Slow dynamics of stepped surfaces

Anna Chame
Département de Recherche Fondamentale sur la Matière Condensée, Commissariat à l’Energie Atomique, 17 Avenue des Martyrs, F-38054 Grenoble Cedex 9, France

Sylvie Rousset
Groupe de Physique des Solides, Université Paris 7 et 6, Laboratoire associé au CNRS, 2 Place Jussieu 75251 Paris, France

Hans P. Bonzel
Forschungszentrum Juelich, Institut für Grenzflächenforschung und Vakuumphysik, D-52425 Juelich, Germany

Jacques Villain
Département de Recherche Fondamentale sur la Matière Condensée, Commissariat à l’Energie Atomique, 17 Avenue des Martyrs, F-38054 Grenoble Cedex 9, France
& Centre de Recherches sur les Très basses températures, CNRS, B.P. 166, 38042 Grenoble Cedex 9
(OCTOBER 21, 2018)

Two kinds of configurations involving steps on surfaces are reviewed. The first one results from an initially planar vicinal surface, i.e. slightly deviating from a high-symmetry (001) or (111) orientation. In some cases, these surfaces separate into domains of different orientations by a mechanism which is very similar to phase separation in mixtures. The domain size initially increases with time and goes to a finite limit, whose value is related to elastic phenomena. The second kind of configurations results from making grooves in a high-symmetry surface. The surface smooths out and takes an intermediate shape with facet-like hills and valleys, which are the source of a controversy which we try to clarify as much as possible.

I. MOTIVATION.

Surfaces are of great technological and fundamental interest since many processes, such as crystal growth, catalytic reactions, production of nanostructures, occur mainly at surfaces.

The surface of an industrial catalyst is too complicated to allow for an observation of the microscopic processes. On the other hand, a high-symmetry, (001) or (111), surface of a cubic crystal is too simple. The only process which occurs is the diffusion of single atoms, which cannot easily be observed.

The present review will be focussed on stepped surfaces of cubic crystals, i.e. surfaces made of large high-symmetry terraces separated by steps of thickness one monolayer (Fig. 1).

The fundamental interest of stepped surfaces is that they are both simple and not too simple. The ensemble of the steps can be arranged into many different structures, due to various factors which can play together or compete among themselves. Simple models can include attachment/detachment of atoms to/from the steps, diffusion or evaporation of atoms, and also step fluctuations. The steps can interact with each other, through short or long range interactions. The effect of a flux of atoms over the stepped surface can be considered, growth can occur through step flow, there can be step bunching, etc. The dynamics of steps gives informations on the microscopic parameters (energy, diffusion constants...) and are a test of our ability to solve problems of nonlinear dynamics.

The experimental observation of steps is relatively easy, for instance by scanning tunnel microscopy (STM). The present review will not be concerned with isolated steps, but only with experiments in which interactions between steps has an influence on their motion. Two examples are given in the next section.

*Permanent address: Instituto de Física, Universidade Federal Fluminense, 24210-340, Niterói RJ, Brazil.
II. EXPERIMENTS

Solids are generally not in their equilibrium shape, and that is a good thing since otherwise one could not make, for instance, tools or artwork. However, small solids particles can reach their equilibrium shape at high enough temperature.

A. Grooves

A case of interest in the present review is that of a crystal surface in which periodic grooves have been made. Figure 2 shows the example of periodically modulated Ni(110) and Ni(100) surfaces which have been annealed at 800 °C to obtain a steady state profile shape. This shape is sinusoidal in the first case but trapezoidal in the second. If annealed for long times, both profiles will decay and approach a flat surface. If the profile has a short enough wavelength and the temperature is high enough (wavelength $\lambda \approx 10 \mu m$, typical temperatures $T$ between 900 – 1300 K) the profile smoothens after reasonably short times.\textsuperscript{2,3} (Fig. 2).

The relevant questions in context with this experiment are: i) How does the amplitude $2h(t)$ decay? Exponentially or not? ii) What is the transient shape of the profile? iii) How does the relaxation time $\tau$ depend on the wavelength $\lambda$? Mullins\textsuperscript{4} has given a simple theory (reviewed in chapter III) valid above the roughening transition (we shall recall later what this means). Mullins’ answers to the above questions, under the assumption of small slopes, are the following: i) The decay is exponential. ii) The profile is sinusoidal or becomes rapidly sinusoidal if it is initially not. iii) The relaxation time $\tau$ is proportional to a power of $\lambda$ which depends on the type of dynamics. Mullins’ theory will be reviewed in chapter III.

Early experimental observations\textsuperscript{3} evidenced that, for initially prepared sinusoidal profiles on Ni(100), (110) and (111) single crystals, the evolution towards equilibrium was found to be different depending on which surface the profile is created. For (110) surfaces the profile maintains the sinusoidal shape during the decay and the time law is strictly exponential. The relaxation time scales with the fourth power of the wavelength of the profile. In contrast, in the case of the high symmetry (111) and (001) surfaces, flat regions, reminiscent of facets, form at the maxima and minima. The decay of these profiles with time is slower than for the ones on Ni(110).\textsuperscript{5,6} Non-sinusoidal profile shapes were also observed\textsuperscript{7} for the (100) and (111) surfaces of gold shown in Figure 3. This case, however, is even more complicated than Ni, because vicinal Au(100) and (111) surfaces are unstable and facet. This problem will be discussed in parts II B and XIII.

B. Phase separation on vicinal surfaces

A vicinal or miscut surface is a surface obtained by cutting a crystal along a plane making a small angle $\alpha$ with a low index plane, (001) or (111) for instance. The ideal structure of a vicinal surface then consists of high symmetry terraces separated by equally spaced steps of atomic height. Indeed, such configurations have been observed, for example on vicinal copper surfaces at room temperature.\textsuperscript{8,9} or on vicinal Si(111) surfaces at elevated temperature.\textsuperscript{10} Although thermal fluctuations have been studied in detail on vicinal surfaces, and are responsible for a terrace width distribution\textsuperscript{11}, the average distance between steps is usually consistent with the ideal expected value.

However, it has been known for a long time\textsuperscript{12} that upon thermal treatment, some stepped surfaces are unstable and separate into parts (or ‘facets’) of two or three different orientations. This separation is analogous to phase separation of unstable mixtures and the resultant morphology is a hill-and-valley structure. Such a situation occurs for instance on Au(111) vicinal surfaces.\textsuperscript{12} Two examples are shown in figures \textsuperscript{3} and \textsuperscript{4}, namely Au(11,9,9) and Au(5,5,4). Both surfaces are tilted by about 6° with respect to the (111) orientation and can be figured out as consisting of [1,-1,0] monoatomic steps which are initially equally spaced by about 24A. Both surfaces are unstable. After a thermal treatment in ultra high vacuum, a faceted morphology is clearly seen in figures \textsuperscript{3} and \textsuperscript{4}. In the simplest case, the unstable surface evolves towards an array of step bunches separated by high symmetry terraces. For instance, a (11,9,9) gold surface (Figure \textsuperscript{3}) transforms into (111) terraces of 35 Å width, separated by small portions of another vicinal surface, namely the (7,5,5) orientation. In the case of the (5,5,4) surface (Figure \textsuperscript{4}), the transformation leads to facets which are both portions of vicinals. All steps have still the same sign. The phase with the greatest slope corresponds to a (3,3,2) orientation, whereas the other one is misoriented from (111) by about 4°. The additional long range order displayed by the faceted morphologies will be discussed in section XII. The stability of the facets may be interpreted as caused by an interaction between steps which is not uniformly repulsive, as will be seen in subsection V B.
Another possible cause of faceting is surface melting. For instance, Frenken et al. have shown, using medium energy ion scattering, that vicinal Pb(111) can separate into two surfaces of non-zero step density, a melted one and a dry one.

Measurements of the faceting of vicinal Si(111) surfaces show that this surface also rearranges into a hill-and-valley structure. At high temperature this surface consisted of a uniform density of steps and at low temperatures two “phases” appear: the \((7 \times 7)\) reconstructed (111) facets and the unreconstructed step bunches.

As in ordinary phase separation, the two coexisting phases can be deduced by the so-called double tangent construction if one knows the thermodynamic potential as a function of the relevant variable (the concentration in the case of a mixture, orientation in the case of a surface).

This thermodynamic potential, in the case of a stepped surface, can be in principle deduced, or at least understood, from the knowledge of the interactions between steps, which are the subject of section \[V\).

III. VARIOUS TYPES OF KINETICS AND MULLINS' THEORY

In order to model the experiments reported in Subsection \[II B\), we consider a crystal surface which is approximately a plane parallel to the \(xy\) direction, but for a small initial perturbation which slowly decays in time. We wish to study this decay. We can consider for instance an initially sinusoidal (unidirectional) profile of wavelength \(\lambda\), namely:

\[
z(x, t = 0) = h(0) \cos \frac{2\pi x}{\lambda}.
\]

The important quantity which drives the relaxation process is the chemical potential \(\mu\), i.e. the thermodynamical potential per particle. If the surface is out of equilibrium, \(\mu\) is not constant on the surface and can be related to the surface free energy density by the Herring-Mullins formula. This formula can be written in a simple way if one introduces the free energy density \(\varphi\) per unit area of the projection onto any reference plane, e.g. the \(xy\) plane:

\[
\mu = \mu_0 - a^2 \left[ \frac{\partial}{\partial x} \left( \frac{\partial \varphi}{\partial z_x} \right) + \frac{\partial}{\partial y} \left( \frac{\partial \varphi}{\partial z_y} \right) \right],
\]

where \(z\) is the height of the surface above the \(xy\) plane and \(z_\alpha = \partial z/\partial x_\alpha\). This formula makes sense if \(\varphi\) is an analytical function of \(z_x\) and \(z_y\). If it is so, the surface is called non-singular. The remainder of this section is devoted to the simple case of a surface which is non-singular in all its orientations. As will be seen in the next section this is not the case of stepped surfaces, but the forthcoming study will provide us the opportunity to introduce several useful concepts.

For not too high temperatures, atoms can neither evaporate nor diffuse through the solid, so that surface relaxation takes place through diffusion of atoms on the surface. This case is called surface diffusion dynamics. One can then write a conservation equation which expresses the absence of evaporation:

\[
\partial z/\partial t = -a^2 \nabla \cdot \vec{j}_s.
\]

where \(a\) is the atomic distance.

Mullins wrote the surface current density \(\vec{j}_s\) in (3) as

\[
\vec{j}_s = -a^2 \beta \tilde{D}_s \nabla \mu
\]

where \(\mu\) is the local chemical potential, \(\beta = 1/(k_B T)\) and \(\nabla = (\partial_x, \partial_y)\). The surface “mass diffusion constant” \(\tilde{D}_s\) is defined as \(\tilde{D}_s = a^2 \rho_0 D\), where \(\rho_0\) is the adatom density at equilibrium and \(D\) is the adatom diffusion constant (we suppose that the advacancy contribution to diffusion is negligible compared to the adatom contribution).

Mullins approximated \(\varphi\) by a quadratic function which will be assumed isotropic for the sake of simplicity. This procedure is usual in liquids and yields:

\[
\varphi(z_x, z_y) \approx \frac{c^2}{2} \left( z_x^2 + z_y^2 \right)
\]

where \(c\) is the interatomic distance along the \(z\) axis.

Relations (2) and (5) yield

\[
\mu = \mu_0 - a^2 c^2 \tilde{\sigma} (z_x x + z_y y).
\]
Inserting (6) into (4) and (3), one finds
\[ \partial z/\partial t = -a^2 K \nabla^2 (\nabla^2 z), \] (7)
where \( K = c^2 \beta \tilde{D} \tilde{\sigma} > 0 \). This equation of motion is linear, so that an initially sinusoidal profile remains sinusoidal:
\[ z(x, t) = h(t) \cos \frac{2\pi x}{\lambda}, \] (8)
Using (7), the amplitude \( h(t) \) in (8) is seen to decay exponentially with the time \( t \),
\[ h(t) = h(0) \exp(-t/\tau) \] (9)
with a relaxation time
\[ \tau(\lambda) = \frac{\lambda^4}{16a^2 \pi^4 K}. \] (10)

For an arbitrary, but periodic initial profile, the shape will anyway become sinusoidal after some time since it can be regarded as a sum of many sinusoids of different wavelengths (Fourier decomposition). At long times, only the component of longest wavelength persists.

The above results hold for surface-diffusion kinetics. The comparison with experiment allows it to determine systematically the diffusion constant \( \tilde{D} \) on the (110) face of fcc metals.

Another case is when matter is carried through the vapour. This process, important at high temperature, is called evaporation-condensation kinetics. For simplicity, the chemical potential of the vapour is always uniform and equal to the value \( \mu_0 \) of the bulk solid. The evaporation rate at a point of the surface where the chemical potential is \( \mu \) is proportional to the difference \( \mu - \mu_0 \):
\[ \dot{z} \propto \mu - \mu_0 \] (11)
Then using expression (6) for the chemical potential, one obtains
\[ \dot{z} = A(z_{xx} + z_{yy}) \] (12)
where \( A \) is a temperature-dependent coefficient. Since (12) is a linear equation, there are again sinusoidal solutions which satisfy eqs. (5) and (7). However, for evaporation-condensation kinetics, the above equations yield \( \tau \propto \lambda^2 \) in contrast with (10).

A third way to transport matter, and thus to allow for the relaxation of the profile, is bulk diffusion. When this process dominates, it can be shown that, in the non-singular case, \( \tau \propto \lambda^3 \).

### IV. STEPPED SURFACES

The free energy of a stepped surface is the sum of the free energy of the high symmetry parts and the free energy of the steps. The simplest case is that of a regular array of straight, parallel steps at distance \( \ell \) (Fig. 6). If the step energy per unit length is \( \gamma \) and if \( \ell \) is so large that the interaction between steps can be neglected, the projected free energy density resulting from high symmetry parts is independent of \( \ell \) while the free energy of the steps is \( \gamma/\ell \). The total projected free energy density can be written as
\[ \varphi(z_x, z_y) = \varphi(0, 0) + \gamma(z_x^2 + z_y^2)^{1/2} \] (13)
In contrast with (3), this expression is not analytic in \( z_x \) and \( z_y \) (Fig. 6b). A high symmetry surface is singular and Mullins’ theory is not applicable.

More precisely, a high symmetry surface is singular below its roughening transition which occurs at a temperature \( T_R \). Above \( T_R \), \( \gamma \) vanishes, (13) does not apply, and one can argue that (3) applies. For the (001) and (111) faces of most fcc materials, \( T_R \) is very close or equal to the melting temperature. Low symmetry surfaces also have roughening transitions, which occur at much lower temperatures.

In the case of stepped surface, the three types of kinetics (surface-diffusion, evaporation-condensation, bulk diffusion) are still possible. However, surface-diffusion kinetics subdivide into two classes. i) In the first class, atoms are easily trapped by steps as soon as they meet one. The slow process is migration on the terraces. This is migration-limited surface-diffusion-kinetics. ii) In the second class, diffusing adatoms hardly feel steps. The slow process is
attachment on steps (and detachment from steps). This is attachment-detachment-limited surface-diffusion-kinetics. We shall generally consider migration-limited surface-diffusion-kinetics.

Attachment-detachment-limited surface-diffusion-kinetics is somewhat analogous to evaporation-condensation kinetics, since the adatoms may be considered to have a uniform chemical potential \( \mu_0 \) as if there were a vapour bathing the surface. The exchange of matter between this mobile layer and the steps is assumed proportional to the difference between \( \mu_0 \) and the local chemical potential \( \mu \) determined by surface energy changes resulting from surface displacements.

The equilibrium shape of crystals have facets parallel to singular orientation. As seen in the previous section, facet-like flat regions also appear in the transient shape of unstable grooves. A priori, both phenomena are expected to have the same origin.

However, there are significant differences. At equilibrium, the chemical potential \( \mu \) is the same everywhere. The size of a facet cannot decrease without locally increasing the density of adatoms (and therefore the chemical potential) near the facet, and the extra adatoms cannot be removed unless they go back to the facet, which thus comes back to its previous shape. On the other hand, in the case of the surface perturbations (not at equilibrium), the chemical potential deviates from its equilibrium value by a positive amount in the convex regions (top) and by a negative amount in the concave parts (bottom) and the removal of adatoms can be accomplished by transferring them to a bottom facet. Thus, if facets are for instance artificially made, they may be unstable with respect to exchange of atoms from top facets to bottom facets. Whether this occurs or not is a matter of dynamics: if the exchange of atoms between facets requires too much time, facets can persist until complete smoothing. This dynamical problem is controversial, as will be seen.

A simple method is to replace the true free energy (13) (actually the improved expression 14 below, which takes step interactions into account) by a regularized form (Fig. 3). This approach yields facets, and actually the transient groove shape is not very different from the equilibrium shape. However, the regularization procedure does not give much insight into what really happens near facets, and it is desirable to devise more microscopic methods. Before doing that, it is necessary to discuss interactions between steps.

V. INTERACTIONS BETWEEN STEPS

Formula 13 consists of just the first two terms of an expansion. The next terms depend on interactions between steps.

Interactions may be short ranged or long ranged. The definition which will be accepted in this review is that an interaction is called ‘short ranged’ if it decays faster than any power \( r^{-\alpha} \) with the average distance \( r \). Short range interactions generally depend on the microscopic features of each particular material and each particular orientation, while long range interactions have rather general features which make them especially interesting.

A. Long range interactions

Electrostatic interaction

The most evident interaction between steps may be the electrostatic one: symmetry considerations suggest that steps carry an electric dipole moment. It is in fact a corollary of the electrostatic interaction between adatoms. Actually, even a flat surface carries an electric moment density: it is the correction to this electric moment due to the step that we are considering here.

The interaction between two dipole moments at distance \( r \) on the surface of a solid is proportional to \( 1/r^3 = (x^2 + y^2)^{-3/2} \), just as in a homogeneous medium. However, the proportionality factor is not easy to evaluate. In the case of a metal, different evaluations have been given by Kohn & Lau and by Lannoo & Allan. Note that two dipoles at the interface between two metals would have no long range interaction because of screening.

If we come back to the case of steps, we can obtain the interaction energy between two straight, parallel steps at a distance \( \ell \) by integrating the dipole-dipole interaction \( (\ell^2 + y^2)^{-3/2} \) over \( y \). The resulting interaction is proportional to \( 1/\ell^2 \), and of course to the length of the steps. The free energy density of a regular array of steps at distance \( \ell \) is obtained by multiplying by the step density which is itself proportional to \( 1/\ell \). The free energy density per unit projected area \( \varphi \) (introduced in formula 8) is then, for \( |z_x|, |z_y| \ll 1 \)

\[
\varphi(z_x, z_y) = \varphi(0, 0) + g_1(z_x^2 + z_y^2)^{1/2} + g_3(z_x^2 + z_y^2)^{3/2}
\]  
(14)
where $g_1 = \gamma$ is the step free energy per unit length and the constant $g_3 = g_3^{\text{elec}}$ can be positive or negative, depending of the orientation of the dipoles.

**Elastic interaction**

Another type of long range interaction arises from the elastic stress which is unavoidably exerted by a step (like any other defect) on the surface. This stress produces a strain which is of course maximum near the step, and decreases as $1/r^2$ with the distance $r$ to this step. As a result, an elastic interaction energy between two parallel steps at distance $\ell$ arises, which is proportional to $1/\ell^2$, just as the electrostatic interaction! For steps of identical sign, this interaction is repulsive. When it is taken into account, the resulting surface free energy density of a vicinal surface has still the form (14), but $g_3$ now contains an elastic contribution $g_3^{\text{elas}}$, which is always positive in contrast with $g_3^{\text{elec}}$.

A noteworthy exception to the $1/\ell^2$ rule is the elastic interaction between steps in the case of an adsorbed epitaxial layer which has a different lattice parameter from that of the substrate. In this case, the (elastic) dipole-dipole interaction has to be integrated over the whole misfitting terrace, not only over the step edge: the interaction becomes thus logarithmic!

**Entropic interaction**

A third type of interaction between steps arises from the fact that steps cannot cross each other. This can be regarded as an infinite contact repulsion. If the free energy density is calculated as a function of the average distance $\ell$ between steps, this contact repulsion turns out to generate a term proportional to $\ell^{-3}$, just as in the case of elastic and electrostatic interactions. This term may be understood as resulting from the reduction of the entropy of a step by its neighbours. Indeed, the entropy is essentially the logarithm of the number of degrees of freedom and a step looses degrees of freedom every time it meets a colleague, since it has no right to cross it. This effective interaction may therefore be called entropic. It is obviously repulsive since each step tries to have as much space as possible.

When the contact repulsion is taken into account, the projected free energy density $\varphi$ has still the form (14), but a new term $g_3^{\text{ent}}$, which is positive as $g_3^{\text{elas}}$, has to be added to obtain $g_3$. The calculation of $g_3^{\text{ent}}$ uses the analogy between an array of mutually-avoiding steps and the trajectories of non-interaction, one-dimensional fermions. The result is

$$g_3^{\text{ent}} = \frac{\pi^2 (k_B T)^2}{6\tilde{\gamma}}. \quad (15)$$

where $\tilde{\gamma}$ is the line stiffness. This result is twice as large as that obtained by Jayaprakash et al. because of a factor $1/2$ in the second term of equations (3) and (13) of these authors.

All three interactions of $g_3 = g_3^{\text{elec}} + g_3^{\text{elas}} + g_3^{\text{ent}}$ are equivalent to a force proportional to $\ell^{-2}$ between pairs of steps, or to a term proportional to $\ell^{-3}$ in the free energy density. However, there are important differences: the entropic interaction is a repulsion between nearest neighbour steps only while elastic and electrostatic interactions relate all pairs of neighbours.

**Experiments**

The case of the solid-superfluid interface of helium is particularly accessible to experiments because equilibrium is much more rapidly established than in other materials. Certain experiments suggest an interaction which decreases slower than $r^{-2}$. A similar suggestion has been made by Arenhold et al. for Pb. A theoretical attempt to explain that have been made (in the case of He) by Uwaha. On the other hand, Balibar et al. have pointed out that experimental results must be very cautiously interpreted.

**B. Oscillating and short range interactions**

As said before, short range interactions are generally particular to each material and it is difficult to say anything general. Oscillating interactions have similar effects since they have local minima at short distances. One can mention the following mechanisms.

**Oscillating electronic interactions**
For certain metal surfaces there is a partially unfilled electronic surface band. Then a phenomenon analogous to Friedel oscillations generates an oscillating interaction between point defects. This interaction is proportional to $r^{-2}\cos(2k_F r)$, where $k_F$ is the Fermi wavevector and $r$ the distance between defects. Integrating along a row generates an interaction between parallel line defects (e.g. steps) which is proportional to $r^{-1}\cos(2k_F r)$. Since it oscillates with distance, the absolute minimum corresponds to a finite value of the distance $\ell_0$ between steps. The effect is very important since surface orientations with steps larger than $\ell_0$ can become unstable as observed experimentally in certain cases (see subsection II A). Oscillations are washed out when $r$ becomes longer than the electron mean free path, and therefore the interactions between parallel steps on a clean surface are likely to decay as $1/r^2$ at long distances in all cases. An oscillating interaction appears also without partially unfilled electronic surface band, but it decreases faster with distance.

**Interactions resulting from reconstruction**

Surface reconstruction may have a similar effect, i.e. make certain orientations more favourable than the intermediate one, in other words, create an oscillating interaction between steps. A typical example of reconstruction is provided by the (001) surface of silicon or any semiconductor. Semiconductors usually have the diamond structure, in which atoms have a very low coordination (4 neighbours). Creating a (001) face in a rigid lattice would reduce the coordination of surface atoms to two neighbours and that would cost a lot of energy. Therefore the surface atoms form ‘dimers’, thus reducing the symmetry. This symmetry reduction with respect to that of the rigid lattice is called *surface reconstruction*. Now, step positions which would cut dimers are unfavourable, and this disadvantages certain distances between steps.

The orientations which are favoured by reconstruction are sometimes called ‘magic’.

**VI. MEAN FIELD THEORY FOR A WELL-CUT SINGULAR SURFACE**

After having recalled the various general properties of surfaces and steps, we come back to the experiments on groove smoothing on Ni(001) and Ni(111) described in subsection I A. The case of Au(001) and Au(111), whose vicinals are unstable, is excluded here and will be addressed in section XIII. Steps are complicated objects and in this section we shall yield to the temptation to consider them as straight lines (Fig. 7 a). This is only possible if the average surface is initially perfectly cut along a symmetry orientation and if there are no dislocations. Even then, steps are not straight, but fluctuating lines (Fig. 7 b). Neglecting these lines (Fig. 7 a). This is only possible if the average surface is initially perfectly cut along a symmetry orientation.

Surface reconstruction may have a similar effect, i.e. make certain orientations more favourable than the intermediate one, in other words, create an oscillating interaction between steps. A typical example of reconstruction is provided by the (001) surface of silicon or any semiconductor. Semiconductors usually have the diamond structure, in which atoms have a very low coordination (4 neighbours). Creating a (001) face in a rigid lattice would reduce the coordination of surface atoms to two neighbours and that would cost a lot of energy. Therefore the surface atoms form ‘dimers’, thus reducing the symmetry. This symmetry reduction with respect to that of the rigid lattice is called *surface reconstruction*. Now, step positions which would cut dimers are unfavourable, and this disadvantages certain distances between steps.

The orientations which are favoured by reconstruction are sometimes called ‘magic’.

**VI. MEAN FIELD THEORY FOR A WELL-CUT SINGULAR SURFACE**

After having recalled the various general properties of surfaces and steps, we come back to the experiments on groove smoothing on Ni(001) and Ni(111) described in subsection I A. The case of Au(001) and Au(111), whose vicinals are unstable, is excluded here and will be addressed in section XIII. Steps are complicated objects and in this section we shall yield to the temptation to consider them as straight lines (Fig. 7 a). This is only possible if the average surface is initially perfectly cut along a symmetry orientation and if there are no dislocations. Even then, steps are not straight, but fluctuating lines (Fig. 7 b). Neglecting these fluctuations may be called a "mean field approximation". This approach was chosen by Rettori & Villain and Ozdemir & Zangwill, who assumed an interaction energy proportional to $L/\ell^2$ between nearest neighbour steps of length $L$ at distance $\ell$. These features are those of the entropic interaction addressed in subsection V A.

We will recall here the results of Rettori & Villain and Ozdemir and Zangwill. Below $T_R$, the analytic form of the projected free energy $\varphi$ is not correct. Instead, one should use (15), where $g_3$ is given by (13) in the absence of step interactions except contact interaction. In a continuum approximation, the instantaneous shape of the surface can be described by a height function $z(x, t)$ (if the perturbation is unidirectional) and (13) takes the form

$$\varphi = g_1 |z_x| + g_3 |z_x|^3$$

(16)

Using (3) and (16), one obtains the excess chemical potential as $\delta \mu = -6a^2 g_3 |z_x|^3 z_{xx}$

(17)

where $z_{xx} = \partial^2 z / \partial x^2$.

If the relaxation occurs by surface diffusion, we can still write (3) and (4), and together with (17) the equation of motion is obtained

$$\frac{\partial z}{\partial t} = -G_3 \frac{\partial^2}{\partial x^2} |z_x|^3 z_{xx}$$

(18)

where $G_3 \propto g_3 D_s / k_B T$ and $D_s = a^2 \rho_0 D$ as before. Eq. (18) is non-linear and until now no analytic solution has been found for it.

Since $\delta \mu$ should vary smoothly in space, (17) is consistent with a singularity near the top ($\delta x \simeq 0$) of the type

$$z = h(t) - C(t)|\delta x|^{3/2}$$

(19)
where \( h(t) \) is the amplitude of the profile at time \( t \).

The singularity (19) is the same as predicted at equilibrium near a facet. However, according to Rettori & Villain and to Ozdemir & Zangwill no facets are expected to form during flattening. Indeed, the decay of the top (and bottom) terraces (should they form facets or not) is due to the junction of the top (or bottom, respectively) ledges. When two top (or bottom) ledges approach from each other, why should lower ledges stay behind instead of keeping contact with them? If top ledges keep contact with lower ledges, no facet is expected in the decaying profile. Therefore, according to (19), the profile is predicted to be sharper than a parabola at its top (and at its bottom as well).

Ozdemir & Zangwill have solved (18), or more precisely a discrete version of (18), and found under certain assumptions (shape preserving solution) that the amplitude \( h(t) \) decays with time \( t \) as

\[
h(t) = h(0) \frac{1}{1 + t/\tau_{\lambda}}
\]

where \( \tau_{\lambda} \simeq \lambda^5 \). Relation (20) is often quoted but it is not always mentioned that \( \tau_{\lambda} \) has to depend on \( h(0) \). Indeed, if (20) holds for a particular value \( h_0 \) of \( h(0) \), with a particular value \( \tau_{\lambda}^0 \) of \( \tau_{\lambda} \), it follows, for any time \( t_1 \) \((0 < t_1 < t)\),

\[
h(t) = h(0) \frac{1}{1 + t_1/\tau_{\lambda}^0} \frac{1 + t_1/\tau_{\lambda}^0}{1 + t/\tau_{\lambda}} = h(t_1) \frac{1 + t_1/\tau_{\lambda}^0}{1 + (t - t_1)/(t_1 + \tau_{\lambda}^0)} = \frac{h(t_1)}{1 + h(t_1)(t - t_1)/(h_0\tau_{\lambda}^0)}
\]

If the time origin is translated to \( t_1 \), this coincides with (21), but \( \tau_{\lambda} \) is proportional to \( 1/h(0) \):

\[
\tau_{\lambda} = \tau_{\lambda}^0 h_0/h(0)
\]

The weakness of the above theory is that any interaction between steps of opposite sign (at the top and the bottom of the profile) is ignored. This would be acceptable if the ledges were straight (Fig. 7a). In reality, they have fluctuations (Fig. 7b). We shall try to take these fluctuations into account in section VII.

**VII. FACET-PREDICTING THEORIES OR THE AMBIGUITY OF THE CHEMICAL POTENTIAL**

A paradox of the mean field theory outlined in the previous section is the energy release which results from the pairwise annihilation of ledges at the top and bottom of the profile when they are assumed to be straight. Spohn have proposed a completely different theory of groove smoothing which does not show this paradox, at least in the case of surface diffusion kinetics. In the case of evaporation-condensation kinetics, both approaches predicts the same singularity, a sharpening of the profile at maxima and minima for long times: \( z \sim |\delta x|^{4/5} \) (this prediction is only valid in the limit of a slowly varying surface profile, i.e., a minimum sample size is needed).

The remainder of this section is devoted to surface diffusion kinetics. In this case, Spohn’s results regarding the shape of the profile are in strong contrast with those described in section VI. He finds, indeed, that facets form in the transient regime.

As pointed out by Tang, the reason of the disagreement lies in different expressions of the local chemical potential \( \mu \) on a surface which is not at equilibrium. Since the current is a function of \( \nabla \mu \) as seen above, the consequences are crucial.

The chemical potential \( \mu \) is the sum of its value \( \mu_0 \) in the solid far from the surface, and an excess \( \delta \mu \) resulting from the surface tension.

If a system has \( N \) atoms and a free energy \( F \), its chemical potential is \( \mu = F/N \).

Now, let us consider the topmost terrace of the profile of Figure 7a. If its width is \( \ell \) and if the sample length is \( L \), then the number of atoms in the terrace is \( N = \ell L/a^2 \) while, if interactions between steps are neglected, the free energy excess resulting from the surface energy is \( \delta F = 2\gamma \ell L \) where \( \gamma \) is the step free energy per unit length. If the whole terrace is removed, the corresponding variation of free energy is \( N\mu_0 + \delta F \) hence \( \delta \mu = \delta F/N \) or

\[
\delta \mu = 2\gamma a^2/\ell
\]

Experiments are performed on macroscopic samples, where this expression is much larger than the term coming from step interactions.

If (22) is applied to grooves, the same formula holds for the bottom terrace with an opposite sign, \( \delta \mu = -2\gamma a^2/\ell \) if the bottom terrace has the same width. The average chemical potential gradient is therefore \( \nabla \mu = 4\gamma a^2/(\ell \lambda) \) and the current from the top to the bottom is of order \( 4D\gamma a^2/(\ell \lambda) \). If \( \ell \) is small, the bottom terraces are rapidly filled and
the top terraces are rapidly peeled, and after some time, only the intermediate terraces are left, and facets appear at the top and at the bottom. This is Spohn’s description.

In section VI, on the other hand, an underlying idea is the following: if the edges of the topmost terrace move so that the width changes by small amount $d\ell$, the number of atoms of that terrace changes by $dN = 2Ld\ell/a^2$, but the total length of the edges does not change, it is always $2L$, and therefore the chemical potential is, disregarding interactions between steps, $\delta\mu = 0/dN$ or

$$\delta\mu = 0$$

(23)

Instead of a straight step, it is of interest to consider also a closed, e.g. circular terrace of size $R$. It contains $N = \pi R^2/a^2$, where $a^2$ is the atomic area, and its free energy excess is $\delta F = 2\pi \gamma R$. The formula analogous to (22) is

$$\delta\mu = \delta F/N = 2\gamma a^2/R$$

while, arguing along the lines of section VI, one obtains

$$\delta\mu = d(\delta F)/dN = \frac{\gamma a^2}{R}$$

(24)

Formulae (24) and (25) are still different, but just by a factor 2. The results which can be deduced from both formulae are just quantitatively different, not qualitatively. In any case smaller terraces have the higher chemical potential and therefore decay first.

Formulae (24) and (25) are in contradiction. Which one is correct at equilibrium? It depends.

For a single terrace on a high symmetry surface, (25) is correct for a circular terrace of radius $R$, while $\delta\mu = 0$ for a stripe-shaped terrace, as can be obtained from (25) by replacing the ledge radius $R$ by $\infty$.

However, if a finite crystal has an approximately circular facet of radius $R$ at equilibrium, $\delta\mu$ can be obtained by removing a whole atomic layer from a facet. The step interaction energy is not much modified in that operation, and therefore (24). If the crystal is obliged to have the shape of a bar, $\delta\mu$ is given at equilibrium by (22). Of course, it is also given by (17), and both expressions should be equal at equilibrium.

Out of equilibrium, there is no reason a priori to write (22) or (23), (24) or (25). A careful analysis of the dynamics is necessary to solve the controversy.

Relation (25), which relates the chemical potential to the curvature, is a two-dimensional form of the Gibbs-Thomson formula.

An objection to Spohn’s theory is that it does not describe how pairs of top (or bottom) steps merge. The peeling of extreme layers are accompanied by fluctuations which are not be better taken into account by him than by Rettori & Villain and Ozdemir & Zangwill. In the next section we shall try to find a solution of the controversy in simulations.

VIII. SIMULATIONS

The relaxation of profiles have been simulated in (1+1)D and (2+1)D by many authors. The solid-on-solid (SOS) model have been used by most of them. Its Hamiltonian is

$$\mathcal{H} = J \sum_{xy,x'y'} |h_{xy} - h_{x'y'}|$$

(26)

where $h_{xy}$ denotes the height of the surface at site $xy$, the sum runs over nearest-neighbours pairs of sites and $J$ is the bonding energy.

Both diffusion and evaporation dynamics were considered in the simulations, and in general the standard Metropolis algorithm was used.

For evaporation-condensation, a conserved dynamics is sometimes used, in the form of a detailed balance of particle exchange between the surface and the surrounding gas: a surface atom can move from its initial position to some other, arbitrarily distant site (conserved number of surface atoms). In some works, non-conserved dynamics are used. For (2D+1) and $T > T_R$, the simulation results agree well with the predictions of Mullins: the profile relaxes as a sinusoid. For $T < T_R$ it was observed that the profile fluctuates, in time, between a sinusoidal and a “trapezoidal” form. Selke and Bieker observed that these fluctuations are accompanied by two distinct time scales in the flattening procedure, reflecting the step wandering and the shrinking of islands. They assumed that the meandering stage leads to the dominant time scale and their results for the relaxation time $\tau$ are compatible with
\( \tau \propto \lambda^3 \), but they speculate that for larger systems sizes, \( \tau \propto \lambda^4 \). Actually, recent large scale simulations by Tang\(^5\) confirmed the exponent 4, but with a correction in the power law.

For diffusion, the number of particles must be conserved and particle exchange occur between nearest-neighbors sites. For temperatures above \( T_R \) the results of the simulations agree well with the predictions of Mullins (sinusoidal profile decay, the value \( n = 4 \) was obtained for the scaling law \( \tau \propto \lambda^n \) of the relaxation time\(^2\)). For temperatures \( T < T_R \), some authors\(^3\) found that the scaling behaviour breaks down after some time and then cusps and plateaus develop at the top and bottom of the profile, others\(^6\) found that the shape of the relaxation profile fluctuates in time between having a flat top to having a rounded top (sinusoidal). We remark that these authors have considered typically small initial profile heights \( h = 4, 5 \). Different scaling laws for the typical relaxation time \( \tau \) were obtained: \( n = 4 \) (obtained by Searson et al\(^5\)), \( n = 3.5 - 4 \) (obtained by Erlebacher et al\(^3\)), \( n = 5 \) (obtained by Ramana Murty et al\(^3\)).

We mention that most authors performed their simulations using standard Monte Carlo algorithms, and from that they obtained time dependent laws for the quantities of interest. Presently it becomes more clear only if the relation –for instance considering a single fluctuating line between two straight lines

relaxation time \( \tau \) introduced, especially, small samples have been considered (small heights, or small widths).

condensation. Due to that, in many simulations (for diffusion dynamics) some short-circuit artefact have been found that the shape of the relaxation profile fluctuates in time between having a flat top to having a rounded top (sinusoidal).

Another important point is that, since in the evaporation-condensation dynamics atoms are exchanged between the surface and the vapour and in diffusion dynamics it is necessary to consider the motion of the atoms from a site to another (in general a nearest-neighbour), surface diffusion takes much more computing time than evaporation-condensation. Due to that, in many simulations (for diffusion dynamics) some short-circuit artefact have been introduced, especially, small samples have been considered (small heights, or small widths).

In what concern the choice of small samples, one of the problems is that to obtain the correct scaling laws (e.g. the relaxation time \( \tau \) vs the wavelength \( \lambda \)), the amplitude \( h \) and the average distance between steps \( \ell = a\lambda/(4h) \) must be large with respect to the atomic distance \( a \).

**What is a short sample?**

The problem related to the width \( L \) of the system in the direction of the grooves is different. In available analytical or numerical theories, elastic or electrostatic interactions between the steps which form the profile are not considered, and then the only interaction which remains is the contact repulsion. As seen in section VA, in analytic theories\(^1\), \( f_{\text{cut}} \) on the relaxation of grooves.

\[ f_{\text{cut}} = L \left( \frac{\pi k_B T}{6 \gamma \ell^2} \right)^2 \]  

for each pair of steps at average distance \( \ell \).

Here, \( \gamma \) is the line stiffness related to the energy \( W \) per kink by the relation

\[ \beta \gamma a = 1 + \frac{\exp(\beta W)}{2} \]  

Since steps are not straight at finite temperatures, it is useful to define the average distance \( \xi \) between kinks along a step, given by

\[ \xi \approx a \left( 1 + \frac{\exp(\beta W)}{2} \right). \]  

Formula \(^{26}\) is correct only for long distances \( \ell \). Moreover \(^{27}\) makes sense only for large \( L \). An exact calculation\(^2\) –for instance considering a single fluctuating line between two straight lines\(^2\) at distance \( 2\ell \)– shows that \(^{27}\) holds only if the relation

\[ L \gg \xi \ell^2/a^2 \]  

is satisfied. This yields a first condition on \( \xi \)

\[ \xi \ll L(4h/\lambda)^2. \]  

Whether this condition is satisfied or not depends on the temperature \( T \), which should anyway be smaller than \( T_R \). An order of magnitude of \( T_R \) is given by writing that the free energy of an isolated step per atom, which is \( W - k_B T \ln[1 + 2 \exp(-\beta W)] \) at low temperature, vanishes. Thus

\[ \exp \frac{W}{k_B T_R} \approx 2 \]  

\(^{(32)}\)
As a matter of fact, if one wishes to check the analytic predictions made for singular surfaces, it is safer to choose $T$ much lower than $T_R$. Indeed the aspect of a surface on short distances is very similar just below $T_R$ and just above $T_R$. In particular, closed terraces are present between steps, and steps exhibit “overhangs” which are generally ignored in available theoretical treatments. The choice $T < T_R/2$ seems reasonable. This implies, according to (20) and (32), a second condition on $\xi$

$$\xi > 3a$$  \hspace{1cm} (33)

It turns out that conditions (31) and (33) are not always simultaneously satisfied in simulations, specially when diffusion kinetics is considered. The simulation by Ramana Murty and Cooper is a special case, since they used sufficient long samples, and actually Ramana Murty and Cooper do find the scaling law $\tau \propto \lambda^5$ predicted by Ozdemir and Zangwill. Note, however, the very low value of $\lambda$ in all simulations. The choice of all lengths ($\lambda$, $h$, $L$) results from a compromise between too large values which would saturate computers, and too short sizes which would have no relation with reality.

A conclusion which can be drawn from simulations is that facets do appear at least in certain cases, but it is not quite sure that this phenomenon is not related to the small sample size. For a given sample length, facets seem to be observed in simulations at low temperature, where the steps have but few contact points. On the other hand, at higher temperatures, the profile is roughly sinusoidal. In the following section, an explanation of the results on short samples is presented.

**IX. THE TRANSIENT ATTRACTION**

The interactions between steps we considered so far are thermodynamic. They correspond to terms of the free energy, and have an effect on the equilibrium state. When writing kinetic equations, these thermodynamic interactions appear in the detailed balance relation

$$p_A^B \exp(-\beta E_A) = p_B^A \exp(-\beta E_B)$$  \hspace{1cm} (34)

where $p_A^B$ denotes transition probability per unit time from a state $A$ to state $B$ and $E_A$ is the energy of state $A$.

In a non-equilibrium situation, we will prove that a clustering of steps of identical sign can occur in the case of surface diffusion kinetics. This can be interpreted as arising from an attraction between such steps, even though there is no thermodynamic interaction, i.e. $E_A = E_B$ has the same value for all configurations of interest.

Unfortunately, a quantitative theory of this attraction can only be done for a 1-dimensional surface (Fig. 8 a) which is a good representation of a short sample. The one-dimensional model is fully characterized by the probabilities per unit time and unit length, $\alpha^+ (\ell)$ and $\alpha^- (\ell)$, for two neighbouring steps at distance $\ell$, to exchange an atom in one direction or in the other one. The case of interest is when both steps have identical sign. Consider the configuration $B$ obtained from a configuration $A$ by transferring one atom downward from a step to the neighbouring one at distance $\ell$.

The transition probability per unit time from $A$ to $B$ is, by definition, $\alpha^+ (\ell)$. The transition probability per unit time from $B$ to $A$ is $\alpha^- (\ell + 2a)$ because the terrace width in $B$ is $\ell + 2a$. In the absence of interaction between steps, the detailed balance relation writes

$$\alpha^- (\ell + 2a) = \alpha^+ (\ell)$$  \hspace{1cm} (35)

If the distance $\ell$ between both steps is large, most of the emitted atoms go back to the step where they started from. The transfer probabilities $\alpha^- (\ell)$ and $\alpha^+ (\ell)$ are therefore expected to decrease with increasing $\ell$.

More precisely, it can be shown that:

$$\alpha^+ (\ell) = a_0 \frac{a}{\ell + \ell_s + a}$$  \hspace{1cm} (36)

and

$$\alpha^- (\ell) = a_0 \frac{a}{\ell + \ell_s - a}$$  \hspace{1cm} (37)

where $a_0$ is a constant and the “Schwoebel length” $\ell_s$ (equal to 0 in most of available simulations) depends on the detachment probability of atoms from steps. The emission rate $a_0 a$ per lattice site is obtained if one notices that, at equilibrium, adatom emission by steps is compensated by absorption. The absorption rate is proportional to the
product of the adatom density $\rho_0$ by the adatom jumping rate $4D/a^2$, where $D$ is the adatom diffusion constant. Therefore

$$\alpha_0 = \frac{4D\rho_0}{a}.$$  \hfill (38)

There is no thermodynamic interaction between steps at equilibrium since (36) and (37) satisfy the detailed balance relation (35). However, $\alpha^- (\ell) > \alpha^+ (\ell)$, which means that atom exchange between two steps of identical sign tends to shorten their distance. It is hardly avoidable to interpret this as a kind of attraction between neighbouring steps of identical sign.

Of course, all steps should be taken into account, and the effect disappears for a regular array of equidistant steps (an equilibrium configuration) but it is present for the periodic profile of Fig. 8a, as demonstrated by Monte-Carlo simulations.\(^5\) The result is a blunting of the profile: steps of identical sign attract themselves, so that the maximal slope increases, and consequently the top and the bottom flatten.

The following exercise helps to understand the nature of the interaction. Consider a one-dimensional profile made of alternating pairs of up and down steps (Fig. 8b). Let the distance between two consecutive steps be initially uniform and equal to $\ell_0$. It will first be assumed that steps of opposite sign cannot annihilate—an unphysical model which has the advantage to have a non-trivial equilibrium state in which the average distance between two consecutive steps is $\ell_0$. In this model the average distance $<\ell(t)>$ between two consecutive steps of identical sign will first decrease because of the attractive interaction, until collisions take place. Then, as an effect of the contact repulsion, $<\ell(t)>$ will increase and come back to its equilibrium value $\ell_0$. Thus, the attraction has just a transient effect. For this reason, we will call it transient attraction.

In a one-dimensional profile with alternating groups of $2h/c$ up steps and $2h/c$ down steps, the transient attraction does produce an initial clustering of identical steps, which produces facets, which are observed in Monte-Carlo simulations.\(^5\) In these simulations, steps of opposite sign are allowed to annihilate, and it turns out that facets persist until the profile completely flattens. This is a surprise, but the effect seems to be observed only on one-dimensional samples or in two-dimensional ones which are too short in the groove direction. Therefore, the transient attraction will be ignored in the following sections.

### X. STEP FLUCTUATIONS AT THE TOP AND BOTTOM

Analytic theories of Rettori and Villain\(^4\) and Ozdemir and Zangwill\(^2\) are mean field ones, where fluctuations are neglected. Away from the top and bottom, step fluctuations are expected to be reasonably taken into account by the entropic interaction. The challenge is now to introduce step fluctuations of the top and bottom ledges into these theories. The following calculation\(^6\) is an attempt to solve this problem.

Because of these fluctuations, finite terraces, i.e. closed step loops, form at the top of the profile, which have a typical length $L_1$ (Fig. 7b). The width of the loop should be comparable with the distance $2\ell_1$ between both topmost infinite steps of each period. Each finite terrace terminates by a tip whose radius is of order $\ell_1$, so that the excess chemical potential before the tip is

$$\delta \mu = \frac{\gamma a^2}{\ell_1}.$$  \hfill (39)

The velocity $v$ of the tip is proportional to the current density of adatoms flowing from the tip which is equal to $\beta \rho_0 D \nabla \mu$. Since the tip is at distance $\ell_1$ of the terrace edges, the order of magnitude of $\nabla \mu$ should be expression (39) divided by $\ell_1$, so that

$$v \approx \frac{\beta \rho_0 D \gamma a^4}{\ell_1^2}.$$  \hfill (40)

The time $\tau_1$ necessary to peel the upper layer is obviously

$$\tau_1 = L_1/v$$  \hfill (41)

so that (40) yields

$$\tau_1 \approx \frac{L_1 \ell_1^2}{\beta \rho_0 D \gamma a^4}.$$  \hfill (42)
The nucleation time of a finite terrace after the previous one has disappeared is expected to have the same order of magnitude \( \tau \) as the lifetime of a finite terrace.

Topmost steps can only fluctuate by emission of atoms. These atoms can only go to the lowest steps. This suggests that step fluctuations arise from the exchange of atoms between topmost and lowest terraces. This exchange is of course biased, and preferably from the top to the bottom. But it is also partly stochastic. Its mean square fluctuation will be calculated without taking the bias into account. The exchange rate in each direction is expected to be given by a formula analogous to (36) or (37) where the distance \( \ell \) is replaced by the half-wavelength \( \lambda/2 \) while the proportionality factor is given by (38). Thus, the average number \( d\nu/(dtdL) \) of atoms exchanged from the top to the bottom per unit length in the unit time is (neglecting bias)

\[
\frac{d\nu}{dtdL} \approx \frac{k\rho_0 D}{\lambda} \tag{43}
\]

The average \( < \nu > \) of the number \( \nu \) of particles emitted by a length \( b \) of a topmost step in the time \( \tau_1 \) is the product of this quantity by \( b\tau_1 \). The mean square fluctuation \( < \delta\nu^2 > \) of this number is, if the various absorption and emission processes are independent:

\[
< \delta\nu^2 > = < \nu > b\tau_1 \tag{44}
\]

This fluctuation of the number of atoms produces a fluctuation \( \delta\ell \) of the distance between the topmost steps on a length \( b \). Expression (44) can therefore be identified with the square of the area \( b\delta\ell \), so that

\[
< \delta\ell^2 > = \frac{a^4}{b^2} < \nu > b\tau_1 \tag{45}
\]

The length \( b \) should be chosen as the most efficient one, which maximises (45). Therefore, \( b \) should be chosen as short as possible. However, expression (45) cannot be larger than the thermal fluctuation, so that \( < \delta\ell^2 > < k_B Tb/\gamma \). The appropriate choice of \( b \) is therefore

\[
b = \frac{\gamma < \delta\ell^2 >}{k_B T} \tag{46}
\]

The topmost steps meet when \( < \delta\ell^2 > = \ell^2 \). This relation, together with (45), (42), (10) and (13), yields an expression for \( L_1 \):

\[
L_1 \approx \frac{\gamma^2 \lambda \ell^2}{8k_B^2 T^2} \tag{47}
\]

The average current density \( j \) from a top terrace is obtained by calculating the total current from each tip, which is proportional to the product of (40) by \( \ell \), and dividing by the distance \( L_1 \)

\[
j \approx \frac{\rho_0 \beta D \gamma a^2}{L_1 \ell_1} \tag{48}
\]

This can be identified with the current density of atoms from the top to the bottom terrace, which can also be roughly evaluated by dividing the chemical potential difference \( 2\delta\mu \) (given by formulae (17) and (19)) by \( \lambda/2 \) (in order to obtain the chemical potential gradient) and then multiplying by the same kinetic coefficient \( \rho_0 \beta D \) as in (43).

\[
j = \frac{27C^2 \rho_0 \beta D gsa^2}{2\lambda} \tag{49}
\]

Identification of (18) and (49) yields

\[
L_1 = \frac{2\lambda \gamma}{27C^2 g3\ell_1} \tag{50}
\]

Eliminating \( L_1 \) between (50) and (17), one obtains

\[
\ell_1^3 \approx \frac{16(k_B T)^2}{27C^2 g3\gamma} \tag{51}
\]
If $g_3$ is replaced by its value \([13]\), this relation reduces to $\ell^3 \approx C^{-2}$. This is just what could be deduced from \([19]\) by replacing $h - z$ by 1 and $\delta x$ by $\ell_1$. In other words, the results of the mean field theory of section \([\mathbf{V}]\) would not be considerably modified if fluctuations were taken into account.

An approximate expression of $C(t)$ as a function of the modulation amplitude $h(t)$ can be obtained if one assumes that \([19]\) is approximately correct for $z = 0$. Then, since $\lambda \gg \ell_1$,

$$C(t) \approx h(t) \left(\frac{\lambda}{4}\right)^{-3/2}$$

(52)

The peeling time of the top layers is given by inserting \([50]\) and \([51]\) into \([42]\). One obtains

$$\tau_1 \approx \frac{\gamma^2 \lambda}{8k_B T^2 \beta \rho_0 D \alpha^4} \approx \frac{\gamma^2 \lambda}{8k_B T^2 \beta \rho_0 D \alpha^4} \left[ \frac{16(k_BT)^2}{2\gamma g_3}\right]^{4/3} C^{-8/3}$$

and, using \([52]\),

$$\tau_1 \approx \frac{\gamma^2}{2k_B T^2 \beta \rho_0 D \alpha^4} \left[ \frac{16(k_BT)^2}{2\gamma g_3}\right]^{4/3} \left(\frac{h(t) - 8/3}{\gamma/4}\right)^5$$

(53)

The quantity which can easily be measured is the time after which the amplitude $h$ has been reduced by a factor 2 for instance. This decay time is

$$\tau_{\text{dec}} \approx \tau_1 h \approx h^{-5/3} \lambda^5$$

(54)

The power $\lambda^5$ is the same as obtained by Ozdemir and Zangwill (see formula \([24]\) but expression \([21]\) was proportional to $1/h$. The amplitudes $h$ used in Monte-Carlo simulations are too small to decide which formula is correct, and so far as we know, there is no experiment which can prove or disprove \([54]\).

**XI. MISCUT SURFACES**

Metal surfaces cannot easily be cut along a high-symmetry direction. There is generally a small miscut angle $\alpha$. If $x$ is the direction common to the high symmetry plane and to the miscut average surface, the groove direction is defined by its angle $(\pi/2 + \psi)$ with $x$. A sinusoidal surface modulation causes the steps to assume a specific shape. For $\psi = 0$ they are sinusoidal in an projected on-top view while for $\psi = \pi/2$ they are straight, with their separation modulated sinusoidally. Staying with a low amplitude/wavelength ratio (surface slopes small compared to $\alpha$) and using a surface free energy of the kind in eq. \([14]\) solutions for the rate of profile decay via migration-limited, surface diffusion kinetics were derived by Bonzel and Mullins \([\mathbf{4}]\) for two particular cases: $\psi = 0$ and $\psi = \pi/2$. In the first case the rate is proportional to $(g_1 + 3g_3 \tan^2 \alpha)/\sin \alpha$, which is approximately equal to $g_1/\sin \alpha$ because $g_3 \tan^2 \alpha \ll g_1$. Thus the step self-energy is the important energetic quantity, driving the profile decay. This is understandable because the wavy steps want to reduce energy by becoming straight which is equivalent to a reduction in profile amplitude. For $\psi = \pi/2$, on the other hand, the decay rate is proportional to $6g_3 \sin \alpha/\cos \alpha$, i.e. it is driven by the step interaction energy only. Since the steps are basically straight from the beginning, the total energy can only be reduced by a redistribution of all steps, so that their separation becomes about equal. This redistribution of steps causes the amplitude to decrease. The ratio of rates for these two types of modulation is approximately $g_1/(6g_3 \sin^2 \alpha)$ for $\alpha < 10^\circ$ assuming equal surface diffusion coefficients normal and parallel to steps. Since $g_1$ is believed to be larger than $g_3$, this ratio can be a large number, depending on the choice of $\alpha$. An experimental verification of the effect was given for $1.5^\circ$ and $5^\circ$ miscut Au(111) surfaces that had been modulated in the $\psi = 0$ and $\psi = \pi/2$ modes. Figure \(\mathbf{3}\) shows the experimental amplitude decay at 1023 K of two profiles in orthogonal orientations on the $5^\circ$ miscut Au(111) surface. The substantial difference in decay rates illustrates the predominant influence of step and step interaction energy, respectively.

Strictly speaking, since there are unstable orientations near the (111) facet of Au, the theory by Bonzel and Mullins is not valid. This case will be addressed in section \([\mathbf{XII}]\).

Unfortunately, this kind of experiment always yields products of surface diffusion coefficient times surface energy term, and unravelling these two factors seems difficult. A combination of kinetic and equilibrium experiments offers a possibility to separate them but the total effort is substantial.

Profile decay is exponential with time on vicinal surfaces for the small slope approximation \([\mathbf{4}]\) and the relaxation time $\tau$ is proportional to $\lambda^5$. This is the same result \([\mathbf{14}]\) as for a non-singular surface.
A numerical investigation beyond the small slope approximation has also been done for the $\psi = \pi/2$ case. The calculated decay is linear with time. It also does no longer obey a $1/\sin \alpha$ dependence but rather saturates with decreasing miscut angle (Fig. 10). For $\psi = 0$, the corresponding profile shape is sinusoidal for small slopes and more trapezoidal when larger slopes are permitted. This blunting can be understood intuitively as follows. Near an isolated step, $\delta \mu$ is proportional to the step curvature as seen from (23). Therefore, the steps try to decrease $\delta \mu$ by increasing their radius of curvature, where it is most easy, namely at the top and at the bottom, while in the intermediate region they are squeezed together, so that they cannot change their shape much. The increase of the radius of curvature results in a blunting of the profile. For small amplitudes, the squeezing effect is absent and the profile remains sinusoidal. Another interpretation of the blunting is the following. The miscut has the effect to suppress the singularity of the free energy as a function of $z_x$ (14), so that the Bonzel-Preuss calculation applies, which does predict a blunting. Simulations showed that increasing the step interaction energy relative to the step energy causes the steep portion between maximum and minimum of the profile to become less steep, as one expects.

Keeping the step energy parameters constant, the influence of $\alpha$ on profile shape was also studied using the same algorithm. The smaller the miscut $\alpha$, the flatter the tops and bottoms of the profile. The behavior of the interesting $\psi = \pi/2$ case for larger slopes, where steps of opposite sign would be generated by the modulation, has not been dealt with so far. The question whether such profiles would facet or not remains unresolved. This case is, from an experimental point of view, an enormous challenge because the positioning of the profile parallel to the intrinsic steps would have to be very accurate. Bonzel & Mullins have also treated the decay of a periodic profile of small amplitude ($h/\lambda \ll \alpha$) when there is a crossover from migration-limited to attachment-detachment surface-diffusion kinetics. The crossover occurs in the vicinity of a wavelength $\lambda^*$. The above relation $\tau \propto \lambda^4$, characteristic of migration-limited kinetics, holds only for $\lambda \gg \lambda^*$, while $\tau \propto \lambda^2$, characteristic of attachment-detachment-limited kinetics, holds only for $\lambda \ll \lambda^*$. This is a fairly remarkable result which contrasts with the case of competition between surface diffusion kinetics and evaporation-deposition kinetics on non-singular surfaces. Then, $\tau$ is proportional to $\lambda^4$ for short wavelengths and to $\lambda^2$ for long wavelengths.

**XII. LONG RANGE INTERACTIONS**

To our knowledge, all computer simulations have been made without taking long range interactions into account, while theoretical treatments use an entropic interaction in $1/\ell^2$ between neighbouring steps, which corresponds to a contact repulsion. This is a questionable choice, because Météo has experimentally shown that the elastic or electrostatic interaction is larger than the entropic interaction even at fairly high temperature.

In the present section, we briefly discuss the expected effect of long range, repulsive interactions... and find quite disappointing results.

As seen in section IIIA, the total elastic and electrostatic interaction per unit length between two steps at distance $\ell$ is $C/\ell^2$ for steps of identical sign, and $C'/\ell^2$ for steps of opposite sign, where $C$ and $C'$ are constants.

We shall first adress the case $C = C' > 0$, neglecting step fluctuations. Then, the sign of the steps is irrelevant, and therefore a state with equally distant steps (Fig. 11) is an equilibrium state, since it is an equilibrium state when all steps have the same sign. For appropriate step signs, one can give to this equilibrium state any arbitrary height $h$ and wavelength $\lambda$. The existence of an equilibrium state of arbitrary height and wavelength in the absence of step fluctuations suggests a very slow decay when step fluctuations are taken into account. The profile has a zigzag shape without facets. This picture is very far from experiments.

Can we do better by assuming $C > C' > 0$? It is easily seen from a perturbative treatment that there is still an equilibrium state of arbitrary height and wavelength in the absence of step fluctuations, at least if $C'$ is not too different from $C$. The profile has again a zigzag shape without facets. The tops and bottoms are even sharper. We do not get closer to experiments although the fluctuation-induced relaxation can be somewhat faster.

In the case $C' > C > 0$, the perturbative treatment shows that there is also an equilibrium state of arbitrary height, but now the profile has facets. However, an extremely slow relaxation is expected.

These results are quite disappointing. On one hand, steps should interact. On the other hand, taking interactions into account yields results which disagree with experiments. This paradox disappears if the surface is miscut.
XIII. UNSTABLE ORIENTATIONS

In section II, we mentioned that vicinal (001) and (111) faces of Au are thermodynamically unstable. This property may be related to an interaction between steps which is not uniformly repulsive in contrast with the assumptions made, for instance in section IV B. The origin of this interaction may be one of those addressed in subsection IV B. However, although it is well known that Au(111) possesses a $22 \times \sqrt{3}$ reconstruction, the role played by the surface reconstruction is not so clear as in the case of vicinal Au(100) surfaces or vicinal Si(111) surfaces. “Magic vicinals” have been invoked, both theoretically and experimentally, in order to explain the remarkable stability of particular vicinals. Such surfaces are characterised by a strong relationship between the terrace width and the reconstruction mesh. It has been observed for example on vicinals Au(100) and also on vicinal Pt(100). The role of surface reconstruction is clearly evidenced in the pioneering work of Williams et al. on Si(111), which is reported in subsection III B.

As pointed out initially by Marchenko and more explicitly by E. Williams and her colleagues, elastic effects are important in the “phase separation” phenomenon described in subsection II B. Without taking elasticity into account, an unstable surface, e.g. Au(11 9 9) would separate into domains whose size would increase indefinitely with time.

Elasticity limits the size of the domains, because each surface element of each “phase” exerts a stress on the solid, the result of which is an elastic interaction proportional to $1/|\mathbf{r} - \mathbf{r}'|^3$ between two surface elements $d\mathbf{r}$ and $d\mathbf{r}'$ at points $\mathbf{r}$ and $\mathbf{r}'$. The total energy of a stripe of size $\ell$ is obtained by summing over the two coordinates of the points atoms $\mathbf{r}$ and $\mathbf{r}'$. This operation multiplies by the sample width $L_y$ and introduces 3 integrals which transform the function $1/|\mathbf{r} - \mathbf{r}'|^3$ into a divergent function of $\ell$ proportional to $\ln \ell$. Similarly, the energy of a periodic array of stripes of two different orientations is proportional to $L_y \ln \ell$ per period, so that the elastic energy density is proportional to $\ln \ell/\ell$. The coefficient turns out to be positive if the average orientation is unstable. Since the energy density resulting from domain boundaries is proportional to $1/\ell$, too large domains are thermodynamically unstable with respect to domain wall formation. To summarize, an unstable surface can reach an equilibrium state by forming a periodic structure of alternate “phases”. The value of the period is given by a balance in energy between the elastic energy and the energy cost of boundaries. Indeed, a long range order is present on the stepped surfaces of Au(111) described previously in subsection II B (figures 4 and 5). The morphology of the faceted Au(11,9,9) surface (figure 5) is clearly periodic. The value of the period is about 65 Å, as it was determined both using diffraction technique (LEED) and statistical analysis of STM images. In the case of Au(5,5,4), the quasi-period is about 1800 Å. The factor of more than 20 between the values of both surfaces can be qualitatively understood as follows.

The surfaces of interest are vicinals of (111) defined by Miller indices (mmp), with $m/p$ close to 1. They all correspond to [1,1,0] steps, but these steps have a different structure for $m/p < 1$ and for $m/p > 1$ (compare fig. 4a and 4b). Their energy can therefore be quite different. Moreover, since the elastic energy is proportional to $\ln \ell$, the equilibrium domain width $\ell_{eq}$ is an exponential function of the step energy, and this can explain the very high ratio between the widths in figures fig.5a and 4b. Details are given by Rouset et al. It should be pointed out that, so far, no evolution of the faceted morphologies has been found by increasing, either the temperature of annealing (since 400°C until 700°C), or the time of annealing (since a few minutes until 24 hours). This suggests that the observed morphologies are close to the equilibrium state. Perhaps not quite the equilibrium state. Indeed, the evolution toward the thermodynamically stable state can be expected to be very slow. This slow evolution results from the attractive interaction between steps which has been seen to be presumably responsible for the instability. This interaction favours the formation of step bunches observed in Fig. 4. The motion of these bunches is presumably more difficult than that of isolated steps, just as big particles diffuse less easily in any medium than slow particles. Moreover, if the bunches are close to the optimal size $\ell_{eq}$, the evolution toward this size requires breaking the bunches, which is certainly very difficult. More precisely, the evolution toward equilibrium should be rather slow until the period reaches a value of order $\ell_{eq}/2$, and much slower yet afterwards. The above discussion holds for mmp surfaces with $m/p < 1$, whereas the case $m/p > 1$ is more complicated.

The attraction between steps is also expected to produce a very slow decay of grooves on Au(111) and Au(001). These grooves are completely different from those on Ni(111) and Ni(001), whose vicinals are stable. In particular, there is no objection to the formation of facets since unstable orientations result from attractive interactions between steps of identical sign, while the instability of facets, advocated by certain theorists, is related to the repulsive interaction. Moreover, these facets are expected to decay very slowly since the upper and lower steps are tightly bound to their colleagues and can but hardly detach from them and combine with the opposite step of opposite sign.

Groove healing has also been observed on Au(111) vicinal surfaces ($\alpha = 1.5^\circ, 5^\circ$), where the decay of perturbations of orientations $\psi = 0$ and $\psi = \pi/2$ were observed ($\psi$ is defined in section 8). These profiles could not be treated under the small slope approximation. Initially the etched profiles have nearly square wave shapes, but after some time of annealing, sharp edges are eliminated. The decay of the $\psi = 0$ profiles is much faster than the one for $\psi = \pi/2$ profiles. The former shows a well-rounded shape after some time of annealing, while the $\psi = \pi/2$ profile
does not become sinusoidal even after a very long time.

For $\psi = \pi/2$ a (111) facet is present, in addition to an extra facet which is flat bounded by edge-like features indicative of missing orientations. The profile in this case becomes very asymmetrical. A possible explanation is that, when the profile is etched on a vicinal surface, the terrace widths are not the same. When the terrace widths are smaller than a given minimum, if the average orientation of this part of the profile is close to a magic orientation, it is energetically more favorable for the surface to present a flat region than to maintain the structure of steps/small terraces.

XIV. CONCLUSION

We have reviewed the state of the art of groove smoothing.

When the average surface is non-singular and far from any singular orientation, everything is clear and there is nothing to add to Mullins' theory.

When the average surface is singular and the neighbouring orientations are unstable, the situation is pretty clear too. Facets should appear at the top and at the bottom, they have sharp edges, and the decay is expected to be generally very slow. An experimental check of the theory is not yet available, and can obviously be made only if the decay is not too slow.

When the average surface is singular and the neighbouring orientations are stable, e.g. Ni(001), the situation is more complicated, except for a miscut surface.

Let the controversial state of the art be summarized in the case of a singular surface of an ideal, perfectly cut crystal, when the neighbouring orientations are stable. The most common theoretical approach is a generalization of Mullins' theory, using the non-equilibrium chemical potential $\mu$. However, the choice of the appropriate formula for $\mu$ is controversial. A correct theoretical treatment should correctly take into account the peeling of the successive layers, and therefore the fluctuations of the top and bottom ledges. The attempt presented in section X tends to confirm the results obtained without taking fluctuations into account, i.e. there is no facet on a well-cut profile. However, the treatment of fluctuations in section X is far from being exact. The most recent experiments suggest that facet do appear in well-cut surfaces as well. This is in agreement with certain theories, although these theories do not take fluctuations into account in a satisfactory way either.

A point which requires further investigation is the ‘transient’ attraction investigated in section IX. It is clearly effective for an (unphysical) one-dimensional surface. It appears between two steps of identical sign because an atom diffusing from the lower to the upper step has a shorter path and therefore a lower probability to come back. It does produce a blunting of a one-dimensional profile. Whether it produces a similar effect on real surfaces is still unclear.

Most of existing theoretical treatments of the groove problem ignore long range (elastic or electric) interactions between steps. The attempt which was done here does not yield satisfactory results. However, these interactions are extremely important in the other problem reviewed here, namely phase separation of vicinal surfaces. A careful comparison of both types of experiments in the same materials would probably lead to a better understanding of interactions between steps.
1 E.D. Williams, R.J. Phaneuf, J. Wei, N.C. Bartelt, T.L. Einstein, Surf. Science 294, 219 (1993). Thermodynamics and statistical mechanics of the faceting of stepped Si(111); E.D. Williams, Surface Sci. 299/300, 502 (1994). Surface steps and surface morphology: understanding macroscopic phenomena from atomic observations.

2 J. M. Blakely, H. Mykura, Acta Metall. 10, 565 (1962). Surface self diffusion and surface energy measurements on Platinum by the multiple scratch method.

3 K. Yamashita, H.P. Bonzel, H. Ibach, Appl.Phys. 25, 231 (1981). Steady state shapes of periodic profiles on (110), (100) and (111) surfaces of Nickel.

4 W.W. Mullins, J. Appl.Phys. 28 333 (1957) Theory of thermal grooving.; 30, 77 (1959) Flattening of a nearly plane solid surface due to capillarity.

5 H.P. Bonzel, E. Preuss, Appl.Phys. A35, 1 (1984). The dynamical behaviour of periodic surface profiles on metals under the influence of anisotropic surface energy.

6 H.P. Bonzel, E. Preuss, B. Steffen, Surface Sci. 145, 20 (1984). Periodic surface profiles under the influence of anisotropic surface energy: a steady-state solution.

7 H.P. Bonzel, U. Breuer, B. Voigtlander, E. Zeldov, Surface Sci. 272, 10 (1992). Temperature-dependent morphologies of gold surfaces.

8 J.C. Girard, thèse (1993) and ref. therein.

9 L. Masson, thèse (1994) and ref. therein.

10 C. Alfonso, J.M. Bermon, J.C. Heyraud, J.J. Metois Surface Sci. 262, 371 (1992). The meandering of steps and the terrace width distribution on clean Si(111).

11 M. Flytzani-Stephanopoulos and L.D. Schmidt, Prog. in Surf. Sci. 9, 83 (1979). Morphology and etching process on macroscopic metal catalysts.

12 F. Pourmir, S. Rousset, S. Gauthier, M. Sotto, J. Klein, J. Lecoeur, J.P. Bellier, Surface Science 324, L337 (1995). Superperiodicity in the thermal faceting of Au(111) vicinal surfaces.

13 Ph. Nozières, J. de Physique 50, 2541 (1989). Surface melting and crystal shape.

14 J.C. Heyraud, J.J. Métois, J.M. Bermond, J. Cryst. Growth 98, 355 (1989). Surface melting and equilibrium shape: the case of Pb on graphite.

15 H. M. van Pinxteren, B. Pluis and J.W.M. Frenken, Phys. Rev. B 49, 13798 (1994). Temperature dependence of surface-melting-induced faceting of surfaces vicinal to Pb(111).

16 R.J. Phaneuf, N.C. Bartelt, E.D. Williams, W. Swiech and E. Bauer, Phys.Rev.Lett. 67, 2986 (1991). Low-energy electron-microscopy investigations of orientational phase separation on vicinal Si(111) surfaces.

17 P. Nozières (1991) in “Solids far from equilibrium”, ed C. Godreche (Cambridge University Press). Shape and growth of crystals.

18 J. Vilain, A. Pimpinelli, Physique de la Croissance Cristalline, Eyrolles-Alea-Saclay, Paris (1994) and english version, to be published.

19 C. Herring, in “Structure and properties of solid surfaces”, ed. R. Gomer and C.S. Smith (University of Chicago Press, Chicago) pp. 5-81 (1953). The use of classical macroscopic concepts in surface energy problems.

20 W.W. Mullins in “Metal Surfaces: Structure, Energetics and Kinetics”, Am. Soc. Metals, Metals Park, Ohio, p. 17. (1963) Solid surface morphologies governed by capillarity.

21 H. van Beijeren, I. Nolden, in “Structure and Dynamics of Surfaces”, II, Ed. W.Schommers and P. von Blanckenhagen, “Topics in Current Physics ” 43 (Springer, Berlin) (1987).

22 P. Nozieres, J. Physique 48, 1605 (1987). On the motion of steps on a vicinal surface.

23 J.W. Cahn, J.E. Taylor, Acta Metall. Mater. 42, 1045 (1994). Surface motion by surface diffusion.

24 W.C. Carter, A.R. Rosen, J.W. Cahn, J.E. Taylor, Acta Met.43, 4309 (1995). Shape evolution by surface diffusion and surface attachment limited kinetics on completely faceted surfaces.

25 H.P. Bonzel, E. Preuss, Surf. Sci. 336, 209 (1995). Morphology of periodic surface profiles below the roughening temperature: aspects of the continuum theory.

26 H.P. Bonzel, P. Wynblatt, Z. Phys. Chemie 198, 246 (1997) A comparison of equilibrium crystal shapes and periodic surface profiles below Tg.

27 M.D. Thompson, H.B. Huntington, Surface Sci. 116, 522 (1982). Adatom binding at the surface ledges of a jellium metal.

28 W. Kohn, K.H. Lau, (1976) Solid State Comm. 18, 553. Adatom dipole moments on metals and their interactions.

29 M. Lannoo, G. Allan (1978) Solid State Comm. 28, 715. Band effects and the dipole interaction between two adatoms on a metal surface.

30 V.I. Marchenko, A Ya. Parshin, Sov. Phys. JETP 52, 129 (1980/81?). Elastic properties of crystal surfaces.

31 O.L. Alerhand, D. Vanderbilt, R.D. Meade, J. D. Joannopoulos, Phys.Rev. Lett. 61 1973 (1988) Spontaneous formation of stress domains on crystal surfaces.; O.L. Alerhand, A.N. Berker, J.D. Joannopoulos, D. Vanderbilt, R.J. Hamers, J.E.
Demuth, Phys.Rev.Lett. 64 1990 (1990). Finite temperature phase diagram of vicinal Si(100) surfaces.

32 E.E. Gruber, W.W. Mullins, J. Phys. Chem. Solids 28, 875 (1967) On the theory of anisotropy of crystalline surface tension.

33 V.L. Pokrovskii, A.L. Talapov, Phys. Rev. Lett. 42, 65 (1979). Ground state, spectrum and phase diagram of two-dimensional incommensurate crystals.

34 F.D.M. Haldane, J. Villain, J. de Physique 42, 1673 (1981). Commensurate–incommensurate transitions of physisorbed monolayers on anisotropic substrates.

35 P.G. de Gennes, J. Chem. Phys. 48, 2257 (1968).

36 J. Villain (1980) in "Ordering in strongly fluctuating condensed matter systems", ed. T. Riste (Plenum, New York). Two-dimensional solids and their interaction with substrates.

37 C. Jayaprakash, C. Rottman, W.W. Mullins, J. Villain, Journal de Physique I France 9, 82 (1996). Magic vicinal surfaces stabilized by reconstruction.

38 O.A. Andreeva, K.O. Keshishhev, JETP Lett. 64, 5013 (1990). Morphological equilibration of a corrugated crystalline surface.

39 M. Uwaha, J. Phys. France 51 2743 (1990). Possible long range step interaction in He due to step oscillations.

40 S. Balibar, C. Guthmann, E. Rolley J. de Physique I 3, 1475 (1993). From vicinal to rough crystal surfaces.

41 K. H. Lau, W. Kohn (1978) Surface Sci. 75, 69. Indirect long range interaction between adsorbed atoms.

42 D.J. Liu, J. Weeks, Phys.Rev. Lett. 79, 1694 (1997). Interactions between fluctuating steps on vicinal surfaces: Edge energy effects in reconstruction induced faceting.

43 A. Bartolini, F. Ercolessi, E. Tosatti, Phys.Rev.Lett. 63, 1989. “Magic” vicinal surfaces stabilized by reconstruction.

44 A. Rettori, J. Villain, J. Phys 49, 257 (1988). Flattening of grooves on a crystal surface: a method of investigation of surface roughness.

45 M. Ozdemir, A. Zangwill, Phys.Rev.B 42, 17468 (1990). Equilibration of vicinal surfaces. from step dynamics to continuum theory.

46 Z. Jiang, C. Ebner, Phys.Rev.B 40, 316 (1989). Simulated healing of crystal surfaces.

47 Z. Jiang, C. Ebner, Phys.Rev. B 53, 1146 (1996). Simulations of low-temperature annealing of crystal surfaces.

48 J.D. Erlebacher, M.J. Aziz, Surf. Sci. 374, 427 (1997). Morphological equilibration of rippled and dimpled crystal surfaces: the role of terrace-width fluctuations.

49 M.V. Ramana Murty, B.H. Cooper, Phys.Rev.B 54, 10377 (1996). Dynamics of surface profile evolution through surface diffusion.

50 P.C. Searson, R. Li, K. Sieradzki, Phys. Rev. Lett. 74, 1395 (1995). Surface diffusion in the Solid-on-solid model.

51 W. Selke, P.M. Duxbury, Phys.Rev.B 52, 194 (1995). Equilibration of crystal surfaces.

52 W. Selke, P.M. Duxbury, Z. Phys.B 94, 311 (1994). Surface profile evolution above roughening.

53 E. Adam, A. Chame, F. Lançon, J. Villain, Journal de Physique I France 7 (nov. 1997). Relaxation of a grooved profile cut in a crystalline surface of high symmetry.

54 W. Selke, J. Oitmaa, Surf. Science Lett. 198, L346 (1988). The roughening transition and the flattening of periodic surface profiles.

55 W. Selke, Bieler, Surface Science 281, 163 (1993). Morphological changes of periodic surface profiles.

56 M. Kotrla, Computer Physics Communications 97, 82 (1996). Numerical simulations in the theory of crystal growth.

57 M.E. Fisher, D.S. Fisher, Phys. Rev. B 25, 3192 (1982). Wall wandering and the dimensionality dependence of the commensurate-incommensurate transition.

58 E. Adam, private communication.

59 G. Ehrlich, F.G. Hudda, J. Chem. Phys. 44, 1039 (1966). Atomic view of surface diffusion: tungsten on tungsten.

60 R.L. Schwobel, E.J. Shipsey, J. Appl. Phys 37, 3682 (1966) Step motion on crystal surfaces; R.L. Schwobel, J. Appl. Phys 40, 614 (1969).

61 J. Villain, A. Chame, F. Lançon, P. Politi, G. Renaud, I. Villan, to be published in a special section of International Journal of Modern Physics B 11 n. 31 (1997). Three mysteries in surface science.

62 C. Dupont, A. Chame, W.W. Mullins, J. Villain, Journal de Physique I France 6,1095-1125 (1996). Decay of grooves cut in a surface with singular orientation when the neighbouring orientations are unstable.

63 H.P. Bonzel, W.W. Mullins, Surf. Sci. 350, 285 (1996). Smoothing of perturbed vicinal surfaces.

64 Y. Samson, S. Rousset, S. Gauthier, J.C. Girard and J. Klein, Surf. Sci. 315, L969 (1994) STM study of vicinal structures on Au(100).
FIG. 1. Stepped areas found on a Au(111) surface misoriented by 50°. Note that steps are straight on the right and lower part of the figure, whereas kinks are present on the left and upper part. All steps are monoatomic, 2.35 Å high. The size of the STM image is 1020 Å × 1020 Å. Light white lines, running perpendicular to the steps, are the sign of the 22 × √3 reconstruction.

FIG. 2. Interference micrographs of periodic profiles on Ni(110) and Ni(100) single crystal surfaces, both annealed at 1173 K for several hours. The profiles exhibit a wavelength of 12 micrometers and amplitudes of 0.21 and 0.27 micrometer, respectively. Note the completely different shapes in the two cases. From Yamashita et al.

FIG. 3. Interference micrograph of a periodic profile on a Au(111) surface annealed at 1123 K. The wavelength and amplitude are 7.0 and 0.125 micrometer, respectively.

FIG. 4. Decomposition of an unstable surface: Au(11,9,9). (a) Hard sphere model of the ideal Au(11,9,9). Note that the steps consist of {100} microfacets, displayed in grey. (b) STM image of the Au(11,9,9) faceted surface. The size of the image is 356 Å × 314 Å. All steps are monoatomic (2.35 Å high) and aligned along the zone axis < 0, 1, −1 >.

FIG. 5. Decomposition of an unstable surface: Au(5,5,4). a) Hard sphere model of the ideal Au(5,5,4). Note that the steps consist of {111} microfacets, displayed in grey. (b) STM image of the Au(5,5,4) faceted surface. The size of the image is 1.07 µm × 1.07 µm. (c) zoom in of the frontier between both phases, and located at the white spot on fig. 5b. On the left part, terraces are 13 Å wide, whereas on the right part they are about 35 Å wide.

FIG. 6. a) A vicinal surface. b) Free energy as a function of the slope

FIG. 7. a) Decay of grooves considered as arrays of straight steps. b) Effect of fluctuations

FIG. 8. a) The one-dimensional surface of a two-dimensional crystal. b) The same as in the previous figure when the height is just two layers

FIG. 9. Log-plot of profile amplitude versus annealing time for two profiles of 4.3 micrometer etched on a 5° miscut Au(111) crystal in the $\psi = \pi/2$ and $\psi = 0$ orientations. The ratio of decay rates at 1023 K is 25. From Surnev et al.

FIG. 10. Numerically calculated decay rate versus amplitude of periodic profiles with modulation $\psi = 0$ for three different miscut angles $\alpha$. Parameters: step free energy = 0.4, step interaction energy = 0.16, wavelength = 4. From Bonzel & Mullins
FIG. 11. A stable configuration (in the absence of fluctuations) in the case of steps interacting through a long range interaction independent of the sign of the steps.
This figure "fig1.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig2a.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig2b.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig3.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig4a.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig4b.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig5a.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig5b.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig5c.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig6a.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig6b.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig7a.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig7b.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig8a.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig9.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig10.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1
This figure "fig11.jpg" is available in "jpg" format from:

http://arxiv.org/ps/cond-mat/9912188v1