The strangest liquid: Why water is so weird

03 February 2010 by **Edwin Cartlidge**
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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.

Quite an oddity (Image: Shinichi Maruyama

1 more image

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.

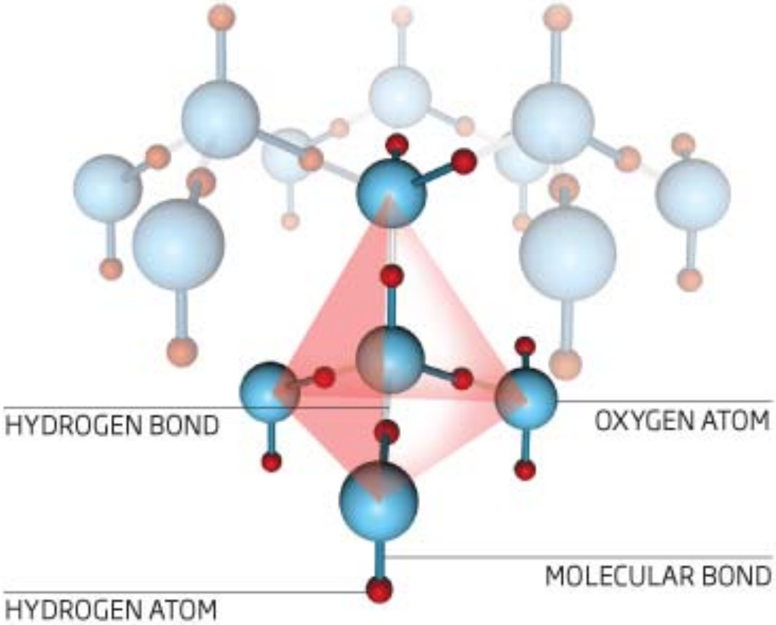
True, some physicists had claimed that water placed under certain extreme conditions may separate into two different structures (see "Extreme water"), but most had assumed it resumes a single structure under normal conditions.

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."

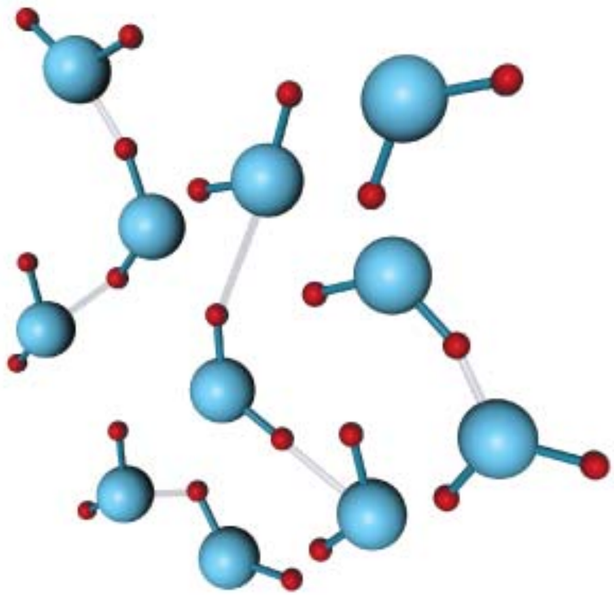
The two faces of water

Each water molecule has the potential to form hydrogen bonds with four neighbouring molecules: one via each of its hydrogen atoms plus two via its oxygen atom. Fluctuations between the two resulting structures could explain water's unique properties

With all four hydrogen bonds in place, the result is a regular **tetrahedral structure**



Water molecules are more densely packed when they are in a more random, **disordered structure**



> What we saw in the water was sensational, so we had to get to the bottom of it

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.

Edwin Cartlidge is a journalist based in Rome, Italy. To enjoy more stunning images of water in motion by Shinichi Maruyama, visit his website: www.shinichimaruyama.com

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The many mysteries of water

18:00 03 February 2010 by **David Robson** and **Michael Marshall**

No liquid behaves quite as oddly as water. It exhibits a raft of unusual behaviours, many of which are essential for life as we know it. We list water's peculiarities below.

In *The strangest liquid*, we look at how a controversial new theory could finally explain water's weird behaviour. Here we explain how the theory could explain 10 of water's behaviours – and then take a quick look at its many other peculiarities.

Read more: Martin Chaplin of London South Bank University has posted a much more detailed and technical discussion of these anomalies.

Water's mysteries

Picturing water as a liquid that can form two types of structure, one tetrahedral and the other disordered, could explain many of its unusual properties. Here are 10 of them.

Water is most dense at 4 °C

EXPLANATION: Heating reduces the number of ordered, tetrahedral structures in favour of a more disordered arrangement in which molecules are more densely packed. However, the heat also agitates the molecules in the disordered regions, causing them to move further apart. Above 4 °C, this effect takes precedence, making the water less dense

Water has an exceptionally high specific heat capacity: it takes a lot of heat energy to raise water's temperature by a given amount

EXPLANATION: Much of the extra heat energy is used to convert more molecules from the tetrahedral structures to the disordered structures, rather than into increasing the kinetic energy of the molecules, and hence the temperature.

Specific heat capacity is at a minimum at 35 °C but increases as the temperature falls or rises, whereas the heat capacity of most other liquids rises continuously with temperature.

EXPLANATION: Between 0 and 35 °C, increasing the temperature steadily removes regions of ordered, tetrahedral structure, reducing water's ability to absorb heat. Above 35 °C, so few of the tetrahedral regions are left that water behaves like a regular liquid.

Water's compressibility drops with increasing temperature until it reaches a minimum at 46 °C, whereas in most liquids, the compressibility rises continuously with temperature

EXPLANATION: As the temperature rises, the dense, disordered regions become more prevalent, and these are more difficult to compress. However, rising temperature also forces molecules within these regions further apart and hence makes them more compressible. This effect takes precedence beyond 46 °C.

Water is particularly difficult to compress

EXPLANATION: The strong attraction between water molecules keeps them more closely packed than the molecules of many other liquids.

This effect is particularly marked when the higher-density disordered structure dominates

The speed of sound in water increases with temperature up to 74 °C, after which it starts to fall again

EXPLANATION: This is the result of the interplay between water's unusual density and compressibility profiles, which directly stem from the changing balance between the two types of structure.

Water molecules diffuse more easily, not less easily, at higher pressures

EXPLANATION: High pressure converts more molecules to the disordered structure, in which they are more mobile.

Unlike many liquids, water becomes less viscous, not more viscous, at higher pressures

EXPLANATION: Molecules are freer to move when in the disordered structures, which are favoured at higher pressures, than when they are in the ordered, tetrahedral structure.

Increasing the pressure increases the amount by which water expands on heating

EXPLANATION: Rising temperature causes disordered regions to expand more rapidly than ordered, tetrahedral ones, and high pressure favours fluctuations to the disordered regions.

Properties such as viscosity, boiling point and melting point are significantly different in "heavy" water - made from the heavier hydrogen isotopes deuterium and tritium - compared with their equivalents in normal water.

EXPLANATION: The heavier isotopes change the quantum mechanical properties of water molecules, altering the balance of the disordered and tetrahedral regions.

Phase anomalies

Water has an unusually high melting/freezing point.

Water has an unusually high boiling point.

Water has an unusually high critical point. This is the temperature at which the distinct liquid and gas states cease to exist. Instead, there is only a supercritical fluid, which can diffuse through solids just like a gas but also dissolve things just like a liquid. Water's critical point is at a temperature of 374 °C and a pressure of 217 atmospheres: above this temperature, it is a supercritical fluid.

Solid water exists in a wider variety of stable (and metastable) crystal and amorphous structures than other materials.

The thermal conductivity of ice falls with increasing pressure.

The structure of liquid water changes at high pressure.

Supercooled water – that is, water that has been cooled below its freezing point without it becoming a solid – behaves strangely. It has two phases and a second critical point at about -91°C.

Liquid water is easy to supercool, but difficult to turn into a glass-like solid.

Liquid water exists at very low temperatures and freezes on heating.

Liquid water may be easily superheated: that is, heated to a temperature above its boiling point without it boiling.

Hot water may freeze faster than cold water – the Mpemba effect.

Warm water vibrates longer than cold water.

Density anomalies

The density of ice increases on heating (up to a temperature of -203 °C). Normally, solids expand and become less dense when heated.

Water shrinks on melting, when most substances expand.

Pressure reduces ice's melting point, when it normally increases it: pressure normally encourages a substance to become a solid.

Liquid water has a high density that increases on heating (up to 3.984 °C). Heating a liquid normally causes it to expand, reducing its density.

The surface of water is denser than the bulk. This may be because the density of the surface water does not vary with temperature as the density of the bulk does.

Pressure reduces the temperature of maximum density.

There is a minimum in the density of supercooled water.

Water has a low thermal expansivity: for a given increase in temperature, it does not expand as much as it might be expected to.

Water's thermal expansivity decreases at low temperatures. Below 4 °C, it becomes negative – so if you heat water that is below this temperature, it will shrink.

The number of nearest neighbours that each water molecule has increases on melting. Normally, because the molecules of a liquid are moving around so much more, any one molecule is likely to have fewer nearest neighbours than if it were part of a solid.

The number of nearest neighbours increases with temperature. This happens because the increasing temperatures break down the hydrogen bond network holding the molecules in place, allowing them to move closer to each other.

There is a maximum in the compressibility-temperature relationship, probably near the temperature at which the density is lowest.

The speed of sound may show a minimum.

High-frequency sounds travel as "fast sound", because for these frequencies water behaves as if it is a glassy solid rather than a liquid. Water also shows a discontinuity at higher pressure, probably as a result of the water molecules rearranging themselves.

Nuclear magnetic resonance (NMR) spin-lattice relaxation time is very small at low temperatures. In other words, if the nuclei of the atoms making up water are excited to a higher energy level – for instance by a magnetic field – they return to their previous, lower energy level unusually fast.

The NMR shift increases to a maximum at low (supercool) temperatures.

The refractive index of water – that is, how much light is slowed down, and thus deflected, when it enters water – has a maximum value at just below 0 °C.

The change in volume as liquid water changes to gas is unusually large.

Material anomalies

No aqueous solution is ideal. In other words, there is no substance that can be dissolved in water without any heat being absorbed or released. This is because dissolving a substance in water always involves disrupting the clustering of the water molecules.

The mean kinetic energy of water's hydrogen atoms increases at low temperature.

When different substances are dissolved in water, they have varying effects on properties such as density and viscosity.

The solubilities of non-polar gases in water decrease with temperature to a minimum and then rise.

The dielectric constant of water is high.

The dielectric constant shows a temperature maximum.

Proton and hydroxide ion mobilities are anomalously fast in an electric field. This may be because the protons can use quantum tunnelling to travel rapidly between neighbouring water molecules.

The electrical conductivity of water rises to a maximum at about 230 °C.

For weak acids in water, the acidity constants (a measure of the strength of the acid when dissolved) show temperature minima.

X-ray diffraction shows an unusually detailed structure.

Under high pressure, water molecules move further away from each other with increasing pressure.

Thermodynamic anomalies

Water's heat of fusion – the amount of heat energy that 1 mole of it must absorb to melt – is at a maximum at -17 °C.

Liquid water has over twice the specific heat capacity of ice or steam. In other words, it takes almost twice as much energy to increase its temperature by the same amount.

The specific heat capacity also has a maximum, at about -45 °C.

The specific heat capacity has a minimum with respect to pressure.

The heat capacity also has a maximum.

Water's heat of vaporization – the energy required to transform it from a liquid into a gas – is unusually high.

Its heat of sublimation, the energy needed to change it from a solid directly into a gas – without becoming a liquid in between – is also unusually high.

Water's entropy of vaporization – the increase in disorder caused by changing it from a liquid to a gas – is high.

The thermal conductivity of water is high and rises to a maximum at about 130 °C. In other words, energy is transferred unusually fast from regions of hot water to regions of cooler water, and this rate of transfer reaches a maximum at around 130 °C.

Physical anomalies

Water is surprisingly viscous: although it is "thin", it is surprisingly resistant to force.

Water's viscosity decreases with pressure at temperatures below 33 °C.

At low temperatures, the self-diffusion of water increases as the density and pressure increase.

The thermal diffusivity, water's ability to adjust its temperature to that of the surroundings, rises with pressure until it reaches a maximum at a pressure of about 7900 atmospheres.

Water has unusually high surface tension.

Some salts exhibit the Jones-Ray effect when dissolved in water: when the salt is at a very low concentration, the surface tension of the water reaches a minimum.

Some salts stop small bubbles from coalescing.

Read more: A much more detailed and technical discussion of these anomalies has been posted by Martin Chaplin of London South Bank University.

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