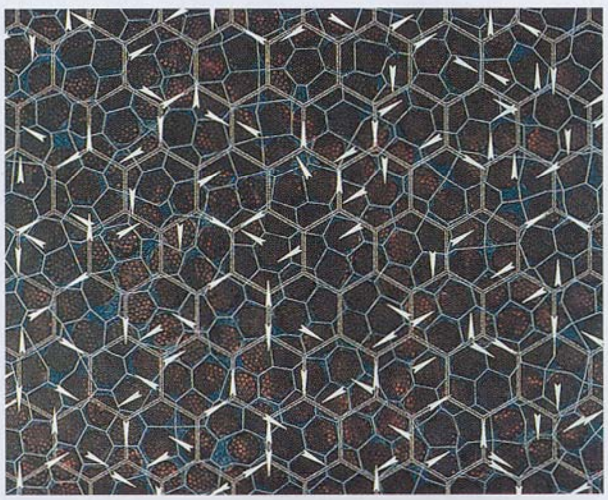
Cold Feat

A new kind of ice that contracts when it freezes

WHEN MY FRIEND'S FIVE-YEAR-OLD SON, DAVID, ACCIDENTally stored a can of Coca-Cola in the freezer, he soon discovered a virtually unique property of water. Unlike most liquids, water expands when it freezes. Now the computational physical chemists Kenichiro Koga and Xiao C. Zeng of the University of Nebraska-Lincoln and their colleague Hideki Tanaka of Kyoto University in Japan have described freezing conditions under which water *contracts* into a crystal structure that makes an entirely novel form of ice.

It must be emphasized that the discovery, reported recently in *Physical Review Letters,* has not been confirmed experimentally; it was made instead through a computer simulation of molecular dynamics. Such simulations are powerful tools that enable computational chemists to explore physical systems under conditions not readily accessible to existing experimental techniques. Molecular dynamics is an increasingly reliable predictor of reality, and any discovery suggesting a new form of water is fundamental to science.



Andrea Way, Jets, *1987*

In the computer model, the investigators were studying the properties of a film of liquid water confined between two parallel plates of water-repellent material that were spaced only a nanometer apart. According to Zeng, when the computer simulated the cooling of the water to around minus-forty degrees Celsius at a pressure of 493 atmospheres, Koga noticed a sudden change in the potential energy of the simulated molecules. (The pressure on the water kept it from freezing at the usual zero degrees Celsius.) To Koga, the change in potential energy immediately signaled the transition from liquid to solid. The confined layer of virtual water had frozen. "Our finding was totally unexpected," Zeng said.

A detailed analysis of the frozen molecular structure showed that it is like no other ice ever known before. Twelve other kinds of crystalline ice have been experimentally established, but they all have three-dimensional structures, in which the water molecules form tetrahedral frameworks. In contrast, the new virtual crystal is essentially two-dimensional: it is made up of a bilayer of water molecules, arranged so that their atoms define two parallel and almost flat lattices of distorted hexagons.

Investigating molecular dynamics with a computer is a rapidly growing discipline in which "simulation precedes and guides experimentation," Zeng notes. What makes it trustworthy in this case? In spite of its unusual characteristics, the simulated ice displays a feature common to all known crystal ice structures: every water molecule is attached by hydrogen bonds to four neighboring water molecules. That property, Zeng says, makes him and his colleagues confident that the simulated crystal can be synthesized in the laboratory.

Indeed, theoretical calculations predict that once formed, the crystal would be stable enough for one of the confining plates to be removed. If so, that would be good news to experimenters. The exposed surface could then be scanned with an atomic force microscope (AFM). The instrument measures the surface topography of a material by monitoring the force between the surface and a sharp probe suspended just above it. As the probe scans the surface, the instrument generates three-dimensional images with atomic resolution. An AFM image of the novel ice could confirm its predicted structure and—not incidentally—prove once and for all the power of computer simulations to explore chemical and biological systems.

Research groups at the University of California, Davis, and at Chiba University in Japan are trying to make the new ice in the laboratory. So far neither one has succeeded, but Zeng remains confident of success within a year or so. "When this work was started, we never imagined that water, as we know it, could contract and freeze in such a small hydrophobic slit," Zeng says. "But nature always finds a way."

—REGINA RAZ