Evolution of Crystal Shape

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ABSTRACT: We have developed a mathematical model to track facets appearing and disappearing during the evolution of crystal shape. The model also gives the crystal shape at steady state that is consistent with the predictions from the Wulff-Chernov approach (Chernov, A. A. *Sov. Phys. Crystallogr.* **1963**, *7*, 728). We show that under constant growth rate conditions, the steady state shape of a crystal is unique, stable, and independent of the seed crystal shape. The predicted shape of solution grown succinic acid is shown to be in excellent agreement with experimentally grown shapes. This model explains the experimentally observed uniqueness of the steady-state shape of crystals with respect to the random seed shapes.

Introduction

It is well-known that crystals grow in a variety of shapes in response to both internal and external factors. Some of these factors can be manipulated (e.g., solvent type, solution temperature, and supersaturation, etc.) by crystal engineers to steer crystals toward a target shape or away from undesired shapes. The shape of crystals is an important factor for organic materials in the product and process design of pharmaceutical, agricultural, and specialty chemicals,¹ and for inorganic materials in the design of metal, semiconductor applications.^{2,3} Techniques for predicting the steady state morphology of vapor-grown organic crystals,4,5 and solution grown crystals are known.^{6,7} Despite more than a century of research on crystallization, there is relatively little known on the dynamics of the evolution of crystal shape from a seed to a steady-state shape.

Experiments performed on the growth of crystals from spherical seeds have shown that flat faces appear during growth. Some of the faces that appear eventually disappear, while others grow in size, eventually leading to a fully facetted stationary (steady state) shape.^{9,10} The shape of crystals at the thermodynamic equilibrium can be determined using Gibbs' approach of minimality of the total surface free energy per unit volume.¹¹ This thermodynamic equilibrium condition leads to the Wulff construction to determine crystal shape:¹²

$$\frac{\gamma_i}{h_i} = \text{constant}, \ i = 1, ..., N$$
 (1)

where γ_i is the specific surface free energy of face *i*, and h_i is the perpendicular distance between the origin and face *i*. Only small particles can undergo rapid shape change to reach equilibrium, during which the size change is not substantial. For large particles, however, the number of elementary transport processes that have to occur to achieve significant changes in shape is so large compared with the lowering of the surface free

* To whom correspondence should be addressed, 3323 Engineering II, University of California, Santa Barbara, CA 93106. Telephone: (805) 893-5309. Fax: (805) 893-4731. E-mail: mfd@ engineering.ucsb.edu. energy that the rate of equilibration becomes negligible.¹³ For crystals grown from seeds, steady-state shapes (that have self-similar growth) are therefore observed more often than the equilibrium shapes. Wulff's condition was modified by Chernov⁸ (also see Cahn et al.¹⁴) to determine the crystal shape at steady state given as

$$\frac{R_i}{h_i} = \text{constant}, \ i = 1, \dots, N \tag{2}$$

where R_i is the perpendicular growth velocity of face *i*. A number of mechanisms and models are available to estimate the perpendicular growth velocities of facets (e.g., BFDH, attachment energy, etc.), but only two models, nucleation and growth, and the screw dislocation model (BCF model) have the proven capability to correctly estimate the relative growth rates of crystals grown from solution.^{6,7,15–17} Moreover, single-crystal experiments can be performed to measure the perpendicular growth velocities.¹⁸

Modeling Crystal Shape Evolution

Succinic acid grown from aqueous solution exhibits a hexagonal platelike crystal shape at steady state with the [100] form dominant.¹⁹ Facetted crystals with a dominant flat face can be effectively represented by a two-dimensional projection of the crystal on the dominant face. A projection on the dominant [100] form allows for a model that accounts for the length of a face in the projection as a representation of the face itself. The rate of change of the length of each face is given as

$$\frac{v_{i} = \frac{dl_{i}}{dt}}{(R_{i+1} - R_{i}\cos\alpha_{i,i+1})\sin\alpha_{i-1,i} + (R_{i-1} - R_{i}\cos\alpha_{i-1,i})\sin\alpha_{i,i+1}}{\sin\alpha_{i-1,i}\sin\alpha_{i,i+1}},$$

$$i = 1, ..., N (3)$$

where v_i is the tangential growth velocity, l_i is the length, and R_i is the perpendicular growth velocity of face *i*, $\alpha_{i,j}$ is the angle between the normal directions of adjacent faces *i* and *j*, and *N* is the total number of faces



Figure 1. (a, b) Predicted shape evolution of succinic acid grown from water.

in the projection. To determine the shape at any given time for an evolving crystal, a convenient choice of variables is to use the length of faces relative to the perimeter of the two-dimensional projection, given by a set of ordinary differential equations

$$\frac{dx_i}{d\xi} = u_i - x_i, \ i = 1, ..., \ N - 1 \tag{4}$$

$$L = L^0 \exp(\xi) \tag{5}$$

where $x_i = (I_i/L)$ is the relative length of face *i* to the perimeter, $u_i = (v_i/V)$ is the relative velocity of face *i* to the sum of tangential velocities of all faces (for given perpendicular growth rates, u_i has a constant value during crystal growth), $L = \sum_{i=1}^{N} I_i$ is the perimeter of the crystal at any time, L^0 is the perimeter of the seed crystal (time t = 0), and $V = \sum_{i=1}^{N} v_i$ is the sum of tangential velocities of all faces. Here, ξ represents a dimensionless warped time, and is related to the real time *t* by $\xi = \ln(1 + Vt/L^0)$. Gadewar and Doherty²⁰ provide a detailed derivation of the model together with a description of its properties. The shape evolution model can be applied to both organic as well as inorganic crystals; however, since reliable methods for predicting the growth rates of inorganic crystals are not known, our methodology has been applied only to organic crystals.

Equation 4 is written in a matrix notation as

$$\frac{d\boldsymbol{x}}{d\xi} = \boldsymbol{A}\boldsymbol{x} + \boldsymbol{u} \tag{6}$$

where A = -I is the negative of the identity matrix I of dimensions $(N - 1 \times N - 1)$, **x** is a vector of N - 1

relative face lengths, and \boldsymbol{u} is the vector of N-1 relative tangential growth velocities. There are (N-1) eigen values for matrix \boldsymbol{A} , each having the value -1. The steady-state condition for the crystal shape evolution is obtained by equating the right-hand side of eq 6 to zero, and this condition is equivalent to eq 2. All the eigen values are real and negative; therefore, the steady state for the linear ordinary differential eqs 6 is stable and unique.^{20,21} This implies that for given perpendicular growth velocities, the steady-state crystal shape is unique and stable.

Application to Succinic Acid Grown from Water

Succinic acid is a widely studied crystal system. Docherty and Roberts²² used the attachment energy model to predict the vapor-grown shape, and Davey et al.¹⁹ published the effect of solvents such as 2-propanol and water on the crystal shape. Facetted portions of crystals are believed to result from a layer-by-layer growth.²³ For succinic acid grown out of water, a standard attachment energy simulation and interplanar spacing calculation was performed to estimate the likely faces, the intermolecular bond energies and distances.⁷ All the likely low index faces provided by the Bravais, Freidel, Donnay and Harker (BFDH) analysis were chosen as the likely crystal faces for which the growth rates are estimated. The estimated likely growth forms are [100], [020], [021], and [011]. More faces can be added at will according to the number of faces desired on the seed crystal. Physical properties such as the kink free energy and edge free energy are calculated using models that account for the effect of a polar solvent on the surface free energy.²⁴ A screw dislocation model is then used to determine the perpendicular growth rates



Figure 2. Steady-state shape of succinic acid grown from water.

of the likely forms, and have the following values relative to the unit growth rate of form [100]: R[020] =4.19, R[021] = 4.45, R[011] = 2.98, and R[002] = 5.72. These growth rates depend not only on the lattice geometry, intermolecular bonds, and interplanar spacing but also on the solute-solvent interaction. Both the BFDH and the attachment energy models do not provide a precise mechanism for incorporating solvent effects. The BFDH and attachment energy models were therefore not used to estimate the relative growth rates. A more detailed description on the estimation of the relative growth rates using the screw dislocation model, and its comparison with other growth rate models can be found in Winn and Doherty.^{7,25} Using the estimated growth rates with the evolution model in eqs 3-5, the shape of growing crystals is determined. The initial condition for the model is defined by the seed shape. The predicted evolution of succinic acid crystals for two different seed shapes is shown in Figure 1. The projection of the shape on form [100] at increasing time is shown by concentric polygons with the seed shape given by the innermost polygon.

The shape evolution from a random triangular seed shape is shown in Figure 1a. The projection on form [100] is defined by the faces (021), (002), and $(0\bar{1}\bar{1})$. As the crystal grows, faces (021) and (002) start to disappear, and faces (020), (011), $(0\bar{1}1)$, $(0\bar{2}0)$, $(01\bar{1})$ appear and grow. During growth, face (002) disappears first, and eventually face (021) disappears from the crystal shape. The shape that satisfies the steady-state condition for eq 4 is shown in Figure 2. Two faces present in the seed shape disappear, while five faces appear during growth.

Starting with a seed shape shown with 12 sides of the projection on form [100] (14 faces including face (100) and ($\overline{1}$ 00)), the shape evolves with the form [002] disappearing with growth as shown in Figure 1a. During further growth, the form [021] also disappears giving a shape bound by forms [100], [020], and [011]. On further growth, the steady-state condition for eq 4



Figure 3. Experimental setup for growing organic crystals from solution.

is again satisfied by the shape shown in Figure 2. Six faces that were present in the seed shape disappear during growth. The steady-state shape is therefore independent of the seed crystal shape. If different faces were chosen as likely faces, and if a different growth rate model was used, the steady-state shape can be different from the one in Figure 2. The steady-state shape would still be unique, and independent of the seed crystal shape.

Crystal Shape Experiments

Experiments were performed in a 4 L fluidized bed batch crystallizer for growing succinic acid crystals out of water. The experimental setup is shown in Figure 3. In the right side of the apparatus, crystals are grown in an undercooled solution in a fluidized bed. A part of the solution is removed at the top of the vessel into a funnel and flows into the left side of the apparatus. In the left side of the apparatus, the solution can be heated to dissolve the fine crystals in the solution, which are created by nucleation, crystal breakage, etc. The solution is cooled as it flows into the growth zone at the bottom of the fluidized bed. The flow of the solution is driven by a motor driven four-blade propeller. The temperature in the apparatus is maintained by circulating chilled water in the cooling jackets using microprocessor control (NESLAB RTE-111).

The crystallizer was operated at 22 °C, for a solution with a saturation temperature of 24 °C. The metastable zone width was 2.2 °C (determined using the polythermal method published by Söhnel and Mullin²⁶), and therefore the operating temperature of 22 °C was found to be suitable for growth. The dissolution vessel dis-



Figure 4. (a–e) Experimental measurement of the shape evolution of succinic acid grown from water.

solves the fines, allowing growth only on the inserted seed crystals. Approximately 50 seeds of random shape (obtained by grinding larger crystals) were inserted in the crystallizer. The size of the seeds was in the range of $450-500 \,\mu\text{m}$. Samples of growing crystals were taken and observed under a Zeiss light microscope.

Two pictures of each sample taken at various time intervals are shown in Figure 4. Figure 4a shows that the seeds are of random shapes. At a time interval of 1 h, the crystal shape is evolving shown in Figure 4b. After 2:15 h in the crystallizer, most of the crystals reach steady state shape; however, some of the crystals shapes are still evolving as shown in Figure 4c. The steady state shape of the crystals was achieved after approximately 3:30 h as shown in Figure 4d. Some agglomeration begins to appear at larger time periods in the crystallizer (>3 h). The experiments were repeated with another set of random seed crystals, and the steady state shape from the new set of experiments is shown in Figure 4e. Figure 4 shows that the steady state shape of the crystals is unique and independent of the shape of the seed crystals, and repeated experiments confirm the reproducibility of this observation. The experimentally measured steady state shape is in excellent agreement with the theoretically predicted shape shown in Figure 2.

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