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School on Synchrotron and Free-Electron-Laser Sources and their Multidisciplinary Applications

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X-ray Photon Correlation Spectroscopy (XPCS)

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ICTP school on Synchrotron and Free-Electron-Laser Sources and their Multidisciplinary Applications
Trieste, May 6 - 2010

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ID10A homepage:
http://www.esrf.eu/UsersAndScience/Experiments/SoftMatter/ID10A/

Outline:

1/ X-ray coherence

2/ X-ray Photon Correlation Spectroscopy (basics)

3/ The beamline

4/ Examples of research

Motivation: To be able to study **dynamics** in a range of time and space which is inaccessible by other techniques

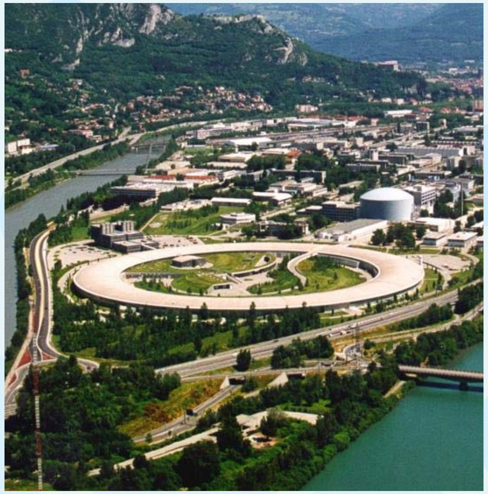
How: time-correlation spectroscopy of scattered X-ray photons (**XPCS**)

Needs: A **brilliant** X-ray source generating a partially **coherent** X-ray beam and a suitable **detector** to measure the fluctuating **speckle pattern**

Future developments: XPCS at an **X-FEL** source

X-ray coherence

….or how to get coherent radiation from an incoherent source



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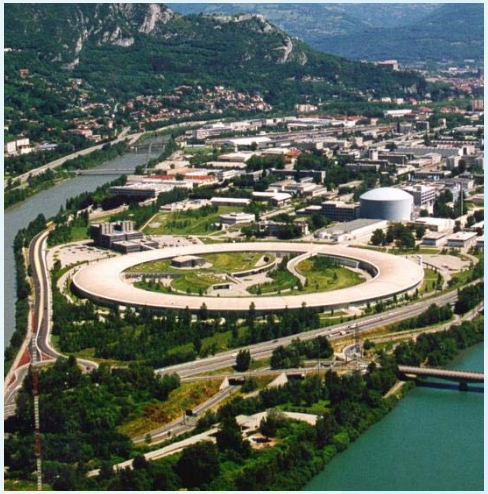
based on
spontaneous light emission



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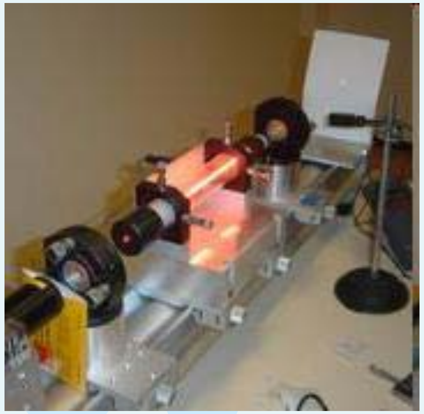


based on
stimulated light emission

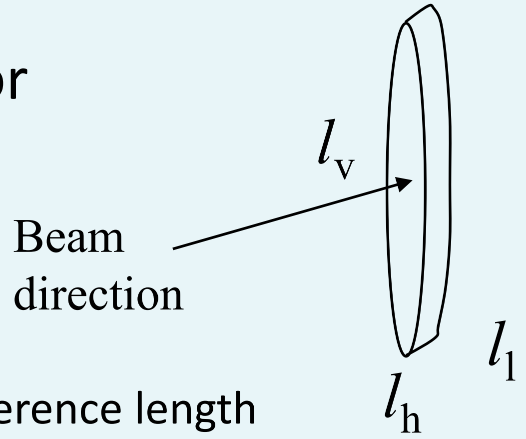
Two types of sources

- Chaotic sources (spontaneous emission)
  - Lab. X-ray generators
  - Synchrotron and Neutron sources
  - Radioactive nuclei

- One-mode sources (stimulated emission, Glauber light)
  - Unimodal lasers

Important parameter : N_C=photons pr. coherence volume

N_C ~10^{-3} for typical ESRF undulator
N_C ~10^{7} for typical optical laser



Coherence volume $V_C \propto l_h \, l_v \, l_l$
horizontal, vertical and longitudinal (temporal) coherence length

Coherence

- Quantum mechanics → probability amplitudes (waves)
- Optics → Young's double slit experiment, interference
- X-ray (and neutron) scattering

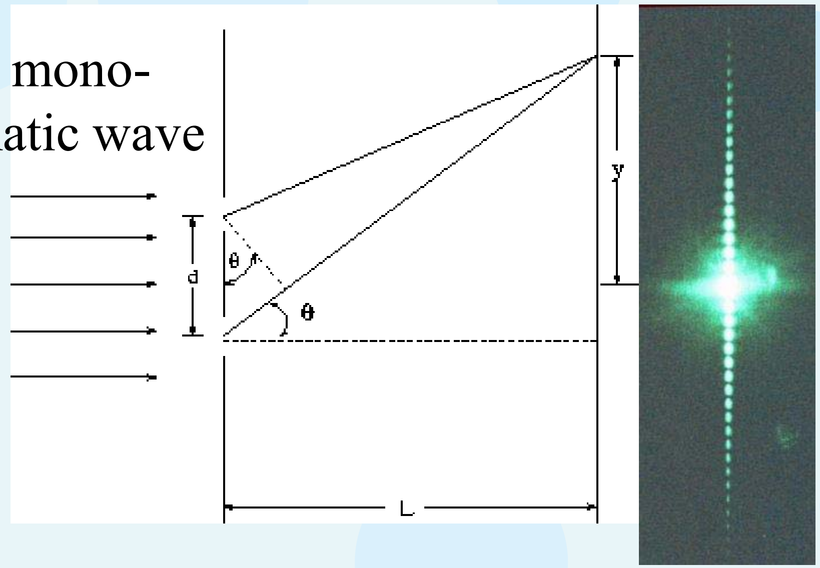
It's all about probability amplitudes and interference !!!

Example: Young's double slit experiment (Thomas Young, 1801)

[wave-character of quantum mechanical particles (photons)]

Plane, mono-chromatic wave

Laser beam



$P=|\Sigma_j \Phi_j|^2$

Φ: probability amplitude

$\Phi_j \sim \exp[-i(\omega t-kl_j)]$

$\omega=ck$, $k=2\pi/\lambda$, $l_j(L,y)$

$P(y) \sim \cos^2(\pi yd/\lambda L)$

$\Delta y=\lambda L/d$

Reasons for loss of coherence/visibility

1) Incoherent superposition of probability amplitudes $P=\Sigma_j|\Phi_j|^2$
(distinguishable alternatives, uncertainty principle, partial coherence)

2) Intensity interference is only observed if event is repeated many times; repetition under non-ideal conditions washes out the visibility

Non-ideal conditions:

- E_{in}, E_{out}, $\mathbf{k}_{in}$, $\mathbf{k}_{out}$ not well defined in the experiment
- Disorder or dynamics in the scattering sample
- Limited detector resolution (temporal and spatial)

Chaotic source (ESRF undulator)

(spontaneous, independent emission in all modes)

Longitudinal (or temporal) coherence

At times $>> \tau_0$ the field amplitudes from a chaotic source are no longer correlated due to the spread in wavelength

$$g^{(1)}(\tau) = \frac{\langle E^*(t)E(t+\tau)\rangle}{\langle |E(t)|^2\rangle} \propto e^{-\tau/\tau_0}$$

(Gaussian 1st order time-correlation function)

$\tau_0 = 1/\Delta\nu = \lambda^2/(c\Delta\lambda) \sim 3$ fs (Δλ/λ=1e-4)

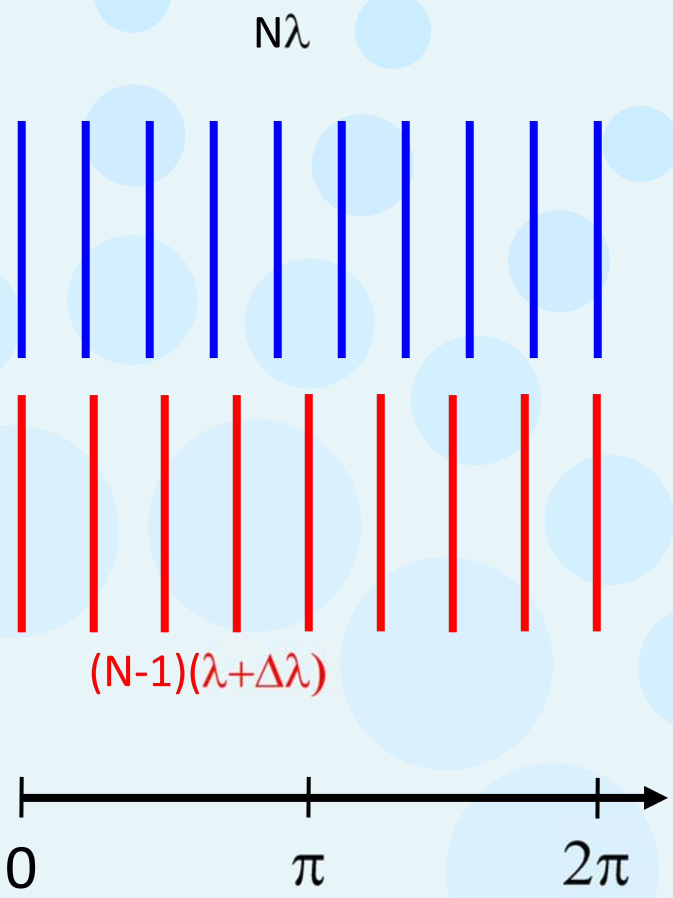
Longitudinal coherence length $l_l = c\tau_0 = \lambda/(\Delta\lambda/\lambda) \sim 1\ \mu m$

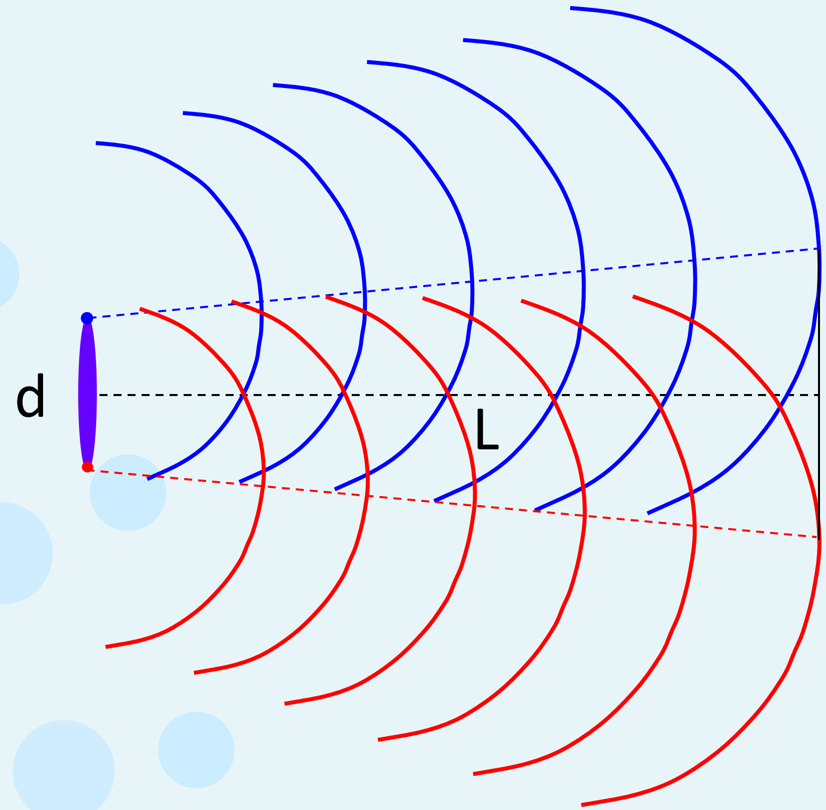
Spatial coherence

Analogy with Young's double slit experiment :

Transverse coherence length (v,h) : $l_{v,h} = \lambda L/d_{v,h} \sim 2\text{-}150\ \mu m$

Coherence lengths

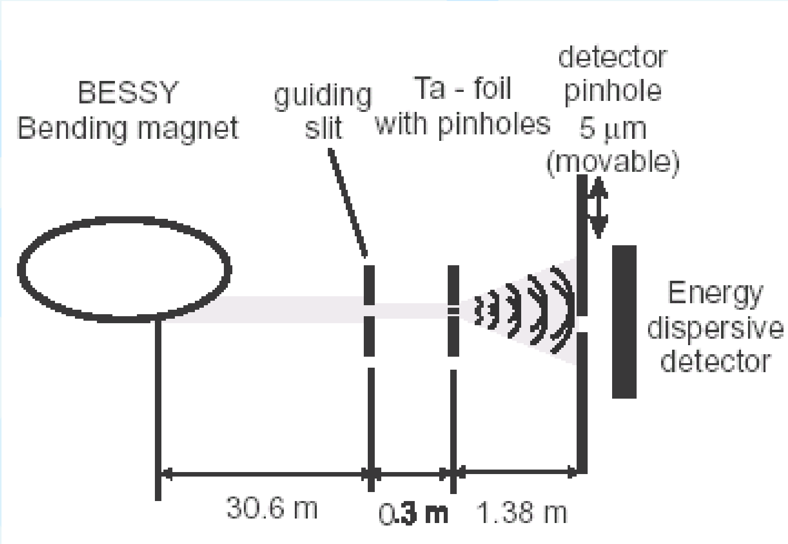




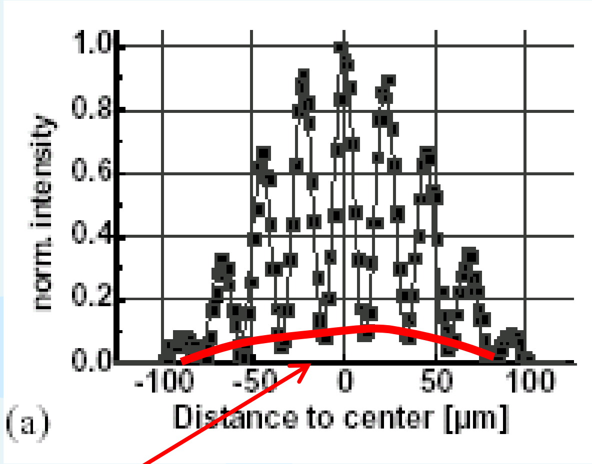
Longitudinal coherence length $\lambda^2/\Delta\lambda$

Transverse coherence length $\lambda L/d$

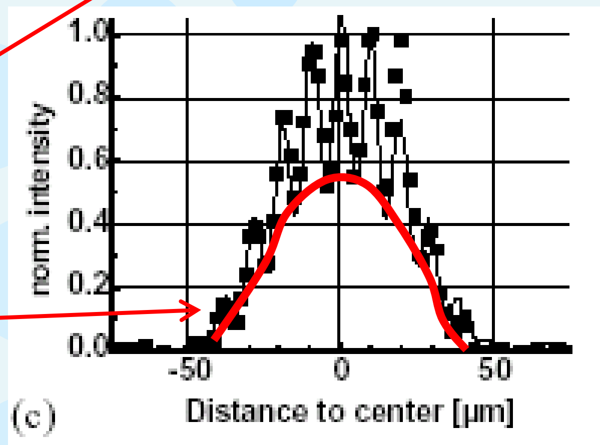
Young's double slit experiment with hard X-rays



Leitenberger *et al.*
Physica B ***336***, *36 (2003)*



λ=2.1Å, d=11μm
Visibility(β) ~ 80%



λ=0.9Å, d=11μm
Visibility(β) ~ 30%

Incoherent background

$$\Delta y = \lambda L/d$$

How many coherent photons from a chaotic source?

How many photons are in the coherence volume?

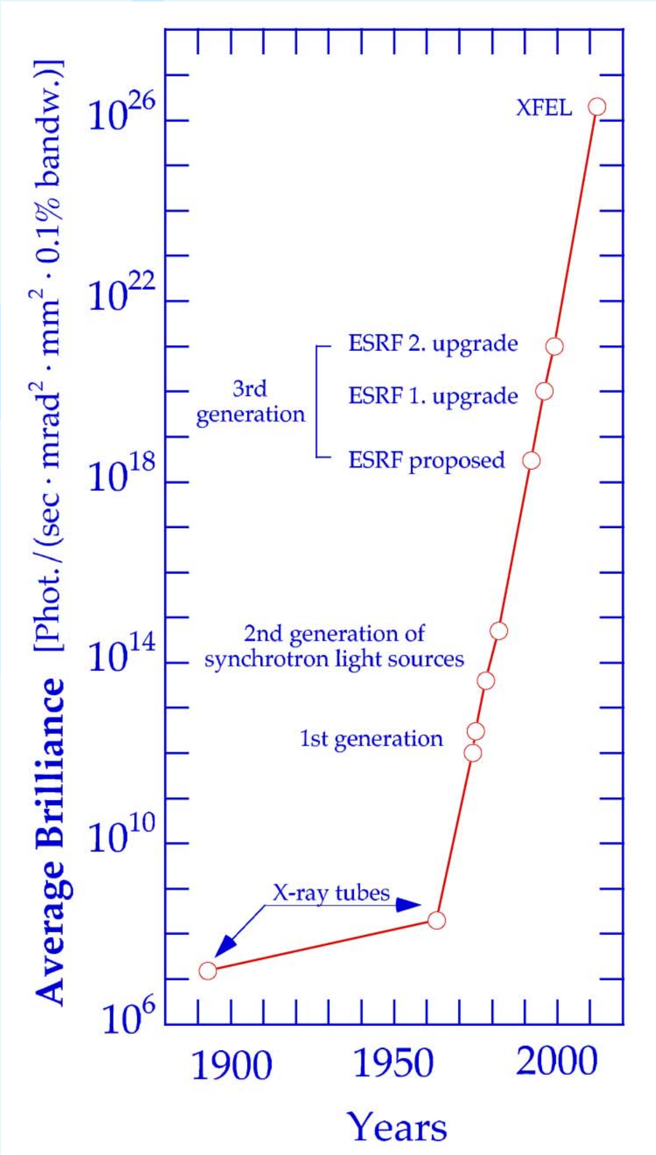
Coherent flux: $I_C = B\,\lambda^2 / 4$

B: Brilliance

$$B = \frac{\text{ph/s}}{\text{mrad}^2 \times \text{mm}^2} \text{ in a bandwidth of } 10^{-3} (\Delta\lambda/\lambda)$$

State of the art: $B > 10^{20}$
(beamlines at 3rd generation synchrotrons
e.g. ESRF, APS and SPring8). $I_c > 10^{10}$ ph/s

Evolution of state-of-the-art X-ray sources



Coherent flux: $I_C = B\,\lambda^2 / 4$

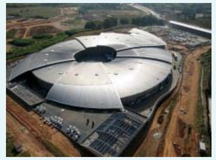
B: Brilliance

“Old” high energy 3rd generation sources:



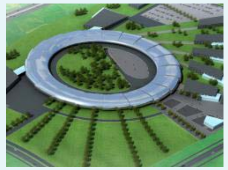
Other 3rd generation sources:



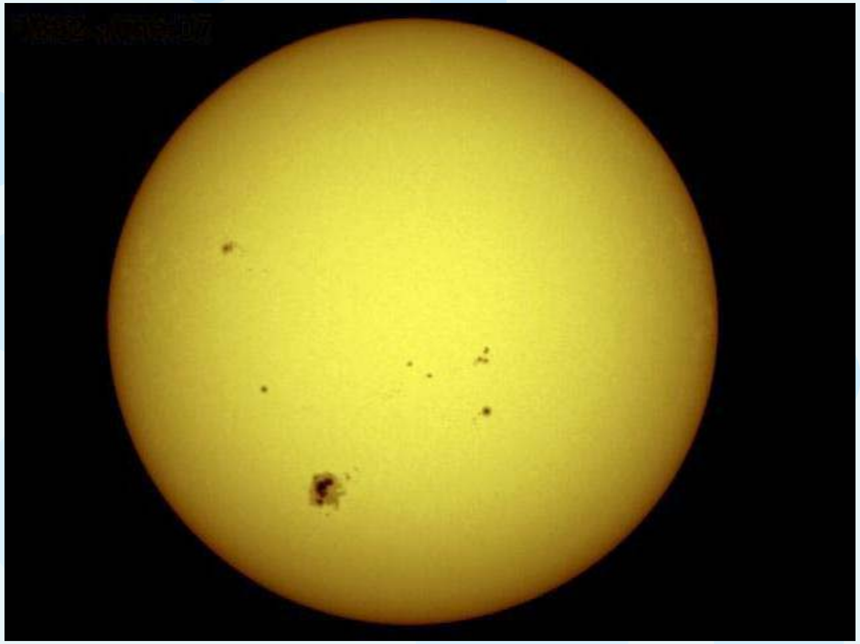
Diffraction limited sources:



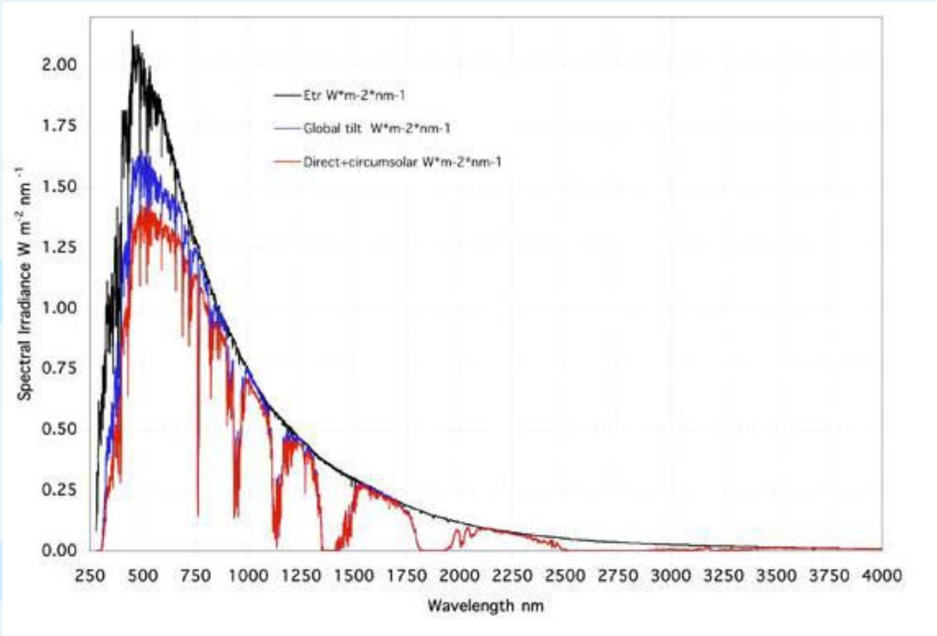


X-ray free electron lasers:

Comparison with a well known source



Sun's spectral irradiance at earth



Peak ~ 1 W/m^2 (@500nm, 0.1%bw)

i.e. 2.5×10^{18} $ph/s/m^2$ at earth.
$1 m^2$ in earth's distance (150Mkm) subtends 4.4×10^{-17} $mrad^2$
Sun's projected area ~ 1.5×10^{24} mm^2

B ~ 4×10^{10} $ph/s/mm^2/mrad^2$/0.1%bw @ 500nm

Coherent X-ray scattering

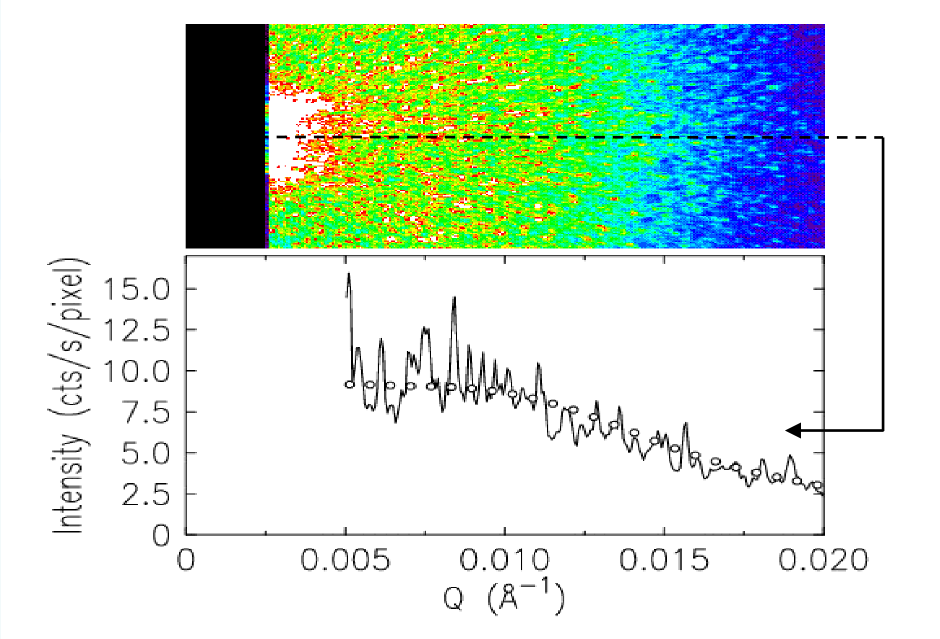
If (partially) coherent light is scattered from a disordered system it gives rise to a random (grainy) diffraction pattern, known as a **speckle pattern**. A speckle pattern is an interference pattern and related to the **exact spatial arrangement** of the scatterers in the disordered system.

$$I(Q,t) \propto S_c(Q,t) \propto \left| \sum e^{iQ \cdot R_j(t)} \right|^2$$

j in coherence volume $V_c = l_v\, l_h\, l_l$

Aerogel SAXS, λ=1Å
CCD (22 μm pixels)
beamsize d = 10 μm

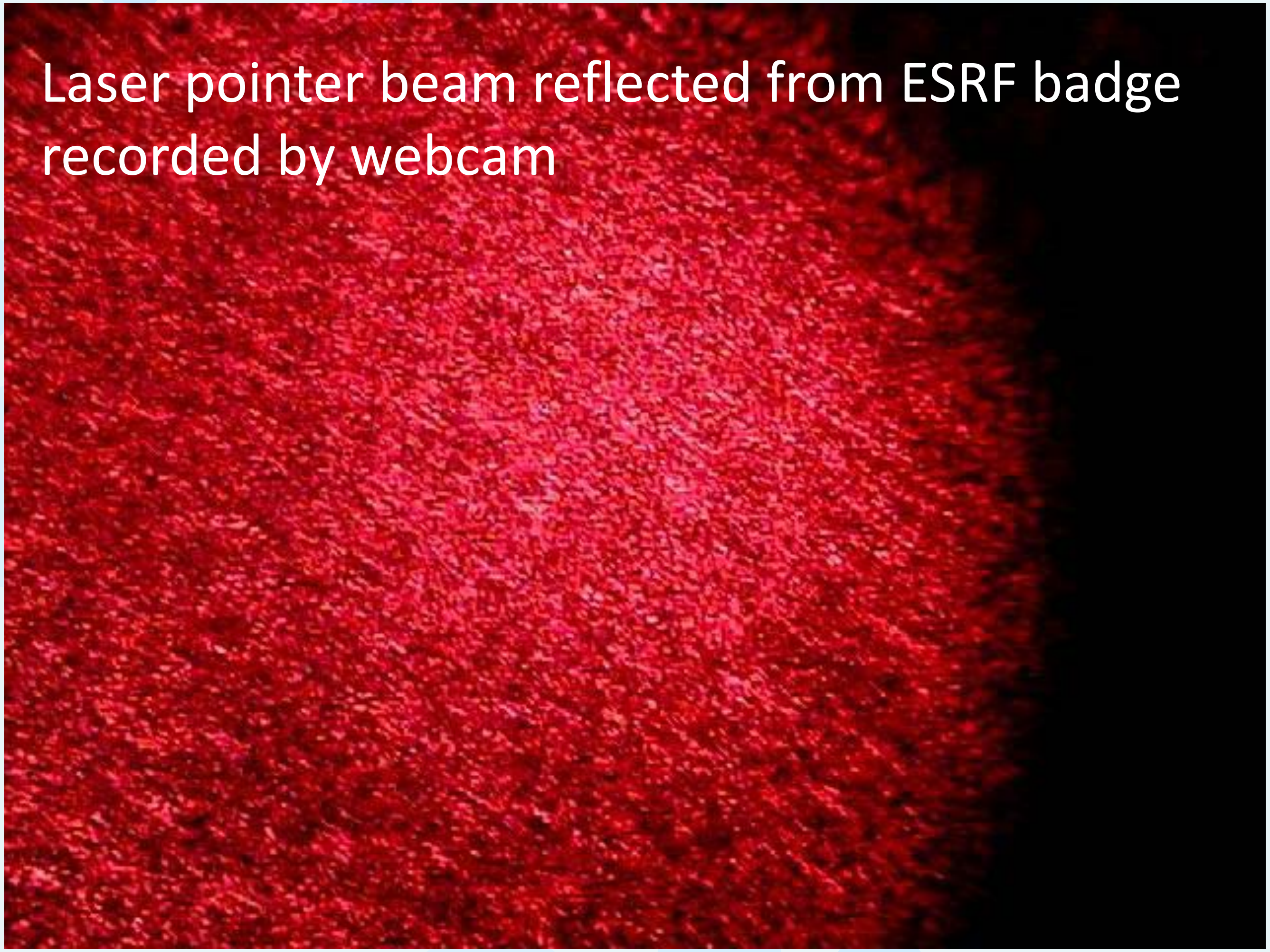
angular speckle size ~λ/d



Information beyond average properties

D. Abernathy *et al*, *J. Sync. Rad*. **5**, 37 (1998)

Speckle pattern



angular speckle size: λ/D

D: beam size

Speckle pattern

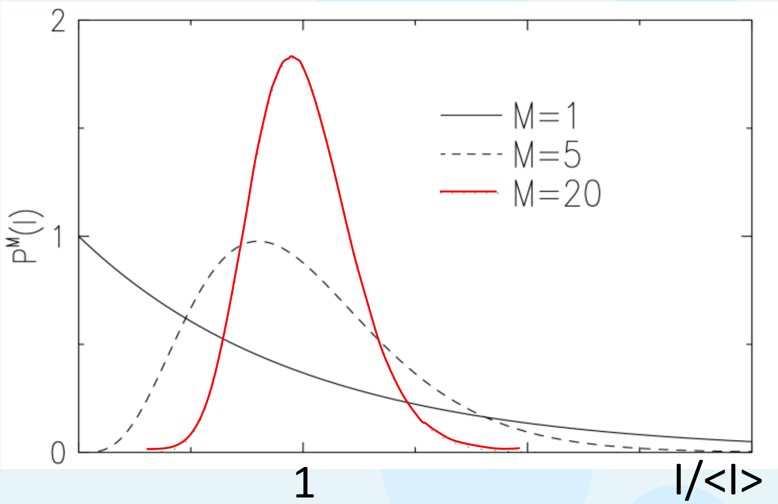
For a "perfectly" random sample, i.e. random scattering amplitudes and phase shifts, the statistical properties of the speckle pattern depends on the coherence properties of the incident beam

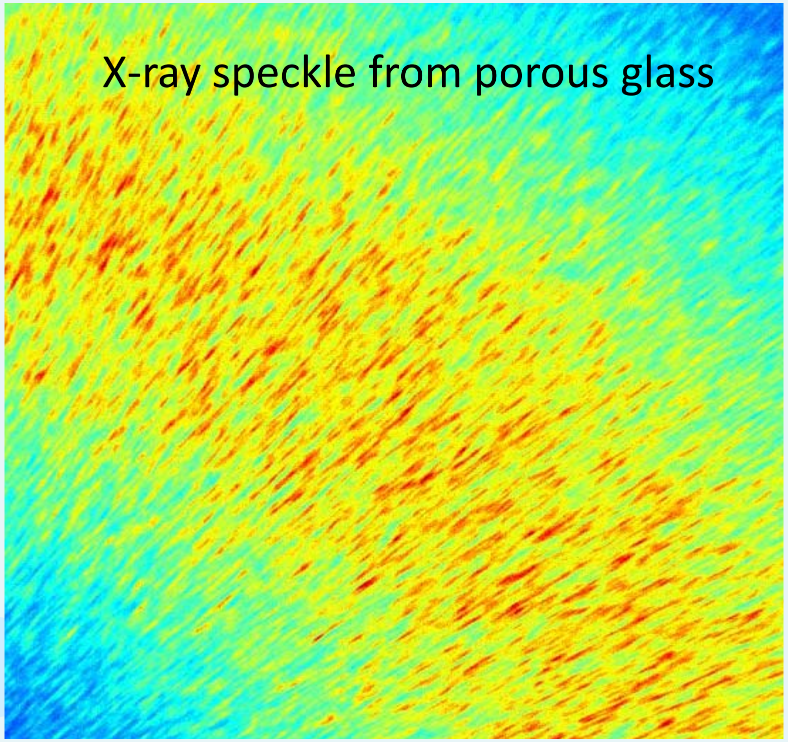
Gamma-Poisson distribution of intensity coming from M statistically independent superimposed speckle patterns

$P_M(I)=(M/<I>)^M I^{M-1} \exp(-MI/<I>)/\Gamma(M)$

$\sigma^2=<I>^2/M,\ 1/M=\beta$

Histogram of intensity

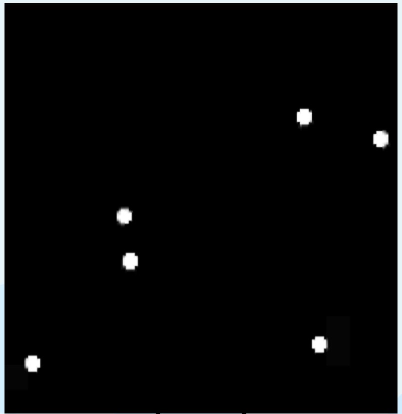


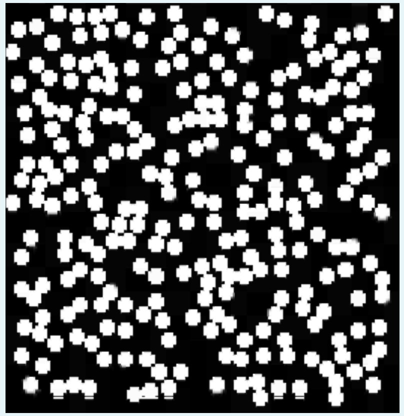


$M \approx V_{scat}/V_{coh}$

contrast (visibility) = 1/M

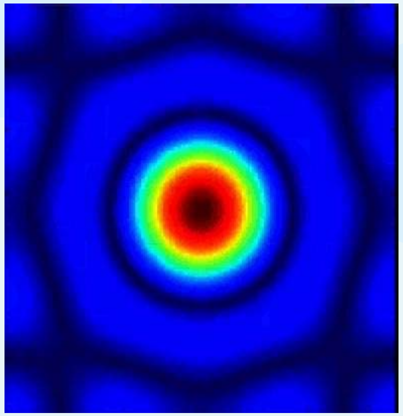
Speckle pattern

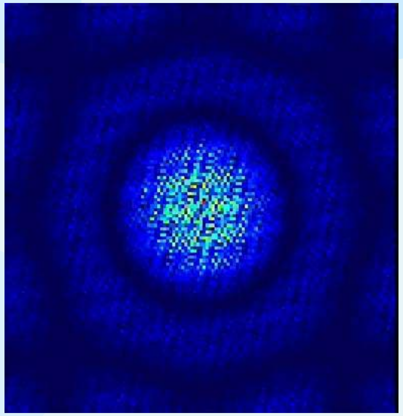


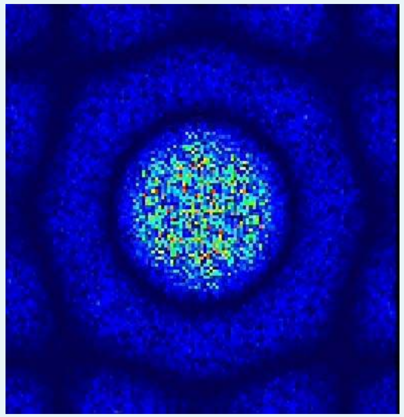


Non-coherent
(M=10000)

Coherent
(M=1)







<I(Q)>

I(Q,t)

I(Q,t)

Kinetics

Dynamics

Outline:

1/ X-ray coherence

Summary:

- Synchrotrons are chaotic sources based on spontaneous emission
- In this case transverse coherence is inv. prop. to the solid angle the source subtends
- Longitudinal coherence is obtained by use of a monochromator
- The source Brilliance determines how many coherent photons are available
- Scattering with coherent radiation leads to speckle patterns
- Speckle patterns depend on the sample and on the degree of coherence
- Speckle carry information beyond the average properties obtained by regular scattering

Outline:

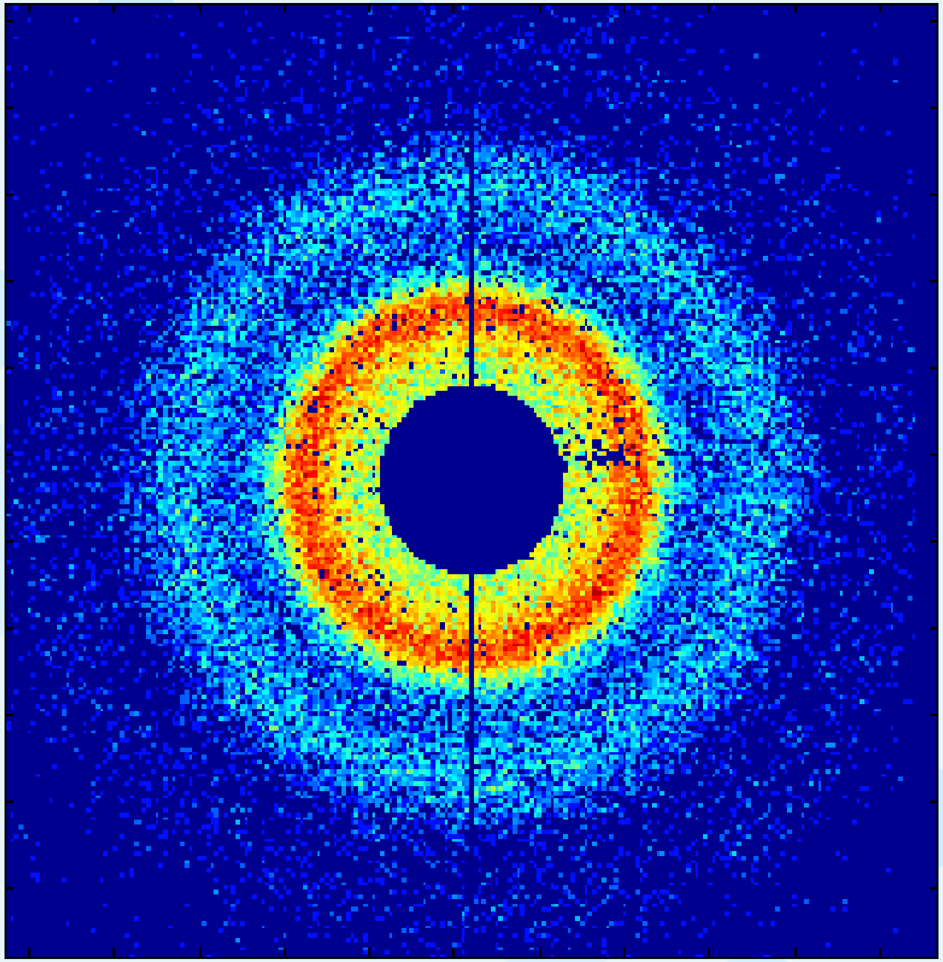
1/ X-ray coherence

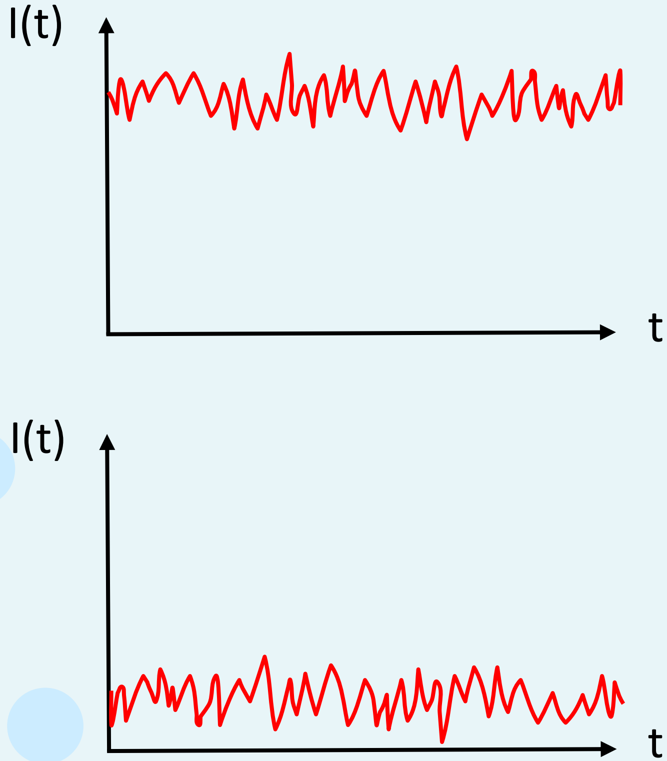
2/ X-ray Photon Correlation Spectroscopy (basics)

3/ The beamline

4/ Examples of research

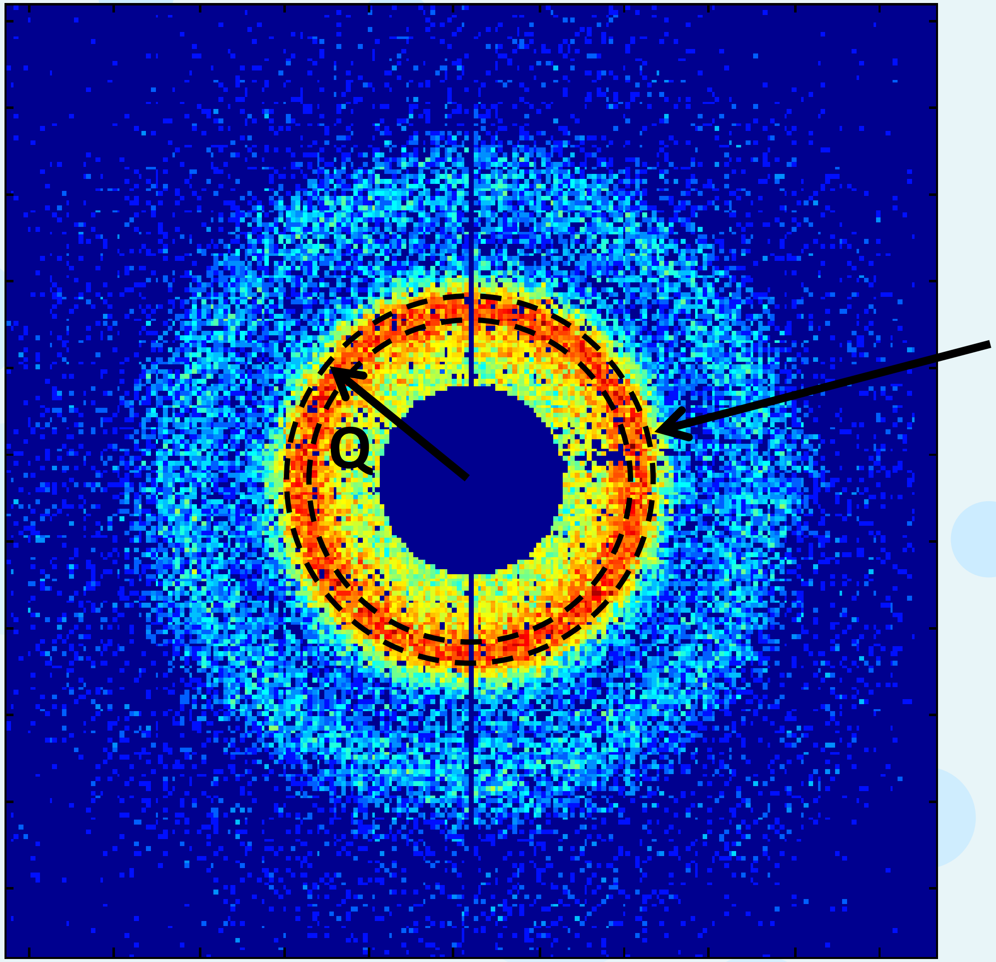
X-ray Photon Correlation Spectroscopy





Calculate the temporal
autocorrelation function
of the intensity in the pixels

X-ray Photon Correlation Spectroscopy



Average over time and possibly over ensemble (pixels)

$$g^{(2)}(t) = \frac{\langle I(\tau)I(\tau+t)\rangle}{\langle I\rangle^2}$$

$$= \frac{1}{M} \mid f(Q,t)/ f(Q,0) \mid^2 +1$$

Don't forget that if M is too big there's no signal!

X-ray Photon Correlation Spectroscopy

Temporal intensity auto-correlation function

$$g^{(2)}(\mathbf{Q},\tau) = \frac{\langle I(\mathbf{Q},t)I(\mathbf{Q},t+\tau)\rangle}{\langle I(\mathbf{Q})\rangle^2}$$

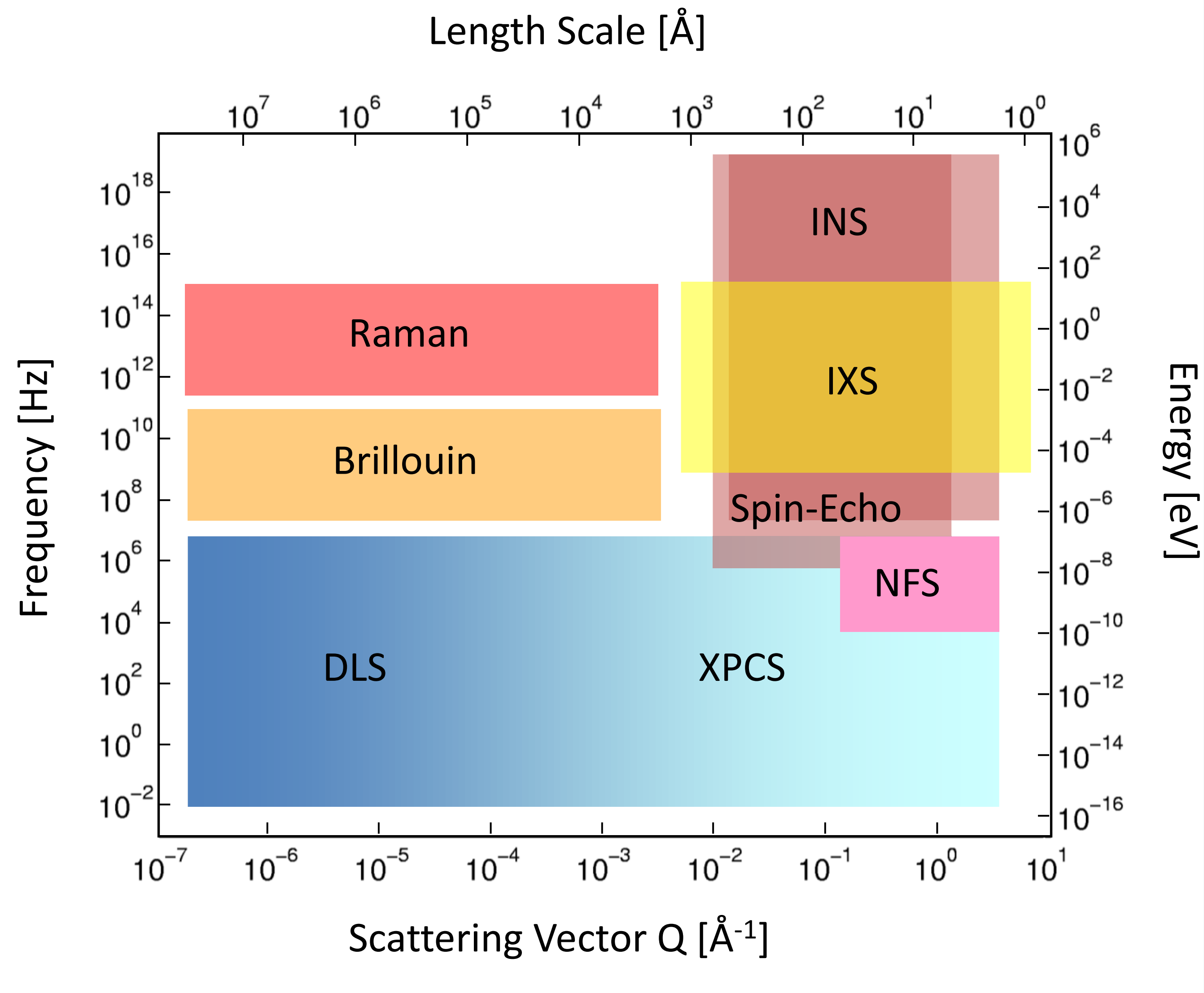
Siegert relation

$$M(g^{(2)}(\mathbf{Q},t)-1) = |f(\mathbf{Q},t)/f(\mathbf{Q},0)|^2 = (\mathrm{Re}\{\tilde{S}(\mathbf{Q},\omega)\})^2$$

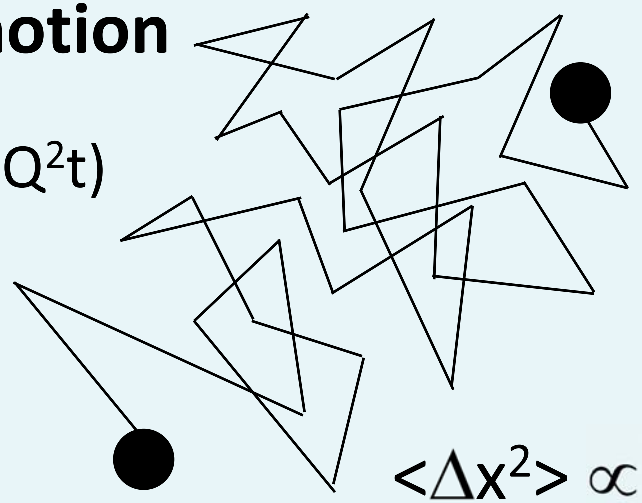
$$|f(\mathbf{Q},t)| \propto \int_V \int_V b_n(\mathbf{Q}) b_m(\mathbf{Q}) \exp(i\mathbf{Q}\cdot[\mathbf{r}_n(0)-\mathbf{r}_m(t)])$$

Intermediate scattering function: information about the density correlations in the sample and their time dependences

Comparison with other techniques



Example: Brownian motion



$$f(Q,t)=\exp(-D_0Q^2t)$$

$$g^{(2)}(Q,t)=\beta\exp(-2t/t_0)+1$$

$$t_0=1/(D_0Q^2)$$

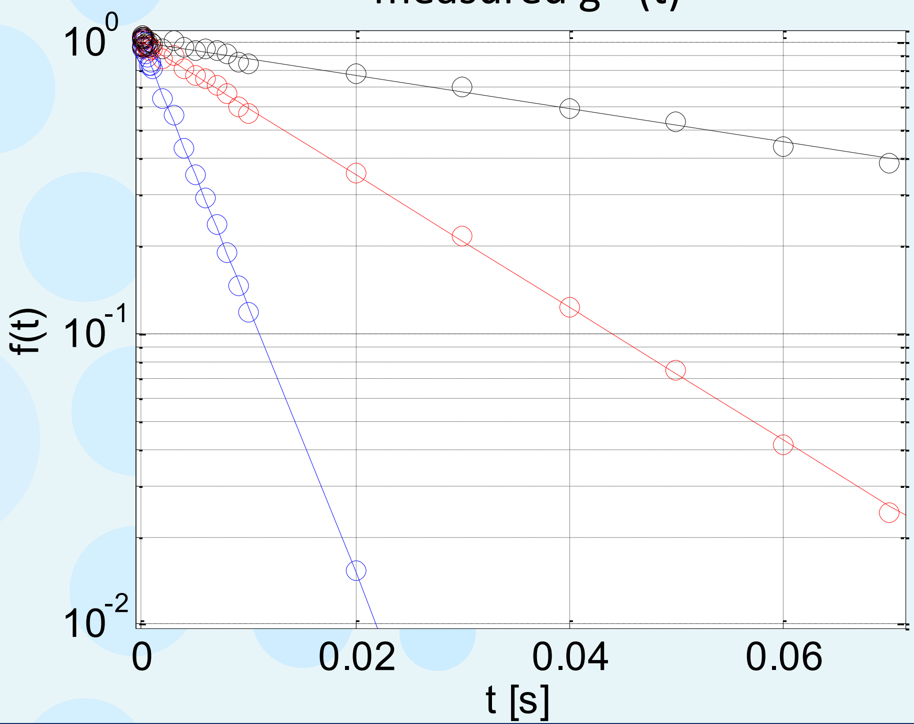
$$\beta=1/M$$

$<\Delta x^2> \propto t$

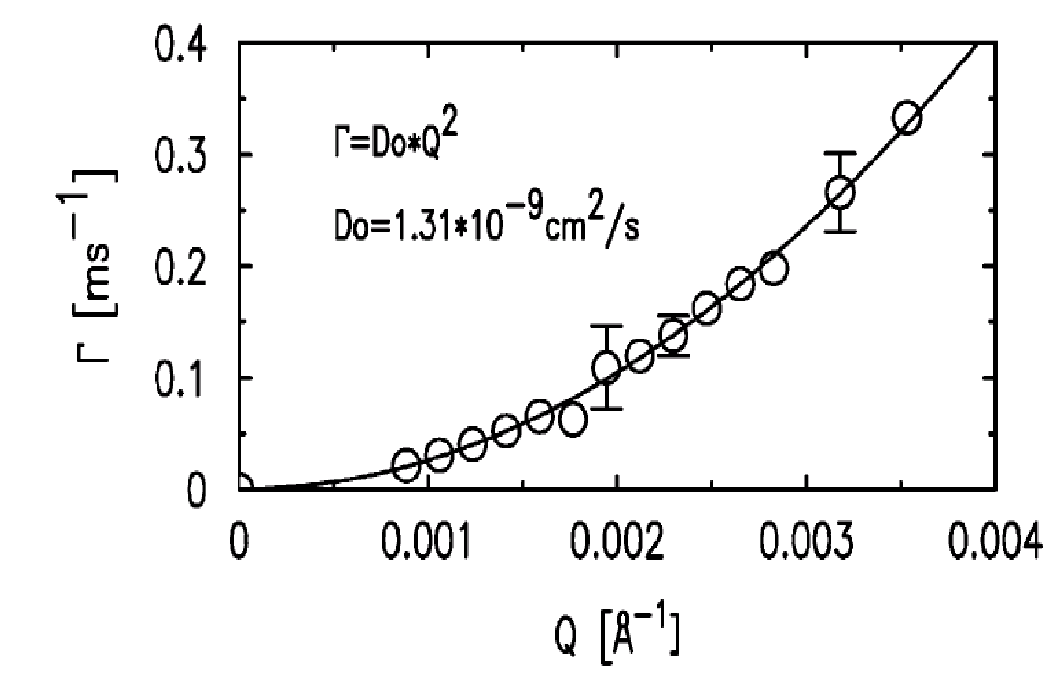
Example: dilute suspension of silica spheres in H_2O:

$Q=1e\text{-}3$ Å^{-1}	$t_0=76.3$ ms
$Q=2e\text{-}3$ Å^{-1}	$t_0=19.1$ms
$Q=4e\text{-}3$ Å^{-1}	$t_0=4.8$ ms

$$1/t_0 \propto Q^2$$



Example: Brownian motion



Stokes-Einstein free diffusion coefficient

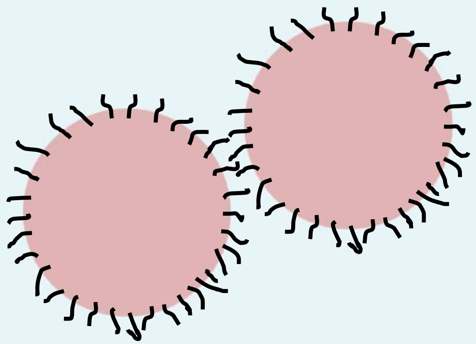
$$D_0 = \frac{k_B T}{6\pi\eta R}$$

geometrical factor

viscosity

particle radius (hydrodynamic)

Hydrodynamic radius > particle radius (SAXS)



Fight van der Walls attraction (agglomeration) by steric- or charge stabilization

X-ray Photon Correlation Spectroscopy

more complex analysis (real science…)

Aim: To quantify non-stationary dynamics (out-of-equilibrium) and non-Gaussian fluctuations

Non-stationary dynamics:

The time averaging in $g^{(2)}(t)=\langle I(\tau)I(\tau+t)\rangle/\langle I\rangle^2$ becomes a problem

Solution: Don't time average…………

Non-Gaussian fluctuations:

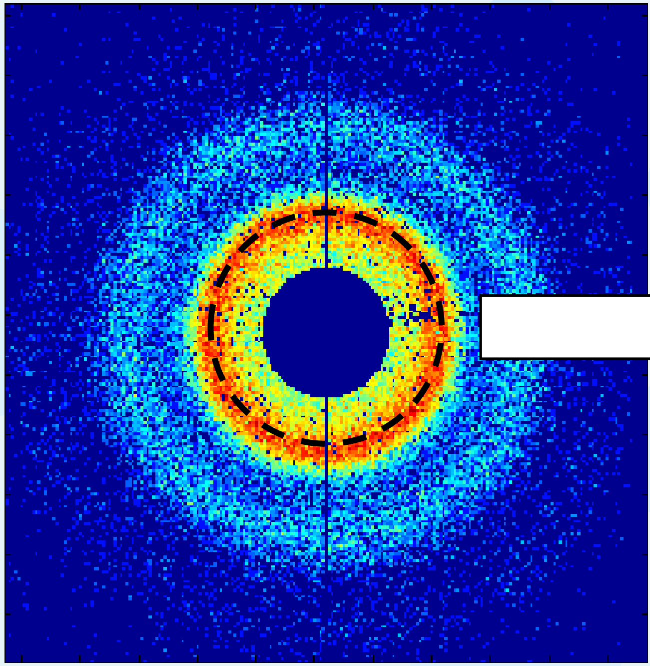
The Siegert relation is not valid and f(t) is not readily obtained from $g^{(2)}$

Solution: Heterodyne detection or higher-order correlations…..

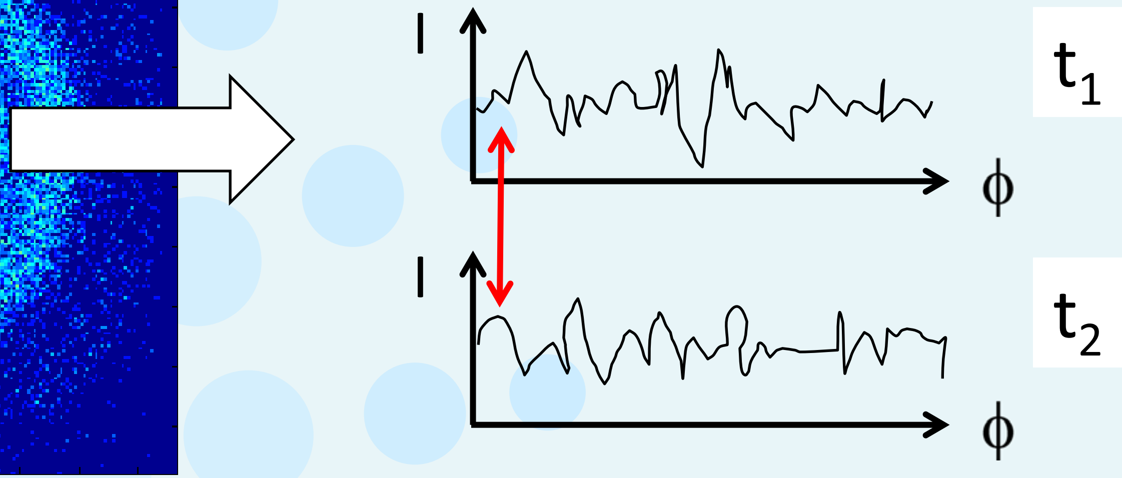
Non-stationary dynamics by XPCS

The time averaging in $g^{(2)}(t)=\langle I(\tau)I(\tau+t)\rangle/\langle I\rangle^2$ becomes a problem

Solution: Don't time average............



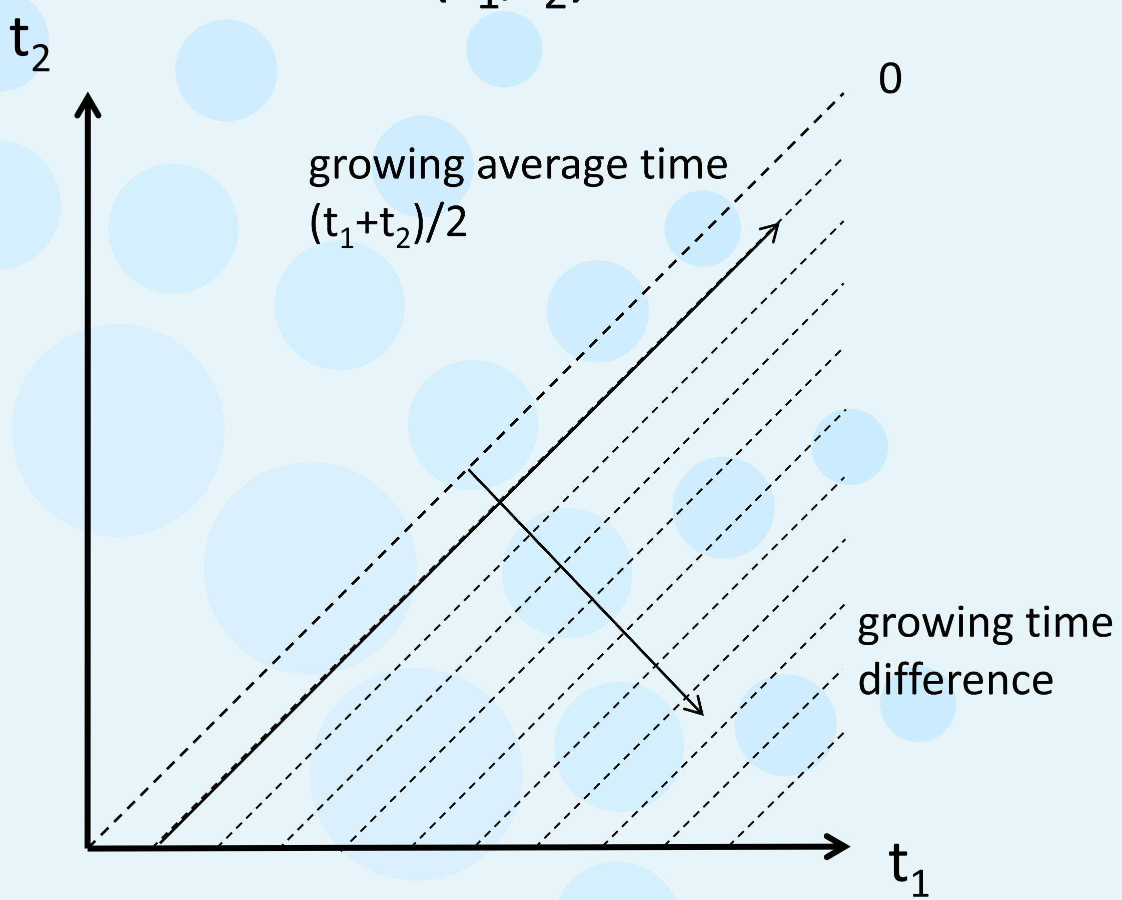
$$G(t_1,t_2)=\langle I(t_1)I(t_2)\rangle/\langle I(t_1)\rangle\langle I(t_2)\rangle$$



This can only be performed by use of a 2D detector

Non-stationary dynamics by XPCS

$G(t_1,t_2)$



time difference:

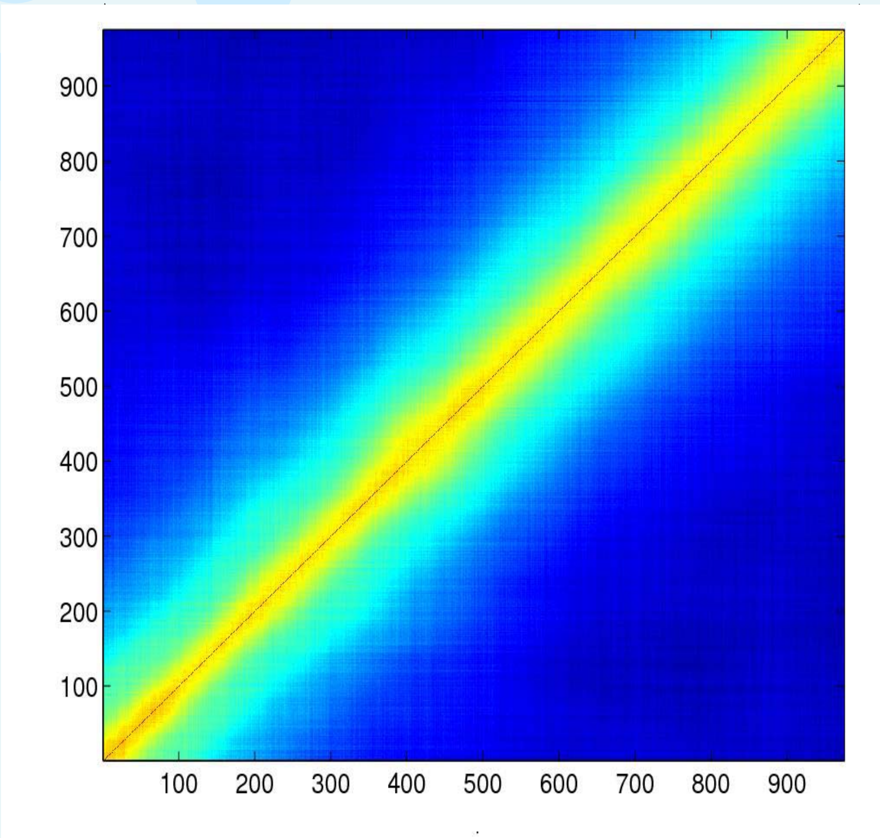
$t=t_1-t_2$

age:

$(t_1+t_2)/2$

Non-stationary dynamics by XPCS

$G(t_1,t_2)$



t_2 (vertical axis), t_1 (horizontal axis)

time difference:

$t=t_1-t_2$

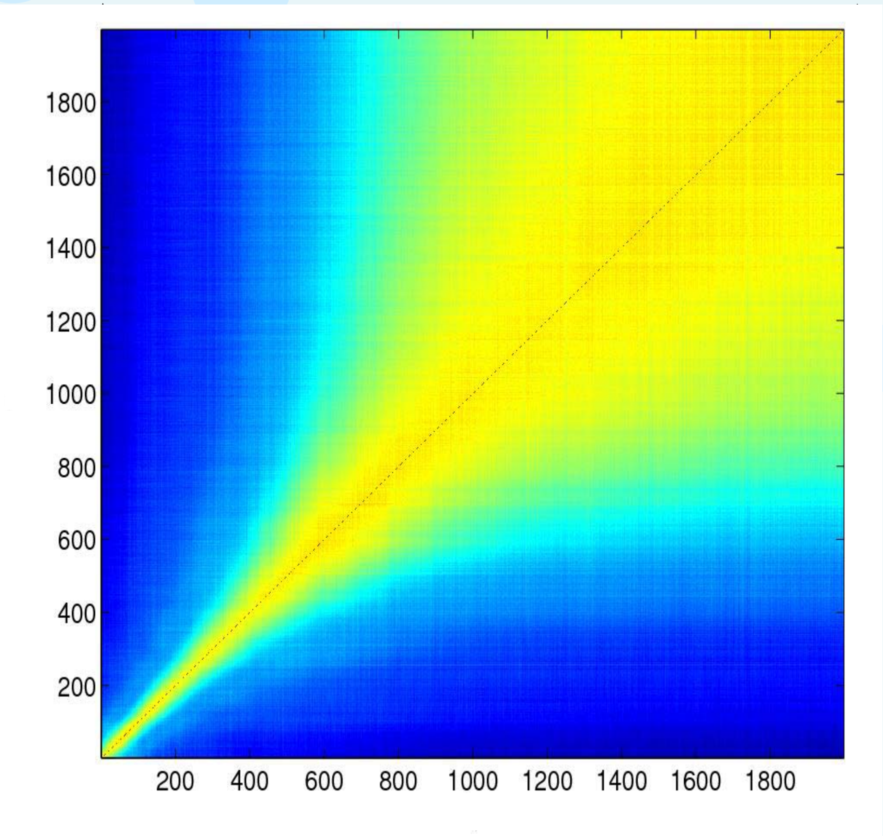
age:

$(t_1+t_2)/2$

Non-stationary dynamics by XPCS

$G(t_1,t_2)$

t_2



t_1

time difference:

$t=t_1-t_2$

age:

$(t_1+t_2)/2$

Slowing down of dynamics
"aging"

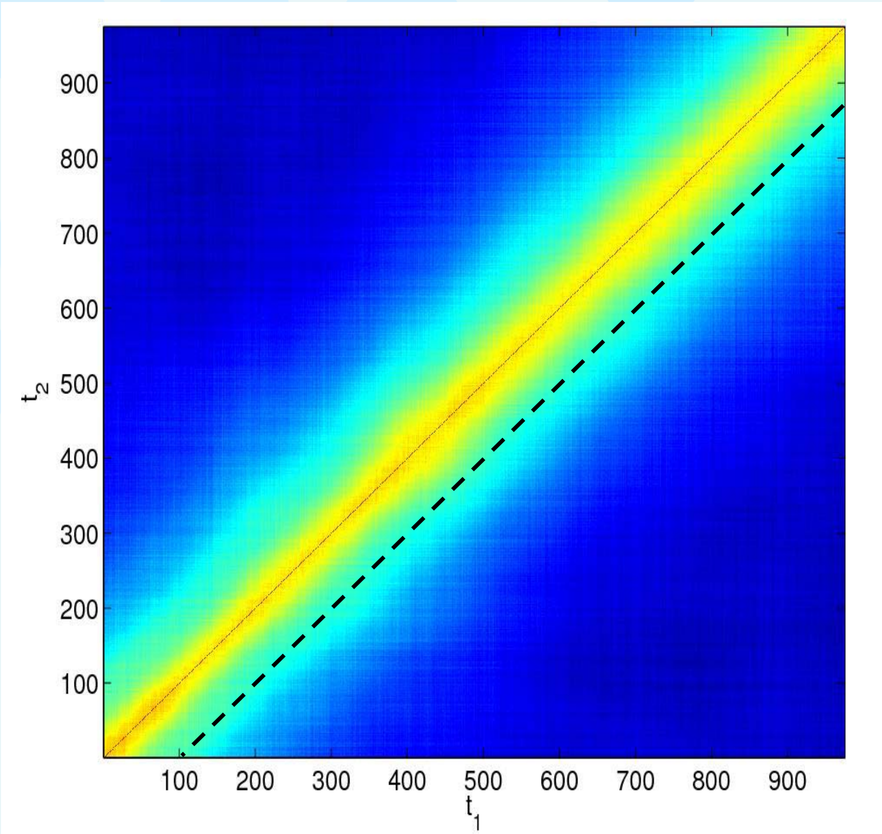
age 0? - rejuvenation?
arrested state? - Q dependence?

Non-gaussian fluctuations by XPCS

Non-Gaussian fluctuations:

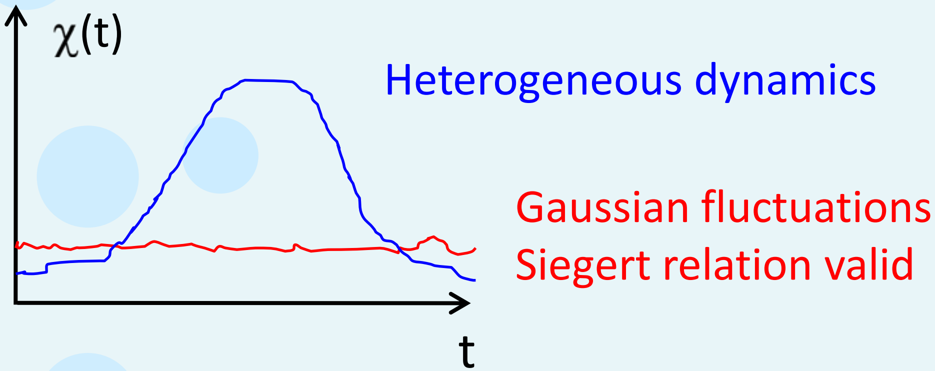
The Siegert relation is not valid and f(t) is not readily obtained from $g^{(2)}$

Solution: Heterodyne detection or higher-order correlations…..



$\Leftarrow$ $G(t_1,t_2)_{t=const}$

$Var(G)=<G^2>-<G>^2$ dynamical susceptibility $\chi(t)$



Outline:

2/ X-ray Photon Correlation Spectroscopy (basics)

Summary:

- XPCS is the X-ray counterpart to DLS – Dynamic Light Scattering
- It provides unique possibilities for investigating slow (ns-hrs) dynamics
- XPCS gives access to the intermediate scattering function f(Q,t)
- time-resolved XPCS can provide information about non-equilibrium dynamics
- A variance analysis of $G(t_1,t_2)$ can demonstrate non-Gaussian fluctuations

Outline:

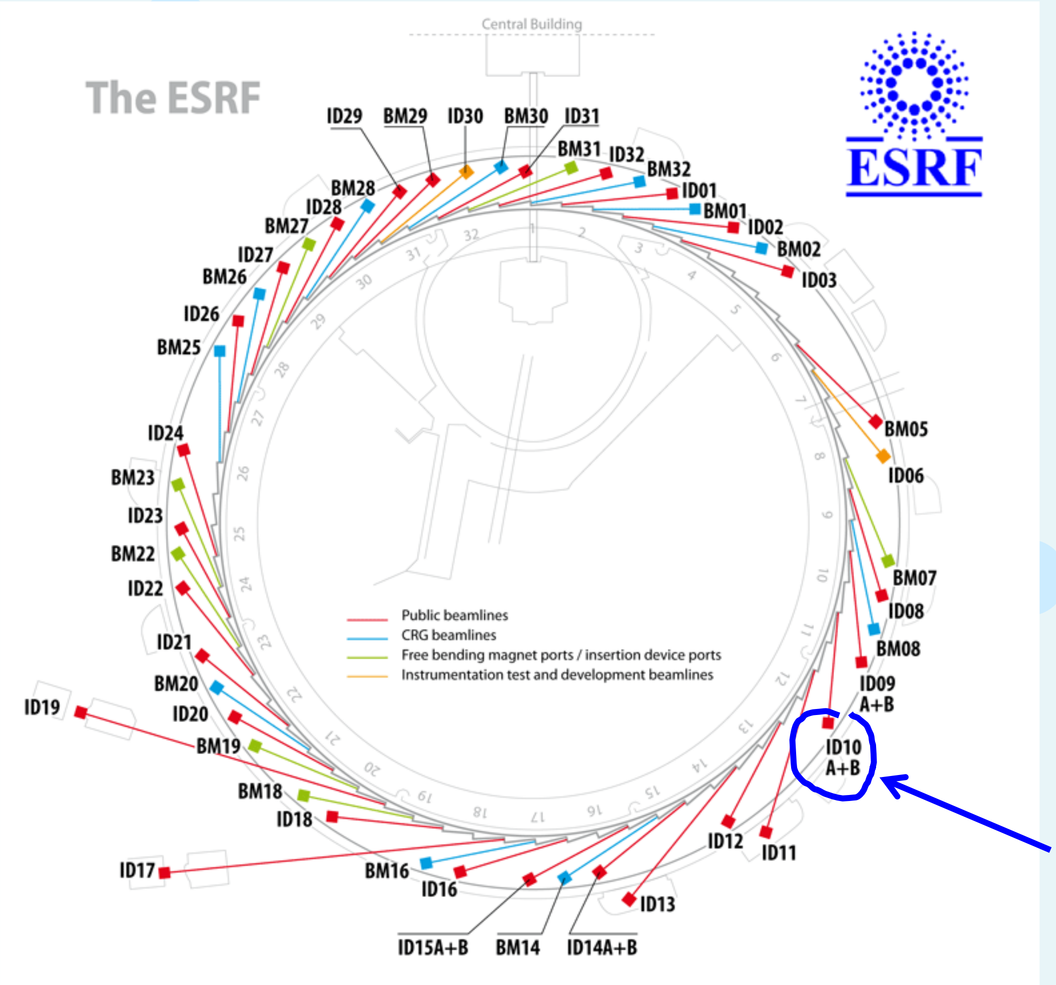
1/ X-ray coherence

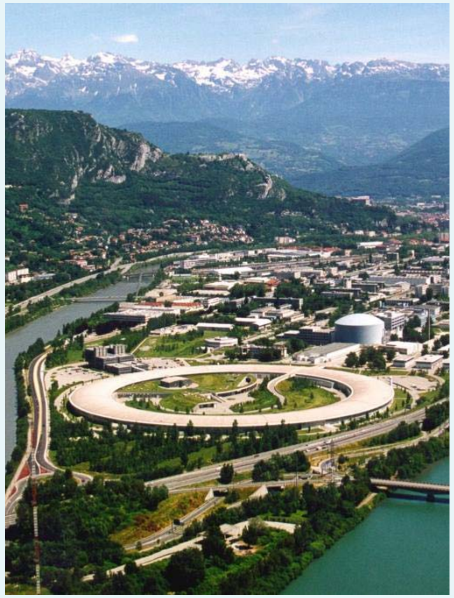
2/ X-ray Photon Correlation Spectroscopy (basics)

3/ The beamline

4/ Examples of research

European Synchrotron Radiation Facility





ESRF, Grenoble, France

> 50 experimental stations

TROÏKA

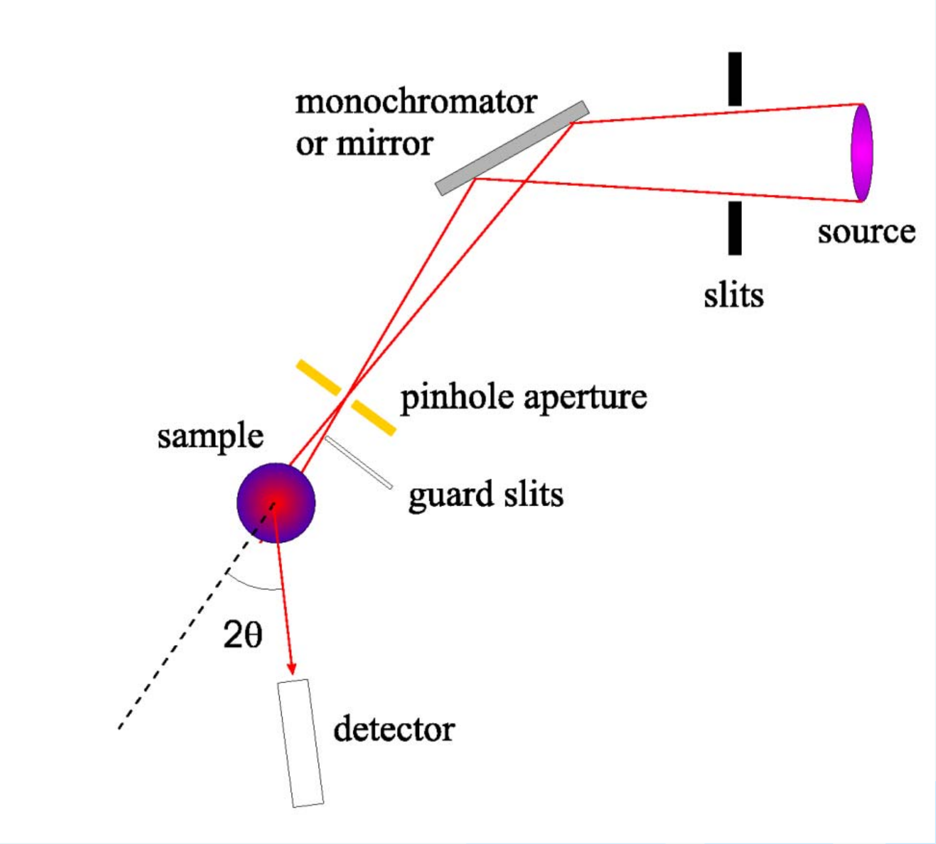
3 experimental stations

Troika I: XPCS and WAXS

Troika II: GID, XR, GISAXS

Troika III: CXDI, C-SAXS, XPCS

The beamline setup



Keywords: collimation and monochromatization

M ≈ 10000 in the raw synchrotron beam → no coherence (no XPCS)

Collimate the beam and select a narrow bandwidth in λ to the match the scattering volume to the coherence volume, i.e. M ≈ 1

$$l_t = \lambda L/d$$

$$l_l = \lambda/(\Delta\lambda/\lambda)$$

Point detectors:

- Fast (ns) Avalanche Photo Diode detector
- Scintillation counter
- Solid state detector

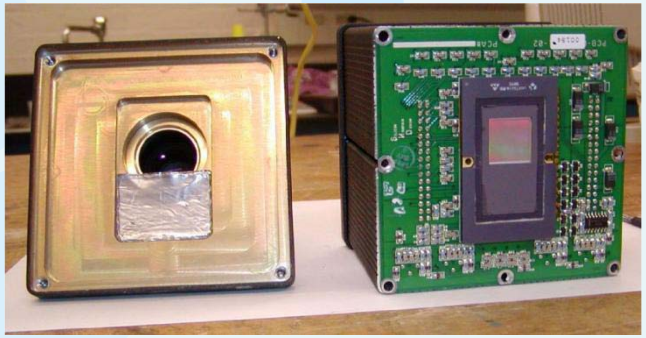
Area detectors for multi-speckle XPCS

Advantages:
- Ageing and non-Gaussian fluctuations accessible
- More efficient data-taking (10^6 pixels) with 2d detector
- Beam induced sample damage minimized

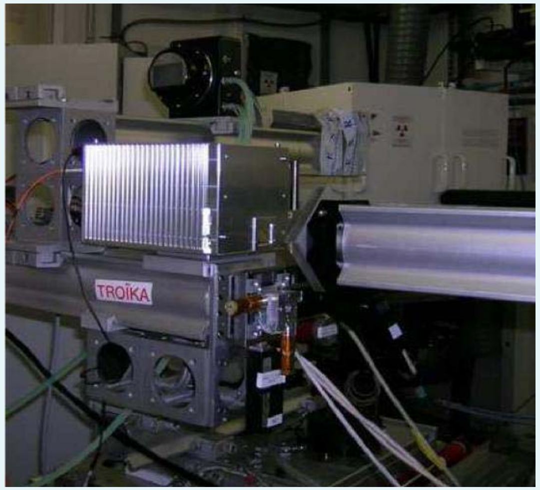
Drawbacks:
2d detectors are slow, can be noisy, have limited dynamic range, are not always photon counting, have limited resolution, radiation hardness can be a problem……..

Princeton Instruments

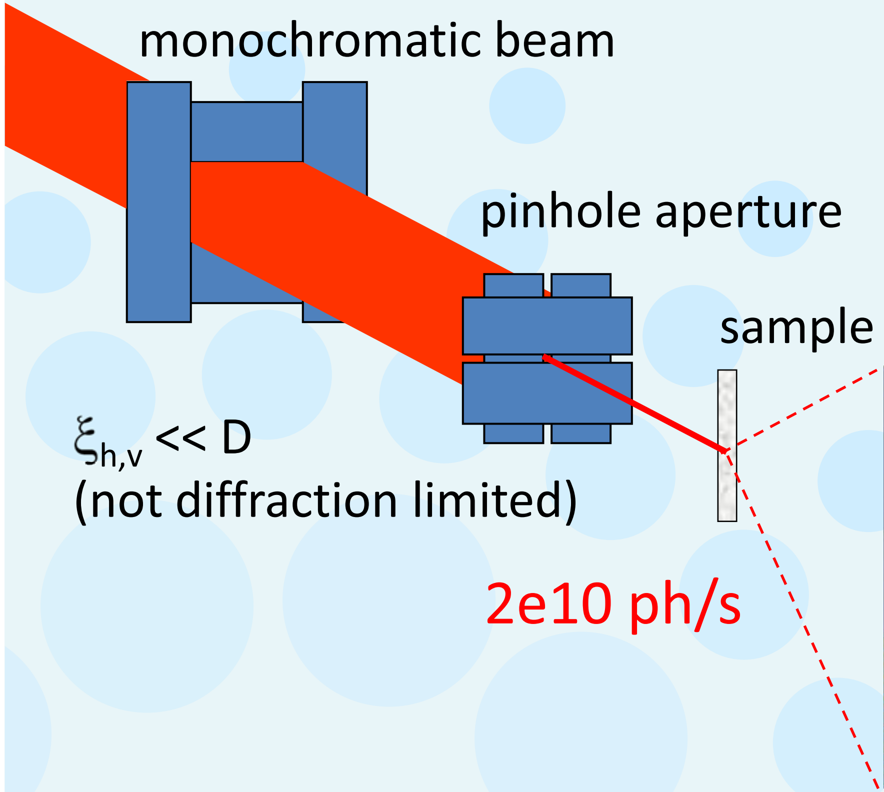
Dalsa



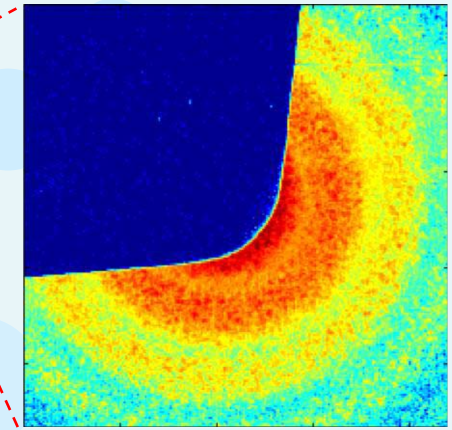
MAXIPIX (1kHz)



Why detectors are so important for XPCS



Coherent illumination of disorder leads to speckles



Static sample

CCD image
140s exp
speckle size λ/ξ
(~10 μrad)

Far field (Fraunhofer regime):
Scattered intensity in every pixel of the CCD is

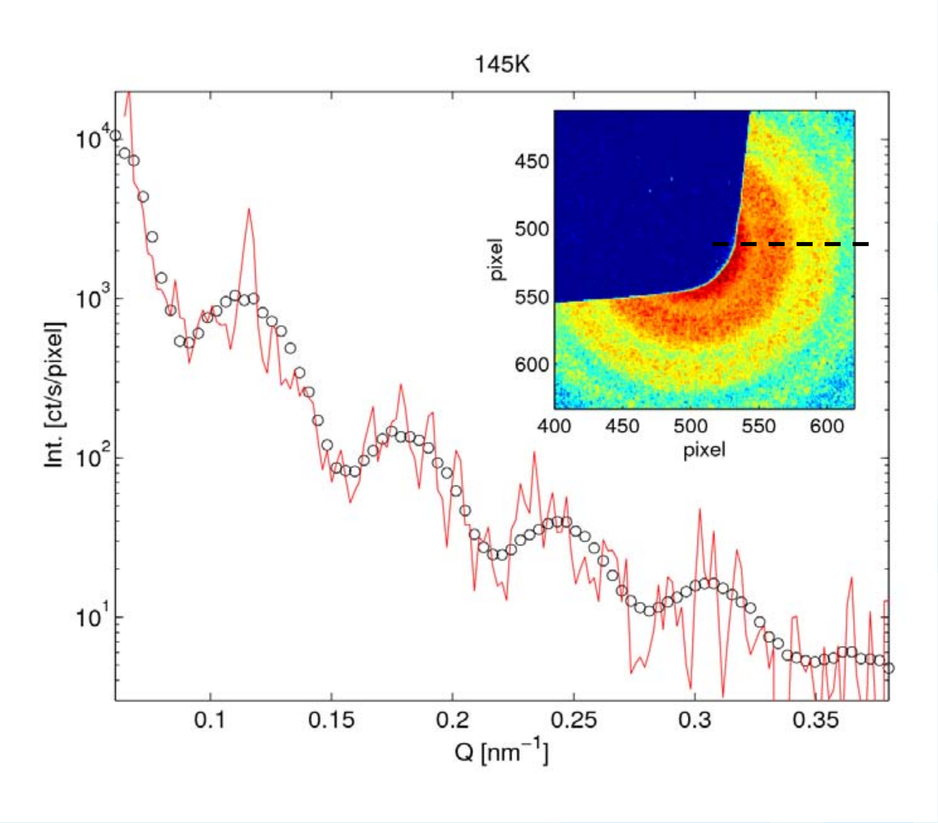
$$E(\mathbf{Q}) \sim \int \rho(\mathbf{R}) \exp[i\mathbf{Q}\cdot\mathbf{R}]\, d\mathbf{R}$$

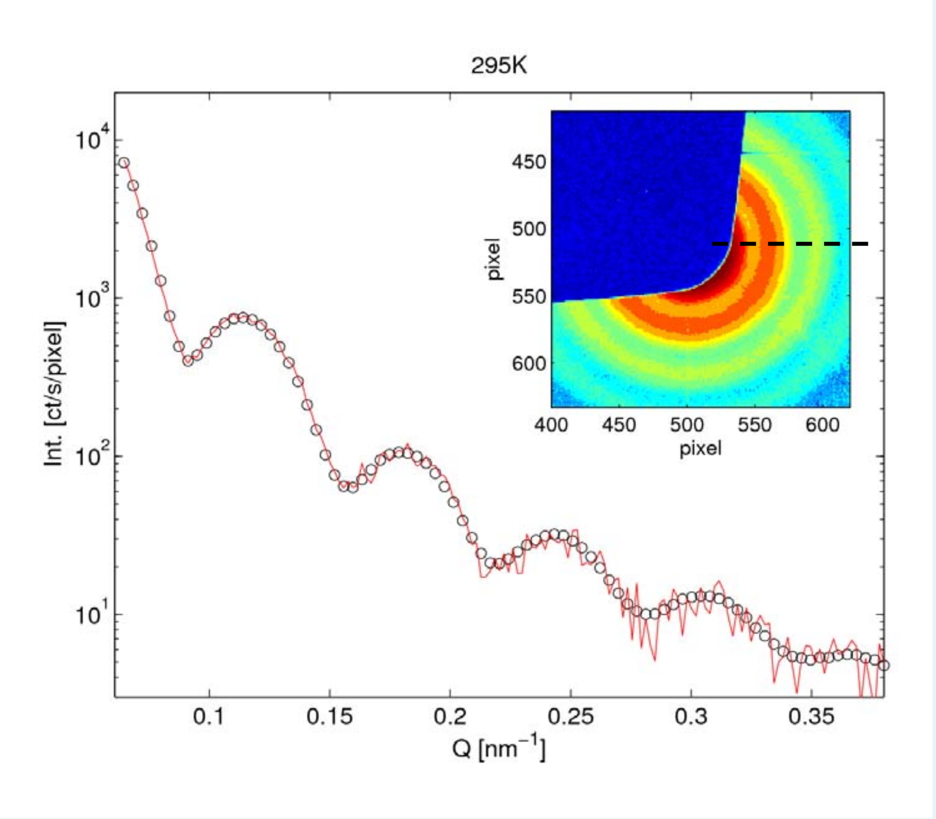
$$I(\mathbf{Q}) = E(\mathbf{Q})E^{*}(\mathbf{Q}) = |E(\mathbf{Q})|^2$$

Speckles visible because illuminated volume ~ coherence volume

Why detectors are so important for XPCS

Averaging kills the speckles





by azimuthal averaging
the speckles disappear
(back to average quantities)

if the particles move fast
the speckles also disappear
(back to average quantities)

Outline:

3/ The beamline

Summary:

- Essential to ensure coherent illumination
- Collimation and monochromatization throws a factor of 10^4 away!
- Thanks to the huge Brilliance there's still 10^{10} ph/s left for the experiments
- Detectors (speed, resolution, sensitivity) are of extreme importance

Outline:

1/ X-ray coherence

2/ X-ray Photon Correlation Spectroscopy (basics)

3/ The beamline

4/ Examples of research

Examples of XPCS research

Physical chemistry, soft matter, hard condensed matter physics, surface science

1/ Dynamics of nano-particles in a glass forming solvent

2/ Ageing of a transient depletion gel

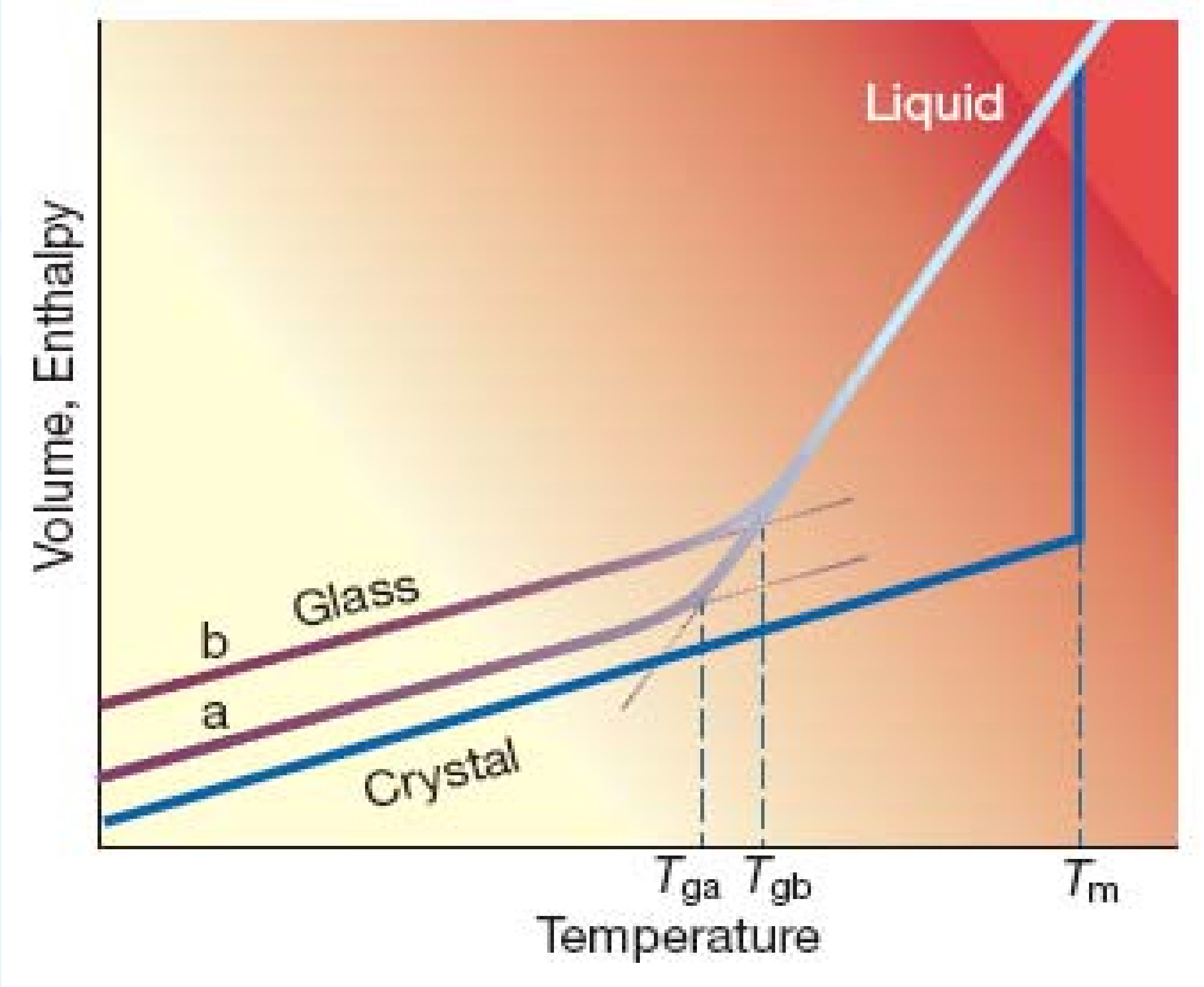
3/ Heterogeneous dynamics in ………….

4/ Liquid surface dynamics by grazing incidence XPCS

5/ Atomic diffusion in an alloy

Dynamics of nanoparticles in a glass forming solvent

The supercooled liquid-to-glass transition



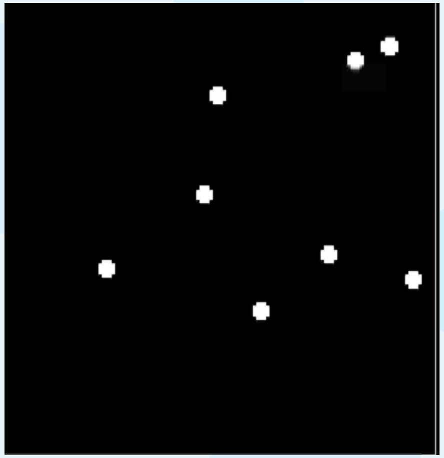
Pablo G. Debenedetti and Frank H. Stillinger, Nature (2001)

Dynamics of nanoparticles in a glass forming solvent

Simple diffusion and hyper-diffusion

Ballistic motion: $x = v \cdot t$ → $\langle[x(t)-x(0)]^2\rangle = \Delta x^2 = v^2t^2$ → $Q \propto 1/x \propto 1/t = \Gamma$

Brownian (random walker) motion: $\langle[\mathbf{r}(t)-\mathbf{r}(0)]^2\rangle = 6D_0t$ → $Q^2 \propto \Gamma$



D_0 : self-diffusion constant

$D_0=k_BT/6\pi\eta R$ (Einstein, 1905)

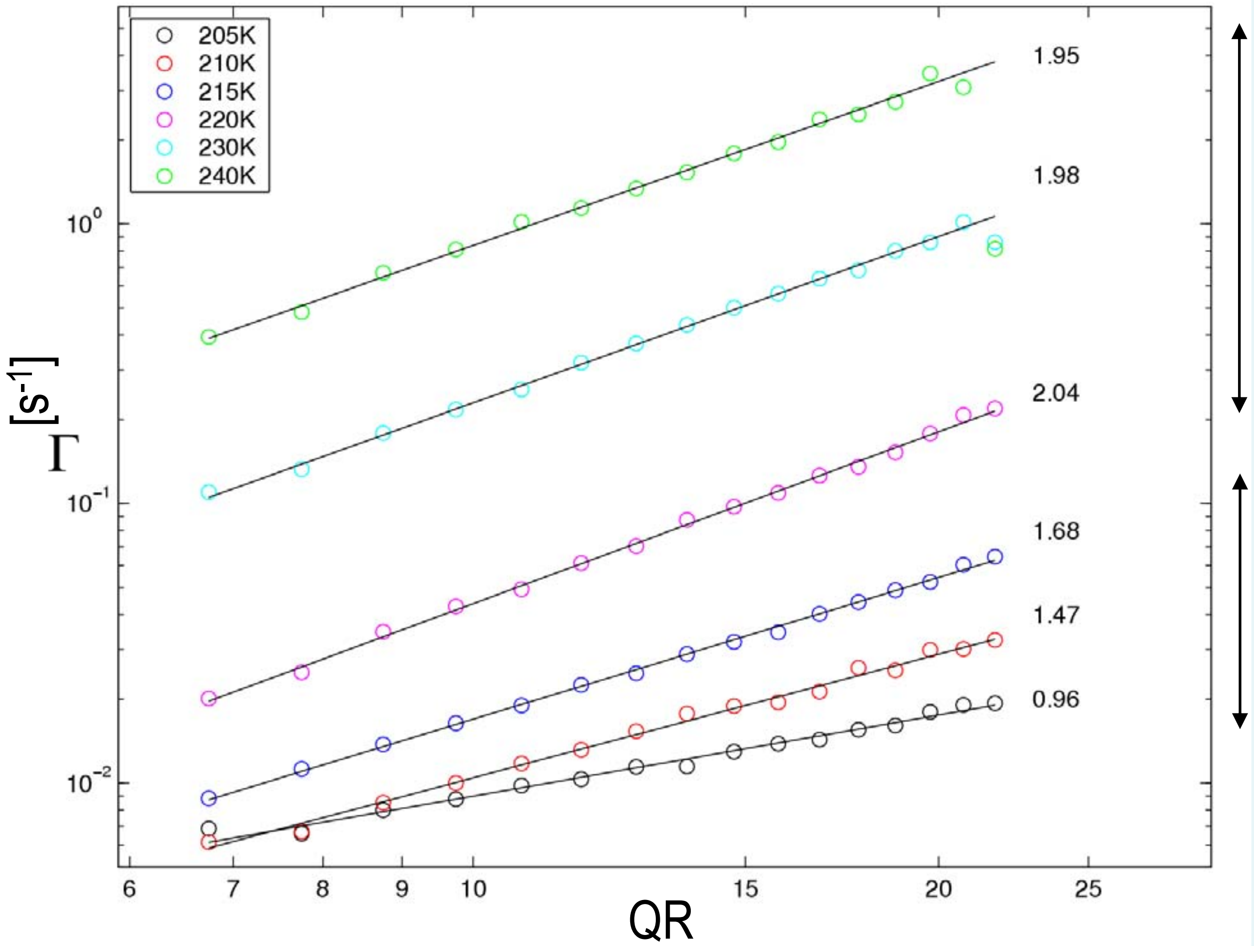
$$\boxed{g^{(2)} \sim 1 + \exp(-2\Gamma t)}$$

$\Gamma = D_0Q^2$ for Brownian motion

Dynamics of nanoparticles in a glass forming solvent

Silica nano-particles (R=250nm, 1% vol.)
in supercooled propanediol

Tg~170K



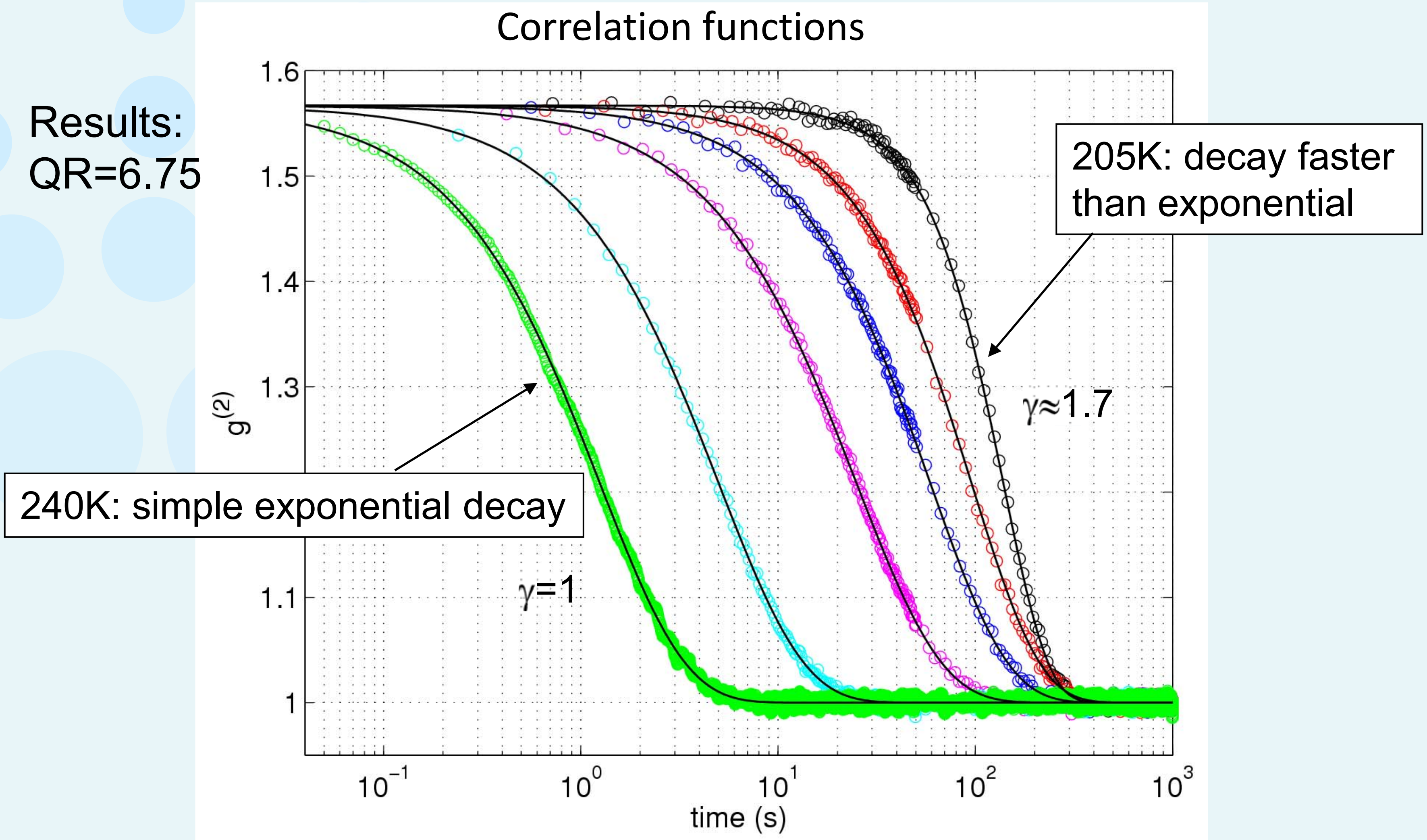
n=2
(Brownian motion)

n→1
(Hyper diffusion?)

Phys. Rev. Lett. **100**, 055702 (2008)

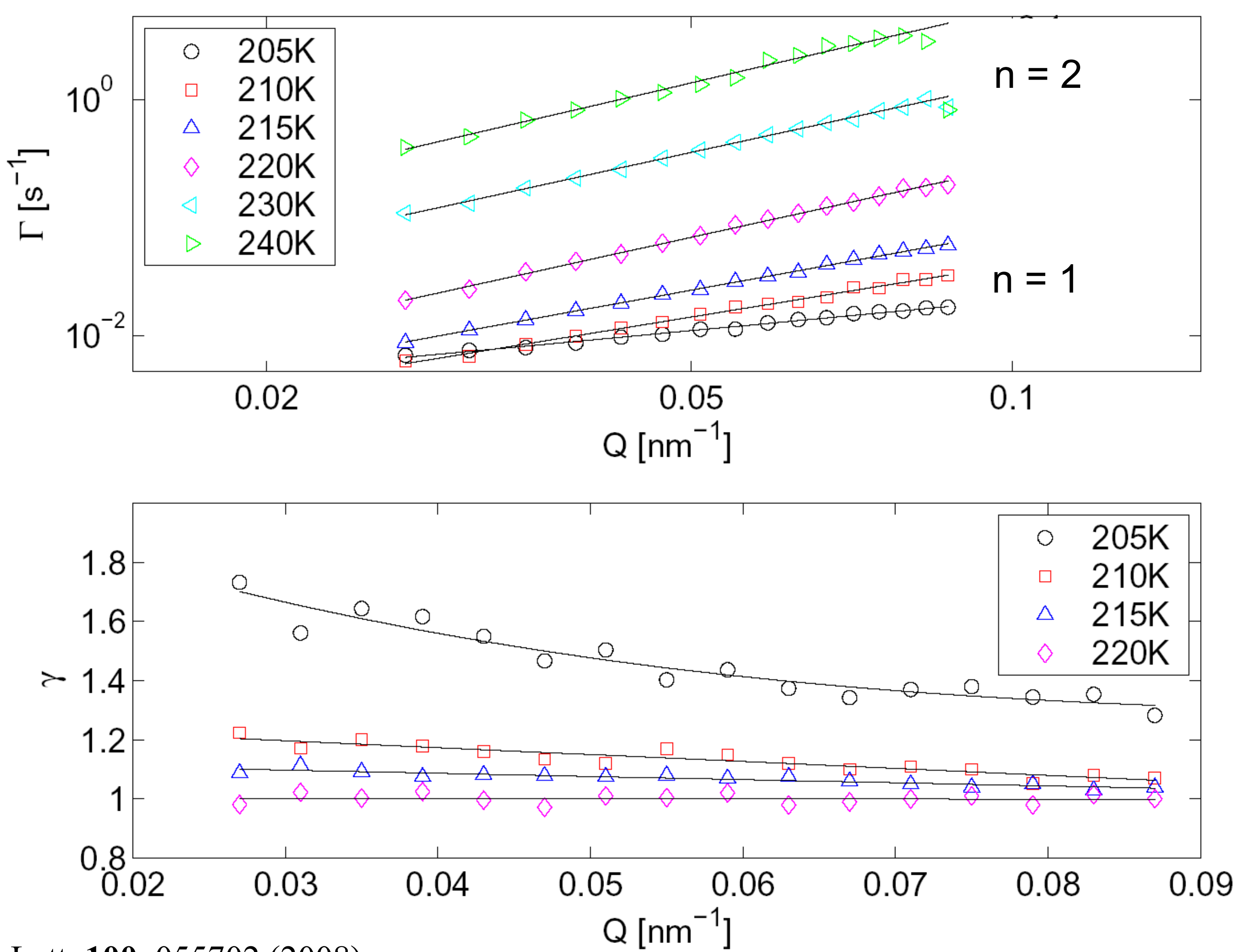
Dynamics of nanoparticles in a glass forming solvent

Results:
QR=6.75



Fits with empirical model (KWW): $g^{(2)} = 1+\exp(-2(\Gamma t)^{\gamma})$

Dynamics of nanoparticles in a glass forming solvent

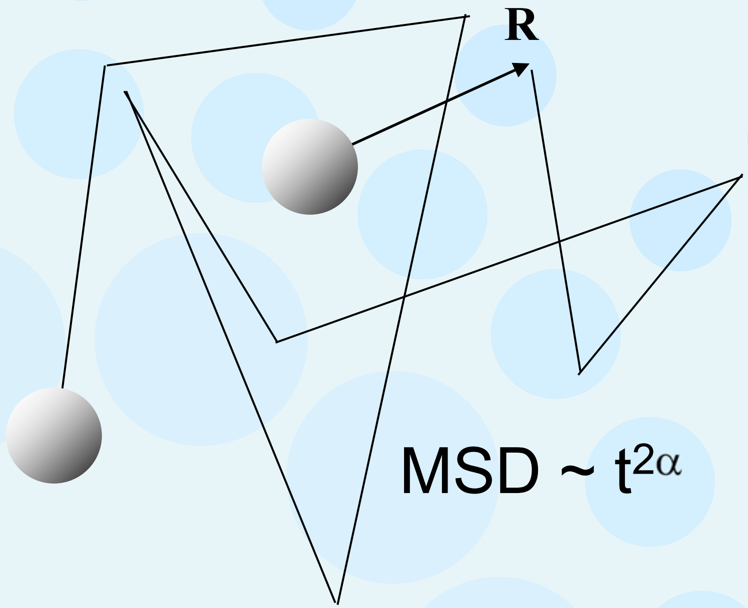


Phys. Rev. Lett. **100**, 055702 (2008)

Dynamics of nanoparticles in a glass forming solvent

Model for particle dynamics

Continuous time random walk model



MSD ~ $t^{2\alpha}$

$$g^{(2)}(Q,t) = \left| \sum_{N=0}^{\infty} P_t(N) h(Q,N) \right|^2 + 1$$

$$P_t(N) = \frac{\exp(-\Gamma_0 t)(\Gamma_0 t)^N}{N!}$$

$$h(Q,N) = \left\langle \exp(-iN^{\alpha} \mathbf{Q} \cdot \mathbf{R}) \right\rangle$$

P(**R**) : distribution of **R** (Gaussian)
$\langle |\mathbf{R}| \rangle = \delta$

α = 1: $h(N+1)=h(N)h(1)$ (ballistic motion)

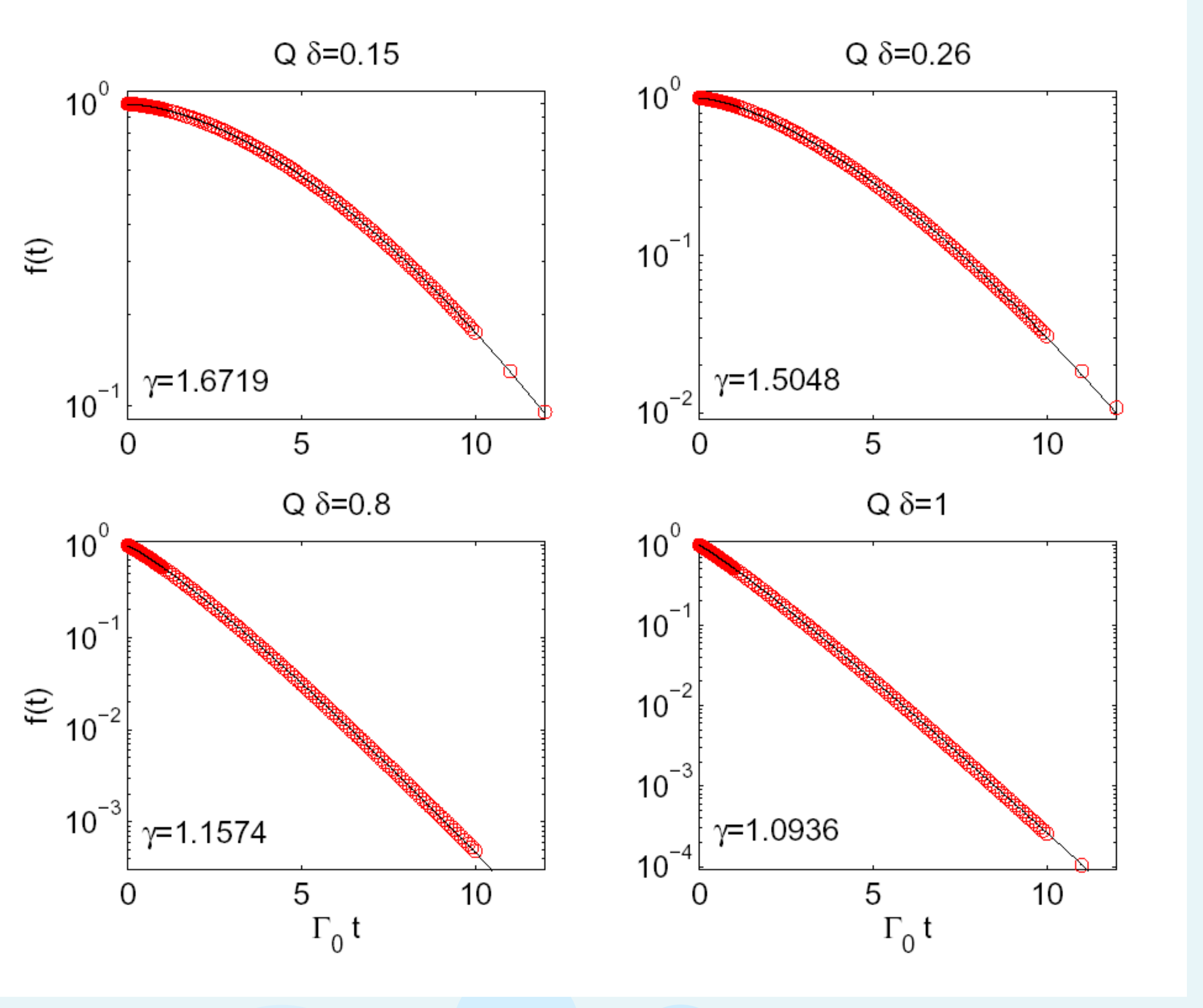
α = 1/2: Brownian motion (simple diffusion)

α < 1/2: sub-diffusion

α > 1/2: hyper diffusion

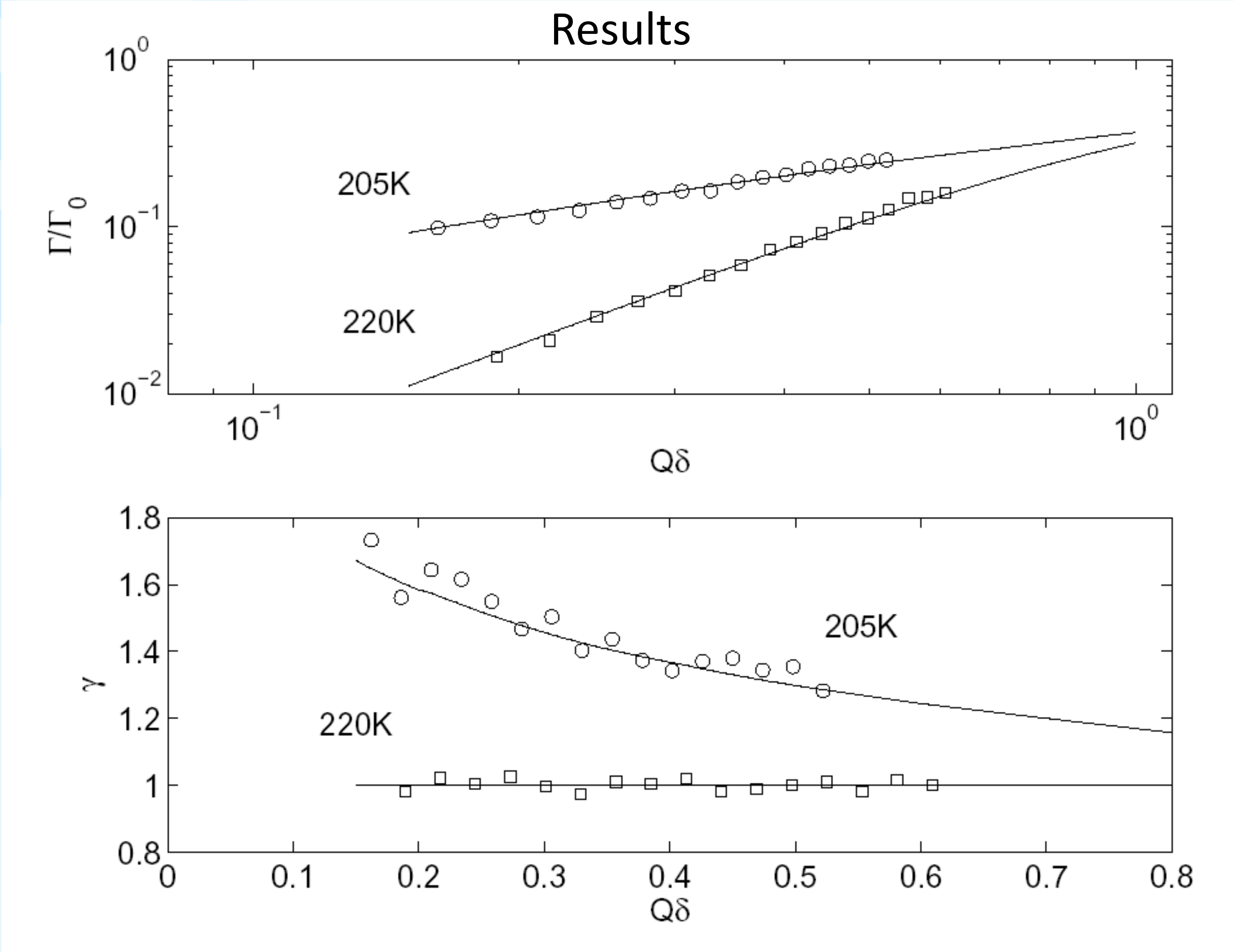
Dynamics of nanoparticles in a glass forming solvent

α=1
(ballistic)



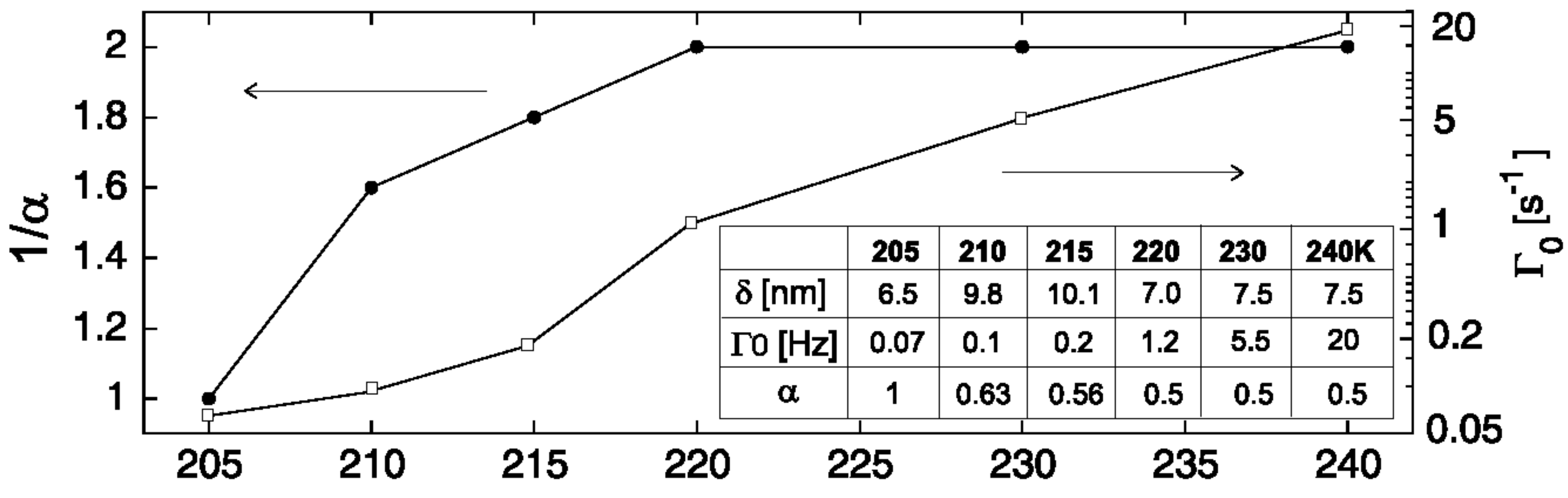
The fits with the KWW form $f(t) = \exp(-(\Gamma t)^{\gamma})$ are perfect:
The model explains the KWW exponent γ !

Dynamics of nanoparticles in a glass forming solvent



Phys. Rev. Lett. **100**, 055702 (2008)

Dynamics of nanoparticles in a glass forming solvent



	205	210	215	220	230	240K
δ [nm]	6.5	9.8	10.1	7.0	7.5	7.5
Γ0 [Hz]	0.07	0.1	0.2	1.2	5.5	20
α	1	0.63	0.56	0.5	0.5	0.5

Tg=170K (by DSC)

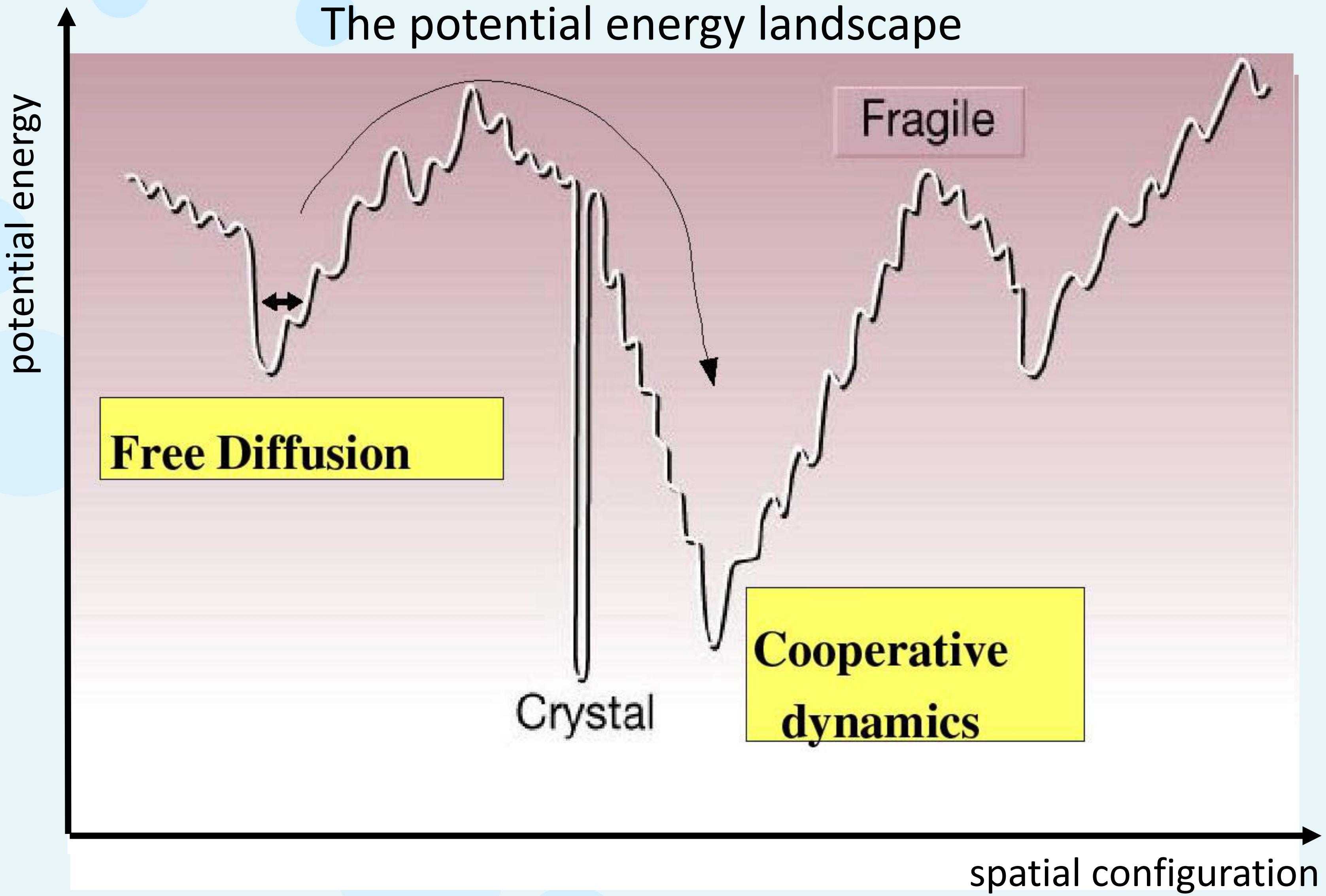
Striking similarities with dynamics of stress relaxations

but $\gamma \rightarrow 2$ for $Q \rightarrow 0$

ballistic motion observed at ~1.2*Tg

the potential energy landscape of the solvent may play a role………

Dynamics of nanoparticles in a glass forming solvent



Examples of XPCS research

Physical chemistry, soft matter, hard condensed matter physics, surface science

1/ Dynamics of nano-particles in a glass forming solvent

2/ Ageing of a transient depletion gel

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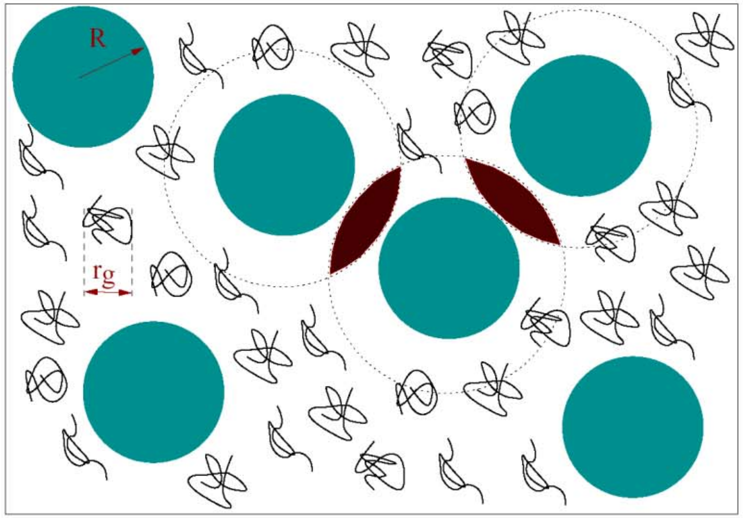
5/ Atomic diffusion in an alloy

Ageing of a transient depletion gel

Depletion gel

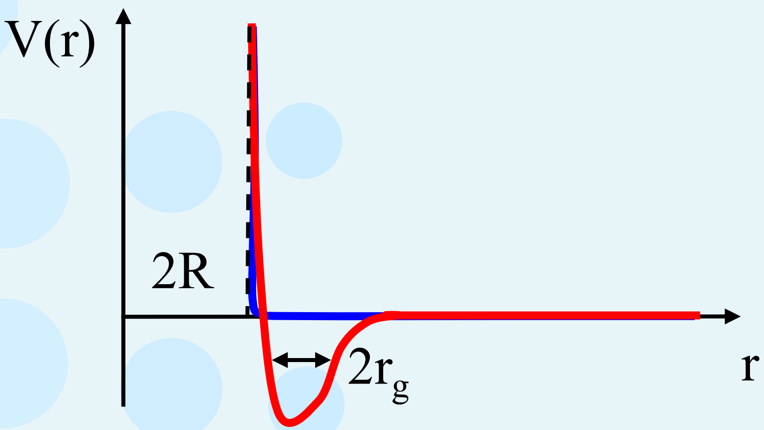


- Mixture of Poly(MethylMethacrylate) PMMA particles (spherical, R ≈ 1000 Å) coated with poly-12-hydroxystearic acid and free polymer (polystyrene) in cis-decalin
- Entropic forces between the polymer coatings layers → infinite repulsion
- Depletion effect due to the free polymer → attractive potential

Complex phase diagram

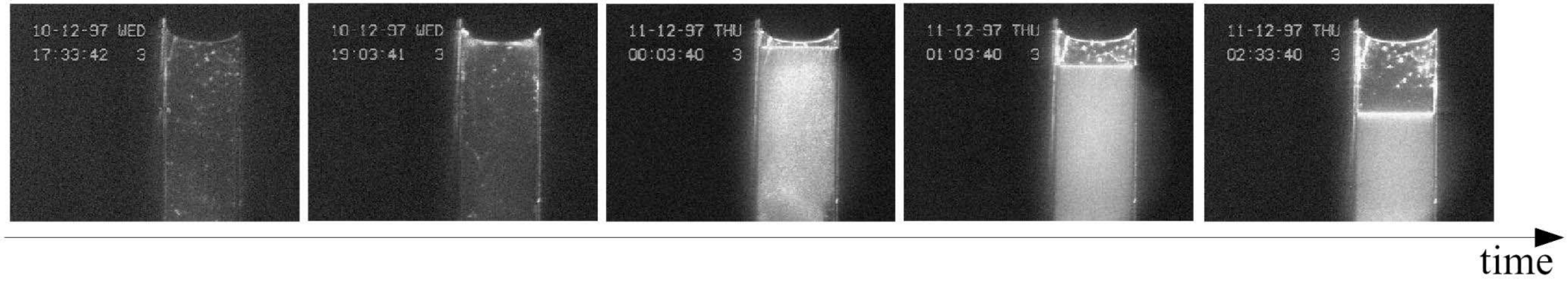
r_g/R (0.1) , ϕ (20%), c_p (4.3mg/cm^3)

Inter-particle interaction potential

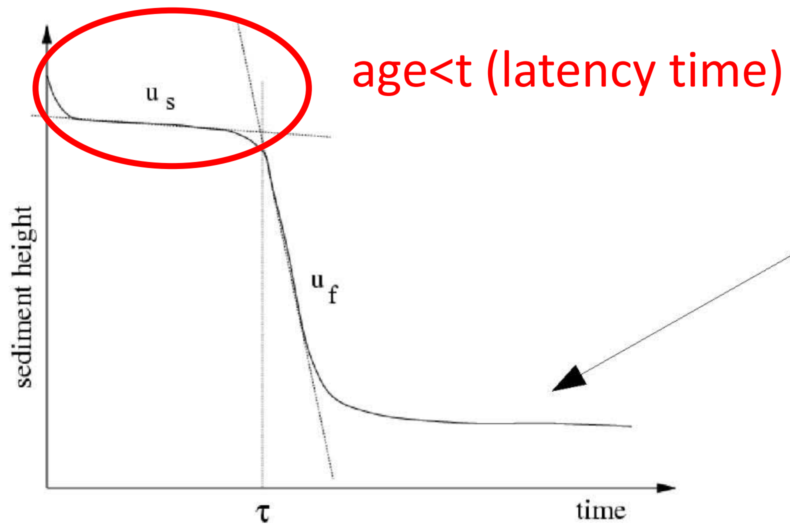


Ageing of a transient depletion gel

The gel phase is transient…..



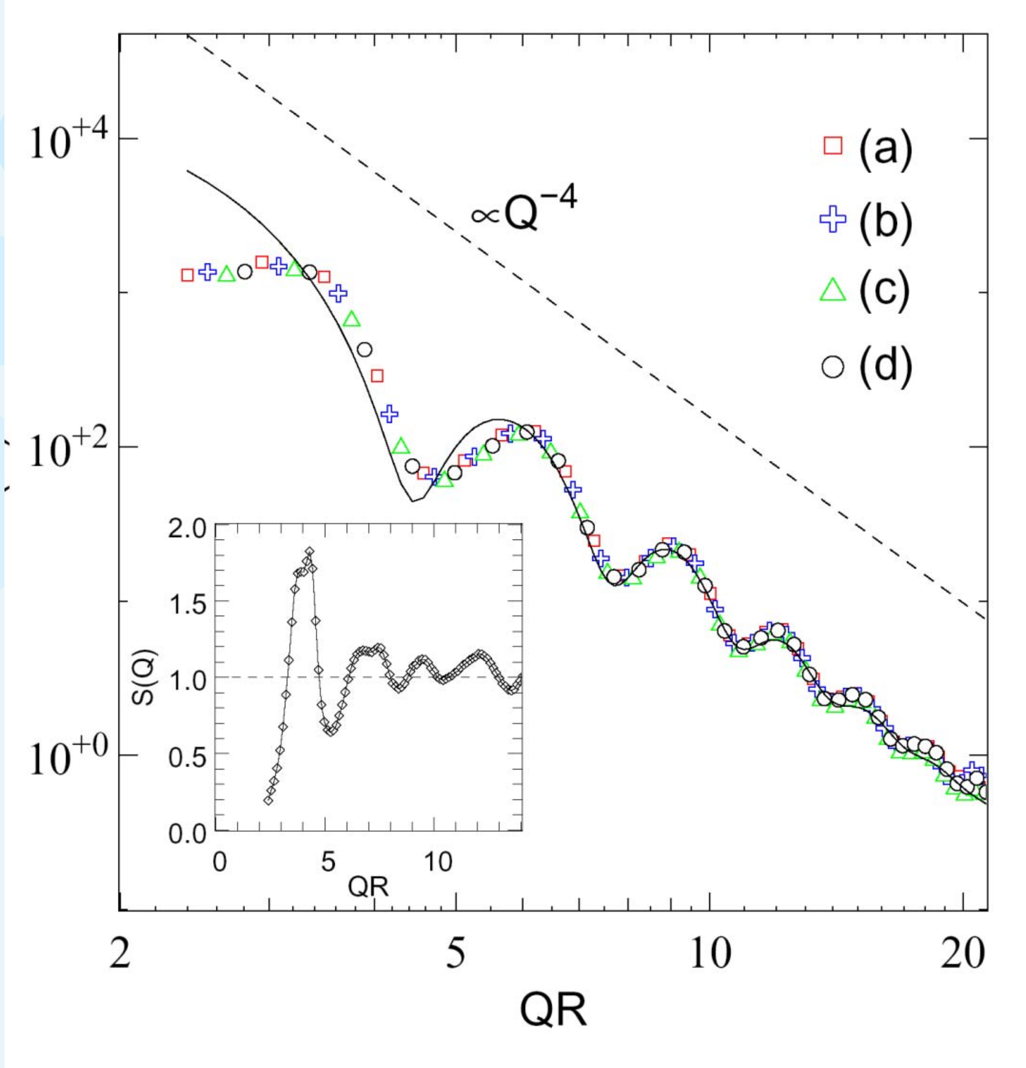
W. C. K. Poon *et al*, Faraday Discuss. **112**, 143 (1999)



delayed sedimentation

Ageing of a transient depletion gel

…but the structure is constant in the accessible Q-range

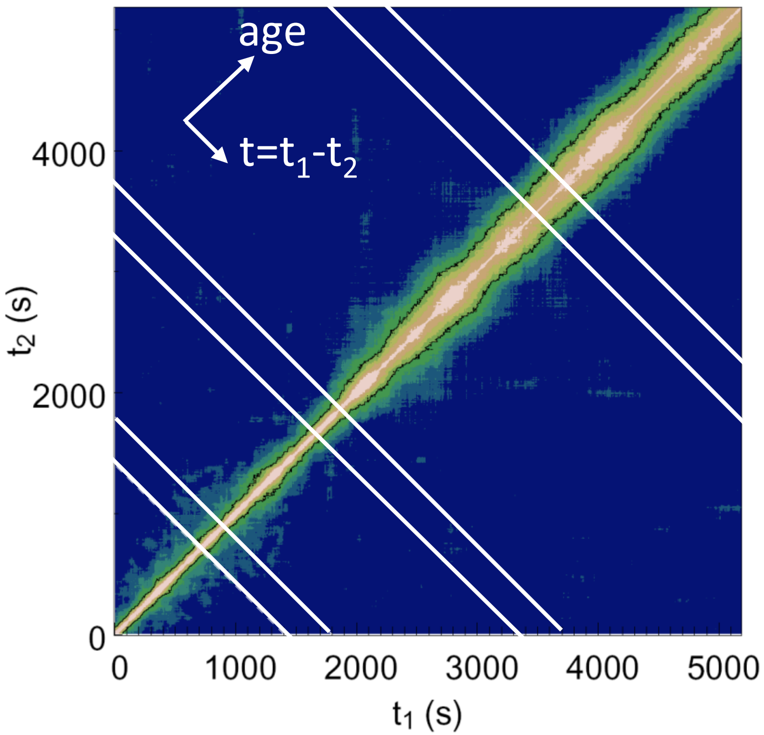


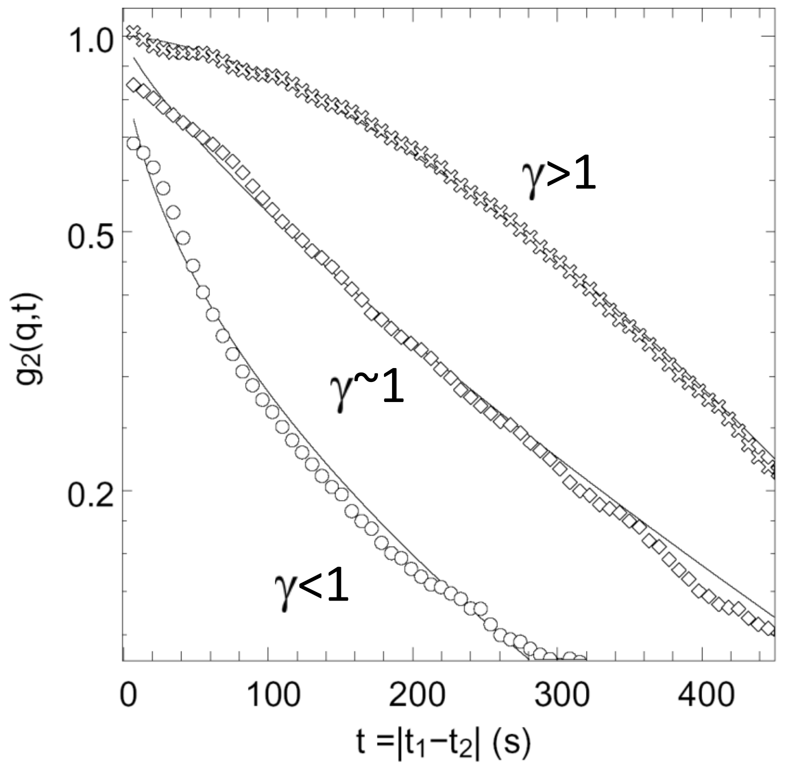
Fit: sphere form-factor

Phys. Rev. E **76**, 010401(R) (2007)

Ageing of a transient depletion gel

Two time analysis





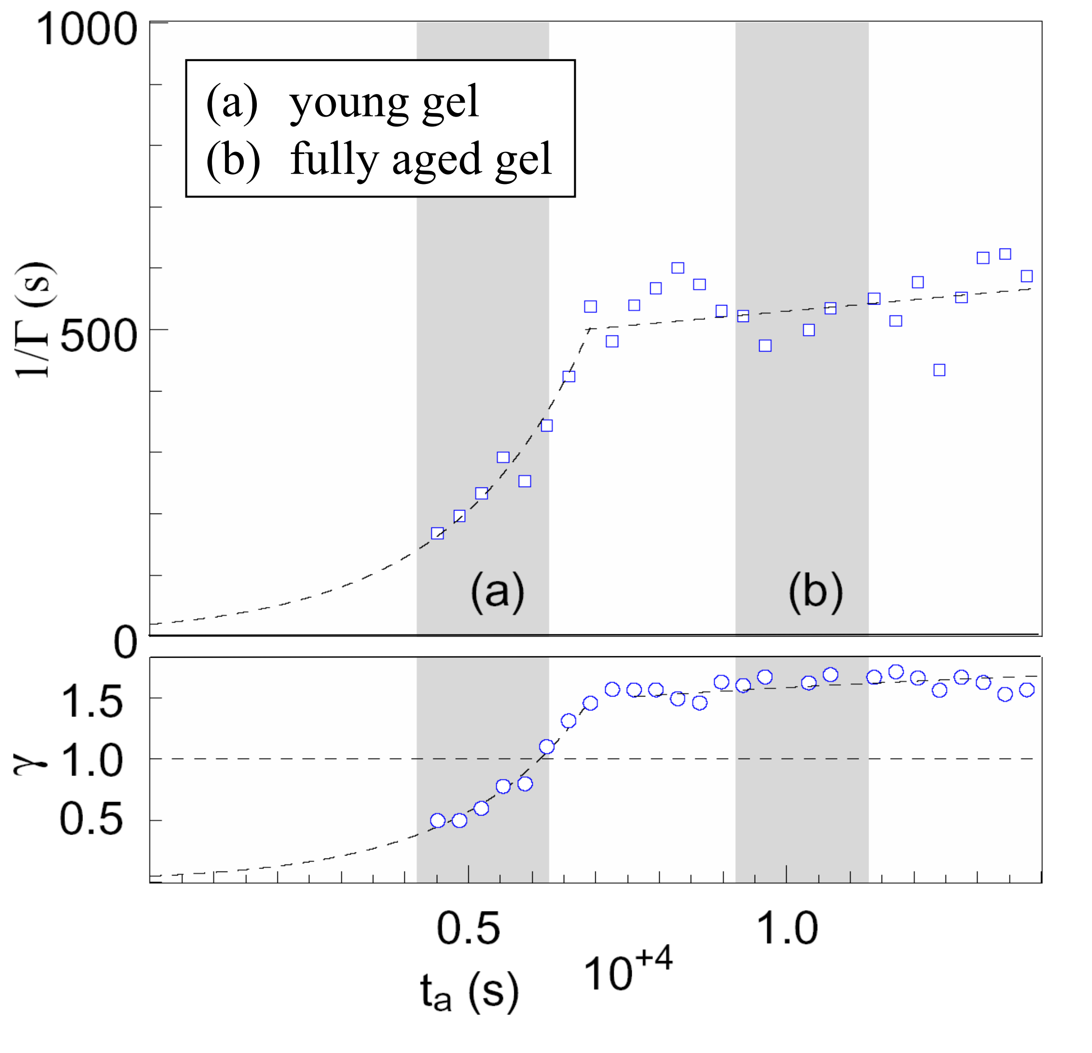
$$G(Q,t_1,t_2) = \frac{\langle I(Q,t_1)I(Q,t_2)\rangle_\phi}{\langle I(Q,t_1)\rangle_\phi \langle I(Q,t_2)\rangle_\phi}$$

Kohlrausch-Williams-Watts (KWW):
$g^{(2)}(t) = 1+\exp(-2(\Gamma t)^\gamma)$

Phys. Rev. E **76**, 010401(R) (2007)

Ageing of a transient depletion gel

A jamming transition?



relaxation time vs. age

"stretching exponent" vs. age

Analogous to the glass transition ??

Phys. Rev. E **76**, 010401(R) (2007)

Ageing of a transient depletion gel

Jamming:

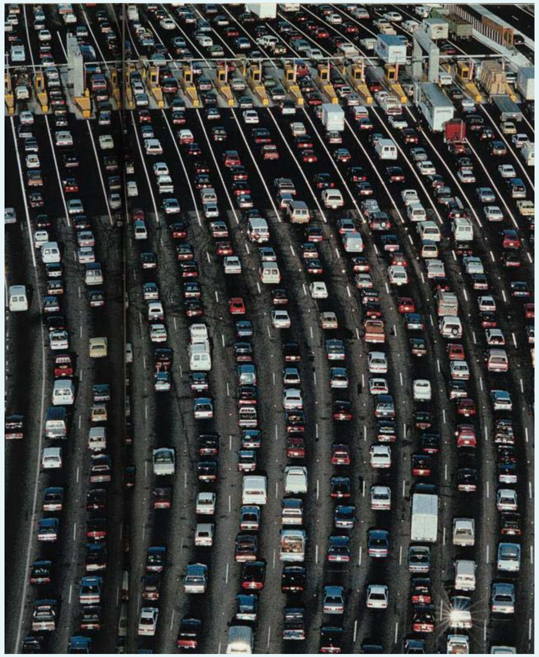
Micro-collapses due to stress relaxations

Kohlrausch-Williams-Watts (KWW):
$g^{(2)}(t) = 1+\exp(-2(\Gamma t)^{\gamma})$ with γ~1.5

Bouchaud & Pitard, EPJE **6**, 231 (2001)

Characteristic features

- crowded media
- intermittent dynamics
- $<\Delta x^2> \propto t^2$ (or $Q \propto \Gamma$)
- cooperative behavior
- aging — V. Trappe *et al*, Nature **411**, 772 (2001)



Examples of XPCS research

Physical chemistry, soft matter, hard condensed matter physics, surface science

1/ Dynamics of nano-particles in a glass forming solvent

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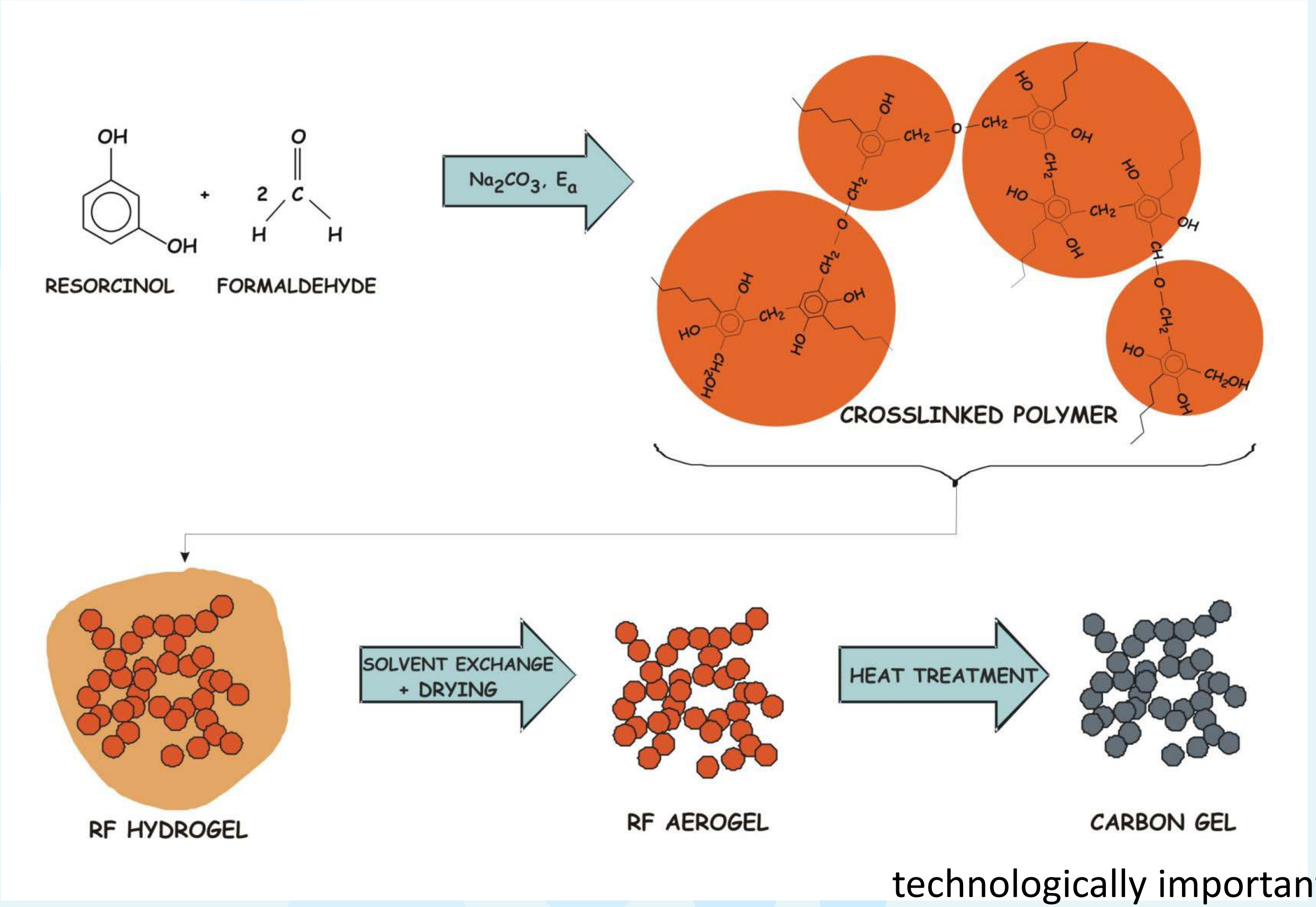
3/ Heterogeneous dynamics in an aerogel

4/ Liquid surface dynamics by grazing incidence XPCS

5/ Atomic diffusion in an alloy

Heterogeneous dynamics in an aerogel

RF aerogel

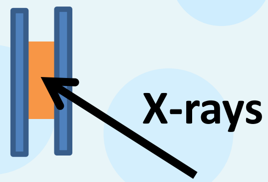


technologically important material, e.g. catalyst support ,..

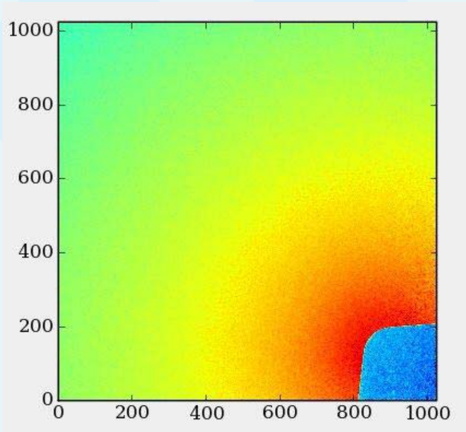
Heterogeneous dynamics in an aerogel

Non-equilibrium dynamics of an aerogel

RF polymer aerogel
under constant strain

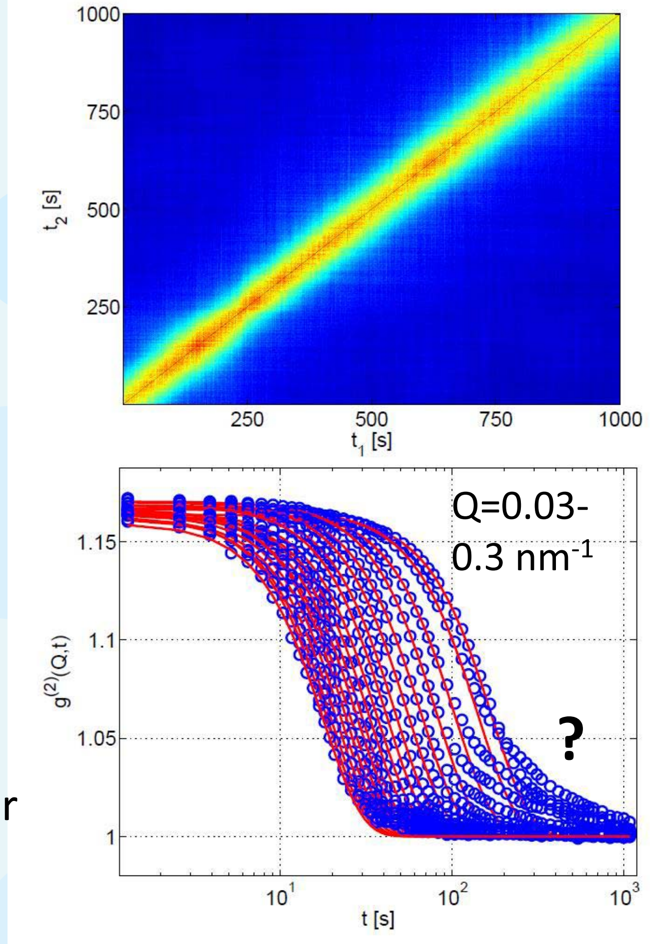


SAXS

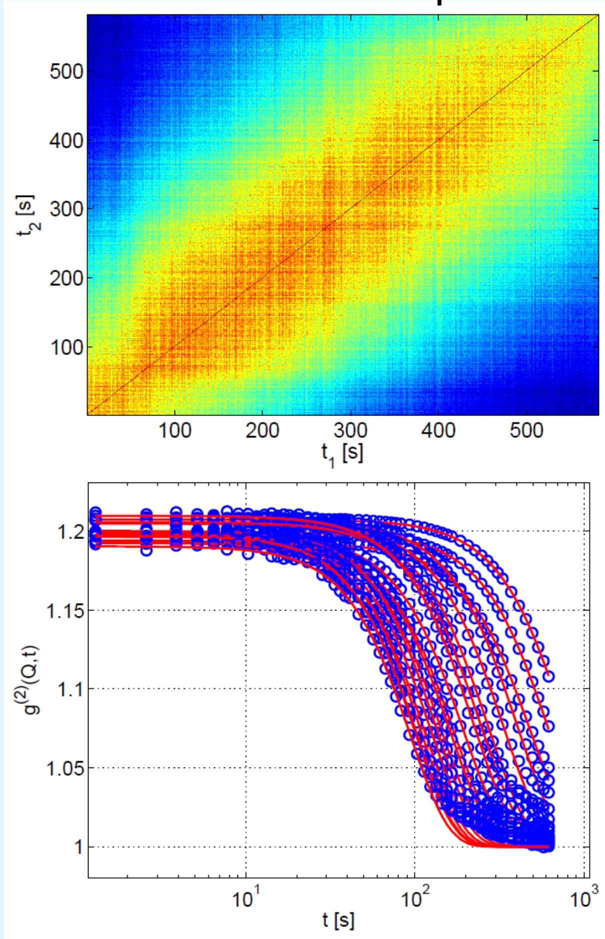


Dynamics 200 times slower after 3 hrs. $Q \propto \tau^{-1}$

5 min “old” sample



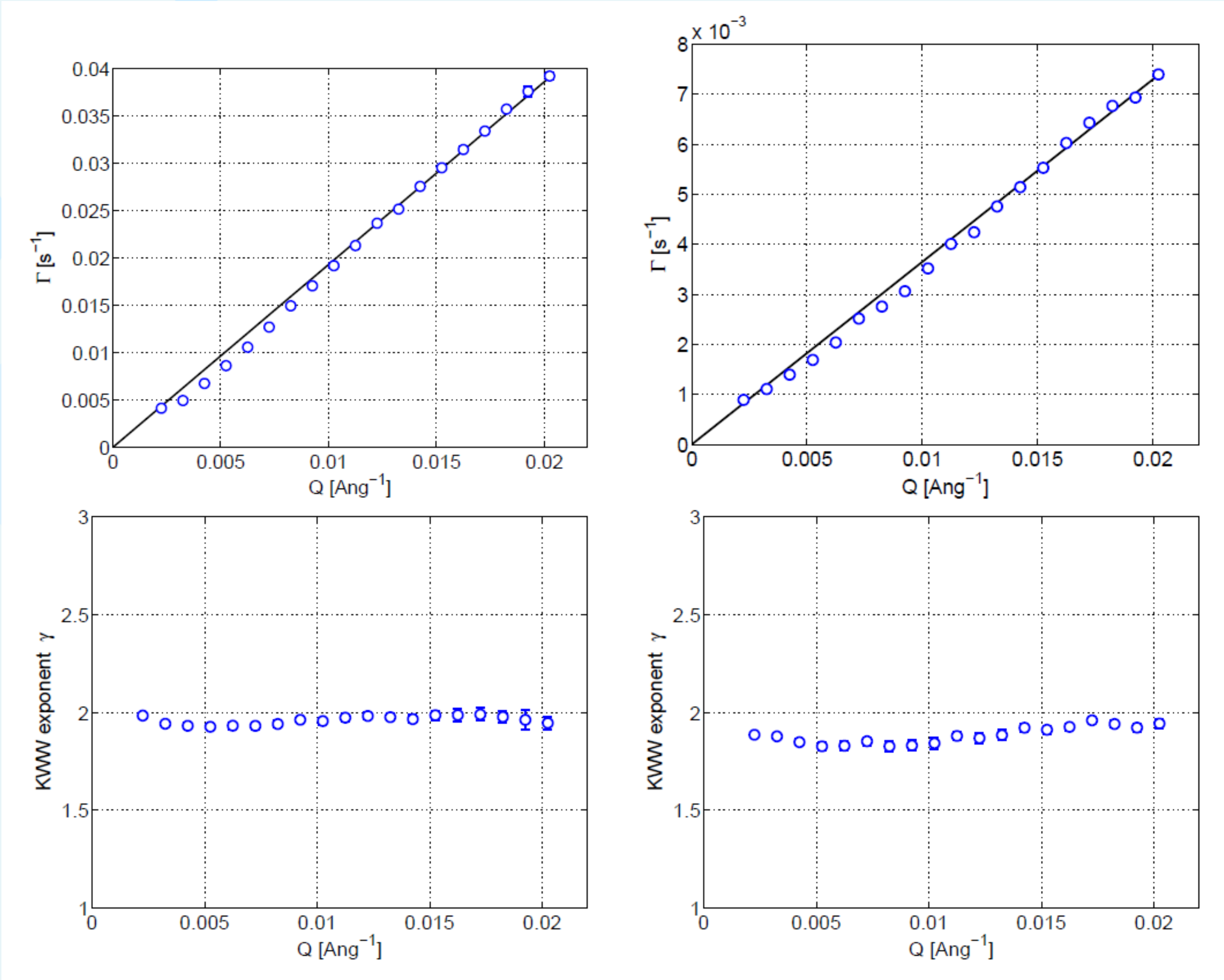
3 hrs “old” sample



A. Madsen *et al*, NJP (in print)

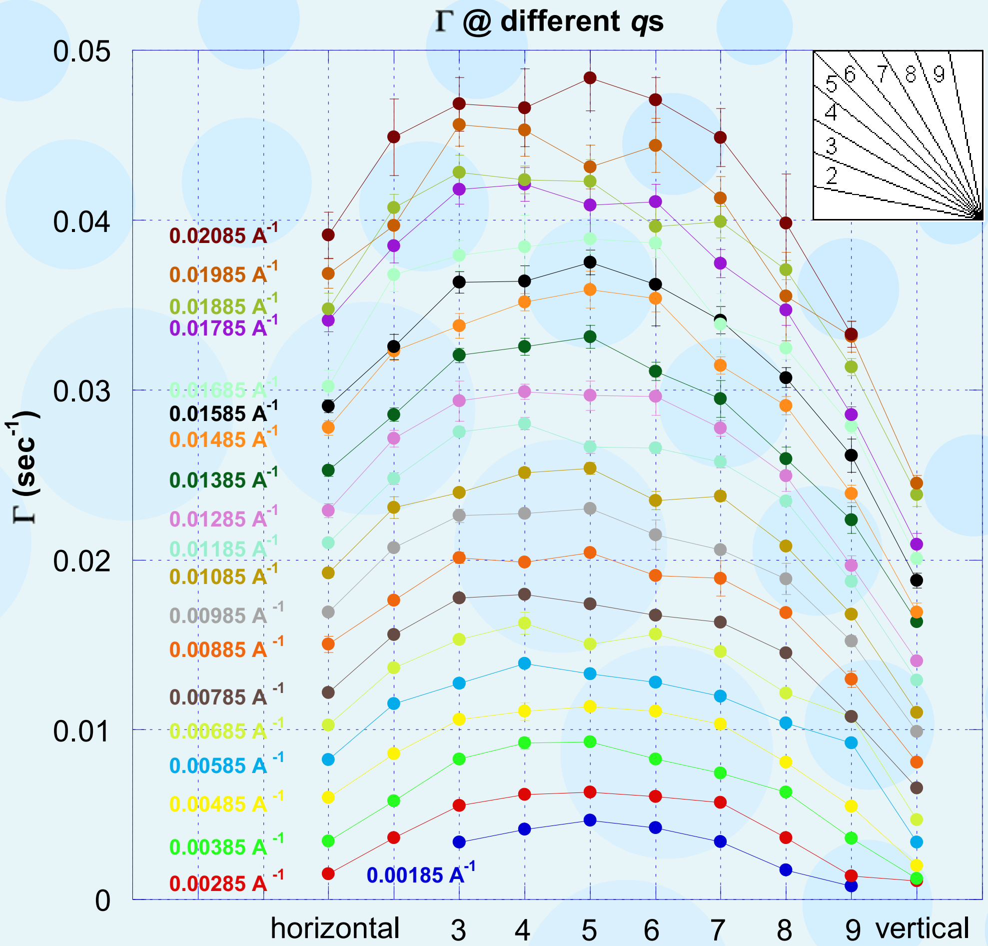
Heterogeneous dynamics in an aerogel

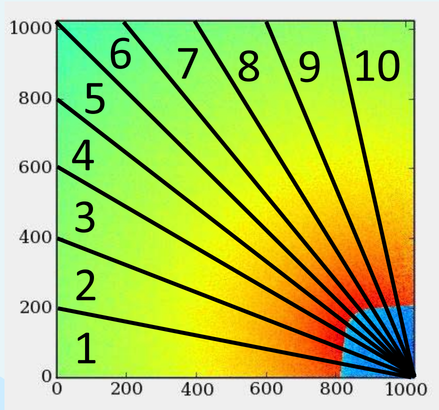
5 min “old” sample   3 hrs “old” sample



Heterogeneous dynamics in an aerogel

Angular dependence (5 min. old sample)



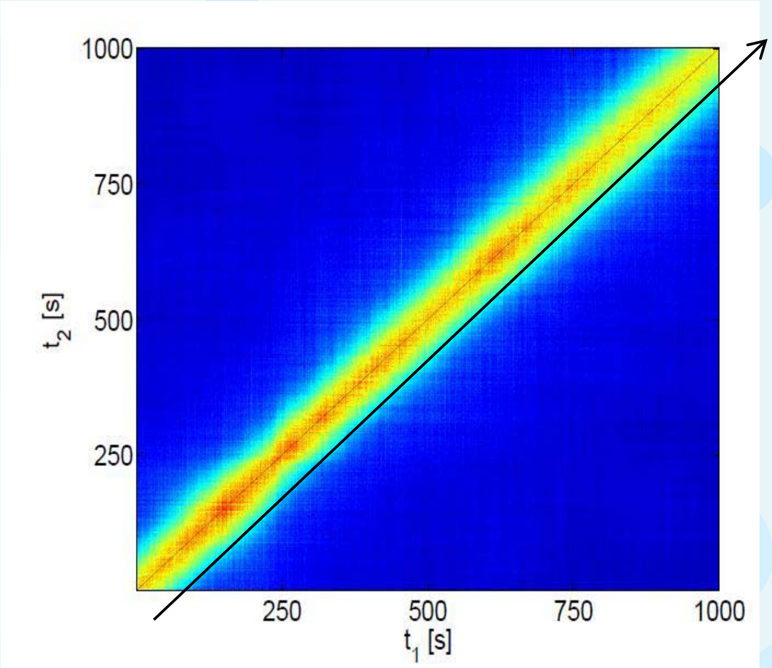


Azimuthal mask

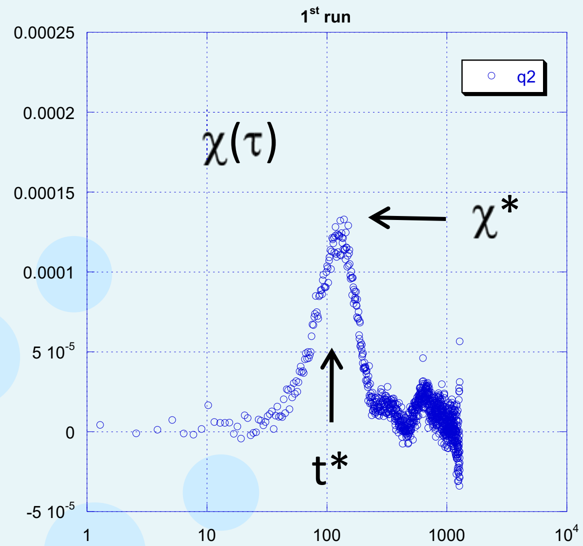
Which kind of dynamics is this and what causes the anisotropy? (stress relaxations, shear,…)

O. Czakkel *et al*, in progress

Heterogeneous dynamics in an aerogel

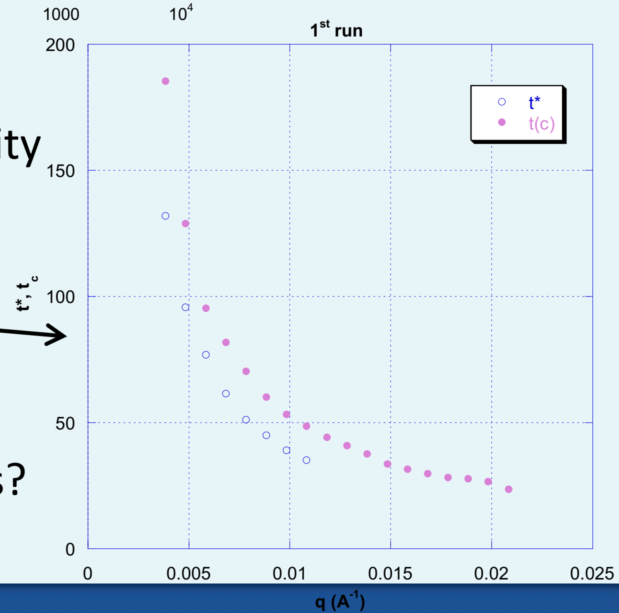


$\chi(t)$=Var(G(|t_1-t_2|=t)), sign of dyn. heterogeneity

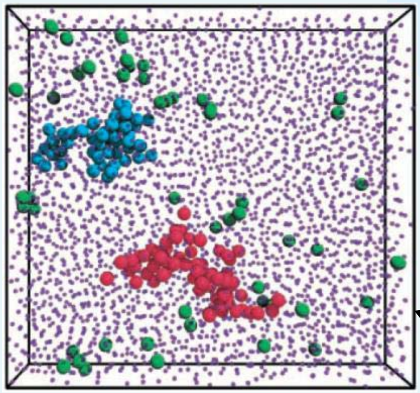


Non-Gaussian fluctuations

Unpublished data



Typically, the dynamical heterogeneity peaks at **times shorter** than the characteristic correlation time but obeys the same Q-scaling….



Weeks *et al*, Science (2000)

Link to spatial heterogeneity (χ_4) observed in colloidal (near) glasses?

Examples of XPCS research

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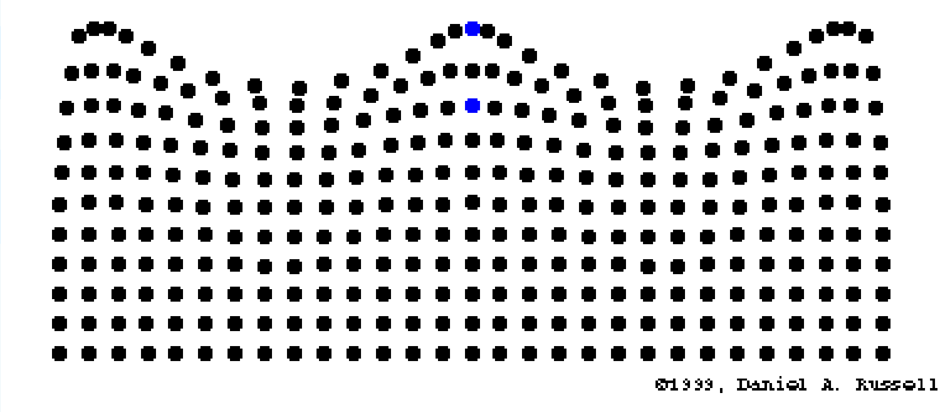
Liquid surface dynamics by grazing incidence XPCS



Capillary waves on highly viscous liquids: $\Gamma = 2\sigma/\eta\ Q$

What happens as $\eta \rightarrow \infty$ i.e. at the transition from a supercooled liquid to a glass ?

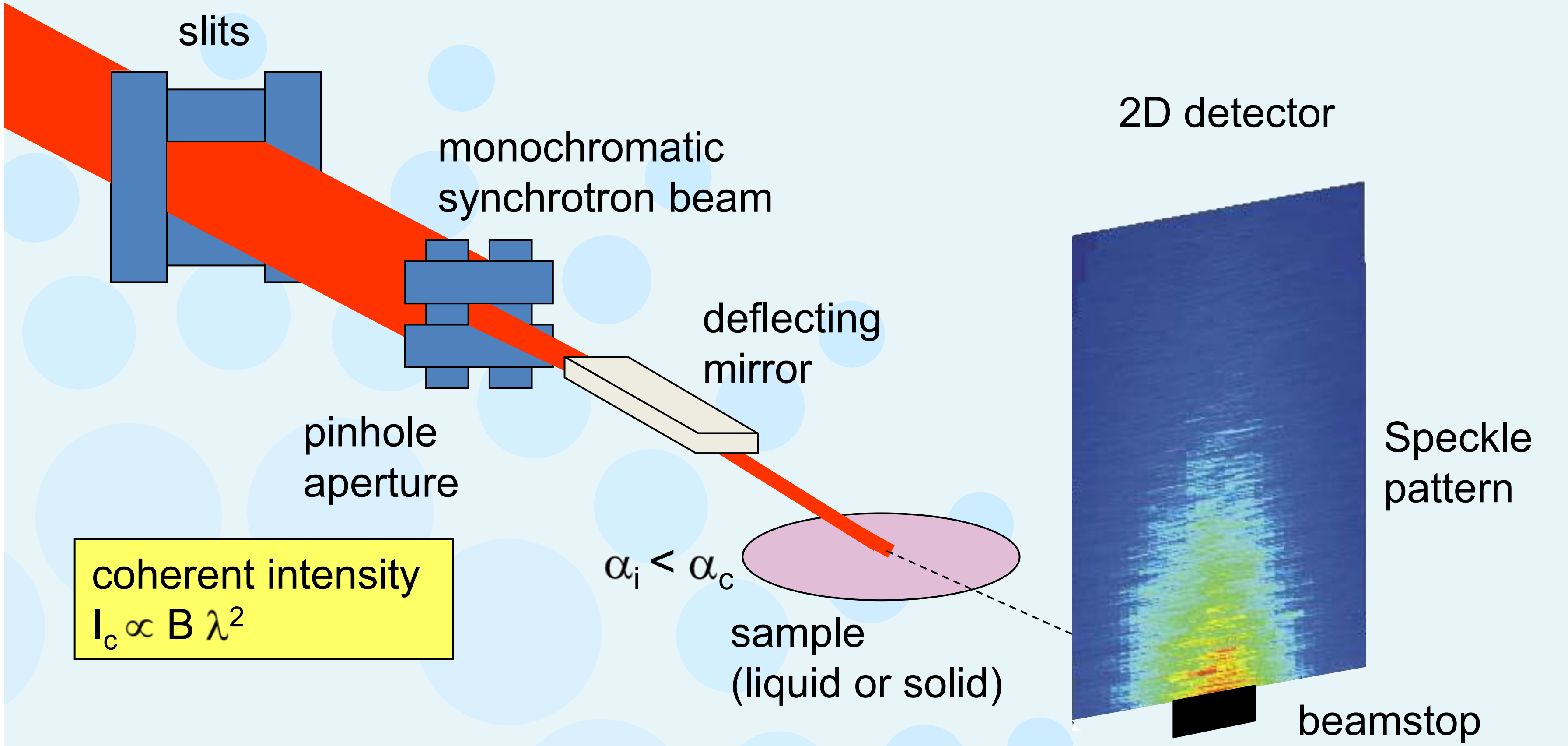
What happens with the shear response as the liquid solidifies?

RHEOLOGY (modulus=stress/strain)

Liquid: deforms cont. under stress
Solid: equilibrium deformation under stress

Liquid: stress relaxes under a constant strain
Solid: constant stress level under constant strain

Liquid surface dynamics by grazing incidence XPCS



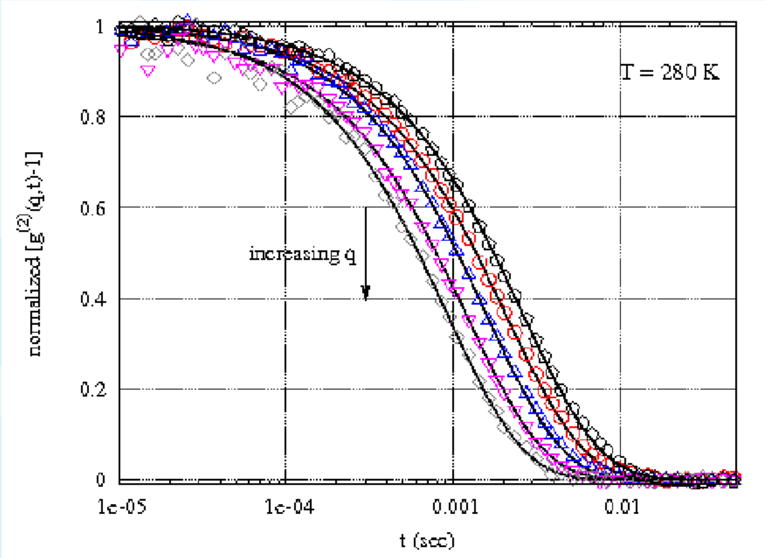
coherent intensity
$I_c \propto B \lambda^2$

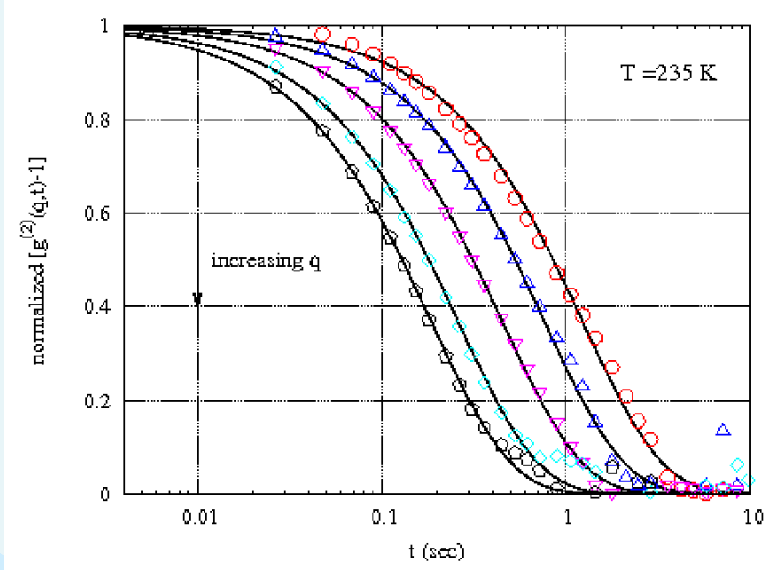
Intensity fluctuations of the speckle pattern reflect the dynamics of the sample

XPCS → Intensity auto-correlation function $g(q,t) = \dfrac{\langle I(q,0) I(q,t) \rangle}{\langle I(q,t) \rangle^2}$

Liquid surface dynamics by grazing incidence XPCS

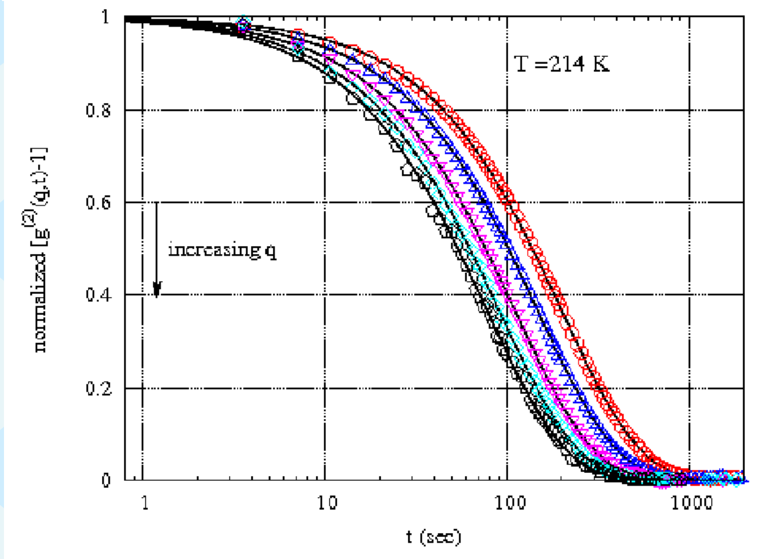
CW dynamics on supercooled poly-propylene glycol (PPG)





All functions are simple exponential decays

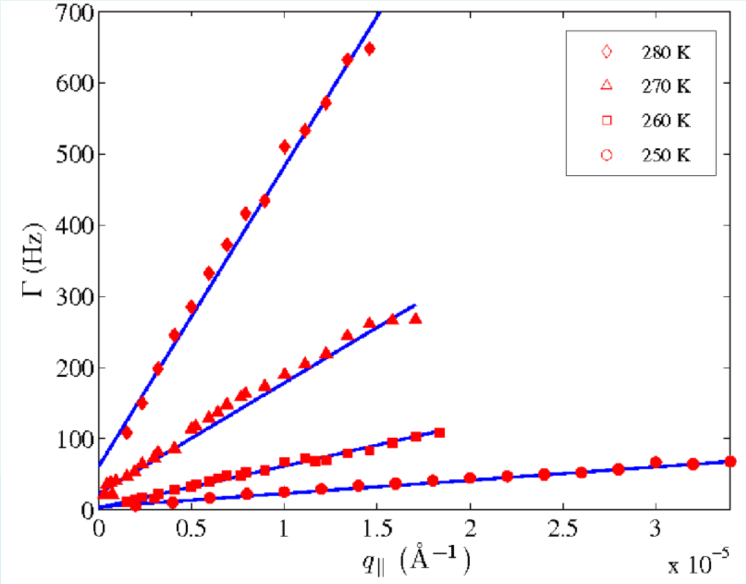
$$g^{(2)}(Q,\tau) = 1 + \exp(-2\Gamma\tau)$$

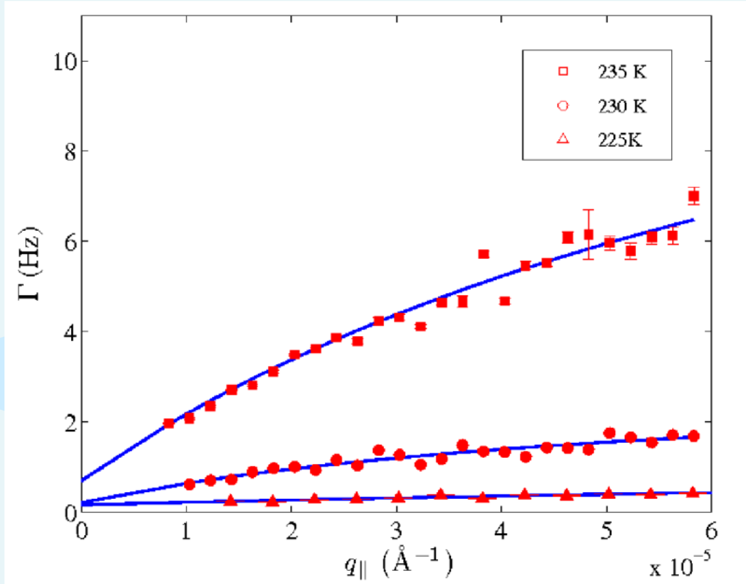


Characteristic times change 5 orders of magnitude from 280 to 214K ($T_g \sim$ 205K)

Europhysics Lett. **83**, 36001 (2008)

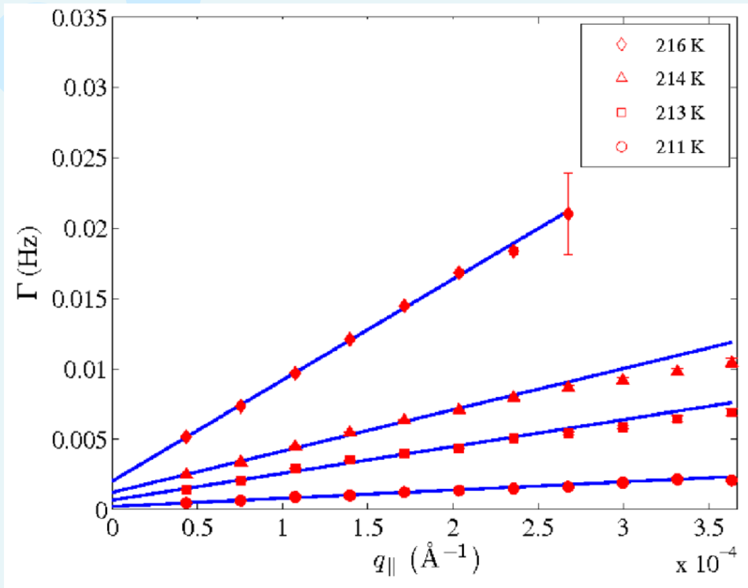
Liquid surface dynamics by grazing incidence XPCS





Newtonian liquid

$$\Gamma = \frac{\gamma}{2\eta} Q$$



Liquid surface dynamics by grazing incidence XPCS

Liquids near the glass transition

Viscosity and elasticity become important → viscoelasticity

Maxwell-Debye model
(viscoelastic liquid)

$$G(\omega) = i\omega\eta(\omega)$$

$$\eta(\omega) = \frac{\eta_0}{1 + i\omega\tau}$$

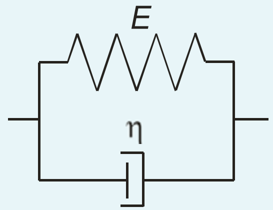
$$\Gamma = \frac{\gamma q}{2\eta_0}\left(1 + \frac{\gamma q}{2G}\right)^{-1}$$

$$\Gamma(0) = 0$$

Over-damped capillary waves
Newtonian liquid

$$\Gamma = \frac{\gamma q}{2\eta}$$

Kelvin-Voigt model
(viscoelastic solid)



$$G(\omega) = i\omega\eta_0 + E$$

$$\eta(\omega) = \eta_0 + \frac{E}{i\omega}$$

$$\Gamma = \frac{\gamma q}{2\eta_0} + \frac{E}{\eta_0}$$

This is what we observe even far above Tg !

$$\Gamma(0) = \frac{E}{\eta_0}$$

Liquid surface dynamics by grazing incidence XPCS

Liquids near the glass transition

Viscosity and elasticity become important → viscoelasticity

Combined Maxwell-Debye and Kelvin-Voigt model

$$G(\omega) = i\omega\eta(\omega) + E$$

Maxwell Debye

$$\eta(\omega) = \frac{\eta_0}{1 + i\omega\tau}$$

$$E$$

Elasticity from Voigt-Kelvin

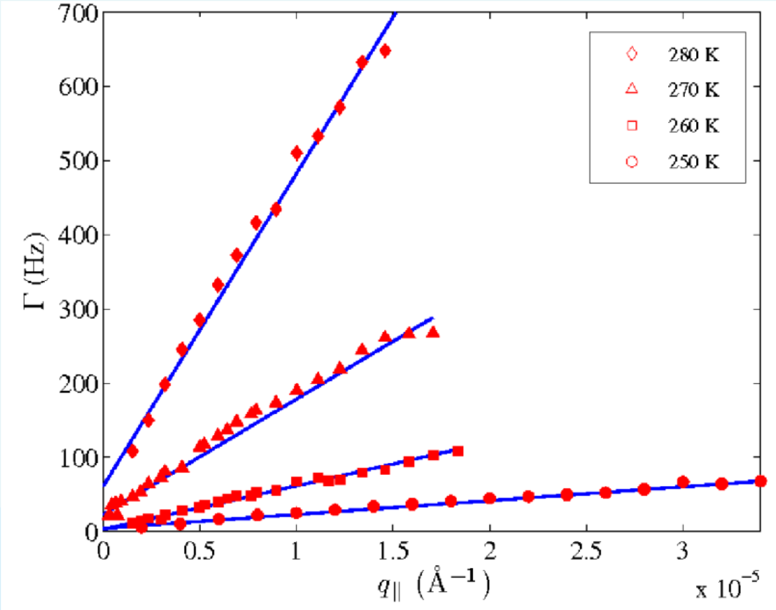
$$\Gamma = \frac{\gamma(q+q_0)}{2\eta_0}\left(1 + \frac{\gamma(q+q_0)}{2G(\infty)}\right)^{-1}$$

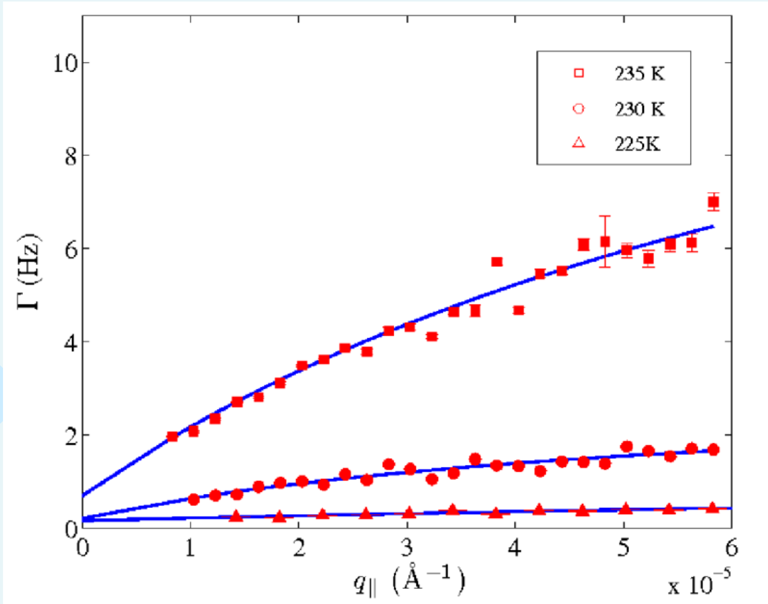
$q_0 = 2E/\gamma$

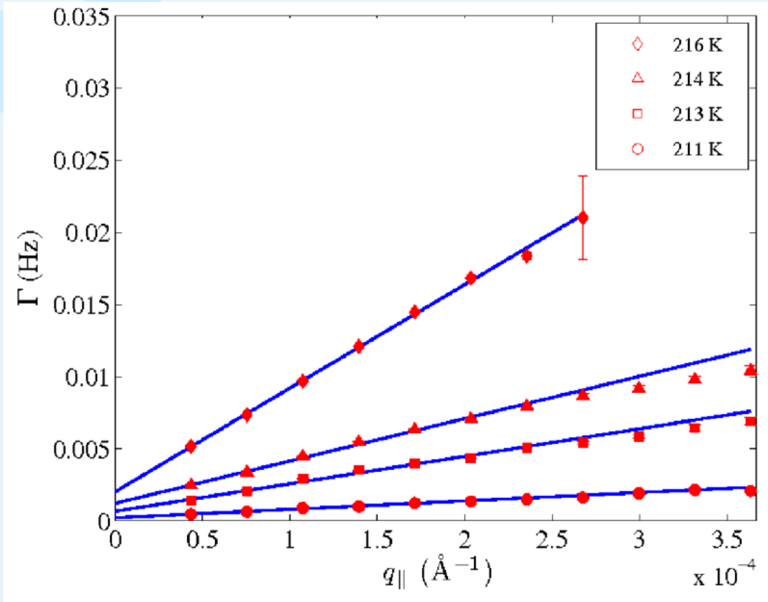
$\Gamma \rightarrow E/\eta$ for $q \rightarrow 0$

$\Gamma \rightarrow G(\infty)/\eta$ for $q \rightarrow \infty$

Liquid surface dynamics by grazing incidence XPCS





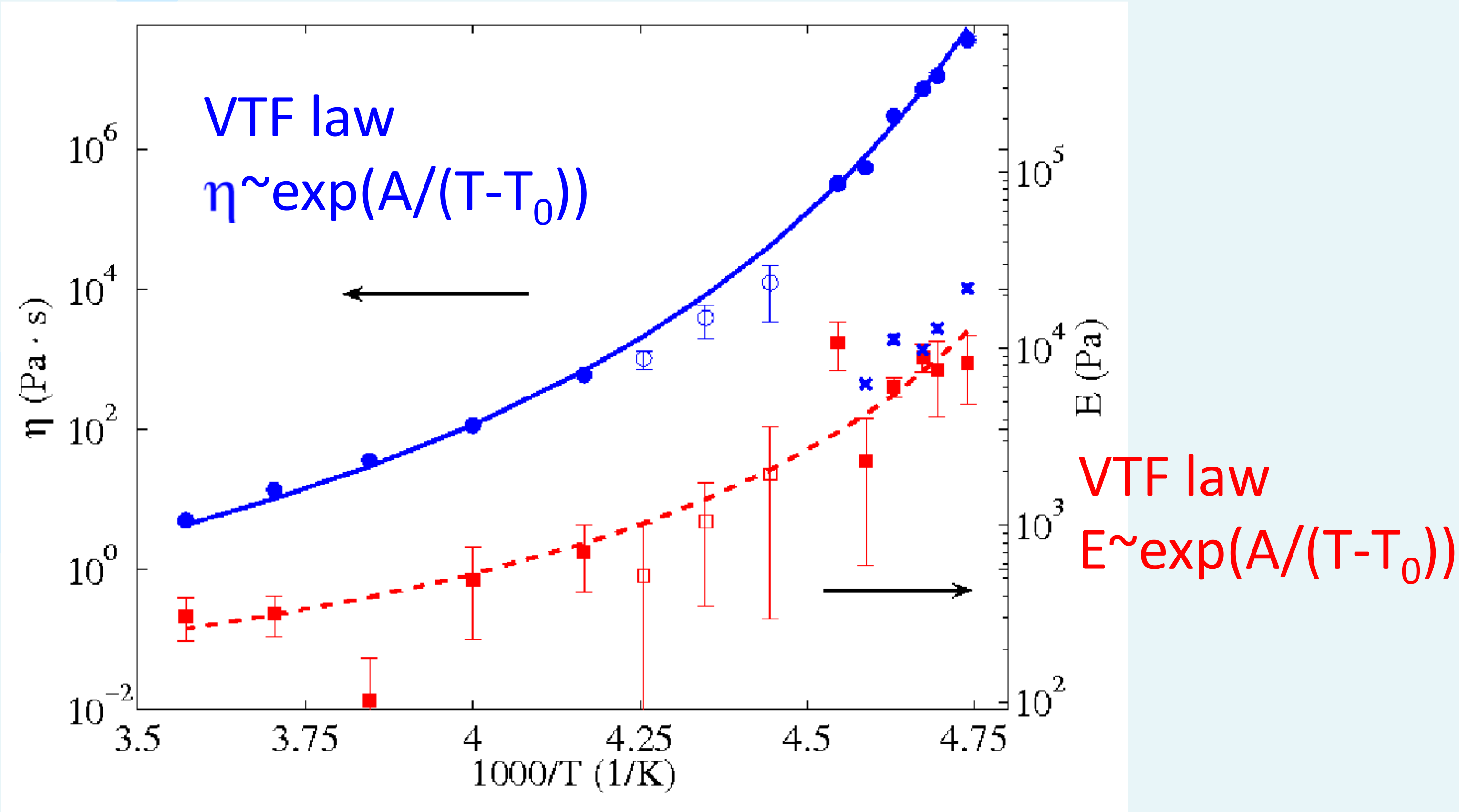


$$\Gamma = \frac{\gamma(q+q_0)}{2\eta_0}\left(1+\frac{\gamma(q+q_0)}{2G(\infty)}\right)^{-1}$$

Europhysics Lett. **83**, 36001 (2008)

Liquid surface dynamics by grazing incidence XPCS

Viscoelasticity of poly-propylene glycol (PPG)



Low-frequency elastic behavior of supercooled liquids is an extremely controversial topic in the literature and non-invasive experimental methods are missing

Europhysics Lett. **83**, 36001 (2008)

Examples of XPCS research

Physical chemistry, soft matter, hard condensed matter physics, surface science

1/ Dynamics of nano-particles in a glass forming solvent

2/ Ageing of a transient depletion gel

3/ Heterogeneous dynamics in ………….

4/ Liquid surface dynamics by grazing incidence XPCS

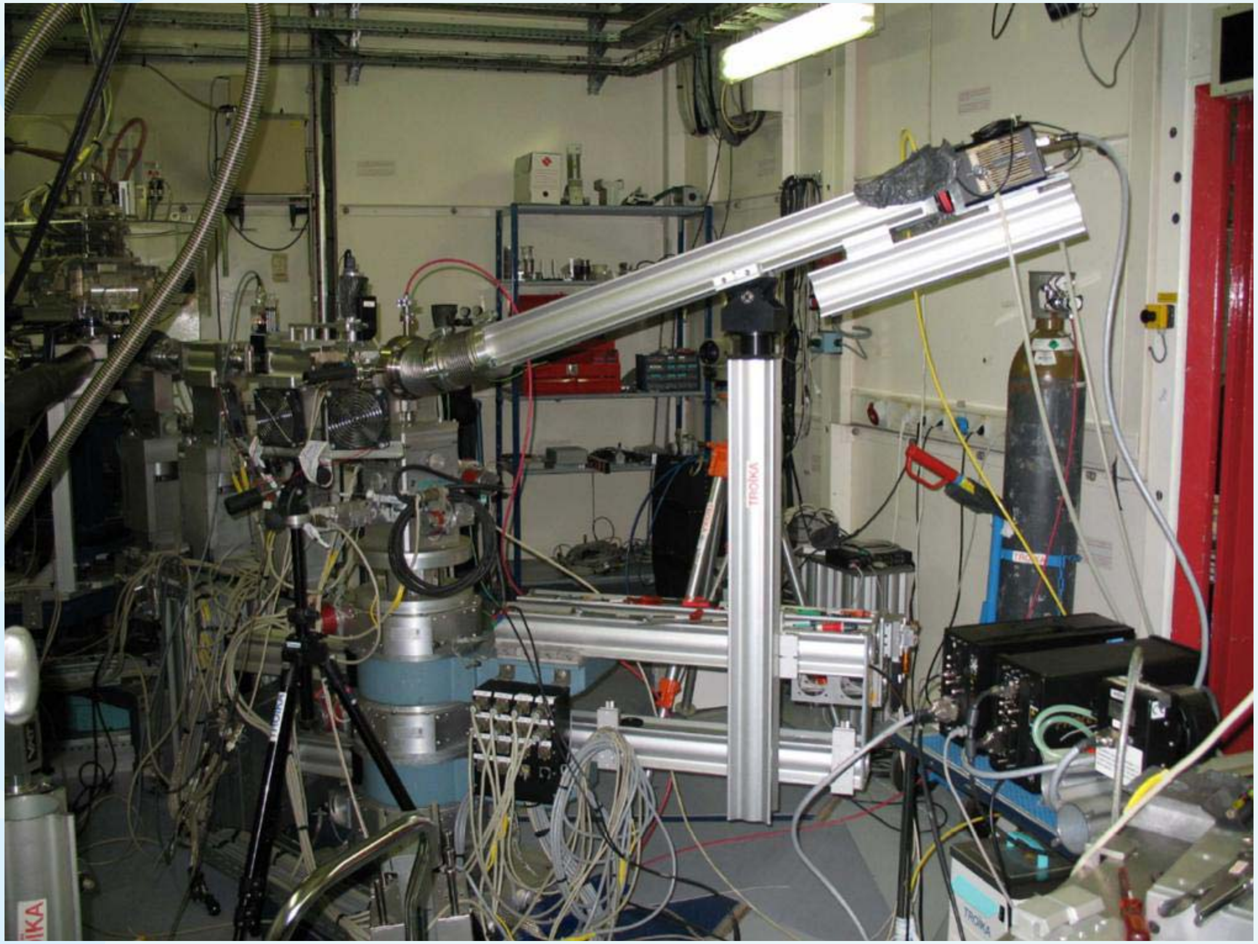
5/ Atomic diffusion in an alloy

Atomic diffusion in an alloy

Diffuse scattering on a crystalline lattice

Cu-10at.%Au at 270^{o}C,
$|Q|=1.75Å^{-1}$

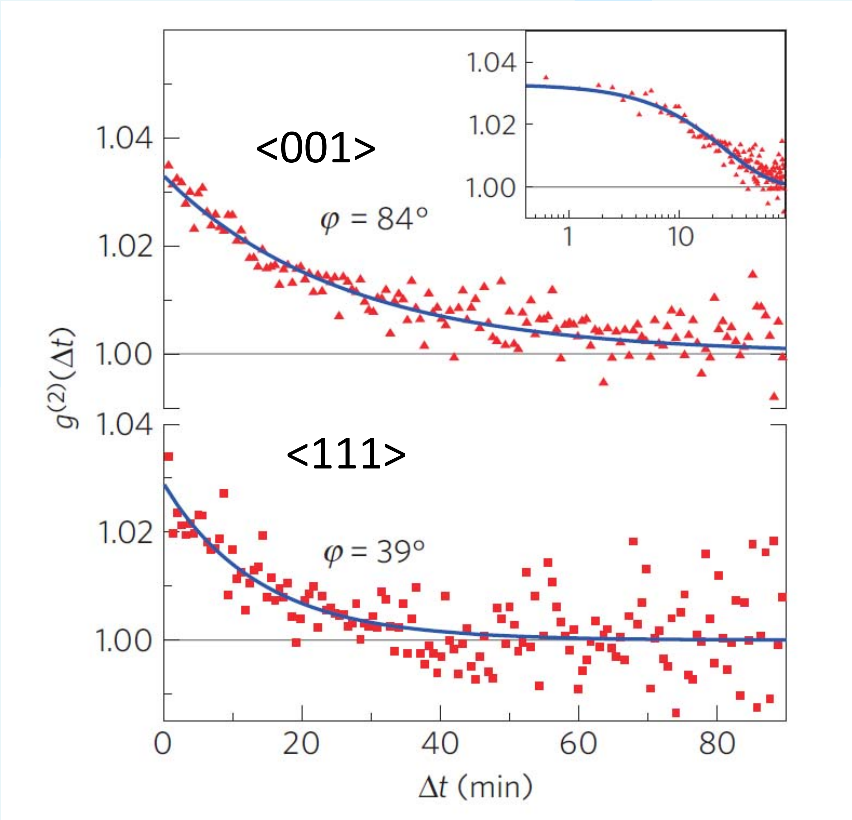
Intensity ~1e-3 ph/pixel/s



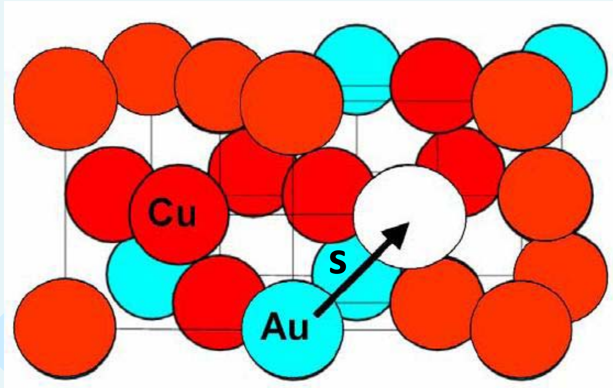
Atomic diffusion in an alloy

System: Au(10%)-Cu(90%) alloy

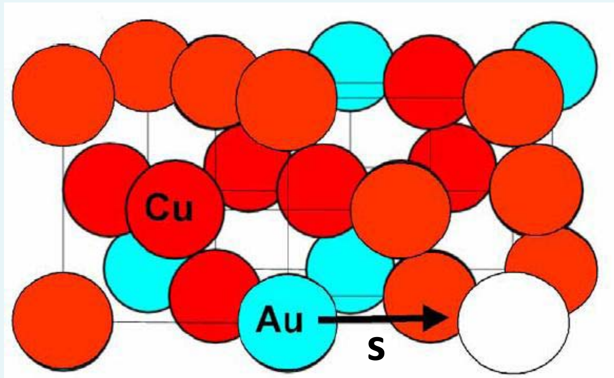
$2\theta=25^o$, $|Q|=1.75$ Å^{-1}



NN jumps

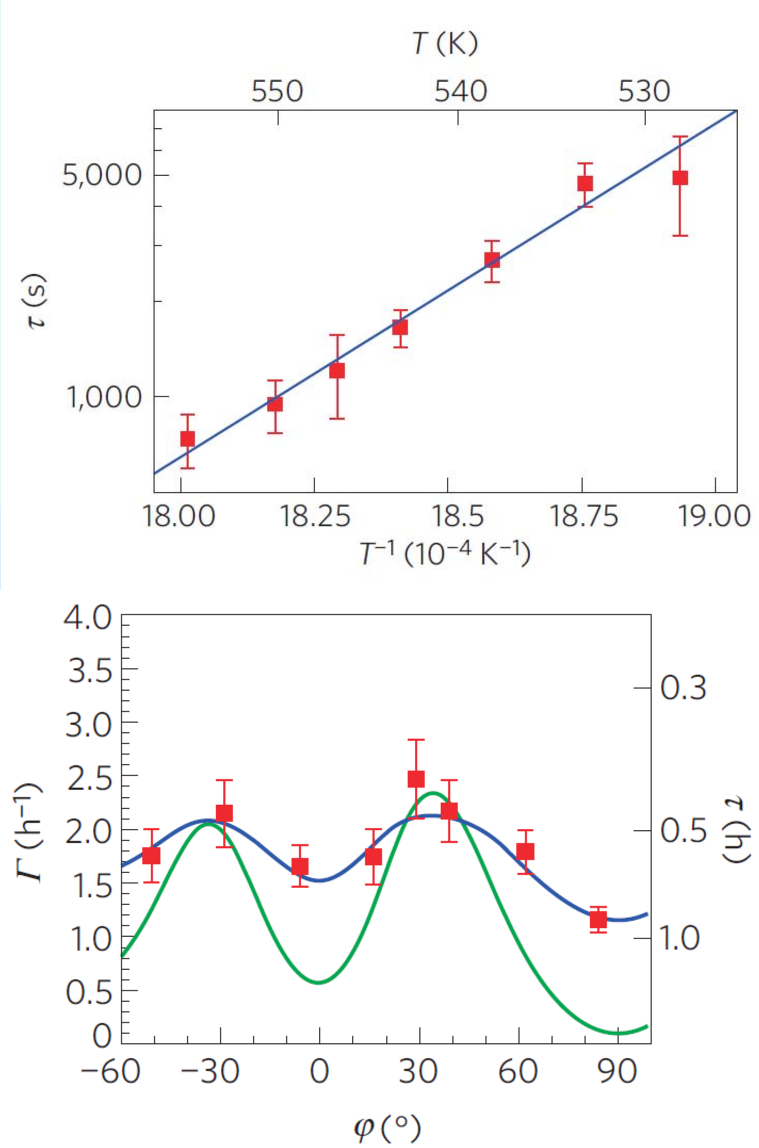


2nd NN jumps



Leitner, Sepiol *et al.*, Nature Materials **8**, 717 (2009)

Atomic diffusion in an alloy



Hypothesis:

$$\tau(\mathbf{Q}) = \tau_0 \frac{I_{SRO}(\mathbf{Q})}{1-\sum_i p_i \cos(\mathbf{s_i}\cdot\mathbf{Q})}$$

confirmed taking NN jumps and SRO into account

Demonstrates the possibility of investigating atomic motion with XPCS

To be continued with the XFELs…….

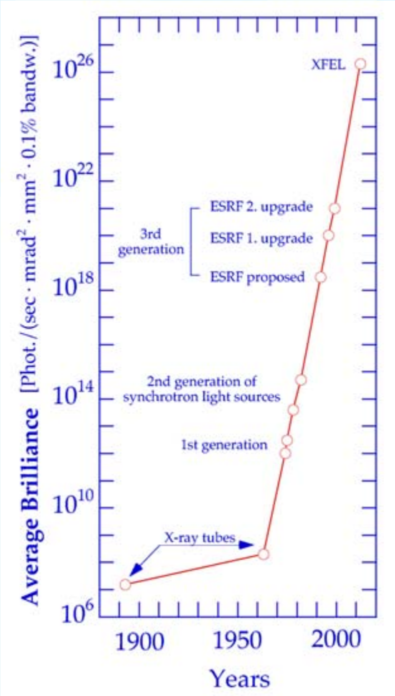
Leitner, Sepiol *et al.*, Nature Materials **8**, 717 (2009)

XPCS at the X-FEL

XFELs are pulsed sources, i.e. the continuous illumination needed for traditional XPCS is not possible. We need to come up with a different scheme.

XFELs are not lasers but thanks to their excellent transverse coherence properties and the huge gain thanks to the SASE principle the coherent flux (Brilliance) is enormous

The potential gain with the XFEL is huge in measuring fast (fs-ps-ns) dynamics at Å and nm lengthscales.



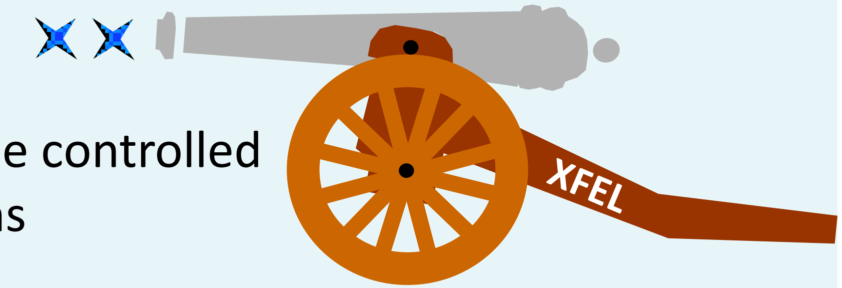
but,

…. a mono is still needed for WA-XPCS (e.g. diamond 1e-5 bw.)

…. samples must survive the intense X-ray pulses

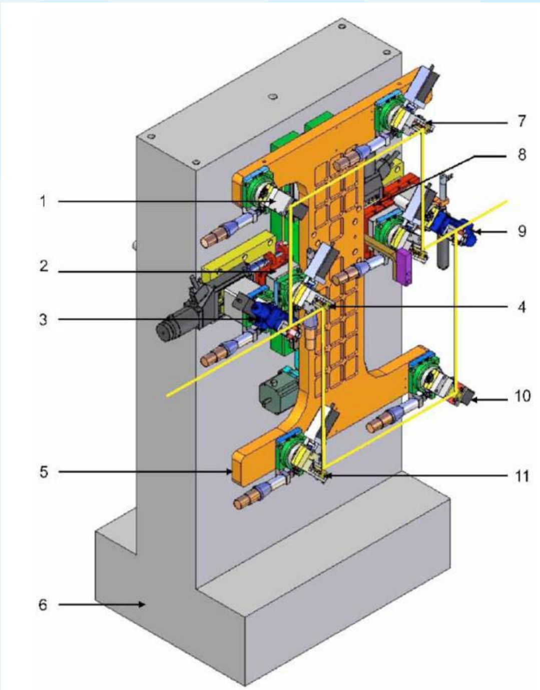
…. detectors must be custom made and have on-chip memory

XPCS at the X-FEL



Double exposures: delay between pulses must be controlled and variable to map out the correlation functions

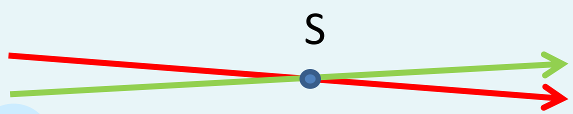
Delays generated in the Linac or by a special split-delay line



X-ray split-delay line
W. Roseker *et al*, Optics Letters **34**, 1768 (2009)

Si(511) Bragg reflectors, efficiency <1%
300 μm path difference gives 1 ps delay
Resolution down to 17 ps achieved

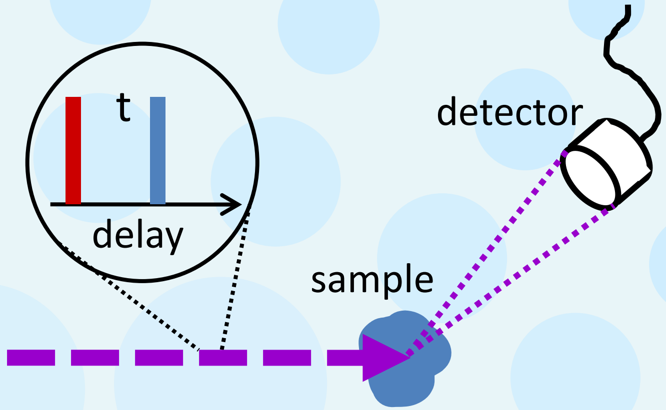
Combination of Bragg and Laue optics:



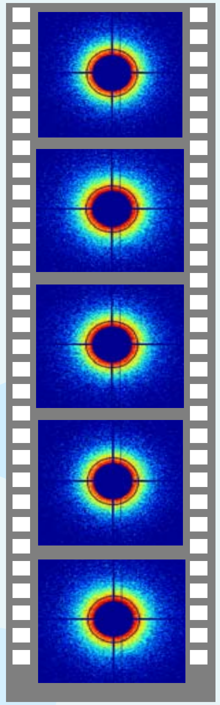
X-ray pump, X-ray probe..

XPCS at the X-FEL

Contrast/visibility of speckle pattern obtained by $Var(I(q))/\langle I(q)\rangle^2$ or by looking at the Gamma-Poisson distr.

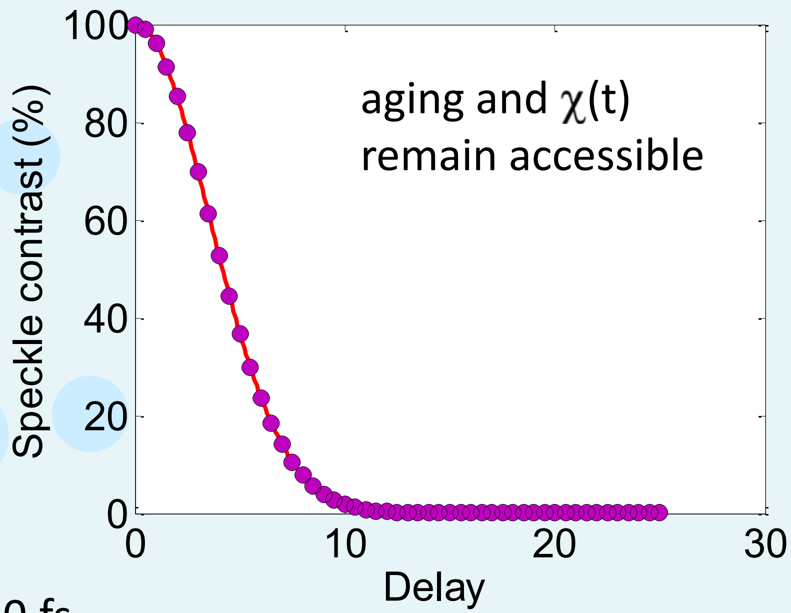


Split-delay line
or delay from linac



Long series of
double-exposures

Contrast analysis leads to $g^{(2)}$

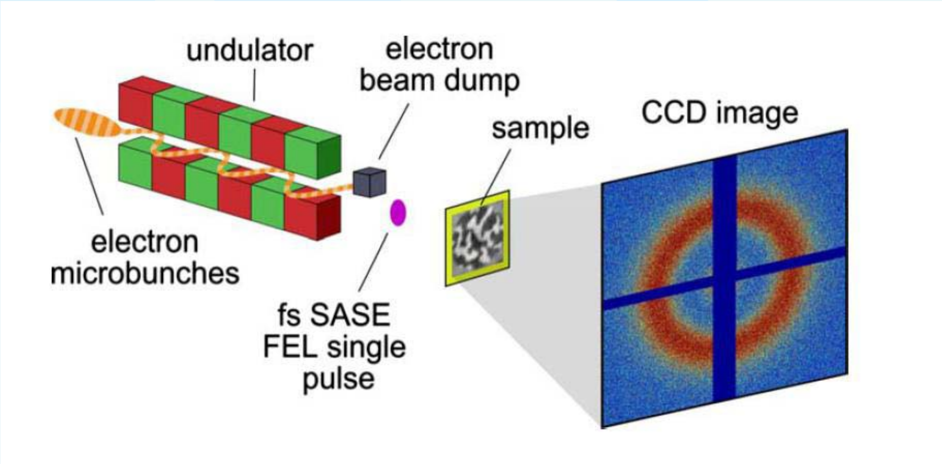


First experience from LCLS shows a pulse duration of 10 fs
Experience from FLASH and calculations indicate that beam damage can be dealt with

XPCS at the X-FEL: Ultrafast processes in cond. matter

Nano/pico/femto-second dynamics on nanoscale in condensed matter

- Molecular excitations (vibrational, rotational)
- Brillouin scattering (phonons)
- Chemistry
- Magneto dynamics
- Polymers and bio-materials



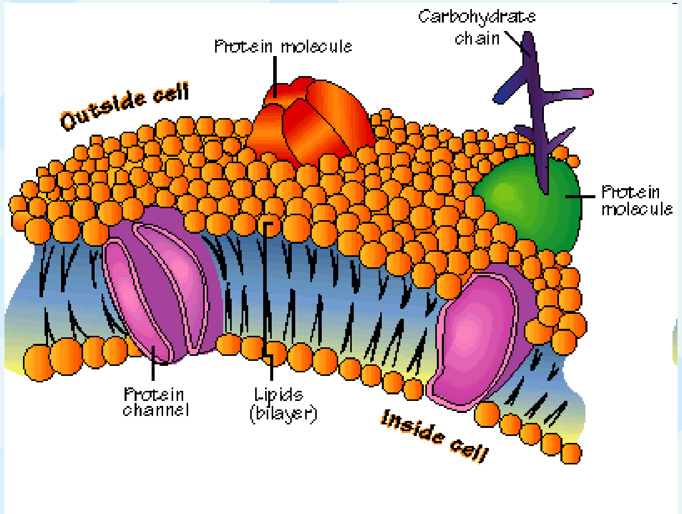
Resonant magnetic scattering
with single XFEL pulses (30 fs) at FLASH

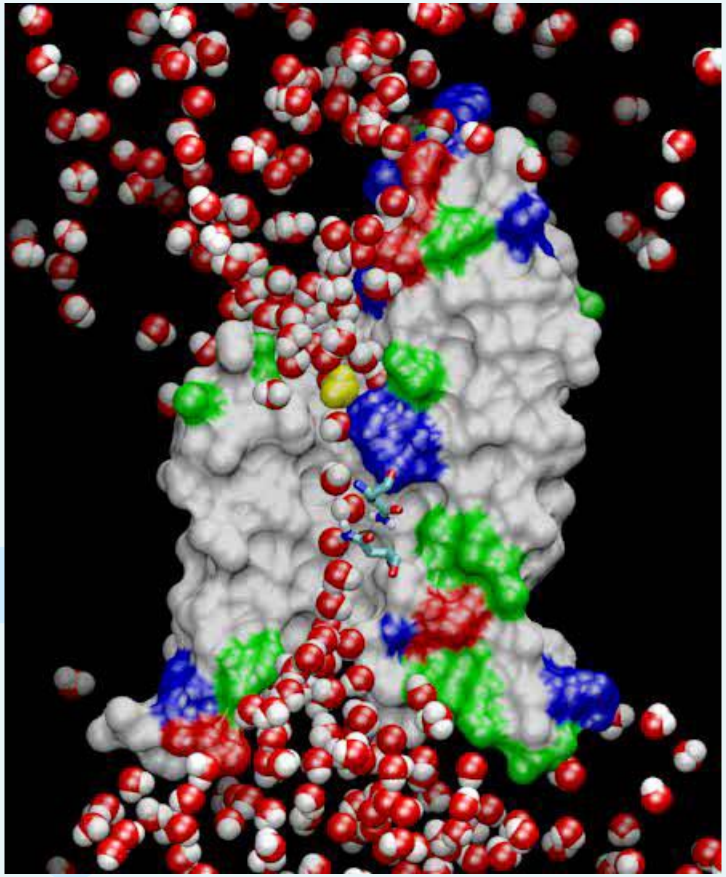
Non-destructive and non-pertubative
below threshold

C. Gutt *et al*, PRB **81**, 100401(R) (2010)

Co/Pt multilayer, λ=20.8 nm (Co $M_{2,3}$ edge)

XPCS at the X-FEL: Ultrafast processes in bio- and soft matter





Movie: Theoretical and Computational Biophysics group, University of Illinois

Dynamics of functional biomolecules
all length scales and timescales matter

a cell can quasi-instantaneously switch on or off its permeability for a protein over the whole surface; that can only be understood as a collective dynamical phenomenon

Sources of additional information

G. Grübel, A. Madsen and A. Robert: X-ray Photon Correlation Spectroscopy, Chapter 18 in *Soft Matter Characterization; R. Borsali and R. Pecora (editors). Springer 2008*
http://www.springer.com/materials/book/978-1-4020-4464-9

ID10A homepage: http://www.esrf.eu/UsersAndScience/Experiments/SoftMatter/ID10A/

MID workshop: http://www.xfel.eu/events/workshops/2009/mid_workshop_2009/

XFEL TDR and science case: http://xfel.desy.de/tdr/tdr/

LCSL homepage: http://lcls.slac.stanford.edu/