Roughening at wetting: step free energy

LETTER TO THE EDITOR

Roughening at wetting: step free energy

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Abstract. Build-up of roughening fluctuations in an interface at the wetting (unbinding) transition can be measured by the free energy of a step-like formation due to a stepped substrate. For the 2D solid-on-solid model of line interface unbinding, exact calculations are presented. It is found that the step free energy vanishes linearly as the wetting transition is approached, as opposed to the well known quadratic vanishing of the interfacial binding energy (per unit length). Step–step interaction free energy is also calculated, for large step separation.

The geometrical features of an interface, such as roughness and step formation [1–4], are important for understanding a variety of interfacial phenomena (e.g. equilibrium crystal shapes). A distinction between rough and smooth interfaces can be made by considering the excess step free energy, f_s, the vanishing of which indicates the interfacial roughness.

It has been well established (e.g. [5]) that fluctuating (unbound) interfaces in two-dimensional Ising-type systems are rough for all temperatures $0 < T < T_c$, i.e. $f_s = 0$ for such interfaces. An interface with a step, which is at the same time bound to a substrate due to substrate interactions, will have $f_s > 0$. Consequently, the step free energy of a bound interface should vanish as the unbinding (wetting) transition is approached. Abraham and Newman [6] recently considered the three-dimensional model of wetting with a simultaneous wetting–roughening transition. In their model the two-dimensional interface delocalises and becomes rough at the same temperature [6, 7].

In this work we investigate the behaviour of the step free energy near the wetting transition by exact calculation for the lattice solid-on-solid (SOS) interface model in 2D [8–11]. (In a related work, in a different physical context, Levi and Tosatti [12] used mean-field theory to analyse the formation and roughening for steps on solid-liquid interfaces. A related Monte Carlo calculation has also been performed [13].) A step-like formation in the interface can be introduced, e.g. by the appropriate choice of boundary conditions which pin the interface ends at different heights [8, 14–16]. However, for interfaces near walls, this is not the most convenient method since too many geometrical features are involved. Instead, we consider an interface attracted to a *stepped substrate* by a short-range potential. For low enough temperatures such an interface is bound to the substrate, and its shape follows that of the stepped substrate.

Consider a square lattice of Ising spins below the critical temperature T_c, with boundary spins fixed to have an interface separating the predominantly + from predominantly − regions. The boundary has a step of one lattice spacing, as shown in figure 1(*a*). Within the SOS model description of the interface [8, 14], the interfacial
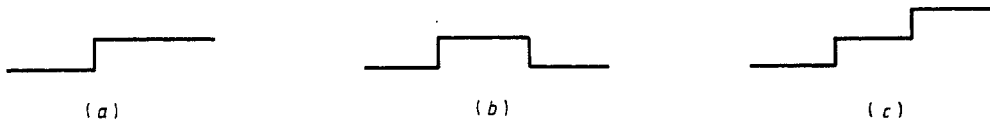
(a)   (b)   (c)

Figure 1. Single- and two-step substrates.

energy is given by

$$H/k_B T = \sum_y [\, U|n_y - n_{y-1}| + (U - W\delta_{1n_y}) \,].$$ (1)

Here $U > 0$ represents the surface tension contribution while the 'contact' pinning potential $W > 0$ describes the short-range substrate attraction. Note that the connection between the full Ising model and the SOS model specified by (1) can be established at low temperatures if we take $U = 2K$ and $W = 2(1-a)K$, where K is the nearest-neighbour coupling constant and $a = (U - W)/U$ is the parameter $(0 < a < 1)$ which specifies the modified substrate interactions. The integer distances $n_y = 1, 2, 3, \ldots$ measure the displacements of the interface from the substrate. In what follows we will consider the restricted SOS model where $|n_y - n_{y-1}| = 0, 1$. It is convenient to introduce the notation $0 < u \equiv \exp(-U) < 1$ and $w \equiv \exp(W) > 1$. The thermodynamic behaviour of this model is obtained in the usual manner [14] from the symmetric transfer matrix T with elements

$$T_{nm} = u^{|n-m|} w^{(\delta_{1n} + \delta_{1m})/2} (\delta_{0,|n-m|} + \delta_{1,|n-m|}).$$ (2)

The method of solution of the eigenproblem for this matrix is well known. We first recall briefly the solution in the case of a flat substrate (no steps) [14].

The transfer matrix eigenvector for the discrete spectrum has the form $g_n \propto \gamma^n$ and corresponds to the largest eigenvalue $\lambda_1 = 1 + u(\gamma + 1/\gamma)$. Introducing the notation $1/u = 1/u_c - wt/(w-1)$, with $u_c = (w-1)/(2-w)$, the eigenvalues can be expressed in the form $\lambda = 1 + 2u + 2u\varepsilon$. It turns out that t measures the displacement from the wetting transition point. Indeed, the largest eigenvalue is discrete, with $\varepsilon_1(t) > 0$, for $t < 0$. In this notation $\gamma = 1 + \varepsilon - \sqrt{\varepsilon(2+\varepsilon)}$, so that for $\varepsilon > 0$ we have $\gamma < 1$. The largest eigenvector is exponentially decaying and describes a 'non-wet' solution, i.e. an interface pinned to the substrate, with the wetting layer extending the distance $\xi_\perp \sim (-\ln \gamma)^{-1}$. This is obtained when $u < u_c$, i.e. $t < 0$. In addition, there is a continuum of delocalised solutions for $1 - 2u \leqslant \lambda_{\text{delocalised}} \leqslant 1 + 2u$ representing the 'wet' configurations. As $u \to u_c^-$ (i.e. $\gamma \to 1$), the interface unbinds via a second-order wetting transition. For small negative t, when the transition is approached from below, the singular part of the free energy behaves as $f_{\text{sing}} = -(w-1)t^2/w$. The parallel and perpendicular correlation lengths diverge as $\xi_\parallel \approx wt^{-2}/(w-1)$, $\xi_\perp \approx (-t)^{-1}$, as $t \to 0^-$. Above the wetting transition (for $t \geqslant 0$) we have $f_{\text{sing}} = 0$, $\xi_\parallel = \infty$, and $\xi_\perp = \infty$.

For a single step, the step free energy is defined by

$$f_s = -\ln(\mathcal{Z}_s / \mathcal{Z}_0)$$ (3)

where $\mathcal{Z}_s$ is the partition function for the substrate with a single step, while $\mathcal{Z}_0$ is that for the substrate with no step. The 'stepped' problem is solved by the same transfer matrix approach. At the step, a special transfer matrix must be considered, and it enters only via its matrix elements between the eigenvectors of T corresponding to λ_1. For the single-step free energy we get, after some algebra,

$$f_s = -\ln\left(\frac{w}{w\gamma^2 - \gamma^2 + 1} \frac{u(\gamma^2/\sqrt{w} + \gamma^2 + 1)(1 - \gamma^2) + \gamma + 2u\gamma^4}{\lambda_1} \right).$$ (4)
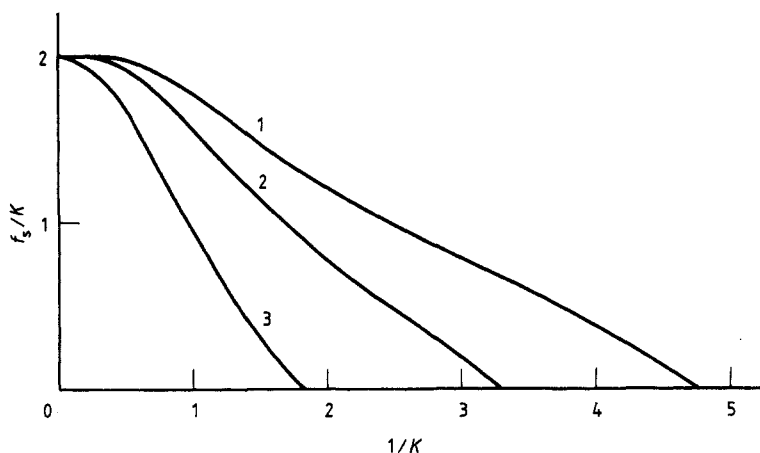
Figure 2. Variation of the single-step free energy f_s with temperature. The coupling constant $K = -\frac{1}{2}\ln u$ is proportional to the inverse temperature. The substrate interactions are specified by (1) $a = 0.2$, (2) $a = 0.5$ and (3) $a = 0.8$; see text.

The temperature dependence of s_s obtained from (4) is shown in figure 2. As the wetting transition is approached from below, we have $\gamma \to 1$ and the step free energy vanishes as $f_s \simeq (1 - 2/\sqrt{w} + 2/w\sqrt{w})(-t)$, where $t \to 0^-$. Above the wetting transition $f_s = 0$. Thus, at the transition the step free energy has a kink-like singularity. This should be contrasted with the interfacial binding free energy per unit length $|f_{\text{sing}}|$ which vanishes $\sim t^2$, as $t \to 0^-$.

Using similar methods, the free energy of *two* steps can be obtained in closed form. If the steps are separated by a large distance L, the step–step interaction energy has the exponential form $\sim \exp(-L/\xi_\parallel)$. This behaviour is valid for large step separations $L \gg \xi_\parallel$ and is controlled by the gap between the leading and next-to-leading transfer matrix eigenvalues. It is interesting to note that the results are identical for two-step substrates of both types shown in figures 1(*b*) and 1(*c*). One can likewise obtain the interaction energy for three steps in a closed form. However, both two- and three-step results for all separations are expressed in terms of hypergeometric functions and are not particularly illuminating.

In summary, we have analysed the behaviour of the step free energy of an interface below and on approach to the wetting (unbinding) transition in 2D. We found that the step free energy vanishes linearly at the wetting transition.

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