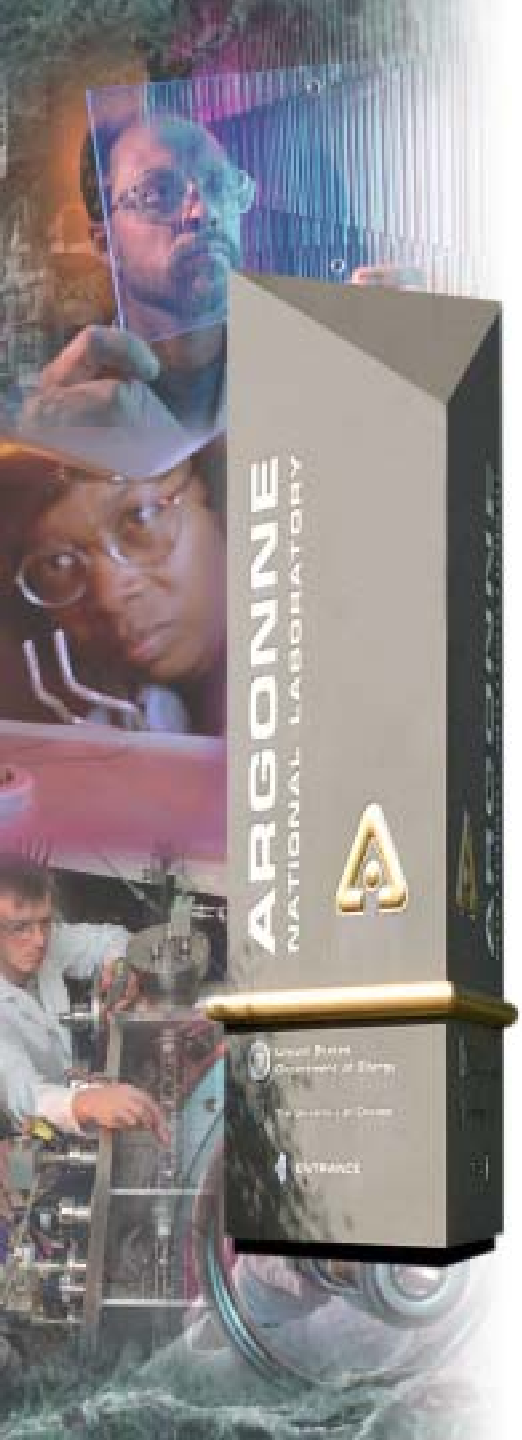

Grazing-Angle X-ray Techniques for Studying Membranes and Ultrathin Films

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Future Scientific Directions for the Advanced Photon Source

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Argonne National Laboratory

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Collaborators

- **Drs. Suresh Narayanan, Rodney Guico, Xuefa Li (XFD/ANL)**
- **Prof. Ken Shull**
  - Au/polymer nanocomposite thin Films
- **Dr. Dong Ryeol Lee (XFD/ANL) and Prof. Sunil Sinha (UCSD)**
  - DWBA calculations
- **Profs. Martin Caffrey (Ohio State U.), Michael J. Bedzyk (Northwestern), Dr. Tom Penner (Kodak)**
  - Diffuse double layer at model membrane surfaces

The experiments have been done at beam line 1-BM of the APS and D1 station of CHESS. Support by Sector 1 and CHESS staff is acknowledged. This work and the use of the APS are supported by the U. S. DOE under Contract No. W-31-109-Eng-38. CHESS is supported by the National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences under award DMR00-225180.

Outline

- **Grazing-angle x-ray techniques for surface studies**
- **Diffuse-double layer at model membrane surfaces**
  - Ionic distribution
  - Reversibility during *p*H titration
- **Anisotropic nanoparticle diffusion in ultrathin polymer films**
  - Perpendicular to interfaces
  - Lateral motion
- **Conclusions**

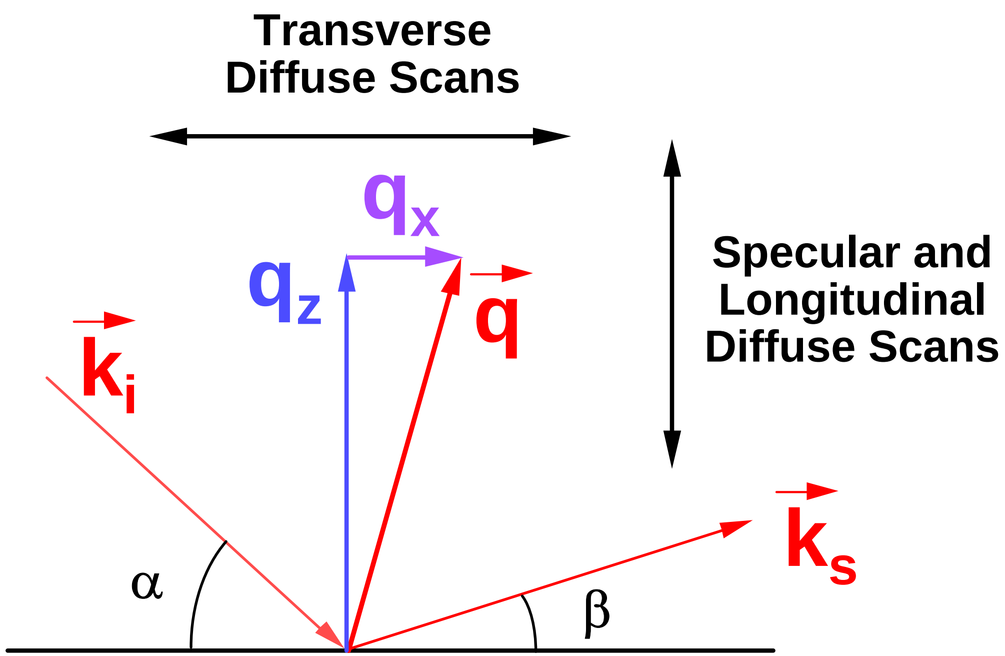
Surface Sensitive X-ray Techniques

- Reflectivity (XRR)
- Diffuse scattering
- X-ray standing waves (XSWs)
- Grazing-incident small angle scattering (GISAXS)

- Nonintrusive, *in situ* capabilities
- Ideal for studying membrane kinetics and dynamics
- Well-suited for ultrathin films

X-ray Reflectometry

- X-ray reflectivity to probe electron-density distribution normal to the film surfaces: L.G. Parratt, Phys. Rev. **95**, 359 (1954)
- X-ray diffuse scattering to probe in-plane density fluctuation: S.K. Sinha *et al*. Phys. Rev. **B38**, 2297 (1988)



$$q_z = \frac{2\pi}{\lambda}(\alpha + \beta)$$

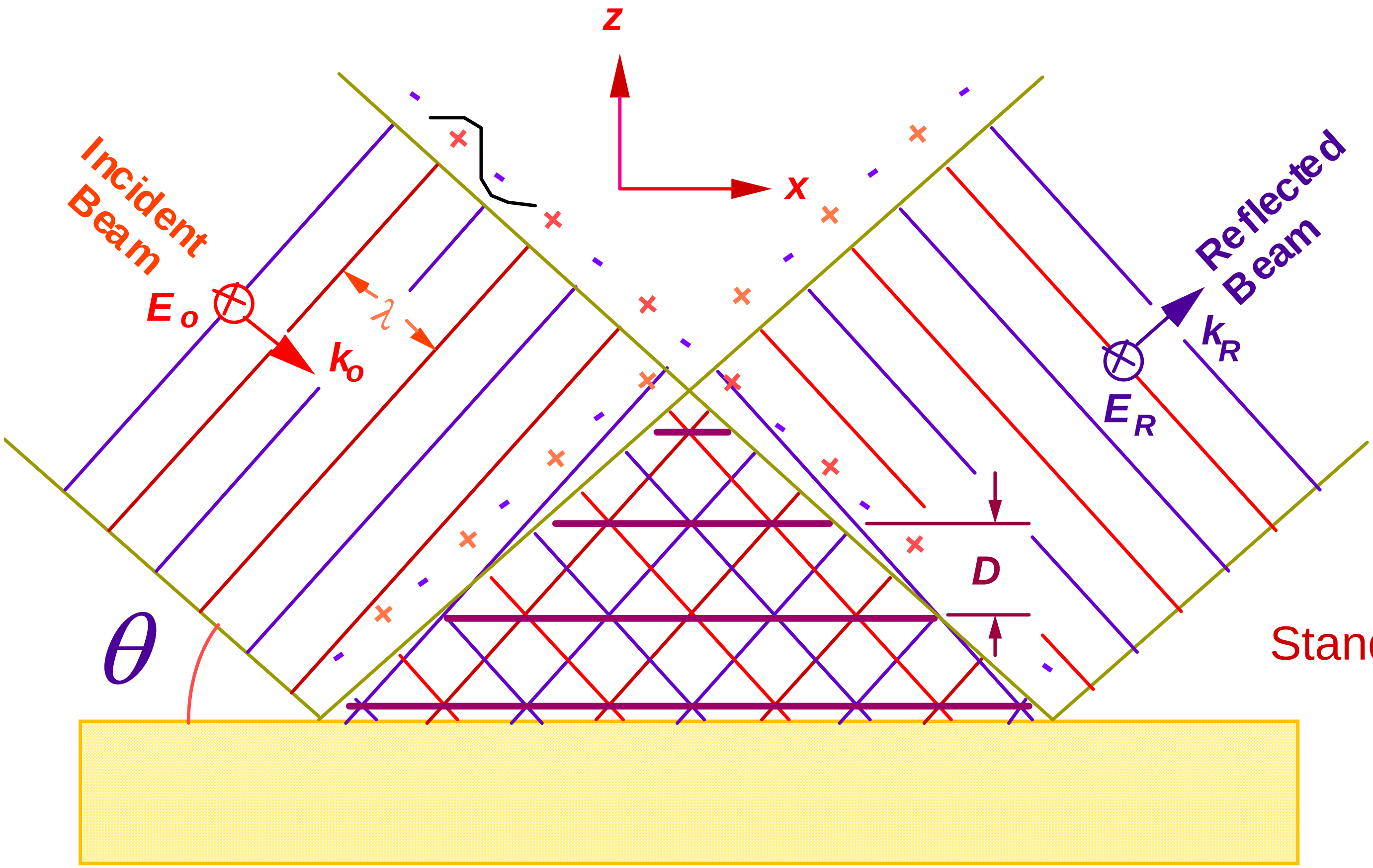
$$q_x = \frac{1}{2} q_z (\alpha - \beta)$$

Membrane Surface or Interface

Kent, Nagle, Huang, Schlossman

X-Ray Standing Waves by Total External Reflection

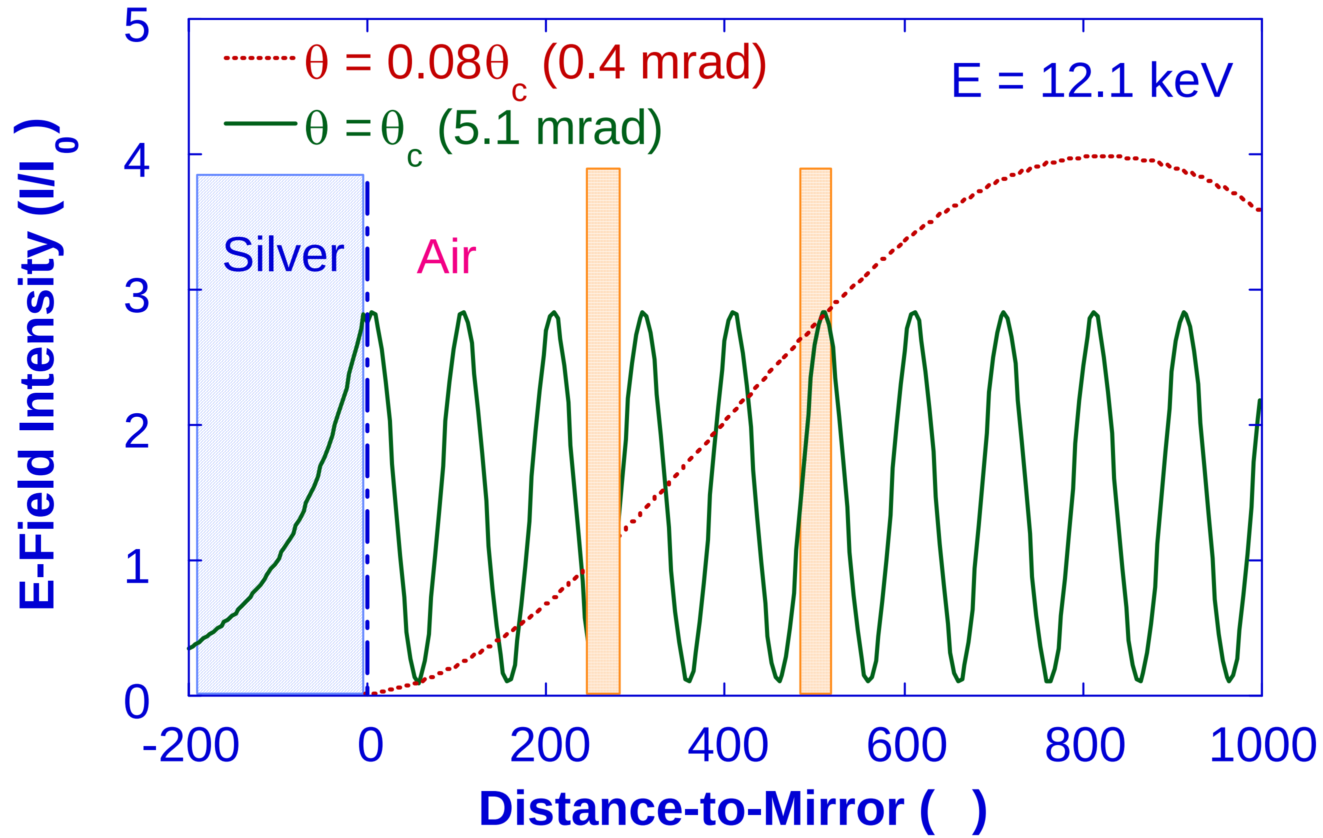
M.J. Bedzyk *et al*. Phys. Rev. Lett. **62** 1376 (1989)



Standing Wave Period:

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

E-Field Intensity vs. Angle

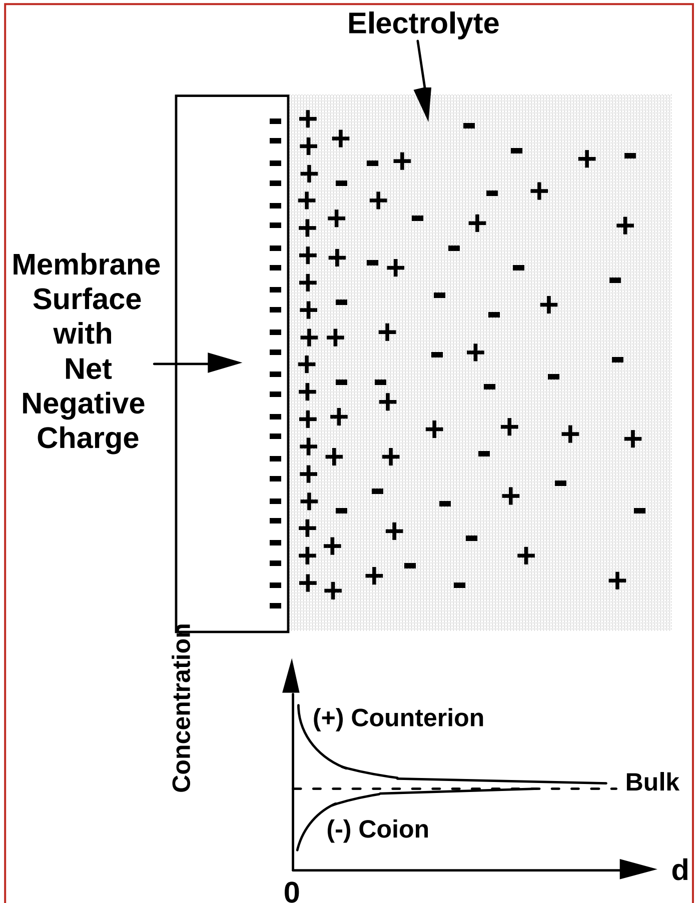


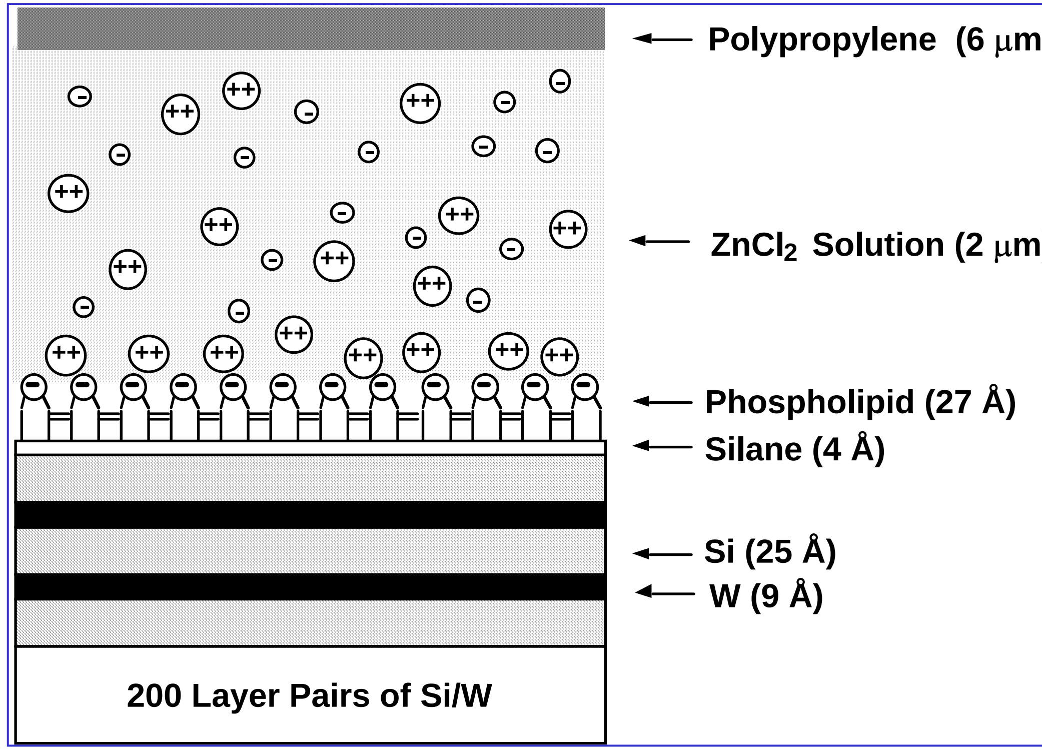
$$I(z,\theta) = \left|E_0 + E_R\right|^2 = I_0\left[1 + R + 2\sqrt{R}\cos\left(\phi^R - 2\pi q_Z z\right)\right]$$

Fluorescence Yield: $Y(\theta) = \int I(z,\theta) \cdot \rho(z)\, dz$

Charged Membrane Surfaces

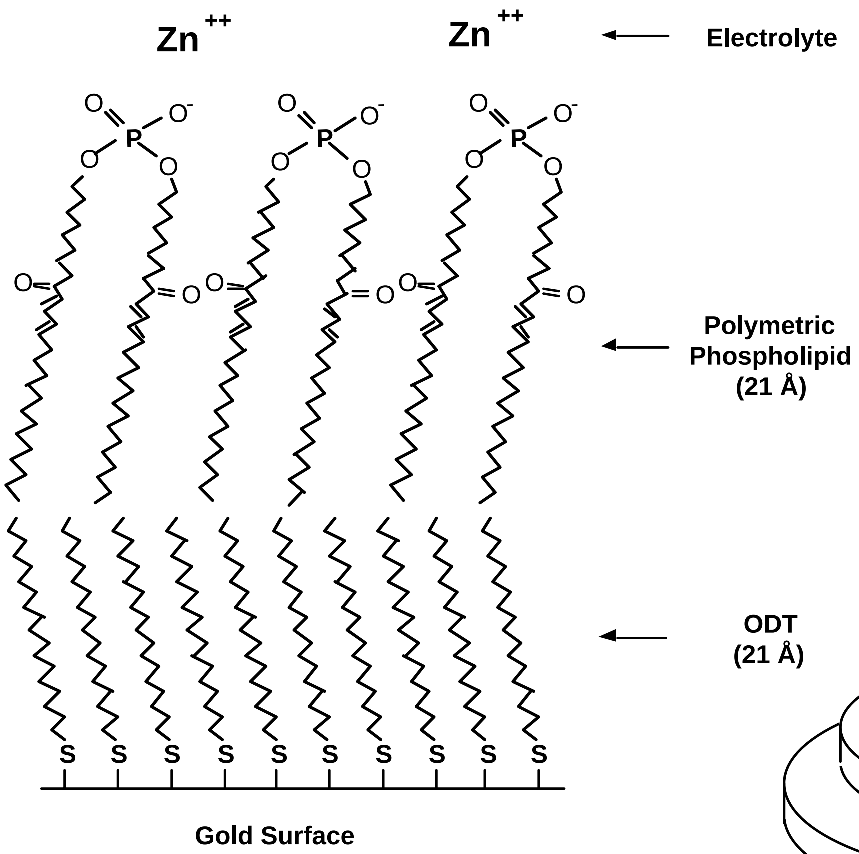
- Charged membrane in contact with electrolytes (ion transport)
- Model by Helmholtz, Gouy-Chapman, Stern

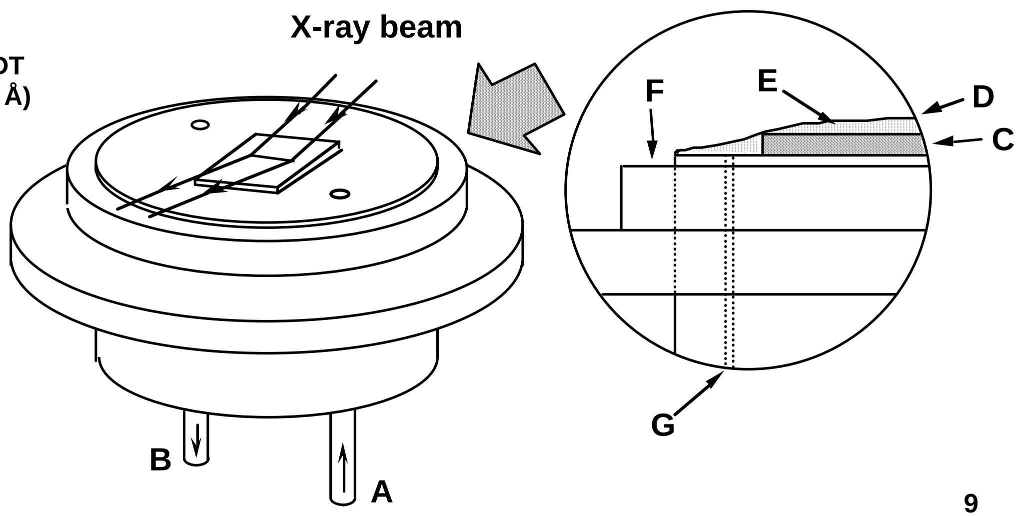




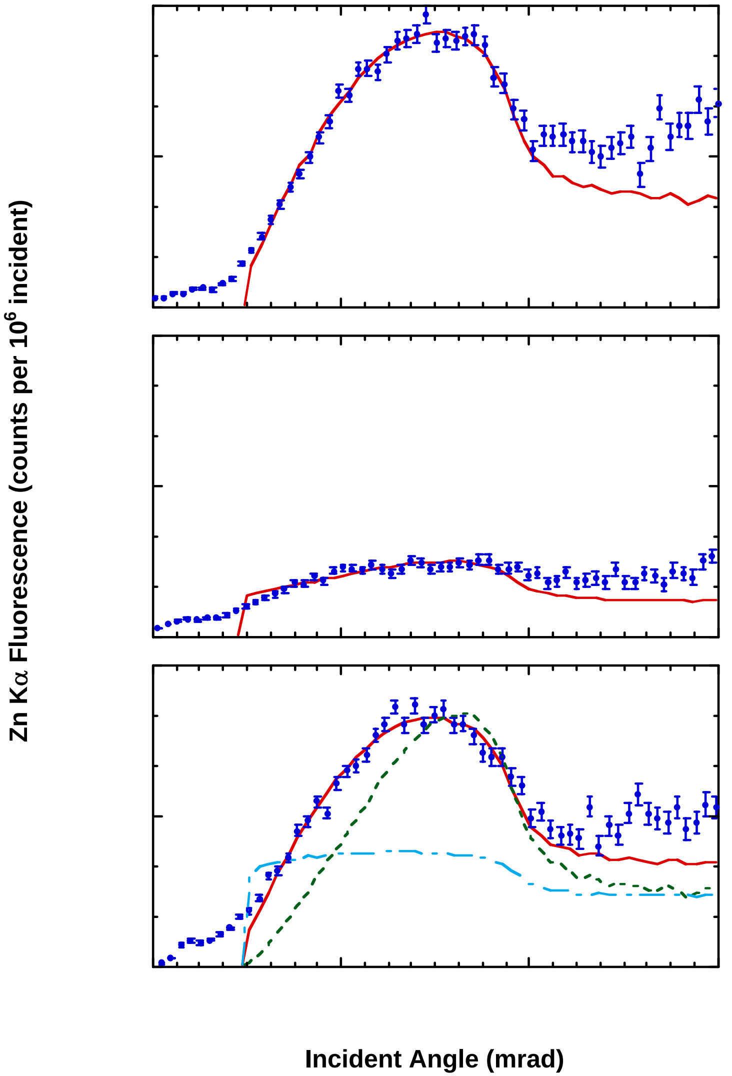
Bedzyk, Bommarito,Caffrey, Penner, Science 248, 52 (1990)

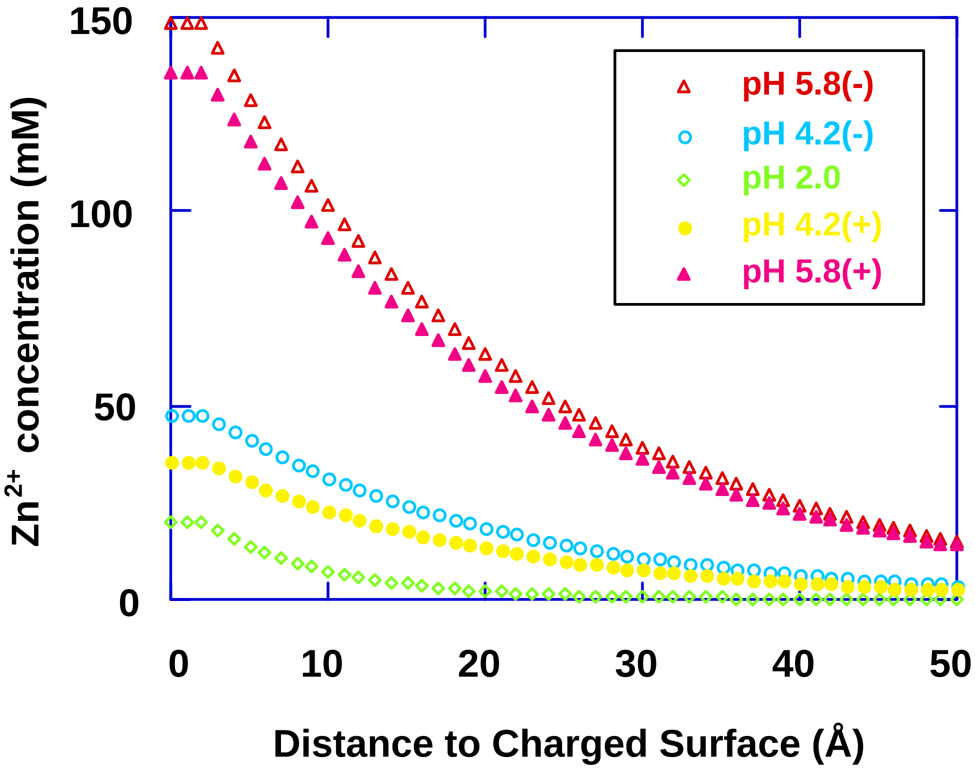
Experiment Setup





DDL Reversibility by pH





Jin Wang, Martin Caffrey, Mike Bezyk, Tom Penner

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

Summary

As H+ concentration increased upon changing pH from 5.8 to 2.0, the amount of zinc in the DDL decreased from 122 mM to a low of ca. 19 mM.

Recovery of the pH 5.8 distribution profile was essentially complete upon back-titration from pH 2.0.

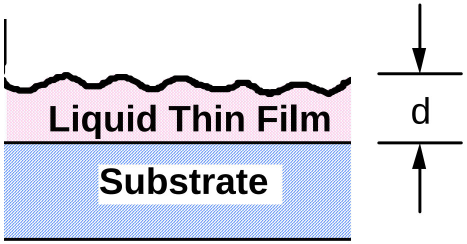
These results demonstrate clearly that within the experimental error of the measurement ion distribution at the charged membrane interface is reversible.

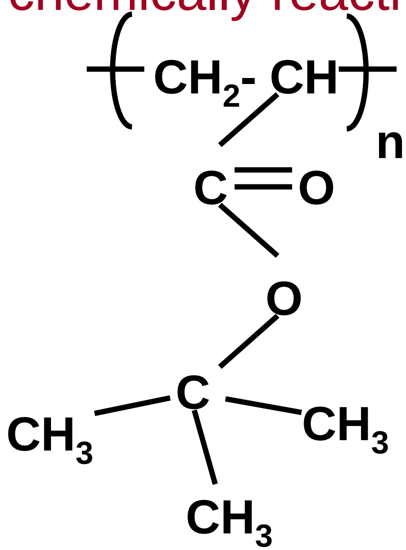
Nanoparticles in Ultrathin Films

- **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**
  - X-ray 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

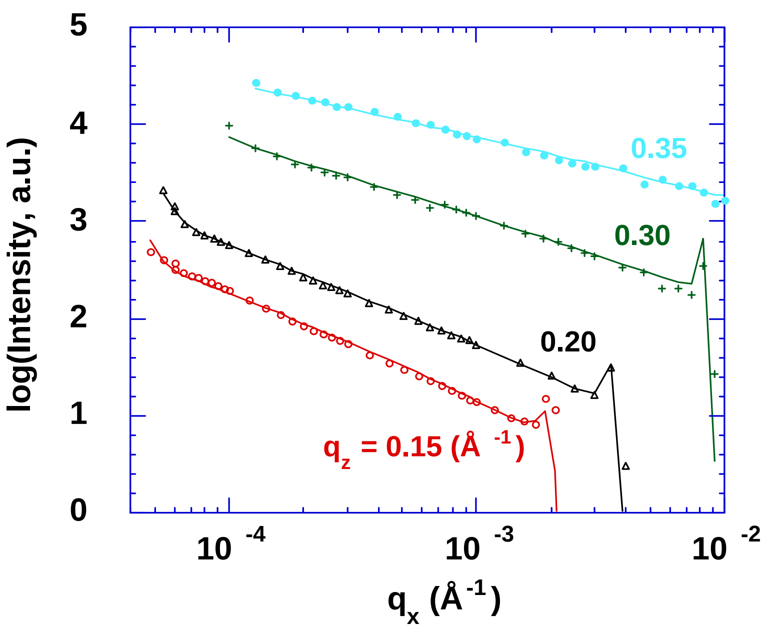
Model: Au NP in Homopolymer

- Poly (tert-butyl acrylate)
- Amorphous homopolymer
- Glass transition temperature (T_g) = 49 °C
- Molecular weight (MW) = 352,000 g/mol
- Radius of gyration (R_g) = 150 Å
- Film thickness = 150 Å to 600 Ås
- Not chemically reactive to gold

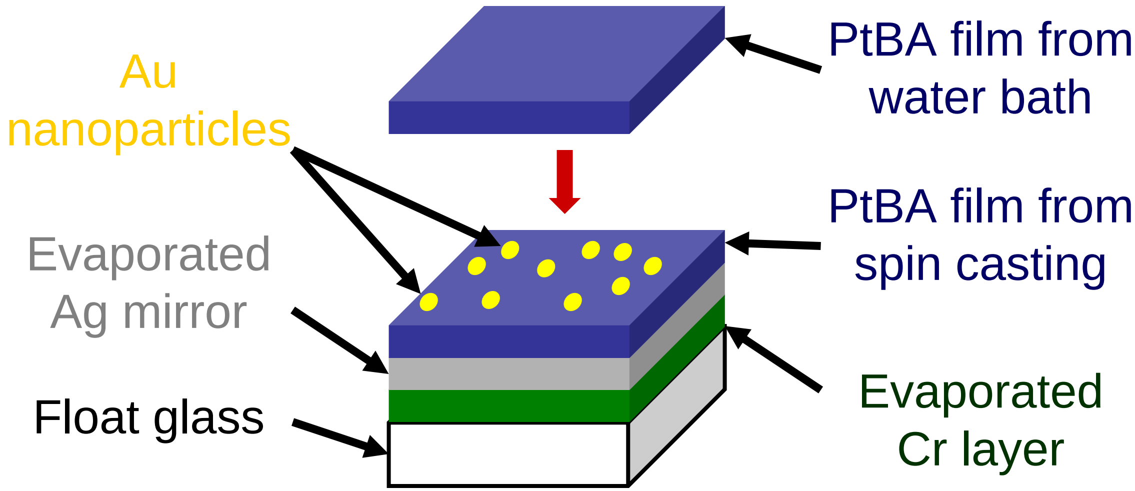


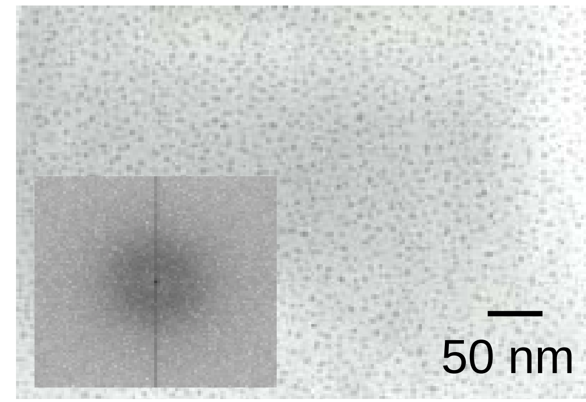


d = 1215 Å, T = 70s°C

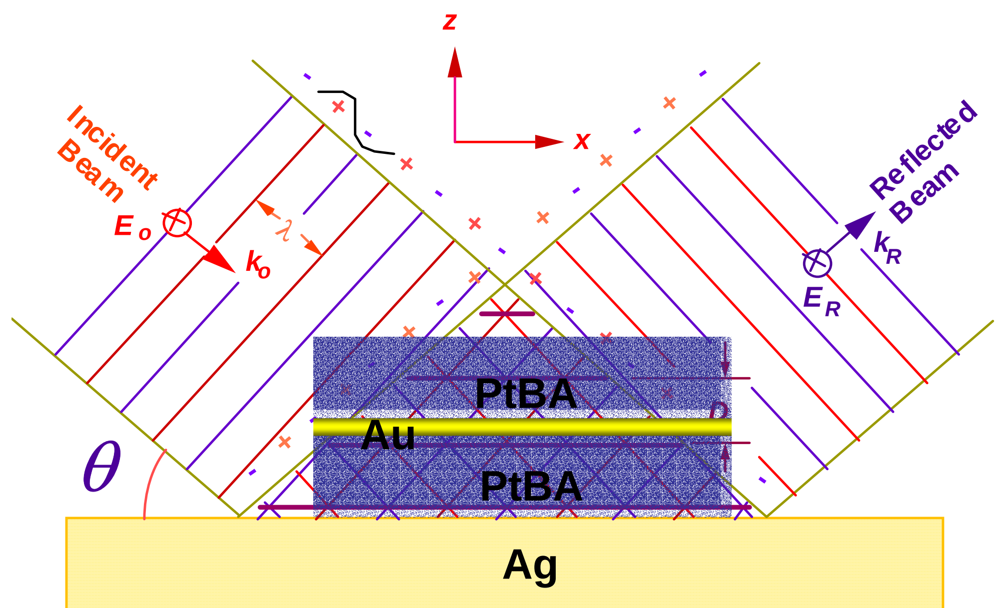


Vertical Diffusing

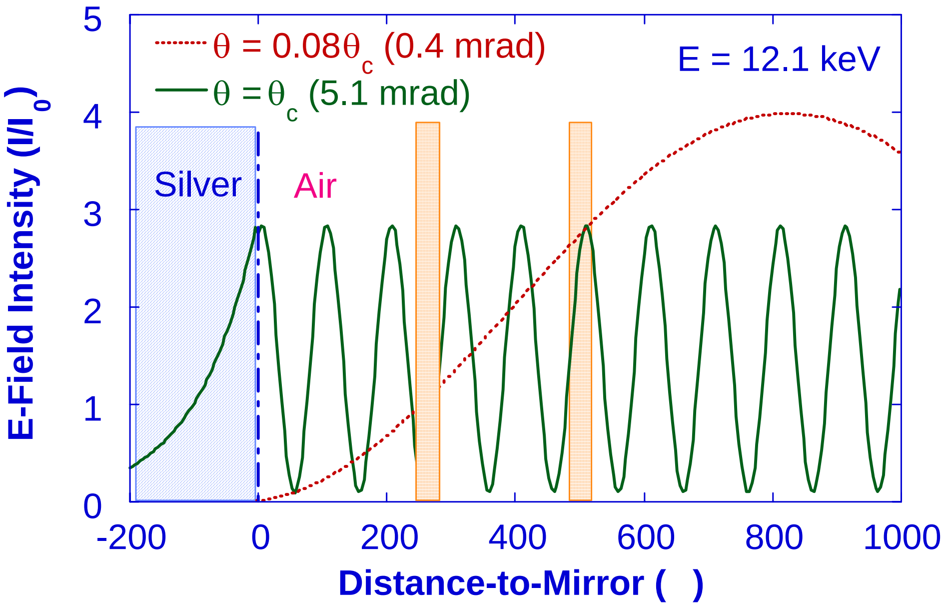


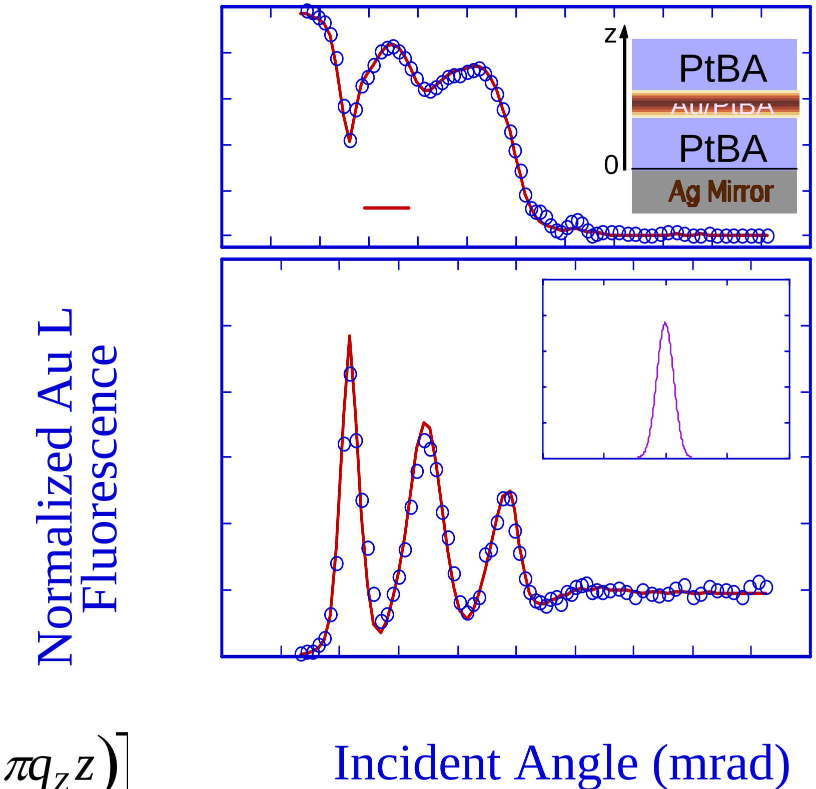


X-ray Standing Waves



XSW Data





$$I(z,\theta) = \left|E_0 + E_R\right|^2 = I_0\left[1 + R + 2\sqrt{R}\cos\left(\phi^R - 2\pi q_Z z\right)\right]$$

X-ray Fluorescence Yield

$$Y(\theta) = \int I(z,\theta)\cdot\rho(z)\,dz$$

- A few Å spatial resolution
- A few s temporal resolution

Diffusion Coefficient

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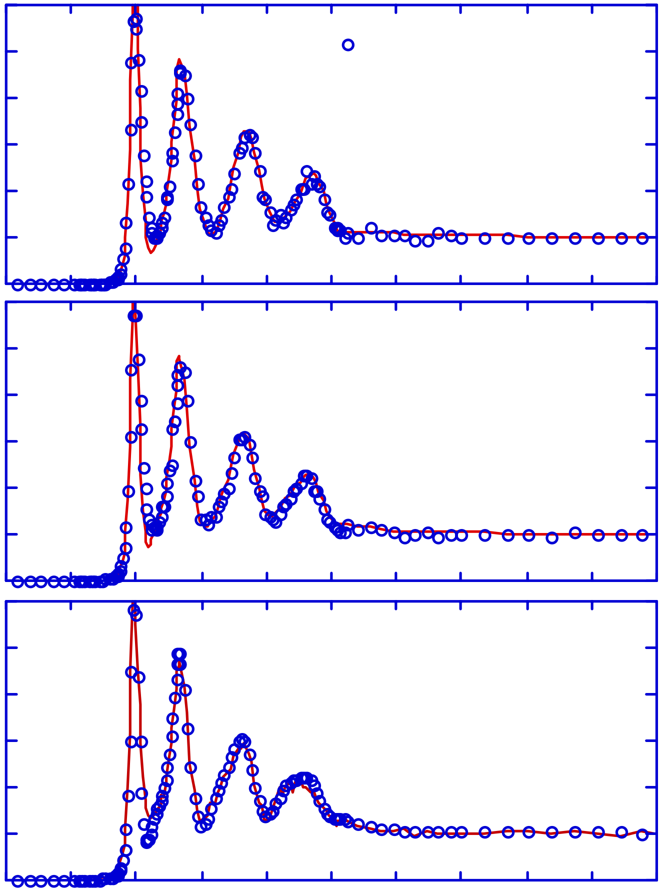
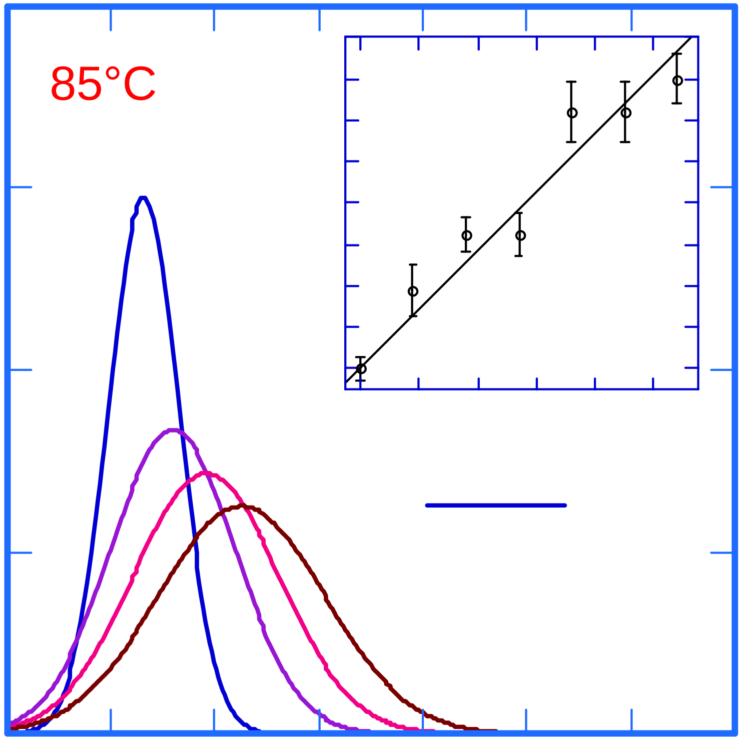


Incident Angle, θ, (mrad)



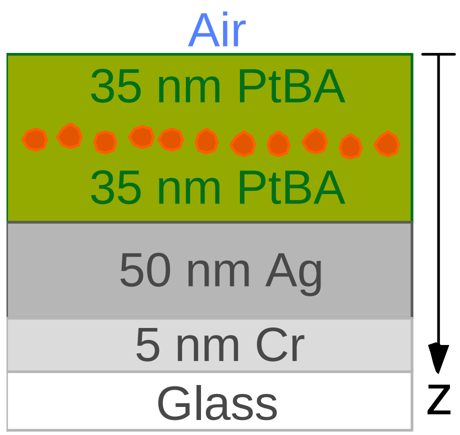
Diffusion coefficient

5×10^{-18} cm^2/s

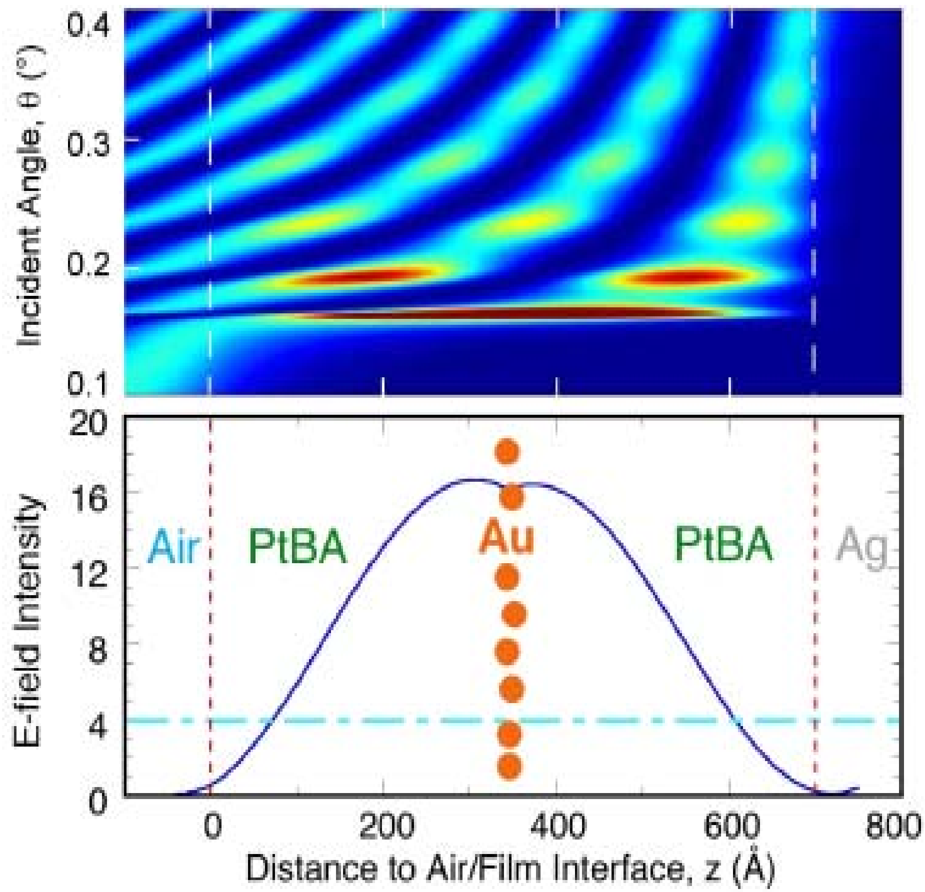
Guico, Narayanan, Wang, Shull, Macromolecule, accepted

Wave-Guiding Effect

Resonance Enhancement

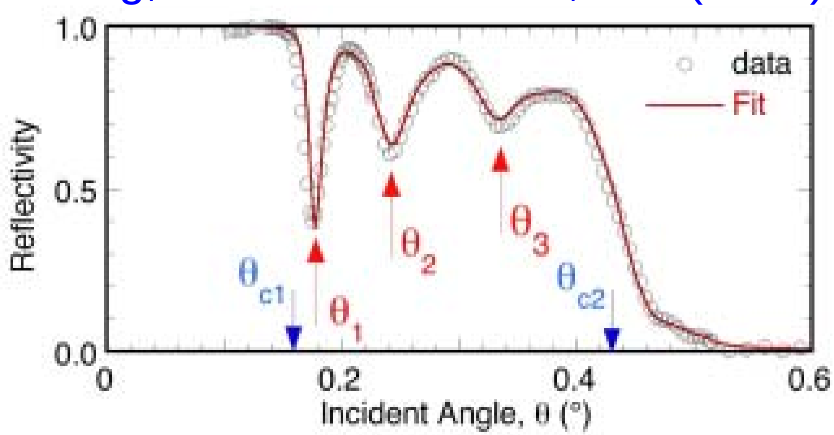


Electric Field distribution and enhancement



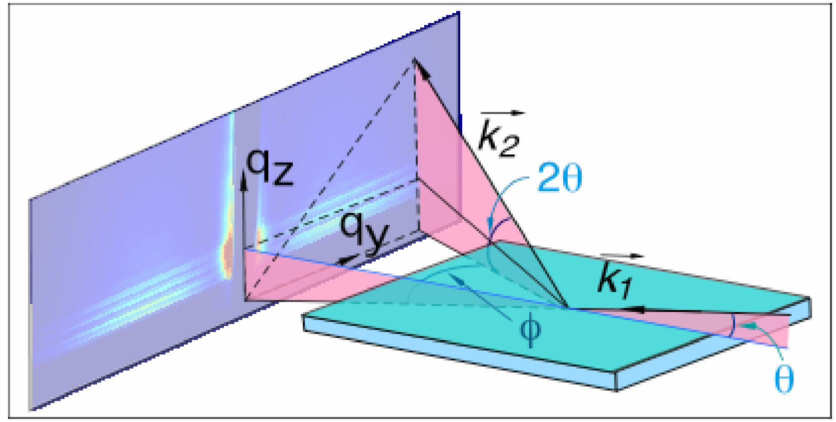
Wave-guiding effect at several angles

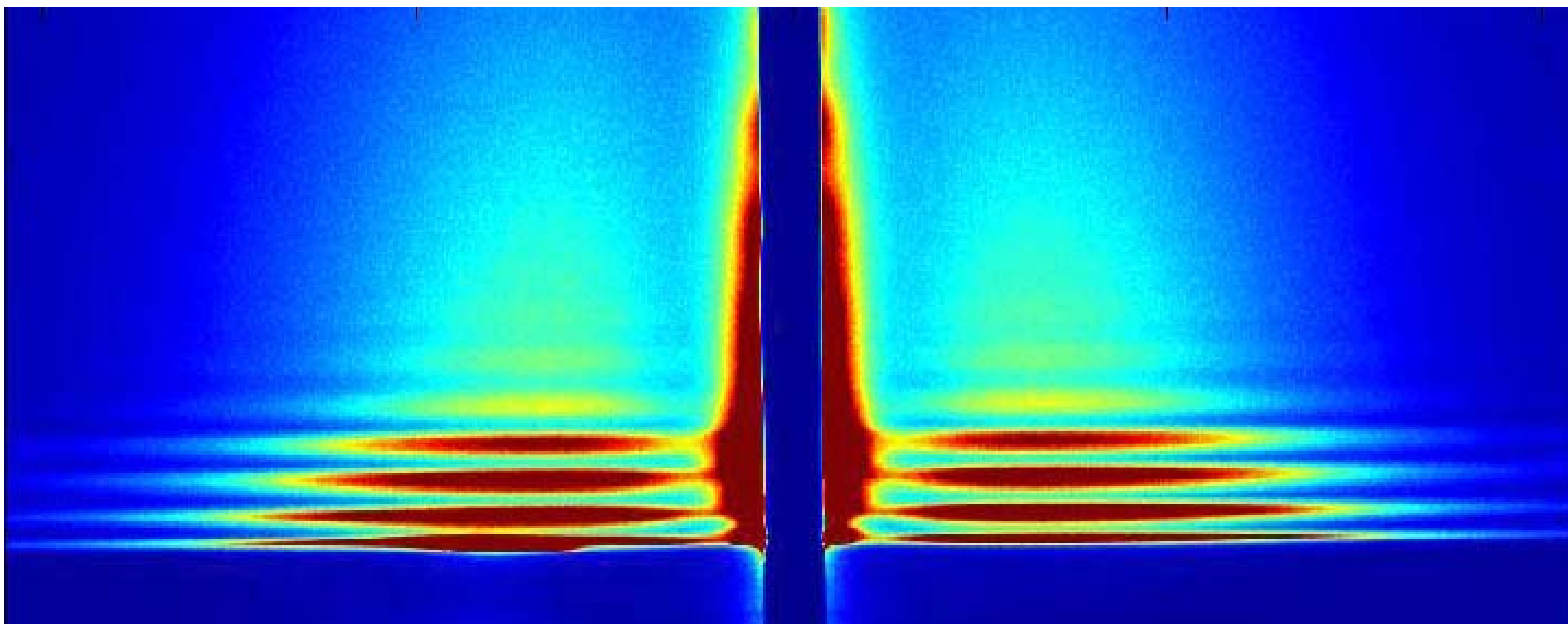
Wang, *et al.* *Science* **258**, 775 (1992)



GISAXS with Enhancement

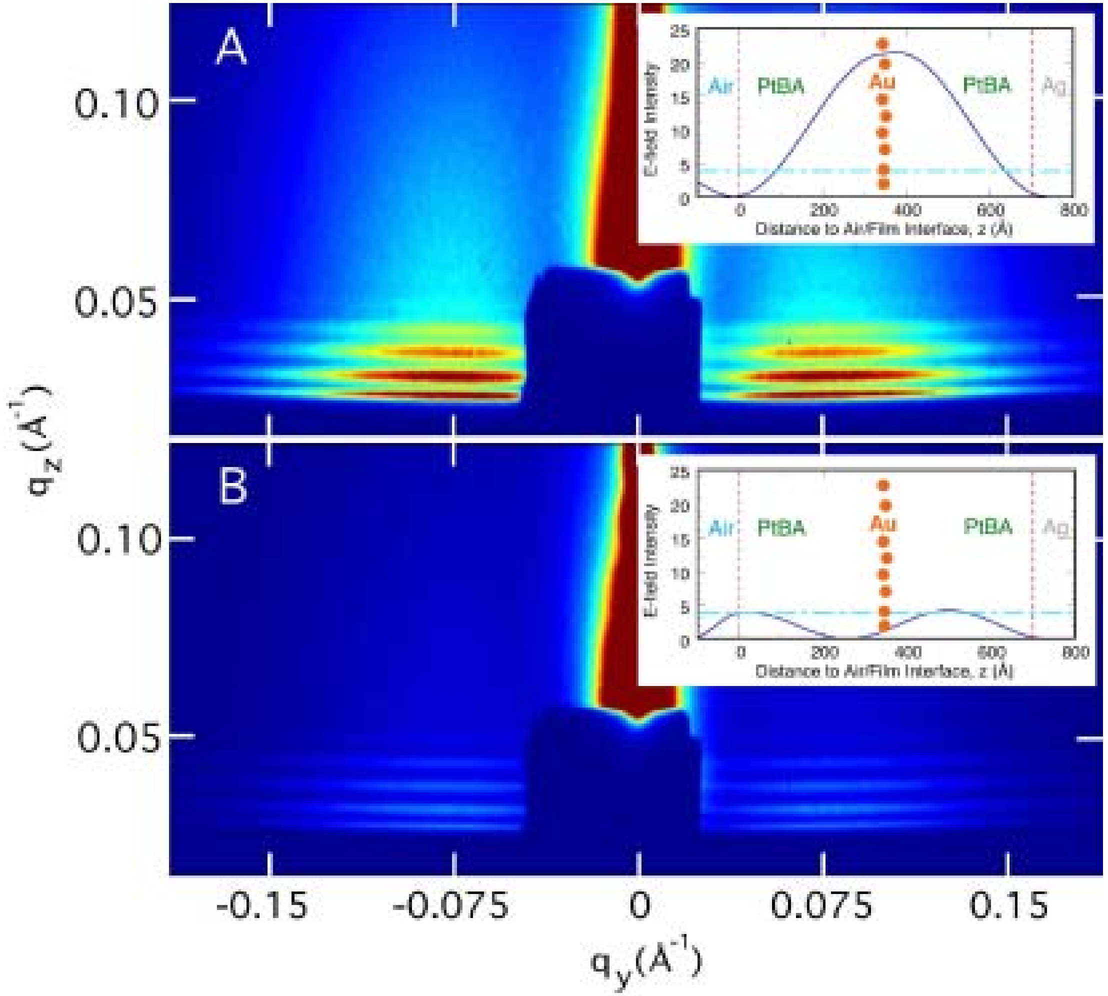
- And something more





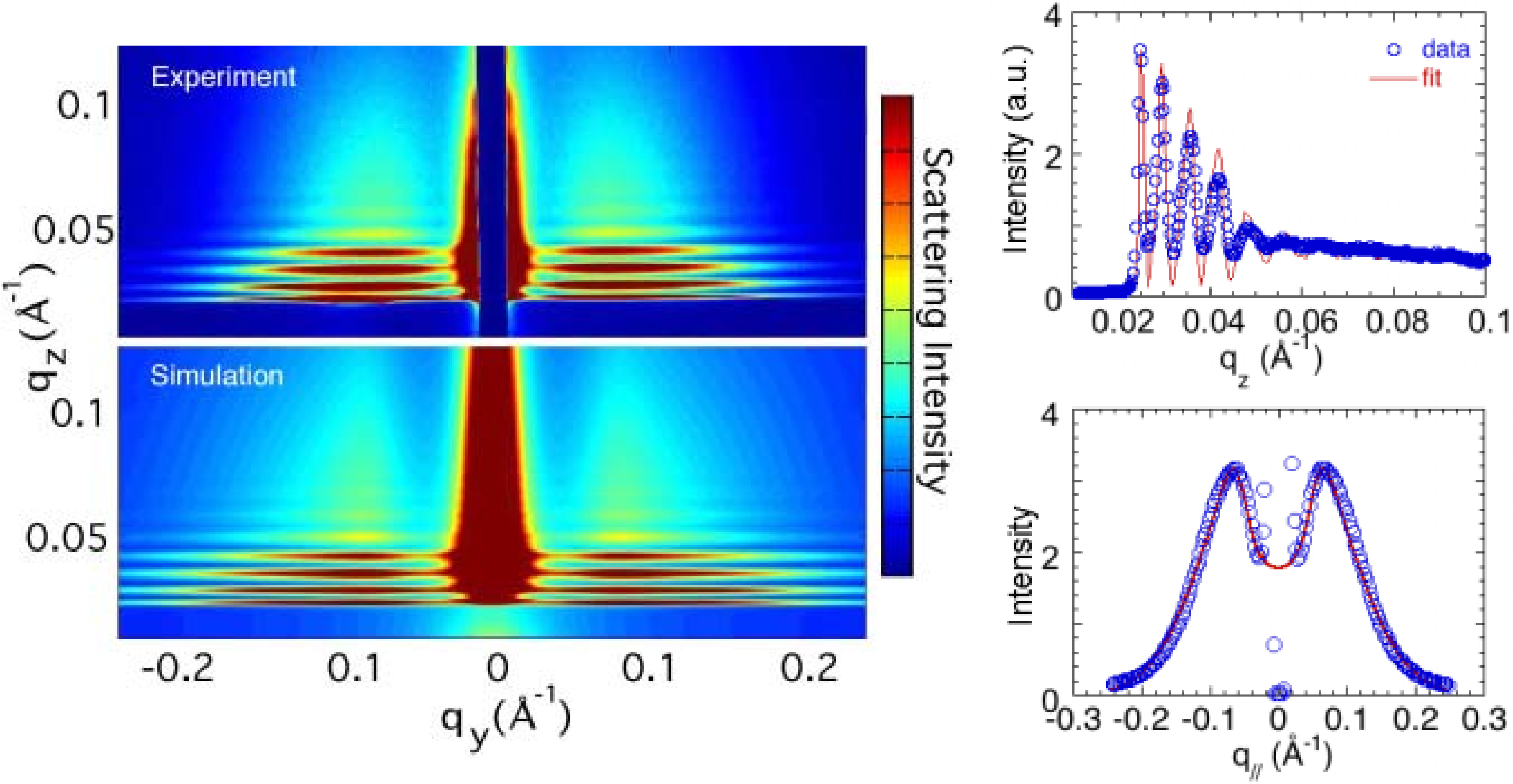
Effect of the Enhancement

- **Enhancement is apparent at different incident angles**

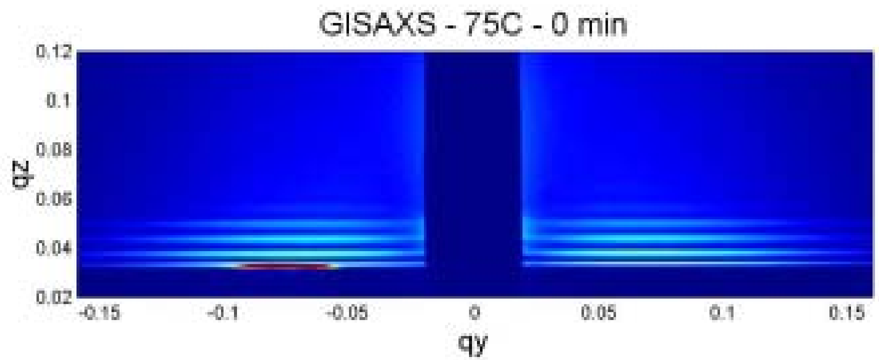


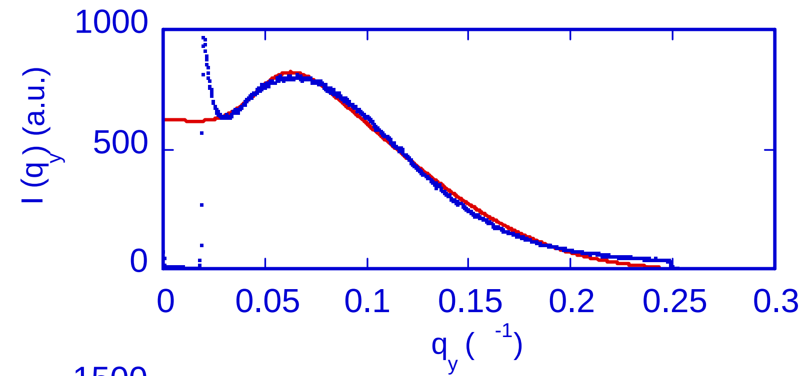
Simulation of the GISAXS

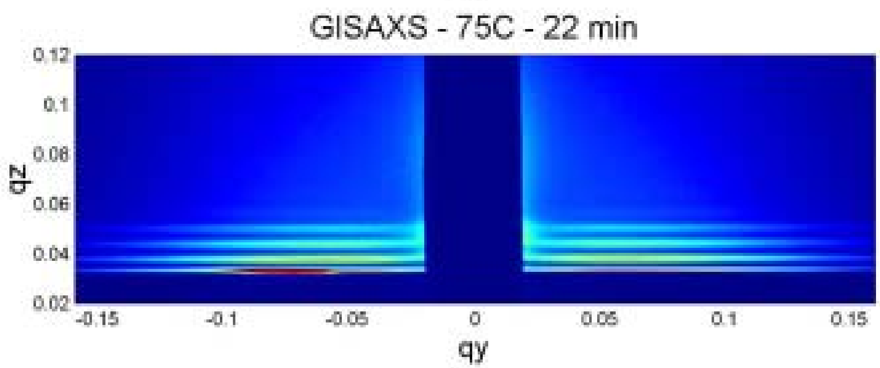
- Optical reciprocity explains the modulation in q_z direction
- DWBA yield satisfactory simulation (see Prof. Sunil Sinha's talk)

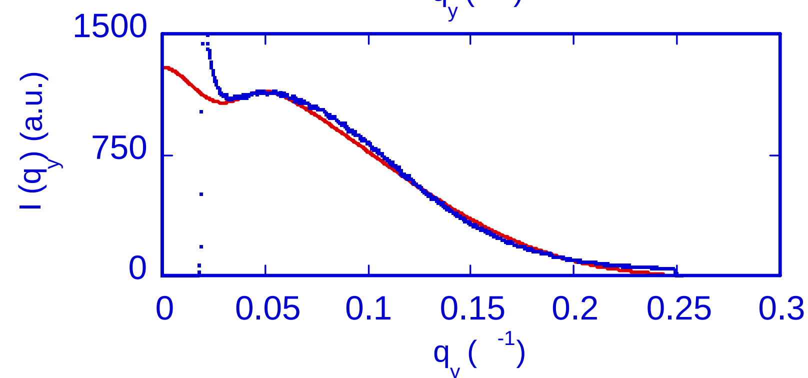


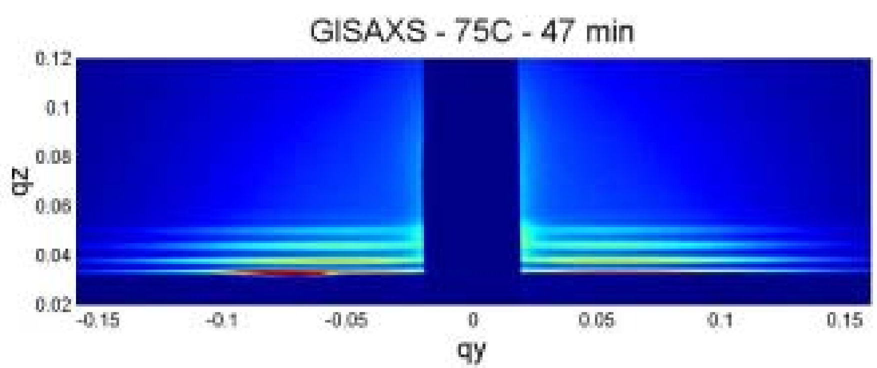
Real Time Measurement

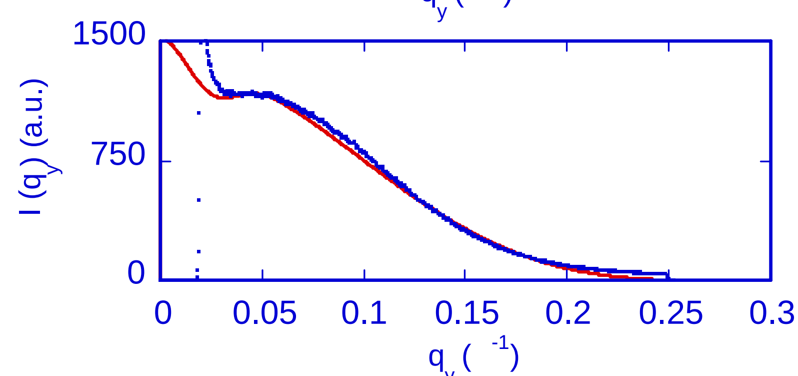




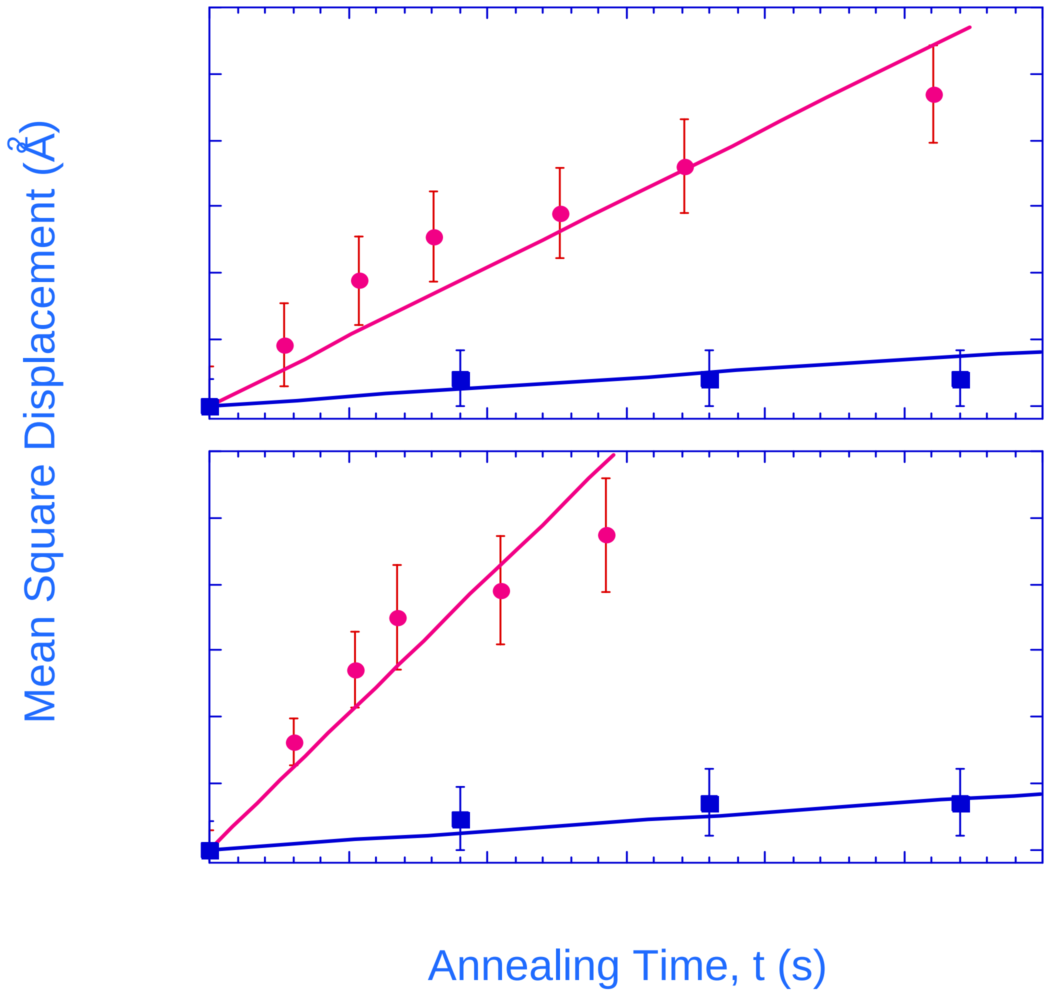








Anisotropic Motion



Narayanan, Guico, Lee, Sinha, Wang, Submitted to Phys. Rev. Lett.

Summary

- Anisotropic diffusion or motion properties has been observed: 10 times faster in the plan than normal to the surfaces
- Thin-film-based wave-guiding effects greatly enhance GISAXS signals, 100, and, with location selectivity
- The enhancement will be extremely useful for correlation spectroscopy using coherent beam: scattering intensity is a limit, 100-fold of enhancement will be certainly help!
- Grazing-incident is powerful to obtaining the location-dependence of the kinetics and ordering

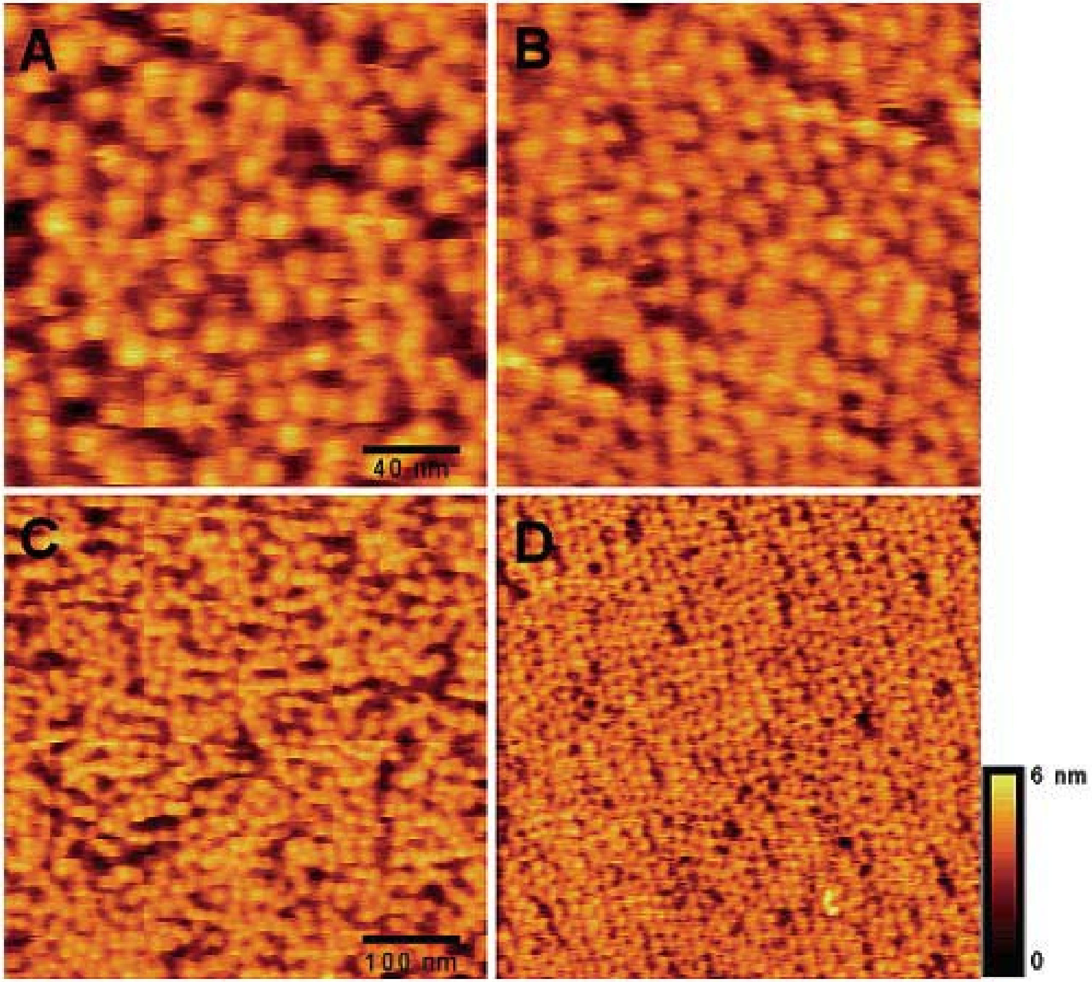
Density Fluctuations in Co-Polymer

- For weak contrast systems such as diblock co-polymers for time-resolved studies: in progress
- Interface with <3% interfacial electron density difference

Collaboration with M. Foster (Akron)

Membrane Protein Structure

- **3-D crystallography of 2D crystal?**
  - Nanoparticulate phospholipid bilayer disk with membrane scaffold protein
  - T. Bayburt *et al*. *Nano Letters* **2**, 853 (2002)



Membrane Protein Unfolding

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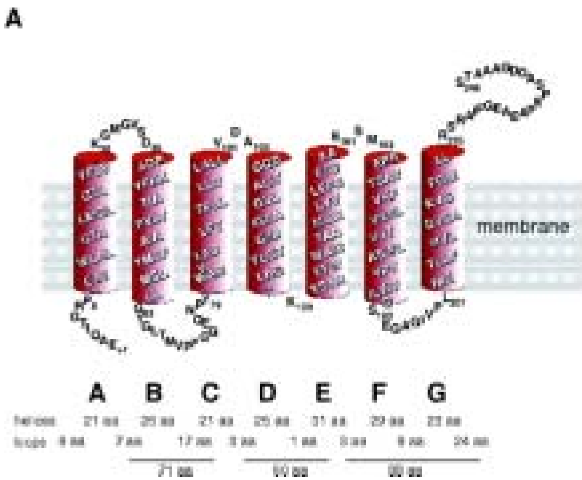
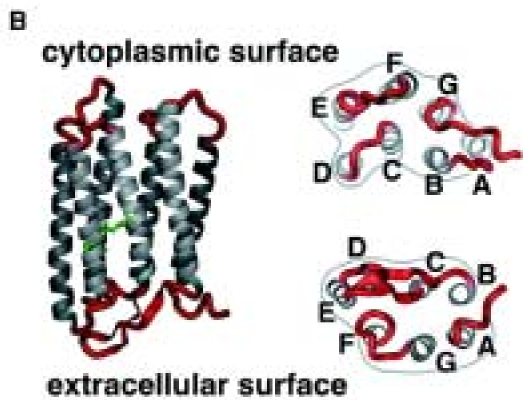
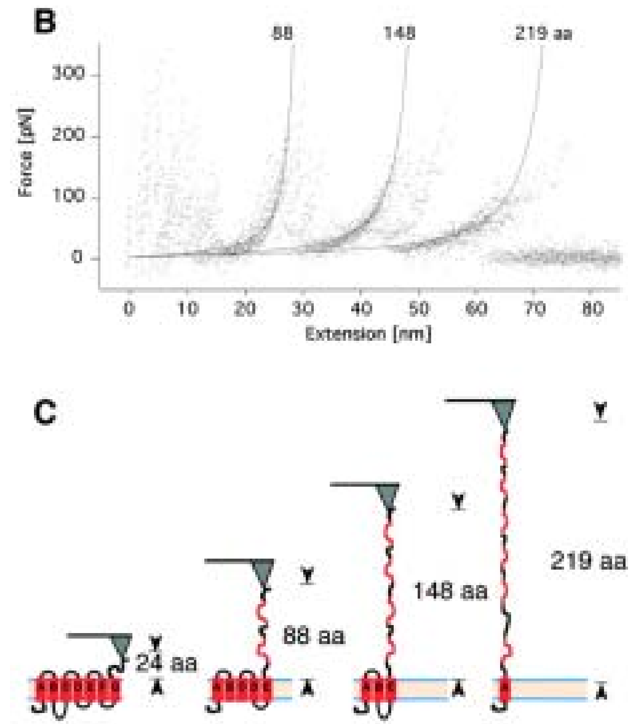
Argonne National Laboratory

- Induced by AFM tips
- F. esterhelt, et al. Science **288**, 143 (2000)







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