Use of Coherence in Hard X-rays to study Dynamics and Structure

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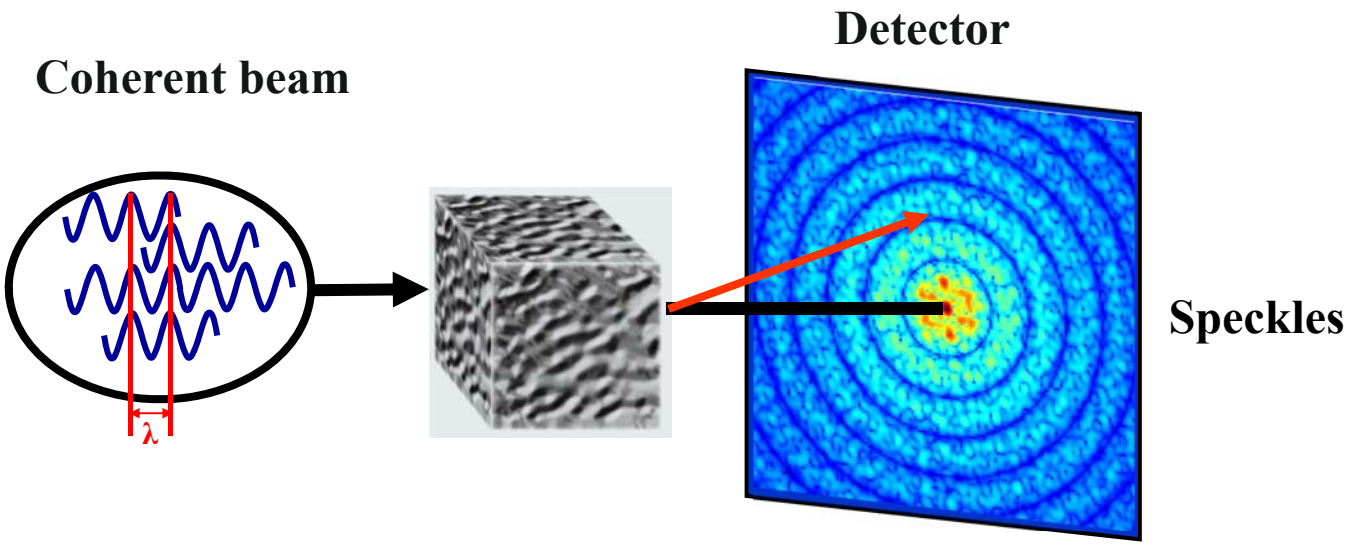
Coherent X-ray Scattering

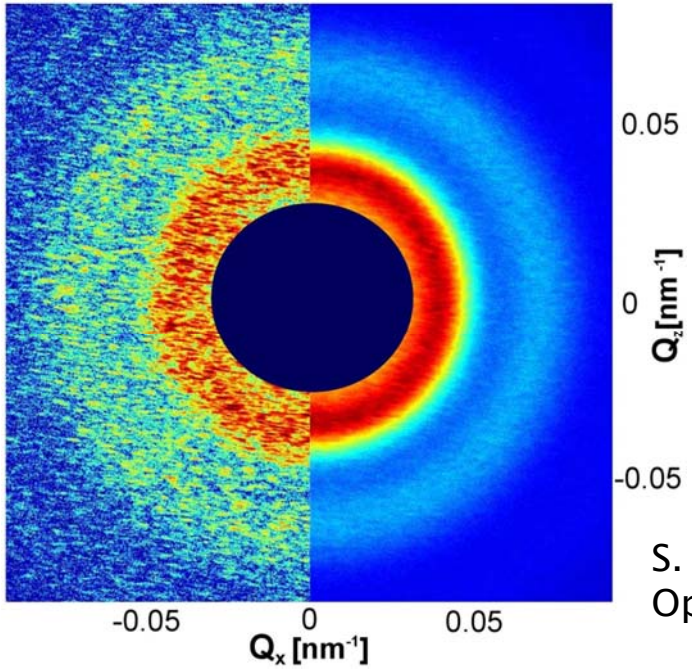


$$\rho_e\left(\vec{r}\right)\rho_e\left(\vec{r}-\vec{r''}\right)\approx\left\langle\rho_e\left(\vec{r}\right)\rho_e\left(\vec{r}-\vec{r''}\right)\right\rangle\equiv g\left(\vec{r}\right)$$

For coherent x-rays one measures the Fourier transform of the exact density distribution, not the average. What one observes is a speckle pattern superposed on the average scattering pattern.

Coherent *vs.* Incoherent

Small-angle X-ray scattering pattern of silica nanospheres

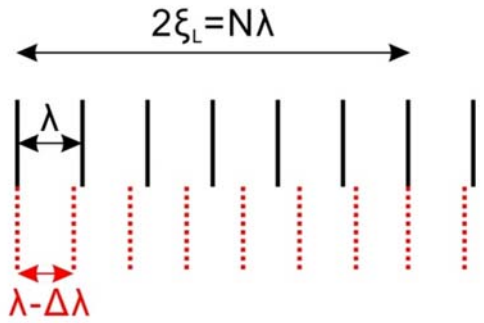


S. Lee, *et al.*,
Optics Express **21**, 24647 (2013).

Coherent scattering
- Speckle pattern directly related to the electron density
- Speckle arising from the path length difference of X-rays in the sample

Incoherent scattering
- Statistical average of scattering regions
- No speckle
- Local information lost

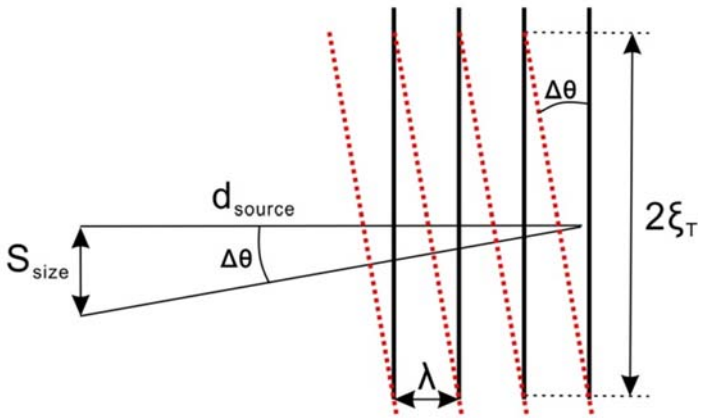
Coherence Lengths



In the plane wave approximation:

- Longitudinal coherence length ξ_L: $\xi_L = \frac{1}{2}\frac{\lambda^2}{\Delta\lambda}$

: related to the monochromaticity of the beam.



- Transverse coherence length ξ_T: $\xi_T = \frac{\lambda}{2}\frac{d_{source}}{S_{size}}$

: related to the source size and source distance.

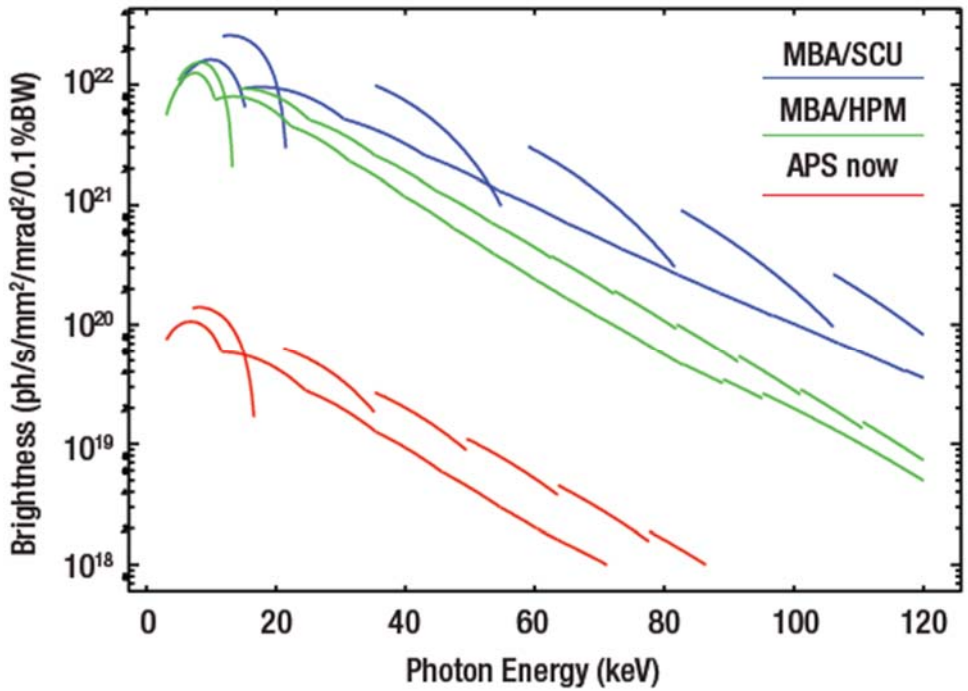
Photon degeneracy in the coherence volume : $D_{photon} = \frac{\mathcal{B}\times\lambda^3}{4c}$

$$\text{Brilliance (B)} = \frac{\text{Photons/second}}{(\text{mrad})^2(\text{mm}^2\text{ source area})(0.1\%\text{ BW})}$$

3rd Gen. vs Diffraction Limited Storage Ring

	3rd Gen.	DLSR
Brilliance	10^{20}	10^{22}
Source size	280μm×11μm (H×V)	8μm×10μm (H×V)
Transverse coherence lengths (9keV)	12μm×340μm (H×V)	420μm×340μm (H×V)
Photon degeneracy at 9keV	~10^{-4}	~10^{-2}
Pulse length	80ps	35-70ps
Repetition rate	~650MHz	10-100 MHz

Coherence in Hard X-rays



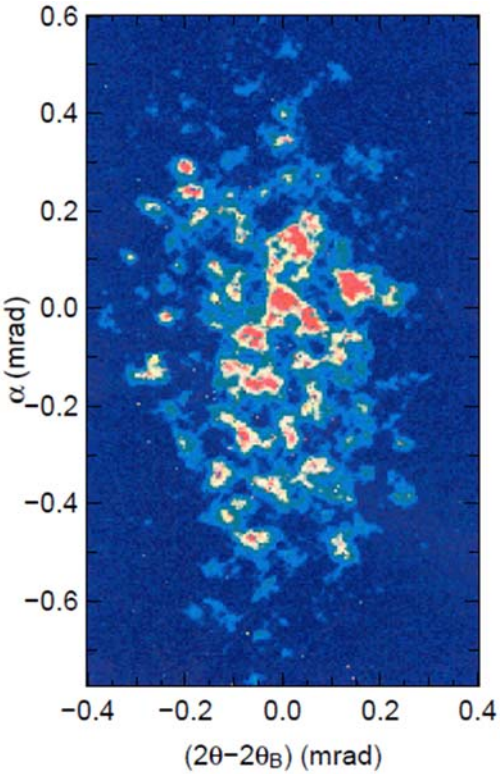
$$D_{photon} = \frac{\mathcal{B} \times \lambda^3}{4c}$$

>100 times higher at same energy

- Reaching higher q
- Reaching smaller length scale
- Measuring in solution
- Measuring in-situ with various environment

"Speckle" ⇒ Coherence based Techniques

First X-ray Speckle



Speckle of (001) Cu_3Au

Imaging:
Coherent X-ray Diffraction (CXD)

Fourier Transform Holography
….

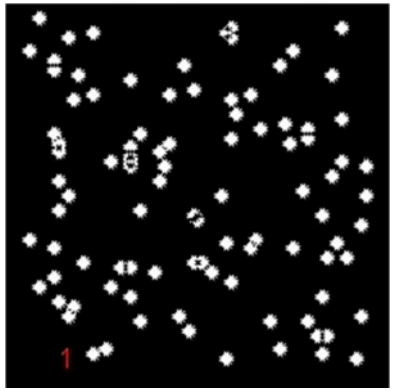
Studying Dynamics:
X-ray Photon Correlation Spectroscopy (XPCS)

M. Sutton, S.G.J. Mochrie, T. Greytak, S.E. Nagler, L.E. Berman, G.A. Held, G.B. Stephenson, Nature **352**, 608 (1991).

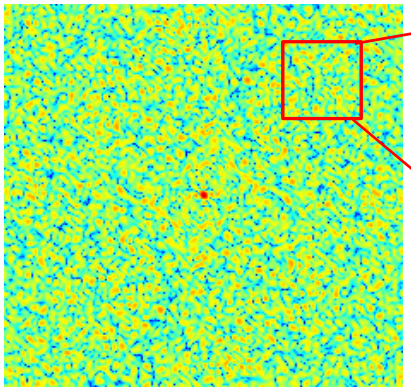
X-ray Photon Correlation Spectroscopy

(Intensity Fluctuation Spectroscopy)

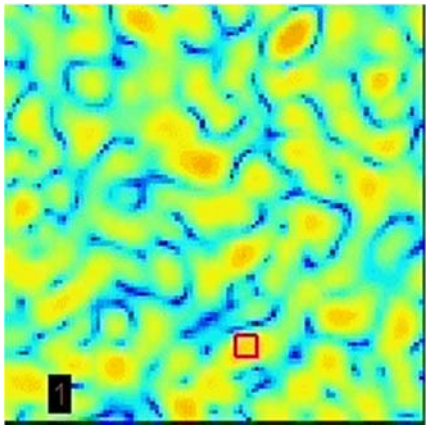
Brownian motion of 100 particles

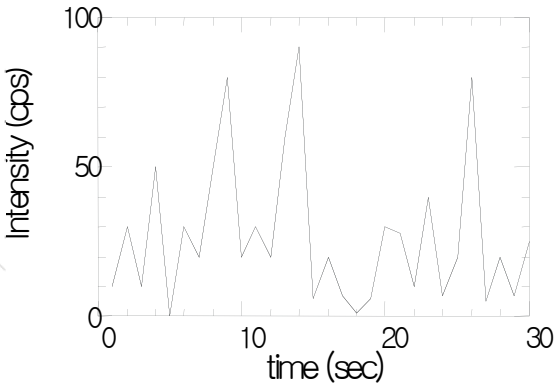


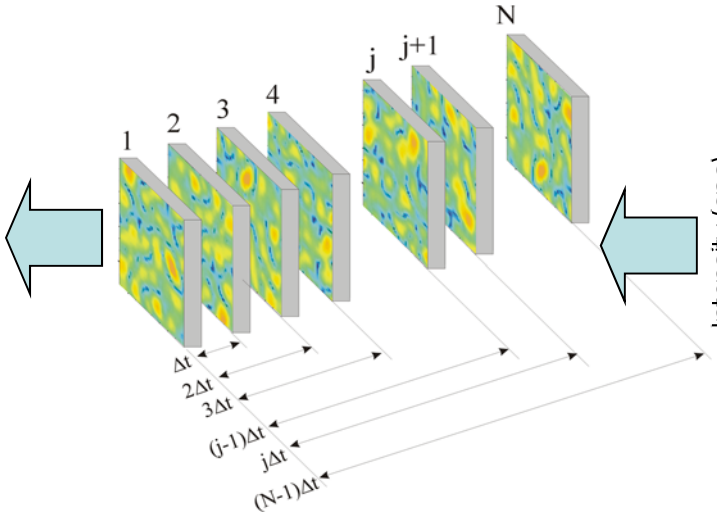
Diffraction Pattern



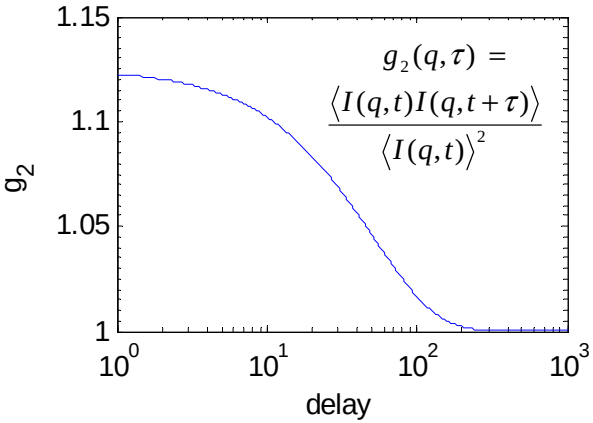
Speckles







Intensity-intensity auto correlation

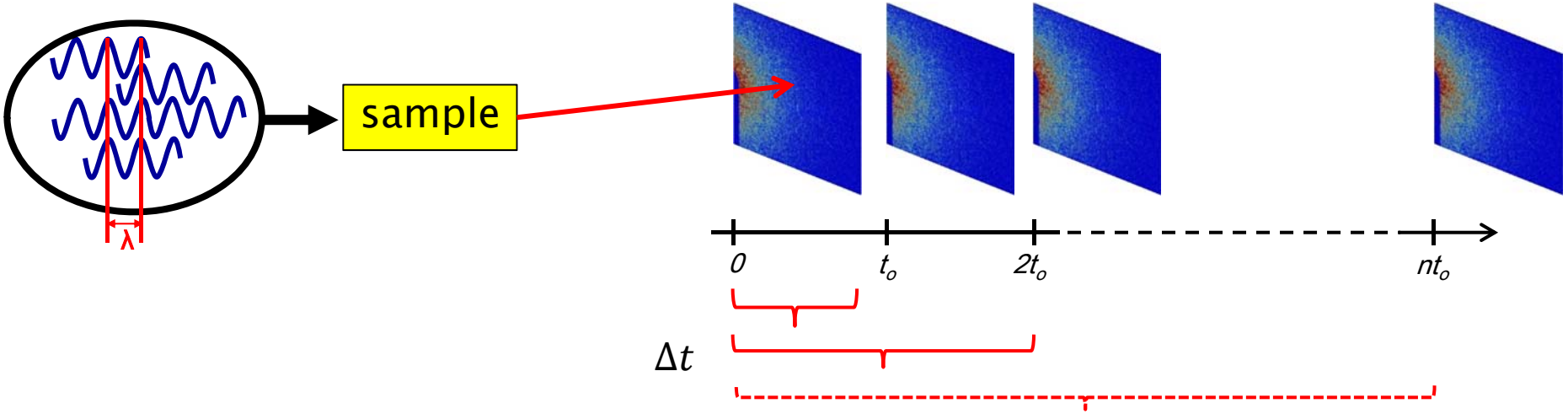


→ S(Q, t) Dynamic Structure Factor

In courtesy of J. Zhang

X-ray Photon Correlation Spectroscopy

Coherent beam



Intensity autocorrelation $g_2(\boldsymbol{q},\Delta t) = \dfrac{\langle I(\boldsymbol{q},t)I(\boldsymbol{q},t+\Delta t)\rangle}{\langle I(\boldsymbol{q},t)\rangle^2}$

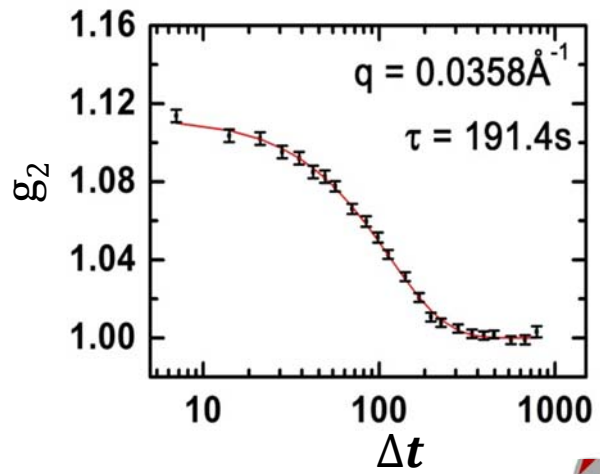
Siegert relation

$$\boldsymbol{I_{obs}} \Leftrightarrow \boldsymbol{f(t)} = \frac{\langle \boldsymbol{E(0)E^*(\tau)}\rangle}{\langle \boldsymbol{EE^*}\rangle}$$

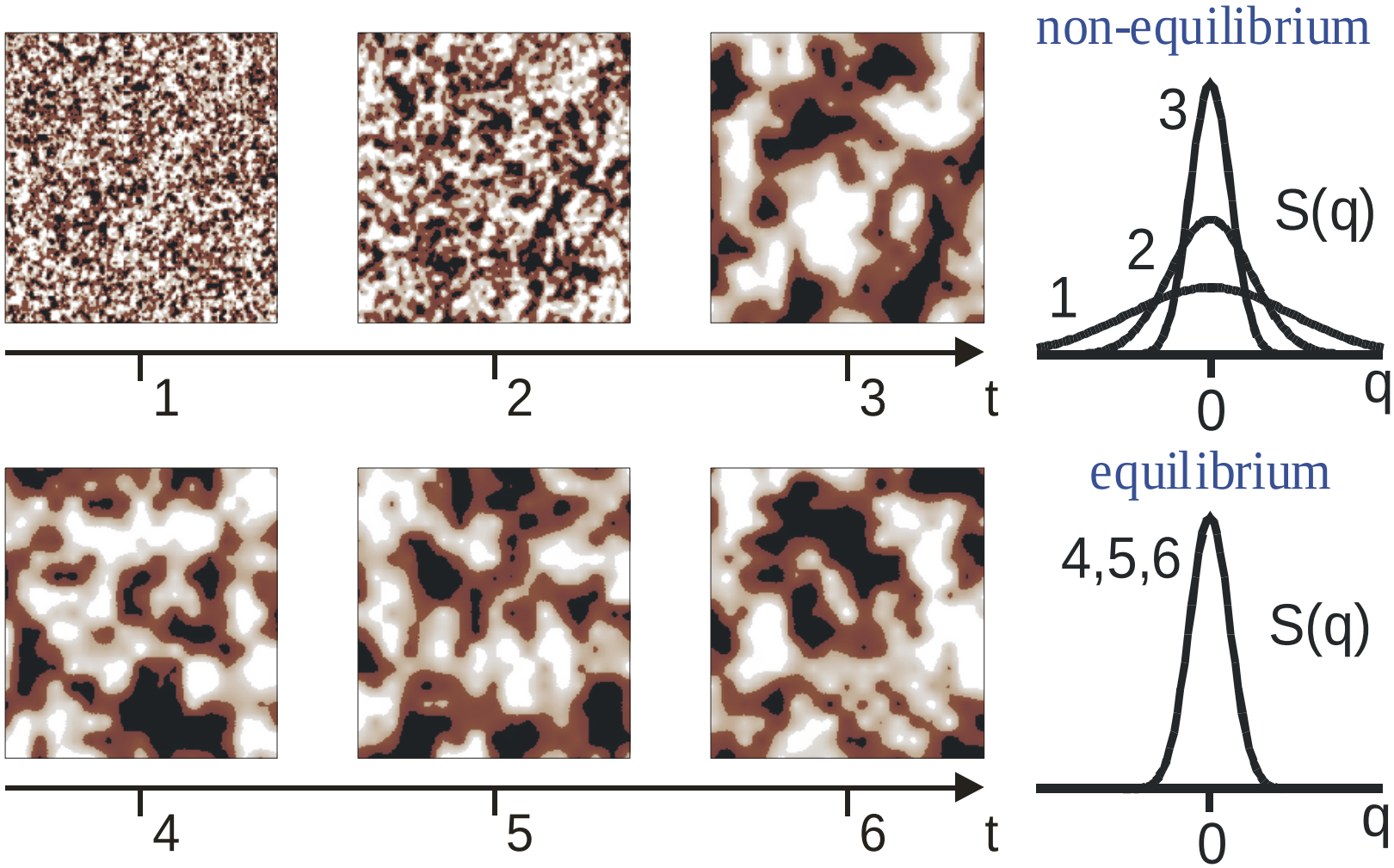
$g_2(\boldsymbol{q},\Delta t) = 1 + \beta|f(\boldsymbol{q},\Delta t)|^2$

f = normalized intermediate scattering function

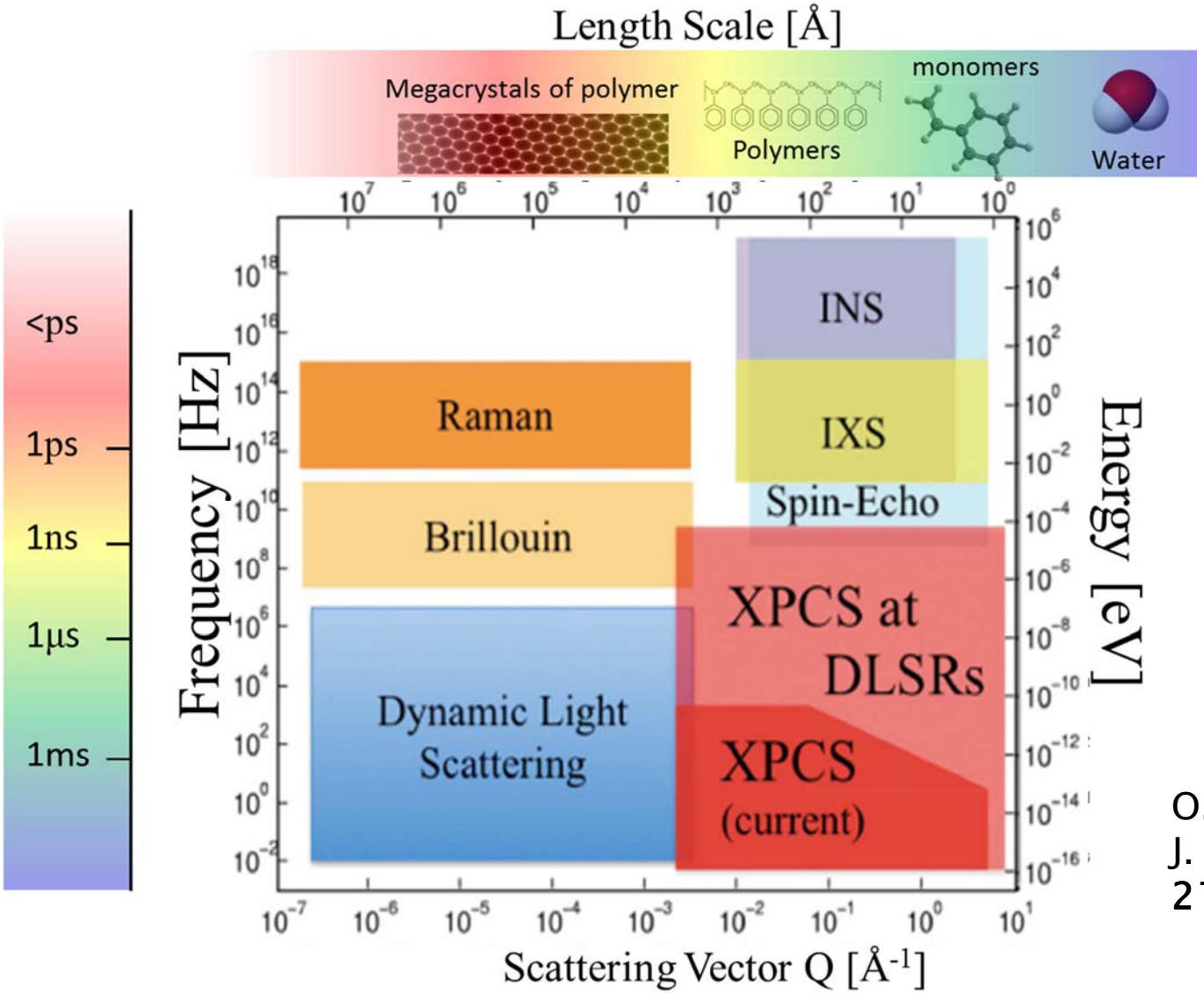
Choose an adapted model for f $\xrightarrow{\textit{fit}}$



Non-equilibrium kinetics *vs.* equilibrium dynamics



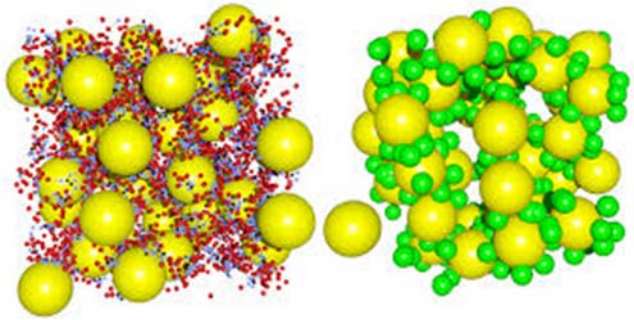
Techniques for dynamic study

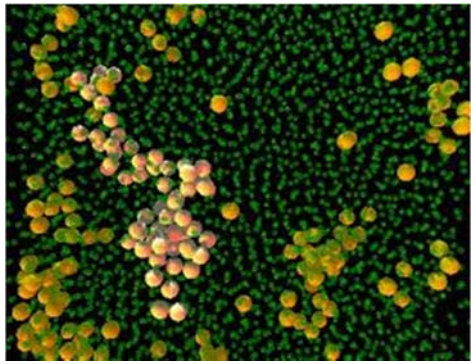


O. Shpyrko, J. Synchrotron Rad. 21, 1054 (2014).

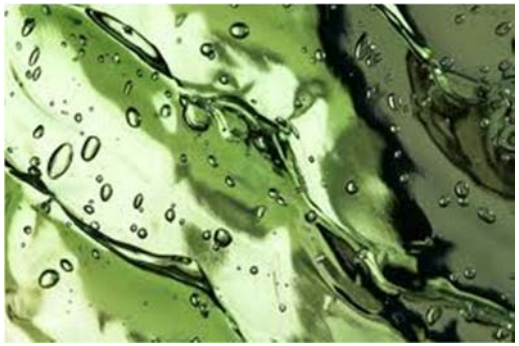
Dynamics in Soft Matter

– Colloids, Magnetic Colloids, Nanocomposites, Clay

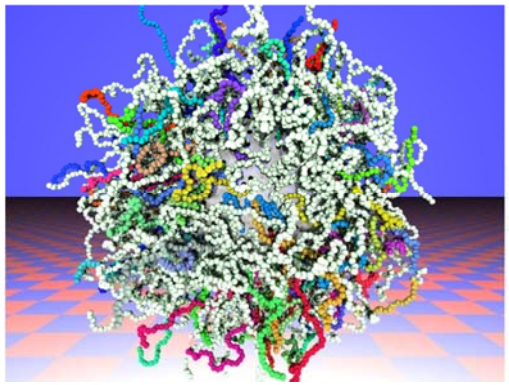


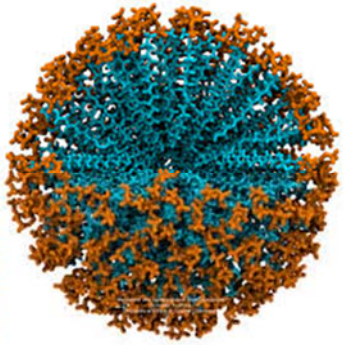


– Glasses, Gels



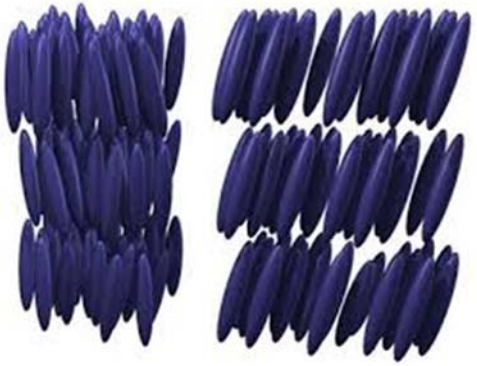
– Polymer: Vesicles, Micelles, Melts





– Liquid, Ferrofluid

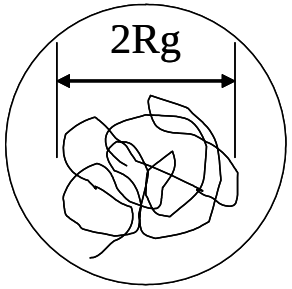
– Liquid Crystals

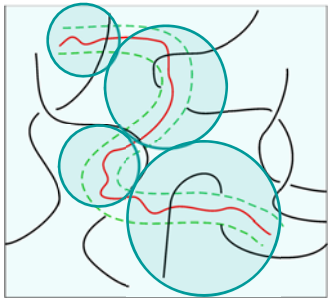


- Diffusion, Phase Transition, Hydrodynamic Fluctuations
- Ordering & Relaxation Dynamics
- Atomic Diffusion

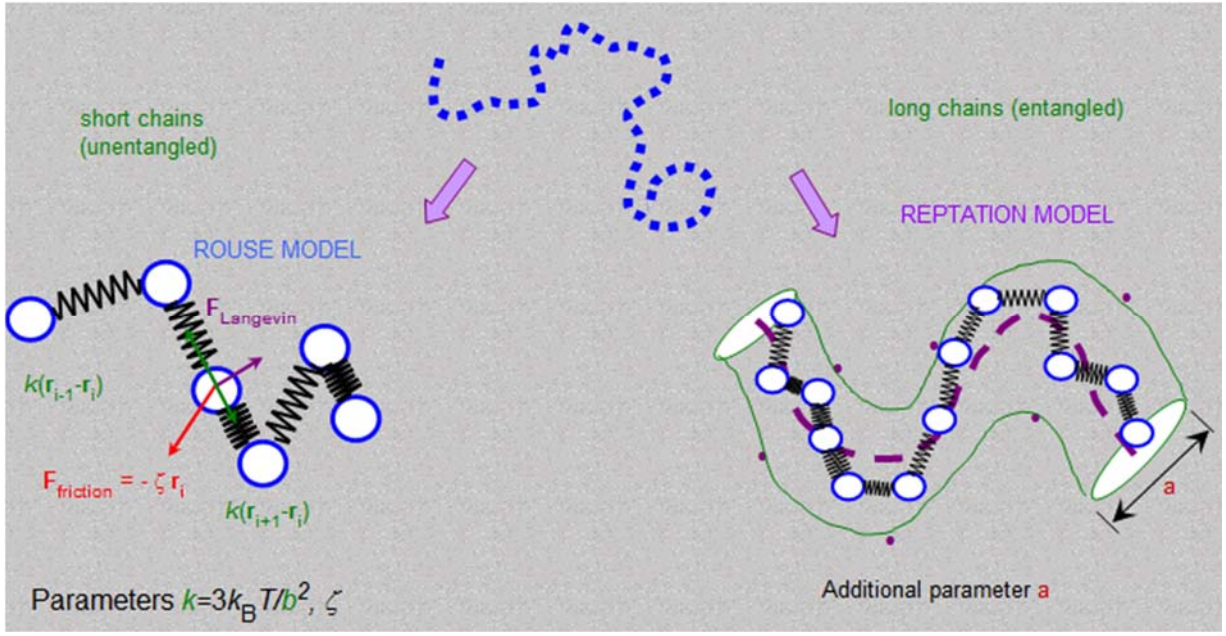
Polymer Dynamics

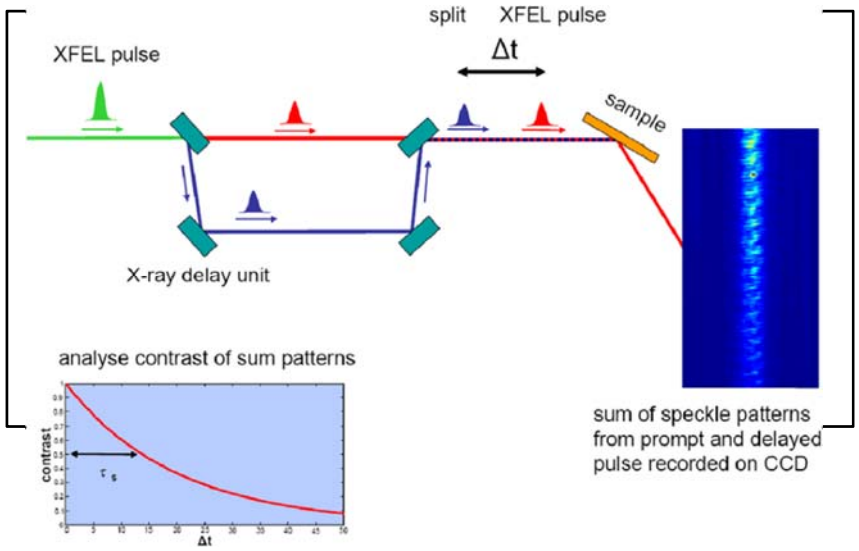
de Gennes has established a number of predictions regarding how polymer chains and their individual parts can move, i.e. what physicists call polymer dynamics. These predictions often have the character of "**scaling laws**": they say that conditions shall be similar for certain combinations of the starting variables (such as polymer concentration in a solution, and temperature). These are properties that can sometimes be controlled experimentally, and many works on polymer dynamics have been performed using neutron-scattering techniques.

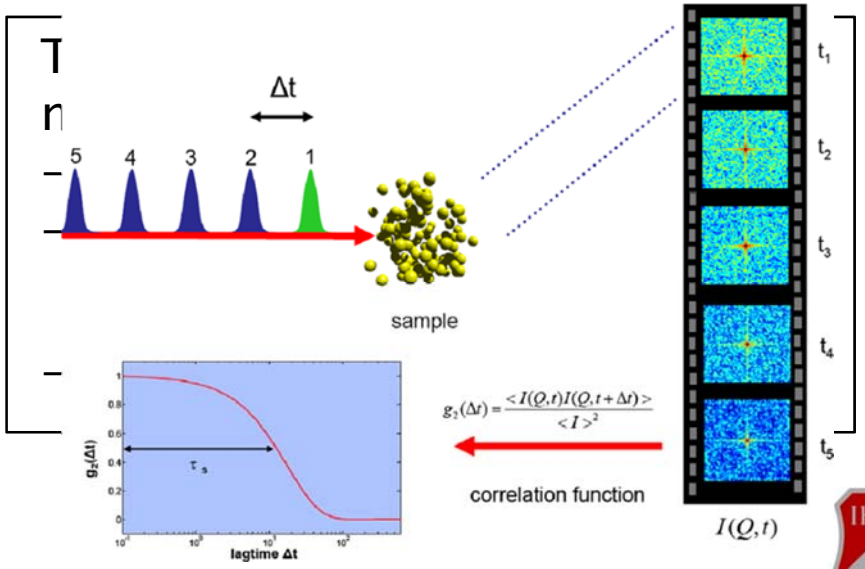




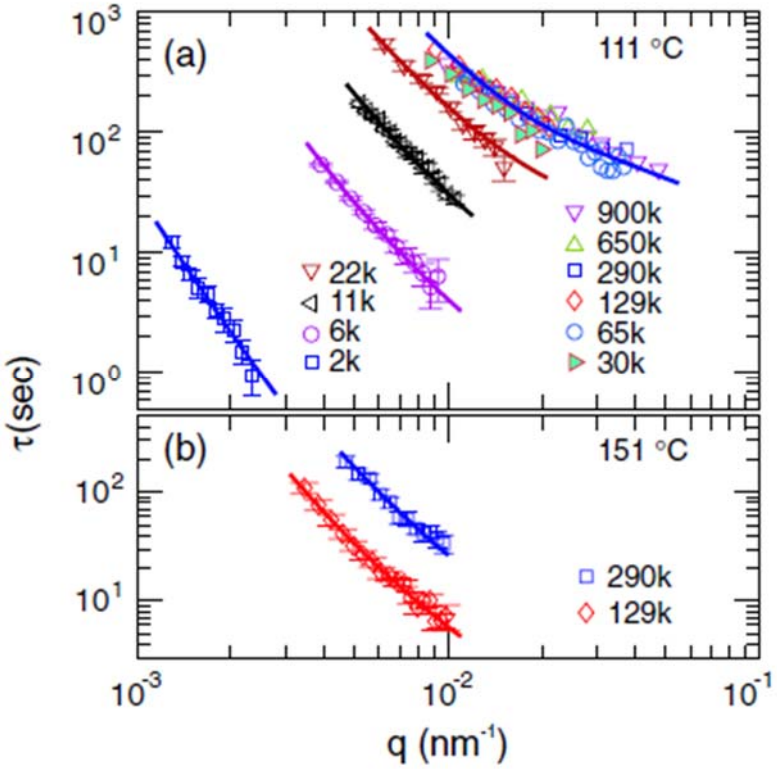
Polymer Dynamics with XFEL

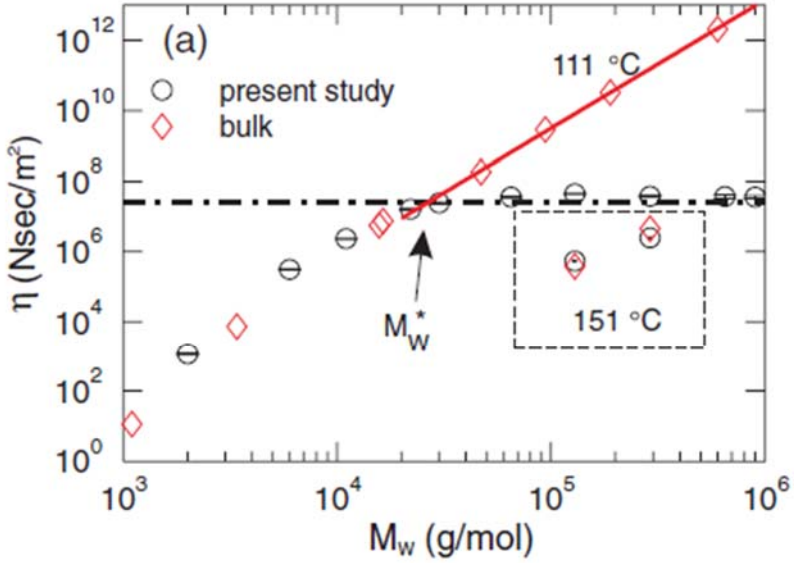




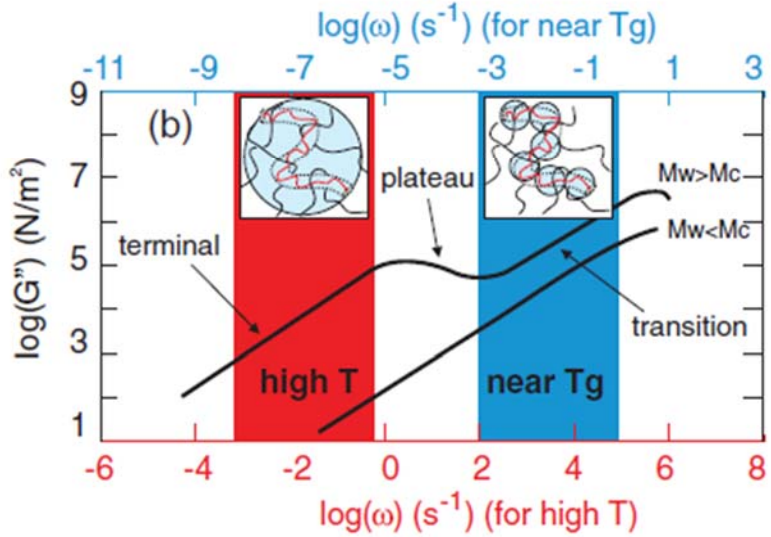


Close to T_g



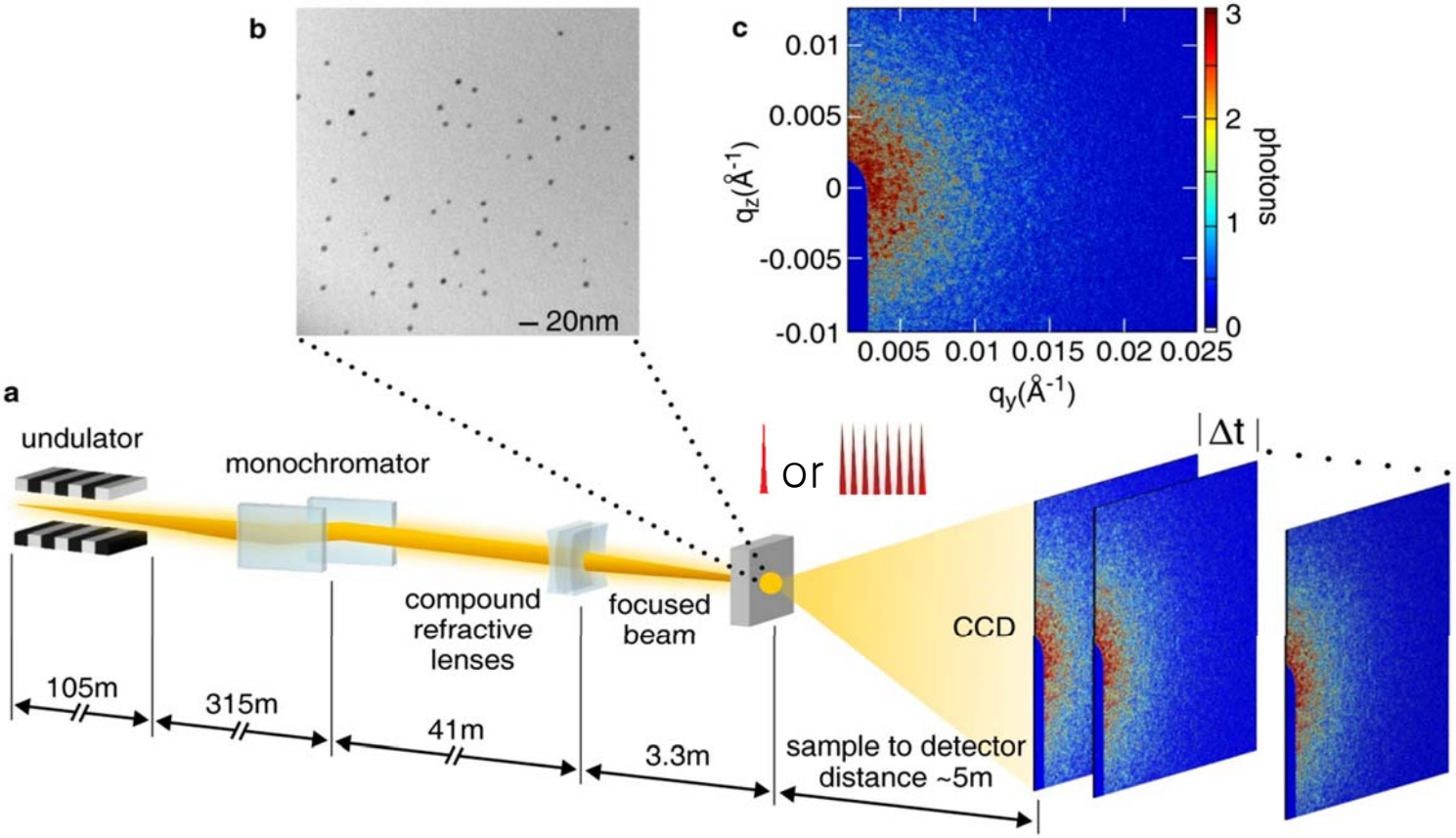


Rouse dynamics

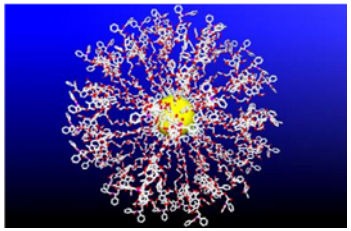


Z. Jiang et.al., Phys. Rev. Lett. 101, 246104 (2008).

Experimental Setup



Gold Nanoparticles of 5.5 nm dia.
grafted with polystyrene (M_w=30kg/mol)
in a polystyrene matrix
(M_w :42kg/mol to 1000kg/mol)



XCS, LCLS

Diffusion of a Particle in Polymer Melt

- If particle size is smaller than tube diameter (R < a), topological interactions between chains do not affect particle motion.
  : Rouse modes of these sections contribute to effective viscosity "felt" by the particle.

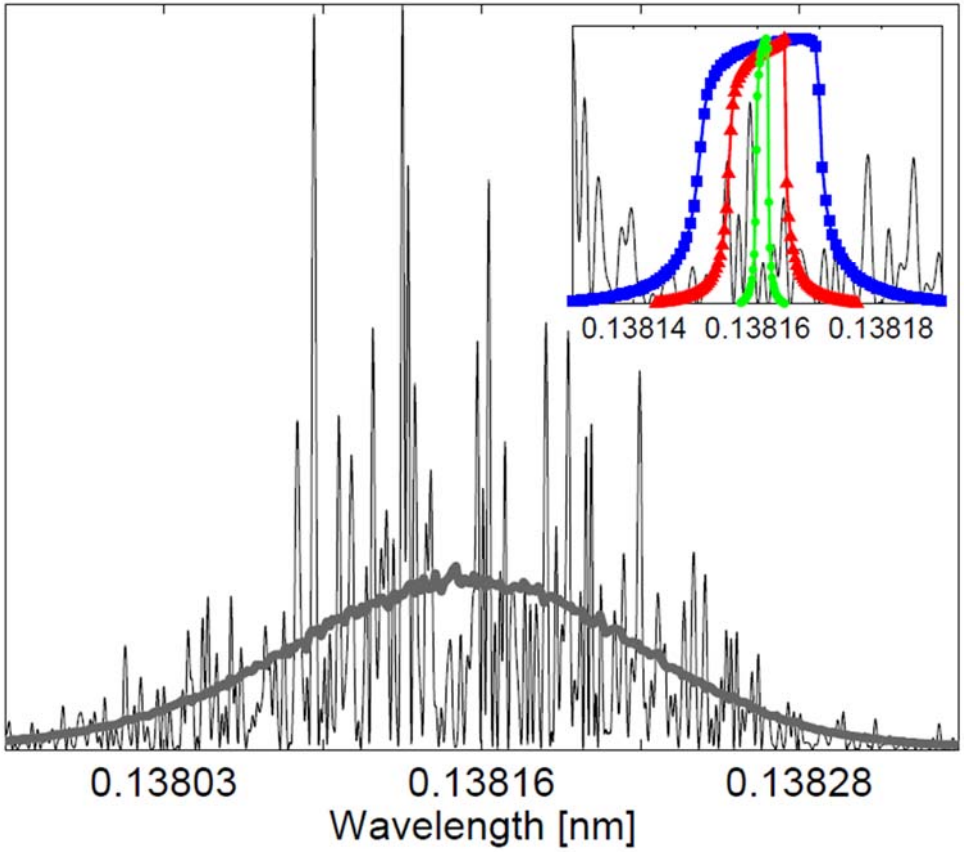
  Number of monomers in a chain section of particle size $g=(R/b)^2$
  $\eta = \eta_0 g = \eta_0 (R/b)^2$,

$$D \approx kT/(\eta R) \sim D_0 b^3 / R^3$$

- If particle is larger than tube diameter (R>a), it becomes trapped and has to wait for chains to reptate away before it can diffuse further.
  : Diffusion of particles (with R>a) is determined by melt viscosity.

$$D = \frac{kT}{6\pi\eta R} \sim R^{-1}$$

Spectrum from XFEL



The random nature of the SASE emission process for XFEL radiation implies pulse to pulse variations of

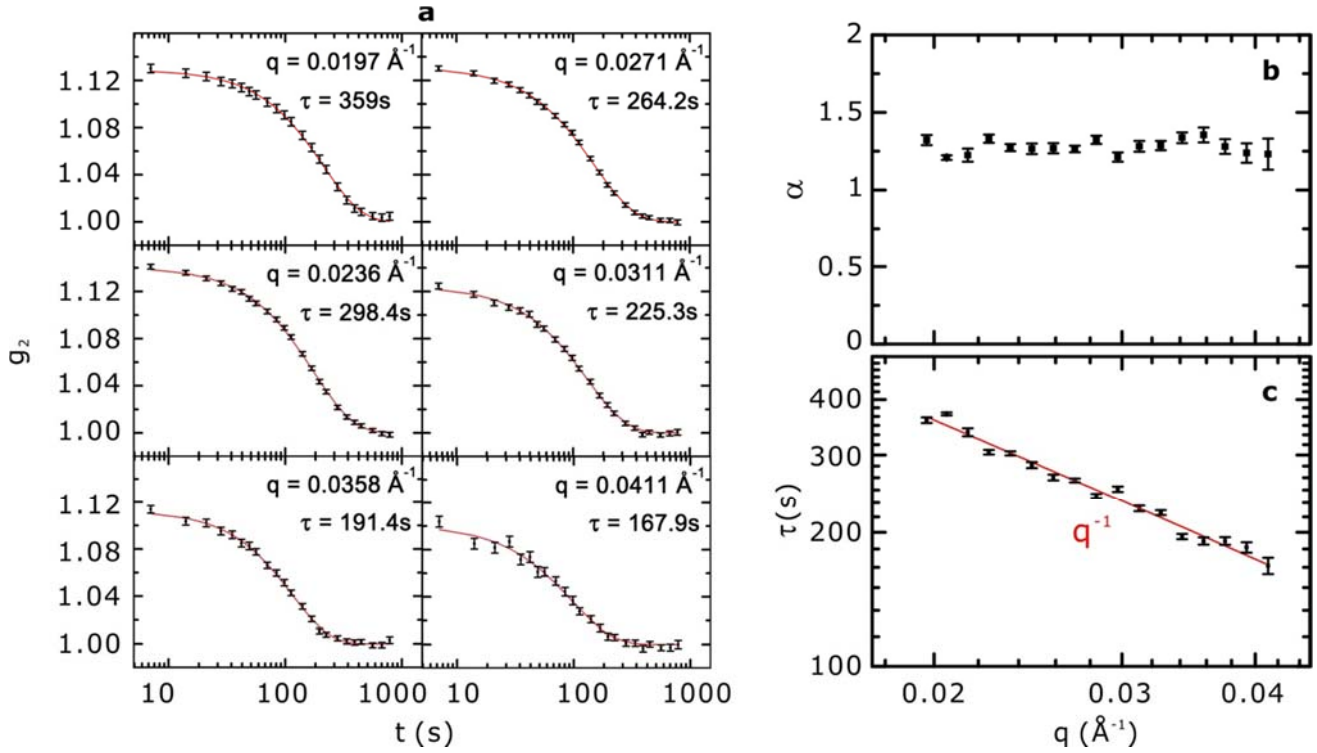
- Flux
- Beam position
- Energy

- black line: a single shot LCLS spectrum simulated The
- gray line: the average of 1000 single-shot spectrums
- blue square, red triangle and green circle: diffraction curves of Si (111),(220) and (511) reflections, respectively.

S. Lee, et.al., OPTICS EXPRESS 20, 9791 (2012).

Measured g_2 functions

T=120°C 100 pulses/frame



Stretching Exponent: $\alpha \sim 1.28$

Relaxation time scaling: $\tau \sim q^{-1}$

$$g_2(\boldsymbol{q},t') = \frac{\langle I(\boldsymbol{q},t) I(\boldsymbol{q},t+t') \rangle_t}{\langle I(\boldsymbol{q},t) \rangle_t^2} = 1 + \beta \left| f(\boldsymbol{q},t') \right|^2$$

$$f(\boldsymbol{q},t) = e^{-(t/\tau)^{\alpha}}$$

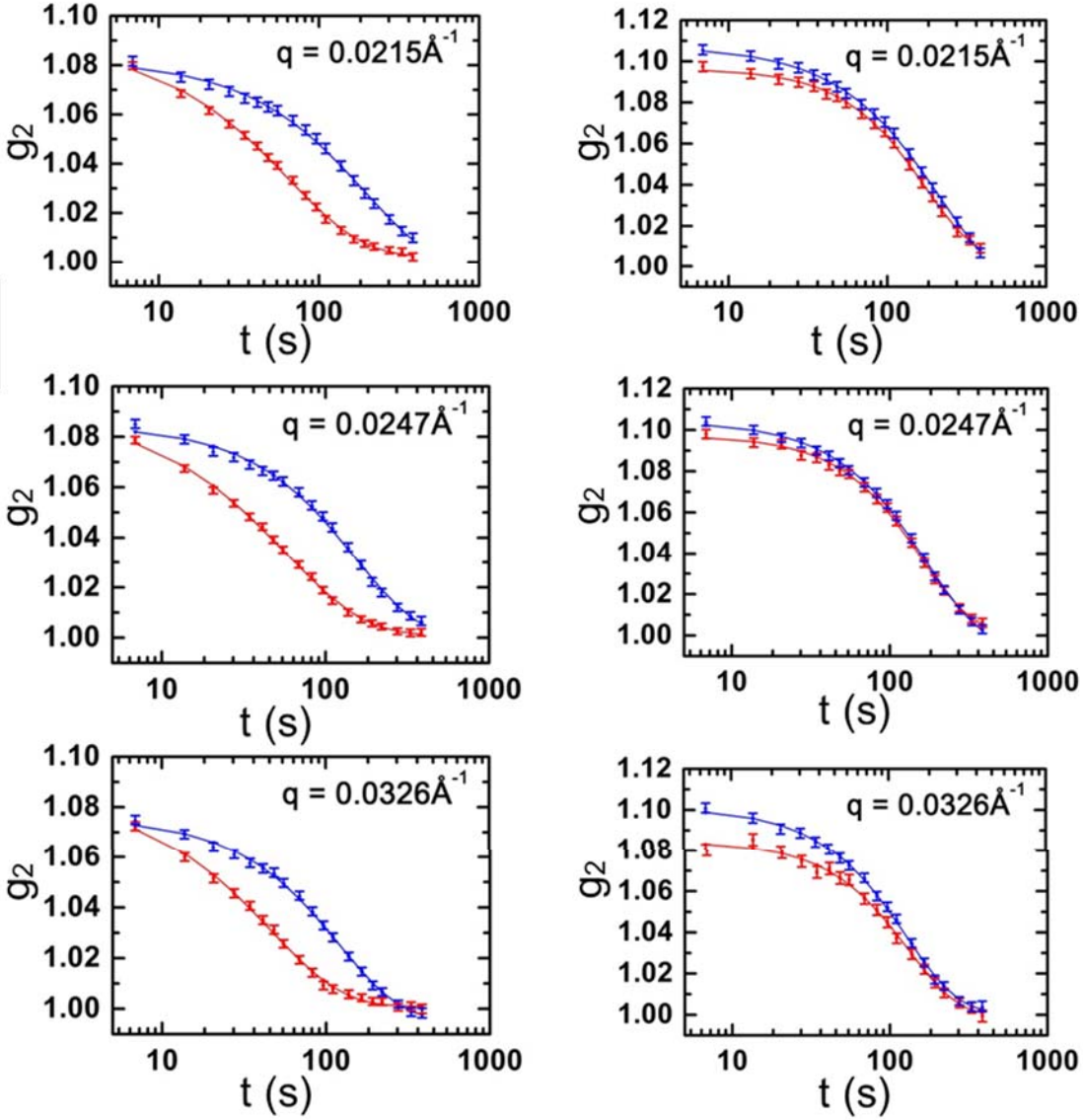
f intermediate scattering function

α stretching exponent

Aging or Sample Damage?

After 103min.

After 477min.

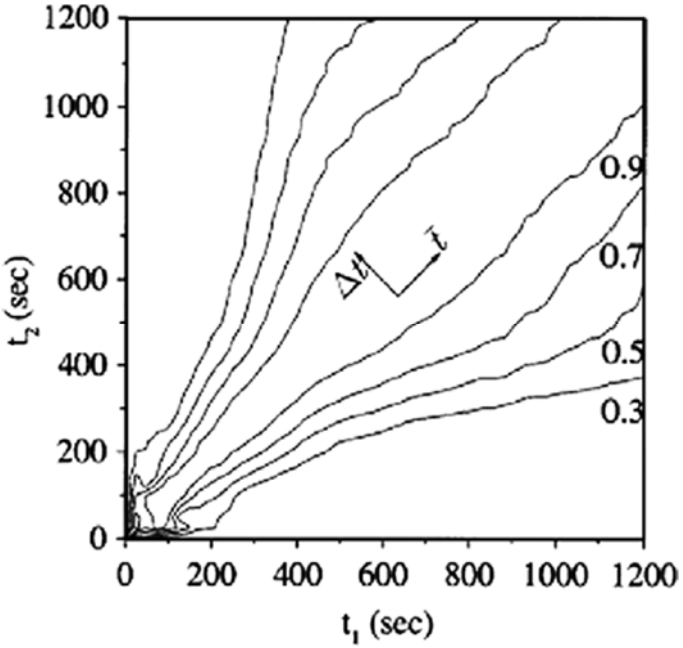


75 first frames
75 last frames

75 frames: 8.5 min. total X-ray exposure of ~0.38ns.

Two-time intensity correlation

: Study of samples out of equilibrium



$$C(\boldsymbol{q},t_1,t_2)=\frac{\langle I(t_1)I(t_2)\rangle_t-\langle I(t_1)\rangle_t\langle I(t_2)\rangle_t}{\sqrt{\langle I^2(t_1)\rangle_t-\langle I(t_1)\rangle_t^2}\sqrt{\langle I^2(t_2)\rangle_t-\langle I(t_2)\rangle_t^2}}$$

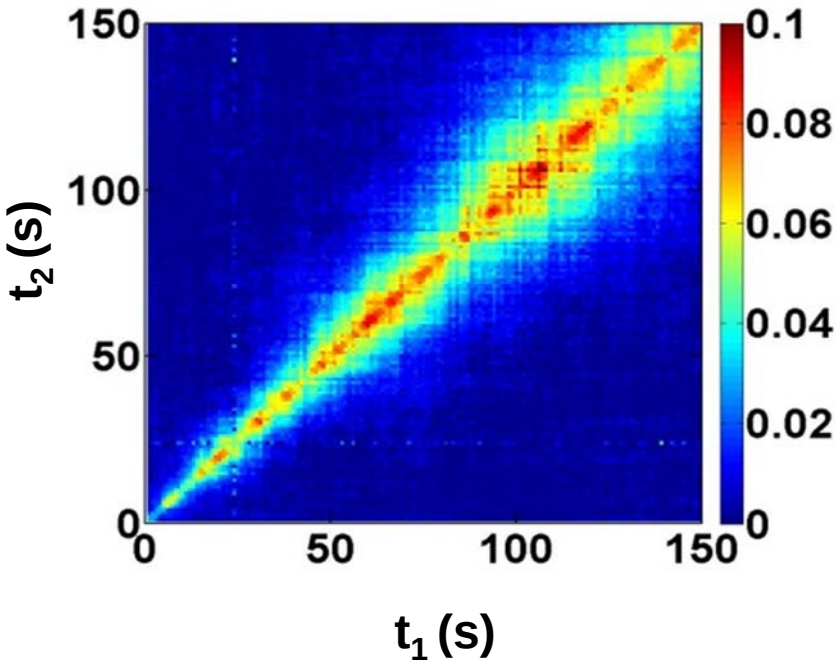
- Age is represented by $\bar{t}$.
- Usual g_2 is obtained by cutting along Δt.
- Now g_2 depends also on the age of the sample: $g_2(\mathbf{q},t,\bar{t})$

Grübel *et. al*. NIM B **262**, 357(2007).

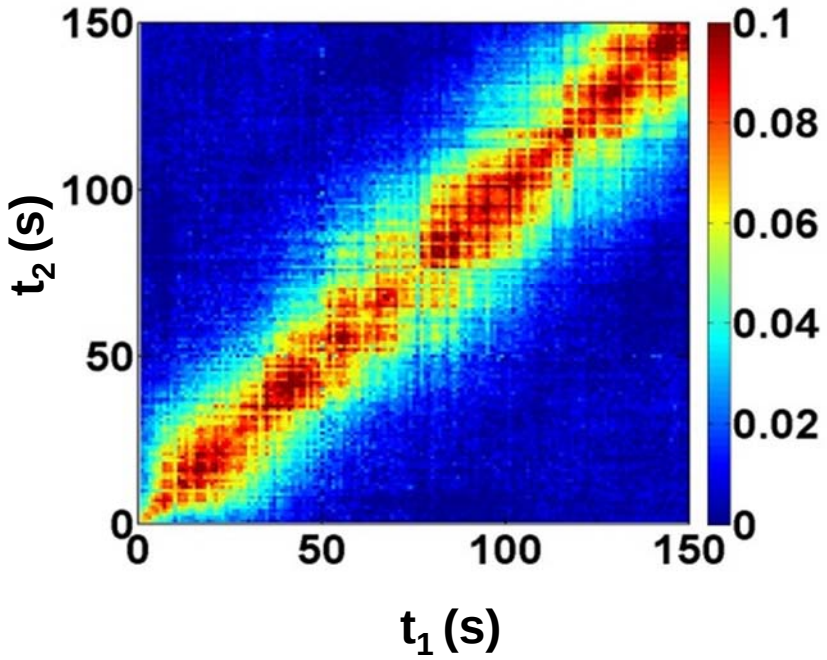
Two-time Intensity Correlation

T=120°C, q=0.0215Å^{-1}

After 103min.



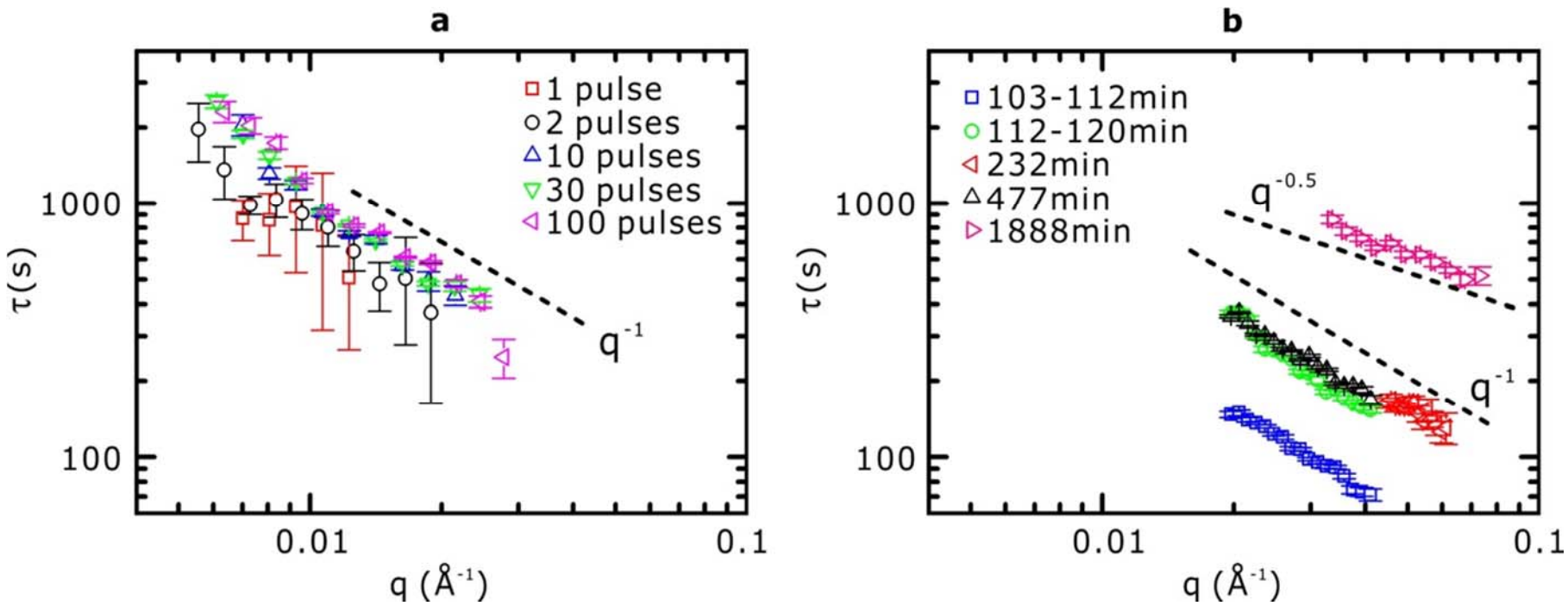
After 477min.



Two-time intensity correlation function:

$$C(\boldsymbol{q},t_1,t_2)=\frac{\langle I(\boldsymbol{q},t_1)I(\boldsymbol{q},t_2)\rangle_t-\langle I(\boldsymbol{q},t_1)\rangle_t\langle I(\boldsymbol{q},t_2)\rangle_t}{\sqrt{\langle I^2(\boldsymbol{q},t_1)\rangle_t-\langle I(\boldsymbol{q},t_1)\rangle_t^2}\sqrt{\langle I^2(\boldsymbol{q},t_2)\rangle_t-\langle I(\boldsymbol{q},t_2)\rangle_t^2}}$$

τ(q)



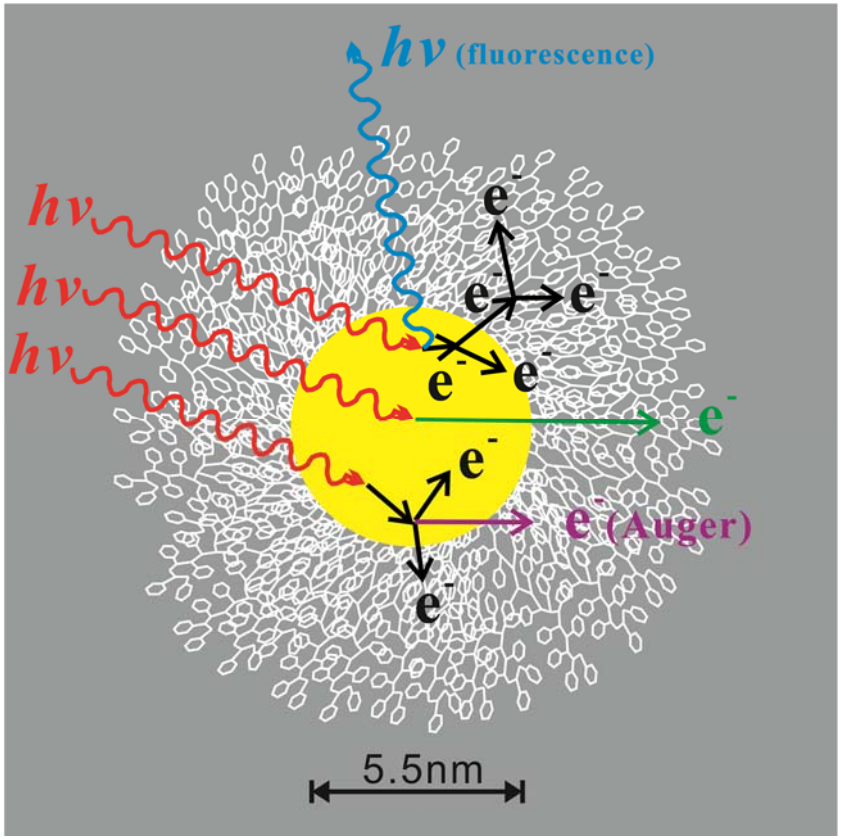
- τ(q) gets slower even with increasing pulse numbers.
- Not compatible with sample heating.
- Aging-like behavior

Sample heating and size effect

Adiabatic heating (contribution of 1 pulse)

$2.4*10^9$ photons/pulse at 8.7keV
4.7μm×3.3μm (H×V)

~10K/atom in PS
~10000K/atom for gold



Photoelectric absorption by M-shell electrons (Binding E: ~2 to 3keV)

Average M-shell fluorescence yield: 2.7~2.9%

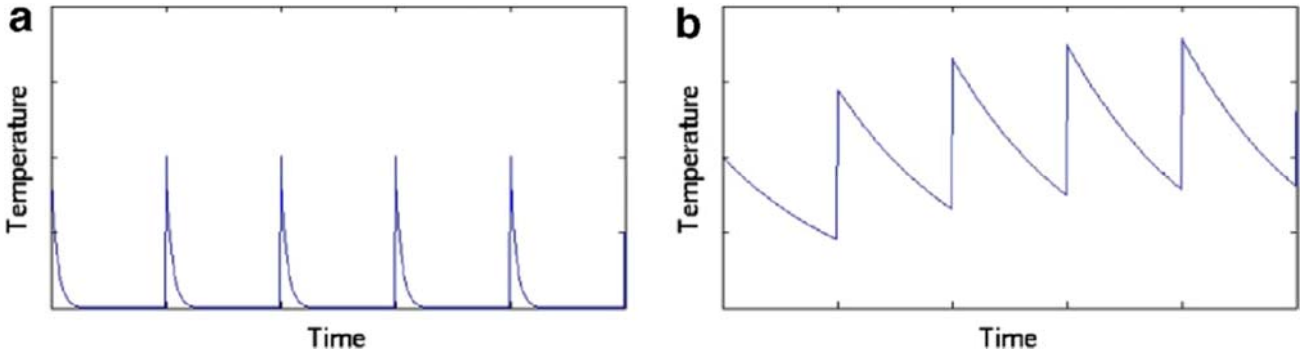
Inelastic mean free path of primary electrons: ~5 to 6nm

Inelastic mean free path of Auger electrons (main peaks at ~2keV): ~2.2nm

Main part of the energy is released in the PS matrix.

Sample steady-state heating

Estimated single-pulse heating of the PS matrix from the absorption: ~18K

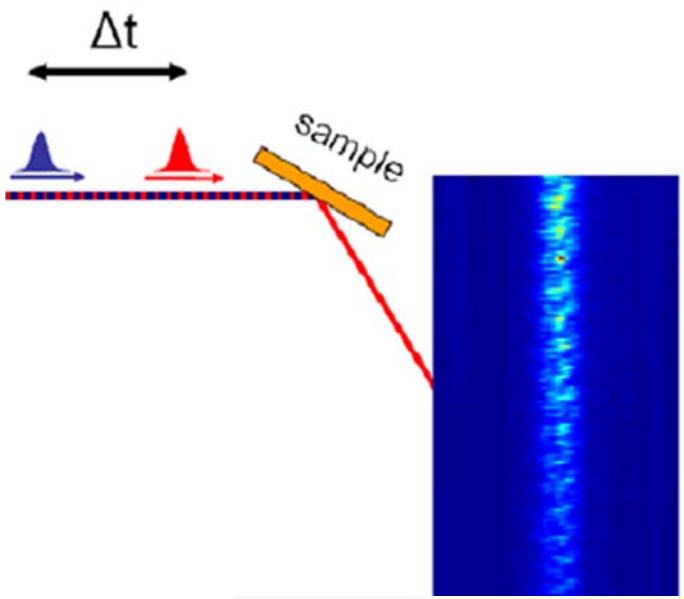


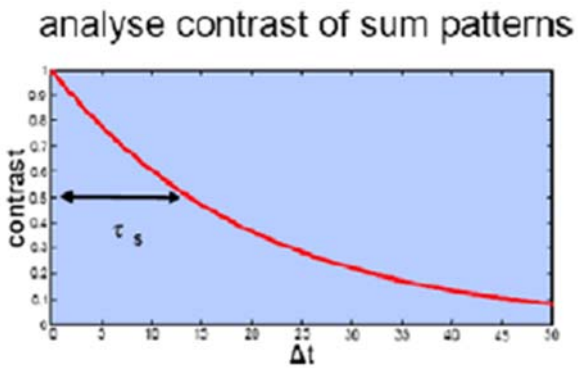
Grübel, G *et al*. *NIM B* **262** , 357(2007)

Temperature response to a pulse train, with a thermal constant smaller (a) or larger (b) than the pulse spacing.

Time constant for thermal diffusion: $\tau = \frac{r^2}{4D_{th}} \sim 6.3 \times 10^{-5} s \ll 8.3 ms$

Study of dynamics with DLSR



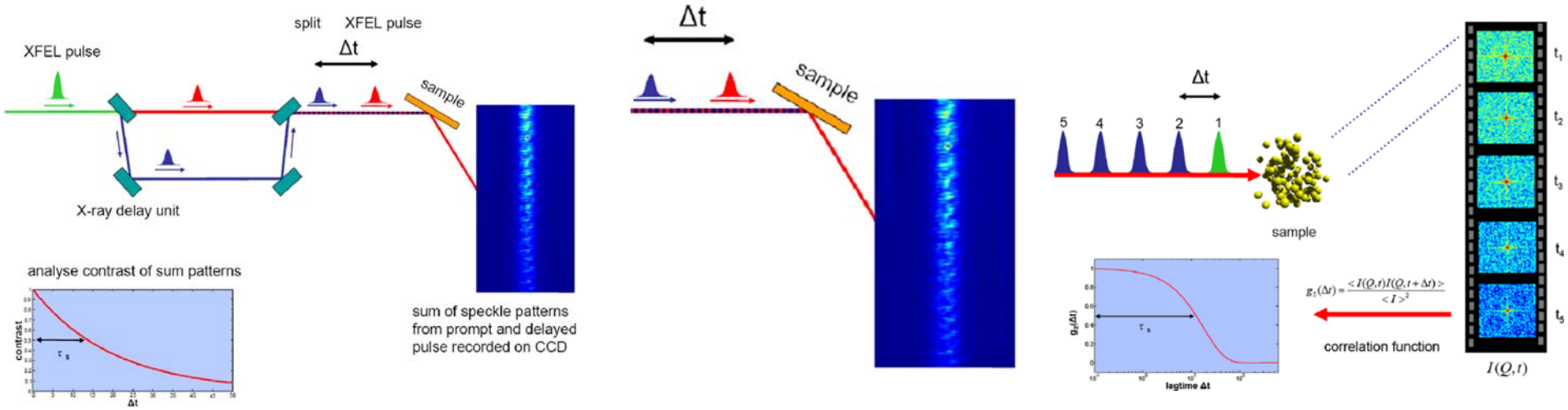


G. Grűbel et al., Nucl. Instr. and Meth. in Phys. Res. B **262**, 357 (2007).
C. Gutt, et.al., Optics Express **17**, 55 (2009).

Summary

With coherence available in Hard X-ray regime with DLSR, the study of dynamics in soft matters will get benefit :

- Reaching higher q
- Reaching smaller length scale
- Time range >10-100 nsec
- Measuring in solution
- Measuring in-situ with various environment



<5ns 10-100ns ms-sec

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Thank you very much for your attention!