Europhys. Lett., **39** (6), pp. 633-638 (1997)

Effect of surface roughness on bulk-disorder–induced wetting

G. Sartoni[1](*), A. L. Stella[2], G. Giugliarelli[3] and M. R. D'Orsogna[2]

[1] *Dipartimento di Fisica and Sezione INFN, Università di Bologna I-40126 Bologna Italy*
[2] *INFM-Dipartimento di Fisica and Sezione INFN, Università di Padova I-35131 Padova, Italy*
[3] *Dipartimento di Fisica and INFN (Gruppo Collegato di Udine) Università di Udine I-33100 Udine, Italy*

(received 17 April 1997; accepted in final form 11 August 1997)

PACS. 68.45Gd – Wetting.
PACS. 05.70Fh – Phase transitions: general aspects.
PACS. 82.65Dp – Thermodynamics of surfaces and interfaces.

Abstract. – Transfer-matrix results in 2D show that wetting of a rough, self-affine wall induced by bulk bond disorder turns discontinuous as soon as the wall roughness exponent ζ_W exceeds $\zeta_0 = 2/3$, the spatial anisotropy index of interface fluctuations in the bulk. For $\zeta_W < 2/3$ critical wetting is recovered, in the same universality class as for the flat-wall case. These and related findings suggest a free-energy structure such to imply first-order wetting also without disorder, or in 3D, whenever ζ_W exceeds the appropriate ζ_0. The same thresholds should apply also with van der Waals forces, in cases when ζ_0 implies a strong-fluctuation regime.

Disorder induced critical wetting [1]-[3] is a remarkable phenomenon in the physics of interfaces in random media [2], [4], [5]. Even at temperature $T = 0$, under the effect of quenched bulk impurities, an interface can undergo depinning from an attractive (smooth) wall [1]. An example is offered by the 2D Ising model on semi-infinite lattice. At $T = 0$, with suitable boundary conditions, the interface can be localized on a line of weak ferromagnetic bonds along the edge (wall). If the bulk couplings are disordered, upon reducing wall attraction depinning eventually occurs. This ill-condensed matter version of critical wetting in 2D belongs to a different universality class as similar transitions controlled by thermal fluctuations alone. Indeed, the mean wall-interface distance $\overline{h}$ diverges as $\Delta\epsilon^{-\psi}$, where $\psi = 2$ [1] and $\Delta\epsilon$ measures the deviation from critical edge attraction conditions. $\psi = 1$ holds for the thermal case without disorder [6].

An as yet unanswered question concerns the possible effect of additional, geometrical surface disorder on this type of wetting. Rough substrate walls with self-affine geometry, are produced in experiments [7], [8] and adsorption phenomena have been already observed on them [8]. On the other hand, interface depinning belongs to a more general class of disorder-induced delocalization phenomena of fluctuating manifolds from extended defects [9].

(*) Present address: Instituut-Lorentz, Rijks Universiteit Leiden, 2300 RA Leiden, The Netherlands.

In the present letter we show that a self-affine roughness of the attractive wall can indeed have dramatic effects on the wetting induced by bulk disorder. By extensive calculations in 2D and by a study of the interfacial free energy, we show that wetting turns first-order as soon as the wall roughness exceeds that of the interface in the bulk. If, on the contrary, the wall is smoother than the bulk interface, critical wetting persists, in the same universality class as with flat wall. For first-order wetting due to roughness our results allow to draw a general scenario, encompassing also cases in 3D, with ordered bulk or long-range substrate forces.

The possibility for geometrical surface disorder to drive wetting first-order has been recently envisaged by some of us for pure systems and in the context of hierarchical models [10]. A key issue here is to assess whether and up to what extent this disorder, which is correlated in the case of self-affine roughness, can determine modifications when acting simultaneously with uncorrelated bulk randomness.

Here wetting of a rough boundary is studied by means o the model illustrated in fig. 1. To each bond b of a square lattice, a random energy ϵ_b is independently assigned from a uniform distribution in $(0,1)$. The interface configurations are directed paths with one end in the origin O and t steps (t measures also the longitudinal distance). At $T=0$ the only interface configuration is that minimizing the total energy of a path P, given by

$$E_P = \sum_{b\in P} \epsilon_b - \sum_{b\in W\cap P} \epsilon_W \,. \tag{1}$$

Our paths cannot trespass the wall W, whose profile is fixed together with the set $\{\epsilon_b\}$ in a given disorder configuration. Substrate attraction is accounted for by assigning an extra energy gain $-\epsilon_W$ ($\epsilon_W > 0$) to each step of P on W. Directed wall configurations are sampled at random through an algorithm [11] producing $x_W(t)$'s such that

$$\left(\overline{(x_W(t_1) - x_W(t_2))^2}\right)^{1/2} \sim_{t_2-t_1>1} (t_2-t_1)^{\zeta_W} \,, \tag{2}$$

where the bar indicates averaging over wall disorder, x_W are transverse wall coordinates, and ζ_W is a preassigned wall roughness exponent ($0<\zeta_W<1$).

Information on the optimal path properties at time t can be transferred to $t+1$ if, for each possible x ($x_W(t) \le x \le t$), the energy, $E(t,x)$, and the total number of steps on the wall, $N(t,x)$, are known for the minimal-energy path joining the origin with the point of coordinates (t,x). Indeed, the following recursion holds:

$$\begin{aligned} E(t+1,x) = \min\big\{ & E(t,x+1) + \epsilon_{b_1} - \epsilon_W \delta_{x+1,x_W(t)} \delta_{x,x_W(t+1)} \,; \\ & E(t,x-1) + \epsilon_{b_2} - \epsilon_W \delta_{x-1,x_W(t)} \delta_{x,x_W(t+1)} \big\} \,, \end{aligned} \tag{3}$$

where b_1 and b_2 are bonds connecting the point $(t+1,x)$ to its upper left and lower left nearest neighbor (n.n.), respectively. Of course, minimization in eq. (3) trivially involves only one term when x is at its upper or lower bound and only one such n.n. point exists. For N we have

$$N(t+1,x) = N(t,y) + \delta_{x,x_W(t+1)} \delta_{y,x_W(t)} \,, \tag{4}$$

where $y = x+1$ or $y = x-1$, depending on which one of the two terms in eq. (3) satisfies minimization.

We considered four different values of ζ_W: $\zeta_1 = 1/2$, $\zeta_2 = \frac{\ln 4}{\ln 12} = 0.557\ldots$, $\zeta_3 = \frac{\ln 4}{\ln 6} = 0.773\ldots$ and $\zeta_4 = \frac{\ln 6}{\ln 8} = 0.861\ldots$. For these ζ_W and a wide range of t's we calculated quantities like $x_{\min}(t)$ such that $E(t, x_{\min}(t)) = \min_x\{E(t,x)\}$, $h(t) = x_{\min}(t) - x_W(t)$ and $n(t) = N(t, x_{\min}(t))/t$, and their quenched averages over disorder. We made extrapolations of these quantities to infinite t. We could average over at least 50 different bulk and wall random configurations in correspondence to the longest paths ($t = 1.5\times 10^5$).

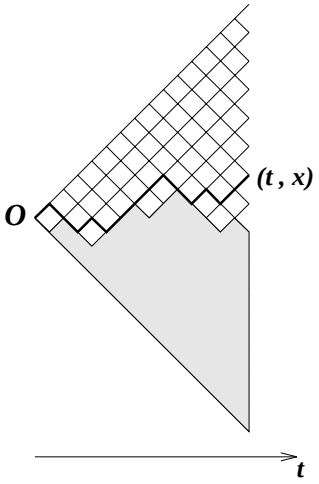

Fig. 1

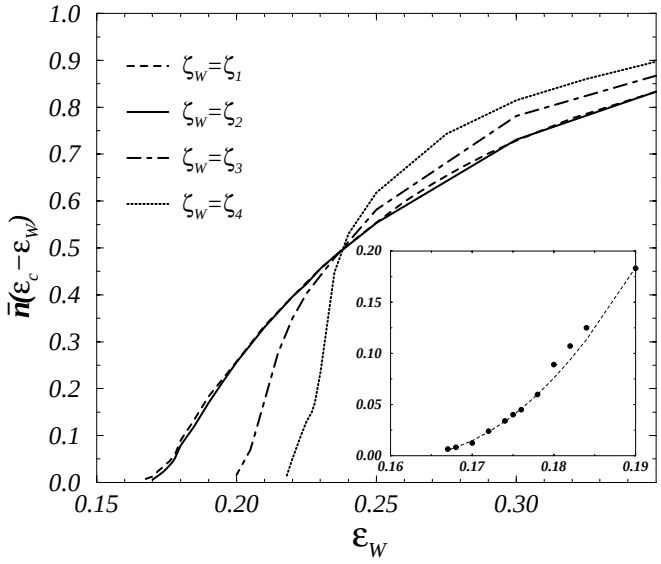

Fig. 2

Fig. 1. – The thick line represents an interface with origin in O and end point at (t, x) after t steps. The shaded area represents the substrate bounded by the rough wall. Both interface and wall are directed paths.

Fig. 2. – $\overline{n}(\epsilon_W - \epsilon_c)$ *vs.* ϵ_W for the four different values of ζ_W. Note the parabolic vanishing of $\overline{n}$ when $\zeta_W < 2/3$. The insert displays the fit of $\overline{n}$ for $\zeta_W = \zeta_1$, to the critical behavior $\propto \Delta\epsilon^{\psi}$: $\psi = 2.0 \pm 0.1$ and $\epsilon_c = 0.162 \pm 0.001$.

For each ζ_W, upon lowering ϵ_W, a threshold $\epsilon_c(\zeta_W)$ is always reached, below which $\overline{h} = \lim_{t\to\infty} \overline{h}(t) = \infty$ and $\overline{n} = \lim_{t\to\infty} \overline{n}(t) = 0$. For $\zeta_W = \zeta_1$ and ζ_2, $\overline{h}$ and $\overline{n}$ diverge and approach zero, respectively, as power laws in $\Delta\epsilon = \epsilon_W - \epsilon_c$, when $\Delta\epsilon$ approaches zero. Quite remarkably, best fits of our data are well consistent with $\overline{h} \propto \overline{n}^{-1}$, and with $\overline{h} \propto (\Delta\epsilon)^{-\psi}$, with $\psi = 2.0 \pm 0.1$, and 2.1 ± 0.1, respectively, for $\zeta_W = \zeta_1$ and ζ_2 (fig. 2). These exponents are also fully consistent with finite-size scaling collapse fits for $\overline{h}(\Delta\epsilon, t)$ or $\overline{n}(\Delta\epsilon, t)$. *E.g.*, for $\overline{n}$ we test the scaling form $\overline{n}(\Delta\epsilon, t) = \Delta\epsilon^{\psi} f(t\Delta\epsilon^{\psi})$, taking into account that the transverse lengths controlling crossover are t and $\Delta\epsilon^{-\psi}$.

These results strongly suggest that, at least for $\zeta_W \leq \zeta_2$, wetting remains critical, and in the same universality class as with flat walls [1]. Thus, geometric disorder of the boundary does not seem to affect the nature of the wetting transition here. The only effect of surface geometric disorder is a slight increase of ϵ_c with increasing ζ_W.

The behaviors of $\overline{n}$ and $\overline{h}$ radically change for $\zeta_W = \zeta_3$ and ζ_4. At both these ζ_W values, the curves for $\overline{n}$ are much steeper soon above threshold (slopes, respectively, two and four times larger than in the previous smoother cases), with an initial behavior at threshold which cannot be fitted in terms of the previous power law (fig. 2). In order to better characterize the wetting transition with rougher walls, we analyzed distributions of the fraction n of adsorbed interface steps at different t's, based on rich enough samples of disorder configurations (~ 300), and up to $t \sim 5 \times 10^4$. Figure 3 shows a series of histograms for $n(t)$ at a value of $\epsilon_c \lesssim \epsilon_W$, for $\zeta_W = \zeta_4$. A very marked two-peak structure can be recognized. This is a most convincing indication of a first-order transition. The mechanism of $\overline{n}$ vanishing appears to be a depletion of the peak at nonzero n values in favor of that at the origin. This depletion takes place in

a relatively narrow range of ϵ_W values for finite t and is responsible for the peculiar behavior of $\overline{n}$ just above threshold. Similar results are obtained for $\zeta_W = \zeta_3$. This behavior openly contrasts with that of the smoother walls we tested. For those walls a single-peak structure is manifest and the vanishing of $\overline{n}$ is due to a progressive shift of the peak location towards the origin. This is consistent with the expected continuous character of the transition.

The arrangement of the four tested ζ_W values is such that the above results already feature $\zeta_W = 2/3$ as a plausible threshold for the instauration of first-order wetting. Indeed, $\zeta_0 = 2/3$ is the intrinsic roughness of the interface when it wanders in the bulk [4], and it makes sense that this number plays a crucial role here. We did not attempt a finer numerical exploration in the interval $\zeta_2 < \zeta_W < \zeta_3$. This would be very time consuming and would not provide sharp enough results. Rather, we argue the precise location of the tricritical threshold as follows.

Let us consider generally situations at nonzero T, so that overbars indicate quenched averages of thermal expectation values. As discussed below, in the presence of bulk disorder, nonzero T is not expected to alter the scenario [1], [9]. The continuum interface Hamiltonian description of wetting leads to the identification of different contributions to the free energy density [2], [12]. An ubiquitous term in the Hamiltonian density is the square gradient of the interfacial profile, $(\nabla h)^2$. For an interface bound at average distance $\overline{h}$ from a flat wall, this term is expected to be $\propto \Sigma \overline{h}^{-\tau(\zeta_0)}$, where Σ is a positive interface stiffness, and $\tau = 2(1-\zeta_0)/\zeta_0$, with $\zeta_0 = 2/3$ in the case of random bonds in the bulk [2], [12]. This follows from dimensional considerations, by estimating the distance between successive wall-interface contacts as $\propto \overline{h}^{1/\zeta_0}$, and thus the above gradient as $\propto \overline{h}^{(1-\zeta_0)/\zeta_0}$. In the flat case, one can also argue that the random potential due to bond-impurities should provide an additional term, with the same $\overline{h}$-dependence [2]. The presence of this extra term is crucial. Indeed, the stiffness term, being positive and most long-ranged, needs to be possibly compensated, for the interface to be able to continuously depin, upon approaching wetting. Other contributions to the free energy, like the entropic one [2], [12], can indeed be shown to decay to zero at infinity more rapidly ($\propto \overline{h}^{-3/2}$) than the stiffness one in the presence of bulk bond disorder. Since the reference free energy of the interface in the bulk is put equal to zero, only discontinuous depinning could occur, with a positive free-energy barrier always present at large $\overline{h}$.

Based on the estimate of the leading free-energy density as $\propto \overline{h}^{-\tau(\zeta_0)}$ and on the identification of $\overline{h}$ with $\xi_\perp$, the transverse correlation length ($\xi_\parallel \propto \xi_\perp^{3/2}$ is the parallel one), Lipowsky and Fisher [2] could derive $\psi = 2$. Our results for $\zeta_W < 2/3$ are clearly consistent with the free-energy leading terms retaining the same power law behavior as in the case of flat wall. Thus, the arguments of ref. [2] still apply. If the wall is less rough than the interface, the stiffness term remains determined by the anisotropy of interface fluctuations, rather than by the geometry of the substrate. At the same time, the continuous character of wetting shows that bulk disorder contributions, which are again linked to interface wandering, remain able to balance this stiffness term.

For $\zeta_W > 2/3$ we must argue differently. The positive stiffness term of the bound interface must certainly be modified to $\Sigma \overline{h}^{-\tau(\zeta_W)}$, because wall geometry now determines the gradient. Indeed, the dominant stiffness free energy originates from the fact that now the bound interface has to adapt to wall roughness, rather than to bulk disorder. Moreover, $\tau(\zeta_W) < 1$, for $\zeta_W > 2/3$. Thus, the stiffness free-energy term is now even more dominant at large $\overline{h}$. On the other, we can convince ourselves that, for given $\overline{h}$, the disorder-induced fluctuations of the interface are still controlled by ζ_0 and are not wide enough to compensate the stiffness term in the free energy. Moreover, this is fully consistent with the fact that first-order wetting is observed: only with the stiffness term left as the dominating one at large $\overline{h}$ an excess positive free-energy barrier can be maintained for the transition. Thus, we conclude that, as soon as

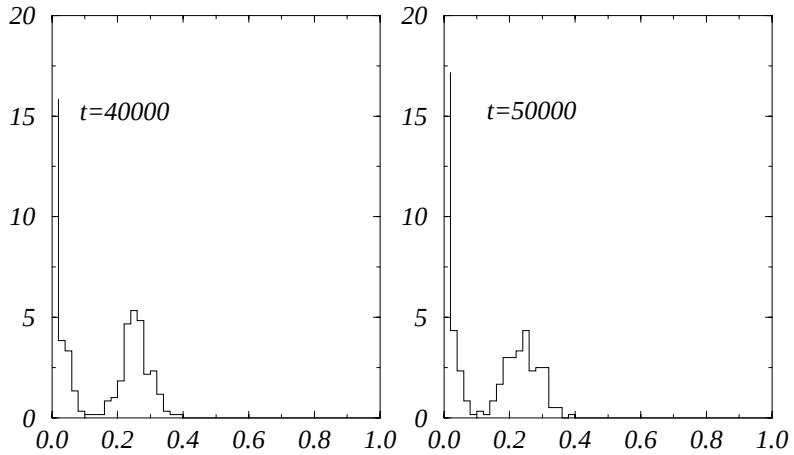

Fig. 3. – Histograms of $n(t)$, at different t's, for $\zeta_W = \zeta_4$ and $\epsilon_W = 0.22$. Asymptotically $\overline{n}(\epsilon_W - \epsilon_c) = 0.057 \pm 0.005$.

$\zeta_W > 2/3$, if wetting does occur, it is first order.

The above picture is fully consistent with our numerical results and elucidates the role of $\zeta_W = \zeta_0 = 2/3$ as a threshold for discontinuous wetting. Thus, geometric surface disorder plays a very crucial role in determining the nature of the wetting transition. First-order wetting in 2D and with short-range forces is quite exceptional [3]. We know of only one special setup in which a first-order depinning with bulk disorder was obtained in 2D [13]. In that example, bulk disorder is fully correlated parallel to a flat wall, *i.e.* the random potential depends on x alone, not on t. Here we find a subtle and physically realistic way in which correlations of the disorder in direction parallel to the wall can produce a first-order transition. Indeed, in our system, a nontrivial long-range longitudinal correlation pertains to the self-affine boundary fluctuations (see eq. (2)) and does not involve the whole bulk. Nevertheless, upon tuning ζ_W, this effect is such to induce a tricritical point for the wetting transition.

By producing histograms like those in fig. 3, in the absence of bond disorder and at $T > 0$, we also find conclusive numerical evidence that $\zeta_W \simeq \zeta_0 = 1/2$ is the threshold for first order in this case, as previously conjectured [10]. With ordered bulk in 2D, $\tau(\zeta_0) = \tau(1/2) = 2$ and the entropy falls as $\overline{h}^{-2}$. Also here we argue that, as soon as $\zeta_W > 1/2$, the stiffness term $\Sigma \overline{h}^{-\tau(\zeta_W)}$, with its asymptotic dominance, is such to create an extra positive energy barrier, which leaves first-order wetting as the only possibility.

Our arguments are naturally generalized in 3D, where $\zeta_0 \sim 0.41$ with bulk bond disorder [5]. The gradient squared term in the Hamiltonian still leads to a long-range stiffness free energy decaying with $\tau(\zeta_0) \sim 2.9$. Thus, even if the critical wetting exponents are not known for the flat case, we anticipate first-order wetting for $\zeta_W > 0.41$. Similarly, in the case of ordered bulk in $3D$ ($\zeta_0 = 0$), we expect first-order as soon as $\zeta_W > 0$, which turns the stiffness term from exponentially [12] to power law decaying [14].

Finally, we consider long-range forces with the substrate, inducing an interface potential $V(\overline{h}) = u/\overline{h}^{\sigma-1} + v/\overline{h}^{\sigma}$ [2], [12]. With flat walls, critical wetting falls in a regime of mean field (MF) if $\zeta_0 < 2/(\sigma+2)$, of weak fluctuation (WFL) if $2/(\sigma+2) < \zeta_0 < 2/(\sigma+1) = \zeta^*$, and of strong fluctuation (SFL) if $\zeta_0 > \zeta^*$. Such regimes have been discussed for both ordered and random bulk, and their exponents are known in many cases [2], [12]. Within a local potential approximation, the effect of roughness added to V has been shown to be irrelevant as long as

$\zeta_W < \zeta^*$, in the sense that only subdominant corrections to V are introduced [15]. On the other hand, for $\zeta_W > \zeta^*$, self-consistent scaling and renormalization group (RG) calculations yield a modified total potential $\propto \overline{h}^{-\tau(\zeta_W)}$ for the bound interface. This agrees with our analysis for short-range forces, which also fall in SFL regimes. There we argued a stiffness term of this form for $\zeta_W > \zeta_0$. In the light of our discussion of the short-range cases, it is natural to expect continuous or first-order wetting transitions for $\zeta_W < \zeta_0$ or $\zeta_W > \zeta_0$, respectively, in a SFL regime. For $\zeta_W < \zeta_0$ the transition should occur with the exponents of the flat case, while first order should be induced by the extra positive free-energy barrier at large $\overline{h}$ when $\zeta_W > \zeta_0$. In MF or WFL regimes there will be no change in the critical transitions and their exponents as long as $\zeta_W < \zeta_0$ ($< \zeta^*$). A very interesting case occurs when $\zeta_0 < 2/(\sigma+2) < \zeta_W < \zeta^*$. Here we expect still critical wetting, but with WFL exponents determined by ζ_W [15] (*e.g.*, $\psi = (\tau(\zeta_W) - \sigma + 1)^{-1}$ [12]), in place of the MF ones of the flat case. Similarly, a roughness-dominated WFL critical wetting should prevail for $2/(\sigma+2) < \zeta_0 < \zeta_W < \zeta^*$. A drastic change into first-order wetting should again occur when $\zeta_W > \zeta^* > \zeta_0$. To confirm these predictions numerical or RG calculations would be useful.

In summary, we fully elucidated the role of self-affine wall roughness in determining the nature of wetting, for short-range forces and with or without bulk disorder in 2D. We could generalize our arguments to 3D, and even to cases in which long-range forces are present. In SFL regimes, first-order wetting is always anticipated when $\zeta_W > \zeta_0$, as with short-range forces. Our results are expected to generalize also to interfaces in random field systems [2], or quasi-crystals [16].

***

ALS acknowledges useful conversations with Prof. M. E. Fisher and Prof. J. O. Indekeu.

REFERENCES

[1] Kardar M., *Phys. Rev. Lett.*, **55** (1985) 2235.
[2] Lipowsky R. and Fisher M. E., *Phys. Rev. Lett.*, **56** (1986) 472.
[3] Forgacs G., Lipowsky R. and Nieuwenhuizen Th. M., in *Phase Transition and Critical Phenomena*, Vol. 14, edited by C. Domb and J. L. Lebowitz (Academic Press) 1991.
[4] Huse D. A. and Henley C. L., *Phys. Rev. Lett.*, **54** (1985) 2708.
[5] Halpin-Healy T. , *Phys. Rev A*, **42** (1990) 711.
[6] Abraham D. B., *Phys. Rev. Lett.*, **44** (1980) 1165.
[7] Krim J., Heyveart I., Van Haesendonck C. and Bruynseraede Y., *Phys. Rev. Lett.*, **70** (1993) 57.
[8] Pfeifer P., Wu Y. J., Cole M. W. and Krim J., *Phys. Rev. Lett.*, **62** (1989) 1997.
[9] Balents L. and Kardar M., *Phys. Rev. B*, **49** (1994) 13030.
[10] Giugliarelli G. and Stella A. L., *Phys. Rev. E*, **53** (1996) 5035.
[11] The algorithm is a modified random version of one first introduced by Mandelbrot B. B., *Phys. Scripta*, **32** (1985) 257. By an iterative procedure we generate walls satisfying eq. (2) with ζ_W equal to the ratio of the logarithms of two even integers.
[12] Fisher M. E., *J. Chem. Soc., Faraday Trans. II*, **82** (1986) 1569.
[13] Nieuwenhuizen Th. M., *J. Phys. A*, **21** (1988) L567.
[14] In an MF treatment for short-range forces in 3D (Parry A. O., Swain P. S. and Fox J. A., *J. Phys. A*, **8** (1996) L659), a similar effect appears.
[15] Kardar M. and Indekeu J. O., *Europhys. Lett.*, **12** (1990) 161; Li H. and Kardar M., *Phys. Rev. B*, **42** (1990) 6546.
[16] Lipowsky R. and Henley C. L., *Phys. Rev. Lett.*, **60** (1988) 2394.