Available online at www.sciencedirect.com
SCIENCE DIRECT
Surface Science 598 (2005) L355–L360
SURFACE SCIENCE
www.elsevier.com/locate/susc

Surface Science Letters

A facet is not an island: Step–step interactions and the fluctuations of the boundary of a crystal facet

Alberto Pimpinelli [a,b,*], M. Degawa [a], T.L. Einstein [a], Ellen D. Williams [a]

[a] Department of Physics, University of Maryland, College Park, MD 20742-4111, United States
[b] LASMEA, UMR 6602 CNRS/Université Blaise Pascal—Clermont 2, F-63177 Aubière cedex, France

Received 7 October 2004; accepted for publication 28 September 2005
Available online 26 October 2005

Abstract

In a recent paper [P.L. Ferrari, M. Prähofer, H. Spohn, Phys. Rev. E 69 (2004) 035102(R)], the scaling law of the fluctuations of the step limiting a crystal facet, as a function of the facet size, was computed. Ferrari et al. use rigorous, but physically rather obscure arguments. Approaching the problem from a different perspective, we rederive more transparently the scaling behavior of facet edge fluctuations as a function of time.

Keywords: Single-crystal surfaces: curved surfaces; Stepped surfaces; Surface structure; Morphology

In a recent very interesting, stimulating paper [1], Ferrari et al. have computed the scaling of equilibrium fluctuations of an atomic ledge bordering a crystalline facet. These authors derive an intriguing exact result, concerning how the step-edge width w scales as a function of the linear size L of the facet. This result differs from what is expected, and actually found, for the step bordering a 2D island, which performs a random walk so that $w \sim L^{1/2}$. Ferrari et al. find instead $w \sim L^{1/3}$. They prove that the origin of the unusual $L^{1/3}$ scaling lies in the step–step interactions between the facet ledge and the neighboring steps.

Ferrari et al.'s formidable calculation is based on the use of free fermions, transfer matrices, random-matrix properties, Airy functions, and specific models; as a purely static result, it does not address the question of the time behavior of step fluctuations.

In this letter, we compute the time scaling of step-edge fluctuations using two approaches. First, we address the problem from the perspective of simple scaling arguments, using the exact result of

* Corresponding author. Address: LASMEA, UMR 6602 CNRS/Université Blaise Pascal—Clermont 2, F-63177 Aubière cedex, France. Tel.: +33 473 405159; fax: +33 473 407340.
E-mail addresses: pimpinel@lasmea.univ-bpclermont.fr (A. Pimpinelli), einstein@umd.edu (T.L. Einstein).
URL: http://www2.physics.umd.edu/~einstein (T.L. Einstein).

0039-6028/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2005.09.023

Ferrari et al. as a starting point. Second, we derive a continuum-equation description of the step bordering a crystal facet. Then, using simple power counting we rederive Ferrari et al.'s result, as well as the power-law scaling of edge fluctuations with time.

The most easily accessible experimental quantity is the step autocorrelation function $G(t) = \langle [x(t) - x(0)]^2 \rangle$, which is expected to have a power-law behavior at short times: $G(t) \sim t^{2\beta}$. The value of exponent β depends on the atomistic processes responsible for the fluctuations of the step, but also on the position of the step with respect to a crystal facet, as we prove here.

We start from Ferrari et al.'s result that $w \sim L^{1/3}$. We then use Pimpinelli et al.'s argument [2] for finding the time scaling. The argument goes like this. Consider a portion of step of length ℓ. Because of several transport processes (notably, terrace diffusion and step-edge diffusion), $N(t)$ atoms continually enter and leave this step region during any time interval t. On average, the net flux through the region vanishes, but the instantaneous number fluctuates around the vanishing mean, the typical size of the fluctuation δN being of order $\sqrt{N(t)}$. If Ω is the atomic area, we can estimate the size w of a protrusion along the step edge (the amplitude or width of a typical step fluctuation of length ℓ) from $w \times \ell \approx \Omega\sqrt{N(t)}$. We now have to estimate $N(t)$. If L_s is a diffusion length in the direction perpendicular to the step edge, then ℓL_s is the surface area feeding the fluctuation. Calling c_{eq} the equilibrium particle density, the number of atoms diffusing to and from the step edge during time t is proportional to the number of atoms in the region feeding the step, $c_{eq}\ell L_s$, and to the fraction of time the atoms spend in this region, t/τ^*. The characteristic time τ^* depends on the specific transport process (see below). Then, as in Ref. [2]:

$$N(t) \approx \frac{c_{eq}}{\tau^*} \ell L_s t. \tag{1}$$

Specifically, we consider the two primary examples: (i) conservative mass transport (step-edge diffusion); (ii) non-conservative mass transport (attachment–detachment to/from the step edge, with fast terrace diffusion).

If mass transport takes place through step-edge diffusion along a portion of step of size ℓ, then $1/\tau^* \approx D_e/\ell^2$, where D_e is the edge diffusion coefficient. Also, L_s is of order the lattice spacing a in this case. Thus, Eq. (1) becomes

$$N(t) \approx t c_{eq} D_e a/\ell. \tag{2}$$

Letting $\delta N = \sqrt{N}$, we now find

$$w^2\ell^2 \approx (\delta N)^2 \approx N, \tag{3}$$

or

$$w^2 \approx t c_{eq} D_e a/\ell^3. \tag{4}$$

We now need one more equation relating w, t and ℓ. This is provided by the scaling relation

$$w \sim \ell^\alpha,$$

that holds at equilibrium, with $\alpha = 1/2$ for an isolated (large, see below) island or for an isolated step [2]. The result of Ferrari et al. shows that it also holds with $\alpha = 1/3$ for the edge of a facet. Then, letting $w \sim \ell^{1/3}$ yields

$$t \sim \ell^{11/3}, \tag{5}$$

or

$$w \approx t^{1/11}, \tag{6}$$

so that

$$G(t) \sim t^{2/11}, \tag{7}$$

for a crystal facet fluctuating through step edge diffusion. This is to be compared with $G(t) \sim t^{1/4}$ for a straight step or an isolated (large) 2D island [2].

If mass transport takes place through detachment–attachment of atoms from/to the step edge, then $1/\tau^* \approx k$, with k an appropriate kinetic coefficient. If surface diffusion is fast, the step effectively exchanges atoms with a "2D adatom vapor" on the surface. Then, $L_s \approx a$, and Eq. (1) yields

$$w^2\ell^2 \approx k c_{eq} \ell a t. \tag{8}$$

Using $w \sim \ell^{1/3}$ yields $\ell^{5/3} \sim t$, and eventually

$$w \sim t^{1/5}, \tag{9}$$

so that

$$G(t) \sim t^{2/5}, \tag{10}$$

for a crystal facet fluctuating through detachment–attachment from and to its edge. This is to be compared with $G(t) \sim t^{1/2}$ for a straight step or an isolated 2D island [2].

We will now approach the same problem from a different perspective. With appropriate approximations, we describe the motion of the edge of a crystal facet through a Langevin equation. In polar coordinates, the facet radius (the position of the edge) in the direction θ and at time t, $r(\theta,t)$ satisfies the stochastic differential equation

$$\frac{\partial r(\theta,t)}{\partial t} = f[r(\theta,t), \partial r/\partial\theta] + \eta(\theta,t). \tag{11}$$

The function f describes the deterministic relaxation of the fluctuations, and $\eta(\theta,t)$ is a white noise, which can be conservative or non-conservative, according to the nature of the mass transport process.

To obtain the deterministic part f of the Langevin equation, we assume that the facet is delimited by a closed step of free energy per length $\beta(\theta)$ and that it sits over a second layer of fixed radius $R > r$. Neglecting step–step interactions and letting $r_\theta \equiv \partial r/\partial\theta$, the free energy of the facet reads

$$F = \int_0^{2\pi} \beta(\vartheta)\sqrt{r^2 + r_\theta^2}\,\mathrm{d}\theta, \tag{12}$$

where ϑ is the local direction of the step [3].

For simplicity and clarity, we consider an isotropic step free energy $\beta(\theta) = \beta$, and thus a circular facet. Then, it is straightforward to compute the excess chemical potential, with respect to a perfectly circular facet, which is given by the Gibbs–Thomson relation (see [4,5])

$$\delta\mu = \Omega\beta(\kappa - 1/\rho_0), \tag{13}$$

where the step curvature κ is

$$\kappa = \frac{r^2 - r r_{\theta\theta} + 2r_\theta^2}{(r^2 + r_\theta^2)^{3/2}}. \tag{14}$$

In order to study fluctuations around the average facet radius ρ_0, it is useful to introduce the new variable $\tilde{r}(\theta,t) = [r(\theta,t) - \rho_0]/\rho_0$. In terms of this variable, the excess chemical potential reads

$$\delta\mu = \frac{\Omega\beta}{\rho_0}\frac{(1+\tilde{r})(1+\tilde{r}-\tilde{r}_{\theta\theta}) + 2\tilde{r}_\theta^2}{[(1+\tilde{r})^2 + \tilde{r}_\theta^2]^{3/2}} - \frac{\Omega\beta}{\rho_0}. \tag{15}$$

Expanding around $\tilde{r} = 0$, we discard all terms in $\tilde{r}$, compared to 1, but we keep the lowest nonlinear terms in the derivative $\tilde{r}_\theta$. We obtain then

$$\delta\mu \approx \frac{\Omega\beta}{\rho_0}\left(-\tilde{r}_{\theta\theta} + \frac{1}{2}\tilde{r}_\theta^2\right). \tag{16}$$

Now that we have the chemical potential, we can model the fluctuations of the step edge as a Langevin equation. We present here two examples, corresponding to two different atomistic kinetic processes at the step edge. The first is attachment–detachment (AD), and the second is step-edge diffusion (SED). AD is conveniently thought of as a non-conserved dynamic process, with atoms "evaporating from" and "condensing into" the step edge. Accordingly, we write [4,5]

$$\frac{\partial\tilde{r}(\theta,t)}{\partial t} = -\frac{\Gamma_{\mathrm{AD}}}{k_{\mathrm{B}}T}\delta\mu(\tilde{r},\tilde{r}_\theta,\tilde{r}_{\theta\theta}) + \eta(\theta,t), \tag{17}$$

where Γ_{AD} is the attachment–detachment kinetic coefficient, and $\eta(\theta,t)$ is a gaussian white noise. Similarly for SED, we use conserved dynamics to represent atomic diffusion along the step edge. Accordingly, we write [4,5]

$$\frac{\partial\tilde{r}(\theta,t)}{\partial t} = \frac{\rho_0^2}{k_{\mathrm{B}}T}\frac{\partial^2}{\partial\theta^2}\delta\mu(\tilde{r},\tilde{r}_\theta,\tilde{r}_{\theta\theta}) + \eta_{\mathrm{C}}(\theta,t), \tag{18}$$

where Γ_{SED} is the step-edge-diffusion kinetic coefficient, and $\eta_{\mathrm{C}}(\theta,t)$ is a conserved gaussian white noise.

Putting Eq. (16) into Eq. (17) for AD kinetics we find

$$\frac{\partial\tilde{r}(\theta,t)}{\partial t} = \frac{\Gamma_{\mathrm{AD}}}{k_{\mathrm{B}}T}\frac{\Omega\beta}{\rho_0}\left[\frac{\partial^2\tilde{r}}{\partial\theta^2} - \frac{1}{2}\left(\frac{\partial\tilde{r}}{\partial\theta}\right)^2\right] + \eta(\theta,t). \tag{19}$$

Inserting Eq. (16) into Eq. (18) for SED kinetics we find

$$\frac{\partial\tilde{r}(\theta,t)}{\partial t} = \frac{\rho_0^2}{k_{\mathrm{B}}T}\frac{\Omega\beta}{\rho_0}\left[-\frac{\partial^4\tilde{r}}{\partial\theta^4} + \frac{1}{2}\frac{\partial^2}{\partial\theta^2}\left(\frac{\partial\tilde{r}}{\partial\theta}\right)^2\right] + \eta_{\mathrm{C}}(\theta,t). \tag{20}$$

Note that Eqs. (19) and (20) look like the Kardar–Parisi–Zhang (KPZ) [6] equation, and its conserved counterpart (the so-called Montreal model)

[7], respectively. However, the non-linear terms come from the equilibrium curvature of the interface here, while they are induced by non-equilibrium effects in the KPZ and montreal models. Should we expect to observe KPZ or Montreal exponents in the fluctuations of facets or islands? The question is rather subtle, as we discuss below. In fact, we will see that KPZ or Montreal exponents (see for instance Ref. [8]) are expected for the fluctuations of the edge of an island, if it is small enough. A facet, on the contrary, is expected to exhibit the exponents that we have computed in the first part of this Letter, which are neither KPZ nor Montreal.

Eqs. (19) and (20) represent, of course, limiting cases for a real crystal facet, since in general one expects step-edge diffusion and attachment–detachment to coexist. For the sake of simplicity, we will examine them independently, using scaling arguments to extract power-law behaviors.

In order to set the stage and to see how scaling arguments work, let us consider what happens with a straight step. In this case, a more appropriate description uses cartesian coordinates (x, y), y being parallel to the step edge, and $x(y)$ describing the step profile. Then, the fluctuations of the step edge obey a linear equation [4,5], which reads

$$\frac{\partial x(y,t)}{\partial t} = \frac{\Gamma_{\mathrm{AD}}\Omega\beta}{k_{\mathrm{B}}T}\frac{\partial^2 x}{\partial y^2} + \eta(\theta,t), \tag{21}$$

for attachment–detachment kinetics, and an equation equivalent to (20) for step-edge diffusion.

The equation is linear and can be solved. However, we will use it to show how the scaling argument works. Assume that the linear size ℓ along the step edge is dilated by a factor b, $\ell' = b\ell$ (we use here and throughout primed variables to denote rescaled quantities). Scaling implies that the width w of a fluctuation varies as $w \sim \ell^{\alpha}$, so that $w' = b^{\alpha}w$. The typical time needed to develop a fluctuation of size ℓ scales as $t \sim \ell^{z}$, so that $t' = b^{z}t$. The time derivative in Eq. (21) scales then as

$$\frac{\partial x'(y',t')}{\partial t'} = b^{\alpha-z}\frac{\partial x(y,t)}{\partial t}. \tag{22}$$

The second-derivative term scales as

$$\frac{\partial^2 x'(y',t')}{\partial y'^2} = b^{\alpha-2}\frac{\partial^2 x(y,t)}{\partial y^2}. \tag{23}$$

Equating Eqs. (22) and (23) yields $z = 2$. The scaling exponent α depends on the scaling behavior of the noise term, and this in turn depends on the problem one investigates.

If the step is isolated, the step edge should be treated as a 1D interface. Then, the noise term scales as

$$\eta'(y',t') = b^{-(1+z)/2}\eta(y,t). \tag{24}$$

Equating Eqs. (22) and (24) and using $z = 2$ yields

$$\alpha = 1/2. \tag{25}$$

The value 1/2 of the exponent α is characteristic of a random walk.

If the step is inside a train, as on a vicinal surface, then its fluctuations take on a 2D character. The noise term now scales as

$$\eta'(y',t') = b^{-(2+z)/2}\eta(y,t). \tag{26}$$

Equating Eqs. (22) and (24) and using $z = 2$ yields $\alpha = 0$. Indeed, the amplitude turns out to scale logarithmically, $w \sim \ln\ell$, in this case (cf. Ref. [9]).

We are now ready to analyze the scaling behavior of Eqs. (19) and (20). These equations are non-linear, and the non-linearity dominates the scaling.

It can be seen that the non-linearity comes from the curvature of the step edge (Gibbs–Thomson effect). What then is the difference between a facet and an island, implied by the title? The difference is indeed subtle. Contrary to the boundary step of a facet, an island edge is free to fluctuate, the amplitude w of its fluctuations being limited only by the size of the island. Because of the hindrance of neighboring steps, the fluctuations of a facet are constrained to smaller amplitudes than those of an island of comparable size. Note also that an island has to be small (compared to the capillary length $k_{\mathrm{B}}T/\beta$) in order for the non-linear term to become important. As shown by Krishnamachari et al. [10], the radius of an island has to be larger than a minimum value in order for the island to be stable. We will give more details elsewhere [11].

The conclusion is that the step edge bordering an island may have larger amplitude fluctuations than the edge of a facet, the latter being limited by the presence of the neighboring steps. As a con-

sequence, the noise terms scale differently for a facet and for an island, giving rise to different temporal and spatial scaling behaviors. Again w is the width of a step-edge protrusion of size ℓ. Proceeding as in Hentschel and Family [12], $S_\ell \approx \sqrt{w^2+\ell^2}$ is the length of the step edge. Of course, if the protrusion amplitude is small, $S_\ell \approx \ell$ (small amplitude fluctuations), and $S_\ell \approx w$ in the opposite case (large amplitude fluctuations). Assuming atoms are added (or subtracted) randomly to the step edge (either by attachment–detachment or by step-edge diffusion), the relative fluctuations of the length of the edge are just $\Delta S_\ell/S_\ell \approx 1/\sqrt{S_\ell}$. We will thus assume that the noise term in our stochastic equations scales as $1/\sqrt{S_\ell}$.

Consider first a facet fluctuating by attachment–detachment, Eq. (17). In this case, step fluctuations are limited in amplitude by neighboring steps. Noise scales then as

$$\eta'(y',t') = b^{-(1+z)/2}\eta(y,t). \tag{27}$$

Equating the time derivative to the noise term Eq. (27) yields

$$z = 2\alpha + 1. \tag{28}$$

The non-linear term $\tilde{r}_\theta^2$ scales as

$$\left(\frac{\partial \tilde{r}'}{\partial \theta'}\right)^2 = b^{2\alpha-2}\left(\frac{\partial \tilde{r}}{\partial \theta}\right)^2. \tag{29}$$

Equating Eq. (29) to the noise term Eq. (27) yields

$$4\alpha + z = 3. \tag{30}$$

From Eqs. (28) and (30) we finally get

$$\alpha = 1/3, \tag{31}$$

i.e. Ferrari et al.'s result

$$\tilde{r} \sim \ell^{1/3}. \tag{32}$$

The dynamic scaling of step fluctuations turns out to be what we computed previously: From Eqs. (28) and (32), e.g., we obtain

$$\alpha/z = \beta = 1/5, \tag{33}$$

which, recalling that $G(t) \sim t^{2\beta}$, coincides with Eq. (10).

Facet fluctuations driven by step-edge diffusion obey Eq. (20). The conserved noise term scales as

$$\eta'_C(y',t') = b^{-(3+z)/2}\eta_C(y,t). \tag{34}$$

The conserved non-linear term scales now as

$$\frac{\partial^2}{\partial \theta'^2}\left(\frac{\partial \tilde{r}'}{\partial \theta'}\right)^2 = b^{2\alpha-4}\frac{\partial^2}{\partial \theta^2}\left(\frac{\partial \tilde{r}}{\partial \theta}\right)^2. \tag{35}$$

Equating (34) and (35) yields

$$4\alpha + z = 5. \tag{36}$$

Equating the time derivative to the noise term Eq. (34) yields

$$2\alpha = z - 3. \tag{37}$$

Together Eqs. (36) and (37) yield

$$\alpha = 1/3, \quad z = 11/3, \tag{38}$$

and also

$$\beta = 1/11, \tag{39}$$

as derived above, Eq. (6).

As mentioned above, KPZ-like or Montreal-like exponents are expected to show up in the fluctuations of a small island edge, for non-conserved and conserved dynamics, respectively. In the latter case, fluctuations are not hindered, and the noise scales as

$$\eta'(\theta',t') = b^{-(\alpha+z)/2}\eta(\theta,t). \tag{40}$$

It is then straightforward to show that the scaling relations $\alpha + z = 2$ and $3\alpha = z$ follow, implying $\alpha = 1/2$ as for a random walk (cf. Eq. (25)), as well as

$$\beta = 1/3. \tag{41}$$

The prediction of KPZ-like exponents for the fluctuations of the step edge of an island is new. However, it clearly applies only to small islands for which the curvature is large. Otherwise, the same scaling as for a straight step is expected.

Acknowledgments

This work was supported by the NSF-funded MRSEC at University of Maryland. AP received travel funding from CNRS under the USA/CNRS 2005-07 grant. We acknowledge helpful communications from H. Spohn, H.P. Bonzel, and J. Krug.

References

[1] P.L. Ferrari, M. Prähofer, H. Spohn, Phys. Rev. E 69 (2004) 035102(R).

[2] A. Pimpinelli, J. Villain, D.E. Wolf, J.J. Métois, J.C. Heyraud, I. Elkinani, G. Uimin, Surf. Sci. 295 (1993) 143.

[3] $\vartheta = \theta - \arctan(r_\theta(\theta)/r(\theta))$, as derived in S.V. Khare, S. Kodambaka, D.D. Johnson, I. Petrov, J.E. Greene, Surf. Sci. 522 (2003) 75;
S. Kodambaka, S.V. Khare, V. Petrova, D.D. Johnson, I. Petrov, J.E. Greene, Phys. Rev. B 67 (2003) 035409.

[4] S.V. Khare, N.C. Bartelt, T.L. Einstein, Phys. Rev. Lett. 75 (1995) 2148;
S.V. Khare, N.C. Bartelt, T.L. Einstein, Phys. Rev. B 54 (1996) 11752.

[5] A. Pimpinelli, J. Villain, Physics of Crystal Growth, Cambridge University Press, Cambridge, 1998.

[6] M. Kardar, G. Parisi, Y.C. Zhang, Phys. Rev. Lett. 56 (1986) 889.

[7] T. Sun, H. Guo, M. Grant, Phys. Rev. A 40 (1989) 6763.

[8] E.g. A.-L. Barabási, H.E. Stanley, Fractal Concepts in Surface Growth, Cambridge University Press, Cambridge, 1995.

[9] N.C. Bartelt, T.L. Einstein, E.D. Williams, Surf. Sci. 276 (1992) 308.

[10] B. Krishnamachari, J. McLean, B. Cooper, J. Sethna, Phys. Rev. B 54 (1996) 8899.

[11] M. Degawa, A. Pimpinelli, T.L. Einstein, E.D. Williams, unpublished.

[12] H.G.E. Hentschel, F. Family, Phys. Rev. Lett. 66 (1991) 1982.