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Structure and Dynamics of Polymer Nanocomposites by Grazing-Incidence X-Ray Techniques

High Temperature Membrane Working Group Meeting

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Advanced Photon Source

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Advanced Photon Source

- 3rd generation synchrotron x-ray facility built by US DoE for basic and applied research
- 3000 Users/Year: physics, chemistry, materials science, biology, energy …

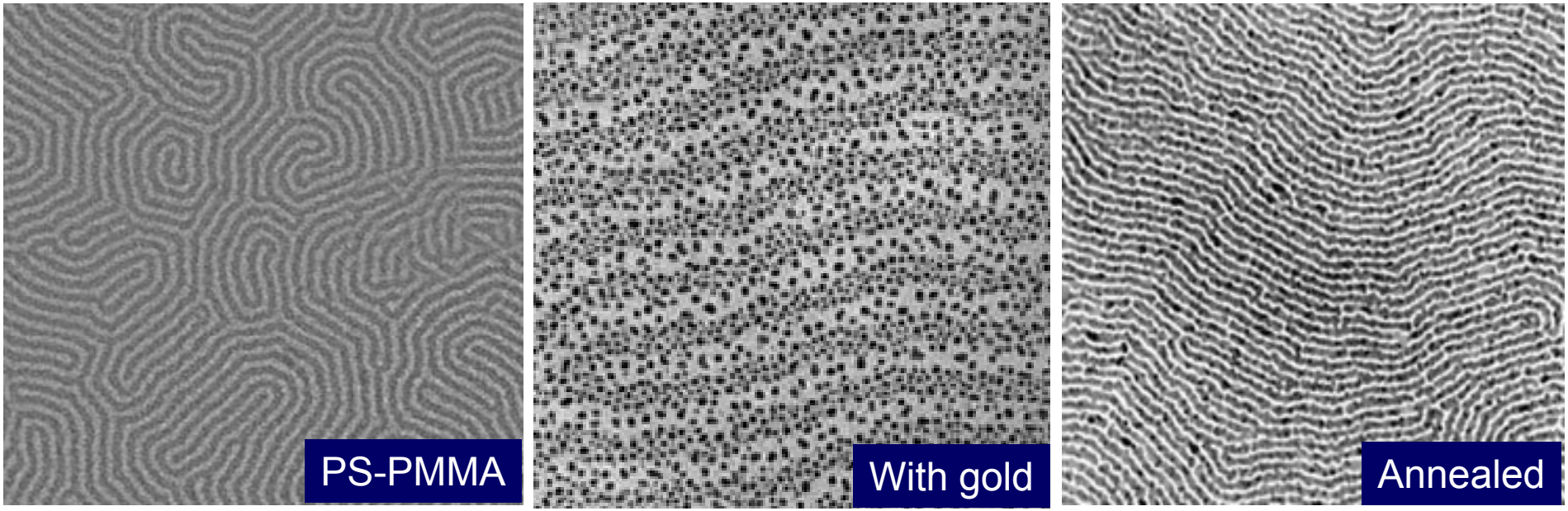
Outlines

- Scientific opportunities and motivations
- Structure, kinetics and self-assembly in thin films of polymer nanocomposites
  - Anisotropic nanoparticle diffusion and dynamics in ultrathin polymer films
  - Self Assembly of 2D diblock copolymer single crystal by graphoepitaxy
  - Diblock copolymer/nanoparticle self assembly
- Ionic distribution near membrane surfaces using x-ray standing waves
- Membrane research with surface sensitive x-ray technqiues

Motivations

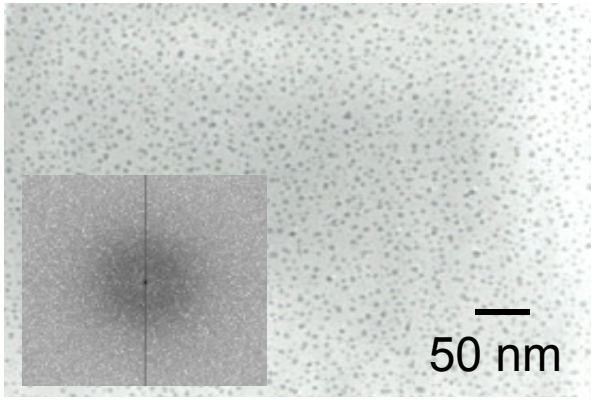
- Self-assembly of nanostructure is mostly an art.
- The self-assembly is NOT an equilibrate process.
- A controlled self-assembling needs to be guided by a thorough understanding of ordering kinetics.

*Lopes & Jaeger, Nature **414**, 735 (2001)*



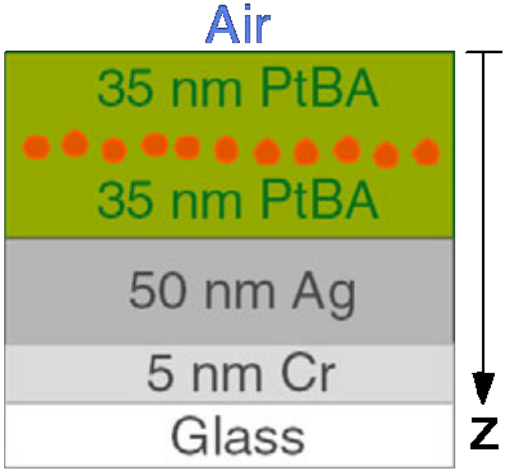
Nanoparticle Diffusion in Ultrathin Polymer Films

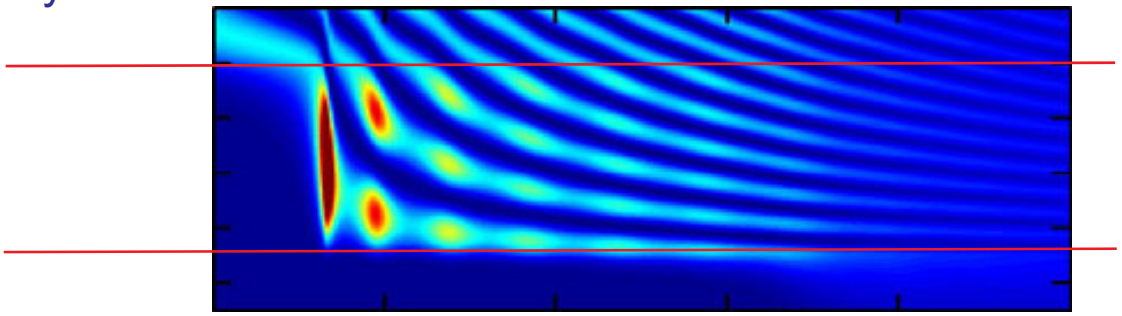
- Understanding the diffusion of nanoparticle metal particle in ultrathin polymer films
  - molecular dynamic in confined geometry
  - drastically different diffusion properties than in bulk
  - van der Waals interactions, steric forces, chemical affinities
- A host of x-ray techniques can be applied
  - Reflectivity and standing waves: diffusion perpendicular to interfaces
  - X-ray photon correlation spectroscopy: local short time dynamics
  - GISAXS using x-ray wave-guides: in-plane motion
- Complementary techniques
  - TEM
  - SPM



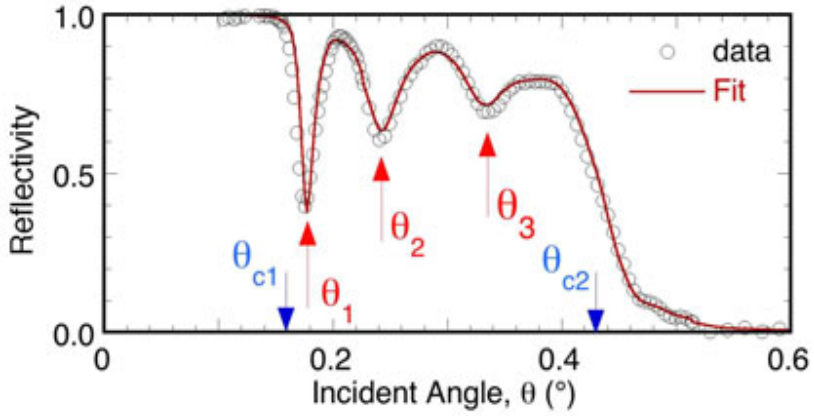
Grazing-Incident Techniques - X-ray Reflectivity and More

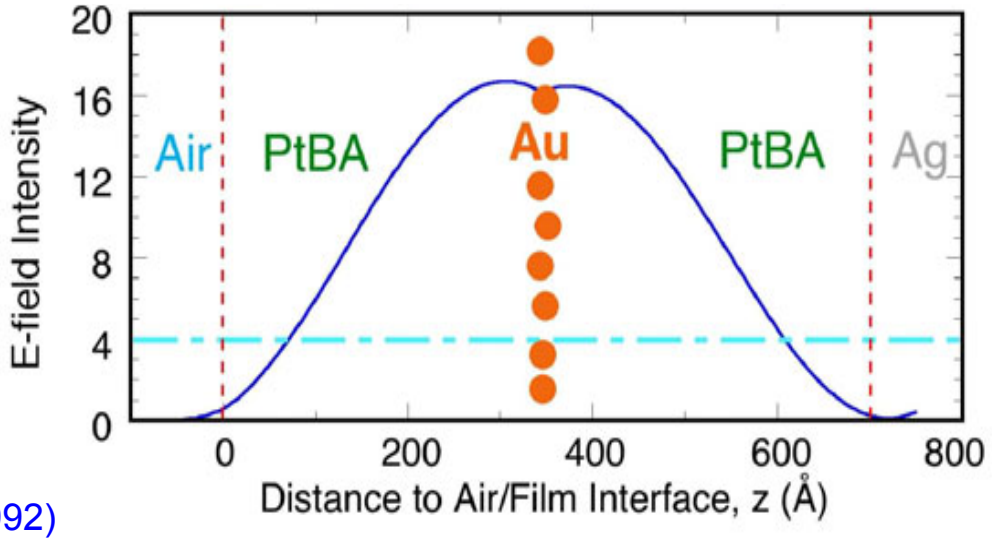
- Nanoparticles embedded in polymer films





Resonance-Enhanced Electric Field



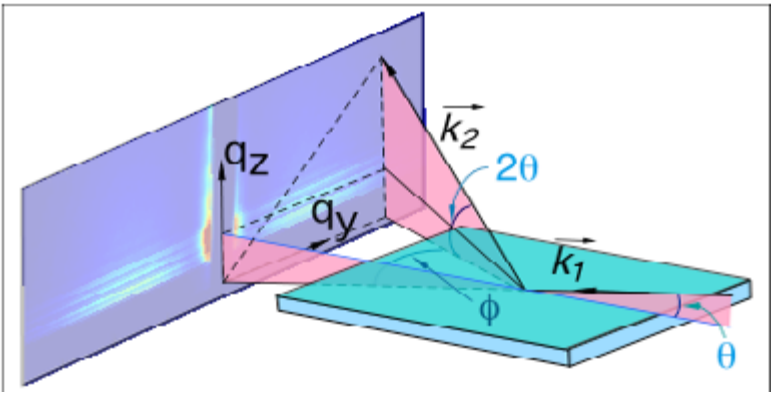


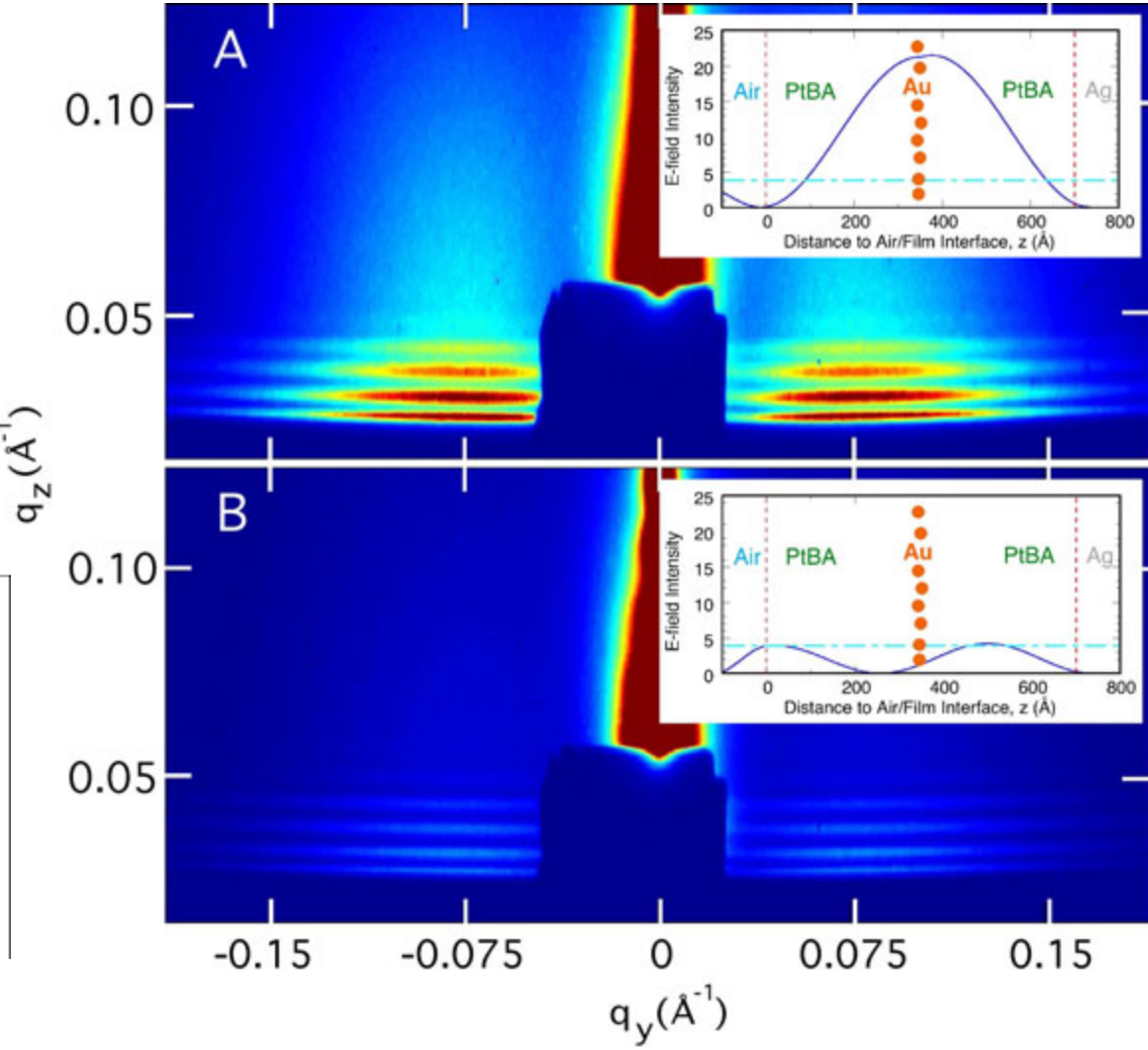
Waveguiding effect: Wang, *et al.* *Science* 258, 775 (1992)

Feng, *et al. PRL*, 71, 537 (1993)

GISAXS with Enhancement

- Scattering in x, y, z directions reveals the sample structure in 3D
- Enhancement due to waveguides is apparent at different incident angles

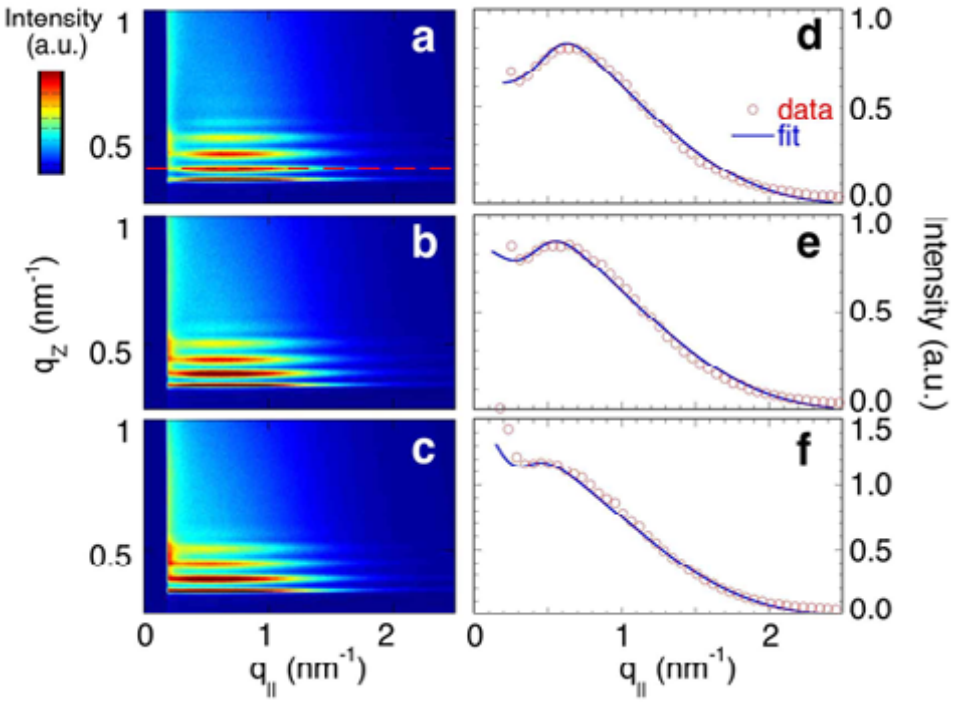


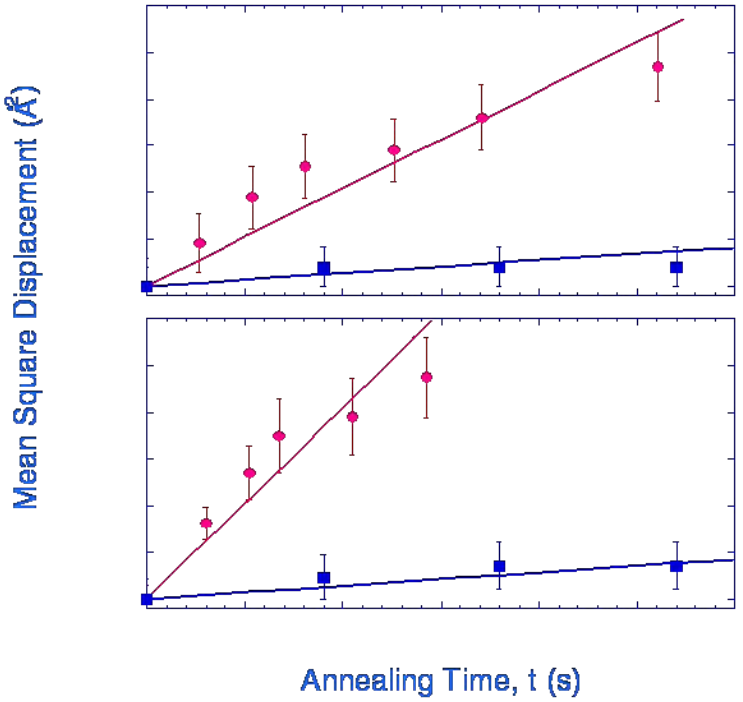


Narayanan, Lee, Guico, Sinha, Wang, Phys. Rev. Lett. 145504 (2005)

Real-Time Measurements: Kinetics

- Particle lateral diffusion reveal by $q_{//}$ scans





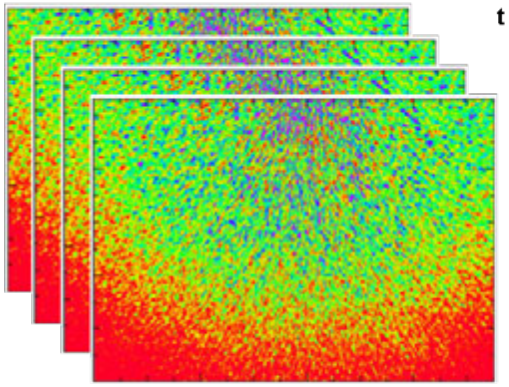
- Nanoparticles are moving faster in plane
- This constitutes the base of forming self-assembly in 2D

Narayanan, Lee, Guico, Sinha, Wang, Phys. Rev. Lett. 145504 (2005)

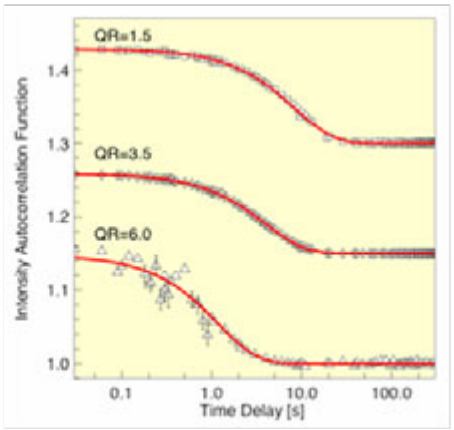
Dynamics of Nanoparticles in Polymer Films

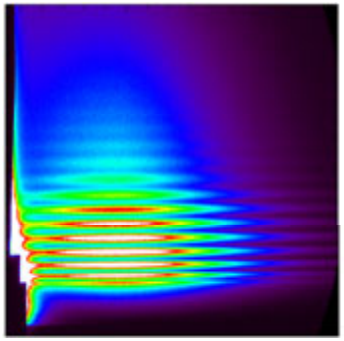
- Dynamics of single nanoparticles ultimately determines their diffusion
- Dynamical light scattering (DLS) is not effective because of q-range
- X-ray photon correlation spectroscopy (XPCS) is well-suited
- X-ray beams at the APS can be effectively used for XPCS (8-ID).

A = Optical Contrast = Beamline Figure of Merit



$$g_2(\vec{Q},t) = 1 + A[S(\vec{Q},t)/S(\vec{Q})]^2 = \frac{\langle I(\vec{Q},t\ )I(\vec{Q},t\ +\tau)\rangle_\tau}{\langle I(\vec{Q},\tau\ )\rangle_\tau^2}$$

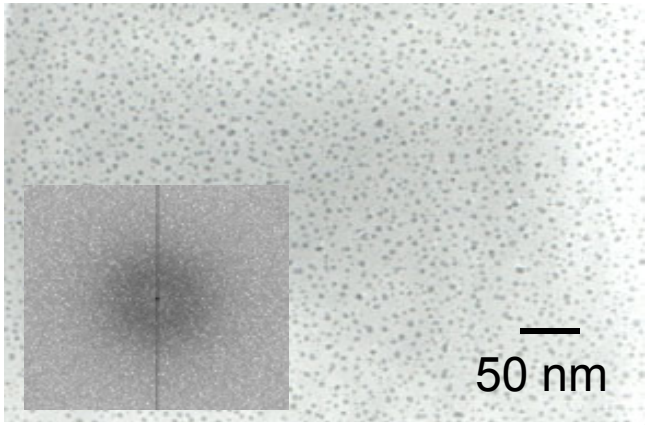


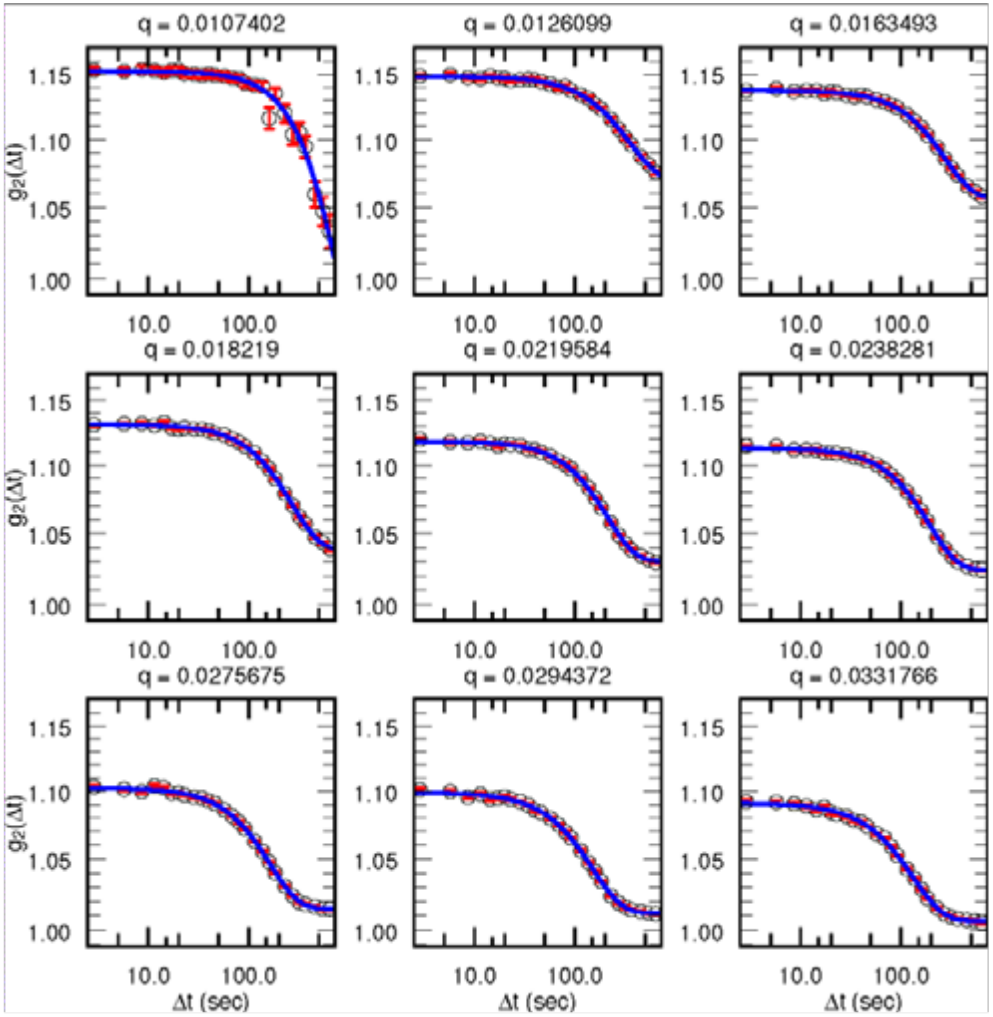


Q_p

XPCS Results

- Au nanoparticles on MW 120K 700 Å PS





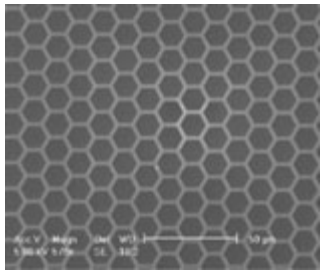
• Exhibits Ballistic motion with a Drift Velocity 1/(τQ) of ~0.1 Å/sec

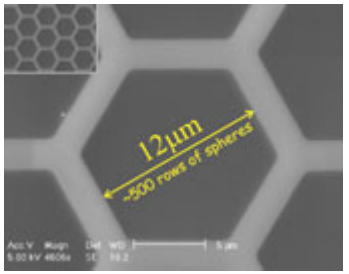
• Such behavior observed in systems aging with time viz. colloidal glass, gels …

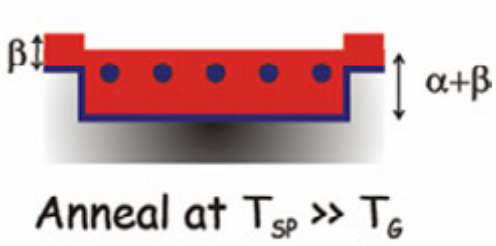
Narayanan, Lee, Hagman, Li, Wang, Phys. Rev. Lett. 185506 (2007)

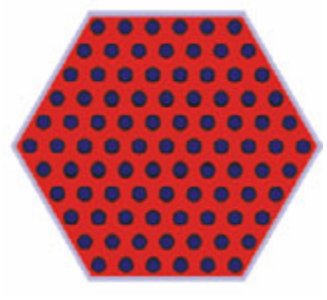
Self Assembly of Diblock Copolymer 2D Crystals

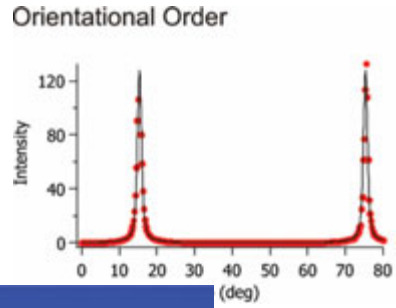
- Samples: PS-P2VP thin film
- Substrate: patterned surface
- Graphoepitaxy

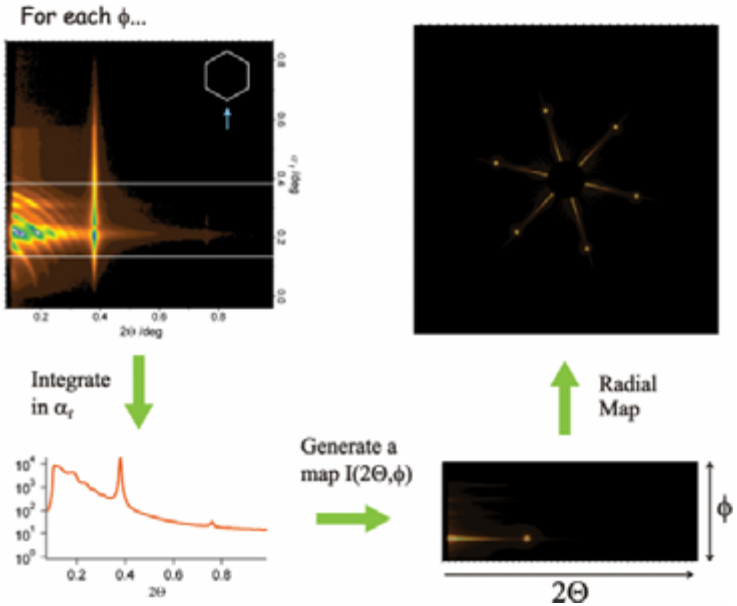


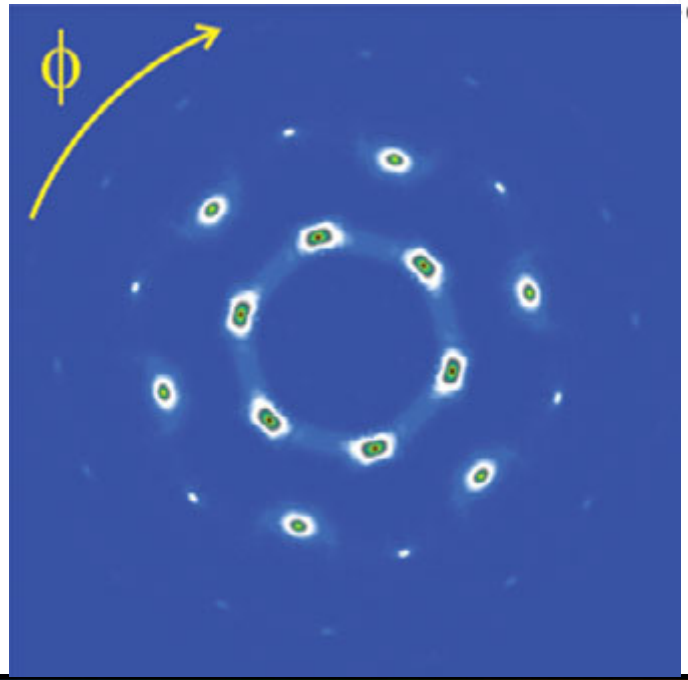




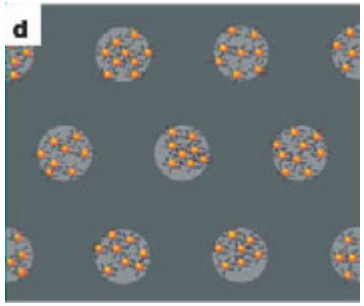






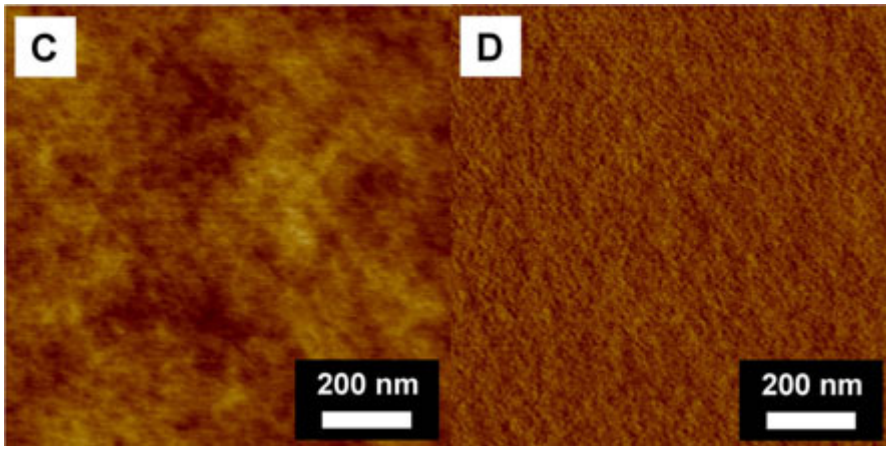


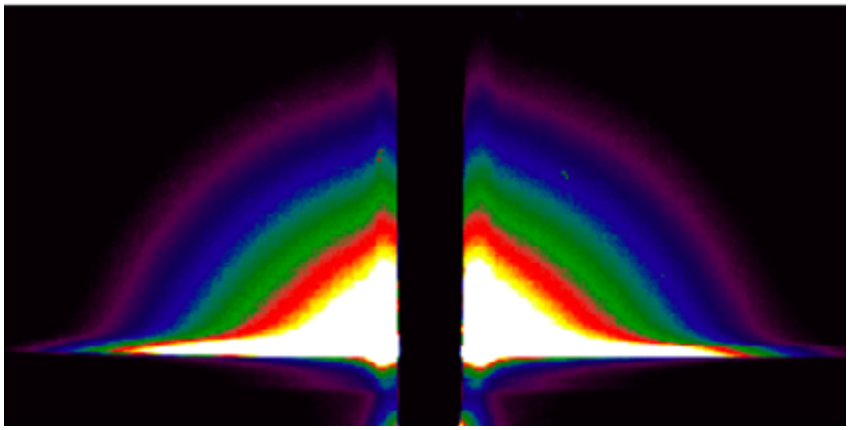
Diblock Copolymer/Nanoparticle Co-Self-Assembly

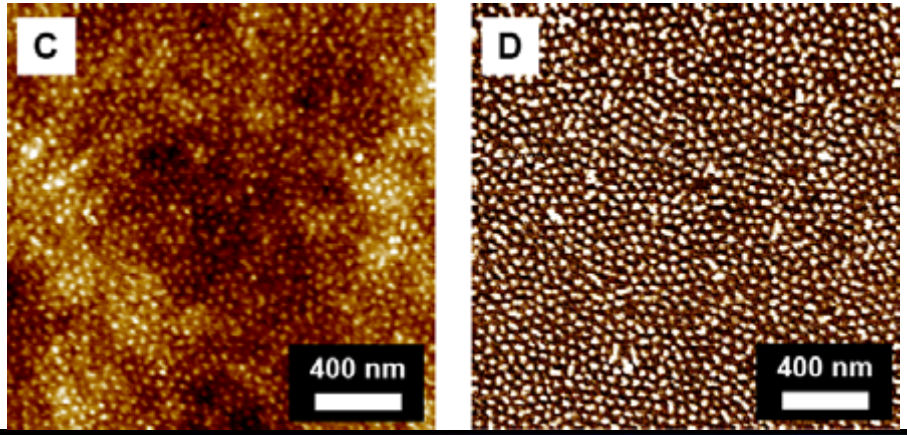


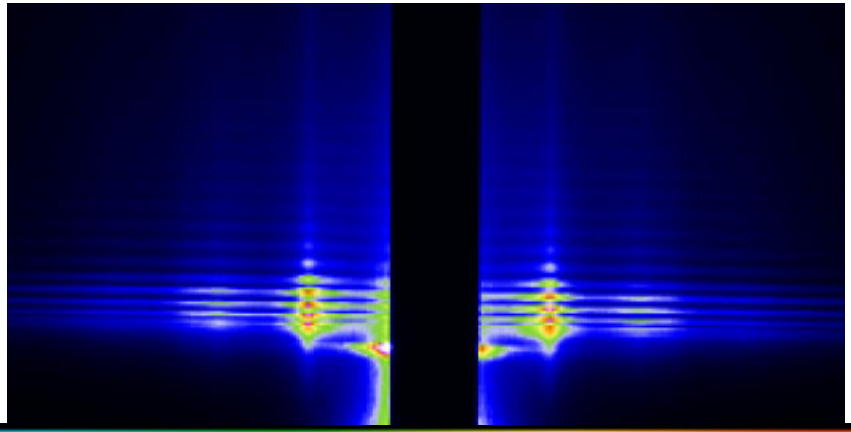
- Nanoparticle-facilitated PS-P2VP self assembly (CdSe particle)
  - Nanoparticle changed the energy state and phase diagram of the system

Before Anneal





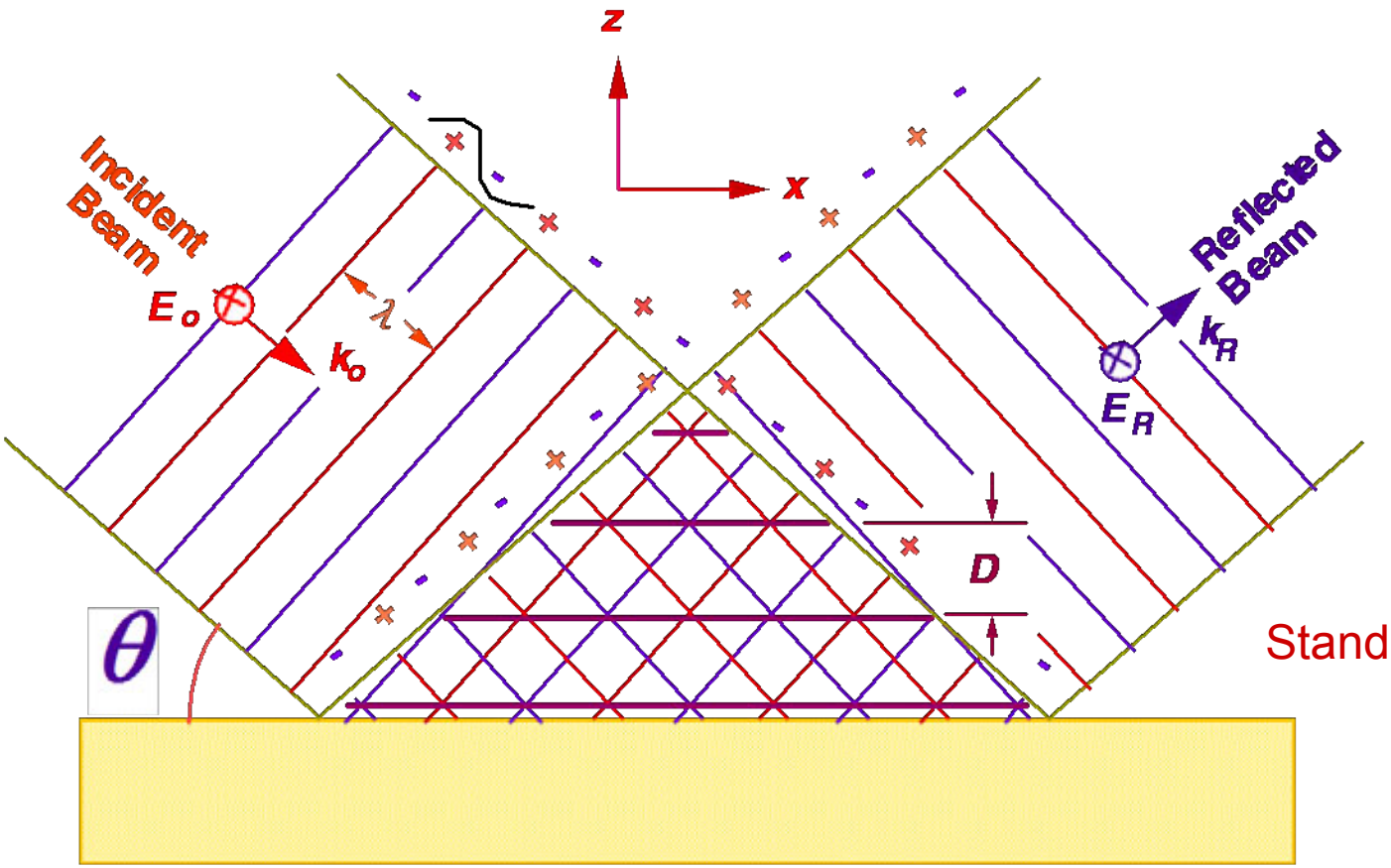




Y. Lin, *et al*. Self-directed self-assembly of Nanoparticles/Copolymer Mixtures, Nature, **434**, 55, 2005

X-ray Standing Waves

- **X-Ray Standing Waves by Total External Reflection**

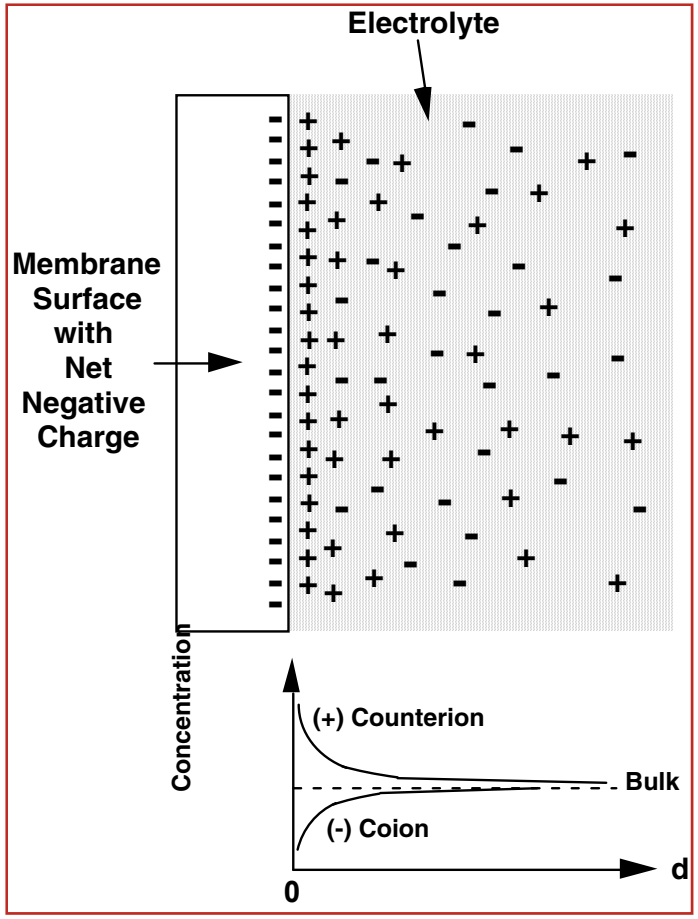


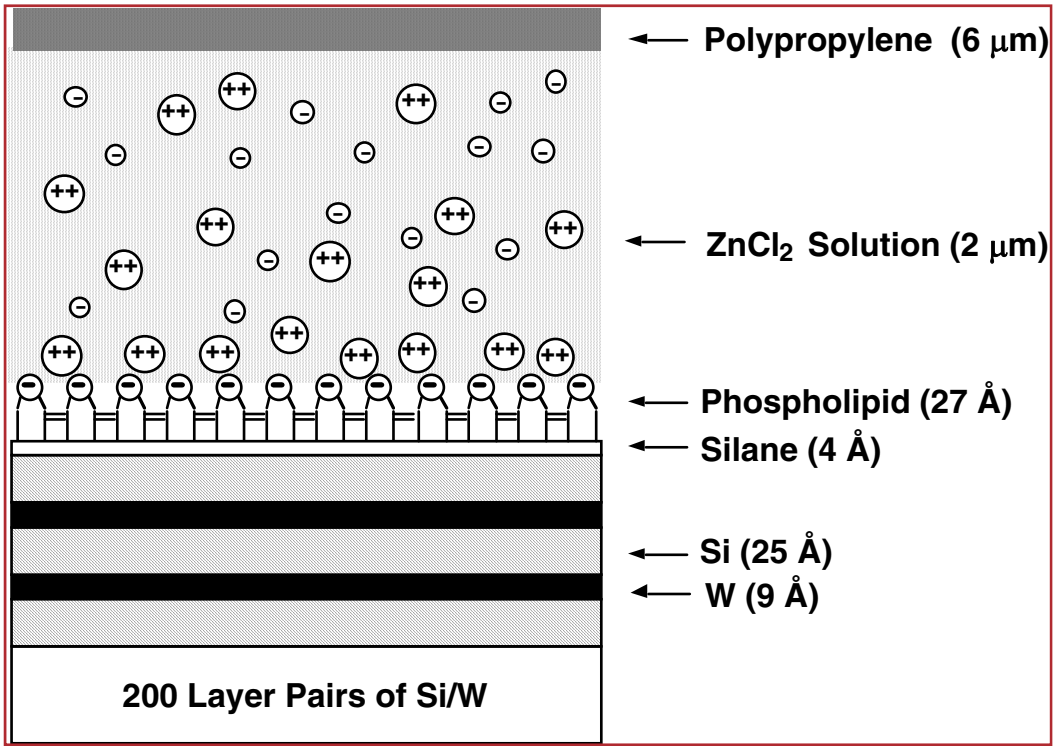
Standing Wave Period:

$$D = \frac{\lambda}{2\sin\theta}$$

Charged Membrane Surfaces

- Charged membrane in contact with electrolytes (ion transport)
- Model by Helmholtz, Gouy-Chapman, Stern

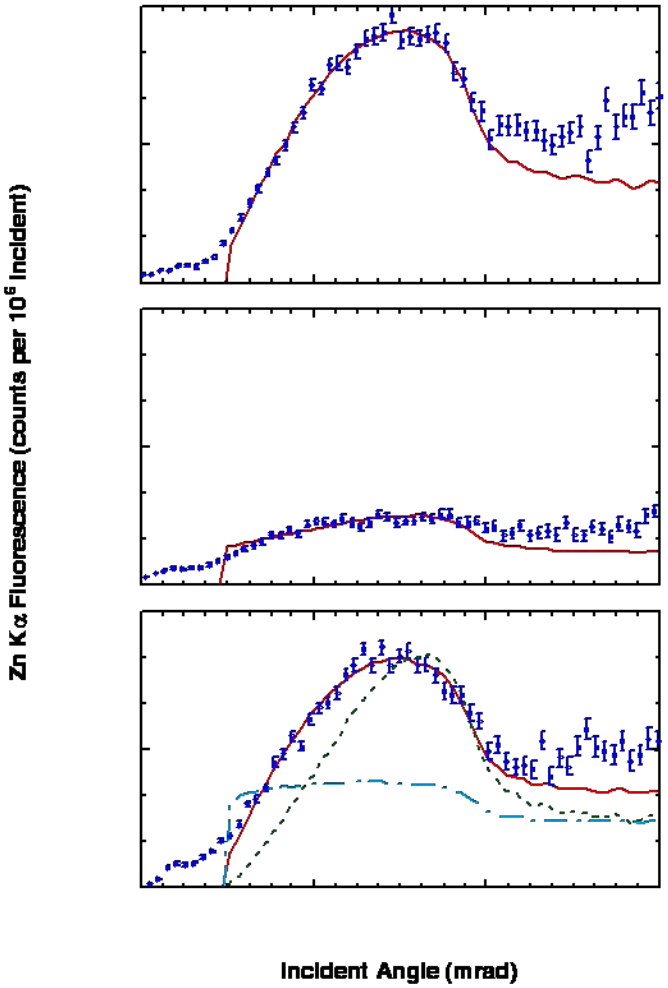


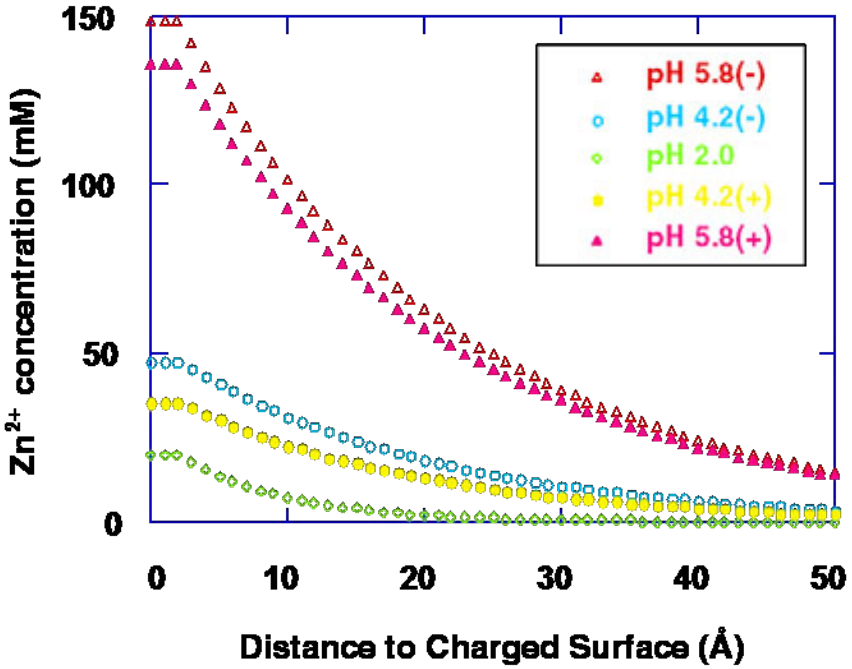


Bedzyk, Bommarito,Caffrey, Penner, Science 248, 52 (1990)

DDL Reversibility by pH

- As H+ concentration increased, the amount of zinc in the DDL decreased
- Recovery of the pH 5.8 distribution profile was essentially complete





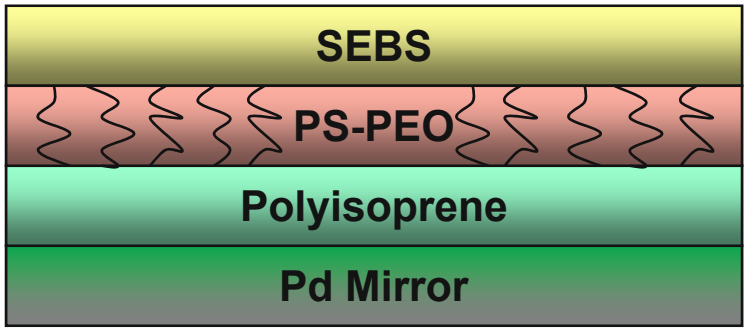
Jin Wang, Martin Caffrey, Mike Bezyk, Tom Penner

Langmuir, **17**. 3681 (2001)

Ionic Distribution Near Polymer Brush/Membrane

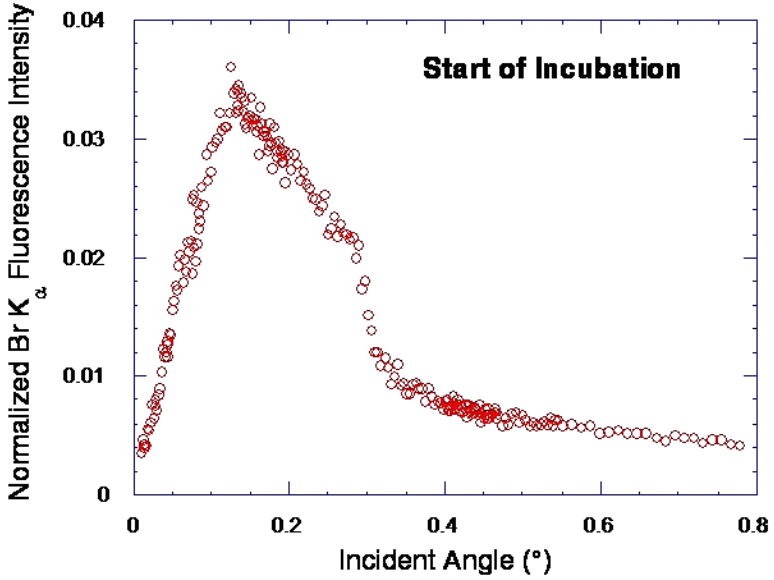
- Standing wave measurements can yield the Br ion distribution between membranes.

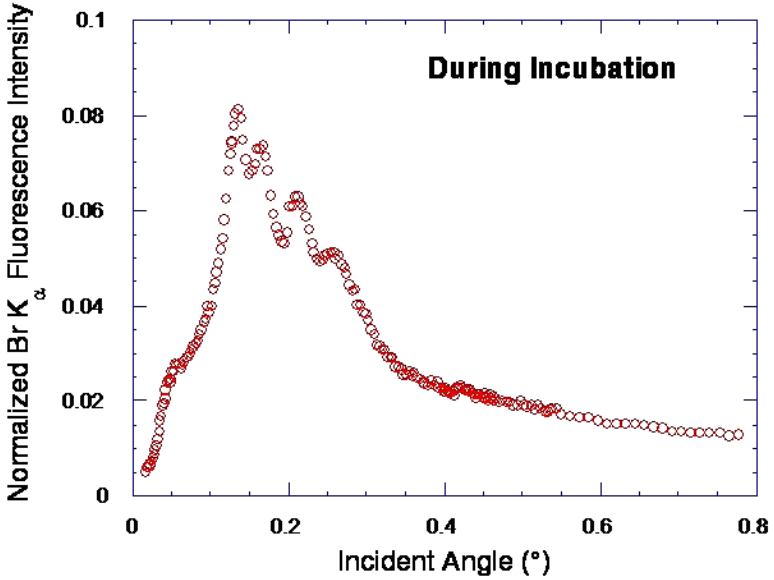
Rafael Bras, Yan Sun of Ken Shull's group @ Northwestern U.



← in aqueous Potassium Bromide solution environment (KBr); Langmuir-Blodgett (LB) method for obtaining PS-PEO layer

Preliminary results:





Summary

- Surface Sensitive X-ray Techniques suitable for membrane structure/kinetics/dynamics characterization
  - Reflectivity (XRR)
  - Diffuse scattering
  - X-ray standing waves (XSWs)
  - Grazing-incident small angle scattering (GISAXS)

- Nonintrusive, in situ capabilities
- Sensitive for thin films

Practical Challenges

Fundamental and understanding is necessary to control the formation of membranes on all length scales and time scales

Organic-membranes: Polymeric matrix and composites
Nature of Hydrophilic/hydrophobic interaction for fouling
Specific and nonspecific adsorption and absorption
Porosity control
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