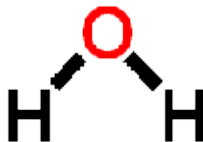


Water Clusters: Introduction

[← Overview of the structure of liquid water](#)



[Water](#) (H₂O) is the third most common molecule in the Universe (after H₂ and CO), the most abundant substance on earth and the only naturally occurring inorganic liquid, a billion cubic kilometers of which reside in our oceans and 50 tons of which pass through our bodies in our lifetimes. It has been very well studied with a number of [model structures](#) having been proposed and refined.^a Notwithstanding this, extensively [hydrogen-bonded](#) liquid water is unique with a number of [anomalous properties](#). It has commonly been stated that no single model is able to explain all of its properties [1, 53a, 54]. In particular, successful models for water must encompass the [radial distribution function](#), the [pressure-viscosity](#) and [temperature-density](#) behavior and the effects of [solutes](#). Much work has been invested in developing [models](#) for individual [water molecules](#) for use in molecular dynamics simulations [2, 3]. These models are very useful, particularly for investigating short-range order, but have difficulty addressing the totality of the unusual nature of water including the long-range ordering that has been described around macromolecules [4, 5, 6]. In particular, they only show approximate agreement with the radial distribution functions and most have difficulty explaining the position and size of the [peak at about 3.7 Å](#) [3, 7]. A number of [interstitial models](#) have been described based on dodecahedra [8, 8b], the [ice Ih](#) structure [9, 10] or from computer simulation [66]. These involve the presence of water molecules within cavities in the hydrogen-bonded network. A percolation model, where the degree of hydrogen-bonding decreases as temperature increases, has also been developed [11]. Although good at explaining some, but not all, of the properties of water, its nature is still unclear.

More recently, explanations of the properties of water have been in terms of non-bonded interactions in a fully bonded network [12], significant bending in the hydrogen bonds [13], [competition between bonded and non-bonded interactions](#) [14, 311] or equilibrium between structural components containing hexagonal, pentagonal and dodecahedral water arrays [15]. The unusual properties of water at mixed hydrophilic/hydrophobic surfaces has been explained in terms of the presence of both high-density water and strongly associated (low-density) water [851]. Reviews outlining the relationship between liquid, supercooled and [low-density amorphous ice](#) (LDA) [16] and the relationship between the bulk structure of water and calculated and experimental data on small water clusters [226] have appeared recently. The present review has its roots in a recent paper [55] that includes elements of several of these approaches. A brief history of the development of the water clustering concept^b is given on [another page](#).

Whilst the molecular movements within [liquid water](#) require the constant breaking and reorganization of individual hydrogen bonds on a picosecond timescale, it is thought by some that the instantaneous degree of [hydrogen-bonding](#) is very high (>95%, [13, 168] at about 0 °C to about 85% at 100 °C [168]) and gives rise to extensive networks, aided by bonding cooperativity. It has been suggested that there will be a temperature-dependent competition between the ordering effects of hydrogen-bonding and the disordering kinetic effects [17]. There are [many pieces of evidence](#) indicating that the time-averaged hydrogen-bonded network possesses a large extent of order. These include the [fine structure](#) in the diffraction data [9], microwave dielectric relaxation measurements on glucose solutions [6], vibrational spectra that have indicated the presence of large clusters [18], collective dipole orientation fluctuations with time scales 50,000 times slower than expected [1034], and the formation and properties of low-density water in gels [4]. There is some evidence that water is self-organizing [581] and can exist as macro-scale (10-120 μm) clusters [1329].

A random network model has been described for LDA [19], liquid [261] and supercooled water [20]. However, although this model is simple, requiring no 'fitting' parameters, and has proven to be useful [261], it fails to describe some of water's properties unless made inhomogeneous; for example the entropy of LDA is much lower than can be explained by this model [21]. A variation of this model concentrates on pentagonal rings and cavities [366]. Several workers suggest that the structure of liquid water should be related to crystalline ice structures [6, 22], although this structuring must be significantly different due to the ease with which water supercools and its high heat of fusion. It has similarly been proposed to be a mixture of almost equal quantities of low (LDA) and high-density amorphous ice (HDA) [262] or related, if less well defined, clusters [732]. Recently, a [two-state network model](#) including [ice Ih](#) (hexagonal ice) and [ice-two](#) (ice II) substructures, locally rearranging on a picosecond timescale, has been used to explain many of the properties of water [23, 56, 57, 268]. Although attractive, the inclusion of explicit ice-two clusters in this model leads to some difficulties, such as the pressure requirement for the extensive ice-two cluster formation necessary to achieve the density of water, the ordered nature of the hydrogen bonding in ice-two and consequent extremely low dielectric constant (3.7 [94]) which is not apparent in liquid water, and the number of unit cells (at 12 molecules per unit cell) required per cluster for the experimental non-bonded close contacts; indeed recently less emphasis has been placed on the explicit inclusion of ice-two in this model by its proposers [60, 409]. In many respects the outer-structure two-state mixture model [409] is, however, not inconsistent with the model described here with mutual agreement concerning both the 'key features' [409] of O...O [next near-neighbor distances](#) and O...O...O hydrogen bond angle distribution. A related two-state model including [ice Ih](#) and [ice-three](#) (ice III) substructures has been used to explain hydration thermodynamics [318]. Other workers have used less explicit two-state models possessing high and low-density components to explain the properties of supercooled water [24, 790], the pressure-dependent growth of the [peak at about 3.7 Å](#) in the radial distribution function [25] and many other anomalies [86].

Water dodecahedra have been found in aqueous solutions [26, 27], crystals [1652], and in the [gas phase](#) [28]. Dodecahedral water clusters have also been reported at [hydrophobic](#) and [protein](#) surfaces [89], where low-density water with stronger hydrogen bonds and lower entropy has been found [29]. Similar dodecahedral cavities have been found in LDA [30] and form relatively easily in water during molecular simulations [31].

In these pages a [structural model for water is proposed](#) that both builds on, and is consistent with, many of these different approaches. The basis of this model is a network that can convert between lower and higher density forms without breaking hydrogen bonds. It contains a mixture of hexamer and pentamer substructures and contains cavities capable of enclosing small solutes. The model was developed by arranging [alternating sheets of boat-form and chair-form water hexamers](#) from the lattices of [hexagonal](#) and [cubic ice](#) respectively. This structure was folded to form an icosahedral three-dimensional network with capacious pores capable of partial collapse due to competition between bonded and non-bonded interactions.

In order to develop the ([icosahedral water clusters](#)) model described, molecular model building and dynamics were performed using the HyperChem ([Hypercube Inc.](#), Ontario, Canada) molecular modeling package. To obtain the co-ordinates, the network was optimized using the AMBER force field with special parameters (O...O stretch $28 \text{ kJ mol}^{-1} \text{ \AA}^{-1}$, O...O distance 2.84 \AA ; O...O...O bend (k_{θ}) varying about $4 \text{ kJ mol}^{-1} \text{ rad}^{-2}$, from 109.47° ; van der Waals $\sigma = 3.536 \text{ \AA}$, $\epsilon = 0.636 \text{ kJ mol}^{-1}$). These parameters were chosen as reasonable to create the model but were not critical. All data reported is derived from structures with average O...O and O-H nearest neighbor distances of 2.82 \AA and 0.96 \AA respectively. Hydrogen atoms were not treated explicitly, being placed such that each oxygen has two near and two far hydrogen neighbors after model building was completed.

Footnotes

Small clusters of liquid, but structured, water molecules within molecular 'test tubes' (carbon nanotubes) have been visualized using a transmission electron microscope [931]. The pictures however still need much interpretation.

Some authors prefer the terms 'dynamic heterogeneities' or 'density fluctuations' to 'clusters', but this site does not. The same type of structuring is meant in most of these cases.

Source: <http://www1.lsbu.ac.uk/water/intro.html>