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The velocity source concept

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Abstract

Traditional kinematic wave theory neglects considerations involving free energy of a surface and nucleation at the boundary of a surface. As a consequence, strictly speaking this theory is only applicable to freely floating perfect crystals, and when applied to more complex situations the conclusions may be false. In this paper we argue that boundary conditions, to be taken into account at interface junctions, affect the shape of the crystal. The effect is either microscopic or macroscopic. In the first case, we have a "kinetic meniscus", a curved transition of the size of the critical radius. In the second case, the growth rate is affected macroscopically and we may consider the boundary as a "velocity source" for the affected interface. These concepts are essential elements in a version of kinematic wave theory that is applicable to all physically relevant situations. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the traditional kinematic wave theory as introduced by Frank [1] and Chernov [2], shape evolution of crystal surfaces is considered from a continuum point of view. This description deals with the evolution of a free surface obeying a certain $R(n)$ function (R = perpendicular growth rate, $\boldsymbol{n}$ = orientation vector). This is a standard textbook subject [1,2,4,6]. However, this "traditional" discussion neglects boundary conditions which might arise at boundaries of a surface, such as 3-junctions (where three interfaces meet), D-junctions (where a dislocation meets an interface), 4-junctions, edges and vertices. As a consequence, traditional kinematic wave theory is only fully relevant for "freely floating perfect single crystals", a fact which is not always properly recognised. Geometrical effects due to boundary conditions as mentioned above are neglected.

In this paper we argue that the consideration of these boundary conditions is essential in those cases which are *not* just freely floating perfect single crystals, i.e. the majority of technical situations. We

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show that under certain conditions, the boundaries can prescribe the growth or etch rate of a macroscopic part of the crystal. In such a case we may call them "velocity sources". Well-known examples avant la lettre are dislocation junctions and twin-plane reentrant edges. In growth or etch fabrication processes for semiconductor devices using inert masks, the mask-junction may act as a velocity source. In that case, the commonly accepted construction by Jaccodine [7] and Shaw [8], neglecting the extra boundary conditions, leads to false conclusions. Indeed, we have found evidence for such behaviour in etching experiments on silicon in alkaline solutions [9].

In the following we use an operator notation for compact formulation of shape-related equations. The vector operators $\boldsymbol{P}$ and $\boldsymbol{Q}$ work on scalar quantities, which are functions of orientation $\boldsymbol{n}$, a unit vector variable on the unit sphere:

$\boldsymbol{P}$, polar-plotting vector operator:

$$\boldsymbol{P}\Psi(\boldsymbol{n}) = \boldsymbol{n}\Psi(\boldsymbol{n}). \tag{1}$$

$\boldsymbol{Q}$, "Gibbs – Wulff" vector operator:

$$\boldsymbol{Q}\Psi(\boldsymbol{n}) = \boldsymbol{n}\Psi(\boldsymbol{n}) + \partial/\partial\boldsymbol{n}\{\Psi(\boldsymbol{n})\}. \tag{2}$$

where $\partial\Psi/\partial\boldsymbol{n} = \boldsymbol{e}_1\partial\Psi/\partial\varphi + \boldsymbol{e}_2 \quad \partial\Psi/\partial\vartheta)$, where $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are orthonormal vectors in the plane tangent to $\boldsymbol{n}$, and φ and ϑ are the related tilt angles. There are two such functions Ψ relevant to crystal growth. The first is $\Psi = \gamma$, the surface free energy. $\boldsymbol{Q}\gamma(\boldsymbol{n})$ is the equilibrium shape of a crystal, which can be obtained by applying the well-known Gibbs–Wulff construction [3,5,10] to the polar plot of the surface free energy $\boldsymbol{P}\gamma(\boldsymbol{n})$. The second is $\Psi = R$, the growth rate. Analogously, $\boldsymbol{Q}R(\boldsymbol{n})$ is identical to the growth shape of a crystal.

Furthermore, we define the vector velocity $\Re$ of a point in a moving surface as the velocity in the direction of the kinematic wave trajectory [1], i.e. the trajectory that preserves orientation. The kinematic wave theory presupposes that R depends on $\boldsymbol{n}$ only, which yields the identity $\Re = \boldsymbol{Q}R(\boldsymbol{n})$. The motion of structural elements such as junctions, edges and vertices can also be represented by vector velocities $\Re_j$.

Equations for the mechanical behaviour of an interface can also be written with the aid of the operators introduced above. The force exerted by a surface on an edge or junction with other surfaces, aligned with unit vector $\boldsymbol{l}$, is given by [3,10]

$$\boldsymbol{F} = \boldsymbol{Q}\gamma(\boldsymbol{n}) \wedge \boldsymbol{l}. \tag{3}$$

where $\wedge$ denotes the vector exterior product.

2. Boundary conditions relevant to junctions

The interfaces meeting at a junction are in general different and therefore have their own growth rate and surface free energy functions $R_i(\boldsymbol{n})$ and $\gamma_i(\boldsymbol{n})$. The following boundary conditions (BC) apply in general:

(1) *The connectivity BC*, ensuring that the junction keeps contact with all, say n, interfaces connected in the junction: ($\boldsymbol{n}_i$ is the orientation of interface i)

$$\Re_j \cdot \boldsymbol{n}_i = R_i(\boldsymbol{n}_i) \quad (i = 1, 2, \ldots, n). \tag{4}$$

(2) The following BCs (2a) and (2b) are mutually exclusive. They are related with the free energy or the step-generating activity of interfaces and dislocations. Both are based on the difference in bond structure between boundary- and nonboundary positions. The BC (2a) applies to the case that nucleation is negligible which may be considered as the near-equilibrium case, and is to be replaced by the BC (2b), if necessary, which can be seen as the kinetic extension of (2a).

(2a) *Mechanical-equilibrium BC*: For simplicity we restrict to the case of a linear 3-junction where three interfaces meet in a line. In a plane perpendicular to this line the force-equilibrium condition reads [3,10]

$$\sum_{i=1}^{3} \boldsymbol{Q}\gamma_i(\boldsymbol{n}_i) = 0. \tag{5}$$

When all three $\gamma_i(\boldsymbol{n})$ functions and the junction-line direction are given, only one orientational degree of freedom is left for the system.

(2b) *Nucleation BC*: In the case of faceted interfaces growing or dissolving below the roughening temperature, interface motion is essentially related with step motion and a boundary may have an active role in the nucleation of new steps. Such step-nucleation imposes an interface velocity and as a consequence also an orientation, just as BC (2a). However, it cannot be expressed in a kinetically extended version of Eq. (5), because the junction is a hybrid object that is not really continuous. At the junction "atomistic" phenomena like the nucleation of steps take place intermittently. The statistical result is an imposed point on the ***QR*** curve, to be obtained from experiment or from Monte Carlo simulation. The mathematical effect is identical as for BC (2a).

3. The wall-junction or "single-mobile 3-junction"

The simplest possible case of a mobile 3-junction is the contact line between a moving crystal interface and an immobile wall, i.e. the wall of a growth vessel or a mask as used in growth or etch techniques for semiconductor devices. This case, with only one mobile interface and a single orientation variable φ, has been considered by Shaw [8]. We use his analysis as a point of departure. We start from a situation where a crystal/parent phase interface of orientation φ_∞ extends towards the wall, see Fig. 1 (inset). Such a situation may occur, for instance, when a freely growing single crystal has just hit the wall of the growth vessel. We assume that the orientations φ_∞ and φ_w (that of the wall) can both be chosen freely relative to the crystal. In the approach followed by Shaw, the $\boldsymbol{QR}(\varphi)$ curve is drawn with its origin in the junction at $t = 0$, see Fig. 1. Shaw's procedure to construct the shape after unit time is as follows. The φ_∞ half-plane is translated along the vector $\boldsymbol{QR}(\varphi_\infty)$. From the point $\boldsymbol{QR}(\varphi_\infty)$ the shape is continued along the $\boldsymbol{QR}(\varphi)$) curve. "Ears" beyond self-intersections of the curve, if any, are cut off because they are nonphysical. Finally the shape obtained by this procedure is confronted with the wall which acts as a knife. This means that it is a "wall" in the sense that it prevents the interface to extend beyond it, *but it does not affect the orientation of the interface.*

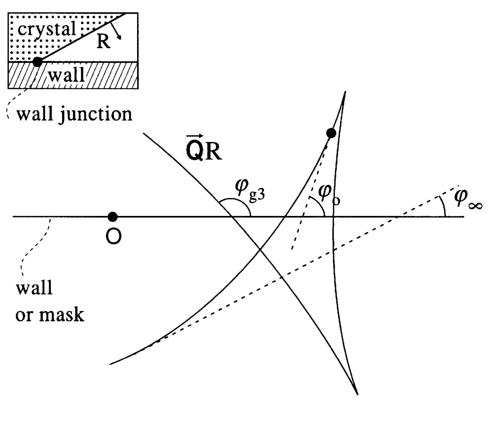

Fig. 1. Relative orientation and shape of wall and ***QR*** curve for the wall-junction.

For further discussion, we make two special choices which together can illustrate all phenomena induced by boundary conditions: one for the shape of $\boldsymbol{QR}(\varphi)$ and one for the orientation of the wall relative to that shape, see Fig. 1. In Fig. 2, we have drawn the function $S(\varphi) = R(\varphi)/|\sin\varphi|$, i.e. the velocity of the wall junction *if the orientation φ of a moving interface would extend throughout the wall*; i.e. a possibly "virtual" velocity. The real velocity is called $\Re_j$. The angle φ, ranging from 0 to 180°, is defined so that $\varphi = 0$ describes an interface parallel to the wall and approaching it. The maxima and minima of this function correspond with the intersections of the $\boldsymbol{QR}(\varphi)$ curve in Fig. 1 with the wall.

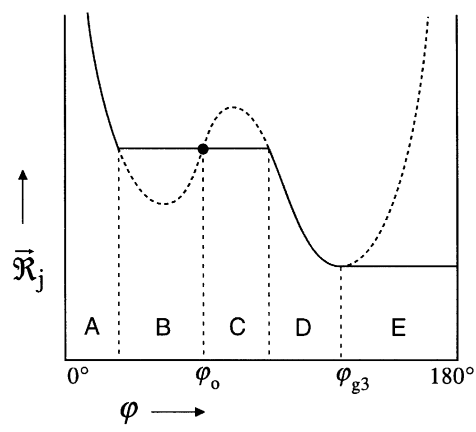

Fig. 2. Virtual and actual wall-junction velocities corresponding with Fig. 1. Continuously curved and partly dotted line = $S(\varphi)$; solid line = $\Re_j(\varphi)$ = actual wall-junction velocity; regions B and C: velocity source behaviour, no kinetic meniscus; regions A, D and E: kinetic meniscus, "classical" behaviour of junction velocity.

Now we make a third special choice: i.e. the orientation φ_0 as imposed by BC (2) is chosen in the first ascending section of the S function, as indicated in Fig. 2. The total φ range between 0 and 180° can now be divided into the five regions A, B, C, D and E which are defined by the position of φ_0 and of the extrema in the S function as indicated in Fig. 2. Special cases of the interface shapes emerge when φ_∞ is situated in each of these ranges, see Fig. 3a–Fig. 3e:

In case A ($\varphi_\infty < \varphi_0$, $S(\varphi_\infty) > S(\varphi_0)$) the construction according to Shaw predicts a value $\Re_j(\varphi_\infty)$ which exceeds $S(\varphi_0)$. So there is obviously a paradox with BC (2). The solution of this paradox is that the basic assumption of kinematic wave theory, i.e. that the growth rate depends on orientation only, is not obeyed in the vicinity of the junction. The φ_0-oriented interface at the junction cannot stay behind physically; this induces a concave curved section that joins the orientation φ_0 at the wall with the orientation φ_∞ further on. The curvature induces a pressure difference between the bulk phases and therefore increases the driving force for crystallisation or etching (Gibbs–Thomson effect). This curvature-induced shift in the driving force provides a mechanism that accelerates the φ_0-oriented interface automatically, until it keeps up with the φ_∞-oriented interface. But this implies that in this curved part of the interface, the prerequisite of the traditional version of kinematic-wave theory, i.e. constant driving force all over the surface, is no longer obeyed. When R is known as a function of $\boldsymbol{n}$ and the driving force, the stationary shape of the curved part can in principle be calculated from the identity $\Re = \Re_j(\varphi_\infty)$ for all points on the curve. In Ref. [11] we have shown that the size of the curved part is roughly the size of the critical nucleus for the applied driving force. Such a curved part may properly be called a *kinetic meniscus*, in analogy with a gravity-induced meniscus in a fluid surface near a container wall.

In case B ($\varphi_\infty < \varphi_0$, $S(\varphi_\infty) < S(\varphi_0)$) the φ_∞-oriented interface at the wall can escape from the value $S(\varphi_\infty)$ predicted in the absence of BC (2). The re-entrant edge between φ_0 and φ_∞ moves away from the junction and a growing, i.e. macroscopic part of the interface is "nucleated" with orientation φ_0. This interface is planar in the vicinity of the junction: there is no kinetic meniscus. The vectors $\boldsymbol{QR}(\varphi_0)$ and $\Re_j$ diverge. This case is an example of a velocity source that *accelerates* the junction and the velocity of the interface.

In case C ($\varphi_\infty > \varphi_0$, $S(\varphi_\infty) > S(\varphi_0)$) we have a similar effect as in case B but now the edge between φ_0 and φ_∞ is *protruding*. Consequently, the junction is a velocity source that *decelerates* the junction and the velocity of the interface.

In case D ($\varphi_\infty > \varphi_0$, $S(\varphi_\infty) < S(\varphi_0)$) we have a kinetic meniscus again: now $S(\varphi_0) > S(\varphi_\infty)$ but the φ_0-interface cannot overtake the junction physically. Again, a kinetic meniscus is generated.

Finally, in case E ($\varphi_\infty > \varphi_{g3} > \varphi_0$, $S(\varphi_\infty) < S(\varphi_0)$ but $S(\varphi_\infty) > S(\varphi_{g3})$) the construction according to Shaw does no longer predict the orientation φ_∞ to occur at the wall but rather φ_{g3}, the orientation of the $\boldsymbol{QR}$/wall intersection with the lowest velocity. As $S(\varphi_0)$ is faster, we have a kinetic meniscus.

4. Generalisations and conclusions

As it is impossible to work out a complete picture of velocity-source phenomenology for all possible junctions within the framework of a short paper, we have restricted ourselves to a single tailored example. For a more thorough discussion we refer

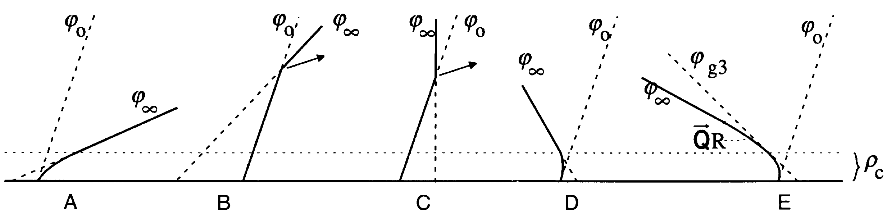

Fig. 3. Shape evolution for cases A–E of Fig. 2.

to [11,12]. General remarks derived from these extended discussions include:

- Velocity source behaviour is not a property of a junction as such; it is a property of a junction + interface *pair*. A junction can nucleate none, one or more of the interfaces attached to it.
- The casuistics of more complex cases than the example used above (2- and 3-mobile 3-junctions, 4-junctions, vertices etc.) is quite extended. The concepts "velocity source" and "kinetic meniscus" and their phenomenology, however, are generally applicable.
- Certain cases of edges and vertices in single crystals seem to show velocity-source behaviour too. This case arises in cases where $\gamma + \partial^2\gamma/\partial\varphi^2 < 0$ which destabilises a planar surface ("zigzag instability" [11]).

Acknowledgements

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