Neutron Reflectometry Investigations of Thin Films and Interfaces

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UT-BATTELLE

Outline

- **Neutrons and neutron reflectometry**
- **Examples of Soft Condensed Matter:**
  - **Polymers at solid/liquid interfaces**
  - **Advanced drug delivery systems**
- **Same principles apply to any thin film materials**

Why Use Elastically Scattered Neutrons to Probe Soft Matter?

Neutron WAVELENGTH ~ atomic/molecular dimensions:

- •interference
- •reflection
- •refraction

Neutrons are NEUTRAL particles:

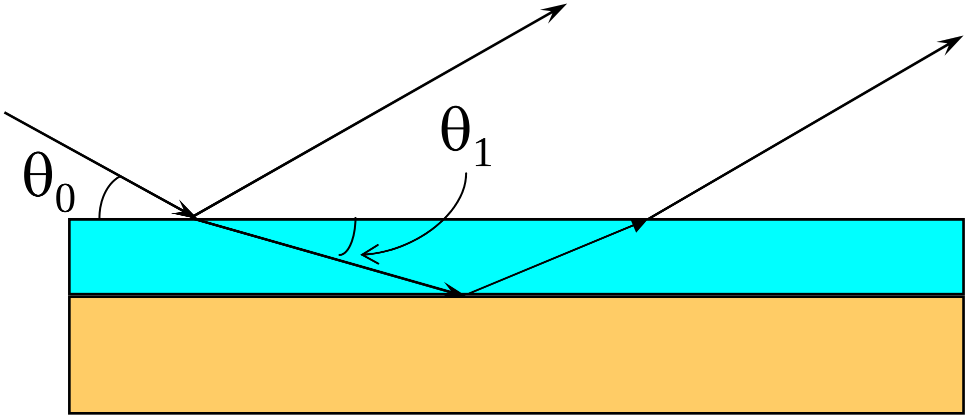
- •highly penetrating
- •nondestructive probe
- •sample environments

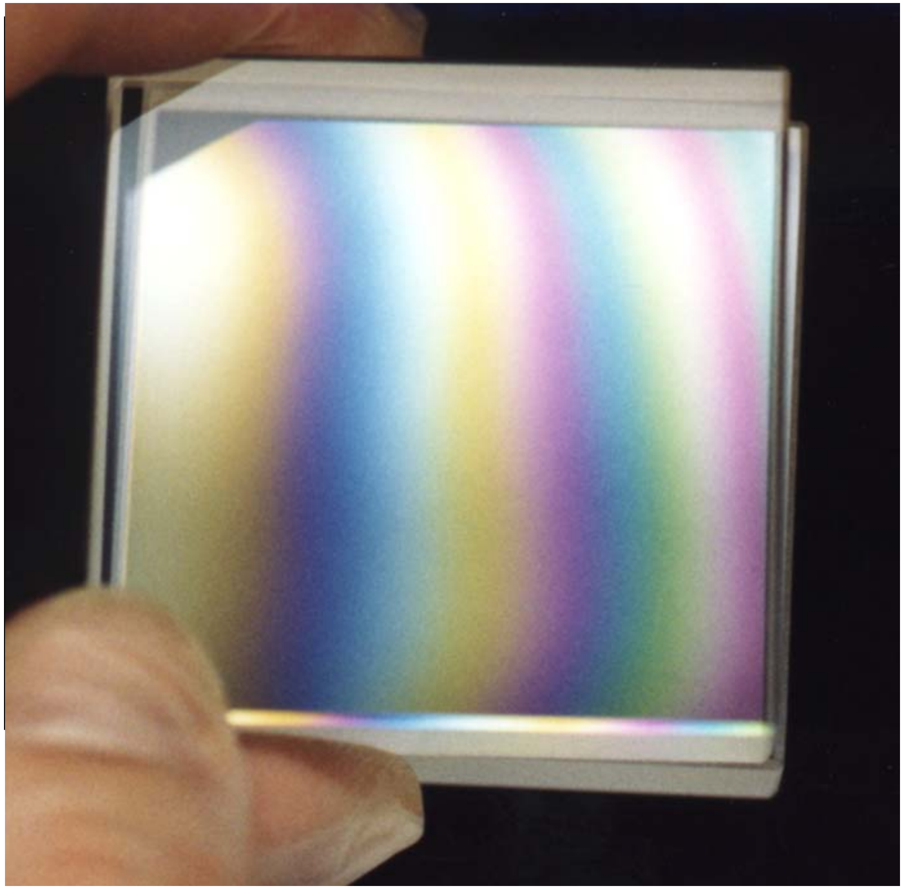
Neutrons interact with atomic NUCLEI:

- •sensitive to light atoms
- •can exploit isotopic substitution
- •contrast matching

Neutron Reflectometry and the Wave Nature of the Neutron

The effects seen in light scattering are also seen in neutron interactions- reflection, refraction, and interference





Contrast Variation in Action!

ORNL-DWG 8767-86

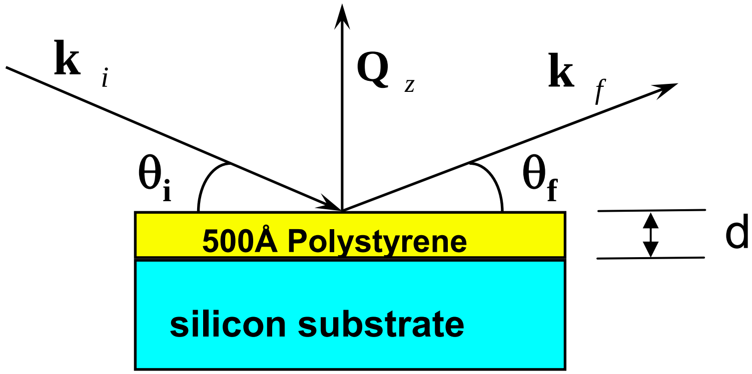
A B

When the monster came, Lola remained undetected.
Harold, of course, was immediately devoured.

BOTH TUBES CONTAIN BOROSILICATE BEADS IN GROUND PYREX FIBERS AND SOLVENT:
A. REFRACTIVE INDEX OF SOLVENT MATCHES THAT OF GROUND PYREX.
B. REFRACTIVE INDEX SOLVENT IS DIFFERENT TO THAT OF GROUND PYREX OR GLASS BEADS AND SCATTERING FROM THE PYREX FIBERS DOMINATES.

Courtesy of G.D. Wignal

Neutron Reflection from a single layer on a substrate

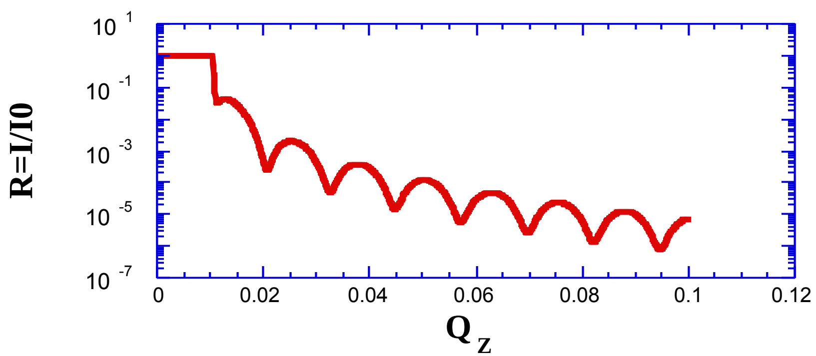


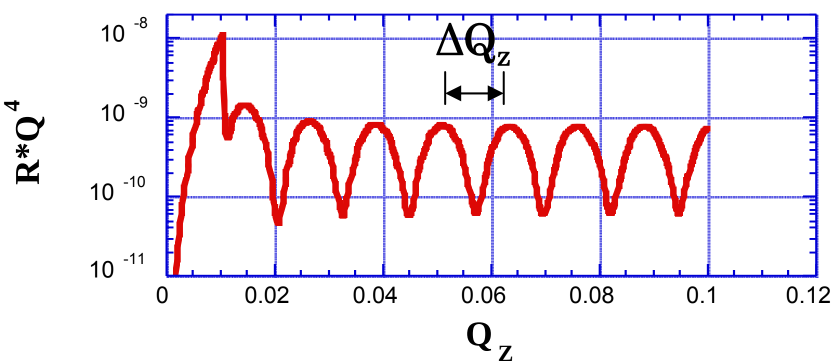
$$|\mathbf{k}_i| = |\mathbf{k}_f| = \frac{2\pi}{\lambda}, \qquad m\mathbf{v} = \hbar \mathbf{k}$$

$$\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i, \qquad Q_z = \frac{4\pi \sin(\theta)}{\lambda}$$

For $Q_z > Q_c$:

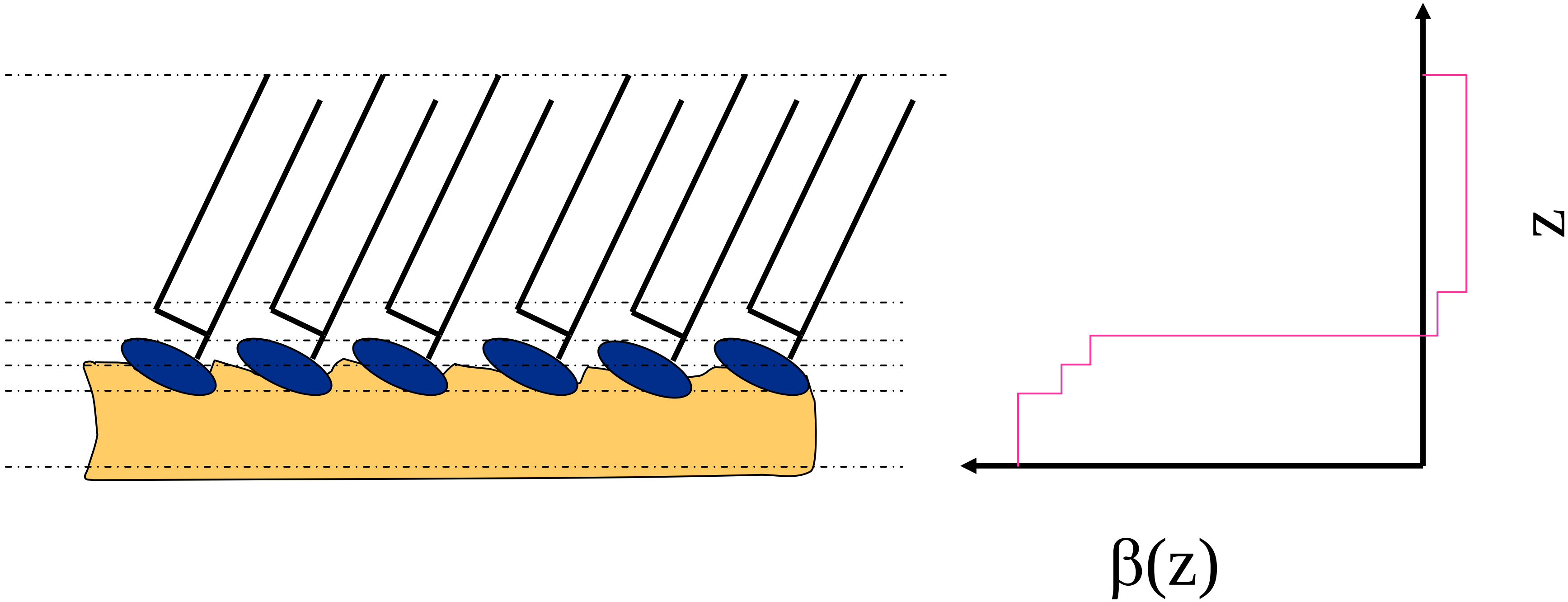
$$R(Q_z) \approx \frac{1}{Q_z^4} \left| \int \frac{d\beta(z)}{dz} e^{-iQ_z z} dz \right|^2$$





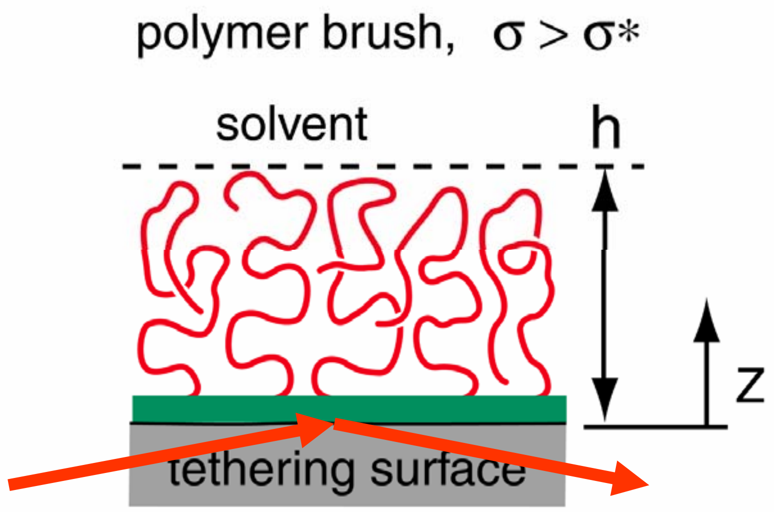
- Incident neutron has velocity, v
- Snell's Law, $\theta_i = \theta_f$
- Momentum transfer Q along z-axis
- Reflectivity defined as I/I_0
- Interference fringes with spacing $\Delta Q_z = 2\pi/d$
- Reflectivity good for films 0.2-500 nm

More complex structures



- For complex potentials approximate by multilayers
  - Interpenetration
  - Thickness
  - Roughness

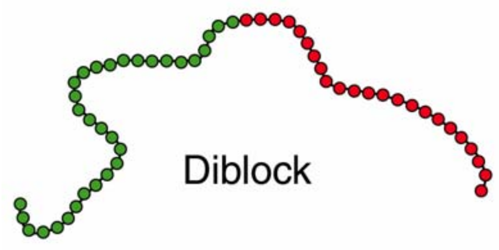
Example I :Grafted Polymer Brushes



solvent

– h = brush height
– σ = grafting density

- Already studied by reflectometry
- Parabolic brush density profile



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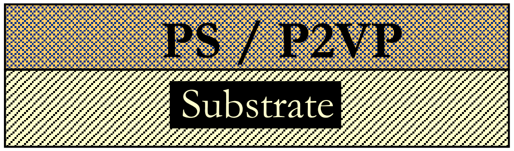
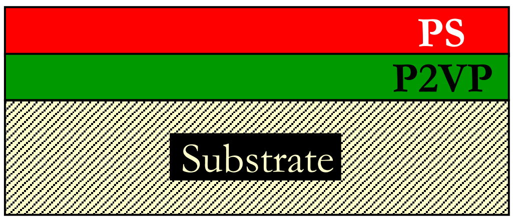
Model System: Dense Polymer Brushes

50:50 PS-P2VP



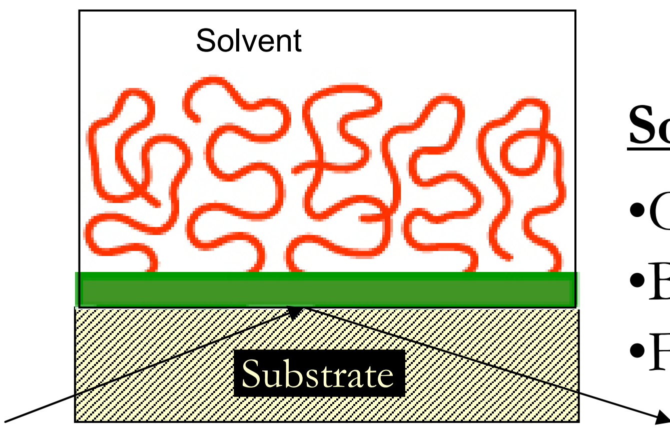
Spin-coat filtered polymer solution

124k dPS-hP2VP



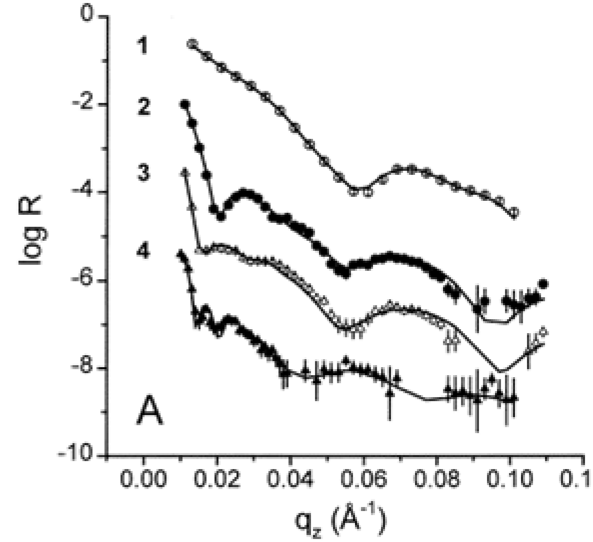
Anneal above T_g

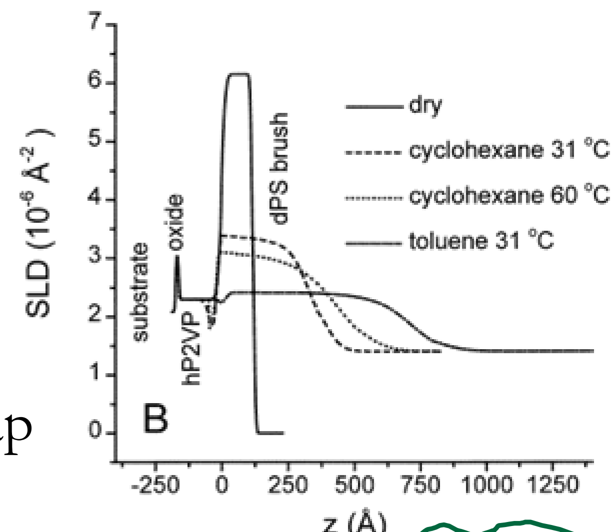
180C for 24 hours



Solvate

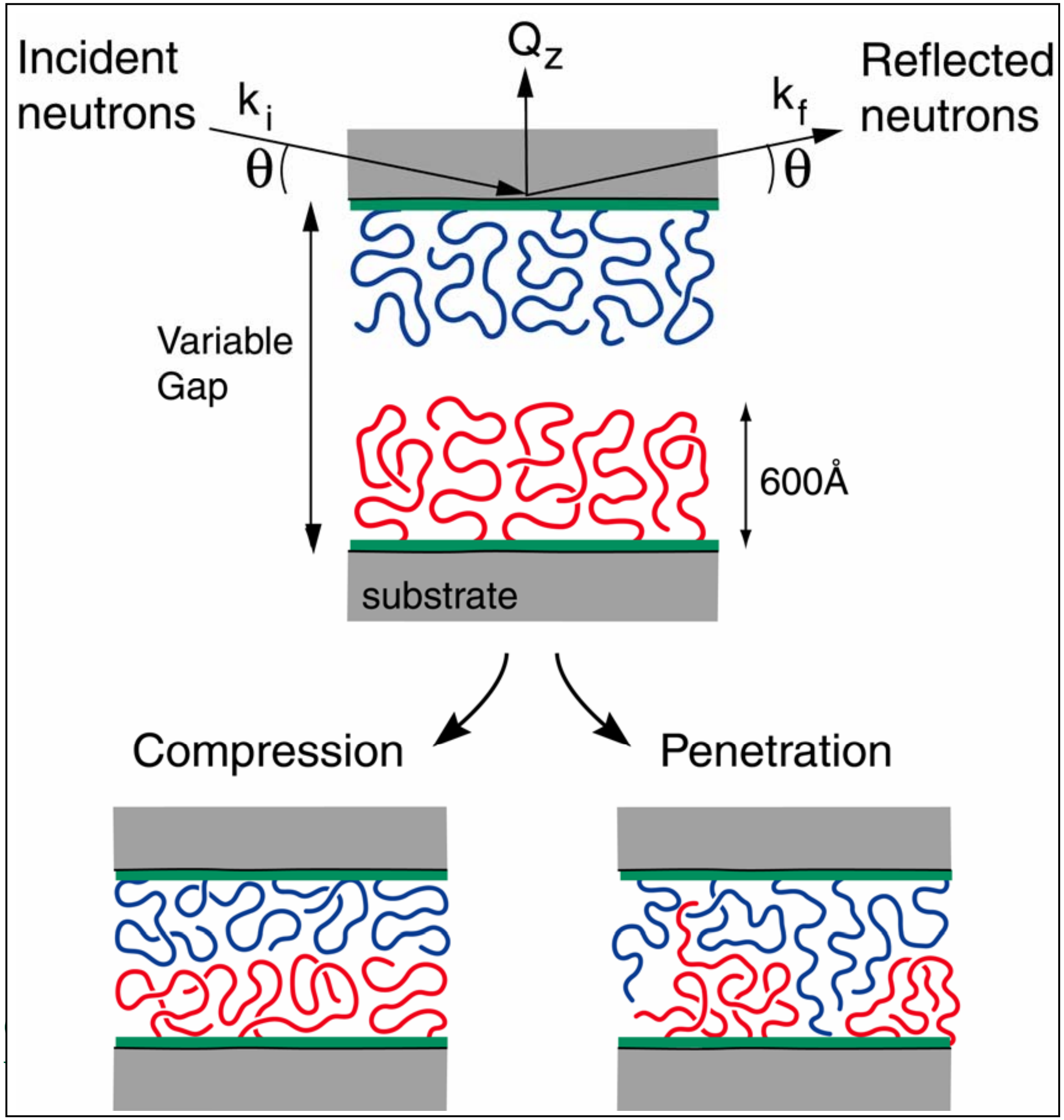
- Contrast Variation
- Brush extension
- Flattens with chain overlap





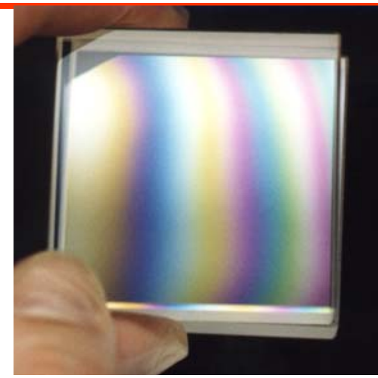
Levicky, et al Macromolecules 1998

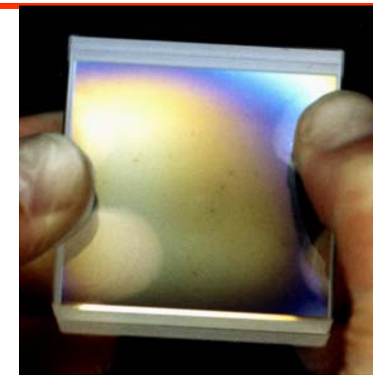
Problem: What happens to confined brushes?



- Polymer brushes in good solvent
- Studied with SFA but no structural data
- Gap smaller than chain extension
- Measure the segment density profile

Neutron Penetration: Confinement Cell





Substrates:

5cm sq. or round

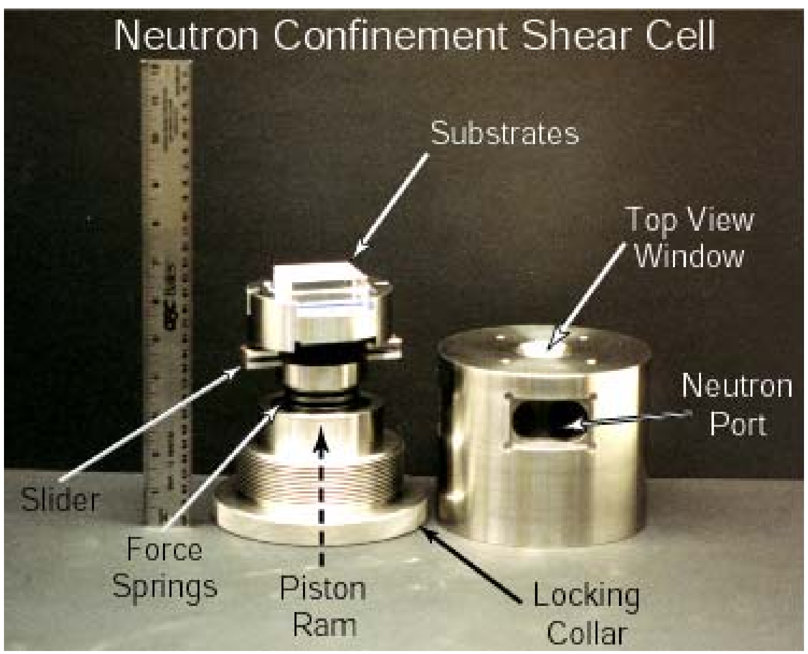
- Silicon

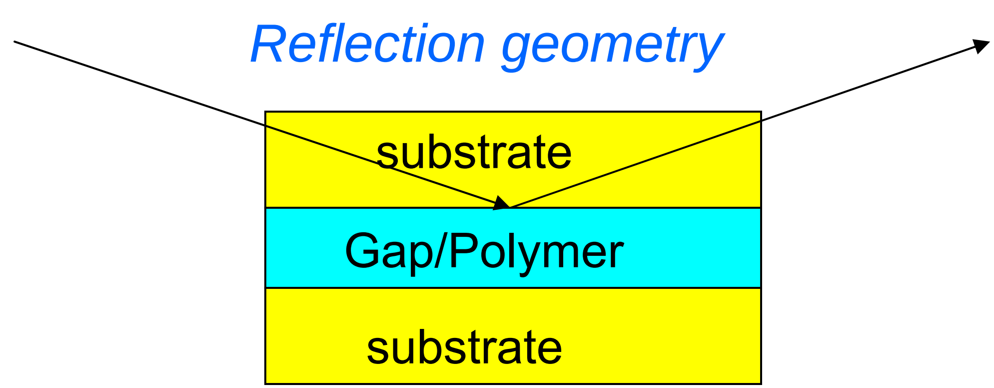
- Quartz

- Sapphire

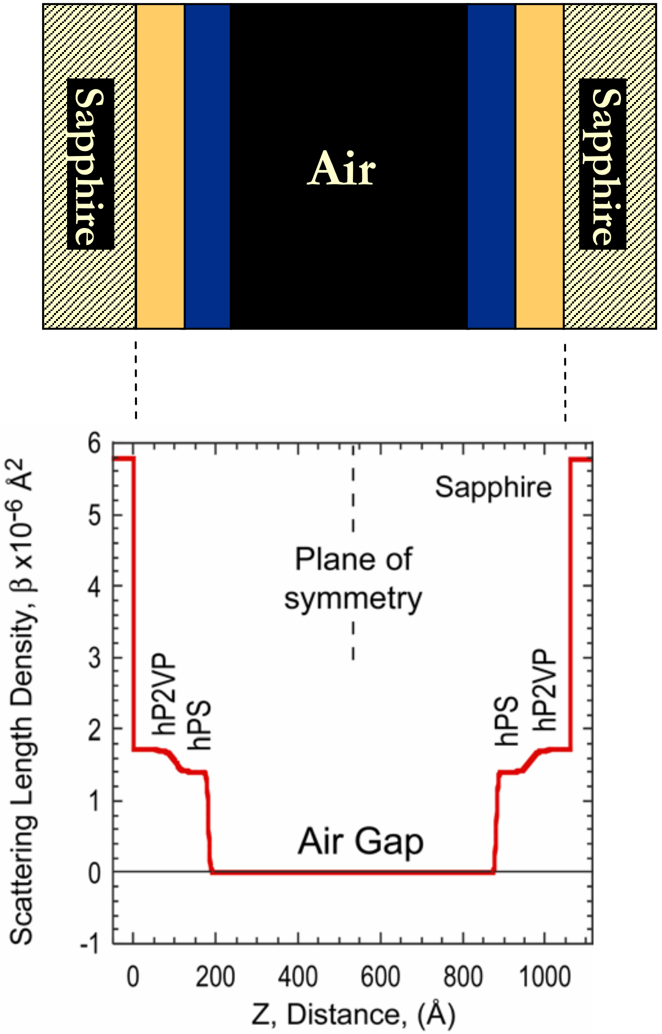
Flatness < λ/25

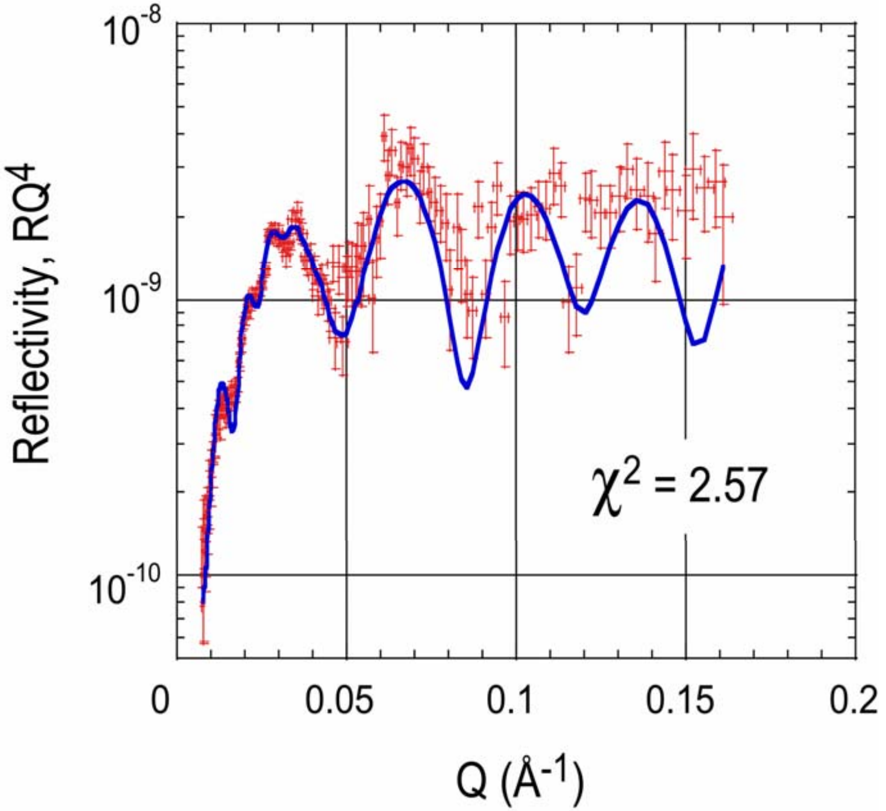
- Need constant gap ~1000 Å over few cm^2
- Transparent material to neutrons
- Squeeze substrates parallel
- Cell assembled in clean environment





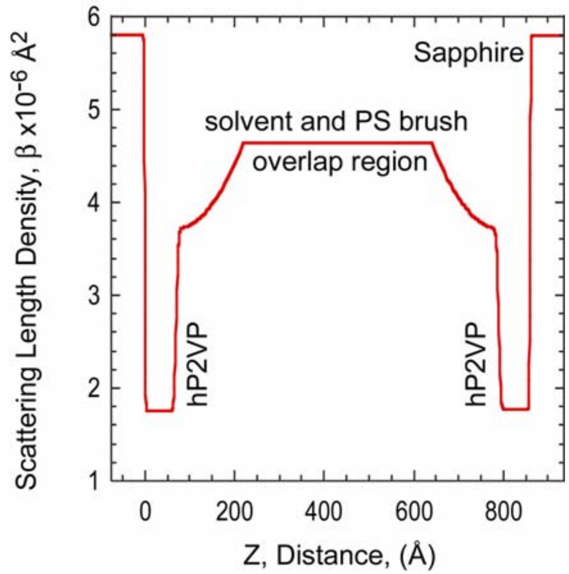
Confined Polymer Layers: No Solvent

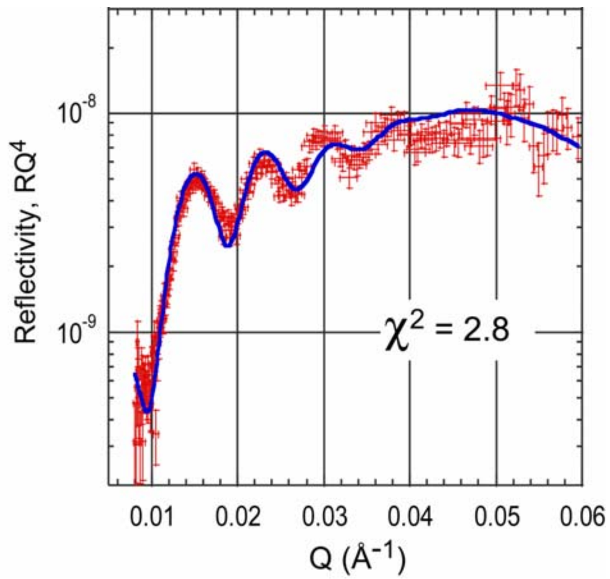


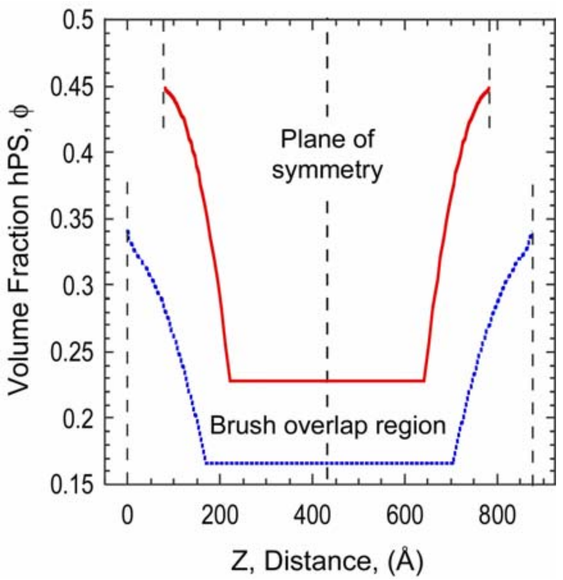


hPS	78 Å	β 1.42
hP2VP	104 Å	β 1.85
Air	697 Å	Inc 60 Å

Solvated Polymer Brush – Smaller Gap 850Å



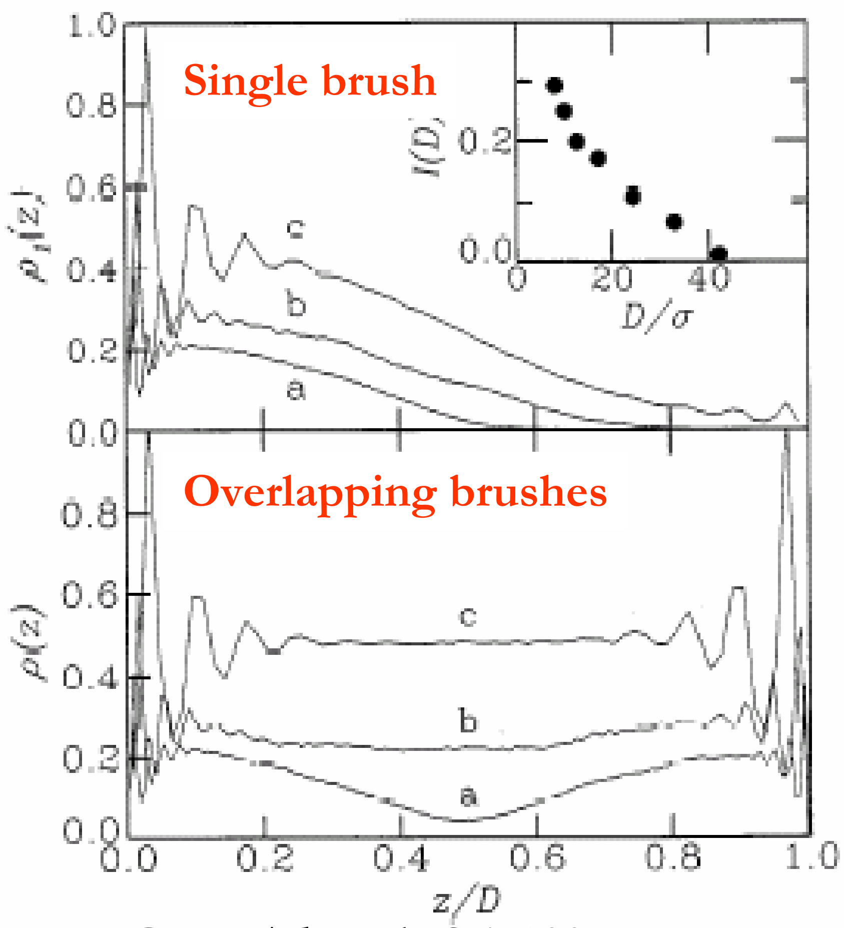




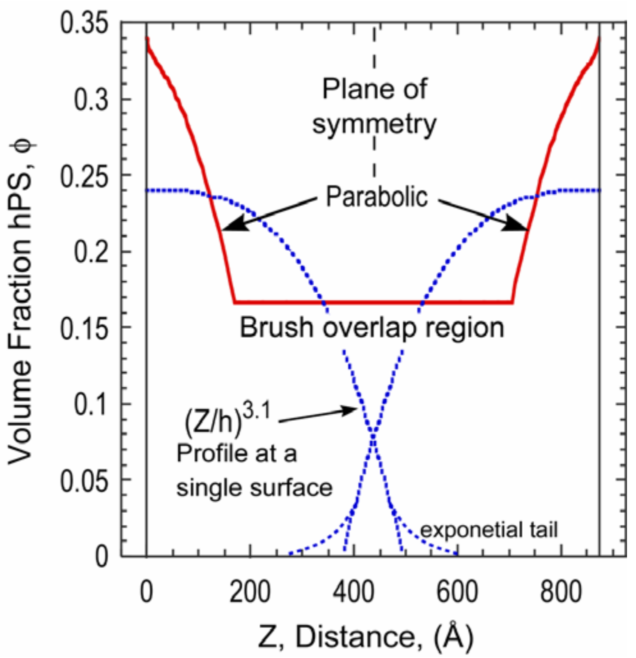
$$\beta(z) = \phi_{PS} * \beta_{PS} + \phi_{solvent} * \beta_{solvent}$$

- **Gap thickness dependent on sample prep**
- **With smaller gap density of overlap region increases**
- **Density increases at the P2VP-substrate surface**

Volume Fraction Profiles: Comparison with MC Calculations



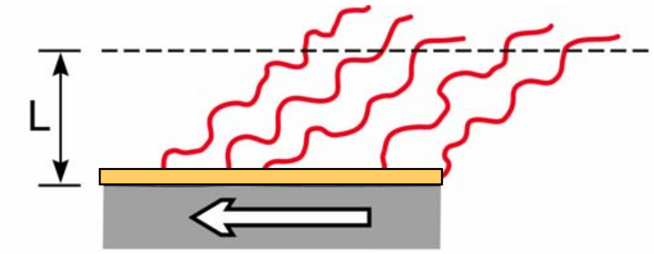
Grest, Adv Poly Sci, 1998



- MD calculations predict that brushes overlap
- Central region density shown to increase with overlap
- No prediction on the compression at the walls

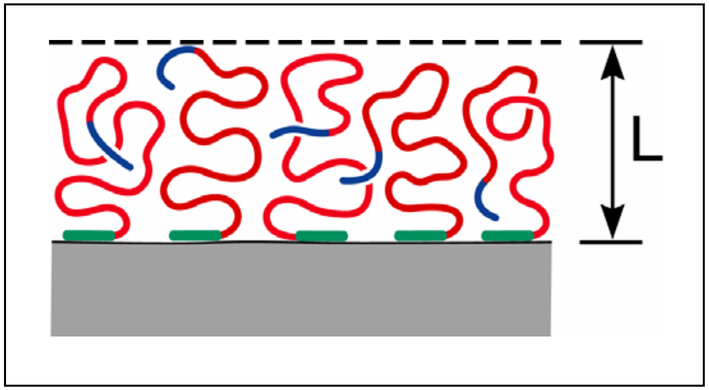
Conclusions

Future Work



$.001\ s^{-1} < \dot{\gamma} < 10{,}000\ s^{-1}$

75 nm < plate separation < 10000 nm

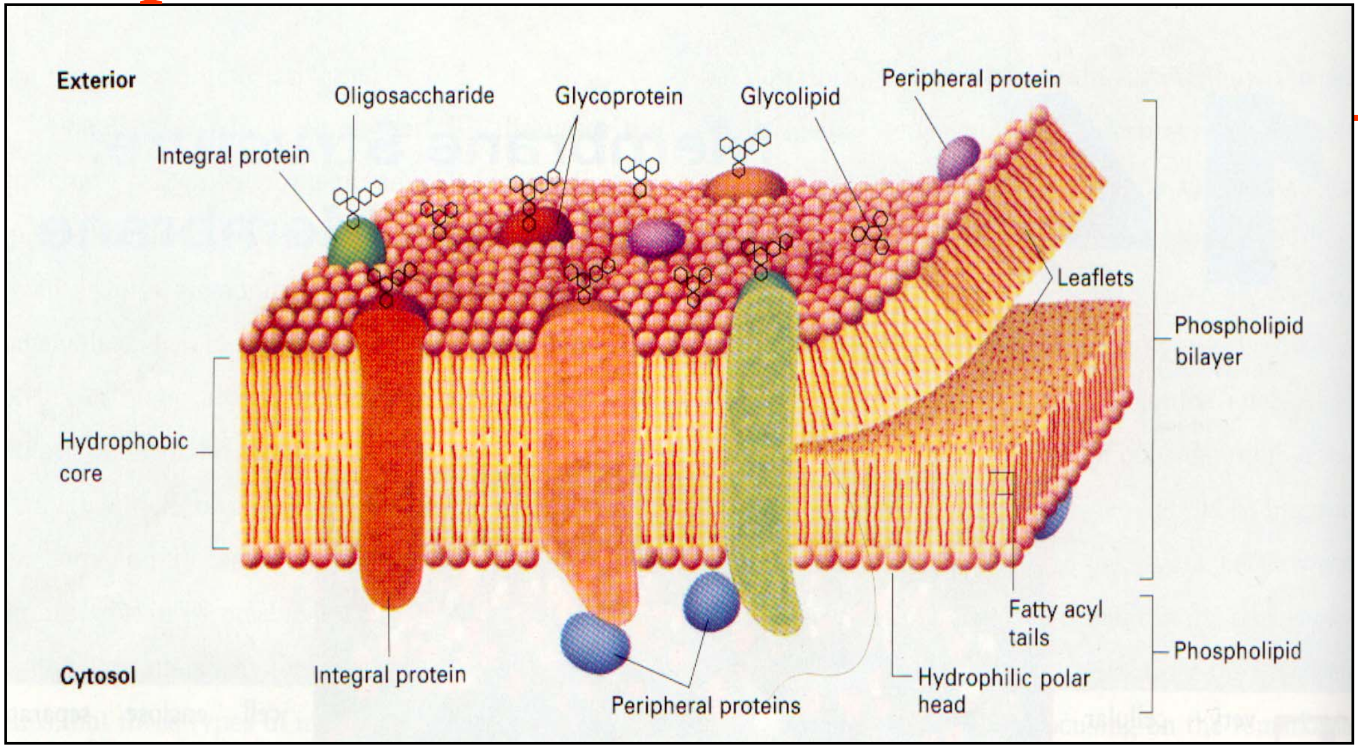


- Neutron reflectivity with new cell yield segment density profiles
- High density polymer brushes serve as model systems for confinement studies
- Chain overlap consistent with predictions, but near-surface compression a surprise

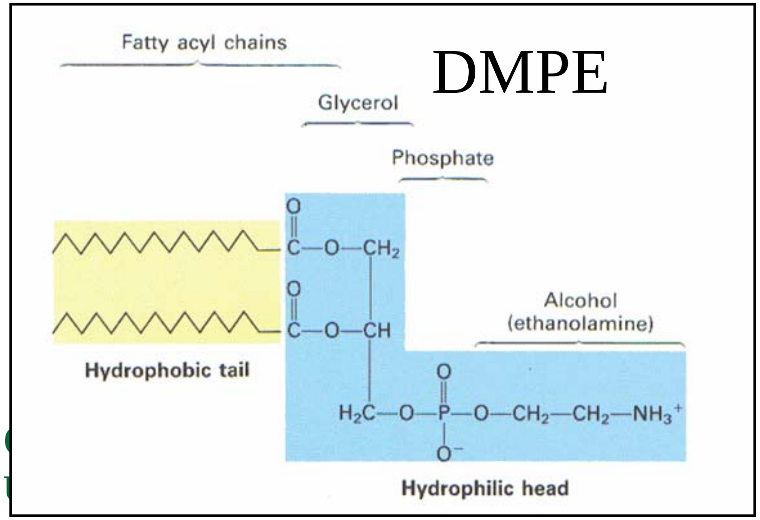
Example 2

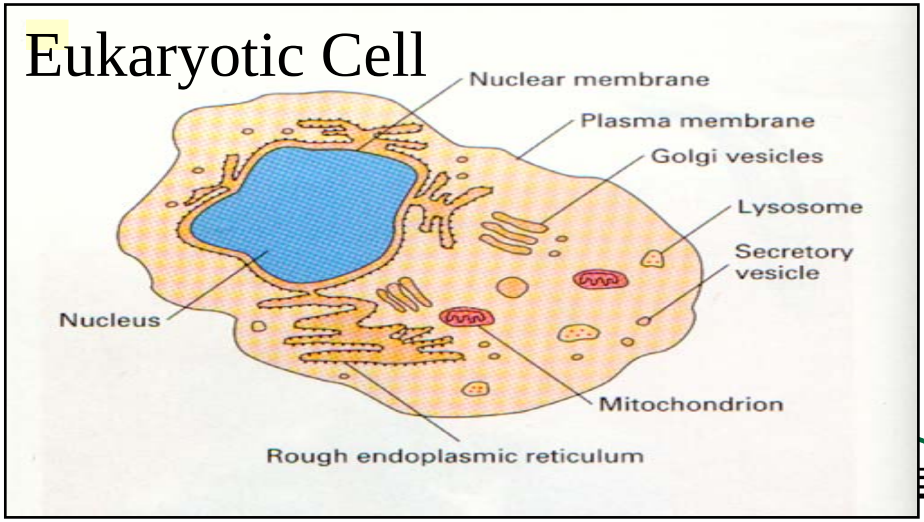
The Structure of PEG-Lipid/Lipid Monolayers at Air/Water and Solid/Water Interfaces

Lipids Form Cell Membranes

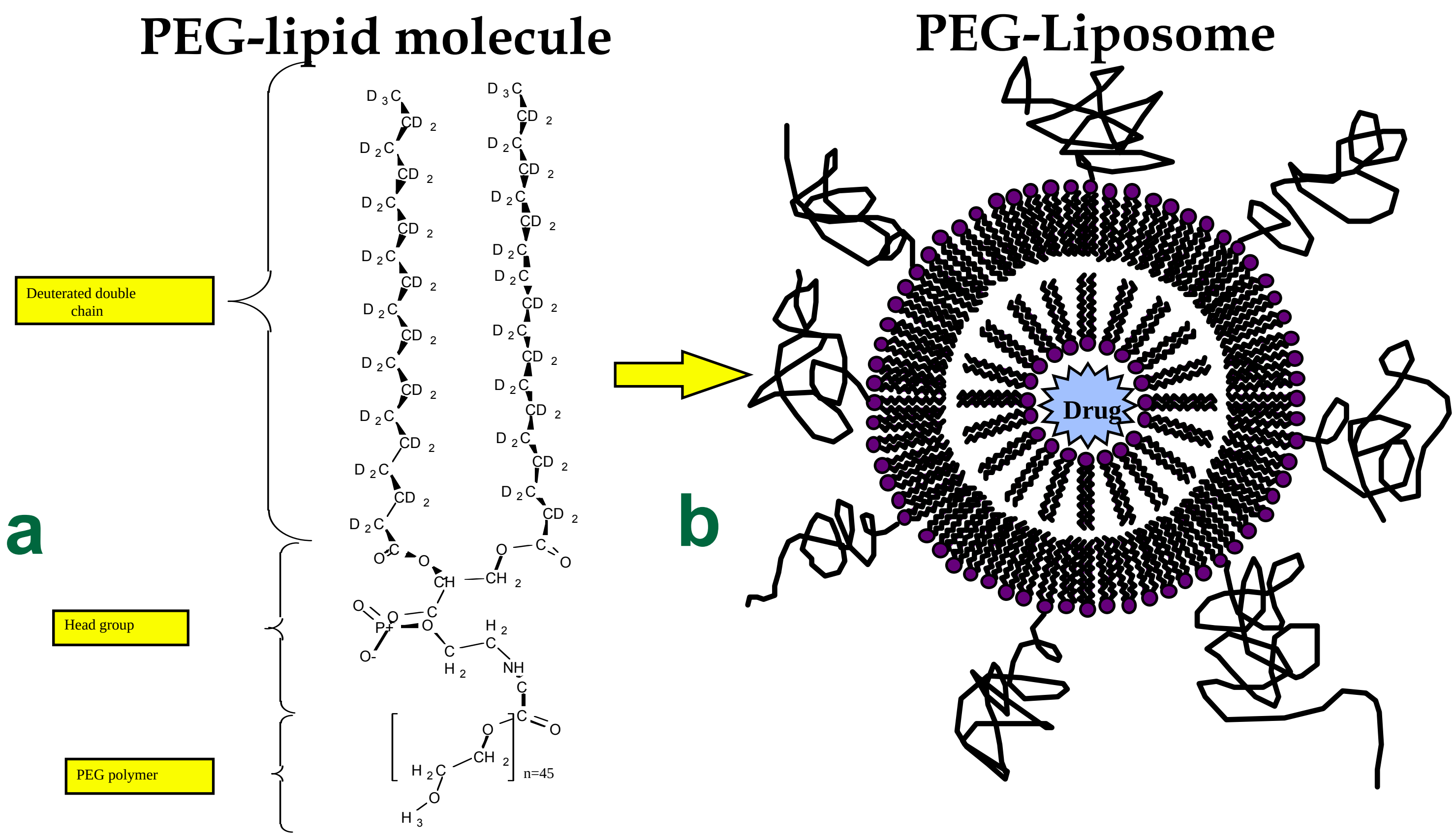


- Found in all membranes
- Contains proteins
- Bilayer structure





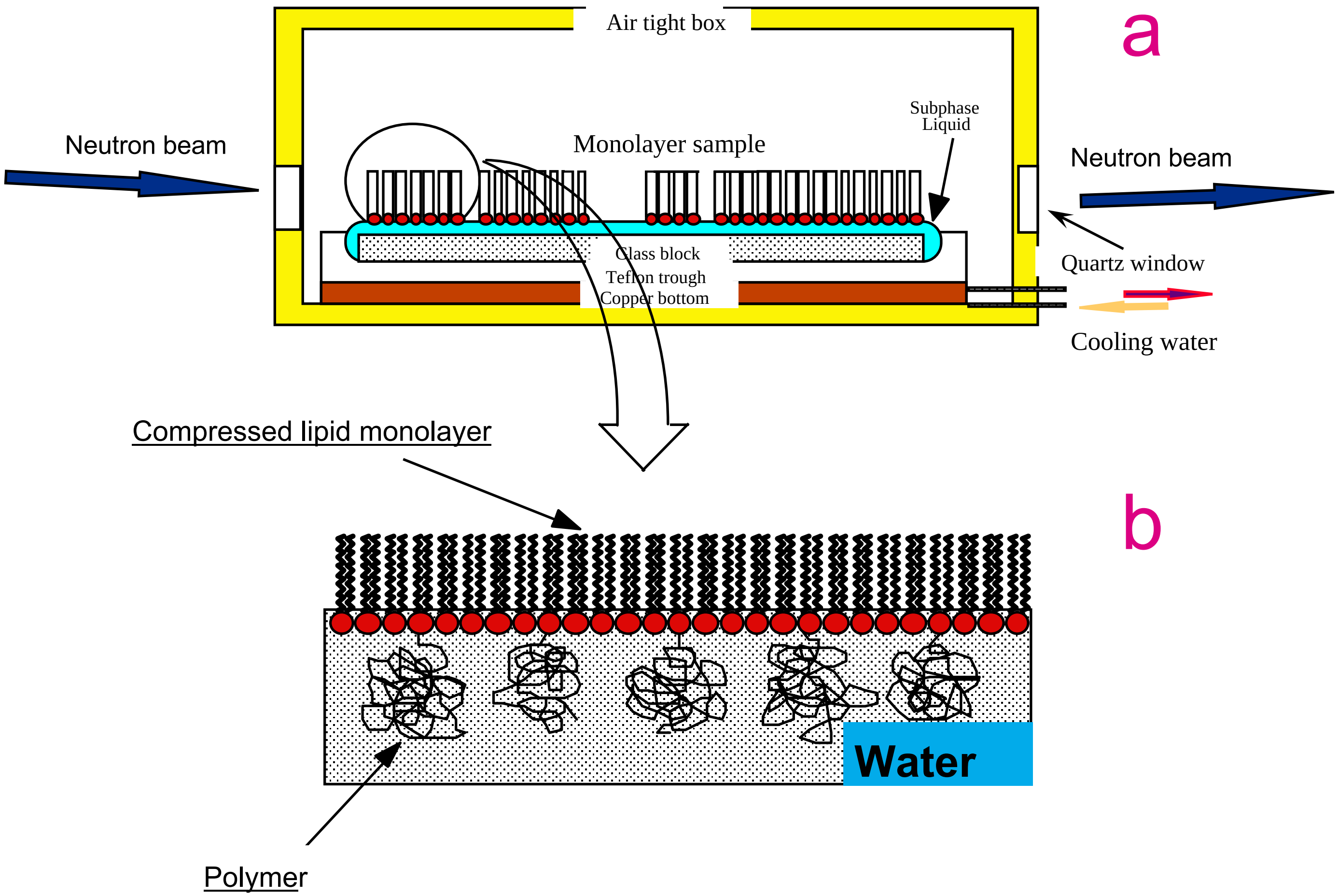
What are PEG Lipids?



Why study PEG Lipids?

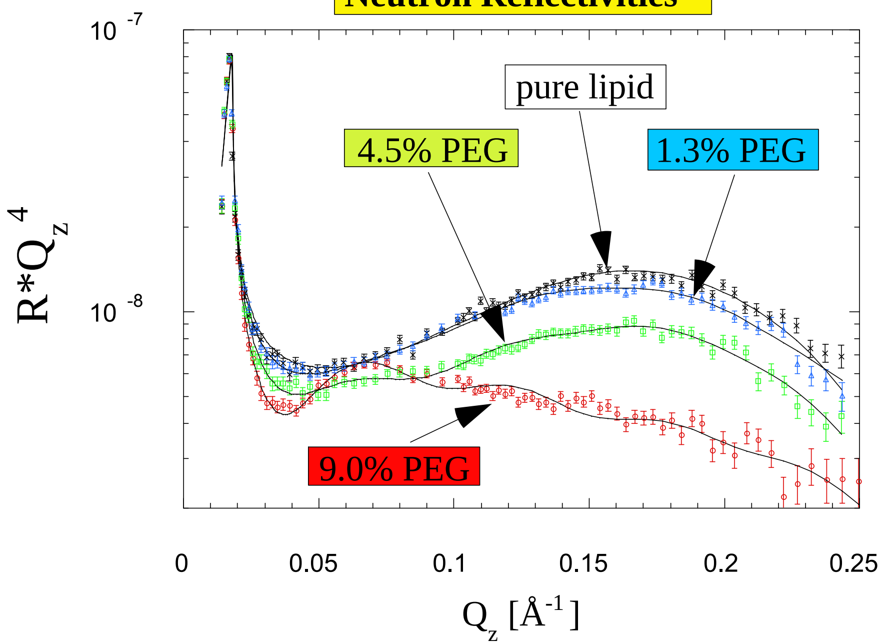
- **advanced drug delivery**
- **monolayers with enlarged hydrophilic headgroups**
- **model of lipid-associated proteins (lipo-proteins)**
- **grafted polymers in good solvent conditions**
  - ***interaction between polymer chains***
  - ***polymer density profiles vs. surface coverage***
  - ***“mushroom” to “brush” transition***

A Schematic View of the Langmuir Trough for Scattering Experiments

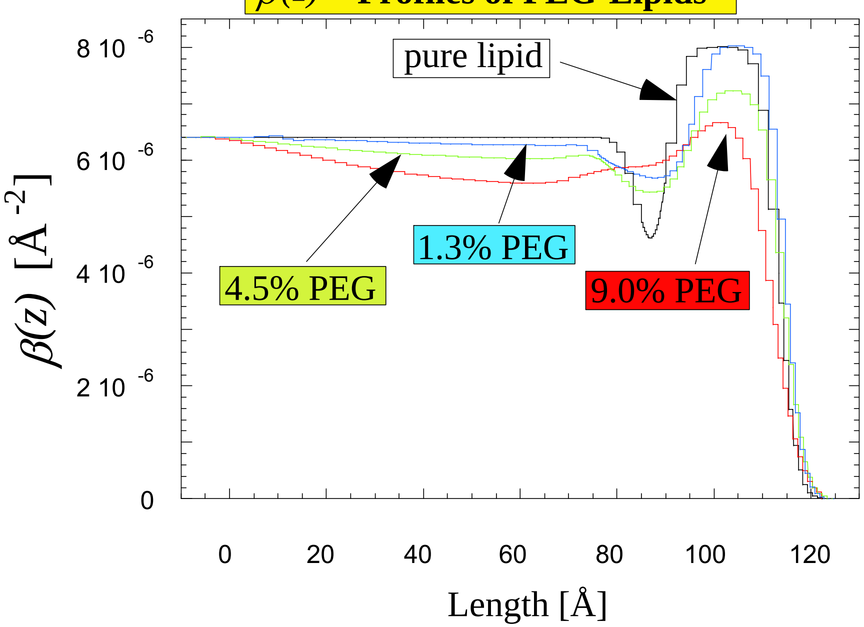


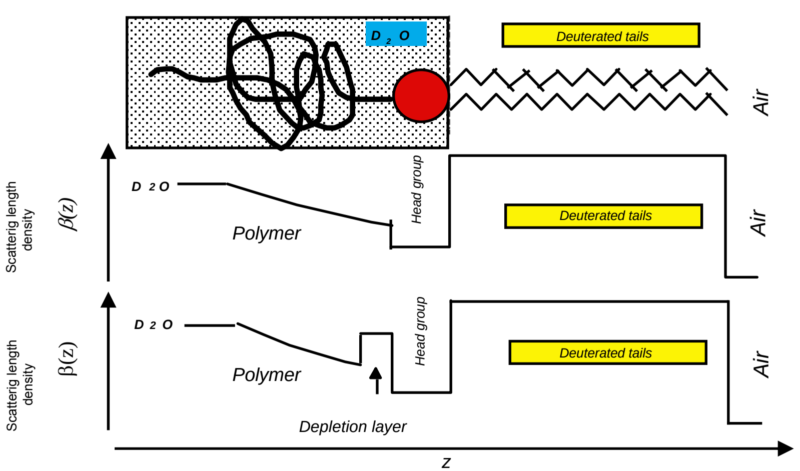
Neutron Reflectivity Data from PEG-Lipid/Lipid Mixtures

Neutron Reflectivities



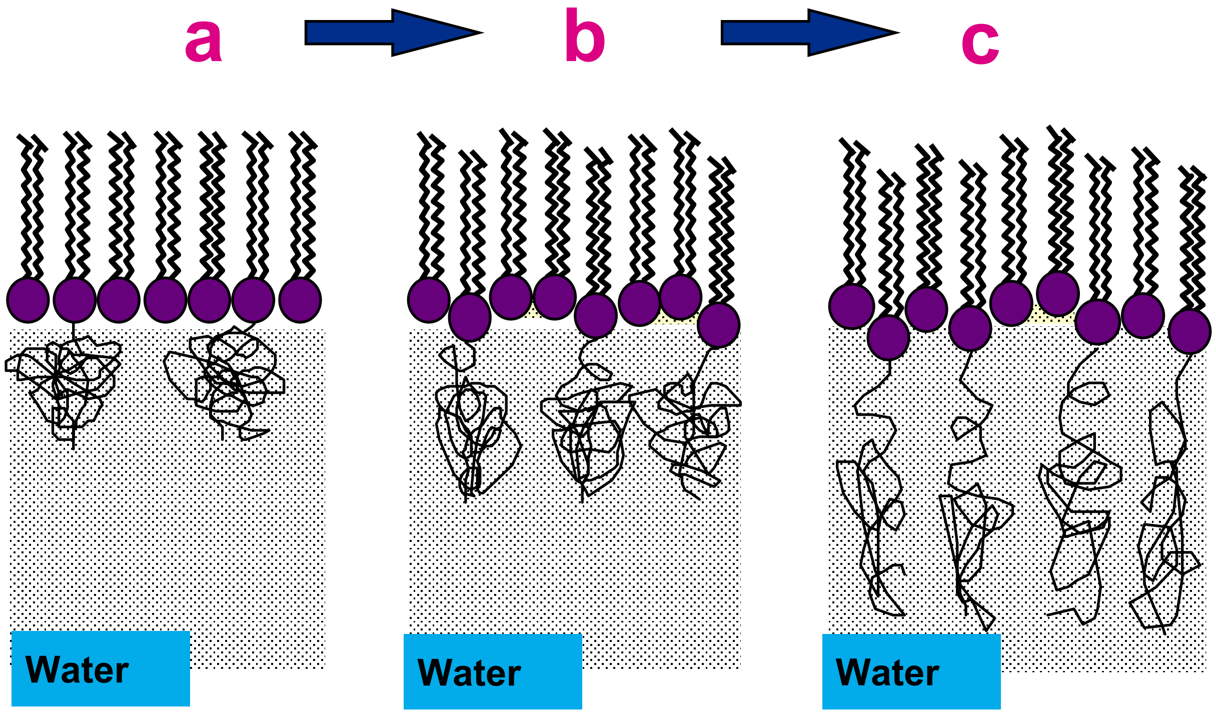
***β(z)* Profiles of PEG-Lipids**





- Parabolic polymer profile
- No depletion layer
- Admixing of tails and water

A model of the behavior of the PEG chain monolayer



Conclusions:

- **PEG portions of the molecules extend into the water subphase.**
- **Lipids are constrained to the interface.**
- **Extension of the PEG chains from the interface increases with increasing concentration of PEG-lipids in the monolayer.**
- **Data is consistent with “mushroom” to “brush” transition.**
- **The air-water interface proportionally roughens with the addition of PEG-lipids.**
  - ***increase in lipid protrusions due to the increased solubility of PEG-lipids,***
  - ***relaxation of the lateral force between PEG portions by staggering of the lipid headgroups.***

Neutron reflectivity summary

- Study solid/air, solid/liquid, liquid/air interfaces
- Model systems with length scales from a few tenths to a few hundred nm
- Contrast variation- highlight molecules
- Model fitting to understand the data
- Other information not here
  - Magnetic thin films
  - Off specular scattering
    - Rough surfaces
    - Grazing Incidence Diffraction

Collaborators

Tonya Kuhl, UC Davis

Dennis Mulder, UC Davis

Jae-Hie Cho, ORNL

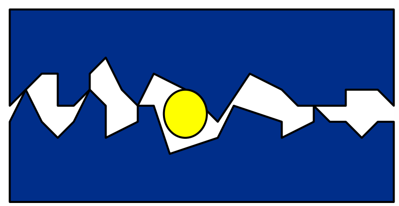
Bill Hamilton, ORNL

J. Israelachvili, UCSB

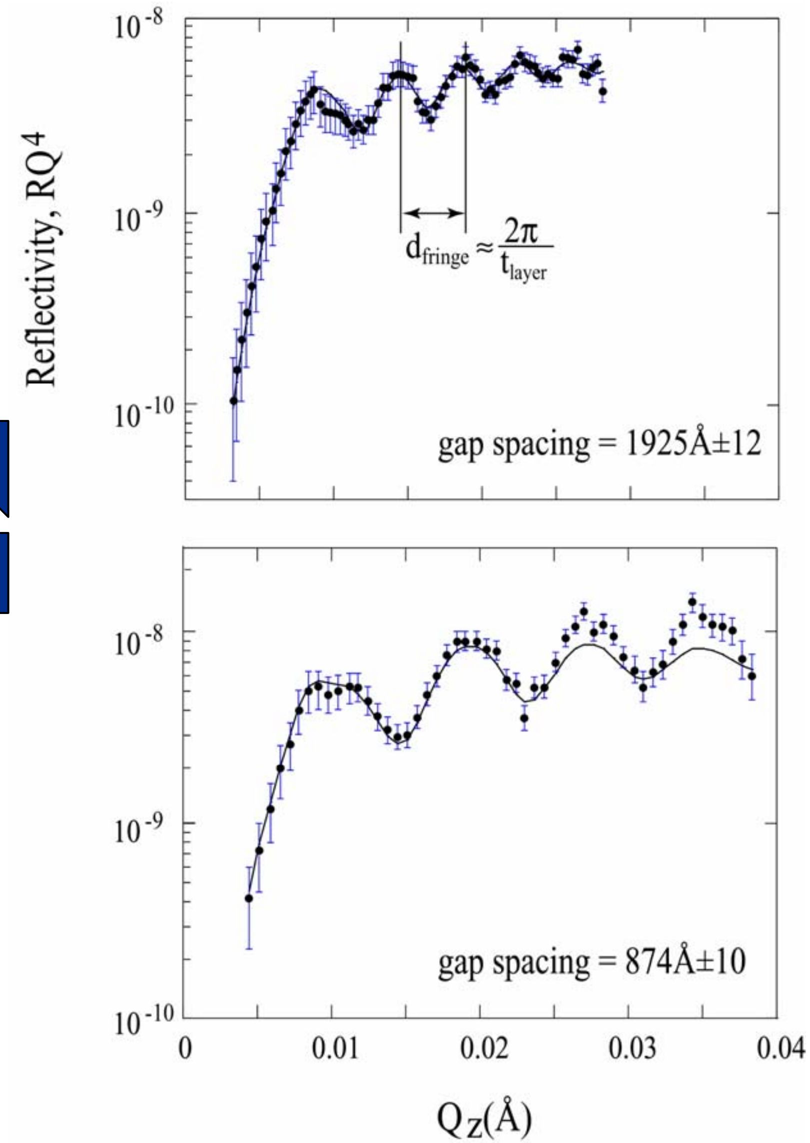
J. Majewski, LANL

Demonstration: No Polymer

- Long wavelength "waviness"
  - –peak to peak <250Å
- Dust
- Quartz, silicon, or sapphire
- OTS or OPA- hydrophobic

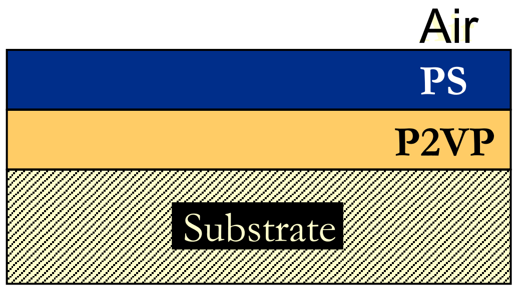


Parameter†	Large Air Gap	Small Air Gap
Intra-substrate separation (Å)	1925±4 (Å)	874±3 (Å)
Quartz β (10^{-6} Å^{-2})	4.17*	4.17*
Sapphire β	5.70*	5.70*
Air gap β	0.00*	0.00*
OTS on quartz β	-0.4*	-0.4*
OTS on quartz thickness (Å)	24* (Å)	24*
OPA on sapphire β	-0.4*	-0.4*
OPA on sapphire thickness (Å)	15* (Å)	15*
Gap variation - σ_w (Å)	66±3 (Å)	47±5 (Å)



Dry Polymer on Single Surface in Air

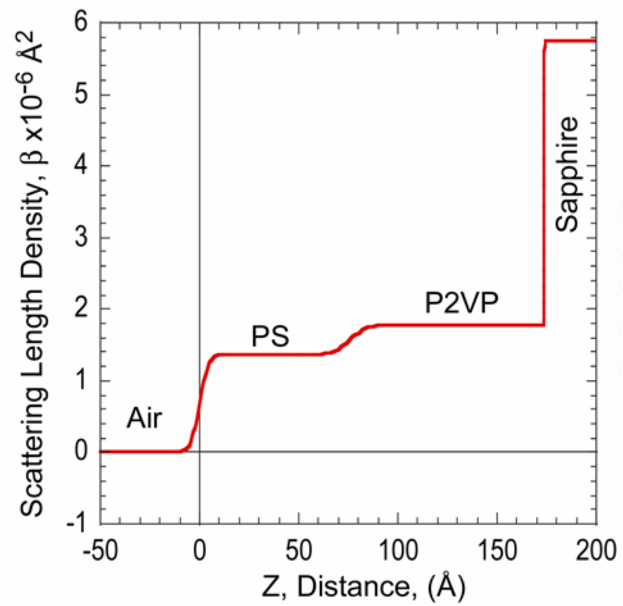
136k hPS-hP2VP

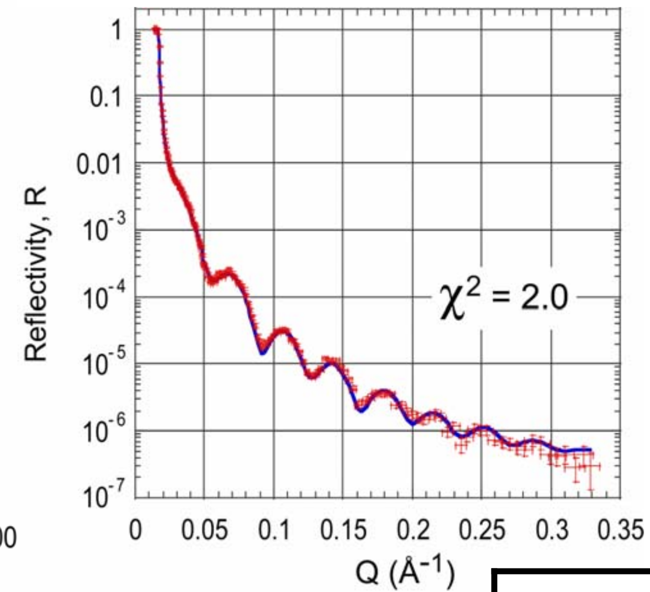


•Reflectivity fits with bilayer model

•Consistent with earlier studies

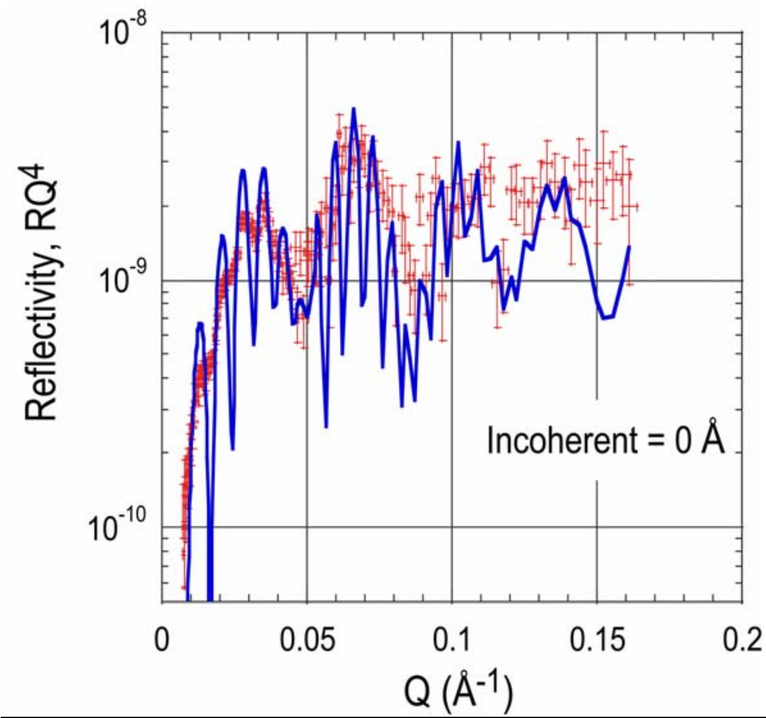
• β's consistent with calculated values for protonated polymer

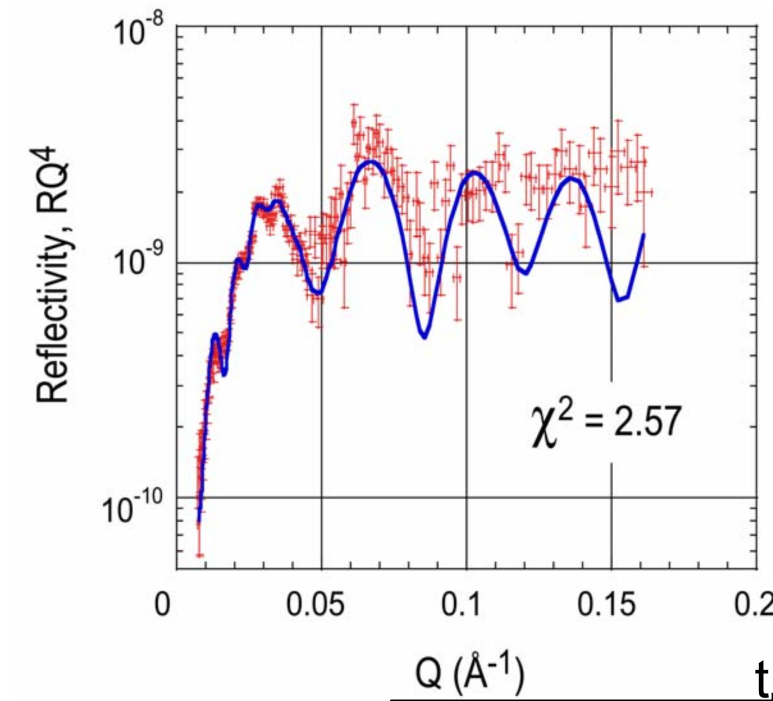




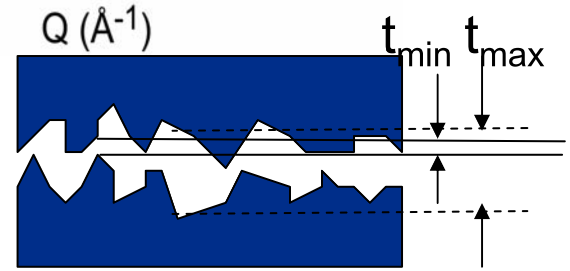
hPS	75 Å	β 1.42
hP2VP	100 Å	β 1.85

Incoherent Averaging





$$R(q_z, t_{nom}) = \frac{1}{\sigma\sqrt{2\pi}} \int R(q_z, t)\, e^{-\frac{(t - t_{nom})^2}{2\sigma^2}}\, dt$$

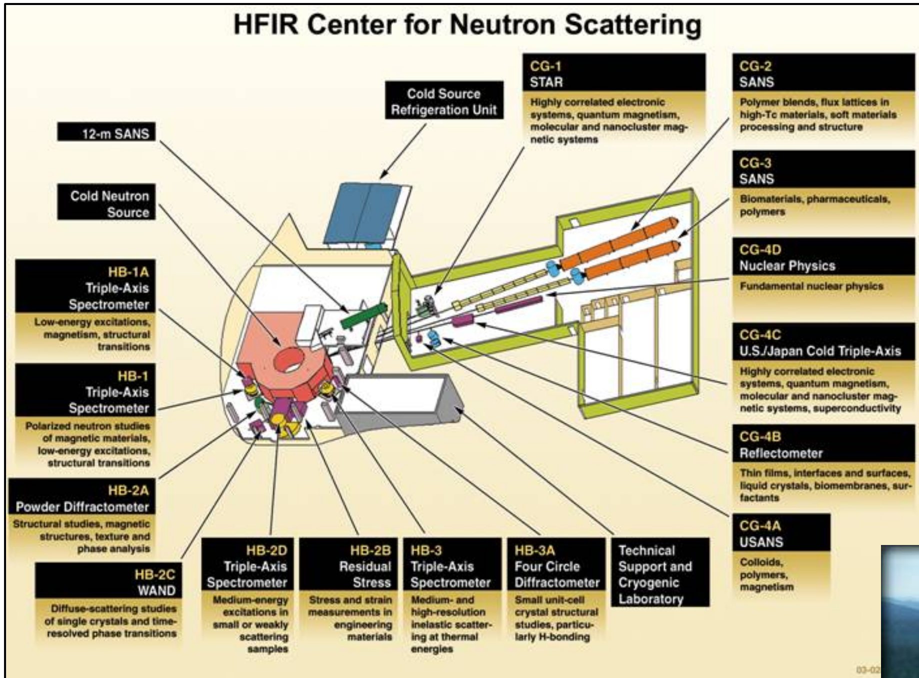


hPS	**78 Å**	**β 1.42**
hP2VP	**104 Å**	**β 1.85**
Air	**697 Å**	Inc 0 Å

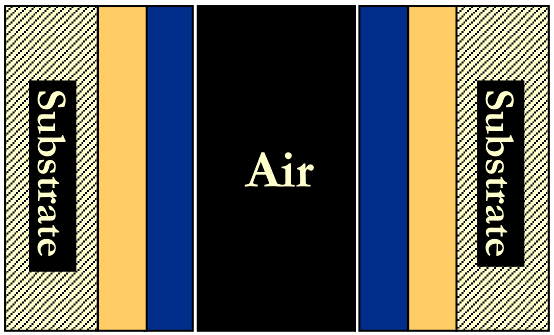
hPS	**78 Å**	**β 1.42**
hP2VP	**104 Å**	**β 1.85**
Air	**697 Å**	Inc 60 Å

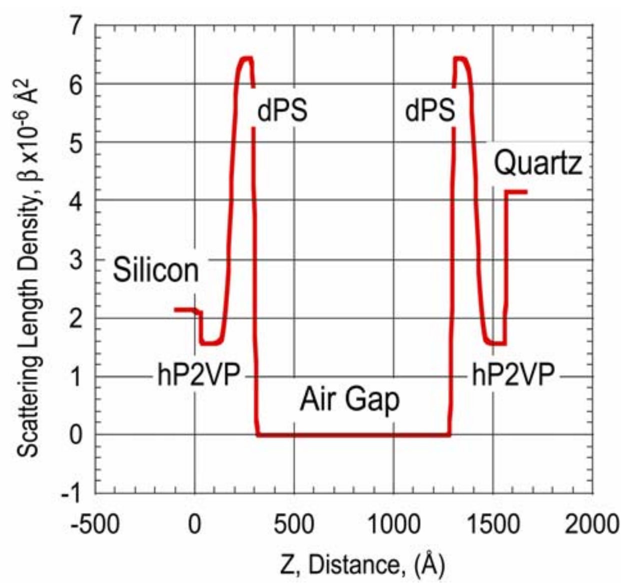
HFIR and SNS

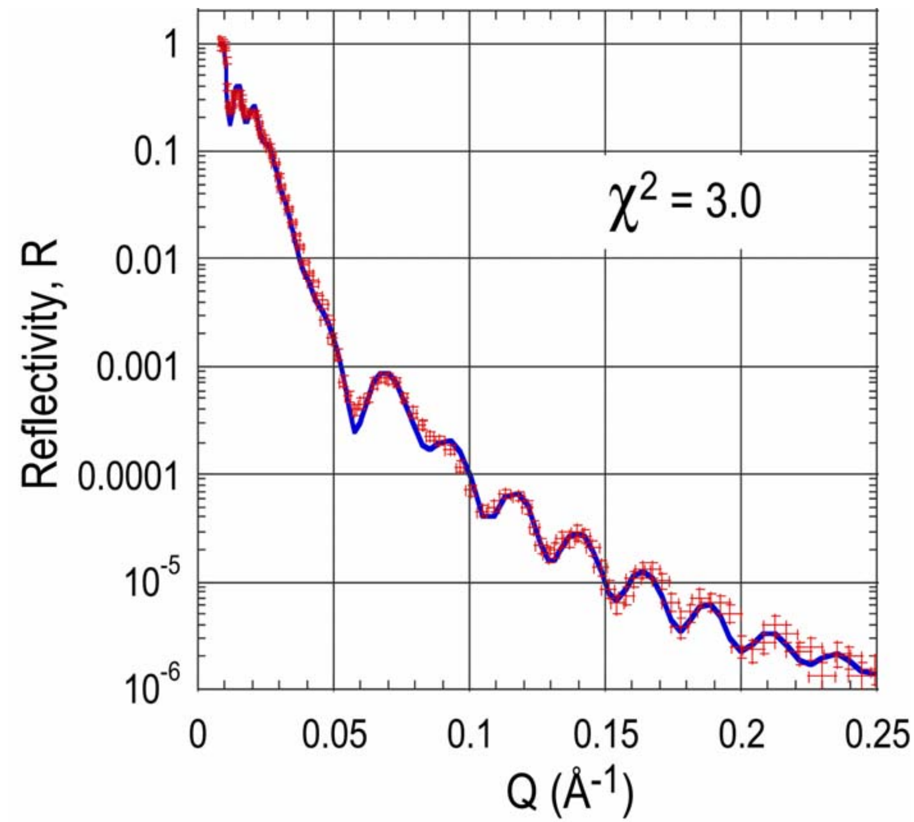
- World's most powerful neutron sources
- National user facilities
- 15 instruments at HFIR
    - 2 Small Angle Neutron Scattering
- 23 instruments at SNS
    - 2 Reflectometers



Contrast Variation

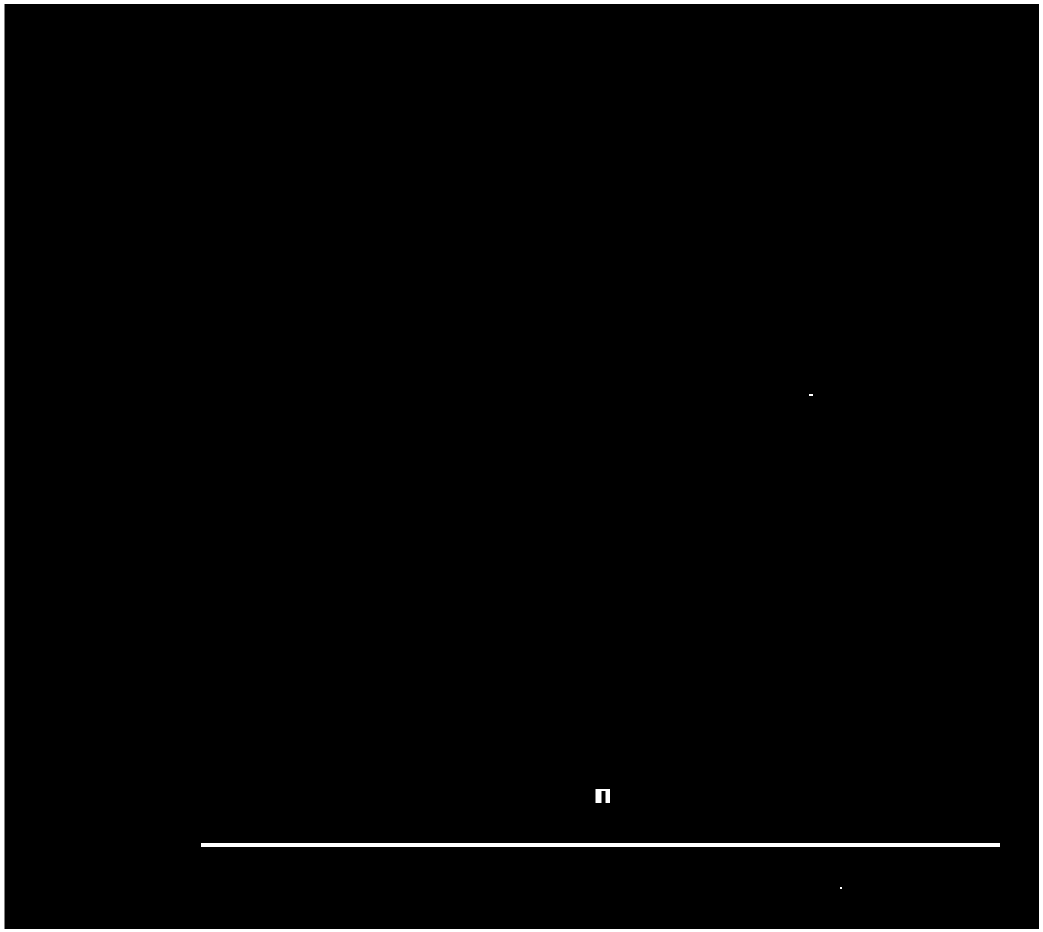




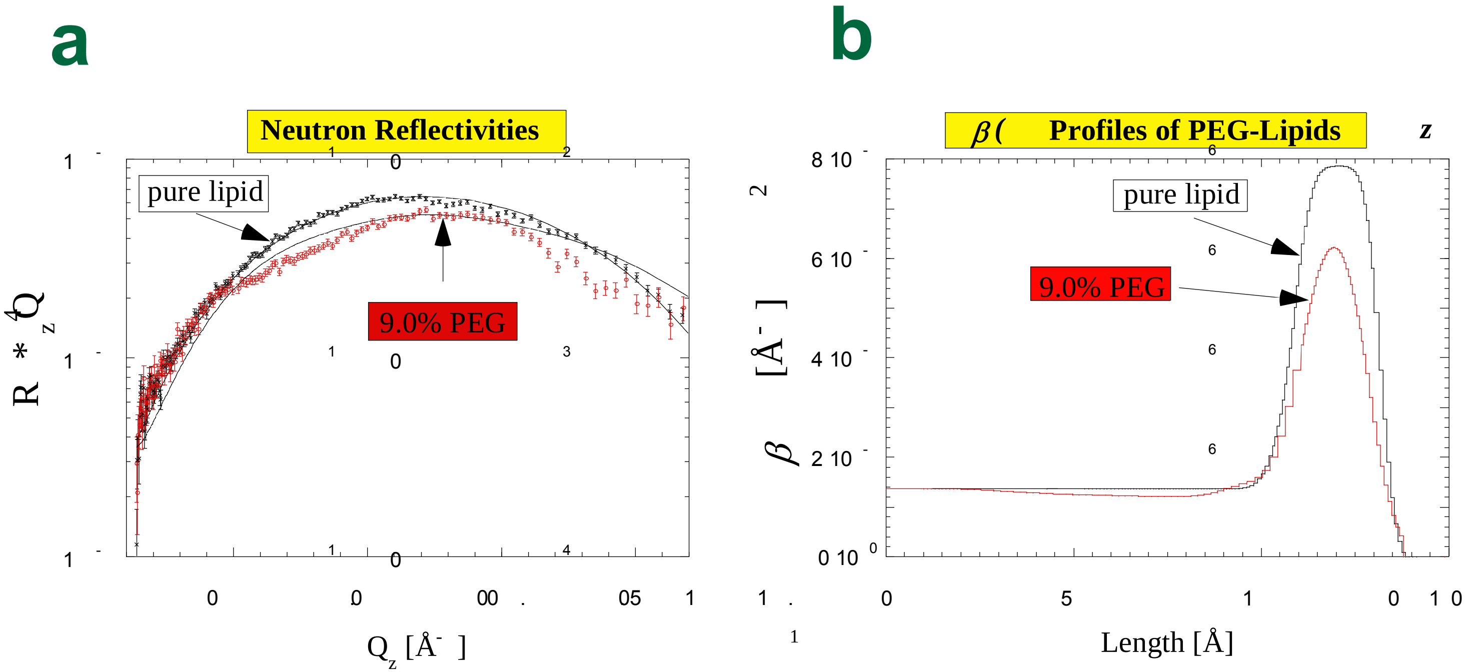


dPS	119 Å	β 6.3
hP2VP	148 Å	β 1.6
Air	995 Å	Inc 60 Å

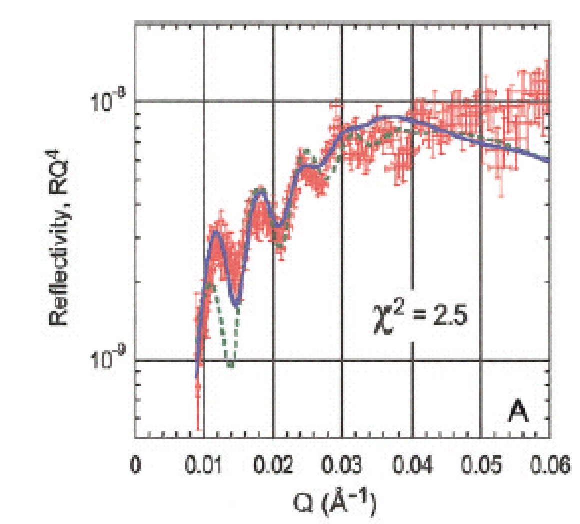
monolayers at 20^{o}C on water. All presented reflectivity measurements were done at a pressure 42 mN/m.

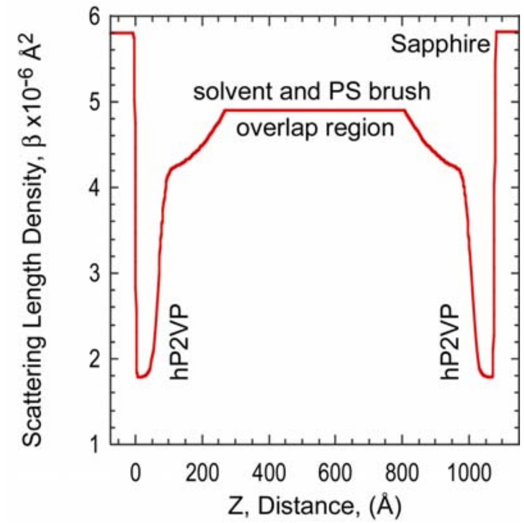


profiles (b) for lipid/PEG-lipid monolayers on (0.7:0.3) $H_2O:D_2O$ mixture. Lipid tails were deuterated.

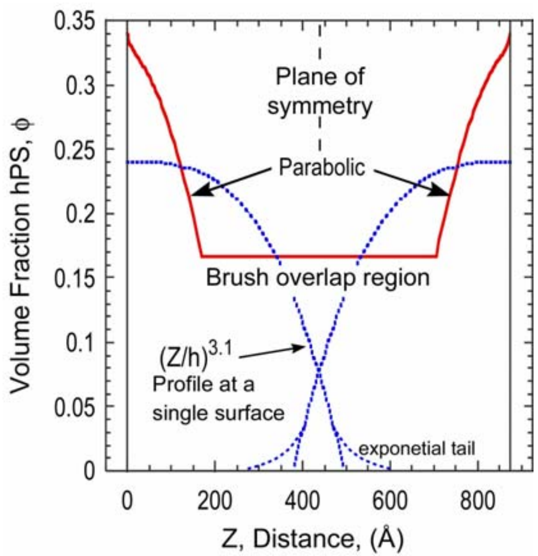


Solvated Polymer Brush – Large Gap 1100Å



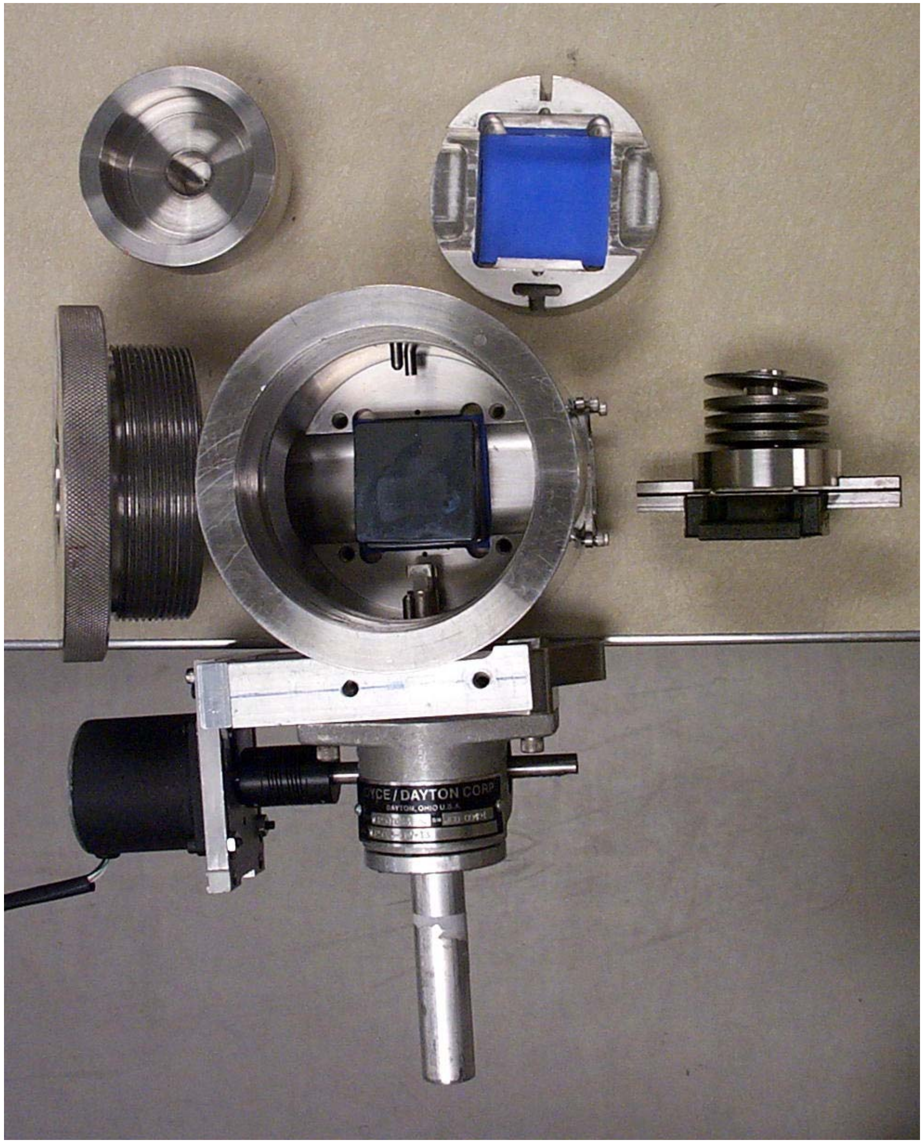


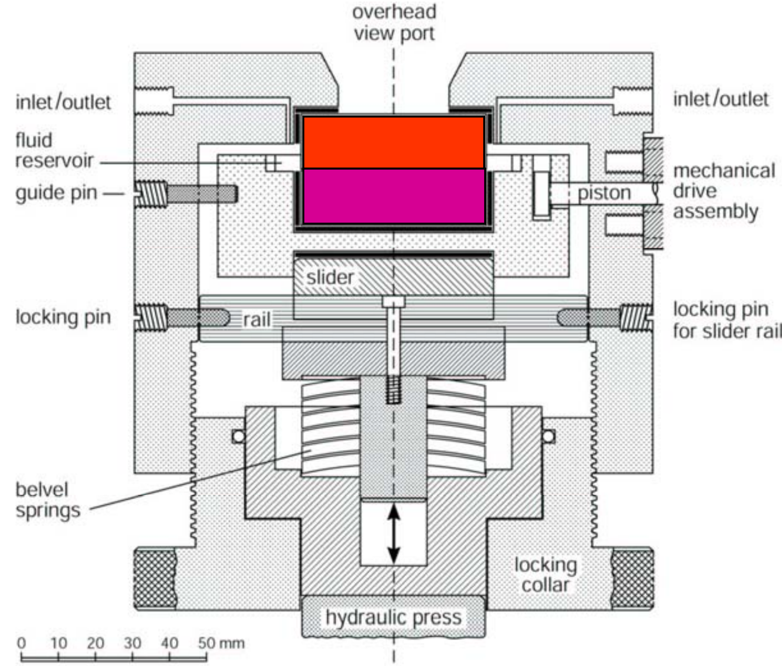
$$\beta(z) = \phi_{PS} * \beta_{PS} + \phi_{solvent} * \beta_{solvent}$$



- High density PS brush in deuterated toluene
- β modeled with parabolic density profile and constant density region
- Tails of brushes overlap in flat central region
- Polymer compresses w/r single brush at substrate wall

Modified Shear/Confinement Cell

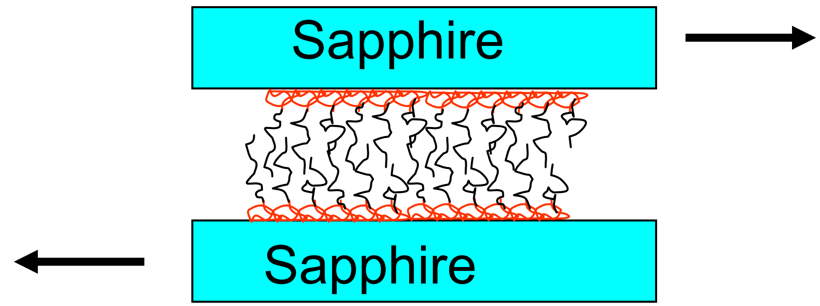


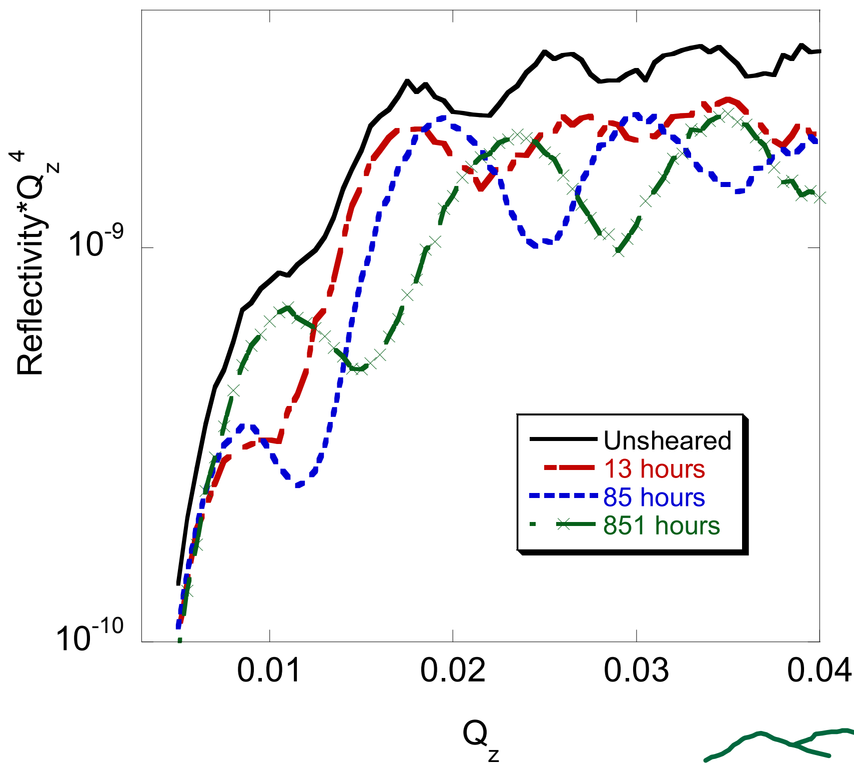


- Incorporated slide mechanism with stepper motor drive
- Drive speeds from 6 μ/s to 5mm/s
- Shear rates from 60 to 50,000 s^{-1}
- Continuous and oscillatory shear

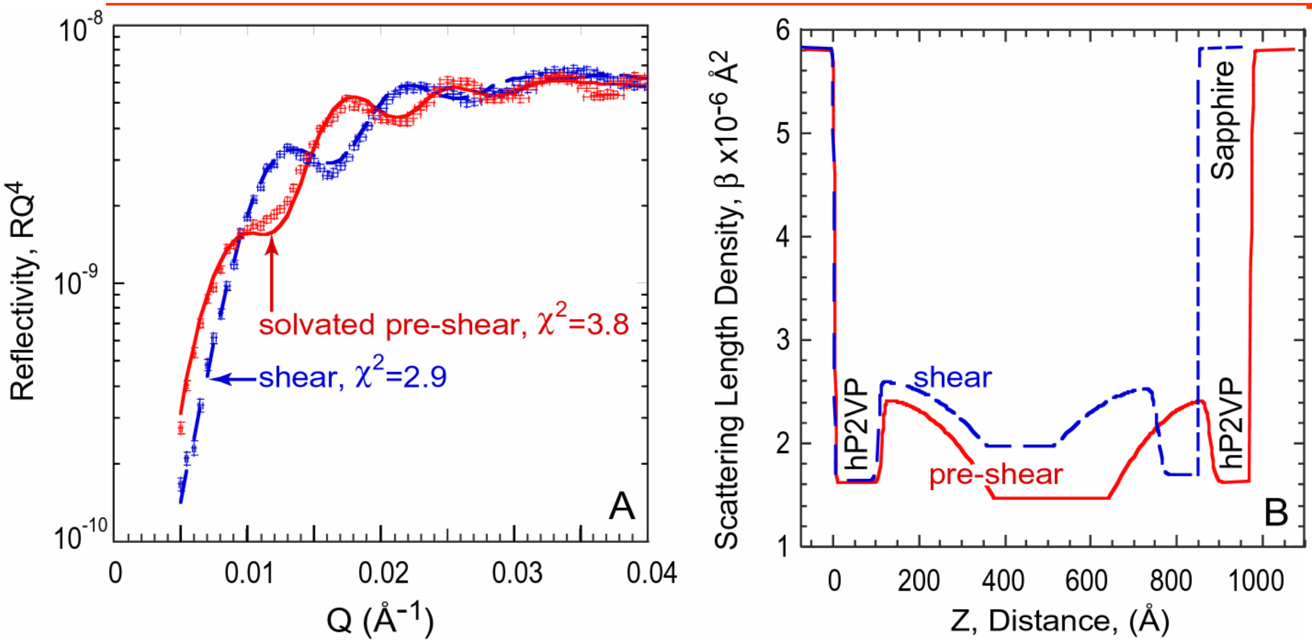
First shear experiments on PS-PVP diblock copolymers

- **Previously studied system (d-PS in h-toluene)**
- **High grafting density**
- **Zero shear**
  - **Dry**
  - **Solvated**
  - **Repeatable**
- **First measurements (NIST)**
  - **Solvate and shear**
  - **Solvate then move ~ 1mm/s ($10{,}000 s^{-1}$)**
- **Large decay constant**

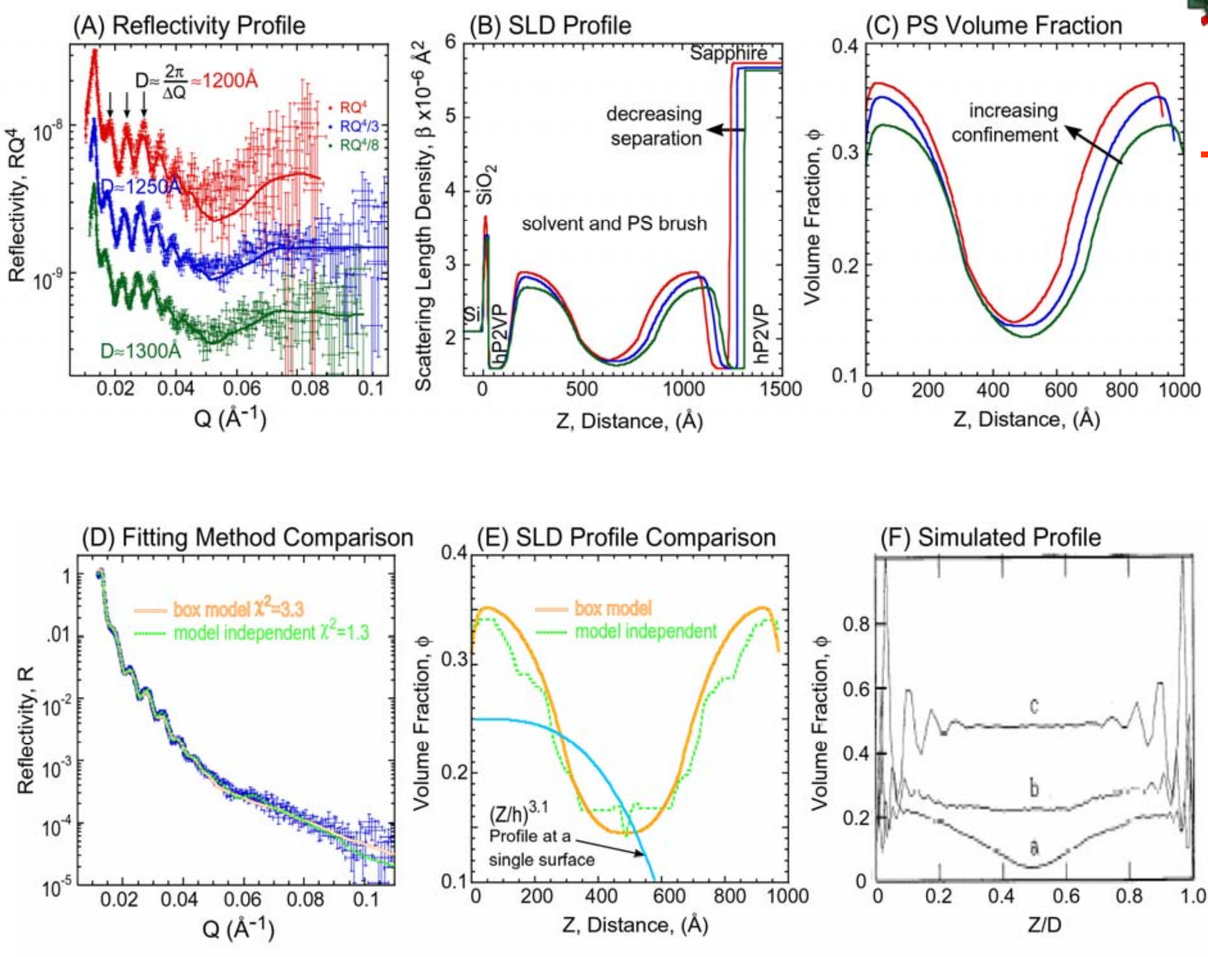




Analysis to date



- Brushes show some interpenetration before shear
- After shear the brushes follow gap thickness
- Overall gap between the substrates decreases with time
- The effective waviness of the surfaces decreases (76-53 Å)



(A) Reflectivity profile for 3 different compressions of dPS-P2VP brushes, 136k MW, concentration ~20 times σ^*. Solid curves are fits to the data based on the SLD profiles shown in **(B)**. **(C)** is the corresponding volume fraction profile. **(D)** and **(E)** compare a box model to our model independent fitting routine. Similar profiles are obtained, but the model independent routine yields a much higher quality fit, $\chi^2=1.3$. The brush profile at a single interface is also shown [1]. (F) MD simulation of the polymer volume fraction between two surfaces bearing grafted chains of 100 monomers [2].