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A proposal for the structuring of water

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Abstract

In spite of much work, many of the properties of water remain puzzling. A fluctuating network of water molecules, with localised icosahedral symmetry, is proposed to exist derived from clusters containing, if complete, 280 fully hydrogen-bonded molecules. These are formed by the regular arrangement of identical units of 14 water molecules that can tessellate locally, by changing centres, in three-dimensions and interconvert between lower and higher density forms. The structure allows explanation of many of the anomalous properties of water including its temperature–density and pressure–viscosity behaviour, the radial distribution pattern, the presence of both pentamers and hexamers, the change in properties and 'two-state' model on supercooling and the solvation properties of ions, hydrophobic molecules, carbohydrates and macromolecules. The model described here offers a structure on to which large molecules can be mapped in order to offer insights into their interactions.

Keywords: Water structure; Low-density water; Water clusters; Amorphous water; Icosahedral network

1. Introduction

Water is the most abundant substance on earth and has been very well studied with a number of model structures having been proposed and refined. Notwithstanding this, it remains an anomalous liquid where no single model is able to explain all of its properties [1]. In particular, successful models must encompass the radial distribution function, the pressure–viscosity and temperature–density behaviour 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

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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 [4–6]. In particular, they only show approximate agreement with the radial distribution functions and have difficulty explaining the position and size of the 3.5-Å peak [3,7]. A number of interstitial models have been described based on dodecahedra [8] or the ice 1h structure [9,10]. 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] or equilibrium between structural components containing hexagonal, pentagonal and dodecahedral water arrays [15]. A review outlining the relationship between liquid, supercooled and low-density amorphous ice (LDA) has appeared recently [16].

Whilst the molecular movements within liquid water require the constant breaking and reorganisation of individual hydrogen bonds on a picosecond timescale, it is thought that the instantaneous degree of hydrogen bonding is very high ($> 95\%$, [13]) 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] and the formation and properties of low density water in gels [4].

A random network model has been described for LDA [19] and supercooled water [20]. However, the entropy of LDA is much lower than can be explained by this model [21]. Several workers suggest that the structure of liquid water should be related to ice structures [6,22], although this structure must be significantly different due to the ease with which water supercools and its high heat of fusion. Recently, a two-state network model including ice 1h and ice II substructures, locally rearranging on a picosecond timescale, has been used to explain many of the properties of water [23]. Although attractive, this model leaves some questions unanswered, such as the pressure requirement for the extensive ice II cluster formation necessary to achieve the density of water and the required number of non-bonded close contacts. Other workers have used less explicit two-state models possessing high and low density components to explain the properties of supercooled water [24] and the pressure-dependent growth of the 3.5-Å peak in the radial distribution function [25].

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

In this paper a structural model for water is proposed that both builds on, and is consistent with, 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.

2. Methods

Molecular model building and dynamics were performed using the Hyperchem 5.11 (Hypercube Inc., Ontario, Canada) molecular modelling package. In order to obtain the co-ordinates, the network was optimised using the AMBER force field with special parameters (O···O stretch 28 kJ mol^{-1} Å^{-1}, O···O distance 2.84 Å; O···O···O bend (k_θ) varying close to 4 kJ mol^{-1} rad^{-2}, from 109.47°; van der Waals $r^* = 3.536$ Å, $\varepsilon = 0.636$ kJ mol^{-1}, hydrogen atoms were not treated explicitly, being placed such that each oxygen has two near and two far hydrogen neighbours after model building was completed). These parameters were chosen as reasonable to create the model but were not critical. All data reported are derived from structures with average O···O and O–H nearest neighbour distances of 2.82 Å and 0.96 Å, respectively.

3. Results and discussion

The network is based on the regular arrangement of 14-molecule units (Fig. 1). Twenty of these slightly flattened tetrahedral units, together containing 280 molecules of water, form a 3-nm diameter icosahedral structure (Fig. 2a); small differences in geometry throughout being taken up by bonding flexibility. This is managed by each of the four tetrahedral chair-form hexameric faces forming three hydrogen bonds to neighbouring units, so creating structural units identical to the cell of hexagonal ice (Fig. 3a). Each tetrahedral edge forms a fifth part of two 15-membered pentagonal boxes made up from five boat-form hexamers (Fig. 3b). In forming these links, eight-membered structures are formed on each edge near the vertices (Fig. 3c). At its vertices each tetrahedron donates one molecule to the formation of a dodecahedron (Fig. 3d). Although such a

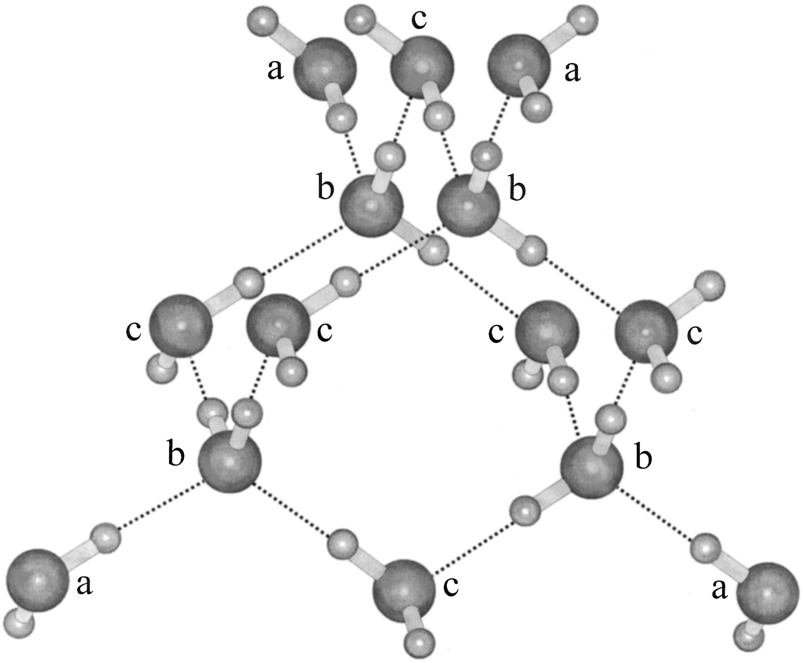

Fig. 1. The arrangement of 14 water molecules within a slightly flattened tetrahedral unit; three edges are 5% shorter than the other three. The three different environments for the water molecules are labelled a–c. The water molecules labelled (a) form the corners of the tetrahedron and are involved in both boat-form hexamers and pentamers. The remaining 10 molecules form an adamantane-type ring structure, identical to a 10-molecule unit recently found in a crystalline supramolecular complex [32], and as found within the 18-molecule cubic ice cell. The four molecules labelled (b) are involved in both boat and chair-form hexamers and the remaining six (c) molecules in pentamers and boat and chair-form hexamers.

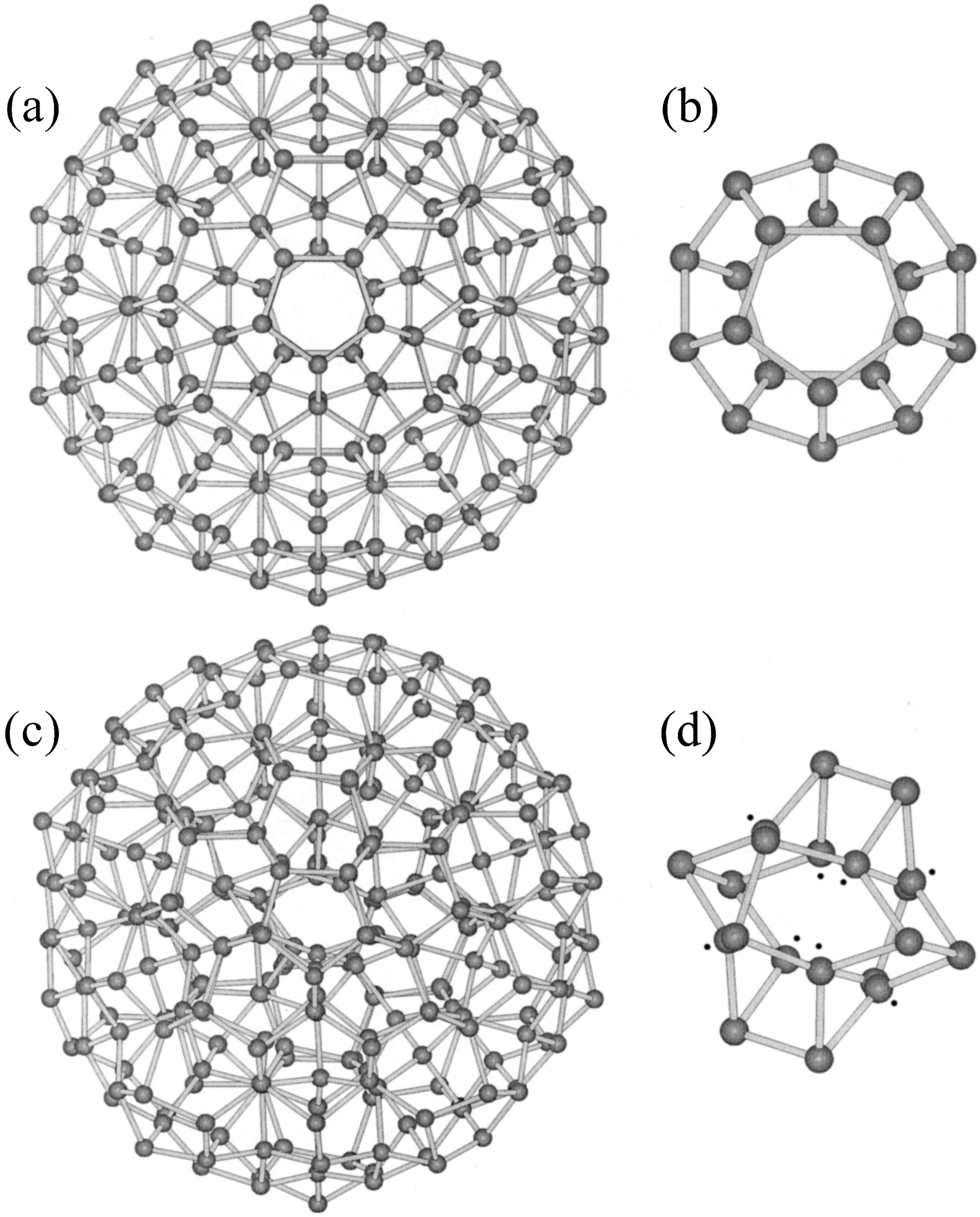

Fig. 2. (a) ES: 280-Molecule expanded icosahedral water cluster, as viewed down a water–pentamer lined axis through four pentagonal boxes and the central dodecahedron, shown separately in (b). Only the network of oxygen atoms is shown for clarity. (c) CS: The ES structure collapsed into the puckered central dodecahedron, shown separately in (d). The puckering, considered here, is symmetrical with 12 outer positions at 4.15 Å from the centre and eight inner ones (arranged at the vertices of a 3.14-Å cube and indicated by dots) at 2.71 Å from the centre.

cluster is capable of tessellation in three dimensions, albeit increasingly strained with increased size, it is incapable of forming a crystalline structure due to its fivefold symmetry.

Each 280-molecule icosahedron contains a variety of substructures with each water molecule being involved in four hydrogen bonds; two as donor and two as acceptor. Pentamers of water

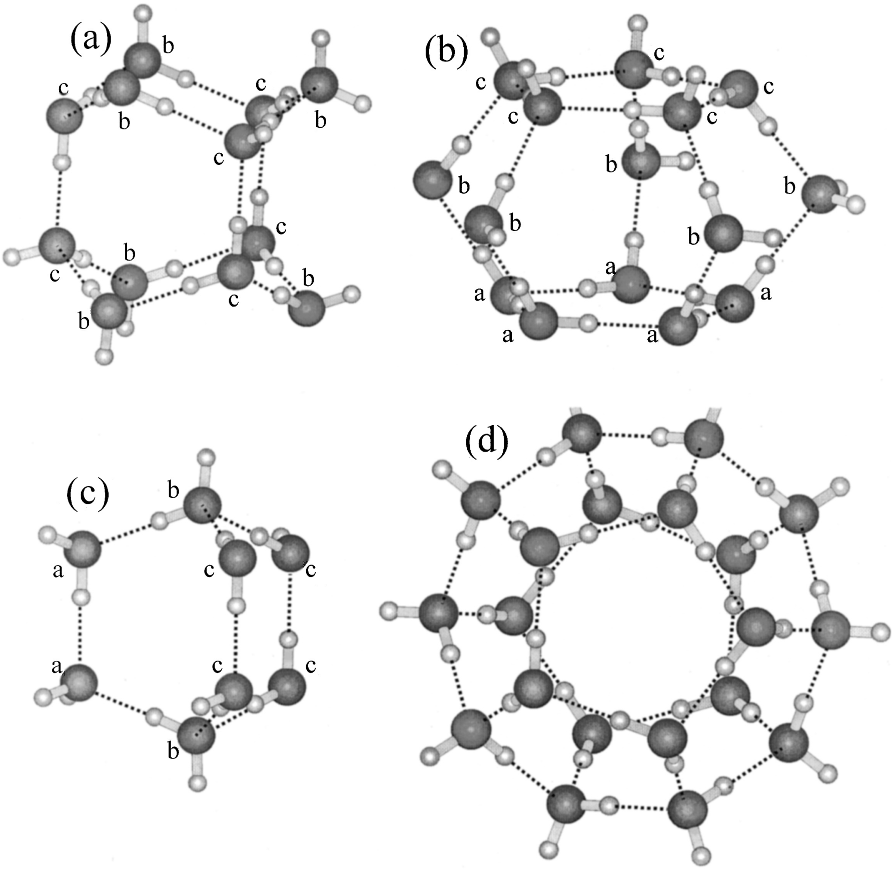

Fig. 3. Structural units formed within ES. Water molecule positions are labelled from the environments indicated in Fig. 1; (a) hexameric box formed by the faces of the tetrahedra; (b) pentagonal box formed by the edges using similar molecules from five tetrahedron edges, meeting at two pentagonal faces. Each tetrahedron unit has a fifth share in each pair of such units that form on each of its six edges; (c) eight-membered structure, arranged similar to the carbon atoms in bicyclo [2,2,2]octane and each containing three boat-form hexamers; (d) dodecahedron formed by the vertices of the tetrahedra (all molecules are type a).

have bond angles of 108°, which are 1.47° closer to the supposedly most stable H–O–H angle as evident in water vapour (104.52°) than are the tetrahedral angles (109.47°) in ice, which may strengthen the hydrogen bonding that forms the spines of the cluster. The clusters can tessellate in three-dimensions as each cluster has 12 potential sites at its icosahedral vertices for use as centres of neighbouring overlapping clusters. As the network grows the structure becomes more distorted. It is likely that this tessellation is achieved by the clusters flickering between different central dodecahedra; a theory in line with that of Luck [18], who used vibration data to suggest clusters of 240 molecules with relatively disordered boundaries at room temperature. Such network structures represent the time-averaged positions and are likely to be incomplete at higher temperatures. Full, if strained or imperfect, tessellation may be possible, as the TIP4P water model has been shown to form infinite four-coordinated hydrogen-bonded networks in low density supercooled water [33].

The stability of the network is finely balanced, being able to fluctuate between an expanded low density structure (ES, Fig. 2a) and a more dense collapsed one (CS, Fig. 2c) without breaking any hydrogen bonds and consequent on small changes in the hydrogen-bond strength relative to the non-bonded interactions. Using a k_θ of 3.68 kJ mol^{-1} rad^{-2} in the model, the central dodecahedron is fully expanded, and the standard deviation of the angles about the tetrahedral angle is 1.3°. Reducing the k_θ by 1% to 3.64 kJ mol^{-1} rad^{-2} (here used as a mechanism to mimic a slight reduction in the relative strength of the hydrogen bonding) causes the central dodecahedron to pucker inwards and increases this standard deviation to 13.6° about a mean of 108°. The expanded structure (ES, Fig. 2a) with central convex dodecahedra (Fig. 2b) is formed when stronger hydrogen bonds are present. This may occur because of the presence of structuring solutes or surface interactions. If the hydrogen bonds are weaker such that non-bonded interactions are more important then the cluster forms the partially collapsed structure (CS, Fig. 2c) due to the formation of puckered dodecahedra (Fig. 2d). As there are five equivalent ways that the central dodecahedron can pucker, the actual CS structure will be a fluctuating mixture of interconverting puckered forms with similar radial distribution functions. The density of ES is 0.94 g cm^{-3} and that of CS, 1.00 g cm^{-3}. The former may be compared with the density of low density water found around macromolecules [4] at 0.96 g cm^{-3}, supercooled water (−45°C) at 0.94 g cm^{-3} and the density of low density amorphous ice (LDA) at 0.94 g cm^{-3} [30,34], whilst the latter compares with the density of water at 0°C of 1.00 g cm^{-3}. With appropriate parameters mimicking weaker hydrogen bonding or greater pressure, CS is capable of further collapse increasing this density. Collapse of all dodecahedral structures gives a density of 1.18 g cm^{-3} similar to that of high density amorphous ice (1.17 g cm^{-3}, [34]).

Although this model can explain the anomalous properties of water, so can other models. The strongest direct evidence for the model is the agreement with the radial distribution functions. The CS model was used to generate a radial distribution of the $O \cdots O$ distances. Fig. 4 compares this radial distribution function with that from the X-ray data at 4°C [9], which shows a great deal of fine structure. Although the peaks are in the same positions, they are less distinct in the X-ray data indicating the relative movements expected of a liquid. There are 16 peaks or troughs plus a further 34 inflections evident using the first derivative. All 50 positions show correspondence between the X-ray data and the calculated function for CS, except that between approximately 7.9 Å and 8.5 Å where only corresponding inflections are found for CS. However, if all 50 data are considered, the standard deviation of the differences is only 0.065 Å. There is also good correspondence with the $O \cdots O$ radial distribution functions derived from the neutron diffraction data (Fig. 5), although this shows less fine structures. The $O \cdots O$ radial distribution function using the SPC/E, PCC and TIP4P models for water [3] do not show the fine structure evident from the diffraction data but do show agreement with the structure of CS by giving second neighbour broad peaks at approximately 4.6 Å.

The 2.8-Å peak from CS shows the presence of 4.34 nearest neighbours where 0.34 of these are contributed by the shoulder evident at approximately 3.2 Å. This compares well with the reported 4.4 nearest neighbours as calculated from the diffraction data [8], which also includes the shoulder at 3.2 Å. The size of the 3.7-Å peak compared to the 2.8-Å peak (0.69:4) from CS is close to that required from the radial distribution function (Fig. 4). It is also possible that very weakly hydrogen-bonded molecules may occupy a small number of the interstitial sites. If only 1% of the water molecules occupied such sites, which is well within the 5% limit [13] possible, this peak would increase by approximately 50% due to multiple interactions. The presence of pentagons increases the number of second-neighbour distances, at between 4 and 5 Å, to first-neighbour distances in the ratio of 13.4:4 in contrast to the 12:4 ratio in ice 1h or ice 1c based structures and the substantially lower ratio in two-state structures containing ice II [22].

The radial distribution functions of $O \cdots H$ and $H \cdots H$ distances can be calculated from the model (Fig. 5). This is less useful for testing the model, however, due to the lack of detail in the neutron scattering data, its variability between laboratories, the higher temperatures used (25°C), the presence of D_2O and the necessary, but possibly

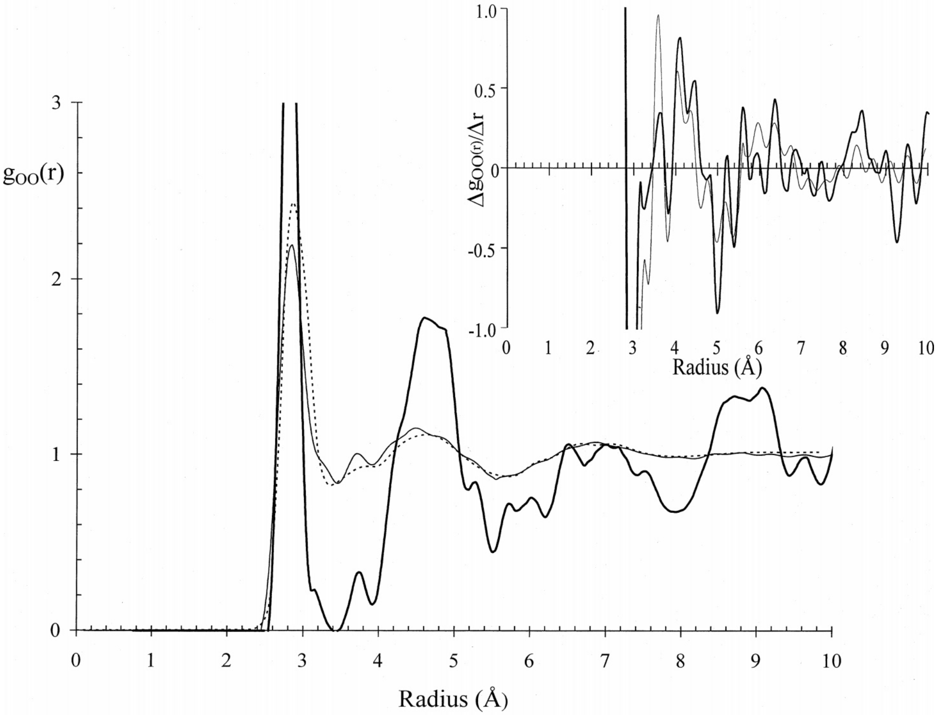

Fig. 4. Comparison of the calculated O ··· O radial distribution function of CS (———) with the X-ray diffraction data of water [9] at 4 °C (———). The model peaks have been broadened using a normal distribution with a standard deviation of 0.1 Å. The radial distribution of oxygen atoms, as determined by neutron scattering, is also shown [35] (- - - -). The validity of this neutron diffraction data has recently been confirmed [36]. The first derivative of the data is shown in the top right; that from the diffraction data has been scaled ×5.

misleading, assumptions that must be made when calculating from the model that the hydrogen bonds are linear and all hydrogen-bonding arrangements are equally probable. However, the model gives H ··· H peaks at 2.35 Å, 3.9 Å and 4.6 Å with a small peak at 2.9 Å and O ··· H peaks at 1.85 Å and 3.3 Å with smaller peaks at 4.55 Å and 5.25 Å similar to published data [17,35,37].

Support for the structure of ES comes from its agreement with radial distribution functions of solutions, supercooled water and LDA. The cavity–cavity distribution function of supercooled water peaks at 5.5 Å [38] and the neon–neon distribution function in water peaks at 6 Å [38]. Both values are close to the cavity–cavity distribution function peak of ES at 5.4 Å. The radial distribution function of ES around its centre consists of a number of spherical shells surrounding a dodecahedral cavity, where structure-forming ions or solutes may reside. The radius of this dodecahedron is 3.94 Å, agreeing with the minimum cage radius found [39], at 3.9 Å.

There are many examples of the formation of dodecahedral clathrates in aqueous solutions [26,27]. Such cavity formation is easy in water, increasing the strength of hydrogen bonding in their neighbourhood [31]. The Hofmeister series, whereby ions affect the stability of proteins in solution by either creating or destroying the structure of water, may be explained in part by how well the ions may sit passively in the dodecahedra, stabilising ES, relative to how strongly they create their own environment [40]. Cations that stabilise proteins in solution also create low-density water [29]. The tetramethylammonium ion is most effective [29] and its effect on the structure of water has been investigated. In ES, expansion of the inner cavity to a radius of 4.60 Å, due to

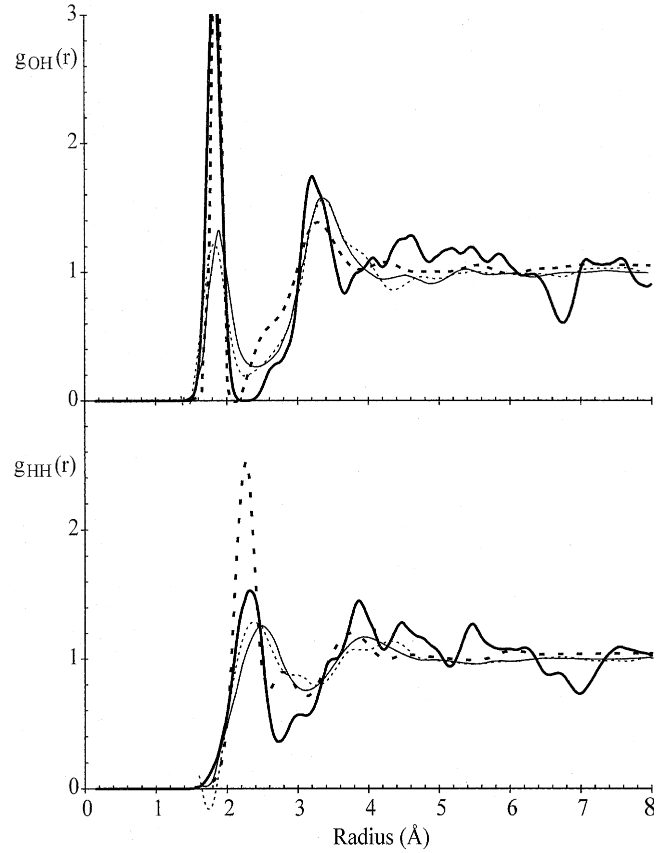

Fig. 5. Comparison of the calculated O ⋯ H and H ⋯ H radial distribution functions of CS (———) with the neutron diffraction data of water; (- - - - -) [35], (·······) [17], (———) [37].

charge or steric effects, causes the next two shells in ES to expand to 7.23 Å (smaller peak) and 8.13 Å (larger peak). These three peaks may be related to those found at 4.6 Å, 7.2 Å (smaller peak) and 8.2 Å (larger peak) around the tetramethylammonium ion of 0.5 M TMA^+Cl^- in D_2O [39], as the 4.6-Å radius for the dodecahedral cavity is only slightly larger than half the sum of the TMA ion (5.8 Å) [39] and water molecule (2.85 Å) diameters. The ES structure provides approximately 1.4 dodecahedral sites per molecule for a 0.5 M solution. When higher concentrations of TMA^+Cl^- were used, demanding more dodecahedral sites than can be provided by ES, the neutron diffraction peak detail was lost. In solutions of TMA^+Cl^-, the chloride had a co-ordination number to water of 5 and the $TMA^+ \cdots Cl^-$ distance was 5.3 Å [39]. Both agree with the chloride ion sitting asymmetrically in the nearest pentagonal box to a TMA ion situated within a dodecahedron, as this gives a co-ordination number of 5 to a dodecahedral face and a $TMA^+ \cdots Cl^-$ distance of 5.34 Å, given a $H_2O \cdots Cl^-$ distance of 3.24 Å. This study [39] also showed little effect of the salt on the structure of water despite the presence of water dodecahedra, which strengthens the argument that such dodecahedral structures are present in pure water. At high salt concentrations where more than one dodecahedral site is required per 70 water molecules, further sites may arise from tessellated, if distorted, dodecahedra (five water molecules per dodecahedron site) or a tessellated structure formed from dodecahedra separated by single pentagonal boxes

(25 water molecules per dodecahedron site). Microwave dielectric relaxation measurements have indicated a critical behaviour of water at a mole fraction (x_w) of 0.83 [6]. Although this can be explained by tessellated water dodecahedra which have the required number of interstitial sites per water molecule ($x_w = 0.83$), it is also close to the number of large interstitial sites available in the icosahedral water cluster ES ($x_w = 0.84$).

The radial distribution functions of ES show similarities to those of LDA. Both include features similar to cubic and hexagonal ices [41]. Neutron diffraction data have been used to suggest the presence of pentamers, boat and chair hexamers and partial dodecahedra [42]. LDA gives an O···O radial distribution function with peaks at 2.79, 4.56, 6.95 and 8.60 Å from X-ray data [43] whereas the ES gives peaks at 2.80, 4.57, 5.38, 7.06, 7.93, 8.88 and 9.16 Å which reduce to just four peaks at 2.8, 4.6, 6.7 and 9.0 Å, on Gaussian broadening, showing close agreement. The neutron diffraction data [20] gives peaks at 1.8, 2.3, 3.3 (shoulder), 3.8, 4.6, 5.2 (shoulder), 7.7, 8.4 and 9.1 Å and troughs at 2.7 and 6.4. Å. This compares favourably with the calculated distribution function from ES, which gives peaks at 1.8, 2.3, 3.2, 3.8, 4.6, 5.3, 7.3, 8.0 and 9.2 Å and major troughs at 2.8 and 6.8 Å. This material is the same density [34] as ES and may bear some relationship to it, particularly as clusters with icosahedral symmetry cannot form crystals and therefore must form amorphous solids. The sharp transition between the puckered and non-puckered water clusters seen in the molecular mechanics optimisations may be the cause of phase transitions found by some in supercooled water [44,45]. An ordered arrangement of cavities has been proposed from the diffraction data of LDA [30], also in agreement with the ES model. It has been reported that the entropy of LDA is only a sixth of that than can be explained from a random network model [21] but in good agreement with the much more ordered ES (Fig. 3a). A Raman spectral study of LDA showed the presence of at least two, or possibly three, distinct species [46] in line with three in the ES model (see Fig. 1).

In this paper, clathrate-like structures are proposed as being part of the normal structure of water, albeit in a mainly puckered state at ambient temperatures. Shear viscosity and self-diffusion studies have demonstrated the existence of high concentrations of clathrate-like structures in supercooled water [47]. In particular, water was shown to diffuse through many hydrogen-bonded water pentagons, such as occur through the spines of ES (see Fig. 2a), where all water molecules line pathways of large cavities (see Fig. 3b), separated by pentagons.

Vibrational spectra have shown the presence of both large clusters (n approx. 240) [18] and water pentamers [48] in agreement with CS. Puckering of the pentamers was found to increase with temperature [48]. There are a number of facts that support the presence of some very bent weaker hydrogen bonds in the structure of water. These include the high ice-water energy of fusion, which has been suggested as due to the distortional weakening of a proportion of the hydrogen bonds, and the vibrational Raman spectra [35] that indicates a range of weaker hydrogen bonds. It has been proposed that the observed heat of fusion (6.0 kJ mol^{-1}) is due solely to an increase in bond bending going from ice to water [49]. The average root mean square distortion occurring in CS is 13.7°, which gives a value very close (5.2 kJ mol^{-1}), and also agrees with the 16° distortion estimated from the 600-cm^{-1} libration band [47].

The minimum number of possible arrangements of hydrogen bonds in the fully occupied low density icosahedral network (ES) is $2^{130} \times 7^{12}$ ($= 1.50^{280}$) as determined during the molecular building. This is in agreement with the minimum entropic factor expected of 1.5 structural variations per molecule [8].

The anomalous temperature-density behaviour of water can be explained as previously [13,14] utilising the range of environments within whole or partially formed clusters with differing degrees of dodecahedral puckering. The density maximum is brought about by the opposing effects of increasing temperature, causing both structural collapse that increases density and thermal expansion that lowers density. At lower temperatures there is a higher concentration of ES whereas at higher temperatures there is more CS, but it expands with temperature. The change from ES to CS as the temperature rises is accompanied by positive changes in entropy and enthalpy due to the less ordered structure and greater hydrogen-bond bending respectively. Water's pressure–viscosity behaviour can be explained by the increased pressure causing deformation, so reducing the strength of the hydrogen-bonded network, which is partially responsible for the viscosity. Such ease of deformation, due to the presence of the large cavities, also explains water's anomalously high compressibility and the growth in the peak at approximately 3.5 Å with increasing temperature [50] or pressure [51], due to the collapsing structure.

The proposed structure fits the theory of how sugar molecules interact with water, based on anisotropic ice 1h-type interactions [5,52], but allows sugars a wider range of orientations. Thus, in a solution of scyllo-inositol, each hydroxyl group can not only donate a hydrogen bond but also accept one so long as it is situated in one of the 80 chair-form hexagonal sites with different orientations within each 280-molecule cluster. ES may form a major part of the low-density water reported to form in gels and at the surface of some macromolecules [4] where an orientation effect may be expected to strengthen the hydrogen bonding in the water.

The basic expanded network structure of the cluster is mechanically strong, having close to tetrahedrally-positioned bonds, and could be found in the, as yet undiscovered, alkane $C_{280}H_{120}$.

The model described here offers a structure, not possible with other models such as a random network [19] for LDA, on which large molecules can be mapped in order to investigate their interaction with water within a three-dimensional hydrogen-bonded network, and should offer new insights into the ways macromolecules interact with each other in aqueous solution.

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