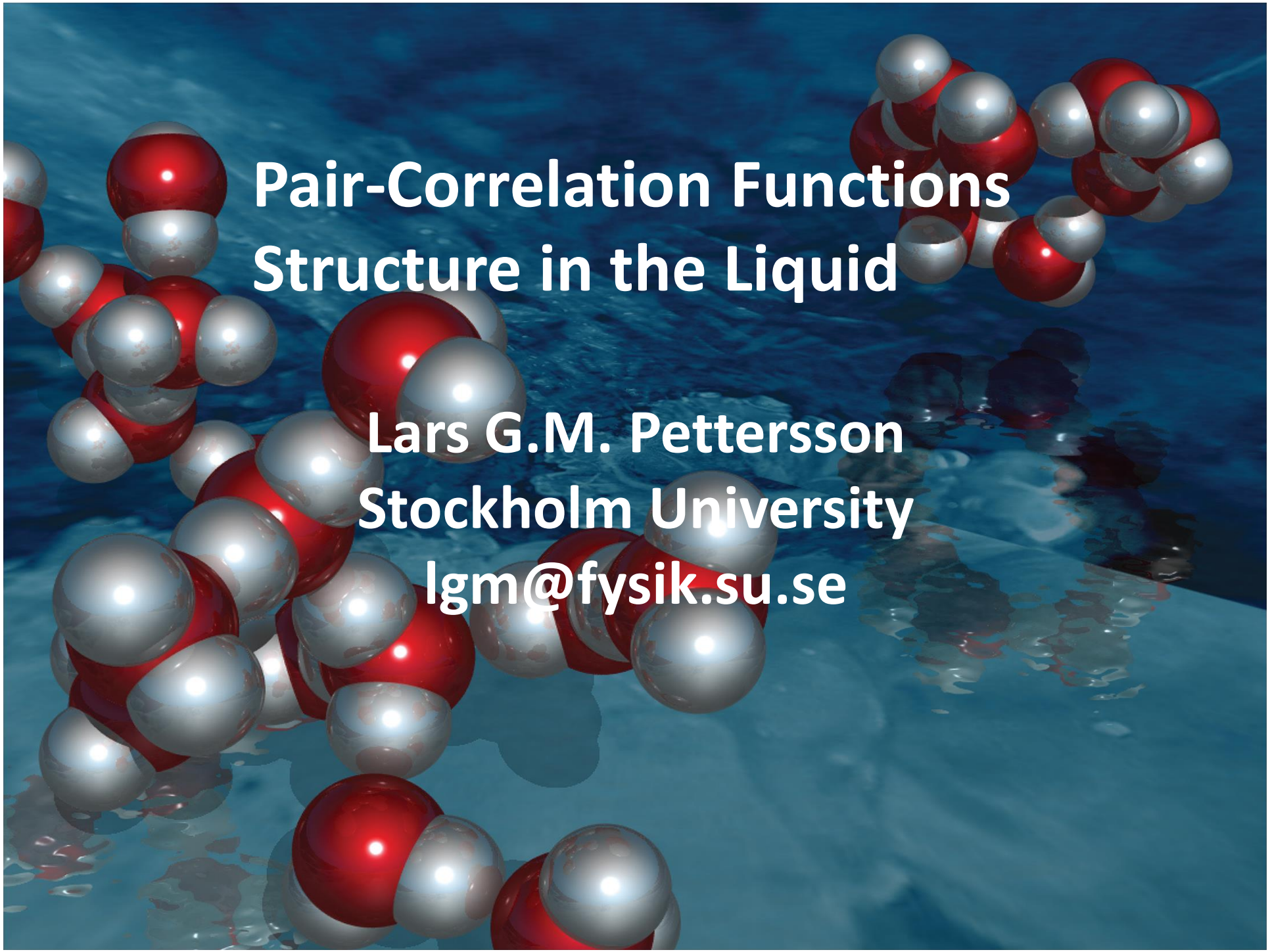

Pair-Correlation Functions
Structure in the Liquid

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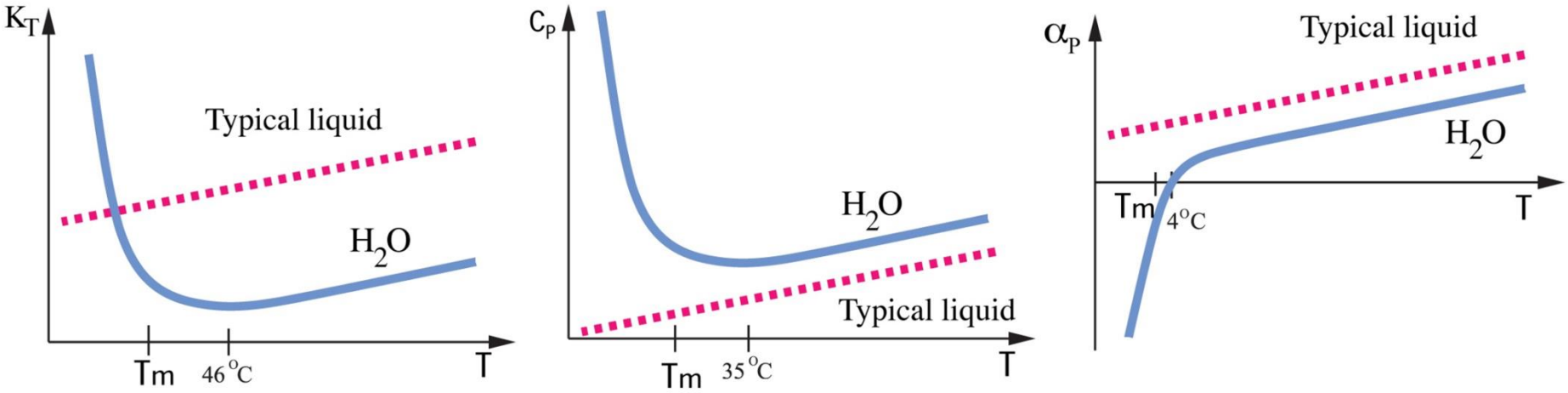
Stockholm University
lgm@fysik.su.se

Anomalous Properties of Water
Structural Fluctuations

Isothermal Compressibility

Heat Capacity

Thermal expansion



$\langle(\delta V)^2\rangle = V k_B T \kappa_T$

$\langle(\delta S)^2\rangle = N k_B c_p$

$\langle(\delta S\, \delta V)\rangle = V k_B T \alpha$

Density fluctuations

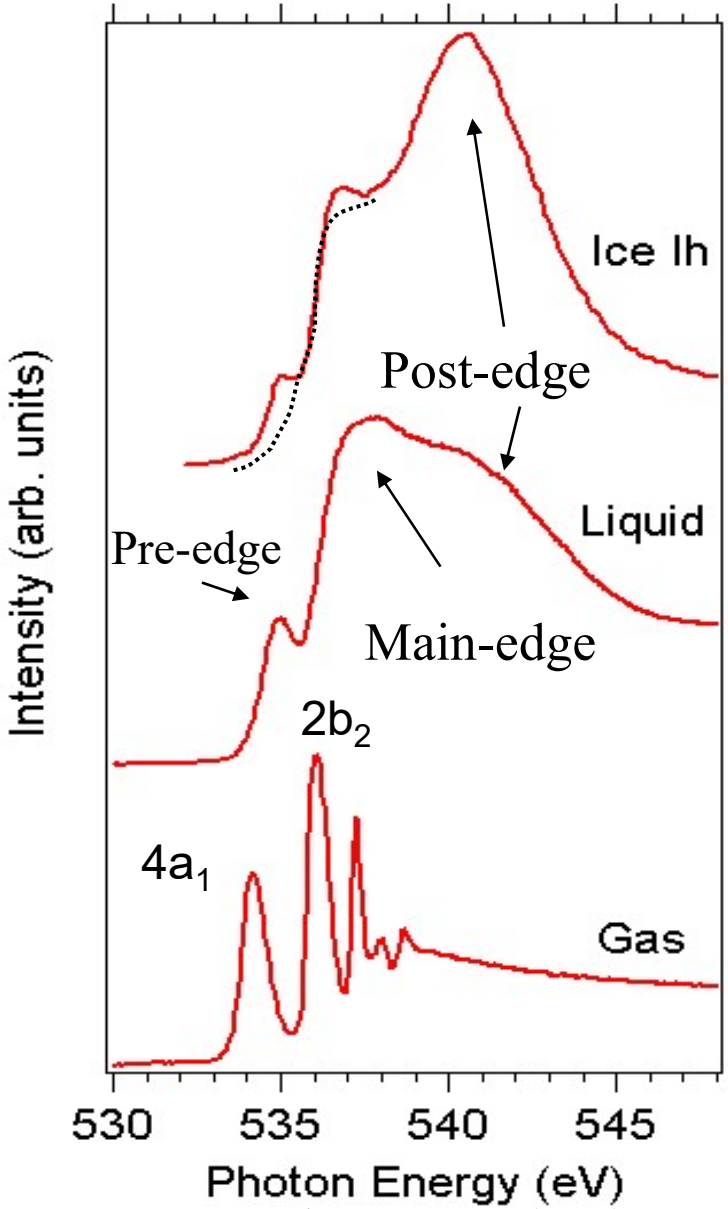
Entropy fluctuations

Cross of density and entropy fluctuations

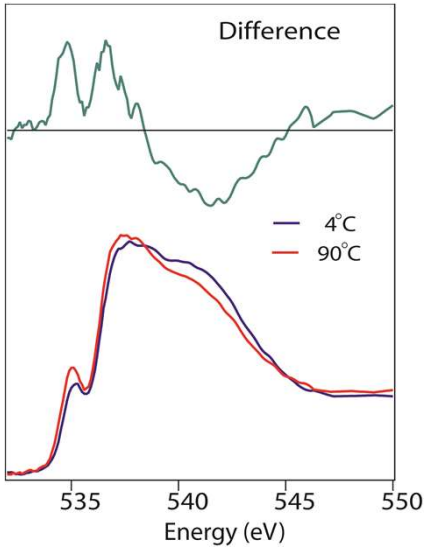
Divergence towards a mysterious temperature of -45 ° C
BUT anomalies set in already at ambient conditions…

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

X-ray Absorption Spectroscopy (XAS) of Water

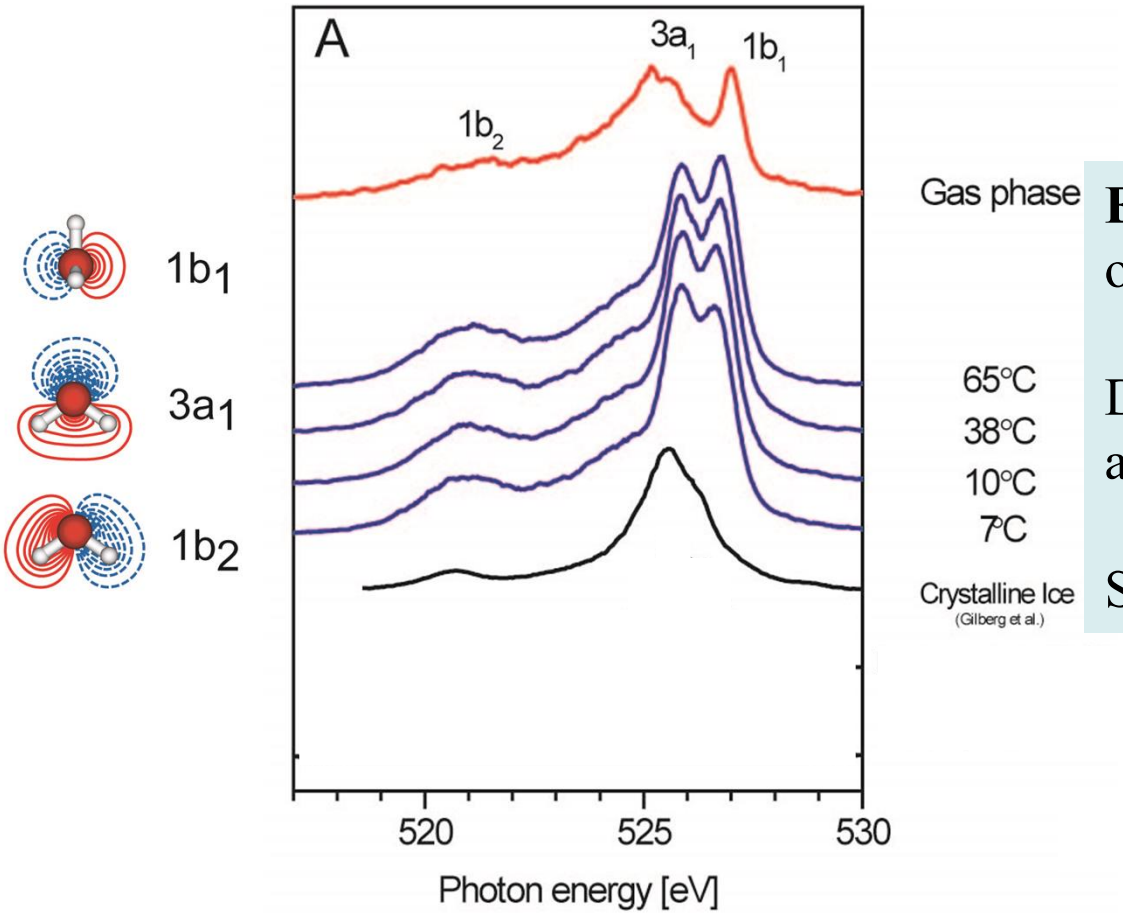


Wernet *et al.*, *Science* **304** (2004) 995
Myneni *et al. J. Phys. Condens. Matter* **14** (2002) 213



Absorption spectroscopy
Measures unoccupied (antibonding) states
Sensitive to structure

X-ray Emission Spectroscopy (XES) of Water



Emission spectroscopy measures occupied states

Depends on phase (gas, liquid, solid) and for the liquid on temperature

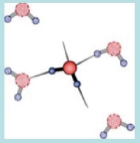
Structural sensitivity

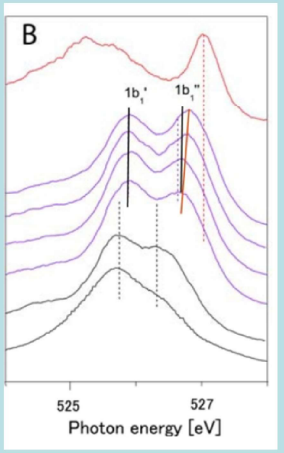
Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387

”HDL/LDL” Fluctuations in Ambient and Supercooled Water

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

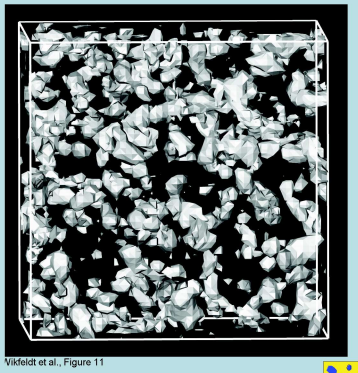
  Wernet *et al*., Science **304** (2004) 995





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

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

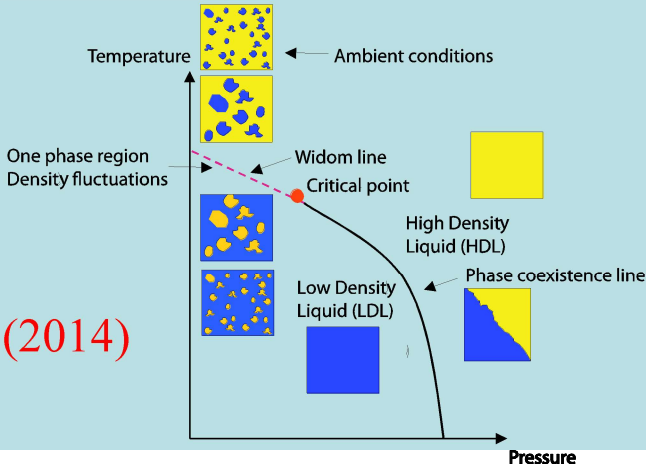


- **SAXS** shows *density fluctuations* Enhanced upon cooling

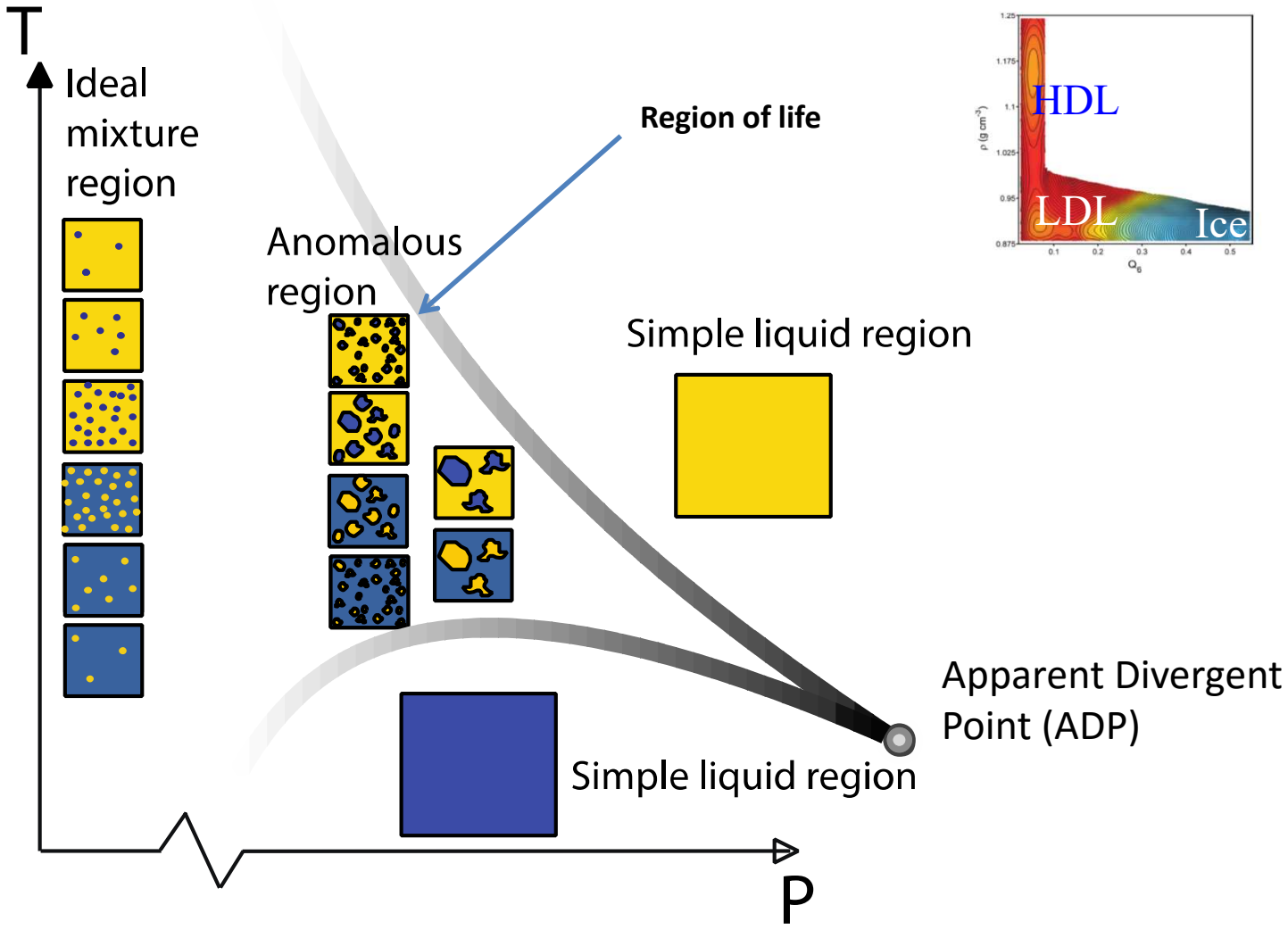
  Huang *et al*., PNAS **106**, 15214 (2009); JCP **133**, 134504 (2010)

- **XRD** shows *accelerated transition to LDL* on supercooling to T~227 K

  LCLS free-electron laser; Sellberg et al., Nature **510**, 381 (2014)

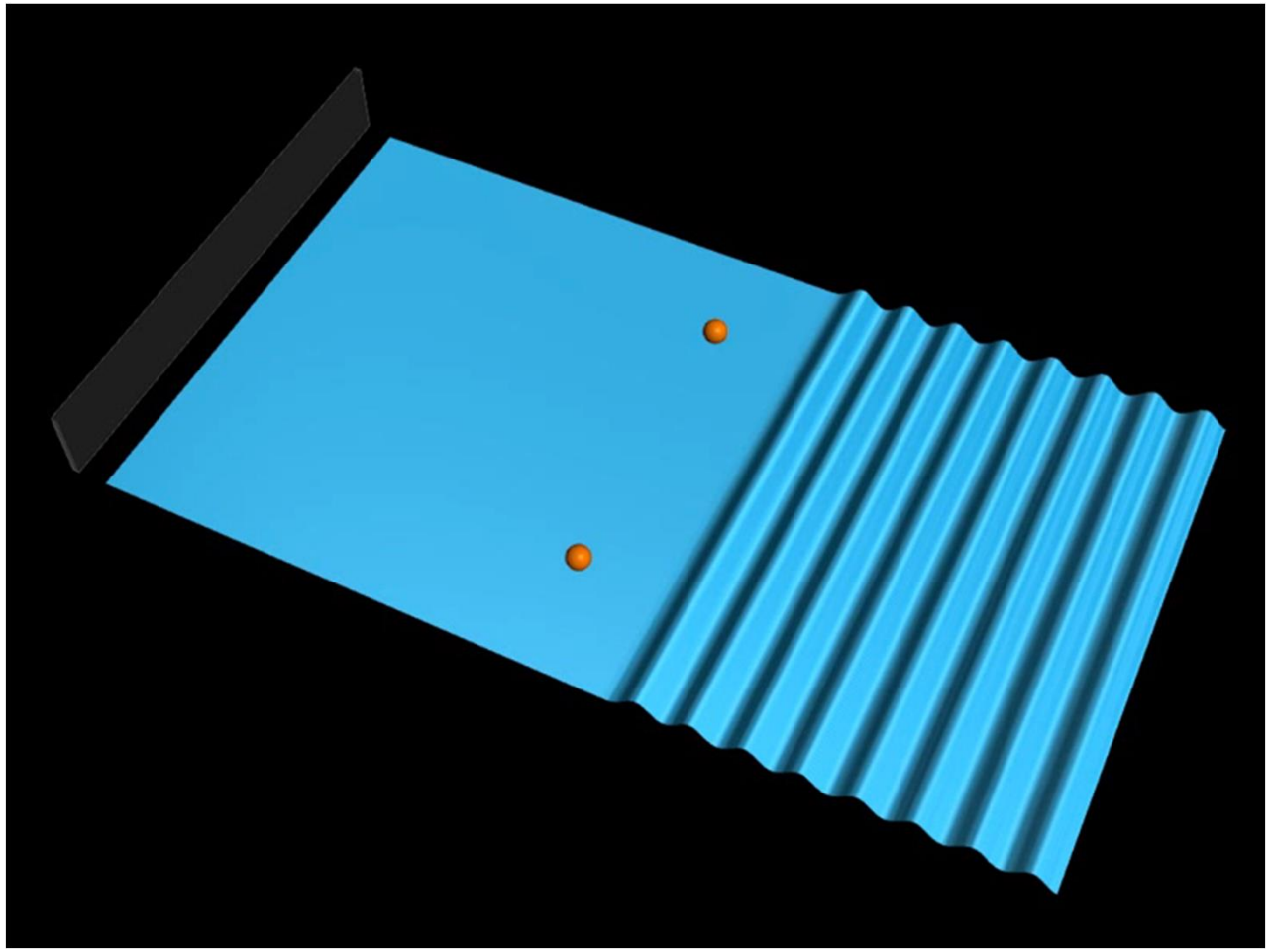


We Live in the "Funnel" of an ADP



Nilsson and Pettersson, Nature Communications **6**, 8998 (2015)

Scattering from a Molecule



- **X-ray scattering** is one of the most useful techniques for **revealing structure** of a molecule

Elastic X-ray Scattering

Initial amplitude: $\boldsymbol{\varepsilon} \cdot e^{i\boldsymbol{k}\cdot\boldsymbol{r}} |\Psi_i(\boldsymbol{r};\boldsymbol{R})\rangle$

Final amplitude: $\boldsymbol{\varepsilon}' \cdot e^{i\boldsymbol{k}'\cdot\boldsymbol{r}} |\Psi_i(\boldsymbol{r};\boldsymbol{R})\rangle e^{-i\Delta\boldsymbol{k}\cdot\boldsymbol{R}_{CM}}$

Scattering amplitude:

$$F_T \sim (\boldsymbol{\varepsilon}'^{*} \cdot \boldsymbol{\varepsilon}) \int \Psi_i^*(\boldsymbol{r_1}, \boldsymbol{r_2}, .., \boldsymbol{r_N}; \boldsymbol{R}) e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \, \Psi(\boldsymbol{r_1}, \boldsymbol{r_2}, .., \boldsymbol{r_N}) d\boldsymbol{r_1} d\boldsymbol{r_2} \ldots d\boldsymbol{r_{N-1}} d\boldsymbol{r}$$

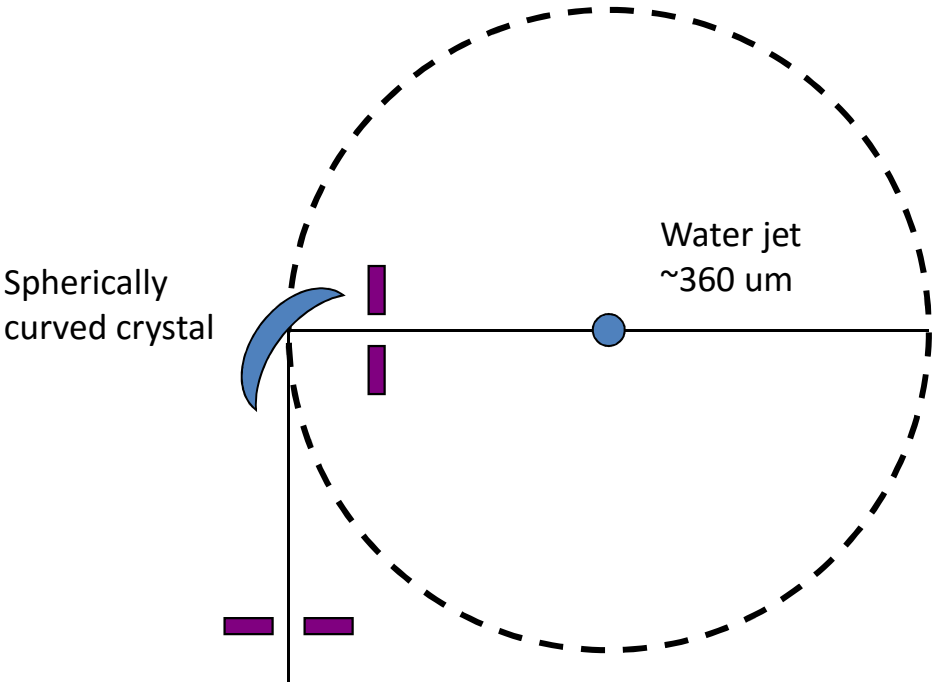
Electronic density:

$$\rho(\boldsymbol{r}) = N \int \Psi^*(\boldsymbol{r_1}, \boldsymbol{r_2}, .., \boldsymbol{r_N}) \, \Psi(\boldsymbol{r_1}, \boldsymbol{r_2}, .., \boldsymbol{r_N}) d\boldsymbol{r_1} d\boldsymbol{r_2} \ldots d\boldsymbol{r_{N-1}}$$

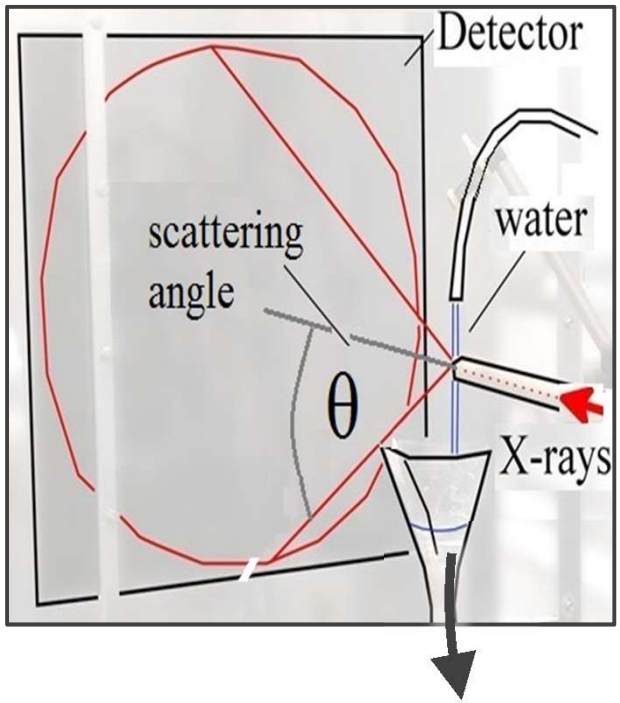
Scattering amplitude Fourier transform of the electronic density: $F_T \sim (\boldsymbol{\varepsilon}'^{*} \cdot \boldsymbol{\varepsilon}) \int \rho(\boldsymbol{r}) \, e^{i\boldsymbol{q}\cdot\boldsymbol{r}} \, d\boldsymbol{r}$

Wide Angle X-ray Scattering Measurements

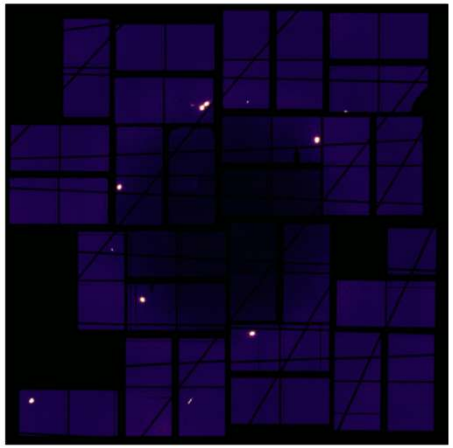
17 keV at SSRL



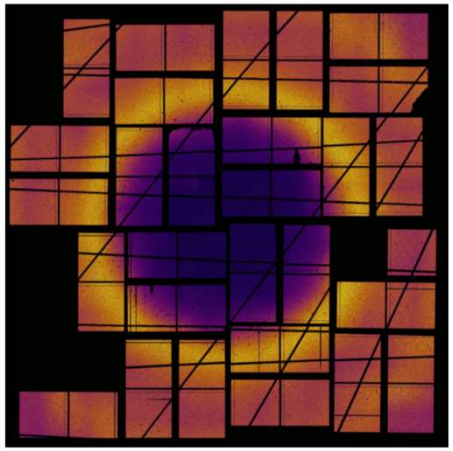
100 keV at APS



Scattering Patterns



Crystalline Ice
Bragg spots



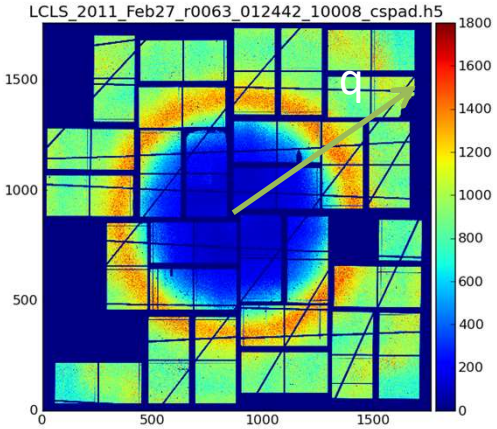
Liquid water
Water ring

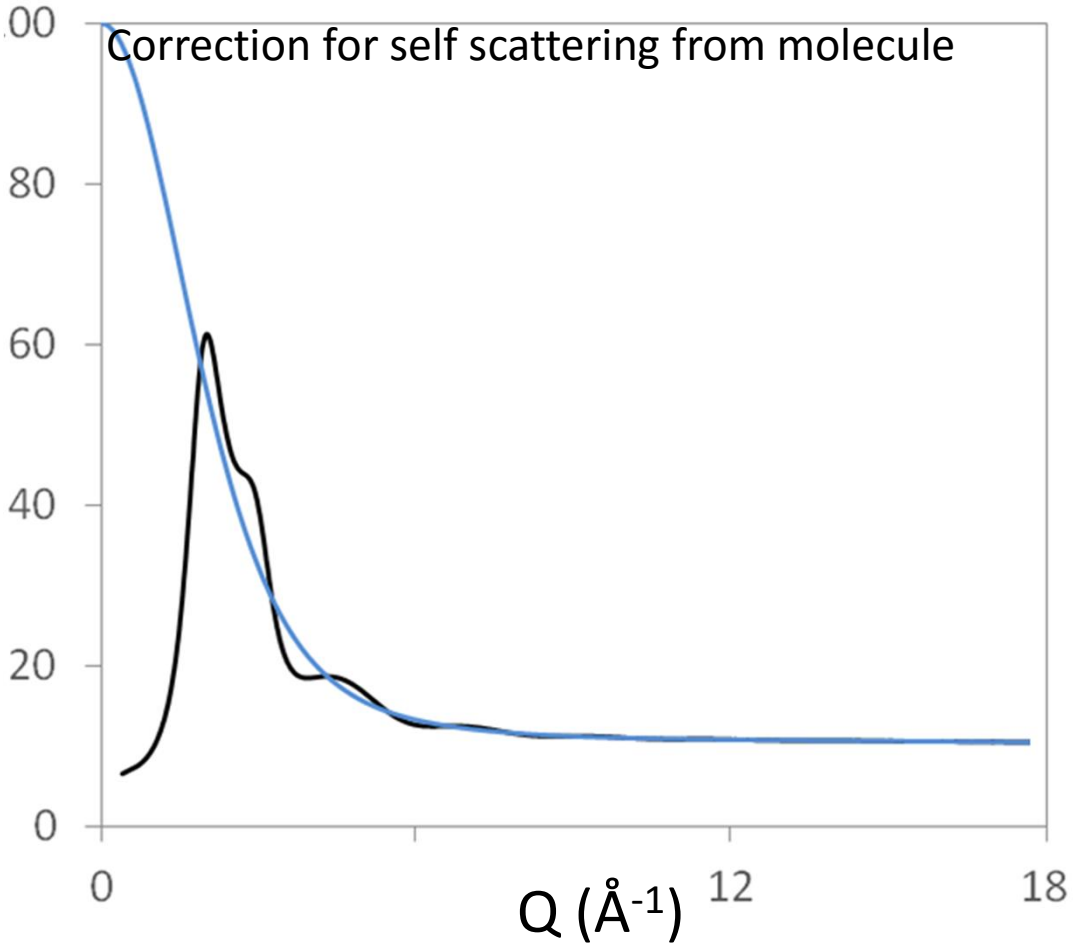
Raw Diffraction Signal

$$I_X(Q) = I_X^{self}(Q) + I_X^{intra}(Q) + I_X^{inter}(Q).$$

I (Q)

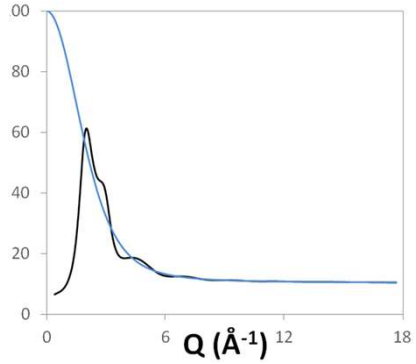
Angular integration





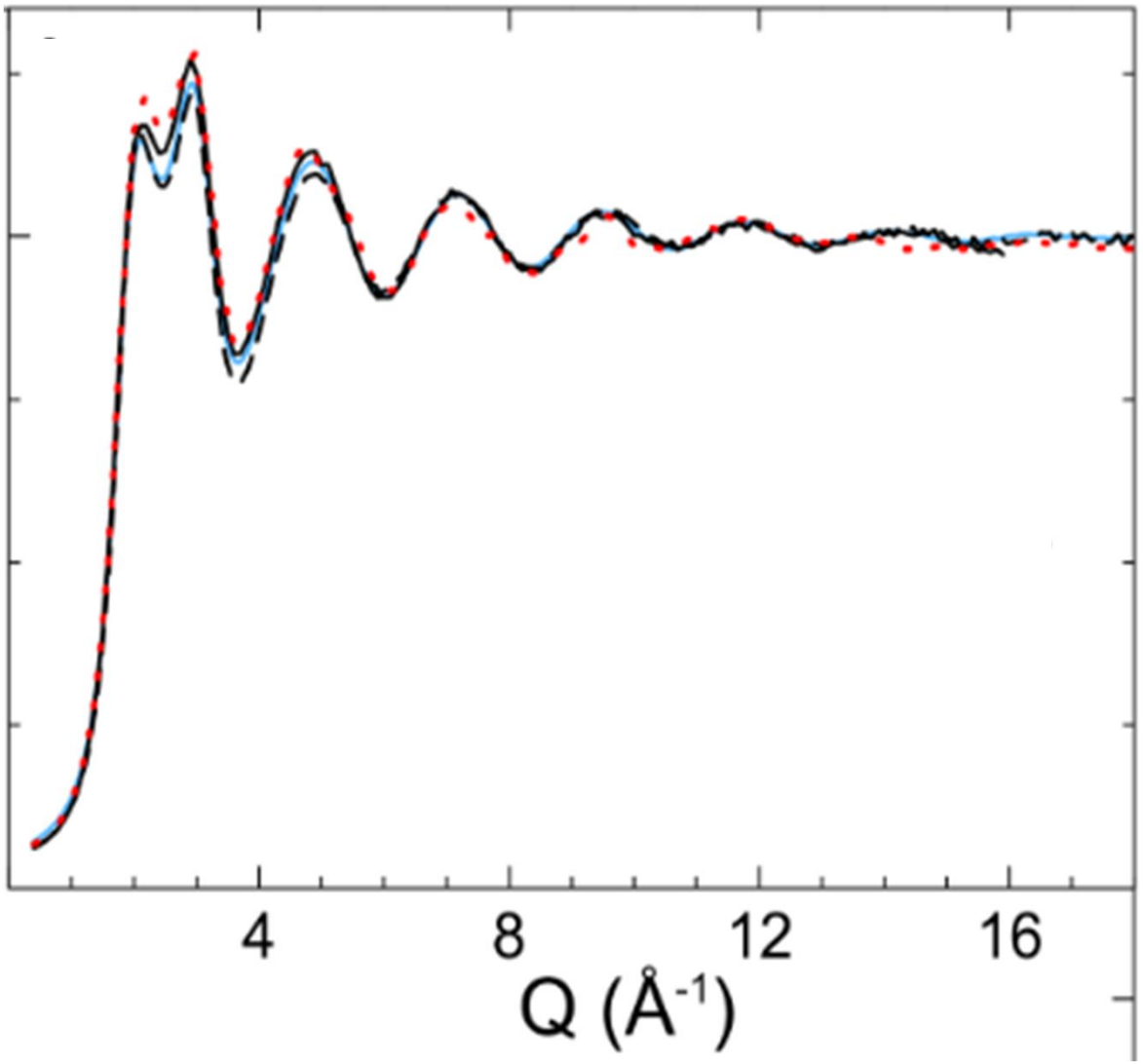
LB Skinner *et al.* J. Chem. Phys. (2013)

Structure Factor

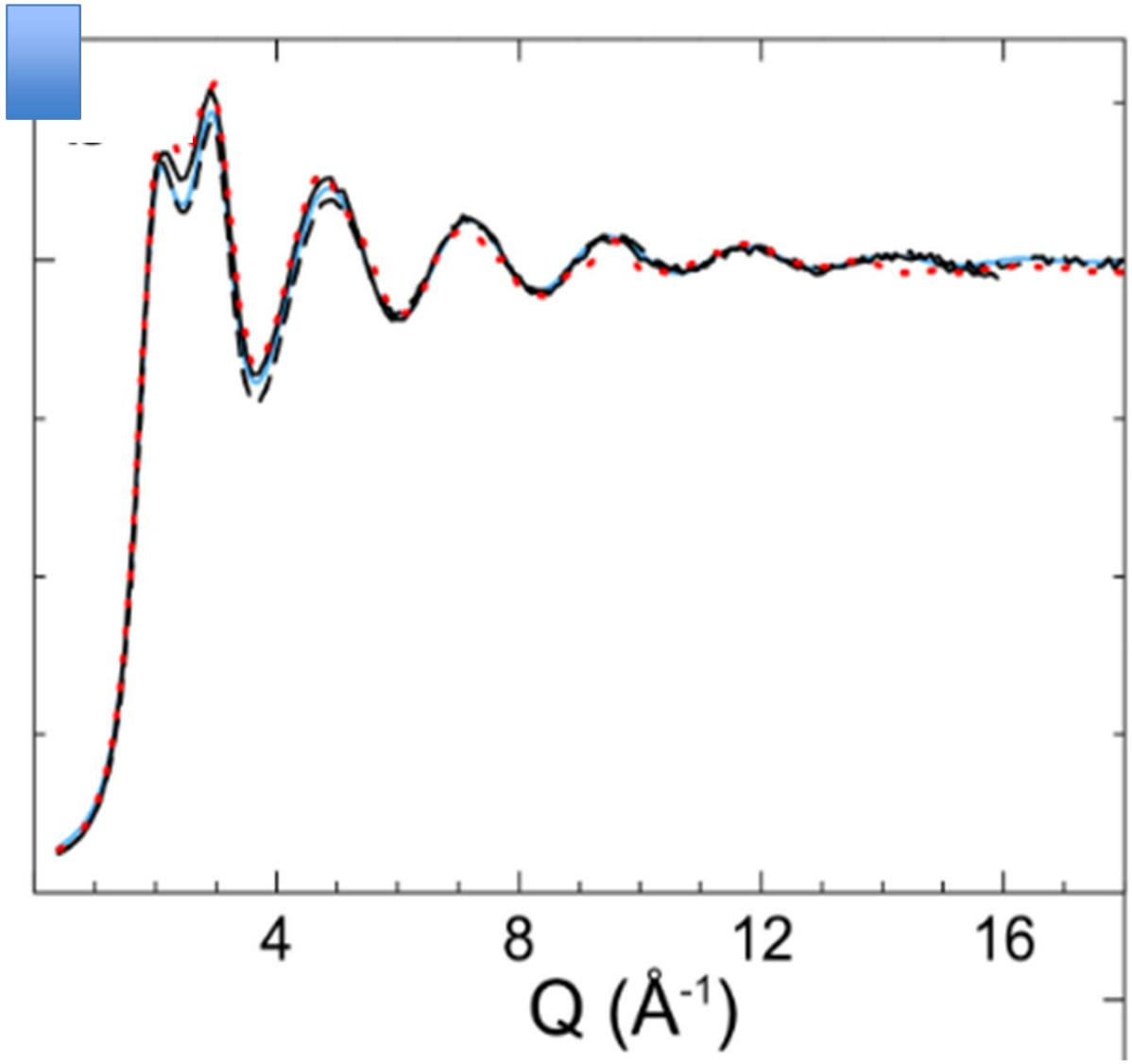


Remove self scattering to obtain intermolecular structure factor

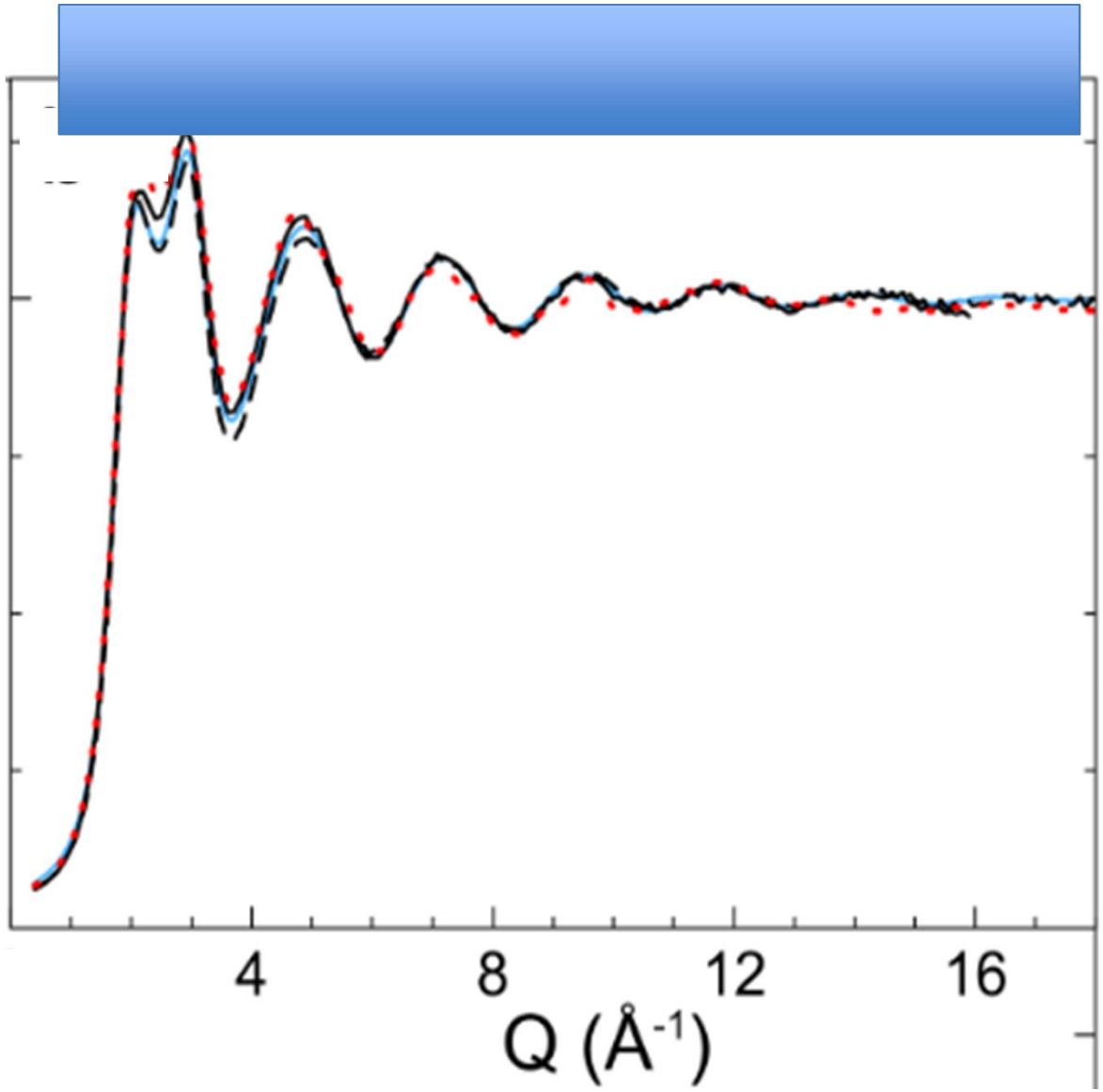
O-O > O-H >> H-H



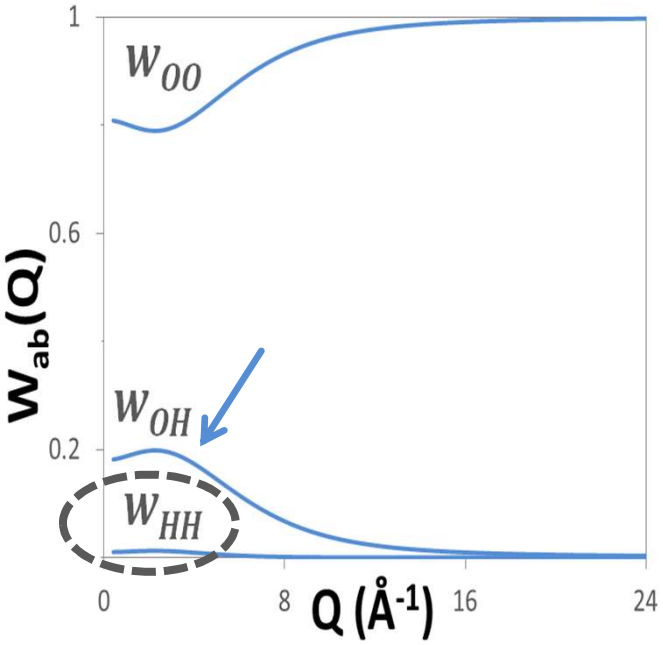
Small Angle Region Q<0.5 Å^{-1}



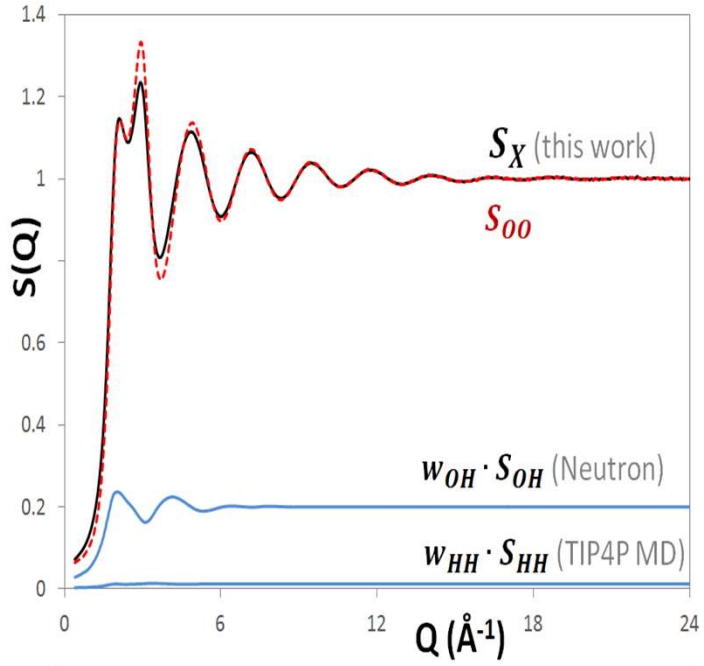
Wide Angle Region Q>0.5 Å^{-1}

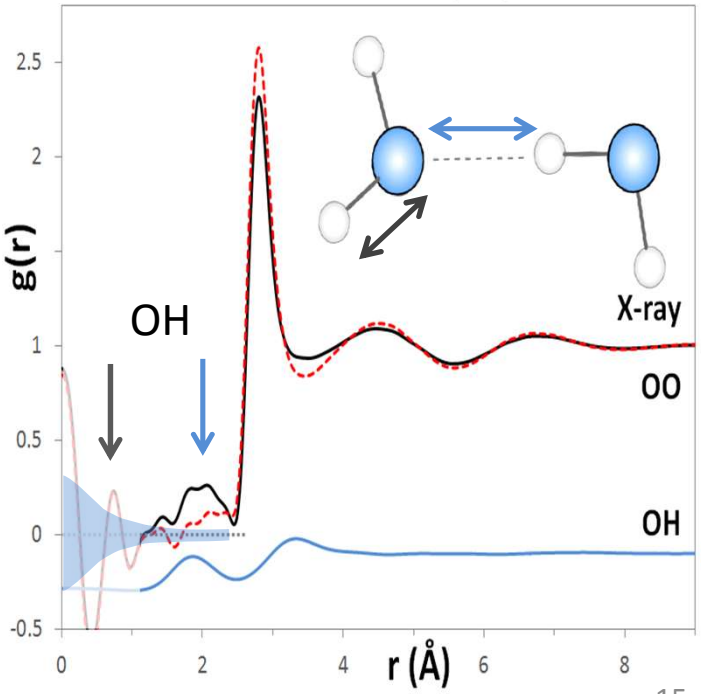


OH Subtraction



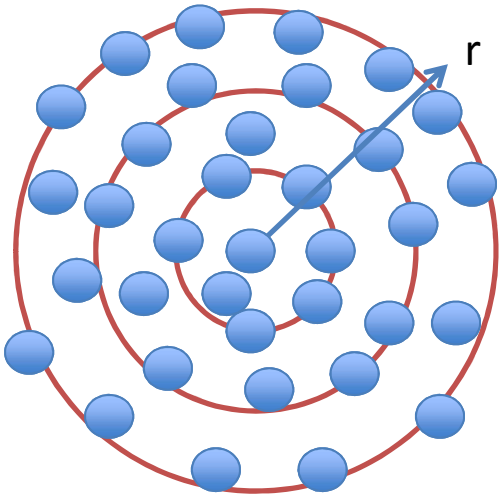
Fourier Transform

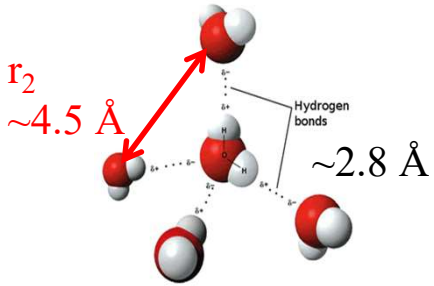


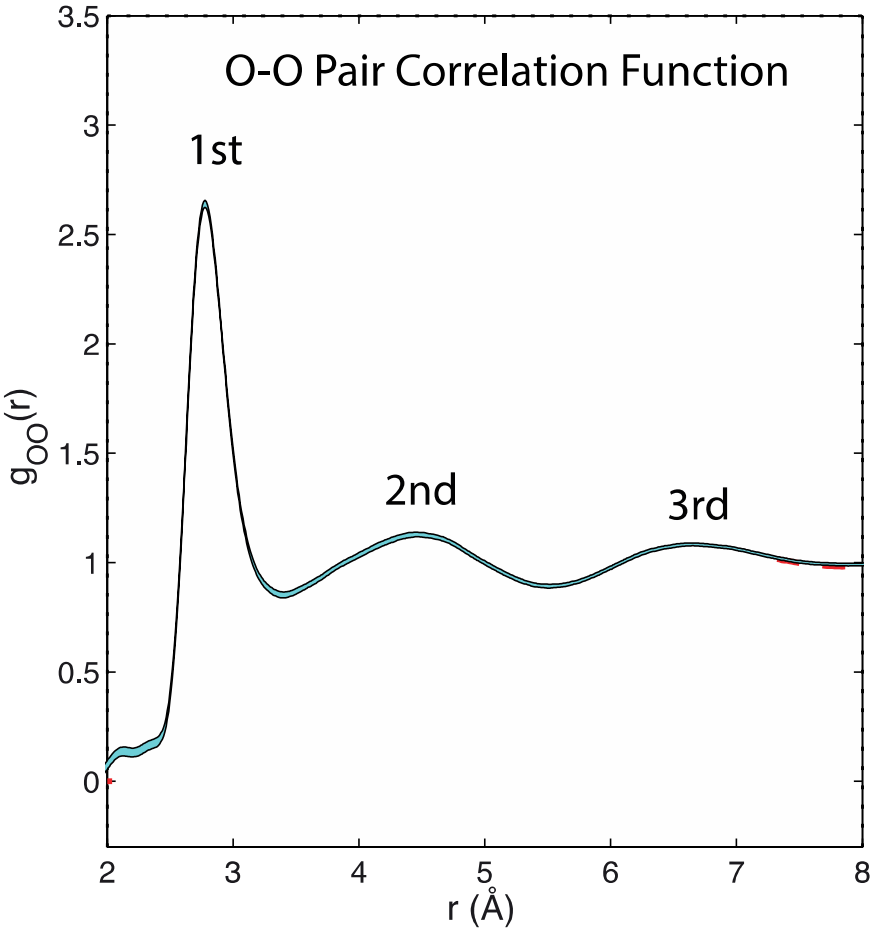


Skinner et al. J. Chem. Phys. **138**, 074506 (2013).

Pair-Correlation Functions

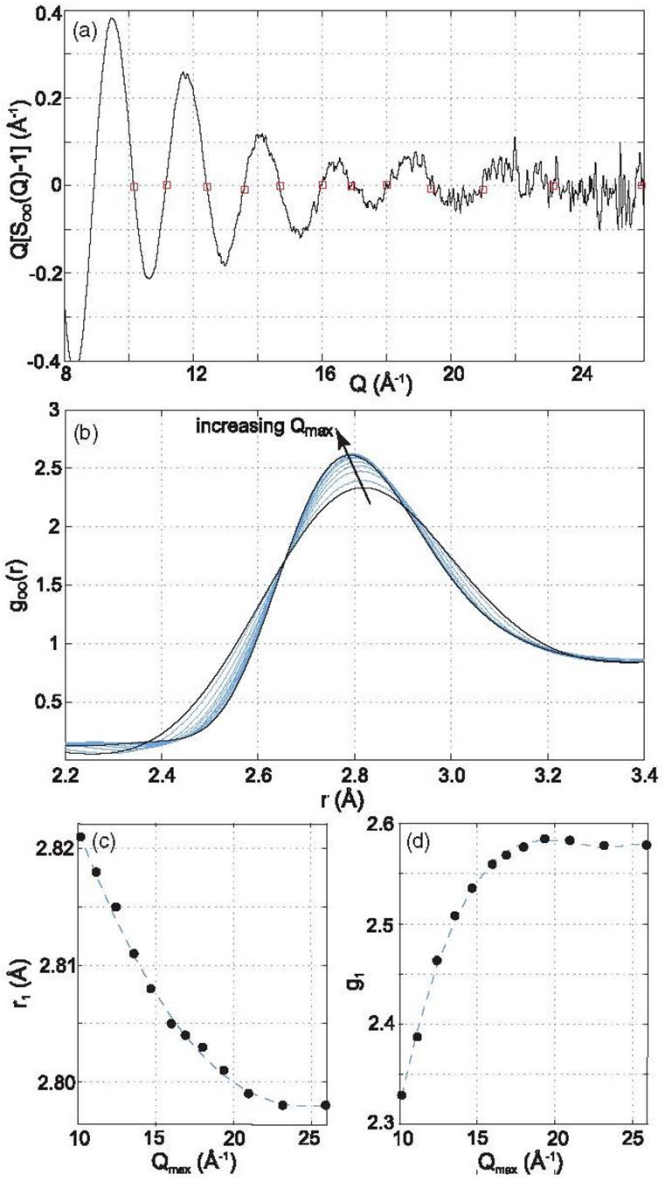






Skinner et al. J. Chem. Phys. **138**, 074506 (2013).

Fourier Transform



$$g(r) = 1 + \frac{1}{2\pi^2 \rho r} \int_0^{Q_{max}} M(Q, \Delta(r)) Q\,[S(Q) - 1] \times \sin(Qr)\, dQ,$$

Important to have long enough Q-range

$Q_{max} > 18$ Å^{-1}

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

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:

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

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

Sensitivity

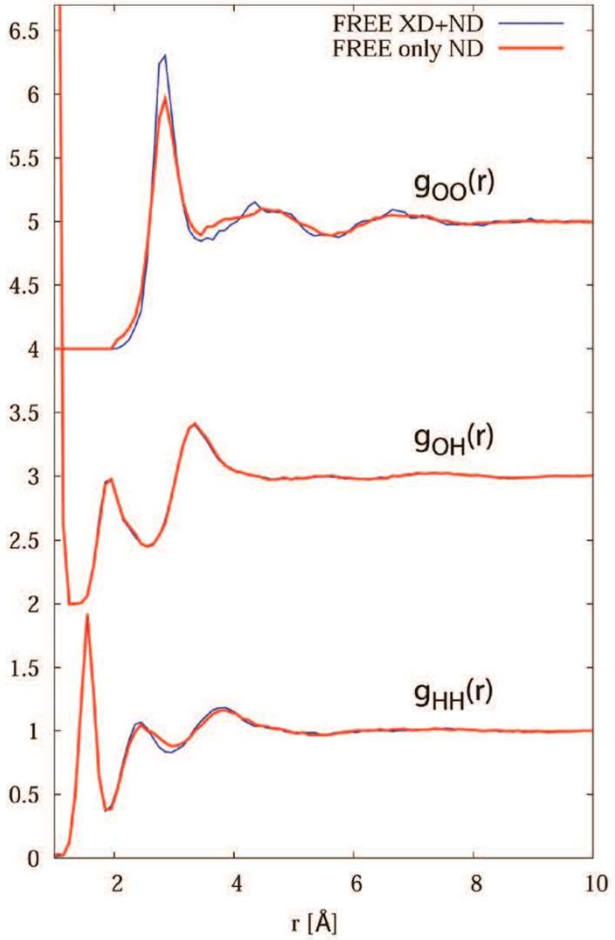
$$S_{ND}(k) = \sum_{\alpha}\sum_{\beta} c_\alpha c_\beta \langle b_\alpha \rangle \langle b_\beta \rangle \left(S_{\alpha\beta}(k) - 1\right)$$

$$S_{XD}(k) = \sum_{\alpha}\sum_{\beta} c_\alpha c_\beta f_\alpha(k) f_\beta(k) \left(S_{\alpha\beta}(k) - 1\right) / \left(\sum_i c_i f_i(k)^2\right)$$

c_α concentration of species α
b_α scattering length of species α
$f_\alpha(k)$ form factor of species α

Data set	% O-O	% O-H	%H-H
100% D_2O	9.2	42.3	48.6
75% D_2O	17.3	48.6	34.1
50% D_2O	44.1	44.6	11.3
25% D_2O	51.6	40.4	8.0
100% H_2O	19.1	49.2	31.7
XD $\alpha_H = 0.0$	70.2	27.1	2.6
XD $\alpha_H = 0.5$	79.8	19.1	1.1

Important to combine data



Unconstrained RMC fits to neutron data only or combined with x-ray data

O-O correlation better defined with XRD

Wikfeldt et al., J. Phys. Chem. B **113**, 6246 (2009)

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:

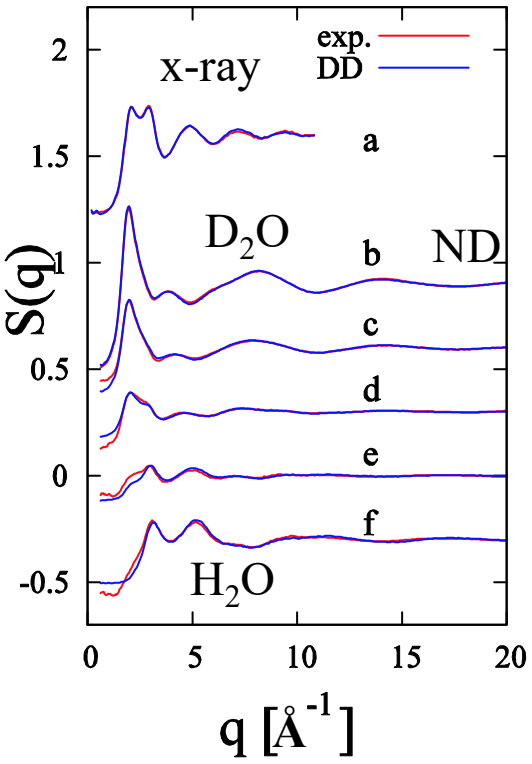
- Fit data AND maximize number of H-bonds to get **maximally symmetric model**

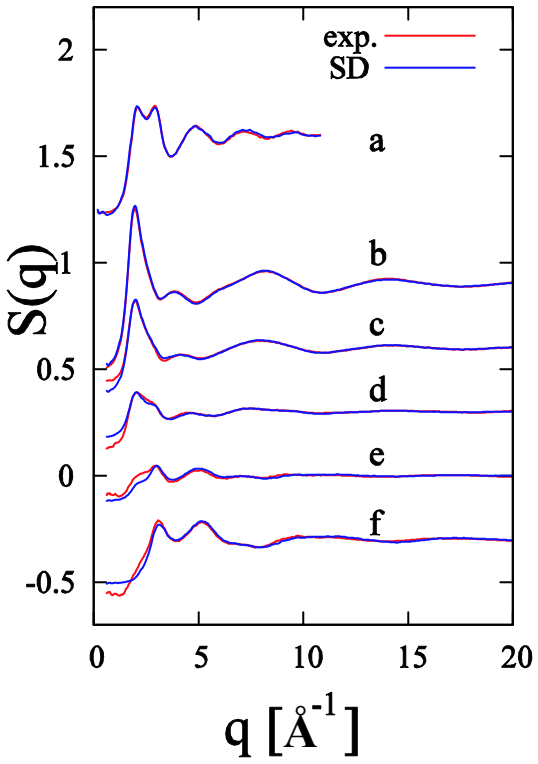
– OR –

- 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





- X-ray and neutron data fitted together with E-field
- Equally good fit in both cases
- Diffraction data give NO preference

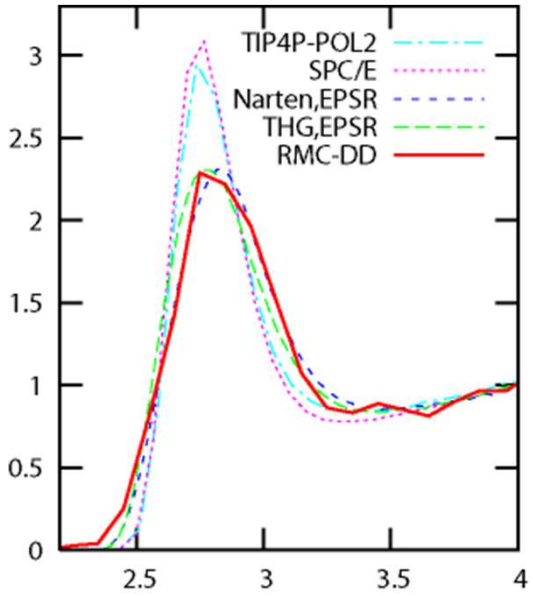
DD: 74%
SD: 21%
ND: 5%

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

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

O-O and O-H Pair Correlations

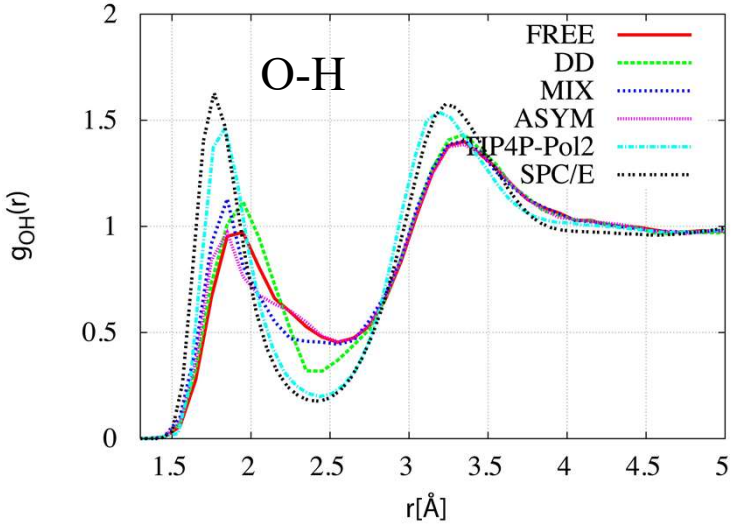
O-O Pair Correlation



RMC fitted O-O correlation
Compare with EPSR fit to the same data set
Soper, J. Phys.: Cond. Mat. **19**, 335206 (2007).

Very similar distributions with
EPSR and RMC
Very similar distributions from
Hura *et al*. and Narten data (Soper 2007)
Poor agreement for SPC/E and TIP4P
Softer potential needed

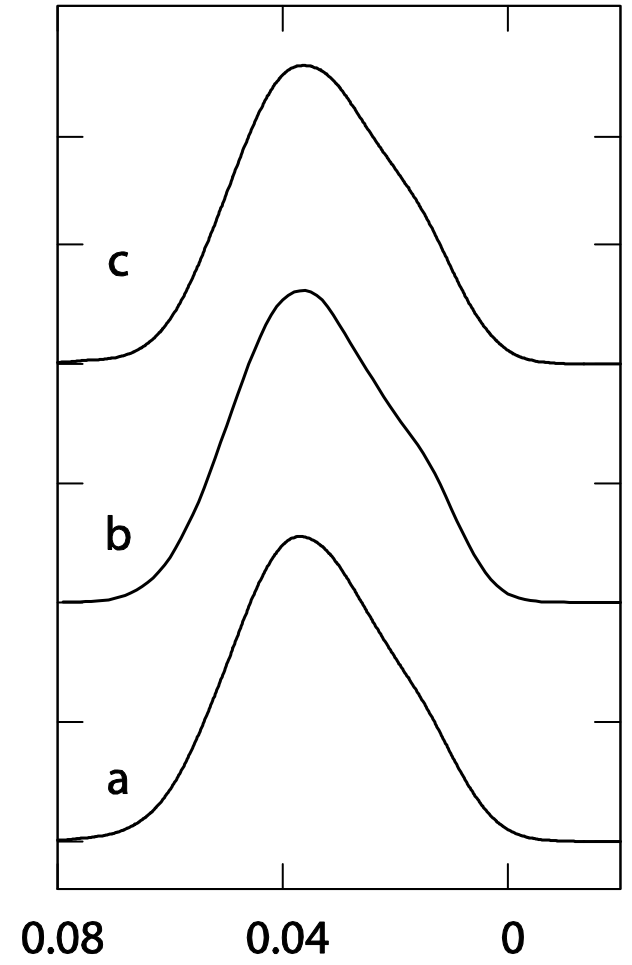
Leetmaa *et al*., J. Chem. Phys. **129**, 084502 (2008)



O-H correlation not well-defined
Wikfeldt *et al*. JPC B **113**, 6246 (2009)

Raman Spectrum: E-field Distribution

- E-field projected along individual OH
- Distribution can represent Raman spectrum (HOD in D_2O)
- Take as reference the E-field distribution for TIP4P-pol2
- Both DD and SD model reproduce the correct distribution (and XRD+ND)
- Both extreme models equally valid (and a range in between)

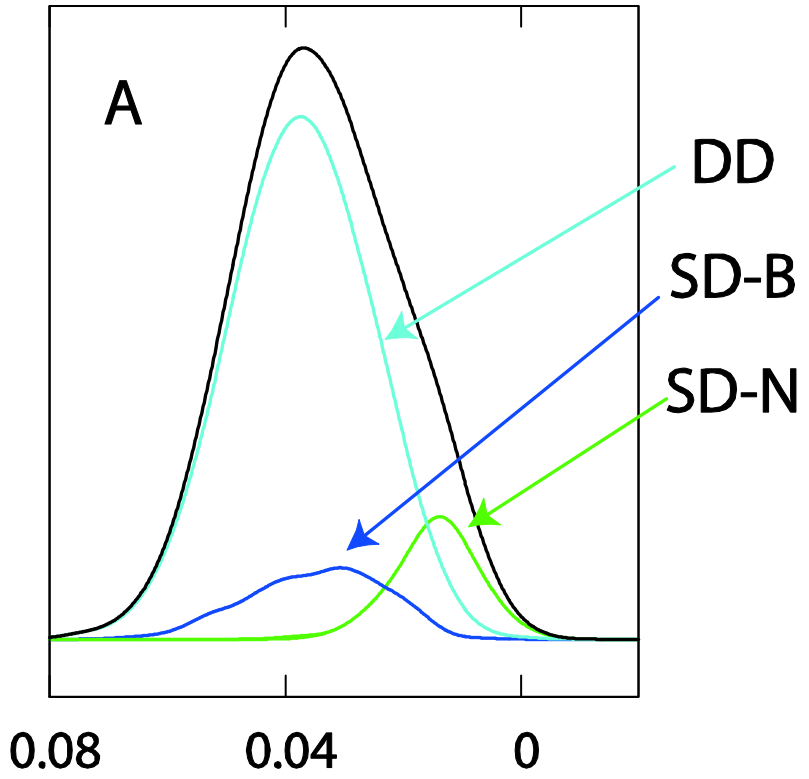


Structure only known from MD!

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

Raman Spectrum
Decomposition – Symmetric (DD) Model

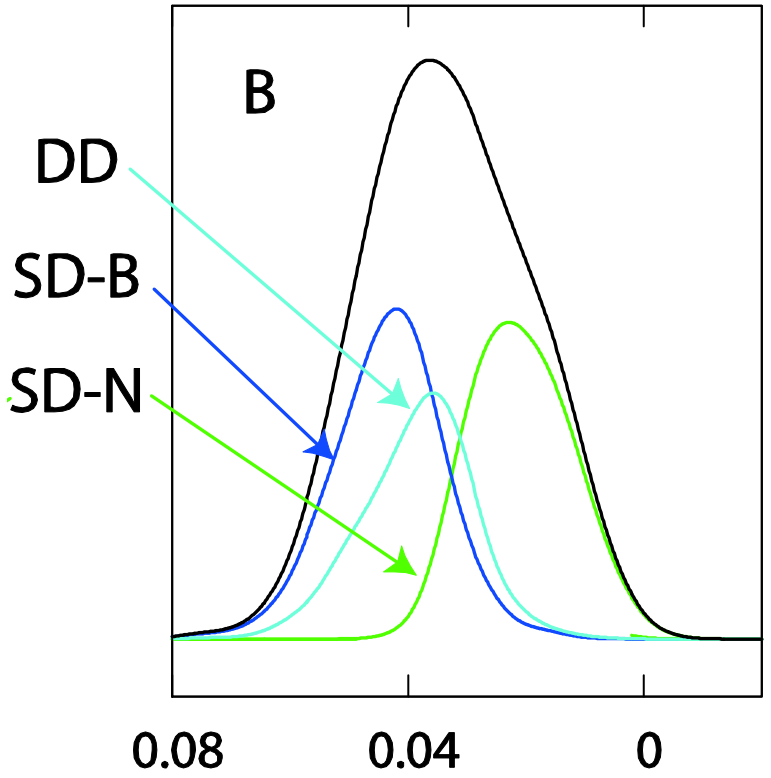
- Ultra-fast pump-probe see fast frequency shifts: H-bond dynamics
- H-bonded DD dominates
- Pump at blue – response in center → H-bond reformed
- H-bonds broken ”only fleetingly”
- Ultra-fast memory loss
- Valid picture



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

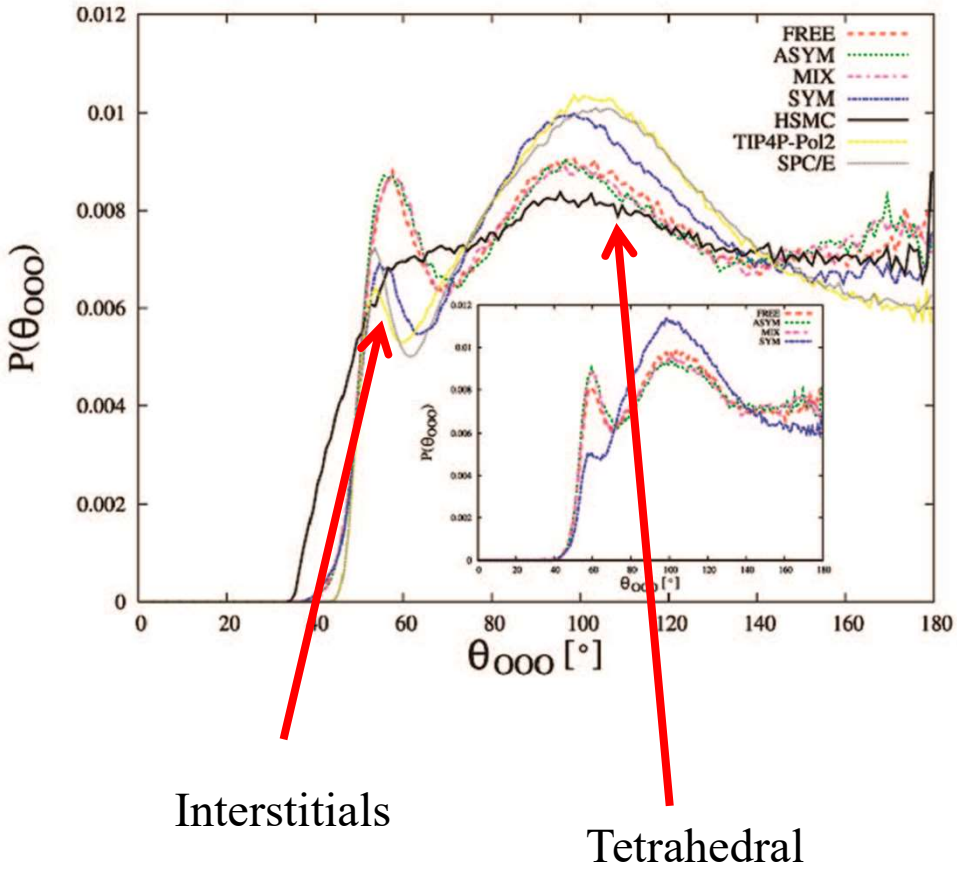
Raman Spectrum
Asymmetric (SD) Model

- Ultra-fast pump-probe
- SD species dominates
- Pump at blue – response in center → H-bond reoriented
- H-bond situation not affected
- Ultra-fast reorientation in non-H-bonded cavity
- Equally valid picture



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

Angular Correlations
Tetrahedrality

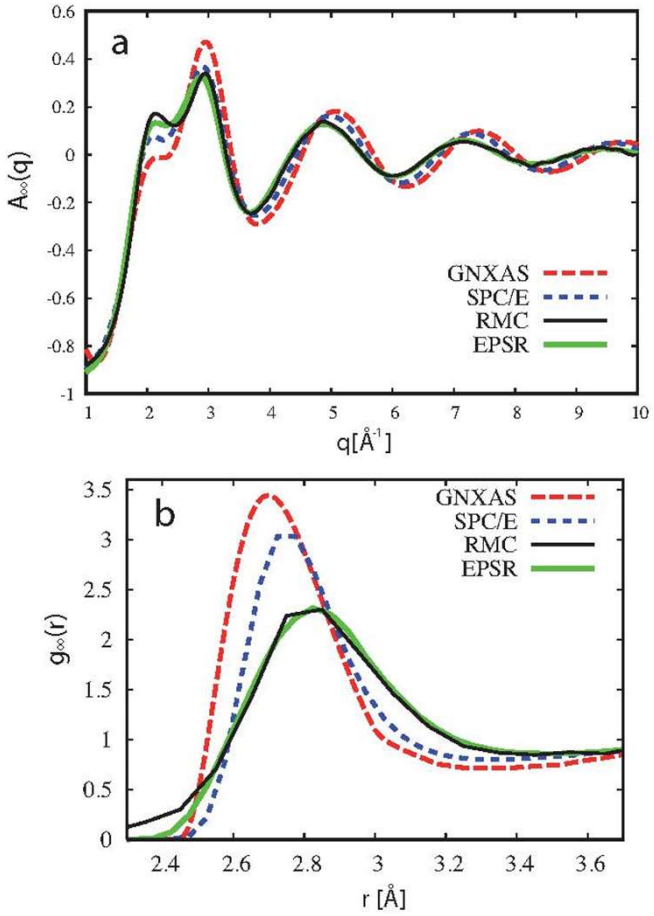


Distribution of O-O-O angles for different models (no Raman):

FREE no structural constraints
ASYM enhance broken bonds
SYM enhance intact bonds
MIX 3:1 mix of ASYM and SYM
HSMC hard spheres
TIP4P-pol2, **SPC/E** force-fields

Inset: E-field included to model Raman → no difference between SD and DD

O-O Pair-Correlation from EXAFS

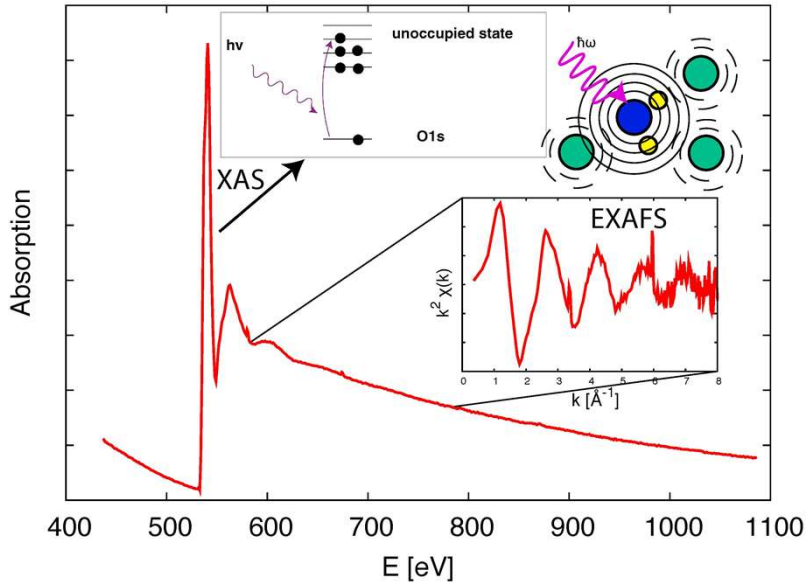


Structure factor determined by Bergmann et al. J. Chem. Phys. **128**, 089902 (2008) from EXAFS wiggles in X-ray Raman Spectroscopy of water.

The derived PCF was highly peaked towards short distances compared to RMC and EPSR fits to neutron data (Soper) and x-ray data (Hura et al.)

Wikfeldt et al., J. Chem. Phys. **132**, 104513 (2010)

EXAFS
Extended X-ray Absorption Fine-Structure

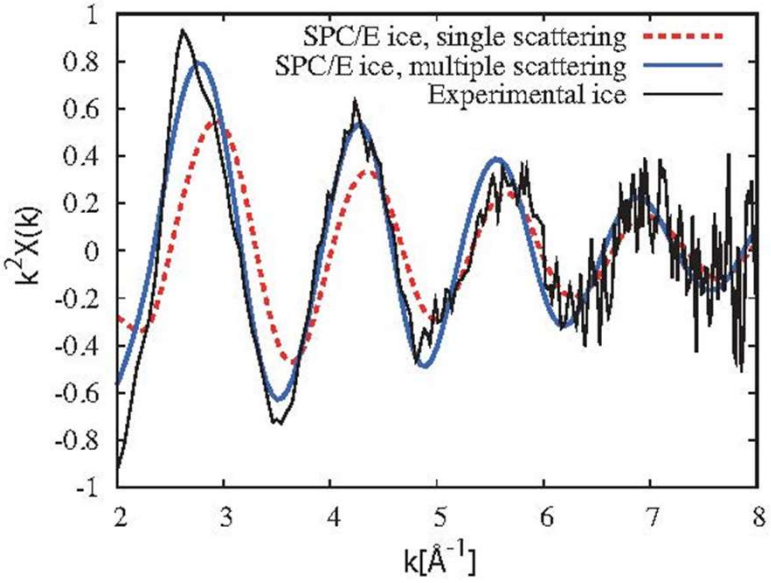


Photoelectron scattering against surrounding atoms

”Particle in a box”

Resonances contain information on e.g. distances

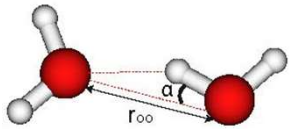
Multiple Scattering



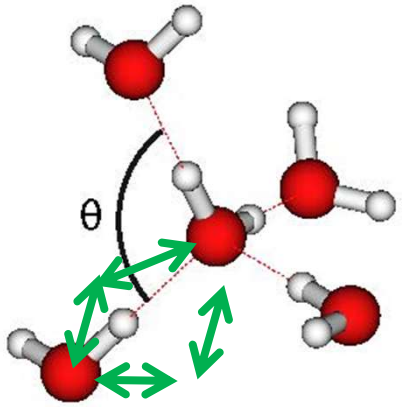
Multiple scattering important

Focusing effect

H-bonded structures give enhanced signal



Single



Multiple

Wikfeldt et al., J. Chem. Phys. **132**, 104513 (2010)

SpecSwap-RMC
Multiple-Data Set Fitting

Any experimental data set that depends on structure and can be computed from a structure can be used

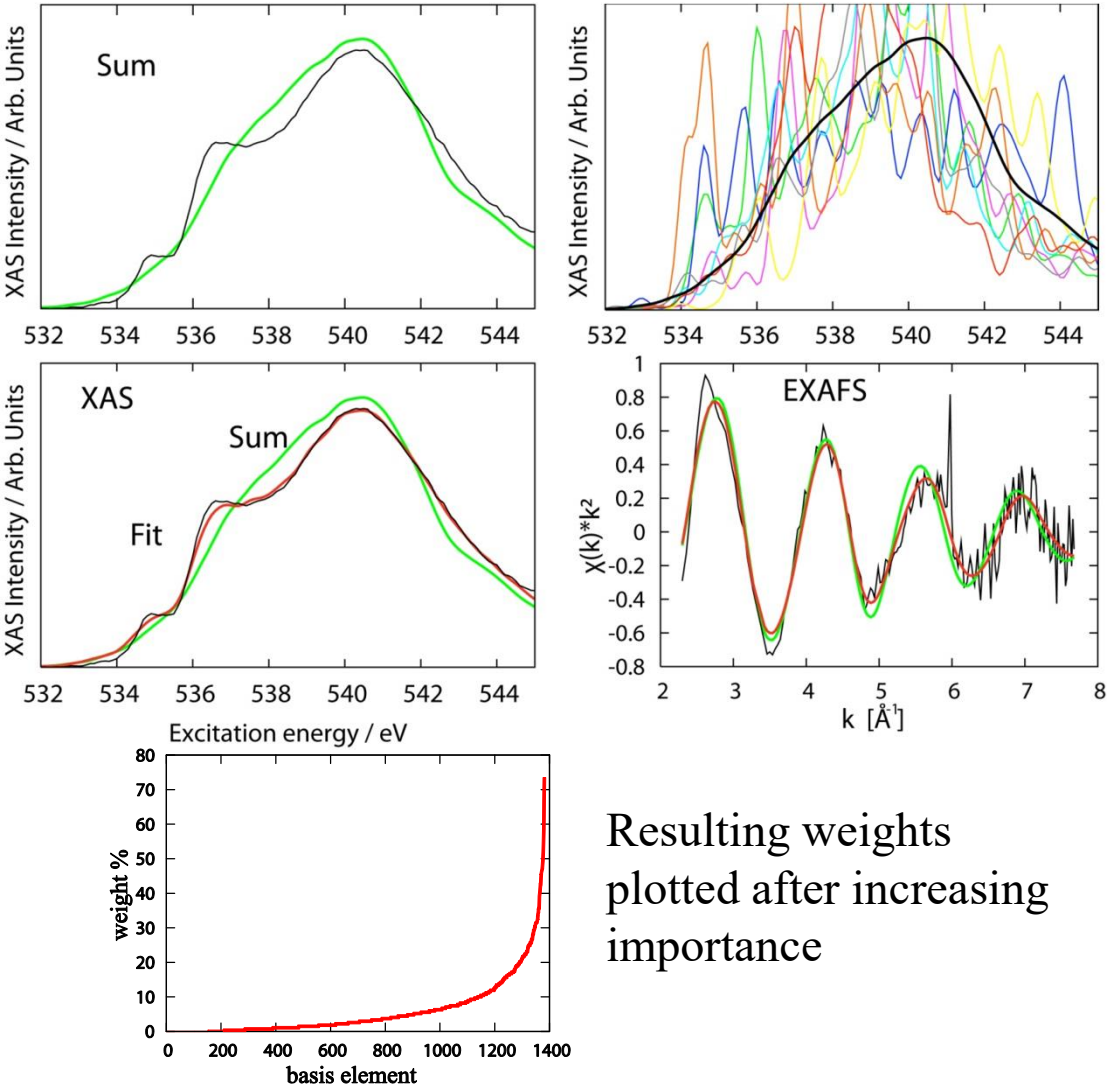
Use large set of possible structures, calculate the property
Structure + property is a basis function in a library

Choose a set of *m* basis functions from the library, calculate the deviation from the experimental data of the sum of these functions

Make random replacements in a reverse Monte Carlo procedure

https://github.com/leetmaa/SpecSwap-RMC/blob/master/doc/user_manual_v1.0a0.pdf

SpecSwap-RMC: XAS+EXAFS on Ice Ih



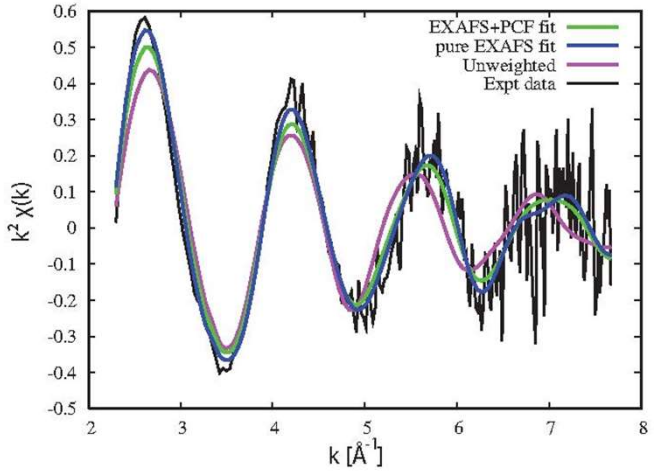
Resulting weights plotted after increasing importance

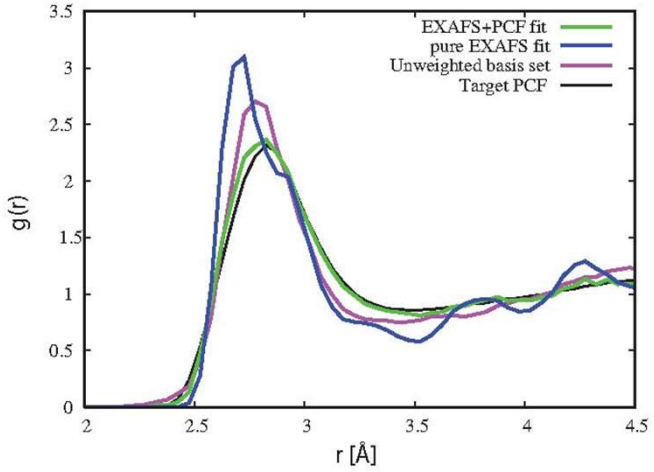
- Huge number of computed spectra (each 3x12 hours)
- None looking like experiment
- Total spectrum sum of contributions
- Do RMC on spectra to reweight the summation

- 1382 clusters (39 molecules) from PIMD on ice 200K
- Compute XAS spectra and EXAFS signal ➡ basis
- Sample set 80 spectra on which RMC is done
- 10^8 attempted moves; 1.2 10^6 accepted
- Collect statistics….
- Connect to structures…
- VERY GENERAL - ANY DATA

Leetmaa et al., J. Phys.:Cond. Mat. **22,** 135001 (2010)
Wikfeldt et al., J. Chem. Phys. **132**, 104513 (2010)

Combine XRD+ND with EXAFS





Fit simultaneously EXAFS signal and PCF

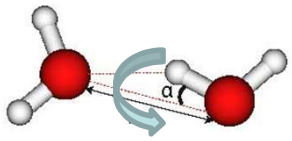
Joint solution possible

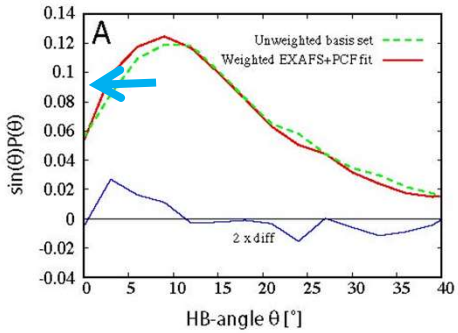
EXAFS very sensitive to strong, directional H-bonds

XRD+ND sees all situations

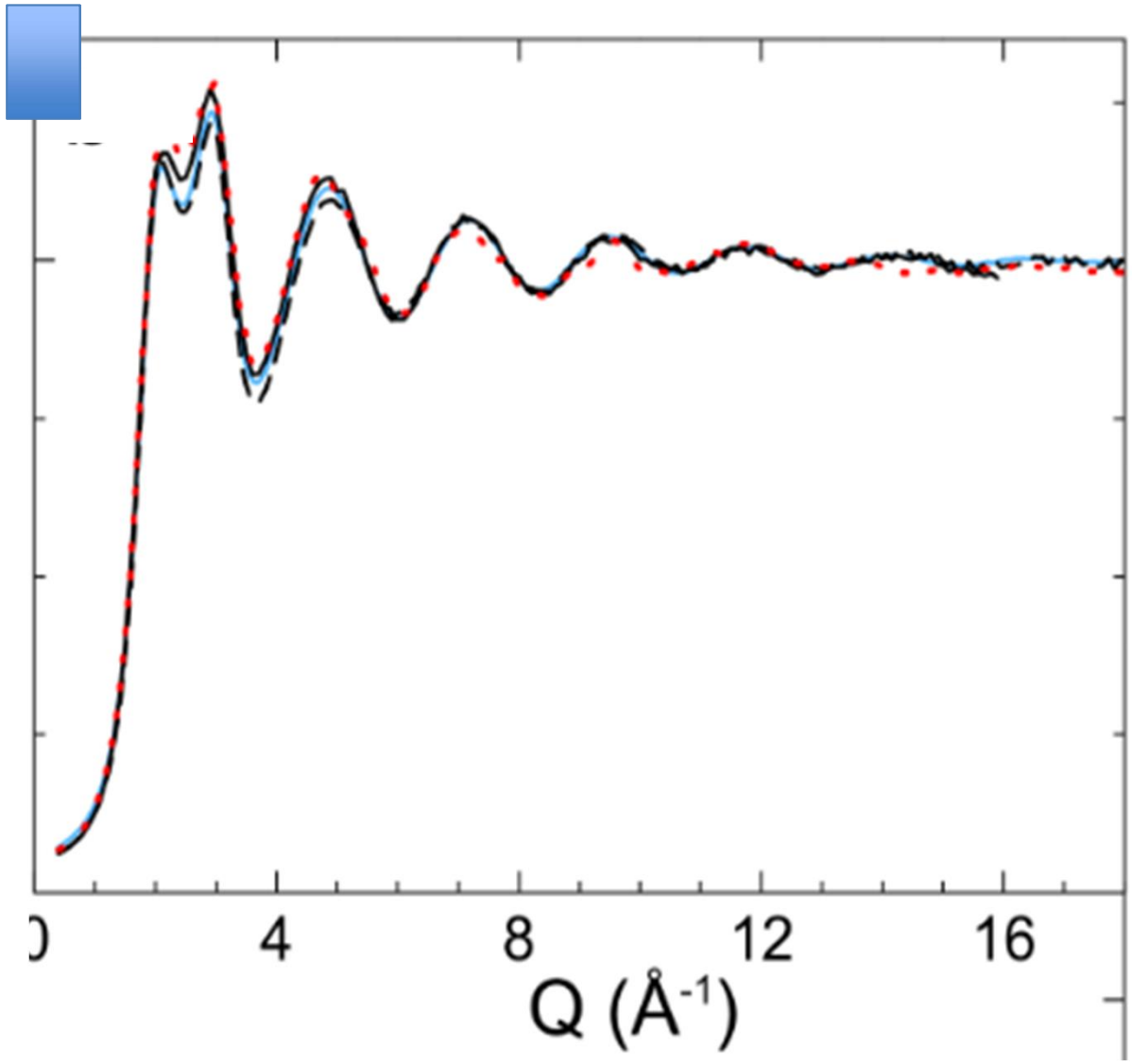
EXAFS enforces a subclass of structures with well-defined H-bonds

Complementary information

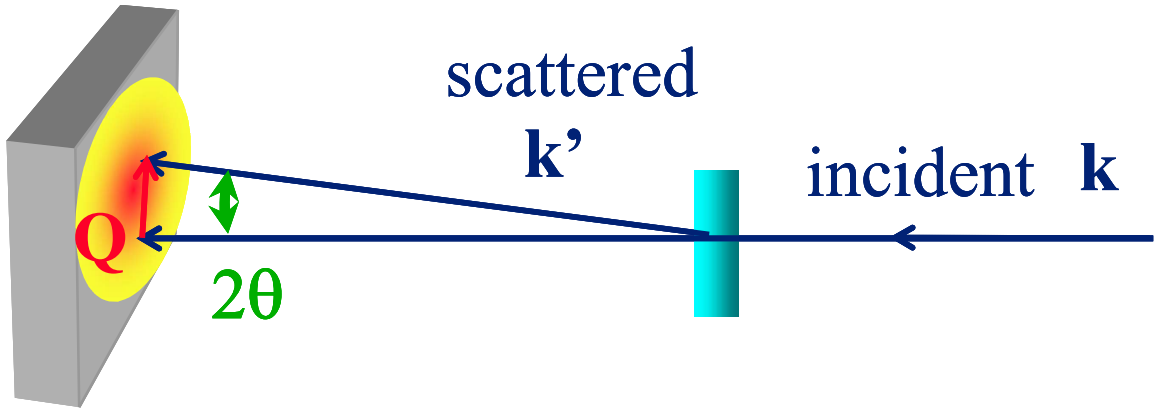




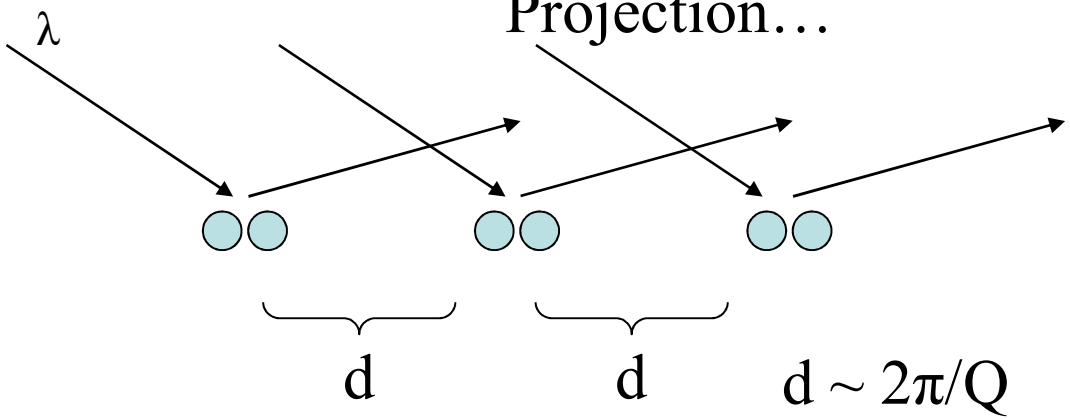
Small Angle Region Q<0.5 Å^{-1}



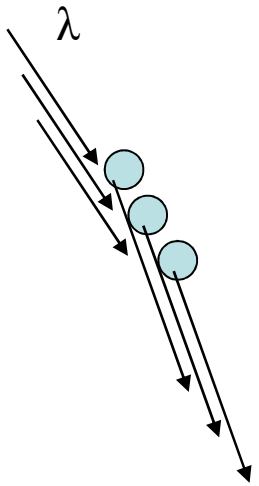
Small-Angle X-ray Scattering (SAXS)



Small angles "trick" the light that distances are short Projection…

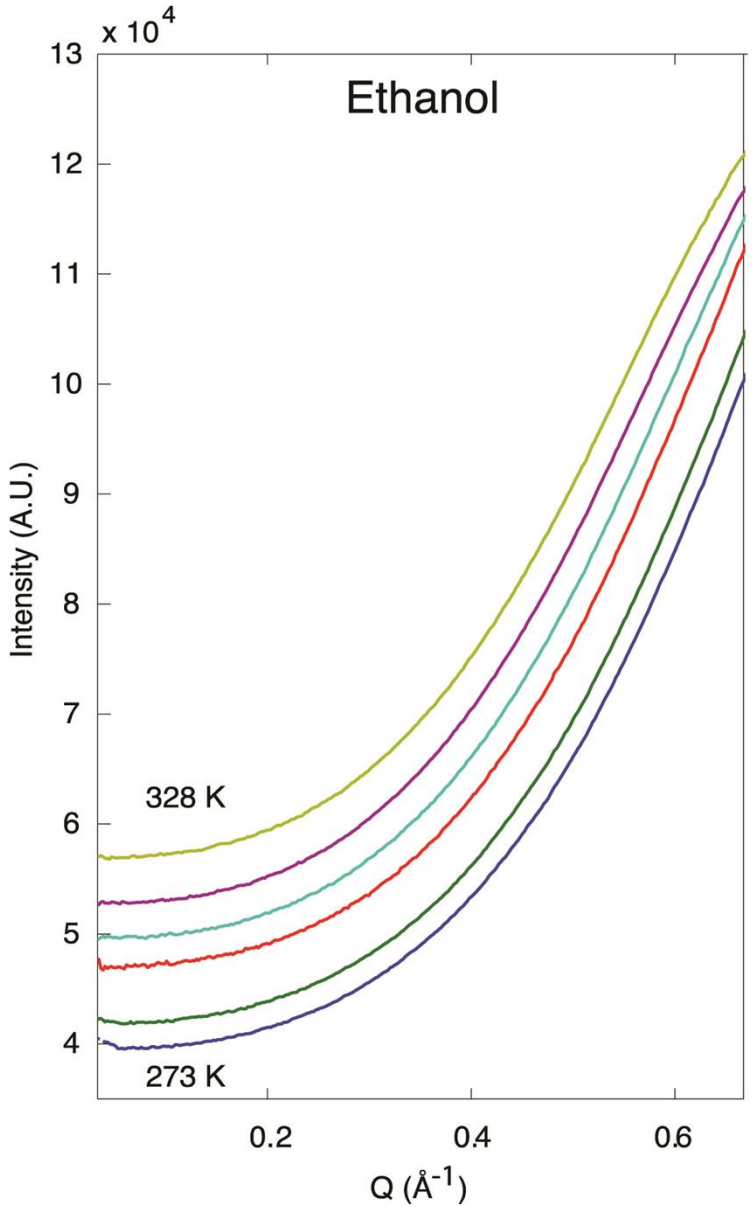


$d \sim 2\pi/Q$



Measures density contrast
Size of macromolecules, colloids etc (Guinier analysis)
Critical density fluctuations (Ornstein-Zernike)

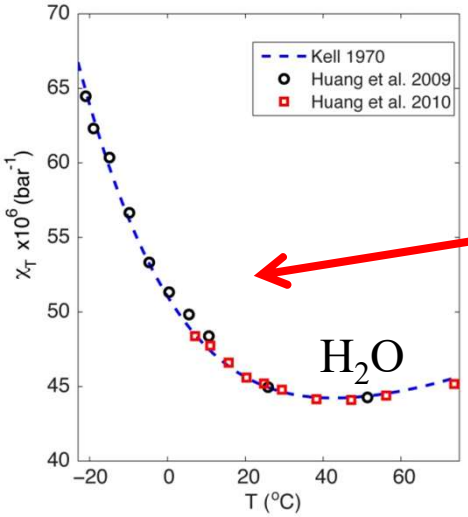
SAXS: Normal Liquid vs Water



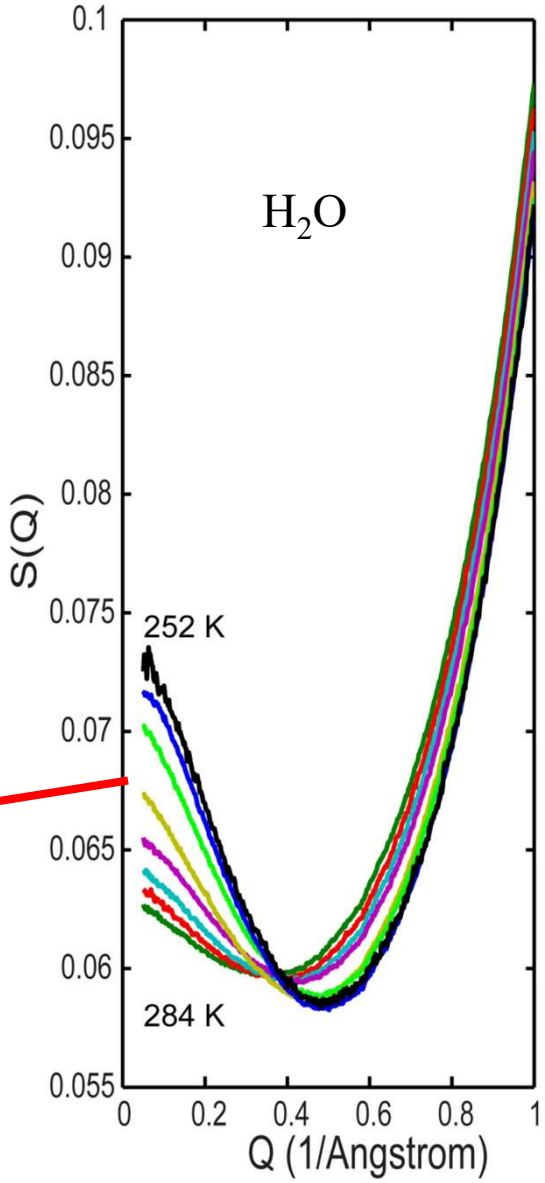
Normal liquid

The isothermal compressibility χ_T

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



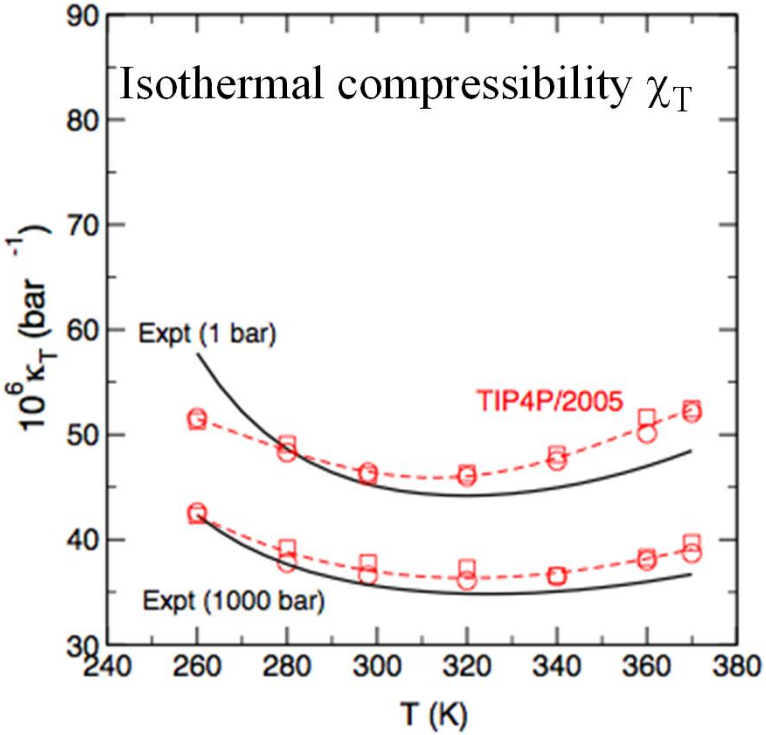
χ_T

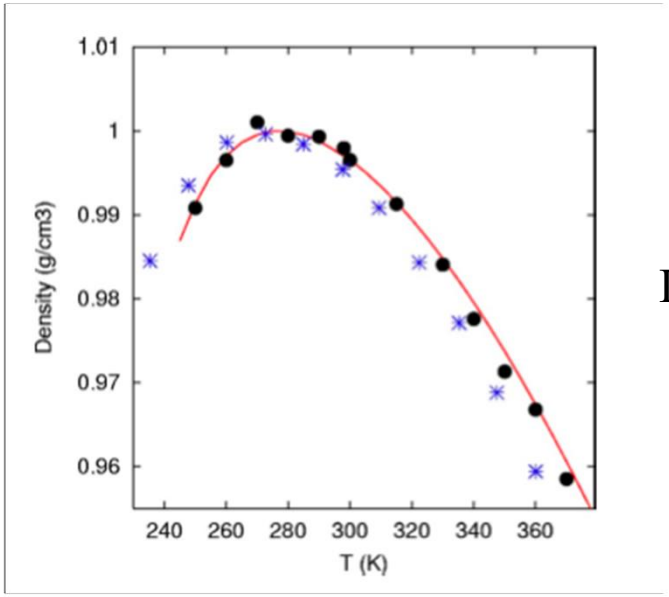


TIP4P/2005

- 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)]

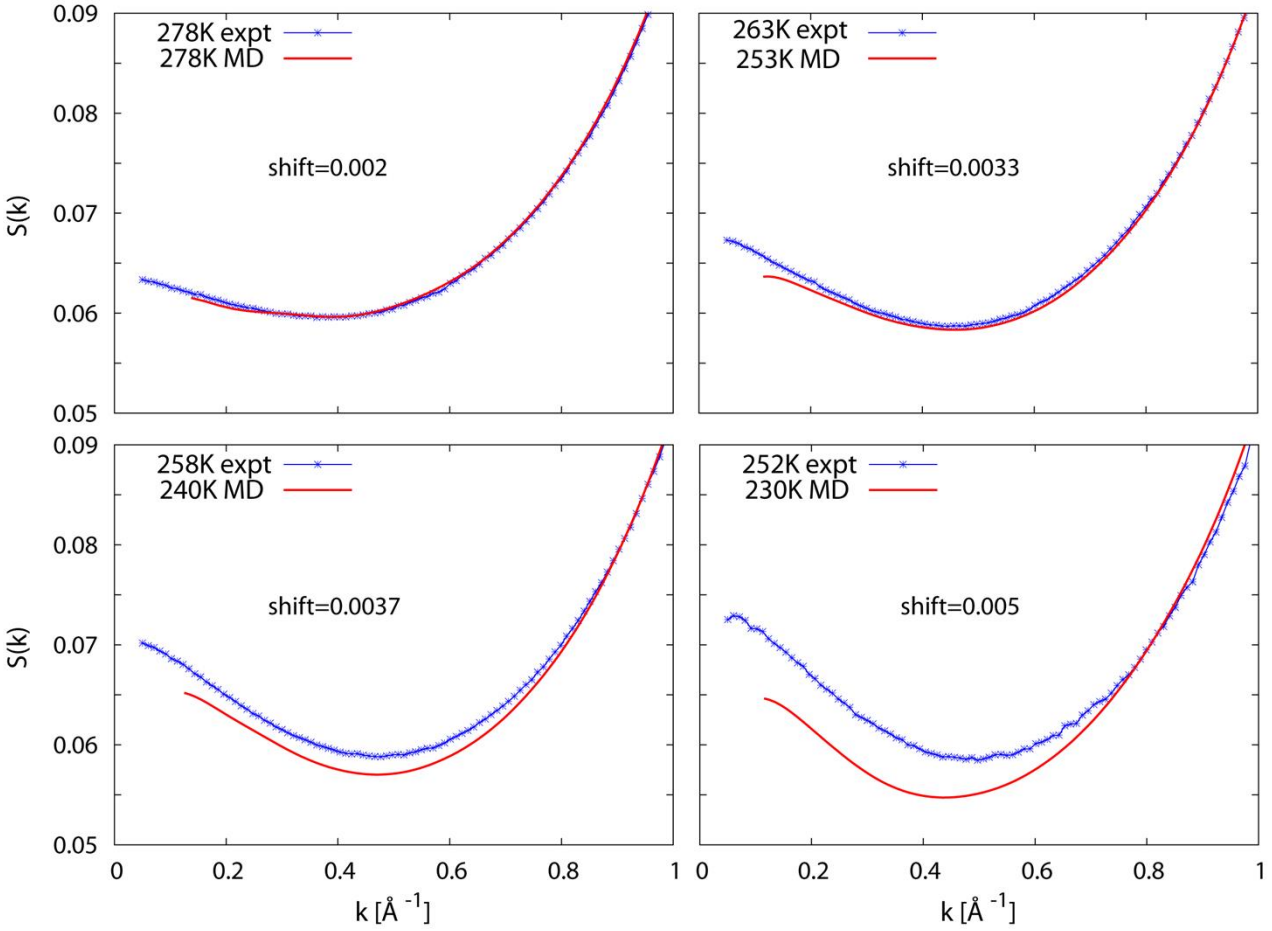
- Need *very* large simulations for SAXS, here 45,000 molecules (Q~2π/R)
- Need long equilibration times to reach equilibrated long-range correlations
- Need to average RDFs over long time intervals to average out spurious fluctuations in low-*q* structure factor $S(q) = 1 + 4\pi\rho \int w(r) r^2 [g(r)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





Density

SAXS and TIP4P/2005



45,000 molecules

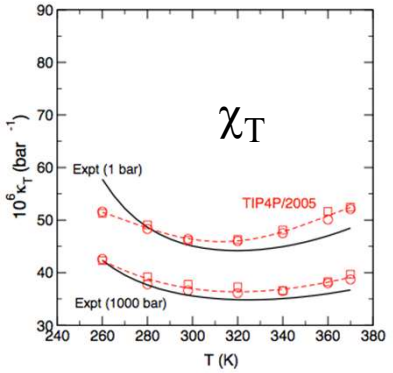
Excellent representation but:

278 K slight underestimate

Lower T shift both in T and in S(k) needed

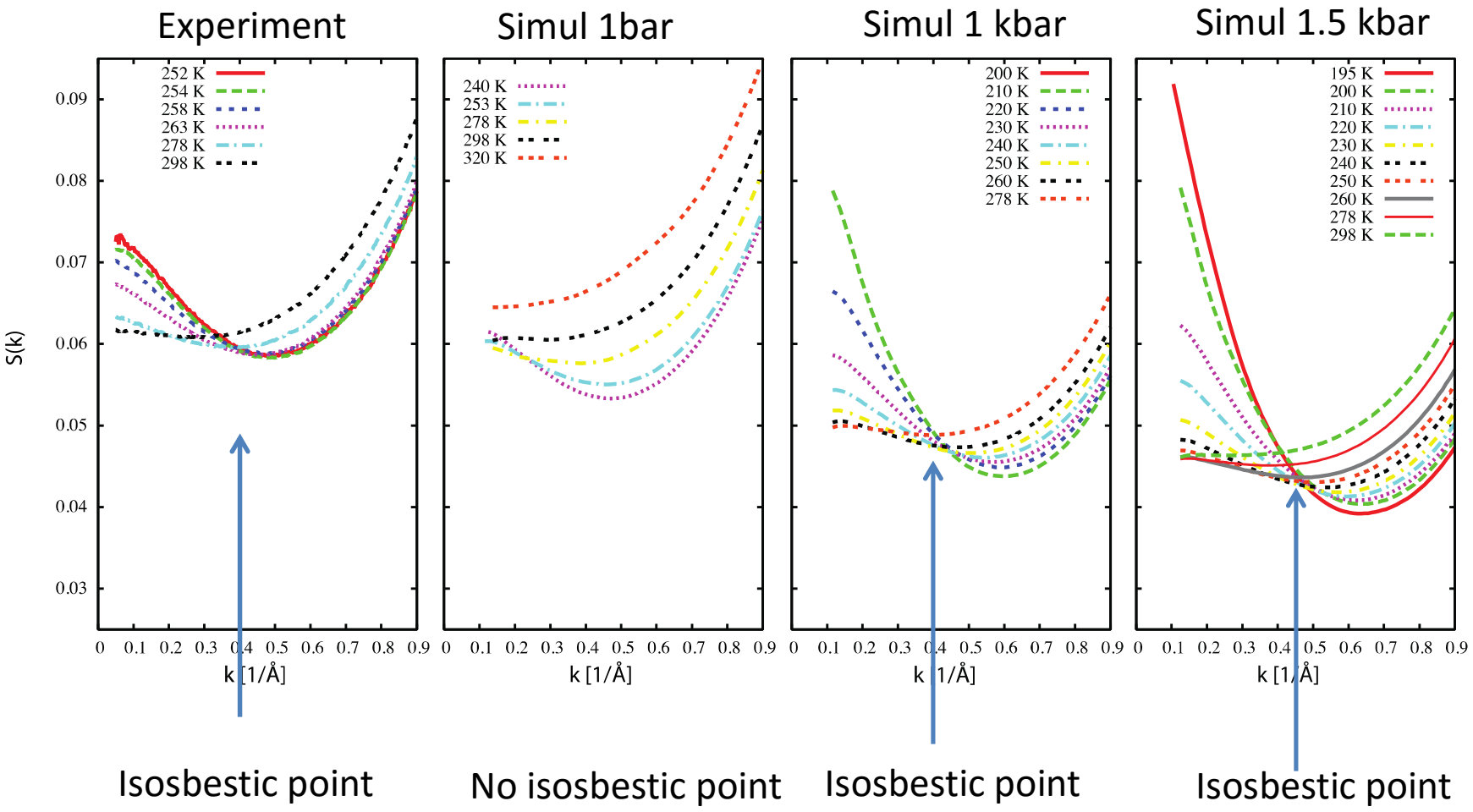
At 230 K maximum but smaller than expt. 252 K

Real liquid larger effect



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

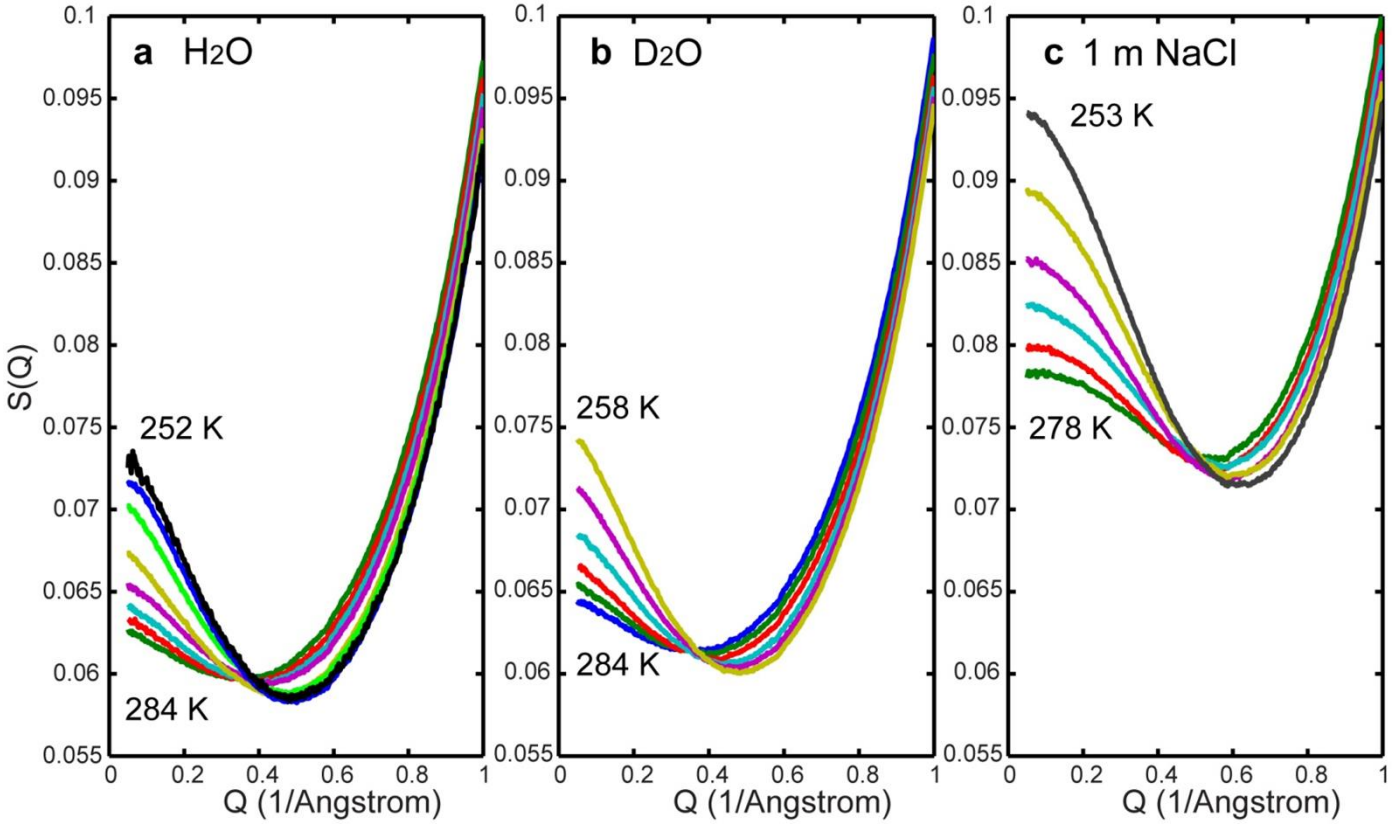
Shift in Pressure for TIP4P/2005



Demonstrate similar behavior with a shift of 1-1.5 kbar

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

SAXS
Isotope and Salt Effects

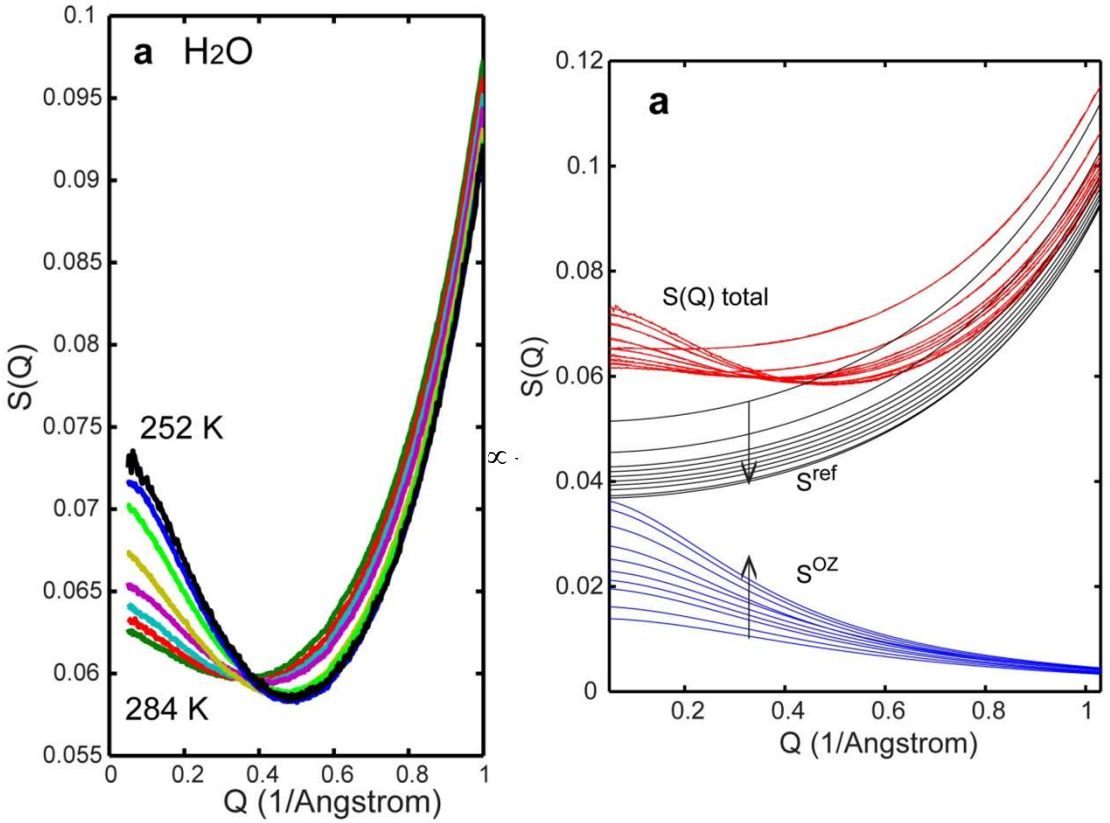


- Density fluctuations grow more quickly in size for D_2O
- H-bond strength reduced by quantum effects (Walker and Michaelides, JCP **133** (2010) 174306)
- Fluctuations towards LDL less favorable for H_2O

Steeper rise for salt solution
Adding salt ~ "increasing pressure"
Leberman and Soper, Nature **378,** 364 (1995)

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

SAXS
Ambient to Supercooled Regime



$\propto$

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:

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

Anomalous contribution from Ornstein-Zernike theory:

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

σ – hard sphere diameter

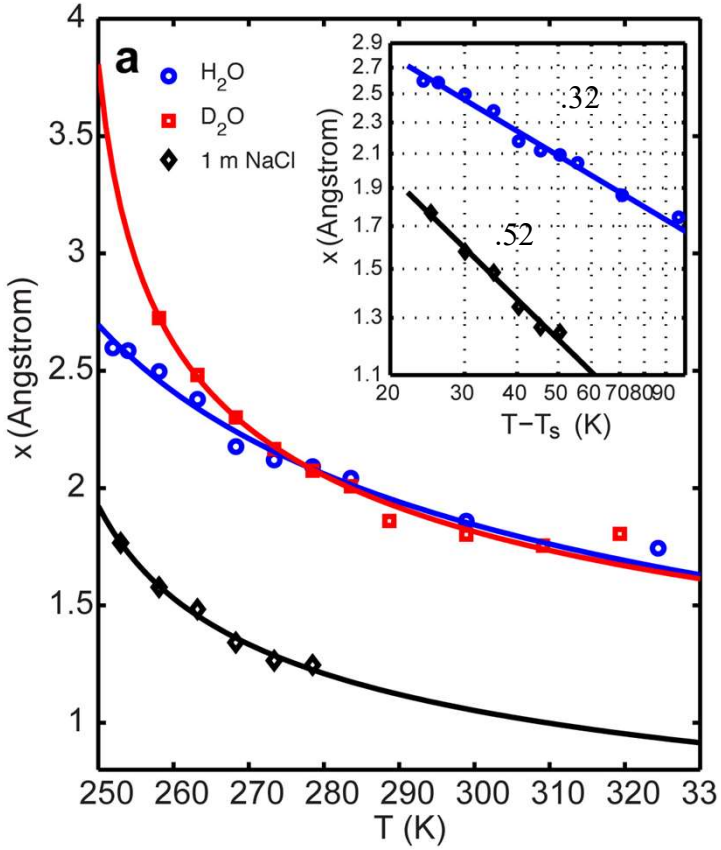
η- volume fraction of water

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

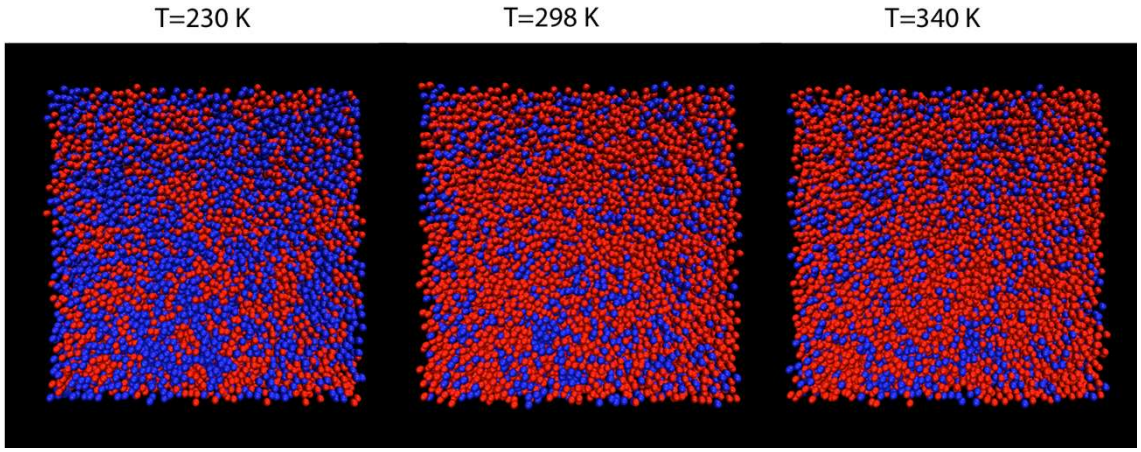
Huang *et al.*, JCP **133**, 134504 (2010)

Apparent Power Law – Widom Line

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

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

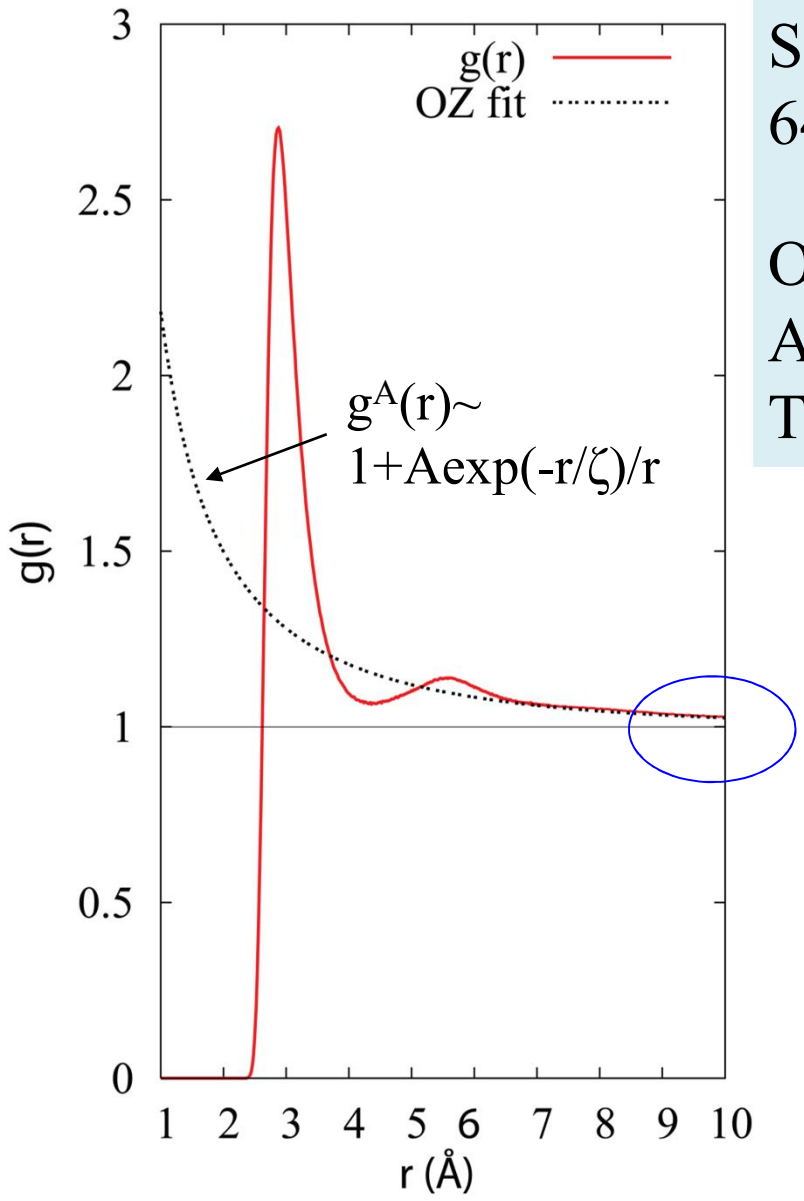
with

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

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

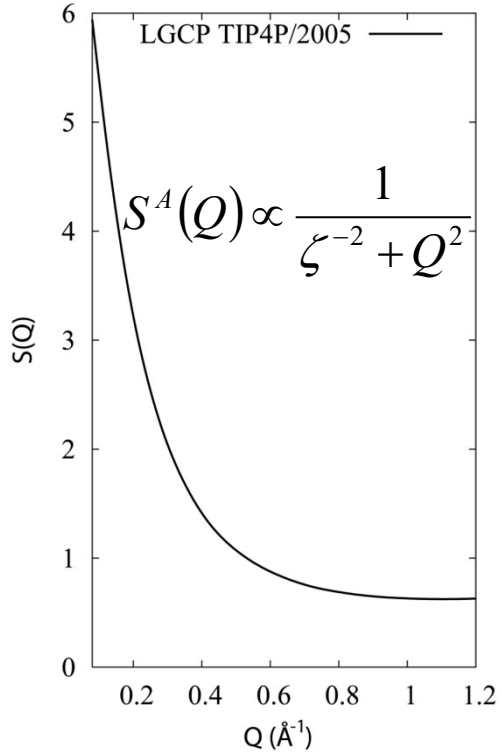
Wikfeldt et al., PCCP **13**, 19918 (2011)

Correlation Length Liquid-Gas CP

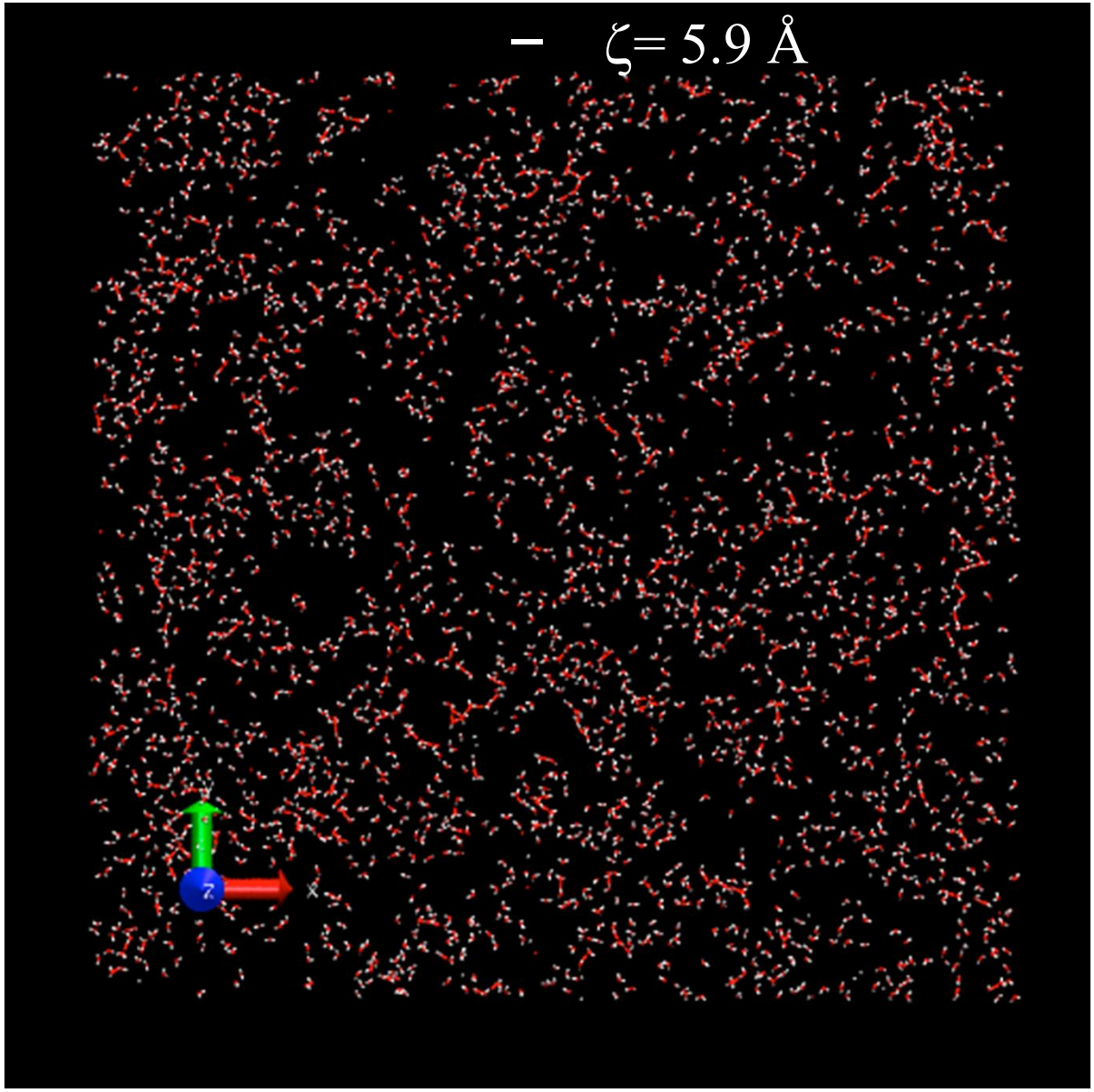


Simulate liquid-gas critical point at
640 K ρ=310 kg/m^3 (Vega et al. JCP 125 (2006) 34503)

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



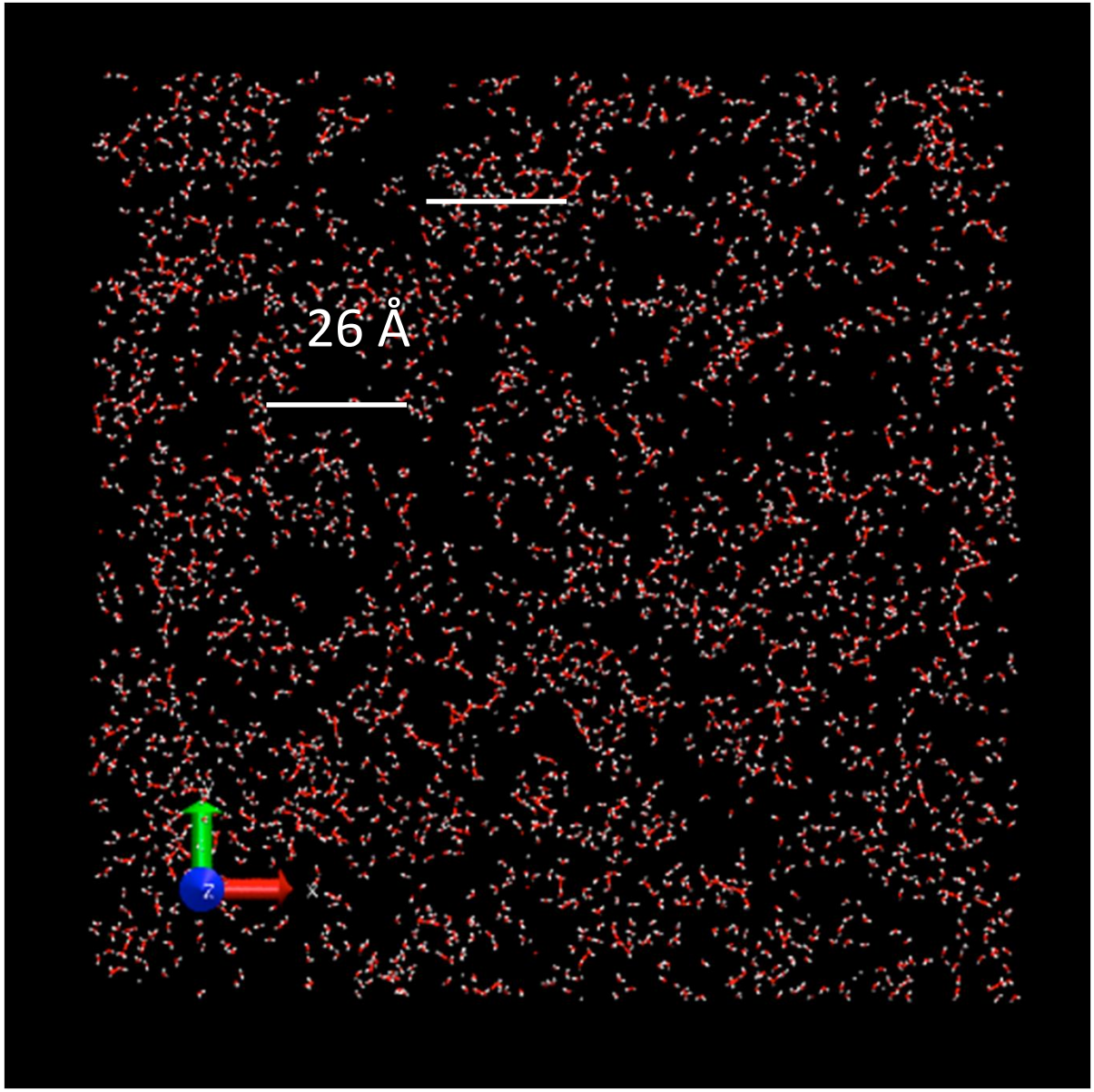
Real Structure Liquid-Gas CP



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

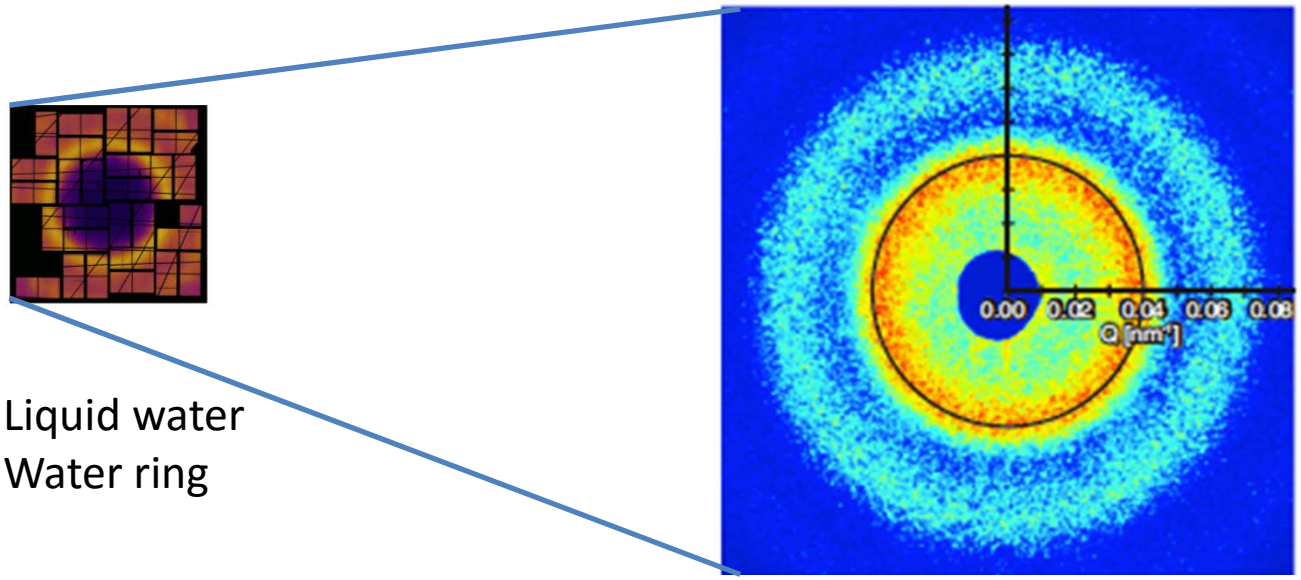
we get D=26 Å

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

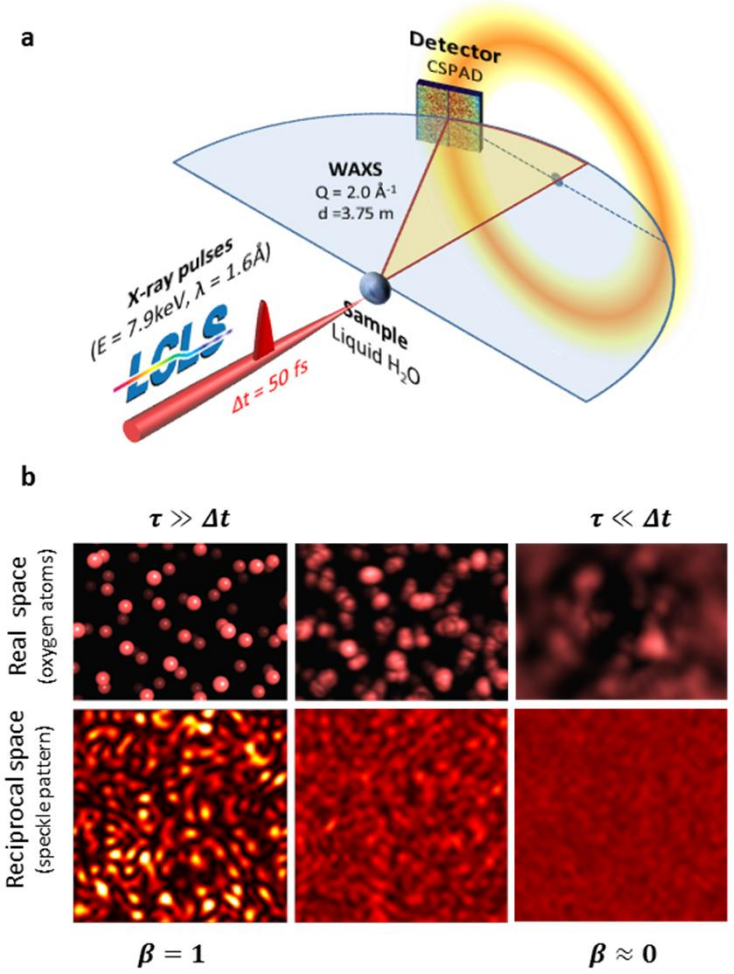
Scattering Patterns
Speckles



Liquid water
Water ring

Granularity (speckles) due to
the instantaneous local structure

Speckle Dynamics
XPCS



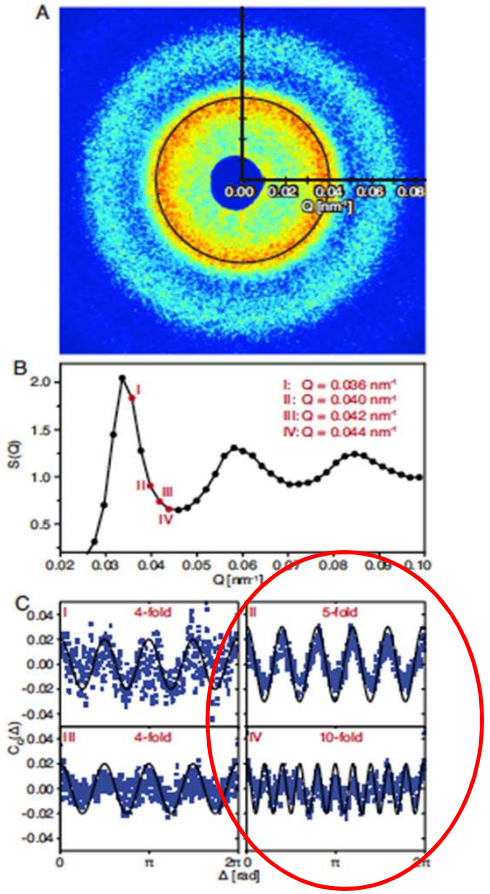
Real space

Speckles

X-ray scattering collected within specific pulse length

Speckle contrast determined by extent of atomic motion during the x-ray pulse

Speckle Correlations
XCCA



Perform autocorrelation analysis in Q, Q´ and Δφ to discover hidden symmetries in the liquid

Here polystyrene spheres suspended in solution from Wochner et al. X-ray cross correlation analysis uncovers hidden local symmetries in disordered matter. *Proc. Natl. Acad. Sci. (USA)* **106**, 11511 (2009)

$$C_{Q_1,Q_2}(\Delta) = \frac{\left\langle \left(I(Q_1,\varphi) - \left\langle I(Q_1,\varphi)\right\rangle\right)\left(I(Q_2,\varphi+\Delta) - \left\langle I(Q_2,\varphi)\right\rangle\right)\right\rangle}{\left\langle I(Q_1,\varphi)\right\rangle\left\langle I(Q_2,\varphi)\right\rangle}$$

Next Lecture….

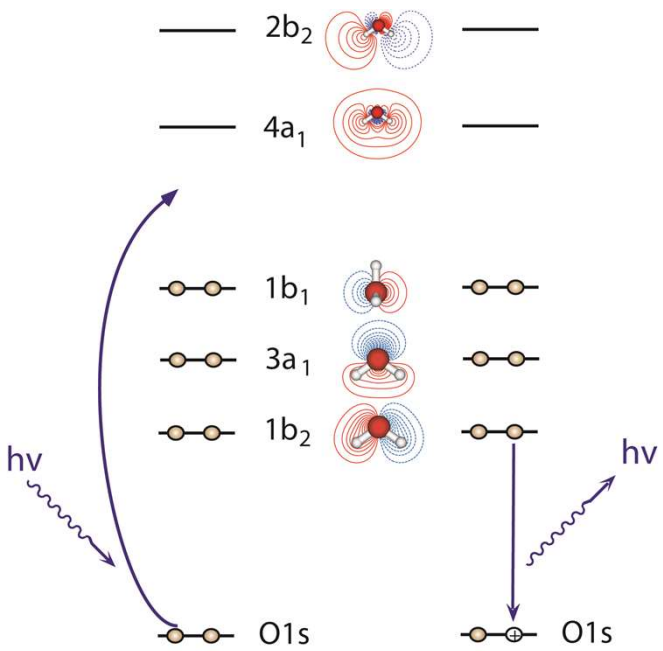
XAS and XES

XAS

X-ray Absorption Spectroscopy

Core electron excited into unoccupied state

Measures unoccupied

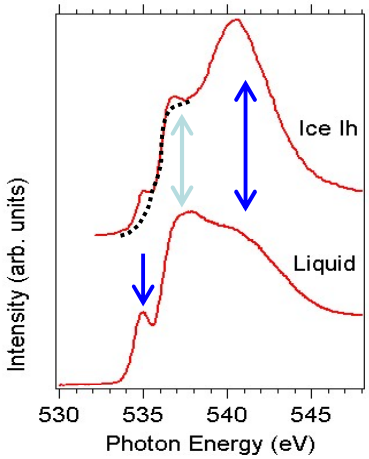


XES

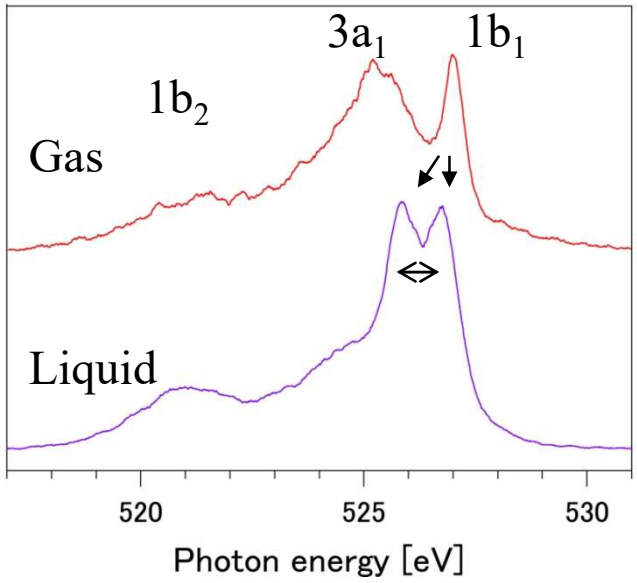
X-ray Emission Spectroscopy

Valence electron decays to fill hole created by XAS

Measures occupied states

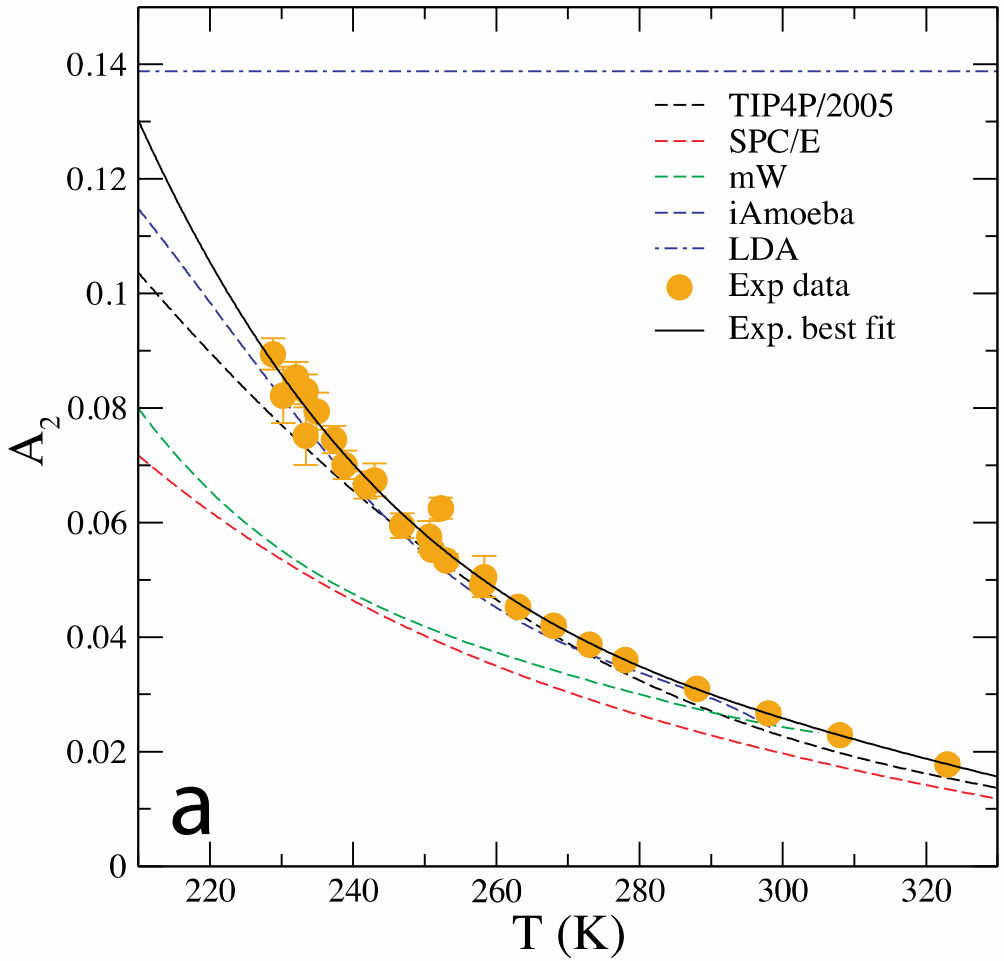


~3-4 *fsec*



Experimental Variation of the Tetrahedrality

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



LDA

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

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

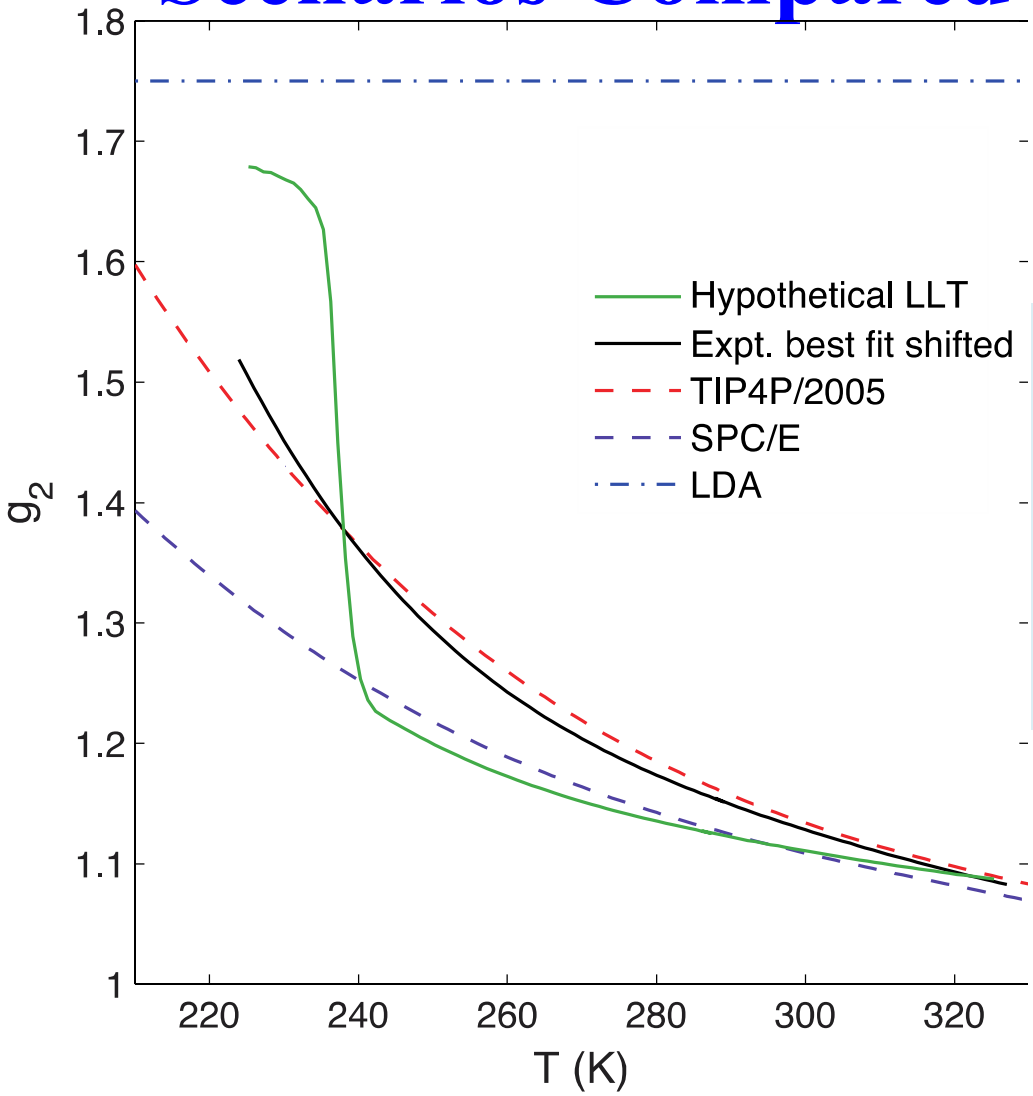
The transformation is **continuous**

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

Simulations underestimate the transformation

Sellberg et al., Nature **510**, 381 (2014)

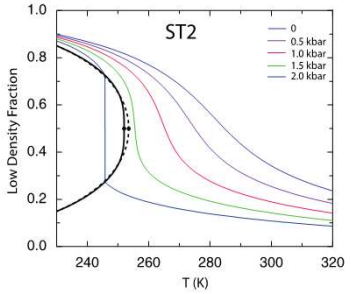
The Change in Structure in Different Scenarios Compared to Experiment…



Data inconsistent with a LLT at 0 bar
Not singularity free scenario

Temperature dependence consistent with ADP / LLCP

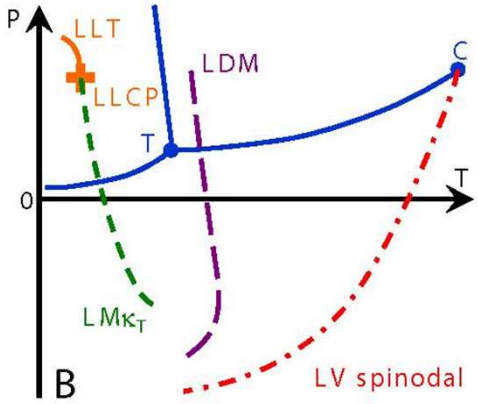
Maybe critical pressure at 1500±250 bar



Nilsson and Pettersson, Nature Communications **6**, 8998 (2015)

Several Scenarios

Stability limit scenario



2nd critical point scenario

Critical point free scenario

Singularity free scenario