Asymptotic solutions for the equilibrium crystal shape with small corner energy regularization

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Dynamic models for facet formation 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 two dimensions. Using matched asymptotic expansions we determine the explicit solution for the corner shape in the presence of the regularization. Our results show that for a class of surface energy anisotropy models the regularized solution approaches the classic sharp-corner results as the regularization approaches zero. The results validate the use of the regularization in numerical calculations for the equilibrium problem. Finally, a byproduct of the analysis is an *exact* solution for the equilibrium shape of a semi-infinite wedge in the presence of the regularization.

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I. INTRODUCTION

The role of surface energy anisotropy in determining the equilibrium shape of a solid particle in a liquid is a classic materials science problem that has been studied for over a century. Herring [1,2] reviewed the work on the so-called Gibbs-Curie problem for the equilibrium shape of a solid particle, including Wulff's construction [3] of the equilibrium shape and corrections and extensions of Wulff's proof. Post-dating Herring, many elegant alternative descriptions of the equilibrium crystal shape have been developed, such as the tangent angle formulation in Burton, Cabrera and Frank [4], the Frank plot [5], the double-tangent construction of Cabrera [6,7], the Cahn-Hoffman ξ vector [8], and Andreev's construction [9]. A modern perspective of the equilibrium crystal shape problem appears in books such as in Refs. [10] or [11].

Following Refs. [1,2], consider the two-dimensional case where the angular orientation of the surface normal is θ and the surface energy is $\gamma(\theta)$. Depending on the details of $\gamma(\theta)$, the equilibrium crystal shape ("Wulff shape") can have flat and/or curved sides which are connected smoothly or by corners (Fig. 1 illustrates the case where the shape consists of curved sides connected by corners). Flat sides correspond to facets and are possible if $\gamma(\theta)$ has cusps (local minima where γ is not differentiable). Corners can occur when it is energetically favorable to exclude high energy orientations, which occurs when the "surface stiffness" $\gamma+\gamma''$ is negative.

While the equilibrium problem is well understood, implementation of anisotropy in models for the *dynamics* of evolving surfaces creates two difficulties, the first due to cusps in $\gamma(\theta)$ and the second due to ill posedness when the surface stiffness is negative. The presence of cusps in $\gamma(\theta)$ depends on whether the system is above the thermal roughening temperature or not. We restrict our attention here to the case where the surface is thermally rough and cusps are not present. Even without the presence of facets, the issue of ill posedness due to orientations with negative stiffness makes the dynamic model intractable unless the evolution model is regularized. Without a regularization, a planar surface oriented so that it has negative stiffness will be unstable to surface wrinkling with a growth rate for the instability that diverges as the length scale of the wrinkling goes to zero [12,13]. In numerical simulations this ill posedness would manifest itself as "blow-up" on the finest scale. A regularizing term smooths the small-scale instability and removes the ill posedness.

One approach that has been used extensively in the literature for regularizing the ill-posed problem is to add a higher-order term to the surface energy [13–27]. The main idea is to include an additional term in the surface energy, which penalizes sharp corners and makes them rounded on a small length scale. A simple model for the two-dimensional problem is [1,13,14,17,18]

$$\gamma = \gamma_0(\theta) + \beta\kappa^2, \tag{1}$$

where κ is the curvature of the surface and β is taken as an isotropic "corner energy" parameter. Sharp corners correspond to $|\kappa|\to\infty$ and thus make the effective surface energy γ divergent. In the equilibrium problem, minimization of the

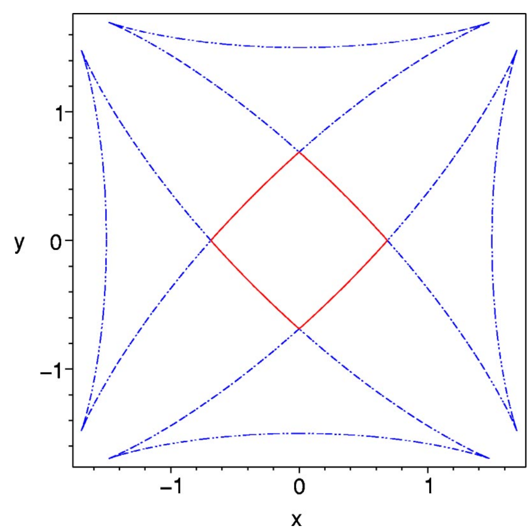

FIG. 1. (Color online) Equilibrium crystal shape for $\gamma(\theta)$ given by Eq. (14) with $\alpha=0.5$ and $\mu=1$. The crystal shape is shown as solid (red) curves, and the unphysical "ears" are shown as dashed (blue).

effective surface energy should lead to corner rounding. Since a large curvature at the corner has high energy because of the regularization, and a small 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.

This regularization was first proposed by Herring for the equilibrium problem in Ref. [1]. Herring determined a crude order-of-magnitude estimate of the effect of this regularization by replacing the corner between two facets with a rounded corner with constant radius of curvature. The regularization was first suggested for the dynamic problem in Ref. [14] and then studied in Ref. [13] (see also Refs. [17]). This model or a linearized version of it has been used in the dynamic models of facet formation in Refs. [15,16,18–21,23–25], calculation of equilibrium island shapes in strained epitaxial films [28], and in equilibrium and dynamic calculations of void shapes in stressed solids [26]. In Ref. [18] the regularization is derived from the interaction of atomic-scale steps near a corner. The thermodynamics of this regularization and its correct representation in three-dimensional models involving surface diffusion and phase transitions has appeared in Ref. [22], and Ref. [27] includes this regularization in a comprehensive general treatment of thermodynamics and kinetics of evolving interfaces.

The plausibility of the regularization for rounding corners is clear, however, to our knowledge there has not yet been a concrete description of how this regularization affects the basic problem of equilibrium crystal shapes. It is expected that as $\beta \rightarrow 0$ we should recover the Wulff shape, but since the additional higher-order term is a nonlinear singular perturbation it is not obvious that the $\beta = 0$ results are recovered in the limit of $\beta \rightarrow 0$. Herring's original work [1] suggested that adding a curvature dependence to the surface energy would round corners of the Wulff shape. In this work, however, the true equilibrium shape was not determined. Rather, an order-of-magnitude estimate was obtained by assuming that the corner would have a constant radius of curvature. From energy minimization of corners with constant radius of curvature it was found that the radius of curvature ρ was proportional to $\beta^{1/2}$. Technically, however, imposing a constant radius of curvature at the corner does not satisfy the conditions of equilibrium for the regularized problem, and so the question of the actual corner shape was not resolved.

More recent work has studied the regularization in more detail, but has not addressed the equilibrium shape problem directly. DiCarlo *et al.* [13] was the first to study the regularization extensively, but the work focuses on the regularization in the context of dynamics for an evolving interface. Liu and Metiu [16] discuss the equilibrium problem in the absence of regularization, and use the regularization in the dynamic problem, but do not consider the effect of the regularization for the equilibrium problem. Siegel *et al.* [26] determine the equilibrium shape of a void numerically for a particular choice for the anisotropy $\gamma_0(\theta) = \gamma^*[1 + 0.15\cos(4\theta)]$ and show that the Wulff shape is recovered as the regularization is reduced to zero. While it is expected that similar results would hold for other values of the parameters and other functional forms for the anisotropy, such results have not been demonstrated in general, so it is not clear if the Wulff shape is always recovered for any form of the anisotropy.

The scope of the present work is to use asymptotic analysis to show in general that there are no surprises regarding the effect of this regularization on the equilibrium shape, even though it enters as a nonlinear singular perturbation. For a broad class of anisotropies, the Wulff shape is always recovered as the regularization approaches zero. Moreover, a central result of the work is an explicit solution for the shape near the corner in the presence of the regularization, as well as a description of the entire equilibrium shape. Finally, in deriving these results we also obtain the *exact* regularized solution for the semi-infinite wedge geometry.

For clarity, we restrict our attention to a two-dimensional system corresponding to a solid particle surrounded by a liquid (or vapor) (see Fig. 1). The generalization to three dimensions is not trivial and is not attempted here. We also restrict ourselves to the case where $\gamma(\theta)$ is sufficiently smooth (twice differentiable), so we do not consider the case where γ has cusps and the equilibrium shape has facets.

The equilibrium shape is constructed using matched asymptotic expansions [29]. Away from a corner the regularization term is not important and the shape is governed by the Wulff construction. Near the corner, the local behavior is governed by a nonlinear differential equation in which the corner energy plays a controlling role. The nonlinearity of the corner problem poses a challenge for the construction of solutions which round the corner and match the appropriate "Wulff" angles of the outer solution. However, we show that the corner problem can be reduced to a linear double-eigenvalue problem, and the only solution to this eigenvalue problem that corresponds to a rounded corner is the one which precisely matches the Wulff angles at the corner. The resulting composite solution consists of the rounded corner solution near the corner and the Wulff shape away from the corner. The results mean that for a class of surface energy anisotropies the regularized solutions recover the Wulff shape as the regularization goes to zero. The convergence of the asymptotic results also provides a validation for using the regularization in computations of the equilibrium shape; numerical calculations should converge to the Wulff-shape provided the regularization is sufficiently small, as seen in the numerical example of Ref. [26].

The asymptotic solution near the corner is similar to some of the analytical results for the dynamics of corners in Refs. [23–25] (see also related work in Refs. [18–21]). The main difference is that here the fully nonlinear regularization is employed in the corner region, whereas in Refs. [23–25] the model equation contains only the linearized regularization term. When the regularization term is linearized, as is appropriate for a small-slope theory of an evolving interface, there is a strong parallel between slope selection at a facet corner and spinodal decomposition in the Cahn-Hilliard equation and the convergence of the regularized solutions to the zero-regularization solution is easily established [25] (see also the discussion in Ref. [18]). The analysis presented here extends the small-slope results to the case where nonlinear effects are important at the corner (but only for the case of equilibrium). Another work related to the corner problem in the presence of the regularization is Ref. [30], where existence and uniqueness results were demonstrated for a semi-infinite wedge with a rounded corner and prescribed far-field orientations. The paper is primarily concerned with the dynamics of evolving corner solutions, but one part of the work applies to the equilibrium problem and is potentially applicable to the local corner problem. However, the work is restricted to orientations for which the stiffness is negative and thus the work does not apply to equilibrium crystal shape problem for which the corner orientations are stable and with positive stiffness.

The rest of this paper is organized as follows. In Sec. II we formulate the problem in nondimensional variables. In Sec. III we review the Wulff shape obtained by setting the corner energy parameter to zero. In Sec. IV we use matched asymptotic expansions to construct the equilibrium shape when the corner energy parameter is small. We find explicit solutions for the corner behavior and demonstrate that it can always match to the corner angles prescribed by the Wulff shape. In Sec. V we present the solution for a semi-infinite wedge, obtained as a by-product of our analysis. Finally, in Secs. VI and VII we discuss and summarize the main results.

II. FORMULATION

Let the solid surface be described by a closed curve in (x_*, y_*) space, parametrized by the orientation angle θ and the arclength s_*, where s_* traverses the boundary of the solid with the solid on the right and θ is measured clockwise from a fixed reference orientation, say $(0,1)$. The local curvature of the surface is taken as positive for a solid bump, which is given by

$$\kappa_* = + \frac{d\theta}{ds_*} \tag{2}$$

when the solid is interior to the boundary (but includes a minus sign when the solid is exterior to the boundary).

The total surface energy per unit length of the surface is described by an anisotropic surface energy density $\gamma_*(\theta)$ and a corner regularization $\frac{1}{2}\beta_*\kappa_*^2$ [1,13,14,18],

$$\tilde{\gamma}_* = \gamma_*(\theta) + \tfrac{1}{2}\beta_*\kappa_*^2 . \tag{3}$$

The total energy of the surface is

$$E_* = \int \tilde{\gamma}_* ds_* . \tag{4}$$

Minimizing the total energy of the surface subject to the constraint of fixed solid area A_* enclosed by the curve gives the modified form of Herring's equation [31] for the chemical potential μ_* at the surface of the solid, which here includes the effect of the regularization [13],

$$\mu_* = \Gamma_*(\theta)\kappa_* - \beta_* C_*(\kappa_*), \tag{5}$$

where

$$\Gamma_*(\theta) = \gamma_*(\theta) + \gamma_*''(\theta) \tag{6}$$

is the surface stiffness and

$$C_*(\kappa) = \frac{d^2\kappa_*}{ds_*^2} + \tfrac{1}{2}\kappa_*^3 \tag{7}$$

is a corner energy term. At equilibrium the surface satisfies $\mu_* = \text{const}$, and bounds a solid with prescribed area A_*.

Without loss of generality we can restrict our attention to the case $\mu_* \geqslant 0$. The case $\mu_* < 0$ is equivalent to the case $\mu_* > 0$ under the transformations $\mu_* \to -\mu_*$ and $\kappa_* \to -\kappa_*$, 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 in the presence of the regularized corner term.

In the following derivation of equilibrium shapes, we shall consider a general form for $\gamma_*(\theta)$. We only require that $\gamma_*(\theta)$ and its derivatives up to γ_*'' are 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 a fourfold anisotropy,

$$\gamma_*(\theta) = \gamma_0[1 + \alpha\cos(4\theta)], \tag{8}$$

where $0 \leqslant \alpha < 1$ measures the degree of anisotropy.

We define a length scale L as a characteristic radius of the solid region from $A_* = \pi L^2$. Let γ_0 be a characteristic value of the surface energy. In nondimensional form, the equilibrium condition becomes

$$\mu = \Gamma(\theta)\frac{d\theta}{ds} - \beta\left[\frac{d^3\theta}{ds^3} + \tfrac{1}{2}\left(\frac{d\theta}{ds}\right)^3\right], \tag{9}$$

where

$$\Gamma(\theta) = \Gamma_*(\theta)/\gamma_0 , \tag{10}$$

$$s = s_*/L, \tag{11}$$

$$\beta = \beta_*/(\gamma_0 L^2), \tag{12}$$

and

$$\mu = \mu_* L/\gamma_0 . \tag{13}$$

In the above equations, the parameter β measures the relative contribution of the corner energy $\beta_*\kappa_*^2 \sim \beta_*/L^2$ to the surface energy $\gamma \sim \gamma_0$. The nondimensional area constraint is A, and in nondimensional form the surface energy model for the example is

$$\gamma(\theta) = 1 + \alpha\cos(4\theta). \tag{14}$$

Finally, the value of μ is unspecified, but is determined so that the area of the solid particle satisfies the area constraint.

III. SOLUTIONS IN THE ABSENCE OF REGULARIZATION

The equilibrium shape problem when $\beta=0$ has been solved from a variety of approaches [1–9]. We summarize the results here in some detail, as they play an important role in the regularized case discussed later. We follow most closely to Refs. [6,7] and [4].

When $\beta=0$, the chemical potential can be absorbed into the length scale. Defining

$$\tilde{s}=s\mu \tag{15}$$

the outer problem becomes

$$\Gamma(\theta)\frac{d\theta}{d\tilde{s}}=1. \tag{16}$$

The shape of the particle is found from Eq. (16), and it has a corresponding area $\tilde{A}$. The area constraint is then satisfied by choosing μ appropriately so that $\tilde{A}=\mu^2 A$, giving

$$\mu=\sqrt{\tilde{A}/A}. \tag{17}$$

Put another way, in the absence of the corner energy term, the shape of the crystal is independent of the crystal size and can be found by solving the problem for $\mu=1$, giving a crystal with area $\tilde{A}$. The effect of μ is to modify the length scale, so by choosing μ appropriately crystals of different area can be constructed. Viewed in this way, μ scales inversely with the dimensions of the crystal: small particles correspond to $\mu\to\infty$ while large particles correspond to $\mu\to 0^+$. The special case $\mu=0$ corresponds to a semi-infinite domain and will be discussed in Sec. V.

The crystal shape determined from integrating Eq. (16) is

$$s=\int_0^\theta \Gamma(\theta)d\theta, \tag{18}$$

which gives an implicit definition of $\theta(s)$. The shape in (x,y) coordinates can then be determined from integrating

$$\frac{dx}{ds}=\cos(\theta), \tag{19}$$

$$\frac{dy}{ds}=-\sin(\theta). \tag{20}$$

It can be shown [4] that the resulting solutions are equivalent to

$$x=\gamma'(\theta)\cos(\theta)+\gamma(\theta)\sin(\theta), \tag{21}$$

$$y=-\gamma'(\theta)\sin(\theta)+\gamma(\theta)\cos(\theta). \tag{22}$$

Construction of the crystal shape depends on the details of $\gamma(\theta)$. If $\Gamma(\theta)=\gamma+\gamma''\geqslant 0$ then the crystal shape is given exactly by the above description. If $\Gamma(\theta)<0$ for some orientations then the surface has orientations with negative "stiffness." In a dynamic setting, a negative stiffness makes the evolution problem ill-posed: orientations with negative stiffness have Fourier components with temporal growth rates that diverge as the spatial frequency becomes large. In the equilibrium shape problem, the orientations with negative stiffness generate a crystal shape with nonphysical "ears." See Fig. 1 for an example.

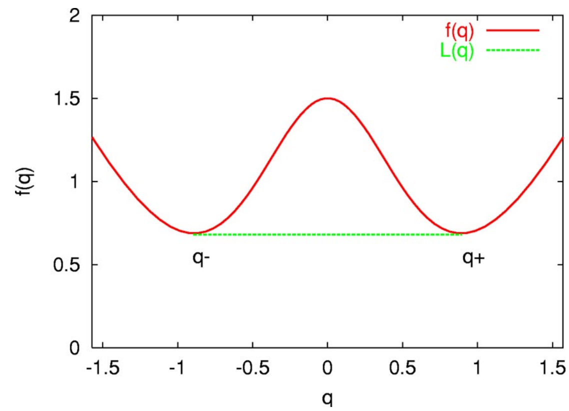

FIG. 2. (Color online) Projected surface energy $f(q)$ and common tangent construction $L(q)$ for the $\cos(4\theta)$ model with $\alpha=0.5$.

In the case where the crystal has nonphysical ears, one can determine the corner orientations by locating the points where $[x(\theta),y(\theta)]$ crosses itself. Without loss of generality, we can orient the crystal so that $\gamma(0)$ is a local maximum and $\Gamma(0)<0$. The corner orientations on either side of the corner, $\theta=\theta_c^-,\theta_c^+$, are given from the two jump conditions

$$[x]\Big|_{\theta_c^-}^{\theta_c^+}=0, \tag{23}$$

$$[y]\Big|_{\theta_c^-}^{\theta_c^+}=0. \tag{24}$$

For the special case where $\gamma(\theta)$ is symmetric with respect to the reference orientation, then the corner is symmetric with orientations given by $\pm\theta_c$ where $\theta_c>0$ is the root of

$$\tan(\theta_c)=-\frac{\gamma'(\theta_c)}{\gamma(\theta_c)}. \tag{25}$$

Cabrera [7] showed that truncating the unphysical ears of the crystal does, in fact, correspond to minimizing the energy. This was done by formulating the solution to the energy minimization problem in terms of a common-tangent convexification of a nonconvex energy function. In this reformulation, the common tangent spans the range of orientations which are missing at the corner, and the ears correspond to portions of the energy surface which lie above the common tangent and are hence higher energy (see Fig. 2). To show this analogy in detail, define the surface slope of the crystal as

$$q=\tan(\theta), \tag{26}$$

where $-\pi/2<\theta<\pi/2$, and define the projected energy on the x axis as

$$f(q)=\frac{\gamma(\theta)}{\cos(\theta)}. \tag{27}$$

The convexity of $f(q)$ is determined by the sign of the surface stiffness, since

$$\frac{d^2f}{dq^2}=\cos^3(\theta)[\gamma(\theta)+\gamma''(\theta)]. \tag{28}$$

Cabrera showed that if $\gamma+\gamma''>0$ for all orientations then $f(q)$ is convex and the stable equilibrium shape consists of all orientations. If $\gamma+\gamma''<0$ for some orientations, then $f(q)$ has regions which are nonconvex. In this case, the energy is minimized by the convex envelope to $f(q)$, in which the portion of the energy surface containing the nonconvex region is replaced by the common tangent $L(q)$. The energy minimizing shape is then obtained by omitting those orientations spanned by the common tangent to the double-well curve (see Fig. 2). Thus, the end points of the common tangent (q_- and q_+) give the slopes at the corner of the crystal associated with minimum energy. Furthermore, since Eqs. (21) and (22) for the equilibrium shape are equivalent to

$$x=\frac{df}{dq}, \tag{29}$$

$$y=f-q\frac{df}{dq}, \tag{30}$$

the end points of the common tangent also correspond to the crossover points marking the ears on the equilibrium shape. To see this, use Eqs. (29) and (30) in the corner conditions [Eqs. (23) and (24)] to obtain

$$\left[\frac{df}{dq}\right]\Bigg|_{q_-}^{q_+}=0, \tag{31}$$

$$\left[f-q\frac{df}{dq}\right]\Bigg|_{q_-}^{q_+}=0, \tag{32}$$

which are precisely the statement of the conditions for the common tangent to $f(q)$ at q_-,q_+; Eq. (31) requires that the slope of the tangents at both points is the same, and Eq. (32) requires that the tangents have the same f intercept. Thus, truncating the unphysical ears of the equilibrium shape obtained from Eqs. (21) and (22) is identical to the energy minimizing shape obtained from the common tangent construction in which orientations spanned by the common tangent are omitted at the corner.

IV. ASYMPTOTIC SOLUTIONS

We now determine how the Wulff shape of Sec. III is modified by the corner energy regularization. When $\beta=0$ the equilibrium crystal shape has sharp corners with a well-defined jump in orientations across the corner. For $\beta>0$ it is expected that the corner energy term penalizes regions of high curvature and so leads to a rounded corner. 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 corner rounding. In physical terms, this means that the atomic dimensions usually associated with the corner are much smaller than the dimensions of the crystal, which is satisfied except for nanoscale crystals.

Inspection of Eq. (9) shows that β enters with a higher-order derivative and is thus a singular perturbation. When $\beta=0$ the surface equation is a first-order differential equation, while for $\beta>0$ the equation is a third-order differential equation. A reasonable approach then is to treat the $\beta=0$ problem as the "outer" problem and then look for boundary layer solutions which round the corners and connect adjacent pieces of the outer solution.

A. Corner problem and solution

Without loss of generality, we take the reference orientation for θ to lie in the range of missing orientations, $\Gamma(0)<0$. This means the corner orientations are of opposite sign with $\theta_c^-<0$ and $\theta_c^+>0$.

We define $s=0$ at the corner of the outer solution and look for a corner-layer solution for $s\ll 1$. Letting

$$s=\epsilon S \tag{33}$$

and

$$\theta(s)=\tilde{\Theta}(S), \tag{34}$$

we find a dominant balance in Eq. (9) when $\epsilon=\beta^{1/2}$, and the resulting inner problem is

$$\beta^{1/2}\mu=\Gamma(\tilde{\Theta})\frac{d\tilde{\Theta}}{dS}-\left[\frac{d^3\tilde{\Theta}}{dS^3}+\tfrac{1}{2}\left(\frac{d\tilde{\Theta}}{dS}\right)^3\right]. \tag{35}$$

We then seek an inner solution as an expansion in $\beta^{1/2}$,

$$\tilde{\Theta}(S)=\Theta(S)+\beta^{1/2}\Theta_1(S)+\beta\Theta_2(S)+\cdots. \tag{36}$$

The $O(1)$ problem for the corner shape is the nonlinear third-order differential equation

$$\frac{d^3\Theta}{dS^3}-\Gamma(\Theta)\frac{d\Theta}{dS}+\tfrac{1}{2}\left(\frac{d\Theta}{dS}\right)^3=0. \tag{37}$$

Note that μ does not appear in the leading order problem and so the corner problem is generic in the sense that it is independent of μ (and hence independent of the crystal size) in the limit of $\beta\to 0$. For our corner shape we seek a solution that rounds the corner and decays to a constant orientation far away,

$$\Theta\to\Theta_\infty^\pm \quad \text{as } S\to\pm\infty. \tag{38}$$

To match the $\beta=0$ solution with corner orientations $\theta_c^\pm$, we would need the far-field values of the inner solution to be identically the corner orientations $\Theta_\infty^\pm=\theta_c^\pm$. Noting that the inner problem is autonomous, the final boundary condition specifies the origin for the inner problem,

$$\Theta = 0 \quad \text{at } S = S_0. \tag{39}$$

In the special case where the surface energy is symmetric with respect to the corner, the symmetries can be used in the inner problem. The symmetric version of the inner problem and its solution are presented in the Appendix.

Because the inner problem is nonlinear, it is not obvious that there exist solutions which round a corner and approach constant orientations $\Theta_\infty^\pm$ far away. Even if solutions of this type exist, it is also not clear that there is sufficient freedom to choose the orientations $\Theta_\infty^\pm = \theta_c^\pm$ far away. Despite these apparent uncertainties, we shall show that this matching can always be accomplished.

In principle, the nonlinear equation (37) is difficult to solve for arbitrary $\Gamma(\Theta)$. However, the problem can be transformed by first treating Θ as the independent variable and defining

$$K = \frac{d\Theta}{dS} \tag{40}$$

as the dependent variable as in Ref. [13] to obtain

$$K\left[\frac{d^2}{d\Theta^2}\left(\tfrac{1}{2}K^2\right) + \left(\tfrac{1}{2}K^2\right) - \Gamma(\Theta)\right] = 0. \tag{41}$$

Excluding the trivial solution $K = 0$ and defining

$$Q(\Theta) = \tfrac{1}{2}K^2 \tag{42}$$

we obtain the *linear* problem

$$\frac{d^2 Q}{d\Theta^2} + Q = \Gamma(\Theta). \tag{43}$$

The boundary conditions on $Q(\Theta) = \frac{1}{2}K^2$ now correspond to the behavior of the curvature. Far away we seek a solution in which the curvature approaches zero as the orientation approaches its far-field value. Thus the boundary conditions on $Q(\Theta)$ are two-point boundary values,

$$Q = 0 \quad \text{at} \quad \Theta = \Theta_\infty^\pm. \tag{44}$$

However, since $Q'(\Theta) = K^2(dK/dS)$, and since $dK/dS \to 0$ as $\Theta \to \Theta_\infty^\pm$, we also have the additional boundary conditions

$$\frac{dQ}{d\Theta} = 0 \quad \text{at } \Theta = \Theta_\infty^\pm. \tag{45}$$

The transformed problem for $Q(\Theta)$ now is now linear and second order, but the four boundary conditions make the problem overdetermined. The extra degrees of freedom needed to satisfy the boundary conditions come from the choice of $\Theta_\infty^\pm$. In this new formulation, $\Theta_\infty^\pm$ play the role of eigenvalues for the inhomogeneous problem. While it seems possible that $\Theta_\infty^\pm$ might be found to construct the inner solution, at this stage it seems questionable that these eigenvalues would necessarily match the required corner orientations $\theta_c^\pm$.

The explicit solution to the linear problem is straightforward to construct. Recalling that $\Gamma = \gamma + \gamma''$ it is seen that the particular solution to the differential equation is just $Q(\Theta) = \gamma(\Theta)$ and the general solution is explicitly given by

$$Q(\Theta) = \gamma(\Theta) + A\cos(\Theta) + B\sin(\Theta), \tag{46}$$

where A and B are constants. The boundary conditions give

$$A = -[\gamma(\Theta_\infty^+)\cos(\Theta_\infty^+) - \gamma'(\Theta_+)\sin(\Theta_\infty^+)], \tag{47}$$

$$B = -[\gamma(\Theta_\infty^+)\sin(\Theta_\infty^+) + \gamma'(\Theta_\infty^+)\cos(\Theta_\infty^+)], \tag{48}$$

with Θ_∞^+ and Θ_∞^- determined by

$$[\gamma(\Theta)\cos(\Theta) - \gamma'(\Theta)\sin(\Theta)]\Big|_{\Theta_\infty^-}^{\Theta_\infty^+} = 0, \tag{49}$$

$$[\gamma(\Theta)\sin(\Theta) + \gamma'(\Theta)\cos(\Theta)]\Big|_{\Theta_\infty^-}^{\Theta_\infty^+} = 0. \tag{50}$$

Note that Eqs. (49) and (50) are precisely those used in the determination of the corner orientations in the outer problem, Eqs. (21) and (24), and hence are also equivalent to the common tangent conditions (31) and (32). Thus, given that the outer problem does in fact have a corner, then the existence of the common-tangent construction for the outer solution, [Eqs. (31) and (32)], guarantees existence of the solution for the eigenvalues in the inner problem [Eqs. (49) and (50)], as the conditions determining these eigenvalues are identical with the conditions determining the common tangent. Further, the correspondence of the common-tangent conditions and inner boundary conditions means that *equilibrium solutions which correspond to rounded corners can only exist between orientations determined by the common-tangent construction.* Finally, since the conditions on $\Theta_\infty^\pm$ in the inner solution and $\theta_c^\pm$ are determined by the same equations, the inner solution always matches the Wulff angle of the outer solution,

$$\Theta_\infty^\pm = \theta_c^\pm, \tag{51}$$

and guarantees matching of the inner and outer solutions. It then follows that if self-consistent corner orientations are prescribed for the outer solution, then the resulting $Q(\Theta)$ is unique.

Once $Q(\Theta)$ is known, we invert to find the curvature

$$K = \pm\sqrt{2Q(\Theta)}, \tag{52}$$

where we choose the $+$ sign to obtain the physically relevant corner solution for a solid lying on the interior of the boundary. For K to be real, we need $Q(\Theta) \geqslant 0$. This is, in fact, true but not obvious from Eq. (46). To show that it is true, define q and $f(q)$ as in Eqs. (26) and (27) replacing θ by Θ and let the common tangent to $f(q)$ from q_- to q_+ be the line

$$L(q) = mq + b. \tag{53}$$

Then identifying $A=-b$ and $B=-m$ we can rewrite Eq. (46) as

$$Q(\Theta)=\cos(\Theta)[f(q)-L(q)]. \tag{54}$$

Since $L(q)<f(q)$ in $q_-<q<q_+$ by the common-tangent construction, it follows that

$$Q(\Theta)>0 \quad \text{for} \quad \Theta_\infty^-<\Theta<\Theta_\infty^+. \tag{55}$$

Therefore real values of K are also guaranteed.

Finally, the inner solution in terms of (Θ,s) can be found from integration of Eq. (40) to obtain

$$S=\int_0^\Theta \frac{1}{K}d\Theta+S_0, \tag{56}$$

where S_0 determines the local surface coordinate where $\Theta=0$. Once $S(\Theta)$ is determined, it can be inverted to find $\Theta(S)$ since $d\Theta/dS>0$ for $\Theta_\infty^-<\Theta<\Theta_\infty^+$.

B. Matching of outer and corner solutions

Having constructed the local corner solution we now verify that it matches the outer Wulff shape. As we have confirmed that $\Theta_\infty^\pm=\theta_c^\pm$ in the preceding section, we expect matching to be satisfied without difficulty.

Consider matching $\Theta\to\Theta_\infty^+$ as $S\to\infty$. We define the intermediate variable

$$s_*=s/\eta, \tag{57}$$

where $\beta^{1/2}\ll\eta\ll 1$. Expanding the inner solution (56) in the intermediate variable we find

$$\tilde{\Theta}=\Theta_\infty^+-C\exp(-\lambda s_*\eta/\beta^{1/2})+O(\beta^{1/2}), \tag{58}$$

where C is a constant and

$$\lambda=\sqrt{Q''(\Theta_\infty^+)}\ >\ 0 \tag{59}$$

gives exponential decay of the second term in Eq. (58). Expanding the outer solution (18) in the intermediate variable we find

$$\theta=\theta_c^++\eta\frac{s_*}{\Gamma(\theta_c^+)}+\cdots. \tag{60}$$

Thus, by virtue of Eq. (51) the inner and outer solutions match at leading order. The matching problem as $S\to-\infty$ is similar to that for $S\to+\infty$.

C. Composite solution

The above analysis describes the local behavior near a single corner. Each corner of the outer solution has its own inner solution describing the rounding of the corner. Let the corners of the outer solution be denoted by i and the inner solution at corner i be θ_{inner}^i. The leading-order composite solution is constructed from

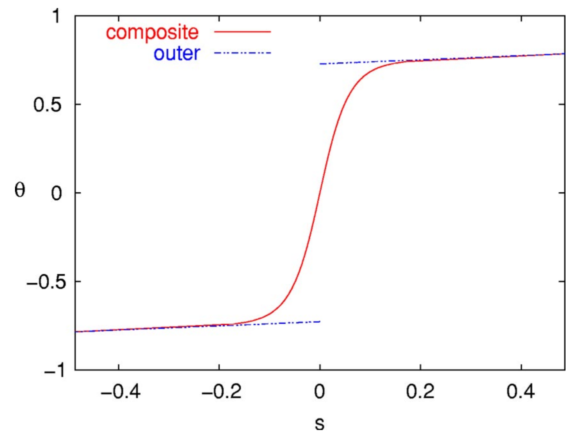

FIG. 3. (Color online) Asymptotic solution for corner with regularization. Shown is the orientation θ versus arclength coordinate s. The dashed (blue) curve is the outer solution with a jump in orientation at the corner corresponding to the Wulff shape. The solid (red) curve is the composite solution from the asymptotic analysis with a transition layer thickness of order $\beta^{1/2}$. The parameters here are $\alpha=0.5$ and $\beta=0.01$.

$$\theta(s)=\theta_{outer}+\sum_i\ [\theta_{inner}^i-\theta_{match}^i], \tag{61}$$

where θ_{match}^i is the matching behavior of θ_{outer} and θ_{inner}^i in the neighborhood of corner i.

D. Summary

The above results describe the leading-order approximation to the equilibrium shape as an expansion in the small corner energy parameter β. In this solution, each corner has a local solution which rounds the corner between angles of the Wulff shape. The width of this corner-rounding region scales with $\beta^{1/2}$ and the radius of curvature in this region is of order $\beta^{1/2}$, as in Herring's original estimate [1]. As β decreases, the scale of the corner rounding decreases but the shape of the corner is preserved. Thus, in the limit $\beta\to 0$ the equilibrium shape converges to the Wulff shape with infinitesimal corner rounding.

E. Example

As a specific example, consider the fourfold anisotropy model in Eq. (14) for $\alpha=0.5$ with a corner energy $\beta=0.01$. We apply the above general results to this model to determine how the corner is rounded by the regularization. The outer solution has corners centered at $\theta=0$ and increments of $\pi/2$ as shown in Fig. 1.

Figure 3 shows the local behavior near the corner at $\theta=0$. The outer solution has a discontinuous jump in θ at the corner. The composite solution smoothes the jump transition in θ over a transition layer of thickness $O(\beta^{1/2})$.

The equilibrium shape in (x,y) coordinates is obtained using Eqs. (19) and (20) to integrate $\theta(s)$ from Fig. 3 to find the shape in the (x,y) coordinates. The results are shown in Fig. 4. The composite solution rounds the corner in a transition region of thickness $O(\beta^{1/2})$, but away from the corner it

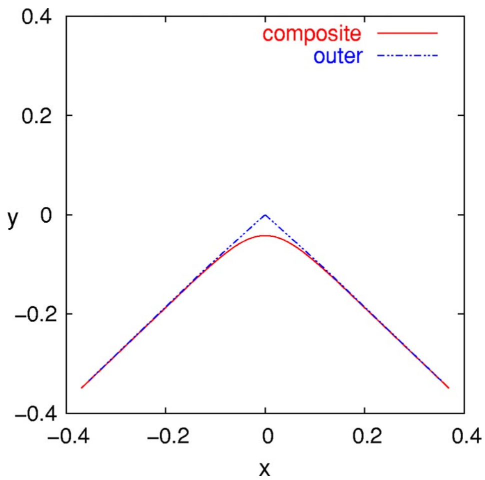

FIG. 4. (Color online) Asymptotic solution for corner with regularization. The dashed (blue) curve is the outer solution with a jump in orientation at the corner. The solid (red) curve is the composite solution from the asymptotic analysis with a transition layer thickness of order $\beta^{1/2}$. The parameters here are $\alpha=0.5$ and $\beta=0.01$.

precisely matches the outer solution obtained from setting $\beta=0$.

One feature of the composite solution apparent from Fig. 4 is that the corner rounding causes a decrease in the area of the enclosed region. Since the corner rounding is of $O(\beta^{1/2})$ over a width of $O(\beta^{1/2})$ the decrease in area is $O(\beta)$. As discussed earlier, the choice of μ controls the overall area of the crystal via the outer solution. To retain the area of the original outer solution, the value of μ would have to be adjusted by an order β correction. Alternatively, if one views μ as prescribed, say for a particle in an environment with constant chemical potential, then the corner rounding corresponds to a small dissolution of the corners to maintain constant chemical potential on the surface of the crystal.

V. SEMI-INFINITE WEDGE SOLUTION

Here we describe the *exact* solution for the equilibrium shape of a semi-infinite wedge in the presence of the corner regularization. The problem for the semi-infinite wedge in dimensional form is obtained by taking $\mu_*=0$ in Eq. (5) with the boundary conditions,

$$\theta\to\theta_\infty^\pm \quad \text{as} \quad s_*\to\pm\infty, \tag{62}$$

$$\theta=0 \quad \text{at} \quad s_*=s_*^0. \tag{63}$$

Defining a length scale as $L=(\beta^*/\gamma_0)$ and defining a nondimensional arclength $S=s_*/L$, with $\Theta(S)=\theta(s_*)$, we obtain the nondimensional wedge problem

$$\Gamma(\Theta)\frac{d\Theta}{dS}-\left[\frac{d^3\Theta}{dS^3}+\tfrac{1}{2}\left(\frac{d\Theta}{dS}\right)^3\right]=0, \tag{64}$$

$$\Theta\to\Theta_\infty^\pm \quad \text{as} \quad S\to\pm\infty \tag{65}$$

$$\Theta=0 \quad \text{at} \quad S=S_0, \tag{66}$$

which is exactly the same form as Eqs. (37)–(39) for the leading-order solution to the inner problem. In Eqs. (40)–(56) we derive the exact solution to this problem and show that the only permissible far-field orientations for the wedge are those given by the common-tangent construction for the Wulff angles. Thus, in the context of the semi-infinite wedge, influence of the regularization determines that the only possible wedge solutions are those that correspond to Wulff orientations far away from the corner.

VI. DISCUSSION

The main result of this analysis is that there are no surprises regarding the effect of the corner regularization term on the equilibrium shape in two dimensions. For any anisotropy $\gamma(\theta)$ which has continuous derivatives up to γ'', the local asymptotic solution rounding the corner can be constructed when corner regularization β is small. As the regularization approaches zero, the size of the rounded corner region approaches zero and the equilibrium shape approaches the Wulff shape. The robustness of the corner regularization results may also be interpreted as a validation of using the regularization in numerical calculations of the equilibrium shape; if the regularization is small enough, the calculated shapes should correspond to the sharp-corner results in the absence of the regularization. While the "no surprises" result holds for the equilibrium problem in two dimensions, there are important extensions for which the role of the regularization is still not clear.

Generalization to three dimensions. The generalization to three dimensions is not trivial. What were corners in two dimensions become either edges or apex points in three dimensions. The local problem for an apex between three different orientations would require finding an inner solution to the nonlinear partial differential equation which matched the three far-field orientations corresponding to the neighboring orientations of the apex. While some of the ideas here might apply to the three-dimensional case, such an extension is a significant challenge.

Effect of stress on corner angles. In many applications elastic energy is an important factor in the determination of the equilibrium crystal shape. For example, in strained solid films, elastic strain causes the formation of "islands" in films which would be planar in the absence of strain (see, for example, Ref. [28]). When the crystal has sharp corners it has been shown that elastic energy should not affect the permissible *microscopic* corner angles determined from surface energy alone [32,33] (see also Ref. [34]). However, whether this conclusion holds for the regularized model has not been firmly established. As with the problem without stress, the issue is that the regularization enters as a singular perturbation and the behavior might be different than the results in the absence of the regularization. The only analysis so far on this question is in the work of Siegel *et al.* [26], who numerically determine the effect of the regularization on corner angles of voids in the presence of elastic stress. Their numerical results show that in the presence of the regularization, elastic stress can make the apparent corner angle different from the Wulff angle, and that this difference persists as the regularization becomes small. These results suggest that there may be a generalization of the analysis presented here in which the influence of elastic energy in the regularized corner region alters the permissible matching behaviors for the outer solution, in effect modifying the Wulff angle.

VII. SUMMARY

We have considered the effect of a small corner-energy regularization on the equilibrium shape of a crystal in two dimensions. By taking the corner-energy parameter as small, we were able to construct a leading-order solution using matched asymptotic expansions. The ''outer'' problem corresponds to the Wulff shape. The ''inner'' problem for the corner is a nonlinear problem. By transforming the nonlinear problem into a linear eigenvalue problem we have shown that there is only one local solution that rounds a corner, and it necessarily must match the equilibrium Wulff shape. In particular, by formulating the problem in terms of the projected surface energy as a function of the slope, we show that the common tangent construction for minimizing the energy of the crystal in the absence of the corner energy also plays a critical role in determining the shape of the rounded corner. The main results of the analysis are the following.

(1) We demonstrate that the regularized solutions approach the classic equilibrium shape as the regularization approaches zero.

(2) We give an analytic formulation for the shape of the corner in the presence of the regularization.

(3) The work validates the use of the corner-energy regularization in numerical calculations of equilibrium shapes in two dimensions; for sufficiently small regularization the regularized solutions can be made arbitrarily close to the classic sharp-corner results.

(4) A by-product of the work is an exact solution for the equilibrium shape of a semi-infinite wedge in the presence of the regularization. Regularized wedge solutions only exist for far-field orientations corresponding to Wulff angles.

Finally, the generalization of these results to include the effects of elasticity and/or three dimensions was discussed.

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APPENDIX A: SYMMETRIC CORNER SOLUTION

Here we present the simplified results for the inner problem when surface energy is symmetric with respect to the corner orientation. The symmetric corner shape $\Theta(S)$ is given by the nonlinear third-order differential equation (37) as in the nonsymmetric case. The boundary conditions (38) and (39) are replaced by

$$\Theta \to \Theta_\infty \quad \text{as} \quad S \to +\infty, \tag{A1}$$

$$\Theta = 0 \quad \text{at} \quad S = 0, \tag{A2}$$

$$\frac{d^2\Theta}{dS^2} = 0 \quad \text{at} \quad S = 0. \tag{A3}$$

Applying the transformation in Eqs. (40)–(42) yields Eq. (43) with the boundary conditions

$$\frac{dQ}{d\Theta} = 0 \quad \text{at} \quad \Theta = 0, \tag{A4}$$

$$Q = 0 \quad \text{at} \quad \Theta = \Theta_\infty, \tag{A5}$$

$$\frac{dQ}{d\Theta} = 0 \quad \text{at} \quad \Theta = \Theta_\infty. \tag{A6}$$

Here there are three boundary conditions for the second-order problem. In analogy with the nonsymmetric case, Θ_∞ plays the role of an eigenvalue. The explicit solution to the linear problem is given by Eq. (46) with the simplified constants

$$A = -\gamma(\Theta_\infty)\cos(\Theta_\infty) + \gamma'(\Theta_\infty)\sin(\Theta_\infty), \tag{A7}$$

$$B = 0, \tag{A8}$$

and with Θ_∞ determined by

$$\gamma(\Theta_\infty)\sin(\Theta_\infty) + \gamma'(\Theta_\infty)\cos(\Theta_\infty) = 0. \tag{A9}$$

Here the eigenvalue condition (A9) is the same as Eq. (25) that determines the corner orientations for the symmetric case. Thus, the same comments made regarding matching, existence and uniqueness of the solution in the nonsymmetric case apply here. Finally, the curvature and surface shape can be determined as in Eqs. (52)–(56).

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