# Shocks Preempt Continuous Curvature Divergence in Interface Motion

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The dichotomy between two approaches to interface motion is illustrated in the context of two-dimensional crystal growth. Analyzing singularity formation based on the curvature of the interface predicts a continuous divergence of curvature in contrast to the discrete loss of orientations predicted when the evolution is described by an equation for the two-vector of the interface. We prove that the formation of a shock in the latter approach preempts continuous curvature divergence predicted in the former approach. The results are broadly applicable to kinematic interface motion problems, and we connect them with experiments reported by Maruyama *et al.* [Phys. Rev. Lett. **85**, 2545 (2000)].

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An understanding of the motion of interfaces constitutes a broad enterprise in physical and mathematical science; in the former case practitioners are often motivated by a particular setting, such as pattern formation in condensed matter systems, and in the latter case, a principal goal deals with the development of methodologies that apply in many settings. Although an interface may separate, for example, two immiscible fluids, phases, or magnetic states of a single phase, it is predicting the space-time evolution of that interface that captures interest. For example, in a Hele-Shaw cell, a flow drives the interface separating two immiscible fluids, and in crystal growth, disequilibrium drives a solidification front, but possible topological changes in the interface, in particular the formation of finite time singularities, are central to the dynamics of these and other systems (e.g., [1,2]). Here, we describe several basic features of interface motion during crystal growth in which a dual description of singularity formation leads to a paradox which we resolve using mathematical proof. The relevance of the principal results may span many interface motion problems.

A broadly useful illustration of interface motion arises in the context of geometric models for the evolution of a two-dimensional phase boundary wherein the local normal growth velocity does not depend on curvature and is only a function of the local orientation of the surface normal for a given thermodynamic growth drive [3]. Two approaches, one based on the global shape dynamics of the two-dimensional curve, the other describing the local curvature evolution, have been suggested [3]. While shocks are associated with the first approach, a continuously divergent curvature is a dramatic aspect of the second. The global shape dynamics is determined by the properties of the solutions to the evolution equation

$$\frac{\partial \vec{C}}{\partial t} = -V\vec{N}, \tag{1}$$

where $\vec{C} = \vec{C}(u,t)$ is an evolving plane curve parametrized by a variable $u$, $\vec{N}$ is the (inward pointing) unit normal vector, and $V(\theta, \Delta\mu)$ is the normal growth velocity. The angle between the positive $x$ axis and the unit tangent vector $\vec{T}$ is defined by $\theta$, and the (constant) thermodynamic growth drive $\Delta\mu$ is the departure of the chemical potential of the solid phase from that at bulk coexistence.

Exact solutions for this type of evolution equation can be expressed in terms of characteristics which represent straight rays along which the orientation of the normal is preserved [4]. The characteristic for a given orientation $\theta$ is given by [5]

$$\vec{r}(\theta,t) = \vec{r}_0(\theta) + [-V(\theta)\vec{N} + V'(\theta)\vec{T}]t\,. \tag{2}$$

In contrast, if we parametrize Eq. (1) by the angle $\theta$, we obtain for the evolution of curvature $\kappa$ along the trajectory of the location on the boundary with fixed orientation of the normal

$$\kappa(\theta,t) = \frac{\kappa_i(\theta)}{1 + \tilde{V}(\theta)\kappa_i(\theta)t}\,, \tag{3}$$

where $\kappa_i(\theta)$ is the curvature at the location on the initial seed crystal's boundary with orientation $\theta$, $\tilde{V} = V + V''$, and the primes denote differentiation with respect to $\theta$ [3,6]. One observes that the curvature decreases with time for all orientations with $\tilde{V} > 0$. The curvature grows continuously and diverges at finite time for all orientations with $\tilde{V} < 0$, and is stationary at the zeros of $\tilde{V}$.

Growing shapes resulting from Eqs. (1) and (3) have been analyzed in detail [3,4,7] for various functional forms of the growth function $V(\theta)$. The analysis in [3] predicted that for a general class of $V(\theta)$ the growth shape contains areas of decreasing curvature both at the roughest and vicinal orientations. The region between these flattening areas grows with increasing curvature and develops a corner that eventually absorbs all rough orientations. The prediction has since been confirmed by experiment [6].

We describe the contrast in these approaches by focusing on the problem of diverging curvature. Previously, numerical evidence led to a conjecture that curvature divergence is preempted by the formation of a shock [3]. According to Eq. (3) the divergence of curvature is a continuous limiting

  

process, and curvature tends to infinity on both sides of the orientation for which curvature blows up. On the contrary, according to Eq. (2), the orientation of the normal experiences a jump at the shock, and curvature is described by a delta function at $\theta = \theta_{\text{shock}}$, but it is well defined and bounded everywhere else. We outline the proof of the above conjecture thereby resolving this contradiction.

A shock is initiated when two characteristics intersect. Each member of an intersecting pair of characteristics corresponds to a certain orientation; we denote the two orientations corresponding to a generic intersecting pair by $\theta_1$ and $\theta_2$. Let $t_0$ be the time when a shock is initiated. We now think of $\theta_1$ and $\theta_2$ as functions of time defined by the following: for each value of $t > t_0$, let $\theta_1$ and $\theta_2$ be the orientations for which the corresponding characteristics intersect at time $t$. We write the intersection of characteristics as

$$\vec{r}(\theta_1(t), t) = \vec{r}(\theta_2(t), t). \tag{4}$$

Differentiating Eq. (4), applying Eq. (2) and the Frenet equations, and denoting $\kappa_i^{(1)} = \kappa_i(\theta_1)$ and $\kappa_i^{(2)} = \kappa_i(\theta_2)$, we obtain the following system of ordinary differential equations for $\theta_1(t)$ and $\theta_2(t)$ [5]:

$$\frac{1}{\kappa_i^{(1)}} \frac{d\theta_1}{dt}(1 + \tilde{V}_1 \kappa_i^{(1)} t)\vec{T}_1 - \frac{1}{\kappa_i^{(2)}} \frac{d\theta_2}{dt}(1 + \tilde{V}_2 \kappa_i^{(2)} t)\vec{T}_2 = \frac{1}{t}[\vec{r}_0(\theta_1) - \vec{r}_0(\theta_2)]. \tag{5}$$

A shock is initiated at time $t_0$ with the termination of a single orientation $\theta_0$. At any $t > t_0$, two characteristics, one with $\theta < \theta_0$, the other with $\theta > \theta_0$, intersect. Then, the initial conditions applied at $t_0$ read

$$\theta_1|_{t=t_0} = \theta_0, \quad \left.\frac{d\theta_1}{dt}\right|_{t=t_0} > 0;$$

$$\theta_2|_{t=t_0} = \theta_0, \left.\frac{d\theta_2}{dt}\right|_{t=t_0} < 0. \tag{6}$$

Equation (5) can satisfy conditions (6) only if $t_0 = -[\kappa_i(\theta_0)\tilde{V}(\theta_0)]^{-1}$, and a shock is initiated at the orientation $\theta_0$ where $\tilde{V}$ is minimum. According to Eq. (3), $t_0$ is also the minimum curvature blowup time.

Assume that the curvature blowup time $t_b$ for an orientation $\theta_2 < \theta_0$ is smaller than the time $t_2$ when the characteristic for this orientation hits the shock. Clearly, $\tilde{V}(\theta_2) \equiv \tilde{V}_2 < 0$, and Eq. (3) tells us that $1 + \tilde{V}_2 \kappa_i^{(2)} t_b = 0$, and $t_2 > t_b$, from which we conclude that $1 + \tilde{V}_2 \kappa_i^{(2)} t_2 < 0$. Hence, at time $t_2$ we can write Eq. (5) in the following form:

$$\vec{r}_0(\theta_1) - \vec{r}_0(\theta_2) = a\vec{T}_1 + b\vec{T}_2, \tag{7}$$

where $\vec{T}_1$ corresponds to the orientation $\theta_1$ whose characteristic hits the shock at the same time $t_2$. Here the coefficient $b$ is

$$b = -\frac{1}{\kappa_i^{(2)}} \left.\frac{d\theta_2}{dt}\right|_{t=t_2} (1 + \tilde{V}_2 \kappa_i^{(2)} t_2) < 0, \tag{8}$$

since $\theta_2(t)$ is a monotonically decreasing function, and $a$ has a similar form in terms of $\theta_1$.

The crystals we are interested in have at least fourfold symmetry. Hence, we may restrict our demonstration to orientations such that $|\theta_1(t) - \theta_2(t)| < \pi/2$. Then, for any convex initial curve, the vector $\vec{r}_0(\theta_1) - \vec{r}_0(\theta_2)$ described by Eq. (7) can be represented only as a linear combination of vectors $\vec{T}_1$ and $\vec{T}_2$ if both $a$ and $b$ are positive (see Fig. 1). Thus, because $b < 0$, the assumption $t_b < t_2$ leads to a contradiction. Analogously, this contradiction would have arisen if we had assumed that the blowup time for an orientation $\theta_1$ less than $\theta_0$ is smaller than the shock intersection time. Therefore, the orientations terminate at the shock before any possible blowup of curvature.

Now we develop a simple model of $V(\theta, \Delta\mu)$ that captures all the features described above as well as qualitatively reproduces experimental observations [6]. We again consider fourfold crystallographic symmetry, even though minor modifications to the model lead to similar results for crystals with other types of symmetry. In particular, we define a local normal velocity $V(\theta, \Delta\mu)$ that: (i) is periodic in $\pi/2$ and preserves the fourfold symmetry of the surface, (ii) has a nonzero derivative at $\theta = 0$, allowing the facets to spread, (iii) possesses a negative $\tilde{V}$ at vicinal orientations and, possibly, positive $\tilde{V}$ at the roughest orientations, and (iv) describes activated growth at the facets. Because of symmetry and crystal structure the growth velocity has a minimum at facet orientations. According to

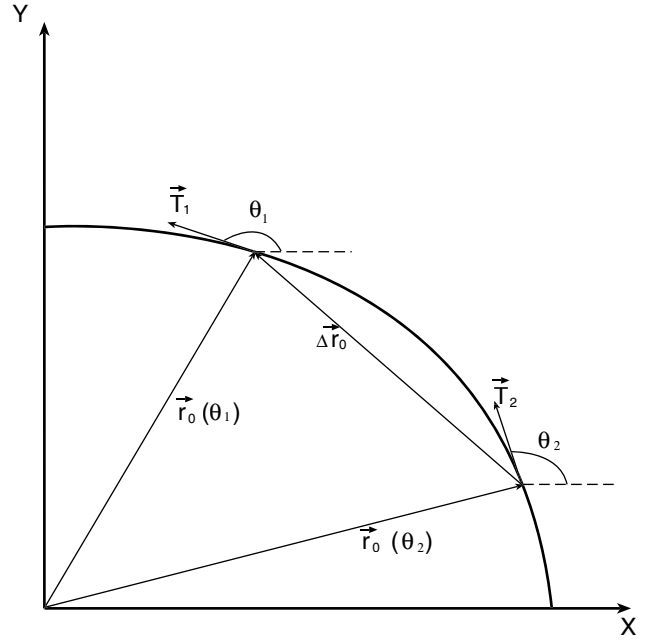


FIG. 1. Convex shape and two orientations on it. Since the shape is convex, $\Delta\vec{r}_0$ can be represented only as a linear combination $a\vec{T}_1 + b\vec{T}_2$ if both $a$ and $b$ are positive.

Eq. (2), if $V'(0) = 0$, facets move only perpendicular to themselves. If, on the other hand, $V(\theta)$ has a cusp at singular orientations, characteristics for $\theta = 0$ have a tangential component, which implies that the facet motion has a component parallel to the facet, and facets spread. It is possible to show [4,5] that the geometric problem described by Eq. (1), with a cusped $V(\theta)$, has a unique solution that involves a fan of characteristics emanating from the edge of the facet. Property (iii) implies that a corner forms in finite time at vicinal orientations, and possibly that the roughest orientations grow with decreasing curvature.

The simplest form of $V(\theta, \Delta\mu)$ possessing the above properties is [3]

$$V(\theta, \Delta\mu) = V_f(\Delta\mu)\xi(\theta) + V_r(\theta, \Delta\mu). \quad (9)$$

Here $V_f(\Delta\mu)$ is the normal growth rate at facet orientations

$$V_f(\Delta\mu) = c_f g(\Delta\mu) \exp\left(-\frac{\pi\sigma^2}{kT\Delta\mu}\right), \quad (10)$$

whereas for nonsingular orientations we express the linear response to the growth drive as

$$V_r(\theta, \Delta\mu) = c_r \Delta\mu (a|\sin 2\theta| - b \sin^2 2\theta). \quad (11)$$

In the expressions above $\sigma$ is the free energy of a critical nucleus on the facet (e.g., [8]), $T$ is the temperature, and $\xi(\theta)$ is a smooth function periodic in $\pi/4$, with the properties $\xi(0) = 1$ and $\xi(\pi/4) = 0$. This model departs from the form of $V(\theta, \Delta\mu)$ suggested earlier [3] in that it incorporates a cusp at singular orientations.

At fixed $\Delta\mu$ and low temperatures nucleation at facets is slow and hence $V(\theta) \approx V_r$,

$$\tilde{V} = -3a \sin 2\theta - b(\sin^2 2\theta + 8 \cos 4\theta), \quad (12)$$

and

$$V(0) = 0, \quad V'(0) = 2a, \quad \tilde{V}(0) = -8b,$$
$$\tilde{V}(\pi/4) = 7b - 3a.$$

Since $\tilde{V}(0) < 0$, the curvature at vicinal orientations grows with time. If, however, $a < 7/3b$, the roughest orientations evolve with *decreasing* curvature. We also find that $V(\theta)$ has extrema at $\theta = \pi/4$ and $\theta = (1/2)\sin^{-1}(a/2b)$. If $a < 2b$, $V(\theta)$ has a minimum at $\theta = \pi/4$ which can possibly be ascribed to the effect of a diffusion flux towards singular orientations [3,9]. For $a > 2b$, on the other hand, $V(\theta)$ grows monotonically with $\theta$ and is maximum at $\pi/4$. Thus, models with $2b < a < 7/3b$ describe a physical situation wherein formation and expansion of facets is accompanied by decreasing curvature at rough orientations. This occurs even though the proximity of a facet may not introduce a critical change to the normal growth velocity at vicinal orientations which maintain a maximal velocity where the step density is the highest. From Eq. (12) we also find that $\tilde{V}$ has a minimum at $\theta_0 = (1/2)\sin^{-1}(3a/31b)$. For $2b < a < 7/3b$, $\theta_0 \sim 0.1$, so that the shock is initiated in the immediate vicinity of the facet. It is easy to see that if $t_0$ is the time of corner formation, the facet collides with a shock at $t \sim 1.1t_0$, that is, almost immediately after shock initiation; this is exactly the situation observed in [6].

We note here that Eq. (9) is consistent with the general conclusions of the layer-by-layer surface growth described by the motion of the steps [10,11]. According to the theory, the step velocity $v_s$ is a monotonically increasing function of the terrace width; in other words, $v_s$ is a monotonically decreasing function of $\theta$. Recalling that $v_s(\theta) = V(\theta)/\sin\theta$, and analyzing $v_s(\theta)$ with $V(\theta)$ from Eq. (11), we find that for $2b < a < 7/3b$, $v_s(\theta)$ is indeed a decreasing function of $\theta$.

Next we consider the applicability of geometric models to crystal growth from the melt wherein some surface orientations are below their roughening temperature. The rate of growth from a melt is limited by one of the two processes: removal of latent heat of fusion via thermal diffusion through the bulk of the phases (diffusion regime), and surface attachment kinetics (kinetic regime), and the relative importance of these two regimes is determined by a dimensionless parameter $\delta = \beta^T T_Q R/a_l$ (see, e.g., [11,12]). Here $\beta^T$ is a kinetic coefficient for attachment at steps, $a_l$ is a thermal diffusivity, $R$ is a crystal size that determines a typical length scale of the thermal field, and $T_Q = L/c$ is the ratio of the latent heat of solidification to heat capacity of melt. Small values of the parameter $\delta \ll 1$ indicate the kinetic regime, while for $\delta \gg 1$ the crystal grows in the diffusion regime.

We base our estimates on the recent experiments [6,13] conducted on carbon tetrachloride, $CCl_4$, and ice crystals, even though the resulting conclusions are quite general and should be applicable to a wide range of systems. A typical value of the kinetic coefficient both for carbon tetrachloride and ice is $\beta^T > 10^{-2}$ m/s K. For $CCl_4$, $a_l \sim 10^{-7}$ m$^2$/s, and $T_Q \sim 200$ K, so that $\delta$ is small for submicron-size crystals. Since the size of the crystals studied in [6] is of the order of 0.1–1 mm, $\delta$ is large, and growth is limited by thermal diffusion. The characteristic interface velocity associated with it is given by $V_d \sim a_l \Delta T/RT_Q$, where $\Delta T$ is the supercooling far away from the surface. We would then expect $V_d \sim 10^{-6} - 10^{-5}$ m/s, which indeed *is* the velocity measured in [6], indicating purely diffusion limited growth. However, the authors also showed that the data on the evolution of the interface can be explained quantitatively by the geometric kinematic theory, Eq. (1). In particular, while the interface velocity at the roughest orientation $\theta = \pi/4$ stays constant, the curvature at this orientation decreases linearly with time, and the surface undergoes significant transformations including the formation and propagation of corners — features predicted by the theory. Paradoxically, in the diffusion regime the growth velocity is inversely proportional to the size of the crystal, hence any normal growth of the surface should result in a decreasing velocity.

To resolve the paradox, we notice that both the theory and the observations deal with initial crystal shapes

containing orientations below their roughening temperatures, i.e., partially faceted. On a microscopic scale, vicinal and rough surfaces can be seen as molecularly smooth terraces separated by steps of monomolecular layer height [10]. At low growth drives, in the absence of nucleation at facets, as in [6], growth of surfaces below their roughening temperature is described by the motion of steps. Steps at vicinal orientations, where their separation is large, are known to move much faster than steps at rough orientations [11]. Nevertheless, the normal growth velocity is typically a maximum at the roughest orientations which have a maximal step density. It is the *normal growth velocity* at rough orientations that determines how far the interface moves in time $t$, and therefore, to what extent the growth drive $\Delta\mu$, and hence the interface velocity itself, are modified by this surface dynamics. On the other hand, the *shape* of the interface may change kinematically on a much shorter time scale: the velocity of the steps at vicinal orientations immediately adjacent to the facets (extremely small $\theta$), can be orders of magnitude higher than that of the steps at rough orientations. Then, facets and vicinals may spread at the expense of rough orientations, leading to noticeable transformations of the interface long before the latter moves perpendicular to itself a distance comparable to the size of the crystal. The model we presented above clearly demonstrates such behavior; $|\tilde{V}(\theta_0)| \approx 9V(\pi/4)$, and assuming the curvature is the same everywhere on the curved part of the initial interface, this implies that $V(\pi/4)t_0\kappa_i \ll 1$. The latter inequality indicates that the *size* of the crystal ($\sim\kappa_i^{-1}$) does not change much while the *shape* undergoes significant transformations. Therefore, the motion of the interface does not modify $\Delta\mu$ at the interface, and a geometric model is applicable at the early stages of interface evolution, $t < t_0$, and additionally for some period of time $t > t_0$.

As a final point we emphasize that the appearance of a corner results in the formation of a dynamic facet; a region of constant step density [6]. Under large growth drives, the dynamic facet consequently transformed into a concave region. However, it has been proved [5] that local geometric models preserve the convexity of the interface, and hence the observed concavities must be due to the diffusion dynamics of the surface rather than its kinematics. Therefore, while the early stages of evolution of such a shape can be described by a geometric model, at later times the thermal field at the surface becomes modified by the transforming interface. We thus conclude that while the velocity of the interface is determined by thermal diffusion, the shape of the interface of crystals below their surface roughening transition may undergo significant changes while the growth drive itself is not changed by diffusion. These shape transitions originate in the anisotropy of interfacial motion — lateral motion of steps can be dramatically more rapid than the fastest normal motion.

In summary, we have shown that apparently dual approaches to interface motion lead to a contradictory description of corner formation. The approach based on the evolution of the curvature of the interface predicts a continuous divergence of curvature in contrast to the discrete loss of orientations predicted when the evolution is described by an equation for the two-vector of the interface. We have proved that it is the formation of a shock in the latter approach that preempts the curvature divergence predicted in the former approach, and we have developed a geometric model that describes recent experiments.

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