

# Methoden moderner Röntgenphysik: Streuung und Abbildung

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Lecture 17	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2018 G. Grübel, A. Philippi-Kobs, <u>F. Lehmkuhler</u> , O. Seeck, L. Frenzel, M. Martins, W. Wurth		
Location	Lecture hall AP, Physics, Jungiusstraße		
Date	Tuesday	13:00 - 14:30	(starting 3.4.)
	Thursday	8:30 - 10:00	(until 12.7.)



# Soft Matter – Timeline


- Di 29.05.2018 Soft Matter studies I: Methods & experiments  
*Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, ...*
- Do 31.05.2018 Soft Matter studies II: Structure  
*SAXS & WAXS applications, X-ray cross correlations, ...*
- Di 05.06.2018 Soft Matter studies III: Dynamics  
*XPCS applications, diffusion, dynamical heterogeneities, ...*
- Di 12.06.2018 Case study I: Glass transition  
*Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, ...*
- Do 14.06.2018 **Case study II: Water**  
*Phase diagram, anomalies, crystalline and glassy forms, FEL studies, ...*



Quick links ▼ Print

# WATER STRUCTURE AND SCIENCE

*Martin Chaplin*



## Water Structure and Science

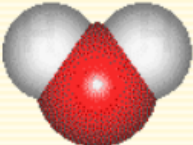
This page forms the entrance to a website concerned with the physical, chemical and biological properties of water.

[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<sub>2</sub>O) 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. ⇒

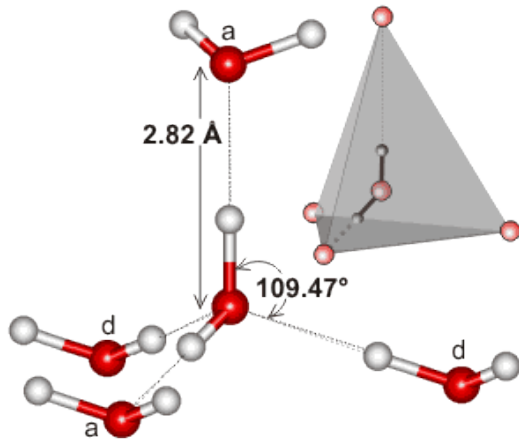


Although we drink it, wash, fish and swim in it, and cook with it (although probably not all at the same time), we nearly always overlook the special relationship it has with our lives. Droughts cause famines and floods cause death and disease. It makes up over about half of us and, without it, we die 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<sub>2</sub>O is the second most common molecule in the Universe (behind hydrogen, H<sub>2</sub>), 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?

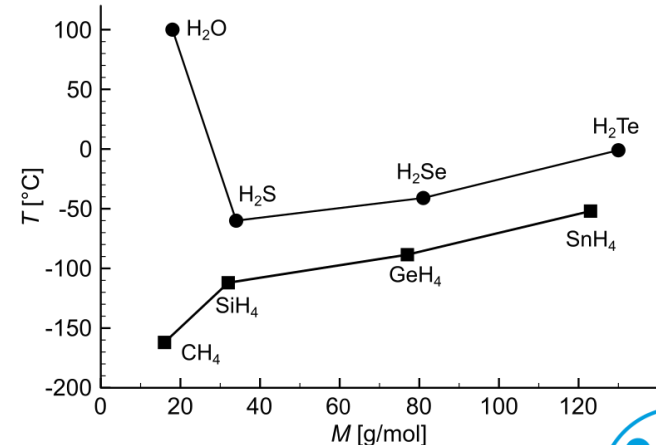
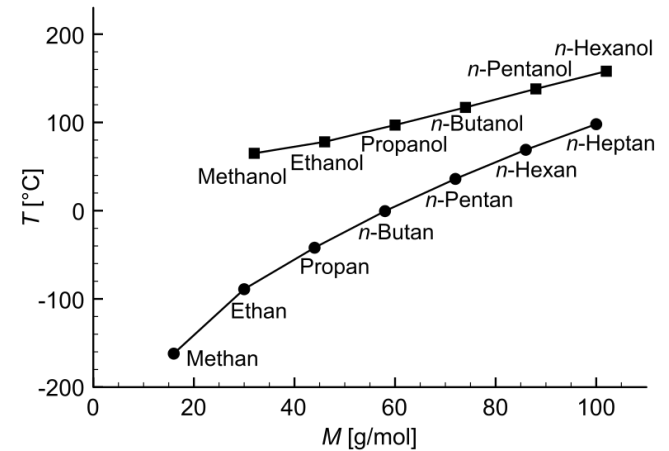
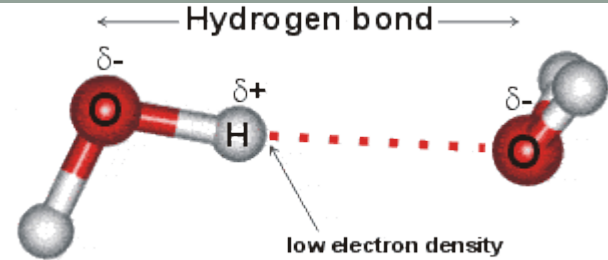


Most important liquid for life (biology), as solvent (chemistry), geo-science, ...

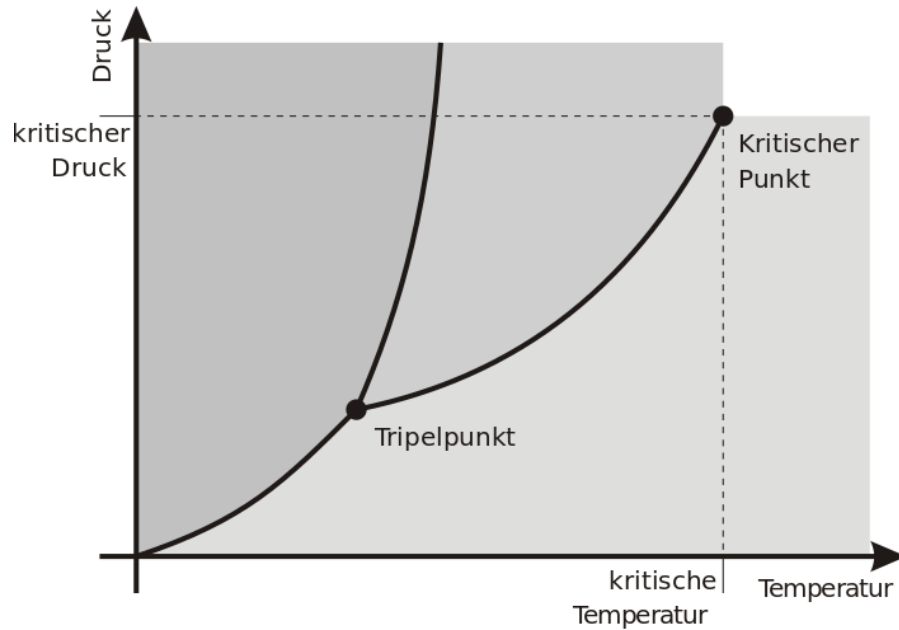
Complex **hydrogen bond** network

- Strength O-H...O: ~21 kJ/mol+
- Tetrahedral coordination

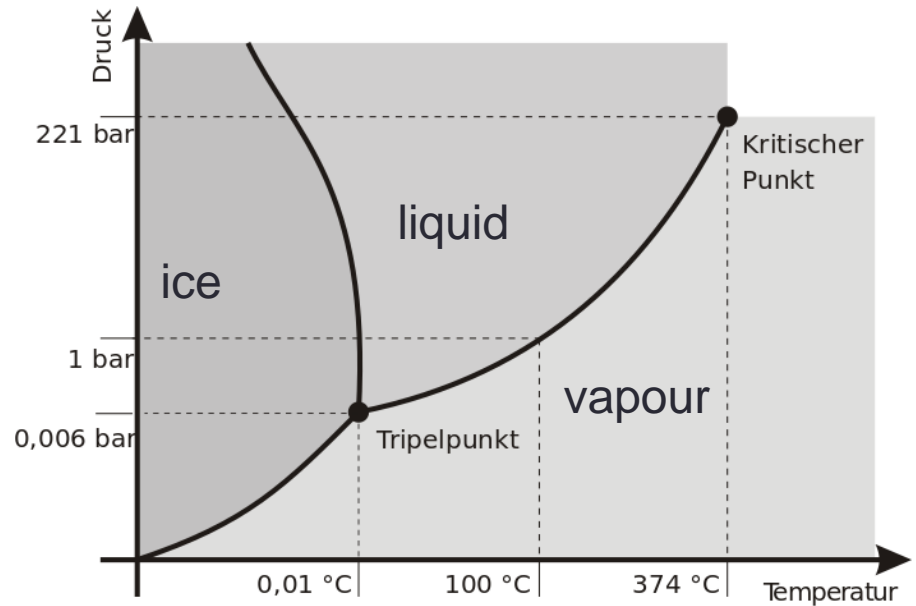
<http://www1.lsbu.ac.uk/water/>



# Water – phase diagram



Normal liquid

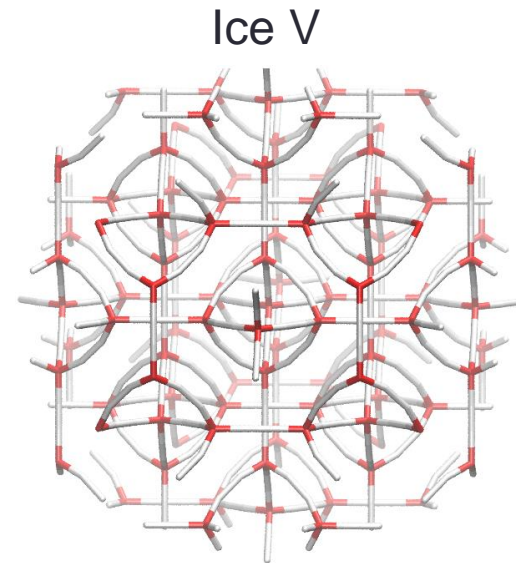
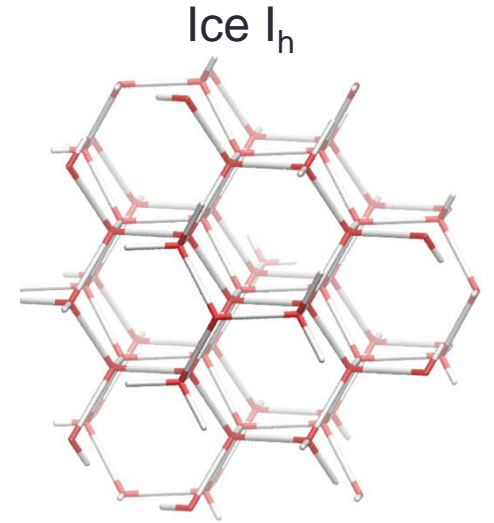
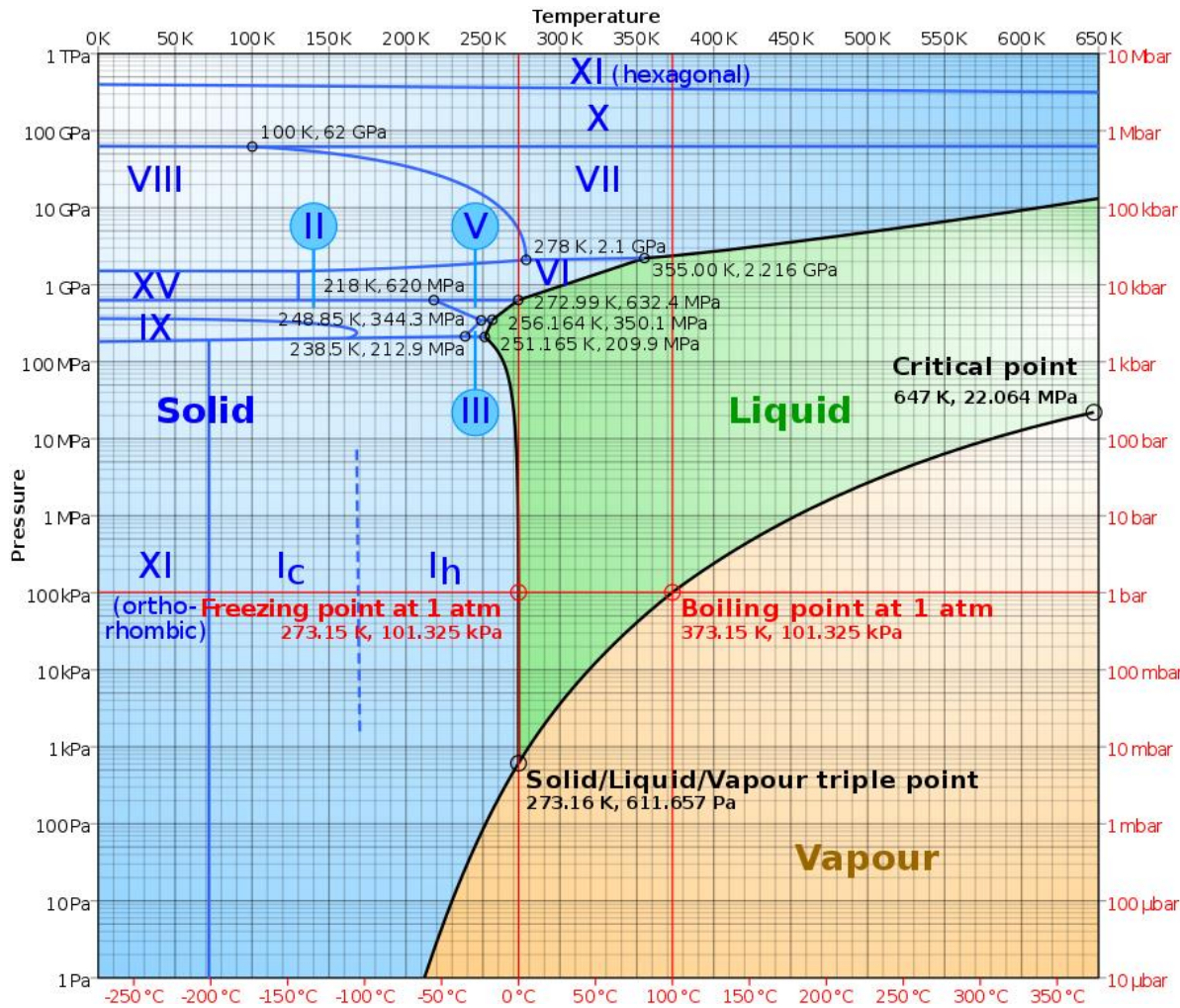


Water  
→ anomalies

Figures: wikipedia



# Crystalline ice – polymorphism

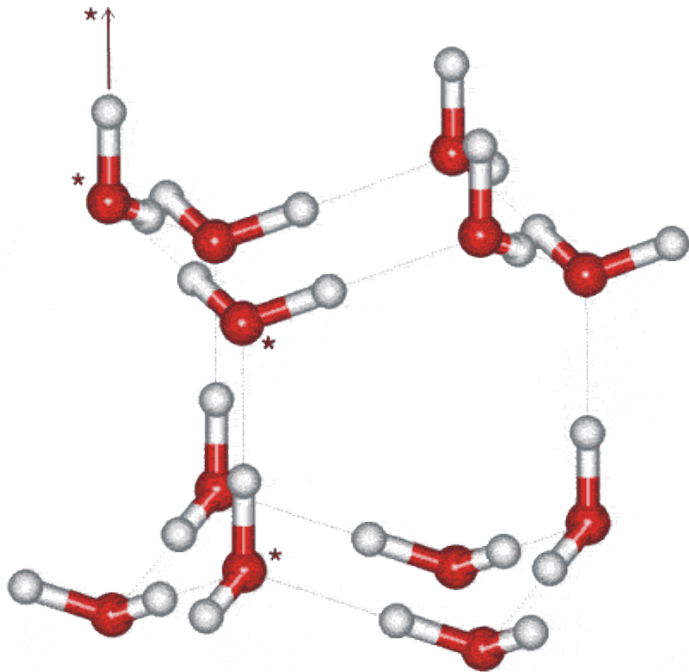


Phase diagram: wikipedia



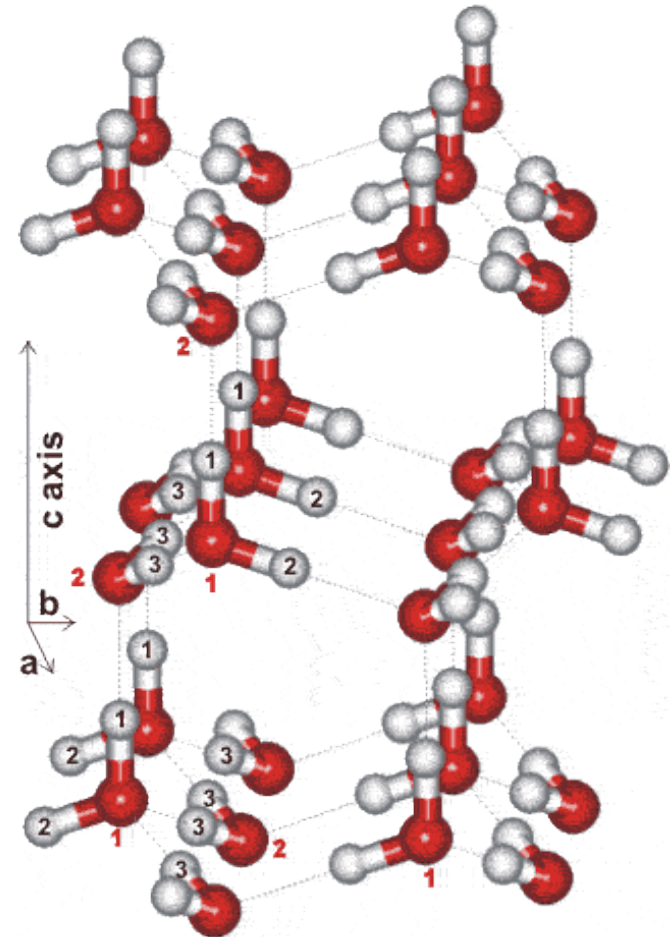
# Crystalline ice – polymorphism

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



Tetrahedral coordination  
4 H-bonds per molecule

Ice rule: one hydrogen  
between two oxygens



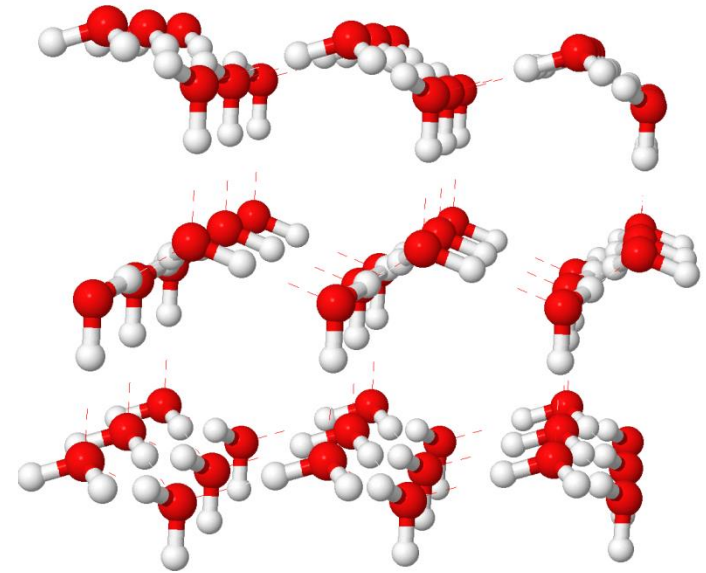
<http://www1.lsbu.ac.uk/water>



## Crystalline ice – polymorphism

There are hydrogen-disordered and hydrogen-ordered ice phases

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  $I_h$



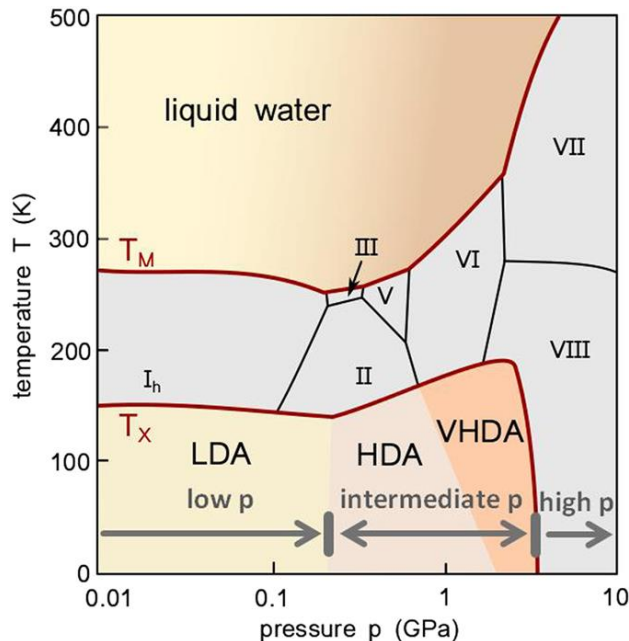
## Amorphous ice

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

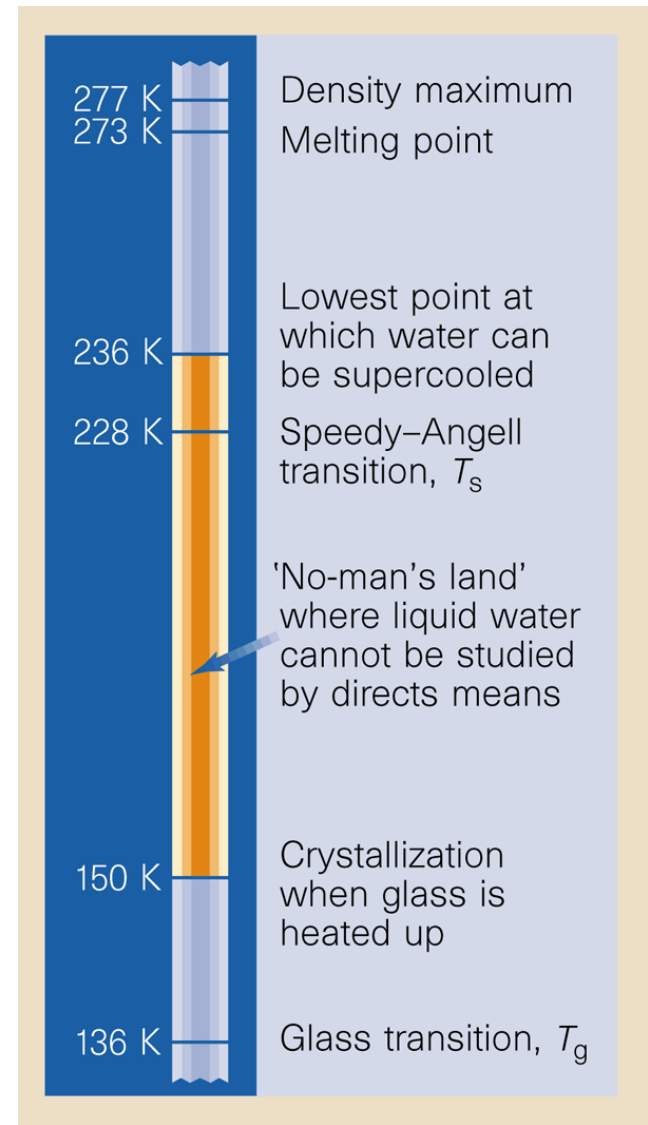
### Three forms of amorphous ice

- Low-density (LDA),  $0.92 \text{ g/cm}^3$
- 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



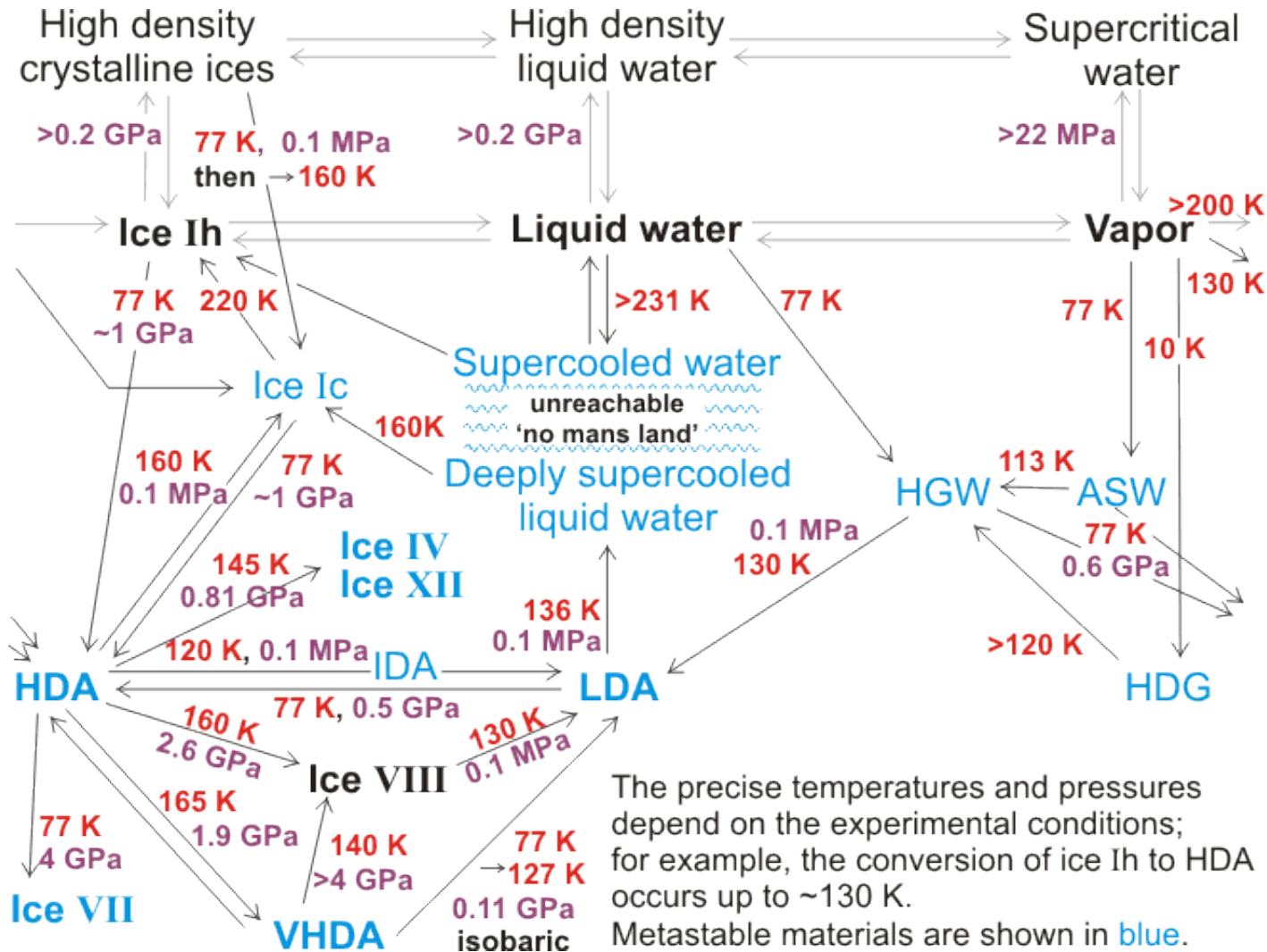
J. Stern and T. Loerting.  
 Sci. Rep. 7, 3995 (2017)



S. Sastry. Nature 398, 467 (1999)



## Water – solid states



ASW –  
amorphous solid  
water

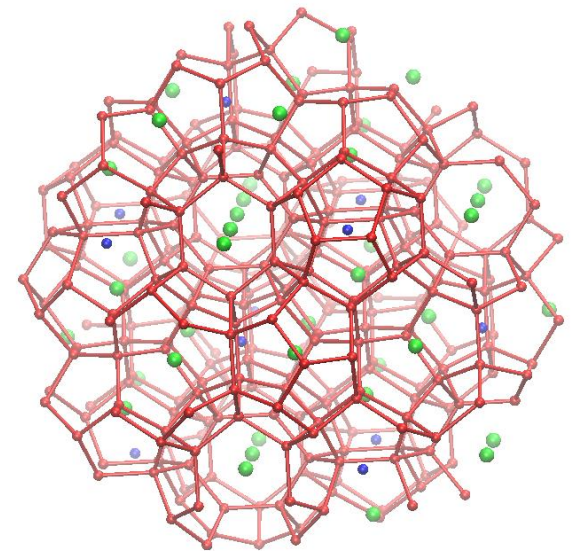
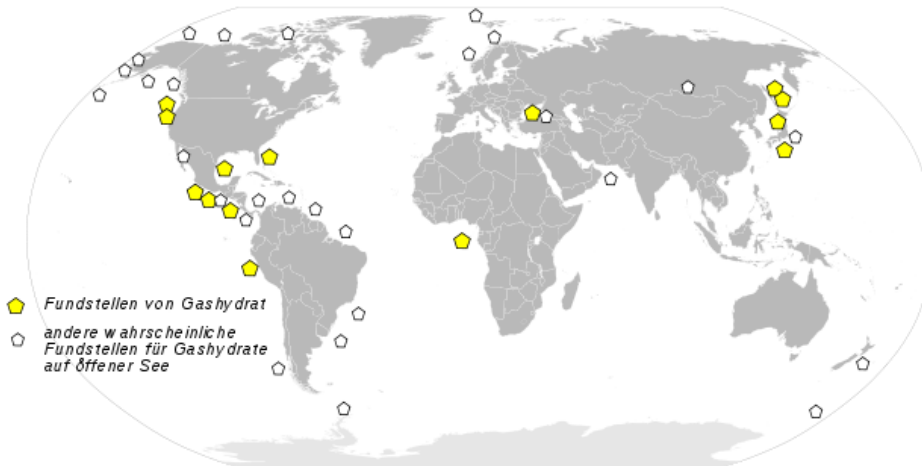
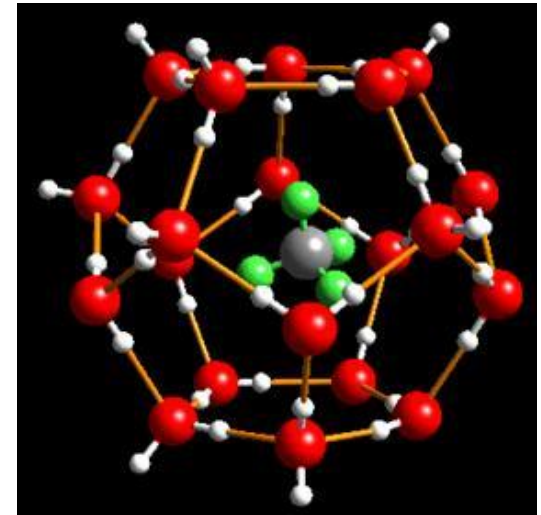
HGW –  
Hyperquenched  
glassy water

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



## Clathrate hydrates

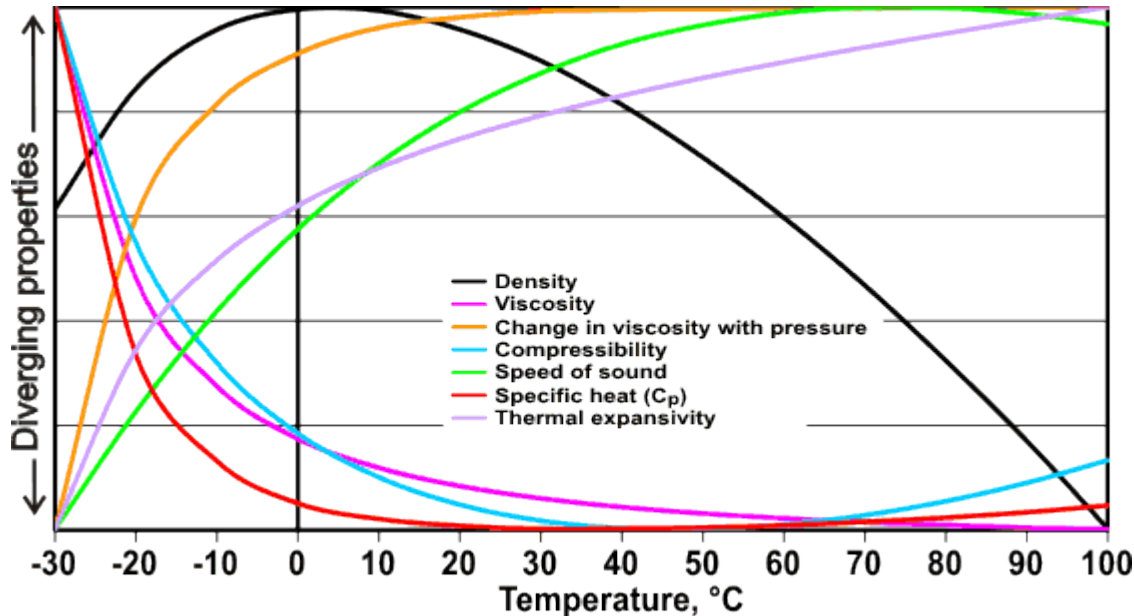
- In presence of gas molecules (e.g. methane,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2$ , ...) water forms ice-like inclusion compounds
- Typically "more stable" than ice
- Methane hydrate at ocean floor and in permafrost regions



## 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>



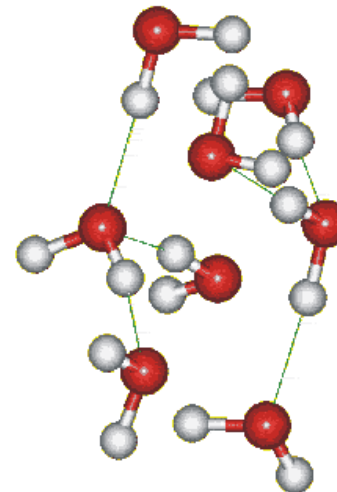
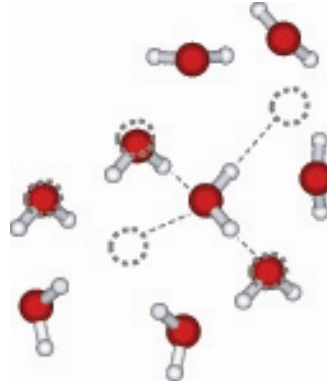
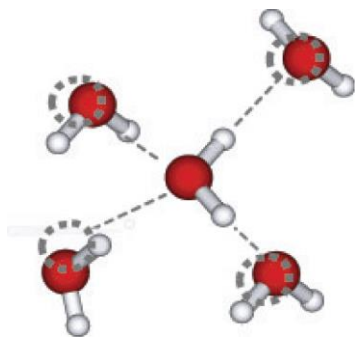
## Liquid water: continuum and mixture models

Long-standing debate: Liquid water as...

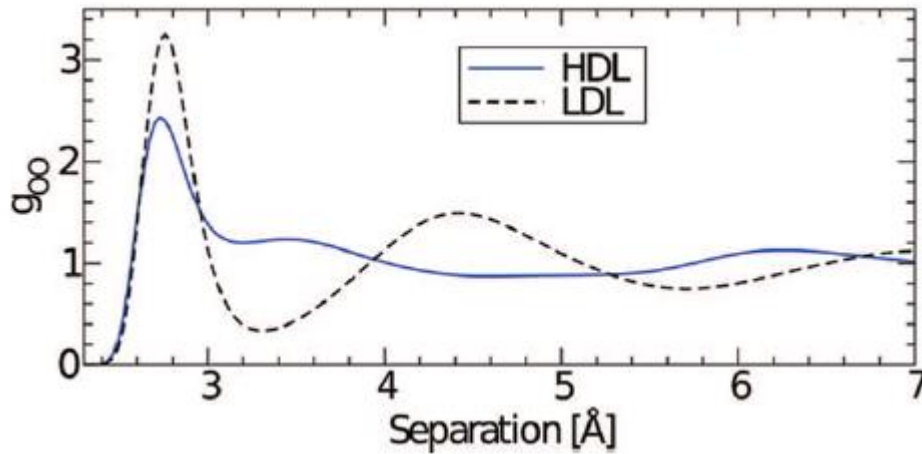
- (1) network of disordered tetrahedrally coordinated molecules with  $\sim 3.5$  hydrogen bonds per molecules
- (2) Mixture of different species with different geometry (goes back to Röntgen 1892 to explain anomalous properties of water)

In more recent years: two-liquids hypothesis

- Low density liquid (LDL): strong tetrahedral coordination
- High density liquid (HDL): broken hydrogen bonds  $\rightarrow$  higher density  
Dominates at room temperature



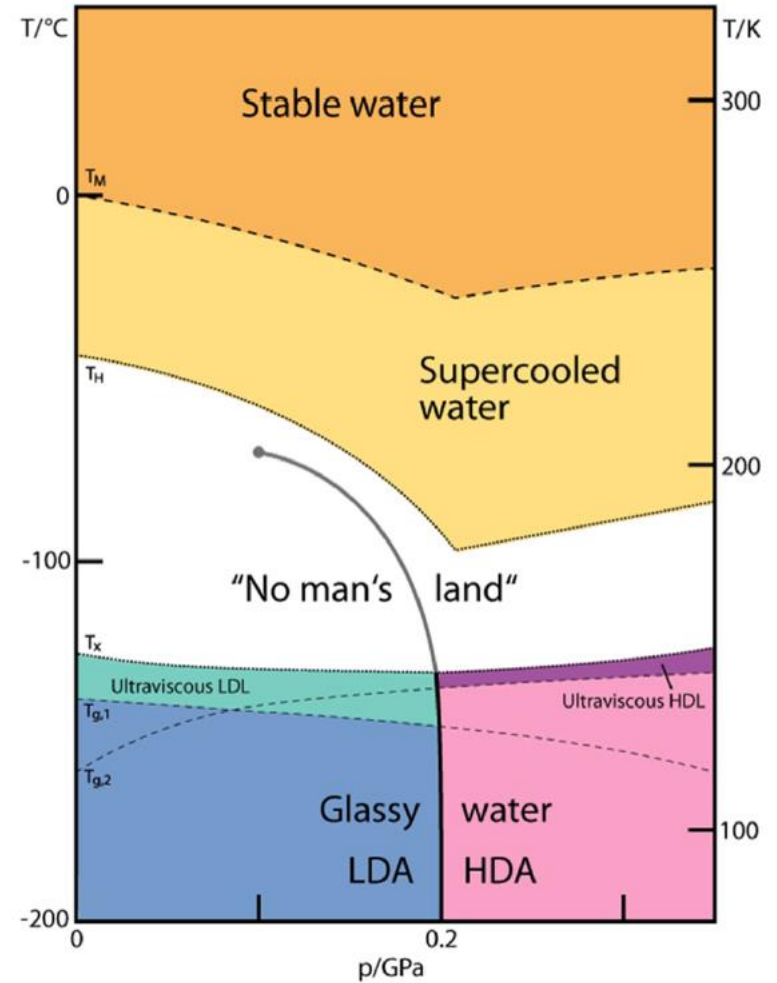
## Liquid water: continuum and mixture models



Molecular dynamics simulations:

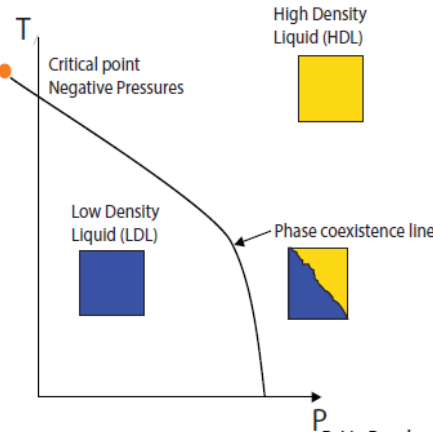
- LDL: tetrahedral liquid
- HDL: broken hydrogen bonds

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

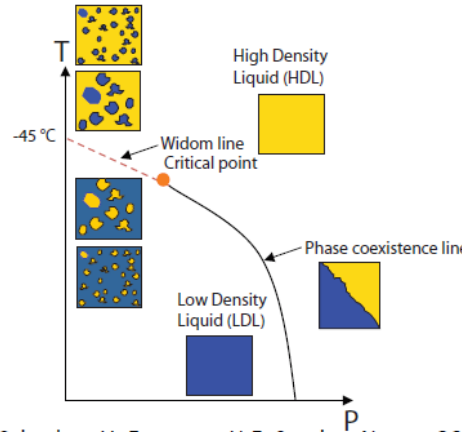


# Liquid water: continuum and mixture models

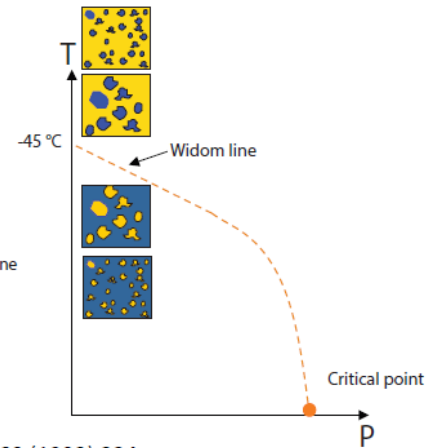
Critical Point Free Model  
Critical Point at -P



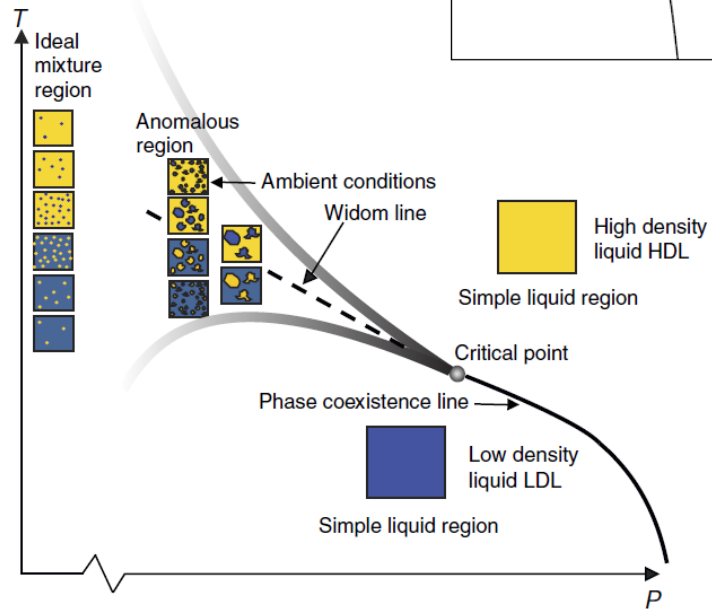
Critical Point Model  
Critical Point at +P



Singularity Free Model  
Critical Point at 0K



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

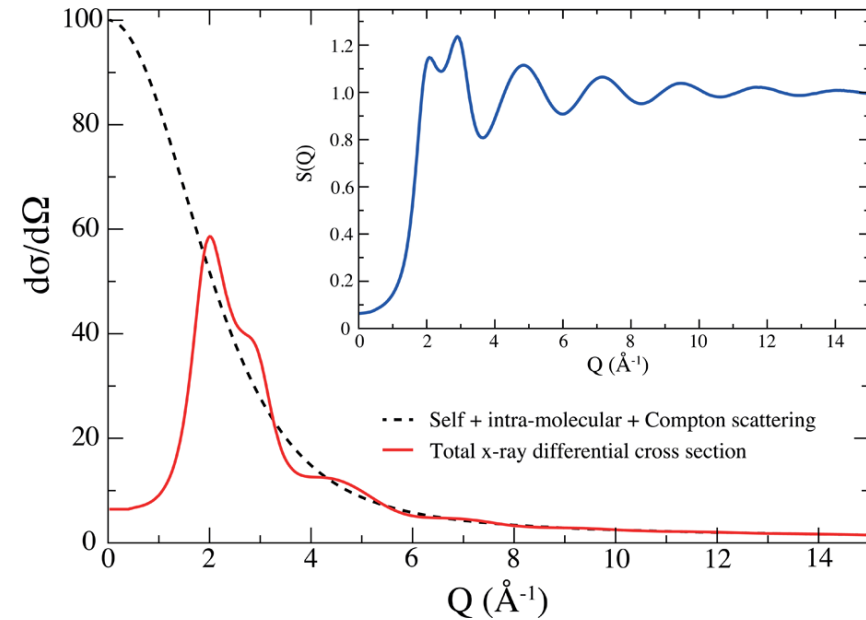


If there are two liquids, will there be a (2nd) critical point?

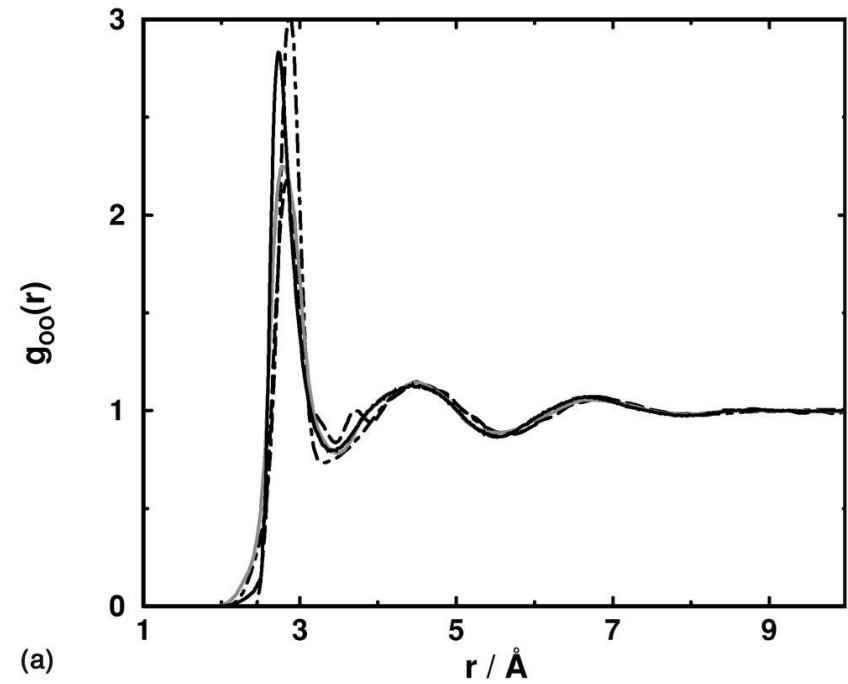
Nat. Comm. 6, 8998 (2015)



## X-ray studies: structure factors



Chem. Rev. 116, 7570 (2016)



(a)

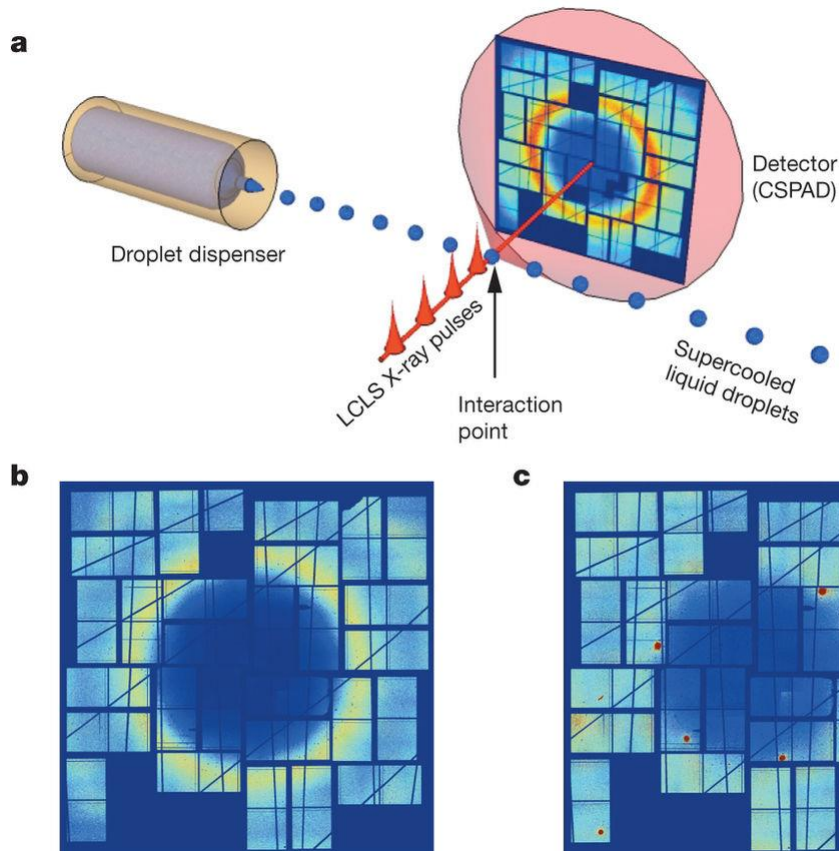
J. Chem. Phys. 113, 9140 (2000)

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

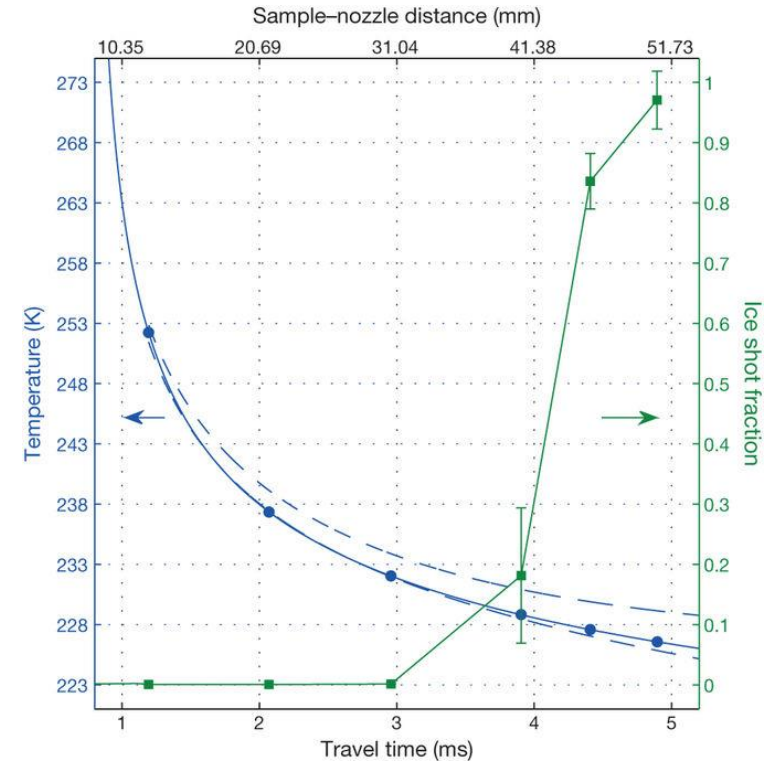
Experimental limit:  $\theta = 180^\circ \Rightarrow q_{max} = \frac{4\pi}{\lambda} \approx 8 \text{ \AA}^{-1}$  for 8 keV  $\rightarrow$  high-energy X-rays ( $\geq 50$  keV) for pair-distribution function (pdf) studies



## Liquid water: structure factors



Nature 510, 381 (2014)

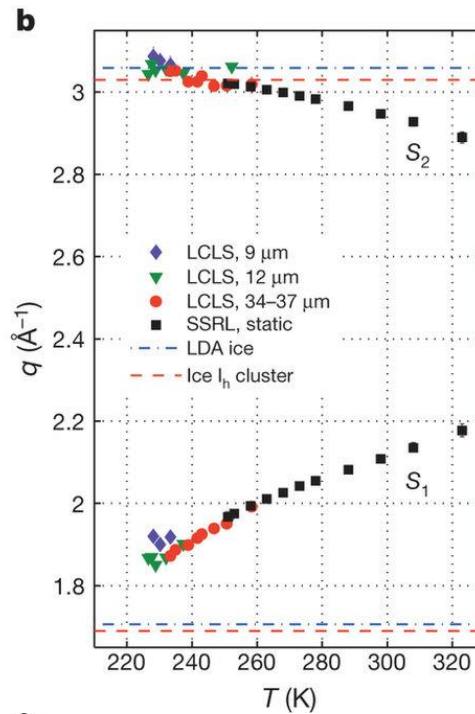
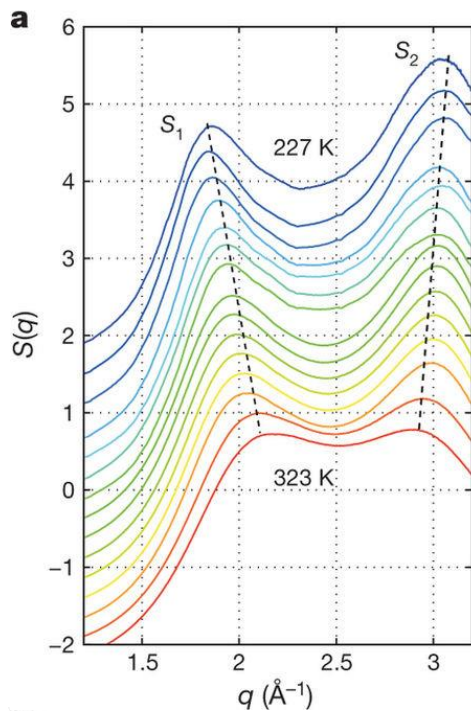


Liquid microdroplets: supercooling due to evaporation in vacuum

Ultrafast probing: FEL (~100 fs)

→ XRD patterns from single droplets



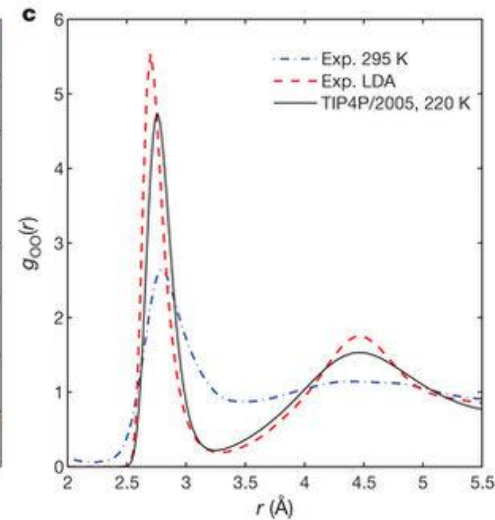
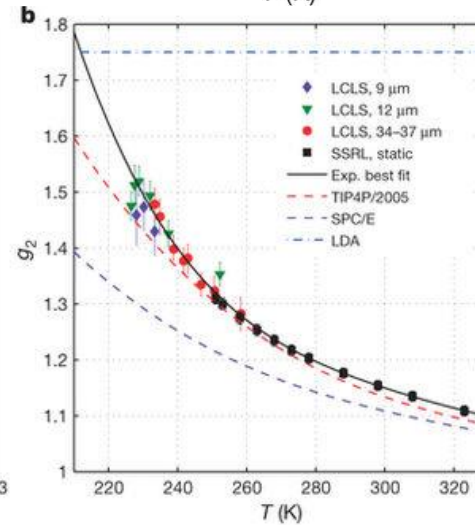
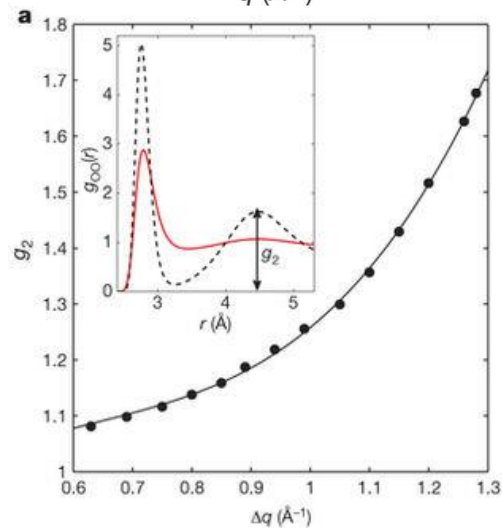


Structure factors: peaks shift upon supercooling

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

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

Towards low-density liquid water?

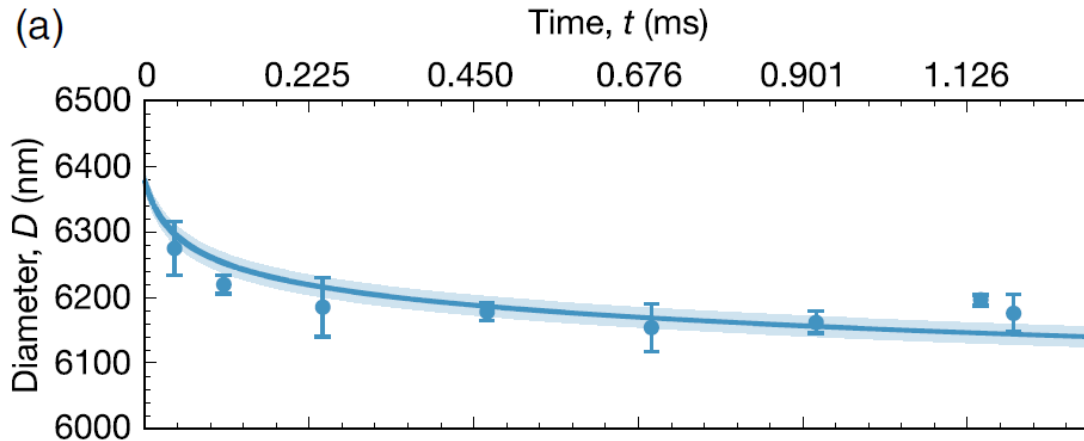


Nature 510, 381 (2014)

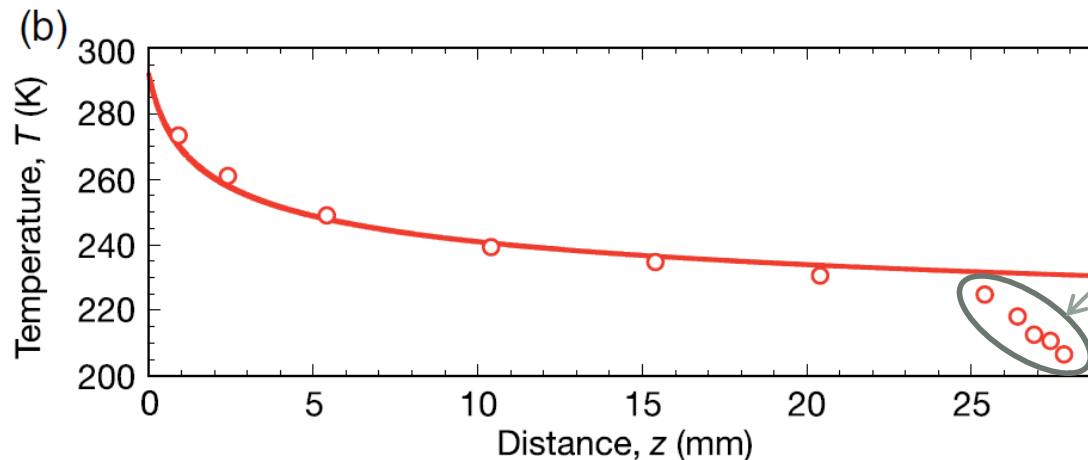


## How to measure temperature of water droplets?

Raman scattering → Interpretation debated



Droplet diameters from vibrational spectroscopy & Knudsen model of evaporation



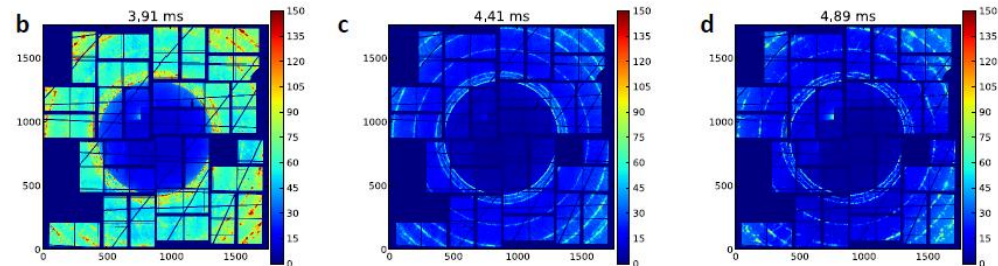
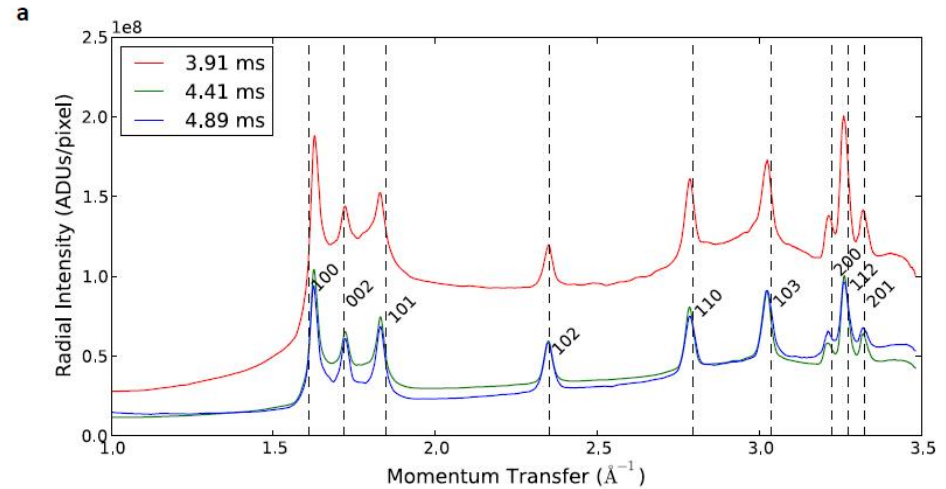
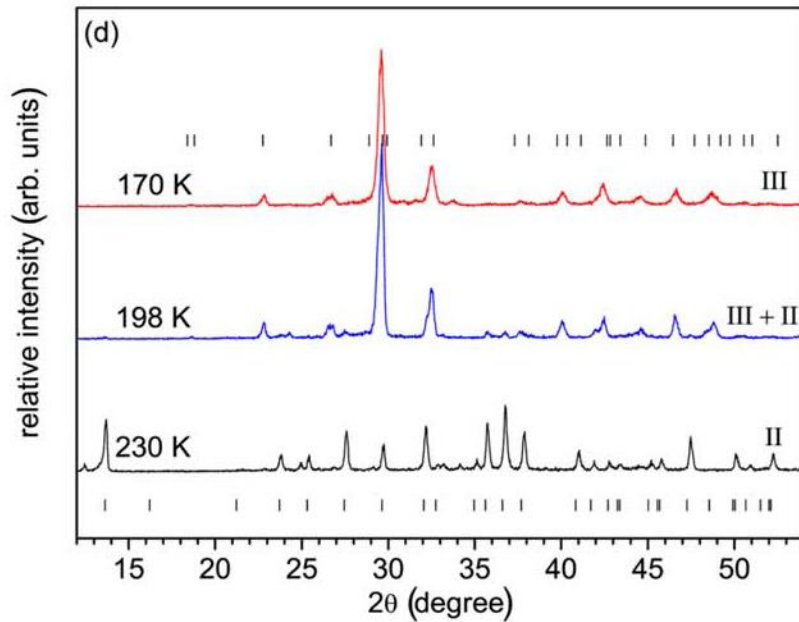
Ice formation

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

## X-ray diffraction: ices

Typical example: XRD of ice(s)

Fingerprint of structure  $\rightarrow$  no "new" ice without XRD proof

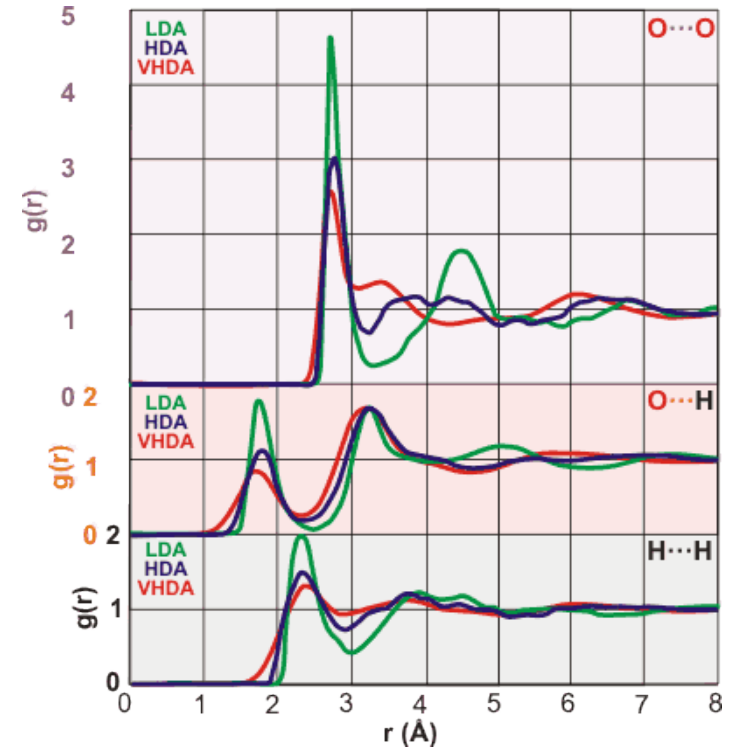
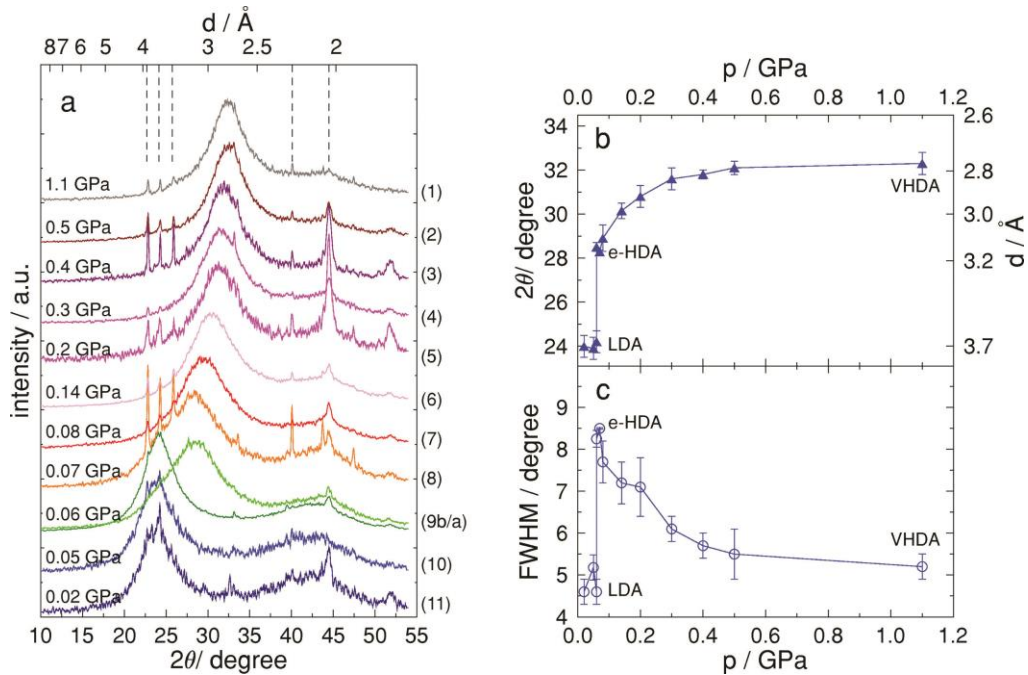


Crystallisation upon fast cooling

Nature 510, 381 (2014)

Phys. Rev. B 77, 220105 (2008)

## Transition of amorphous ices

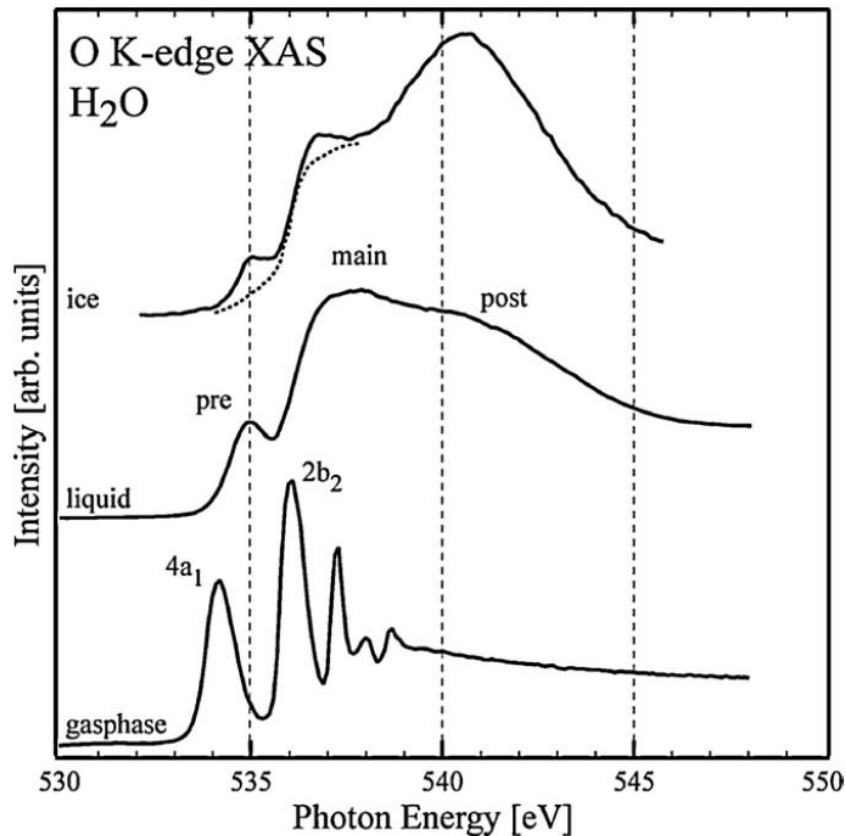


Isothermal decompression of VHDA at 140K to several selected pressures

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

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

## X-ray spectroscopy



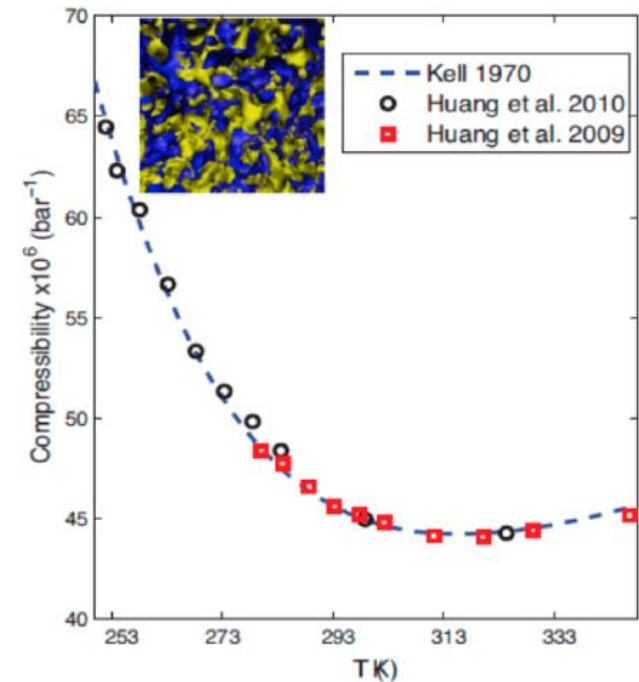
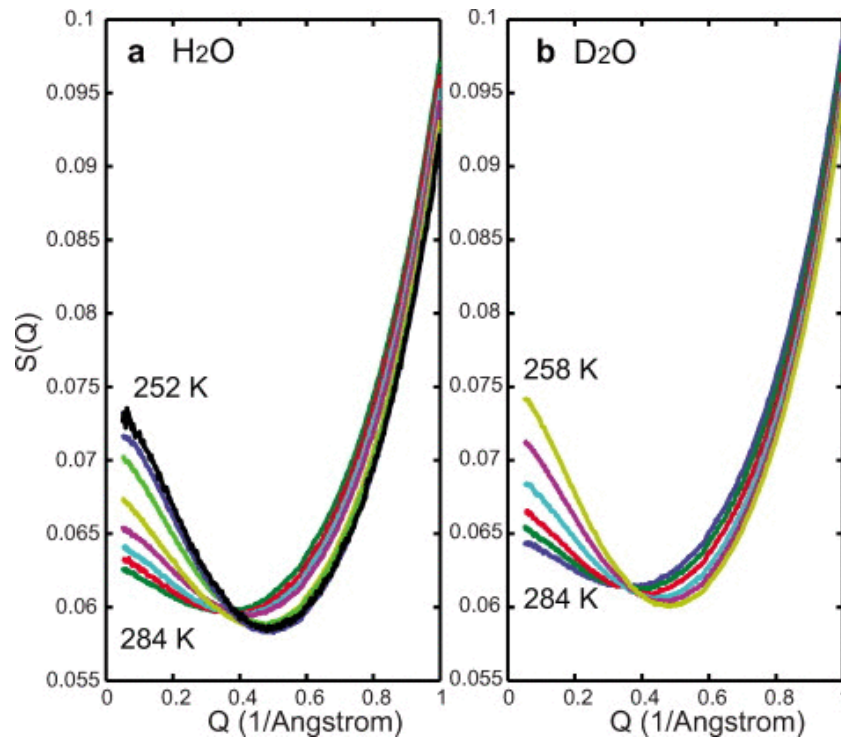
- XAS = X-ray Absorption Spectroscopy
- Fine structure of absorption edge ↔ local structure of sample
- Only indirect access, need e.g. DFT calculations
- Intense debate to which extent XAS results provide information on water models (e.g. LDL/HDL)

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

## Liquid water: SAXS

Small  $q$  limit in SAXS:  $S(q \rightarrow 0) \propto$  density fluctuations (see Lecture 7)

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!

## The inhomogeneity at ambient conditions

C. Huang<sup>1</sup>, K. T. Wilkinson<sup>2</sup>, Y. Horikawa<sup>3</sup>, M. L. Huggins<sup>4</sup>, L. G. M. Pettersson<sup>5</sup>

<sup>1</sup>Stanford Synchrotron Radiation Laboratory, 510691 Stockholm, Sweden; <sup>2</sup>Department of Chemistry, Hokkaido University, 060-0810 Sapporo, Japan; <sup>3</sup>Department of Chemistry, Institute for Solid State Physics, University of Tokyo, 113-8670 Tokyo, Japan; <sup>4</sup>Department of Chemistry, University of California, San Diego, 92093 La Jolla, CA, USA; <sup>5</sup>Department of Chemistry, University of Cambridge, CB2 3RQ, UK

Small-angle X-ray scattering (SAXS) reveals the presence of density fluctuations in a liquid with a length-scale of ~1 nm, while the magnitude of these fluctuations is enhanced with decreasing temperature. Based on X-ray scattering data we propose a model of water in which the inhomogeneity is due to a fluctuation of hydrogen-bonded distorted tetrahedral regions in high density water. We propose a model of water in which the inhomogeneity is due to a fluctuation of hydrogen-bonded distorted tetrahedral regions in high density water. We propose a model of water in which the inhomogeneity is due to a fluctuation of hydrogen-bonded distorted tetrahedral regions in high density water.

Liquid water shows properties such as capacity (1–4). In the liquid point, these properties, related to a and low density water anomalies (5). Above supercooled region where most of waters' of importance occurs, has traditionally been of near-tetrahedral with thermal fluctuation picture has been characterized by Raman (XRS) and coherent X-ray scattering (CXRS) (6), and X-ray scattering two distinct local and a highly hydrogen majority. In particular structure has been characterized by refs. 7 and 8 for data SAXS and small-angle direct probes of density in a liquid. Through an momentum transfer,  $Q$ , density at different length

## LETTER

### Is ambient water the nanometer scale

According to a recent regard as inhomogeneity is made on the basis of absorption/emission 0 value of the structure

where  $N$  is the number of fluid and the angle of density fluctuation substantially at low  $Q$  in noncritical ambient water is heterogeneous. To understand water a noncritical fluid,  $S_d(Q)$  density and the intensity (2), and that the correlation unimodal in fluctuations from small system (4) suggest the amplitude given by

where  $\phi$  is the volume density difference between "correlation volume"  $S_d(0)$  or  $v_c$  can be defined fluid far away from known, this would suggest Eq. 2 indeterminate.

## LETTER

### Reply to Soper et al. on water around a bimodal local hydrogen-bonded structural motifs

Soper et al. (1) propose that the low  $Q$  in the small-angle X-ray ref. 2 is caused by stochastic in liquids and that these fluctuations for water. Water, however, exhibits fluctuations both at higher and driving force cannot be the same. In ref. 2, we suggest that the tetrahedral regions) and contribute the driving force dominating a creatively enhanced H bonds in hedral regions may play an important

Eq. 2 of ref. 1 applies to two boundaries and a bimodal distribution advocated in ref. 2; the LDL in noncritical ambient water is heterogeneous. To understand water a noncritical fluid,  $S_d(Q)$  density and the intensity (2), and that the correlation unimodal in fluctuations from small system (4) suggest the amplitude given by

A recent pressure-dependent rise at small  $Q$  to vanish consistent with the picture in ref. 2 with increasing pressure, disordered motifs undergoing fluctuations, with a redshift and a decrease in intensity.

There is a recent water simulation which displays nanometer-scale coordination (assigned in ref. 4 more disordered (high-temperature SAXS intensity enhancement, even at 300 K, nearly 100 K above transition at low temperature in simulations can thus persist in similar specific model studied in ref. 4 cooperatively enhanced H bonds additionally favor forming structures

## Small-angle scattering of ambient liquid

Gary N. I. Clark<sup>1</sup>, Greg L. Hura<sup>2</sup>, Jos

<sup>1</sup>Department of Biomechanical Engineering, University of Berkeley, CA 94720; <sup>2</sup>Laboratoire Leon Brillouin, Scientifiques (CEA/CNRS), CEA Saclay, 91191 G Technology Facilities Council (STFC) Rutherford

Edited by John D. Weeks, University of Mary

Structural polymorphism has been proposed in the experimentally inaccessible metastable liquid region, theory of a liquid-liquid critical point separates two water species of high and low angle X-ray scattering study has claimed species postulated in the supercooled state at ambient conditions. We analyze scattering data on ambient liquid water synchrotron sources, and large 32,000 v using the TIP4P-Fw model of water, to regions measures standard number density with water's isothermal compressibility; study shows that there is no support for in water structure at room temperature scattering data, as it is consistent with tetrahedral liquid at ambient conditions

anomalous scattering | density distribution | structural polymorphism

Water appears to be a unique liquid exhibiting several anomalous features dynamics, and dynamics. Both experimental simulation have shown that supercooled region exhibits response properties that appear to diverge near transition temperature, experimental are polymorphic states of water, in of low-density amorphous and high-density (2, 3). This polymorphism has been identified in the anomalous thermodynamics, such as the large increase in density with decreasing temperature, experimentally inaccessible supercooled amorphous underlies one of the main: critical point hypothesis (5), i.e., the liquid-liquid critical point from which two fluctuating species of high and low and LDL.

However, recent studies have shown low-temperature criticality in the ST2 need to invoke an explanation for a set based on structural polymorphism (it possible to explain the existing anomalous thermodynamic singularity, in free interpretation (4, 7). Sastry and co a finite increase in isothermal compressibility of a liquid that expands to a thermodynamic necessity, and was a lattice model that has no singularities alternative explanations for the thermodynamic

*Pure Appl. Chem.*, Vol. 82, No. 10, pp. 1855–1867, 2010.  
doi:10.1039/PAC-CON-09-12-16  
© 2010 IUPAC, Publication date (Web): 30 June 2010

## Recent water myths

Alan K. Soper

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**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,  $\approx 5$  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  $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , 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-

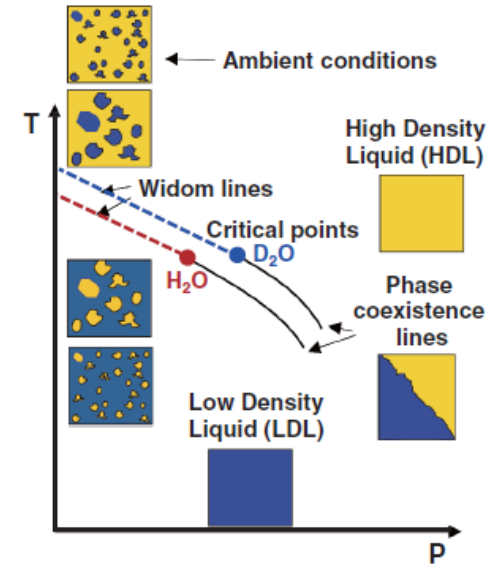
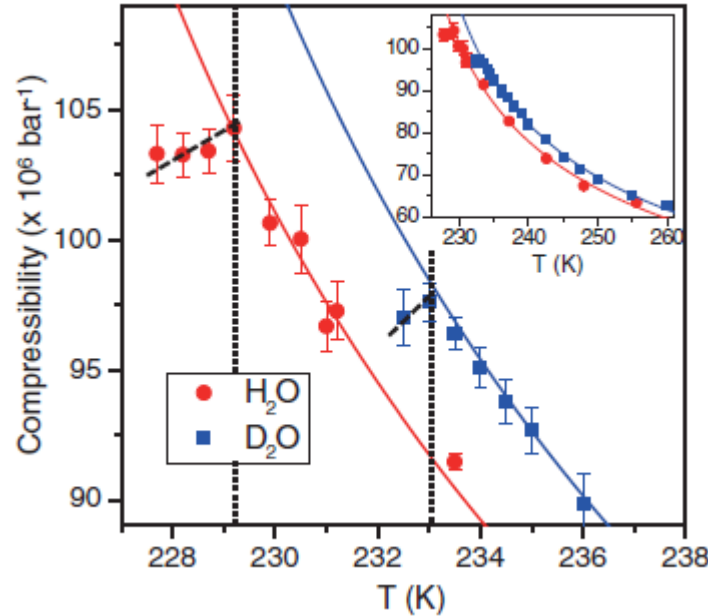
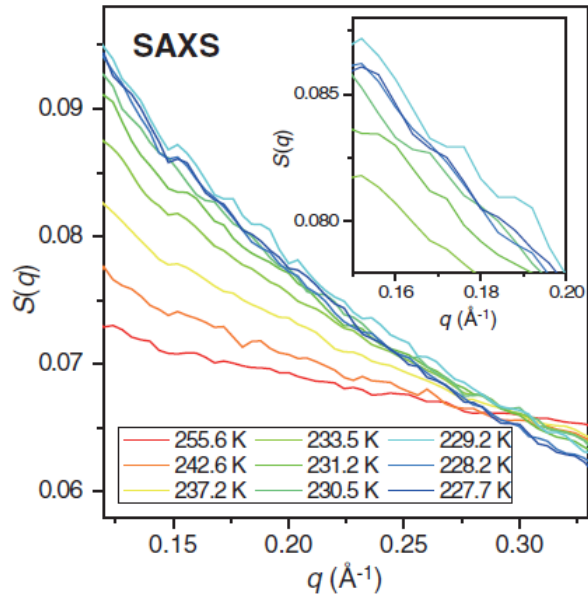
\*Paper based on a presentation at the 31<sup>st</sup> International Conference on Solution Chemistry (ICSC-31), 21–25 August 2009, Innsbruck, Austria. Other presentations are published in this issue, pp. 1855–1973.





# Liquid water: SAXS at FEL

Microdroplets → stronger supercooling possible



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

Compressibility

Proposed phase diagram

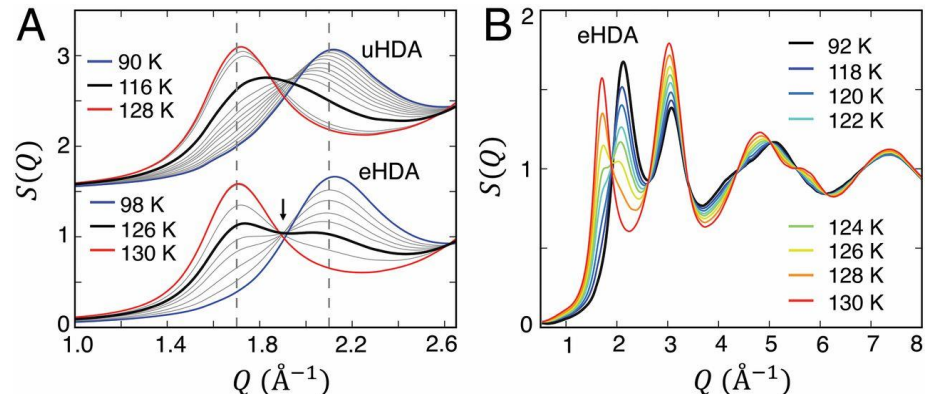
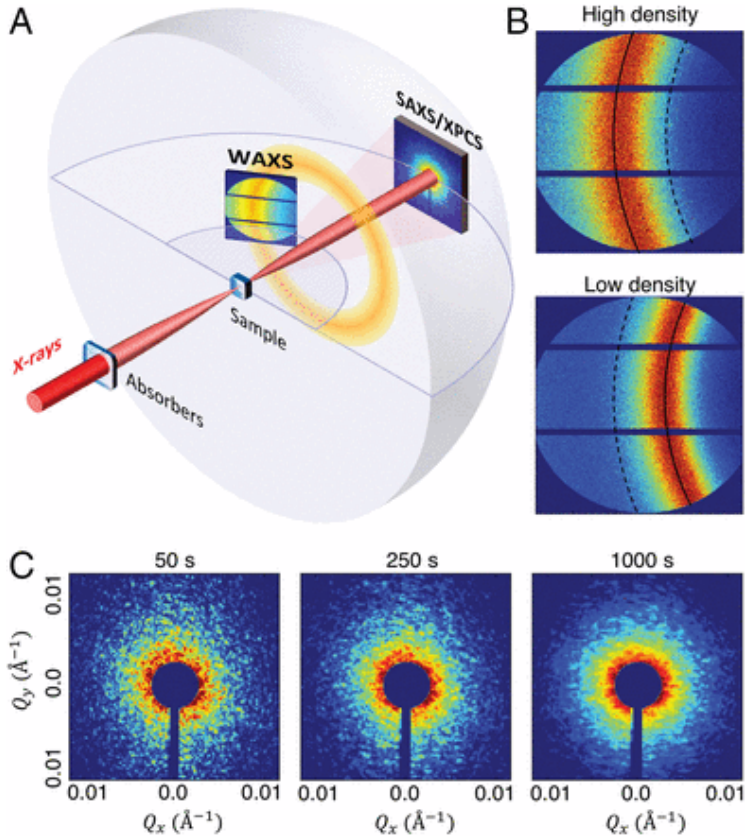
Science 358, 1589 (2017)

→ Compressibility maximum by crossing the Widom line

→ But: depends on the estimation of water density



# Dynamics in amorphous ices & liquid water



## X-ray diffraction

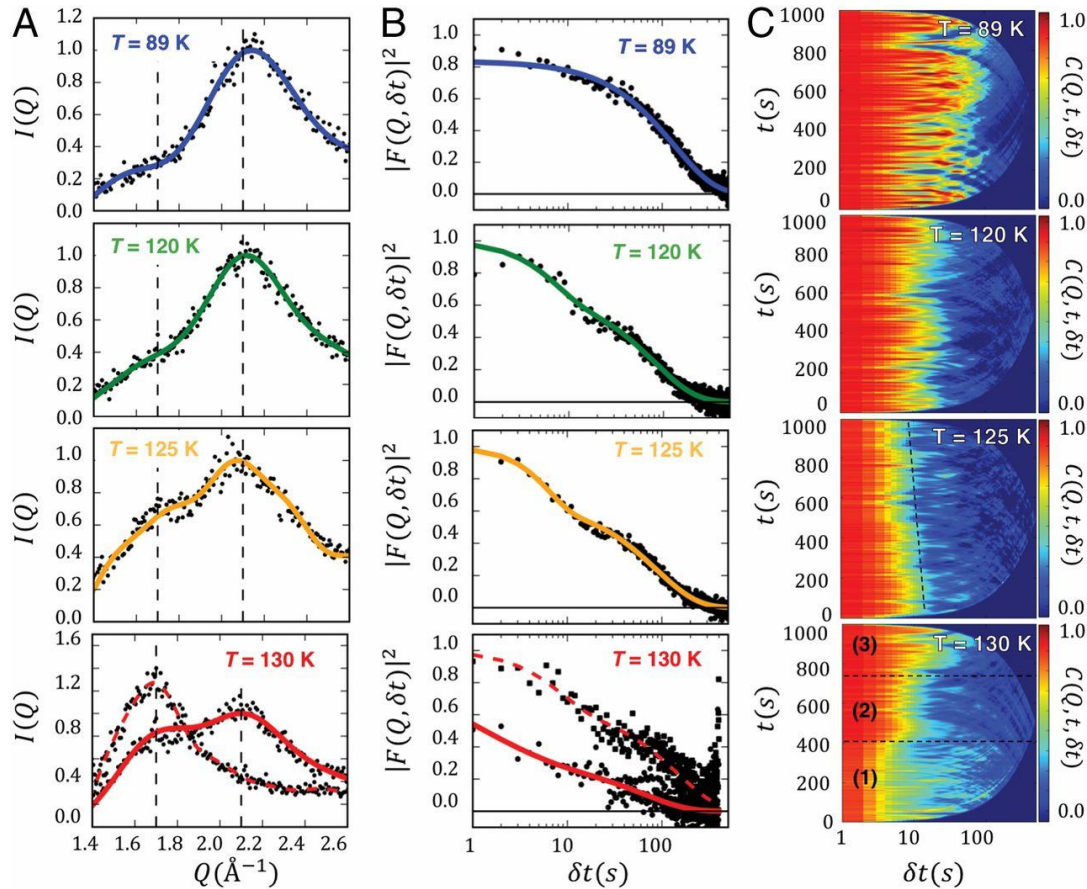
- Double peak for eHDA: coexistence of high- and low-density form
- Decomposition of  $S(Q)$  (and  $g(r)$ ) in two (main) contributions possible

## Transition of HDA to LDA

PNAS 114, 8793 (2017)

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

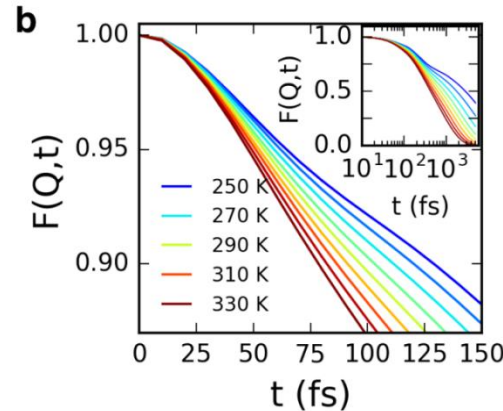
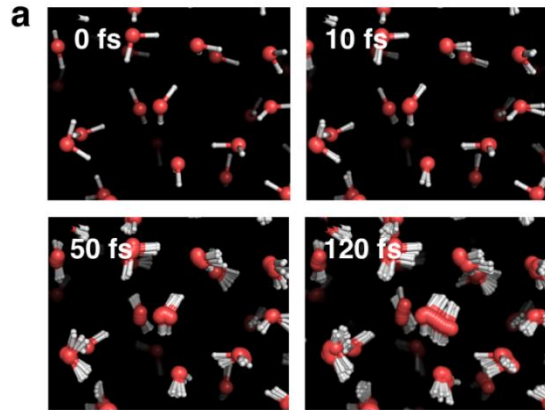
# Dynamics in amorphous ices & liquid water



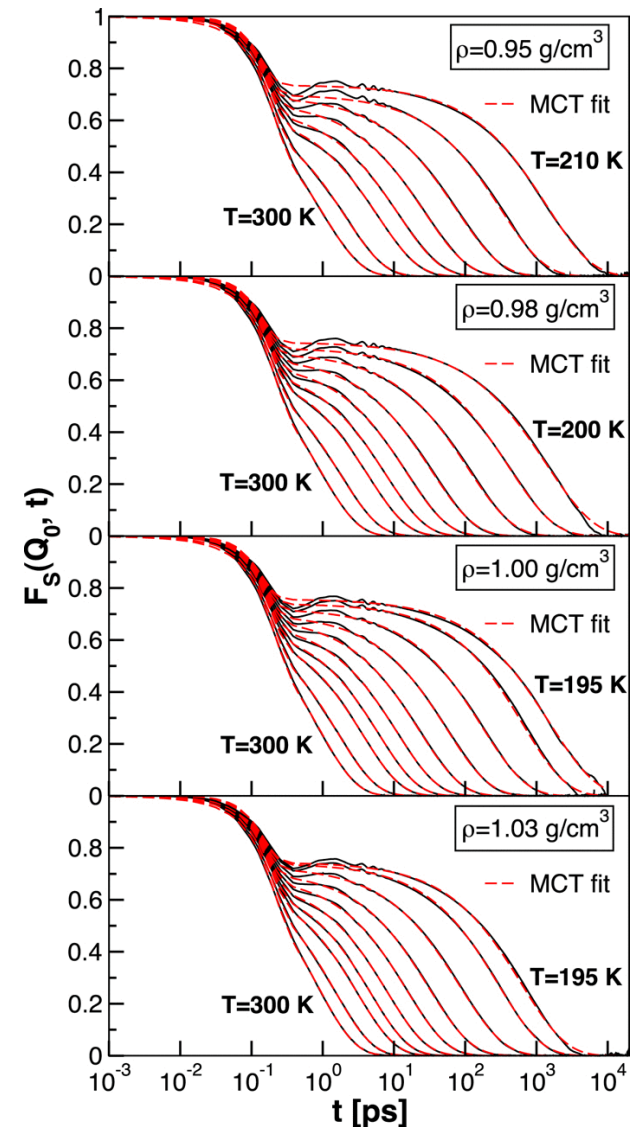
- $T < 110$  K: viscoelastic relaxation of HDA
- Onset of diffusive dynamics for  $T \geq 110$  K
- HDA domains transform to ultraviscous **HDL**
- Around  $T = 130$  K: transformation to ultraviscous **LDL**

PNAS 114, 8793 (2017)

## 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

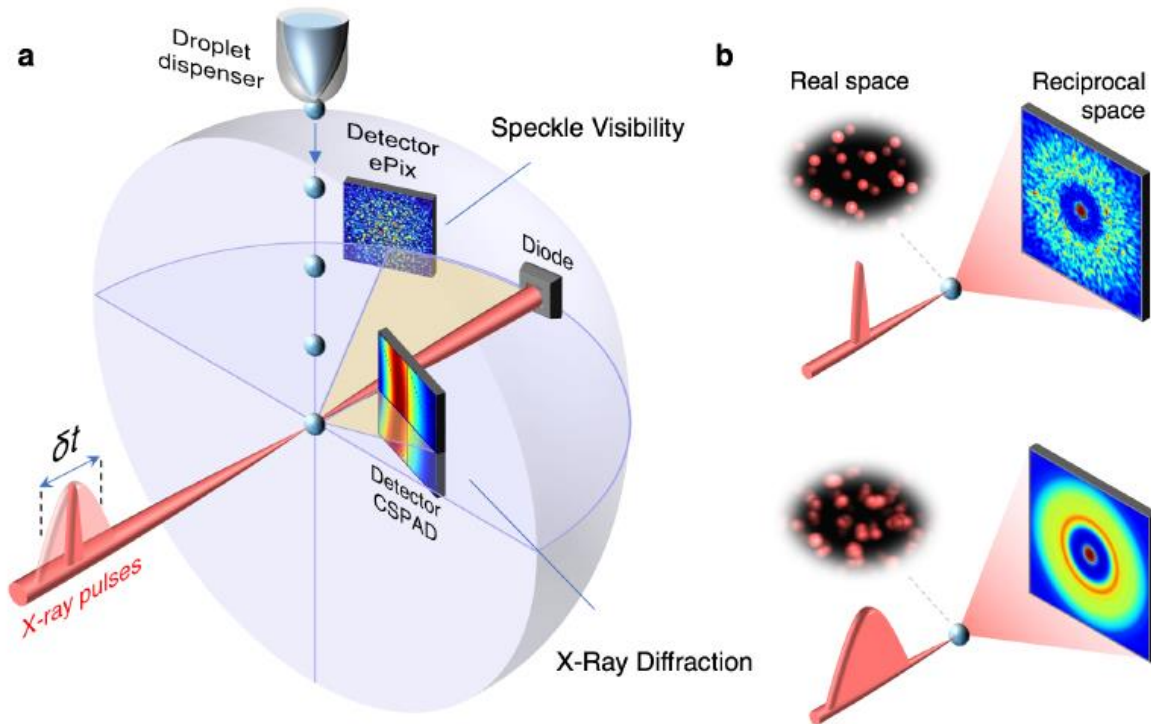


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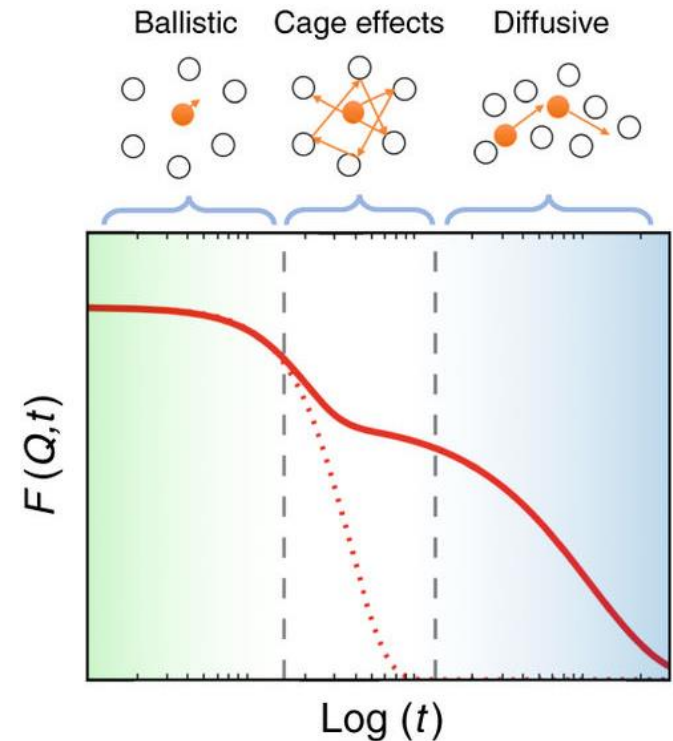
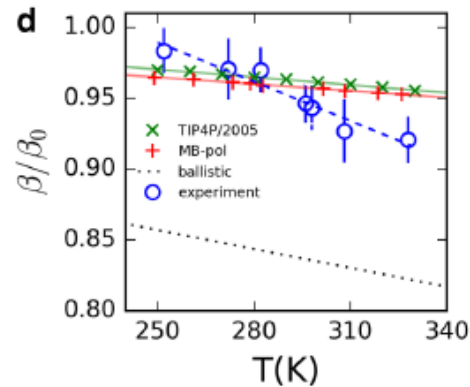
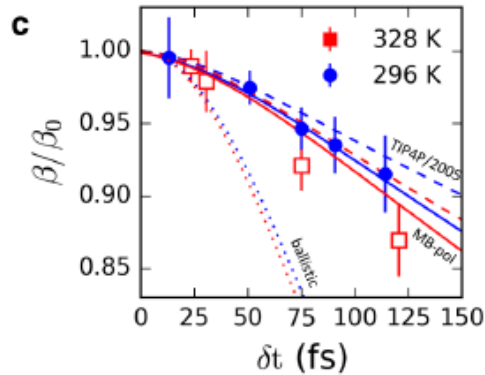
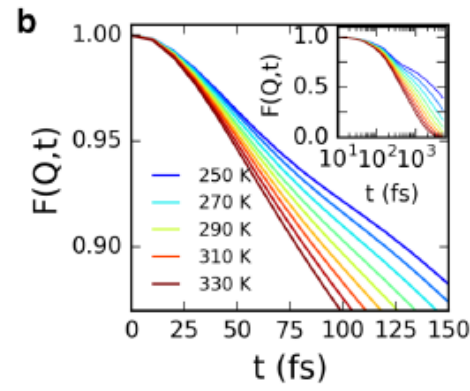
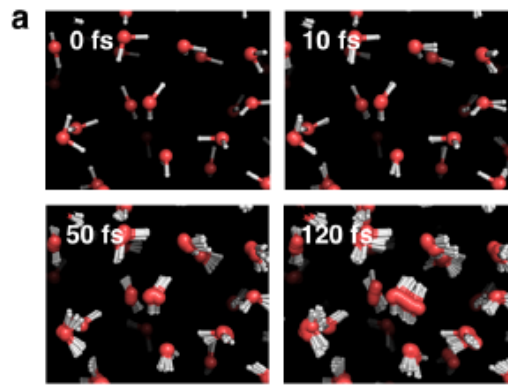


## Dynamics in amorphous ices & liquid water



- XSVS experiment
- 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"

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