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Flattening of grooves on a crystal surface : a method of investigation of surface roughness

A. Rettori and J. Villain

Universita de Firenze, Dipartimento di Fisica Largo Enrico Fermi, 2, 50125 Firenze, Italy
 Institut für Festkörperforschung, der Kernforschungsanlage Jülich, Postfach 1913, D-5170 Jülich, F.R.G.

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Résumé. — L'évolution de sillons creusés à la surface d'un monocristal en dessous de sa température de transition rugueuse est étudiée théoriquement de façon qualitative. Dans le cas d'une modulation bidirectionnelle, la hauteur $h(t)$ est une fonction linéaire du temps t et le temps de vie est proportionnel à $\lambda^3 h(0)$, où λ est la longueur d'onde. Comme l'ont suggéré Bonzel *et al.*, la formation de facettes est une indication sensible que la surface est en dessous de sa transition rugueuse. Près des facettes, le profil présente une singularité en $(x - x_0)^{3/2}$, comme dans le cristal à l'équilibre. Le cas d'une modulation unidirectionnelle est encore peu clair, bien que des hypothèses heuristiques appropriées mènent à des résultats qualitatifs en accord avec les résultats expérimentaux.

Abstract. — The decay of a profile artificially produced on a crystal surface below its roughening transition is studied by means of a qualitative theory. In the case of a bidirectional modulation the height $h(t)$ is a linear function of time t and the lifetime τ is proportional to $\lambda^3 h(0)$, where λ is the wavelength. As suggested by Bonzel *et al.* the formation of facets is a sensitive information to determine whether a surface is below its roughening temperature. Near the flat part the profile has a $(x - x_0)^{3/2}$ singularity as in a crystal at equilibrium. The case of a unidirectional modulation is still open although some heuristic treatments give a qualitative agreement with experimental results.

1. Introduction.

It is well known that the surface of a crystal in equilibrium with its melt or its vapour can undergo a roughening transition at a temperature T_R which depends on the surface [1-3]. Below this temperature, on the atomic scale, the surface is smooth while it becomes rough above. The transition is generally of Kosterlitz-Thouless type. Experimentally the roughening transition has been reported in many different systems: helium crystals in equilibrium with superfluid helium [4-7], crystallites of lead [8] and indium [9], Zn-Bi-In alloys [10], and Cu and Ni crystals both for low Miller index orientation and vicinal surfaces [11-14].

The roughening transition has important macroscopic consequences: according to whether the surface is in the smooth or in the rough state, both the growth kinetics [15] and the equilibrium shape of crystals [3, 16] are very different. The latter is particularly important in order to observe experimentally the roughening transition. Above T_R the

surface is rounded while below T_R we have the formation of facets which are macroscopically flat. A facet in the equilibrium crystal-shape is obtained from the Wulff construction as a consequence of the existence of a cusp in the surface tension $\gamma(\hat{n})$ plot [3, 16] (\hat{n} indicates the orientation).

Recently, one of us [17] has studied the smoothening kinetics of a rough surface due to surface diffusion when the crystal is cooled down from $T > T_R$ to $T \ll T_R$. The model developed there, analogous to the Lifshitz-Slyozov theory of the growth of clusters in a supersaturated binary solution [18] is valid for nearly flat surfaces where terraces do not interact. It predicts that after a long time t the surface is flat on lengthscales smaller than $R(t) \approx t^{1/3}$.

On the other hand, existing experimental data correspond to a different situation, namely artificial, one-directional grooves [19]. A theory of Mullins [20, 21] predicts a lifetime proportional to the fourth power of the wavelength λ above T_R . The

present paper deals with the same problem below T_R , but in the case of strong surface modulation, where steps are so close to each other that their interaction is not negligible. We assume here contact interactions [22-25] rather than elastic or electrostatic ones [24] which, anyway, would make the theory of reference [17] invalid.

As a matter of fact, a theory of the decay of one-directional grooves below T_R was already given by Bonzel *et al.* [26]. This theory has the merit of explaining the very interesting qualitative results obtained experimentally by Yamashita *et al.* [19]. These authors observed the time evolution of the geometry of initially prepared sinusoidal profiles (Fig. 1) with various amplitudes and periodicities on Ni (100), (110) and (111) single crystals for temperatures between 1073-1327 K. The evolution toward the equilibrium was found very different depending on which surface the profile is created. For the (110) surface the profile maintains the sinusoidal shape during the decay (Fig. 2a) while, on the contrary, the profiles on the (100) and (111) surfaces assume a trapezoidal shape (Fig. 2b) and decay more slowly with time [19]. This difference can be interpreted as follows: in this range of temperature the (110) surface is rough [13], so that the theory of Mullins [20, 21] can be applied. This theory predicts that an initially sinusoidal profile keeps a sinusoidal form

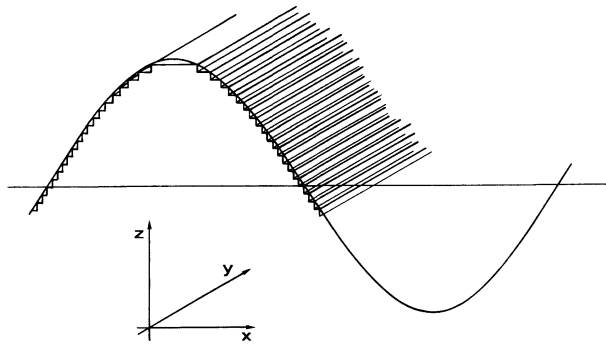


Fig. 1. — Initial profile (at a realistic scale the number of steps would be much larger).

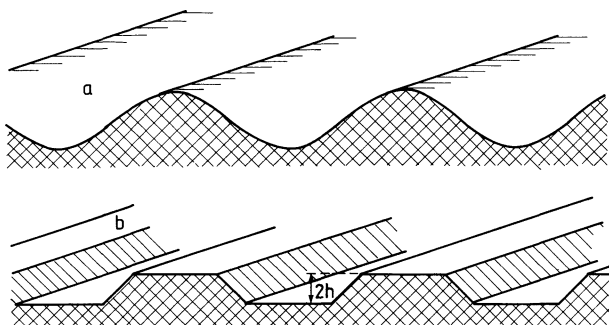


Fig. 2. — Profile experimentally observed after some time. a) Above the roughening transition temperature; b) below T_R [19, 26]. Ledges have not been shown.

when decaying. On the contrary, the [100] face is smooth (in contradiction with the claims of reference [14], but in agreement with references [11-13] as well as the [111] face, so that a new theory was necessary. That of Bonzel *et al.* [26-28] could explain the trapezoidal shape below T_R , and thus revealed the interest of this experimental method for the investigation of roughening. However this theory failed, for instance, to give the analytic dependence of the relaxation time as a function of the wavelength. The present investigation was undertaken in the hope to obtain these informations. However, the decay of unidirectional grooves turned out to be a more difficult problem than we expected and we preferred to solve the easier problem of a bidirectional modulation. The difficulties related to a unidirectional profile are explained in sections 2 to 4 and our solution in the bidirectional case is presented in sections 5 and 6.

In this paper it is always assumed that the dynamics is governed by surface diffusion. Transport through the bulk and through the vapour is neglected as in references [26-28]. The wavelength $4L$ of the profile as well as the amplitude h are assumed to be much larger than the interatomic distance. The ratio h/L is assumed to be of order 0.1 or less as in the experiments [19].

2. The equations of motion above T_R , and why they fail below T_R .

In this section we recall the calculation of Bonzel *et al.* [26-28] in the one-directional case.

Throughout this paper it is assumed that atoms move only at the surface. Let z be the direction normal to the average surface, y the direction of the grooves and x the direction perpendicular to y and z (Fig. 1). The height z of the surface obeys the continuity equation

$$\dot{z} = -\partial j / \partial x \quad (2.1)$$

where j is the current density of atoms. In addition to this *exact* equation, Bonzel *et al.* assume the following equation which is phenomenological, but standard [21]:

$$j = -D \partial \mu / \partial x \quad (2.2)$$

where μ is the local chemical potential which is assumed to be zero for a flat surface due to an appropriately chosen origin. Now, μ is given by a formula of Herring [29, 20, 21], (rederived here in Sect. 3) namely

$$\mu = \frac{\partial}{\partial x} \frac{\partial G}{\partial z'}, \quad (2.3)$$

where $z' = \partial z / \partial x$ and $G(z')$ is the free energy per unit *projected* surface area on the xOy plane. Thus, the surface tension is

$$\gamma = G(z') / \sqrt{1 + z'^2}. \quad (2.4)$$

Formula (2.3) will be rederived in section 3. Above the roughening transition, G is an analytic function of z' :

$$G = G_0 + \frac{1}{2} G_2 z'^2 + \frac{1}{4} G_4 z'^4 + \dots \quad (T > T_R). \quad (2.5)$$

At sufficiently long times or for sufficiently smooth initial profiles one can neglect fourth and higher order terms. Equations (2.1) to (2.5) yield

$$\dot{z} \approx DG_2 z'''. \quad (2.6)$$

Thus, an initially sinusoidal profile remains sinusoidal. The [110] Ni surface has this property at about 1 100 to 1 200 K [19], but not the [111] and the [100] faces. The only possible explanation is that these surfaces are below their roughening transition temperature. It turns out that the initially sinusoidal profile transforms into a faceted one (Fig. 2) after some time in the case of [111] and [100] nickel faces. Since facets are known to appear below T_R at equilibrium [3, 4, 5, 8, 9, 16, 21, 30] it is not too surprising that they also appear in a dynamical pattern. However, the extension of the classical theory of faceting [3, 16] to a dynamic case is not straightforward since the chemical potential μ oscillates around a vanishing value. In the static case, instead, μ is constant and it is sufficient to solve the single equation (2.3), which yields the Wulff construction. In the dynamical problem one should work with three equations (2.1) to (2.3). But there are more fundamental difficulties.

As noticed by Bonzel *et al.* [26] the analytic form (2.5) is not correct below T_R . Instead one should use the Gruber-Mullins-Pokrovski-Talapov formula [22, 23, 30]

$$G = G_0 + g|z'| + \frac{1}{3} G_3 |z'|^3 + \dots \quad (2.7)$$

Bonzel *et al.* inserted (2.7) into (2.3), obtaining

$$\mu = gz'' \delta(z') + 2 G_3 |z'| z''. \quad (2.8)$$

Then they solved numerically the system (2.1, 2.8), replacing the continuum by a lattice and the delta function by a sharply peaked one. The correctness of this trick is questionable. As a matter of fact, (2.8) is already dubious since $z'' \delta(z') = 0 \times \infty$ is undetermined on flat parts, and flat parts occupy a large proportion of the surface according to experimental results. Replacing the δ -function by an analytic one, Bonzel *et al.* force μ to vanish on facets. In reality μ should be allowed to vary on facets, reflecting a variable density of mobile atoms and holes.

Another difficulty is the following : the second term of (2.7) is just proportional to the number of

steps. So, it corresponds to an attractive energy between the two top steps of figure 1. If these 2 steps recombine, there is an energy gain $2g$ per unit length in the y direction. However, this is a *contact* interaction. If both upper edges are very far from each other, as experiments suggest (Fig. 2), they do not feel each other ; this suggests that the first term of the right hand side of (2.8) should be omitted or at least replaced by some more complicated term, possibly non-local in time, since the steps require some time to establish contact.

Some unsuccessful attempts to overcome this difficulty will be described in section 4. In section 5 a different geometry will be considered where this problem does not arise.

3. Equations of motion below T_R in the sloping parts.

In the non-horizontal parts of the profile, equations (2.1, 2.2, 2.3) and (2.7) will be applied. The validity of (2.2) has been questioned by Nozières and for this reason it is discussed in this section. It is assumed that almost all mobile atoms are on ledges, so that it is sufficient to know the chemical potential μ_n of an atom lying on the n 'th ledge (Fig. 3). μ_n is equal to the difference $\phi - \phi_n^-$, where ϕ is the free energy per atom when these atoms are present, and ϕ_n^- is the free energy when they are removed. We assume

$$\phi = \phi_0 + \sum_n \varphi(\ell_n) \quad (3.1)$$

where ℓ_n is the average distance between steps n and $(n-1)$. ϕ_n^- is given by the same expression except that ℓ_n and ℓ_{n+1} are replaced by $(\ell_n) + 1$ and $(\ell_{n+1}) - 1$ respectively. The chemical potential is therefore, for large ℓ_n

$$\mu_n = \varphi(\ell_n) + \varphi(\ell_{n+1}) - \varphi(\ell_n + 1) - \varphi(\ell_{n+1} - 1)$$

or

$$\mu_n = \varphi'(\ell_{n+1}) - \varphi'(\ell_n) \quad (3.2)$$

where

$$\varphi'(\ell) = d\varphi(\ell)/d\ell.$$

As previously promised we can now derive relation (2.3). In the continuum limit the value of μ_n at a

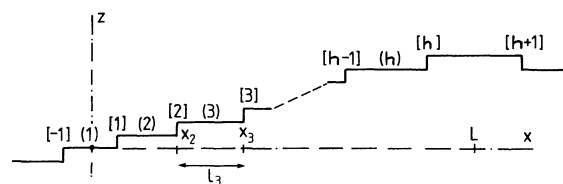


Fig. 3. — Labelling of ledges [] and terraces (). In contrast with us, Nozières [32] puts terrace (n) at the right of ledge $[n]$.

point where ℓ_n has the value ℓ is given by the following relation derived from (3.2).

$$\mu = \ell \frac{d}{dx} \varphi'(\ell) = \ell \frac{d\ell}{dx} \varphi''(\ell)$$

or, since $\ell = 1/z'$ where $z' = \partial z / \partial x$,

$$\begin{aligned} \mu &= \frac{1}{z'} \varphi''(\ell) \frac{\partial}{\partial x} 1/z' = \\ &= -z'^{-3} z'' \varphi''(1/z'). \end{aligned} \quad (3.3)$$

On the other hand, the function G of (2.3) is related to ϕ by $G = \phi/\ell = G_0 + \varphi/\ell$, therefore

$$\begin{aligned} \varphi''(1/z') &= [\partial/\partial(1/z')]^2 (G/z') \\ &= [\partial/\partial(1/z')][G - (1/z') \partial G/\partial(1/z')] \\ &= - (1/z') [dz'/d(1/z')]^2 \partial^2 G/\partial z'^2 \\ &= -z'^3 \partial^2 G/\partial z'^2. \end{aligned}$$

Insertion into (3.3) yields (2.3) as promised.

Below T_R and for large ℓ , $\varphi(\ell) = \ell(G - G_0)$ is given, according to (2.7), by

$$\varphi(\ell) = g + \frac{1}{3} G_3/\ell^2. \quad (3.4)$$

It is of interest to recall the statistical mechanical meaning of this equation : if ℓ is small, each ledge is squeezed against its neighbours and has less entropy, therefore more free energy. Insertion of (3.4) into (3.2) yields

$$\mu_n = G_3(\ell_n^{-3} - \ell_{n+1}^{-3}) \quad (3.5)$$

μ_n has been defined as the free energy loss per atom when an atomic row is removed at the n 'th ledge. For large n , it is also seen to be equal to the free energy gain per atom when an atomic row is added. Thus, if $\mu_n = \mu_{n-1}$, one can transfer the atoms from the ledge $N^\circ n$ to the ledge $N^\circ n-1$ (or vice versa) with a free energy change $\mu_n - \mu_{n-1} = 0$. Thus, the current density j_n between step n and step $n-1$ (counted as positive if atoms move to the right) should vanish when $\mu_n = \mu_{n-1}$. It is reasonable to assume a linear relation

$$j_n = -K(\mu_n - \mu_{n-1})/\ell_n. \quad (3.6)$$

This is the discrete version of the standard equation (2.2) which can be found in textbooks [31]. However, it is worth recalling the meaning of these equations since Nozières [32] suggested D might have a singular behaviour which ℓ goes to ∞ . j_n may be seen as a sum of the current j_{n-1}^+ from ledge $(n-1)$ to ledge n , and a current j_n^- in the opposite direction. These currents are nearly equal, and strictly equal if the chemical potentials μ_n and μ_{n-1} are equal. Otherwise the detailed balance principle yields

$$j_{n-1}^+ e^{-\beta\mu_{n-1}} + j_n^- e^{-\beta\mu_n} = 0.$$

When $(\mu_n - \mu_{n-1})$ is small the total current is

$$\begin{aligned} j_n &= j_{n-1}^+ + j_n^- = j_n^- [1 - e^{-\beta(\mu_n - \mu_{n-1})}] \\ &\simeq \beta j_n^- (\mu_n - \mu_{n-1}). \end{aligned}$$

It may be convenient to consider the case when almost all atoms which reach the $(n-1)$ 'th ledge are adsorbed by it. In this case j_n is the current of particles which start from the n 'th ledge and reach the $(n-1)$ 'th ledge (Fig. 4). This is the product of the current emitted by the n 'th ledge in the negative direction, multiplied by the probability $p(\ell_n)$ that a particle can accomplish a random walk of length ℓ_n without coming back to its starting point before ; $p(\ell)$ can easily be calculated from the equation $p(2\ell) = \frac{1}{2}p(\ell)$ which results from the observation that, if the particle is just midway, it has the same probability 1/2 to reach the goal or to come back to the starting point. It results $p(\ell) \sim 1/\ell$ and formula (3.6). A quite different argument has been given in reference [17]. An apparent weakness of both derivations is that it neglects the fluctuations of the distance ℓ . In particular two neighbouring ledges have contact points where $p(\ell)$ becomes equal to 1. However, it is easily seen that the number of contact points is proportional to $1/\ell_n^2$, so that they cannot produce a divergence of K in (3.6). We conclude that K has a well-defined value, which will be calculated in section 6.

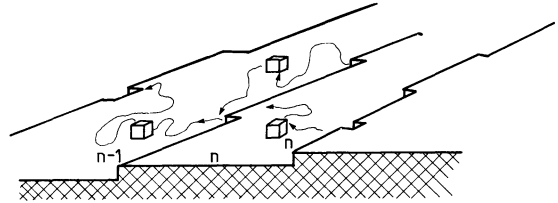


Fig. 4. — Diffusion of atoms between ledges. Atoms are shown as cubes.

Nozières [32] used equation (3.6) without the denominator ℓ_n . The reason is that he assumes the chemical potential to be well-defined for terraces rather than for ledges. Then, since two neighbouring terraces are in contact, there is no reason for the factor $1/\ell_n$ in (3.6). In practical situations when a current is present it is presumably not strictly possible to define a chemical potential neither for terraces (as Nozières does) nor for ledges (as we do). However, our assumption that diffusion along ledges is very fast so that ledges reach thermal equilibrium before atoms can be exchanged between ledges is acceptable, in this sense that it does not violate any physical law. Nozières' assumption would imply serious complications for at least two reasons.

Firstly, on the top terrace, which is very broad, the chemical potential is *not* uniform. Secondly, since the free energy and chemical potentials are expressed as functions of ledge location, it is much easier to assume they are defined on ledges rather than on terraces. Anyway the essential results (Sect. 6) would probably not be much altered if one uses Nozières' formula as will be argued in section 7.

It is of interest to check that the equilibrium shape of a bar can be obtained from (3.5) if $\mu_n = \mu$ is constant. In the continuum limit one obtains

$$-2 G_3 z' z'' = \mu \quad (3.7)$$

which does reproduce the standard Wulff construction.

4. How does the top of the wave look like ?

As noticed in section 2, the non-analytic nature of the chemical potential (2.8) creates difficulties for $z' = 0$. These difficulties are also related to the existence of a *contact*, attractive interaction between the two top ledges which may be very *far* from each other, as explained at the end of section 2.

Suppose one starts, as in the experiment [19] with a sinusoidal profile prepared at room temperature and then heated to 1 000 K. Thermal fluctuations establish after some rather short time τ , the contacts between ledges which, away from the top and the bottom of the wave, are responsible for the repulsive Gruber-Mullins-Pokrovskii-Talapov interaction (3.4) or (2.8) between ledges of the same « sign ». The « sign » of a ledge is here defined « plus » if the upper terrace corresponds to larger x values, « minus » in the opposite case. On the other hand, the upper (or lower) two ledges of each period have

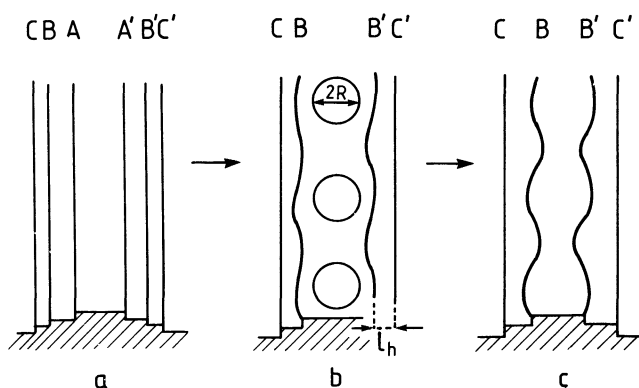


Fig. 5. — Top view of the top of the profile : a) initial state ; b) when closed terraces are present ; c) when they have disappeared. This picture neglects fluctuations and is only locally true : closed terraces may be present at some place and have already disappeared somewhere else. The anisotropy of the problem is not reproduced : the closed terraces of (b) would be elongated ellipses in a realistic picture.

an attractive interaction, which results after a time of order τ in a decay of the upper terrace into a series of smaller terraces (Fig. 5b). If those terraces have a radius of order R , they are expected [17] to emit a current $j \sim \text{Const.}/R^2$ and to decay in a time proportional to $1/R^3$. This has the effect to repel the other terraces, and this is in agreement with the experimental observation that the top of the profile forms a facet [19]. However, when the closed terraces have disappeared (Fig. 5c) the upper two ledges B, B' do not touch each other, so that the attractive interaction between them is not effective. Then, the effect which pushes the upper two ledges together again is the pressure of the lower ledges, but this seems to imply that all ledges come back together, thus preventing the formation of a facet. This would disagree with experiment.

We see several possible explanations to this puzzle.

- a) The model might be wrong : transport through the gas and the solid might be effective. We do not expect this effect to favour faceting, and this does not seem to be a satisfactory explanation.
- b) The unidirectional profile might be unstable with respect to periodic perturbations parallel to the ledges (Fig. 6).

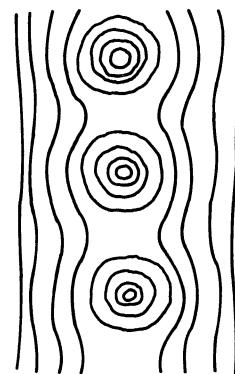


Fig. 6. — A possibility, to be tested by further numerical calculations : the one-directional profile might become unstable.

- c) The alternation of the situations of figures 5b and c might influence only the upper ledges. There would not be facets in a strict sense, but the tops would just be very flat.

The possibilities (b) and (c) should be tested by numerical analyses which are not extremely easy. We prefer to leave the question open and to concentrate on a bidirectional modulation (Fig. 7) which does not show the same difficulties as the unidirectional one. This problem will be treated in the next section.

Before doing that, we close this study of the

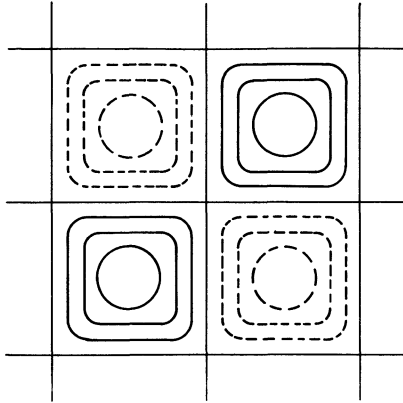


Fig. 7. — Top view of the initial two dimensional profile. Full lines : $z \geq 0$; dashed lines : $z < 0$.

unidirectional case by mentioning a last (unsuccessful !) attempt. The situation of figure 5c may reasonably be expected to have a longer duration than figure 5b since the closed terraces have a rather short lifetime. Since the attractive interaction between B and B' is ineffective in figure 5c, one may try to neglect them. Then equations (3.5) and (3.6) yield

$$j_n = -KG_3 \left(\frac{2}{\ell_n^3} - \frac{1}{\ell_{n-1}^3} - \frac{1}{\ell_{n+1}^3} \right) / \ell_n \quad (1 < n < h). \quad (4.1)$$

Here h is the index of the left hand upper ledge (B on Fig. 5c, A on Fig. 5a). For $n = 1$, the symmetry of the problem implies $\ell_{n+1} = \ell_{n-1}$ and (4.1) can be written as

$$j_1 = -2KG_3 \left(\frac{1}{\ell_1^3} - \frac{1}{\ell_2^3} \right) / \ell_1. \quad (4.2)$$

Finally for the upper step $n = h$, we just neglect the attractive interaction with the next step as explained before and write

$$j_h = -KG_3 \left(\frac{2}{\ell_h^3} - \frac{1}{\ell_{h-1}^3} \right) / \ell_h. \quad (4.3)$$

This is the crucial approximation of the theory. The remaining equations are

$$\ell_n = x_n - x_{n-1} \quad (4.4a)$$

$$\ell_1 = 2x_1 \quad (4.4b)$$

where x_n is the position of the n 'th step, the motion of which is given by

$$\dot{x}_n = j_{n+1} - j_n. \quad (4.5)$$

This equation holds for $1 \leq n \leq h$ and also $n = h$ provided one defines

$$j_{h+1} = 0 \quad (4.6)$$

since the current vanishes at the top of the wave because of symmetry.

Finally h is defined as the largest value of n which satisfies

$$x_n \leq L \quad (4.7)$$

where $4L$ is the wavelength of the profile.

After disappearance of transients the structure is expected to take a form which corresponds to weak currents j_n . This conjecture is correct in a linear system (e.g. in the present problem above T_R) since long-lived eigenmodes correspond of course to weak currents. Thus it is reasonable to neglect j_n in (4.1) and (4.3). It follows

$$1/\ell_{h-n}^3 = (n+1)/\ell_h^3. \quad (4.8)$$

A straightforward calculation shows that the current deduced from (4.1) and (4.3) is weak and therefore the treatment is self-consistent.

Formula (4.8) can be written as $dz/dx \sim (h-z)^{1/3}$ or $h-z \sim (L-x)^{3/2}$. The curvature is thus infinite at the top of the profile, in total disagreement with experiment. The law $\delta z \sim (\delta x)^{3/2}$ is known to describe the neighbourhood of a facet in an equilibrium configuration [30] and this is not surprising since we have neglected the current, which of course is zero at equilibrium, so that the equations we solved are precisely the equilibrium equations. Unfortunately, we failed to reproduce the facet. This proves that attractive interaction between top ledges should be taken into account.

5. Bidirectional modulation.

In this section we study the decay of a profile modulated in two orthogonal directions with a wavelength $4L$ (Fig. 7). The initial height of the surface at coordinates x, y may for instance be chosen to be

$$z(x, y, t = 0) = h_0 \sin(\pi x/2L) \sin(\pi y/2L). \quad (5.1)$$

This geometry is more difficult to realize in practice... but more accessible to theory. Indeed the difficulties related to the disappearance of closed terraces as in figure 5b are avoided since all terraces are closed.

Above T_R a linear equation which generalizes (2.6) may be written. (5.1) is seen to be the stable profile form, if h_0 is replaced by $h_0 \exp(-t/\tau_L)$ with $\tau_L \sim L^{-4}$. From now on we consider the problem below T_R .

One essential difference between the unidirectional profile of sections 3 and 4 and the bidirectional profile considered now is that the chemical potential of an atom on a ledge of average radius R contains a term g/R in addition to (3.5). Here g is a constant (we use the notations of Ref. [17]). The fact that the shape of the terrace is described by the single

parameter R involves of course approximations. The chemical potential on the n 'th step is

$$\mu_n = G_3(\ell_n^{-3} - \ell_{n+1}^{-3}) + g/R_n \quad (5.2)$$

where

$$\ell_n = R_n - R_{n-1}. \quad (5.3)$$

The second term of (5.2) is very large for small R_n and has no reason to be compensated by the first term. Therefore, it is a natural Ansatz to neglect the first term for small radii R_n . In that case the argument of reference [17] can be applied and predicts that only the inner terrace shrinks while the others swell. This swelling will presumably be limited by the repulsion between ledges, i.e. by the first term of the r.h.s. of (5.2). It is thus expected that after some time a « quasi-equilibrium » is reached, where all ledges except the inner one are almost immobile. This inner terrace has thus a different behaviour and can be compared with the closed terraces of figure 5b, while the other ledges are comparable to the infinite ones. Therefore we shall denote h the last nearly immobile ledge, i.e. the next to last ledge. For the ledge $N'h$ (5.2) is replaced by

$$\mu_h = G_3 \ell_h^{-3} + g/R_h \quad (5.4)$$

as soon as the last ledge ($N'h + 1$) is far enough, so that ℓ_{h+1}^{-3} can be neglected.

Now we need equations from the currents. The current j_n from the n 'th step to the $(n - 1)$ 'th is again given by

$$j_n = -K(\mu_n - \mu_{n-1})/l_n \quad (3.6)$$

for $n \leq h$. Inside the h 'th step one can no longer disregard the atoms which are between the h 'th and the $(h + 1)$ 'th ledge since those are responsible for the decay of the last terrace. These atoms, which are not on ledges, will be called « free ». Since holes as well as atoms contribute to the decay, we shall speak of free « particles », as in reference [17]. The density ρ of free particles between ledges $N'h$ and $(h + 1)$ satisfy with a good approximation the equation $\dot{\rho} = \Lambda \nabla^2 \rho = 0$, as argued in reference [17]. Hence

$$\rho(r) = \rho_0 + A \ln r \quad (5.5)$$

where ρ_0 and A are given by the following boundary conditions on terraces $N'h$ and $h + 1$

$$A\Lambda/R_h = \gamma - \bar{\gamma}(\rho_0 + A \ln R_h) \quad (5.6a)$$

$$A\Lambda/R_{h+1} = -\alpha + \bar{\alpha}(\rho_0 + A \ln R_{h+1}) \quad (5.6b)$$

where Λ is the diffusion constant, α , γ and $\bar{\alpha}$, $\bar{\gamma}$ respectively the particle emission and absorption probability by a ledge. We have changed the signs of reference [17] because we want to count positively currents going toward the centre, consistently with (3.6).

We want to know the particle flux $J_{h+1} = rj = A\Lambda$, which is readily obtained from (5.6), namely (in the limit of large R_h, R_{h+1})

$$J_{h+1} = \Lambda \frac{(\gamma/\bar{\gamma}) - (\alpha/\bar{\alpha})}{\ln(R_h/R_{h+1})} \quad (5.7)$$

$\gamma/\bar{\gamma}$ satisfies the detailed balance equation

$$\gamma/\bar{\gamma} = \exp -\beta(E_0 - \mu_h) \quad (5.8)$$

where $\beta = 1/K_B T$ and the constant E_0 is essentially the energy difference between an atom on a ledge and an atom running on a terrace (one of the little cubes in Fig. 3). Relation (5.4) yields

$$\gamma/\bar{\gamma} = \exp -\beta(E_0 - g/R_h - G_3 \ell_h^{-3} + G_3 \ell_{h+1}^{-3}). \quad (5.9a)$$

Analogously

$$\alpha/\bar{\alpha} = \exp -\beta(E_0 - g/R_{h+1} - G_3 \ell_{h+1}^{-3}) \quad (5.9b)$$

ℓ_{h+1}^{-3} is negligible most of the time. Assuming $g/R_h \ll K_B T \equiv 1/\beta$ and $G_3/\ell_h^3 \ll K_B T$, (5.7) and (5.9) yield

$$J_{h+1} = \beta \Lambda e^{-\beta E_0} \left(\frac{g}{R_h} - \frac{g}{R_{h+1}} + G_3 \ell_h^{-3} \right) / \ln \left(\frac{R_h}{R_{h+1}} \right) \quad (5.10)$$

which is the flux between the last terrace and the next one.

The two-directional geometry of the profile implies a complication near $z = 0$ (or $n = 0$). Indeed the second term of (5.2) does not vanish, but goes to a positive limit g/R_1 when n goes to zero. It is so on all hills, while in valleys it goes to $-g/R_1$. In fact both terms of (5.2) should obey the symmetry rule $\mu(x, y) = -\mu(-x, y) = \mu(-x, -y)$. Thus, the difference in chemical potential between the lowest ledge on a hill and the highest ledge in a neighbouring valley has the rather large value $2g/R_1$. This implies that flat parts appear in the plane $z = 0$ which corresponds to the position of the surface at infinite time. These flat parts form an infinite facet (Fig. 8). Thus, R_1 is not nearly equal to L as might

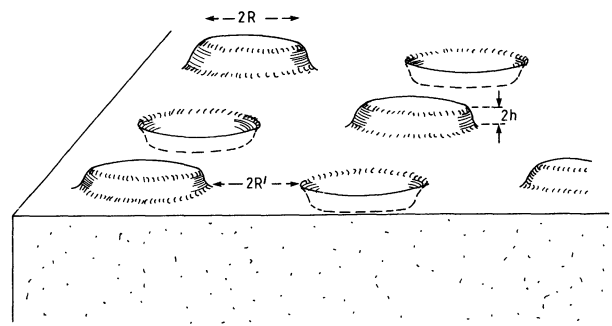


Fig. 8. — The two-dimensional profile after some time.

be expected. It will be seen in section 6 that, if h/L is sufficiently small, then $R_1 \approx R \approx 0.6 L$.

Equations (5.2), (5.3), (5.4), (5.10) and (3.6) should be completed by

$$\dot{R}_n = j_n - j_{n+1} \quad (n < h) \quad (5.11a)$$

and

$$\dot{R}_h = j_h - J_{h+1}/R_h. \quad (5.11b)$$

The resulting system of equations might be solved numerically but we prefer to give an approximate solution valid for if the height h is much smaller than the facet radius R .

6. Approximate solution.

Since $z' = 1/\ell$ is expected to vanish continuously when approaching a facet, it is a reasonable Ansatz (to be checked later) to neglect the term containing G_3 in (5.10).

$$J_{h+1} \approx \beta \Lambda \times \\ \times e^{-\beta E_0} \left(\frac{g}{R_h} - \frac{g}{R_{h+1}} \right) / \ln(R_h/R_{h+1}) \quad (6.1)$$

or

$$|J_{h+1}| = \beta \Lambda e^{-\beta E_0} (g/R_h) f(R_h/R_{h+1}) \quad (6.2)$$

where $f(x)$ increases monotonically from 1 to ∞ when x increases from 1 to ∞ . $f(x)$ takes the value 2 for $x = 3.5$ and is therefore of order 1 most of the time. The divergence for very small R_{h+1} should have no consequence since the quantity of matter to be evacuated is then very small. If one compares (6.1) with (3.6) and (5.4) for $G_3 = 0$ and $R_h/R_{h+1} \approx 1$ one finds

$$K = (\Lambda/K_B T) \exp(-E_0/K_B T). \quad (6.3)$$

According to (6.2) the average value of $|J_{h+1}|$ should be around

$$|J| \approx 1.3 K g / R. \quad (6.4)$$

We shall now give an approximate solution of (3.6). We make the Ansatz (the selfconsistency of which should be checked later) that (in agreement with the picture of Sect. 5) all terraces are immobile. This implies that the total current $J_n = j_n R_n$ is a constant J . (3.6) can be written in the continuum limit on the sloping parts as

$$K \partial \mu / \partial x = |J| / (L - x).$$

Integration yields

$$\mu = (|J|/K) \ln \frac{L}{L-x} + \text{Const.}$$

If the left hand side is replaced by (5.2) and if the notations $z' = \partial z / \partial x = 1/\ell$, $z'' = \partial z' / \partial x$ are used, one obtains in the continuum approximation

$$-3 G_3 z' z'' = \frac{|J|}{K} \ln \frac{L}{L-x} - \frac{g}{L-x} + \text{Const.} \quad (6.5)$$

Now we replace the right hand side by its Taylor expansion around the point x_1 where its second derivative vanishes.

$$x_1 = L - 2 g K / |J| \quad (6.6)$$

(6.5) reads

$$-3 G_3 z' z'' = f_1 \xi - f_3 \xi^3 + \dots \quad (6.7)$$

where $\xi = x - x_1$,

$$f_1 = \frac{|J|}{K} (L - x_1)^{-1} - g (L - x_1)^{-2} = \\ = J^2 / 4 g K^2 \quad (6.8a)$$

$$f_3 = \frac{|J|}{3 K} (L - x_1)^{-3} + g (L - x_1)^{-4} = \\ = J^4 / 48 g^3 K^4 \quad (6.8b)$$

(6.7) may be compared with the equilibrium equation (3.7).

Expansion (6.7) will be seen to be qualitatively correct even near the facets if h/L is reasonably small (say, $h < L/10$). In other words the right hand side is finite near a facet (as it is at equilibrium) and of order $f_1 \xi$. Of course, (6.7) does not hold inside a facet. Integration of (6.7) yields, away from facets,

$$3 G_3 (z_M'^2 - z'^2) = f_1 \xi^2 - \frac{1}{2} f_3 \xi^4 + \dots \quad (6.9)$$

where z_M' is the value of z' for $x = x_1$.

The location of the facets is given by putting $z' = 0$ into this equation. Neglecting terms of order ξ^4 and higher, one finds

$$\xi^2 \approx z_M'^2 G_3 / f_1.$$

The horizontal width L' of the steep parts in figure 8 is equal to the distance between both solutions of this equation. On the other hand $z_M' \approx h/L'$. Thus, L' satisfies the condition

$$L'^4 \approx h^2 G_3 / f_1$$

or, inserting (6.8a)

$$L'^4 \approx g G_3 h^2 K^2 / J^2$$

and according to (6.4)

$$L'^4 \approx (G_3/g) h^2 R^2. \quad (6.10)$$

R can now be determined if one remarks that L is the sum of L' , the radius R of the upper terrace and the half-distance R' between bumps (Fig. 8). Since the total current $J = j_n R_n$ is independent of n , relation (3.6) yields for $n = 1$

$$|J|/R_1 = K \mu_1 / R'.$$

Now, as seen at the end of section 5, $\mu_1 = \frac{g}{R_1}$ while $|J| \approx 1.3 Kg/R$ according to (6.4). It follows $R' \approx 0.6 R$ and $L' \approx L - 1.6 R$, so that (6.10) reads

$$(L - 1.6 R)^2 \approx hR \sqrt{G_3/g}. \quad (6.11)$$

G_3 is related to thermal fluctuations of ledges, so that G_3/g is very small at low temperature. Even at the temperature of interest, $T \approx 1000$ K, G_3/g is expected to be fairly small as can be seen from a standard calculation [33]. In the experiments which have been performed [19] h/R is pretty small. In this situation, the width L' of the steep parts is rather small with respect to L , as seen from (6.11). Since $R' \approx 0.6 R$ the equality $L' + R + R' = L$ yields

$$R \approx 0.6 L. \quad (6.12)$$

The current J is of order

$$J \approx \dot{h}R^2 \approx \dot{h}L^2.$$

Equating this to (6.4) and integrating one obtains (Fig. 9)

$$h(0) - h(t) \approx Kgt/L^3. \quad (6.13)$$

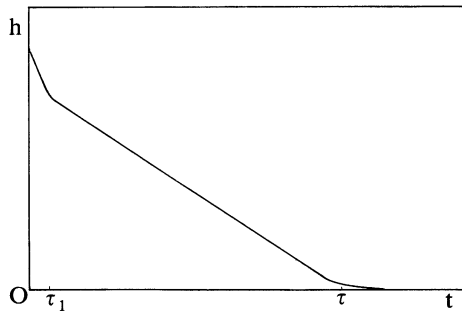


Fig. 9. — Amplitude of the profile modulation as a function of time.

The lifetime of the profile is therefore

$$\tau \approx h(0) L^3 / Kg. \quad (6.14)$$

Near a facet, (6.9), (6.8a) and (6.4) imply

$$z'^2 \approx (g/G_3) R^{-2} L' \delta x \quad (6.15)$$

where δx is the distance to the edge of the facet.

Integration of this equation yields the same law as near a facet at equilibrium [30], namely

$$z \sim (\delta x)^{3/2}. \quad (6.16)$$

It is of interest to know the value $1/\ell_h$ of z' near a facet. It is obtained by replacing δx and $1/z'$ by ℓ in (6.15)

$$1/\ell_h \approx (gL'/G_3 R^2)^{1/3}. \quad (6.17)$$

The essential results of our calculation are equation (6.11) which gives the radius R of the facets, (6.13) and (6.14) which describes the evolution of the profile, and (6.16) which gives the shape. Now we have to check the self-consistency of the Ansätze which have been made. Firstly, it is legitimate to neglect higher order terms in (6.9) even near the facets since $f_3 L'^2/f_1 \approx L'^2/R^2$ is rather small compared to L according to (6.11).

Then, we can check that $G_3 \ell_h^{-3}$ is much smaller than g/R_h and g/R_{h+1} in (5.10) since (6.11) and (6.17) imply

$$(G_3/g) R \ell_h^{-3} \approx L'/R \approx L'/L.$$

The last Ansatz to be checked is that the current $j_n R_n$ does not depend much on n . This is true if R_n does not depend much on time, and actually it is so far $h \ll R$ since all $R_n \approx L$ according to (6.11). More precisely one finds by differentiation of (6.11) that

$$\frac{\dot{R} h}{R \dot{h}} \approx (h/R) \sqrt{G_3/g}.$$

Since both factors are at the right hand side rather small with respect to 1 it is reasonable to assume a constant current.

7. Discussion.

The results obtained here can be compared with that of reference [17] where *non-interacting* ledges (i.e. with very large ℓ) were considered. The lifetime of terraces of size L was found to be proportional to L^3 . Formula (6.14) of the present work may be seen as an extension of this result for terraces of height $h > 1$ interatomic distance.

It may be interesting to mention a by-product of the present calculation, namely the motion of two parallel ledges with identical « sign » and average distance ℓ . The difference in chemical potential is $2 G_3/\ell^3$ according to (3.5) and the equation of motion is given by (3.6), namely

$$\ell = |j| = 2 KG_3/\ell^4.$$

Therefore $\ell(t) \sim t^{1/5}$ instead of $t^{1/4}$ as would be the case in the presence of a vapour [34].

It is interesting to compare our results with those of Bonzel *et al.* [26]. Although these authors investigated the unidirectional geometry (Fig. 1), their results fit fairly well our results obtained for the two-directional geometry (Fig. 7 and 8). In particular, curves b, c and c' in figure 8 of Bonzel *et al.* [26] become linear functions if plotted in linear rather than in logarithmic coordinates, and this is in agreement with our equation (6.13).

In the case of unidirectional grooves (Fig. 1), the equations of sections 3 and 4 would predict facets at

the top and at the bottom (Fig. 2b) provided the current is assumed to be constantly of order Kg/R^2 . Since this has no obvious reason to be true in the situation of figure 5c, we consider this argument purely phenomenological, and for the same reason we would qualify the theory of Bonzel *et al.* a phenomenological one. However, we have not been able to do better in the unidirectional case !

It would be nice to have experiments for the bidirectional geometry and to compare with figure 8. Possibly the cliffs would be less steep due to evaporation and diffusion through the vapour and the solid.

Although this work leaves some questions open and therefore suffers deficiencies, it would have been much worse if its first version (devoted to the unidirectional problem of Fig. 1) had not been read by two distinguished censors, Ph. Nozières and H. van Beijeren. Ph. Nozières drew our attention to the difficulties of the unidirectional geometry mentioned in section 4. Moreover, in that first version we assumed the chemical potential on the upper ledge to be of order g/R , which is the value at equilibrium for a system of finite size. R. H. van Beijeren pointed out that this was in contradiction with

equation (4.3) if one assumes $j \approx g/R^2$ (see Eq. (6.4)). It is interesting to note that the change in chemical potential along the steep parts is much smaller than g/R although it is of order g/R on the flat parts. So to speak, nothing very important happens in the rather narrow sloping parts. For this reason the essential results (6.13) and (6.14) would not be affected if one used the equations of Nozières [32] instead of (3.6).

We are also indebted to F. Lançon who solved numerically equations similar to (4.3) and checked that a profile roughly looking like (4.8) is obtained after some time.

It is a pleasure to thank W. Selke for discussions. He gave a Monte Carlo treatment of a related problem which will be submitted soon. However, he assumed a different dynamics because the two-dimensional diffusion would imply a fantastically long computer time.

Finally, the present work would not have been done, had we not benefitted of H. Bonzel's suggestions. He is really responsible for the basic idea expressed by the title of this article. This idea directly stems from the works of him and his coworkers.

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