

Flowers of Ice—Beauty, Symmetry, and Complexity: A Review of *The Snowflake: Winter's Secret Beauty*

Reviewed by John A. Adam

Growing up as a child in southern England, my early memories of snow include trudging home from school with my father, gazing at the seemingly enormous snowdrifts that smoothed the hedgerows, fields and bushes, while listening to the soft “scrunch” of the snow under my Wellington boots. In the country, snow stretching as far as I could see was not a particularly uncommon sight. The quietness of the land under a foot of snow seemed eerie. I cannot remember the first time I looked at snowflakes per se; my interests as a small child were primarily in their spheroidally shaped aggregates as they flew through the air. Many years later, as I cycled home from my office in Coleraine, Northern Ireland, I remember being intrigued by a colored blotch of light to the west of the Sun at about the same elevation. Little did I know then that these two events of snowfall and “sundogs” (of which more anon) were intimately connected. Since that time I have learned rather more about meteorological optics, and this book about the beauty of snowflakes has challenged me to learn more of the physics and mathematics behind crystal formation in general and ice crystal formation in particular.

As in an earlier review [1], I will divide this review into two main sections; Libbrecht's book

contains no mathematics, so the first section will address the qualitative features of snow and snowflakes discussed by the author. I will draw on some of the general descriptions of snow and its properties both from this book and those by others mentioned below. I have decided to comment on every chapter individually, because each can be treated to some extent independently of the others. The second section takes the form of a mathematical appendix devoted to an outline of some of the mathematical aspects of crystal formation, with particular emphasis on ice crystals. In some sense, I hope, this will become a parallel “mathematical universe” to the first section. However, the growth of crystals is a complex combination of thermodynamics and statistical physics, and no review of this nature could do justice to the immense theoretical edifice that has been erected on this topic.

This slim volume is informally yet clearly written, and the photographs (mostly taken by Patricia Rasmussen) are quite stunning. Obviously, it is aimed at a popular audience. In one sense, though, it is the latest in a disjoint set of popular books on pattern formation in nature: D'Arcy Thompson's *On Growth and Form* [38]; Stevens's *Patterns in Nature* [32]; Ball's *The Self-Made Tapestry* [3]; Stewart's *Nature's Numbers* [33] and *What Shape Is a Snowflake?* [34]; and finally, from a very different perspective, Bejan's *constructal theory* as expounded in *Shape and Structure, from Engineering to Nature* [5]. With the exception of [34], none of these address the nature of the snowflake to any great extent. Some of Libbrecht's low-key yet vivid

John A. Adam is a professor of mathematics at Old Dominion University. His email address is jadam@odu.edu.

The *Snowflake: Winter's Secret Beauty*, by Kenneth Libbrecht, with photographs by Patricia Rasmussen, Voyageur Press, Inc., 2003, hardcover, \$20.00, ISBN 0-89658-630-8.

descriptions captured my imagination, and I would certainly recommend this book to any person wishing to “experience” something of the physical intuition of a scientist.

As might be expected, the study of snowflakes is not new; no doubt people have been fascinated by their beauty and symmetry since time immemorial. According to [4], [16] the Chinese awareness of this was recorded in 135 B.C., while in Europe the Dominican scientist, philosopher, and theologian, Albertus Magnus, studied them around 1260 A.D. Not surprisingly, the astronomer and mathematician Johannes Kepler was intrigued by snow crystals, writing a small treatise entitled *On the Six-Cornered Snowflake*. In 1611 he asked the fundamental question: *There must be some definite cause why, whenever snow begins to fall, its initial formation invariably displays the shape of a six-cornered starlet. For if it happens by chance, why do they not fall just as well with five corners or seven?* In his treatise he compared their symmetry with that of honeycombs and the seed arrangement inside pomegranates [4]. However, nothing was known in Kepler’s era of the molecular structure of water, which ultimately determines the hexagonal shape of ice crystals, so Kepler was unable to explain their shape in mechanical terms, though he did attempt to do so using entirely reasonable packing arguments. (Indeed, finding the densest (not necessarily periodic) packing of spheres is now known as the Kepler problem [14].) In 1665 the scientist Robert Hooke published *Micrographia*, in which he described his observations of snowflakes using a microscope. More historical details may be found in [4].

In the first chapter of *The Snowflake* (“The Creative Genius”), the author asks the fundamental questions: *How do crystals grow? Why do complex patterns arise spontaneously in simple physical systems?* These are very profound questions, of course, and a considerable portion of past and present literature in applied mathematics and theoretical physics is devoted to attempting to answer them. Obviously, the second question goes well beyond the “mineral kingdom” of crystal formation into the “animal and vegetable” ones of patterns in (and on) living things. In particular, though, Libbrecht reminds the reader that snowflakes are the product of a rich synthesis of physics, mathematics, and chemistry and that they are even fun to catch on one’s tongue! The range of such comments reflects the underlying parallel approaches of the book: on the one hand, a good qualitative and nontechnical description of the scientific aspects of snowflake formation and, on the other, the sheer fun of doing science. It is worth noting that in Libbrecht’s terminology, snow crystal to snowflake is as tulip to flower. In other words, a snowflake can be an individual snow crystal or collection of the same,

depending on context. The two words will be used synonymously here unless otherwise noted.

The short Chapter 2 is entitled “Snowflake Watching”. In it, Libbrecht records a partial history of snowflake watchers from Descartes to the present day. In particular, he makes mention of Wilson Bentley, a Vermont farmer who dedicated much of his life to photographing snowflakes. In the late 1920s Bentley worked with physicist W. J. Humphreys to publish a book containing more than 2,000 of his snow crystal images. (There is a 1962 Dover edition of this book, *Snow Crystals*.) The scientific discussion begins in earnest in the third chapter (“Snow Crystal Symmetry”). It starts with the following quote from Richard P. Feynman (*The Feynman Lectures on Physics*, 1963):

Poets say science takes away from the beauty of the stars—mere globs of gas atoms. I too can see the stars on a desert night, and feel them. But do I see less or more?... What is the pattern, or the meaning, or the why? It does not do harm to the mystery to know a little about it. For far more marvelous is the truth than any artists of the past imagined it.

A quote from Kepler in 1611 is included as he pondered the sixfold symmetry of snowflakes, and although Libbrecht makes no mention of it, a quote from D’Arcy Wentworth Thompson [38] is particularly appropriate here:

The beauty of a snow-crystal depends on its mathematical regularity and symmetry; but somehow the association of many variants of a single type, all related but no two the same, vastly increases our pleasure and admiration.... The snow-crystal is further complicated, and its beauty is notably enhanced, by minute occluded bubbles of air or drops of water, whose symmetrical form and arrangement are very curious and not always easy to explain. Lastly, we are apt to see our snow crystals after a slight thaw has rounded their edges, and has heightened their beauty by softening their contours.

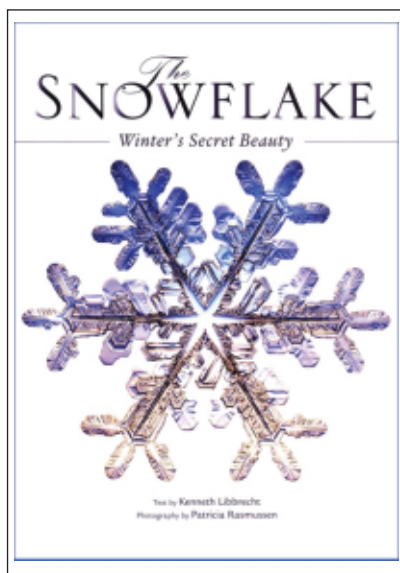
Returning to the question of complex patterns in nature, we may not be surprised to be reminded by Libbrecht that all crystals demonstrate the organizational ability to self-assemble. Starting with a random collection of molecules, this is an example of spontaneous pattern formation. The best non-mathematical book I know on the broad spectrum of pattern formation is *The Self-Made Tapestry* [3], and the present book, much narrower in scope, is a good introduction to some of the underlying

concepts explained therein. For example: Libbrecht does a pretty good job of explaining to a nontechnical readership the physics of crystal facets and their formation. One basic snow crystal shape is the hexagonal prism, which possesses two basal facets

and six prism facets, and depending on which of the two types grows faster, the prism can become a long column or a thin plate. The slowest moving facets eventually define the shape of the crystal. At this point the author asks a very significant question: *How can molecular forces, operating only at the nanoscale, determine the shape of large crystals?* Answers to this and related questions are hinted at in the following two chapters.

And so to Chapter 4 (“Hieroglyphs from the Sky”), in which it is stated that the real puzzle of snowflakes is their combination of symmetry

and complexity and that major progress in solving this puzzle was made by the physicist Nakaya in the 1930s. Eventually, he succeeded in growing individual snow crystals in his laboratory under many different humidity levels and temperatures, and it was only a matter of time before he was able to classify the symmetry and considerable variety displayed by these crystals. He developed his famous morphology diagram, demonstrating the remarkable sensitivity of the snow crystal form to its environmental conditions. This diagram is reproduced on page 45 of *The Snowflake*. Basically, at low but fixed levels of supersaturation (degree of humidity), as the temperature decreases below 0°C to about -35°C, snow crystals are essentially plates, then solid prisms, and then plates again. At higher supersaturation levels, the evolution is from dendrites to needles, hollow columns, sectorial plates and dendrites, and then columns again. Essentially, the overall crystal shape, whether it is platelike or columnar, reveals something about the temperature at which the crystal grew, and the complexity of the structure indicates something about the humidity. However, each crystal falling on one’s nose is a product of the cumulative history it has undergone as it has been wafted hither and yon by air currents through many different atmospheric conditions. In mathematical terms, we might think of its shape being defined by a line integral over its path through space and time. Generally, the length scale of variations of temperature and humidity will be much larger than the dimension of the crystal, so each vertex or arm of the crystal experiences the



same conditions at each moment of time; their symmetry is evidently a reflection of their shared history.

It should be noted that while Nakaya’s 1954 book *Snow Crystals: Natural and Artificial* is referred to on page 44, no mention is made of the im-

portant work by Furukawa, who studied under Kuroda and Kobayashi, both of whom were students of Nakaya. Many valuable details and references on the history and science of snow crystal research can be found in Furukawa’s essay (<http://www.lowtem.hokudai.ac.jp/~frkw/english/aletter.html>).

In Chapter 5 (“Morphogenesis on Ice”) the search for an explanation of snow crystal complexity is taken yet further. Touching on a point made earlier in this review, Libbrecht temporarily broadens his perspective by noting that while a flower is an example of biological morphogenesis, even simpler physical systems exhibit this feature. Thus whether it be waves on the oceans or ripples on snowdrifts and sand dunes, they are all relatively simple pattern-forming systems in which complexity arises spontaneously, but for Libbrecht the snowflake is the poster child of morphogenesis. Here as in earlier chapters he does a good job of introducing the concept of self-organization in physical (and, in passing, biological) systems. This is all to the good, given the preoccupation in some quarters with the concept of “intelligent design” (with all due respect to my fellow Christians). In a sentence that I find very appealing, Libbrecht notes that instabilities like those discussed here are the heart of pattern formation, and nature is one unstable system heaped on top of another.



Scientifically, the real meat of the book is to be

The three photographs of snowflakes (above) were provided by Yoshinori Furukawa of Hokkaido University, who also provided the photographs from which the background snowflakes came. The ordinary symmetry of snowflake growth is really extraordinary.

found in this chapter. There are several key comments made by Libbrecht that bear repeating as written: *Growth is the key ingredient for the generation of snow-crystal patterns. Left in isolation for a long time, an ice crystal will eventually turn into a plain hexagonal prism.... Ornate patterns appear only when a snow crystal is out of equilibrium, while it is growing.* Such circumstances are often referred to as nonequilibrium conditions. Another important concept introduced is that of *diffusion-limited growth*. A snow crystal grows by assimilating molecules of water vapor into the existing ice lattice, provided the humidity is high enough. However, continuing crystal growth gradually depletes the vapor from layers of air adjacent to the crystal, and the remaining water vapor molecules must diffuse over increasingly larger distances. Since the travel time for diffusion (other things remaining unchanged) is proportional to the square of the distance traveled, it is clear that the growth rate of the crystal will be inhibited; the growth is now diffusion-limited.

An initial “seed” crystal consisting of several hundred or thousand molecules has a molecularly rough boundary. Depending on the crystallographic orientation, some orientations may grow more rapidly than others (under a spatially uniform growth drive), and thus a surface is created with both positive and negative curvature. “Flatter” portions of the boundary are called *facets*, and while a *completely* rough seed will not have facets, it may still grow anisotropically. The curved regions “fill in” more readily than the facets, from which it is seen that ultimately the slower-growing facets define the crystal shape in the absence of significant branching (a mechanism discussed below). Combining the above two mechanisms, in diffusion-limited growth one might expect that the crystal vertices would “harvest” water vapor molecules faster than facets by virtue of their projection further into the medium (if the mean free path of the vapor phase is of order the size of the system). This can induce a positive feedback loop known as a *branching instability*. As will be noted in the second section of this review, if this instability occurs, there is usually a self-limiting stabilizing mechanism, akin to surface tension, that eventually balances the destabilizing one. If this diffusion-limited branching instability is iterated over and over, a type of snow crystal known as a *dendrite* will develop. Ultimately, this may give rise to some kind of self-similar or fractal-like structure over several orders of magnitude of scale, not unlike a fern leaf. This branching process is more pronounced in regions of higher vapor pressure, since then the diffusive transport of water vapor molecules is more effective. Conversely, faceted growth is more likely to occur in a lower vapor pressure environment. Ultimately, the complex interplay between

faceting and branching is what determines the form of a given snow crystal in a kind of morphological balancing act, and this in turn depends on the temperature and humidity history of the growing crystal and also its size. Libbrecht speculates that if snowflakes occur in other planetary atmospheres, they may well be different from the ones we know and love.

Although he does not identify it as such, the branching instability Libbrecht refers to is the *Mullins-Sekerka instability* (see the second section of this article for more details). Nobody could fault him for simplifying physical phenomena in a book of this kind, but as he implies elsewhere, the picture is just not that straightforward. Indeed, I am indebted to Professor J. S. Wettlaufer for the following comment (in reference to a statement made in [2]) that puts into perspective the complexity of the problem:

The initial question that needs to be asked is: How does a hexagon emerge from a nucleus of some 1,000 molecules that, at the point of nucleation, do not necessarily reflect that symmetry? This has nothing whatever to do with the structure of the background diffusion field, but rather it is solely controlled by the statistical mechanics of adsorbates on the seed. The seed is much smaller than the mean free path in the vapor phase. The enhancement of the vapor field at a corner, generically understood as the “point effect of diffusion” or the “Berg-effect”, may or may not lead to an instability. The conditions must be carefully determined; for example, is the size of the seed much smaller than the characteristic scale of the diffusion field? There is a plethora of outstanding physical and mathematical problems related to the transition between nucleation, interface controlled growth and diffusion limited shapes. Therefore, if and/or when a diffusive/Mullins-Sekerka instability occurs, understanding the habit of the crystal still requires an understanding of the initial value problem and thus the evolution of a crystal from its birth.

In Chapter 6 (“Snowflake Weather”) Libbrecht makes some statements about snow crystal quantities that might form the basis for several interesting estimation problems, but first it is necessary to note some facts about snow. Consider first a small ice cube 1 cm^3 in volume. This has a mass of one gram, and since the mass of a water molecule is about $3 \times 10^{-23} \text{ g}$, there are about 3×10^{22} molecules in this ice cube. A typical snow crystal

of mass 3×10^{-5} g therefore may contain about 10^{18} molecules. Depending on the type of crystal, temperature, wind speed, and other factors, including the density of packing, snow has considerable variation in its water content. An eight-foot blanket of fresh snow may contain as little as 1 inch of water per unit of surface area or as much as 3 feet. According to [16], the majority of U.S. snows have a water-to-snow ratio in the range of 0.04 to 0.10. I had to dig around for most of this information; I wish that facts such as these had been incorporated into the book as an appendix.

In the beginning of this chapter we read: *Snowflakes are being manufactured in the atmosphere at an astounding rate—around a million billion crystals each second. Every ten minutes that's enough snow to make an unstoppable army of snowmen, one for every person in the world....* Let's think about this: on the basis of these numbers, after ten minutes there are about $10^{15} \times 6 \times 10^2 = 6 \times 10^{17}$ crystals, and estimating a typical snowman to be composed of two identical spheres of diameter 1.5 ft. gives a volume of about 3.5 ft.^3 or approximately $3.5 \times (0.3)^3 \approx 0.1 \text{ m}^3 = 10^5 \text{ cm}^3$. If we assume that all the crystals formed make their way to the ground (a rather dubious assumption) and take an average water-to-snow ratio of 0.07 for U.S. snow (!), then the mass of crystals falling in a ten-minute interval is approximately 2×10^{13} g. Meanwhile, the mass of our typical snowman is given by the product $10^5 \times 0.07 = 7 \times 10^3$ g. This means our army of

snowmen numbers about 3×10^9 , or about one half of the present world population. A factor of two is not a large discrepancy in this context, and in any case, that's a lot of snowmen. (There is a delightful "Peanuts" cartoon showing a vast army of snowmen built on a cloudy day by that precocious genius, Linus. He marches up and down declaring their military invincibility under any and all circumstances. Then the Sun comes out. I use this particular cartoon in mathematical modeling classes to emphasize the dangers of making false (or at best, weak) assumptions.)

Later, another estimation beckons us. Libbrecht states that the total global precipitation per day is equivalent to about 10^{15} liters of water, and each of us typically exhales about 1 liter of water per day into the atmosphere. By simple proportion, therefore, and using his figures, we infer that if our contribution to the water cycle were uniformly distributed around the globe (seemingly yet another flawed assumption), then our average contribution to the total water content of a snow crystal is about $10^{18} \div 10^{15} = 10^3$ molecules. On this number, not surprisingly, we agree.

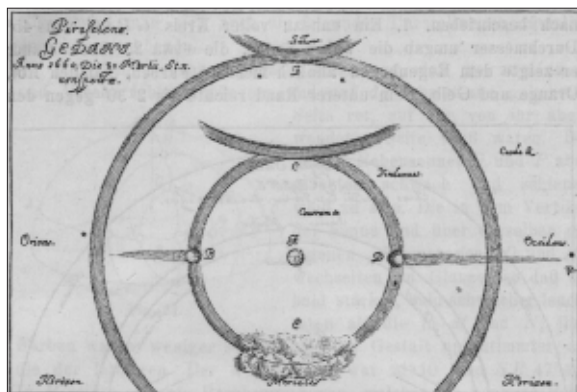
The chapter closes with a nice little section about ice nucleation: how water molecules, like adolescents, eventually learn to settle down and become very cool (or freeze, in the case of the former). There is also a rather intricate table classifying some of the many types of snow.

Chapter 7 ("A Field Guide to Falling Snow") is by far the longest in the book and is accompanied by many beautiful photographs. We are introduced to a veritable zoo of snow crystals: diamond dust (of which cirrus clouds are made), stellar dendrites, sector plates, columns and needles, hollow columns, needles and bullets, capped columns, split stars and split plates, twinned crystals, twelve-sided snowflakes and double stars, chandelier crystals, spatial dendrites, triangular crystals, and rimed snowflakes!

What type of ice crystal then was responsible for the sundog I mentioned earlier (such patches of colored light are also known as *mock suns* or *parhelia*)? Billions of slowly falling horizontally oriented hexagonal plate like crystals (present in cirrus clouds) 30 microns or larger are the culprits. They behave like tiny prisms and refract light entering one vertical face (say face 1) and exiting face 3. Unlike rainbow formation, there is no reflection involved, and so the red portion is always closest to the Sun. They occur at least 22° away from the Sun. There are many other related phenomena one may observe, such as ice crystal halos, and



This photograph of atmospheric halos was taken at the South Pole, where conditions are frequently favorable. It was provided by Walter Tape, now at the University of Alaska in Fairbanks. It is one of many photographs in his book [35].



This drawing of halos was made in Danzig, 1661 by the astronomer Hevelius. It is one of several early records described in the book on meteorological optics by J. M. Pernter and F. M. Exner.

some of them very rare. A common example is the 22° halo around the Sun (or the Moon, but it is much fainter for obvious reasons). However, only small (less than about 20 microns in size) columnar crystals are responsible for this particular optical manifestation. Again, light is refracted between alternate faces of the hexagonal columns, but the crystals are small enough to tumble, and so are randomly oriented as they fall. I see these halos, or parts of them, at least once a month on the average, and sometimes they can last for an hour or two. There are many other types of halos; details and further references may be found in [2] and [35]. A general mathematical setting for halo theory is available in [36] (see also [18], in which the use of symmetry arguments is further explored, together with some speculations on possible halo forms produced in the atmosphere of Titan!)

In passing, Libbrecht briefly addresses the question: Why (not who) is snow white? To which we may add: Why does it seem so quiet outside after a snowfall? In fact, let us generalize the first question by asking why it does appear white, while ice (in sufficient quantities, as in a glacier) appears somewhat blue in color. Snow is made of small crystals of ice, as we well know by now. There are myriads of tiny surfaces from which light is reflected, resulting in a very efficient scattering process in which very little absorption takes place. This high reflectivity, incidentally, is also the main reason why snow is melted more by warm air than by direct sunlight. By contrast, ice is a continuous medium (on the scale of ice crystals, at least), and so sunlight is more readily absorbed because of the longer path-length between scattering centers. Blue light is absorbed rather less efficiently than are longer wavelengths, but this is not obvious in something as small as an ice cube! Large quantities of ice allow an accumulation of the effects of scattering and absorption by not only the ice molecules but the plentiful supply of dust, air bubbles, and other

particulate matter. As to the question not asked in the book: sound waves are readily absorbed by a thick covering of fresh snow, because all the air pockets are prone to trapping the waves to a certain extent. As noted in [16], as snow ages, it changes from being light and fluffy to smooth and hard, and in this state it can become an efficient reflector of sound waves, and sounds may seem clearer and be heard from greater distances.

Chapter 8 (“In Search of Identical Snowflakes”) addresses what might be termed “the question we have all been waiting for”: *Is every snowflake unique?* In a recently used phrase, the answer to this question depends on what is meant by the word “is”. Less flippantly, the answer does depend on how powerful a “magnifying glass” one wishes to use to provide an answer. It is an axiom of fundamental physics that all electrons are identical, so at this scale the components of all snowflakes are identical. However, since this applies to elephants and teapots as well, the concept is not particularly helpful. Moving up in size from electrons, it is also true that “ordinary” (as opposed to “heavy”) water molecules are identical. Heavy water is water composed of deuterium, a stable isotope of hydrogen, occurring with a frequency of about one deuterium atom for every 5,000 of the lighter hydrogen atoms. Another stable isotope of oxygen has a relative frequency of occurrence of about one in 500, so while a snow crystal might contain water molecules, about 1 in 500 water molecules will be different from the rest. The number of configurations containing these heavier oxygen atoms is combinatorially enormous, so the likelihood of two snowflakes being identical is equivalent to that of the sustained existence of the proverbial snowball in the proverbial very hot place. But as Libbrecht reminds us, crystals contain impurity atoms, stacking faults, and other types of defects. And this does not help matters, to say the least.

If we relax our requirement of mathematical uniqueness at the atomic and molecular level, using a good optical microscope with resolution down to about 10^{-3} mm, it might well be possible to find two hexagonal plates that appear indistinguishable, but the more complex crystals are very intricate, with all sorts of minor asymmetries, so the problem gets worse again. Just as with the early stages of male pattern baldness, it all depends on how closely one looks.

The “afterword” by photographer Patricia Rasmussen is beautiful, not least because of her obvious love for poetry. And with mention of the word *beauty*, it is appropriate to quote both Poincaré (as stated in Chapter 8 of the book) and Kenneth Libbrecht himself as he ends this, his last chapter.

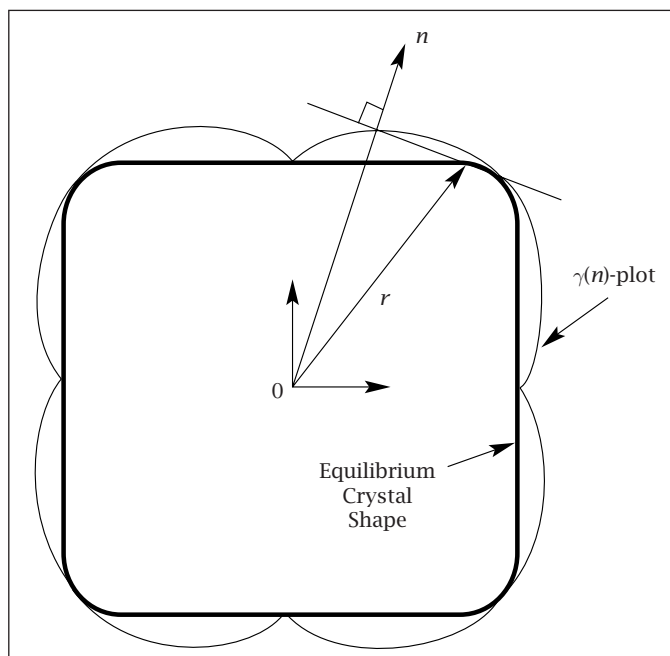


Figure 1: The equilibrium crystal shape (for cubic symmetry) formed from the Wulff construction; the boundary is shown in bold. It is the interior envelope of the set of perpendiculars to radial rays intersecting the $\gamma(\mathcal{N})$ (surface free energy) polar plot. (From [43].)

The scientist does not study nature because it is useful; he studies it because he delights in it, and he delights in it because it is beautiful. (Jules Henri Poincaré, 1908)

There is great beauty in a large, symmetrical stellar crystal. The beauty is enhanced by the magnifying lens that brings out the fine structures in the ice. The beauty is enhanced still further by an understanding of the processes that created it. (Kenneth G. Libbrecht, 2003)

Is Seeing Believing?

By searching through both old and recent snowflake photographs with a computer search tool specially designed for the task, candidates for indistinguishable flakes have been found. Because of the poorer quality of the picture on the left, however, some difficult work remains to be done. These photographs were taken on the first day of April, which might account for the similarity of the flakes.



A last word on the topic of snow crystals may be of interest:

Thanks to the sharp eyes of a Minnesota man, it is possible that two identical snowflakes may finally have been observed. While out snowmobiling, he noticed a snowflake that looked familiar to him. Searching his memory, he realized it was identical to a snowflake he had seen as a child in Vermont. Weather experts, while excited, caution that this may be difficult to verify.

See more about snow crystals on Kenneth Libbrecht's website www.snowcrystals.net.

Mathematical Appendix

A snow crystal pattern is an interfacial phenomenon, occurring at the boundary between the solid phase and vapor phase of water. By contrast, an ice crystal grows at a solid/liquid boundary. There is a plethora of theoretical papers on the subject of crystal formation (for a sample, see the references), only a small proportion of these, understandably, being devoted to snow or ice crystals. I will attempt to provide a general overview of the topic and then address some of the particular models of snow and ice crystal formation.

As noted already several times, many nonbiological patterns in nature arise at the moving interface between two domains or phases, such as an ice-water vapor boundary, with competition between forces tending to stabilize and destabilize the boundary. However, in contrast to complex biological systems, crystal growth perhaps represents a conceptually simpler example of spontaneous pattern formation and self-organization, based on the existing "laws" of thermodynamics, statistical mechanics, kinetics, and transport theory. Nevertheless, many of the theoretical problems associated with these phenomena are quite formidable mathematically.

A snowflake with its planar hexagonal symmetry is a good illustration of some of the questions

that can be asked in a more general context. They are patterns that have emerged, apparently, from a structureless environment, and as has been noted previously, they are very sensitive to that environment. Depending on the history of each ice crystal as it moves through regions of different temperature, supersaturation, and airspeed, there will be formed several different types of ice structure; and since each history is (presumably) unique, so in principle is each snow crystal.

According to the review by Langer [19], regularly faceted crystals will form under a wide variety of conditions when the molecules are tightly bound on crystallographic planes. At the other extreme, when the surface molecular binding is sufficiently weak (as in many metals and alloys), growth is dominated by the mechanism of diffusion close to the solidification front (and may be rapid). In such cases, the fluid-solid interfaces are macroscopically smooth but microscopically rough. Ice falls between these two extremes: facets grow slowly parallel to the basal plane, but rapidly in the hexagonal directions, and surfaces tend to be rounded.

There are two basic types of mechanism that contribute to the solidification process: diffusion control (involving long-range processes) and interface control (involving local processes). In [42], models based on these mechanisms are referred to respectively as *nongeometric* and *geometric* growth models. In the latter, the interfacial growth velocity is determined by local conditions only, and hence diffusion-driven morphological instabilities are absent. However, even this is something of an oversimplification, because a geometric model may be used to examine diffusion-limited growth if the interfacial speed is sufficiently large. (In this context the appropriate length scale L is essentially the diffusivity divided by the interface speed; large gradients can exist, and the boundary layer of thickness L effectively defines the interfacial region.) A model is considered geometric if the normal velocity at an interfacial point depends only upon the shape and shape-dependent quantities of the interface.

By contrast, nongeometric models pertain to growth on surfaces that are everywhere rough and are usually formulated as some type of free boundary problem. It transpires that such diffusion-controlled models of simple geometric shapes such as planes, cylinders, and spheres are commonly unstable. For example, if a plane solid interface develops a small bump extending into the vapor phase or liquid phase, the temperature gradient is locally larger than in its immediate neighborhood (because the isotherms are closer at that point), latent heat diffuses away more rapidly, and the bump continues to grow, at least until the stabilizing effect of surface tension (via the curvature of the interface) becomes comparable. How does

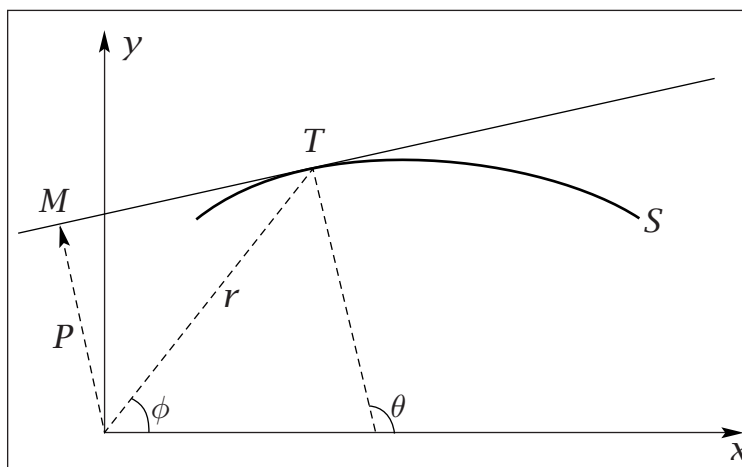


Figure 2: A portion of the crystal boundary S used in establishing equations (4) for the total free energy \mathcal{F} and the “area” of the two-dimensional crystal. (The notation of [9] is used in this figure.)

this stabilizing effect come about? The surface molecules on a bump with positive curvature have fewer nearest neighbors than do those on a plane surface and are thus more susceptible to being removed, and the bump will tend to move back to the plane configuration. This corresponds to a reduction in the melting temperature of the bump. Similarly, molecules on the surface of a negatively curved region have more nearest neighbors and are more tightly bound; the melting temperature has been raised.

Thus, a moving interfacial boundary is driven by a diffusion field gradient and inhibited by curvature-related forces. A common feature of such competition between stabilizing and destabilizing influences is the existence of a characteristic length scale for the resulting pattern. It is often difficult to predict the pattern selection principles that operate in these systems. Such patterns, as noted above, are sensitive to the system geometry and external conditions in general. A valuable review of pattern formation models in this context can be found in [17]. Mathematically, the problem of a moving and developing interface between two distinct media is a Stefan problem, wherein a nonlinear system evolves dynamically in time. As noted in [7], this problem is especially interesting when the interface motion is a nonequilibrium problem, where the configuration is initially such that the free energy of the system is not at an absolute minimum.

A very useful resource for mathematicians interested in the subject of crystal formation is the review in [37]. Therein, an important convex set, known as the *Wulff shape* (or equilibrium crystal shape) is introduced. The equilibrium crystal shape is the shape which minimizes the total surface free energy per unit area $\gamma(\mathcal{N})$ for the volume it encloses, and its boundary \mathcal{W}_γ is defined as

$$(1) \quad \mathcal{W}_y = \{\mathbf{r} : \mathbf{r} \cdot \mathcal{N} \leq y(\mathcal{N}) \forall \mathcal{N}\}.$$

$y(\mathcal{N})$ is orientation-dependent, \mathcal{N} is the unit normal vector, and \mathbf{r} is the radius vector of any point on the equilibrium crystal surface (see Figure 1). \mathcal{W}_y is determined uniquely by the *Wulff Theorem (or construction)*, one proof of which is given below. Another important boundary is the steady-state growth shape \mathcal{W}_V defined by

$$(2) \quad \mathcal{W}_V = \{\mathbf{r} : \mathbf{r} \cdot \mathcal{N} \leq V(\mathcal{N}) \forall \mathcal{N}\},$$

where $V(\mathcal{N})$ is the growth rate in the direction \mathcal{N} . For further references to the Wulff construction, see [11].

Wulff's Theorem

In a crystal at equilibrium, the distances of the faces from the centre of the crystal are proportional to their surface free energies per unit area [9]. The proof and notation therein for the two-dimensional case will be followed here. The fundamental idea is to relate the equilibrium shape of the “crystal” to the polar plot of the surface free energy. This is done via the Wulff construction (again, see Figure 1), which is the interior envelope of the set of perpendiculars to radial rays intersecting the latter [43]. The equilibrium shape is determined by the requirement that the total free energy for a given crystal “area” is a minimum.

We consider a point $P(x, y)$ on the boundary S of the crystal; the polar coordinates of P are (r, ϕ) . Here the arc length parameter will be denoted by θ for consistency with [9], but also to emphasize that we are dealing with rather general equilibrium boundary curves as opposed to the circular ones discussed in the model below. (Note that θ will be used in two other ways in the models below.) The line segment OM (see Figure 2) is the perpendicular from the origin to the tangent line to S at P ; it has length p . Denoting the edge free energy per unit length of a boundary element by $f(\theta)$, the total free energy F and the area n (related to the number of molecules) are respectively given by

$$(3) \quad \begin{aligned} F &= \int f(\theta) ds = \int f(\theta) (\dot{x}^2 + \dot{y}^2)^{1/2} d\theta \\ \text{and } n &= \frac{1}{2} \int (x\dot{y} - y\dot{x}) d\theta, \end{aligned}$$

where $\dot{x} = dx/d\theta$, etc. From the figure and standard algebra,

$$p = x \cos \theta + y \sin \theta.$$

The locus of M as the point P moves around the boundary curve S will be the pedal curve of S . The expression above and its derivative with respect to θ can be inverted to obtain

$$x = p \cos \theta - \dot{p} \sin \theta \quad \text{and} \quad y = p \sin \theta + \dot{p} \cos \theta.$$

Hence

$$(4) \quad F = \int (p + \dot{p}) f(\theta) d\theta \quad \text{and} \quad n = \frac{1}{2} \int (p + \dot{p}) p(\theta) d\theta.$$

The total free energy must be minimized subject to the constraint $n = \text{constant}$. If the choice of Lagrange multiplier λ is made such that we can define the quantity

$$(5) \quad Q(\theta, p, \dot{p}, \ddot{p}) = \frac{1}{2}(p + \dot{p})p - \lambda(p + \dot{p})f,$$

then the appropriate Euler-Lagrange equation is

$$(6) \quad \frac{\partial Q}{\partial p} - \frac{d}{d\theta} \left(\frac{\partial Q}{\partial \dot{p}} \right) + \frac{d^2}{d\theta^2} \left(\frac{\partial Q}{\partial \ddot{p}} \right) = 0.$$

It follows that

$$(7) \quad (p + \dot{p}) - \lambda(f + \dot{f}) = 0,$$

with solution

$$(8) \quad p(\theta) = C \sin(\theta - \theta_0) + \lambda f(\theta)$$

for arbitrary constants C and θ_0 . By choosing the origin in such a way that the crystal has some rotational symmetry about it, the choice $C = 0$ is permissible. Then

$$(9) \quad p(\theta) = \lambda f(\theta),$$

which establishes that the polar diagram of the edge free energy is proportional to the pedal of the equilibrium shape of the crystal.

It is important to note that the steady-state shape of a crystal is not as general as the Wulff shape for an equilibrium crystal, because it is not obtained from an initial value problem. Not all initial shapes will in fact reach this steady-state shape, and neither does it indicate what class of geometric models results in a convex form from an initial shape. Further details on this and other aspects of the problem may be found in [41].

A “Toy” Model for Crystal Growth

As a precursor to the more physically significant models of crystal growth discussed below, let us examine a specific yet simple evolution equation for the interface in a two-dimensional geometrical model and comment on its stability. The model that follows is not particularly realistic physically—only the lowest order curvature term is retained to exhibit the desired behavior of the boundary—but it must be emphasized that it is merely a mathematical simile; it cannot be derived from the kinetics of crystal growth for realistic crystals. In fact, a model of this type is one in which the boundary layer effectively defines the interface: as noted earlier, the characteristic length scale L is the ratio of the diffusion coefficient to the interfacial speed, and this would be true in practice only if the crystal growth speeds were excessively high. Nevertheless, for applied mathematicians, toy models are

the aesthetic equivalent of “back-of-the-envelope” calculations for engineers!

If \mathbf{x} is the position vector of a point on the interface corresponding to outward unit normal \mathcal{N} , then we assume that

$$(10) \quad \mathcal{N} \cdot \frac{d\mathbf{x}}{dt} = U(\mathbf{x}; s, \kappa),$$

where the speed U is a function of the local surface geometry, being dependent on position, and implicitly on arc length s and curvature κ . What form might U take? One choice is [7]:

$$(11) \quad U = V(\kappa) + \gamma \frac{\partial^2 \kappa}{\partial s^2}.$$

The second term corresponds to the stabilization mechanism for short wavelengths when $\gamma > 0$. Heuristically we may choose the “curvature potential” V to take the form of a cubic for the following reasons. A planar interface cannot move at all (except under very special circumstances), so $V(0) = 0$. The growth rate of a spherical crystal (or circular in two dimensions) behaves like R^{-1} for large R , so we would expect $V \approx \alpha\kappa$ for small κ . Noting further that a solid with large curvature will contract due to forces of surface tension, U must become negative for some value of κ . Hence there must be a minimum “bubble” size for nucleation, and this corresponds to a term $-\beta\kappa^3$ in V , where β is related to the minimum size for nucleation. A quadratic term, $\mu\kappa^2$, is also included in the expression for V to account for an asymmetry in the solidification process between the freezing and the remelting of the dynamic interface, so we write

$$(12) \quad V(\kappa) = \alpha\kappa + \mu\kappa^2 - \beta\kappa^3.$$

Stability Criteria

In terms of the unit tangent vector \mathcal{T} to the curve at a point with polar angle θ (s being arc length along the boundary curve), the curvature vector κ is variously defined as

$$\begin{aligned} \kappa &= d\mathcal{T}/ds = (d\mathcal{T}/d\theta)/(ds/d\theta) \\ &= (d\mathcal{T}/d\theta)/|d\mathbf{x}/d\theta|, \end{aligned}$$

where $\mathbf{x}(\theta)$ is the position vector. For a circle with time-dependent radius $r(t)$ and the special case of $U = V(\kappa) = \kappa$ (with the unit of length chosen to fix $\alpha = 1$ [7], [8]), the equation

$$\mathcal{N} \cdot \frac{d\mathbf{x}}{dt} = U(\mathbf{x}; s, \kappa)$$

reduces to

$$(13) \quad \frac{dr}{dt} = V\left(\frac{1}{r}\right),$$

with solution

$$(14) \quad r(t) = [2t + r^2(0)]^{1/2}.$$

Performing a linear stability analysis around this solution, following [8] (see also [42]) we consider radial perturbations only, because tangential terms can be eliminated by a suitable gauge transformation (equivalently, they can be shown to drop out of the linear stability analysis). Thus

$$(15) \quad \mathbf{x} = \hat{\mathbf{r}}[r(t) + \varepsilon(t, \theta)].$$

Then

$$(16) \quad \kappa = |\kappa| = \frac{1}{r} - \frac{1}{r^2} \left(\frac{\partial^2}{\partial \theta^2} + 1 \right) \varepsilon \equiv \kappa_0 + \kappa_\varepsilon,$$

where $\kappa_0 = r^{-1}$, and

$$(17) \quad \frac{\partial^2 \kappa}{\partial s^2} = -\frac{1}{r^4} \frac{\partial^2}{\partial \theta^2} \left(\frac{\partial}{\partial \theta^2} + 1 \right) \varepsilon.$$

Since

$$V(\kappa_0 + \kappa_\varepsilon) = V(\kappa_0) + \kappa_\varepsilon V'(\kappa_0) + O(\kappa_\varepsilon^2),$$

the linear perturbation $\varepsilon(t, \theta)$ may be shown to satisfy the equation

$$(18) \quad \begin{aligned} \frac{\partial \varepsilon}{\partial t} &= -\frac{V'(\kappa_0)}{r^2} \left(\frac{\partial^2}{\partial \theta^2} + 1 \right) \\ &\quad \times \varepsilon - \frac{\gamma}{r^4} \frac{\partial^2}{\partial \theta^2} \left(\frac{\partial}{\partial \theta^2} + 1 \right) \varepsilon. \end{aligned}$$

Seeking eigenfunctions of the form

$$(19) \quad \varepsilon(t, \theta) = \varepsilon_m e^{\sigma_m t} \cos m\theta,$$

we see that the linear growth rate

$$(20) \quad \sigma_m = \frac{(m^2 - 1)}{r^2} \left[V' \left(\frac{1}{r} \right) - \frac{\gamma m^2}{r^2} \right].$$

The $m = 1$ mode corresponds to a uniform rotation of the circle and is a neutrally stable perturbation. As noted in [8], the first term is stable for all $m (\neq 1)$ if $V'(1/r) > 0$, and since for sufficiently large radii $V \sim \kappa$, this will occur even for nonzero μ and β in the complete expression for V . This simple result is the analog of the Mullins-Sekerka instability as discussed in [29], [30] (see also [10], [31], [46]). The second term is always stabilizing for $m > 1$ (with γ playing a role analogous to that of surface tension), so this will act to limit the range of m -values that are in the unstable regime.

More Sophisticated Models

Based on more detailed theoretical physics, how might the interface evolution of a crystal be characterized mathematically? Following the approach in [42], we consider the boundary of a two-dimensional crystal to be represented by the closed curve $C[x(u, t), y(u, t)]$ in the plane, with time dependent components parametrized by the variable

u . Let the arc length s be related to u via the relation

$$(21) \quad s(u, t) = \int_0^u \left| \frac{\partial C(u', t)}{\partial u'} \right| du'.$$

Further, let $W = |\partial C(u, t)/\partial u| = ds/du$. θ is now defined to be the angle between the positive x -axis and the unit tangent vector $\mathcal{T} = (\cos \theta, \sin \theta) = W^{-1} \partial C(u, t)/\partial u$, and the unit normal vector \mathcal{N} is inward pointing. The boundary evolves in terms of the normal velocity function $V(\theta, \delta\mu)$ according to

$$(22) \quad \left(\frac{\partial C}{\partial t} \right)_u = -V \mathcal{N}.$$

The initial-value problem with V defined as above can be solved exactly by the method of characteristics, since the normal velocity of the interface depends explicitly on the surface orientation alone. They are rays of the form $\mathbf{x}(t) = \mathbf{x}_0 + \mathbf{d}(\theta_0)t$, \mathbf{x}_0 being a point on the initial curve, and $V(\theta_0; \mathbf{x}_0)$ is in the direction $\mathbf{d}(\theta_0)$. The surface normal direction is preserved along each characteristic, and so the curve C at time t is defined by the set of all points $\mathbf{x}(t)$.

To discuss the curvature evolution, both global and local, we require that the two appropriate Frenet equations for the unit tangent (\mathcal{T}) and normal (\mathcal{N}) vectors at a point on the boundary curve are

$$\frac{\partial \mathcal{T}}{\partial s} = \kappa \mathcal{N} \quad \text{and} \quad \frac{\partial \mathcal{N}}{\partial s} = -\kappa \mathcal{T},$$

($\kappa = \partial \theta / \partial s$). If arc length is used to parametrize these quantities in terms of the closed interfacial boundary curve C [42], then

$$(23) \quad \mathcal{T}(s, t) = \frac{\partial C}{\partial s}, \quad \kappa(s, t) = \left| \frac{\partial^2 C(s, t)}{\partial s^2} \right|,$$

$$\text{and } \mathcal{N}(s, t) = \kappa^{-1}(s, t) \frac{\partial^2 C(s, t)}{\partial s^2}.$$

Following [13] and also [42], we can prove the following identities:

$$(24) \quad \frac{\partial W}{\partial t} = \kappa V W; \quad \left[\frac{\partial}{\partial t}, \frac{\partial}{\partial s} \right] = -\kappa V \frac{\partial}{\partial s},$$

$$\frac{\partial \mathcal{T}}{\partial s} = -\frac{\partial V}{\partial s} \mathcal{N}; \quad \frac{\partial \theta}{\partial t} = -\frac{\partial V}{\partial s}.$$

Since W is essentially a measure of the length of an infinitesimal displacement on the boundary, the differential equation for W represents its rate of dilation. The corresponding equations in \mathcal{T} and θ describe the rotation rates of those quantities, as determined by the anisotropy of V . After some subtle reformulation (involving gauge invariance arguments), a nonlocal integrodifferential equation for the curvature evolution can be derived, namely:

$$(25) \quad \left(\frac{\partial \kappa(s, t)}{\partial t} \right)_s = - \left(\frac{\partial^2 V}{\partial s^2} + \kappa^2 V \right) - \frac{\partial \kappa}{\partial s} \int_0^s \kappa V ds'.$$

As pointed out in [8], when the curve C is parametrized by θ rather than by u or s , then the evolution equation for κ becomes strictly local. This is a consequence of the fact that its rate of change at fixed θ is given by

$$(26) \quad \left(\frac{\partial \kappa}{\partial t} \right)_\theta = \left(\frac{\partial \kappa}{\partial t} \right)_u - \left(\frac{\partial \theta}{\partial t} \right) \left(\frac{\partial \kappa}{\partial \theta} \right) \equiv \frac{\partial \kappa}{\partial \tau}.$$

Thus

$$(27) \quad \frac{\partial \kappa}{\partial \tau} = -\kappa^2 \tilde{V}(\theta),$$

where $\tilde{V} = V + V''$ is named the “velocity stiffness” in [42]. These results also can be derived by considering the curve as a set of complex numbers in the plane [8]. For finite \tilde{V} this equation has solution

$$(28) \quad \kappa = \frac{\kappa(0)}{1 + \kappa(0) \tilde{V} \tau},$$

in terms of the initial curvature $\kappa(0)$. If $\tilde{V} > 0$, the curvature will decrease monotonically in time at nonfaceted orientations for which $\kappa(0) \neq 0$. For orientations in which $\tilde{V} < 0$, the curvature diverges at finite time, $\tau = -(\kappa(0) \tilde{V})^{-1}$. In fact, as discussed below, a shock (intersection of characteristics) develops before the minimum blow-up time.

In defining a local normal velocity with reference to a weak “growth drive” $\delta\mu$ (the chemical potential difference between the surface and external phase), two different kinetic processes are merged via a convexity type of argument involving a transition function $\xi(\theta)$ to form an expression for the local normal velocity of a crystal with n -gonal symmetry. This is

$$(29) \quad V(\theta, \delta\mu) = V_f(\delta\mu) \xi(\theta) + V_r(\theta, \delta\mu) (1 - \xi(\theta)),$$

where

$$(30) \quad V_f(\delta\mu) = c_f g(\delta\mu) \exp \left(\frac{-\pi \sigma^2}{kT \delta\mu} \right),$$

and

$$(31) \quad V_r(\theta, \delta\mu) = c_r \delta\mu \left[1 + \cos^p \left(\frac{n\theta}{2} \right) \right],$$

where p is an even integer. V_f (for *facet*) is the normal growth rate at facet orientations under the “growth drive” $\delta\mu$, while V_r (for *rough*) describes the normal interfacial motion at vicinal and molecularly rough orientations (due to surface migration of adsorbed molecules away from facets). Since $0 \leq \xi(\theta) \leq 1$, this function is a measure of

the distribution between facetlike and roughlike growth. It is periodic in $2\pi/n$, and $\xi(\theta_f) = 1$, $\xi(\theta_f + \pi/n) = 0$ for a facet orientation θ_f . In [42] the choice of $\xi(\theta) = \cos^m(n\theta/2)$, $m \geq p$ being even, is made. If in particular $\theta = \pi/4$ and $n = 4$ in the definition of \tilde{V} , then for $m = p = 2$, $\tilde{V} = c_r\delta\mu + 8V_f$, which implies that the rate of curvature decrease increases with $\delta\mu$. In short, the polygonalization of crystals corresponds to decreasing curvature in rough orientations.

Thus, in general, a crystal has slowly growing molecularly smooth faces (facets) and more rapidly growing faces that are rough at the molecular level. At this level, both structures are sensitive to temperature, as one might expect. Facet locations are associated with minima of the surface free energy, and indeed a crystal shape may be only partially faceted, but a major question for crystal growth is to find what processes are responsible for the evolution of an initial “seed crystal” towards a faceted asymptotic growth shape. This is called *global kinetic faceting* and has been observed to occur experimentally and numerically [26] and has been predicted theoretically [42]. In this process, the rough orientations of partially faceted shapes grow out of existence with decreasing curvature. Such a decrease implies the presence of discontinuities in surface slope (or a jump in the normal to the surface), so it is of considerable interest to be able to tie the time-dependence of the local curvature to the ultimate shape of the crystal boundary. Mathematically, discontinuities of this kind are associated with both singularities in the interfacial curvature and the intersection of characteristics [39]. The latter viewpoint, while complementary to the former, corresponds to the existence of shocks in the solution of the surface evolution equation. The dynamics of such shocks, when they exist, are of great importance in the interpretation of experimental data. Furthermore, it has been shown in [41] that if the initial seed crystal is convex, then convexity is preserved throughout the whole growth process. Forms of V that possess cusps at faceted orientations also explain the formation of expanding facets separated from rough orientations by a corner, called *shocking facets* in [40]. Specifically, in place of expression (29) for $V(\theta, \delta\mu)$, now

$$(32) \quad V(\theta, \delta\mu) = V_f(\delta\mu)\xi(\theta) + V_r(\theta, \delta\mu),$$

where

$$(33) \quad V_r(\theta, \delta\mu) = c_r\delta\mu (a|\sin 2\theta| - b\sin^2 2\theta),$$

where the coefficients a and b are related to certain angular rates of change. It transpires in this case that models with the parameter range $2b < a < 7/3b$ correspond to the formation and expansion of facets accompanied by decreasing cur-

vature at rough orientations. Further, if t_0 is the time of corner formation, the facet collides with the shock at $t \approx 1.1t_0$ almost immediately after shock formation, consistent with observations [40].

Green's Functions

The literature on this subject abounds with examples of the application of Green's function techniques to the growth and development of crystals and might well be a useful source of examples for graduate classes. This particular analysis is based on the approach in [40] (but see also [25]). In connection with shocking facets, the temperature field T around an expanding surface with a constant density of heat sinks is computed using Green's functions for the two-dimensional diffusion problem. The expression for the field at $(x, z; t)$ is

$$(34) \quad u(x, z; t) = u_0(x, z) - \int_0^t dt' \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G(x - x', z - z'; t - t') \times Q(x'z'; t') dx' dz',$$

where $u = (T - T_\infty)/T_\infty$, T_∞ being the melt temperature far from the interface. The temperature field before the formation of a shocking facet is u_0 , and the standard Green's function for the diffusion problem

$$(35) \quad \left[\frac{\partial}{\partial t} - k\nabla^2 \right] G(x, z; t) = \delta(x)\delta(z)\delta(t)$$

is

$$(36) \quad G(x, z; t) = \frac{1}{4\pi kt} \exp\left(-\frac{x^2 + z^2}{4kt}\right),$$

k being the thermal diffusivity of the melt. The source term is

$$(37) \quad Q(x, z; t) = qH(vt - x)H(x)\delta(z),$$

in terms of the Heaviside step-function H and the Dirac delta function δ (remember that distribution theoretic distinctions and subtleties are usually suppressed in much of the scientific literature). The term q is a heat flux constant, proportional to the surface density of heat sinks. After some rearrangement

$$(38) \quad u(x, z; t) - u_0(x, z) = -\frac{q}{4k} \int_0^t dt' \frac{e^{-z^2/4k(t-t')}}{t - t'} I,$$

where

$$I = \sqrt{4k(t - t')} \int_{-\alpha}^{-\alpha+\eta} e^{-n^2} dn, \\ \alpha = x/\sqrt{4k(t - t')}, \\ \eta = vt/\sqrt{4k(t - t')}.$$

Experimentally, the authors found that $vt \ll \sqrt{4kt}$. Under the experimentally reasonable assumption that $\eta \ll 1$,

$$I \approx \eta \sqrt{4k(t-t')} e^{-a^2};$$

whence

$$(39) \quad \begin{aligned} u(x, z; t) - u_0(x, z) &\equiv \tilde{u}(x, z; t) \\ &\approx -\frac{qvt}{4k} \int_{(x^2+z^2)/4kt}^{\infty} \frac{e^{-\lambda}}{\lambda} d\lambda. \end{aligned}$$

Noting that the exponential integral [6] is defined as

$$(40) \quad \begin{aligned} E_1(x) &= \int_{\theta}^{\infty} \frac{e^{-\lambda}}{\lambda} d\lambda \\ &= -\ln \theta - \gamma + \sum_{n=1}^{\infty} \frac{(-1)^{n+1} \theta^n}{n \cdot n!}, \end{aligned}$$

where γ is the Euler-Mascheroni constant, it follows that when $(x^2 + z^2)/4kt \ll 1$,

$$(41) \quad \tilde{u}(x, z; t) \approx -\frac{qvt}{4k} \left(-\gamma + \ln \frac{4kt}{x^2 + z^2} \right).$$

At the other extreme, for short times such that $4kt \ll x^2 + z^2$, \tilde{u} is exponentially small. Using experimental data, Tsemekhman and Wettlaufer [40] estimate that the geometric model begins to fail at $t \approx 10$ s. From this and related observations, the authors conclude that geometric models of the entire interface are very accurate up to about $t = 15$ s. Ultimately the model breaks down when q is no longer constant, and nonlinear effects become significant. Studies such as this one confirm that geometric models are very useful in describing the early stages of the evolution of a crystal surface. Some of these models predict the possible formation of a shocking facet and are still applicable for some time beyond this point. Indeed, according to Wettlaufer [private communication], even the timescales cited above do a great injustice to the utility of the geometric approach: for solid helium growing from a superfluid, the geometric model is the only model of significance, and it never breaks down!

Summary

There are many other mathematical aspects of crystal formation that have been investigated over the last several decades. It is a field rich in theory, experiment, and applications (particularly interesting, for example, but outside the scope of the present review, is the asymptotic analysis found in [44], [45]). Interesting theoretical papers on dendrite formation are presented in the set [20]–[24], [27], [28]. In addition, many theoretical developments are to be found outside the “standard” applied mathematical literature: some of the papers cited below are published in the *Journal of Crystal Growth*, and *Physical Review E*, for example, so it is incumbent on those of us interested in entering a field such as this sometimes to walk in pastures new.

Personally, I have been both pleasantly surprised and pleased to encounter such a broad swath of thoughtfully written papers addressing crystal growth. I hope that this review will be a useful (but clearly not exhaustive) resource for readers wishing to pursue the subject further. However, a caveat is in order: a review of this nature must maintain a balance between material of interest to mathematicians while at the same time doing justice to the physics of the problem. Inevitably, the simple models and oversimplified physical descriptions presented here will not satisfy crystal theorists, but as in all topics on the interface between two magisterial disciplines, compromises must be made. This article is no exception, and I will end it with a warning: The mathematical physics of snow crystal formation is *much* more complicated than might be inferred from the discussion presented here!

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Simulating Snowflakes

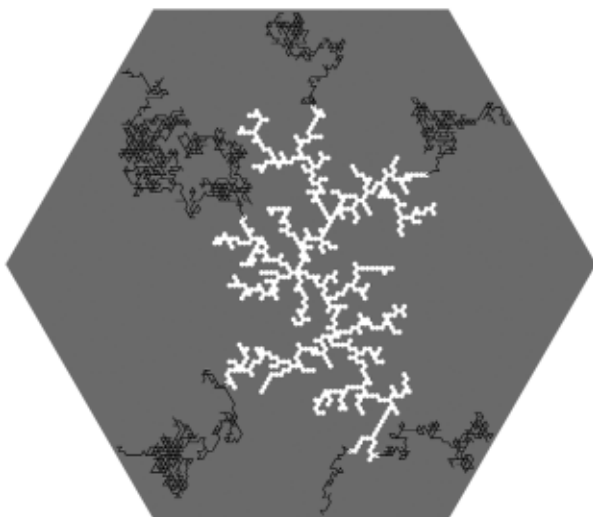
Snowflake formation is very complicated, and one would not expect a purely theoretical account to explain all that occurs. There have been many attempts to simulate the process in software. Even here, the complexities are overwhelming. The principal focus of effort has been to understand the extraordinary sixfold planar symmetry of snowflakes coexisting with a complicated dendritic structure. All simulation attempts seem to have been in a restricted two-dimensional environment.

The central problem is that the symmetry suggests deterministic growth, the dendritic structure randomness. Of course some of the randomness is contributed by a rapidly changing environment. But although the environment is uniform on the scale of a snowflake, the symmetry of real snowflakes is not exact, and this also suggests that local randomness on the snowflake is important.

Other considerations suggest the role of randomness. It is easy enough to construct dendrites in software that, at least locally, look somewhat like snowflakes. The simplest process in which this happens in a physical manner is **diffusion-limited aggregation**, or **DLA**, in which particles wander around randomly and stick irreversibly onto a central, growing core whenever they hit it.

Diffusion-Limited Aggregation

Particles were initially randomly distributed on a hexagonal lattice with a single particle in the



Diffusion-Limited Aggregation. Particles were initially randomly distributed on a hexagonal lattice with a single particle in the central core. The paths show the motion of the particles wandering in randomly from the boundary of the region to attach to the core.

central core. The paths show the motion of particles wandering in randomly from the boundary of the region to attach to the core.

The characteristic feature of DLA is that bump growth is unstable: high curvature means a high gradient in the distribution of particles, which are therefore attracted to bumps. This instability combined with microscopic randomness presumably does play a role in snowflake growth.

Diffusion Instability

Bumps attract diffusing particles, which follow the gradient of a certain potential field. As it grows, the gradient increases, so a bump grows unstably.



Diffusion Instability. Bumps attract diffusing particles, which follow the gradient of a certain potential field. As it grows, the gradient increases, so a bump grows unstably.

The results of DLA do not look much like snowflakes. One simple explanation for this is that dendrites formed in a DLA process are fractal,

which means that they possess a similar structure at all scales. In snowflakes surface tension forbids this and in any realistic simulation must be taken into account. The combined effect of surface tension and DLA is to establish a certain characteristic length involved in the growth process.

Up until about 1985 all attempts to simulate snowflakes built the symmetry in by constructing one arm and then reflecting and rotating it. But then Nittman and Stanley showed that a truly random process could in fact give rise to a good approximate symmetry without artificial forcing. Their process was an extension of DLA in which sites next to the growing core freeze only when they encounter several diffusing free particles. This requirement is already one that assures a certain stability in the process and leads to quasi-symmetry but gives rise only to a very restricted range of snowflake shapes. In addition, they introduced a somewhat artificial parameter that generates thicker dendritic arms. With this, quasi-symmetry is maintained and a wider range of shapes arises. Unfortunately, their construction seems to have little to do with physics.

A much more physically realistic account was that of Yokoyama and Kuroda (of Hokkaido University). Their simulations involved a fairly detailed account of actual surface motion of molecules in ice formation, as well as a detailed analysis of how diffusion behaves at corners. Although extensive dendritic growth does not occur in their models, it does not seem too far away.

One recent attempt at imitating snowflakes has been done with a 2D cellular automaton by Clifford Reiter. The only randomness built into his construction is in the initial state, however, and although some of his figures do resemble snowflakes, it is hard to see what this process has to do with real life.

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—Bill Casselman, Graphics Editor