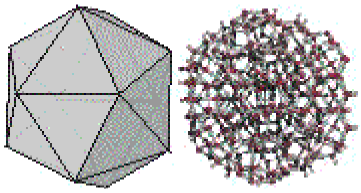
Water Clusters: Overview

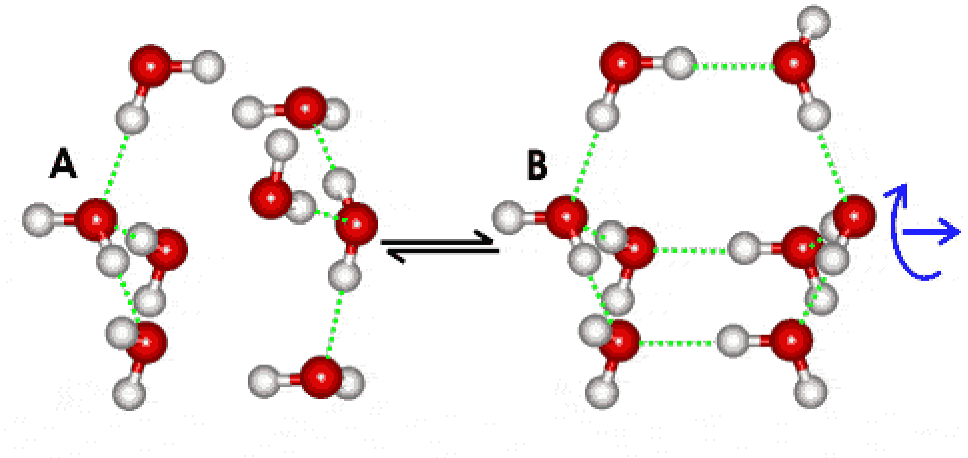
Plato thought that water could be represented by an icosahedron.
So do I. Read on and decide if we may be correct.



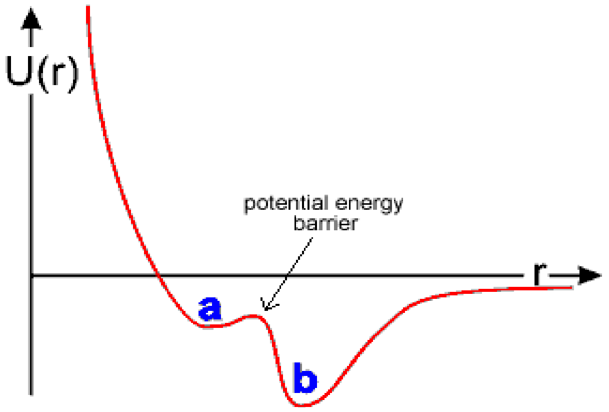
Water clustering

It is clear that life on Earth depends on the unusual structure and anomalous nature of liquid water. Organisms consist mostly of liquid water. This water performs many functions and it can never be considered simply as an inert diluent; it transports, lubricates, reacts, stabilizes, signals, structures and partitions. The living world should be thought of as an equal partnership between the biological molecules and water.

In spite of much work, many of the properties of water are puzzling. Enlightenment comes from an understanding that water molecules form an infinite hydrogen-bonded network with localized and structured clustering [1866]. The middling strength of the connecting hydrogen bonds seems ideally suited to life processes, being easily formed but not too difficult to break. An important concept, often overlooked, is that liquid water is not homogeneous at the nanoscopic level (*e.g.* see [993]).



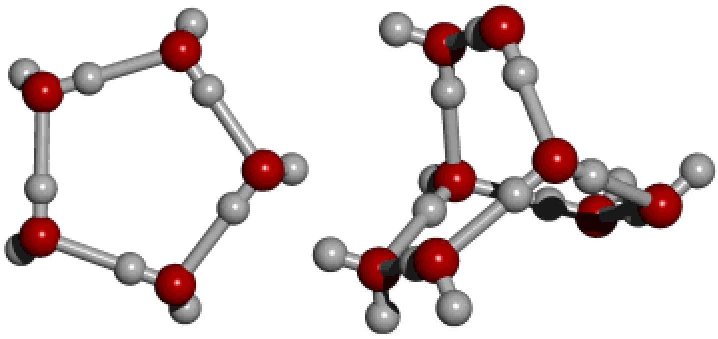
Small clusters of four water molecules may come together to form water bicyclo-octamers. The molecular arrangement (**A**) also occurs in high-density ice-sevenwhereas, with 60° relative twist, (**B**) is found in low density hexagonal ice; (see animated gif, 129 kB). Structures similar to**A** have greater numbers of 3-hydrogen bonded and 5-coordinated water molecules as found at higher temperatures in liquid water, whereas structures similar to **B** have greater numbers of 4-hydrogen bonded and 4-coordinated water molecules as found at lower temperatures in liquid water [1773]. Such equilibria are balanced due to the existence of two minima in the potential energy (U) - molecular separation (r) diagram below, which shows the approach of the water tetramers.



This competition between maximizing van-der Waals interactions (**A**, yielding higher orientation entropy, higher density and individually weaker but more numerous water-water binding energies) and maximizing hydrogen bonding (**B**, yielding more ordered structuring, lower density and fewer but stronger water-water binding energies) is finely balanced, easily shifted with changed physical conditions, solutes and surfaces. The potential energy barrier between these states (see below left) ensures that water molecules prefer either structure **A** or **B** with little time spent on intermediate structures. An individual water molecule may be in state **A** with respect to some neighbors whilst being in state **B** with respect to others (for example,ice-seven).

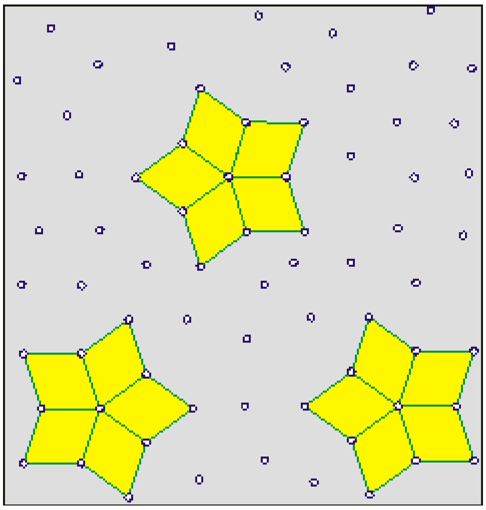
Certainly, recent simulations using *ab initio* van der Waals interactions support this mechanism for the density fluctuations in liquid water [1756].

The shallow minimum (**a**), due to non-bonded interactions, lies up to 20% inside the deeper minimum (b) due to hydrogen bonding (even allowing for a 15% closer approach of individual hydrogen bonded water molecules). In spatial terms, minimum (**a**) is far more extensive as the hydrogen-bonded minimum (**b**) is restricted in its geometry, being highly directional. At lower temperatures (particularly below the temperature of maximum density) and pressures, the less dense structure with more extensive hydrogen bonding at the lower minimum (**b**) will be preferred even though it involves a more ordered (lower entropy) structure. At higher temperatures, non-bonded interactions dominate causing breakdown of the clustering (Figure inspired by [16]).
The hydrogen bonding, although cohesive in nature, is thus holding the water molecules apart. It is the conflict between these two effects, and how it varies with conditions, which endows water with many of its unusual properties.
These bicyclo-octamers may cluster further, with only themselves, to form highly symmetric 280-molecule icosahedral water clusters that are able to interlink and tessellate throughout space. A mixture of water cyclic pentamers and tricyclo-decamers can bring about the same resultant clustering.



Cyclic pentamer **Bicyclo-octamer** **Tricyclo-decamer**

As all three of these small clusters are relatively stable, it is likely that their interaction will produce these larger icosahedral clusters. Such clusters can dynamically form a continuous network of both open, low-density, and condensed structures. [**Back to Top**]

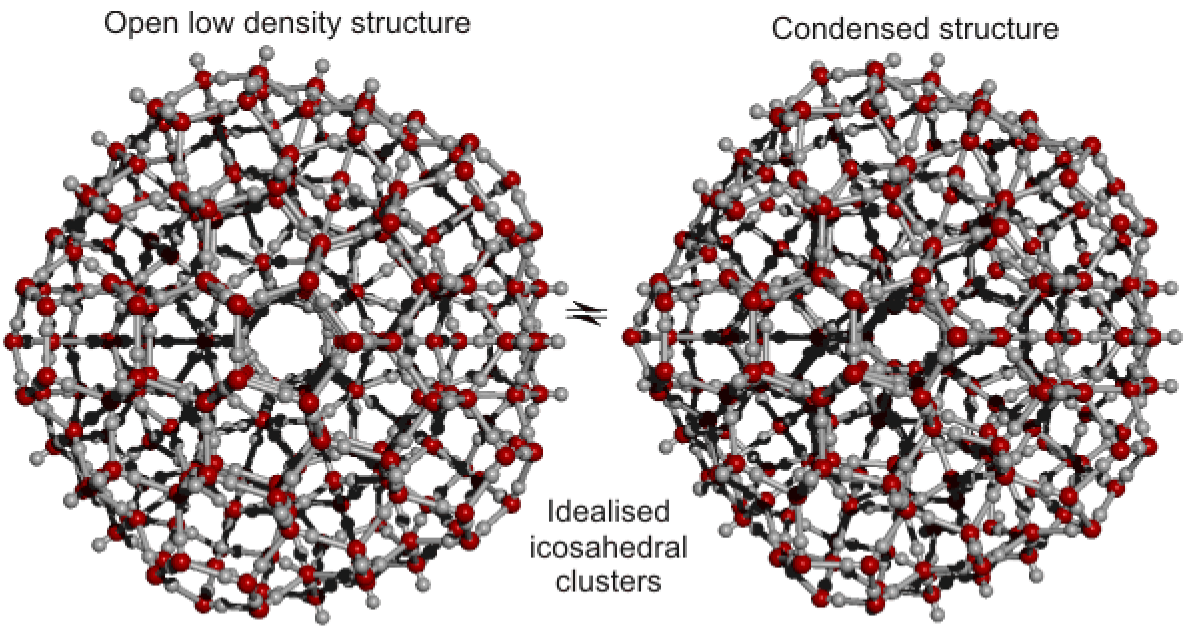


Cluster and hydrogen-bond lifetimes are independent

Cartoon to aid the understanding of how the lifetimes of clusters are independent of the lifetime of individual linkages. The cartoon shows a two-dimensional representation of a three-dimensional phenomenon. The actual clusters of water molecules are not represented. It is supposed (opposite) that the star clusters (shown yellow filled) may reform around key structures (shown as rhombuses, sometimes red, but closed ring oligomers of H_2O in water). For each shifting cluster a few units move to break up the existing cluster and help create a new cluster. The new clusters are identical to the old ones but only contain a proportion of the units. Clusters may reform around any of the star arms. Although the hydrogen bonds between water molecules in ice have equally short lifetimes to those in water, ice cubes, which can be considered as enormous ice clusters, can last forever at 0 °C in water.

There is a similarity, in principle, with John Conway's game "life"[b] in the persistence of some of its structures [1609]. [**Back to Top**]

Icosahedral water clusters



Such a fluctuating self-replicating network of water molecules, with localized and overlapping icosahedral symmetry, was first proposed to exist in liquid water in 1998 [55] and the structure subsequently independently found, by X-ray diffraction, in water nanodrops in 2001 [417]. The clusters formed can interconvert between lower and higher density forms by bending, but not breaking, some of the hydrogen bonds. Structuring may also flicker between statistically and topographically equivalent clusters but involving different molecules by shifting their cluster centers. These polyhedral structures are idealized as given, and are considerably distorted and fragmented by thermal effects, but the existence of long-lived ring fragments is nevertheless considered to be well-founded [2053]. The cluster size required for ice formation has been estimated at about 400 molecules (one further layer of water arond the icosahedral water core), although the structure of this core structure was indeterminable [2088]. As the temperature increases the average cluster size, the cluster integrity and the proportion in the low-density form all decrease. This structuring accommodates explanation of many of the anomalous properties of water including its temperature-density and pressure-viscosity behavior, the radial distribution pattern, the presence of both cyclic pentamers and hexamers, the change in properties on supercooling[a] and the solvation and hydration properties of ions, hydrophobic molecules, carbohydrates and macromolecules. The model described here offers a "two-state" structural model on to which large molecules can be mapped in order to offer insights into their interactions.

Footnotes

[a] As the temperature of supercooled water drops further below 0 °C, the density, self-diffusion, thermal conductivity, enthalpy and entropy all decrease whereas compressibility, viscosity, thermal convection, specific heat (C_P) and gas solubility all increase. As the pressure increases on supercooled water, viscosity and freezing point decrease whereas entropy and self-diffusion increases. [Back]

[b] The Game of Life is 'played' on an infinite two-dimensional grid of squares, each of which is in one of two possible states, *alive* or *dead* (see right for an example). Every cell interacts with its eight adjacent neighbours using the four rules:

1. Any live cell with fewer than two live neighbours dies, as if caused by under-population.
2. Any live cell with two or three live neighbours lives on to the next generation.
3. Any live cell with more than three live neighbours dies, as if by overcrowding.
4. Any dead cell with exactly three live neighbours becomes a live cell, as if by reproduction.

Source: http://www1.lsbu.ac.uk/water/abstrct.html