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

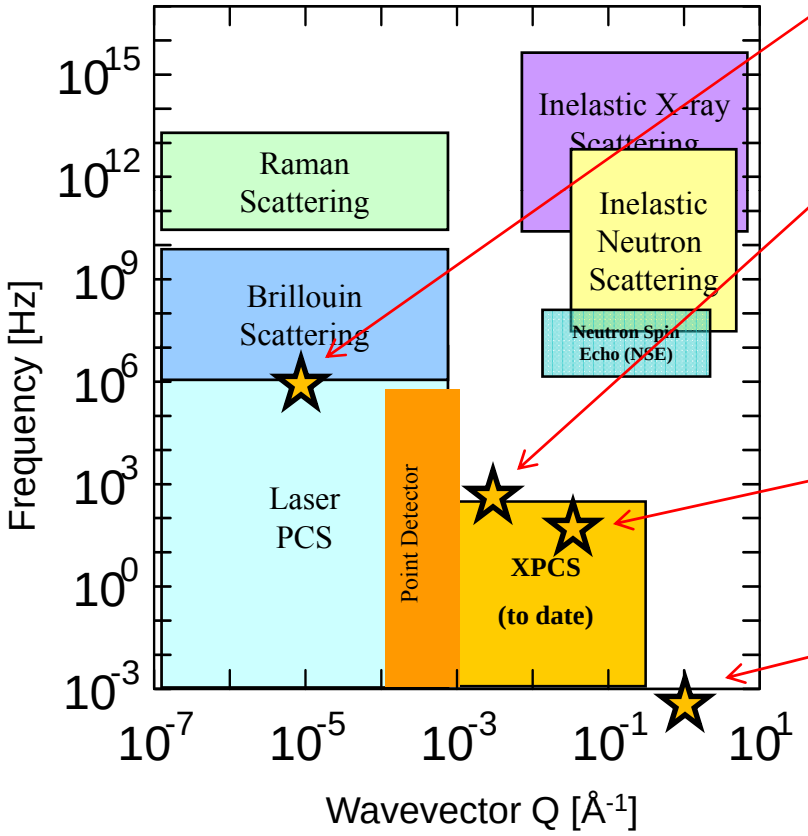
Laurence Lurio
Department of Physics
Northern Illinois University

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

Outline

- Theory of X-ray Photon Correlation Spectroscopy
- Some examples of work done using XPCS
- Experimental tricks of the trade
- The future of XPCS

XPCS and Dynamics in Soft Matter



Liquid Surface Capillary Waves

Gutt *et. al.* PRL 91, 076104, (2003)

Colloidal Diffusion

Grübel *et. al.* in Slow Dynamics in Complex Systems

Protein Diffusion

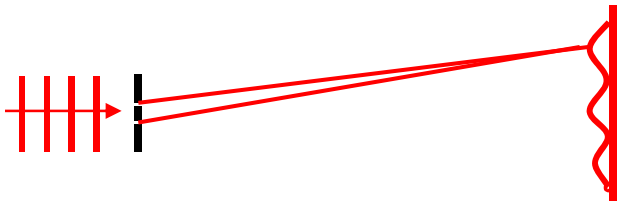
Debartolo et. al. (unpublished)

Atomic Diffusion in CuAu Alloy

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

What is Coherence?

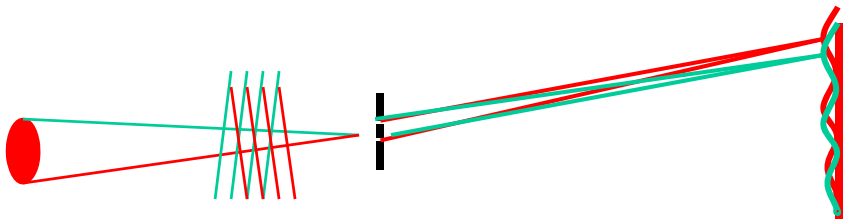
Ideal Young's double slit experiment



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

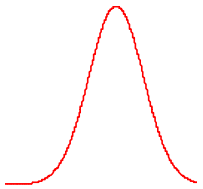
$$I = 2I_0\left[1+\beta\cos\left(2\pi d\sin(\theta)/\lambda\right)\right]$$

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

Coherence Length and Contrast

It is generally convenient to assume the source has a Gaussian intensity profile

$$I(x) = \frac{I_0}{\sqrt{2\pi}\xi} \exp\left[-\left(x - x_0\right)^2 / 2\sigma^2\right]$$



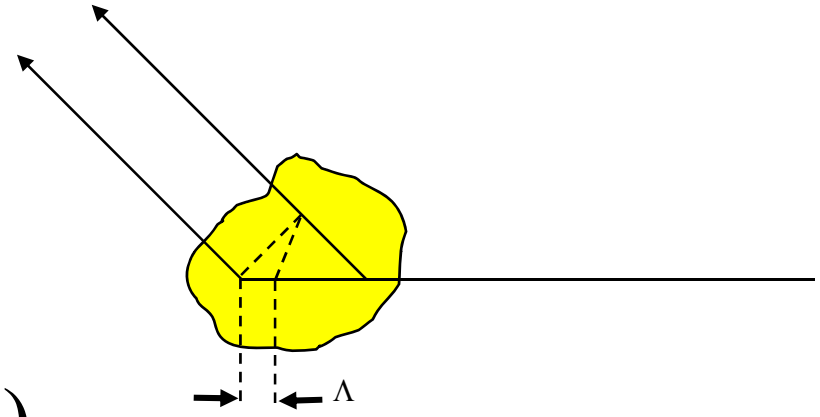
One can then define a coherence length

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

This characterizes the distance over which two slits would produce an interference pattern, or more generally the length scale over which any sample will produce interference effects.

A more rigorous theory can be found in e.g. Born and Wolf

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.

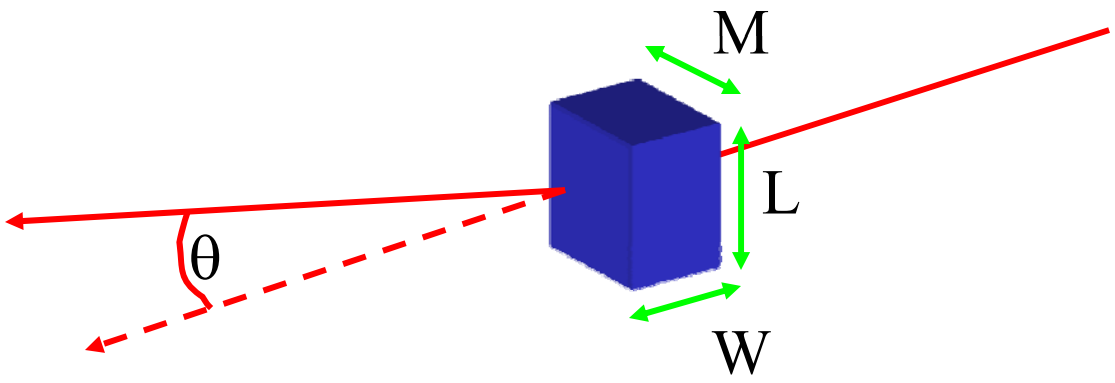
Can also be viewed as a coherence time $T_c = \Lambda/c$

Speckle Size and Contrast

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

$$\Delta\theta \sim \lambda / L$$

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

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

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

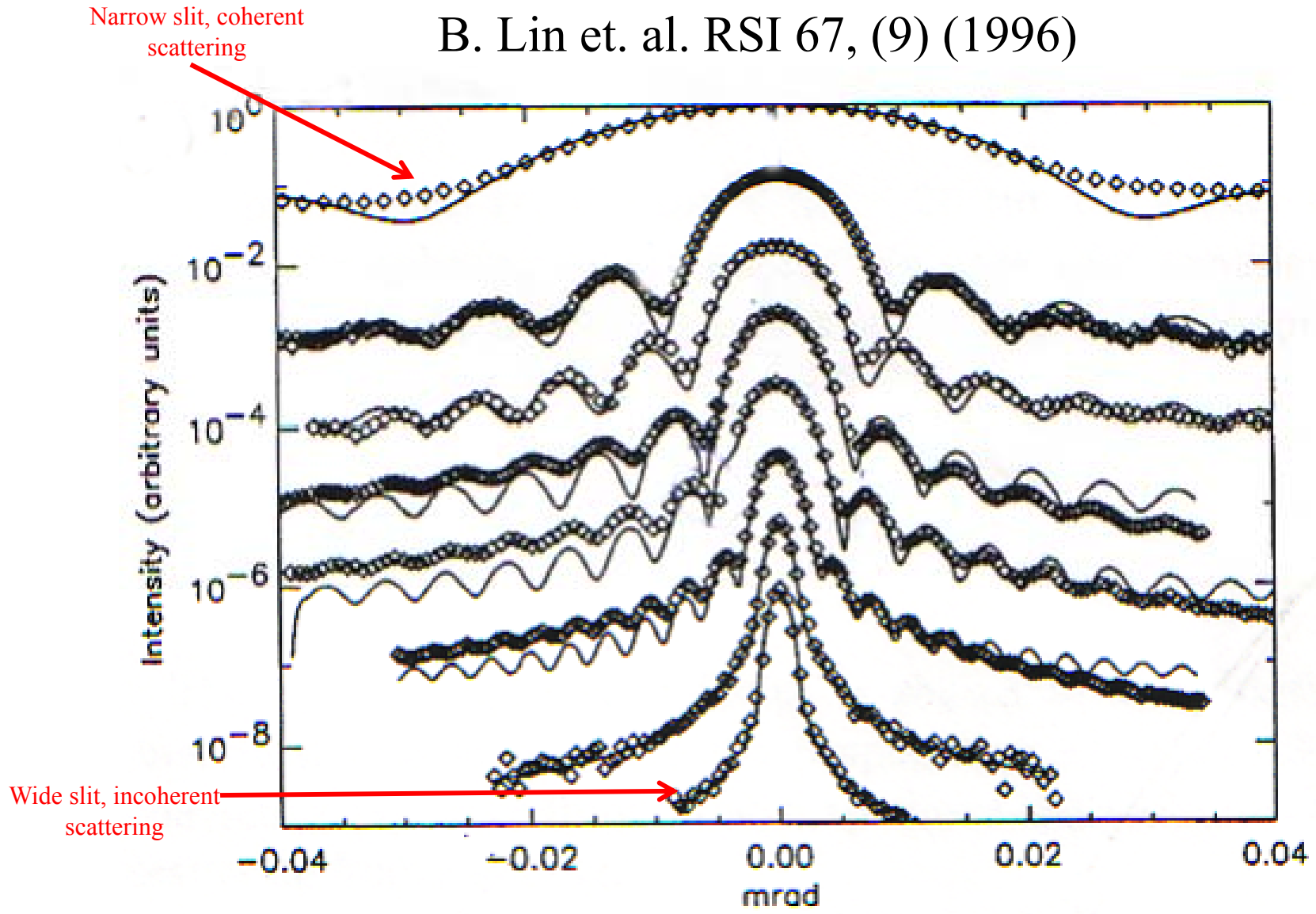
$$\xi_y = \frac{\lambda R}{2\sigma y\sqrt{\pi}} = 306\mu\text{m}$$

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

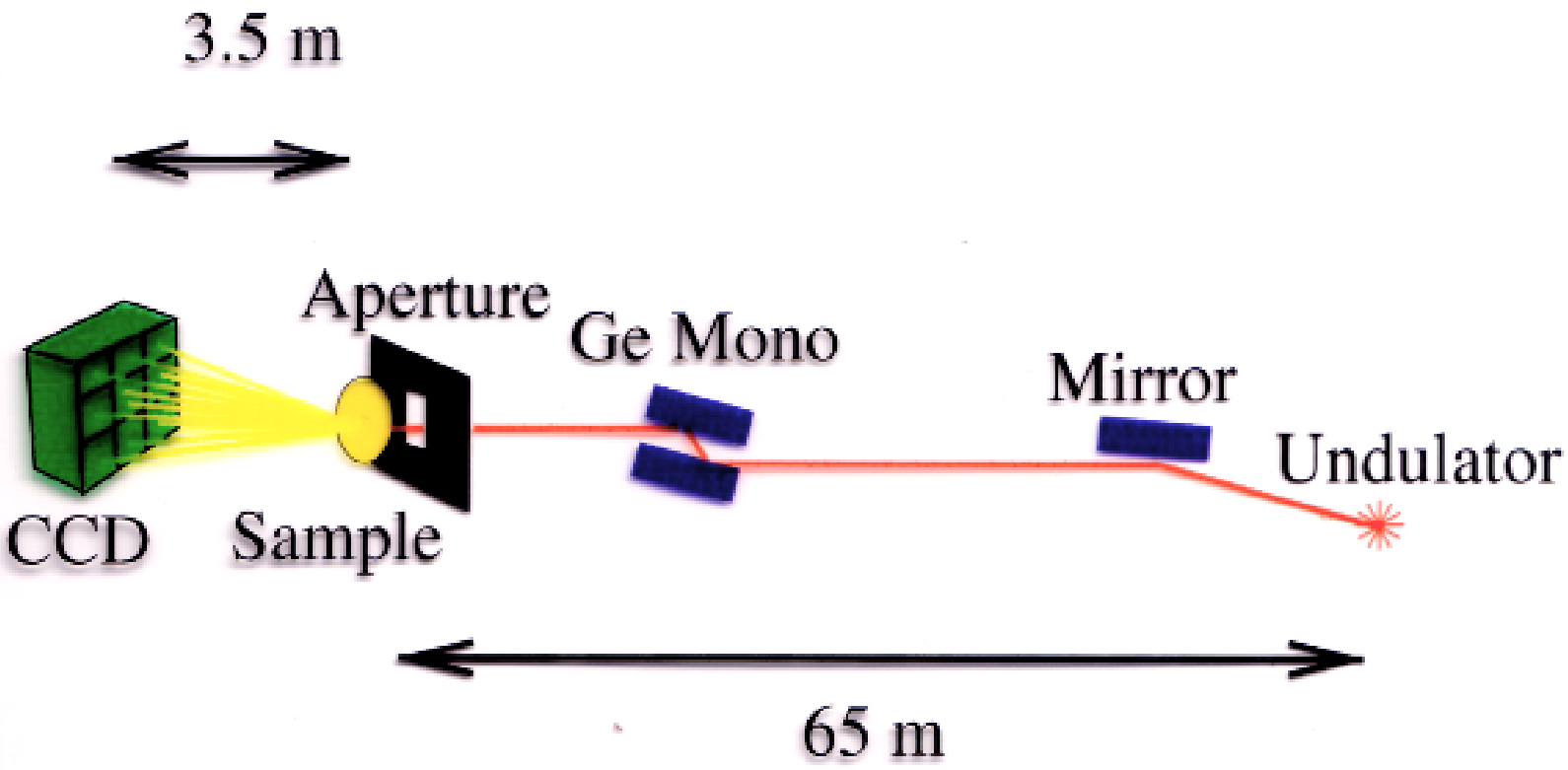
$$\sim 3\times10^{10}\,\text{Photons/Coherence Area}$$

Fraunhofer X-ray Diffraction from a Slit

B. Lin et. al. RSI 67, (9) (1996)



Setup for XPCS at Sector 8 of the APS



Optics must preserve coherence

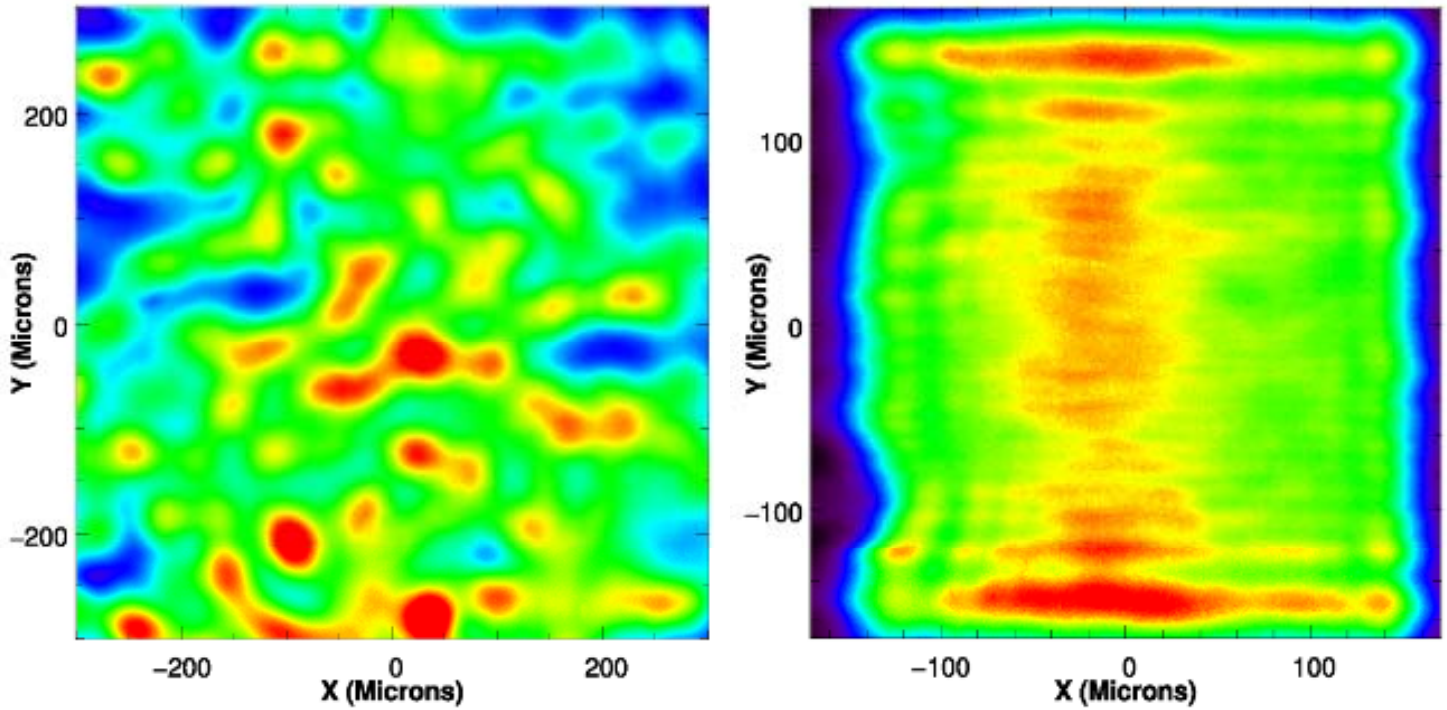


Image of x-ray beam reflected from channel cut monochromator (left) vs. artificial channel cut which allows better polish of interior faces.

S. Naryanan, A. Sandy, M. Sprung, D. Shu and J. Sullivan

Scattering of Coherent X-rays

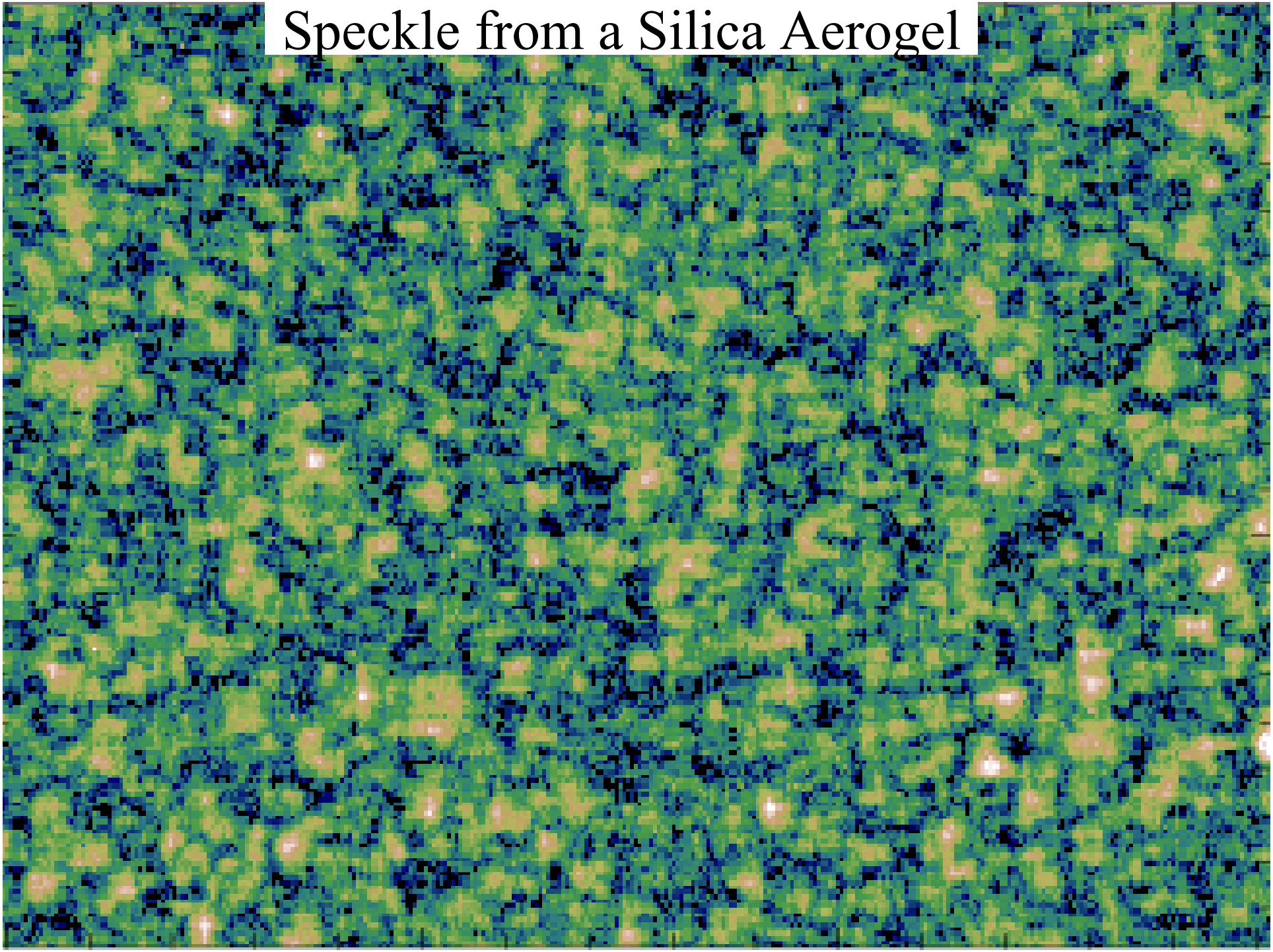
$$I(Q) \sim \int\int e^{i\vec{Q}\cdot\vec{r}} \rho_e\left(\vec{r}+\vec{r}'\right)\rho_e\left(\vec{r}'\right) d\vec{r}d\vec{r}'$$

For incoherent x-rays the measured scattering represents a statistical average over many incoherent regions within the sample and one obtains:

$$\rho_e\left(\vec{r}+\vec{r}'\right)\rho_e\left(\vec{r}'\right) \Rightarrow \left\langle \rho_e\left(\vec{r}+\vec{r}'\right)\rho_e\left(\vec{r}'\right)\right\rangle$$

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.

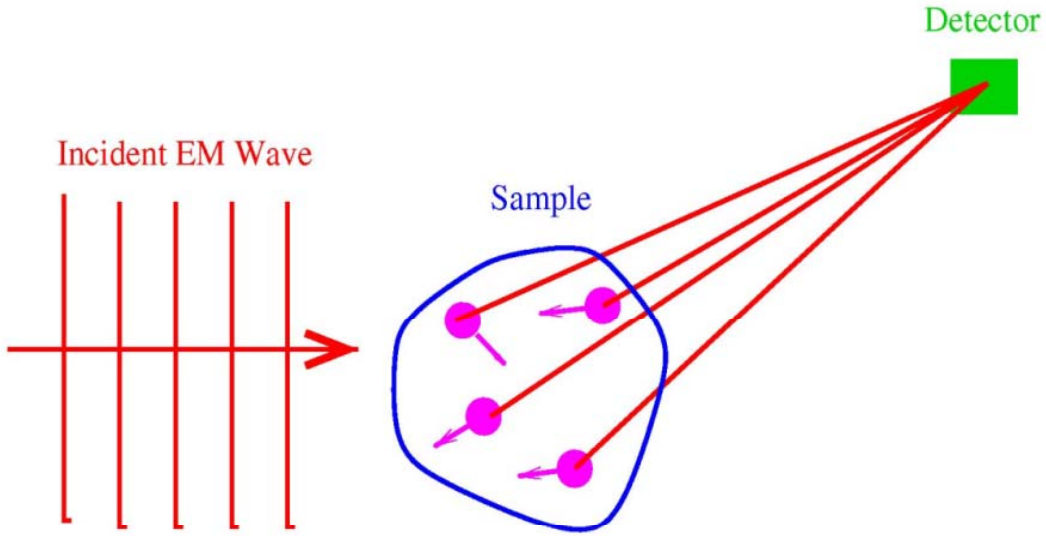
Speckle from a Silica Aerogel

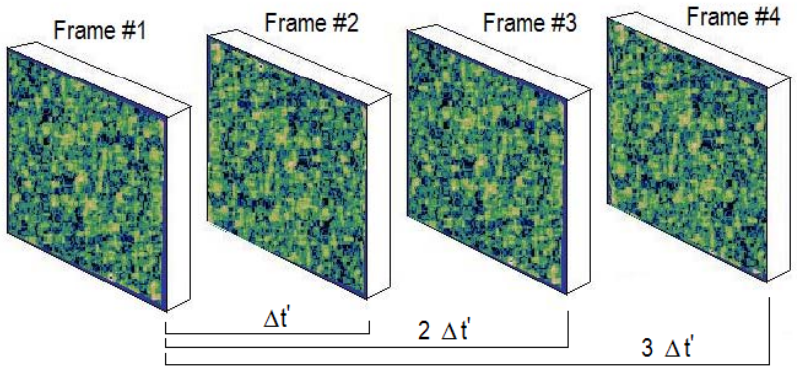


What to do with coherent x-rays?

- Try to invert the speckle to get information about the exact structure factor. (--- phase retrieval x-ray imaging---) Generally to slow to obtain dynamics information.
- Ignore the details of the exact structure factor, but use the time fluctuations of the pattern to study dynamics of the material (XPCS)

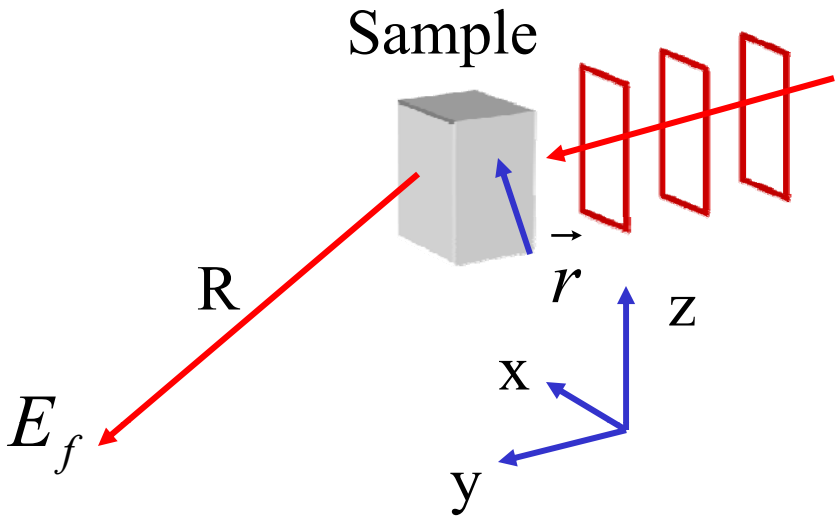
Measuring Dynamics





$$g_2(q,t) = \frac{\langle I(q,t')I(q,t'+t)\rangle}{\langle I(q,t')\rangle^2}$$

The Intensity-Intensity Correlation Function



$$g_2(Q,\tau) \equiv \langle I(Q,t) I(Q,t+\tau) \rangle / \langle I \rangle^2$$

$$= \frac{V\left(\hat{e}_f \cdot \hat{e}_i\right)^4 r_0^{\,4}}{R^4} \int\int\int\int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \exp\left(-i\left(\left(\vec{Q}+\vec{s}_1\right)\cdot\left(\vec{r}_1-\vec{r}_2\right)+\left(\vec{Q}+\vec{s}_2\right)\cdot\left(\vec{r}_3-\vec{r}_4\right)\right)\right)$$

$$\left\langle \rho_e\left(\vec{r}_1,t\right)\rho_e\left(\vec{r}_2,t\right)\rho_e\left(\vec{r}_3,t+\tau\right)\rho_e\left(\vec{r}_4,t+\tau\right)\right\rangle$$

$$\left\langle E_i\left(x_1,0,z_1,t-\frac{\left(\vec{Q}+\vec{s}_1\right)\cdot\vec{r}_1}{\omega}\right)E_i^{\,*}\left(x_2,0,z_2,t-\frac{\left(\vec{Q}+\vec{s}_2\right)\cdot\vec{r}_2}{\omega}\right)\right.$$

$$\left.E_i\left(x_3,0,z_3,t+\tau-\frac{\left(\vec{Q}+\vec{s}_1\right)\cdot\vec{r}_3}{\omega}\right)E_i^{\,*}\left(x_4,0,z_4,t+\tau-\frac{\left(\vec{Q}+\vec{s}_2\right)\cdot\vec{r}_4}{\omega}\right)\right\rangle$$

How to calculate g_2 (skipping most of the equations)

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

$$G_2(Q,\tau)=\int \exp(iQ\cdot r')\langle E_f^2(r,t)\, E_f{}^2(r+r',t+t)\rangle_{r,t} dr'$$

- The fourth order correlations in E, can be reduced to pairs of second order correlation functions

- Assume correlation lengths are smaller than sample size, and the scattering can be factored into independent space and time parts.

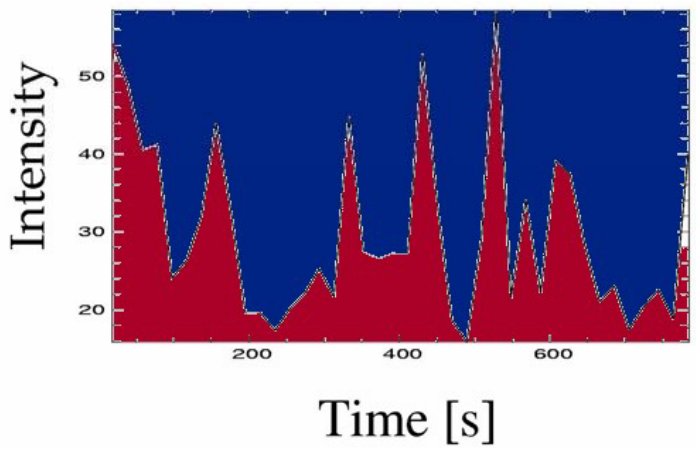
Final Result

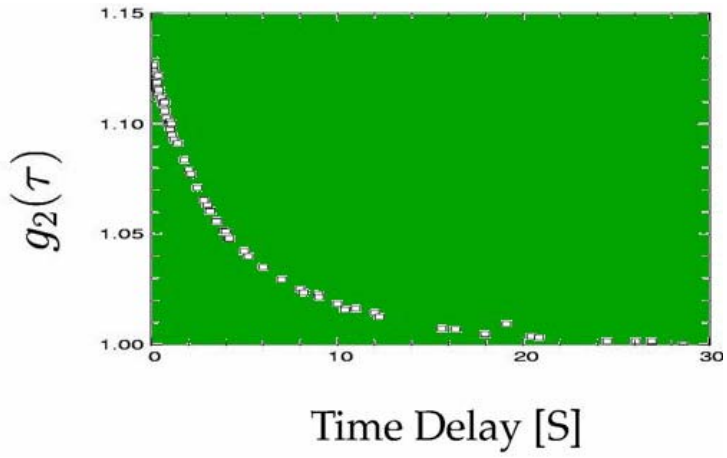
$$G_2(\vec{Q},\tau) = \langle I \rangle^2 \left[1 + \beta f(Q,\tau)^2 \right]$$

The contrast factor, β, is related to the degree of coherence and can be between 0 and 1

$$f(\vec{Q},\tau) = S(\vec{Q},\tau) / S(\vec{Q},0)$$

$$S(\vec{Q},\tau) = \left\langle \int e^{i\vec{Q}\cdot\vec{r}} \rho_e(0,0)\, \rho_e\left(\vec{r},\tau\right) d\vec{r} \right\rangle$$



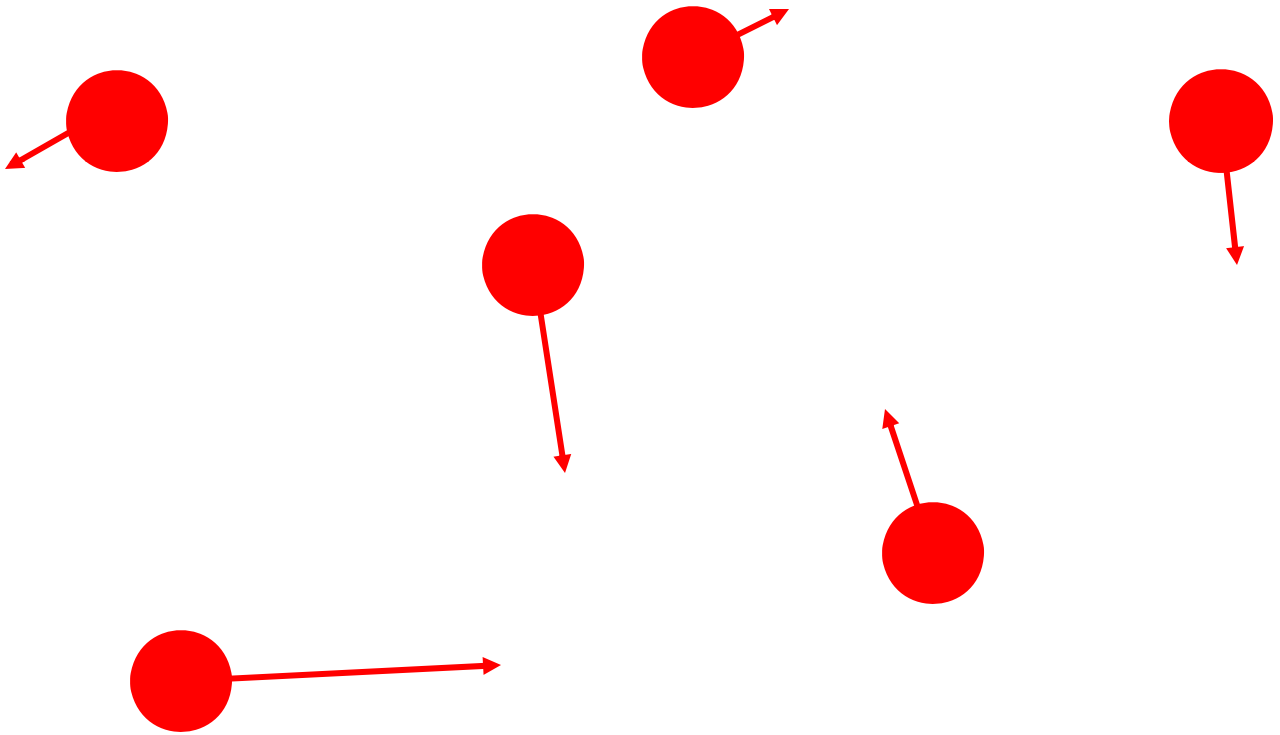


Typical Applications

The average structure is constant, but the local structure fluctuates.

- Diffusion of particles in solution
- Concentration fluctuations in binary liquids
- Fluctuations of order parameter in a crystal
- Thermally driven surface height fluctuations in a viscous fluid
- Vibrations of a membrane
- Aging: evolution of the "equilibrium" dynamics with time.

A dilute colloidal suspension (71 nm Latex in Glycerol)



To theoretically calculate the dynamic scattering factor one has to take the correlation functions for a collection of point scatterers diffusing in the liquid.

$$f(\vec{Q},\tau) = \frac{1}{N}\sum_{i,j}\left\langle \exp(i\vec{Q}\cdot\left(\vec{r}_i(t) - \vec{r}_j(t+\tau)\right)\right\rangle$$

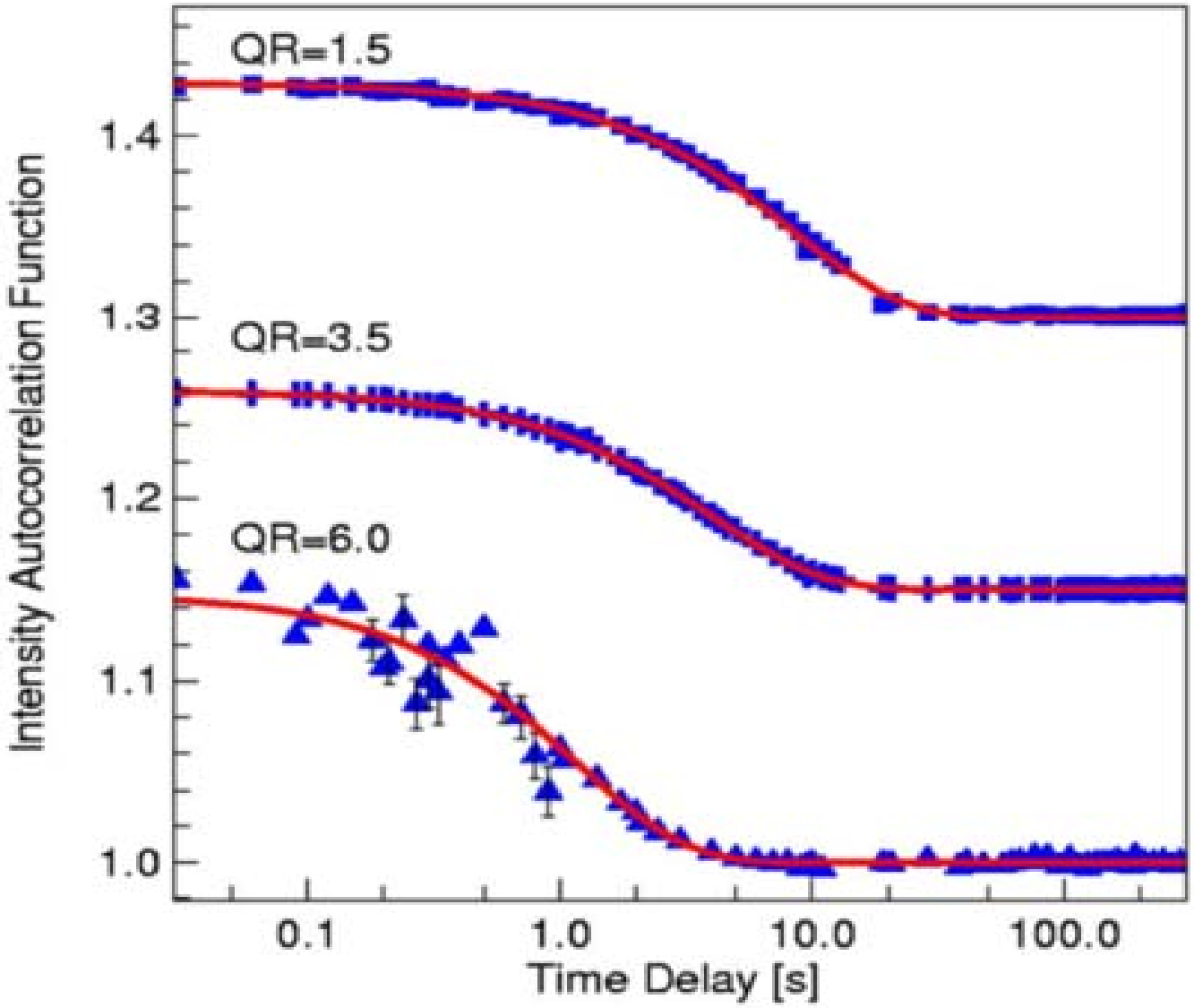
For Brownian motion, this can be reduced to an exponential decay proportional to the diffusion coefficient.

$$f(Q,\tau) = e^{-DQ^2\tau}$$

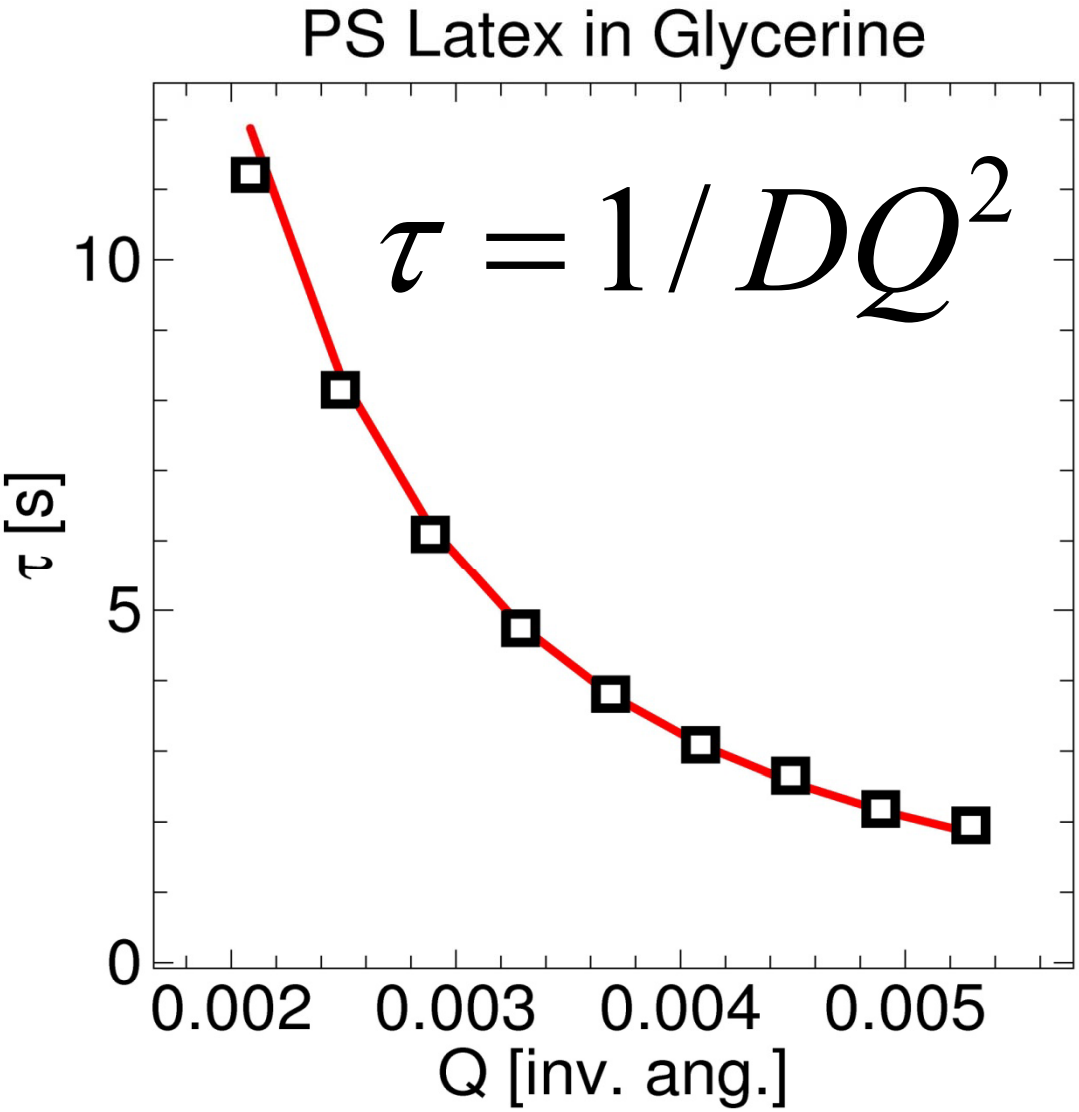
Here, the diffusion coefficient is related to the viscosity, η and the radius a, via the Stoke-Einstein relation:

$$D = k_B T \; / \; 6\pi\eta a$$

Correlation Functions



Wavevector Dependence

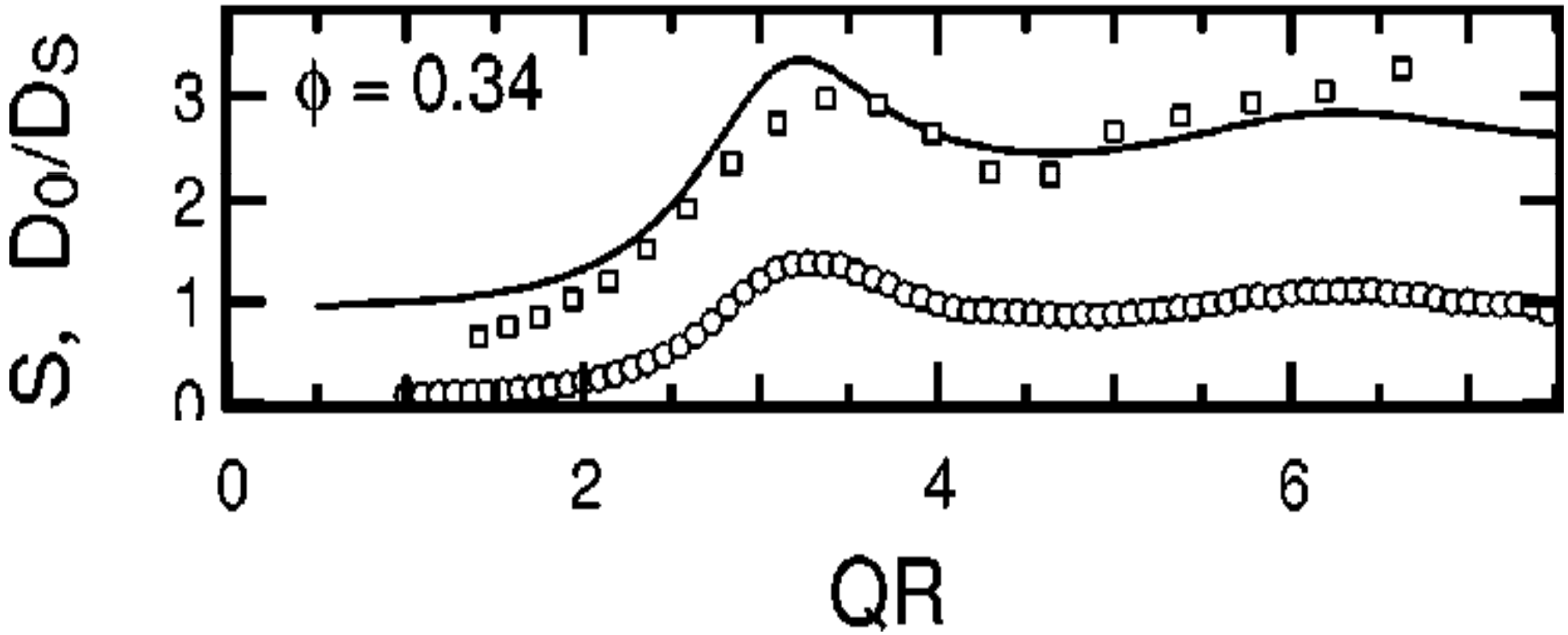


Short Time Diffusion Constants in Concentrated Suspension

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,t) will not generally be an exponential at long times.

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

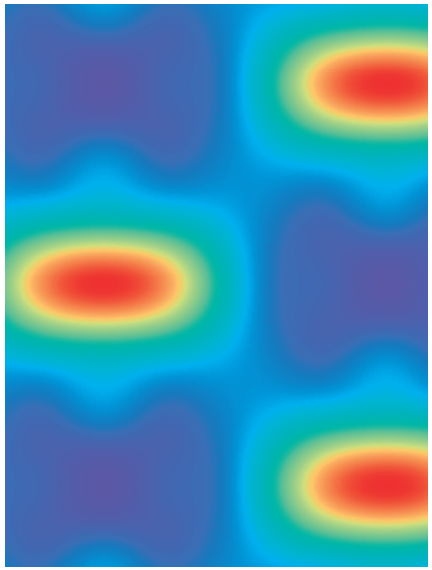
Deviations for Stokes-Einstein Diffusion

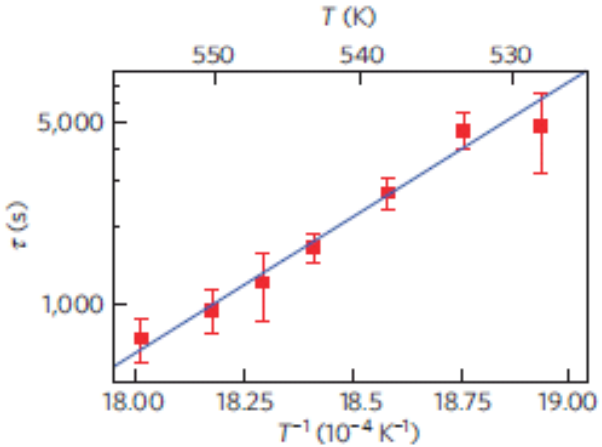


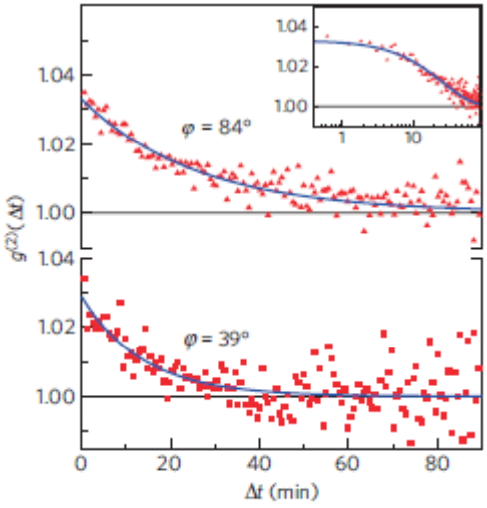
Example 2

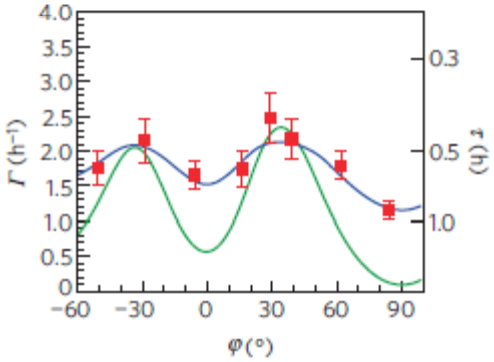
Atomic Diffusion in Metal Alloys

Leitner et. al. Nature Materials, 2009





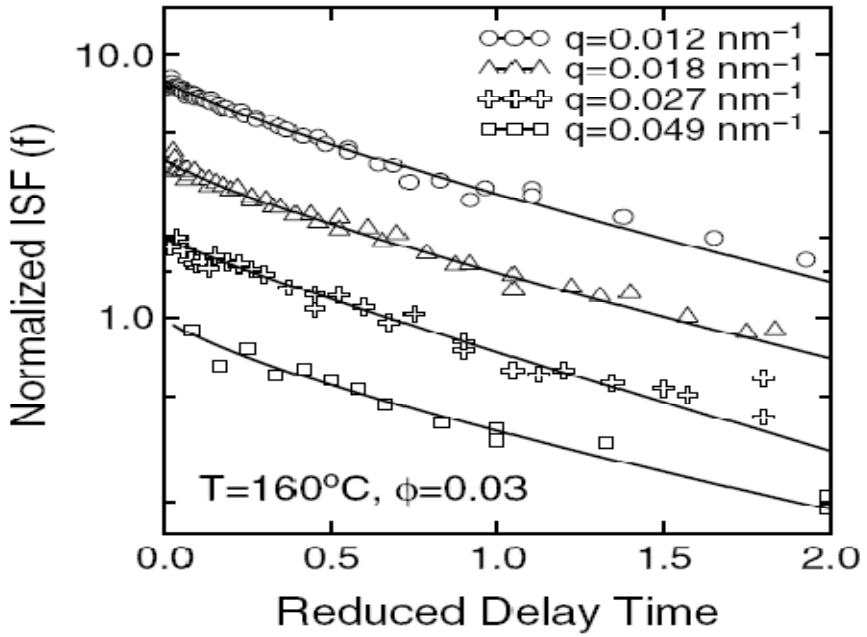




Example 3 Concentrated Polymeric Vesicles

Concentrated Block Copolymer Vesicles

Falus et. al. PRL 94, 16105, 2005

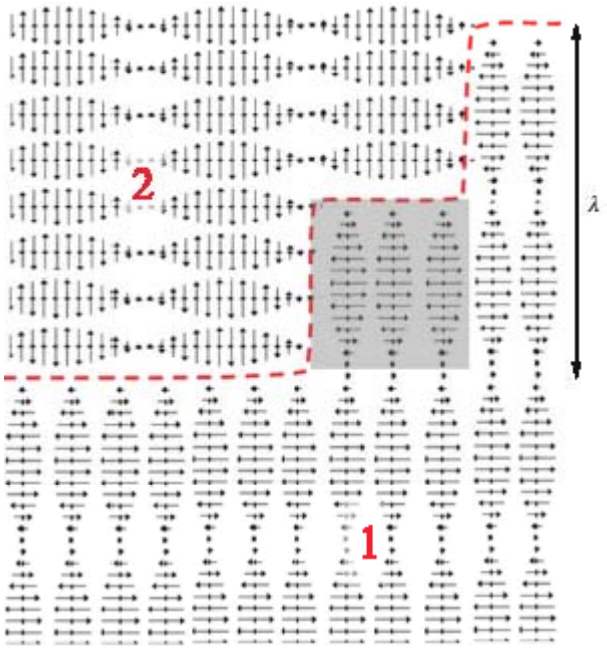


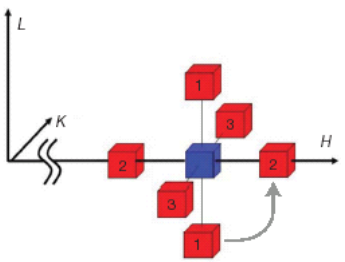
In Liquid State, Near
Tg Exponential Decays
Become Stretched

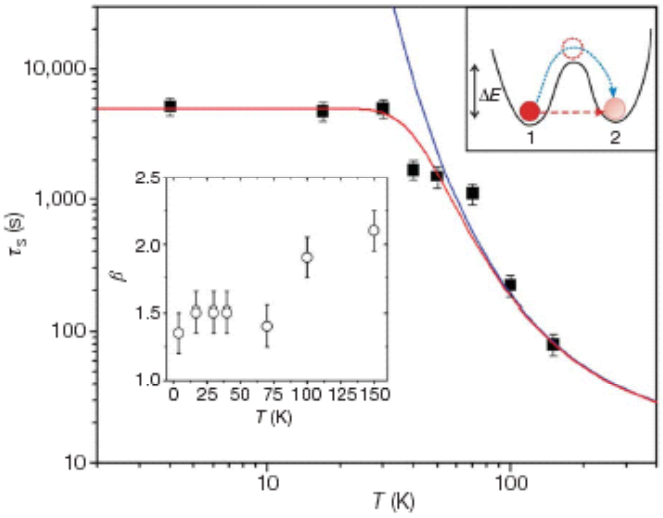
Example 4

Antiferromagnetic Domain Fluctuations

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

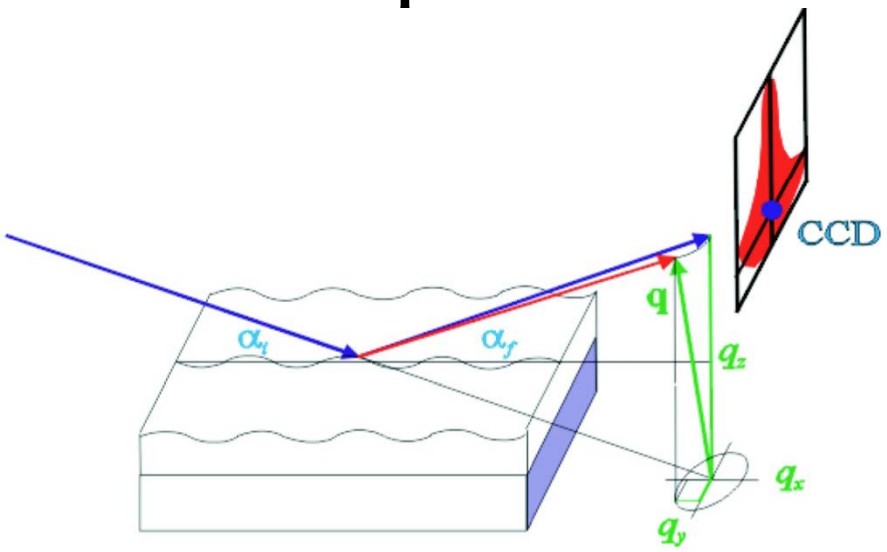


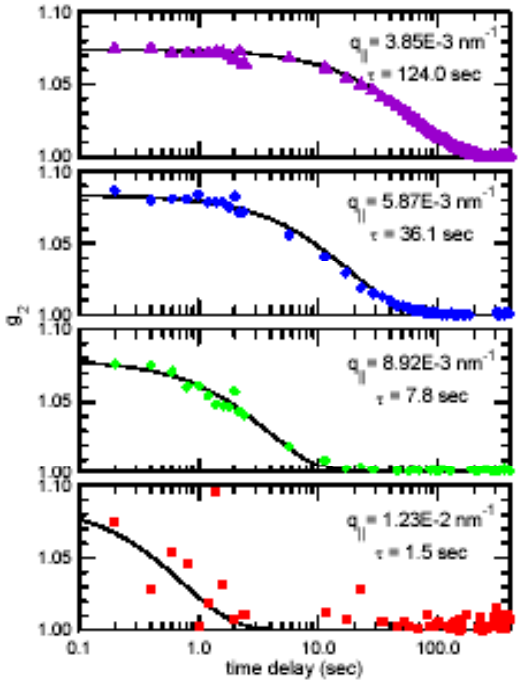


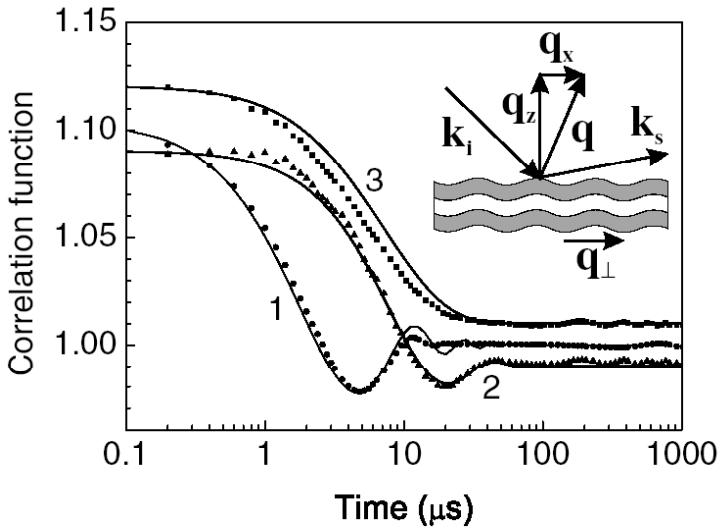


Note that although the length scale of the fluctuations is large (>10 nm) they require x-rays with wavelengths ~0.1 nm in order to be visible.

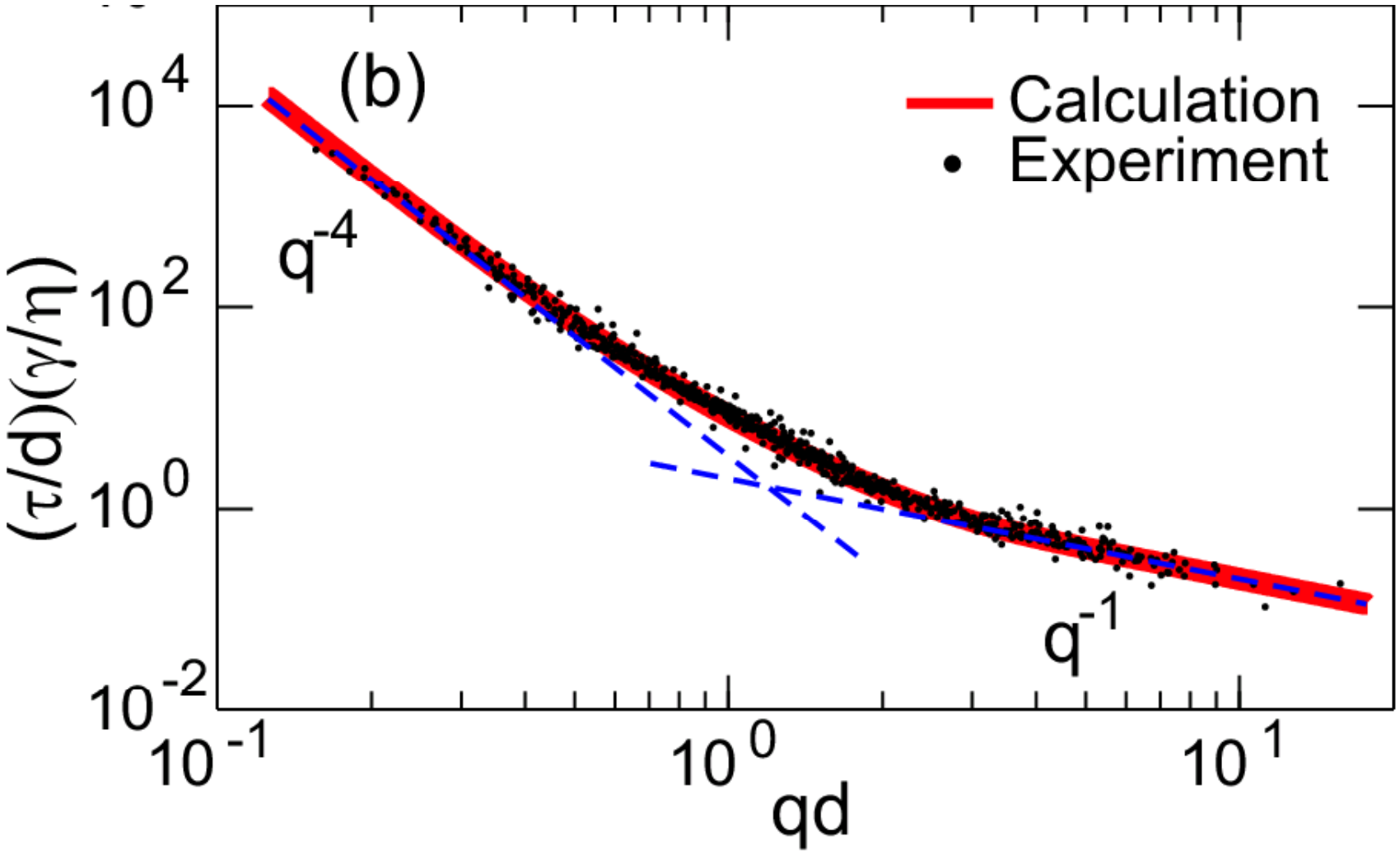
Example 5: Dynamics of Liquid Surfaces







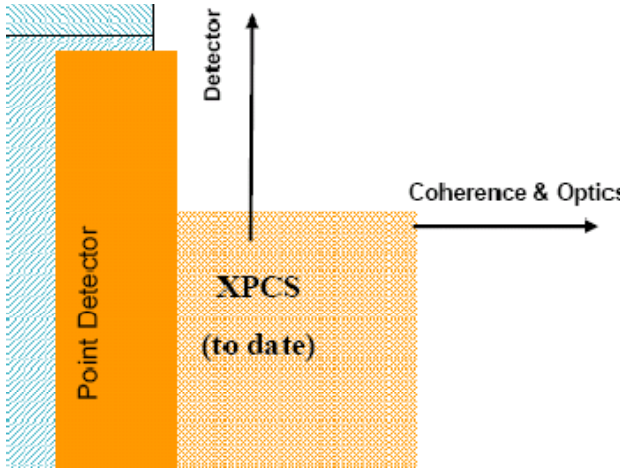
- Polystyrene films on Si wafers (Kim, PRL 2003) are highly viscous and show exponential decay
- Thin liquid crystal membranes (Sikharulidze, PRL 2002) show transition from oscillatory to overdamped behavior.



From Jiang et. al. PRL, 246104, 2008

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)
- Too little flux (Poor signal to noise)

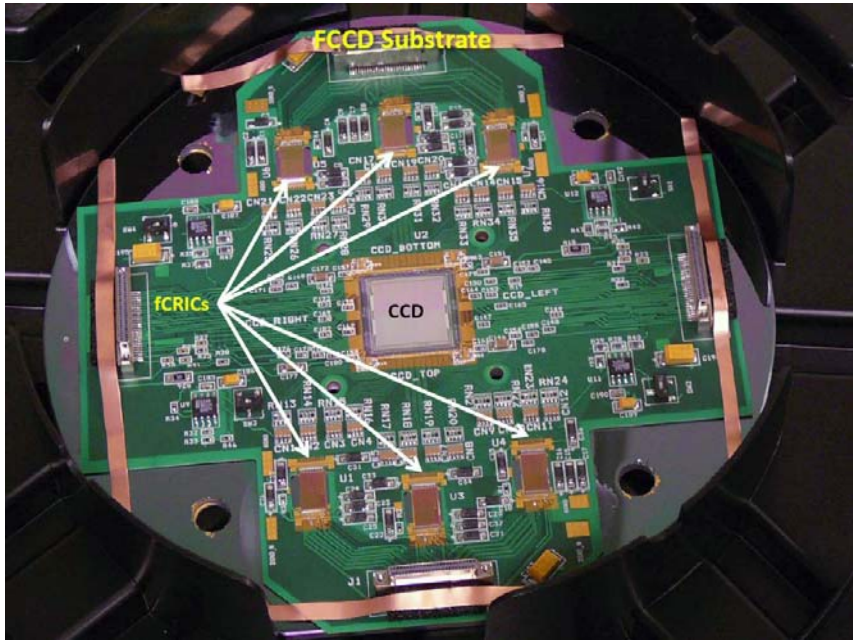


Some tricks of the trade …

Multispeckle Detection

- Falus, Borthwick, Mochrie, RSI (2004)
- SNR increases as $\sqrt{N}$
- Limitations:
  - Readout rate presently around 60 Hz
  - Efficiency < 50%

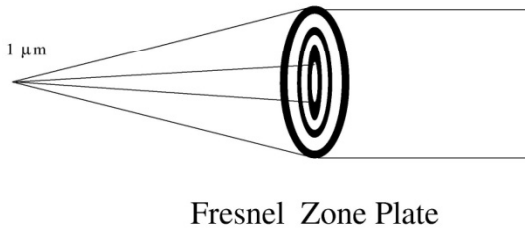
- New Camera under development at LBL and APS ~500 Hz at 100% efficiency. (John Weizeorick and Alec Sandy) Should see first light this cycle.



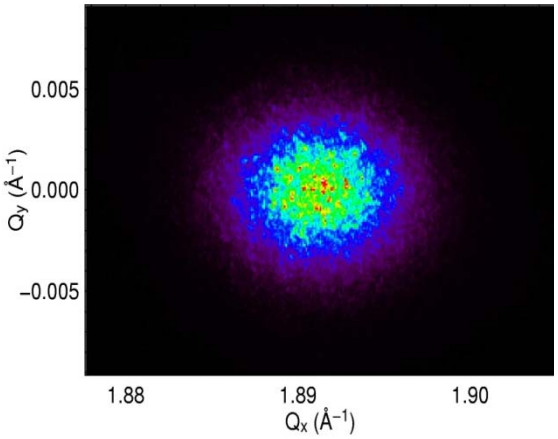
Focusing

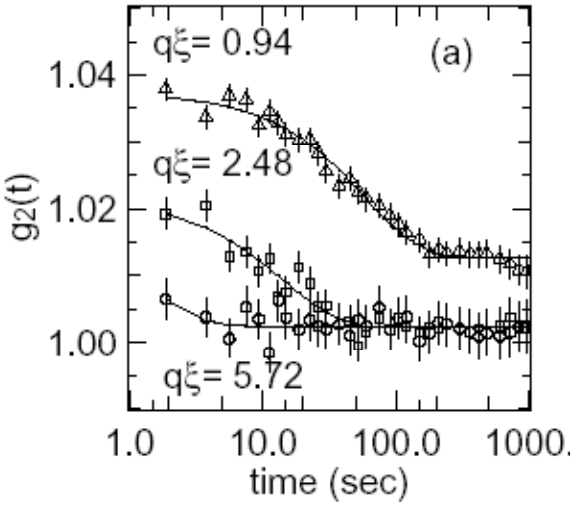
Khalid Laaziri and Mark Sutton

- 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

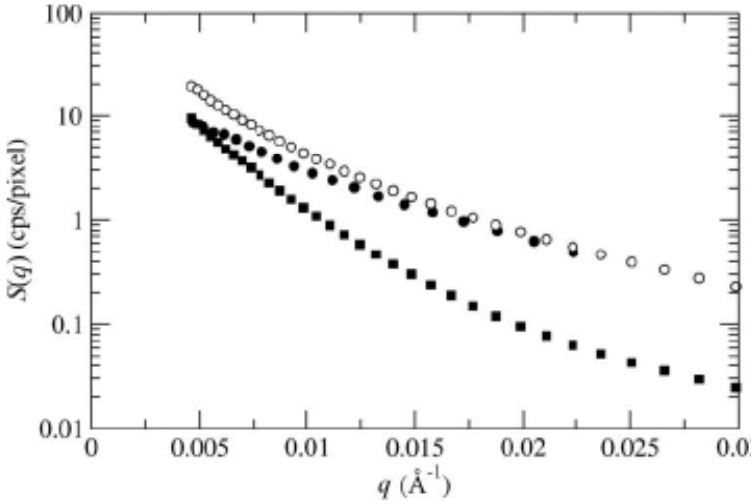


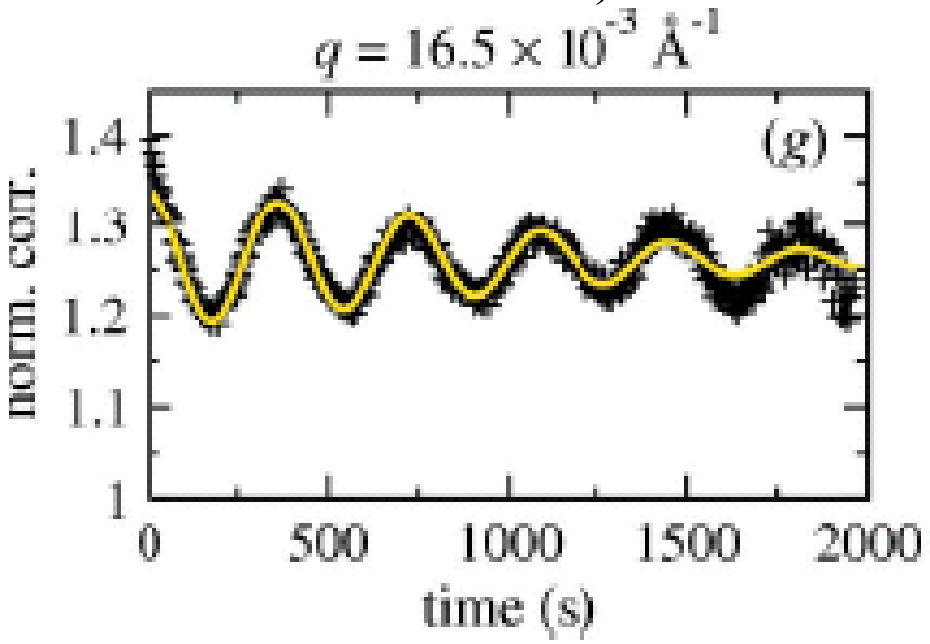


Heterodyne Detection

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)





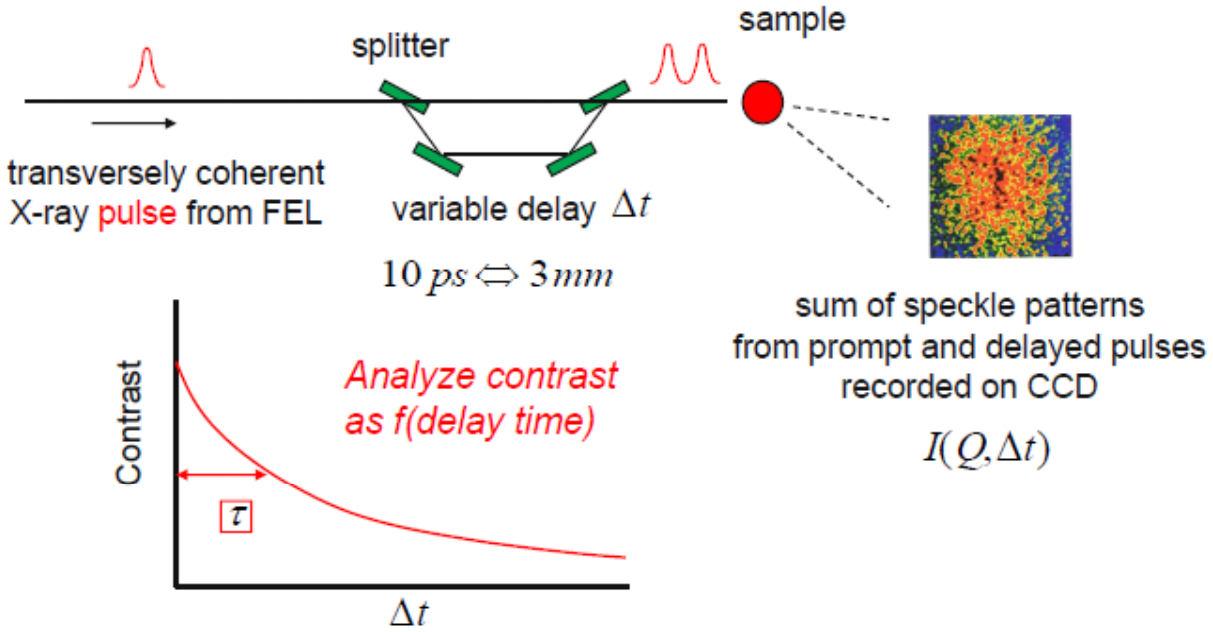
What is in the Future for XPCS ?
X-ray Free Electron Lasers

LCLS at Stanford

European Free Electron Laser at Hamburg

Ultrafast XPCS using 'Split Pulse' Mode

Femtoseconds to nanoseconds time resolution
Uses high *peak* brilliance



References

- **This talk:** http://www.niu.edu/~llurio/coherence/
- **XPCS:**
  - G. Grübel, *et al*. (2008). X-Ray Photon Correlation Spectroscopy (XPCS). Soft-Matter Characterization. R. B. a. R. Pecora. Heidelberg, Springer.
  - M. Sutton, (2008). "A review of X-ray intensity fluctuation spectroscopy." Comptes Rendus Physics **9: 657-667.**
- **Dynamic Light Scattering:**
  - B. Berne and R. Pecora, "Dynamic Light Scattering", Dover, 2000.
- **Coherence:**
  - J. Goodman, "Statistical Optics", Wiley, 1985.
  - M. Born and E. Wolf, "Principles of Optics", Pergamon, 1965
- **X –ray Free Electron Lasers**
  - Proposed Science for European XFEL G. Grübel *et. al., NIM* ***262, 357 (2007).***
  - LCLS "The First Experiments: Studies of Nanoscale Dynamics in Condensed Matter Physics ", Stephenson *et. al.* **SLAC-R-611 (2003)**