Shocks and Curvature Dynamics: A Test of Global Kinetic Faceting in Crystals

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(Received 8 May 2000)

We investigate the microscopic mechanisms underlying the dynamical faceting of crystals. Partially faceted crystal shapes of CCl_4 are formed from a melt contained in a Bridgman apparatus and pressure is used to control growth which is observed using optical microscopy. In contrast to predictions of models in which the local interfacial motion is greatest where the step density is the highest, the loss of rough orientations is observed to occur via a local decrease in curvature which results in the formation of discontinuities—shocks—in the surface of the growth forms, a feature predicted by a recent theory of kinetic faceting.

PACS numbers: 81.10.Aj, 81.30.Fb, 82.65.Dp

The study and manipulation of crystallization forms have captured the interest of artists, engineers and scientists since at least the Bronze Age [1]. Nevertheless, fundamental tests of the tenets of the theory of crystal growth constitute a central and active area of contemporary condensed matter science [2]. Crystal growth provides a setting in which microscopic phenomena control macroscopic shapes, and a natural testing ground for pattern formation in driven systems [3,4]. In the context of the growth of semiconductors, microscopic models can often be tested using the ultrahigh-vacuum probes of surface science [5]. However, many growth forms found in the natural environment and in metallurgical contexts evolve from the melt phase and involve length scales that span many orders of magnitude. The paucity of tests of theories of relevance in this latter situation motivates the present study.

The qualitative picture of the growth of partially faceted crystals has a rich history originating in the work of Wulff [6], Frank [7], and Chernov [8]. Weakly driven growth forms evolving from partially faceted equilibrium shapes become more faceted during growth [9]. Qualitatively one can argue that this is principally because the accretion of material normal to facets is an activated process whereas no nucleation barrier exists for rough orientations. Hence, for a spatially uniform growth drive, the rough orientations grow more rapidly leaving facets to dominate the shape. Although this much is known, the general mechanisms underlying the process have remained obscure. Here we present observations that test the most robust features of the process. In contrast to predictions of models in which the local interfacial motion is greatest where the step density is the highest, we observe that the loss of rough orientations occurs via a local decrease in curvature which results in the formation of discontinuities—shocks—in the surface of the growth forms, a feature predicted by a recent theory of kinetic faceting [10].

Precisely *how* the rough orientations are lost depends on the microscopic details influencing the attachment of additional molecules. Intuitive models, in which the local normal motion is maximal at locations in which the step density is the highest, predict that the rough orientations grow out of existence with *increasing curvature*. In contrast, models including effects such as surface diffusion find that the growth rate is not a maximum where the step density is the highest, and the prediction is that the rough orientations grow out of existence with *decreasing curvature*. These two extremely different qualitative predictions provide the rostrum for the experimental test described here.

Growth theories generally treat a single interfacial state, faceted or rough, or the transition between them, but on a single closed surface both types of surface structure can coexist. Typically, when the motion of the interface is limited by local interfacial processes it can be modeled as *geometric* in the sense that 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 long-range diffusion in the bulk (see, e.g., the review in Ref. [11]). Some of the many situations wherein such a model is applicable include the early stages of snowflake growth, when the mean free path in the vapor is larger than the characteristic size of the crystal, the growth of electronic materials via molecular beam epitaxy, the growth of ferromagnetic or ferroelectric domain walls, grain growth, and stress-driven-zone migration. Here we focus on the weakly driven growth of a crystal containing both facets and rough regions which is a situation linking the disparate interfacial kinetic processes associated with these distinct types of surface to the global driving force.

A fourfold symmetric crystal is well suited for comparison with theory, and hence as an experimental system we choose carbon tetrachloride (CCl_4) grown from the melt under pressure. Owing to a rhombohedral unit cell with 90° in the lattice angle [12], CCl_4 grows in a cubic form [13,14]. Moreover, growth from the melt at fixed temperature and at moderately high pressures (<1000 bars)

enables us to accurately control parameters such as initial curvature and growth drive [15]. Pressure transmits to the sample quickly and uniformly under hydrostatic conditions. Hence, through simultaneous pressure manipulation and visual inspection, we can produce a partially faceted crystal with some curvature in rough orientations and then grow it at very small growth drives. This offers an ideal test of geometric models.

At a constant temperature of 5 °C, liquid CCl_4 sealed in an elastic fluorocarbon tube is pressurized by manual operation of a hand pump. The liquid freezes spontaneously at approximately 1000 bars into a polycrystalline solid. A single crystal is obtained by reducing the pressure below an equilibrium value (~750 bars) and melting the polycrystal until only one crystallite remains. A cubic crystal can be made with continuous curvature between the facets and subsequently grown. Upon imposition of a small growth drive to such a partially faceted crystal, we observe the essential tenets of the theory of global kinetic faceting as shown in Fig. 1. First, discontinuities in the surface slope form abruptly, thereby separating rough orientations from vicinal and faceted orientations. Such discontinuities are associated with the formation of shocks in the global curve dynamics [10]. Second, rough regions grow out of existence with a *decreasing* curvature; the facets are not mobile and eventually dominate the overall shape. We now show that neither of these features is predicted by models

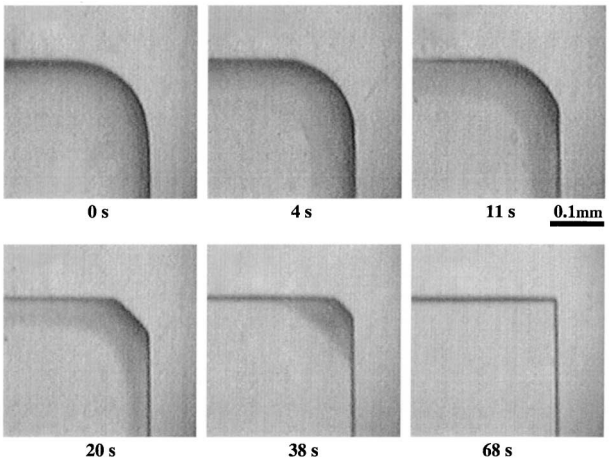

FIG. 1. Growth sequence of a CCl_4 crystal in a high pressure melt. The initial shape contains facets and rough regions and we display the upper right hand quadrant of a cubic crystal. The growth drive (pressure deviation $\Delta P = 1$ bar) is applied at 0 s when the shape is equilibrated at $T = 5.33$ °C and $P_m = 754$ bars; $\Delta\mu$ is proportional to ΔP and $\Delta P = 1$ bar corresponds to $\Delta\mu/kT = 1.4 \times 10^{-4}$ [14,15]. Note the following: (i) Discontinuities in the surface slope form abruptly after 4 s and are more pronounced at 11 s, thereby separating rough orientations from vicinal and faceted orientations. Such discontinuities are associated with the formation of shocks in the global curve dynamics [10]. (ii) The rough orientations grow out of existence with *decreasing* curvature, while facets do not grow at all. The three-dimensional features are clearer at later stages.

in which regions of high local curvature, where the surface density of steps is highest, grow the fastest.

The experimentally realizable limits are distinguished in terms of the magnitude of the growth drive $\Delta\mu$, the chemical potential difference between a molecule in the parent phase and that on the solid. The first regime occurs for extremely small $\Delta\mu$, wherein the accretion of mass is much slower than all of the available relaxation processes, so that the crystal surface is indistinguishable from the equilibrium crystal shape. This "thermodynamically slow" or "shape preserving" regime has been observed at temperatures above, below, and very near the roughening transition of the prism facet of ice growing from water (Fig. 3 of Ref. [15]) and can be described via a continuous expansion of the Wulff shape [16]. (The result is also trivially correct for isotropic surface free energy, a crystal surface everywhere above its roughening transition, or a liquid drop. One then simply expands a sphere.) In the second regime $\Delta\mu$ is larger, but nonetheless smaller than the activation barrier for two-dimensional nucleation on the facets $\Delta\mu_c$. The facets are then pinned and the rough orientations accrete mass to take the Wulff shape of an "equilibrium" crystal of increasing size [10,16]. Ultimately the rough orientations grow themselves out of existence leaving a fully faceted growth form behind. The third regime is attained again by increasing $\Delta\mu$ to a value that is above $\Delta\mu_c$ but below the threshold necessary to induce kinetic roughening on the facets, $\Delta\mu_{kr}$, where we therefore expect slow normal growth by nucleation and spreading of monolayers.

We concentrate on two dimensions, which is relevant to the growth of nuclei on a facet [17,18], the growth of highly anisotropic materials such as ice [19,20], the evolution of monolayer surfactant films [21,22], or the growth of axisymmetric three-dimensional crystals as described here. Our geometric model is built around an equation for the local normal velocity $V(\theta, \Delta\mu)$ that explicitly accounts for activated growth on facets, nonactivated growth in rough regions, and their modification in the vicinal orientations in a continuous manner [10]. $V(\theta, \Delta\mu)$ depends on a spatially uniform driving force, $\Delta\mu$, and the orientation of the surface with respect to the underlying lattice θ as follows:

$$V(\theta, \Delta\mu) = V_f(\Delta\mu)\xi(\theta) + V_g(\theta, \Delta\mu)[1 - \xi(\theta)]. \tag{1}$$

V_f, V_g, and ξ are defined as $V_f(\Delta\mu) = f(\Delta\mu) \times \exp(\frac{-\pi\sigma^2}{kT\Delta\mu})$, $V_g(\theta, \Delta\mu) = g\Delta\mu[1 + \cos^p(\frac{n\theta}{2})]$, and $\xi(\theta) = \cos^m(\frac{n\theta}{2})$, where V_f and V_g are the growth laws on facets and rounded orientations, respectively, σ is the free energy of a critical nucleus on the facet, and ξ determines the nature of the transition between facetlike and rough growth. The mobility coefficients f, g are influenced by the molecular attachment kinetics, and the growth rate in vicinal regions has contributions from both

the birth and spreading of supercritical islands on terraces *and* molecular attachment directly to kinks in moving steps. The combined influence of these two effects on the normal growth rate is embodied in the second term of $V_g(\theta, \Delta\mu)$. An essential qualitative point is that, for a given $\Delta\mu$, $V_f \ll V_g$. The equation is valid for n-fold symmetry, and m and p are even integers such that $m \geq p$. The differential geometry of curves in the plane [4,10,18,19] allows us to express the evolution of the curvature κ of the surface as

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

where $\tilde{V} \equiv (V + \frac{\partial^2 V}{\partial \theta^2})$ is the "velocity stiffness" in *analogy* with surface stiffness, and $\frac{\partial}{\partial \tau}$ is taken at constant θ. The curvature evolution at each point of the interface with initial curvature κ_i follows immediately as

$$\kappa = \frac{\kappa_i}{1 + \kappa_i \tilde{V} \tau}\,. \tag{3}$$

For orientations between the facets, for cubic symmetry ($n = 4$) and $m = p = 2$, or $m = 4$ and $p = 2$, we have $\tilde{V} > 0$, so it is predicted that the curvature will *decrease* monotonically in time from the initial value at that orientation. This decrease is due to a tendency toward a constant surface density of steps; in vicinal regions surface diffusion on the terraces enhances motion normal to the interface, increases the density of sites for attachment, and drives the region toward a more constant step density. In contrast, models in which regions with the highest surface density of steps grow the fastest have $\tilde{V} < 0$ and this is inconsistent with the experiments as seen visually in Fig. 1 and as we now show quantitatively.

The relation between V and $\Delta\mu$ is measured for facets and rounded orientations (at $\theta = \pi/4$) and is shown in Fig. 2. We observe that the rough orientations grow linearly with $\Delta\mu$, whereas activated growth is observed on facets, which supports the applicability of the theoretical models described above to the CCl_4 system. Because the rough orientations rapidly grow out of existence, observations of curvature evolution are made at the smallest growth drives. The radius of curvature of the curved surface between the facets is measured directly as a function of time. This is the curvature averaged about the $\theta = \pi/4$ orientation rather than the local value. The results are plotted in terms of curvature in Fig. 3 for different initial curvatures and growth drives. The accuracy in curvature measurements is approximately 10%. The curvature *decreases* linearly with time and the rate at which it does so increases with the growth drive as predicted by Eq. (3). We therefore find that $\tilde{V} > 0$ at $\theta = \pi/4$, and we can estimate the value by assuming that $\tilde{V}$ is the same order of magnitude as $V(\approx 1\ \mu\mathrm{m/s})$. For experimental values of $\kappa_i \approx 10^4\ \mathrm{m}^{-1}$ and $\tau \approx 20$ s, $\kappa_i \tilde{V} \tau \approx 0.2$, allowing us to approximate Eq. (3) using the relation $\kappa \approx \kappa_i - \kappa_i^2 \tilde{V} \tau$. The fits for rate of curvature decrease $\kappa_i^2 \tilde{V}$, as displayed in Fig. 3, give the following estimates: $\tilde{V} = 3$–$4\ \mu\mathrm{m/s}$ at $\Delta\mu/kT = 1.4 \times 10^{-4}$ and $\tilde{V} = 5$–$9\ \mu\mathrm{m/s}$ at $\Delta\mu/kT = 2.8 \times 10^{-4}$.

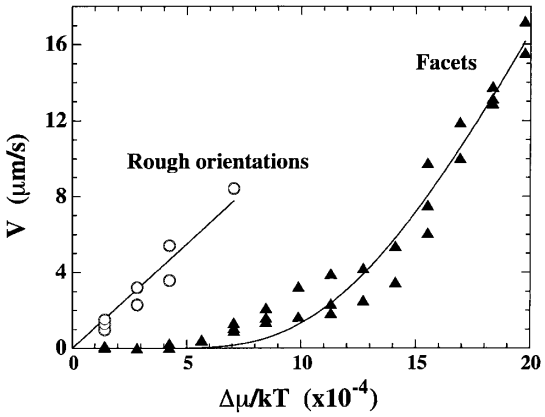

FIG. 2. V versus $\Delta\mu/kT$ for rough orientations at $\theta = \pi/4$ and facets. Fits are linear and exponential, respectively. For rough orientations V cannot be measured at larger $\Delta\mu$ due to rapid faceting.

The observations reported here display the macroscopic influence of the difference in microscopic crystal growth kinetics: the relaxation rate at rough orientations is negligible compared with that on the facets, and hence the latter spread to dominate the growth form. Confirmation of the principal features of the two-dimensional theory has been found and quantitative agreement with curvature evolution is excellent until very late times when the influence of faceting and dimensionality becomes important. The

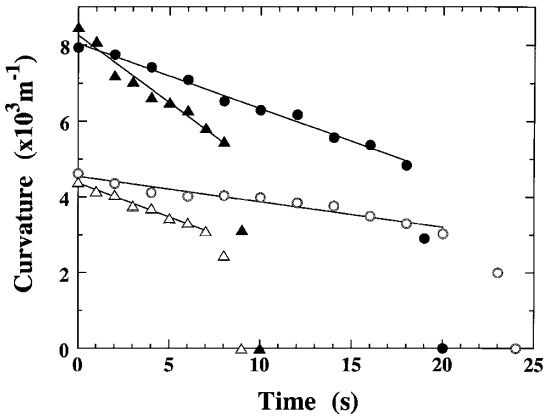

FIG. 3. Curvature evolution and fits for $\tilde{V}$ at two initial curvatures and two growth drives. Solid symbols are at $\kappa_i \approx 8 \times 10^3\ \mathrm{m}^{-1}$, $T = 5.33\,^{\circ}\mathrm{C}$, and $P_m = 754$ bars; open symbols are at $\kappa_i \approx 4 \times 10^3\ \mathrm{m}^{-1}$, $T = 5.08\,^{\circ}\mathrm{C}$, and $P_m = 749$ bars. Circles are at $\Delta\mu/kT = 1.4 \times 10^{-4}$ ($\Delta P = 1$ bar); triangles are at $\Delta\mu/kT = 2.8 \times 10^{-4}$ ($\Delta P = 2$ bars). Because the region of rough orientation between the discontinuties must shrink during the faceting process, the curvature eventually changes abruptly and the effects of dimensionality become important.

study forces us to examine the underlying assumptions of commonly accepted models and provides a framework for broad based testing of the kinetics of crystal growth in two and three dimensions.

Conversations with J. G. Dash and Y. Furukawa are gratefully acknowledged. W. C. Carter led us to Ref. [1] and A. Rempel provided comments on the manuscript. This work has been supported by NSF Grants No. INT97-25945, No. CHE99-80125, ONR Grant No. N00014-94-1-0120, and Grant-in-Aid No. 09640405 from Ministry of Education, Japan.

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