Methoden moderner Röntgenphysik: Streuung und Abbildung

Lecture 21	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2021		
	G. Grübel, O. Seeck, F. Lehmkühler, A. Philippi-Kobs, V. Markmann, M. Martins		
Location	online		
Date	Tuesday	12:30 - 14:00	(starting 6.4.)
	Thursday	8:30 - 10:00	(until 8.7.)

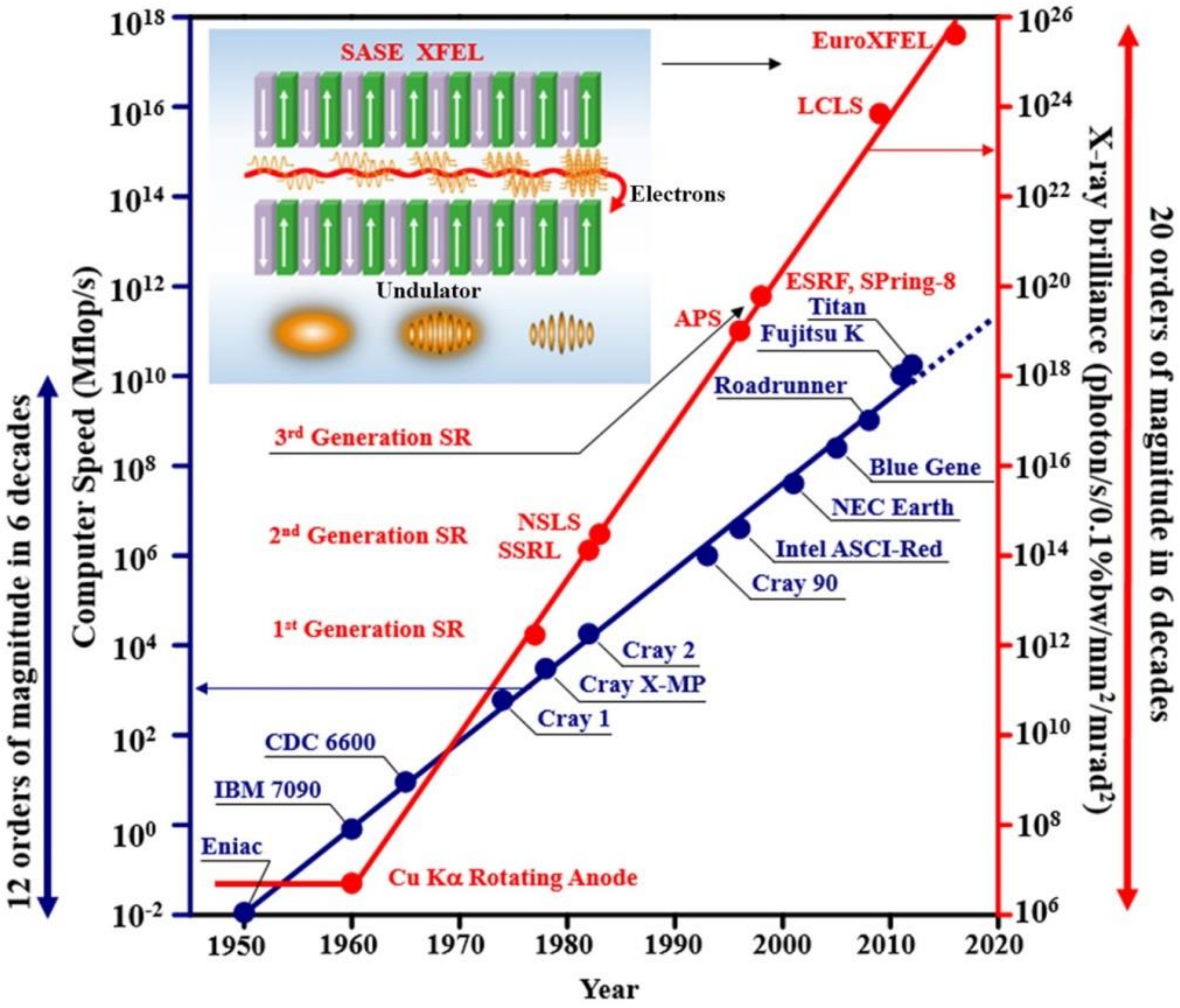
Soft Matter – Timeline

- Do 27.05.2021 Soft Matter studies I: Methods & experiments
  Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, **…**
- Di 01.06.2021 Soft Matter studies II: Structure
  SAXS & WAXS applications, X-ray cross correlations, **…**
- Do 03.06.2021 Soft Matter studies III: Dynamics
  XPCS applications, diffusion, dynamical heterogeneities, …
- Di 08.06.2021 XPCS & XCCA simulations and modelling
- Do 10.06.2021 Case study I: Glass transition
  Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, …
- Di 15.05.2021 Case study II: Water
  Phase diagram, anomalies, crystalline and glassy forms, FEL studies, …
- Do 17.06.2021 Outlook: Opportunities at new facilities

New facilites

- Synchrotron radiation facilites worldwide
- Free-electron lasers facilities
- Next-generation synchrotron radiation facilities: diffraction-limited storage rings

lightsources.org



- Brilliance as „source quality“:

$$B = \frac{N_{photons}}{t \cdot \Delta\Omega \cdot A \cdot BW}$$

- With time t (s); $\Delta\Omega$ = divergence (mrad^2), cross section A (mm^2), energy bandwidth BW (0.1%)

- Beating Moore‘s law

- Towards „small“ and „fast“ at new sources:

    - FEL: About >10^{12} photons per pulse

    - Storage rings: About >10^{12} photons per second

http://www.physics.ucla.edu/research/imaging/research_CDI.html

Free-electron lasers

- FLASH at DESY
- FERMI (Trieste, Italy)

Soft X-rays (Spectroscopy) → below 1 keV → see e.g. lectures by A. Philippi-Kobs

- LCLS (Stanford, USA)
- SACLA (Japan)
- PAL-FEL (Korea)
- SwissFEL (PSI, Switzerland)
- European XFEL (Schenefeld/Hamburg)

Hard X-rays (Scattering) → around 10 keV

- Full transverse coherence

- Repetition rates
  - Typically ~10 to 100 Hz (e.g. LCLS, SACLA)
  - European XFEL: up to 4.5 MHz

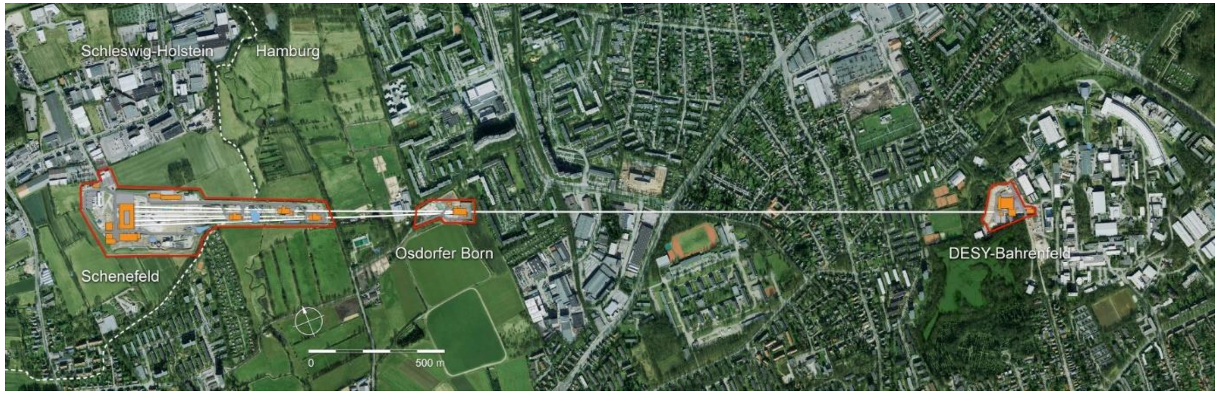
- Time scales
  - Pulse lengths: 1 to 100+ fs
  - Pump-probe schemes (up to ns regime)

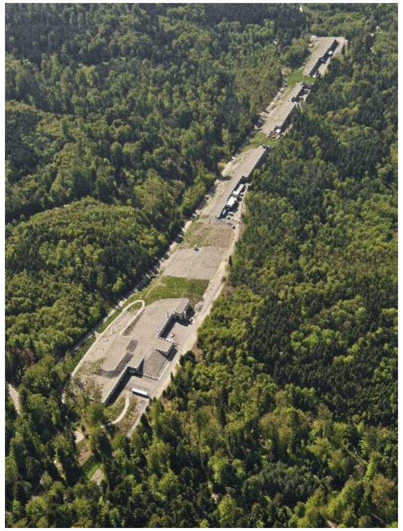
But:

- Limited number of beamlines / instruments (e.g. 20 to >40 at synchrotron radiation facilities vs. 1 to 3 at FEL sources)

- High data rates! >TB to PB within few days of experiments


SXU
HXU
LCLS-II-HE
LCLS-II
LCLS
Cu-linac

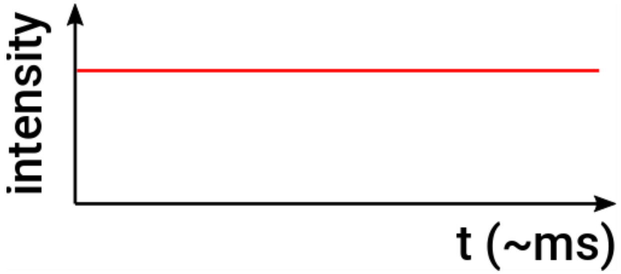

Schleswig-Holstein
Hamburg
Osdorfer Born
Schenefeld
DESY-Bahrenfeld
0
500 m



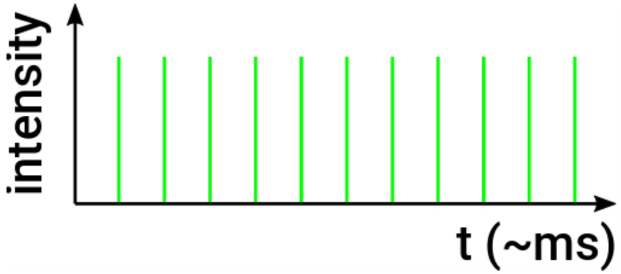

PAL-XFEL
PAL 4세대방사광가속기

Research at free-electron lasers: Time-resolution

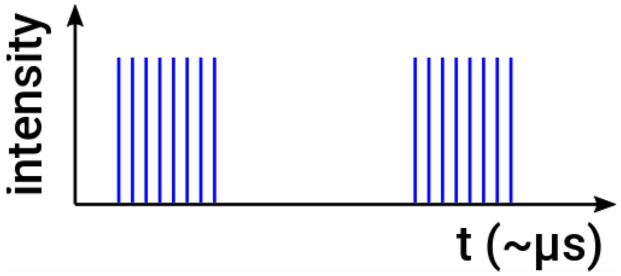
Storage ring
- Quasi-continuous light source
- $\sim10^{12}$ photons per second



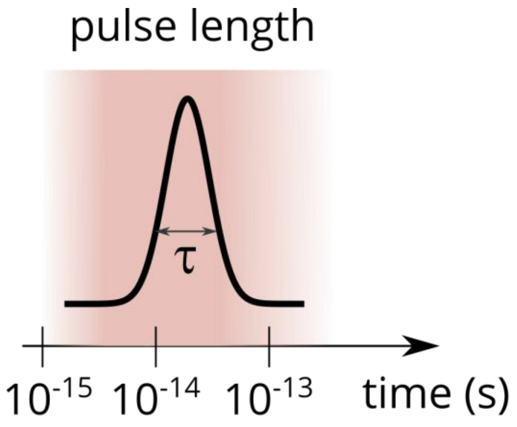
LCLS / SACLA / PAL-FEL
- 60 – 120 Hz repetition rate
- ~10 – 100 fs long pulses
- $\sim10^{12}$ photons per pulse

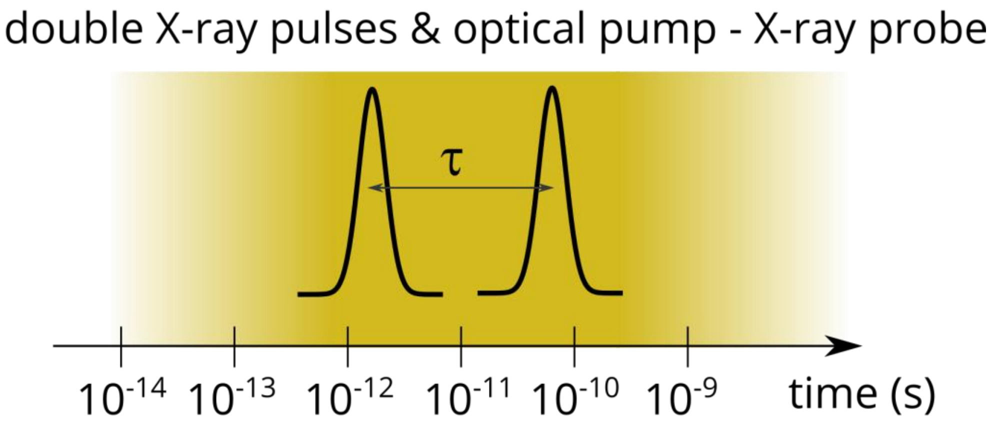


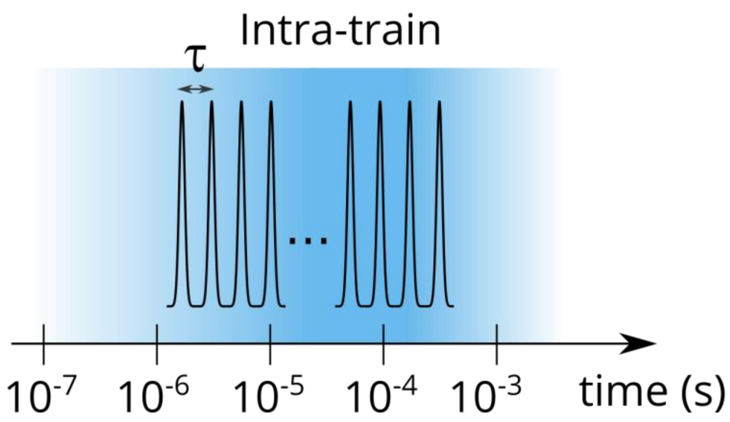
European XFEL
- Pulse trains of 2700 pulses
- Train repetition rate: 10 Hz
- Pulse repetition rate: 4.5 MHz
- ~10 – 100 fs long pulses
- $\sim10^{12}$ photons per pulse

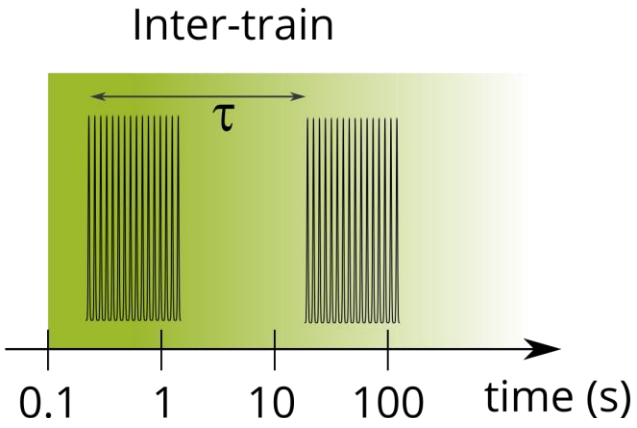


Research at free-electron lasers: Time-resolution at European XFEL


pulse length


double X-ray pulses & optical pump - X-ray probe

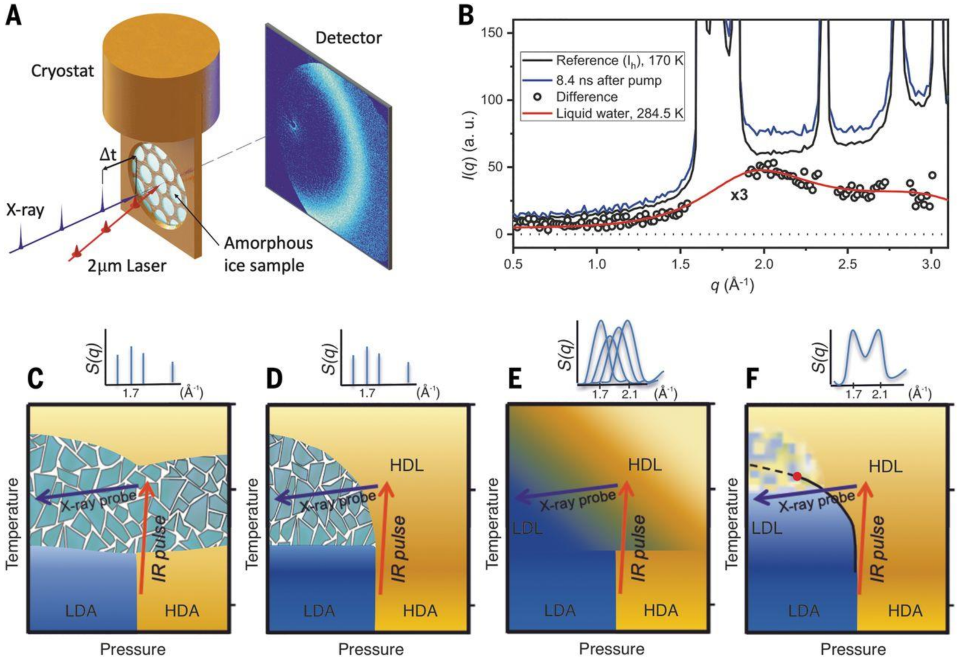

Intra-train

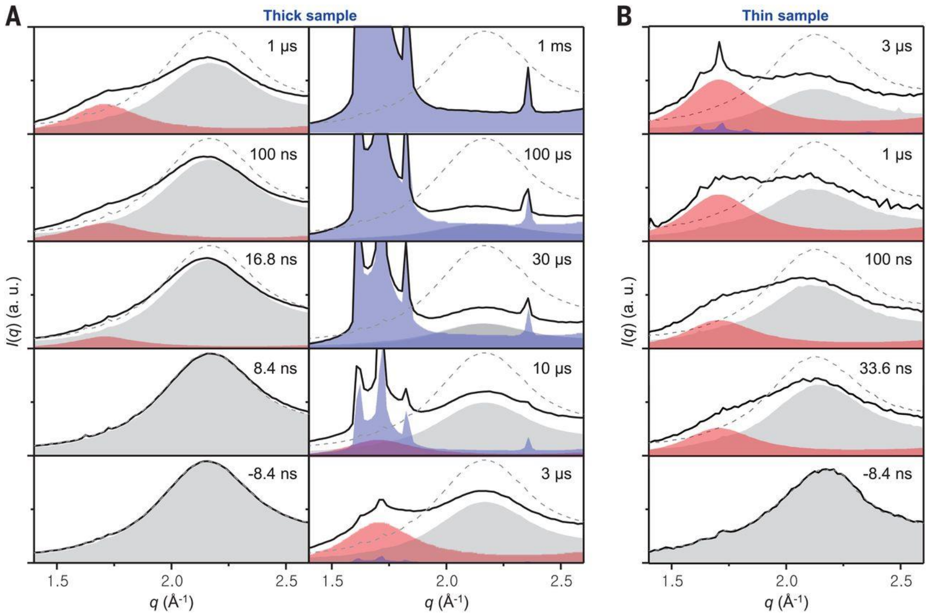

Inter-train

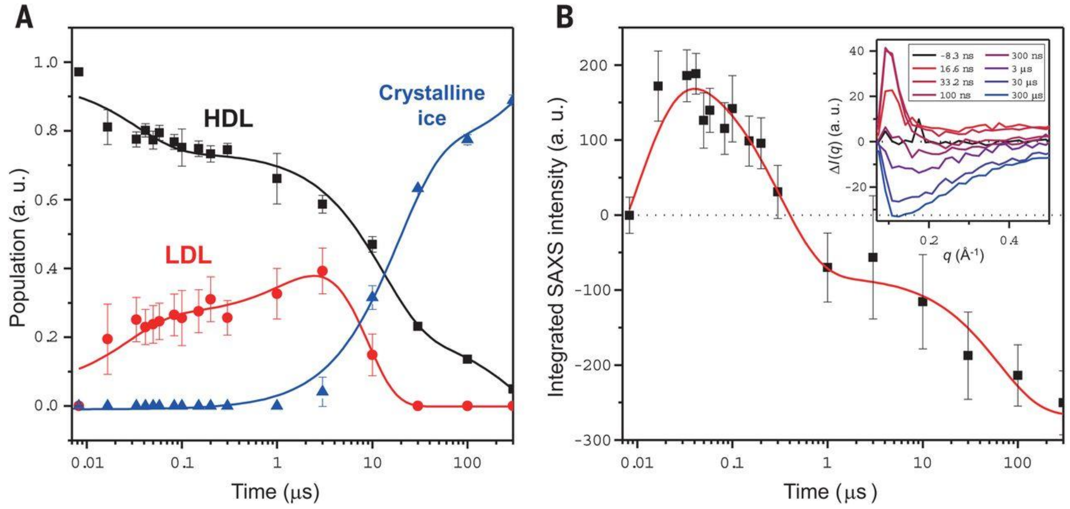
Water and ice: new results

Pump-probe on amorphous ice (PAL-FEL)

- Ice heated rapidly by short IR laser pulses (pump)
- Track structural changes by X-ray pulse with variable time delay (probe)
- Different scenarios expected





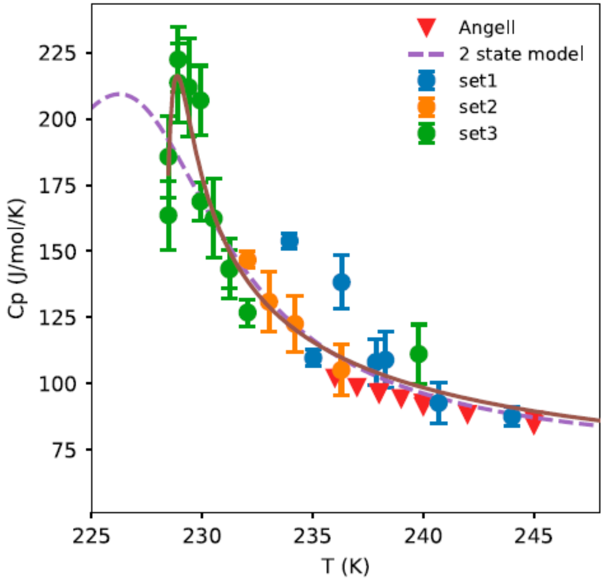


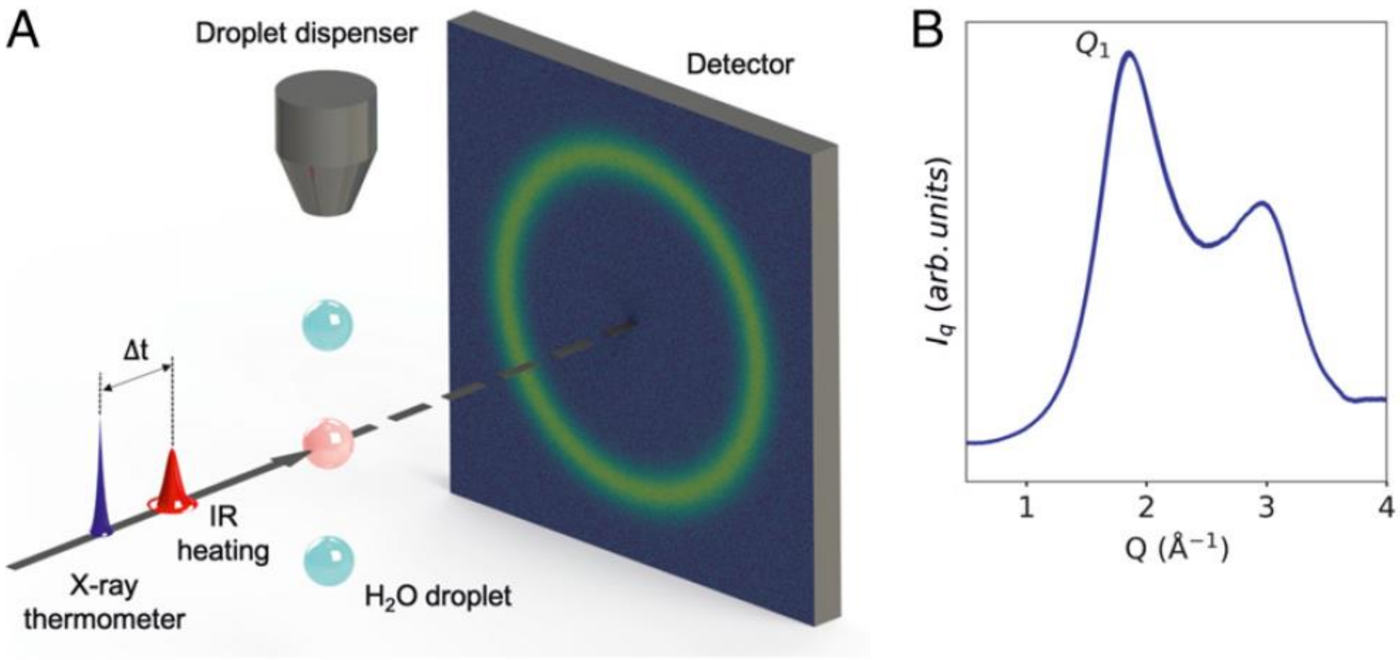
Science 370, 978 (2020)

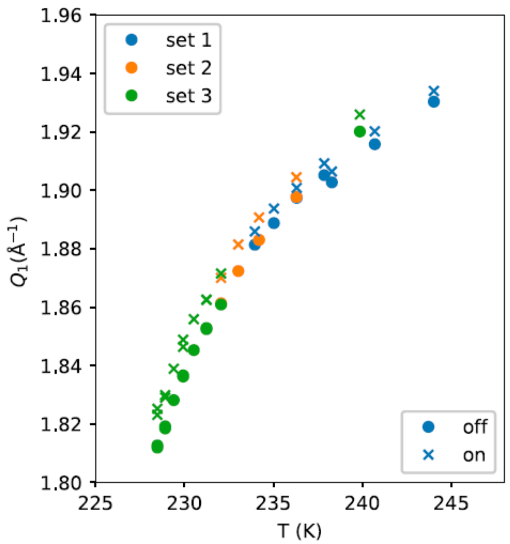
Water and ice: new results

Pump-probe on liquid water (SwissFEL)

- Liquid microdroplets: strong supercooling possible
- IR pulses to heat sample, probe by XFEL pulses
- Shift of structure factor peak as temperature measure → obtain specific heat c_p

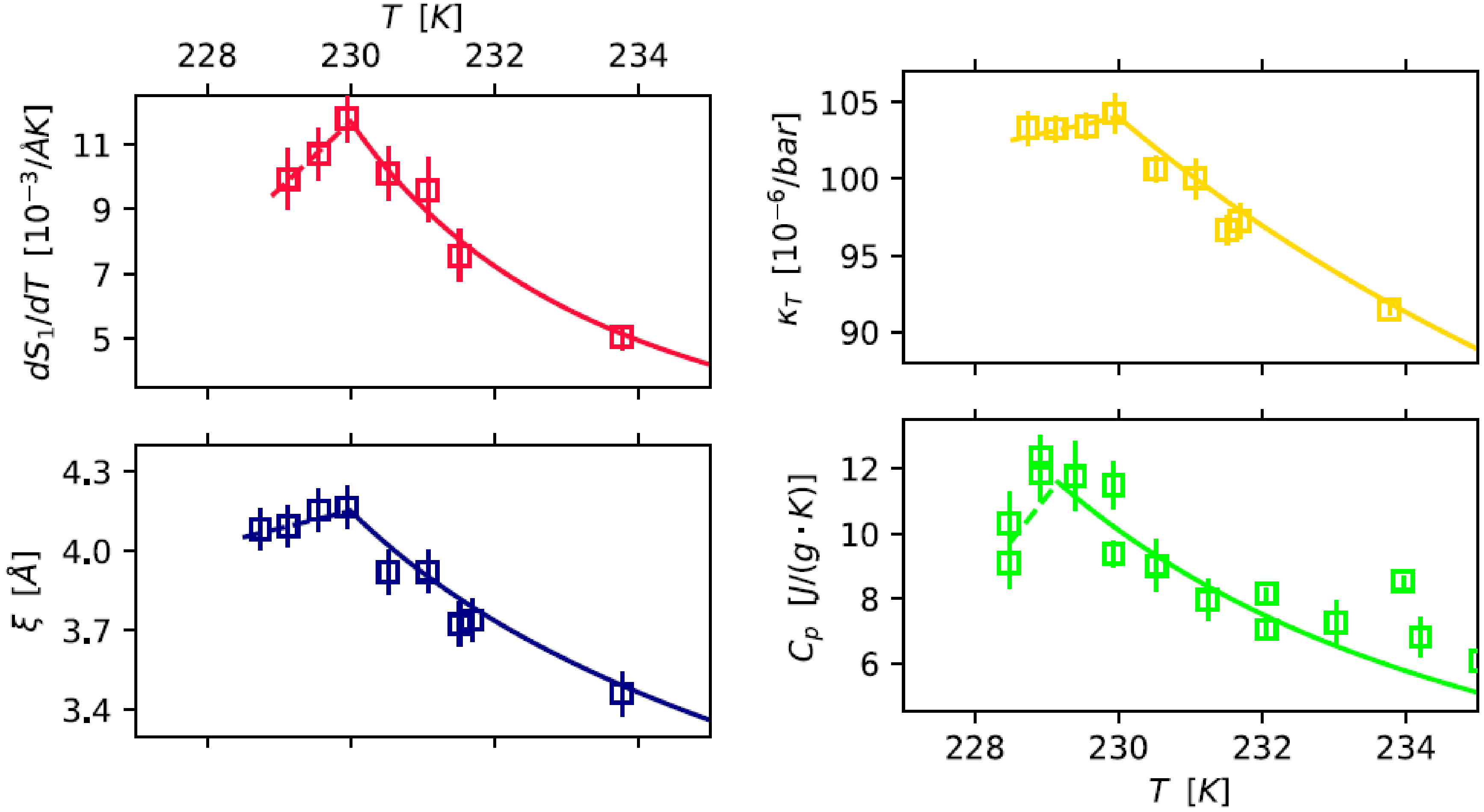






PNAS 118, e2018379118 (2021)

Water and ice: new results



Combining new results from FEL experiments suggest the existence of a liquid-liquid critical point

→ water as two liquids

→ Further proof by dynamics pending

→ Lower temperatures possible?

PNAS 118, e2018379118 (2021)

Dynamics: XPCS at FEL

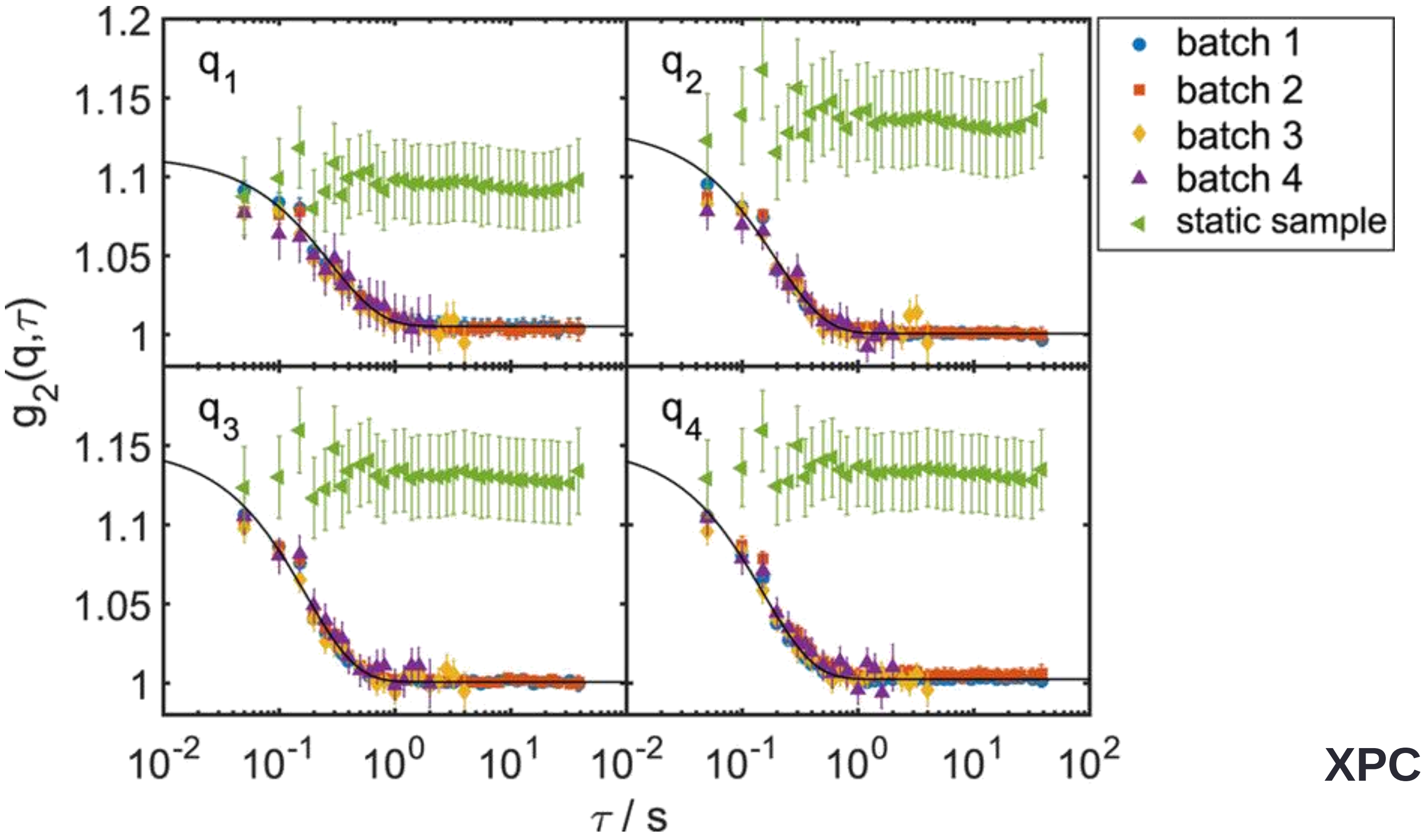
Parameter	Storage ring	FEL
Time Structure	Continuous	Pulses
Coherence	Partial	Full
Intensity	Stable	Fluctuations
Position / pointing	Stable	Fluctuations
Energy spectrum	Stable	Fluctuations
Time lag	Detector- and flux-limited ($\geq 10^{-6}$ s)	Repetition rate (60/120 Hz: LCLS/SACLA >MHz: E-XFEL)

} Challenging!

State-of-the-art detectors at storage rings

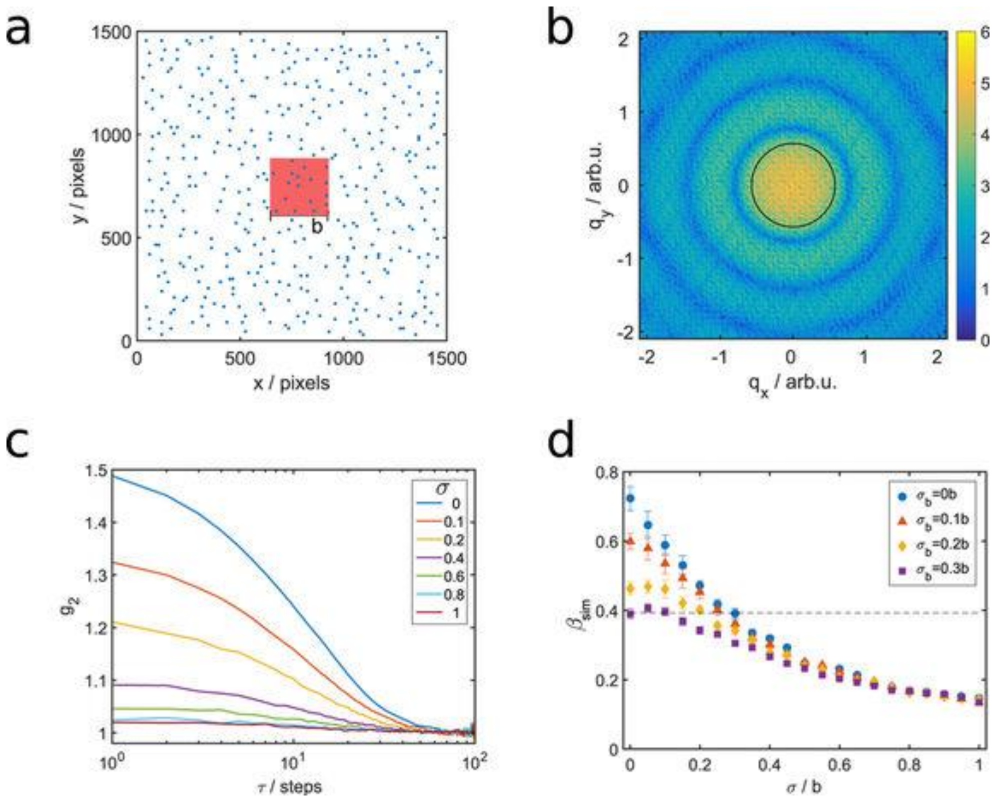
e.g. Eiger, Lambda	~ kHz
(Prototype) detectors with special modes	~MHz

XPCS example – XPCS at FEL



Diffusion of nanoparticles in glycerol and static sample with 20 Hz rep. Rate

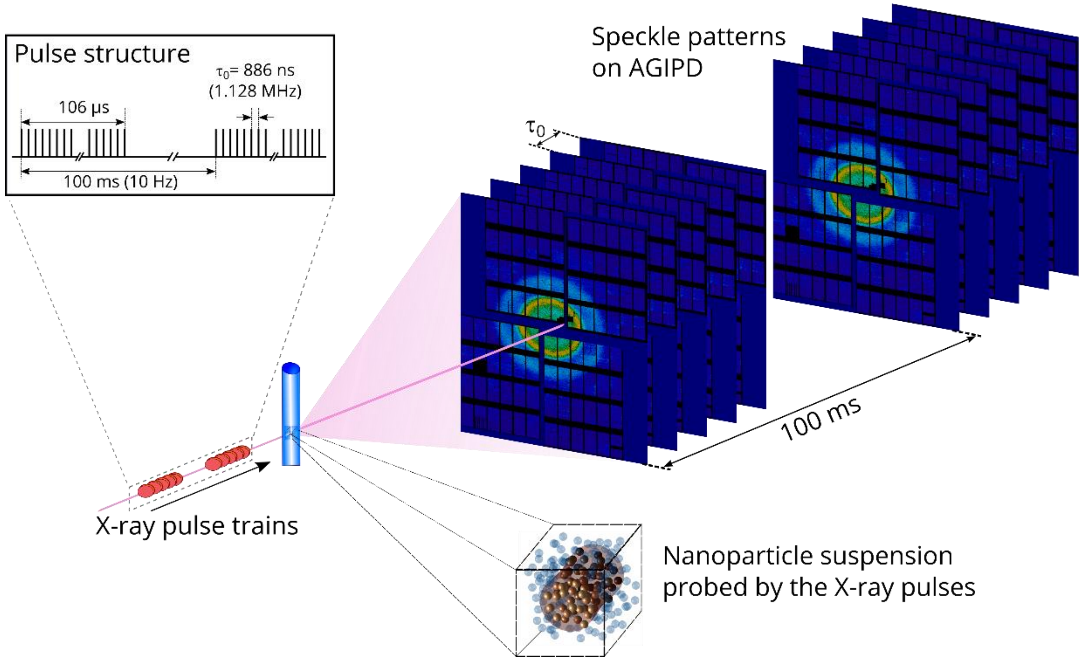
Sci. Rep. 5, 17193 (2015)



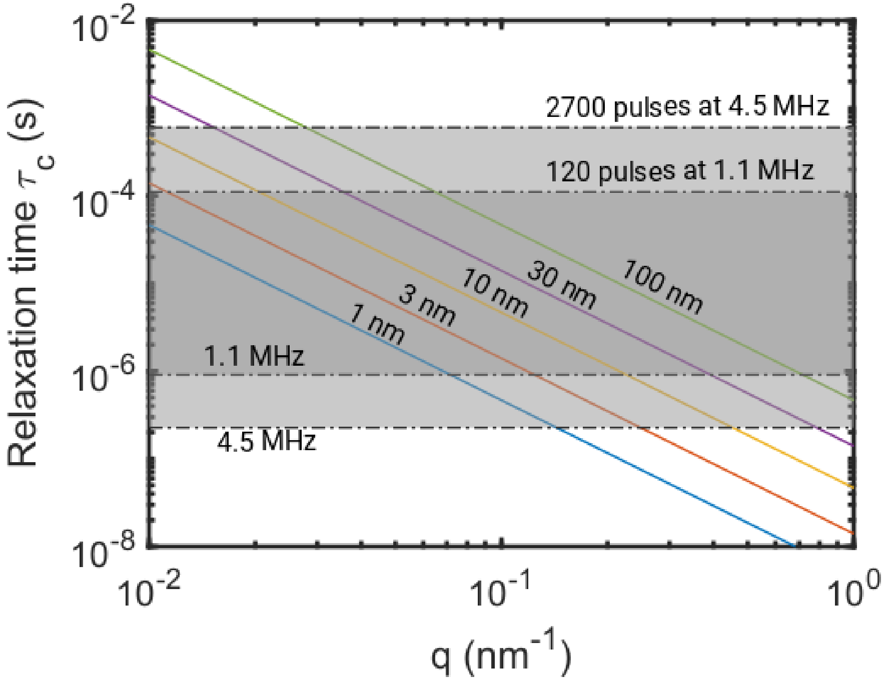
XPCS simulations

- Moving beam & beam size modifications on shot-to-shot basis
- Drop of effective contrast

XPCS example – µs XPCS at European FEL



Diffusion of colloidal particles with $r = 68$ nm dispersed in water

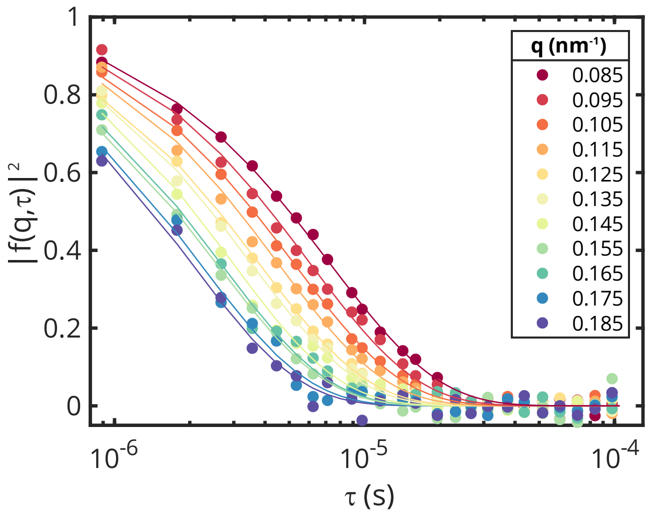


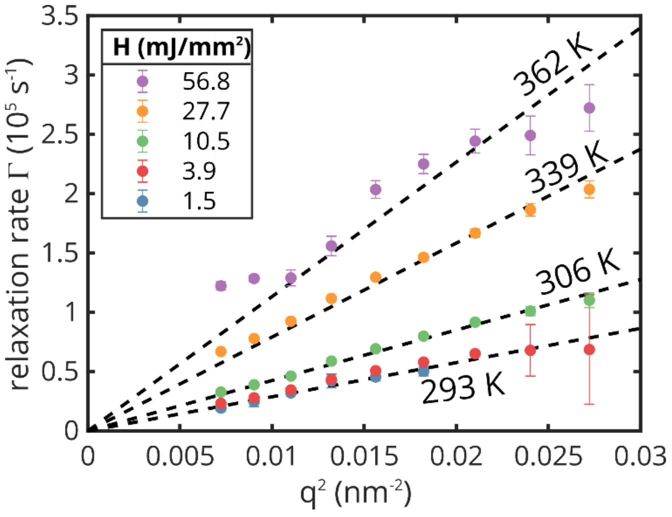
Expected relaxation times for diffusion of different particles in water

$$\frac{1}{\tau_c} = Dq^2 = \frac{k_B T}{6\pi\eta r q^2}$$

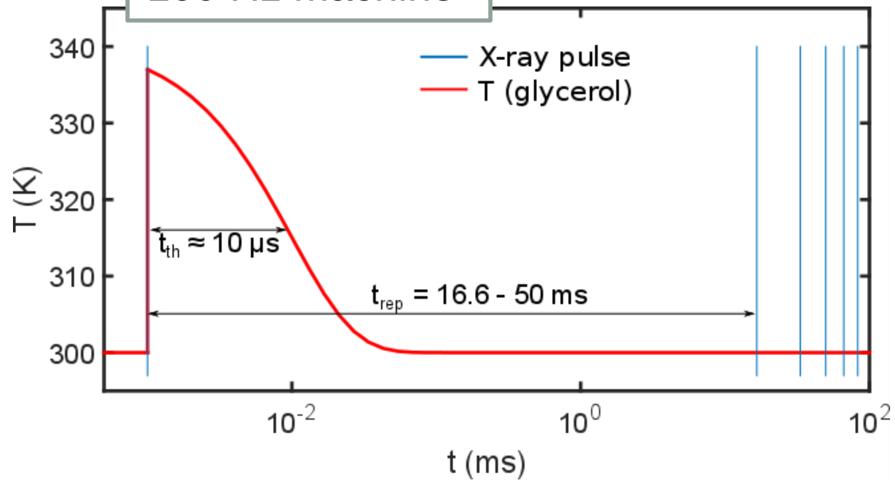
→ typical soft matter case needs sub-µs time scales

XPCS example – µs XPCS at European FEL

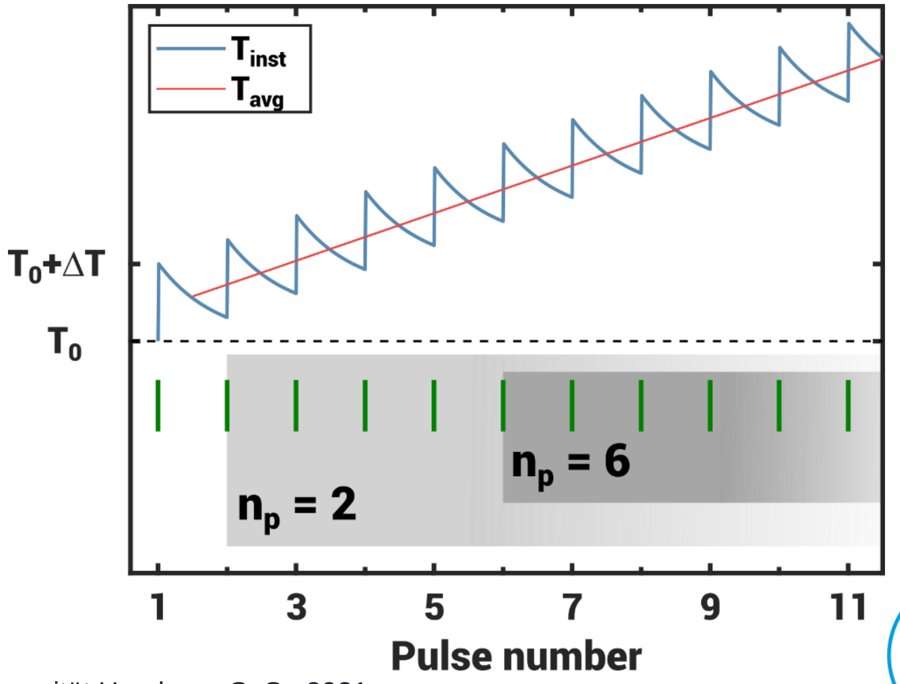




100 Hz machine



MHz machine

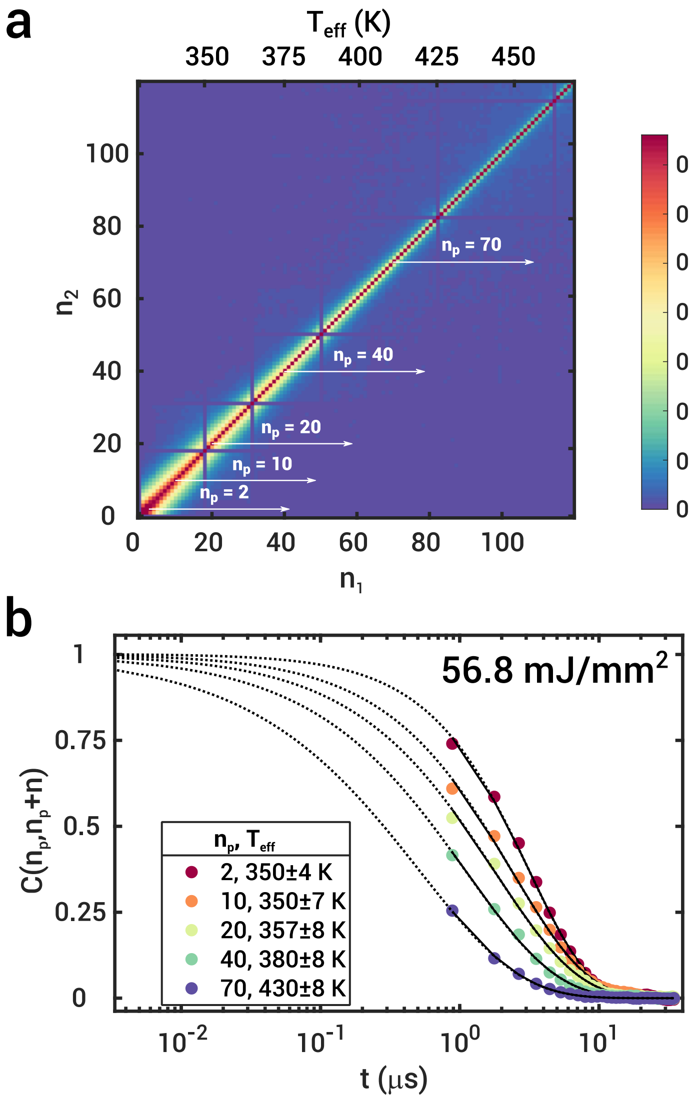


- High stability during pulse trains
- Single-train correlation function
- q-dependence of relaxation $g_2 - 1 = \beta\,\exp(-2\Gamma\tau)$

→ Diffusion $\Gamma = Dq^2 = \frac{k_B T}{6\pi\eta(T)r}\,q^2$

Indication for beam-induced heating
→ Increase of effective temperature with pulse intensity

Quantify heating via two-time correlations



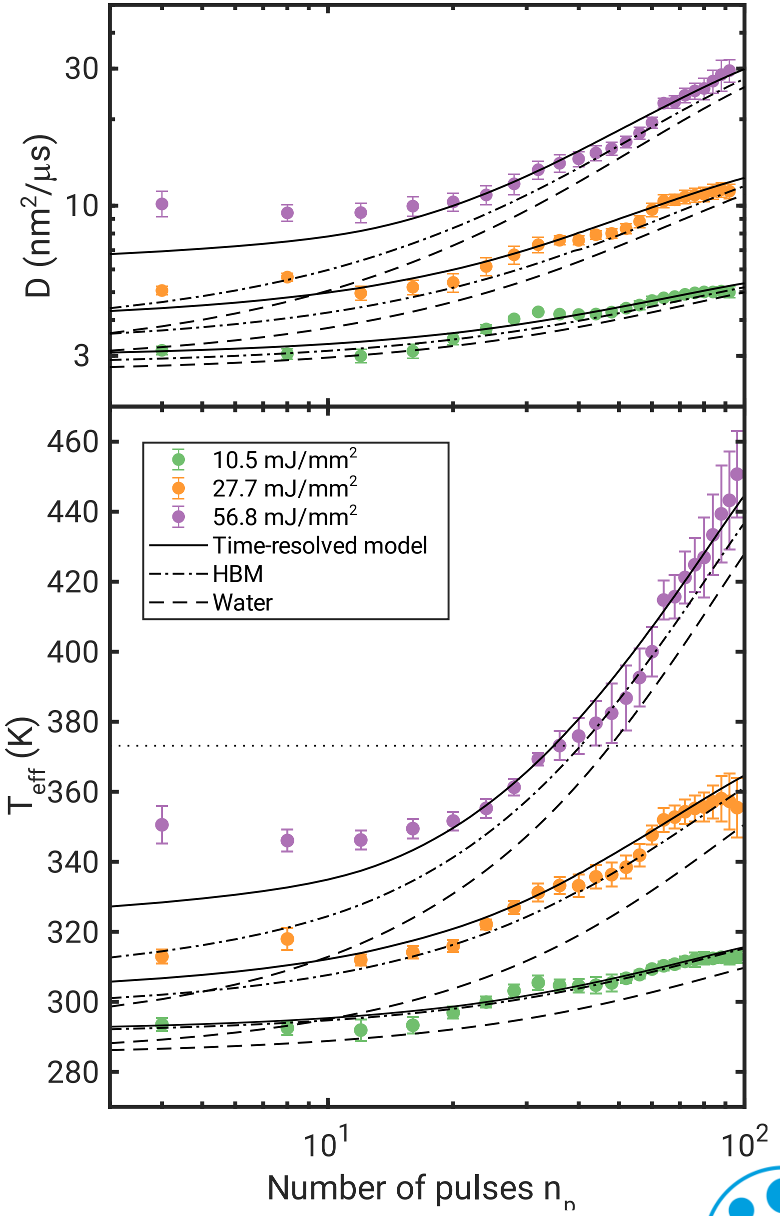
Diffusion coefficient D as function of n_p

a) **Water heating** only

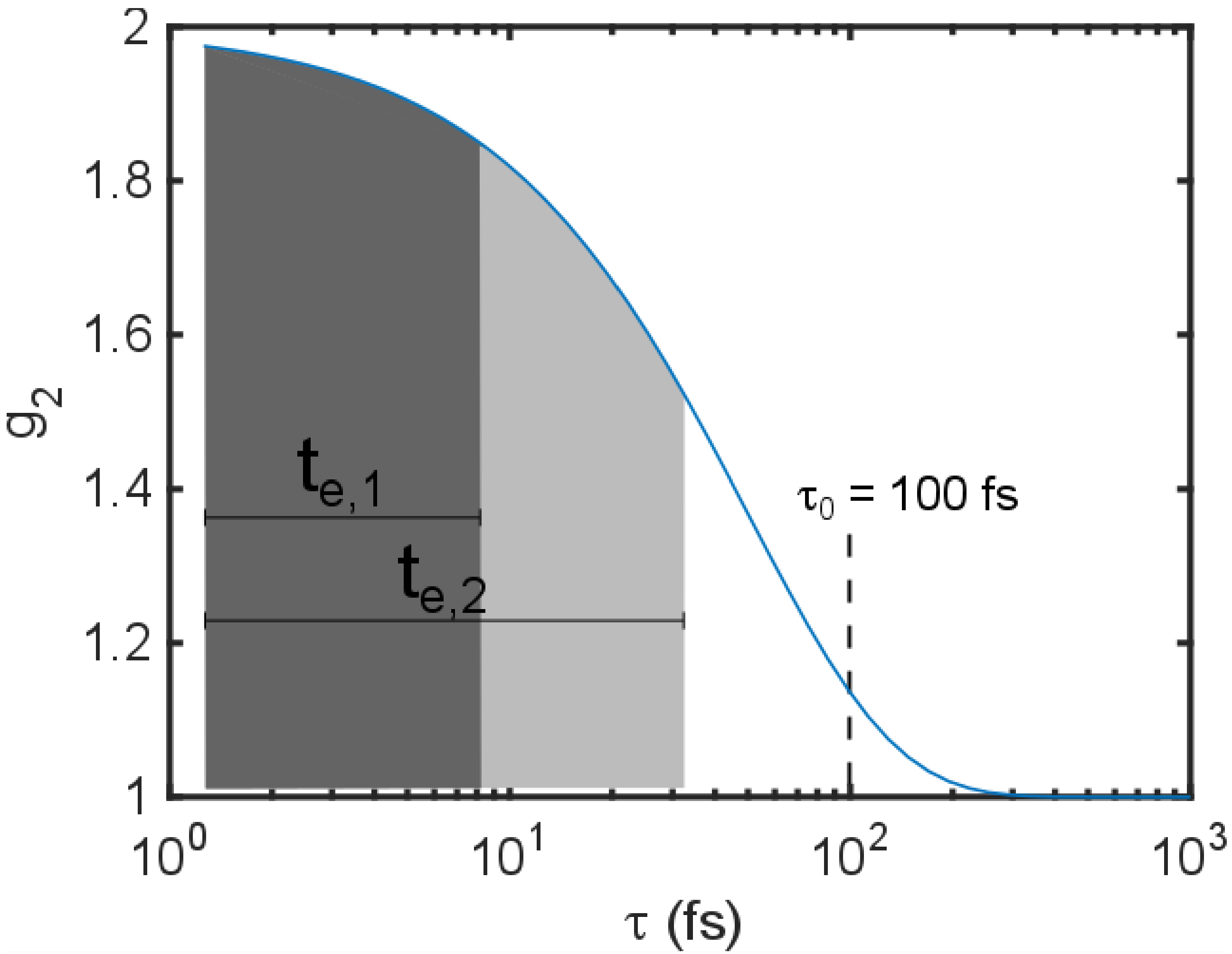
b) **Hot Brownian motion***: „hot“ particle diffusion in „colder“ environment, with water temperature from a

c) **Time-resolved model**: Use the actual time-resolved temperature profile of particles and water

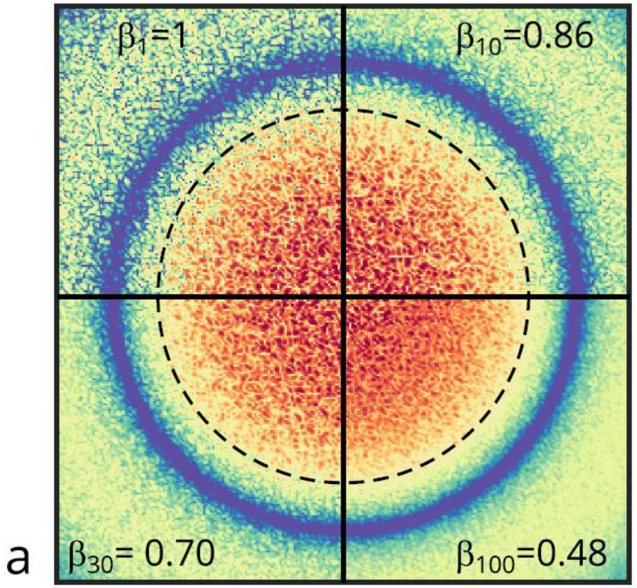
- Increase of T_{eff} above 373 K → Water still in a liquid state (diffusive dynamics) → superheating of water
- Initial temperature increase still underestimated



Ultrafast XPCS: X-ray Speckle Visibility Spectroscopy



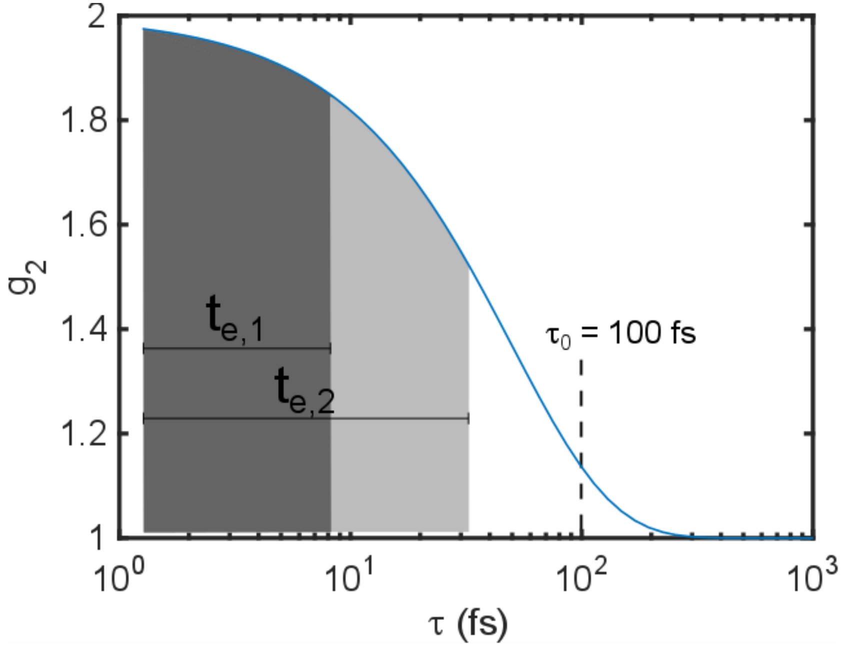
- So far: short exposure time $t_e \ll \tau_0$
- Dynamics change during exposure → reduction of contrast
- Typical FEL pulse length: $\tau_0 = 100$ fs

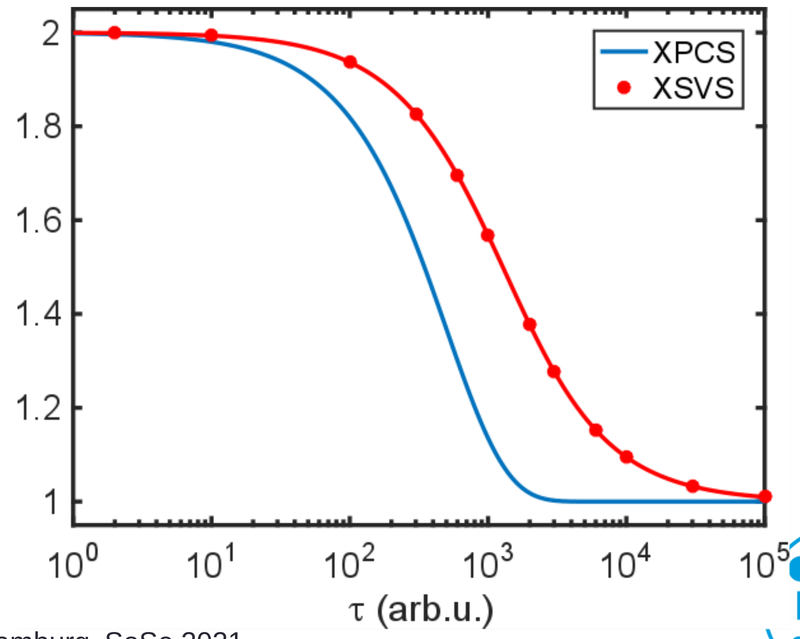


Ultrafast XPCS: XSVS

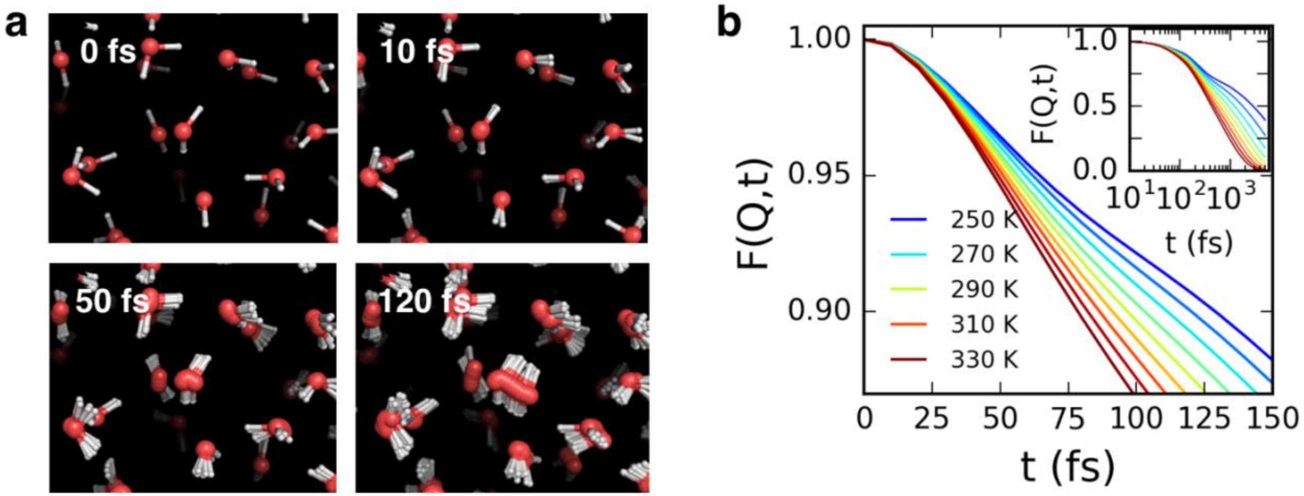
Finite pulse lengths

- Contrast as function of exposure ($\beta^2 = \frac{\langle I^2 \rangle}{\langle I \rangle^2} - 1$)
- $\beta^2(q, t_e) = \frac{2\beta_0^2}{t_e} \int_0^{t_e} \left(1 - \frac{\tau}{t_e}\right) |f(q,\tau)|^2 d\tau$
- For diffusion, this can be solved analytically (→ Exercise!)
- Limited by accessible exposure times
  - Pulse lengths (FEL)
  - Detector read out & flux (storage rings)
- FEL: pulse lengths variations & split-pulse applications





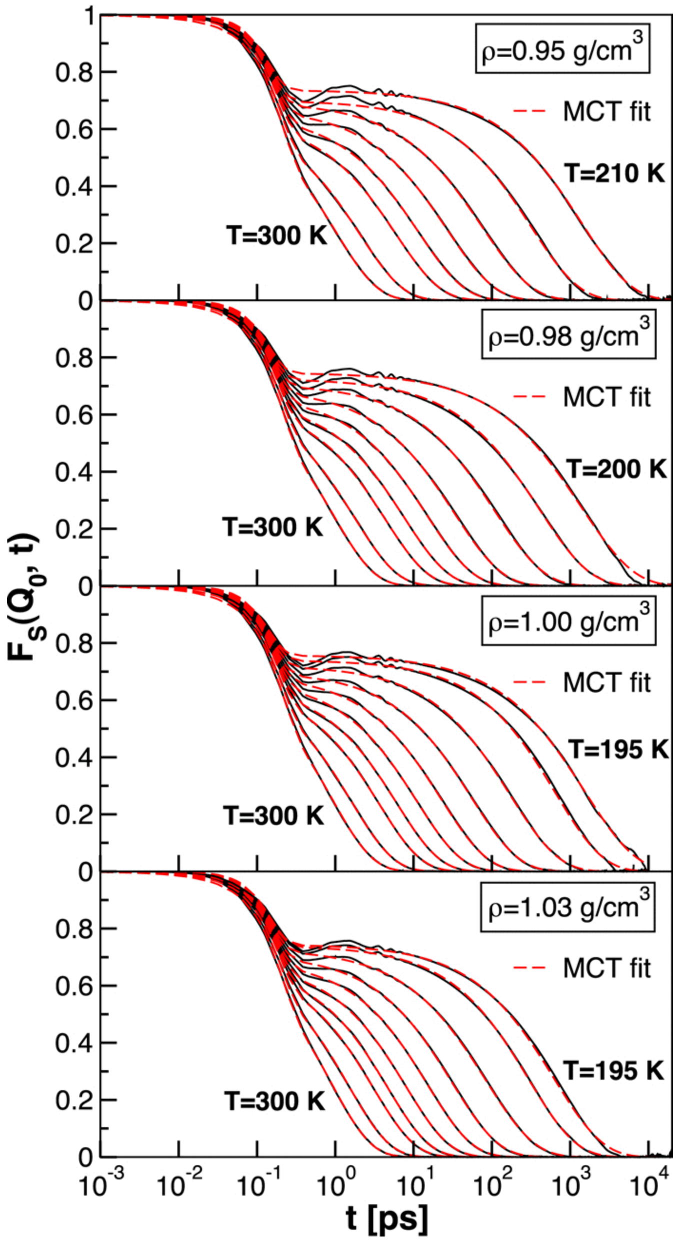
Dynamics in liquid water



- Liquid water: fs dynamics → FEL pulse length

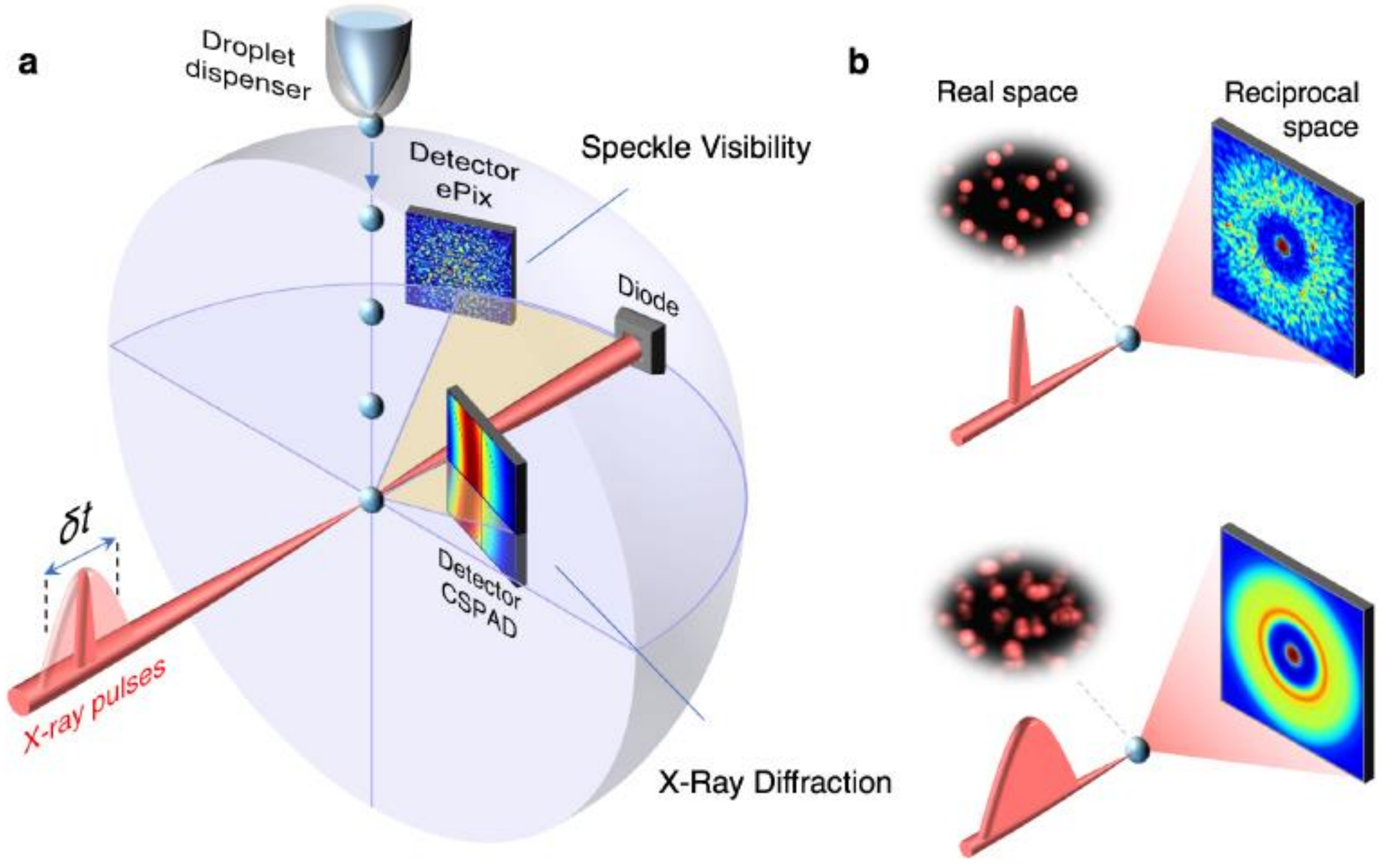
- MD simulations of liquid water show two-step decay of intermediate scattering function
  - → fragile-to-strong crossover
  - → LLCP hypothesis

Nature Comm. 9, 1917 (2018).



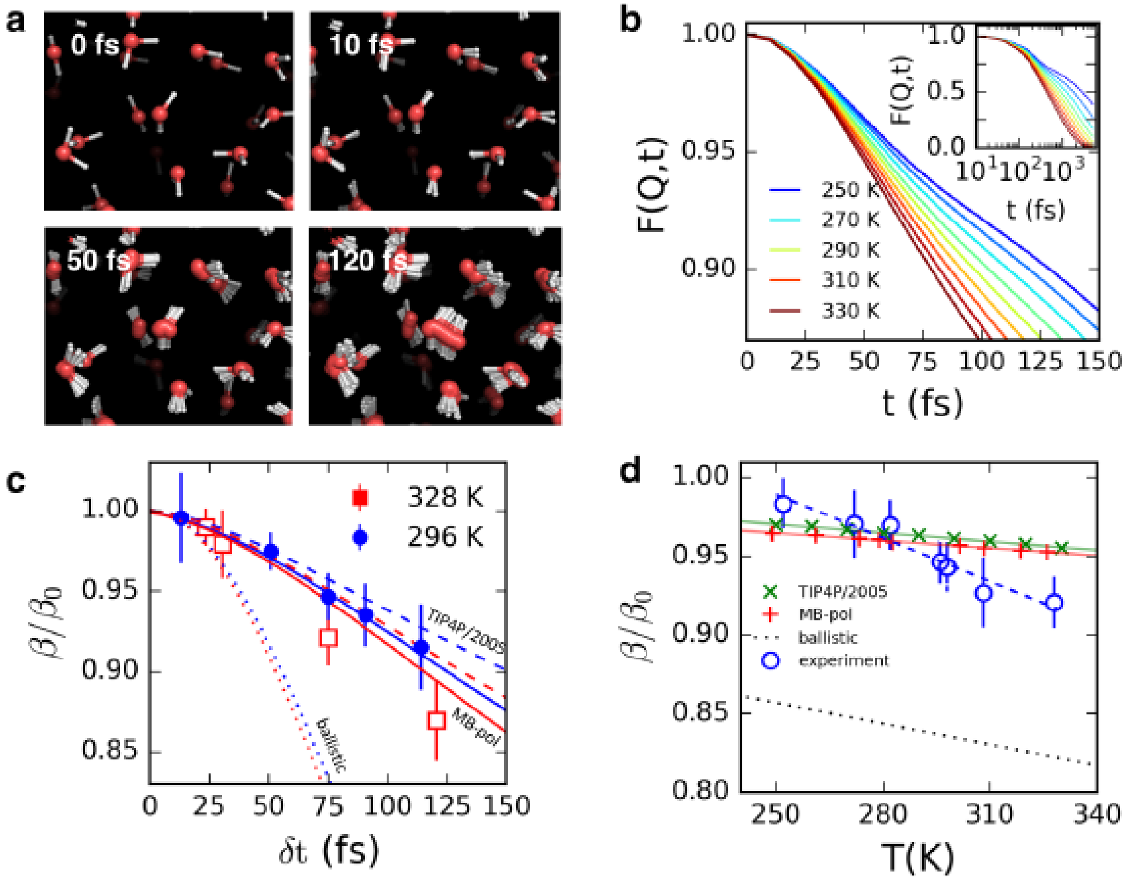
JCP 144, 074503 (2016)

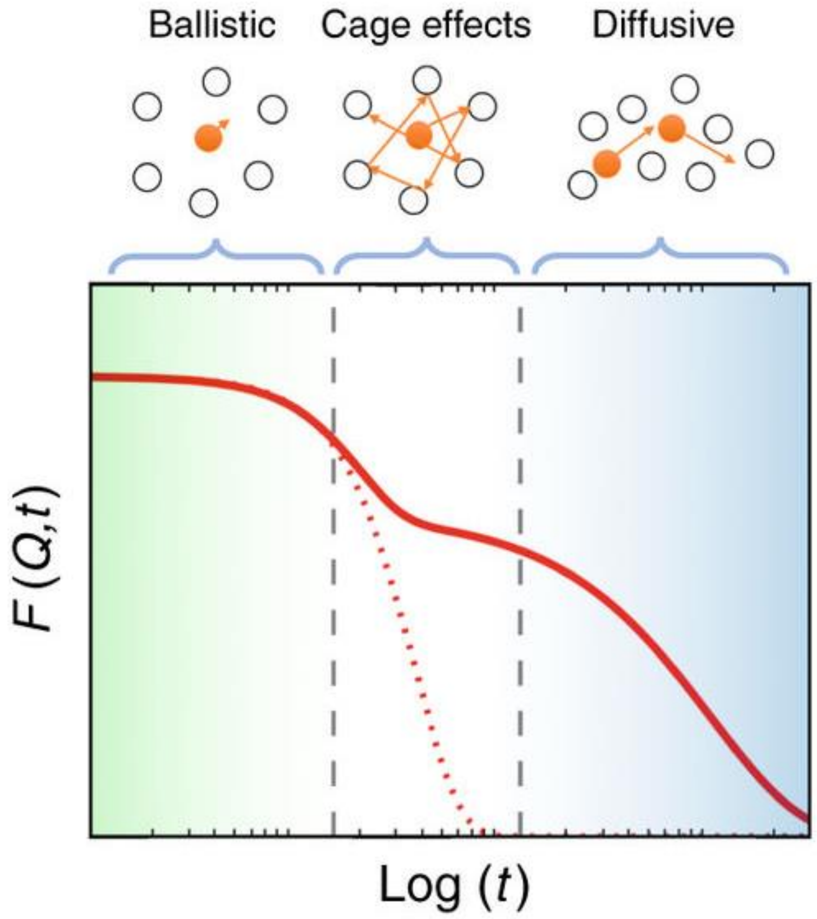
Dynamics in amorphous ices & liquid water



- XSVS experiment
- FEL pulse length variation between 10 fs to 130 fs
- Water structure factor peak around 2 Å^{-1}
- >10000 shots per setting

Nature Comm. 9, 1917 (2018).



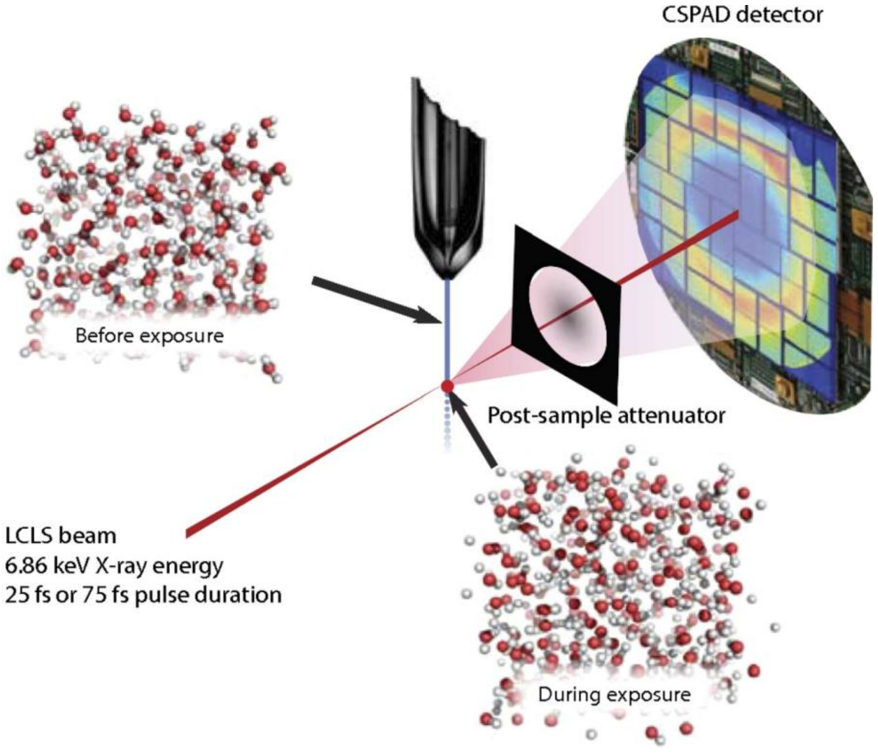


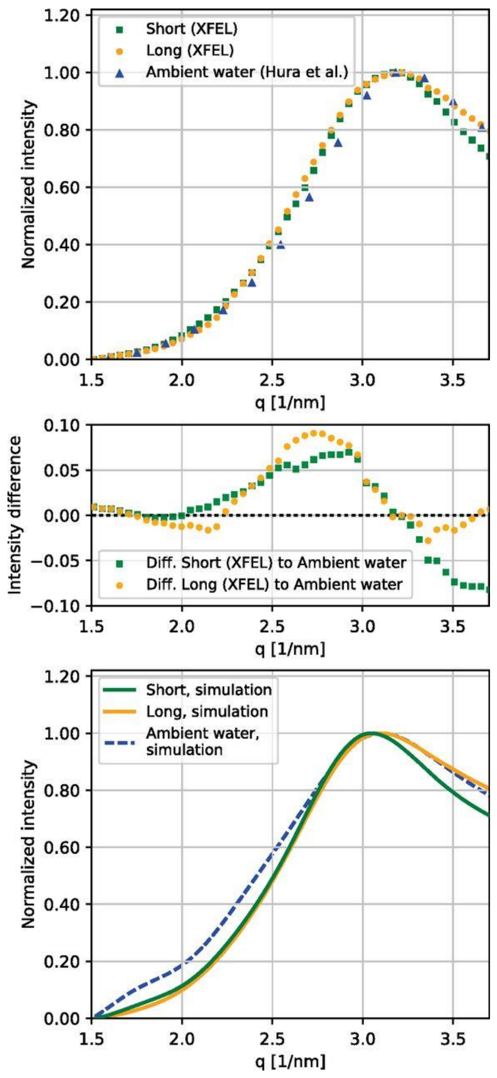
- Molecular dynamics in real time experiments
- Influence from H-bonding at sub-100 fs time scales
- "Cage effects"

Nature Comm. 9, 1917 (2018).

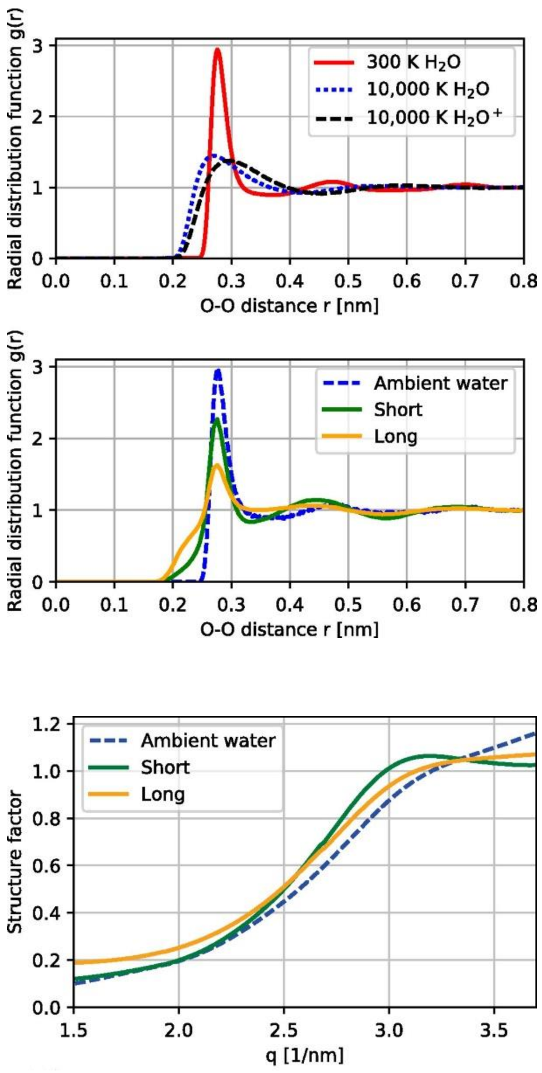
REMINDER - Fast water heating at FEL sources

Microdroplets → stronger supercooling possible





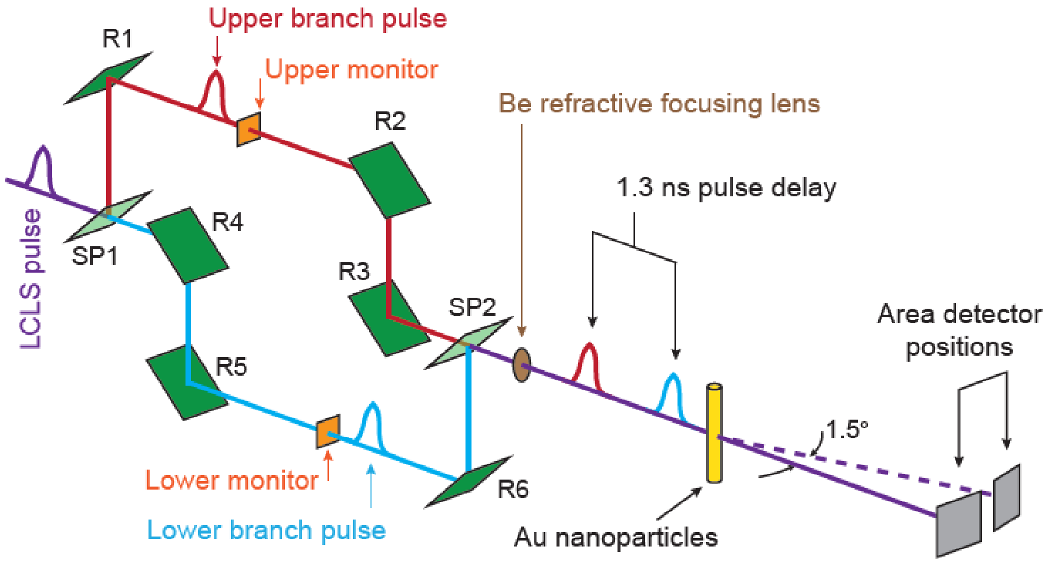
Pulse-length dependence of structure factor

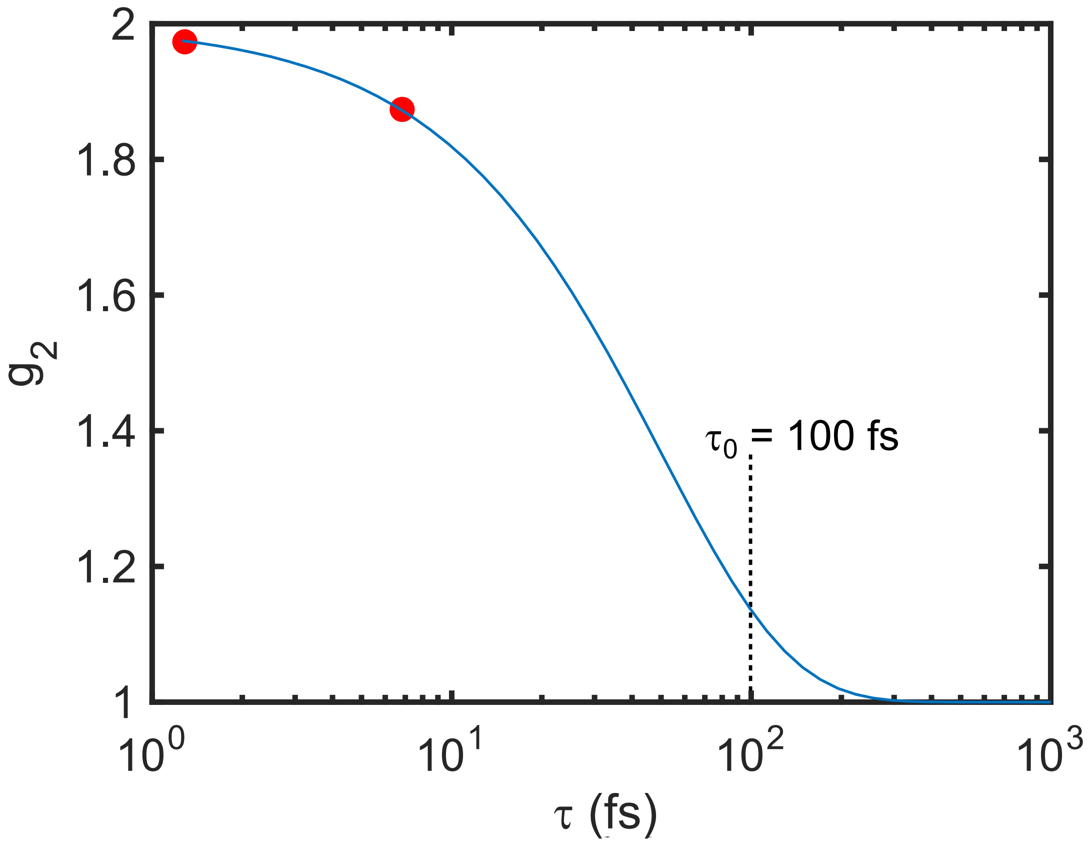


Simulation results

PNAS 115, 5652 (2018)

Ultrafast XPCS: double shot

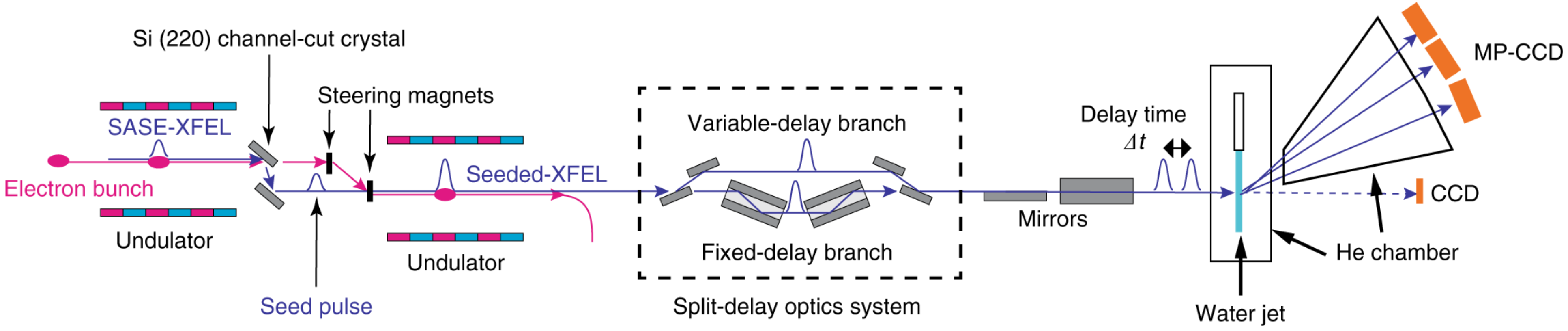


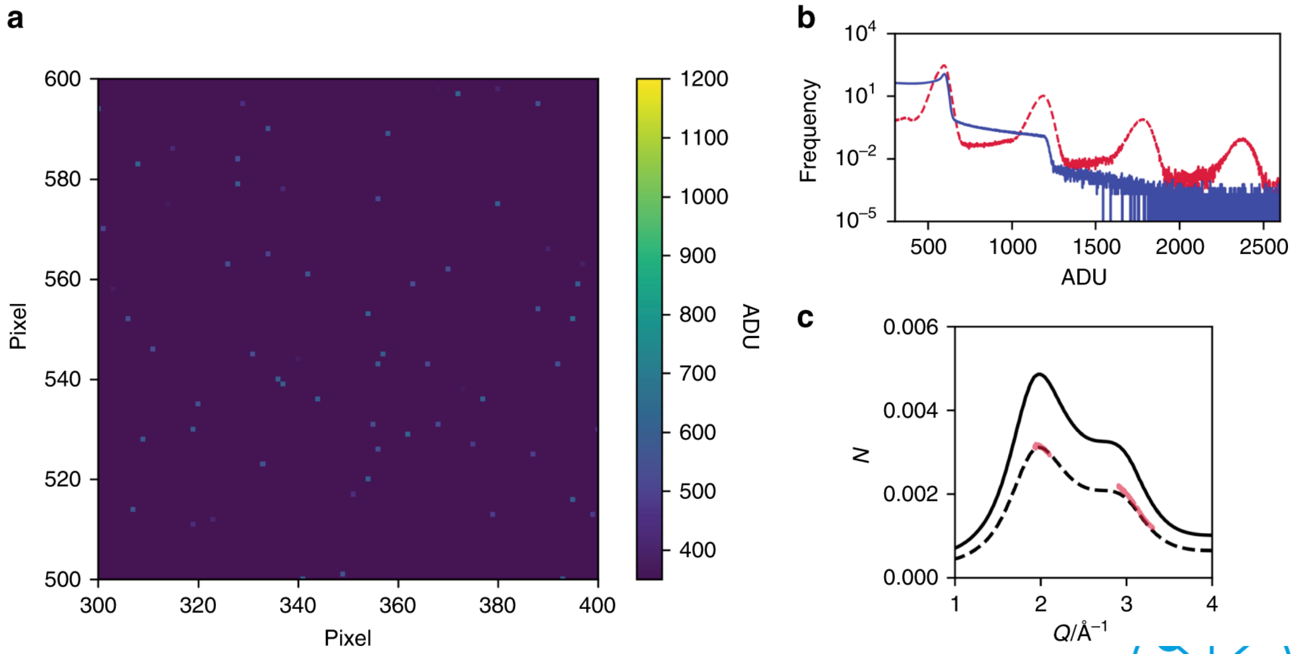


- Split FEL pulse in two and delay one of them
- Speckle pattern: sum of two patterns
- XSVS-type of analysis
- Typically low count rates → obtain contrast from distribution functions of intensity

W. Roseker et al. Nature Comm. 9, 1704 (2018)

Ultrafast XPCS: double shot

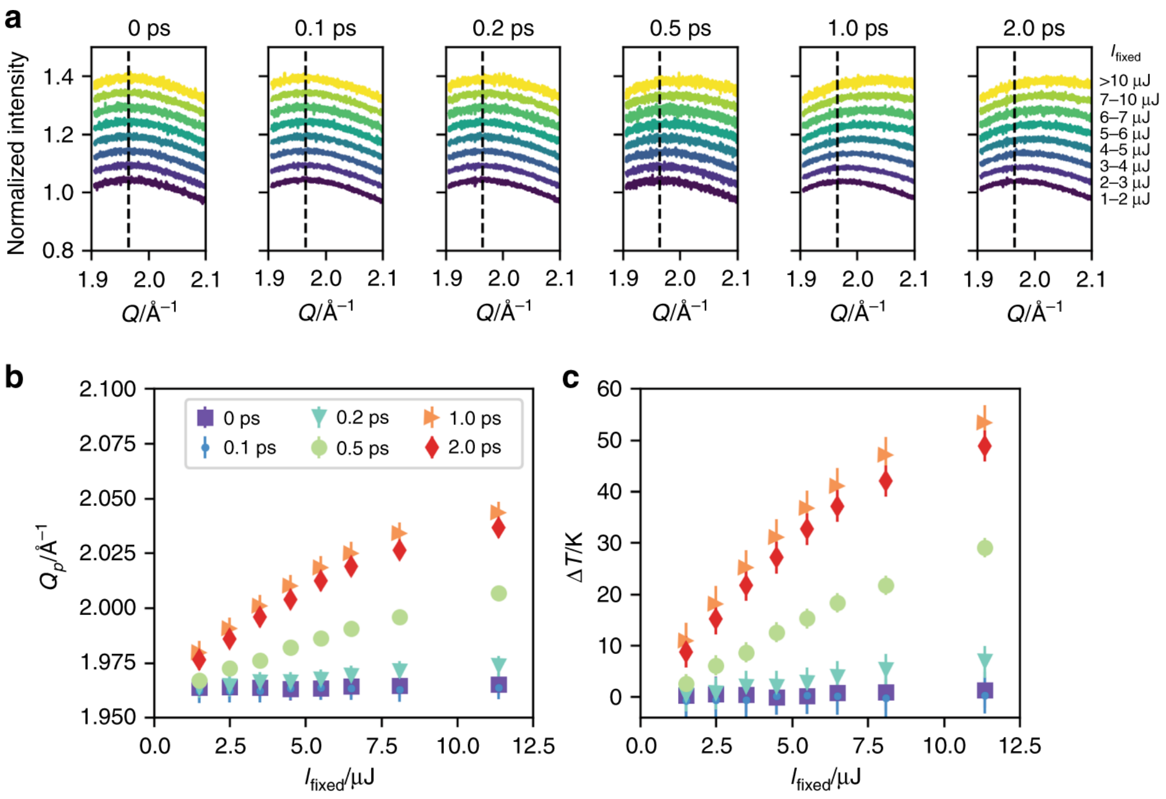


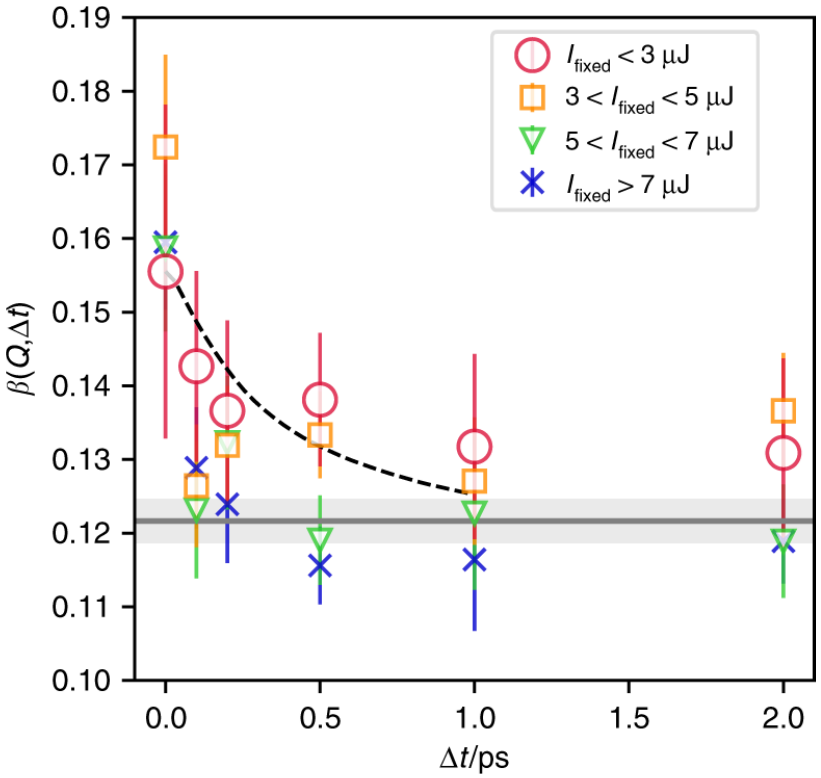


- Double pulse study on dynamics in liquid water at SACLA
- Pulse delays up to 2 ps
- Detector at large angles ($q \sim 2$ Å^{-1})
- Self-seeding to reach lower bandwidth → reduced longitudinal coherence
- Low countrate: $> 10^5$ patterns per delay
- Optimized analysis: droplet algorithm

Nature Comm. 11, 6213 (2020)

Ultrafast XPCS: double shot





XSVS result follow expecations for low intensities, but suggest induced dynamics for high intensities

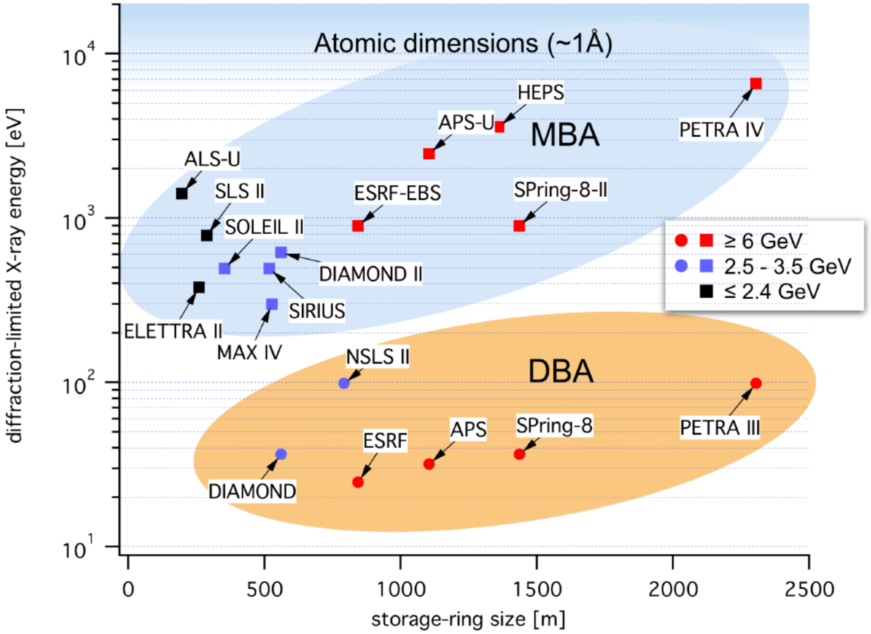
Temperature increases with longer delay times

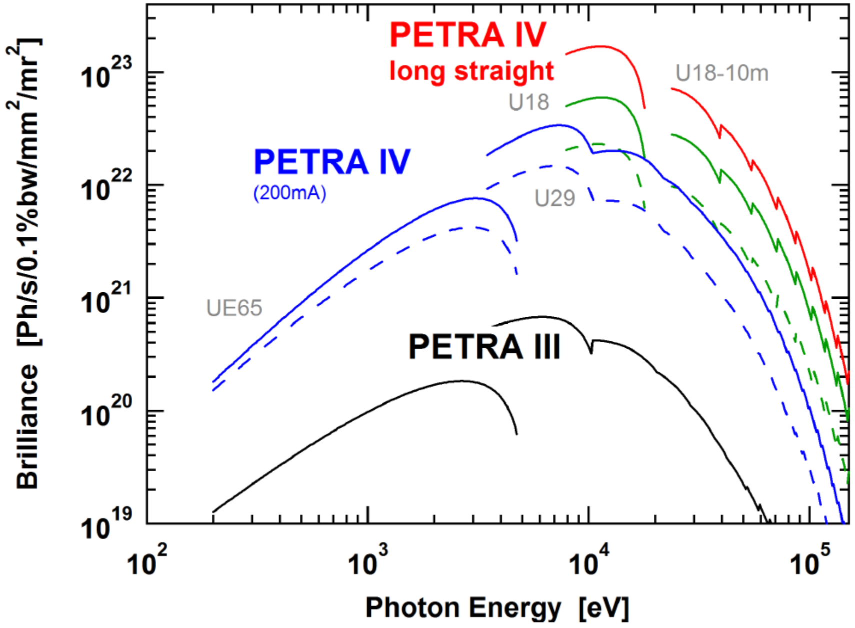
Nature Comm. 11, 6213 (2020)

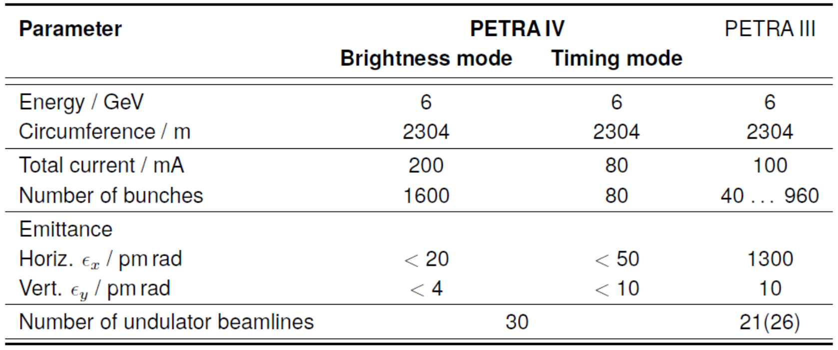
Diffraction-limited storage rings in a nutshell

New design of storage ring layout, especially magnets

- Reduce beam emittance
- Increase brilliance by ~2 orders of magnitude
- Diffraction limit: $\lambda_{DL} = 4\pi\epsilon$
- For $\lambda \geq \lambda_{DL}$: brightness dominated by single electron properties → source with generate coherent radiation → no increase of brightness at further decrease emittance values







Parameter	**PETRA IV**		PETRA III
	Brightness mode	**Timing mode**	
Energy / GeV	6	6	6
Circumference / m	2304	2304	2304
Total current / mA	200	80	100
Number of bunches	1600	80	40 . . . 960
Emittance			
Horiz. ϵ_x / pm rad	< 20	< 50	1300
Vert. ϵ_y / pm rad	< 4	< 10	10
Number of undulator beamlines	30		21(26)

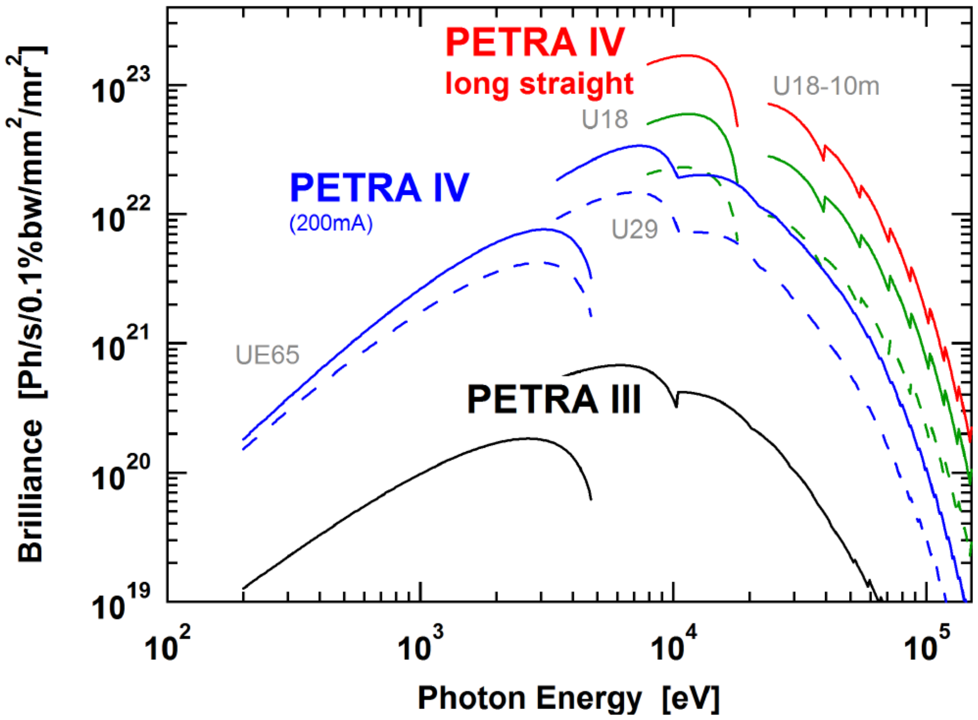
Diffraction-limited storage rings worldwide

(Almost) every synchrotron radiation source plans to upgrade

Name	Location	Circumference	Electron energy	Operational?
MAX IV	Lund, SWE	528 m	3 GeV	Yes
Sirius	Brasil	518 m	3 GeV	
ESRF-EBS	Grenoble, F	844 m	6 GeV	Yes
APS-U	Chicago, USA	1104 m	6 GeV	Technical concept phase
Spring-8 II	Japan	1436 m	6 GeV	
PETRA IV	Hamburg	2304 m	6 GeV	Technical concept phase
Diamond II	Didcot, UK	561 m	3 GeV	

Diffraction-limited storage rings - consequences

- Increase of brilliance
- Increase of coherence: coherent scattering & imaging will benefit
- Focussing to even smaller beams will become possible → nm beam sizes
- Coherence at higher energies: similar coherence at 100 keV as now for 10 keV
- Scattering and imaging with high energies: buried interfaces, high pressure chambers etc.



XPCS – signal to noise

- Reasonable definition $SNR = \frac{g_2 - 1}{\sqrt{\mathrm{var}(g_2)}}$

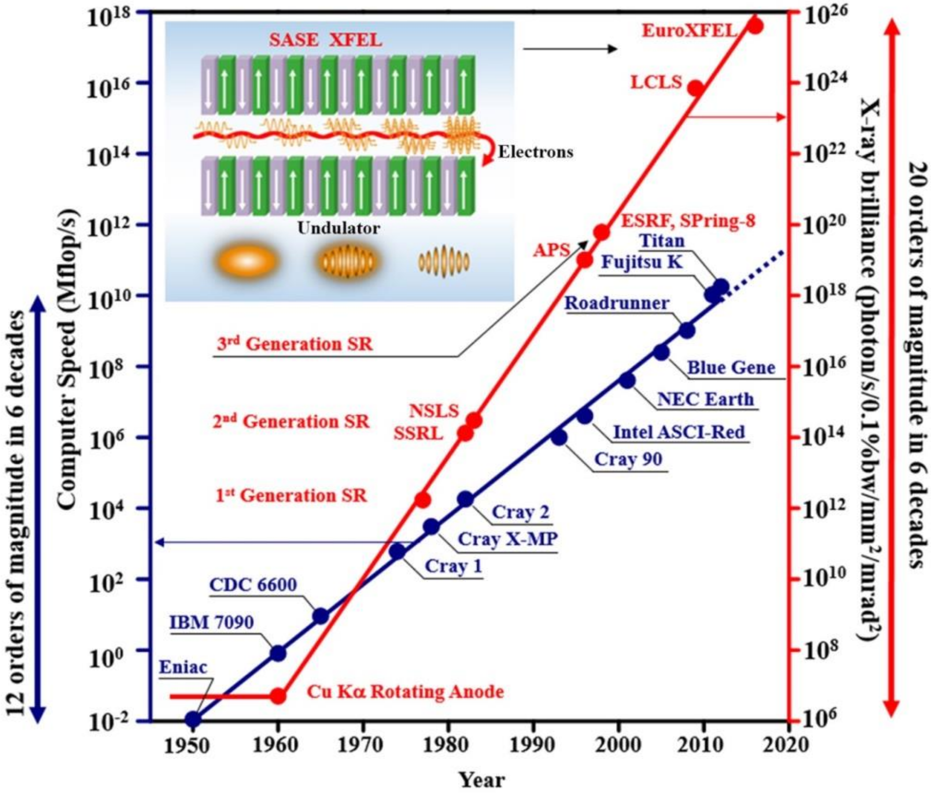
- $\mathrm{var}(g_2) = \frac{g_2}{N_p \langle n_c \rangle} = \frac{g_2}{n_x n_y T t_a I^2}$
  - N_p number of correlated pairs averaged for g_2
  - $\langle n_c \rangle$ mean number of counts per exposure time
  - Using count rate I per pixel, accumulation time t_a, number of pixels $P = n_x n_y$, total experimental duration T.

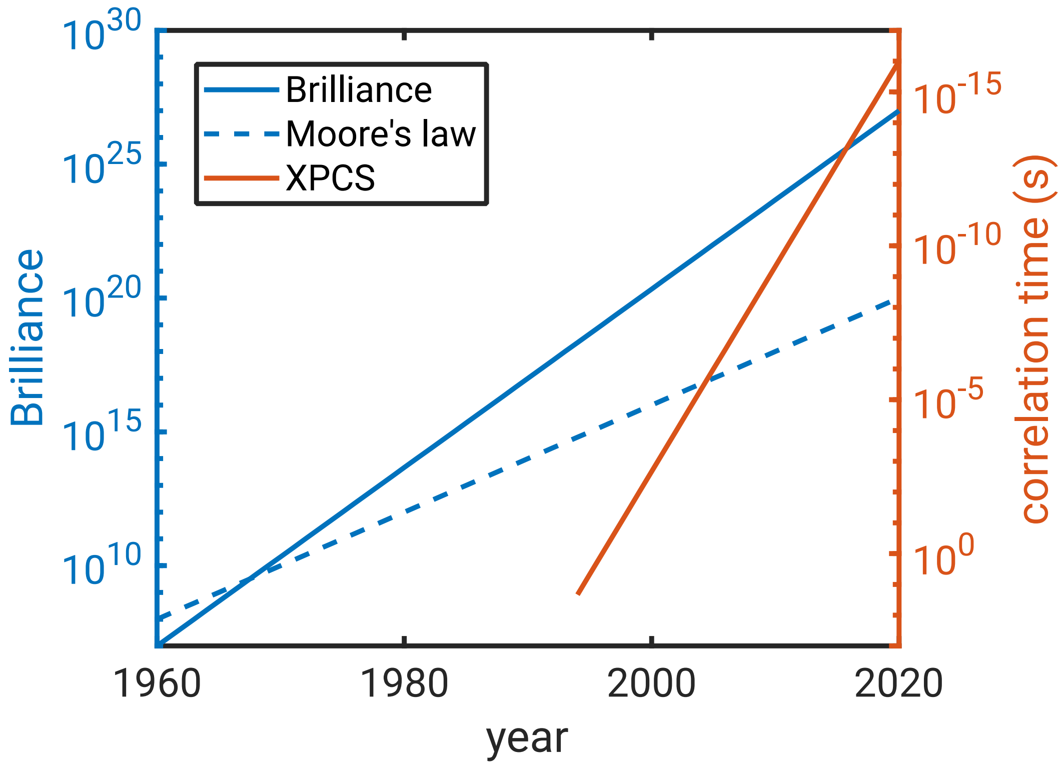
- $SNR = \frac{g_2 - 1}{\sqrt{\mathrm{var}(g_2)}} = \sqrt{PTt_a/g_2} \cdot I(g_2 - 1)$
  - Substitute g_2 with the limit of $\tau \to 0$: $g_2 = \beta^2 + 1$
  - Low contrast limit: $\sqrt{g_2} \approx 1$

→ $SNR = \beta^2 I \sqrt{PTt_a}$

- Consequence: Increase of I by 10 → accessible time scale 100x smaller at same SNR

see P. Falus et al. J. Synchr. Rad. 13, 253 (2006)





- Today: $\tau_c \geq 1$ µs
- Next-generation storage rings: 10^4 gain in $\tau_c \Rightarrow \tau_c \approx$ ns
- European XFEL (avg. Brilliance): 10^{10} gain in $\tau_c \Rightarrow \tau_c \approx$ fs
  - Limitations by pulse length and repetition rate

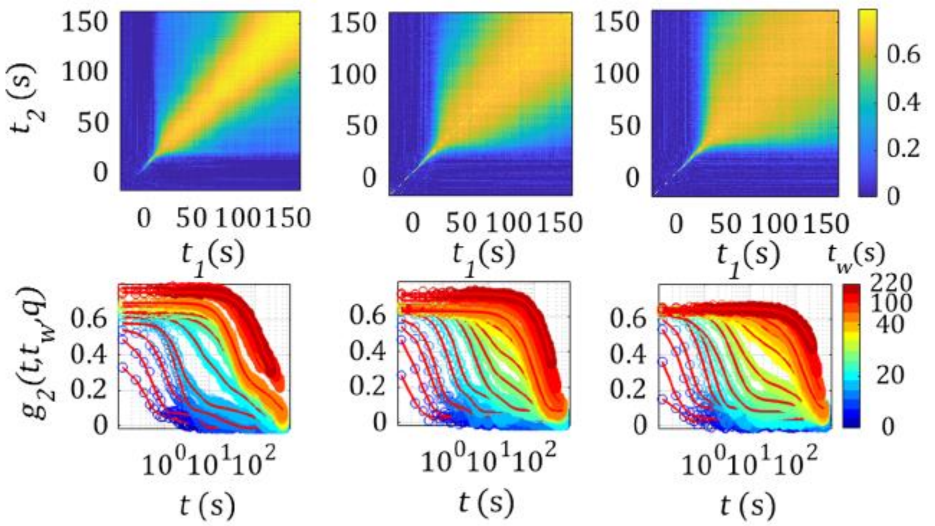
Dynamics of biological systems

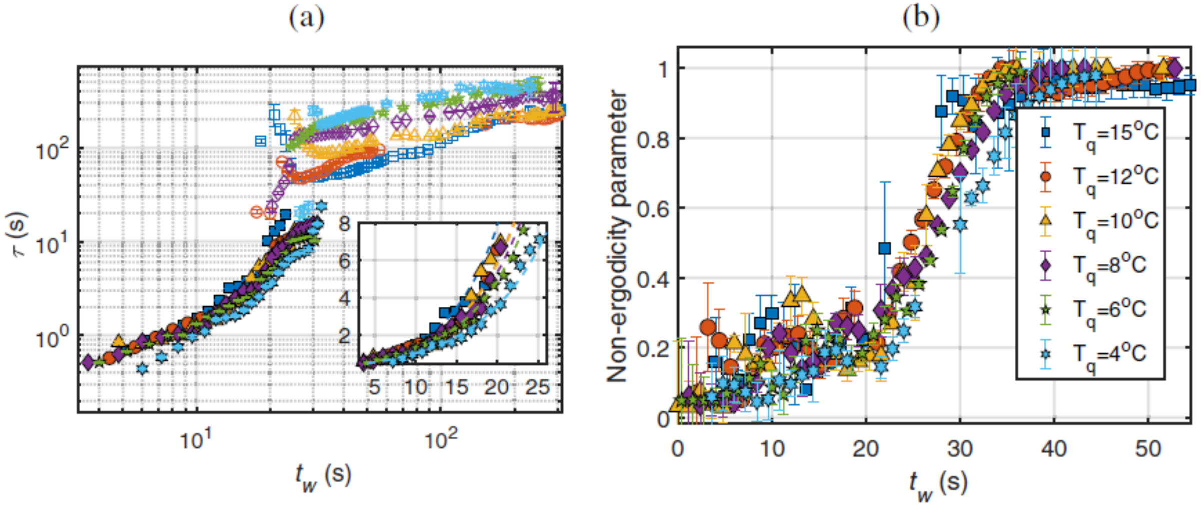
Liquid-liquid phase separation in dense protein solutions

Here γ globulin (Ig) in a concentrated aqueous polyethylene glycol (PEG) solution

Low-dose XPCS: large X-ray beam → low photon density
→ to be optimized in future: higher X-ray energies

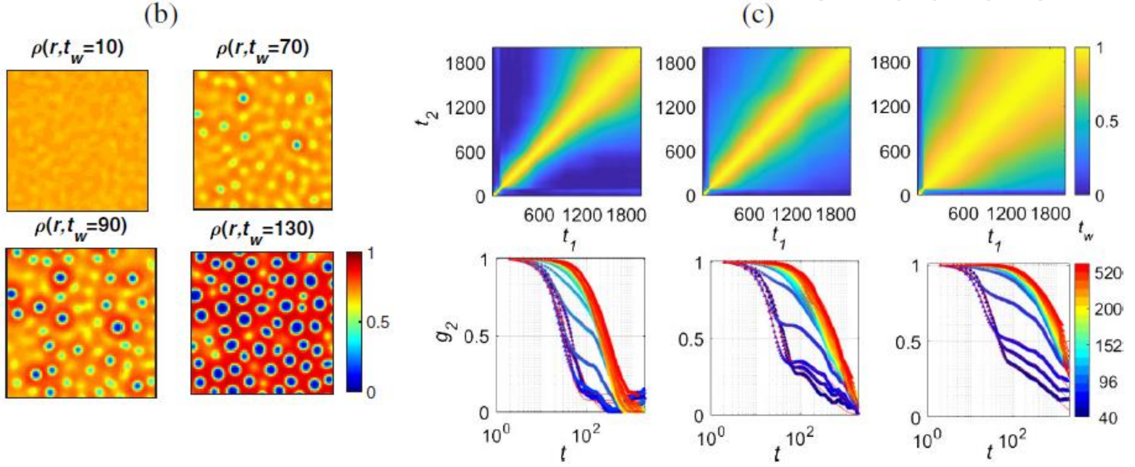
Experiment at different temperatures





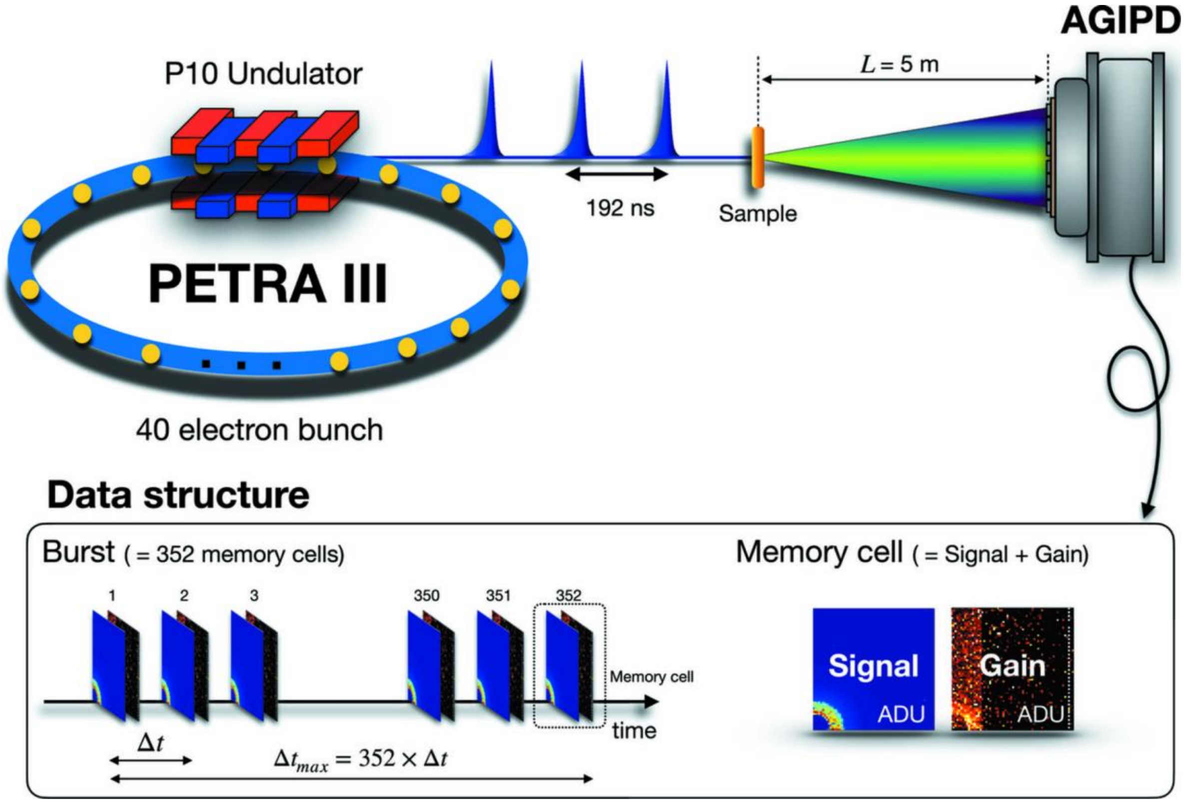
Phys. Rev. Lett. 126, 138004 (2021)

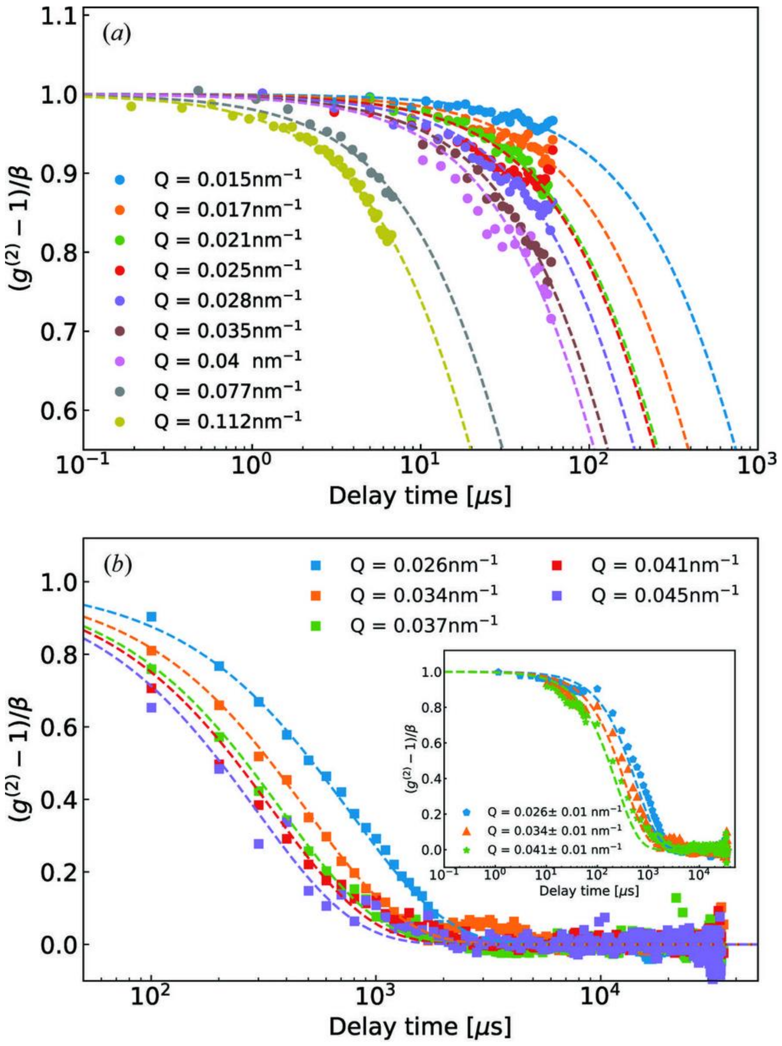
Simulations



Pulse-pulse XPCS at storage rings

- At DLSR pulse-pulse XPCS will become possible
- Storage rings will be no longer treated as continuous sources
- Recent demonstration using AGIPD (XFEL detector) at PETRA III probing pulse-pulse correlations with 192 ns separation



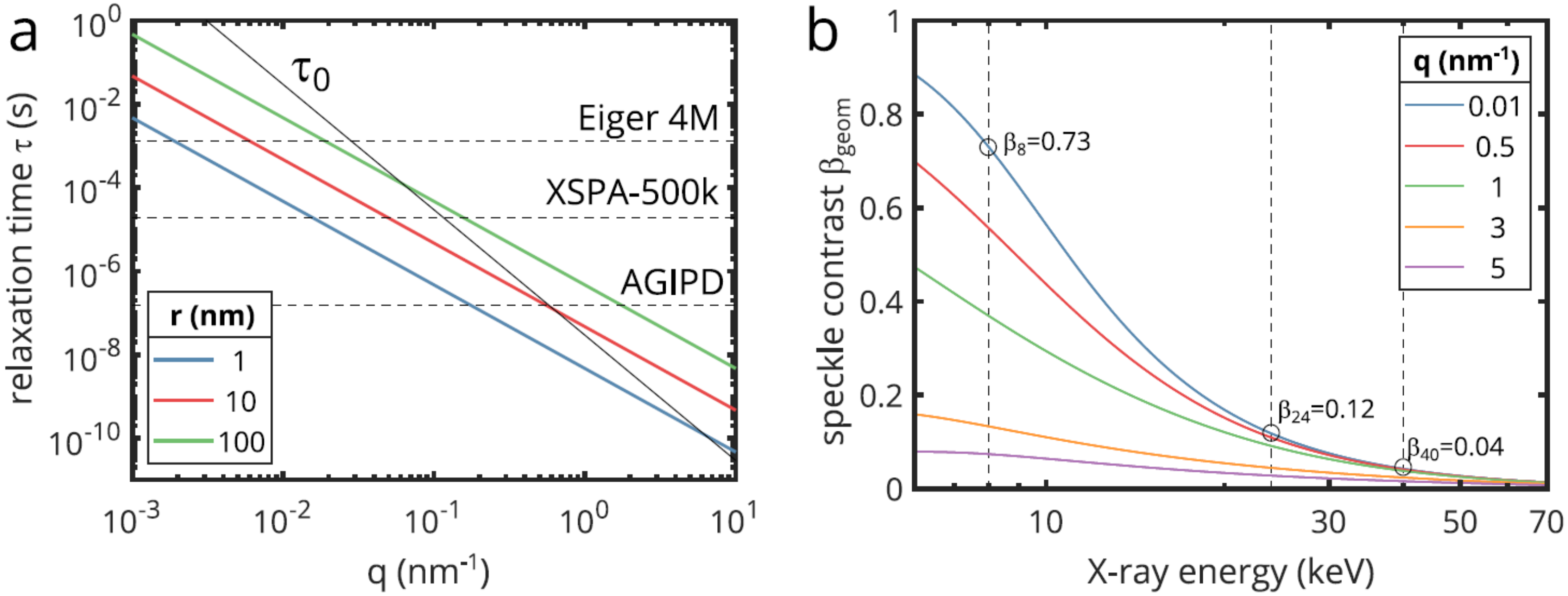


W. Jo et al. IUCrJ 8, 124 (2021)

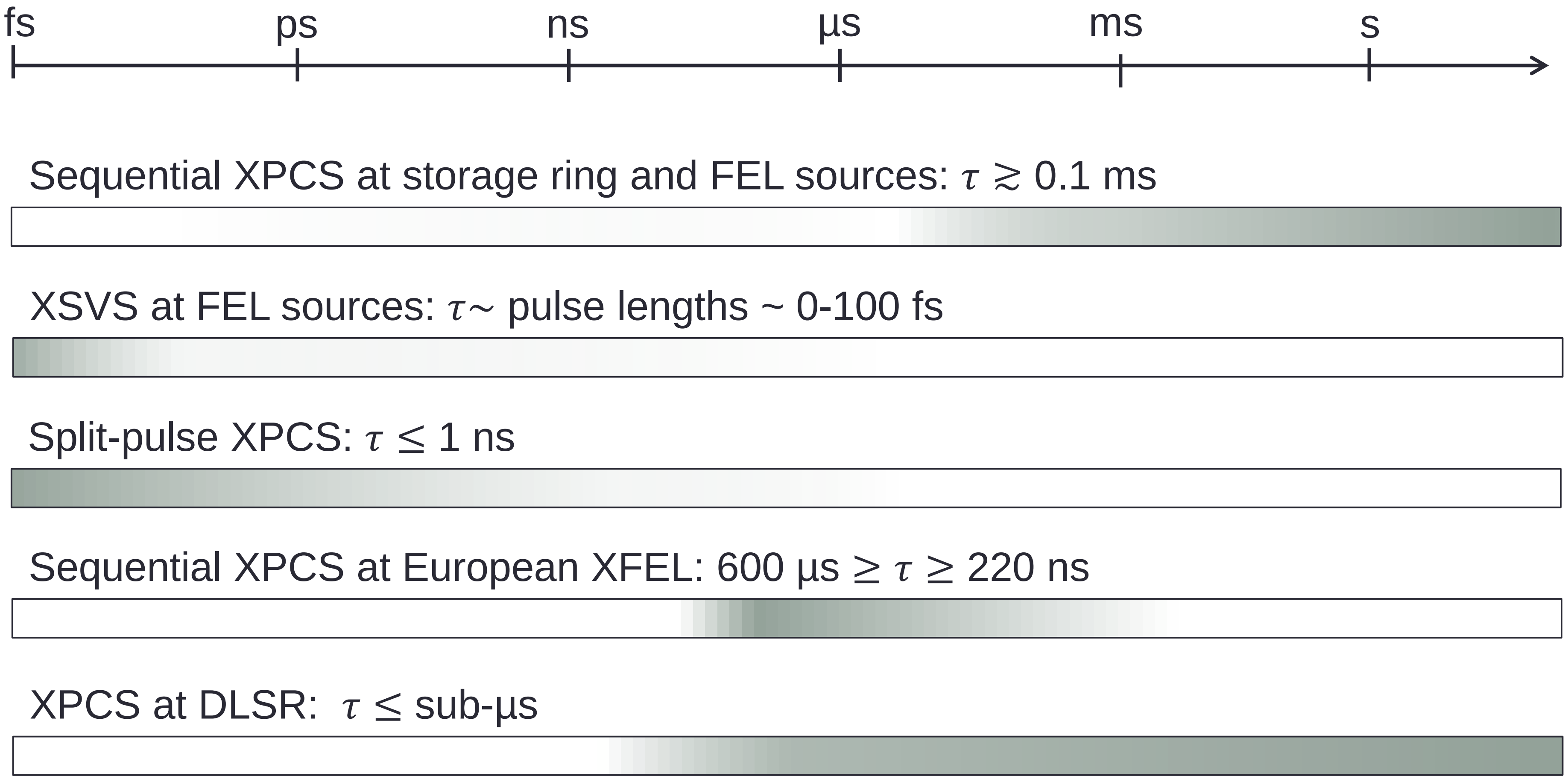
Limitations and challenges: XPCS at DLSR

- Detectors: need high repetition rates and single-photon counting
- High coherent flux at high energies – but bandwidth limit → use higher reflection monochromators on cost of intensity
- New detection schemes possible? E.g. even-based read-out
- High-data rates!
- 1 Megapixel Detektor at 100 kHz repetition rate (~1 MB per pattern (8 bit counter depth))

→ 100 GB/s raw data → how to analyze??? → need to compress data / use sparse data



Accessible timescales for XPCS



Sequential XPCS at storage ring and FEL sources: $\tau \gtrsim 0.1$ ms

XSVS at FEL sources: $\tau \sim$ pulse lengths ~ 0-100 fs

Split-pulse XPCS: $\tau \leq 1$ ns

Sequential XPCS at European XFEL: 600 µs $\geq \tau \geq$ 220 ns

XPCS at DLSR: $\tau \leq$ sub-µs

Further questions, interest, master thesis etc.

Soft matter, colloids, coherent X-ray scattering (XPCS, XCCA, …), water

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