Coherent X-ray Scattering and X-ray Photon Correlation Spectroscopy

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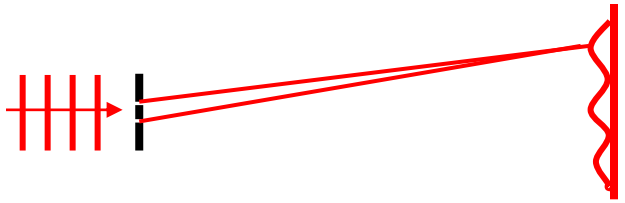
http://www.niu.edu/~llurio/coherence/

What is Coherence?

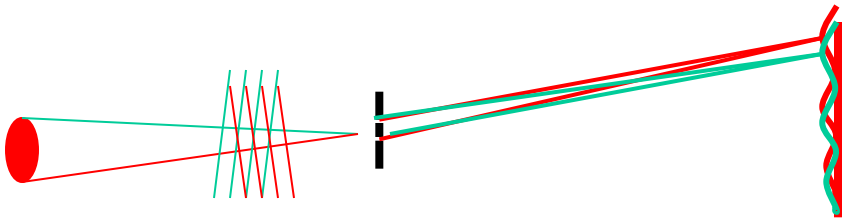
Ideal Young's double slit experiment



Intensity varies as

$$I = 2I_0\left[1+\cos\left(2\pi d\sin(\theta)/\lambda\right)\right]$$

Real Young's double slit experiment



Intensity varies as

$$I = 2I_0\left[1+\beta\cos\left(2\pi d\sin(\theta)/\lambda\right)\right]$$

β is the contrast, determined by the angular size of the source

What Can You Do With Coherence?

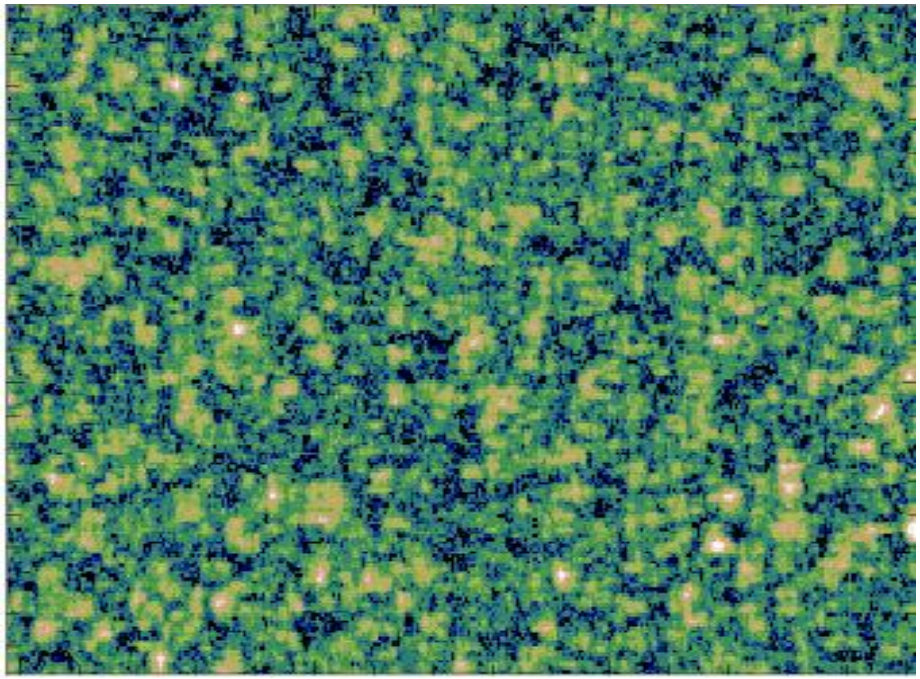
The cross section for x-ray scattering involves a F.T. of the electron density

$$I(Q) \propto \iint e^{i\vec{Q}\cdot(\vec{r}-\vec{r}')}\rho_e(\vec{r})\rho_e(\vec{r}')d\vec{r}d\vec{r}'$$

For incoherent x-rays the scattering is a statistical average over many incoherent regions

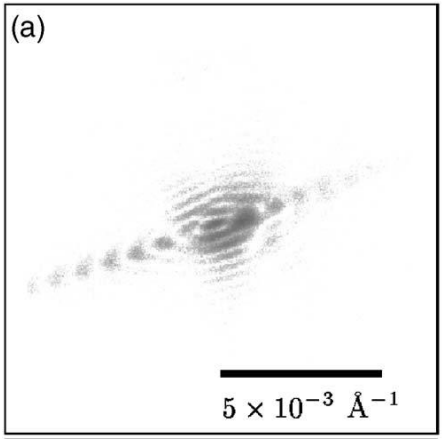
$$\rho_e(\vec{r})\rho_e(\vec{r}-\vec{r}') \approx \left\langle \rho_e(\vec{r})\rho_e(\vec{r}-\vec{r}') \right\rangle \equiv g(\vec{r})$$

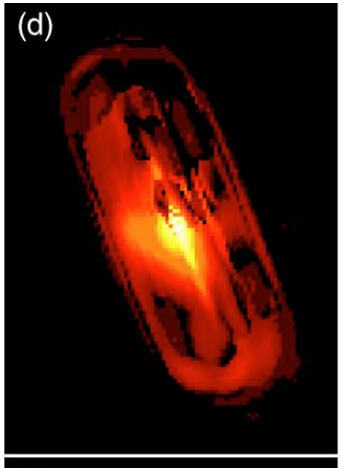
For coherent x-rays one measures the Fourier transform of the exact density distribution, not the average. What one observes is a speckle pattern superposed on the average scattering pattern.



Inverting Speckle Patterns

- A reverse F.T. of the speckle pattern can give the exact arrangement of atoms in the sample. Even though the phase is lost, there are techniques for recovering this.
- Speckle inversion requires collecting data from several angles and to high statistical accuracy.
- Measuring sample dynamics via repeated speckle inversion as a function of time seems impractical.





Reconstruction of structure of a gold crystallite. G. J. Williams, M. A. Pfeifer, I. A. Vartanyants, and I. K. Robinson, PRB 73, 94112

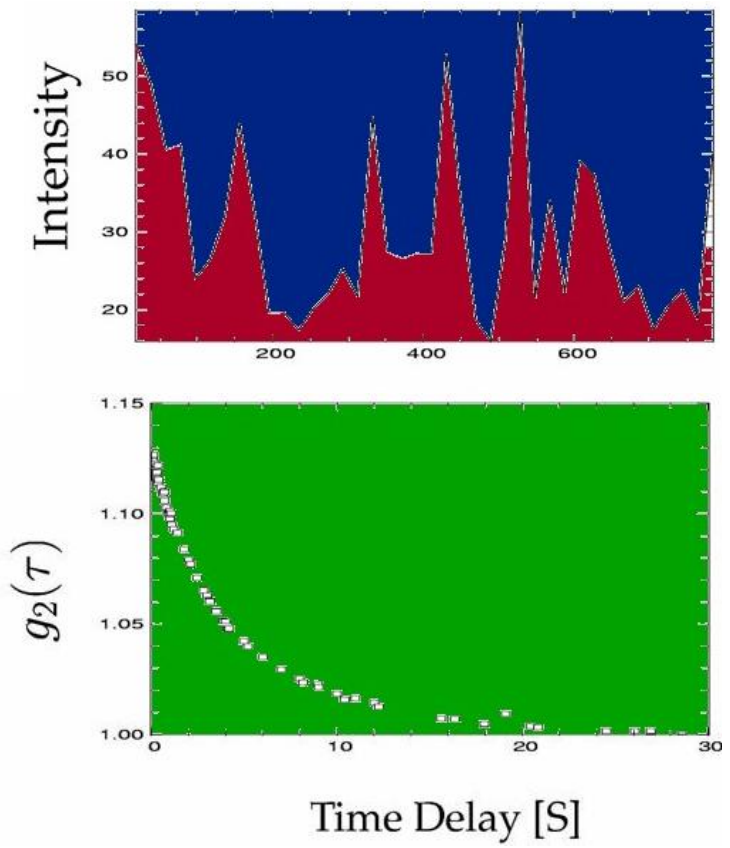
Time Correlation Functions

(X-ray Photon Correlation Spectroscopy)

Consider the time correlation function of the intensity within a single speckle of a coherent scattering pattern.

$$g_2(\tau) = \langle I(t)I(t+\tau)\rangle / \langle I\rangle^2$$

This function is called “g-2” since it is a second order correlation (e.g. it correlates intensities instead of electric field amplitudes). The correlation function contains information about the dynamics of the sample. By correlating the intensity within a single speckle at a particular scattering wavevector Q, one learns about the dynamics for fluctuations with that wavevector.



How to connect g_2 with sample dynamics

•Calculate electric field intensity correlation function at the observation point:

$$g_2(Q,\tau)=\int e^{iQ\cdot r'}\langle E^2(r,t)\,E^2(r+r',t+t)\rangle_{r,t}dr'/I^2$$

•Under reasonable assumptions, the fourth order correlations in E, can be reduced to pairs of second order correlation functions.

$$g_2(Q,\tau)=1+\beta\langle E(Q,0)\,E(Q,\tau)\rangle^2/I^2$$

•The electric field correlation yields the normalized dynamic structure factor (called the intermediate scattering function):

$$\langle E(Q,0)\,E(Q,\tau)\rangle/I=F(Q,\tau)/F(Q,0)=f(Q,\tau)$$

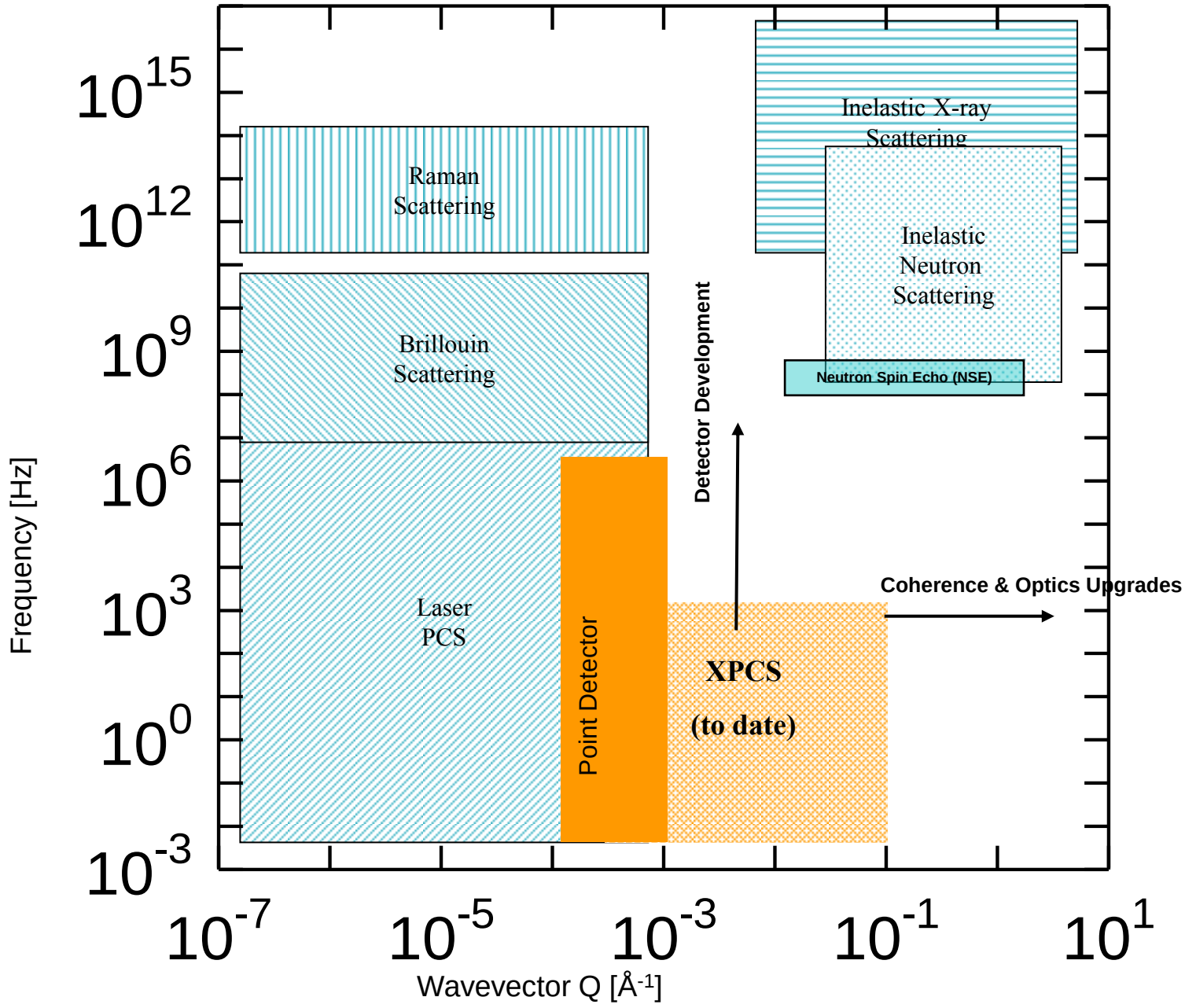
where $F(Q,\tau)=\int e^{iQ\cdot r}\langle\rho(0,0)\rho(r,\tau)\rangle dr$

Significance of the Intermediate Scattering Function $f(Q,\tau)$

The intermediate scattering function gives information on fluctuations of a sample in equilibrium.

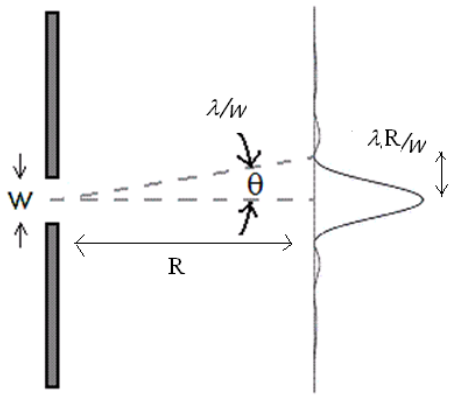
- Brownian Motion and Diffusion
- Surface and Membrane Fluctuations
- Density Fluctuations
- Concentration fluctuations in a binary fluid or solid
- Fluctuations of the order parameter of a crystal.
- Atomic fluctuations about lattice positions

While time resolved x-ray scattering can measure changes in average structure with time, fluctuations about the average structure are invisible to incoherent x-rays. This is the chief value of X-ray Photon Correlation Spectroscopy (XPCS)


Inelastic X-ray Scattering
Raman Scattering
Inelastic Neutron Scattering
Brillouin Scattering
Neutron Spin Echo (NSE)
Detector Development
Coherence & Optics Upgrades
Laser PCS
Point Detector
XPCS
(to date)
Frequency [Hz]
10^{15}
10^{12}
10^{9}
10^{6}
10^{3}
10^{0}
10^{-3}
10^{-7}
10^{-5}
10^{-3}
10^{-1}
10^{1}
Wavevector Q [Å^{-1}]

How Coherent are Undulator Sources?

The coherence length of an x-ray source (assuming the source is initially incoherent) is approximately the size of the first diffraction minimum from a slit the size of the source

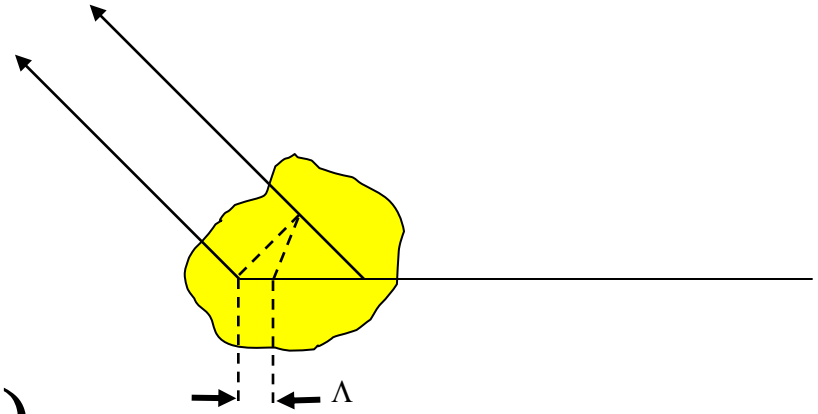


More exactly: for a Gaussian source profile of width σ the coherence length of the source is given by:

$$\xi = \frac{\lambda R}{2\sigma\sqrt{\pi}}$$

At current third generation synchrotron sources this is typically of order a few tens of microns.

Longitudinal coherence



$$\Lambda \approx \lambda(E / \Delta E)$$

e.g. the number of wavelengths that can be added before the uncertainty adds up to a full wavelength.

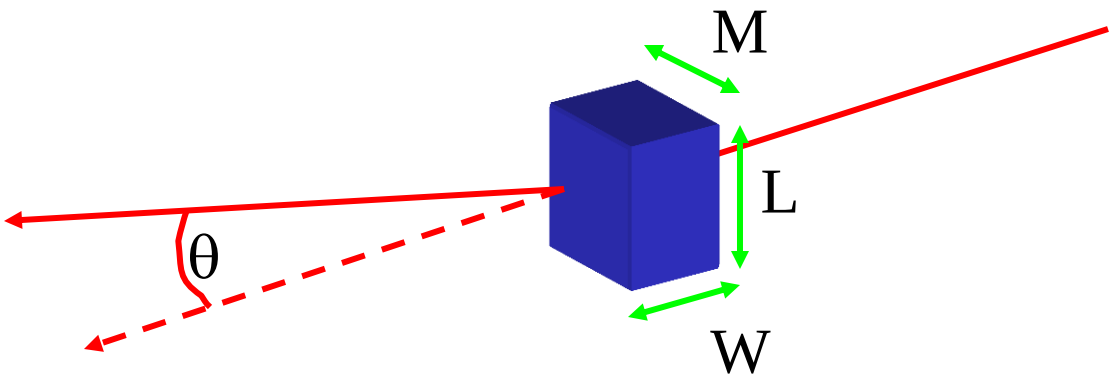
Can also be viewed as a coherence time $T_c = \Lambda/c$

Speckle Size and Contrast

The speckle widths are approximately the size of the diffraction pattern from a slit the size of the sample:

$$\Delta\theta \approx \lambda / L$$

The contrast is given by the ratio of the scattering volume to the coherence volume, $\Lambda\xi_x\xi_y/MLW\sin(\theta)$



Exact numbers require integrals over the sample volume and electric field spatial correlation function. For small angles, the scattering volume is much smaller than the sample volume.

How Practical is it to Make X-rays Coherent?

Consider a point 65 meters downstream of an APS Undulator A

$$\lambda = 0.2\text{nm}, \quad \Delta\lambda/\lambda = 3\times10^{-4}$$

Ge 111

$$\sigma_x = 254\mu\text{m}, \sigma_y = 12\mu\text{m}$$

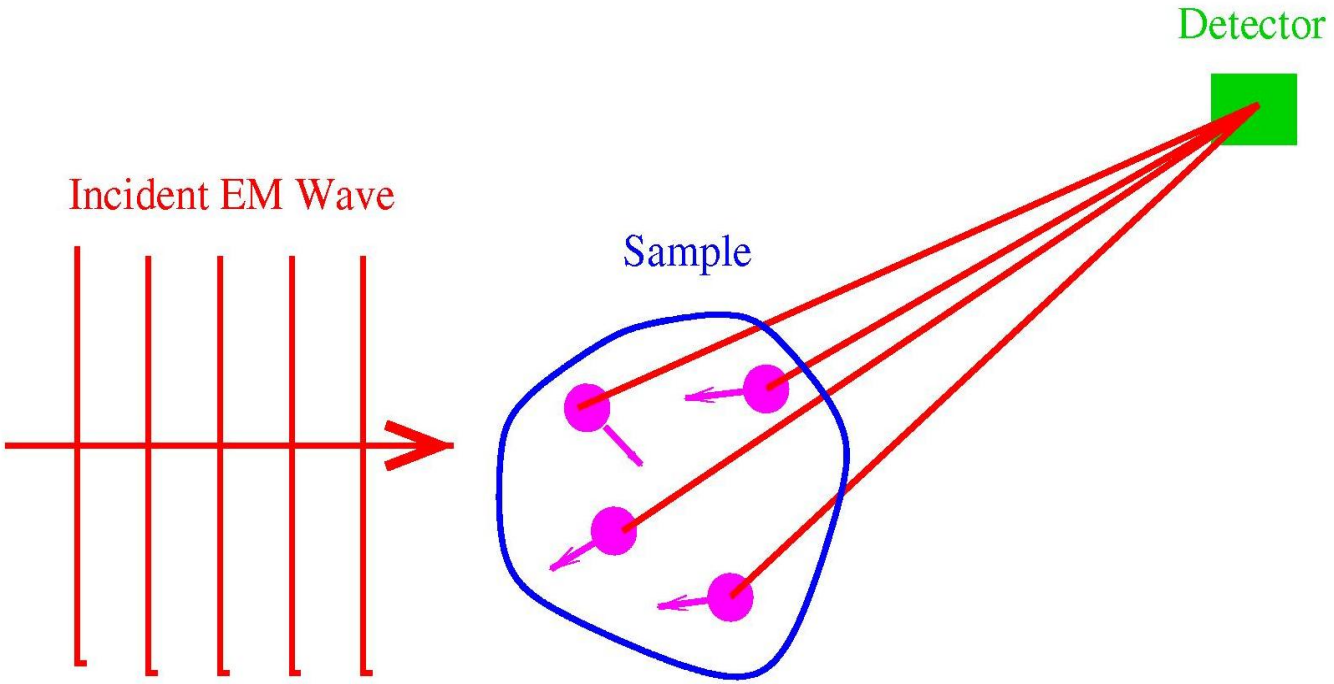
$$\xi_x = \frac{\lambda R}{2\sigma_x\sqrt{\pi}} = 14\mu\text{m}$$

$$\xi_y = \frac{\lambda R}{2\sigma y\sqrt{\pi}} = 306\mu\text{m}$$

$$\Lambda = 0.66\mu\text{m}$$

$\sim 3\times10^{10}$ Photons/Coherence Area

A simple example: Brownian motion of colloidal particles



How to calculate $f(Q,\tau)$ for diffusion of point particles (colloids)

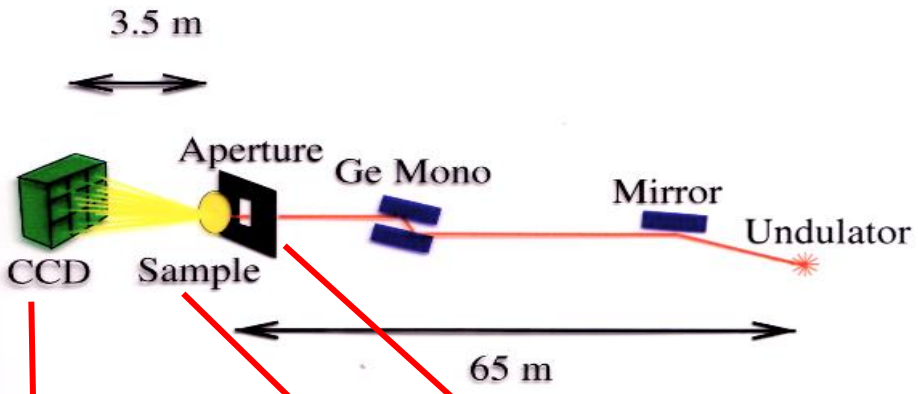
$$f(\vec{Q},\tau)=\frac{1}{N}\sum_{i,j}e^{i\vec{Q}\cdot\left(\vec{r}_i(0)-\vec{r}_j(\tau)\right)}\approx\frac{1}{N}\sum_{i}e^{i\vec{Q}\cdot\left(\vec{r}_i(0)-\vec{r}_i(\tau)\right)}=\left\langle e^{i\vec{Q}\cdot\Delta r(\tau)}\right\rangle$$

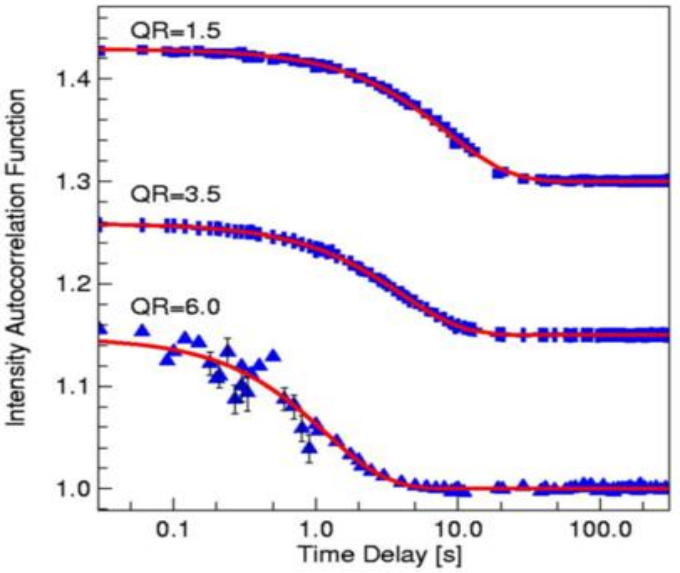
$$\left\langle\sum_i e^{i\vec{Q}\cdot\overrightarrow{\Delta r_i}}\right\rangle=e^{-\frac{1}{2}\left\langle\left(\vec{Q}\cdot\overrightarrow{\Delta r(\tau)}\right)^2\right\rangle}=e^{-\frac{1}{6}Q^2\left\langle\Delta r(\tau)\right\rangle^2}=e^{-DQ^2\tau}$$

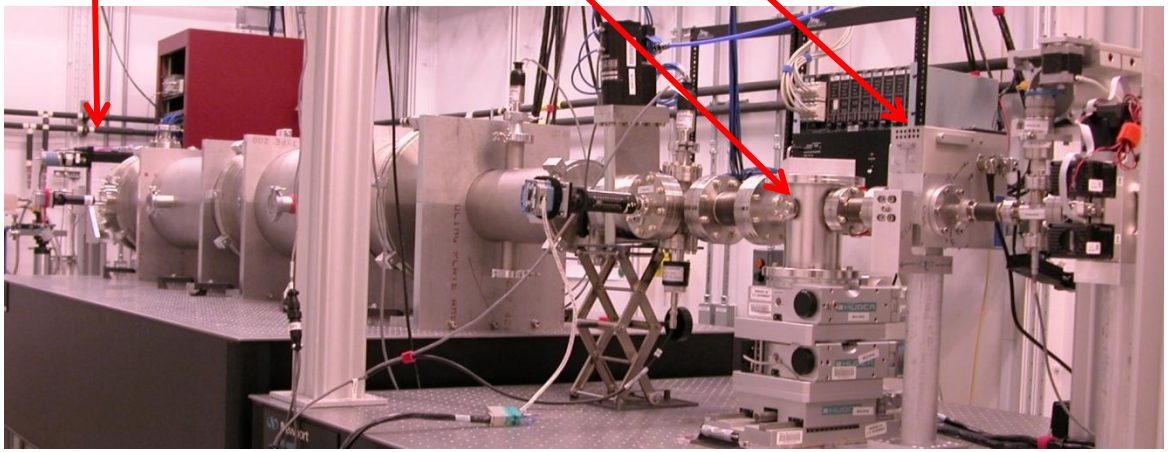
Conclusion: For simple diffusive motion; $f(Q,\tau)=\exp(-\Gamma\tau)$ with $\Gamma=DQ^2$.

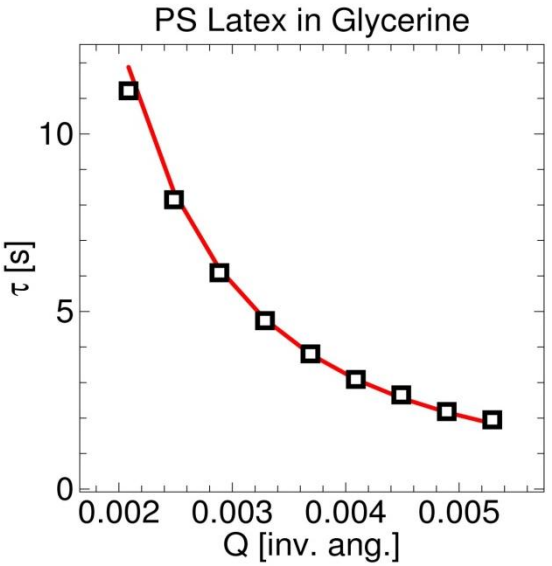
In fact, this is generally true that diffusive behavior leads to an exponential decay in f.

A dilute colloidal suspension (R=71 nm Latex in Glycerine)









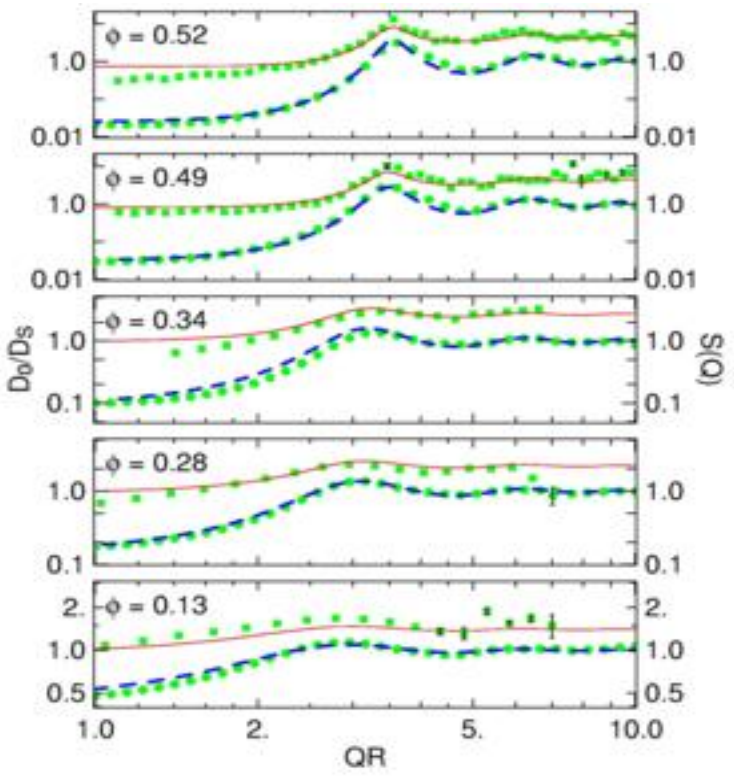
Some XPCS scientific examples

Example 1: Diffusion in concentrated colloidal suspensions

PRL Lurio *et. al.* 2000

1. Structural correlations lead to a slowing down of dynamics
2. Hydrodynamic interactions further modify the dynamics at high concentration
3. These effects can be calculated for the initial decay rate of the correlation function, but the $f(Q,\tau)$ will not generally be an exponential at long times. The diffusion coefficient will be increased by a hydrodynamic factor $H(Q)$ and decreased by the sample structure factor $S(Q)$:

$$D(Q)=D_0(Q)H(Q)/S(Q)$$

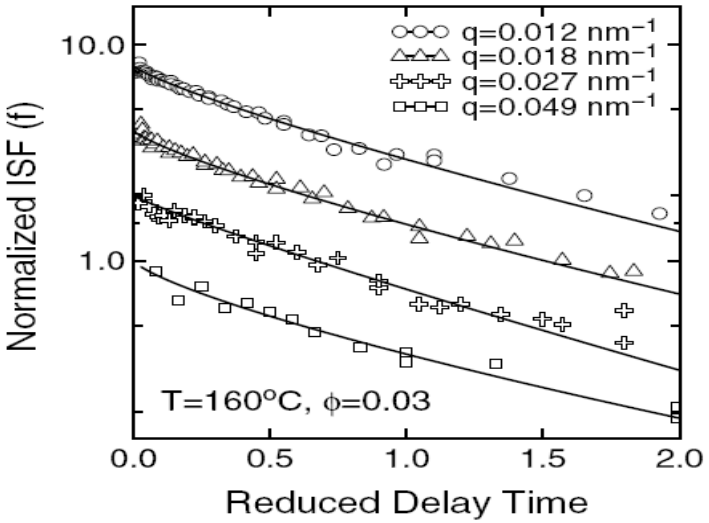


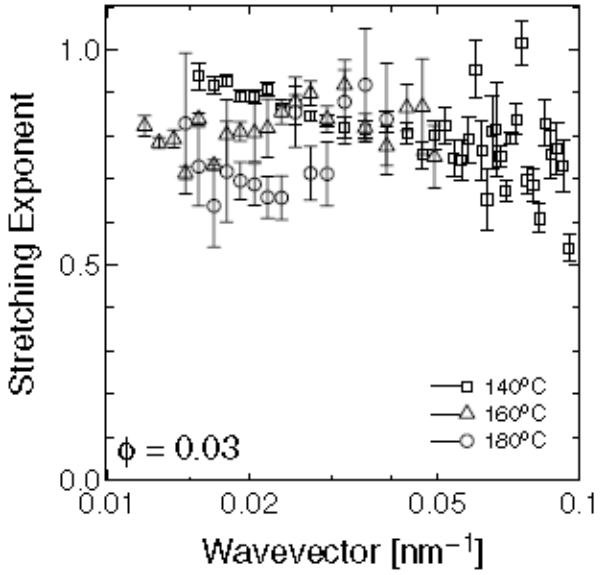
Example 2: Diffusion in Concentrated Polymeric Vesicles

PRL Falus *et. al.* 2005

In polymeric vesicle systems the ISF shows a stretched exponential:
$f(Q,\tau)=\exp[-(\Gamma\tau)^{\alpha}]$.

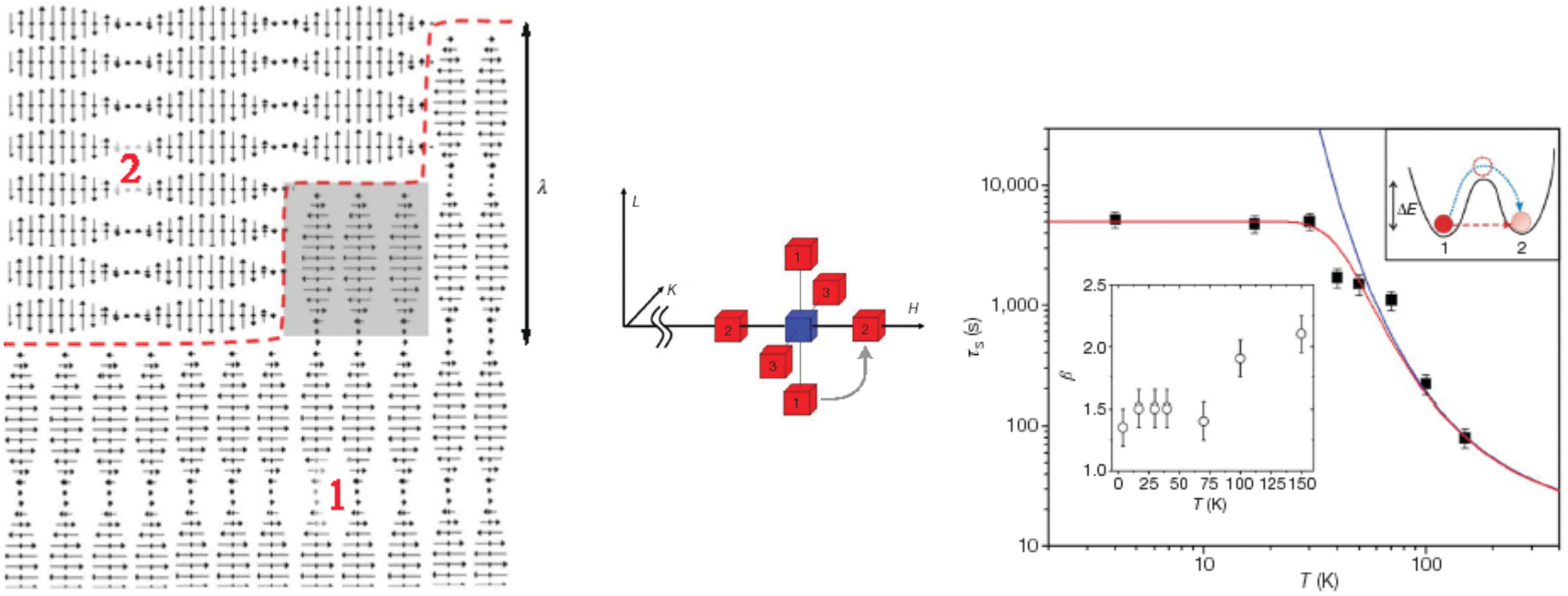
Theory predicts α=.67
experiment give α=.8 ±1





Example 3: Antiferromagnetic Domain Fluctuations

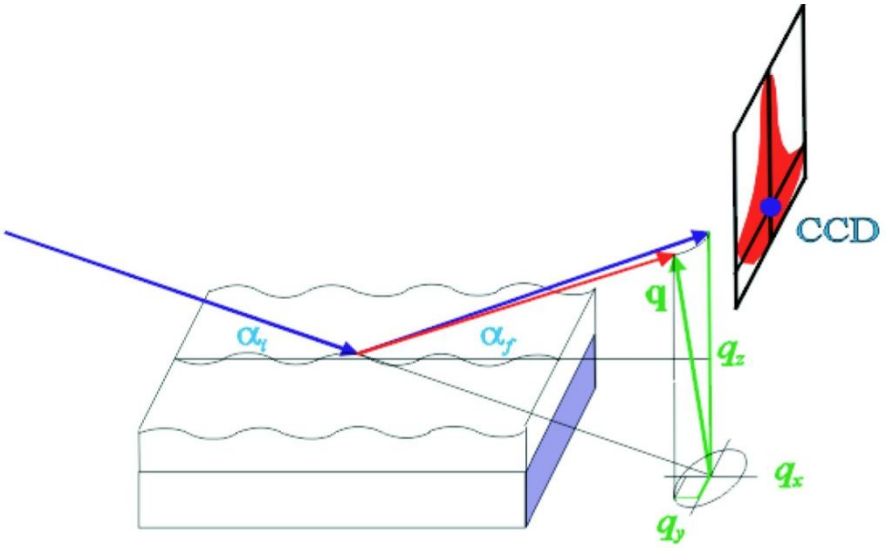
Nature Shpyrko *et. al.* 2007.

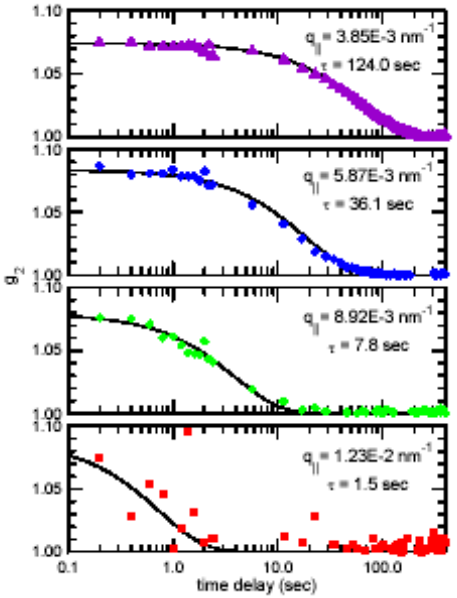


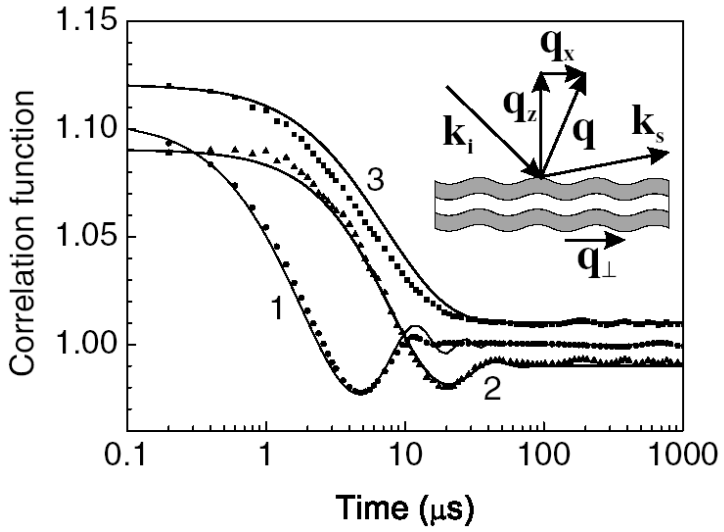
Note that although the length scale of the fluctuations is large (>10 nm) they require x-rays with wavelengths ~0.1 nm in order to be visible. In this case, compressed exponentials are seen α>1 indicating relaxation of stress (nonequilibrium behavior).

Example 4: Dynamics of Surfaces

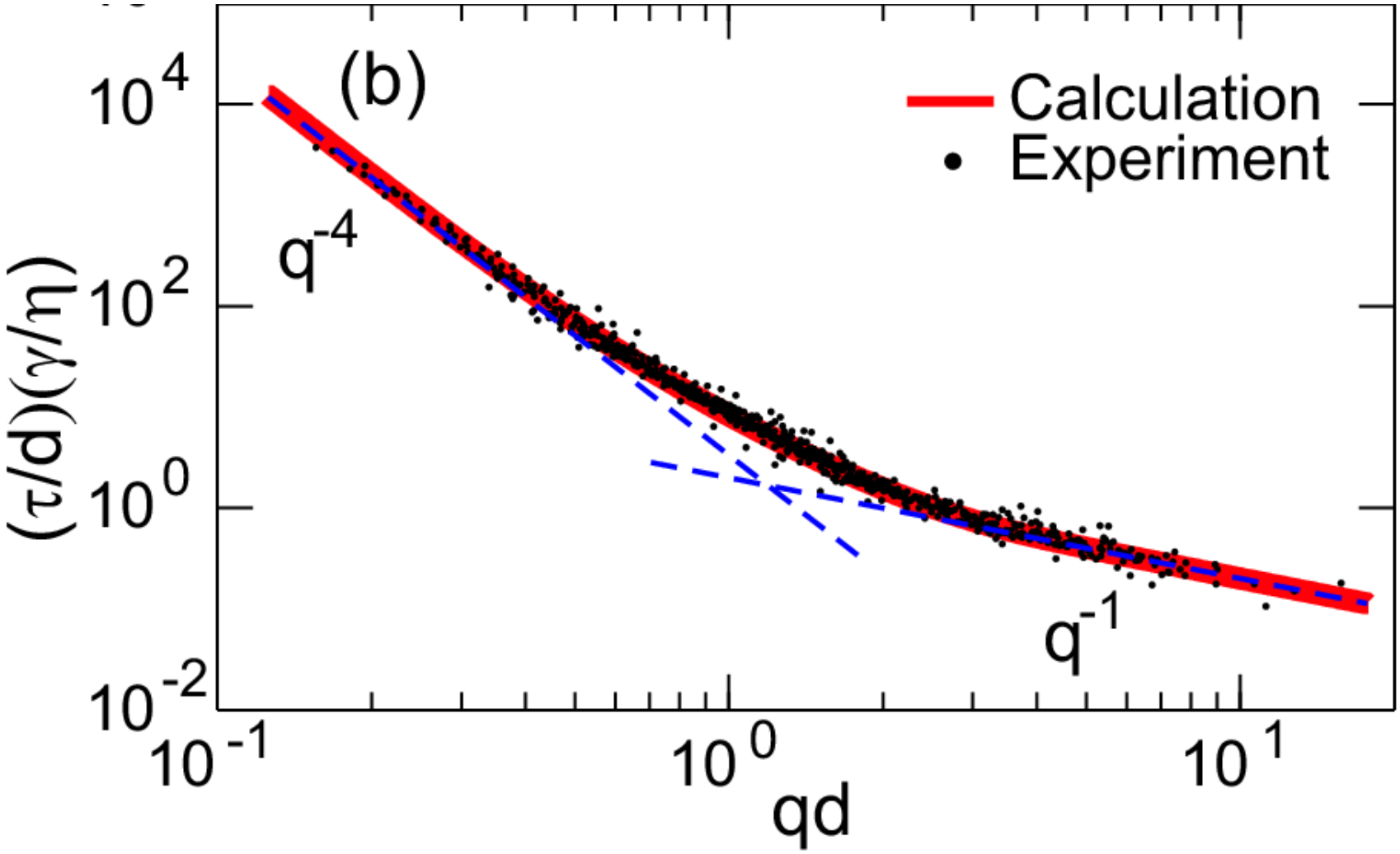
PRL Kim *et. al.* 2003 PRL Sikharulidze *et. al.* 2002







- Polystyrene films on Si wafers (Kim) are highly viscous and show exponential decay
- Thin liquid crystal membranes (Sikharulidze) show transition from oscillatory to overdamped behavior.

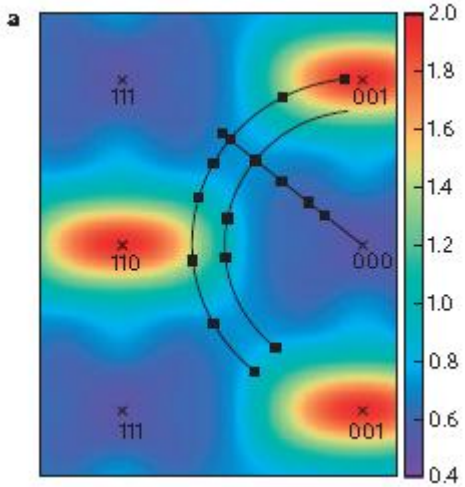


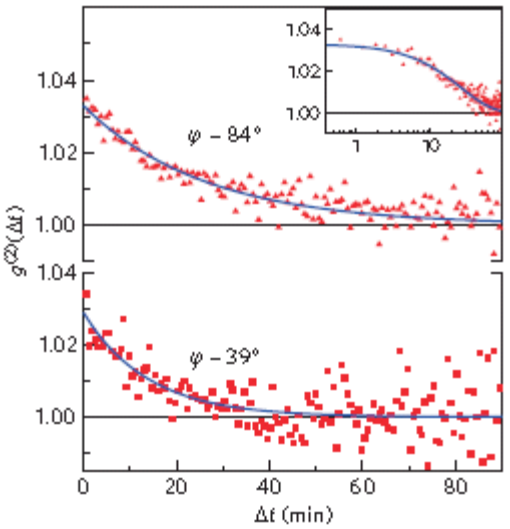
From Jiang et. al. PRL, 246104, 2008

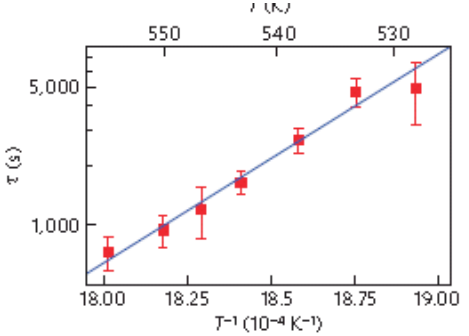
Example 5 atomic jumps in a binary alloy

M. Leitner, B. Sepiol, L.-M. Stadler, B. Pfau, and G. Vogl, Nature Materials **8, 717-20 (2009).**

Measure XPCS from thermal diffuse scattering between Bragg peaks. Study CuAu alloy so as to have strong scattering cross section. Dynamics corresponds to Cu-Au place exchange. At low temperature this dynamics is of order tens of minutes.

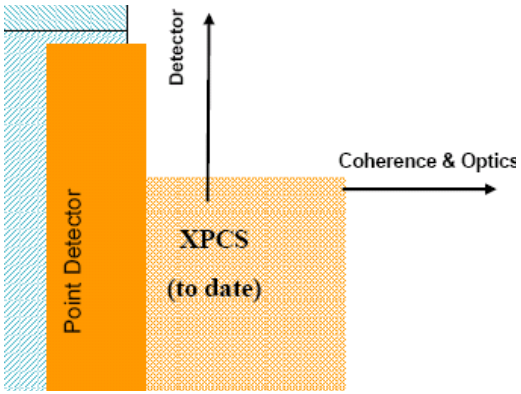






Limitations of XPCS

- Too much flux (X-ray damage)
  - Radiation can cause cross linking of polymers and charging of colloids.
  - A reasonably radiation resistant polymer (PS) in vacuum can absorb around ~10^7 Gy. (10 min in surface reflection geometry)
  - Protein in water can absorb ~10^5 Gy (10 sec in transmission geometry)
  - At very high fluxes (such as LCLS) heating can melt sample.
- Too little flux (Poor signal to noise)



Some tricks of the trade …

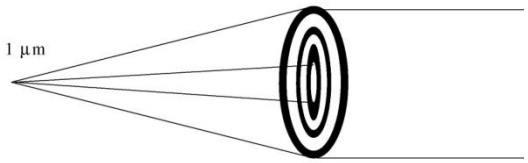
Multispeckle Detection

- Falus, Borthwick, Mochrie, RSI (2004)
- SNR increases as $\sqrt{N}$
- New Camera under development at LBL and APS ~50 Hz at 100% efficiency. (Alec Sandy, John Weizeorick, Tim Madden)

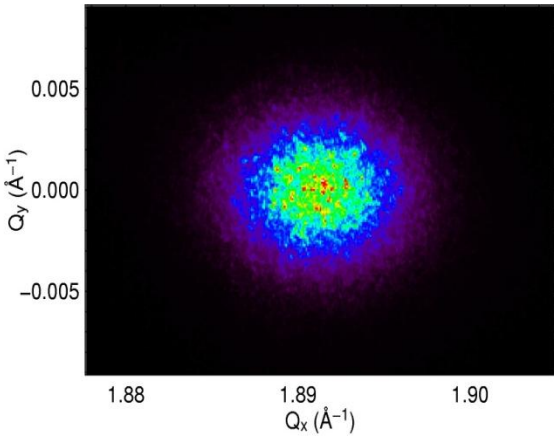
Focusing

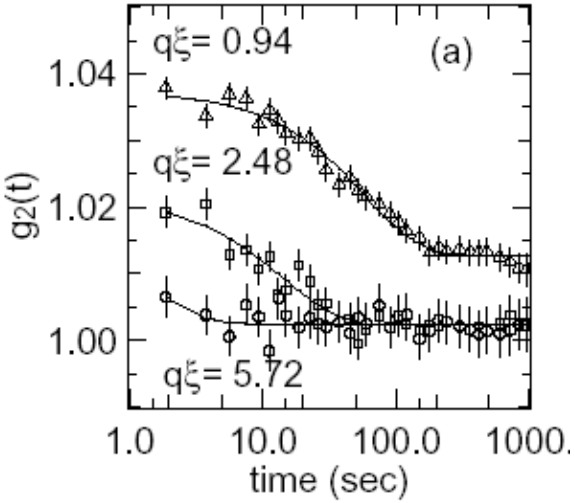
Khalid Laaziri and Mark Sutton

- Focusing the x-ray beam down to a small spot (~1 μm) maintains flux, but increases the speckle size. SNR ~ photons/speckle, so SNR goes up. Disadvantage is that radiation damage goes up as well.
- Fluctuations in Fe_3Al



Fresnel Zone Plate





Flowing Sample

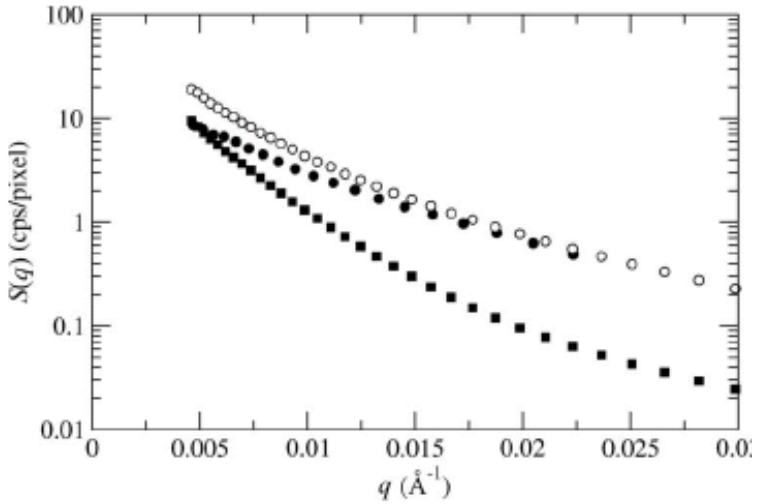
Marchand, Mukhopadhyay, Lurio

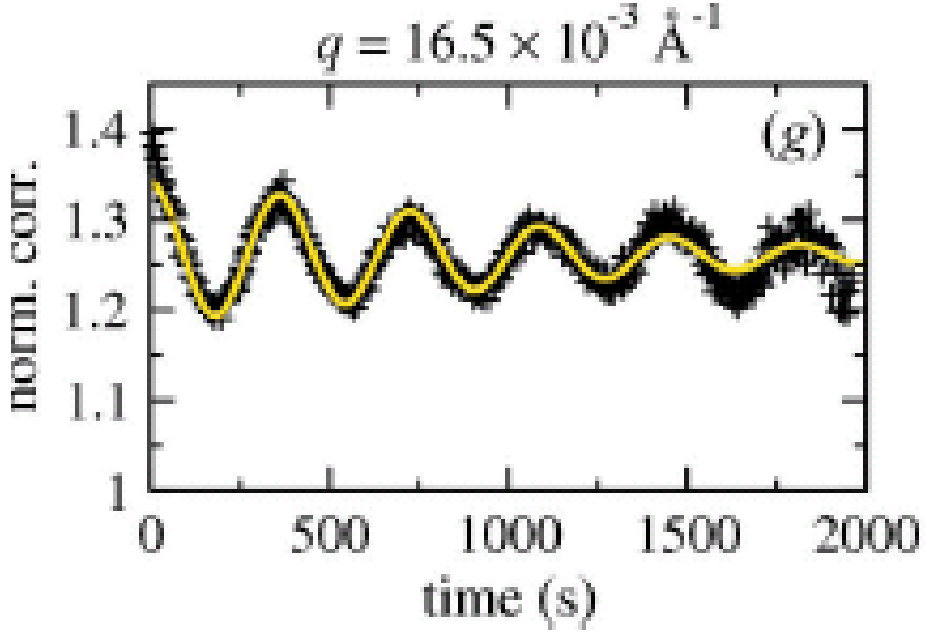
- Continuously flow sample so as to reduce damage.
- Alternately, step sample over short intervals to reduce damage.

Heterodyne Detection

Livet. et. al. JSR (2006)

- Mix a static signal with a weaker dynamic signal.
- For diffusive motion relaxation times are longer: exp(-Γt/) instead of exp(-2Γt).
- Constant flow can be detected, which is invisible to homodyne. (example aerosil + carbon-black rubber)





Future Developments

- Better Detectors: Faster detectors with higher efficiencies would yield immediate improvement in XPCS with no commensurate increase in x-ray damage
- Better Optics: Preserve coherence, tailor coherence lengths and speckle size. Tradeoff of flux damage with focusing.
- Better X-ray sources: Longer undulators, Energy Recovery Linacs. (NSLS II and APS Refresh)
- X-ray lasers provide completely coherent sources with extremely high intensity. However flux damage is a serious issue.

References

- **This talk:** http://www.niu.edu/~llurio/coherence/
- **XPCS:**
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