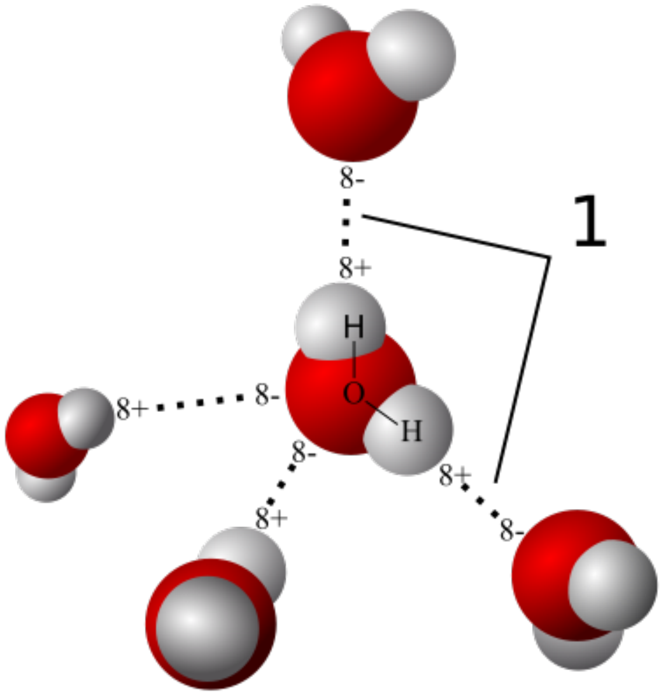
Combinatorial calculus and the entropy of hexagonal ice (Pauling, 1935)

Edoardo Milotti, Advanced Statistics course

The hydrogen bond

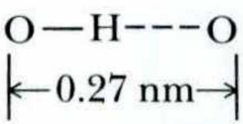
A hydrogen bond is the electrostatic attraction between polar molecules that occurs when a hydrogen atom bound to an electronegative atom experiences attraction to some other nearby electronegative atom.

The hydrogen is not a true bond but a particularly strong dipole-dipole force and should not be confused with a covalent bond.

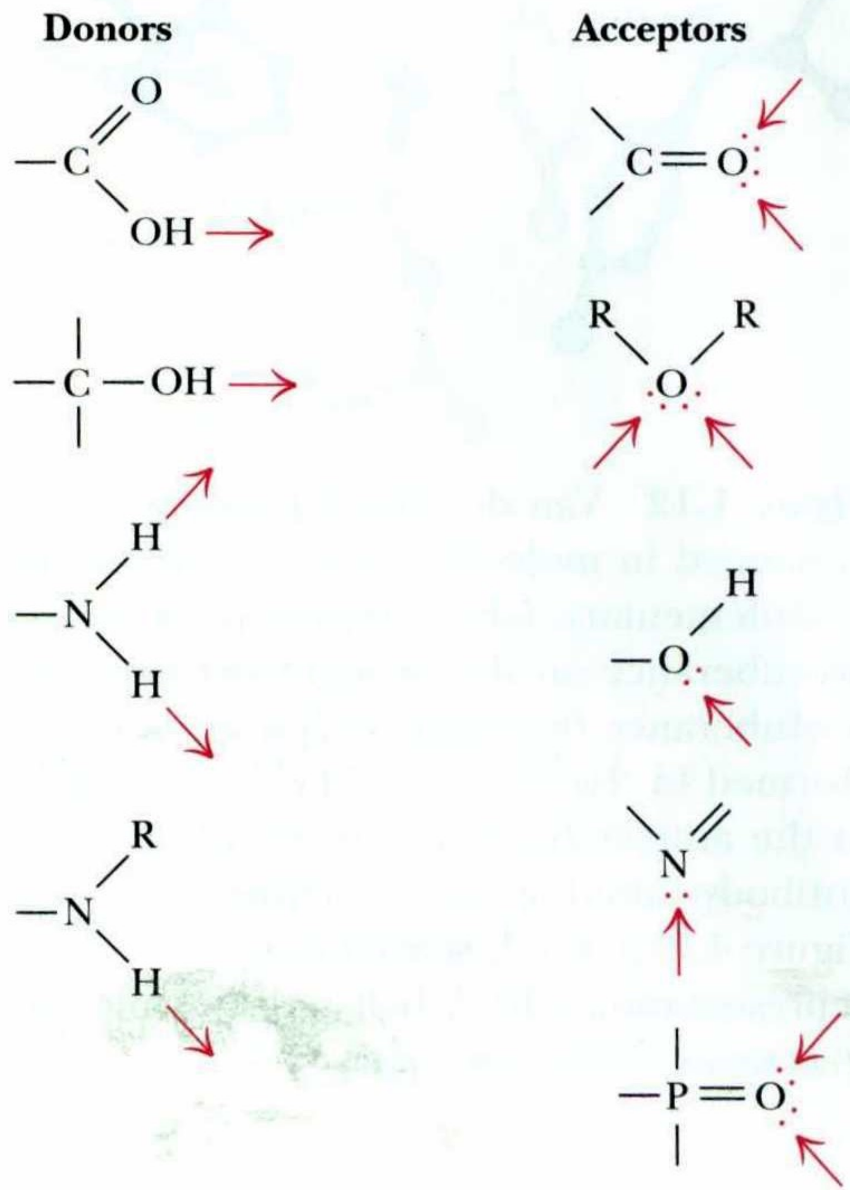


Bonded atoms	Approximate bond length*
O—H---O	0.27 nm
O—H---O$^-$	0.26 nm
O—H---N	0.29 nm
N—H---O	0.30 nm
N$^+$—H---O	0.29 nm
N—H---N	0.31 nm

*Lengths given are distances from the atom covalently linked to the H to the atom H-bonded to the hydrogen:



Functional groups which are important H bond donors and acceptors:



Biologically important H-bonds and functional groups

The strength of these bonds is intermediate between Van der Waals interactions (about 0.3 kcal/mol ≈ 1.3 kJ/mol), and covalent chemical bonds (about 100 kcal/mol ≈ 420 kJ/mol).

Note that the strength of the **hydrogen bond in liquid water** is

23.3 kJ/mol (≈ 5 kcal/mol) ≈ 0.24 eV/bond

This must be compared with the thermal energy at room temperature

3/2 kT ≈ 0.04 eV/bond

A quick estimate:

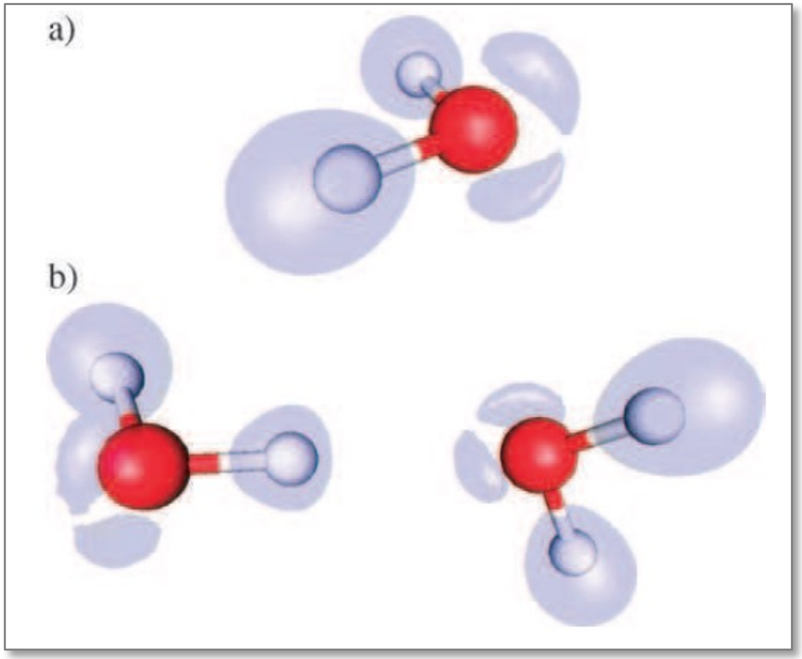
1 mole of water contains 2 moles of bonds ≈ $1.2 \cdot 10^{24}$ bonds

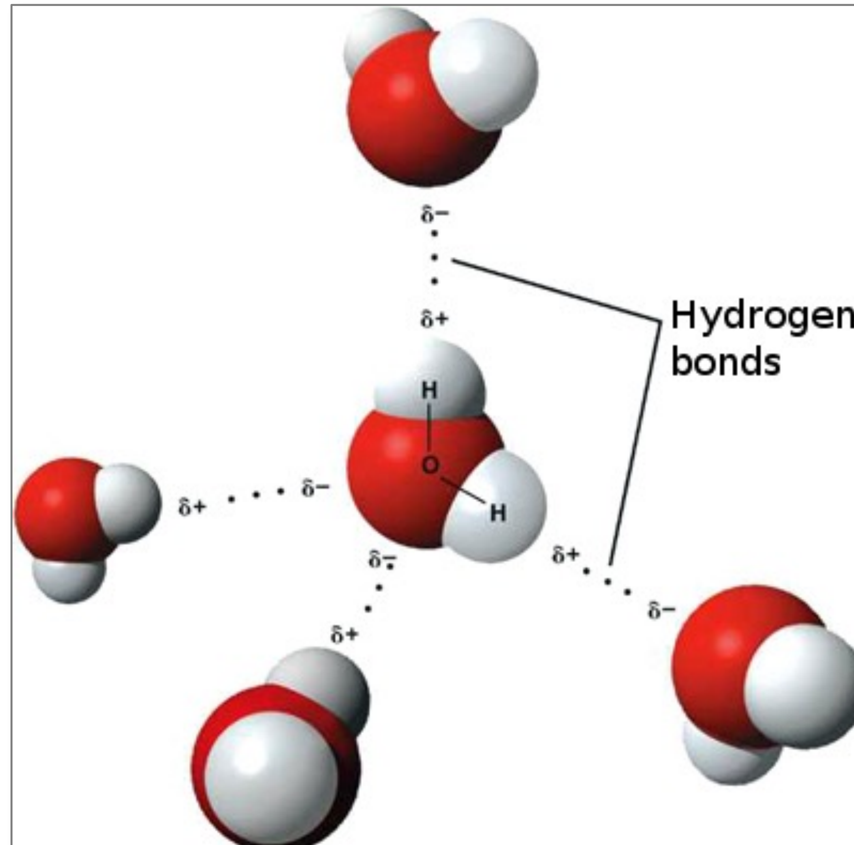
and

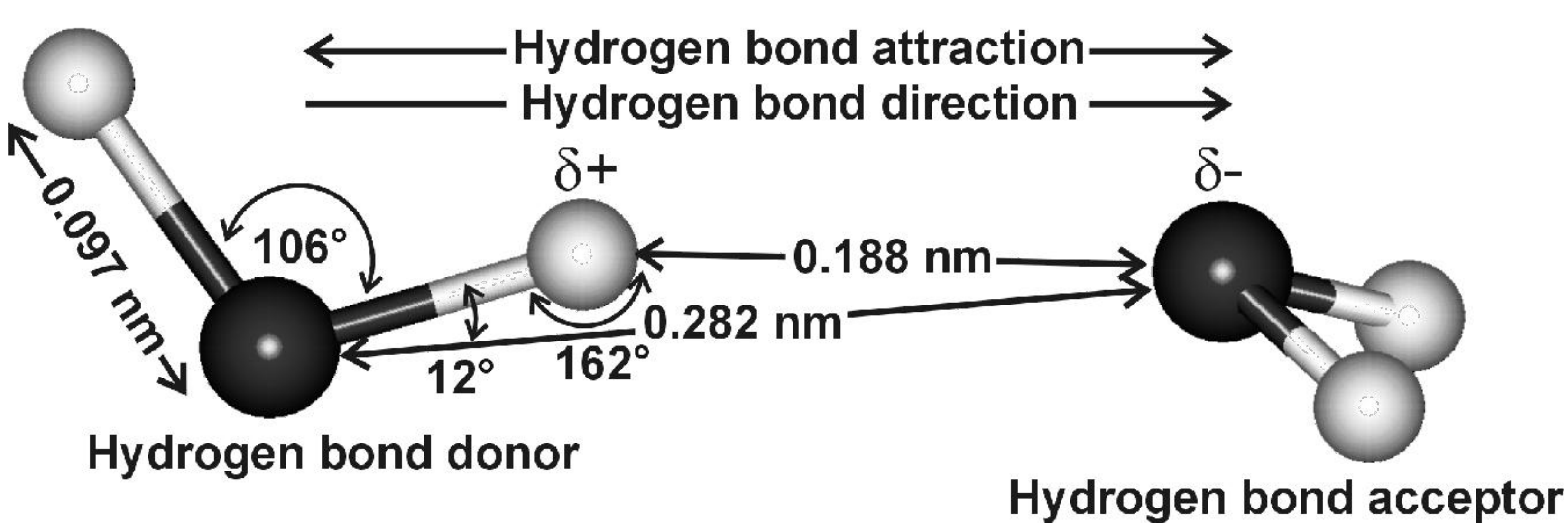
the latent heat of vaporization (enthalpy of vaporization) @ 25°C is ≈ 44 kJ/mol

and this can be used for a rough estimate of the hydrogen bond strength in water:

$3.7 \cdot 10^{-20}$ J/bond ≈ 0.23 eV/bond


a)
b)


δ−
δ+
Hydrogen bonds
H
O
H
δ+
δ−
δ−
δ+
δ+
δ+
δ−



Average parameters for hydrogen bonds in liquid water with nonlinearity, distances and variances all increasing with temperature. There is considerable variation between different water molecules and between hydrogen bonds associated with the same water molecules.

(adapted from M. Chaplin, arXiv:cond-mat/0706.1355)

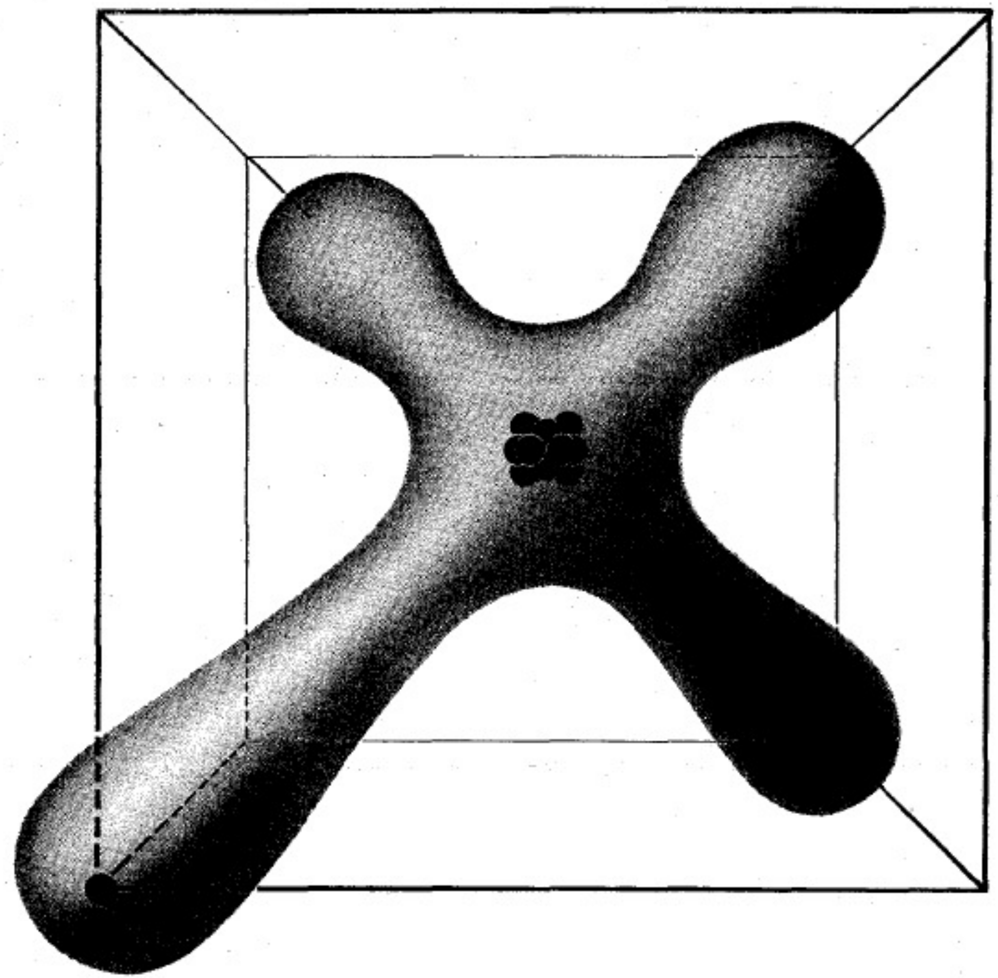
Bernal–Fowler ice rules

(After the British physicists John Desmond Bernal and Ralph H. Fowler who first described them in 1933).

These rules state that:

- **in ice each oxygen is covalently bonded to two hydrogen atoms**
- **that the oxygen atom in each water molecule forms two hydrogen bonds with other oxygens**

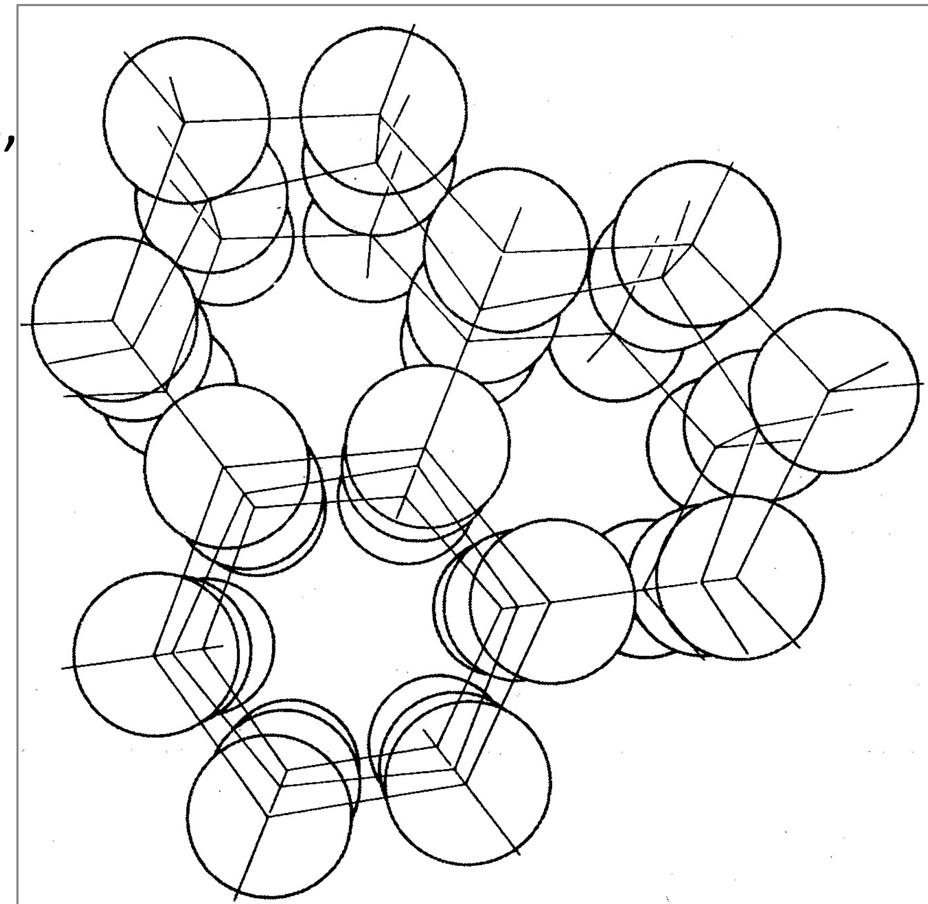
so that there is precisely one hydrogen between each pair of oxygen atoms.

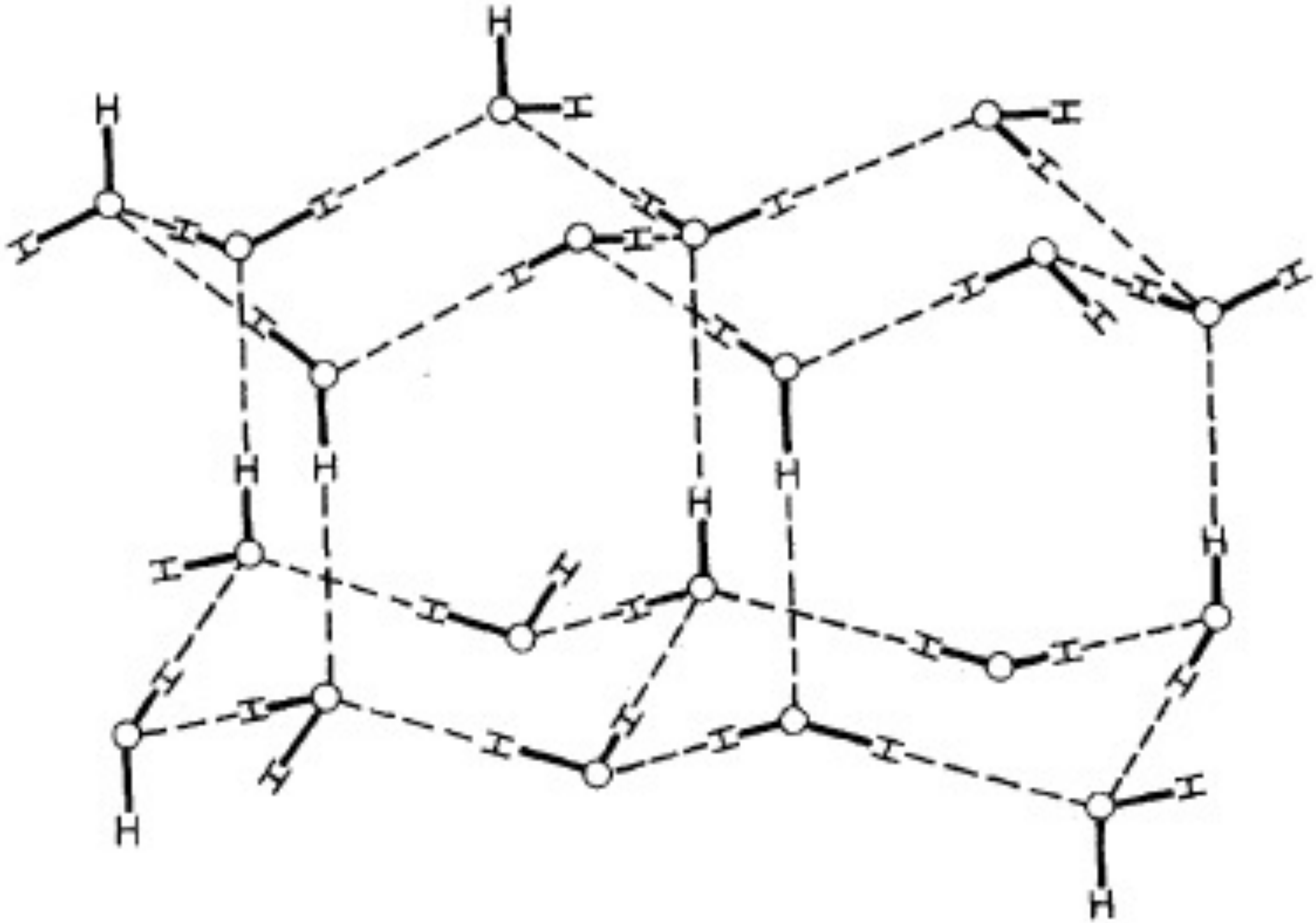


The structure of ice
(hexagonal ice, the most frequent form of ice)

This figure shows the arrangement of the O atoms, as it was found early on, from X-ray crystallography.

Where are the H atoms?





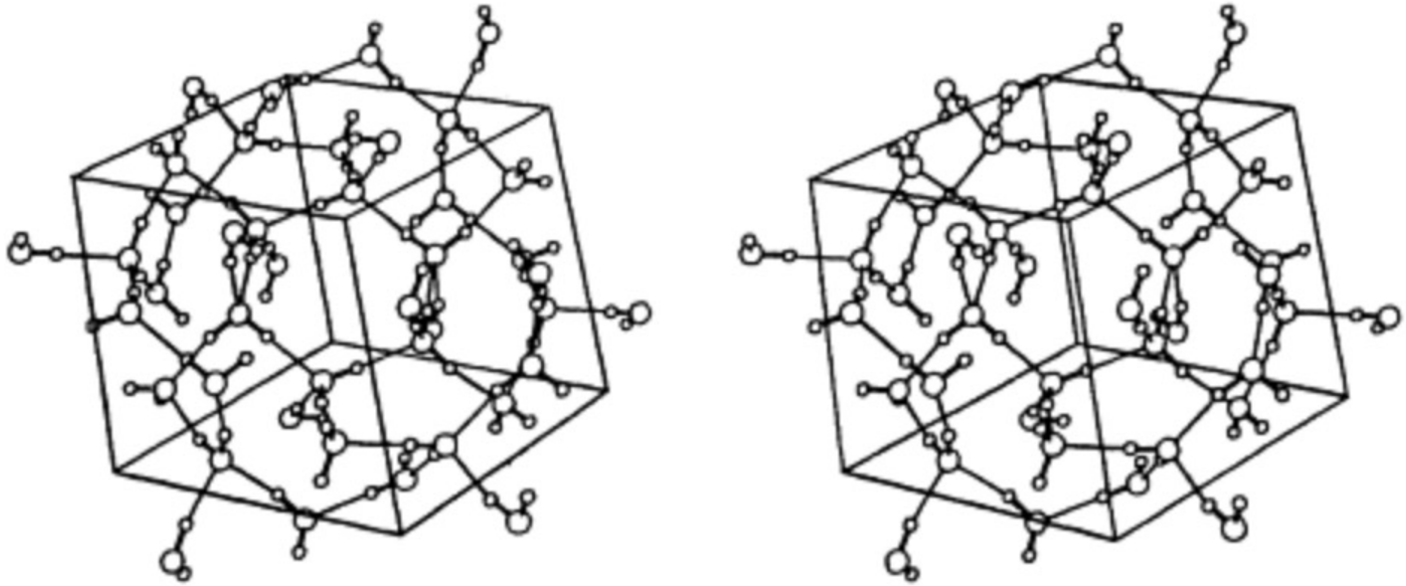
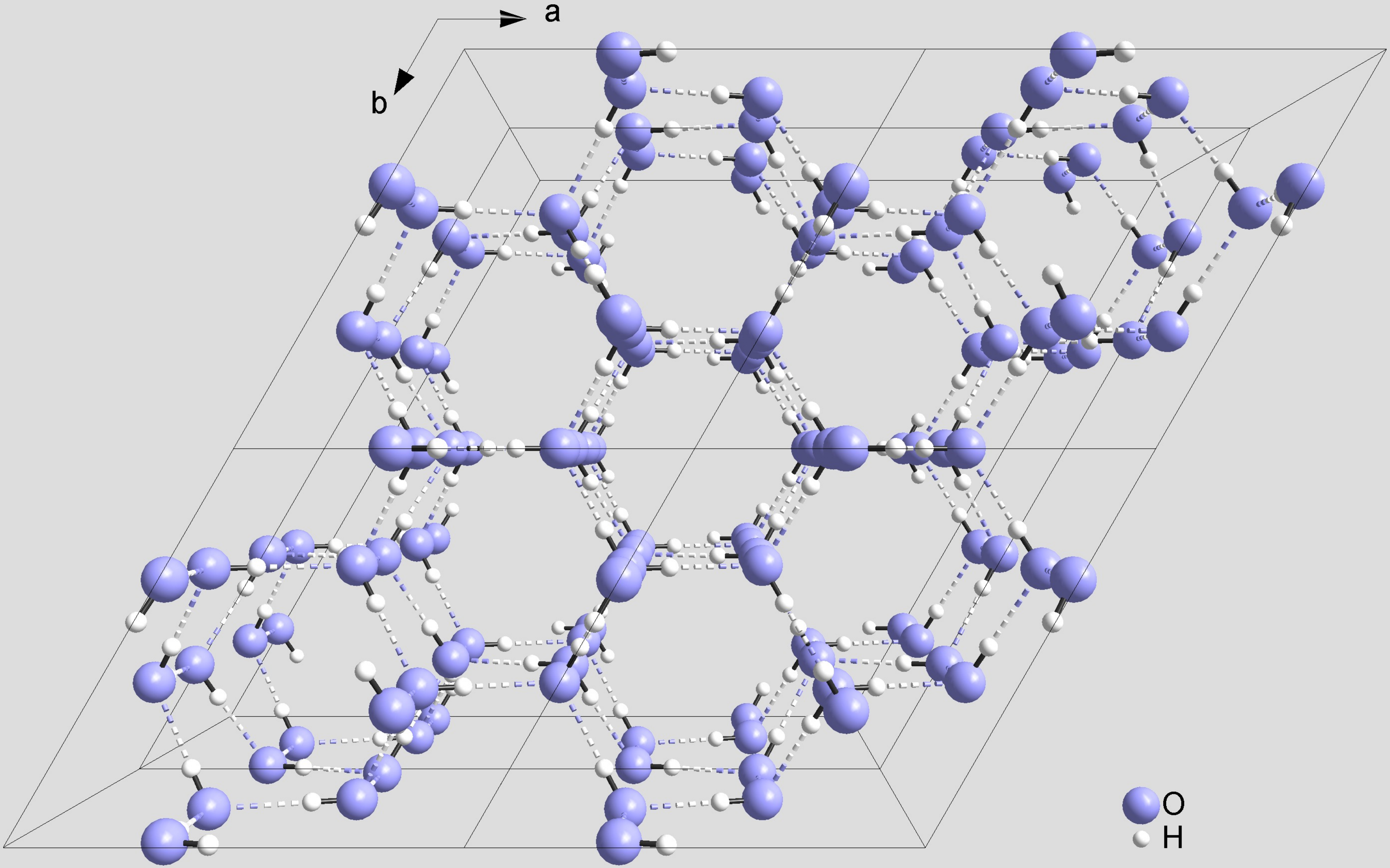
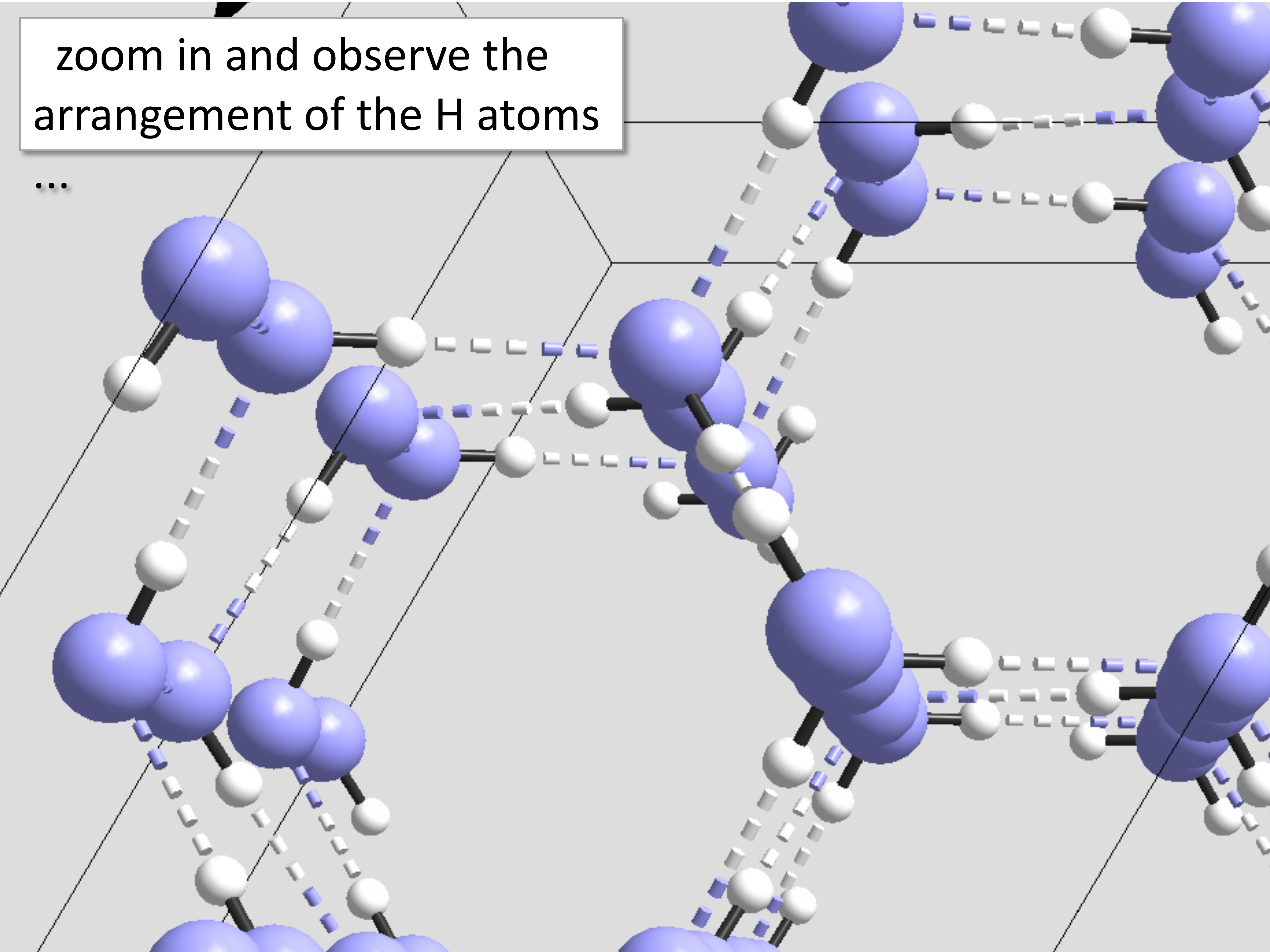


Fig. 11.9 Pair of stereo images of the structure of ice II viewed at an angle of about 30° to the hexagonal *c*-axis. The contents of one rhombohedral unit cell and portions of adjacent cells are shown. (From Kamb *et al.* 1971.) Readers not already familiar with viewing such stereo pairs should hold the page close to the face so that one image is in front of each eye but out of focus. Then move the page slowly away while trying to keep the eyes relaxed and looking towards the distance. Three images will be seen and the central one of these becomes the stereo-image, but avoid trying to focus on it until its three-dimensional character has become clear. If this cannot be made to work, try viewing through two 10 cm converging lenses, one in front of each eye. It is worth the effort!

... a possible arrangement of the H atoms in hexagonal ice ...



zoom in and observe the arrangement of the H atoms …

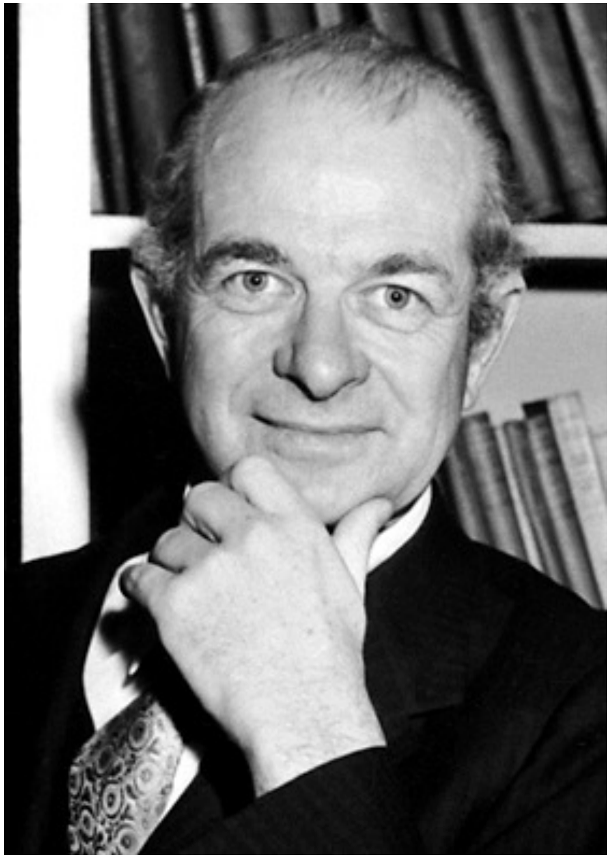


The many possible arrangements of protons around oxygens in water lead to the

residual entropy of ice

i.e., a configurational entropic contribution that persists down to absolute zero.

Ice is the first substance where residual entropy was actually studied.

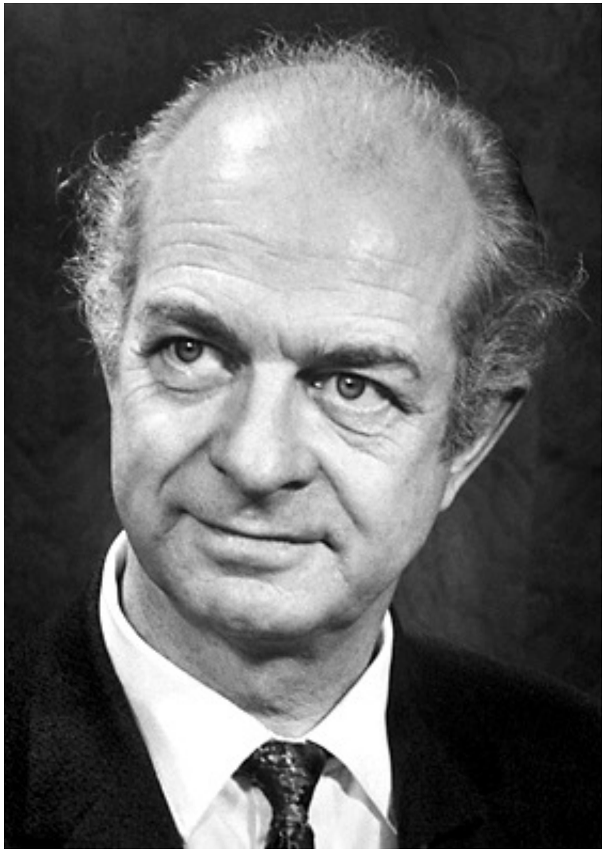


Linus Carl Pauling

Born: 28 February 1901, Portland, OR, USA

Died: 19 August 1994, Big Sur, CA, USA

Nobel Prize in Chemistry in 1954 "for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances”



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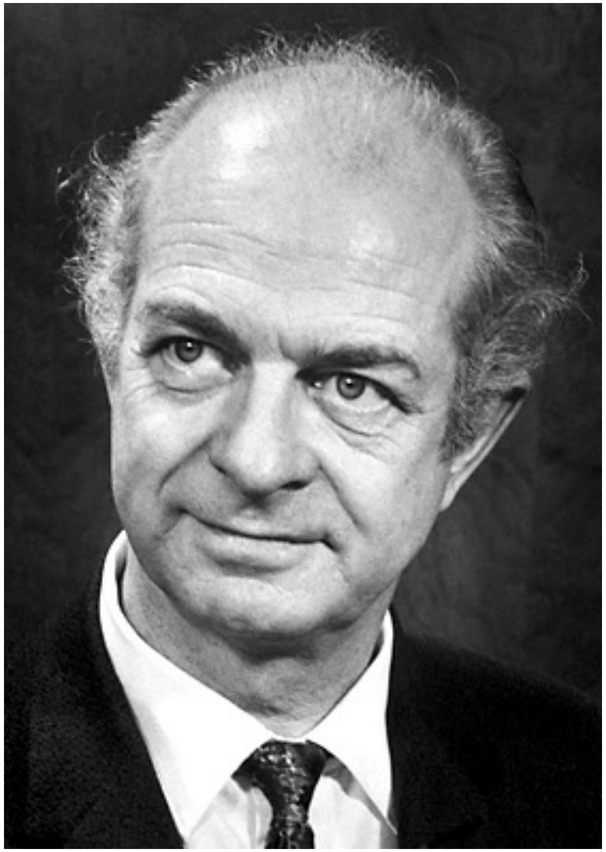
Nobel Peace Prize 1962, for arms control and disarmament**, the only person who has won two undivided Nobel Prizes**

See biography at this link
http://www.nobelprize.org/nobel_prizes/peace/laureates/1962/pauling.html




J. Am. Chem. Soc. 57, 2680 (1935).

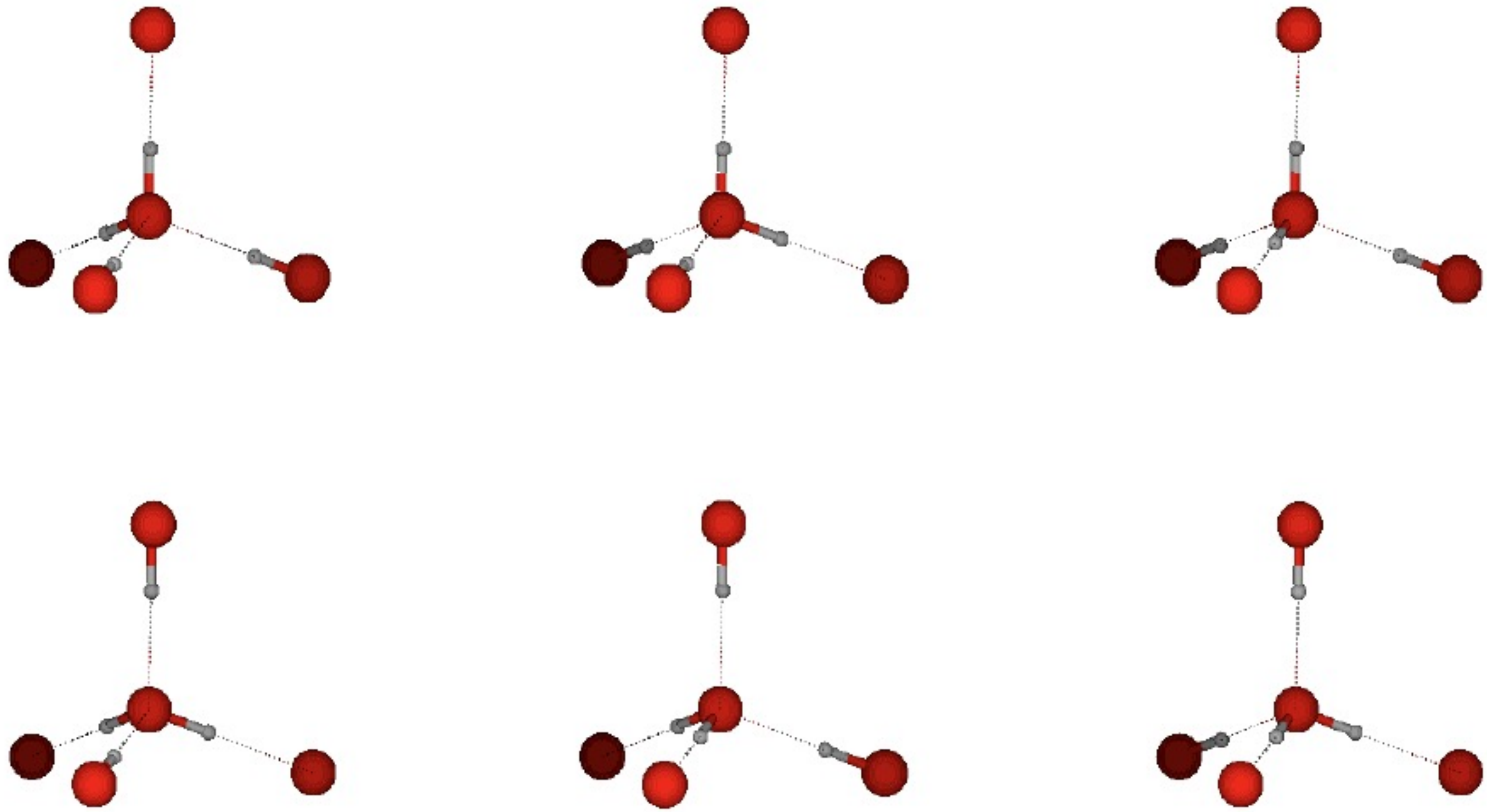
The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

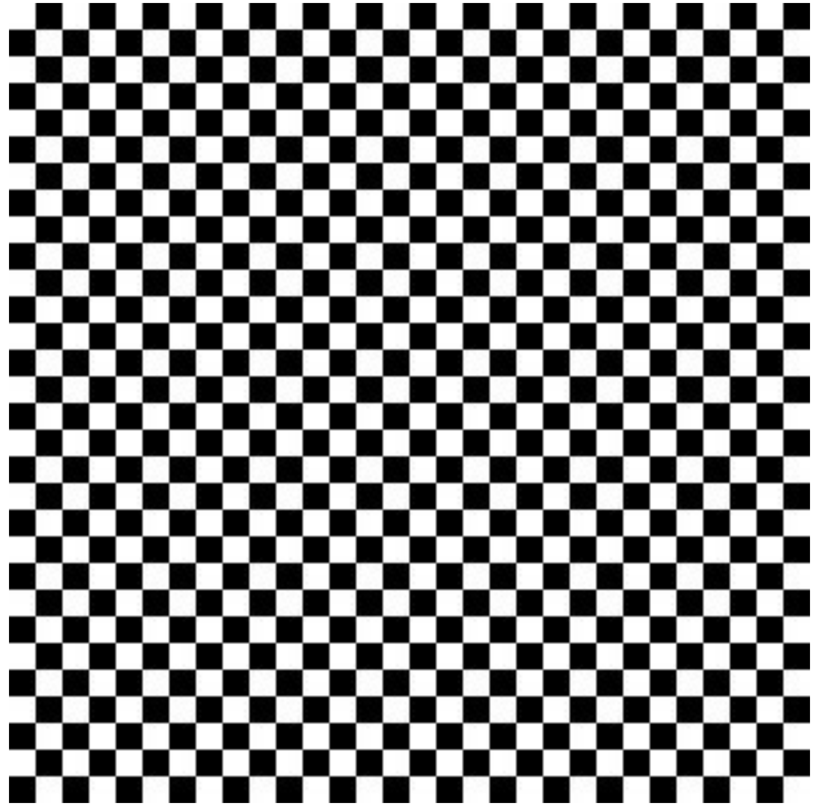
By Linus Pauling

The basic idea in the paper is that each O atom is surrounded by 4 possible bonds and the H atoms can fill 2 of these bonds. Then there are

$$\binom{4}{2} = 6$$

ways to fill these bonds.





“checkerboard pattern” in 2D: black (white) sites are independent, because they are spatially disconnected; Pauling considered a similar configuration in 3D.

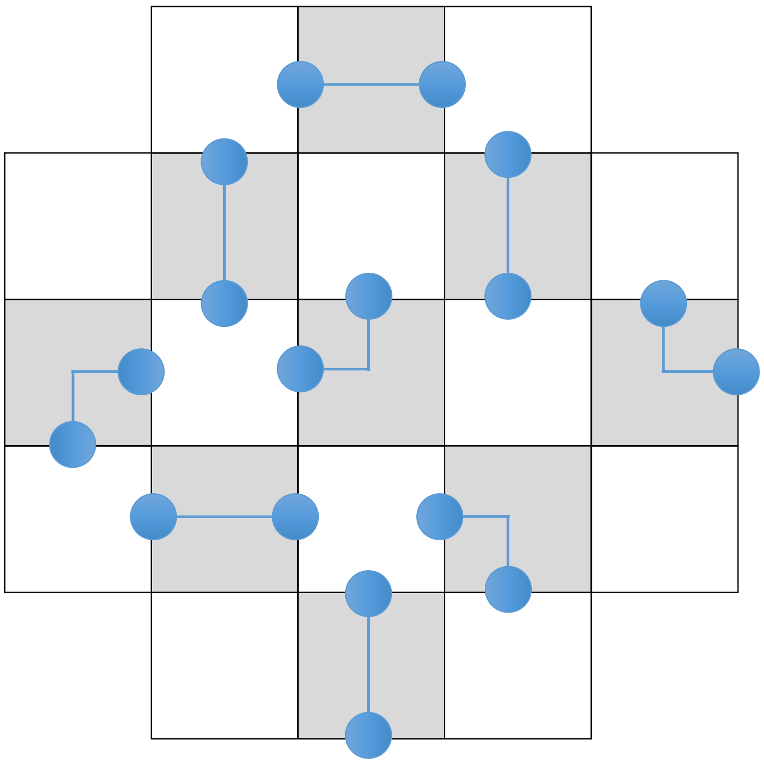
We can subdivide the whole ice lattice with N oxygen atoms in two sublattices, each with $N/2$ atoms. The atoms in each sublattice are independent, within a given sublattice.

Then, there are $6^{N/2}$ ways to fill the bonds for the O atoms in the first sublattice.

However, this is likely to produce a wrong configuration in the other sublattice. Since the arrangements in the first sublattice yield $2^4 = 16$ ways to fill/not-fill the bonds for an atom in the adjacent sublattice, but only 6 are correct, the probability of randomly filling the bonds in the first sublattice and still find a correct configuration is 6/16 per atom in the adjacent sublattice.

Then there are approximately $6^{N/2}\,(6/16)^{N/2}$ *configurations.*

2D example



This means that the residual entropy of ice is

$$S \approx k_B \ln\left[6^{N/2}\left(\frac{6}{16}\right)^{N/2}\right] = \frac{Nk}{2}\ln\frac{9}{4} = Nk_B \ln\frac{3}{2} \approx 0.405\, Nk_B$$

and for one mole of ice this corresponds to

$$\begin{aligned} S &\approx 0.405\, N_A k_B \\ &\approx 0.405\, R \\ &\approx 3.37\ \mathrm{J\ mol^{-1}\ K^{-1}} \\ &\approx 0.806\ \mathrm{cal\ mol^{-1}\ K^{-1}} \end{aligned}$$

Experiment: $S_{\mathrm{exp}} \approx 0.82(5)\ \mathrm{cal\ mol^{-1}\ K^{-1}}$

... this is in extremely good agreement with experiment.

- The problem of the exact evaluation of residual entropy has led to the development of the so-called “ice models” in statistical mechanics.

- Exact solution of 2D “square ice” in 1967 (Lieb)

- There are no exact solutions, but only analytical approximations for 3D ice models

- Further estimates can be obtained from numerical solutions for 3D ice models

EXACT SOLUTION OF THE PROBLEM OF THE ENTROPY OF TWO-DIMENSIONAL ICE

Elliott H. Lieb*
Department of Physics, Northeastern University, Boston, Massachusetts
(Received 16 February 1967)

The entropy of two-dimensional ice has been found by the transfer-matrix method. Entropy $= Mk \ln W$, with $M =$ No. of molecules and $W = (\frac{4}{3})^{3/2}$.