On the motion of steps on a vicinal surface

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(Reçu le 6 juillet 1987, accepté le 21 juillet 1987)

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’attache 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, \( n(x) = \frac{1}{d} \), is related to the tilt angle \( \theta \) according to \( \tan \theta = na \), where \( a \) is the \( \sigma \)-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 \( n\xi < 1 \) : 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

\[
E(n) = E_0 + \beta n + \phi n^3 + ... \tag{1}
\]

\( \beta \) 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 \( n \varepsilon(n) \) and (1) corresponds to \( \varepsilon(d) = \phi / d^2 \).

From \( E(n) \), we may define a “step chemical potential”

\[
\xi(n) = \frac{dE}{dn} = \beta + 3\phi n^2 + ...
\]

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

\[
F_{\text{int}} = -\frac{\partial \xi}{\partial x} = -\frac{dE}{dn} \frac{\partial n}{\partial x} = -6\phi n \frac{\partial n}{\partial x} + ...
\tag{2}
\]

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

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

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 \( \varepsilon(d) \)

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

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

- 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

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

(hence the step velocity $w = vd/a$). Such a picture certainly holds in the rough state $(n\xi >> 1)$ - it is tempting to extend it to the vicinal regime $n\xi << 1$. 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.
Note that the interface velocity \( v \) responds to the second derivative \( \frac{\partial^2 \mu}{\partial z^2} \), instead of \( \mu \), 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

\[
J^+ = \alpha \left[ \mu_n - \mu - b^4 \frac{\partial \xi_n}{\partial x} \right]
\]

(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

\[
J^- = -\alpha \left[ \mu_n - \mu_{n-1} - b^4 \frac{\partial \xi_n}{\partial x} \right]
\]

(9b)
describes atom transfer from terrace \((n-1)\) to step \( n \).

The step velocity \( w_n \) follows from mass conservation

\[
w_n = b^4 \left[ J^+ - J^- \right]
\]

(10)

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

\[
\dot{q}_n = J^+_n - J^-_{n+1}
\]

(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 \( \mu_n \),

\[
\mu_n = \mu_s - \frac{b^4}{2} \left[ \frac{\partial \xi_n}{\partial x} + \frac{\partial \xi_{n+1}}{\partial x} \right]
\]

(12a)

from which we infer the current \( J \)

\[
J = \frac{\alpha b^4}{2} \left[ \frac{\partial \xi_{n+1}}{\partial x} - \frac{\partial \xi_n}{\partial x} \right] = \frac{\alpha b^4}{2} \frac{\partial^2 \xi}{\partial x^2}
\]

(12b)

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

\[
J = -\frac{\alpha}{2} \frac{\partial \mu}{\partial x}
\]

(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

\[
\begin{align*}
\frac{d}{dx} = & \frac{b^4}{2} \frac{\partial J}{\partial x} = \frac{\alpha b^4}{2n} \frac{\partial^2 \xi}{\partial x^2} \\
\frac{dJ}{dx} = & -ab^2 \frac{\partial J}{\partial x} = -n \alpha \frac{\partial \mu}{\partial x}
\end{align*}
\]

(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

\[
\frac{d\xi}{dx} = \frac{2J}{\alpha b^2 n} = \frac{2J}{\alpha a b^2 x}
\]
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

\[
z' = \left[ \frac{a J_0}{2\phi a^2} (h^2 - z^2) \right]^{1/3}
\]

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

\[
2\ell = \left( \frac{2\phi a^2}{a J_0} \right)^{1/3} \int_{-h}^{+h} \frac{dz}{(h^2 - z^2)^{1/3}} = 2.59 \left( \frac{2\phi a^2}{a J_0} \right)^{1/3}
\]

(16)

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

\[
h - x \approx \left( \frac{a J_0 h}{\phi a^2} \right)^{1/3} \left[ \frac{2}{3} (\ell - x) \right]^{3/2}
\]

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.

Acknowledgments.

This work was triggered by discussions with J. Villain, to whom I am extremely grateful.

References

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