Use of x-ray coherence to study dynamics in thin films, layered systems and membranes

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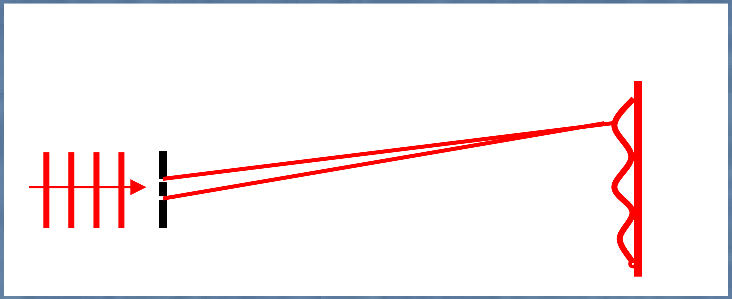
What is Coherence

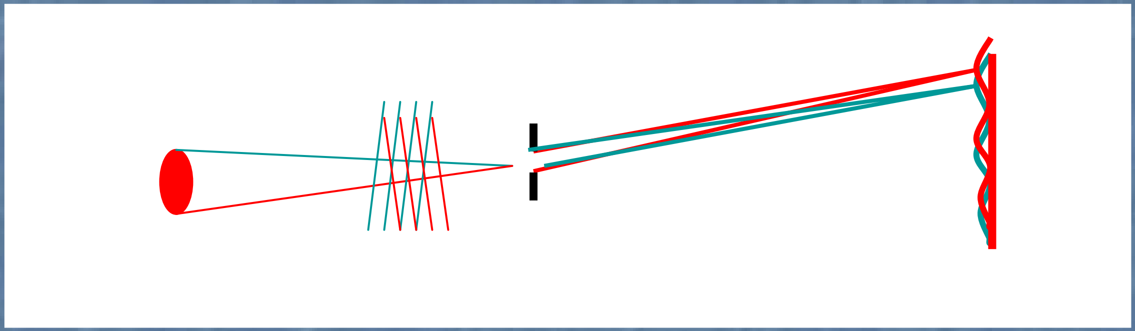
Ideal Young's double slit experiment



Intensity varies as

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

Real Young's double experiment



Intensity varies as

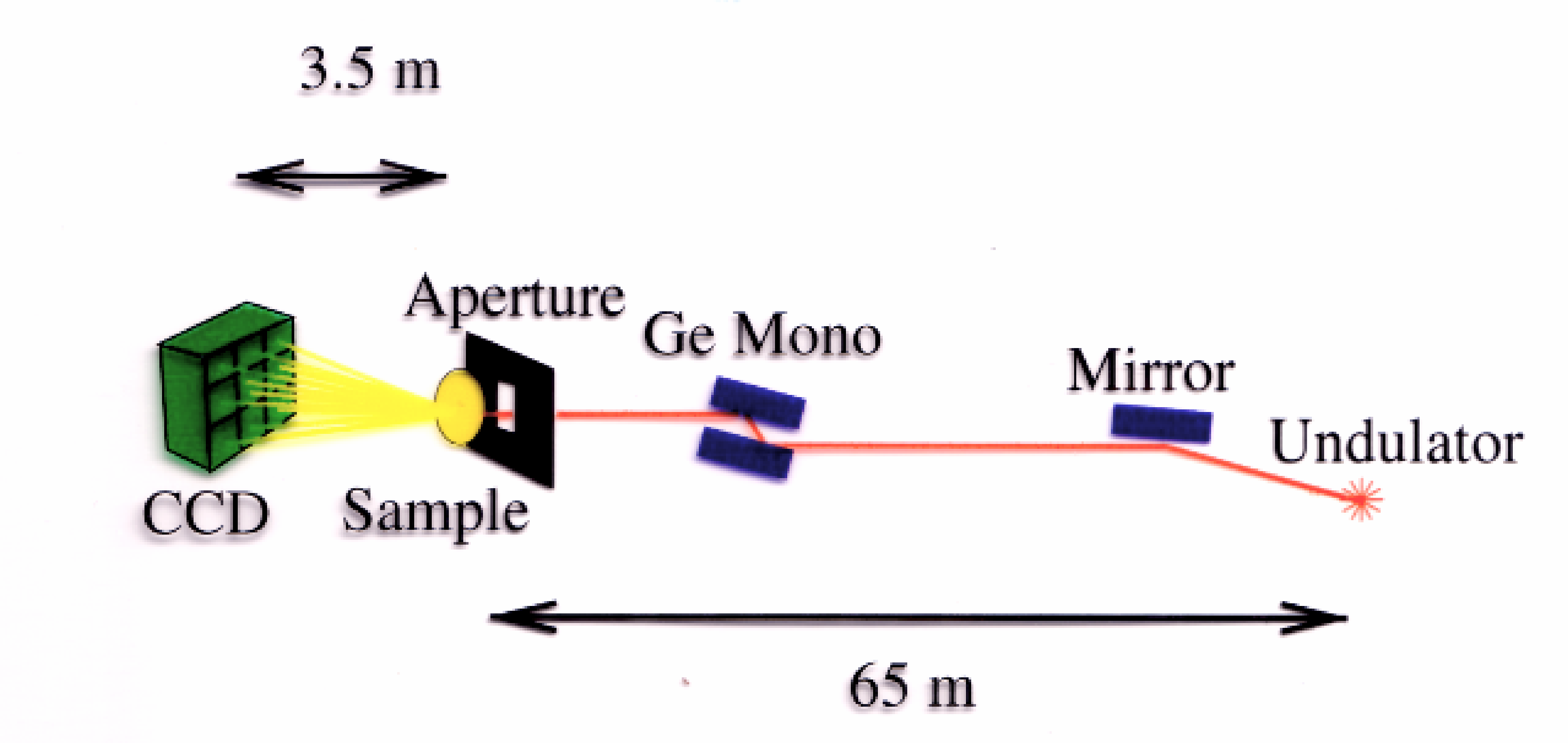
$$I = 2I_0\left[1 + \beta\cos\left(2\pi d \sin(\theta)/\lambda\right)\right]$$

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

How Practical is it to Make X-rays Coherent

- X-rays passing through a slit will spread out due to diffraction $\Delta\theta = \lambda / D$
- Collimate x-rays, so angular divergence equals diffraction.
- This is a very small angle. At 65 m from the x-ray source the beam only diffracts out to around 50 μm
- 50 μm x 50 μm has 10^{10} Photons/s

Setup for XPCS at Sector 8 of the APS



Scattering of Coherent X-rays

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

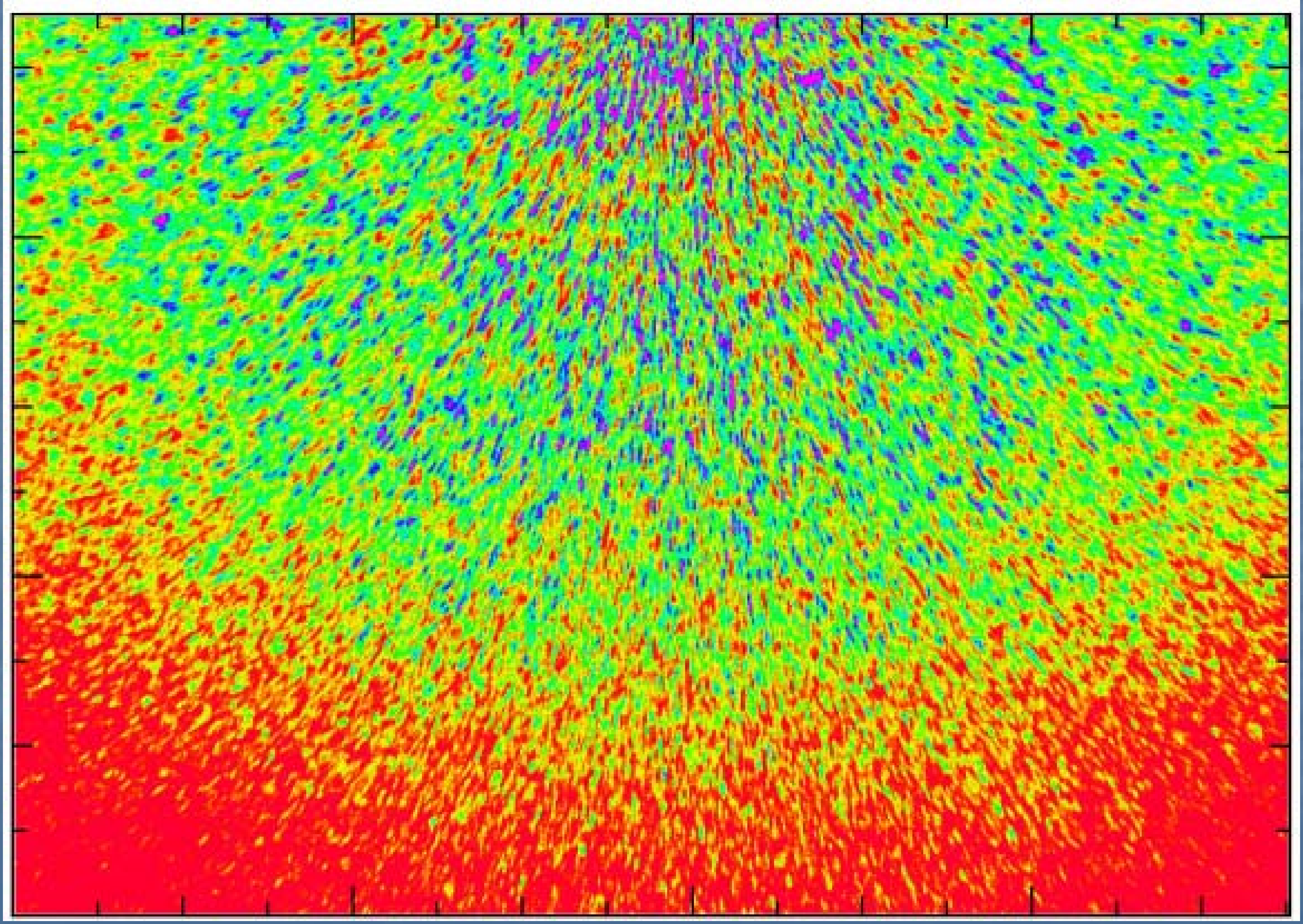
Coherent x-rays: exact distribution, results in a speckle pattern.

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

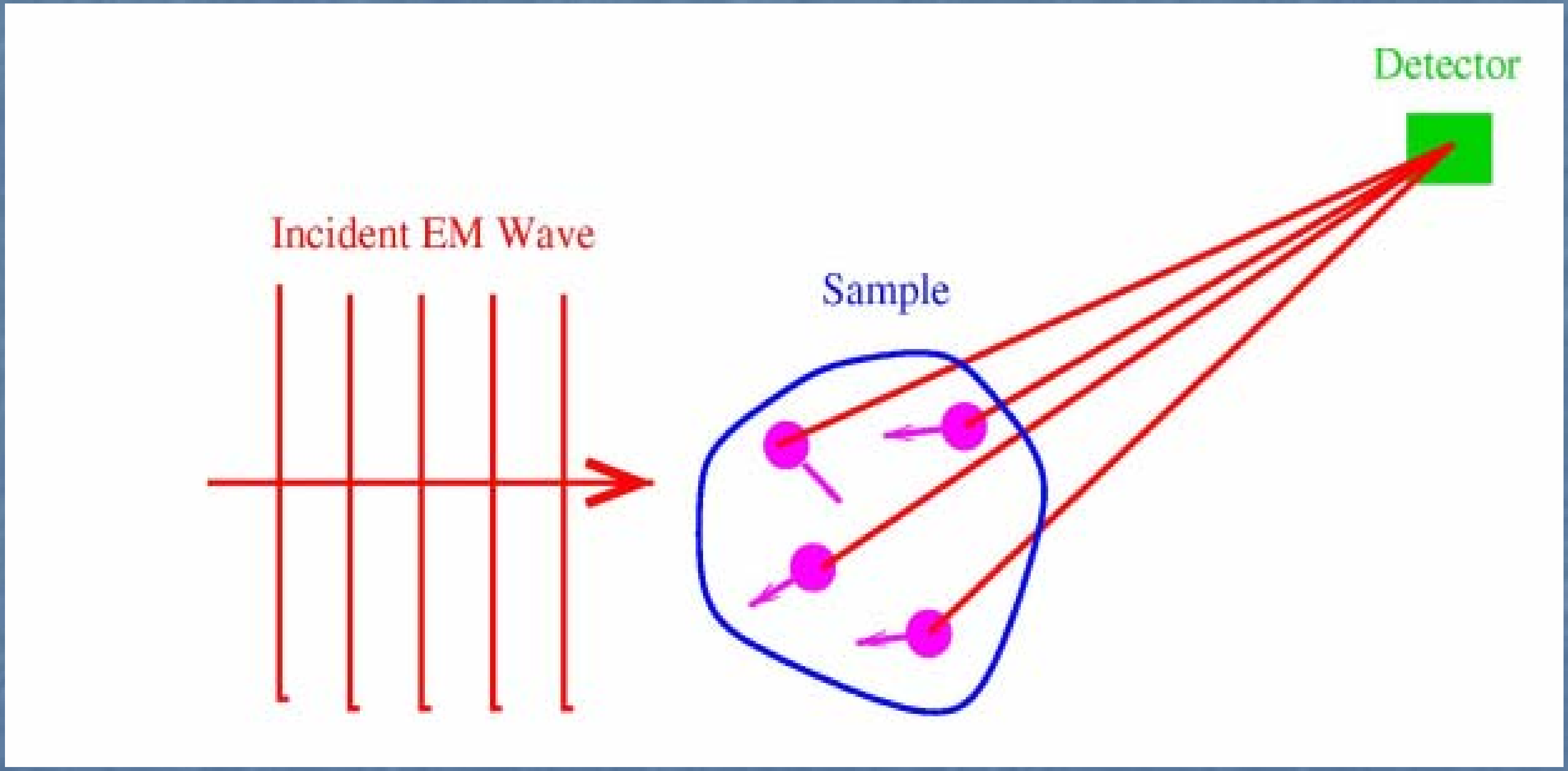
Incoherent x-rays: statistical average

Equilibrium Dynamics are Only Visible to Coherent X-rays!

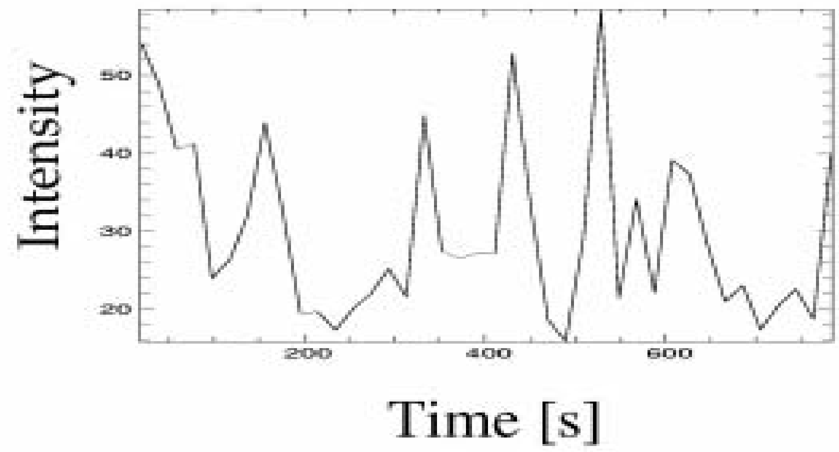
Coherent Scattering from a Silica Aerogel



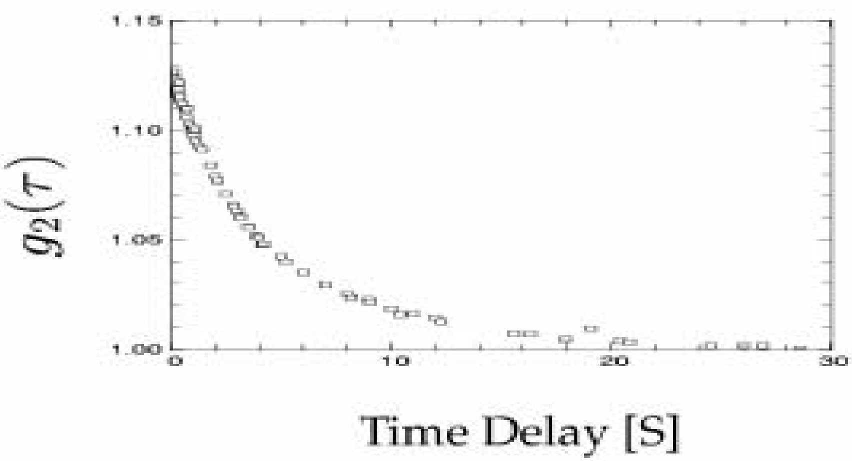
Measuring Dynamics



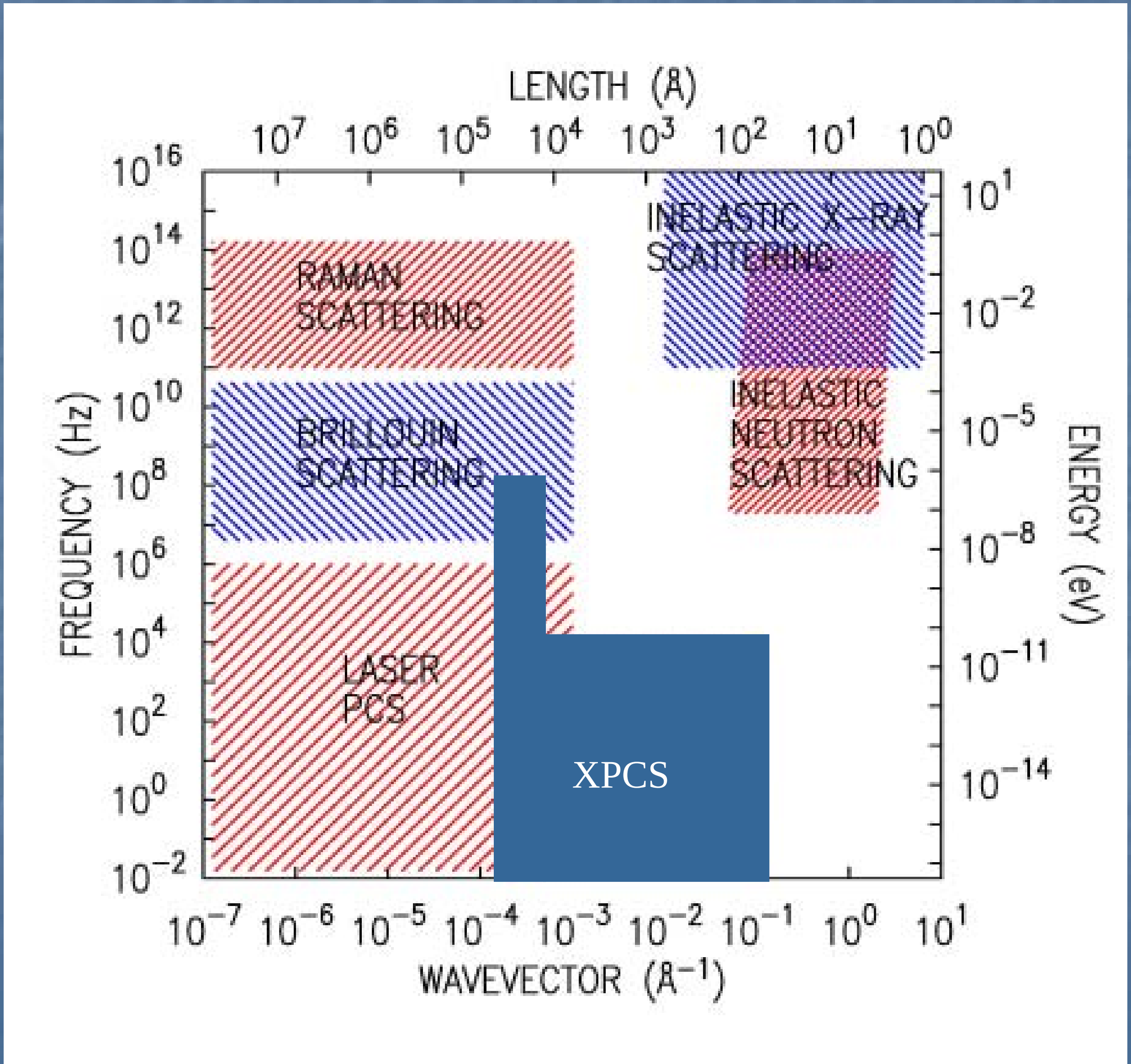
Example of a time correlation Function



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



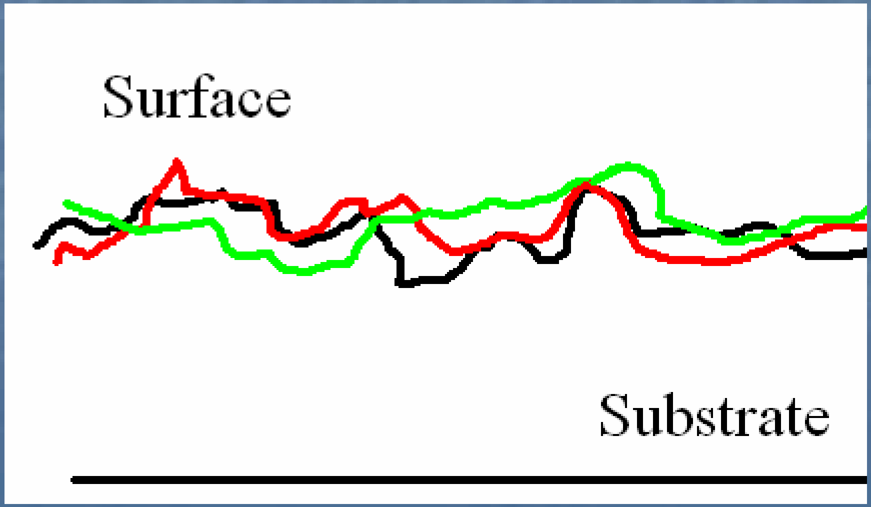
Phase space for XPCS



Dynamics in Polystyrene Films

Hyunjung Kim, A. Ruhm, L. B. Lurio et al., Physical Review Letters **90** (6), 068301 (2003).

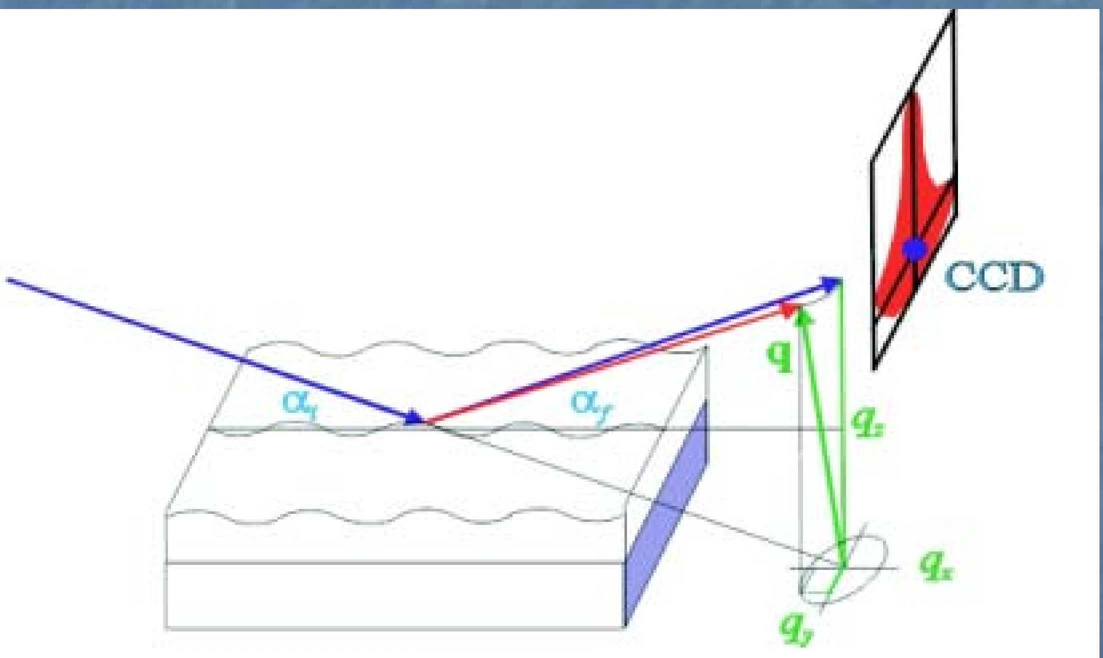
- Surface height fluctuations in PS films driven by thermal energy
- Surface configuration diffuses from one random configuration to another
- XPCS measures relaxation time vs. length scale

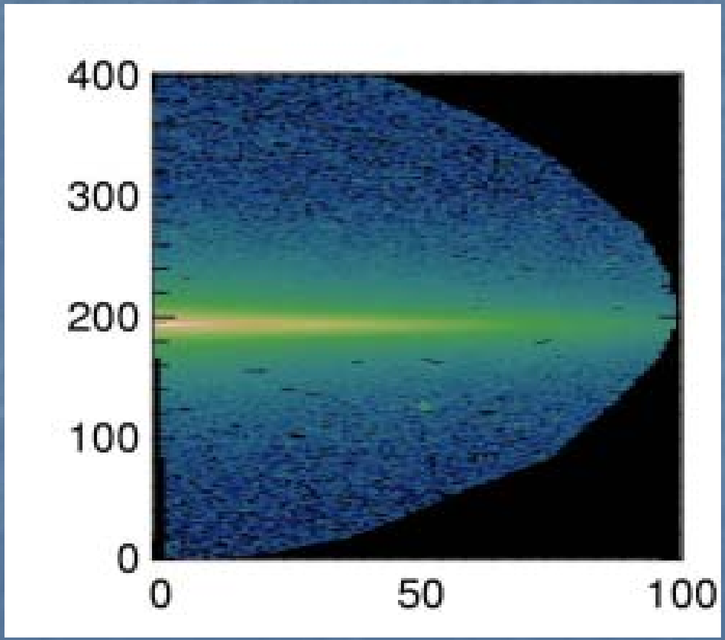


What do you learn

- Relaxation time as a function of in-plane wavelength measures the ratio of viscosity to surface tension
- Surface displacement is due to motion throughout film.

Scattering Geometry

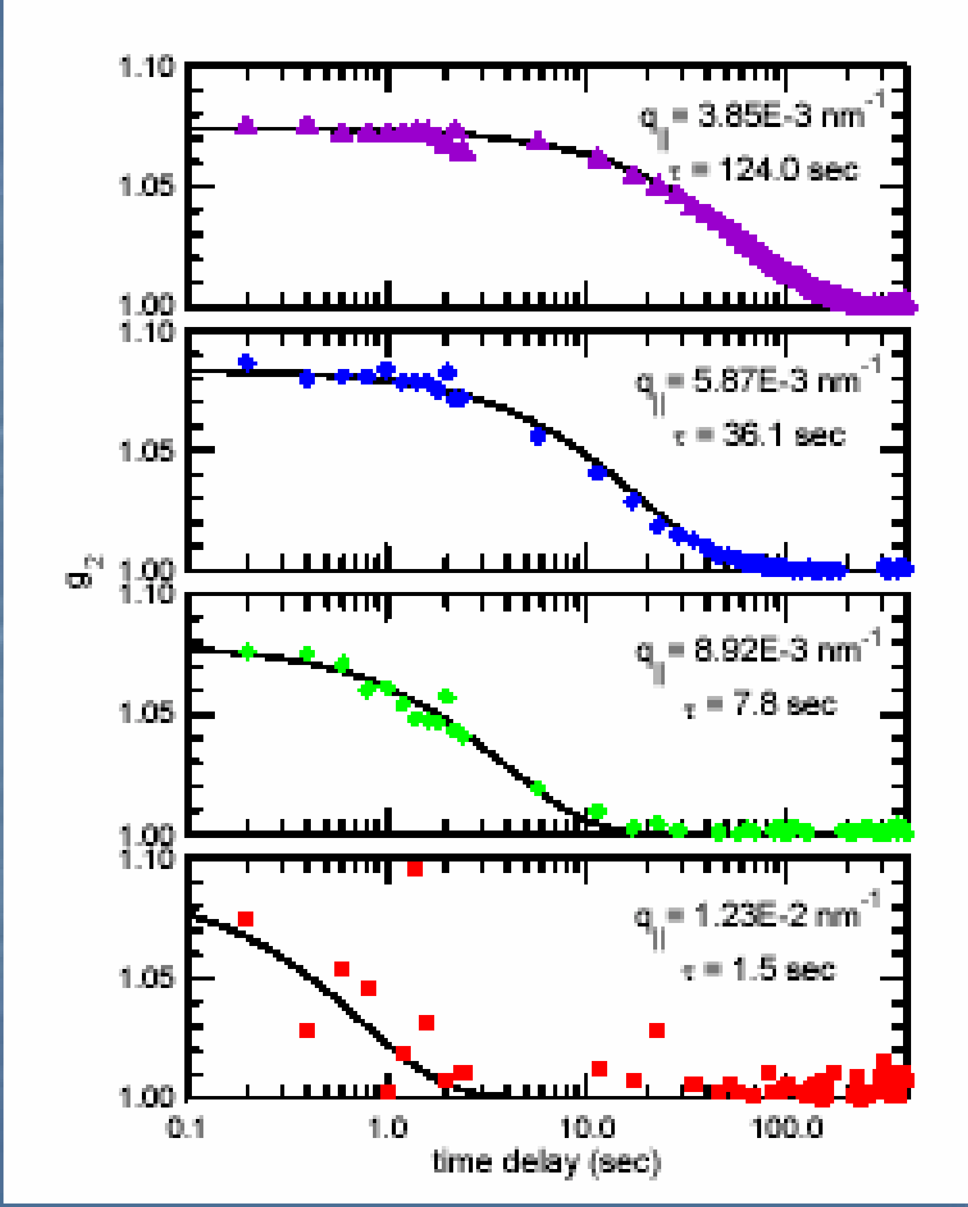




Time Correlation Functions

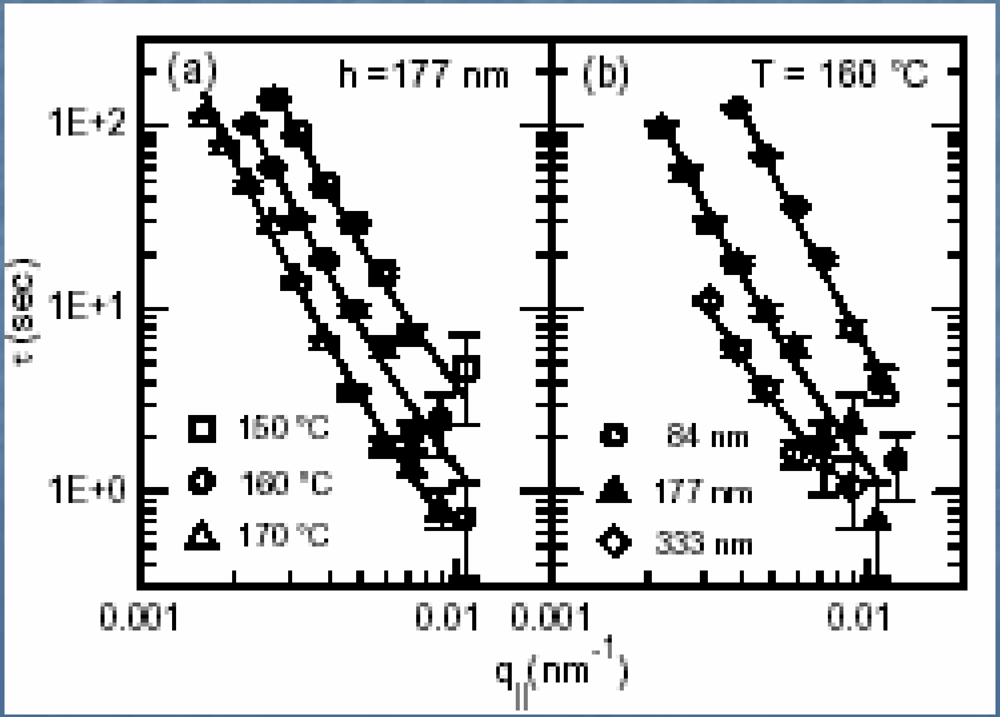
$$g_2(\tau) = \frac{\langle I(t)I(t+\tau)\rangle_t}{\langle I\rangle^2}$$

$$\tau = \frac{2\eta\left[\cosh^2(qh) + q^2h^2\right]}{\gamma q\left[\sinh(qh)\cosh(qh) - qh\right]}$$



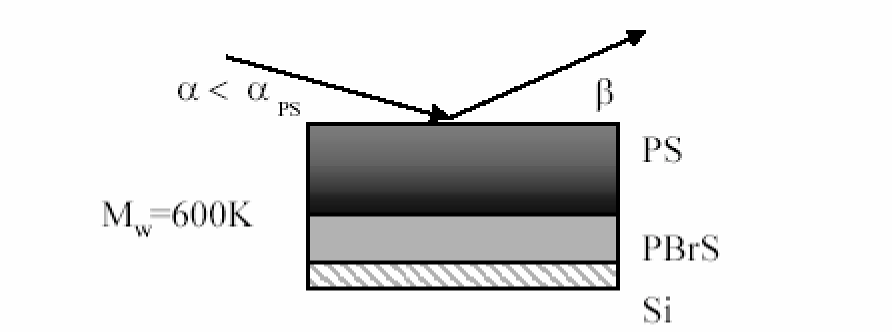
Depth and wavelength dependence agree with theory

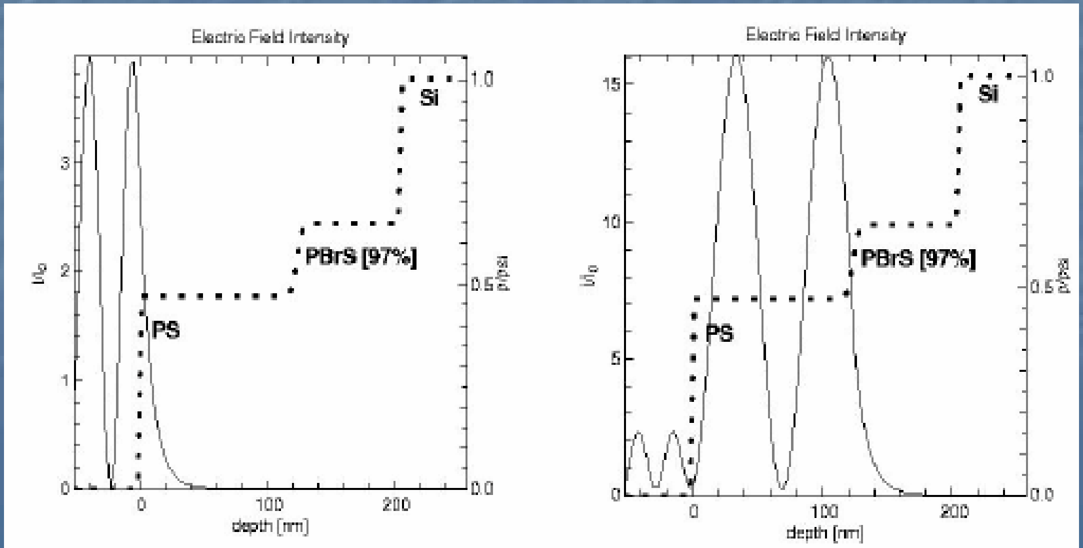
(Choose viscosity as independent parameter, within a factor of 2)

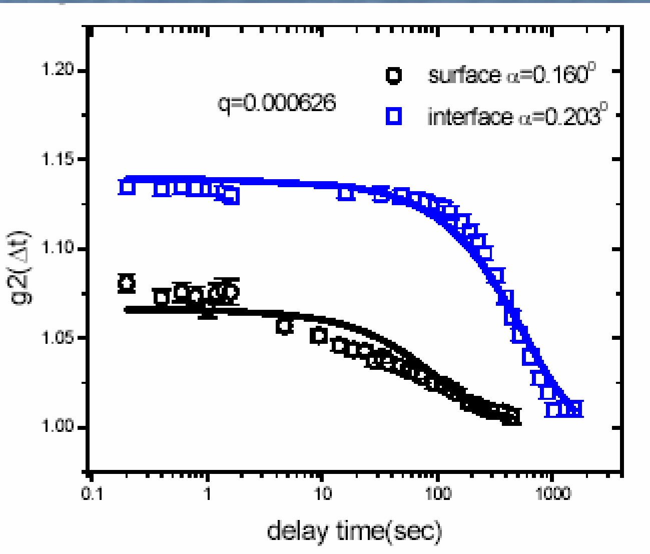


What about Multilayer Films?

- PS-PBrS Bilayers: X. Hu, X. Jiao, S. Narayanan, L. Lurio and J. Lal







Dynamics of Smectic Membranes

Irakli Sikharulidze, Igor P. Dolbnya, Andrea Fera et al., Physical Review Letters **88** (11), 115503 (2002).

- Smectic membranes: Thin liquid crystal membranes (~μm) freely suspended from an aperture. (Smectic A phase)
- Dynamics within membrane can be determine from continuum elastic theory.
- Equation of motion for membrane:

$$\rho_0 \frac{\partial^2 u(r)}{\partial t^2} = \eta_3 \frac{\partial}{\partial t} \nabla_\perp^2 u(\mathbf{r}) + (B\nabla_z^2 - K\Delta_\perp^2) u(\mathbf{r})$$

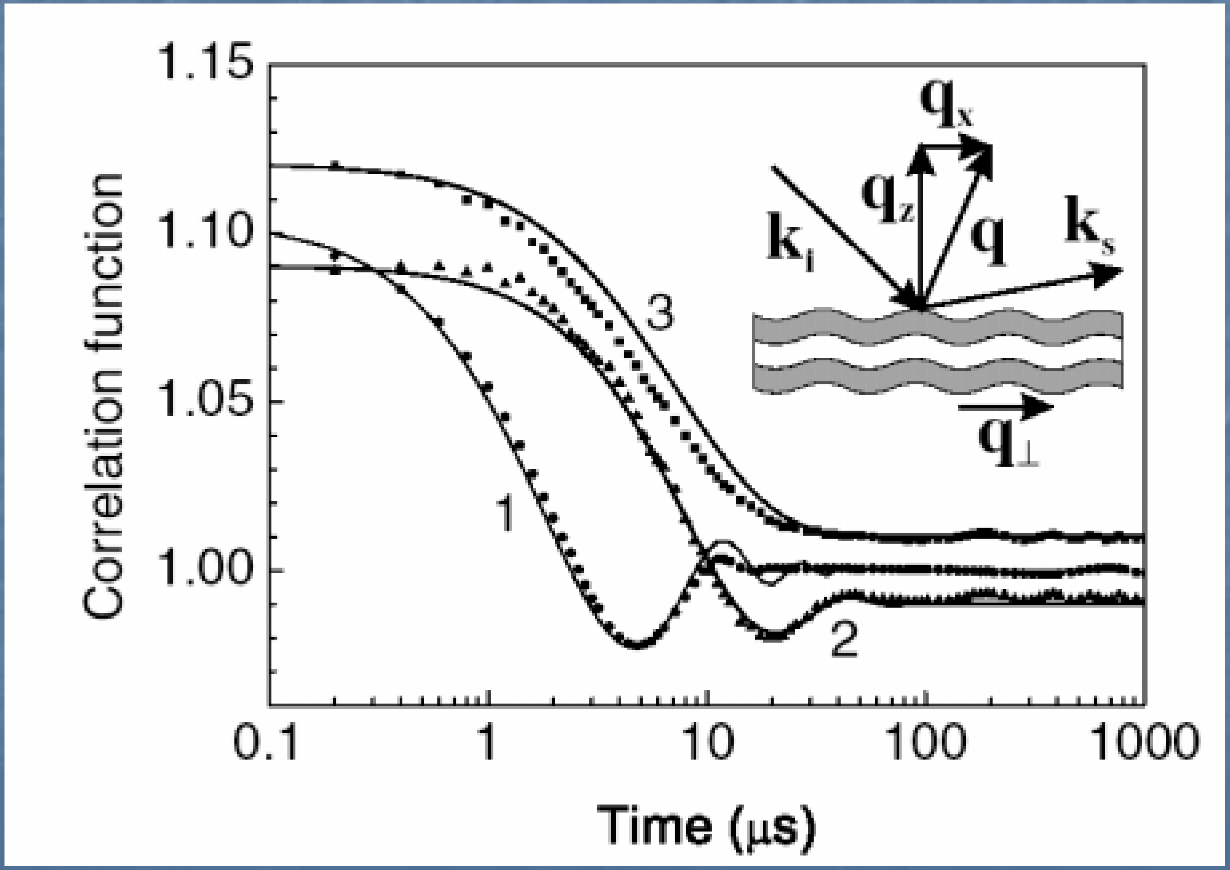
Predicted Dynamics

- Can map equation of motion onto a damped harmonic oscillator
- Underdamped case: Single elastic mode
- Overdamped case: Two exponentially decaying modes. (high compressibility limit)

$$\tau_{1,2} \approx \frac{2\rho_0}{\eta_3 q_\perp^2}\left(1 \mp \sqrt{1 - \frac{8\rho_0\gamma}{q_\perp^2 \eta_3^2 L}}\right)^{-1}.$$

$$G(q_\perp, t) = \frac{k_B T \tau_1 \tau_2}{L\rho_0(\tau_1 - \tau_2)}\left[\tau_1 \exp\left(-\frac{|t|}{\tau_1}\right) - \tau_2 \exp\left(-\frac{|t|}{\tau_2}\right)\right]$$

Crossover from overdamped to underdamped



What do you get?

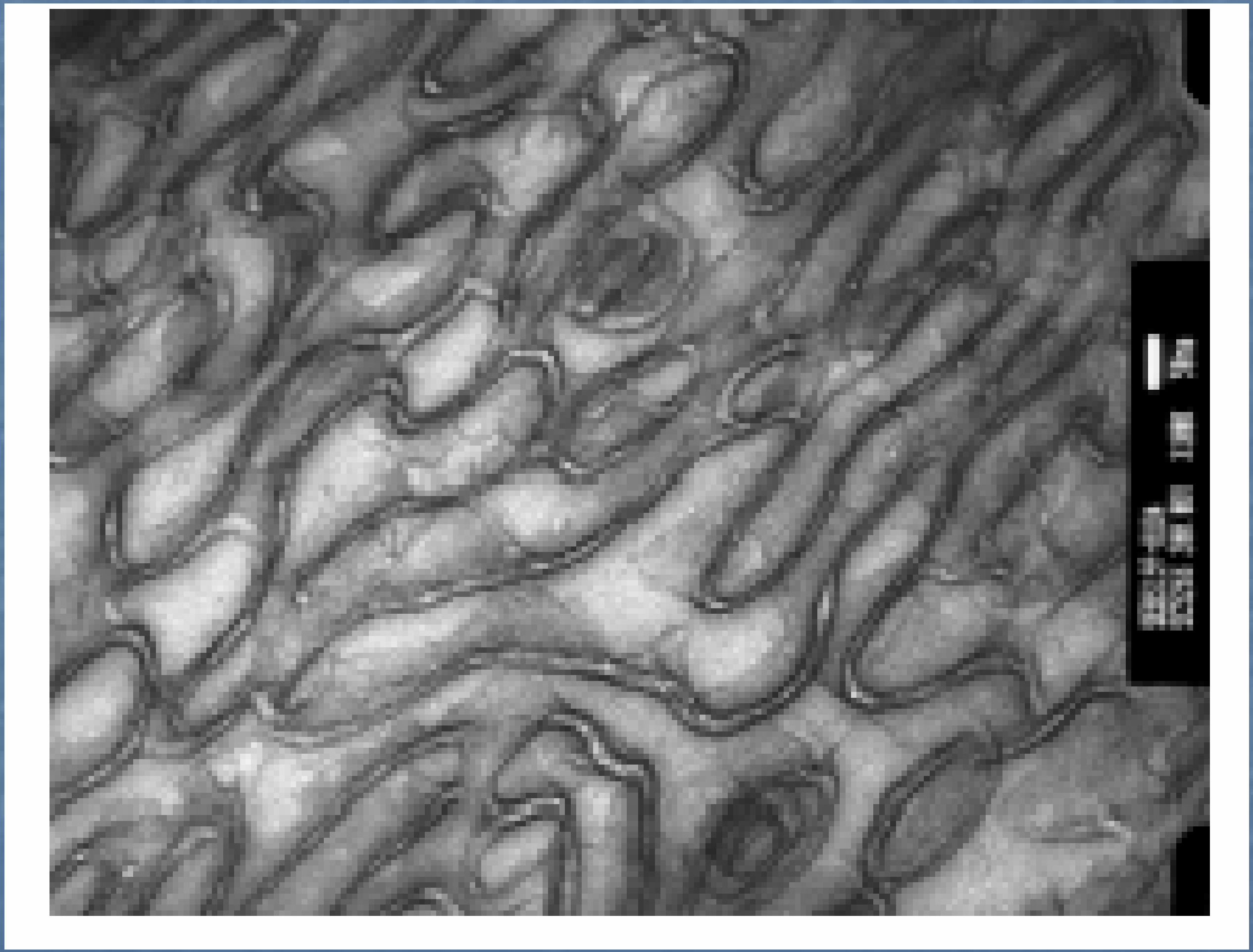
- Dynamics can probe surface tension and viscosity (lowest order results insensitive to elastic constants)
- Can measure very fast dynamics (overlaps with neutron spin echo)
- Cannot measure modes with large in-plane wavelengths.

Fluctuation Dynamics in Block-Copolymer Vesicles

Peter Falus, Simon Mochrie and Matt Borthwick.
(Yale & MIT)

- Block Copolymer Amphiphiles
- L-3 Symmetric Sponge Phase Thermally driven spontaneous shape fluctuations in Vesicles (L4 Phase)

Poly(styrene-ethylene/butylene-styrene) triblock + short chain PS



Cryogenic TEM image of vesicle phase in PSEBS-PS

Theoretical Predictions for Dynamics

- Slower dynamics allows measurement of wider wavevector range (CCD measurement vs. point detector)
- Only see overdamped modes
- Results depend on viscosity bending modulus. (ξ is a long length scale cutoff)
- Expect non-exponential decay

$$f(q,t) = \exp[-(\Gamma t)^{\alpha}],$$

where $\alpha \simeq \frac{2}{3}(1+\nu)$, and

$$\Gamma = \left[0.025\left(\frac{12.56\kappa}{\xi^3\eta}\right)^{\nu}\left(\frac{k_B T}{\kappa}\right)^{1/2}\left(\frac{k_B T q^3}{\eta}\right)\right]^{1/(1+\nu)}.$$

Correlation functions

- Stretched exponential with stretching exponent of ~2/3 as predicted.
- Time constants agree closely with predictions values based on bulk values of viscosity and bending modulus.

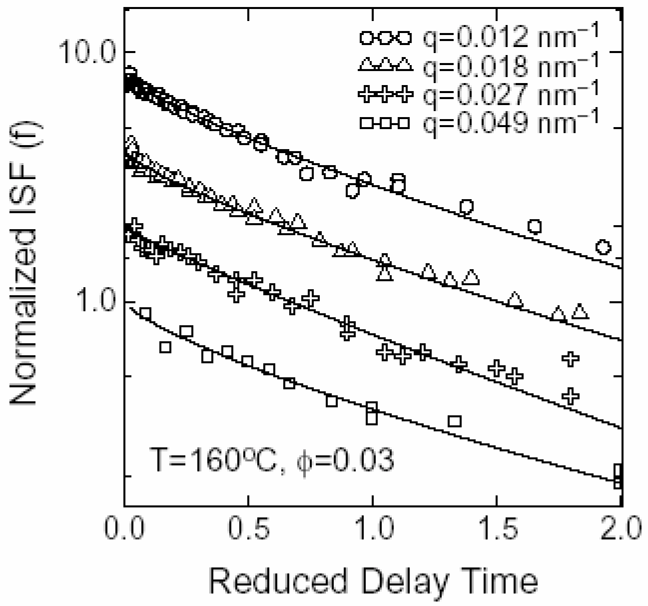


Figure 2: Normalized intermediate scattering functions [f] plotted *vs.* reduced delay time (Γt) at $160^{o}C$. The data and fitted curves are identical to Fig. 1. For clarity the data has been multiplied 1, 2, 4, 8 for the respective wavenumbers.

Future Prospects for XPCS measurements of membranes and films

- Extend measurements to larger in-plane wavevectors at faster times.
- Use x-ray standing waves to probe specific interfaces
- Composite Materials: Nanoparticles embedded in films; measure dynamics of film and particles separately
- Biomembranes in water (?) Lots of challenges: fast dynamics, damage, but possible in next 5 years.