Scientists solve mystery of glassy water

January 31 2008

Water has some amazing properties. It is the only natural substance found in all three states — solid, liquid and gas — within the range of natural Earth temperatures. Its solid form is less dense than its liquid form, which is why ice floats. It can absorb a great deal of heat without getting hot, has very high surface tension (helping it move through roots and capillaries — vital to maintaining life on Earth) and is virtually incompressible.

A less commonly known distinction of water, but one of great interest to physical chemists, is its odd behavior at its transition to the glassy phase. The "glassy state" is a sub-state of matter — glassy water and ice, for example, are chemically identical and have the same state (solid), but have a different structure. Put another way, ice is crystalline, whereas glass is, well, chunky. As water makes the transition to its glassy state, it behaves very oddly, a fact that has baffled scientists.

Arizona State University Regents Professor C. Austen Angell has found a vital clue that helps explain water's bizarre behavior at the glass transition and, along the way, gained important insights into phases of liquid water as well. His research is published in the Feb. 1, 2008 issue of the journal *Science*.

"We know a lot about glasses that form from ordinary silicates, sugars and metals," Angell says. "They're making golf clubs out of glassy metals these days. But how important is the glassy state of water" And what can it tell us about ordinary water, which is such an anomalous liquid""

Most glassy forms of matter experience a gradual increase in heat capacity — the amount of energy it takes to heat a sample by one degree Kelvin — until a key transition point is reached. At that point (called the “glass temperature”), these materials suddenly up-jump to a new, 100 percent higher, heat capacity zone and change from a solid to very viscous liquid phase — as if a solid brick of cold honey were heated and suddenly became a sticky liquid again. This occurs even in solutions in which water is the chief component.

In pure water, however, something quite different happens. As cold, glassy water is heated, its heat capacity barely changes until about 136 K (-215 F), where it begins to increase slightly. Then, abruptly at 150 K (-190 F), it crystallizes and stops being glassy. Approached from the other direction, supercooling water produces a similarly odd effect: Heat capacity remains constant as the water cools until around 250 K (-10 F), when it begins to increase very rapidly with decreasing temperature.

Angell wanted to know what was transpiring in the “no man’s land” between 150 and 250 K (-190 and -10 F). Where, he wondered, was the “real” glass transition for glassy water"

He solved the problem by looking at the behavior of both supercooled water and “nanoconfined” glassy ice. Nanoconfined water is water that has been squeezed into pores with a diameter of about 20 angstroms, or 20 hundred-millionths of a meter (roughly five times the scale of atoms and chemical bonds). Using the behavior of water in these states and combining it with a hypothetical behavior of bulk water deduced using the laws of thermodynamics, he was able to bracket the possible heat capacity of water in the “no man’s land” and come up with a novel cooperative transition to explain the substance’s odd behavior.

“Water’s heat capacity suddenly goes crazy near this transition and, before we can see what is happening, it crystallizes,” Angell says. “One trick for finding out what is going on in there is to put the water in a confinement — to make it nanoscopic so that it forgets how to crystallize. We see the same behavior but with no data gap."

According to Angell, water does not behave like the usual glass formers and therefore lacks the characteristic heat-capacity jump (glass transition) to the glassy phase; instead, because of its unusual hydrogen bond network, it behaves as if it is in a crystalline phase, making what is known as an "order-disorder transition." This sucks out all of the heat capacity at temperatures around 220 K and explains why the glass transition in water (near 136 K) is so undramatic compared to other substances.

It also gave Angell an idea for a new scenario to explain the odd behavior of supercooled water, one that is compatible with observed behavior but does not require a critical point.

"I wanted to find the answer to the puzzle of what was happening in 'no man's land,'" Angell says. "And so I worked up from the glassy state and nanoconfinement."

"In the end, we say, 'Well that that's not what bulk water would do — that's been thrust upon it by making it so tiny,'" he explains. "But nevertheless it's an important part of the picture and it supports the conclusion that we've got a different sort of thermodynamics in water than we have in any of these other molecular glass-forming liquids."

Source: Arizona State University

Citation: Scientists solve mystery of glassy water (2008, January 31) retrieved 20 April 2024 from https://phys.org/news/2008-01-scientists-mystery-glassy.html