1. WHAT THIS IS ABOUT

An interface between two different materials (which in this paper will be restricted to the interface between a crystalline solid and air) has potential energy due to the unfilled electron orbitals of the surface molecules. This potential energy (called surface free energy) will in general depend on the orientation of the surface relative to the interior of the material. Thus, the surface free energy as a function of direction is determined by the internal structure of the material, for it is related to the number of molecules with unfilled electron orbitals, or, more simply, the number of bonds broken by slicing the substance in a given direction. In the typical example of a crystal, which possesses a rigid symmetrical structure, it is clear that the surface energy function should depend on the direction in which the crystal is sliced, because two different cutting directions will break a different number of bonds (Fig 1).

The fundamental problem of crystallography is predicting the equilibrium shape of the crystal from its internal structure; this is yet to be solved in full generality. Physics mandates that the optimal shape of the crystal possess the minimal total surface free energy of all possible shapes. In order to avoid worrying about the size of the crystal and concentrate on the shape, surface energy is replaced with surface tension, which is the surface energy per unit surface area. This is now a minimization problem, which would appear to belong to the realm of variational calculus, if the shapes were nice, smooth functions. The shapes of crystals, however, are known to be polyhedral, so a more suitable approach is geometric.

In this paper I will present a geometric algorithm of finding the minimizing crystal shape, and describe some of the mathematics involved in proving its existence and uniqueness. Then I will go on from this static problem to considering some of the dynamics of crystal growth by modeling the velocity of propagation of the crystal surface. The model will be simplified, but even in the restricted version, the PDE that will be derived will be unpleasant, unless we assume a crystalline shape and simplify the problem to a system of ODEs.

2. A LITTLE ABSTRACTION

It is time to introduce some terminology. The surface tension function is a function on the set of oriented planes through the origin (the surfaces) whose range is the positive reals - the surface tension of a particular planar surface:

\[ F : G_0(3, 2) \to \mathbb{R}^+ \]

Functions like this are called constant coefficient 2-dimensional oriented integrands on \( \mathbb{R}^3 \). In the mathematical model, it is these integrands that formally define a crystal. They can be integrated over any surface which has an oriented tangent plane \( \text{Tan}(S, x) \) at almost every point (reasonably
nice surfaces). The integral of \( F \) over this surface \( S \) is (with \( \mathcal{H} \) being 2-dimensional Hausdorff measure):

\[
\int_S F(Tan(S, x)) d\mathcal{H}x
\]

This integral expresses the total surface tension of the crystal defined by the integrand \( F \), and thus it is the quantity which is minimized by the physics of crystal growth. We will define the crystal associated with the integrand \( F \) to be the result of a geometric algorithm called the Wulff construction, to be presented below. First, I will motivate the construction with a little geometry.

3. Crystalline Lattice and the Dual Lattice

The interior of a crystal is distinguished from other solids by possessing a translationally invariant set of equivalent points called the crystalline lattice. Equivalence of lattice points means that the inside of the crystal looks identical from each point; translational invariance implies the existence of a basis set of vectors such that linear combinations of the basis vectors with integer coefficients leave the lattice unchanged. (Fig 2) That is, if \( \{v_1, v_2, v_3\} \) is the basis of the lattice, then any lattice point \( v \) can be written (uniquely) as

\[
v = av_1 + bv_2 + cv_3
\]

The numbers \( a, b, c \) are integers; the origin is set at an arbitrary lattice point, since they are all equivalent. This periodic structure is highly symmetric, not only translationally, but also possessing rotational and reflectional symmetries, as well as combinations of both. Lattices can be characterized by their symmetries - each lattice has a corresponding crystallographic group which is the collection of all said symmetries. The demands of periodicity are so restrictive that only 17 planar crystallographic groups are in existence, and in 3D there are 230. I will not use this symmetric information about crystals explicitly in this paper, but it is important to realize that for any specific crystalline material the most fundamental information is its crystallographic group.

This is the time to introduce the dual lattice, which is (not surprisingly) the dual space to the lattice spanned by the basis vectors. Specifically, if \( \{v_1, v_2, v_3\} \) is the basis of the original lattice, then the dual lattice is spanned by vectors \( \{v_1^*, v_2^*, v_3^*\} \) where the dual basis vectors obey:

\[
v_i \cdot v_j^* = \delta_{ij}
\]

The dual lattice is very useful in describing the geometry of lattice planes, which are defined as 2-dimensional sublattices of the 3-dimensional lattice. Any lattice plane can be described by the equation:

\[
kx + ly + mz = \text{integer},
\]
where \( x, y, z \) are coordinates in the \( \{v_1, v_2, v_3\} \) basis. This equation decomposes the lattice into a stack of parallel planes - one for each integer. And when \( x, y, z \) are integers, it corresponds to a point in the lattice. That equation can also be written as

\[
(kv_1^* + lv_2^* + mv_3^*) \cdot (xv_1 + yv_2 + zv_3) = \text{integer}
\]

The dual basis vectors contain information about the spacing of lattice planes in the given direction. Take two successive planes \( kx + ly + mz = 0 \) and \( kx + ly + mz = 1 \). Let \( (a, b, c) \) be a lattice point in the second plane. The separation between two planes is the norm of the projection of the vector \( (a, b, c) \) onto the direction \( (k, l, m) \), and this length is:

\[
d = \frac{(a, b, c) \cdot (k, l, m)}{|(k, l, m)|} = \frac{ka + lb + mc}{|(k, l, m)|} = \frac{1}{|(k, l, m)|}
\]

This is the connection between the dual lattice and the lattice planes of the original one: the length of the dual vector \( (k, l, m) \) is reciprocal to the distance between the lattice planes orthogonal to the vector. This may be why crystallographers call the dual lattice the reciprocal lattice.

The concept of directional density now comes in; it is defined to be the number of lattice points that you encounter per unit length as you move in a specified direction. For any direction that is in the dual lattice, we can now decompose the lattice into a stack of planes normal to the dual lattice vector. It is clear that the directional density should be inversely proportional to the interplanar spacing in our stack - since the bigger the distance between planes, the fewer lattice points you will encounter per unit length while traveling in this direction. The previous result implies that the length of a dual lattice vector \( (k, l, m) \) is proportional to the density of the lattice in the direction \( (k, l, m) \).

It is now time to come back to crystal growth, by noting that crystal surfaces are composed of lattice planes (which is why they are polyhedral). This foray into lattice geometry now bears fruit, because the surface free energy of a lattice plane is (assumed to be) inversely proportional to the directional density and thus proportional to the interplanar spacing. Thus, given a crystalline lattice, we can plot the surface energy (normalized version) as a function of direction. (Fig 3)

The crystal grows by adding layers of molecules to the existing surfaces, so the larger the spaces between parallel planes, the faster the growth of the crystal in that direction. Thus, there is an inverse relationship between density of a crystal as you look in a direction and its growth rate in that direction. The equilibrium shape is the one with the minimal surface free energy, so by the above relationship between surface energy and interplanar distances, the planes with the smallest surface energy will be the ones with the smallest interplanar spacing, and thus with the slowest rate of growth. This is known as Bravais’s Law, which states that: The faces that appear on a crystal will be parallel to the lattice planes with the greatest density. This
is one of the most fundamental properties of crystals, but it may appear paradoxical: the crystal planes that grow fastest will grow themselves out of existence, and the slowest ones will persevere. (Fig 4) This law is very close to reality, although physical crystals are not point lattices, which sometimes causes deviations from this ideal.

4. The Construction

From the geometric and sometimes heuristic explanations of the previous section, a relationship between the internal structure and the external shape of a crystal is emerging. George Wulff noticed the relationship between directional density and surface energy (around 1900) and came up with an algorithm for constructing the ideal crystal form. The construction (in the non-rigorous form) is rather simple:

- Taking a lattice point as the origin, plot the surface free energy as a function of direction.
- Construct planes perpendicular to the radial vector at every point of the plot.
- The smallest convex region bounded by these planes is the ideal crystal shape.

For an ideal crystal we assume the surface energy as a function of direction to be proportional to the directional density of the lattice, so given a lattice, one can construct the surface energy plot and thus find the crystal shape. (Fig 5)

For a precise mathematical description, a more rigorous (and perhaps less enlightening) definition is needed. Now we can formally define the crystal of an integrand $F$ to be the result of the Wulff construction: Define the dual function on the unit sphere $F^*(v) = F(v^*)$, where $v^*$ is in the dual space of the sphere, which is the space of oriented tangent planes. Plot $F^*$ radially (for each $v$ on the unit sphere, go out a distance $F^*(v)$ in the direction $v$). At each point of this polar plot, discard the oriented half space whose boundary contains that point and has tangent plane $-v^*$. The remaining set is the result of this construction.

As advertised, the Wulff construction gives the unique shape $W_F$ which minimizes the integral of $F$ over the boundary $\delta W_F$. The following theorem states it precisely:

**Wulff’s Theorem** $F(\delta W_F) < F(\delta T)$ for every integral current $T$ such that $M(T) = M(W_F)$, $T$ is positively oriented $\|T\|$ almost everywhere and $T$ is not $W_F$ or its translation.

(An integral current is a rectifiable current whose boundary is also a rectifiable current, and an n-dimensional rectifiable current is an element of the space dual to the space of n-forms, such that the current $S$ may be defined as

\[
T(\phi) = \int_T \langle T(x), \phi \rangle \mu(x) dH
\]
with the requirement that \( S \) have compact support.

\( M(T) \) is defined to be the mass of an integral current, also denoted \( \|T\| \).

The proof of this theorem is well beyond the scope of my possible understanding; it is generally relegated to the technical journals.

5. **Dynamics of Crystal Growth**

For the first part of this paper I have ignored an important aspect of crystal growth: the time dimension. As the crystal propagates, one can try to model the normal velocity of the crystalline surface, which will depend on both space and time. It is not easy, for in the messy physical world, there is an intractable number of variables that can influence propagation of the crystal. There are environmental variables such as temperature and concentration gradients, as well as the interior structure of the crystal. The model that I will consider ignores some of these influences by postulating that the surface velocity depend only on the position and local shape of the surface. Because it essentially depends on the spatial structure of the crystal, such a model is called geometric; it discards effects away from the surface of the crystal (which could conceivably be of importance, such as concentration gradient that supplies more material to the surface). Diffusion-controlled crystal or dendrite growth is not geometric.

In this simplified situation, a material will propagate in a way such that its surface tension decreases as its volume grows. The thermodynamic driving force responsible for this motion has two components: the weighted mean curvature \( wmc \), which expresses the decrease in the integral of the specific surface free energy and a volume change \( \Omega \) which represents the volume change. Depending on the material, the force may have more or less effect, which is modeled by the mobility of the crystal \( M \). The expression for the normal velocity of the crystalline surface at any point is given by:

\[
(9) \quad v = M(\Omega + wmc)
\]

In general, this equation can be exceedingly complicated and highly non-linear. \( wmc \) and \( \Omega \) can both depend on the microstructure of the crystal, on the orientation of the surface, and on temperature at the surface, and the mobility \( M \) can, in addition, depend on the velocity \( v \) itself. More simplifications must be made, if one actually wants to solve the problem.

6. **Wulff to the Rescue**

If one assumes a polyhedral shape of the crystal, like the Wulff shape, then the PDE is converted into a system of ODEs. This approach can be used if that the surface energy \( \gamma \) and the mobility \( M \) are each given only on a certain common finite set of normal directions \( \{n_i\} \). Then the Wulff construction is performed on this finite set of values of \( \gamma \). The initial surfaces that are best for this approach are polyhedral shapes with planes normal to the directions \( \{n_i\} \).
Consider an example with no surface energy, so the equation of motion of any of the planes of the polyhedral surface are given by:

\[
\frac{ds_i}{dt} = \Omega M(n_i)
\]

for each i. This is easily integrated to yield:

\[
s_i(t) = s_i(0) + t\Omega M(n_i)
\]

The only complication is with figuring out the corners where the planes meet, which can be found by solving the simultaneous system of linear equations. One singular event that may happen is the disappearance of some of the surfaces (the ones with faster rate of growth). The planes with slower growth rate will squeeze them out until two planes that were not adjacent suddenly become neighbors; in the context of a PDE this would be called a shock. However, this method makes tracking such events simpler than using the method of characteristics in the PDE problem.

Now for the case where \( \gamma \neq 0 \); instead of blindly differentiating the equation, we use the idea that the mean curvature of a 2D surface is the rate of decrease of surface energy with respect to volume under small deformations of the surface. For a well-behaved polyhedral surfaces it can be computed that the weighted mean curvature of a segment \( S_i \) should be defined to be:

\[
-\frac{1}{\text{area}(S_i)} \sum_{j \neq i} \delta_{ij} f_{ij} l_{ij}
\]

where \( l_{ij} \) is the length of the intersection of planes \( S_i \) and \( S_j \) (and so is 0 if the two planes are not adjacent), \( \delta_{ij} \) is 1 or -1 depending on the orientation of the surface, and \( f_{ij} \) is a numerical factor determined by the geometry of the Wulff shape, specifically:

\[
f_{ij} = \frac{\gamma(n_j) - c_{ij}\gamma(n_i)}{\sqrt{1 - c_{ij}^2}}
\]

where \( c_{ij} = n_i \cdot n_j \). This is the general formulation of the problem: the motion is modeled to be by propagating existing plane segments (while shrinking or enlarging them) while keeping their combinatorial structure (same neighbors), according to the equation:

\[
\frac{ds_i}{dt} = M(n_i)[\Omega - \sum_{j \neq i} \delta_{ij} f_{ij} l_{ij} / \text{area}(S_i)]
\]

7. Hamilton-Jacobi Equation

Another approach to tackling the problem of the moving crystalline surface is to define a function \( u \) (of space and time) that at any given time takes on a particular value along the crystal surface. The motion of the
surface can then be described by following the level set of $u$ over time. For any differentiable function $u$, with small $\Delta x$ and $\Delta t$,

\begin{equation}
(15)\quad u(x + \Delta x, t + \Delta t) \approx u(x, t) + \nabla u \Delta x + u_t \Delta t
\end{equation}

Here $\nabla u$ is the spatial gradient of $u$, i.e. $\nabla u = \left( \frac{\partial u}{\partial x_1}, \frac{\partial u}{\partial x_2}, \frac{\partial u}{\partial x_3} \right)$ and $u_t = \frac{\partial u}{\partial t}$.

If $x$ is on the level set of $u$ at time $t$ (say $u(x, t) = 0$) and $x + \Delta x$ is on the level set at time $t + \Delta t$ then $u(x + \Delta x, t + \Delta t) = u(x, t)$ and so

\begin{equation}
(16)\quad -\frac{\nabla u \Delta x}{\Delta t} \approx u_t
\end{equation}

Since $\nabla u$ is always perpendicular to level sets of $u$, if we take $\Delta x$ to be normal to the crystal surface, it will be a scalar multiple of $-\nabla u/|\nabla u|$. Thus, the limit of $\Delta x/\Delta t$ as $\Delta t \to 0$ is

\begin{equation}
(17)\quad v = \frac{u_t}{|\nabla u|}
\end{equation}

Thus, if we want to write $v$ as a function of time, space, and normal direction, a PDE in which every level set moves by that normal velocity is:

\begin{equation}
(18)\quad \frac{\partial u}{\partial t} - |\nabla u|v(x, t, -\nabla u/|\nabla u|) = 0
\end{equation}

This equation can be solved using the method of characteristics when the normal growth rate $v$ is a function of position, time and normal direction but not a function of curvature. Take $\gamma = 0$ and $v(x, t, n) = \Omega(x, t)M(x, t, n)$. It is convenient to assume that $v$ can be extended on all vectors so that $v(x, t, rn) = rv(x, t, n)$ for all $r > 0$. The PDE then simplifies to:

\begin{equation}
(19)\quad \frac{\partial u}{\partial t} - v(x, t, -\nabla u) = 0
\end{equation}

Now let us write $u$ as $t - \tau(x)$, where $\tau$ denotes the arrival time of the crystal at a point. Then the normal to the crystal surface becomes $\nabla \tau/|\nabla \tau|$, a unit normal in the direction of increasing $\tau$. The general equation now becomes this non-linear first order PDE:

\begin{equation}
(20)\quad v(x, \tau, \nabla \tau)
\end{equation}

A first-order PDE can be solved by the method of characteristics, and that is what this simplification has achieved.

8. Ending

The problem of ideal crystal shape has been solved by crystallographers to be the result of Wulff construction and proven by mathematicians to be the shape of minimal surface energy, provided that there are no effects aside from an idealized bond structure within a perfect lattice. This works surprisingly well for many crystalline surfaces, but fails for some that have other effects such as dependence on environmental factors. This can be taken into account in the dynamic model, although complicated dependencies will make the PDE very difficult to solve.
If it is clear that surface will stay purely polyhedral, it is most useful to use that to convert the equation into ODEs. Otherwise, one can use the indirect model with Hamilton-Jacobi equations and use methods such as characteristics, which work for a quasi-linear PDE. Not surprisingly, assumption have to be made in all of these cases if any results are to be achieved. There are still a lot of unsolved questions in the area being studied, as researchers try to relax the restrictions and obtain more general results.

9. Bibliography

Fig. 1. The cut on the left breaks five bonds, whereas the slicing on the right is responsible for

Fig. 2. Lattice basis vectors.

Fig. 3. A typical radial plot of crystalline surface energy.

Fig. 4. How fast-growing directions grow out of existence.

Fig. 5. Wulff shape of a pretty surface energy function.