Fluctuations in Ambient Water

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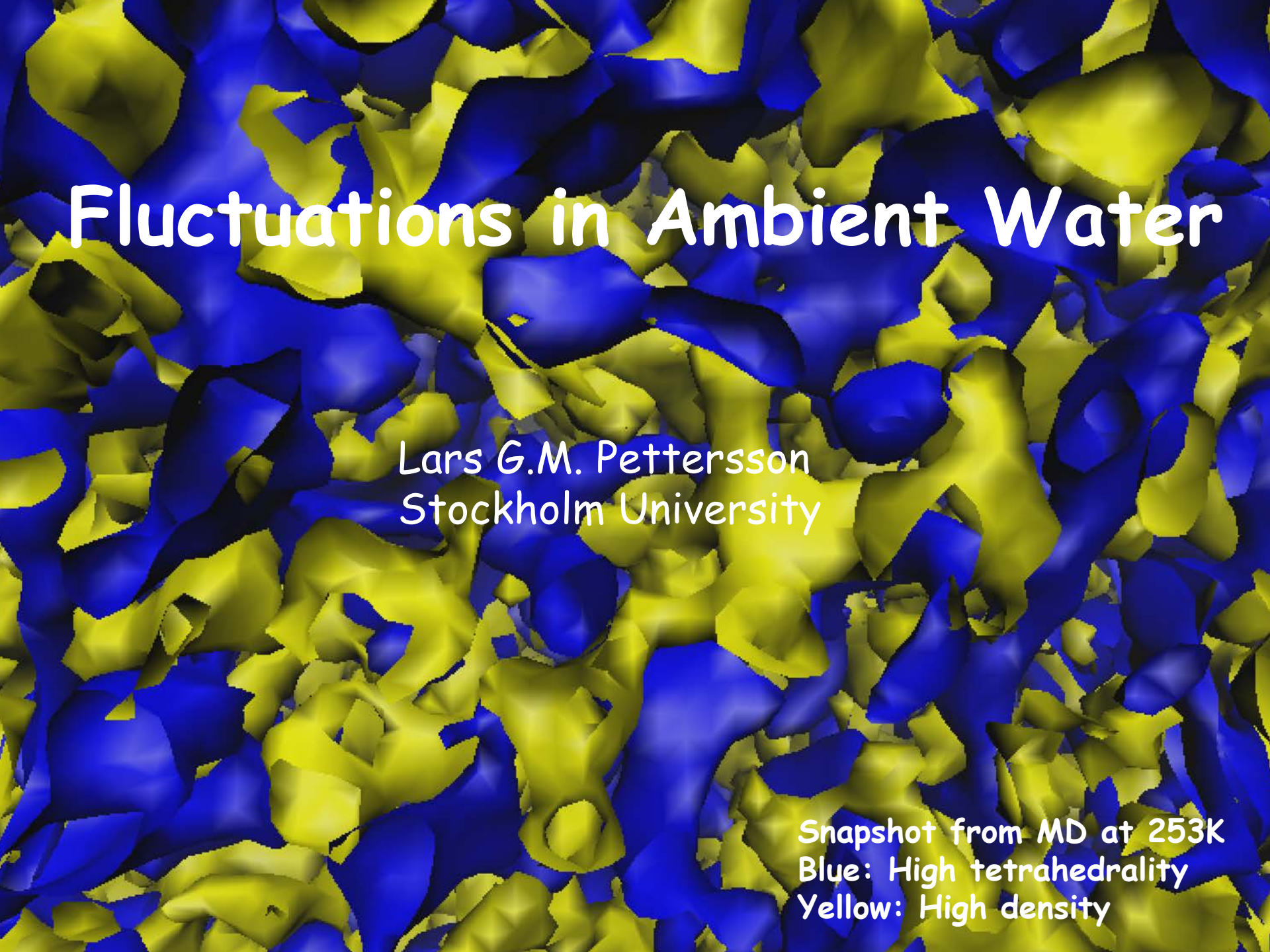
Stockholm University



Snapshot from MD at 253K
Blue: High tetrahedrality
Yellow: High density

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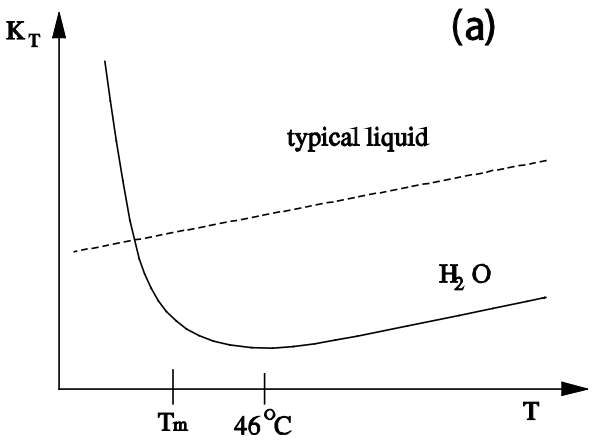
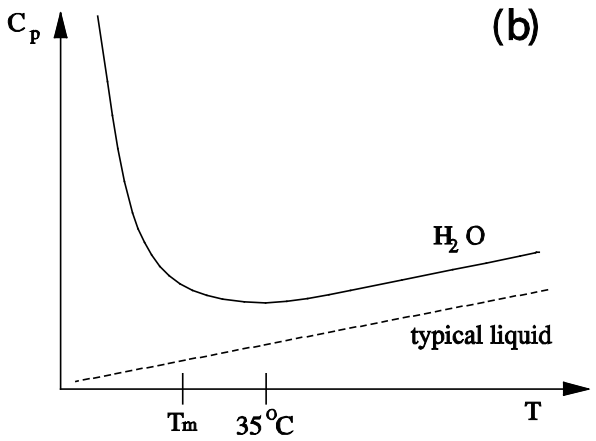
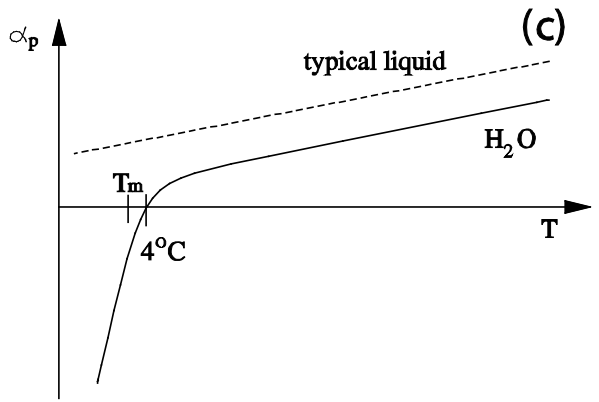
Anomalous Properties of Water

J. Phys.: Condens. Matter 19 (2007) 205126 G Franzese and H E Stanley







Isothermal compressibility

$$K_T \equiv -(\partial \ln V / \partial P)_T$$

Fluctuations, δV

$$K_T = \left(\left(\delta \overline{V}\right)^2\right) / k_B T \overline{V}$$

Specific heat, C_P

$$C_P \equiv T\left(\partial S / \partial T\right)_P$$

Fluctuations, δS

$$C_P = \left(\left(\delta S\right)^2\right) / N k_B$$

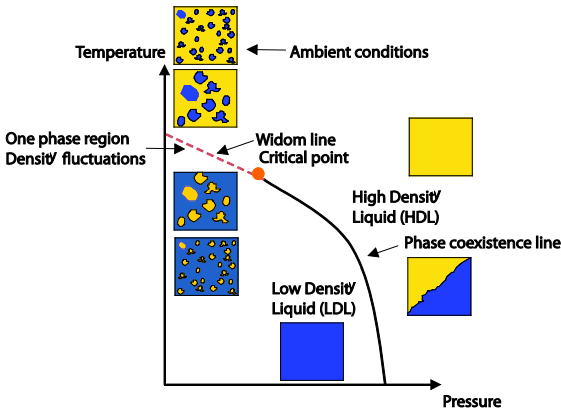
Thermal expansivity

$$\alpha_P \equiv \left(\partial \ln V / \partial T\right)_P$$

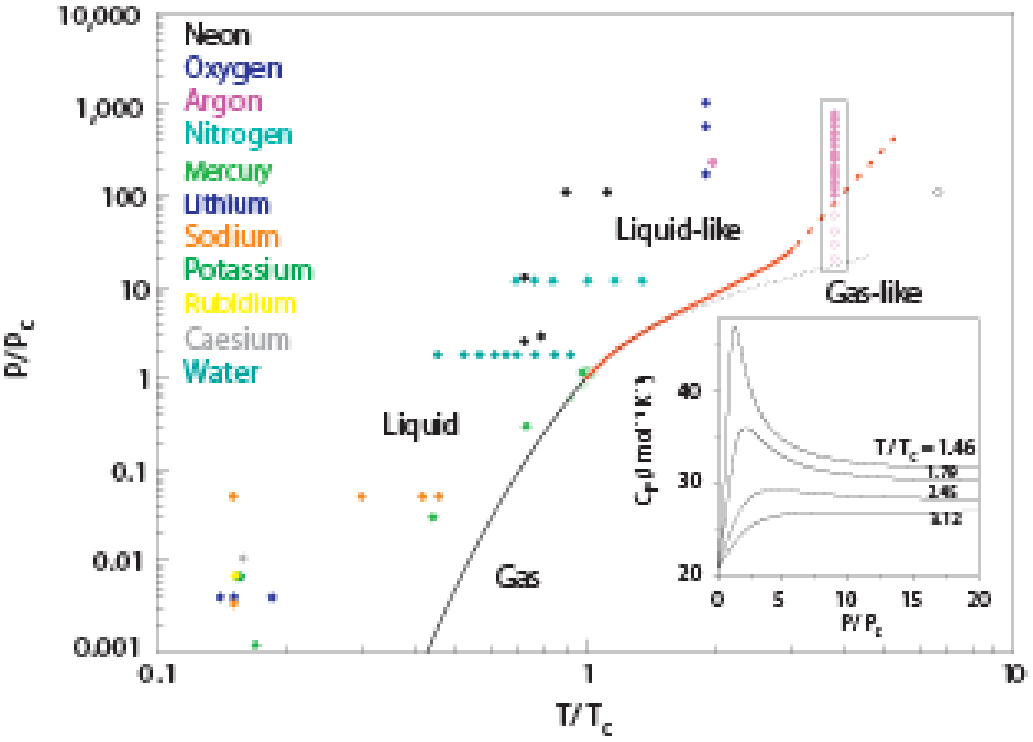
Fluctuations, δS, δV

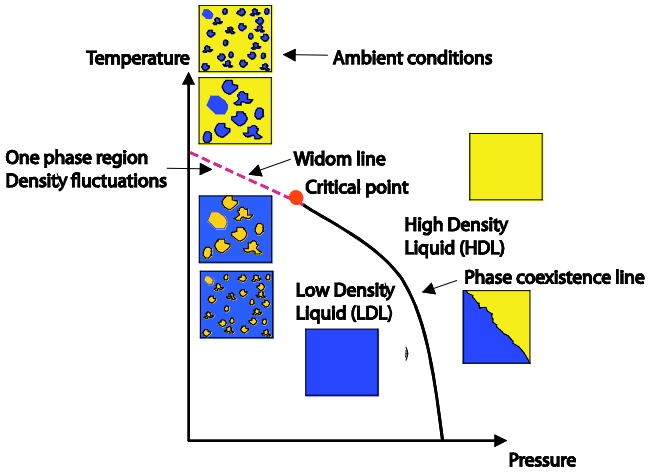
$$\alpha_P = \left(\left(\delta S \delta \overline{V}\right)\right) / k_B T \overline{V}$$

Apparent divergence upon approaching
T ~ 228 K at ambient pressure (-45 ˚C)
BUT, anomalies set in at physiological temperatures



Critical Phenomena: Properties At and Beyond the Widom Line





Simeoni *et al*. Nature Physics **6**, 503 (2010)
From velocity of nanometric acoustic waves in supercritical fluid argon at high pressures by inelastic x-ray scattering and MD simulations.
Sharp change upon crossing Widom line
One phase, but different properties in some respects

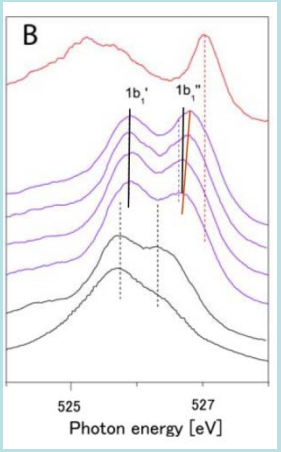
Ambient water is far from T of a liquid-liquid transition (228K)

Could an LLCP (liquid-liquid critical point, real or virtual) affect also ambient water?

”HDL/LDL” Structure of ***Ambient*** Water: ”New” Spectroscopies and Data

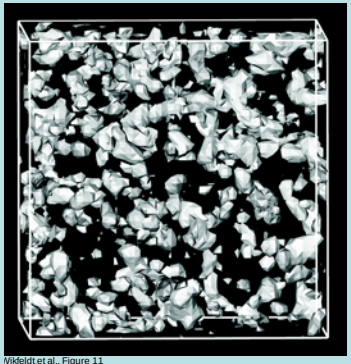
- **XAS** indicates predominant asymmetrical coordination with fewer H-bonds than in tetrahedral model

  Wernet *et al*., Science **304** (2004) 995



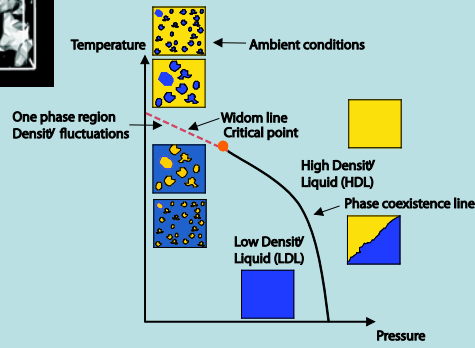
- **XES** shows two motifs: strongly tetrahedral (”LDL”) and very disordered (”HDL”); 25:75

  Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387



- **SAXS** shows density fluctuations Enhanced upon cooling

  Huang *et al*., PNAS **106**, 15214 (2009); JCP **133**, 134504 (2010)



- What’s the driving force?

  Enthalpy vs. Entropy -- Quantized librations; 2nd critical point

- **XRD** shows continuous transition on supercooling to T~223 K

  LCLS free-electron laser; Sellberg et al., submitted

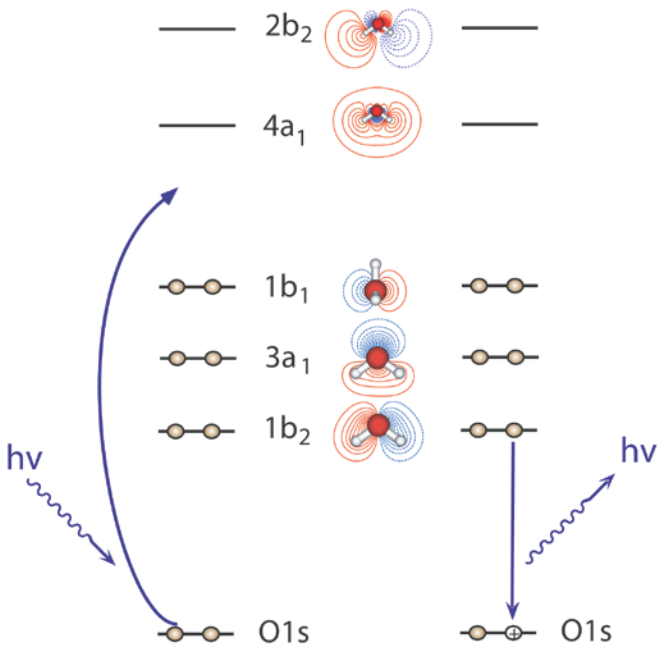
XAS and XES

XAS

X-ray Absorption Spectroscopy

Core electron excited into unoccupied state

Measures unoccupied

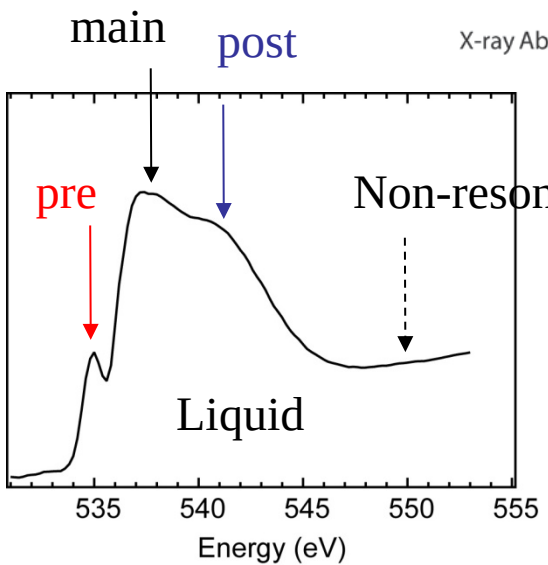


XES

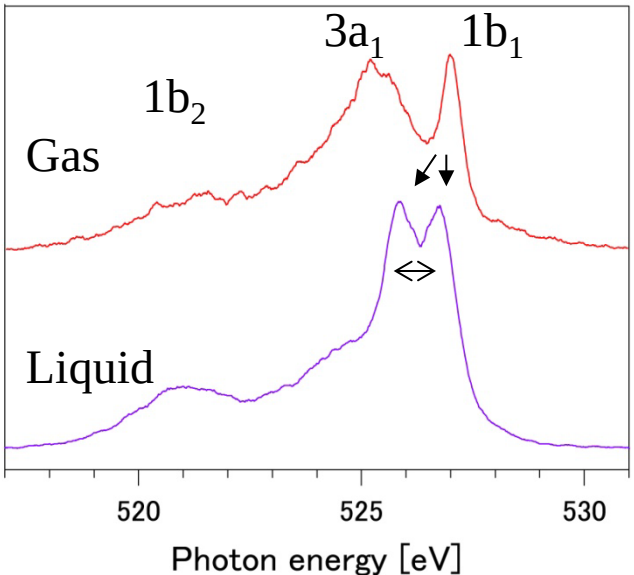
X-ray Emission Spectroscopy

Valence electron decays to fill hole created by XAS

Measures occupied states



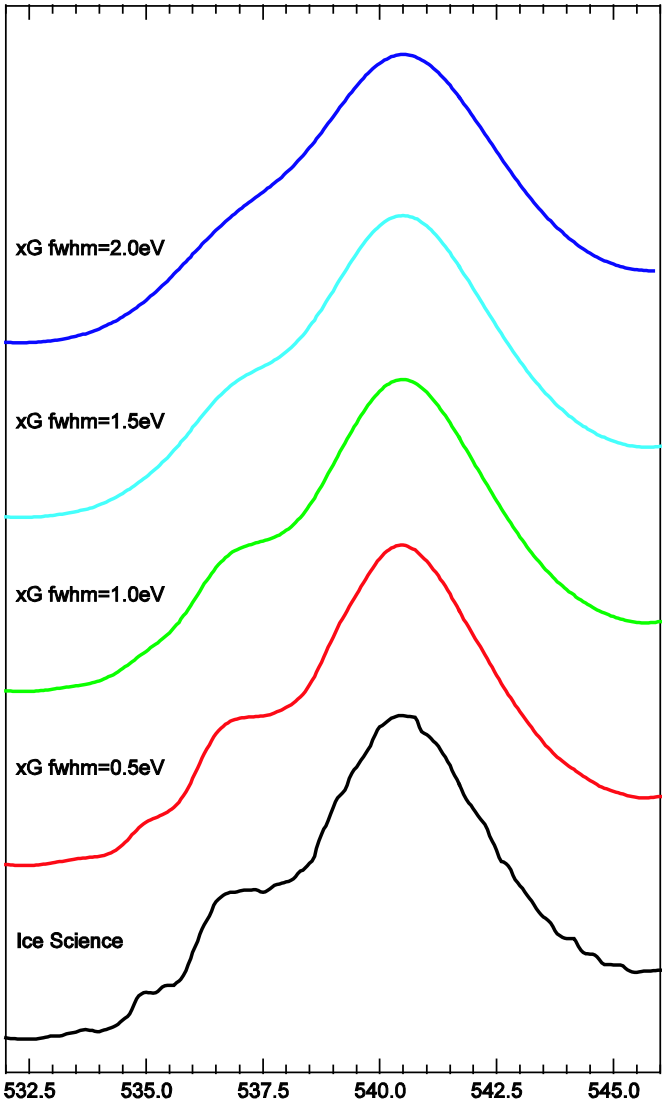
~3-4 *fsec*



XAS on Liquid Water

- Glycine on Cu(110) in UHV at 100 K not a *perfect* model for biomolecules bonding to metal implantates
- Need water – bad combination with UHV
- Soft x-rays on water meniscus in He atmosphere
- No intention to study water
- Needed background water spectrum to subtract to see bio contribution...

XAS: What to Expect for Established Tetrahedral Model of Water



Bondlength with the ruler:

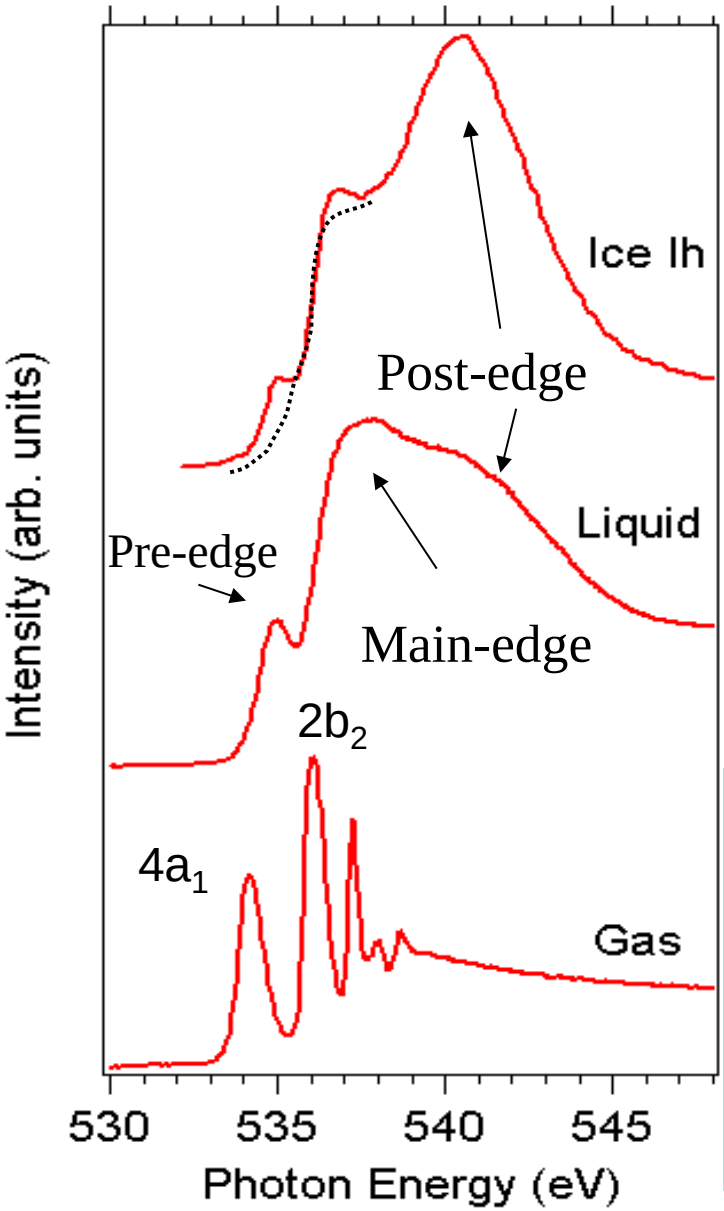
If the molecules in the liquid bind similar to ice, but with more disorder then the spectrum should be like a broadened ice spectrum....

More disordered

Some disorder

Ice

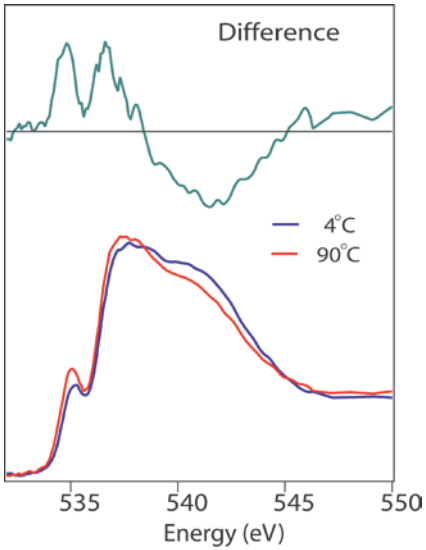
X-ray Absorption Spectroscopy of Water

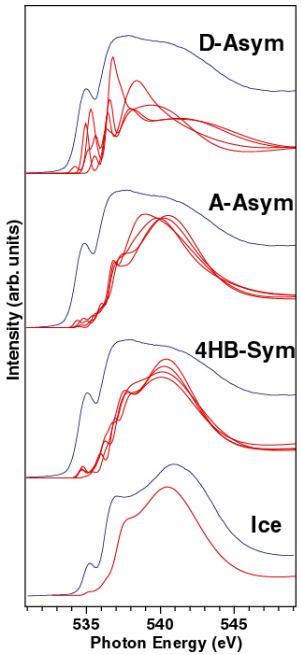


Wernet *et al.*, *Science* **304** (2004) 995

Myneni *et al. J. Phys. Condens. Matter* **14** (2002) 213

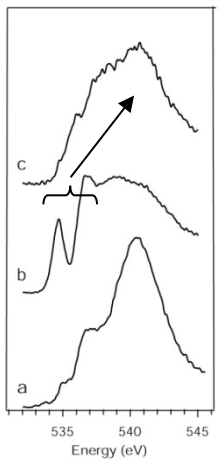
X-ray Raman Scattering
High-resolution

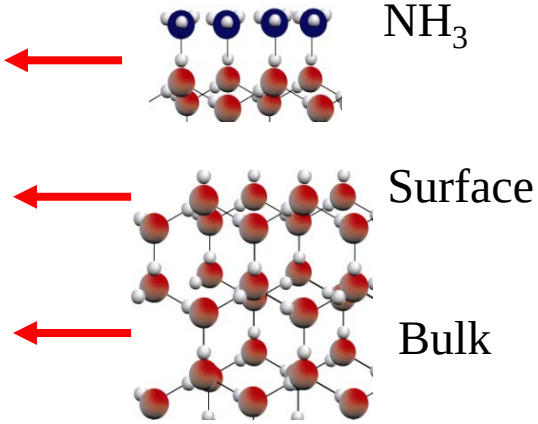




Simulations

Pre-edge from asymmetric donating H-bonds one broken or distorted
Post-edge: H-bonds



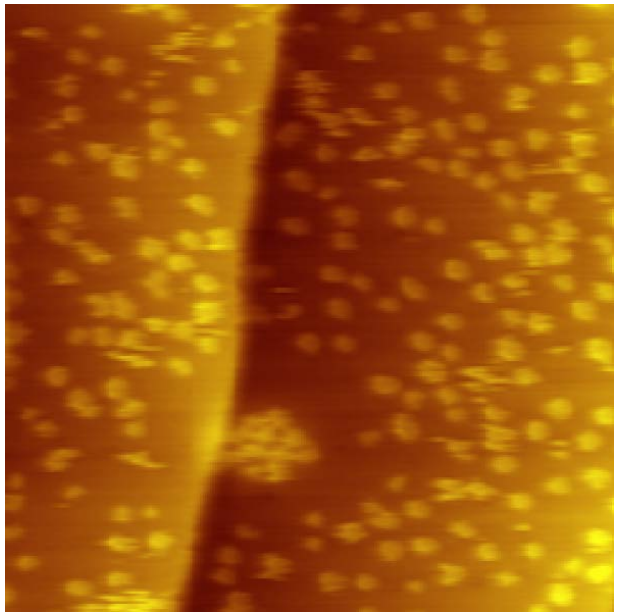


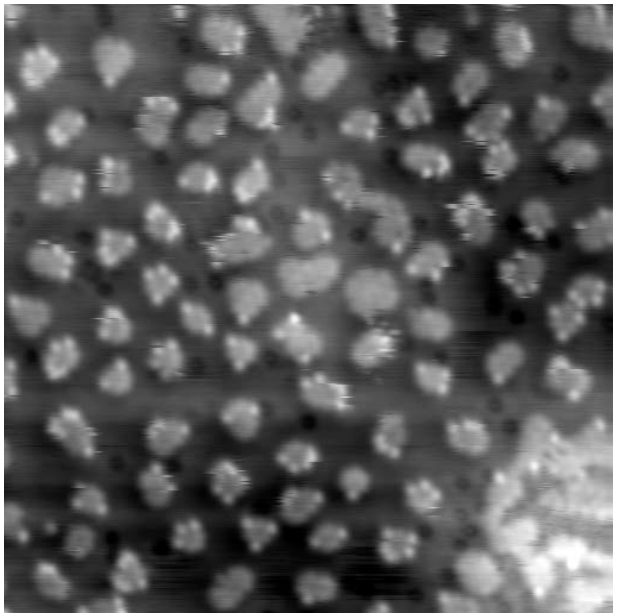
Nilsson et al., J. Electron Spec. Rel. Phen. **177**, 99 (2010)

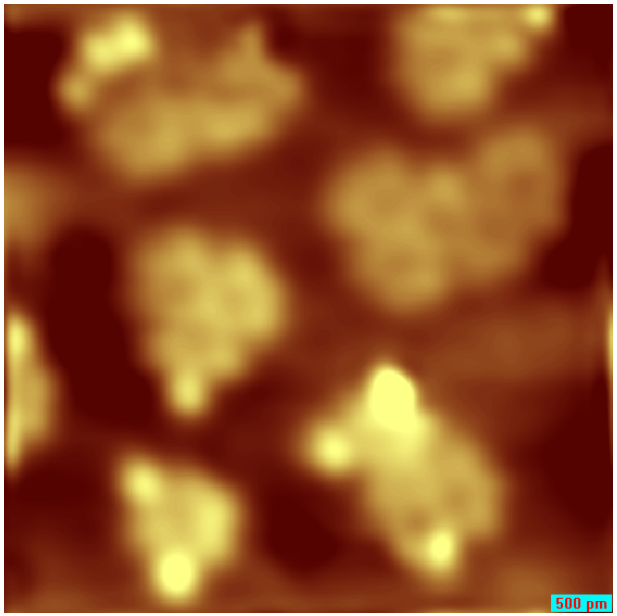
Water Clusters on Surfaces

Scanning Tunneling Microscopy (STM) of Water on Ru(0001)

Nordlund et al., Phys. Rev. B **80**, 233404 (2009)







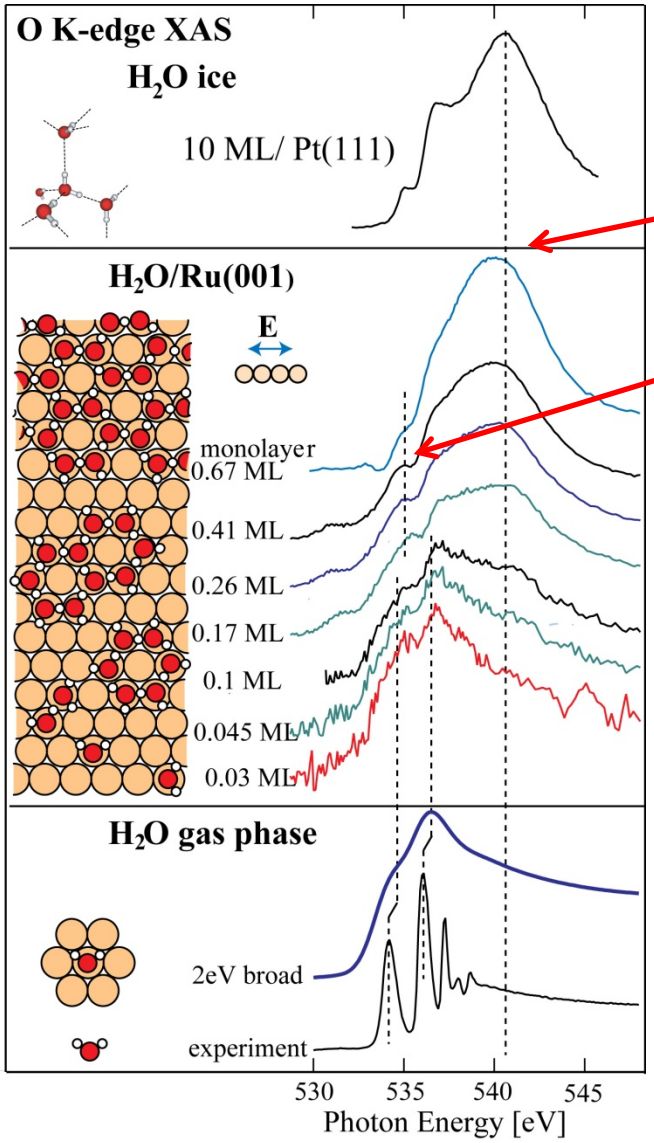
Deposited at 50 K

Annealed to 130 K imaged at 50 K

IR shows that water molecules are adsorbed flat with the HOH plane parallel to the surface

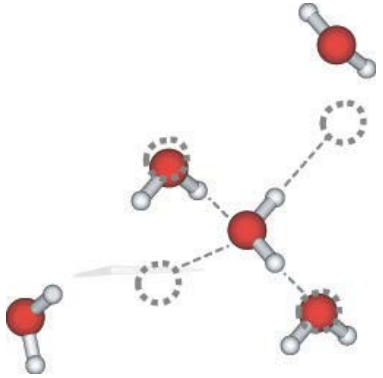
A. Hodgson et al.

Two-Dimensional Water Structures



H-bond signal

Dangling OH



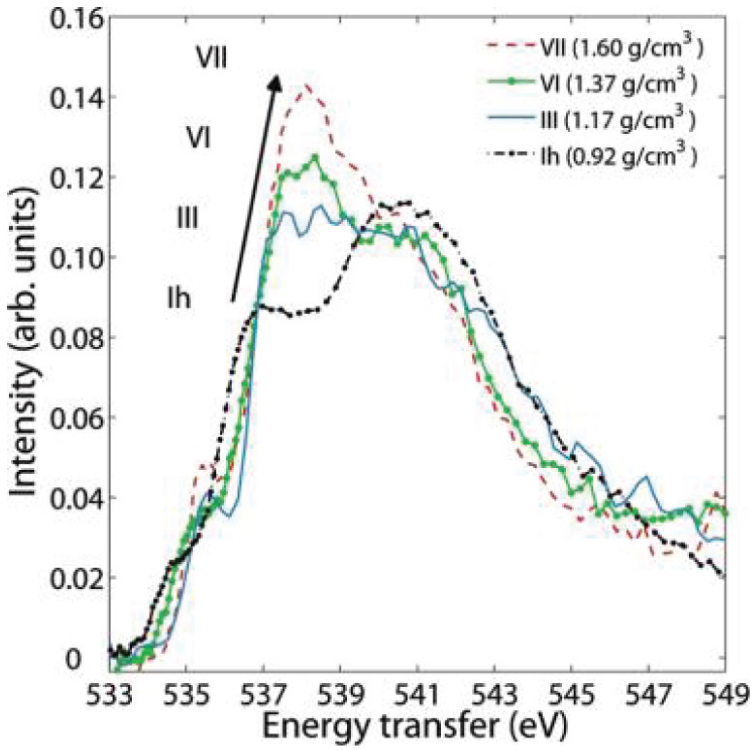
Asymmetrical distortions

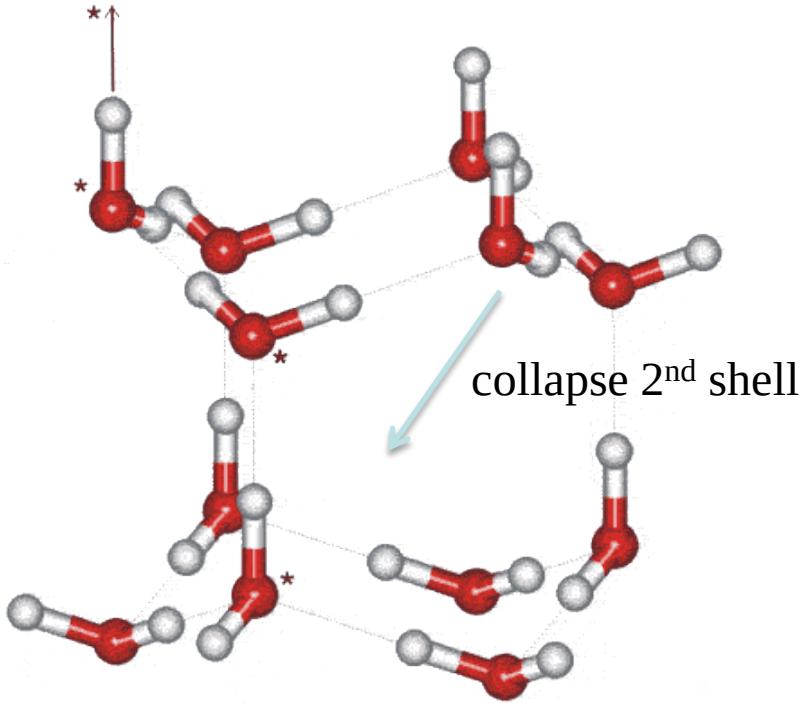
Follow spectrum development for known water structures on Ru(0001)
No donated (ND) to 1 donated (SD) to 2 donated (DD)

Nordlund et al., Phys. Rev. B **80**, 233404 (2009)

Main-edge; Collapse of 2nd Shell High Density Form

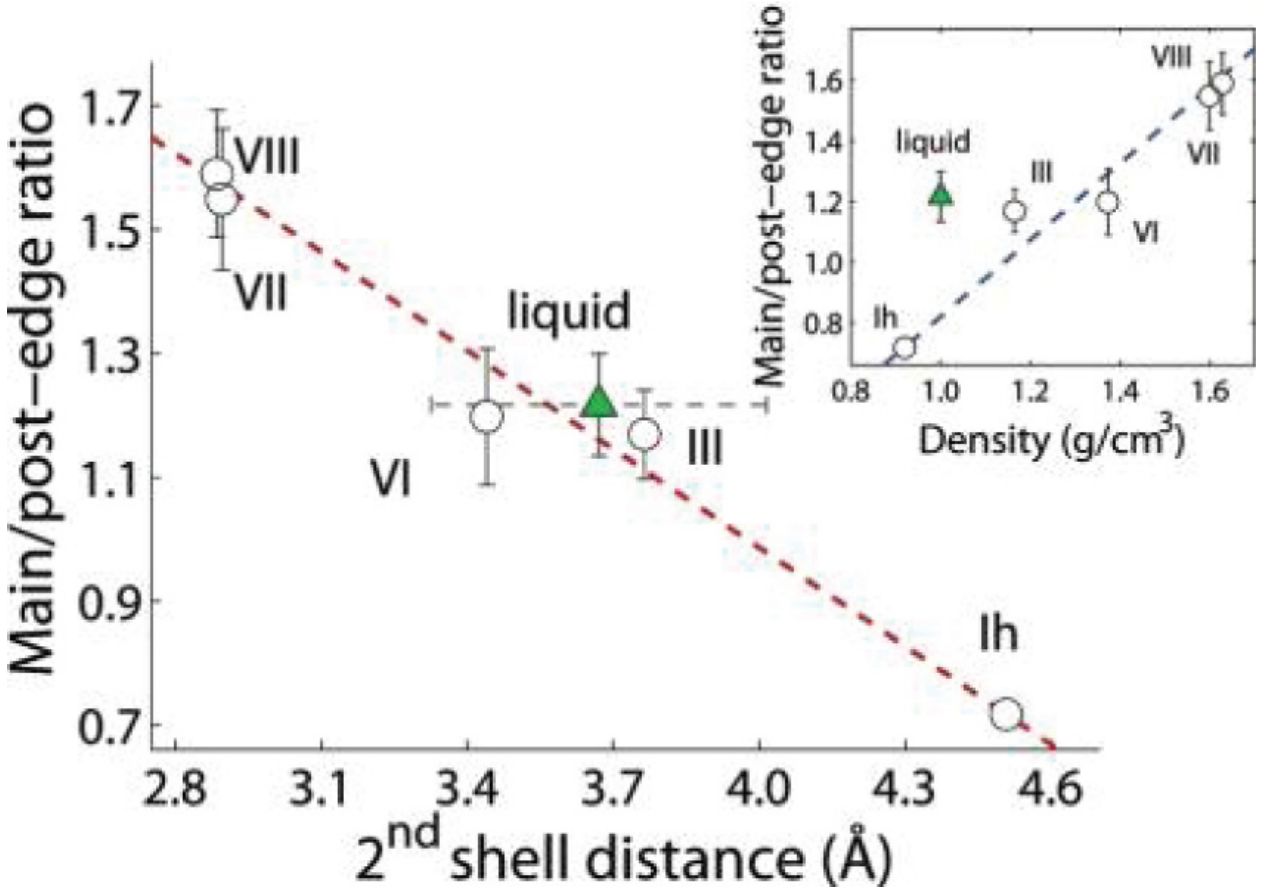
X-ray Raman scattering of high pressure ices
Strong increase in main-edge





Pylkkänen et al., *J. Phys. Chem. B 2010, **114**, 3804*

Main-edge; Collapse of 2nd Shell High Density Form



Water should have a collapsed 2nd shell
High Density Liquid (HDL)

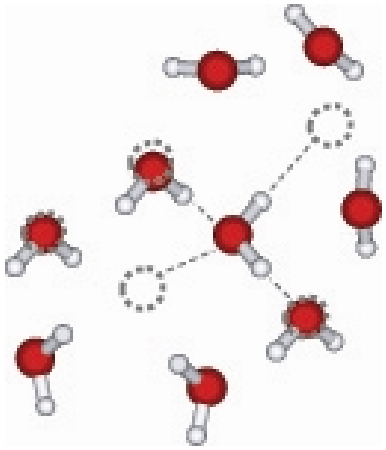
Pylkkänen et al., *J. Phys. Chem. B 2010, **114**, 3804*

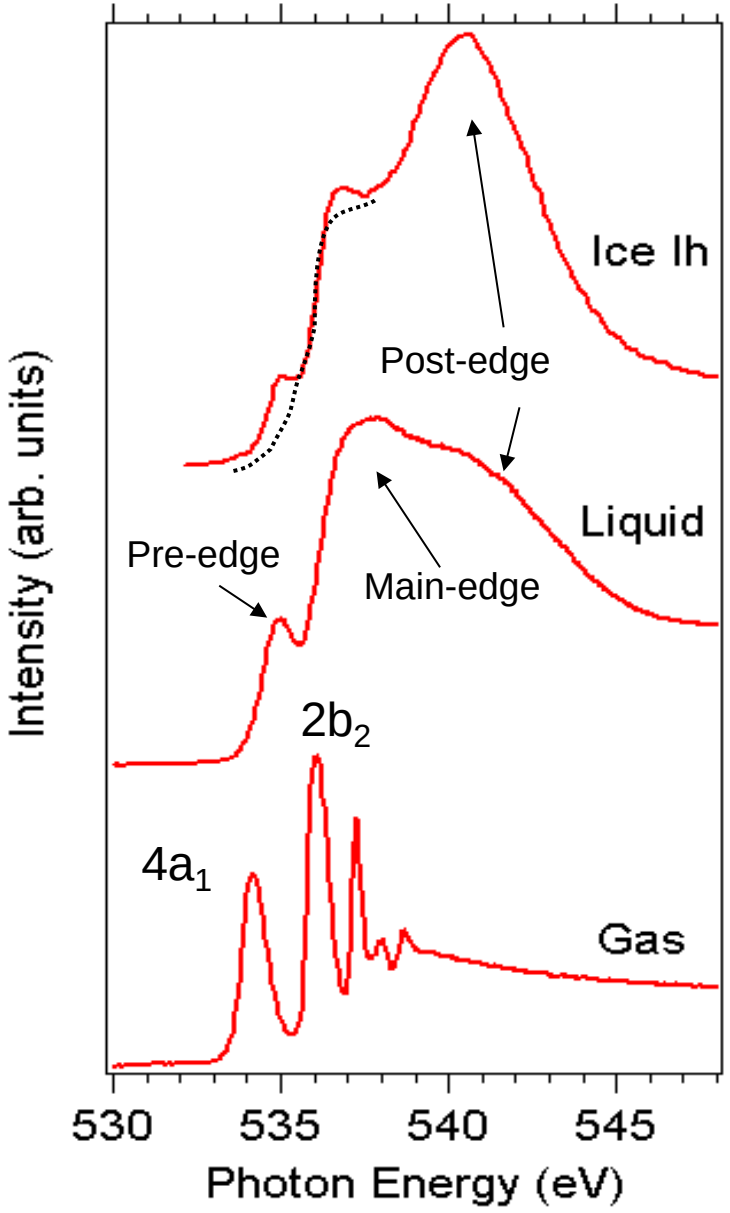
Summary XAS

Post-edge is related to directed H-bonds
Position shifts with H-bond length
Tetrahedral structures in water at similar H-bond length as in ice

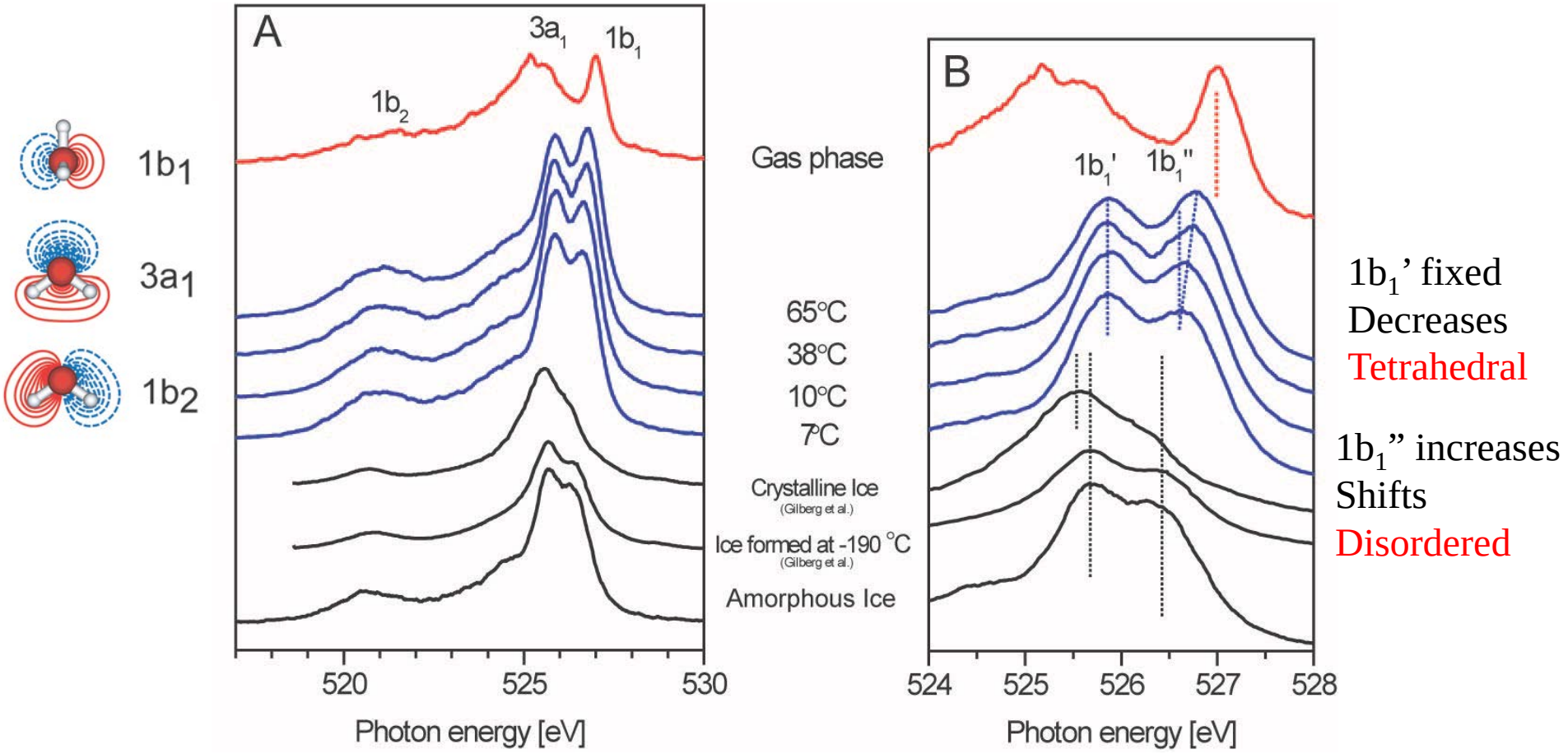
Pre-edge is related to weakened/broken H-bonds (ambient T ~ 80%)
Intensity and energy position change depending on distortions

Main-edge intensity is related to collapse of 2nd shell
High density liquid structures
Non-donor (angular distortion)





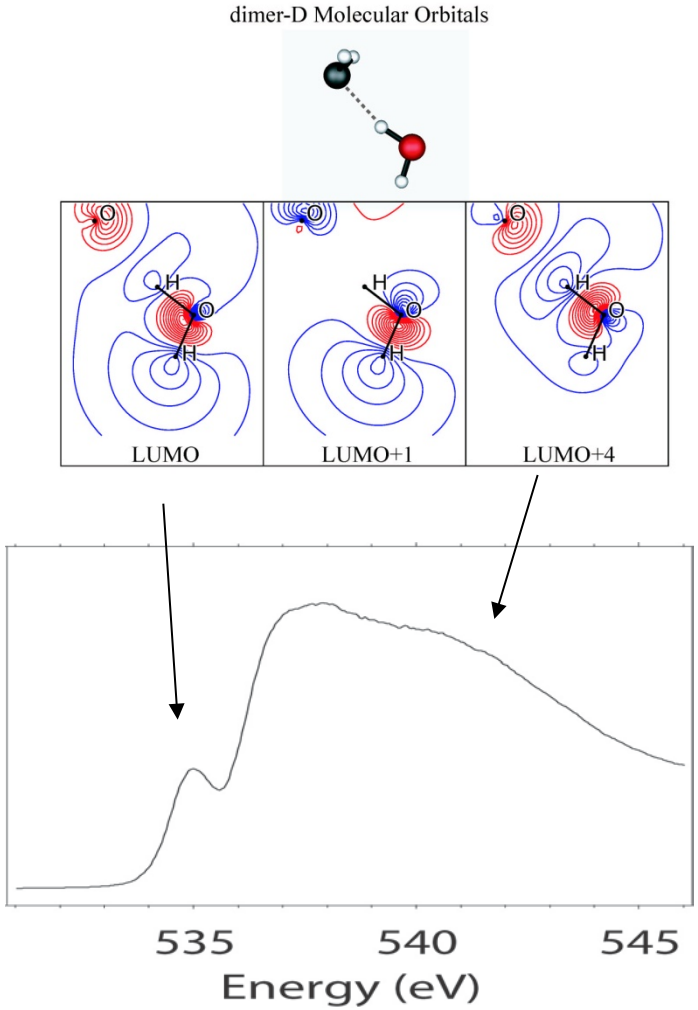
XES H_2O: Temperature dependence



- Intensity transferred from $1b_1$' to $1b_1$" as temperature is increased (fewer H-bonds)
- NO broadening, NO new peaks: Either tetrahedral *OR* very disordered

Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387

Orbital Localization



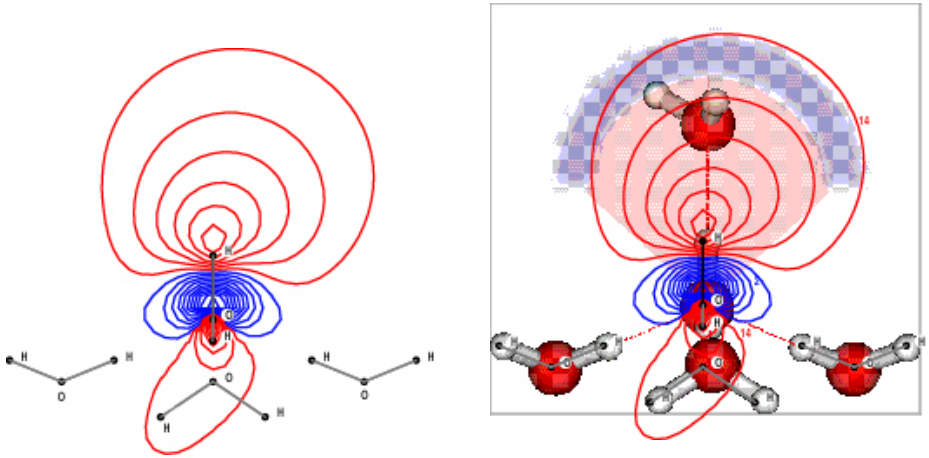
The two OH groups different in molecule

OH group orbital localization

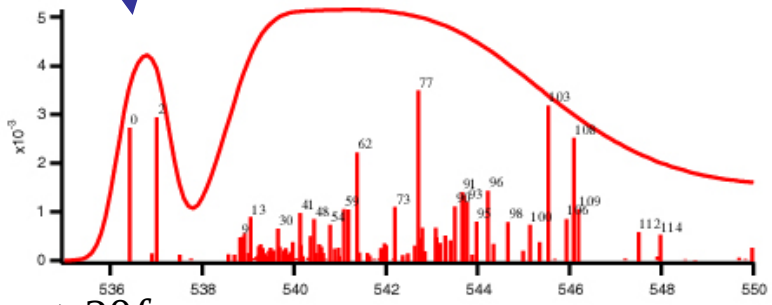
Cavalleri et al., Chem. Phys. Letters **364**, 363 (2002)

Non-H-bonded

Sensitive!!



Computed XAS ice surface



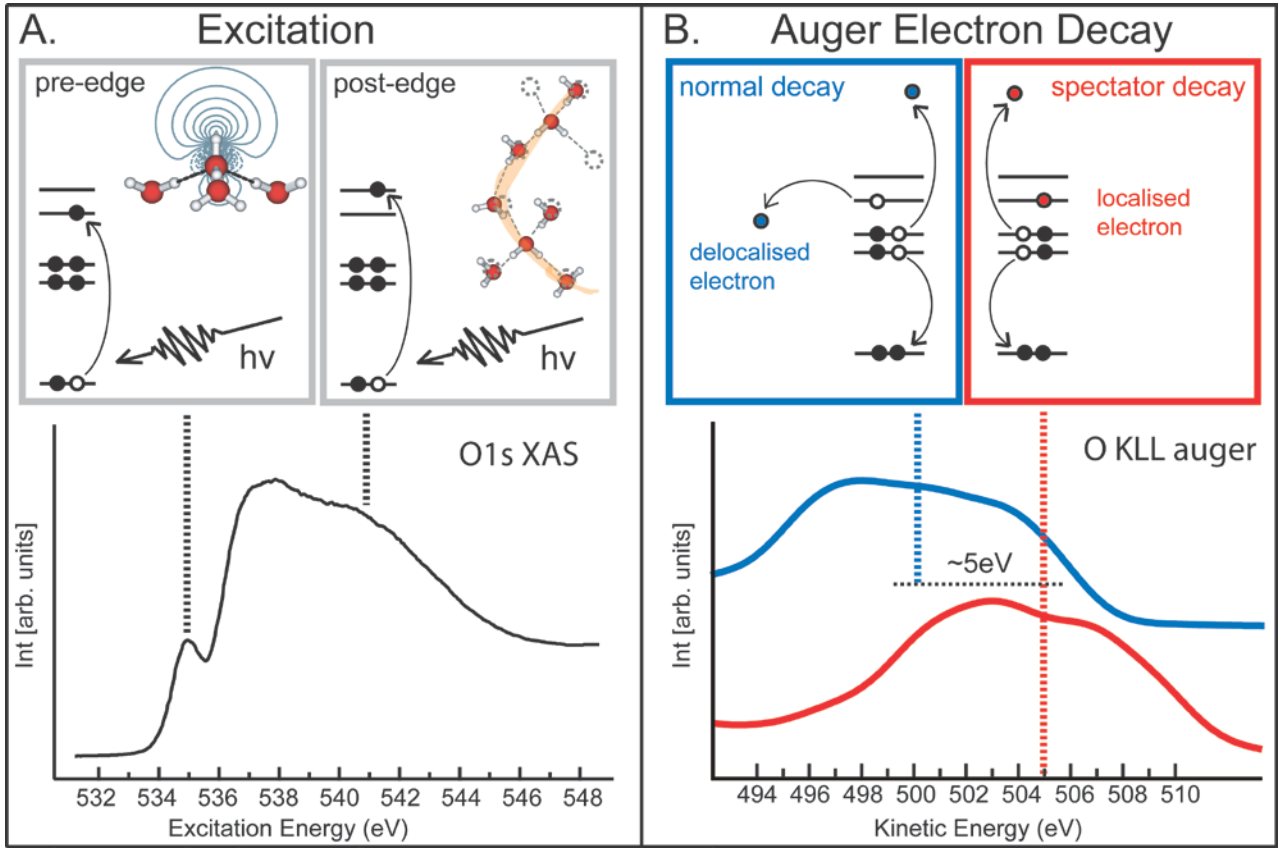
>20*fs*

<500*as*

Resonant Auger gives residence time

Wernet et al., *Science* **304** (2004) 995

Auger Decay
Resonant Photo-Emission Spectroscopy (RPES)



- Dominant decay process

Normal

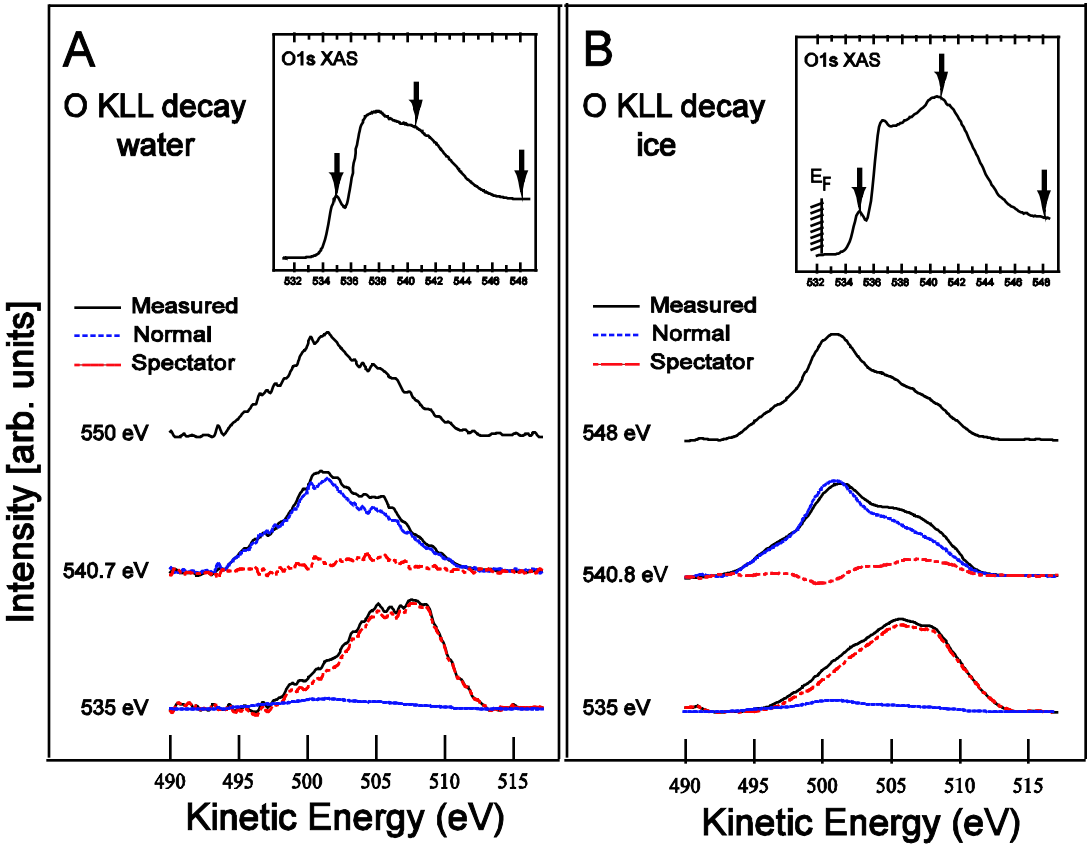
- Decay from ionized state (excited electron gone)

Spectator

- Excited electron present when decay occurs
- Causes an ~5 eV shift

Nordlund et al., PRL **99**, 217406 (2007)

Resonant Auger (RPES) Measurements of Delocalization Rates



$\tau_{CT}=\tau_c*(f_{aug}^{-1}-1)$

f_{aug} fraction normal Auger
τ_c core hole life time
τ_{CT} delocalization rate

Core hole clock
Björneholm et al., PRL **68**, 1892 (1992)

Post-edge delocalization faster than 500*as* along H-bond network
Important in biology – e^- transport

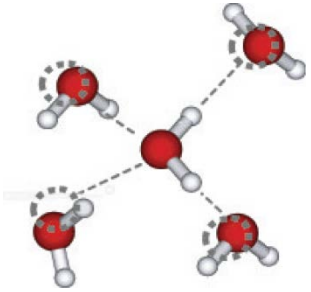
Pre-edge remains localized longer than 20*fs*

Nordlund et al., PRL **99**, 217406 (2007)

Summary X-ray Emission Spectroscopy

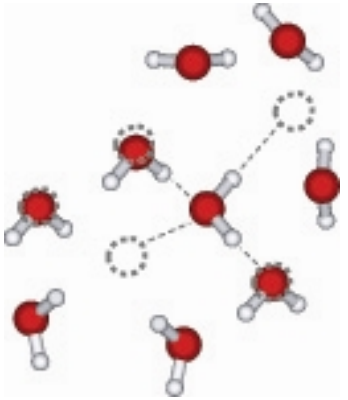
- Bimodal structural distribution

- Tetrahedral loses intensity with temperature, but peak at fixed energy



20-30 %

- Distorted gains intensity and disperses with temperature



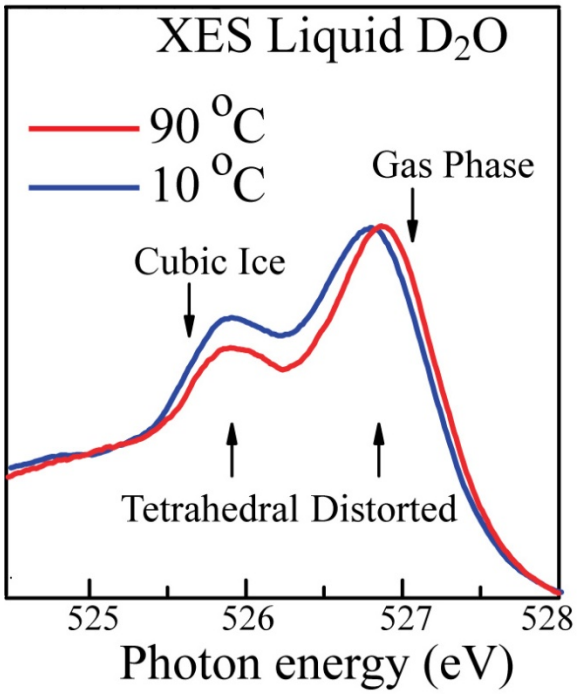
70-80 %

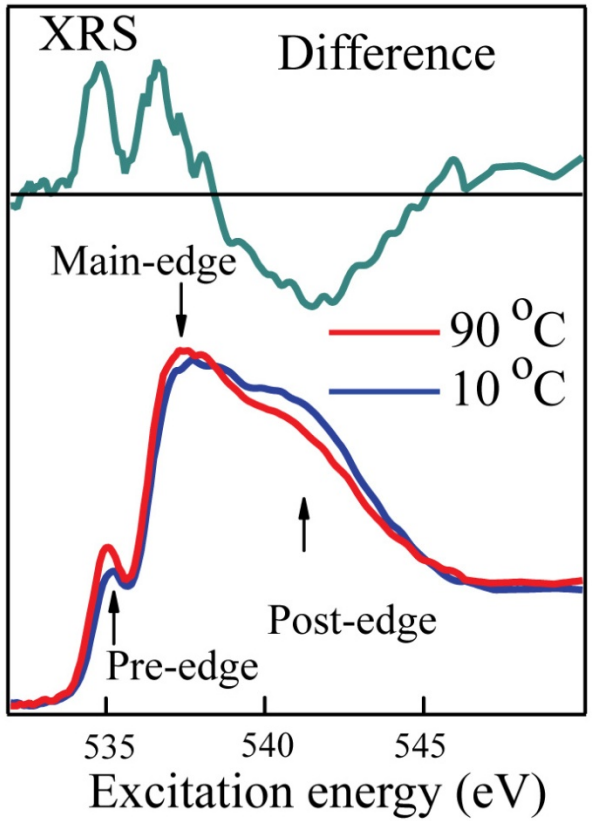
- Energy taken up through:
  - Thermal excitation of distorted species
  - Breaking up a fraction of tetrahedral species

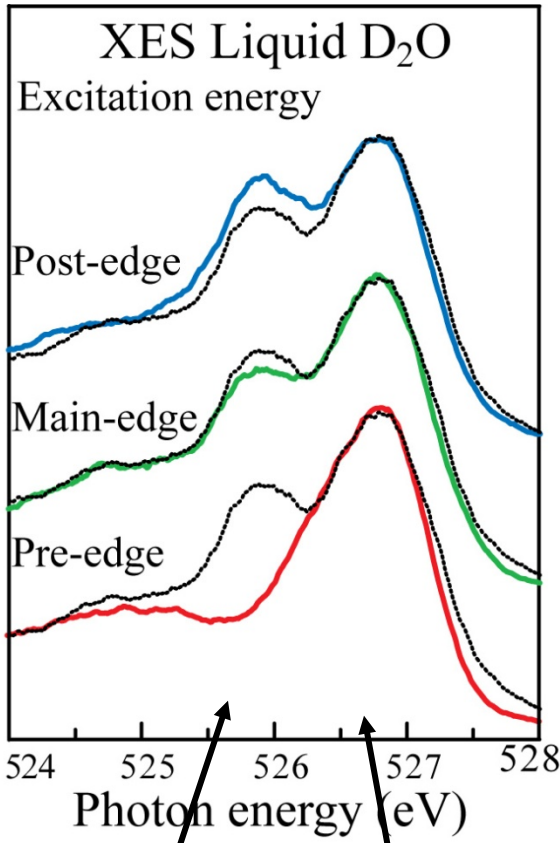
Tokushima *et al.*, Chem. Phys. Lett. **460** (2008) 387

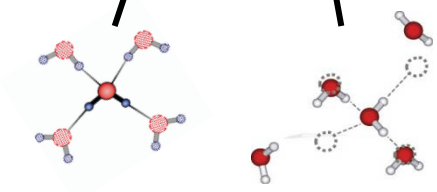
Huang *et al.*, PNAS. **106** (2009) 15214

Connection between XAS/XRS and XES









* XRS = X-ray Raman Scattering

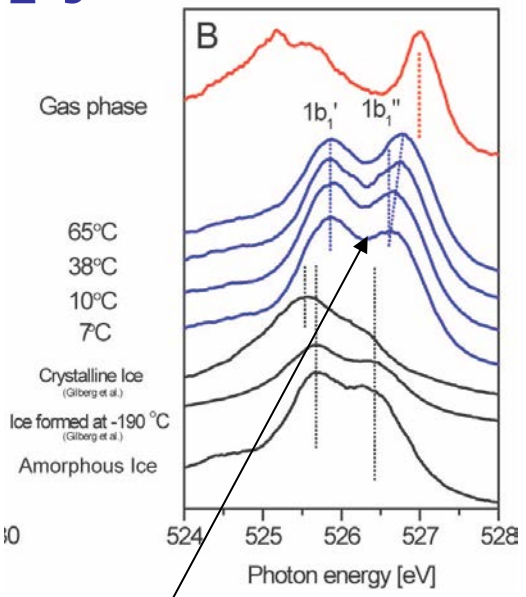
Tokushima *et al.*, Chem. Phys. Lett. **460** (2008) 387

Huang *et al.*, PNAS. **106** (2009) 15214

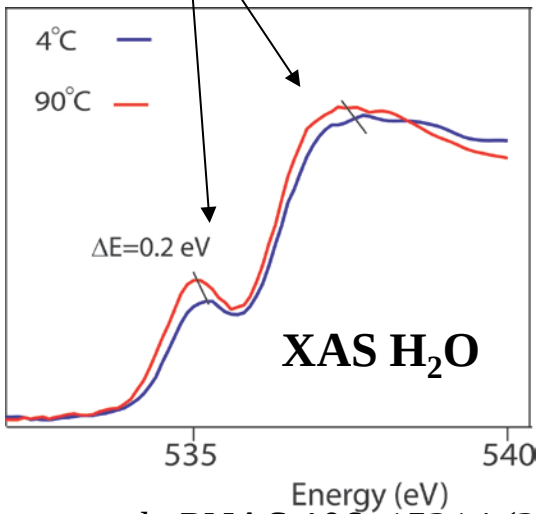
Enthalpy vs. Entropy

XES H_2O

- **Tetrahedral loses intensity** with temperature, but peak at fixed energy
- **Distorted gains intensity and disperses** with temperature in both XES and XAS
- **Energy taken up through**:
  - Thermal excitation of distorted species
  - Breaking up a fraction of tetrahedral species
- **Required**: Active modes in partition function



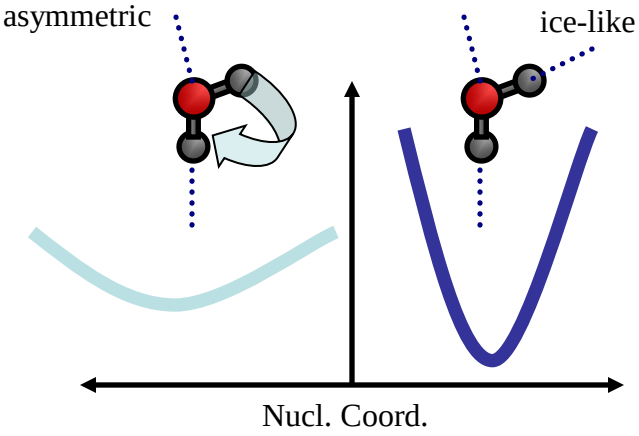
Energy shifts consistent



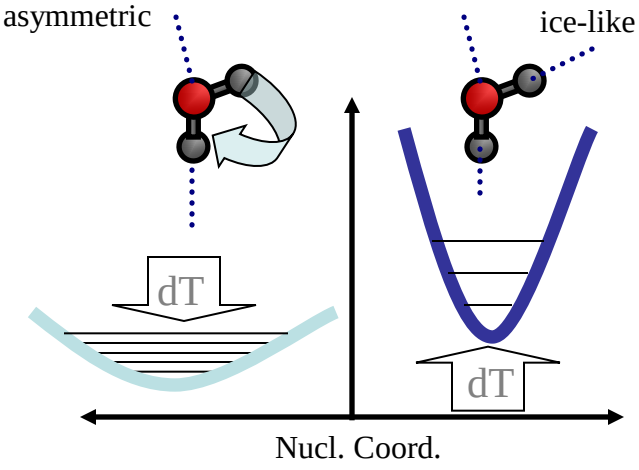
Tokushima *et al.*, Chem. Phys. Lett. **460** (2008) 387

Huang *et al.*, PNAS **106**, 15214 (2009)

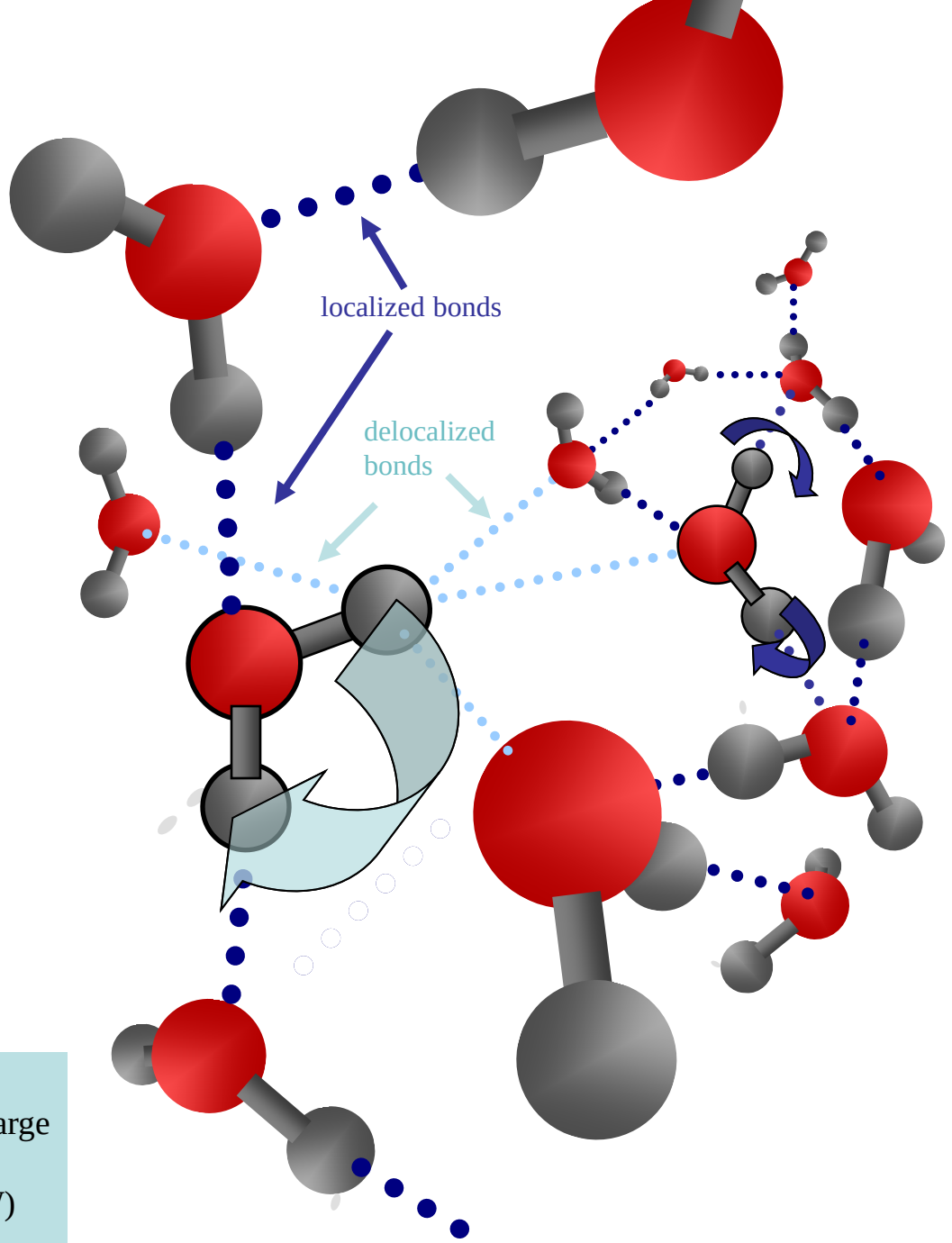
Enthalpy (H)



Gibbs Free Energy
dG = dH - SdT

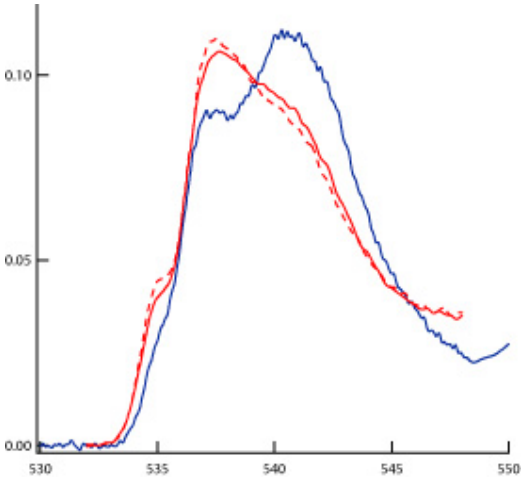


Librational modes quantized
Level-spacing in tetrahedral ice (~800 cm^{-1}) too large
No thermal excitation, no entropy contribution
Less specific, but more H-bond interactions (vdW)
(distorted species) lowers spacing to kT (”HDL”)



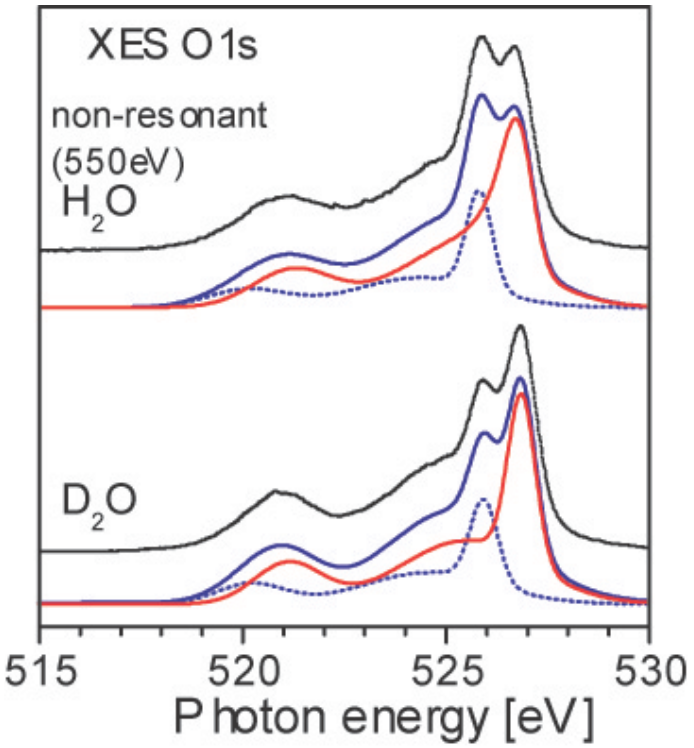
Motifs Population

XAS/XRS



Decompose based on ice spectrum

XES



Decompose as two shifted spectra

Species	Disordered	Tetrahedral
XAS	60-80%	20-40%
XES	70-80%	20-30%
MD	20-40%	60-80%

What Do Diffraction+IR/Raman Say?
RMC Modeling

What do the data actually allow when there are "NO" assumptions *i.e.* when MD potentials or force-fields do not guide the analysis?

Use reverse Monte Carlo (RMC) to determine water structures that reproduce:

a) X-ray diffraction (Hura *et al*., 2003 Q_{max}=10.8 Å^{-1})
b) Neutron diffraction (Soper, Q_{max}=50 Å^{-1})
c) E-field distribution (Raman spectrum)
d) Internal geometry distribution (from PI-CPMD; Sterne and Bern, JCP **115** (2001) 7622)

- Random Monte Carlo moves to minimize $\chi 2$ difference between model and experiment → maximally disordered structure consistent with data and constraints

TARGET – Explore extreme limits:

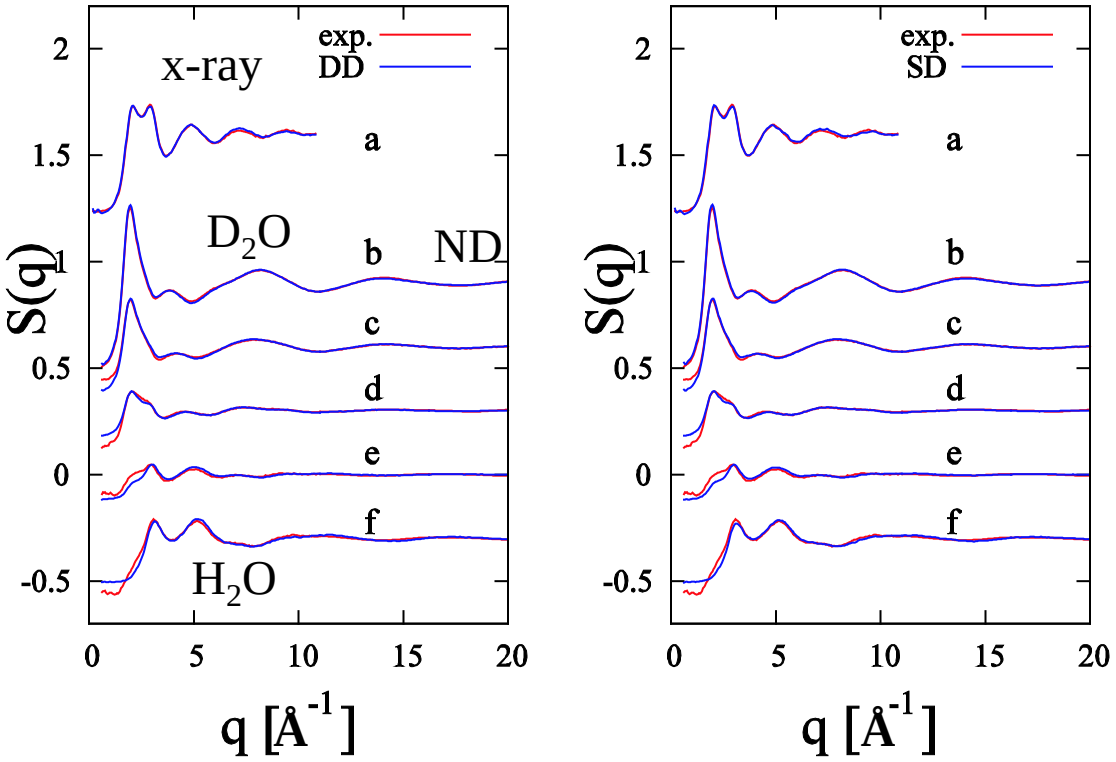
- Fit data AND maximize number of H-bonds to get **maximally symmetric model**

– OR –

- Fit data AND maximize number of asymmetric species to get **maximally asymmetric model**

Leetmaa *et al*., J. Chem. Phys. **129**, 084502 (2008)
Wikfeldt *et al*. J. Phys. Chem. B **113**, 6246 (2009)

RMC Fit of Diffraction Data



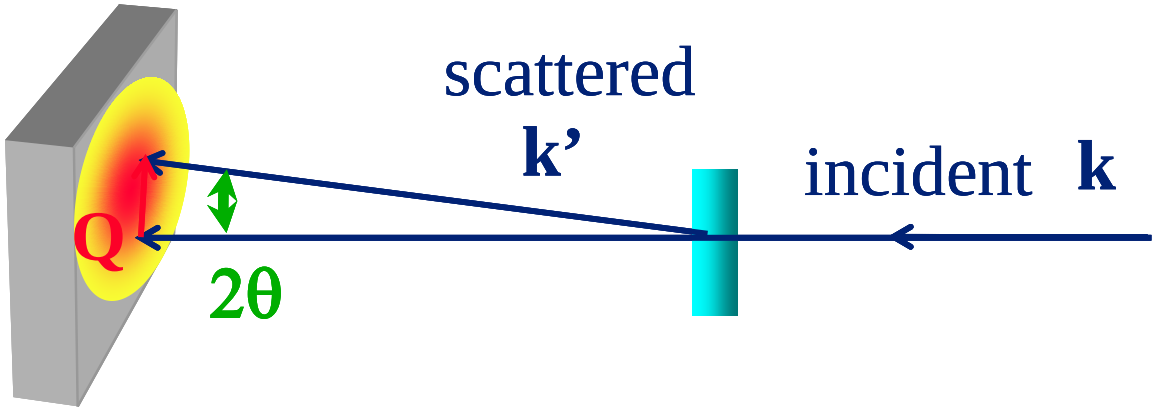
DD: 74%
SD: 21%
ND: 5%

DD: 18%
SD: 81%
ND: 1%

- X-ray and neutron data fitted together with E-field
- Equally good fit in both cases
- Diffraction data give NO preference
- IR/Raman equally good fits (E-field)

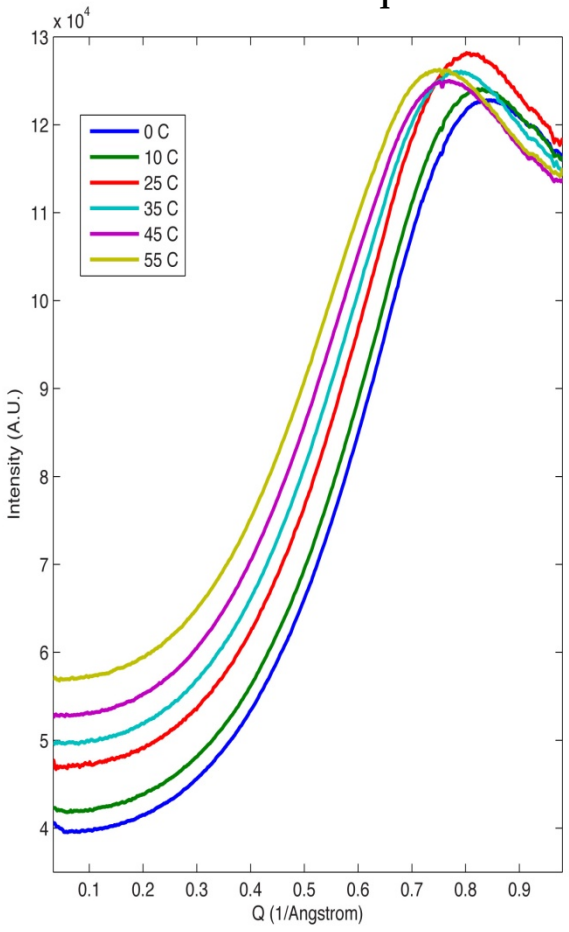
Leetmaa *et al.*, J. Chem. Phys. **129**, 084502 (2008)

Two Classes: Instantaneous Inhomogeneities? Small-Angle X-ray Scattering (SAXS)

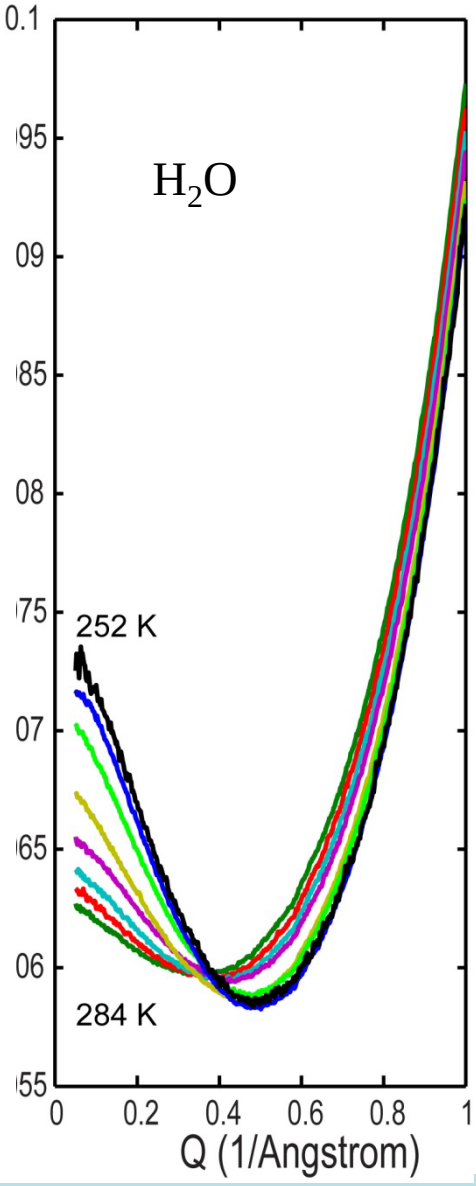


Water – Ambient to Supercooled Regime

C_2H_5OH
Normal liquid



Huang et al., unpublished



At low Q range

S(Q) shows an unusual enhancement

$$S^A(Q) \propto \frac{1}{\zeta^{-2} + Q^2} \quad Q<<1)$$

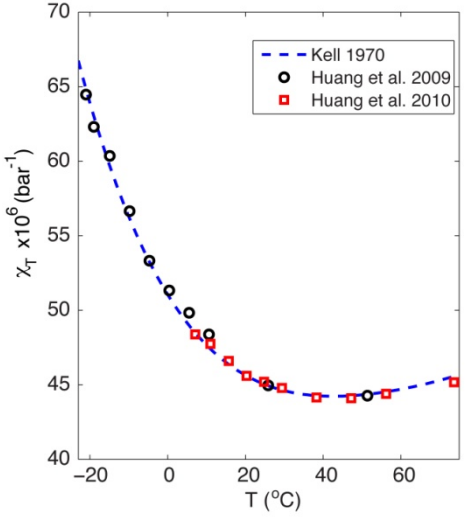
⇕ F.T.

$g^A(r) \sim \exp(-r/\zeta)/r \quad (r>>1)$

The isothermal compressibility χ_T

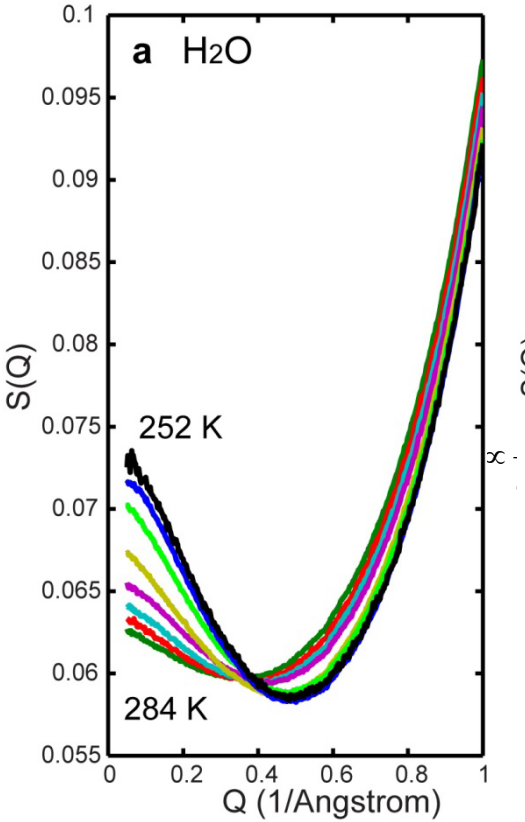
$$S(0) = k_B T n \chi_T$$

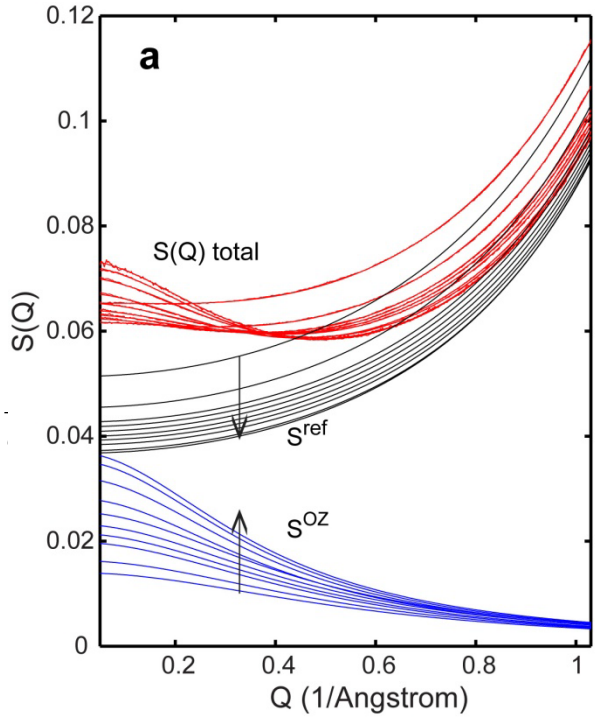
Very good fit to previous data



Huang *et al.*, PNAS **106**, 15214 (2009); PNAS **107**, E45 (2010); JCP **133**, 134504 (2010)

SAXS
Ambient to Supercooled Regime





Having both wide and small angle data from the same measurement we fit a normal and anomalous contribution:

Normal contribution from the Percus-Yevick approximation:

$$1/S^{ref} \propto 1 - 12\eta \frac{\left[\eta\left(3-\eta^2\right)-2\right]}{(1-\eta)^4} \frac{j_1(Q\sigma)}{Q\sigma}$$

$$\eta = \pi n \sigma^3 / 6$$

Anomalous contribution from Ornstein-Zernike theory:

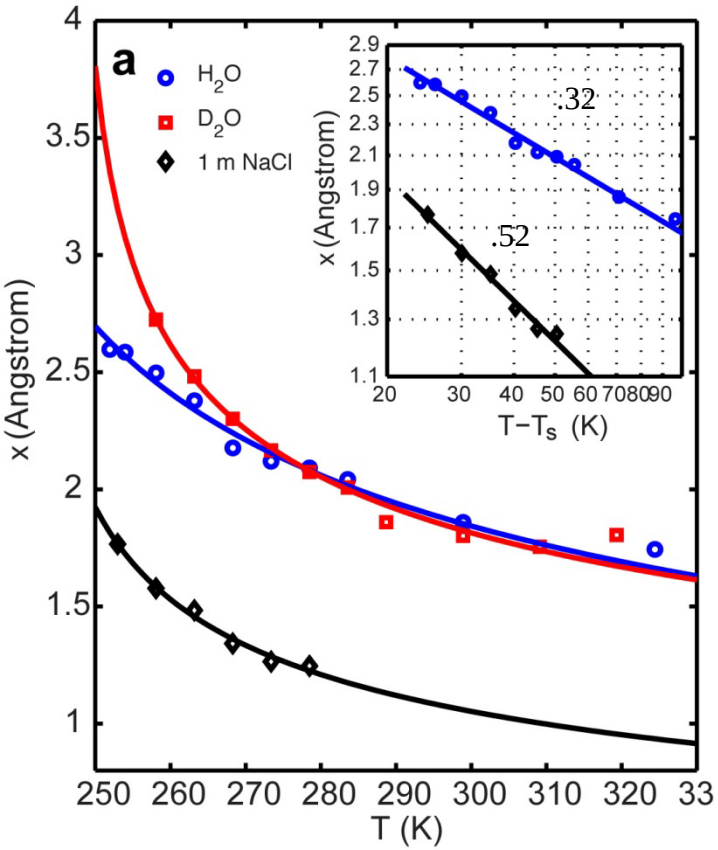
$$S^A(Q) \propto \frac{1}{\zeta^{-2} + Q^2}$$

Extract correlation length ζ

Huang *et al.*, JCP **133**, 134504 (2010)

Apparent Power Law – Widom Line

Critical phenomena characterized by power laws with critical exponents



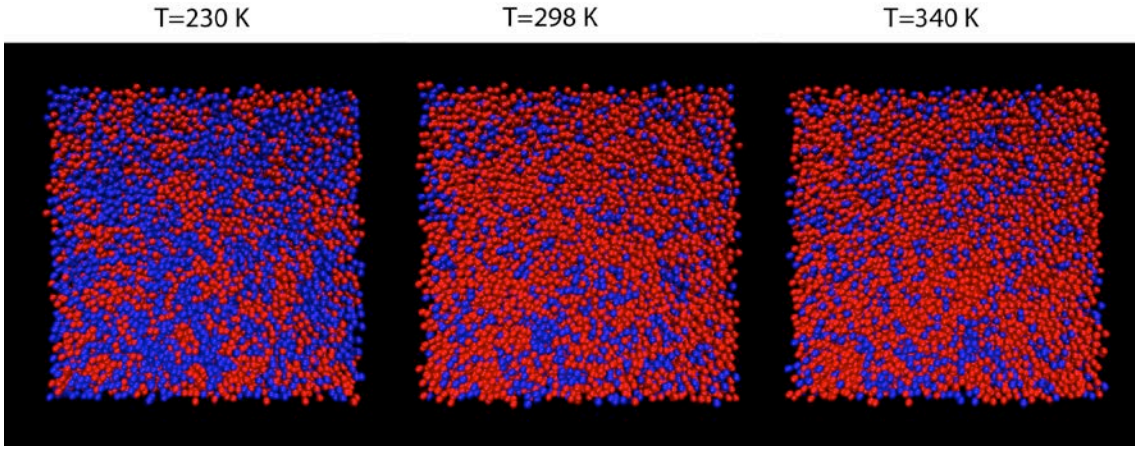
Fit ζ to (apparent) powerlaw

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

with

$\varepsilon = T/T_s - 1$ with T_s=228 K

Fluctuations from disordered into tetrahedral
Real-space ~1 nm

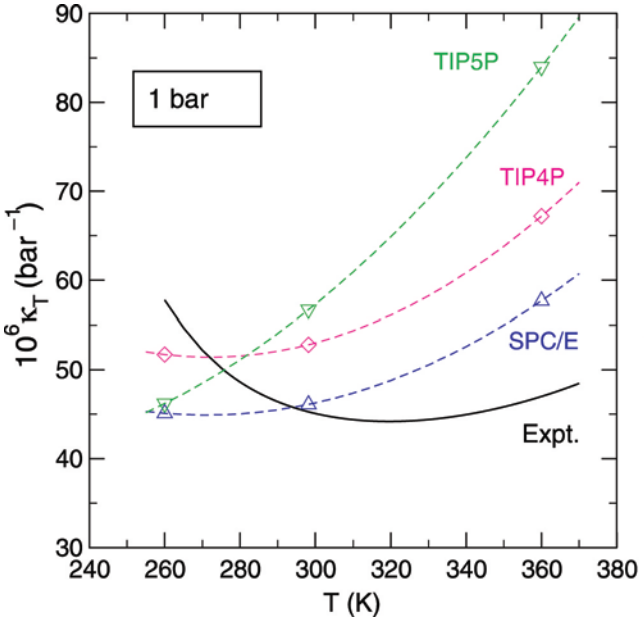


TIP4P/2005 simulations
Blue LDL, Red HDL
based on inherent structure

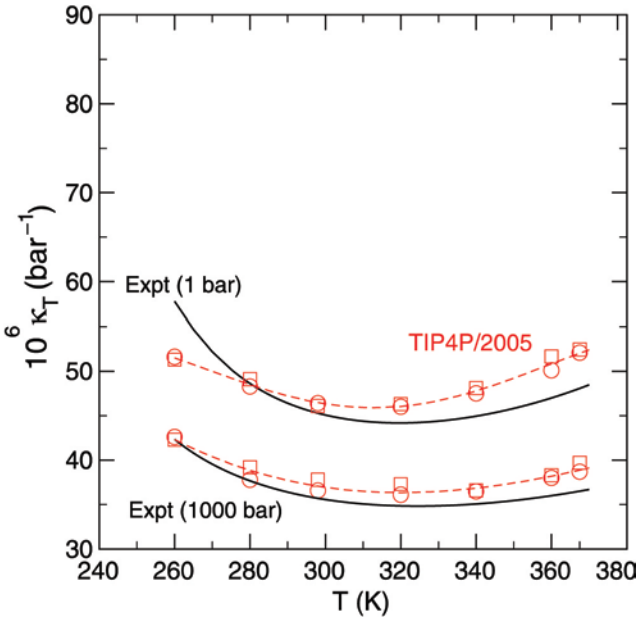
Huang et al., JCP **133**, 134504 (2010)

Wikfeldt et al., PCCP **13**, 19918 (2011)

Isothermal Compressibility H_2O: Different Force-Fields



Normal liquid behavior



Minimum about right, **but**:
Overestimate at high temperatures
Underestimate at low temperatures

Agreement better at high pressure

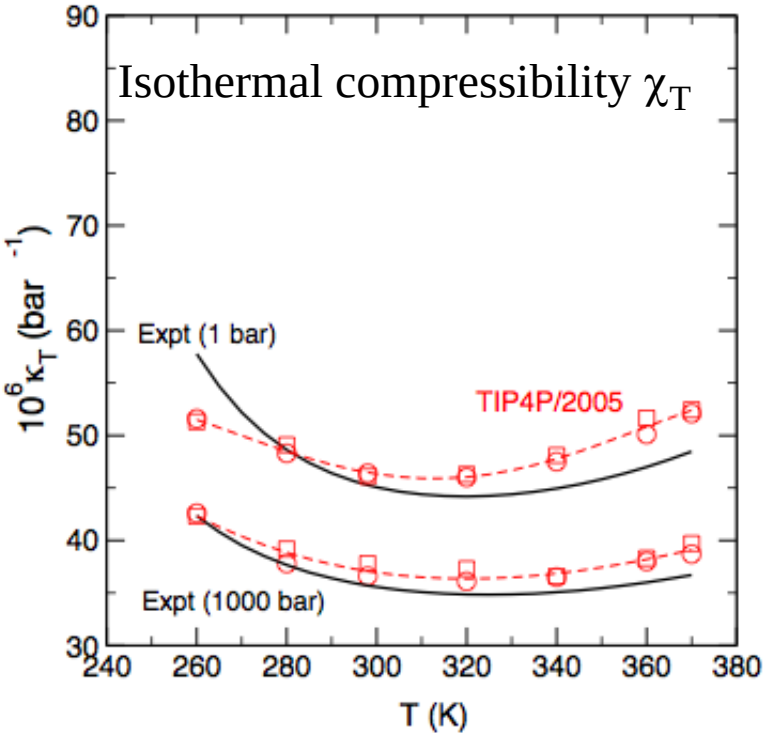
Corresponding states: Limmer and Chandler
http://arxiv.org/pdf/1305.1382.pdf

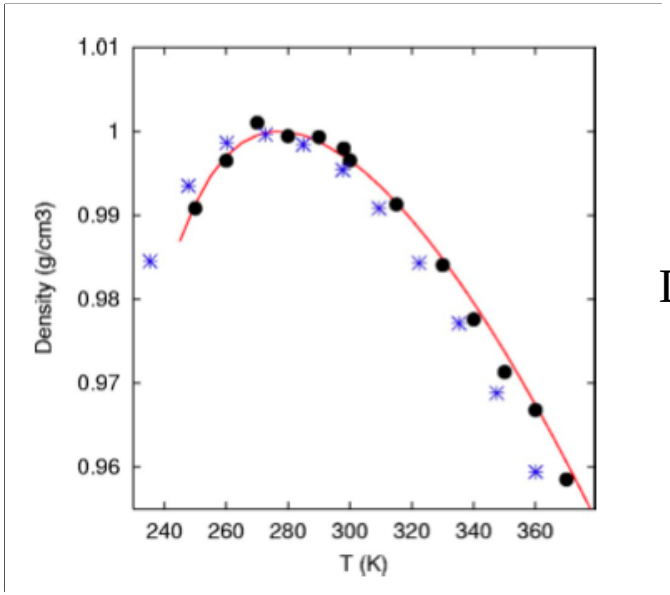
Pi et al., Mol. Phys. **107**, 365 (2009)

TIP4P/2005

- TIP4P/2005 reproduces density maximum and qualitatively minimum in χ_T
- LLCP at T_C = 193 K, P_C = 1350 bar [Abascal and Vega, J. Chem. Phys. 133, 234502 (2010)]

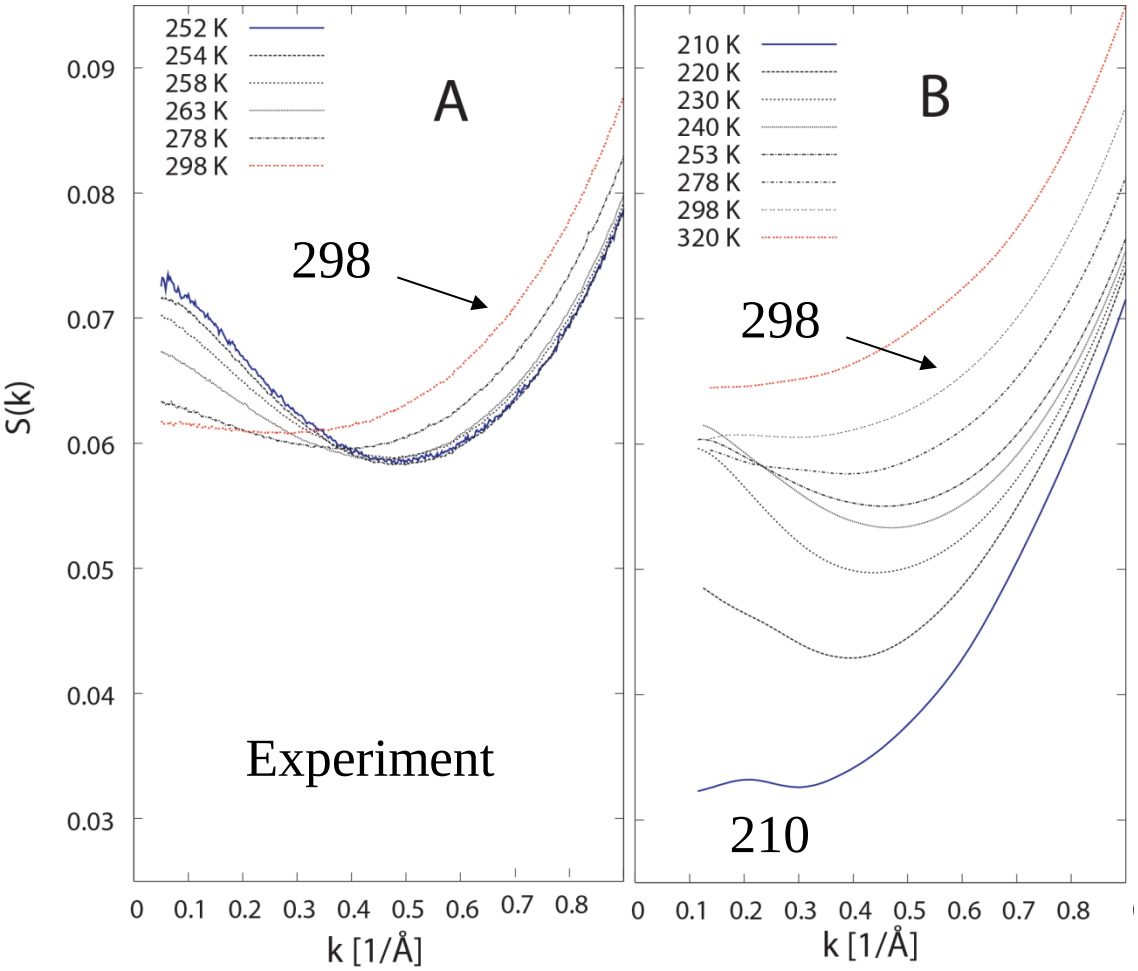
- Need *very* large simulations for SAXS, here 45,000 molecules (Q~2π/R)
- Need long equilibration times to reach equilibrated long-range correlations
- Need to average RDFs over long time intervals to average out spurious fluctuations in low-*q* structure factor $S(q) = 1 + 4\pi\rho \int w(r) r^2 [g(r) - 1] \frac{\sin(qr)}{qr} dr$





Density

SAXS from TIP4P/2005



Huang *et al.*, JCP **133**, 134504 (2010)

Simulated SAXS

We obtain SAXS signal from the MD, but **weaker** than experiment.

Trend is reproduced
Connect to experiment

Going down in temperature we see:

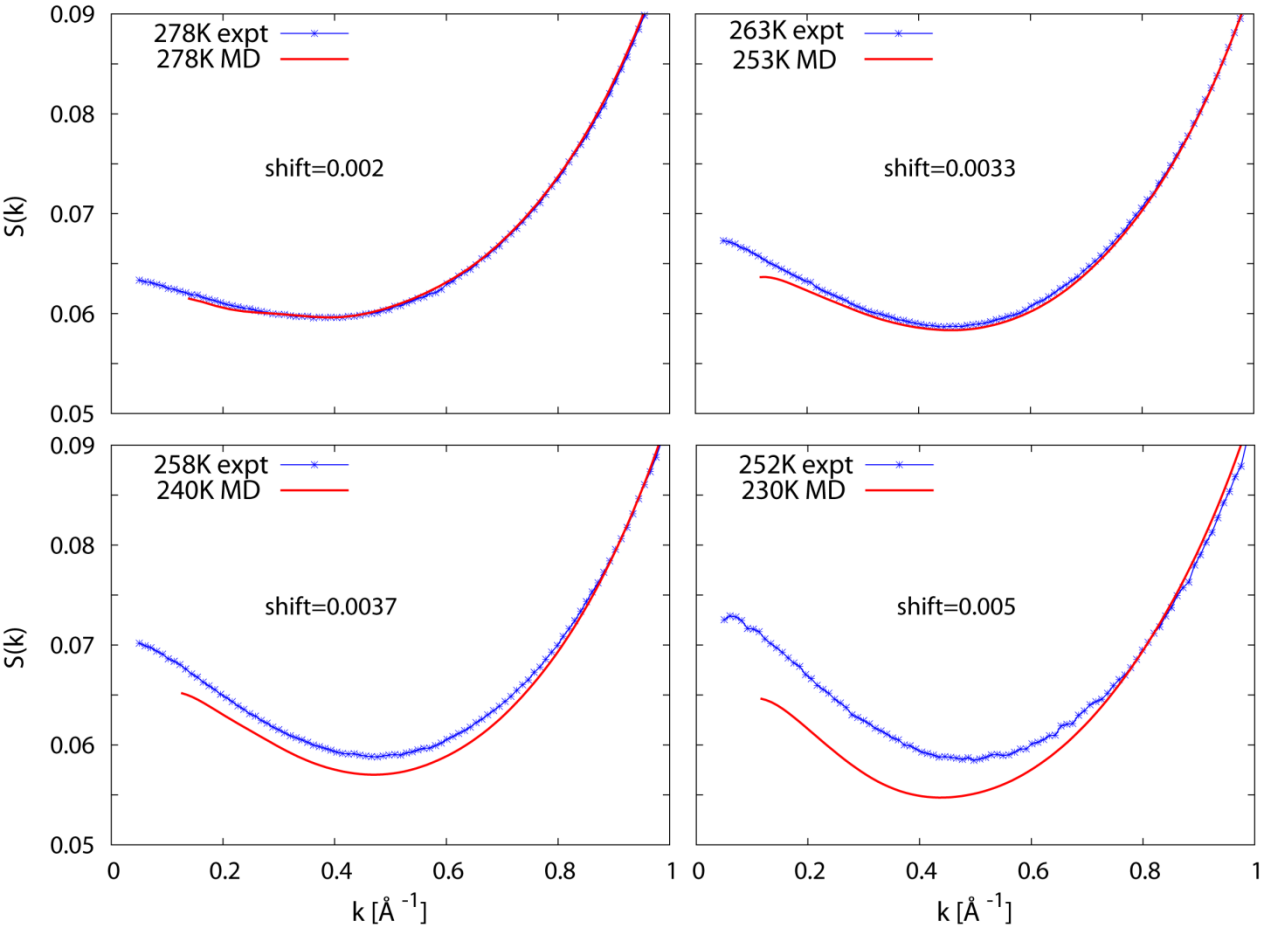
First additional enhancement

A maximum

Then reduced SAXS signal

Wikfeldt et al., J. Chem. Phys. **134**, 214506 (2011)

SAXS and TIP4P/2005



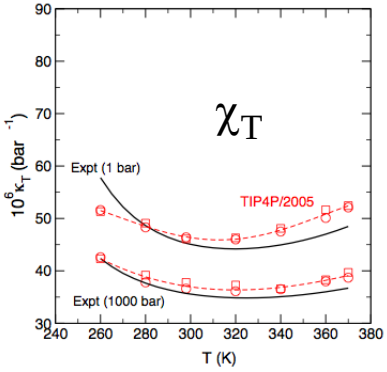
Excellent representation but:

278 K slight underestimate

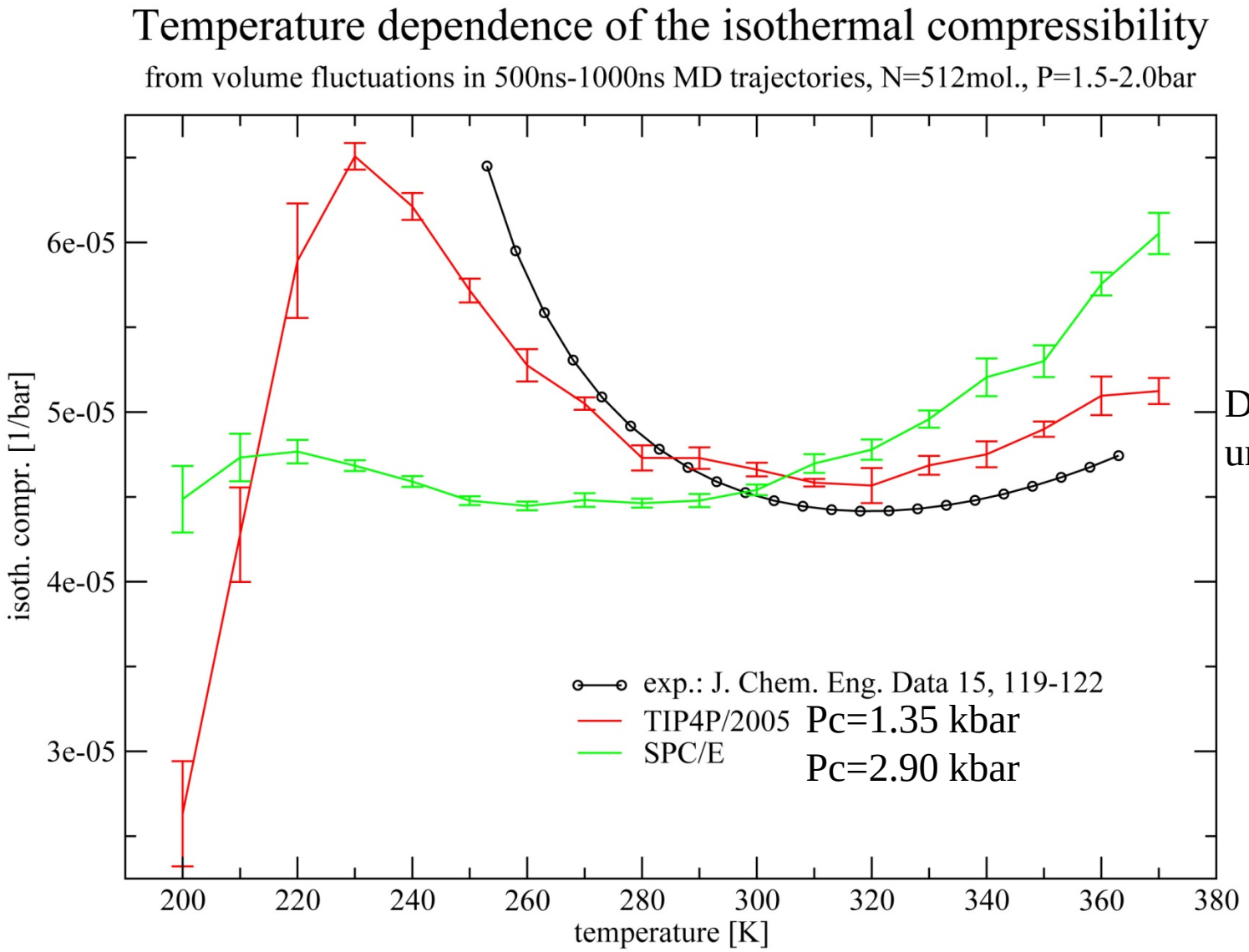
Shift both in T
and in S(k) needed

At 230 K maximum but smaller than expt. at 252 K

Real liquid closer to LLCP



Wikfeldt et al., J. Chem. Phys. **134**, 214506 (2011)



D. Schlesinger, unpublished.

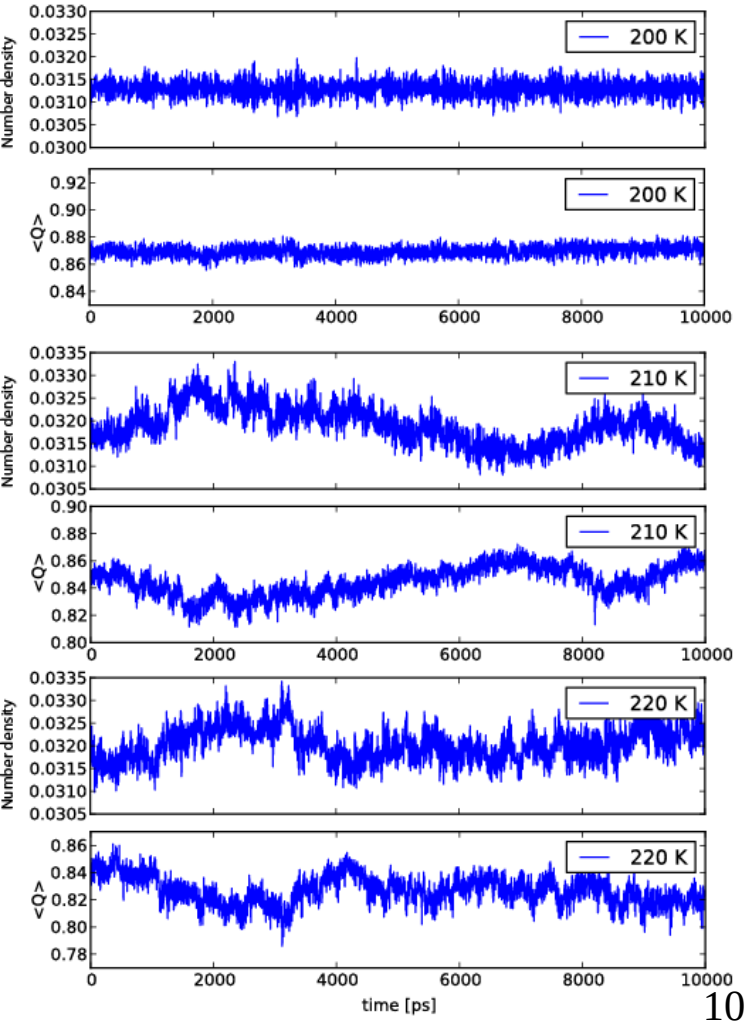
Enhancement at Widom line depends on distance to critical point (LLCP)
Real water may have a LLCP at close to ambient pressure (130-500 bar *)
This would give enhanced fluctuations and anomalous properties at ambient conditions

* Holten & Anisimov, arXiv:1207.2101v1; Mishima, JCP **133**, 144503 (2010)

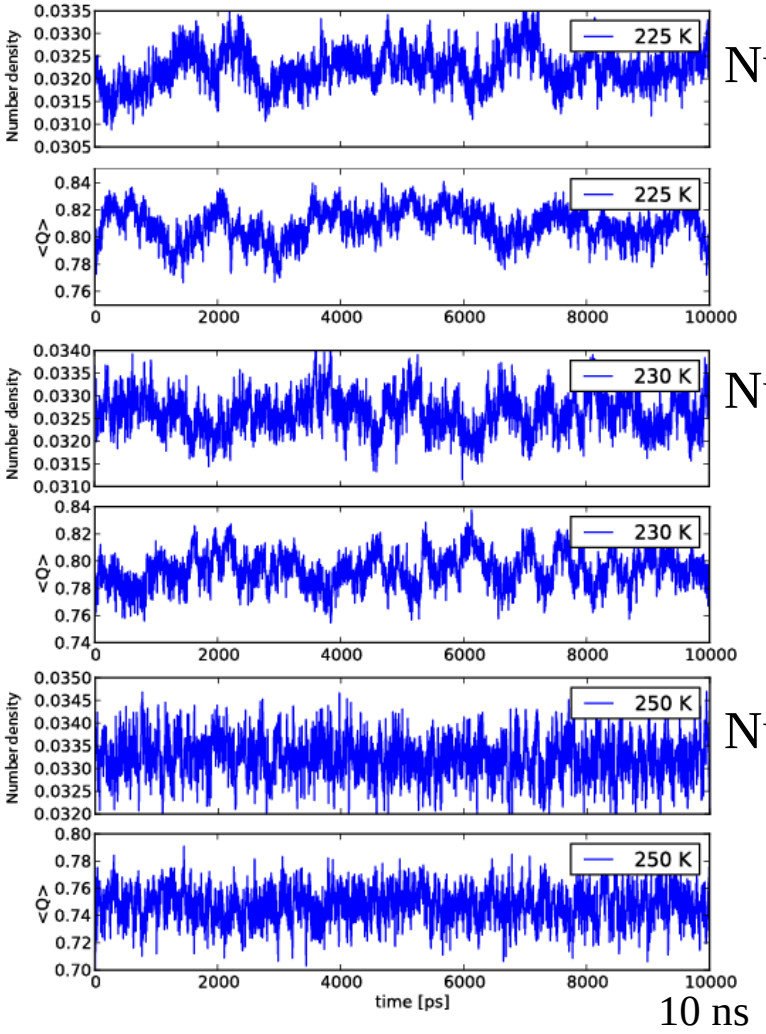
Tetrahedrality vs. Density: Anti-Correlated Fluctuations

Tetrahedrality <Q>

$$q_i = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\theta_{jik} + \frac{1}{3}\right)^2$$



10 ns



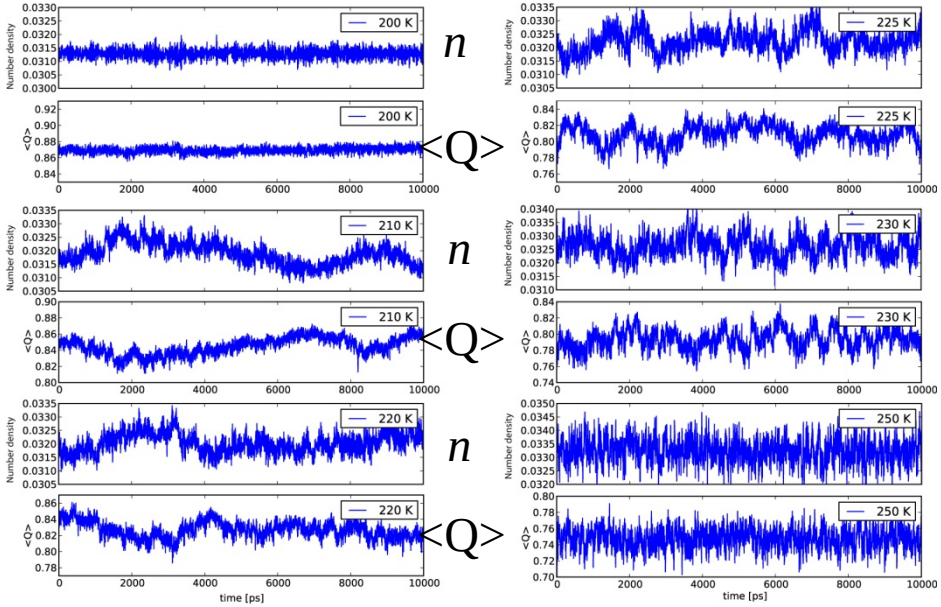
10 ns

Number density fluctuations on different time scales

Wikfeldt et al., J. Chem. Phys. **134**, 214506 (2011)

Density Fluctuations in TIP4P/2005 Water

Number density (n) and structural (<Q>) fluctuations with temperature: 200≤T≤250 K

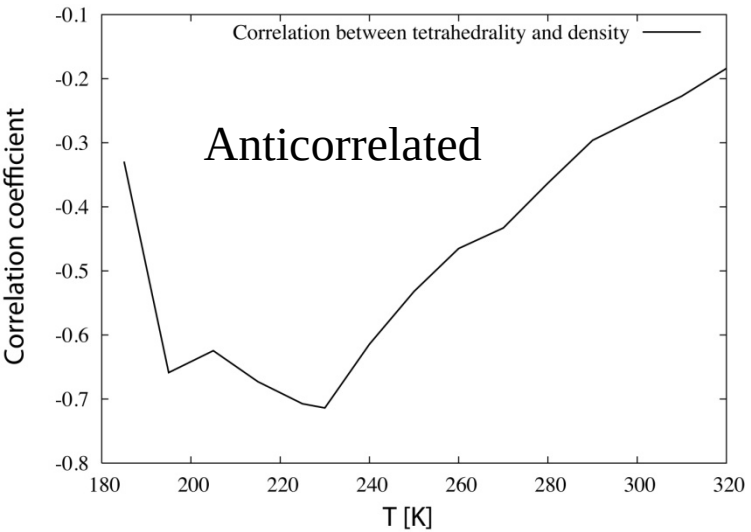


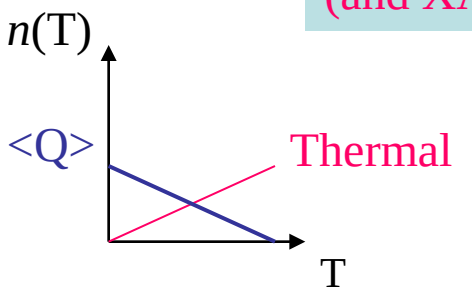
Two types of density fluctuations: Structural and Thermal

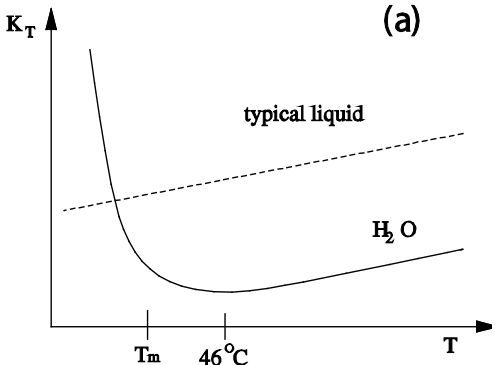
At low T: slow density fluctuations anti-correlated with <Q>; disordered to tetrahedral

At high T: simple thermal motion

Simulation gives the qualitative picture but fluctuations **too small** to give SAXS (and XAS, XES)

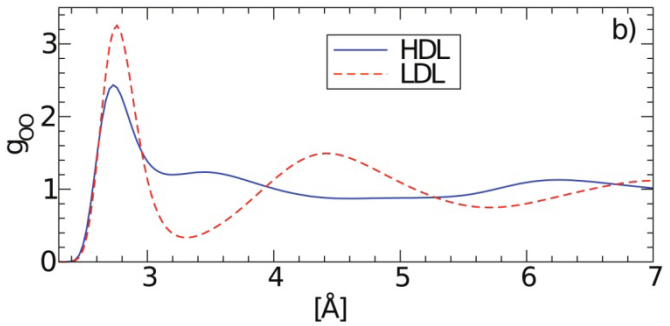




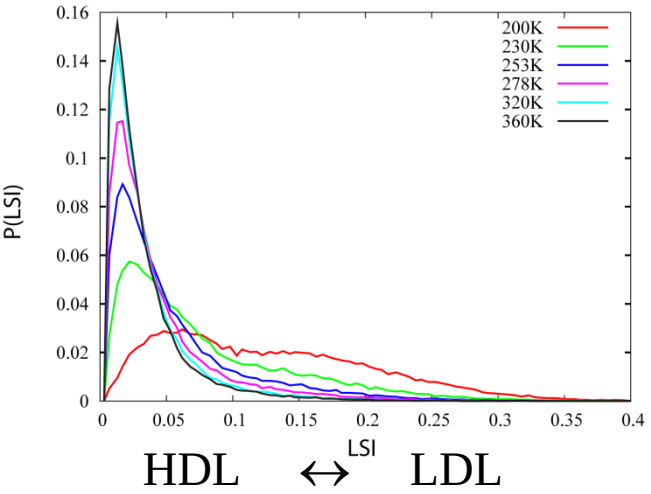


Local Structure Index (LSI)

Order molecules according to distance from molecule *i* as
$r_1 < r_2 < r_3 < \cdots < r_{n(i)} < 3.7\ \text{Å} < r_{n(i)+1}$
where $n(i)$ is the number of molecules that are within 3.7 Å from molecule *i*



Soper & Ricci PRL **84** (2000) 2881



HDL ↔ LDL

Define: $\Delta(j;i) = r_{j+1} - r_j$

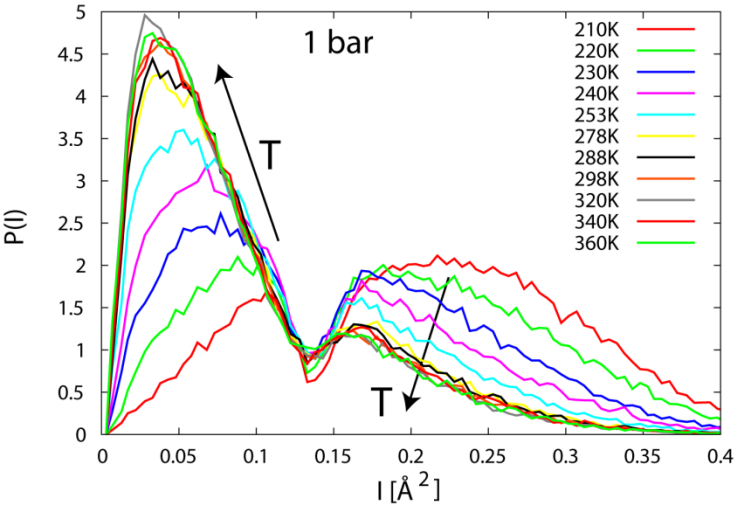
Average: $\overline{\Delta}(i)$ is the average of $\Delta(j;i)$ over all neighbors *j* of molecule *i* within cutoff

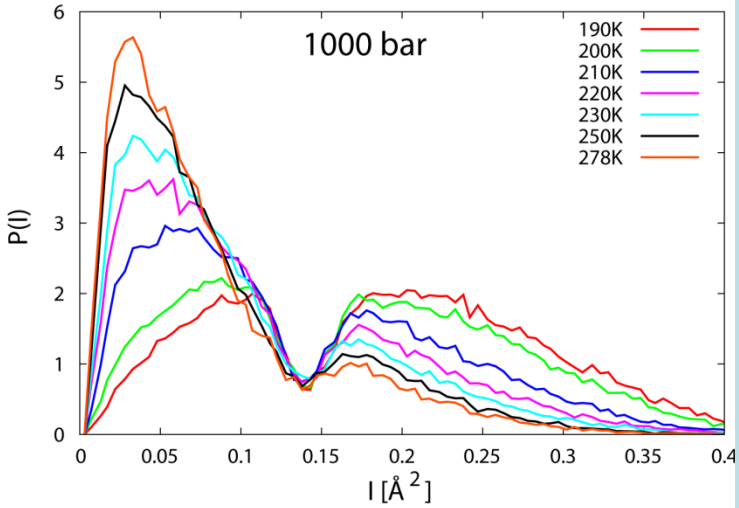
LSI: $$I(i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} \left[\Delta(j;i) - \overline{\Delta}(i)\right]^2$$

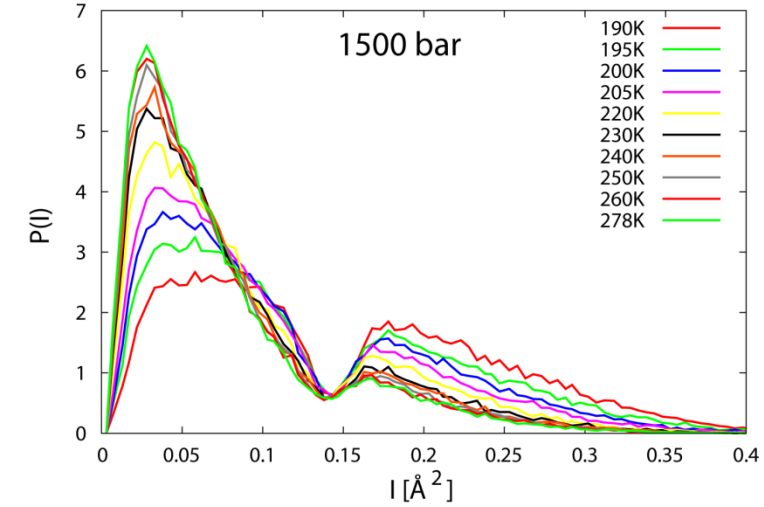
Measures degree of order

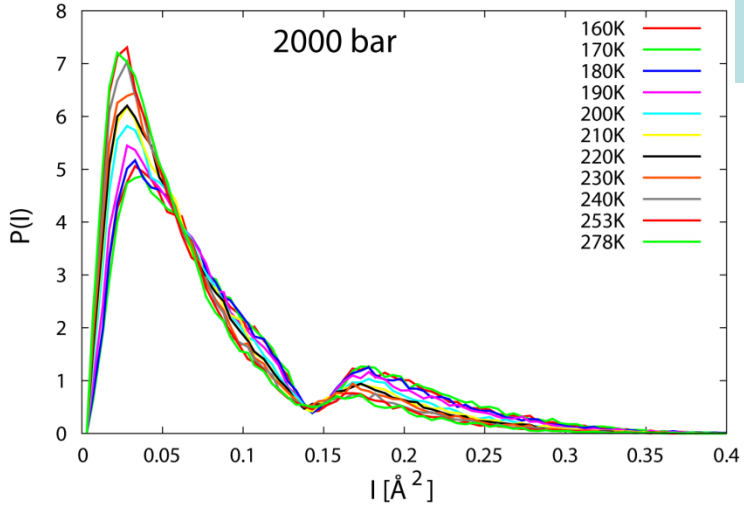
Shiratani & Sasai *J Chem Phys* **104,** 7671 (1996)
Shiratani & Sasai *J Chem Phys* **108,** 3264 (1998)
Appignanesi et al. *Eur. Phys. J. E* **29**, 305 (2009)
Accordino et al. *Eur. Phys. J. E* **34**, 48 (2011)
Wikfeldt et al., PCCP **13**, 19918 (2011)

Bimodality in Inherent Structure









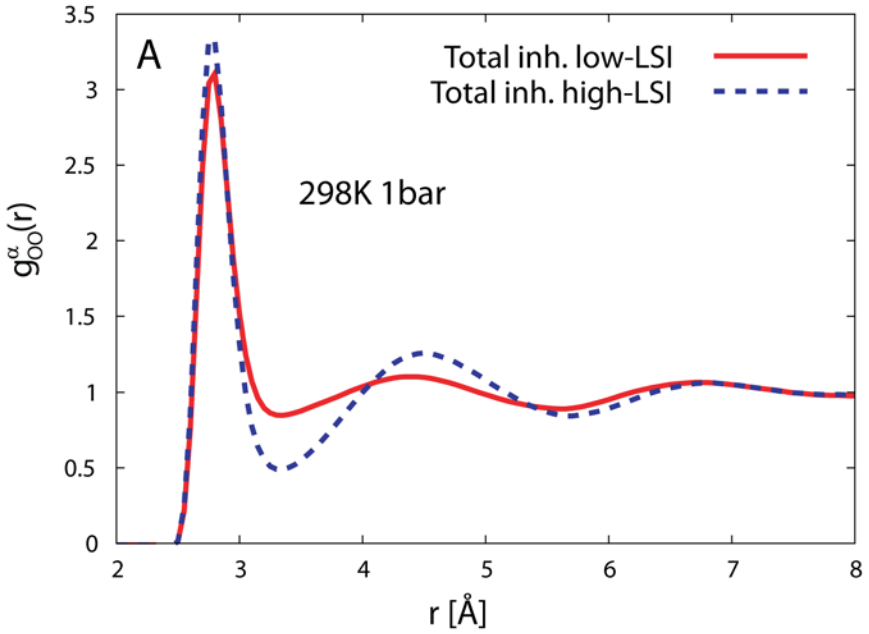
Inherent Structure: Quench to 0 K, i.e. minimize the energy for each dump

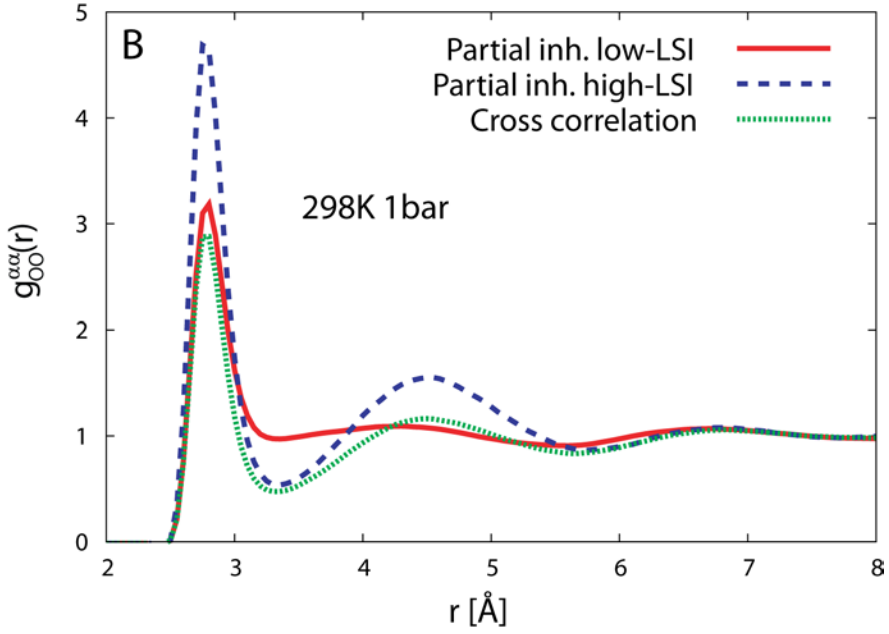
Bimodal

Minimum independent of temperature and pressure

Wikfeldt et al., PCCP **13**, 19918 (2011)

HDL and LDL





Classify molecules in ”Real Structure” according to LSI in Inherent Structure

Pair-correlation as LDL and HDL

Pair-correlation among species: high-high, low-low, and cross-correlation high-low

Cross-correlation weak → spatial separation

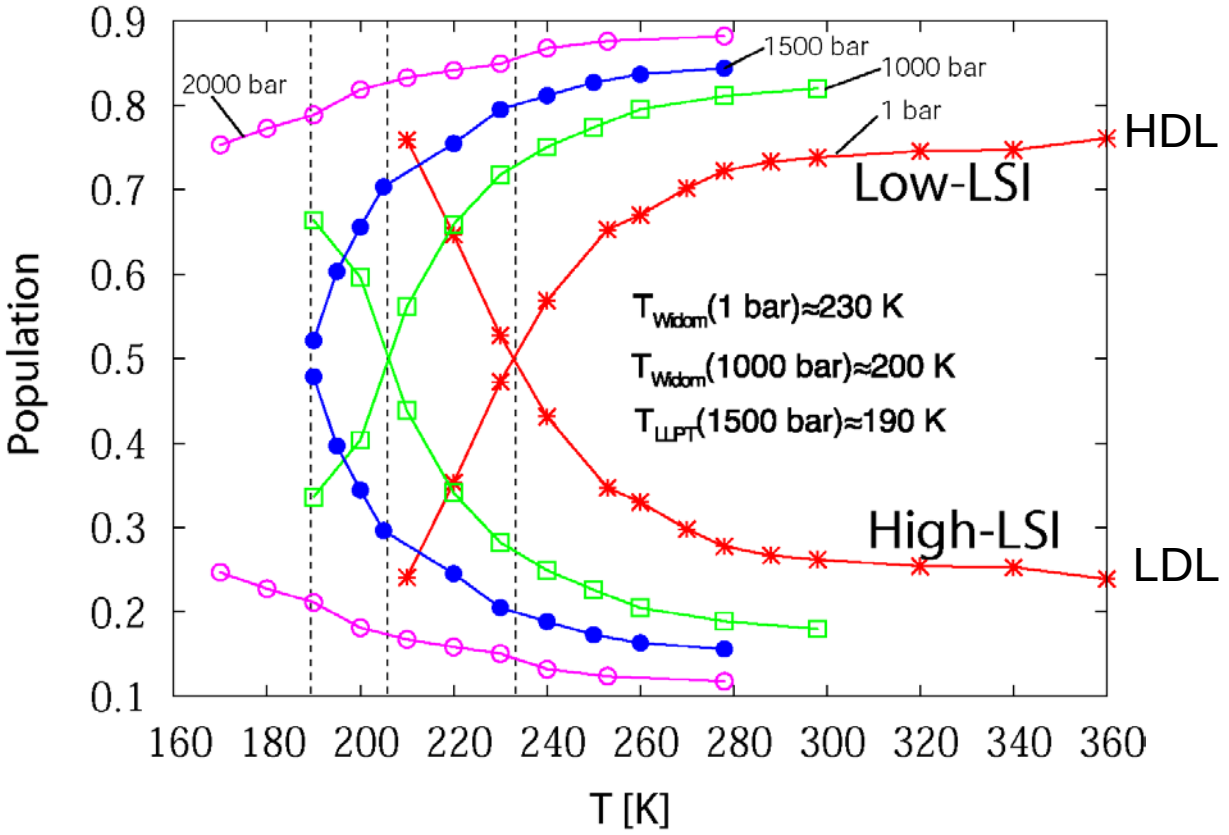
Wikfeldt et al., PCCP **13**, 19918 (2011)

Temperature and Pressure Dependence

Ambient conditions:
~75% HDL, 25% LDL
(≡ XAS, XES)

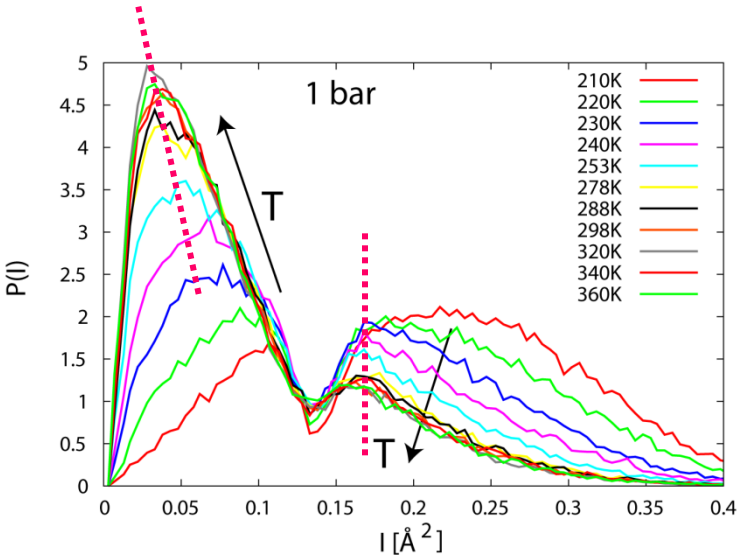
Widom line:
50% HDL, 50% LDL
Maximum fluctuations
(κ_T, C_P)

Increasing pressure:
Fraction HDL increases

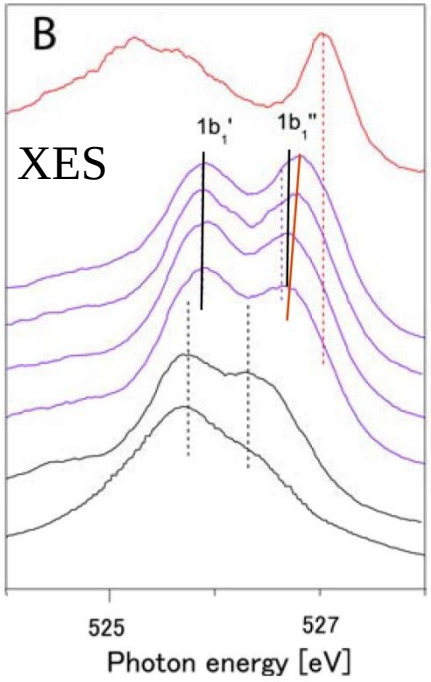


Wikfeldt et al., PCCP **13**, 19918 (2011)

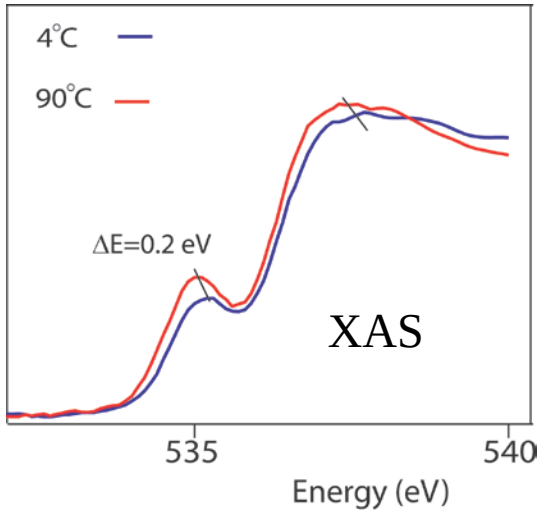
Temperature Dependence LSI vs XES



LSI inherent structure
High LSI fixed (LDL)
Low LSI disperses (HDL)

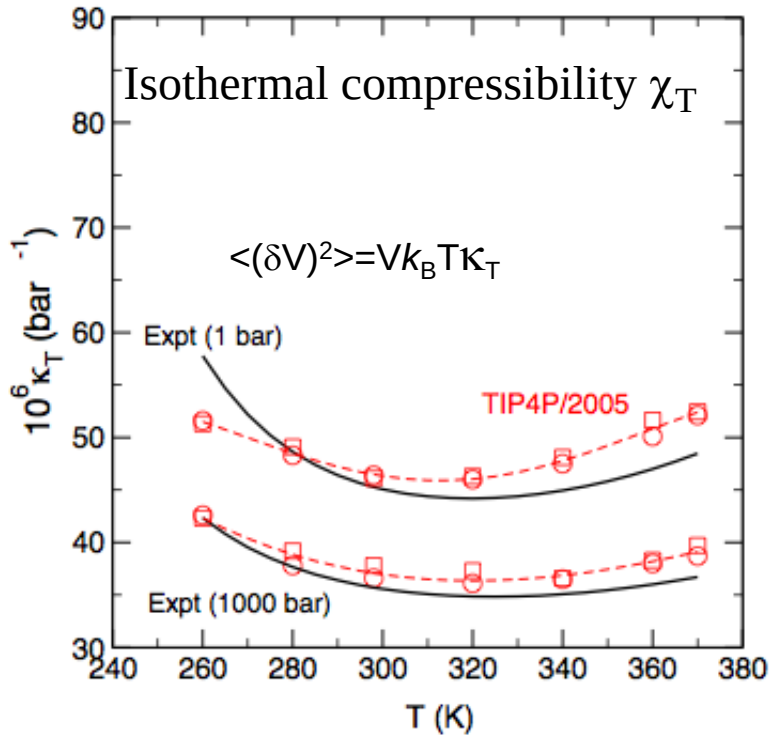


XES/XAS
”LDL”-like fixed
”HDL”-like disperses



Bimodality with similar temperature dependence in LSI inherent structure and in XES/XAS
Smeared out in real structure

Bimodality Washed out in Real Structure

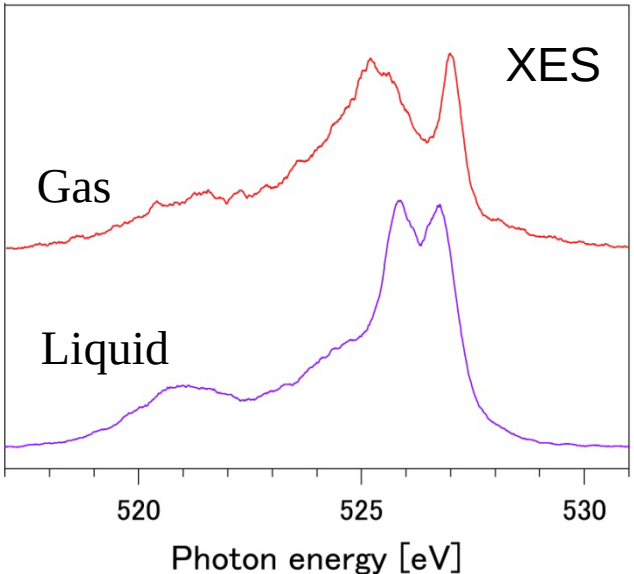


Strong bimodality only in inherent structure ≠ XAS, XES

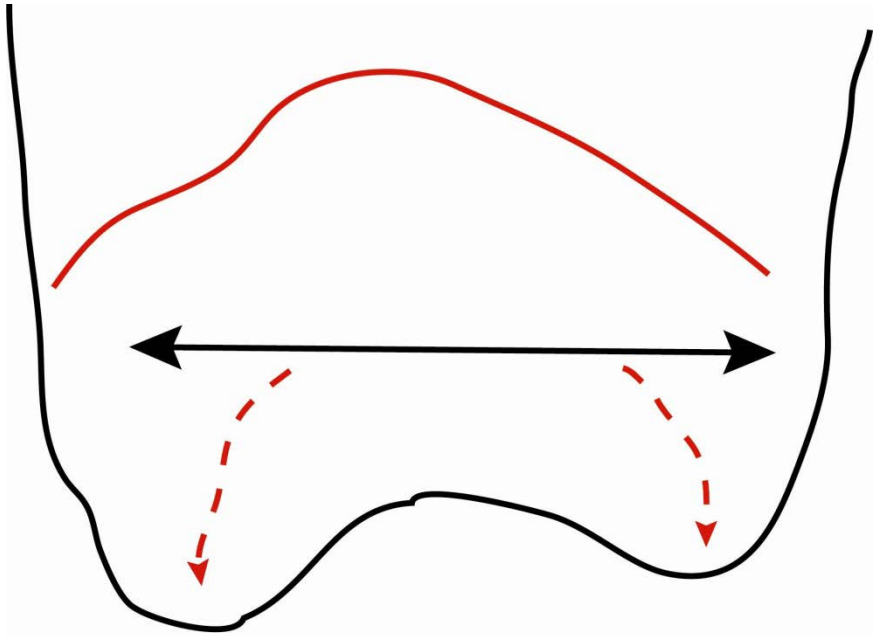
Above 320 K thermal fluctuations are overestimated

Below 280 K structural LDL/HDL fluctuations are underestimated

Potential surface not sufficiently corrugated? Simulation moving too far above? XES/XAS say bimodal…



Bimodality Smeared Out

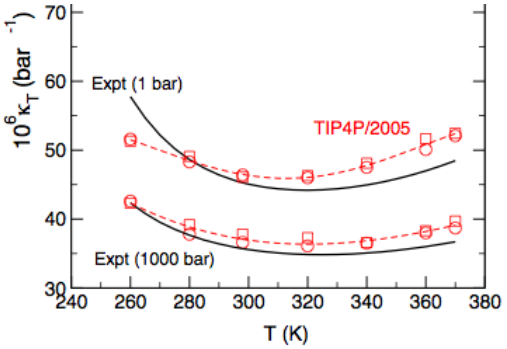


HDL LDL

Strong bimodality only in inherent structure ≠ XAS, XES

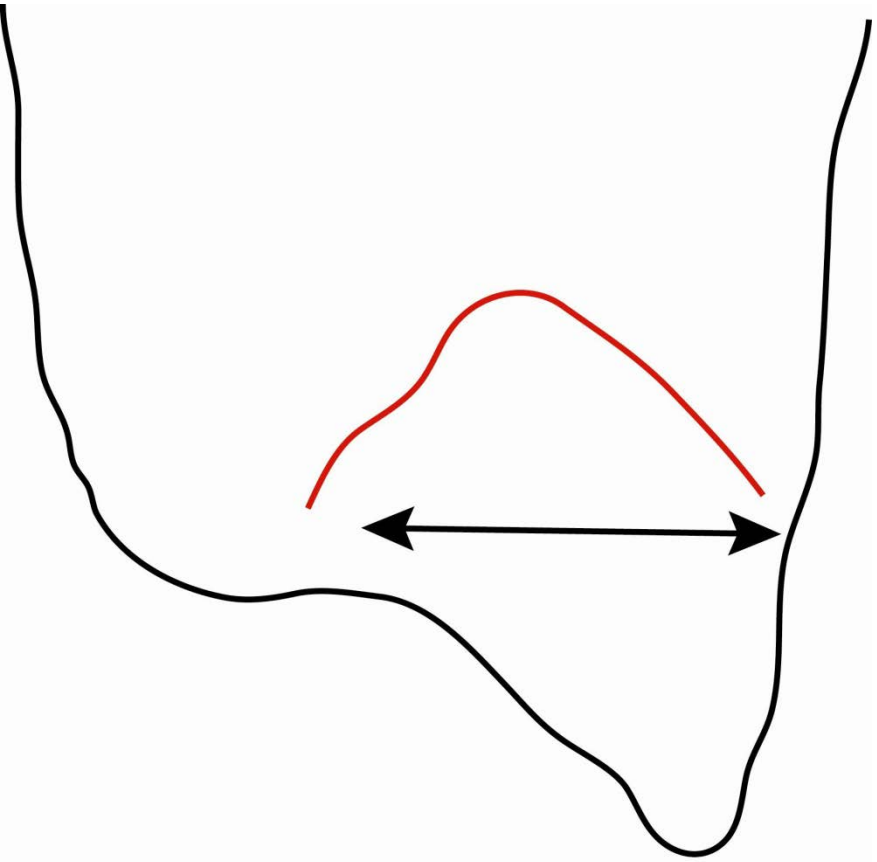
Above 320 K thermal fluctuations are overestimated

Below 280 K structural LDL/HDL fluctuations are underestimated



Potential surface not sufficiently corrugated? Simulation moving too far above? XES/XAS say bimodal…

Add Electronic Cooperativity



HDL LDL

Cooperativity and anticooperativity effects (QM electronic structure)

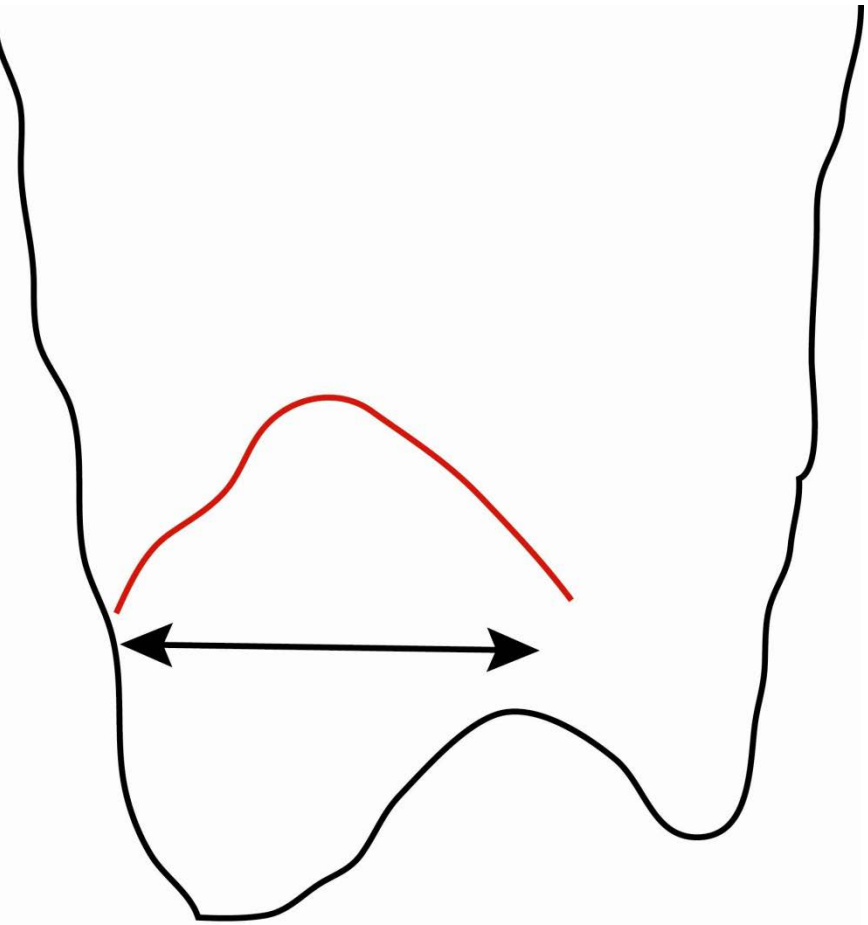
Cooperativity: The central H-bond in a chain of 7 molecules has maximum strength Ojamäe & Hermansson, J. Phys. Chem. 98, 4271 (1994)

Anticooperativity: DA and DDAA favored over imbalance between donors and acceptors

Not described by polarizable FF
Nilsson et al., J. Chem. Phys. **122**, 154505 (2005)

DFT GGA: Favors H-bond formation
Enhances tetrahedral LDL strongly

Add Non-Local Correlation (vdW)



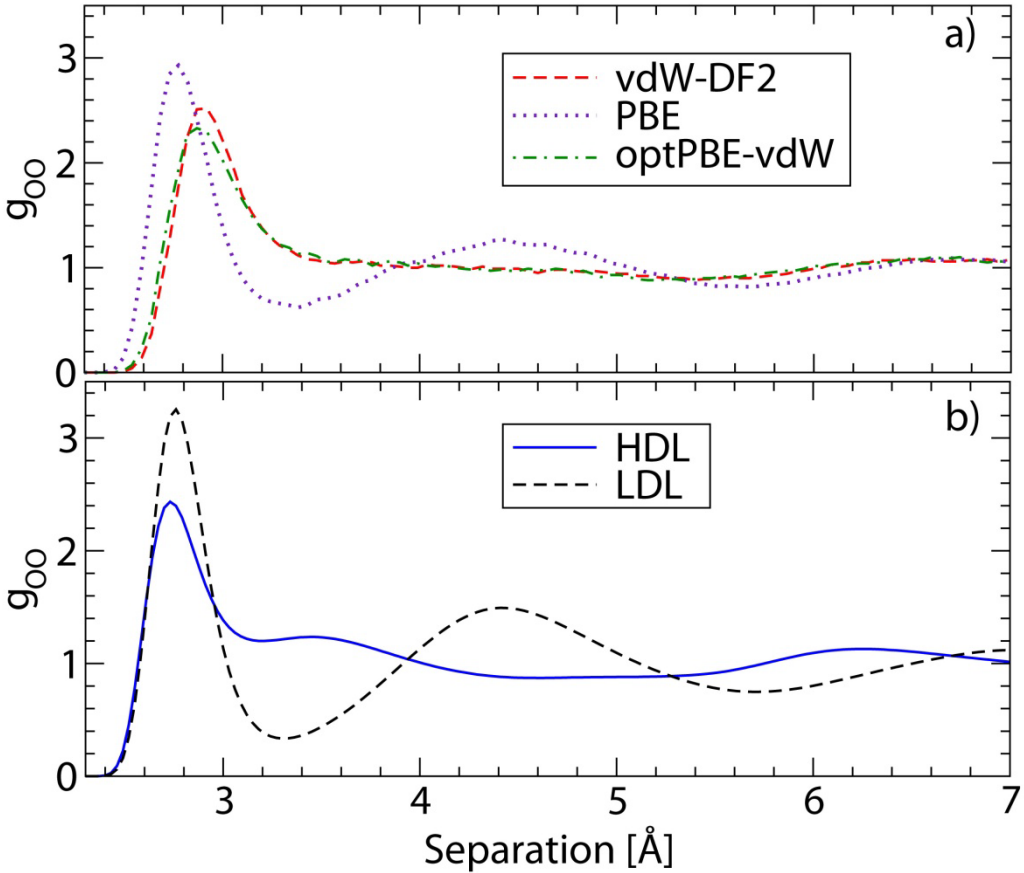
HDL LDL

Non-directional vdW favors close-packing (HDL) over tetrahedral (LDL)

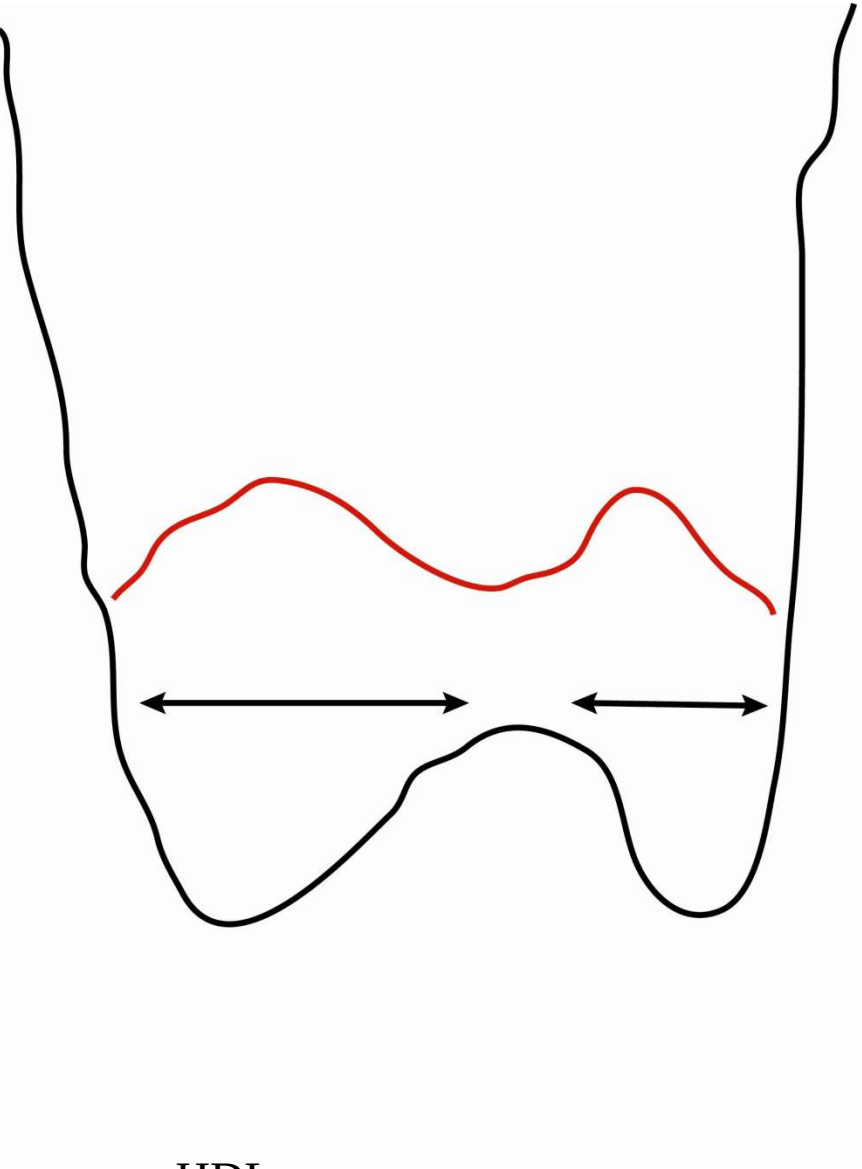
Wang et al., JCP **134**, 024516 (2011)

Møgelhøj et al., JPC B **115**, 14149 (2011)

Extent depends on implementation

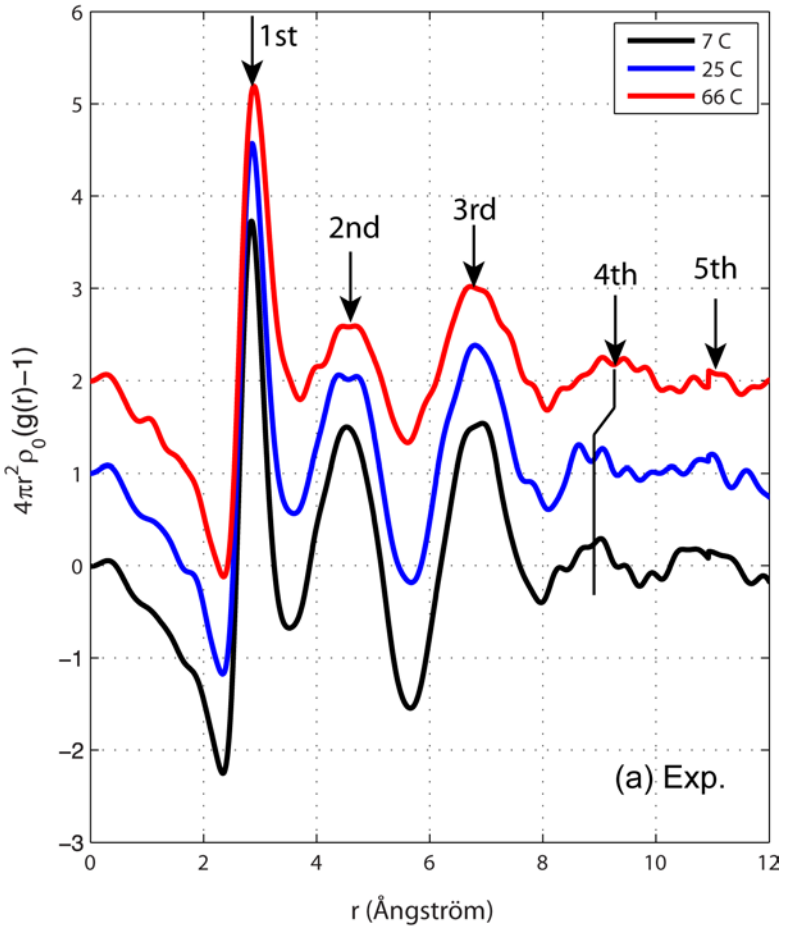


Increase the Size



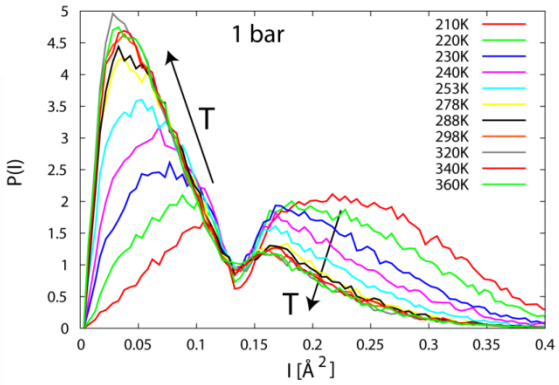
HDL LDL

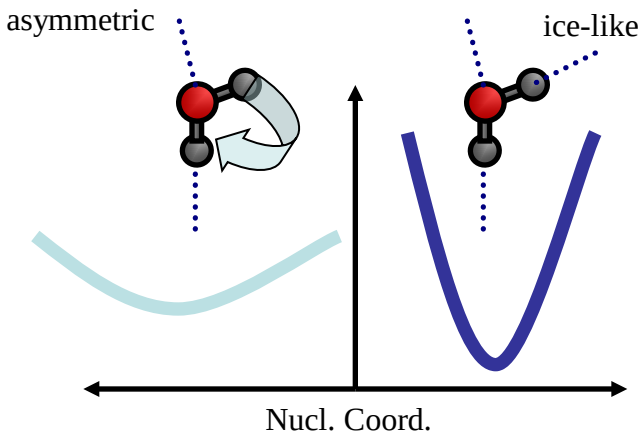
Structure observed out to 5-6 shells
Mainly LDL
Large box required
1000-10000 molecules?



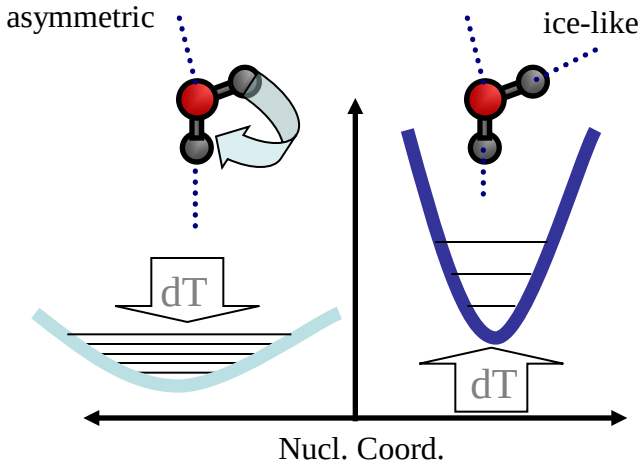
Huang et al., PCCP. **13**, 19997 (2011)

Add Quantum Effects





Gibbs Free Energy
dG = dH - SdT



LDL disfavored by entropy

HDL LDL

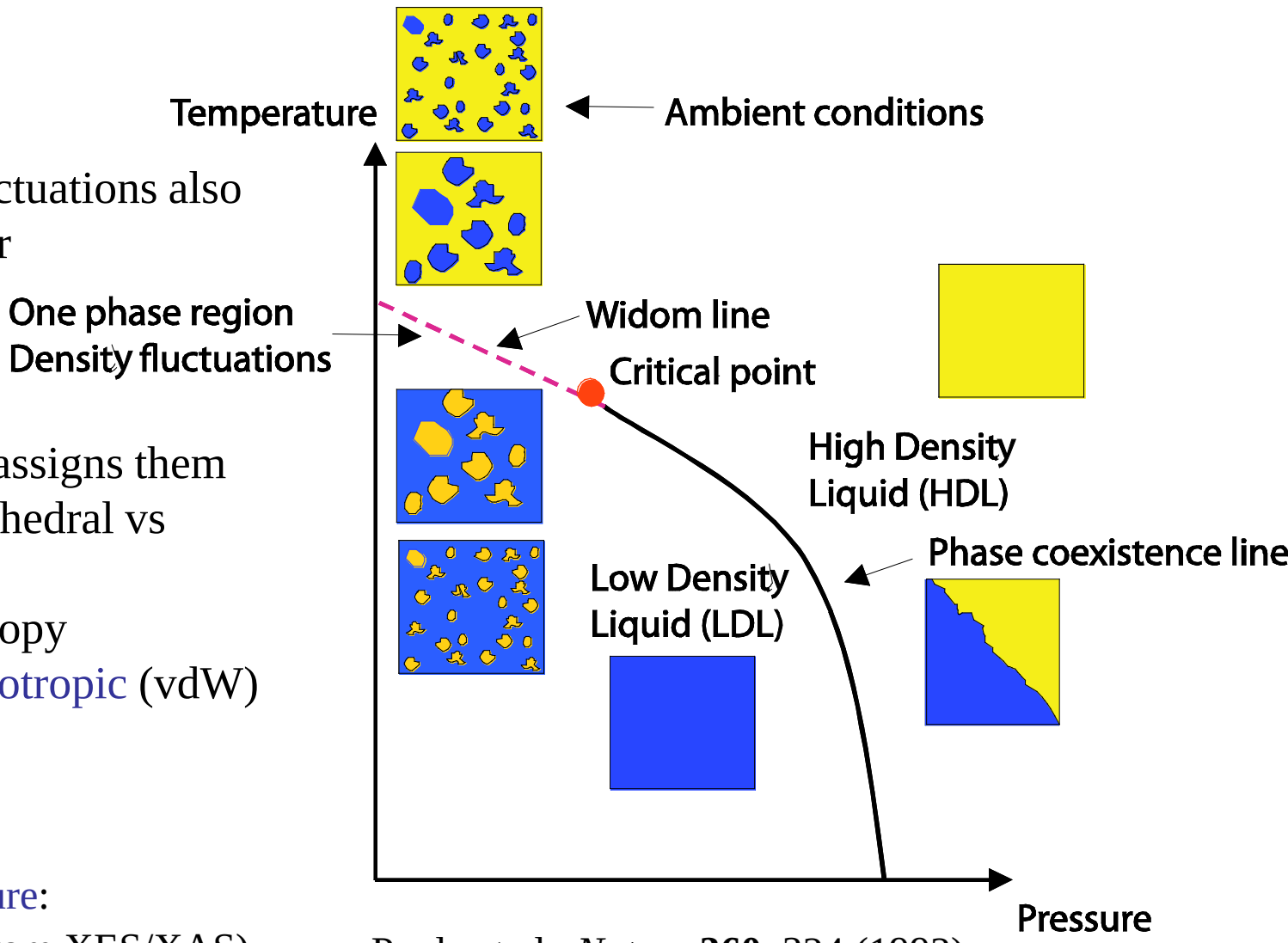
Librational modes quantized
Level-spacing in tetrahedral ice (~800 cm^{-1}) too large
No thermal excitation, no entropy contribution
Less specific, but more H-bond interactions (vdW)
(distorted species) lowers spacing to kT (”HDL”)

Consistent with Existence of Widom Line and 2nd Critical Point Scenario (real or virtual)

SAXS shows fluctuations also for ambient water

XAS/XRS/XES assigns them structurally: tetrahedral vs disordered
Enthalpy vs. entropy
Directional vs. isotropic (vdW)
Small Δρ
Large Δ(H-bond)

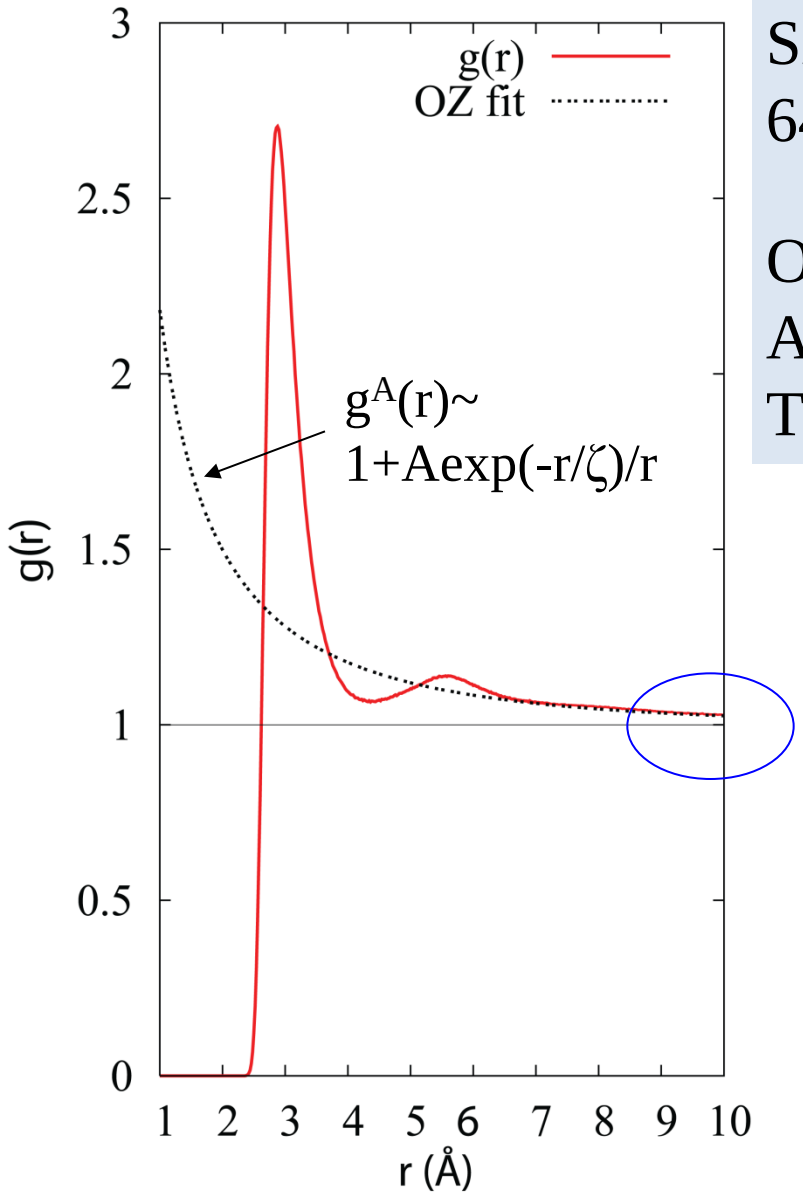
Ambient temperature:
HDL dominates (from XES/XAS)



Poole et al., *Nature* **360**, 324 (1992)

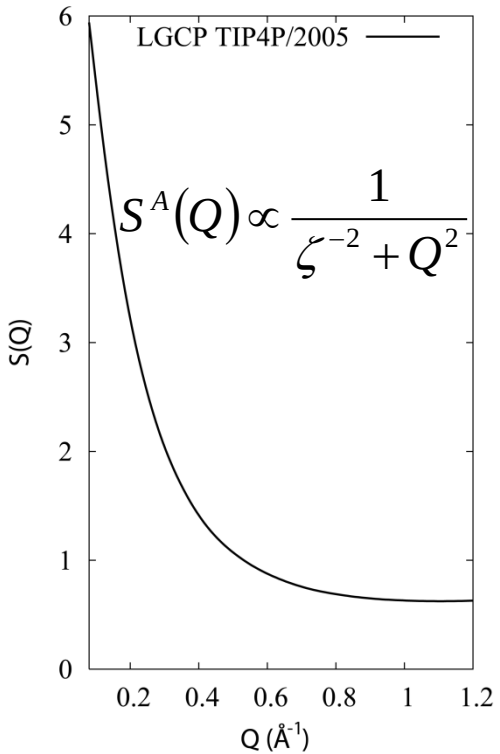
Correlation length

Correlation length Liquid-Gas CP

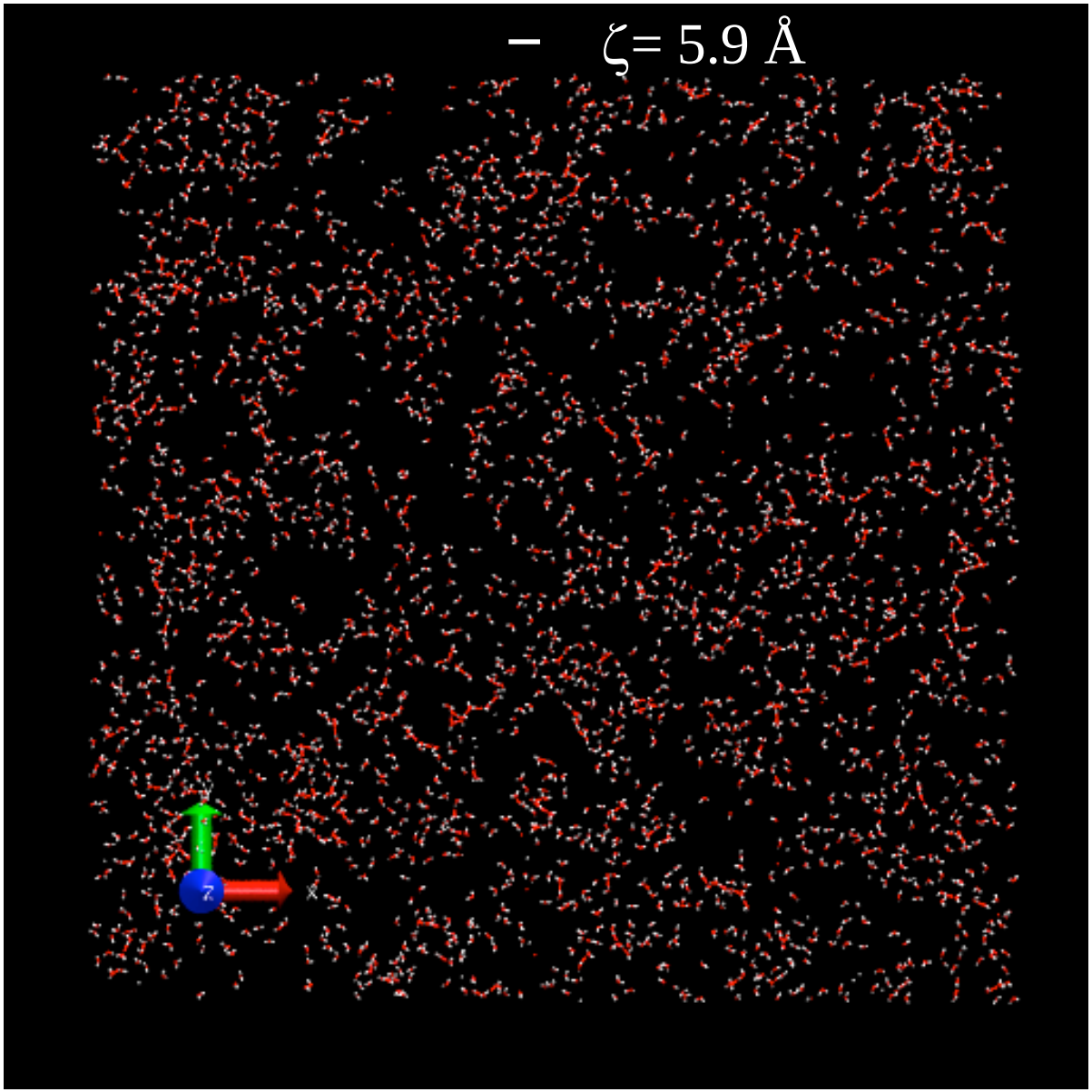


Simulate liquid-gas critical point at
640 K ρ=310 kg/m^3 (Vega et al. JCP 125 (2006) 34503)

OZ correlation length small: ζ= 5.9 Å
Affects O-O PCF to large distance
There is **no** well defined distance



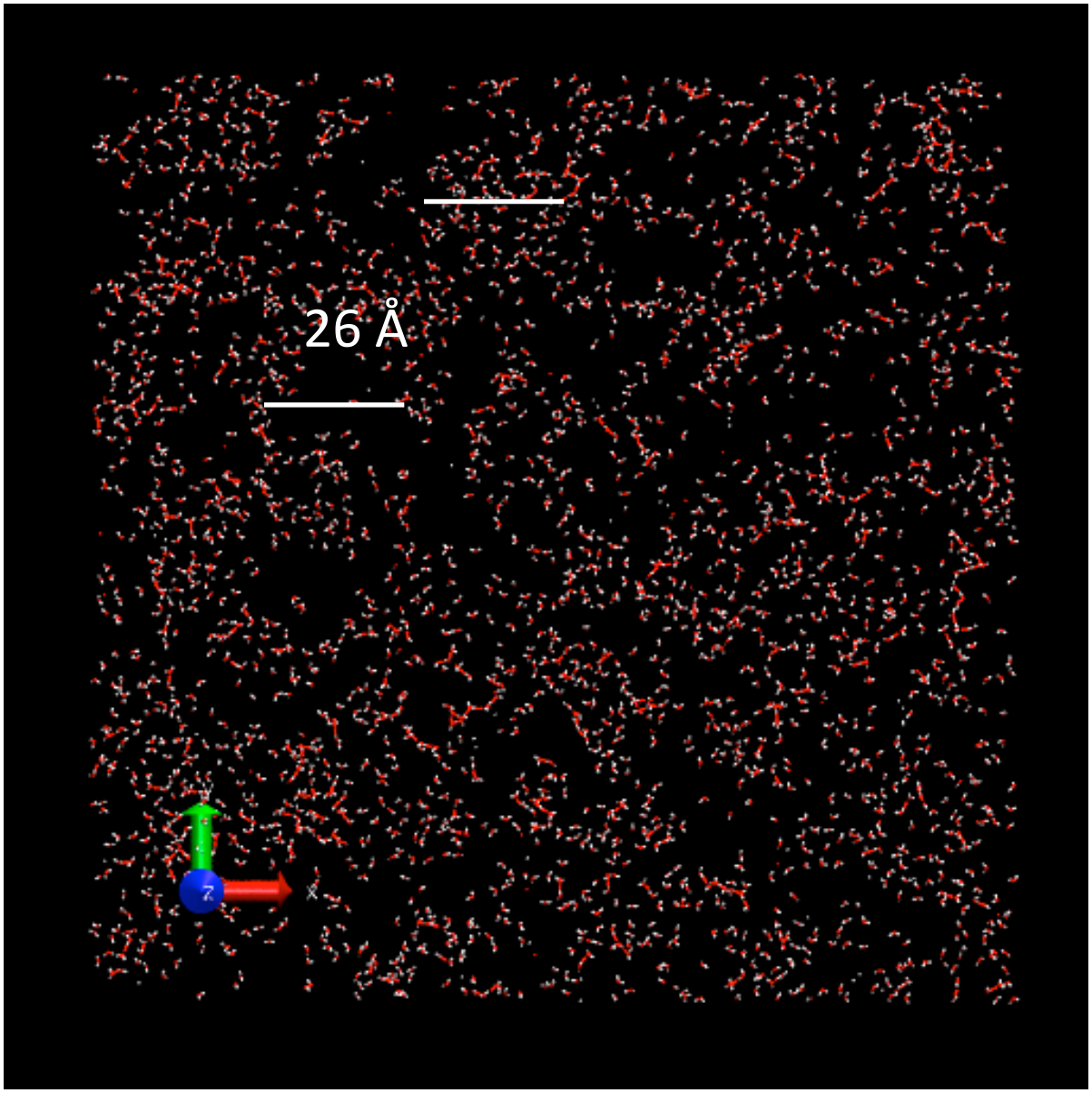
Real Structure Liquid-Gas CP



The correlation length is not a measure in real space that can be compared with a molecular length scale

SAXS measures instantaneous heterogeneities in the electron density

Real Structure Liquid-Gas CP



To obtain a rough approximate dimesion in real space

Assume static nanoparticle

Guinier radius $R_G = \sqrt{3}\xi$

Assuming spherical shape

$D = 2\sqrt{5/3}R_G$

With ζ= 5.9 Å

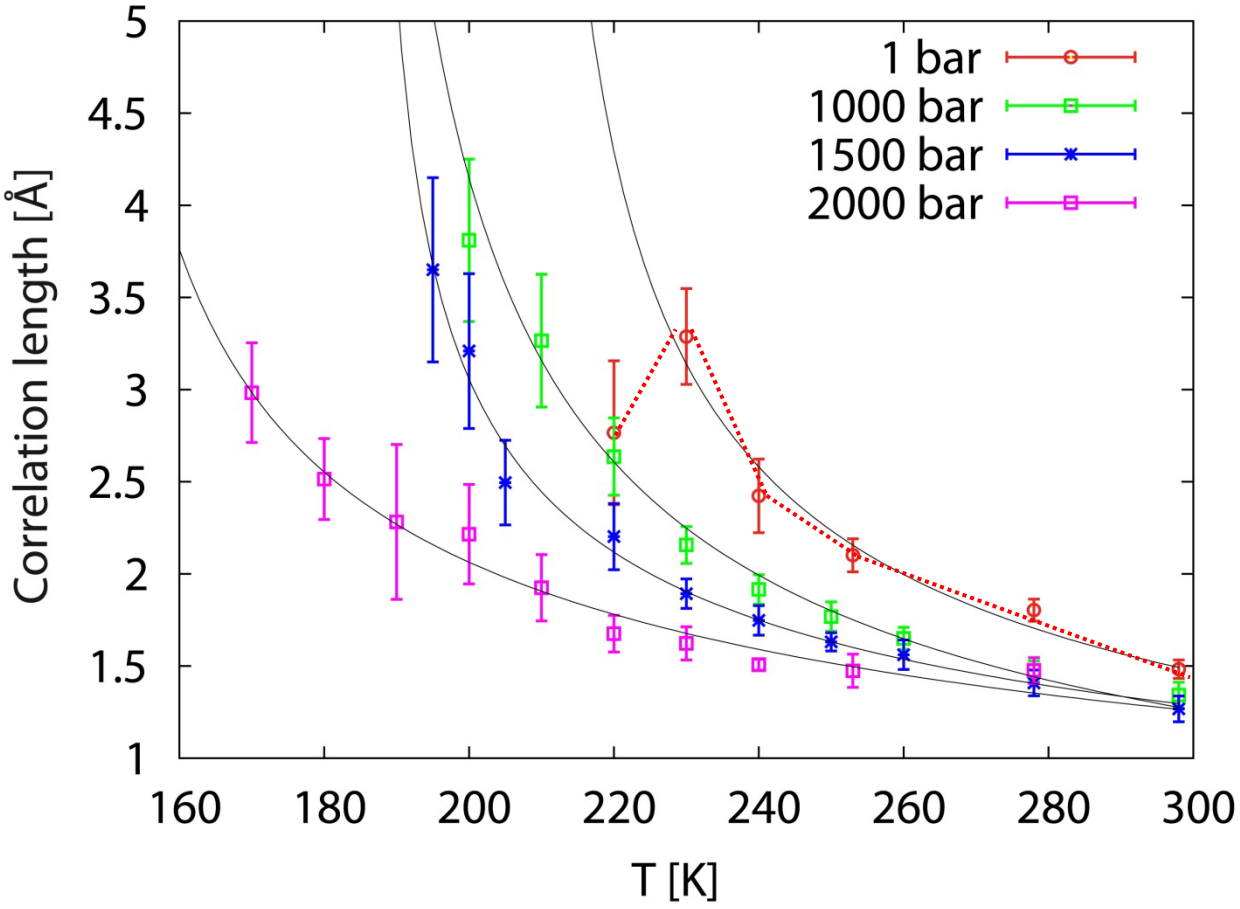
we get D=26 Å

It gives a sense of size range of inhomogeneity

It is not 5.9 Å nor 59 Å

There are many sizes but an average could be 26Å

Correlation Length – Apparent Power Law



Extract OZ correlation length as in experiment

Pressure moves the increase to lower T

Maximum and then decrease – **Widom line** (in the model)

Here: from computed SAXS signal which can be related to experiment

Fit ζ to

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

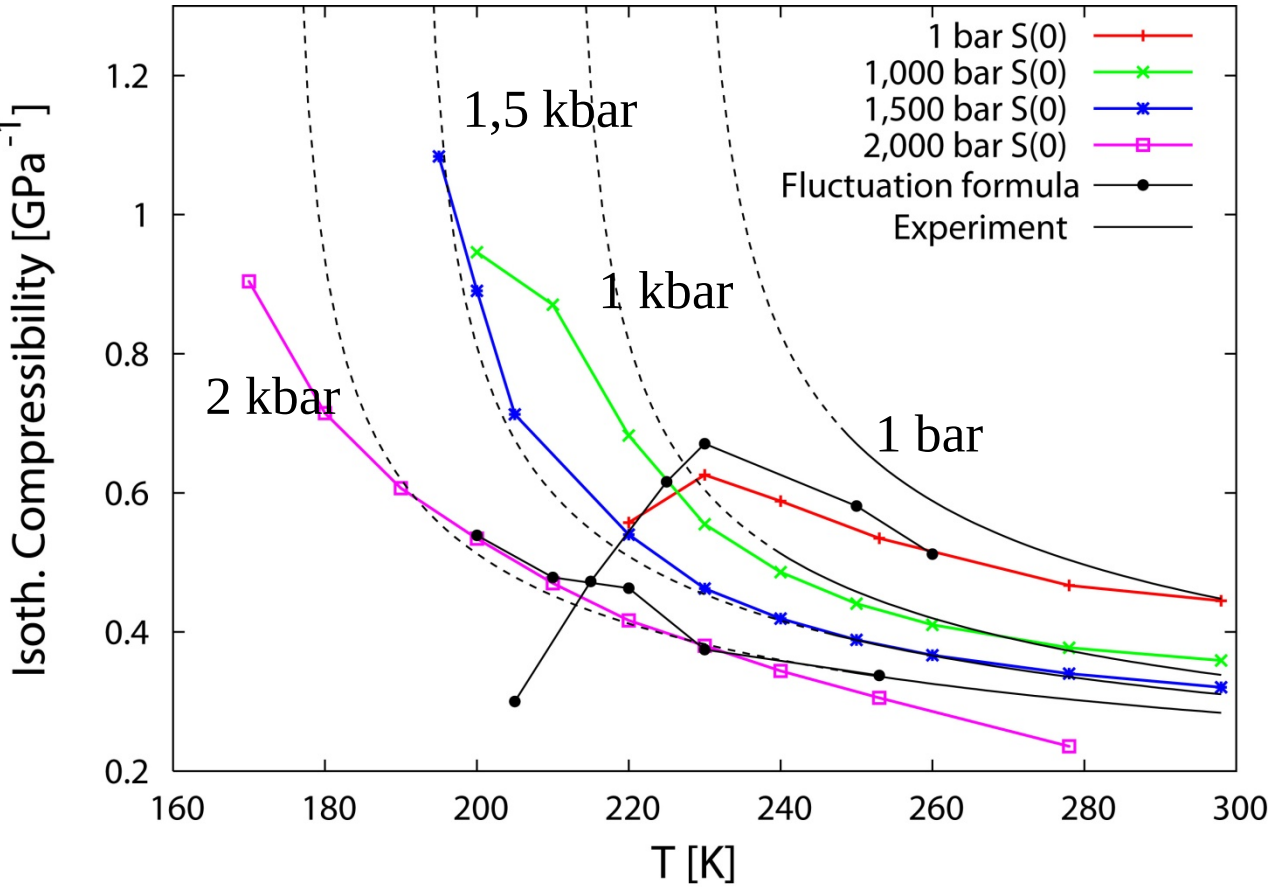
with

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

Correlation length small ~1.5-4 Å

Wikfeldt et al., J. Chem. Phys. **134**, 214506 (2011)

Isothermal Compressibility



Isothermal compressibility increases, shows a maximum (Widom line) and then a decrease

Values from extrapolation of SAXS (45,000 molecules) or from fluctuation formula (360 molecules)

Excellent agreement for higher pressures

Wikfeldt et al., J. Chem. Phys. **134**, 214506 (2011)

Expt: R.J. Speedy and C.A. Angell, J. Chem. Phys. **65**, 851 (1976)
H. Kanno and C. A. Angell, J. Chem. Phys. **70**, 4008 (1979)