Effect of kink-rounding barriers on step edge fluctuations

Jouni Kallunki, Joachim Krug

Fachbereich Physik, Universität Essen, 45117 Essen, Germany

Abstract

The effect that an additional energy barrier E_{kr} for step adatoms moving around kinks has on equilibrium step edge fluctuations is explored using scaling arguments and kinetic Monte Carlo simulations. When mass transport is through step edge diffusion, the time correlation function of the step fluctuations behaves as $C(t) = A(T)t^{1/4}$. At low temperatures the prefactor A(T) shows Arrhenius behavior with an activation energy $(E_{det} + 3\epsilon)/4$ if $E_{kr} < \epsilon$ and $(E_{det} + E_{kr} + 2\epsilon)/4$ if $E_{kr} > \epsilon$, where ϵ is the kink energy and E_{det} is the barrier for detachment of a step adatom from a kink. We point out that the assumption of an Einstein relation for step edge diffusion has lead to an incorrect interpretation of step fluctuation experiments, and explain why such a relation does not hold. The theory is applied to experimental results on Pt(111) and Cu(100).

Key words: Models of surface kinetics, Atomistic dynamics, Surface diffusion, Stepped single crystal surfaces, Monte Carlo simulations *PACS:* 68.35.Fx, 05.70.Ln, 66.30.Fq, 81.10.Aj

1 Introduction

In thin film growth the detailed knowledge of the microscopic elementary processes is essential since the large scale morphology is determined by the competition between the nonequilibrium deposition flux and the different relaxation mechanisms [1]. Clear demonstrations of this are for example growth instabilities on high symmetry or vicinal crystal surfaces, which are known to produce self-organized nanoscale patterns [2,3]. In both cases, mound formation on singular [4] and step meandering on vicinal surfaces [5], the size of the structures is set by the relation between the time scales of deposition and relaxation kinetics [6]. Thus the knowledge of the relaxation kinetics opens a possibility to control the size of the structures by controlling the external parameters such as deposition rate and temperature. The most important elementary process on surfaces is the hopping of individual atoms. The motion of an adatom from one lattice site to another is a thermally activated process and takes place at rate

$$\Gamma_i = \Gamma_{i,0} \exp\left(-\beta E_i\right),\tag{1}$$

where $\beta = 1/k_B T$ is the inverse temperature, $\Gamma_{i,0}$ is an attempt frequency, and E_i is the activation energy of the process *i*. Thus knowledge of the activation energies gives access to the elementary rates. Unfortunately the activation energies are very rarely accessible by direct measurement; it is extremely difficult to follow a single atom diffusing on a surface and to extract activation energies from its trajectory. Thus one has to rely on measurements of mesoscopic quantities and try to compare these with theoretical predictions in order to extract the microscopic parameters. Examples of such an approach are the determination of the adatom diffusion barrier from the island density [7], the estimate of interlayer diffusion barriers from second layer nucleation experiments and mound shapes [8,9], and the extraction of activation energies for processes at step edges from the characteristic length scales of growth instabilities on vicinal surfaces [10–12].

An elegant method for measuring energetic and kinetic parameters of atomistic processes at steps exploits the time correlation function of equilibrium step fluctuations, see [13,14] for recent reviews. In this paper we revisit the theoretical basis of these experiments for the case of mass transport dominated by step edge diffusion, and take into account the possibility of a significant kink rounding barrier, which prevents adatoms migrating along a step from hopping around a kink. The kink-rounding barrier is the one-dimensional analog of the well-known Ehrlich-Schwoebel (ES) barrier [15] suppressing the inter-layer mass transport on crystal surfaces. It is worth noting that also a three-dimensional analog of the ES barrier, inhibiting atoms going around facet edges, has been observed [16]. The existence of the kink rounding barrier is still under debate; numerical calculations support its existence [17,18], but until now experimental observations are few [19,20]. If present, the kinkrounding barriers have great impact on the patterns formed under unstable epitaxial growth [11,21-25] as well as on the shape relaxation of islands and other nanostructures [26,27]. In this paper we show how kink-rounding barriers affect equilibrium step fluctuations, thus providing an alternative way of determining the barriers experimentally. In addition, in Sect.4 we clarify a misconception in the theory of step fluctuations which has lead to an incorrect data analysis in some cases.

2 Step fluctuations and the adatom mobility

On a vicinal surface the mono-atomic steps, separating high symmetry terraces, are not perfectly straight but wander due to thermal fluctuations. Here we will consider a situation where adatoms cannot detach from the steps, thus the only possible mass transfer process is migration of adatoms along the steps. The Langevin theory of step fluctuations then yields the expression [13,14]

$$C(t) \equiv \left\langle \left[\zeta(x,t) - \zeta(x,0) \right]^2 \right\rangle = a_{\perp}^2 \frac{\Gamma(3/4)}{\tilde{\gamma}\pi\beta\Omega^{1/2}} \left(2\sigma\tilde{\gamma}t \right)^{1/4} \tag{2}$$

for the time correlation function of the step edge position $\zeta(x, t)$ with the initial condition of a flat step, $\zeta(x, 0) \equiv 0$. Here $\tilde{\gamma}$ is the step stiffness, a_{\perp} the lattice spacing perpendicular to the step, Ω is the atomic area, $\Gamma(3/4) \approx 1.2254...$, and σ denotes the adatom mobility along the step edge. It is defined through the relation

$$j = -\sigma \partial_x \mu = \sigma \partial_x \Omega \tilde{\gamma} \partial_{xx} \zeta \tag{3}$$

between the mass current along the step and the chemical potential gradient driving it. In the last equality the Gibbs-Thomson relation has been used.

To make use of the expression (2) for the analysis of experimental data, the parameters $\tilde{\gamma}$ and σ of the continuum description must be expressed in terms of the rates of the elementary processes. This can be done exactly if the step is modeled as a one-dimensional solid-on-solid (SOS) surface with energy barriers proportional to the number of lateral bonds in the initial state (Arrhenius kinetics); see Sect.3 for a precise definition. In this case one obtains [28]

$$\sigma = \frac{a\Gamma_0\beta}{2}\exp\left(-\beta E_{det}\right) \tag{4}$$

and

$$\beta \tilde{\gamma} = a^{-1} (\cosh\left(\beta\epsilon\right) - 1), \tag{5}$$

where E_{det} denotes the energy barrier for detachment of a step atom from a kink site, the kink energy ϵ is the energy cost of creating a kink, a is the lattice constant parallel to the step, and Γ_0 is the attempt frequency, which is assumed to be the same for all processes. Since the detachment of a kink atom creates two kinks, within the Arrhenius model $E_{det} = E_{st} + 2\epsilon$, where E_{st} is the energy barrier for diffusion along the straight (unkinked) step. Figure 1 shows



Fig. 1. A schematic picture of a monoatomic step with the activation energies of the elementary processes.

a cartoon of a step displaying the relevant processes. The relation $\sigma \sim e^{-\beta E_{det}}$ has also been derived within a Kubo formalism [29,30].

Putting everything together yields

$$C(t)/a_{\perp}^2 = g \times \left(\frac{t}{\tau_{st}}\right)^{1/4} \tag{6}$$

where g is a numerical constant of order unity, and $\tau_{st} \sim \tilde{\gamma}^3/\sigma$ is the characteristic time for the step to fluctuate one lattice constant. In the low temperature limit $\beta \epsilon \gg 1$ one finds

$$\tau_{st} \sim \exp\left[\beta(E_{det} + 3\epsilon)\right].\tag{7}$$

Equations (6) and (7) form the basis of the experimental determination of kinetic barriers from step edge fluctuations. Measuring the coefficient of the $t^{1/4}$ -behavior of the correlation function (6), the activation energy of the characteristic time (7) can be obtained. Provided the kink energy ϵ is known from other sources (e.g., from the analysis of *static* step fluctuations [13,14]), this yields an estimate of the detachment barrier E_{det} .

To see how (7) has to be modified in the presence of kink rounding barriers, we first rederive τ_{st} from a scaling argument. The elementary process driving the step fluctuations is the transport of an atom from one kink to another, which allows the kinks to diffuse along the step. In order to move the step by a distance a_{\perp} , a kink must diffuse over a distance of the order of the mean kink spacing $\ell_k = (1/2)ae^{\beta\epsilon}$. The detachment rate of atoms from a kink site is $\Gamma_{det} =$ $\Gamma_0 \exp(-\beta E_{det})$. The probability P_{att} for an emitted adatom to reach another kink at distance ℓ_k before it reattaches to the original kink can be calculated from a random walk theory [31], yielding $P_{att} \approx \ell_k^{-1}$. Thus the diffusion rate of a kink is $\Gamma_{det}P_{att}$ and the characteristic time for a step to fluctuate over a single lattice constant reads $\tau_{st} \sim \ell_k^2/(\Gamma_{det}P_{att}) \sim \exp[\beta(3\epsilon + E_{det})]$, in agreement with (7).

When atoms diffusing along the step experience an extra barrier E_{kr} for going around a kink site, as drawn in Fig.1, the probability P_{att} of the adatom to attach to a kink at distance ℓ_k is altered. After reaching the distant kink the adatom still has to overcome the kink rounding barrier in order to attach to it. This yields [31]

$$P_{att} \approx (\ell_k + 1/p_{kr})^{-1},\tag{8}$$

where $p_{kr} \approx \exp(-\beta E_{kr})$ is the probability for going around a kink. Comparing ℓ_k with p_{kr}^{-1} it is obvious that the kink rounding barriers are relevant if $E_{kr} > \epsilon$. In this case (7) has to be replaced by

$$\tau_{st} \sim \exp\left[\beta(2\epsilon + E_{det} + E_{kr})\right].$$
(9)

As shown before the characteristic time is generally a combination of the adatom mobility and the step stiffness, $\tau_{st} \sim \tilde{\gamma}^3/\sigma$. Since the step stiffness does not depend on the dynamics of the adatoms along the step, but only on the energetics, we may conclude that the adatom mobility is reduced to

$$\sigma \sim \exp(-\beta (E_{det} + E_{kr} - \epsilon)) \tag{10}$$

by the kink-rounding barrier, when $E_{kr} > \epsilon$. The expression (8) suggests the interpolation formula

$$\sigma = \frac{1}{2} a \Gamma_0 \frac{e^{-\beta E_{det}}}{1 + e^{\beta (E_{kr} - \epsilon)}} \tag{11}$$

for the mobility, which recovers (4) for $E_{kr} \ll \epsilon$.

3 Monte Carlo simulations

In order to confirm the validity of the arguments of the previous section we have conducted Monte Carlo simulations of a simple one-dimensional SOS model. The position of the step at site i is h_i and the atoms may hop along the step to neighboring sites $(i \rightarrow i \pm 1)$ with rate

$$\Gamma_{i,i\pm 1} = \Gamma_0 \exp(-\beta E_{i,i\pm 1}) \tag{12}$$



Fig. 2. The time correlation function (Eq. (14)) for $\epsilon\beta = 2.5$ and $E_{kr}/\epsilon = 0.0/0.4/1.2/1.6/2.0$ (from top to bottom). The dashed line is the best fit $At^{1/4} + B$. Time is measured in units of the inverse diffusion rate along flat a step, $t_0 \equiv 1/(\Gamma_0 \exp[-\beta E_{st}])$

where the activation energy depends on the local configuration as

$$E_{i,i\pm 1} = E_{st} + 2\epsilon n_i + [1 - \delta(h_i - h_{i\pm 1} - 1)] E_{kr}.$$
(13)

Here $n_i = 0, 1, 2$ is the number of lateral nearest neighbors of the atom at initial site *i* and E_{kr} is an extra barrier suppressing kink rounding; whenever the hop from $i \to i \pm 1$ is not along flat step *i.e.* $h_i - h_{i\pm 1} \neq 1$, the extra barrier E_{kr} is added. In the simulations we used a lattice of size L = 131072, starting with a straight step $h_i(0) \equiv 0$.

The hopping rate $\Gamma_0 \exp[-\beta E_{st}]$ of a free step edge atom on an unkinked step segment determines the time scale of the model, and can be set to unity in the simulation. For the kink energy we used the value $\epsilon = 0.1$ eV. The kink-rounding barrier E_{kr} was varied between 0 and 0.24 eV, and the inverse temperature in the interval $\beta \epsilon = 1.25 - 3.5$, corresponding to T = 331 - 928K.

The time-correlation function

$$C(t) \equiv \sum_{i=1}^{L} h_i(t)^2 \tag{14}$$

measured from the simulations is shown in Fig. 2. It has a clear $t^{1/4}$ time dependence and the prefactor in Eq. (2) was determined by fitting the data



Fig. 3. The adatom mobility along the step edge obtained from the prefactor of the correlation function in Fig. 2, with $\epsilon = 0.1$ eV and kink rounding barrier $E_{kr}/\epsilon = 0.0(\bigcirc), 1.2(\diamondsuit), 1.6(\bigtriangleup), 2.4(*)$. The full lines are best fits to an Arrhenius form.

in the long time limit with $C(t) = At^{1/4} + B$. Using Eqs.(2) and (5), the mobility σ can be extracted from the prefactor. The mobility obtained from the simulation results is shown in Fig. 3 and the activation energy for the mobility E_{σ} , determined from a fit to the Arrhenius plot, is shown in Fig. 4. There is a cross-over in the behavior of the activation energy E_{σ} as the kinkrounding barrier roughly equals the kink energy $E_{kr} \approx \epsilon$. Thus the simulation results are in good agreement with the analytical results (Eqs. (4) and (10)) of the previous section.

4 No Einstein relation for step edge diffusion

In the literature [14,32,33] the interpretation of experimental step fluctuation data is often based on an Einstein relation [34–36]

$$\sigma = \frac{n_{st} D_{st}}{k_B T} \tag{15}$$

for the mobility, where n_{st} is the (one-dimensional) concentration of step adatoms and D_{st} denotes the tracer diffusion coefficient for an adatom migrating along a kinked step. The latter can be estimated by considering the motion of an adatom in a model potential where kink sites are represented as traps of depth E_{det} spaced at the mean kink distance [32,33]. The resulting activation energy for D_{st} is $E_{det} - \epsilon$. Since a step adatom can be viewed as a



Fig. 4. The activation energy for the adatom mobility obtained from the fits in Fig 3. A clear cross-over in the behavior is seen at $E_{kr} \approx \epsilon = 0.1$. The full lines are the theoretical predictions Eqs. (4) and (10).

double kink, the concentration of step adatoms in equilibrium is $n_0 \sim e^{-2\epsilon/k_B T}$, and hence the activation energy of σ is predicted by (15) to be $E_{det} + \epsilon$, in disagreement with the exact result (4).

The problem with (15) was already noted in [30]. Since step adatoms are continually absorbed and emitted at kinks, they do not constitute a conserved species, and it is difficult to consistently define D_{st} and n_{st} . In fact, strictly speaking $D_{st} \equiv 0$: It can be shown [37,38] that the mean square displacement of a marked step adatom moving along a kinked step grows *sublinearly*, as $\langle (x(t) - x(0))^2 \rangle \sim t^{7/8}$. This reflects the fact that a trapped adatom runs a considerable risk of being overgrown by a large step fluctuation, and hence the probability distribution of trapping times has a very broad tail. Representing the migration of an adatom along a kinked step by the diffusion of a particle in an external potential neglects both the possibility of long term trapping due to step fluctuations, and the fact that a kink site is not actually "filled" when an adatom attaches to it – it is merely shifted.

Nevertheless a relation of the form (4) does hold, if D_{st} is replaced by the diffusion coefficient $(1/2)a^2\Gamma_0 \exp[-\beta E_{st}]$ for the migration along a *straight* close packed step, and the bond counting relation $E_{det} = E_{st} + 2\epsilon$ is assumed. Then (15) simply expresses the balance between the detachment and attachment of step adatoms at the kinks.

5 Conclusions

We have studied the time fluctuations of a monoatomic step when the mass transport is restricted to migration along the step. The scaling arguments presented in this paper [Eqs. (9) and (10)], show how the adatom mobility along the step is reduced if the kink-rounding hops are suppressed with an extra barrier. The results of our Monte-Carlo simulations confirm the validity of the scaling arguments.

Time-dependent step fluctuations open a possibility for the experimental measurement of the activation energies of elementary processes on a stepped surface [13,14]. The results presented here show that kink-rounding barriers have to be taken into account in the analysis of such experiments. Provided the kink energy ϵ is known, the temperature dependence of the prefactor of the time correlation function C(t) gives access to the activation energy E_{σ} of the adatom mobility. In general, Eqs.(4) and (10) show that E_{σ} is an upper bound on the detachment barrier E_{det} . For example, the interpretation of the results presented in [33] in the light of our work shows that $E_{det} \leq 1.50 \pm 0.16$ eV for close-packed steps on Pt(111).

When additional information on the energy barriers is available, the analysis of time fluctuations may be used to determine the strength of the kink-rounding barrier itself. For the close-packed [110]-step on Cu(100), the re-interpretation of the experimental results of [32] for the time fluctuations, supplemented with a result of [10] for the diffusion barrier E_{st} at a straight step, yields the estimate $E_{kr} \approx 0.41$ eV [11].

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