Philip Ball

H_2O

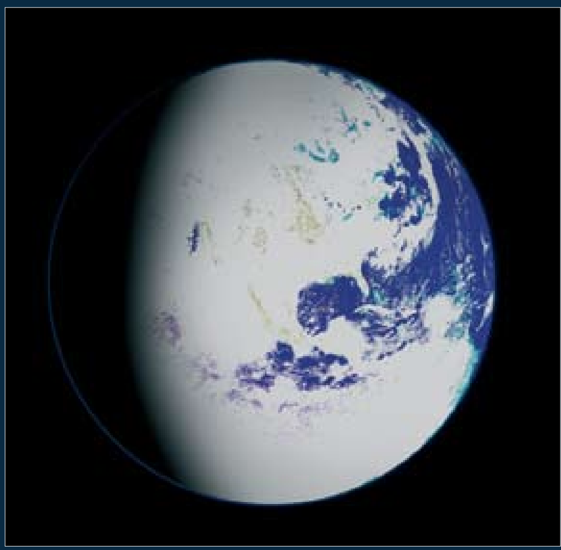
Key words
hydrogen bond
phase
heat capacity
pathological science

Hot ice and the mysteries of water

Water, ice, steam – they are all H_2O. Water is everywhere, so you might think that scientists would understand everything about this apparently simple substance. But water is complicated, even mysterious, as Philip Ball explains.

In Kurt Vonnegut's 1963 novel Cat's Cradle, the world is devastated by an environmental catastrophe as all the oceans turn to ice: 'The moist green world was a blue-white pearl.'

Some scientists suspect a similar thing really happened around 700 million years ago, when the Earth's climate cooled down and the ice sheets grew past some critical 'tipping point'. Because bright ice reflects the Sun's rays back into space whereas the dark seas absorb them, more ice cover means less heat received from the Sun, and there could be a positive feedback process that leads the ice to just keep growing until it covers virtually the whole globe: a scenario called the Snowball Earth.



A computer-generated image of the Snowball Earth scenario. Hundreds of millions of years ago, most of the Earth's surface may have been covered in a thick layer of ice. Most living species died out but those which survived exploded into evolutionary diversity.

But Vonnegut's icy Earth was worse than that. In his book, the oceans are not covered in ice but frozen solid from top to bottom. And it's no ordinary ice like the stuff in summer drinks or glaciers and ice caps. It was a fictional type called ice-nine, discovered by a scientist named Felix Hoenikker, which freezes at 114.4°C – well above water's usual boiling point of 100°C.

So ice-nine stays resolutely frozen at the ordinary temperatures on the Earth's surface. And Vonnegut explains that if a speck of ice-nine comes into contact with ordinary water, it will act as a seed that rearranges the water molecules into the pattern of ice-nine, so that the seed will grow and grow, just like a crystal of ice spreading through a puddle on a cold winter night. All water that touches ice-nine becomes ice-nine itself. And that's inevitably what happens, as a shard of Hoenikker's ice-nine eventually falls into the sea.

Fourteen phases

But of course, there's no such thing as ice-nine, right? Wrong. There are, at the latest count, something like 14 different forms of ice, and one of them is ice-nine, or ice-IX. Ah, but it's not the stuff that Vonnegut imagined – it melts at around minus 100°C, and exists only if ordinary ice is squeezed to several thousand times atmospheric pressure. Yet ice that stays frozen up to 100°C and beyond does exist. It is not ice-nine but ice-seven (ice-VII), and it is very hard and dense.

The catch is that ice-VII, like all the forms of ice other than the familiar ice-I we know from snowflakes and freezers, can exist only at high pressures. All the same, this proliferation of ices is very unusual. Most substances have only one or a few solid forms (called phases), which may be interconverted by changes of temperature or pressure. Generally speaking, squeezing favours the formation of denser solid phases, where the atoms or molecules are packed together more compactly.

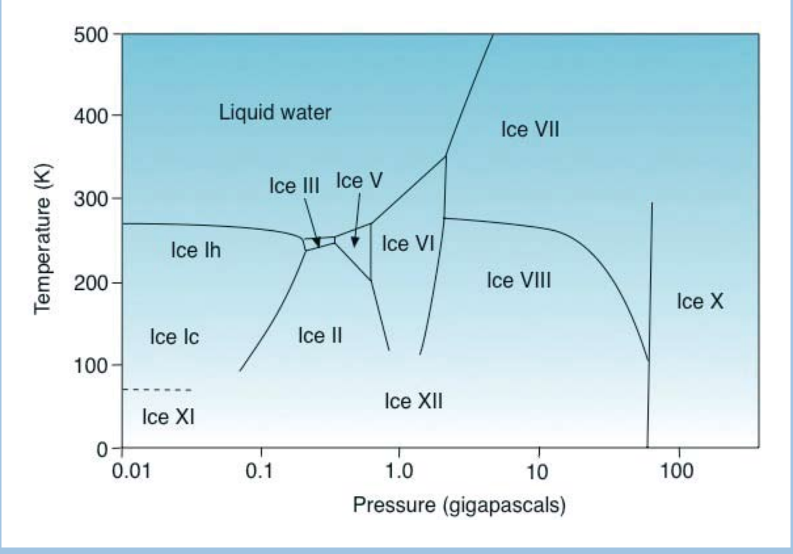
Water oddities

The fact that ice has so many phases is just one of the peculiarities of water itself. It's odd that ice is less dense than water: most liquids get denser when they freeze. Water is actually densest at 4°C, whereas most liquids just get steadily denser as they cool. And there may in fact be two kinds of liquid water, although they exist only well below water's normal freezing point.

All these so-called anomalies stem from the same cause. Water molecules have the chemical formula H_2O, containing two hydrogen atoms linked to one oxygen atom in a bent shape (Figure 1a). And the hydrogen atoms on one molecule can form weak intermolecular chemical bonds, called hydrogen bonds, to the oxygen atoms of another. This means that water molecules may become bound together by temporary 'handclasps' that are continually breaking and reforming, as hydrogen bonds form and then break because of the jiggling influence of heat.

Box 1 The many phases of water

When Kurt Vonnegut wrote about his fictional ice-nine, it was already known that ice has several phases, as shown in the diagram. The first new form of ice was discovered in 1900, and several were found subsequently by the American scientist Percy Bridgman at Harvard University, a pioneer in experiments at high pressure. No doubt this was why Vonnegut chose to call it ice-nine, for he was trained as an engineer and probably knew that ice-II, ice-III and so on had already been discovered.



The phase diagram of some of the known forms of ice, showing where they are stable at different temperatures and pressures. 1 gigapascal is 10 000 times atmospheric pressure.

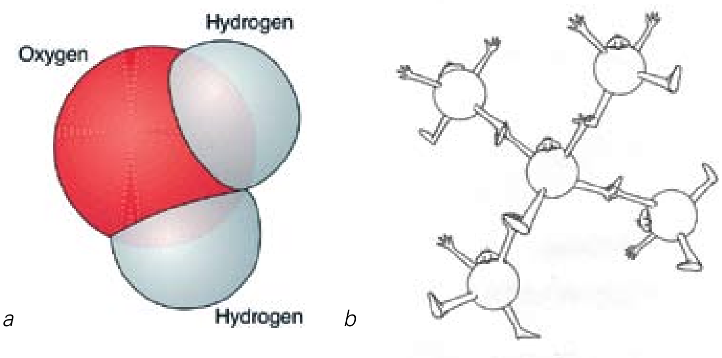


Figure 1 *a The structure of the H_2O molecule.*
b Each water molecule can form four hydrogen bonds to its neighbours, like hands grasping neighbours' feet in a perpetual dance.

Each water molecule can form four hydrogen bonds: two via its hydrogen atoms, and two in which hydrogen from other molecules fasten onto the central oxygen atom. In effect, you could say that water has two hands to grasp other waters, and two feet that others can grasp (Figure 1b). The hydrogen bonds link water molecules into a gigantic network whose links are forever breaking up and rearranging. In liquid water this network is disorderly (Figure 2a), but in ice it has a more rigid shape in which H_2O molecules are joined in hexagons (Figure 2b). This underlying hexagonal symmetry of ice explains why snowflakes are sixpointed (Figure 3). And it is because the hexagonal rings encircle a lot of empty space that ice is less dense than water.

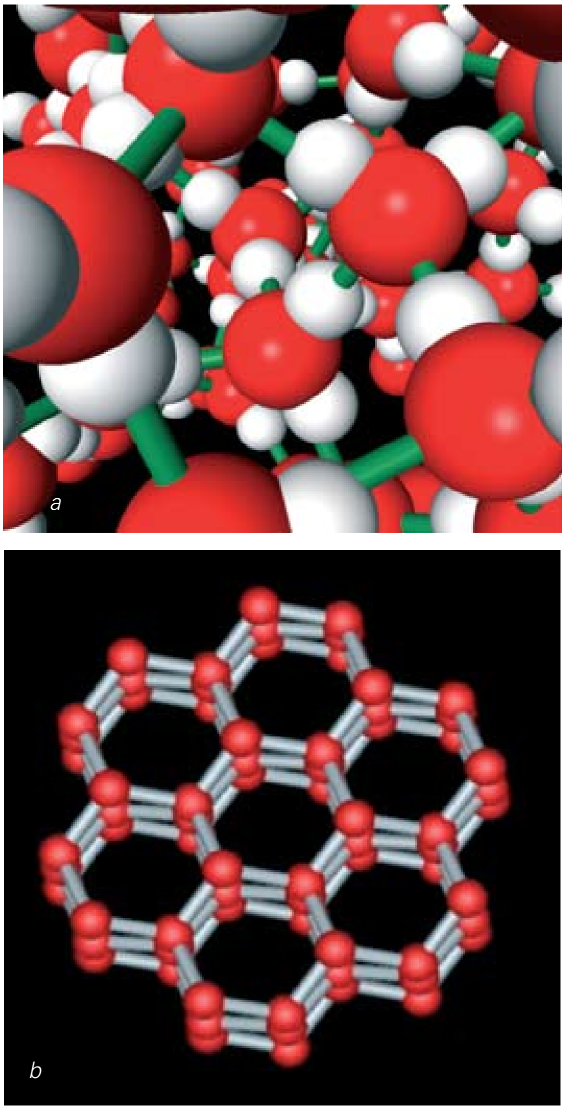


Figure 2 *a The disorderly hydrogen-bond network of liquid water. b In ice, hydrogen bonds link the molecules into orderly hexagonal rings.*

Figure 3 *The hexagonal symmetry of a snowflake*

As the Snowball Earth theory demonstrates, the behaviour of water has profound implications for the entire planet. It is only because of the unusual fact that solid water floats on liquid water, for example, that we have an Arctic ice cap (although maybe, if the planet continues to warm as fast as it is, not for much longer). Because a coating of ice on a lake insulates the water below, this helps prevent shallow lakes from freezing solid in winter and so ensures the survival of living things within them. And because water has an unusually large **heat capacity** – it takes a lot of energy to raise its temperature by a degree – warm ocean currents can redistribute vast amounts of energy around the globe, helping for example to keep the climate of northern Europe temperate. (For the same reason, however, kettles take a long time to boil.)

The delicate interplay between the molecular structure and the properties of water is perhaps most important of all in biology. Once scientists used to think of living cells as bags of biomolecules such as proteins and DNA that interact with each other in exquisite ways while simply being suspended in a liquid solvent of water. Now they have come to realise that these biomolecules actually fine-tune the water around them, using hydrogen bonds as handles to rearrange the molecules into new configurations that help the biomolecules themselves to come into contact and feel each other's presence. Proteins and nucleic acids seem to rebuild their own watery environment, you might say. Some line water molecules up in chains that can act as 'wires' for transporting hydrogen ions in catalytic processes (Figure 4). Others use water molecules as snap-on tools to help capture and transform their target molecules. It's the ability of water to shape and respond to molecules within it that makes life possible.

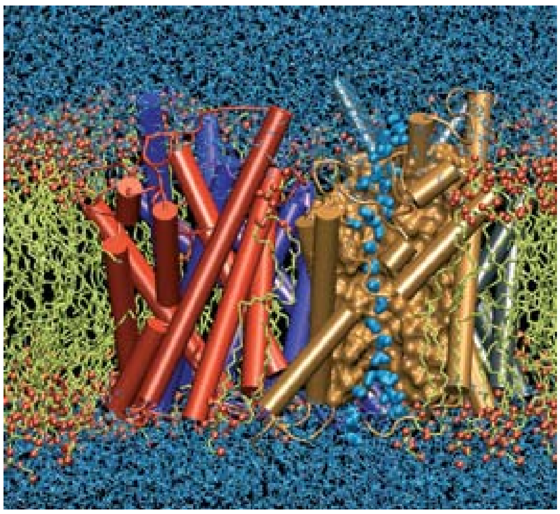


Figure 4 *A snapshot of water molecules (blue) around a protein called aquaporin, embedded in a cell membrane (yellow). Aquaporin controls the water coming in and out of cells, like a kind of molecular sluice gate. The water passes through a narrow channel in the protein, where the molecules get lined up in a chain, linked by hydrogen bonds.*

Artificial snow

The cinema, television and advertising industries make great use of artificial snow. This is often a frozen mixture of water and paper or plastic. Look for the gallery at *www.snowbusiness.com*

Blowing artificial snow … and outside Willy Wonka's chocolate factory

Odd ideas

But because liquid water remains still so hard to understand – its complicated hydrogen-bonded structure is hard to fully capture in computer models – and because it features so deeply in our stories and myths, it seems to have a limitless capacity to spawn strange and eccentric scientific ideas (see Box 2). One is that water possesses a 'memory', somehow retaining an imprint of molecules that have been dissolved in it so that it can mimic their behaviour when they are removed. This idea arose from experiments seeming to show that some solutions of biological molecules retain their biological activity when diluted until none of the molecules actually remained in the water. It's wrong, but is now often put forward as an 'explanation' for homeopathy. Many other spurious proposals have been made that water can act as an energy source, a kind of fuel.

Nils Volkmer/bigstockphoto

These claims, which generally rely on evidence that is barely detectable and hard to reproduce, are examples of what the American chemist Irving Langmuir called **pathological science**. And in a weird coincidence, Langmuir is allegedly the model for Vonnegut's Felix Hoenikker, the discoverer of ice-nine. It's said that Langmuir once tried to persuade H. G. Wells to take up an idea for a science-fiction story about a new form of ice, when Wells visited Langmuir's lab at General Electric in Schenectady, New York. Wells wasn't convinced. But also present at that meeting was the company's publicity officer, one Bernard Vonnegut, who later passed on the idea to his brother…

Box 2 Pathological science: the polywater fiasco

Vonnegut's ice-nine catastrophe of the oceans was echoed just a few years after his book was published when Russian scientists led by Boris Deryagin in Moscow claimed to find a new form of water. This, they said, forms only in very narrow glass capillaries, and it is extremely sluggish, rather like Vaseline. Other scientists speculated that it was a kind of polymer form of water in which the molecules had somehow become linked together via stronger bonds than ordinary hydrogen bonds, and it became known as polywater. When word reached the West in the late 1960s, a frenzy of research on polywater brokea out, with various other groups claiming to have made some.

In 1969, one researcher suggested that polywater might be 'the most dangerous material on Earth', because it might do just what Vonnegut's sliver of ice-nine had done: seed a transformation of the oceans, in this case turning them to goo. Several more influential scientists quickly ridiculed this idea. And by the start of the 1970s, it started to become clear that polywater didn't exist at all – it was probably just some gunk made from impurities in the water used by the Russian scientists, such as silicate ions dissolved from the glass of the capillary tubes. Before long, polywater had become a massive embarrassment to the community of scientists who studied water, but it was by no means the last outbreak of 'pathological' water science.

***Philip Ball** is an editor of the top science journal* Nature. *He is author of* H_2O: A Biography of Water *(Phoenix, 2000).*

Look here!

There's a huge amount of information about water on the web site maintained by Martin Chaplin of South Bank University:
http://www.lsbu.ac.uk/water/