

Physical chemistry

Wafer-thin surface of water

How thick is the surface of water? A combination of vibrational spectroscopy and molecular calculations reveals that only the surface layer of water at the interface with air has a distinctly different structure from the rest. See Letter p. 192

Pavel Jungwirth

The next time you drink a glass of water, take a moment to consider the surface of the liquid. It might surprise you to learn that the molecular structure of this seemingly unremarkable air–water interface has long been the subject of controversial theories. On page XXX of this issue, Stiopkin *et al.*¹ weigh into the debate by reporting the results of spectroscopic and theoretical studies of this interface. Their findings strongly contradict the recurring idea that external interfaces with water, or compounds dissolved within it, can generate long-range molecular order in the liquid.

There have been two popular, mutually interconnected misconceptions about liquid water.

According to the first, water can ‘remember’, for extended periods of time, patterns imposed on it by the environment or by solute molecules². This idea, among others, lent credence to a central tenet of homeopathy: that solutions of compounds could maintain biological activity even when repeatedly diluted to such an extent that effectively no molecules of those compounds remained in solution. But the ‘memory of water’ effect is not reproducible³ and the idea is now

scientifically unacceptable — although this doesn't seem to have affected the commercial success of homeopathy yet.

The second misconception is that long-range order across many, i.e., hundreds or even thousands of molecular layers can exist in liquid water. An early incarnation of this idea was the report⁴ of polywater — a syrupy liquid apparently produced when water was repeatedly forced through capillary tubes, and which was thought to be polymerized water. Similarly to the 'memory of water', the existence of polywater has also been debunked,⁵ but similar ideas have proven to be more durable in the scientific literature. Indeed, there has been a renaissance of the notion that long-range order can be imposed on water by an interface of the liquid with air, by an interface with another immiscible liquid or an interface with a solid such as the containing vessel⁶.

Moreover, the dust has been blown off the picture of bulk water as a mixture of regions of two distinct liquid forms, a concept first proposed⁷ heuristically by Wilhelm Röntgen more than a century ago. In the most recent variant of this idea⁸, robust X-ray scattering data of liquid water have been fitted into Röntgen's elderly model. And, in keeping with the theory that liquid water is structured by surfaces, it has been proposed that long-range water patterning occurs around proteins and other biomolecules. This in turn has led to the enigmatic concept of 'cellular water'⁹ — the elusive idea that all water molecules in cells are ordered, which has been assumed to be crucial for biological function.

Stiopkin *et al.*¹ have therefore performed a valuable service by looking with great detail and with little prejudice at the structure of an archetypal aqueous interface, that between water and air. They posed a seemingly simple question: how thick is this interface? In other words, how deep into bulk water does the patterning imposed by the surface propagate? In fact, for liquid water with its highly dynamical and volatile surface, this is a difficult question to answer.

The authors succeeded by applying a combination of two state-of-the-art techniques, which they also helped to develop. The first technique was experimental: they used a sensitive version of surface-selective vibrational spectroscopy to study oxygen–hydrogen bonds in water that stick out into the air, and which are therefore not hydrogen-bonded to another water molecule. (Actually, for technical reasons, they studied oxygen–deuterium bonds of water labeled once or twice with deuterium.) Such free or dangling bonds (Fig. 1) exist only at the surface and can thus be used as sensitive ‘antennas’ for detecting interactions of surface water molecules with molecules in the underlying sub-surface water layer.

Stiopkin and colleagues’ second approach was to perform sophisticated and accurate molecular calculations to model vibrations of water molecules in the liquid. This allowed them to compare the strength of hydrogen bonds between water molecules in the interfacial layer with that of those in the bulk (Fig. 1). They also used an old but neat trick, known as isotopic dilution, to disentangle the contributions of intramolecular and intermolecular couplings of individual water molecules to observed spectral shifts. This involved analysing a set of samples prepared by mixing together varying fractions of ordinary water (H₂O) and doubly deuterated water (D₂O).

By now, the reader may be waiting impatiently for the great news concerning amazing structural patterns discovered at the surface of water. If so, then the reader will be disappointed — Stiopkin *et al.* found that the surface does not have a long-range impact on water and that the strength of interactions of surface water molecules with those in the sub-surface layer is comparable to that between water molecules in the bulk. This means that only the surface layer is distinctly different in structure from the rest of the liquid, and that the thickness of the water surface is equivalent to that of one water layer, which is about 0.3 nanometres. More complex (e.g., charged) interfaces or solutes may slightly extend this width, but not to more than a small number of water layers^{10,11}.

In this context, the main implication of Stiopkin and colleagues' study is that the old models of long-range patterning in liquid water and their newer incarnations are not substantiated. The fact that these models are not always perceived merely as historical curiosities warrants broad attention to the authors' work. The present findings¹ may seem to represent a 'negative' result, however, by offering a sober view of the fascinating and important — but by no scientific means magical — properties of liquid water, they should have a most welcome, positive effect.

Pavel Jungwirth is at the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nam. 2, 16610 Prague 6, Czech Republic.

e-mail: pavel.jungwirth@uochb.cas.cz

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Figure 1 Structure of the interface between liquid water and air. This image taken from a classical molecular dynamics simulation reveals the features of liquid water at an air–water interface. Most water molecules form hydrogen bonds to each other, but some at the surface do not (these are known as dangling bonds). Stiopkin *et al.*¹ report evidence that the surface has a

depth of only one layer of molecules, contradicting theories that interfaces with water impose long-range order deep into the liquid bulk. The surface layer of water molecules thus sits atop a sub-surface layer, the properties of which already approach those of bulk water. Red atoms are oxygens, white ones are hydrogens.

