Prospects for X-ray Photon Correlation Spectroscopy from Liquid and Soft Matter Surfaces and Interfaces

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Outline

- Review of current XPCS measurements on liquid and soft matter interfaces.
- Some ideas for the next generation of experiments.
- Discussion of required technology.

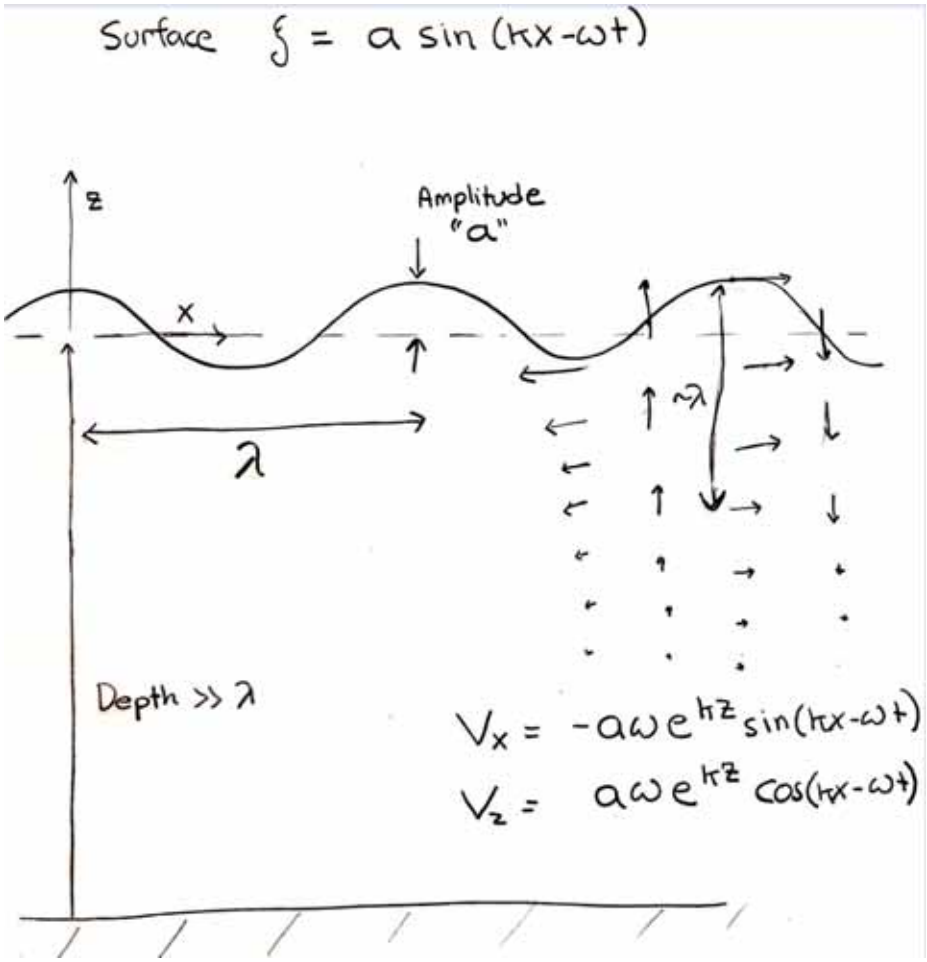
Dynamics at a Simple Liquid Interface: Capillary Waves

Static Structure from Interfacial Energy

$$H = \int d^2\vec{r}\left(\frac{\gamma\Delta h^2}{2} + g\rho h^2 / 2\right)$$

Dynamics from Linearized Navier-Stokes Equation

$$\rho\frac{d\vec{v}}{dt} = -\vec{\nabla}P + \eta\nabla^2\vec{v}$$



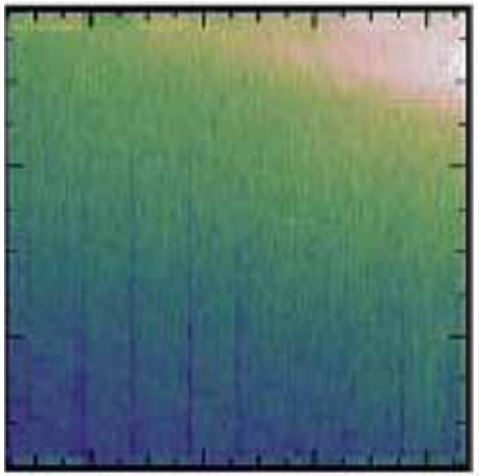
Diffuse Scattering from Capillary Waves

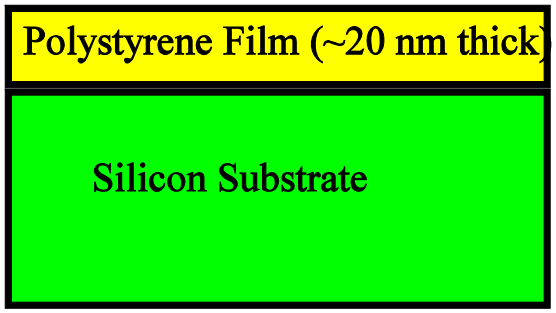
Thin Molten Polymer Films

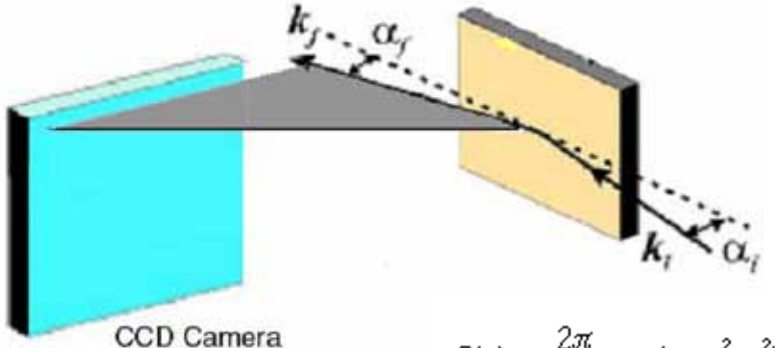
$$d\sigma/d\Omega = \rho_e^2 r_e^2 A \left|T(\alpha)\right|^2 \left|T(\beta)\right|^2 S(\vec{q})$$

$$S(q) \approx k_B T / \gamma q_r^2$$

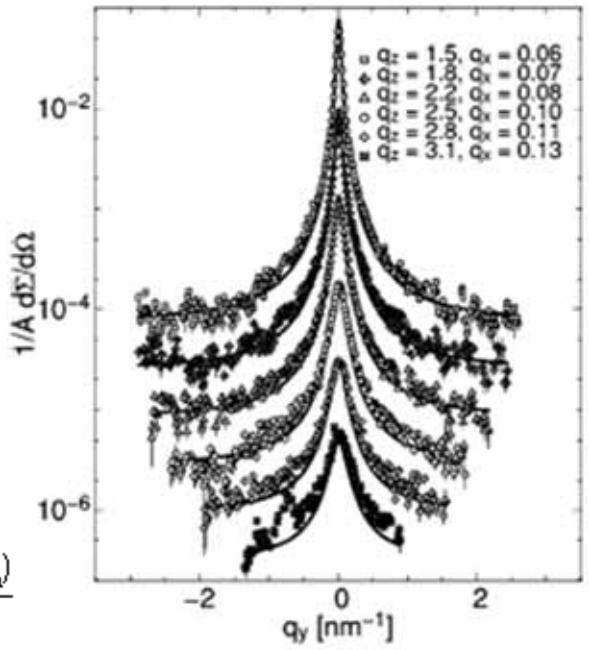
Can measure surface tension of a thin polymer film, as well as characterize any other forces which act of the surface and their range of interaction.







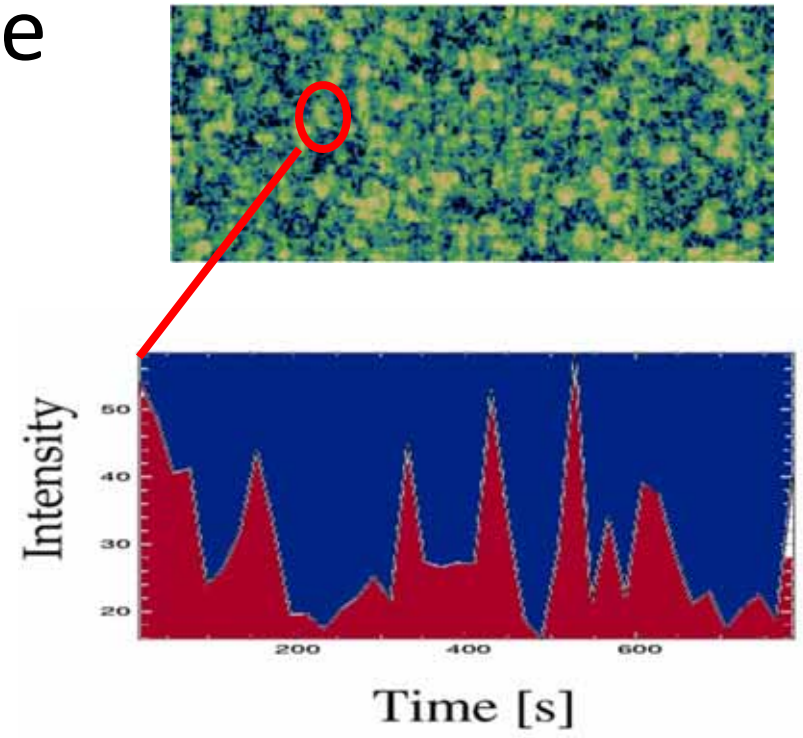
$$S(q) \approx \frac{2\pi}{q_z^2} \exp(-\sigma_0^2 q_z^2) \left(\frac{4\pi}{q_u e^{\gamma_e}}\right)^{\eta} \left(\frac{q_R}{2}\right)^{\eta/2-1} \left(\frac{2\pi}{q_u}\right)^{1-\eta/2} \times \frac{K_{1-\eta/2}(2\pi q_R/q_u)}{\Gamma(\eta/2)}$$



Time Correlation Functions and Dynamics of a Speckle

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

The time correlation function is measured at a single speckle, corresponding to a particular value of *q*. The averaging can be over the initial time, t, or over many speckle at equivalent values of *q*.

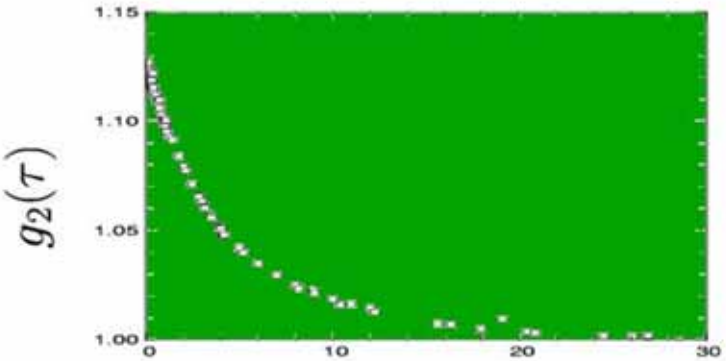


$$g_2(\vec{q},\tau) = \left[1 + \beta f(\vec{q},\tau)^2\right]$$

β is a contrast factor (β=1 for perfect coherence)
$S(q,\tau)$ is the dynamics structure factor

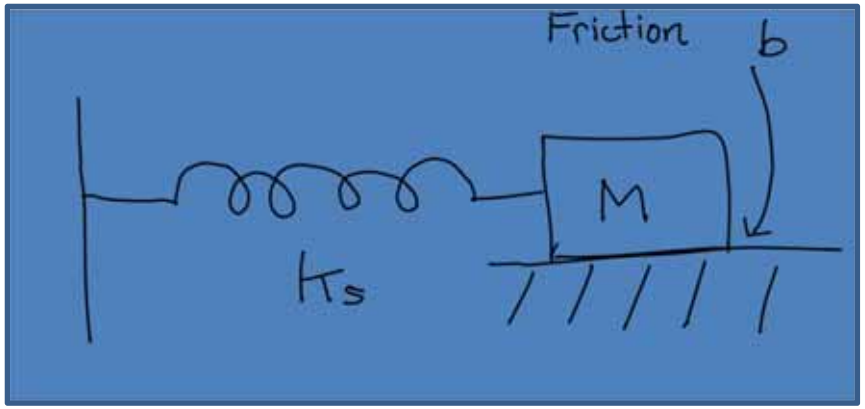
$$f(\vec{q},\tau) = S(\vec{q},\tau) / S(\vec{q},0)$$

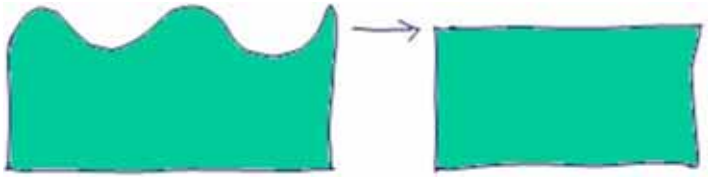
$$S(\vec{q},\tau) = \left\langle \int e^{i\vec{q}\cdot\vec{r}} \rho_e(0,0) \rho_e(\vec{r},\tau) d\vec{r} \right\rangle$$



For simple diffusive motion $g_2(\tau) = 1 + \beta e^{-2\Gamma\tau}$

Calculation of Time Constants





For a film of finite thickness *h* there can be additional factors of *qh*

Overdamped $\tau \to b / k_s$

For deep waves, use dimensional analysis

only dimension is wavevector, $q = 2\pi / \lambda$

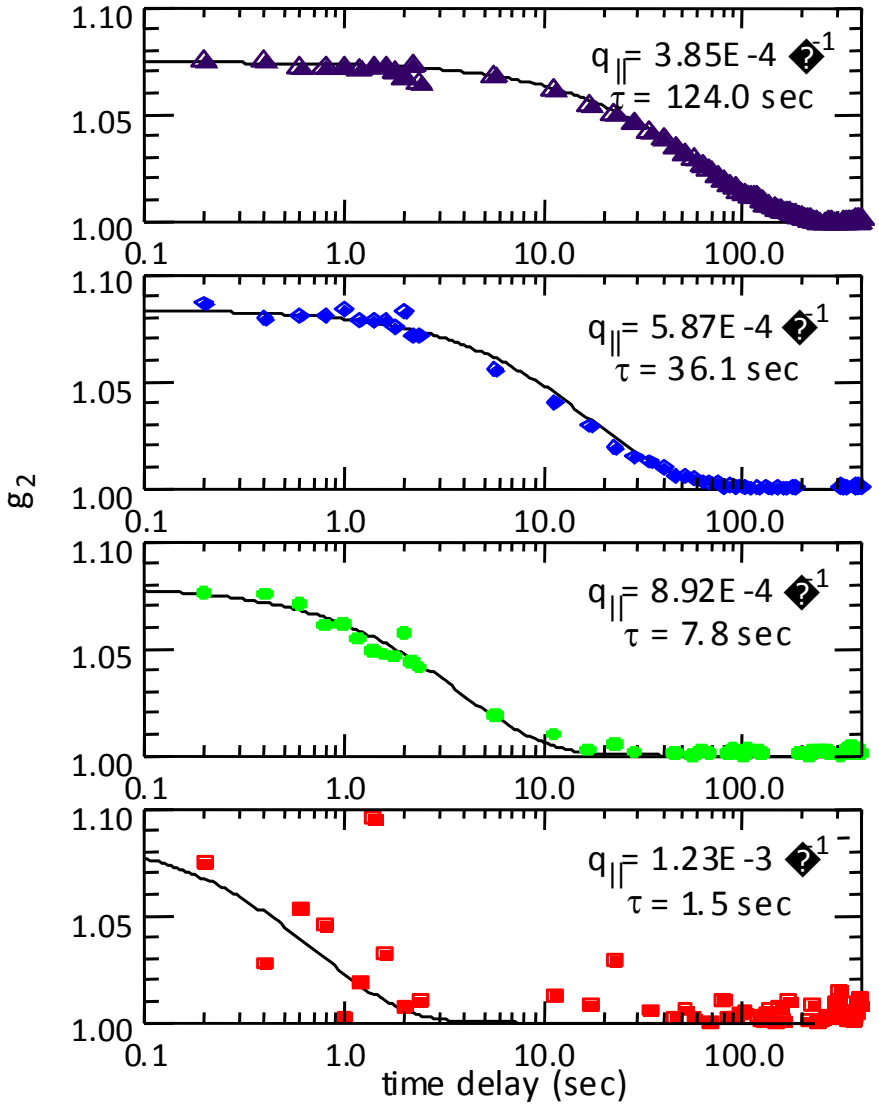
$k_s \to \gamma q^2$

$b \to \eta q$

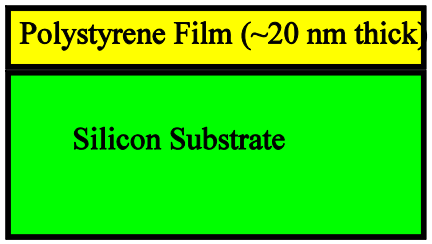
Expect $\tau \sim \eta / q\gamma$, actual $\tau = \eta / 2q\gamma$ (deep waves)

Dynamics for PS films supported on Silicon

Hyunjung Kim et. al. PRL 2003, Jiang et. al. PRL 2008

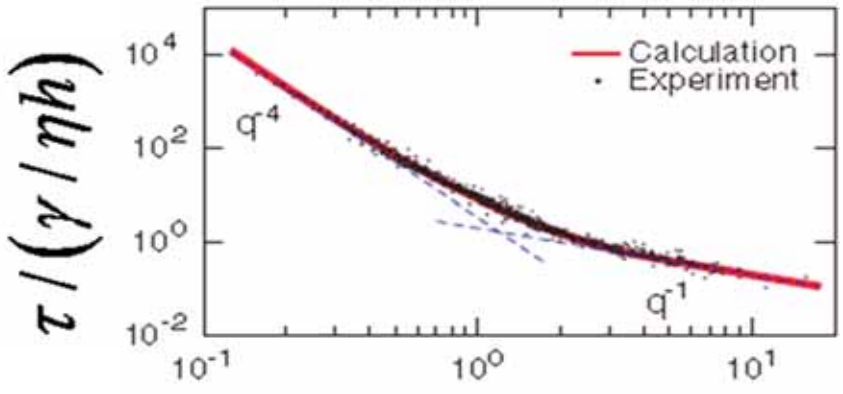


Finite Depth

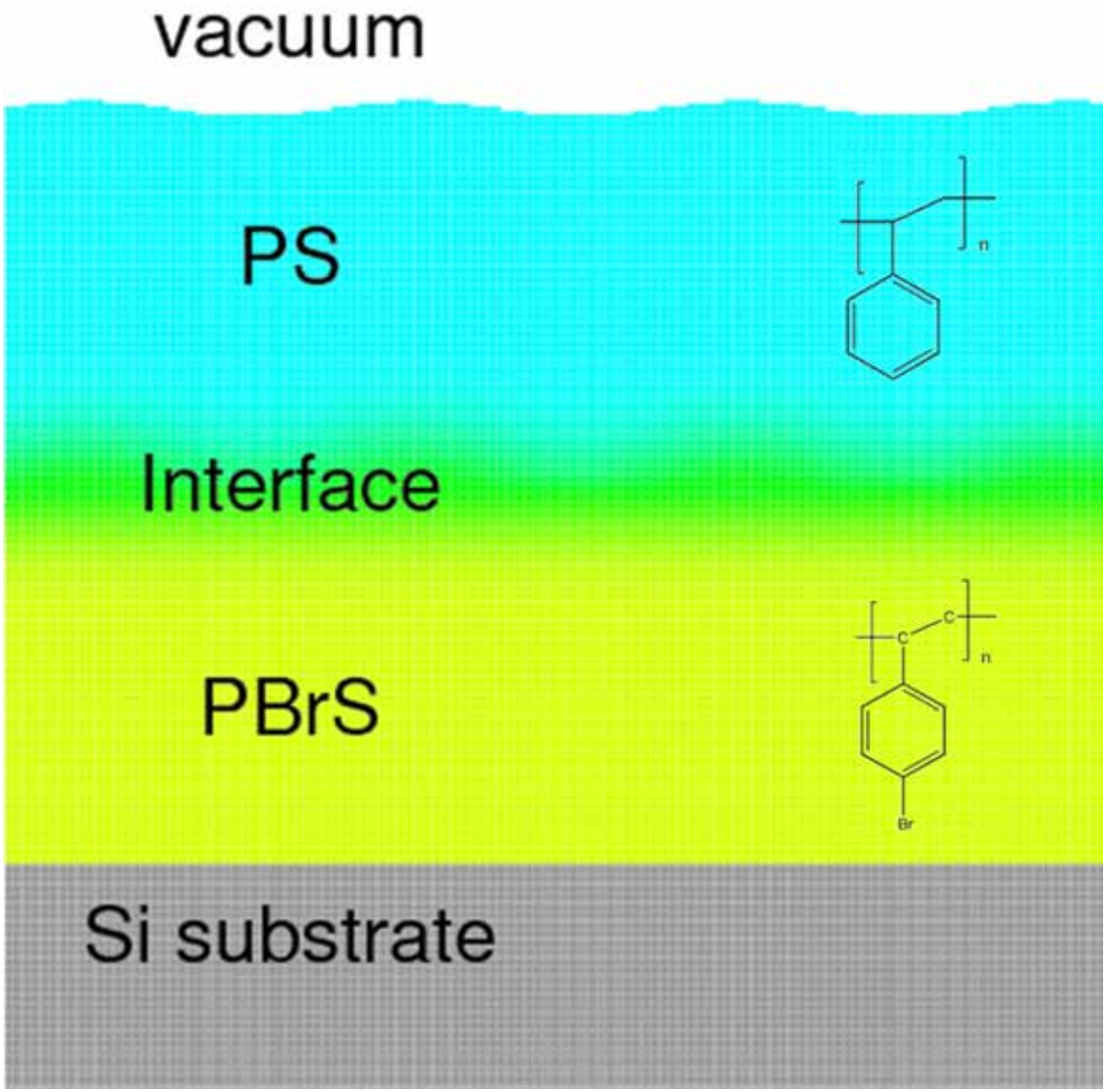


$$\tau = \frac{q_\parallel \gamma \left[-2q_\parallel h + \sinh\left(2q_\parallel h\right) \right]}{2\eta \left[1 + 2h^2 q_\parallel^{\,2} + \cosh\left(2hq_\parallel\right) \right]}$$

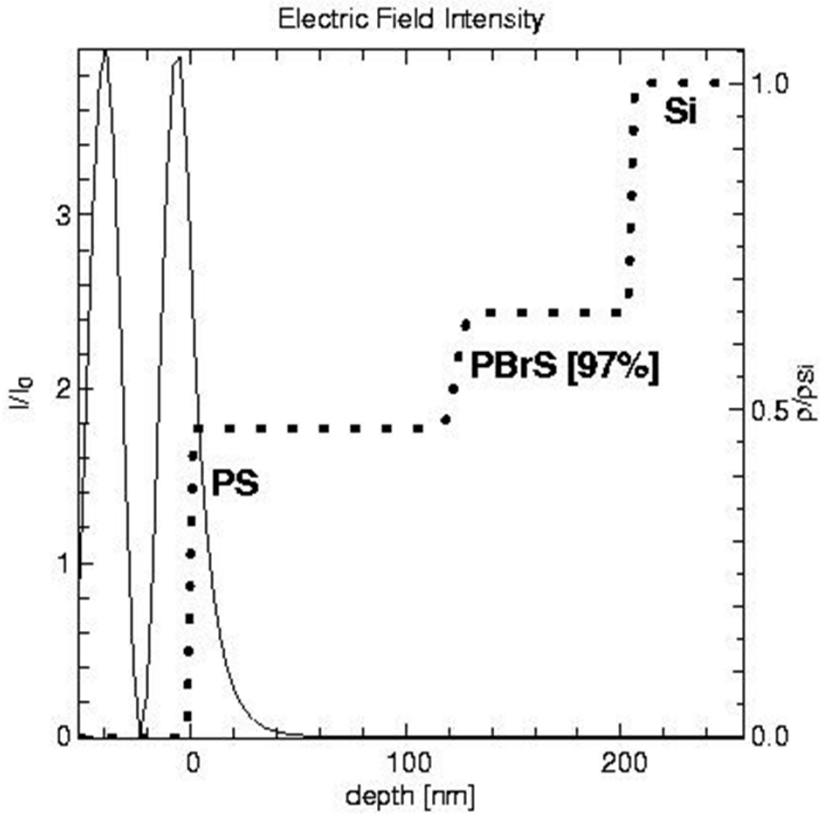
J. Jäckle, J. Phys.: Condens. Matter 10 (1998) 7121.

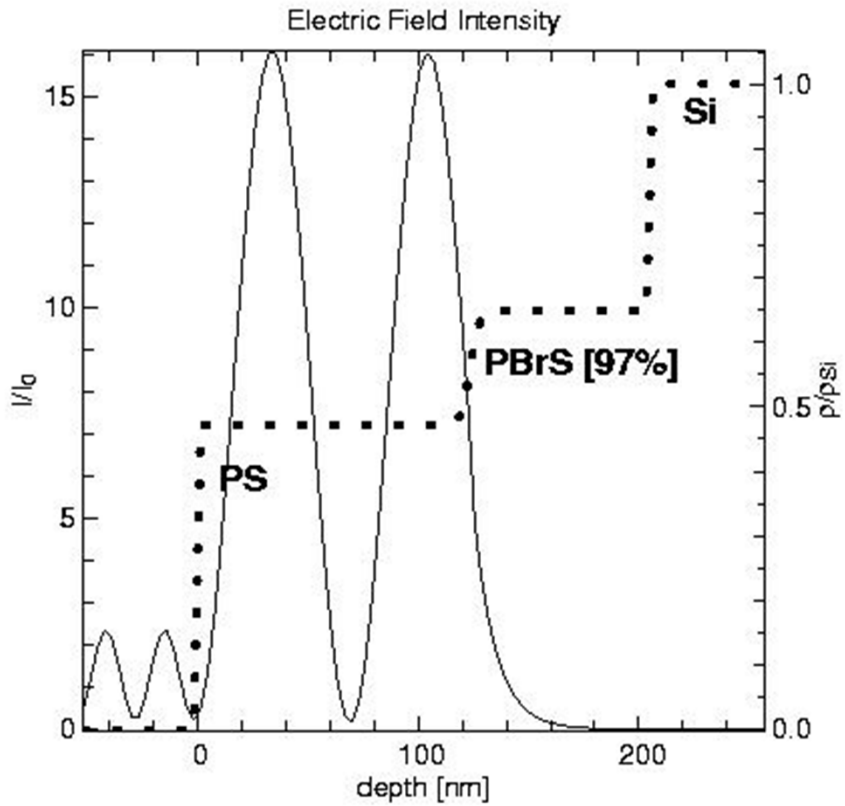


Use XPCS and X-ray standing waves to study Dynamics within a polymer bilayer



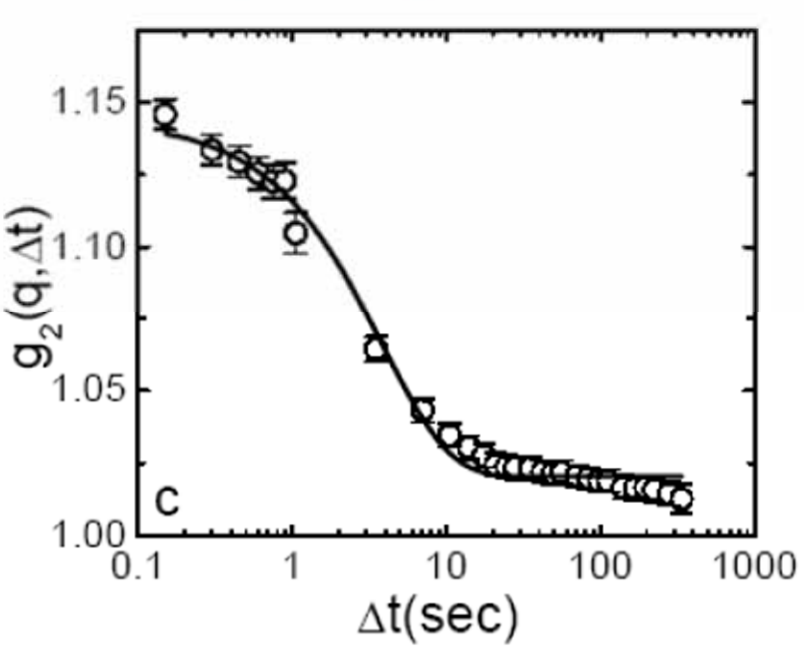
Select an interface using an x-ray standing wave excited through a grazing incidence beam



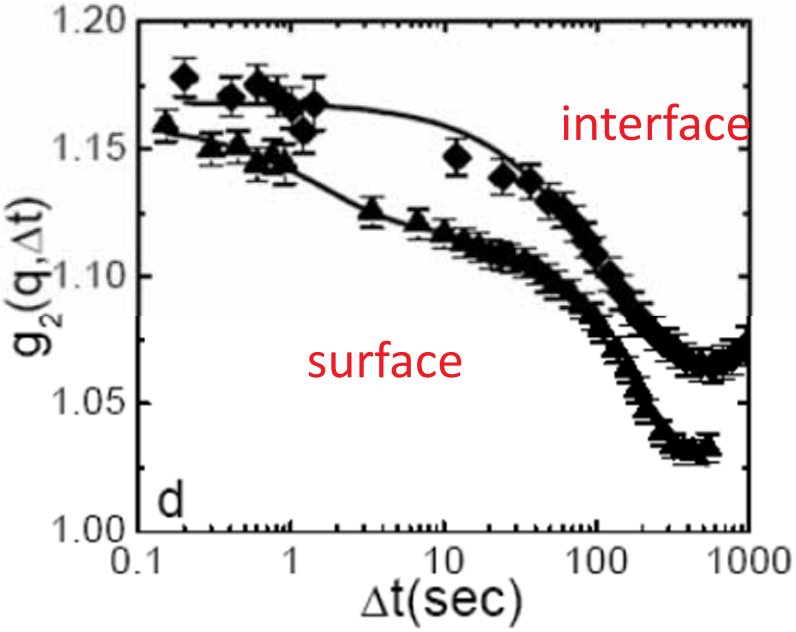


Autocorrelation functions-205°c

Single layer PS

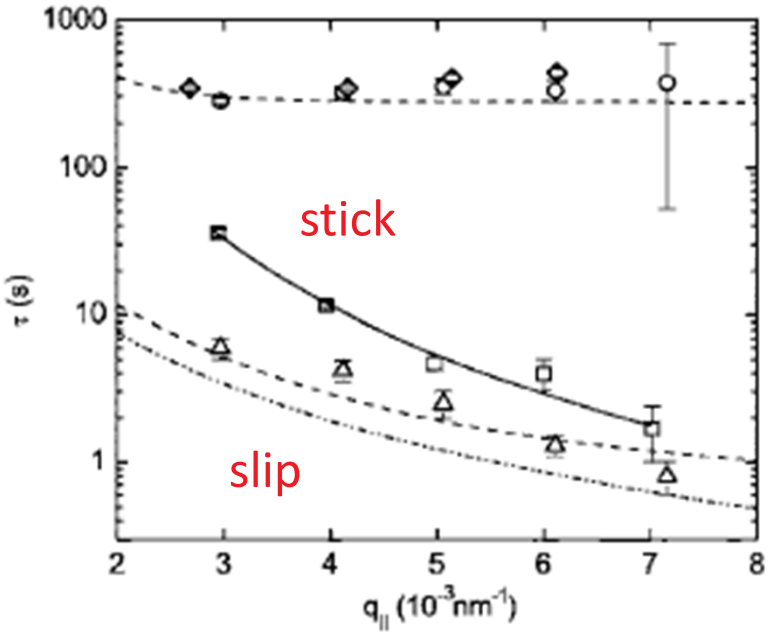


Bilayer



$$g_2(t) = 1 + \beta\left[(1-r)e^{-t/\tau_1} + re^{-t/\tau_2}\right]^2$$

Fast mode can be described via a two layer model, with a low viscosity interface at the PS/PBrS boundary. However this may be equivalent to a change in boundary conditions to something intermediate between stick and slip



195C 100 nm PS/200 nm PBrS

(triangles) Bilayer top surface fast mode

(circles) Bilayer top surface slow mode

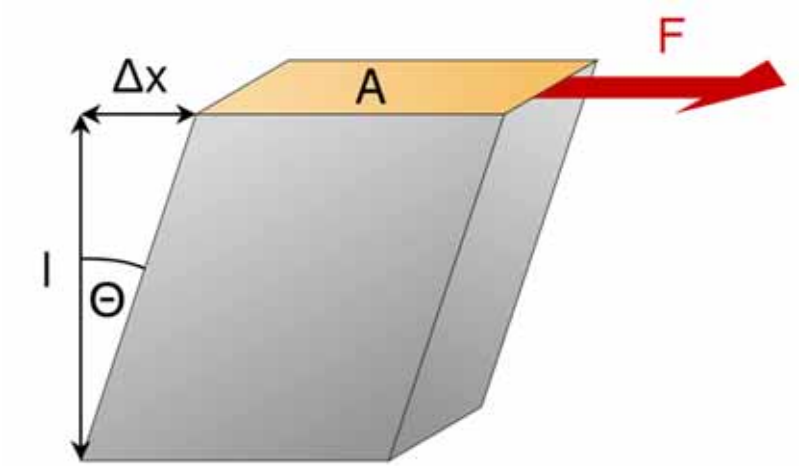
(diamond) Bottom surface mode

(square) single layer ps

But, how to explain the q-independent slow mode?

Include a Static Shear Modulus

$$G(\omega) = \frac{F(\omega)/A}{\Delta x(\omega)/l} = \mu - i\omega\eta$$



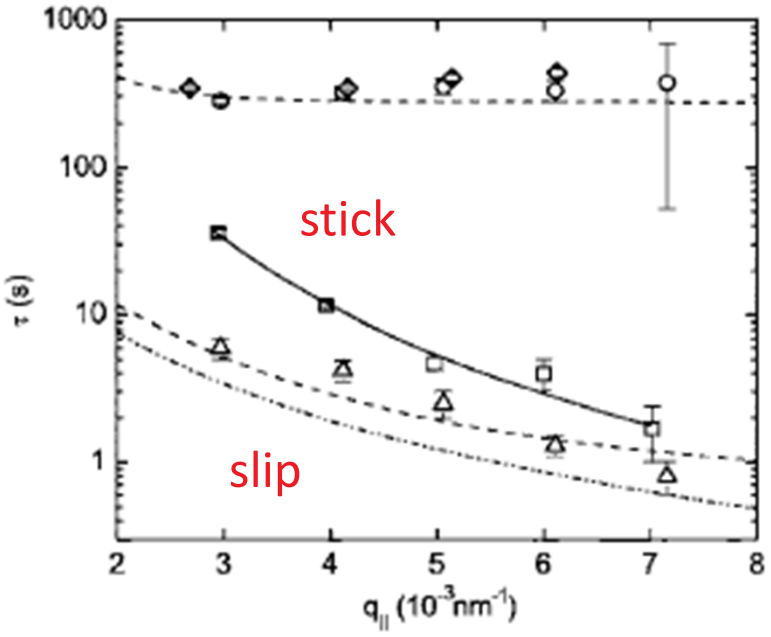
Sheer modulus

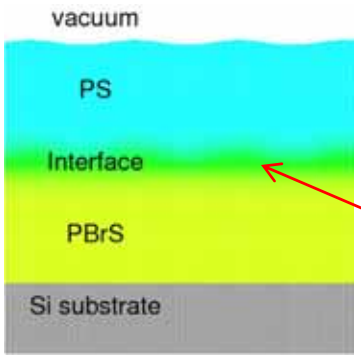
Viscosity

Changes dynamics

$$\tau(q) = \frac{\tau_0(q)}{1 + \tau_0(q)\mu/\eta}$$

For large sheer modulus, get q independent relaxation times





How to explain the q- independent slow mode?

$$\tau(q_\parallel)=\frac{\tau_0(q_\parallel)}{1+\tau_0(q_\parallel)\mu/\eta}$$

$\tau = \eta / \mu$
μ= 18 N/m^2
η = 327 Ns/m^2

Dynamics come from interfacial region, not lower layer

Future experiments (1) capillary wave dynamics on polymers at high *q*

What is gained by going to high wavevector?

Polymer dynamics can be described within the context of the reptation model, which includes three regimes of dynamics. Rause dynamics at short times, reptative dynamics at intermediate times and diffuse motion at long times.

Simplest version of reptation theory assumes that the constraints imposed by neighboring polymers are fixed. However more complete theories must include the effect of constraint release. How is such constraint release modified near a surface?

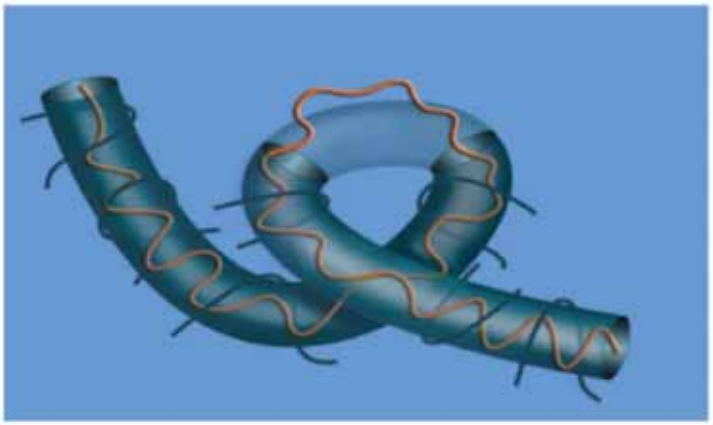
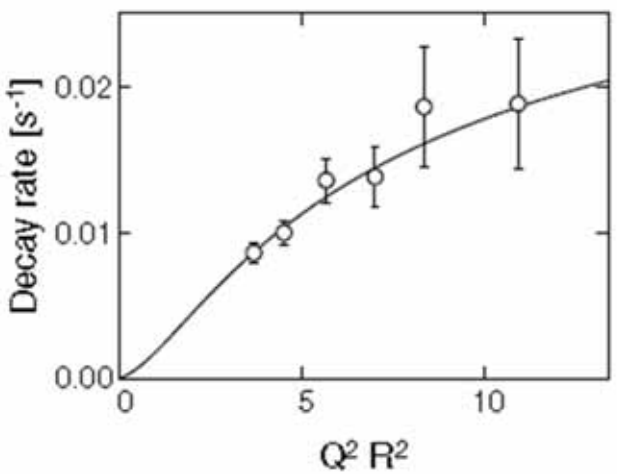
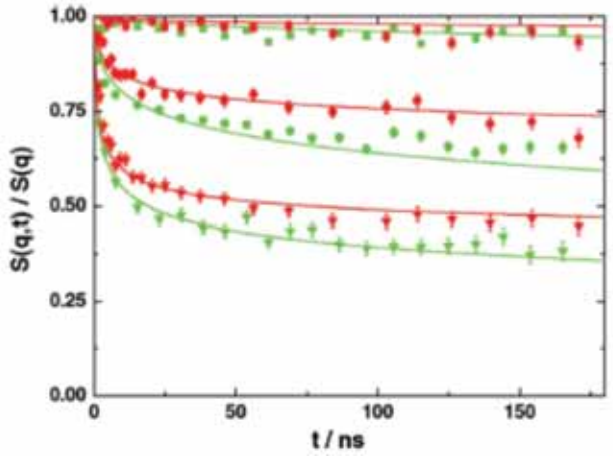


Figure 3
Schematic presentation of the CR mechanisms: the dissolving of entanglements allow chain motions beyond the initial tube constraints.



XPCS measurements by Lumma et. al (PRL 2001) on binary polymer mixtures (PEO-PMMA) show a transition from diffusive behavior at small Q to reptative behavior at larger Q.



Neutron spin echo measurements by Richter (J. App. Cryst. 2007) show transition from Rause like dynamics at short times, to reptative dynamics at longer times.

- The surface can be employed as a contrast mechanism to image polymer dynamics.
- The effect of the surface on constraint release may explain changes in the glass transition near surfaces.
- Measurements at larger Q can probe details of reptation around the entanglement length (~7 nm) which can shed light on the reptation mechanism
- Need high flux and ability to measure microsecond dynamics

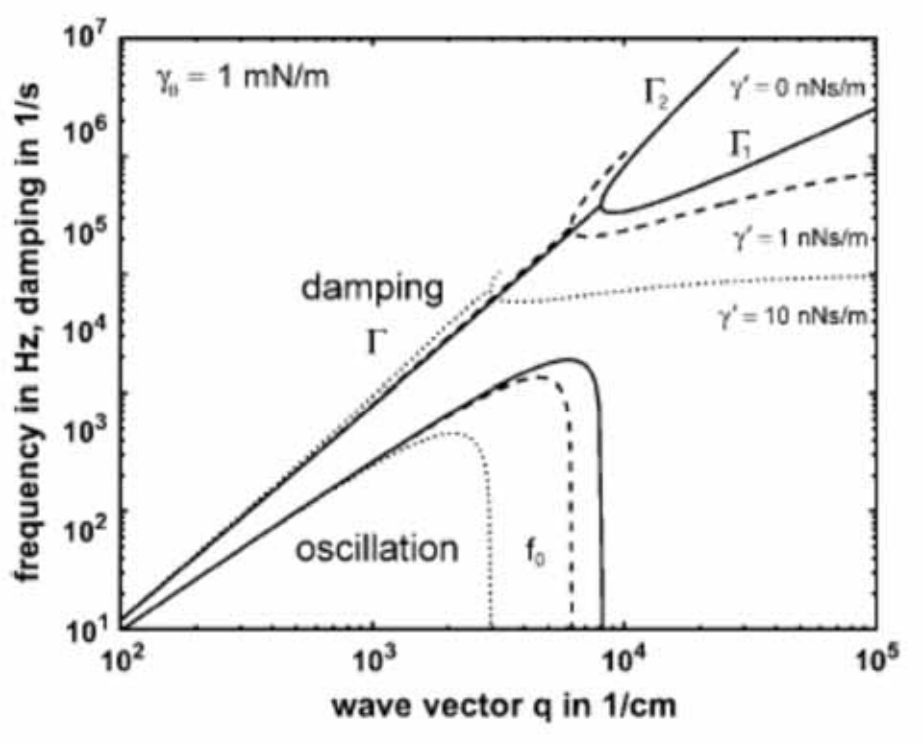
Future experiments (2) dynamics of biomembranes

Membrane fluctuations are important in biology for their relevance to membrane interactions, membrane fusion, thermodynamics equilibrium of membranes, and effect on the rates of membrane bound reactions .

The difference in membrane fluctuations may significantly effect the function of biomimetic solid supported membranes.

For biologically relevant studies must examine membranes in water.

A typical time constants for fluctuations is $\gamma_0/\gamma' \sim 10\ \mu s$.



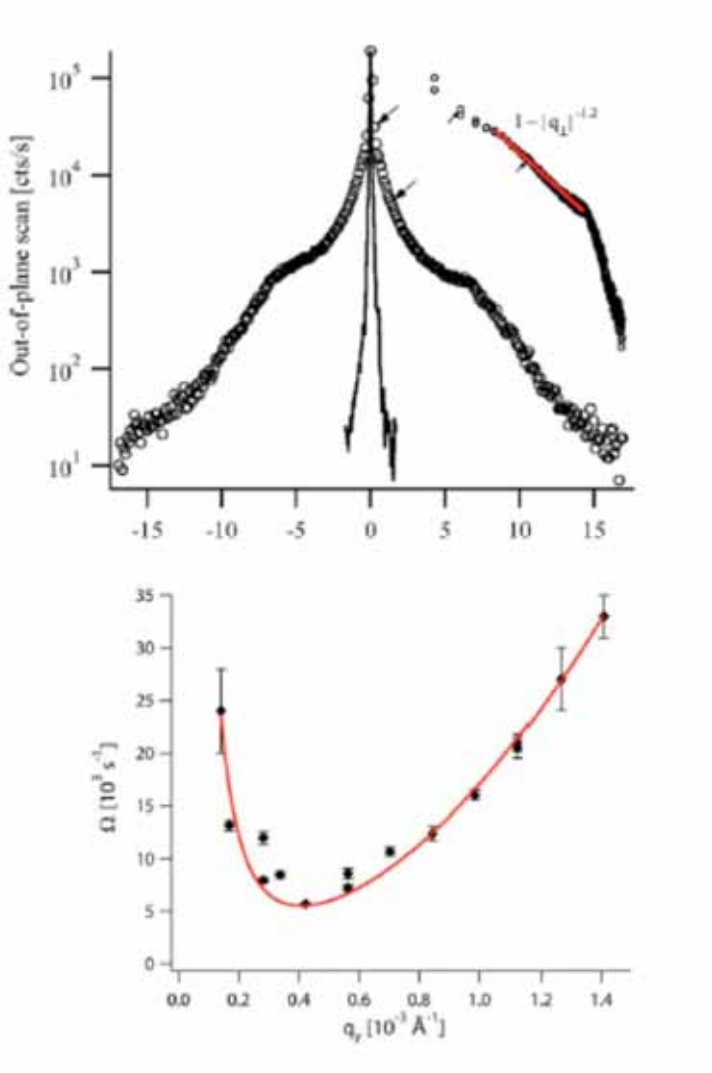
M. F. Hildenbrand, and T. M. Bayerl, Biophys. J. **88**, 3360-7 (2005).

Multilayer membrane stacks

Studying stacks of membranes increases flux, and has allowed some experiments to be done at lower q.

However, low q fluctuations include membrane-membrane couplings and examine different physics than single membrane studies.

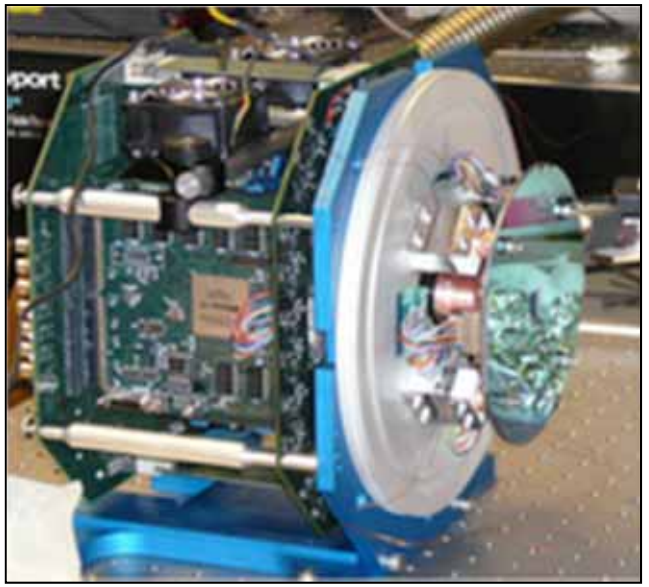
At larger q, membrane fluctuations become independent again, but this requires more flux and coherence



Constantin *et. al.* PRE 2006

Technical Considerations

- Need fast camera with microsecond readout capability.
- Need optics to shape speckle size
- If area detectors are too slow, need multiple point correlators which can be arrayed along a scattering ring.
- Software/hardware needed to handle data flow.



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