Computing liquid water as a transient gel

Water, the most common liquid on Earth, is also among the least typical and most puzzling of liquids. Many of its key properties, such as the way its density depends on temperature, differ sharply from those of other liquids. These peculiarities become even more pronounced when water is carefully cooled to temperatures below its normal freezing point.

Scientists still don't know exactly how the motion of water molecules and the formation of hydrogen bonds — each bond representing the attractive force between a hydrogen atom in one water molecule and the oxygen atom of another — add up to such anomalous liquid behavior. But a team of researchers, using computer simulations of water molecules in motion, has now found a remarkable pattern of hydrogen-bond formation and dissolution that may eventually lead to an explanation for water's many strange characteristics.

"Our long-term goal is to elucidate the dynamics of water," says H. Eugene Stanley of Boston University. "This [study] is an important first step because it focuses on the bond network itself." Stanley, Francesco Sciortino, Peter H. Poole and Shlomo Havlin report their findings in the April 2 PHYSICAL REVIEW LETTERS.

The researchers picture liquid water as a transient gel consisting of a random network of hydrogen bonds linking water molecules over large distances. Because the hydrogen bonds break and reform on a picosecond time scale, the network restructures itself rapidly. But at any given time, enough bonds remain intact to keep it from falling apart.

To find out how the hydrogen-bond network in water evolves, the team computed the motion of 216 water molecules in a cubic box at five different temperatures, keeping track of how long individual hydrogen bonds last. And to get a better grip on the effects of molecular movements on the hydrogen-bond network, they adopted an unconventional definition of what constitutes a hydrogen bond.

"We take into account all the bonds," Sciortino says. "If there is a little bit of an interaction, this is already a bond for us." Normally, scientists count as hydrogen bonds only those representing an attractive force higher than a certain cutoff value.

An analysis of the simulation results shows that for this particular model, the distribution of bond lifetimes fits a mathematical relationship known as a power law. That startling finding suggests that hydrogen bonds in water don't have a characteristic lifetime; instead, some last a short time and others a very long time.

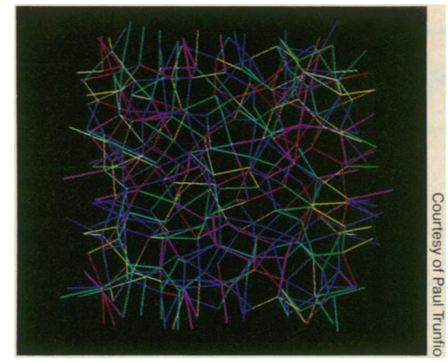
This seems to contradict what many researchers have long believed. If the energy required to make or break a hydrogen bond has a particular value, there should be a characteristic time for a bond to break, they say.

The group also found that the average bond lifetimes increase rapidly as the temperature declines, especially at temperatures below the normal freezing point. Other researchers have seen similar power-law behavior in experimental studies of temperature-dependent properties such as the rate of diffusion in water.

Trends in both the experimental results and the computer simulations suggest that liquid water may undergo some kind of transformation, perhaps to a glassy state, at roughly -46°C. However, no one has yet succeeded in cooling liquid water to such a low temperature without ending up with solid ice.

"Our . . . results may provide a microscopic interpretation for the experimental evidence that suggests a region of power-law behavior in the dynamic properties of liquid water," the Boston scientists conclude. Computations based on alternative molecular models of liquid water produce similar results.

— *I. Peterson*



Courtesy of Paul Trunfio

In this frame from a computer simulation showing the hydrogen bonds between 216 water molecules, colors correspond to how long the bonds last. Blue bonds have the shortest lives, white bonds the longest.

Plastic coating traps indoor air pollutants

A Canadian chemist has developed a plastic coating to filter several toxic pollutants, including formaldehyde and acidic gases, from indoor air. Air filters coated with the plastic might one day help furnaces, box fans and air conditioners remove some of the indoor air contaminants responsible for so-called sick-building syndrome (SN: 9/23/89, p.206), suggests Hyman D. Gesser of the University of Manitoba in Winnipeg. In preliminary tests, the newly patented coating absorbed susceptible pollutants for at least one month — the recommended life of most furnace filters.

Polyethyleneimine (PEI) is a water-soluble plastic used in applications ranging from adhesion and disinfection to carbon dioxide absorption. It comprises three types of amines — subunits derived from ammonia. These primary, secondary and tertiary amines are distinguished by whether one, two or all three of the hydrogens in ammonia have been replaced by a carbon-based molecular fragment.

Because amines bind aldehydes, Gesser reasoned that PEI might trap formaldehyde. Indeed, his first tests confirmed that PEI's primary and secondary amines would absorb the pollutant from air recirculating through a filter coated with the plastic. However, as soon as all molecules on the coating's surface reacted with formaldehyde — within 10 days or so — its pollutant-trapping activity ceased.

The problem, Gesser discovered, was that the originally gooey PEI coating quickly dried and hardened, anchoring its molecules fairly firmly. So he added glycerol to soften the plastic. This allowed PEI molecules to remain mobile so that those on the surface could trade places with others underneath, effectively replenishing the surface until nearly every molecule had reacted. In the April ENVIRONMENTAL SCIENCE AND TECHNOLOGY, he and Shali Fu report filtering out roughly 96 percent of the formaldehyde in air (at concentrations of 2, 5 and 10 parts per million) by drawing the air through a PEI/glycerol-coated filter at 500 milliliters per minute.

Since PEI is alkaline, Gesser also tested the coating against three acidic gases: sulfur dioxide, nitrogen dioxide and hydrogen sulfide. Again, it chemically neutralized 98 percent of them. Here, however, the tertiary amines proved not only active but also the most potent agents. Some of the acid also dissolved into the glycerol, becoming trapped there.

"An abatement technology like this is useful," comments George Semeniuk, who works in EPA's indoor chemical control division in Washington, D.C. However, he notes, materials that give off indoor gases will sometimes increase their emission rates to compensate, at least temporarily, for a lowering in their air concentrations. That's one reason why EPA's program to reduce indoor formaldehyde focuses on limiting emissions from their sources, such as pressed wood, Semeniuk says.

For a "few dollars" in material costs, Gesser says, "it looks like we can now develop a [filter] coating to work for up to six months." He is about to begin testing prototypes in homes insulated with urea-formaldehyde foam or containing new particle board and other building materials that initially emit high levels of formaldehyde.

— *J. Raloff*