X-ray Photon Correlation Spectroscopy Study of the Dynamics of a Polymer Bilayer

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Collaborators

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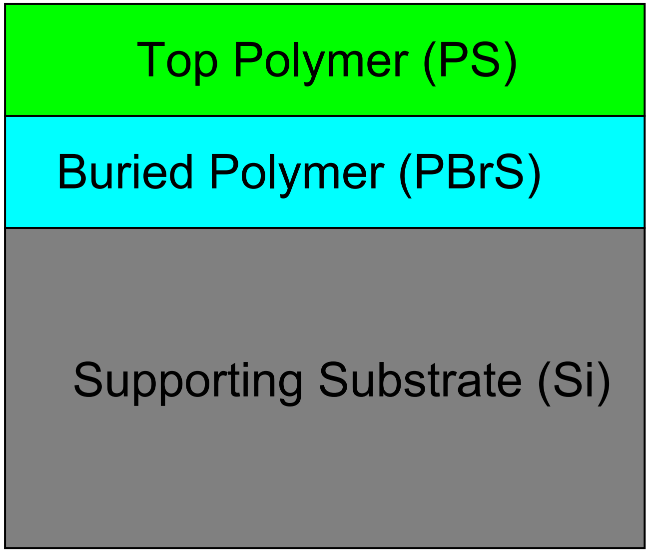
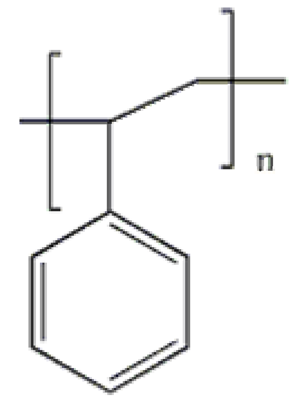
Polymer Bilayer Dynamics

- Technologically important system
  - Co-extrusion of polymers
  - Mechanical toughness
  - Optical multilayers
- Physics of the polymer interface
  - Physical parameters: viscosity, interfacial tension.
  - Intermixing, Entanglement, Slip
  - De-wetting Mechanisms
  - Tg depression
  - Van der Waals interactions
- Develop a Methodology for XPCS within buried layers.

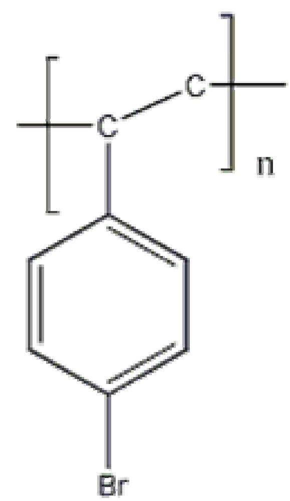


PS-PBrS as a model system

- Need a small interaction paramter (ξ) to get two dissimilar polymers to wet. Can tune ξ by changing bromination ratio.
- PS has fairly good radiation resistance.
- Good x-ray contrast between PS and PBrS
- Dynamics of PS monolayers has been previously characterized.
- Monodisperse PBrS Obtained from Miriam Rafaelovich

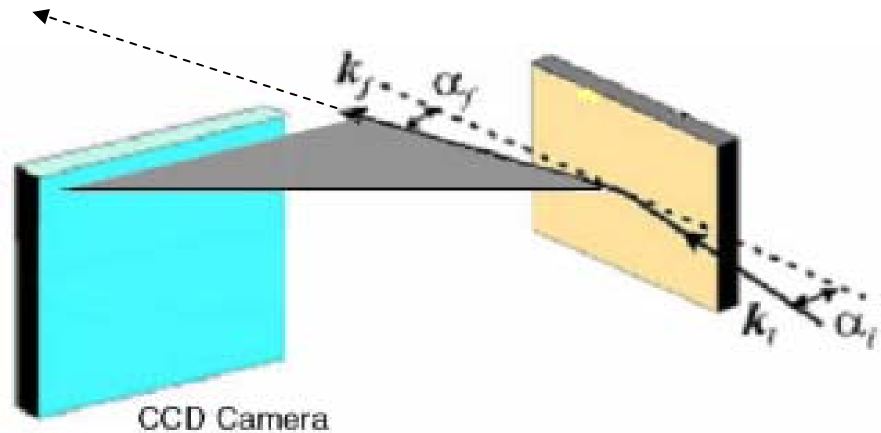


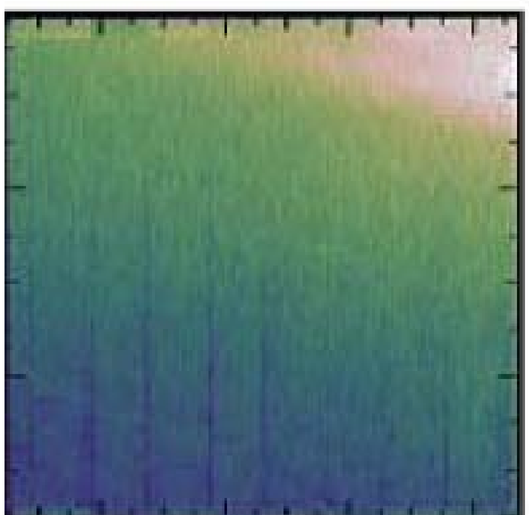
PS

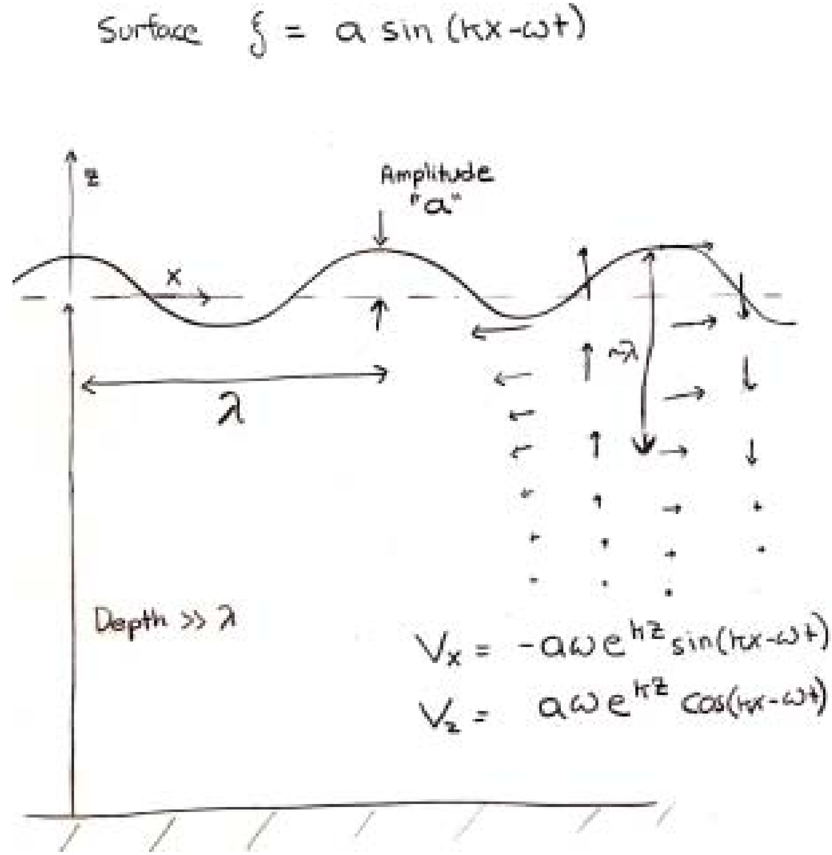


PBrS

Thermal Capillary Waves

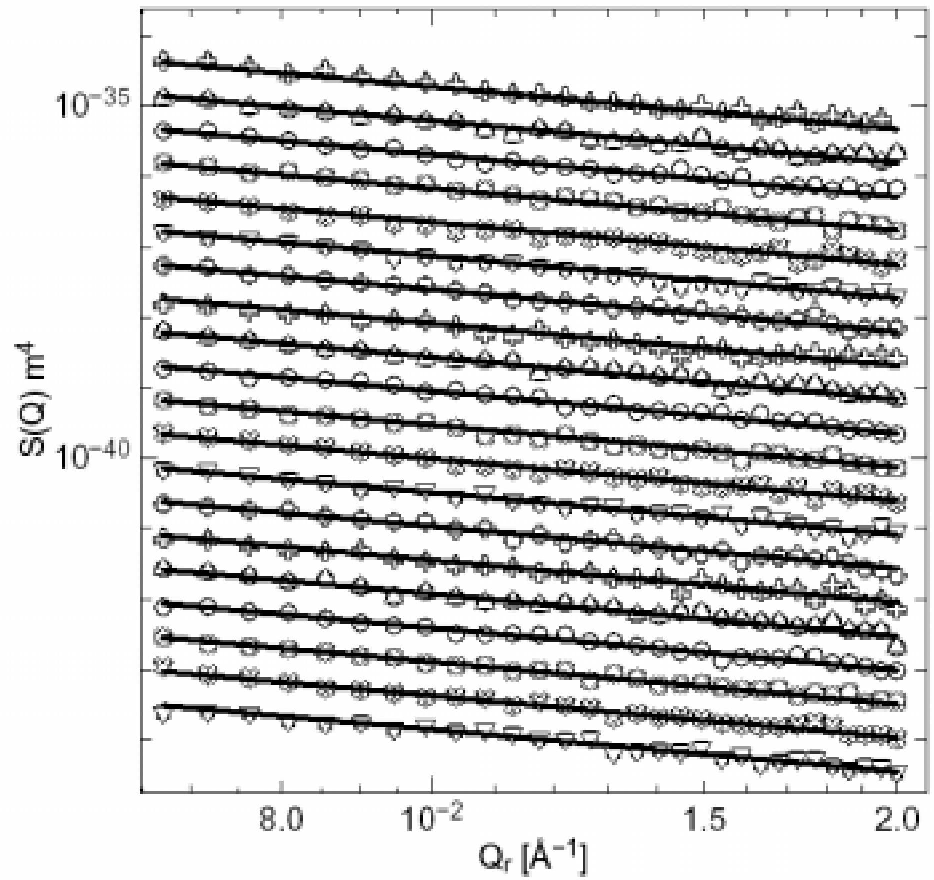






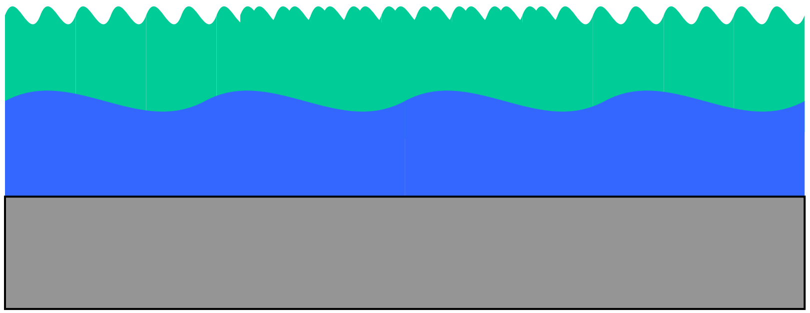
Diffuse Scattering from a PS Homolayer

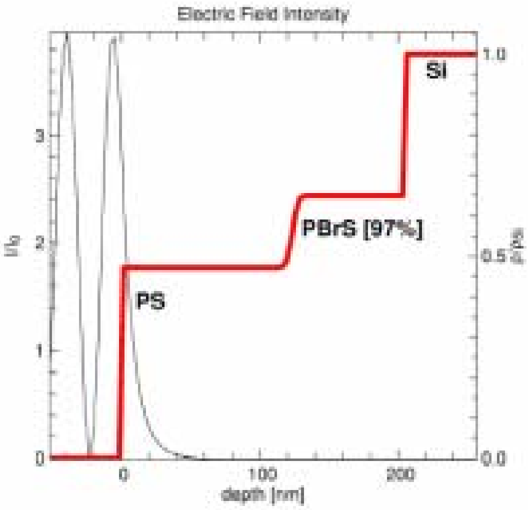
- $S(q)=k_B T/\gamma q^2$
- Thick Polystyrene Film (100 nm)
- Small q_z
- $q_{\parallel}$>> resolution.
- Only adjustable parameter is the surface tension (29 mN/m vs. 32 for bulk)

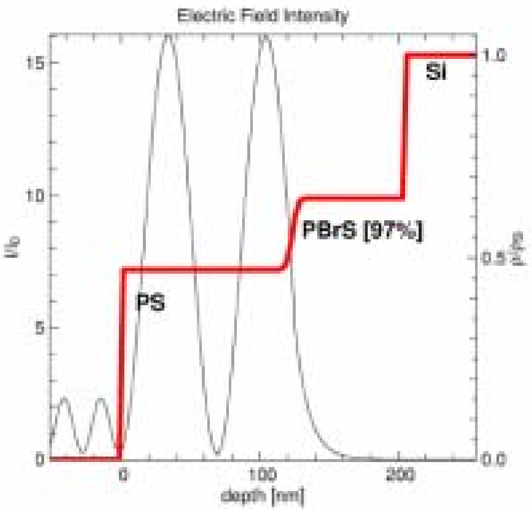


Diffuse Scattering from a Bilayer

- PS (200k)
- PBrS (350k) 89% Brominated
- PS 100nm thick.
- PBrS 100 or 200 nm thick
- Use x-ray standing wave to selectively illuminate each interface

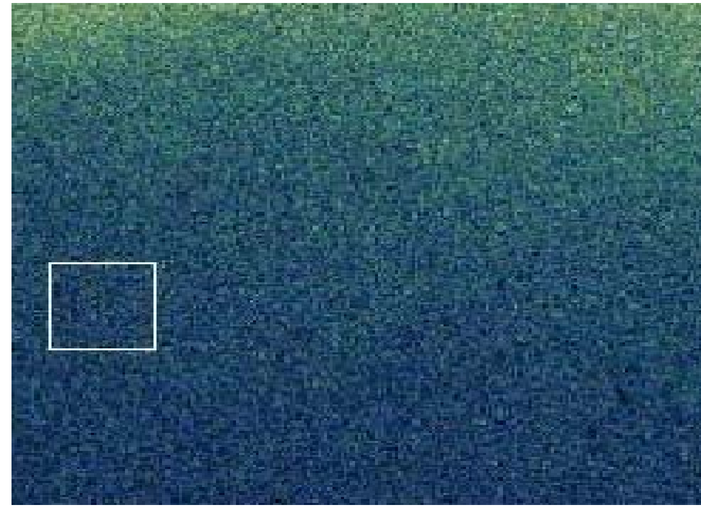


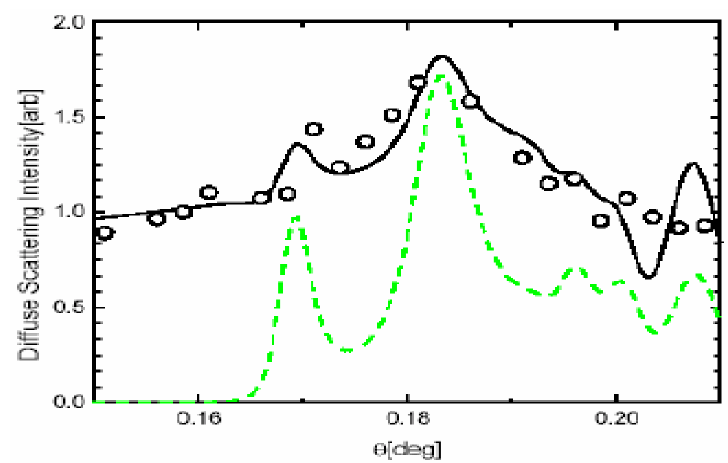




Two layer Static Results

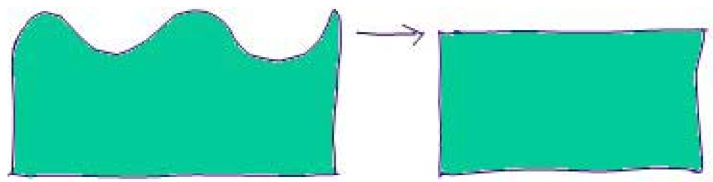
- Depending on standing wave condition, diffuse scattering comes from either the surface or the polymer-polymer interface
- Can compare measured scattering intensity with interfacial tension predicted from Flory-Huggins interaction parameter. Get good agreement. (~25%)





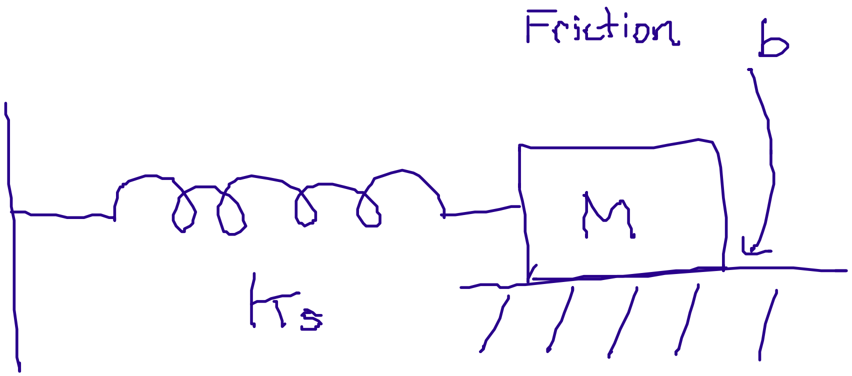
Single Layer Dynamics

- Time required for a surface mode of wavevector $q=2\pi/\lambda$ to relax.



- Use linear response theory to calculate the susceptibility of surface height fluctuations. For viscous fluid find overdamped modes which decay exponentially.
- Time correlation of the x-ray scattering pattern yields the decay times $g(q,\tau) \propto \exp\left[-2t/\tau\left(q\right)\right]$

Single Layer Time Constants



$$\tau = \frac{k\gamma\left[-2kh+\sinh\left(2kh\right)\right]}{2\eta\left[1+2h^2k^2+\cosh\left(2hk\right)\right]}$$

Overdamped $\tau \to b/k_s$

For deep waves, use dimensional analysis

only dimension is wavevector, k

$k_s \to \gamma k^2$

$b \to \eta k$

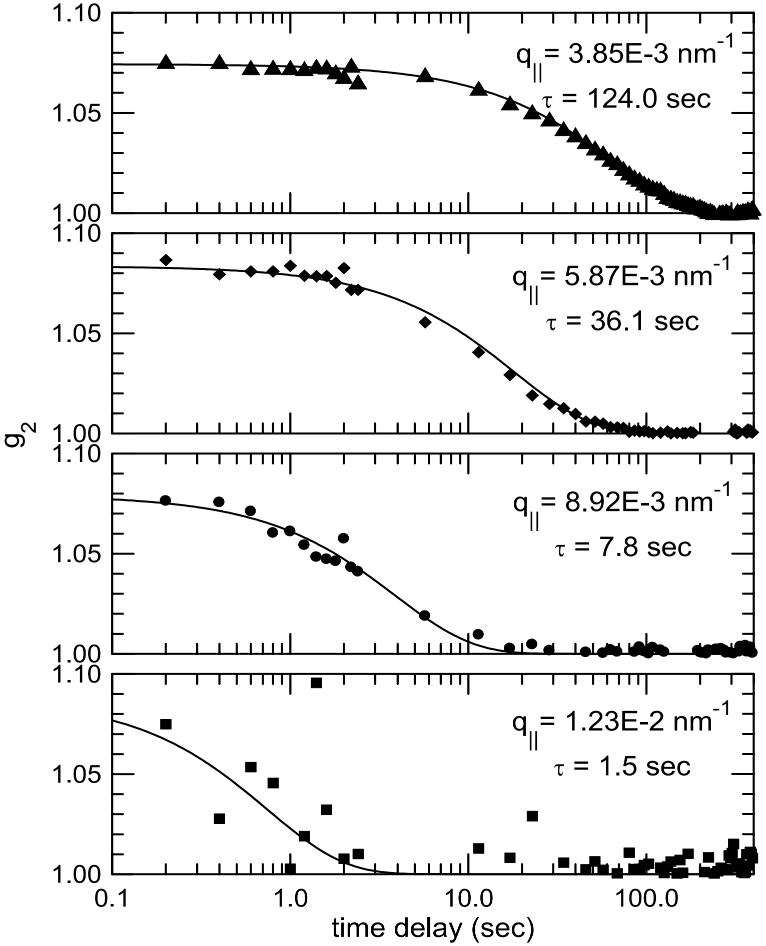
Expect $\tau \sim \eta / k\gamma$

$$\tau \to \frac{2\eta}{\gamma k} \sim \frac{1}{k} \quad \text{for } kh \to \infty$$

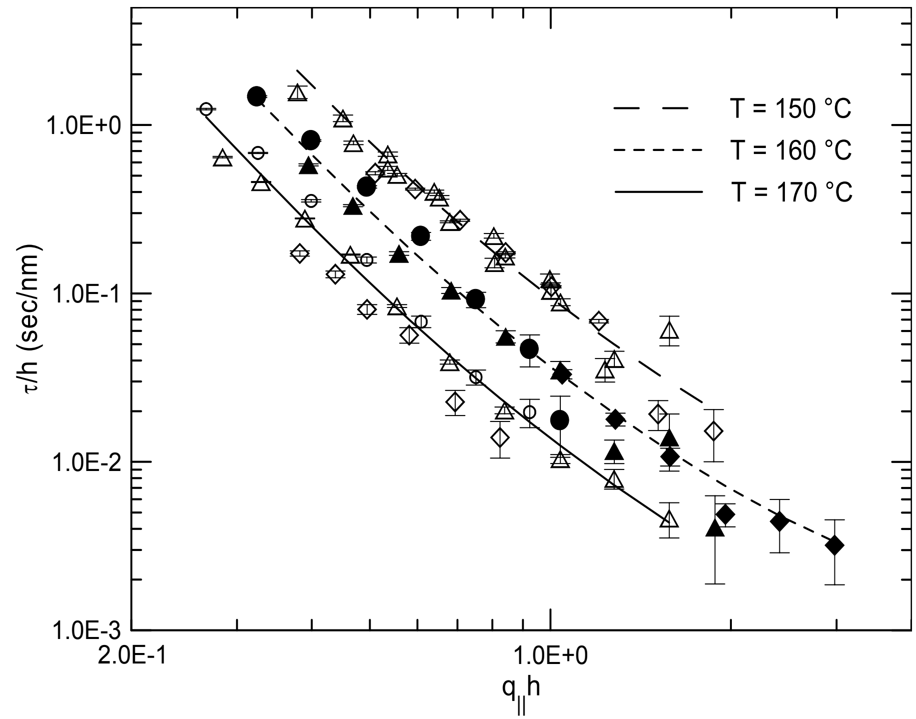
$$\tau \to \frac{2\eta}{\gamma k}\left[\frac{3}{2\left(kh\right)^3}\right] \sim \frac{1}{k^4} \quad \text{for } kh \to 0$$

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

Dynamics for PS films supported on Silicon
Hyunjung Kim et. al. PRL 90, 068302



84 nm film



84 nm (circles), 177 nm (triangles), and 333 nm (diamonds).

What might happen for a bilayer? Bottom Layer

- For a viscous bottom layer (PBrS), bottom layer moves (approximately) independently of top.
- For a thin top layer, expect surface tension of the top layer to supply restoring force.
- For a thick top layer expect surface tension of the interface to supply restoring force

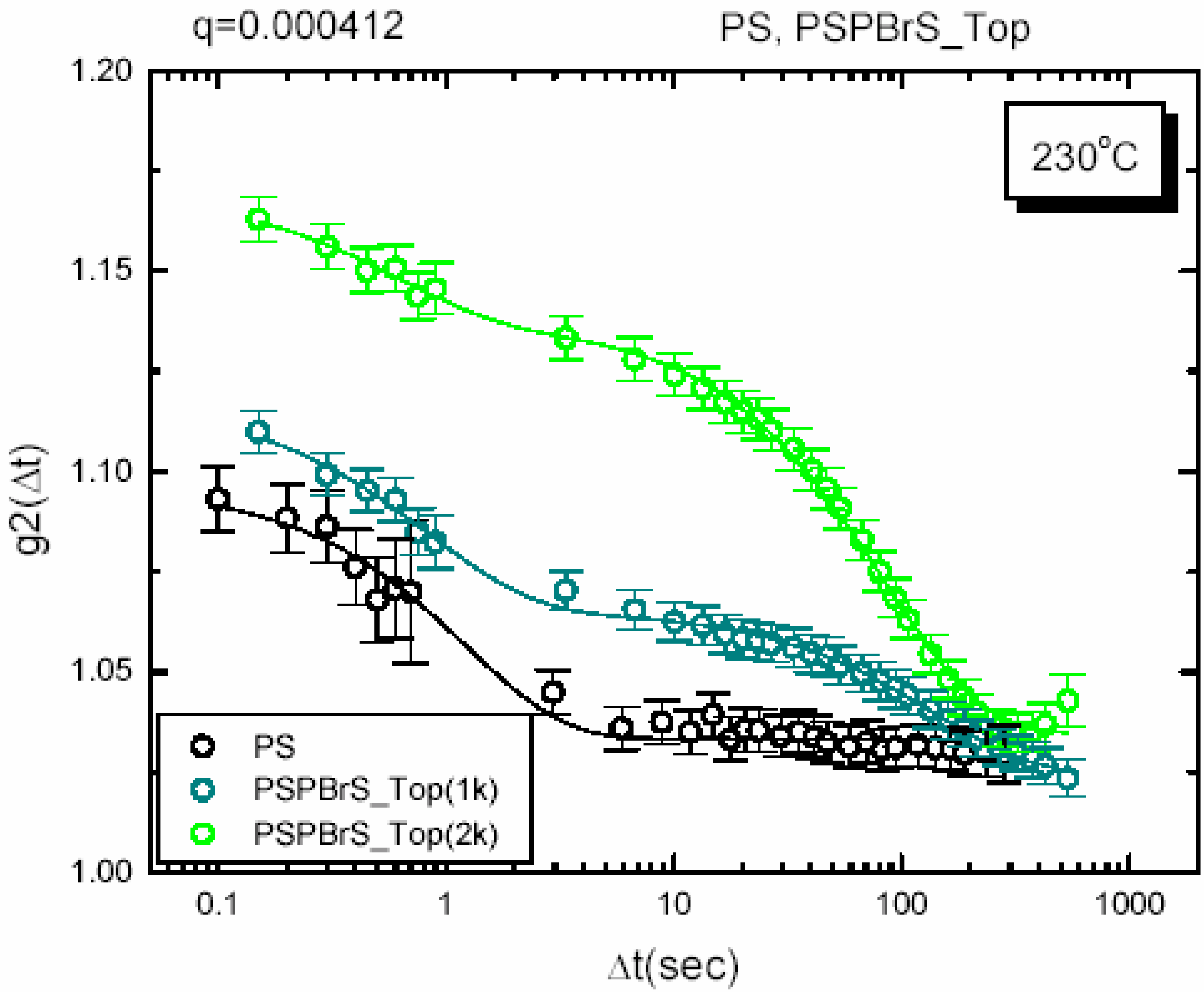
Top Layer

- For a low-viscosity top layer expect top layer to move almost independently of bottom. Should see single layer results.
- For thin top layer, top layer will ride along on top of bottom layer. Expect to see two modes.
- Second mode should be similar to the bottom layer mode.

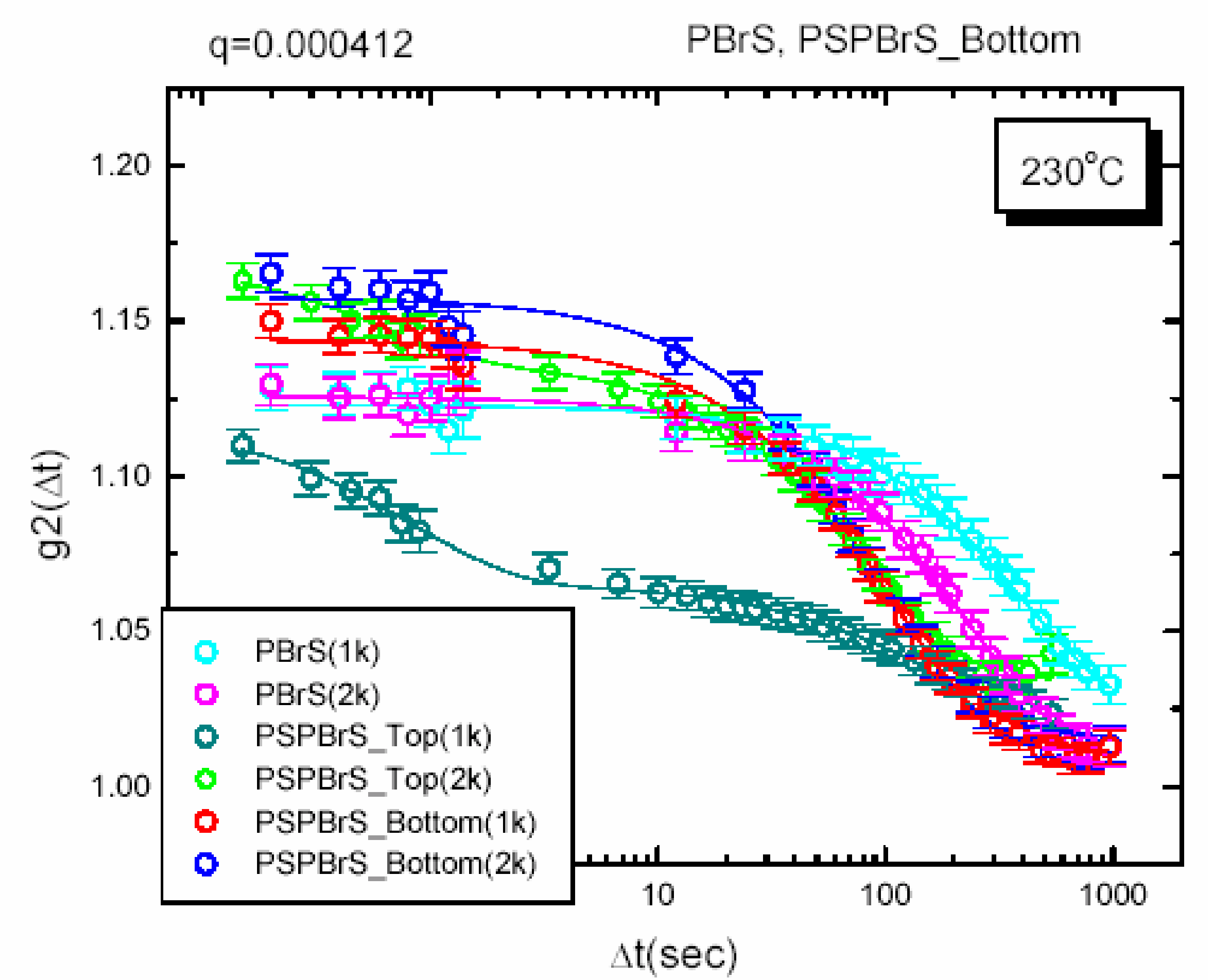
Theoretical Model

- Calculate the susceptibility of each surface to a sinusoidal pressure field
- Solve for time-constants of overdamped modes
- Equations more complicated (have to match boundary conditions at 3 interfaces). Solve numerically.

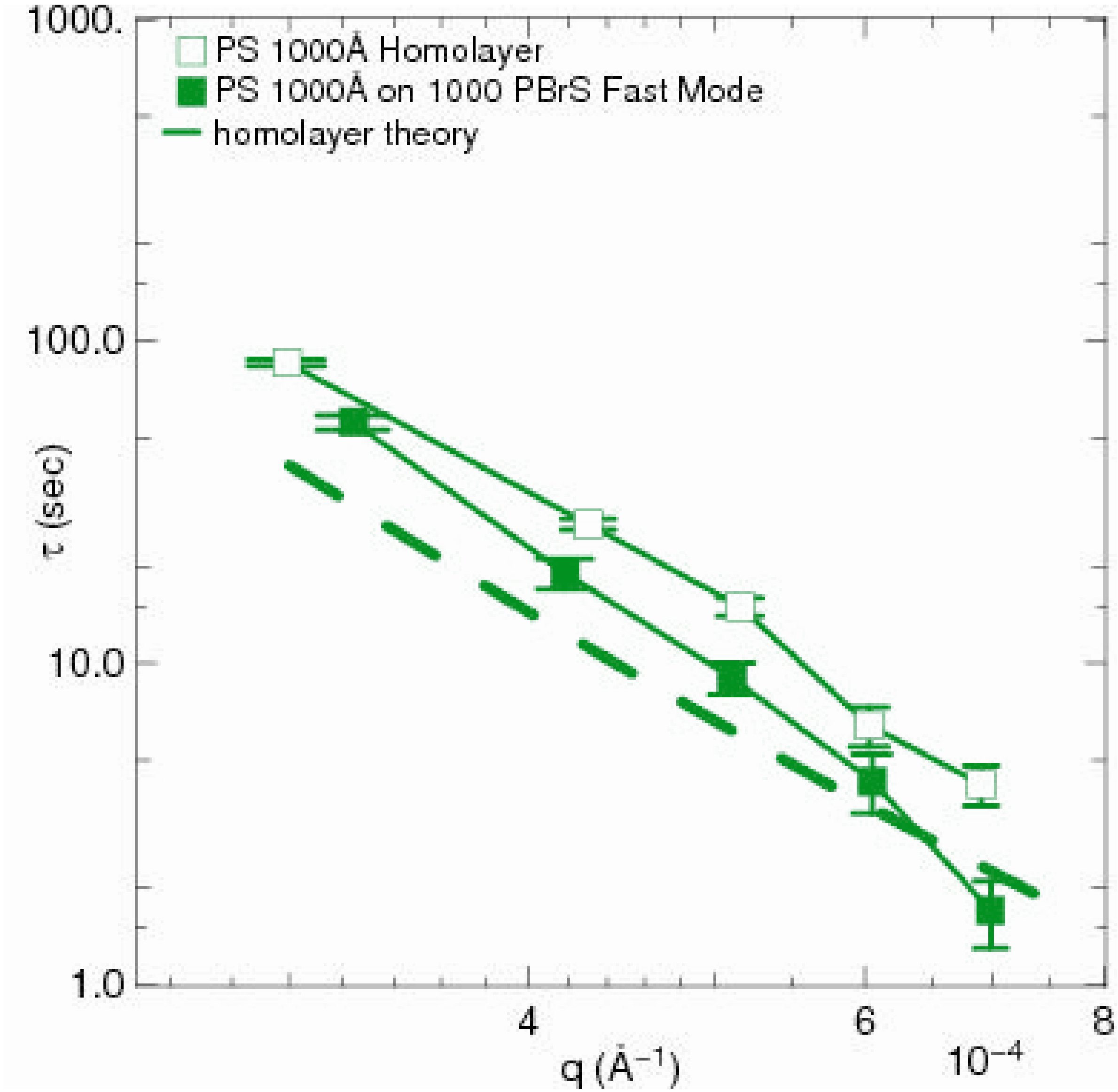
XPCS from Bilayer (top surface)



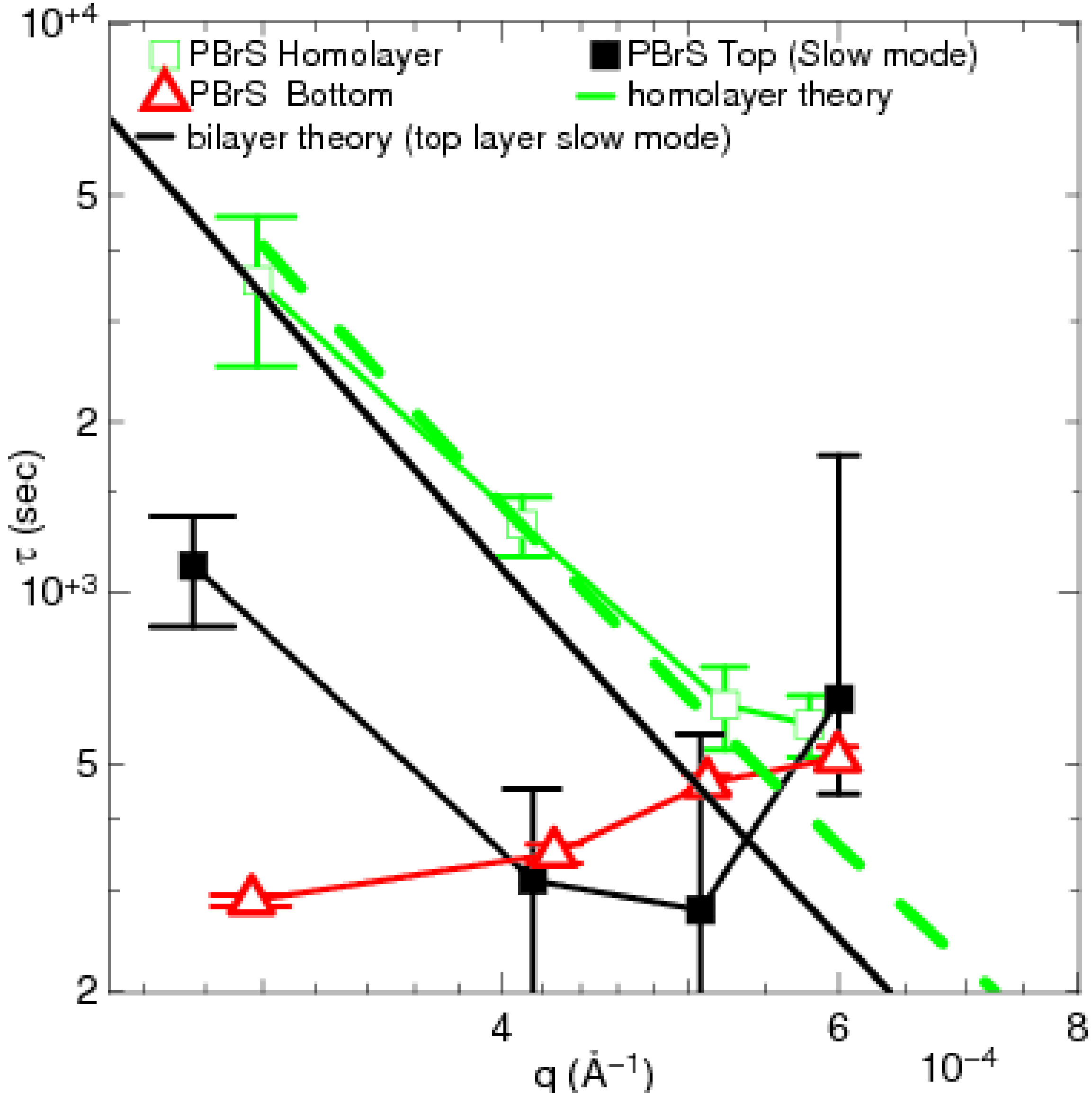
XPCS (Bottom surface)



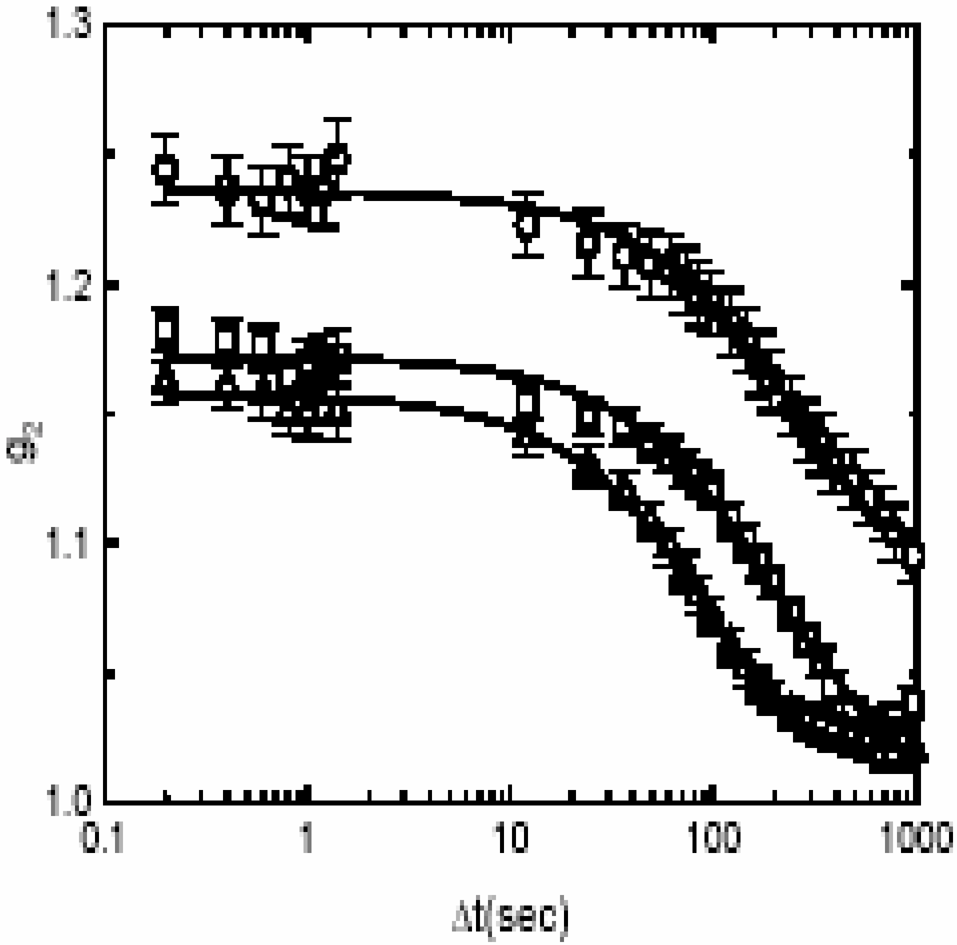
Results for Fast Mode 180C



Results for Slow Mode 200 C
100nm / 100 nm



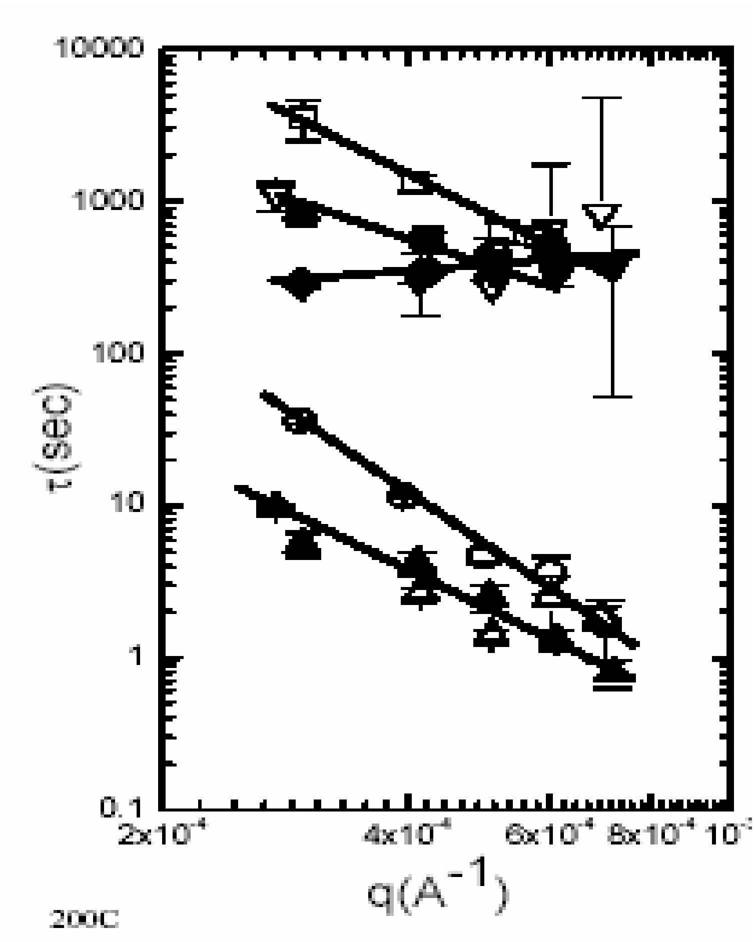
Temperature Dependence of Slow Mode



$q=0.0005A^{-1}$

180C PS (1000A)/PBrS(2000A)(circle)
200C PS (1000A)/PBrS(2000A)(square)
230C PS (1000A)/PBrS(2000A)(triangle)

No Dependence on PBrS Layer Thickness



PBrS(2000A)(solid square)
PS(1000A)/PBrS(1000A)[Top,T2](downtriangle)
PS(1000A)/PBrS(2000A)[Top,T2](solid downtriangle)
PS(1000A)/PBrS(1000A)[Bottom](diamond)
PS(1000A)/PBrS(2000A)[Bottom](solid diamond)
PS(1000A)(circle)
PS(1000A)/PBrS(1000A)[Top,T1](uptriangle)
PS(1000A)/PBrS(2000A)[Top,T1](solid uptriangle)

Is the slow mode a result of X-ray damage or beamline instability?

- Time constants depends on temperature.
- Top layer shows a slow mode even though beam never reaches PBrS.
- The slow mode for the top layer is very close to the mode of the bottom layer.
- Pure PS and PBrS only show one mode
- Pure PBrS is slower than bilayer but shows the correct q dependence

What is the cause of the flat q-dependence?

- Bilayer calculation still preliminary
- Slip at the polymer-polymer interface
- Non-equilibrium fluctuations (Stress driven?)
- Composition fluctuations
- PS/PBrS intermixing → graded fluid
- Substrate effects
- Entanglement effects
- Heterodyne mixing

Conclusions

- Have coupled XPCS with an x-ray standing wave.
- Measure the dynamics at both interfaces within a PS/PBrS bilayer
- Bottom layer of more viscous PBrS shows a single slow relaxations mode.
- Top layer shows a two-mode structure, with fast mode comparable to PS homolayer and slow mode similar to mode of the bottom layer
- Flat q-dependence of slow mode not understood.