Wetting in Random Systems

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Complete wetting and critical wetting transitions are studied in d-dimensional systems with quenched random impurities and general interactions. New but more universal singular behavior is predicted: For example, under random fields the wetting-layer thickness at complete wetting should diverge as $h^{-1/2}$ for $d=3$, where h measures the deviation from the bulk phase boundary. Wetting exponents are expressed in terms of a single spatial anisotropy or roughness exponent, ζ, defined via $\xi_\perp \sim \xi_\parallel^\zeta$ where $\xi_\perp$ and $\xi_\parallel$ are the wetting correlation lengths.

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Interfacial wetting phenomena arise in the interplay of three distinct thermodynamic phases.[1–4] Sometimes, one of those phases is an inert solid which acts as a rigid boundary leaving a *two-phase system* in contact with a *wall*; the bulk or "spectator" phase, α, may then be separated from the wall by a wetting layer of phase β. If the $\alpha\beta$ interface between the wetting layer and the spectator phase is *rough,* the layer thickness, $\bar{l}(T,h)$, may diverge to ∞ in a continuous fashion as a function of the temperature, T, or the field, h, which represents the deviation from the bulk $\alpha\beta$ phase boundary as, say, a chemical potential difference $\delta\mu$. If this happens as T is varied with $h=0$, i.e., precisely *at* bulk $\alpha\beta$ coexistence, one has a *critical wetting transition* at, say, T_{cW}. On the other hand, if $\bar{l}\to\infty$ as $h\to 0$ for fixed $T\neq T_{cW}$, one has *complete wetting.*

Currently, critical wetting transitions and complete wetting have been studied theoretically only for pure equilibrium systems.[1–4] Here we consider such phenomena generally in systems with *quenched random impurities.* If α and β are fluids a physical realization is provided by a binary mixture within a gel matrix which should, by virtue of differential interactions with the two species, act as a random ordering, i.e., phase-separating, field.[5] In a solid-state context a ferromagnet with frozen nonmagnetic impurities provides an example with random thermal fields or "random bonds." More generally, impurities which, on the microscopic level, distinguish between the phases α and β are equivalent to *random* (ordering) *fields* whereas those that do not may be described by *random-bond* models.

If the bulk spatial dimensionality, d, lies below or at the lower critical dimension, $d_<$, the presence of quenched impurities leads, by definition, to the complete destruction of the bulk transition and $\alpha\beta$ coexistence. Theoretical arguments yield $d_<=2$ for random fields,[6,7] and $d_<=1$ for weak random bonds.[8] Here we presuppose $d>d_<$ and, furthermore, assume that the randomness is *sufficiently weak* that the bulk transition survives so that wetting is possible in principle.

Our analysis shows that both random fields and random bonds change the singular behavior at wetting whenever $d_<<d<5$ even though the effects on the bulk phases may be relatively small. The most accessible case experimentally is complete wetting in $d=3$ dimensions. If the impurities act like *random fields* we find that the layer thickness, $\bar{l}$, diverges as $h^{-1/2}$ for systems governed by (i) retarded and (ii) nonretarded van der Waals forces and likewise (iii) if only short-range forces act. A similar result is found for *random bonds.* By contrast, at complete wetting in pure systems $\bar{l}$ diverges as $h^{-1/3}$, $h^{-1/4}$, and $\ln h$ in cases (i)–(iii), respectively. Consequently, the singular behavior at complete wetting is not only different in the presence of quenched randomness but is also *more universal* than in the pure (or annealed) case.

It is convenient to use Ising-model language in describing the α and β phases. Then h corresponds simply to the bulk magnetic field with $h>0$ favoring the spectator phase, α, of "up" spins. If the interactions between two spins at separation $\mathbf{r}$ decay as $1/|\mathbf{r}|^{d+\sigma}$ when $|\mathbf{r}|\to\infty$ (with $\sigma>0$) the effects of the boundary wall are equivalent to a surface (magnetic) field, $h_s(z)$, which decays as $1/z^\sigma$ for large distances, z, from the wall.[2] We will suppose that h_s yields a wetting (or "prewetting")[2] layer of β phase, or "down" spins, in contact with the wall. In addition to these uniform interactions we consider *either* a random (magnetic) field with zero mean *or* random short-range couplings; as customary,[6–8] we suppose that the randomness exhibits only short-range correlations.

To proceed, let $\mathbf{x}\equiv\mathbf{r}_\parallel=(x_1,\ldots,x_{d-1})$ be a coordinate parallel to the wall and call the fluctuating distance of the $\alpha\beta$ interface from the wall $l(\mathbf{x})$. The uniform interactions then lead to an effective potential, $V_W(l)$, which tends to bind the interface to the wall. For the power-law couplings described this may be represented as[9]

$$V_W(l)=hl+w/l^{\sigma-1}+u/l^\sigma, \tag{1}$$

where we will consider only the case $u>0$.[10] For short-range underlying forces, however, the wall po-

tential becomes[11]

$$V_W(l) = hl + we^{-l/\xi_\infty} + ue^{-2l/\xi_\infty}, \quad (2)$$

where ξ_∞ is the bulk correlation length in the wetting phase, β. When $w \equiv w(T)$, which may be regarded as the thermal parameter, is positive only complete wetting arises (as $h \to 0+$); however, a critical wetting transition can occur when w increases from negative values (with $h = 0+$).

On the other hand, the quenched impurities also act on the interface and should give rise to an inhomogeneous, random potential $V_R(\mathbf{x},l)$ within which the interface wanders, even at $T \to 0$, in order to find the lowest free energy. We conclude that the interface may be described by the effective Hamiltonian

$$\mathcal{H}\{l\} = \int d^{d-1}x[\tfrac{1}{2}\tilde{\Sigma}(\nabla l)^2 + V_W(l) + V_R(\mathbf{x},l)], \quad (3)$$

where $\tilde{\Sigma}$ is the nonuniversal interface stiffness which depends on the details of the spin-spin interactions, etc., but may, here, be regarded as a constant.

Now the effects of the random potential, $V_R(\mathbf{x},l)$, on the behavior of the interface in the *absence* of a wall (i.e., $V_W \equiv 0$) have recently been studied by a variety of techniques.[6-8] The results indicate that the interfacial fluctuations in the presence of quenched randomness alone can be characterized by a single *spatial anisotropy* or *roughness exponent* which we call ζ: The typical transverse excursion, $L_\perp$, normal to the mean orientation of an interfacial segment of linear, longitudinal dimension $L_\parallel$ scales according to $L_\perp \sim L_\parallel^\zeta$. Note, to start with, that for a *free interface,* subject only to thermal fluctuations (i.e., $V_R \equiv 0$), one has[12]

$$\zeta(d) = \tfrac{1}{2}(3-d) \text{ for } 1 < d \leq 3, \quad (4)$$

which includes the well known result $\zeta = \frac{1}{2}$ for $d = 3$ (where the interface is representable by a Brownian path).[3] On the other hand, the theories for *random fields* indicate[6,7]

$$\zeta(d) = \tfrac{1}{3}(5-d) \text{ for } 2 < d \leq 5. \quad (5)$$

Only a single result is available for *random bonds,* namely,[8]

$$\zeta = \tfrac{2}{3} \text{ for } d = 2, \quad (6)$$

but this is exact and, furthermore, one expects ζ to decrease monotonically to $\zeta = 0$ at $d = 5$.[8] We will accept these values and use them to make concrete predictions for wetting exponents. Our analysis is, however, more general and should apply whatever the actual values of ζ. Indeed, we recover all the previous results for wetting in *pure* systems[4,9,11,12] when (4) is used to characterize a free interface.

Consider, now, complete wetting when $h \to 0+$ with $w > 0$ (or $T > T_{cW}$). At $h = 0$ the interface is no longer bound to the wall and its fluctuations due to the randomness will be characterized by $L_\perp \sim L_\parallel^\zeta$ on all scales large compared with the lattice spacing. Thus the transverse difference correlation function, $\Delta C(\mathbf{x})$, should obey

$$\Delta C(\mathbf{x}) \equiv \langle [l(\mathbf{x}) - l(\mathbf{0})]^2 \rangle \sim x^{2\zeta}, \quad (7)$$

when $x \to \infty$ with $h = 0$. If $\xi_\parallel(h)$ is the longitudinal correlation length which describes the decay of $[\langle l(\mathbf{x})l(\mathbf{0})\rangle - \langle l\rangle^2]$ for $h > 0$, scaling then implies $\Delta C(\mathbf{x},h) \approx \xi_\parallel^{2\zeta}\Omega(\mathbf{x}/\xi_\parallel)$. This, in turn, means that the roughness of the interface is described by

$$\xi_\perp(h) \equiv \langle (l - \langle l\rangle)^2\rangle^{1/2} \sim [\xi_\parallel(h)]^\zeta, \quad (8)$$

as could have been anticipated. In this light, let us estimate the free energy per unit $(d-1)$-dimensional area of the interface for typical configurations which may be visualized as varying through a transverse displacement $\xi_\perp$ over regions of longitudinal dimensions $\xi_\parallel$. Thus, the gradient and random potential contributions, which should be of comparable magnitude when $h \to 0+$, can, via (3), be estimated by

$$f_R \approx \tilde{\Sigma}(\xi_\perp/\xi_\parallel)^2 \sim \xi_\parallel^{-2(1-\zeta)} \sim \xi_\perp^{-2(1-\zeta)/\zeta}. \quad (9)$$

In this we have assumed that there is no renormalization of $\tilde{\Sigma}$ (in contrast to a normal bulk critical point where the corresponding coefficient varies as ξ_∞^η). This expression is consistent with the previous studies[6-8] which found f_R scaling as $L_\parallel^{2\zeta-2}$. Note, on the other hand, that (9) does *not,* in general, satisfy *hyperscaling* which would require $f \sim \xi_\parallel^{-(d-1)}$. This need not be a concern, however, since random critical behavior should normally be described by a *zero-temperature* renormalization-group *fixed point* for which hyperscaling is *not,* in general, expected to be valid.[13] Nevertheless, when (4) is used for a *free* interface hyperscaling is recaptured, as expected for a nonrandom thermal transition and, as mentioned, the standard results for pure wetting are reproduced.[4,9,11,12]

We now aim to determine the mean interface position $\bar{l} \equiv \langle l\rangle$ by minimizing total effective free energy $f \simeq f_R + U$, where by (3) we may take the effective wall potential as

$$U(\bar{l}) \approx h\bar{l} + w/\bar{l}^{\sigma-1}, \quad (10)$$

provided (i) $\bar{l}$ *greatly exceeds* $\xi_\perp$, the latter measuring the interface roughness. If one first neglects f_R one finds $U_{\min} \simeq \sigma w/\bar{l}^{\sigma-1}$ with

$$\bar{l} \sim h^{-\psi}, \quad \psi \equiv -\beta_s = 1/\sigma. \quad (11)$$

Then, assuming (i) and the condition

$$\zeta < \zeta^* \equiv 2/(\sigma+1), \quad (12)$$

one finds $f_R \ll U_{\min}$ which justifies the neglect of f_R.

Thus the unbinding of the interface is controlled by the wall potential U alone when $\zeta < \zeta^*$. The correlation lengths follow from $\xi_{\|}^{-2} = (\partial^2 f/\partial l^2)_{\bar{l}}$ and via (8): They diverge as $h \to 0$ with the *complete wetting* exponents

$$\nu_{\|} = \tfrac{1}{2}(\sigma+1)/\sigma, \quad \nu_{\perp} = \tfrac{1}{2}\zeta(\sigma+1)/\sigma. \tag{13}$$

Finally, the original *Ansatz* (i) is justified since $\psi > \nu_{\perp}$ when $\zeta < \zeta^*$.

Suppose, on the other hand, one has[14] (ii) $\bar{l} \simeq \xi_{\perp}$; the repulsive term in (10) is then of order $w/\xi_{\perp}^{\sigma-1}$ which can be neglected relative to f_R when $\zeta > \zeta^*$. Minimization of f then leads to

$$\psi = \nu_{\perp} = \zeta/(2-\zeta), \quad \nu_{\|} = 1/(2-\zeta). \tag{14}$$

Thus for $\zeta > \zeta^*$ the complete wetting exponents should depend only on ζ. For *random fields* and $d=3$ one has $\zeta = \frac{2}{3}$ by (5) and thus the *universal value* $\psi = \frac{1}{2}$ for $\sigma > 2$ (which turns out to include short-range forces). The best available estimate for *random bonds* when $d=3$ is[8] $\zeta \simeq 0.4_0$ which implies $\psi \simeq 0.25$; certainly, as mentioned, we expect $\zeta < \frac{2}{3}$ for $d=3$ so that the interface should unbind more rapidly under random fields than with random bonds.

These heuristically based results for complete wetting are fully confirmed by a perturbative treatment of the interface Hamiltonian (3) along the lines of Ref. 9a. The technical details are somewhat involved and will be presented elsewhere.[15] Both approaches can be applied to *critical wetting transitions.* In this case three regimes are found: (i) a *mean field* (MF) regime for $\zeta < \zeta^{\dagger} \equiv 2/(\sigma+2)$ where $\bar{l} \gg \xi_{\perp}$; (ii) a *weak fluctuation* (WFL) regime for $\zeta^{\dagger} < \zeta < \zeta^*$ where $\bar{l} \simeq \xi_{\perp}$; and (iii) a *strong fluctuation* (SFL) regime for $\zeta > \zeta^*$ where again $\bar{l} \simeq \xi_{\perp}$. In all regimes $\bar{l}$, $\xi_{\|}$, $\xi_{\perp}$ and the singular part of the free energy per unit area, f_s, can be described by scaling forms like

$$f_s(w,h) \approx |t|^{2-\alpha} W(h/|t|^{\Delta}), \tag{15}$$

where $t = w - w_c$. In the MF and WFL regimes one has $w_c = 0$ but the SFL regime should be characterized by $w_c < 0$. The exponents (for t variation) in the MF regime are

$$\alpha = 2-\sigma, \quad \Delta = \sigma+1, \quad \psi = 1, \quad \nu_{\|} = \tfrac{1}{2}(\sigma+2) = \nu_{\perp}/\xi. \tag{16}$$

In *both fluctuation regimes* (9) applies with $f_s \sim f_R$ so that $\alpha = 2(1-\nu_{\|}+\nu_{\perp})$; likewise, $\nu_{\|}^{\zeta} \equiv \nu_{\|}/\Delta$ and $\psi^c = \nu_{\perp}^c \equiv \nu_{\perp}/\Delta$, which determine the h divergences when $t=0$, are given by

$$\nu_{\|}^{\zeta}\zeta = \nu_{\perp}^c = \psi^c = \zeta/(2-\zeta); \tag{17}$$

compare with (14). The gap exponent in the WFL regime is found to be

$$\Delta = (2-\zeta)/[2-(\sigma+1)\zeta], \tag{18}$$

which, along with α, $\nu_{\|}$ and $\nu_{\perp}$, diverges when $\zeta \to \zeta^*-$, so signaling the SFL regime. On the other hand, Δ cannot be found in the SFL regime by the arguments described since these rely on the assumption, self-consistently justified, that the transition remains at $w_c = 0$; but even in the pure case one finds[9] a shifted value, $w_c < 0$, in the SFL regime. An analogous shift is, thus, to be expected in the presence of randomness leading to new SFL thermal exponents (although the SFL h exponents $\nu_{\|}^{\zeta}$, etc., for $t \geq 0$ should remain the same as in the WFL regime).

In a somewhat speculative vein one may, for *short-range forces* in $d=2$, appeal to random-walk ideas and the necklace model.[3] This indicates[15,16] $\nu_{\|} = 1/(1-\zeta)$ and so from $\alpha = 2(1-\nu_{\|}+\nu_{\perp})$ one finds $\alpha = 0$ independent of ζ. (Indeed, by analogy with the pure case in $d=2$, we expect this to be valid for all $\zeta > \zeta^*$.) The gap exponent now follows from $\Delta = \nu_{\|}/\nu_{\|}^{\zeta} = 2-\alpha-\nu_{\perp}$ yielding $\Delta = (2-\zeta)/(1-\zeta)$. Finally, for *random bonds* (6) leads explicitly to

$$\bar{l} \sim \xi_{\perp} \sim |t|^{-2}, \quad \xi_{\|} \sim |t|^{-3} \quad (d=2). \tag{19}$$

This power law for l and the result $\alpha = 0$ have also been found recently by Kardar[17] who used a replica technique.

For $d > 2$ we have not yet determined Δ (or α). One might contemplate Monte Carlo simulations but relaxation to equilibrium is likely to be slow.[18] Numerical renormalization-group methods may prove fruitful. Indeed, in studies[15] using Wilson's approximate renormalization group for pure systems[19] a nontrivial ($w_c < 0$) SFL fixed point has been found where both repulsive and attractive parts of the wall potential are irrelevant. In the WFL regime the repulsive part becomes relevant and $w_c = 0$; in the MF regime both parts are relevant. It seems likely that these conditions remain valid in the presence of randomness.

In summary, we have determined all exponents for complete wetting transitions in systems with quenched randomness. Our arguments extend also to critical wetting transitions except for $d > 2$ if only short-range forces act or if the roughness exponent, ζ, exceeds $\zeta^* = 2/(\sigma+1)$ when the forces decay as $1/r^{d+\sigma}$. The results are testable by experiment.

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[10]Our results are readily generalized to describe multicritical wetting transitions in which u changes sign but higher-order terms, not shown in (1) and (2), are then required.

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[12]M. E. Fisher and D. S. Fisher, Phys. Rev. B **25**, 3192 (1982); when $\zeta=0$, at $d=3$ for free interfaces, a logarithmic dependence on $L_\parallel$ arises. Our present analysis extends to commensurate-incommensurate transitions along the lines of this reference yielding $\bar{\beta}=\zeta/2(1-\zeta)$. This relation has also been given by T. Nattermann [Phys. Status Solidi (b) **119**, 209 (1983)], who considered random bond disorder. Unfortunately, the relation Nattermann proposed for $\zeta(d)$ is incorrect; consequently his quoted results for $\bar{\beta}(d)$ also fail. Where he predicts $\bar{\beta}(3)=\frac{1}{2}$ we find $\bar{\beta}(3)\simeq 0.3_3$. In addition, M. Kardar and D. R. Nelson [Phys. Rev. Lett. **55**, 1157 (1985)], have obtained the exact results $\bar{\beta}=1$ and $\alpha=0$ (for the specific heat) for the $d=2$ random bond commensurate-incommensurate transition. They then argued, via the $(\bar{\beta},\zeta)$ relation, that (6) should be exact; see also Huse, Henley, and Fisher, Ref. 8.

[13]See, e.g., M. A. Moore and A. J. Bray, to be published; D. S. Fisher, Phys. Rev. Lett. **56**, 416 (1986) (this issue).

[14]On physical grounds $l < \xi_\perp$ can be rejected.

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[16]For generalized random walks characterized by a roughness or wandering exponent ζ (<1) the probability of being at point x after n steps starting at the origin must, by normalization, satisfy $p_n(x) \approx n^{-\zeta}\Phi(x/n^\zeta)$. It follows that the probability of return to the origin for the *first time* on the nth step decays as $1/n^\phi$ with $\phi=2-\zeta$: See, e.g., Ref. 3, Eq. (2.12) *et seq.* Then, in the necklace model, which describes "beads" of interface, of constant tension Σ_0, wandering away from the wall separated by "strings" of bound interface held close to the wall, the longitudinal correlation or bead length exponent is given generally by $1/\nu_\parallel=\phi-1=1-\zeta$: See Ref. 3, Eq. (6.22). There is an associated singular term in the free energy, arising from Σ_0, with exponent $2-\alpha_0=\nu_\parallel$ [see Ref. 3, Eq. (6.18)], which satisfies hyperscaling. However, for quenched impurities this represents only a higher-order correction to the wandering free energy given by (9) (see also Kardar and Nelson, Ref. 12), which yields $2-\alpha=2(\nu_\parallel-\nu_\perp)$.

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[18]Heuristic arguments (Ref. 15) indicate that, when h (>0) is set equal to zero, the layer thickness grows with time, τ, as $(\ln\tau)^\theta$ with $\theta=\max(\zeta,\zeta^*)/(d-3+2\zeta)$.

[19]The approximation as used is exact to linear order in the potential. For $d=2$ it gives wetting exponents accurate to within a few percent.