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The behaviour of steps on a crystal facet under small supersaturation

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Résumé. — La géométrie des marches sur une facette cristalline dépend de l’énergie de marche anisotrope $\beta(\varphi)$. En nous appuyant sur les efforts effectifs agissant sur un élément de marche, nous discutons brièvement la forme de cette marche, ses angles de raccordement avec le bord de la facette ou avec la paroi. Lorsque la marche est issue d’une dislocation-vis, la facette peut être métastable lorsque cette dislocation est décentrée. Lorsque le nombre de dislocations-vis est élevé, nous montrons qu’au-delà d’un seuil de sur-saturation $F$ les marches piégées se comportent comme si elles étaient libres (par réarrangements successifs). Pou des marches longues et presque alignées, ce seuil $F$ est très inférieur au seuil de Frank-Read habituel pour une paire de dislocations ± voisines. Nous illustrons ce comportement « collectif » des sources de Frank-Read sur quelques exemples.

Abstract. — The geometry of individual steps on a crystal facet is fixed by the anisotropic step energy $\beta(\varphi)$. On the basis of effective stresses on a step element, we briefly discuss the step shape and its matching angles with the facet edge or with a wall. When the step originates from a single screw dislocation, the facet may be metastable if the dislocation lies off centre. When the number of screw dislocations is large, we show that for a large enough supersaturation $F$ the trapped steps behave as if they were free (through successive rearrangements). For long nearly aligned steps, this threshold $F$ is much lower than the usual Frank-Read threshold for neighbouring ± dislocations. We illustrate this « collective behaviour » of Frank-Read sources on a few examples.

The properties of steps on a crystal surface are well known. Their structure and mobility are responsible for the shape and growth of crystal facets [1]. In this paper, we are concerned with steps under a very small supersaturation — a problem which is relevant for the growth of solid $^4$He out of the superfluid. In such a case, bulk dissipation is often irrelevant, and one may hope to observe directly interface details which are often hidden in more conventional situations. The remarks that follow are in fact quite straightforward : we only want to draw attention to simple properties of these steps. (Although we have $^4$He in mind, our remarks are more general.)

A step below the roughening transition is characterized by its free energy $\beta$ (per unit length), and its width $\xi$. $\xi$ incorporates both the natural width at $T = 0$ (sharp for a solid-gas interface, somewhat larger in the solid-liquid case due to blurring of the interface), and the thermal width due to microscopic meandering of the step (typically the size of thermal terraces). We take it as a global parameter, measuring the minimum scale above which the step may be considered as a structure-less stretched string. In the fluctuation limited regime, $\beta \xi \sim T$. The step, in turn, may contain discrete kinks, due to the in plane periodicity (the step arises from periodicity perpendicular to the interface). As a result, $\beta(\varphi)$ depends on the azimuthal angle $\varphi$ of the step. For a classical system at $T = 0$, $\beta(\varphi)$ displays cusps when the step is kink free — such singularities however, are washed out at finite temperature, due to spontaneous formation of thermal kink-antikink pairs. (Note that the kink energy is very small if $\xi$ is large.) Even at
At $T = 0$, quantum fluctuations (1) may produce kinks, making $\beta(\varphi)$ regular. Having $^4$He in mind, we shall thus consider the free energy $\beta(\varphi)$ as a phenomenological, regular property of individual steps.

For a perfect crystal (dislocation free), the interface profile may be viewed as a distribution of steps, characterized by their local orientation $u$ and density $n$ along the lattice planes. (The inclination $\theta$ of the interface with respect to these planes is such that $\tan \theta = na$, where $a$ is the lattice spacing.) Clearly, such a step picture only makes sense if the steps are well separated entities, i.e. if $n \ll 1$. One may then define the step energy density $E(n)$ and their « chemical potential » $\zeta = \partial E/\partial n$ : $\zeta$ depends on $n$ because of step interaction, on $\varphi$ because of anisotropies. It has been argued elsewhere [4] that the equilibrium shape could be interpreted as an equilibrium of steps, under the combined influence of their interaction and of a normal supersaturation « external » force when $\rho_s$ and $\rho_l$ are the solid and liquid densities, $\delta p_l$ the liquid pressure measured from the nominal equilibrium pressure $p^*$ for a flat interface. We want to pursue that interpretation further, paying attention to the shape of steps more than to their interaction.


Let us consider first a terrace enclosed by a step. If the total area of the terrace is given, the shape is determined by the condition that the total step free energy be minimum. This is obviously equivalent to finding the equilibrium shape of a cylindrical crystal and the solution is given by the two-dimensional Wulff construction:

$$\frac{\beta}{R} = \text{const.} \quad (1)$$

where $\beta = \beta + \partial^2 \beta / \partial \varphi^2$ and $R$ is the local radius of curvature (defined only if $R \gg \xi$). This equation expresses the balance of forces acting on the step. In figure 1 we show the « stresses » acting on a step element (2). In addition to the tension force $\beta$ there is a torque $d\beta / d\varphi$ which tends to orient the step to lower energy directions. Under a given pressure, the normal resultant on a bent element must compensate the supersaturation force $F$, so that

$$\frac{\beta}{R} = F \quad (2)$$

(in the Wulff language, $F$ is the Lagrange multiplier which fixes the terrace size). We recover (1) (the resultant of tangential forces is zero, as it should : the torque is essential). Note that the equilibrium shape of a closed loop is always unstable : this loop is nothing but a critical two dimensional nucleus, which either expands or collapses. Only pinned steps with less than half the loop perimeter can be stable.

A flat facet on the crystal cannot be smaller than the critical nucleus (otherwise, the step at the edge shrinks : the facet collapses). In the absence of facet growth mechanisms, any larger facet is permissible : the facet is then metastable, with a shape and size controlled by the surrounding rough parts of the interface [4]. If however we let the facet height relax, there exists an equilibrium size for the facet, such that the free energy be conserved when a step loop collapses from the edge to the center. The corresponding equilibrium condition is

$$\int \zeta(\varphi) \, dl = FS$$

where $S$ is the facet area and $dl$ the edge element. $\zeta$ depends on the density $n_0$ of steps at the edge, i.e. on the matching angle of the round parts at facet edge. Usually, this angle is zero (tangential matching), and $\zeta = \beta$. For an isotropic problem ($\beta = \text{const.}$, circular facet), the equilibrium facet radius $r^*$ is then twice the critical radius $r_c = \beta / F$. More generally, one might

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(1) The possibility of quantum kinks was stressed by Andreev and Parshin [2], who considered the kink as a quantum excitation with a finite band width $2W$ : if $W$ exceeds the energy $\epsilon_0$ of a kink at rest, kinks appear spontaneously. An equivalent description is to consider the kink as a soliton in a one dimensional Sine Gordon model : it is well known that quantum fluctuations may wash out the pinning periodic potential [3] : such a transition makes the step « free », and it is equivalent to the spontaneous formation of kinks in the groundstate.

(2) These forces are not the mechanical stresses at the liquid solid interface : they are fictitious forces whose work characterizes the energy gain upon step displacement, i.e. upon crystal growth.
expect that the equilibrium facet shape should be an enlargement of the critical nucleus shape, reflecting anisotropies of $\beta(\varphi)$: this is wrong. The equilibrium facet shape depends on the geometry of the container (1).

A single step on a facet can terminate either at the edge of the facet or at the wall (see Fig. 2): the effective forces of figure 1 can be used to ascertain the matching angles at these contacts. At the edge of the facet, for instance, the step coming from the facet continues, with a sharp angle $\delta$, along the edge. The net force on a parallel to the edge must vanish. For an isotropic $\beta$, we thus find

$$\beta \cos \delta = \zeta(n_0).$$

(3)

If the round part meets the facet tangentially, $n_0$ vanishes: $\delta$ is also zero and the step merges into the edge tangentially. In what follows, we shall only consider that simple case.

Similarly, consider a facet which meets a wall at right angle. The step end $B$ is subject to a force along the intersection

$$\zeta_w = \alpha(\gamma_s - \gamma_l)$$

Fig. 2. — A facet in contact with a wall. Steps on the facet terminate at screw dislocations or the edge of facet; (a) schematic bird’s-eye view, (b) symbolic notation.

(4) Generalization to an anisotropic $\beta$ is straightforward: $\beta \cos \delta_w$ is replaced by $(\beta \cos \delta_w + \beta' \sin \delta_w)$.

where $\gamma_s$ and $\gamma_l$ are the wall interfacial energies with the two phases. This force must be balanced by the component of step tension along the wall. Hence a matching angle $\delta_w$ (see Fig. 2) given by (4)

$$\beta \cos \delta_w = \zeta_w.\tag{4}$$

Matching is possible only if $\zeta_w < \beta$. More generally, if the crystal axis makes an angle $\alpha$ with the wall, $\zeta_w$ should be replaced by an effective quantity

$$\zeta_w^\text{eff}(\alpha) = \frac{\zeta_w - a \gamma_0 \sin \alpha}{\cos \alpha} \tag{5}$$

where $\gamma_0$ is the facet surface energy. (Eq. (5) is derived by considering the change in facet area due to addition of one step, and it is a special case of (7) in Ref. [4]. Equation (4) is then possible only if

$$\zeta_w^\text{eff}(\alpha) < \beta.\tag{6}$$

Equation (6) determines the finite range of permissible contact angles $\alpha$ between the facet and the wall. If it is violated, steps are generated at the wall and the facet shrinks until it no longer touches the wall.

In view of the above boundary condition, a step cannot exist alone on a facet unless it originates somewhere inside — in practice at a screw dislocation exposed on the surface. Let us first assume that this single dislocation lies at the centre of a circular facet, with radius $R$; for tangential matching, the step is a half circle with radius $R/2$. The step will be in equilibrium if its radius is the critical radius $r_c = \beta/F$ (for which supersaturation balances line tension). We thus recover the equilibrium radius of a circular facet, $R^* = 2r_c$.

If this condition is not met, the step rotates around the dislocation, and the facet grows or melts according to the well-known spiral mechanism. Assume now that the dislocation lies a distance $D$ away from the centre. If $R$ is such that

$$R - D < 2r_c < R + D$$

the step has two equilibrium positions with radius $r_c$ shown in figure 3, one stable (S) and one unstable (U). The facet is thus metastable for a range of forces

$$\frac{2 \beta}{R + D} < F < \frac{2 \beta}{R - D} \tag{7}$$

(the step must overcome a potential barrier in order to make one turn). After one full revolution, the energy has increased by $\Delta E = 2 \pi R \beta - \pi R^2 F$: full thermodynamic equilibrium corresponds to $\Delta E = 0$, i.e. $F = 2 \beta/R$ — but one cannot reach that equilibrium without thermal fluctuations.

(1) Consider for instance a facet between two parallel plates: the facet is an infinite strip, not a circle!
2. Collective behaviour of Frank Read sources.

We now assume that a large number of ± screw dislocations are exposed on the facet, with densities \( q_\pm \) per unit area. (The distance between dislocations, \( d \sim q^{-1/2} \), is much smaller than the facet size \( R \).) In equilibrium, non intersecting steps, with curvature \( r_c \), join ± dislocation pairs — the well known Frank Read sources [5]. In addition, there may exist unpaired steps, originating from a statistical excess of dislocations of one sign. If \( Q_+ \sim Q_- \sim \frac{R^2}{d^2} \) is the total number of dislocations on the facet, one may have for instance \( \Delta Q = (Q_+ - Q_-) \sim \sqrt{Q_\pm} \sim \frac{R}{d} \). The « bachelor » steps issued from such excess dislocations will reach the edge of the facet, where they will merge tangentially with the round parts.

For a single ± pair, a distance \( l \) apart, the usual Frank Read [5] growth threshold corresponds to a half circle step

\[
F_d = \frac{2\beta}{l}
\]

(for an anisotropic \( \beta (\phi) \), the threshold step is half the perimeter of a critical nucleus). In the configuration that minimizes the energy, the steps are as short as possible; they tend to join neighbouring dislocations. It follows that \( l \sim d \); the growth threshold is high for large \( q_\pm \). One might think that the unpaired \( \Delta Q \) dislocations would be enough to produce growth: if they lie well inside the facet, the « bachelor » steps are long, and they may spiral with the threshold [7]. In fact, these bachelor steps are of no help. When they rotate, they sweep by other dislocations: at each intersection, steps exchange, and the unpaired dislocation moves closer to the facet edge. In the end, all unpaired dislocations lie as close to the edge as possible, in a strip of width \( \Delta R \) such that \( \frac{2\pi R \Delta R}{d^2} \sim \Delta Q \). It follows that \( \Delta R \sim d \); the growth threshold of « bachelor » steps is comparable to that of individual Frank Read sources (5).

The only way to lower the threshold is to have long steps, with a length \( l \gg d \). Since they cannot intersect, the steps must be nearly parallel, as shown in figure 4b: we shall say that the steps are polarized. Such a polarization is obtained by tilting the interface with respect to the crystal plane. In the resulting vicinal surface, the only effect of dislocations is to cut the steps into finite segments: the fewer the dislocations, the longer the segments. A brief discussion of this polarization concept is given in the appendix: here we only explore the effect of step lengthening on the growth threshold.

When a small supersaturation force \( F \) is applied, each step bulges with a radius of curvature \( r_c = \beta / F \). The midpoint of a step with length \( l \) moves by an amount \( l^2/2 r_c \). The step thus sweeps an area \( \sim l^3/r_c \). If a dislocation lies in that area, steps rearrange: even though each individual step is bound by two dislocations, on the whole they behave as if they were free. Steps can « creep » from dislocation to dislocation, through successive rearrangements every time a new crossing occurs. The threshold for this « quasi continuous » step behaviour is

\[
\frac{l^3}{r_c d^2} \geq 1 \rightarrow F \geq F_c = \frac{\beta d^2}{l^3}.
\]

Due to the step lengthening, \( F_c \) is much smaller than the simple Frank Read threshold \( F_d \).

The above rearrangement will produce an equilibrium configuration if all final steps are parallel non

(5) Note that the tangential matching of bachelor steps to the edge is possible only if \( R > r_c \): we recover the well known collapse threshold for a facet.
intersecting circle arcs with the same radius of curvature $r_c$. Such a configuration is possible only if the area covered by the steps is smaller than $2r_c$ — otherwise, bent steps necessarily cross, thereby initiating rearrangement and growth. Once the condition (8) is met, growth will proceed whenever the « quasi continuous » steps exceed the Frank Read half circle. A simple example is shown in figure 5, in which a weakly misaligned grain produces long steps between two rows of dislocations, a distance $h$ apart (outside the strip, random Frank Read sources produce short steps of length $\sim d$). The facet grows if $2r_c < h$. Note that individual long steps need not exceed the half circle. The argument is global for the whole strip, the point being that bent steps are forced to cross each other if $h > 2r_c$.

Fig. 5. — Step structure in a slightly misaligned strip with width $h$.

As another, less trivial, example, consider a situation where a large number $N_0$ of $+$ dislocations is located near the origin, the rest of the surface being covered with the usual density $q = d^{-2}$ of $\pm$ dislocations. The $N_0$ steps coming from the origin must find $N_0$ ($-$) dislocations to terminate: their average length is

$$l_0 \sim d \sqrt{N_0}.$$

In the region $r < l_0$, $(+)$ dislocations remain alone, and they must look further out in order to find a partner — hence the geometry of figure 6. At a distance $r$ away from the origin, steps have a length $l(r)$ such that

$$\frac{2 \pi rl(r)}{d^2} = N_0$$

(the flux of steps away from 0 is conserved and equal to $N_0$). Lengthening will stop when $l(r) \sim d$, i.e. at a distance

$$r_p \sim dN_0.$$

When a pressure is applied, the steps bend and the central part begins to wind. The steps are « quasifree » as long as the rearrangement condition (8) is met, i.e. up to a distance $r_m$ such that

$$l(r_m) = (r_c d^2)^{1/3} \rightarrow r_m \sim N_0 \left( \frac{d}{r_c} \right)^{1/3}$$

(note that $r_m \ll r_p$). If $r_m > 2r_c$ an equilibrium configuration is impossible, and the whole pattern starts rotating, thereby producing spiral growth which ultimately extends to the whole facet. (Rotation lengthens the neighbouring steps, which in turn start moving). The threshold for this growth corresponds to

$$r_c \sim dN_0^{3/4}.$$

The corresponding force is considerably smaller than the Frank Read threshold $F_d$ for a simple pair (by a factor $\sim N_0^{3/4}$).

These few examples show that cooperative response of Frank Read sources may lower the threshold for growth considerably: the whole issue is to decide whether the steps are polarized, as discussed in the Appendix. If they are lengthened, the steps move as continuous entities beyond the threshold force [8]. Such considerations might be relevant in understanding the appreciable facet growth rates observed in $^4$He at low temperatures $T \ll T_R$ and small supersaturation $F$ [6]. In that limit, homogeneous nucleation is negligible; moreover, the estimated dislocation density, derived from heat conductivity, is large, making the standard Frank Read threshold $F_d$ higher than $F$. The growth of facets at low $F$ is then somewhat of a mystery (unless there are few exposed screw dislocations, for an unknown reason). Any mechanism which could lower the threshold is worth studying — but lacking any information on crystal defects on the surface, one cannot conclude: we only call attention to a possible explanation.

As a conclusion, let us emphasize again that the points raised in this brief paper are simple applications of well known concepts [1, 5]. Our main purpose was to stress the importance of steps: all the physics of crystal facets may be derived from the step energy and mobility, both anisotropic.
Appendix.
Consider a facet with many steps anchored on screw dislocations. The unit vector normal to the lattice planes is \( n \). On that facet, draw a line element \( dl \), with a normal vector \( dS = n \times dl \) oriented from side 1 to side 2. \( dl \) is crossed by \( dN_+ \) steps going from 1 to 2, by \( dN_- \) steps going from 2 to 1. The net change in interface height is

\[
dl = a[dN_+ - dN_-]. \tag{A.1}\n\]

For a small \( dl \), \( dz \) is a linear function of \( dS \), and we thus set

\[
dN_+ - dN_- = p \cdot dS. \tag{A.2}\n\]

Equation (A.2) is our definition of the step polarization \( p \). If we integrate (A.2) over a closed circuit, we see that \( p \cdot dS \) is the algebraic number of steps emerging from that circuit — i.e. the net dislocation « charge » inside. Thus we have

\[
\text{div } p = q_+ - q_- . \tag{A.3}\n\]

Alternately, we may set \( p = n \times g \), so that

\[
dN_+ - dN_- = g \cdot dl, \quad \text{curl } g = q_+ - q_- .
\]

In the absence of dislocations, \( g \) is a gradient, which according to (A.1) is simply

\[
g(r) = \frac{1}{a} \text{grad } z(r). \n\]

(\( z \) is then a well defined single valued function). If \( (q_+ - q_-) \neq 0 \), the crystal height \( z \) is no longer well defined. (It is multivalued). The concept of local polarization remains valid, but \( g \) is no longer curl free.

Another, more transparent, definition of \( p \) is obtained by averaging (A.2) over a small surface element \( d\sigma = dx dy \) (yet larger than the distance \( d \) between steps). Moving a line element \( dx \) or \( dy \) across \( d\sigma \), it is easily verified that

\[
p = \frac{1}{d\sigma} \sum_{\text{all steps in } d\sigma} dl \tag{A.4}\n\]

\( p \) thus reflects the local orientation and density of steps, whether infinite or ending at dislocations. In equilibrium, the steps are oriented at random, with a length \( -d : p \) is zero. As long as \( pd \ll 1 \) polarization may be achieved by orienting the steps without changing their length appreciably: the cost in energy is small. On the other hand, large polarizations, \( pd \gg 1 \), may be obtained only with the long, parallel steps of figure 4b. The length \( l \) of a step must be such that

\[
p = \frac{l}{d^2}. \n\]

Step lengthening is forced by the polarization, due in turn to the tilt in the interface.

The energy density of steps per unit area is proportional to their total length

\[
E = \beta \cdot \sum_{\text{all steps}} dl.
\]

In highly polarized states, all \( dl \) are nearly parallel, and

the energy is proportional to the polarization

\[
E \sim \frac{\beta l}{d^2} \sim \beta p. \n\]

We recover the usual behaviour of vicinal surfaces: the replacement of infinite steps by finite segments ending at dislocations does not matter much. If, however, \( pd \ll 1 \), the energy remains of order \( \beta d/d^2 = \beta/d : \) dislocations round up the cusp of \( E(p) \) at \( p = 0 \).

The total surface free energy may be written as

\[
E = \sum_{\text{all steps}} \beta \int dl - \frac{1}{2} F \int r \times dl \cdot n. \tag{A.5}\n\]

The first term is the line tension and the second term is the work done by the external force \( F \), which is proportional to the area of an atomic layer bound by the steps (measured from an arbitrary reference). In the limit \( pd \gg 1 \), (A.5) becomes

\[
E = \int d^2 r \left\{ \beta p(r) - \frac{1}{2} F (r \times p(r) \cdot n) \right\}. \tag{A.6}\n\]

The polarization \( p(r) \) is determined by minimization of the free energy, which gives, along with (A.3)

\[
\text{div } p(r) = q_+(r) - q_-(r)
\]

\[
\text{rot } \hat{p}(r) = \frac{1}{r_c} n \tag{A.7}\n\]

where \( \hat{p} \) is the unit vector along \( p \) : as expected the « average » steps have curvature \( r_c \). (A.7) provides a macroscopic description of interfaces with a large dislocation density.

References


