

## Chapter 1: The Structure of Liquid Water

### 1.1 The Water Molecule

In the isolated water molecule, two hydrogen atoms are associated with the two of four  $sp^3$  hybrid electron pairs of an oxygen atom. Two other  $sp^3$  hybrid electron pairs are left as lone pairs. The formation of the  $sp^3$  hybrid orbitals from the atomic orbitals of an oxygen atom and the tetrahedral arrangement of these orbitals are shown in Figure 1.1. In a perfect tetrahedral arrangement the bond-bond, bond-lone pair and lone pair-lone pair angles would all be  $109.47^\circ$ , which can be observed for example in hexagonal ice ( $I_h$ ) (Eisenberg and Kauzmann 1969). However in an isolated water molecule, the bond-bond angle is reduced to  $104.5^\circ$  due to the repulsion of lone pair electrons.

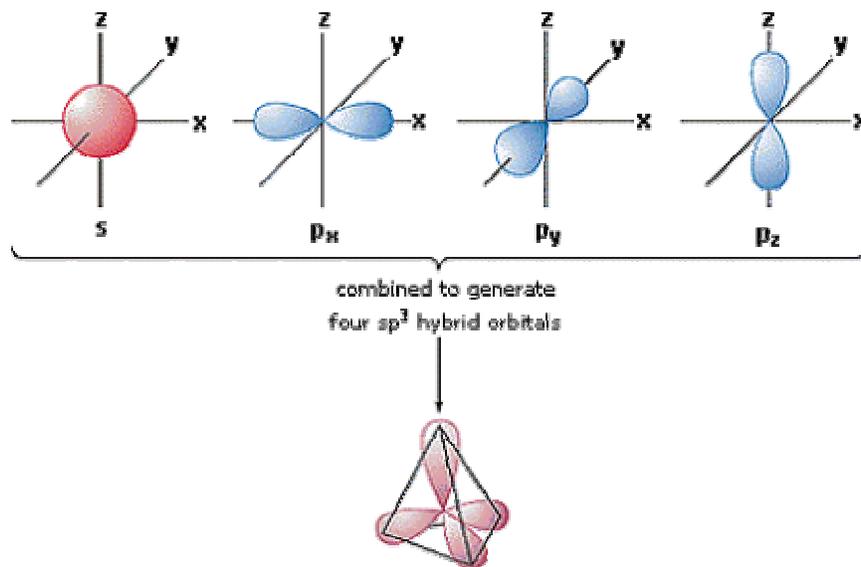


Figure 1.1: Formation of the  $sp^3$  hybrid atomic orbitals on the oxygen atom of a water molecule.  
Reproduced from <http://www.chem.msu.edu/~reusch/VirtualText/intro3.htm>

The O-H bonds in a water molecule have a polar character. This is because the oxygen atom has a higher electronegativity ( $\chi_{\text{O}} = 3.5$ ) than the hydrogen atom ( $\chi_{\text{H}} = 2.2$ ). As a result, negative partial charging of the oxygen atom and positive partial charging of the hydrogen atoms occurs. This partial charging is important for the hydrogen bonding of water molecules. Besides the electrostatic contribution, there are other contributions to the hydrogen bonding. These are the contribution from the molecular orbital interactions, and the contribution from the delocalization of the proton in the double minimum potential well of an H-bond.

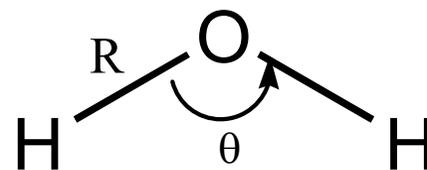


Figure 1.2: The O-H bond length and the H-O-H bond angle in a water molecule:  $R = 0.9584 \text{ \AA}$   $\theta = 104^{\circ}27'$ .

Two important features of the hydrogen bond are that it possesses direction and linearity. By convention the direction of the H-bond is from the shorter covalent bond to the lone pairs of neighbouring oxygen atom (O-H  $\cdots$  O). This means the oxygen atoms act as H-bond acceptor with their lone pairs and the H atoms act as H-bond donors with their partial positive charges ( $\delta^+$ ). Accordingly, the O-H hydrogen atom of a covalent bond is donated to the oxygen atom of another water molecule, in forming an H-bond. The linearity of the H-bond means that the hydrogen atom generally lies on the same line that connects two oxygen atoms. Therefore, the O-H $\cdots$ O bond angle is  $180^{\circ}$  in an ideal H-bond having symmetric double minimum potential.

The strength of an H-bond varies in a wide range for different interacting molecules (e.g. HF, HBr, NH<sub>3</sub>) and in different environments. The zero point corrected H-bond energy ( $E_{\text{H}}$ ) in the **water dimer** is 4.85 kcal/mole (Keutsch and Saykally 2001) and the length of the O-H $\cdots$ O distance is 2.952 Å. In **liquid water**, the H-bond energy may vary according to the interpretation of the H-bonding interaction. Several factors that are considered are the orientation and position of other H-bonded and non-bonded molecules around the central one, and the cooperative effects associated with the coordination of H-bonding molecules (Frank 1958; Nemethy and Scheraga 1962). In addition

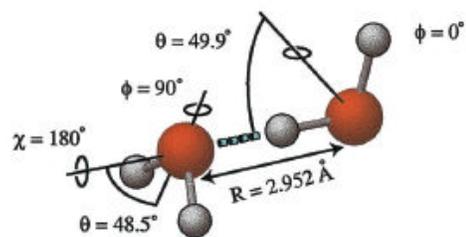


Figure 1.3: The equilibrium structure of the water dimer. The hydrogen bond deviates  $2.3^{\circ}$  from linearity; the O $\cdots$ O distance is 2.952 Å. After (Keutsch and Saykally 2001)

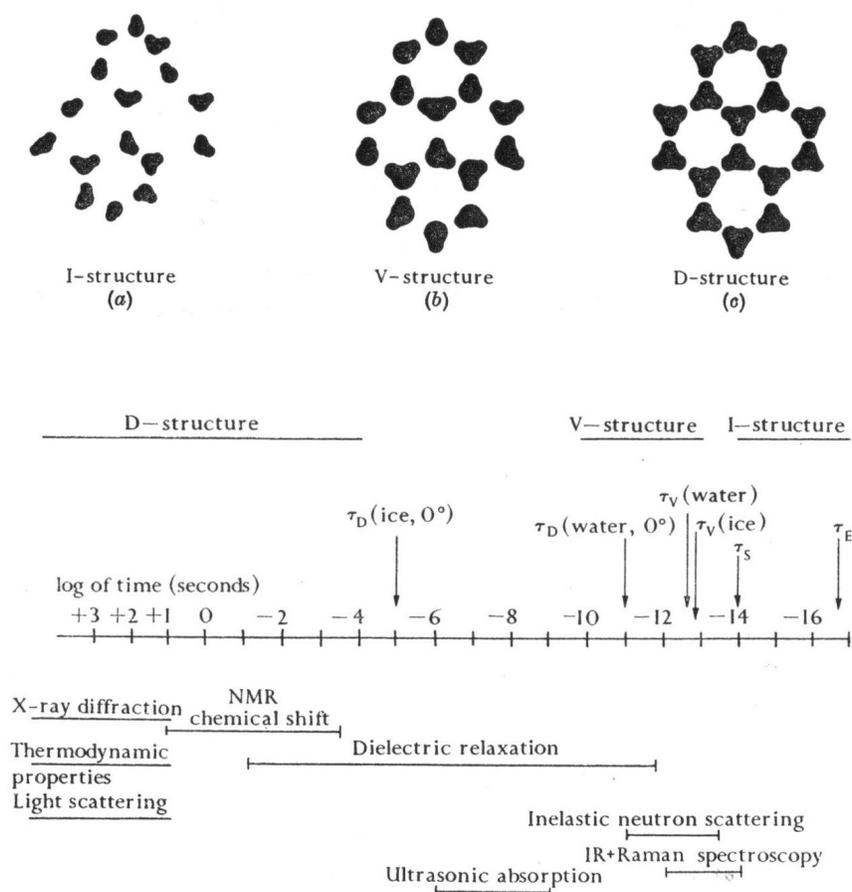
both the bond length and the bond angle vary slightly with temperature (Eisenberg and Kauzmann 1969; Dougherty and Howard 1998). The H-bond strength in liquid water is calculated to be 1.32 kcal/mole by Nemethy and Scheraga (Nemethy and Scheraga 1962).

### 1.2 The Structure of Liquid Water

The structure of liquid water and its dynamics are mostly determined by H-bond rearrangement. The unique properties of liquid water such as high melting and boiling points, high specific heat, the density maximum and the negative thermal expansion coefficient is a result of significant hydrogen bonding and the intermittent dynamics of H-bonded network structure (Chaplin 2007); (Stanley, Buldyrev et al. 1998).

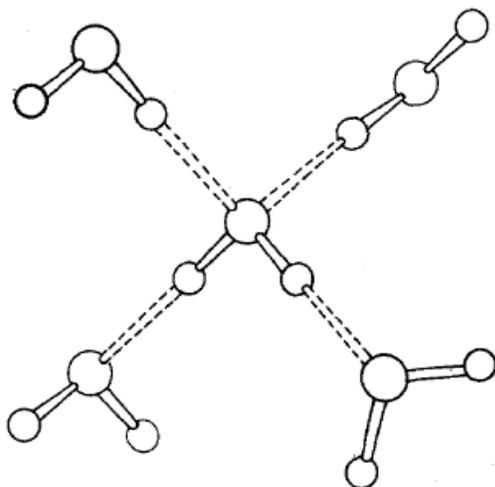
According to Eisenberg and Kauzmann (Eisenberg and Kauzmann 1969) water has instantaneous (I), vibrational (V) and diffusional (D) structure corresponding to different time domains of observation (see also Figure 1.4). The orientations of the molecules in the I-structure are the result of random vibrational motions. Averaging the vibrational motions in a short-time scale would lead to a snapshot of tetrahedral arrangement of water molecules. This is called as V-structure. Waiting for longer times, one obtains the diffusional-averaged D-structure. The D-structure in ice will be a clearer picture of the tetrahedral arrangement of water molecules. In liquid water, the D-structure will be blurred due to the rapidly diffusing water molecules.

The I-structure of water has been investigated in a recent X-Ray absorption study (XAS) by Wernet et al (Wernet, Nordlund et al. 2004). This method involves the excitation of core electrons of a water molecule to the unoccupied molecular orbitals in the valence shell. The energies required for such excitations are sensitive to the local environments of water molecules within the lifetime of an electronic excitation ( $\leq 10^{-15}$  s). Therefore this method gives information on the instantaneous structuring of water in sub-femtosecond time scales (Chaplin 2007). According to their results, Wernet et al suggested that 80 % of the water molecules of ordinary liquid water have one strong bonded O-H group and one weakly bonded O-H group. The remaining 20 % are tetrahedrally coordinated.



**Figure 1.4:** The illustration of the instantaneous (I), vibrational (V), and the diffusional (D) structure of ice; and the time scales of molecular processes in ice and liquid water.  $\tau_D$  and  $\tau_V$  are the periods for molecular displacement and oscillation.  $\tau_S$  is the period for an O-H stretching vibration and  $\tau_E$  is the time required for an electron to complete one circuit in the innermost Bohr orbit. The horizontal lines below the time scale show the time intervals for which various experimental techniques have yielded information on ice and water. After (Eisenberg and Kauzmann 1969).

Saykally et al (Smith, Cappa et al. 2004; Smith, Cappa et al. 2006) have also analyzed the spectral features of liquid water near the O (1s) ionization edge (these are being the pre-edge region ( $\sim 535$  eV) and post-edge regions ( $\sim 541$  eV)). They concluded that the large population of broken-donor bonds found by Wernet et al could actually be the distorted H-bonds in the local tetrahedral structure of liquid water. They also presented calculated X-Ray Absorption Spectra XAS for 11 molecule clusters and configurations taken from MD simulation with symmetric (SPC/E) and asymmetric potentials (SAP). These spectra, when compared with the experimental XAS and Raman Spectra, show that the rings and chains model for liquid water suggested by Wernet et al is incompatible.



**Figure 1.5: Average orientations of near neighbour molecules in liquid water. Large local and instantaneous deviations from the above given configuration and a distribution of H-bond angles about the mean value of  $180^\circ$  is noted.**  
After (Narten 1972)

Narten 1972; Bosio, Teixeira et al. 1981; Chen, Teixeira et al. 1982; Bellissent-Funel, Teixeira et al. 1987; Bellissent-Funel and Bosio 1995; Soper 2000).

These experiments revealed two important results: The first one is that there is a short range local order around a central molecule in liquid water, which resembles the local tetrahedral structure in ice. One can arrive at this result by comparing the radial distribution functions (rdf) of liquid water and ice, and by noting the match of the peak positions to a large extent.

On the other hand the total match of the diffraction patterns is not 100 %. Particularly the area under the first peak of the radial distribution curves differ in liquid water and ice. The average number of nearest neighbours calculated from these area for liquid water is found to be 4.4, which is larger than four. This result led to the second conclusion that there occur large local and instantaneous deviations from the average tetrahedral orientation in the first coordination shell of liquid water. In addition, the temperature induced Raman isosbestic points and the temperature and pressure induced structural isosbestic points from neutron and X-ray scattering experiments indicate an equilibrium between two different kinds of water species having different coordination environments (Robinson, Cho et al. 1999).

An open discussion that arises on the structure of liquid water is the explanation of apparent number of molecules being larger than four in the first coordination shell. Subject to different

Another recent experimental study on the I-structure of liquid water has been conducted by Compton scattering by Hakala et al (Hakala, Nygard et al. 2006). They have found 3.9 hydrogen bonds ( $R_{O-O} < 3.2\text{\AA}$ ) around each water molecules. The **V-** structure of liquid water is searched through infrared and Raman spectroscopy (Walrafen 1964; Walrafen 1967; Monosmith and Walrafen 1984; Mizoguchi, Hori et al. 1992; Lock and Bakker 2002), as well with X-ray and neutron scattering experiments (Morgen and Warren 1938; Danford and Levy 1962; Narten and Levy 1969;

points of views, various approaches are developed to describe the dynamics of an apparent **fifth water molecule**. These approaches led to continuum and mixture models of liquid water which will be discussed in detail in the following sections.

In addition to structural research, the thermodynamic and transport properties of liquid water, which are related to D-structure, have been studied covering a wide range of pressure and temperature (Dorsey 1940; Eisenberg and Kauzmann 1969; Franks 1973; Debenedetti 2003). The relaxation processes related to water dynamics is made known by NMR and dielectric relaxation techniques (Meiboom 1961; Hindman 1974; Price, Ide et al. 1999; Lock and Bakker 2002; Chen, Mallamace et al. 2006). On the other hand several authors formulated thermodynamic potential functions  $g(T,p)$  (also called fundamental equation of state) (Feistel, Wagner et al. 2005) and equation of states [such as  $p = p(\rho, T)$ ] (Jeffery and Austin 1999; Kiselev and Ely 2003) to calculate the thermodynamic properties of liquid water.

Finally the increase of computational power allowed molecular dynamics studies to become popular search tools for the investigation of structure and dynamics of liquid water. A large number of water potentials are developed, which are used to describe the interaction between pairs of water molecules in a molecular dynamics (MD) simulation. Currently, more than 40 water potentials are listed (Chaplin 2007). The commonly used ones are SPC/E, ST2 (Stillinger and Rahman 1974) and TIP4P. Valuable information were obtained through MD studies on the H-bond rearrangement, the defect dynamics and the relaxation processes in liquid water (Sciortino, Poole et al. 1990; Geiger and Mausbach 1991; Ohmine and Saito 1999; Paschek and Geiger 1999; Mazza, Giovambattista et al. 2006). Homogeneous nucleation of ice is also simulated to search for the mechanism of ice nucleation in supercooled liquid water (Matsumoto, Saito et al. 2002; Radhakrishnan and Trout 2003; Vrbka and Jungwirth 2006).

### 1.3 The Location and the Dynamics of the Fifth Water Molecule

X-ray diffraction experiments are used to obtain information on the local order of water molecules in liquid water. This information refers not to the instantaneous local ordering, due to relatively long times of probing the molecules in comparison to the timescales of diffusional motion and H-bond network rearrangement. However, it can be related to the vibrational structure by the ergodic hypothesis. This means that the D-structure is taken as the space average of all local V-structures that are simultaneously present in the liquid. In this way, the radial distribution function for water is treated as an average of radial distribution functions for several V-structures. The average number of nearest neighbours can be calculated from the area under the first peak of radial distribution curve. This gives a number gradually changing from 4.4 to 4.9 with the increase of temperature from 1.5 to 83 °C (Eisenberg and Kauzmann 1969).

Some important information that is revealed by the X-ray diffraction experiments are:

1. At room temperature the local order in liquid water does not extend beyond the second coordination shell of neighbouring molecules.
2. The radial distribution functions change gradually with temperature. With the increase of temperature the short range order extends less far. With decreasing temperature it is extended to somewhat longer ranges. At 200 °C,  $g(R)$  approaches to unity beyond 6 Å. In supercooled liquid water (at -25°C), the characteristic size of correlated regions reaches up to 8 Å (Bosio, Teixeira et al. 1981)
3.  $g(R)$  vanishes for  $R < 2.5$  Å indicating that the closest approach of molecules is 2.5 Å in liquid water.

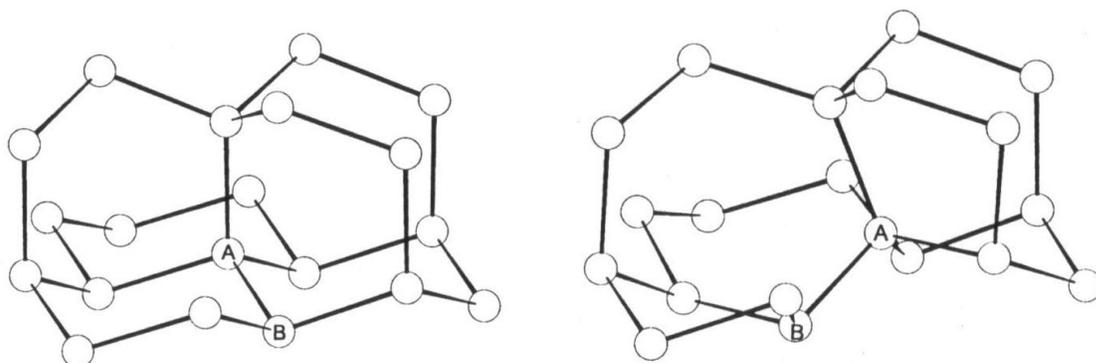
The average nearest neighbour number being calculated bigger than 4 is subject to many discussions on the structure of liquid water and the H-bond network arrangement. According to the continuum / distorted H-bond models (Pople 1950), apparent numbers of nearest neighbors greater than four arise from the superposition of the second and third neighbors as a result of bent H-bonds. In the random network models it is assumed that water consists of irregular network of H-bonded molecules that leads to 5- 6- 7- member rings. Similar to bent H-bond model, the

superposition of water molecules due to the random arrangement of H-bonded molecules is responsible from the apparent fifth water molecule in the first coordination shell.

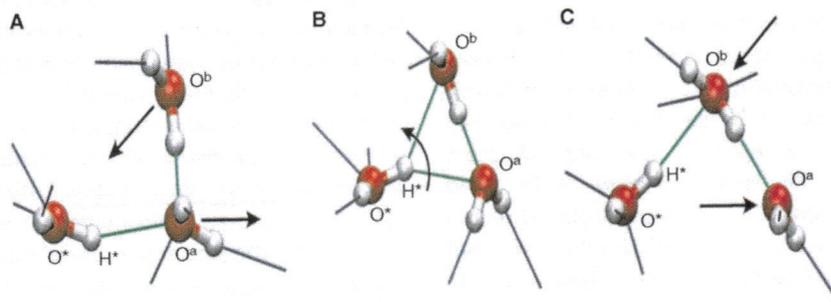
The common point of view of continuum and random network models is that the apparent fifth water molecule is a result of superposition and it is not truly described as a different species. In contrast, in the mixture models the fifth water molecule is treated as a distinct water species having different coordination environment. The mixture models -by the use of ergodic hypothesis- can fit calculated radial distribution curves to the experimental results (Danford and Levy 1962).

In a recent article of (Laage and Hynes 2006) the attention is brought once more to the continuum and bifurcated bond models in connection with the dynamics of a fifth neighbour molecule. Laage and Hynes suggested that a second hydration shell molecule acts as a fifth neighbour, in catalysing the H-bond exchange on the central molecule (see also Figure 1.6). They obtained this result from the interpretation of SPC/E-MD simulations. Their result supports the findings of Eaves (Eaves, Loparo et al. 2005) that broken H-bonds are unstable and survive for very short times. However, they were also criticised by Ludwig (Ludwig 2007) pointing out to the possible deficits of using a rigid water potential in explaining such rapidly occurring processes.

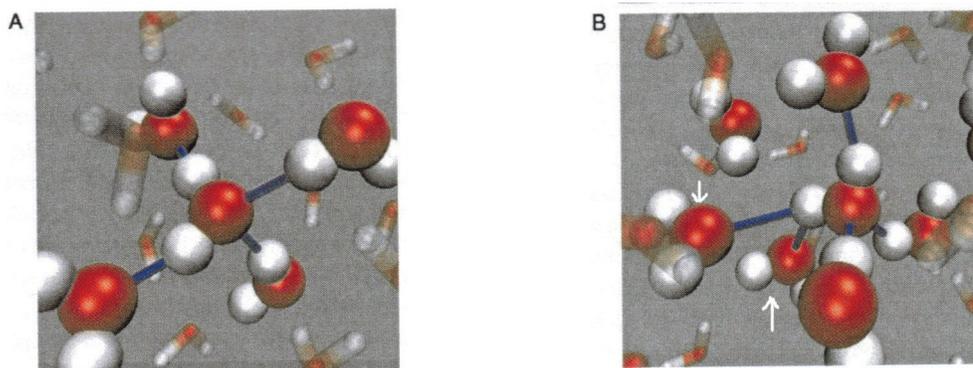
Whatever the model concerned, the presence of a fifth water molecule is necessary to be considered in explaining the molecular mechanism of defect formation and H-bond network rearrangement. It seems that the interstitial/mixture models and the random network/continuum models point out to different transient regimes of similar molecular reorientation processes in water. The interstitial models support the idea that broken H-bonds can survive through interstitial molecules before newer bonds are formed. The continuum/distorted bond models suggest that the fifth water molecule forms bifurcated-bonds before an H-bond exchange occurs. The bonds must not be broken before the exchange occurs. In this respect the interstitial models may refer to the more instantaneous step of molecular reorientation, which might not be seen in MD simulations. On the other hand, Formation of a bifurcated bond offers lower energy pathways for H-bond dynamics and molecular reorientations in liquid water. (Ohmine and Saito 1999; Paschek and Geiger 1999)



**Left:** A view of a piece of an ice- $I_h$ -crystal. Both the chair and boat conformation of oxygen atoms are seen. **Right:** Formation of five- and seven-member rings by the movements of molecules A and B. As a result, the lattice structure of ice is destroyed. Taken from Rehtanz (2000)(Rehtanz 1999)



The different steps of H-bond exchange mechanism according to Laage and Hynes (2006). The formation of a bifurcated bond between a water molecule and its second hydration shell neighbor is shown in **A** and **B**. The network is reconstructed in **C** with the exchange of first and second coordination shell neighbors.



**A:** Typical tetrahedral arrangement of a water molecule with linear H-bonds to four neighbours. **B:** In a bifurcated arrangement, one linear H-bond is replaced by two weaker H-bonds in the presence of an extra molecule giving an over coordinated configuration. (Five neighbors)  
Taken from Ludwig (2007)(Ludwig 2007).

**Figure 1.6: Illustrations of defect formation and molecular reorientation processes in ice and liquid water.**

### 1.4 Water Models – Historical Development

The evaluation of experimental data on the thermodynamic properties of liquid water and the interpretation of physical properties in relation to its structure require a water model. In this respect, a large number of water models have been introduced until now, which can be separated into two broad categories. These are the (a) **distorted hydrogen bond or continuum models** and the (b) **mixture/interstitial models**.

#### 1.4.1 The Continuum Models

The continuum models date back to (Bernal and Fowler 1933). From their X-Ray diffraction data Bernal and Fowler proposed quartz like network structure of tetrahedrally H-bonded water molecules. Pople (Pople 1950) extended the model by introducing “bent” hydrogen bonds. According to Pople, the melting of ice results in bending of the H-bonds instead of being broken.

H-bonds are never broken in the liquid according to the continuum models. In this respect, these models are very close to solid state. The rigidity of these models makes them insufficient to successfully explain all the physical and thermodynamical properties of liquid water. On the other hand the concept of distorted hydrogen bonds is not fully disputed, and often used to explain the several phenomena related to the dynamics of H-bonded systems.

Most modern interpretation of the continuum models were done by Stanley et al (Stanley and Teixeira 1980; Stanley and Blumberg 1983; Blumberg, Stanley et al. 1984; Sciortino, Poole et al. 1990). They proposed that liquid water is composed of a continuous gel-like H-bonded network above its percolation threshold. However, water can not behave like a gel. This is because the H-bonds are being broken and reformed very frequently with a very short characteristic time ( $\tau_{\text{HB}} \sim 10^{-12}$  s).

Stanley et al also assumed that the four bonded molecules are correlated and tend to come together forming clusters. In this way they were able to explain the reason of density fluctuations in liquid water. Their models can be regarded as mixture models, in line with this idea.

Finally (Dougherty and Howard 1998) performed a molecular dynamics study proposing that water structuring prevails different geometries in the random-structural network of liquid water, depending on the temperature. The equilibrium shifts in the dominant structures is attributed to the change of hydrogen bond length and energy as a function of temperature.

### 1.4.2 The Mixture Models

According to the common point of the view of the mixture models (Franks 1973), water consists of a well-ordered ice-like component and a second component having less order. Since density of liquid water is bigger than that of ice ( $\rho_{\text{liq}} > \rho_{\text{ice}}$ ), the second component should be “denser” than the bulky component.



The basic distinction between the mixture and continuum models is that the mixture models allow the presence of intact and broken hydrogen bonds (Ludwig 2001). There are different formalisms of the mixture models according to the interpretation of ice-like and dense species.

In the interstitial models, the dense water is described as water molecules being located in the caves of the ice lattice ( $I_{\text{h}}$ ) (Samailov 1956). A special case for the interstitial models is the clathrate hydrate formalism (Frank and Quist 1961), where bulk water is treated to resemble a clathrate network, and the dense water results from water species occupying the cavities of clathrates. The clathrate model worked well in explaining the solvation of hydrocarbons, which are partitioned to make interstitial solutions with bulk water, and regular solutions with dense water. However, it stayed weak at explaining thermodynamical properties of water, one of which is the heat capacity (Franks 1973).

Starting from 1960's statistical thermodynamic calculations had become a popular tool to calculate the physical and thermodynamic properties of liquid water. Some authors suggested that the properties of liquid water can be described by prevailing structures of H-bonded water clusters. Assuming discrete energy levels for each H-bonded species, these authors succeeded to

calculate the concentration of different H-bonded species and the prevailing structures in liquid water.

The significant structure theory applied to water by (Marchi and Eyring 1964; Jhon, Grosh et al. 1966), the band model of water by (Vand and Senior 1965), the statistical thermodynamic model of Nemethy and Scheraga applied to water (Nemethy and Scheraga 1962), liquid D<sub>2</sub>O (Nemethy and Scheraga 1964), aqueous solutions of hydrocarbons (Nemethy and Scheraga 1962), and aqueous solutions of alcohols (Laiken and Nemethy 1970) can be cited as examples to statistical thermodynamic evaluation of mixture models. (Eadie 1971) extended Nemethy and Scheraga's work to the homogeneous ice nucleation in liquid water. He estimated the free energy of ice-germ formation in supercooled liquid water and the surface contribution to this process.

Levine and Perram (Levine and Perram 1968) applied the statistical thermodynamic approach to the continuum model of liquid water. They calculated the fractions of 1-, 2-, 3-, 4- bonded and non-bonded water species, without making a *priori* assumption on the formation of clusters.

### 1.4.3 Nemethy and Scheraga's Statistical Thermodynamic Model

Nemethy and Scheraga's statistical thermodynamic model (Nemethy and Scheraga 1962) is widely quoted among the early mixture models that are used to describe the thermodynamic properties of liquid water. These authors assumed that water is composed of "small, near-spherical" clusters, which mostly have tridymite like or similar structure, and non-bonded water molecules filling in the space between spherical clusters.

According to this scheme, the interior of the clusters contain water molecules having four hydrogen bonds. Three-, two-, and one-hydrogen bonded species can be found on the periphery of the clusters. Finally, the molecules occupying the space between clusters have no-hydrogen bonds. Functional forms were obtained to describe the relative amounts different H-bonded species, by counting and averaging over the clusters in the range between 12 and 150 water molecules.

Nemethy and Scheraga provided a canonical partition function, to calculate the mole fractions of different H-bonded species and the average cluster size in liquid water. They assumed the energy is partitioned according to the H-bonding state of molecules. Discrete energy levels and equal energy spacing were assumed for the four-, three-, two-, one- hydrogen-bonded, and non-bonded water molecules. The ground state is assigned to the 4-bonded molecules. In addition “cell-type”<sup>1</sup> molecular partition functions for translational, rotational and vibrational motions specific to five different molecular species were introduced. Intermolecular vibrational frequency assignments are made according to the H-bonding state of molecules, and based on the comparison of infrared and Raman spectra of water and ice.

The cluster sizes and mole fractions of the species at different temperatures are found by equating the canonical partition function to the maximum term, and solving for the necessary parameters, which are the size of clusters, the fraction of non-bonded molecules, and fraction of the surface molecules that interact with non-bonded molecules to increase their H-bonding state. The results of Nemethy and Scheraga have shown that the average size of four-bonded clusters in liquid water reach up to 90 near the melting point of ice. These results had also explained the temperature dependence of internal energy, entropy and molar volume with a good match to the experimental results. On the other hand a poor match is obtained for constant volume heat capacity  $c_v$ .

### 1.4.4 Modern Theories on the Structure of Liquid Water

Both the continuum and the mixture models had been modified and improved constantly to favour the experimental data for the properties of water. At the point that is reached on the knowledge of structure and behaviour of liquid water, there is a continuous transition between the two extremes of continuum and mixture model views (Ludwig 2001). This perceptive is best described by Stanley et al in the following way (Blumberg, Stanley et al. 1984) :

...depending on which question to be asked, either viewpoint can emerge... For example, measurements like neutron scattering experiments, designed to

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<sup>1</sup> All second and higher neighbor interactions, all correlations of the motions of molecules are neglected.

investigate the average microscopic structure of liquid water, will favour the continuum picture, whereas the measurement of fluctuation-determined thermodynamic properties like the compressibility or heat capacity will be explained by the presence of structured patches.

With the development of experimental techniques and methodology, it is now possible to collect reliable data on the structure of liquid water, also in the deeply supercooled region (Torre, Bartolini et al. 2004; Chen, Mallamace et al. 2006; Souda 2006). In the light of current experimental data, it is proposed that liquid water consists of low density regions (LDL), where well-ordered, ice-like structure dominates, and high density regions (HDL), which have less ordered structure, mostly having interstitial/fifth water molecules. The presence of these regions with different densities in supercooled liquid water are also revealed by X-Ray and neutron scattering experiments (Mishima, Calvert et al. 1984; Bellissent-Funel, Teixeira et al. 1987; Bellissent-Funel 1998; Robinson, Cho et al. 1999).

Temperature dependent equilibrium exists between LDL and HDL structures. With the effect of decreasing temperature this equilibrium starts to favour the LDL structures. As a result the extent of local order, which arises from highly coordinated water molecules, increases. It is also shown that LDL/HDL equilibrium couples to the dynamics of homogeneous ice nucleation (Kabath, Stöckel et al. 2006).

Besides its structure and thermodynamic properties, another point of interest is the dynamic behaviour of liquid water. Water has anomalous dynamic behaviour, which becomes more significant, particularly in the supercooled region with decreasing temperature. It is first discussed by Speedy and Angell (Speedy and Angell 1976; Angell 1983) that water has a singularity behaviour at a temperature of about  $T_s = -45$  °C. These authors based their reasoning on the observed diverging behaviour of several thermodynamic and transport properties of supercooled liquid water near  $T_s$ . Therefore they proposed that approaching  $T_s$  from the side of supercooled liquid water, water becomes mechanically unstable: Its thermodynamic and transport properties diverge in a power-law behaviour, and become discontinuous at  $T_s$ . Indeed,  $T_s$  is dependent on pressure and there exists a pressure-dependent spinodal line  $T_s(P)$ .

Above view is at present called as “**Stability Limit Hypothesis**”. It was the first attempt to explain the nature of anomalous behaviour of supercooled liquid water. However it was a “purely dynamic model”, and was not sufficient enough to account for the “rich and anomalous thermodynamic behaviour” observed in metastable phases of supercooled liquid water (Torre, Bartolini et al. 2004). That’s why other models such as “**Liquid-Liquid Phase Transition Hypothesis**” (Mishima and Stanley 1998) have been developed. The second critical point phenomena, that is proposed according to the phase transition hypothesis gives the basic inspiration to the current view of LDL /HDL mixture model of liquid water.

### 1.5 Supercooled Liquid Water

Supercooled liquid water attains more ordered structure that is similar to ice, with the decrease of temperature. Consequently, the number of broken hydrogen bonds is reduced, and the four-bonded water molecules become more concentrated. Besides, the decrease in the density and the increase in the viscosity points out to the increasing extent of four-bonded ice-like domains in the liquid. Therefore the ice-likeness of water increases at high degree of supercoolings (Rasmussen and MacKenzie 1973; Pruppacher 1995).

Several stable and metastable phases of supercooled liquid water and glassy water is shown in Figure 1.7 in relation to the “Second Critical Point” (or equivalently called as Liquid-Liquid Phase Transition) hypothesis. As seen in Figure 1.7, the homogenous nucleation temperature  $T_H$  of liquid water occurs at  $-35\text{ }^\circ\text{C}$  at atmospheric pressure. Homogeneous nucleation rates of liquid water has a very strong temperature dependence; therefore a few degrees below  $T_H$  liquid water freezes very rapidly making it highly impractical to obtain experimental data on the nature and structure of liquid water in a macroscopic scale.

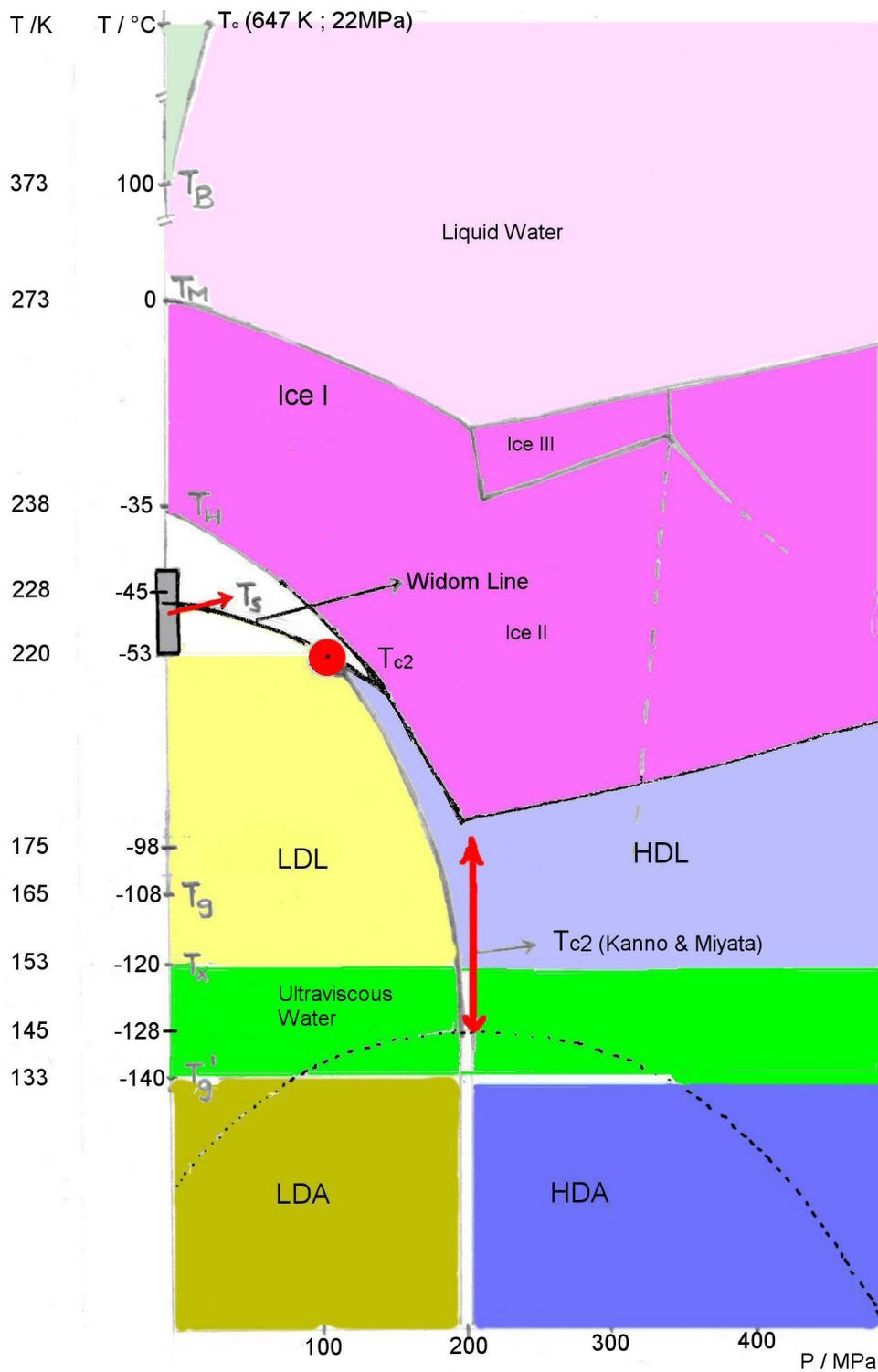


Figure 1.7: Phase relations between the stable and the metastable phases of liquid and glassy water.

The so-called singularity temperature  $T_s$  of supercooled liquid water falls just below the homogeneous nucleation limit, which makes it rather difficult to experimentally confirm the suggested discontinuous behaviour at  $T_s$ . According to the simple view of Mode Coupling Theory (MCT) of glass transition, the  $T_s$  should be the temperatures of dynamical structural arrest (Torre, Bartolini et al. 2004). However, since water is a very fragile glass former (Angell), it avoids dynamical arrest and crystallizes suddenly.

A rather new interpretation of the  $T_s$  is that the supercooled liquid water avoids singularity behaviour by sudden variation of its nature near  $T_s$ ; having a crossover from a fragile behaviour to strong behaviour. This kind of behaviour is supported by a recently conducted experimental study with confined water. Chen et al (Chen, Mallamace et al. 2006) obtained the self-diffusion coefficient and translational relaxation time data by nuclear magnetic resonance and quasi-elastic neutron scattering experiments. These data verifies that supercooled liquid water has a fragile to strong crossover (FSC) behaviour near 225 K, where also the decoupling of transport properties occurs (breakdown of the Stokes-Einstein relation).

The data of Chen et al challenges the stability limit hypotheses for the dynamic behaviour of supercooled liquid water, and supports the “**Singularity-Free Hypothesis**”, which suggests strong changes in thermodynamical properties of liquid water near  $T_s$ , but a thermodynamic continuity above and below this temperature. These data also support the second critical point (SCP) hypothesis, since the decoupling of transport properties, i.e. the breakdown of Stokes-Einstein relation, implies “a dynamical or spatial” heterogeneity (Souda 2006). The spatial heterogeneity is thought to be caused by the coexistence of the LDL and HDL phases in the deeply supercooled regime.

The 2<sup>nd</sup> critical point is first proposed by Poole and Stanley et al (Poole, Essmann et al. 1992; Mishima and Stanley 1998). From the discontinuous behaviour of melting curves of high pressure ices, these authors suggested that SCP is at 220 K and 100 MPa as denoted by a big red point in Figure 1.7. According to SCP, it is possible to separate liquid water into two phases below a certain temperature near the coexistence line that lies under the second critical point. These phases are low-density liquid (LDL) and high density liquid (HDL) phases, which resemble the two amorphous forms of glassy water (ASW). The glassy water that is obtained below 140 K

shows polymorphism. Depending on the pressure two amorphous phases can be obtained: The Low density amorphous (LDA) water and the high density amorphous (HDA) water. The amorphous phases can be experimentally obtained. However the LDL and HDL phases can not be reached, since they lie below the homogenous nucleation limit of supercooled liquid water. Therefore LDL and HDL domains of liquid water fall into the region of “no man’s land” (Mishima and Stanley 1998). On the other hand it is possible to access this region by confining liquid water to nanopores.

The location of the second critical point is also one of the current debates. Kano and Miyata (Kano and Miyata 2006) recently proposed that the SCP should be somewhere in between  $145 \text{ K} < T_{C2} < 175 \text{ K}$  and  $P_{C2} \approx 200 \text{ MPa}$ . They based their proposal to the DTA data for homogenous ice nucleation of emulsified liquid water and aqueous solutions at low temperatures and high pressures. They first realized that the break point of  $T_H$  at  $-92 \text{ }^\circ\text{C}$  and  $200 \text{ MPa}$  becomes “acuter” with the addition of solutes. Further analysing and comparing the peak heights and HWHM of DTA traces they concluded that they had supporting evidence for the above proposed location of the 2<sup>nd</sup> critical point.