X-ray Photon Correlation Spectroscopy (XPCS)

at Synchrotron and FEL sources

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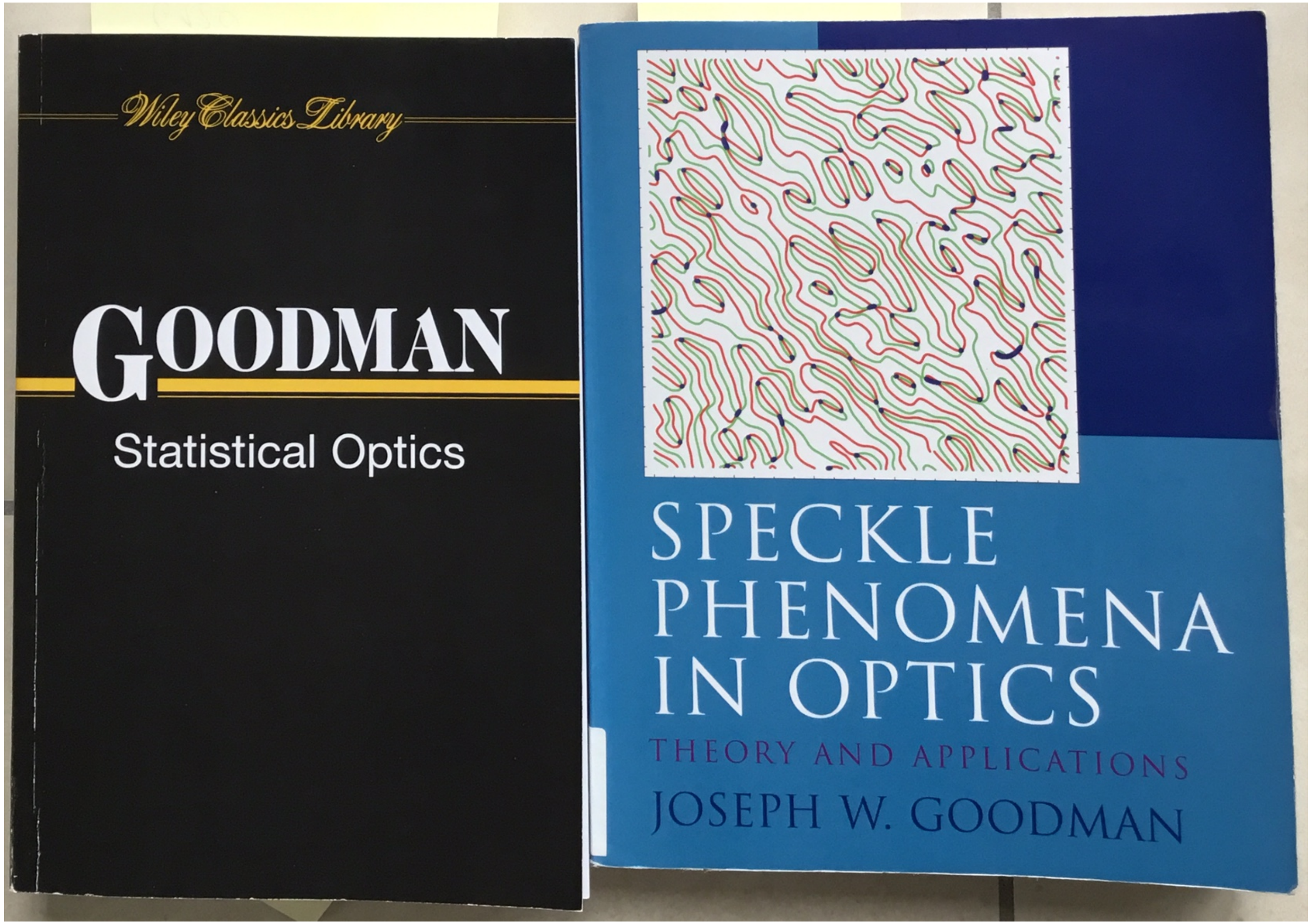
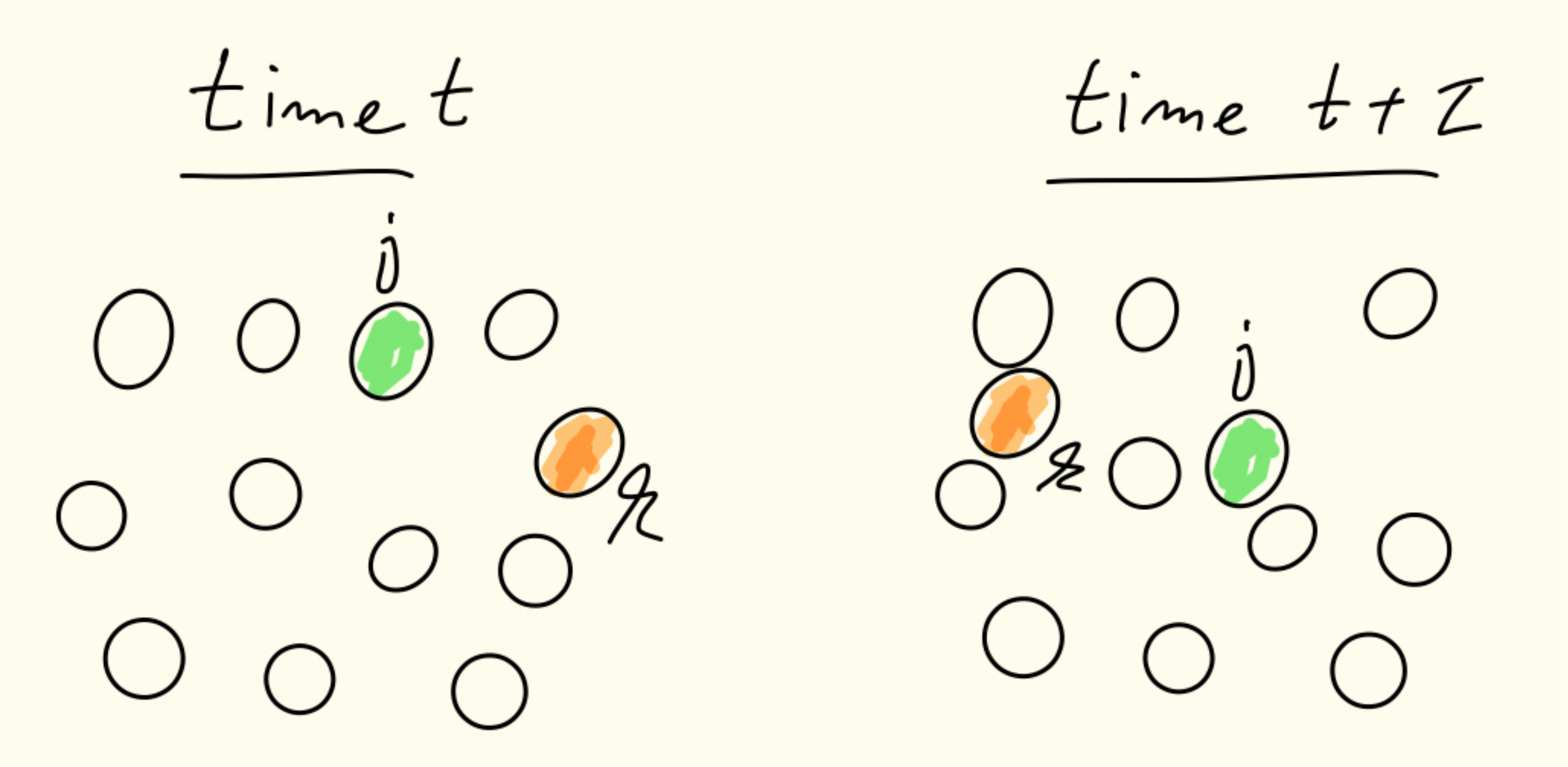
Outline

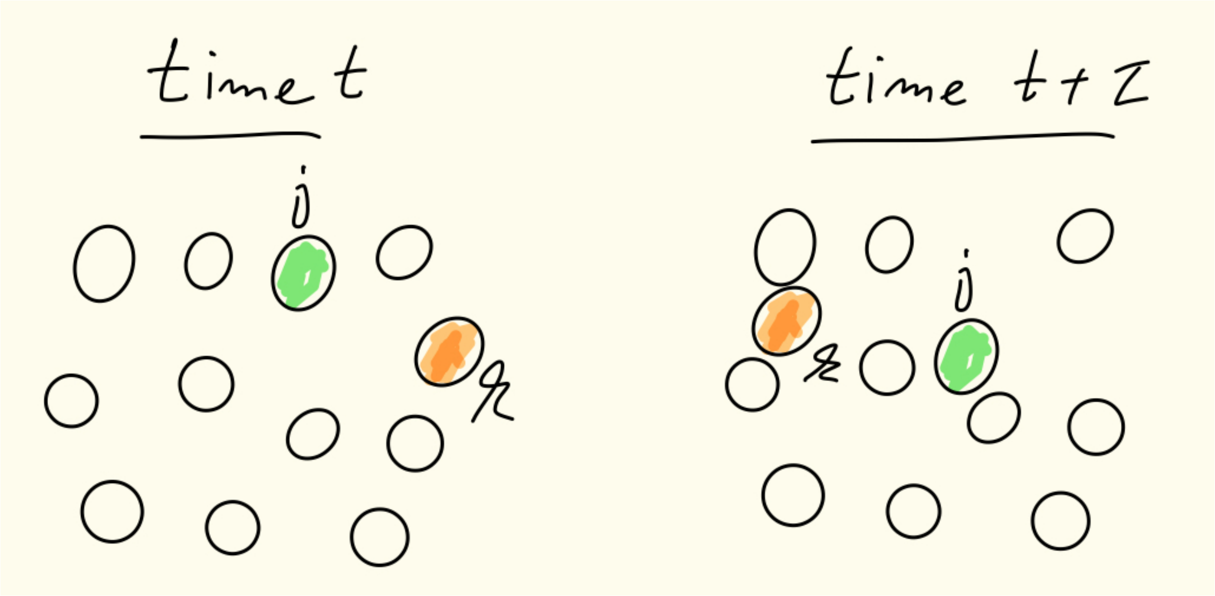
- How to measure dynamics in condensed matter systems
- Coherence
- X-ray speckle patterns
- How to exploit X-ray intensity fluctuations
- Examples for slow dynamics
- XPCS at FEL sources


Wiley Classics Library
GOODMAN
Statistical Optics
SPECKLE PHENOMENA IN OPTICS
THEORY AND APPLICATIONS
JOSEPH W. GOODMAN

How to measure dynamics in condensed matter systems



How to measure dynamics in condensed matter systems



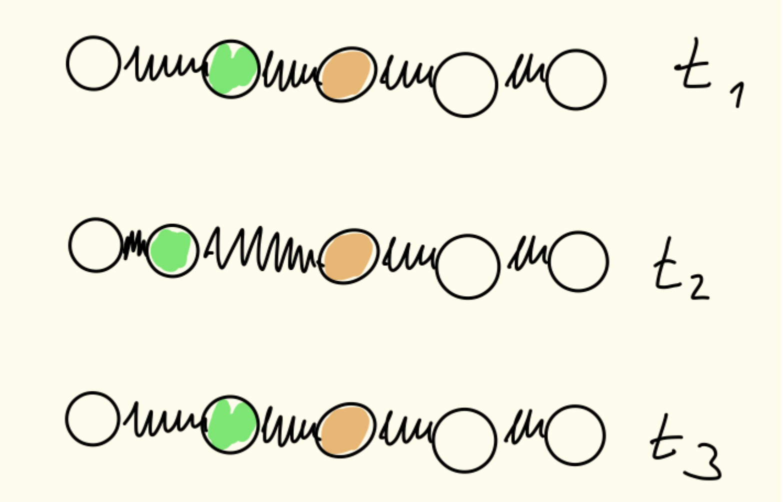
$$F(Q,\tau) = \frac{1}{N} \sum \sum \exp(iQ(r_j(t) - r_k(t+\tau))$$

Time domain
intermediate scattering function

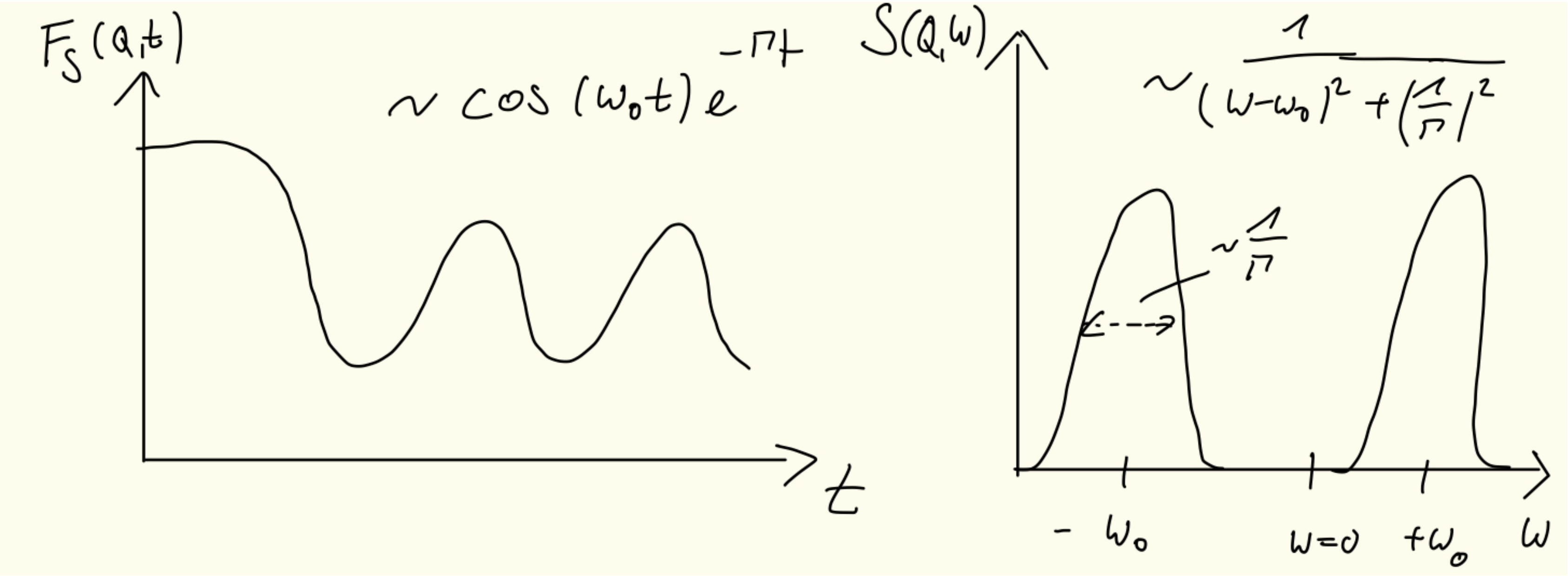
$$S(Q,\omega) = \int F(Q,\tau) \exp(i\omega\tau)\, d\tau$$

Frequency domain
dynamic structure factor

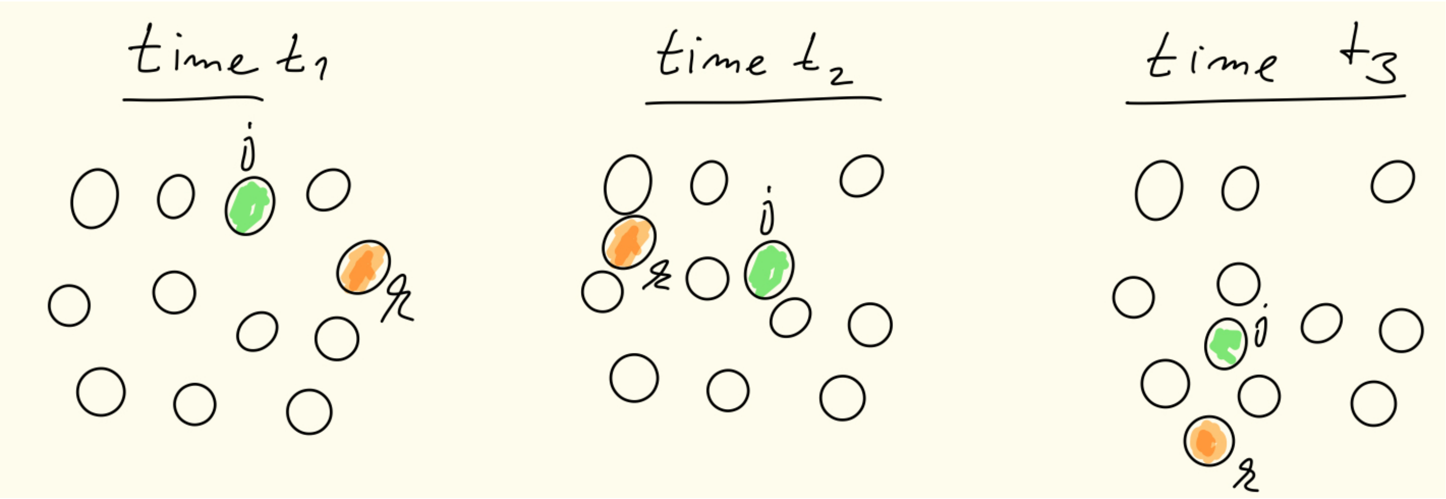
Elastic processes – waves, phonons…



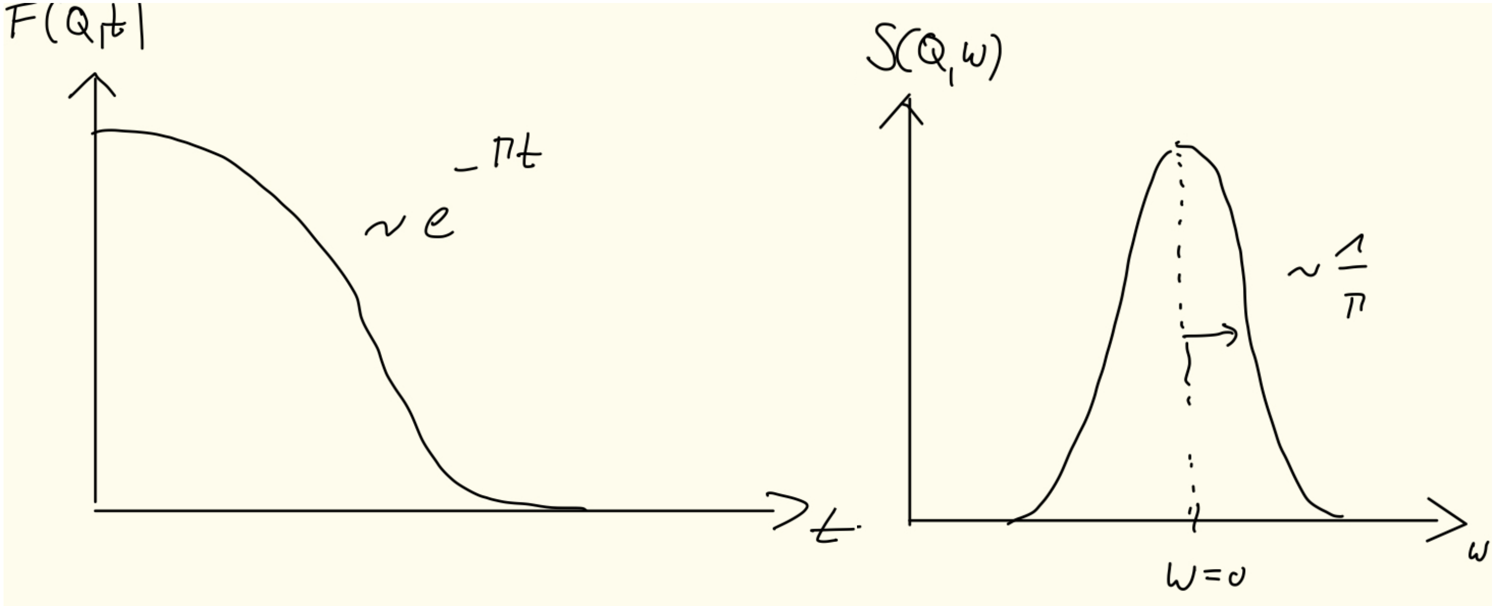
Restoring force – the system goes back to its previous configuration

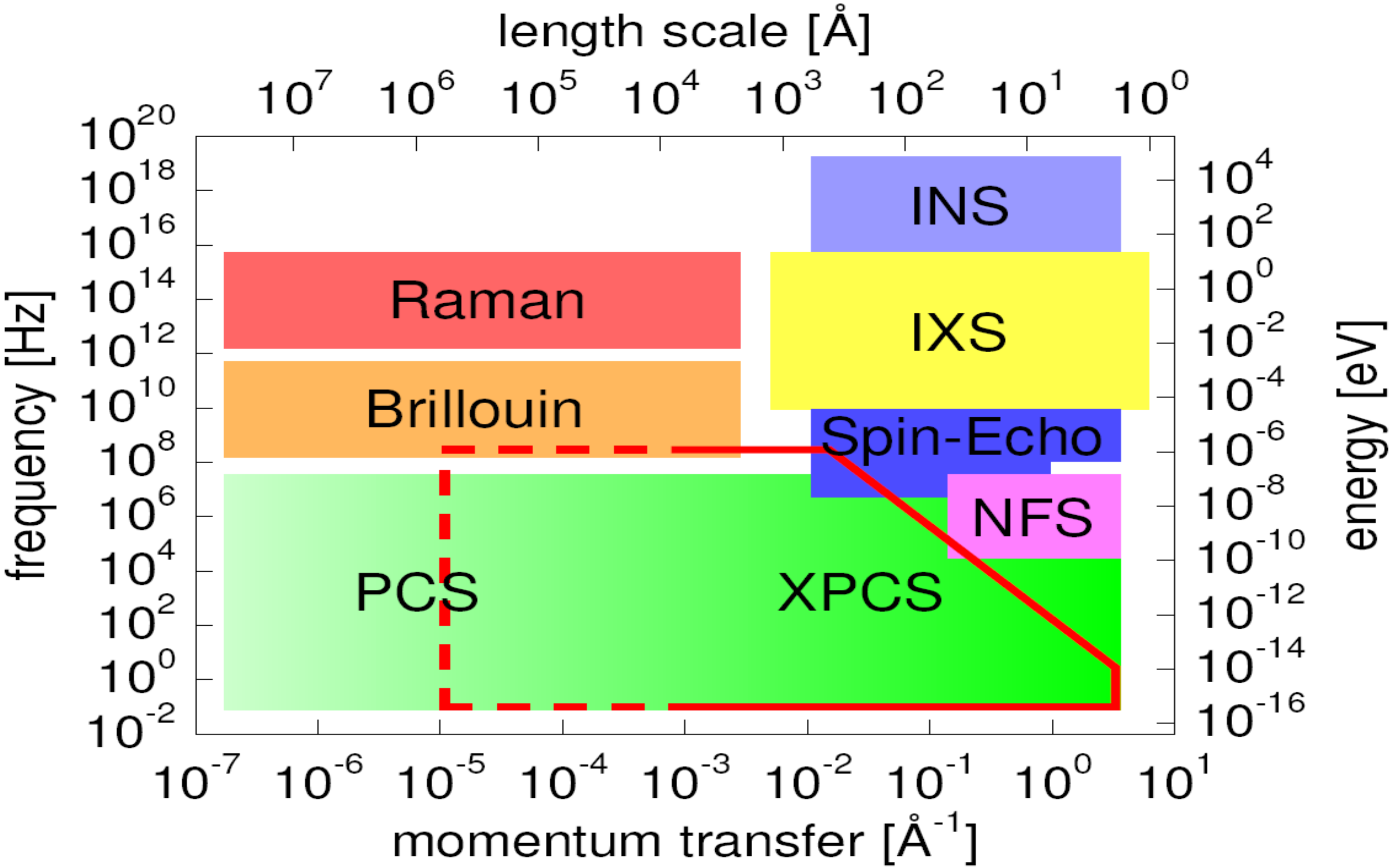


Relaxational processes – diffusion, viscosity...



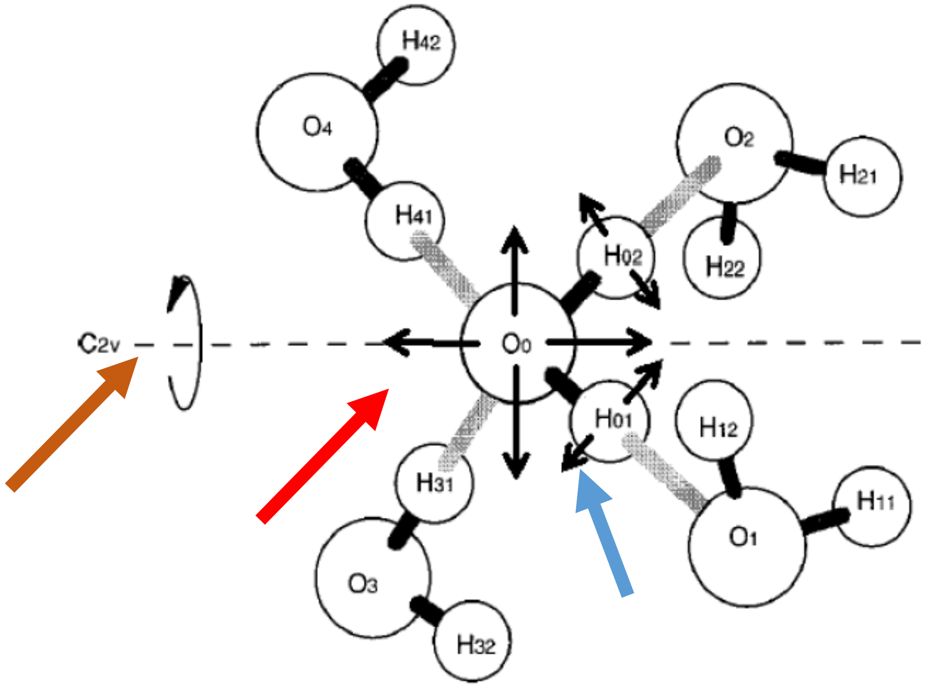
**No restoring force –
the system evolves with time
and does not come back**

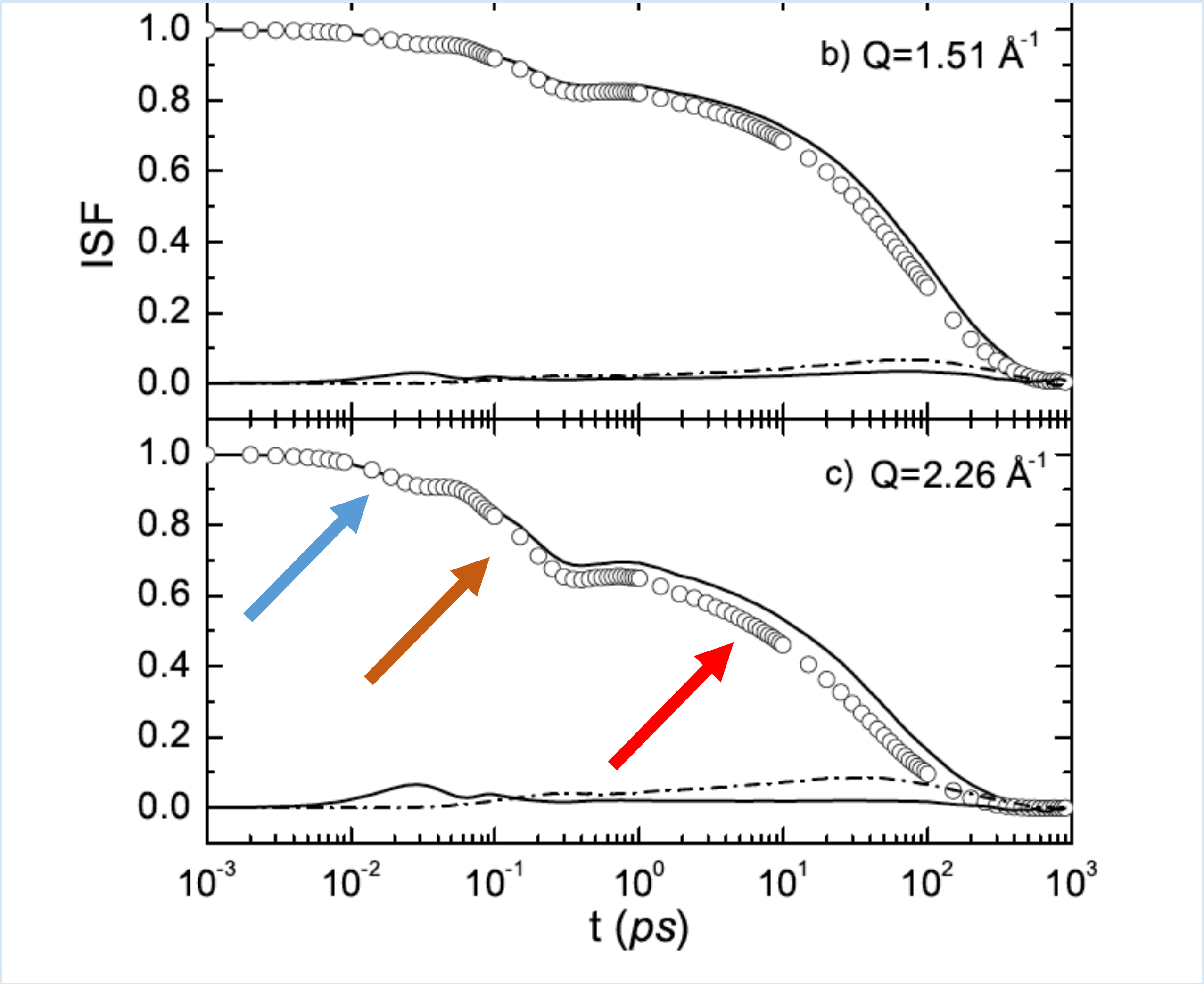


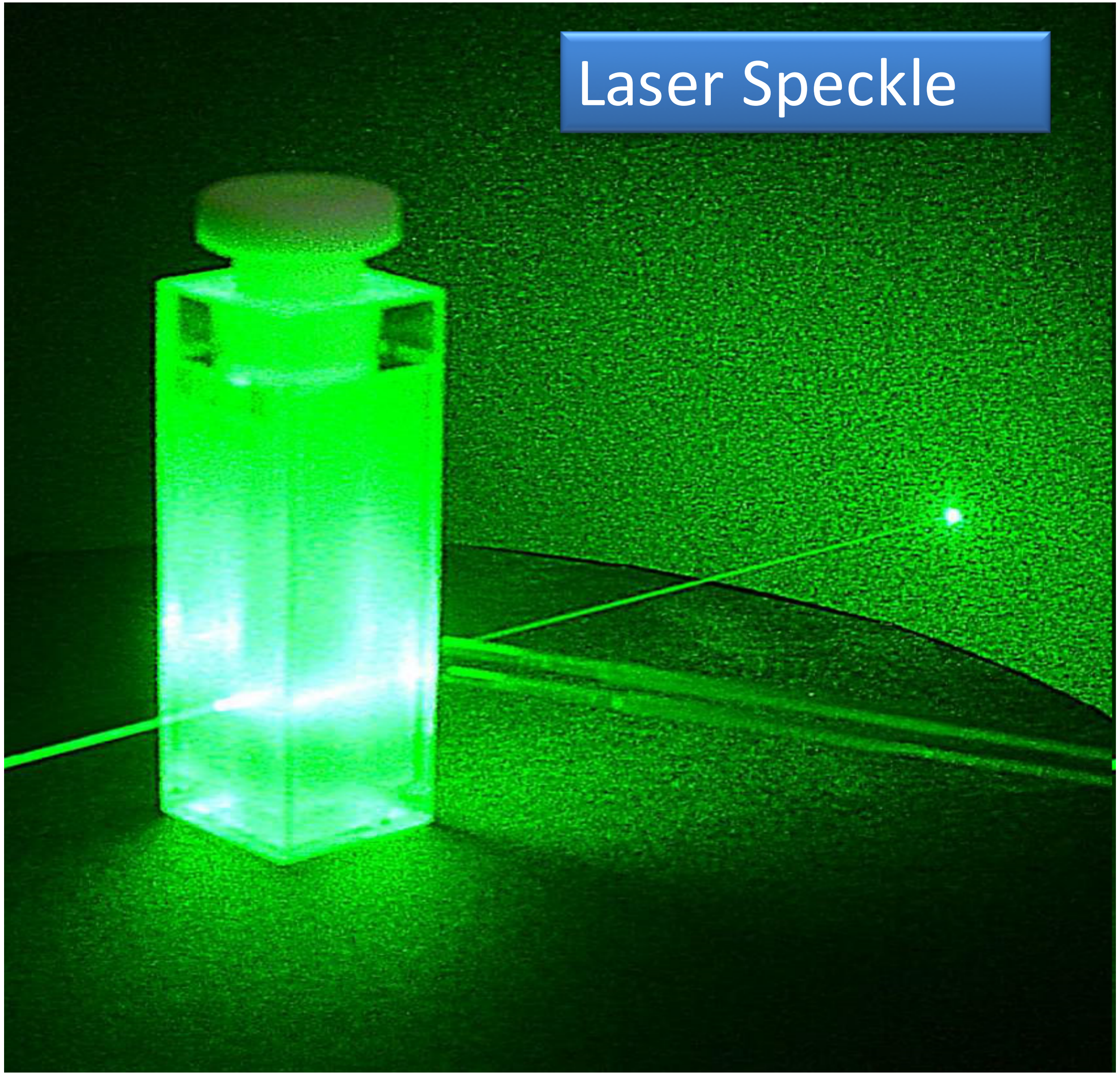

length scale [Å]
10^7
10^6
10^5
10^4
10^3
10^2
10^1
10^0
frequency [Hz]
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^8
10^6
10^4
10^2
10^0
10^{-2}
energy [eV]
10^4
10^2
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
INS
Raman
IXS
Brillouin
Spin-Echo
NFS
PCS
XPCS
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^0
10^1
momentum transfer [Å^{-1}]

An example – molecular dynamics simulation of liquid water

Intermediate scattering function
is complex (many correlation processes)
and spans many orders of magntiude
-> **experiments in the time domain**

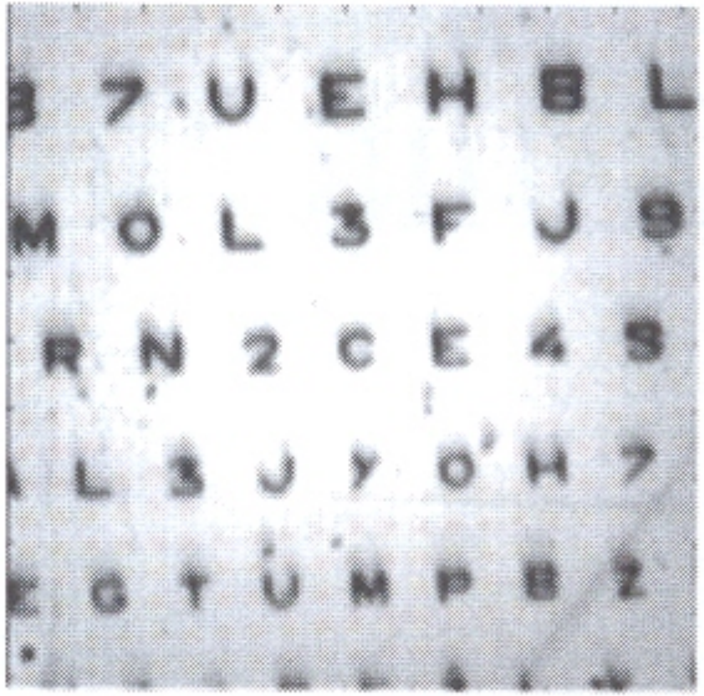




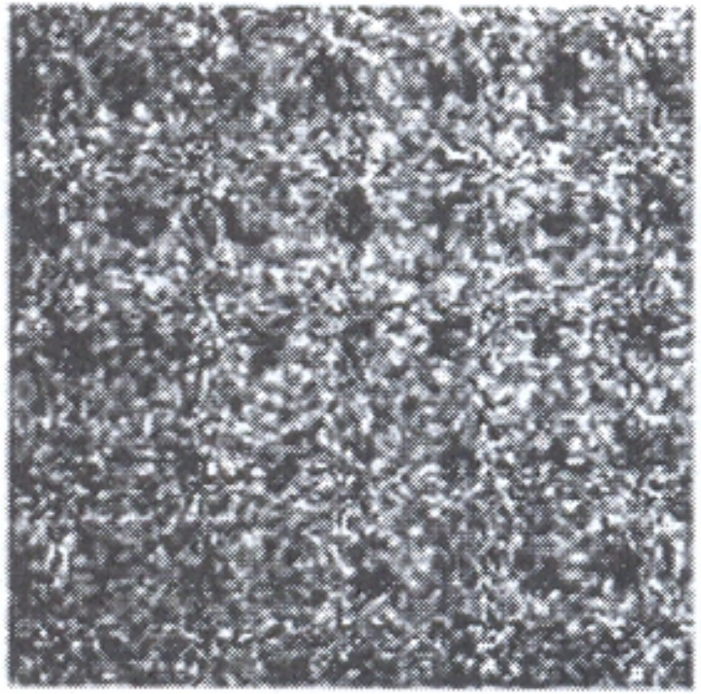


Laser Speckle

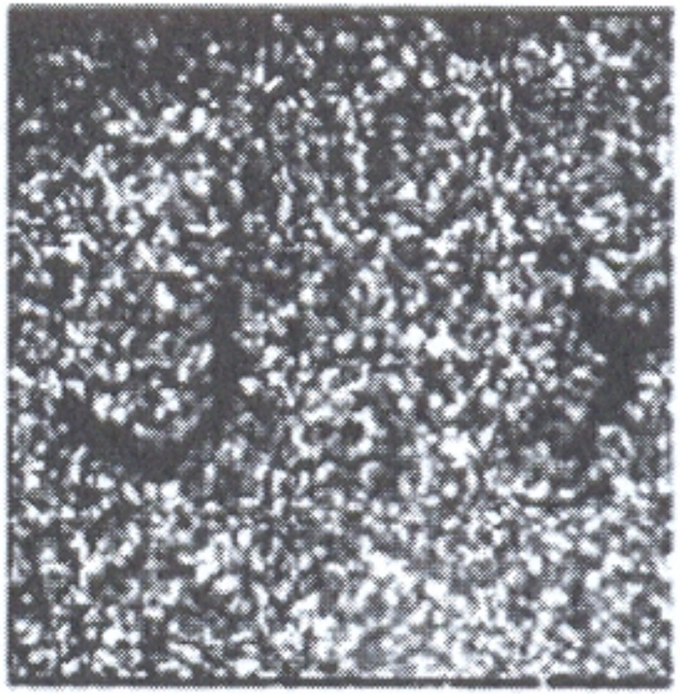
Optical Speckles



Incoherent light



Coherent light

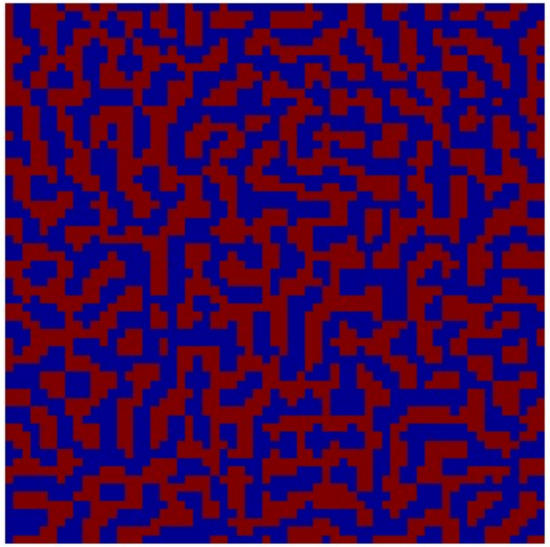


Close up

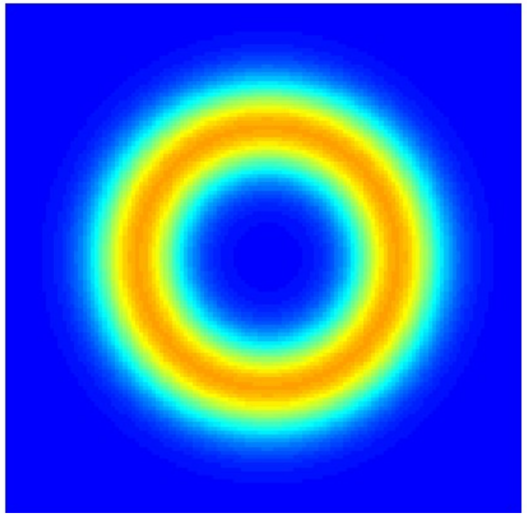
VLC movie

Coherent scattering from disorder: Speckle

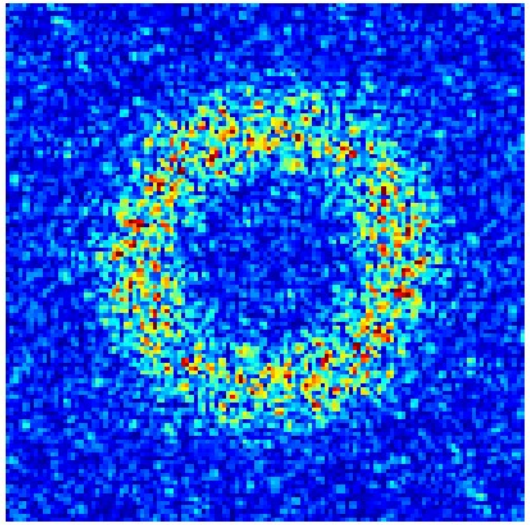
sample with disorder
(e.g. domains)



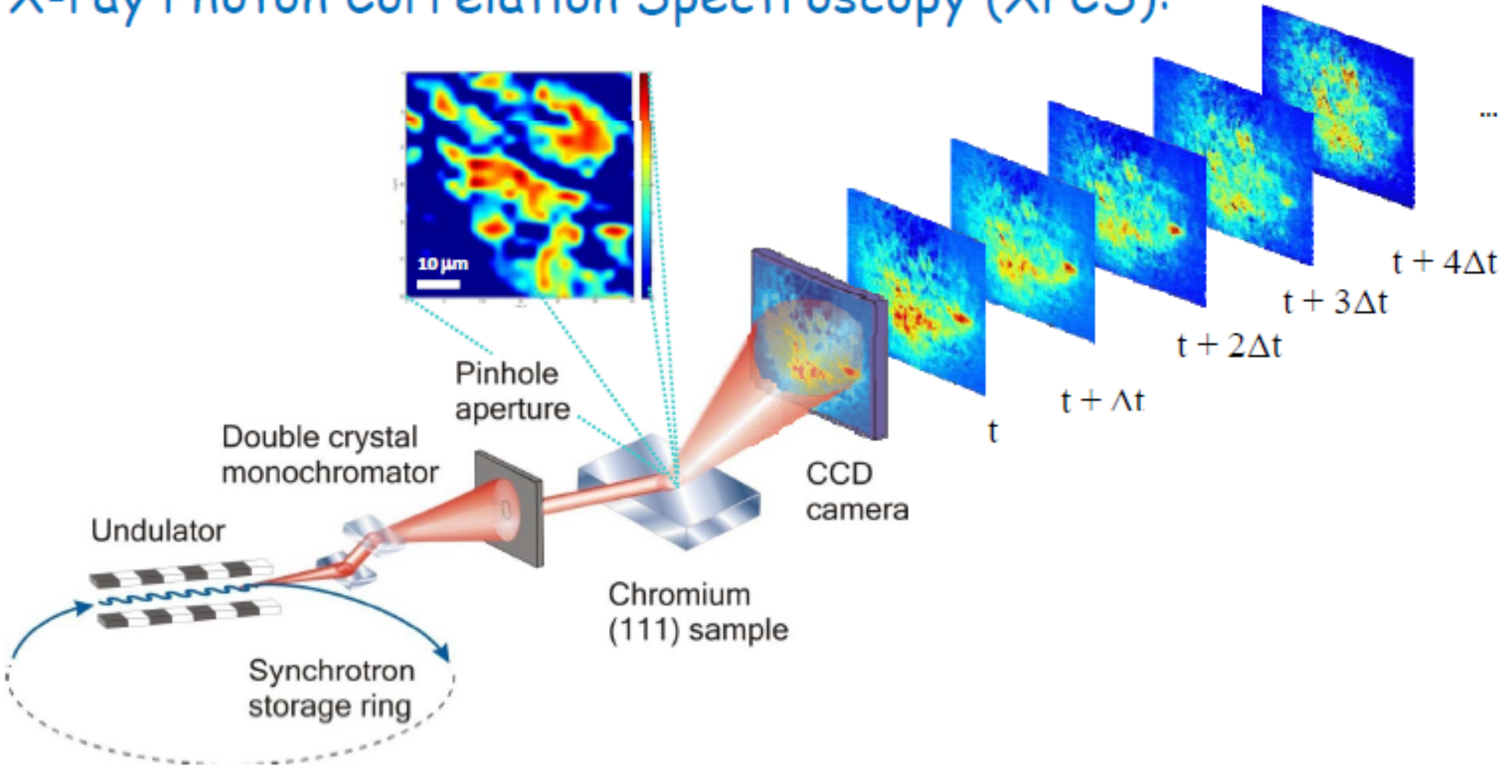
- ***Incoherent Beam: Diffuse Scattering***
  - **Measures averages**

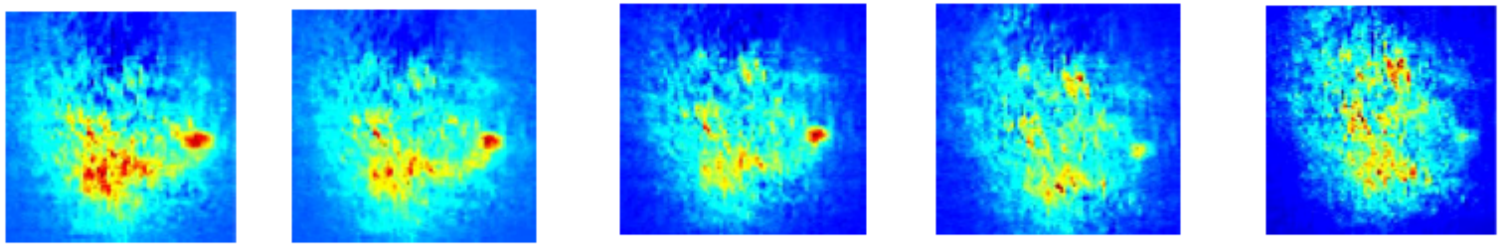


- ***Coherent Beam: Speckle***
  - **Speckle depends on exact arrangement**
  - **Speckel statistics encodes coherence properties**



X-ray Photon Correlation Spectroscopy (XPCS):





t t + Δt t + 2Δt t + 3Δt t + 4Δt

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

XPCS – Theory

$$\langle I(t)I(t+\tau)\rangle = \langle E(t)E^*(t)E(t+\tau)E^*(t+\tau)\rangle$$

Gaussian momentum theorem

$$= \underbrace{\langle E(t)E^*(t)\rangle}_{\langle I(t)\rangle}\underbrace{\langle E(t+\tau)E^*(t+\tau)\rangle}_{\langle I(t)\rangle} + \left|\underbrace{\langle E(t)E^*(t+\tau)\rangle}_{g_1(\tau)}\right|^2$$

$$\frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2} = 1 + \left|g_1(\tau)\right|^2$$

XPCS Theory

$$E(t) = A \sum_{j=1}^{N} b_j \exp(iqr_j(t))$$

$$g_1(q,\boldsymbol{\tau}) = A^2 \sum_{j,k=1}^{N} b_k b_j \exp(iq(r_j(t) - r_k(t+\boldsymbol{\tau}))$$

Time dependent density correlation function

Experiment

$$\frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2} = 1+\beta\left|g_1(\tau)\right|^2$$

Speckle contrast < 1

Speckle blurring leads to small contrast

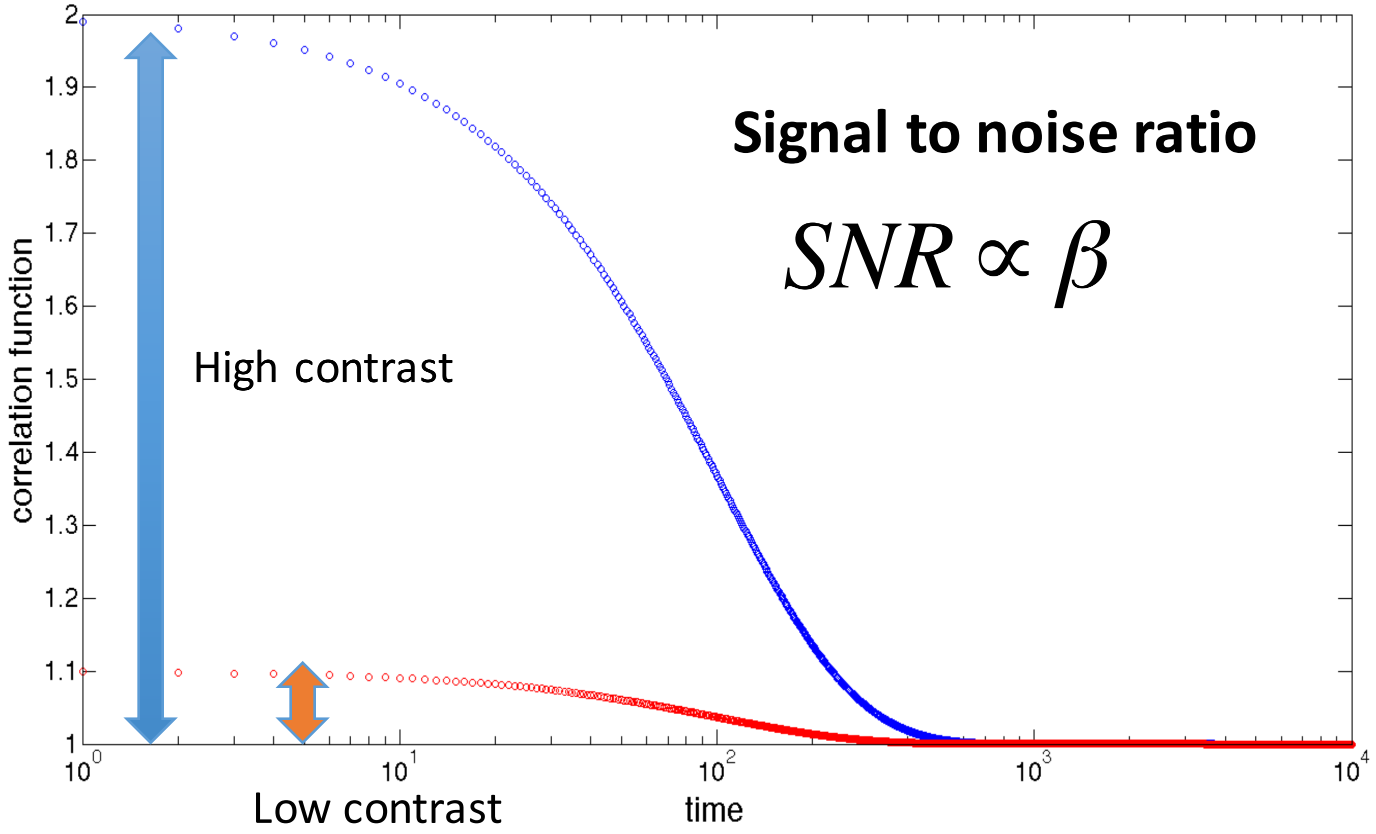
Partial coherence of the x-ray source

Detector pixels P larger than speckle size S

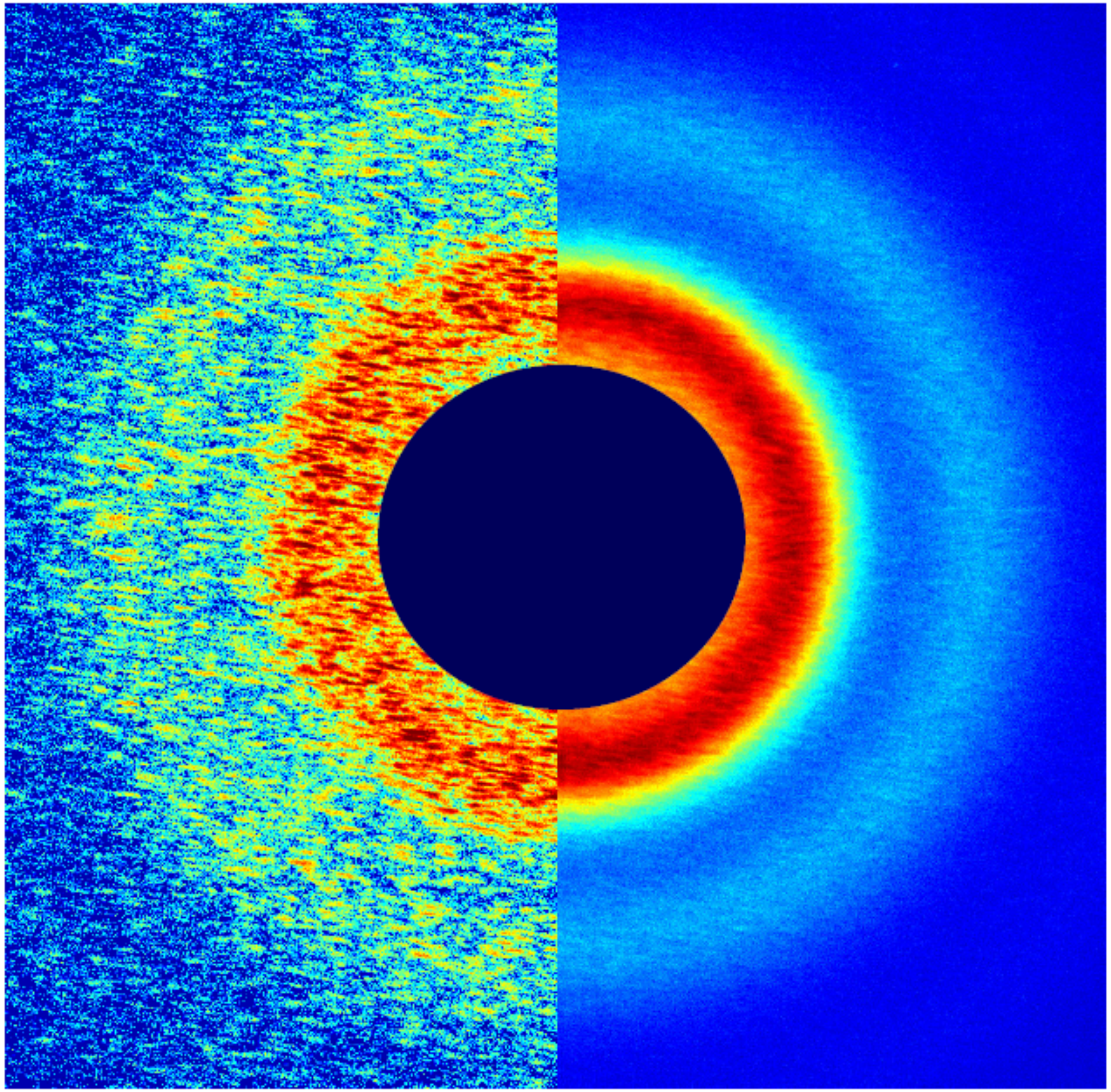
$$S \approx \frac{\lambda}{D} \times L$$

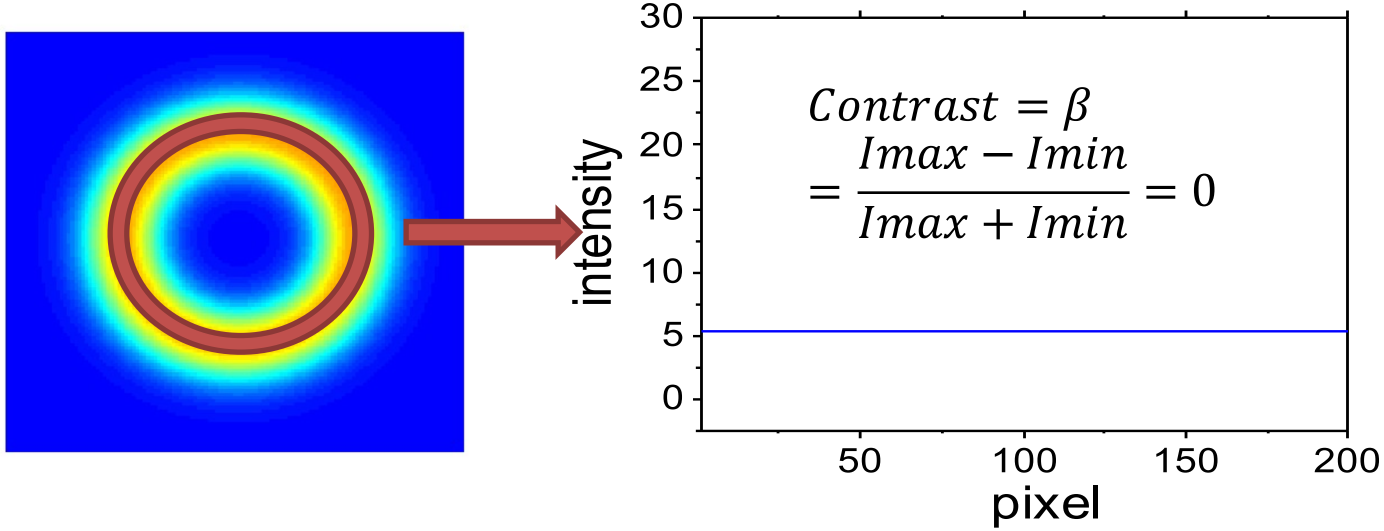
Signal to noise ratio

$$SNR \propto \beta$$

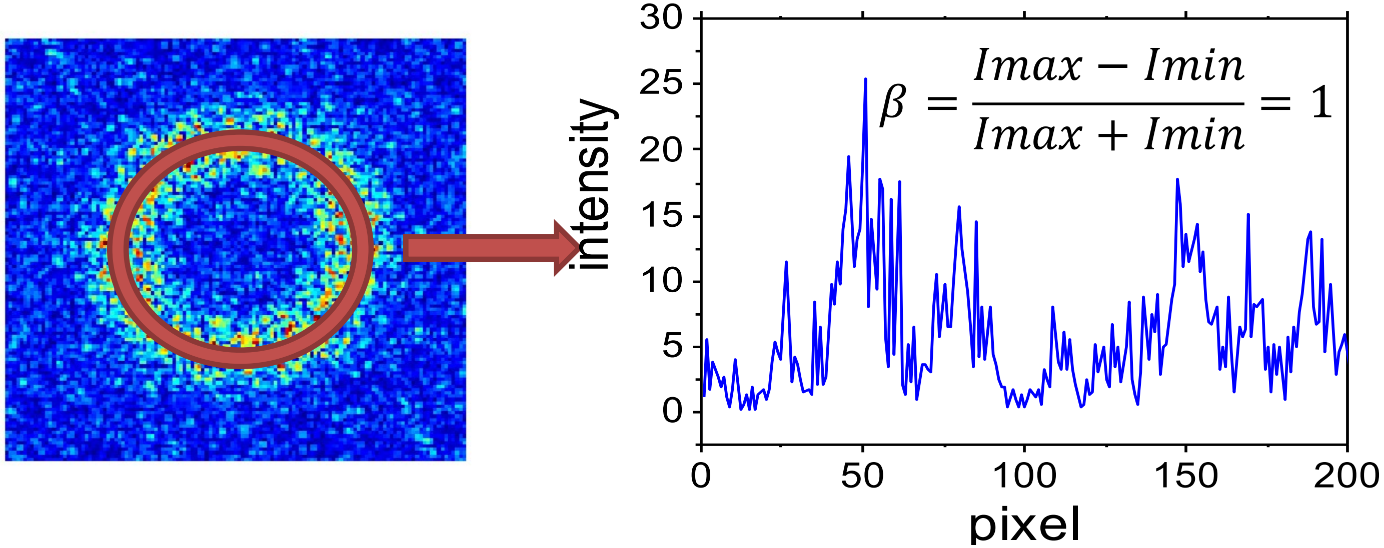


$$\frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2} = 1 + \beta \left| g_1(\tau) \right|^2$$


High coherence
Low coherence

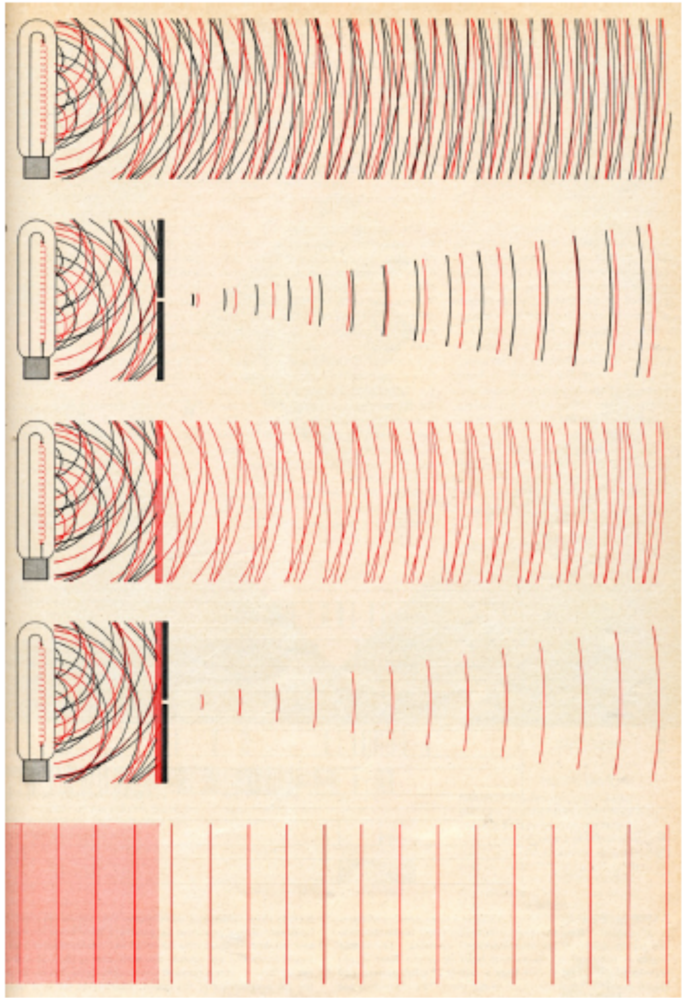


$$Contrast = \beta = \frac{Imax - Imin}{Imax + Imin} = 0$$



$$\beta = \frac{Imax - Imin}{Imax + Imin} = 1$$

Coherence

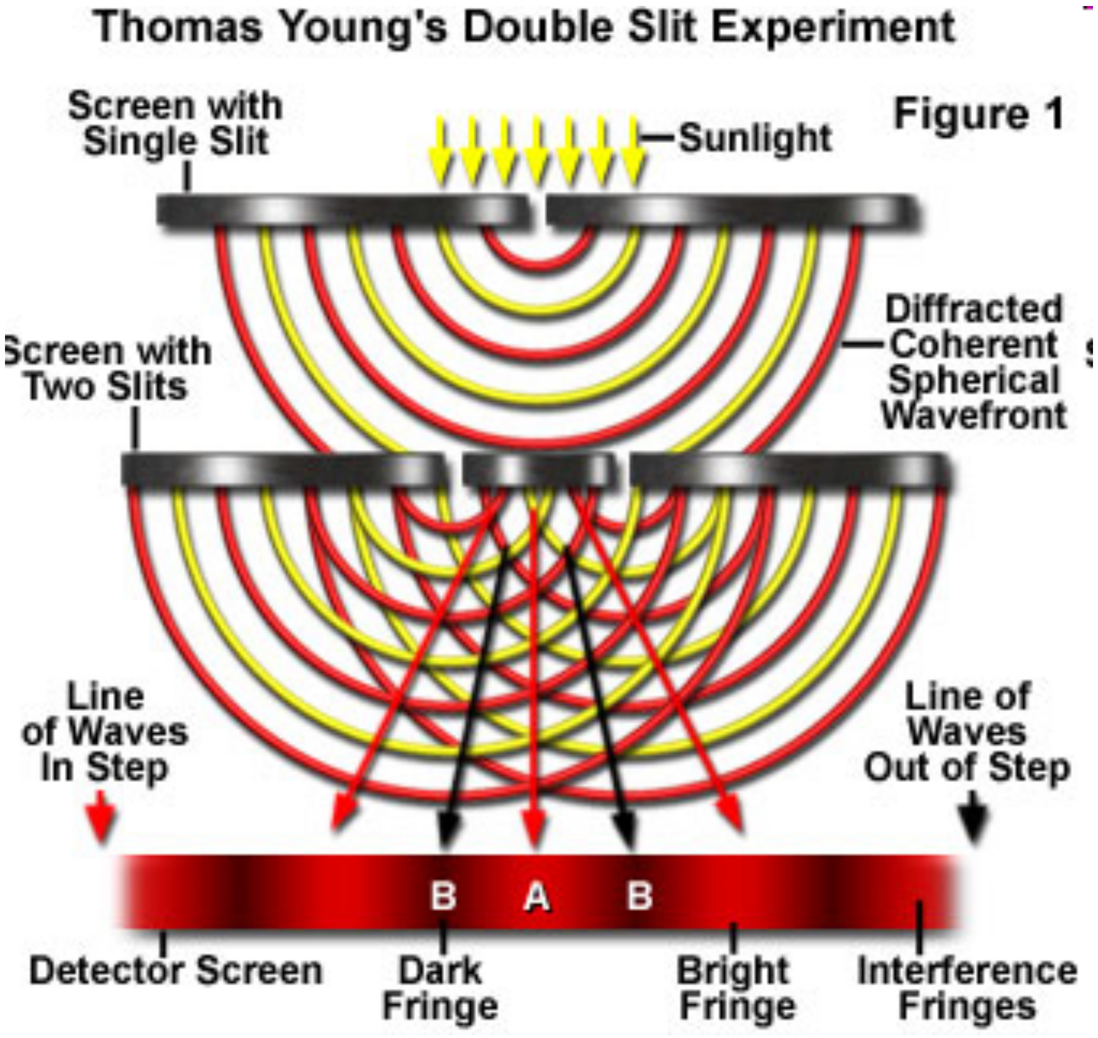


Spatial coherence

Temporal coherence

A. L. Schawlow "Laser Light"
Scientific American, 219 (3), p. 120, (1968)

Young's Double Slit Experiment

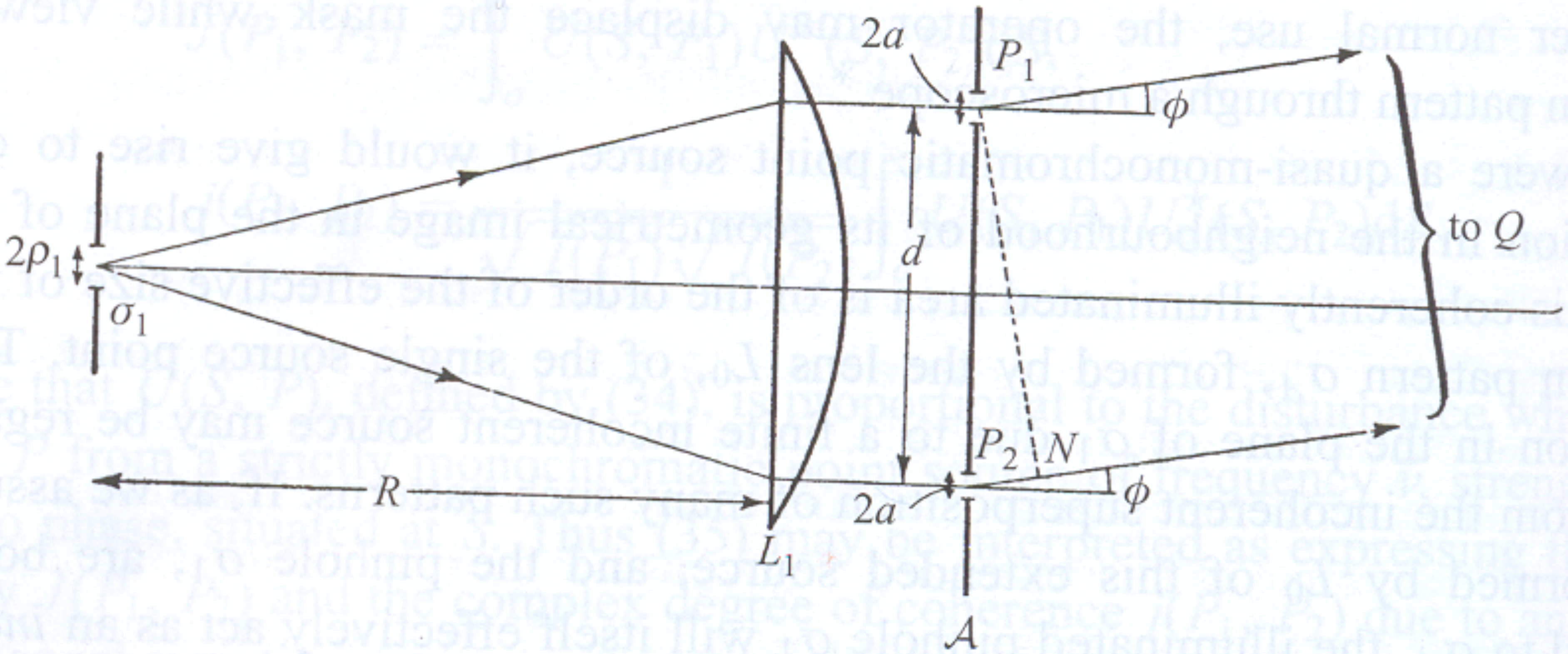


Thomas Young, 1773-1829

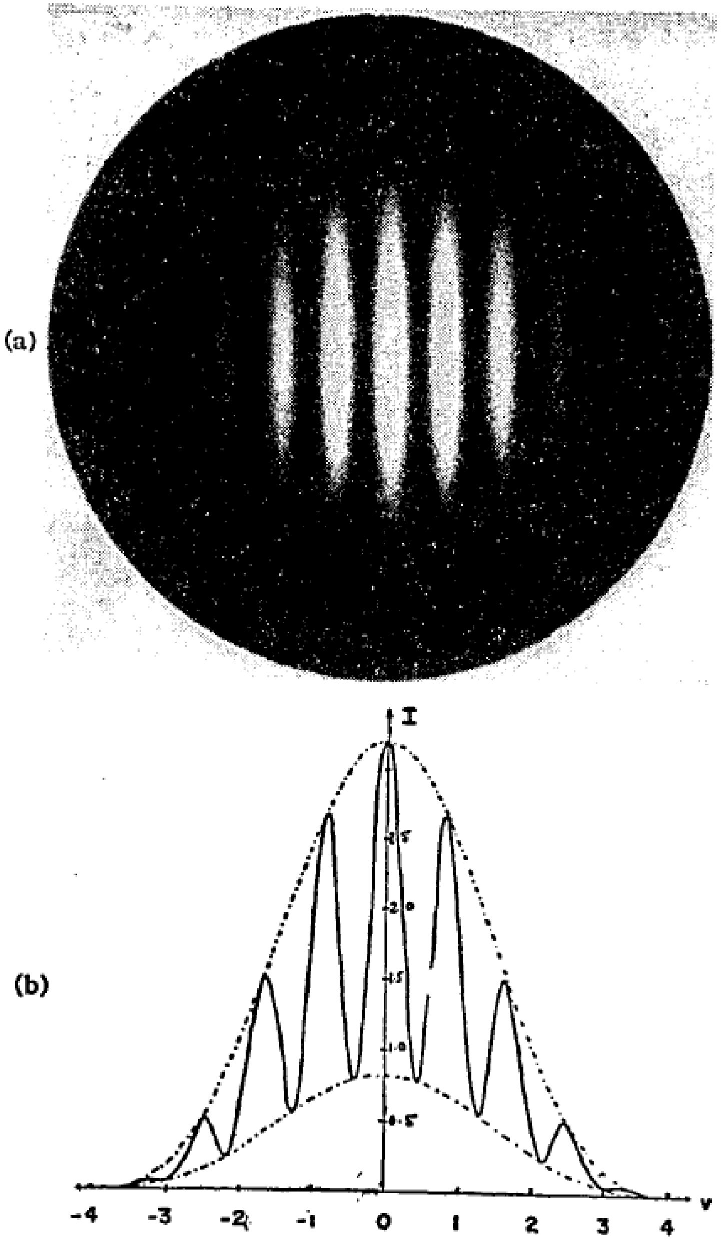
- Light is a wave
- Visibility (coherence)

$$v = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$$

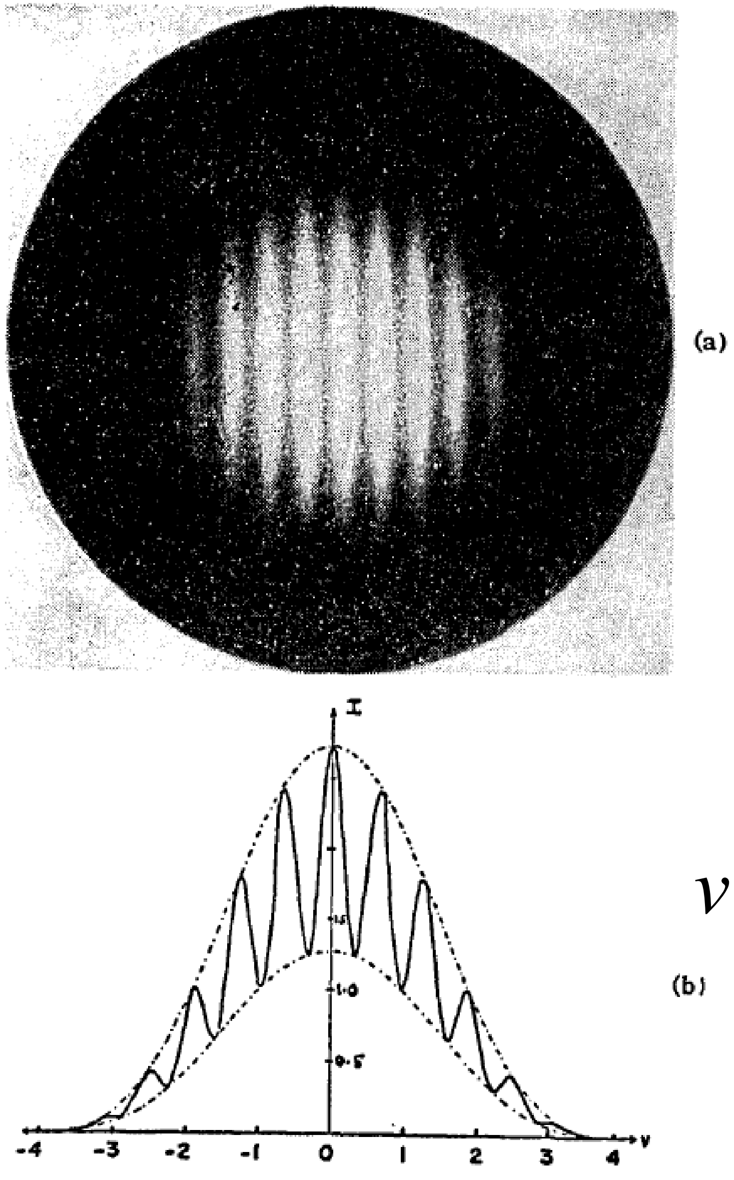
Spatial coherence in Young's Double-Slit experiment



Born and Wolf, Optics

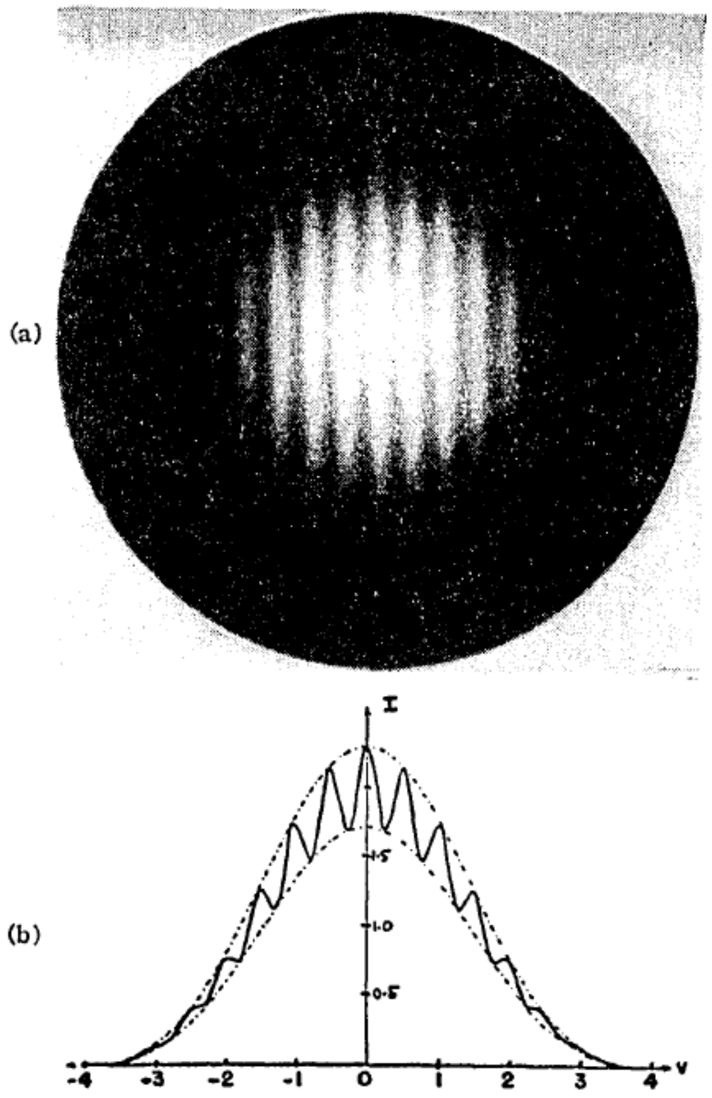


(2h = 0.6 cm., g_{12} = 0.593, β = 0)



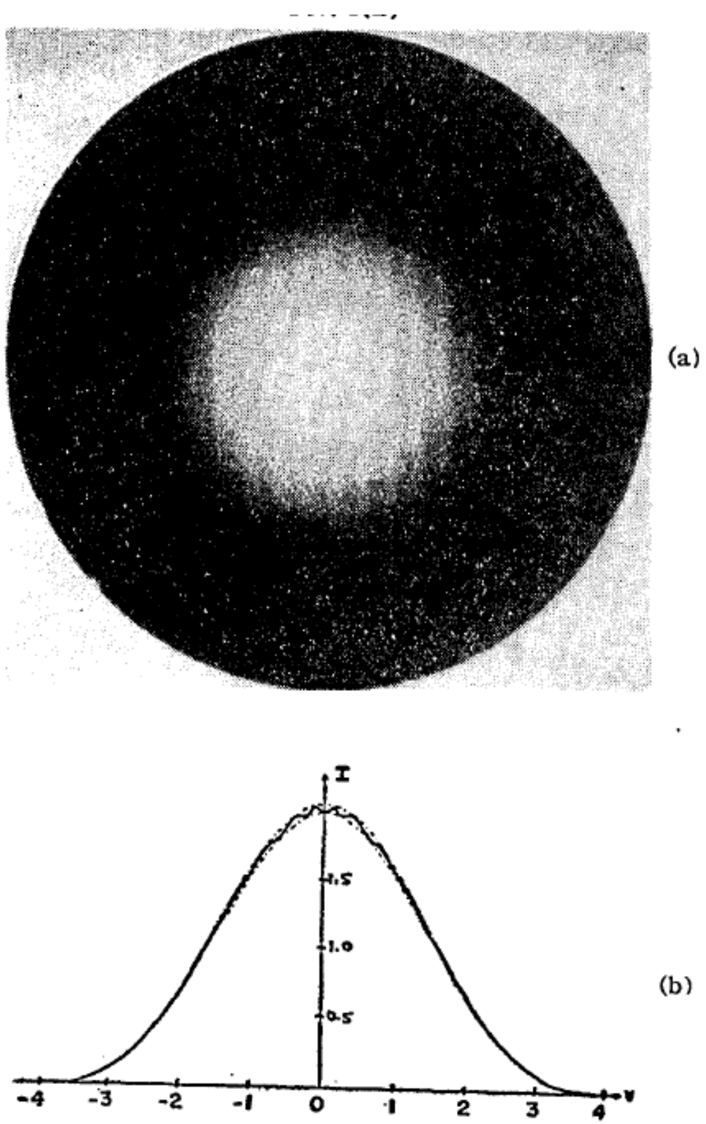
(2h = 0.8 cm., g_{12} = 0.361, β = 0)

$$v = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$$



(2h = 1.0 cm., g_{12} = 0.146, $\beta = 0$)

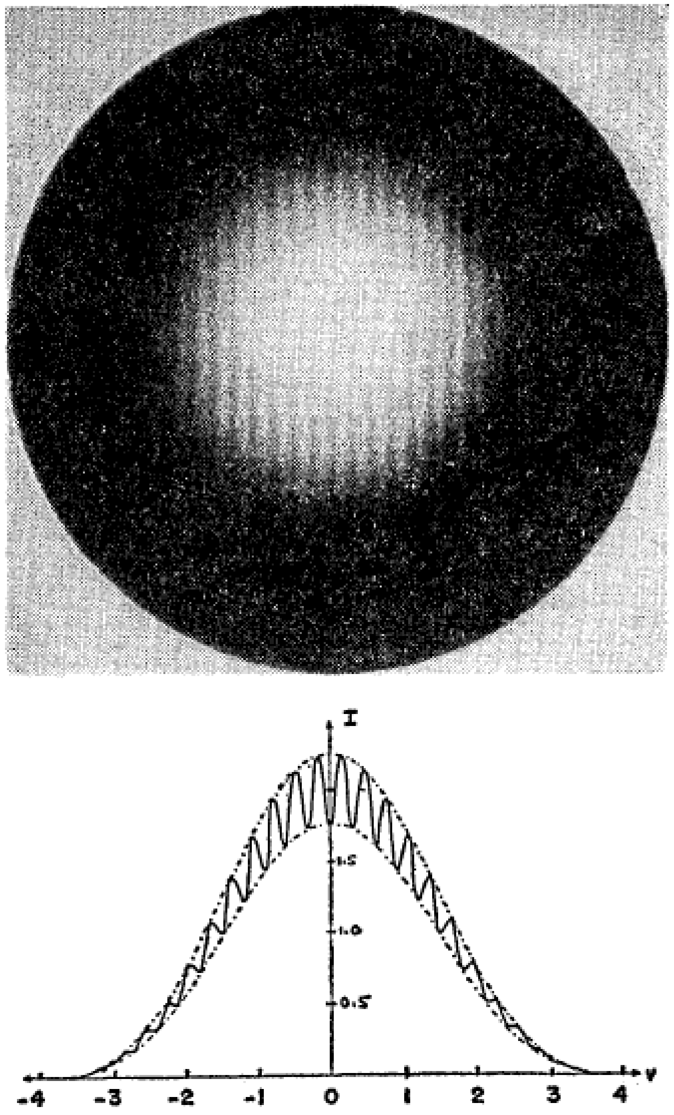
FIG. 4(C)



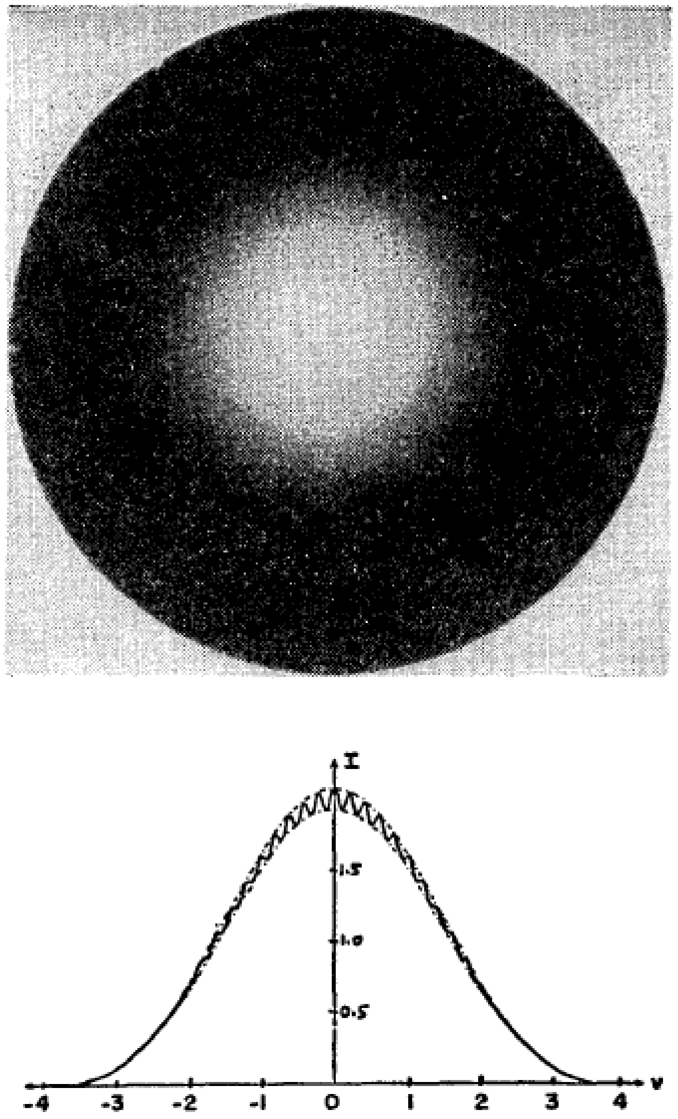
(2h = 1.2 cm., g_{12} = 0.015, $\beta = \pi$)

FIG. 4(D)

$$v = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$$



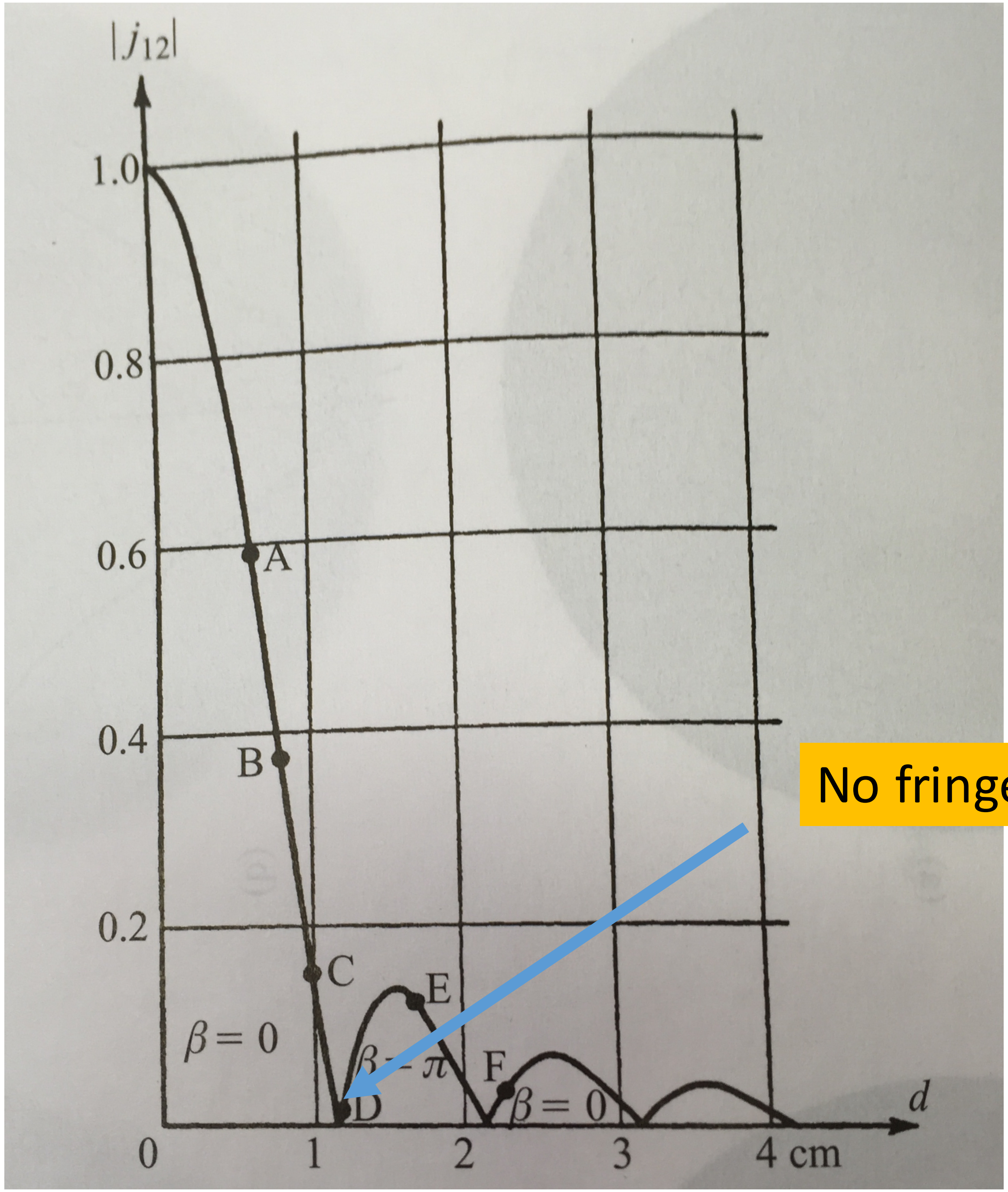
(2h=1.7 cm., g_{12}= 0.123, $\beta = \pi$)



(2h=2.3 cm., g_{12}= 0.035, $\beta = 0$)

$$v = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$$

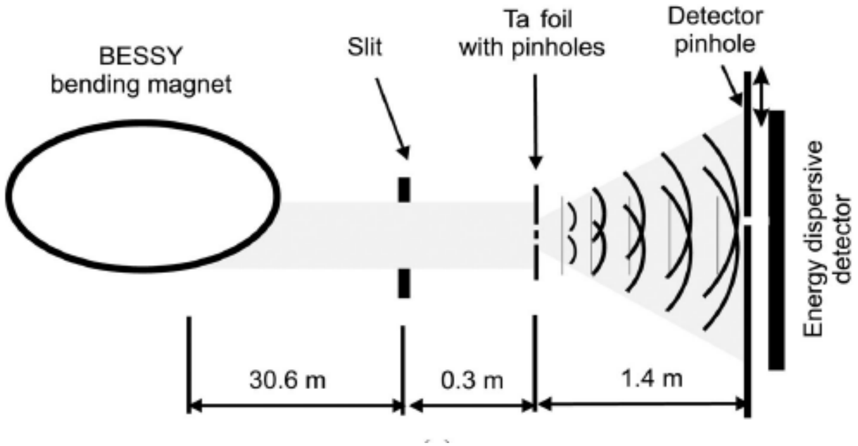
Fringe visibility as a function of distance between the pinholes

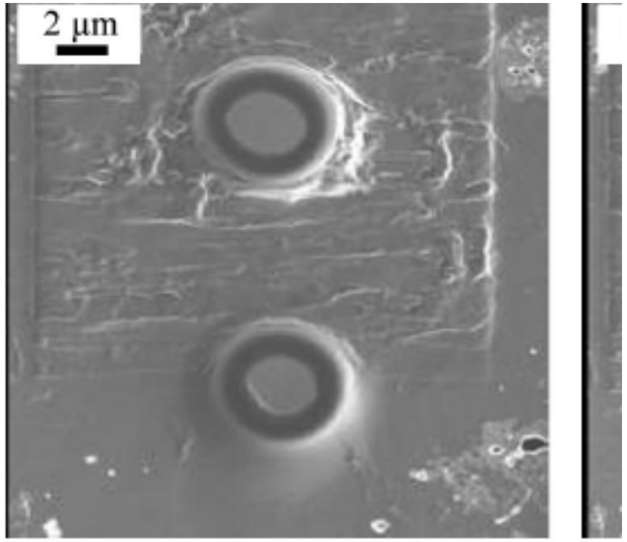


$$\Gamma(r_1, r_2, \tau) =< V^*(r_1, t) V(r_2, t+\tau) >$$

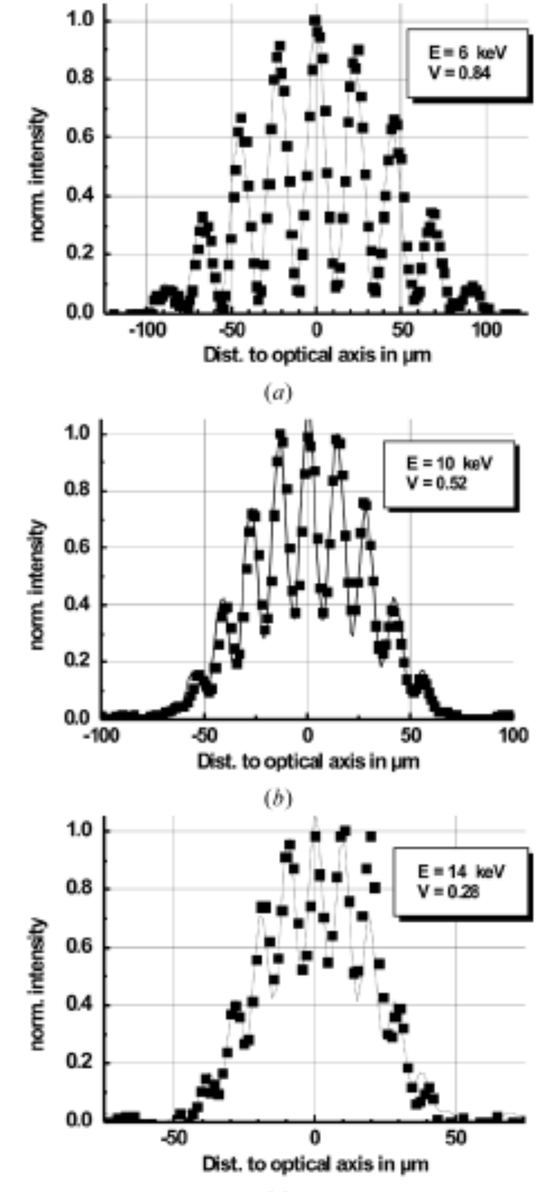
No fringes visibility: „coherence length exceeded“

Young's experiment with X-rays





(*a*)



(*a*)

(*b*)

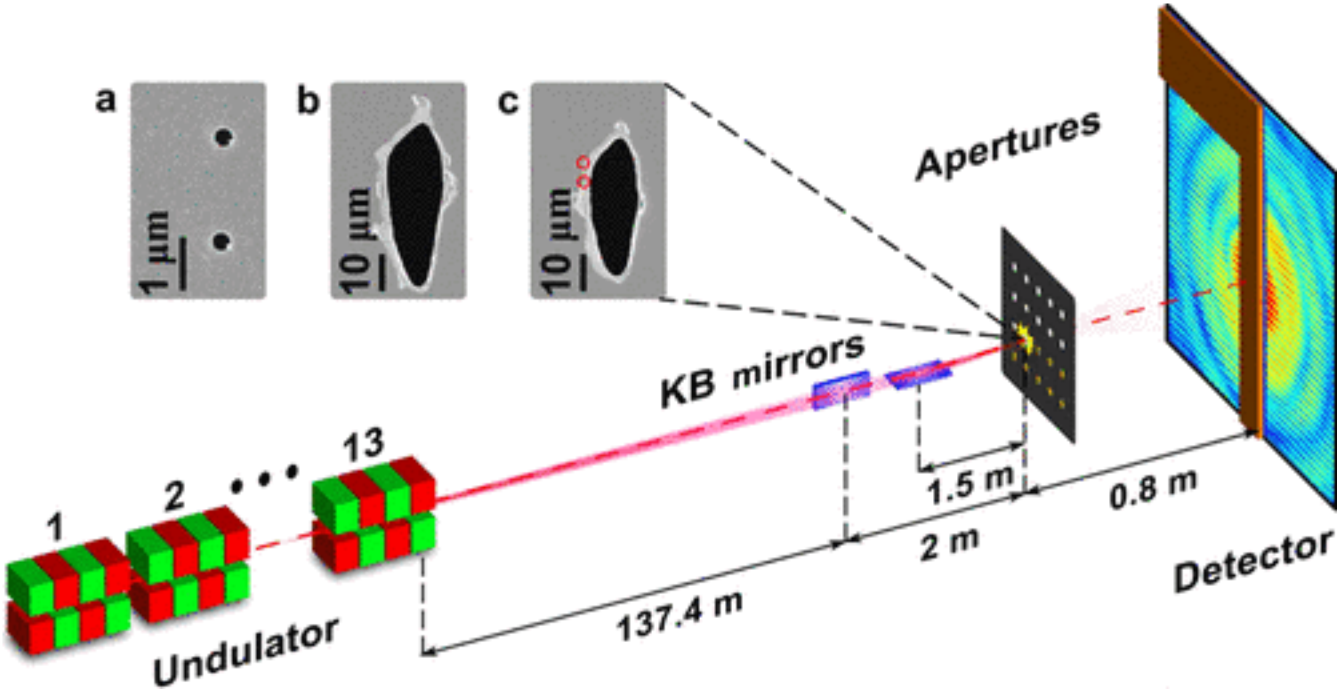
(*c*)

e 9

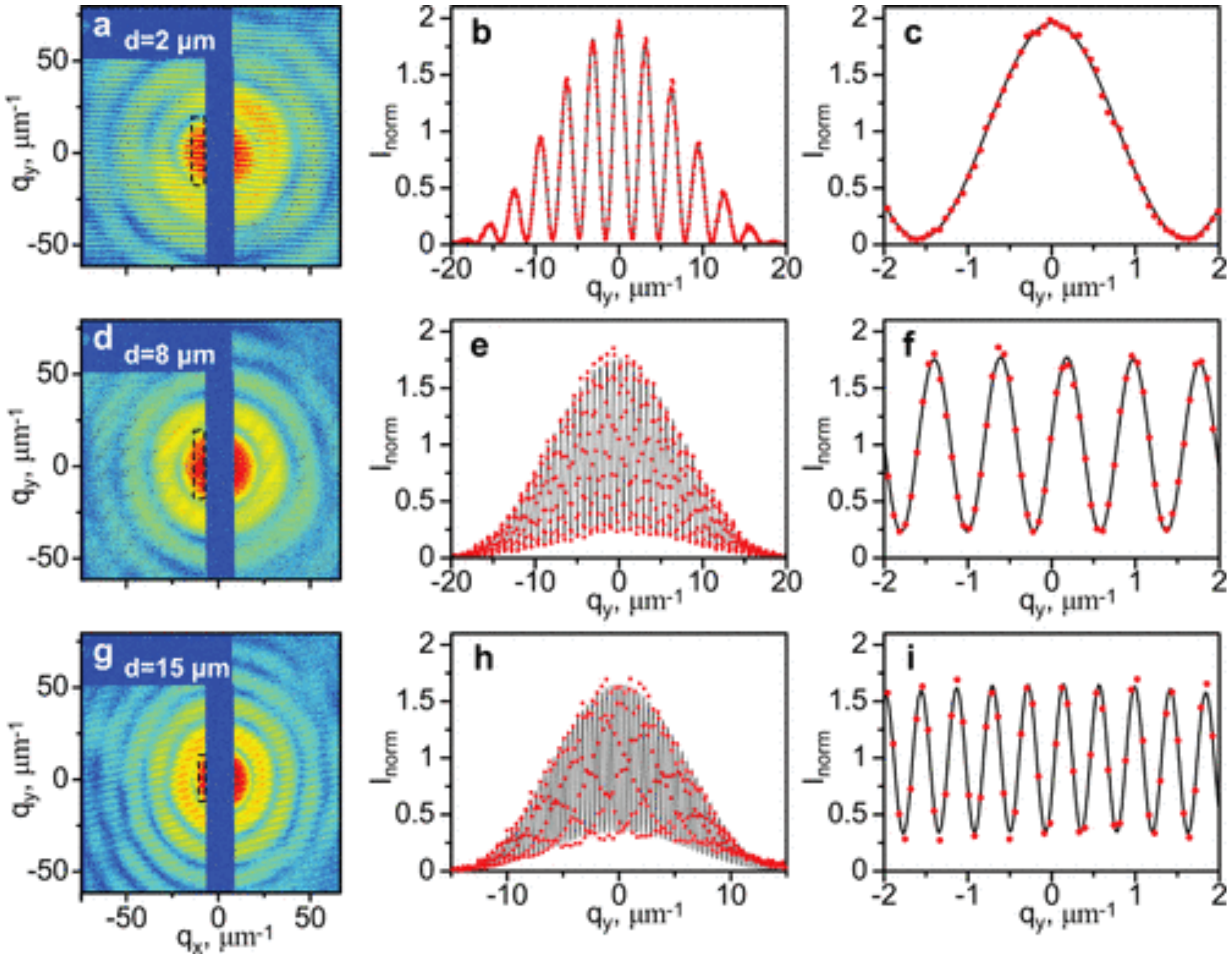
$$v = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$$

Leitenberger et al. J. Synchrotron Rad. 11, 190 (2004)

Young's experiment at an XFEL (here LCLS)

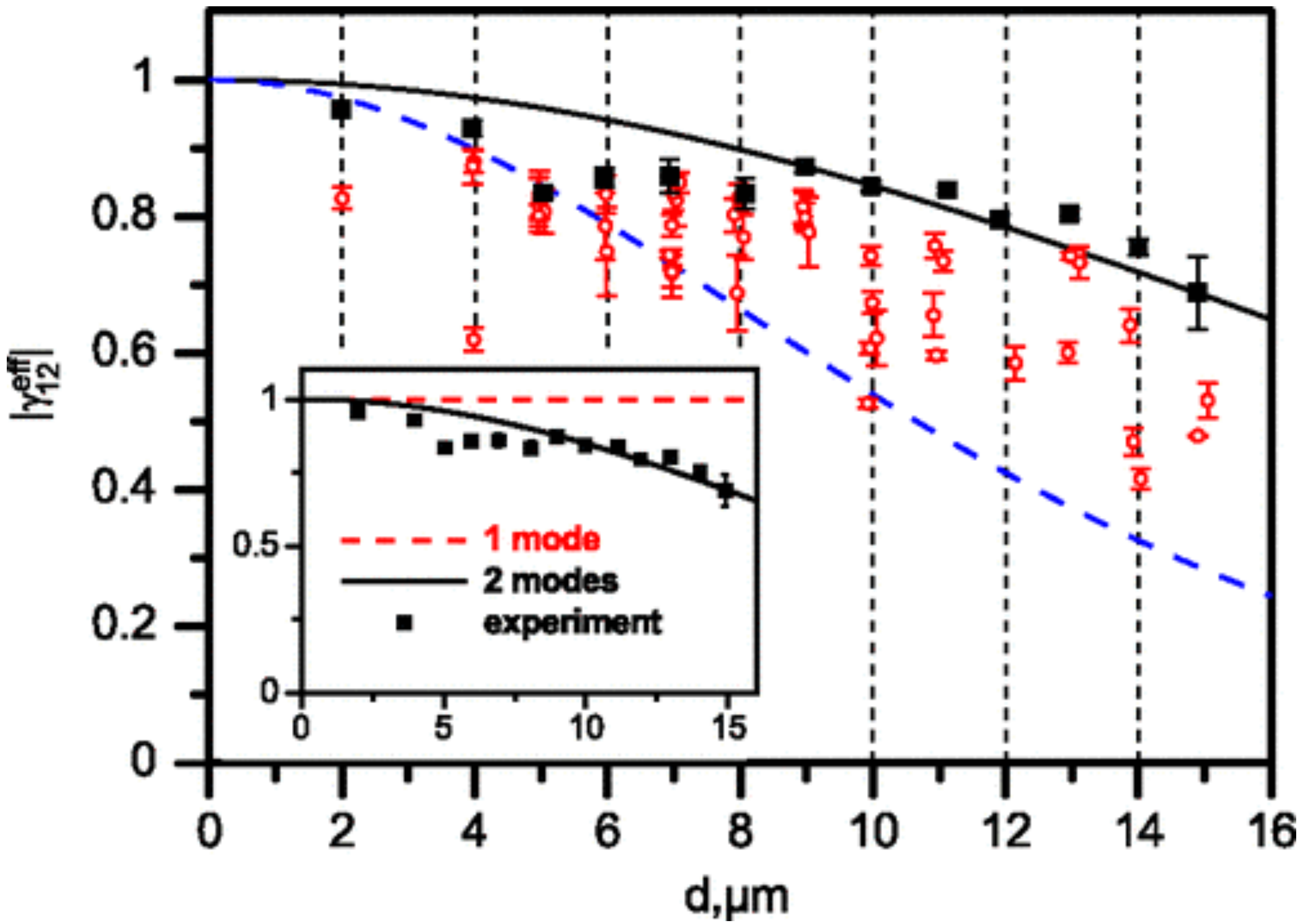


Vartaniants et al. PRL 2012



$$v = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$$

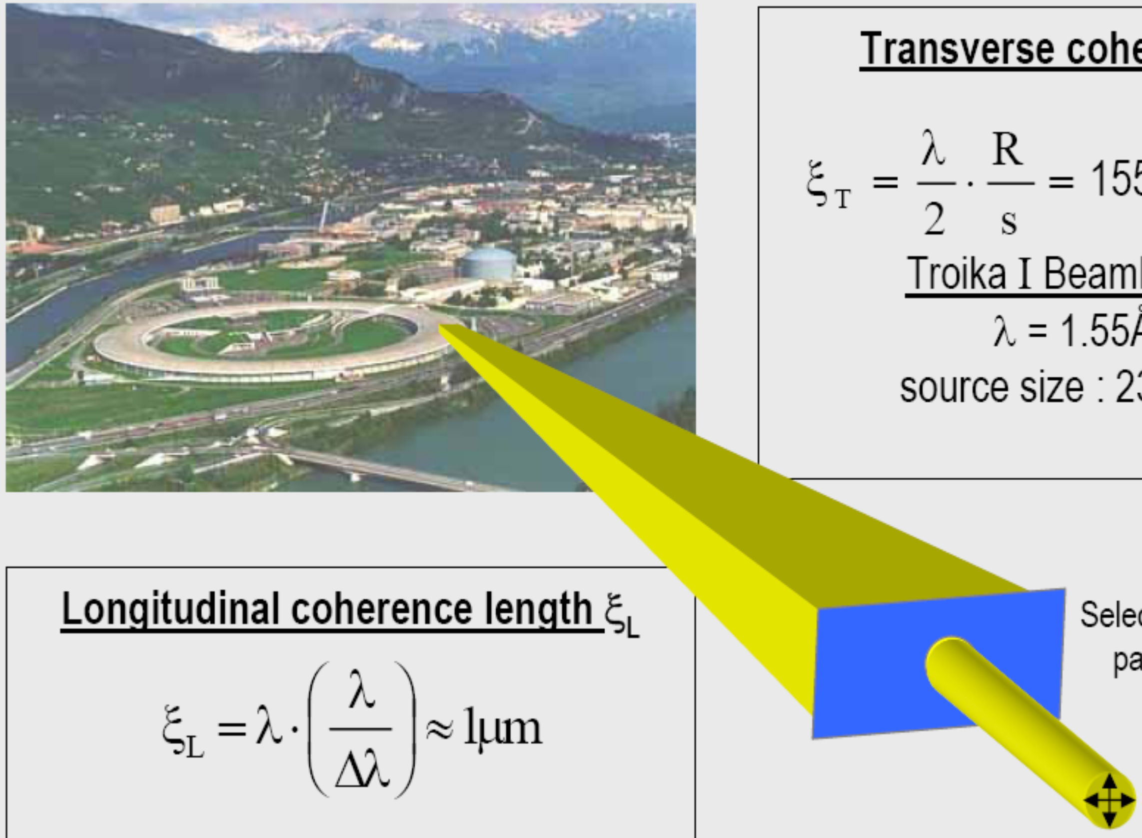
Vartaniants et al. PRL 2012



Vartaniants et al. PRL 2012

Coherent X-rays

third generation synchrotron sources
(ESRF, APS, Spring-8,...)
(and soon : Diamond, Soleil, SLS, Petra-III)



Transverse coherence lengths ξ_T

$$\xi_T = \frac{\lambda}{2}\cdot\frac{R}{s} = 155(V) \times 3.8(H)\ \mu m^2$$

Troika I Beamline parameters
$\lambda = 1.55$Å, R=46m,
source size : $23(V)\times928(H)\mu m$

Longitudinal coherence length ξ_L

$$\xi_L = \lambda\cdot\left(\frac{\lambda}{\Delta\lambda}\right) \approx 1\mu m$$

$\lambda = 1.55$Å , Si(111) $\Delta\lambda/\lambda = 1.4 \cdot 10^{-4}$

Selectioning coherent
part of the beam

beam size $\approx \xi_T \times \xi_T$

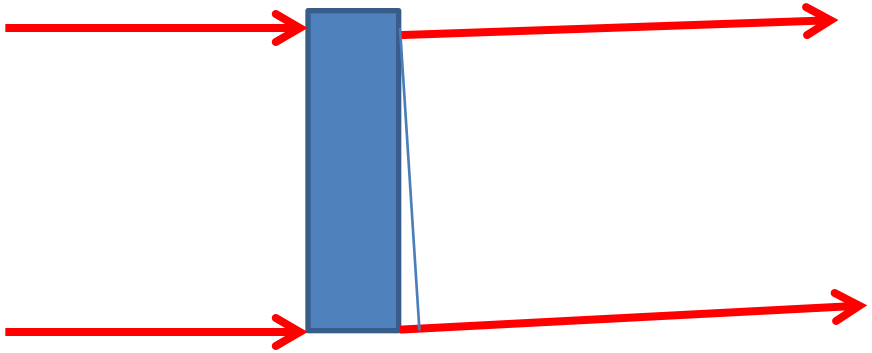
A. Robert, SLAC

Contrast (Visibility) β(Q) of a speckle pattern is determined by the coherence properties of the X-ray beam

$$\beta(Q) = \frac{1}{V^2\langle|E|^2\rangle^2}\int_V\int_V |\Gamma(\vec{r}_2-\vec{r}_1, \vec{Q}\cdot(\vec{r}_2-\vec{r}_1)/ck_o)|^2 d\vec{r}_1 d\vec{r}_2$$

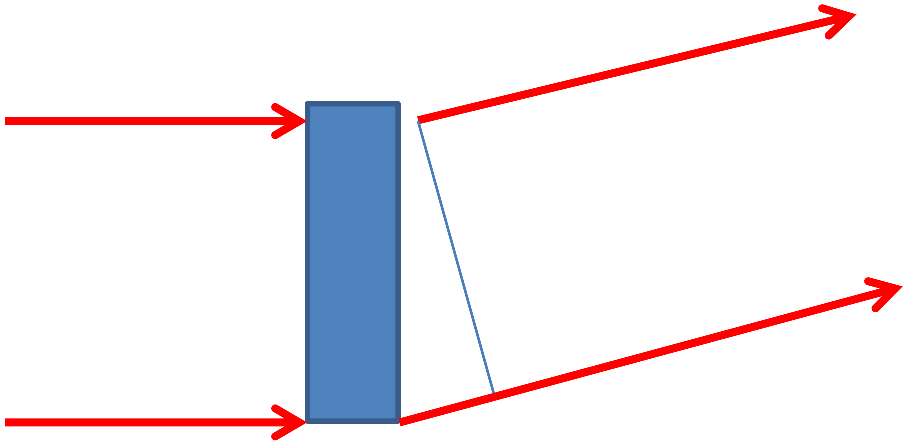
$\Gamma(\mathrm{r},\tau)$ mutual coherence function (MCF)

SAXS Q small
probing transverse coherence $\Gamma(r,0)$

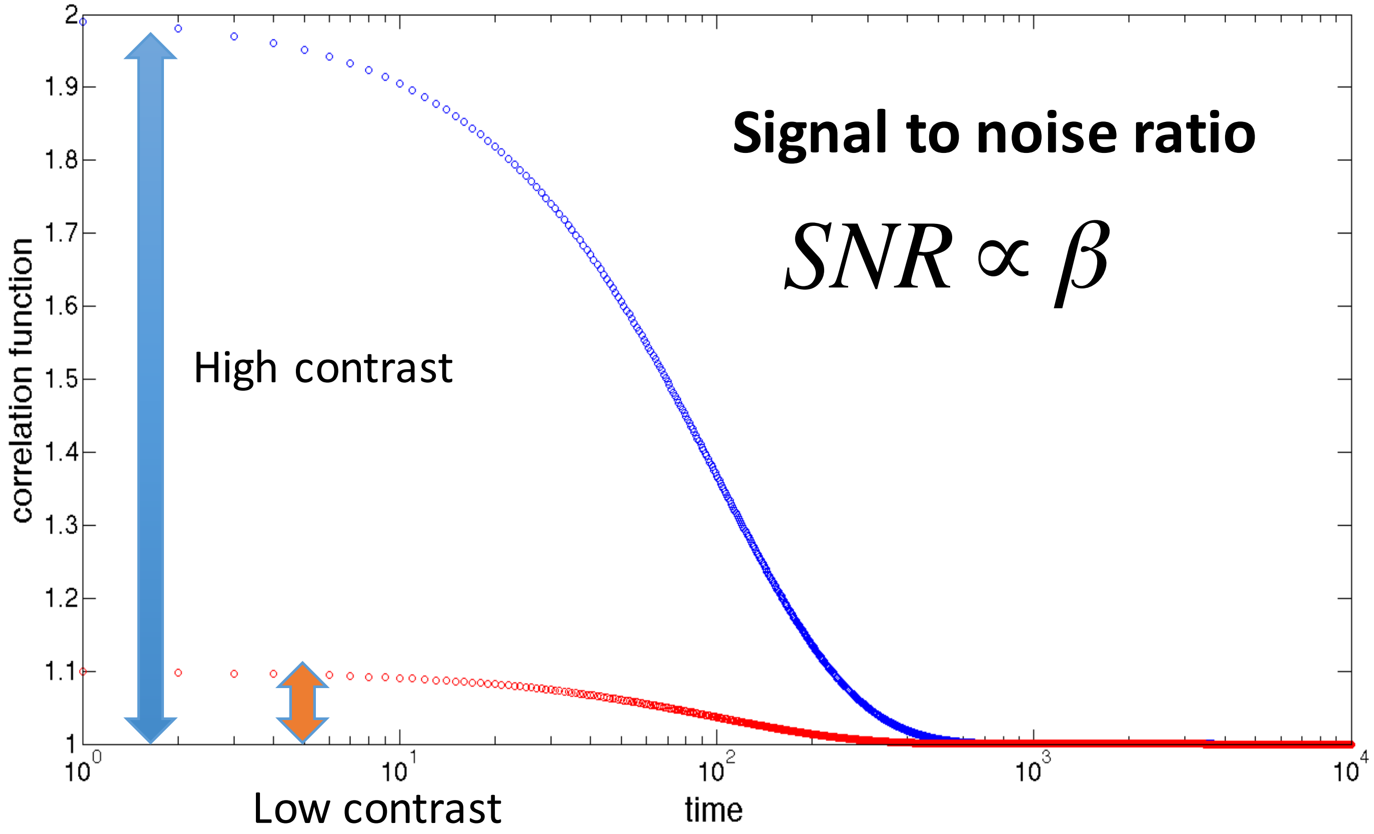


$$\Delta\tau = \frac{Q(r_2-r_1)}{ck_0} \ll \tau_c$$

WAXS Q large
probing transverse AND temporal coherence $\Gamma(r,\Delta\tau)$



$$\Delta\tau = Q(r_2-r_1)/ck_0 \sim \tau_c$$



Signal to noise ratio

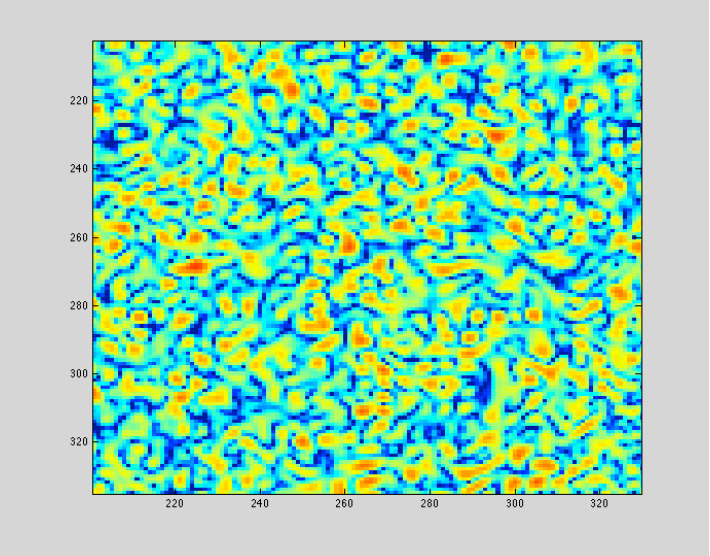
$$SNR \propto \beta$$

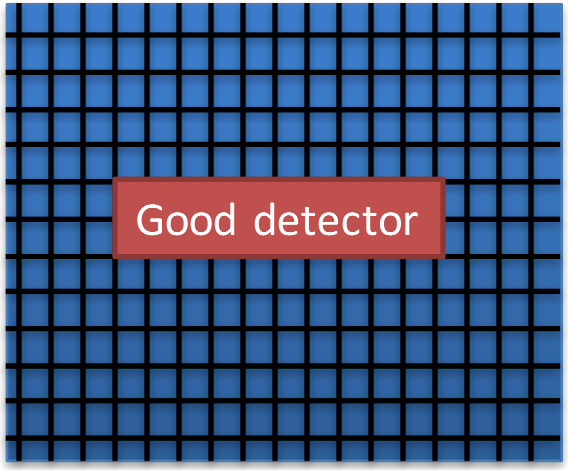
High contrast

Low contrast

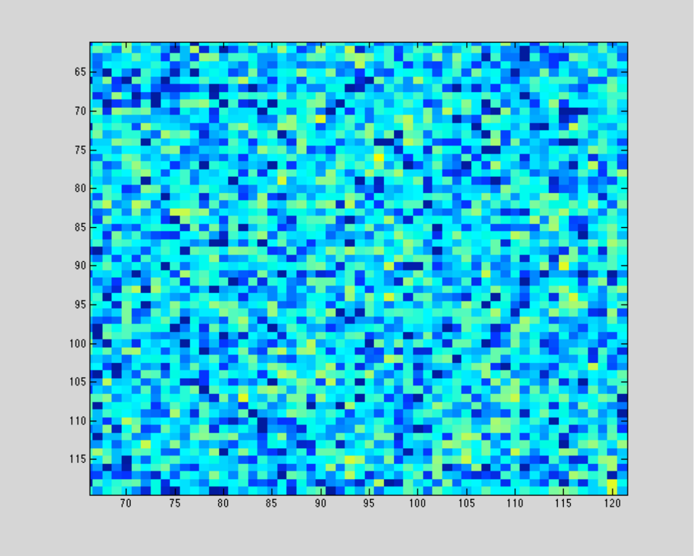
Speckle size needs to match pixel size of detector

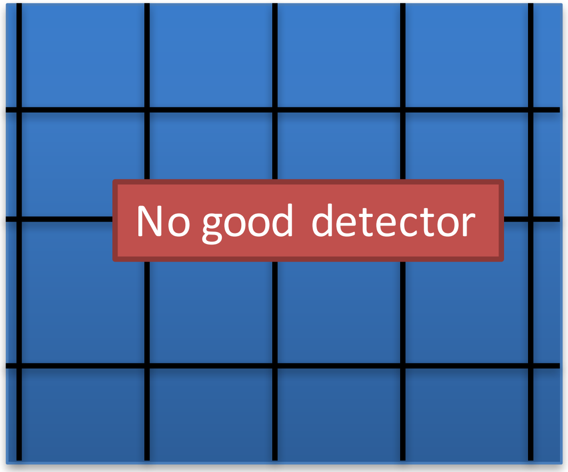
Large speckles



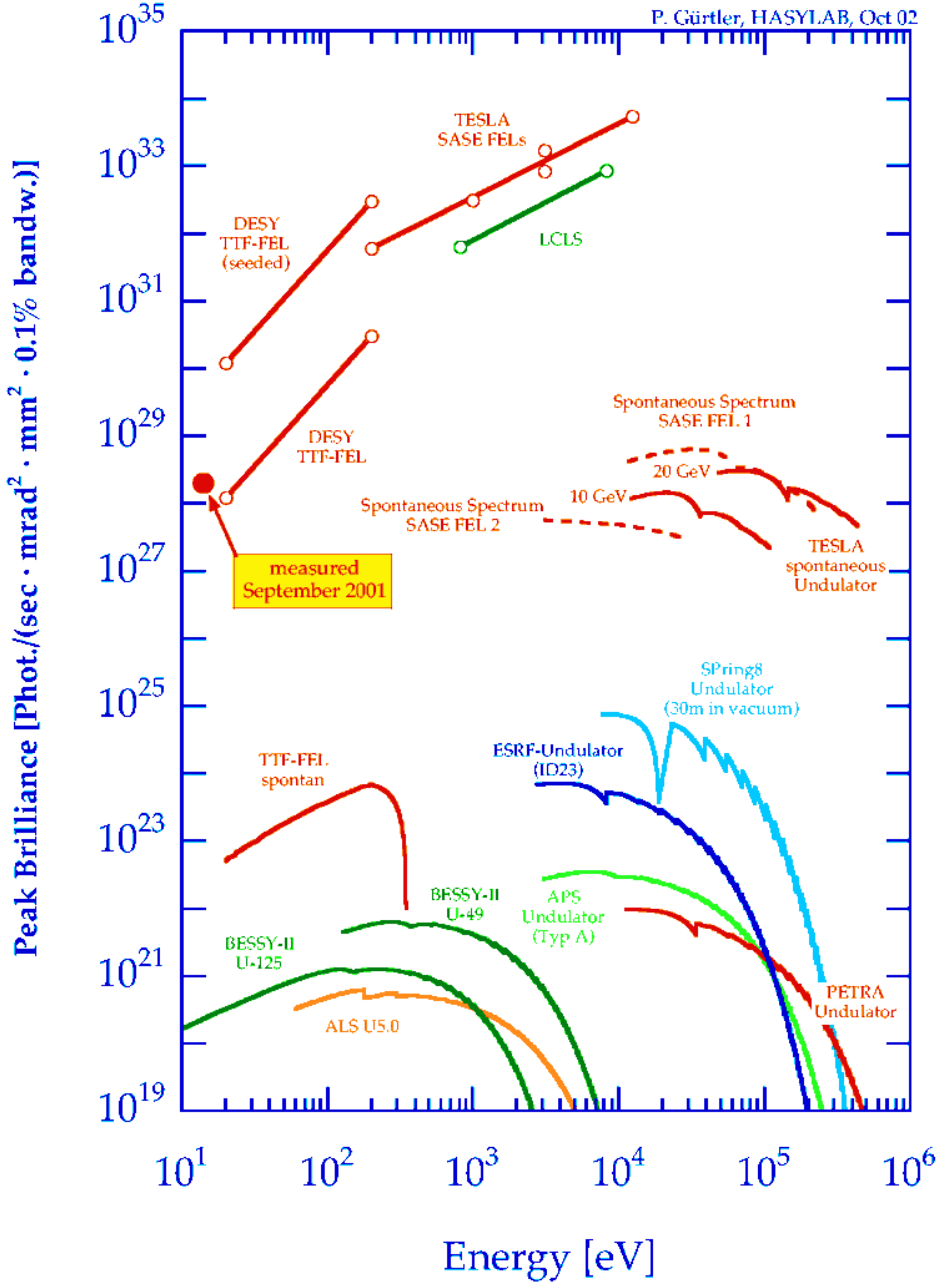

Good detector

Small speckles




No good detector

Brilliance of X-rays Sources



Coherent Flux: F_0= B $\lambda^2(\Delta\lambda/\lambda)$

(ESRF: ID10A $F_0\sim10^{10}$ **ph/s)**

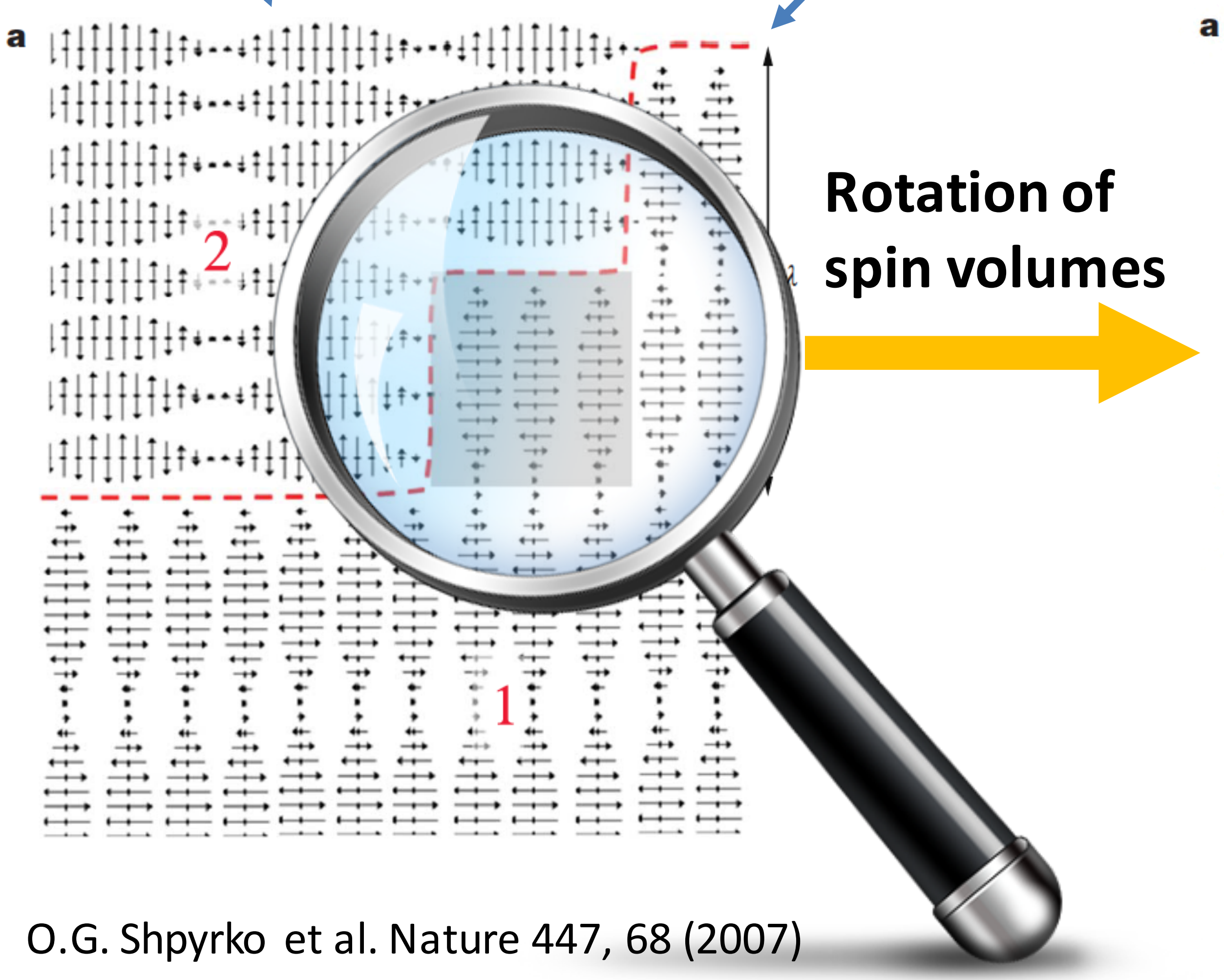
Examples

Antiferromagnetic domain fluctuations in Chromium

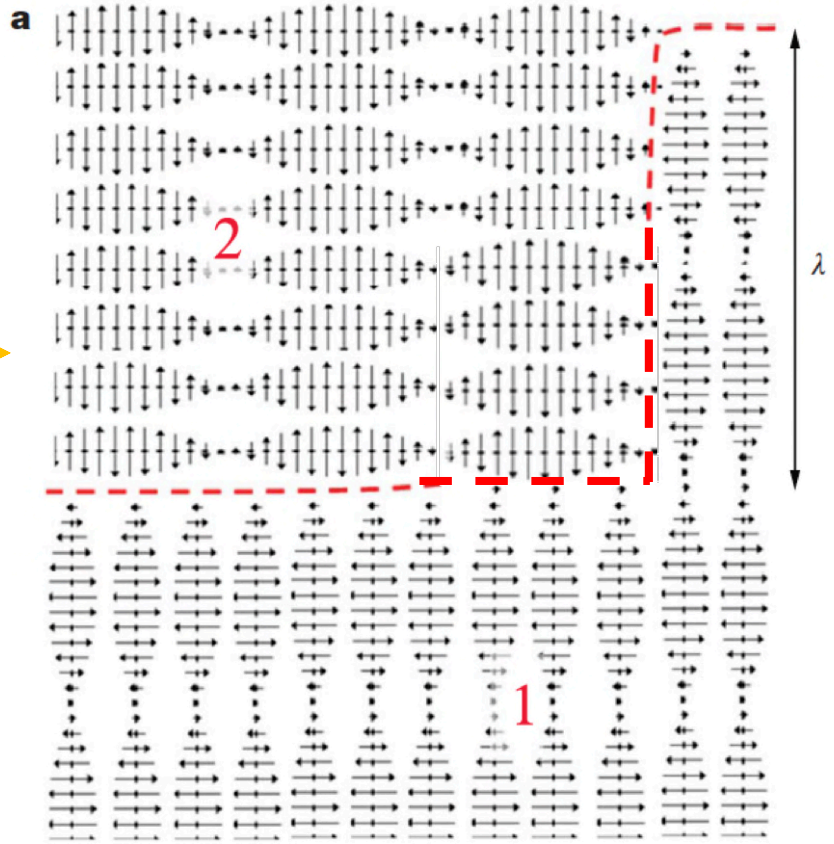
24 51.996
2672 1.6
1857
Cr
[Ar]3d⁵4s
7.19 2,3,6

Spin density waves

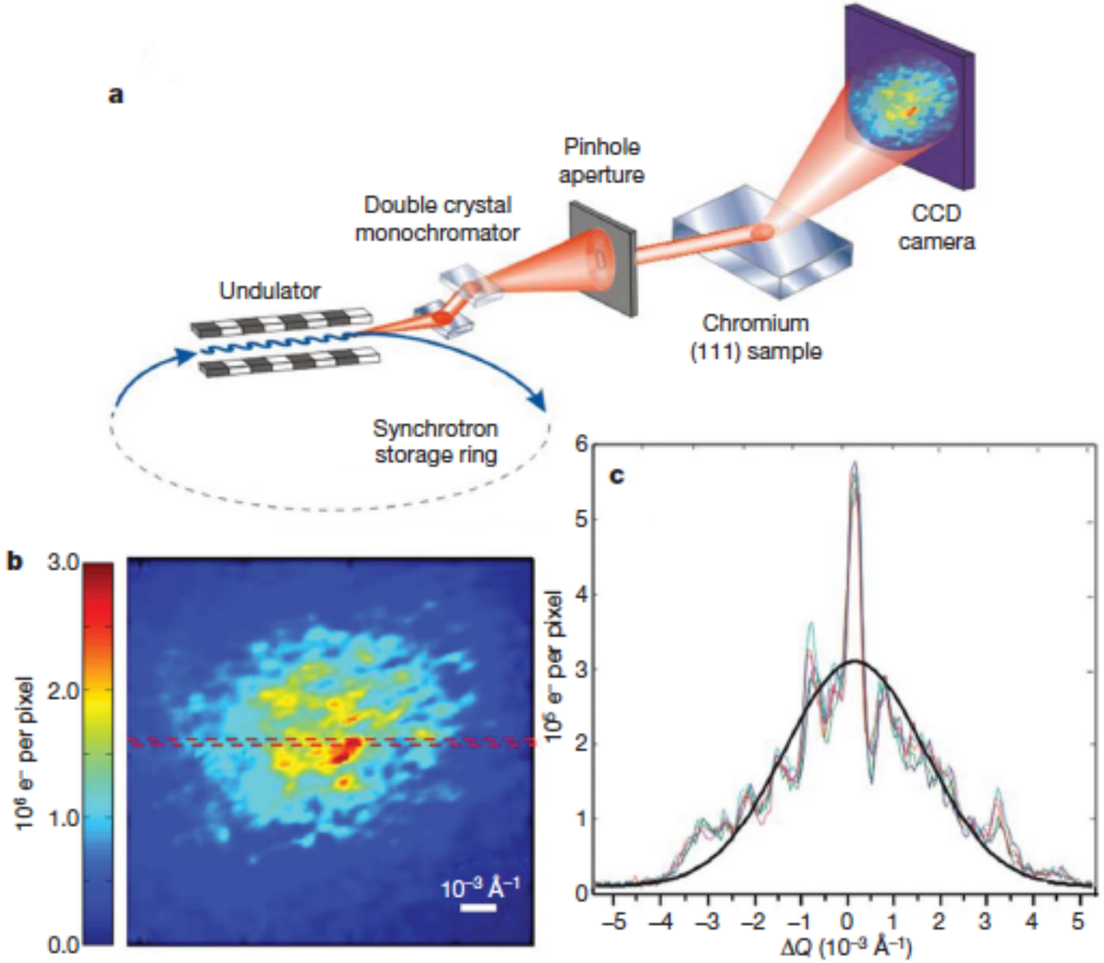
Domain wall

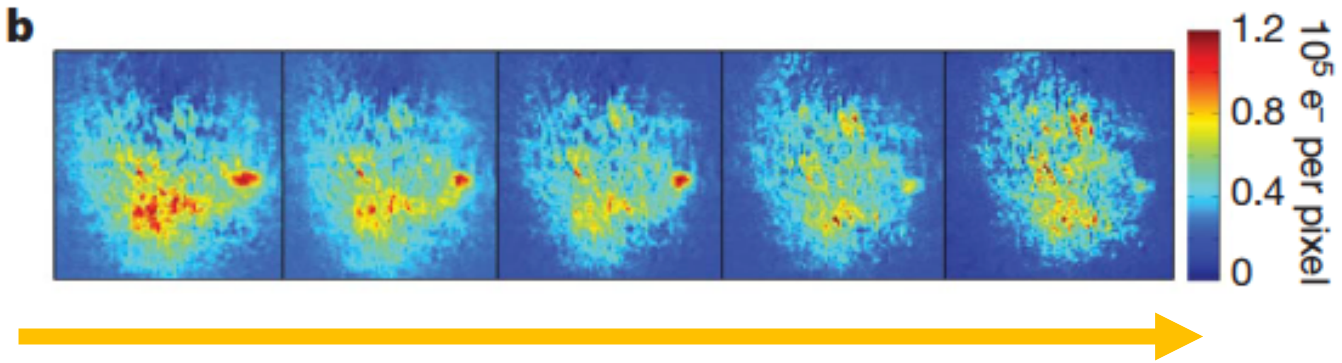


Rotation of spin volumes



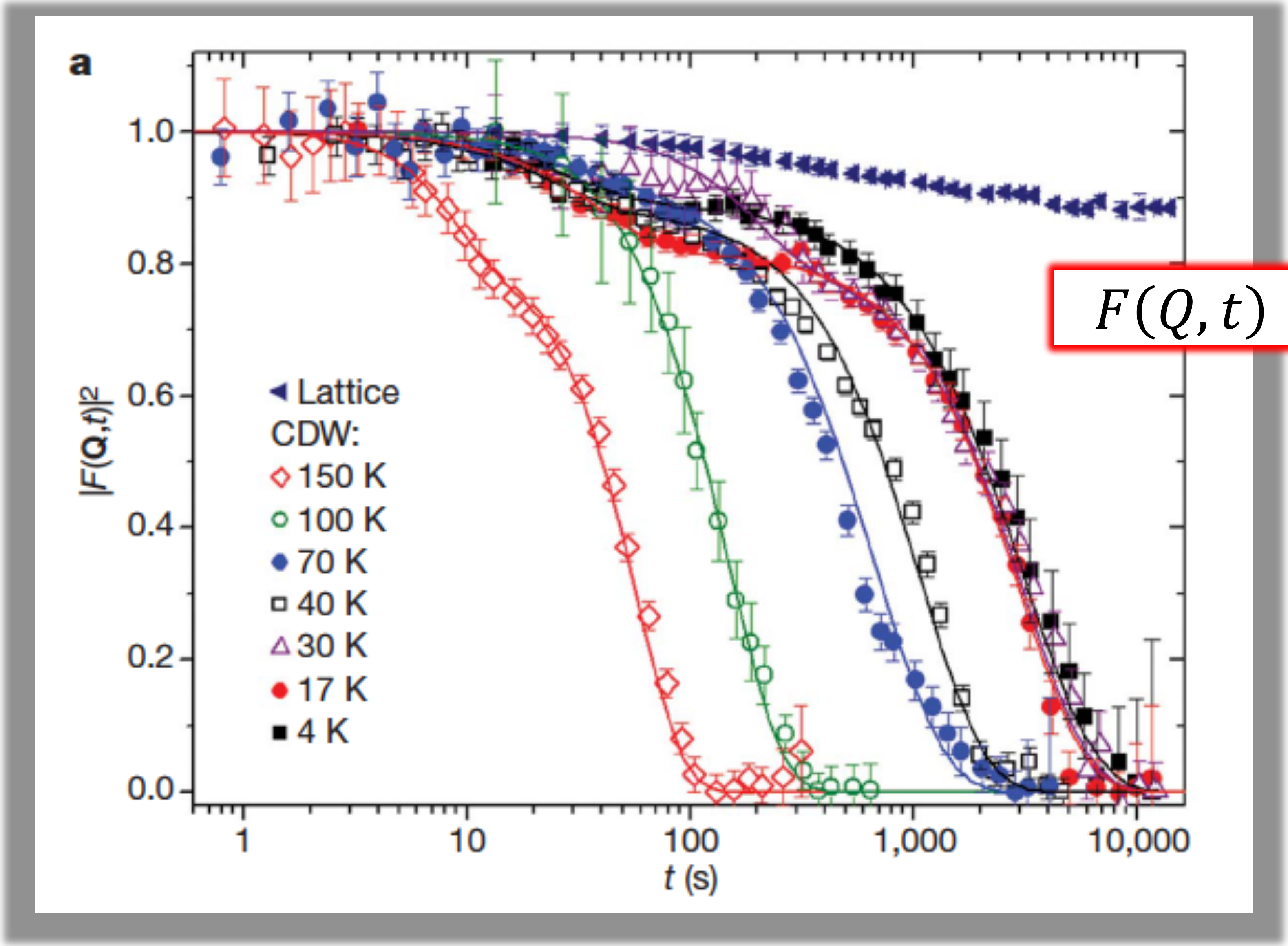
O.G. Shpyrko et al. Nature 447, 68 (2007)


a
Pinhole aperture
Double crystal monochromator
CCD camera
Undulator
Chromium (111) sample
Synchrotron storage ring
b
3.0
2.0
1.0
0.0
10⁶ e⁻ per pixel
10⁻³ Å⁻¹
c
6
5
4
3
2
1
0
10⁶ e⁻ per pixel
−5 −4 −3 −2 −1 0 1 2 3 4 5
ΔQ (10⁻³ Å⁻¹)

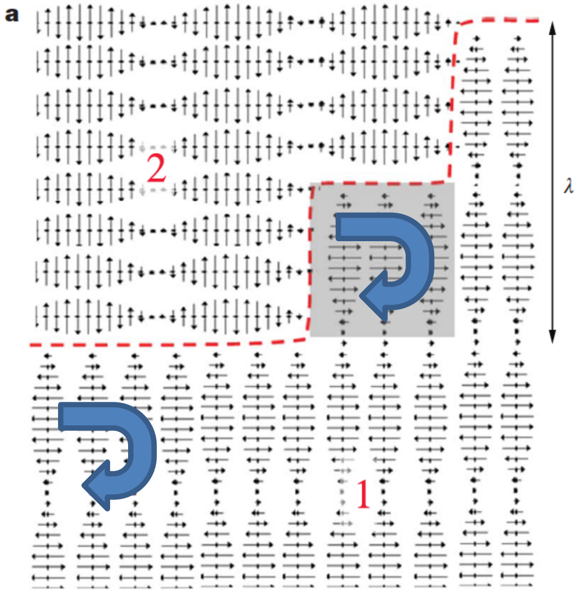

b
1.2
0.8
0.4
0
10⁵ e⁻ per pixel

Time

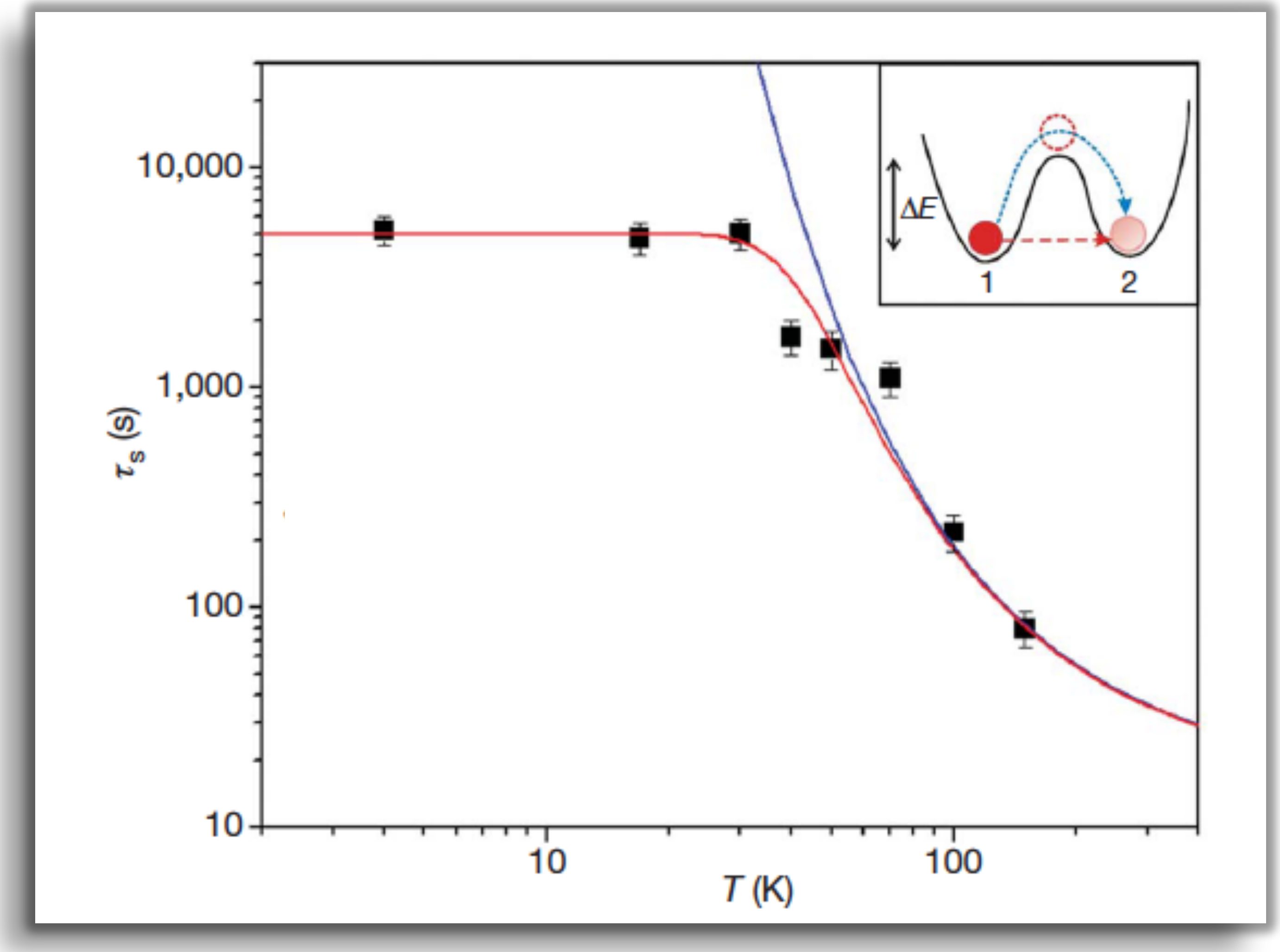
Correlation functions



$$F(Q,t) = \exp(-(t\,/\tau_s)^{\beta})$$



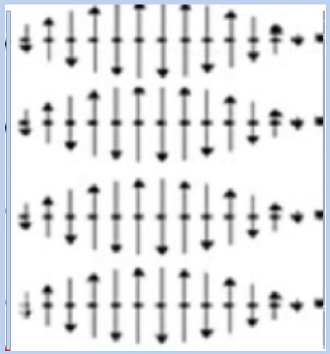
Quantum rotation of spin blocks



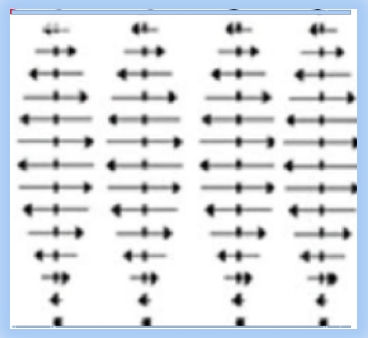
Blue line: Thermally activated jumps over an energy barrier

Red line: Quantum tunneling through an energy barrier

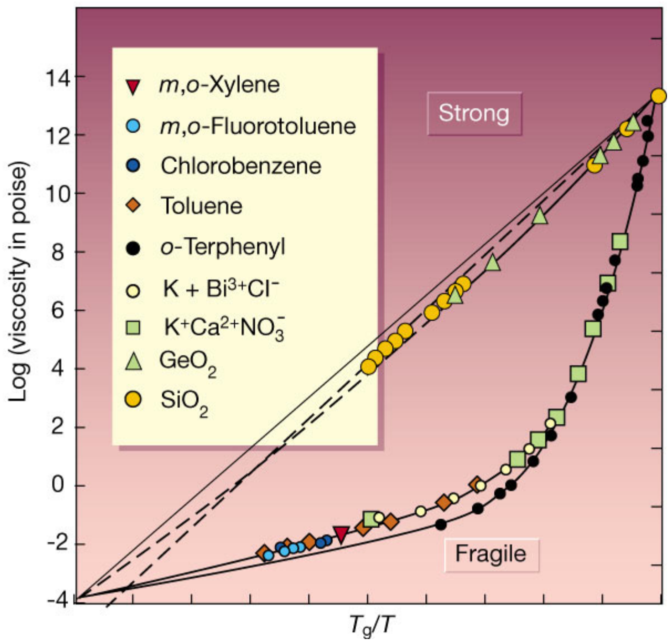
1

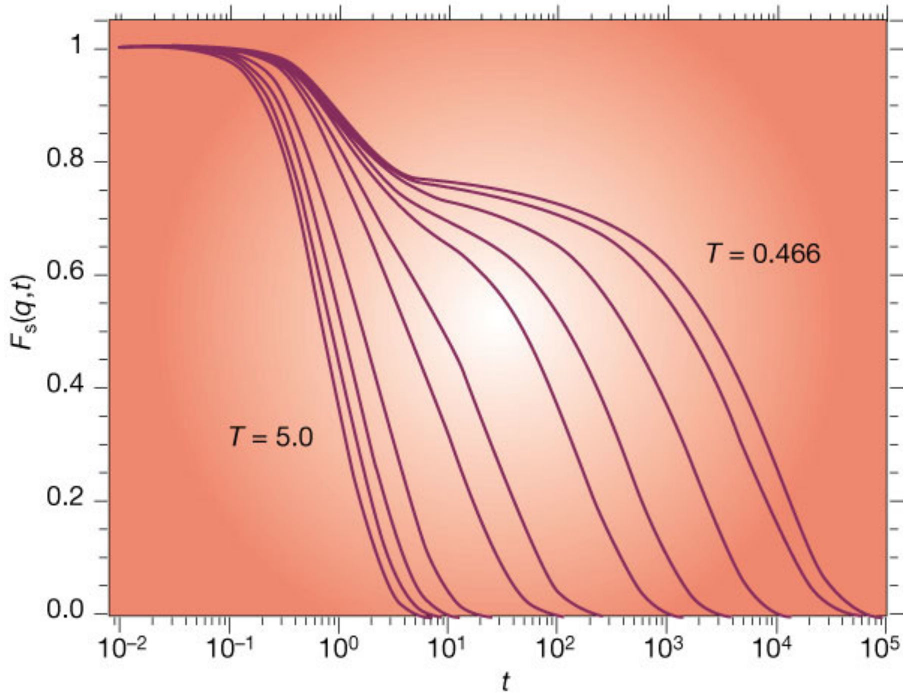


2



How Solid are Glasses ?



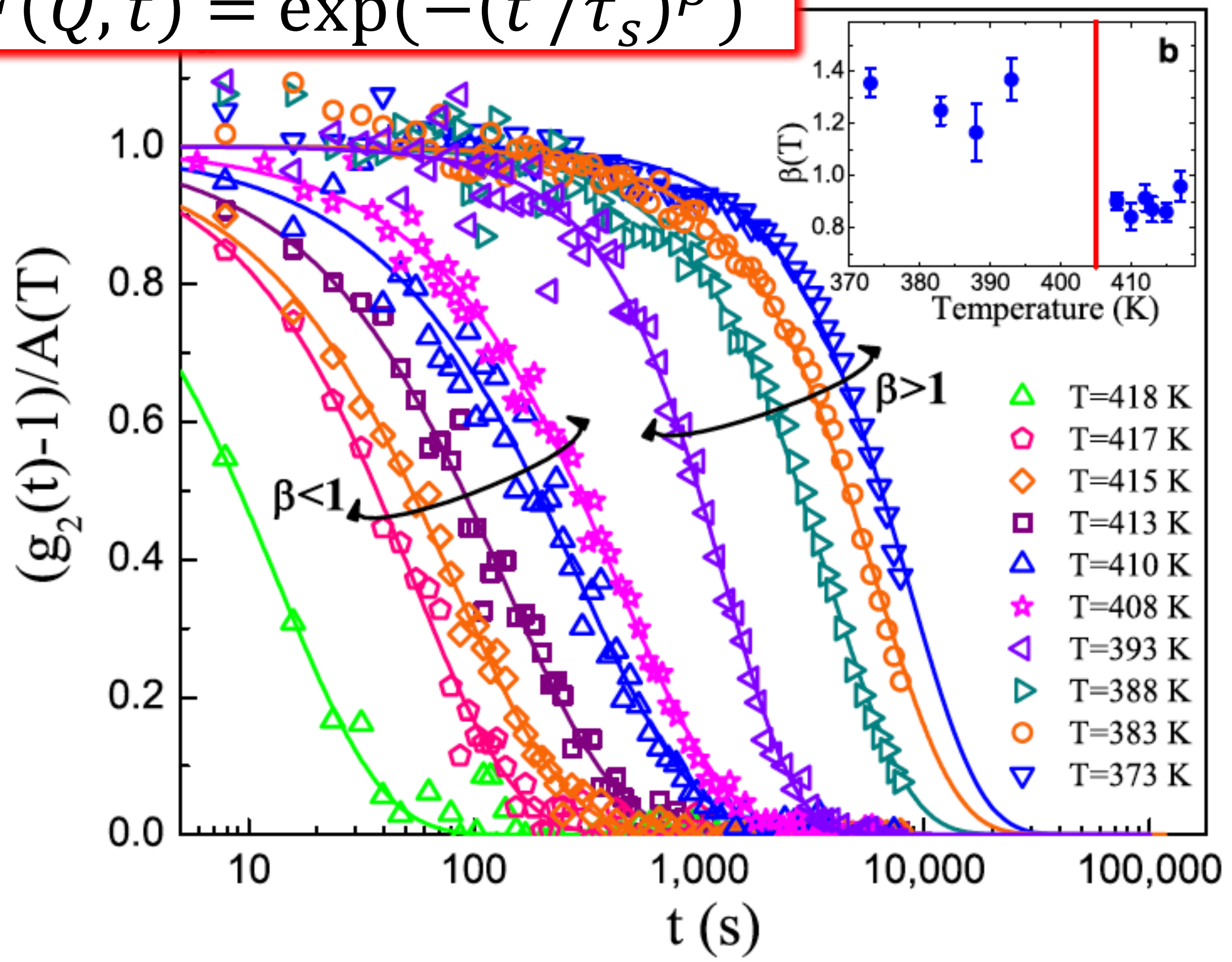


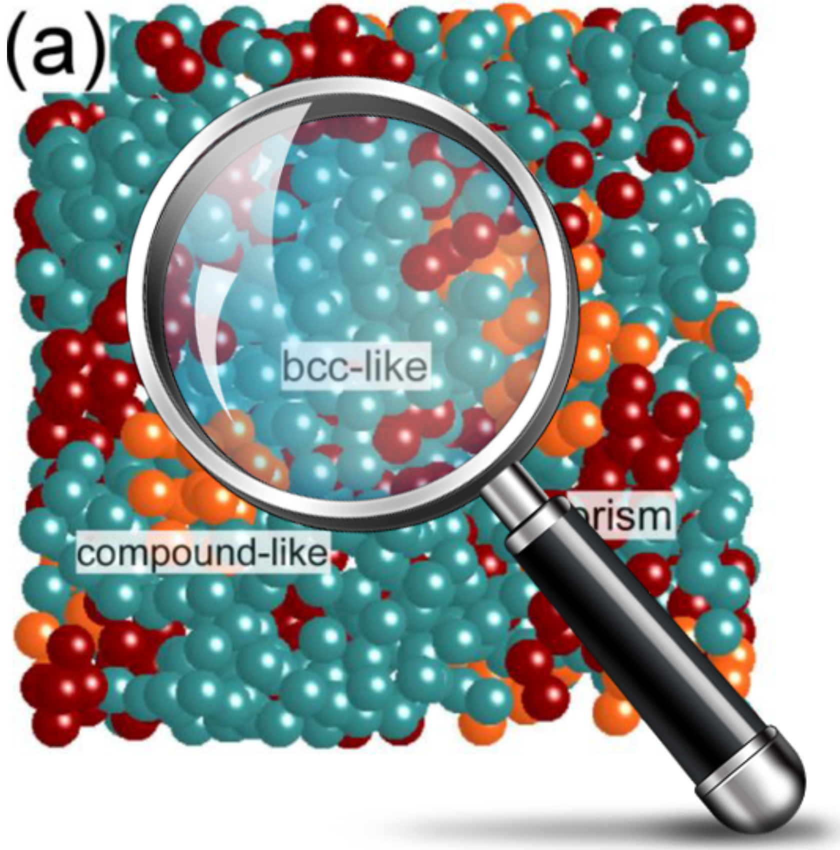
PABLO G. DEBENEDETTI AND FRANK H. STILLINGER,
Nature 410, 259 (2001)

Atomic dynamics in metallic glasses

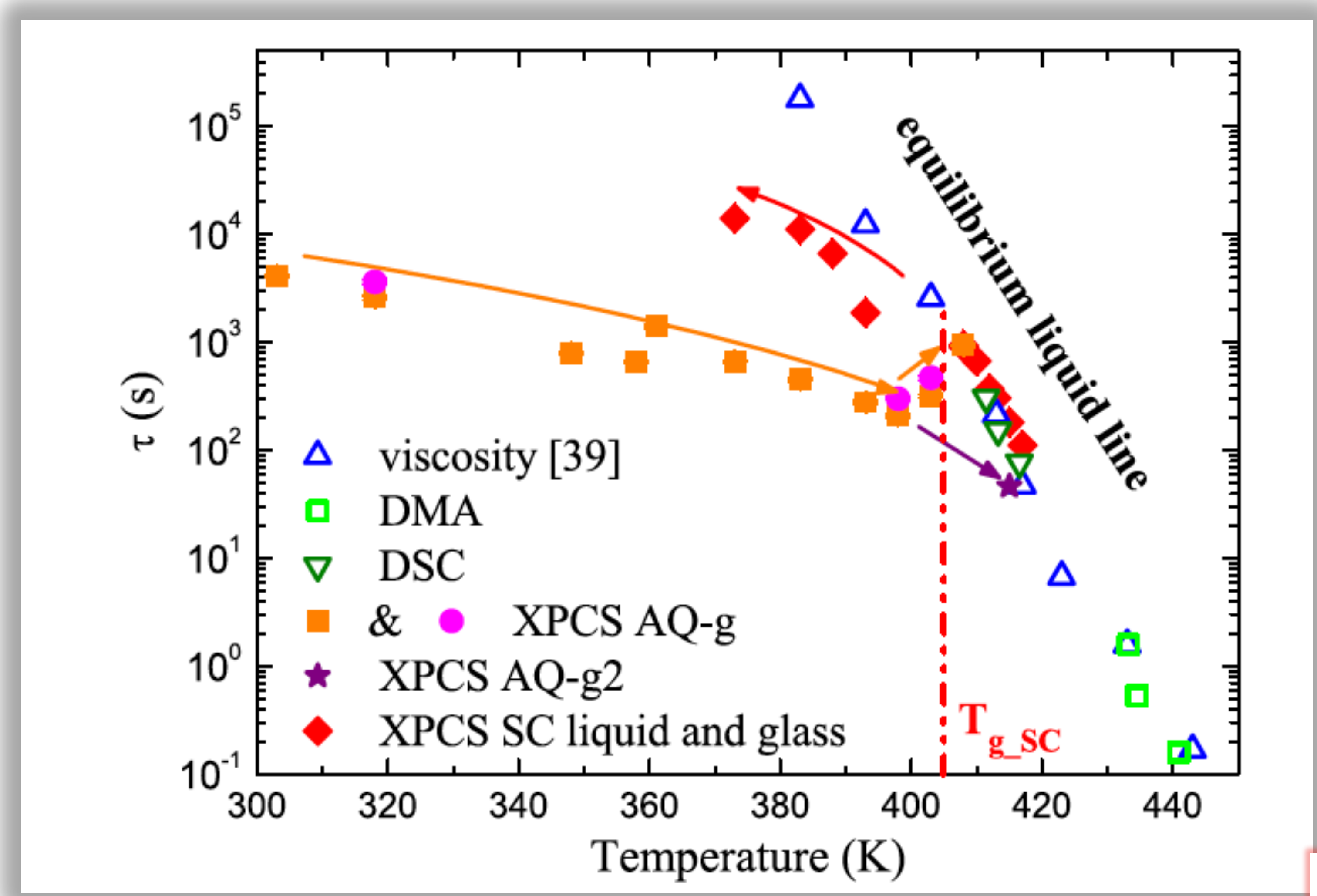
$$F(Q,t) = \exp(-(t/\tau_s)^{\beta})$$

B. Ruta et al. Phys. Rev. Lett. 109, 165701 (2012)
B. Ruta et al. Nature Comm. 5, 3939 (2014)





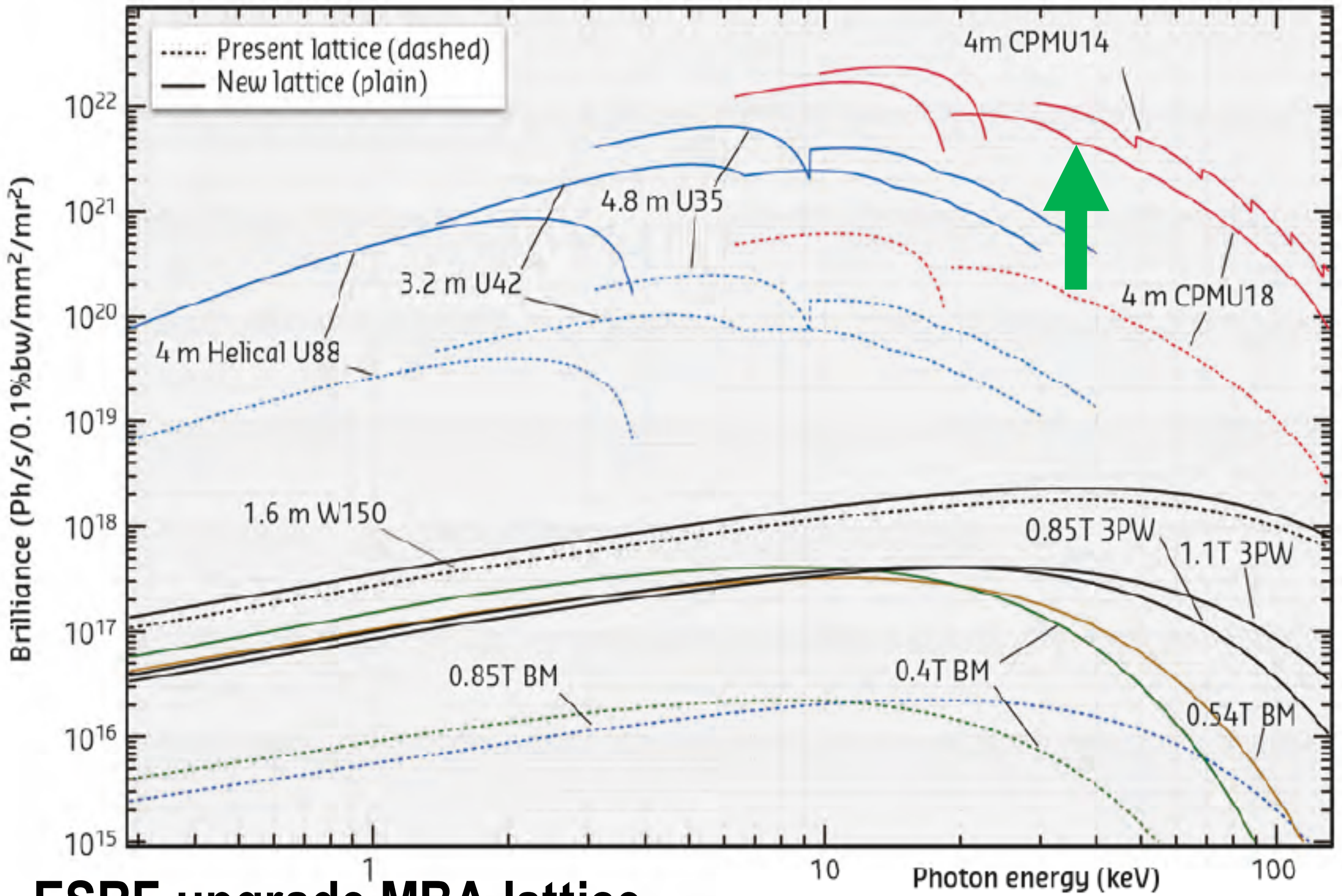
Reality check for glasses



- Fast relaxation dynamics exists below the glass transition temperature Tg.
- Glasses are not completely frozen in
- Stress dominates dynamics below Tg

B. Ruta et al. Phys. Rev. Lett. 109, 165701 (2012)
B. Ruta et al. Nature Comm. 5, 3939 (2014)

XPCS at
diffraction limited strorage rings (DLSR)



ESRF upgrade MBA lattice

Coherent Flux: $F_0 = B\,\lambda^2\,(\Delta\lambda/\lambda)$

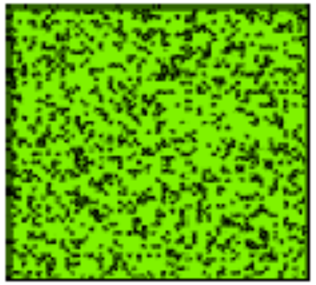
Increase of B by factor 50 - 100

up to 10.000 times faster time scale accessible in XPCS

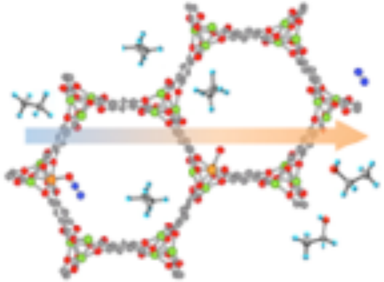
$$\boxed{\tau \sim 1/B^2}$$

unusual scaling because XPCS correlates pairs of photons

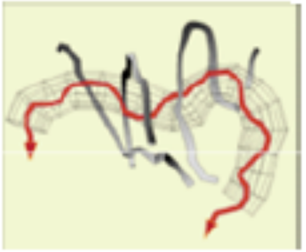
Nucleation kinetics
10.1126/science.1230915



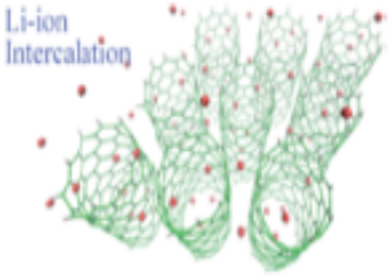
Selective Catalysis
10.1038/nchem.1956



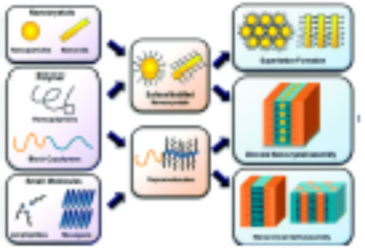
Polymer reptatior

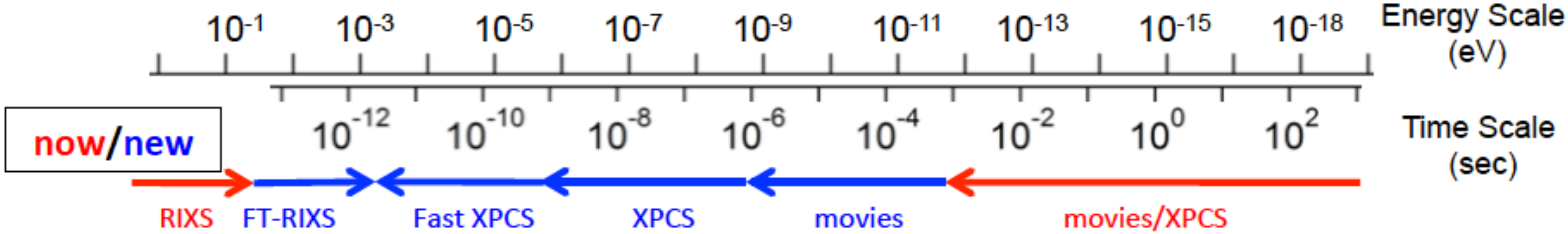


Intercalation kinetics,
10.1039/C0EE00473A



Self assembly





Energy Scale
(eV)

Time Scale
(sec)

now/new

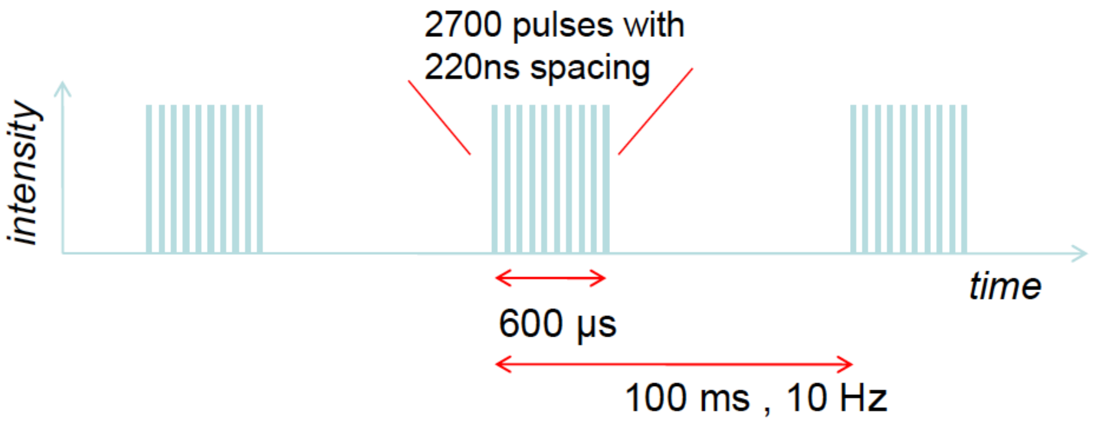
RIXS FT-RIXS Fast XPCS XPCS movies movies/XPCS

Problems that can be adressed at DLSR

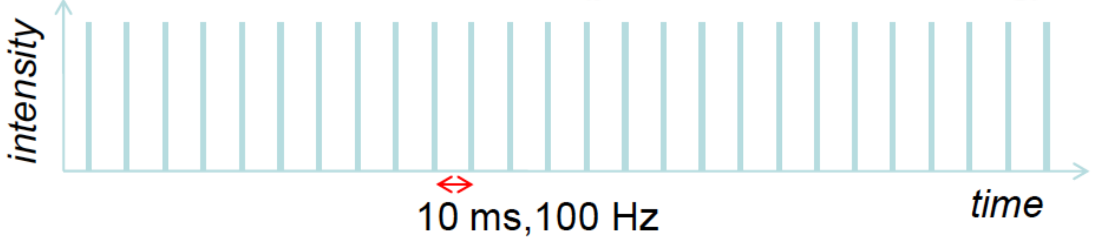
- Dynamics in the supercooled state
- Dynamics in confinement
- Domain fluctuations in hard condensed matter
- Protein diffusion in cells
- Kinetics of biomineralization processes
- Liquids under extreme conditions (e.g. pressure)
- Driven dynamics under external (B,E,T) fields
- Local structures and their relaxations
- ...

XPCS at XFELs

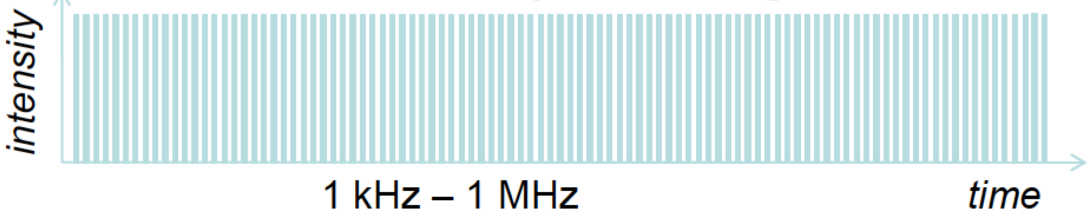
Time structure European XFEL (pulsed superconducting)



Time structure SwissFEL (pulsed normal conducting)

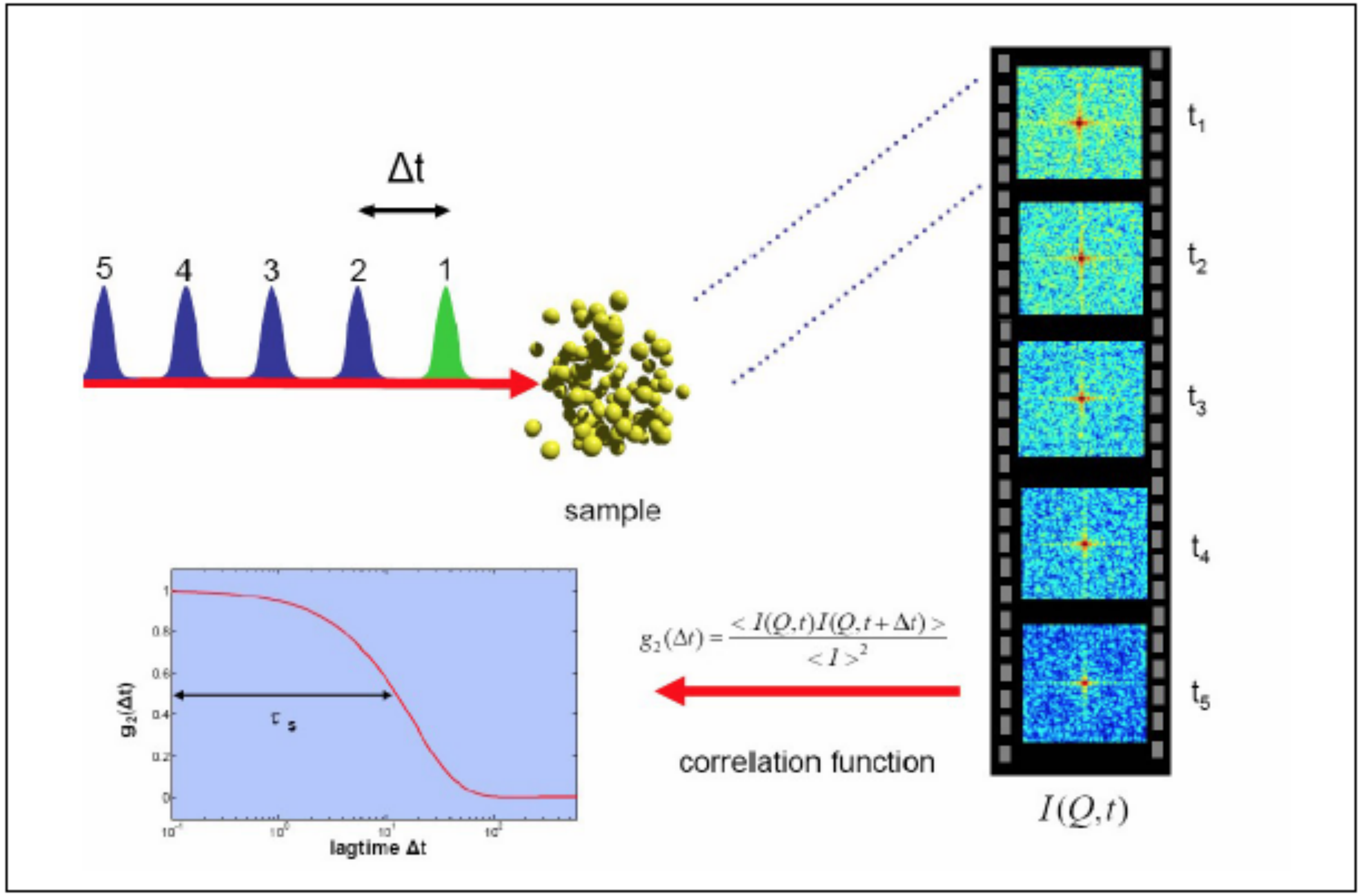


Time structure c.w. super conducting

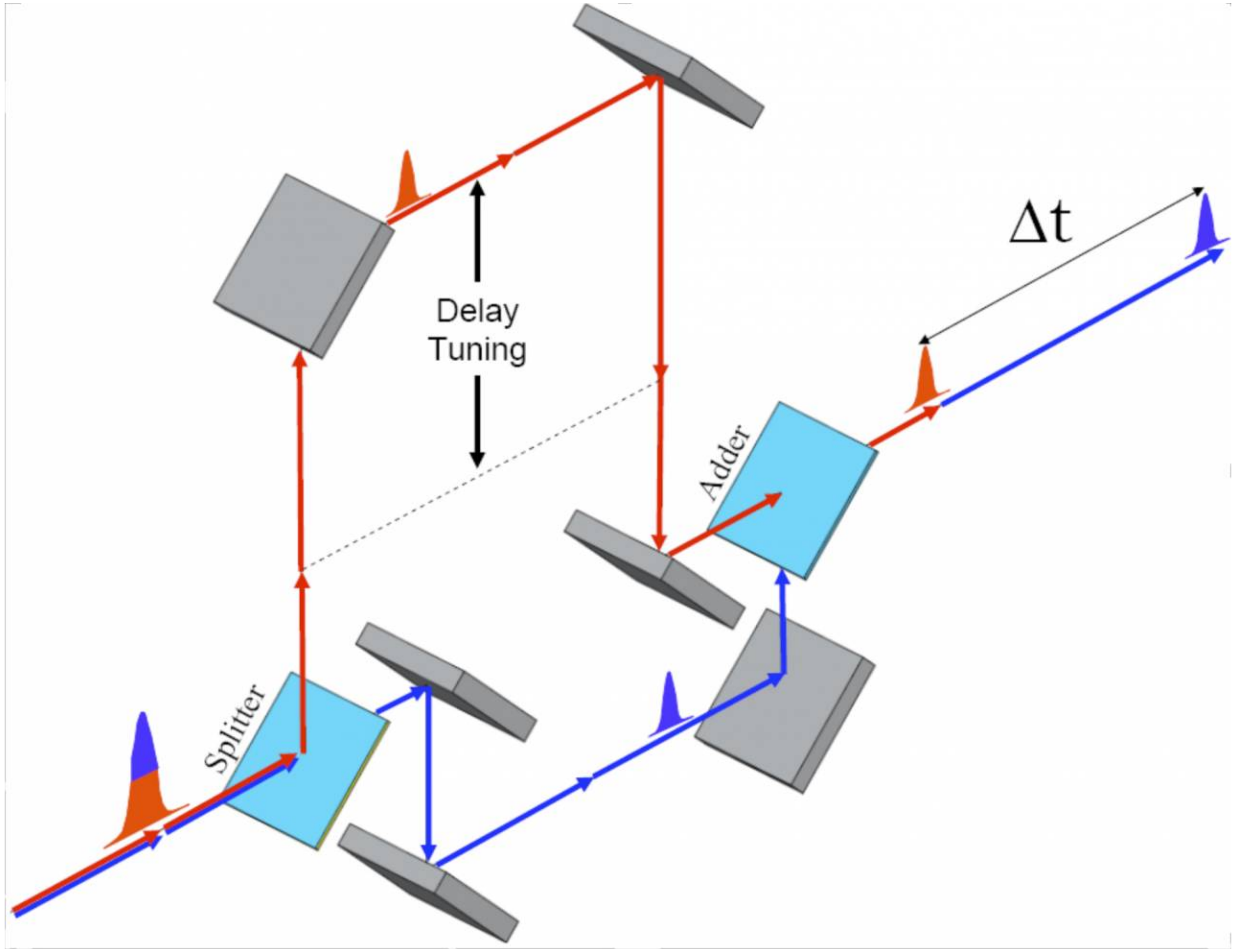


Serial mode

Temporal resolution depends on rep rate of the machine

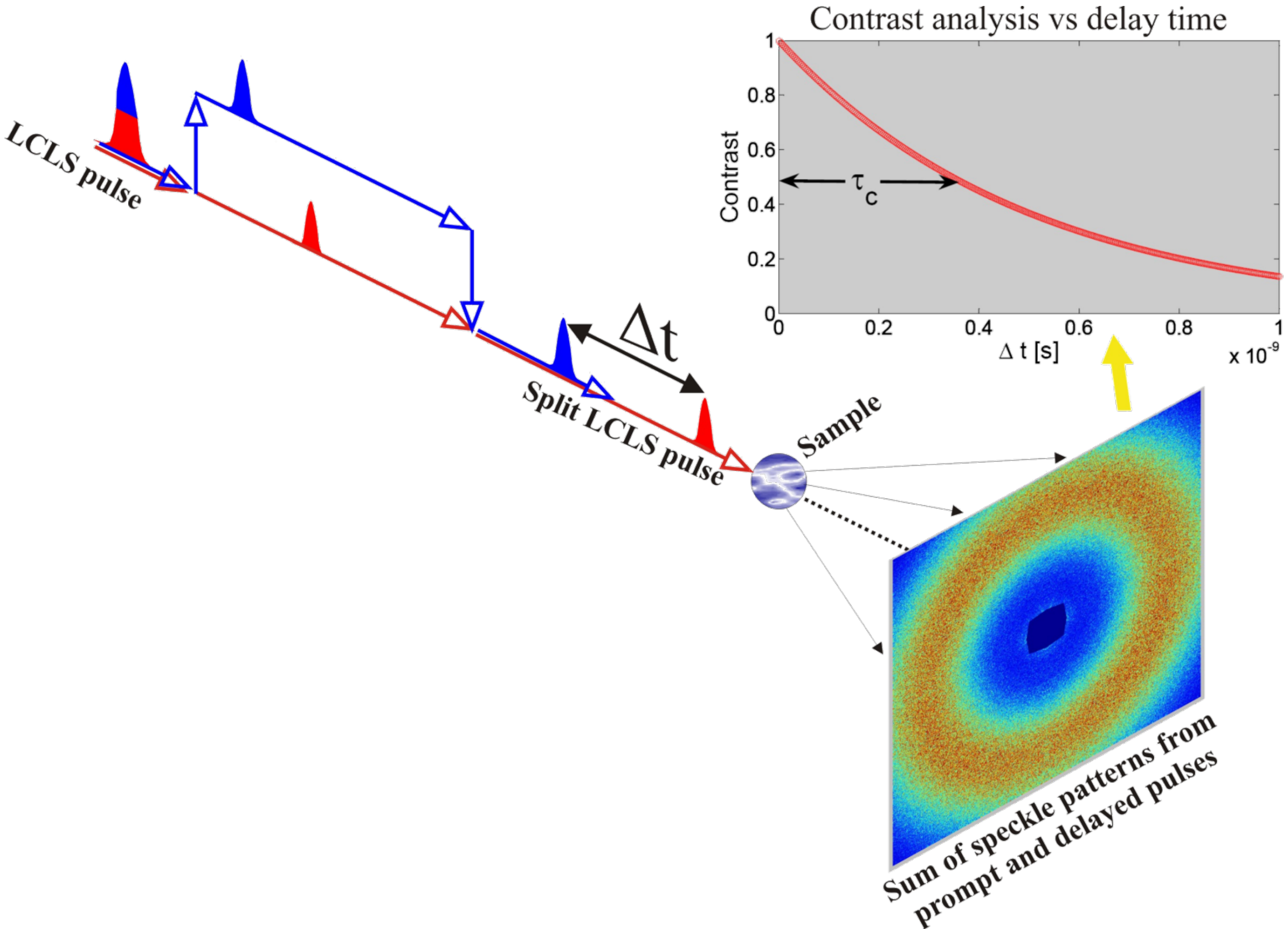


Ultrafast XPCS using a split and delay line



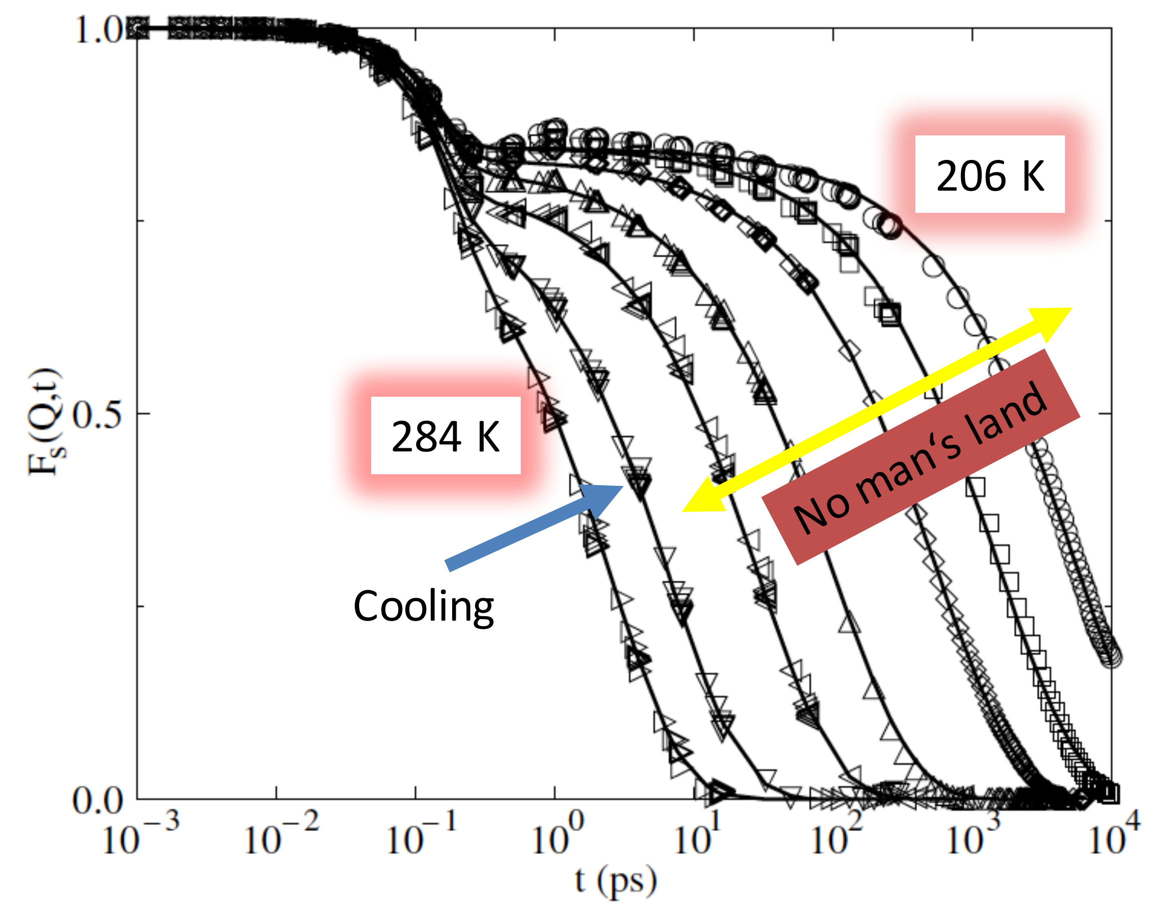
Delay times between 100 fs and 1 ns

Measure speckle contrast as a function of pulse separation

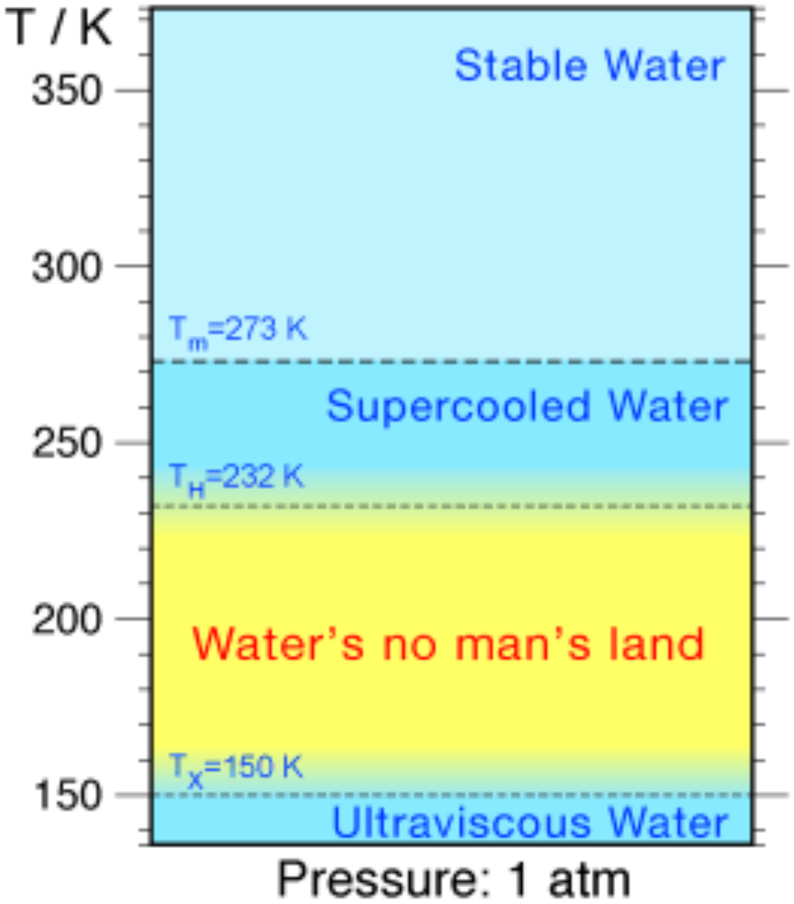


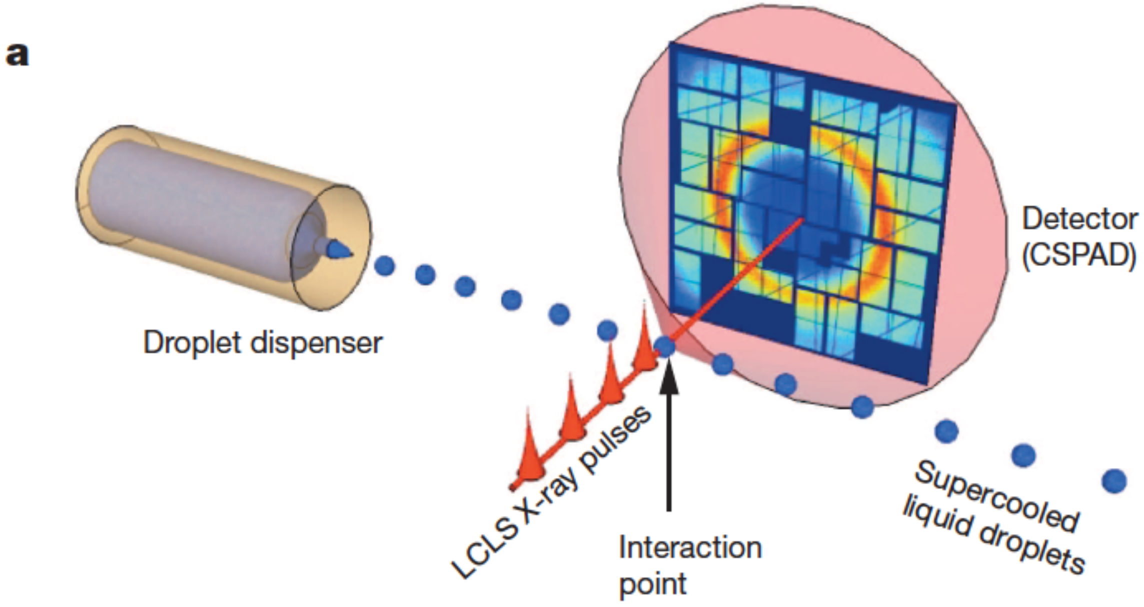
Ultrafast XPCS at XFEL –
dynamics in extreme conditions

Calculated correlation function supercooled liquid water



Dynamics on time-scales ranging from 100 fs to 1000 ps





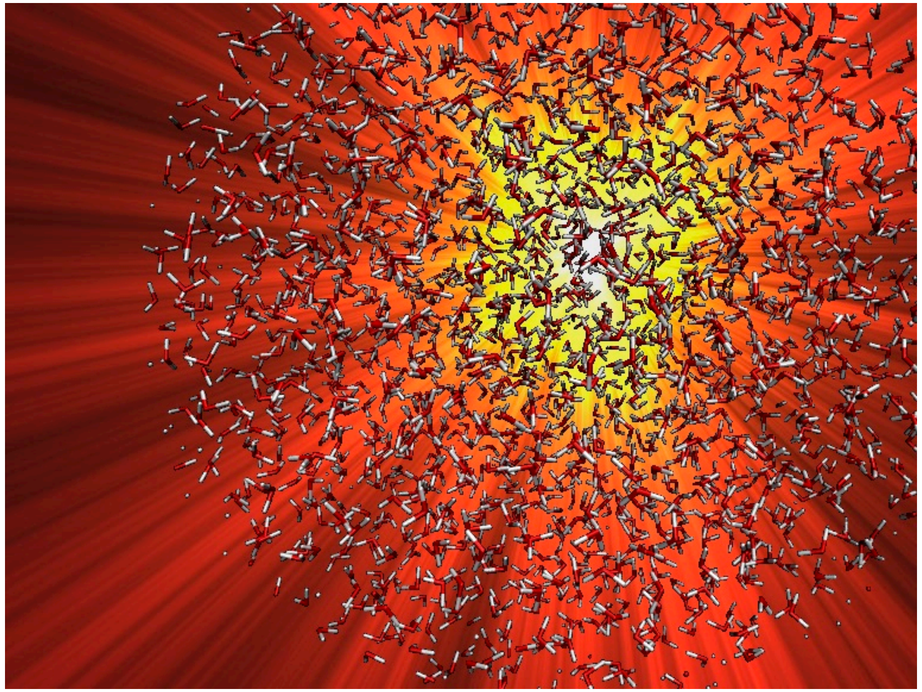
J.A. Sellberg et al. Nature 510, 381 (2014)

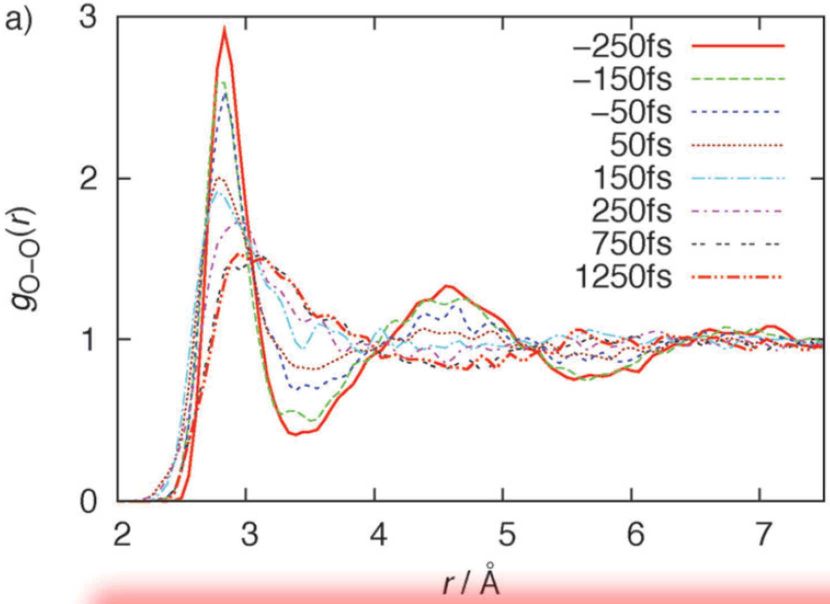
THz Excitation of Water

DOI: 10.1002/anie.201305991

Ultrafast Energy Transfer to Liquid Water by Sub-Picosecond High-Intensity Terahertz Pulses: An Ab Initio Molecular Dynamics Study**

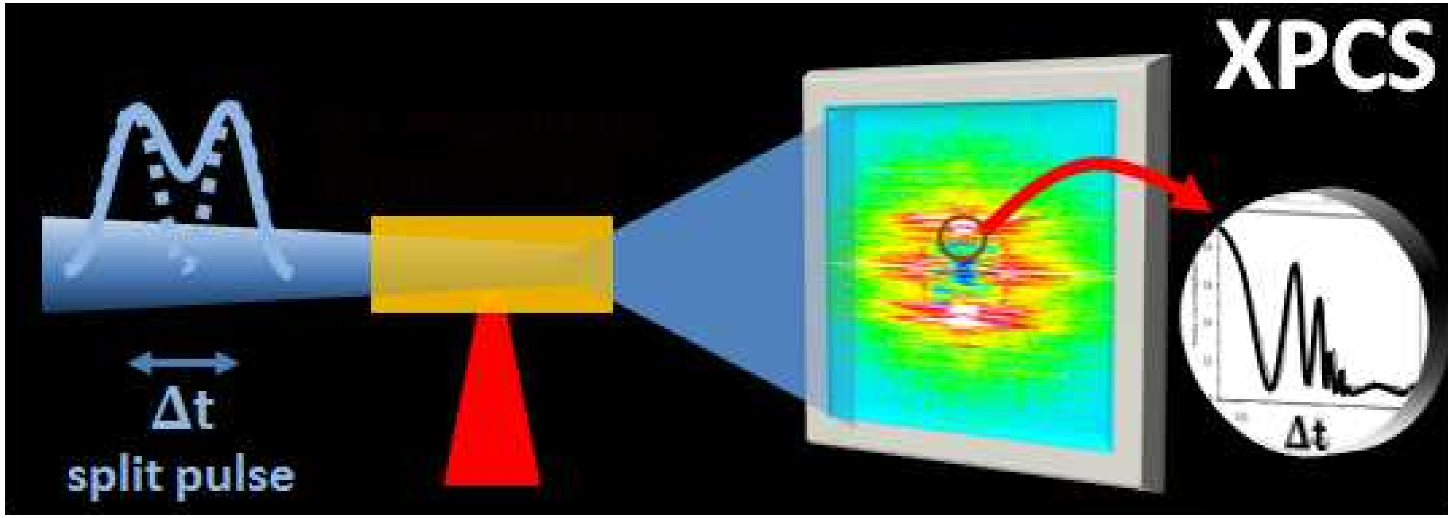
Pankaj Kr. Mishra, Oriol Vendrell, and Robin Santra*

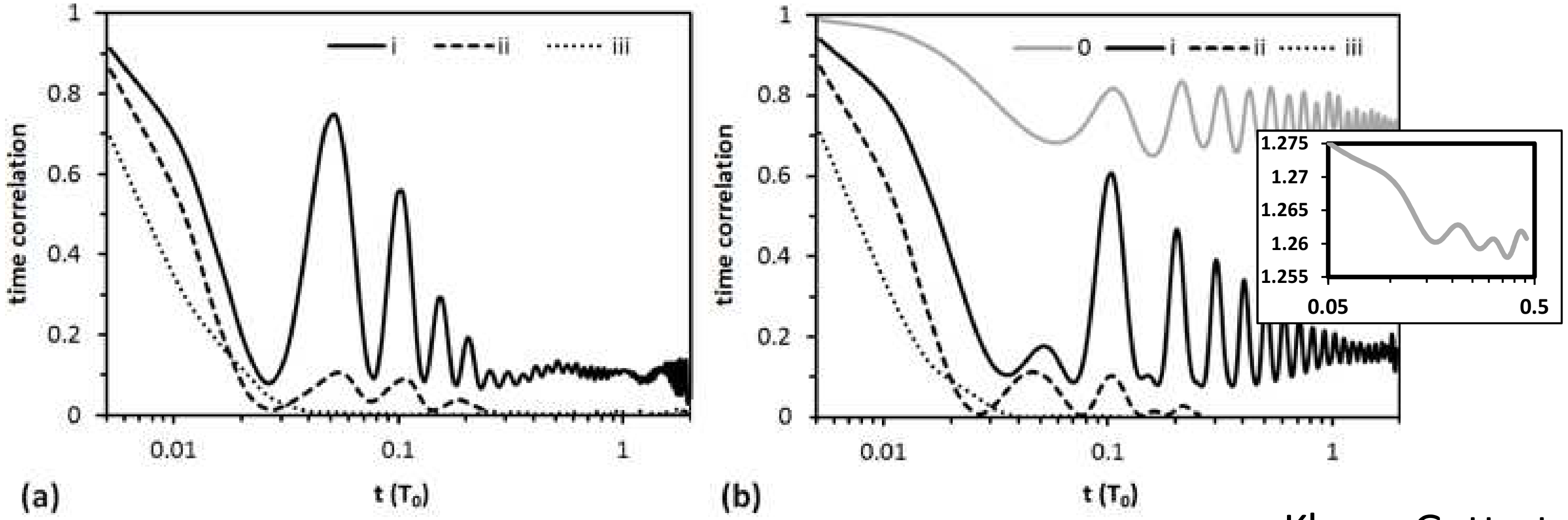




Water at T=1500 K, p = 12 Gpa at least for a few ps

Pump-probe XPCS in Plasma Physics





Kluge, Gutt et al. Plasma Physics 2014

The end