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Part I

Bulk water

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Uniqueness of water

*What makes water so unique? People have asked this question for centuries. Yet the answer seems elusive. Despite all of its complex properties, water has an amazing, deceptively simple chemical composition – just two hydrogen and one oxygen atoms! Yet it exhibits highly unusual and puzzling physical properties. In this chapter we make a list of **six unusual molecular properties** that together could be responsible for the unusual characteristics of water.*

1.1 Introduction

It is fair to state that in the biologically relevant temperature and pressure range, none of the properties of water are like those observed in other common liquids (such as ethanol, benzene or acetonitrile). To begin with, water has remarkably high boiling (100 degree Celsius) and melting (0 degree Celsius) temperatures that are unusual for a liquid consisting of molecules that are so small in size and so light in molecular weight. Additionally, it exhibits a high critical temperature (374°C), compared to the liquids with similar or comparable molecular structure that are mostly in the gaseous state at room temperature and pressure (such as hydrogen sulfide (H₂S) and carbon dioxide (CO₂)). It has large specific heat and exhibits many other thermodynamic anomalies to be discussed later in Chapter 2.

Understanding the origin of the anomalous properties of water has turned out to be an extraordinarily difficult task – a task that is only partly completed. Nevertheless, we need to make a beginning, with whatever understanding we have acquired of bulk water [1–5], in our attempt to understand the diverse (and myriad) roles that water plays in many complex environments, including biology. We discuss below six unique features that can be held responsible for many of the properties of water. But first we present a few of the essential details about a water molecule so that those features can be understood and appreciated.

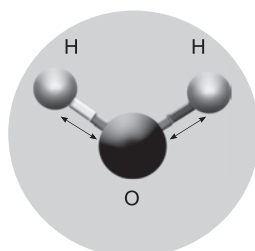


Figure 1.1. Molecular structure of water. The dark and light balls represent oxygen and hydrogen atoms, respectively. The sticks between the oxygen and the hydrogen atoms represent the O–H chemical bond.

1.2 Molecular structure

A water molecule is made of two hydrogen atoms that are attached to an oxygen atom via covalent bonds, making it look “V-shaped” (as shown in Figure 1.1). The O–H bond length is about 0.1 nm (1 Å) and the HOH bond angle is 104.51° (in the gas phase). The oxygen atom has two unused lone pairs of electrons on it and they contribute in no small measure to the unusual properties of water.

Apart from the covalent bonds between oxygen and hydrogen atoms, a water molecule also has the ability to form hydrogen bonds with four other neighboring water molecules. Two hydrogen atoms pair up with two oxygen atoms of two different water molecules while the oxygen atom pairs up with two different hydrogen atoms of two different water molecules. That is, one water molecule can form hydrogen bonds with four different water molecules, and the three-dimensional arrangement is tetrahedral, as shown in Figure 1.2.

A typical hydrogen-bond (O–H \cdots O) distance, that is, the distance between the oxygen atom of one molecule and the hydrogen atom of the participating second water molecule, is 0.25 nm (2.5 Å).

It is worth noting here that Linus Pauling was the first to mention the hydrogen bond, in 1912. In 1935, he first advanced the theory of hydrogen bonds between water molecules. Using quantum mechanics and chemical bonds he evaluated that both covalent bonds and other electrostatic forces – hydrogen bonds – were commencing in water. According to Pauling the covalency in a typical O–H \cdots O hydrogen bond is about 5% [6].

Although the arrangement of oxygen and hydrogen atoms is V-shaped with positive charges localized on the hydrogen atoms and the negative charge on the oxygen atom, the situation is known to be more complex, with the distribution of the electrons of the two lone pairs of electrons which have been recently described as “smeared between two tetrahedral lobes”. As a result, in an approximate sense, the local arrangement of water molecules in liquid water at low temperature can be

1.2 Molecular structure

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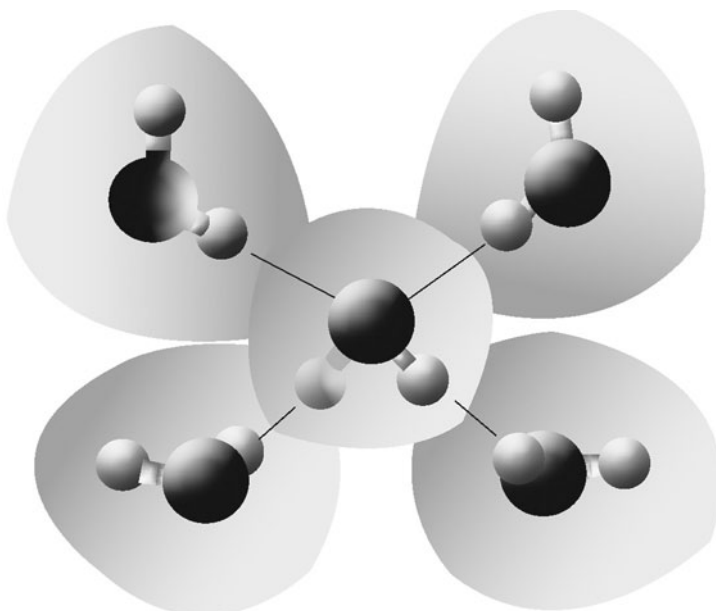


Figure 1.2. Typical molecular arrangement in the HB network around a central water molecule in liquid water. Four other water molecules form HBs (two donor (upper) and two acceptors (lower)) with the central water molecule. The environment around the central water molecule is tetrahedral. (Adapted with permission from http://mi-bitacora-diaria.blogspot.in/2009_02_01_archive.html.)

regarded as a “distorted tetrahedral”, as shown in Figure 1.2, with each water molecule, on average, forming four hydrogen bonds, as mentioned above.

In fact, the delocalized nature of the electron density between the two lobes facilitates a fifth neighbor to approach a tagged water molecule with a hydrogen atom of the incoming molecule pointed towards the oxygen atom of the tagged molecule. This allows formation of a bifurcated hydrogen bond and the existence of a water molecule with five neighbors. The five-coordinate water molecule so formed plays an important role in the thermodynamics and dynamics of liquid water. In Figure 1.3 we present a schematic representation to show how two 4-coordinated water molecules can be converted to one 3-coordinated and one 5-coordinated water molecule.

In Figure 1.3 we show the structure of a 5-coordinated species. Note that the formation of a H bond with a fifth neighbor is already possible even with localized charges on the two tetrahedrally placed lobes of the oxygen atom, and has been observed in many simulations with classical models of localized charges, but the delocalized nature may further facilitate its formation.

The quantum nature of electrons makes a water molecule more responsive and discriminative to external perturbation than possible in the classical world. The

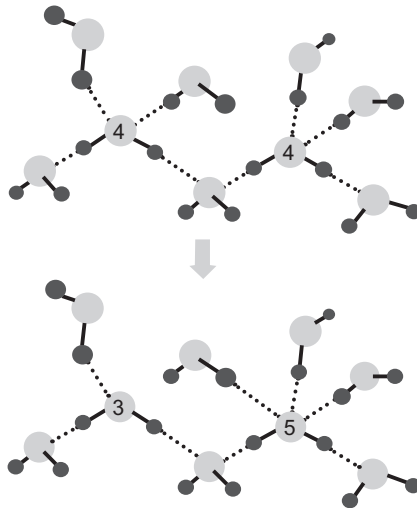


Figure 1.3. Pictorial representation of the conversion scheme from 4- to 5- and 3-coordinated water. Here oxygen atoms are light gray and hydrogen atoms are black.

lengths of the hydrogen bonds are also flexible and they vary considerably at a given time – even among the three or four hydrogen bonds formed by the same molecule.

To summarize, the “perfect” picture given in Figure 1.2 represents an ideal situation. The tetrahedron around the central water molecule is often distorted, except in ice, where collective effects reinforce a tetrahedral geometry. We shall discuss later quantitative descriptions which do more justice to local arrangement of water molecules in the liquid state. But right now we ignore the detailed corrections of the picture depicted above in Figure 1.2 and proceed with it.

In order to form an extended (that is, percolating) network that connects a large fraction of molecules of the entire system, there should be three or more hydrogen bonds per water molecule (unless molecules form large disconnected linear chains, which are unlikely and not seen in liquid water). Since each water molecule can easily form four hydrogen bonds, it can support such a network. Indeed this very ability to form a hydrogen-bond network has always been hypothesized to be the main reason for many anomalies exhibited by water (as shall be discussed later) [1–6].

Although bulk and confined water has been relentlessly studied both theoretically and experimentally for many decades [7], quantitative progress towards understanding the mysteries of water began only after we could study the structure and dynamics of about a thousand molecules via computer simulations. The landmark papers by Stillinger and Rahman [3] in the 1970s marked a turning point in our

understanding of liquid water. We note that these simulations employ classical mechanics and use a rigid model of water where charges are fixed at different sites to mimic the charge distribution of water.

Nevertheless, these simulations led to many important results. First, they confirm the view that water contains an extensive hydrogen-bond network where the two hydrogen atoms participate in one hydrogen bond each while the lone oxygen atom forms two or three hydrogen bonds with the hydrogen atoms of nearest-neighbor water molecules (as shown in Figures 1.2 and 1.3). The average number of hydrogen bonds per water molecule in liquid water under ambient conditions was found to be about 3.5. As we have already mentioned, we need at least three hydrogen bonds by a water molecule to ensure a connected percolating network; these computer simulation studies established that liquid water is a giant gel consisting of water molecules connected by hydrogen bonds. Doubly hydrogen-bonded water molecules are also present in the network, as they connect two extended networks. Some water molecules can be even singly hydrogen bonded and are called dangling bonds. But the fraction of doubly and singly hydrogen-bonded water molecules is small.

However, compared to chemical bonds (like the ones between hydrogen and oxygen atoms in water) these hydrogen bonds are weak, with dissociation energy comparable to thermal energy. As a result, these bonds continuously form and break in liquid water. Hence the lifetime of a hydrogen bond is quite short, of the order of two to three picoseconds (ps) where $1 \text{ ps} = 10^{-12} \text{ s}$.

Thus, the extended network of H_2O molecules in liquid water is a fluctuating network [4]. This fluctuation lets water be responsive to foreign solutes because it allows water to easily rearrange and solvate a large variety of solutes. This feature partly allows water to act as a unique solvent.

1.3 Six unique features

As mentioned above, we can make a list of *six unique features* of water that are responsible for many of its abilities and properties. We now list these properties.

- (i) A water molecule is small in size and low in molecular weight. The first allows it to occupy even relatively confined spaces, such as the grooves of DNA, or the active sites of enzymes. In the latter case, often the presence of a single water molecule plays an important role.
- (ii) Due to the large electro-negativity difference between oxygen and hydrogen atoms there is partial charge separation along the bond giving rise to (approximately) $-0.84e$ charge on the oxygen atom and (again, approximately) $+0.42e$ charge on each hydrogen atom. This distribution of positive and negative

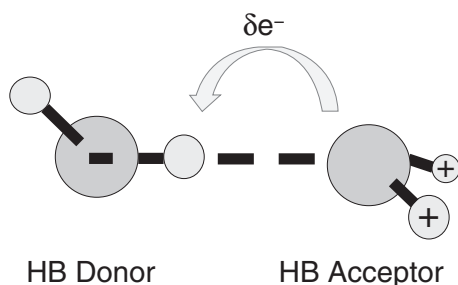


Figure 1.4. Electron cloud migration from the hydrogen-bond (HB) acceptor to the HB donor water molecule. In a water dimer the hydrogen atoms (shown in white) of a better HB acceptor become more positive, while the oxygen (shown in gray) of the HB donor becomes more negative.

charges promotes its hydrogen-bonding ability. Since water is made up of two hydrogen atoms that can form two H bonds and one oxygen atom that can further hold two to three H bonds, *each water molecule can form on the whole four, and even five, hydrogen bonds.*

In addition, water can act as *both* a donor and an acceptor of a hydrogen bond. Thus, *it can stabilize both a positively and a negatively charged atom/group.* This property comes in handy at a protein surface. As mentioned earlier, the electron charge in the lone pairs might be “smeared between the oxygen atoms”, allowing water to react quite differently to an anionic or cationic ligand.

- (iii) An additional aspect of the water–water hydrogen bond not captured in the classical models is the transfer of electron density from the oxygen atom of the acceptor molecule to the hydrogen atom of the donor molecule [8]. See Figure 1.4 for an illustration of this phenomenon.

This electron transfer gives the hydrogen bond a small measure of covalent character, estimated to be about 5% [9].

Note further that the --O--H stretching frequency of the donor molecule decreases proportionally to the strength of the hydrogen bond. This purely quantum effect allows additional cooperativity in hydrogen bonds.

- (iv) A water molecule is characterized by a large dipole moment which is reflected in the large dielectric constant of liquid water, about 80 at room temperature. This large dielectric constant is extremely useful in many chemical processes.

Related to this feature, the two lone pairs of electrons on the oxygen atom render a water molecule polarizable to electric fields from other molecules or from a charged surface. Thus, water molecules can respond to the changing of charge distribution in an external solute (or surface) to lower the energy of an

assembly or molecular arrangement. However, a water molecule is not highly polarizable, and is quite low in polarizability.

In neat liquid water, the polarizability effectively increases the dipole moment of each individual water molecule, and is partly responsible for the large dielectric constant of water.

- (v) *A collection of water molecules can form many structures of nearly equal energy.* This is most evident from a study of water clusters [10]. Also, ice is known to have many polymorphs. As many of these structures are of similar energy this makes a collection of a small number of water molecules highly adaptive to various complex environments [5]. For example, when a layer of water molecules faces a non-polar surface, the spatial arrangement and orientation of water molecules are quite different from those when the layer faces a polar or charged surface. This is because water molecules can adopt many different structures.
- (vi) The remarkable ability of water to sustain a *fluctuating extended hydrogen-bond network* allows facilitation of many dynamic processes that would otherwise be impossible. The marginally stable nature of the hydrogen-bond network arrangement makes it rather easy to initiate the molecular rearrangement. The hydrogen-bond network can easily be distorted. In addition, hydrogen-bond energy in water spans a wide range of energy ($\sim 3\text{--}9 k_{\text{B}}T$ for liquid water at 25°C temperature) [4].

We have made the above list such that each property operates at least somewhat independently. There are obviously correlations among these. Actually the ability of water to sustain multiple timescales is a unique feature of this liquid. Water seems to be able to respond according to the speed of perturbation. It responds slowly to slow perturbation and rapidly to fast perturbation.

In the subsequent chapters we shall try to rationalize the properties of water in complex systems by using these six features.

1.4 Modeling of water

Unfortunately, it has turned out to be exceedingly difficult to accommodate all the unique features of water within any given, classical model. This is reflected in the absence of satisfactory agreement between experiments and any given model [2]. This is a bit unusual (and of course frustrating) because when one usually models a given molecule, such as methane, it is adequate to use a simple functional form such as a Lennard-Jones potential that incorporates a measure of size and a measure of interaction energy at an optimal separation between two molecules. In the case of water molecules, such a simple procedure does not work. Here we have to account

for at least two length scales – one for the molecular size and the other for hydrogen-bond length. Second, one needs to take into account the charge distribution. And as we have already discussed, quantum effects (electron transfer) give rise to a cooperativity in hydrogen-bonding that is hard to mimic within a classical model. Thus, the unique features discussed above prove to be particularly hard to model.

As a result of these complexities, although more than 100 different potential functions have been employed, no fully satisfactory model has yet been developed. But many of these models have been able to explain many of the experimental observables, such as density maximum, values of viscosity and self-diffusion coefficient, specific heat and compressibility, and dynamics of electron transfer reactions.

Thus, it is also not fair to state (as the statement is often made) that “we do not understand water”. Although clearly perspectives differ, one should not lose sight of the successes that have been achieved.

1.5 Conclusion

Liquid water is different from other liquids. Unique (and often termed anomalous) properties of water originate ultimately from the unique molecular features of water. We have made a list of six such features which combine to give rise to the unusual properties of water. The list itself may not be unique or exhaustive but we think that it provides a starting point to rationalize the properties of water.

In fact, an attempt to rationalize the diverse properties in terms of a few basic features is a reductionist view which has a lot of advantages. Most importantly, it is possible to get back to basics when one faces difficulty in explaining the experimentally observed properties. For example, a lot of our difficulties in understanding or describing the behavior of water molecules at the surface of proteins or charged surfaces arise from our difficulty in handling the polarizability anisotropy of water molecules.

In the next chapter, we discuss a few of the well-known anomalies of liquid water. We shall return to the discussion of those anomalies again in the penultimate chapter of the book. In the intervening chapters we shall discuss various properties of water in diverse systems, with a close connection between theory and simulations.

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