The strangest liquid: Why water is so weird

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Quite an oddity (Image: Shinichi Maruyama

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We are confronted by many mysteries, from the nature of dark matter and the origin of the universe to the quest for a theory of everything. These are all puzzles on the grand scale, but you can observe another enduring mystery of the physical world - equally perplexing, if not quite so grand - from the comfort of your kitchen. Simply fill a tall glass with chilled water, throw in an ice cube and leave it to stand.

The fact that the ice cube floats is the first oddity. And the mystery deepens if you take a thermometer and measure the temperature of the water at various depths. At the top, near the ice cube, you'll find it to be around 0 °C, but at the bottom it should be about 4 °C. That's because water is denser at 4°C than it is at any other temperature - another strange trait that sets it apart from other liquids.

Water's odd properties don't stop there (see "Water's mysteries"), and some are vital to life. Because ice is less dense than water, and water is less dense at its freezing point than when it is slightly warmer, it freezes from the top down rather than the bottom up. So even during the ice ages, life continued to thrive on lake floors and in the deep ocean. Water also has an extraordinary capacity to mop up heat, and this helps smooth out climatic changes that could otherwise devastate ecosystems.

Yet despite water's overwhelming importance to life, no single theory had been able to satisfactorily explain its mysterious properties - until now. If we can believe physicists Anders Nilsson at Stanford University, California, and Lars Pettersson of Stockholm University, Sweden, and their colleagues, we could at last be getting to the bottom of many of these anomalies.

Their controversial ideas expand on a theory proposed more than a century ago by Wilhelm Roentgen, the discoverer of X-rays, who claimed that the molecules in liquid water pack together not in just one way, as today's textbooks would have it, but in two fundamentally different ways.

Key to the understanding of water's mysteries is the way its molecules - made up of two hydrogen atoms and one oxygen atom - interact with one another. The oxygen atom has a slight negative charge while the hydrogen atoms share a compensating positive charge. As such, the hydrogen and oxygen atoms of neighbouring molecules are attracted to one another, forming a link called a hydrogen bond.

Hydrogen bonds are far weaker than the bonds that link the atoms within molecules together, and so are continually breaking and reforming, but they are at their strongest when molecules are arranged so that each hydrogen bond lines up with a molecular bond (see diagram). The shape of a water molecule is such that each H_2O molecule is surrounded by four neighbours arranged in the shape of a triangular pyramid - better known as a tetrahedron.

At least, that's the way the molecules arrange themselves in ice. According to the conventional view, liquid water has a similar, albeit less rigid, structure, in which extra molecules can pack into some of the open gaps in the tetrahedral arrangement. That explains why liquid water is denser than ice - and it seems to fit the results of various experiments in which beams of X-rays, infrared light and neutrons are bounced off samples of water.

True, some physicists had claimed that water placed under certain extreme conditions may separate into two different structures (see "Extreme water"), but most had assumed it resumes a single structure under normal conditions.

Then, 10 years ago, a chance discovery by Pettersson and Nilsson called this picture into question. They were using X-ray absorption spectroscopy to investigate the amino acid glycine. The peaks in the X-ray absorption spectrum can shed light on the precise nature of the target substance's chemical bonds, and hence on its structure. Importantly, the researchers had got hold of a new, high-power X-ray source with which they were able to make more sensitive and accurate measurements than had ever been possible. They soon realised that the water containing their glycine sample was producing a far more interesting spectrum than the amino acid. "What we saw there was sensational," Nilsson recalls, "so we had to get to the bottom of it."

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Dramatic implications

The feature that sparked their interest was a peak in the absorption spectrum that is not predicted by the traditional model of liquid water. In fact, in a paper published in 2004 they concluded that at any given moment 85 per cent of the hydrogen bonds in water must be weakened or broken, far more than the 10 per cent predicted by the textbook model (*Science*, vol 304, p 995).

The implications of this finding are dramatic: it suggests that a total rethink of the structure of water is needed. So Nilsson and Pettersson turned to other X-ray experiments to confirm their claims. Their first move was to enlist the help of Shik Shin of the University of Tokyo, Japan, who specialises in a technique called X-ray emission spectroscopy. The key thing about these spectra is that the shorter the wavelength of the X-rays in a substance's emission spectrum are, the looser the hydrogen bonding must be.

The team struck gold: the spectrum of emitted X-rays included two peaks that might correspond to two separate structures. The spike of the longer-wavelength X-rays, the researchers argued, indicates the proportion of tetrahedrally arranged molecules, while the shorter-wavelength peak reflects the proportion of disordered molecules.

Importantly, the shorter-wavelength peak in the X-ray emissions was the more intense of the two, suggesting that the loosely bound molecules must be more prevalent within the sample - an assertion that fitted the team's previous models. What's more, they also found that this peak shifts to an even shorter wavelength as the water is heated, while the other peak remains more or less fixed (*Chemical Physics Letters*, vol 460, p 387).

That suggests that the hydrogen bonds connecting molecules arranged in a disordered way are more likely to loosen upon heating than those linking the more regularly arranged molecules - which again is what the team had predicted. They then reanalysed older experimental data that had seemed to support the traditional picture of water - and now argue that these results, too, are consistent with the new model.

If the team is right, another question arises: how large are the different structures within the liquid? To find out, they turned to the high-power X-rays generated at the Stanford Synchrotron Radiation Lightsource in California, this time measuring how water scatters rays arriving from various angles. The results, they say, reveal that water is dotted with small regions of tetrahedrally arranged molecules, each region being 1 to 2 nanometres across (*Proceedings of the National Academy of Sciences*, vol 106, p 15214).

Combined with further measurements carried out by Uwe Bergmann at Stanford University, they concluded that the ordered structures consisted of roughly 50 to 100 molecules, on average, surrounded by a sea of the more loosely bound molecules. These regions are not fixed, however. In less than a trillionth of a second, water molecules are thought to fluctuate between the two states as the hydrogen bonds break and reform.

Explaining the inexplicable

The changing balance between Nilsson and Pettersson's two types of water provides an explanation for the way water's density peaks at 4 °C. In the disordered regions, water molecules are more closely packed, making them denser than regions where the molecules are arranged in a tetrahedral structure. At 0 °C these disordered regions should be relatively uncommon, but as the water is warmed the extra heat energy tends to shake the more ordered structure apart, so molecules spend less time in the tetrahedral structure and more time in the disordered regions, making it more dense on average.

Counterbalancing this, the loosely bound molecules will move around more vigorously as the temperature rises, gradually forcing them further apart from each other. Once enough of the molecules become loosely bound - at 4 °C - this expansion effect will dominate, and the density will fall with increasing temperatures.

According to Pettersson, the theory offers equally tidy explanations for many of water's other previously inexplicable anomalies - something they say that no other theory can yet achieve (see "Water's mysteries"). Martin Chaplin, a chemist at London South Bank University, agrees. Explanations based on the conventional one-component system have to "go round the houses" to try to accommodate the maxima and minima in various properties as the temperature of water changes, he says. "The dual-structure idea is strongly supported by experiment and can explain water's anomalies far more readily than the conventional picture," Chaplin says.

Nilsson and Pettersson's 2004 paper in *Science* has now been cited over 350 times by other researchers. Yet many remain sceptical. One criticism is that the team's explanation of their X-ray spectroscopy results is based on simulations of at least 50 interacting water molecules - an immensely complex model that can only be resolved approximately. "We need a much more accurate theory in order to make such drastic claims," says Richard Saykally at the University of California, Berkeley. He claims that minor adjustments to the arrangement of the hydrogen bonds in the conventional structure are enough to explain Nilsson and Pettersson's X-ray results. One member of their group, Michael Odelius of Stockholm University, even left the collaboration because he disagreed with their interpretation of the X-ray emission data.

One detail that alienated many sceptics was an assertion in the 2004 paper that the more loosely bound molecules form rings and chains - and indeed Nilsson and his colleagues are now less specific about the structure of the disordered molecules. Eugene Stanley of Boston University, however, does not believe that this fatally damages the team's case. "I don't think they should be condemned forever," he says. Though their argument is not yet watertight, the X-ray scattering results provide "one more piece of supporting evidence", he says.

There is no doubt that Nilsson and Pettersson still face stiff opposition, but the rewards of a comprehensive understanding of the structure of liquid water could be considerable. It could lead to a better understanding of how drugs and proteins interact with water molecules within the body, for example, and so provide more effective medicines. And by giving us a better idea of how water behaves around narrow pores, it might improve water desalination attempts and so increase access to clean water.

"Our understanding of water is an evolving picture," Pettersson says. "Further research by many different groups is needed before this exciting and important journey can end." With so much to gain, who could disagree?

Extreme water

The dual structure of water proposed by Anders Nilsson of Stanford University, California, and Lars Pettersson of Stockholm University in Sweden may be a ghostly echo of the strange properties of "supercool" water - water that has been cooled to below 0 °C without freezing.

Eugene Stanley of Boston University and his colleagues have long claimed that at temperatures below about -50 °C and pressures of more than 1000 times atmospheric pressure, distinct high and low-density forms of supercool water should exist. Several research groups claim they have found evidence for these two structures.

Stanley, however, believes there should be small but discernible traces of this behaviour at higher temperatures too - seen as fluctuations in water's density. Sure enough, the size of the fleeting high and low-density regions seen in Nilsson and Pettersson's X-ray scattering experiments are consistent with his theory's predictions.

However, physicist Alan Soper at the Rutherford Appleton Laboratory in Oxfordshire in the

UK is not convinced that these density differences are anything other than the density fluctuations that can occur in any liquid.

The crux of this dispute concerns the precise statistical distribution of regions of different density. According to Nilsson and Pettersson's model, there should be two peaks at two distinctly different densities, but Soper believes only one continuous distribution is possible.

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