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The roughening transition of vicinal surfaces

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Abstract. Facetting of a vicinal surface is due to an arrangement of parallel primary steps which is commensurate with the substrate in plane periodicity (for instance one step every pth atomic row). It was shown by [4] that such a locking requires an interaction between steps together with a finite step stiffness. But this early approach only reveals part of the story, as it is limited to sharp solid-vacuum interfaces in which thermal excitation of energetically expensive kinks controls all fluctuations. In this paper the problem is taken afresh in a language which applies equally well to "soft" interfaces, with important changes in the conclusions.

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The roughening transition of a regular facet $z = 0$ is a compromise between the capillary energy of the interface and a periodic pinning potential with a period a along the normal z axis. At low temperatures small terraces are bounded by sharp steps. Beyond a critical temperature T_{R} these terraces coalesce, and steps span the whole width of the interface, which becomes rough. Such a transition has been widely studied [2,3]: it is dual to a $2d$ (X, Y) model (the role of low and high temperatures are interchanged). A similar facetting occurs for vicinal surfaces, in which a regular array of parallel steps with distance d acts to tilt the interface. Although in the same universality class as for a regular facet, such a transition is somewhat different, as it corresponds to a *commensurate* arrangement of d with the lattice spacing b along the plane. That problem was studied long ago [4] in the case of solid-vacuum interfaces, for which steps and kinks are essentially atomic entities. The step energy then dominates everything and the roughening temperature T_{R} is close to the kink energy ε within logarithmic corrections. The situation is different for broad steps as befits a solid-liquid interface. We take that problem afresh, using the same approach for both limits, and we show that T_{R} rapidly decreases as d grows. We thus complement the pioneering work of [4].

1 Properties of a planar facet

They were discussed long time ago, for instance by the author in [1]. Consider the (100) facet of an orthorhombic crystal. In a first approximation we ignore the periodicity in the (x, y) plane of the interface: the crystal is a stack of structureless plates. The lattice spacing in the normal z direction is a. We describe the surface distortions within a simple continuous model $z(x, y)$, corresponding to an energy (at finite temperature "energy" means "free energy")

$$E = \int \mathrm{d}x\, \mathrm{d}y \left[\frac{\gamma}{2}\,(\mathrm{grad}\ z)^2 + V \cos\frac{2\pi z}{a}\right] \tag{1}$$

γ is a surface tension, V a potential that pins the surface onto crystal planes. We assume that V is small, as might be the case at a solid-liquid interface. At zero temperature T, such a model allows for "solitons" that connect planar regions $z = 0$ and $z = a$: these are the *crystal steps* of the facet, with a width $\xi_0 \approx a\sqrt{\gamma/V}$ and an energy per unit length $\beta_0 \approx a\sqrt{\gamma V}$. Note that $\beta_0\xi_0 \approx \gamma a^2$. At this stage β does not depend on the azimuth φ of the step in the (x, y) plane.

For an unpinned surface ($V = 0$), thermal fluctuations follow from equipartition of each Fourier component, $\overline{z_k^2} = T/\gamma k^2$. The net fluctuations of the local amplitude z are Gaussian, given by

$$\overline{z^2} = \frac{1}{4\pi^2}\int 2\pi k\, \mathrm{d}k \frac{T}{\gamma k^2} = \frac{T}{2\pi\gamma}\mathrm{Log}\frac{L}{\xi}\cdot \tag{2}$$

The upper and lower cutoffs are respectively the width L of the facet and the step width ξ. When the periodic potential V is restored, it couples fluctuation modes with different k – hence the difficulty. The *roughening transition* at $T = T_R$ separates a high temperature "rough" state in which fluctuations of z diverge logarithmically, from a low temperature facetted state in which they are bounded. As shown in [1], a very simple argument yields T_{R} in lowest order in V: we need only calculate the *first order* average pinning energy U of an $L \times L$ square, which requires the *zeroth order* fluctuations of z:

$$U = V L^2 \, \overline{\cos \frac{2\pi z}{a}} = L^2 V \, \exp\left[-\frac{2\pi^2 \overline{z^2}}{a^2} \right] \cdot$$

Using (2), we obtain

$$U = V \, L^2 \left(\frac{\xi}{L} \right)^{\pi T / \gamma a^2} \cdot$$

Hence two situations:
(i) if $T > \frac{2}{\pi} \gamma a^2$, the power of L is negative: pinning is less and less relevant as the scale L grows, the surface is macroscopically free, hence rough.
(ii) if $T < \frac{2}{\pi} \gamma a^2$ the power is positive: pinning is more and more efficient. Fluctuations stop when $U \approx T$, which defines a characteristic length $L \approx \xi$ – the width of the crystal step.

The roughening transition occurs at

$$T_{\mathrm{R}} = \frac{2}{\pi} \gamma a^2. \tag{3}$$

Such a naive calculation is only exact in first order in V. It holds in all cases if γ is taken to be the surface *free energy at* T_{R} instead of the original $T = 0$ energy (in the renormalization approach of Kosterlitz and Thouless, fixed point properties correspond to $V = 0$). For weak pinning fancy methods are not necessary in order to find T_{R} – in contrast they are crucial in finding critical behaviour *near* the transition.

2 Facetting of a vicinal surface

We now tilt the interface: the normal stays in the (z, x) plane and it is rotated by a small angle θ. We denote by (x, y, z) coordinates referred to the crystal planes, by $(\overline{x}, y, \overline{z})$ those referred to the average surface. Well separated steps parallel to the y axis appear if $\theta \ll a/\xi$: we restrict ourselves to such a *vicinal* regime. The step distance along the x axis is d, such that $\mathrm{tg}\theta = a/d$. The surface energy per unit length dx may be written as

$$E(n) = \gamma_0 + \beta n + E_{\mathrm{int}}(n)$$

$n = 1/d$ is the step density, γ_o the perfect facet surface energy, β the step energy, E_{int} their interaction, whatever their origin (entropic, elastic, electrostatic...). All known mechanisms yield a $1/d^2$ repulsion: we thus write $E_{\mathrm{int}}(n) = \lambda n^3$, where λ is an *ad hoc* coefficient. Since the surface length $\mathrm{d}\overline{x} = \mathrm{d}x / \cos\theta$, it follows that the surface energy of the vicinal surface is $\gamma(\theta) = E(n) \cos\theta$. All the physics lies in $E(n)$ – for instance the equilibrium shape.

A vicinal surface is always rough if there is no periodicity inside the crystal planes: for such a stack of structureless plates steps can slide freely along the interface. Whenever a step sweeps by a given point M, the height shifts by $\pm a$, hence random fluctuations that produce the logarithmic divergence of a free surface (albeit with a much reduced amplitude). The only way to avoid roughness is to lock the steps onto an underlying periodicity in the x direction: a facetted state is then a *commensurate arrangement of steps*, arising from a combination of periodicity and step interactions. The roughening transition is the loss of that commensurability due to thermal fluctuations. We consider only the very simplest case of a $(1, 0, p)$ facet: a step appears every pth row in the x direction, so that the step distance $d = pb$, where b is the lattice spacing along the x axis. Assuming $b \neq a$ allows a clear identification of the roles played by the two periodicities. Our goal is to find the roughening temperature $T_{\mathrm{R}}(p)$ of such a higher order facet using the same naive argument introduced for the original $(0, 0, 1)$ facet. In that way we do not use specific details of the commensurate structure: the only information we need is the "stiffness" γ_{eff} of the vicinal surface, and the "period" a_{eff} along the normal $\overline{x}$ to the real surface. Using (3) we obtain at once $T_{\mathrm{R}}(p)$.

It is clear that a vicinal surface is anisotropic. Let us consider a fluctuation $\overline{z}(\overline{x}, y)$ with wave vector (k_x, k_y): the corresponding cost in energy may be written as

$$\mathrm{d}U = \frac{1}{2} \left[\widetilde{\gamma}_x k_x^2 + \widetilde{\gamma}_y k_y^2 \right] \overline{z}^2 \, \mathrm{d}\overline{x}$$

$\widetilde{\gamma}$ is the effective *surface stiffness* that controls surface deformations. Fluctuations with a wave vector k_x perpendicular to the step correspond to a *compression wave* of the latter: $\widetilde{\gamma}_x$ is due only to step interactions, according to

$$\mathrm{d}U = \frac{1}{2} E''(n) \;\; \delta n^2 \, \mathrm{d}x = \frac{1}{2} E'' \, \frac{\delta\theta^2}{a^2 \cos^3\theta} \, \mathrm{d}\overline{x}.$$

Equating the two expressions of δU yields

$$\widetilde{\gamma}_x = \frac{6\lambda \tan\theta}{a^3 \cos^3\theta} \cdot \tag{4}$$

In contrast fluctuations with wave vector k_y correspond to an *undulation wave* of steps, with three distinct effects:
(i) Steps are *lengthened*, by a factor

$$\left[1 + \frac{1}{2} \left(\frac{\partial \delta u}{\partial y} \right)^2 \right]$$

where $\delta u(y)$ is the local displacement of the steps along the x axis.
(ii) They are *rotated* by an angle $\delta\phi = \partial \delta u / \partial y$, which in turn affects their energy $\beta(\phi)$ (periodicity in the (x, y) plane means loss of rotational invariance: the step parameters β and λ depend on the azimuthal angle ϕ). The joint energy cost of lengthening and rotation may be written as

$$\mathrm{d}U = \frac{1}{2} \widetilde{\beta} \, k_y^2 \, \delta u^2 n \, \mathrm{d}x$$

where $\widetilde{\beta} = \beta + \beta''$ is the "step stiffness", which must be positive for the step to be stable. Strictly speaking the single step energy β should be replaced by the full energy

per step, E/n, which includes the interaction with neighbours: for simplicity we assume that n is small enough for that correction to be negligible.
(iii) Finally the distance between steps is reduced from d to $d\cos\delta\phi$, which affects their interaction. But we just neglected that interaction energy when compared to the bare β: in order to be consistent we should also ignore the correction due to δd. Note that including these effects is straightforward if needed!

In order to transform these data into a $\widetilde{\gamma}_y$, we note that each step which sweeps by a given x raises z by a, from which we infer $\delta z = na\,\delta u$. Since $\mathrm{d}U$ is also

$$\mathrm{d}U = \frac{1}{2}\widetilde{\gamma}_y k_y^2 \delta\overline{z}^2\,\mathrm{d}\overline{x} = \frac{1}{2}\widetilde{\gamma}_y k_y^2 \delta z^2 \cos^2\theta\ \frac{\mathrm{d}x}{\cos\theta}$$

we finally obtain

$$\widetilde{\gamma}_y = \frac{\widetilde{\beta}}{a\,\sin\theta}\cdot \tag{5}$$

What matters for us is the mean square fluctuation of $\overline{z}$ in the absence of inplane periodicity

$$\overline{z^2} = \frac{1}{4\pi^2}\int \mathrm{d}k_x\mathrm{d}k_y \frac{T}{\gamma_x k_x^2 + \gamma_y k_y^2}\cdot$$

Stiffness only enters through the combination

$$\gamma_{\mathrm{eff}} = \sqrt{\gamma_x\gamma_y} = \frac{\sqrt{6\lambda\widetilde{\beta}}}{a^2\cos^2\theta}\cdot \tag{6}$$

The results (4) to (6) are well known (see for instance [1]): we rederive them in order to emphasize the underlying physics. Note that γ_{eff} is nearly constant for a small tilt angle θ: the large variations of γ_x and γ_y cancel out.

We finally need a_{eff}: by definition it is the smallest distance along the $\overline{z}$ axis after which the same surface energy is recovered. It corresponds to a translation by a lattice spacing b in the x direction, not along the z axis. It follows that

$$a_{\mathrm{eff}} = b\sin\theta = \frac{a\cos\theta}{p}\cdot \tag{7}$$

Using (3) we obtain a very simple result for the roughening temperature

$$T_{\mathrm{R}} = \frac{2}{\pi}\,\frac{\sqrt{6\lambda\widetilde{\beta}}}{p^2}\cdot \tag{8}$$

That expression (8) is the central result of this paper. It relies on two approximations, one minor (corrections to λ and $\widetilde{\beta}$ can easily be included), the other one more fundamental (we use zero temperature properties instead of fixed point quantities at T_{R}). Basically we assume that scaling does not renormalize γ_{eff} too much. Let us emphasize again that (7) and (8) are the only new features in our argument: they build on existing knowledge.

Note that facetting depends crucially on step interaction, as surmised correctly by [4]: without interactions a given step would necessarily wander and commensurate locking could not occur! A question then comes naturally to one's mind: can a purely entropic repulsion lead to facetting? A positive answer would be surprising, since more entropy could hardly be expected to produce order! Indeed it cannot occur! The entropic repulsion has been calculated exactly by [5] (the original calculation of [6], using a mapping on a free fermion gas, is off by a factor 2). One thus finds

$$\lambda = \frac{\pi^2 T^2}{6\widetilde{\beta}}\cdot$$

When inserted into (8) that would lead to (9)

$$T_{\mathrm{R}} = T\frac{2}{p^2} \tag{9}$$

(note that the step stiffness $\widetilde{\beta}$ disappears), a condition that can never be met for the large p of a vicinal surface. A standard roughening transition triggerred by entropic step interaction is thus impossible. only genuine mechanical interactions can do the job, as shown by [7].

3 Comparison with the results for solid vacuum interfaces

According to (8), T_{R} goes to 0 as the index of the vicinal surface grows. Such a conclusion looks dramatically different from that of [4], who claim that T_{R} is always close to the kink energy ε: why? The answer to that question sits in the stiffness parameter $\widetilde{\beta}$. While the elastic interaction λ does not depend much on the nature of the interface, the stiffness $\widetilde{\beta}$ is much larger for the narrow steps of a vacuum interface than it would be for the broad steps of a liquid interface. Qualitatively, the only way to make a step wander is to create kinks, and sharp kinks cost energy! The resulting Boltzmann factor leads to a fast increase of $\widetilde{\beta}$ at low temperatures, which dominates everything else.

In order to make that handwaving argument precise, we first define kinks and we calculate the step stiffness directly. A tilted single step develops localized kinks, who have an energy ε of atomic scale. The kink width ζ along the step is such that $\varepsilon\zeta \approx \beta b^2$ (in an atomic picture ζ is the lattice spacing c along the y axis). At any finite temperature there exists a finite density of kinks

$$n_{\mathrm{K}} = \frac{\exp\left(-\varepsilon/T\right)}{\zeta}\cdot$$

Two situations may then hold:
(i) $T \gtrsim \varepsilon$: thermal kinks are numerous, the step moves freely. The anisotropy of $\beta\left(\phi\right)$ is not dramatic and $\widetilde{\beta}$ is comparable to the step energy β. The result (8) should then hold as such.
(ii) $T \ll \varepsilon$: step fluctuations depends on the displacement of a few kinks and the step is far stiffer. $\widetilde{\beta}$ is easily found calculating the step correlation function

$$G\left(y\right) = \overline{\left[x\left(y\right) - x\left(0\right)\right]^2}$$

for large y in two ways. On a macroscopic scale

$$G=\frac{1}{\pi}\int_0^{\infty}\mathrm{d}k\frac{T}{\widetilde{\beta}k^2}2\left(1-\cos ky\right)=\frac{T\,y}{\widetilde{\beta}}\cdot$$

On the kink scale, kinks are of either sign, leftward or rightward, and step fluctuations are due to a local excess of kinks of one type. A length y of step contains $N=n_K y/c$ kinks, and standard combinatorics yields $G\left(y\right)=Nb^2$. It follows that

$$\widetilde{\beta}=\frac{Tc}{b^2}\exp\left(\varepsilon/T\right). \tag{10}$$

Carrying (10) into (8) we see that the roughening temperature is a solution to

$$\exp\left(\varepsilon/T\right)=\frac{\pi^2}{24}\,\frac{p^4b^2T}{\lambda\,\zeta}\cdot \tag{11}$$

That should be compared with the result [4] which reads

$$\exp\left(\varepsilon/T\right)=\frac{2T}{W_p} \tag{12}$$

W_p is the second derivative of the step interaction energy on a length ζ

$$W_p=\lambda\zeta\left[\frac{1}{\left(d+b\right)^2}+\frac{1}{\left(d-b\right)^2}-\frac{2}{d^2}\right]\approx\frac{6\lambda\zeta}{p^4b^2}\cdot$$

In practice the two results agree in that limit, but for numerical factors!

In such an “atomic limit”, what matters is the value of ε. A roughening temperature cannot be much smaller than ε: if it were the stiffness $\widetilde{\beta}$ would increase exponentially, thereby blocking fluctuations. In the opposite limit of a small ϵ the stiffness does not vary much with temperature: the behaviour predicted by (8) is then clearly apparent (if p increases one always returns to the strong coupling limit). It is interesting, however, to note that (8) is always valid: the $1/p^2$ behaviour is just hidden when $\widetilde{\beta}$ is calculated in the strong coupling limit!

Our conclusion is that the roughening transition of vicinal surfaces provides a useful test of step interactions, with one caveat: the result of [4] holds only for sharp vacuum interfaces, and it should not be used inconsiderately.

References

1. P. Nozières, in *Solid far from equilibrium*, Lectures of the Beg Rohu Summer School, edited by C. Godrèche (Cambridge University Press, 1991).
2. S.T. Chui, J.D. Weeks, Phys. Rev. B **14**, 4978 (1978).
3. P. Nozières, F. Gallet, J. Phys. **48**, 353 (1987).
4. J. Villain, D.R. Grempel, J. Lapujoulade, J. Phys. F **15**, 809 (1985).
5. Y. Akutsu, N. Akutsu, T. Yamamoto, Phys. Rev. Lett. **61**, 424 (1988).
6. C. Jayaprakash, C. Rottman, W.F. Saam, Phys. Rev. B **30**, 6549 (1984).
7. E. Le Goff, L. Barbier, L. Masson, B. Salanon, Surf. Sci. **432**, 139 (1999).