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**On the motion of steps on a vicinal surface**

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**Résumé.**-En général, on suppose que la croissance d'un interface cristal-vide est contrôlée par la diffusion des atomes le long de la surface. Nous proposons un mécanisme différent pour des surfaces *vicinales* (marches bien séparées), où la croissance est contrôlée par l'attachement des atomes sur chaque marche. La loi de croissance ainsi obtenue est différente d'une équation purement diffusive. A titre d'exemple, nous considérons la forme stationnaire d'un cristal entre deux facettes parallèles.

**Abstract.**- Usually, the growth of a crystal vacuum interface is described in terms of atom diffusion along the surface. We propose an alternate mechanism for *vicinal* surfaces (well separated steps), in which the growth is controlled by the attachment of atoms at individual steps. The resulting growth law differs from a purely diffusive equation. As an example, we consider the steady shape of crystals between two parallel facets.

We consider a cylindrical crystal surface, characterized by its cross-section  $z(x)$ . We assume that the  $(xy)$  basal plane is a low index symmetry plane of the crystal (say 100) - then the surface may be viewed as an array of *parallel straight steps* along the  $y$ -axis. The step density,  $n(x) = 1/d$ , is related to the tilt angle  $\theta$  according to  $\tan\theta = na$ , where  $a$  is the  $z$ -lattice spacing (see Fig.1). Such a step picture only makes sense in the *vicinal regime*, in which steps are well separated entities, with a *width*  $\xi$  such that  $n\xi \ll 1$ : we only consider that limit. We then define the interfacial free energy  $E(n)$  per unit  $dx$  (the free energy per unit actual area is  $\gamma = E/\cos\theta$ ). In this vicinal limit, we may expand  $E(n)$  as

$$E(n) = E_0 + \beta n + \phi n^3 + \dots \quad (1)$$

$\beta$  is the individual step free energy, the following terms correspond to step interactions, whether statistical or mediated by elastic strain. Assume for instance a pair interaction energy  $\varepsilon(d)$  between nearest neighbour steps (such a simplification is by no means essential: we give it as an illustration). The corresponding contribution to  $E(n)$  is  $n\varepsilon(d)$  and (1) corresponds to  $\varepsilon(d) = \phi/d^2$ .

From  $E(n)$ , we may define a "step chemical potential"

$$\xi(n) = \frac{dE}{dn} = \beta + 3\phi n^2 + \dots$$

from which we infer the *interaction force* exerted by its neighbours on a given step

$$F_{\text{int}} = -\frac{\partial \xi}{\partial x} = -\frac{d\xi}{dn} \frac{\partial n}{\partial x} = -6\phi n \frac{\partial n}{\partial x} + \dots \quad (2)$$

In order to make the definition of  $F_{\text{int}}$  quite clear, assume that we displace the step pattern by a amount  $u(x)$ . The new step density is

$$\bar{n}(x+u) = \frac{n(x)}{1 + \frac{\partial u}{\partial x}} \rightarrow \delta n = (\bar{n} - n) = -\frac{\partial}{\partial x}[nu]$$

For a localized deformation, the corresponding change in energy may be written as

$$\delta E = \int \frac{dE(n)}{dn} \delta n \, dx = \int \frac{\partial \xi}{\partial x} nu \, dx$$

The energy of each step is thus shifted by  $[-F_{\text{int}}u]$ , which defines  $F_{\text{int}}$ . The physical picture is even clearer if we express  $\xi$  in terms of the pair interaction  $\varepsilon(d)$

$$\begin{cases} \xi - \beta = \varepsilon(d) - \frac{\partial \varepsilon}{\partial d} \\ F_{\text{int}} = \frac{\partial d}{\partial x} \cdot d \frac{\partial^2 \varepsilon}{\partial d^2} \end{cases}$$

(remember that  $d = 1/n$ ). The left steps exerts a force  $f = -\partial\varepsilon/\partial d$  calculated at  $x = -d/2$ , while the right step pushes in the opposite direction, by an amount  $[-f [x = +d/2]]$ . The resultant  $[-d(\partial f/\partial x)]$  is noth-

ing but  $F_{\text{int}}$ .

This interaction force  $F_{\text{int}}$  (on individual steps) must be balanced by an appropriate external force  $F$  in order to achieve equilibrium : if it is not balanced, steps move with a velocity  $w$ , and the crystal grows (or melts) with a normal velocity (along  $z$ )

$$v = -n a w \quad (3)$$

At this stage, the situation depends on the environment of the crystal surface.

### 1. Phase equilibrium : crystal in contact with a fluid phase

Such a "mother phase" - whether liquid or vapour is a reservoir of atoms, with a well defined chemical potential  $\mu_L$ . Let  $\mu_S$  be the free energy per site of the crystal. If a unit length of step moves by an amount  $u > 0$  (see Fig.1),  $u/b^2$  sites go from crystal to fluid ( $b$  = in plane lattice spacing) - hence a change in energy  $u(\mu_L - \mu_S)/b^2$  and a *supersaturation force* on the step

$$F = \frac{\mu_S - \mu_L}{b^2}$$

$F$  is fixed by the fluid reservoir.

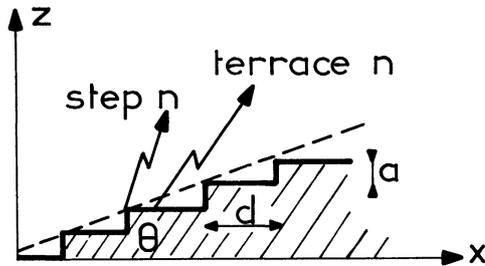


Fig.1.- The step structure of a tilted interface.

The competition between  $F$  and  $F_{\text{int}}$  has been discussed extensively elsewhere [1]. Here we only quote a few salient features of our one dimensional geometry :

- The condition  $F + F_{\text{int}} = 0$  is equivalent to the Wulff construction.  $\xi$  is then a linear function of  $x$  from which  $n(x)$  is inferred :

$$\xi[n(x)] = F x + \text{Const.} \quad (4)$$

- At a wall, the contact angle fixes  $n$ , hence  $\xi$ . Similarly, tangential matching to a flat *facet* implies  $\xi = \beta$ ,  $n = 0$ . (4) thus provides the width of the curved region for a fixed  $F$ .

- Near the edge  $x_0$  of a facet,  $\partial n^2 / \partial x = F/3\phi$ , hence a variation  $n \sim (x_0 - x)^{1/2}$ ,  $z \sim (x_0 - x)^{3/2}$  which is a direct consequence of the  $1/d^2$  step interaction.

- Off equilibrium, the step moves with a velocity  $w = \eta[F + F_{\text{int}}]$ , where  $\eta$  is a *step mobility*.

It is enlightening to view the mobility  $\eta$  in terms of attachment kinetics of atoms onto the step. When an atom sticks, a length  $b$  of step moves a distance  $d$  to the left (Fig.1) - hence a change of energy

$$\Delta E = b^2 [F + F_{\text{int}}] = \mu_S - \mu_L - b^2 \frac{\partial \xi}{\partial x} \quad (5a)$$

The balance between attachment and detachment results in a net atom flow  $j$  from the step to the liquid (per unit step length) such that

$$j b = \frac{w}{b} = \frac{1}{\tau} \frac{\Delta E}{T} \quad (5b)$$

where  $\tau$  is a characteristic atomic time. The resulting mobility is  $\eta = b^3/\tau T$ .

### 2. Crystal-vacuum interface : diffusion of atoms along the surface

In such a case, there is no reservoir : atoms drift from step to step along the surface. Usual treatments assume that the limiting feature is *diffusion*. The atom current density  $J$  (in the  $x$ -direction) is written as :

$$J = -\lambda \frac{\partial \mu}{\partial x} \quad (6)$$

$\mu$  is the local chemical potential (for individual atoms : the chemical potential per unit solid volume is  $\mu/\Omega$ , where  $\Omega = ab^2$  is the volume of a unit cell).  $\lambda$  is an *atom mobility* (more exactly,  $\lambda/\nu$  where  $\nu$  is the density of moving atoms per unit area). The net growth rate follows from particle conservation

$$v = -\Omega \frac{\partial J}{\partial x} = \lambda a b^2 \frac{\partial^2 \mu}{\partial x^2} \quad (7)$$

(hence the step velocity  $w = vd/a$ ). Such a picture certainly holds in the *rough* state ( $n\xi \gg 1$ ) - it is tempting to extend it to the *vicinal* regime  $n\xi \ll 1$ . The chemical potential  $\mu(x)$  should then reflect the interaction between steps. More precisely, one may assume that the step pattern responds instantaneously to an *effective* local supersaturation  $F = (\mu_S - \mu)/b^2$  [growth is controlled by particle drift, not by step motion]. One should then have  $F = -F_{\text{int}}$ , i.e.

$$\mu = \mu_S + b^2 F_{\text{int}} = \mu_S - b^2 \frac{\partial \xi}{\partial x} \quad (8)$$

For low  $\theta$ , this may be written in the more conventional form

$$\mu = \mu_S - \Omega \frac{\partial}{\partial x} \left[ \frac{\partial \gamma}{\partial \theta} \right] \quad (8')$$

Note that the interface velocity  $v$  responds to the second derivative  $\delta^2 \mu / \partial x^2$ , instead of  $\mu = \mu_L$  in the presence of a reservoir.

The results (6) to (8), due to Mullins [2], rely on a *diffusion controlled* process - a situation which is unlikely to hold in a truly vicinal surface, for which attachment to the steps is the limiting feature. Let us number by an integer  $n$  the successive steps and the interlying terraces, as shown in figure 1. We assume that particles thermalize quickly on each terrace - and also that crossing a terrace is an easy process which does not require any driving force : each terrace is then characterized by an atomic chemical potential  $\mu_n$  (Note the difference with the previous treatment :  $\mu_n$  is constant throughout a given terrace, a statement that diffusion across the terrace is easy). The step  $n$  exchanges atoms with both the left terrace ( $n-1$ ) and the right terrace  $n$ , which act as reservoirs for the step. in analogy with (5), we may write the flow of atoms from step  $n$  to terrace  $n$  as

$$j_n^+ = \alpha \left[ \mu_S - \mu_n - b^2 \frac{\partial \xi_n}{\partial x} \right] \quad (9a)$$

( $\alpha b^4$  has the dimension of a step mobility  $\eta$  - but it is clearly not the same as for a solid liquid interface, since the microscopic sticking processes are different). Similarly

$$j_n^- = -\alpha \left[ \mu_S - \mu_{n-1} - b^2 \frac{\partial \xi_n}{\partial x} \right] \quad (9b)$$

describes atom transfer from terrace ( $n-1$ ) to step  $n$ . The step velocity  $w_n$  follows from mass conservation

$$w_n = b^2 [j_n^+ - j_n^-] \quad (10)$$

(9) and (10) provide the response of the interface to  $\mu_n$ . Conversely,  $j_n^\pm$  control the time dependence of  $q_n$ , the number of diffusing atoms on terrace  $n$  at a given time :

$$\dot{q}_n = j_n^+ - j_{n+1}^- \quad (11)$$

From  $q_n$  and the terrace width, we infer the density, hence the chemical potential  $\mu_n$  at fixed  $T$ . The system is thus closed : we have coupled equations for  $j_n$  and  $q_n$ . The physics is completely different from (6)-(8) : here dissipation is localized *at the steps*, terraces acting only as "capacitances" that can store diffusing atoms.

In order to proceed, we make one further assumption (which looks quite reasonable) : the capacitances are *small*. A tiny variation of  $q_n$  is enough to change  $\mu_n$  appreciably, thereby locking the inflow

of atoms on each terrace. If  $\dot{q}_n$  may be neglected, we have  $j_n^+ = j_{n+1}^- = J$  : atoms *cross* the terrace  $n$  without stopping. This condition fixes  $\mu_n$ ,

$$\mu_n = \mu_S - \frac{b^2}{2} \left[ \frac{\partial \xi_n}{\partial x} + \frac{\partial \xi_{n+1}}{\partial x} \right] \quad (12a)$$

from which we infer the current  $J$

$$J = \frac{\alpha b^2}{2} \left[ \frac{\partial \xi_{n+1}}{\partial x} - \frac{\partial \xi_n}{\partial x} \right] = \frac{\alpha b^2}{2} d \frac{\partial^2 \xi}{\partial x^2} \quad (12b)$$

Combining (12a) and (12b), we may write

$$J = -\frac{\alpha}{2} d \frac{\partial \mu}{\partial x} \quad (13)$$

The atom current  $J$  is still proportional to  $\frac{\partial \mu}{\partial x}$ , as in (6), but the coefficient is proportional to  $d = 1/n$ . The step velocity  $w$  and interface velocity  $v$  follow at once

$$\begin{cases} w &= b^2 d \frac{\partial J}{\partial x} = \frac{\alpha b^4}{2n} \frac{\partial}{\partial x} \left[ \frac{1}{n} \frac{\partial^2 \xi}{\partial x^2} \right] \\ v &= -\alpha b^2 \frac{\partial J}{\partial x} = -n \alpha w \end{cases} \quad (14)$$

(14) is the new result put forward in this note, amounting to the statement that the diffusion parameter  $\lambda$  of equation (6) is proportional to the step distance,  $\lambda = \alpha d / 2$ . Thus the growth of a vicinal surface is different from that of a rough surface.

### 3. An example : steady shape between two facets

We consider the geometry of figure 2 : atoms are created on the upper facet by some appropriate nucleation processes. They spill over to the lower facet where they annihilate by the reverse process : in the end, the height difference  $2h$  between the two facets relaxes [3]. We assume that a net atom current  $J_0$  flows from top to bottom (the current in the  $x$  direction is  $J = -J_0$ ). We look for the *steady* shape of the curved region. This region matches tangentially to the facets for  $x = \pm \ell$  : what is the relationship between  $h$ ,  $J_0$  and  $\ell$  ?

For a solid fluid interface, a steady shape does not exist : a *linear*  $\xi(x)$  cannot be equal to  $\beta$  (facet edge) both at  $x = +\ell$  and  $x = -\ell$  (if a supersaturation  $F$  exists, the hollow parts fill in spontaneously). In the diffusive case, on the other hand, the solution does exist. Since  $J$  is constant (steady state), it follows from (12b) that

$$\frac{d\xi}{dx} = \frac{2J}{\alpha b^2} n = \frac{2J}{\alpha a b^2} z$$

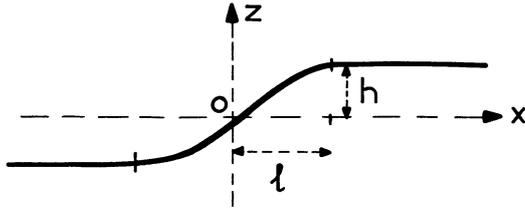


Fig.2.- A curved section between two flat facets.

But in lowest order in step interaction

$$\frac{d\xi}{dx} = 6\phi n \frac{\partial n}{\partial x} = \frac{6\phi}{a^2} z' z''$$

hence a simple differential equation for  $z(x)$ , with a first integral

$$z' = \left[ \frac{aJ_0}{2\phi\alpha b^2} (h^2 - z^2) \right]^{1/3} \quad (15)$$

(tangential matching implies  $z' = 0$  when  $z = \pm h$ ). Numerical integration of (15) provides the detailed shape. The width of the curved region is

$$2\ell = \left( \frac{2\phi\alpha b^2}{aJ_0} \right)^{1/3} \int_{-h}^{+h} \frac{dz}{(h^2 - z^2)^{1/3}} = 2,59 \left( \frac{2h\phi\alpha b^2}{aJ_0} \right)^{1/3} \quad (16)$$

Note that  $\ell \rightarrow \infty$  if  $J_0 \rightarrow 0$  : as quoted earlier, there exists no *equilibrium* profile between two facets. Near the edge of the facet, (15) yields easily

$$h - z \approx \left( \frac{aJ_0 h}{\phi\alpha b^2} \right)^{1/2} \left[ \frac{2}{3} (\ell - x) \right]^{3/2}$$

The shape is again  $x^{3/2}$ , but with a coefficient that depends on  $J_0$ .

#### 4. Conclusion.

We have shown that the growth of vicinal surfaces may be described in terms of *step motion* (attachment of atoms to the step). For a crystal vacuum interface, in which atoms diffuse along the surface, the resulting kinetics is *not* a plain diffusion equation (see Eq.(14)). One should be careful in transposing results established for a rough surface to the vicinal case.

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- [3] This relaxation of "grooves" has been studied by Rettori and Villain, to be published.