"Physical Characteristics" of water.
Structure?

This is a very large topic with an enormous literature, and many different models. In addition it is very difficult to build a theoretical model that satisfactorily takes care of the many diverse and unusual properties of water. However, many of the properties of the macromolecules are tied directly to the characteristics of water – their structures and dynamic responses, as well as their interactions with other macromolecules or small molecule ligands (specific ligands, ions, membrane components, etc.). We must understand the properties of water as a solvent, before we can understand how macromolecules carry out their functions in their aqueous milieu.

A comment on the name **"structure" of water**. If there is a structure it is very ephemeral, and changes rapidly, - the picosecond scale. Nevertheless what is meant is that there are *configurations of the water molecules that are allowed*, and *more likely that others*, which are **peculiar to water**. This is related to the tetrahedral structure of water, and to the extensive H-bonding configurations in bulk water.

There are some interesting general characteristics of water that do not concern the molecular properties directly, but are very important for biology:

1) It is the only inorganic substance and chemical compound that is found in all three phases – gas, liquid, and solid – in nature.

2) 93% of blood plasma, 80% of muscle, and 60% of red cell mass is water.

3) 80% of fresh water is in the frozen state (e.g. glacial ice).

4) < 3% of all water on the surface of the earth is fresh.

5) 95% of the fresh water that is in the liquid state, is in ground deposits.

6) 2/3 of the planet is covered by water.

TABLE 18.1. The hydrologic cycle.

Phase of cycle	Annual water volume (km³)
Evaporation from the ocean surface	419,000
Precipitation onto ocean	381,000
Precipitation on land surfaces	107,000
Runoff from land to ocean	38,000
Evapotranspiration from land	69,000

7) 10^5 km^3 H$_2$O passes through the photosynthetic pathway.
H$_2$O is the most reduced form of O, and CO$_2$ is the most oxidized form of carbon.
These two molecules are the end products of the metabolism in the mitochondria
C$_6$**H**$_{12}$O$_6$ + **3O$_2$** + 3O$_2$ + 38ADP + 38Pi -> 6CO$_2$ + **6 H$_2$O** + 38ATP

An average human produces 300 gm of H$_2$O per day, and used 7600 kJ/day to produce
ATP.

8) Some interesting physical characteristics of H$_2$O:
- **High dielectric constant** = 78.5 D (Debye); MeOH has 32.6 and H$_2$S has 9.3. So it is
  a very polar solvent. Electrically charged molecules are easily dissociated in H$_2$O.

TABLE 18.2. Dielectric constants of selected compounds.

Substance	Dielectric constant (at 298 K)
Water	78.5
CH$_3$OH	32.6
CH$_3$CH$_2$OH	24.0
H$_2$S	9.3
C$_6$H$_6$	2.2
CCl$_4$	2.2
CH$_4$	1.7
Air	1.000059
Mica	5.4
Polystyrene	2.55

The dielectric constant of ice is greater for ice than it is for liquid water. This is very
unusual.
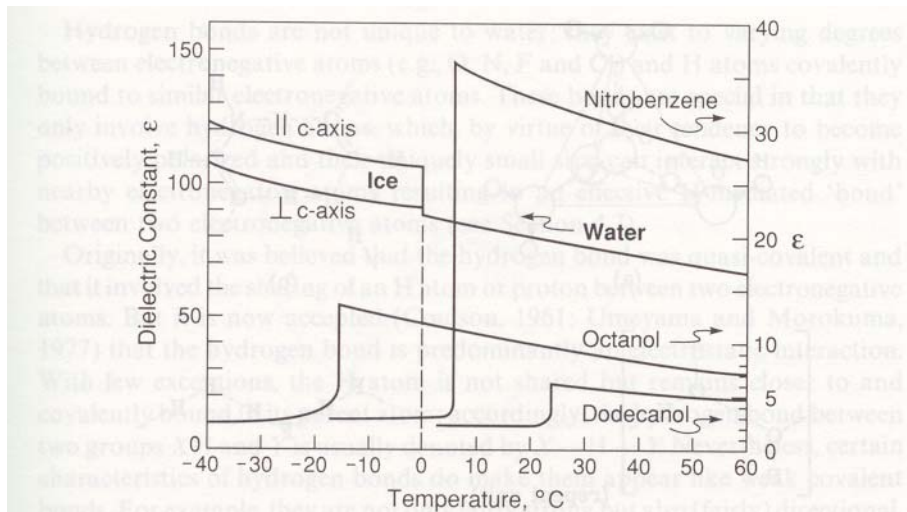
Fig. 8.1. Static dielectric constants as a function of temperature of some 'normal' polar
liquids and water. For all the 'normal' liquids ε falls abruptly on freezing to a value that
is close to the square of the refractive index, indicating that the thermal rotations of the
dipolar molecules have stopped. However, for water ε rises on freezing, and continues to
rise down to $-70°C$, after which it falls. The high polarizability of water is believed to
arise from proton hopping along the H-bond network (see Fig. 8.2a) rather than molecular
rotations. Data compiled from Landolt-Börnstein (1982), Hasted (1973) and Hobbs (1974).
For theories of the dielectric constant of ice see Pauling (1935) and Hollins (1964).

- Water has a **very high heat capacity** – it can act as a thermal buffer. This is required to keep the temperature in biological cells constant.
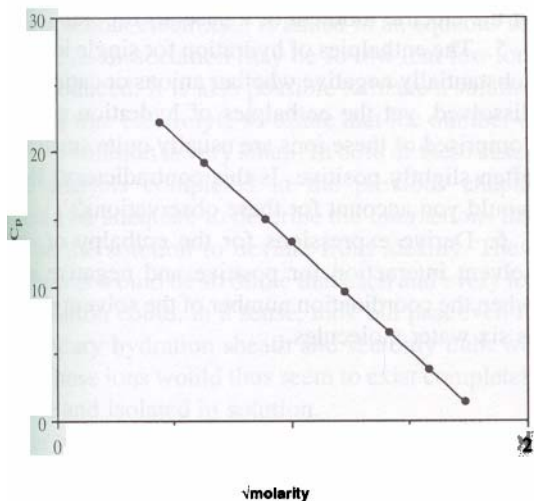

FIGURE 19.15. **Plot of the heat capacity (C_p) for a solution** of KBr in water at various concentrations.

The relatively large heat capacity of water "disappears" with larger concentration of ions; this points to the reduction of entropy when the ions are added to the solution. This is usually attributed to the structuring effect of water around the ions. The normal H-bonds of water do not (supposedly) exist around the ions. In water there are a large number of microstates (high entropy) available for the water molecules in bulk water. Remember the enthalpy of hydration of these ions is highly negative, because of the number of primary and secondary hydration sheaths around the ions, as well as the H-bond energy that is lost when the bulk water structure is perturbed.

TABLE 19.3. **Enthalpies of hydration for single ions.**

Ion	$\Delta H_{hydration}$ (kJ mol^{-1})
H$^+$	-1071
Li$^+$	-548
Na$^+$	-485
K$^+$	-385
Ca^{2+}	-1715
Al^{3+}	-4807

Also, the existence of an ionic atmosphere where the H-bonds do not exist not only accounts for the fact that the heat capacity decreases as the ion concentrations increase, but also accounts for the smaller volume of the water surrounding the ions (this is usually called electrostriction). The hexagonal "structure" of the water is perturbed.

- Very high heat of vaporization (40 kJ/mol). This is due to the large extent of H-bonding in bulk water (all solvents that have such extensive H-bonding, have relatively high heats of vaporization). This is of course important for cooling by perspiration

TABLE 18.3. Heats of vaporization for selected substances.

Substance	Heat of vaporization (kJ mol^{-1})
Water	40.7 @ 373 K
Acetic acid	41.7 @ 391 K
Ethanol	40.5 @ 351 K
Hexane	31.9 @ 341 K

It is interesting to compare the heat of vaporization of water to other compounds that have the same number of electrons and those where the hydride structures are the same, and the atoms of the hydrides are from the same group as oxygen. This emphasizes the unusual properties of water.

TABLE 18.5. The heats of vaporization as well as the melting and freezing points of water compared to its isoelectric series and related hydrides.

Isoelectronic series	Melting point (K)	Boiling point (K)	Heat of vaporization (kJ mol^{-1})
CH_4	89	112	9.21
NH_3	195	240	23.22
H_2O	273	373	40.65
HF	181	292	30.20
Ne	24	27	1.74

Hydride series	Melting point (K)	Boiling Point (K)	Heat of vaporization (kJ mol^{-1})
H_2O	273	373	40.65
H_2S	187	213	18.67
H_2Se	207	232	19.70
H_2Te	224	271	19.20

- Liquid water has a density larger than ice. This has important consequences for fish and aquatic life, and probably for evolution. Also, the action and movement of glaciers depends on this. In addition, this is very important for the ability of water to slowly destroy rock structures, which is a major process forming the structure of the surface of the earth.

- Water has a very high surface tension, and this has an important effect of minimizing the surface areas of water. This is also important for capillary action. In lungs, surfactants must be present to open alveolar spaces for respiration. These are biological molecules that are made by the organisms. If these are not present, or not enough of them, this leads to respiratory diseases, and even to death.

- Water has a larger conductivity (proton conductivity) than would be expected from its ionization constant (which is very low). The conductivity of ice is just as high. This is probably due to a brigade mechanism for transport through large conjugates of H-bonds.

The **structure of a water molecule** can be thought of as a **sphere**:
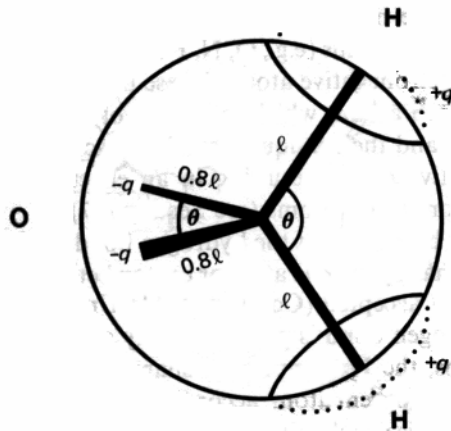
Fig. 8.3. ST2 model of water molecule; $q = 0.24e$, $l = 0.1$ nm, $\theta = 109°$.

The electron distribution and the relative size of the atoms, makes the molecule approximately spherical. The structure of the molecule is approximately tetrahedral, where the lone electron pairs are at two of the apexes and the hydrogen atoms at the others. The angles are all nearly perfect tetrahedral (109°). The hydrogens have an angle of 104.5 °) In ice, only 42% of the volume is filled by the van der Waals volumes of the atoms, compared to 74% for spherical close packing.

There is a ver y large degeneracy of possible states that water can participate in when the molecule is in the liquid phase. These very large number of states leads to a large entropy. In a way, the H-bonding propensity of the water together with the tetrahedral geometry of the water molecule, leads to a higher entropy in the bulk phase. When the water molecules are removed from the bulk water, they assume fewer microstates – fewer ways to H-bond. This has lead to models such as the "flickering iceberg" model, which emphasizes the cooperativity of the H-bonded state. But this model is no longer really proposed, at least not in its original form.

It is interesting to compare H_2O and H_2S:

TABLE 18.7. Comparison of thermodynamic parameters of water and hydrogen sulfide.

| Property	H_2O	H_2S
$T_{\text{solid-liquid, 1 atm}}$	273 K	187 K
$T_{\text{liquid-gas, 1 atm}}$	100 K	213 K
Density$_{\text{solid}}$ @ T_m	0.9998 kg dm^{-3}	1.80 kg dm^{-3}
$C_{p, \text{liquid}}$	76.02 J mol^{-1} K^{-1}	36.1 J mol^{-1} K^{-1}
$C_{p, \text{gas}}$	36.44 J mol^{-1} K^{-1}	41.56 J mol^{-1} K^{-1}
$\Delta H_{\text{solid-liquid, 1 atm}}$	6.003 kJ mol^{-1}	2.386 kJ mol^{-1}
$\Delta H_{\text{liquid-gas, 1 atm}}$	40.656 kJ mol^{-1}	18.747 kJ mol^{-1}
Conductivity at $T_{\text{liquid-gas, 1 atm}}$	4×10^{-10} Ω^{-1} m^{-1}	1×10^{-13} Ω^{-1} m^{-1}

There is a **very extensive H-bonded network** that is much more extensive and three-dimensional than for other H-bonding structures.
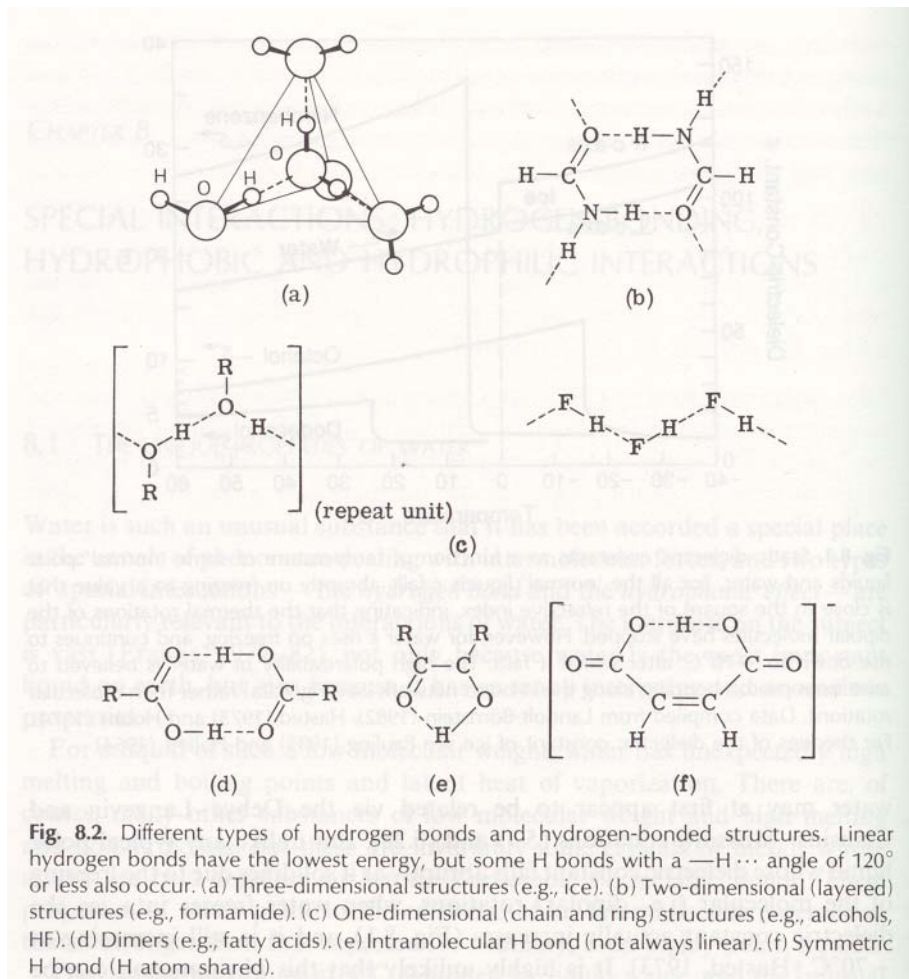
Fig. 8.2. Different types of hydrogen bonds and hydrogen-bonded structures. Linear hydrogen bonds have the lowest energy, but some H bonds with a —H··· angle of 120° or less also occur. (a) Three-dimensional structures (e.g., ice). (b) Two-dimensional (layered) structures (e.g., formamide). (c) One-dimensional (chain and ring) structures (e.g., alcohols, HF). (d) Dimers (e.g., fatty acids). (e) Intramolecular H bond (not always linear). (f) Symmetric H bond (H atom shared).

Radial distribution function of water:
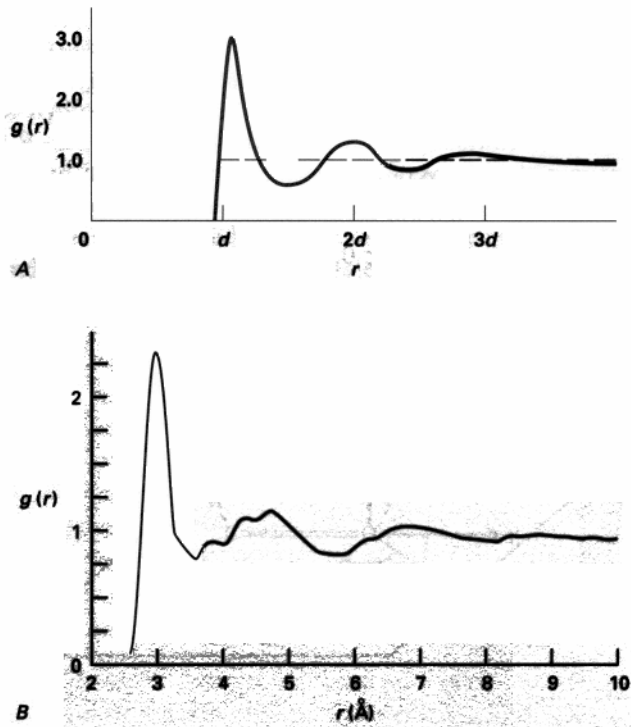
FIGURE 4.5
Radial distribution function of a normal liquid *(A)* and of water at 4°C *(B)*. The probability of finding other atoms at radial distance *r* from a central molecule is given by $g(r)$ times the density of the liquid. The distance *r* is expressed in *A* in terms of the van der Waals diameter of the molecule, *d*. The experimental curve for water measured using X rays is given in *B*; X rays are scattered primarily by the oxygen atom of the water molecule. (From A. H. Narten and H. A. Levy, *J. Chem. Phys.* 55:2263–2269, 1971.)

The centers of the four oxygen molecules of the nearest neighbors are 2.82 Å(for ice it is 2.76 Å) away from the central oxygen atom, and the next nearest neighbors are 4.5 Å away. The number of nearest neighbors in water is 4.4, just a little more than in ice (where it is 4).

Water molecules seem to have the ability to form "clathrate" type structures (remember the comment about "structure") around many **nonpolar** substances. The water in the immediate vicinity of these nonpolar structures is not in a rigid structure, but the structure is very labile, but it seems to have fewer possibilities of fulfilling its desire for H-bonding conformations than does the bulk water molecules. You have to remember that these are in general hypothesized "structures" and are not seen directly in any experiment. They are surmised mainly from thermodynamic parameters, and from statistical mechanical calculations.

Tetrahedrally
coordinated
water molecules
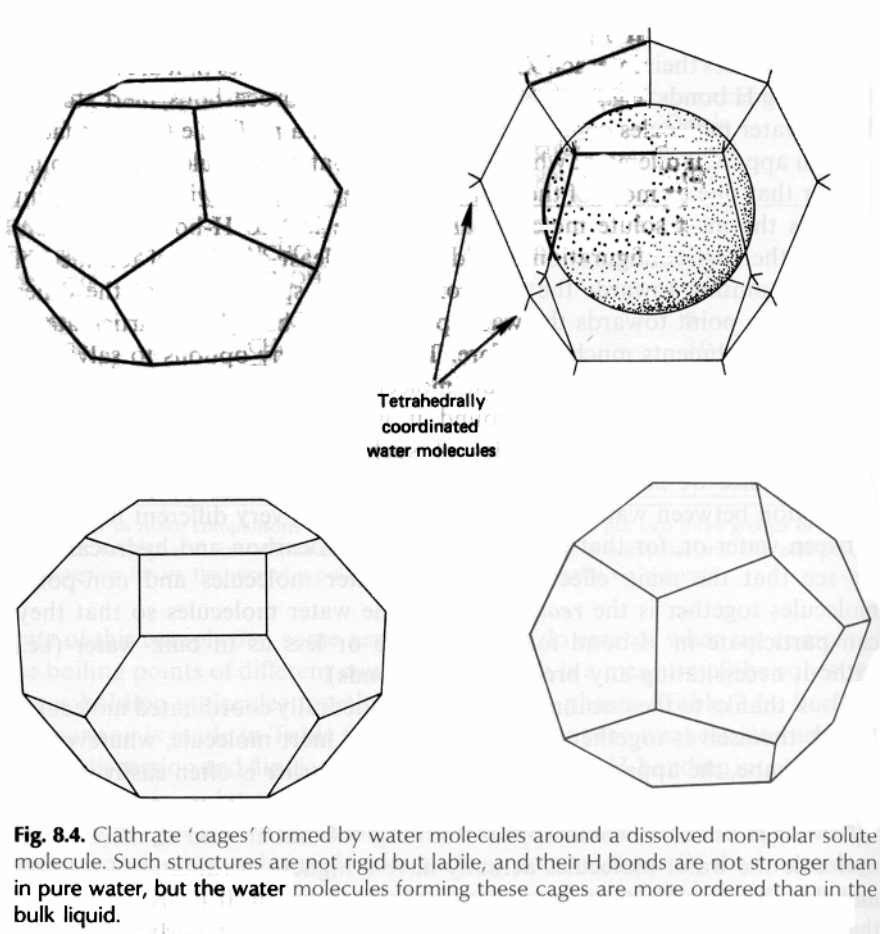
Fig. 8.4. Clathrate 'cages' formed by water molecules around a dissolved non-polar solute molecule. Such structures are not rigid but labile, and their H bonds are not stronger than in pure water, but the water molecules forming these cages are more ordered than in the bulk liquid.