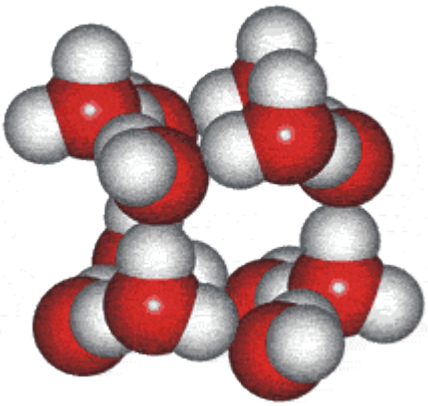
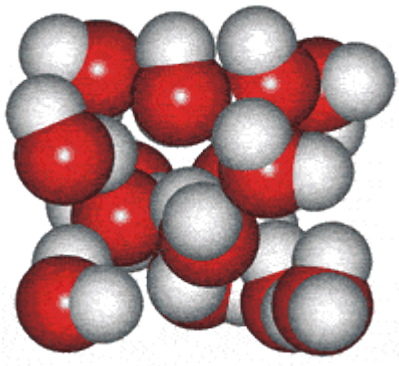
Water Cluster History

The anomalous properties of water have excited chemists to attempt explanation for many years. These hypotheses have mainly involved consideration of the existence of different water clusters within liquid water. Such clusters are either low density (similar in density to that of hexagonal ice) or of higher density; their changing relative concentrations determining the changes in physical properties.



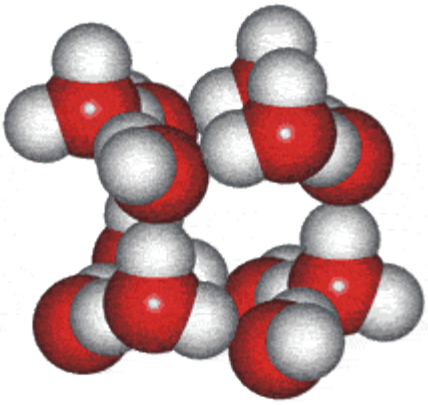
Low-density ice-like particles



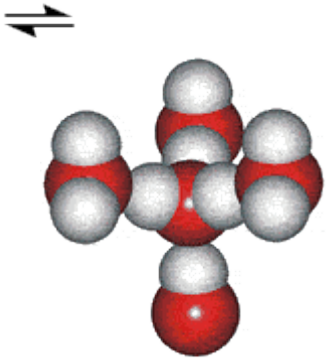
Higher-density liquid matrix

1884

The first reported suggestion for clusters being responsible for water's anomalous density maximum was by Whiting in 1884 [764]. Melting ice was proposed to release solid low-density ice crystals (left) which remained within the higher density matrix (right). Whiting proposed that the concentrations of these solid particles changed with temperature and pressure. Chadwell [765] reviewed the first 40 years in the development of this idea.



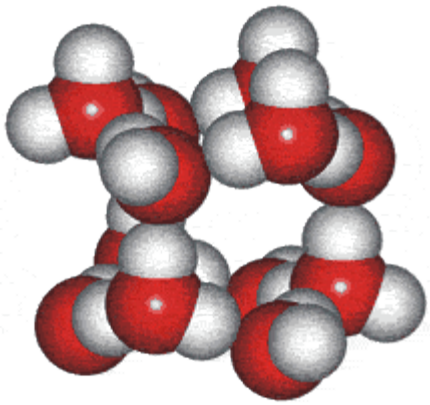
Low-density ice-like clusters



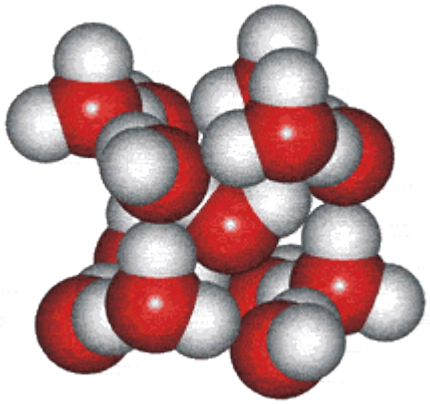
Higher-density clusters

1933

In 1933, Bernal and Fowler developed this model in two important respects [1177]. Firstly the denser matrix was proposed to be made up of 'quartz-like' clusters (right) that may pack closer together. Secondly, and significantly, they introduced the idea of equilibration of water molecules interconverting between the clusters [766].



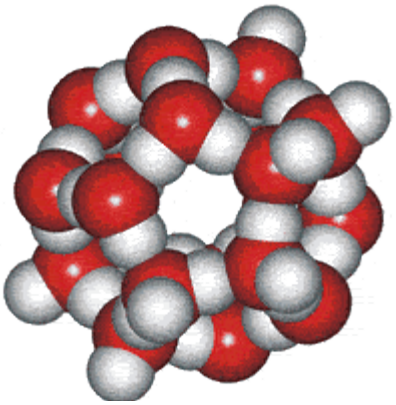
Low-density ice-like clusters



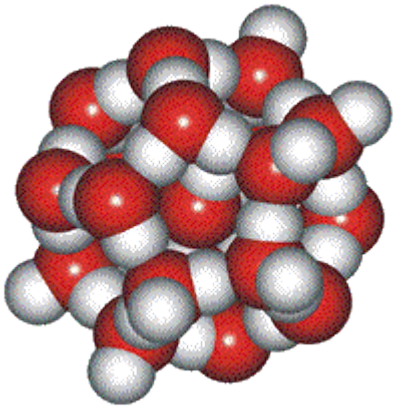
Cluster plus an interstitial molecule

1946

An interesting idea, based on interstitial water molecules within the ice hexagonal box (right) was put forward in 1946 [767]. Such clusters are not now generally thought to be present in significant quantities, although some researchers still make use of this hypothesis [2009].



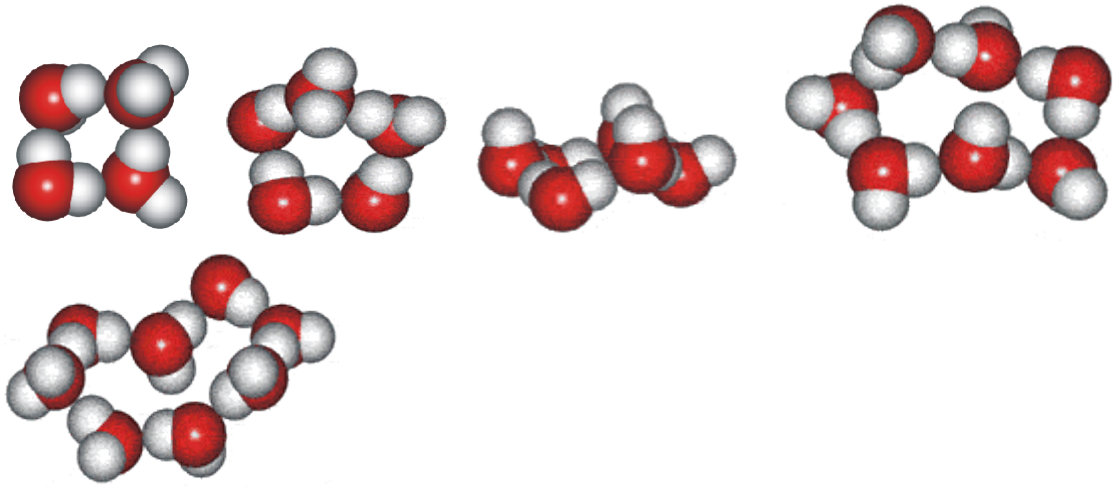
Low-density clathrate clusters



Cluster plus an interstitial molecule

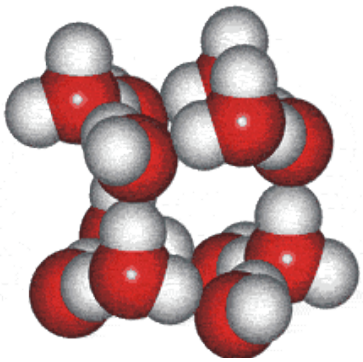
1959

Pauling suggested another interstitial arrangement in 1959, making use of his interest in clathrate structures [8b]. These clusters were quickly dismissed, however, for being unable to explain the available diffraction data if the main constituents in liquid water.



1975

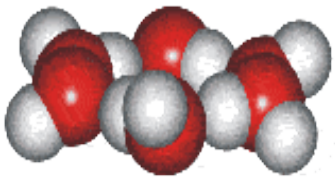
A random network model of water, also introduced by Bernal [1177] and published in 1975 [19], contained a mixture of water clusters including 4-, 5-, 6-, 7- and 8-membered rings. Some success has been had using this model but its homogeneous nature is not universally applicable or productive.



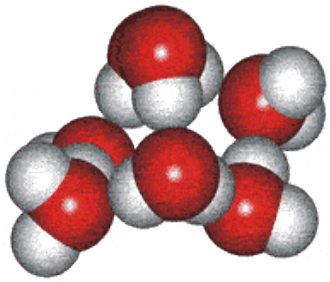
An ice Ih cluster

1987

Wilse Robinson's research group introduced the outer structure two-state mixture model in 1987, which involved a mixture of water clusters related to ices 1h, IIand III. The group went on to produce a number of papers using the model to successfully and quantitatively explain many of water's anomalies (for example, [23, 56,57, 60, 69, 73, 148, 1354]).

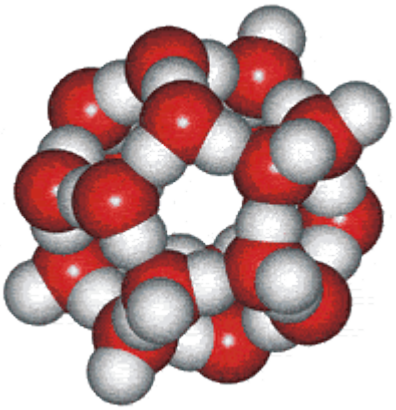


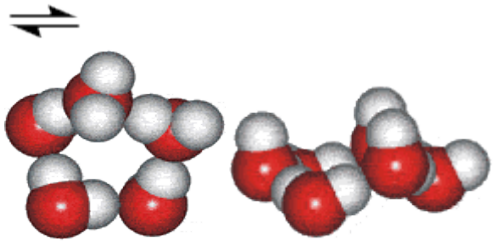
An ice II cluster



An ice III cluster

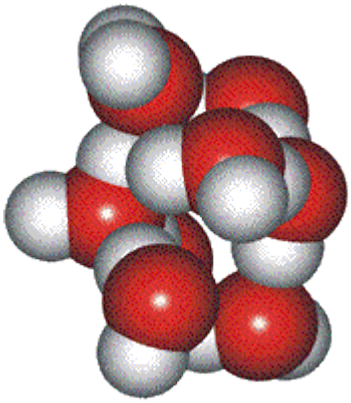
The only difficulty with this model concerned whether such clusters could exist for significant time in liquid water and so the clusters were more realistically considered as rapidly fluctuating 'indicative' structures [1354c].



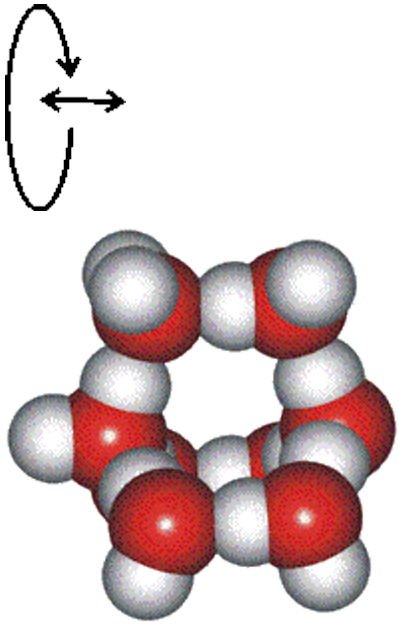


1998

In 1998 Dougherty and Howard proposed an equilibrium model for water [15] involving dodecahedra, 5- and 6-membered clusters based on several of water's anomalous properties.



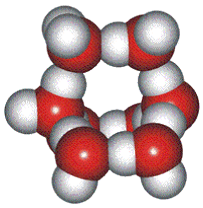
Dense cluster



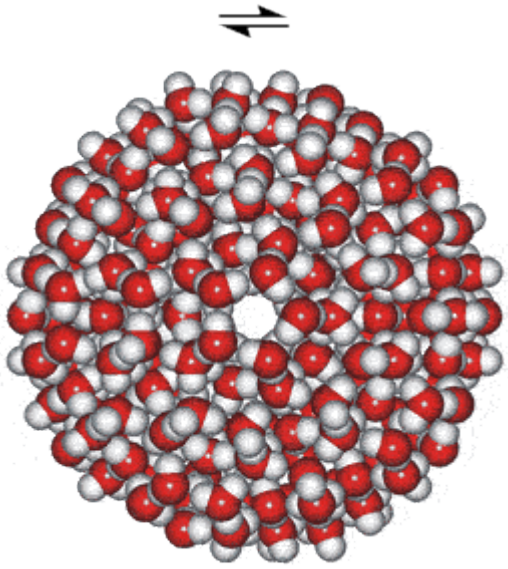
Low-density cluster

2000

These water cluster models lead logically on to theicosahedral water cluster model , published in 2000 [55] and described at this site. This model is based on dense and less dense clusters equivalent to an equilibrium opposite (see animated gif). The less-dense bicyclo(2,2,2) structures (right) occur when the hydrogen bonding is strongest and the dense structures occur when the weaker but more numerous van der Waals interactions predominate.



Low-density cluster



Icosahedral cluster

When conditions arise (such as on supercooling at low temperatures) when there is a high concentration of the expanded 8-membered bicyclo clusters, partial to complete icosahedral clusters (right) may arise. A full description of this is given elsewhere on this site. This cluster contains the dodecahedral, ice Ih cell, 5-, 6-membered and 8-membered bicyclo(2,2,2) subclusters included in the historical survey of models, above.

The meaning of the term 'cluster' has evolved during this time as well. In the beginning, water clusters were thought of as discrete entities, like crystals, with long (e.g. > seconds) individual lifetimes where the same molecules were involved throughout. Nowadays, we know that molecules may leave or add to clusters[a] with frequencies that depend on their situation and obey statistical laws with clusters appearing, evolving and disappearing with involvement of physically different molecular constituents. The aqueous environment is heterogeneous with more than one type of environment present and with the relative preponderance of these environments changing with temperature, pressure, solutes and surfaces. Clusters are now thought of as dynamic entities offering a simplified view into a complex, broken and rapidly shifting environment. As such they reveal water's underlying nature.

Footnotes

Some authors prefer the term 'dynamic heterogeneities' to 'clusters', but this site does not. The same type of structuring is meant in both cases.

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