Crystalline variational methods

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A surface free energy function is defined to be crystalline if its Wulff shape (the equilibrium crystal shape) is a polyhedron. All the questions that one considers for the area functional, where the surface free energy per unit area is 1 for all normal directions, can be considered for crystalline surface free energies. Such questions are interesting for both mathematical and physical reasons. Methods from the geometric calculus of variations are useful for studying a number of such questions; a survey of some of the results is given.

Crystalline problems by definition involve a surface free energy function $\gamma : S^{d-1} \rightarrow R^+$ (S^{d-1} denotes unit vectors in R^d and R^+ the positive real numbers) for which the Wulff shape

$$W_\gamma := \{x \in R^d : x \cdot n = \gamma(n) \text{ for every } n \in S^{d-1}\},$$

is a polyhedron. The surface energy of a rectifiable $(d-1)$ -dimensional oriented surface S is

$$\gamma(S) = \int_{x \in S} \gamma[n_S(x)] d\mathcal{H}^{d-1}x,$$

where $n_S(x)$ is the normal direction of S at x , and $\mathcal{H}^{d-1}$ is a Hausdorff $(d-1)$ -dimensional area measure. All the questions that one considers for the area functional [where $\gamma(n) = 1$ for all unit vectors n] can be considered for crystalline surface free energies, and they are interesting for both mathematical and physical reasons. Methods from the geometric calculus of variations are useful for studying a number of such questions.

A variety of results were obtained earlier concerning equilibrium shapes including a construction (1), a catalog of embedded minimizing crystalline cones (2), and an *a priori* bound on the number of facets in a minimizing surface with a given boundary under certain hypotheses (3). Although many questions remain open for such surfaces, attention for the last dozen years has focused on motion problems such as motion by crystalline-weighted mean curvature and crystalline surface diffusion.

Weighted Mean Curvature

Suppose h is a Lipschitz vector field taking R^d to R^d . Define $S_{\lambda h}$, for a real number λ , as the set of points $\{x + \lambda h(x) : x \in S\}$, with the induced orientation from that of S . Define the first variation $\delta S_\gamma(h)$ by

$$\delta S_\gamma(h) = \lim_{\lambda \rightarrow 0} \frac{\gamma(S_{\lambda h}) - \gamma(S)}{\lambda}.$$

It is useful to extend γ to a function on all R^d by defining $\gamma(rn) = r\gamma(n)$ for all $r \geq 0$. In the case where γ is then $C^{2,\alpha}$ and convex (a noncrystalline case), δS_γ is a bounded linear functional when S is smooth, and κ_γ is defined via representation by integration

$$\delta S_\gamma(h) = \int_S \kappa_\gamma n \cdot h \, d\mathcal{H}^{d-1}.$$

Thus $\kappa_\gamma(x)$ is approximately the increase in energy divided by the volume swept out for a deformation λh with small support around x and small λ . Furthermore, $\kappa_\gamma = a_1 \kappa_1 + a_2 \kappa_2$, where κ_i is the i th principal curvature and a_i is the second derivative of γ in the i th principal direction. Equivalently, κ_γ is the surface divergence of the Cahn–Hoffman ξ vector, and $\xi(x) = \nabla \gamma$ evaluated at $n_S(x)$ (again regarding γ as a function on all of R^d) (4, 5).

If γ is crystalline, the first variation is neither bounded nor linear as a function of h , because γ is not differentiable at the normal directions of W_γ . Furthermore, if a surface S is not of least surface energy compared to all deformations $S_{\lambda h}$ with h having small enough support around a point x in S , then the increase in energy divided by the volume swept out goes to minus infinity as $\lambda \downarrow 0$ and as the support of h shrinks down around x (2). We therefore restrict attention to surfaces that are locally γ -minimizing in a neighborhood of each point and consider nonlocal definitions of κ_γ .

For polyhedral S with plane segments parallel to facets of W_γ , one now considers deformations by Lipschitz maps that shift an entire plane segment S_i of S in its normal direction, extending or cutting off adjacent plane segments as needed to maintain

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continuity of the surface. $\kappa_\gamma(S_i)$ is defined as the limit as λ goes to zero of the energy change divided by the volume swept out under such deformations. For the case $d = 2$, the result for a segment S_i of a crystalline curve is

$$\kappa_\gamma(S_i) = \sigma_i \frac{\Lambda(n_{S_i})}{l_i},$$

where $\Lambda(n_{S_i})$ is the length of the segment of the boundary of the Wulff shape with exterior normal n_{S_i} , l_i is the length of S_i , and σ_i is 1, -1 , or 0 depending on whether S is locally convex at each end of S_i , locally concave at each end of S_i , or locally convex at one end and concave at the other. For $d = 3$, the formula is also explicitly computable

$$\kappa_\gamma = \sum_j \frac{\delta_{ij} f(n_{S_i}, n_{S_j}) l_{ij}}{\mathcal{H}^2(S_i)},$$

where the sum is over neighboring segments S_j to segment S_i in S , l_{ij} is the length of the intersection of segments S_i and S_j , δ_{ij} is 1 if S is locally convex along that intersection and -1 if S is locally concave along it, and $f(n_{S_i}, n_{S_j})$ is a factor depending only on W_γ .

Weighted mean curvature was addressed by Gibbs (6), although with different notation. A summary of these ideas appears in ref. 7.

Motions

In motion by weighted mean curvature, the normal velocity v of S at x is

$$v(x) = M[n_S(x)][-\kappa_\gamma(x)]$$

for a given mobility function $M : S^{d-1} \rightarrow R^+$. In motion with an extra bulk driving force Ω (constant or varying in space),

$$v(x) = M[n_S(x)][\Omega(x) - \kappa_\gamma(x)].$$

In surface diffusion, where the dynamics are controlled by the speed of diffusion over the interface rather than by attachment–detachment kinetics,

$$v(x) = \nabla \cdot D \nabla \kappa_\gamma(x)$$

for some positive or positive-definite D (which could vary with normal direction). Motion where both types of kinetics occur follows the law (see ref. 8).

$$v = (\nabla \cdot D \nabla)(\nabla \cdot D \nabla - M)^{-1}[M(\Omega - \kappa_\gamma)].$$

If γ is crystalline, and if the motion is simply changing the distances of the plane segments of S from some point while maintaining the same adjacencies, then the partial differential equations shown above become systems of ordinary differential equations for those distances, because lengths and areas are defined by the distances and the adjacencies. This was investigated for motion by weighted curvature for crystalline curves in refs. 9 and 10. The video of a lecture given in 1989 (11) gives early results on computing $v = M(-\kappa_\gamma)$ and $v = D \nabla^2 \kappa_\gamma$ for crystalline γ and polygonal curves; the video from a lecture in 1991 (12) shows a more fully developed program for curves including triple junctions and fixed boundary points plus early efforts at computing surfaces moving by $M(\Omega - \kappa_\gamma)$.

We say h is the velocity for gradient flow of γ with respect to the inner product $\langle \cdot, \cdot \rangle$ if $\lim_{\lambda \downarrow 0} \gamma(S_{\lambda h}) \leq \lim_{\lambda \downarrow 0} \gamma(S_{\lambda g})$ whenever $\langle h, h \rangle = \langle g, g \rangle$; the constant value of $\langle h, h \rangle$ is such that the Lagrange multiplier in the variational problem is $\frac{1}{2}$. In order for topological changes to occur in S , one has to be more careful with the definition; see the description of the approximating-motions approach of Almgren–Taylor–Wang (13) below.

Motion by weighted mean curvature should be L^2 gradient flow. Thus, this gradient flow is equivalent to h minimizing $\delta_\gamma S(h) + \frac{1}{2} \int_S |h|^2$. Motion by surface diffusion should be gradient flow in the H^{-1} inner product. Surface motion that incorporates both types of kinetics and with constant mobility M and diffusion constant D is gradient flow in the inner product $(1/M)L^2 + (1/D)H^{-1}$ (see ref. 14).

Stepping

The definition given above of κ_γ for a facet assumes that the facet stays whole. However, for some two-dimensional polyhedral surfaces S , there are deformations h that shift parts of a plane segment different distances (with strips of surface connecting those parts to maintain continuity), which achieve a larger decrease in surface energy. Such “steps” then should occur in minimizing surfaces and in the L^2 gradient definition of motion by crystalline curvature. In fact, in motion by weighted mean curvature, a varifold (essentially, a cylindrical portion of surface consisting of infinitesimal steps and more precisely a probability distribution for the normal at each point, these normals being in the family of normals to W_γ) can result from such stepping. In this case, one extends the concept of the weighted mean curvature of a plane segment to that of a line segment in such a cylinder via the limit of the average weighted mean curvature for discrete steps.

The necessity for stepping was demonstrated in refs. 1, 15, and 16 and also investigated independently by Bellettini *et al.* (17). Yunker (18) proved that there is a unique optimal stepping of plane segments under motion by crystalline weighted mean curvature and, more significantly, produced an algorithm to compute it. He defined weighted mean curvature as follows: Let S_i be a plane segment of S with normal n_i , and suppose n_i is the normal of a plane segment W_i of ∂W_γ . Then define

$$\delta E(h) = \sup_{\xi} \int_{S_i} h \operatorname{div} \xi \, dx,$$

where the supremum is taken over all functions ξ defined on S_i with values in W_i and for which $\xi(x)$ for x in $S_i \cap S_j$ lies in $W_i \cap W_j$. Then $-\kappa_\gamma = \operatorname{Min}_h \{ \delta E(h) + \frac{1}{2} \int_{S_i} h^2 dx \}$, and thus also $\kappa_\gamma = \operatorname{div} \xi$ for a minimizing ξ . A step or varifold can begin only where a certain scaled version of a portion of W_i fits inside S_i up against the boundary of S_i in a certain way (18).

Stepping occurs for curves under motion by crystalline curvature with a nonconstant driving term Ω (due to diffusion of latent heat) (19), which is illustrated in the video of ref. 20. Stepping also occurs during surface diffusion for curves in R^2 (21), as is illustrated in a video available through www.ctcms.nist.gov.

Approximating-Motions Approach

Ref. 13 introduced a definition of motion by weighted mean curvature for any surface free energy function γ as a limit of approximating motions; the approximating motions are obtained by solving variational problems. κ_γ is never defined directly; rather, the flow for $v = -\kappa_\gamma$ was defined as a limit of time-step variational problems, and all-time existence for any γ was proved. It applies only to surfaces that separate two regions; denote one of the regions by K . Given time step $\Delta t = 2^{-k}$ and $K = K[(n-1)\Delta t]$ for some positive integer n (initially $n = 0$), the variational problem to be solved is to minimize among all regions L

$$\gamma(\partial L) - \gamma(\partial K) + \frac{1}{\Delta t} \int_{x \in K \Delta L} \operatorname{dist}(x, \partial K) \, dx$$

($K \Delta L$ denotes the symmetric difference between K and L). One then sets $K(n\Delta t)$ equal to the minimizer L (which is proved to exist) and proceeds to find $K[(n+1)\Delta t]$, etc. Almgren *et al.* proved that a limit motion exists as k goes to infinity for the sequence of approximating motions (via proving a Hölder estimate), and that this limit motion is the same as the motion given by solving the appropriate partial differential equation (PDE), when that PDE is classically defined and has smooth solutions (13). The motion continues to exist after times at which classical solutions cease to exist (or never existed). Ref. 22 proved that for crystalline curves in the plane, the motion of ref. 13 agrees with the motion obtained by solving the system of ordinary differential equations for the motions of the segments. For motion by $v = M(\Omega - \kappa_\gamma)$, Yip (23, 24) extended these results.

Approximating-Motions Approach to Triple-Junction Motion

Recently a partial extension (only as long as no topological changes occur and only for initially energy-minimizing triple junctions) has been made of the method of ref. 13 to determine the motion of triple junctions for crystalline curves in R^2 separating regions (25). Here the normal velocity of an interface is taken to be $v = M(\Omega - \kappa_\gamma)$, where Ω is a driving force due to differences in bulk energy (assumed constant on each region) between the regions separated by the interface. If the surface free energy functions γ are identically zero, this latter motion is that based on characteristics first described by F. C. Frank (26) and further explored in ref. 27. If the surface free energy functions are positive and crystalline, then the motion is that of ref. 10. Finally, if the surface free energy functions are written as $\gamma = \varepsilon \gamma_0$, then the limiting motion as $\varepsilon \downarrow 0$ is in general different from the motion for $\varepsilon = 0$; the limiting motion is presumably that explored by Reitich and Sonner (28). Here it emerges naturally and computably from the variational description.

There are conjectures of extensions to topological changes, to surfaces in R^3 , and to the noncrystalline case.

Affine Invariance

A striking result is that motion of curves in R^2 by $\kappa^{1/3}$, where κ is the usual curvature, is affine-invariant (29). This implies that if one does an affine transformation of R^2 and then flows the transformed curve by its curvature to the one-third power, the same result is obtained as if one flowed the curve first and then transformed it. Because there is little physical reason for the one-third power to occur, this result was reexamined for the case of $v = M(n)(-\kappa_\gamma)$, and indeed the presence of the mobility is crucial: if one transforms not only the curve but also makes the appropriate transformations of γ and M , then v itself (i.e., to the power one rather than one-third) is affine-invariant (30).

Other Approaches to Modeling Crystalline Motions

Giga *et al.* (31) defined κ_γ as the value of $\operatorname{div} \xi$ that minimizes $\int_{S_i} |\operatorname{div} \xi|^2 dx$ subject to $\xi \in W_i$ and boundary conditions as in Yunker's definition above. (They also erroneously "proved" that stepping does not occur.) This definition is referred to as the *minimal* one. There is also a *canonical* definition for flows of divergence type in that there is a unique ξ that "makes sense" (32, 33). For curves that are graphs of functions, ref. 34 proves that $v = M(-\kappa_\gamma)$ can be written in this divergence type, and thus this theory applies. It is conjectured that it applies in general to crystalline motion in all dimensions.

Belletini *et al.* define motion for the case $M(n) = \gamma(n)$. A flow is called a curvature flow if the velocity is $-\gamma \operatorname{div} \xi$, with the requirement that the flow be Lipschitz-continuous in space and time and that ξ be in the appropriate facet of ∂W_γ (17). They never characterize $\operatorname{div} \xi$ directly, but the flow only depends on the initial surface. This flow probably is related to the canonical definition through the expectation that there is a unique canonical choice of $\operatorname{div} \xi$.

There is also the approach to modeling surface motion via diffuse interfaces as pioneered in the isotropic case by the Cahn-Hilliard and Allen-Cahn equations (see ref. 14).

Atomic Considerations

In the models described above, when atoms at the interface leave one crystal and/or join another, the area is assumed to be retarded in this motion only by a multiplicative mobility factor M . There are several problems associated with applying such mathematical models to physical crystal-shape changes.

One recently appreciated consideration is that these models assume that crystals retain their same orientation in space as their shapes change. However, when atoms at the interface move from one crystal to another (or to a different phase), they may continue to feel a net sideways tug from atoms in their original crystal. The result can be significant local distortion of the crystal lattices and consequent generation of significant elastic stresses, relieved by a net rotation of a crystal or sliding of grains along the boundary. In the case of isotropic but misorientation-dependent surface free energies, an embedded round crystal that starts with a small misorientation and a small γ can rotate to a larger misorientation and a larger γ due to this coupling of grain boundary motion with tangential shear. Such effects have been observed in molecular dynamics simulations (ref. 35 and S. G. Srinivasan and J. W. Cahn, unpublished results) and currently are being mathematically modeled by using the variational framework described above (J.E.T. and J. W. Cahn, unpublished results).

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