Methoden moderner Röntgenphysik: Streuung und Abbildung

Lecture 13	Vorlesung zum Haupt- oder Masterstudiengang Physik, SoSe 2019
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Location	Lecture hall AP, Physics, Jungiusstraße

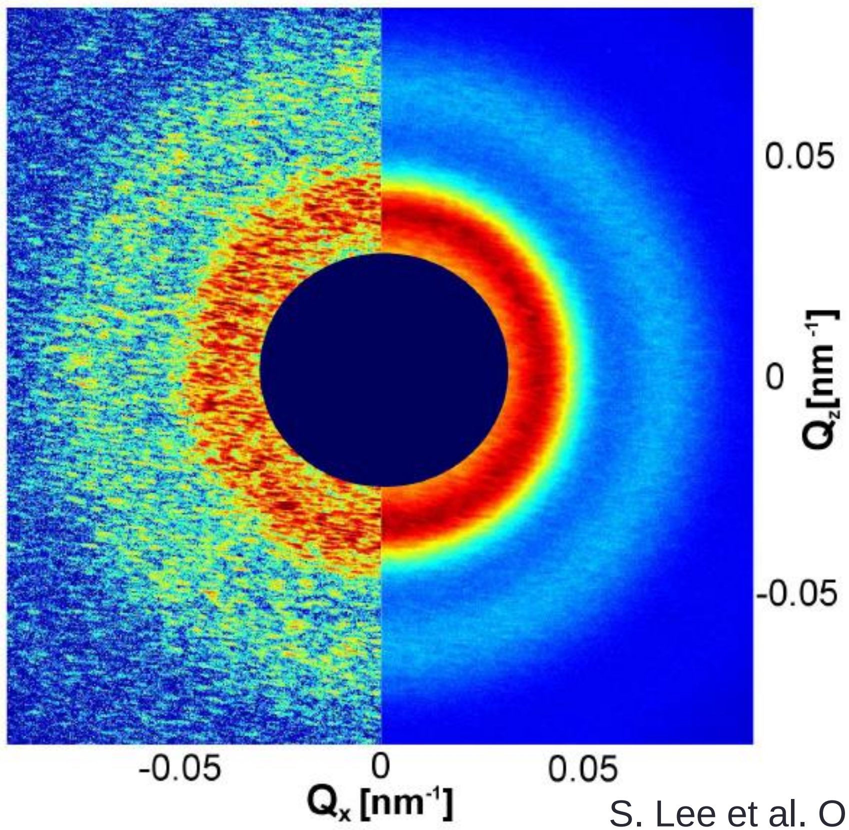
Date	Tuesday	12:30 - 14:00	(starting 2.4.)
	Thursday	8:30 - 10:00	(until 11.7.)

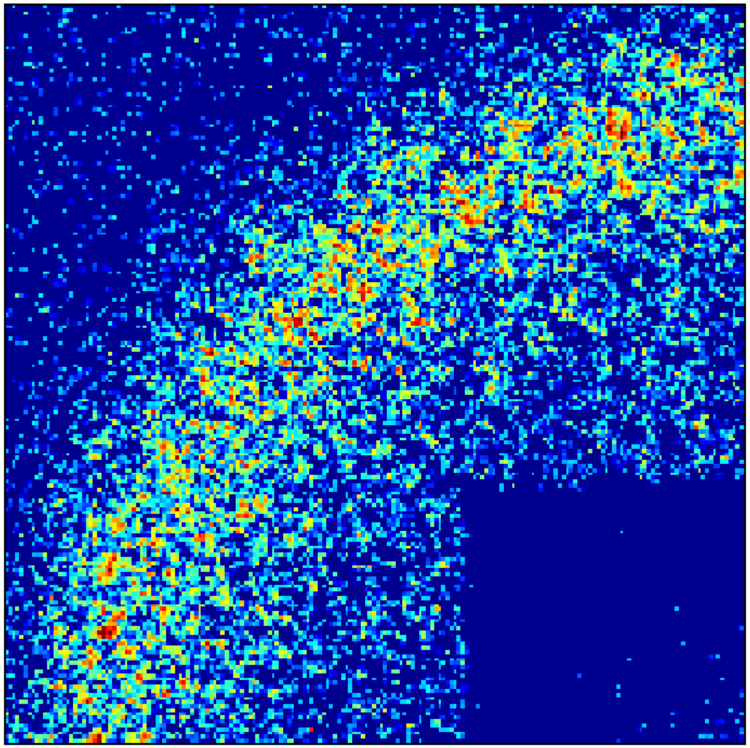
Soft Matter – Timeline

- Di 07.05.2019 Soft Matter studies I: Methods & experiments
  Definitions, complex liquids, colloids, storage ring and FEL experiments, setups, liquid jets, **…**
- Do 09.05.2019 Soft Matter studies II: Structure
  SAXS & WAXS applications, X-ray cross correlations, **…**
- Di 14.05.2019 Soft Matter studies III: Dynamics
  XPCS applications, diffusion, dynamical heterogeneities, ...
- Do 16.05.2019 XPCS and XCCA simulation and modelling
- Di 21.05.2019 Case study I: Glass transition
  Supercooled liquids, glasses vs. crystals, glass transition concepts, structure-dynamics relations, ...
- Do 23.05.2019 Case study II: Water
  Phase diagram, anomalies, crystalline and glassy forms, FEL studies, ...

Probing dynamics with coherent X-rays: X-ray photon correlation spectroscopy (XPCS)

X-ray scattering from disordered samples: speckles
→ structure decoded

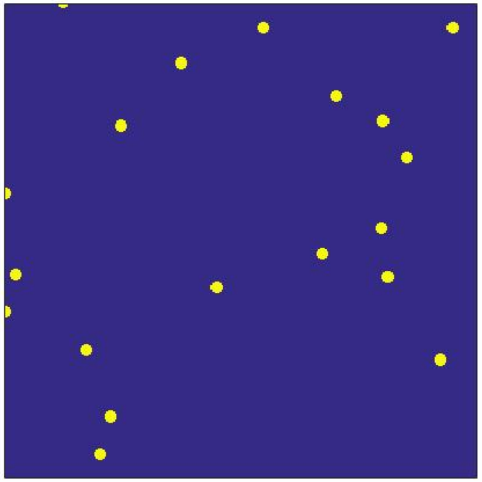




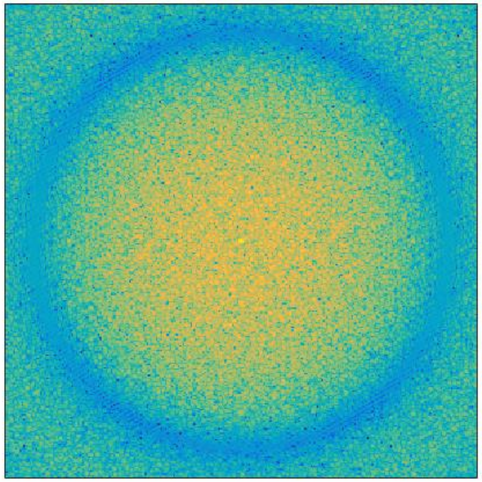
S. Lee et al. Optics Express 21, 24647 (2013)

XPCS

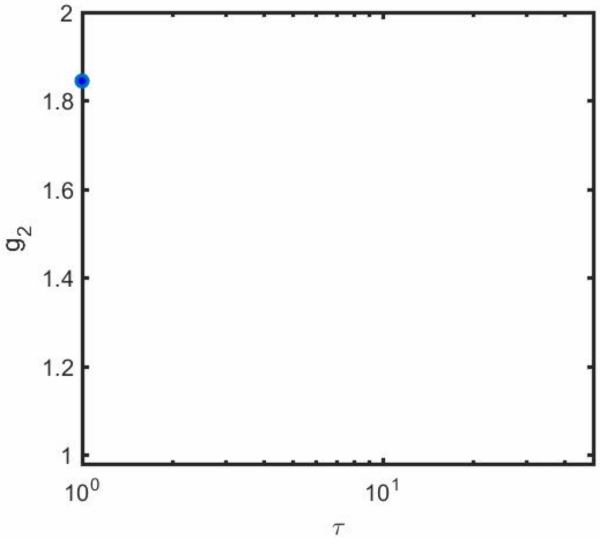
- **Time domain**: changing sample structure → change of speckle pattern
- Correlation function $g_2(q,\tau) = \frac{\langle I(q,t)I(q,t+\tau)\rangle_t}{\langle I(q,t)\rangle_t^2} = 1 + \beta^2 |f(q,\tau)|^2$, speckle contrast $\beta = \mathrm{std}(I)/\langle I \rangle$
- Intermediate scattering function $f(q,\tau) = S(q,\tau)/S(q,0)$



Diffusing particles



Speckle pattern



g_2 function

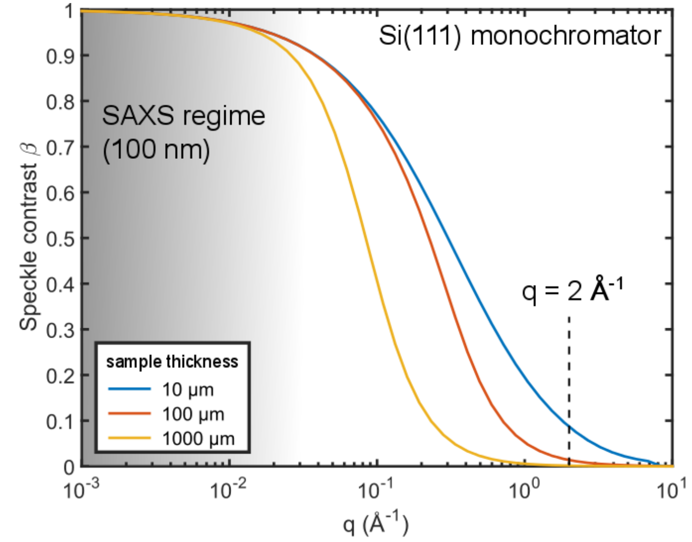
XPCS experiments – requirements

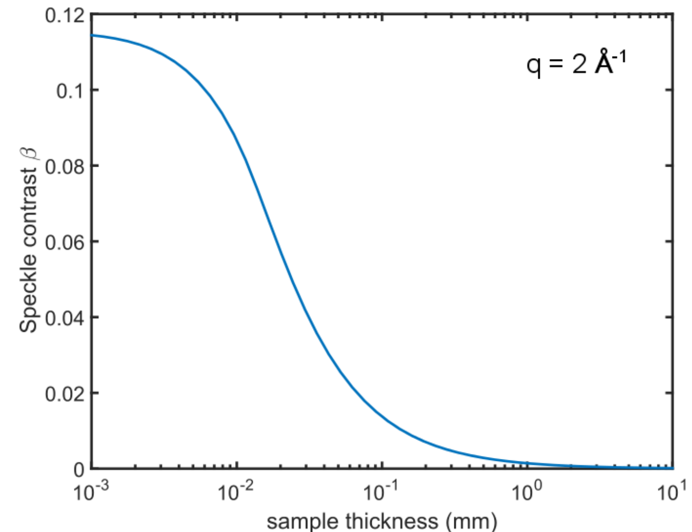
- Degree of coherence → speckle contrast
- Need to resolve speckles
  - speckle size $s \approx \frac{\lambda D}{b}$
  - using hard X-rays ($\lambda \sim 10^{-10}$ m)

  → $\frac{bs}{D} = 10^{-10}$ m

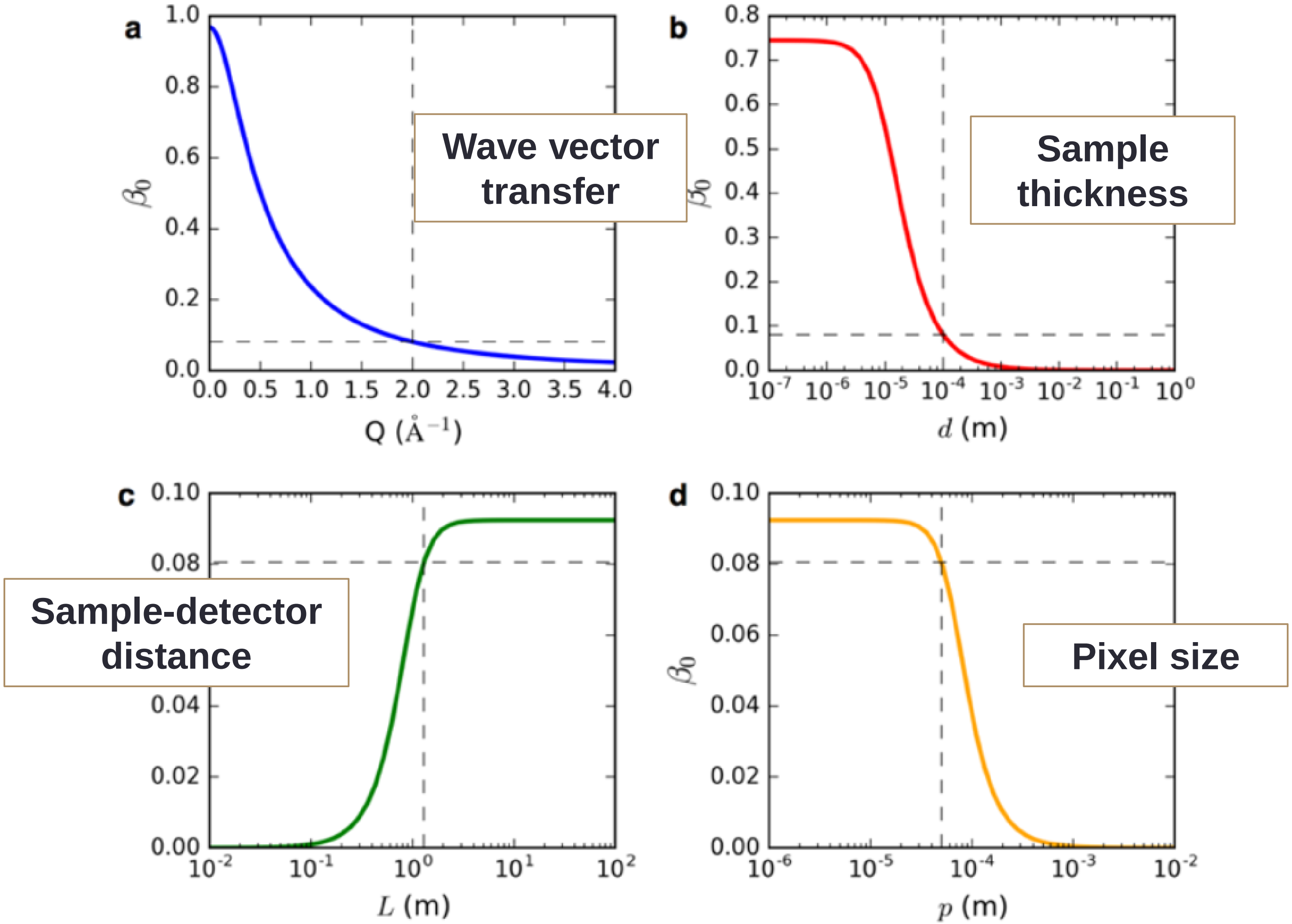
  → $bs \sim 10^{-10}$ m² for $D \sim 1$ m
- Statistics and q-dependence: 2D detectors (e.g. CCD)
  - Typical pixel sizes of $\sim 10 - 100$ µm
  - Consequently beam sizes in the µm regime
- Limit of time scales by detector read-out
  - CCD: ~ seconds
  - Photon counting: >kHz

Large q → molecular lengths





XPCS experiments – requirements



Speckle contrast as a function of various parameters

Nature Comm. 9, 1917 (2018).

Diffusion in Soft Matter

- Brownian motion: random movement of particles (pollen collision with water molecules (Einstein 1905))

- Omnipresent in soft matter systems

- Derivation (after Langevin, here only one direction x):

$$m\frac{d^2x}{dt^2} = F - f\frac{dx}{dt}$$

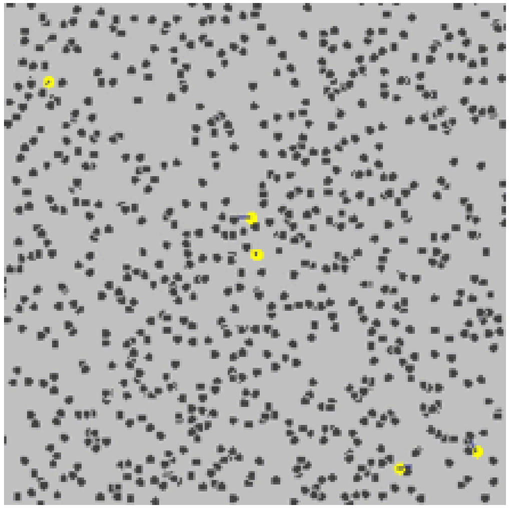
(with force F and viscous friction $F_R = -f\frac{dx}{dt}$)

$$\Leftrightarrow m\frac{d}{dt}\langle v\rangle = \langle F\rangle - f\langle v\rangle$$ (Averaging)

$\langle F\rangle = 0$ for random particle collisons

$$\frac{d}{dt}\langle v\rangle = -\frac{f}{m}\langle v\rangle$$

$$\Rightarrow \langle v(t)\rangle = v(0)\exp\left(-\frac{m}{f}t\right)$$



Diffusion of particles

Diffusion in Soft Matter

→ Mean drift velocity $\langle v \rangle$ decays with time. Back to $m\frac{d}{dt}v = F - fv$. Multiply by instantaneous position r of an particle and average yields:

$$\frac{d^2}{dt^2}\langle r^2 \rangle + \frac{f}{m}\frac{d}{dt}\langle r^2 \rangle = 2\,\langle v^2 \rangle$$

Following the equipartition theorem ($\langle v^2 \rangle = \frac{3k_BT}{m}$) the equation can be solved with the result

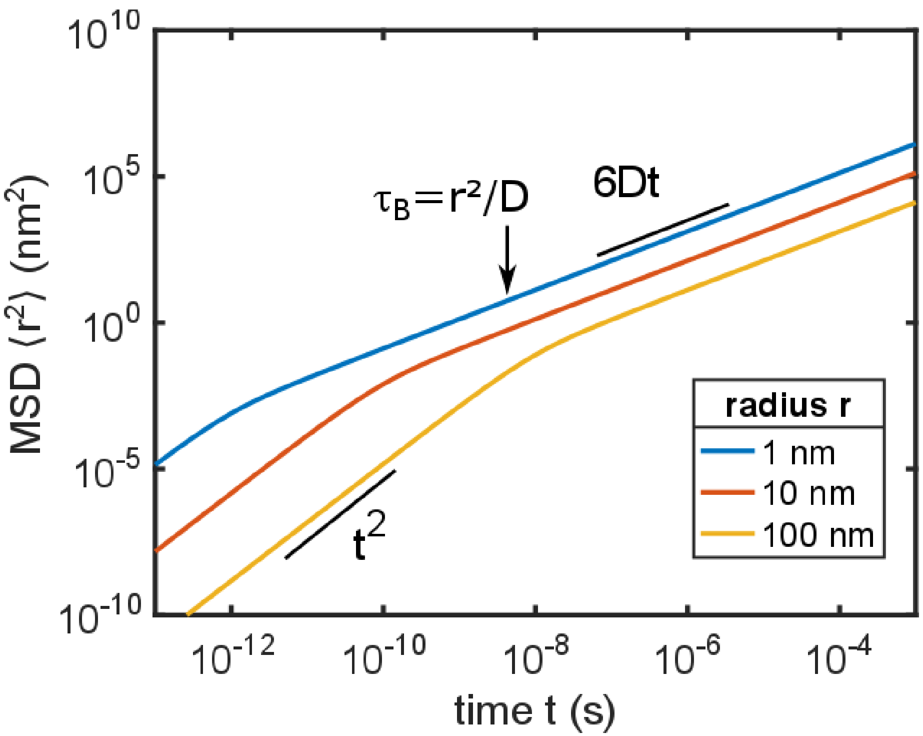
$$\langle r^2 \rangle = \frac{6k_BTm}{f^2}\left(\frac{f}{m}t - \left[1 - \exp\left(-\frac{f}{m}t\right)\right]\right)$$

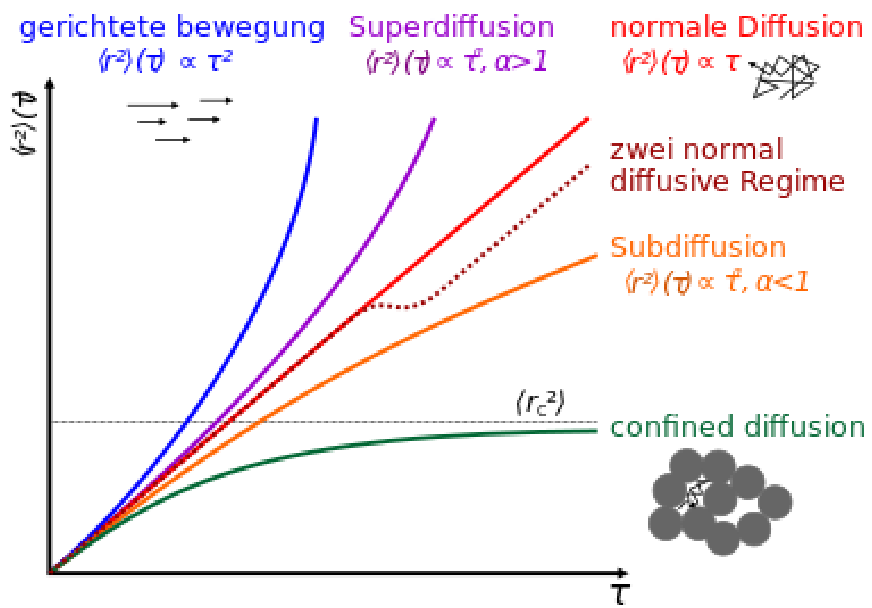
For $t \gg \frac{m}{f}$ we obtain with Stoke's law (friction of spheres, $f = 6\pi R\eta$)

$\langle r^2 \rangle = \left(\frac{k_BT}{\pi R\eta}\right)\, t = 6Dt$ with diffusion coefficient $D = \frac{k_BT}{6\pi\eta R}$

Diffusion in Soft Matter

Mean squared displacement $\langle r^2 \rangle$ – particles in water





Characteristic time $\tau_b = \frac{R^2}{D}$ to move by one radius (here $4.5 \cdot 10^{-9}$ s for $\mathrm{R} = 1$ nm)

Diffusion in Soft Matter – XPCS

Intermediate scattering function $f(q,\tau) = S(q,\tau)/S(q,0)$ with

$$f(q,\tau) = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \exp(i\mathbf{q}\cdot[\mathbf{r_i}(0) - \mathbf{r_j}(\tau)])\right\rangle$$

For diffusion, only single particle properties are probed → cross terms $i \neq j$ average out and $S(q) = 1$ → we obtain

$$f(q,\tau) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \exp(i\mathbf{q}\cdot[\mathbf{r_i}(0) - \mathbf{r}_i(\tau)])\right\rangle$$

And finally (cf. Physica 32, 415 (1966)) the result for diffusion

$$f(q,\tau) = \exp(-Dq^2\tau)$$

DESY.

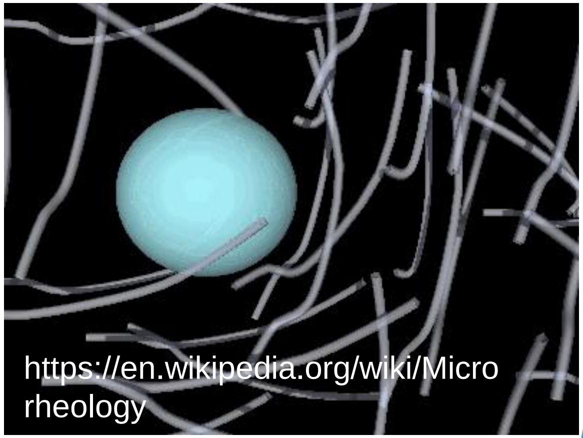
Diffusion by XPCS – Notes

- In XPCS, correlation function for diffusion:
$$g_2(q,\tau) = 1 + \beta^2 |f(q,\tau)|^2 = 1 + \beta^2 \exp(-2Dq^2\tau)$$

- Relaxation time $\tau_0 = \frac{1}{\Gamma} = \frac{1}{Dq^2}$ → characteristic $\tau_0 \propto q^{-2}$

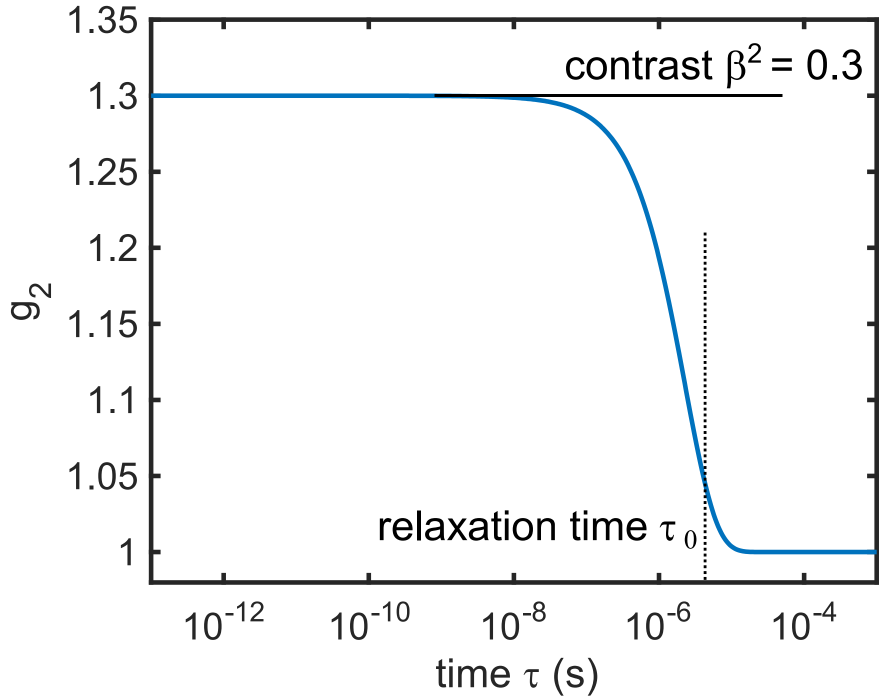
- Measuring g_2 allows to obtain particle size $R = \frac{k_B T \tau_0 q^2}{6\pi\eta}$ when solvent properties are known → Dynamical light scattering

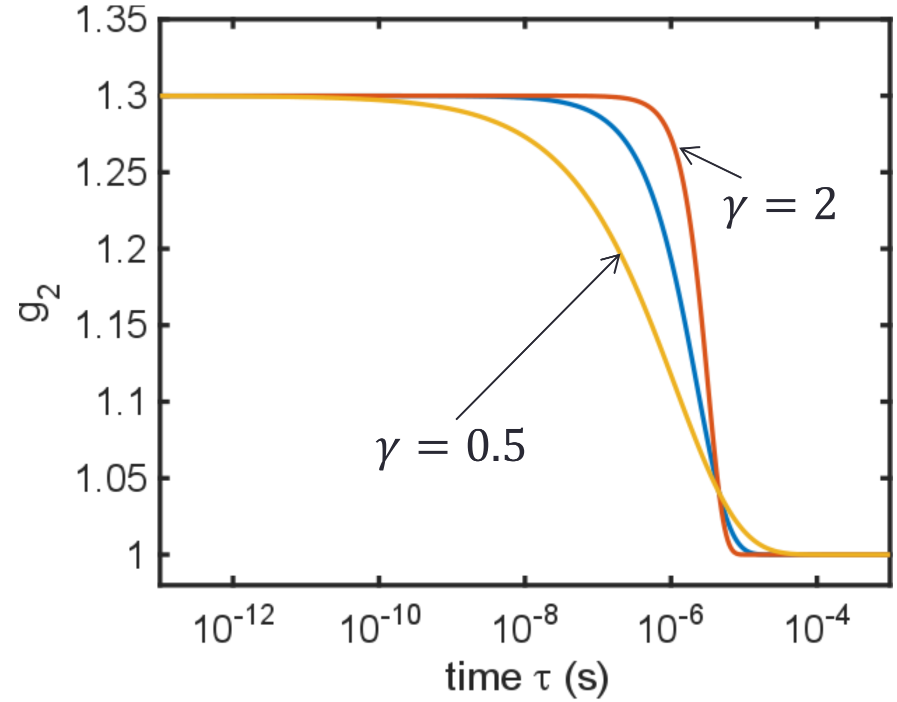
- On the other hand, known particles can be used to probe solvent properties, in particular viscosity η → microrheology


https://en.wikipedia.org/wiki/Microrheology

XPCS – correlation functions

Spherical particles with $\mathrm{R} = 10$ nm in water





- Stretched and compressed correlation functions: Kohlrausch-Williams-Watts function $f(q,\tau) = \exp(-(\Gamma\tau)^{\gamma})$
- Measure of width of distribution of (local) relaxation times

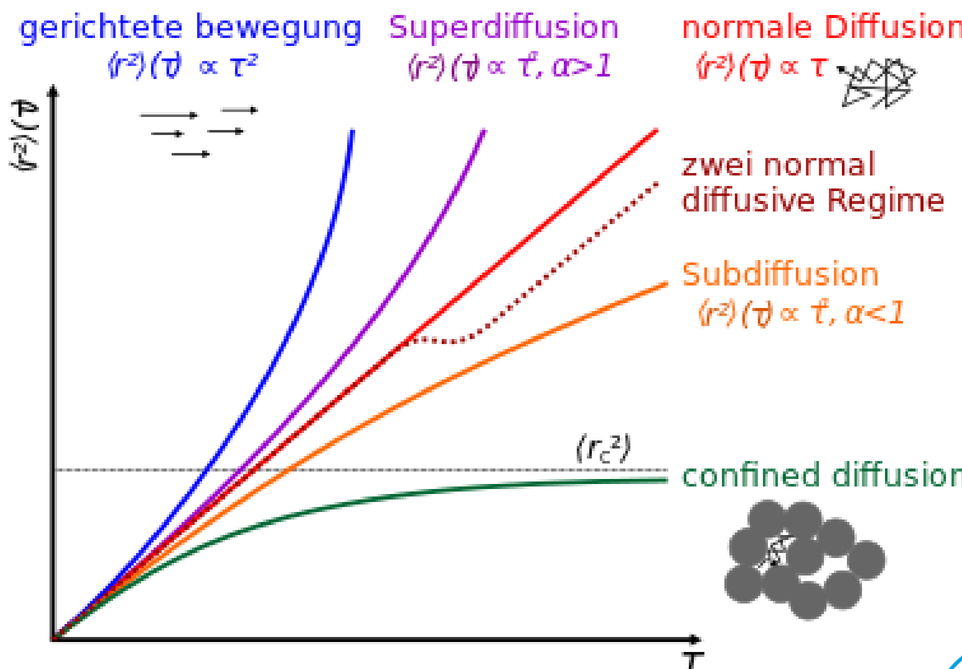
XPCS – correlation functions

Q-dependencies

- Diffusion: $\tau_0 \propto q^{-2}$, $\langle r^2 \rangle \propto \tau$
- More general ($\tau_0 \propto q^{-\delta}$): $\langle r^2 \rangle \propto \tau^{\alpha} \rightsquigarrow \; r \propto \tau^{\frac{\alpha}{2}} \rightsquigarrow \tau \propto q^{\frac{2}{\alpha}} \quad \Rightarrow \quad \alpha\delta = -2$

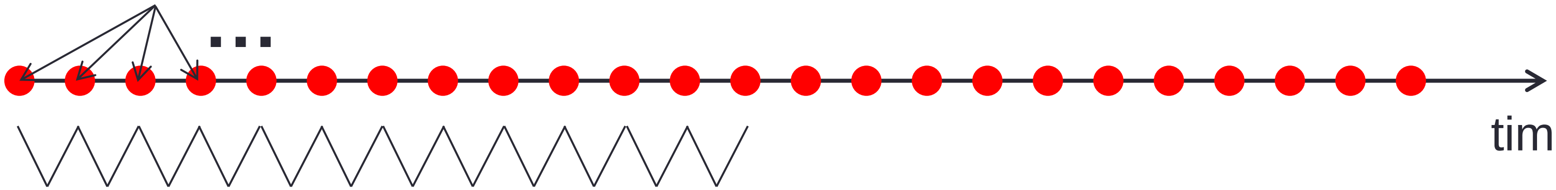
- Diffusion: $\delta = 2$
- Subdiffusion: $\delta > 2$
- Superdiffusion: $\delta < 2$
- Balistic motion: $\delta = 1$

→ The analysis of both exponents γ and δ provides information on the type of dynamics



XPCS – instantaneous correlation function

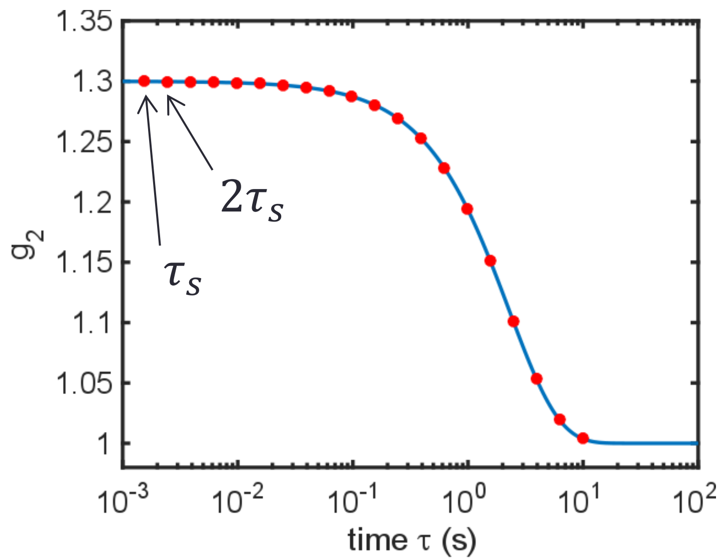
Measured speckle patterns



Correlate & average → Shortest lag time τ_s

Correlate & average → 2nd shortest lag time $2\tau_s$

⋮



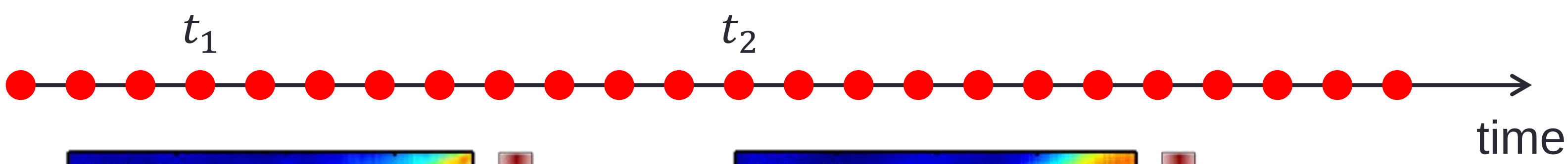
→ $g_2(q,\tau)$ averaged over pairs of same lag time τ (…**and** pixels!) taken during the experimental run

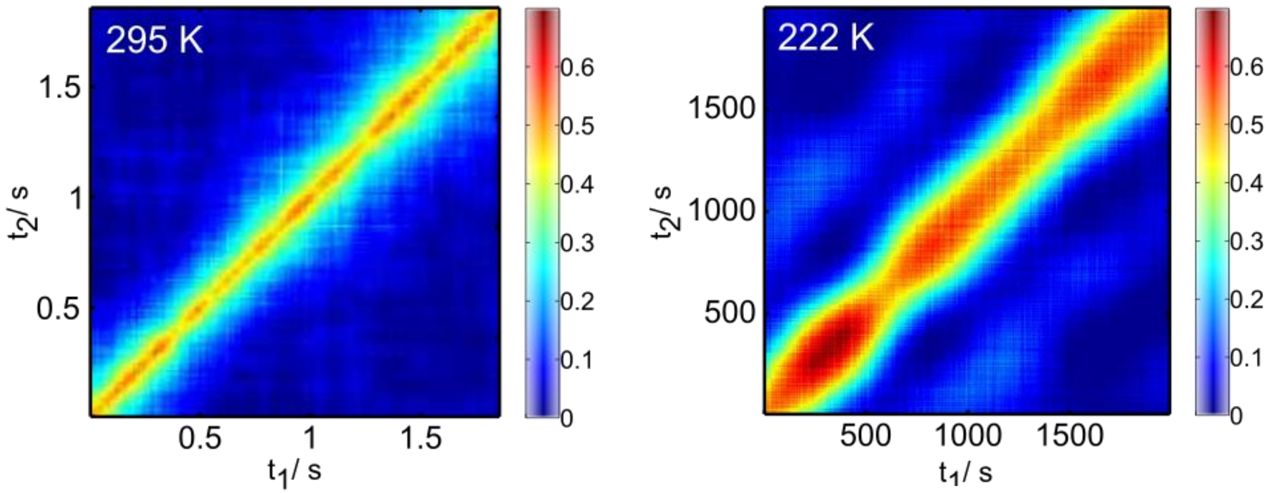
XPCS – instantaneous correlation function

But: sample may change during the measurement

→ Two-time correlation function $C_I(q, t_1, t_2) = \frac{\langle I(q,t_1) I(q,t_2) \rangle}{\langle I(q,t_1) \rangle \langle I(q,t_2) \rangle}$

- t_1, t_2 are points in experiment time, e.g.:





→ Dynamical heterogeneities!

- Sample ages along $t_1 = t_2$ diagonal $t_{age} = \frac{t_2 - t_1}{2}$
- Lag time $\tau = |t_2 - t_1|$

XPCS – signal to noise

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

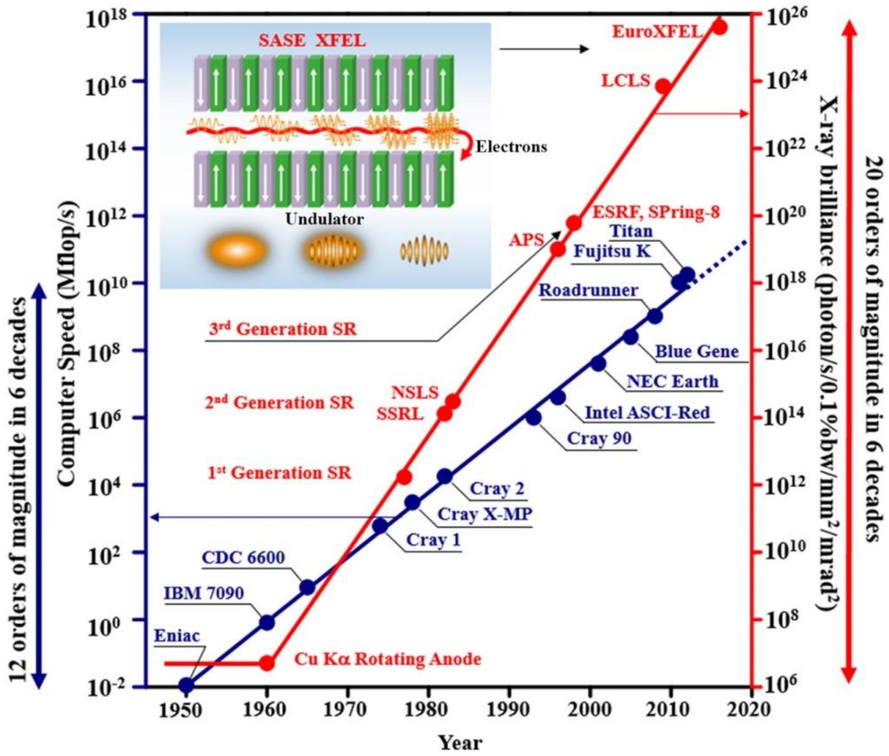
- $\mathrm{var}(g_2) = \frac{g_2}{N_p \langle n_c \rangle} = \frac{g_2}{n_x n_y T t_a I^2}$
  - N_p number of correlated pairs averaged for g_2
  - $\langle n_c \rangle$ mean number of counts per exposure time
  - Using count rate I per pixel, accumulation time t_a, number of pixels $P = n_x n_y$, total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

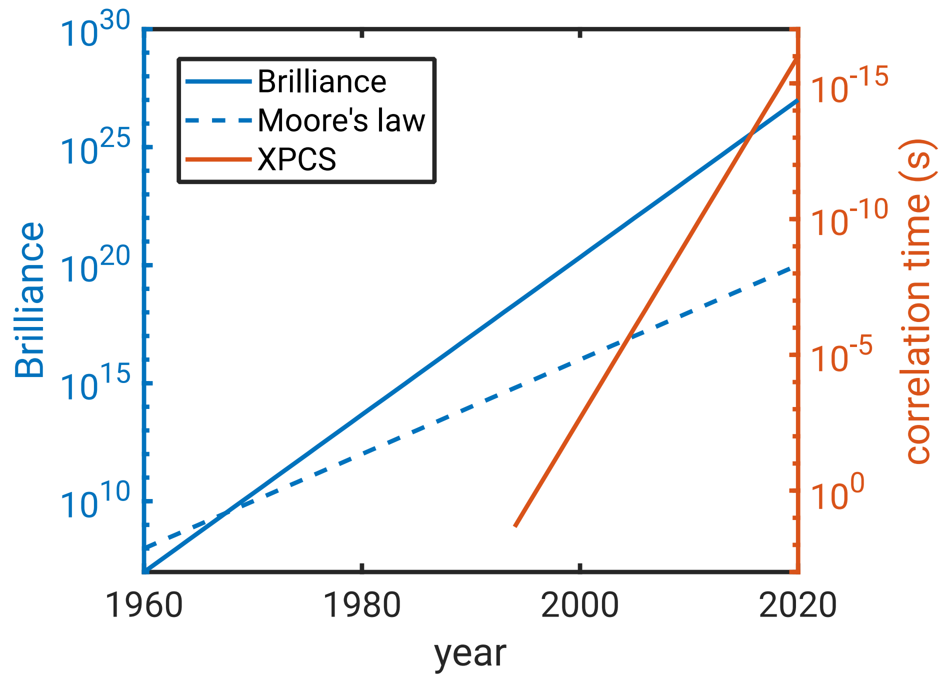
- $SNR = \frac{g_2 - 1}{\sqrt{\mathrm{var}(g_2)}} = \sqrt{PTt_a/g_2} \cdot I(g_2 - 1)$
  - Substitute g_2 with the limit of $\tau \to 0$: $g_2 = \beta^2 + 1$
  - Low contrast limit: $\sqrt{g_2} \approx 1$

→ $SNR = \beta^2 I \sqrt{PTt_a}$

- Consequence: Increase of I by 10 → accessible time scale 100x smaller!

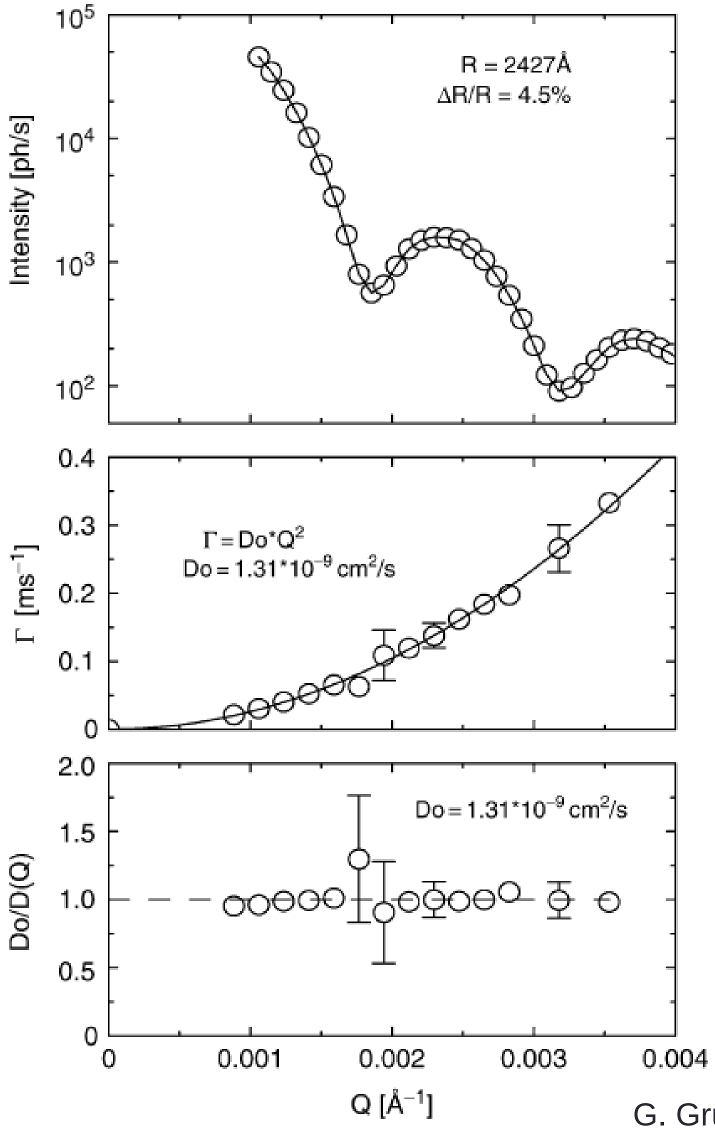
see P. Falus et al. J. Synchr. Rad. 13, 253 (2006)





- 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

XPCS example 1 – dynamics in colloidal systems

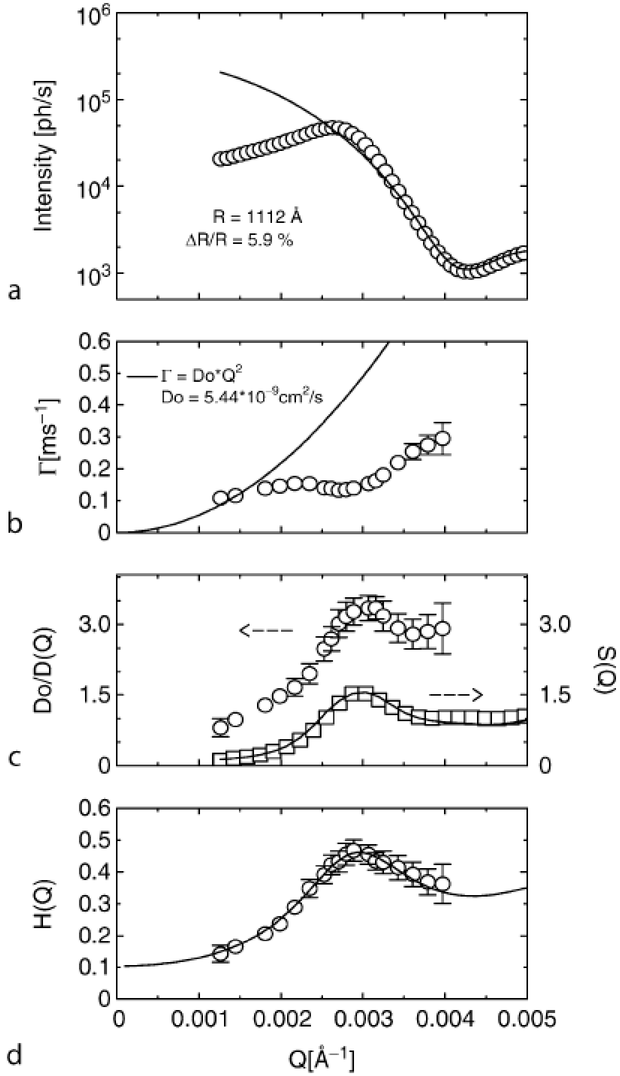


SiO_2 colloids in glycerol/water

- Low concentration: volume fraction 1%
- SAXS: Formfactor
- XPCS: diffusion with $\Gamma \propto q^2$

G. Grübel et al. In "Soft Matter Characterization", Springer (2008)

XPCS example 1 – dynamics in colloidal systems



PMMA particles in decalin

- High concentration: volume fraction 37%
- SAXS: Structure factor
- XPCS results deviate from $\Gamma \propto q^2$
- Effective diffusion constant $D(q) = D_0 H(q)/S(q)$ for short times, hydrodynamic function $H(q)$
- $H(q) = 1 \Rightarrow D(q) = D_0/S(q)$: de Gennes narrowing, i.e. slowing down around next-neighbour distances.

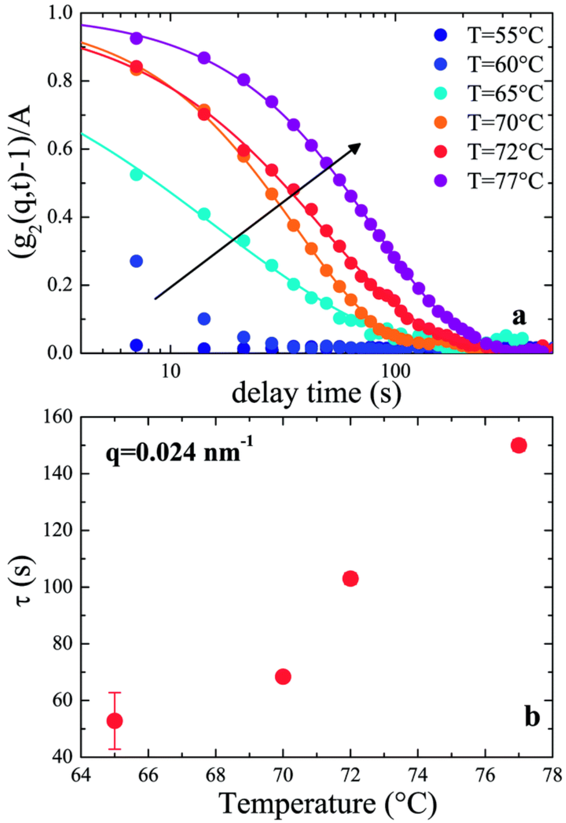
G. Grübel et al. In "Soft Matter Characterization", Springer (2008)

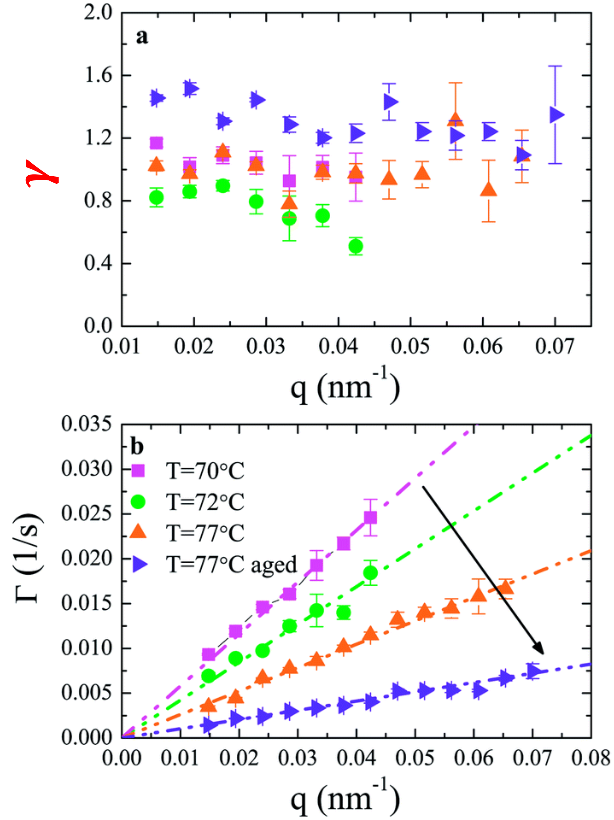
XPCS example 2 – microrheology

Tracer particles to measure solvent properties

- Weak scattering signal from solvent
- Large q-region has to be probed (low speckle contrast)
- Slower dynamics in SAXS regime
- Indirect access to solvent properties only
- Length scale of several 10 nm given by the tracer particle size
- Low tracer particle concentrations, so that $S(q) = 1$ for the particles → avoid any particle-solvent interactions

XPCS example 2 – microrheology



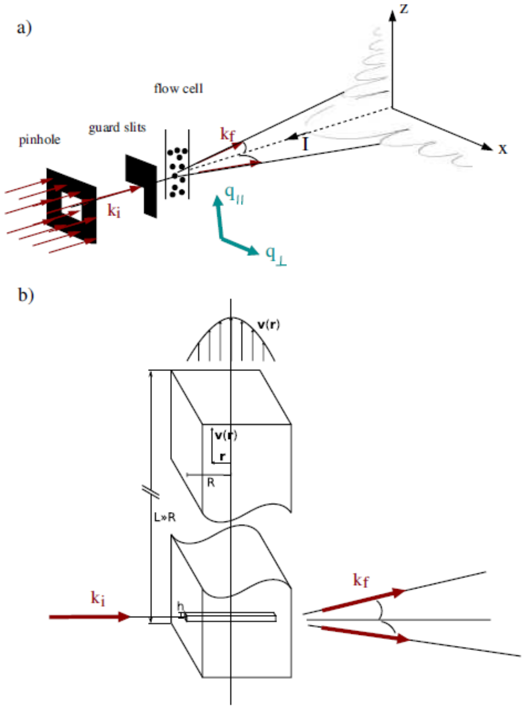


B. Ruta et al. Soft Matter 10, 4547 (2014)

Glass transition studies: →Lecture 15

- SiO_2 particles as tracer for gelation of methylcellulose in water
- Gel-gel-transition: Turbid gel for $T \geq 60$ °C
- Stretched ($\gamma < 1$) to compressed ($\gamma > 1$) transition (KWW exponent!)
- Hyper-diffusive & compressed at high temperatures → stress-dominated

XPCS example 3 – directed motion



Sample undergoes (shear) flow

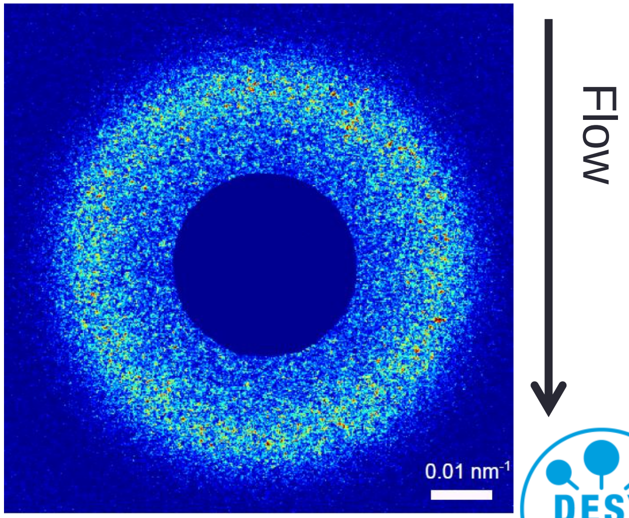
- Flowing sample to avoid radiation damage
- Sedimentation of particles

- $f(q,\tau)$: product of diffusive and advective contributions
  $f(q,\tau) = f_d(q,\tau) \cdot f_a(q,\tau) = \exp(-\Gamma t) \cdot f_a(q,\tau)$

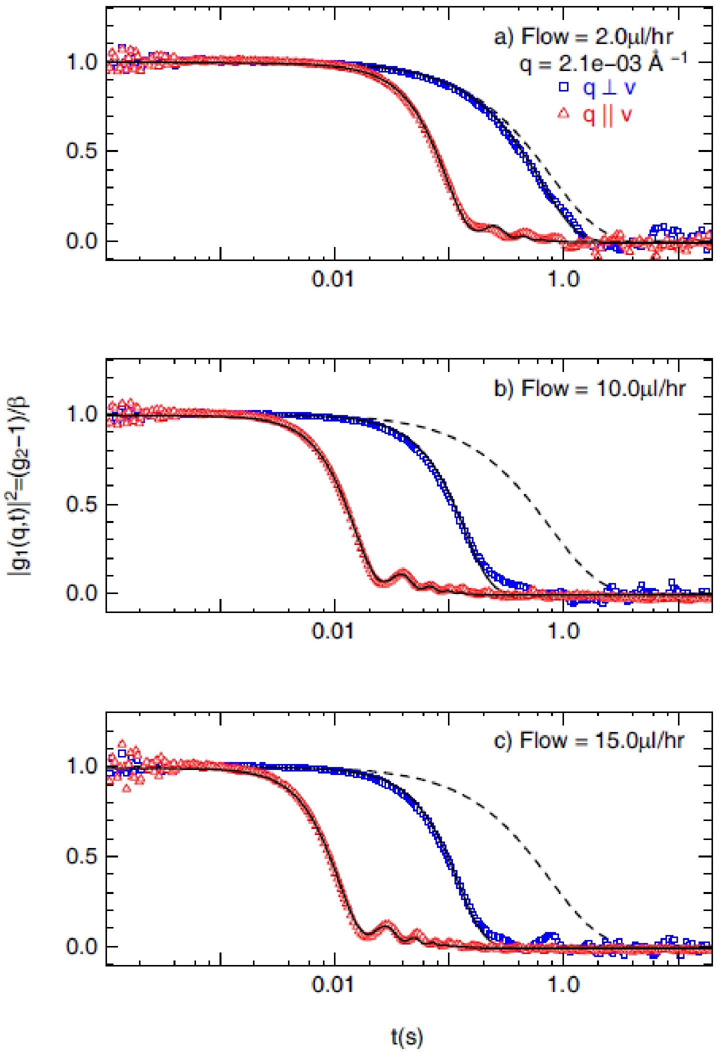
- $f_a(q,\tau)$ can become complicated

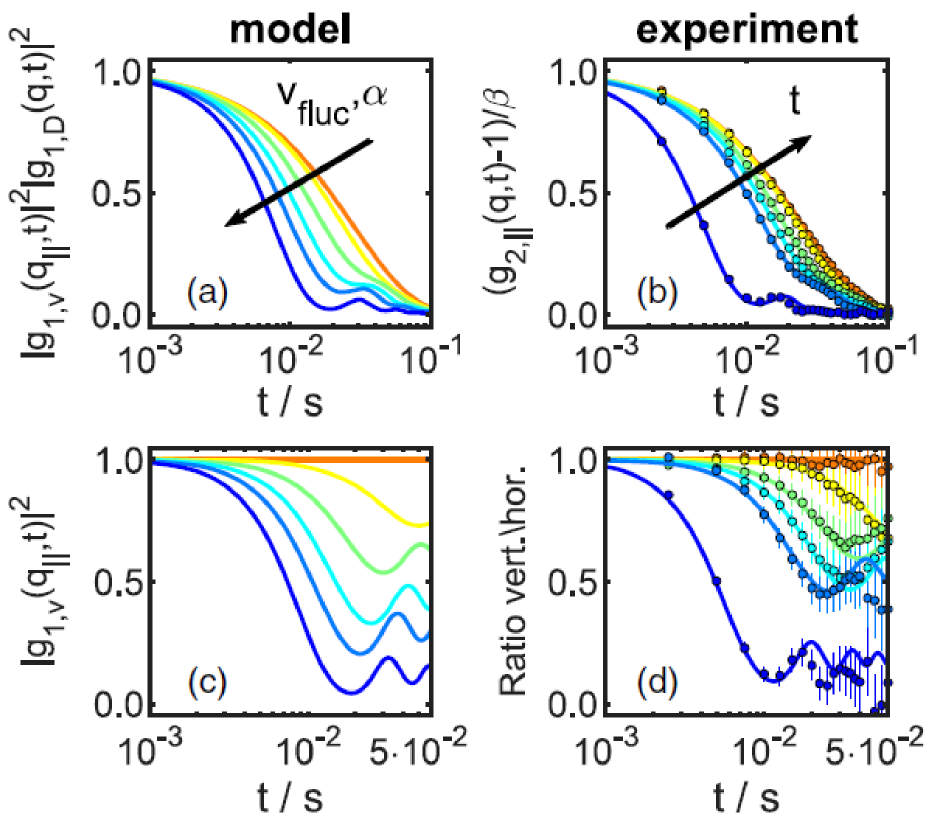
Perpendicular to flow it simplifies to
$g_{2,\perp}(q,\tau) = 1 + \beta^2 \exp(-2\Gamma\tau) \exp(-(\nu_{tr} t)^2)$,
transit-induced frequency ν_{tr}

In flow direction: oscillating behaviour



XPCS example 3 – directed motion





Particle sedimentation

J. Möller et al. PRL 118, 198001 (2017)

S. Busch et al. Eur. Phys. J. E 26, 55 (2008)

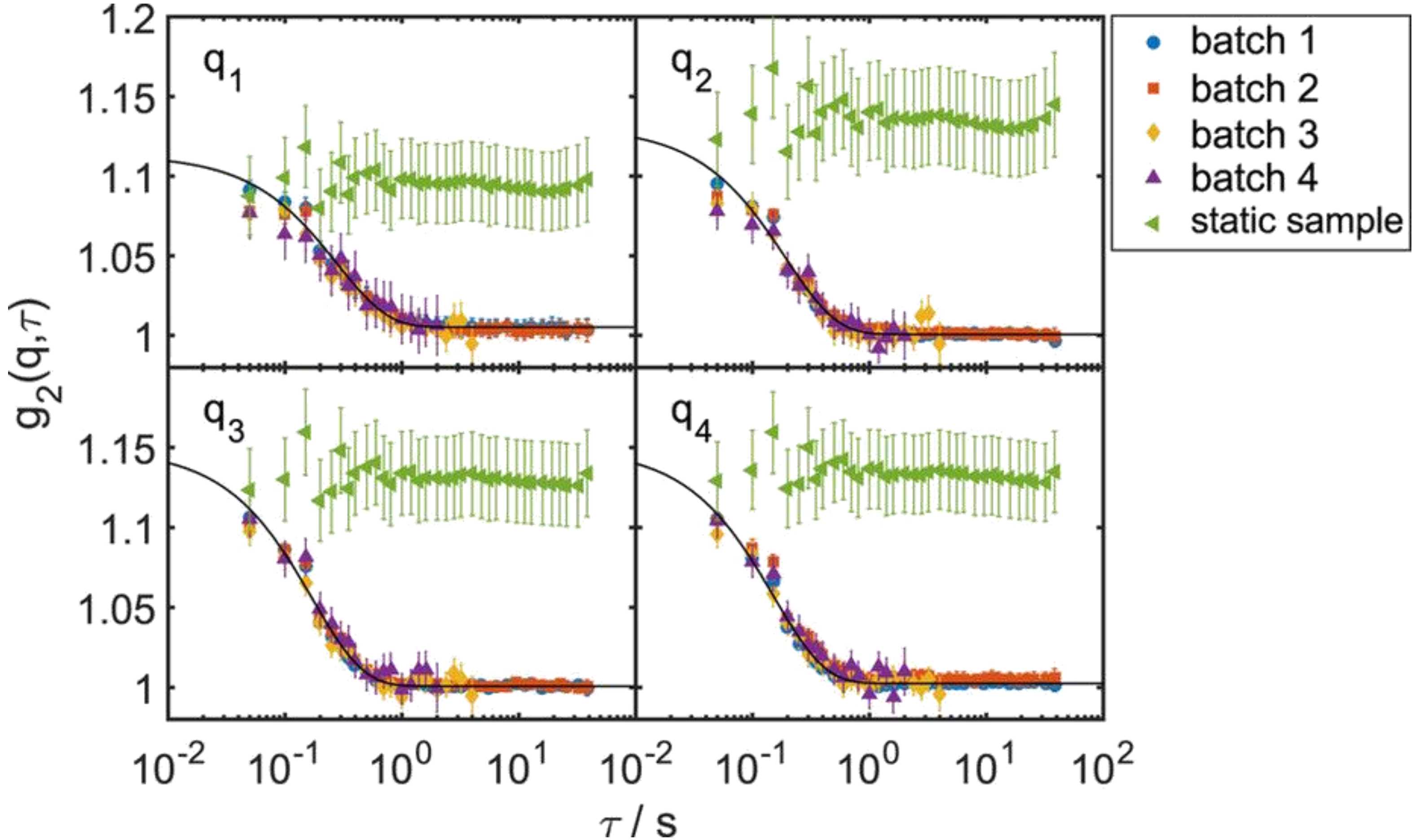
XPCS example 4 – XPCS at FEL

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)

State-of-the-art detectors at storage rings

Maxipix (ESRF) ~ 300 Hz
Lambda (PETRA III, APS) ~ >2 kHz
Eiger (PETRA III, NSLS-II, ESRF) ~ kHz

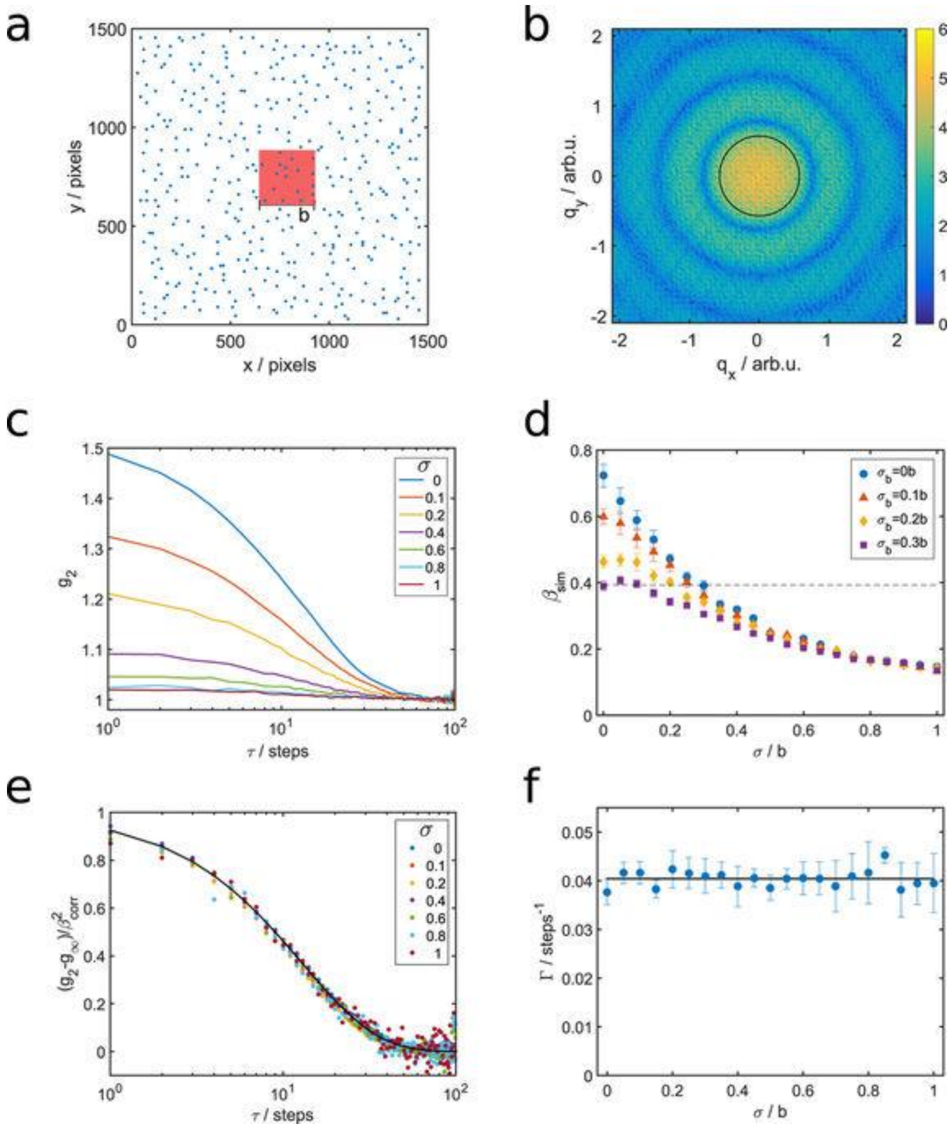
XPCS example 4 – XPCS at FEL



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

FL et al. Sci. Rep. 5, 17193 (2015)

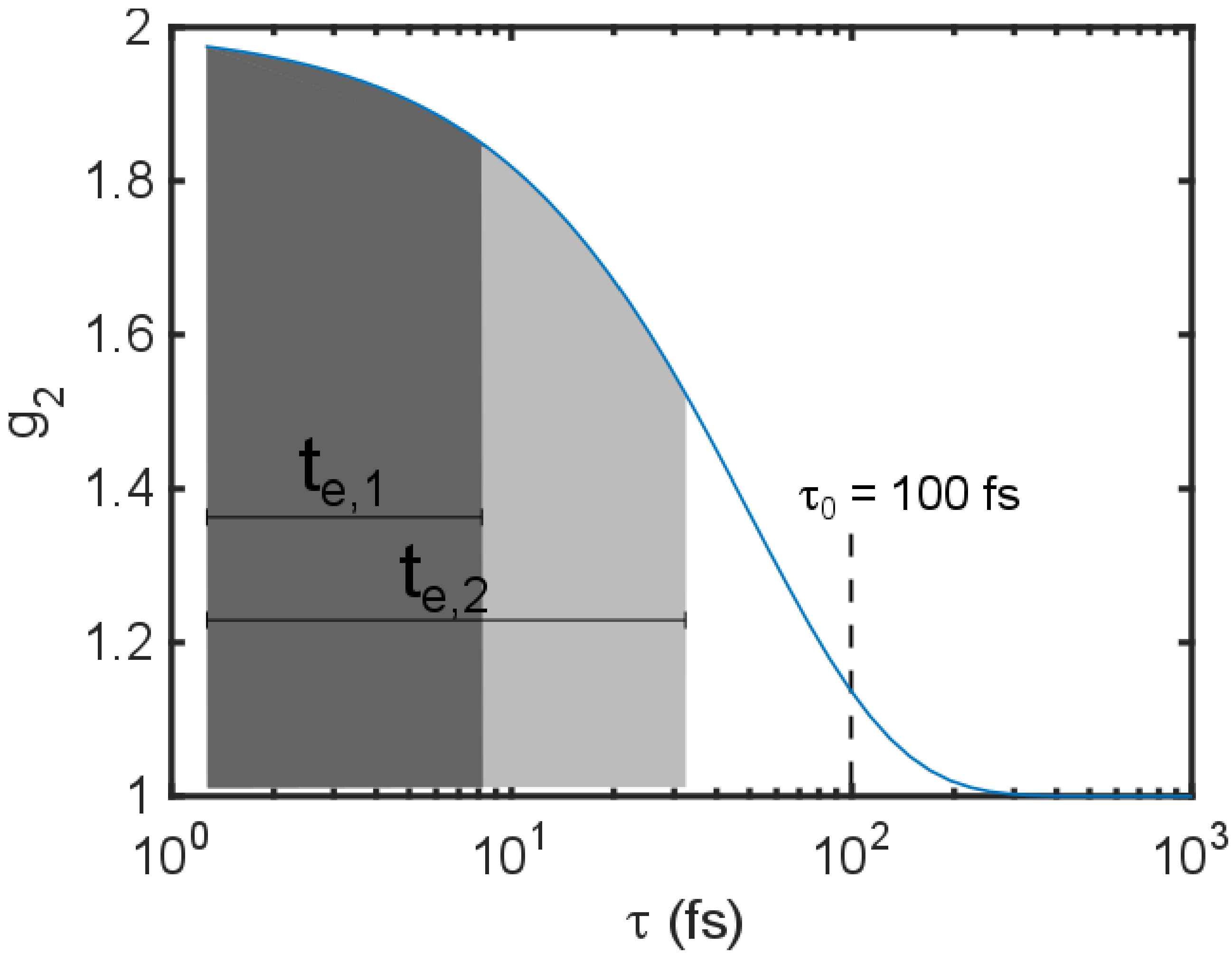
XPCS example 4 – XPCS at FEL



- XPCS simulations
- Moving beam & beam size modifications on shot-to-shot basis
- Extracted relaxation rates well-described by diffusion
- Drop of effective contrast

FL et al. Sci. Rep. 5, 17193 (2015)

XPCS example 5 – ultrafast XPCS: XSVS

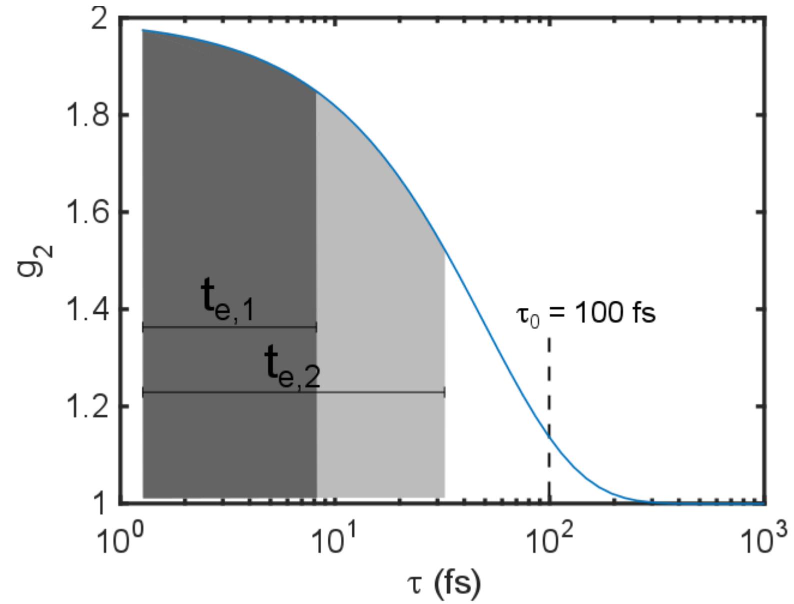


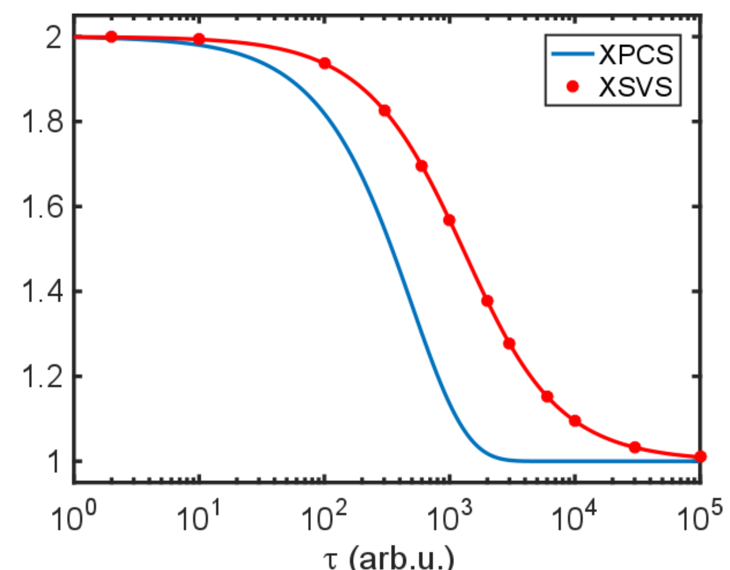
- So far: short exposure time $t_e \ll \tau_0$
- Dynamics change during exposure → reduction of contrast
- Typical FEL pulse length: $\tau_0 = 100$ fs

XPCS example 5 – ultrafast XPCS: XSVS

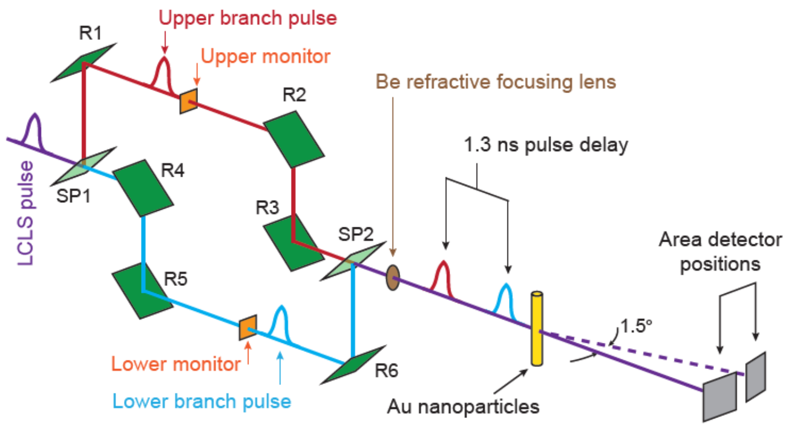
Finite pulse lengths

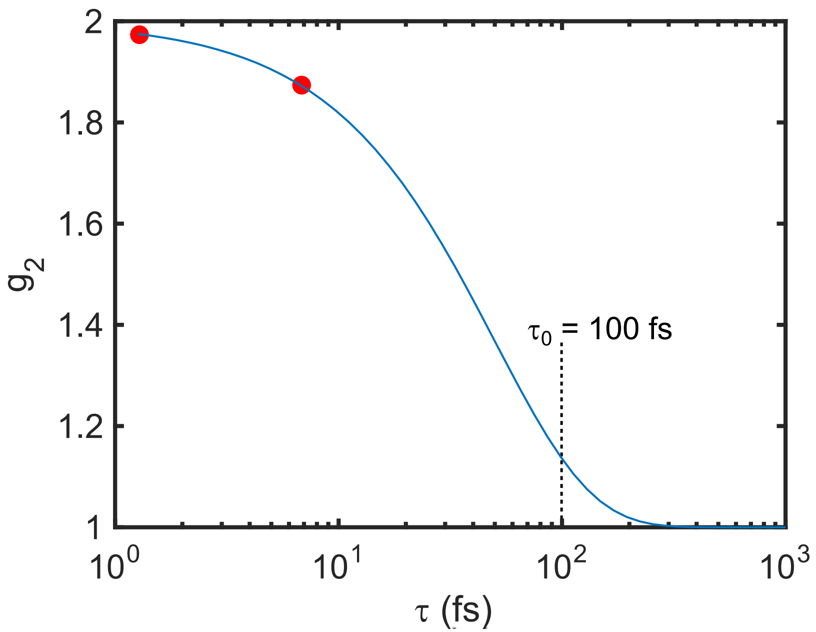
- Contrast as function of exposure ($\beta^2 = \frac{\langle I^2 \rangle}{\langle I \rangle^2} - 1$)
- $\beta^2(q, t_e) = \frac{2\beta_0^2}{t_e} \int_0^{t_e} \left(1 - \frac{\tau}{t_e}\right) |f(q,\tau)|^2 d\tau$
- For diffusion, this can be solved analytically (→ Exercise!)
- Limited by accessible exposure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





XPCS example 5 – 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)

XPCS: further examples

- Glass dynamics and glass transition (→ lecture 15)
- In general, large q experiments
  - Water (→ lecture 16)
  - Domain wall dynamics
  - Network glasses (SiO2, …)
  - …
- Liquid surfaces: capillary waves → oscillating ISF
- …
- Relation to neutron spin echo and dynamic light scattering

Accessible timescales for XPCS