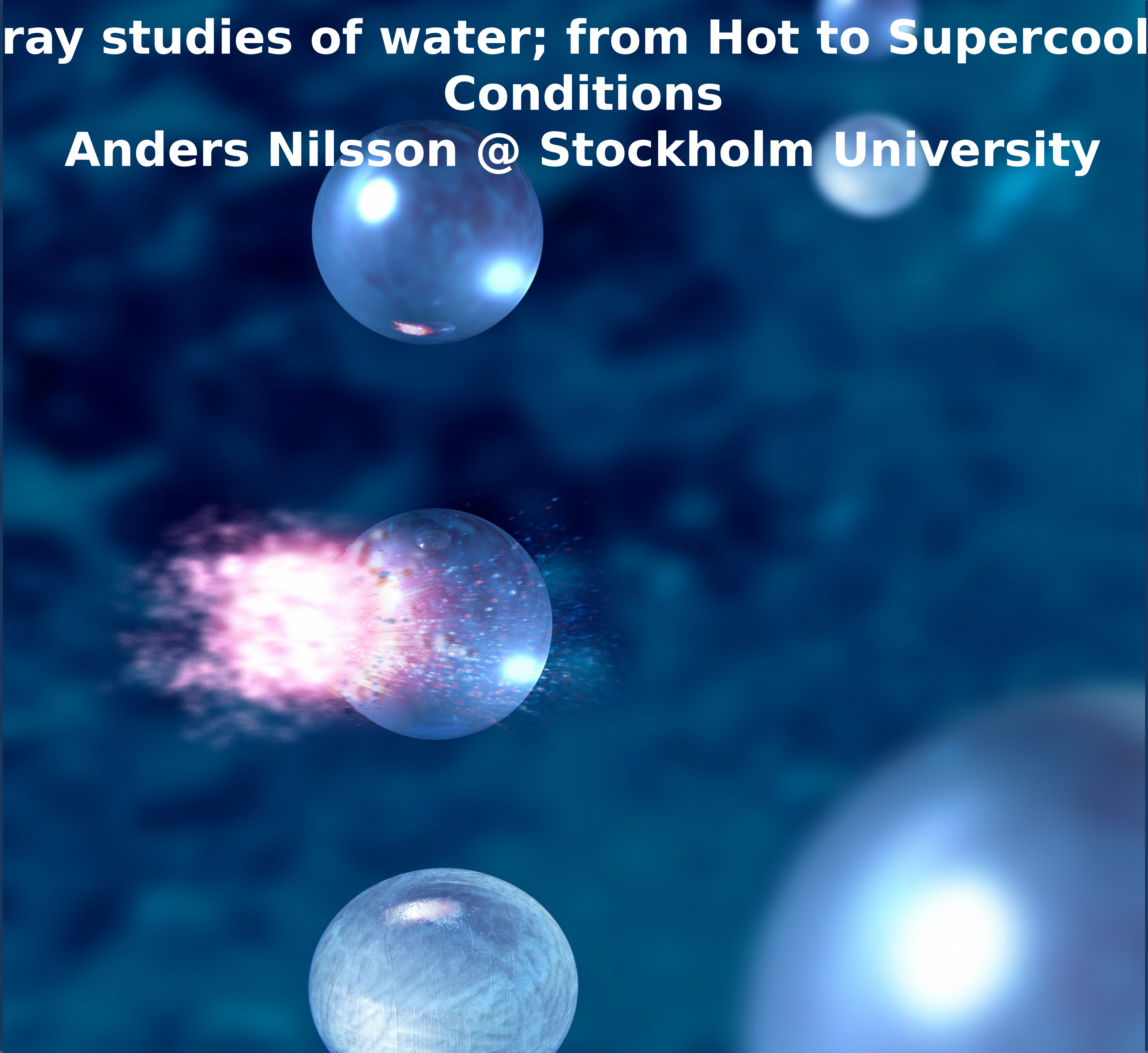
X-ray studies of water; from Hot to Supercooled Conditions

Anders Nilsson @ Stockholm University



11 reviews from the 2014 Nordita meeting in Stockholm

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European Research Council

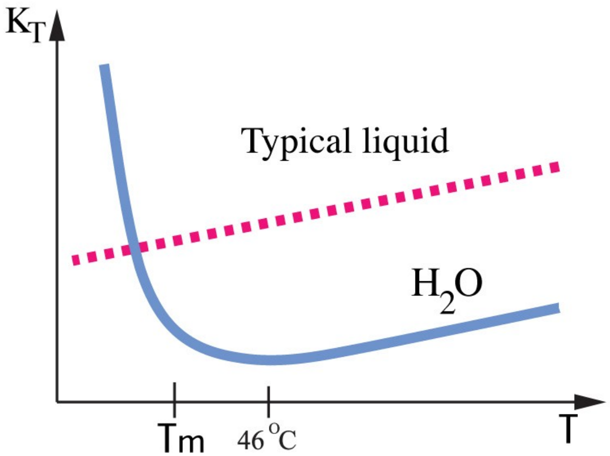
Established by the European Commission

Vetenskapsrådet

Anomalous Properties of Water

Total 63 anomalous properties

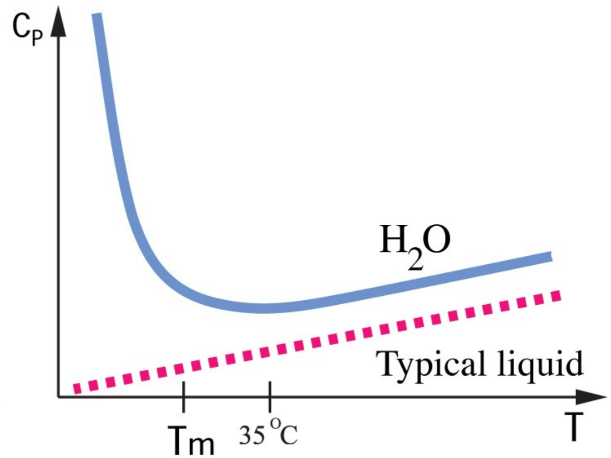
Isothermal Compressibilit
y



$<(\delta V)^2>=Vk_B T\kappa_T$

Density fluctuations

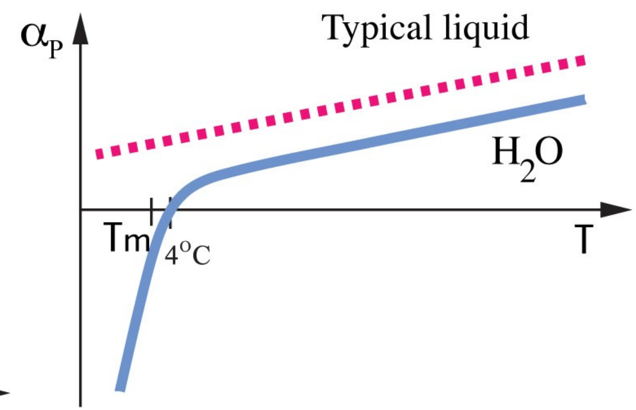
Heat Capacity



$<(\delta S)^2>=Nk_B c_p$

Entropy fluctuations

Thermal expansion



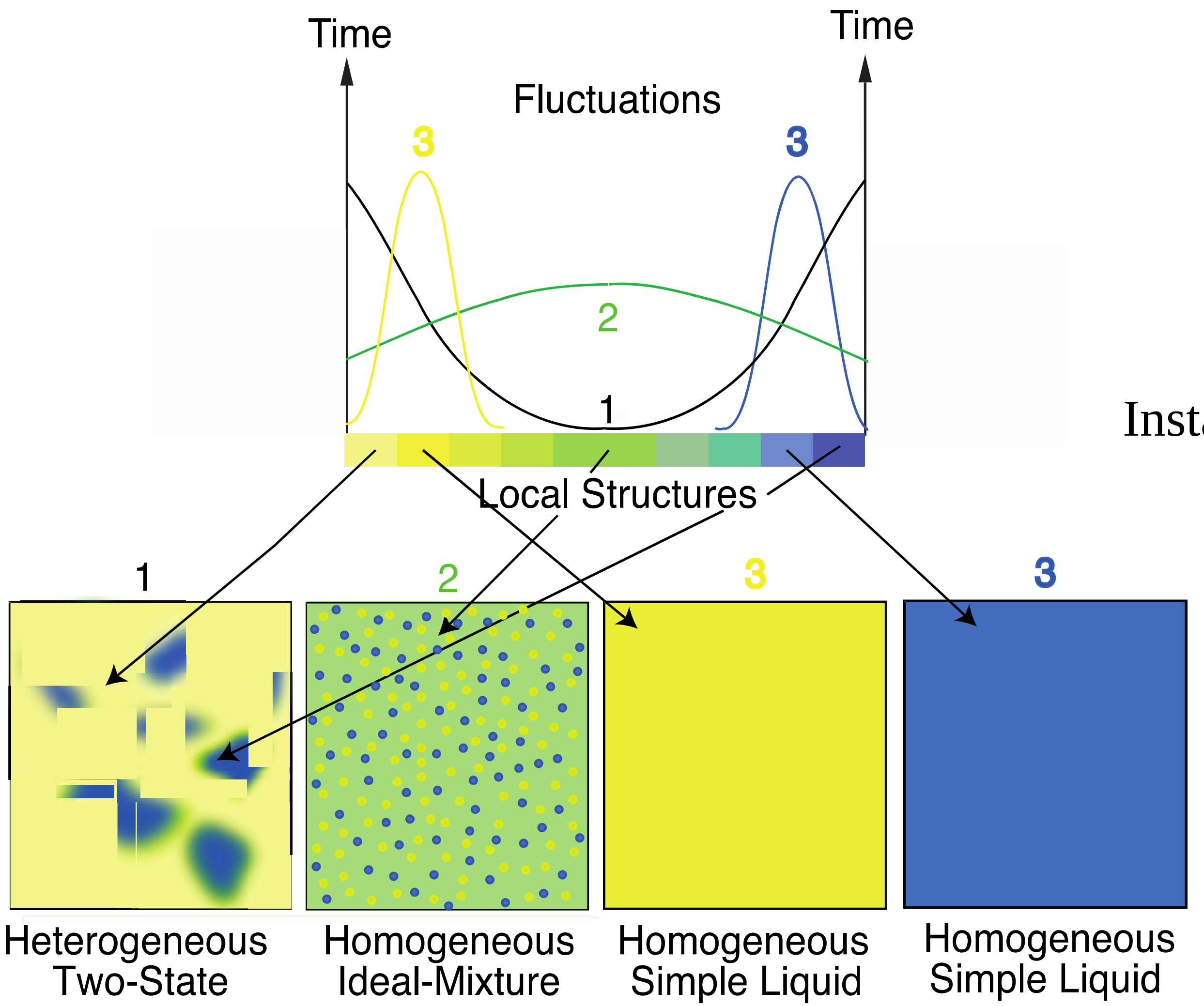
$<(\delta S\ \delta V)>=Vk_B T\alpha$

Cross of density and entropy fluctuations

Divergence towards a mysterious temperature of -45 °C

P. Kumar, S. Han, H.E. Stanley, J. Phys.: Condens. Matter **21** (2009) 504108.

Synergy of Mixture and Continuum Models
Fluctuating Heterogeneous Model

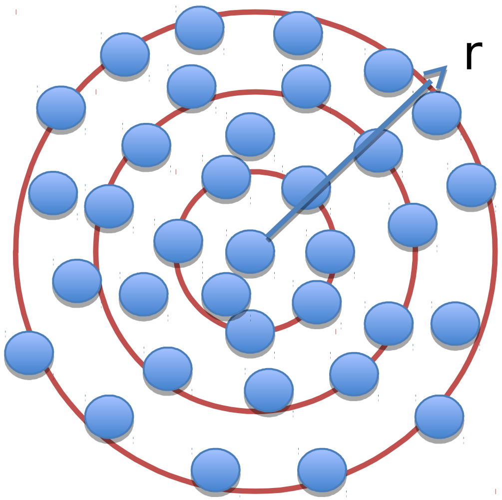


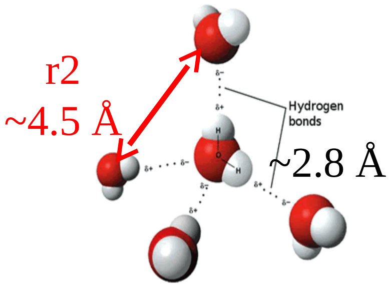
Pendelum

Instantaneous snapshots

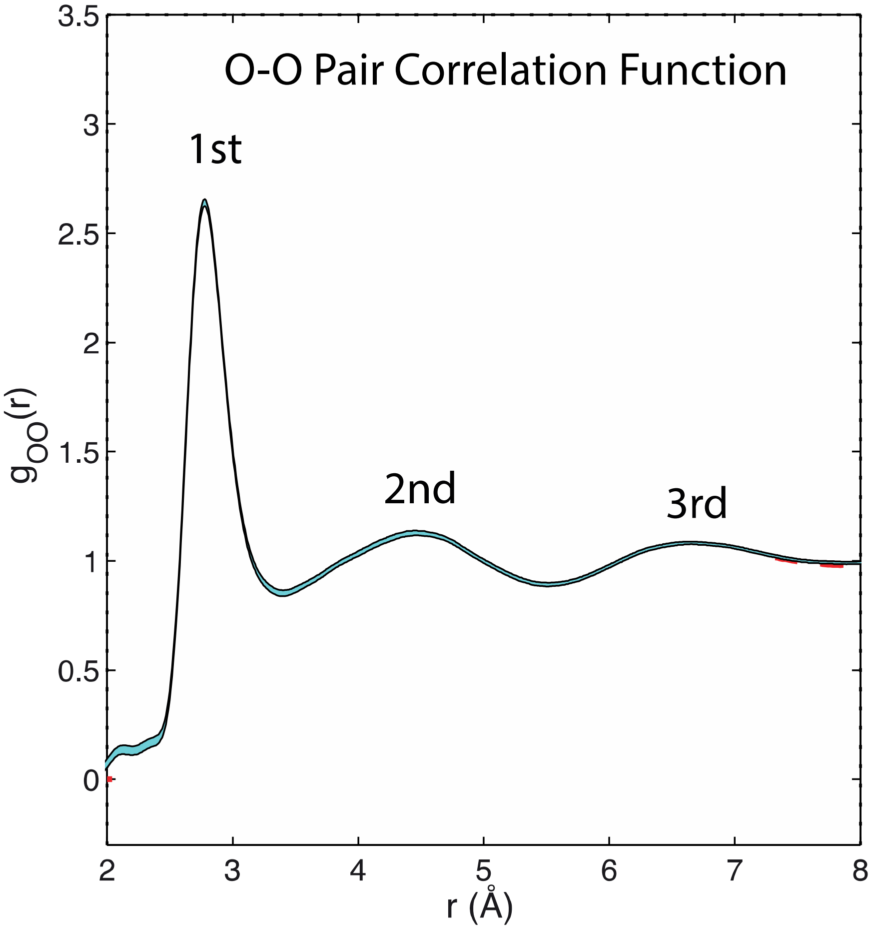
A. Nilsson and L. G. M. Pettersson Nature Communication **6** 8998 (2015)

Pair Correlation Functions





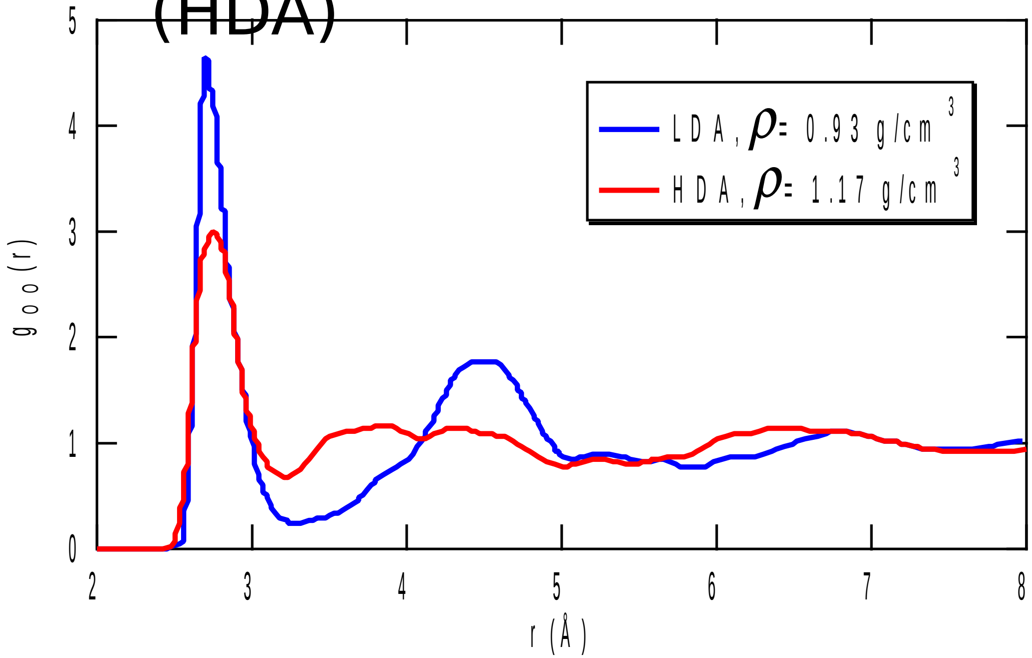
Water at 298 K

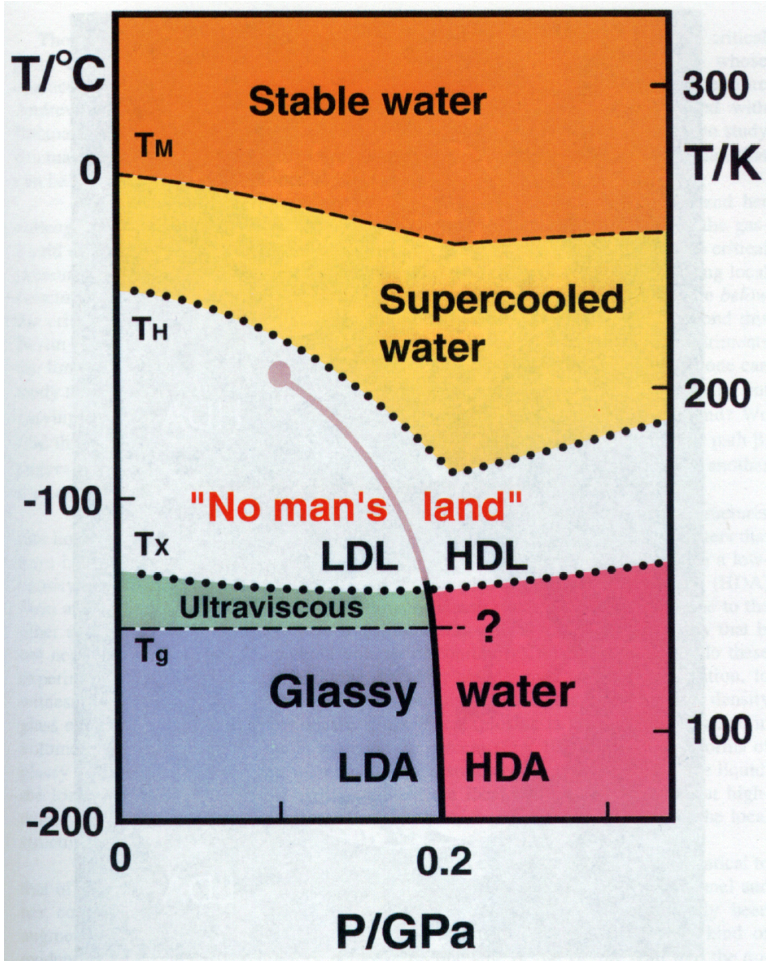


Skinner et al. J. Chem. Phys. **138**, 074506 (2013

Amorphous Phases of water

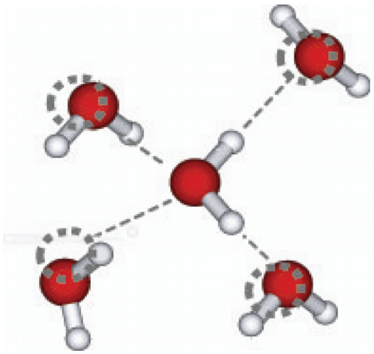
- Polyamorphism
  - Low-density amorphous ice (LDA)
  - High-density amorphous ice (HDA)





J. L. Finney *et al.*, *Phys. Rev. Lett.* **88**, 225503 (2002)
H. E. Stanley, *Mysteries of Water,* Les Houches Lecture (1998)

Hypothesis Two Local Structures



Bond Energy

Low Density Liquid (LDL)

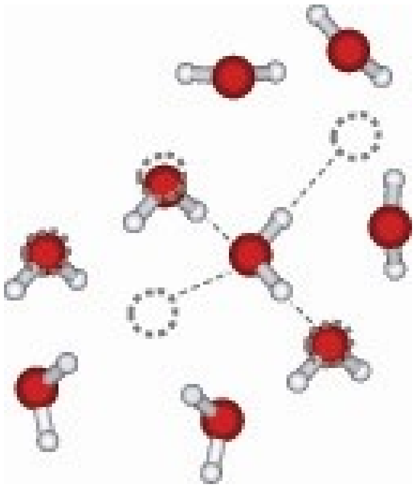
is connected to strong tetrahedral coordination

High Density Liquid (HDL)

is connected to species with higher coordination with the expense of breaking hydrogen bonds

Asymmetrical species

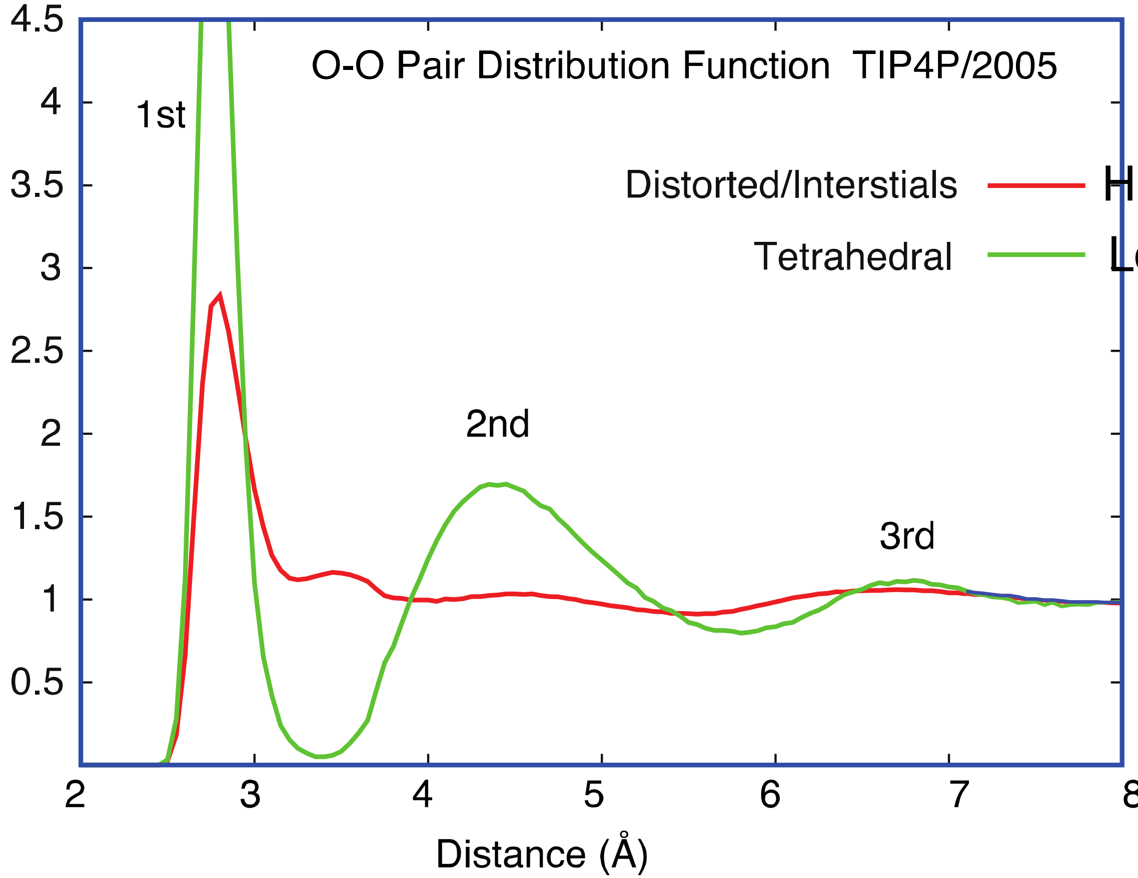
Importance of van der Waals interactions

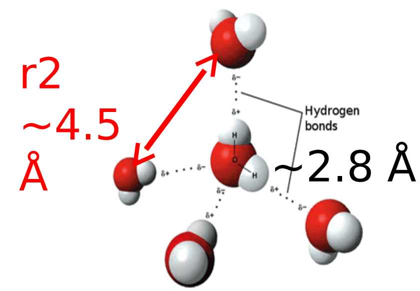


Dominates at RT!!!!

Entropy

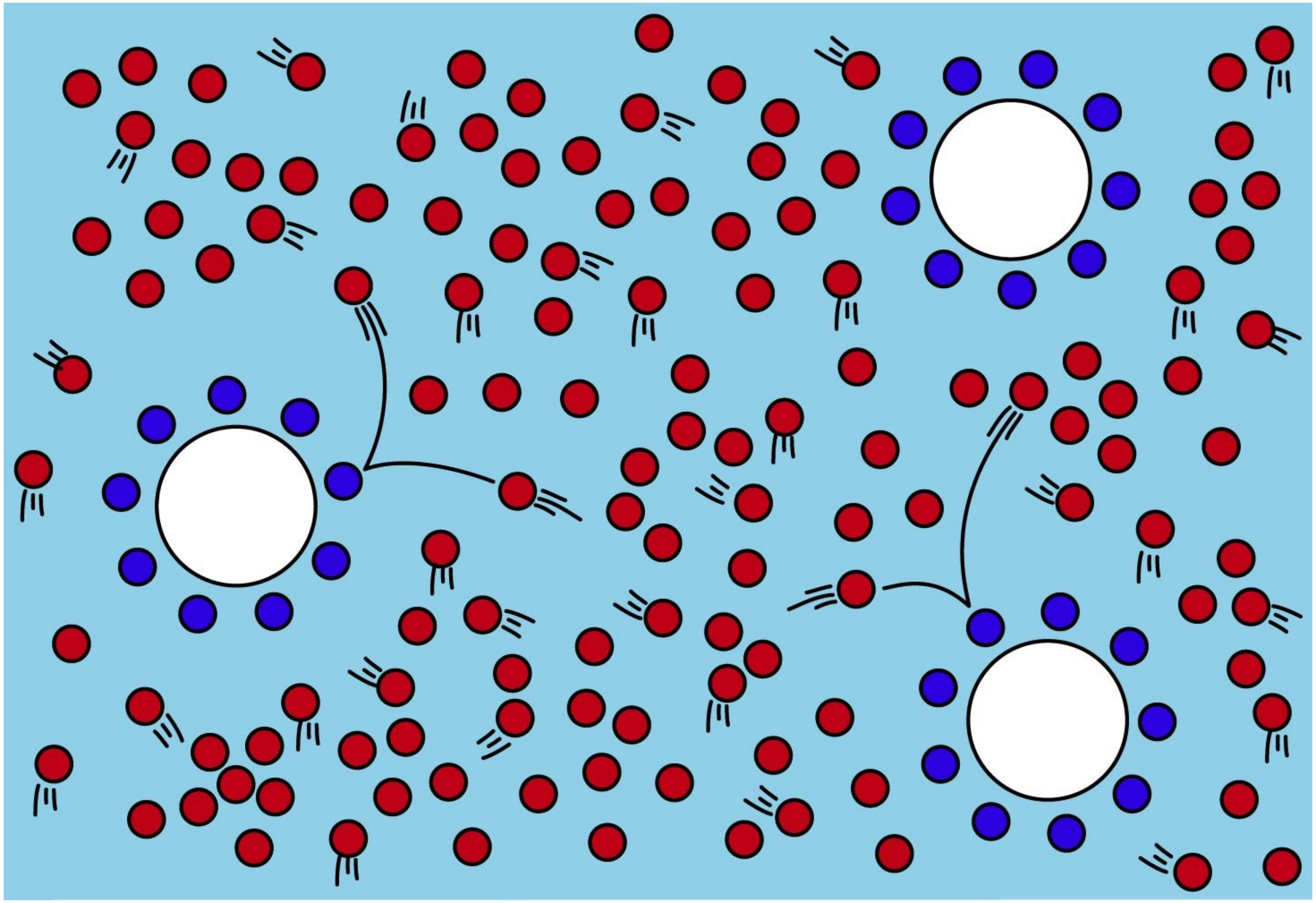
Different Liquid Structures in MD



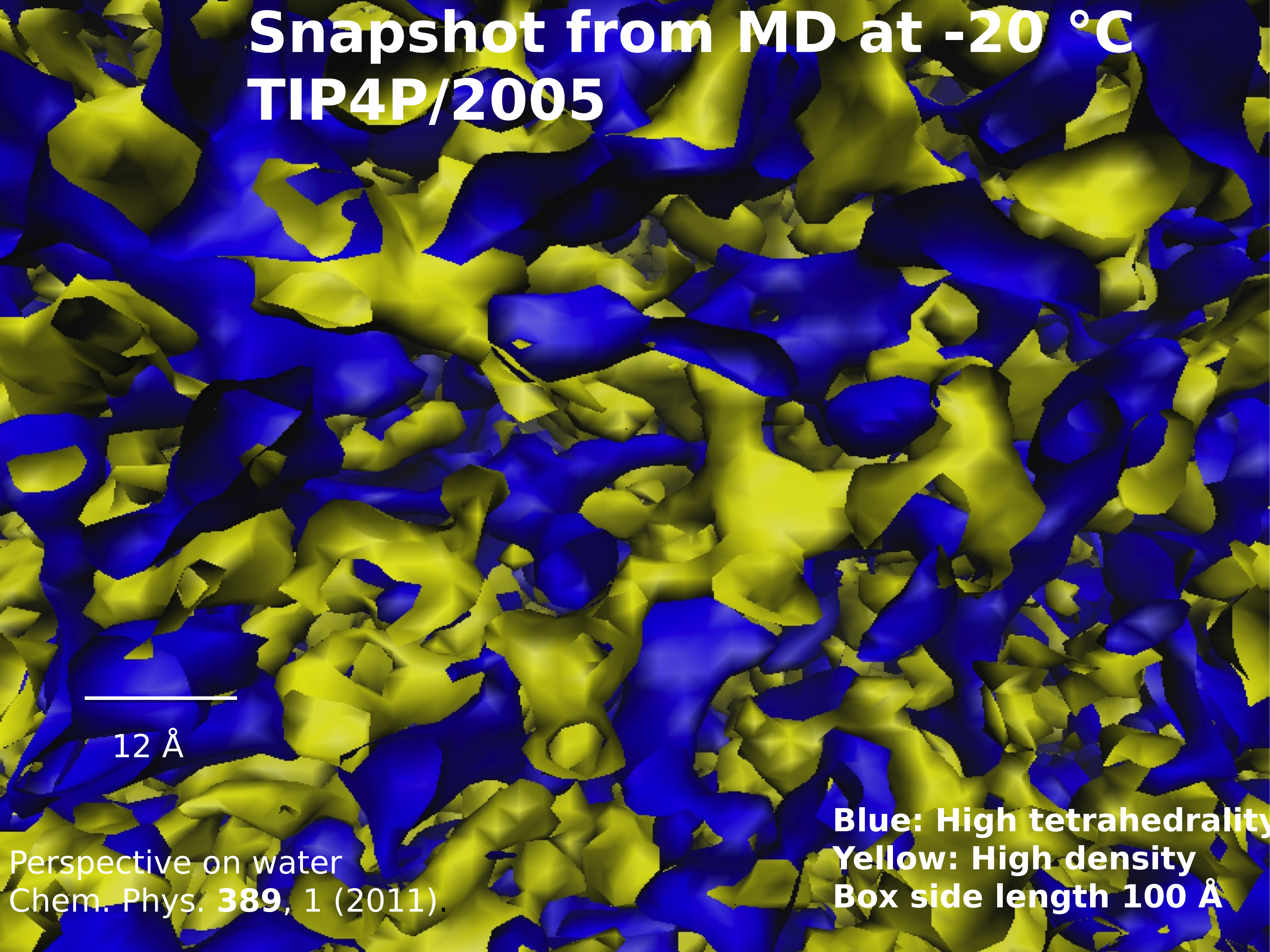


A. Nilsson and L. G. M. Pettersson Nature Communication **6** 8998 (2015)

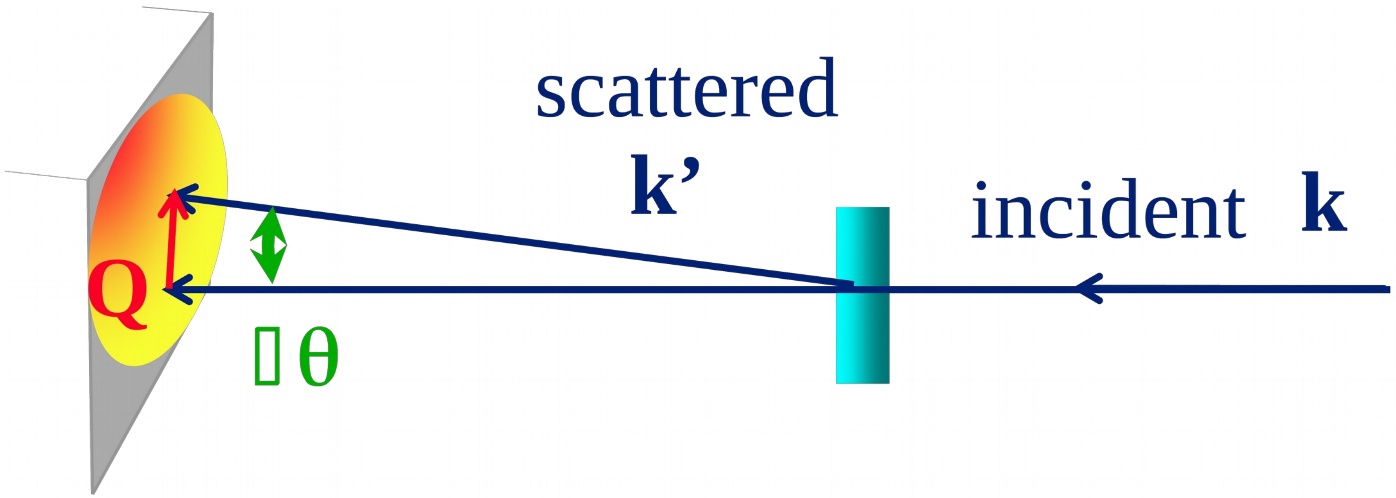
Dance Restaurant

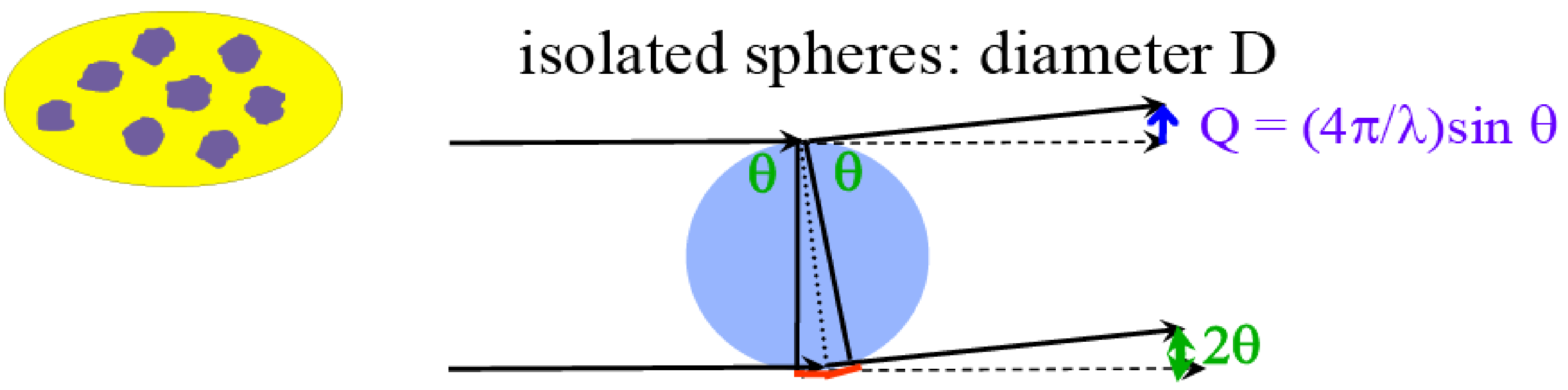


People at the table are more socially bonded, local order, low density
People dancing are disordered but excited and moves around, higher density
Exchange between dancing and sitting people


Snapshot from MD at -20 °C
TIP4P/2005
12 Å
Perspective on water
Chem. Phys. 389, 1 (2011).
Blue: High tetrahedrality
Yellow: High density
Box side length 100 Å

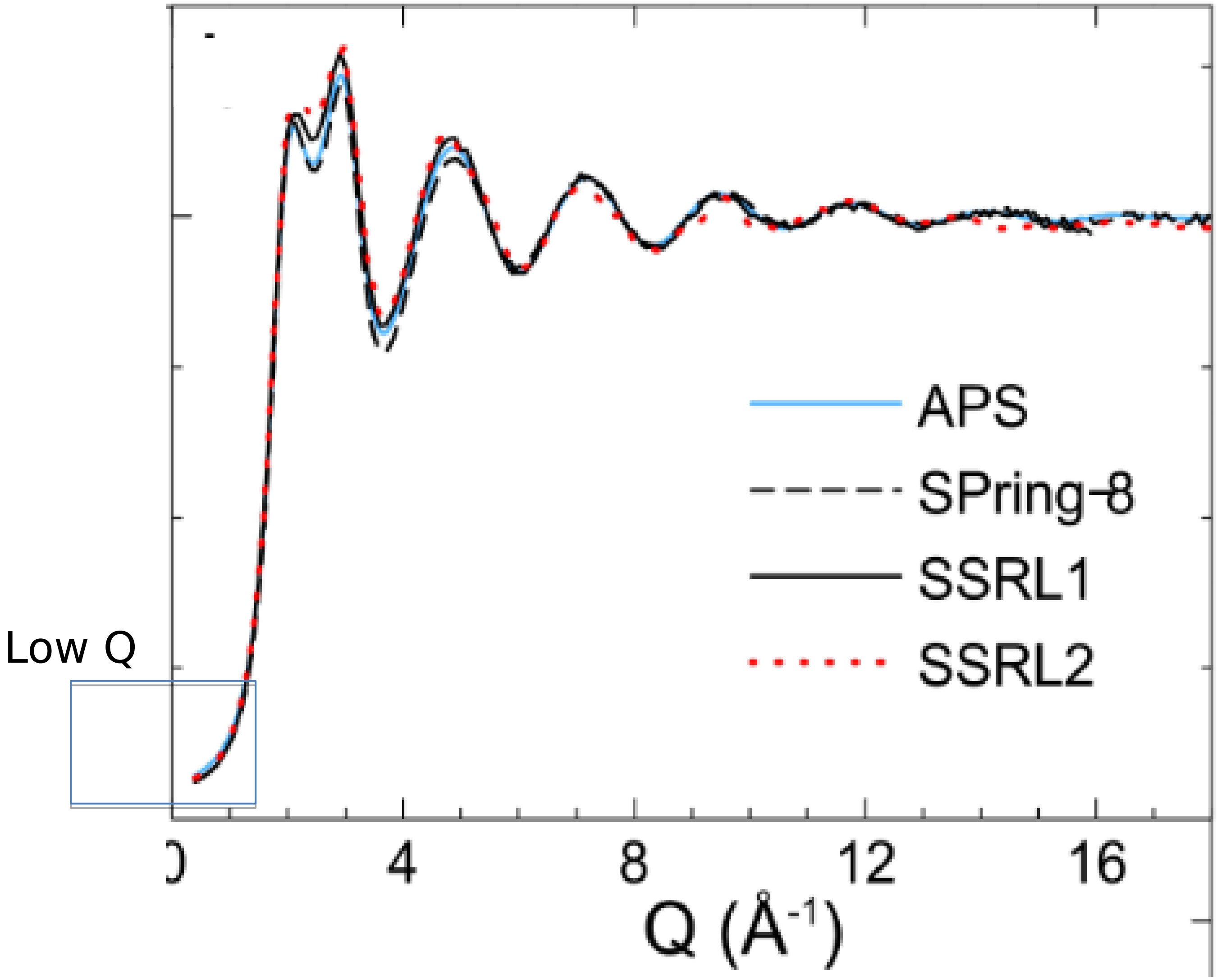
Small Angle X-ray Scattering (SAXS)



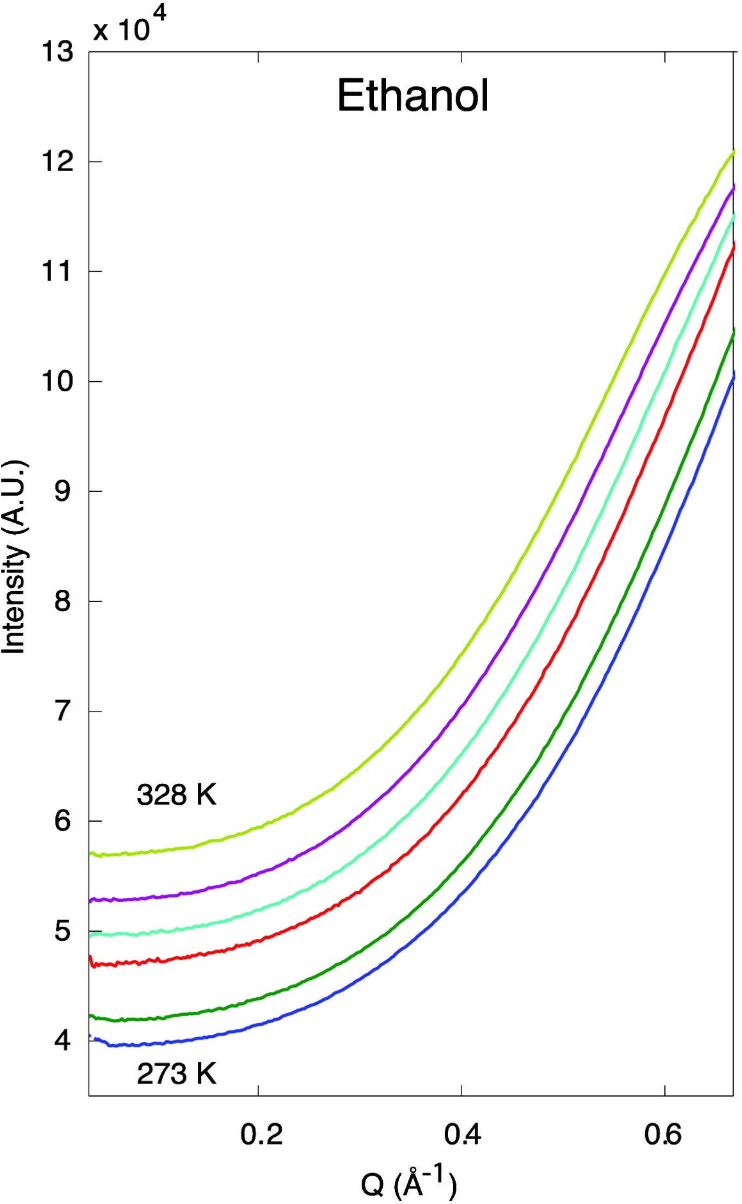


Courtesy Mike Toney

Structure Factor



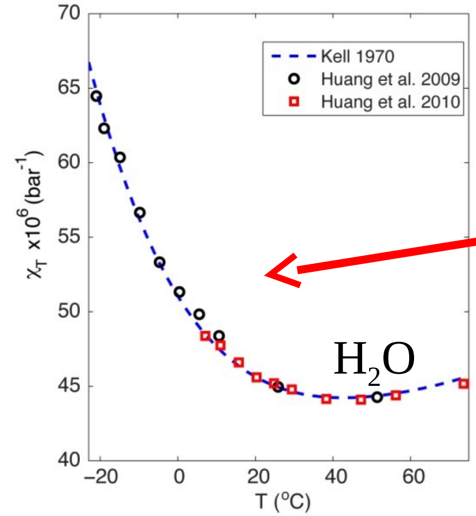
SAXS: Normal Liquid vs Water



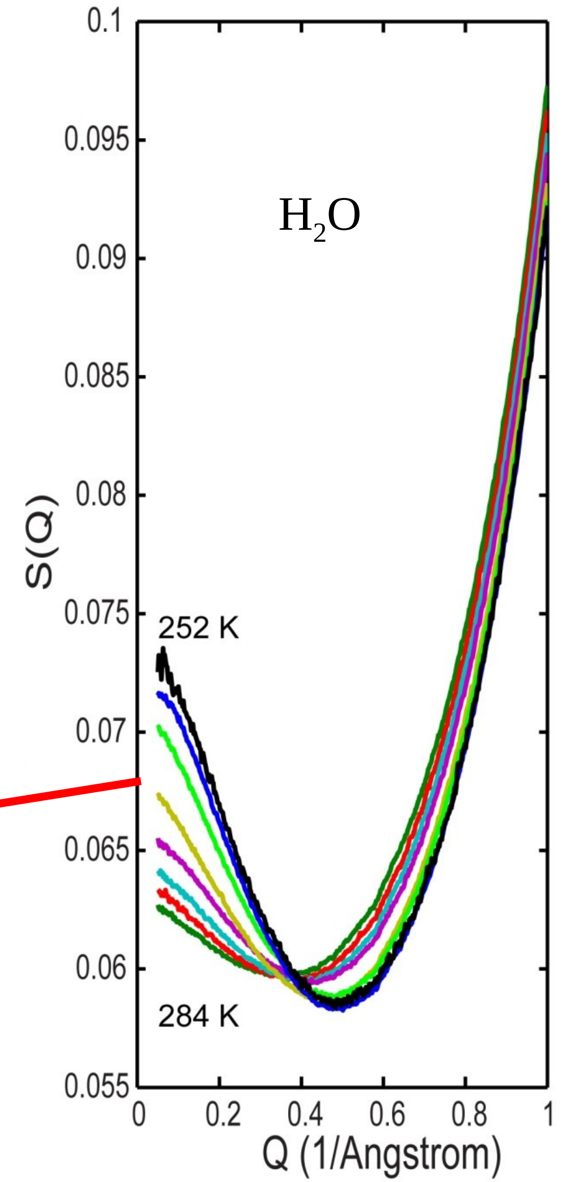
Normal liquid

The isothermal compressibility χ_T

$$S(0) = k_B T n \chi_T$$



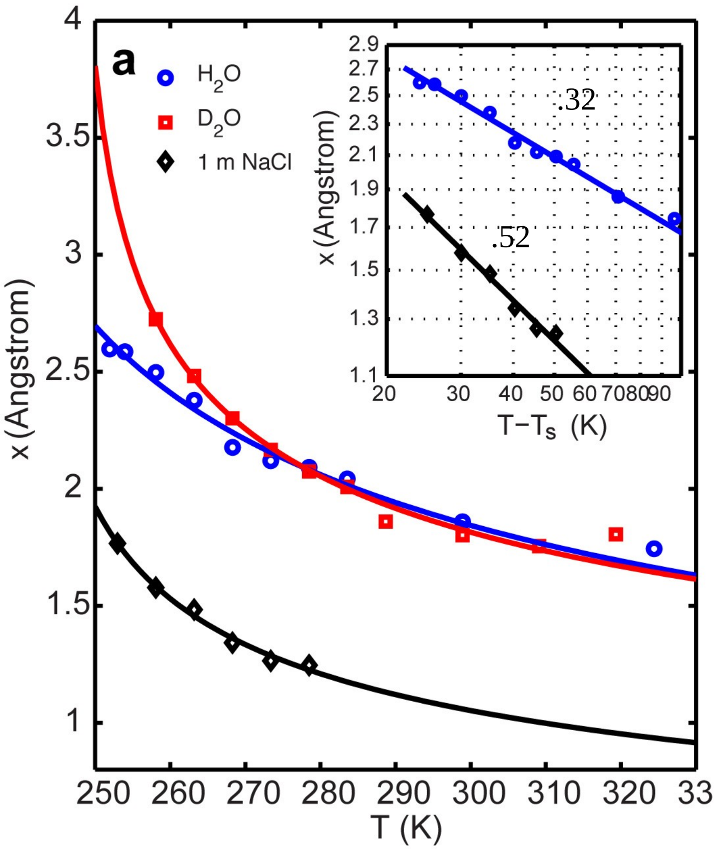
χ_T



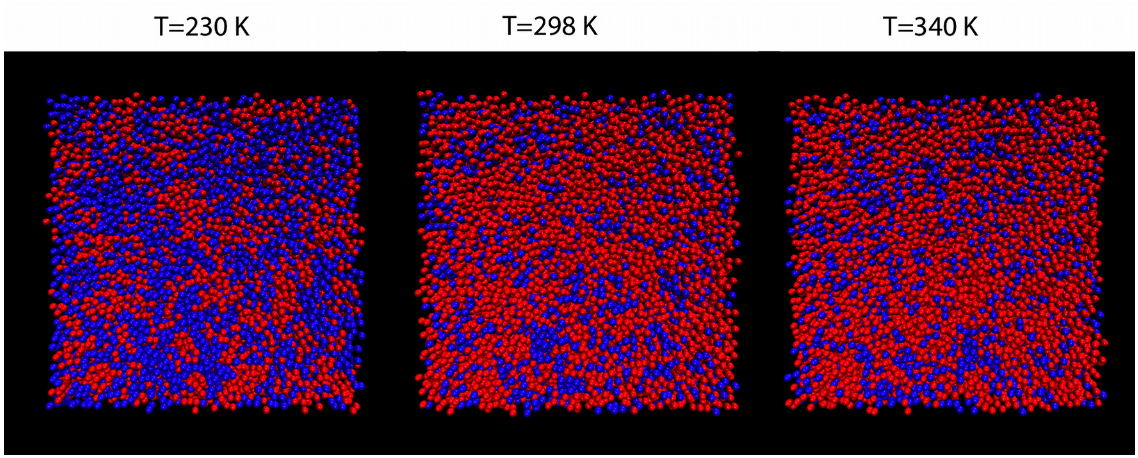
Huang et al. JCP **133**, 134504 (2010)
Nilsson et al. Mol. Liq. **176**, 2 (2012)

Apparent Power Law

Critical phenomena characterized by power laws with critical exponents



2nd critical point scenario
Fluctuations between
HDL/LDL
Poole *et al.*, *Nature* **360**, 324 (1992)



TIP4P-2005 simulations
Blue LDL Red HDL
based on inherent structure

Fit ζ to (apparent) powerlaw

$$\xi = \xi_0 \varepsilon^{-\nu}$$

with

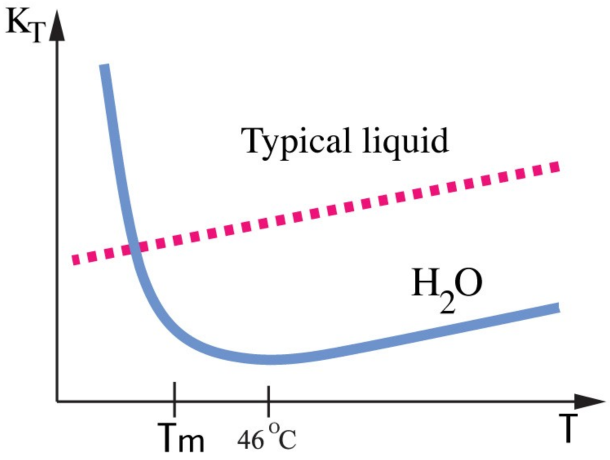
$$\varepsilon = T/T_s - 1$$

Huang et al. JCP **133**, 134504 (2010) Wikfeldt et al., PCCP **13**, 19918 (2011)

Anomalous Properties of Water

Total 63 anomalous properties

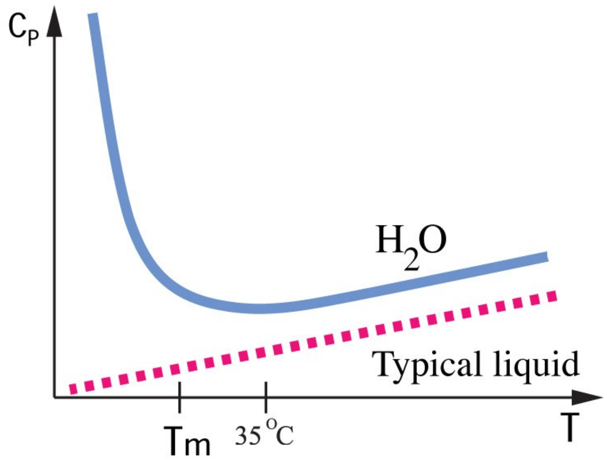
Isothermal Compressibilit
y



$<(\delta V)^2>=Vk_BT\kappa_T$

Density fluctuations

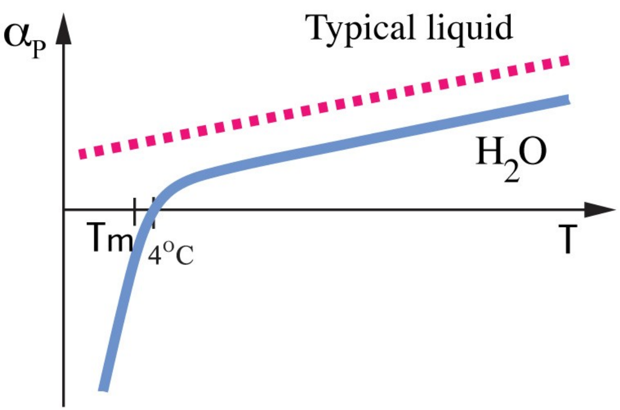
Heat Capacity



$<(\delta S)^2>=Nk_Bc_p$

Entropy fluctuations

Thermal expansion



$<(\delta S\ \delta V)>=Vk_BT\alpha$

Cross of density and entropy fluctuations

Divergence towards a mysterious temperature of -45 °C

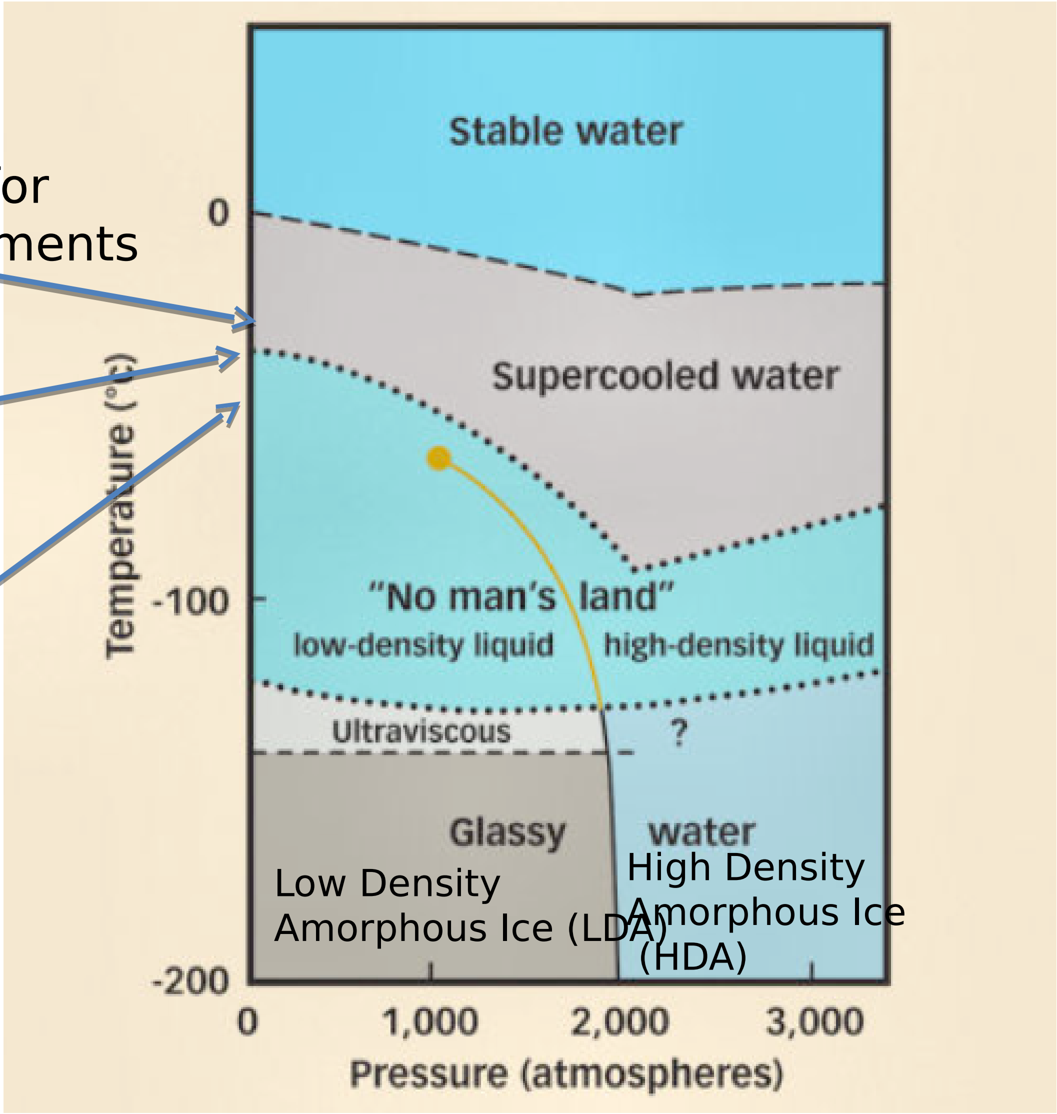
P. Kumar, S. Han, H.E. Stanley, J. Phys.: Condens. Matter **21** (2009) 504108.

ater Phase Diagram; No Man's Land

Practical Limit for Water Measurements --20 to -33 °C

Homogenous Ice Nucleation Limit -38 °C

-45 °C in "no mans land"



ρ(HDA)=1.17 g/cm^3

ρ(LDA)=0.94

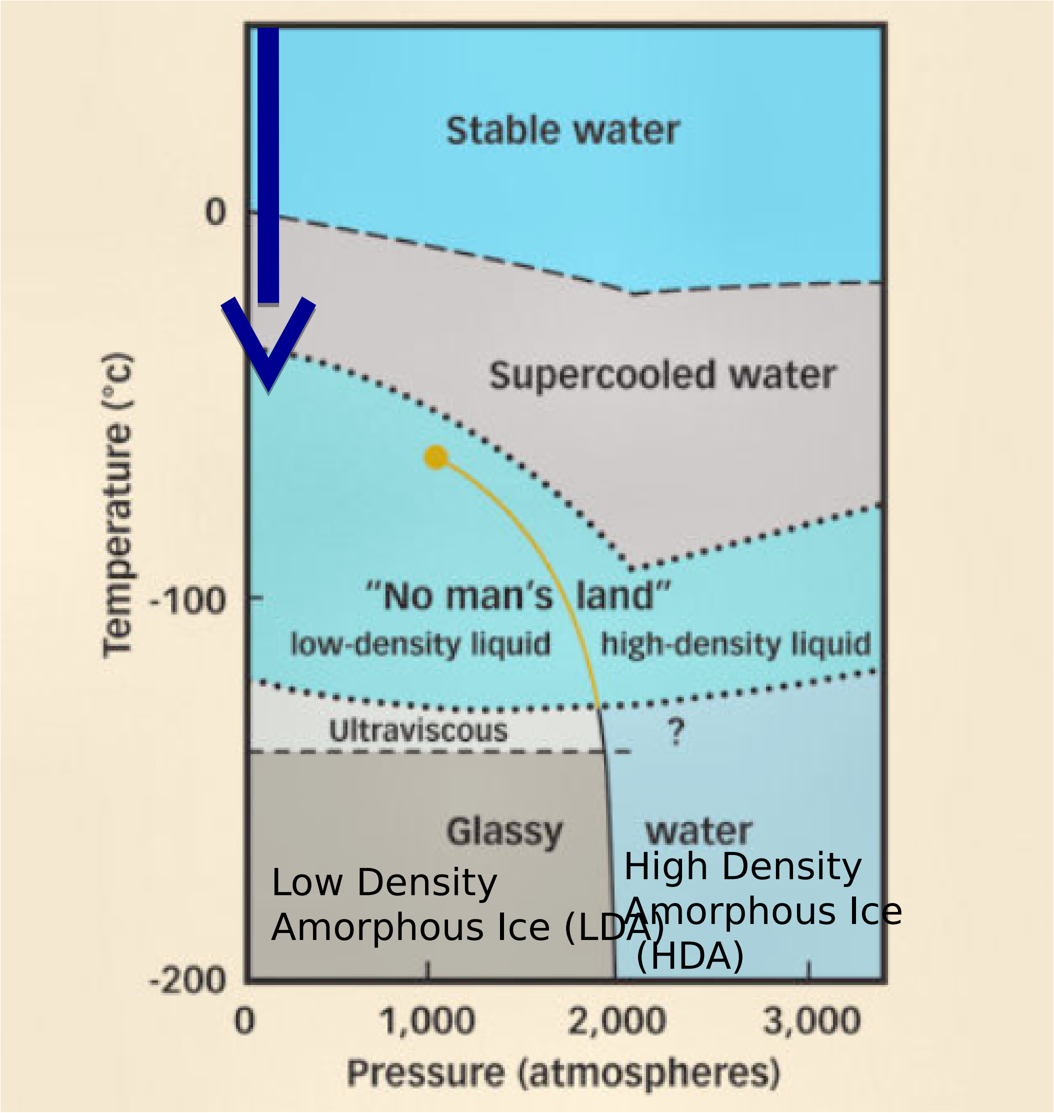
ρ(Ih)=0.92

ρ(Ic)=0.92

H. E. STANLEY "Mysteries of Water" Les Houches Lecture, May 1998

Originally Proposed P.H. Poole, F. Sciortino, U. Essmann, H.E. Stanley, Nature 360, 3 (1992)

o Approaches; From Above No-Man's Land



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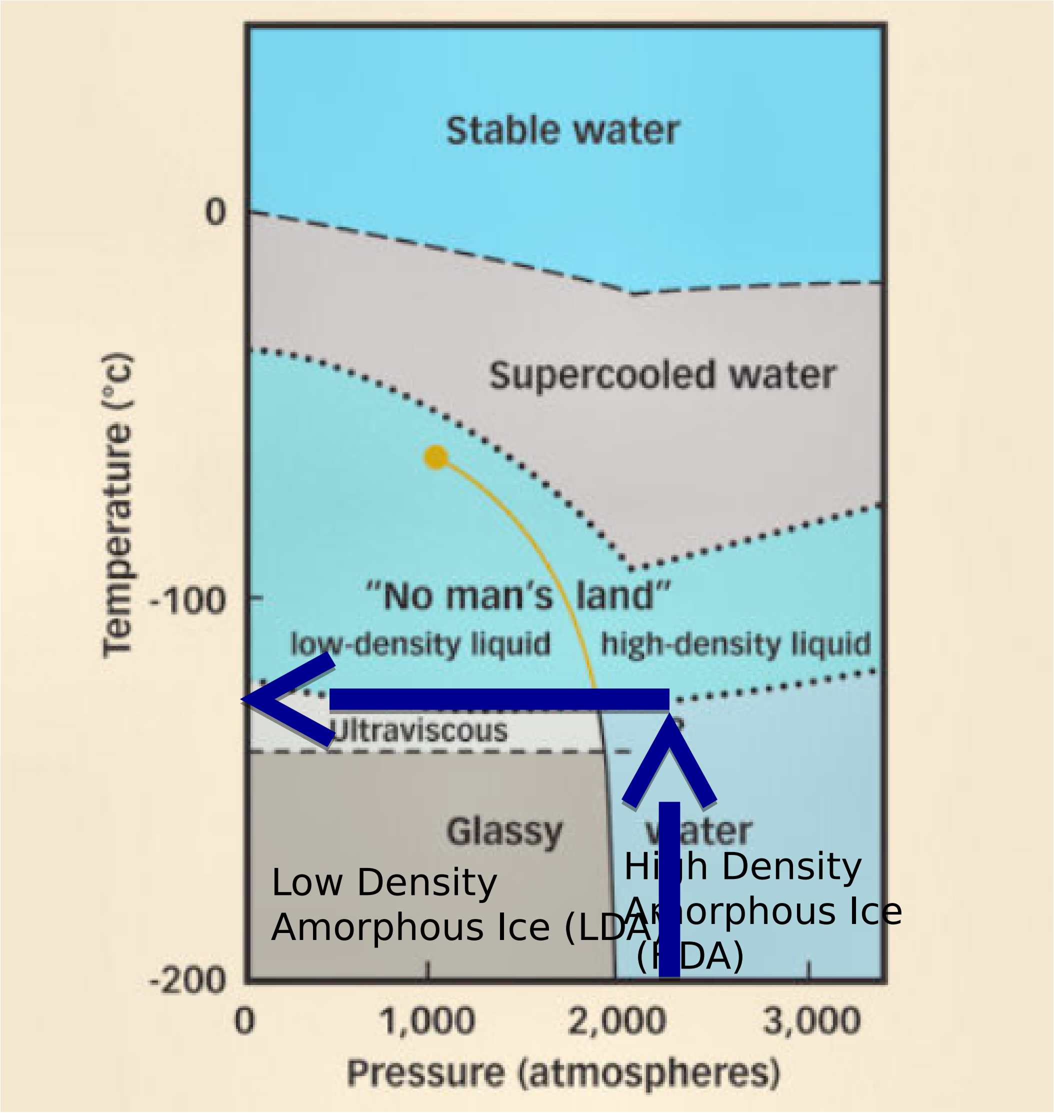

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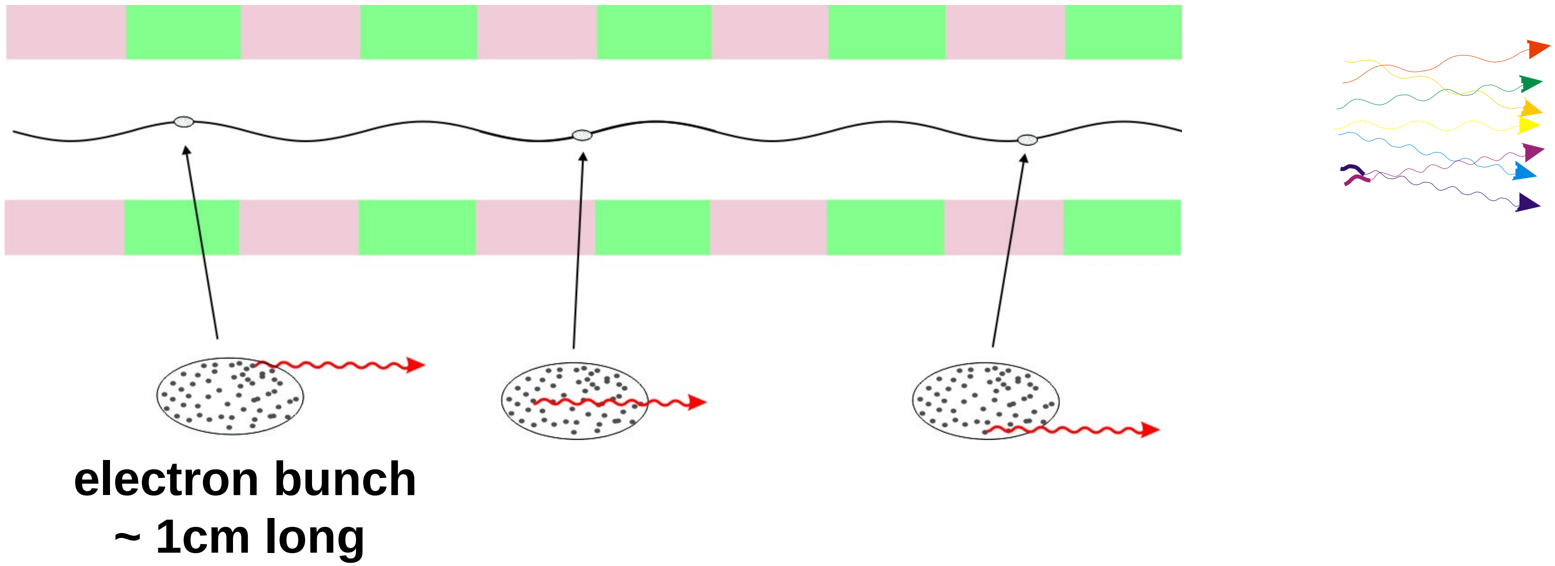
Synchrotron radiation from undulator in storage ring

Electron bunch is “stored” in ring and used over and over…..



Each bunch contains $N_e \sim 10^9$ electrons

…but electrons emit spontaneously

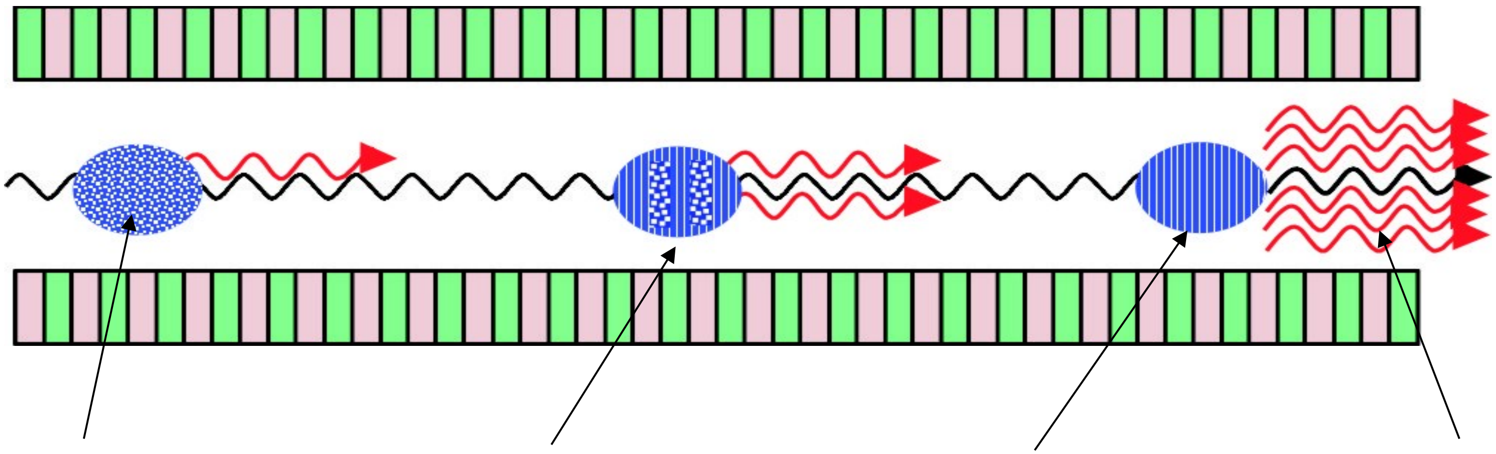
photons not coherent

Intensity limited by independent photon emission – scales as N_e

Concept of a free electron x-ray laser

- Replace storage ring by a linear accelerator
  allows compression of electron bunch – use once, then throw away

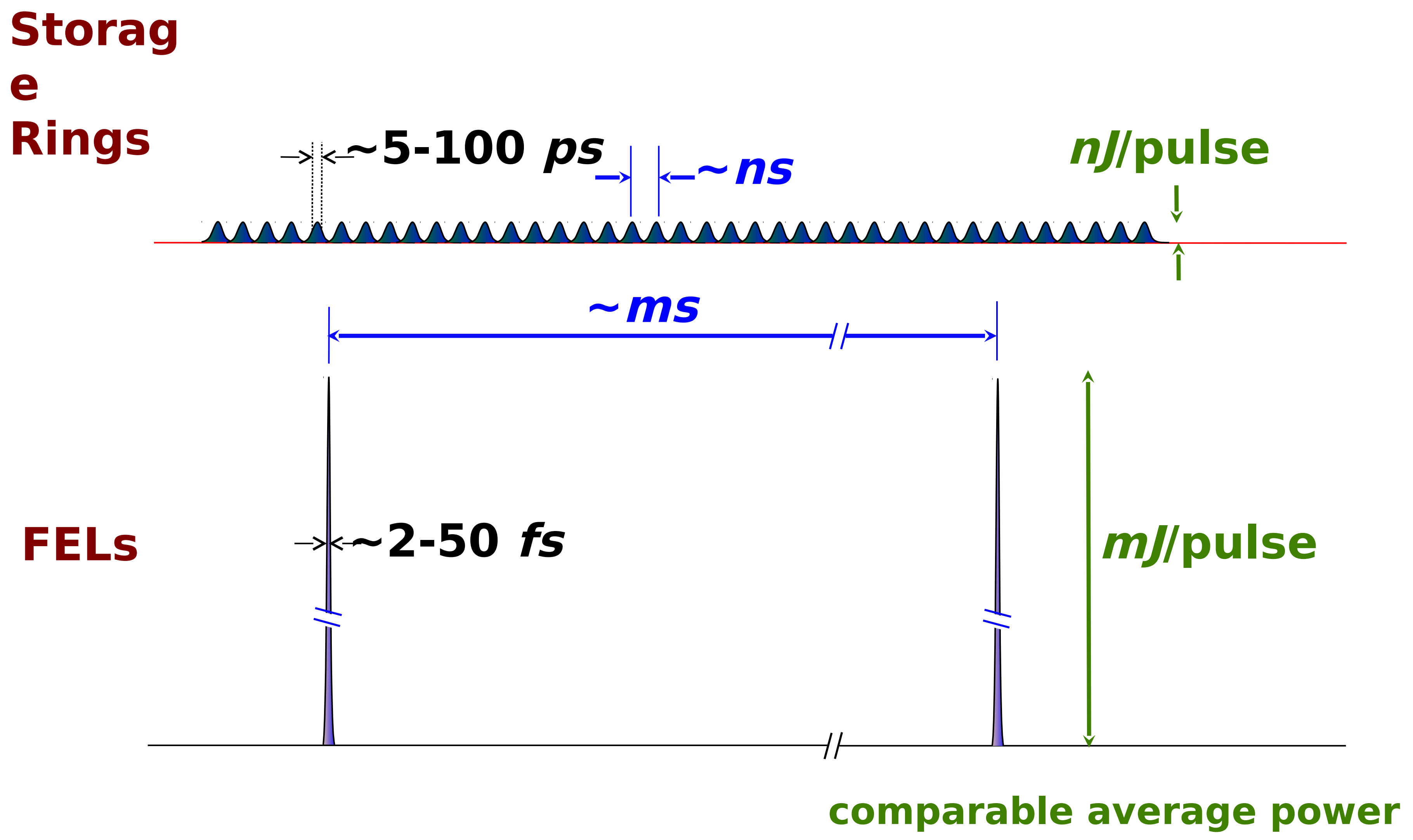
- Send electron bunch through a very long undulator



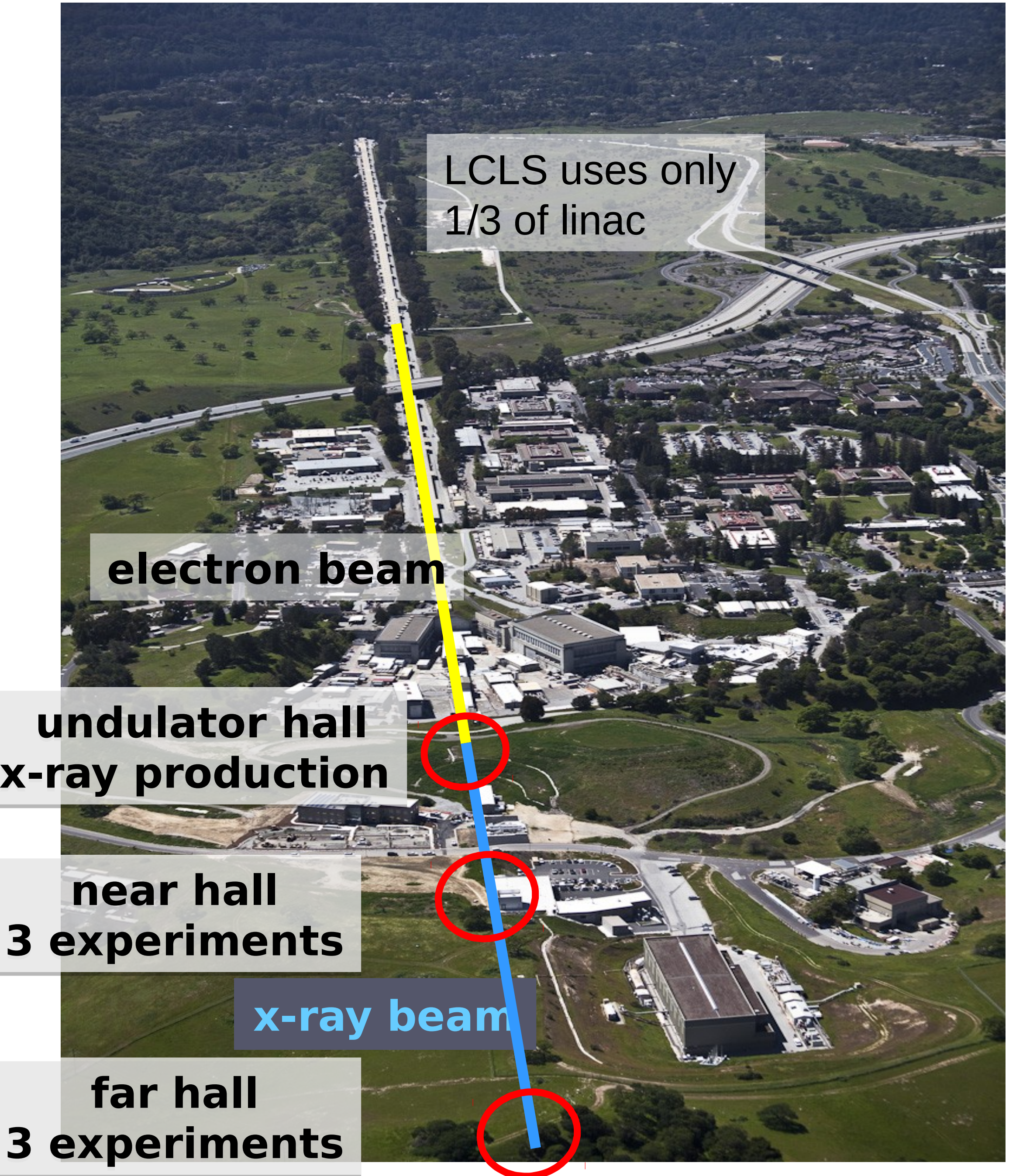
very short bunch length micrometers	**spontaneous** photons from back of bunch create order	ordered electrons enhance **stimulated** photon emission	amplified photons completely coherent

Intensity scales as N_e^2 or increased by 10^9

storage rings and x-ray lasers today

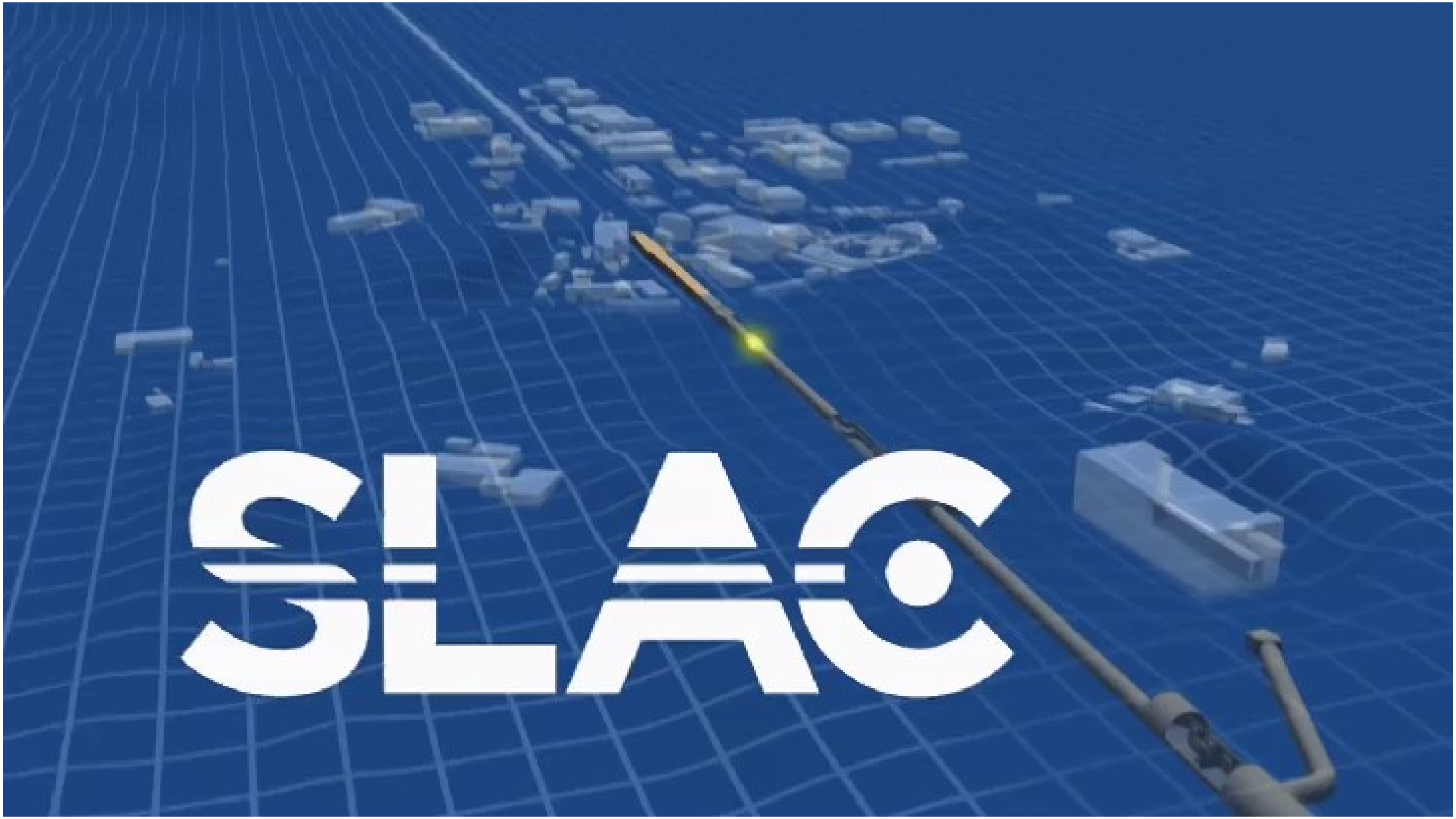


Linac Coherent Light Source



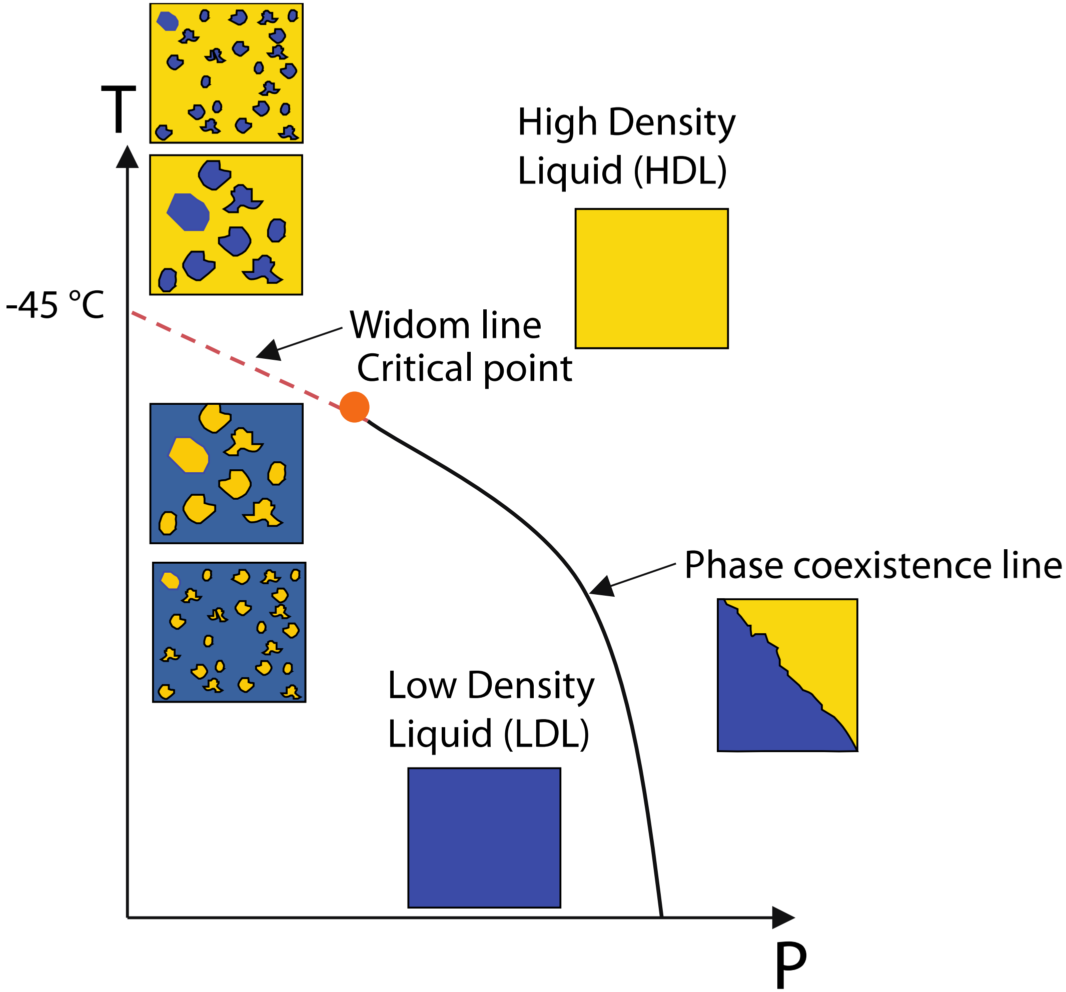
- Electron Energy: **15 GeV**
- Photon Energy: **0.5-10 keV**
- Pulse length: **5-500 fs**
- Flux: **10^{12}**
- Frequency: **120 Hz**
- E. Bandwidth: **0.1-2%**
- Machine Length: **2 km**

LCLS Movie



Different Models

Liquid-Liquid Transition (LLT) and Liquid-Liquid Critical Point (LLCP) Model

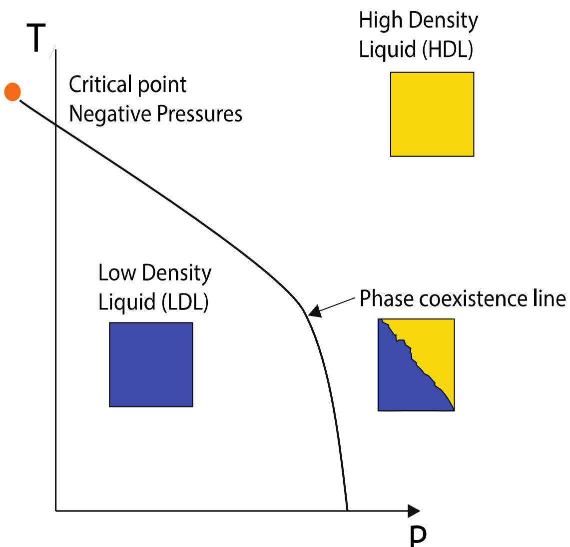


P.H. Poole, F. Sciortino, U. Essmann, H.E. Stanley, Nature **360** (1992) 324.

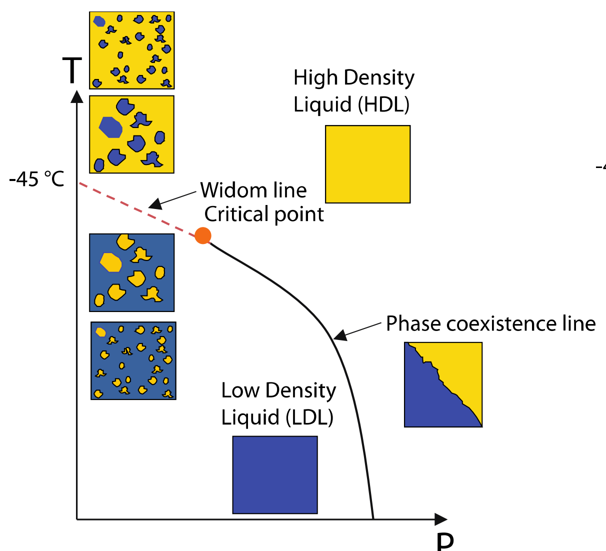
Unifying models Stokely et al. *PNAS* **107**, 1301 (2010)

Different Models Which is most likely Experiments?

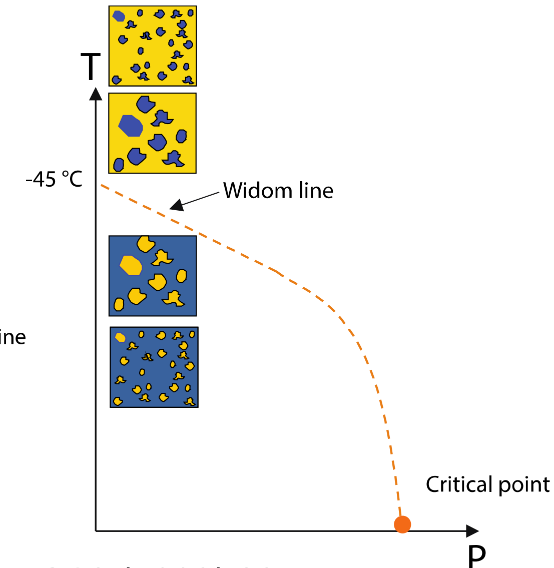
Critical Point Free Model Critical Point at -P



Critical Point Model Critical Point at +P



Singularity Free Model Critical Point at 0K

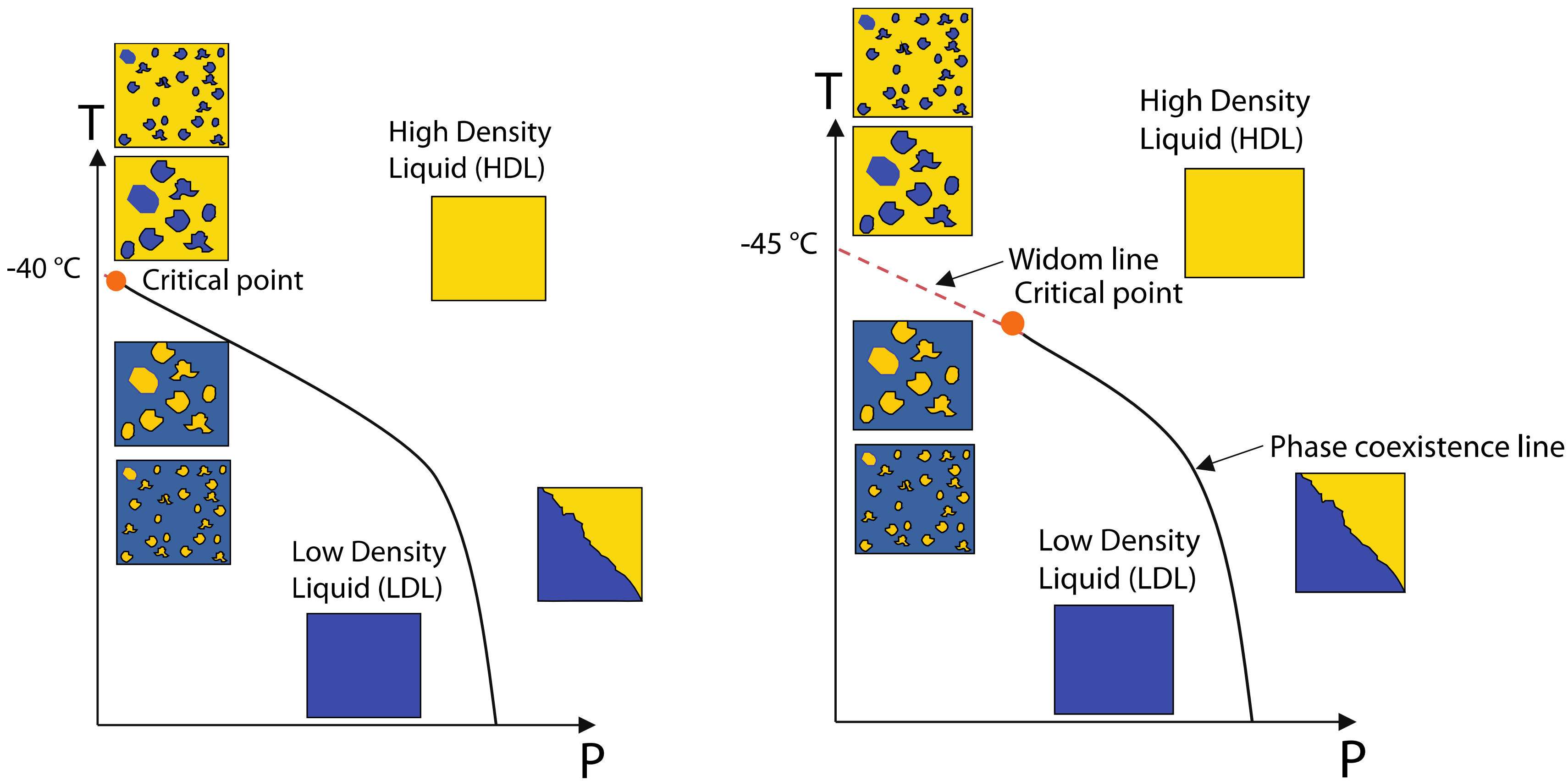


P.H. Poole, F. Sciortino, U. Essmann, H.E. Stanley, Nature **360** (1992) 324.

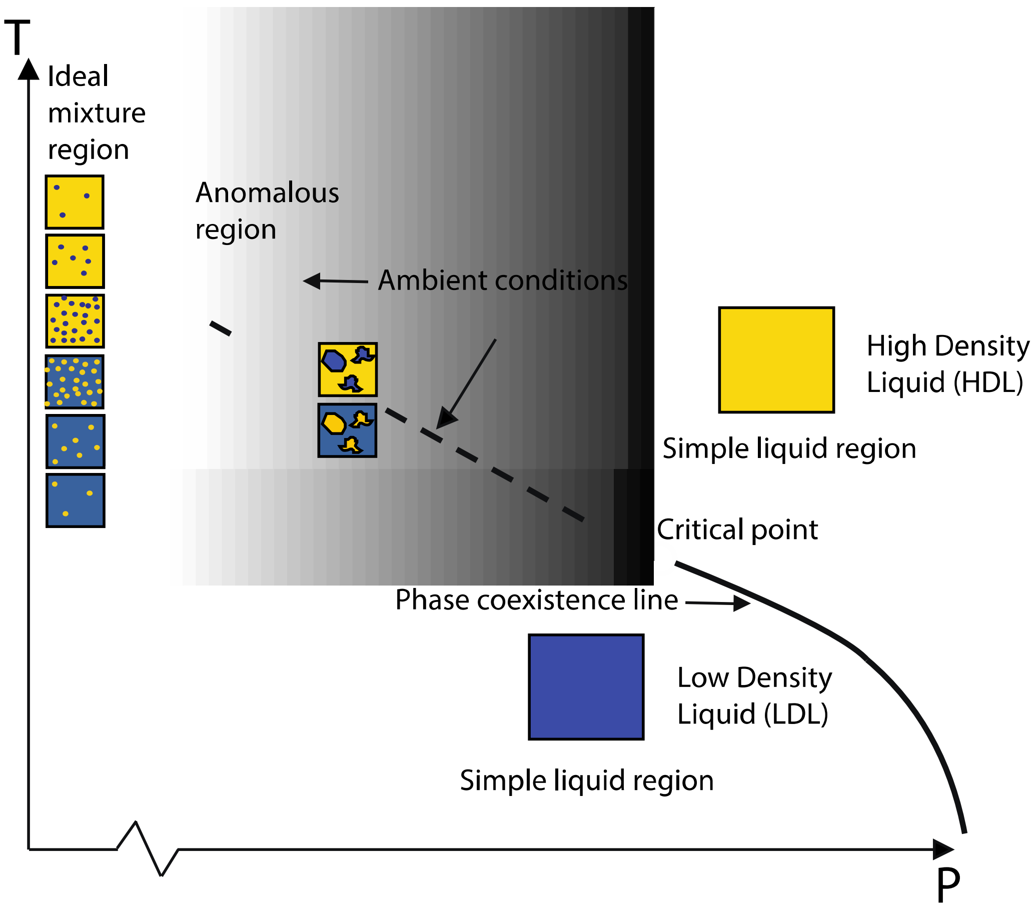
C.A. Angell, Science **319** (2008) 582.

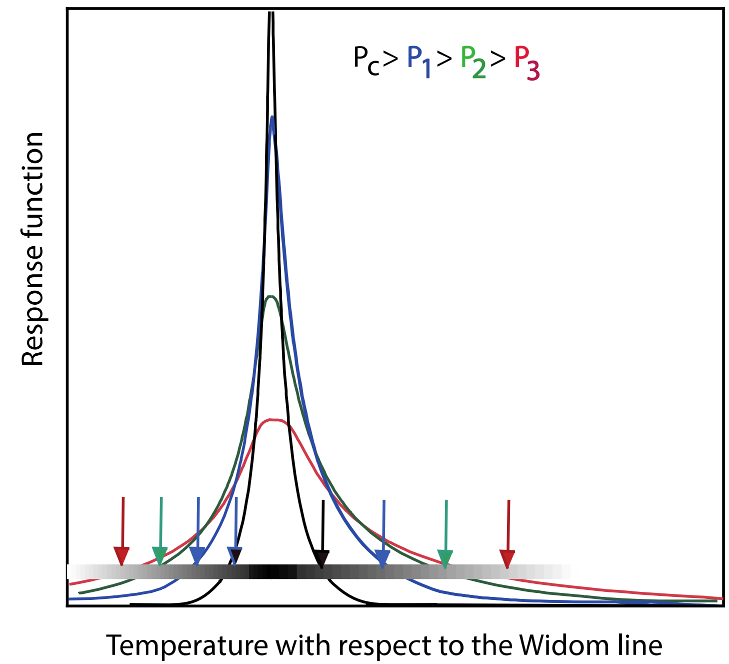
S. Sastry, P.G. Debenedetti, F. Sciortino, H.E. Stanley, Phys. Rev. E **53** (1996) 6144

Liquid-liquid Critical Point (LLCP) Model
If correct, at what pressure ?
Experiments?



Anomalous Region



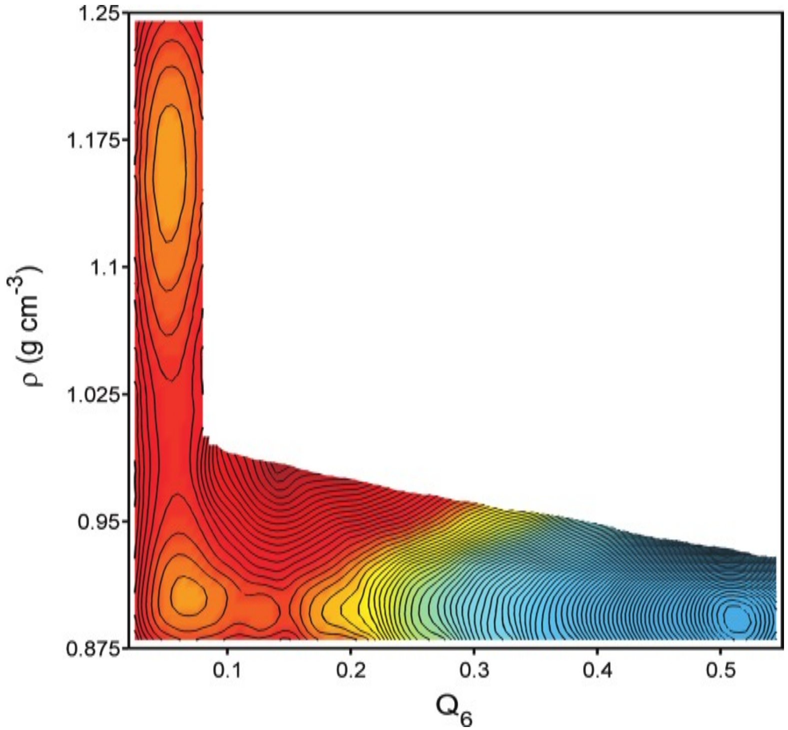


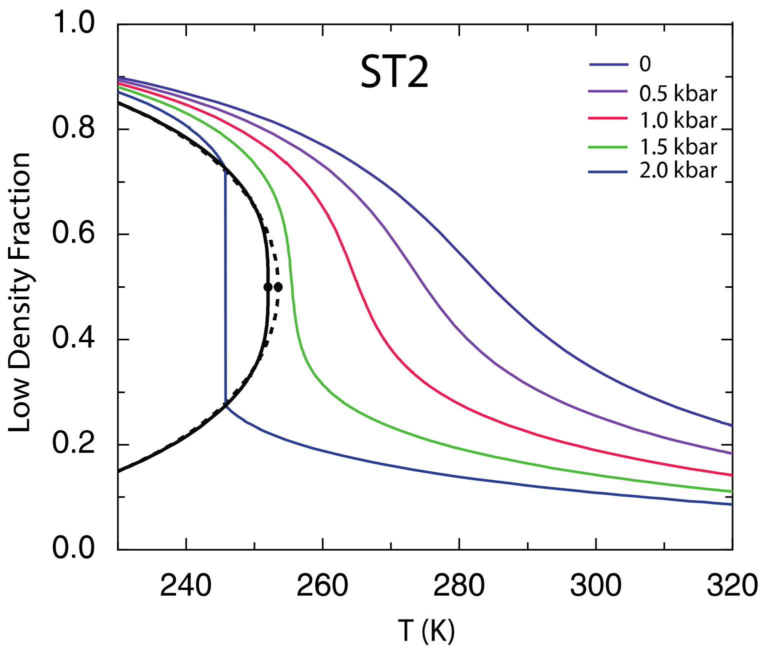
Nilsson and Pettersson, review in Nature Communication 6 8998 (2015)

Two State Upon Supercooling

ST2 shows the existence of LLT

Major variation in LDL temperature depende

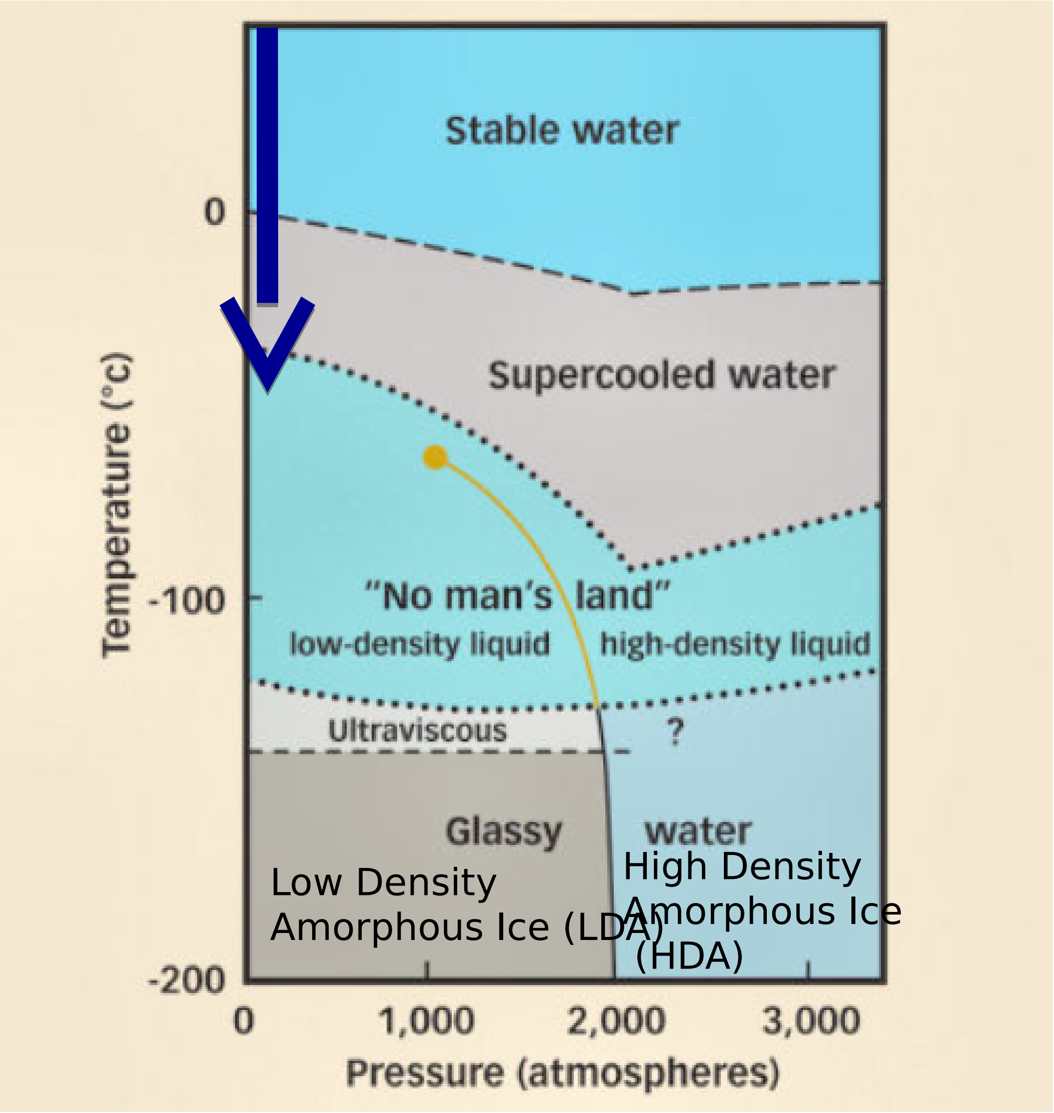




C. Palmer, F. Martelli, Y. Liu, R. Car,
. Z. Panagiotopoulos, P. G. Debenedetti, *Nature*, **385** (2014).

Vincent Holten , Jeremy C. Palmer , Peter H. Poole ,
Pablo G. Debenedetti , and Mikhail A. Anisimov *JCP* **140**, 104502 (2

rom Above No-Man’s Land



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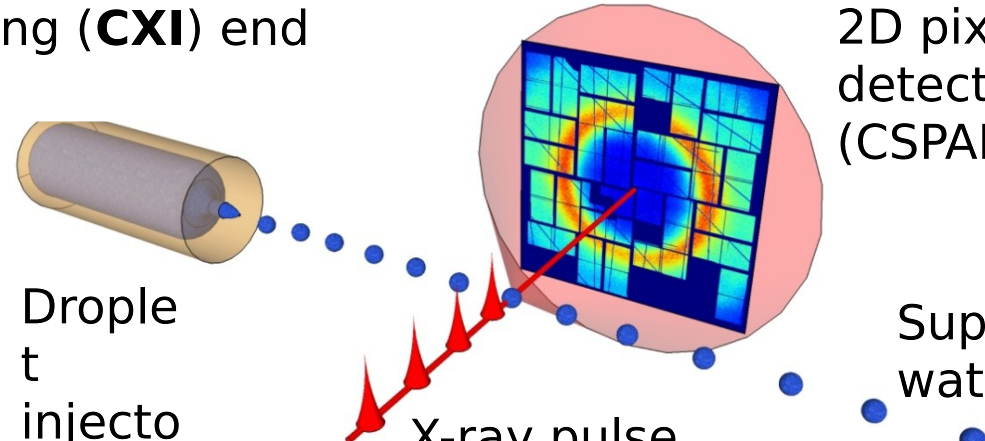
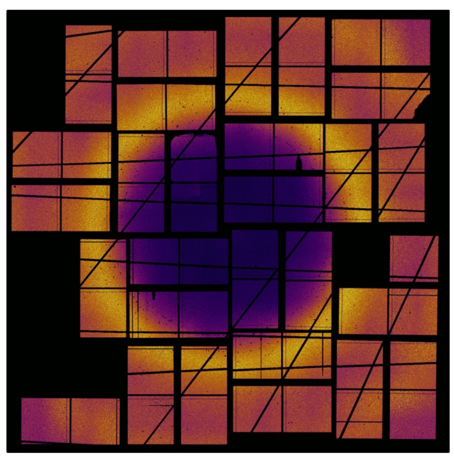
New Experiment to Probe Water in "No-man's Land

Linac Coherent Light Source (**LCLS**)
Coherent X-ray Imaging (**CXI**) end station

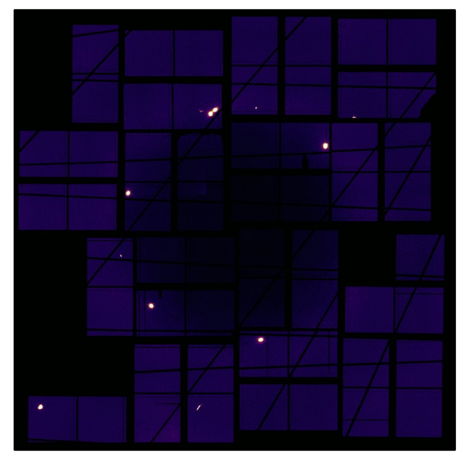
Beam energy: 9.4 keV
Wavelength: 1.32 Å
Pulse duration: 50 fs
Repetition rate: 120 Hz
Flux: 2×10^{12} photons/pulse
Focus: 1 and 10 μm^2



Water



Crystalline Ice

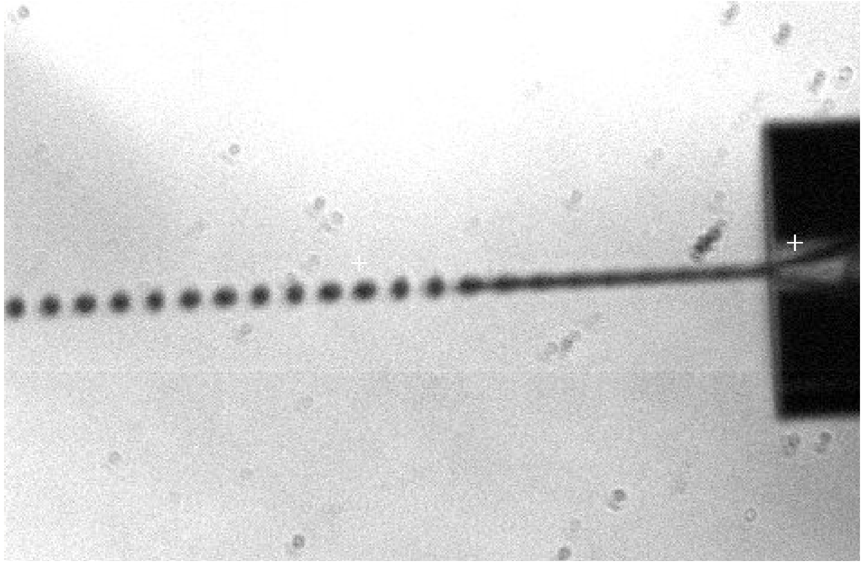


lberg et al. Nature 510, 381 (2014)

Water Droplet Sources

Gas Dynamics Virtual Nozzle
GDVN
Diameter ~ 9-13 μm

Drop-on-Demand (MicroFab)
DoD
Diameter ~ 40 μm

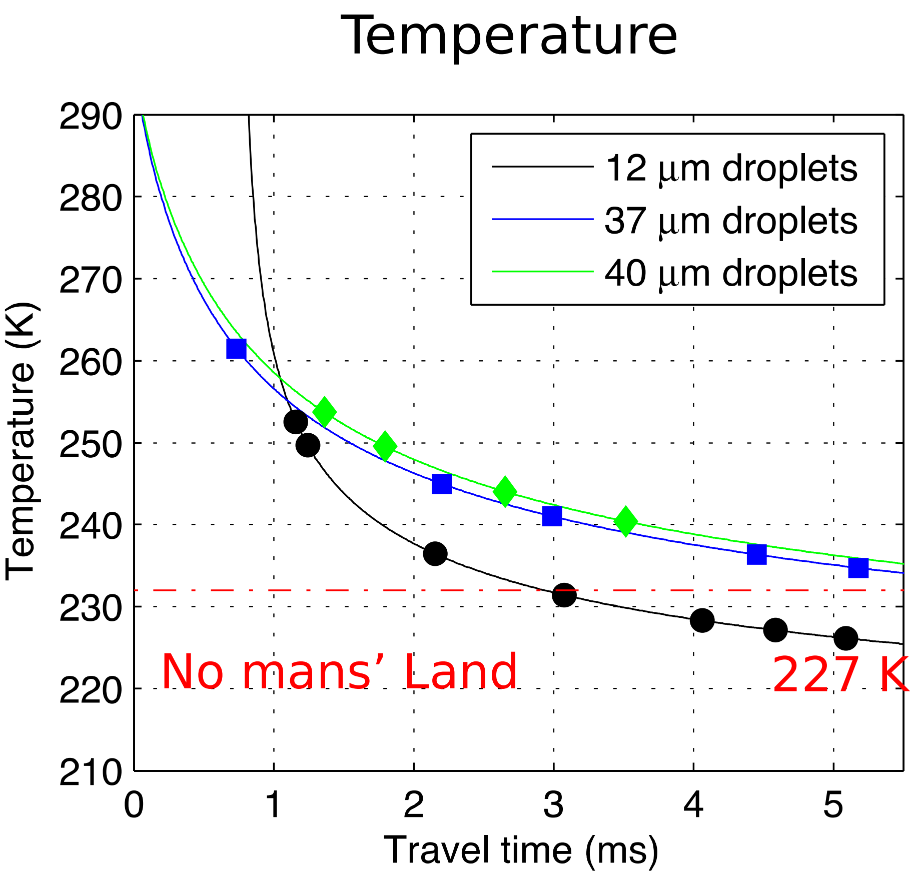


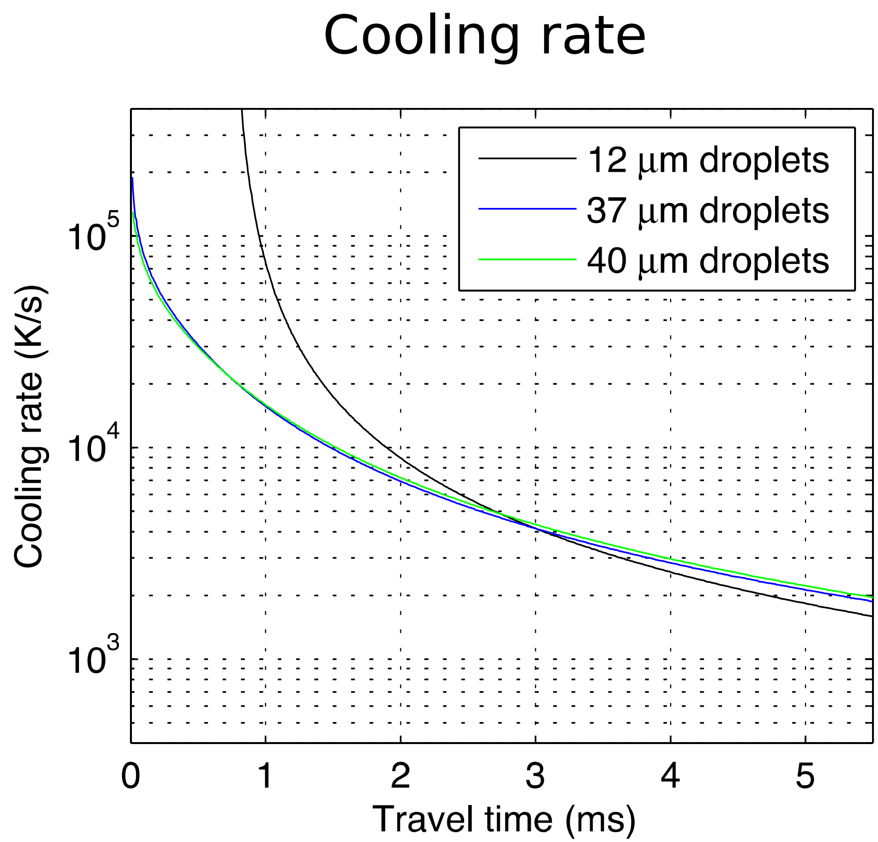
D. Deponte et al. *J. Phys. D: Appl. Phys.* 41, 195505 (2008).

arly liquid jet development M. Faubel *Z. Physik D* **10**, 269 (1988)

lberg et al. Nature 510, 381 (2014)

Temperature Calibration using Ballistic Evaporation Model





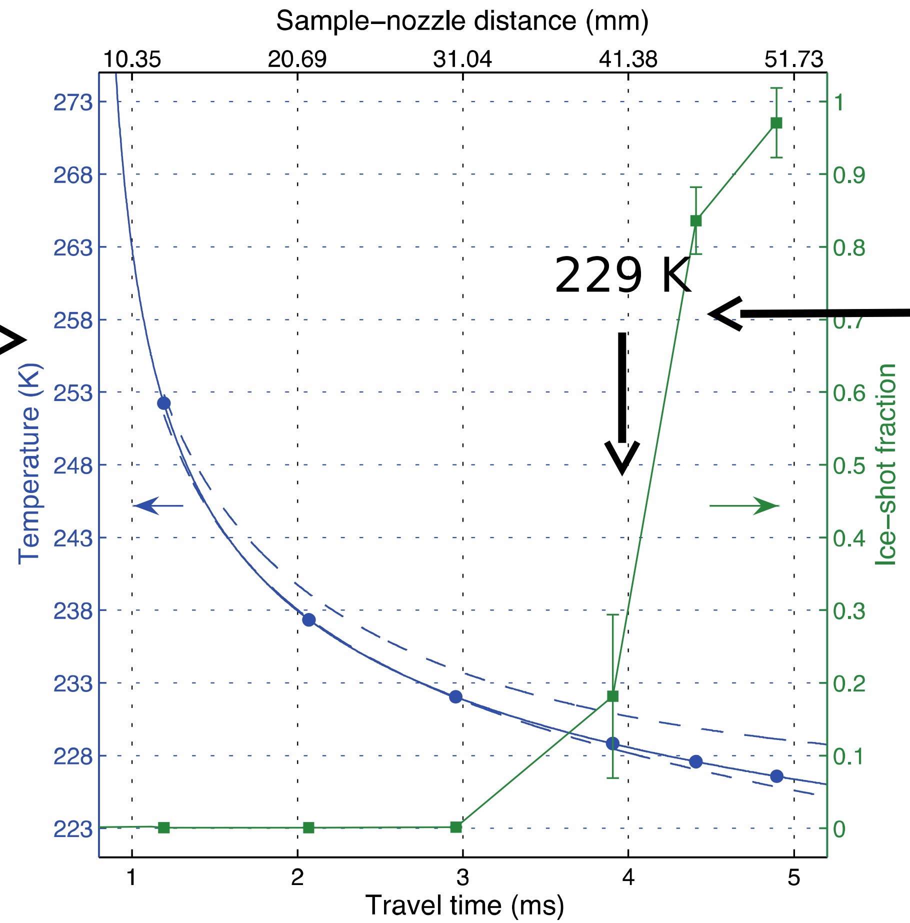
J. D. Smith et al. *J. Am. Chem. Soc.* 128, 12892 (2006).
I. W. Eames et al. *Int. J. Heat Mass Transfer.* 40, 2963 (1997).
lberg et al. Nature 510, 381 (2014)

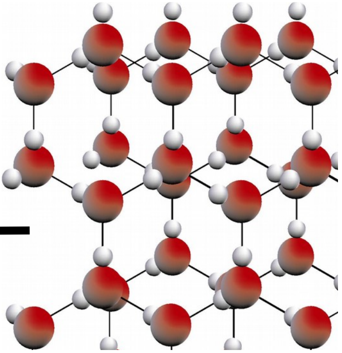
Formation of Ice

Droplets with detected ice

Ice fraction

Temperature



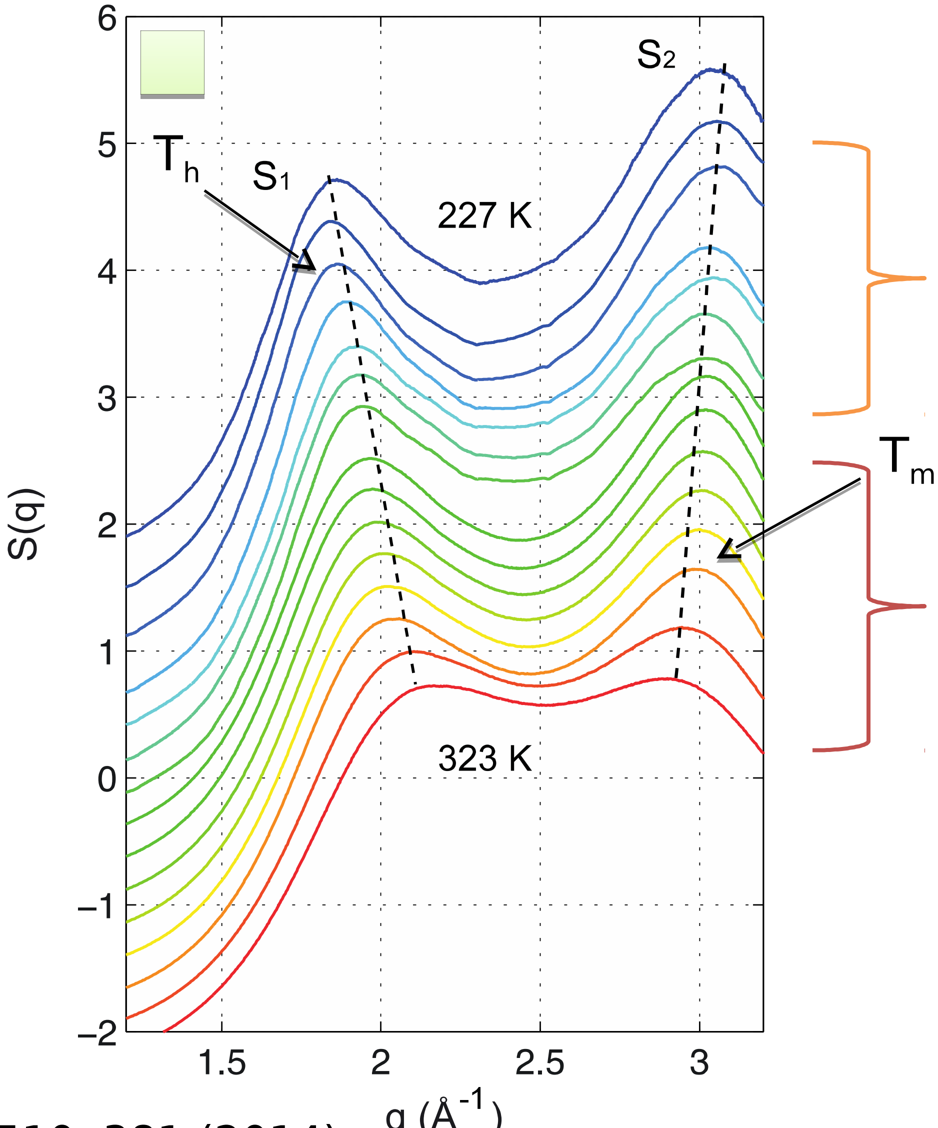


Travel time

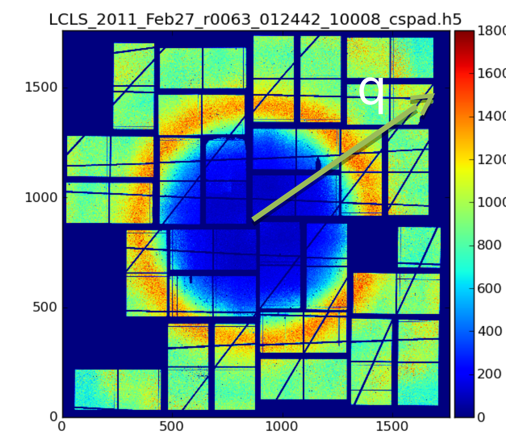
Water is metastable on 0.1-1 millisecond timescales

Sellberg et al. Nature 510, 381 (2014

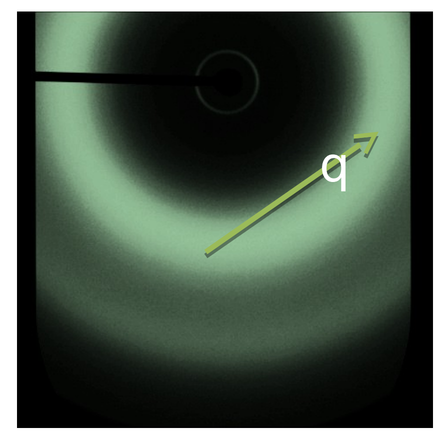
Split of the 1st water scattering S(q) peak



LCLS CXI, CSPAD

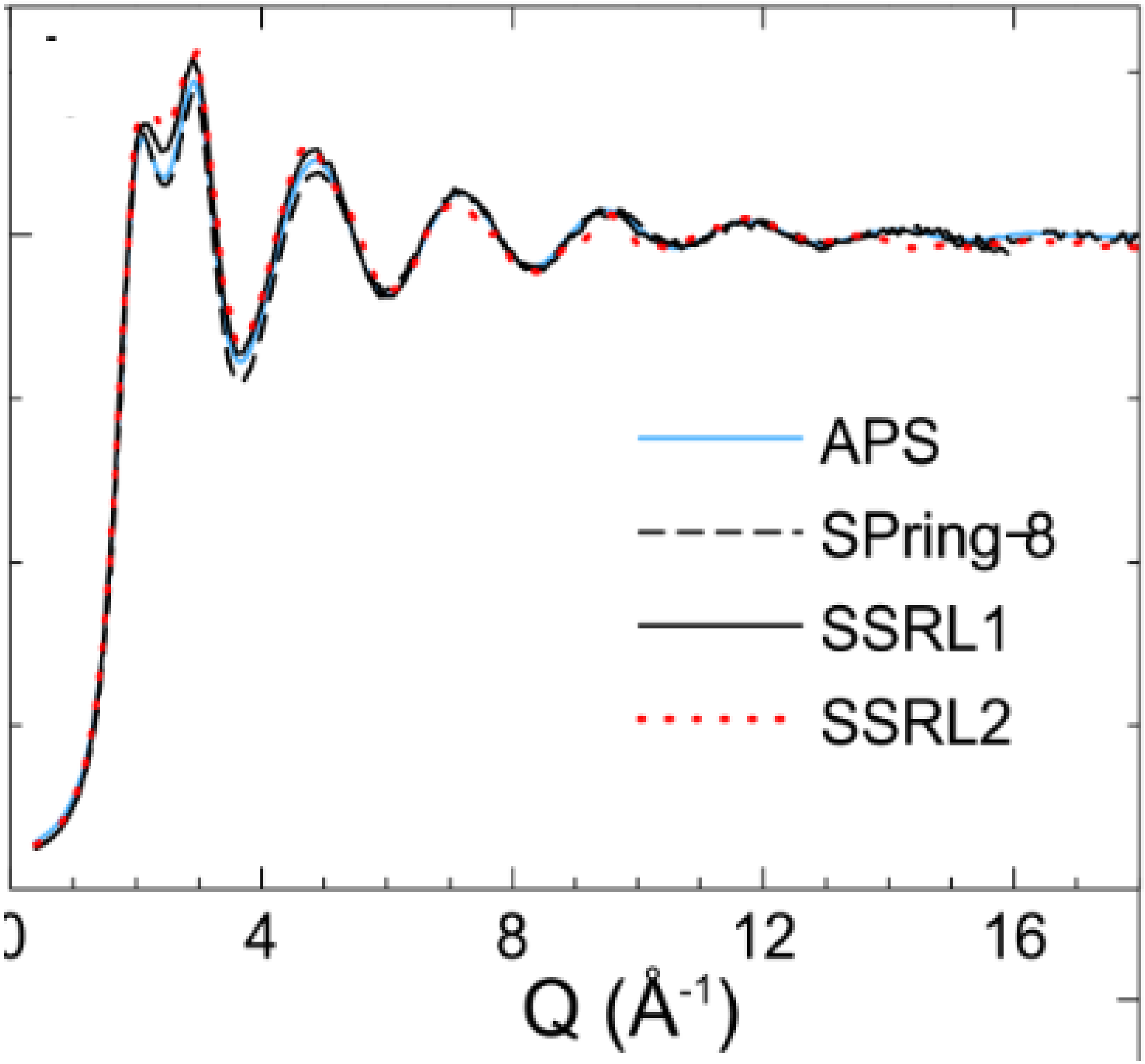


SSRL BL4-2
Rayonix MX225-HE



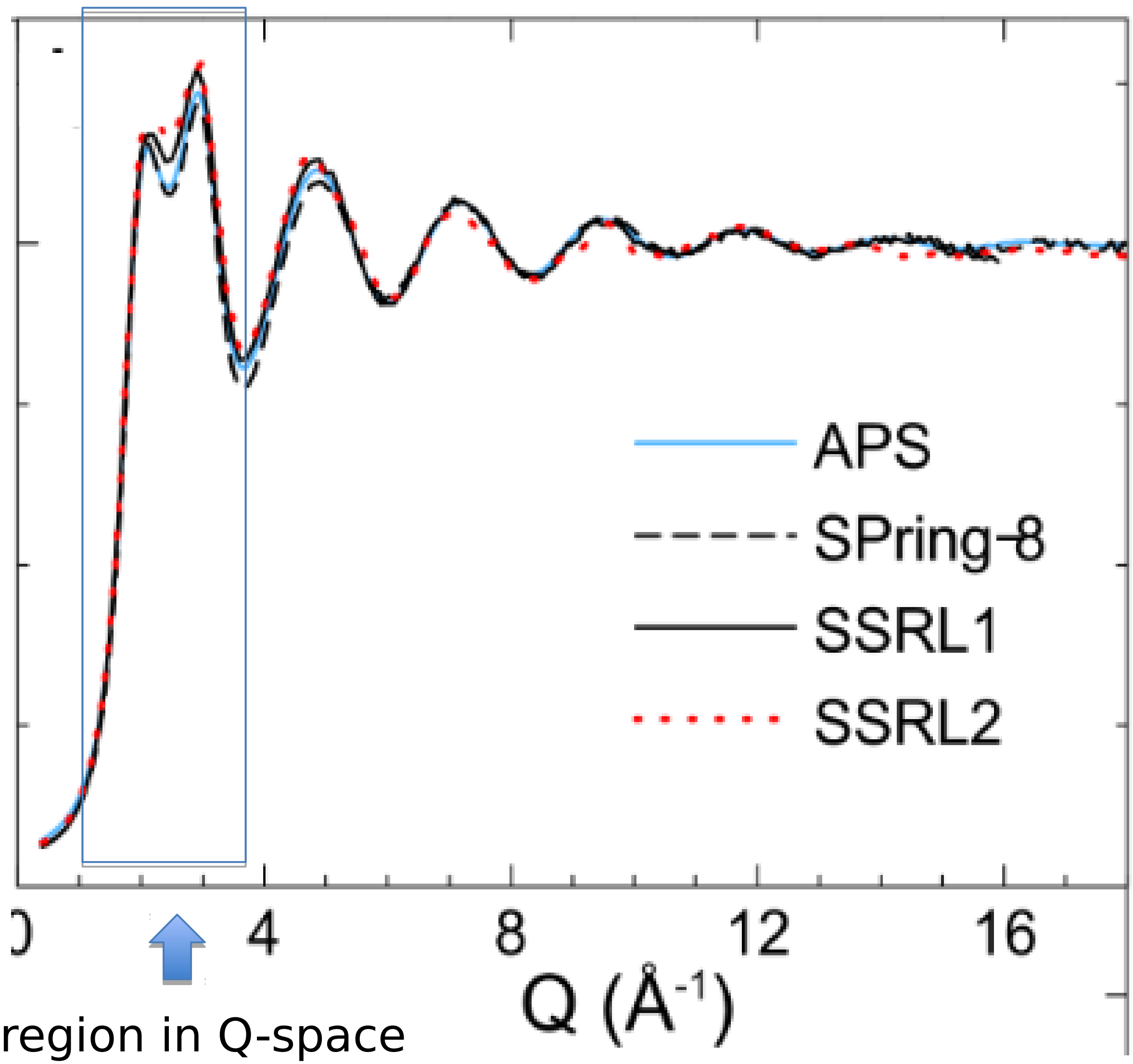
lberg et al. Nature 510, 381 (2014)

Structure Factor from X-ray Scattering



kinner et al. J. Chem. Phys. **138**, 074506 (2013).

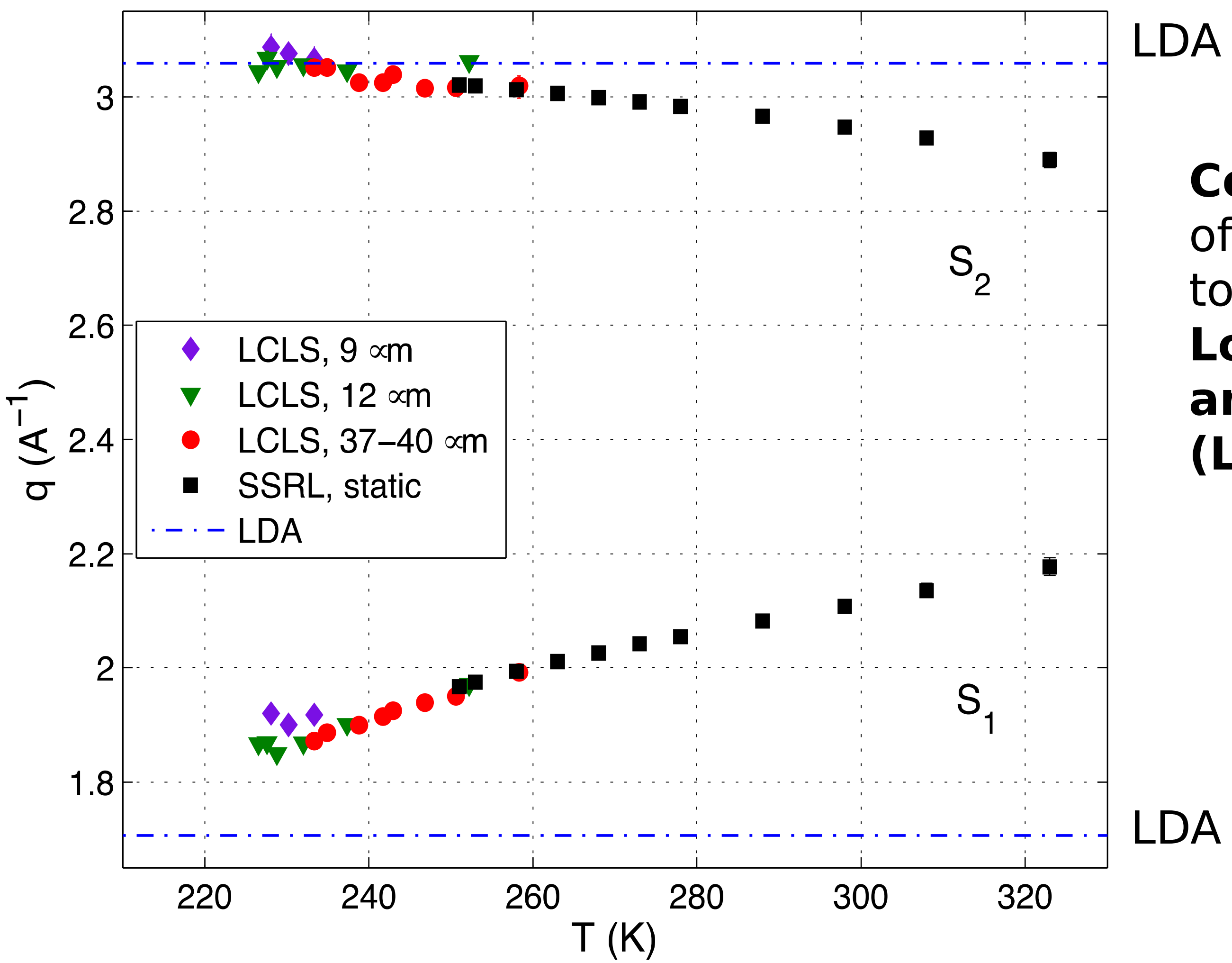
Structure Factor from X-ray Scattering



region in Q-space

kinner et al. J. Chem. Phys. **138**, 074506 (2013).

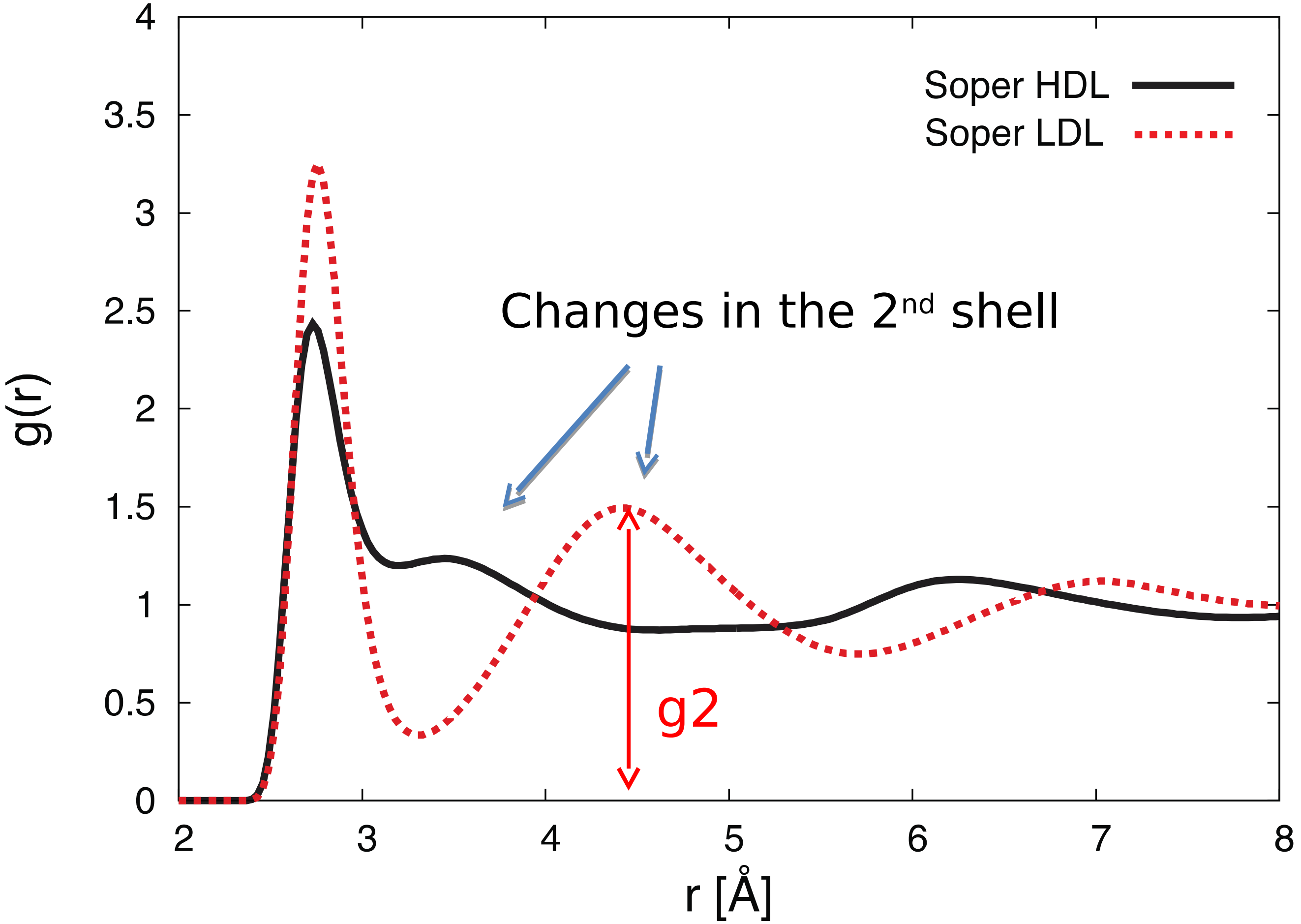
emperature dependence of S1 and S2 peak positi

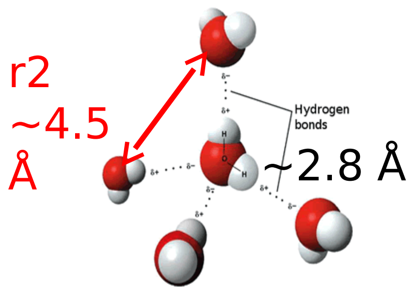


Continuous change of the liquid structure towards **Low density amorphous ice (LDA)**

lberg et al. Nature 510, 381 (2014)

S(q) split is a fingerprint of **tetrahedrality** of liquid water

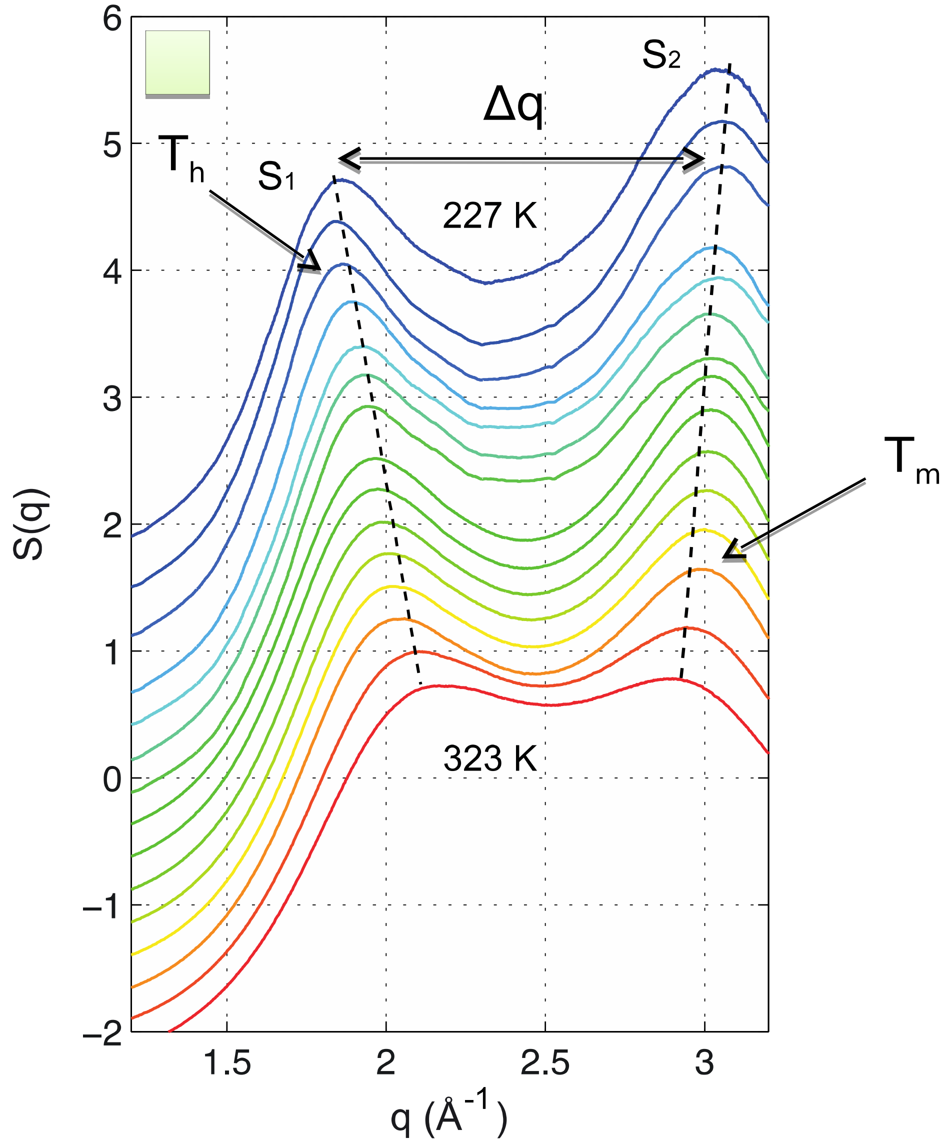


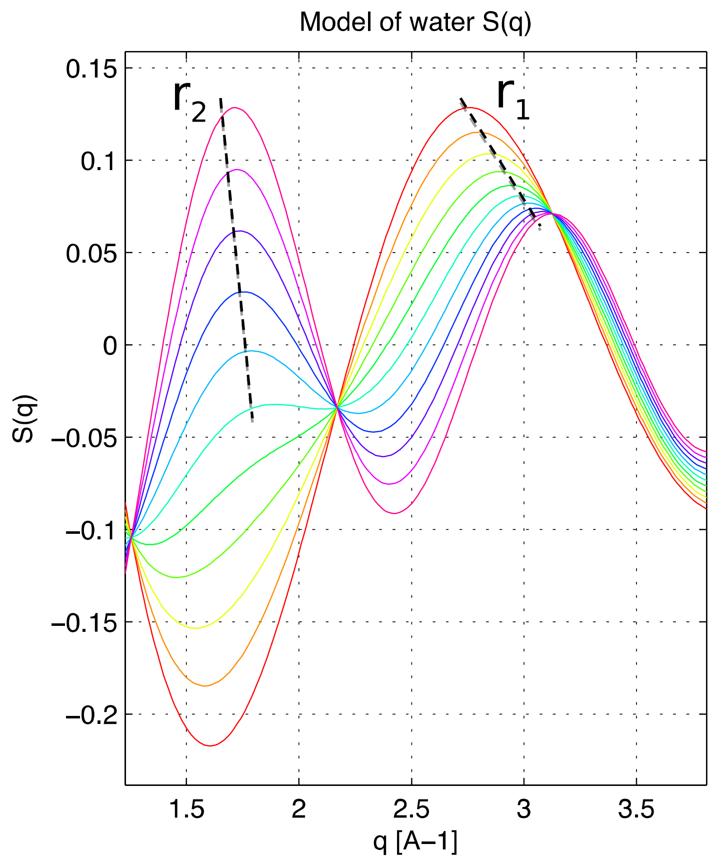


g2 Height of 2nd shell in the O-O Pair Correlation function
Directly related to amount and ordering of tetrahedral water (LDL)

Ricci and Soper, Phys. Rev. Lett. **84**, 2881 (200

Structure Factor



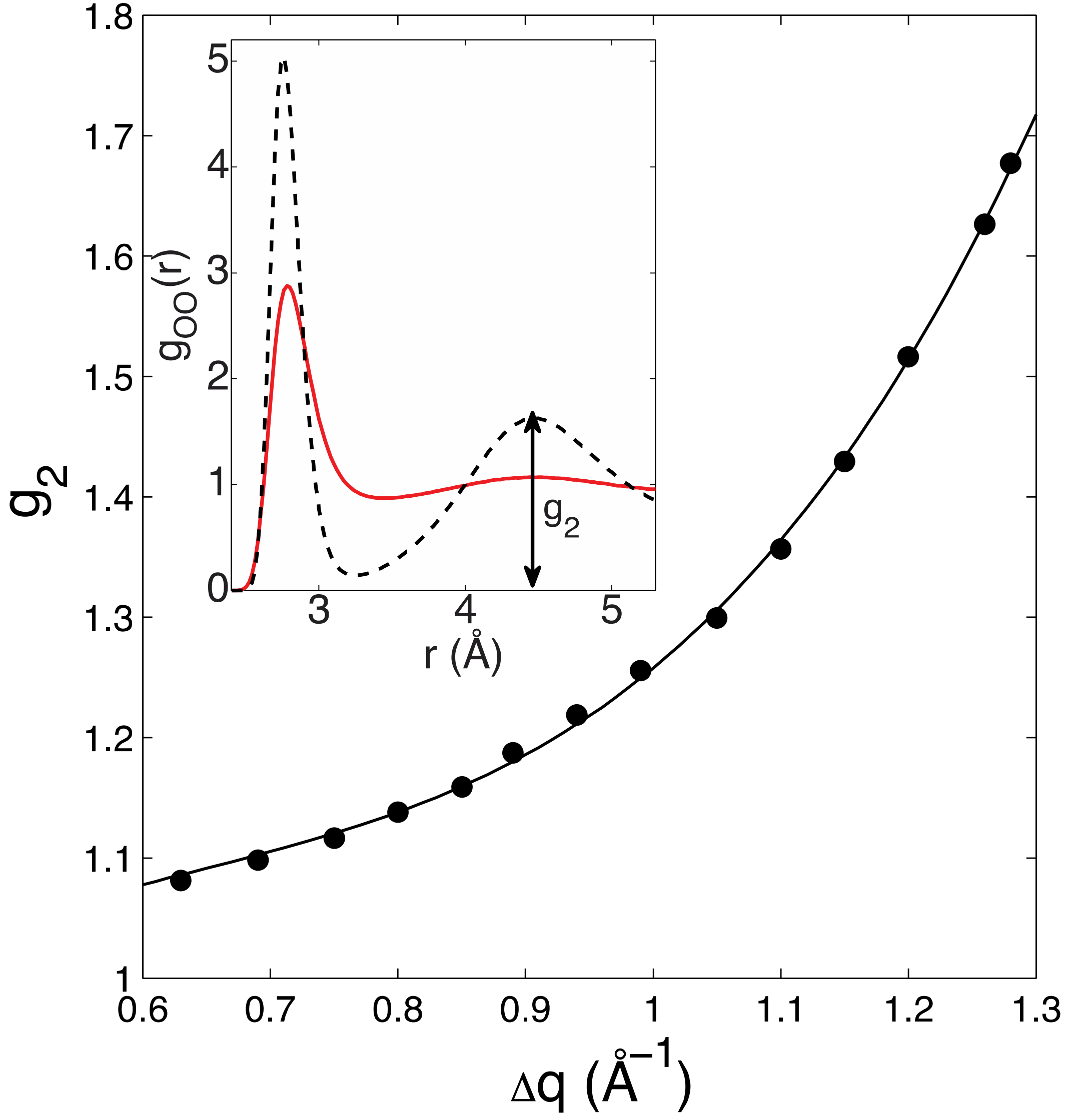


$$S = \frac{\sin(qr_1)}{qr_1} + \frac{\sin(qr_2)}{qr_2}$$

r_1 = 2.8 Å, r_2 = 4.5 Å

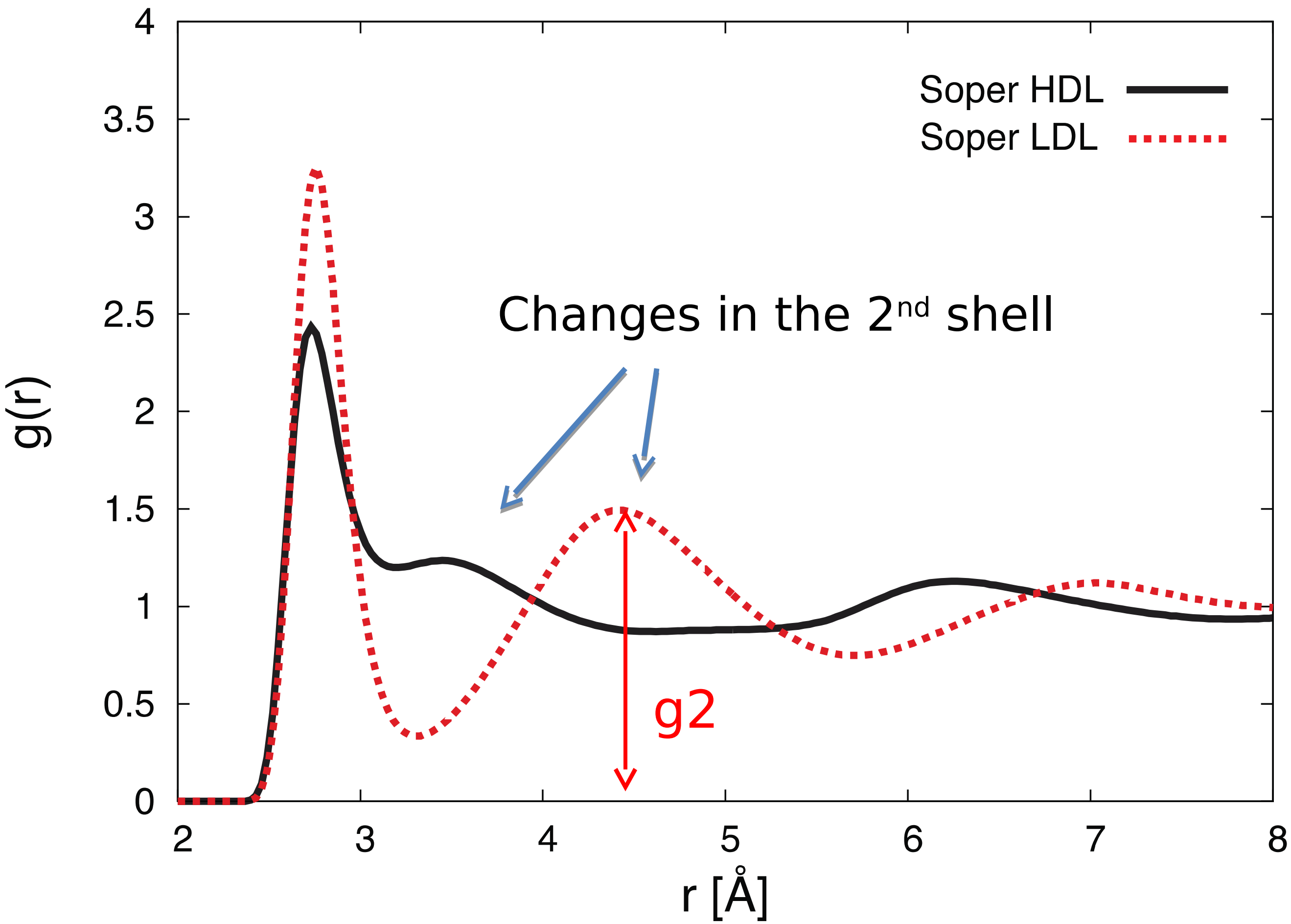
Quantify the relationship between S(q) Split (Δq) and the tetrahedrality (g2)

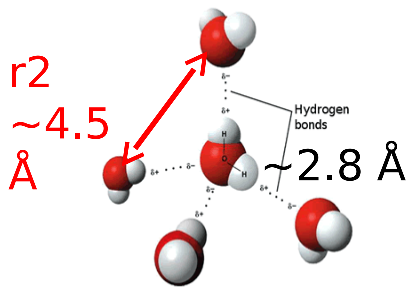
Using **TIP4P/2005 MD water model**



lberg et al. Nature 510, 381 (2014)

S(q) split is a fingerprint of **tetrahedrality** of liquid water



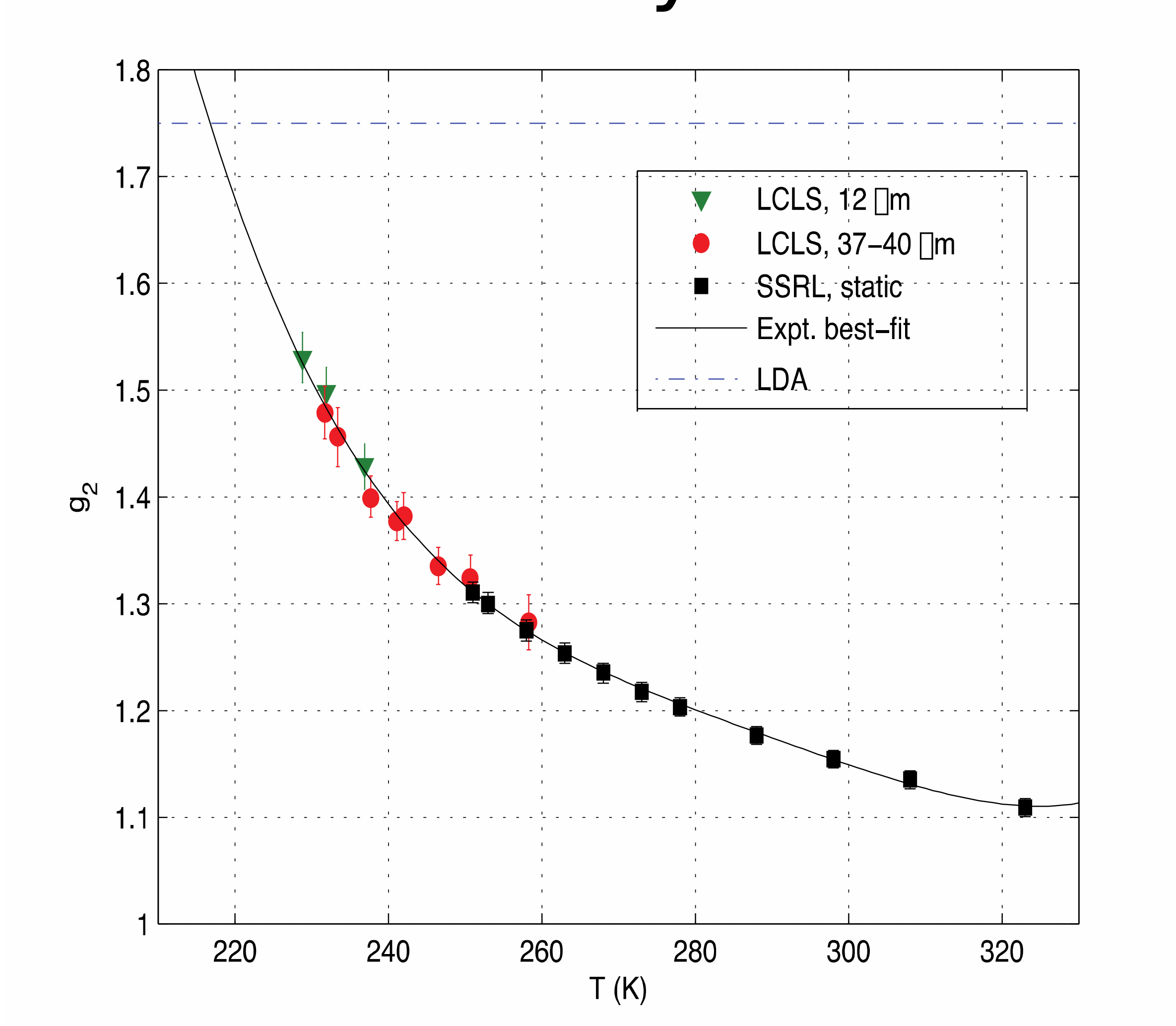


g2 Height of 2nd shell in the O-O Pair Correlation function
Directly related to amount and ordering of tetrahedral water (LDL)

Ricci and Soper, Phys. Rev. Lett. **84**, 2881 (200

Experimental variation of the tetrahedrality

g_2 is the 2nd shell distance as a measure of tetrahedrality



LDA

Transition from **HDL to a LDL** dominated liquid

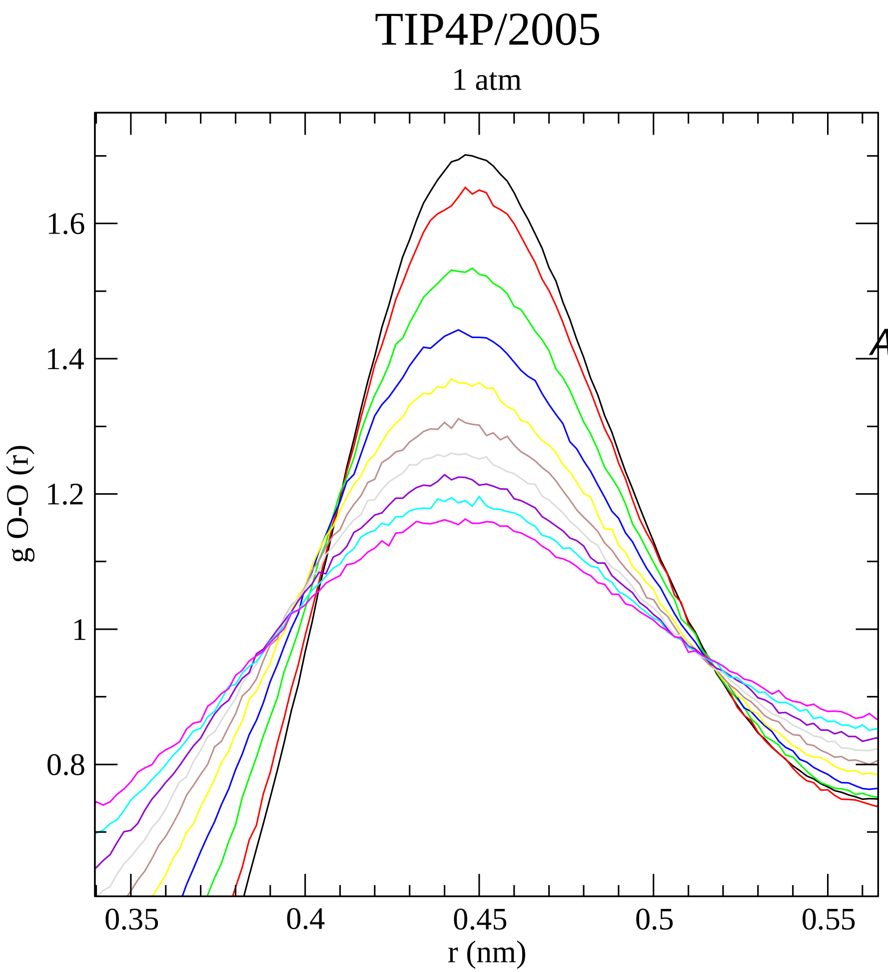
At lowest temperatures it is **getting quite close to LDA**

The transformation is **continuous**

The transformation is **strongly accelerated** below 240 K

lberg et al. Nature 510, 381 (2014)

Defining peak area



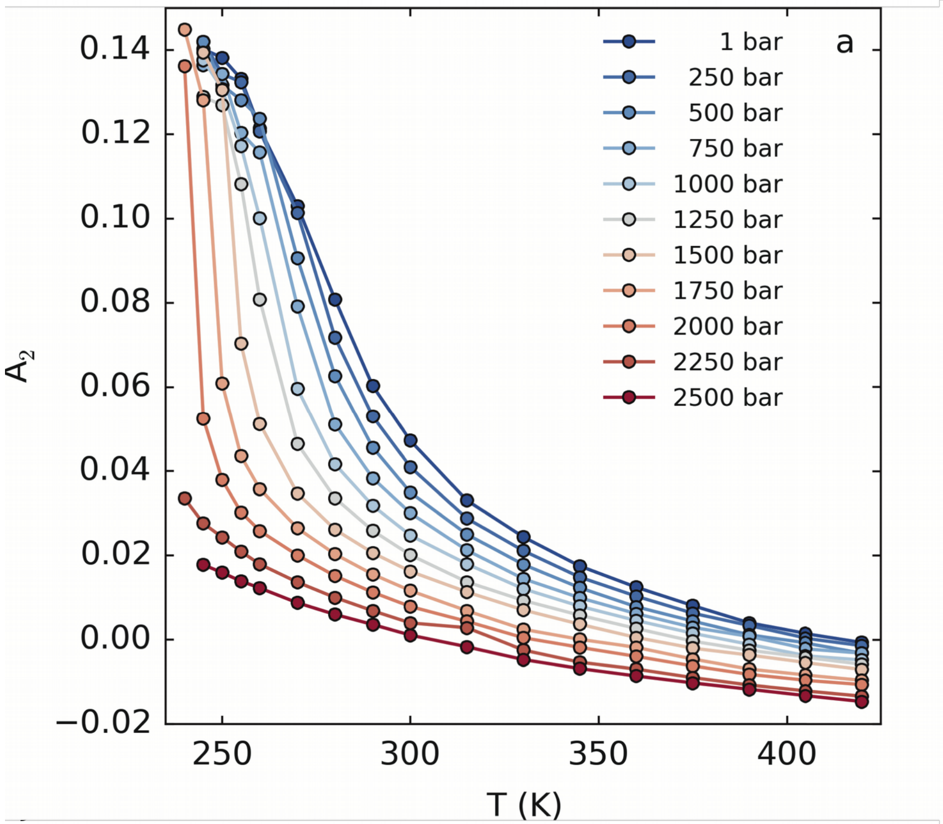
$$A_2 = 4\pi \int_{r_1}^{r_2} \left(g_{OO}(r) - 1\right) r^2 dr$$

$A2 =$

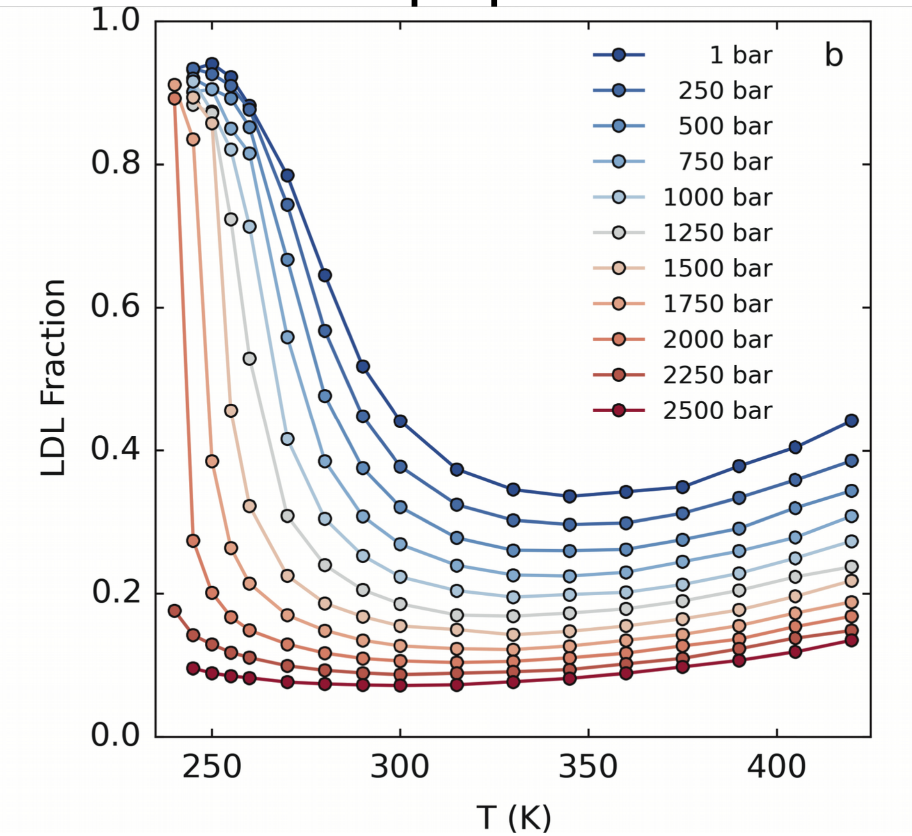
Relative number of excess O atoms (excess wrt bulk) around a central oxygen atom within a range of r1 to r2

ST2

A2



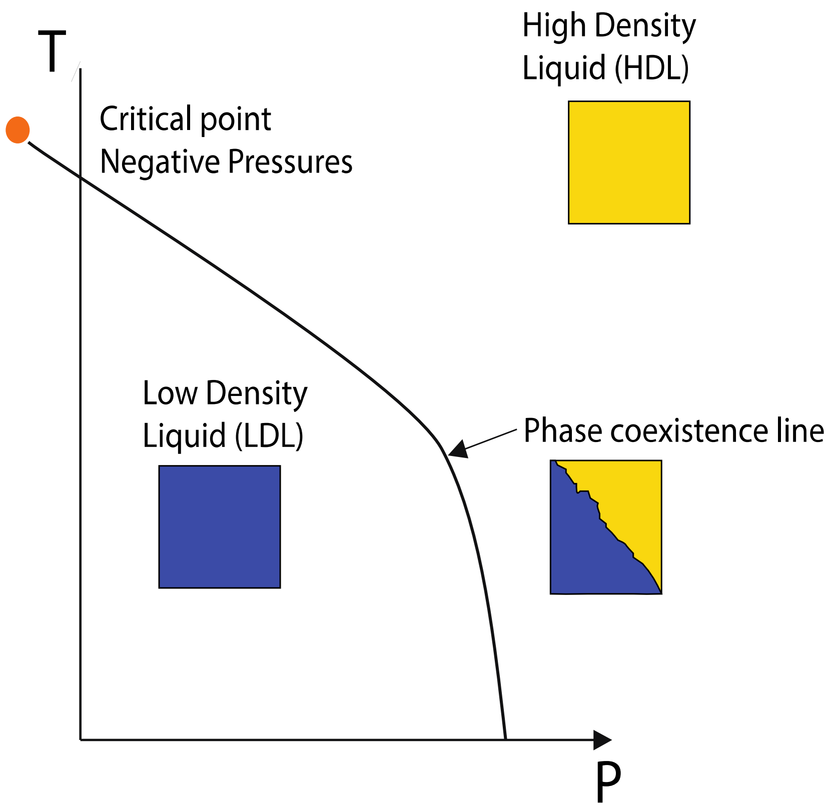
LDL population

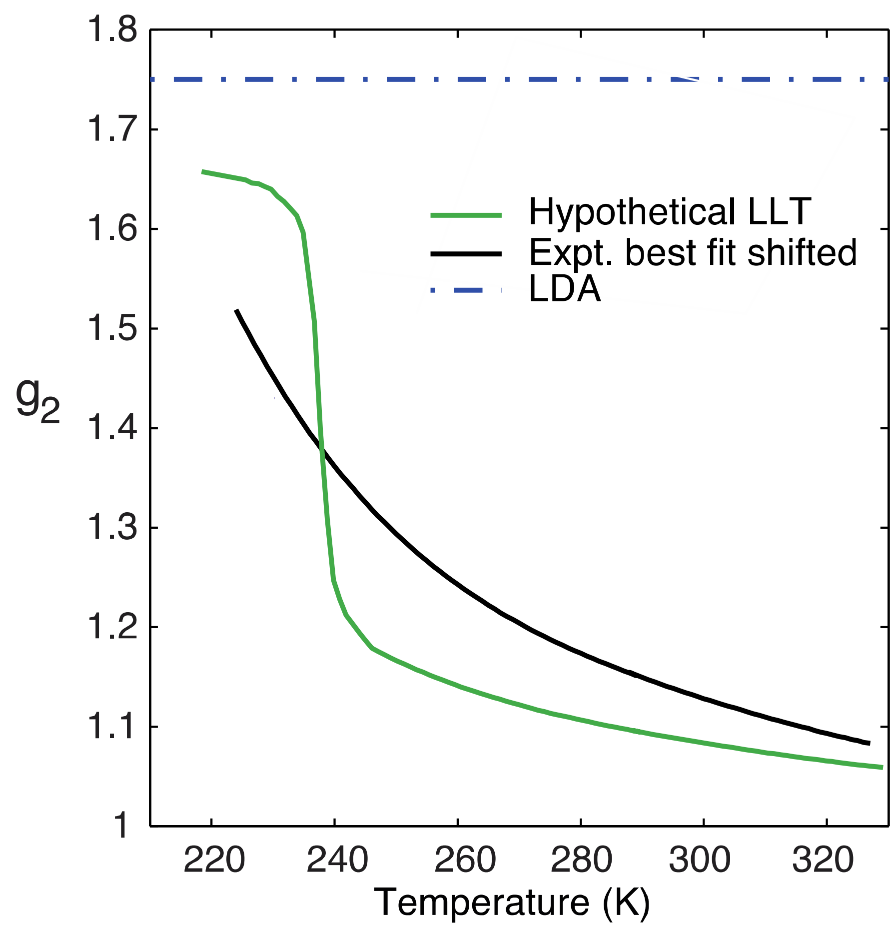


A2 and LDL population follows the same trend
Gets steeper towards a critical point

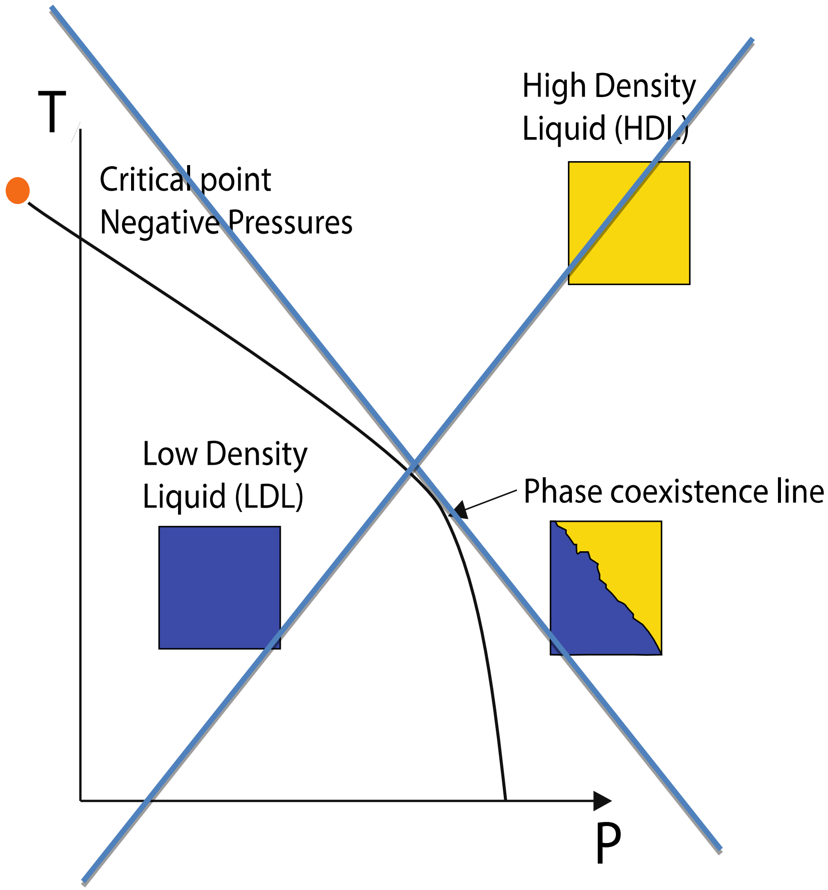
H. Pathak et al., submitted

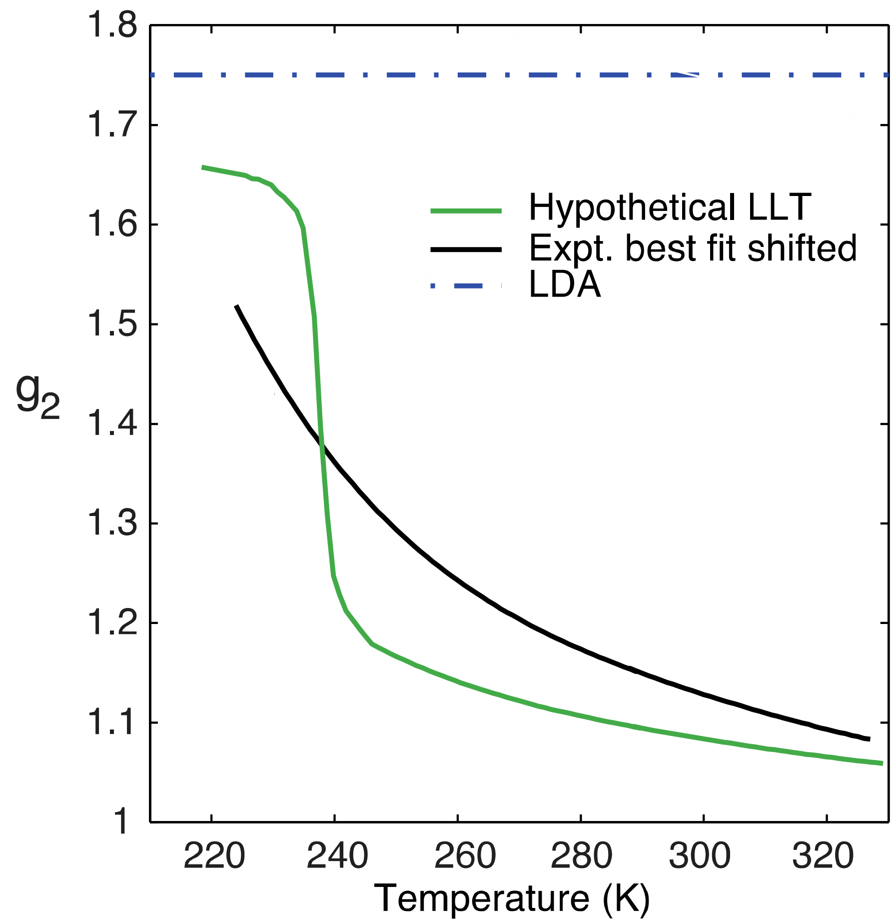
Liquid-Liquid Transition at 1bar?





No Liquid-Liquid Transition at 1bar!



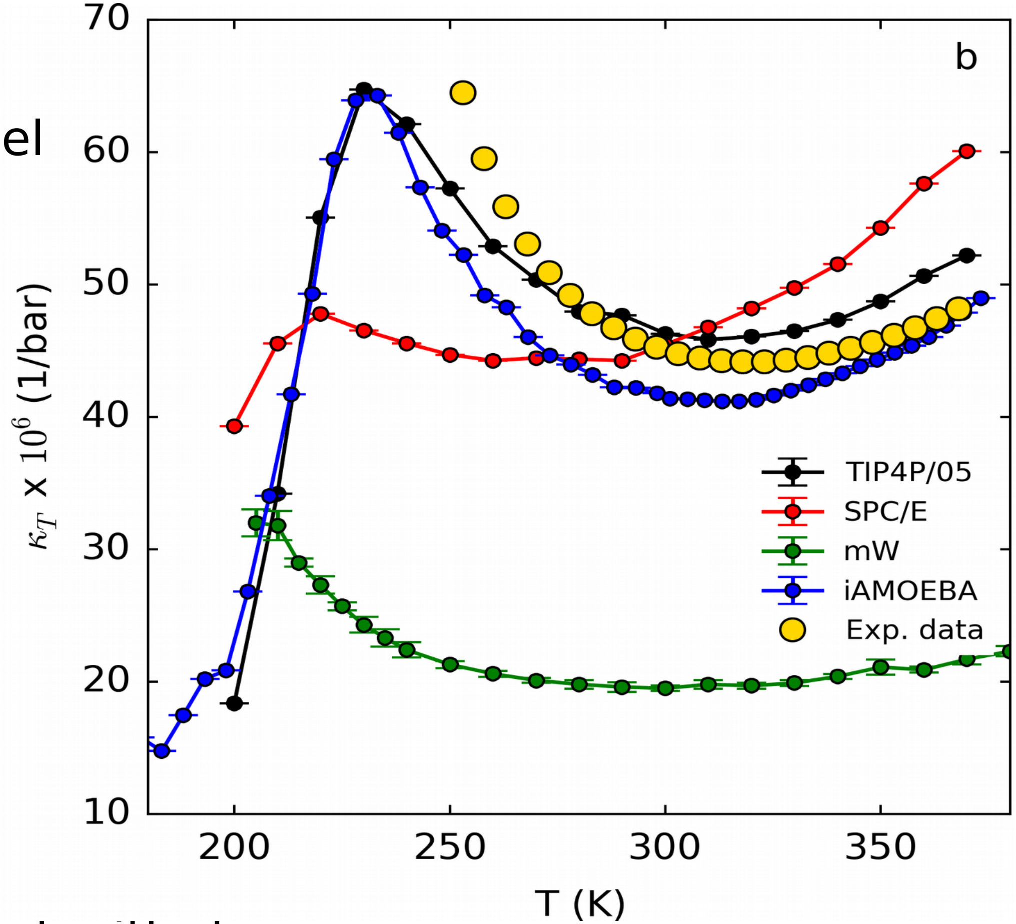


Isothermal Compressibility

TIP4P/2005 LLCP 193 K and 1.35 kbar
SPC/E LLCP 130 K and 2.90 kbar Real or Virtual?

TIP4P/2005 shows Widom line at 230 K
SPC/E very faint Widom line at 220K
Singularity Free Model?

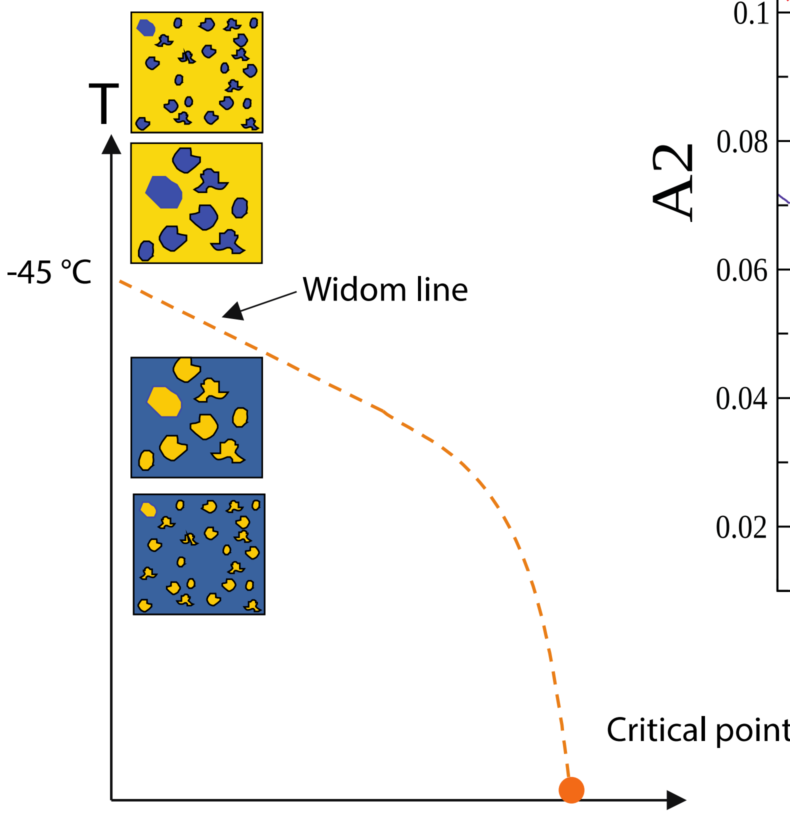
ingularity Free Model

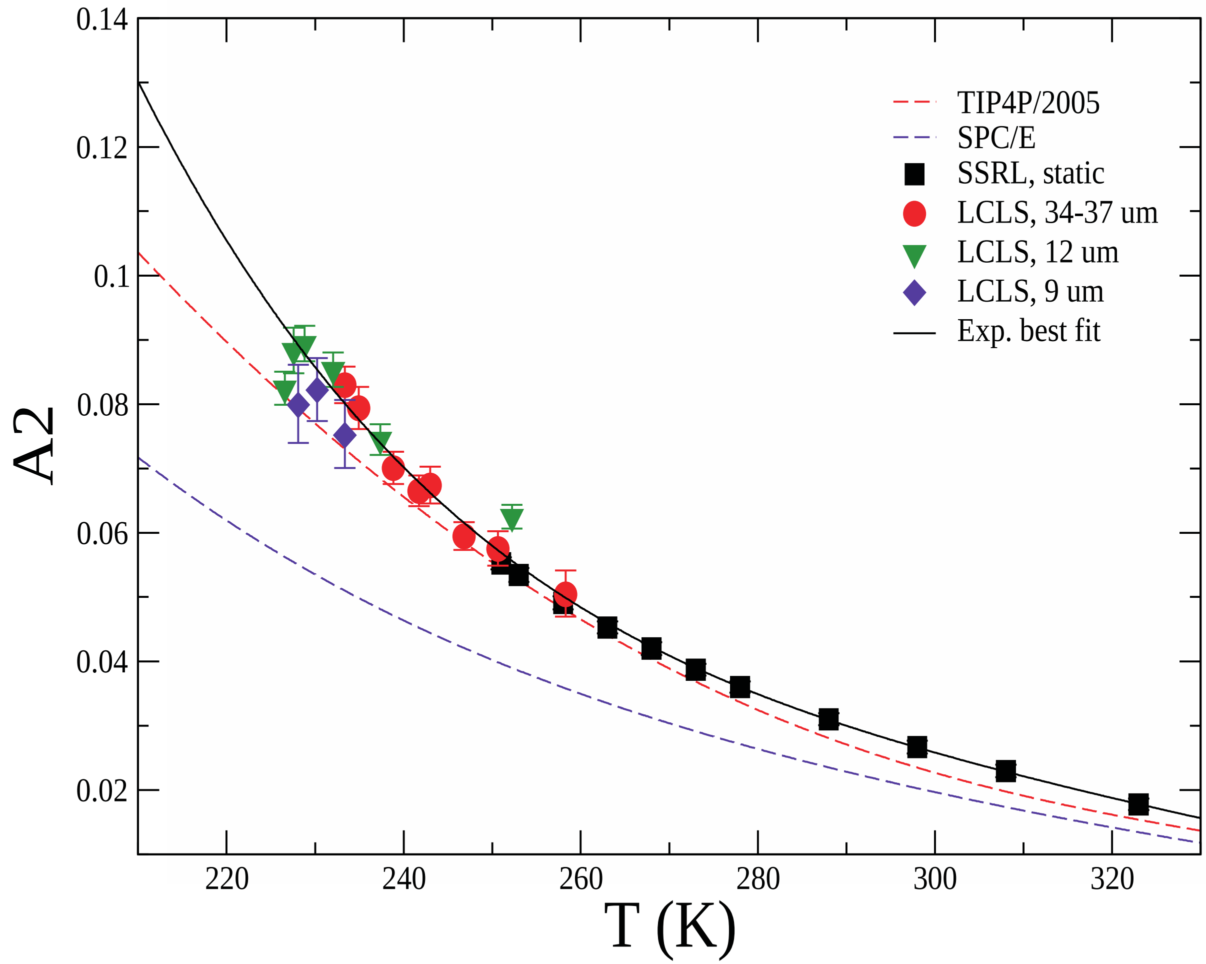


H. Pathak et al., submitted

Enhanced Fluctuations from Singularity Free Model

Singularity Free Model
Critical Point at 0K



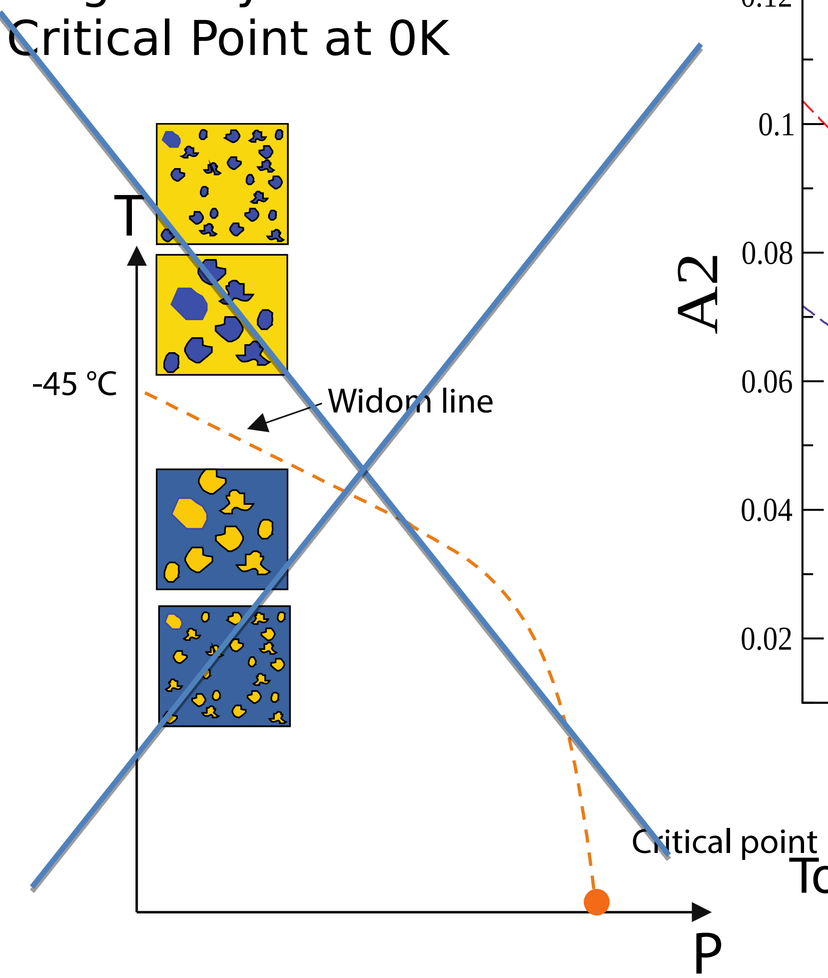


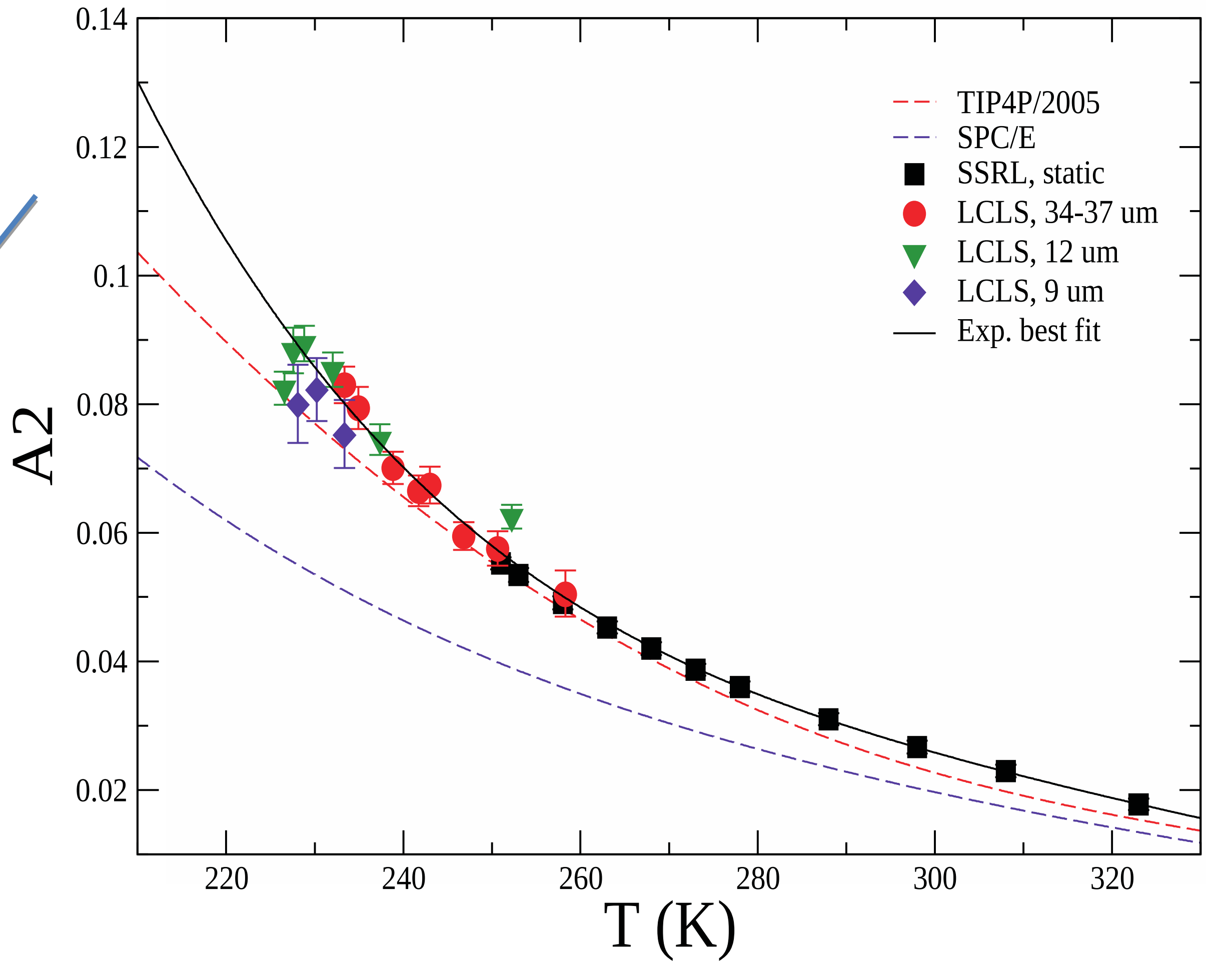
SPC/E shows to weak change

H. Pathak et al., submitted

Enhanced Fluctuations from Singularity Free Model

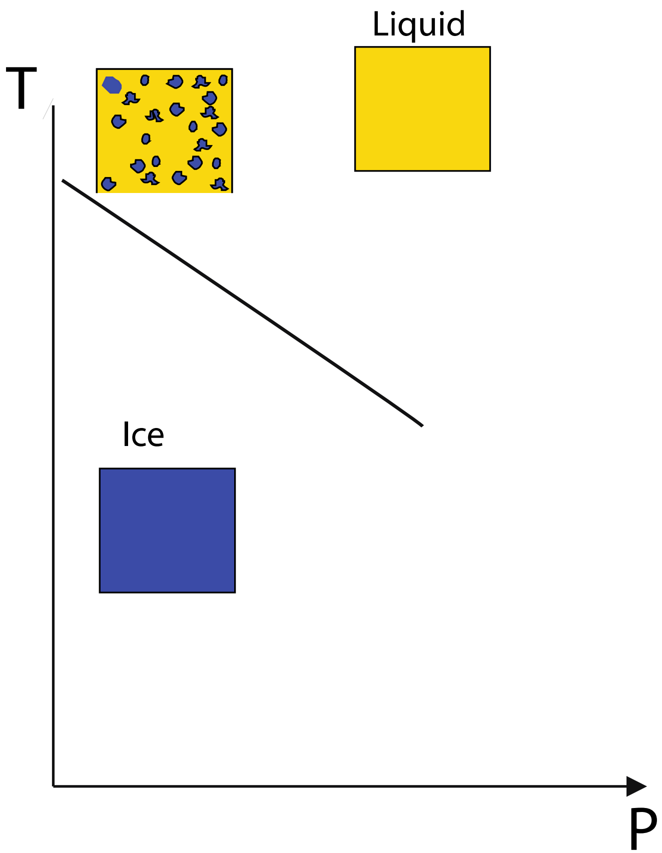
Singularity Free Model
Critical Point at 0K

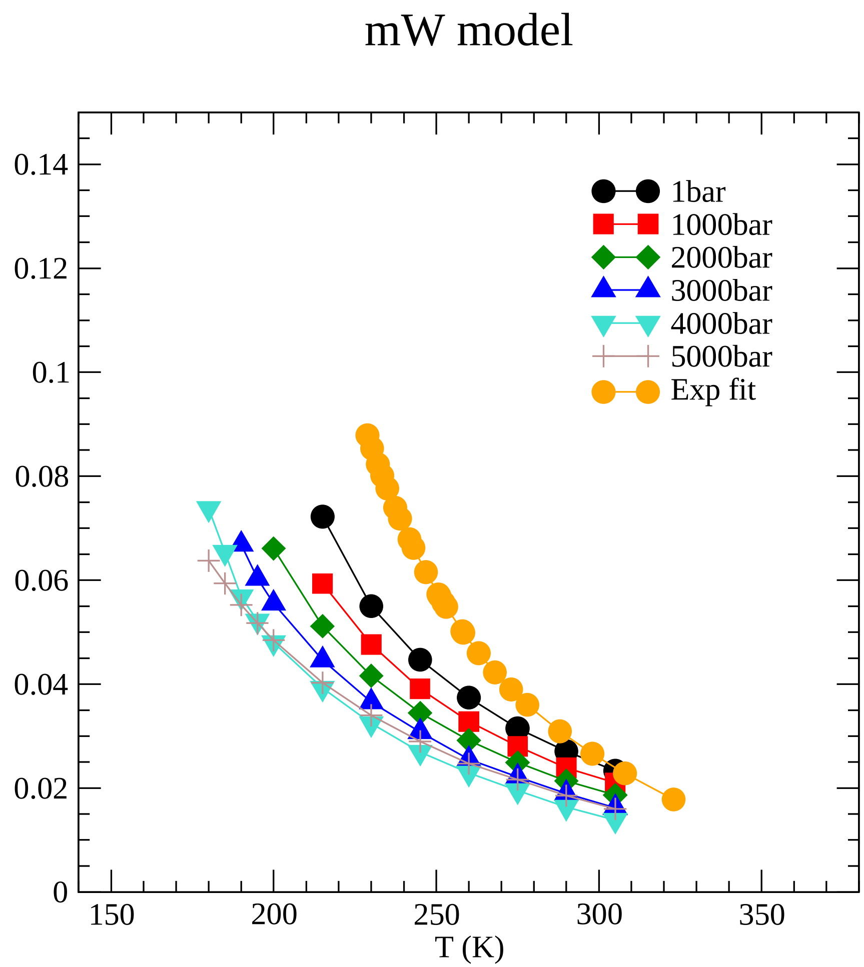




To weak fluctuations into tetrahedral structures

Enhanced Fluctuations due to Ice format

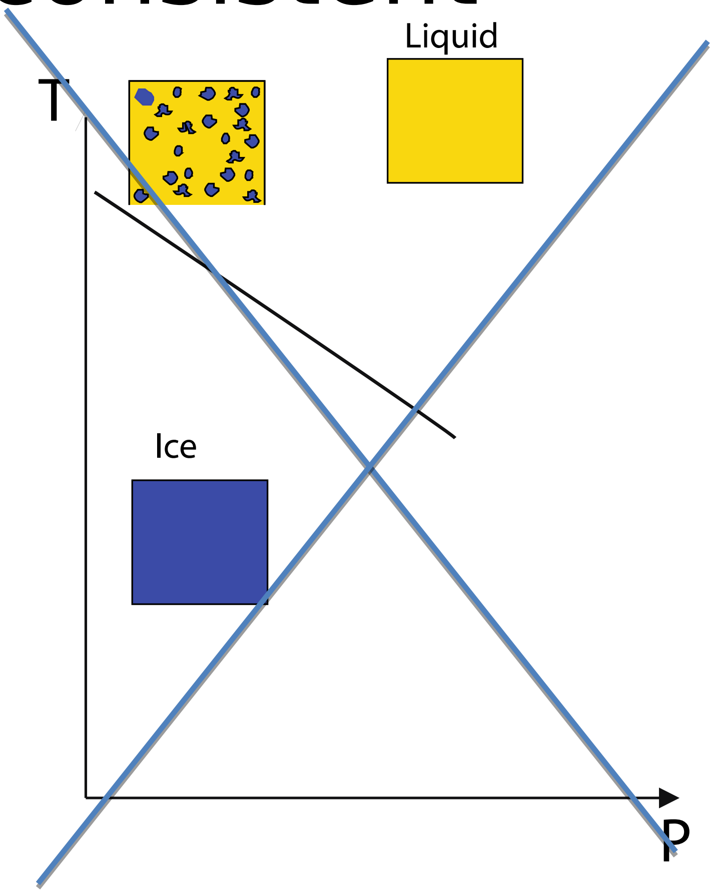




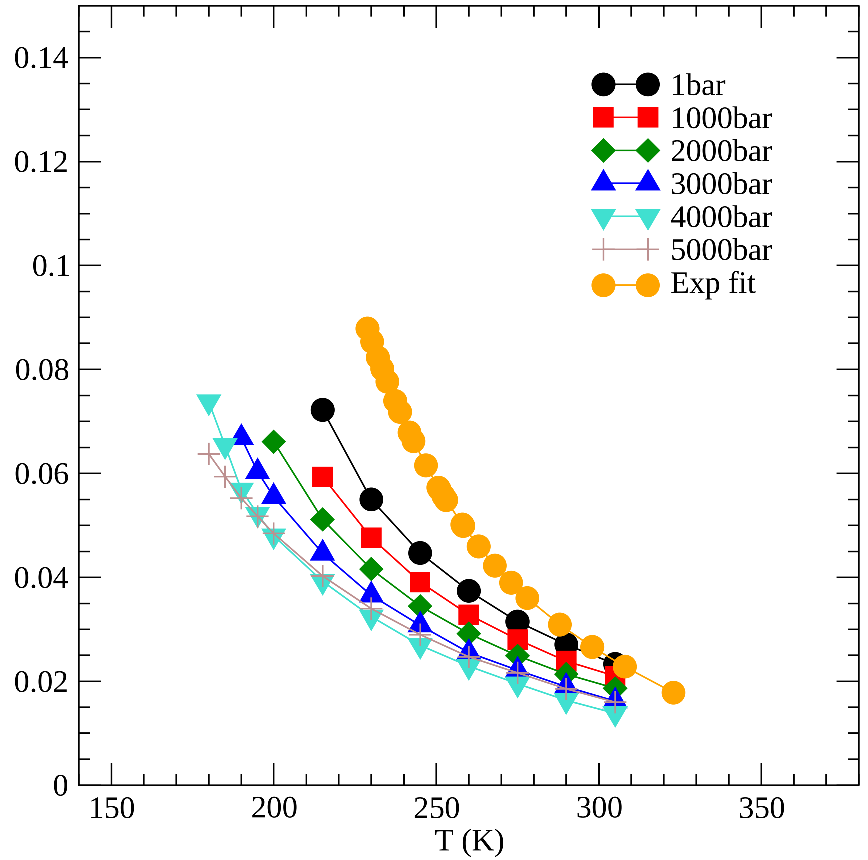
Fluctuations into tetrahedral structures more significant in the experiment even with a temperature shift

. B. Moore and V. Molinero, Nature **479**, 506–508 (2011).

Enhanced Fluctuations due to Ice formation based on mW model not consistent



mW model



Cannot explain the experimental observations

. B. Moore and V. Molinero, Nature **479**, 506–508 (2011).

iAMOEBA model

J. Phys. Chem. B 2013, 117, 9956−9972

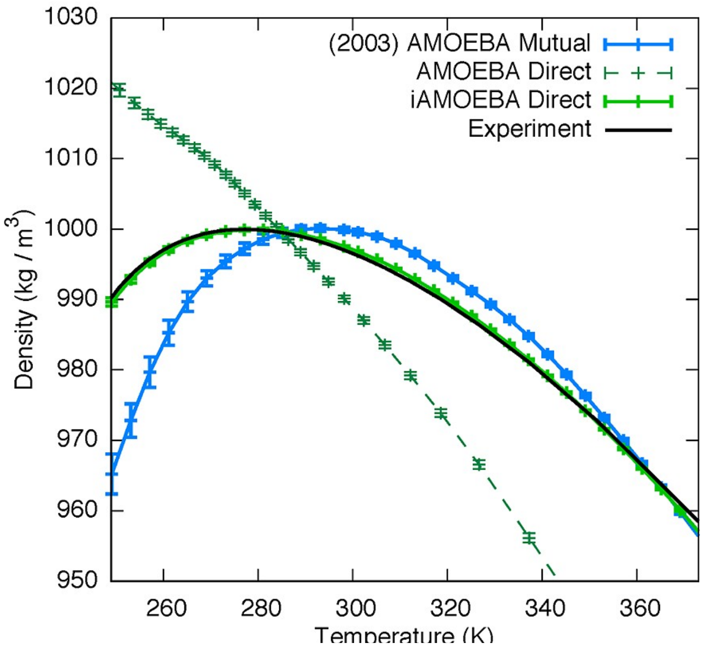
THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

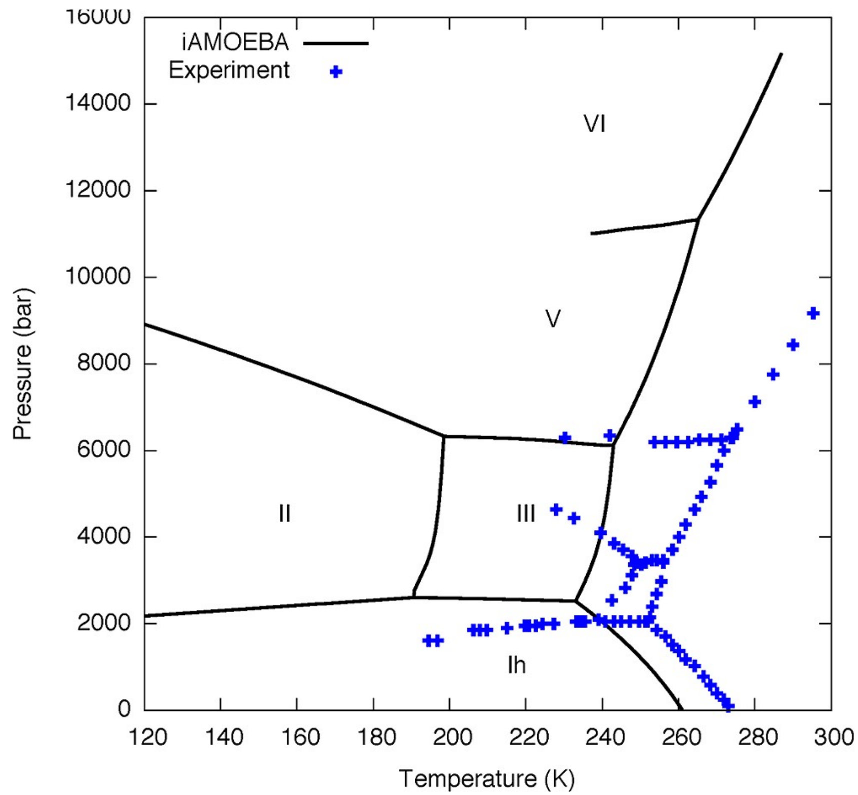
pubs.acs.org/JPCB

Systematic Improvement of a Classical Molecular Model of Water

Lee-Ping Wang,[†] Teresa Head-Gordon,[‡] Jay W. Ponder,[§] Pengyu Ren,[∥] John D. Chodera,[⊥]
Peter K. Eastman,[†] Todd J. Martinez,[†] and Vijay S. Pande*[,†]



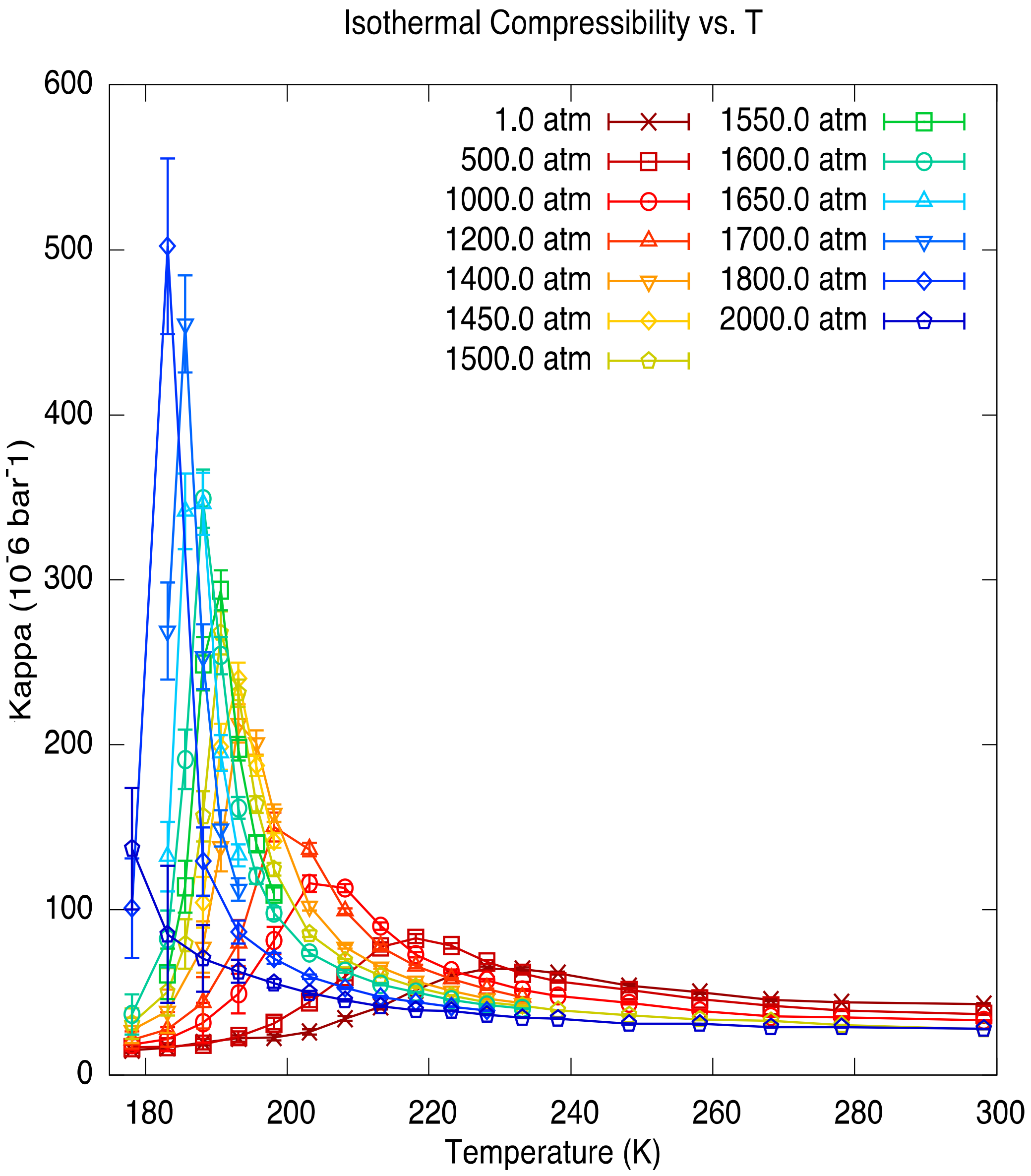
Excellent Density Maximum



Melting point 261 K

Small shift in pressure of 200-300 bar for minimum in melting cu

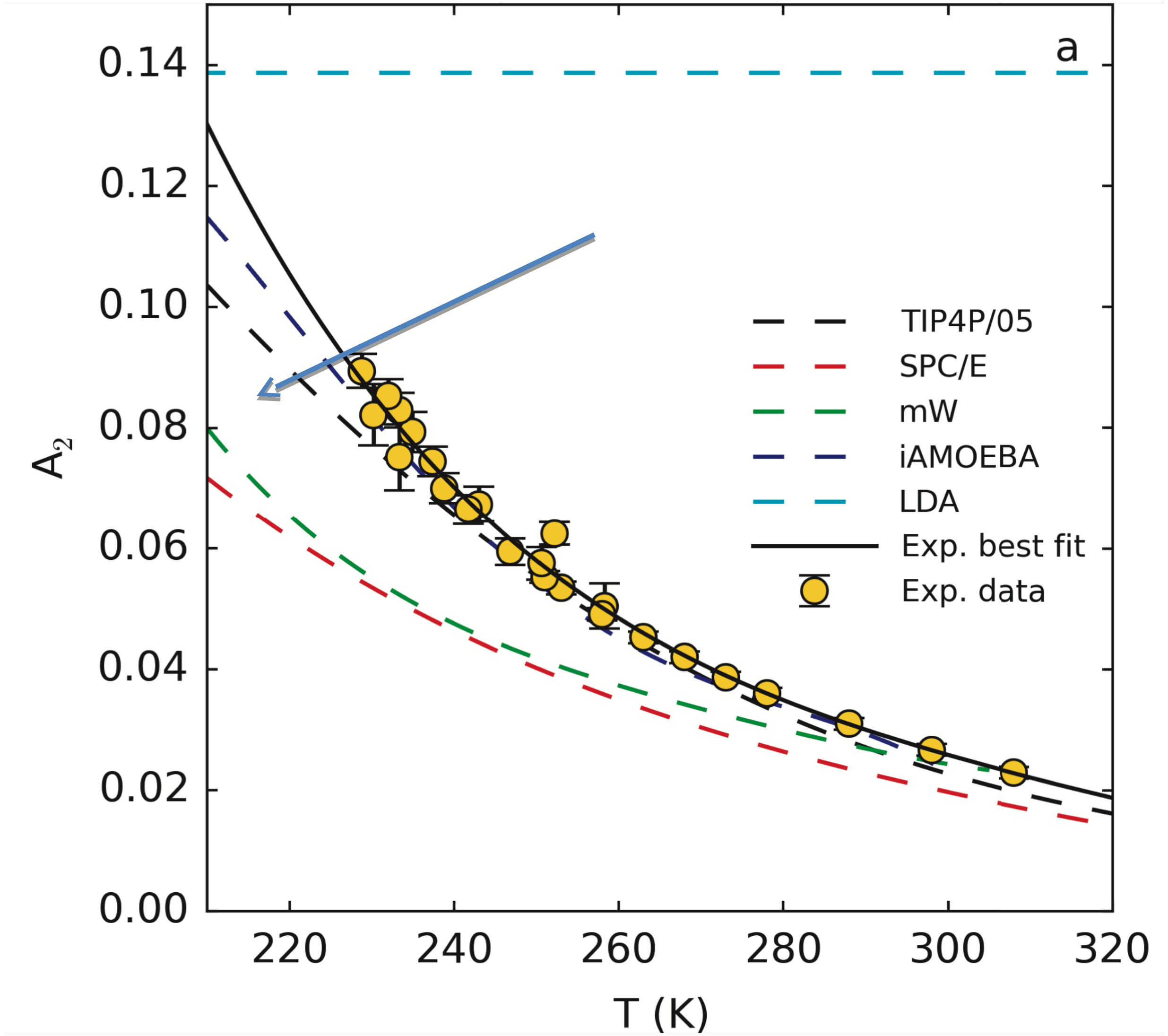
iAMOEBA-Compressibility



Maximum at 1700 bar 188
Lee Ping Wang
Private Communication

An Apparent Diverging Point
Instead of LLCP until clearly proven criticality

iAMOEBA- Very good agreement



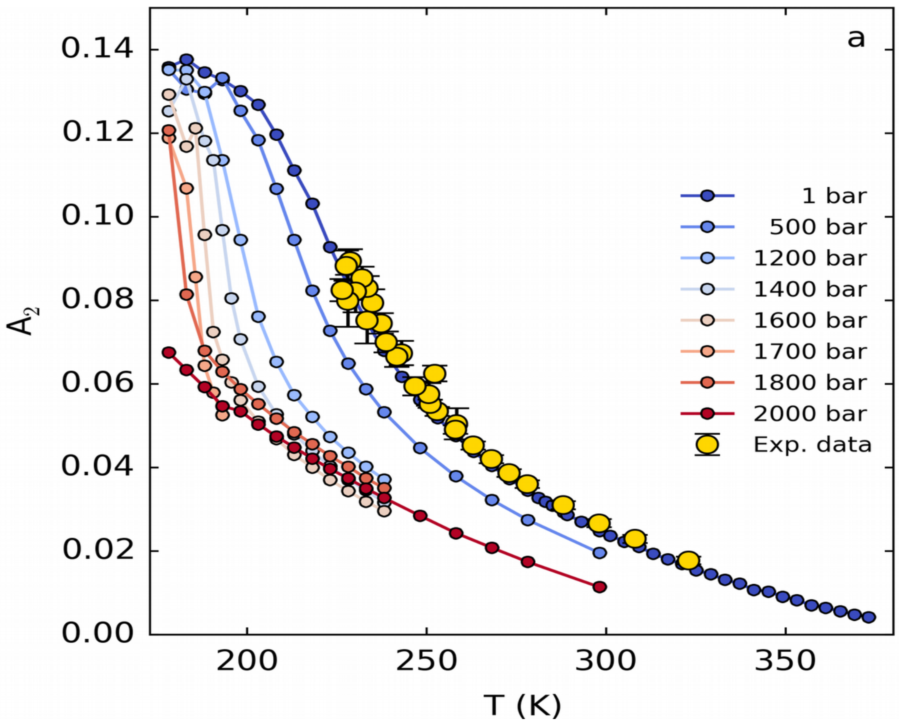
LDA

H. Pathak et al., submitted

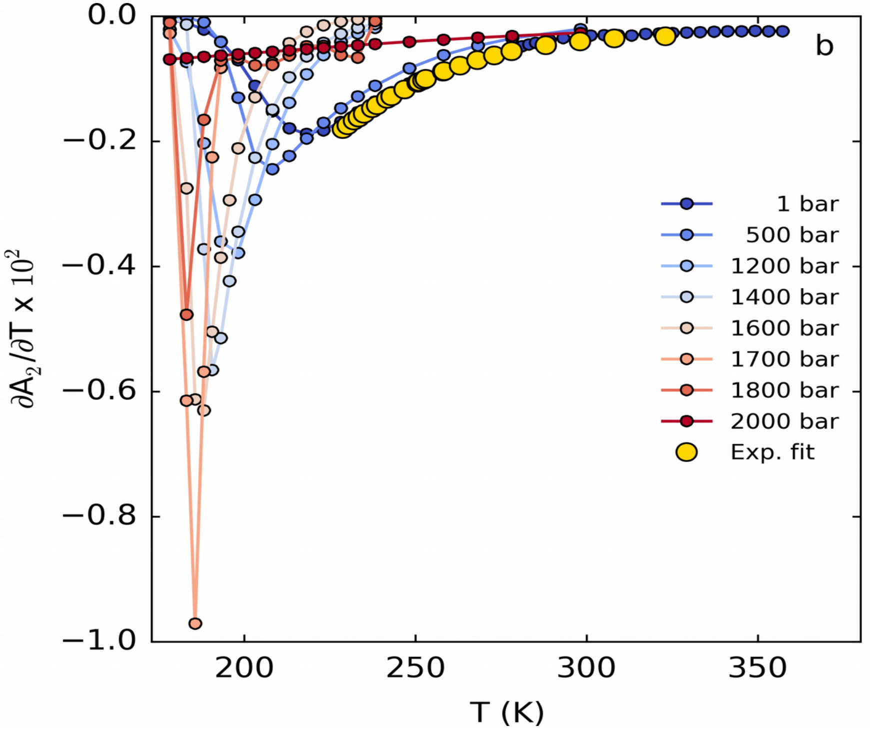
Pressure Dependence iAMOEBA

Similar Dependence as for ST2
Consistent with the existence of an ADP in the iAMOEBA model

A2

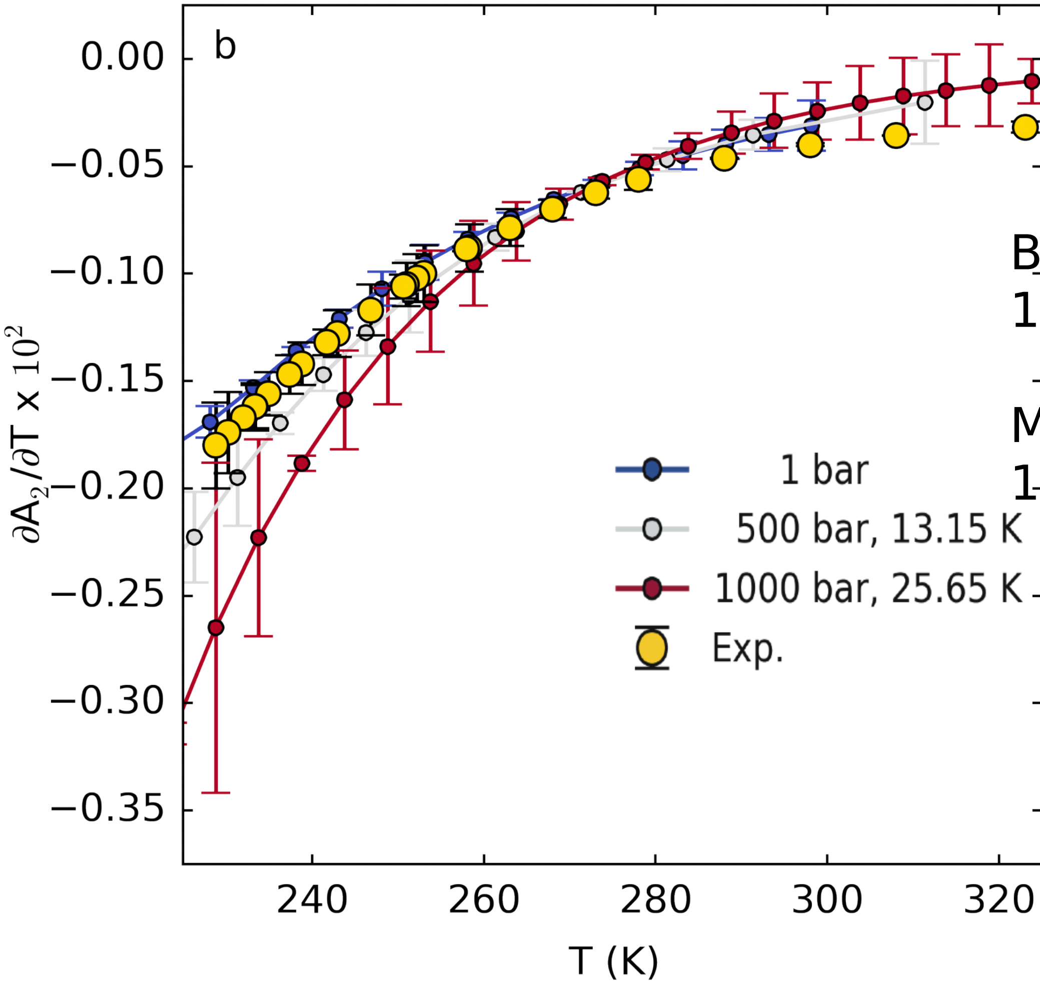


Derivative A2



H. Pathak et al., submitted

Fine Tuning Sloop A2



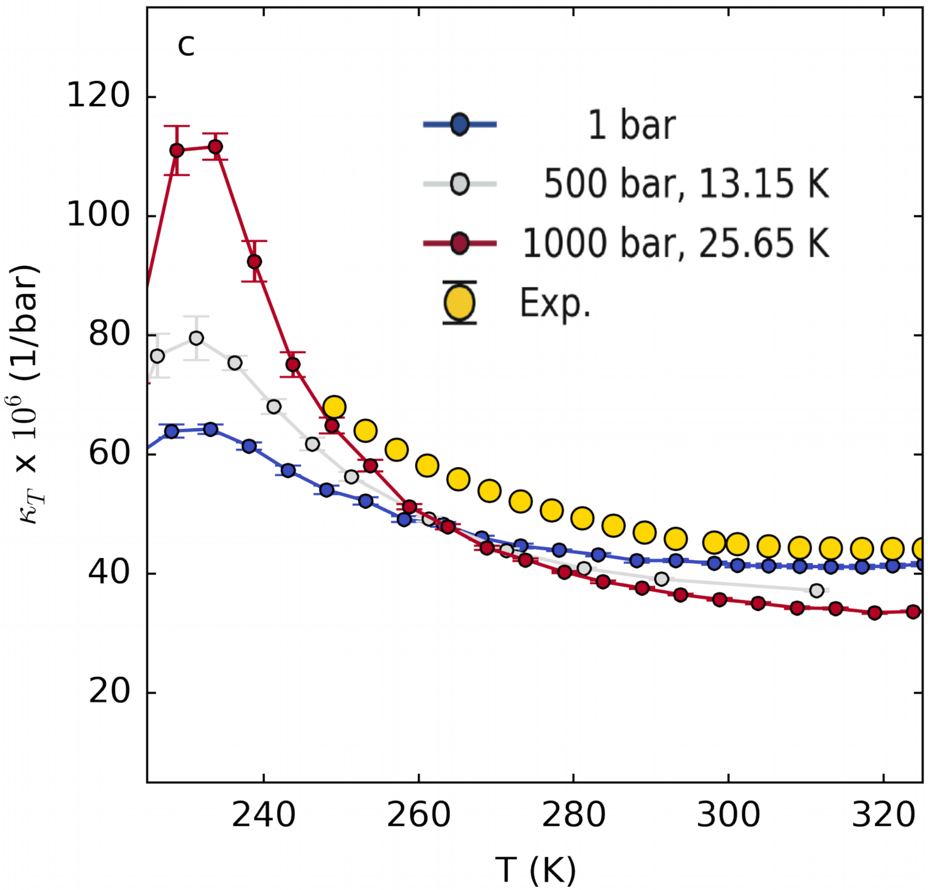
Shifted in temperature at higher
Location of Widom line in T is constant

Best agreement is between
1 and 500 bar

Meaning that ADP is between
1700 bar and 1600-500=1200 bar

H. Pathak et al., submitted

Fine Tuning Compressibility



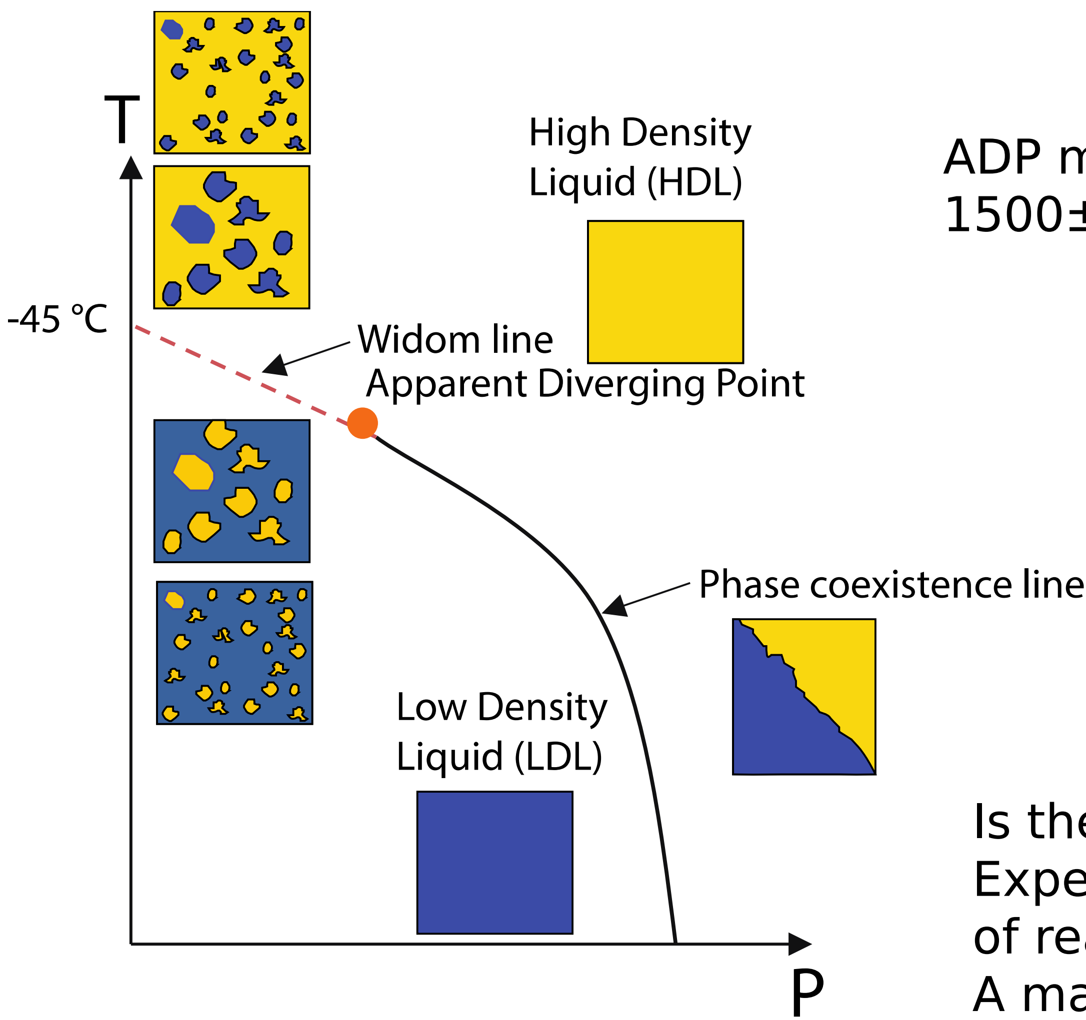
Shifted in temperature at higher P
Location of Widom line in T is constant

Best agreement is between 1 and 500 bar

Meaning that ADP is between 1700 bar and 1600-500=1200 bar

H. Pathak et al., submitted

Apparent Diverging Point
Consistent with experimental data



ADP most likely in the range
1500±250 bar 185-195 K

Is the ADP a LLCP?
Experiment will be necessary
of real bulk water
A major challenge