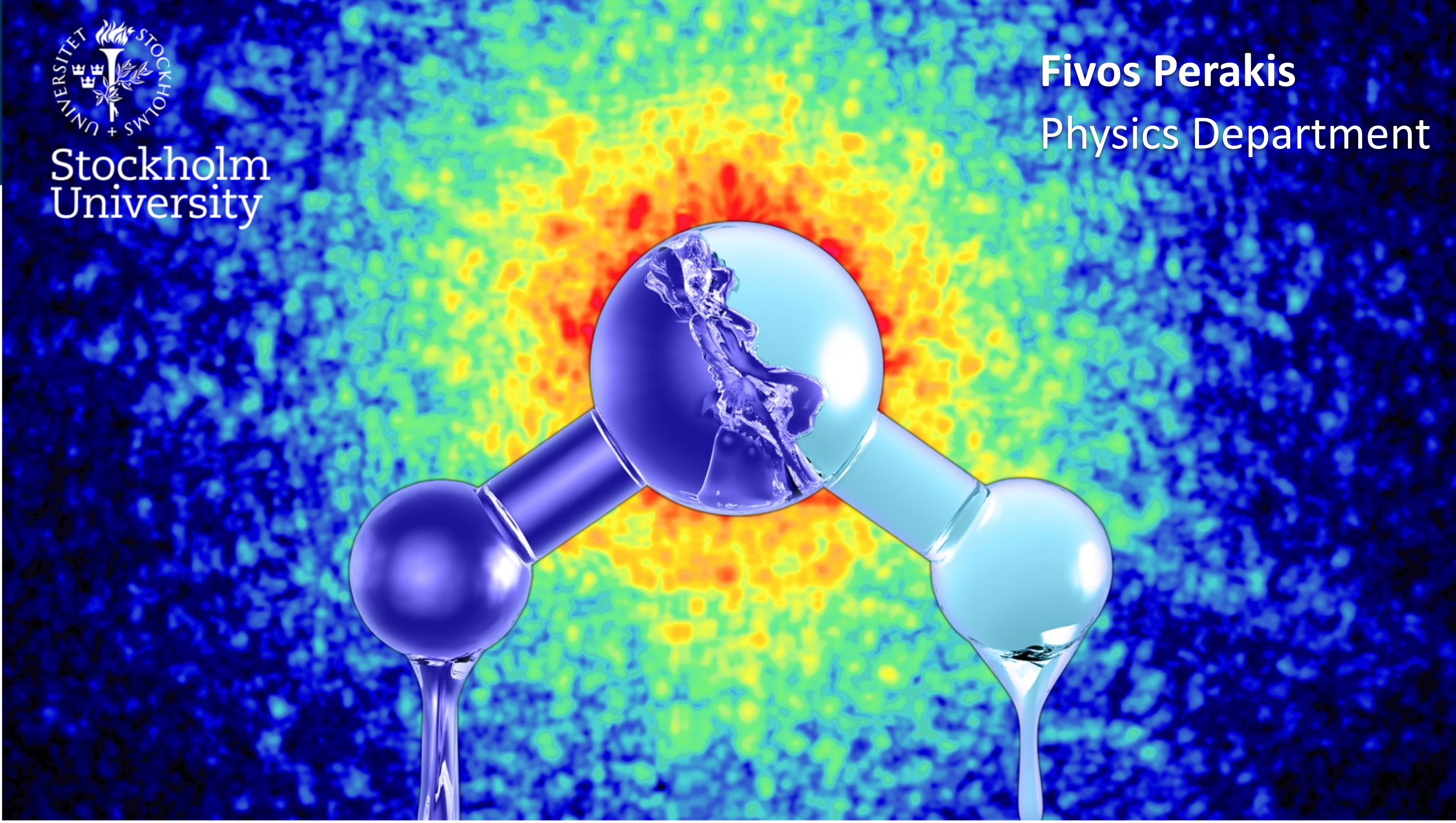


Stockholm University

Fivos Perakis
Physics Department

Dynamics in Complex Systems:

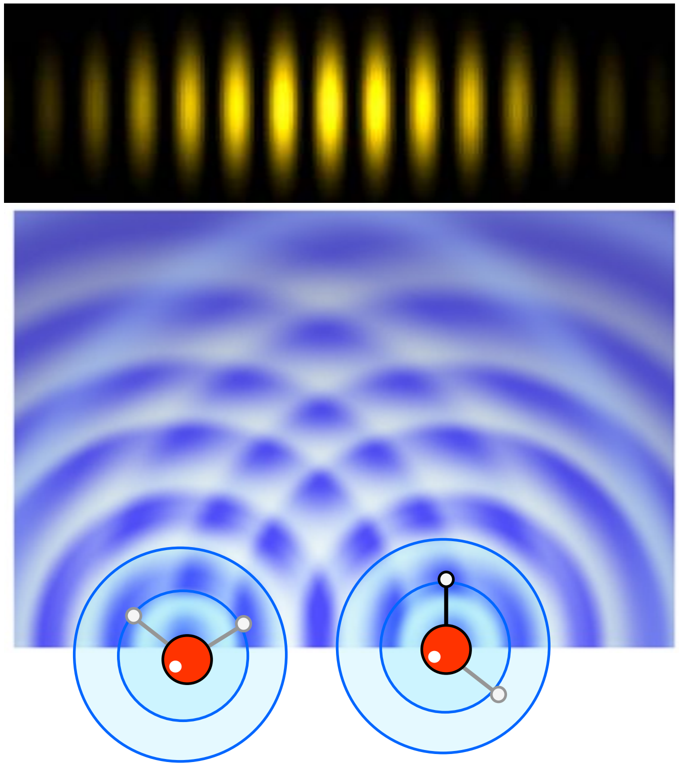
From supercooled and glassy water to protein dynamics

Science Opportunities with Table-Top Coherent X-Ray Sources
Uppsala, 29-30 October 2019

Fivos Perakis

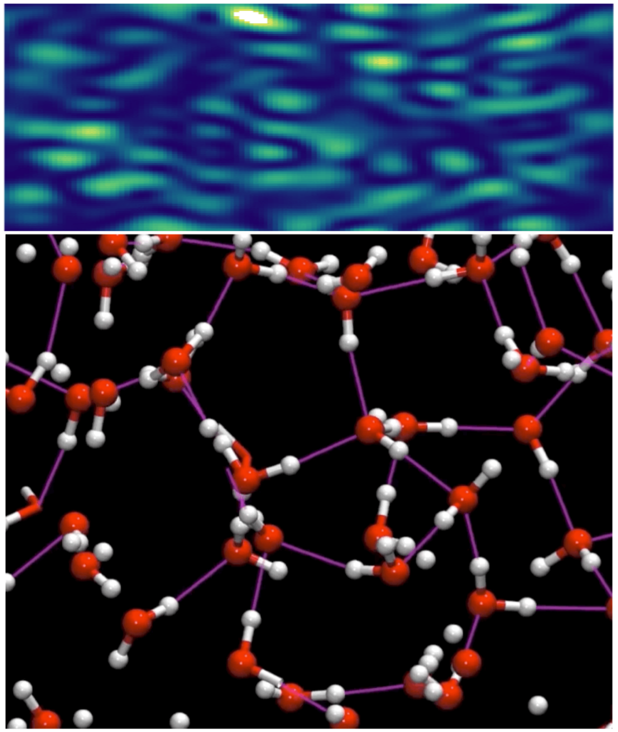
The speckle pattern

Interferogram



2 scattering points

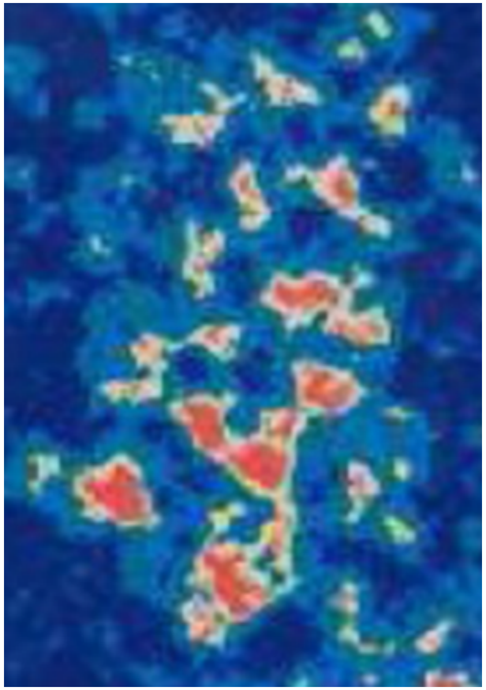
Speckle pattern



Many scattering points

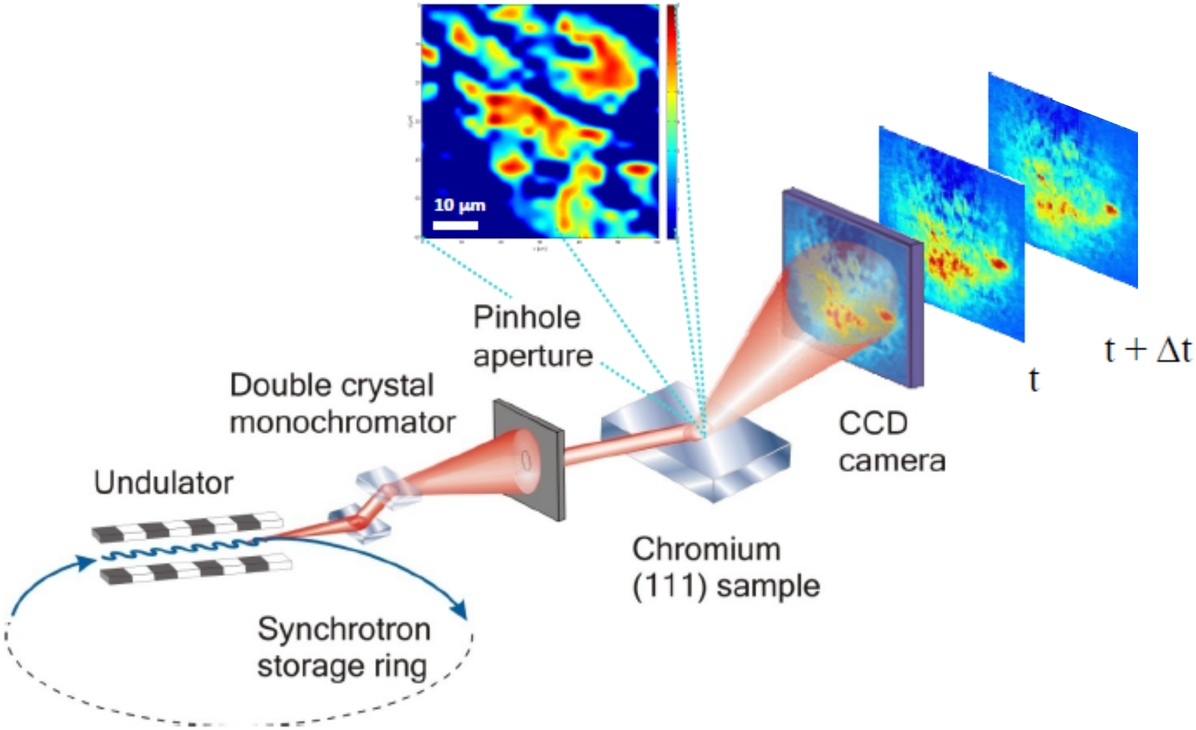
Speckles and Dynamics

Speckle Pattern



Beyond averages:
reflects exact arrangements

X-ray Photon Correlation Spectroscopy



Dynamics by changes of the speckle pattern

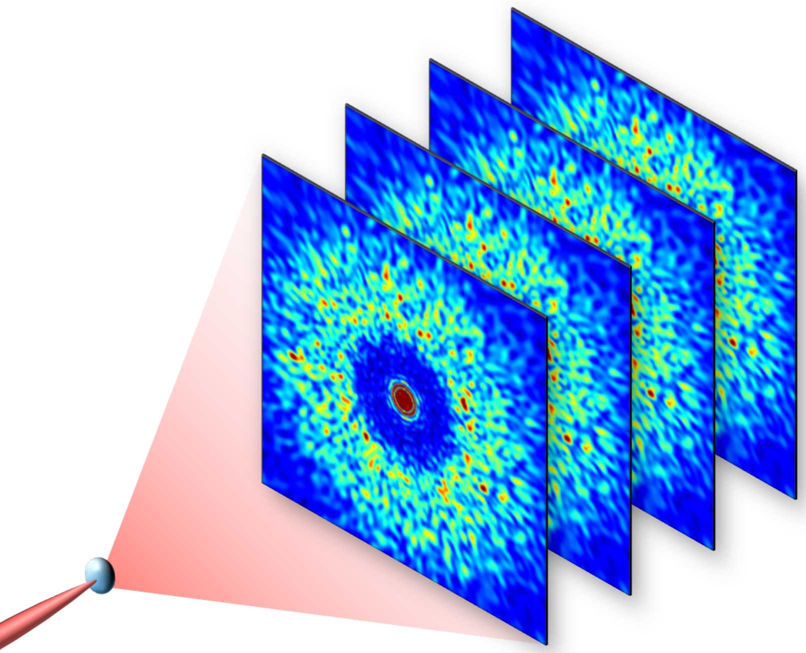
M. Sutton et al.,
Nature 352, 608-610 (1991)

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

X-ray Photon Correlation Spectroscopy

Intensity Autocorrelation Function

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



Changes of the Speckle pattern

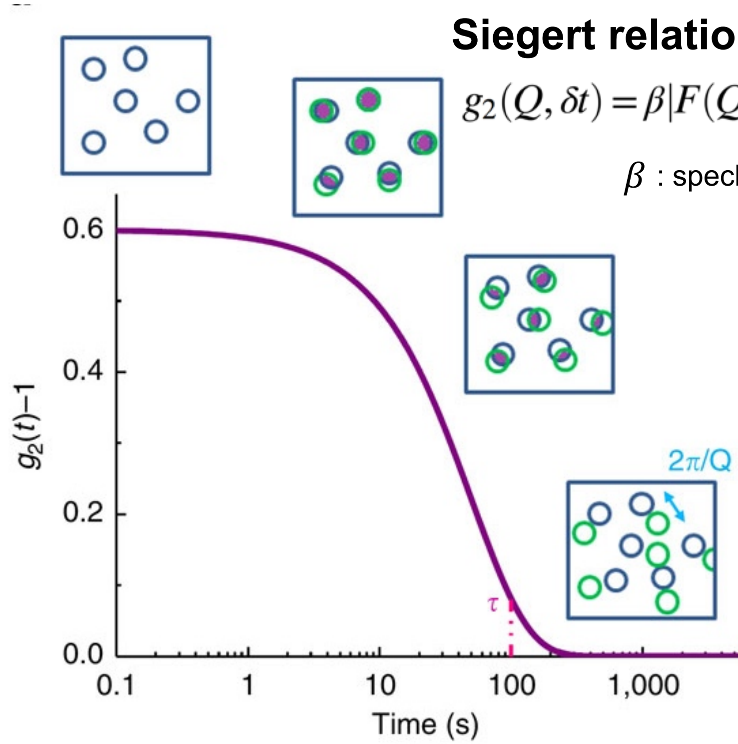
Intermediate scattering function

$$F(Q,t) = \frac{1}{N}\langle \sum_{i=1}^{N}\sum_{j=1}^{N} e^{i\mathbf{Q}\cdot[\mathbf{r}_i(t)-\mathbf{r}_j(0)]}\rangle$$

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)

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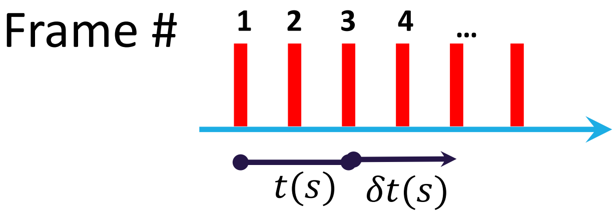
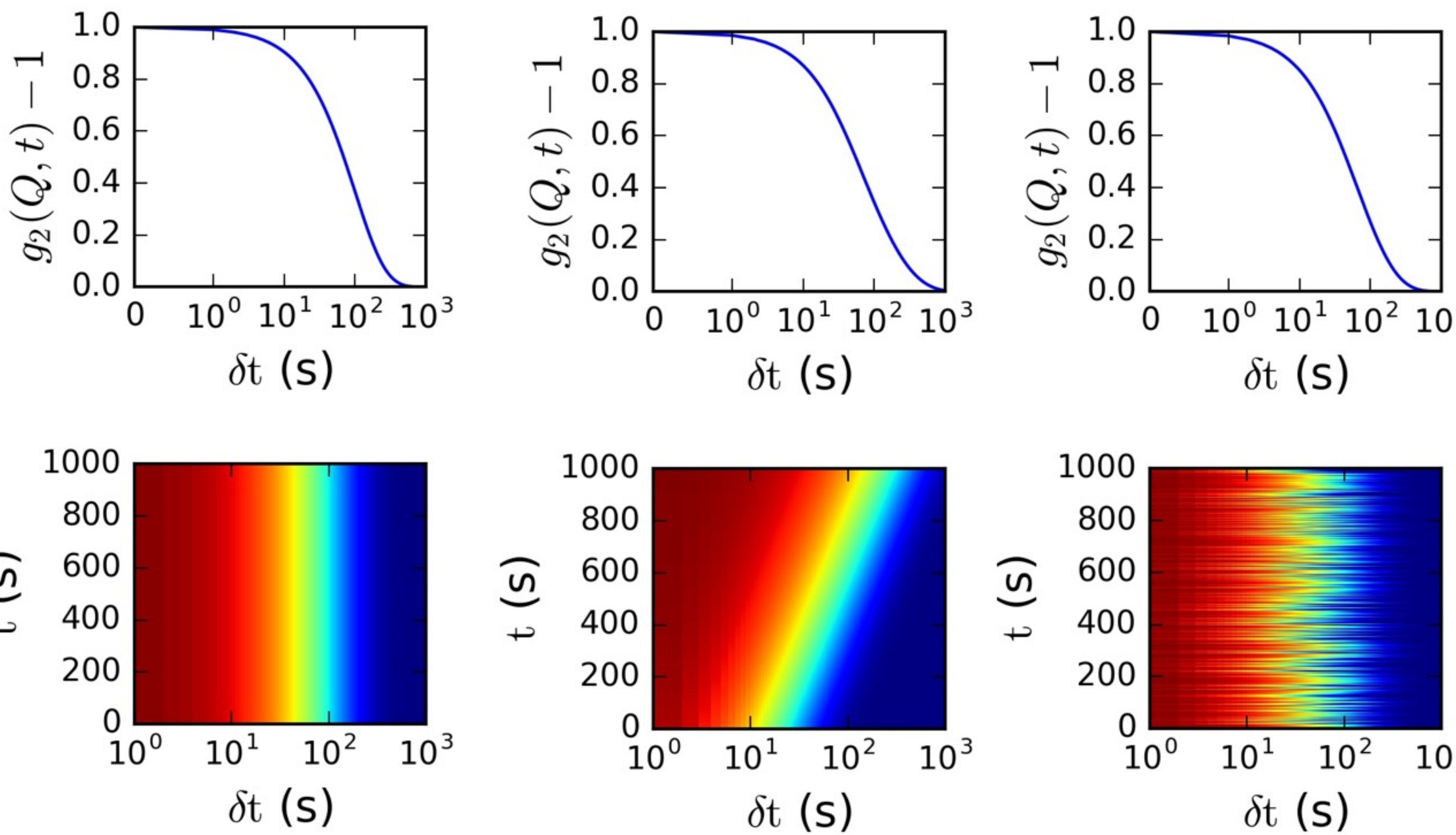
two-time correlation functions



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

1D-XPCS

2D-XPCS



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

Synchrotron Experiments

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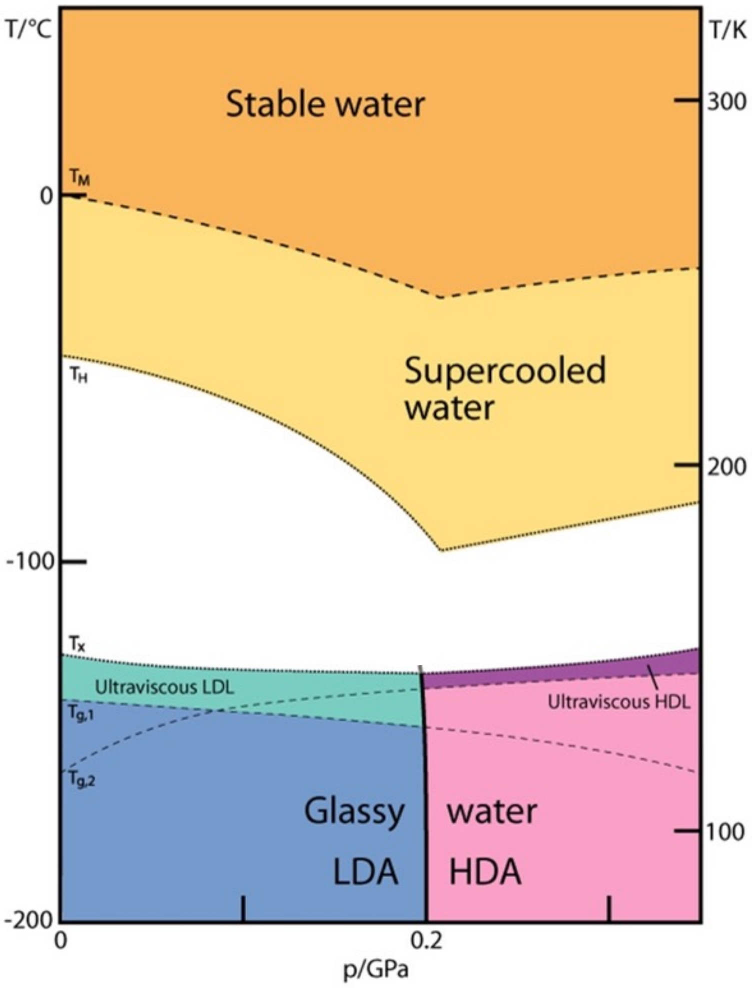
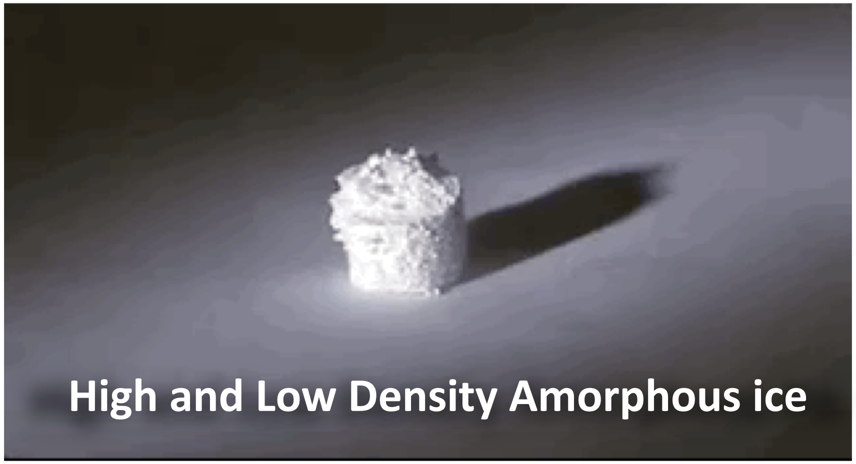
The two-liquid hypothesis





ρ(LDA)=0.94 g/cm^3 ρ(HDA)=1.17 g/cm^3

Close to hexagonal ice

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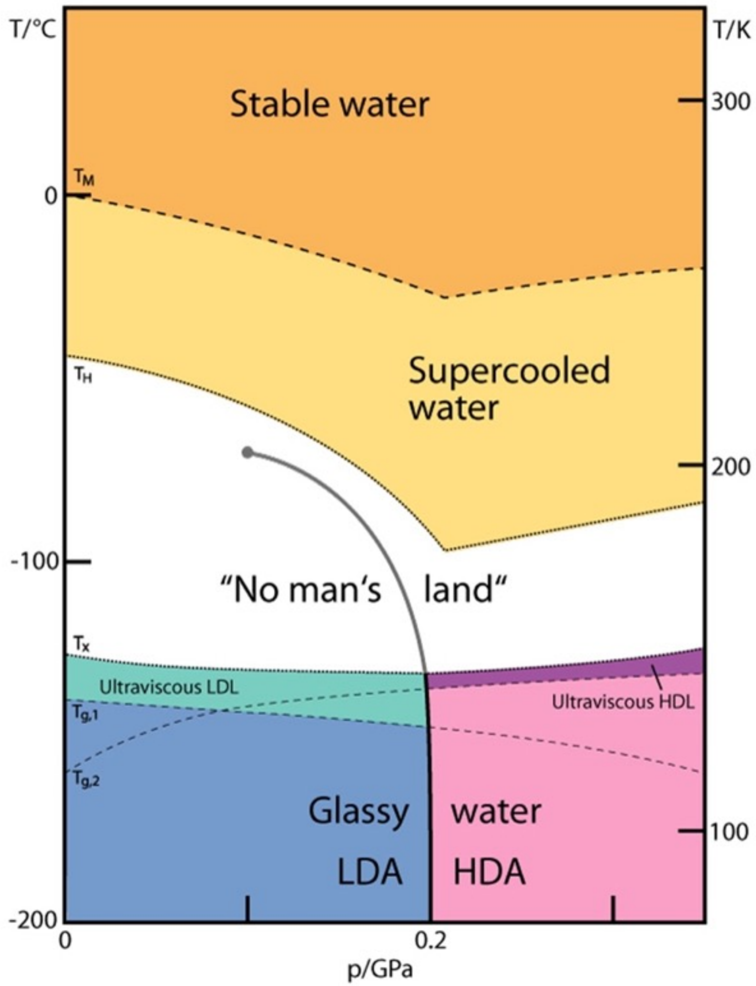
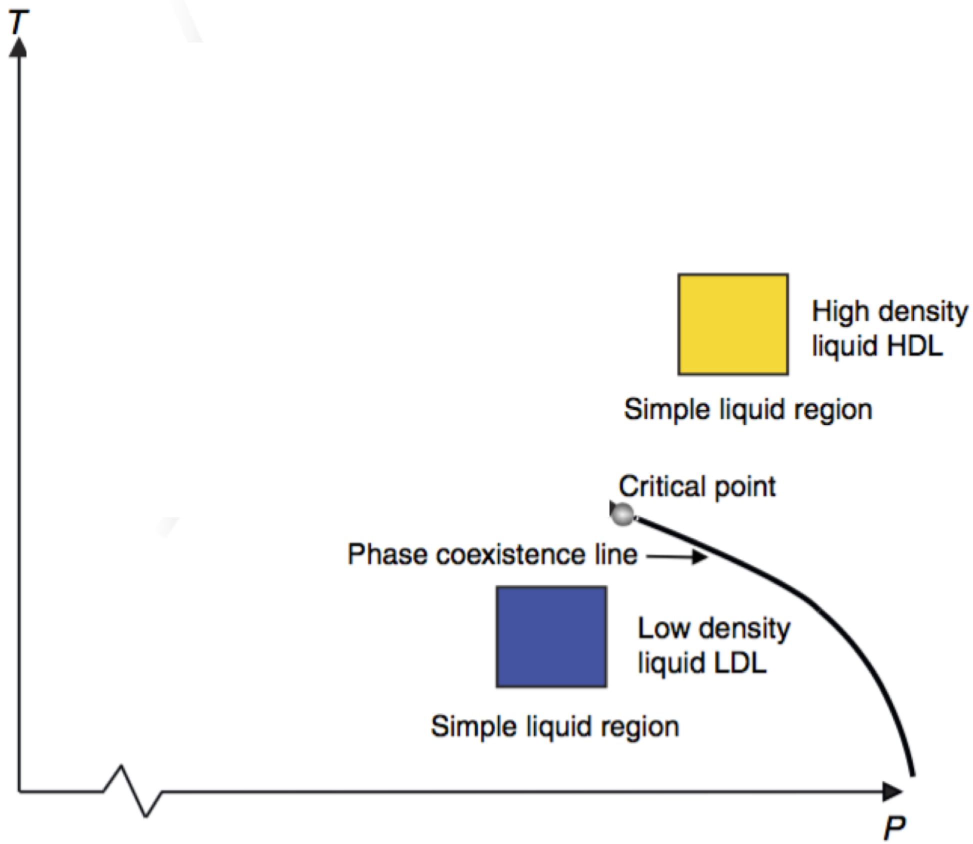
The two-liquid hypothesis

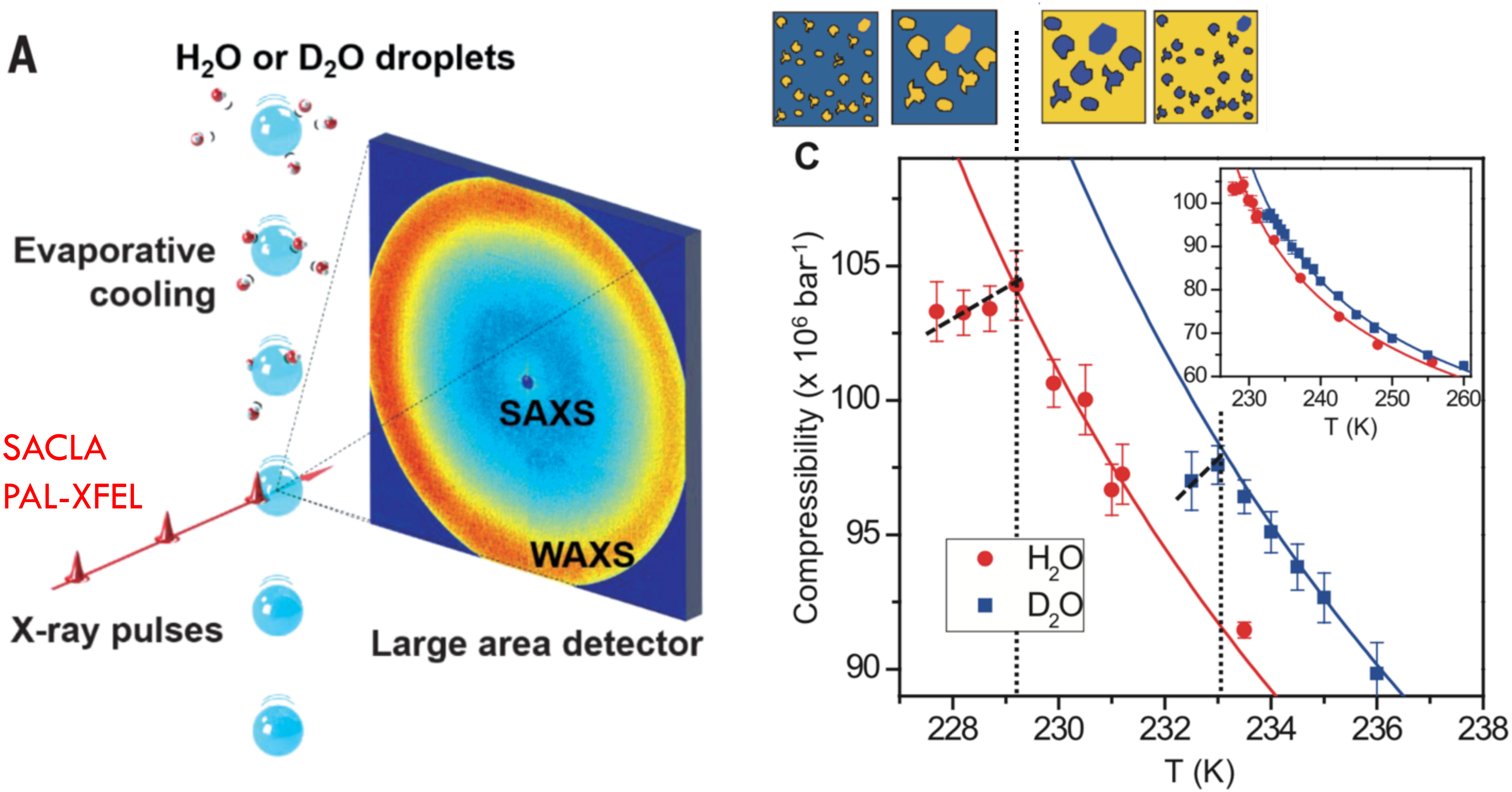




Poole et al.
Nature 360,1992

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

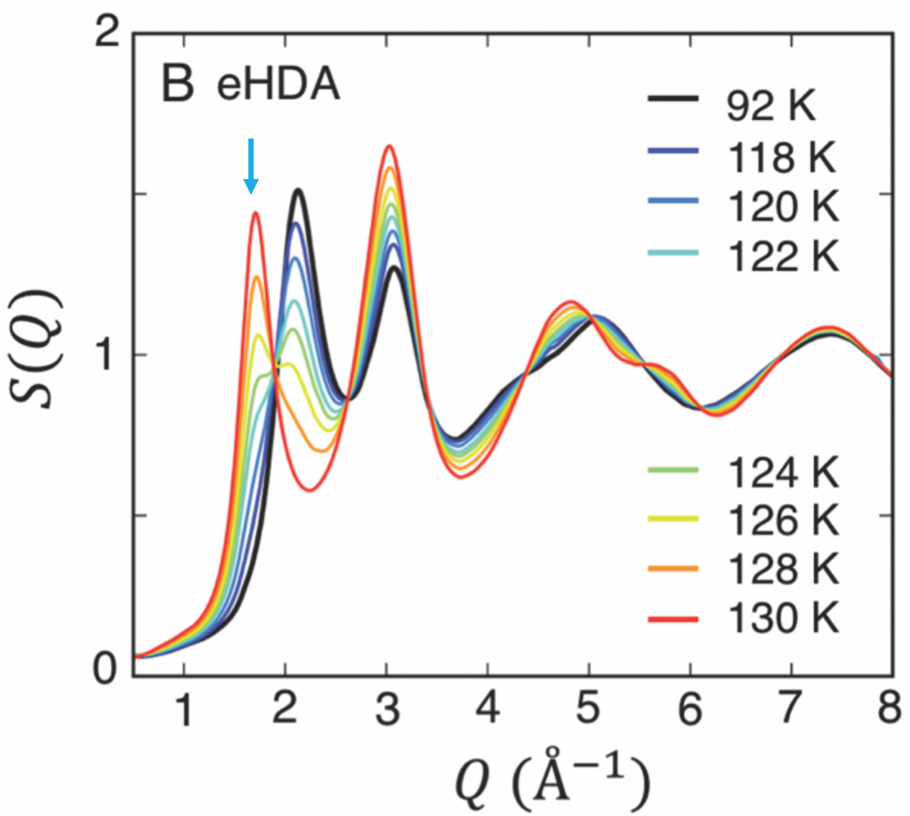
Experimental Evidence: Widom line 229K



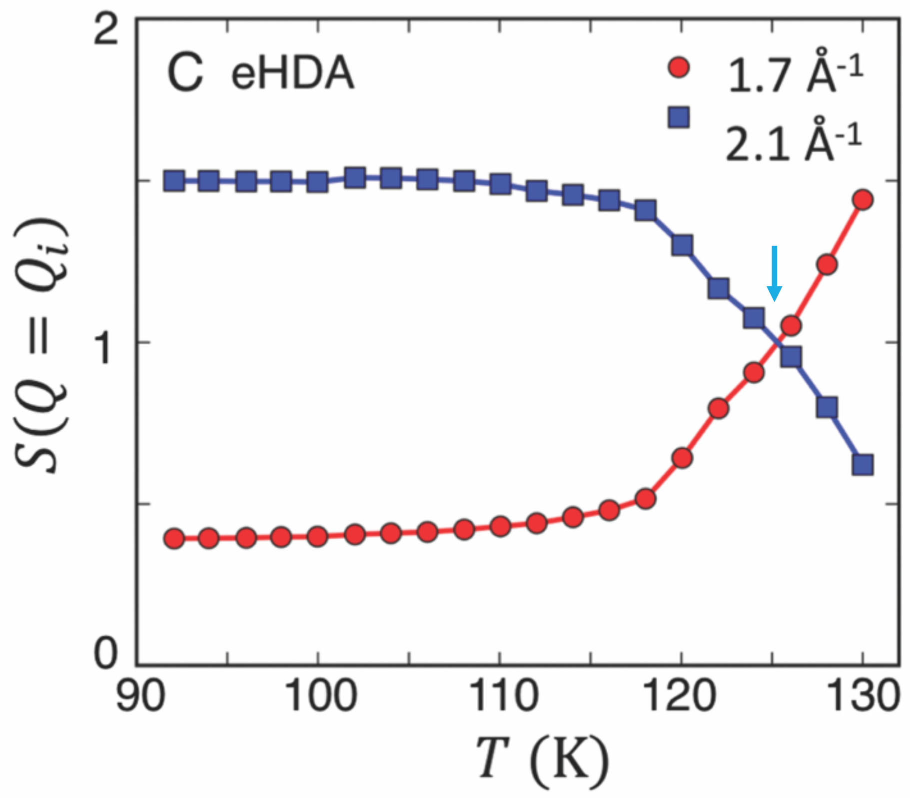
K.H. Kim et al. Science **358**, 1589 (2017)

High energy diffraction experiments

Static Structure factor

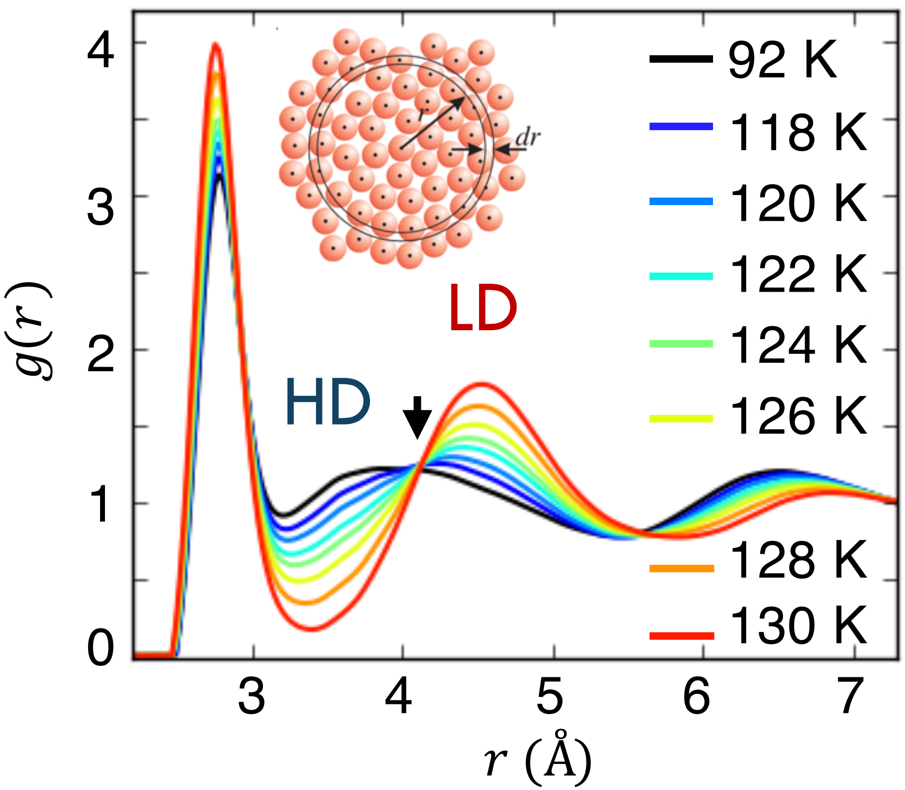


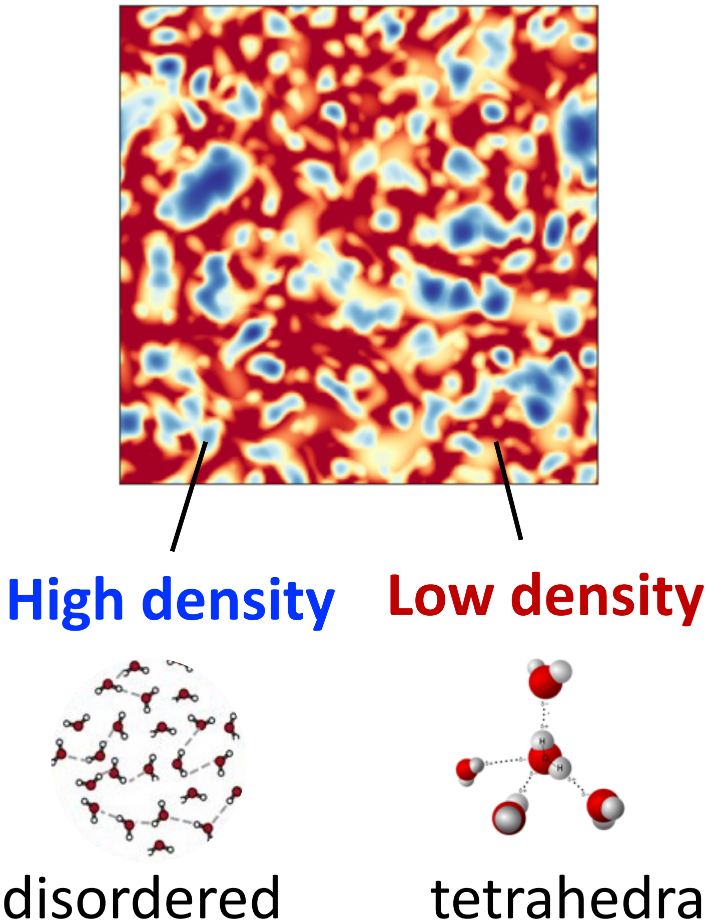
High to low density transition



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

High energy diffraction experiments

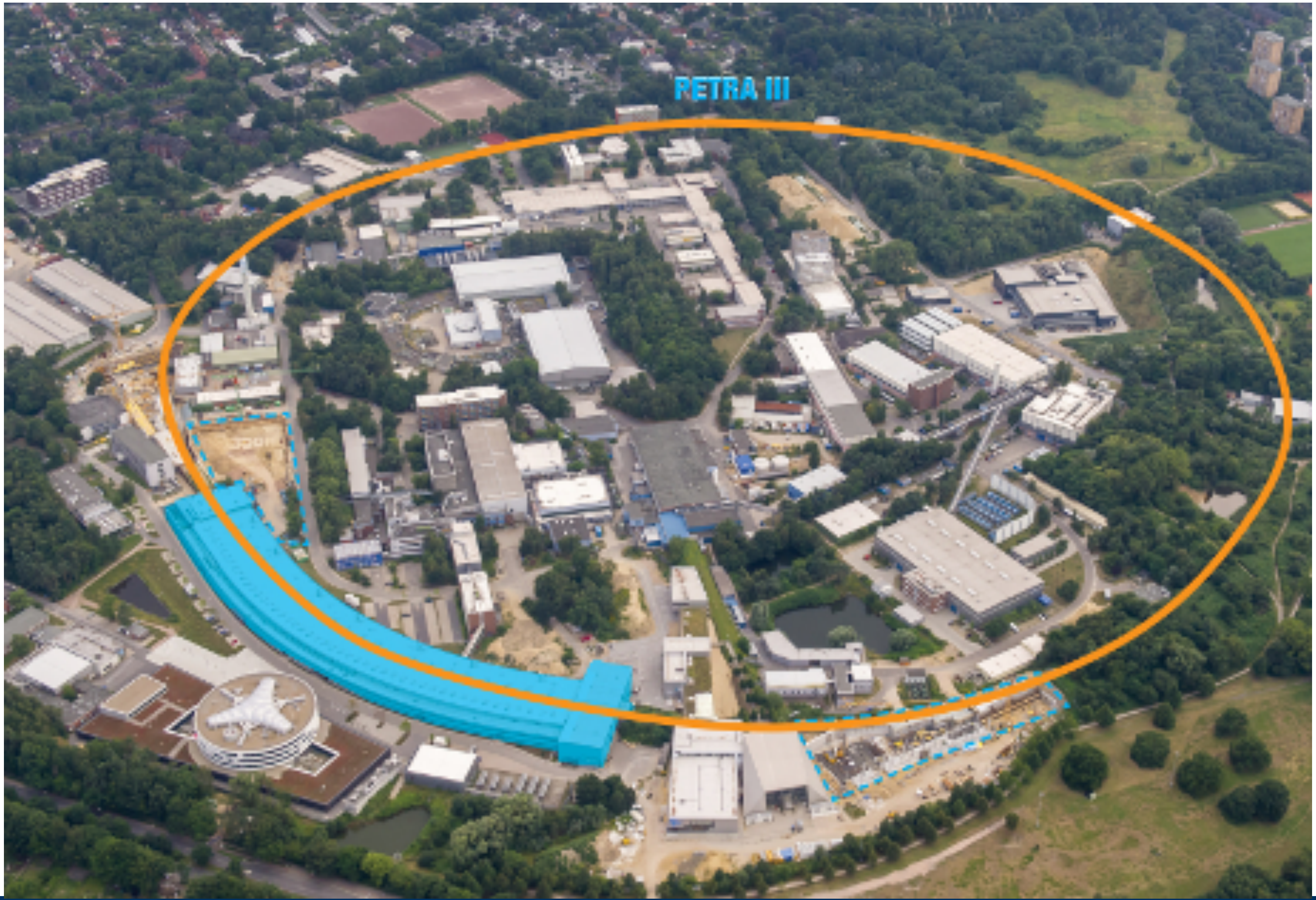




F. Perakis, K. Amman-Winkel et al.
PNAS 114, 8193 (2017)

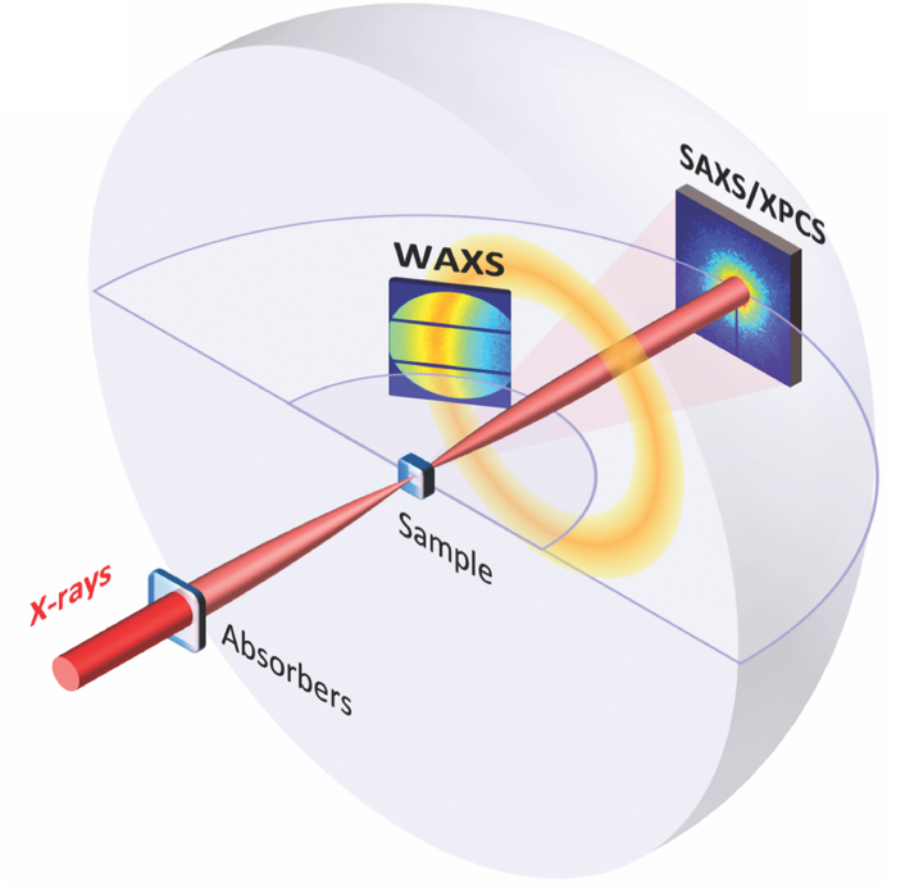
Fivos Perakis

PETRA III, HAMBURG



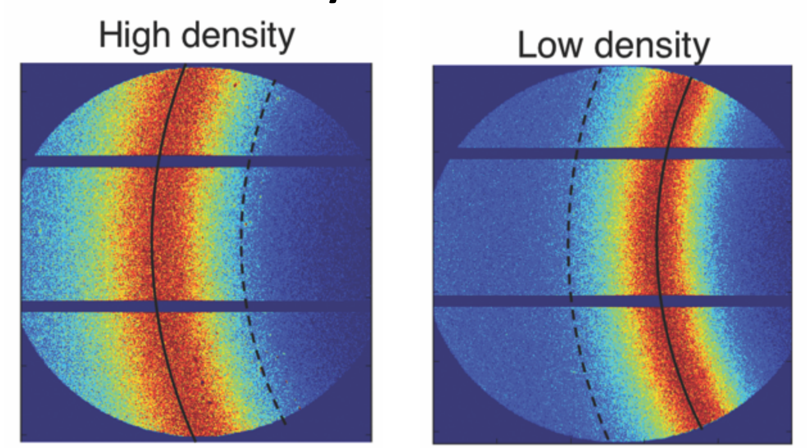
P10 Coherence Applications Beamline

The experimental setup

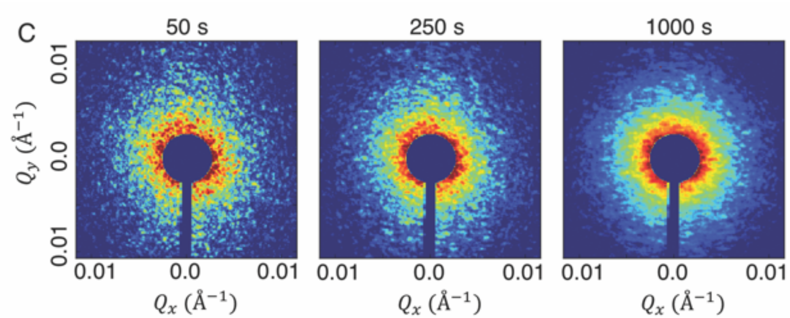


8.4 keV, Si(333), PILATUS 300k, Lamda, 3x3um focus

X-ray diffraction



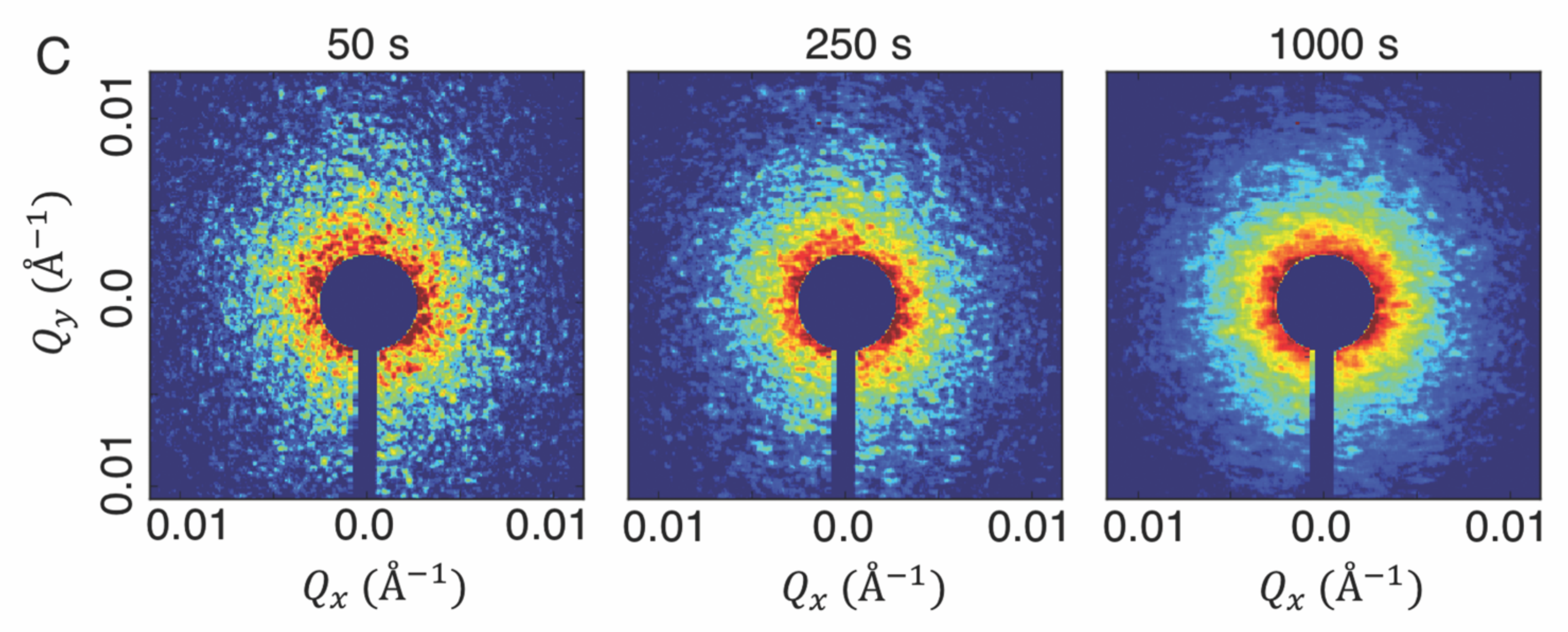
X-ray Photon Correlation Spectroscopy



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

X-ray Photon Correlation Spectroscopy

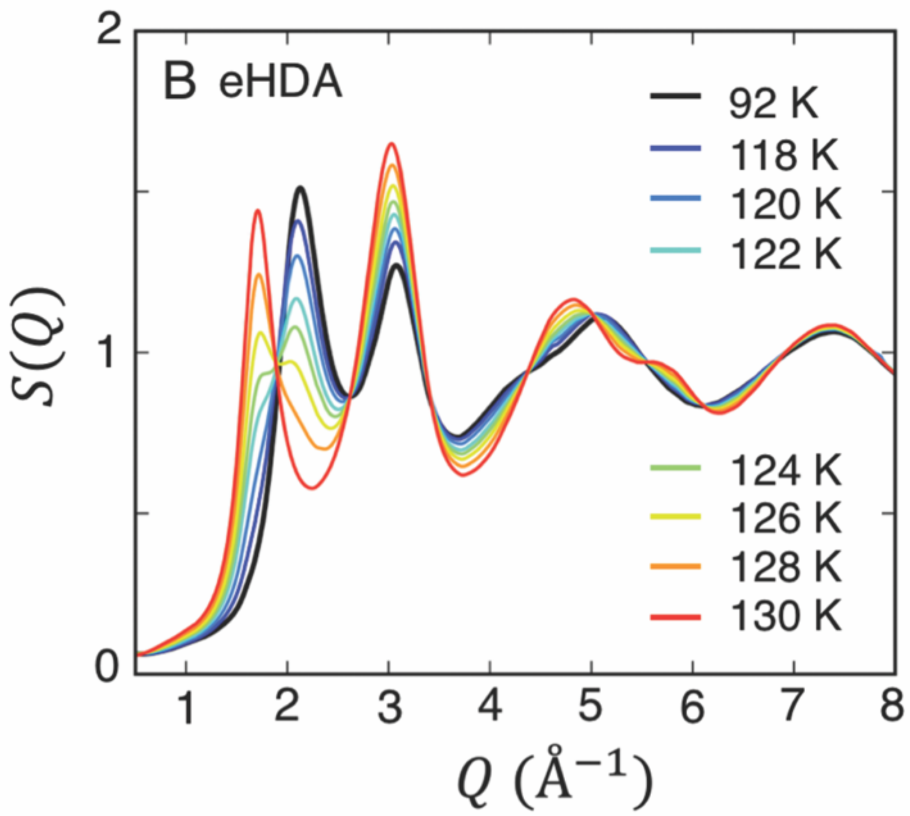
Nanoscale dynamics of water near the glass transition



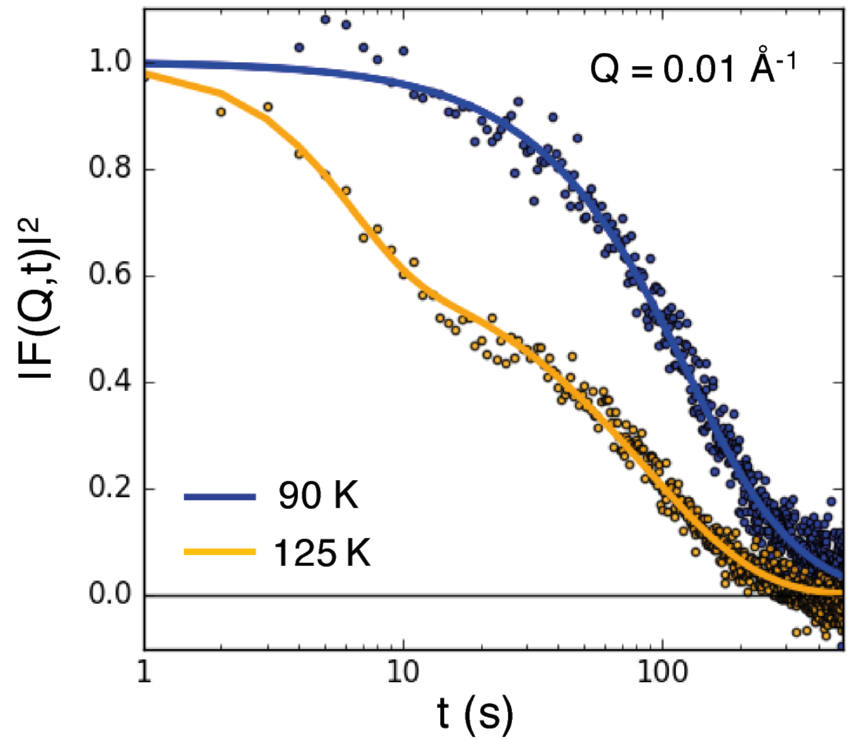
F. Perakis, K. Amman-Winkel et al.
PNAS 114, 8193 (2017)

Probing Structure and Dynamics

Static Structure factor



Dynamic Structure factor



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

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

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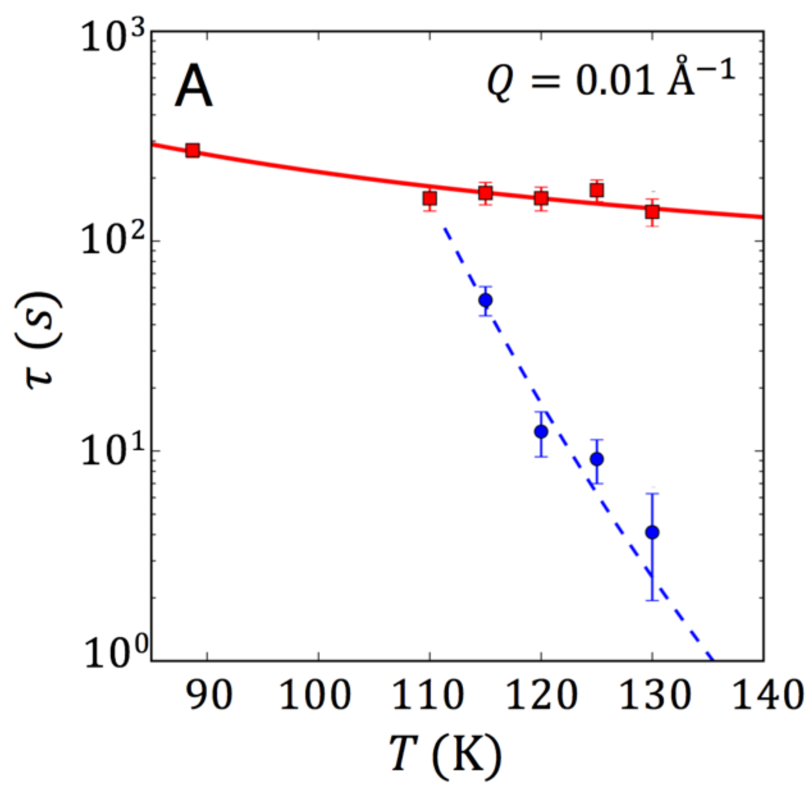
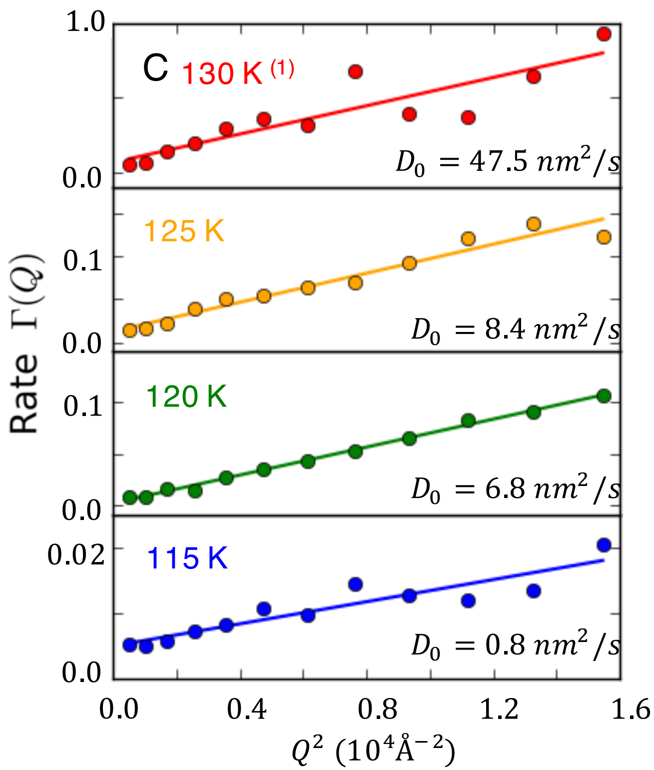
Temperature and Q-dependence

Fast component appearing at 110 K



Diffusive motion ~100nm



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

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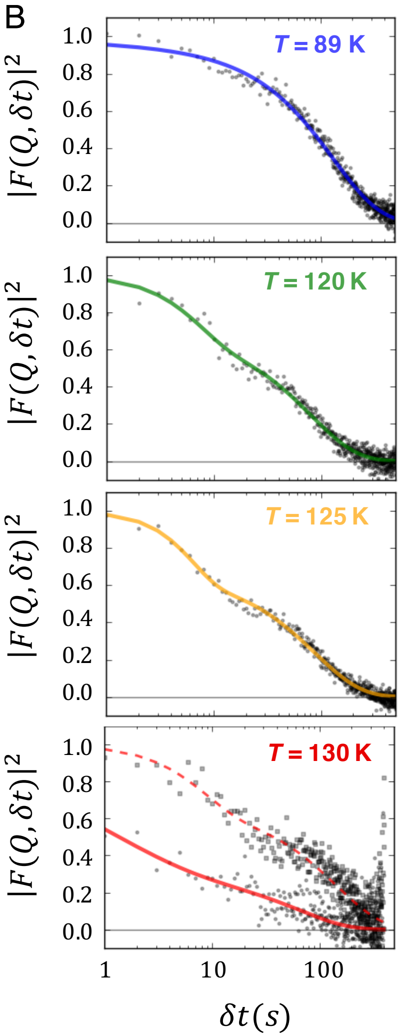
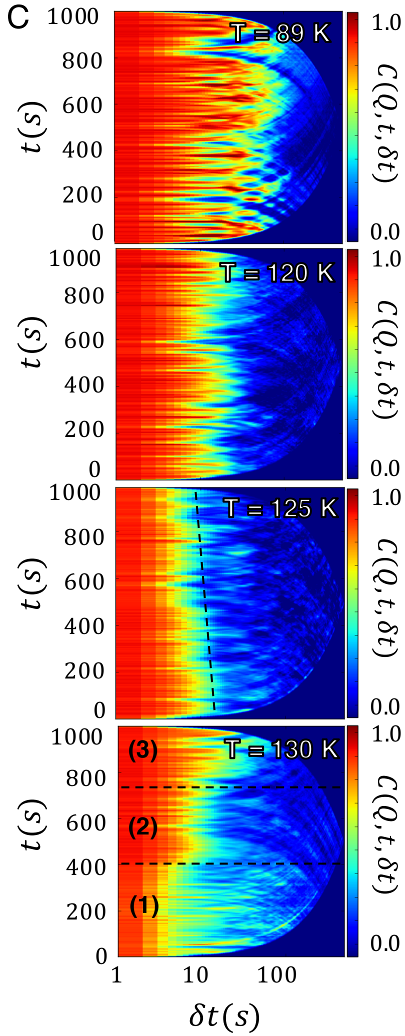
Dynamical heterogeneities

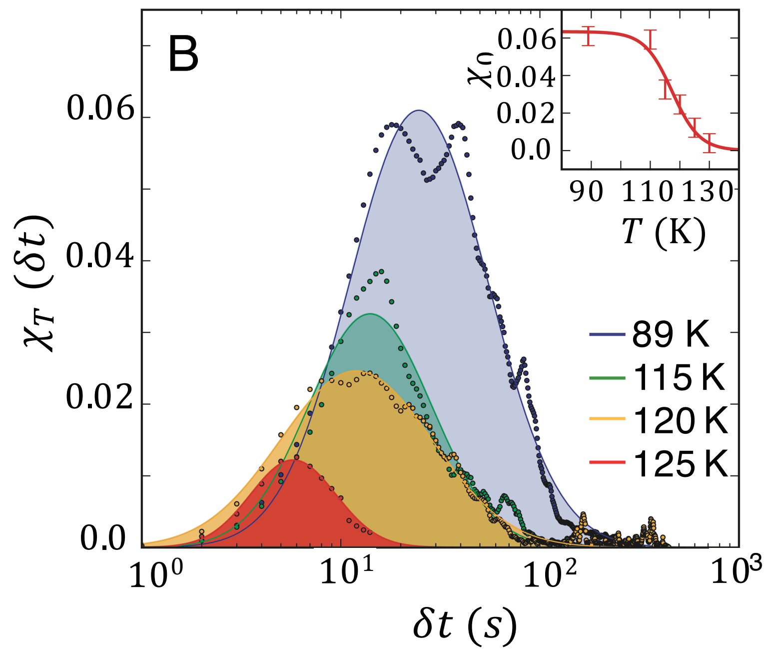
XPCS (1D)



XPCS (2D)



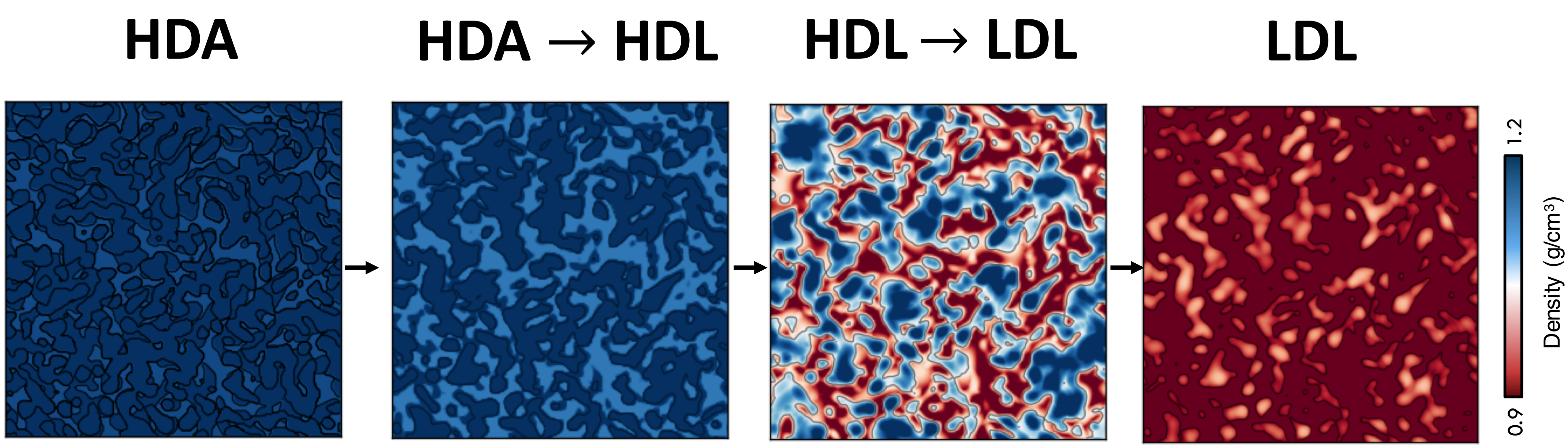
Normalized variance



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

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

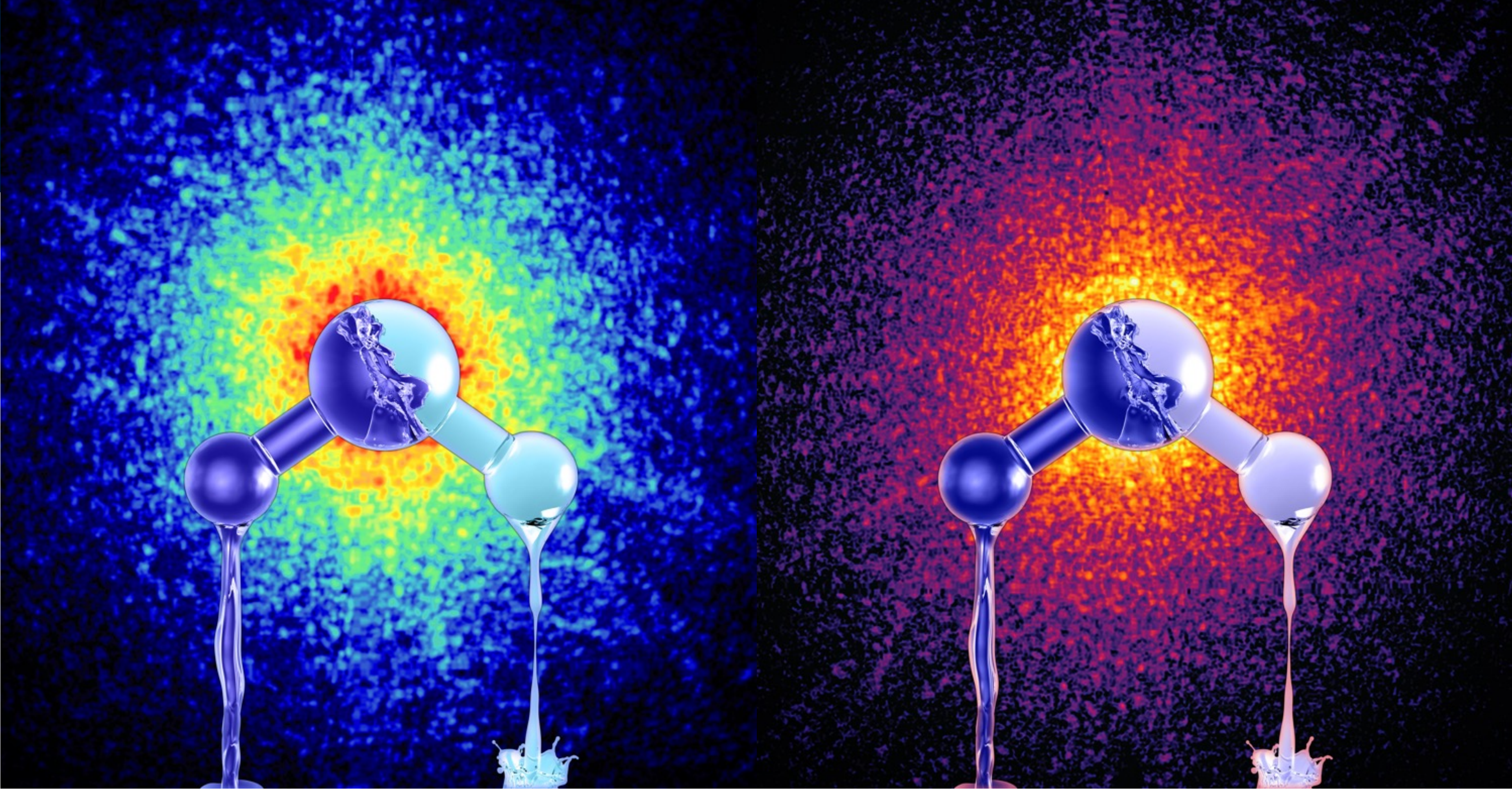
Take-home message I:



"Slow" and "fast" components: Glass transition

High and low density coexistence

low-density diffusive dynamics



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

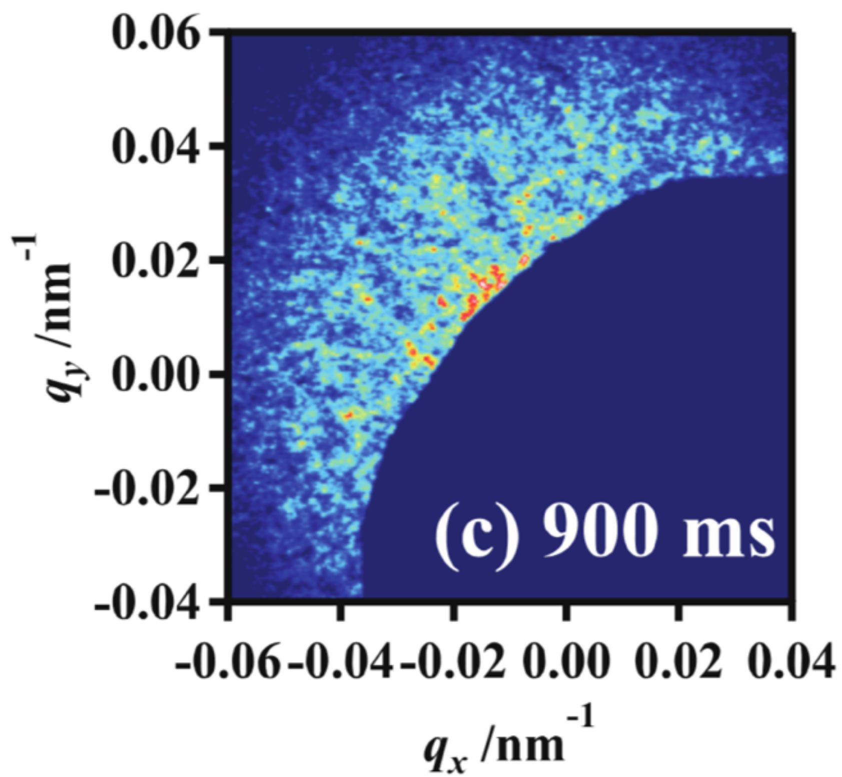
FEL EXPERIMENTS, XCS@LCLS

Fivos Perakis

X-ray Speckle Visibility Spectroscopy

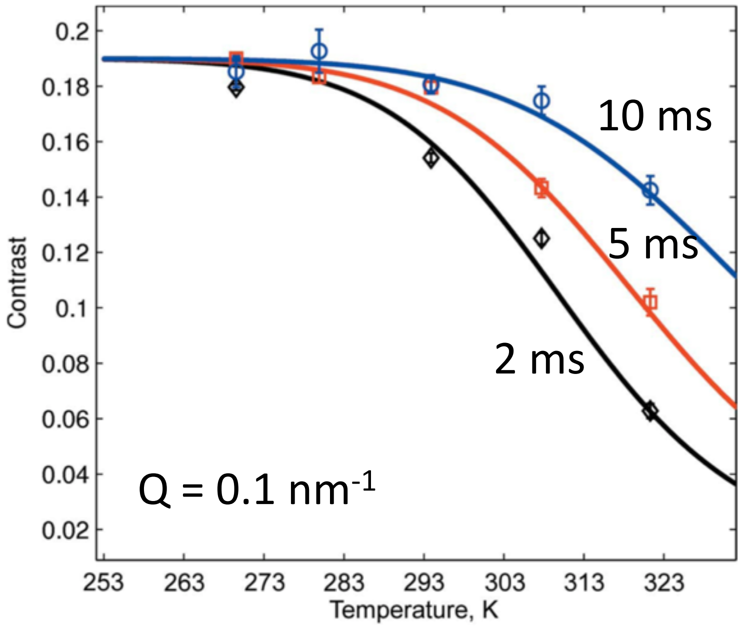
Exposure Time-dependence

polystyrene nanospheres in glycerol



Temperature-dependence

latex nanospheres in glycerol



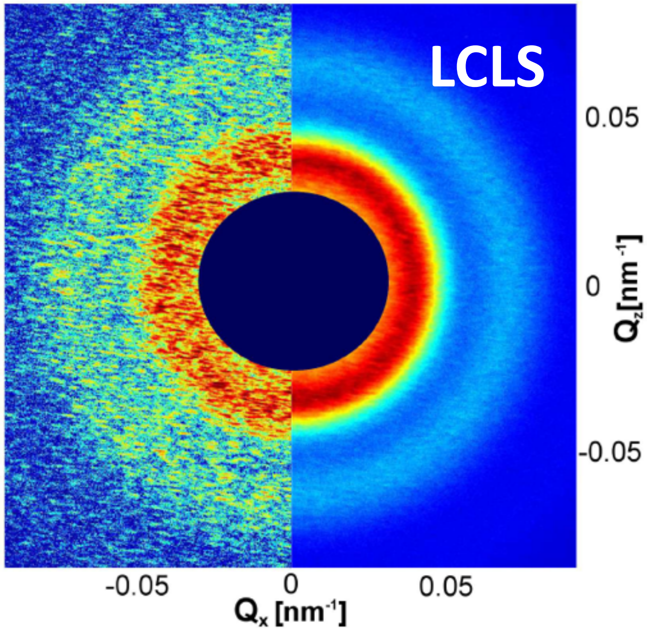
latex in glycerol

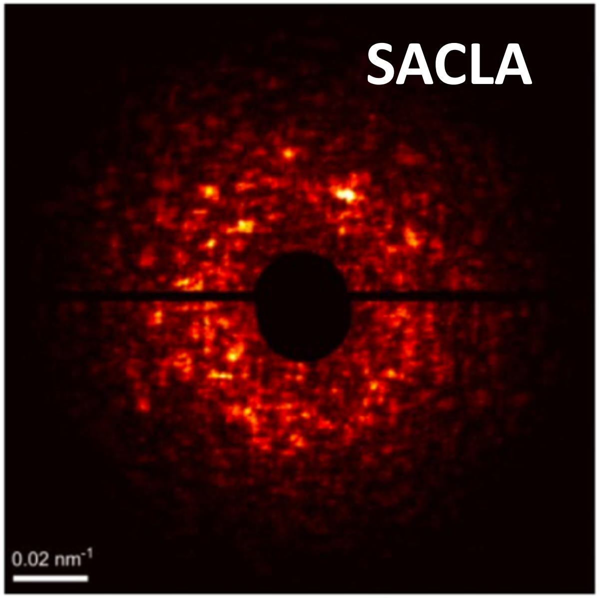
I. Inoue et al
Optics Express 20, 26878 (2012)

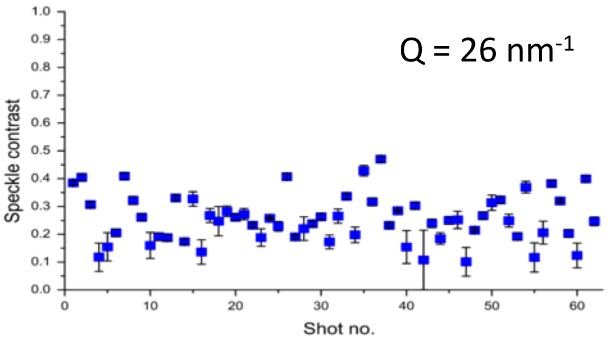
C. DeCaro et al.
J. Synchrotron Rad. 20, 332–338 (2013)

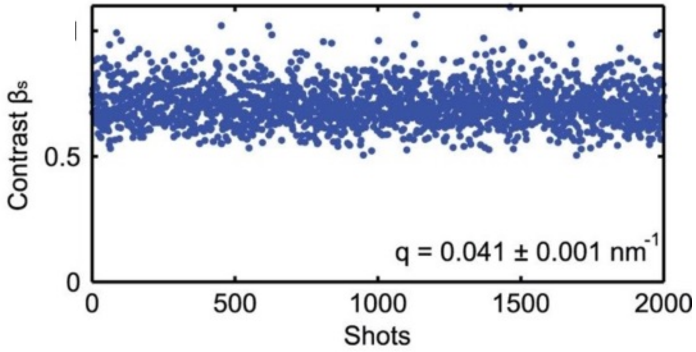
Fivos Perakis

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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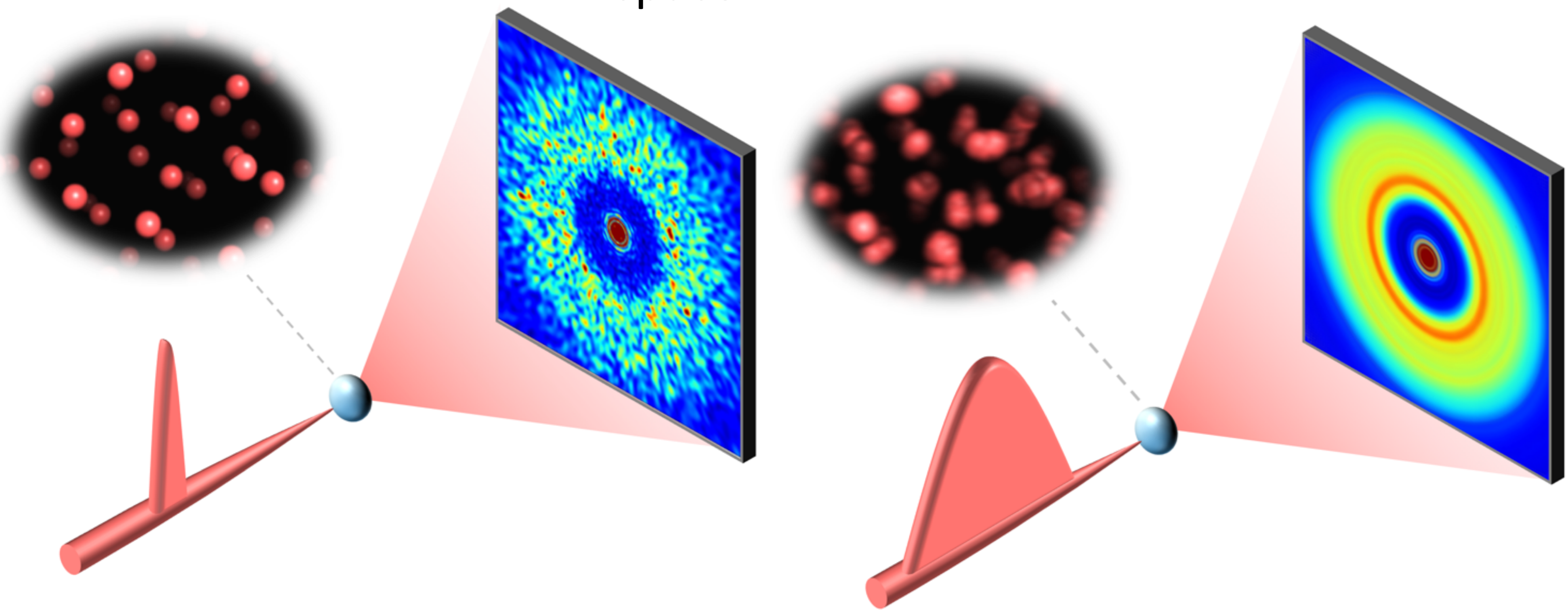
X-ray Speckle Visibility Spectroscopy



The challenges

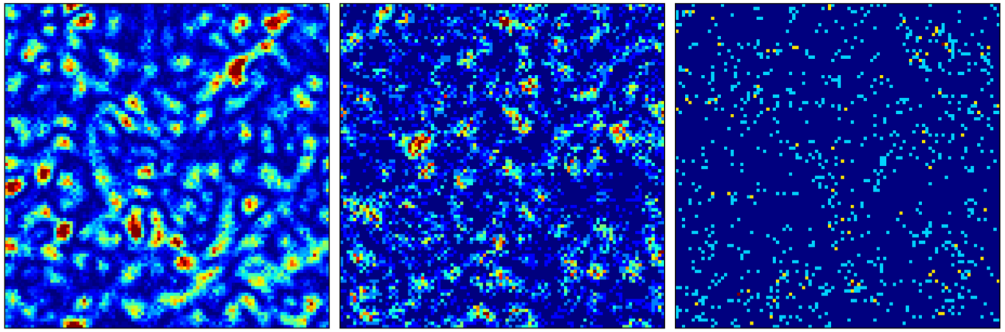
Water is a weak scatterer

in the hard X-ray range (8.2keV)

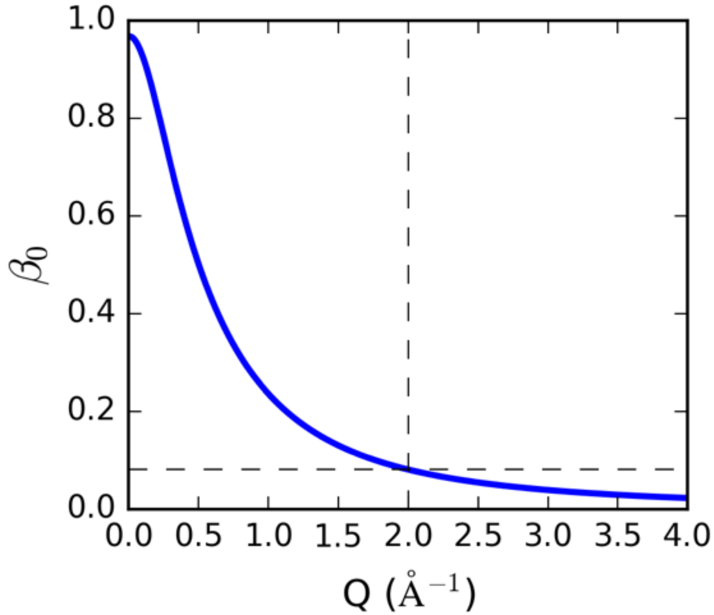
Contrast is low in WAXS

atomic lengthscales (Q = 1.9Å^{-1})

Mean Photon Density $\bar{k}$



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



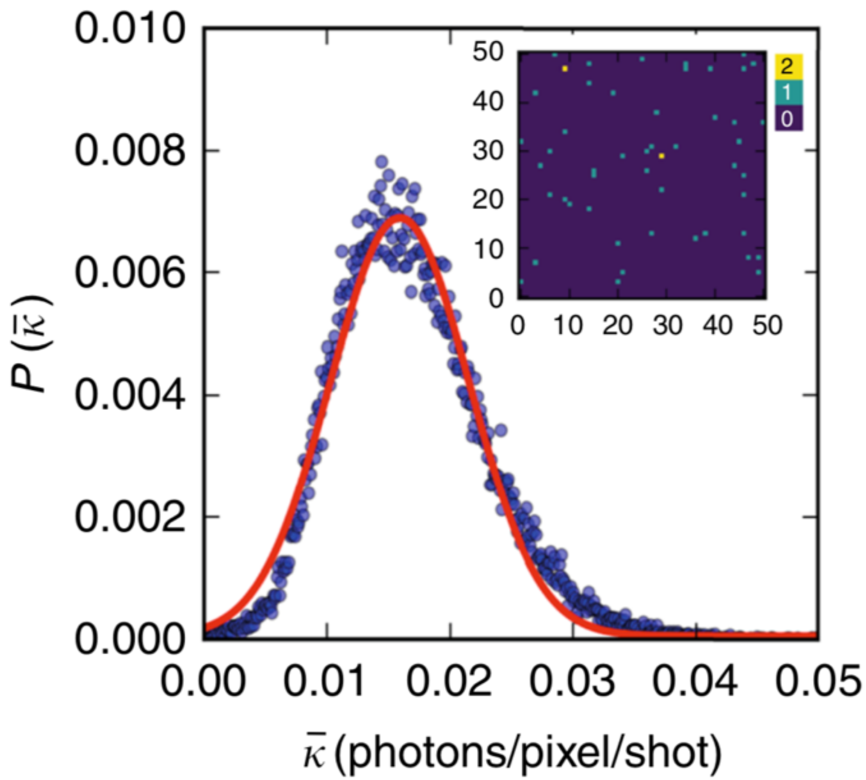
X-ray Studies of Water, A. Nilsson and F. Perakis,
Synchrotron Light Sources and Free-Electron Lasers, Springer (2019)

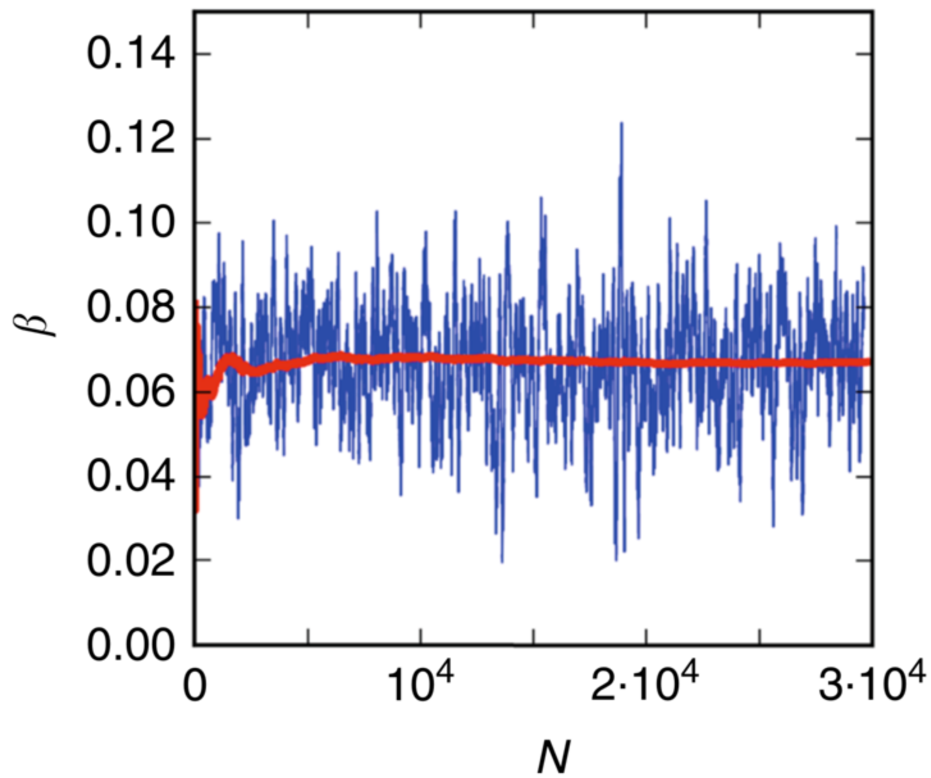
Photon counts and contrast

TJ Lane Felix Lehmkühler

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

Contrast 0.069

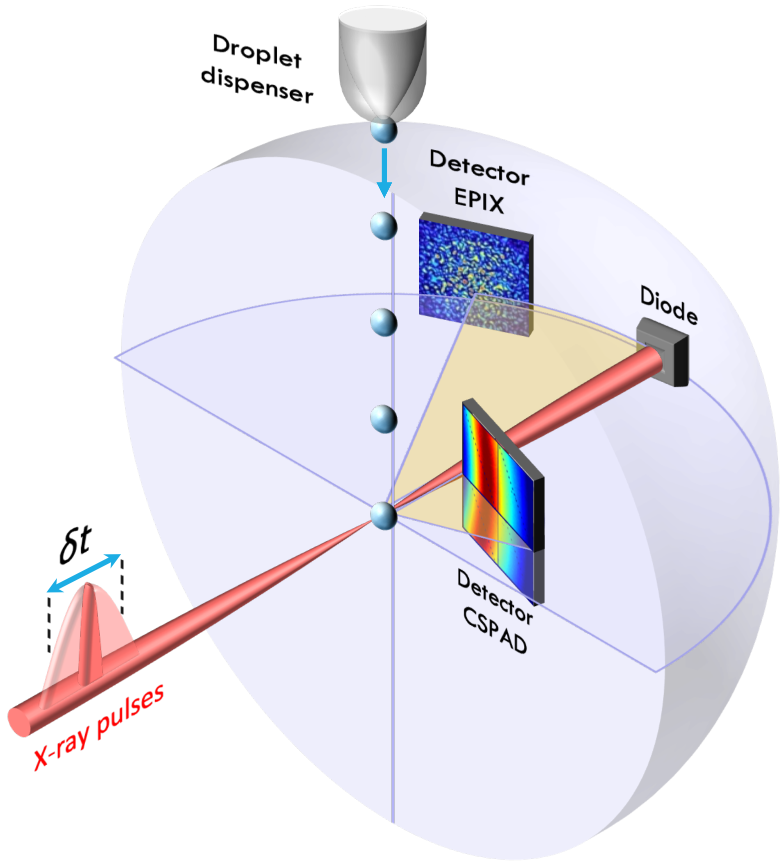




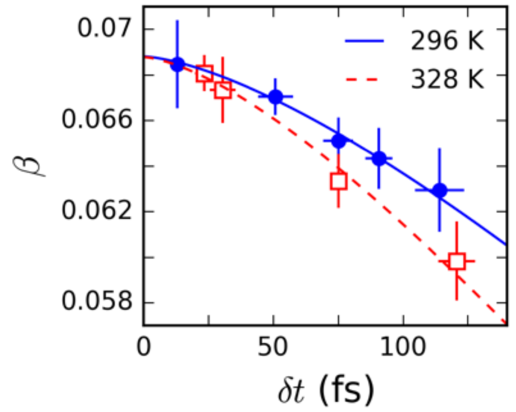
F. Perakis et al
Nature Comm. 9, 1917 (2018)

Fivos Perakis

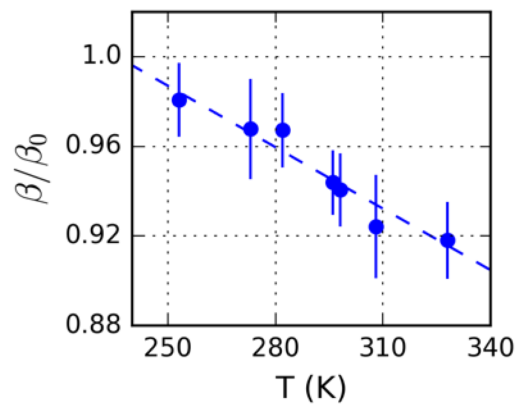
The experiment in a nutshell



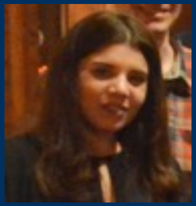
Varying pulse duration



Varying temperature

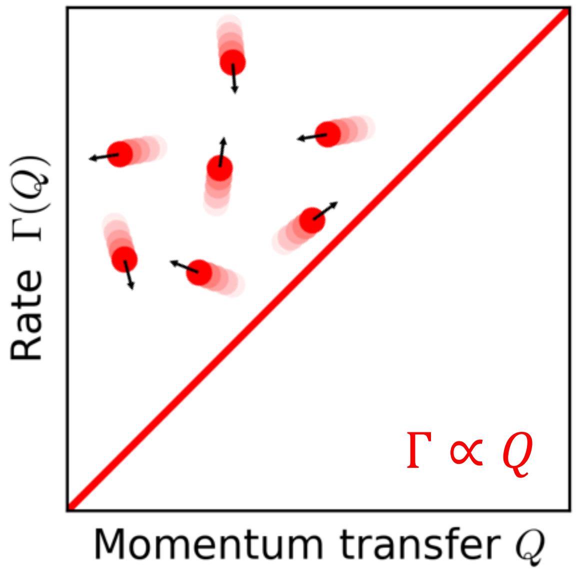


Molecular Simulations



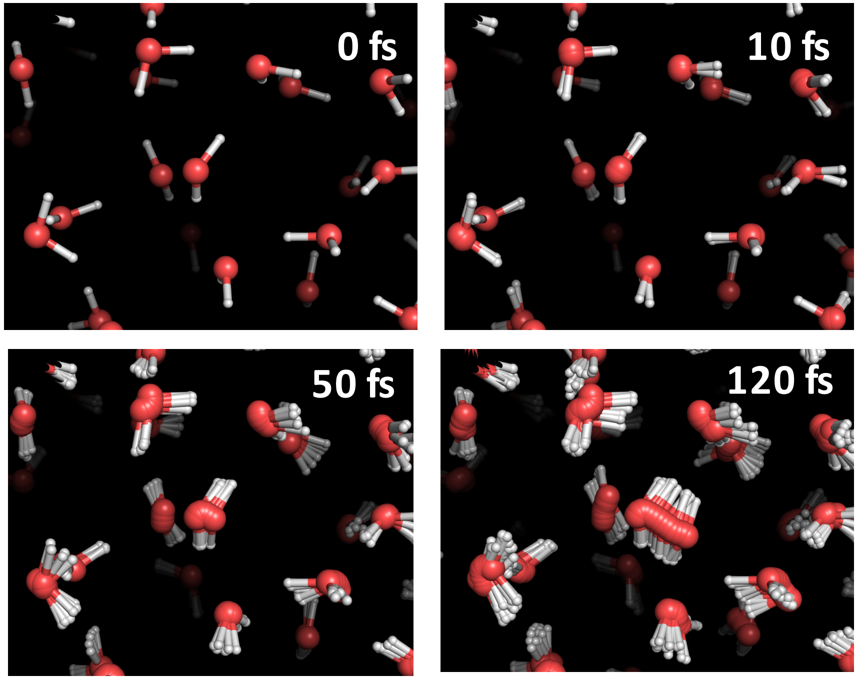
Gaia Camisasca

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)

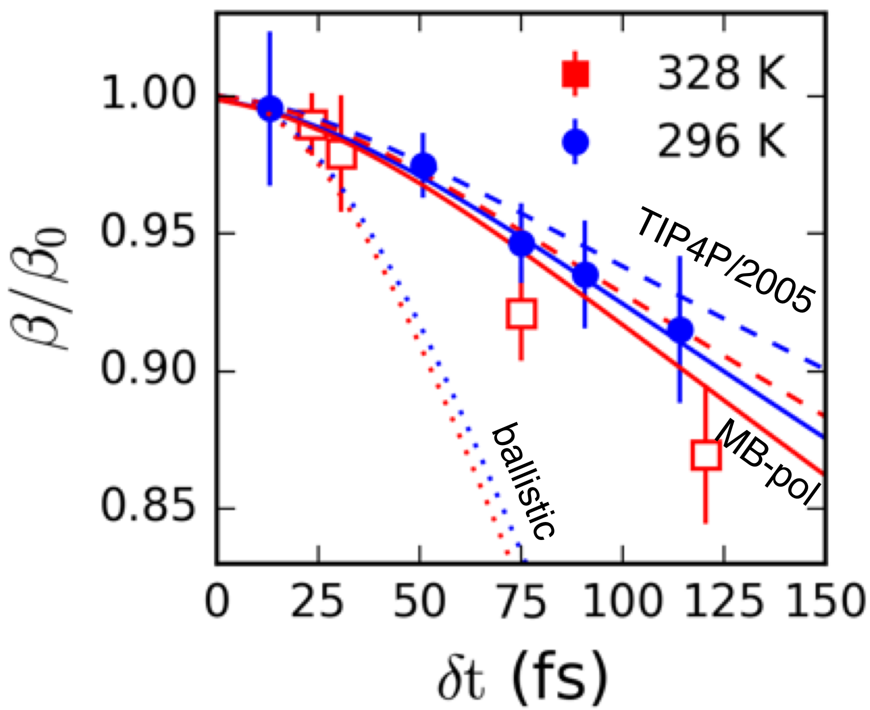
Comparison with experiment

XSVS:
Siegert relation

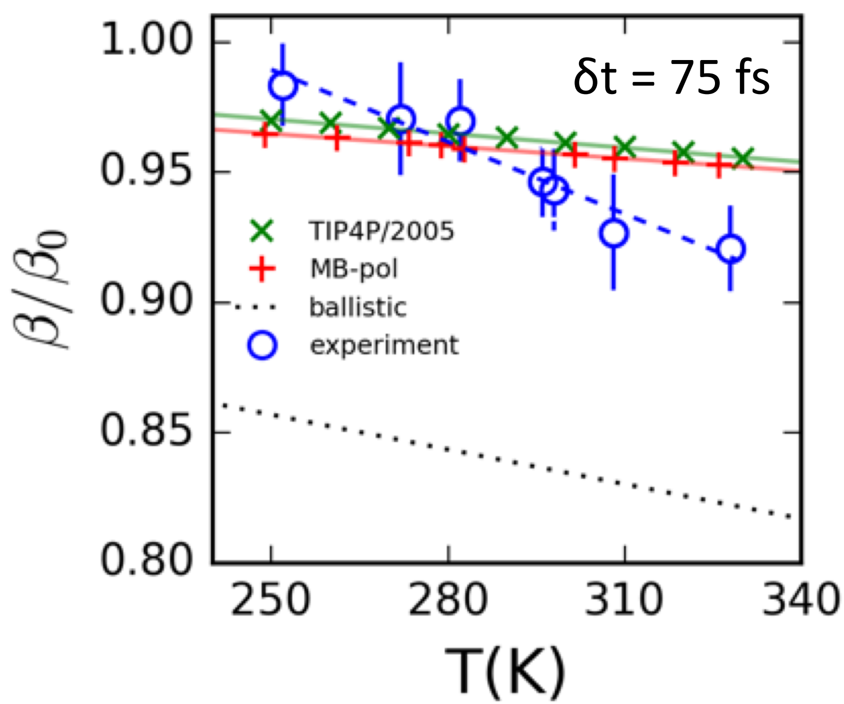
$$\beta(Q,\delta t) = 2\cdot\beta_0 \int_0^{\delta t}\left(1-\frac{t}{\delta t}\right)|F(Q,t)|^2\,\frac{dt}{\delta t}$$

Dixon & Durian
PRL 90, 184302 (2003)

Pulse duration dependence

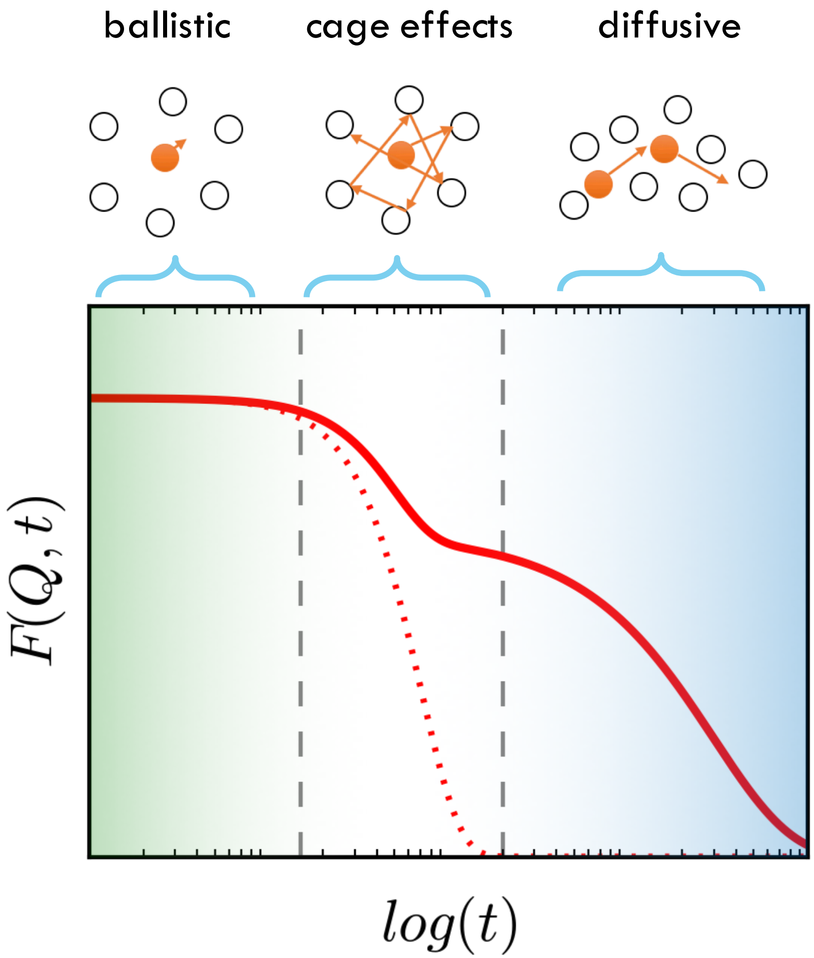


Temperature dependence



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.**

Foivos Perakis
Chemical Physics

Stockholm University

Stockholm University

Rafat Yousif
Maddalena Bin
Sudipta Das
Sharon Berkowicz
Ifi Tsironi

A. Nilsson
L. Pettersson
K. Amann-Winkel
A. Späh
H. Pathak
M. L. Parada
G. Camisasca
T. Hansson
R. Thomas
D. Schlesinger

KTH VETENSKAP OCH KONST

J. Sellberg
T. Karpouzoglou

DESY

G. Gruebel
F. Lehmkühler
W. Roseker
A. Jain

SLAC NATIONAL ACCELERATOR LABORATORY

TJ Lane
S. Song
A. Robert
D. Zhu

Thank you for your attention!