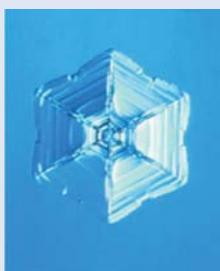


Snow and ice crystals

Yoshinori Furukawa and John S. Wettlaufer

Highly dendritic snowflakes are an aesthetic source of wonder, but the greater challenge for physicists lies in understanding the “simpler” prismatic and planar forms.

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Vast regions of our planet are seasonally or perennially covered with snow and ice; the ground becomes rock hard, lakes and oceans freeze, and snow falls from the sky. If you live in New England or Hokkaido, look out the window in winter and you will see those inescapable consequences of Earth's seasonal cycles. For nearly everyone, snow crystals induce a visceral response, be it an annoyance during one's commute or the enthusiasm of an impending ski trip. The distribution of ice throughout the universe and close to home has central implications in astrophysics and geophysics—from the agglomeration of matter in stellar nebulae to the state and fate of Earth's climate. Like all materials, ice exhibits basic phase-transition phenomena. But its study does not require ultrahigh-vacuum or cryogenic apparatus, so it is an ideal test bed for physicists.

Vermont farmer and Sapporo physicist

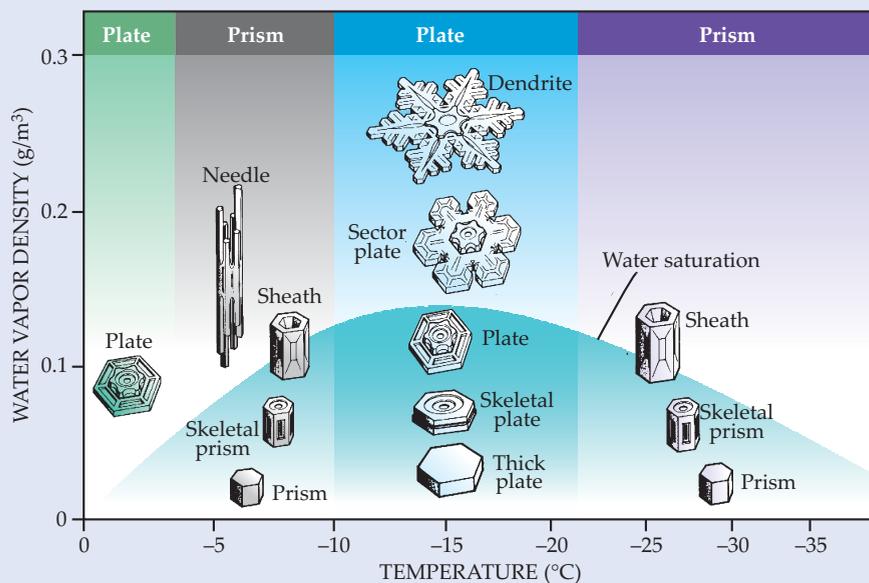
Snow crystals are simply ice crystals grown from the water vapor present in air, and the varied forms they take during their transit through the clouds are the basis of science, art, and the culture of cold regions. In his 1611 book *A New Year's Gift of Hexagonal Snow*, Johannes Kepler considered the origin of the hexagonal shapes of snow crystals, like those shown at left in photographs taken by one of us (Furukawa). Kepler argued that the hexagonal form had to do with the packing of spheres, an idea that led to his famous conjecture on the densest possible filling of space by spheres. During the winter of 1635, René Descartes made strikingly detailed observations of snow crystals. Three centuries later the most extensive catalog of its time was made by the Vermont farmer Wilson Bentley, who published the book *Snow Crystals* with William Humphreys in 1931. Bentley's dedication and passion were evident: “Was ever a life history written in more dainty or fairy-like hieroglyphics? How charming the task of trying to decipher them.”

The snowflake has substantially shaped the fabric of life in Hokkaido, the northern island of Japan. The imagination of Hokkaido University nuclear physicist Ukichiro Nakaya was captivated by *Snow Crystals*, and in 1932 he began his own ob-

servational program. In the course of taking more than 3000 photographs in a few years, Nakaya classified snow crystals into some 40 morphological categories. He surmised that the shapes were a consequence of the temperature and supersaturation of the atmosphere through which the crystals moved, and he quantified his intuition by creating nearly all of the natural morphological categories in the laboratory. His results, which have since been reproduced by his students and by many others around the world, are elegantly summarized in the so-called Nakaya diagram that appears on the next page. In the diagram, one can read the meteorological information written on a snow crystal. That is, one can infer much of the temperature and humidity history of the snow crystal by observing its morphology on the ground. Hence, Nakaya was often quoted as referring to the snow crystal as “a letter from the sky.”

Much of the focus on snowflakes deals with the highly dendritic forms, but physicists generally understand how such shapes arise out of diffusive instabilities associated with the vapor, as mediated by the underlying anisotropy that shapes the inner hexagonal form. Nakaya clearly appreciated that the complex spacetime history of an object in a turbulent, nonequilibrium environment cannot be captured in its entirety. Nonetheless, the Nakaya diagram embodies the basic physics associated with the principal dynamic shape transitions, even if it doesn't include all snow crystal forms. One of its salient features is that, depending on the temperature regime of growth, the forms at small supersaturation are either hexagonal plates or prisms, and the transitions from one regime to the other are abrupt. For some 50 years, many researchers have grappled with the challenge of explaining that alternating plate-prism growth sequence.

A crystal's facets reflect the symmetry of the underlying crystal structure. And its surface energy depends on the sum of the energies of all the bonds broken per unit area during the creation of its surface by cleavage. Strictly speaking, facets, beautifully reflected in the crystals at the bottom of the Nakaya diagram, are orientations that are smooth on all scales down to the molecular scale.



The shape of snow crystals depends on the temperature and humidity of the atmosphere in which they have grown. In this Nakaya diagram, the vertical axis shows the density of water vapor in excess of saturation with respect to ice. Reading from left to right at low supersaturation, one sees abrupt morphological changes (dynamical phase transitions) from hexagonal plate to prism to plate and back to prism. The curved line shows the saturation with respect to liquid water as a function of temperature.

An ideal, dislocation-free crystal is fully faceted at absolute zero and becomes rougher as its temperature increases. Some facets persist right up to the bulk melting point T_m , and some become rough at lower temperatures. The surface roughness, its equilibrium and nonequilibrium manifestations, and liquidity itself all conspire to influence the transitions on the Nakaya diagram. Here we point out the essential ingredients of the conspiracy.

Liquid and vapor interfaces

It is commonly thought that ice skating is possible because of pressure melting; the pressure applied by the skate melts the ice below it, and the water film allows the blade to glide. That fact alone, however, cannot explain the slipperiness of ice; the answer involves not only frictional melting but also surface melting, which describes the natural state of the free surface of ice as being covered by a thin liquid film of water.

Detailed experiments on the surfaces of semiconductors, metals, rare-gas solids, and molecular solids, including ice, show that the process of surface melting begins at a temperature below T_m . It is due to the weaker binding of the surface atoms or molecules, which are thus more susceptible to thermal disorder than the bulk interior. Further temperature increases lead to the breakdown of the surface layers and an increase in the defect density; hence the atomic and molecular mobility increases. That mobility eventually becomes the same as in the bulk liquid phase, and finally the liquid film thickness becomes arbitrarily large at T_m ; surface melting is completed, and bulk coexistence is reached.

Liquidlike layers persist on ice at temperatures as low as a few tens of degrees below 0°C when, as under atmospheric conditions, appreciable surface impurities are present. The different facets of an ice crystal in the Nakaya diagram have microscopic films, but the film thickness depends on the facet. As the temperature is lowered, the films thin. The surface energy of a “dry” facet depends on the distribution of ledges, corners, edges, and point defects such as single molecules and vacancies in the surface. The cost of all of those contributions determines whether the surface is faceted or rough: The transition between the two situations is called the roughening transition.

On an infinite two-dimensional surface, the energy required to form a step vanishes at a roughening temperature $T_r \leq T_m$, and thermal fluctuations liberate the surface from

the ordering influence of the underlying lattice. Although finite crystals are different in detail, it is qualitatively accurate to say that if $T > T_r$, the crystal’s equilibrium shape will be rough.

When a crystal grows, it receives additional molecules from the vapor phase. If a molecule lands on a region that is molecularly rough, it will find a ready place for incorporation into the solid. In contrast, a molecule landing on a facet has many options: It can diffuse along the facet until it finds a ledge, corner, or edge to attach to; it can meet up with a number of other diffusing molecules and create an expanding island on the surface; or it can detach and return to the vapor. Moreover, if the growth is so rapid that new material can’t settle before being buried by more molecules, a surface will kinetically roughen. Thus the growth process depends sensitively on the nature of the surface, which sets the stage for anisotropic growth. Much of the discussion of the Nakaya diagram does and must deal with the confluence of surface growth processes and their dependence on vapor density, surface temperature, and the size of the crystal.

Here’s the rub. Independent experiments by Michael Elbaum and Minoru Maruyama established that roughening depends on whether ice is in contact with water or water vapor. Therefore, as the temperature rises, surface melting begins to become important—in natural snow the precise temperature depends sensitively on the impurity level. A thin film develops between ice and vapor, the nature of the roughening transition changes, and that change depends on which facet one scrutinizes. Is the change dramatic? Evidently so, but the key issue is to extract the underlying physics that weds surface melting to roughening in systems driven away from equilibrium. If you succeed in doing it, there will be a diagram named after you.

Additional resources

- ▶ J. G. Dash, A. W. Rempel, J. S. Wettlaufer, “The Physics of Premelted Ice and Its Geophysical Consequences,” *Rev. Mod. Phys.* **78**, 695 (2006).
- ▶ Y. Furukawa, “Fascination of Snow Crystals: How Are Their Beautiful Patterns Created?” available at <http://www.lowtem.hokudai.ac.jp/ptdice/english/aletter.html>.

The online version of this Quick Study provides links to further resources and to René Descartes’ snowflake sketches and comments.