Confined water

▾ Hydrophobic confinement
▾ Hydrophilic confinement
▾ Capillary rise
◂ Interfacial water and water-gas interfaces
◂ Nanobubbles

Confined water is found widespread in nature in granular and porous material and around and within macromolecules,supramolecular structures and gels. It has recently been reviewed [1592]. When water is confined there is conflict between the energetic minimization of the hydrogen-bonded network, interactions with the relatively large cavity surface and the fit within the space available. The physical properties and state of the contained water may vary widely depending on the molecular characteristics of the cavity surface and the confinement dimensions, as well as temperature and pressure. The properties of the confined water are difficult to predict and may be very different from those of bulk water. This is particularly true when the confinement is on the nano-scale. [**Back to Top ▲**]

Hydrophobic confinement

Water at hydrophobic surfaces is similar to that at the liquid gas interface but confinement prevents movement of the water molecules towards the surface and van der Waals dispersion interactions loosely hold the outer molecules in preferred positions and orientations relative to the surface atoms.
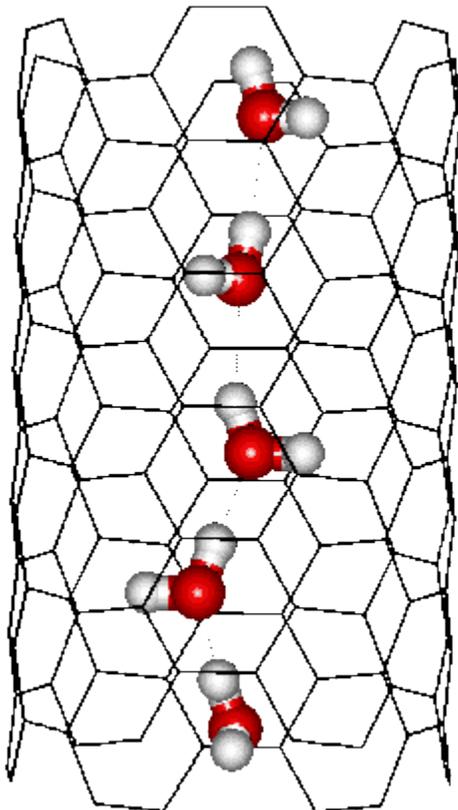
Much theoretical and experimental work has concerned water in carbon nanotubes; made up of a hexagonal lattice of carbon atoms rolled up into cylinders with diameters of a nanometer or so. Such structures are often thought of as hydrophobic cylinders but that can underestimate the importance of the surface. The carbon atoms provide a high number of van der Waals interactions in an orderly hexagonal lattice arrangement that varies between the different types of nanotube and with their diameters. Although uncharged, these surfaces provide extensive pi-electron orbitals that can interact with and be polarized by the water molecules to cause effects significantly different from that expected of a flat and uniform hydrophobic cylinder.

Opposite is shown a one-dimensional strand of water molecules within a (6; 6) carbon nanotube, diameter 0.81 nm. The water self-aligns to give an almost all-trans zigzag arrangement possessing similar entropy to that found in bulk water [1397]. Each water molecule has two cooperative hydrogen bonds plus multiple van der Waals interactions from the carbon nanotube. Such organized water chains are determined by the confinement rather than interaction with the pore surface [1398] and make rapid proton conductors due to the Grotthuss effect[1041].
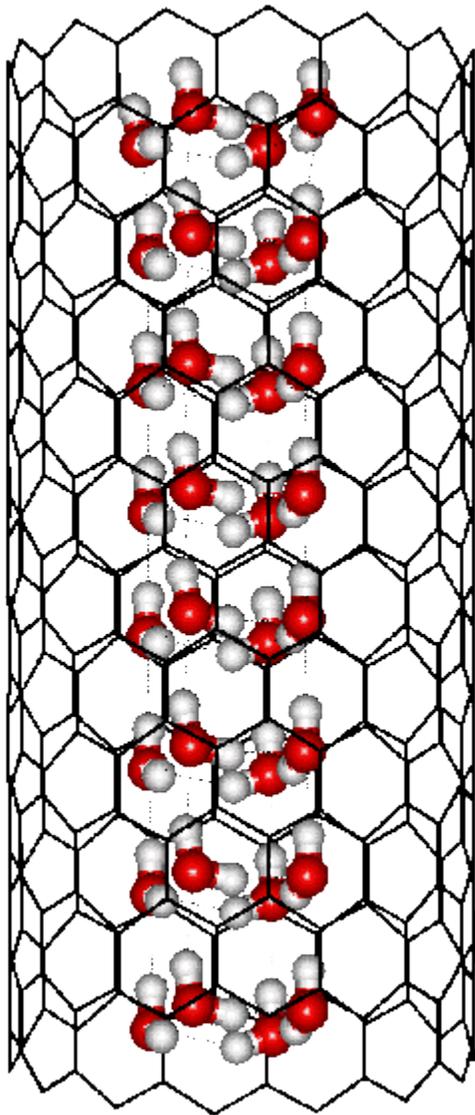
In modeling studies, penetration of water into nanotubes is modulated by small changes in the polarity of the wall and the dimensions of the cavity [1396]. The cohesive nature of the hydrogen-bonded network may allow water to travel easily through such pores, with the molecules leaving the pore pulling through a following stream of water. Thus, submicrometer-thick membranes made from graphene oxide (a mixed hydrophilic/hydrophobic material) , which are completely impermeable to all other liquids, vapors, and gases, allow unimpeded permeation of water [1778]. Graphene sheets with nanoscale pores also function well as desalination membranes [1900].

A phase diagram of water within carbon nanotubes has been proposed for tube diameters up to 1.7 nm. This suggests that there may be at least nine phases possible within the cylindrical space, including those found by x-ray diffraction and by simulation. The global maximum freezing point is found to be for 'square' ice at 290 K [1400].

Shown opposite.is such a square ice nanotube formed within a (14; 0) carbon nanotube of diameter 1.11 nm.^{c} Each water molecule has four cooperative hydrogen bonds, which are more bent than in hexagonal ice. They also have multiple van der Waals interactions from the carbon atoms.
Other ices (for example, pentagonal, hexagonal and heptagonal nanotubes of water molecules, all with two donor and two acceptor hydrogen bonds) are formed within carbon nanotubes of diameters increasing up to 1.9 nm diameter [1401]. Conversion between these ices can be achieved by increasing the pressure; such that the square ice converts to the pentagonal ice at about 200 MPa at about 275 K [1402]. Water simulated as confined under pressure between flat plates, 0.85 nm apart, forms a twelve-fold symmetrical quasicrystal made up of mostly five-membered rings in two molecular layers [1705].

There is evidence that the protons of confined liquid water exist in a novel quantum state when significant quantum fluctuations in charge take place along the hydrogen bonds [1699]. [**Back to Top** ⏶]

Hydrophilic confinement
At hydrophilic surfaces, polar and hydrogen bonding interactions with the surface may vary between those that are very much weaker than water-water hydrogen bonds to those that are very much stronger. Water will condense from the gas phase onto glass to give at least four layers of absorbed water [1403], with the water next to the silica highly structured, dependent on the surface and distinguishable from more distant water by infrared [1404] and X-ray [1405] spectroscopy. Even the second neighbors to the surface are considerably affected due to the competition between the surface water and the effects of confinement [1406]. When the confinement is less than about 2 nm wide, the viscosity may increase considerably to over a million times that of bulk water, but this viscosity increase is not noticed if the confining surfaces are hydrophobic [1304]. The surface hydroxyls on the pore walls hydrogen bond to the water and control the distortion of the hydrogen bond network and its surface dynamics [1408].
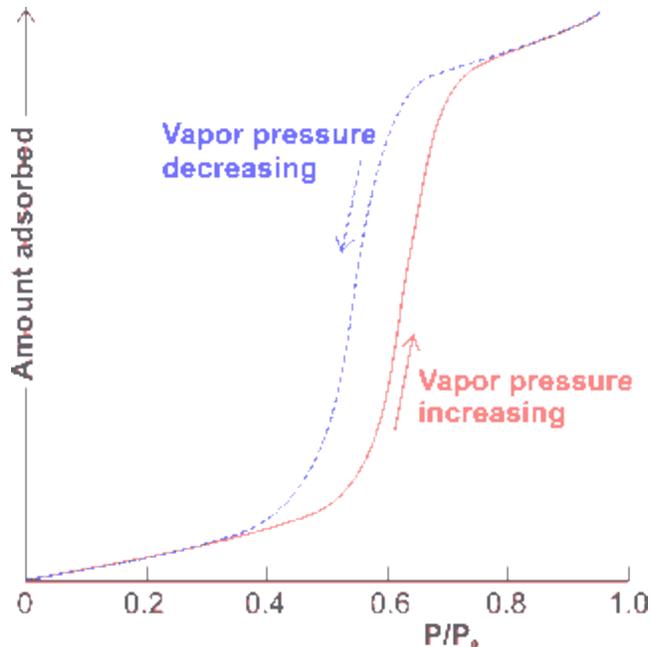
Variation of the spacing between any interaction sites on polar cavity surfaces determine the strength of binding, distribution and organization of several layers of water molecules. Sawtooth-like oscillatory forces may be generated as hydrophilic surfaces approach with about 1 nm periodicity, corresponding to units reducing by clusters with a linear width of five H-bonded water molecules at a time (rather than single water molecule losses) [2105].

The adsorption of water to a bare surface involves continuous changes in structuring due to relaxation of the hydrogen bonding and molecular orientations as the surface becomes covered and further water layers are added. This can give rise to substantial hysteresis (shown opposite) in structure and properties on its removal [1409].

Confinement may cause raised or lowered melting points, dependent on the surface and the space available. Generally, it might be expected that the raised boiling point and depressed freezing point are inversely related to the capillary diameter due to the Gibbs-Thomson effect [1420]. For example, cubic ice may form in 4.2 nm diameter cylindrical silica pores at 232 K [1410]. However, surface interactions and the confinement diameter may cause opposite effects, such as the ice that forms at 400 K in very narrow pores (0.6-1.0 nm diameter) in porous glass [1411].

Water may freeze when confined between flat surfaces such that it can form the optimally ordered hydrogen bonds required. The confined water undergoes significant changes in density and viscosity as the surface separation is varied. For example in a model, water goes from liquid to solid and back again as the space decreases from 0.58 nm to 0.53 nm to 0.47 nm between interacting but non-hydrogen bonding surfaces [1412]. If unable to form the required ordered structures, it may still undergo wide fluctuations in density as it attempts to optimize its structure within the restrictions of the confinement.

When ice does form at strongly binding or atomically rough confining surfaces, there may be no room for expansion and a high density amorphous ice may result [1413]. Different ices may form in interacting confined space, with a high density confined ice (1.2 g cm^{-3}) formed from two helices and crystallizing at ambient temperature in $AlPO_4$-5 zeolite 0.73 nm diameter micropores [1407]. Both cubic and amorphous ices can form at strongly binding silica surfaces at low temperatures

[1406]. However rather than forming ice within confinement, liquid water in confined spaces may leave the confinement on freezing, to crystallize freely external to the cavity, so long as they can easily be replaced by the gas phase under the ambient pressure [1399]. [**Back to Top** ▲]
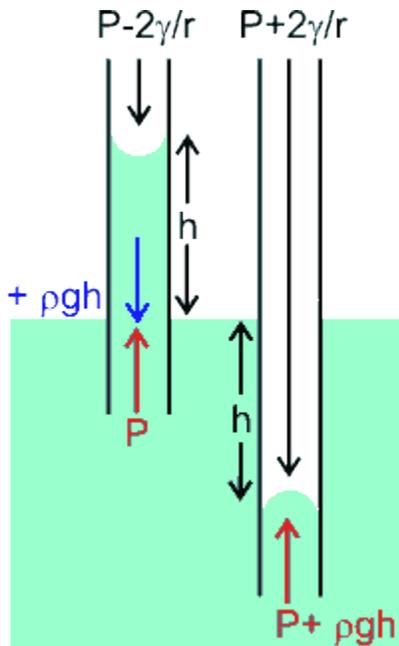
Capillary rise

The movement of water up or down capillary (narrow bore) tubes and confined spaces is due to the Laplace pressure at curved surfaces.[a] Thus, if the water curves towards the surface (hydrophilic surfaces, left in Figure) then water enters the capillary until the pressure of the water above the liquid surface (= weight per unit volume x height) counteracts the reduced pressure (= 2 x surface tension/radius). Thus water will rise (a maximum) 2.94 cm within a glass capillary 1 mm in diameter at 25 °C.[b] An opposite effect occurs in hydrophobic capillaries (far right). It is the presence of the extensive gas-liquid interfaces and many capillary bridges that are responsible for the characteristic of wet sand that allows it to be easily molded into sandcastles [1537].

There are confounding factors when very fine capillaries are considered. The surface will not be uniform but involve a number of molecularly organized environments. Also, strongly bound water will reduce the effective capillary diameter, so increasing any water movement. Although the capillary rise phenomenon does hold for very small diameter capillaries, it is not clear that it can scale down to nanometer or molecularly sized capillaries [1449]. [**Back to Top** ▲]

Footnotes
[a] The rise can also be attributed to the energy of binding of the water at the capillary wall being available to do the work needed to lift the liquid column against gravity. [Back]

[b] If the meniscus does not meet the capillary wall at zero angle ($\theta = 0$) then the contact angle (θ) is related to the radius of curvature R of the meniscus ($\cos\theta = r/R$) and the Laplace pressure is $2\gamma\cos\theta/r$ ($0 < \cos\theta < 1$). rather than $2\gamma/r$. Allowance for the volume within the meniscus is easily made by using the value for the height (h) that gives the actual volume of fluid involved [1448]. In reality the meniscus will not be spherical in shape [1448]. [Back]

[c] The octameric cubic structure $(H_2O)_8$ has also been found by crystallography, trapped within supramolecular metal–
organic networks [2093]. [Back]