PHYSICAL REVIEW E VOLUME 48, NUMBER 4 OCTOBER 1993

Relation of growth and equilibrium crystal shapes

M. Elbaum
Department of Physics, Technion–Israel Institute of Technology, Haifa 32000, Israel

J.S. Wettlaufer
Applied Physics Laboratory HN-10, University of Washington, Seattle, Washington 98105

(Received 24 February 1993)

We consider the shape of a slowly growing single crystal, which in equilibrium contains both facets and rounded regions. In a restricted regime of growth drive, a simple modification of the surface-free-energy minimization relevant to equilibrium reproduces experimentally observed behavior during growth and evaporation in a homogeneous environment.

PACS number(s): 61.50.Jr, 61.50.Cj, 68.35.Md

The topic of crystal shapes has attracted much interest for its relevance to scientific and technical concerns, as well as esthetic ones. Progress has been made in two fields rather independently: equilibrium shapes, and growth forms. The connection between the two has received somewhat less attention than either one separately. A growth form must, on some time scale, relax to the equilibrium shape if the growth drive is removed, but the relevant times are usually very long. Recent experiments have demonstrated the possibility of observing crystals very close to equilibrium [1–5,21]. Here we present a simple construction that reproduces salient qualitative features of experimental observations. Rather than focusing on specific structures or materials, we use the model to develop intuition and to look for general rules governing crystal growth within certain limits.

In equilibrium the shape of a crystal is determined by minimization of the total surface free energy. The specific surface free energy of a crystalline solid is orientation-dependent, so that the total surface-free-energy integral must be expressed as

$$I_S = \int_S \gamma(\hat{\mathbf{n}}) dS' \ , \tag{1}$$

where $\gamma(\hat{\mathbf{n}})$ represents the surface free energy per unit area in the specified orientation of the surface normal vector $\hat{\mathbf{n}}$. For the case of an isotropic liquid drop this minimization is trivial, and yields a spherical shape. (We ignore effects of gravity here.) In general, the minimization of this integral at constant volume is achieved by Wulff's geometrical construction, a transform on the surface free energy itself [6]:

$$\hat{\mathbf{n}} \cdot \mathbf{r} = \lambda\gamma(\hat{\mathbf{n}}). \tag{2}$$

The crystal shape is determined by the inner envelope of a set of planes perpendicular to radial rays, intersecting a polar plot of $\gamma(\hat{\mathbf{n}})$. $\mathbf{r}$ defines a radial vector from the origin to the equilibrium crystal surface. The shapes generated by this construction are geometrically similar at any size, determined by λ above.. Proofs that Wulff's construction does indeed minimize Eq. (1) have been given, among others, by Dinghas [7], Herring [8], and Landau [9]. Qualitatively the shapes of anisotropic crystals in equilibrium may be fully faceted, fully rounded, or may consist of faceted (molecularly smooth) and rounded (molecularly rough) regions. A simple two-dimensional example of the latter is shown in Fig. 1(a).

A finite single crystal may also be characterized in terms of the Gibbs-Thomson-Herring contribution to the thermodynamic potentials appropriate to the bulk equilibrium phases [10]. For the curved phase boundaries on the crystal surface, the relevant shift in chemical potential involves products of the surface stiffness and the local curvature:

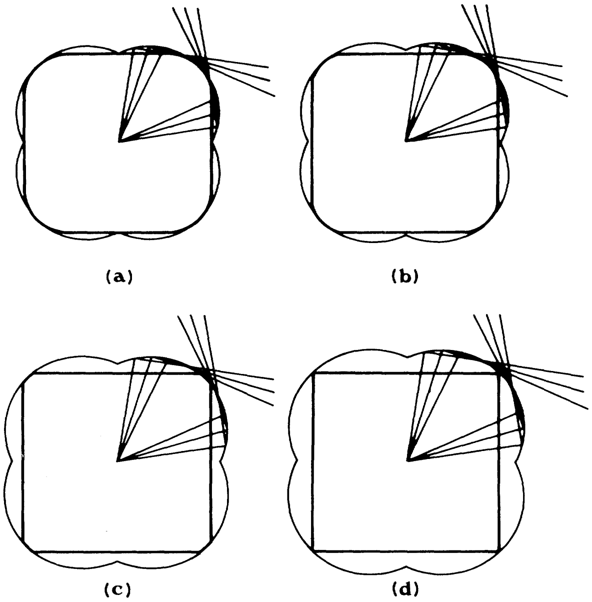

FIG. 1. (a) The equilibrium shape (in bold lines) is formed in the Wulff construction by the interior envelope of the set of perpendiculars to radial rays intersecting a polar plot of $\gamma(\hat{\mathbf{n}})$. (b),(c) The crystal shape under a small departure from equilibrium reflects the large disparity in relaxation rates between facets and rounded regions. The former remain stationary, while the latter take a shape appropriate to an *equilibrium* crystal of increasing size. (d) Eventually, only the facets remain.

$$\Delta\mu = \mu_F - \mu_{S^*} = v\left(\gamma(\hat{\mathbf{n}}) + \frac{\partial^2\gamma(\hat{\mathbf{n}})}{\partial\theta_1^2)}\right)\frac{\partial\phi_1}{\partial s} + v\left(\gamma(\hat{\mathbf{n}}) + \frac{\partial^2\gamma(\hat{\mathbf{n}})}{\partial\theta_2^2}\right)\frac{\partial\phi_2}{\partial s}, \qquad (3)$$

where v is the molecular volume, μ_F is the chemical potential of the bulk coexisting nutrient phase, which would equal that of the bulk solid of infinite size, and μ_{S^*} is the chemical potential of the actual crystal. Externally applied mechanical forces would add additional terms to the right-hand side above. Angles $\theta_{1,2}$ represent the directions of principal curvature, and $\partial\phi_{1,2}/\partial s$ the differential change in surface normal orientation over path length, i.e., the curvature in those same directions. Thus a curved region of crystal surface will be in equilibrium with the nutrient phase if the difference in their chemical potentials is equal to $\Delta\mu$ above. For facets such analysis is indeterminate, due to the nonanalytic nature of γ in those orientations.

For a liquid droplet, Eq. (3) reduces to the familiar Gibbs-Thomson effect that $\Delta\mu = 2v\gamma/R$, where γ is isotropic and R is the radius. Note that increasing size implies *decreasing* curvature on all regions of the liquid surface. For a finite crystal the solution of the minimization problem in Eqs. (1) and (2) requires that the scale parameter relate the size of the crystal to $\Delta\mu$ from above as $\lambda = 2v/\Delta\mu$. Thus a crystal of size characterized by λ is stable *in shape* only in the presence of the uniform positive chemical potential difference $\Delta\mu = \mu_F - \mu_{S^*}$ given in Eq. (3). As the size is inverse to the applied $\Delta\mu$, this represents a point of unstable equilibrium: a small excursion in $\Delta\mu$ will cause the crystal to shrink or grow without bound (assuming an infinite fluid reservoir). This is the source of the critical nucleation size for condensation of liquid drops, and the same principles apply to nucleation of solid grains from a fluid medium.

We now examine the possible crystal shapes during the process of growth into a pure, homogeneous nutrient phase. We distinguish three regimes: "thermodynamically slow," "weakly driven," and "strongly driven." In the first regime, the rate of accretion of material is much slower than all available diffusion and relaxation processes, so that in this limit the growth shape is indistinguishable from that in equilibrium. In the strongly driven regime, the mass accretion rate is so much faster than available relaxation processes that the eventual recovery of the equilibrium shape may be a matter of rhetorical concern only. Here we are concerned with the intermediate regime, where the crystal shape is not identical to that in equilibrium, but would relax to such in an experimentally observable time frame if the growth drive were removed.

We add to the equilibrium picture the familiar observation that the growth rate of facets along the surface normal is far smaller than the analogous rate on rounded surfaces [11]. The normal advancement of facets requires, in the absence of step-generating defects, the nucleation of two-dimensional islands of critical size. Rounded surfaces, by contrast, are molecularly rough in that steps are present on the equilibrium surface by geometric requirement. Burton, Cabrera, and Frank have shown that under small growth drives the normal growth rate of facets is a nonlinear function of the drive [12]. On rounded regions the growth rate is linearly related to the drive, with some orientation-dependent factor accounting for anisotropy.

The basis of our model is the following kinetic limit: in the "weakly driven" regime there exists a range of growth drives for which the facets remain stationary, while the rounded areas easily accommodate accreting material and take a shape appropriate to an *equilibrium* crystal of monotonically increasing size. Growth shapes are generated by expanding the polar surface-free-energy plot uniformly [increasing λ from Eq. (2)], and redrawing the perpendiculars construction, this time with the additional stipulation that the crystal-center to facet-center distance remain fixed. A full sequence is shown in Fig. 1. Note the spreading of the facets, and the change in character, from smooth to abrupt, of the joint between facets and rounded parts. These qualitative features have been observed on crystals of solid He growing into a superfluid [13], of ordinary water ice growing into pure water vapor [14], and of small metal crystals growing into metal vapor [15]. Furthermore, note that the rough sections of the surface take a decreasing curvature as growth progresses between the equilibrium and fully faceted shapes, in analogy with the growth of liquid droplets.

A sequence of shapes such as those in Fig. 1 may be generated from any proposed or measured equilibrium surface-free-energy function. The construction associates a sequence of shapes with a series of monotonically increasing volumes (areas in two dimensions); weakly driven growth beginning from a specific size in equilibrium should bring the crystal through that sequence, with the shapes labeled by the enclosed volumes. Further assumptions would be necessary to fix a time variable to the rate of change of the enclosed volume. In the simplest picture it is determined by the rate of extraction of latent heat from the system. The two major initial hypotheses may also be relaxed in a specific realization of the construction. These are (a) that the surface-free-energy function is unperturbed by the imposition of a growth drive, and (b) that the normal advancement rate of the facet is zero. Again, the incorporation of different rules is straightforward, but additional assumptions are required to suit specific situations.

Figure 2 presents a sequence of dissolution (e.g., evaporation or melting) forms generated according to the same rule as above: the first perturbation away from the thermodynamically slow regime is that the crystal approaches an equilibrium shape of ever-*shrinking* size. To this end, we fix the center-facet distance to be the same as in Fig. 1(a), and generate the dissolution forms by contracting the surface-free-energy plot uniformly, and redrawing the perpendiculars construction. The equilibrium facet is replaced by broad surfaces making very small angles with the facet orientation, in this case forming a shallow "rooftop" shape. The pitch gets steeper with progressing dissolution.

The asymmetry between growth and evaporation forms is perhaps the most striking feature of our con-

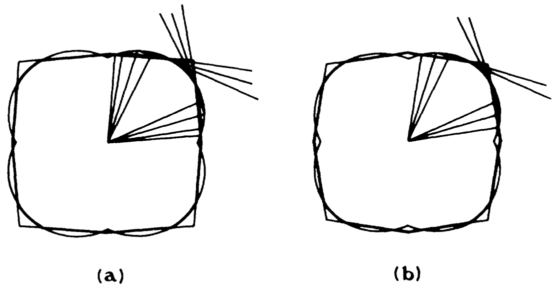
(a) (b)

FIG. 2. Evaporation shapes may be generated by the same construction. The shrinking crystal approaches the equilibrium shape of a progressively smaller crystal. In the figure the center-facet distance is held fixed while the polar plot of γ is reduced in size. Crystallographic facets are replaced by very broad flat areas of vicinal slope. Note that the evaporation shapes are not limited by kinetic faceting effects, as in Fig. 1(d).

struction. As growth forms are more familiar, we present in Fig. 3 monochromatic light images of an isolated H_2O ice crystal evaporating into a pure vapor environment. The orientation is such that the *a* axis points vertically out of the picture. Thin-film interference fringes are formed between top and bottom surfaces. Parallel surfaces would display a uniform grey level. Note the "rooftop" shape (facing trapezoids at the broad sides and triangles at the narrow ones). In real time the fringes drift toward the center of the crystal, while at the same time becoming more dense, indicating a steepening of the surface slope. The order of magnitude of the slopes is indicated by the change in crystal thickness from center to edge, about 1 μm, divided by half the crystal width, about 0.5 mm. Thus these images are in accord with the qualitative indications of Fig. 2. It must be noted, however, that the initial shape in Fig. 3(a) is itself a growth form. In equilibrium the facets cover only a small fraction of the total surface, and this observation would not have been possible.

Mechanistically, during growth the attachment of molecules occurs mainly at the steps which terminate flat terraces; thus the terrace edge advances. The process may continue until all terraces have reached the edges of the crystal and no more steps remain. During evaporation, the rounded regions provide an inexhaustible supply of steps from which molecules may detach far more easily than from the center of a terrace; thus the terrace edge recedes. The ratio of the rate with which steps leave the rounded regions to that with which they recede toward the center determines the slope of the rooftop sides. The rate at which steps arrive at the center determines the rate at which the surface recedes along the facet normal orientation. In a complete model for a specific material, this would have to be taken into account by allowing some (inward) normal motion in this direction.

We must emphasize that the *decreasing* curvature of rounded surfaces with growth is in conflict with intuition derived from the extension to properly faceted crystals of many normal velocity models appropriate to anisotropic growth shapes. For analytic γ the equilibrium crystal shape contains no true facets, though flat regions may appear in growth shapes due to anisotropies in growth rates. Many such models presume simply that regions where the surface density of steps is highest should grow fastest. Thus the flat facets should remain stationary, while the rounded regions grow toward corners with *increasing* local curvature. Local values of thermodynamic parameters (e.g., p, μ) shift in violation of Eq. (3), effectively restabilizing the growth shape against the nutrient phase of an initially higher chemical potential. This is in contradiction to accepted explanations of homogeneous nucleation, grain coarsening, and sintering, all of which depend on an unstable critical nucleation size. Furthermore, the facet edges, which become sharper and more visible in experimental observations, would become flatter and less distinct. On dissolution, the curvature of the remaining rough area at the corners increases in accord with the requirements of Eq. (3) and the instability argument presented for growth above.

In the case of analytic anisotropy in surface free energy [16], we wish to point out that polygonal growth shapes may be generated by decreasing curvature in the relatively slow-growing directions, rather than at corners. Villain has presented a phenomenological example of such a process [17]. Experimental examples include two-dimensional crystals, where the one-dimensional boundary is molecularly rough. The observations reported by

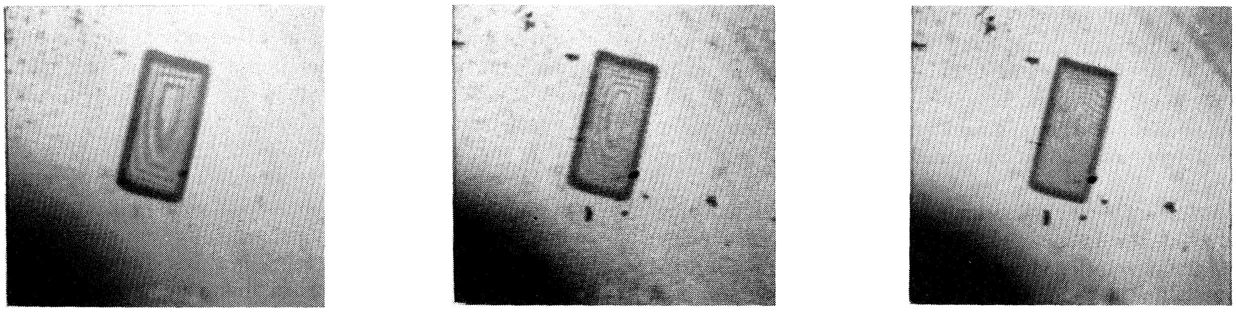

FIG. 3. Sequence of evaporation shapes of an isolated H_2O ice crystal in a pure vapor environment. The field of view is 1.0×1.0 mm. The height difference between adjacent fringes is 0.23 μm. Note the "rooftop" shape of the surface, with pitch steepening as evaporation progresses, in accord with Fig. 2. The experimental starting point is, however, a growth shape rather than equilibrium.

Flesselles, Magnasco, and Libhober [18] may be directly relevant here, though the diffusive background medium may also play an important role. The general field of geometric models of crystal growth has been reviewed recently by Taylor, Cahn, and Handwerker [20]. The present construction is geometric in that it does not depend on long-range diffusion inside the nutrient phase, and it treats specifically the case most challenging to full mathematical modeling, that of mixed faceted and rough surfaces.

A particularly intriguing possibility is raised by the final growth shape in Fig. 1. Note that with the facets held fixed the growth shape overall becomes less and less similar to equilibrium as growth progresses. The broad rounded areas grow, leaving a fully-faceted crystal on which there no longer remains any surface to easily accept accreting material. This is a reasonable lower bound for effects such as kinetic roughening of the facets themselves and the more extreme transition to dendritic behavior if growth takes place in a diffusive medium. In the latter case, our model suggests that the initial stages of dendritic growth are dominated by an extended equilibrium property of the solid itself, and not by the mixing and competition of capillary lengths with the diffusive scale properties of the background medium. Thus the initial symmetry displayed by kinetically dominated growth forms is set by microscopic dynamics that exclude large-scale gradients. In this regard we refer the reader to the photographs of snowflakes in Ref. [19], and note that at the center of each snowflake is a small, fully faceted seed crystal. The equilibrium shape of ice at such temperatures is, however, of the type we treat here: rounded with small facets.

In summary, we have shown that a simple extension of Wulff's construction for equilibrium shapes of crystals leads naturally to dynamical shapes consistent with those observed experimentally. Facets are held stationary along the normal direction, while rounded areas grow with a shape appropriate to an *equilibrium* crystal of changing size. Complete faceting of a rounded equilibrium shape appears as a precursor to kinetic effects typical of strongly driven growth.

Note added: Since the original submission of this work there appeared a paper by Tersoff, Denier Vander Gon, and Tromp [21] on shapes of small Ag crystals. The mechanism described here may be relevant to the interpretation of their results.

The authors wish to thank J.G. Dash, J.W. Cahn, S.G. Lipson, M. den Nijs, M. Wortis, and M. Siegert for their comments and instructive criticisms. M.E. acknowledges NSF, Grant No. INT-9015952, for support at the University of Washington, where this work was begun. J.S.W. acknowledges ONR under Grants Nos. N00014-90-J-0586 and N00014-90-J-1369, and APL/UW.

---

[1] Y. Carmi, S.G. Lipson, and E. Polturak, Phys. Rev. B **36**, 1894 (1987).

[2] M. Elbaum, Phys. Rev. Lett. **67**, 2982 (1991).

[3] K. Koo, R. Anath, and W.N. Gill, Phys. Rev. A **44**, 3782 (1991).

[4] M. Maruyama, J. Crys. Growth **94**, 757 (1989).

[5] J.C. Heyraud and J.J. Métois, Surf. Sci. **177**, 213 (1986); **128**, 334 (1983).

[6] G. Wulff, Z. Krist. **34**, 449 (1901).

[7] A. Dinghas, Z. Krist. **105**, 304 (1944).

[8] C. Herring, Phys. Rev. **82**, 87 (1951).

[9] L.D. Landau, in *Collected Papers of L.D. Landau* (Pergammon, Oxford, 1965), p. 540.

[10] C. Herring, in *Structure and Properties of Solid Surfaces*, edited by R. Gomer and C.S. Smith Publisher, (Chicago, 1953).

[11] A.A. Chernov, *Modern Crystallography III, Crystal Growth* (Springer, Berlin, 1984), p. 122.

[12] W.K. Burton, N. Cabrera, and F.C. Frank, Philos. Trans. R. Soc. A **243**, 299 (1951).

[13] S.G. Lipson (personal communication).

[14] M. Elbaum, S.G. Lipson, and J.G. Dash, J. Cryst. Growth **129**, 491 (1993).

[15] J.C. Heyraud and J.J. Métois, J. Cryst. Growth **82**, 269 (1987).

[16] M. Siegert, Phys. Rev. A **42**, 6268 (1990).

[17] J. Villain, Nature **350**, 273 (1991); see also F.C. Frank, in *Growth and Perfection of Crystals*, edited by R.H. Doremus, B.W. Roberts, and D. Turnbull (Wiley, New York, 1958).

[18] J. Flesselles, M.O. Magnasco, and A. Libchaber, Phys. Rev. Lett. **67**, 2489 (1991); see also B.B. Berge, L. Faucheux, K. Schwab, and A. Libchaber, Nature **350**, 322 (1991).

[19] U. Nakaya, *Snow Crystals, Natural and Artificial* (Harvard Press, Cambridge, 1954); also W.A. Bentley and W.J. Humphreys, *Snow Crystals* (Dover, New York, 1962).

[20] J. Taylor, J.W. Cahn, and C.A. Handwerker, Acta. Metall. **40**, 1443 (1992).

[21] J. Tersoff, A.W. Denier van der Gon, and R.M. Tromp, Phys. Rev. Lett. **70**, 1143 (1993).

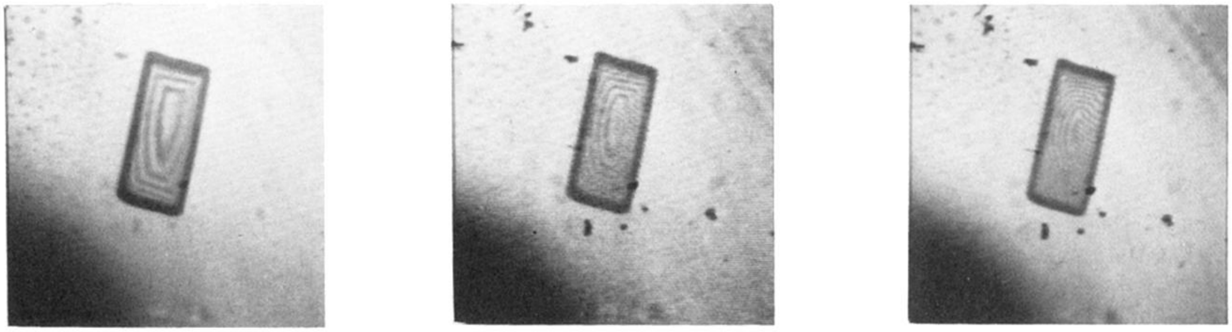

FIG. 3. Sequence of evaporation shapes of an isolated H_2O ice crystal in a pure vapor environment. The field of view is 1.0×1.0 mm. The height difference between adjacent fringes is 0.23 μm. Note the "rooftop" shape of the surface, with pitch steepening as evaporation progresses, in accord with Fig. 2. The experimental starting point is, however, a growth shape rather than equilibrium.