Methoden moderner Röntgenphysik: Streuung und Abbildung

Lecture 16	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2019		
	G. Grübel, F. Lehmkühler, L. Müller, O. Seeck, L. Frenzel, M. Martins, W. Wurth		
Location	Lecture hall AP, Physics, Jungiusstraße		
Date	Tuesday	12:30 - 14:00	(starting 2.4.)
	Thursday	8:30 - 10:00	(until 11.7.)

Soft Matter – Timeline

- Di 07.05.2019 Soft Matter studies I: Methods & experiments
  Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, **…**
- Do 09.05.2019 Soft Matter studies II: Structure
  SAXS & WAXS applications, X-ray cross correlations, **…**
- Di 14.05.2019 Soft Matter studies III: Dynamics
  XPCS applications, diffusion, dynamical heterogeneities, ...
- Do 16.05.2019 XPCS and XCCA simulation and modelling
- Di 21.05.2019 Case study I: Glass transition
  Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, ...
- Do 23.05.2019 Case study II: Water
  Phase diagram, anomalies, crystalline and glassy forms, FEL studies, ...

Quick links ▼ Print

WATER STRUCTURE AND SCIENCE

Martin Chaplin

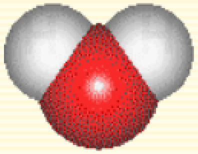
Home

Water Structure and Science

This page forms the entrance to a website concerned with the physical, chemical and biological properties of water.

Table of Contents | Site Map

Liquid water is not a bit player in the theatre of life — it's the headline act

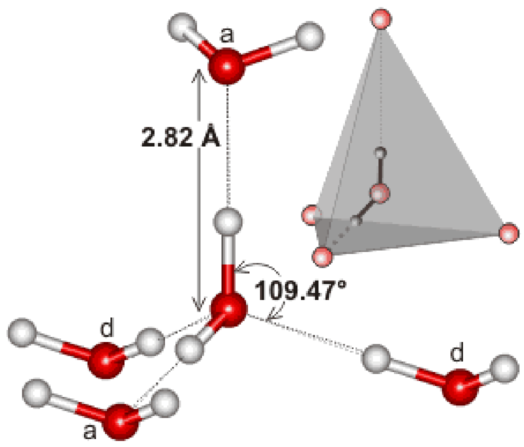


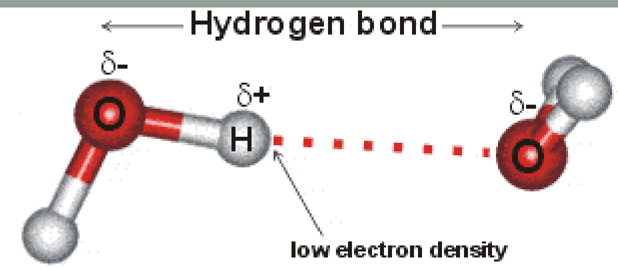
Many regard water (H_2O) as a rather uninteresting substance because it is transparent, odorless, tasteless and ubiquitous. It is the simplest compound of the two most common reactive elements in the universe, consisting of just two hydrogen atoms attached to a single oxygen atom. Indeed, very few molecules are smaller or lighter. Liquid water, however, is the most extraordinary material contradicting its apparently simple molecular constituent. ⇒

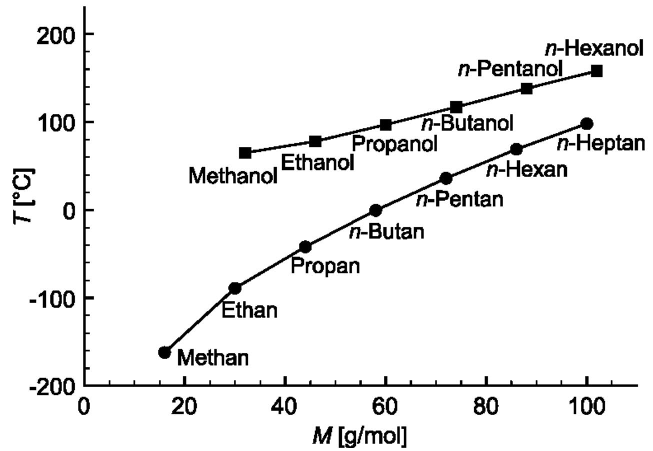
Although we drink it, wash, fish and swim in it, and cook with it (although probably not all at the same time), we nearly always overlook the special relationship it has with our lives. Droughts cause famines and floods cause death and disease. It makes up over about half of us and, without it, we die within a few days. Liquid water has importance as a solvent, a solute, a reactant, a catalyst and a biomolecule, structuring proteins, nucleic acids and cells and controlling our consciousness. H_2O is the second most common molecule in the Universe (behind hydrogen, H_2), the most abundant solid material and fundamental to star formation. There is a hundred times as many water molecules in our bodies than the sum of all the other molecules put together. Life cannot evolve or continue without liquid water, which is why there is so much excitement about finding it on Mars and other planets and moons. It is unsurprising that water plays a central role in many of the World's religions. This web site discusses many aspects of water science. ⇒

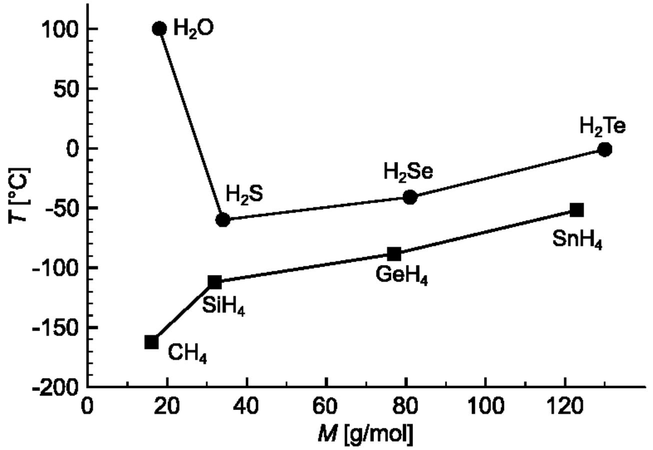
Water science online: http://www1.lsbu.ac.uk/water/

Why study water?









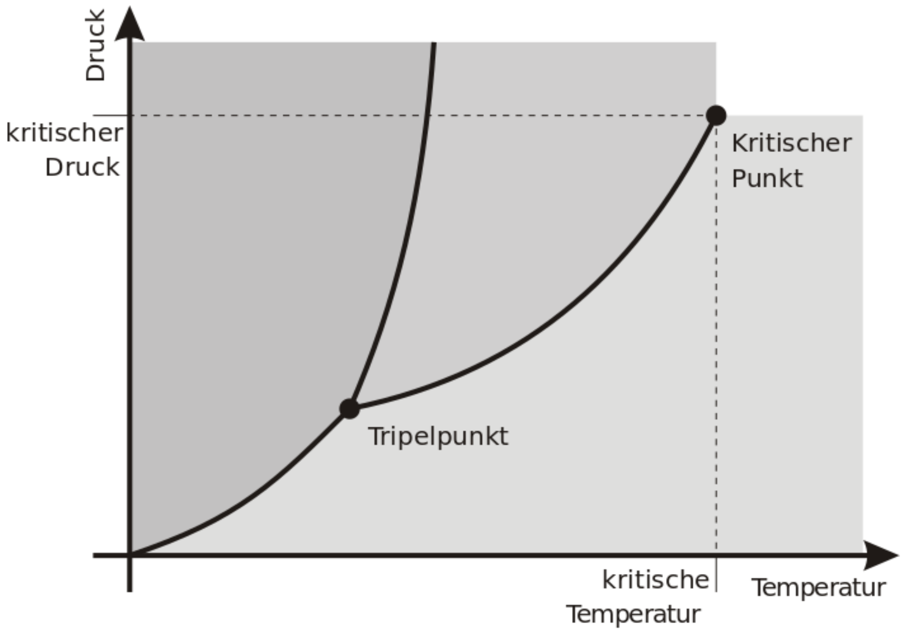
Most important liquid for life (biology), as solvent (chemistry), geo-science, …

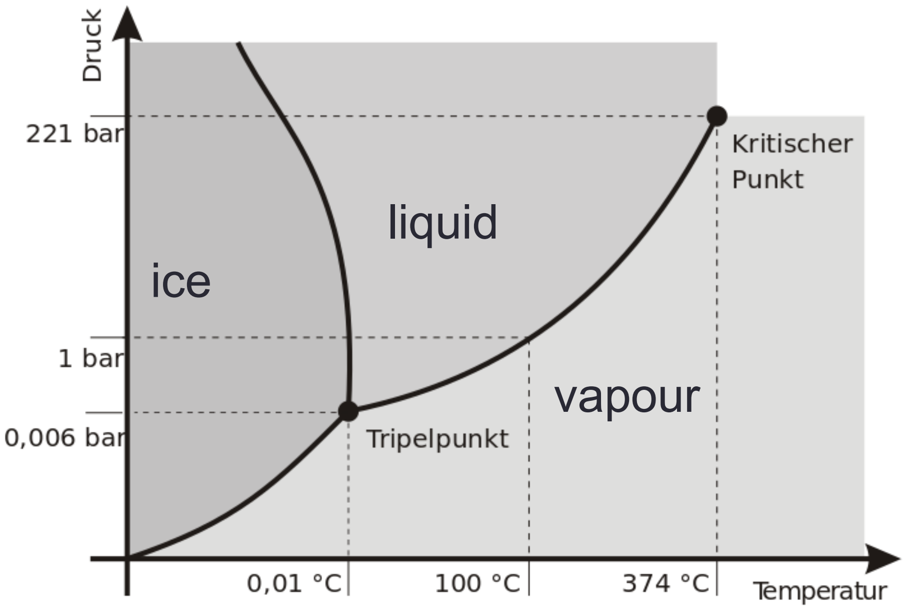
Complex **hydrogen bond** network

- Strength O-H…O: ~21 kJ/mol
- Tetrahedral coordination
- E.g. high boiling points

http://www1.lsbu.ac.uk/water/

Water – phase diagram



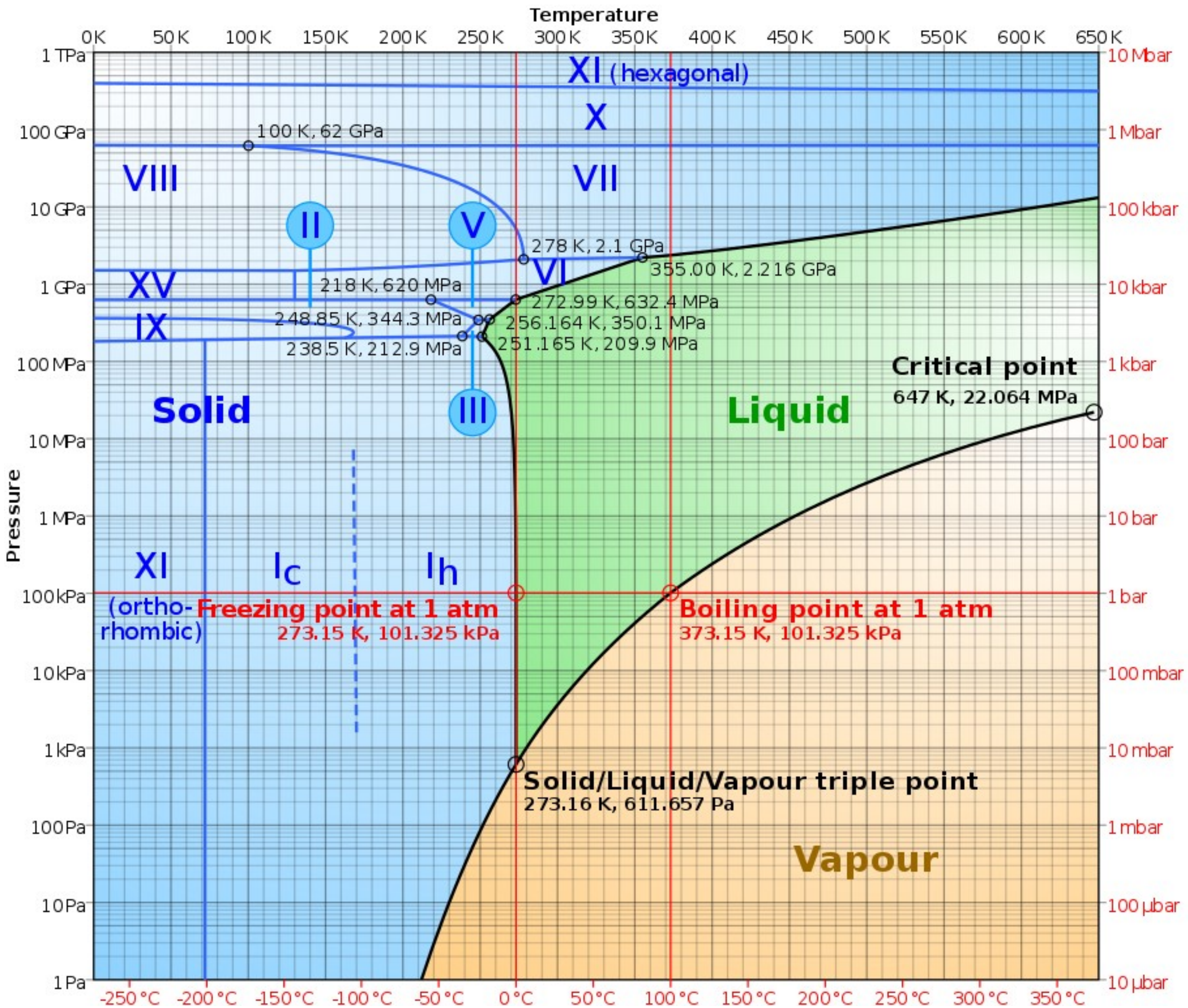


Normal liquid

Water
→ anomalies

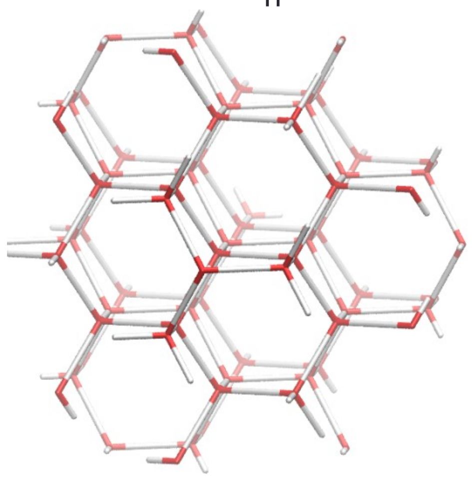
Figures: wikipedia

Crystalline ice – polymorphism

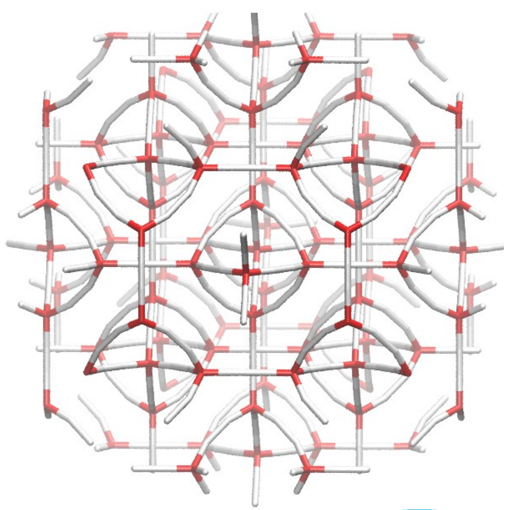


Phase diagram: wikipedia

Ice I_h

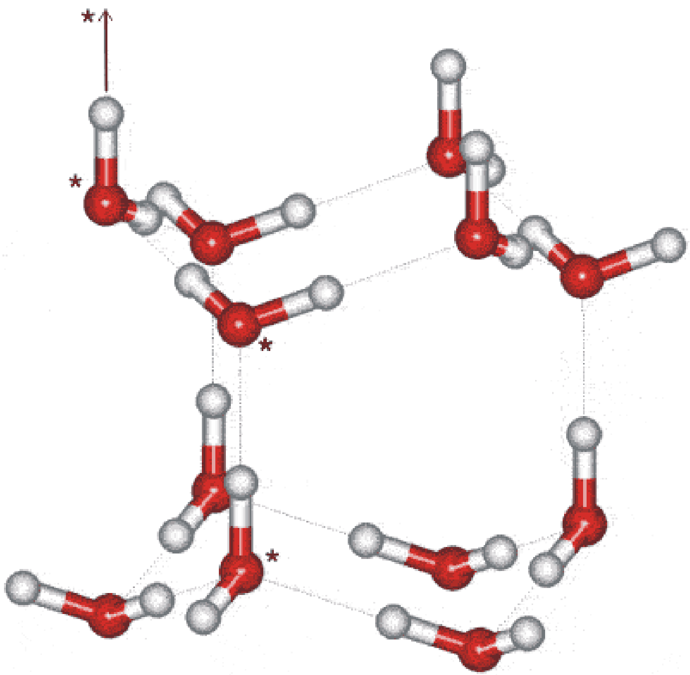


Ice V



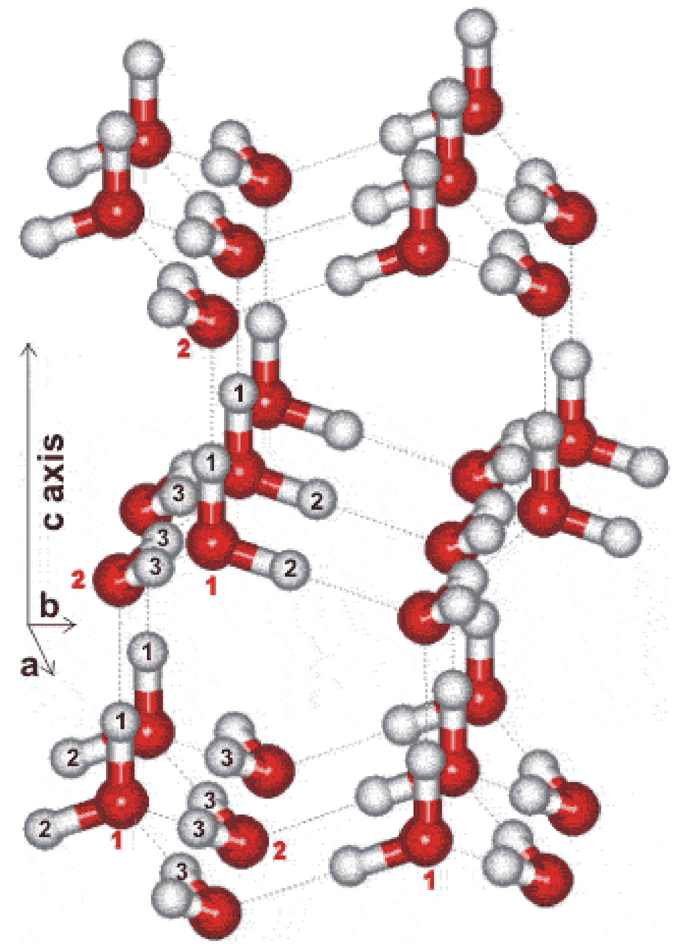
Crystalline ice – polymorphism

Hexagonal ice (ice I_h)



Tetrahedral coordination
4 H-bonds per molecule

Ice rule: one hydrogen between two oxygens

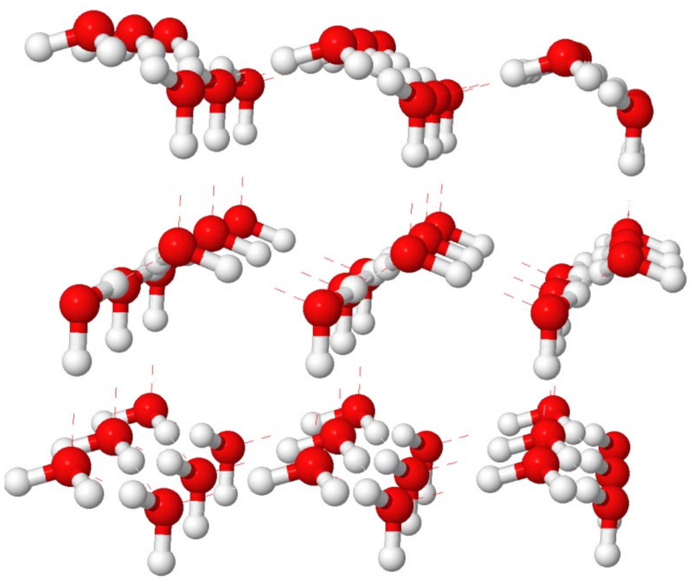


http://www1.lsbu.ac.uk/water

Crystalline ice – polymorphism

There are hydrogen-disordered and hydrogen-ordered ice phases

Disorded phase	Ordered phase	$T_{o \rightarrow d}$
Ih	XI	72 K
III	IX	170 K
VII	VIII	270 K
XII	XIV	100 K
IV	???	-
???	II	-
V	XIII	~120 K
VI	XV	~130 K



Ice XI: hydrogen-ordered form of hexagonal ice I_h

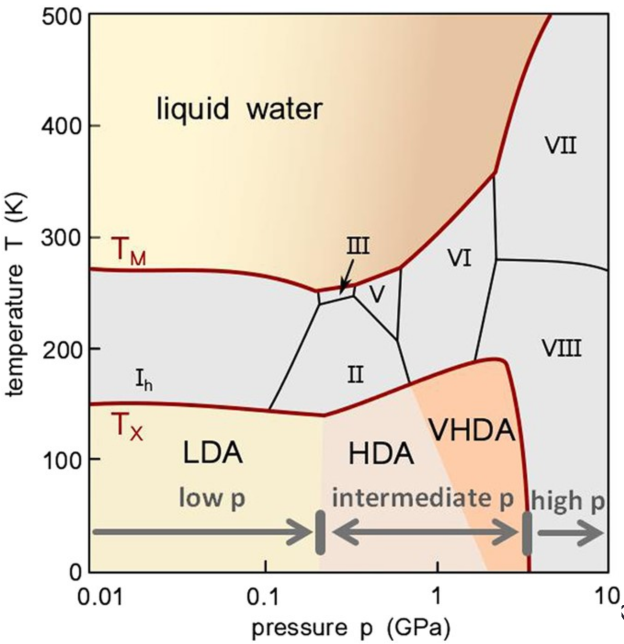
Amorphous ice

- Earth: hexagonal ice
- Space: amorphous forms of ice

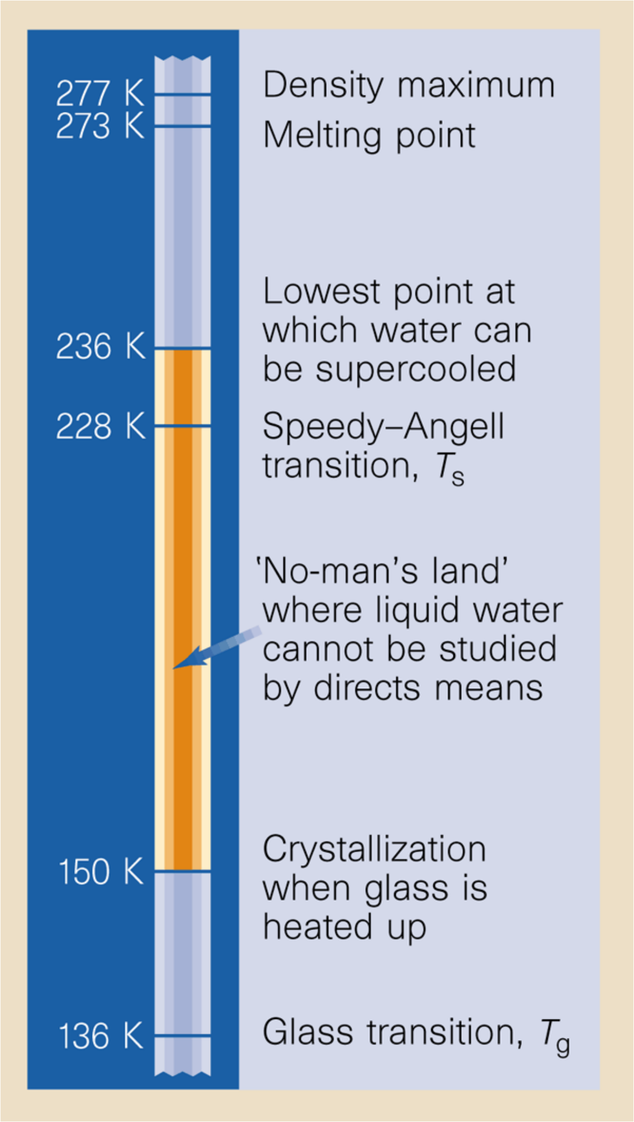
Three forms of amorphous ice

- Low-density (LDA), 0.92 g/cm^3
- High-density (HDA), 1.17 g/cm^3
- Very-high-density (VHDA), 1.26 g/cm^3

Glass transition: no man's land

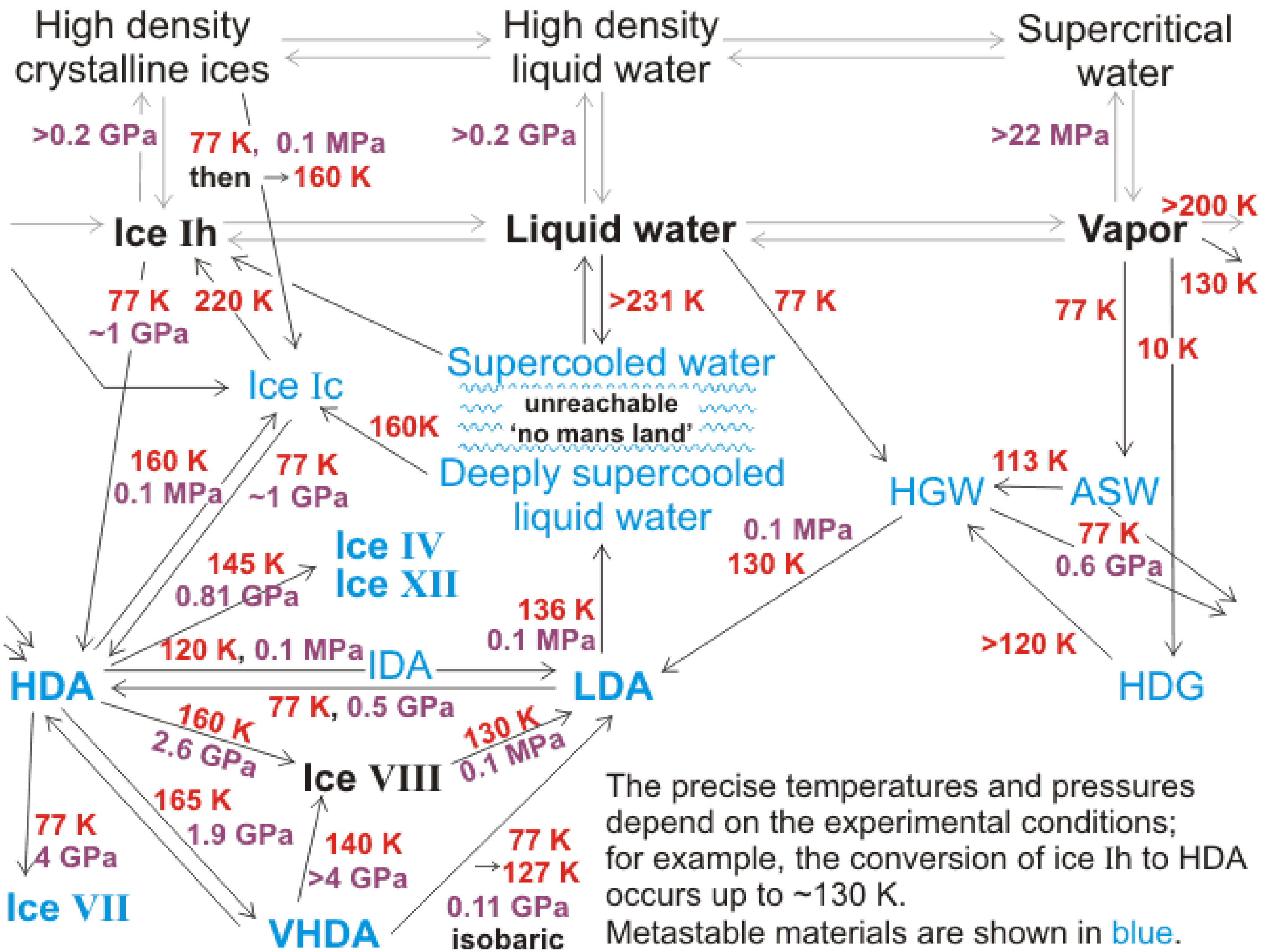


J. Stern and T. Loerting. Sci. Rep. 7, 3995 (2017)



S. Sastry. Nature 398, 467 (1999)

Water – solid states



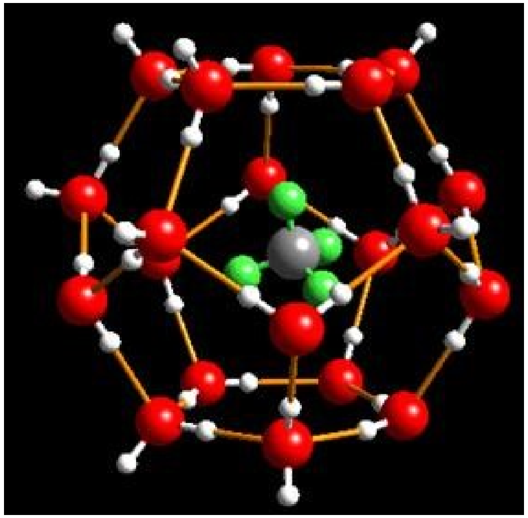
The precise temperatures and pressures depend on the experimental conditions; for example, the conversion of ice Ih to HDA occurs up to ~130 K.
Metastable materials are shown in blue.

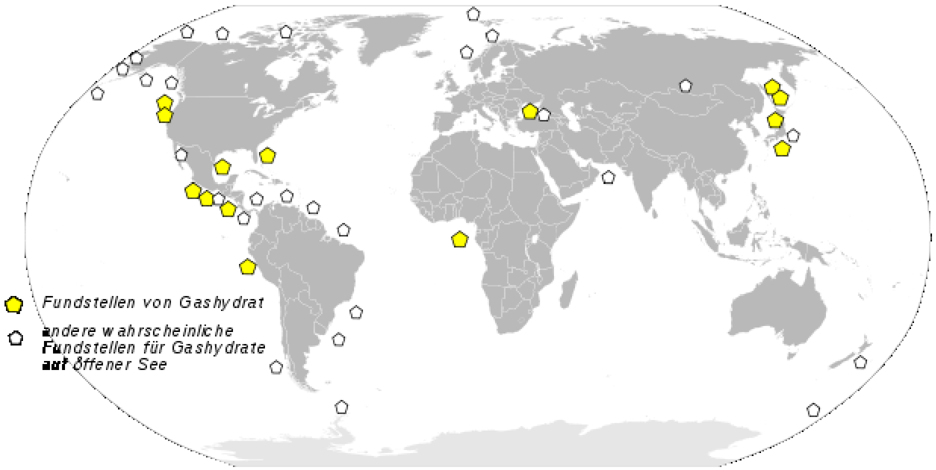
ASW – amorphous solid water

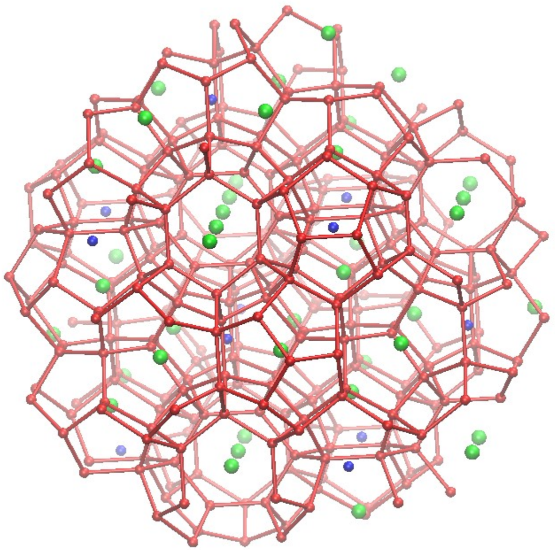
HGW – Hyperquenched glassy water

Clathrate hydrates

- In presence of gas molecules (e.g. methane, CO_2, O_2, H_2, …) water forms ice-like inclusion compounds
- Typically "more stable" than ice
- Methane hydrate at ocean floor and in perma frost regions



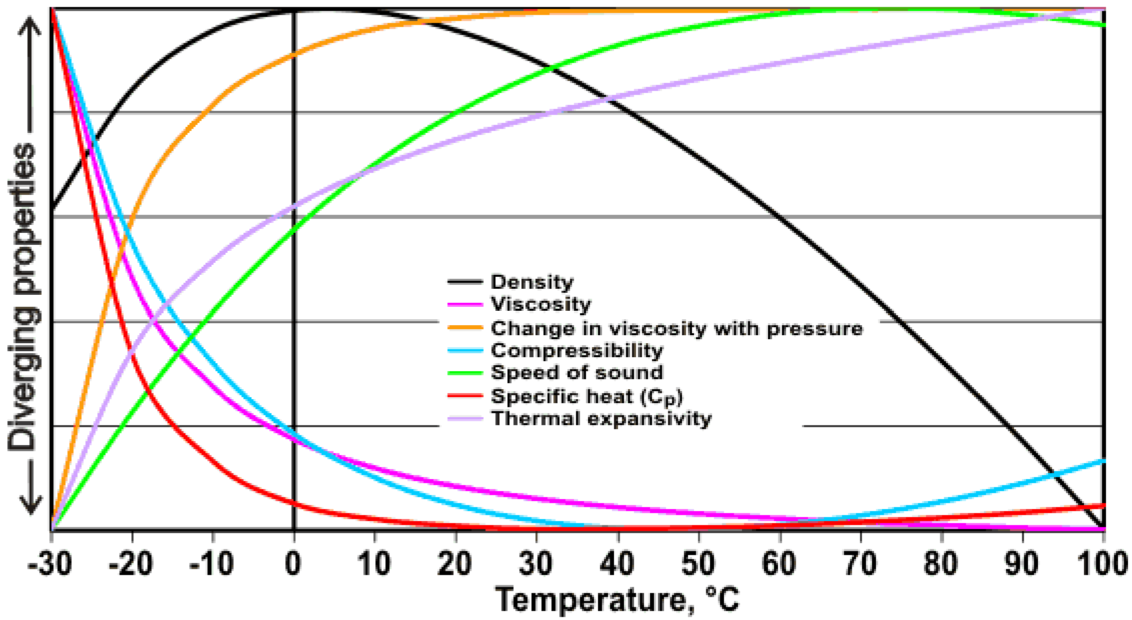




Water – anomalies

Water shows a large number of anomalous properties compared to "simple liquids", e.g.

- Density anomalies (e.g. well-known highest density at 4°C)
- Phase anomalies (e.g. high boiling point)
- Thermodynamic anomalies (e.g. high heat capacity)
- Physical anomalies (e.g. high surface tension)



→ Complex hydrogen bond network

→ Diverging properties upon supercooling around -45°C

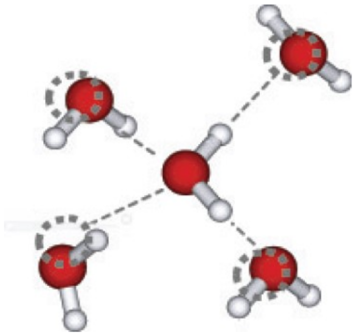
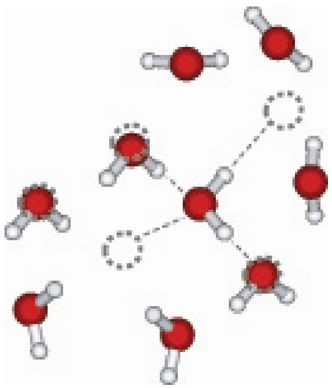
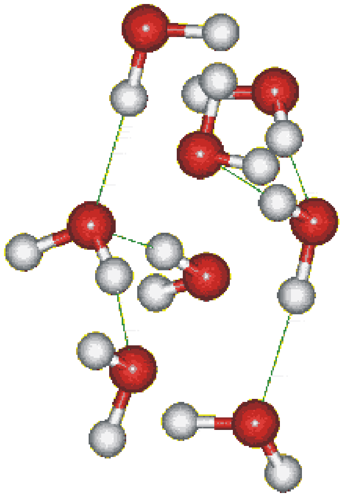
→ Connection to water structure

http://www1.lsbu.ac.uk/water

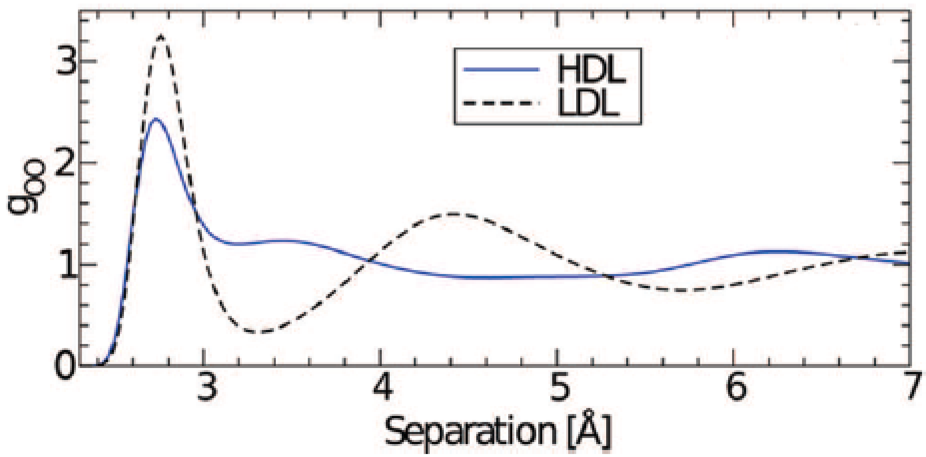
Liquid water: continuum and mixture models

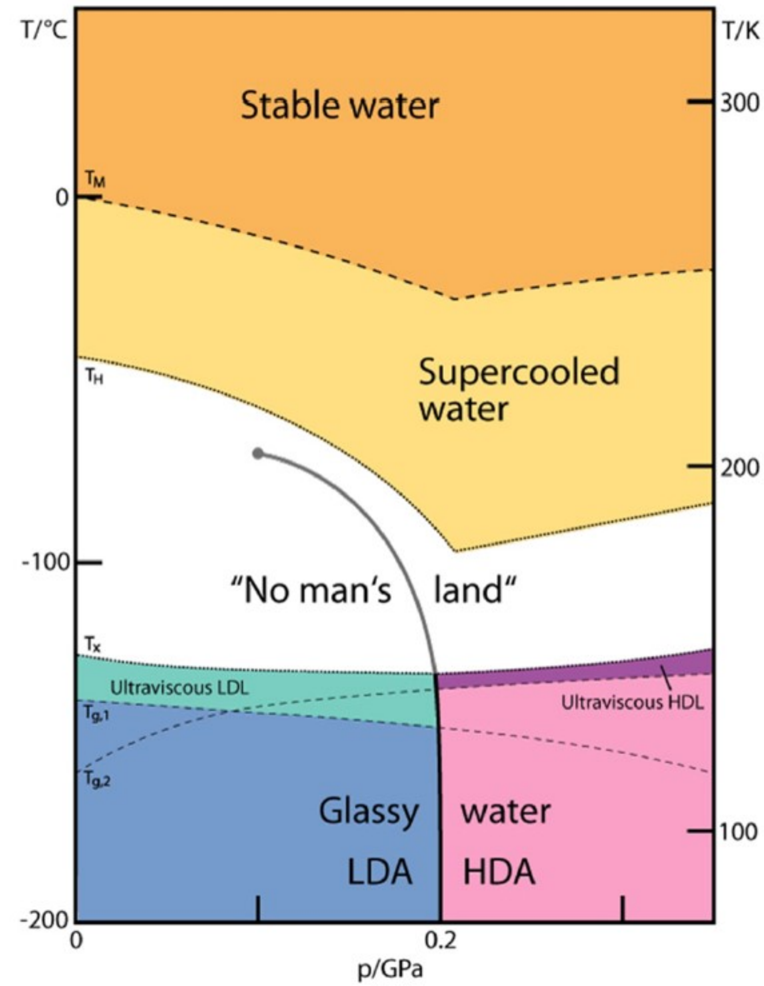
Long-standing debate: Liquid water as…
(1) network of disordered tetrahedrally coordinated molecules with ~3.5 hydrogen boonds per molecules
(2) Mixture of different species with different geometry (goes back to Röntgen 1892 to explain anomalous properties of water)

In more recent years: two-liquids hypothesis
- Low density liquid (LDL): strong tetrahedral coordination
- High density liquid (HDL): broken hydrogen bonds → higher density Dominates at room temperature

Liquid water: continuum and mixture models





Molecular dynamics simulations:

- LDL: tetrahedral liquid
- HDL: broken hydrogen bonds

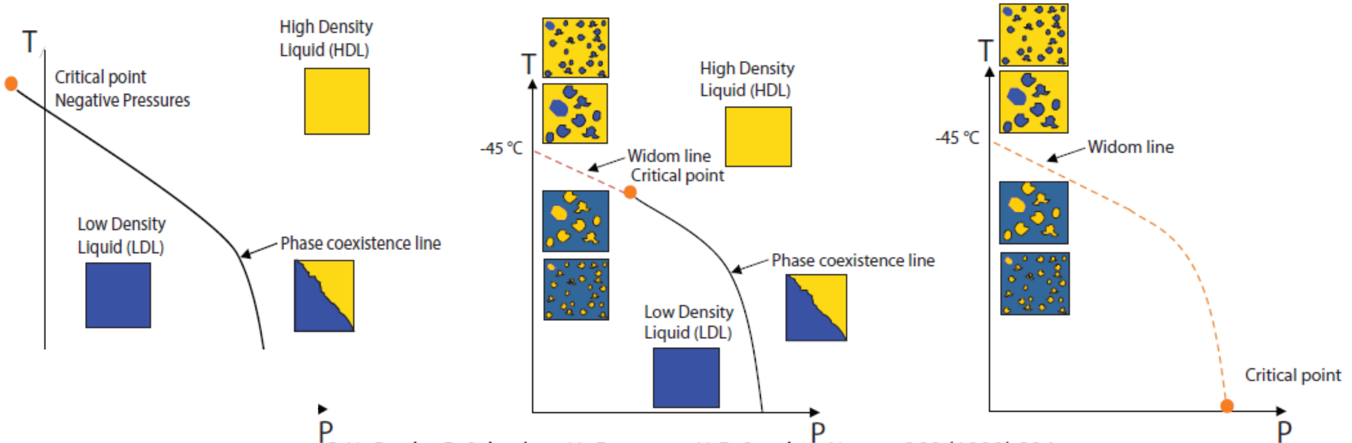
Phase diagram of amorphous water: Reaching "no man's land" to measure HDL/LDL

Liquid water: continuum and mixture models

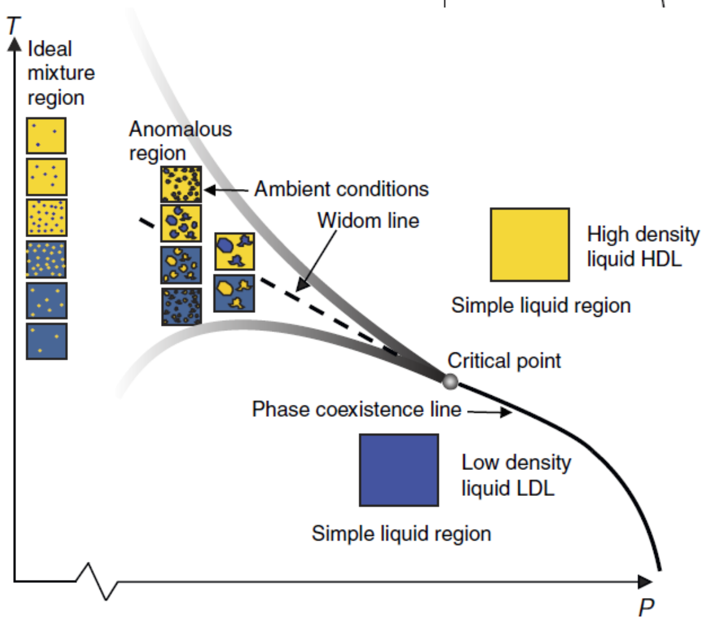
Critical Point Free Model
Critical Point at -P

Critical Point Model
Critical Point at +P

Singularity Free Model
Critical Point at 0K



P.H. Poole, F. Sciortino, U. Essmann, H.E. Stanley, Nature **360** (1992) 324.

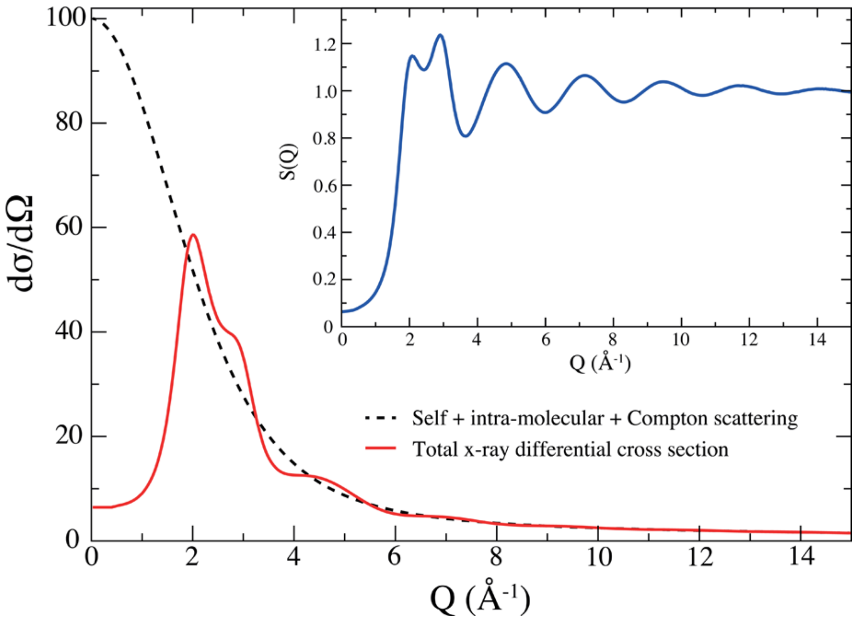


If there are two liquids, will there be a (2nd) critical point?

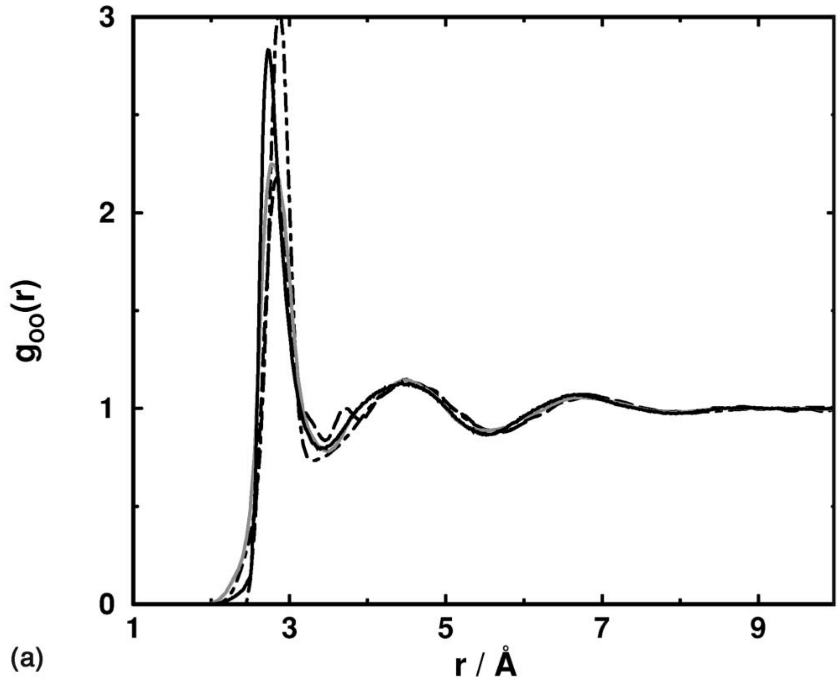
Widom line: locus of correlation length maxima in the pressure-temperature (P-T) plane. Thermodynamic response functions are expected to have maxima

Nat. Comm. 6, 8998 (2015)

X-ray studies: structure factors



Chem. Rev. 116, 7570 (2016)

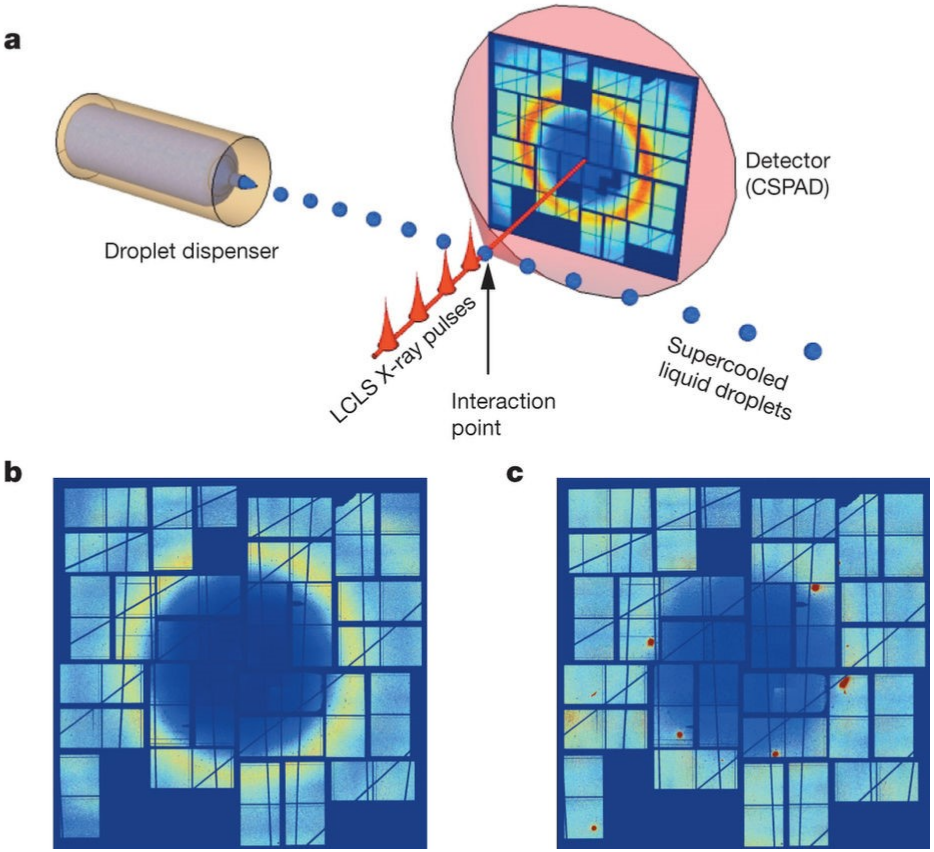


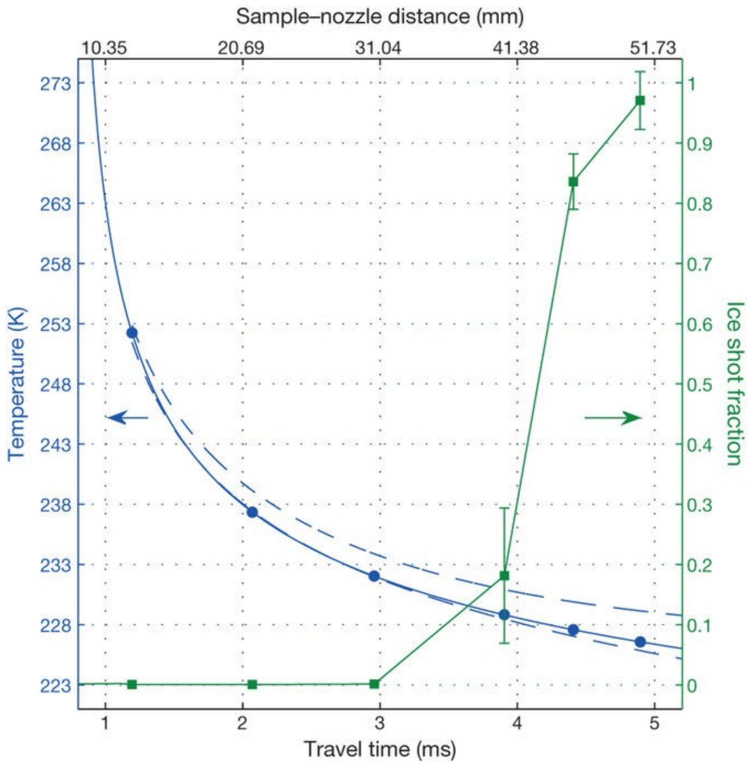
J. Chem. Phys. 113, 9140 (2000)

Structure factor of water around $q = 2$ Å^{-1} → for 8 keV X-rays → $\theta \approx 29°$ → XRD

Experimental limit: $\theta = 180° \Rightarrow q_{max} = \frac{4\pi}{\lambda} \approx 8$ Å^{-1} for 8 keV → high-energy X-rays (≥ 50 keV) for pair-distribution function (pdf) studies

Liquid water: structure factors



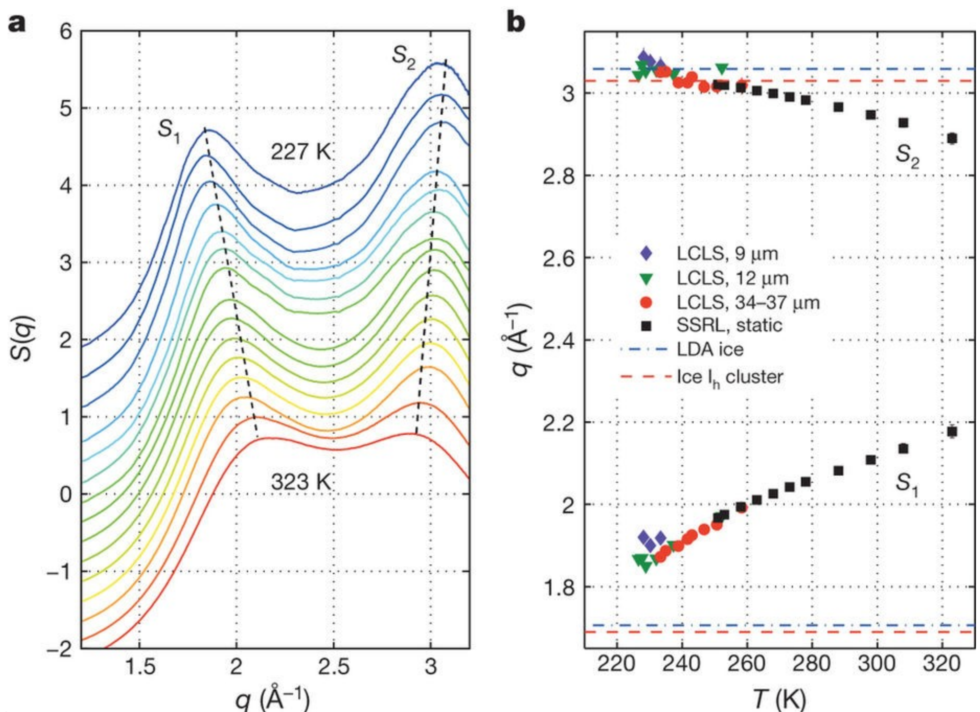


Liquid microdroplets: supercooling due to evaporation in vacuum

Ultrafast probing: FEL (~100 fs)

→ XRD patterns from single droplets

Nature 510, 381 (2014)

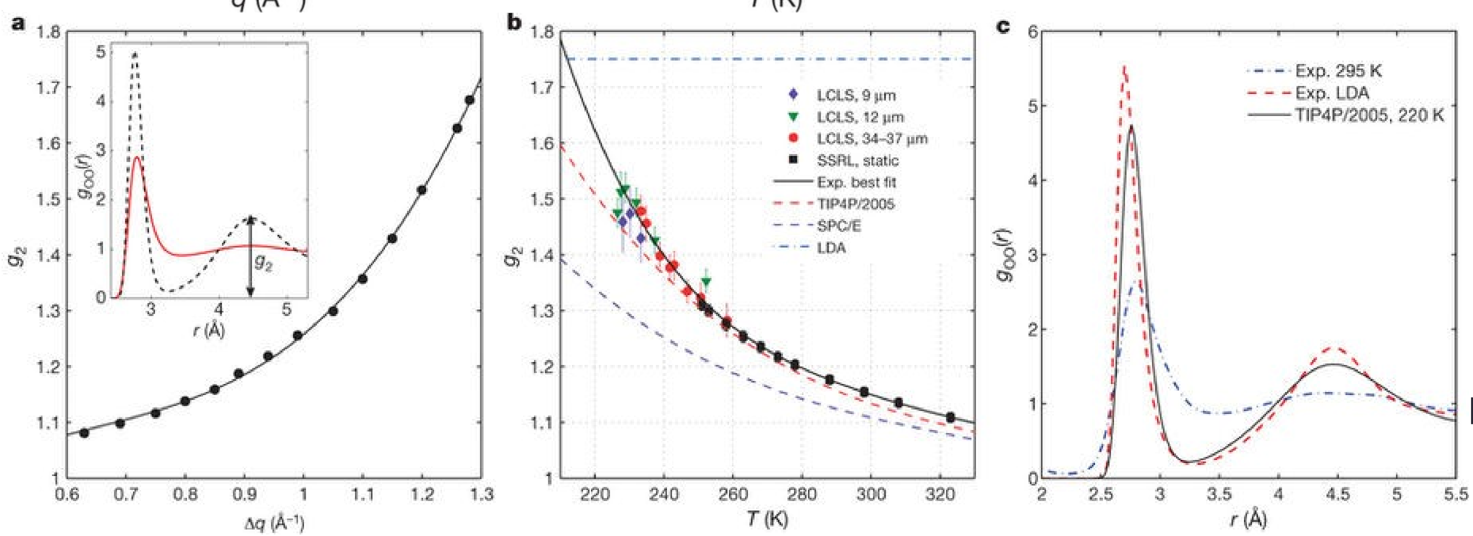


Structure factors: peaks shift upon supercooling

But: here limited to $q \leq 3.2$ Å^{-1}

Degree of tetrahedrality: 2nd peak of $g(r)$

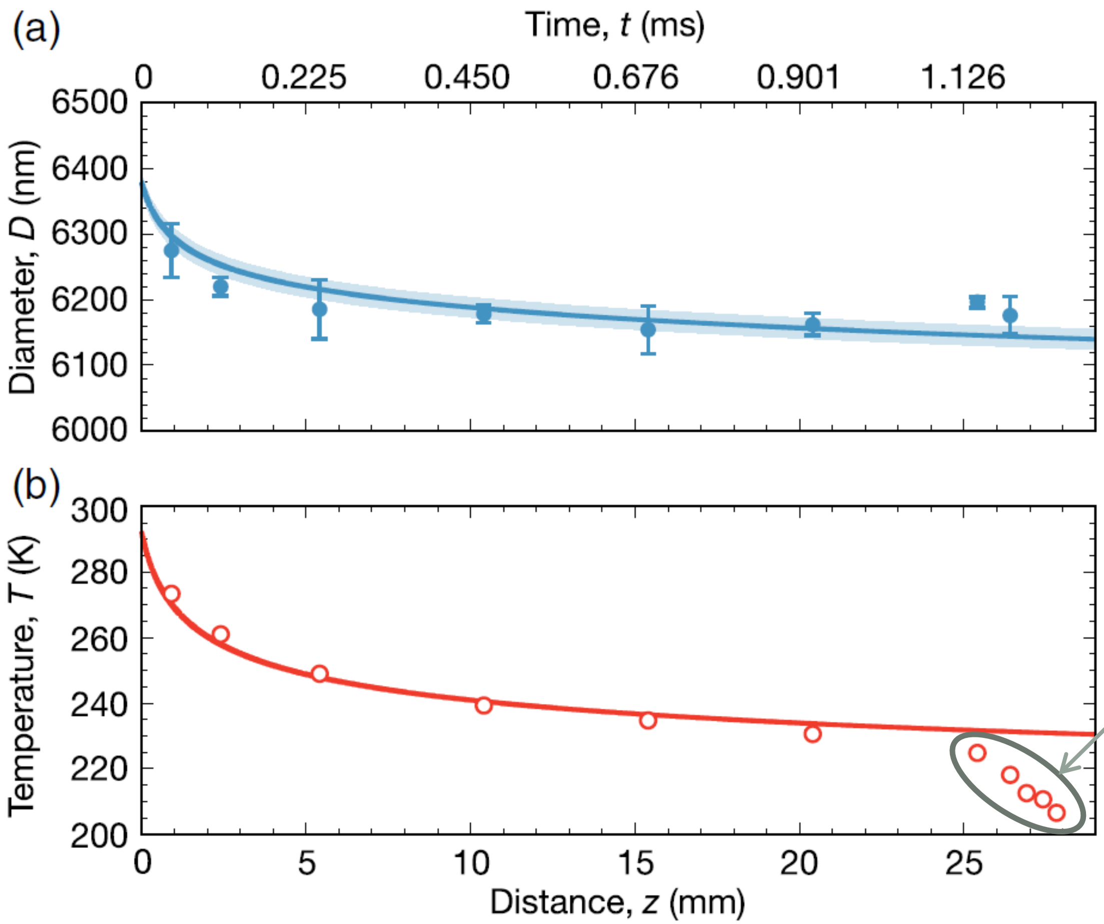
Towards low-density liquid water?



Nature 510, 381 (2014)

How to measure temperature of water droplets?

Raman scattering → Interpretation debated



Droplet diameters from vibrational spectroscopy & Knudsen model of evaporation

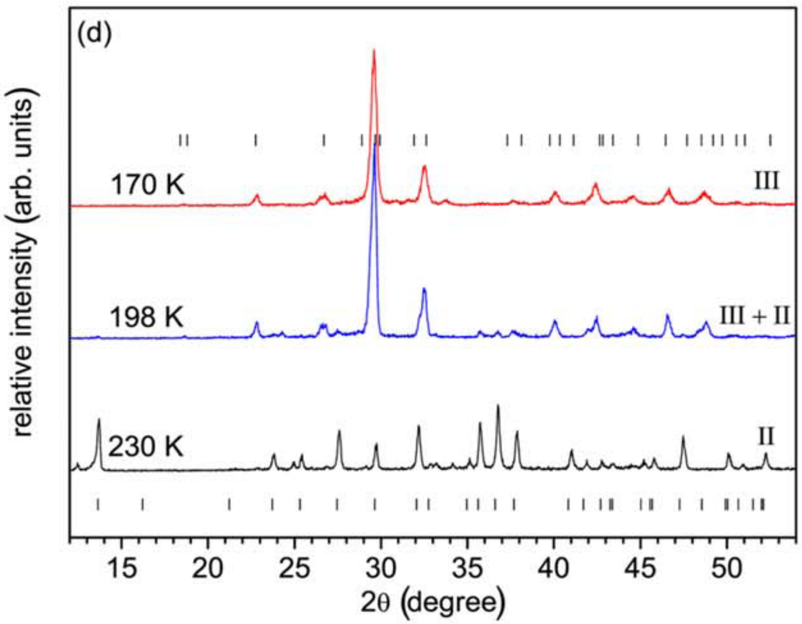
Ice formation

Phys. Rev. Lett.120, 015501 (2018)

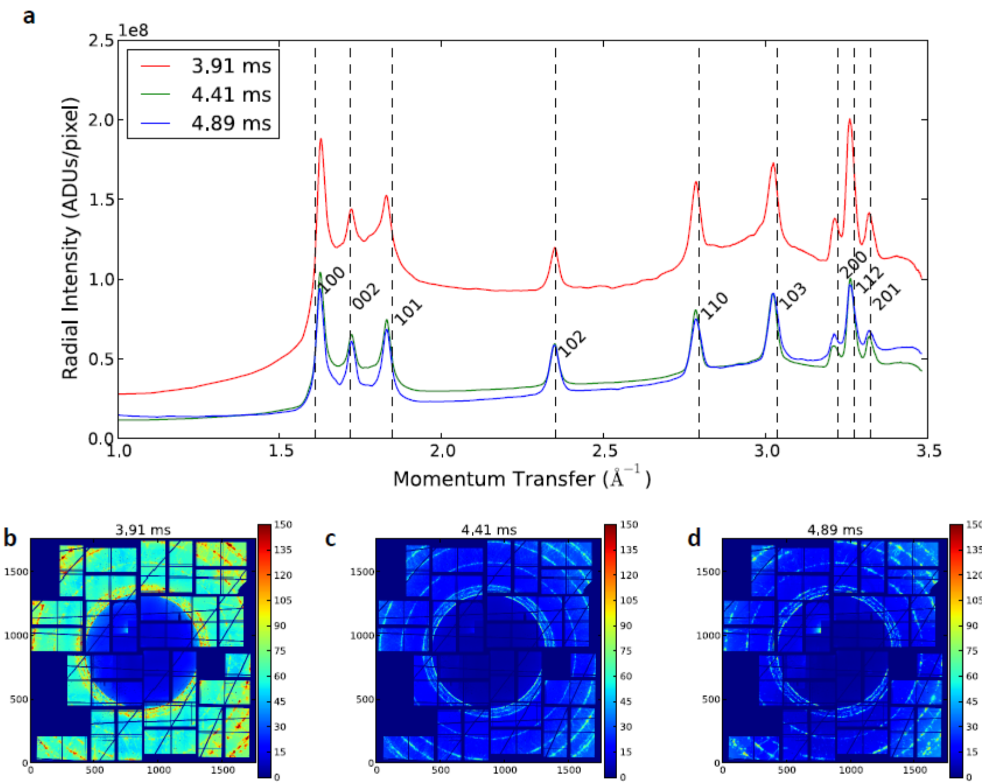
X-ray diffraction: ices

Typical example: XRD of ice(s)

Fingerprint of structure → no "new" ice without XRD proof



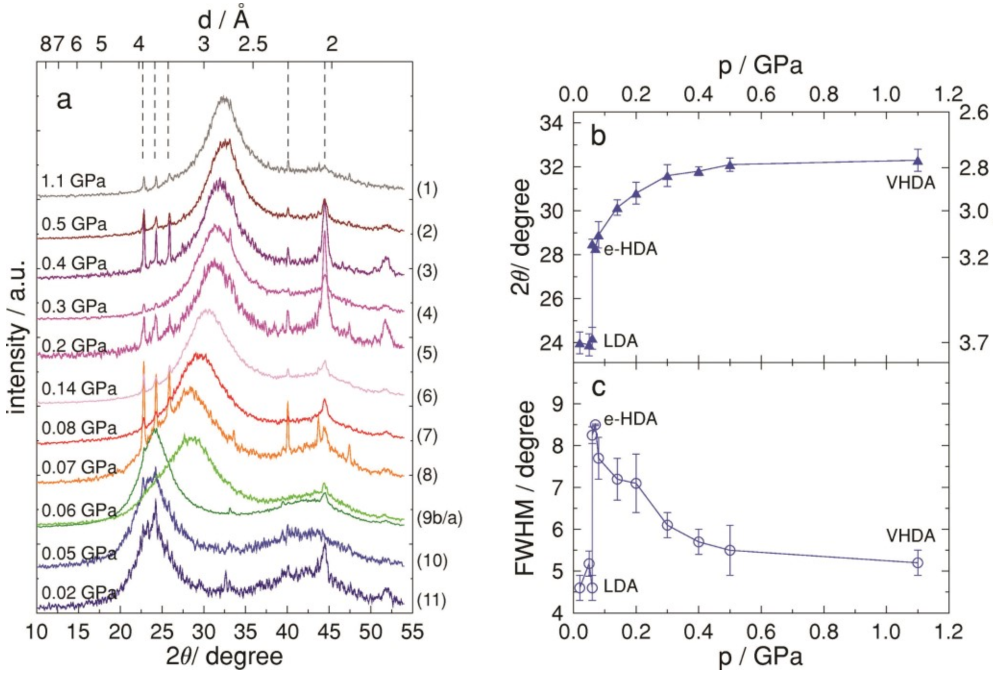
Phys. Rev. B 77, 220105 (2008)

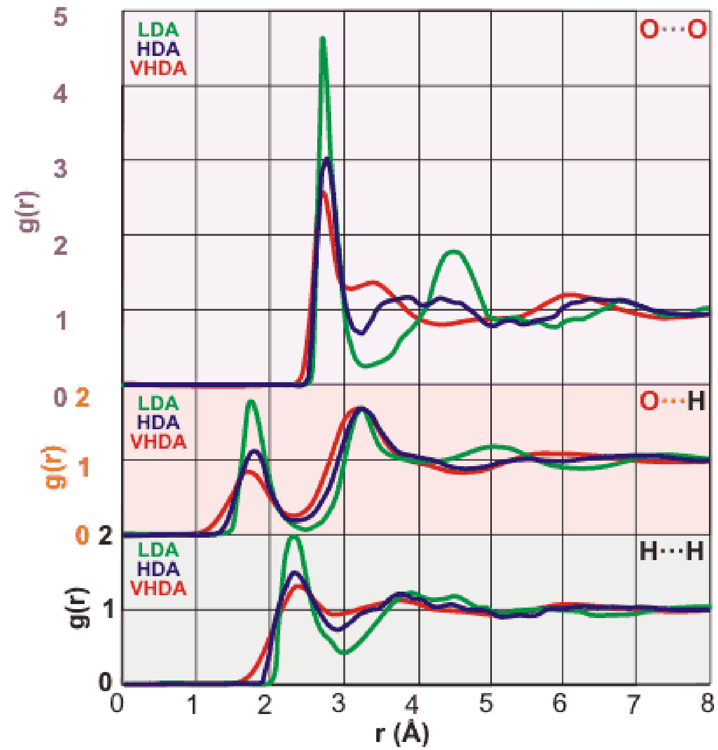


Crystallisation upon fast cooling

Nature 510, 381 (2014)

Transition of amorphous ices



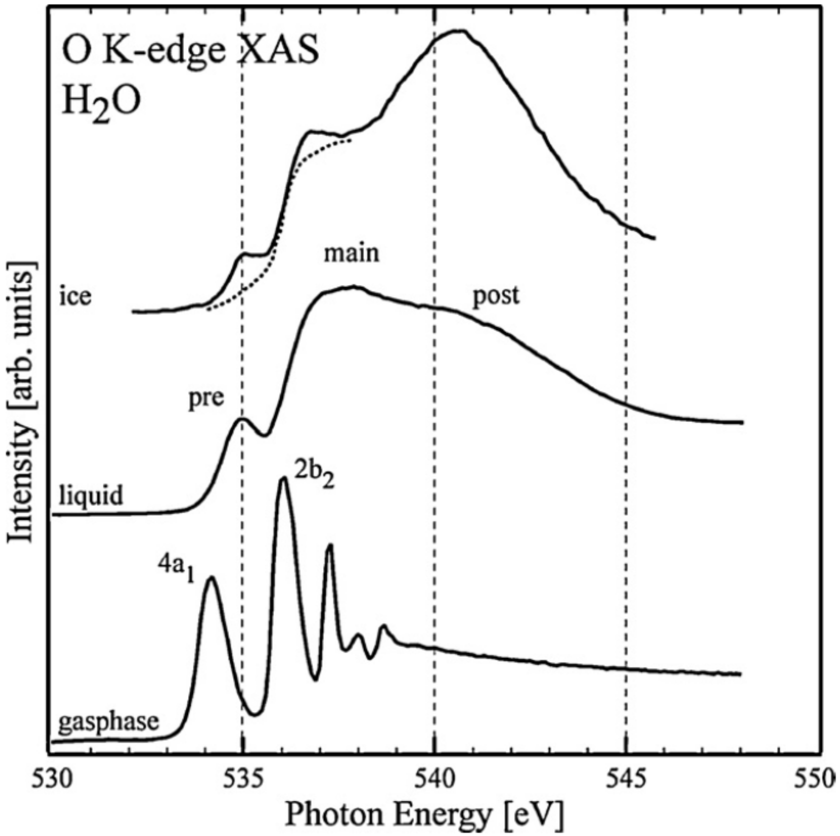


Isothermal decompression of VHDA at 140K to several selected pressures

http://www1.lsbu.ac.uk/water

J. Chem. Phys. doi: 10.1063/1.2830029 (2008)

X-ray spectroscopy

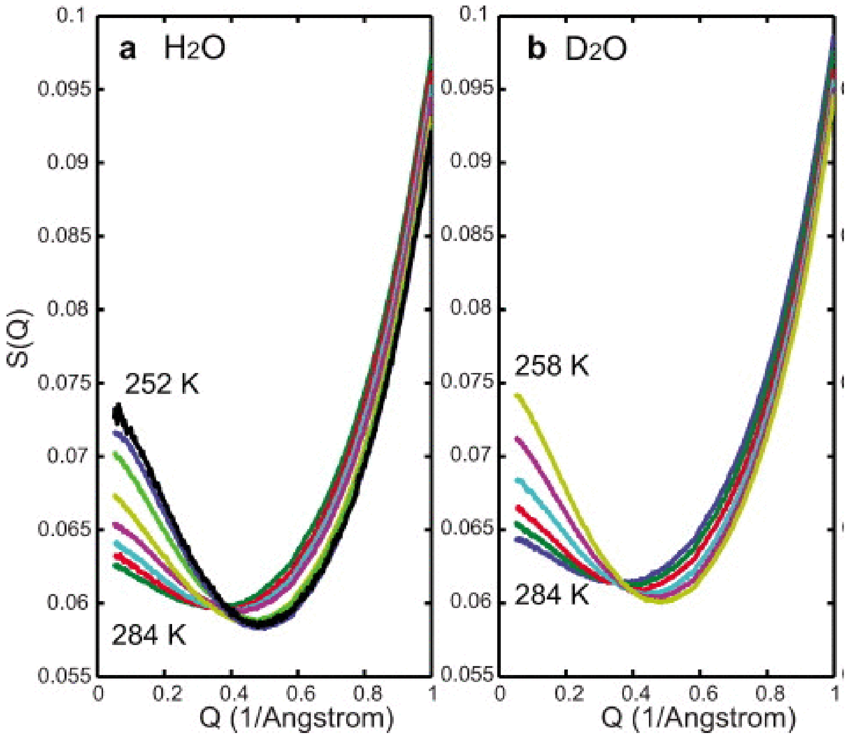


- XAS = X-ray Absorption Spectroscopy
- Fine structure of absorption edge ↔ local structure of sample
- Only indirect access, need e.g. DFT calculations
- Intense debate to which extent XAS results provide information on water models (e.g. LDL/HDL)

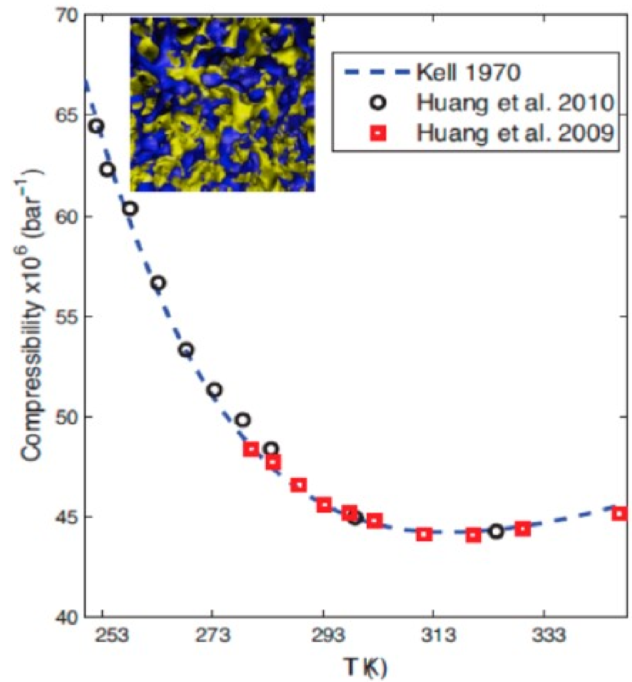
J. El. Spec. Rel. Phen. 177, 99 (2010)

Liquid water: SAXS

Small q limit in SAXS: $S(q \to 0) \propto$ density fluctuations (see Lecture 7)
Isothermal compressibility χ_T can be extracted for $q \to 0$: $S(0) = k_B T \rho_n \chi_T$



J. Chem. Phys. 133, 134504 (2010)



Chem. Rev. 116, 7570 (2016)

Liquid water: SAXS

Is there a connection between compressibility and the two-liquid hypothesis?
→ Strongly debated!

Pure Appl. Chem., Vol. 82, No. 10, pp. 1855–1867, 2010.
doi:10.1351/PAC-CON-09-12-16
© 2010 IUPAC, Publication date (Web): 30 June 2010

Recent water myths

Alan K. Soper

STFC Rutherford Appleton Laboratory, ISIS Facility, Harwell Science and Innovation Campus, Didcot, Oxon, OX11 0QX, UK

Abstract: Recently, there have been a number of claims about the nature of water as a liquid that seem to contradict traditional views. The present paper takes a close look at two of these claims—namely, that water is not the tetrahedral network that it is traditionally regarded as but a chain-like liquid, and that water is intrinsically heterogeneous by nature—and attempts to make sense of them.

Keywords: chain structure; computer simulation; mixture models; neutron diffraction; water; X-ray absorption spectroscopy; X-ray diffraction; X-ray emission spectroscopy; X-ray Raman spectroscopy.

INTRODUCTION

Because it is so important in many different fields of science, water quite naturally attracts an enormous amount of research into its properties and the atom-scale origin of those properties, both in its pure state and in solutions of ions and molecules of all shapes and sizes. Homeopathy, for example, arises from the perceived ability of water to remember its structure around a dissolved entity long after that entity has disappeared, the so-called memory effect of water. Perhaps two of the more bizarre recent claims are that the structure of water is affected by relatively modest magnetic fields [1] and that the structure of water is altered by sunlight [2]. This change in the structure of water due to sunlight appears unlikely: in Britain, for example, the rain during the day is just as wet as the rain at night. In [3] it is stated that water is not the tetrahedral structure traditionally assumed, but consists of chains of water molecules. In [4] it is proposed that ambient water is intrinsically heterogeneous, consisting of a mixture of low- and high-density forms, an idea which has been proposed on many previous occasions for more than 100 years. Given all this often conflicting information, it is not surprising there is much confusion on the true state of water.

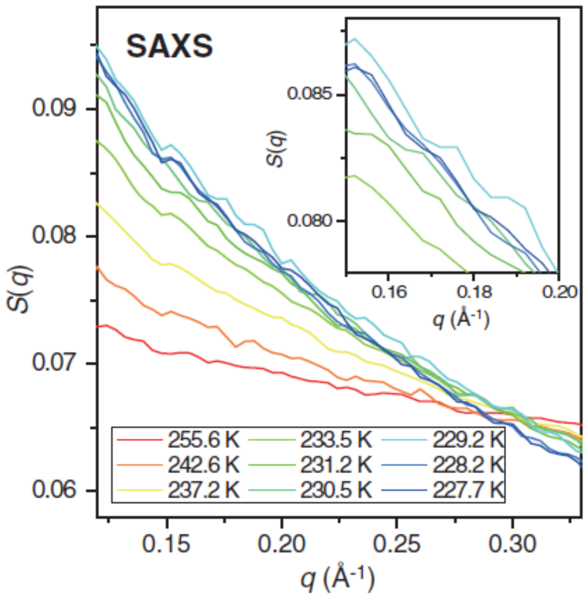
Perhaps one of the most surprising facts about water is that it is a liquid. All of the elements that surround oxygen in the periodic table have hydrides which are gases at ambient temperature and pressure, while hydrogen oxide is definitely a liquid with quite a low vapor pressure, ≈5 mbar. Even more difficult to comprehend is that while water is a liquid with marked "hydrogen" bonds between its constituent molecules, water hydrogen bonds are being formed and broken extremely rapidly, typically around 10^{12} times per second. The diffusion constant is also surprisingly large, around 2×10^{-5} cm^2 s^{-1}, which means that after 1 s any given water molecule has on average moved about 44 µm from its starting position, corresponding to ≈150000 molecular diameters. Therefore, whenever we attempt to develop a picture of water we have to keep in mind the extremely dynamic nature of the underlying water molecules that form this material. Based on these numbers, it is difficult to envisage how water can re-

*Paper based on a presentation at the 31st International Conference on Solution Chemistry (ICSC-31), 21–25 August 2009, Innsbruck, Austria. Other presentations are published in this issue, pp. 1855–1973.

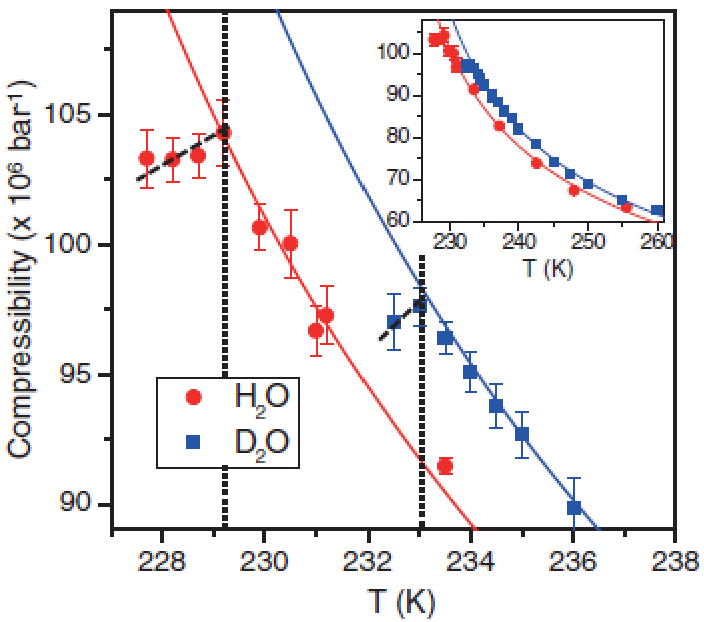
1855

Liquid water: SAXS at FEL

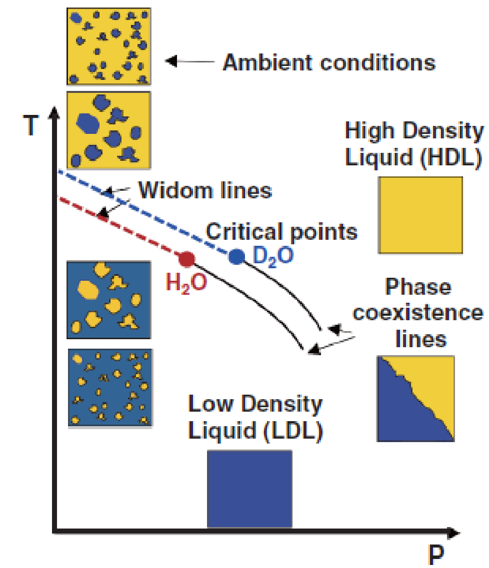
Microdroplets → stronger supercooling possible



SAXS data: $S(q \to 0)$



Compressibility

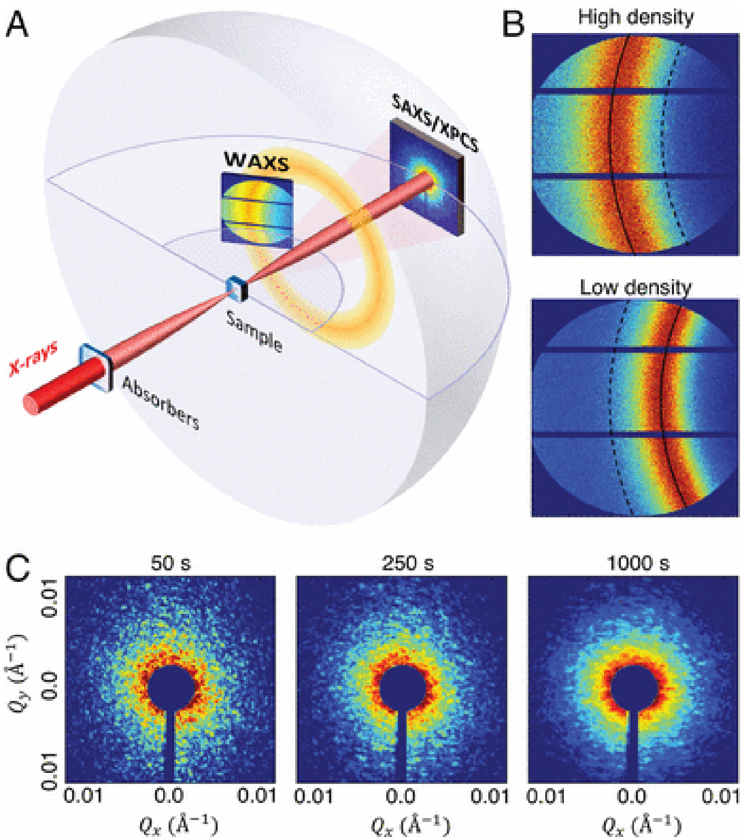


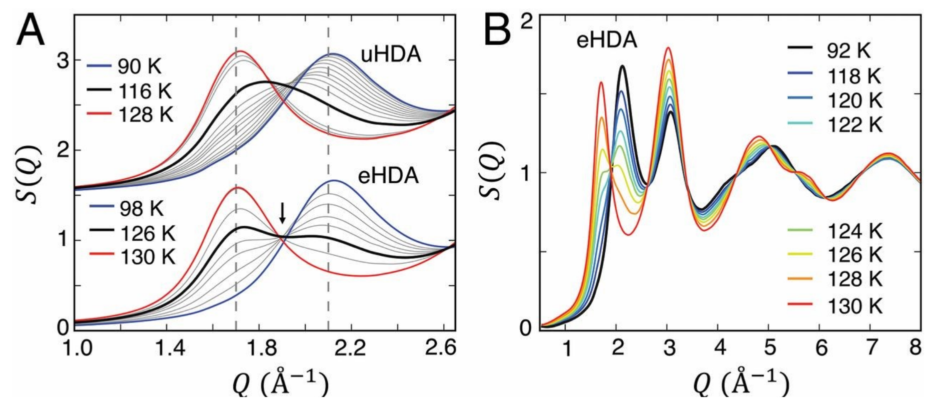
Proposed phase diagram

Science 358, 1589 (2017)

→ Compressibility maximum by crossing the Widom line
→ But: depends on the estimation of water density

Dynamics in amorphous ices & liquid water





X-ray diffraction

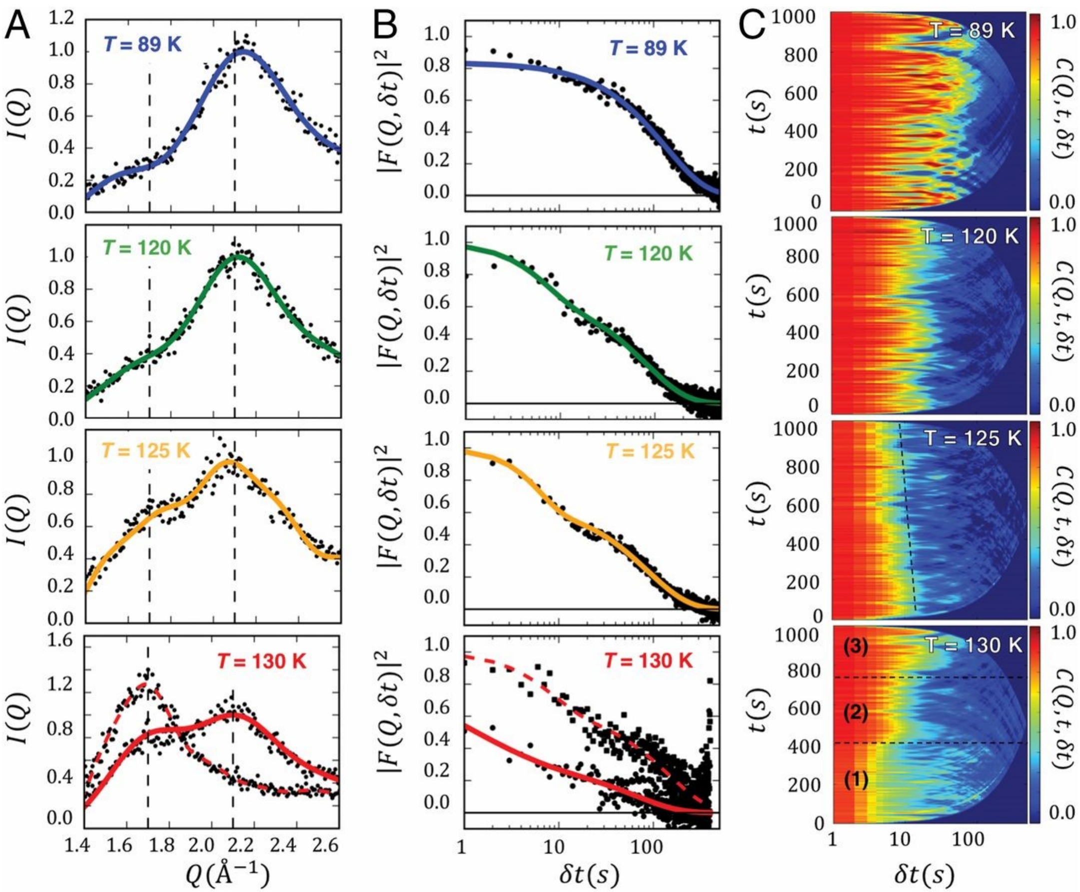
- Double peak for eHDA: coexistence of high- and low-density form
- Decomposition of $S(Q)$ (and $g(r)$) in two (main) contributions possible

Transition of HDA to LDA

Dynamics information to quantify glass-glass or liquid-liquid transition

PNAS 114, 8793 (2017)

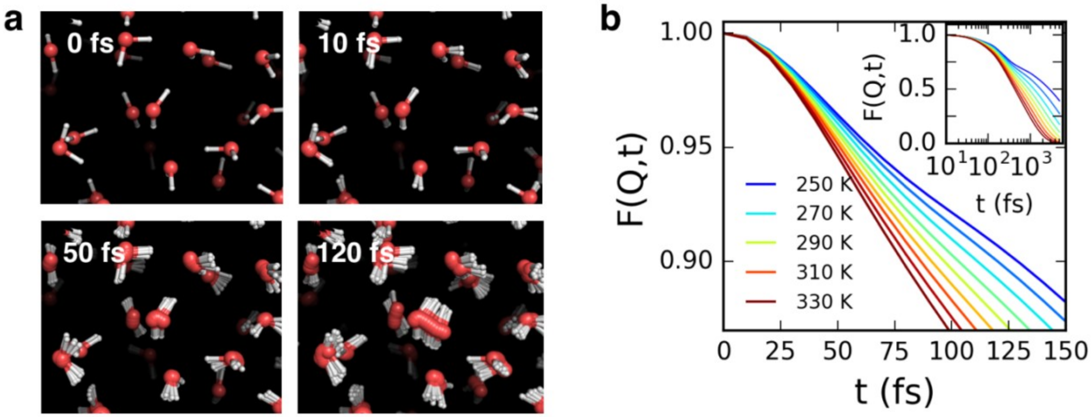
Dynamics in amorphous ices & liquid water

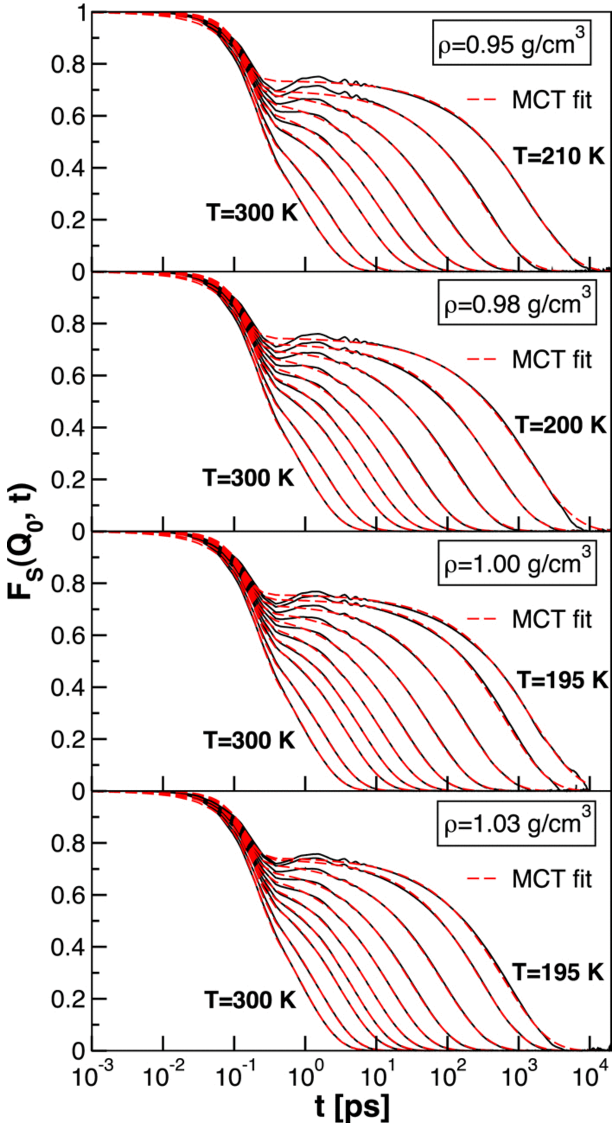


- $T < 110$ K: viscoelastic relaxation of HDA
- Onset of diffusive dynamics for $T \geq 110$ K
- HDA domains transform to ultraviscous **HDL**
- Around $T = 130$ K: transformation to ultravisous **LDL**

PNAS 114, 8793 (2017)

Dynamics in amorphous ices & liquid water





- Liquid water: fs dynamics → FEL pulse length

- MD simulations of liquid water show two-step decay of intermediate scattering function

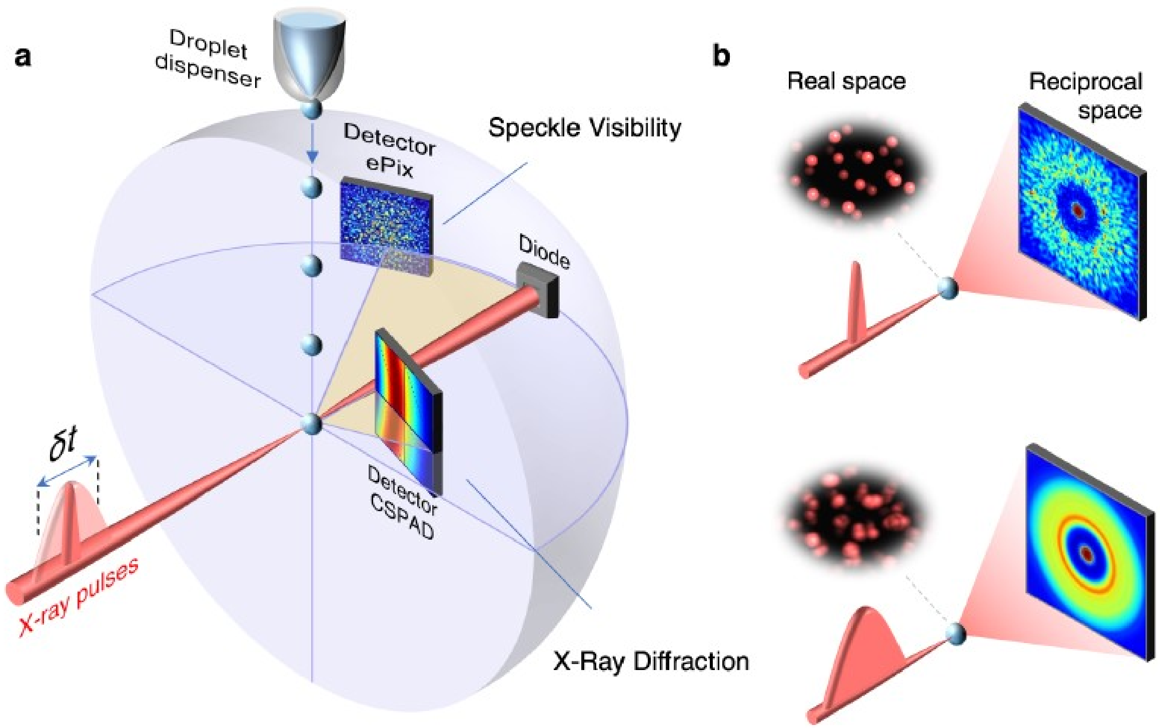
  → fragile-to-strong crossover

  → LLCP hypothesis

Nature Comm. 9, 1917 (2018).

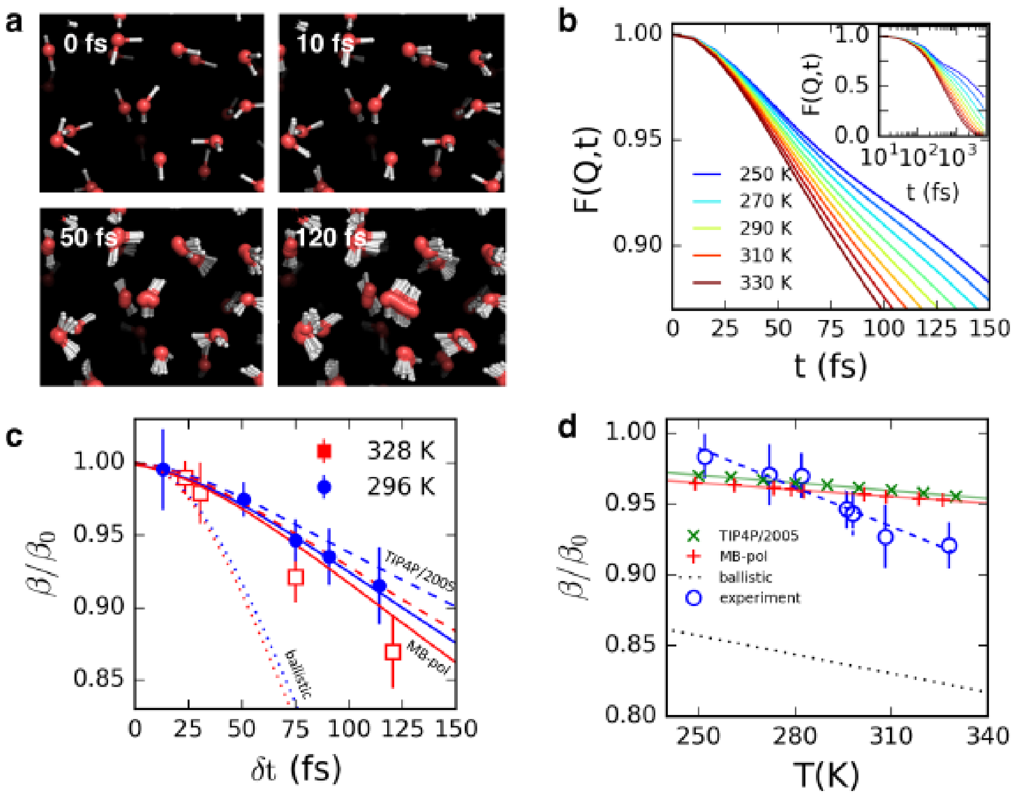
JCP 144, 074503 (2016)

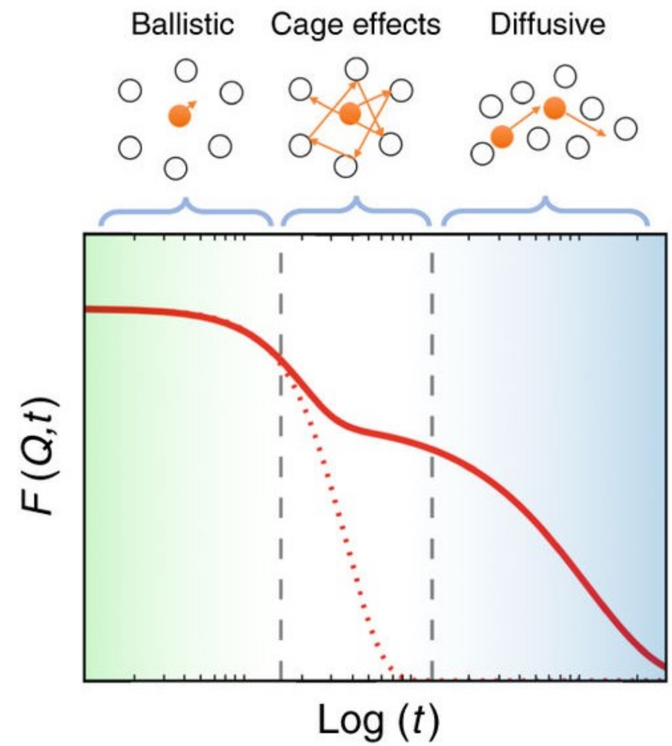
Dynamics in amorphous ices & liquid water



- XSVS experiment
- Water structure factor peak around 2 Å^{-1}
- >10000 shots per setting

Nature Comm. 9, 1917 (2018).





- Molecular dynamics in real time experiments
- Influence from H-bonding at sub-100 fs time scales
- "Cage effects"

Nature Comm. 9, 1917 (2018).

Further questions, interest, master thesis etc.

Soft matter, colloids, coherent X-ray scattering (XPCS, XCCA, …), water

Contact:
Felix.Lehmkuehler@desy.de
Gerhard.Gruebel@desy.de