Crystal Polarity: A Window on Ice Nucleation

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One might think that by now scientists would have developed a reliable quantitative understanding of the freezing of water, a transformation that does not even require chemical reaction. But the tools of equilibrium thermodynamics are inadequate for understanding the intricate mechanisms by which crystals nucleate and grow. One has only to consider the elaborate, nonequilibrium shapes of snowflakes to sense the mystery of this process. Careful structural analysis of some ice nucleators reported in this issue by a group of chemists from Israel's Weizmann Institute of Science provides new experimental support for a mechanism that depends less on detailed structure than do other recent models for nucleation (*1*).

Surface molecules make fewer stabilizing contacts than molecules within a solid. Thus tiny ice particles, with high surface-to-volume ratios, are much less stable than macroscopic ice. Even when cooled 20° or 30°C below its melting point, pure water cannot generate stable nuclei on which ice can grow. This bottleneck provides an opportunity for tinkering. Nature controls freezing in many ways. By making proteins that nucleate ice formation, several bacterial genera raise the temperature at which frost formation damages agricultural plants by as much as 10°C. At the other extreme, fish that inhabit polar seas can live for 30 years at temperatures a degree below the equilibrium melting point of their body fluids. To these fish an adventitious ice sliver on which water could crystallize poses a threat as lethal as Kurt Vonnegut's "ice-nine," the substance that destroyed all of life in *Cat's Cradle* (*2*). As they swim obliviously among the floes, ingesting countless ice particles, the fish are protected by specific proteins and glycoproteins that apparently bind to the surface of ice and prevent its growth.

In 1947, 16 years before *Cat's Cradle*, Bernard Vonnegut, the author's brother, invented the method of nucleating ice formation in clouds by seeding them with a smoke of silver iodide. Because ice nuclei of the critical size are so small, their creation has never been observed directly, and the mechanism by which foreign substances stimulate or inhibit this process remains speculative. Vonnegut had chosen to study silver iodide because the close geometric match between its crystal lattice and that of ice suggested an epitaxial process in which the silver iodide surface would organize water molecules into viable ice nuclei. This plausible rationalization on the basis of a structural match with ice enjoys continued popularity for explaining not only nucleation by the bacterial proteins but also growth inhibition of preexisting ice nuclei in the polar fishes. It is not easy to predict whether a particular substance with a structural match should accelerate freezing by organizing water molecules into viable nuclei or inhibit freezing by binding to critical growth sites on the surface of ice crystals.

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Hoary mystery. How water freezes has yet to be fully explained. [Weinberg-Clark/The Image Bank]

Over the last 2 years, by studying supercooled water droplets covered with a monolayer of long-chain alcohol molecules, Lahav, Leiserowitz, Popovitz-Biro, and their collaborators at the Weizmann Institute have bolstered the view that a structural match can cause ice nucleation (*3*). The 31-carbon alcohol makes water droplets freeze readily at temperatures as high as −0.5°C. Grazing incidence x-ray diffraction showed that its monolayer has a distorted hexagonal lattice providing a close geometric match to the (0001) face of ice.

The effect is sensitive not only to lattice spacing but also to the nature and orientation of the surface groups that must organize the water molecules. Although monolayers of long-chain alcohols with even numbers of carbons atoms have the same lattice structure as those of odd-chain alcohols, water beneath them must be cooled an additional 8°C to induce freezing. Apparently the orientation of OH groups attached to even-carbon chains at the monolayer-water interface is less effective at nucleating ice.

Now the Weizmann group reports studying nucleation by amino acid crystals that have no structural match at all with ice, and they attribute this nucleation to high electric fields within crystal cracks. Since 1861 there has been speculation about the influence of electric fields (*4*), and more recently powders of hydrophobic amino acids have been shown to facilitate freezing. The simple experiment reported in this issue unites these observations.

The experiment requires observing the freezing of water droplets on the hydrophobic surface of paired crystals of nine different amino acids. For each amino acid one of the paired crystals is chiral, containing natural amino acid molecules of uniform handedness. The other crystal is racemic, containing equal numbers of right- and left-handed molecules. Each crystal can be viewed as a series of monomolecular layers stacked in a particular sequential pattern. The two crystals of each amino acid are nearly identical in the structure of their monomolecular layers, but they differ in the stacking pattern.

In every case the paired crystals show a reproducible difference in the temperature at which they induce freezing. These differences range from 2.6° to 5.5°C. For some amino acids the chiral crystal is effective at the higher temperature; for others the racemic crystal is. But a consistent pattern does emerge—in every pair the nonpolar crystal, where successive molecular layers are arranged so that their electric dipolar fields cancel, is a less effective nucleator than the polar crystal, where the dipoles of successive layers reinforce.

Microscopic observation of ice crystals emerging from tiny cracks in the hydrophobic surface of the amino acid crystals, together with computer simulations of ice stabilization in submicroscopic cracks, suggests that ice can nucleate between oppositely charged walls of narrow cracks, whatever their detailed atomic arrangement.

Additional surprises can be anticipated in the search for a more comprehensive understanding of how water freezes and how the freezing process can be controlled. A particularly challenging problem is to determine how large an ordered domain is required to generate a viable nucleus. Further progress will certainly profit from high technology methods, but it is refreshing that careful visual observation of simple materials can still yield original insight.

REFERENCES

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