Three-dimensional equilibrium crystal shapes with corner energy regularization

Antonio Mastroberardino
School of Science, Penn State Erie, The Behrend College, Erie, Pennsylvania 16563-0203

Brian J. Spencer
Department of Mathematics, University at Buffalo, Buffalo, New York 14260-2900

December 17, 2009

Abstract

The evolution equations of crystal growth often employ a regularization of the surface energy based on a corner energy term. Here we consider the effect of this regularization on the equilibrium shape of a solid particle in three dimensions. We determine that a sufficient regularization involves only one of the two isotropic invariants related to curvature. Using a long-wave approximation, we derive a nonlinear equation for the shape of a semi-infinite wedge in the case when the surface energy has cubic symmetry. An analytic description of the solution along an edge is given as well as an exact solution for a special case of anisotropy. Finally, this equation is solved numerically to demonstrate explicit solutions for which the regularization rounds the edges of the unregularized crystal shape.
1 Introduction

The equilibrium shape of a solid crystal in contact with its vapor or liquid phase is determined by minimizing its interfacial free energy under the constraint of constant volume. This is a classic materials science problem that has been studied for over a century. The first solution to this problem was given by Wulff (1901) using a geometrical construction - the Wulff construction - which involves a polar plot of the surface energy, $\gamma({\mathbf{n}})$, where $\mathbf{n}$ is a unit normal to the surface. Herring (1951a, 1953) extended this work and provided corrections to Wulff’s proof. Subsequent descriptions of the equilibrium crystal shape have been developed by Burton, Cabrera and Frank (1951), Frank (1963), Cabrera (1963, 1964), Cahn and Hoffman (1974), and Andreev (1981). A modern perspective of the equilibrium crystal shape problem appears in books by Landau and Lifshitz (1980), Tsao (1993), and Pimpinelli and Villain (1998).

In the absence of anisotropy, the solution to the problem is a circle for a two-dimensional crystal and a sphere for a three-dimensional crystal. The presence of anisotropy alters the shape and, for strong anisotropy, it may be energetically favorable to exclude certain orientations, resulting in the formation of corners, edges, or facets. Fig. 1 illustrates the case where the shape consists of curved sides connected by smooth edges and Fig. 2 illustrates the case where the shape consists of curved sides connected by sharp edges. Flat sides or facets correspond to cusps (local minima where $\gamma({\mathbf{n}})$ is not differentiable) in the polar plot of $\gamma({\mathbf{n}})$.

In this paper, we restrict our attention to the case where the surface is thermally rough and cusps are not present, i.e., the system is above the thermal roughening temperature. Corners and edges arise when it is energetically favorable to exclude high energy orientations. In two dimensions, where the angular orientation of the surface normal is $\theta$ and the surface energy is $\gamma(\theta)$, a sharp corner exists when the “surface stiffness” $\gamma + \gamma''$ is negative. In three dimensions, Sekerka (2005) proved that the onset of missing orientations occurs when $\xi \cdot (\xi_\nu \times \xi_v) < 0$ where $\xi$ is the capillarity vector introduced by Hoffman and Cahn (1972) and subscripts denote differentiation with respect to the surface parameters $u$ and $v$. 
Figure 1: Equilibrium crystal shape for $\gamma(n)$ given by Eq. (3.8) with $\alpha = 0.3$.

The analytical criteria noted above for the onset of missing orientations play critical roles in the dynamics of evolving surfaces. For orientations that satisfy these criteria, evolution equations are ill-posed due to an instability with respect to short-scale wrinkling (Mullins (1963), DiCarlo et al. (1992)). In numerical calculations, this ill-posedness manifests itself as a blow up on the finest scale. To remove the ill-posedness, a regularization which smooths the small-scale instability is required.

The approach that has been used for regularizing the ill-posed problem is to add a higher-order term to the surface energy (DiCarlo et al. (1992), Angenent and Gurtin (1989), Stewart and Goldenfeld (1992), Golovin et al. (1998, 1999), Gurtin and Jabbour (2002)). In particular, adding a dependence on curvature to the surface energy should penalize sharp edges and corners, and make them rounded on a small length scale (Herring (1951a)). Since a large curvature at the corner has high energy because of the regularization, and a small
Figure 2: Equilibrium crystal shape for $\gamma(\mathbf{n})$ given by Eq. (3.8) with $\alpha = 0.8$. The exterior flaps and ears are unphysical mathematical artifacts. The equilibrium shape is the convex surface obtained by truncation of the ears and flaps.

curvature at the corner has high energy because of a larger area with orientations with larger surface energy, the amount of corner rounding that minimizes the energy is determined by a compromise between these two competing energy penalties.

A simple model for the total surface energy in the two-dimensional problem is $E = \int \gamma(\theta) + \beta \kappa^2 \, ds$ (Angenent and Gurtin (1989)) where $s$ is the surface arclength, $\kappa$ is the curvature, and $\beta \geq 0$ is an isotropic corner energy parameter. Recently, Spencer (2004) used asymptotic analysis to show in general that the equilibrium Wulff shape in two dimensions is recovered in the regularized model as $\beta \to 0$, even though the regularization appears as a nonlinear singular perturbation. The asymptotic solution, constructed using matched asymptotic expansions, consists of an explicit solution for the regularized shape near the corner and the Wulff shape away from the corner. It was also shown that matching was
always guaranteed; corner solutions could exist if and only if they precisely matched the
corner geometries prescribed by the classical common tangent construction (Cabrera (1964))
of the Wulff corner angles. These results demonstrate that for any analytical surface energy
anisotropy the regularized solutions converge to the Wulff shape as the regularization goes
to zero, as was observed in the numerical example of Siegel et al. (2003).

While there has been considerable progress on the implementation of a regularization in
two dimensions, little has been done with respect to problems involving a three-dimensional
crystal in either the dynamic setting or at equilibrium. Liu and Metiu (1993) studied
the dynamics of a crystal surface relaxing to an equilibrium shape in the presence of a
regularization attributed to the additional energy of edges and corners. Golovin et al. (1999)
implemented a regularization in the context of dynamics for an evolving surface by adding
a dependence on the total (or twice the mean) curvature to the surface energy. Gurtin
and Jabbour (2002) considered the regularized model
\[ E = \int \gamma(n) + \frac{1}{2} \beta_1 |L|^2 + \frac{1}{2} \beta_2 K^2 \, dA \]
which includes a dependence on two quadratic isotropic invariants of the curvature tensor
\( L \) in a comprehensive treatment of the thermodynamics and kinetics of evolving surfaces.
However, no one to date has addressed the implementation of a regularization at equilibrium
for a three-dimensional crystal.

The goal of this paper is to study the regularization for the equilibrium crystal shape
problem in three dimensions. We start our analysis with the regularized model proposed by
Gurtin and Jabbour. We determine that the energy effects from the two regularization terms
are the same, and thus, propose a model surface energy of the form
\[ \hat{\gamma} = \gamma(n) + \frac{1}{2} \beta K^2 \]
where \( K \) is the total curvature. In the absence of the regularization, the solution is provided
in terms of the surface energy, its first partial derivatives and the spherical polar angles
when there are no missing orientations. When there are missing orientations, we give a
detailed description of exactly which angle orientations are missing at a sharp corner for
a crystal with cubic symmetry. In the presence of the regularization, we construct a long-
wave approximation for the equilibrium condition for a semi-infinite wedge and provide an
asymptotic description of solutions along a smooth edge. For a special case of anisotropy,
we give an exact solution and conclude with a numerical solution of the equation obtained
from the long-wave approximation.
The rest of this paper is organized as follows. In Section 2 we formulate the problem in the general setting with dimensional variables. In Section 3 we discuss the Wulff shape obtained by setting the corner energy parameter to zero. In Section 4 we provide asymptotic and numerical solutions for the equilibrium shape when the corner energy parameter is small by using a long-wave approximation. We also find an exact solution for a special case of anisotropy. Finally, in Section 5 we summarize the main results.

2 Formulation

Consider a closed surface $S$ in $\mathbb{R}^3$ that forms the boundary of a three-dimensional crystal. This surface can be described by the coordinates $(x, y, z)$, where each is parametrized by the polar angle $\phi$ and azimuthal angle $\theta$. The total curvature at a point on the surface $S$ is given by

$$K = tr\, L = k_1 + k_2$$

(2.1)

where $L = -\nabla_S n$ is the curvature tensor, $n$ is the outward unit normal, $\nabla_S$ is the surface gradient, and $k_1$ and $k_2$ are the principal curvatures.

Gurtin and Jabbour (2002) have proposed the model

$$E = \int_S \gamma(n) + \frac{1}{2}\beta_1 |L|^2 + \frac{1}{2}\beta_2 K^2 \, dA$$

(2.2)

for the total energy of the surface of a three-dimensional crystal based on an anisotropic surface energy $\gamma(n)$ and a corner regularization which includes the quadratic isotropic invariants of the curvature tensor $L$. We expect both of these regularization terms to penalize the formation of sharp corners and edges, and thus, round these corners and edges on a small length scale.

The equilibrium condition is derived by minimizing Eq. (2.2) subject to the constraint of fixed volume $V$ enclosed by the surface. Using the concepts of configurational forces and moments, the modified form of Herring’s equation (1951b) for the chemical potential $\mu$ at the surface of the solid, which here includes the effect of the regularization, is given in Gurtin and Jabbour (2002) as

$$\mu = \left[\gamma(n)P + \frac{\partial^2 \gamma(n)}{\partial n^2}\right] \cdot L - \beta_1 C_1(L, K) - \beta_2 C_2(L, K)$$

(2.3)
where
\[ C_1(L, K) = \nabla_3^2 K - \frac{1}{2} K |L|^2 + \text{tr}(L^3) \] (2.4)
\[ C_2(L, K) = \nabla_3^2 K + K |L|^2 - \frac{1}{2} K^3 \] (2.5)
are corner energy terms, \( P \) is the projection operator, and \( \nabla_3^2 \) is the surface Laplacian. At equilibrium the surface satisfies \( \mu = \text{constant} \), and bounds a solid with prescribed volume \( V \).

Note that in the case of a two-dimensional surface enclosing a three-dimensional crystal, we have (Antman (1993))
\[ |L|^2 = k_1^2 + k_2^2 \] (2.6)
\[ \text{tr}(L^3) = k_1^3 + k_2^3 \] (2.7)
and substituting Eqs. (2.1), (2.6) and (2.7) into Eqs. (2.4) and (2.5) yields
\[ C_1(L, K) = C_2(L, K) \] (2.8)
It follows that
\[ \beta_1 C_1(L, K) + \beta_2 C_2(L, K) = (\beta_1 + \beta_2) C_1(L, K) \] (2.9)
and so the contribution to the surface chemical potential from both quadratic isotropic invariants are the same.

This is no surprise if one considers the fact that
\[ |L|^2 = K^2 - 2G \] (2.10)
where \( G = k_1 k_2 \) is the Gaussian curvature. Substituting Eq. (2.10) into Eq. (2.2) yields
\[ E = \int_S \gamma(n) - \beta_1 G + \frac{1}{2} (\beta_1 + \beta_2) K^2 dA \] (2.11)
for the total surface energy. Since the surface \( S \) of the equilibrium shape is a compact oriented surface without boundary, it follows from the Gauss-Bonnet Theorem that the Gaussian curvature term has no effect on the equilibrium condition. Thus, a sufficient regularized model for the surface energy in three dimensions is
\[ \hat{\gamma} = \gamma(n) + \frac{1}{2} \beta K^2 \] (2.12)
where the dependence on the total curvature is the so-called Willmore energy. Using Eq. (2.12), the equilibrium condition that determines a surface of minimum total energy becomes

$$
\mu = \left[ \gamma(n)P + \frac{\partial^2 \gamma(n)}{\partial n^2} \right] \cdot L - \beta(\nabla_\gamma^2 K + K |L|^2 - \frac{1}{2} K^3).
$$

(2.13)

The problem of finding surfaces embedded in $\mathbb{R}^3$ that minimize the integral involving only the Willmore energy, i.e., the case $\gamma = 0$, $\beta \neq 0$, has been studied for quite some time. Using the calculus of variations and the computational tools of Riemannian Geometry, Schadow (Thomsen (1923)) derived the following Euler-Lagrange equation

$$
\nabla_\gamma^2 K + \frac{1}{2} K(K^2 - 4G) = 0
$$

(2.14)
as a necessary condition. Clearly, we must have the following correspondence between Eq. (2.14) and the $\beta$ term of Eq. (2.13)

$$
\nabla_\gamma^2 K + \frac{1}{2} K(K^2 - 4G) = \nabla_\gamma^2 K + K |L|^2 - \frac{1}{2} K^3
$$

(2.15)

and this can easily be demonstrated by substituting Eqs. (2.1) and (2.6) into Eq. (2.15). See Willmore (1993) for an in-depth discussion of this problem and a proof of Eq. (2.14).

To recast Eq. (2.13) in nondimensional form, we let $l$ be a characteristic radius of the solid region and $\gamma_0$ be a characteristic value of the surface energy. Eq. (2.13) becomes

$$
\frac{\mu l}{\gamma_0} = \left[ \tilde{\gamma}(n)P + \frac{\partial^2 \tilde{\gamma}(n)}{\partial n^2} \right] \cdot \tilde{L} - \frac{\beta}{\gamma_0 l^2} \left( \nabla_\gamma^2 \tilde{K} + \tilde{K} |\tilde{L}|^2 - \frac{1}{2} \tilde{K}^3 \right).
$$

(2.16)

We define the nondimensional chemical potential and the nondimensional regularization parameter by

$$
\tilde{\mu} = \frac{\mu l}{\gamma_0},
$$

(2.17)

$$
\tilde{\beta} = \frac{\beta}{\gamma_0 l^2}.
$$

(2.18)

By substituting these nondimensional parameters into Eq. (2.16) and dropping the tilde notation, we recover Eq. (2.13) which is now nondimensional.

In the sections that follow, we will construct solutions to Eq. (2.13) first for the $\beta = 0$ case. For the case $\beta \neq 0$, we will employ a long-wave approximation in order to make the problem tractable. Without loss of generality we can restrict our attention to the case
\( \mu \geq 0 \). The case \( \mu < 0 \) is equivalent to the case \( \mu > 0 \) under the transformation \( \mu \to -\mu \) and \( K \to -K \), i.e. converting an exterior solid (void) domain to an interior (drop) domain or vice versa. The inversion symmetry of interior (drop) and exterior (void) shapes is well-known in the absence of the regularization term. Here we note that this symmetry is also preserved for the regularized corner term.

3 Solutions in the absence of regularization

The equilibrium shape problem when \( \beta = 0 \) has been solved by a variety of approaches (Wulff (1901), Herring (1951a, 1953), Burton et al. (1951) Frank (1963), Cabrera (1963, 1964), Cahn and Hoffman (1974), Andreev 1981)). We will follow the \( \xi \)-vector formalism of Cahn and Hoffman (1972, 1974) as it provides an elegant formula for the onset of missing orientations in the three-dimensional case.

3.1 Cahn-Hoffman capillarity vector

As an alternative to the scalar function \( \gamma(n) \), Hoffman and Cahn (1972) proposed a vector function \( \xi(n) \) to describe the anisotropic surface energy of a crystal. This vector function is defined so that its component in the direction of the unit normal \( n \) represents the tendency of the surface to minimize energy by contraction and its component perpendicular to \( n \) represents the tendency of the surface to minimize energy by rotation. The main advantage of this vector formulation is that, in the case of a crystal with smooth corners and edges, the \( \xi \)-plot is geometrically similar to the Wulff shape.

To represent the capillarity vector \( \xi(n) \) in mathematical terms (Sekerka (2005)), one first extends the function \( \gamma(n) \) to a three-dimensional vector space, \( A \), by defining \( \bar{\gamma}(A) = |A| \gamma(n) \) where \( n = A / |A| \). Then the \( \xi \)-vector is defined by

\[
\xi(n) = \nabla \bar{\gamma}(A) \tag{3.1}
\]

where \( \nabla = \partial / \partial A \) in \( A \) space. This definition yields the following properties (Hoffman and Cahn (1972)):

\[
\xi \cdot n = \gamma \tag{3.2}
\]

\[
n \cdot d\xi = 0. \tag{3.3}
\]
Using these properties, Cahn and Hoffman (1974) proved that

\[
\nabla S \cdot \xi = \left[ \gamma(n)P + \frac{\partial^2 \gamma(n)}{\partial n^2} \right] \cdot L \tag{3.4}
\]

where \(\nabla S\) is the surface divergence operator. In other words, Herring’s equation for the equilibrium shape can be restated

\[
\mu = \nabla S \cdot \xi. \tag{3.5}
\]

Since \(\nabla S \cdot r = 2\), where \(r\) is the position vector, it follows that

\[
\nabla S \cdot r = \frac{2}{\mu} \nabla S \cdot \xi. \tag{3.6}
\]

The equilibrium crystal shape in parametric form becomes

\[
r(n) = L \xi(n) \tag{3.7}
\]

where \(L = 2/\mu\) is a constant scaling factor.

Eq. (3.7) states that the equilibrium shape is similar in shape to the \(\xi\)-plot, which is a polar plot of \(\xi\) as a function of the orientation \(n\), and that, in the absence of the corner energy term, the shape of the crystal is inversely proportional to \(\mu\). Thus, the equilibrium shape is independent of the crystal size, and can be found by solving the problem for \(\mu = 1\). By choosing \(\mu\) appropriately, crystals of different volume can be constructed where small particles correspond to \(\mu \to \infty\) and large particles correspond to \(\mu \to 0^+\). The special case \(\mu = 0\) corresponds to a semi-infinite domain and will be discussed in Sec. 4.

### 3.2 Smooth equilibrium shapes

In the following derivation of equilibrium shapes, we shall consider a general nondimensional form for \(\gamma(n)\). We only require that \(\gamma(n)\) is continuous, and that its second partial derivatives are also continuous. In some instances, it is useful to illustrate the results with a specific example. In such cases we consider the prototype model for surface energy with cubic symmetry,

\[
\gamma(\theta, \phi) = 1 + \alpha \left( n_x^4 + n_y^4 + n_z^4 \right) \tag{3.8}
\]

where \(0 \leq \alpha < 1\) measures the degree of anisotropy and \(n_x, n_y, n_z\) are the coordinates of \(n\), which can be expressed in terms of the spherical polar angles \(\phi\) and \(\theta\).
Using the definition in Eq. (3.1), the $\xi$-vector is given by

$$\xi = \gamma n + \gamma_\theta \theta + \frac{\gamma_\phi}{\sin \theta} \phi \tag{3.9}$$

where $n, \theta, \phi$ are unit vectors of the spherical coordinate system and subscript variables denote derivatives. Converting to cartesian coordinates yields

$$x = \gamma(\theta, \phi) \sin(\theta) \cos(\phi) + \gamma_\theta(\theta, \phi) \cos(\theta) \cos(\phi) - \gamma_\phi(\theta, \phi) \frac{\sin(\phi)}{\sin(\theta)} \tag{3.10}$$

$$y = \gamma(\theta, \phi) \sin(\theta) \sin(\phi) + \gamma_\theta(\theta, \phi) \cos(\theta) \sin(\phi) + \gamma_\phi(\theta, \phi) \frac{\cos(\phi)}{\sin(\theta)} \tag{3.11}$$

$$z = \gamma(\theta, \phi) \cos(\theta) - \gamma_\theta(\theta, \phi) \sin(\theta). \tag{3.12}$$

Construction of the equilibrium crystal shape depends on the details of $\gamma(\theta, \phi)$. Fig. 1 illustrates the case when the shape has smooth corners and edges. For this case, there are no missing angle orientations and the crystal shape is given exactly by the above description.

### 3.3 Equilibrium shapes with missing orientations

As noted previously, however, in the case of severe anisotropy, it may be energetically favorable to exclude certain orientations, resulting in the formation of corners and/or edges. Missing orientations arise when the $1/\gamma$-plot becomes concave, i.e., when the Gaussian curvature changes sign. Based on the convexity of the $1/\gamma$-plot, Sekerka (2005) has recently formulated an analytical criterion for the onset of missing orientations in three dimensions.

Consider the capillarity vector $\xi$ as a function of the surface parameters $u$ and $v$. By showing that the unit normal to the $1/\gamma$-plot is proportional to the $\xi$-vector, Sekerka determined that if $\xi \cdot (\xi_u \times \xi_v) < 0$, then the crystal shape will have missing orientations. Here subscripts denote differentiation with respect to the surface parameters. Using Eq. (3.9), this condition becomes (Sekerka (2005))

$$\left(\gamma + \gamma_\theta\theta\right)\left(\gamma \sin^2 \theta + \gamma_\phi\phi + \gamma_\theta \sin \theta \cos \theta\right) - \left(\gamma_\theta\phi - \gamma_\phi \cot \theta\right)^2 < 0 \tag{3.13}$$

where the spherical polar angles $\phi$ and $\theta$ have been used as the parameters. In this case, Eqs. (3.10)-(3.12) yield a crystal shape with nonphysical ears and/or flaps. Flaps will arise where the crystal shape has a sharp edge and ears will arise when edges of the crystal shape intersect to form a corner.
To illustrate consider the model surface energy in Eq. (3.8). The condition for missing orientations becomes (Sekerka (2005))

\[ \frac{\gamma}{\xi} \left[ 1 - 3\alpha (2 \sin(\phi))^4 - 2(\sin(\phi))^2 + 1 \right] \times \left[ 1 - 3\alpha (10 \sin(\phi))^4 - 10(\sin(\phi))^2 + 1 \right] < 0 \] (3.14)

where \( \xi = |\xi| \). This relation shows that the equilibrium shape will have missing orientations whenever \( \alpha > 1/3 \) (positive anisotropy) or \( \alpha < -2/9 \) (negative anisotropy). Fig. 2 shows a plot of the \( \xi \)-vector for \( \alpha = 0.8 \), which also corresponds to the equilibrium shape with nonphysical ears/flaps.

When there are missing orientations, the nonphysical flaps contain the range of missing orientations. So, the orientations that appear on the crystal can be determined by locating the points where \((x(\theta, \phi), y(\theta, \phi), z(\theta, \phi))\) crosses itself. For the general case of positive anisotropy, note that the edges of the crystal shape are aligned with the planes \( \phi = 0, \phi = \pi/2, \phi = \pi, \phi = 3\pi/2, \theta = \pi/2 \). Consider the edge that lies in the plane \( \theta = \pi/2 \).
Across this edge, there is a jump discontinuity in the $\theta$ coordinate of the unit normal vector $n$, and by the symmetry, this jump discontinuity is symmetric with respect to $\theta = \pi/2$. In other words, if the $\theta$ coordinates of $n$ on either side of the edge are $\theta = \pi/2 - \theta_c^-, \pi/2 + \theta_c^+$, we have $\theta_c^- = \theta_c^+ = \theta_c$ and the missing orientations are given from the three jump conditions

\[
[x]_{\theta = \pi/2 - \theta_c, \phi} = 0 \quad (3.15) \\
[y]_{\theta = \pi/2 - \theta_c, \phi} = 0 \quad (3.16) \\
[z]_{\theta = \pi/2 - \theta_c, \phi} = 0. \quad (3.17)
\]

Using these jump conditions and the symmetry of $\gamma$, $\theta_c > 0$ is the root of

\[
\tan \theta_c = -\frac{\gamma_\theta(\frac{\pi}{2} + \theta_c, \phi)}{\gamma(\frac{\pi}{2} + \theta_c, \phi)}, \quad (3.18)
\]

Similarly, for the edge that lies in the plane $\phi = 0$, $\phi_c^- = \phi_c^+ = \phi_c$ and the missing orientations are given from the three jump conditions

\[
[x]_{\theta} | \theta = \phi_c = 0 \quad (3.19) \\
[y]_{\theta} | \theta = \phi_c = 0 \quad (3.20) \\
[z]_{\theta} | \theta = \phi_c = 0. \quad (3.21)
\]

Using these jump conditions and the symmetry of $\gamma$, $\phi_c > 0$ is the root of

\[
\gamma(\theta, \phi_c) \sin(\theta) \sin(\phi_c) + \gamma_\theta(\theta, \phi_c) \cos(\theta) \sin(\phi_c) + \gamma_\phi(\theta, \phi_c) \frac{\cos(\phi_c)}{\sin(\theta)} = 0. \quad (3.22)
\]

As an alternative to the analytic criterion for the onset of missing orientations determined by Sekerka (2005) for a three-dimensional crystal, Eqs. (3.18) and (3.22) provide explicit conditions for determining exactly which angle orientations are missing from the equilibrium shape for the case of cubic symmetry. In Fig. 3 we have plotted the curves separating the region of missing angle orientations (unshaded) from the regions of angle orientations that appear on the Wulff shape (shaded).

4 Solutions with regularization

In this section, we determine how the Wulff shape of Sec. 3 is modified by the corner energy regularization. When $\beta = 0$ the equilibrium crystal shape has sharp edges with a well-defined jump in orientations across these edges. For $\beta > 0$ it is expected that the corner
energy term penalizes regions of high curvature and so leads to rounded edges. We seek here to describe the behavior for \( \beta \ll 1 \), corresponding to the case of a small corner energy contribution, appropriate when the dimensions of the crystal are large relative to the radius of the edge rounding.

4.1 Long-wave approximation

To obtain analytic and numerical solutions to Eq. (2.13), we take the limit \( \mu \to 0^+ \), so that the size of the solid crystal becomes infinitely large, and thus, the behavior in the vicinity of a corner reduces to that of a semi-infinite wedge. We then employ a long-wave approximation similar to the one given in Golovin et al. (1999) in order to derive a nonlinear partial differential equation for the equilibrium crystal shape in the presence of a corner regularization. Consider a nondimensional form of the surface energy that has cubic symmetry (McFadden et al. (1988)) and a dependence on the total curvature

\[
\gamma_s(\theta, \phi) = 1 + \alpha_4(n_x^4 + n_y^4 + n_z^4) + \alpha_6(n_x^6 + n_y^6 + n_z^6) + \cdots + \frac{\beta}{2} K^2
\] (4.1)

where \( \alpha_4, \alpha_6, \ldots \) are anisotropy constants and \( \beta > 0 \).

For the case of positive anisotropy (see Fig. (1) and Fig. (2)), the crystal can be oriented so that its position is given by \( z = h(x, y) \), with the vertex located at \((0, 0)\) and the edges of the unregularized crystal aligned with the coordinate axes. In this case, the total energy of the surface is

\[
E_* = \int_S \tilde{\gamma}_s \sqrt{1 + |\nabla h|^2} \, dx \, dy
\] (4.2)

where \( \tilde{\gamma}_s \sqrt{1 + |\nabla h|^2} \) is the weighed surface tension. Expanding \( I \) for \( |h_x| \ll 1, |h_y| \ll 1 \) yields

\[
I = \epsilon_0 + \epsilon_1(h_x^2 + h_y^2) + \epsilon_2(h_x^4 + h_y^4) + \epsilon_3(h_x^2 h_y^2) + \cdots + \frac{\beta}{2}(h_{xx}^2 + 2h_{xy} h_{yy} + h_{yy}^2) + \cdots
\] (4.3)

where dots denote higher order terms and

\[
\epsilon_0 = 1 + \alpha_4 + \alpha_6 \quad \text{(4.4)}
\]
\[
\epsilon_1 = \frac{1}{2} - \frac{3}{2} \alpha_4 - \frac{5}{2} \alpha_6 \quad \text{(4.5)}
\]
\[
\epsilon_2 = -\frac{1}{8} + \frac{23}{8} \alpha_4 + \frac{35}{8} \alpha_6 \quad \text{(4.6)}
\]
\[
\epsilon_3 = -\frac{1}{4} + \frac{15}{4} \alpha_4 + \frac{35}{4} \alpha_6 \quad \text{(4.7)}
\]
The equilibrium condition Eq. (2.13) now becomes

\[-m\nabla^2 h - \beta \nabla^4 h + [ah_x^2 + bh_y^2]h_{xx} + [bh_x^2 + ah_y^2]h_{yy} + ch_x h_y h_{xy} = 0\]  (4.8)

where

\[m = 3\alpha_4 + 5\alpha_6 - 1\]  (4.9)
\[a = \frac{69}{2}\alpha_4 + \frac{105}{2}\alpha_6 - \frac{1}{2}\]  (4.10)
\[b = \frac{15}{2}\alpha_4 + \frac{35}{2}\alpha_6 - \frac{1}{2}\]  (4.11)
\[c = 30\alpha_4 + 70\alpha_6 - 2\]  (4.12)

and terms up to the fourth order have been kept.

Note that Eq. (4.8) is invariant under the transformations \(x \rightarrow -x, \ y \rightarrow -y,\) and \(x \rightarrow y,\) which reflects the cubic symmetry of the crystal surface. Without the regularization, i.e., \(\beta = 0,\) Eq. (4.8) yields planar solutions of arbitrary slope. Because of the cubic symmetry, we expect a piecewise solution \(h(x, y)\) that is defined in each of the four quadrants of the \(xy\)-plane by the planes \(-A(x + y),\ A(x - y),\ A(x + y),\) and \(A(y - x)\) respectively, where \(A\) is a constant to be determined. Note that these planes meet along the coordinate axes to form sharp edges with a sharp corner located at \((0, 0)\).

Eq. (4.8) is related to the equation derived by Golovin et al. (1999) which describes the formation of facets and corners in the course of kinetically controlled crystal growth. In nondimensional form, their equation is

\[V_0 \frac{h_t}{t} = -m\nabla^2 h - \beta \nabla^4 h + \frac{V_0}{2} (\nabla h)^2 + [ah_x^2 + bh_y^2]h_{xx} + [bh_x^2 + ah_y^2]h_{yy} + ch_x h_y h_{xy}\]  (4.13)

where \(V_0\) a constant driving force and

\[m = 3\alpha_4 + 5\alpha_6 - 1\]  (4.14)
\[a = 33\alpha_4 + 50\alpha_6 - 1\]  (4.15)
\[b = 6\alpha_4 + 15\alpha_6\]  (4.16)
\[c = 30\alpha_4 + 70\alpha_6 - 2\]  (4.17)

To find stationary solutions of Eq. (4.13), consider the limit \(V_0 \rightarrow 0\) and note that the time derivative and the convective term \(\frac{1}{2} (\nabla h)^2\) are negligible compared to all other terms.
This yields an equation that matches the form of Eq. (4.8), however, our models in the stationary case are different by the fact that the anisotropy coefficients in Eq. (4.10) and Eq. (4.11) are not equal to the anisotropy coefficients in Eq. (4.15) and Eq. (4.16), respectively. This difference occurs because the expansion of the geometric factor in the normal velocity \( h_t/\sqrt{1 + |\nabla h|^2} \) in the original time dependent growth model of Golovin et al. generates \( |\nabla h|^2 \) terms which modify the coefficients in the resulting equation at fourth order.

In conclusion, while Eq. (4.8) is of the same form as the stationary equation in Golovin et al., the coefficients are numerically different and the solutions obtained for both models are similar but with different dependencies on the original parameters of the system.

### 4.2 Solution along an edge

By paralleling the analysis presented in Golovin et al. (1999), we are able to determine that the far-field slope of the equilibrium shape in the presence of the regularization is independent of the regularization parameter \( \beta \) and also, that it matches the form of the far-field slope determined by Golovin et al. when there is no crystal growth. However, because of the difference in anisotropy coefficients noted above, we obtain results that differ from those of Golovin et al.

For nonzero \( \beta \), we expect the edges to become rounded. Using asymptotic analysis, we can determine the shape and slopes of the edges far from the vertex. Specifically, suppose that the shape \( h(x, y) \) has the following asymptotic behavior

\[
h \sim Ay + f(x) \quad \text{as} \quad y \to -\infty
\]  

(4.18)

where \( A \) is the slope of the edge, and \( f(x) \) is a function to be determined. For \( x \to -\infty \) we have \( h \sim Ax + f(y) \). Thus, the function \( f \) must satisfy the compatibility condition

\[
f'(\pm \infty) = \mp A.
\]  

(4.19)

By substituting Eq. (4.18) into Eq. (4.8), we obtain the following equation for \( f(x) \):

\[
-(m - bA^2)f'' + a(f')^2f'' - \beta f'''' = 0
\]  

(4.20)

Substituting an ansatz (Leung (1990))

\[
f' = Q \tanh kx
\]  

(4.21)
into Eq. (4.20) yields
\[ Q^2 = \frac{3}{a}(m - bA^2), \quad k^2 = \frac{aQ^2}{6\beta}. \] (4.22)

Since \( f' = Q \tanh kx \), as \( x \to \pm \infty \) we have the compatibility condition, \( Q^2 = A^2 \), so the slope of the edge far from the vertex is determined to be
\[ A = \sqrt{\frac{3m}{a + 3b}} \] (4.23)
which is independent of the regularization parameter \( \beta \).

In the case of kinetically controlled crystal growth, Golovin et al. (1999) determined the far-field slope of an edge to be
\[ A = \sqrt{\frac{3m - 3V_0\sqrt{3\beta/(2a)}}{a + 3b}} \] (4.24)
where \( V_0 \) is a constant driving force. If there is no growth, i.e. \( V_0 = 0 \), Eq. (4.23) and Eq. (4.24) are equal in form, but as noted previously, they are quantitatively different because of the difference in how the anisotropy coefficients \( a \) and \( b \) depend on the material parameters.

Note that the inclusion of the regularization term has permitted us to determine the far-field slope of edges, and thus, the crystal shape for \( y \to -\infty \), is given by
\[ h(x, y) \sim Ay - \sqrt{\frac{6\beta}{a}} \ln \left[ \cosh(\sqrt{\frac{a}{6\beta}}Ax) \cosh(\sqrt{\frac{a}{6\beta}}Ay) \right]. \] (4.25)

A similar description can be given for the other edges as well.

### 4.3 An exact solution

For the case \( b = 0 \), as in Golovin et al. (1999), we can determine the exact solution of Eq. (4.8) by supposing a solution of the form \( h(x, y) = f(x) + g(y) \). Substituting this into Eq. (4.8) yields two decoupled equations for \( f \) and \( g \) whose solutions can be determined as outlined in Sec. 4.2. The exact solution is given by
\[ h_{\text{exact}}(x, y) = -\sqrt{\frac{6\beta}{a}} \ln \left[ \cosh(\sqrt{\frac{a}{6\beta}}Ax) \cosh(\sqrt{\frac{a}{6\beta}}Ay) \right] \] (4.26)
where \( A = \sqrt{3m/a} \) and \( \pm A \) is the far-field slope of an edge that has been rounded by the regularization. See Fig. 4 for a graph of Eq. (4.26).
4.4 Numerical solution

Now we seek a numerical solution of Eq. (4.8) for arbitrary $a$, $b$, $c$, $m$, and $\beta$. Because of the cubic symmetry, we can restrict our attention to solving for $h(x, y)$ on a square domain of length $L$ in the first quadrant of the $xy$-plane. Since we expect the regularization to round the sharp edges and noting that $h(x, y)$ is an even function by symmetry, we determine that the boundary conditions along the positive coordinate axes are

\begin{align}
    h_x(0, y) &= h_{xxx}(0, y) = 0, \quad y \geq 0, \\
    h_y(x, 0) &= h_{yyy}(x, 0) = 0, \quad x \geq 0.
\end{align}

(4.27) (4.28)

We also expect that away from the corner and edges, the solution is well-approximated by the planar solution obtained when $\beta = 0$, i.e., $h(x, y) \sim -A(x + y)$ for $L$ large enough. This can be characterized by the conditions

\begin{align}
    h_x(L, y) &= -A, \quad h_{xx}(L, y) = 0, \quad y \geq 0
\end{align}

(4.29)
Figure 5: Numerical solution of Eq. (4.8) for $m = 0.5, a = 1.0, b = 0.1, c = 0.3$ and various values of $\beta$.

\[ h_y(x, L) = -A, \quad h_{yy}(x, L) = 0, \quad x \geq 0 \]  

(4.30)

where $A$ is given by Eq. (4.23).

To develop a numerical algorithm, we discretize Eq. (4.8), (4.27)-(4.30) using standard central finite difference schemes on a square grid where the horizontal and vertical mesh sizes, $\Delta x$ and $\Delta y$, are equal to $L/N$ and the number of grid points is $N^2$. This yields a discrete system of the form

\[ F_{i,j}(h_{i,j}, h_{i-1,j}, h_{i+1,j}, \ldots) = 0, \quad i, j = 1, \ldots, N \]  

(4.31)

where each computational molecule centered on $h_{i,j}$ contains 13 nodes. Despite the nonlinearity in Eq. (4.8), we can solve for the center node $h_{i,j}$ in Eq. (4.31) and then perform an iterating procedure where Eq. (4.26) is used as an initial guess, i.e., we set $h_{i,j}^0 = h_{\text{exact}}(x_i, y_j)$ where $A$ is given by Eq. (4.23) and $h_{i,j}^{n+1} = G(h_{i-1,j}^n, h_{i+1,j}^n, \ldots)$. Because the boundary conditions in Eq. (4.27)-(4.30) involve derivatives of $h(x, y)$, we solve for ghost points that lie outside of the computational domain using standard central finite differences. Convergence
of our algorithm is achieved when

\[
\sqrt{\frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} (F_{i,j}(h_{i,j}^{n+1}, h_{i-1,j}^{n+1}, ...))^2} < 10^{-6}.
\]

Fig. (5) illustrates the numerical solution to Eq. (4.8) for \( L = 5, N = 50 \) which closely resembles the exact solution in Fig. (4). This result demonstrates the existence of solutions to the long-wave approximation given in Eq. (4.8) which is one step towards establishing solutions for the fully nonlinear Eq. (2.13).

5 Summary

We have studied a regularization for the equilibrium crystal shape problem in three dimensions based on an anisotropic surface energy and a Willmore energy term. We have determined that even for the three-dimensional case only the single regularization term is needed. For the case of strong anisotropy, we have provided an explicit description of missing angle orientations on the Wulff shape in the absence of the regularization for cubic symmetry. Using a small-slope approximation, we have derived the governing equation for the equilibrium shape of a semi-infinite wedge with cubic symmetry in the presence of the regularization. The wedge solution obtained from this equation is a valid description of the local behavior near a regularized corner. The main results of our analysis of this equation are the following: 1) We have contrasted our model with the one derived by Golovin et al. (1999), 2) we have determined the slope of edges far from the vertex, 3) we have provided an exact solution for a special case of anisotropy, 4) we have solved the equation numerically. These results describe how the corner energy regularization modifies the equilibrium crystal shape when four faceted surfaces join to form a corner.

Acknowledgements

This research was supported by the National Science Foundation under Grant No. DMS-0505497 (BJS).
References


GURTIN, M.E. AND JABBOUR, M.E. (2002) Interface evolution in three dimensions with curvature-dependent energy and surface diffusion: Interface-controlled evol-


