Nearly everyone is familiar with snow crystals—tiny flakes of ice, remarkably crafted into intricate six-fold symmetric patterns, common icons of ski sweaters and holiday shopping malls. But exactly how do snow crystals develop into such intricate, symmetrical shapes? Where is the sculptor that creates these miniature masterpieces of frozen water, quite literally out of thin air? In my lab at Caltech we have been trying to answer these questions, and more general ones relating to the materials science of crystal growth and the underlying physics of morphogenesis, or pattern formation. And what we’re finding is that there’s a world of interesting and sometimes puzzling physics in snow crystals and how they form, much of which derives from the unique surface properties of ice.

Many people think that snow crystals are made from frozen raindrops, but they’re not—rather they grow from water in the gaseous state. In the cold atmosphere above us, this water vapor condenses directly to form solid ice. The process begins with some nucleus, typically a tiny dust grain, to which water molecules can easily attach. If the humidity of the air is above 100 percent (the air is then said to be supersaturated), water molecules freeze onto the dust nucleus, forming a tiny piece of ice, which subsequently grows into a snow crystal as more water molecules condense out of the air. The intricate patterns we see are the result of just how water molecules selectively attach to the growing crystal.

The actual ice in a snow crystal is no different from that in an ordinary ice cube, and, at the molecular level, we understand the physics quite well: quantum mechanics tells us how two hydrogen atoms and one oxygen atom form a single water molecule, and how water molecules line up and fit together to form a hexagonal crystal lattice (opposite). The basic molecular structure of ice was first proposed by Linus Pauling in 1935, and was one of the early triumphs in the application of quantum physics to materials science.
It’s this hexagonal symmetry of the ice crystal that is ultimately responsible for the six-fold symmetry of the snow crystals that fall from the sky. But just how do molecular forces, acting at the subnanometer scale, control the shape of a snow crystal ten million times larger? This same question applies to all crystals that form facets—flat surfaces that define the crystal shape—such as the mineral specimens shown below.

Facets have an interesting history in human society, which has led to some confusing expressions in our language. Many minerals in the earth grow into beautiful faceted shapes, and in early times these crystals were quite valuable. Since nice mineral specimens are rare, people naturally started carving facets into other materials, particularly glass (in which the molecules are randomly arranged, in contrast to the regular arrangement of atoms in a crystal). So now one can go to Macy’s and buy a piece of fine “crystal”—which is in fact glass—with facets cut into it. Diamonds and other gemstones are crystalline materials, but here again the facets are usually of human origin. An amusing recent development has come from the superstition that quartz (and other) crystals possess mystical healing powers, which has greatly increased the demand for attractive mineral specimens. Demand begets supply, and lately I’ve seen “fake” quartz crystals in stores—real quartz, but with artificially made facets, cut to look like natural faceted quartz. I can’t help but speculate that fake facets must diminish the healing powers, but I haven’t explored the matter further.

Getting back to the natural world, the reason many crystals grow into faceted shapes is simply because some crystalline surfaces grow more slowly than others. And this in turn arises from the molecular structure of the crystal. For example, if we imagine beginning with a small, round ice crystal, we would find that the surface was quite rough on a molecular scale, with lots of dangling chemical bonds. Water molecules from the air can readily attach to these rough surfaces, and they grow relatively quickly. The facet planes are special, however, in that they tend to be smoother on a molecular scale, with fewer dangling bonds. Water molecules cannot so easily attach to these smoother surfaces, and so the facets grow more slowly. After all the rough surfaces have grown out, what’s left are the slow-growing faceted surfaces.

A big problem in crystal growth, and not just for ice, is that quantum mechanics cannot really tell us how fast a given surface will grow. It could in principle; but in practice, for essentially all real surfaces, the problem is exceedingly difficult. Supercomputer simulations can produce molecular models of crystals, but typically these elaborate models are not useful for modeling growth rates, because the thermal motions of molecules are very fast, while crystal growth is quite slow. A typical timescale for molecules in a crystal to joggle back and forth is on the order of picoseconds (10^{-12} seconds), whereas the timescale for crystal growth is far longer—typically microseconds (10^{-6} seconds) or more.

Of course we don’t need to keep track of every molecular wiggle, and over the past five decades many excellent theoretical techniques have been developed to describe the statistical mechanics behind crystal growth. Much of this has been driven by commercial concerns, as semiconductor crystal growth is the foundation of a very, very big business, and ever more sophisticated electronic and optical devices require the growth of ever more complex layered crystals. However, despite this huge, commercially funded research effort, crystal growth remains largely an
empirical science, even for simple and well-studied materials like silicon. And we’re now finding that ice has its own very different and quite fascinating story to tell, mainly because, unlike silicon, it has a very high vapor pressure. To tell this story, we must first see what ice crystals growing from water vapor look like.

We can learn a great deal simply by observing the great bounty of snow crystals that appear out of thin air, in snowfall.

The earth’s atmosphere is not a bad laboratory for the study of snow-crystal structure, and it’s all for free. Natural snow crystals exhibit a remarkable variety of crystal shapes. The photos on the first two pages of this article show a collection of beautiful snow crystals that fell from the skies over Wisconsin, and these beauties demonstrate nicely the intricate structure that most of us associate with snowflakes. (A brief note on meteorological terms: a snow crystal refers to a single ice crystal, while snowflakes are clumps of snow crystals that stick together and fall to earth as little puffs). While such fancy specimens are clearly the favorite of snow-crystal photographers, there are many other common shapes that tell us about the physics of snow crystals. The most basic ice-crystal shape is a hexagonal prism, which has two “basal” facets and six “prism” facets (see above). Very simple crystals like these are actually quite common, and the photo shows some examples that were collected at the South Pole. Because the conditions at the Pole are both very cold and very dry, snow crystals in this environment grow extremely slowly and typically don’t become very large. Slow growth is the key factor for making simple snow crystals, and these tiny gems—in snowfall circles called “diamond dust”—probably floated through the Antarctic air for hours before growing as large as the thickness of a human hair. Not exactly ski sweater material, but these examples show the simple faceting that results from the underlying hexagonal symmetry of the ice crystal.

In more hospitable climates, snow crystals tend to grow much more quickly, and have a greater variety of forms. Simple prisms can grow into long, thin columns, which are usually hollow. Faster-growing columns branch into clusters of long, thin, needlelike crystals. Sometimes a snowfall can consist entirely of these columnar and needlelike crystals—quite painful! On another day, a snowfall could drop a preponderance of platelike crystals: small examples are often just simple hexagonal plates, but larger ones tend to have more structure, such as sectored plates or stellar dendrites (“dendrite” means “treelike,” describing the branched structure of these crystals—these are the ones that come to mind when thinking of snow crystals). Platelike crystals are quite common in the wild, and they are the biggest specimens—often several millimeters across and easily seen with the naked eye.

Permutations of the simpler shapes give us a nearly infinite variety of complex snow crystal shapes—dendrites with sectored plate extensions, sectored plates with dendritic extensions, plates with platelike extensions, and even such exotica as “tsuzumi” crystals, which consist of columns capped with plates (named after a Japanese drum with a similar appearance). Some examples of the main types are shown on the opposite page.

Twelve-sided snowflakes (left) can also be found floating through the air, and are not even that uncommon. These are actually two separate platelike crystals joined together at the center, one rotated 30 degrees relative to the other in a process called crystal “twinning.” For the sake of anatomical correctness, however, I must point out that although eight-sided snowflakes are often seen on holiday wrapping paper, on ski sweaters, and even on soup cans (right), they are never found in nature.

Snow-crystal watching is incredibly easy, and can be quite fascinating. Simply pack a magnifying glass on your next ski trip, or whenever you might encounter some snowfall (a small pocket-size fold-up plastic model is perfect—you don’t need the bulky Sherlock...
Snow crystals don’t just come in the ski-sweater variety. Plate-like forms (top, from left to right) include a simple plate, sectored plate, stellar dendrite, and endless variations. Columnar forms range from simple hollow columns (far left) to thin needles (middle). Capped columns, or tsuzumi crystals, can also be seen (right). Holmes variety). On a good day you can see some beautiful crystals—and as with gemstones, photographs rarely do them real justice. You may find yourself echoing the sentiments of Thoreau, who remarked, “How full of the creative genius is the air in which these are generated! I should hardly admire them more if real stars fell and lodged on my coat.”

So how do we make sense of all these different snow-crystal shapes? The first real scientific steps were taken by Japanese physicist Ukichiro Nakaya in the 1930s. Nakaya trained as a nuclear physicist, but on graduation found that no suitable jobs were available in his field. He eventually took a professorship at Hokkaido University in northern Japan, even though they had no nuclear physics department. Undaunted, Nakaya turned his attention to snow crystals, which were available locally in great abundance. After observing and categorizing natural snow crystals in great detail for the first time, Nakaya then developed techniques to grow artificial snow crystals in his laboratory, so that he could study their properties under controlled conditions.

One of Nakaya’s early problems was that it was very difficult to grow individual snow crystals out of supersaturated air—the usual result was a mixed-up jumble of crystals that formed what was essentially a frost. Nakaya experimented with many thin fibers on which he tried to grow individual snow crystals—cotton fiber, silk fiber, metal wire, and even spider’s web. Nothing worked, until he finally happened upon rabbit hair, and on this he was able to grow single crystals that were a great deal like natural specimens. (We tried this briefly in my lab, but without much success—I suspect we were using the wrong kind of rabbit!)

Nakaya discovered that snow crystals grow in different shapes, or morphologies, depending on the conditions in which they grow—in particular on the temperature and supersaturation of the air. Detailed measurements by Nakaya, and subsequently by others, were used to produce a snow crystal “morphology diagram” (next page) showing the crystal shapes that grow under different conditions.

This interesting diagram tells us a great deal about snow-crystal physics. It shows that the
basic shape of a growing crystal depends mainly on temperature: plates form at around –2 °C, columns at –5 °C, plates again at –15 °C, and either columns or plates below –25 °C. The appearance of structure depends more on the level of supersaturation, and therefore on growth rate: when the humidity is high, rapidly growing columns become feathery needle crystals, and hexagonal plates grow into stellar dendrites. An especially remarkable thing about snow crystal growth is the way the shape, or morphology, changes back and forth between plates and columns several times as a function of temperature. And the changes are large: within a few degrees the morphology changes from very long, narrow, needle-like crystals (at –5 °C) to very thin, flat, platelike crystals (at –15 °C). This is pretty bizarre—other materials don’t change their growth morphology with temperature nearly as much as ice does. So what’s going on?

Two main factors produce what we see in the morphology diagram: the intrinsic growth rates of the crystal facets, and diffusion. Let’s look at crystal facet growth first. When the prism facets grow more slowly than the basal facets, we get columnar crystals; when the basal facets grow more slowly than the prism facets, we get platelike crystals. So the morphology diagram already tells us that the prism and basal facets grow at different rates, and both rates depend sensitively on temperature.

In my lab we’ve been working on a series of quantitative measurements to try to figure out in more detail what’s really behind all this. The physics we’re exploring is the statistical mechanics of crystal growth, which in turn depends on the detailed surface properties of ice. Ice is a better material than you might think for doing basic materials physics—it’s a relatively simple substance, and, because of its environmental importance, ice has been studied using practically every experimental and theoretical tool known, so that the material itself is well characterized. Ice also turns out to be very convenient to work with in the lab—the stuff is cheap, it freezes at an easily accessible temperature, and as a chemical it poses no health hazards whatsoever (aside from drowning, which usually isn’t much of a problem).

The basic idea for our experiments is quite simple: we grow snow crystals under controlled conditions, and measure the crystal dimensions as a function of growth time. In these experiments we usually grow only very tiny crystals, smaller even than the Antarctic ones. Smaller crystals grow mainly as simple prisms, which makes the growth much easier to model theoretically. After some roundabout mathematical machinations we’ve been able to infer the growth rates of the different ice surfaces as a function of temperature, supersaturation, and other conditions. And as you
Ice crystals, left, grown at controlled temperatures and humidities in a crystal growth chamber, show the same variations in size and shape predicted by the morphology diagram on the opposite page. From the top, with two examples for each group: small plates formed at −2 °C with low supersaturation; hollow and filled columns at −5 °C with moderately high supersaturation; large plates and stellar dendrites at −15 °C with high supersaturation; and small, fairly thick plates at −30 °C with low supersaturation.

The growth rates of the basal and prism facets depend strongly on supersaturation as well as on temperature, and some recent measurements show that the rates even depend strongly on the background gas in which the crystals are grown. Snow crystals grown in pure water-vapor conditions (i.e., in a vacuum chamber containing no gases other than water vapor) do not grow into the same thin plates or long needles that we see in air, but rather into more nearly isometric simple prisms. Air is relatively inert, and helium gas is even more so, but both nevertheless slow the surface growth rates substantially, even after factoring out the effects of water-vapor diffusion.

We still don’t understand why ice does all of what it does, which is why we continue studying it. But one feature of ice that almost certainly plays a big role in its crystal growth is a phenomenon called surface melting. For any crystal, the surface molecules are not as tightly bound as the molecules deep inside, since surface molecules don’t have so many neighbors to hang on to. Thus, the surface molecules can sometimes jostle loose while still remaining attached to the solid, forming what’s called a quasiliquid layer (see diagram). This layer disappears at very low temperatures, when it’s so cold that the molecules don’t have much jostle in them, and gets thicker at higher temperatures, eventually increasing to effectively infinite thickness at the melting point. Surface melting is present on a large variety of materials, but the physics of this phenomenon is particularly puzzling for high-vapor-pressure materials like ice.

The quasiliquid layer on ice has been studied for a long time (it was first proposed by Faraday in the 1850s to explain some unusual properties of ice), and it seems to play a role in many disparate environmental phenomena. Lightning, for example, is known to arise from collisions between ice particles in clouds—tropical clouds with no ice seldom produce lightning. The charge transfer during these collisions is thought to depend on the details of the ice surface structure, and thus on the quasiliquid layer. On a different front, some of the chemistry that takes place in high-altitude clouds, and which is important for ozone depletion, also occurs on the surface of ice crystals, and is affected by the presence of a quasiliquid layer. And back down on earth, it’s the quasiliquid layer that makes ice especially slippery and helps snow stick together in snowballs.

The quasiliquid layer can affect crystal growth in a number of ways. At low temperatures, when the layer is gone, the facet surface can be very smooth, and so grows slowly. It’s said that the surface has a high nucleation barrier, since molecules on the smooth surface don’t have much to hold on to. At higher temperatures, however, when the quasiliquid layer first starts to form on a facet surface, molecules begin to jostle loose, so that the surface cannot be so smooth any more, and the growth rate shoots up. But then, at still higher temperatures, the quasiliquid layer is so thick it starts to look like a real liquid, and the solid/quasiliquid boundary can itself become smooth, like that between a solid and its melt. Thus there is a nucleation barrier at the solid/quasiliquid interface, and the growth rate goes down again. There’s considerably more to the story, but you get the idea.

When you consider that the properties of the quasiliquid layer, and how they depend on temperature, can be different for the different ice facets, it becomes plausible that ice growth shows the unusual characteristics that it does. But the devil is in the details, and our current research is
aimed at reaching a better understanding of just what’s going on. This is all pretty basic stuff—the structure of ice surfaces, and how it affects crystal growth—but we are surprisingly ignorant of even these fundamental issues, not only for ice but also for most real surfaces.

The second big factor affecting snow crystal shapes is the diffusion of water molecules through the air, and here at least we know the underlying physics fairly well. A growing crystal captures water molecules from the air right around the crystal, and additional water molecules have to make their way through the surrounding air molecules to reach the surface. Diffusion tends to hinder crystal growth, and this produces what turns out to be a fairly common effect, known as the Mullins-Sekerka instability, that goes far in explaining why snow crystals grow into such intricate structures.

If you imagine that our newborn snow crystal is a hexagonal plate, you can see that the corners of the crystal stick out a bit farther into the supersaturated air and thus collect more water molecules. On the nanoscale, below, what appears to be a straight facet actually contains many molecular steps. Diffusing molecules are more likely to hit the corners, but molecules are more likely to stick where the surface is rough, in between the corners.

How snow crystals get their arms. This photo series of a growing crystal shows how a hexagonal sectored plate develops six distinct arms. The hexagonal growth is eventually unstable because the corners of the plate stick farther out into the supersaturated air and thus collect more water molecules. On the nanoscale, below, what appears to be a straight facet actually contains many molecular steps. Diffusing molecules are more likely to hit the corners, but molecules are more likely to stick where the surface is rough, in between the corners.
overall shape of the crystal doesn’t change as it grows. And since the molecular steps are very tiny, the crystal continues to look like a simple hexagonal prism as it grows.

This goes well for a while, but to continue this shape-preserving growth, the center faces become rougher and rougher as the crystal grows larger, until eventually they become so rough that they can’t be any rougher. At this point the center faces can no longer keep up, and the corners really do grow faster, with the end result that our hexagonal snow crystal sprouts six tiny arms. As the arms themselves grow longer, they too come under the influence of the Mullins-Sekerka instability, and can sprout their own side branches. In the end we find that a very complex crystal shape results from a rather simple physical phenomenon. Growth instabilities like these are quite common in nature, and are responsible for a great deal of pattern formation, in the biological world as well as the physical world.

With these tools, we can now can pretty much explain why there’s such a rich variety of symmetrical snow-crystal shapes in nature, or what I like to call the “no-two-alike conjecture.” After a snow crystal is born, it quickly grows into a small hexagonal prism, with the facet surfaces growing more slowly than the other surfaces. Then, as the crystal grows larger, the Mullins-Sekerka instability often kicks in, causing the corners to sprout arms. Exactly how fast the arms grow depends on the local temperature and supersaturation experienced by the crystal, since, as we’ve seen from the morphology diagram, snow-crystal growth is extremely sensitive to environmental conditions.

It’s important to note that the local conditions are essentially the same for each arm on a tiny snow crystal, so that the arms all grow in the same way. Then, as this growing crystal travels through regions of the atmosphere with different temperatures and supersaturations, its growth will change with the conditions, and the arms will all change their growth in unison. The final crystal shape can be very complex, reflecting the complex path the crystal followed through the atmosphere. Yet since the arms all grow at the same time, they tend to look alike, so that the crystal has a sixfold symmetric appearance. And since no two crystals follow exactly the same path through the sky as they fall, each grows into a slightly different shape. So we end up with a myriad of complex, symmetric patterns, with no two alike. In principle, one could look at a snow crystal and decipher the conditions under which it grew. Or, to quote Nakaya, “Snow crystals are hieroglyphs sent from the sky.”

Another area we’ve been exploring in my lab is that of using high electric fields to enhance and control the dendritic instabilities in crystal growth. We started by growing normal dendritic crystals like the one in the photo above, which are very easy to grow at −15 °C when the supersaturation is high. The tip of such a crystal grows at a steady 3–4 microns per second, and side branches appear in a semiregular pattern as dictated by the Mullins-Sekerka instability. Dendritic growth like this has been studied for quite a while (it has applications in metallurgy and the structure of alloys), and we know how to calculate the simpler properties of the growth, such as the steady-state tip velocity, which is the rate at which the tip elongates.
To make life a bit more interesting, we began growing these crystals on the end of a wire connected to a high-voltage power supply. As we turned on the voltage, the electric field near the tip of the growing crystal polarized the water molecules in the surrounding air, and these polarized molecules were attracted to the tip. This enhanced the normal diffusion rate, and the tip velocity increased accordingly—all nicely according to theory. But when the tip velocity was about twice as fast as normal, whoosh! The tip just took off, growing as much as 200 microns per second—greased lightning in the crystal-growth game! The crystals grew into long, thin needles, with tip radii as small as 100 nanometers.

The theory we developed to explain the physics of all this suggested that electrically enhanced growth would work even with nonpolar molecules (water is highly polar), and we recently demonstrated this in the lab by growing iodine needle crystals. Metallic needle crystals have also been grown from certain metal-carbonyl vapors using related techniques, and it’s tempting to speculate that diamond needles could be produced one day using electrically enhanced growth (although I suppose it’s too late to corner the market in phonograph needles).

In our lab, we have a special fondness for growing “c-axis” electric needles of ice (think tiny ice versions of a standard hexagonal pencil). For a long time we found that growing this particular type of needle crystal was a hit-or-miss proposition; some days it worked well, some days it didn’t work at all. At first we thought we were having contamination problems from solvent vapors floating around in our chamber (the laboratory version of air pollution), so we decided to give the chamber a good, long bake to clean it out. To our surprise, when we started our experiments again, we couldn’t get any good needles at all—not one. It turned out we weren’t being hurt by contamination in the chamber; we were actually being helped.

\[ \text{Electric needles, left, were grown at } -5 \, ^\circ \text{C with the application of 2000 volts and chemical vapor additives to induce growth along the c-axis of the crystal. When the voltage was removed and the needles moved to } -15 \, ^\circ \text{C, plates grew. Right: needle growth at } -5 \, ^\circ \text{C.} \]

A designer snowflake. This crystal was grown at $-14 \, ^\circ \text{C}$, except that at approximately periodic intervals it was moved to $-7 \, ^\circ \text{C}$ for just a few seconds. Each move induced the development of side branches at the tips of the growing arms. A movie of this can be seen at snowcrystals.net.
by it. So we tried adding various solvent vapors, at concentrations of only a few parts per million in the air, and Voilà!—we were soon producing beautiful c-axis needles again, very reliably. Acetic acid, the main ingredient in vinegar, seems to work especially well, and we're still puzzling over exactly what physical and chemical mechanisms are controlling the needle growth.

A wonderful feature of c-axis needles is that after growing a long ice needle, we can turn off the voltage and grow a normal platelike snow crystal on its end. Most of this work is done in our vertical diffusion chamber with a convenient temperature gradient—warm at the top, cold at the bottom. By moving the needle from –5 °C, where the c-axis needles grow best, to –15 °C, where plates grow best, we can grow a beautiful snow crystal on the end of the needle, like a tiny ice flower on a thin ice stem.

We've developed these techniques to the point where we can now create "designer" snow crystals, growing shapes of our own choosing by controlling the humidity and temperature of the growth, and some examples are shown in the photos on these pages. It's something of a new art form—miniature ice sculpture. Instead of cutting away material, we design and fabricate using the natural rules of pattern formation. Stellar dendrites, sectored plates, hollow columns can all be made relatively easily, and now we're even learning to control side branching and other features to create more complex and unusual snow-crystal shapes.

So we see that snow-crystal growth is governed by some sophisticated physics, mathematics, and chemistry, all working in concert to create these tiny, filigreed ice sculptures that fall down from the sky. Snow crystals are not only beautiful to look at, but they also teach us about surface physics, the statistical mechanics of crystal growth, and the intricacies of pattern formation processes in nature.

Growing up in Fargo, North Dakota—where it's said there's 10 months of snow and two months of poor sledding—may have inspired Ken Libbrecht's current interest in snow crystals, but for most of his early career he worked at the other end of the temperature spectrum, investigating the internal structure of the sun. A Caltech graduate (BS '80), he returned to join the faculty in 1984, and has been Executive Officer for Physics since 1997. Nowadays, as well as investigating the physics of snow crystals, Libbrecht is involved in advanced detector development for LIGO, the Laser Interferometer Gravitational-wave Observatory. Check out his award-winning Web site, snowcrystals.net, for much, much more on snow crystals, including how to make your own in the kitchen, and how to help locate the snow crystal capital of the world. This article is adapted from a Watson lecture given in January 2001.