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ONE

Snow Crystal Science

How full of the creative genius is the air in which these are generated!
I should hardly admire more if real stars fell and lodged on my coat.

—HENRY DAVID THOREAU, JOURNAL, 1856

This book is about the science of snowflakes. Its overarching objective is to explain why snowflakes grow into those remarkable crystalline structures that can be found floating down from the winter clouds. In these pages, I answer some of the basic scientific questions one might ask while scrutinizing a newly fallen snowflake: Where do snowflakes come from? How does formless water vapor manage to arrange itself, spontaneously, into such a variety of amazingly ornate shapes? What physical processes guide the development of these elaborate, yet symmetrical, patterns? Why does all this happen the way it does?

Comprehending the humble snowflake is a surprisingly challenging task. The seemingly simple phenomenon of water vapor freezing into ice involves a veritable symphony of subtle molecular processes, from diffusive mixing in the air to the complex attachment kinetics that govern how water molecules assimilate into a rigid crystalline lattice. Explaining this intricate act of meteorological morphogenesis requires a rather deep dive into areas of mathematical physics, statistical mechanics, materials science, and the many-body molecular dynamics

of crystal growth. Even now, well into the twenty-first century, snowflake science is very much a work in progress, as several rather basic aspects of the surface structure and dynamics of ice at the molecular level remain quite mysterious.

When I first began reading about this subject in the 1990s, I was immediately struck by just how little was really understood about snowflake formation. Many different morphological types of snowflakes had been observed and cataloged over the years, yet there was no comprehensive explanation for why these different shapes appeared under different growth conditions. As illustrated in Figure 1.2, thin plates and ornate stellar crystals appear when the temperature is around −15°C, while slender needles and columns form when the temperature is near −5°C. Intermediate temperatures generally yield blocky shapes. Small platelike crystals are the norm above −3°C, while sharply faceted columnal crystals form below −30°C. Why does snow crystal morphology depend so strongly on temperature, and why specifically in this manner? I expound at some length on this topic in Chapter 4, as this has been a long-standing
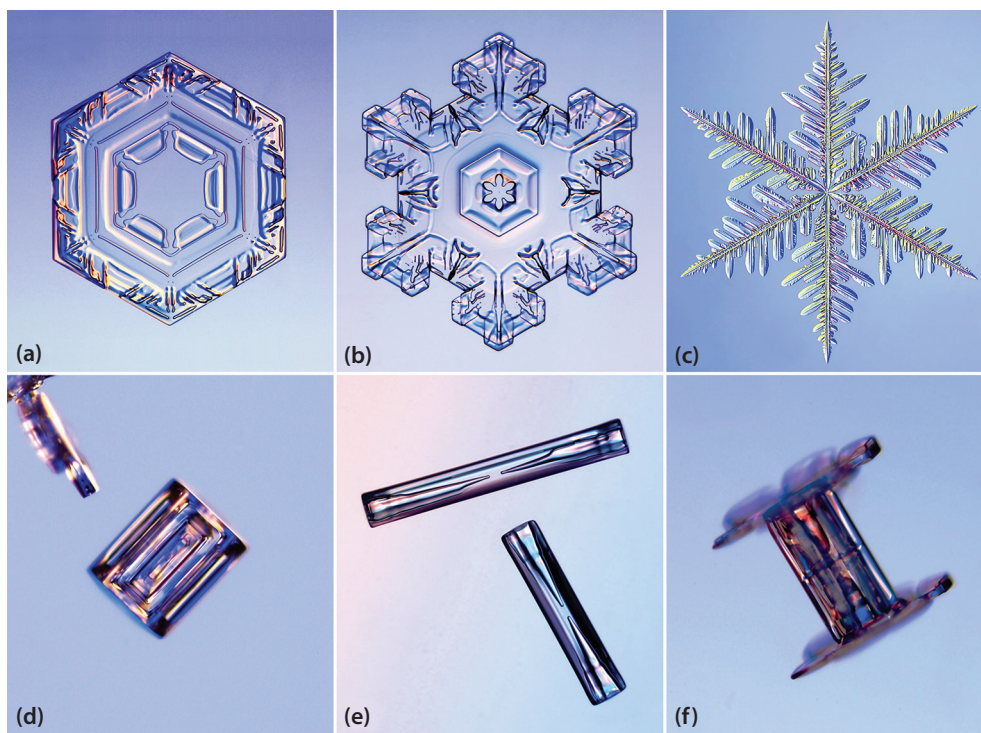
FIGURE 1.2. Natural snow crystals exhibit a remarkable degree of morphological diversity. Platelike examples shown here include (a) a basic hexagonal crystal with symmetrical surface markings; (b) a stellar plate with six broad-branched extensions; and (c) a "fernlike" stellar dendrite, which is an exceptionally thin, flat crystal with copious sidebranching. These types of crystals typically appear when the temperature is in a narrow range around −15°C, although smaller platelike crystals can also be found near −2°C. Other natural specimens include (d) a simple hexagonal prism viewed from the side; (e) a pair of hollow columns, each exhibiting conical voids that almost touch at the crystal centers; and (f) a capped column, resulting when two platelike crystals grow out from the ends of a stout column, like two wheels on an axle. Columnar and needle forms are common near −5°C, while a capped column results when the temperature changes as the crystal grows.

scientific puzzle, and I have developed a few new ideas aimed at solving it. But a complete understanding of even this straightforward observation remains elusive.

At first glance, the snowflake appears to be a somewhat basic natural phenomenon. It is made of little more than pure ice, and it assembles itself, quite literally, out of thin air (Figure 1.3). Nevertheless, trying to understand snowflake formation in detail will take us to the cutting edge of contemporary science. The journey will be neither short nor simple, so let us begin with the basics.

COMPLEX SYMMETRY

I often use the term *snowflake* synonymously with *snow crystal*. The latter is a single crystal of ice, in which water molecules are all lined up in a precise hexagonal array. Whenever you see that characteristic sixfold symmetry associated with snowflakes, you are actually looking at a snow crystal. A snowflake is a more general meteorological term that can mean an individual snow crystal, a cluster of snow crystals that form together, or even a large aggregate of snow crystals that collide and

FIGURE 1.3. A gray winter scene looking out over Lake Superior near Houghton, Michigan. Water vapor evaporating from the warm lake quickly condenses into a mist of water droplets, because the air is substantially colder than the water. But the mist soon evaporates back to water vapor as it rises above the lake. The vapor condenses once again into droplets at higher altitudes, forming thick clouds. Should the clouds cool down sufficiently, most of the liquid droplets will evaporate to feed the formation of snowflakes that fall back into the lake, completing the water cycle.

stick together mid-flight. Those large puff-balls you see floating down in warmer snowfalls are called "snowflakes," and each is made from hundreds or even thousands of individual snow crystals. Snow crystals are commonly called "snowflakes," and this is fine, like calling a tulip a "flower."

A snow crystal is not a frozen raindrop; that type of precipitation is called "sleet." Instead, a snow crystal forms out of water vapor in the atmosphere, as water molecules in the gaseous state transition directly to the solid state. Complex structures emerge as the crystal grows, driven mainly by how water vapor molecules are transported to the developing crystal via diffusion, together with how readily impinging molecules stick to different ice surfaces.

From Clouds to Crystals

To begin our study of snow crystal formation, consider the life of a large, well-formed snowflake that falls from the winter clouds. The story begins as weather patterns transport and cool a parcel of moist air until its temperature drops below the *dew point*, meaning the relative humidity rises above 100 percent and the air becomes *supersaturated* with water vapor. When this happens, the gaseous water vapor in the air tends to condense out as liquid water. Near the ground, the water vapor might condense as dew on the grass (which is why this temperature is called the "dew point"). At higher altitudes, however, water vapor condenses into countless cloud droplets. Each liquid droplet forms around a microscopic particle of dust, and these are typically abundant in the atmosphere. Cloud droplets are so small—about 10–20 microns in diameter—that they can remain suspended in the air almost indefinitely.

If the cloud continues cooling and its temperature drops significantly below 0°C, then the liquid water droplets will start freezing into ice. Not all the droplets freeze at once, and none will freeze right at 0°C. Instead, the droplets become *supercooled* as their temperature drops, often remaining in a metastable liquid state for long periods of time. Some droplets will freeze when the temperature is as high −5°C, but most will freeze somewhere in the vicinity of −10°C. A hearty few may survive unfrozen at −20°C or below, but all will become solid ice before the temperature reaches −40°C.
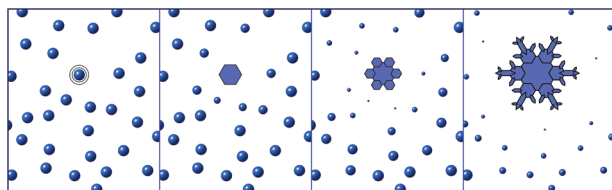
FIGURE 1.4. A snowflake is born when a liquid cloud droplet freezes into ice (left sketch). The ice particle initially grows into a faceted prism, as the growth is limited by anisotropic attachment kinetics on the ice surface. After the crystal grows larger, the diffusion of water molecules through the air causes branches to sprout from the six corners of the prism, which continue growing to become elaborate dendritic structures. The growing crystal removes water vapor from the air, which is replenished by the evaporation of nearby water droplets. About 100,000 cloud droplets evaporate to provide enough material to make one large stellar snow crystal. The flake continues growing inside the cloud until it becomes so heavy that it falls to earth.

FIGURE 1.5. The most basic shape of a snow crystal is a *hexagonal prism* with two basal facets and six prism facets. This shape arises because of the underlying hexagonal structure of the ice crystal lattice.

The freezing temperature of a specific cloud droplet is determined in large part by the speck of dust it contains. Pure water can be cooled to nearly −40°C before freezing, while some materials (silver iodide in particular) will nucleate freezing as high as −4°C. Certain bacterial proteins can even promote freezing at temperatures as high as −2°C. These exotic materials are not much present in the atmosphere, however, so your average speck of dust will nucleate freezing around −10°C. Note that the character of an included dust particle usually has little effect on the final snow crystal shape, because the dust is soon buried within the ice.

Once a cloud droplet freezes, it becomes an embryonic snow crystal that commences its growth by absorbing water vapor from the air around it. Because the vapor pressure of liquid water is higher than that of solid ice (see Chapter 2), the cloud droplets surrounding the nascent snowflake begin to evaporate away, as illustrated in Figure 1.4. During this process, there is a net transfer of water molecules from liquid water droplets to water vapor, and then from vapor to ice. About 100,000 cloud droplets will evaporate away to provide enough material to make one good-sized snowflake. This roundabout route is how the liquid water in a cloud freezes into solid ice.
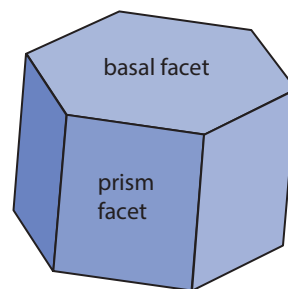
As the temperature inside a cooling cloud falls below −10°C, cloud droplets will begin freezing in large numbers, thus initiating a full-fledged snowfall. By the time the cloud has cooled to around −20°C, however, most of the liquid droplets will be gone, as some will have frozen and many will have evaporated away to form snow crystals. At temperatures below −20°C, it is sometimes said to be "too cold to snow," because nearly all the liquid cloud droplets will have already disappeared before the cloud cools to that temperature. And when no liquid water remains to feed growing snowflakes, there will not be a lot of falling snow.

Faceting and Branching

Soon after a cloud droplet freezes, it initially grows into the shape of a small, faceted hexagonal prism, as illustrated in Figure 1.5. The prism shape is defined by two *basal facets* and six *prism facets* that arise from the underlying sixfold symmetry of the ice crystal lattice (see Chapter 2). The molecular mechanism that creates this faceted shape is one of the key physical processes that guide snow crystal formation, and Figure 1.6 illustrates how it works. Water vapor molecules strike the ice crystal everywhere on its surface, but they are more likely to stick when the surface is molecularly "rough," meaning it has a lot of dangling chemical bonds. The facet surfaces are special, because they are aligned with the lattice
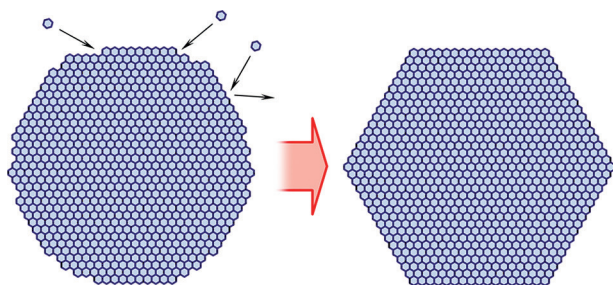
FIGURE 1.6. When water vapor molecules strike a molecularly rough ice surface, they tend to stick and become incorporated into the ice lattice. But when they strike a molecularly smooth facet surface, they are less likely to stick. As the crystal grows, the rough areas soon fill in to yield a fully faceted ice prism.

FIGURE 1.7. As a thin hexagonal plate grows larger, its six corners stick out into the humid air around it. Water vapor condenses preferentially on the corners as a result, making them stick out even farther. This leads to a *growth instability* that causes six branches to sprout from the corners of the hexagon. The same process later yields sidebranches on the main branches.

structure of the crystal, so these surfaces exhibit fewer open molecular bonds. Thus, the facet surfaces accumulate water vapor at a lower rate than do the rough surfaces, and this process soon yields a faceted ice prism. The rate at which impinging water molecules stick to various surfaces is called the *attachment kinetics,* and I discuss this subject in considerable detail in Chapter 4.

If the cloud temperature drops to near −15°C, which is often the case during an ample snowfall, then the basal surfaces will accumulate material especially slowly, while water vapor will condense on the prism facets much more readily. As a result, a frozen droplet in those conditions will soon develop into a thin, flat, hexagonal plate, which is an early stage of what will eventually become a large stellar snow crystal. As the small hexagonal plate is growing, its six corners stick out slightly into the surrounding humid air, causing the tips of the hexagon to absorb water vapor a bit more quickly than other parts of the crystal. The faster growth makes the corners stick out farther still, causing them to grow even faster. This positive-feedback effect causes a set of six branches to sprout from the hexagonal plate, as illustrated in Figure 1.7. I describe this *branching instability* (also known as the *Mullins-Sekerka instability*) at length in Chapter 3, as it is responsible for most of the complex structure seen in snow crystals.

Once the six branches begin to develop, most of the subsequent growth occurs near the branch tips, where
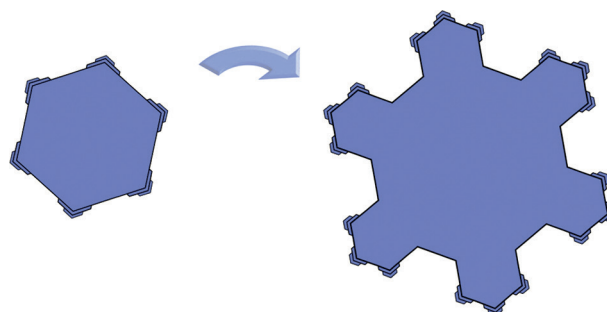
the supply of water vapor is greatest. Moreover, the growth behavior of each branch is quite sensitive to the temperature and humidity of the air surrounding it. As the crystal travels through the inhomogeneous clouds, it experiences ever-changing conditions that modify how the crystal grows. Sometimes the branch tips become faceted, while at other times, they may sprout additional sidebranches. It all depends on the growth conditions seen by the crystal at any given time. The final shape of the branch, therefore, reflects the entire history of its growth, which was determined by the meandering path the flake took through the atmosphere.

The six branches of a snow crystal develop in near synchrony, simply because they all travel together through the cloud. All six branches experience essentially the same growth conditions at the same times, so all six develop into the same elaborate shape, as illustrated in Figure 1.8. Note that the growth of the separate branches is not synchronized by any communication between them, but rather by their common history. And because no two snowflakes follow exactly the same path through the turbulent atmosphere, no two look exactly alike. (The full story of snowflake uniqueness is a bit more involved, as I describe later in this chapter.) The formation of a large stellar snow crystal takes about 30–45 minutes, and we can reproduce the process in the lab
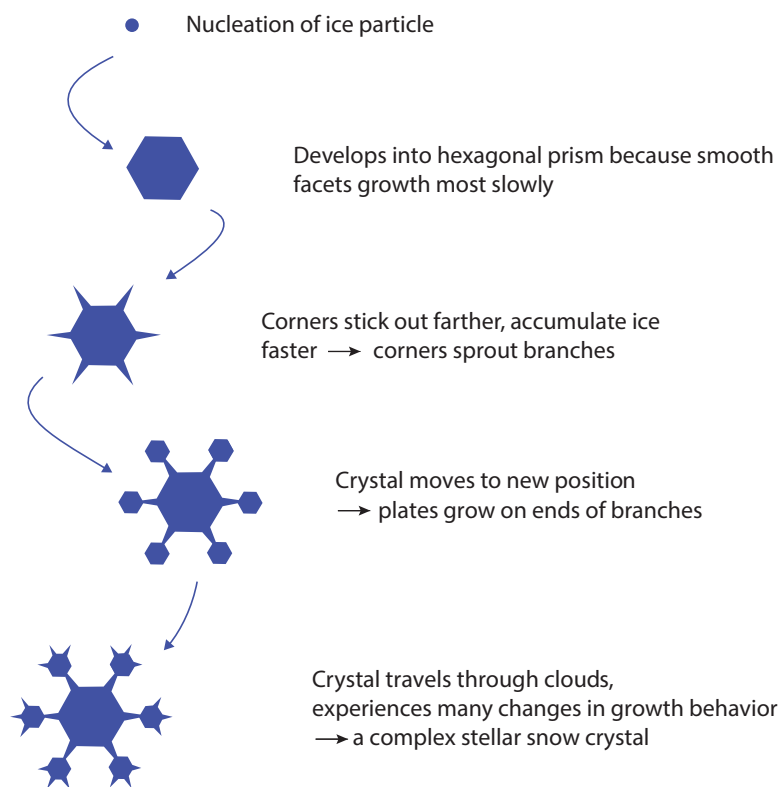
Nucleation of ice particle

Develops into hexagonal prism because smooth facets growth most slowly

Corners stick out farther, accumulate ice faster ⟶ corners sprout branches

Crystal moves to new position ⟶ plates grow on ends of branches

Crystal travels through clouds, experiences many changes in growth behavior ⟶ a complex stellar snow crystal

FIGURE 1.8. The final shape of a complex stellar snow crystal depends on the path it traveled through the clouds. Sudden changes in the temperature and humidity around a crystal can cause abrupt changes in its growth behavior, perhaps stimulating the formation of sidebranches or plates. However, because the six arms see the same changes at the same times, they grow in near synchrony. The final snow crystal thus exhibits a complex structure with an overall sixfold symmetry.

with relative ease, studying how environmental changes induce symmetrical dendritic structures.

Although this narrative reasonably describes the origin of complex symmetry in stellar snow crystals, the story deepens when we also consider the variety of morphological types illustrated in Figure 1.2. The full menagerie of natural snow crystals is presented in Chapter 10, and laboratory studies have found that these can be organized according to the *Nakaya diagram* shown in Figure 1.9, which is also called the *snow crystal morphology diagram*. This empirical chart summarizes the various snow crystal forms that appear at different temperatures and humidity levels, including platelike and columnar forms with varying amounts of structural complexity. Explaining this morphological organization is no easy task, requiring a methodical characterization of the relevant physical processes involved. The quest to fully comprehend the science of snow crystal formation

is the primary focus of this book, continuing an endeavor that has been ongoing for some 400 years.

A BRIEF HISTORY OF SNOW CRYSTAL SCIENCE

I like to think about the snow crystal as something of a case study of scientific reasoning. Science is fundamentally about understanding the natural world, so snowflakes, being part of that world, deserve an explanation. Richard Feynman commented that "nature uses only the longest threads to weave her patterns, so each small piece of her fabric reveals the organization of the entire tapestry" [1964Fey, p. 34]. There is hardly a more fitting example of this truism than the intricate patterns of common snowflakes, as the entire panoply of modern scientific knowledge is still not quite enough to fully explain their origin.
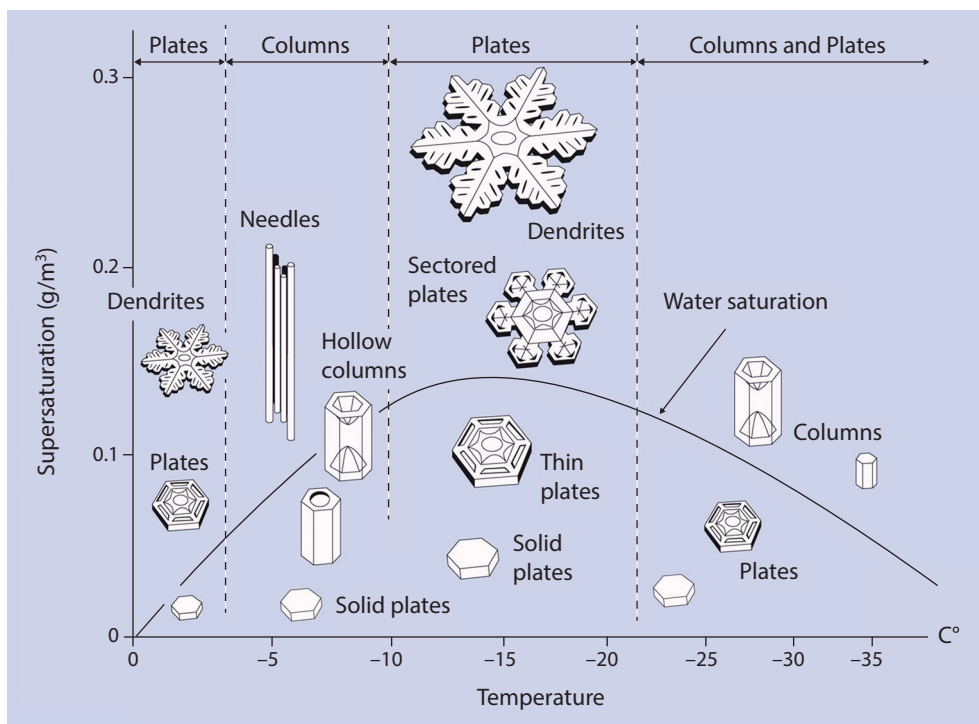
FIGURE 1.9. The *Nakaya diagram* plots the morphological types of snow crystals that develop at different temperatures and humidity levels. Here the supersaturation is shown as the "excess" water vapor density in the air, above the value for saturated air, and the *water saturation* line shows the supersaturation in a dense winter cloud made of liquid water droplets. Explaining why snow crystals experience such varied growth behaviors at different temperatures and supersaturations is a remarkably challenging scientific puzzle, with many parts still unsolved.

The study of snowflake science began when the distinctive sixfold symmetry of individual snow crystals was first recognized as something that could be investigated and possibly understood. Over time, this led to a greater scrutiny of what fell from the clouds, yielding early sketches that began to document the remarkable variety of different morphological types. With advances in technology, snow crystals were examined in greater detail by using optical microscopy and were further documented in extensive photographic studies. And as sophisticated scientific tools became available, researchers progressed from observations of natural snowfalls to scrutinizing laboratory-grown snow crystals, eventually leading to precision measurements of ice growth behaviors, molecular dynamics investigations, and studies using computer-generated snowflake simulations.

In many ways, the snowflake story mirrors the historical development of science itself. As mathematics became intertwined with natural philosophy, the precise symmetry of snow crystal facets suggested an underlying geometrical basis, foreshadowing the molecular order found in crystal lattices. As laboratory-based science emerged, synthetic snowflakes revealed an underlying organization for the observed diversity of natural snow crystal morphologies. And as the nanoscale structure of crystalline materials has become better characterized in the modern era, our understanding of the molecular attachment kinetics governing snow crystal growth has

improved as well. We can only guess as to what future scientific tools will be brought to bear in our effort to comprehend the inner workings of the common snowflake.

Early Observations

The earliest account (of which I am aware) describing the sixfold symmetry of individual snow crystals was written in 135 BCE by Chinese philosopher Han Yin [2002Wan, p. 3], who commented: "Flowers of plants and trees are generally five-pointed, but those of snow, which are called ying, are always six-pointed." Subsequent Chinese authors mentioned snow crystal symmetry as well, an example being the sixth-century poet Hsiao Tung, who penned, "The ruddy clouds float in the four quarters of the cerulean sky. And the white snowflakes show forth their six-petaled flowers" [2002Wan, p. 3].

European authors began documenting snowflakes many centuries after the first Asian accounts, and one oft-quoted reference is the woodcut shown in Figure 1.10, created by Olaus Magnus in 1555 [1982Fra]. It can be seen, however, that the clergyman depicted snowflakes as having a curious assortment of odd shapes, including crescents, arrows, and even one that looked like a human hand, so perhaps this account does not quite warrant being called a historical first. It appears that English astronomer Thomas Harriot was the first in Europe to clearly identify and document the snowflake's sixfold symmetry in 1591 [1982Fra].

French philosopher and mathematician René Descartes recorded the first detailed account of snow crystal structures in his famous *Les Météores* in 1637, including the sketches shown in Figure 1.11. In his essay, Descartes described some remarkably thorough naked-eye observations of snow crystals, which included several uncommon forms [1982Fra, p. 5]:

> After this storm cloud, there came another, which produced only little roses or wheels with six rounded semicircular teeth . . . which were quite
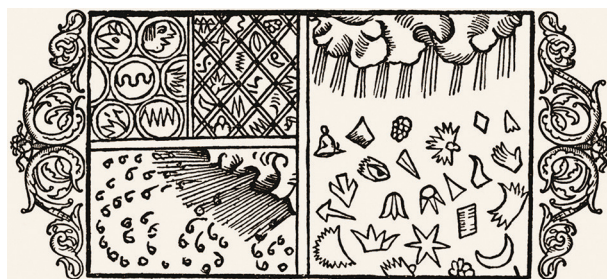

FIGURE 1.10. This 1555 woodcut by Olaus Magnus was perhaps the first European illustration depicting a sixfold symmetrical snow crystal, although the artist was perhaps a bit overzealous in his depiction of morphological diversity. Adapted from [1982Fra].

> transparent and quite flat . . . and formed as perfectly and symmetrically as one could possibly imagine. There followed, after this, a further quantity of such wheels joined two by two by an axle, or rather, since at the beginning these axles were quite thick, one could as well have described them as little crystal columns, decorated at each end with a six-petaled rose a little larger than their base. But after that there fell more delicate ones, and often the roses or stars at their ends were unequal. But then there fell shorter and progressively shorter ones until finally these stars completely joined, and fell as double stars with twelve points or rays, rather long and perfectly symmetrical, in some all equal, in others alternately unequal.

In this passage, we can see snowflakes influencing—in their own small way—the early development of modern science. Descartes was clearly impressed with the geometrical perfection he saw in snow crystal forms, with their flat facets and hexagonal symmetry. Pondering this and other observations, he went on to reason about how the principles of geometry and mathematics play a central role in describing the natural world. Although we take this for granted now, using mathematics to explain ordinary phenomena was still something of an unconventional idea at the time, and a major step forward in science.
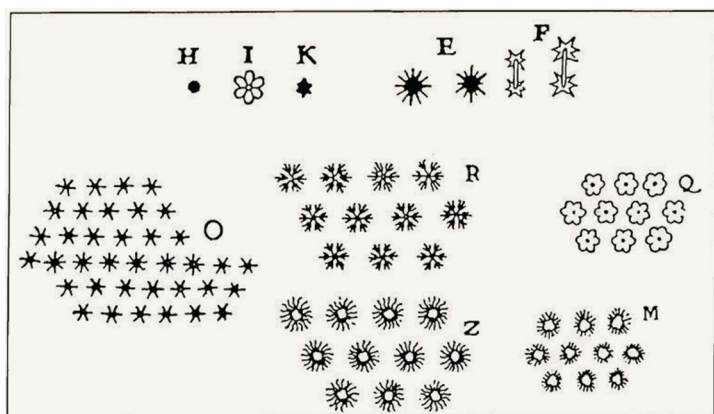
FIGURE 1.11. René Descartes made some of the first accurate sketches of different snow crystal morphologies in 1637, including observations of capped columns (group F in this sketch) [1637Des].

Emerging Science

The first scientist to speculate on a theoretical explanation of the sixfold symmetry of snow crystals was German astronomer and mathematician Johannes Kepler. In 1611, Kepler presented a small treatise titled *The Six-Cornered Snowflake* to his patron, Holy Roman Emperor Rudolf II, as a New Year's Day gift [1611Kep, p. 35]. In his treatise, Kepler contrasted the sixfold symmetry of snowflakes with similar symmetries found in flowers, deducing that the similarities must be in appearance only, because flowers are alive, while snowflakes clearly are not:

> Each single plant has a single animating principle of its own, since each instance of a plant exists separately, and there is no cause to wonder that each should be equipped with its own peculiar shape. But to imagine an individual soul for each and any starlet of snow is utterly absurd, and therefore the shapes of snowflakes are by no means to be deduced from the operation of soul in the same way as with plants.

Kepler saw that a snowflake is a relatively simple thing, made only from ice, compared to the utterly baffling complexity of living things. He offered, therefore, that there might be some relatively simple organizing principle that was responsible for snow crystal symmetry. Drawing on correspondence with Thomas Harriot, Kepler noted that stacking cannonballs also yielded geometric structures with sixfold symmetry, and he further surmised that there might be a mathematical connection between these two phenomena. There was certainly a germ of truth in this reasoning, as the geometry of stacking water molecules lies at the heart of snow crystal symmetry. But this was long before the atomistic view of matter was accepted canon, so Kepler could not carry the cannonball analogy very far.

Kepler realized that the genesis of crystalline symmetry was a worthy scientific question, and he also recognized the similarity between snow crystals and mineral crystals, as they both exhibited symmetrical faceted structures. At the end of his treatise, however, Kepler accepted that the science of his day was not advanced enough to explain any of it. He was certainly correct in this conclusion: Three centuries would pass before scientists knew enough about atoms, molecules, and their arrangement in solid materials to finally answer Kepler's 1611 query.

Microscopic Observations

The invention of the microscope in the mid-seventeenth century quickly led to more and better snowflake observations. English scientist and early microscopist Robert

FIGURE 1.12. Robert Hooke sketched these observations of snowflakes 1665, enabled by his newly invented microscope [1665Hoo].
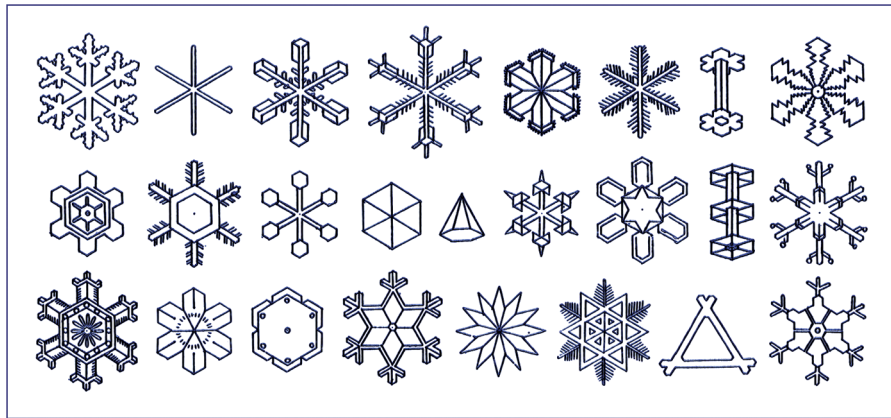

FIGURE 1.13. English explorer William Scoresby made these sketches during a winter voyage through the Arctic, which he recounted in 1820 [1820Sco]. These are the first drawings that accurately depicted many features of snow crystal structure, as well as several rare forms, including triangular crystals and 12-branched snowflakes. Scoresby also noted that the cold arctic climate produced more highly symmetrical crystals than were typically seen in Britain.

Hooke sketched snowflakes (Figure 1.12) and practically everything else he could find for his book *Micrographia*, published in 1665 [1665Hoo]. Although his microscope was crude by modern standards, Hooke's drawings nevertheless began to reveal the complexity and intricate symmetry of snow crystal structures, details that could not be detected with the unaided eye.

As the quality and availability of optical magnifiers improved, so did the accuracy of snow crystal drawings. By the mid-nineteenth century, several observers around the globe had recorded the diverse character of snow crystal forms, and one notable example is shown in Figure 1.13. Given the ephemeral nature of a snowflake, however, observers inevitably had to rely on memory to complete their sketches. As a result, even the best snow crystal drawings lacked detail and were not completely faithful to their original subjects.

Snowflake Photography

It took Wilson Bentley, a farmer from the small town of Jericho, Vermont, to create the first photographic album of falling snow, thus awakening the world to the hidden wonders of snowflakes. Bentley became interested in the microscopic structure of snow crystals as a teenager in the 1880s, and he soon began experimenting with the new medium of photography as a means of recording what he observed. He constructed an ingenious mecha-

nism for attaching a camera to his microscope for this purpose, and he succeeded in photographing his first snow crystal in 1885 when he was 19 years old.

To say Bentley was dedicated to this task is an understatement. Snowflake photography became his life-long passion, and over the course of 46 years, he captured more than 5,000 snow crystal images, all on 4-inch glass photographic plates. He resided his entire life in the same Jericho farmhouse, photographing snowflakes each winter, using the same equipment he constructed as a teenager. Figure 1.14 shows Wilson Bentley demonstrating his apparatus, although the grass at his feet suggests there were no snowflakes to be found that day.

Bentley usually presented his photographs as white snowflakes on a black background, as shown in Figure 1.15, but the original photos had a bright background. A snow crystal is made of pure ice, which is clear, not white (see Chapter 11). When illuminating a snow crystal from behind, as Bentley did, the resulting photo exhibits a somewhat low-contrast "bright-on-bright" appearance. To increase the contrast, Bentley made a copy of each photographic negative and painstakingly scraped away the emulsion from the background areas. A print made from the modified negative then yielded a white snowflake on a black background, as illustrated in the figure. Bentley preferred this high-contrast look, so he modified most of his photos using this technique. Some have accused Bentley of altering his photos to augment what nature had provided, but he did not hide the fact that he processed his photos this way. And he was always quick to point out that he never changed the snow crystal images themselves during this process.

One aspect of his work that Bentley rarely emphasized is that large, symmetrical stellar snow crystals are not the norm, and near-perfect specimens are quite rare (see Chapter 10). Over the course of an entire winter season, he only photographed about 100 crystals on average, reserving his expensive emulsions for only the most photogenic snow crystals he could find. Modern automated cameras that photograph falling snow without

FIGURE 1.14. Vermont farmer Wilson Bentley first developed the art of snowflake photography in the 1880s, eventually producing a large album of images. He is shown here with his specially built snow crystal photomicroscope [1931Ben].

any selection bias confirm that well-formed symmetrical snow crystals are exceedingly rare [2012Gar].

Bentley's photographs appeared in numerous publications over several decades, providing for many their first look at the inner structure and symmetry of snow crystals. And with thousands of snowflakes, each unique, the world was exposed to their incredible variety as well. The now-familiar old chestnut that no two snowflakes are exactly alike appears to have had its origin in Bentley's photographs.

In the late 1920s, Bentley teamed with W. J. Humphreys, chief physicist for the United States Weather Bureau, to publish his magnum opus, containing more than 2,000 snow crystal photographs [1931Ben]. The book appeared in November 1931, and the 66-year-old Vermont farmer died of pneumonia just a few weeks later. In the decades following this seminal work, many others have taken up the challenge of capturing the structure and beauty of snow crystals using photography, and I describe some modern techniques and recent results in Chapter 11.
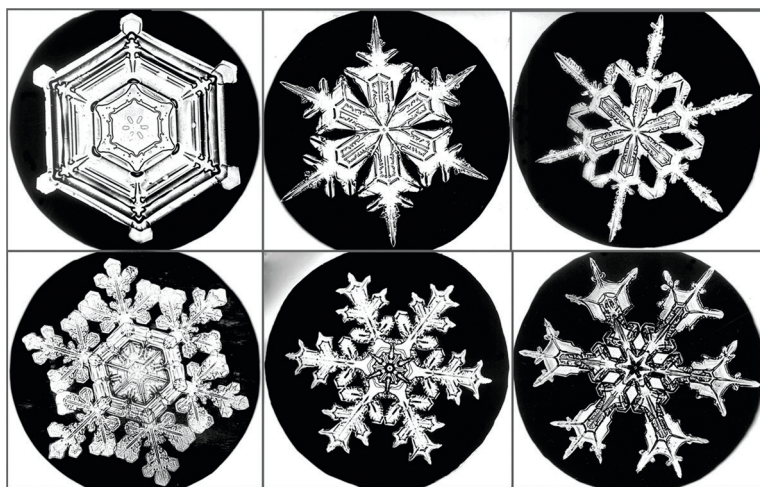
FIGURE 1.15. These are just a few of the thousands of snowflake photographs taken by Wilson Bentley between 1865 and 1931. The original photos showed bright crystals against a bright background, as the clear snowflakes were illuminated from behind. The photos were subsequently modified by essentially cutting each crystal out and placing it on a black background. Adapted from [1931Ben].

Crystallography

The word "crystal" derives from the Ancient Greek *krystallos*, meaning "ice" or "rock ice." Contrary to what the definition implies, *krystallos* was not originally used to describe ice, but rather the mineral quartz. The early Roman naturalist Pliny the Elder described clear quartz *krystallos* as a form of ice, frozen so hard that it could not melt. Pliny was certainly mistaken on this point, as quartz is not a form of ice, nor is it even made of water. Nevertheless, after nearly 2,000 years, Pliny's misunderstanding is still seen in the language of the present day. If you look in your dictionary, you may find that one of the definitions for crystal is simply "quartz."

While mineral collectors have admired beautiful crystalline specimens for millennia, understanding the origin of their faceted structures required a bona fide scientific breakthrough. In 1912, German physicist Max von Laue and coworkers discovered that when X-rays were shone through a crystal of copper sulfate, the crystal acted like a grating and produced a diffraction pattern that could be recorded on photographic film. Australian-born British physicists William Henry Bragg and William Lawrence Bragg (father and son) soon developed a mathematical theory showing how the atomic structures of crystalline materials could be ascertained from these diffraction patterns, thus creating the field of crystallography.

Working with the Braggs in their Cambridge laboratory, William Barnes used X-ray crystallography to determine the structure of ice for the first time in 1929 [1929Bar], discovering the now-familiar hexagonal lattice of normal ice Ih (see Chapter 2), and Figure 1.16 shows Barnes's discovery photograph. In subsequent studies over many decades, numerous additional solid phases of water have been discovered and characterized, mostly at extremely high pressures. Three hundred years after Kepler's initial musings, scientists had finally proven that the geometry of stacking was indeed the underlying source of the snowflake's sixfold symmetry.

In the decades that followed these early crystallographic discoveries, the development of quantum mechanics and quantum chemistry have allowed precise *ab initio* calculations of the water molecule electronic and atomic structure, including two-body and higher order interactions between water molecules. From these fundamental quantum-mechanical calculations, researchers have been able to reproduce the known structures of water in many of its solid phases. As a result, the lattice structure of ice Ih, from which snow crystals are made, is now well understood at a fundamental physical level.
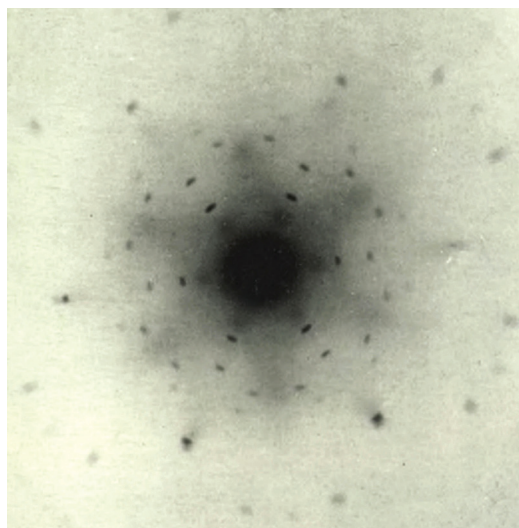
FIGURE 1.16. This X-ray diffraction pattern was made by a crystal of normal ice Ih, allowing William Barnes to first determine the hexagonal lattice structure of the ice crystal. Adapted from [1929Bar].

Attachment Kinetics

While the sixfold symmetry of a snowflake ultimately derives from the symmetry of the ice crystal lattice, how the nanoscale structure of the molecular matrix translates into the large-scale morphology of a growing crystal is a separate matter. For example, quartz and copper are both crystalline minerals, but quartz often exhibits striking faceted features that reveal its lattice structure, while copper rarely does. Why? A big part of the answer lies in the physical processes that govern the formation of faceted surfaces, collectively called the *surface attachment kinetics.*

Around the beginning of the twentieth century, scientists began examining the physics of solidification using the newly discovered laws of statistical mechanics and thermodynamics, which had been developed by James Clerk Maxwell, Ludwig Boltzmann, J. Willard Gibbs, Amedeo Avogadro, Lord Kelvin, and other scientific luminaries throughout the nineteenth century. An early result came from German physicist Heinrich Hertz [1882Her] and independently from Danish phys-

icist Martin Knudsen [1915Knu], who calculated the growth rate of a solid from its vapor phase (like ice from water vapor) from the net flux of vapor molecules striking the solid surface. The resulting Hertz-Knudsen law provides the starting point for the attachment kinetics theory I describe in Chapter 4.

Some decades later, however, it had become clear that the Hertz-Knudsen law did not provide a complete description of the growth of faceted crystalline surfaces. The net flux of molecules striking the surface was only one factor determining the growth rate; another was the probability that an impinging molecule would permanently attach to the surface and become part of the bulk crystal lattice. This probability, ranging from 0 to 1, is now called the *attachment coefficient*, also discussed at length in Chapter 4. Figure 1.6 shows how an anisotropic attachment coefficient produces faceted crystal growth, and this mechanism is also essentially responsible for the appearance of faceted minerals like those shown in Figure 1.17.

Beginning around the 1930s, physicists I. N. Stranski [1928Str], R. Kaischew [1934Str], R. Becker and W. Döring [1935Bec], M. Volmer [1939Vol], and others pushed the field forward by developing a detailed statistical-mechanical theory describing the nucleation and subsequent growth of one-molecule-high *terraces* on flat faceted surfaces. Many researchers fortified this theory in the following decades, notably W. K. Burton, N. Cabrera, and F. C. Frank [1951Bur], building it into the modern theory of crystal growth and surface attachment kinetics that is described in modern textbooks [1996Sai, 1999Pim, 2002Mut, 2004Mar]. This theory provides the starting point for understanding snow crystal growth.

The attachment kinetics are a major factor in determining the growth rates and resulting morphologies in different environmental conditions. For example, the principal difference between a thin platelike snow crystal and a slender columnar form (see Figure 1.2) lies in how readily the impinging water vapor molecules attach to the basal and prism surfaces. As a result, the large-scale
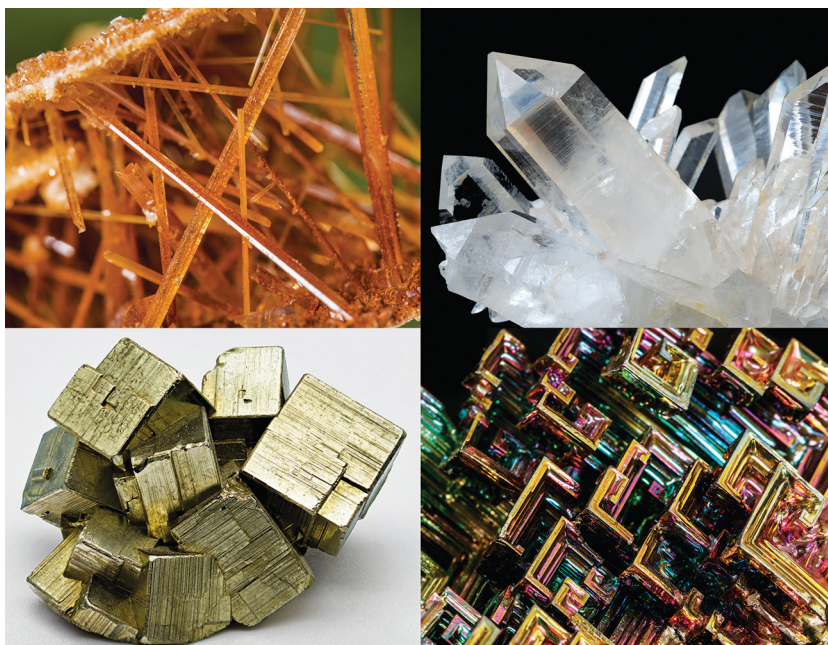
FIGURE 1.17. Besides ice, many other mineral crystals grow into faceted morphologies under the right conditions, as seen in these examples (from upper left to lower right): gypsum, quartz, pyrite, and synthetic bismuth. The lattice structure determines the overall symmetry of each crystalline form, but the attachment kinetics are largely responsible for the appearance of faceted surfaces.

morphology of nearly every snowflake, from platelike to columnar, is determined to a large degree by how the surface attachment kinetics changes with temperature, supersaturation, surface orientation, and other factors.

It is a common misconception that crystallography explains crystal growth, but this is far from the truth. Crystallography refers to the lattice structure of crystalline materials, and this is entirely a statics problem describing the lowest-energy molecular configuration in equilibrium. Crystal growth, by contrast, is a dynamical problem involving many-particle interactions in systems far from equilibrium. Modern science is quite adept at solving statics problems, but less so with many-body dynamics problems. For this reason, the crystallography of ice has been essentially solved for nearly a century, while many important aspects the ice attachment kinetics remain quite puzzling. Terrace nucleation theory nicely explains some aspects of snow crystal attachment kinetics, but certainly

not all. Creating a comprehensive model of this many-body molecular process is very much a work in progress, with many unsolved problems still outstanding.

The Nakaya Diagram

Japanese physicist Ukichiro Nakaya conducted the first true scientific investigation of snow crystals at Hokkaido University in the 1930s. Motivated by the abundant snowfalls in Hokkaido, and inspired by Wilson Bentley's photographs, Nakaya began his investigations by cataloging the different types of falling snow. Unlike Bentley, however, Nakaya looked beyond stellar crystals and focused his attention on describing the full range of different snowflake types, including columns, needles, capped columns, and other less-common forms. Nakaya thus produced the first photographic documentation of the broader menagerie of falling snow.
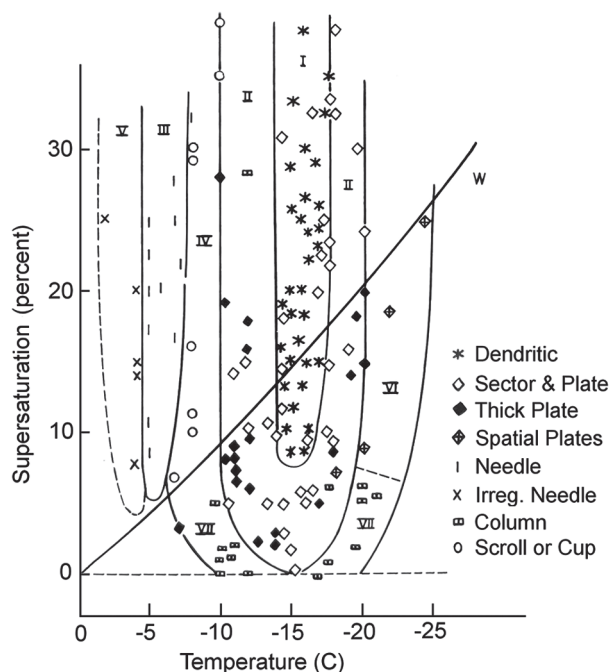
FIGURE 1.18. The original Nakaya diagram [1954Nak, 1958Nak] illustrates snow crystal morphology plotted versus growth temperature and water vapor supersaturation. Nakaya's observations of laboratory-grown snow crystals revealed, for example, that large stellar dendrites only form in a narrow temperature range around −15°C, while slender needle crystals only appear near −5°C. Adapted from [1954Nak].

FIGURE 1.19. A detailed version of the Nakaya diagram, adapted from [1990Yok]. Additional data further indicate that plates grow at all temperatures above −20°C when the supersaturation is sufficiently low [2019Lib1] while columns are common down to −70°C [2009Bai, 2012Bai].

While learning a great deal from observations of natural snow crystals, Nakaya quickly realized that laboratory experiments would be essential for better understanding the origin of what he saw falling from the clouds. To this end, he constructed a walk-in freezer laboratory at Hokkaido, using it for a variety of experimental investigations of ice crystal growth. Prominent among them, Nakaya created the world's first laboratory-grown snowflakes in his lab in 1936 [1954Nak].

Nakaya and his collaborators spent years examining how synthetic snow crystals grew and developed at different temperatures and supersaturations in their growth chamber, soon combining all these observations into what is now called the *Nakaya diagram,* shown in Figure 1.18. Subsequent researchers further refined and expanded the Nakaya diagram [1958Hal, 1961Kob, 1990Yok], and the

most recent of these is shown in Figure 1.19. The more stylized version in Figure 1.9 includes newer observations indicating that simple plates form in low supersaturations at all temperatures above −20°C [2019Lib1]. Bailey and Hallett further extended these results with additional observations, exploring temperatures down to −70°C and finding an abundance of columnar forms in these frigid conditions [2009Bai, 2012Bai].

The Nakaya diagram was immediately recognized as being like a Rosetta Stone for snowflakes. With it, one can translate the shape of a falling snow crystal into a description of its growth history. On seeing a slender needle crystal, for example, one can deduce that it must have grown in high humidity at a temperature near −5°C. A large stellar crystal indicates growth near −15°C, and the amount of sidebranching provides an indication of the level of supersaturation it experienced. The formation of a capped column (see Figure 1.2) arises from an initial period of growth near −5°C (columnar) followed by subsequent growth near −15°C (yielding plates on both ends of the column).

Nakaya liked to remark that snowflakes are like "hieroglyphs from the sky." With the Nakaya diagram, a

spectator on the ground can decipher the observed crystal morphology to ascertain the conditions of the clouds in which it formed, like a kind of meteorological hieroglyphics. The Nakaya diagram also tells us that snow crystal growth is remarkably sensitive to temperature. Even a change of a few degrees can dramatically alter a crystal's growth behavior, which helps explain why snowflakes have such a remarkable diversity of shapes. We will come back to the Nakaya diagram many times in this book, as it has become an essential tool for understanding the variable nature of snow crystal formation.

Crystal Dendrites

In 1917, Scottish zoologist D'Arcy Wentworth Thompson published *On Growth and Form*, in which he pondered on the physical, biological, and mathematical origins of complex structures in nature [1917Tho, 1961Tho]. While confessing that crystal growth was somewhat outside the province of his book, Thompson commented:

> Yet snow-crystals . . . have much to teach us about the variety, the beauty and the very nature of form. To begin with, the snow-crystal is a regular hexagonal plate or thin prism; that is to say, it shows hexagonal faces above and below, with edges set at co-equal angles of 120°. Ringing her changes on this fundamental form, Nature superadds to the primary hexagon endless combinations of similar plates or prisms, all with identical angles but varying lengths of side; and she repeats, with an exquisite symmetry, about all three axes of the hexagon, whatsoever she may have done for the adornment and elaboration of one.

In his celebrated treatise, Thompson used extensive examples to focus scientific attention on the central question of how complex structures arise spontaneously in natural systems. Humans tend to create intricate objects via a subtractive process, beginning with bulk material and carving it into a final desired form, following a preconceived design. At the opposite end of the fabrication spectrum, living things develop into amazingly sophisticated organisms quite spontaneously, using the additive process of growth. Thompson strove to comprehend the underlying physical and chemical principles that guide the development of living organisms, thus pioneering what has become the field of developmental biology.

Like Kepler 300 years before him, however, Thompson found that the whole of biological structure formation presented a challenging problem, to say the least. An easier approach, therefore, might be to consider something like the snowflake, which exhibits an interesting degree of spontaneous structure formation, but in a far simpler physical system. Over time, physicists also began to appreciate that the patterns arising during solidification offered a worthy phenomenon to investigate. Just as the hydrogen atom was a first step toward understanding the complex chemistry of large biomolecules, perhaps the physical origin of structure formation during solidification can provide insights into systems having far greater complexity.

A significant step forward in this direction was made in 1964, when American physicists William W. Mullins and Robert F. Sekerka realized that *growth instabilities* are often associated with pattern-forming systems, with solidification being a specific example. In their seminal paper [1964Mul], the authors showed that many of the simplest solutions to the equations describing diffusion-limited growth were mathematically unstable to small perturbations that developed into complex dendritic structures. This spontaneous branching process that arises during solidification—the *Mullins-Sekerka instability*—plays a central role whenever diffusion limits the solidification of materials, and as described in Chapter 3, growth instabilities are necessary for producing essentially all the complex morphological features seen in snow crystals.

Although dendritic structures had been documented in a broad range of physical and biological systems by D'Arcy Thompson and others for many decades,

the underlying causes of these forms was beyond the reach of early scientific knowledge. Counting the petals on a flower was one thing; explaining their existence was another matter entirely. Indeed, comprehending even quite simple biological structures remains largely an intractable problem to this day. Mullins and Sekerka showed, however, at least for simple physical systems, that it was possible to make some progress toward understanding how complex structures arise spontaneously in nonequilibrium systems.

A systematic study of growth instabilities in laboratory solidification was undertaken in the 1970s by American materials scientist Martin Glicksman and others, who examined the growth of dendritic structures when liquids cooled and solidified [1976Gli, 1981Hua]. In an extensive series of influential experiments, these researchers made detailed measurements of structure formation during the freezing of liquid succinonitrile, choosing this material because it is transparent with a freezing temperature near room temperature, while its growth behavior is similar to most common metals. When unconstrained by container walls, Glicksman found that freezing often yielded branched structures like that shown in Figure 1.20, with growth characteristics that depended mainly on crystal symmetry and the degree of supercooling of the liquid. Similar branching is seen in some stellar snow crystals, like the fernlike stellar dendrite shown in Figure 1.2, and this same kind of dendritic growth behavior has been observed to be quite ubiquitous during solidification from both liquids and vapors over a broad range of materials.

The work of Glicksman and others soon called attention to the Mullins-Sekerka instability and its consequences for structure formation during crystal growth. There followed a concerted push by physicists, material scientists, and applied mathematicians to form a self-consistent theory describing the characteristics of the diffusion-limited growth of dendritic structures. Efforts in the 1980s, led by James Langer [1978Lan, 1980Lan, 1989Lan], Hans Müller-Krumbhaar, Efim Brener, Herbert Levine, and others eventually yielded what has be-
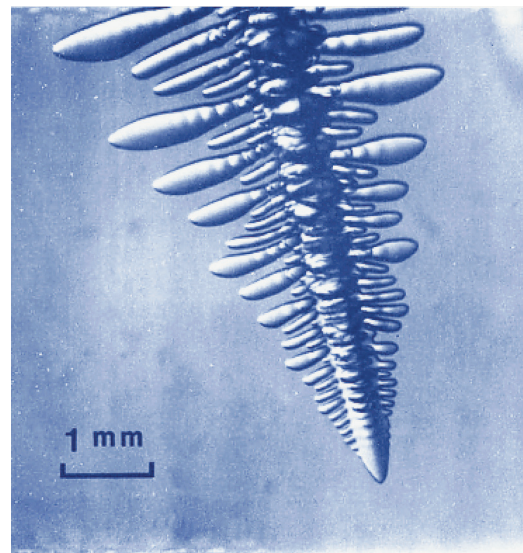
FIGURE 1.20. This photo shows a dendritic crystal of succinonitrile growing into a supercooled melt of the same material. In a vessel with a fixed temperature, the tip advances at a constant growth velocity, while the radius of curvature and overall shape of the tip do not change with time. Adapted from [1981Hua].

come known as *solvability theory*, which explains many of the defining characteristics of dendritic crystal growth. As I describe in Chapter 3, this theory provides an overarching explanation for why there is a marked increase in dendritic structure with supersaturation, as seen in the Nakaya diagram.

TWENTY-FIRST-CENTURY SNOWFLAKES

In the decades following Nakaya's seminal work, many scientists have conducted specific investigations into snow crystal structures and growth, including Matthew Bailey, Norihiko Fukuta, Yoshinori Furukawa, Takehiko Gonda, John Hallett, Jerry Harrington, Katsuhiro Kikuchi, Charles Knight, Teisaku Kobayashi, Toshio Kuroda, R. Lacmann, Dennis Lamb, Basil Mason, Jon Nelson, and Vincent Schaefer. Some of their work is cited throughout the chapters that follow, so I do not

review it separately here. Suffice it to say at this point that much effort has been expended by numerous researchers on this topic, including aspects related to meteorology, material science, chemical physics, and the mathematics of pattern formation.

My primary goal in this book is to help carry the torch forward as snow crystal science advances through the twenty-first century. Review papers are useful in this regard [1987Kob, 2001Nel, 2005Lib, 2017Lib], but their inevitable page limitations make it difficult to give the subject a proper treatment. I found much inspiration in Nakaya's book when I first began studying snowflakes, and it is still a fascinating read [1954Nak]. But there has been no comparable treatise on the subject for nearly 70 years, so clearly an update is long overdue. When written by a single author, books inevitably give a somewhat biased view of a subject, and this book is no exception in that regard. I find certain topics especially intriguing, so I dwell perhaps too long in those areas. And I may skip quickly over related topics that deserve more attention, especially when I do not feel proficient in those subjects. I have made some attempt to provide a broad overview of snow crystal science, but knowledge is a limited commodity, and, like most people, I tend to write about what I know (or what I think I know, as the case may be). I have been studying the physics of snow crystal growth for more than 20 years already, trying to understand the detailed physical processes that govern growth rates and morphological development. During that time, I have photographed more than 10,000 natural snowflakes, measured the growth of countless small ice prisms, and developed techniques for growing complex dendritic structures under well-controlled laboratory conditions. My interest is rooted in the fundamental physics of snow crystal formation, so that is the primary focus in this volume.

The Big Picture

Like most technical subjects, it is impossible to present snow crystal science in an entirely linear fashion. Different topics are invariably interconnected to some extent, so one cannot fully appreciate any individual chapter in this book without having at least some understanding of the material presented in all the other chapters. I believe it is useful, therefore, begin with a brief synopsis of some key areas that form the backbone of this book.

Ice Crystal Structure: Chapter 2

Chapter 2 examines the properties of ice in equilibrium, including lattice structures, crystallography, general material properties, and thermodynamic quantities like latent heats and vapor pressures. Special attention is given to *terrace step energies* on the basal and prism facets, as these play an important role in snow crystal growth. Equilibrium physics is generally quite well understood, so these topics form a foundational basis for studying snow crystal growth. I have some fondness for lattice projections and crystal twinning in natural snow crystals, so these topics are presented in this chapter as well.

Although the lattice structure of crystalline ice is well characterized in the bulk, the molecular structure and chemical physics of the ice surface remains an area of active research [1970Fle, 2004Ike, 2010Pfa]. For example, *surface premelting* has been investigated using a variety of surface probes over a wide range of temperatures, but this phenomenon remains somewhat enigmatic overall [2007Li, 2018Qui]. Surface premelting appears to play a major role in snow crystal growth, and I touch on the topic in this chapter. But there is no comprehensive theory of surface premelting, so its detailed effects on the dynamics of ice crystal growth are not yet understood at even a qualitative level, a fact that has hindered progress for many decades.

This chapter also connects to current research in *molecular dynamics simulations* of the ice crystal surface, which have provided many insights into surface premelting and other ice properties [2002Mat, 2009Pae]. Molecular dynamics (MD) simulations are just beginning to calculate terrace step energies in ice [2020Llo], which have been measured as a function of temperature from

ice-growth experiments. These developments suggest that computational chemistry will soon become an essential tool for better understanding the detailed molecular dynamics governing snow crystal growth.

Diffusion-Limited Growth: Chapter 3

The formation of elaborately branched snow crystal structures results from the *Mullins-Sekerka instability*, which arises from the slow diffusion of water vapor molecules through air. Analytical solutions presented in Chapter 3 indicate that *particle diffusion* and *surface attachment kinetics* are the primary physical processes guiding snow crystal growth. The complex interplay of these two effects yields the full menagerie of observed morphologies that are simultaneously branched and faceted. These same analytical solutions show that *heat diffusion* and *surface energies* play relatively minor roles in snow crystal dynamics, although they can become important considerations in special circumstances.

The physics of particle diffusion is well described by the statistical mechanics of ideal gases, so this aspect of snow crystal science is essentially a solved problem. Applying this theory to the growth of complex structures continues to be a nontrivial challenge, however. Analytic solutions are suitable for especially simple examples, like growing spheres and parabolic needlelike forms, and these are extremely useful for examining scaling relations and revealing the relative importance of competing factors in overall growth behaviors. But numerical modeling (Chapter 5) is needed to reproduce the complexity seen in all but the simplest snow crystals.

This chapter connects to a large body of more-general scientific work examining the growth of dendritic structures during solidification, including work on *solvability theory* [1992Mus, 1997Kar, 2019Liu]. Much of this work pertains to solidification from the melt, however, where heat diffusion and surface energies are dominant forces, while particle diffusion and attachment kinetics are often negligible factors. As a result, the connections are not as strong as one might expect, because solidification from vapor and from liquid can have quite different growth behaviors. This chapter ends with qualitative discussions of numerous specific snow crystal growth behaviors that arise from the interplay of the oft-competing processes of particle diffusion and surface attachment kinetics.

Attachment Kinetics: Chapter 4

In this chapter, I present a comprehensive attachment kinetics (CAK) model that can explain most of the morphological transitions seen in the Nakaya diagram. The model begins with *terrace nucleation theory*, as this physical process nicely explains the growth of large facet surfaces. The theory incorporates *terrace step energies* on the basal and prism facets, which have been measured over a broad range of temperatures. This foundational element of the model relies heavily on a several precision ice-growth measurements that are presented separately in Chapter 7.

The CAK model goes on to incorporate the concept of *structure-dependent attachment kinetics* (SDAK), which stipulates that the molecular attachment kinetics on small faceted terraces can be dramatically different from that on large terraces. Enhanced surface diffusion factors into this phenomenon, facilitated by temperature-dependent surface premelting that differs on the basal and prism facets. The SDAK effect further yields an *edge-sharpening instability* (ESI), which can explain the rather abrupt temperature transitions seen in the Nakaya diagram, including the formation of thin plates at $-15°C$ and hollow columns at $-5°C$. The CAK model extends and improves on earlier models of the snow crystal attachment kinetics, and it makes numerous predictions that are (so far) holding up to experimental scrutiny. The chapter ends with a detailed look at snow crystal measurements near $-5°C$, as this temperature presents an especially interesting nexus of growth behaviors.

The general topic of surface attachment kinetics connects with a great deal of work associated with crystal growth theory and mesoscale molecular dynamics across many areas of scientific research [2007Mic,

2010Zha]. However, while terrace nucleation theory has deep roots in these areas, the SDAK and ESI phenomena appear to be unique to snow crystal growth. The reason is simply that ice is a special material in the world of materials science, as it has a high vapor pressure and is often investigated near the solid/liquid/vapor triple point. The phenomenology of ice crystal growth thus stands apart from that found with the low-vapor-pressure, high-melting-point materials commonly studied for technology applications.

A somewhat different connection is with studies of antifreeze proteins (AFPs) in water, which can strongly inhibit attachment kinetics at the ice/water interface [2003Du, 2009Pet]. Molecular dynamics simulations have become an important tool in these studies, which aim to understand the underlying molecular mechanisms and to develop AFPs for applications in the food industry and in cryobiology. These topics are all related at the molecular level, where they can be grouped into the general area of chemically mediated crystal growth. Notably, the effects of chemical additives on snow crystal growth have been documented by numerous researchers, but there is essentially no theoretical framework to describe the observations at present.

Computational Snow Crystals: Chapter 5

Numerical models of solidification have been extensively studied since the 1980s, but only around 2005 did researchers begin demonstrating realistic model structures that exhibited both branching and faceting. This area has attracted considerable attention from applied mathematicians and metallurgists seeking to better understand the solidification process [2002Bra, 2011Mil]. The snow crystal case involves highly anisotropic attachment kinetics exhibiting deep cusps at the facet angles, requiring specialized computational modeling techniques that are not needed in most metallurgical applications. At the time of this writing, several existing models have reproduced reasonable-looking structures, but only when some nonphysical assumptions are adopted.

Resolving these issues is the subject of current research described in this chapter. Several numerical strategies have been investigated, including *front-tracking methods*, *phase-field techniques*, and *cellular automata*. The cellular automaton models seem to be especially adept at dealing with strongly anisotropic attachment kinetics, and these appear to be winning the race to develop physically realistic computational snow crystals. This area is evolving rapidly, however, and it is difficult to predict how future advances in numerical algorithms will impact the different modeling strategies.

Laboratory Snow Crystals: Chapter 6

Quantitative experimental observations are an essential part of snow crystal science, so this chapter explores some laboratory techniques that have been applied in this area. I examine a variety of ice growth chambers that allow in situ observations of growing snow crystals over a wide range of environmental conditions, along with nucleation methods, sample support mechanisms, and techniques for creating clean ice samples with oriented basal and prism facets. Controlling, measuring, and modeling supersaturation are discussed, as are unwanted systematic errors from substrate interactions, chemical impurities, and other experimental factors. Imaging techniques at all scales are discussed briefly, along with other types of surface probes that can yield information about premelting and other aspects of the ice surface structure.

The technology associated with ice crystal investigations connects with a broad range of studies in atmospheric science [1992Don, 2019Har, 2019Nel2], environmental science [2004Czi, 2012Hoo], atmospheric chemistry [2016Sei], materials science [1999Pet, 2013Dev], planetary science [2002Pou], cryobiology [1987Ban], and ice technology [2009Pat]. Ice has a ubiquitous presence in a broad range of scientific disciplines, linking these areas like no other single material can. Thus, although I treat snow crystal formation as its own microcosm of scientific investigation, the subject is clearly woven into a much larger tapestry.

Simple Ice Prisms: Chapter 7

The surface attachment kinetics comprise the crux of the snow crystal problem—necessary to understand even basic observations like the Nakaya diagram, yet remarkably difficult to comprehend at even a qualitative level. Progress toward developing a comprehensive physical model of the attachment kinetics begins with accurate measurements of the growth of simple ice prisms, a core topic that is examined in this chapter. I examine two key investigations in considerable detail, focusing on experimental techniques, growth modeling, and managing systematic errors. Although this topic is quite specialized, the resulting data provide the empirical foundation for the CAK model presented in Chapter 4, so precision measurements like these are central to our understanding of even the most basic elements of snow crystal formation.

Electric Ice Needles: Chapter 8

Because of the SDAK and ESI phenomena, the growth of simple ice prisms cannot reveal all aspects of the attachment kinetics. Further studies of complex growth morphologies are needed, which must be performed at high supersaturations and ultimately compared with full three-dimensional computational models of diffusion-limited snow crystal growth. This chapter presents what is perhaps the best overall experimental technique so far developed for examining the SDAK and ESI effects under controlled conditions. By growing snow crystals on the ends of slender "electric" ice needles in a dual diffusion chamber, a wide range of growth behaviors can be examined with in situ observations and a well-defined initial seed-crystal geometry.

Designer Snow Crystals: Chapter 9

This chapter examines an especially artistic laboratory technique that exploits the ESI to create thin platelike snow crystals perched atop small, blocky, ice-prism "ped-

estals." While not as flexible or scientifically valuable as the electric-needle method, these *Plate-on-Pedestal (PoP) snow crystals* are nearly ideal for recording high-resolution images of growing stellar-plate crystals. This apparatus has yielded the first photographs of stellar snow crystals that exhibit qualities that are overall superior to the best natural specimens, including better symmetry and sharper faceted features. The PoP technique has also yielded the highest-quality videos of growing stellar snowflakes thus far produced, along with the first observations of "identical-twin" snow crystals.

Natural Snowflakes: Chapter 10

This chapter examines the full menagerie of natural snow crystal types with illustrative sketches and abundant photographic examples. Classification schemes are discussed along with descriptions of a variety of common snow crystal structural features. This chapter presents something of a naturalist's guide to falling snow, suitable for the convenient examination and identification of different types of falling snow crystals.

Snowflake Photography: Chapter 11

Capturing quality imagery of natural snow crystals in cold conditions presents some unusual challenges for aspiring snowflake photographers. Finding especially photogenic specimens is nontrivial; handling them can be challenging; attaining suitable magnification requires special lenses; and lighting is problematic, because single-crystal ice is quite transparent. This chapter looks at each of these issues in detail and presents examples of a variety of innovative techniques that have been pioneered by the community of snowflake photographers.

Reductionism and Holism

My overarching goal in snow crystal science is a combination of reductionism and computational holism. The reductionism side aims to break down the physics of snow

crystal growth into its constituent parts and processes, including crystal structure, attachment kinetics, diffusion-limited growth, and other factors. Each of these can be isolated and examined separately, perhaps right down to the molecular level, with the hope of developing precise mathematical models of all the relevant physics.

Some of the reductionist pieces are already well understood, while others remain quite puzzling. For example, the statistical mechanics of diffusion is well known for ideal gases, and the ideal-gas approximation is more than adequate for describing snow crystal growth. The ice lattice structure and various thermodynamic properties of water and its phase transitions are also quite well understood. However, the structure and dynamics of surface premelting are rather poorly known, and how premelting affects the attachment kinetics is a remarkably difficult problem. Nevertheless, at least in principle, it is possible to isolate, investigate, and ultimately comprehend all the relevant physical process involved in snow crystal growth.

Reductionism, however, is not sufficient to describe all of snow crystal science. Characterizing all the pieces of a puzzle and assembling the puzzle are two different endeavors. Learning the fundamental laws of quantum physics does not immediately explain everything in the field of chemistry, because understanding how atoms assemble into molecules is a separate problem from understanding individual atoms alone. Similarly, comprehending the formation of a complete snow crystal, as illustrated in Figures 1.21 and 1.22, is not the same as characterizing the separate physical processes involved in its growth. Holism in this case is not so much that the whole is greater than the sum of the parts. Rather, seeing the whole requires that you be able to assemble the parts.

Holism thus compels us to create a computational model that incorporates all the known physical processes involved in ice crystal growth, with an accuracy sufficient to yield realistic snow crystal simulations. In principle, using a large enough computer, it would be straightforward to create the necessary algorithms. But the devil is in the details, and computational models involve a lot of details. Numerical inaccuracies and instabilities can be

problematic, and even the fastest supercomputers cannot come close to realizing full molecular resolution in large-scale phenomena. Thus, reductionism and holism tend to separate into distinct aspects of understanding snow crystal growth, and neither can be accomplished with absolute precision. The science of complex systems is always an activity of successive approximations.

In any area of scientific investigation, progress is measured by quantitative comparisons between theory and experiment, and this certainly applies to snow crystals. Creating numerical models that generate snowflakelike structures is a start, but meaningful progress requires direct comparison with laboratory observations. Chapters 5 and 8 point toward this eventual nexus of theory and experiment, when comparisons between laboratory and computational snow crystals are sufficient to determine whether our physical description of snow crystal formation is correct. We are certainly not at that point yet.

Some might argue that creating accurate computer simulations of all types of growing snow crystals would not constitute a true understanding of the underlying phenomenon. Debating this point would require a precise definition of the word "understanding," which is itself a nontrivial philosophical point. Snow crystal formation involves a multitude of complex physical processes acting over a broad range of length and time scales. It may indeed be the case that a single brain cannot simultaneously comprehend all aspects of what is happening. If that is true, then we have little choice but to let our machines do the heavy lifting for us. I would argue that a detailed computer model that reproduces laboratory snow crystals with high fidelity is as close to a true understanding as we are likely to achieve. It is a good place to start, at any rate.

As of this writing, many aspects of this overarching scientific strategy are coming together. Our understanding of the attachment kinetics is beginning to make sense (Chapter 4), suitable computational models are rapidly becoming feasible (Chapter 5), and detailed comparisons between experiments and theoretical models of complex snow crystal morphologies are becoming pos-

FIGURE 1.21. (Above) This "pond crystal" froze from liquid water on the surface of a still pond, and basal faceting yielded a thin platelike sheet. Note how the angular branching exhibits the six-fold symmetry that characterizes the ice crystal. (Below) Frost forms from water vapor near ground level, and the resulting structures can look much like snow crystals. Large specimens like these (about 2 cm in length) are called "hoarfrost" crystals.

sible (Chapter 8). There appears to be no serious road-blocks impeding the path forward, and steady progress is being made on all fronts.

Curiosity-Driven Science

The quest to understand how snow crystals grow and develop is not motivated by any practical applications or societal needs, but rather simply by a desire to explain a common natural phenomenon. The rainbow provides a good analogy (see Figure 1.23), as considerable intellectual determination and scientific advancement was required to fully comprehend its colorful arcs. After centuries of musings and slow progress toward understanding these vibrant meteorological displays, René Descartes described a detailed physical model of the rainbow in his 1637 treatise, *Discourse on the Method* [1637Des], explaining how the primary and secondary rainbows arise
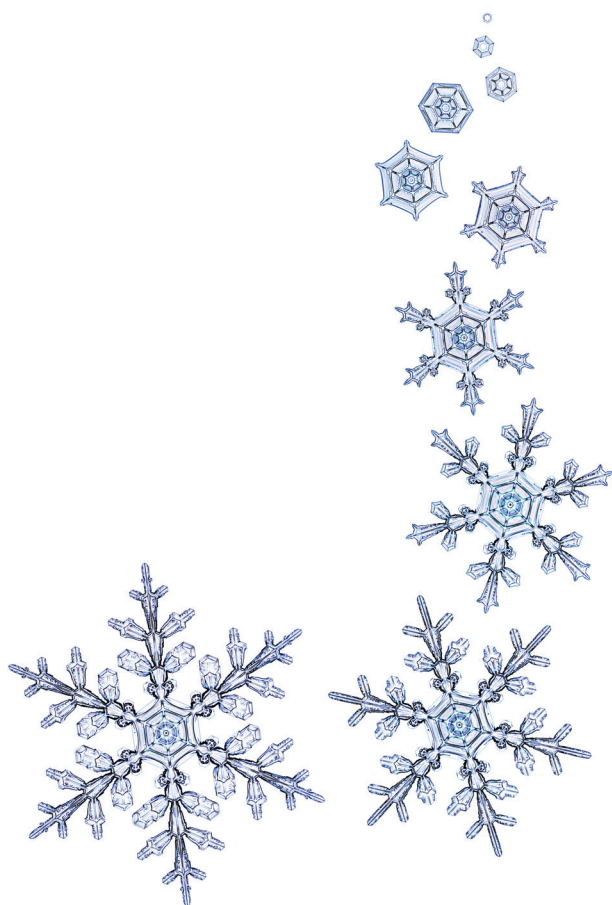
FIGURE 1.22. This series of images shows the growth and development of a laboratory-grown snow crystal. The temperature and supersaturation were changed as the crystal grew, alternating between periods of faceted and branched growth. After the initial seed crystal had grown into a larger hexagonal plate, the conditions were changed to sprout branches from the six corners of the plate. Additional changes were applied to stimulate the growth of sidebranches at various times. Because the six branches experienced the same changing growth conditions, they all developed symmetrically. It took about 45 minutes to grow the full crystal, which measured about 2 mm from tip to tip.

truly solved problem in 1908, when Gustav Mie developed a comprehensive mathematical theory for light scattering from spherical water droplets. Does this knowledge substantially improve the human condition? In 1880, Mark Twain wrote that "we have not the reverent feeling for the rainbow that the savage has, because we know how it is made. We have lost as much as we gained by prying into that matter" [1880Twa, p. 466]. Perhaps, but seeking truth seems to have worked for us in the past, especially in the natural sciences.

The snowflake is following a similar path through scientific history, except it is about 400 years behind the rainbow. We are just now piecing together a rudimentary picture of the attachment kinetics, slowly deciphering the detailed molecular forces that guide growth rates and structure formation. The snowflake and the rainbow are two small parts of nature's tapestry, and that is sufficient reason to justify our curiosity regarding their physical nature. The aim of this book is to push forward this icy microcosm of science just a bit more.

NO TWO ALIKE?

Is it really true that no two snowflakes are alike? I hear this question frequently, perhaps because our elementary-school teachers planted the notion into all our heads as we practiced cutting paper snowflakes, and there it has remained throughout our lives. It is a funny question, almost like a Zen *koan*—if two identical snowflakes fell in the vast winter forests, my inquisitive friend, would anyone ever know? And can you truly be sure that no two are alike, as you cannot possibly check them all to find out? There is indeed a certain level of unknowability to the question of snowflake alikeness, but as a physicist, I feel that I can shed some light on this issue. As I will demonstrate, the answer depends to a large extent on what you mean by the question. (Physics does occasionally have its Zenlike qualities.)

The short answer to the question is yes—it is indeed extremely unlikely that any two complex snowflakes will look exactly alike. It is so unlikely, in fact, that even if

from single and double reflections inside raindrops. Isaac Newton discovered color dispersion three decades later, thereby explaining the rainbow's characteristic colors. And around 1800, Thomas Young further identified the fainter supernumerary bows as a manifestation of the wavelike nature of light. The rainbow only became a

FIGURE 1.23. Explaining the rainbow required a synthesis of many advances in physics, optics, and mathematics, so these colorful arcs were not fully understood until early in the twentieth century. Snow crystal formation is a substantially tougher problem than the rainbow, involving subtle many-body molecular processes at the ice surface. Comprehending the snowflake remains very much a work in progress. Rainbow photo by Steven E. Nelson.

you looked at every one ever made, over all of Earth's history, you would almost certainly not find any exact duplicates. The long answer is a bit more involved, however, as it depends on just what you mean by "alike" and on how you define a "snowflake." For example, I will claim that it is possible that two nano-snowflakes could be exactly alike. When developing the theory of quantum mechanics, physicists discovered that some things in nature are exactly, precisely, perfectly alike—*indistinguishable* is the proper technical term. For example, our understanding of elementary particles indicates that all electrons are fundamentally indistinguishable from one another. This is one of the cornerstones of quantum physics, and alikeness in this arena is a profound concept. Indistinguishability is part of what defines a truly elementary particle.

A water molecule is considerably more complex than an electron, and not all water molecules are exactly alike. If we restrict ourselves to water molecules that contain two ordinary hydrogen atoms and one ordinary ^{16}O atom, then again, physics tells us that all such water molecules are exactly alike. However, about one molecule out of every 5,000 naturally occurring water molecules will contain an atom of deuterium in place of one of the hydrogens, and about one in 500 will contain an atom of ^{18}O instead of the more common ^{16}O. And these rogue atoms can be distinguished from their common cousins.

Because a typical small snow crystal might contain 10^{18} water molecules, we see that about 10^{15} of these will be isotopically different from the rest. These unusual molecules will be randomly scattered throughout the

snow crystal lattice, giving it a unique design. The probability that two snow crystals would have identical placements of these isotopic anomalies is essentially zero. Even with 10^{24} snow crystals being made per year on Earth, the probability that any two would be exactly identical within the entire lifetime of the Universe is zero in any practical sense.

Thus, at this extreme level of atomic precision, no two snow crystals can be exactly alike because of these isotopic differences. However, an exception (there are few absolute statements in science) would be a snow crystal with only a handful of molecules. If we assemble an ice crystal of only six molecules, for example, then it could easily happen that each of the six will contain two ordinary hydrogen atoms and one ordinary ^{16}O atom. Furthermore, a cluster of six molecules will only have a few stable configurations. Therefore, there is a reasonable probability that two six-molecule snow crystals would be exactly alike, quantum mechanically indistinguishable from one another. However, perhaps an assembly of just six molecules does not a snowflake make.

If we restrict ourselves to isotopically pure water molecules, it is still extremely improbable that two macroscopic snow crystals would be exactly alike. When a crystal grows, its molecules do not always stack together with perfect regularity, so a typical snow crystal contains a large number of minor crystal dislocations, which again are scattered throughout the crystal in a random fashion. One can then argue, as with the isotopes, that the probability of two crystals growing with exactly the same pattern of dislocations is vanishingly small. And again, one has the exception of few-molecule crystals, which can easily be free of dislocations.

Another part of this tale is that small snow crystals can at least look alike, even if they are not precisely identical down to the last molecule. So, let us relax our definition of alikeness and say that two snow crystals are alike if they just look alike in an optical microscope. The smallest features one can see in an optical microscope are about 1 micrometer in size, which is 10,000 times larger

than an atom. With this relaxed definition, you could probably find two identical-looking hexagonal prisms falling from the sky if you conducted a diligent search, and it is certainly easy to make such simple crystals in the laboratory. Figure 1.24 shows a pair of identical-looking snowflakes that happened to fall next to one another in my lab. When the overall crystal morphology is little more than a simple hexagon, one looks much like any other.

As the morphology of a snow crystal becomes more complex, however, the number of possible ways to make it soon becomes staggeringly large. To see just how rapidly the possibilities increase, consider a simpler question—how many ways can you arrange books on your bookshelf? With three books, there are six possible arrangements, and you can easily sketch all of them for yourself. Increasing to 15 books, there are 15 choices when you place the first book on the shelf, then 14 for the second, 13 for the third, and so on. Multiply it out and there are more than a trillion ways to arrange just 15 books. With 100 books, the number of possible arrangements goes up to just under 10^{158}, which is about 10^{70} times larger than the total number of atoms in the entire known universe!

If you gaze at a complex snow crystal under a microscope, you can often pick out a hundred separate features if you look closely. Because all those features could have developed differently, or could have appeared in slightly different places, the math ends up being like that with the books, and it applies to fingerprints as well. The exact calculation would depend on the details, along with how you define individual features and their locations. But the details are not important, because the total number of possible ways to make a complex snow crystal soon becomes unfathomably large. Thus, it is essentially impossible that any two complex snow crystals, out of all those made over the entire history of the planet, have ever looked exactly alike.

The story of snowflake alikeness takes another amusing turn when you start looking at complex laboratory-grown crystals. As I described earlier in this chapter, the
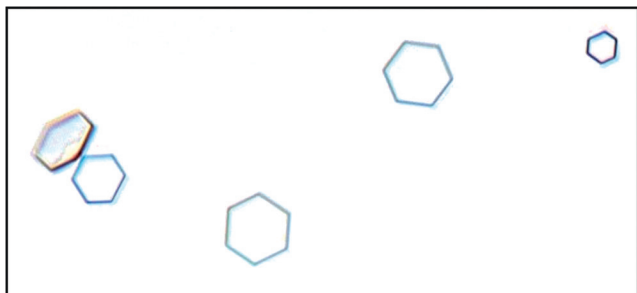
FIGURE 1.24. This laboratory photo shows several small, thin-plate snow crystals that grew while falling freely in air and then landed on a transparent substrate (see Chapter 6). Because the crystals have a simple hexagonal shape, one can easily find a pair of nearly identical specimens next to each other, like the two centered here.

FIGURE 1.25. A pair of laboratory-grown "identical-twin" snow crystals, surrounded by a field of water droplets. These grew side-by-side on a fixed transparent substrate using the Plate-on-Pedestal technique described in Chapter 10. Because both crystals experienced the same growth conditions as a function of time, they grew into nearly identical shapes. Analogous to identical-twin people, these similar snowflakes are clearly related, even though they are not precisely equal in every detail.

final shape of a large stellar snow crystal is determined by the path it traveled through the clouds as it formed. Because the air is usually turbulent to some extent, even under calm conditions, the paths of different snow crystals are typically quite meandering and chaotic. Trajectories that bring two crystals close to one another will soon diverge, separating them again by large distances. In the laboratory, however, it is possible to place two seed crystals near one another on a fixed substrate and then subject them both to the same growth conditions as a function of time. Doing this with some care yields results like that shown in Figure 1.25. As these crystals were developing, I occasionally subjected them to abrupt changes in temperature and/or supersaturation. Because both crystals saw the same changes at the same times, they responded with synchronized growth behaviors. I like to call these "identical-twin" snowflakes, in analogy to identical-twin people. They are clearly so alike that there must have been some underlying connection between them, yet they are not identical in an absolute sense.

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