

# Methoden moderner Röntgenphysik: Streuung und Abbildung

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Lecture 20	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2021 G. Grübel, O. Seeck, <u>F. Lehmkühler</u> , A. Philippi-Kobs, V. Markmann, M. Martins
Location	online
Date	Tuesday                    12:30 - 14:00 (starting 6.4.) Thursday                    8:30 - 10:00 (until 8.7.)

# Soft Matter – Timeline

- Do 27.05.2021      **Soft Matter studies I: Methods & experiments**  
*Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, ...*
- Di 01.06.2021      **Soft Matter studies II: Structure**  
*SAXS & WAXS applications, X-ray cross correlations, ...*
- Do 03.06.2021      **Soft Matter studies III: Dynamics**  
*XPCS applications, diffusion, dynamical heterogeneities, ...*
- Di 08.06.2021      **XPCS & XCCA simulations and modelling**
- Do 10.06.2021      **Case study I: Glass transition**  
*Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, ...*
- Di 15.05.2021      **Case study II: Water**  
*Phase diagram, anomalies, crystalline and glassy forms, FEL studies, ...*
- Do 17.06.2021      **Outlook: Opportunities at new facilities**

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.

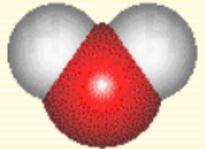
[Table of Contents](#) | [Site Map](#)

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

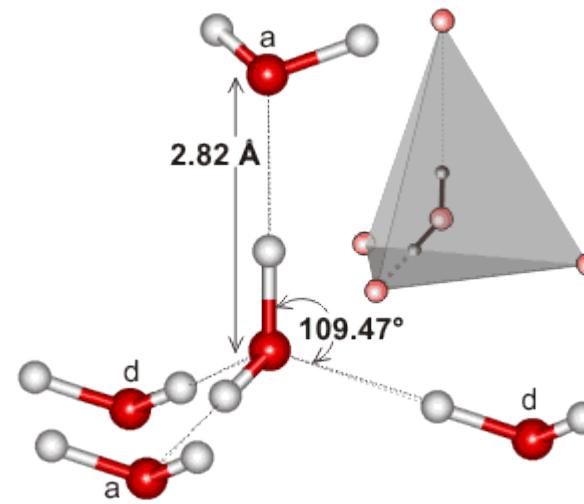
Many regard water ( $H_2O$ ) as a rather uninteresting substance because it is transparent, odorless, tasteless and ubiquitous. It is the simplest compound of the two most common reactive elements in the universe, consisting of just two hydrogen atoms attached to a single oxygen atom. Indeed, very few 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/>

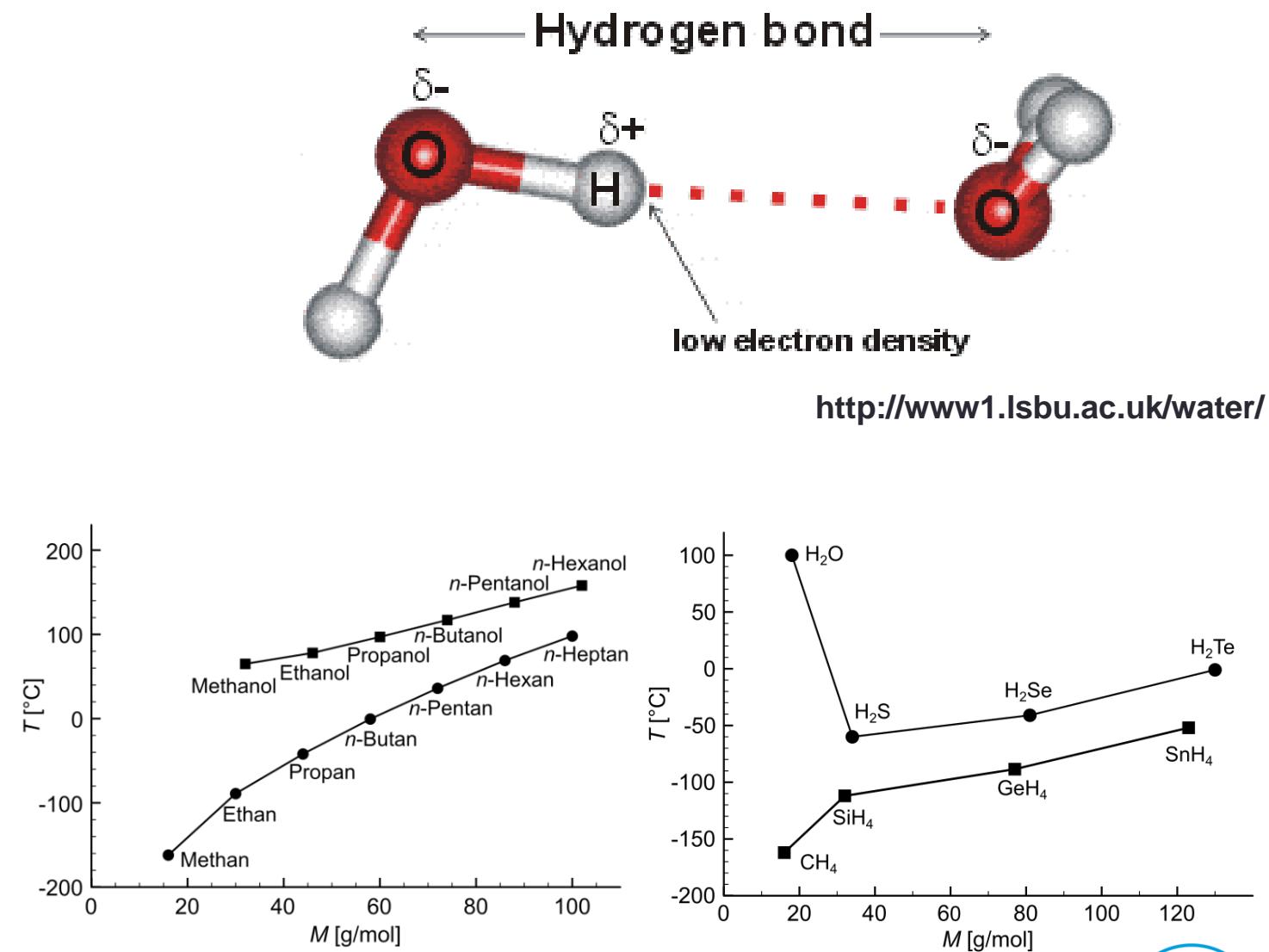
## Why study water?



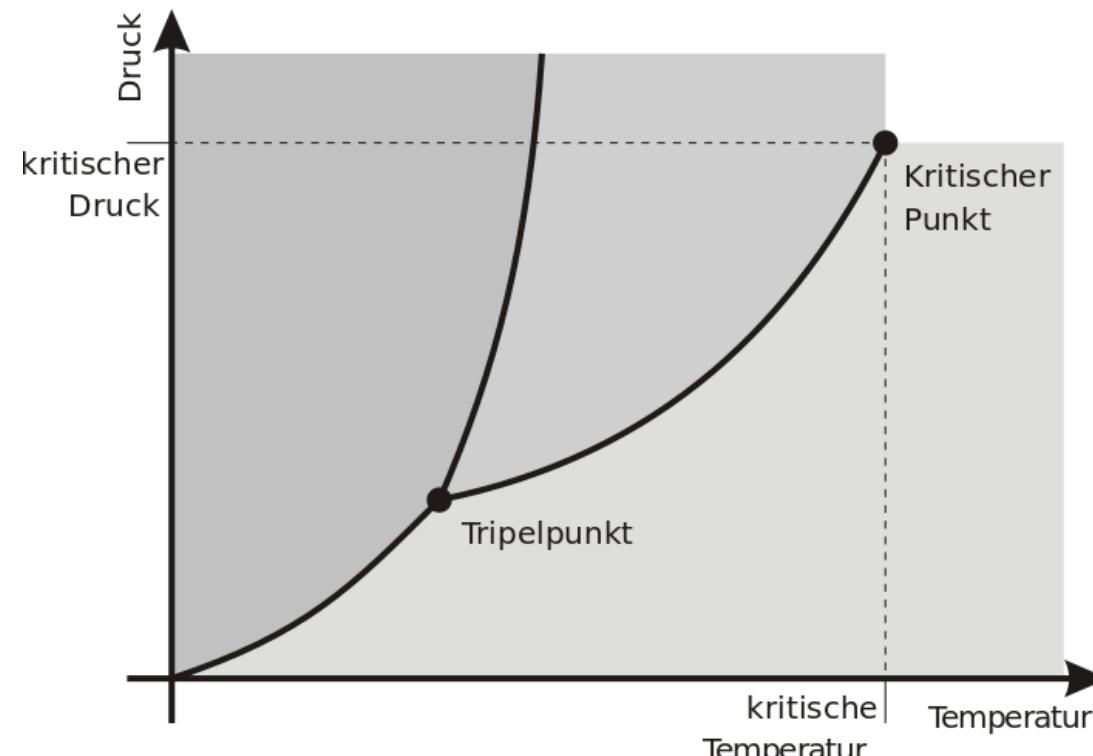
Most important liquid for life (biology), as solvent (chemistry), geo-science, ...

### Complex hydrogen bond network

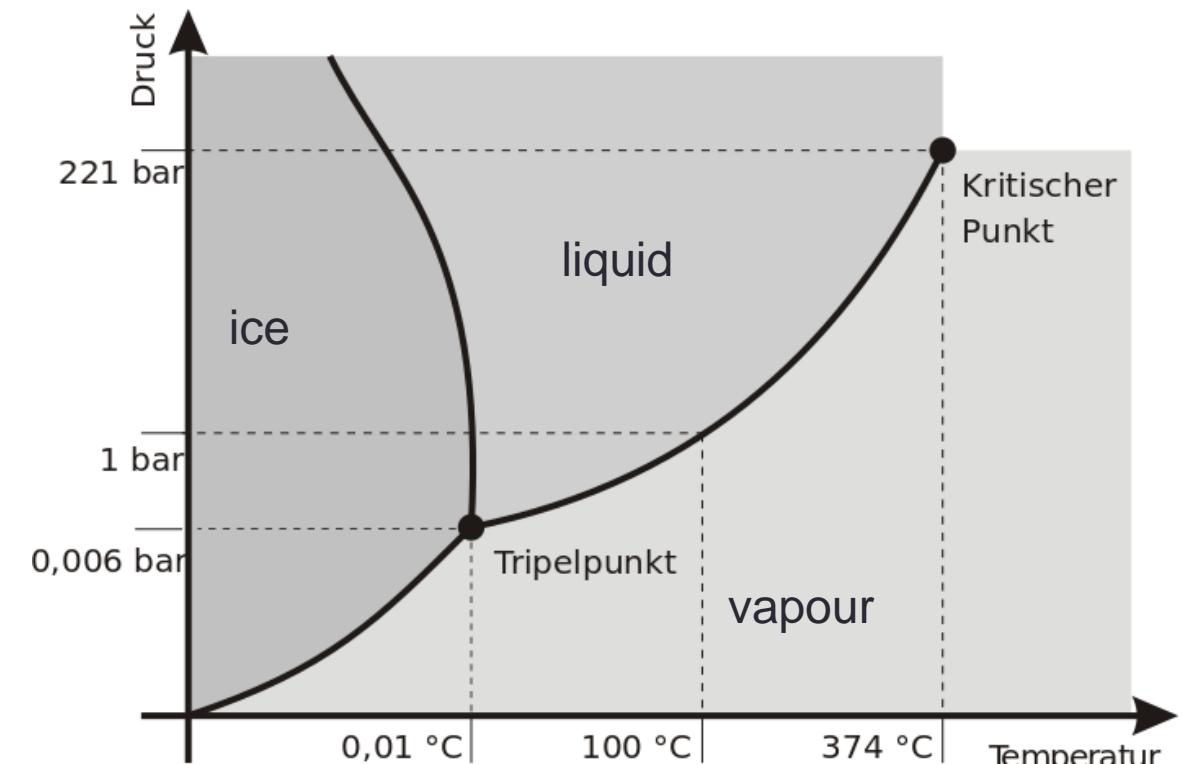
- Strength O-H...O:  $\sim 21$  kJ/mol
- Tetrahedral coordination
- E.g. high boiling points



## Water – phase diagram



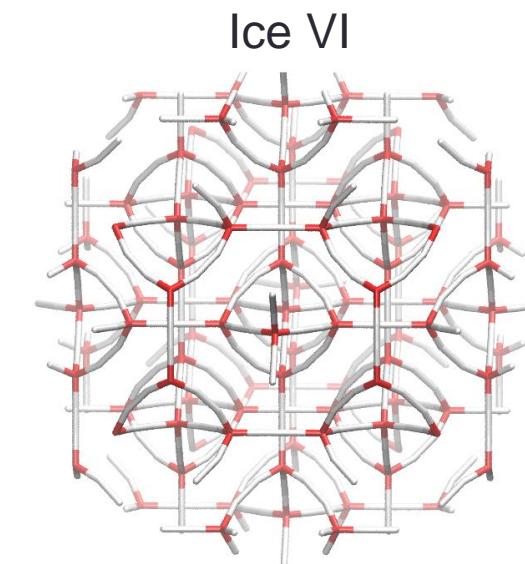
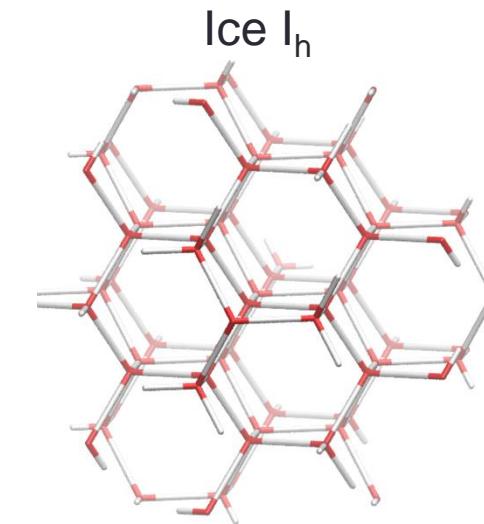
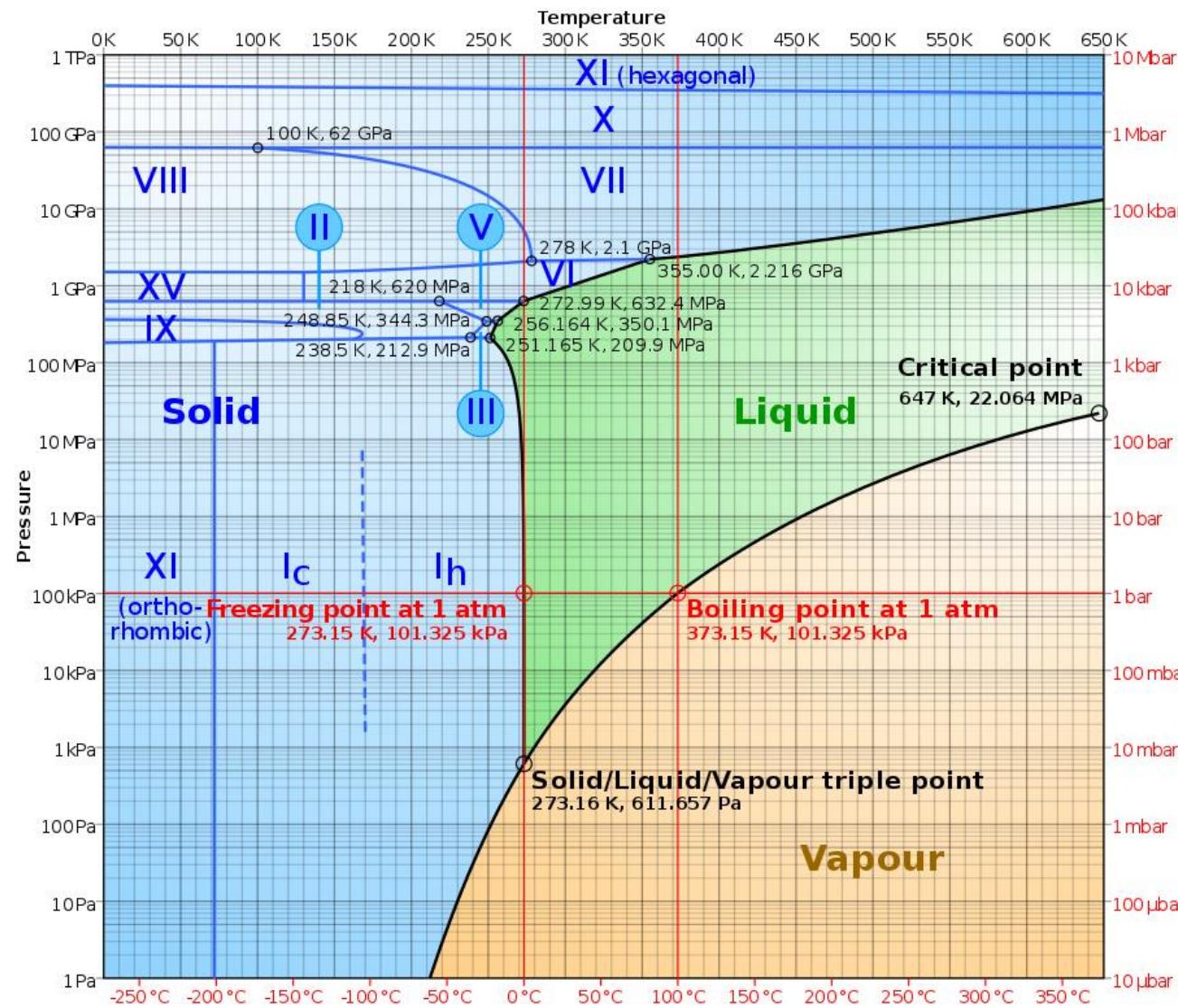
Normal liquid



Water → anomalies

Figures: wikipedia

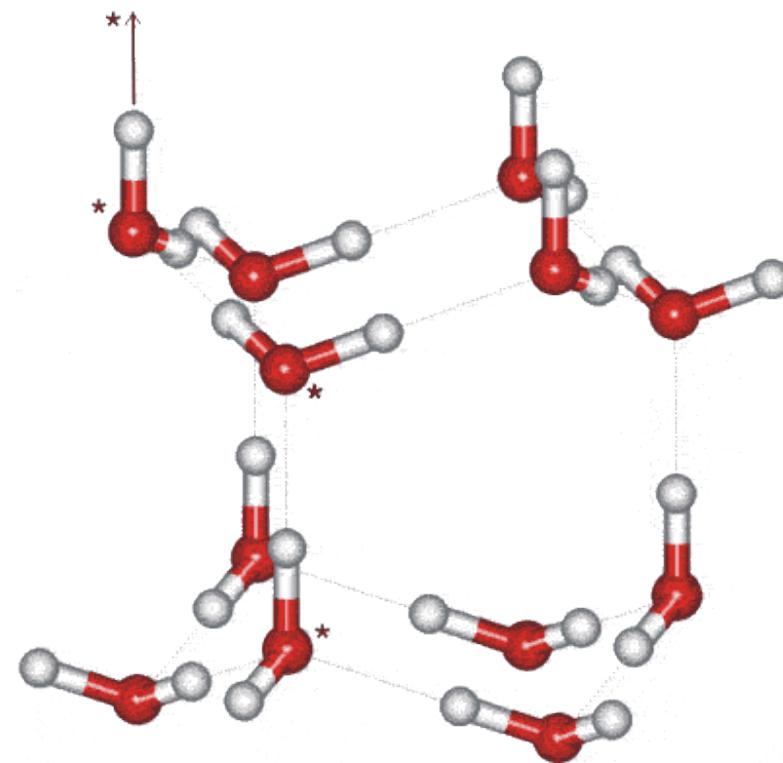
## Crystalline ice – polymorphism



Phase diagram: wikipedia

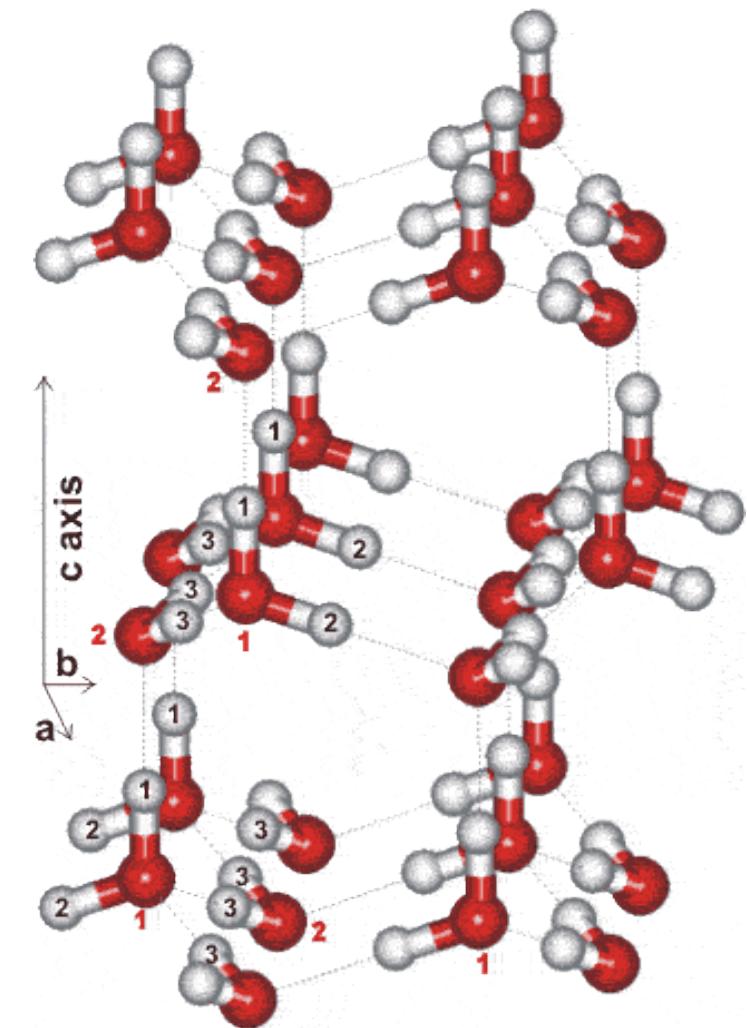
## Crystalline ice – polymorphism

Hexagonal ice (ice I<sub>h</sub>)



Tetrahedral coordination  
4 H-bonds per molecule

Ice rule: one hydrogen  
between two oxygens

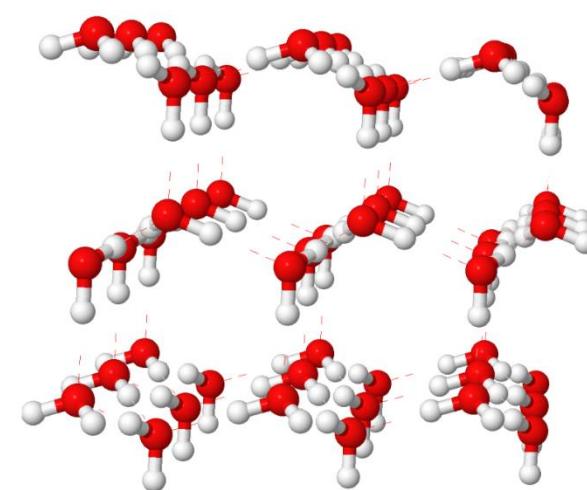
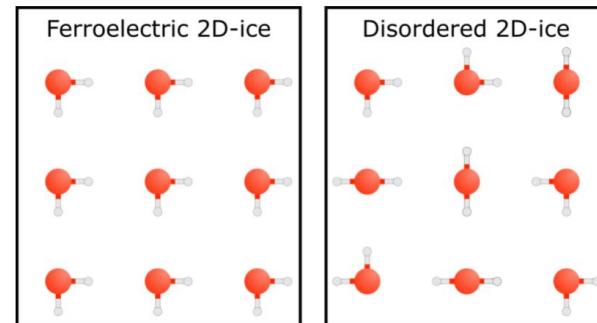


<http://www1.lsbu.ac.uk/water>

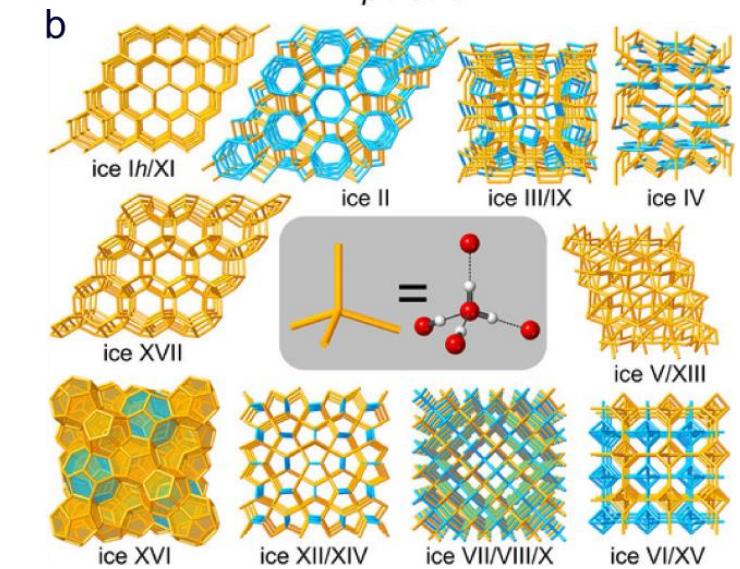
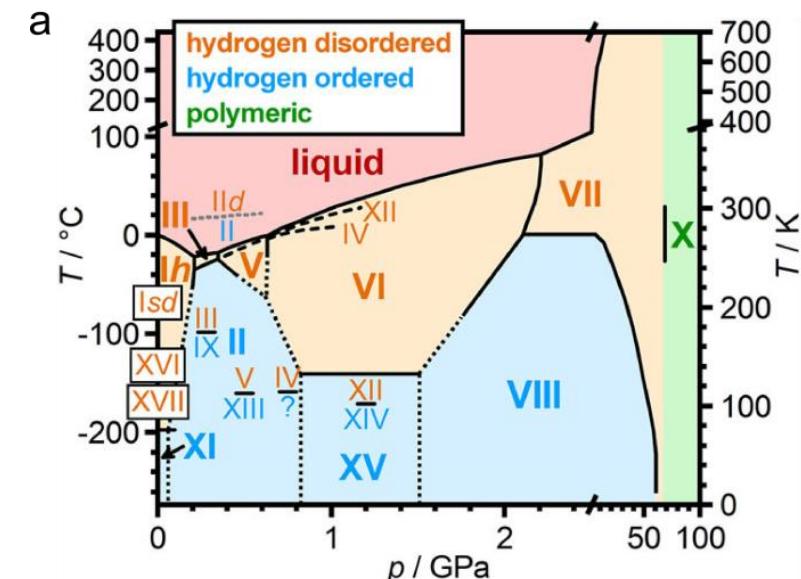
## Crystalline ice – polymorphism

There are hydrogen-disordered and hydrogen-ordered ice phases

Disordered 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	$\sim 120$ K
VI	XV	$\sim 130$ K



Ice XI: hydrogen-ordered form of hexagonal ice  $I_h$



J. Chem. Phys. 150, 060901 (2019).

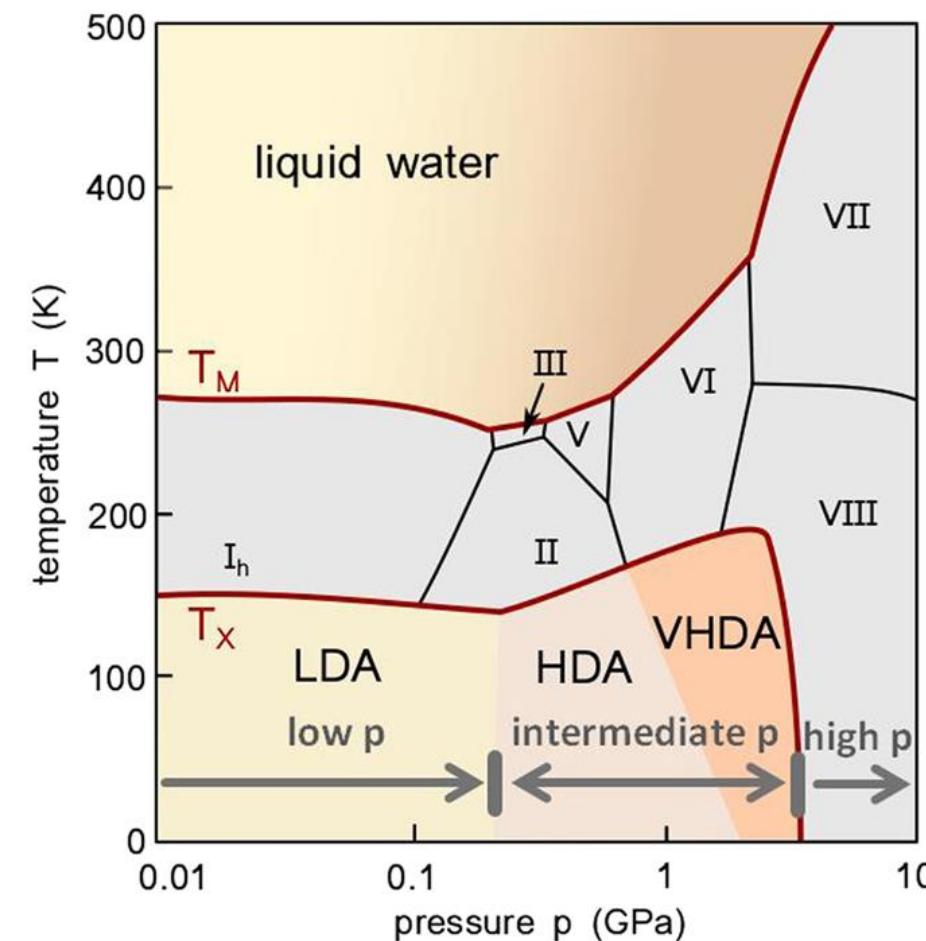
## Amorphous ice

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

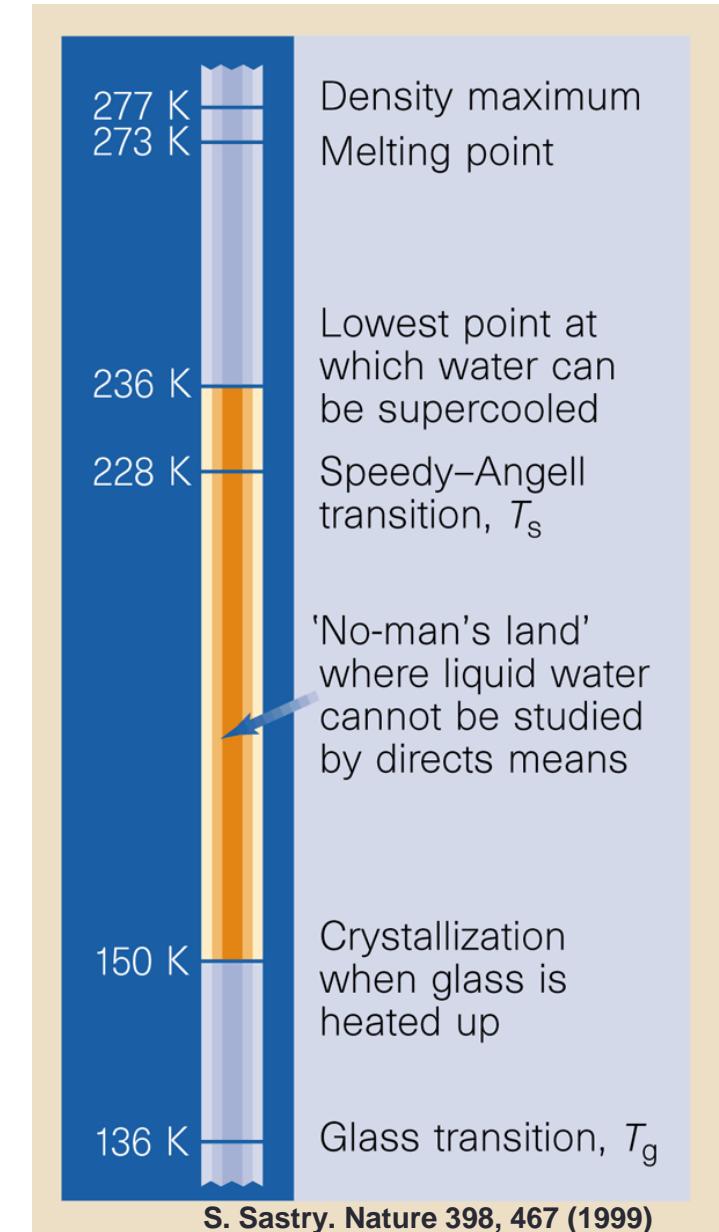
(At least) three forms of amorphous ice

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

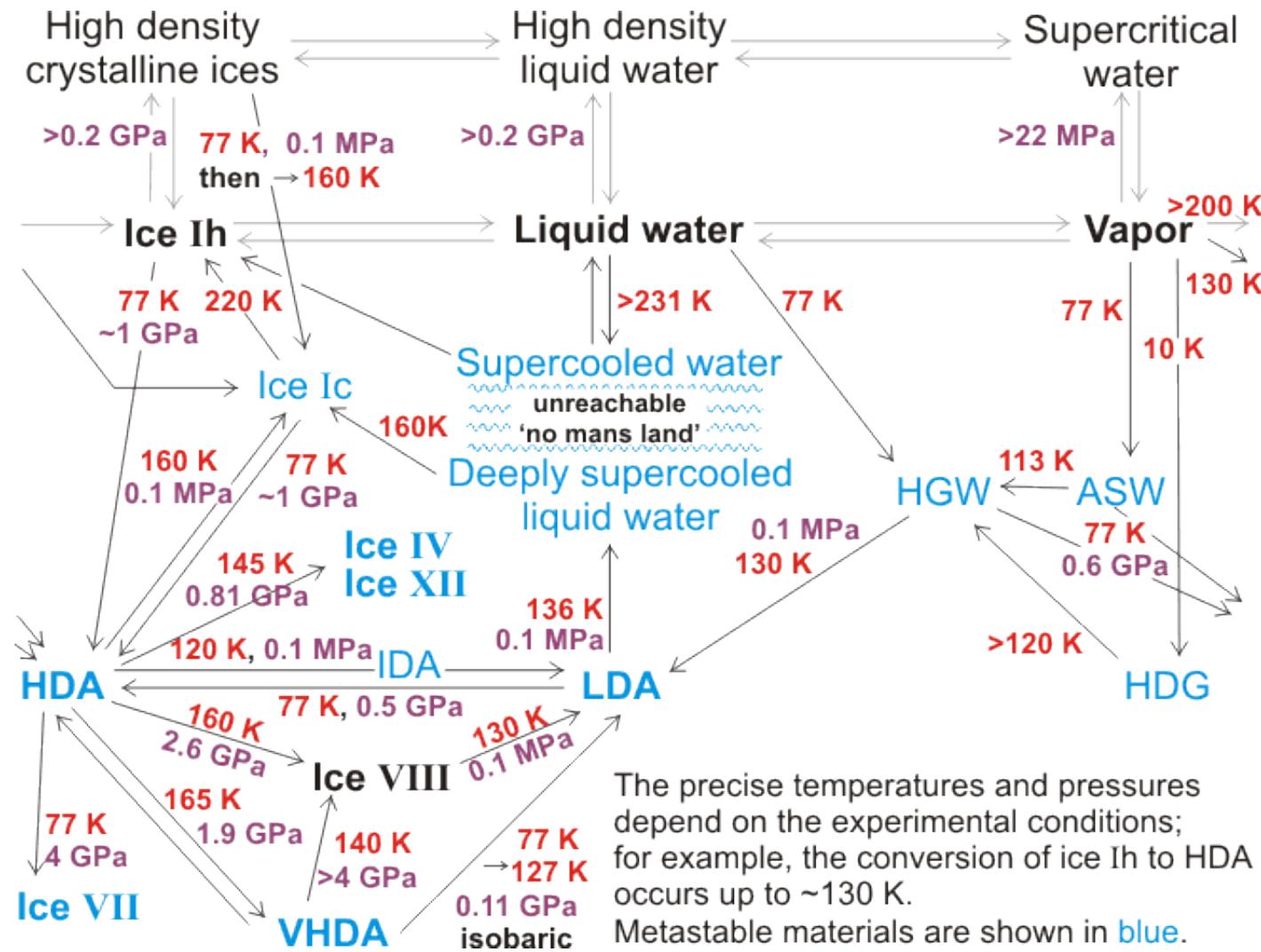
Glass transition: no man's land



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



## Water – solid states



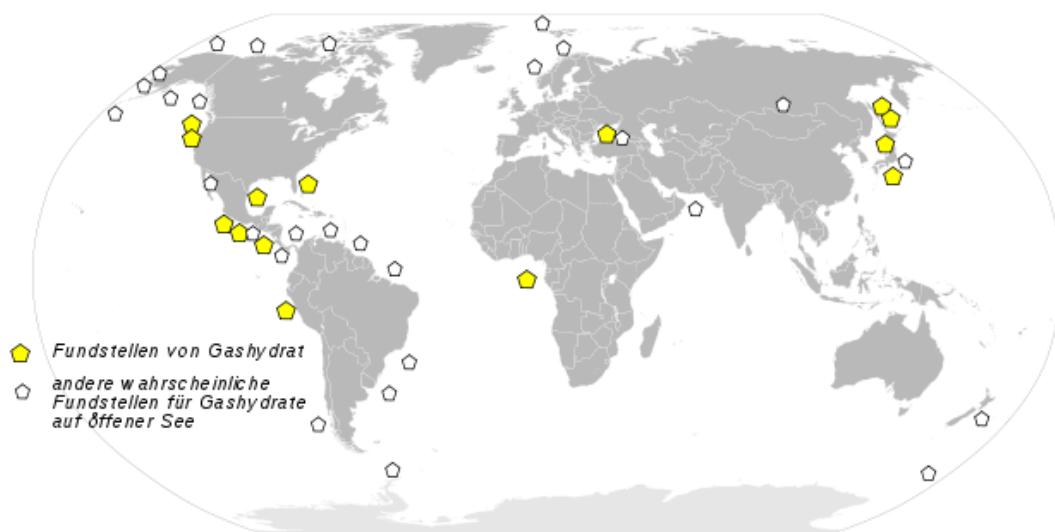
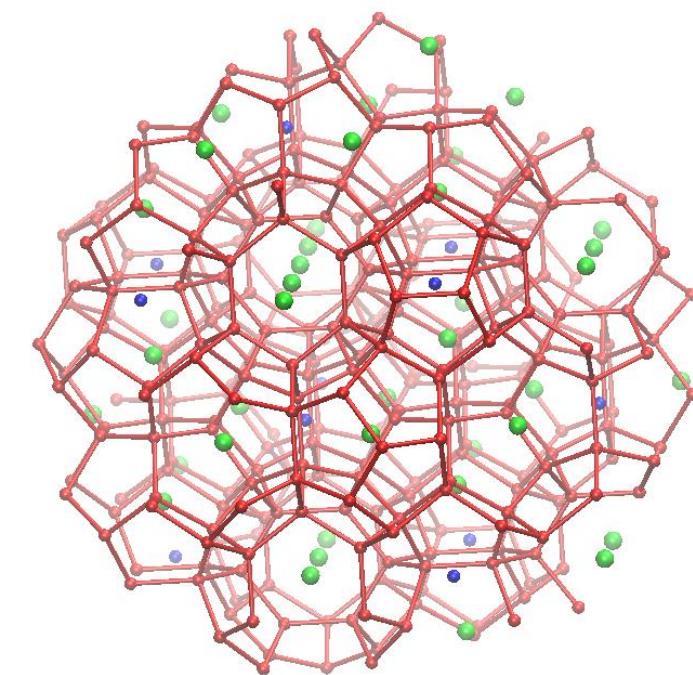
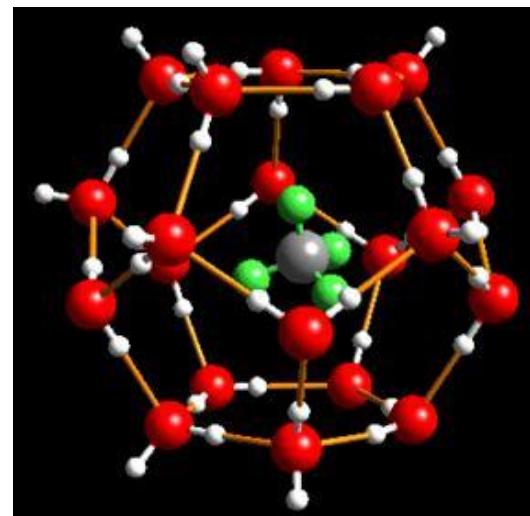
ASW –  
amorphous solid  
water

# HGW – Hyperquenched glassy water

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.

## Clathrate hydrates

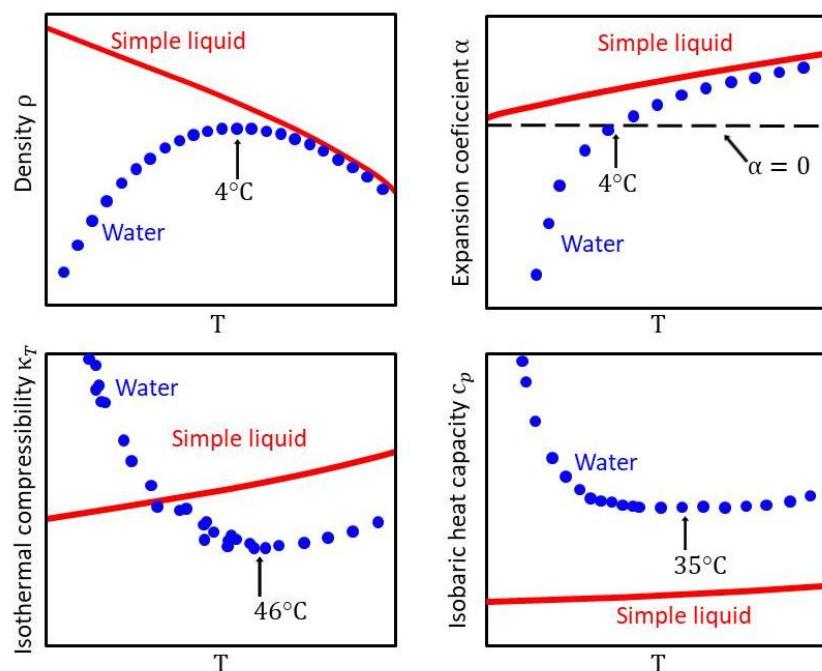
- In presence of gas molecules (e.g. methane, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, ...) water forms ice-like inclusion compounds
- Typically "more stable" than ice
- Methane hydrate at ocean floor and in perma frost regions



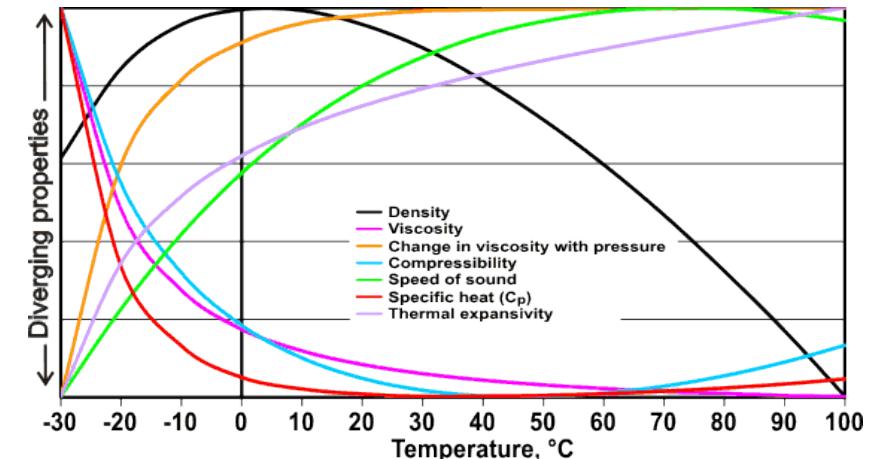
## Water – anomalies

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)



J. Phys.: Cond. Matt. 15, R1669 (2003)



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

- Complex hydrogen bond network
- Diverging properties upon supercooling around -45°C
- Connection to water structure



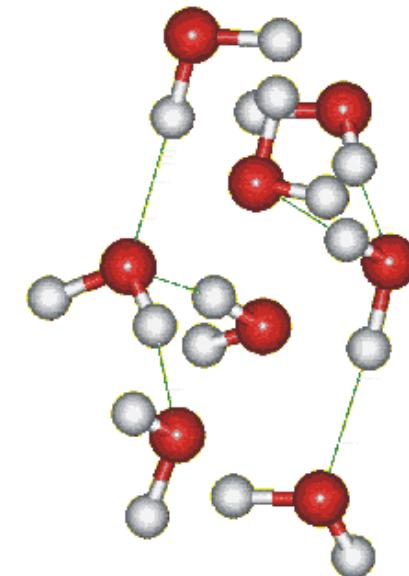
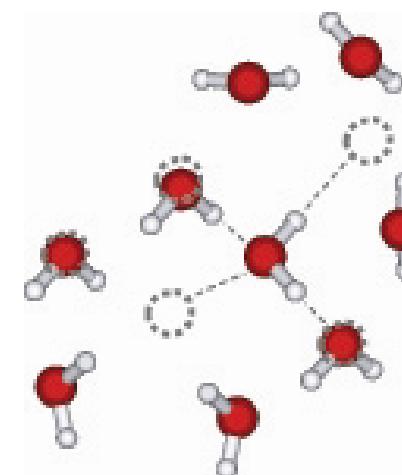
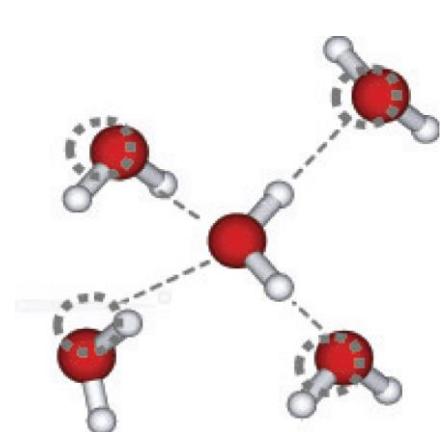
## Liquid water: continuum and mixture models

Long-standing debate: Liquid water as...

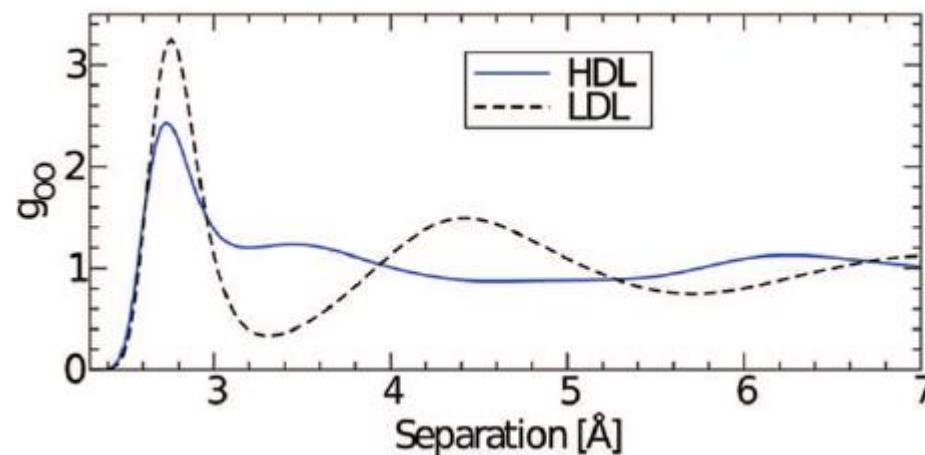
- (1) network of disordered tetrahedrally coordinated molecules with ~3.5 hydrogen bonds per molecule
- (2) Mixture of different species with different geometry (goes back to Röntgen 1892 to explain anomalous properties of water)

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



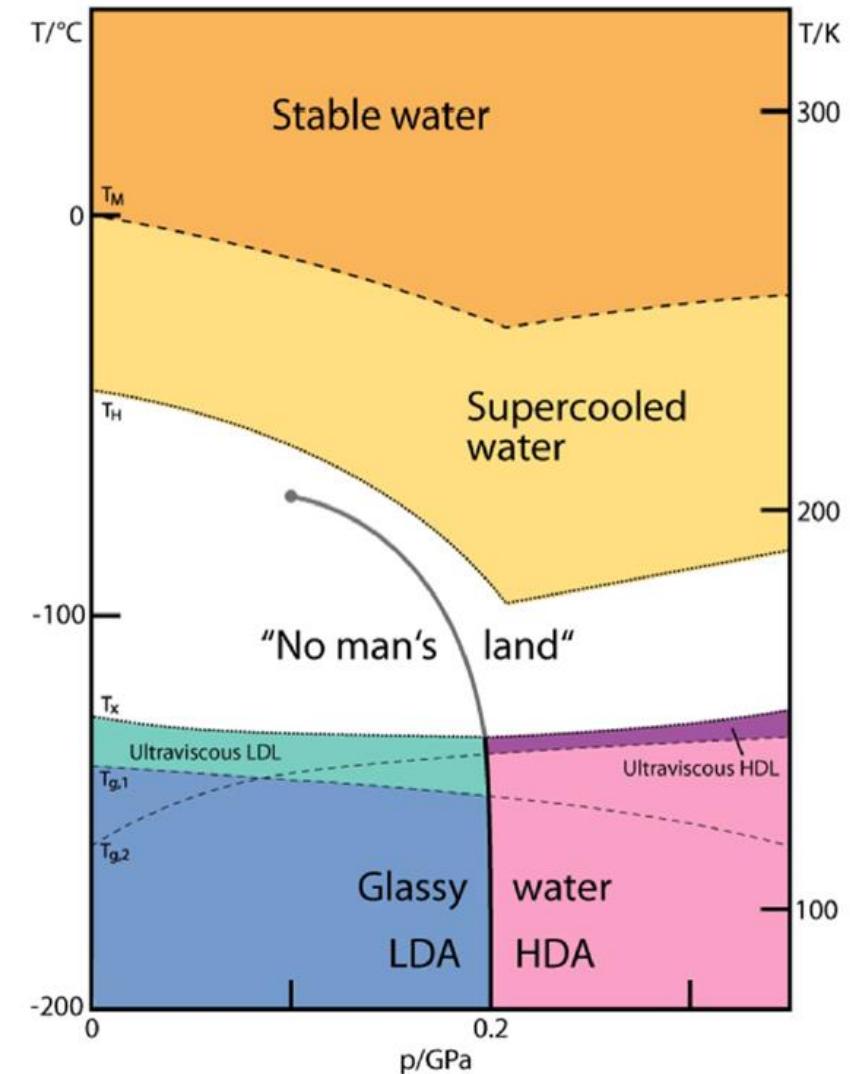
## Liquid water: continuum and mixture models



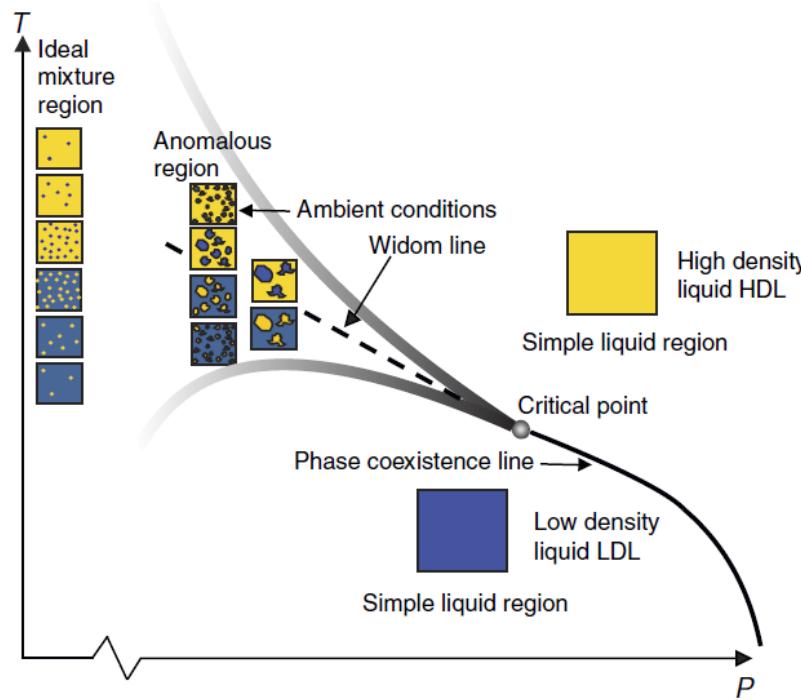
Molecular dynamics simulations:

- LDL: tetrahedral liquid
- HDL: broken hydrogen bonds

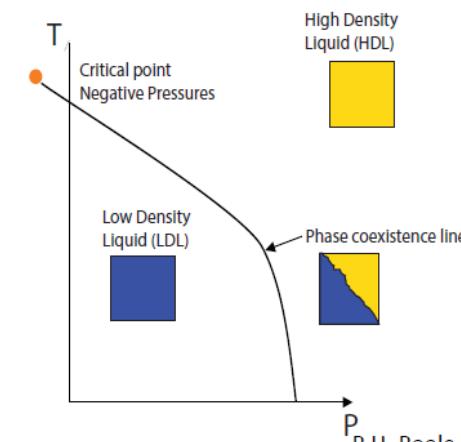
Phase diagram of amorphous water:  
 Reaching "no man's land" to measure  
 HDL/LDL



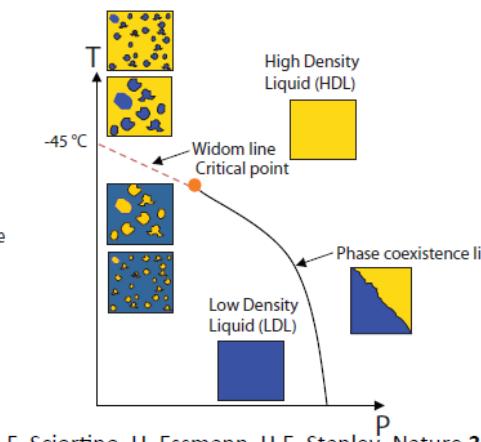
## Liquid water: continuum and mixture models



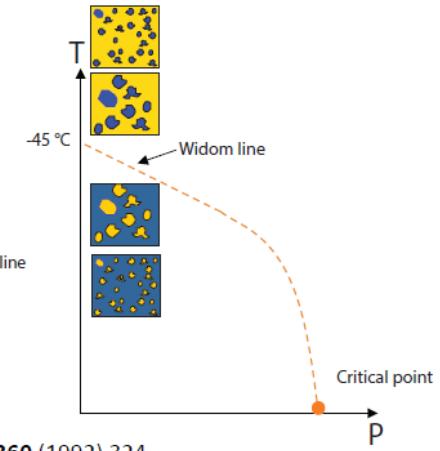
Critical Point Free Model  
Critical Point at -P



Critical Point Model  
Critical Point at +P



Singularity Free Model  
Critical Point at 0K



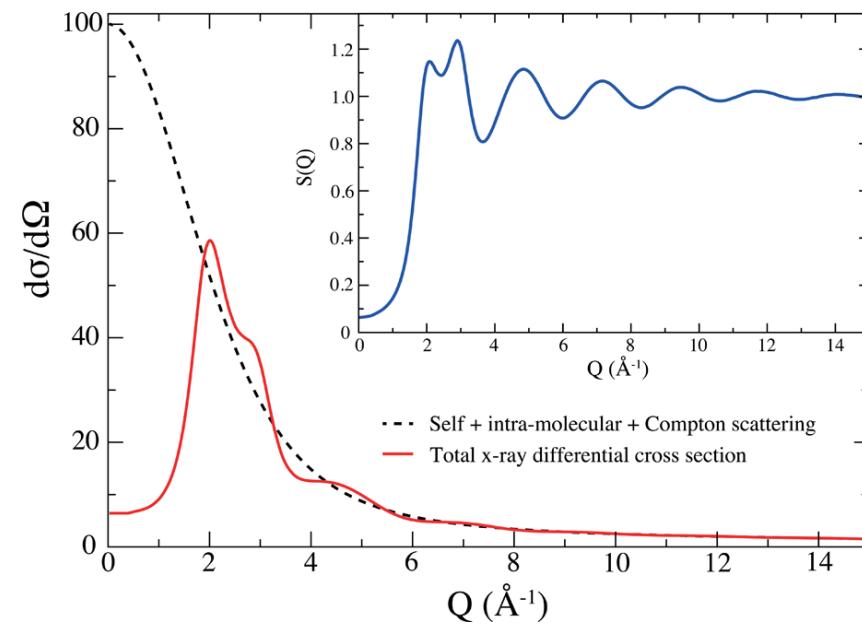
P.H. Poole, F. Sciortino, U. Essmann, H.E. Stanley, Nature 360 (1992) 324.

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

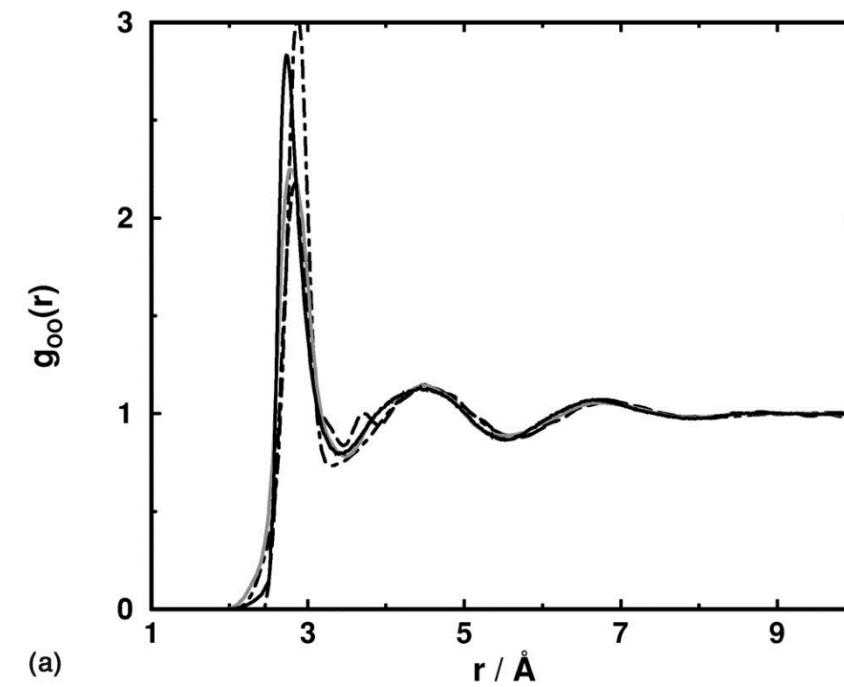
Widom line: locus of correlation length maxima in the pressure-temperature (P-T) plane.  
Thermodynamic response functions are expected to have maxima

Nat. Comm. 6, 8998 (2015)

## X-ray studies: structure factors



Chem. Rev. 116, 7570 (2016)

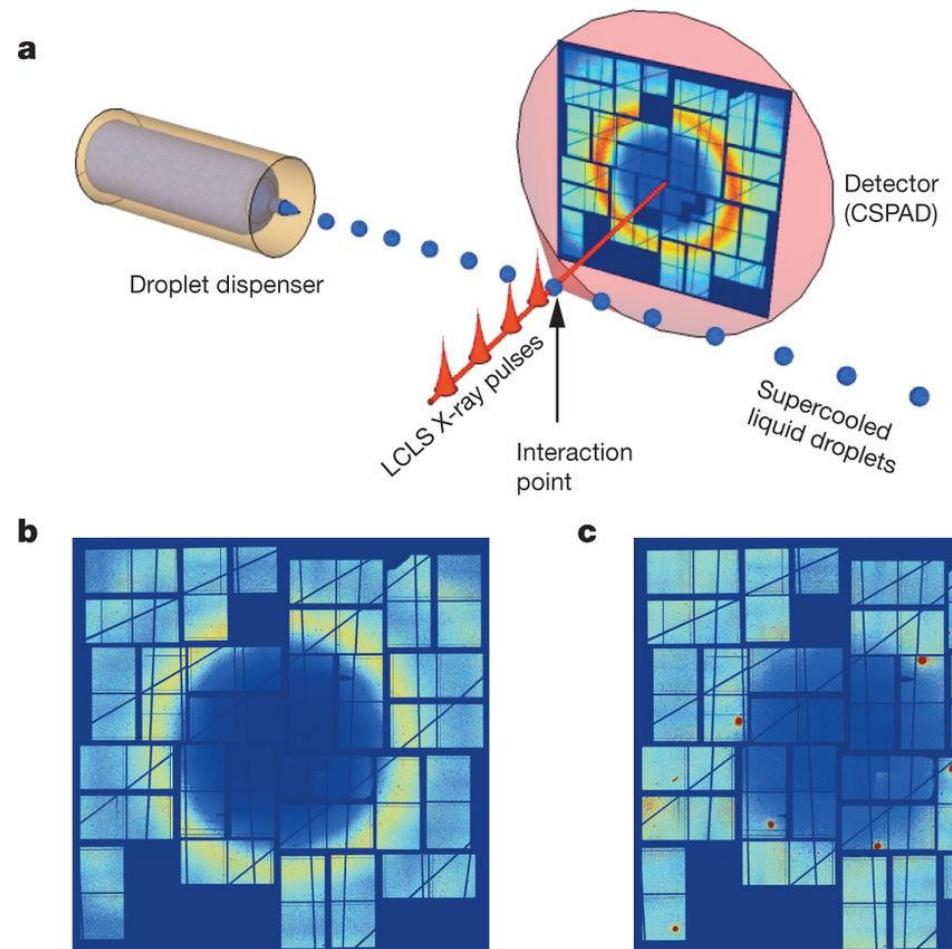


J. Chem. Phys. 113, 9140 (2000)

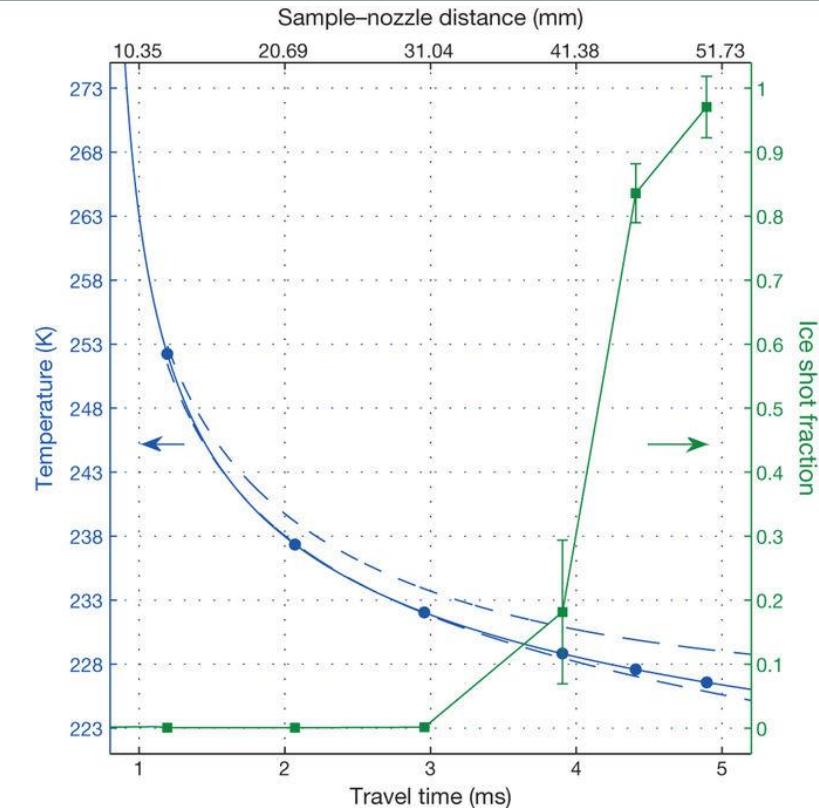
Structure factor of water around  $q = 2 \text{\AA}^{-1} \rightarrow$  for 8 keV X-rays  $\rightarrow \theta \approx 29^\circ \rightarrow$  XRD

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

## Liquid water: structure factors



Nature 510, 381 (2014)

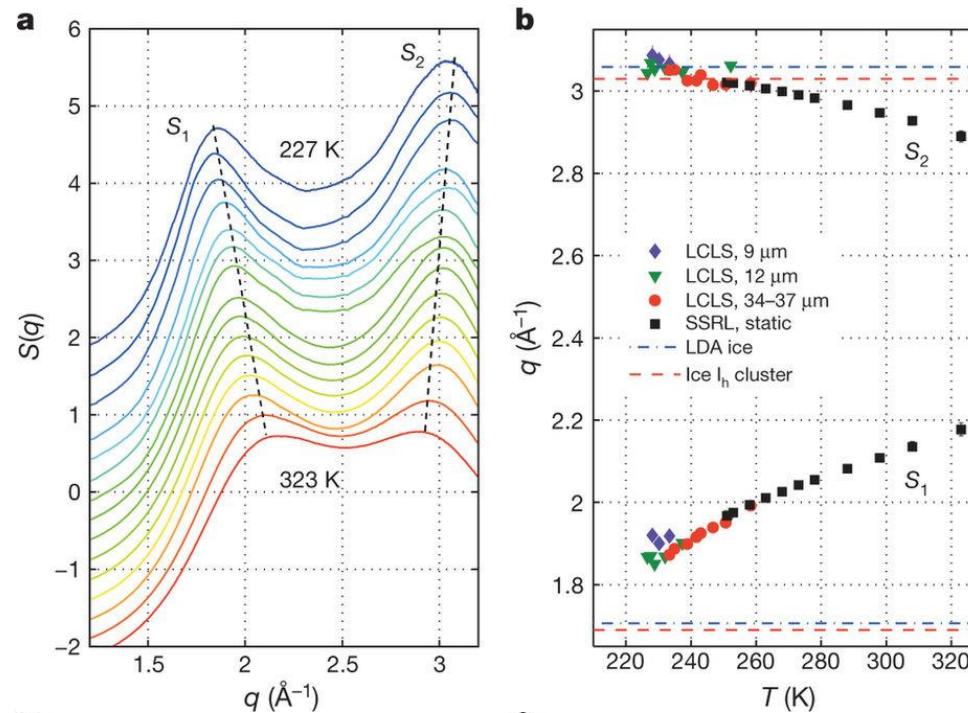


Liquid microdroplets: supercooling due to evaporation in vacuum

Ultrafast probing: FEL ( $\sim 100$  fs)

→ XRD patterns from single droplets



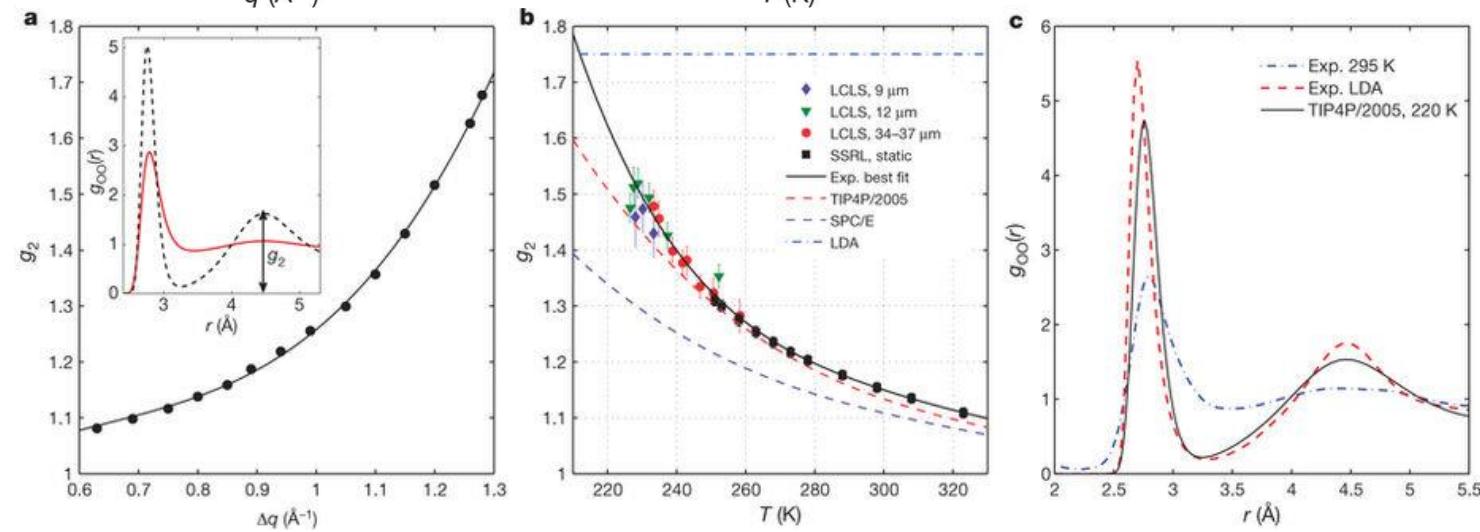


Structure factors: peaks shift upon supercooling

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

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

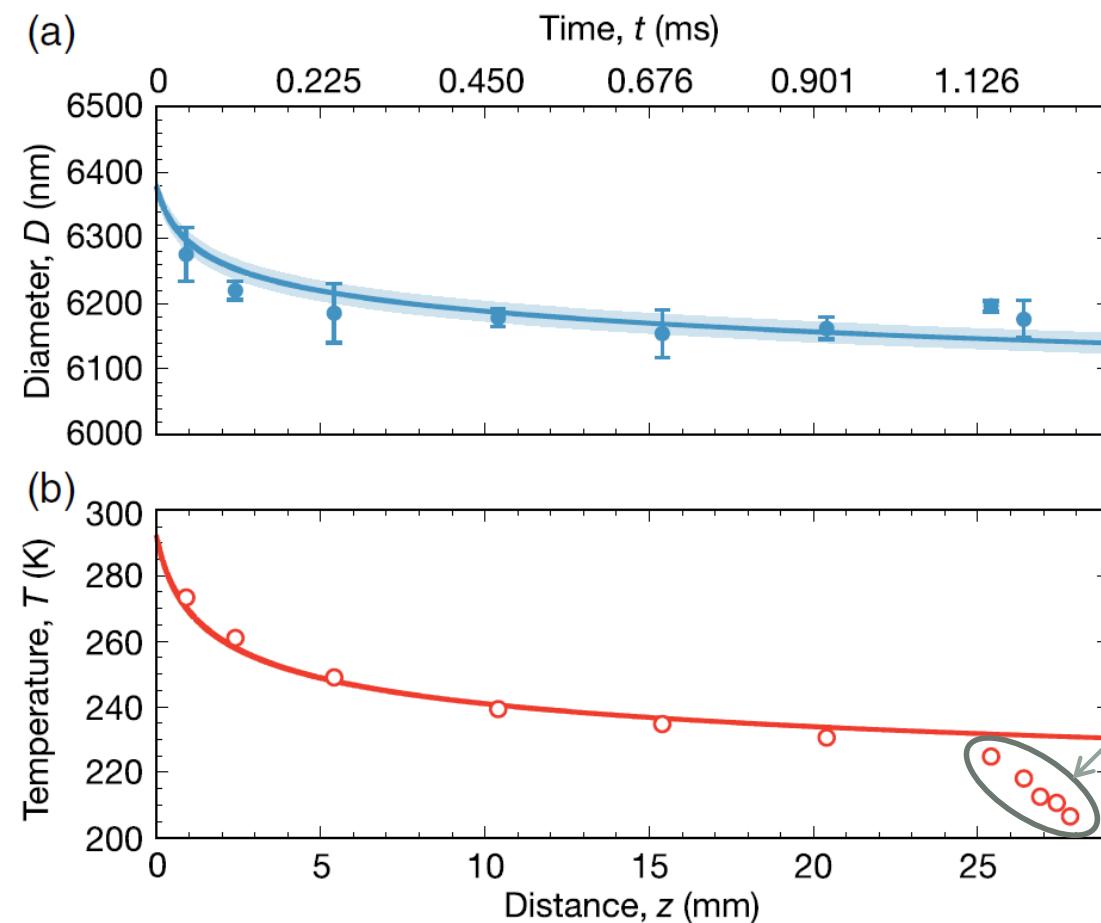
Towards low-density liquid water?



Nature 510, 381 (2014)

## How to measure temperature of water droplets?

Raman scattering for diameter measurement



Droplet diameters from vibrational spectroscopy & Knudsen model of evaporation

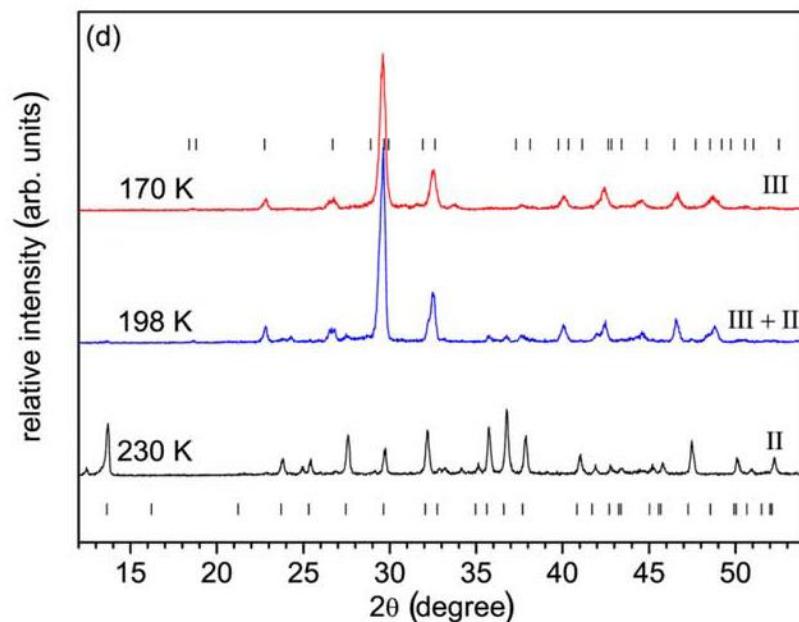
Ice formation

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

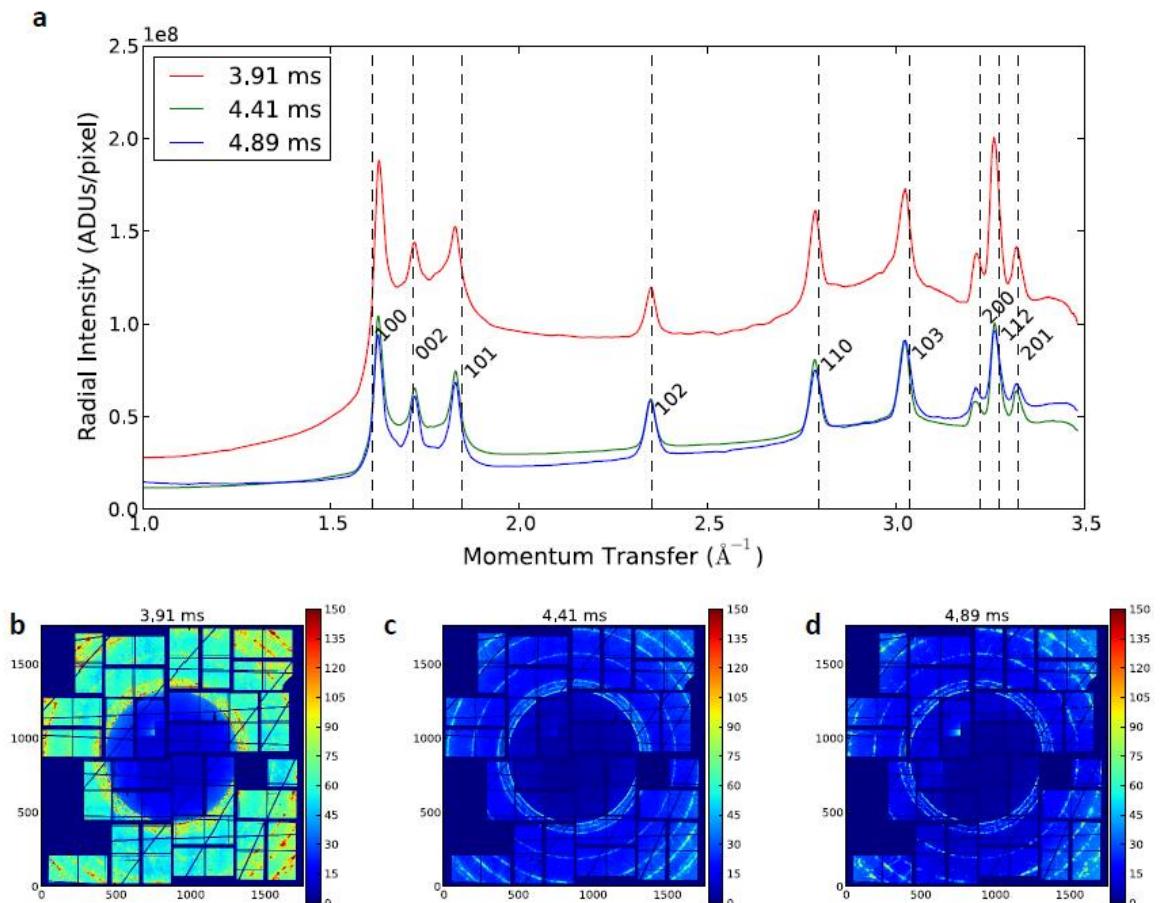
## X-ray diffraction: ices

Typical example: XRD of ice(s)

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



Phys. Rev. B 77, 220105 (2008)

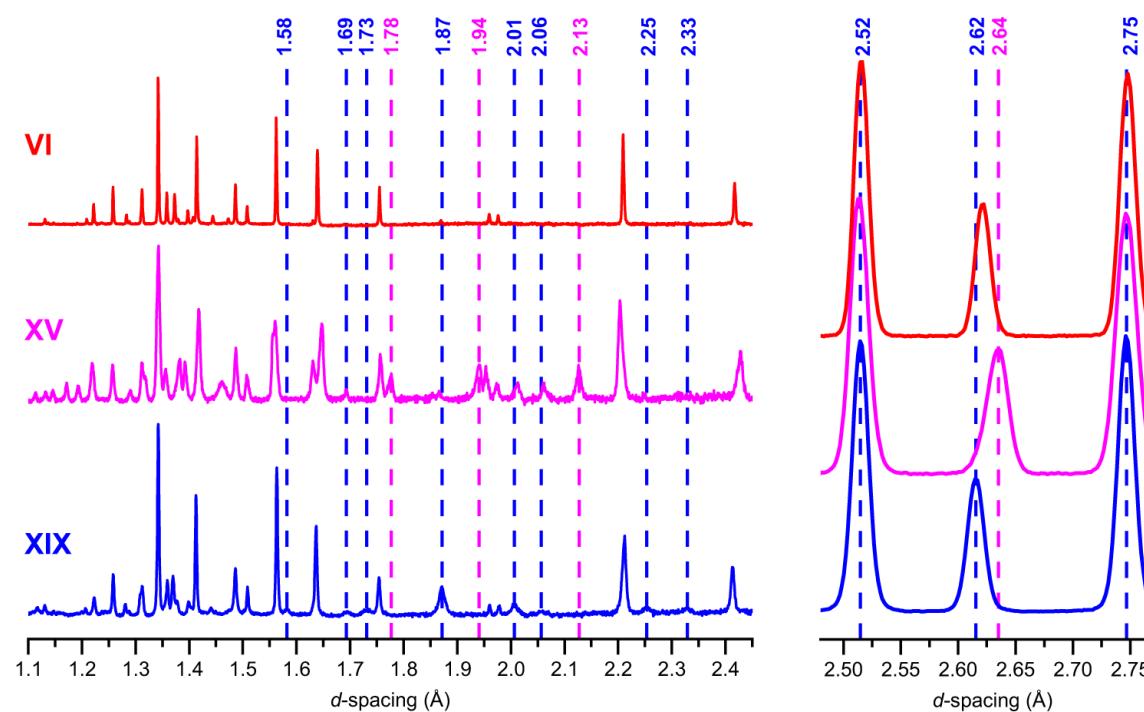


Crystallisation upon fast cooling

Nature 510, 381 (2014)

## X-ray diffraction: Latest ice

Ice XIX as second polymorph of ice VI

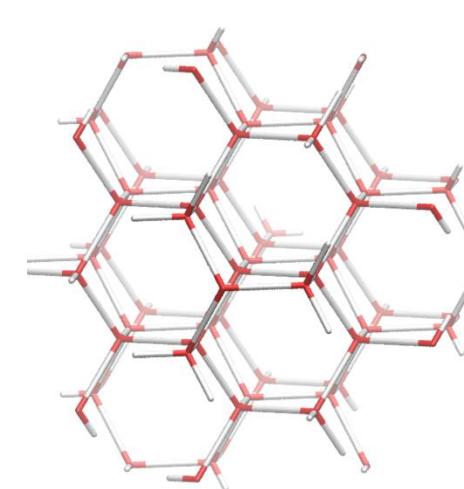


Nature Comm. 12, 1128 (2021)

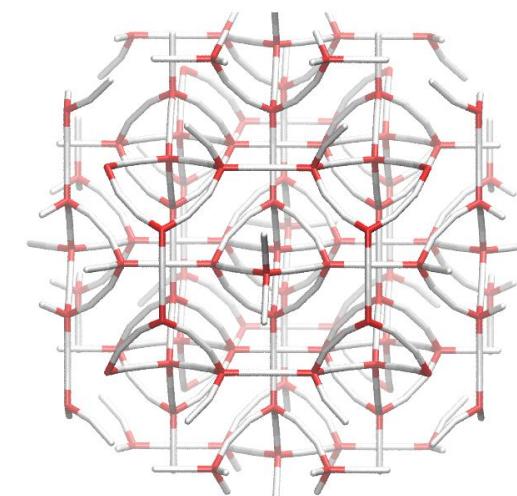
Ice VI: hydrogen disordered

Two different hydrogen-ordered phases: Ice XV and ice XIX

Here: Neutron diffraction to make hydrogen „visible“

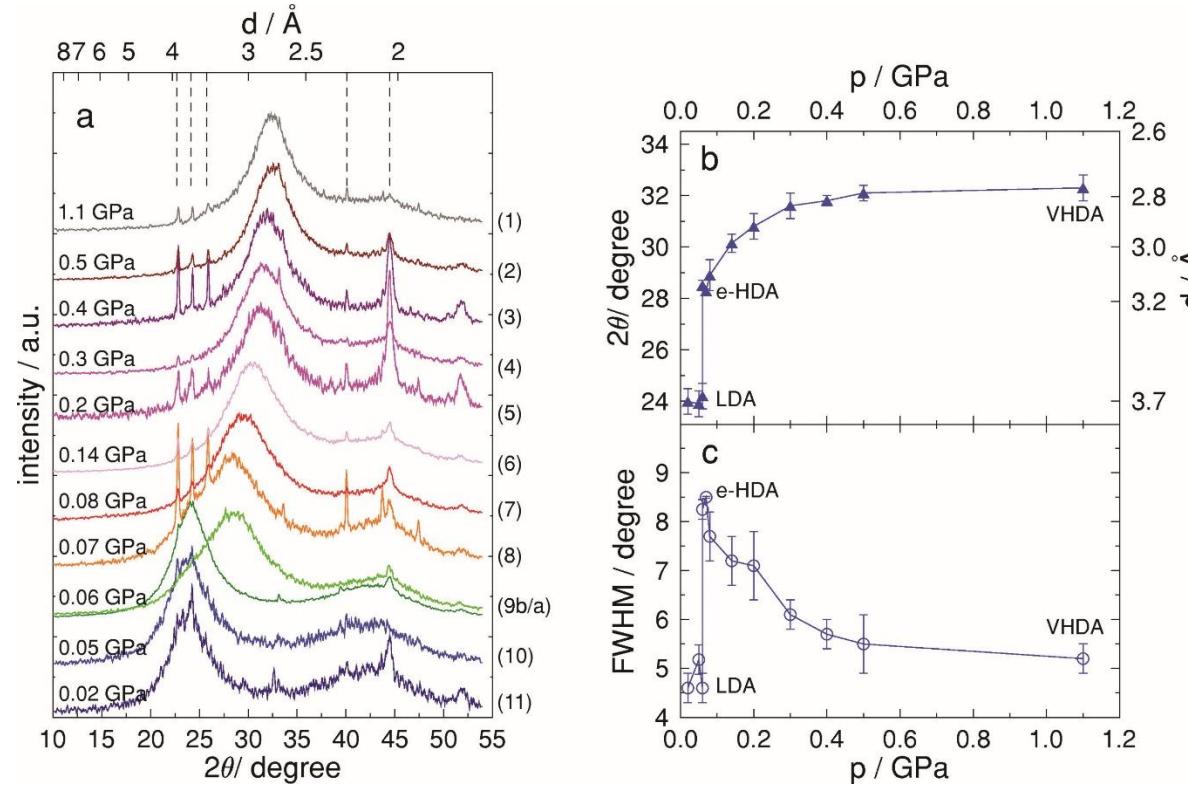


Ice  $I_h$



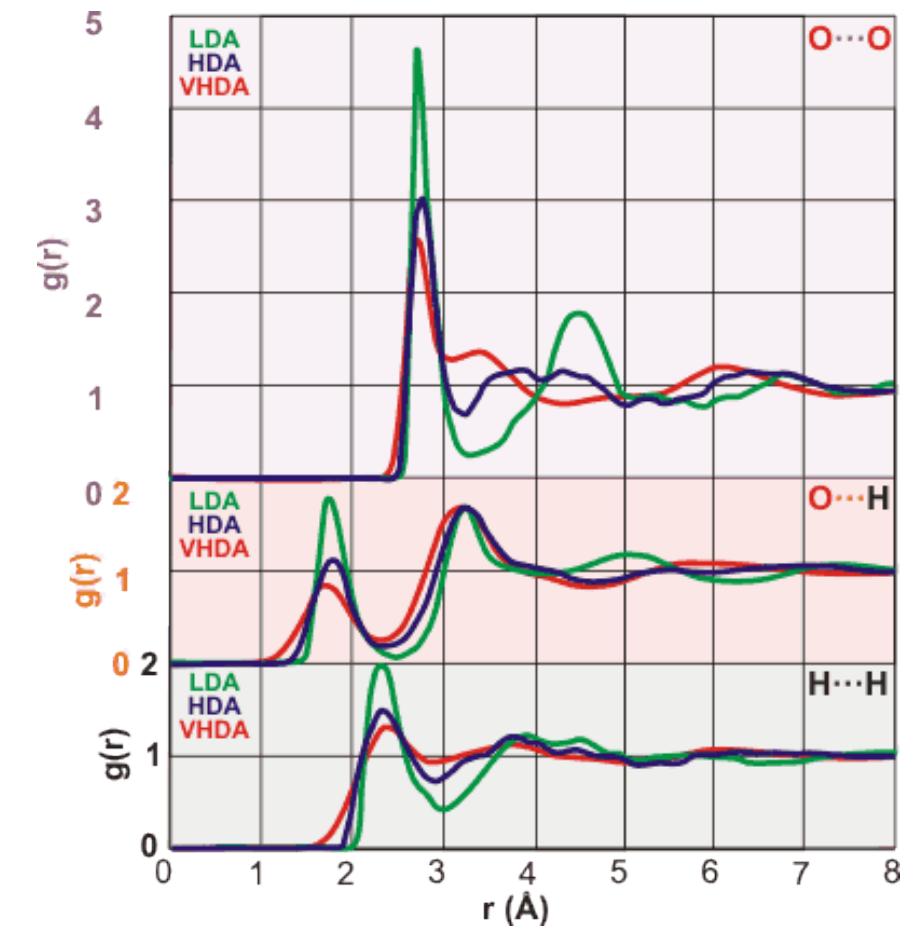
Ice VI

## Transition of amorphous ices



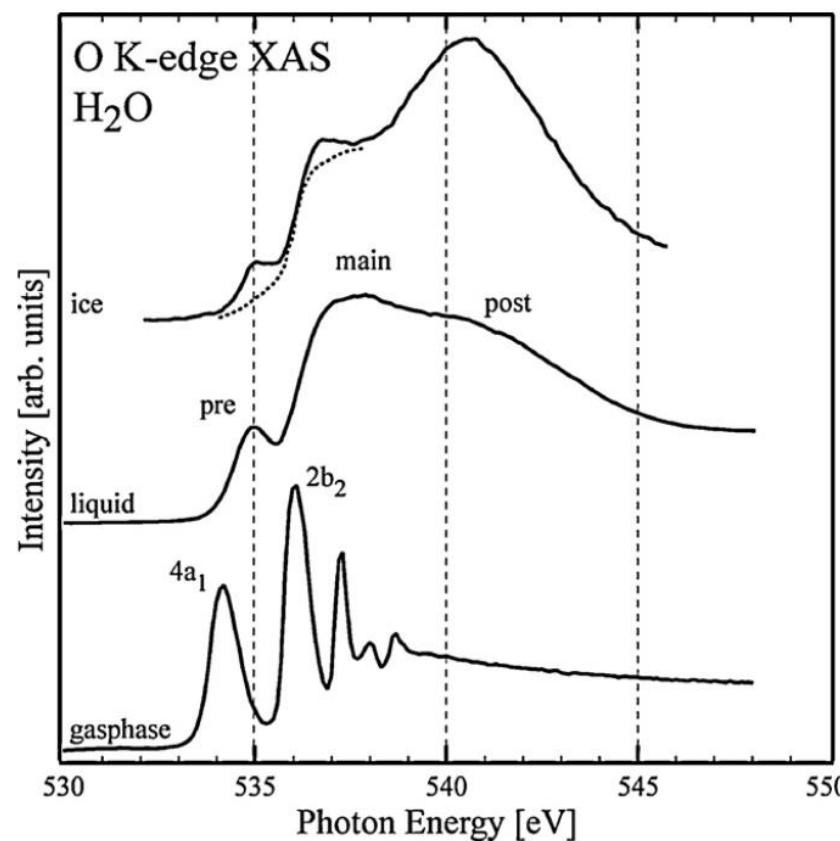
Isothermal decompression of VHDA at 140K to several selected pressures

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



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

## X-ray spectroscopy



- XAS = X-ray Absorption Spectroscopy
- Fine structure of absorption edge  $\leftrightarrow$  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)

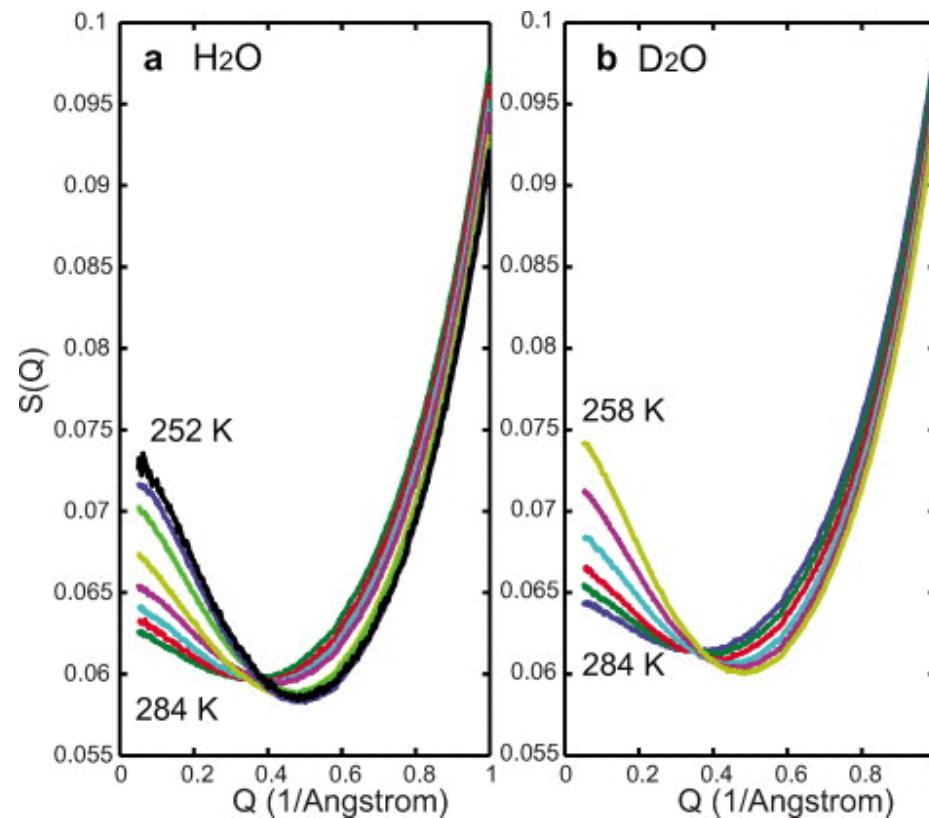
e.g. PNAS 116, 4058 (2019)

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

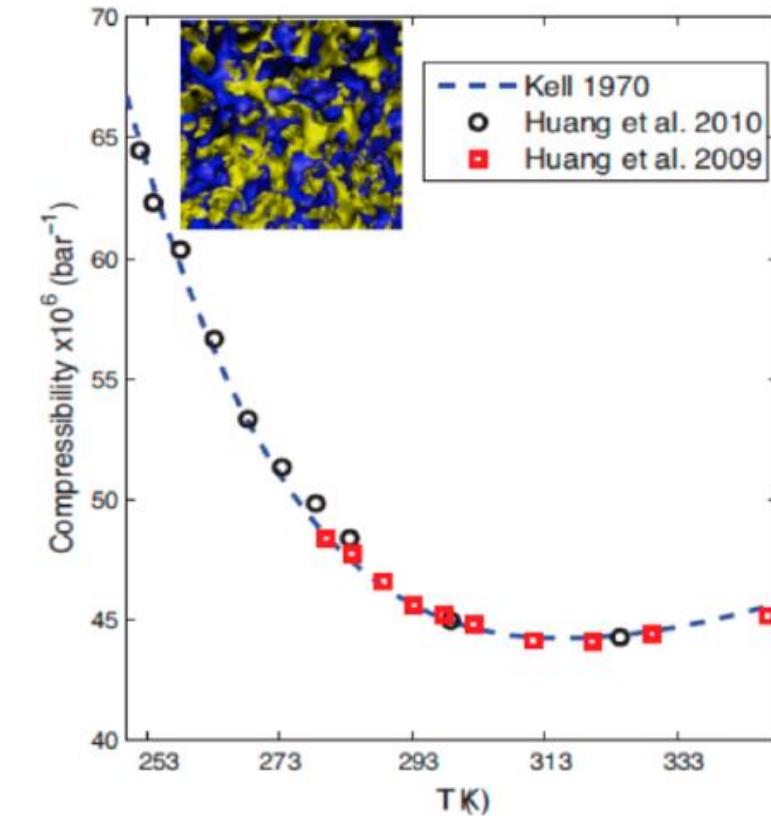
## Liquid water: SAXS

Small  $q$  limit in SAXS:  $S(q \rightarrow 0) \propto$  density fluctuations (see Lecture 6)

Isothermal compressibility  $\chi_T$  can be extracted for  $q \rightarrow 0$ :  $S(0) = k_B T \rho_n \chi_T$



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, Oxfordshire 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 over the true state of water.

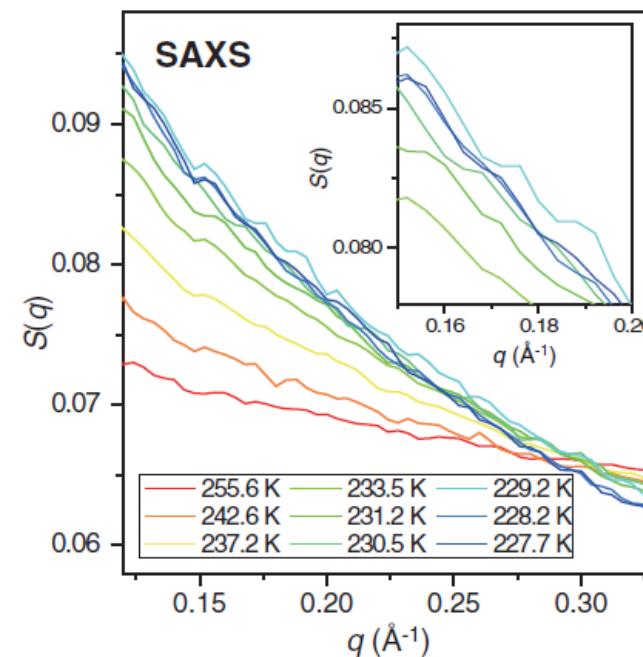
Perhaps one of the most surprising facts about water is that it is a liquid. All of the elements that surround oxygen in the periodic table have hydrides which are gases at ambient temperature and pressure, while hydrogen oxide is definitely a liquid with quite a low vapor pressure,  $\approx 5$  mbars. 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  $2 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ , which means that after 1 s any given water molecule has on average moved about 44  $\mu\text{m}$  from its starting position, corresponding to  $\approx 150000$  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-

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

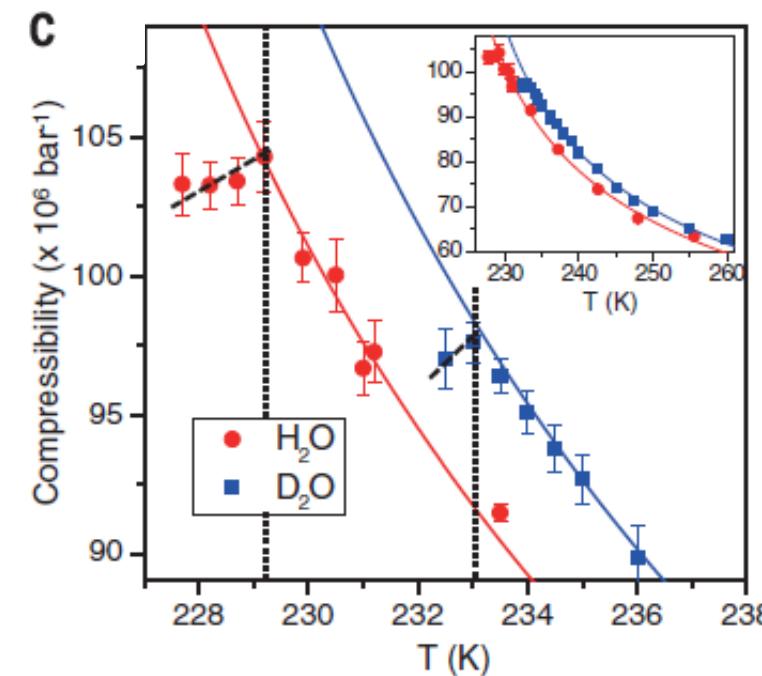


## Liquid water: SAXS at FEL

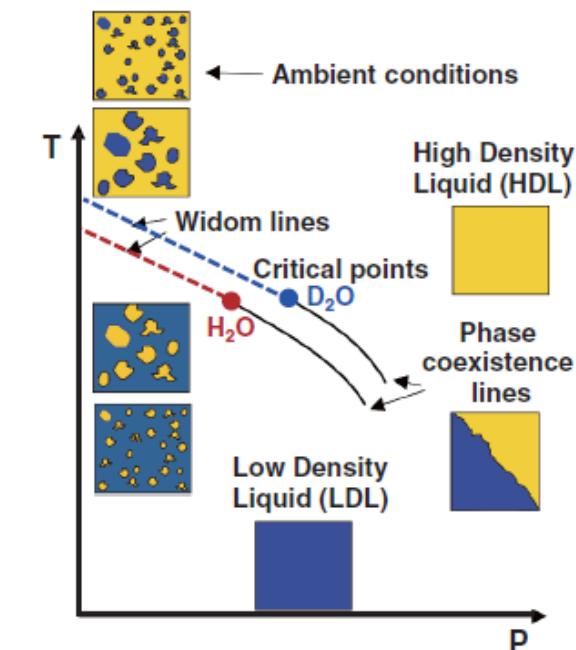
Microdroplets → stronger supercooling possible



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



Compressibility



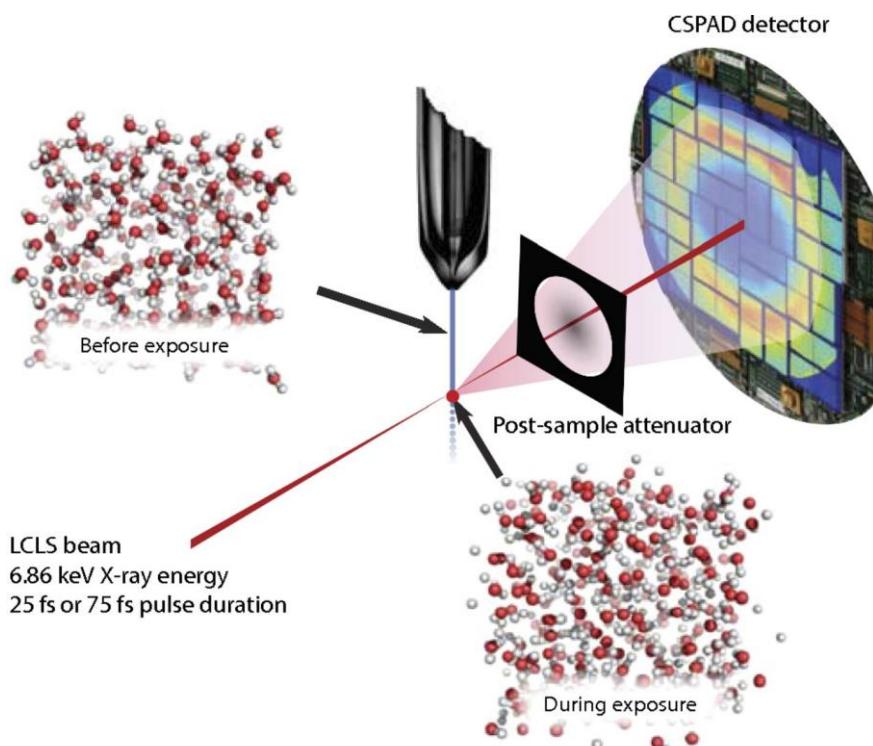
Proposed phase diagram

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

Science 358, 1589 (2017)

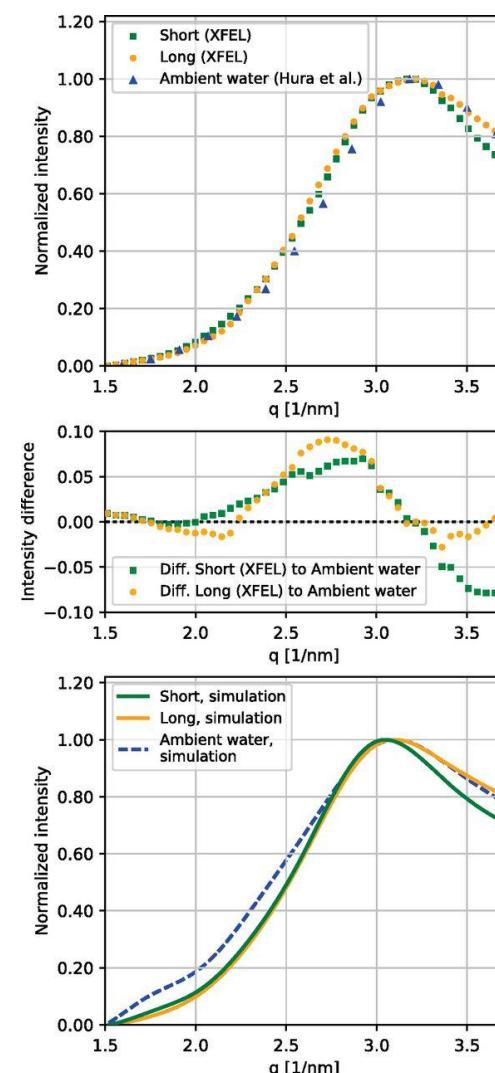
## Fast water heating at FEL sources

### Pulse length dependence

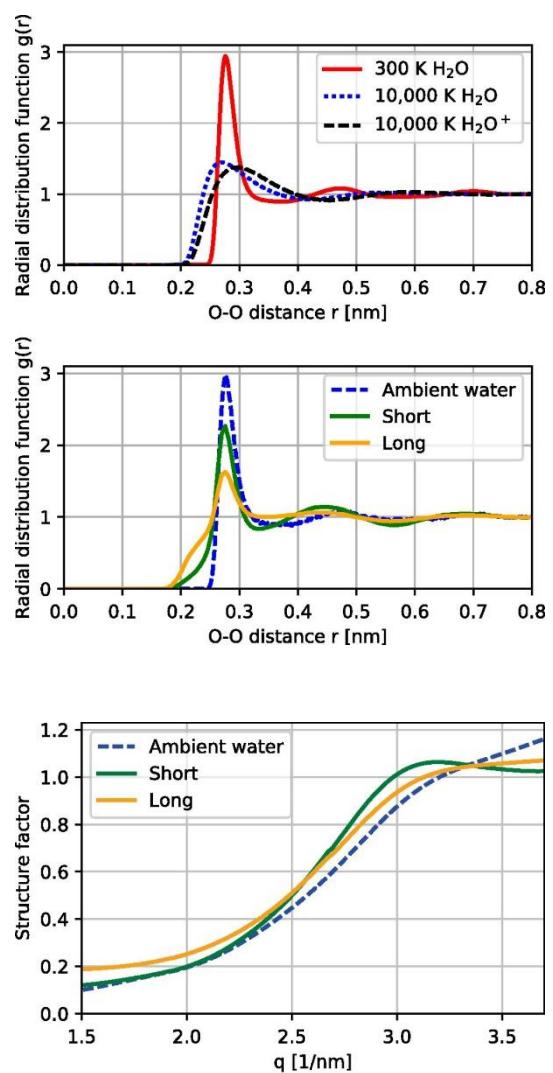


PNAS 115, 5652 (2018)

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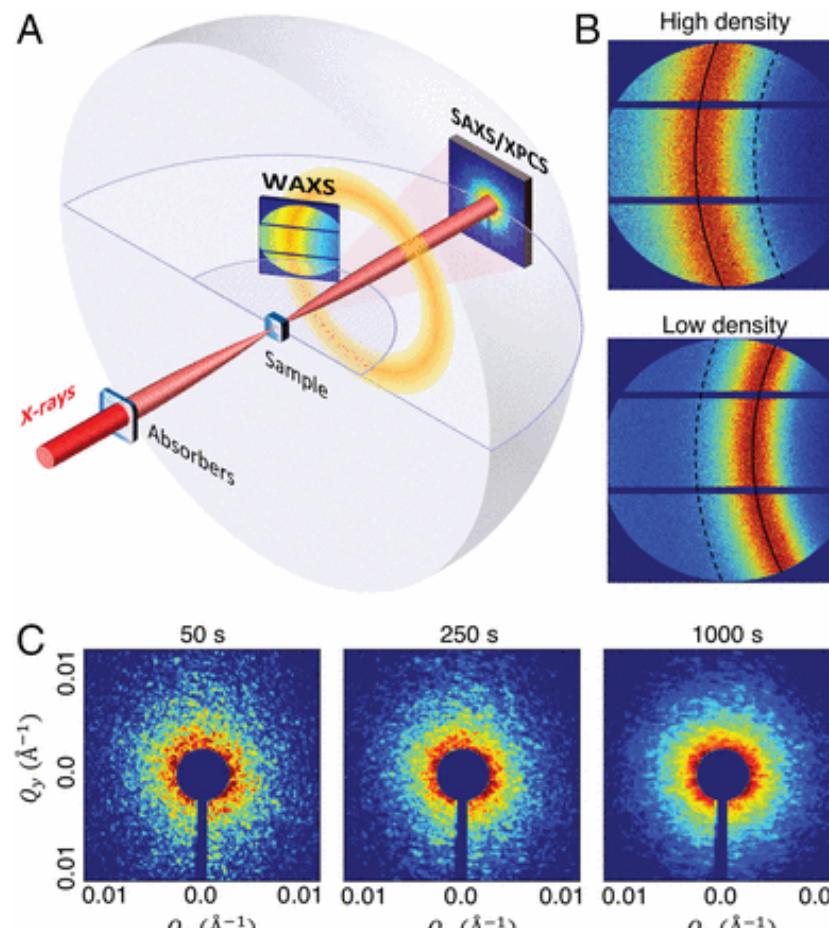
Pulse-length dependence  
of structure factor



Simulation results

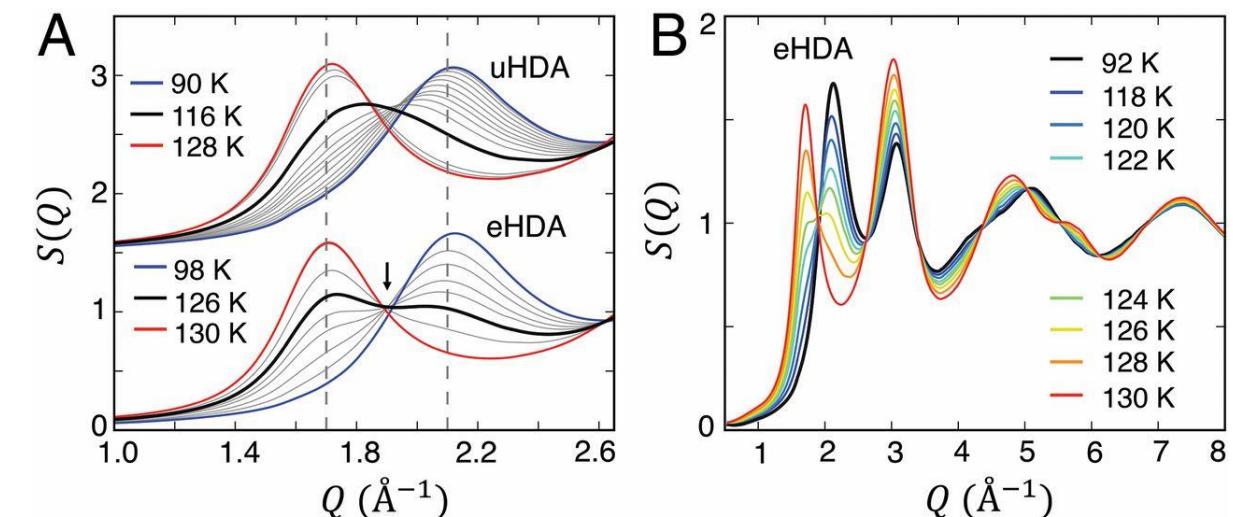


## Dynamics in amorphous ices & liquid water



Transition of HDA to LDA

PNAS 114, 8793 (2017)

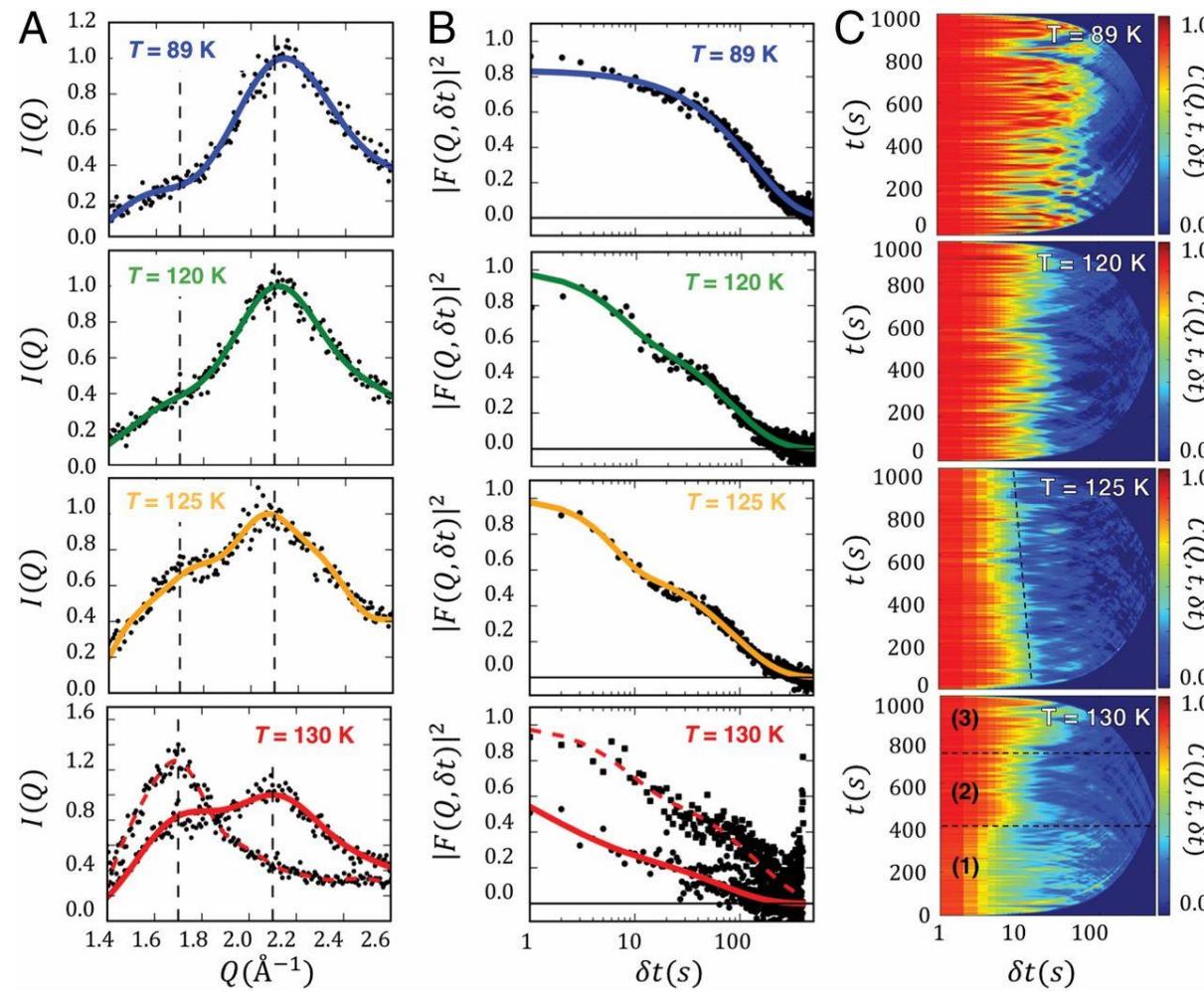


X-ray diffraction

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

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

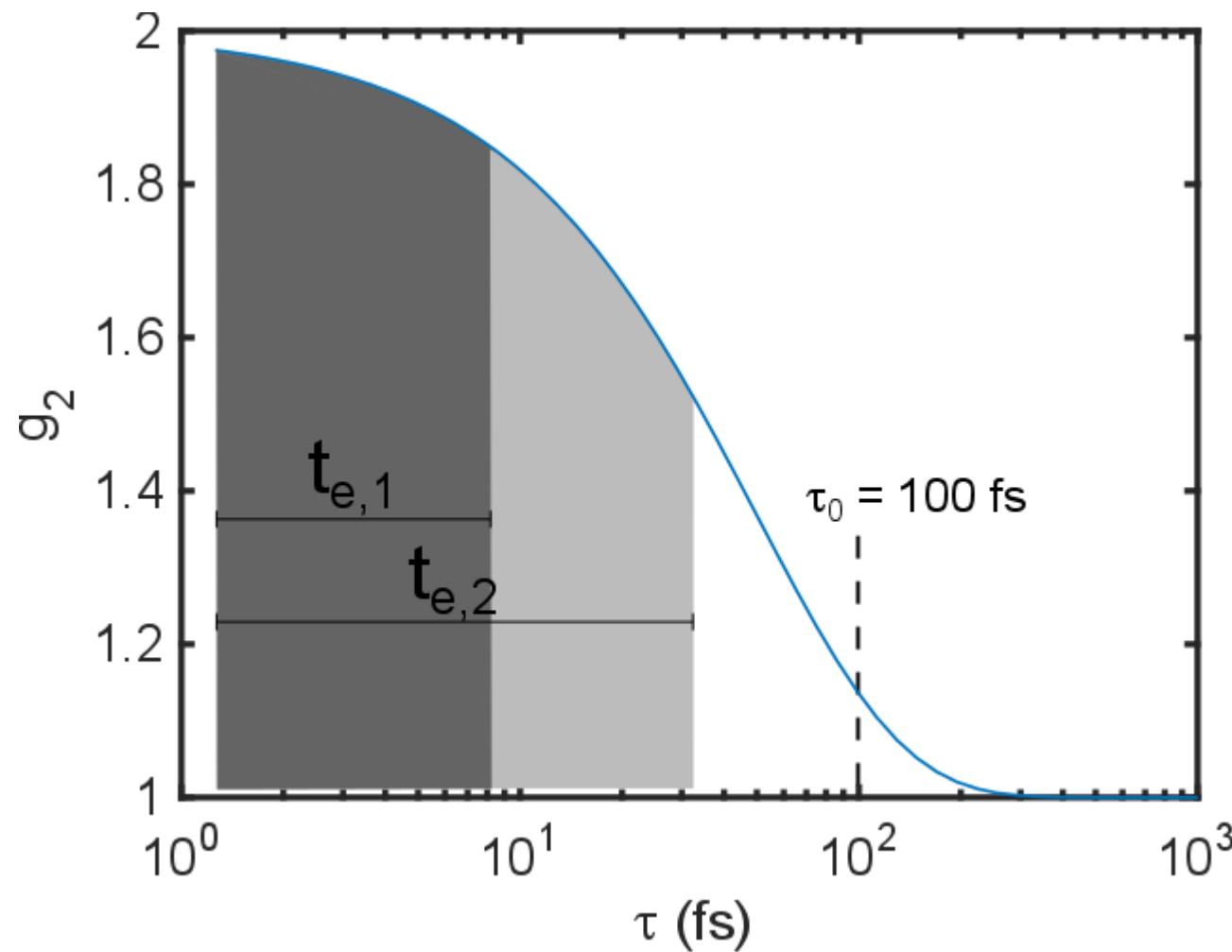
## Dynamics in amorphous ices & liquid water



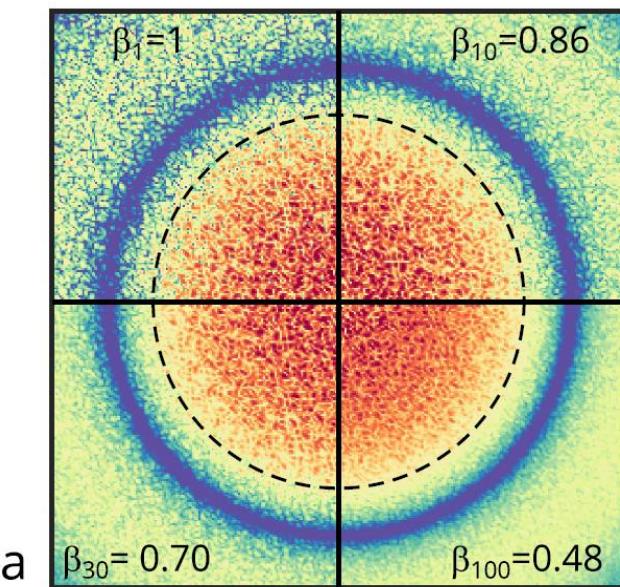
- $T < 110 \text{ K}$ : viscoelastic relaxation of HDA
- Onset of diffusive dynamics for  $T \geq 110 \text{ K}$
- HDA domains transform to ultraviscous **HDL**
- Around  $T = 130 \text{ K}$ : transformation to ultravisous **LDL**

PNAS 114, 8793 (2017)

## Ultrafast XPCS: X-ray Speckle Visibility Spectroscopy



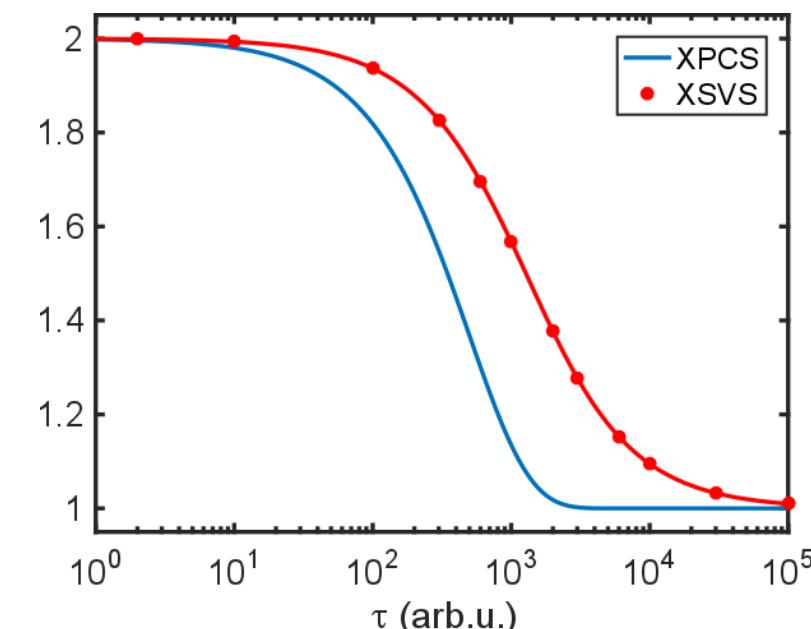
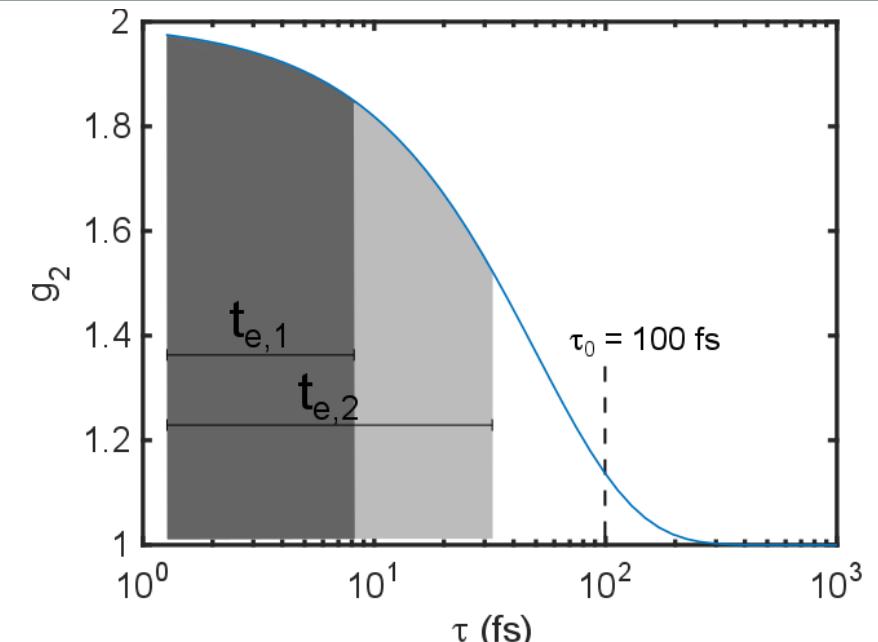
- So far: short exposure time  $t_e \ll \tau_0$
- Dynamics change during exposure → reduction of contrast
- Typical FEL pulse length:  $\tau_0 = 100$  fs



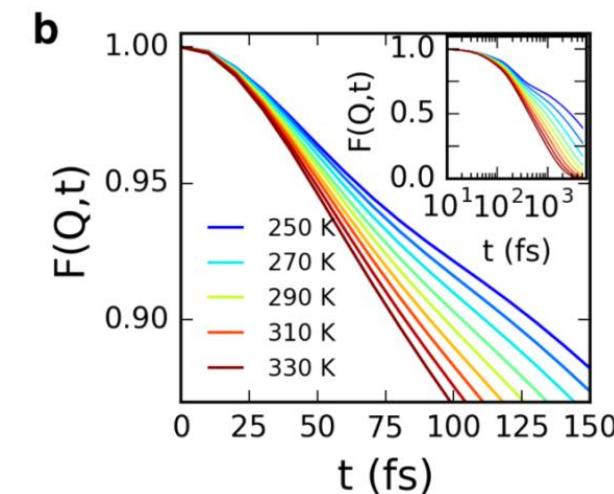
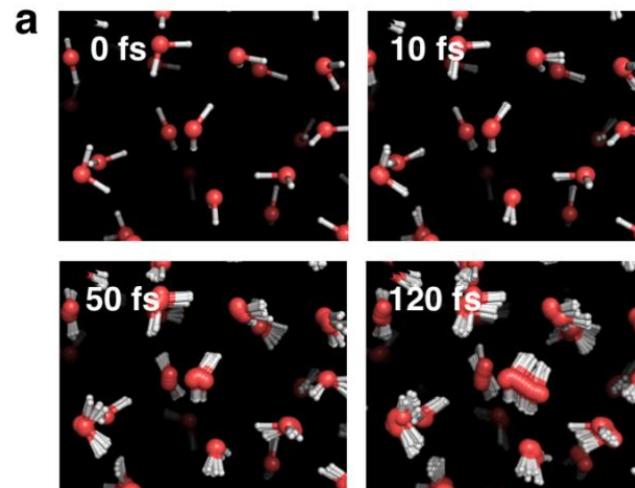
## Ultrafast dynamics: XSVS

### Finite pulse lengths

- Contrast as function of exposure ( $\beta^2 = \frac{\langle I^2 \rangle}{\langle I \rangle^2} - 1$ )
- $\beta^2(q, t_e) = \frac{2\beta_0^2}{t_e} \int_0^{t_e} \left(1 - \frac{\tau}{t_e}\right) |f(q, \tau)|^2 d\tau$
- For diffusion, this can be solved analytically ( $\rightarrow$  Exercise!)
- Limited by accessible exposure times
  - Pulse lengths (FEL)
  - Detector read out & flux (storage rings)
- FEL: pulse lengths variations & split-pulse applications

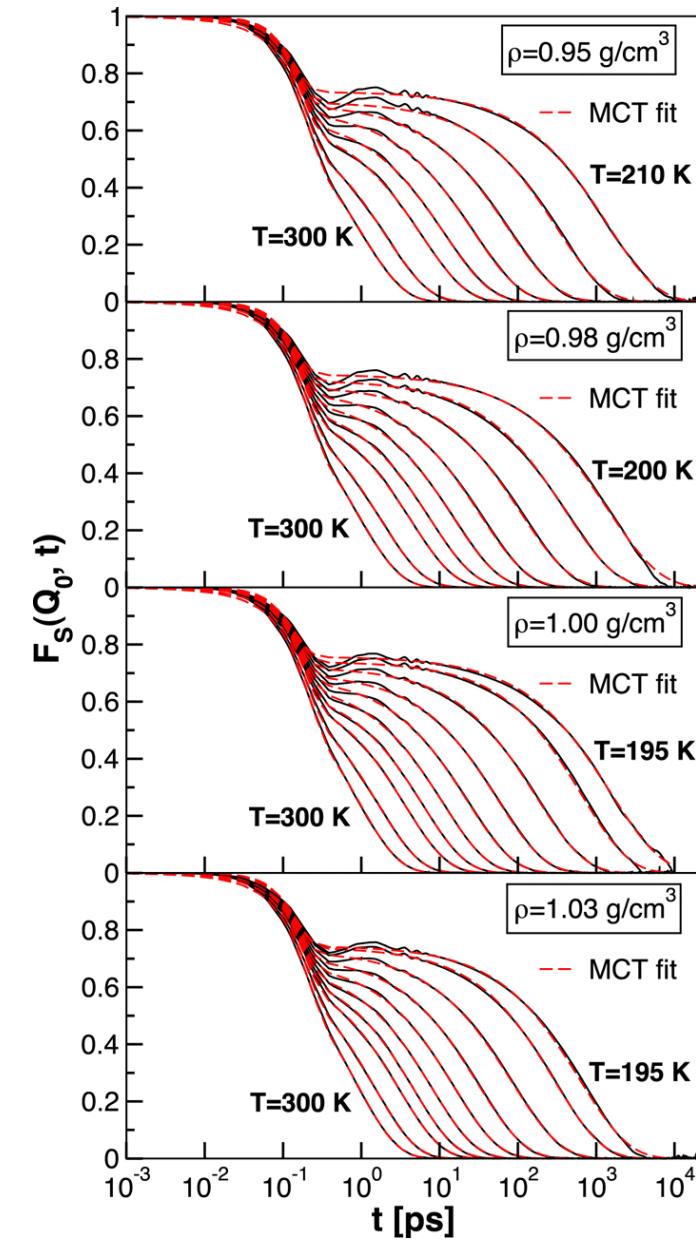


## Dynamics in amorphous ices & liquid water



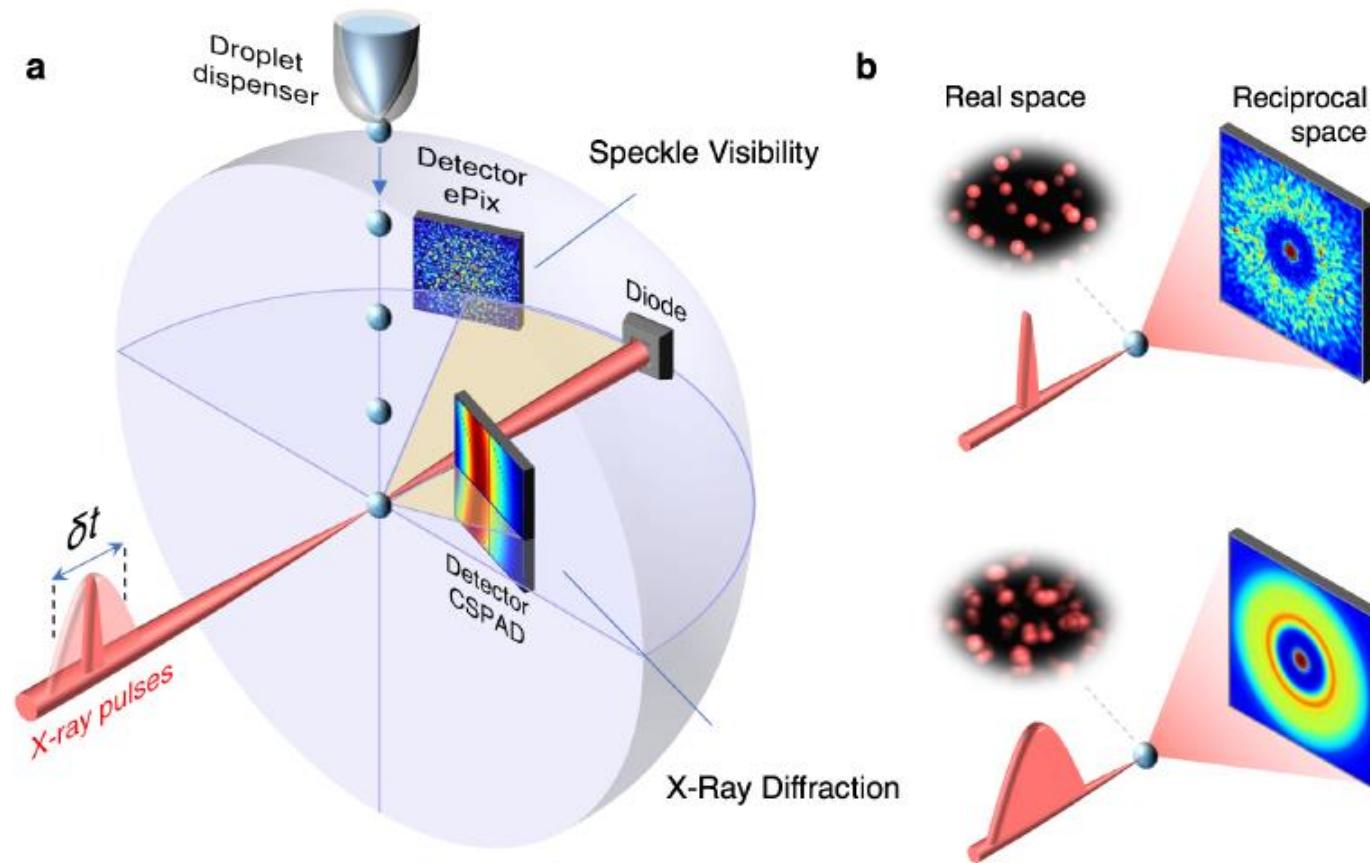
- Liquid water: fs dynamics  $\rightarrow$  FEL pulse length
- MD simulations of liquid water show two-step decay of intermediate scattering function
  - $\rightarrow$  fragile-to-strong crossover
  - $\rightarrow$  LLCP hypothesis

Nature Comm. 9, 1917 (2018).



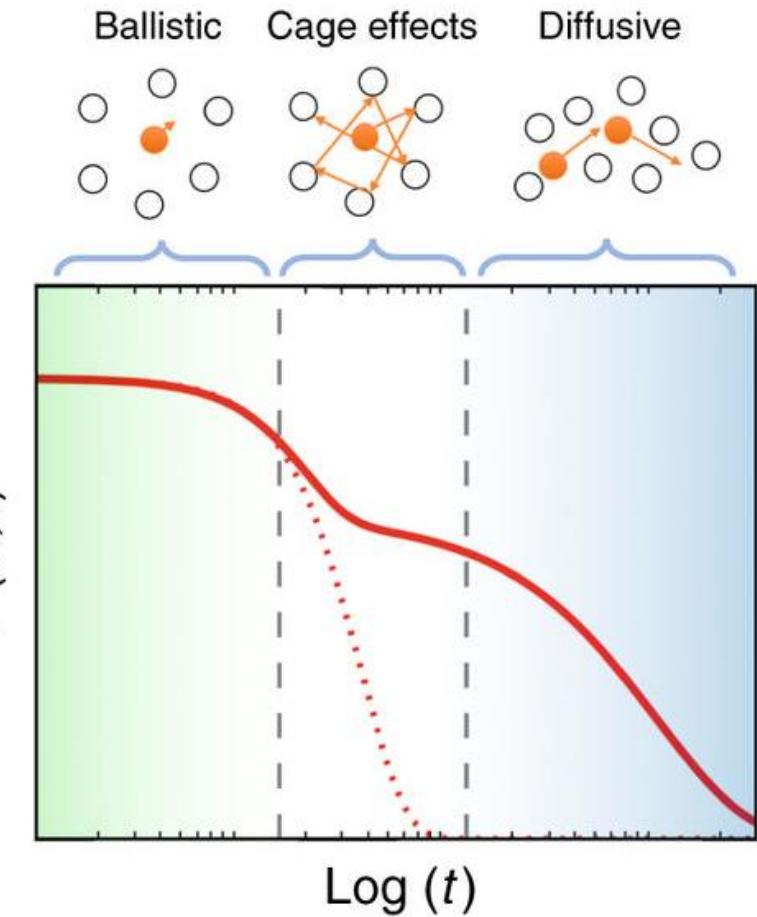
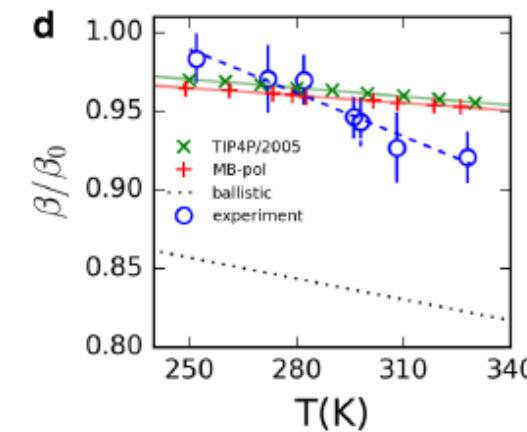
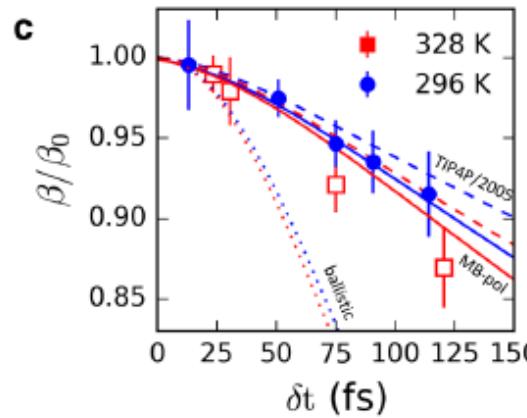
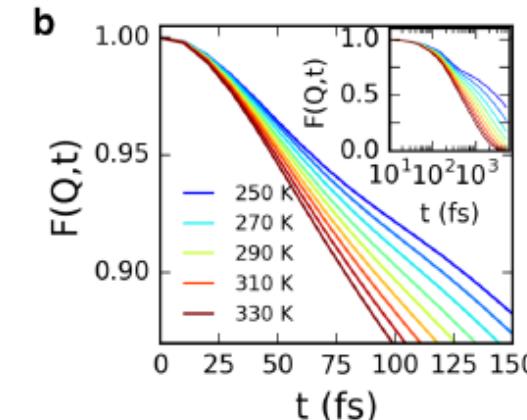
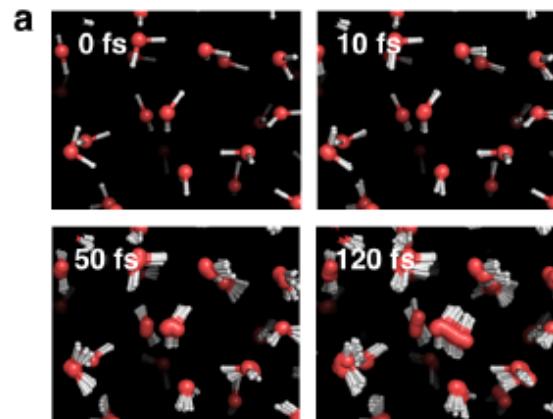
JCP 144,  
074503 (2016)

## Dynamics in amorphous ices & liquid water



- XSVS experiment
- FEL pulse length variation between 10 fs to 130 fs
- Water structure factor peak around  $2 \text{ \AA}^{-1}$
- >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).