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A geometric model for anisotropic crystal growth

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Abstract. Equilibrium crystal shapes are defined uniquely by the Wulff construction. The classical kinematic theory of crystal growth, due mainly to Frank and Chernov, provides a mathematically equivalent prescription for the limiting growth shape. To connect these two well studied states, we derive a local geometric growth model and examine the *transient* shape evolution of an equilibrium form containing both facets and rough regions. Our model is appropriate to the weakly driven growth of a two-dimensional single crystal with n-gonal symmetry and arbitrary closed initial shape. The model links disparate kinetic processes determined by the local interfacial structure to the isotropic growth drive, and reproduces the experimentally observed transition from a partly rounded equilibrium shape to a highly faceted crystal which we term 'global kinetic faceting'. We solve for the transient shape dynamics globally, and locally, and in the latter case present a curvature evolution equation valid for any local growth law. Both approaches show that, during kinetic faceting, rough orientations grow out of existence with *decreasing* curvature.

1. Introduction

Spatiotemporal pattern formation in condensed matter systems has broad technological and scientific interest, with theoretical analogues in hydrodynamic, chemical and biological systems [1]. The example of crystal growth shapes is important in many areas of physics, materials science, physical chemistry, and geophysics. The theoretical approaches to the study of growth shapes depend on whether the interfacial motion is controlled by long-range diffusion or by local processes. It is known that local growth kinetics depend on local interfacial free energy and microscopic structural considerations in the particular crystallographic orientation, but the manner in which they determine the *global* (≡ the entire close surface) crystal shape is often treated *ad hoc*. The geometry of phase boundaries, or interfaces between grains of the same phase, is of interest in many contexts [2]. Studying the case of a single crystal growing from a pure nutrient phase has the advantage of laying bare the essential physics and analysis common among them.

Two broad classes of growth models exist: geometric and non-geometric. Geometric models are appropriate when the interfacial growth velocity may be determined solely by local interfacial parameters, decoupled from diffusional or other long-ranged influences. Hence instabilities associated with diffusional growth are precluded. Geometric models have been reviewed by Taylor *et al* [3], and in addition to their intrinsic mathematical interest [4], they have successfully treated crystal growth, phase–antiphase boundary motion, grain growth, and stress-driven-zone migration, among others. Taylor *et al* [3] view a model as *geometric* if the normal velocity V at an interfacial point depends on the *shape* and *position* of the interface, and not on field variables modified by the interface motion or

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long-range diffusion in the bulk. We consider *geometric* models in the sense that only the *shape*, and *shape-dependent quantities* of the interface determine the motion. Non-geometric models generally treat growth on surfaces that are everywhere rough [5]†, with anisotropy introduced into the interfacial conditions of a particular free boundary problem. Classical normal growth theories of molecular attachment kinetics treat a single interfacial state—faceted (≡ high symmetry) or rough, or the transition between them, but not the coexistence of different surface structures [6]. The anisotropy of specific surface free energy determines the equilibrium crystal shape, while the growth shape is *also* affected by the anisotropy of the mobility or kinetic coefficient. Using a Ginzburg–Landau model, Siegert [7] has shown this from the resulting Allen–Cahn (or Langevin-type) equation with noise, wherein the surface stiffness is anisotropic, but *continuously differentiable* and so cannot treat the problem of an initial shape which contains orientations below their roughening temperatures. Hence, to treat this case, we pursue a kinematic theory for anisotropic growth.

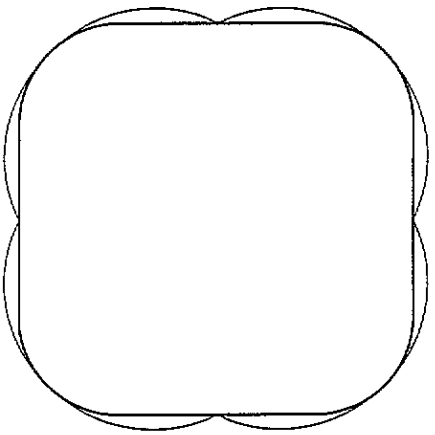

Figure 1. The boundary (full lines) of the equilibrium crystal shape, $\mathcal{W}_\gamma$, formed from the Wulff construction which is the interior envelope of the set of perpendiculars to radial rays intersecting the polar plot of surface free energy (lighter lines). We take this initial shape away from equilibrium according to our growth model, but stress that, since our theory is kinematic, the initial shape need not be an equilibrium shape.

The equilibrium crystal shape is that which minimizes the orientation-dependent total surface free energy per unit area for the volume it contains, and is determined uniquely from Wulff's construction [10]. It may be helpful to recall the salient points here. The boundary of the shape, $\mathcal{W}_\gamma$, is given by

$$\mathcal{W}_\gamma = \{\boldsymbol{r} : \boldsymbol{r} \cdot \boldsymbol{\mathcal{N}} = \gamma(\boldsymbol{\mathcal{N}}) \; \forall \; \boldsymbol{\mathcal{N}}\} \tag{1}$$

where $\gamma(\boldsymbol{\mathcal{N}})$ represents the surface free energy per unit area in the specified orientation of the surface unit normal vector $\boldsymbol{\mathcal{N}}$, and $\boldsymbol{r}$ defines a radial vector from the origin to the equilibrium crystal surface (e.g. [3, 9, 10]). The construction shows that shapes are geometrically similar, with a size determined by the thermodynamic conditions of the problem (given by the Lagrange parameter in the standard variational thermodynamics). Equilibrium forms may be fully faceted, everywhere rough, or may consist of both interfacial structures. An example of the latter is given in figure 1. Previously, we presented a phenomenological model [9] for growth shapes which was based on the kinetically constrained minimization of surface free energy. Motivated by the fact that the relaxation rate at rough orientations can be negligible compared to that on facets, we took the shape of figure 1 very slightly away from equilibrium. In this limit, the facets are pinned, and

† Unless the boundary layer hypothesis is invoked, diffusion-limited growth is not geometric because the interfacial motion depends on the interfacial value of the field variable(s) which are modified by diffusion. In diffusion-limited growth, anisotropy is ascribed to an orientation dependence in the surface tension or the kinetic coefficient, or to both.

the rough orientations accrete mass to take the Wulff shape of an 'equilibrium' crystal of *increasing size*.

Similarly, Chernov [11] (see also [3]) has extended Frank's picture to observe that the *steady-state* growth shape which is spatially bounded at each time has a boundary $\mathcal{W}_V$ which can be written as

$$\mathcal{W}_V = \{r : r \cdot \mathcal{N} = V(\mathcal{N}) \; \forall \; \mathcal{N}\} \tag{2}$$

where $V(\mathcal{N})$ is the growth rate in the normal direction $\mathcal{N}$. The sequence of limiting growth shapes is given by a simple expansion with time. The shape $\mathcal{W}_V$ can be related to Frank's [8] polar plot of slowness $\mathcal{N}/V(\mathcal{N})$ [3]. The shape of the polar plot of $V(\mathcal{N})$ determines the nature of growth anisotropy and the structure of $\mathcal{W}_V$.

In this presentation we take an equilibrium shape $\mathcal{W}_\gamma$ which contains both facets and rough orientations, and investigate its evolution *toward* the limiting shape $\mathcal{W}_V$. We begin with the equilibrium shape, since it experiences the least activation barrier and is therefore most likely to be nucleated. However, our approach can be applied to any closed convex initial shape.

In the next section we present a vector evolution equation for an arbitrary $V(\mathcal{N})$, and then derive a local growth rule for an arbitrary initial shape of n-gonal symmetry. Following this we use the model to study a specific example. Finally, we analyse a scalar evolution equation for local curvature that is derived from the vector evolution equation for the curve. Both equations possess analytic solutions, from which we deduce systematic behaviour applicable to experimental observations.

2. The growth rule

We follow the motion of each point of an equilibrium shape under weak growth drives $\delta\mu$, the chemical potential difference between the surface and the nutrient phase, where the cost of advancing the interface in faceted directions is high relative to the available driving force. The previous model [9] motivates the present one, based on the familiar tenet that there is a range of $\delta\mu$ for which there exists a nucleation barrier to accretion at faceted orientations which is not present at rough orientations [6, 11]. Thus the crystal is at a temperature below the roughening transition of its faceted orientations, and under a growth drive too weak to induce kinetic roughening, allowing us to treat growth in a regime far from standard surface phase transitions [12].

To derive our model we consider a crystal that is uniformly bathed in a homogeneous nutrient phase. On imposition of a weak growth drive, interfacial processes control the rate of advance of the solid phase. Normal motion at facet orientations is limited by the generation of step sources for new layers. Here we restrict attention to those generated by two-dimensional nucleation of solid clusters, though we stress that our formalism can accomodate the other step generation mechanisms. The formation of a nucleated step source requires the coalescence of many molecules in a cluster for which the edge to surface free energy ratio favours spreading at a given drive†. The generation of new layers is a thermally activated process with a nucleation frequency I per unit facet area of the typical Maxwell–Boltzmann form, $I \propto \exp(-\pi\sigma^2/kT\delta\mu)$, where σ is the free energy of a critical nucleus on the facet (e.g. Weeks and Gilmer [6]). Thus, the normal growth rate is $V_\mathrm{f} = \hat{a}IA$,

† The free energy change of the facet/source system (with i_T molecules) on introduction of the nucleus of i molecules is $\Delta G = \Delta G_i - T\Delta S_i$, where ΔG_i is the free energy of formation of the nucleus, and ΔS_i is the configurational entropy associated with the reorganization of i molecules from the vapour to the solid. Since $i/i_T << 1$ we can approximate $\Delta G = \Delta G_i$.

where $\hat{a}$ is the lattice constant and A is the typical facet area. We treat the case in which the nucleus spreading velocity is so large that a nucleated layer covers the facet before the subsequent nucleation event occurs. Moreover, owing to the finite facet size relative to fluctuations which can initiate kinetic roughening [12], experiments clearly exhibit singular growth in this mode. We stress that this is not the case for an infinite facet, or when the facet size is less than the correlation length of the surface [12]. We also emphasize that V_f is less than the facet growth rate by a mechanism involving multiple nuclei (e.g. equation (36) of [12]). Steps are already present at molecularly rough surface orientations, so that growth occurs by random encorporation of nutrient molecules onto the surface; here there is a linear response to a small driving force $V_r \propto \delta\mu$ [6]. Thus, our initial shape will evolve due to (i) slow normal growth of facets by nucleation and spreading of monolayers, (ii) relatively fast normal growth of molecularly rough regions, and (iii) the coupling of the above, wherein the normal growth of the non-singular regions is modified by surface diffusion of admolecules away from the facets.

The essential idea is to develop an expression for the local normal velocity at each point of the interface, and to evolve the global shape under growth resulting from the coexistence of the local kinetics described above. For simplicity we treat the overall shape problem in a two-dimensional symmetric cross section through the crystal, while noting that shape evolution of two-dimensional forms is itself of experimental relevance [14–18]. We model the interface with a closed curve $\mathcal{C}[x(u,t), y(u,t)]$ in the plane having time-dependent components parametrized by a variable u. The arclengths s and u are related by $s(u,t) = \int_0^u |\partial\mathcal{C}(u',t)/\partial u'|\,du'$. We let $W = |\partial\mathcal{C}(u,t)/\partial u|$ so that $ds = W\,du$. We let θ denote the angle between the positive x-axis and the unit tangent vector $\mathcal{T} = (\cos(\theta), \sin(\theta)) = W^{-1}\partial\mathcal{C}/\partial u$. The unit normal $\mathcal{N}$ is inward pointing. Our evolution equation will have the form

$$\left(\frac{\partial\mathcal{C}}{\partial t}\right)_u = -V\mathcal{N} \tag{3}$$

where $V = V(\theta, \delta\mu)$ is a normal velocity function under the drive $\delta\mu$.

Now we define a local normal velocity $V(\theta, \delta\mu)$ which continuously blends V_f and V_r as motivated above. The normal growth rate at facet orientations is written as

$$V_f(\delta\mu) = c_f g(\delta\mu)\exp\left(\frac{-\pi\sigma^2}{kT\delta\mu}\right) \tag{4}$$

whereas for non-singular orientations we express the linear response to the growth drive as

$$V_r(\theta, \delta\mu) = c_r\delta\mu\left[1 + \cos^p\left(\frac{n\theta}{2}\right)\right] \tag{5}$$

where p is an even integer. The second term of V_r models the contribution to the normal interfacial motion at vicinal and rough orientations due to surface migration of admolecules away from facets. This is in analogy to the results of solid-on-solid models [18] wherein it is found that surface diffusion currents of admolecules away from singular orientations increase with surface slope, saturate at a maximal value, and at a slope controlled somewhat by finite-size effects, decrease abruptly to zero. The latter slope is ascribed to a grooved surface state, and we tie this to the roughest orientations on our shape at a given time. Our representation is the simplest form capturing this growth process in the continuum limit [19].

A 'kinematic observer' moving on the surface of the crystal will see activated growth at singular orientations, and a transition to rough growth kinetics while walking away from

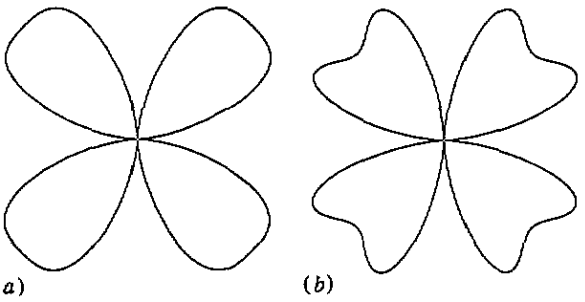

Figure 2. Polar plots of $V(\theta, \delta\mu)$ for (*a*) $m = p = 2$, (*b*) $m = 4$, $p = 2$. $V(\theta, \delta\mu)$ controls the evolution of the initial crystal shown in figure 1 and in figure 3(*a*), where we take $m = p = 2$.

singular faces. We join these disparate kinetic processes into a complete local normal velocity function for n-gonal symmetry via a transition function $\xi(\theta)$

$$V(\theta, \delta\mu) = V_f(\delta\mu)\xi(\theta) + V_r(\theta, \delta\mu)(1 - \xi(\theta)). \tag{6}$$

The function ξ governs the transition between facet-like and rough-like growth. Its essential properties are: ξ is periodic in $2\pi/n$, $1 \geqslant \xi \geqslant 0$, and $\xi(\theta_f) = 1, \xi(\theta_f + \pi/n) = 0$, where θ_f is a facet orientation. For the examples in this paper, we make the simple choice of the transition function $\xi(\theta) = \cos^m(n\theta/2)$, where m is even and $m \geqslant p$ to preserve the n-gonal symmetry. We include two parameters m and p in our model which may be determined by experiment. The function $g(\delta\mu)$ and the mobilities $c_{f,r}$ may also depend on other parameters [20], but the essential point is that for a given $\delta\mu$, $V_f \ll V_r$. Similarly, other geometric growth models (e.g. [3, 4] (Angenent and Gurtin)) represent anisotropy as a product of an orientation-dependent mobility and a linear combination of a bulk phase-change contribution and weighted mean curvature, itself a linear combination of $\gamma(\mathcal{N})$ and $\gamma''(\mathcal{N})$. Polar plots of $V(\theta, \delta\mu)$ are shown in figure 2.

3. Solution and example

An initial value problem for (3) with V given by (6) can be solved *exactly* using the method of characteristics [3]. The method of characteristics is applicable to interface–motion problems when the normal velocity depends explicitly on surface orientation alone (at a given driving force) and not on the interface position or derivatives such as curvature (e.g. [4] Brower *et al*). The characteristics for this class of problems are straight rays, one emanating from each point of the initial curve. These characteristics have the form $\boldsymbol{x}(t) = \boldsymbol{x}_0 + t\boldsymbol{d}(\theta_0)$, where $\boldsymbol{x}_0$ is a point on the initial curve and $\boldsymbol{d}$ is a direction vector whose value is determined by the velocity $V(\theta_0)$ at $\boldsymbol{x}_0$. The surface normal direction is preserved along each characteristic. Thus the curve $\mathcal{C}$ at time t is given by the set of all points $\boldsymbol{x}(t)$.

Figure 3 presents the resulting growth sequence when the initial *equilibrium* shape (given in figure 1) contains both facets and rough regions. The initial shapes are constructed explicitly from Wulff's theorem ($\mathcal{W}_\gamma$ from (1)). Note that the facets spread to dominate the growth shape, broad vicinal regions form, and the rough orientations grow out of existence with *decreasing* curvature. This type of faceting can only occur under an imposed growth drive and we term this '*global kinetic faceting*'. It is the global (the entire closed surface) effect of local dynamics, as distinct from equilibrium faceting or local kinetic faceting that has been observed on crystals grown from solutions [21]. The curvature decrease at rough orientations during this transition is consistent with notions of critical nucleation size [9],

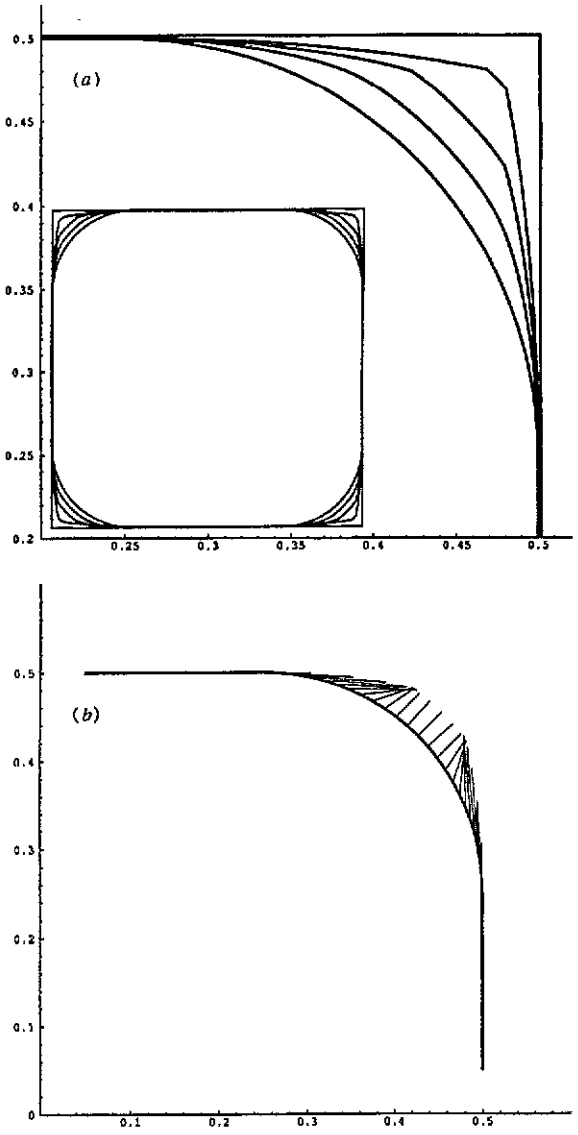

Figure 3. (*a*) A sequence of growth shapes at times $t = 0, 0.018, 0.038, 0.068, 0.35$ of the upper right quadrant of a crystal with cubic ($n = 4$) symmetry, $m = p = 2$, $c_r\delta\mu = 1$, $V_f(\delta\mu) = 0.01$. The units are arbitrary. (*a*) The initial ($t = 0$) equilibrium shape, $\mathcal{W}_\gamma$, is formed by in the Wulff construction and shown in figure 1. The inset shows the full crystal shape at the same times. Note that the rough orientations grow out of existence with a *decreasing* curvature, and that there are sharp joints where the vicinal regions join the rough regions. The curvatures at $\theta = \pi/4$ for $t = 0, 0.018, 0.038, 0.068$ are 4, 3.7, 3.4, 3.1 (the numerical values agreeing with the exact solutions to (7) to one significant figure [25]). As growth progresses, the crystal loses orientations, until it is fully faceted and possesses only four orientations. Note that growth at the facet orientations is so slow that individual time steps are represented by fractions of a line width on this scale. The final shape is geometrically equivalent to that given by $\mathcal{W}_\mathcal{V}$ of (2), *and* that constructed from the polar plot of ∇V, thereby showing the transient evolution between $\mathcal{W}_\gamma$ and $\mathcal{W}_\mathcal{V}$. (*b*). Here we draw the characteristics to illustrate the method of solution and the point that the characteristics are trajectories along which the surface normal is conserved.

and contradicts the common intuition that curvature will increase at orientations where the normal velocity is greatest. Also, consistent with experimental observations [23–25], the edges of the facets become sharper and more visible during the transition. Finally, the steady state that our model captures is equivalent to that obtained by Chernov's construction $\mathcal{W}_V$ on V, that which can be generated from Frank's [8] polar plot of slowness, and that which is obtained by truncating the 'ears' of the Taylor *et al* ∇V plot [3]. Therefore, we see *how* the equilibrium shape $\mathcal{W}_\gamma$, evolves toward the limiting growth shape $\mathcal{W}_V$.

In general, the characteristic rays will begin intersecting after some finite time; that is, shocks will develop (figure 3(*b*)). After the time of the first intersection, the curve $\mathcal{C}$ will not be a simple closed curve, but instead will develop 'ears'. Of course, there is no physical meaning for these ears so the natural procedure is to terminate any characteristics which reach such a shock [3]. Thus the curve $\mathcal{C}$ loses any initial orientation whose corresponding characteristic hits the shock.

4. Local curvature evolution

The result displayed in figure 3 is confirmed by a general analysis of the curvature evolution. We utilize the basic differential geometry of curves in the plane (see the appendix). With the curve parametrized by θ rather than u or s, we derive the local curvature evolution equation

$$\frac{\partial \kappa}{\partial \tau} = -\kappa^2 \tilde{V} \tag{7}$$

where $\tilde{V} \equiv (V + V'')$, the primes denote differentiation with respect to theta, and $\partial/\partial\tau$ gives the rate of change at fixed θ as distinguished from that at fixed u. We call $\tilde{V}$ the 'velocity stiffness' in analogy with surface stiffness.

The derivation of (7) depends solely on identities of differential geometry and does not require us to specify a rule for V. Thus, at this point the physics of the problem for an arbitrary shape is unspecified, and we are poised to address a variety of two-dimensional interfacial evolution problems. In order to study idealized diffusion-limited growth, similar evolution equations have been presented previously [4, 5]. An important distinction is that, for a given driving force, our growth law V, and hence the velocity stiffness, depends only on θ and not κ or its derivatives.

Any seed crystal relevant to our analysis is convex, $\kappa \geqslant 0$, but need not be strictly convex, $\kappa > 0$. For finite $\tilde{V}$, the solution of (7) is given by

$$\kappa = \frac{\kappa_i}{1 + \kappa_i \tilde{V} \tau} . \tag{8}$$

Angenent [26] has found behaviour similar to (8) for a more general class of problems. We consider the three cases of orientations with $\tilde{V} > 0$, orientations with $\tilde{V} = 0$, and orientations with $\tilde{V} < 0$ (figure 4).

At non-faceted orientations with initial curvature κ_i, and $\tilde{V} > 0$, the curvature will decrease monotonically in time from the initial value. This result is quantitatively consistent with the solution to (3), qualitatively consistent with the experimental behaviour mentioned above, and qualitatively consistent with our model of kinetically constrained minimization of surface free energy wherein the rough orientations take the shape of an expanding equilibrium crystal [9]. It is also trivially correct for isotropic surface free energy, e.g. a liquid drop. We can get some insight into our model velocity given in (6) by looking at, for example, the orientaion $\theta = \pi/4$ with $n = 4$. In this case $\tilde{V}(\pi/4) = c_t \delta\mu + 8V_f$. Therefore, for small $\delta\mu$ the *rate* of curvature decrease *increases* with $\delta\mu$.

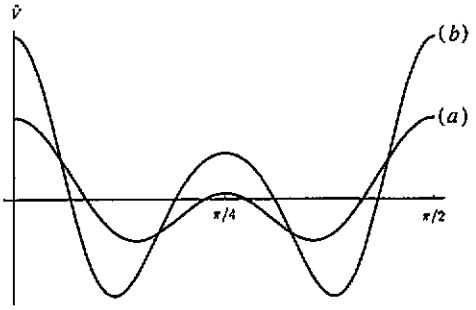

Figure 4. A plot of $\tilde{V}$ for $0 < \theta < \pi/2$. (*a*) $m = p = 2$ (*b*) $m = 4$, $p = 2$.

In general, $\tilde{V}$ will be zero for certain orientations which we denote θ_0. For these orientations, the curvature remains constant. In our model velocity function, $\tilde{V}$ has two zeros between each facet orientation and the centre of the rough orientations. In the case $n = 4$, there are a total of sixteen values of θ_0 (figure 4).

For orientations with $\tilde{V} < 0$ the solution in (8) gives a finite time curvature divergence at time $\tau = -(\kappa\tilde{V})^{-1}$. The minimum 'blow-up' time corresponds to the orientation for which $\tilde{V}$ is minimum. We conjecture that the shock begins developing before the minimum blow-up time, and that the characteristics for orientations with $\tilde{V} < 0$ hit the shock before the blow-up time corresponding to their orientations. We have numerical evidence for this conjecture in the case of our model velocity, and we observe corners on the evolving shape, but never curvature divergence.

For closed curves, shape preserving growth is *not* synonymous with a vanishing time derivative in (7) (e.g. an expanding circle preserves overall shape with decreasing curvature), although for open curves shape preserving solutions can be obtained with this constraint (e.g. needle crystals) [5]. For orientations such that $\tilde{V} > 0$, the long time limit of (8), $\kappa = 1/\tilde{V}\tau$, tells us that the local shape loses memory of the κ_i, *only if* $\kappa_i > 0$, at such an orientation. Thus, under these conditions, an initial seed that is everywhere convex will have an asymptotic curvature that is independent of its initial value at any orientation.

Our analysis of (7) is related to the work of Frank [8] and Chernov [11]. In analogy to the invariance of the chemical potential on the surface of an *equilibrium* crystal, Frank and Chernov showed that there are steady, shape-preserving solutions for interface-controlled *growth*, that satisfy the invariance of the 'kinematic potential' $\kappa\tilde{V} = \lambda(\tau)$. This invariance is the classical constraint for limiting growth shapes. The $\lambda(\tau)$ is a 'constant' (Lagrange parameter) at each time consisting of an arbitrary constant and a decreasing function of time, which provides the length scale of the steady shape. (The invariance of the kinematic potential is equivalent to the Euler–Lagrange equation resulting from the variational solution of the problem of finding the slowest growth shape of all shapes of a given volume at each time.) The interpretation is analogous to the Gibbs–Thomson–Herring equation for an equilibrium crystal shape, where τ plays the role of $\delta\mu$ [9], in the overall expansion of a geometrically similar object. The simplest choice of the Lagrange parameter results in $\tau\kappa\tilde{V} = 1$, which is equivalent to the asymptotic solution of (8). Hence, the invariance is a special case of a more general curvature evolution, and cannot be valid for an *arbitrary* initial shape. As pointed out above, the long time solution is not valid for orientations where $\kappa_i = 0$. The invariance of the kinematic potential in the Frank–Chernov approach is thus a rigorous constraint only for strictly convex initial shapes.

5. Conclusion

In any real crystal growth situation one can hope to begin growth from an equilibrium shape, but it is the *transient* shape that one observes, until and if steady state is reached. We have considered other, more complicated treatments of particular transient effects. For example, one might model the surface diffusion processes via a term $\mathcal{V}\mathcal{T}$ on the right-hand side of (3) rather than as a periodic modulation of the rough growth rate. However, in the most general case the local arc length need not be preserved, which is equivalent to the choice of an 'orthogonal gauge' wherein only the normal growth rule affects the crystal shape [27]. Hence, $\mathcal{V}$ determines solely how the points parametrized by u move along the curve, but it cannot play an explicit role in the shape evolution.

The polygonalization of crystals growing under the conditions we have studied is known. The key to our results is that they indicate this polygonalization is achieved by *decreasing* curvature in rough orientations. In other words, we have found that the transient evolution of an equilibrium shape $\mathcal{W}_\gamma$, containing facets and rough orientations, toward the limiting growth shape $\mathcal{W}_V$, involves a discrete loss in surface orientations. Such an evolution is not captured in a model in which curvature increases in those orientations because the loss of surface orientations can be asymptotically continuous. We have also found the classical constraint of the invariance of the kinematic potential as a special case of a general solution to a local evolution equation for curvature. The invariance holds only when the initial shape is strictly convex, so that one cannot apply it to the study of asymptotic forms of arbitrary, and in particular partially faceted, initial shapes.

A fully faceted crystal contains no surface which can easily accept accreting material. Consistent with our previous result [9] (depending on the size of the crystal, and whether growth takes place in a diffusive medium), such a surface state defines a reasonable lower bound for kinetic roughening of the facets themselves, or the onset of either shape instabilities or oscillations [16]. When the critical nucleation size of a seed crystallite is smaller than the diffusion length in the background material, our model indicates that the initial stage of dendritic growth (or a similar shape instability) is controlled by near-equilibrium microscopic dynamics rather than multiple scale—capillary and diffusive—interactions.

Acknowledgments

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Appendix. Curvature evolution

We outline here the derivation of (7), the curvature evolution equation for an arbitrary normal growth law V. First, we invoke the Frenet equations,

$$\frac{\partial \mathcal{T}}{\partial s} = \kappa \mathcal{N} \qquad \text{and} \qquad \frac{\partial \mathcal{N}}{\partial s} = -\kappa \mathcal{T} \tag{A1}$$

where $\partial\theta/\partial s = \kappa$. We next use the arc length s to parametrize $\mathcal{T}$, κ and $\mathcal{N}$, which by definition are

$$\mathcal{T}(s,t) = \frac{\partial \mathcal{C}(s,t)}{\partial s} \qquad \kappa(s,t) = \left|\frac{\partial^2 \mathcal{C}(s,t)}{\partial s^2}\right| \qquad \mathcal{N}(s,t) = \kappa(s,t)^{-1}\frac{\partial^2 \mathcal{C}(s,t)}{\partial s^2}. \tag{A2}$$

In analogy with the approach of Gage and Hamilton [4] we then compute the following identities:

$$\frac{\partial W}{\partial t} = W\kappa V \qquad \left[\frac{\partial}{\partial t}, \frac{\partial}{\partial s}\right] = -\kappa V \frac{\partial}{\partial s} \tag{A3}$$

$$\frac{\partial \mathcal{T}}{\partial t} = -\frac{\partial V}{\partial s}\mathcal{N} \qquad \frac{\partial \theta}{\partial t} = -\frac{\partial V}{\partial s}. \tag{A4}$$

A more detailed inquiry along these lines will be presented elsewhere [25], but here we give a brief description of each expression in turn. Since the metric W measures the length of an infinitesimal displacement on the boundary, the dilation of the boundary is represented in the first expression. This is obtained by computing $\partial_t(\mathcal{T}\cdot\mathcal{T})$. The commutation relation that follows utilizes the first result, and the next two results describe how $\mathcal{T}$, and the angle θ that defines it, rotate at each point of the curve by an amount which depends on the anisotropy of V. Note that $(\partial/\partial t)_s \neq (\partial/\partial t)_u$, so $[(\partial/\partial t)_u, (\partial/\partial u)_t] = 0$, and when combining (A3) and (A4) a non-local integro-differential curvature evolution equation is obtained (e.g. [4] (Gage and Hamilton) or [27]) which can be written

$$\left(\frac{\partial \kappa(s,t)}{\partial t}\right)_s = -V\kappa^2 + \frac{\partial^2 V}{\partial s^2} - \frac{\partial V}{\partial s}\int_0^s \kappa V \, ds'. \tag{A5}$$

When parametrizing the curve by θ rather than u or s the curvature evolution equation becomes strictly local [4] since $(\partial/\partial t)_\theta = (\partial/\partial t)_u - (\partial\theta/\partial t)\partial/\partial\theta \equiv \partial/\partial\tau$:

$$\frac{\partial \kappa}{\partial \tau} = -\kappa^2 \tilde{V} \tag{A6}$$

where $\tilde{V} \equiv (V + V'')$, and the primes denote $\partial/\partial\theta$. The variable τ is defined above, and one should keep in mind that it is the relevant time variable when thinking about local curvature evolution with κ parametrized by θ. Note the contrast between the curvature decay behaviour in (8) and the weaker curvature decay behaviour in the case $V = c\kappa$, c = constant; the 'curve-shortening equation'. We find a different exponent for the solution of this equation with a circle of initial curvature κ_i having curvature decay $\kappa = (\kappa_i/(1 + c\kappa_i t))^{1/2}$.

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