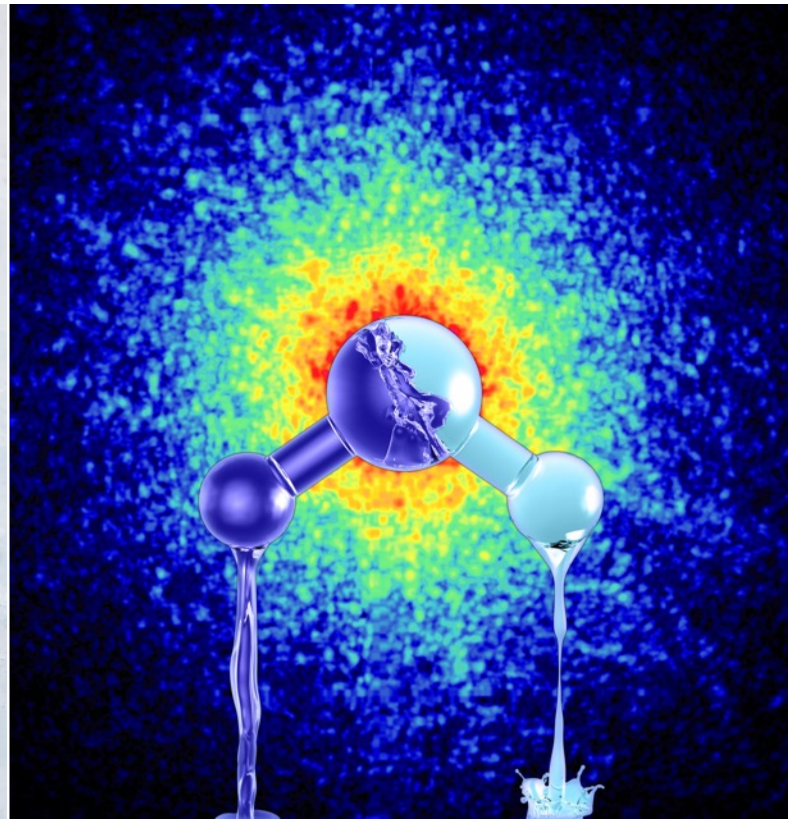
Stockholm University

Foivos Perakis
Physics Department

Temporal correlations in liquid water using x-rays:
from femtoseconds to seconds

Workshop on Coherence at ESRF-EBS
Grenoble, 10 September 2019

Outline



Glassy water

Diffusive dynamics of amorphous ices

Supercooled water

ultrafast cage effects

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Why study water?

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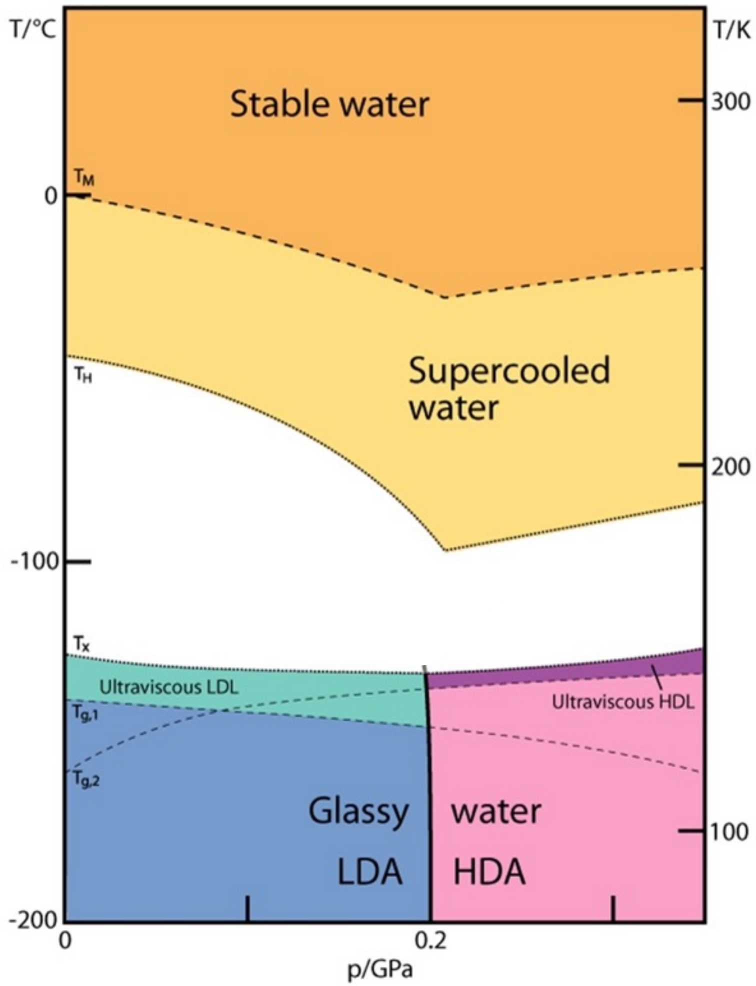
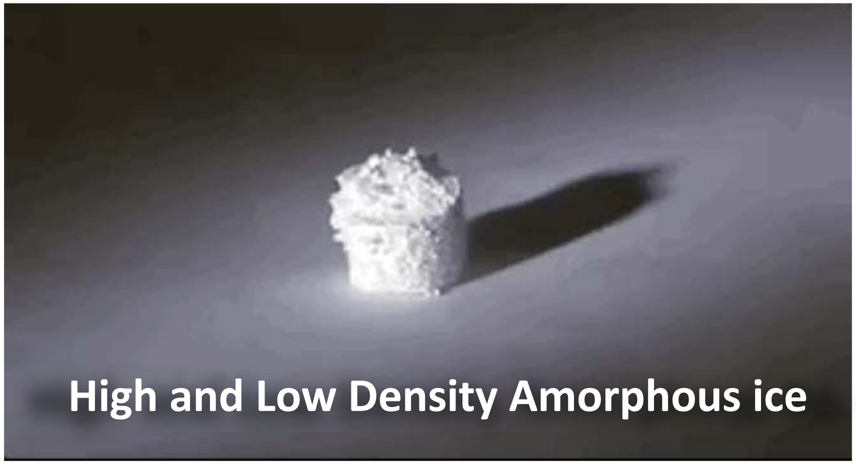
The two-liquid hypothesis





ρ(LDA)=0.94 g/cm^3 ρ(HDA)=1.17 g/cm^3

Close to hexagonal ice

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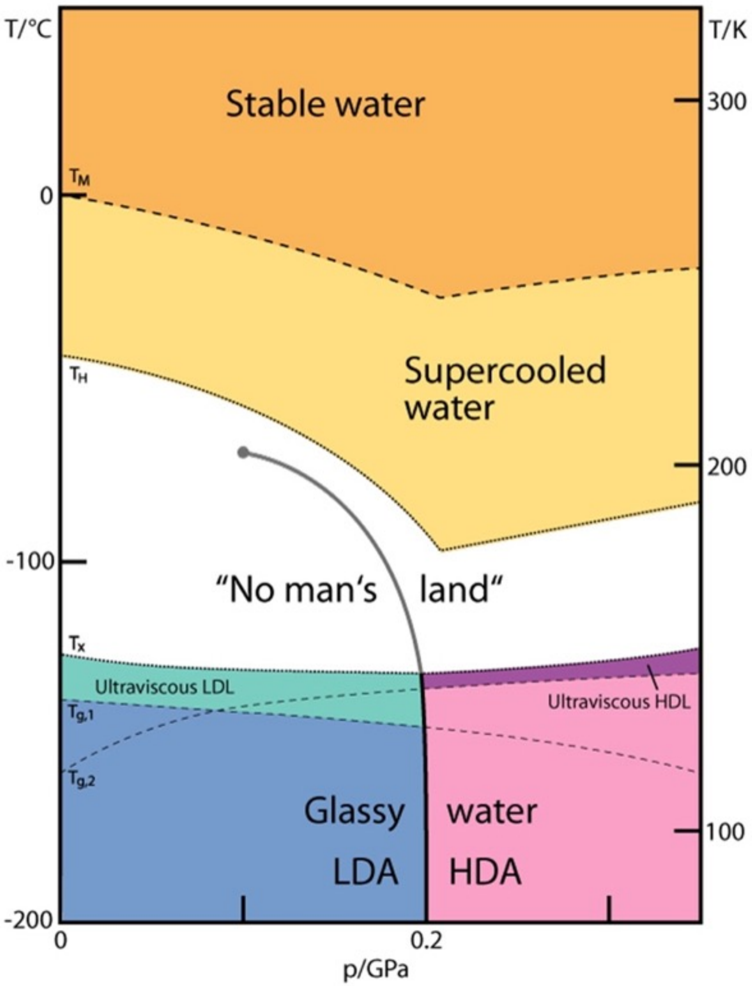
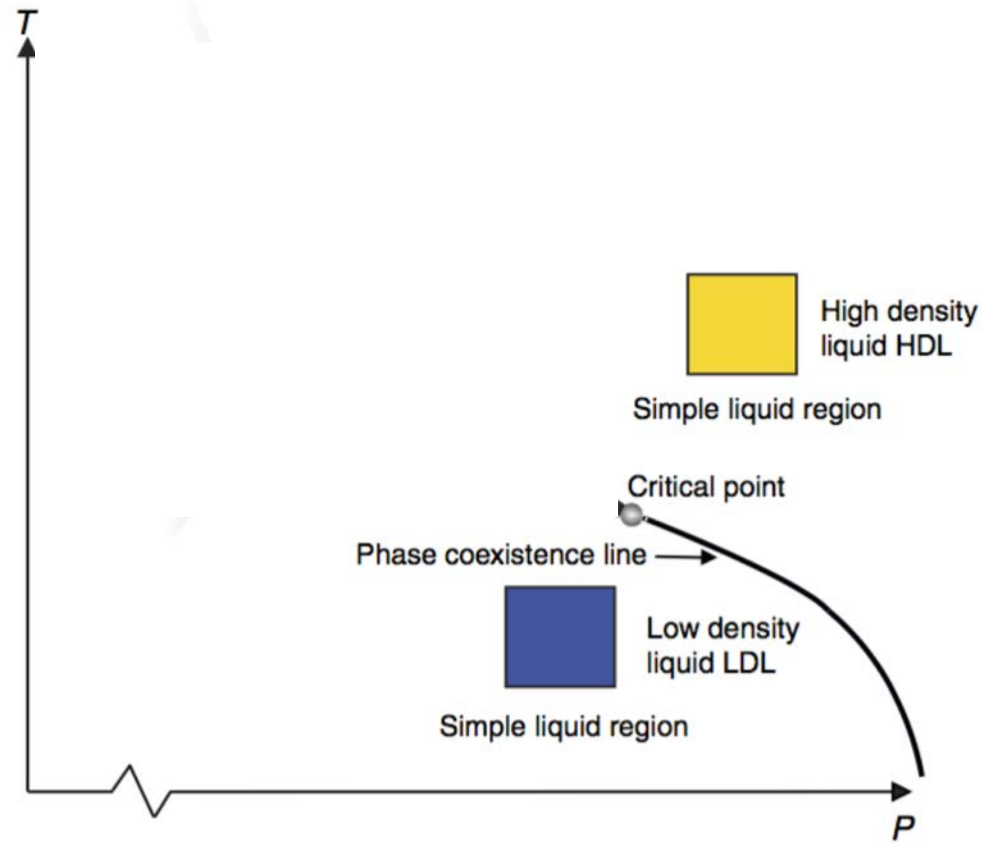
The two-liquid hypothesis

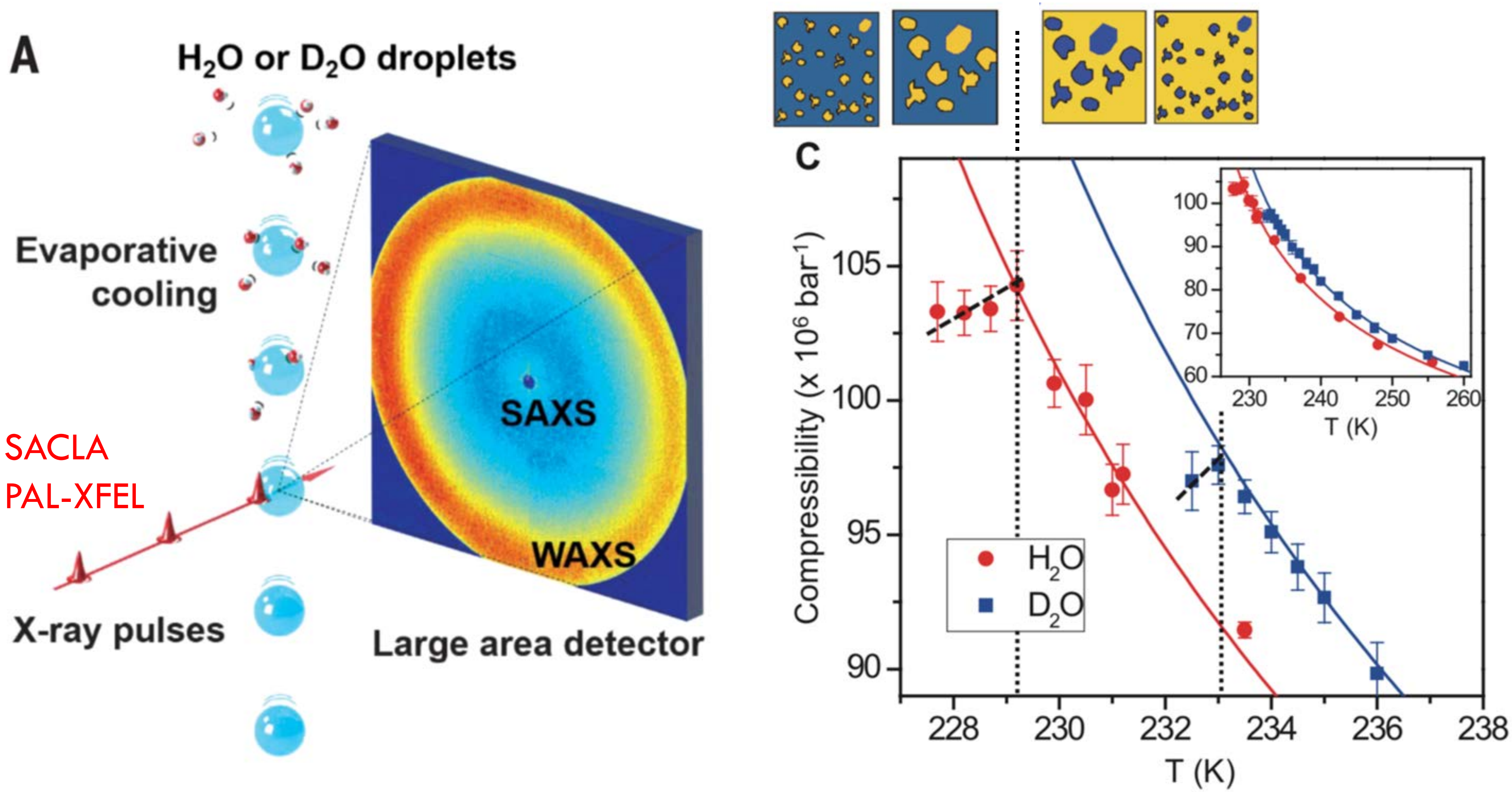




Poole et al.
Nature 360,1992

A. Nilsson & L. Pettersson
Nature Comm. **6,** 8998 (2015)

Experimental Evidence: Widom line 229K

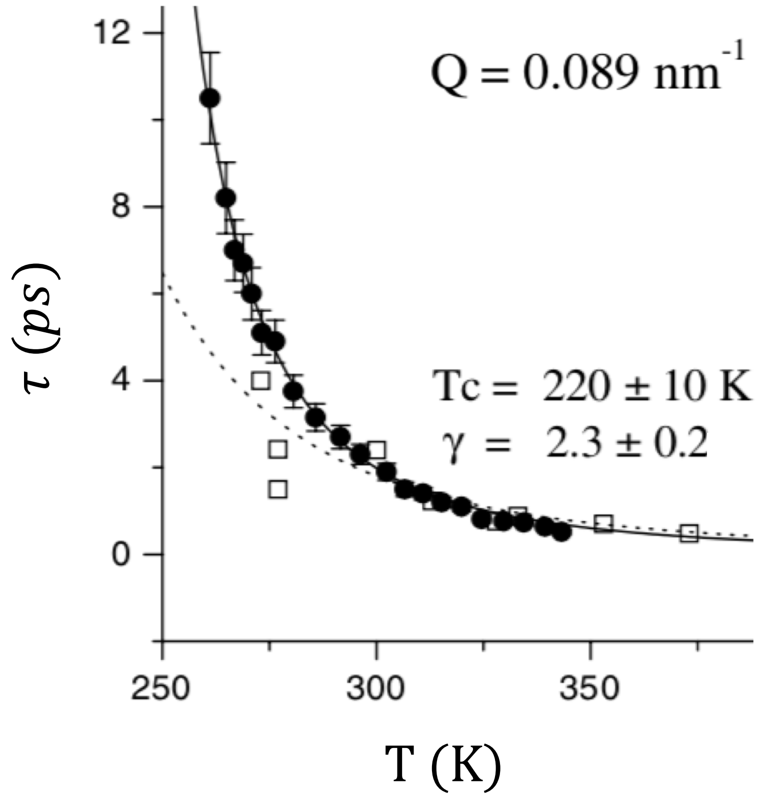


K.H. Kim et al. Science **358**, 1589 (2017)

What about the dynamics?

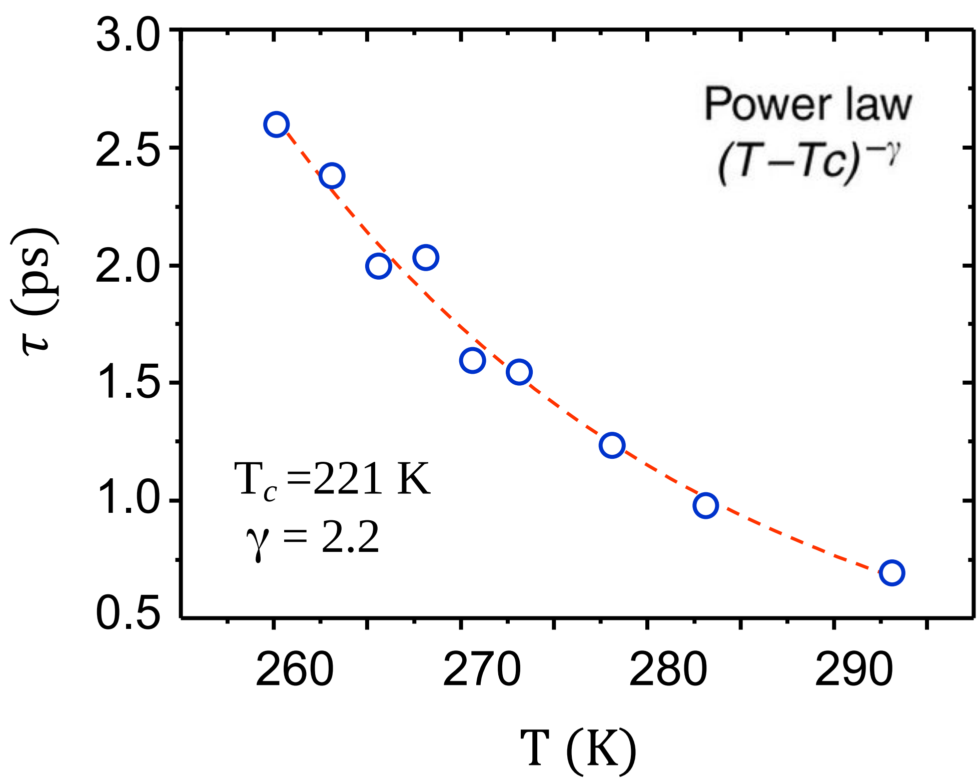
Inelastic UV Scattering

Dynamic structure factor S(Q,ω)



2D-IR Spectroscopy

OH stretch frequency fluctuations



C. Masciovecchio, S. C. Santucci,A. Gessini, S. Di Fonzo, G. Ruocco, and F. Sette PRL 92, 255507 (2004)

F. Perakis, et al
Chem. Rev. 116, 7590−7607 (2016)

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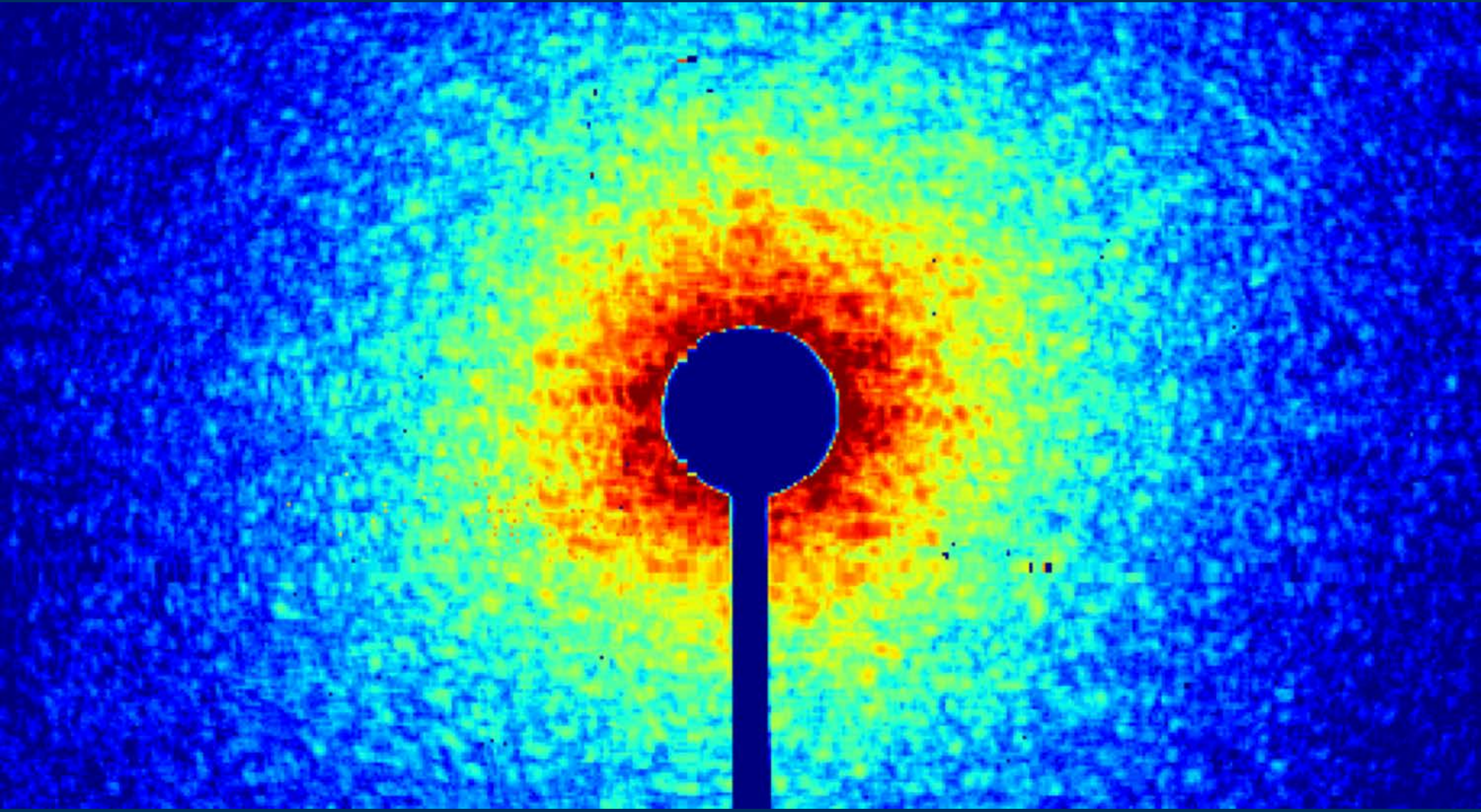
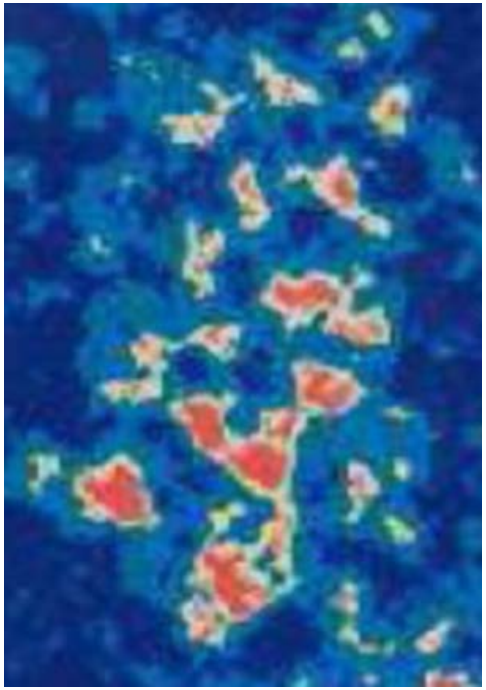
Coherence and dynamics



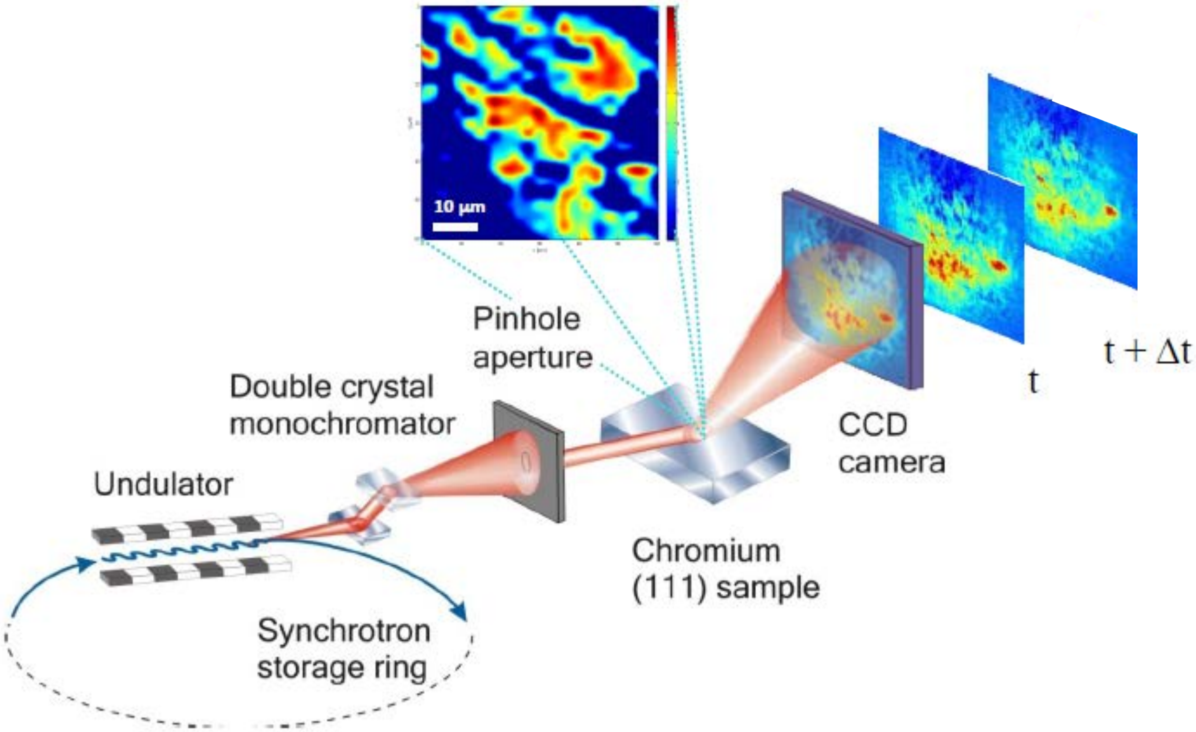
Speckles and Dynamics

Speckle Pattern



Beyond averages:
reflects exact arrangements

X-ray Photon Correlation Spectroscopy



Dynamics by changes of the speckle pattern

M. Sutton et al.,
Nature 352, 608-610 (1991)

O. G. Shpyrko et al
Nature 447, 68 (2007)

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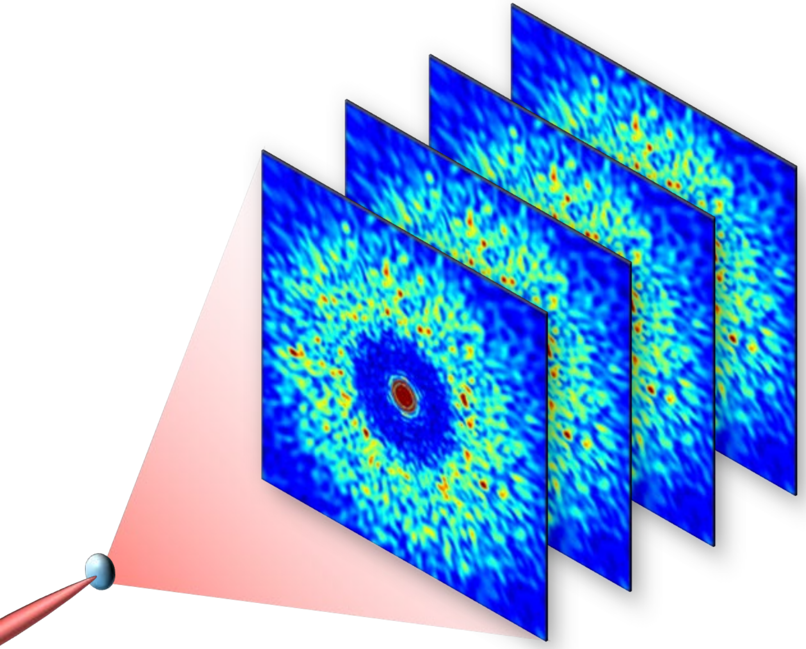
X-ray Photon Correlation Spectroscopy

Intensity Autocorrelation Function

$$g_2(Q,\delta t) = \frac{1}{N}\langle I(Q,t)\cdot I(Q,t+\delta t)\rangle$$

Intermediate scattering function

$$F(Q,t) = \frac{1}{N}\langle \sum_{i=1}^{N}\sum_{j=1}^{N} e^{iQ\cdot[r_i(t)-r_j(0)]}\rangle$$

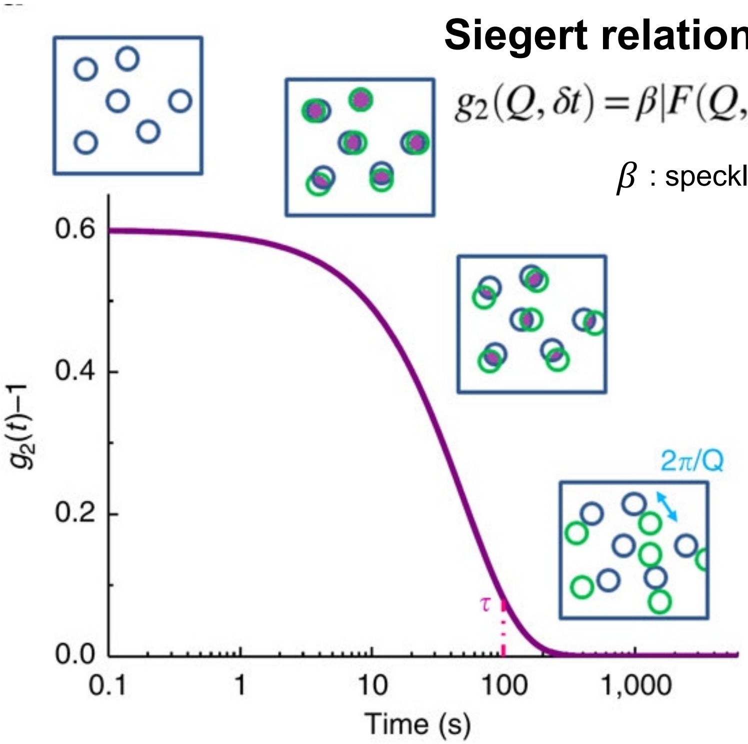


Changes of the Speckle pattern

Siegert relation

$$g_2(Q,\delta t) = \beta|F(Q,\delta t)|^2 + 1$$

β : speckle contrast

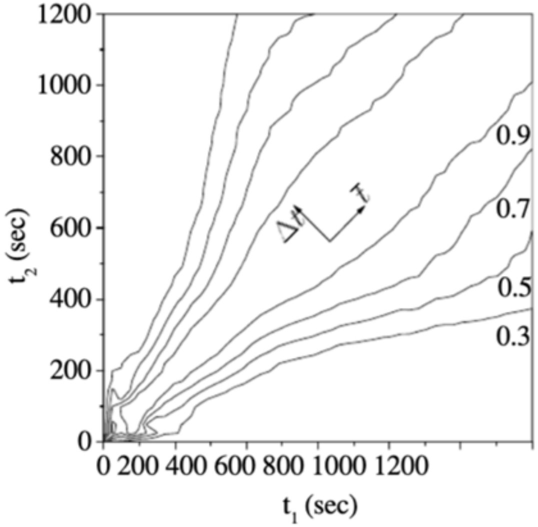


Madsen A., Fluerasu A., Ruta B. (2016)
Structural Dynamics of Materials Probed by XPCS

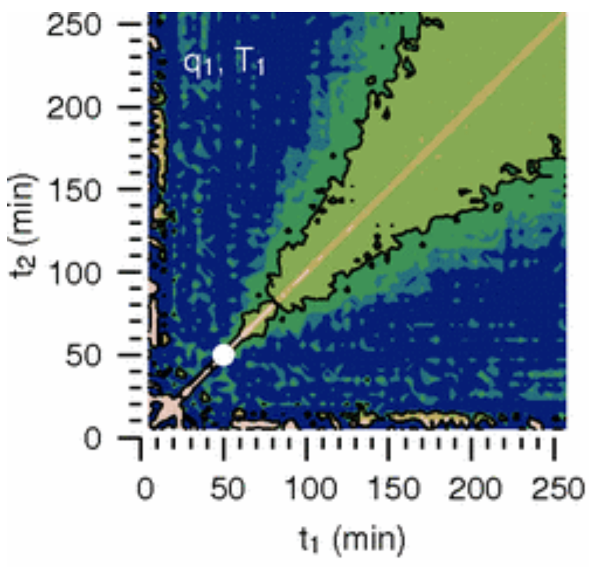
Giordano and Ruta
Nature Comm. 7, 10344 (2016)

two-time correlation functions

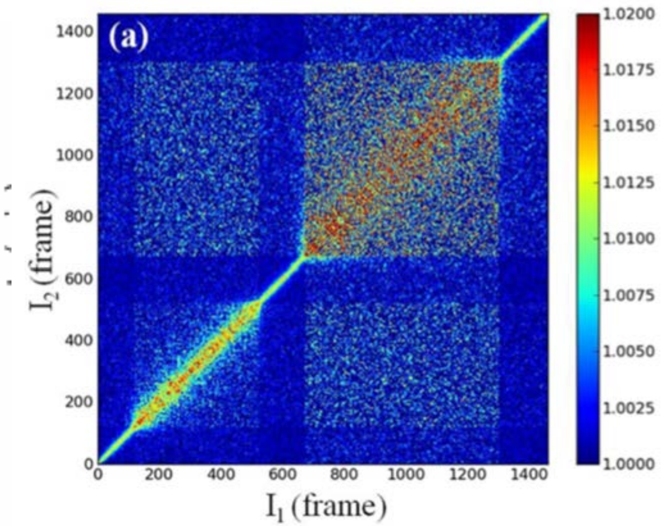
$$g_2(Q,\delta t) = \frac{1}{N}\langle I(Q,t)\cdot I(Q,t+\delta t)\rangle \Leftrightarrow C(Q,t_1,t_2) = \frac{1}{N}\langle I(Q,t_1) I(Q,t_2)\rangle$$



phase separation in sodium borosilicate glass



Order-disorder phase transition in Cu_3Au



Pump and probe of atomic motion in oxide glasses

Malik et al
PRL 81, 832-5835 (1998)

Fluerasu et al
PRL 94, 055501 (2005)

Ruta et al.
Sc. Rep. 7, 3962 (2017)

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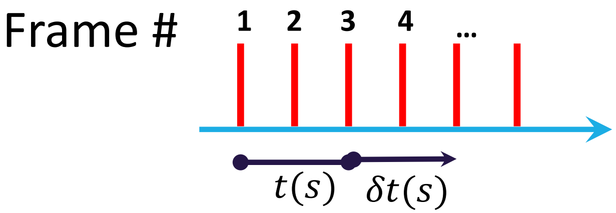
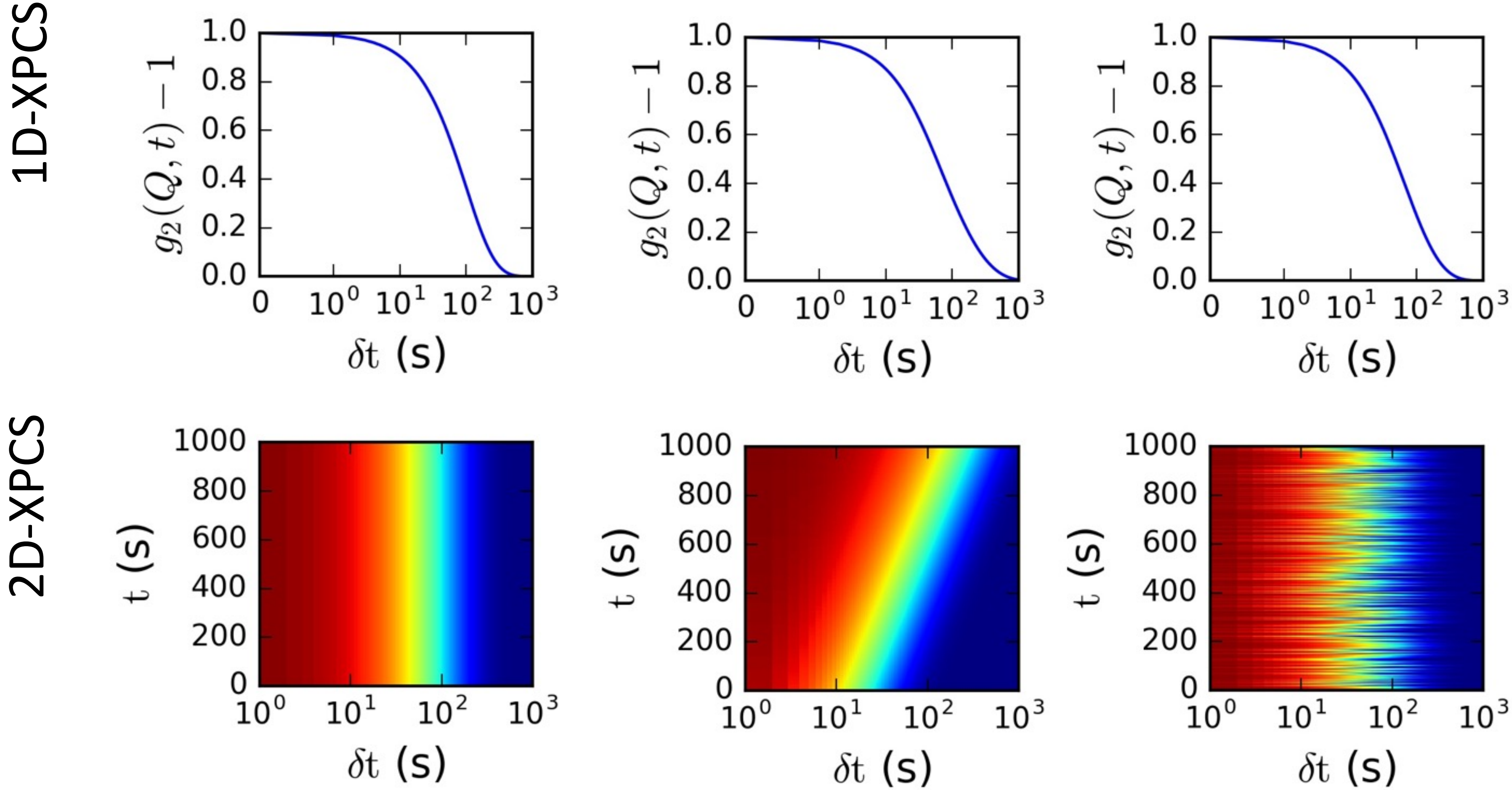
two-time correlation functions



$$g_2(Q,\delta t) = \frac{1}{N}\langle I(Q,t)\cdot I(Q,t+\delta t)\rangle$$



Diffusive dynamics during the high-to-low density transition in amorphous ice

Synchrotron Experiments

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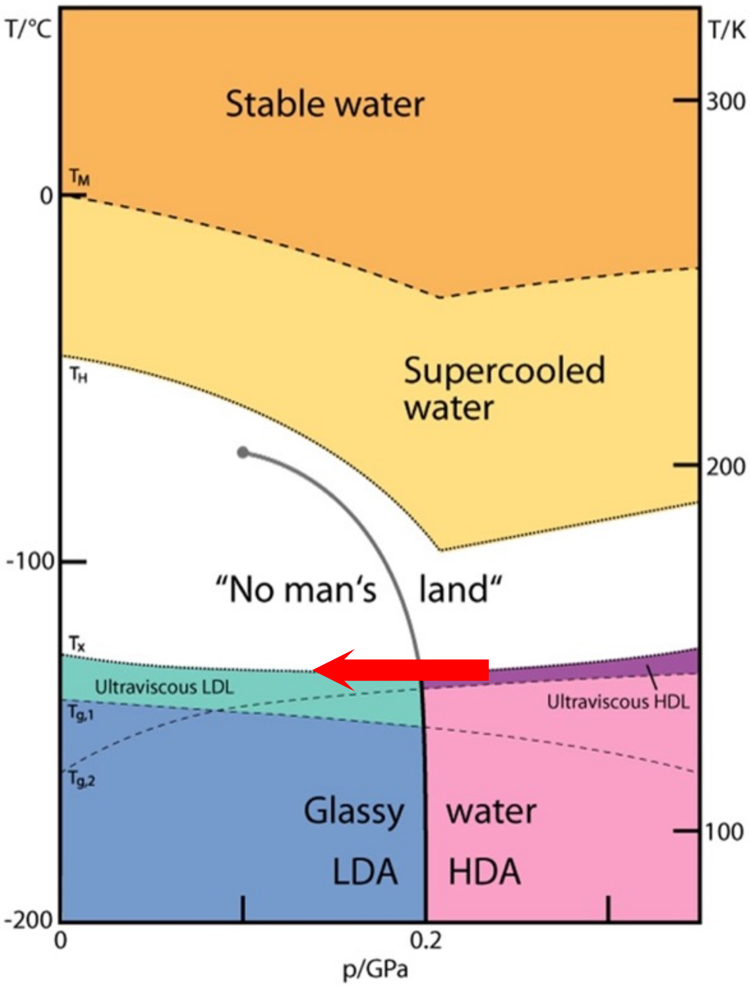
The two-liquid hypothesis



Katrin Amann-Winkel
Thomas Loerting

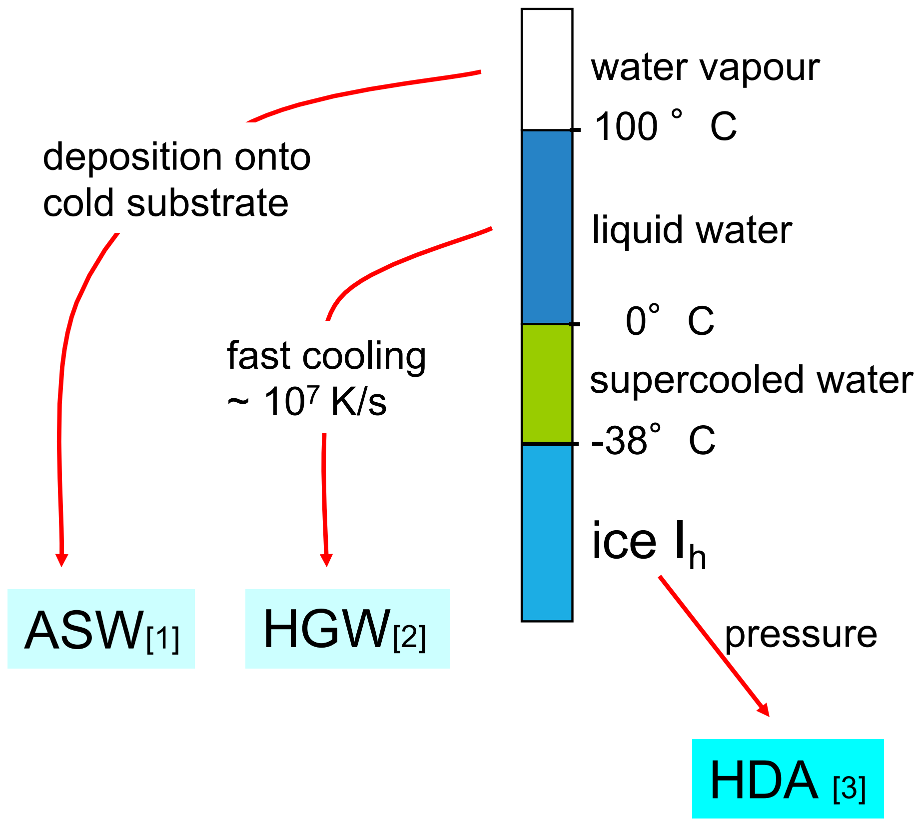
HDA

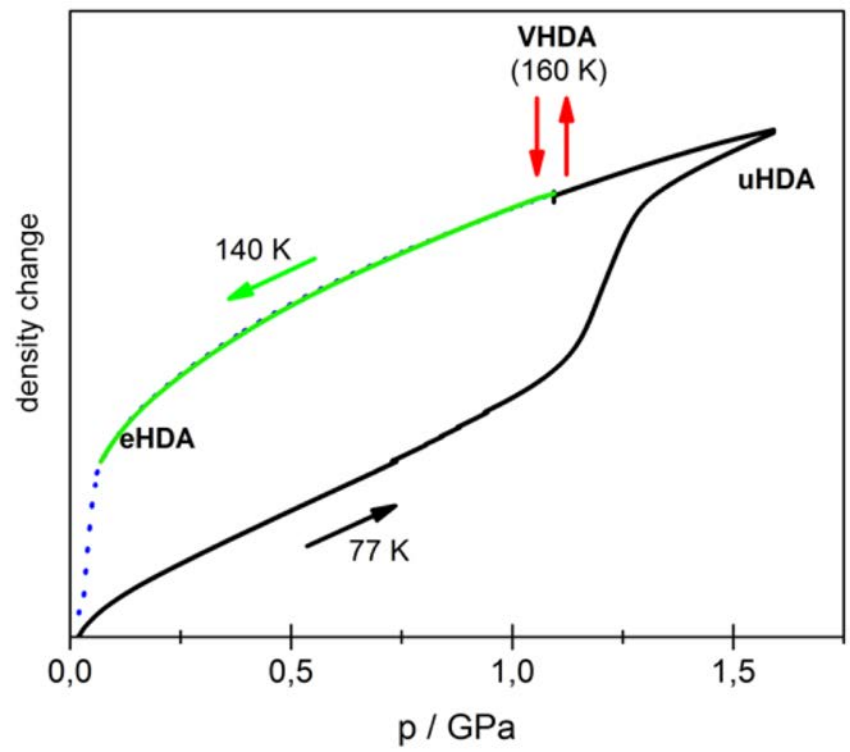
LDA

Poole et al.
Nature 360,1992

K. Amann-Winkel et al.
PNAS, 1311718110 (2013)

High and low density amorphous ice





[1] E.F. Burton and W.F. Oliver, *Proc. R. Soc. A*, 153, 1935
[2] P. Brüggeller, E. Mayer, *Nature,* 288, 1980
[3] O. Mishima, L.D. Calvert, E. Whalley, *Nature*, 310, 1984

K. Amann-Winkel et al.
PNAS, 1311718110 (2013)

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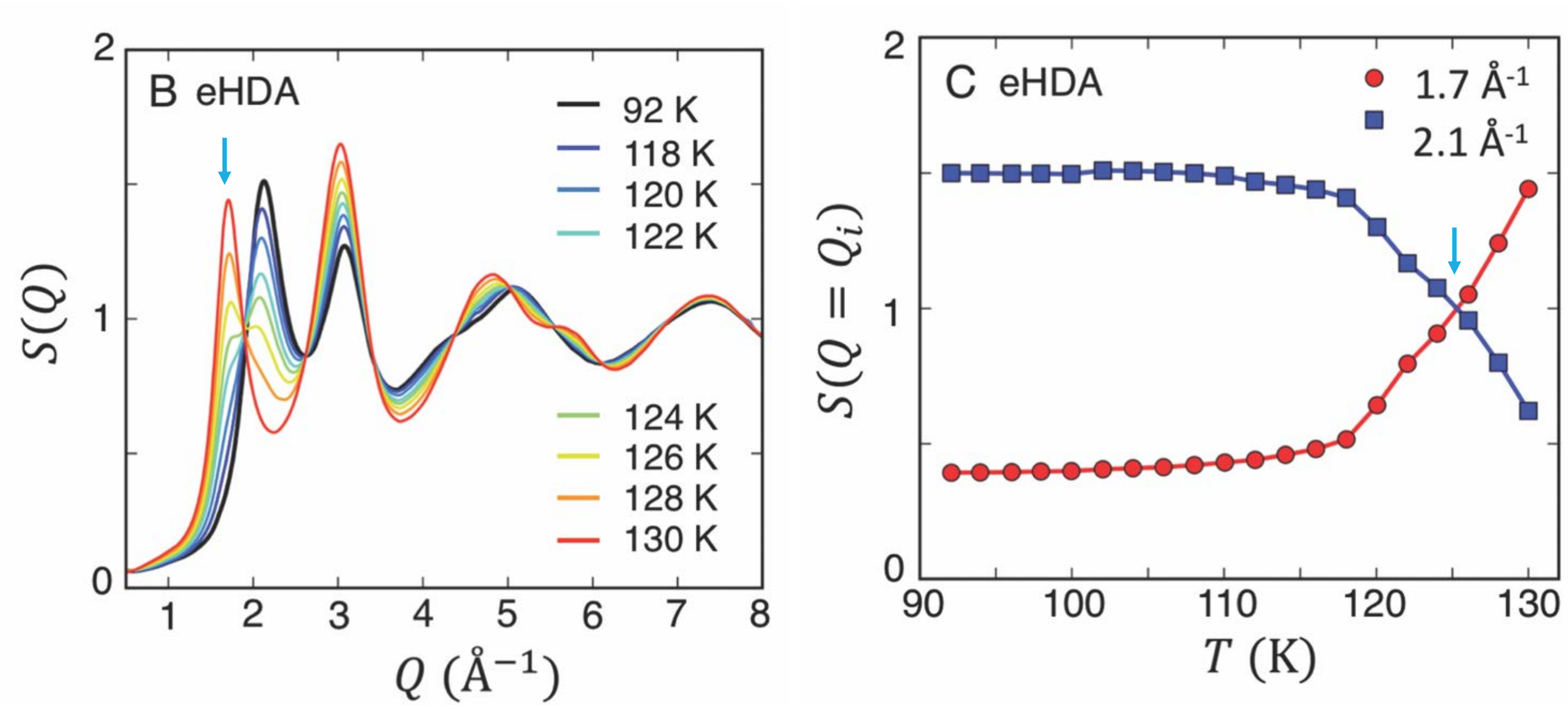
APS, Argonne

High energy diffraction, Beamline 6-ID-D

photon energy E = 100 keV

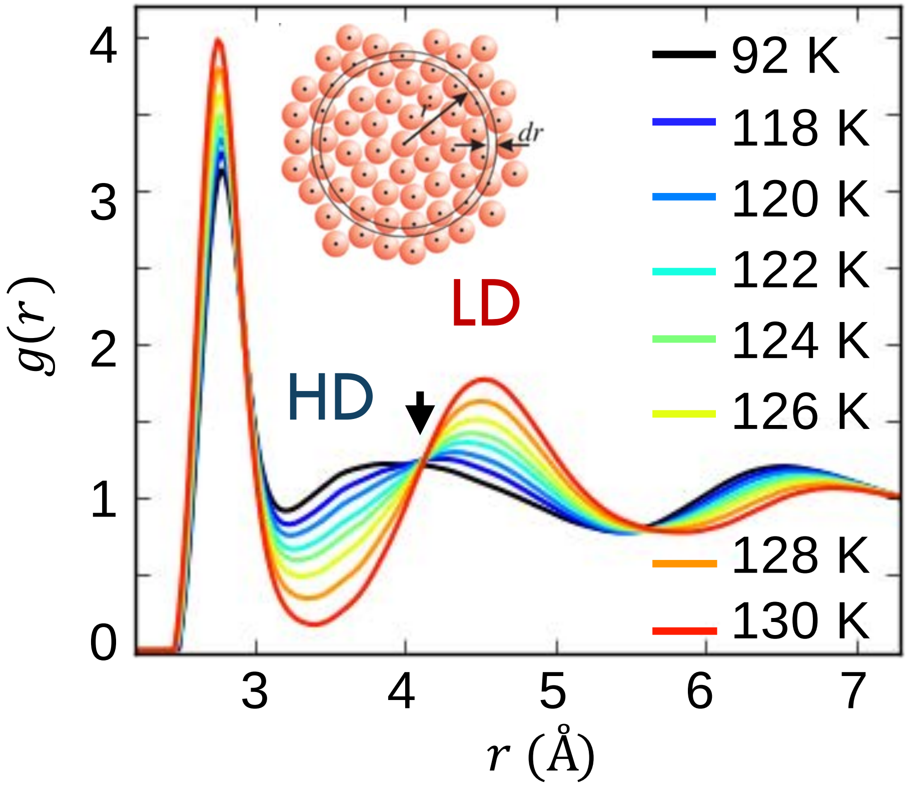
High energy diffraction experiments

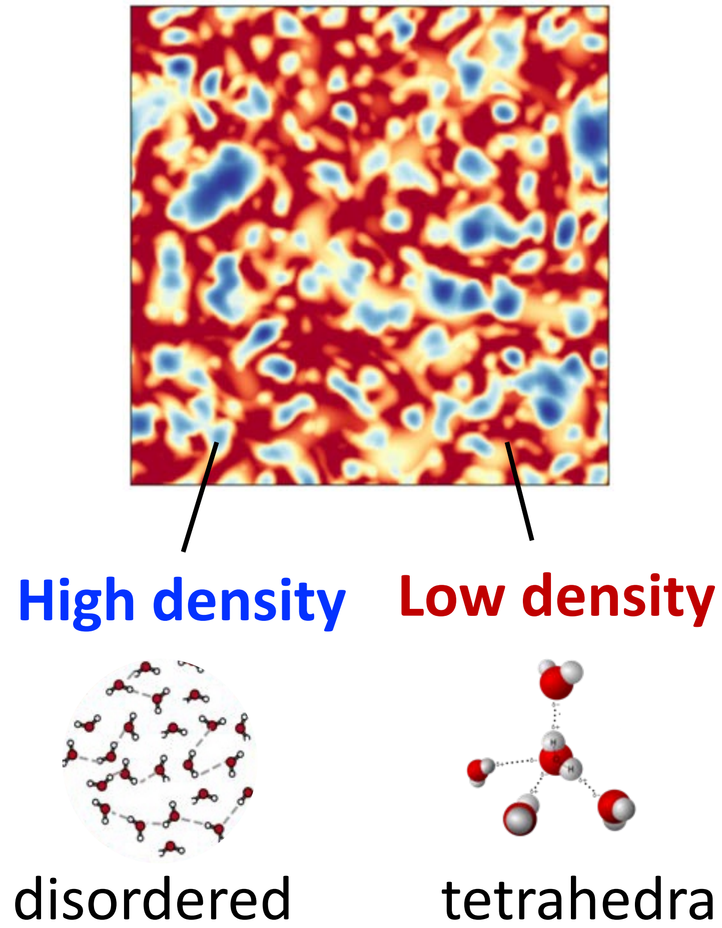
Static Structure factor | **High to low density transition**



F. Perakis, K. Amman-Winkel et al.
PNAS 114, 8193 (2017)

High energy diffraction experiments





F. Perakis, K. Amman-Winkel et al.
PNAS 114, 8193 (2017)

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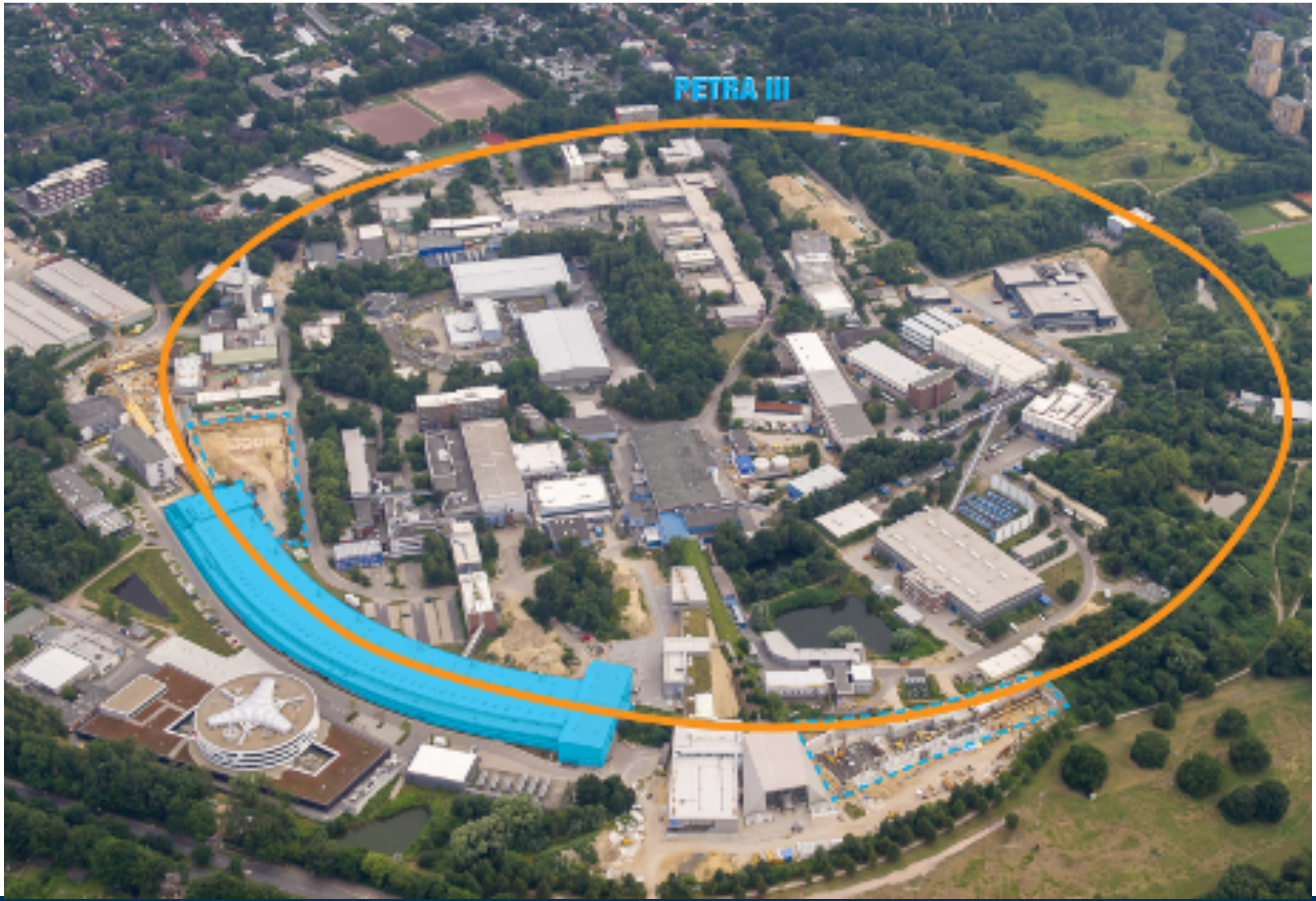
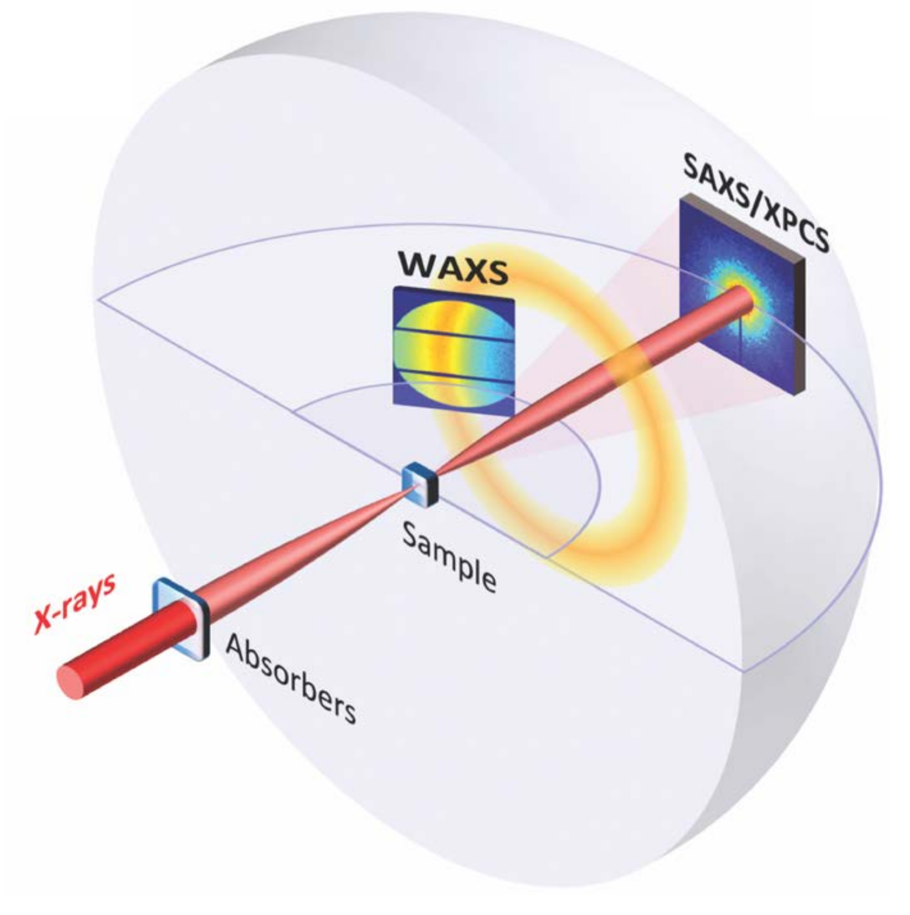
PETRA III, HAMBURG



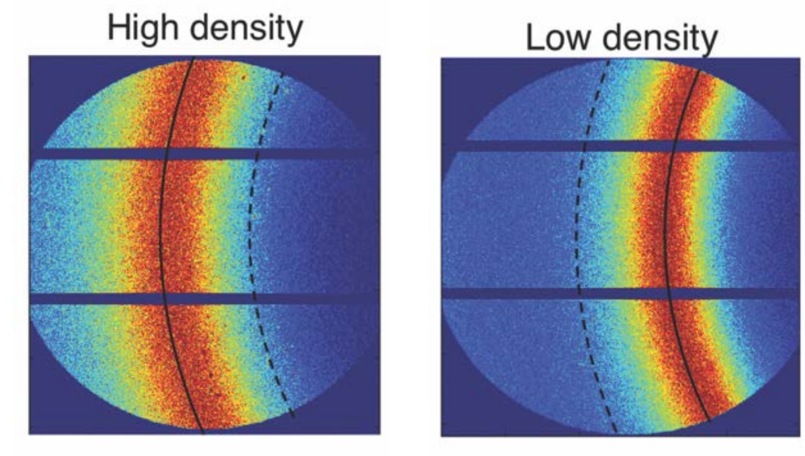
P10 Coherence Applications Beamline

The experimental setup

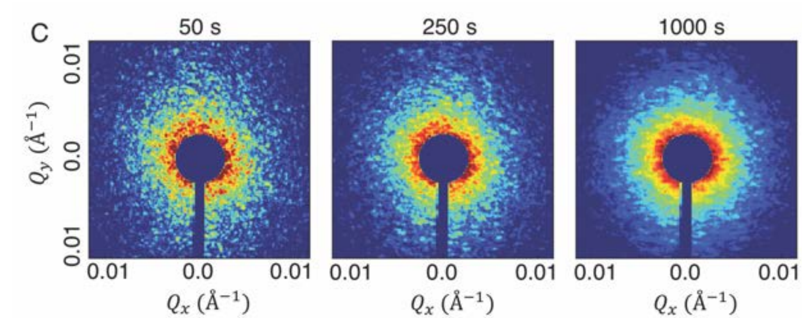


8.4 keV, Si(333), PILATUS 300k, Lamda, 3x3um focus

X-ray diffraction



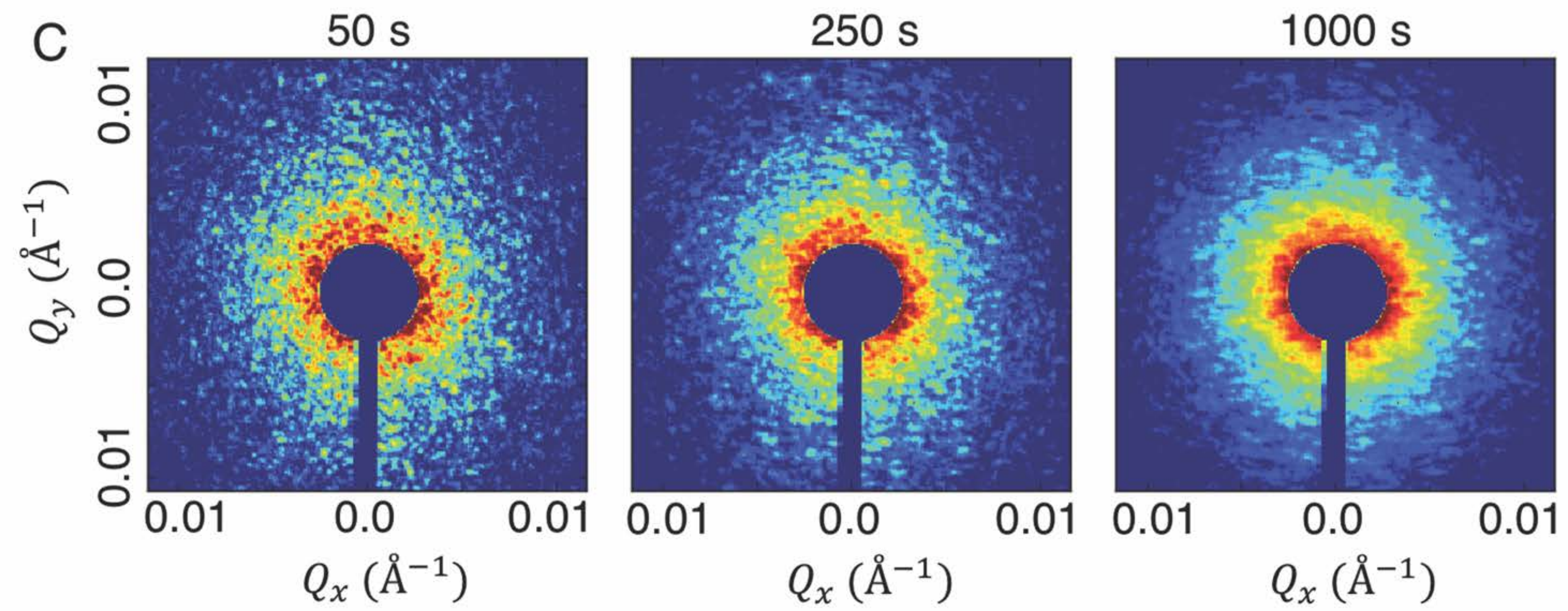
X-ray Photon Correlation Spectroscopy



F. Perakis, K. Amman-Winkel et al.
PNAS 114, 8193 (2017)

X-ray Photon Correlation Spectroscopy

Nanoscale dynamics of water near the glass transition



F. Perakis, K. Amman-Winkel et al.
PNAS 114, 8193 (2017)

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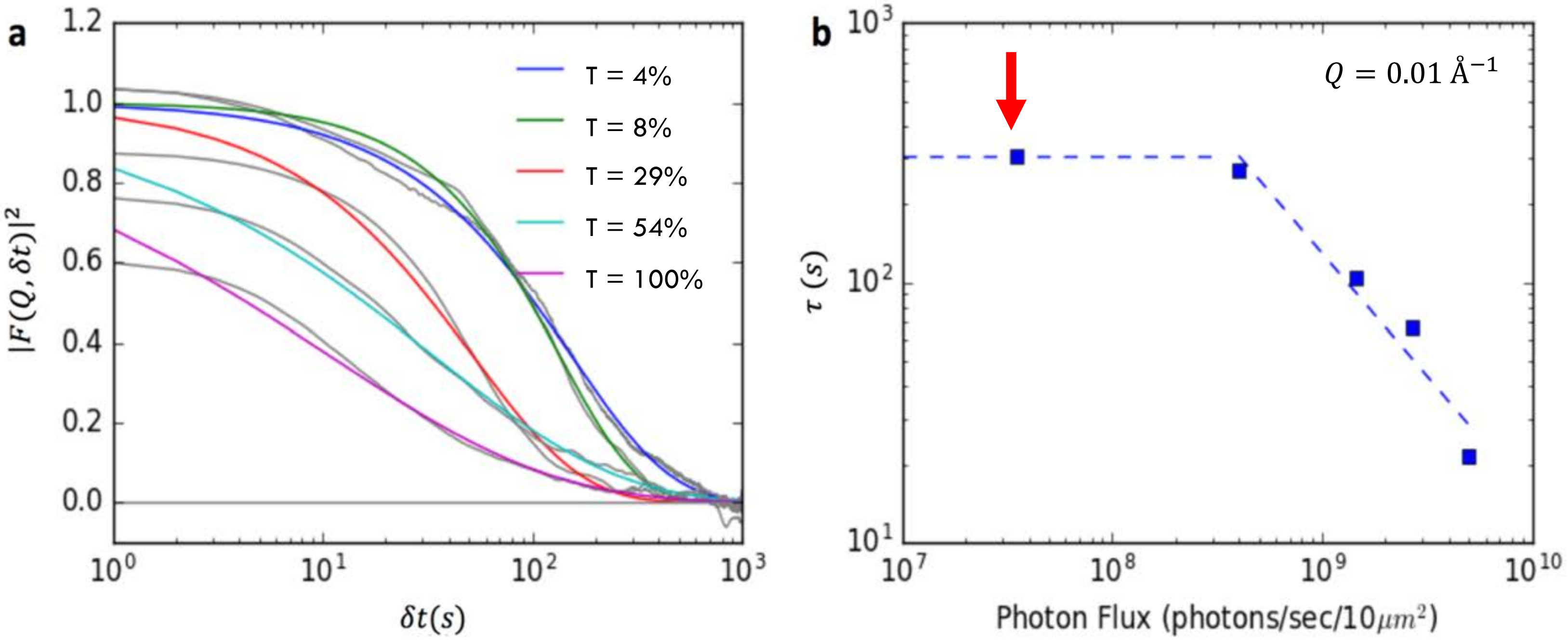
Flux dependence

- Always measure XRD before and after the XPCS measurement
- To minimise beam-induced heating we investigate the flux dependence



Performed measurements in the non-perturbative regime

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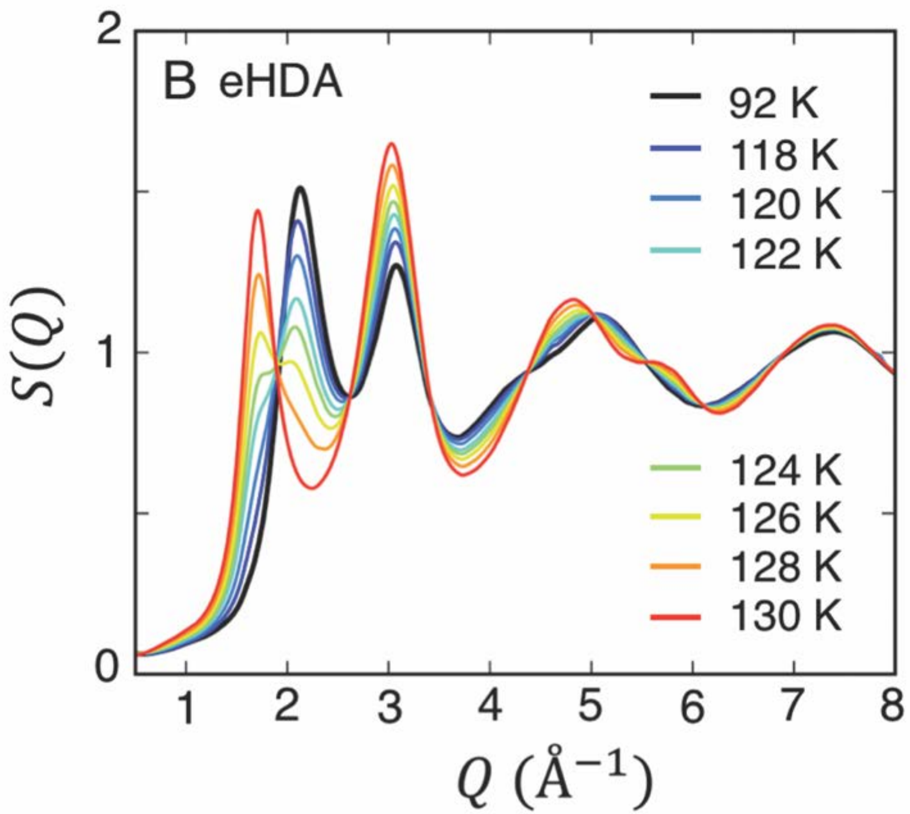
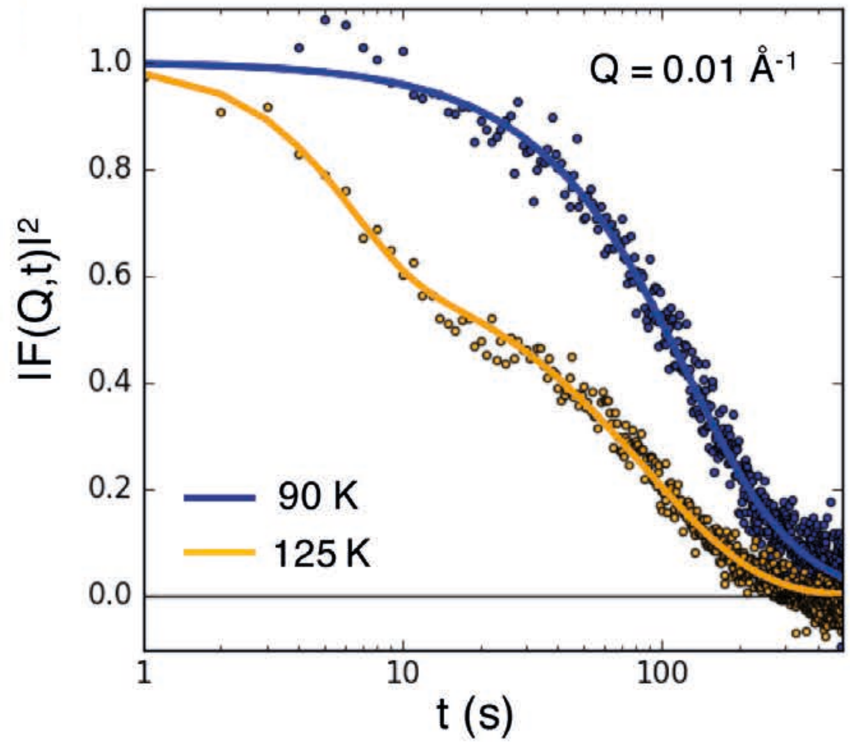
Probing Structure and Dynamics

Static Structure factor



Dynamic Structure factor

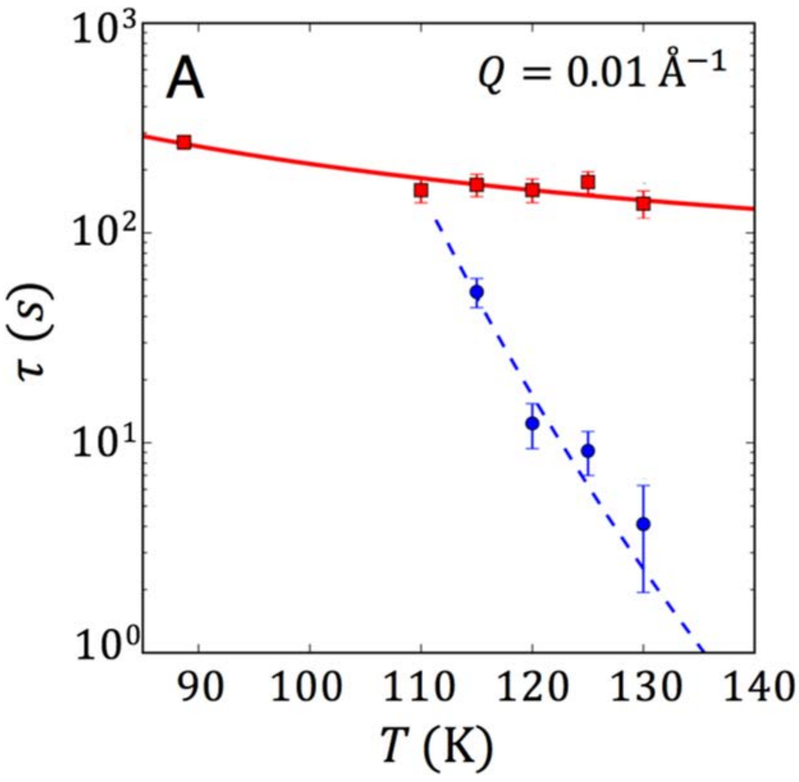


$$g_2(t) = \mathrm{A} \cdot e^{-t/(2\tau_1)} + (\beta - \mathrm{A}) \cdot e^{-t/(2\tau_2)} + c$$

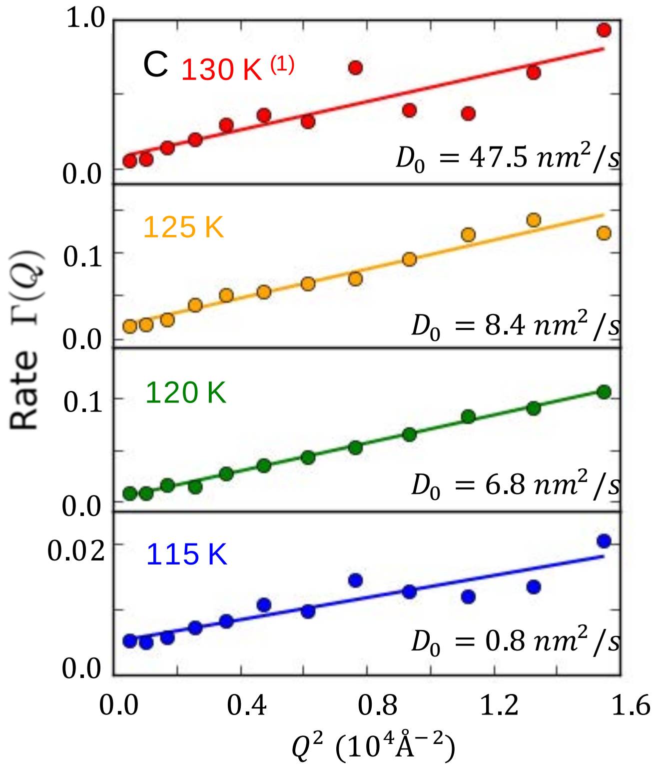
F. Perakis, K. Amman-Winkel et al.
PNAS 114, 8193 (2017)

Temperature and Q-dependence

Fast component appearing at 110 K



Diffusive motion ~100nm



$$\Gamma(Q) \propto D_0 \cdot Q^2$$

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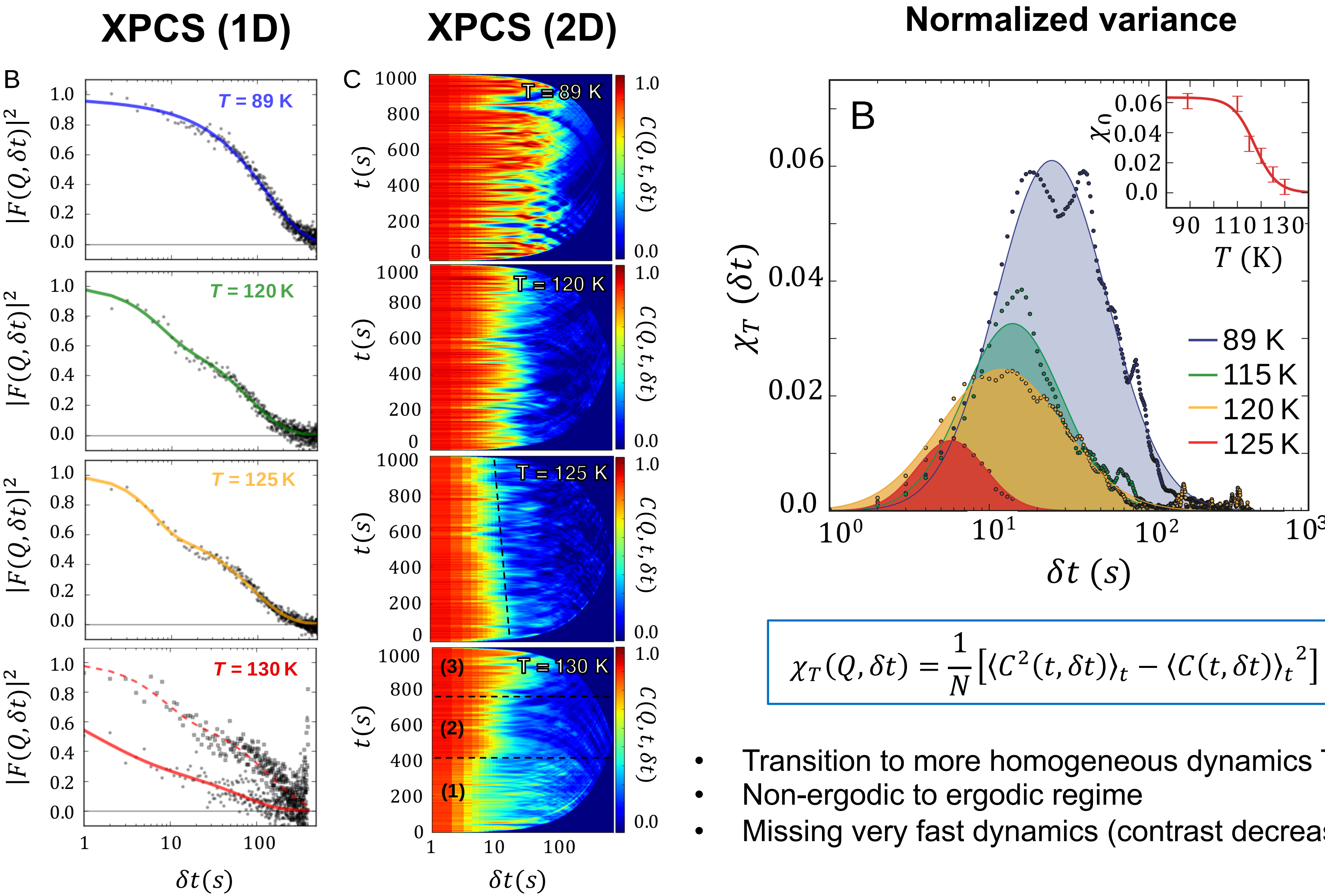
Dynamical heterogeneities



$$\chi_T(Q, \delta t) = \frac{1}{N}\left[\langle C^2(t, \delta t)\rangle_t - \langle C(t, \delta t)\rangle_t{}^2\right]$$

- Transition to more homogeneous dynamics T>115K
- Non-ergodic to ergodic regime
- Missing very fast dynamics (contrast decreases)

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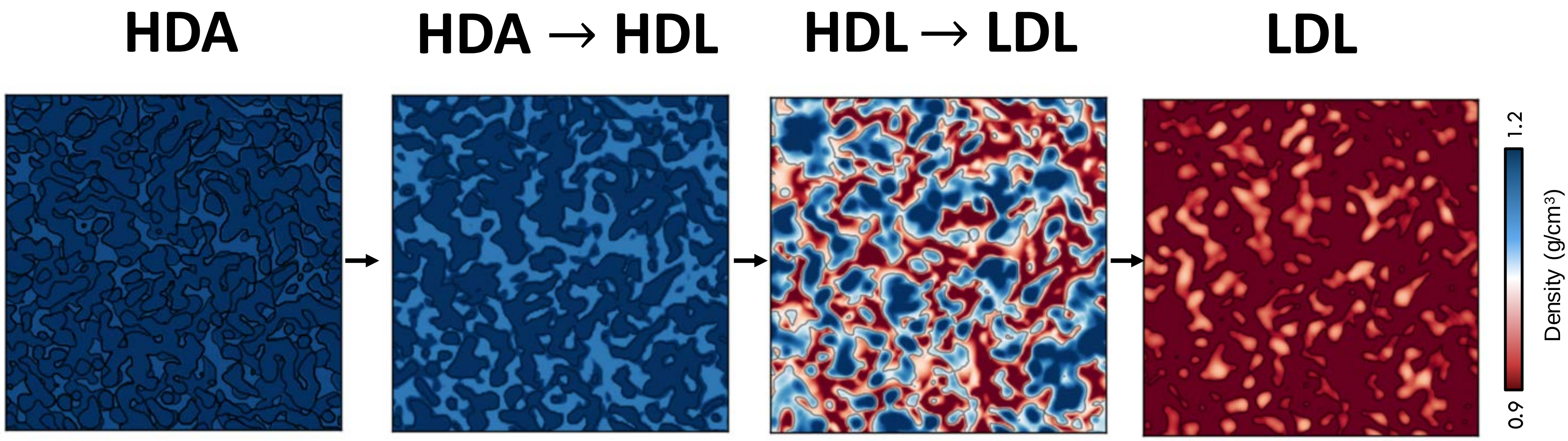
Take-home message I:

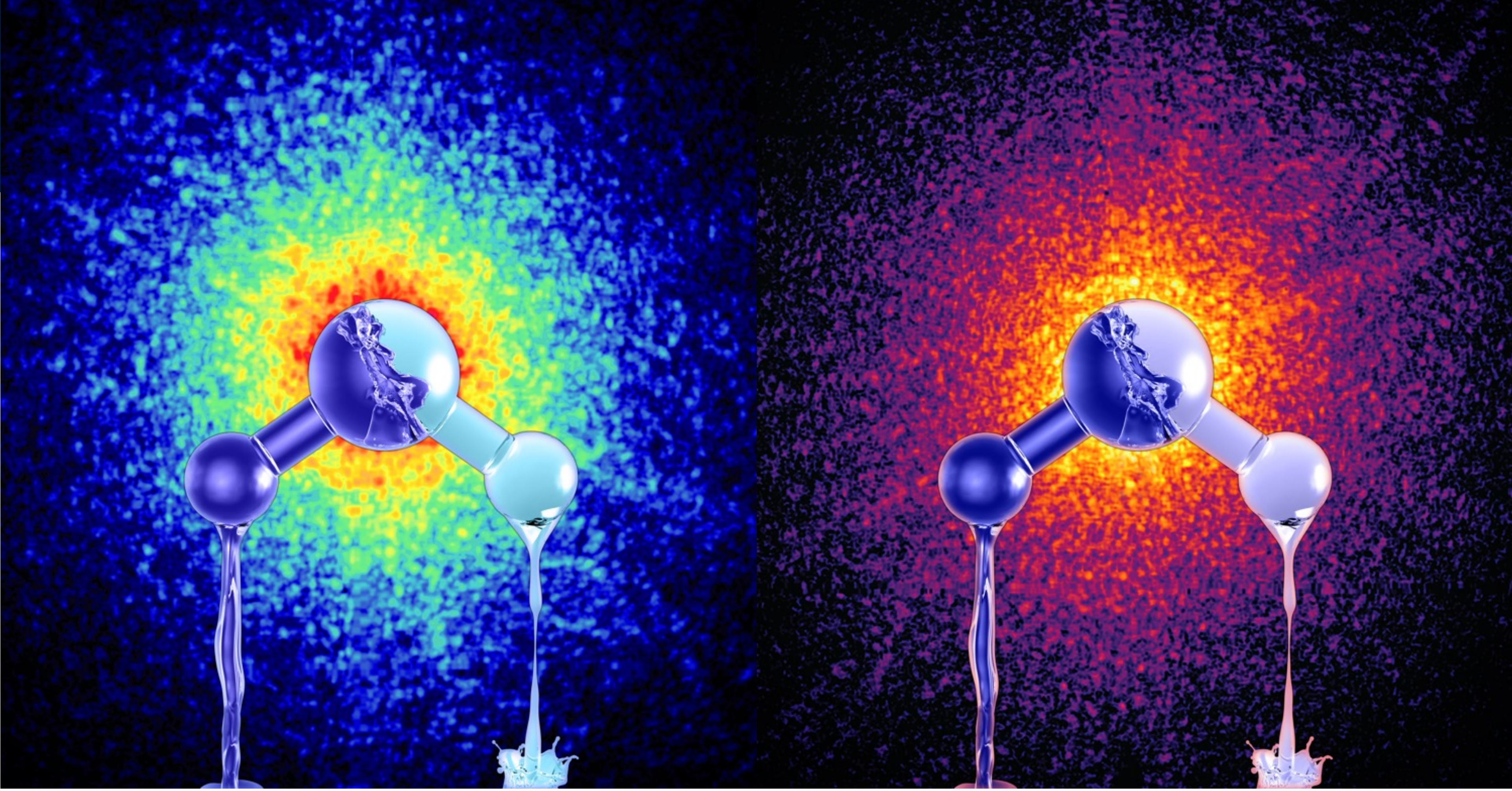


“Slow” and “fast” components: Glass transition

High and low density coexistence

low-density diffusive dynamics

F. Perakis, K. Amman-Winkel et al.
PNAS 114, 8193 (2017)



Coherent X-rays reveal the influence of cage effects on ultrafast water dynamics

FEL EXPERIMENTS, XCS@LCLS

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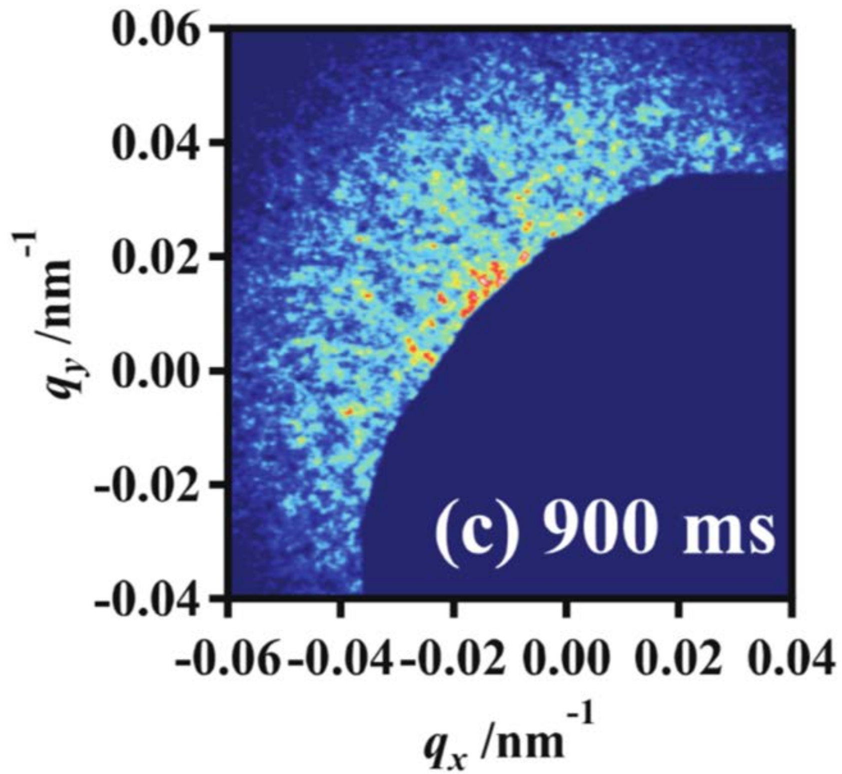
X-ray Speckle Visibility Spectroscopy

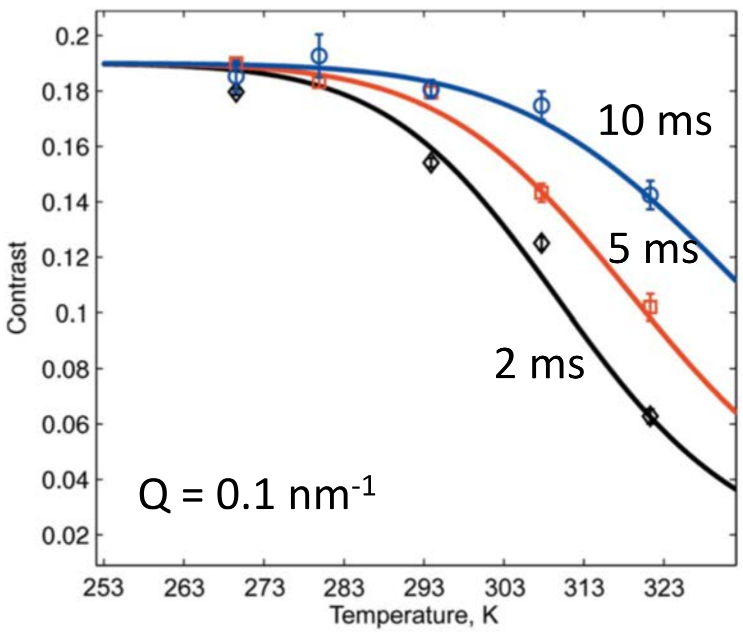
Exposure Time-dependence

polystyrene nanospheres in glycerol



Temperature-dependence

latex nanospheres in glycerol



latex in glycerol

I. Inoue et al
Optics Express 20, 26878 (2012)

C. DeCaro et al.
J. Synchrotron Rad. 20, 332–338 (2013)

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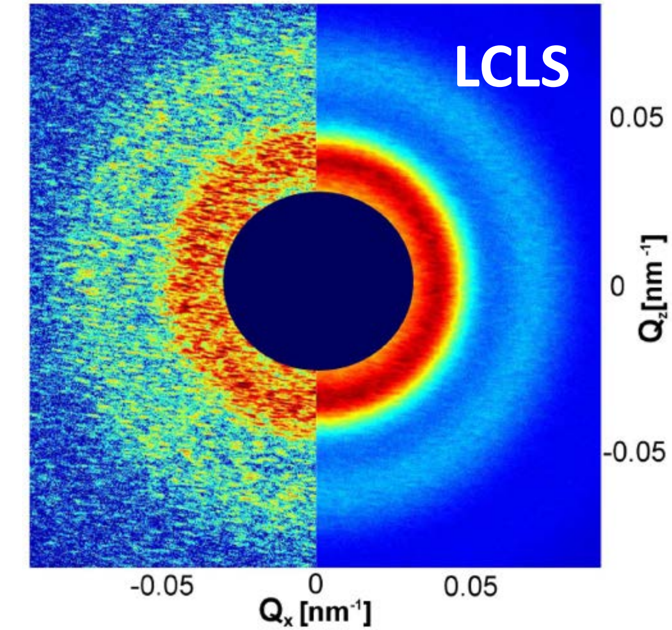
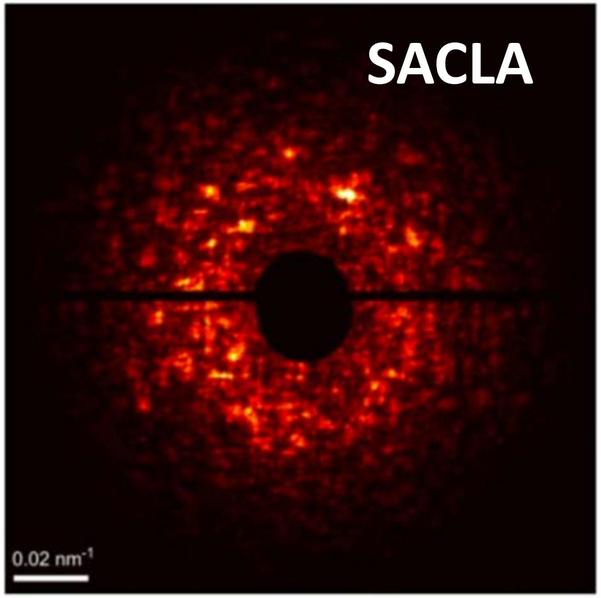
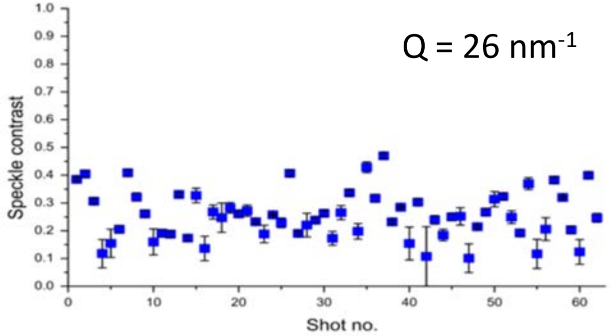
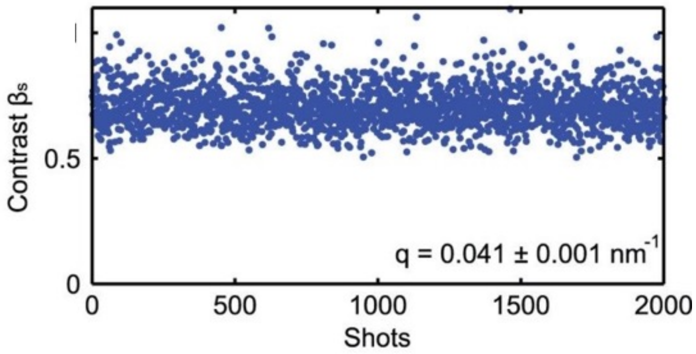
Speckle contrast at XFELs









C. Gutt et al. PRL 108, 024801 (2012)
S. Lee et al. Opt. Exp. 21, 24647 (2013)

F. Lehmkühler et al. Sci. Rep. 4, 5234 (2014)
Sci. Rep. 5, 17193 (2015)

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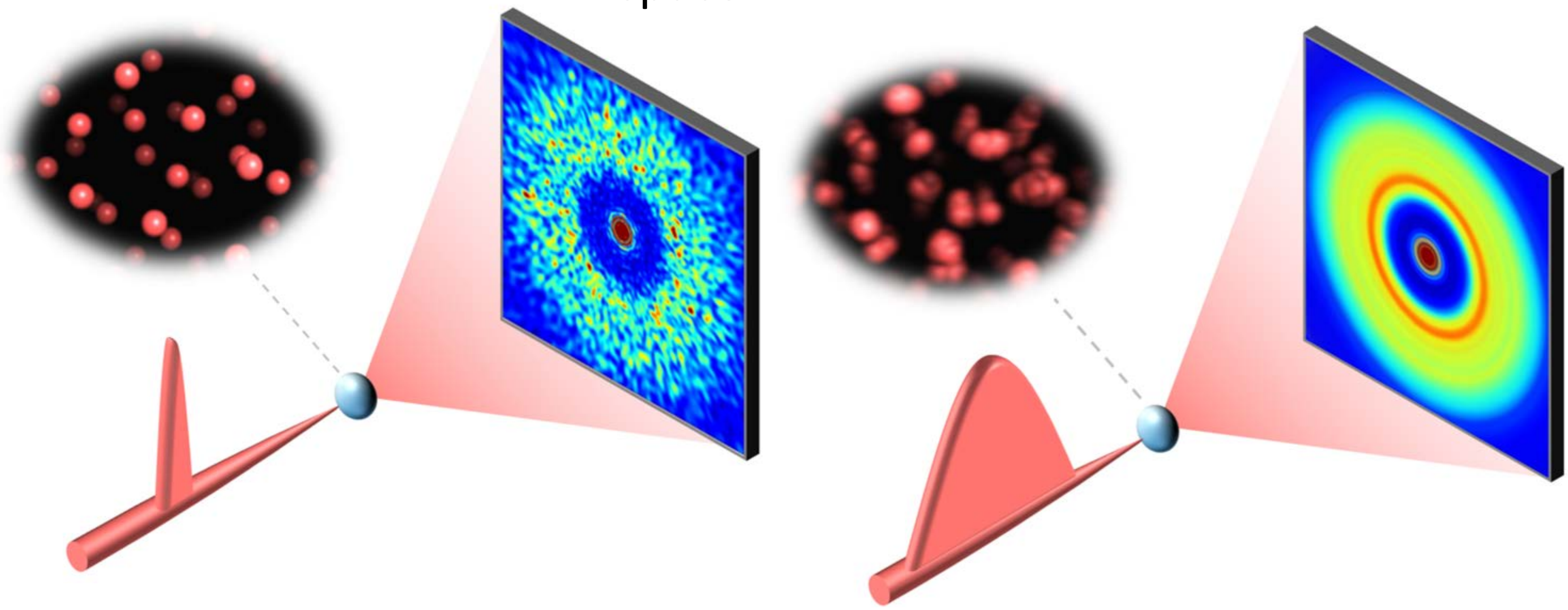
X-ray Speckle Visibility Spectroscopy

Real space

Reciprocal space

"Blurring"

loss of speckle contrast



The challenges

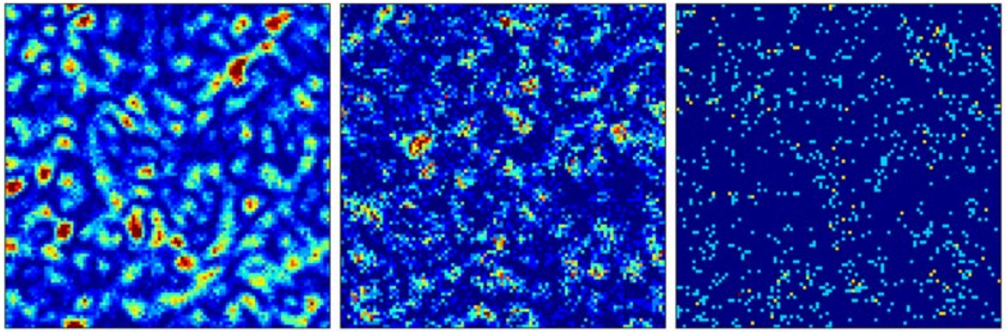
Water is a weak scatterer

in the hard X-ray range (8.2keV)

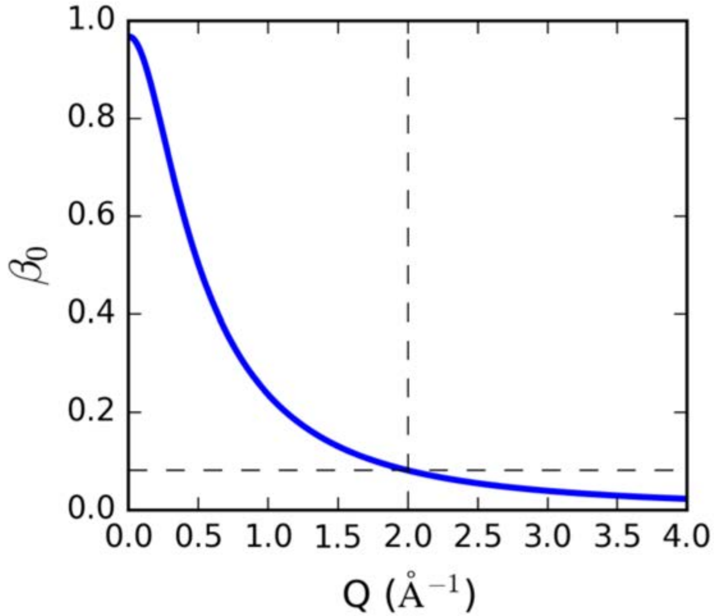
Contrast is low in WAXS

atomic lengthscales (Q = 1.9Å^{-1})

Mean Photon Density $\bar{k}$



10 ph/pix   1 ph/pix   0.1 ph/pix



X-ray Studies of Water, A. Nilsson and F. Perakis,
Synchrotron Light Sources and Free-Electron Lasers, Springer (2019)

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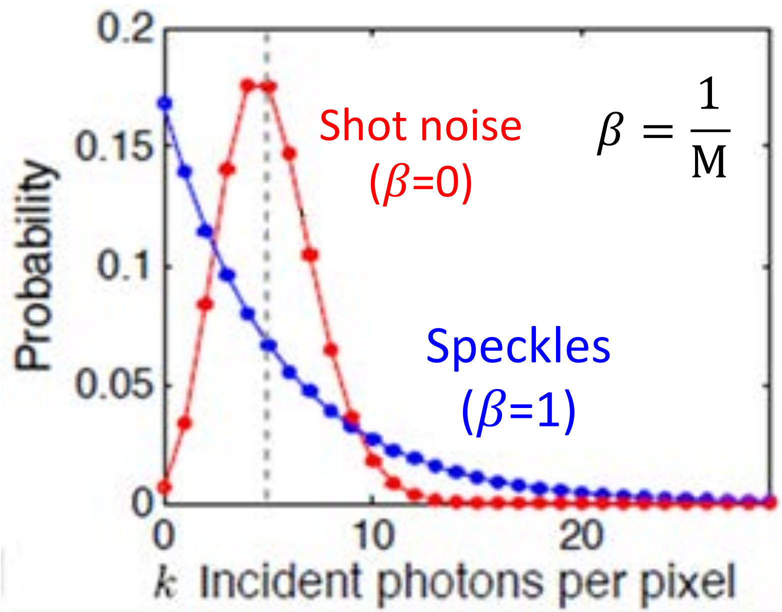
Negative binomial distribution

NB = Poisson $*$ Gamma

$$P(k,\bar{k},M) = \frac{\Gamma(k+M)}{\Gamma(M)\Gamma(k+1)}\left(1+\frac{M}{\bar{k}}\right)^{-k}\left(1+\frac{\bar{k}}{M}\right)^{-M}$$



$$P(1) \equiv P(k=1,\bar{k},M) = M\left(1+\frac{M}{\bar{k}}\right)^{-1}\left(1+\frac{\bar{k}}{M}\right)^{-M}$$

$$P(2) \equiv P(k=2,\bar{k},M) = \frac{M(M+1)}{2}\left(1+\frac{M}{\bar{k}}\right)^{-2}\left(1+\frac{\bar{k}}{M}\right)^{-M}$$

$$R_{12} \equiv \frac{P(2)}{\mathrm{P}(1)} = \cdots \Leftrightarrow$$

$$\beta \equiv \frac{1}{M} = \frac{2\cdot R_{12}-\bar{k}}{\bar{k}(1-2\cdot R_{12})}$$

Hruszkewycz et al,
RPL 1109, 85502 (2012)

Verwohlt et al
PRL 120, 168001 (2018)

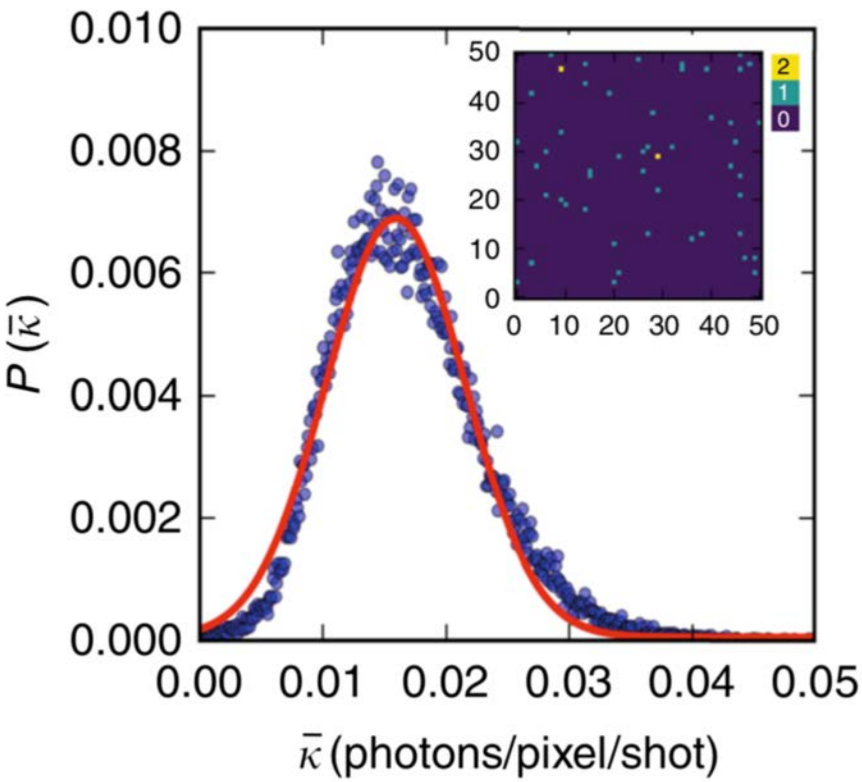
Photon counts and contrast

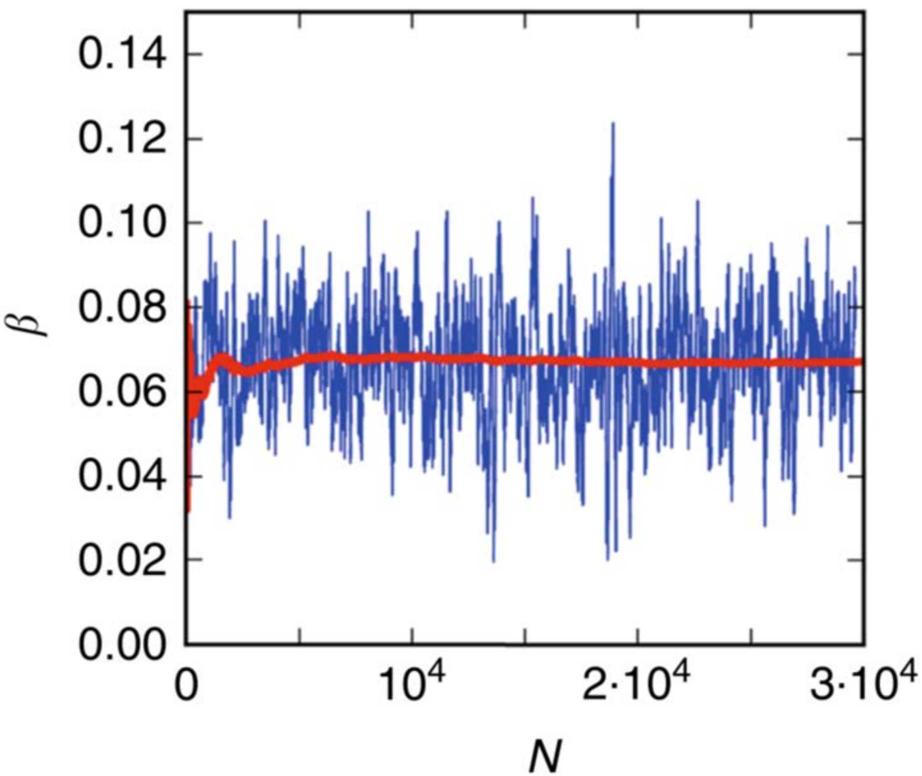
TJ Lane

Felix Lehmkühler

$1.5 \cdot 10^{-2}$ photons/pixel

Contrast 0.069





F. Perakis et al

Nature Comm. 9, 1917 (2018)

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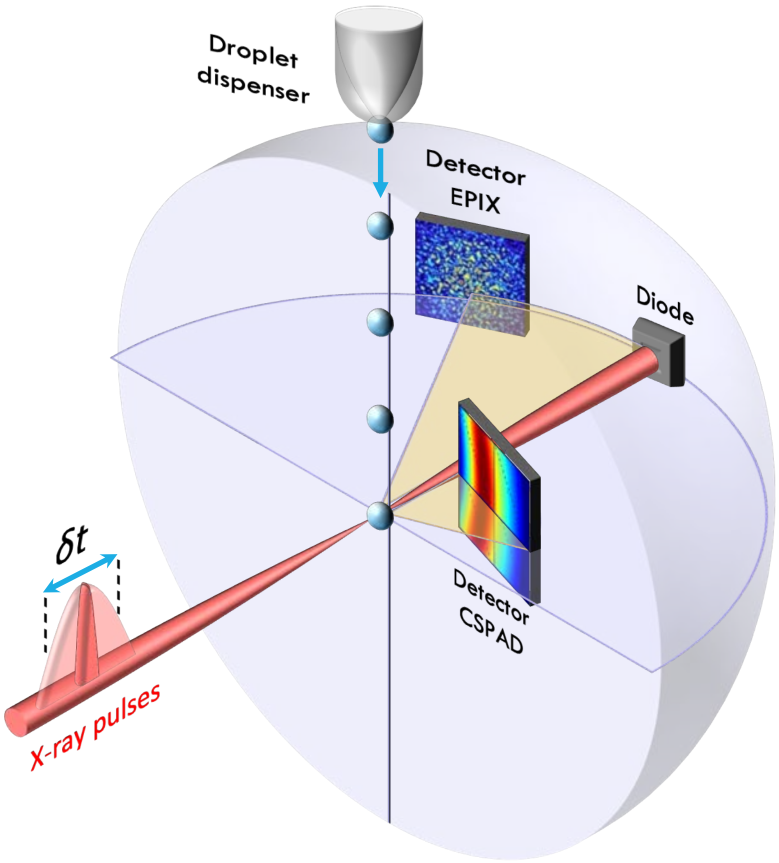
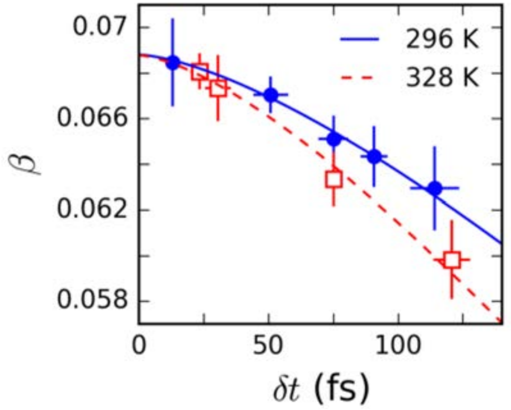
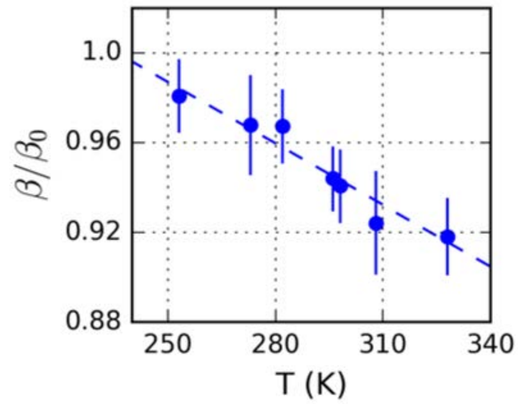
The experiment in a nutshell



Varying pulse duration



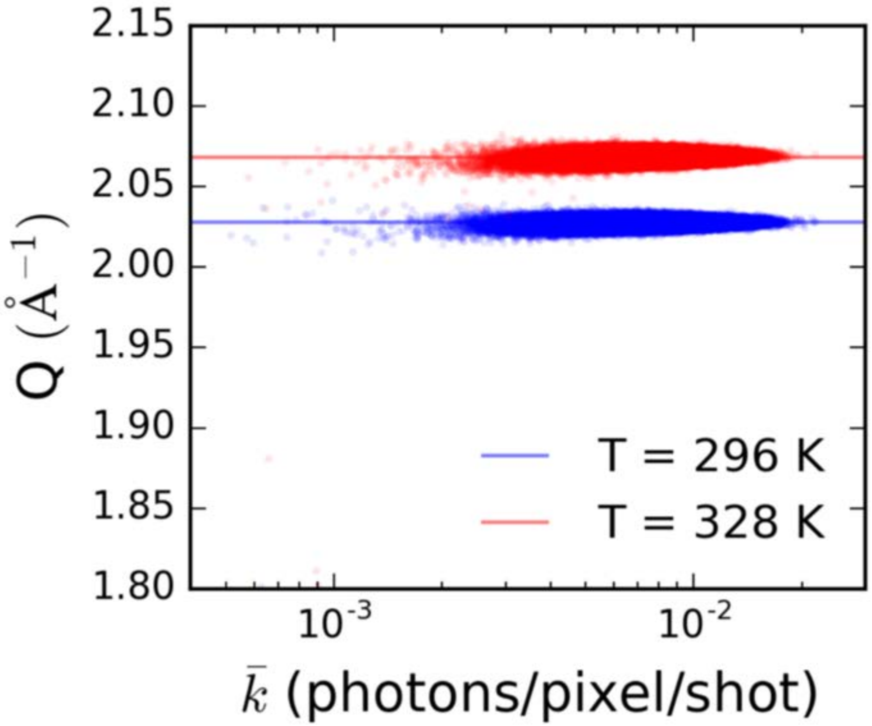
Varying temperature



Flux dependence

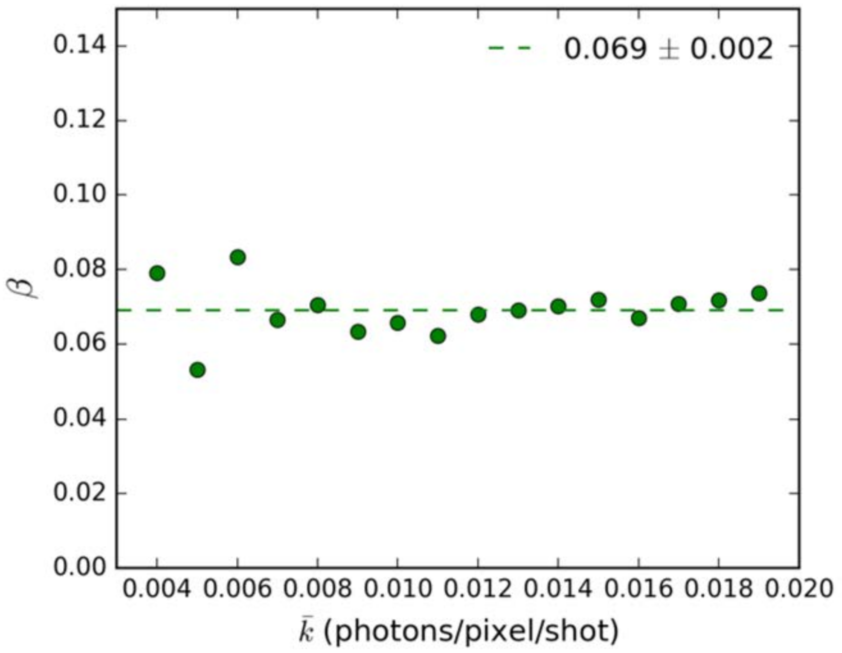
Structure factor

position of the 1st diffraction peak



Speckle contrast

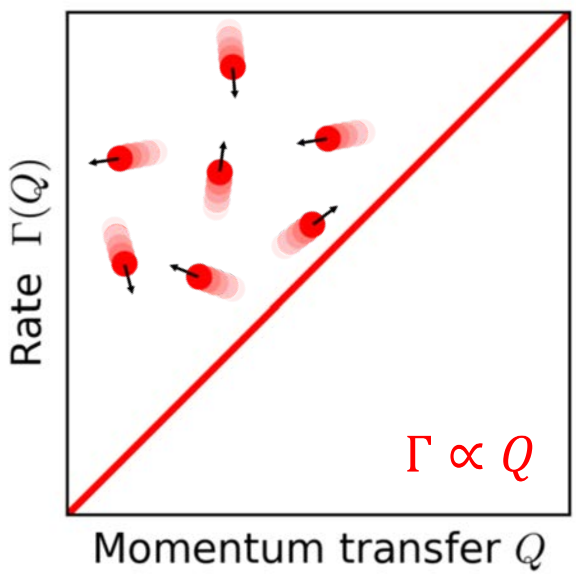
as a function of photon density



Molecular Simulations

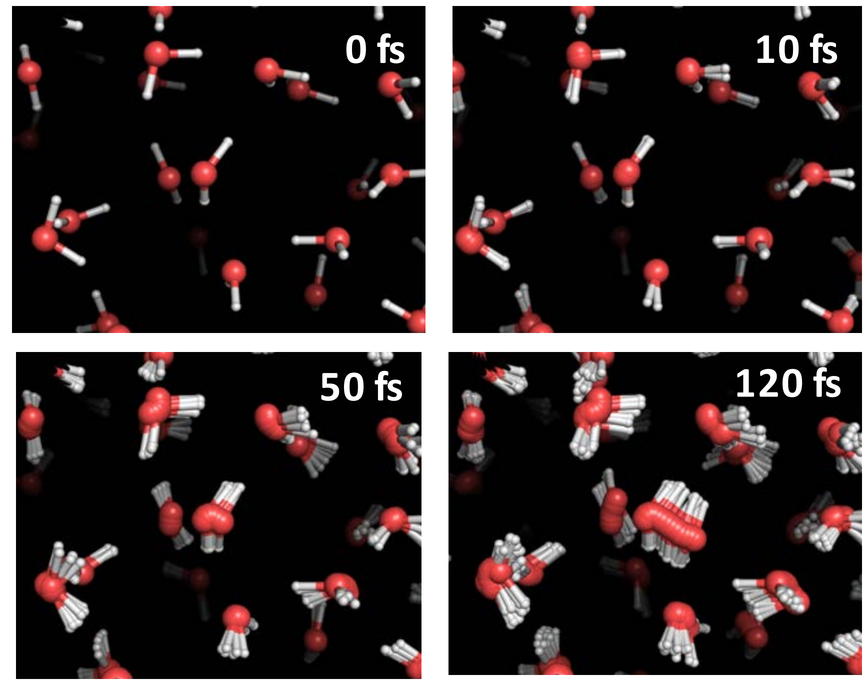
Gaia Camisasca

Pure Ballistic motion



- Thermal fluctuations
- Maxwell-Botzmann distribution

Molecular dynamics (MD)



TIP4P/2005 : rigid planar model, 4-site
MB/pol : flexible, polarizable, many-body

TIP4P/2005: J. L. F. Abascal and C. Vega
J. Chem. Phys. **123**, 234505 (2005)

MB/pol: Reddy et al … F. Paesani
J. Chem. Phys. **145**, 194504 (2016)

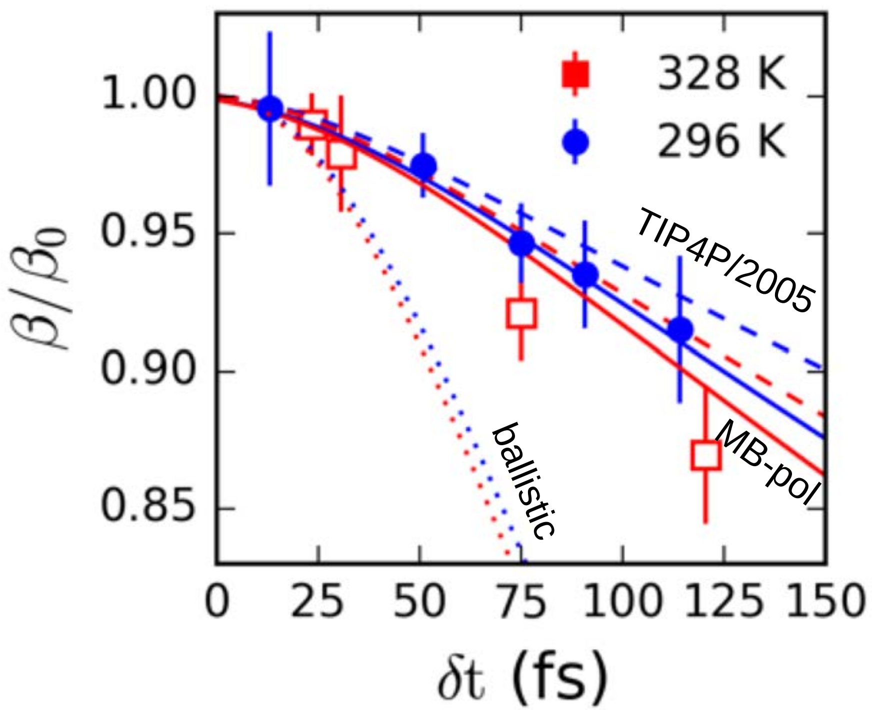
Comparison with experiment

XSVS:
Siegert relation

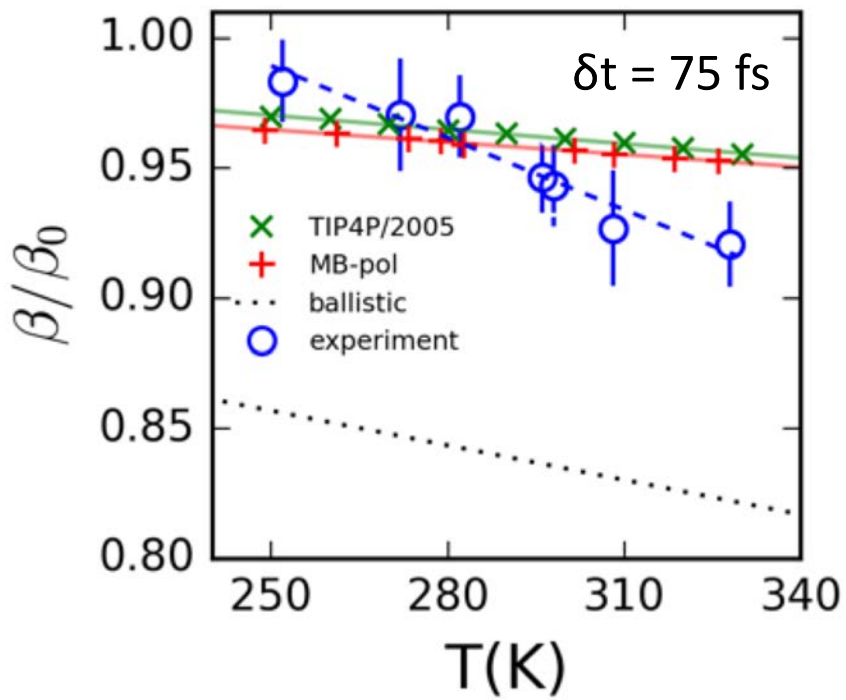
$$\beta(Q,\delta t) = 2 \cdot \beta_0 \int_0^{\delta t} \left(1 - \frac{t}{\delta t}\right) |F(Q,t)|^2 \frac{dt}{\delta t}$$

Dixon & Durian
PRL 90, 184302 (2003)

Pulse duration dependence

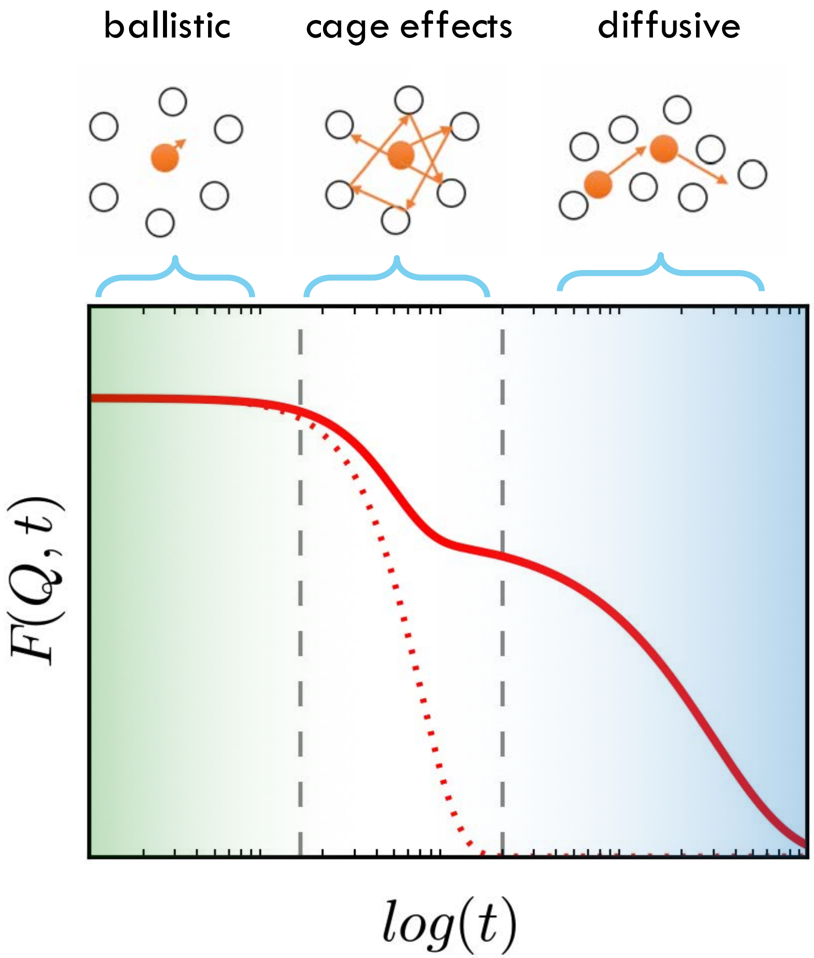


Temperature dependence



F. Perakis et al Nature Comm. 9, 1917 (2018)

Take-home message II:



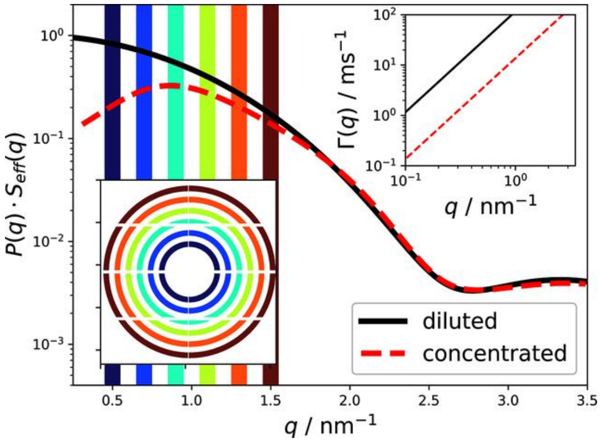
- Probing the transition from **pure ballistic** motion to **diffusion**
- **cage effects**: increased occupation time within the first solvation shell due to O-O oscillations **after 25 fs.**

Outlook: towards the future

DLSR: classes of experiments

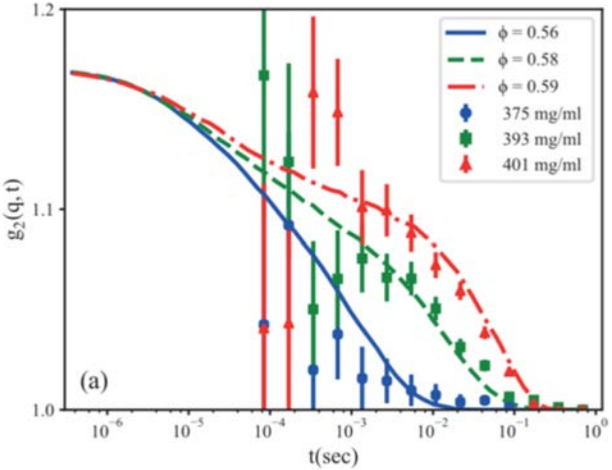
Sensitive

- **radiation sensitive samples**
- Large focus/ high energy
- Large sample-det. distance



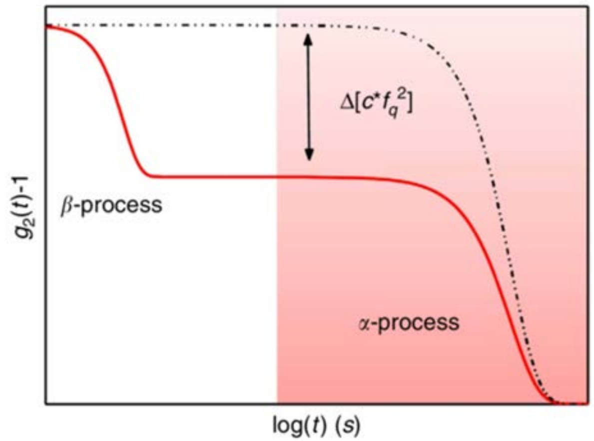
Fast

- **Sub-millisecond dynamics**
- Fast detectors/shutters



Atomic

- **atomic lengthscales**
- Highly monochromatic beams



J. Möller et al
J Synchr. Rad. 6, 794-803 (2019)

Vodnala et al
Phys. Rev. E 97, 020601 (2018)

Giordano and Ruta
Nat. Commun. 7, 10344 (2016)

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