First-order wetting of rough substrates and quantum unbinding

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Replica and functional renormalization group methods show that, with short-range substrate forces or in strong fluctuation regimes, wetting of a self-affine rough wall in two dimensions turns first order as soon as the wall roughness exponent exceeds the anisotropy index of bulk interface fluctuations. Different thresholds apply with long-range forces in mean field regimes. For bond-disordered bulk, fixed point stability suggests similar results, which ultimately rely on basic properties of quantum bound states with asymptotically power-law repulsive potentials. [S1063-651X(98)15309-6]

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Wetting transitions occur when, e.g., an interface separating two coexisting phases unbinds from an attractive substrate, as the wetting temperature T_w is approached from below. In recent literature, much space has been devoted to the effects of different types of disorder on the nature and universality of such transitions [1–4]. This is motivated both by the presence of impurities in actual experiments, and by the expectation that disorder modifies critical behavior. Many studies concentrated on impurities in the bulk, or on the surface of a smooth substrate. Another type of disorder is that due to the roughness of the wall delimiting the substrate. This rather frequent geometrical disorder was discussed especially in connection with measurements of nitrogen adsorption on flash deposited silver [5–8].

Substrate roughness describable by self-affine geometry is often realized and most interesting, from both a fundamental and a physical point of view. Indeed, a wall whose average transverse fluctuation W_L increases as a power of the longitudinal sample size L ($W_L \propto L^{\zeta_w}, 0<\zeta_w<1$), has a random geometry characterized globally by a single roughness exponent ζ_w. Moreover, whether their fluctuations are controlled by temperature or by disorder, bulk interfaces behave as self-affine objects, with appropriate exponents ζ_0 [1,4] describing their transverse fluctuations just as ζ_w does in the case of W_L. Thus, when such substrates are considered, a direct competition between wall and interface roughnesses may be anticipated in wetting phenomena.

In the present paper we show exactly in two-dimensions (2D) that, as soon as the wall wins (i.e., for $\zeta_w>\zeta_0$ with short-range substrate potentials), the above competition is resolved in an unusual, drastic change of the wetting transition, from continuous to first order. In other terms, the average substrate-interface distance diverges discontinuously at T_w, rather than as a negative power of $T_w - T$. We determine exact roughness thresholds for first-order wetting also in other regimes with the substrate exerting long-range forces (e.g., van der Waals) on the interface and discuss, at perturbative level, cases with bond disorder in the bulk. A change from continuous to discontinuous wetting is in fact a quite surprising and unexpected phenomenon, especially in 2D. As a rule, with short-range forces, first-order wetting never occurs in 2D, except in special and *ad hoc* limit situations [9]. Disorder generally acts in the opposite sense of turning into second-order discontinuous transitions [1]. In all cases the mechanism leading to first-order wetting at large ζ_w can be traced back to some basic properties of quantum bound states of a particle in a potential [10].

In 2D, a self-affine wall can be described by a random function $h_w(x)$ (Fig. 1), with probability distribution [7]

$$P_w[h_w] \propto \exp\left[-\int dx \frac{K_w}{2} (\partial^\beta h_w / \partial x^\beta)^2 \right] \tag{1}$$

such that $\overline{|h_w(x)-h_w(x')|} \propto |x-x'|^{\zeta_w}$, with $\zeta_w = \beta - 1/2$ and the overbar indicating the quenched average with respect to

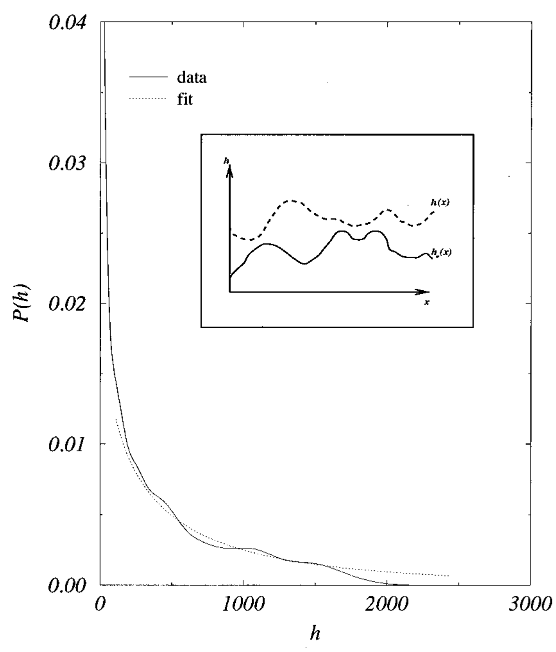

FIG. 1. Inset: sketch of the geometry of wall (continuous) and interface (dashed). Main: probability distribution of h, from a sampling of 500 wall configurations of 100 000 longitudinal steps.

Eq. (1) [11]. In the presence of bulk disorder, the interface Hamiltonian can be put in the form

$$\beta H[h,h_w,V]=\int dx\left[\frac{K}{2}(\partial h/\partial x)^2 + U(h(x)-h_w(x))+V(x,h(x))\right] \quad (2)$$

where V is a Gaussian random potential [$\overline{V}=0$, $\overline{V(x,h)V(x',h')}=\Delta\,\delta(x-x')\,\delta(h-h')$], and U is the potential due to the substrate. K is the interfacial stiffness. If the wall is attractive, but impenetrable, $U(y)=\infty$ for $y\leqslant 0$, and a minimum of U at some $y>0$ allows us to pin the interface. With long-range forces, $U(y)\sim u/y^{\sigma-1}+v/y^{\sigma}$ $(v>0)$, for large y [4].

The disorder due to h_w and V in Eq. (2) makes the partition $Z[h_w,V]=\int\mathcal{D}h\exp(-\beta H)$ a stochastic variable. Thus, we introduce replicas [12] and evaluate

$$\overline{Z^n}=\int\mathcal{D}V\int\mathcal{D}h_wP_v[V]P_w[h_w]\int\prod_{\alpha=1}^{n}\mathcal{D}h_\alpha \times\exp(-\beta H[h_\alpha,h_w,V]) \quad (3)$$

where $\ln(P_v)=\text{const}-(1/2\Delta)\int dx\,dh\,V(x,h)^2$. Integration over $\mathcal{D}V$ is easily performed and allows to interpret $h_\alpha(x)$ as world lines (x corresponding to time) of n quantum particles interacting via attractive two-body δ potentials. Thus, in Eq. (3) we are left with integrations over $\mathcal{D}h_w$ and $\mathcal{D}h_\alpha$, and an effective Hamiltonian:

$$\beta H[h_\alpha,h_w]=\int dx\Bigg(\frac{K_w}{2}(\partial^\beta h_w/\partial x^\beta)^2 + \sum_\alpha\left[\frac{K}{2}(\partial h_\alpha/\partial x)^2+\frac{K'}{2}(\partial h_w/\partial x)^2 + C(\partial h_\alpha/\partial x)(\partial h_w/\partial x)+U(h_\alpha)\right] + \Delta\sum_{\alpha\neq\beta}\delta(h_\alpha-h_\beta)\Bigg). \quad (4)$$

The logarithm of P_w is now included in βH and the couplings K' and C arise from the replacement $h_\alpha\to h_\alpha+h_w$ (initially, of course, $K'=C=K$). A functional renormalization group (RG) [1,7] treatment can be performed exactly up to first order in U and Δ. By summing up $\exp(-\beta H)$ over Fourier modes $\tilde{h}_\alpha(k)$ and $\tilde{h}_w(k)$ with $\Lambda/b<k<\Lambda$, after the rescalings $x\to bx$, $h_\alpha\to b^\zeta h_\alpha$ and $h_w\to b^{\zeta_w}h_w$, one obtains the following RG flow equations ($b=1+dl$):

$$\frac{d\ln(U)}{dl}=1+\zeta h\frac{U'}{U}+\Omega\frac{U''}{U},$$

$$\frac{d\ln(K)}{dl}=2\zeta-1,$$

$$\frac{d\ln(K')}{dl}=2\zeta_w-1,$$

$$\frac{d\ln(C)}{dl}=\zeta+\zeta_w-1, \quad (5)$$

$$\frac{d\ln(K_w)}{dl}=1-2\beta+2\zeta_w=0,$$

$$\frac{d\ln(\Delta)}{dl}=1-\zeta,$$

where Ω is a suitable function of K, K_w, C and the cutoff Λ [7], and h stands for a generic h_α.

We first discuss $\Delta=0$. With $\zeta_w<1/2$ and ordered bulk, for $\zeta=\zeta_0=1/2$ [1,4], there exists a fixed point (FP) of Eqs. (5), with respect to which K' and C are irrelevant [$d\ln(K)/dl=0$, while, e.g., $d\ln(K')/dl<0$]. Thus, substrate fluctuations decouple from the problem. With short-range, or with long-range forces such that $\zeta_0=1/2>2/(\sigma+1)=\zeta^*$ {strong fluctuation (SF) regime [4]}, the FP behavior of U at large h is within the control of a first-order cumulant expansion and turns out to be $U\propto h^{-\tau(\zeta_0)}$, ($\tau(\zeta_0)=2(1-\zeta_0)/\zeta_0=2$) [4,7,13]. This long distance behavior should in fact apply to all of the FP U's necessary to describe the wetting transition in such conditions. These FP's are in general three: one describing pinned interface situations, one for the wet regime with unbound interface, and one, unstable, at the borderline between the domains of attraction of the previous two, describing the transition point behavior. In view of the decoupling of substrate fluctuations, the wetting transition controlled by these FP's, whose U's we can not determine at finite h, is expected to be continuous, with exponents identical to those valid for the flat wall, which are known exactly [1,14]. In the case of short-range forces, numerical evidence of second-order wetting with such exponents has been recently obtained for low enough ζ_w by extensive transfer matrix calculations [8].

The FP's for $\zeta_w>1/2$ have to be found at $T=0$, by setting $\zeta=\zeta_w$ in Eqs. (5). Indeed, now, choosing again $\zeta=1/2$, parameters like K' and C would grow to infinity while K remains fixed. Surface roughness is clearly relevant now. Under a rescaling b, a $T=0$ fixed point is approached as $\beta H\propto b^y(\beta H)^*$ with $(\beta H)^*$ finite and $y>0$, when $b\to\infty$. Such FP's are expected in situations when quenched disorder (due to the wall here) controls the physics [7]. At the $T=0$ FP's with $\zeta=\zeta_w$, K, K', and C are all growing to infinity at the same rate {e.g., $K(l)\sim K^*\exp[(2\zeta_w-1)l]$}, and $U(l)\sim U^*(h)\exp[(2\zeta_w-1)l]$. U^* obeys an equation like the first of Eqs. (5), with the constant term replaced by $2(1-\zeta_w)$, and ζ_w multiplying the second term on the right-hand side in place of ζ. Thus, the discussion of the asymptotic behavior of U^* follows lines similar to those for U in the case $\zeta_w<1/2$ [7]. In particular, with short-range forces or in SF regime, we get now $U^*(h)\propto h^{-\tau(\zeta_w)}$, [$\tau(\zeta_w)<2$]. Such behavior of U^* holds also in MF regime ($\zeta^*>\zeta_0=1/2$ [4]), as soon as $\zeta_w>\zeta^*$.

This asymptotic behavior of U^* and the connection between path integral and quantum mechanics are the key to demonstrate first-order wetting. Indeed, the transition order is revealed by the way in which $\overline{\langle h \rangle}$ diverges to infinity. Consistently with Eqs. (5), upon approaching a $T=0$ FP with $\zeta_w > \zeta_0$, or $\zeta_w > \zeta^*$ in the MF regime, we must define K_w^* such that $K_w(l) = K_w^* \exp[2\zeta_w - 1)l] = \text{const}$. Thus, in the FP action $(\beta H)^*$ we are left with $K_w^* = 0$, as $l \to \infty$. By shifting back integration variables in this action ($h_\alpha \to h_\alpha - h_w$), the terms in K'^* and C^* disappear and the calculation of $\overline{Z^n}$ can be easily converted into that of the ground state energy of a quantum problem in 1D, with $n+1$ particles and Hamiltonian $\mathcal{H} = \Sigma_\alpha [p_\alpha^2/(2K^*) + U(h_\alpha - h_w)]$. In this problem the particle with coordinate h_w has an infinite mass. This circumstance allows to get the ground state wave function of $\mathcal{H}$ exactly in the form $\Pi_\alpha \Psi(h_\alpha - h_w)$, with Ψ satisfying the one-particle Schrödinger equation:

$$-\frac{1}{2K^*}\partial^2\Psi/\partial h^2 + U^*\Psi = \epsilon\Psi. \tag{6}$$

$\overline{\langle h_\alpha - h_w \rangle}$ is proportional to the expectation value, $\langle h \rangle_\Psi$ [15], of h in the ground state $\Psi(h)$ of Eq. (6). We concluded above that, at large h and for $\zeta_w > 1/2$ (or $\zeta_w > \zeta^* > 1/2$ with long range forces in the MF regime), the possible $U^*(h)$, however, behaving at finite h, are repulsive and decay asymptotically to zero with a power $\tau(\zeta_w) < 2$ of h. The FP U^* at the wetting transition must have such a shape to belong to the borderline class between potentials with bound ground state and $\epsilon < 0$, and potentials for which all states have $\epsilon > 0$ and $\langle h \rangle_\Psi = \infty$. These two latter types of potentials characterize dry and wet regimes, respectively. Independent of the details of $U^*(h)$ at short h, a solution of Eq. (6) with $\epsilon = 0$ has a remarkable property for $\tau < 2$ [10]. Indeed, an $\epsilon = 0$ eigenstate necessarily behaves as $\Psi(h) \propto \exp(-ah^s)$, at large h, with $s = 1 - (\tau/2) > 0$. This means that, for $\epsilon = 0$, a repulsive potential decaying slower than h^{-2} creates a too strong barrier at large distances to allow interface delocalization. Thus, the ground state Ψ for U^* representing the transition FP (i.e., a FP potential in the borderline class) must be bound, with $\langle h \rangle_\Psi < \infty$. This implies that, right at the wetting transition, $\overline{\langle h \rangle} < \infty$, while $\overline{\langle h \rangle} = \infty$ as soon as the wet phase is accessed. First-order wetting is thus proved as soon as $\zeta_w > 1/2$ (short range or $\zeta^* < 1/2$), or $\zeta_w > \zeta^* > 1/2$.

A recent numerical study of a 2D model with rough substrate exerting short-range forces, gave evidence in support of first-order wetting for ζ_w sufficiently larger than 1/2 [8]. In order to get a more direct manifestation of the mechanisms implied by Eq. (6), we performed transfer matrix calculations for a model on square lattice with both the wall and interface represented by directed paths, as described in Ref. [16]. Figure 1 reports numerical results for the probability distribution of h. Data are taken just below the depinning temperature for $\zeta_w = 2/3$ $[\tau(2/3) = 1]$. The dotted curve has a behavior $\propto \exp(-ax^{1/2})$, of the form expected right at threshold on an infinite asymptotic range $(s = 1/2)$. A relatively still poor sampling over disorder is largely responsible of some oscillations of the distribution, but the overall trend appears already consistent with our theoretical predictions.

With bulk disorder $(\Delta > 0)$, the perturbative character of Eqs. (5) prevents an exact control of the FP U for $h \to \infty$. On the other hand, we know that, with $\Delta > 0$, $\zeta_0 = 2/3$ is the exact interface anisotropy index [1,4]. For $\zeta_w < 2/3$, by setting $\zeta = 2/3$ in Eqs. (5), we find that both $K(l)$ and $\Delta(l)$ grow proportional to $\exp(l/3)$ (towards a $T=0$ fixed point), while K' and C grow slower, and are thus irrelevant. At the same time, for short-range forces, $U(l) = U^* \exp(l/3)$ gives $U^*(h) \propto h^{-\tau(\zeta_0)}$, with $\tau(\zeta_0) = 1$, at large h. Thus, in the limit of very small bulk disorder, we get an indication that for $\zeta_w < 2/3$ a wetting transition regime identified by $\zeta = \zeta_0 = 2/3$ should imply a decoupling of substrate fluctuations from the problem. At least with very weak bulk disorder, the wetting transition with $\zeta_w < 2/3$ should retain the features of the flat wall case. For this case one indeed expects an effective wall-interface potential decaying as h^{-1} [2,4], and Kardar has determined exactly by Bethe ansatz the second-order character and the exponents of the transition [3]. Consistently with our expectation, numerical results for short-range forces in Ref. [16] support continuous wetting in Kardar's class for ζ_w sufficiently lower than 2/3, even with finite bulk disorder.

Let us consider now $\zeta_w > 2/3$, and short-range forces again. By setting $\zeta = \zeta_w$ in Eqs. (5), we find $\Delta(l) = \Delta(0)\exp[(1-\zeta_w)l]$, while $K(l) = K'(l) = C(l) = K^*\exp[(2\zeta_w - 1)l]$ and $K_w(l) = \text{const}$. Furthermore, $U(l) = U^*\exp[(2\zeta_w - 1)l]$ implies $U^*(h) \propto h^{-\tau(\zeta_w)}$. Since now Δ (still supposed small) grows slower than K, C, and K', it is natural to regard it as an irrelevant parameter with respect to the $T=0$ FP's that would be reached for $\Delta = 0$ strictly. Upon varying $\zeta_w > 2/3$, these FP's span a subset of those already discussed with ordered bulk, for which quantum mechanics implies first-order wetting. Thus, we conclude that for $\zeta_w > 2/3$ a small amount of bulk disorder is irrelevant and leaves the transition under the control of the same mechanism outlined for pure bulk and the same ζ_w. Numerical results in Ref. [16] support this conclusion, giving evidence of first-order wetting for sufficiently large ζ_w and finite disorder. Similar arguments apply to long-range forces in SF and, for $\zeta_w > \zeta^*$, in the MF regime.

In summary, our RG picture demonstrates first-order wetting in 2D with sufficiently rough substrates exerting short-range forces on the interface. This is consistent with earlier numerical work suggestive of discontinuous transitions [8,16]. The threshold for first-order wetting is precisely identified as $\zeta_w = 1/2$ in the case of ordered bulk. For disordered bulk perturbative arguments suggest first-order as soon as $\zeta_w > 2/3$, consistent with a possible general rule that ζ_0 identifies the threshold. We predict roughness induced first-order wetting also with long-range forces, for $\zeta_w > \zeta_0 > \zeta^*$ (SF) or for $\zeta_w > \zeta^* > \zeta_0$ (MF). Discontinuous depinning is due to the repulsive effective wall-interface potential, which becomes too strong, at large distance, to allow for a continuous increase towards infinity of $\overline{\langle h \rangle}$ when depinning is approached. This follows from general quantum properties, independent of the details of U at finite h.

Interesting open problems remain the nature of wetting right at the thresholds and the possible extension to 3D of this type of results, which rely on the connection with quantum mechanics in 1D. A recent mean feld study in 3D suggests the possibility of first-order wetting induced by wall roughness with short-range substrate potential and ordered bulk [17]. Another interesting issue is whether $\zeta_w = \zeta_0$ could be a plausible threshold also in cases in which different kinds of bulk disorder imply different ζ_0's. Relevant examples include random fields [4] and quasicristals [18].

Due to the competition between two qualitatively similar scaling geometries, interactions between a fluctuating manifold and a random boundary can lead to interesting phenomena also in other contexts. An example could be flux lines in high-T_c superconductors with extended rough defects [19]. Also of interest would be polymers or membranes adsorbed by rough walls.

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