That Spirit-Like Force: Homeopathy and the Physics of Water

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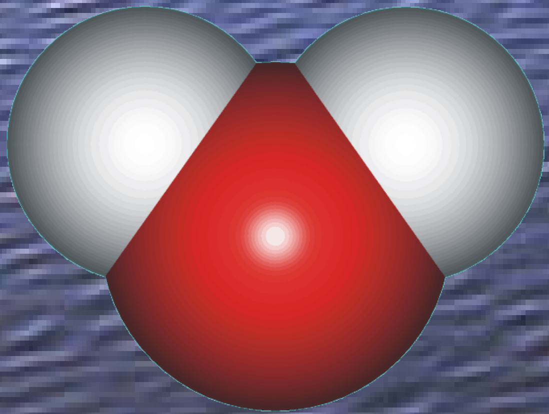


Outline of talk

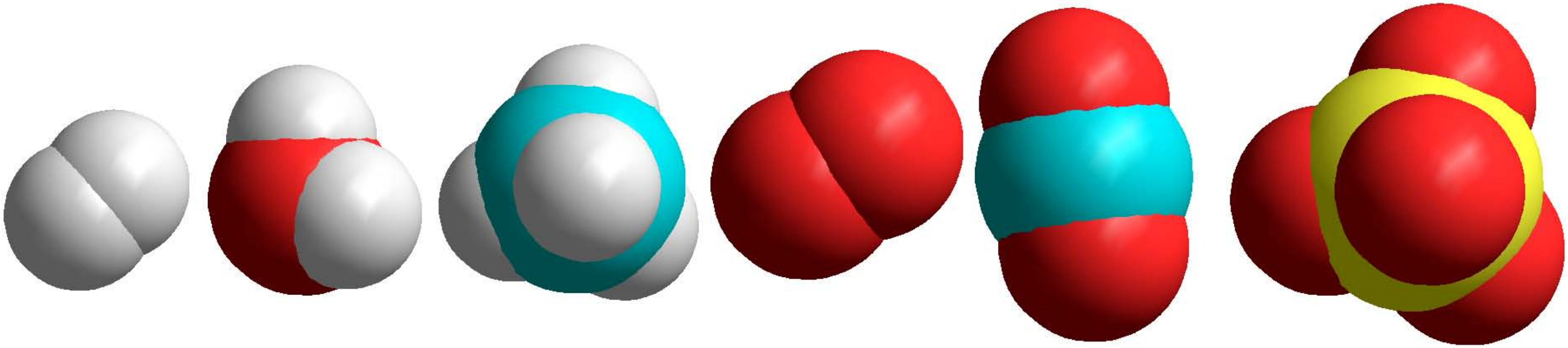
The Physics of Water

Why is water so special?

- The water molecule and hydrogen bonding
- Liquid water has many strange properties
- Water is not just H_2O molecules
- What happens when you shake water
- How succussed water is different from 'just' H_2O
- So. Does water have a memory?
- Conclusions

The water molecule and hydrogen bonding

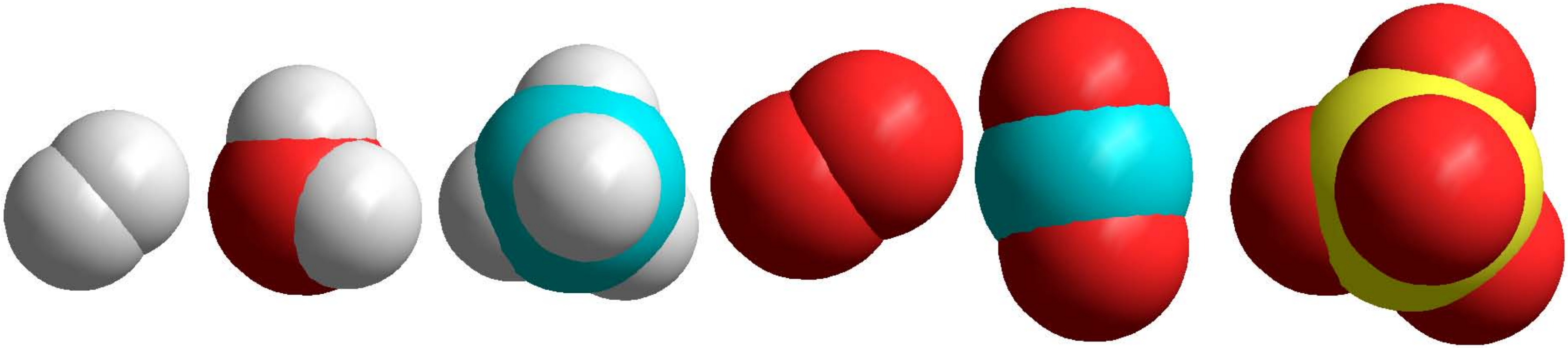
Water is very small



H_2 H_2O CH_4 O_2 CO_2 SO_4^{2-}

Only H_2 and HF are smaller molecules

Water is very small



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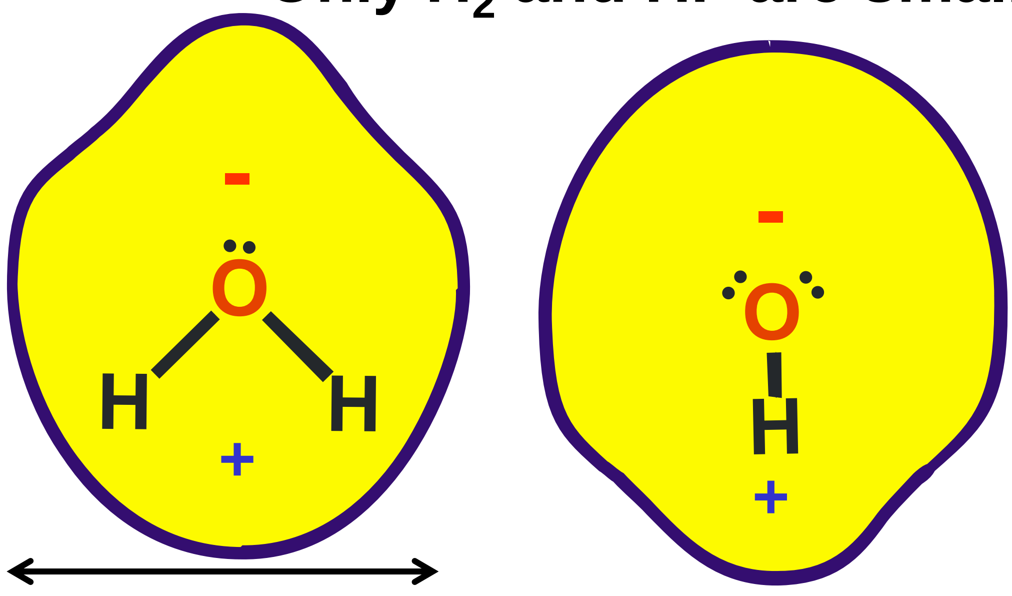


~0.28-0.31 nm

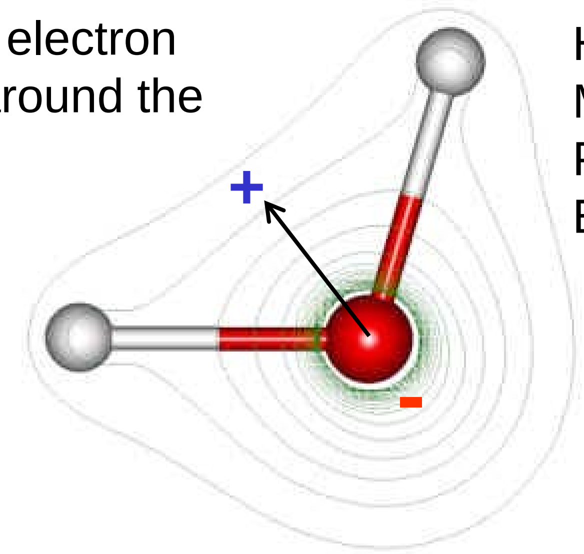
Good solvent

High density

Good penetration into materials

Water has a high dipole

Greatest electron density around the oxygen

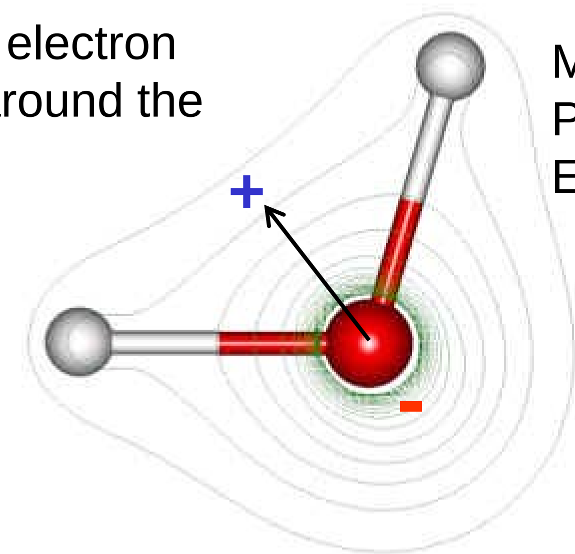


Hydrogen atom
Mass=1
Protons=1
Electrons~1/2

Oxygen atom
Mass=16
Protons=8
Electrons~9

Water has a high dipole

Greatest electron density around the oxygen



Mass=1
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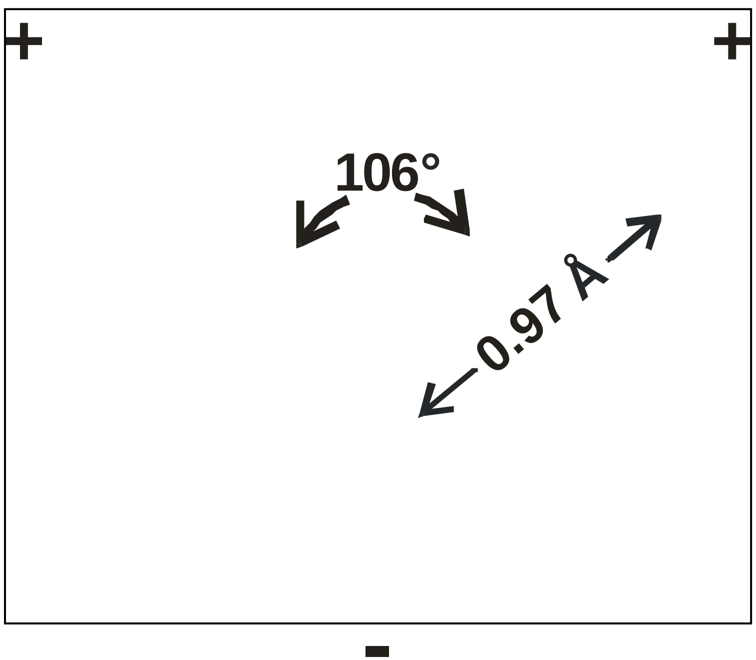
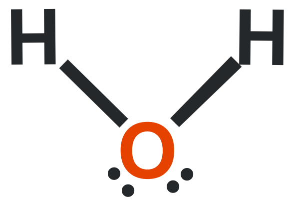


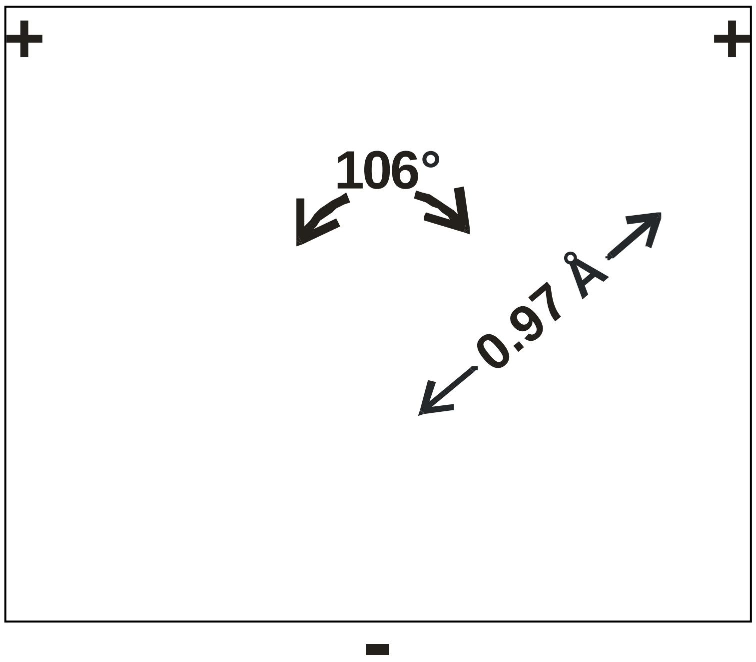
Dipole, 2.95 D (liquid) cf. 1.854 D (gas)

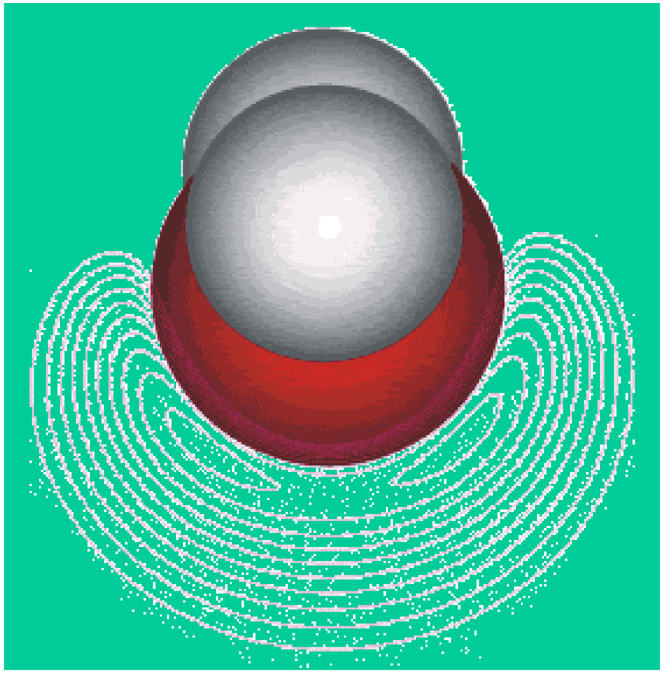
High dielectric constant
Ion solvation
Highly polar
High density
Hydrogen bonding

Water has ‘spare’ electrons



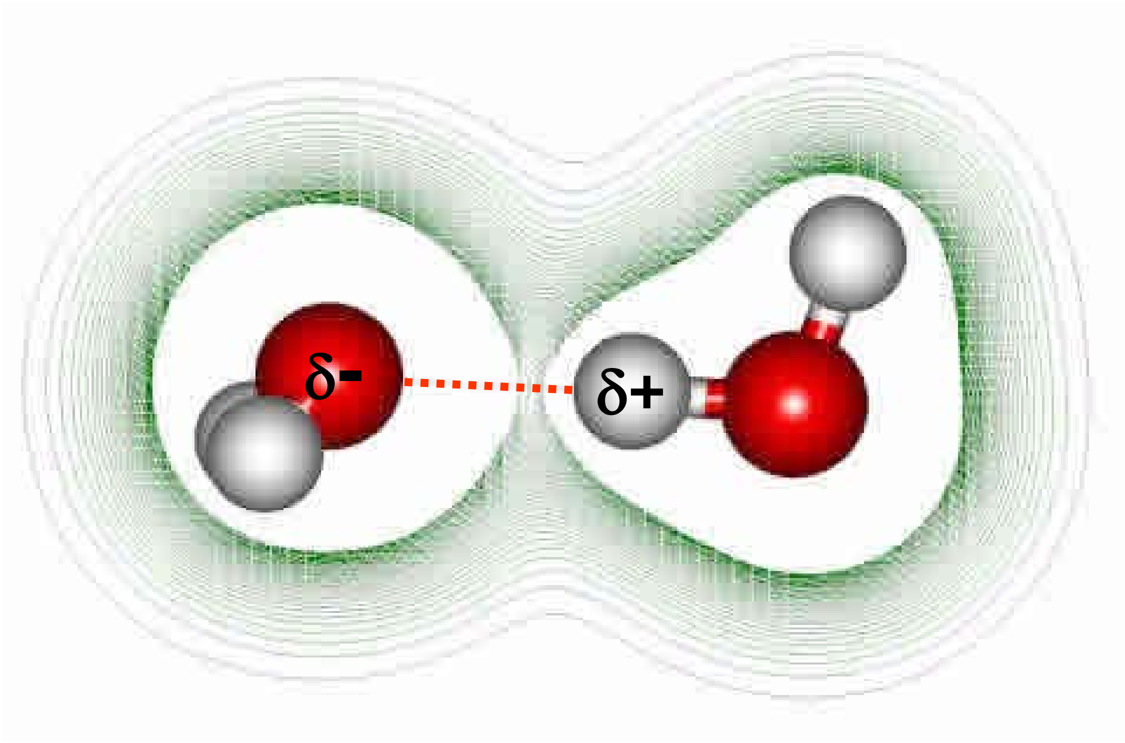
No distinct lone pairs
of electrons





Four electrons in two orbitals, spread out

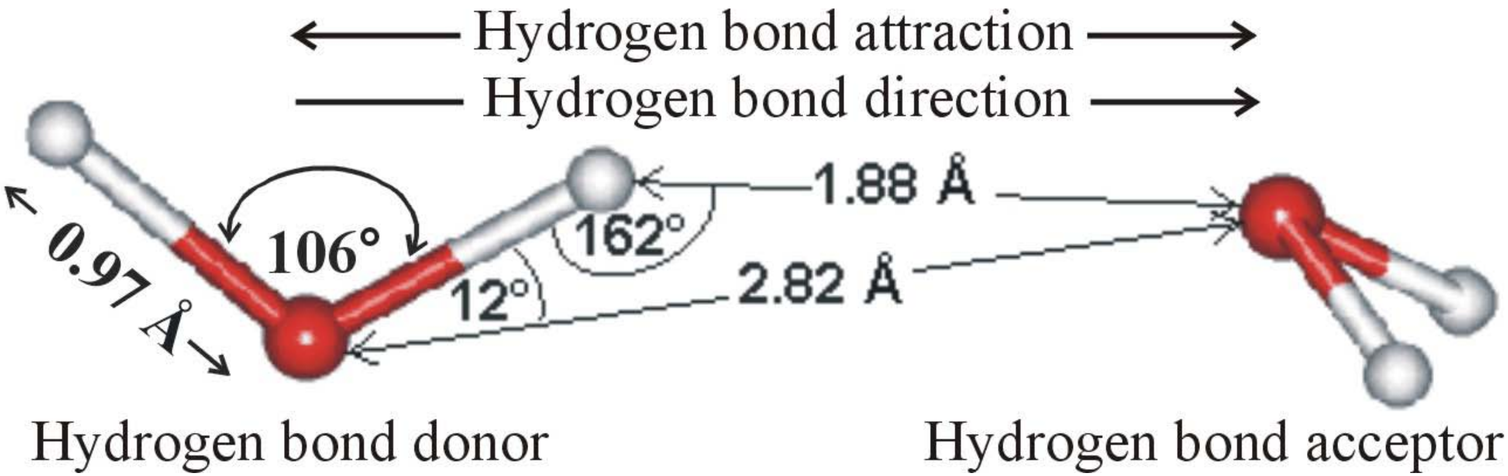
Water forms strong hydrogen bonds



Water's hydrogen bond

H-bond ~23 kJ/mol; O-H covalent bond ~492 kJ/mol

What is liquid water's hydrogen bond?

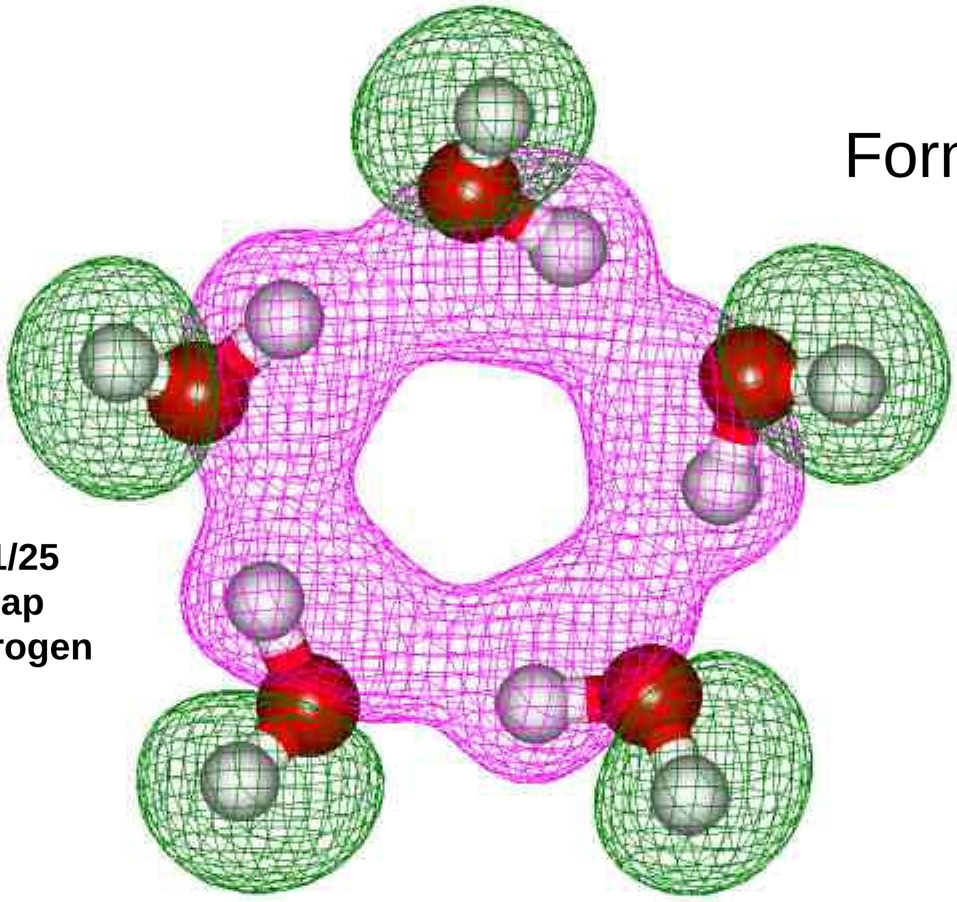


Average values.

In reality, there is much vibration and variation

compare with: van der Waals minimum energy position 3.0 - 3.6 Å

Hydrogen Bonding in Water

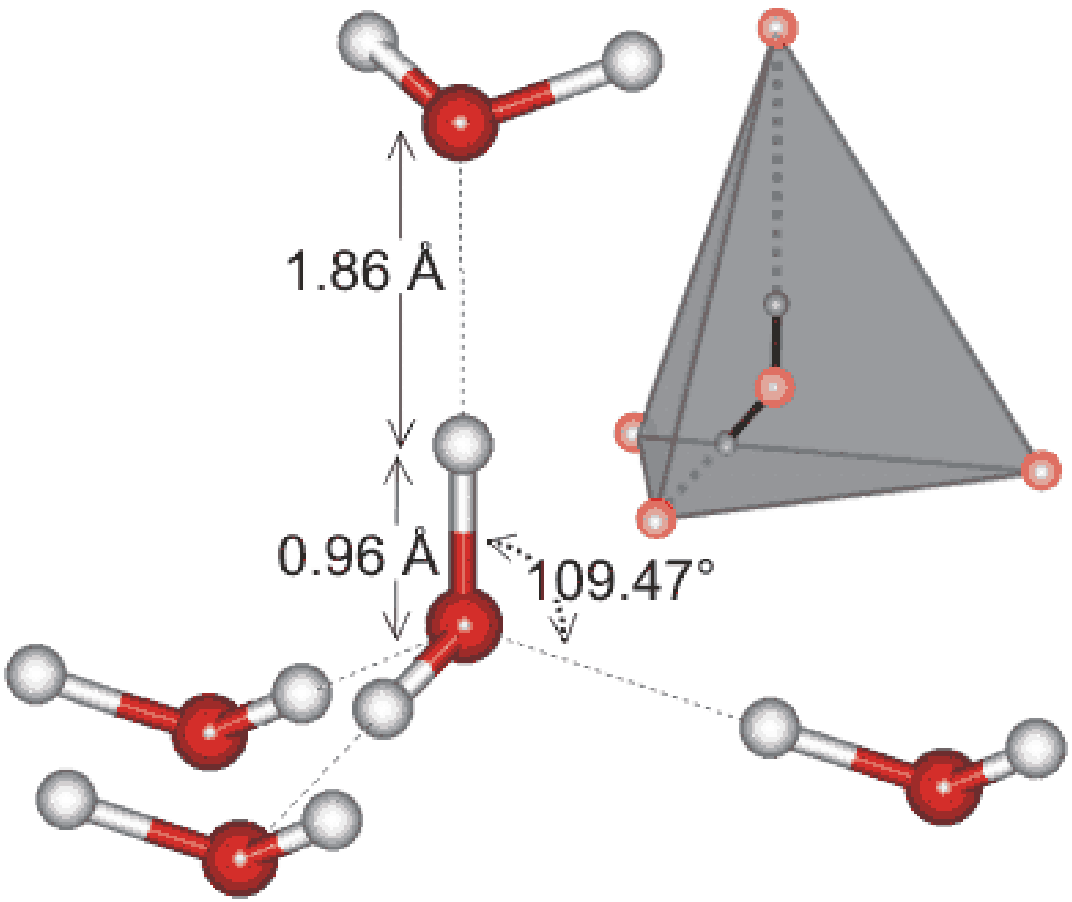


Forms networks

This is molecular orbital 11/25 showing the electron overlap possible for extended hydrogen bonding

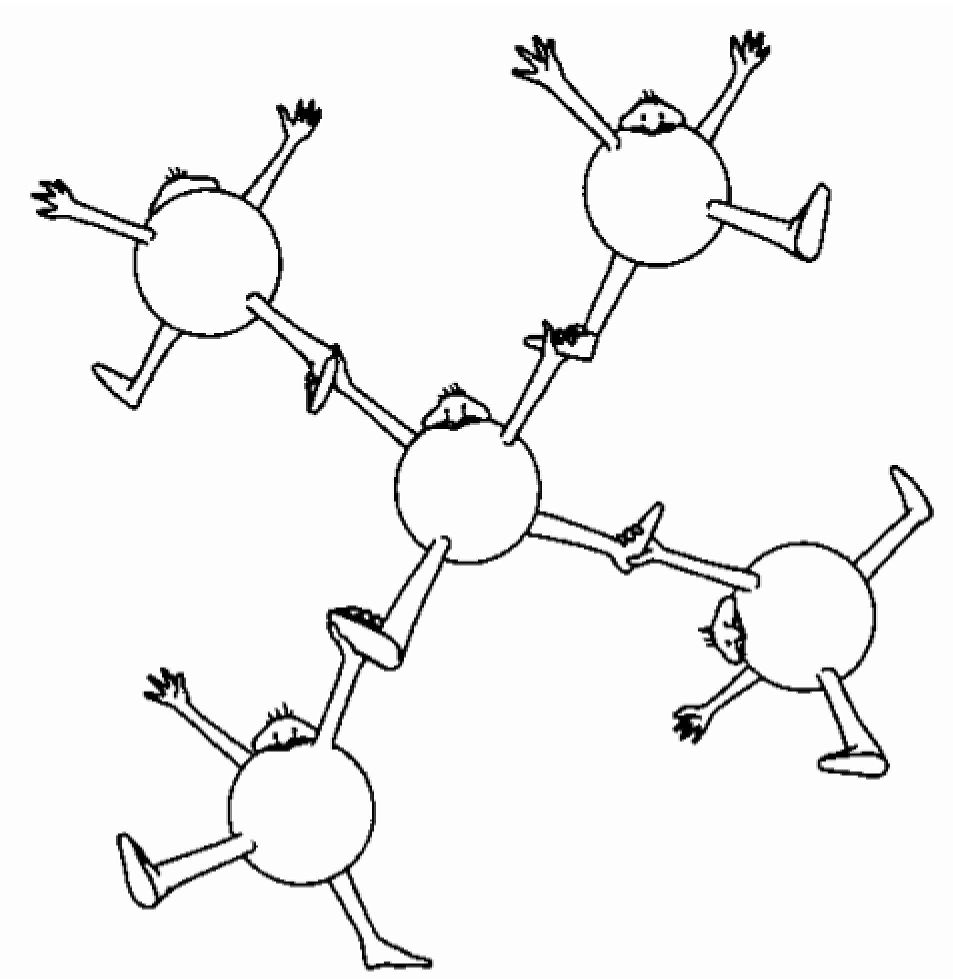
Substantial cooperativity in bond strengthening

Water: tetrahedral pentamer structure

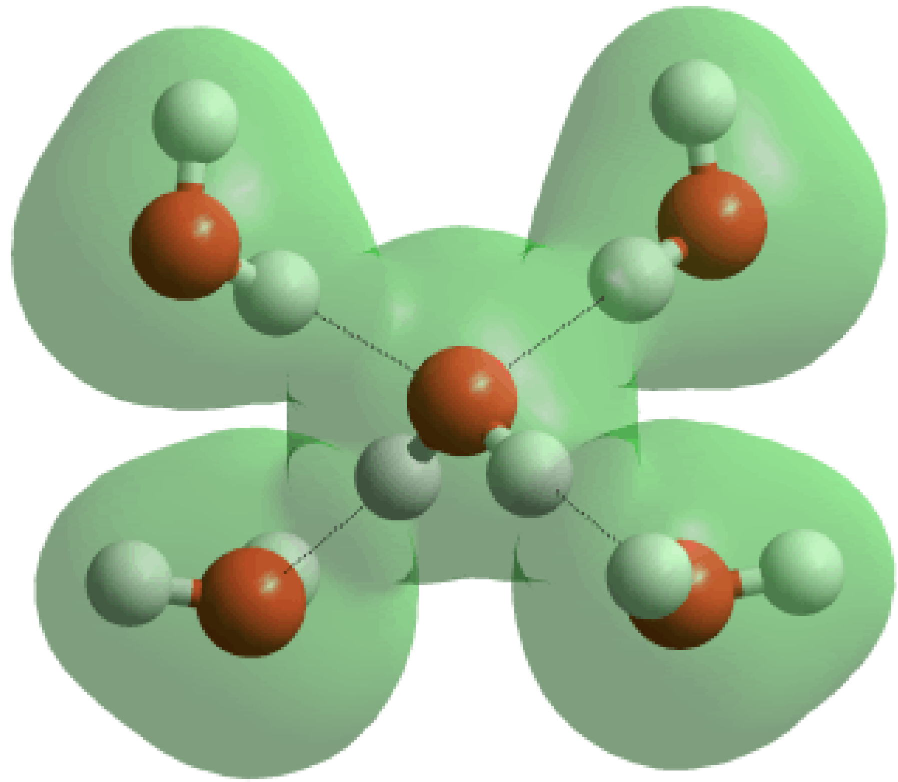


Commonly found tetrahedral arrangement of water molecules
Hydrogen bonds O-H····O are not necessarily straight

Hydrogen bonding



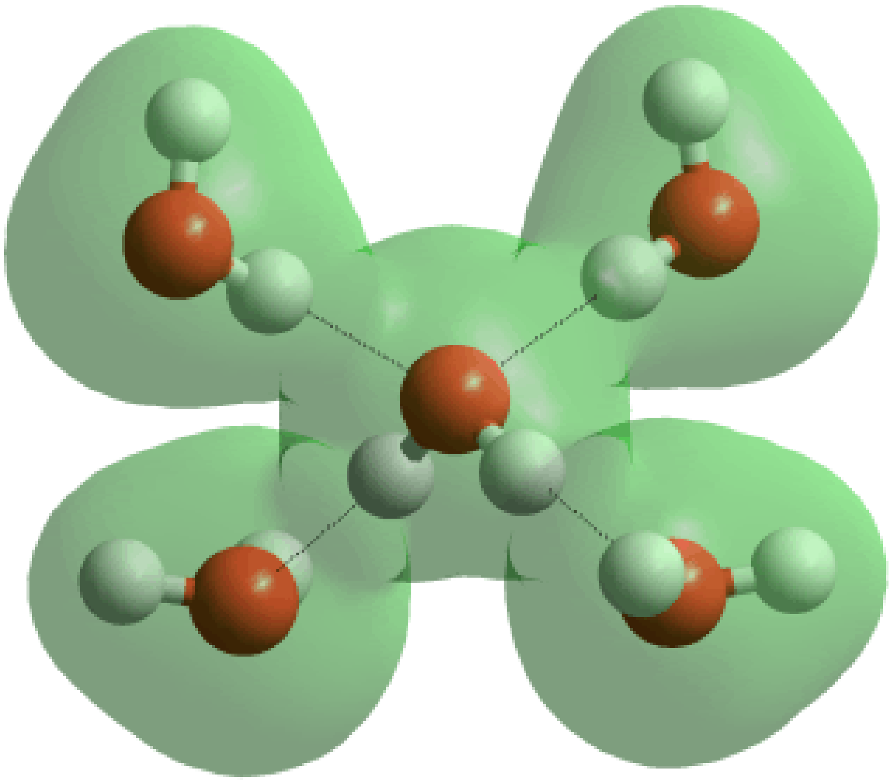
forms 3-dimensional networks



Hydrogen bonding dominates the properties of water. If hydrogen bonds are absent then the water molecule is much more reactive

P. Ball, A biography of water, Weidenfeld & Nicolson, 1999.

Liquid water has many strange properties,
due to hydrogen bonding



High specific heat
High surface tension
High melting point
High boiling point
High heat of vaporization
Good solvation

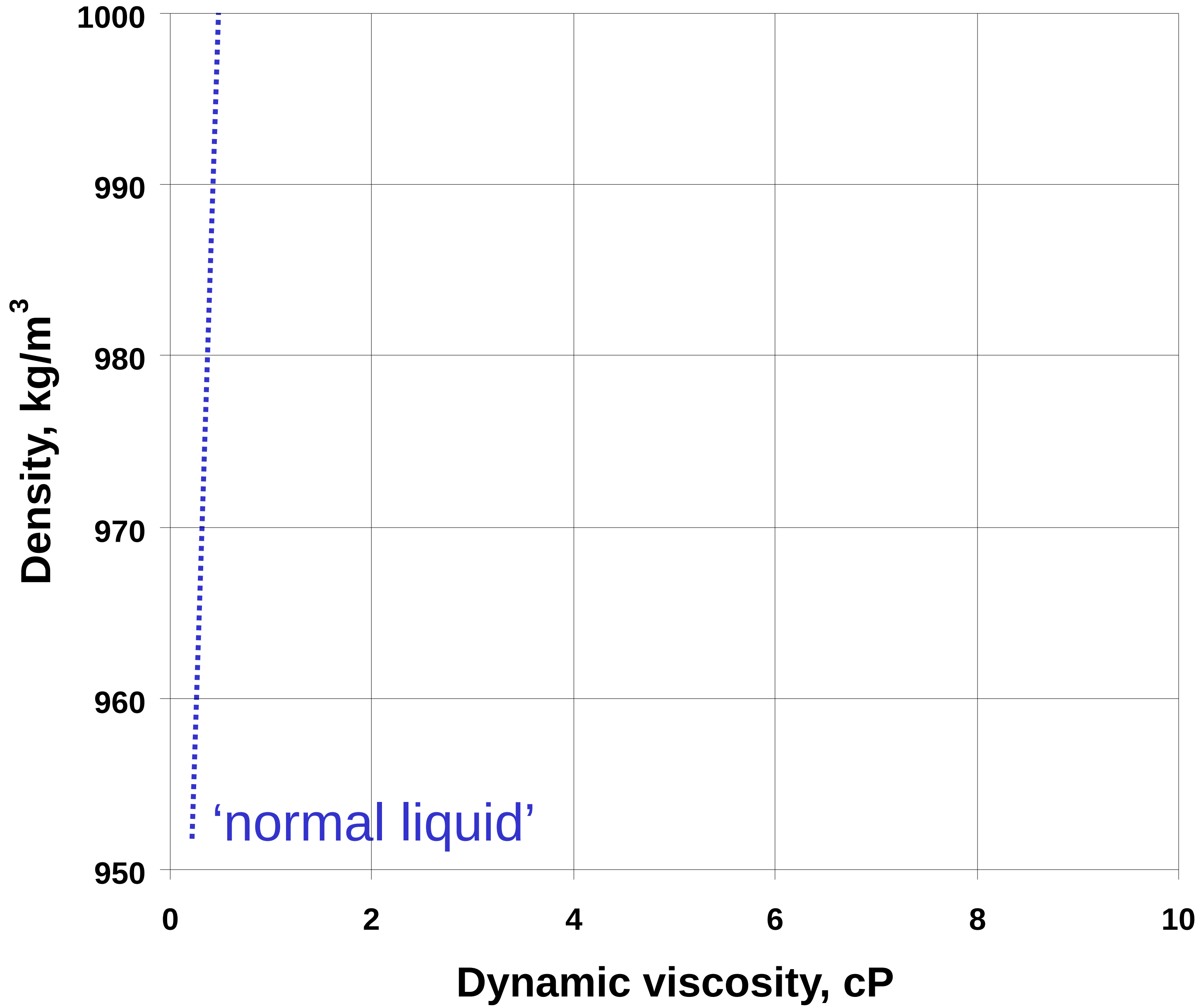
Puzzles
Over 60 unusual properties for a liquid

- **(Cold) Liquid water contracts on heating**
- **Liquid water becomes less organised when compressed**
- **Liquid water molecules move faster if compressed**
- **Liquid water molecules move apart if compressed hard**
- **Liquid water dissolves less gas on heating**
- **Liquid water is more dense than solid water**

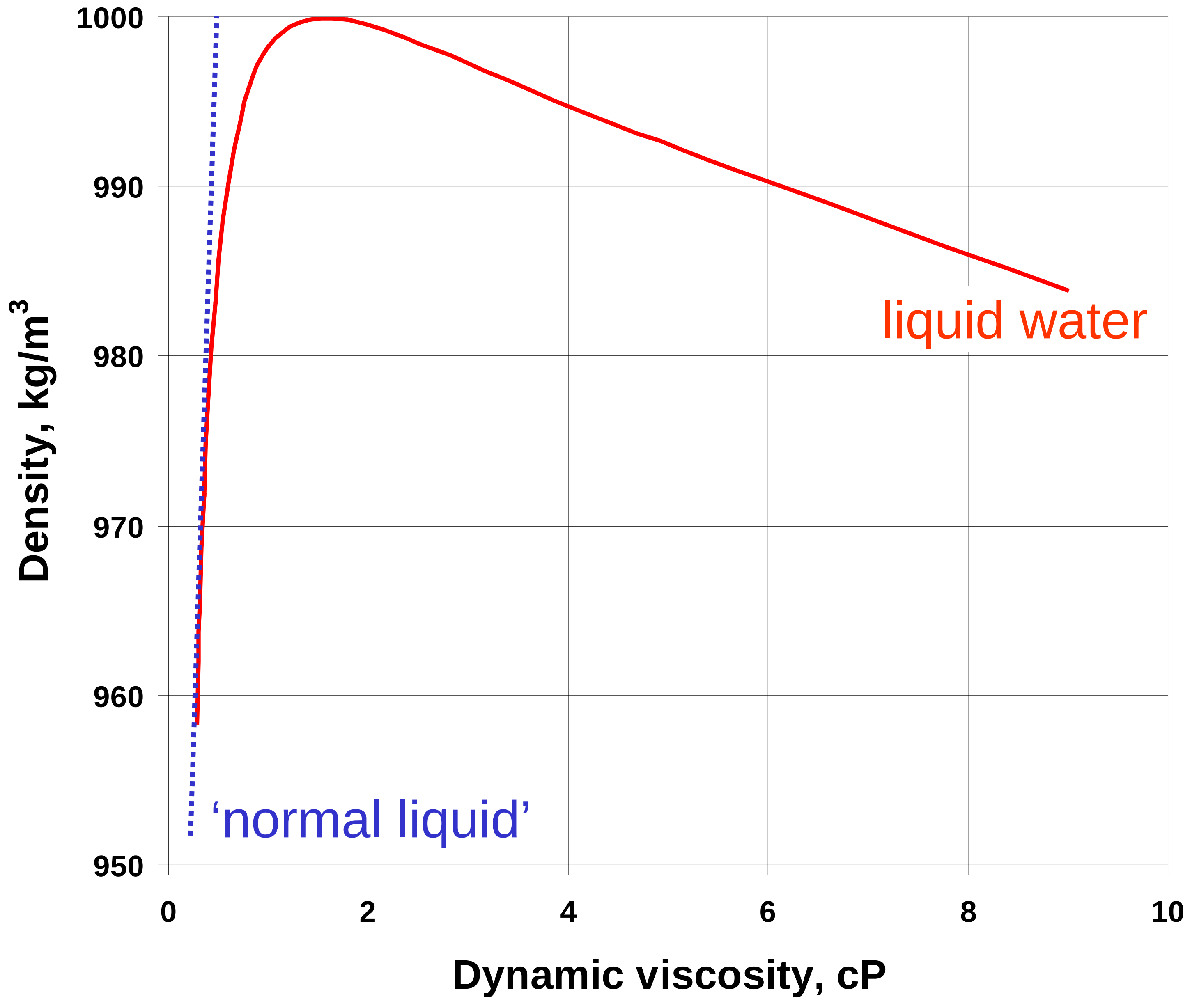
Generally, **cold water behaves in a different manner than does hot water** and **liquid water behaves as a mixture of two aqueous phases**

http://www.lsbu.ac.uk/water/anmlies.html

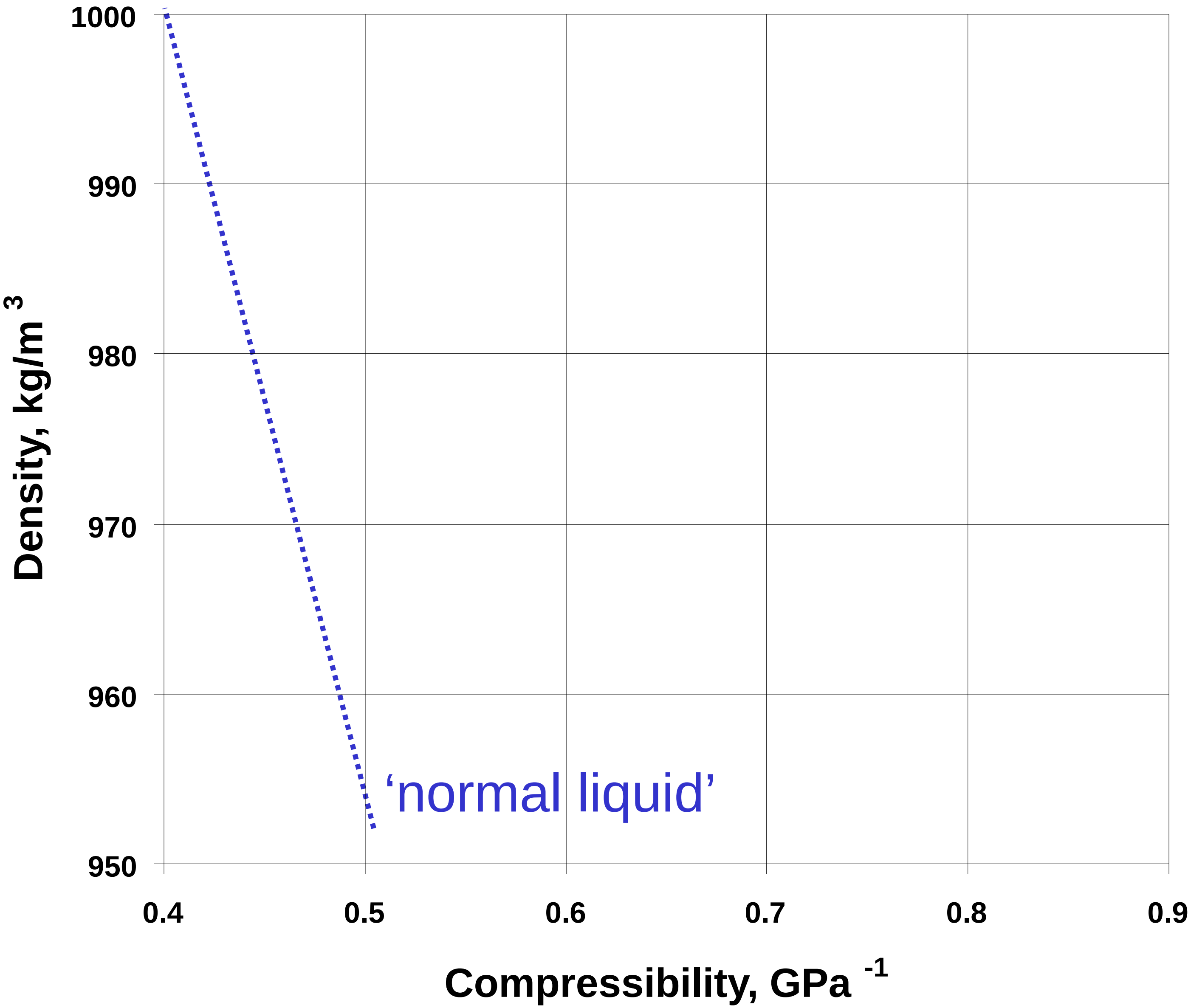
Density versus viscosity for liquid water



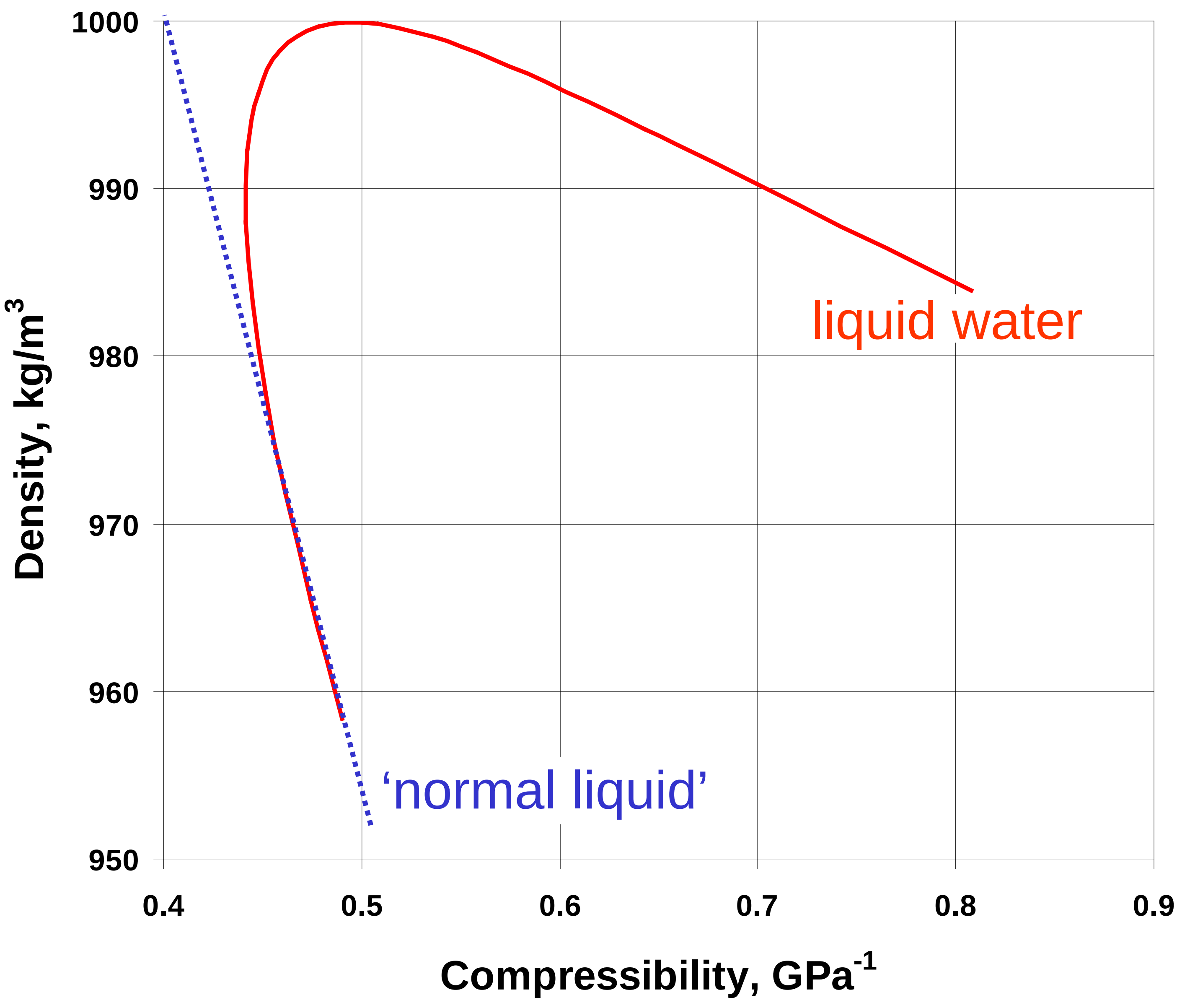
Density versus viscosity for liquid water



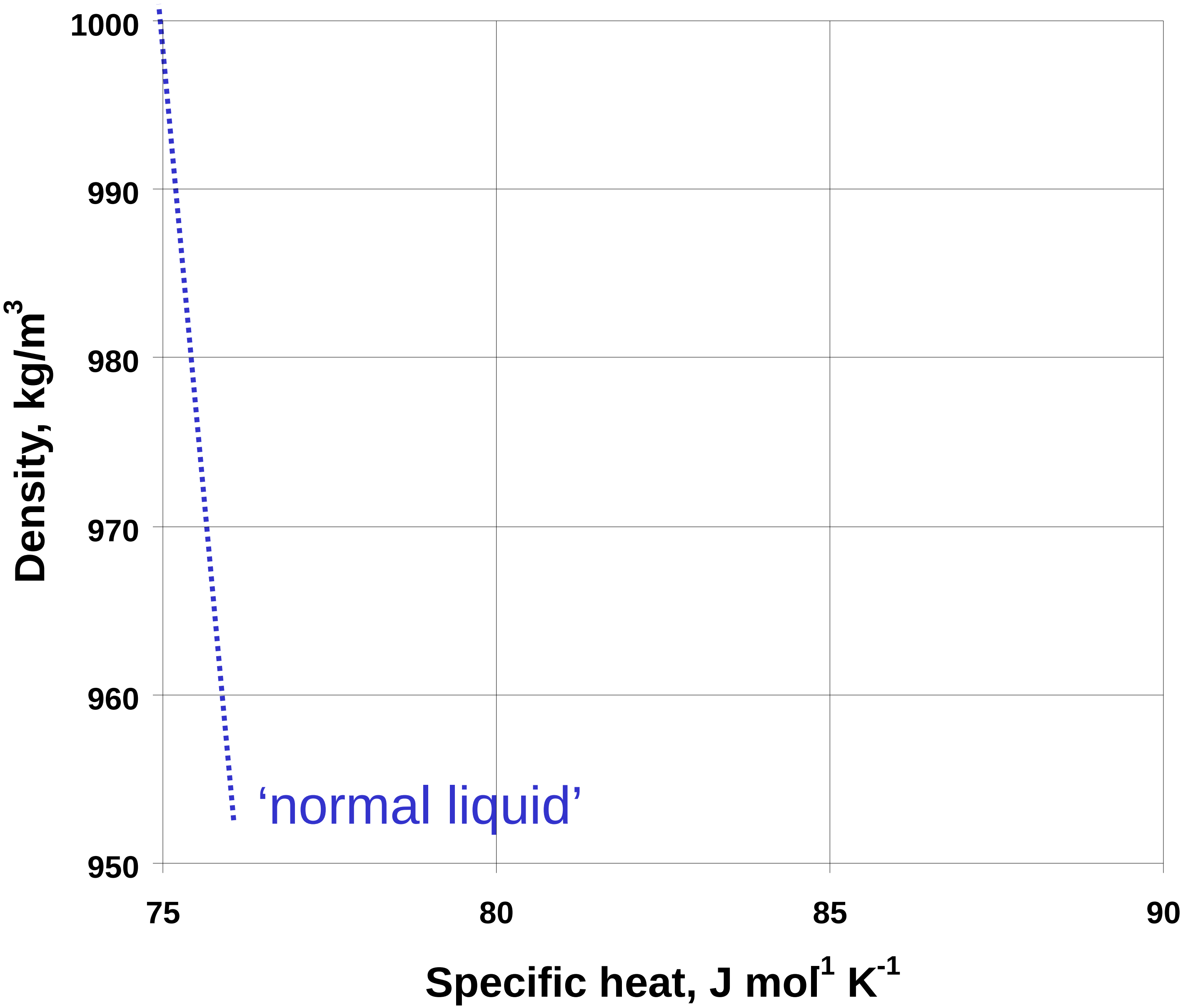
Density versus compressibility for liquid water



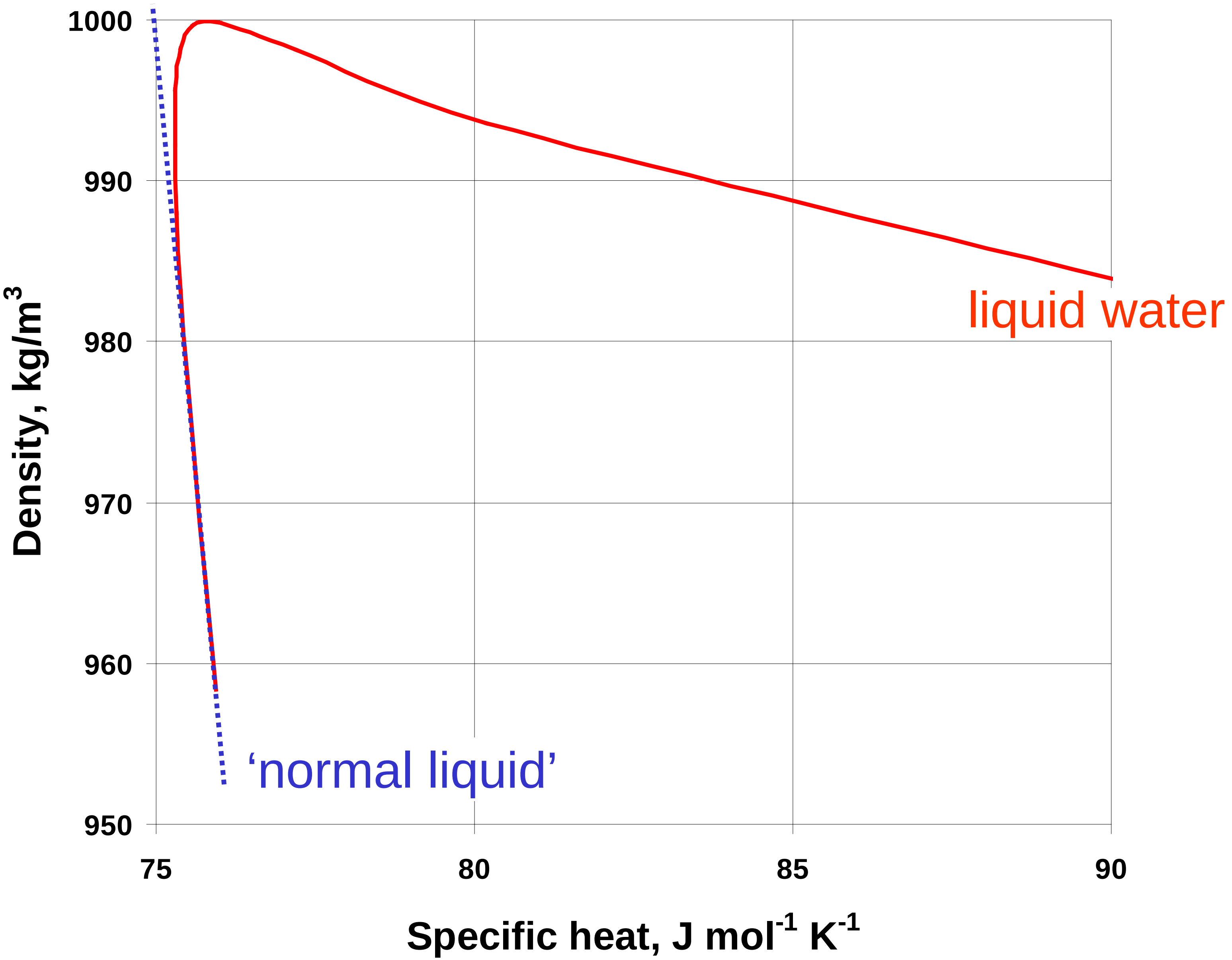
Density versus compressibility for liquid water



Density versus specific heat for liquid water



Density versus specific heat for liquid water



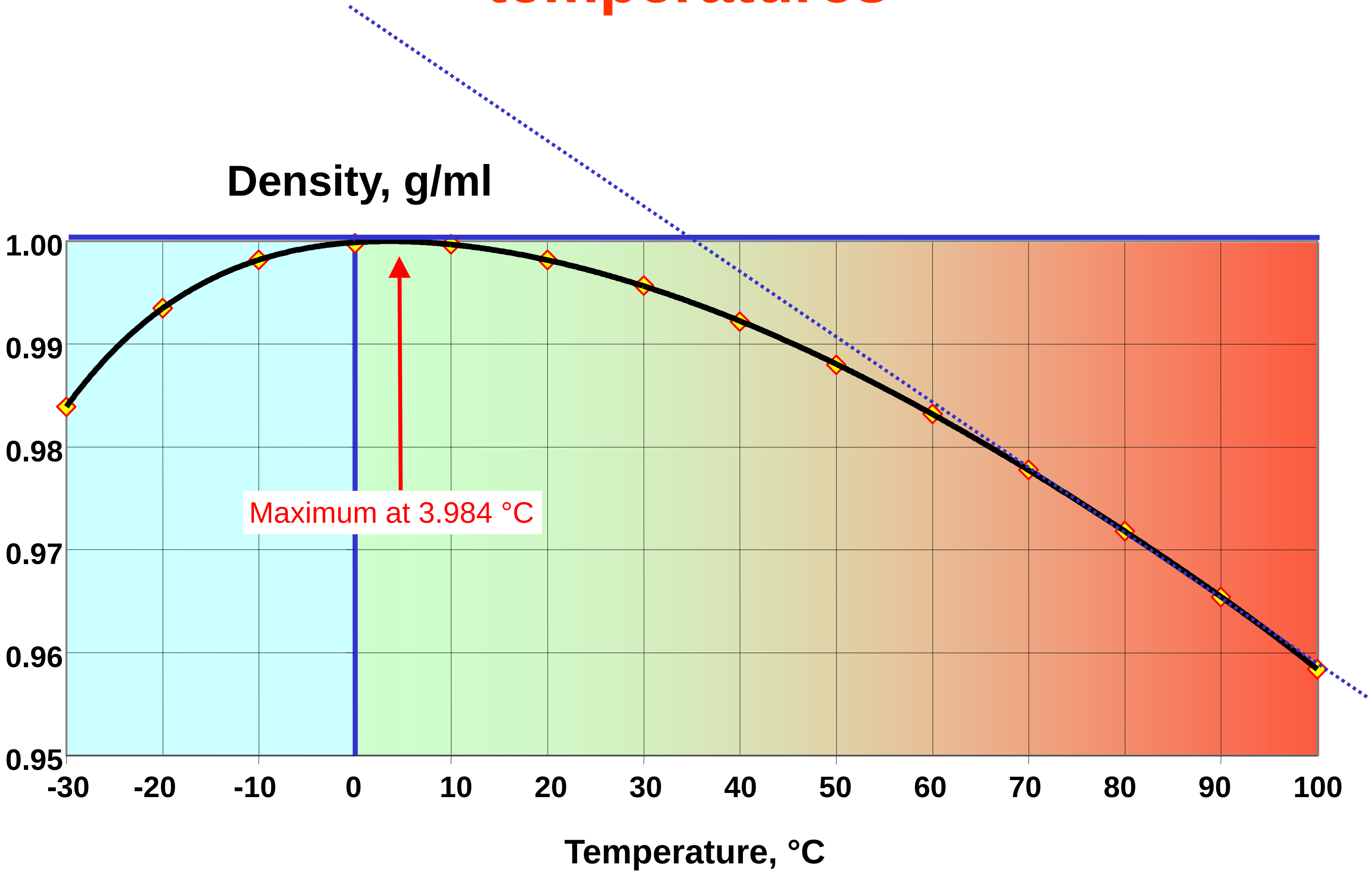
Liquid water behaves as a mixture of two aqueous phases

A second miscible phase of liquid water* appears to be present at low temperatures. It has:

Higher specific heat, lower thermal conductivity
Lower density, greater volume
Different solubility properties, e.g. Higher gas solubility
Low diffusion
High viscosity
High compressibility
High NMR shift and very low NMR spin-lattice relaxation time
Low entropy (well organised)
Low enthalpy (strong intra-molecular bonding)

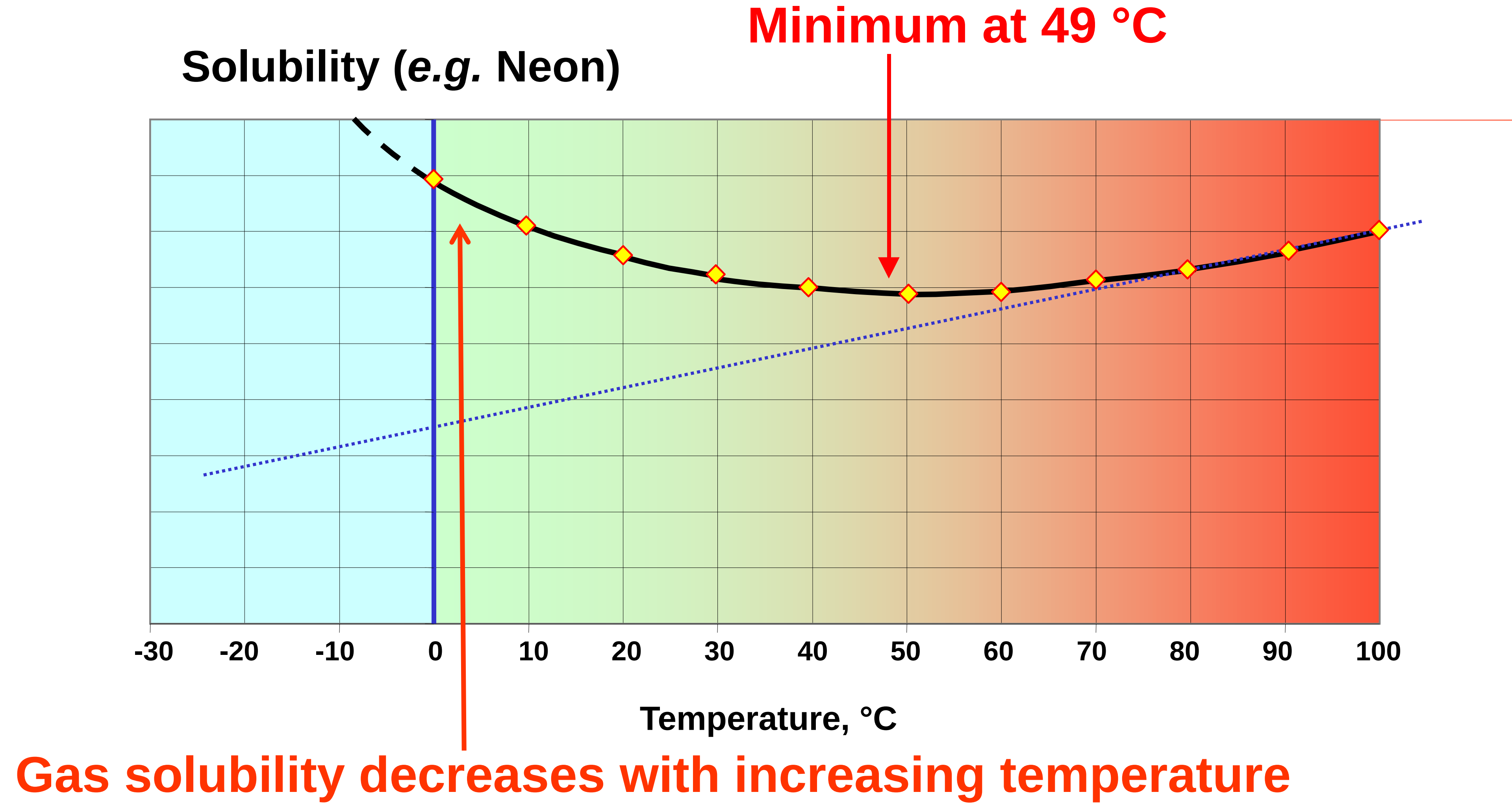
*e.g. G. A. Appignanesi, J. A. Rodriguez Fris and F. Sciortino, Evidence of a two-state picture for supercooled water and its connections with glassy dynamics, *Eur. Phys. J. E* **29** (2009) 305-310. D. Banerjee, S. N. Bhat, S. V. Bhat and D. Leporini, ESR evidence for 2 coexisting liquid phases in deeply supercooled bulk water. *Proc. Nat. Acad. Sci.* **106** (2009) 11448-11453.C. H. Cho, J. Urquidi, S. Singh, S. C. Park and G. W. Robinson, Pressure effect on the density of water, *J. Phys. Chem. A* **106** (2002) 7557-7561. L. Xu, F. Mallamace, Z. Yan, F. W. Starr, S. V. Buldyrev and H. E. Stanley, Appearance of a fractional Stokes–Einstein relation in water and a structural interpretation of its onset, *Nature Phys.* **5** (2009) 565 -569.

Low-density phase is more apparent at low temperatures

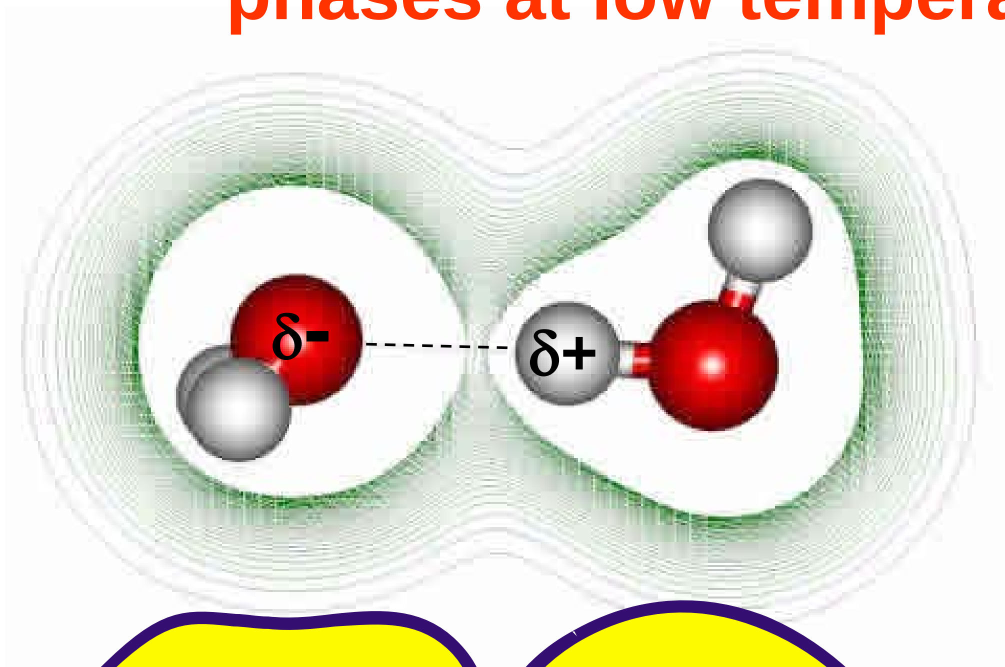


Water shrinks as temperature increases, below 4°C

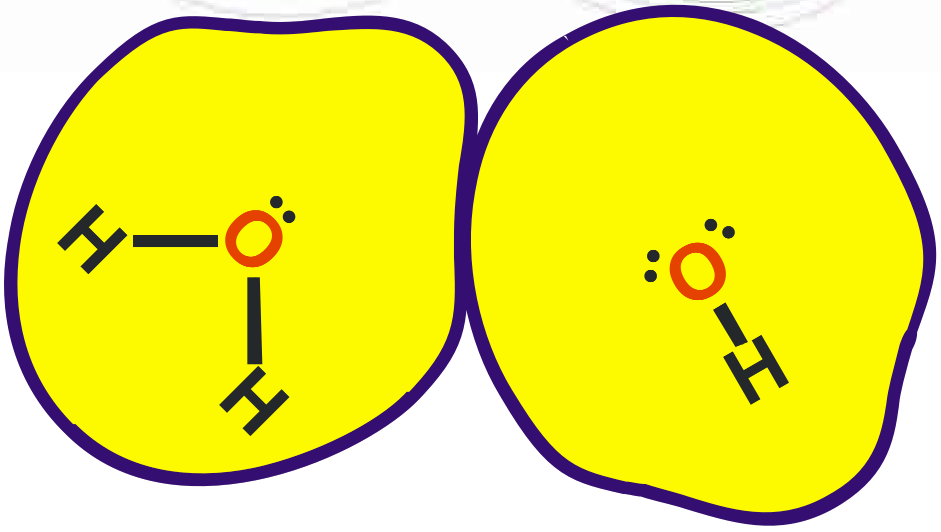
Low-density phase dissolves more gas



Why does liquid water appear to have two phases at low temperatures?



H-bond
low entropy
low enthalpy

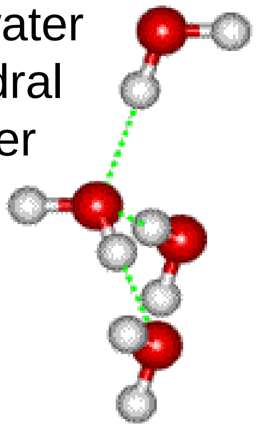


Van der Waals
higher entropy
higher enthalpy

H-bonds preferred at lower temperatures

Equilibrium between the liquid phases of water

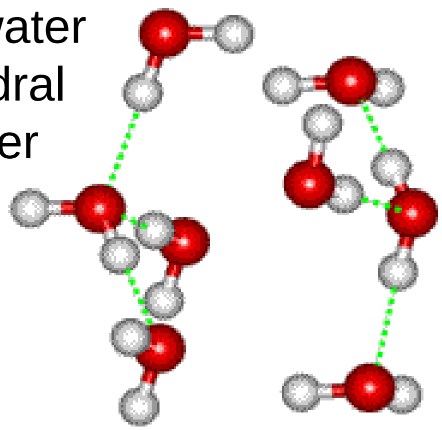
4/5 of water
tetrahedral
pentamer



Dense clusters of water ⟷ Lower density clusters of water

Equilibrium between the liquid phases of water

4/5 of water
tetrahedral
pentamer



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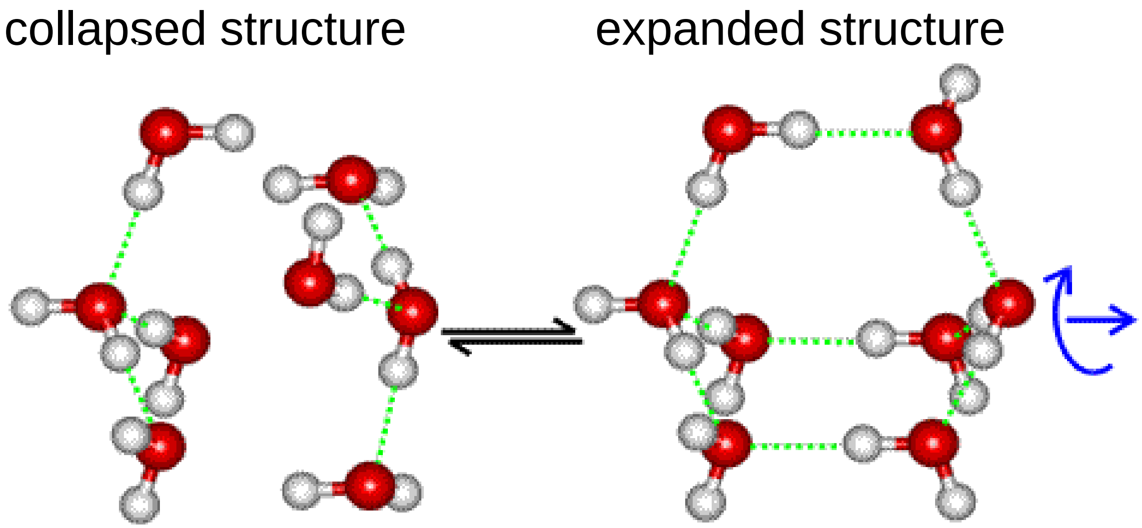

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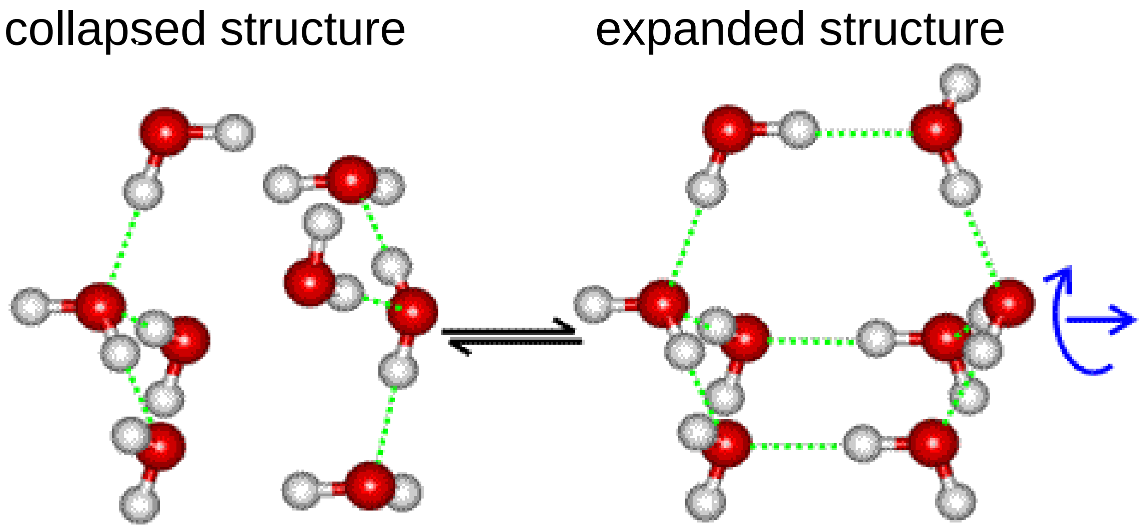
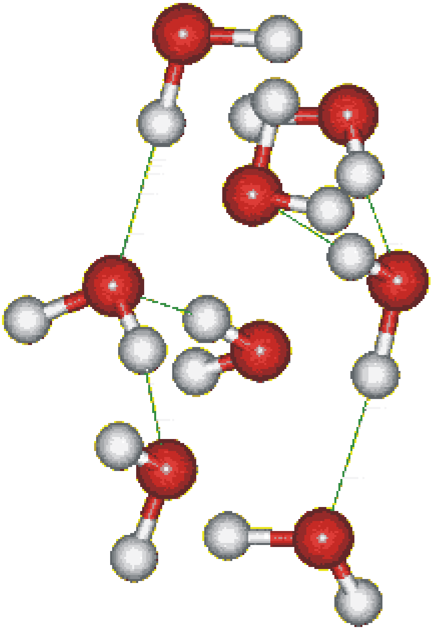
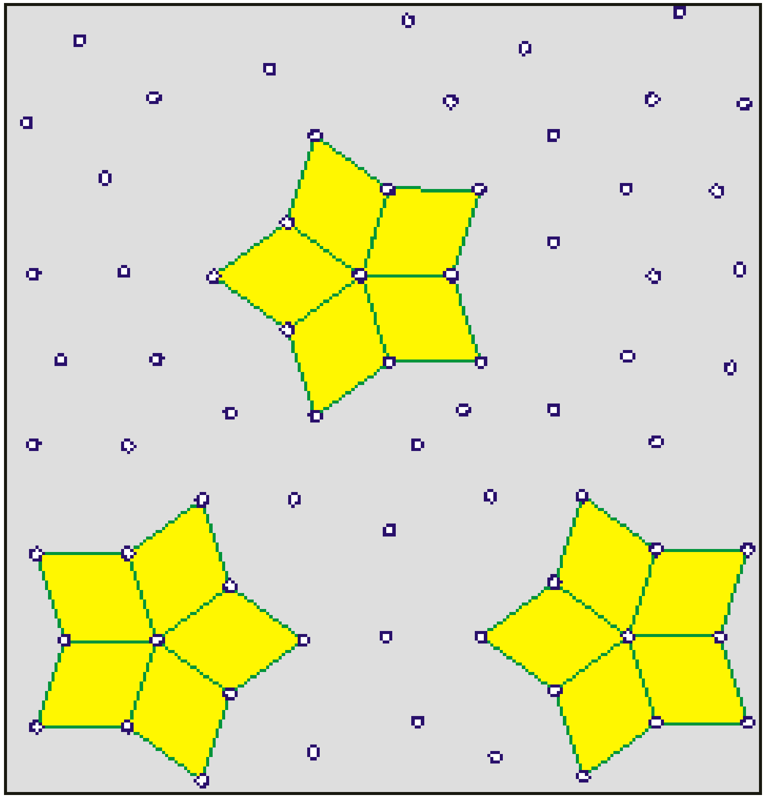




Water: Cluster movement



Movement of molecules as ‘flickering’ clusters.

Individual molecules move every 3 ps at room temperature.

But ‘clusters’ may last for much longer;

as one molecule leaves then another joins

or the same molecule may come back

Water is not just H_2O molecules

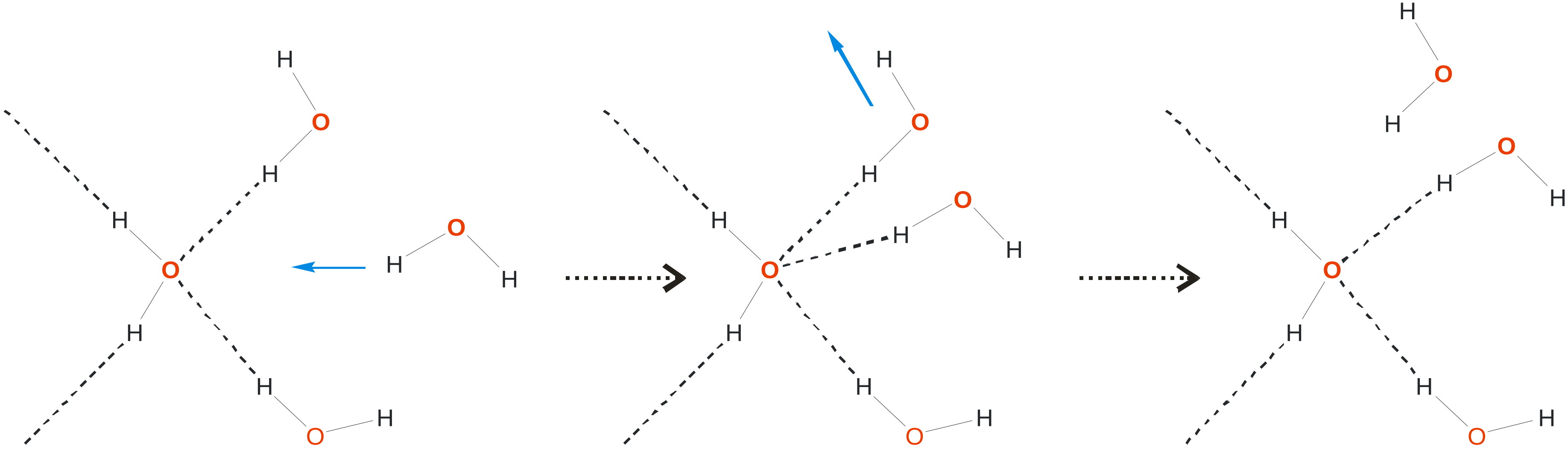
75% ortho-H_2O parallel magnetic nuclear spin, paramagnetic
25% para-H_2O anti parallel magnetic nuclear spin, non magnetic
0.03% (17 mM) HDO; 0.2% (110 mM) $H_2{}^{18}O$
Two sorts of molecular clusters containing 1-, **2-**, 3- **or 4-** H-bonds extending throughout the liquid and affected by solutes, etc.
Hydrogen ions and hydroxide ions
Other ions, even in distilled water and 'deionized' water
Dissolved gasses and other dissolved material
Dissolved and colloidal material from vessels and aerosols
Gas bubbles and nanobubbles
Materials produced from reactions between water molecules and between water and solutes

Even highly diluted solutions contain ALL of the above

What happens when you shake water

Shaking breaks hydrogen bonds

Reactivity of 'collapsed' structure



Collapsed structure allows bifurcated hydrogen bonding, facile hydrogen bond exchange, partner swapping, increased diffusion and greater reactivity.

Shaking can form other molecules in liquid water

In particular, low concentrations of hydrogen peroxide (H_2O_2) may be produced from water (H_2O) by any process that moves clusters of water relative to each other such as mechanical vibration

$$(H_2O)_n(H_2O\cdots HOH\cdots OH_2)(H_2O)_m \rightarrow (H_2O)_n(H_2O + H\cdot + \cdot OH + OH_2)(H_2O)_m$$

$$2\ \cdot OH \rightarrow H_2O_2$$

without the need for molecular oxygen but increased by it, for example,

$$O_2 + \cdot H \rightarrow HO_2\cdot$$

$$HO_2\cdot + \cdot H \rightarrow H_2O_2$$

Also

$$\cdot OH + HCO_3^- \rightarrow H_2O + \cdot CO_3^-$$

The presence of such active oxygen species and gases or their mixtures in water may have significant long term effects.

V. L. Voeikov, Biological significance of active oxygen-dependent processes in aqueous systems, In *Water and the cell*, Ed. G. H. Pollack, I. L. Cameron and D. N. Wheatley (Springer, Dordrecht, 2006) pp 285-298.
V. L. Voeikov, The possible role of active oxygen in the memory of water, *Homeopathy* **96** (2007) 196-202.

Liquid water is a good solvent, and dissolves glass and atmospheric gasses

Glass is preferred over polypropylene tubes in homeopathic preparations.

Solutions made up in glassware contain ~μM silica, including colloidal silica

It should be noted that dissolved silica is capable of forming solid particles with complementary structures (that is, imprints) to dissolved solutes and macromolecules and such particles will 'remember' these complementary structures essentially forever. ‘Dissolved’ silica can re-precipitate at surfaces, so binding other materials there.

Such processes are likely to be more prevalent at the liquid-gas interface

Changes in solutes also cause changes in pH and changes in the glass surface

J.-L. Demangeat, NMR water proton relaxation in unheated and heated ultrahigh aqueous dilutions of histamine: Evidence for an air-dependent supramolecular organization of water. *Mol. Liquids* **144** (2009) 32-39.
D. J. Anick and J. A. Ives, The silica hypothesis for homeopathy: physical chemistry, *Homeopathy* **96** (2007) 203-209.

Liquid water can contain vast numbers of nanobubbles with their associated liquid-gas surfaces

Indeed, a high density of nanobubbles has recently been created in solution and the heterogeneous mixture lasts for more than two weeks.

The total amount of gases in these nanobubble solutions reached 600 ml (in 1.9 x 10^{16} 50-nm radius nanobubbles) per liter of water, and the liquid density was reduced to about 0.988 g.ml.

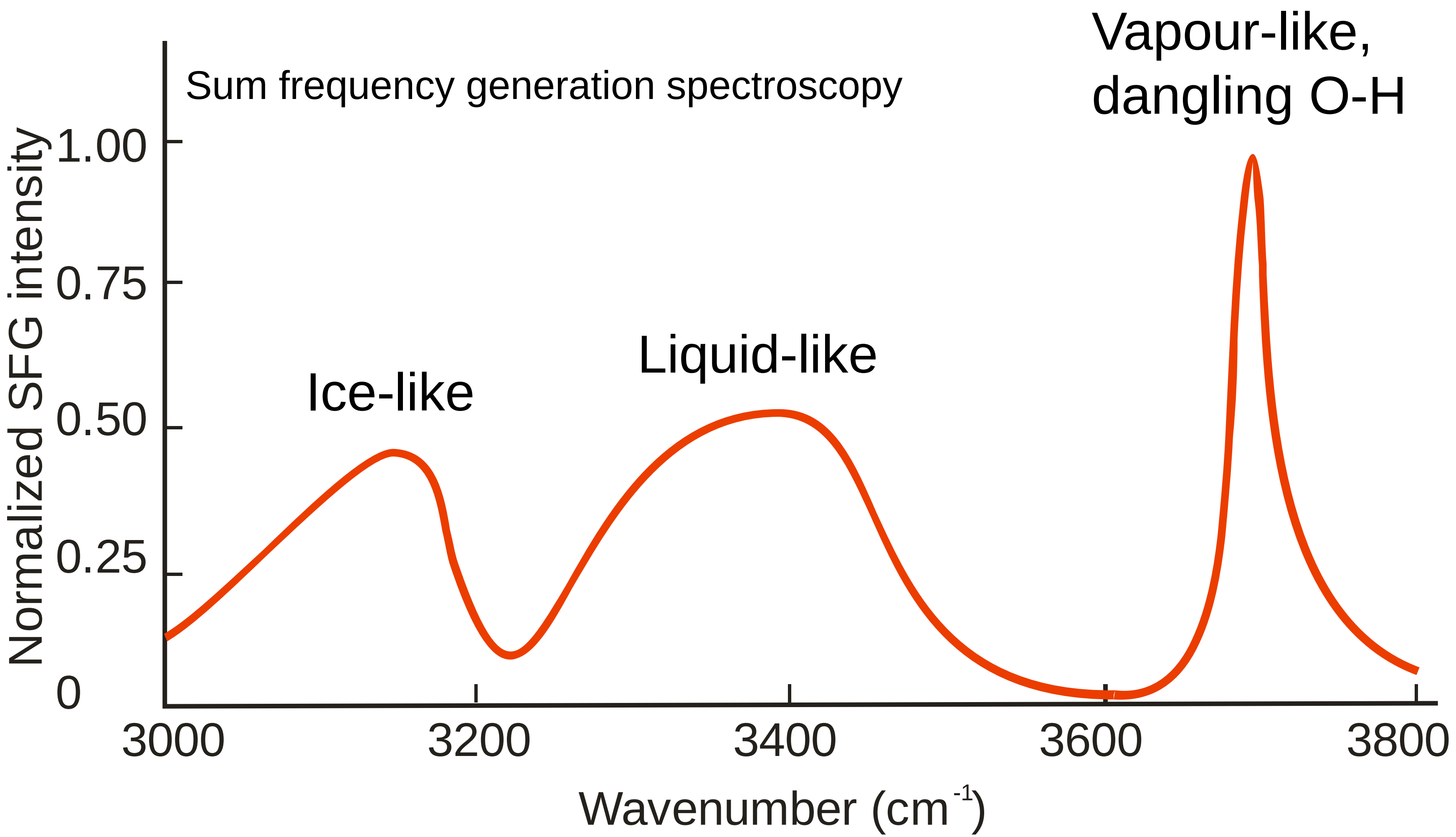
This gives about 600 m^2 of surface per liter. With surface depth of 20 nm (50 nm) this gives a 'surface' volume of about 2% (7%),

K. Ohgaki, N. Q. Khanh, Y. Joden, A. Tsuji and T. Nakagawa, Physicochemical approach to nanobubble solutions, *Chem. Eng. Sci.* **65** (2010) 1296-1300.

How succussed water is different from ‘just’ H_2O

- Solutes, including gasses
- Colloidal particles
- Nanobubbles
- Reaction products
- Three-phase water
- Starting materials?

The surface of liquid water



M. J. Shultz, C. Schnitzer, D. Simonelli and S. Baldelli, Sum frequency generation spectroscopy of the aqueous interface: ionic and soluble molecular solutions. *Int Rev Phys Chem* **19** (2000). 123-153.

Very small concentrations of some materials in water may have unexpected effects on health

e.g. peroxide

“Low micromolar, single doses of hydrogen peroxide were shown to cause dramatic increases in the apparent intracellular accumulation of model compounds with different physicochemical properties in different cell types.”

The immune response is now known to depend on the redox processes, with antibodies utilizing singlet oxygen.

R. S. Funk and J. P. Krise, Exposure of cells to hydrogen peroxide can increase the intracellular accumulation of drugs, *Mol. Pharmaceutics,* **4** (2007) 154-159.

So. Does water have a memory?

So. Does water have a memory?

Yes

So. Does water have a memory?

Yes

A shaken solution can be distinguished from one that has not been shaken and may contain ‘new’ pharmacologically-active material

Homeopathic preparations can be distinguished from their controls*

Both results have rational explanations

*S. Baumgartner, M. Wolf, P. Skrabal, F. Bangerter, P. Heusser, A. Thurneysen and U. Wolf, High-field 1H T1 and T2 NMR relaxation time measurements of H2O in homeopathic preparations of quartz, sulfur, and copper sulfate, *Naturwissenschaften* **96** (2009)1079-1089; U. Wolf, M. Wolf, P. Heusser, A. Thurneysen and S. Baumgartner, Homeopathic preparations of quartz, sulfur and copper sulfate assessed by UV-spectroscopy, *eCAM* (2009) doi:10.1093/ecam/nep036

Possible other effects

Addition of ethanol to water adds an important further area of complexity.

Ethanol forms solutions in water that are far from ideal and very slow to equilibrate. Although usually considered a single phase, such solutions may contain several distinct phases and more generally consist of a complex mixture dominated by water-water and ethanol-ethanol clusters, where hydrogen bonding is longer-lived than in water alone.

Ethanolic solutions also favor nanobubble formation.

Liquid water easily forms aerosols which could contaminate later preparations

Further bibliography

http://www.lsbu.ac.uk/water/memory.html
http://www.lsbu.ac.uk/water/homeop.html
M. F. Chaplin, The memory of water; an overview, *Homeopathy* **96** (2007) 143-150; P. Wilson, Comment on "The memory of water; an overview", *Homeopathy* **97** (2008) 42-43; M. F. Chaplin, Reply to Comment on "The memory of water; an overview", *Homeopathy* **97** (2008) 43-44.

Conclusions

- **Liquid water is a complex material and behaves as a mixture of two aqueous phases where the equilibria involved are affected by solutes, surfaces, magnetic and electrical fields and liquid-gaseous interfaces**

- **Liquid water can form other molecules on mechanical stirring**

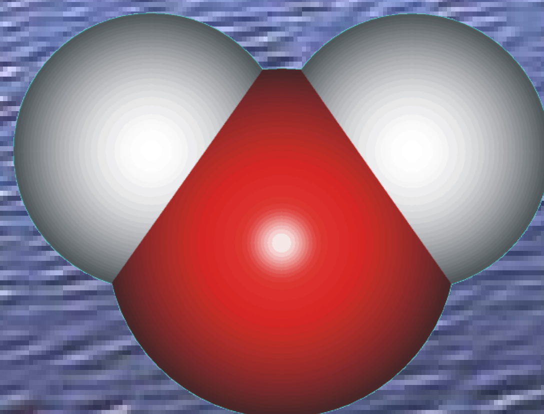
- **Liquid water can contain vast numbers of nanobubbles with liquid-gas interfaces that behave as though a different (third) phase**

- **Liquid water is a good solvent, and dissolves glass and atmospheric gasses to form complex solutions**

- **Very small concentrations of some materials in water may have unexpected effects on health**

That Spirit-Like Force: Homeopathy and the Physics of Water"

Martin Chaplin



More background information at http://www.lsbu.ac.uk/water/

Effects on structure

Electrical fields

Water, being dipolar, can be partly aligned by an electric field The electric field may be found at surfaces.

Electric fields break hydrogen bonds giving less cyclic hydrogen bonded clustering and raising the hydrating ability of the water.

High electric fields (E ~10^9 V m^{-1}) reduce water's permittivity, which will increase the solubility of gasses.

Strong electric fields at surface may cause liquid water to become ‘organized’; ice formation.