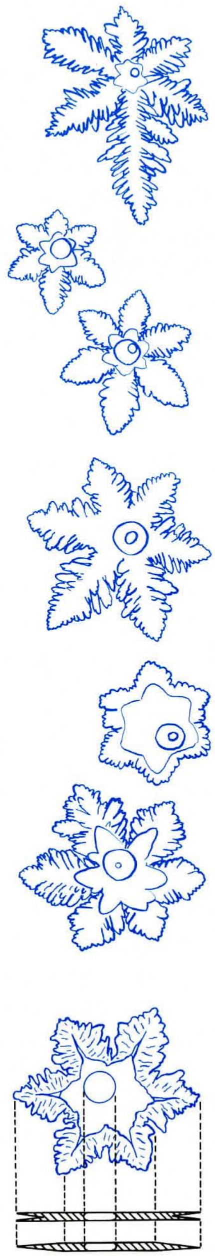
NCAR Quarterly
Summer 1966

Ice Crystal Studies in Atmospheric Research



The fundamental processes of the atmosphere have much to do with transformations of water among its three phases of vapor, liquid, and ice. To investigate details of these transformations, the atmospheric sciences must call on the methods of experimental physics. One aspect of such research, being conducted at NCAR by Charles and Nancy Knight, is a study of the primary processes which determine the formation of ice crystals. In attempting to deal with the difficult theoretical concepts and the perhaps even more difficult physical measurements involved, the Knights have devised some novel techniques for the study of crystal surfaces.

The atmospheric processes by which water and ice change to one another depend more on the nature of the liquid and solid surfaces involved than on the bulk properties, and the Knights have felt that study of the equilibrium form of crystals offers possibly the most direct way to investigate the nature of these surfaces and their interactions.

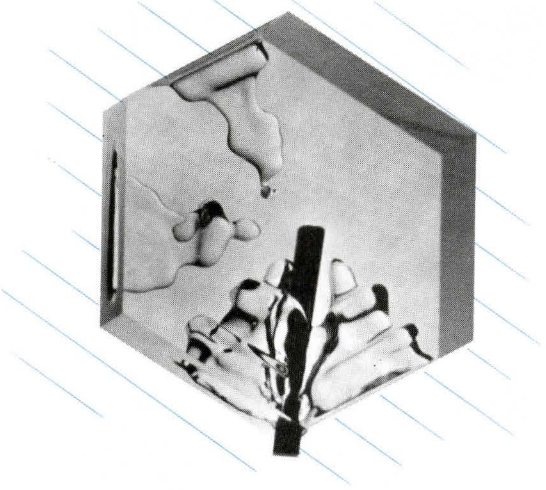
Equilibrium Shape

A crystal held in a constant environment should, in theory, change its shape toward an equilibrium form which expresses the most economical use of the molecular binding forces of the crystal lattice in relation to the energies available in the complete system of crystal and environment. Thus, solid material might evaporate from certain of the crystal faces, or portions of the faces, and other faces might serve as sites of condensation for material from the environment. The result would be a gradual change in shape of the crystal, continuing until an equilibrium shape is reached—a shape which should be related to the surface energies of the crystal faces. If the molecules near the surface are tightly bound to the lattice structure of the crystal interior, the equilibrium shape should be one of clean facets and sharp angles. However, if the lattice becomes disordered near the surface, then the equilibrium shape might well be one in which surfaces and angles are rounded off.

For most crystals at atmospheric pressure such changes, if they do occur, are too slow to be observed by any presently available means. However, under certain rather unusual conditions ice crystal faces do change their shape, presumably toward equilibrium form, within a few days. The changes are observed in "negative crystals," which occur as holes bounded by crystal faces, entirely enclosed in single large ice crystals.

Tyndall Figures

Negative crystals in natural ice were described more than a century ago by the English glaciologist John Tyndall: "Take a slab of lake ice and place it in the path of a concentrated sunbeam. Watch the track of the beam through the ice. Part of the beam is stopped, part of it goes through; the former produces internal liquefaction, the latter has no effect whatever upon the



ice. But the liquefaction is not uniformly diffused. From separate spots of the ice little shining spots are seen to sparkle forth. Every one of these points is surrounded by a beautiful liquid flower with six petals... what is the central spot? A vacuum. Ice swims on water because, bulk for bulk, it is lighter than water, so that when ice is melted it shrinks in size. Can the liquid flower then occupy the whole space of the ice melted? Plainly no. A little empty space is formed with the flowers, and this space, or rather its surface, shines in the sun... In all cases the flowers are formed parallel to the surface of freezing. They are formed when the sun shines upon the ice of every lake; sometimes in myriads and so small as to require a magnifying glass to see them... Here we have the reverse of the process of crystallization. The searching solar beam is delicate enough to take the molecules down without deranging the order of their architecture..."

These Tyndall figures, as they are now known, are negative representations, nearly filled with water, of the characteristic six-sided ice crystal, the same basic crystal structure seen in common snowflakes. (The vacuum in the figures is not complete; the cavities have their own atmospheres of nearly pure water vapor, at about 5 mm Hg pressure.) Tyndall figures offer an inherently more stable environment than do positive crystals, and in recent decades the Japanese physicist Ukichiro Nakaya has developed techniques for experimenting with them. Nakaya used a burning glass to produce the figures in natural ice crystals and found that on refreezing the water, the gas bubble remained as a negative crystal, similar to a natural Tyndall figure, surrounded by ice.

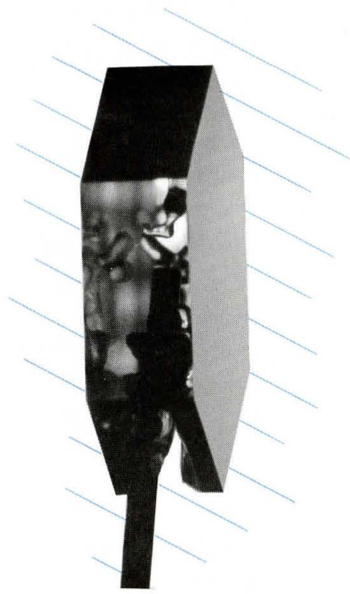
Nakaya studied his negative crystals in a cold chamber kept at about –5° C. He found that ice evaporated from some faces and condensed onto other faces, so that within a few days the crystal cavities became visibly longer and thinner. These changes in shape, however, were due to temperature gradients, and could not be considered strictly a response to equilibrium conditions. It was virtually impossible to keep the experimental chamber at an exactly even temperature throughout, and Nakaya found that a temperature gradient as low as 0.01° C per centimeter between opposite crystal faces was enough to cause evaporation from the warmer face and condensation on the colder face, with the result that the elongating crystal migrated through the ice in the direction of the warmer face. The migrating crystals sometimes left trails of contained bubbles, which Nakaya felt were evidence of strain in the ice crystal, produced during the refreezing process.

Growing Negative Crystals

The Knights, who spent the years from 1962 to 1964 as visiting workers in Nakaya's laboratory at the University of Hokkaido, felt that these experiments offered some interesting possibilities for investigating the equilibrium conditions of ice crystals. If the difficult problem of temperature control could be solved, so that an even temperature could be maintained throughout the crystal, then any changes in the geometry of the faces should come about in response only to forces within the crystal and at its faces.

The first requirement for such experiments was to secure ice crystals free from internal strain. To this end, the Knights began with large, exceptionally perfect crystals quarried from the Mendenhall Glacier in Alaska by Professor A. Higashi of Hokkaido University.

Negative ice crystal, produced by the Knights by the hypodermic needle vacuum technique. The crystal was grown at –14° C, but incomplete temperature control caused some irregularities. The solid remnants left in the negative crystal develop on the fastest growing faces. They persist for a while because of low heat conduction in the 5-mm water vapor atmosphere of the crystal interior, but will eventually detach and fall to the bottom of the cavity.

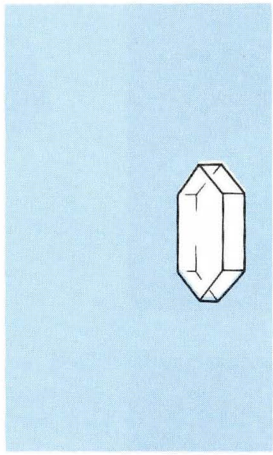


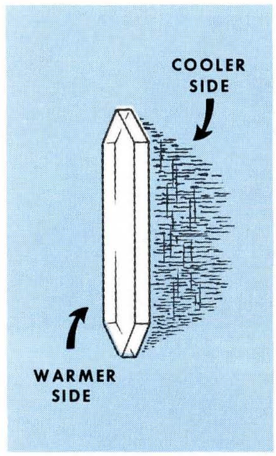
To create their negative crystals, the Knights made a decided innovation over the burning-glass method. They embedded the square-cut end of a hypodermic needle in a small block of ice cut from one of the Mendenhall crystals, and applied a constant vacuum to the other end of the needle. Ice kept below the freezing point sublimates, or transforms directly into water vapor. In this experiment the vapor was removed through the needle, and the high vapor pressure of ice soon allowed a cavity to form at the embedded end of the needle. The cavity grew in the shape of a six-sided negative ice crystal, the exact form being determined by the temperature and by the rate at which the process was carried out. When perfected, the procedure was easy to repeat and resulted in mirror-smooth uncontaminated crystal faces. The ice surrounding the crystal faces was not subjected to strain, because the process involved no re-freezing.

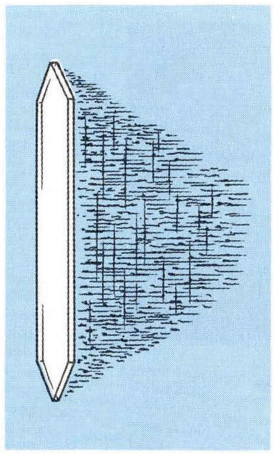
Crystal Faces and Free Energy

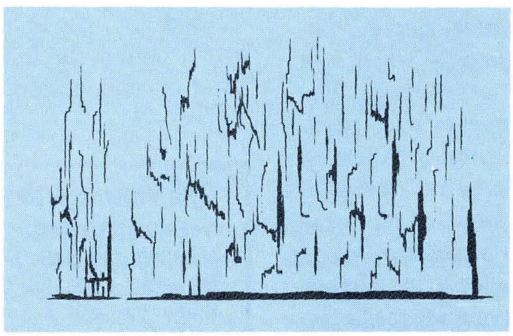
Within a drop of liquid the molecular attractions are approximately the same in all directions, but at the surface the molecules are less strongly attracted in the direction away from the drop than they are toward the interior. The surface molecules thus pull together, like an elastic skin, into the spherical shape which expresses the minimum surface area, or minimum free energy.

Although the binding forces in crystals are stronger than in liquids, the shapes of most crystals also appear to be determined by considerations of minimum free energy. Water chilled below 0° C freezes because at such temperatures ice has a lower free energy than water. But for freezing to start, the ice crystal has to grow from zero size, and some extra energy is required to hold together a group of water molecules to form an incipient ice crystal. The extra energy is made available in part by supercooling—that is, lowering the temperature of the still-liquid water below 0° C—and in part by random energy fluctuations with-









Professor Nakaya studied the migration of Tyndall figures through ice in response to a slight temperature gradient. In a few days' time the figures moved toward the warmer surface, narrowing and elongating as they travelled. The crystals left trails of enclosed bubbles, which Nakaya believes indicate a high degree of internal strain in the ice he used.

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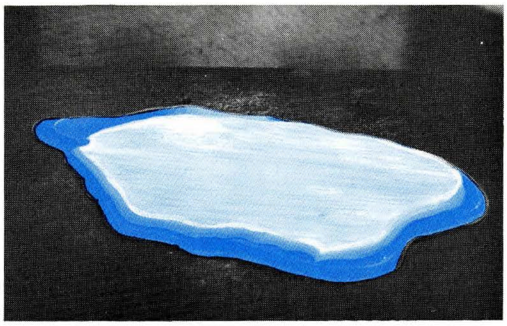

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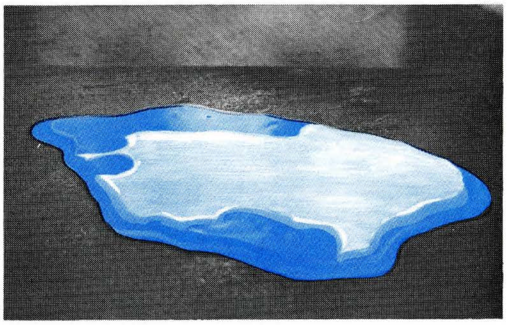

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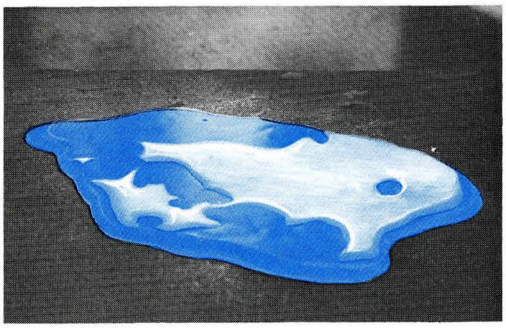
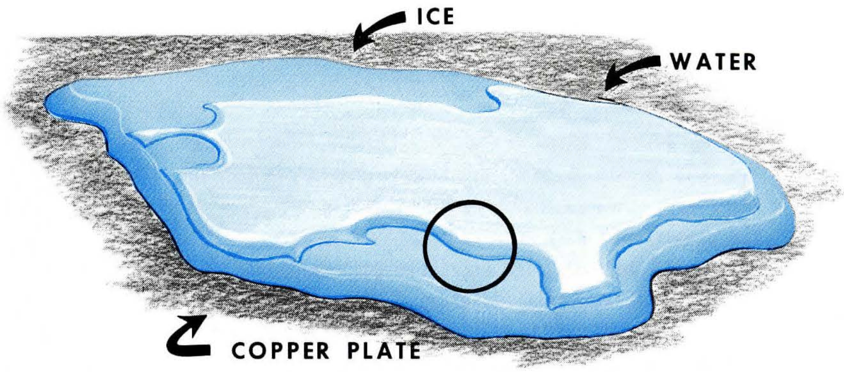
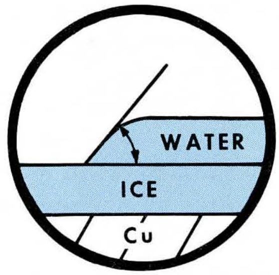


in the supercooled water. The necessary amount of supercooling may be very slight for impure water such as tap water, but may be as low as –39° C before very pure water will begin to freeze.

The amount of energy required to begin the freezing process is related to the molecular attraction, or interfacial energy, between ice and water, a quantity which has thus far defied careful measurement. The Knights hope that experiments with negative crystals may yield some information on the role of interfacial energy in ice nucleation. If, in a carefully controlled temperature environment, and in strain-free ice, a negative crystal changes shape, the change should reveal something about the equilibrium shape of the crystal. This shape determines the surface-to-volume ratio, and thus strongly affects the amount of energy involved in nucleation.





Measurement of the contact angle of a liquid on a solid surface is one way to determine the ratio between the free energy of the solid surface and that of the liquid-solid interface. The contact angle for water on ice, surrounded by air, has always been assumed to be zero, but actual measurement has been impossible due to the difficulty of maintaining the system at 0° C throughout. The Knights tested this assumption in a non-equilibrium experiment in which they poured water onto a copper plate at –70° C. As the water froze upward from the copper, a non-zero contact angle appeared. The experiment did not provide a measurement of the equilibrium contact angle between water and ice, but it did enable the Knights to conclude that the angle must be greater than 12°.

However, while the principle of minimum free energy evidently controls the formation and the shape of most crystal substances, it may not apply in entirely the same manner to ice. The concept requires an equilibrium between crystal and environment that includes equal vapor pressure at all faces, and it seems possible that changes in the shape of negative crystals could result from differential vapor pressures at different faces of the ice crystal. It would be helpful indeed if experiments could determine which concept is correct, and also give a better measure of the interfacial tension of ice.

The required environmental control may prove too difficult to achieve, and the experiments may not be possible. The topic is too important to drop, however, and the Knights and other scientists working on similar problems would then seek alternate routes to the goal. Meanwhile, the Knights' method of producing negative crystals seems certain to find wide application in other crystallographic experiments.

FOR FURTHER REFERENCE

Nakaya, U., 1956: "Properties of Single Crystals of Ice, Revealed by Internal Melting," U. S. Army Corps of Engineers, Snow Ice and Permafrost Research Establishment, *Research Paper 13,* Wilmette, Illinois; also Knight, C. A., 1965: "Negative Crystals in Ice: A Method for Growth," *Science 150,* No. 3705, 1819-1821.