

Scientists chip away at 'Nebraska' ice

Water is one of the most ubiquitous substances on earth. It covers three-fifths of the globe and is essential for life as we know it — but scientists are far from understanding all of its fundamental properties, particularly at the nanoscale level.

That's gradually changing, however, and another piece of the H₂O puzzle has fallen into place with the publication of a paper by two Japanese chemists, Kenichiro Koga of Fukuoka University of Education and Hideki Tanaka of Okayama University, and Xiao Cheng Zeng, associate professor of chemistry at the University of Nebraska-Lincoln, in the Nov.30 edition of *Nature*, the international weekly journal of science.

In the paper, Koga, Tanaka and Zeng describe how they have induced water to form glass instead of ice crystals when it is cooled to minus-10 degrees Celsius in a slit one nanometer (one-billionth of a meter) thick. The paper grew out of a discovery Zeng and Koga made three years ago when Koga was a postdoctoral fellow in Zeng's lab in UNL's Hamilton Hall doing basic research in nanoscience, a major research area at UNL and for the National Science Foundation.

Using a computer model, they made the startling discovery that water contracts rather than expands when it is frozen under extremes of pressure, temperature and confinement (493 atmospheres at minus-40 degrees Celsius between two water-repellent plates spaced one nanometer apart).

In the computer model, the water froze into ice crystals with the hexagonal structure of ice in which each water molecule has a hydrogen bond with its four nearest neighbors - but differed

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from normal ice in that its crystals were two- rather than three-dimensional.

"We were looking for new water glass, or ice glass, but we accidentally found this new crystal. My first reaction was that we had to have made mistakes in creating the computer model, that we would have to go back and double-check everything," Zeng said. "We ran many, many trials for about six months, but we found the water froze into crystals and shrank every time."

Zeng said he informally calls the ice "Nebraska" ice because the name Nebraska comes from the Otoe word for "flat water," and this two-dimensional ice is as flat as flat can be. The glass Koga and Zeng expected to find would have had a mixture of pentagon, hexagon and heptagon molecular structures. They didn't think it would be that hard to produce it, Zeng said, because it's usually easier to get glass than crystals in computer simulations.

But to produce the laboratory results reported in this week's *Nature*, it has taken another three years, with the collaboration of Tanaka, one of the world's leading experts on ice, and grant support by the Nebraska Research Initiative through UNL's Center for Materials Research and Analysis, the NSF and its Japanese equivalent, and the Office of Naval Research.

"Dr. Koga introduced some 'frustration,' a trick people like to use to make glass, to prevent the growth to true crystal," Zeng said. "The frustration he introduced was to hold the two water-repellent plates immobile during the freezing process. This time, he was successful.

"This glass is unique because it not only shows a new ice-glass structure, but it also shows a new piece of important physics. It has a strong first-order transition, meaning you have a large energy change from the liquid phase to the solid phase. When you make regular window glass, the energy change is pretty smooth as a function of temperature, so some people say it's not really a phase transition. But this is a genuine strong first-order transition, which is very, very rare."

Zeng said he doesn't foresee immediate applications for the discoveries, which is often the case with basic research, particularly in nanoscale research. He said the immediate reward is the joy of discovery.

"Being able to find a new ice structure is very exciting because of our curiosity as chemists," he said. "Water is such a fundamental substance that it deserves a lot of attention and we want to understand it from every aspect, from its nanoscale behavior, from its molecular properties, and all the way up."

— University of Nebraska-Lincoln