Neutron Reflectivity of Confined Polymer Brushes

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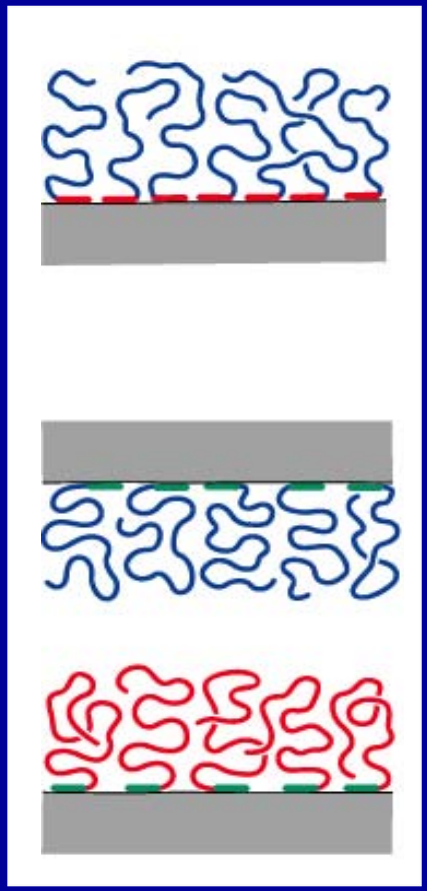
Thank you – DOE support

SNS HFIR User Meeting October 2005

Outline

- Polymers in Restricted Geometries
  - Static confinement
  - Shear measurements
  - Future work
- Biological Systems – see Jarek Majewski's talk Thurs.

Motivation – Polymer Thin-Films at Interfaces



Steric Stabilizers

- Flocculation/Aggregation inhibitors
- Compatibilizers

Lubricants

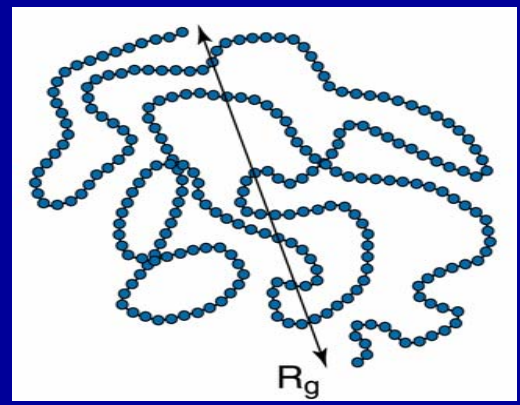
- Lube oils
- Protective surface coatings

Adhesion

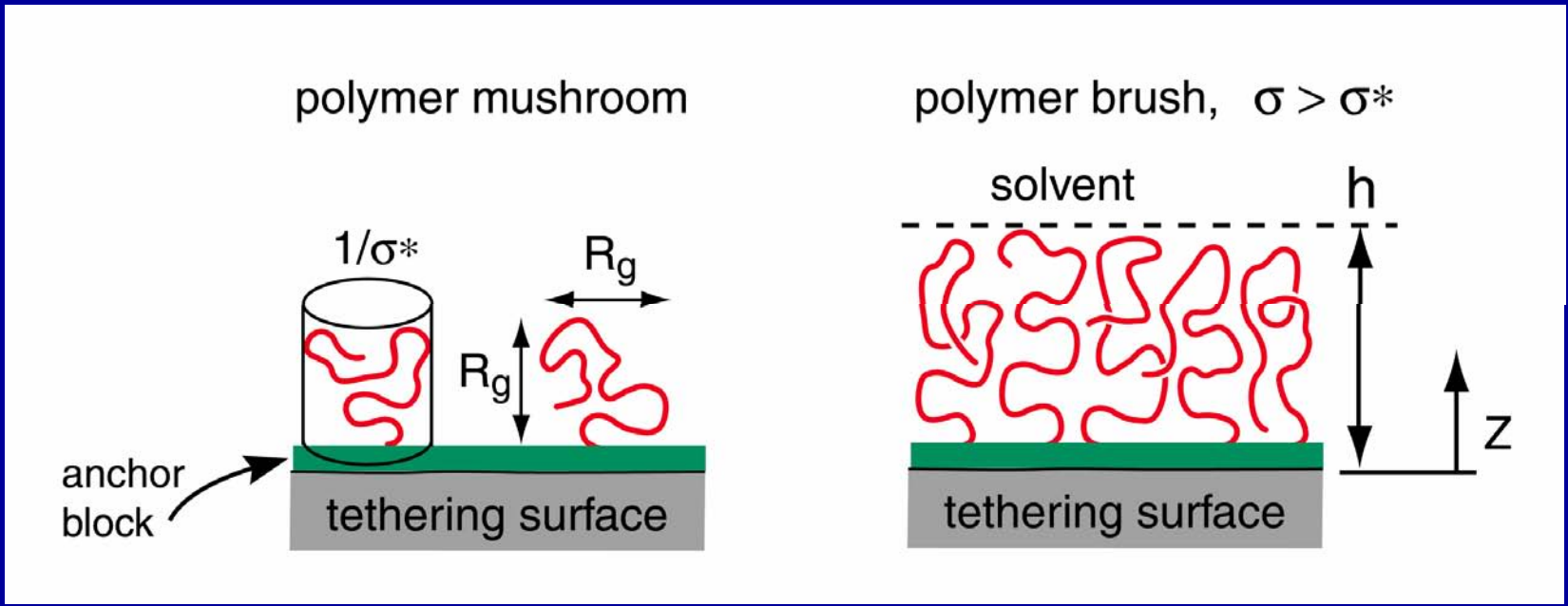
- Interfacial films
- Wetting/dewetting

Structure of Thin Polymer layers

- Solvent-polymer
- Polymer-polymer



Grafted Polymer Brushes – circa 1990-2000

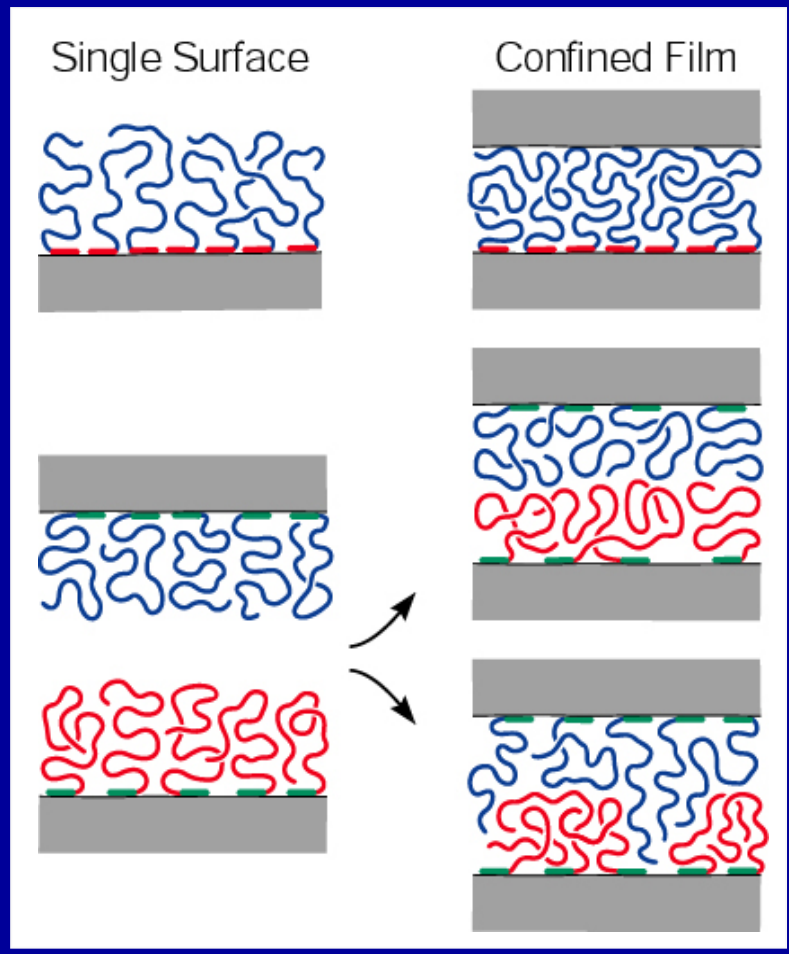


- σ = grafting density
- χ = solvent quality
- h = brush height $h \sim N/\sigma^{1/3}$
- Rg = radius of gyration, $Rg \sim N^{3/5}$
- **ρ = density distribution**

volume fraction

$$\Phi(z) = \Phi(0)\left(1 - \left(\frac{z}{h}\right)^{n}\right)$$

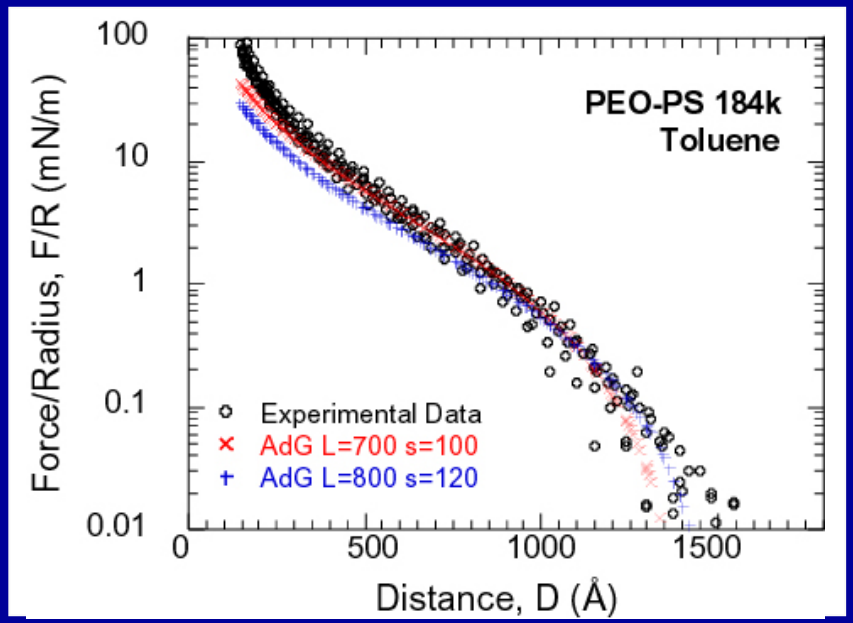
Structure of Polymer Brushes

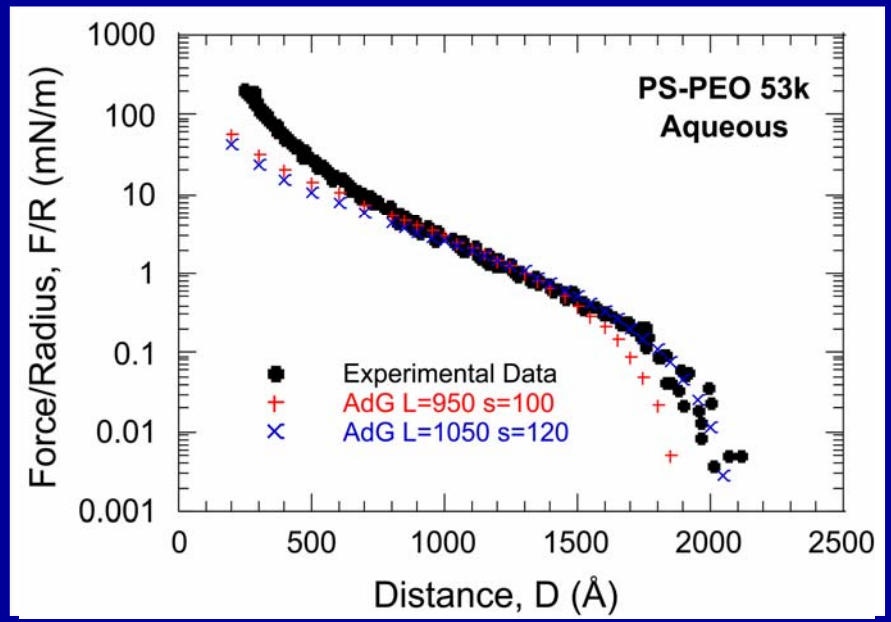


With polymer brushes, theory preceded experiments

Interaction between opposing brushes

Force Profiles

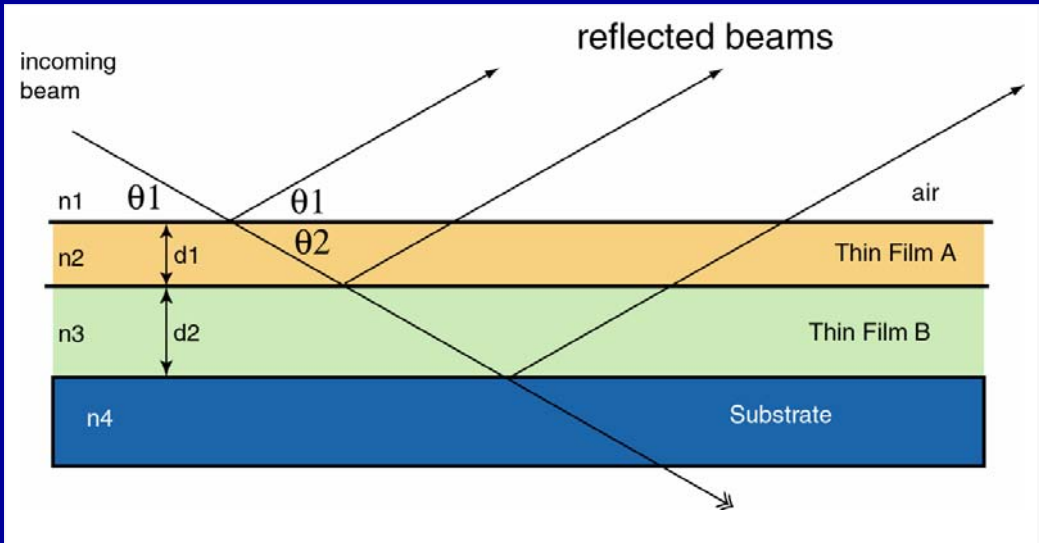




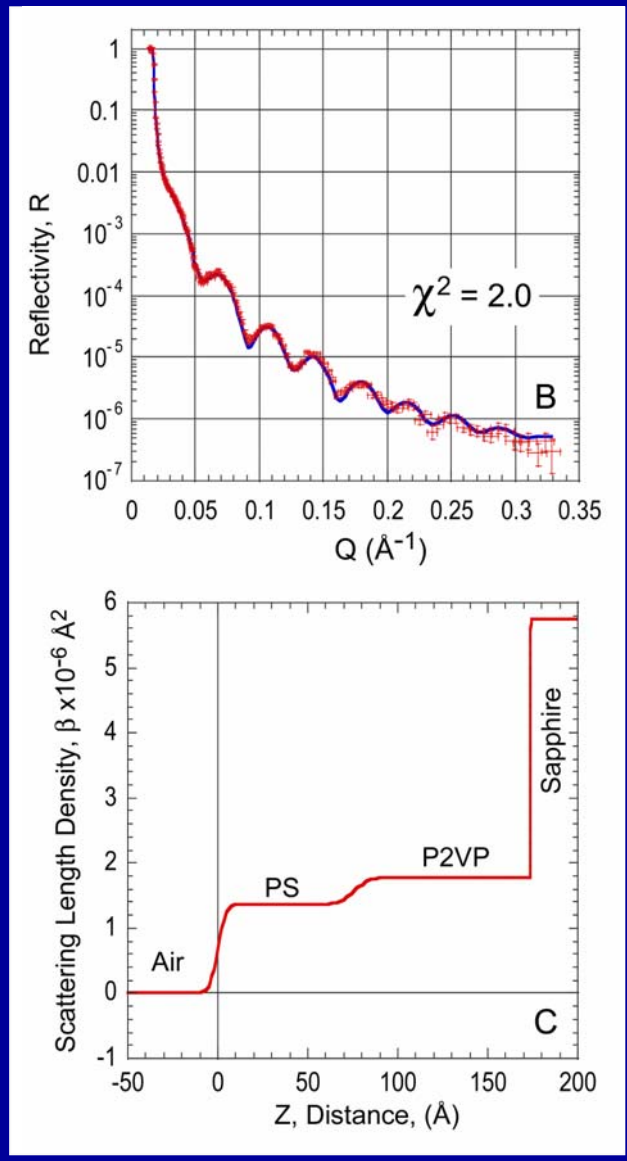
$$h = \frac{Na^{5/3}}{\sigma^{1/3}} = \frac{Na^{5/3}}{s^{2/3}}$$

$$P(D) = \frac{kT}{s^3}\left[\left(\frac{2h}{D}\right)^{9/4} - \left(\frac{D}{2h}\right)^{3/4}\right] \quad \text{for } D < 2h$$

Neutron Reflectivity



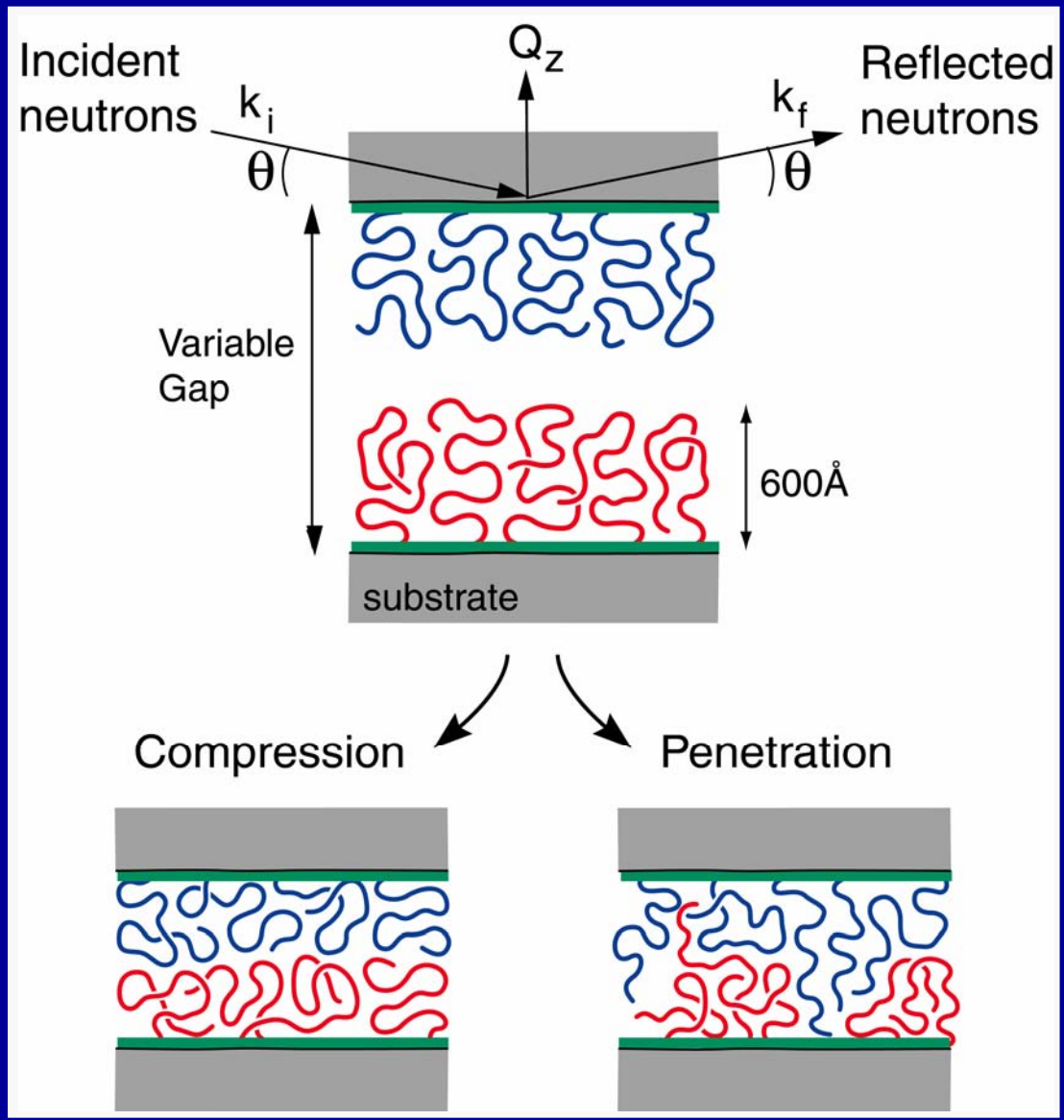
Deuteration → Contrast



Measures:

average density structure **normal** to the interface.
(layer thickness, density and roughness)

Neutron Reflectivity of Opposing Brushes



Neutrons are KEY

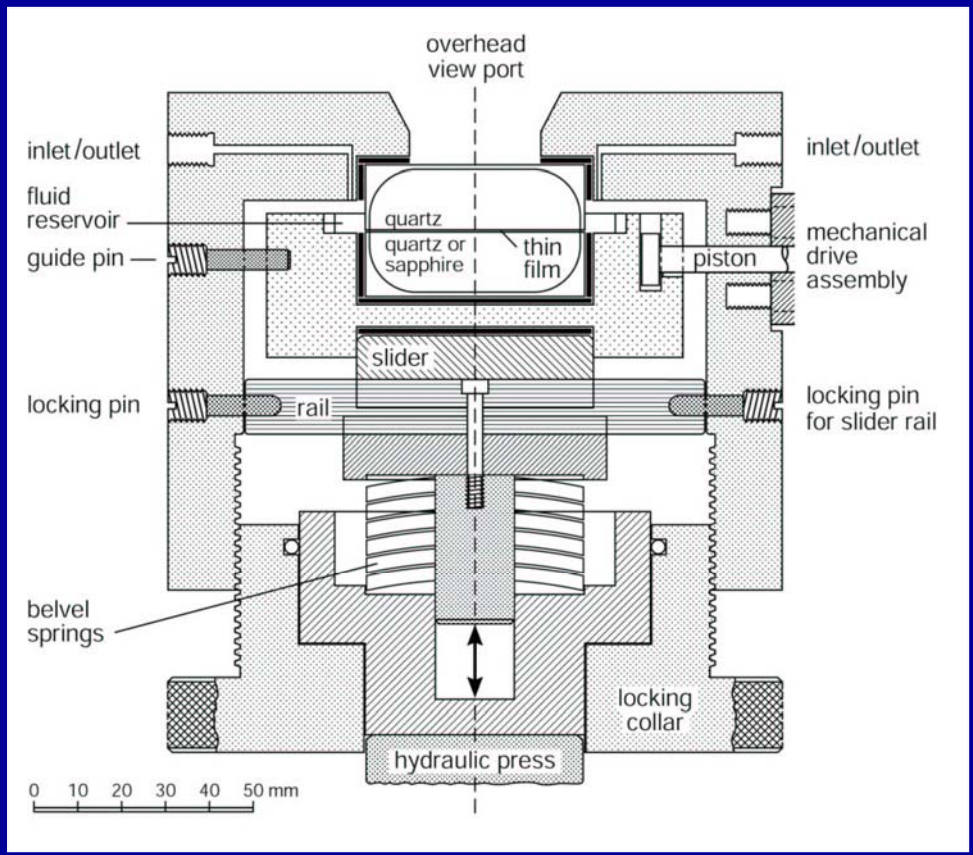
- Probe buried interface
- Depth profiling
- Contrast matching

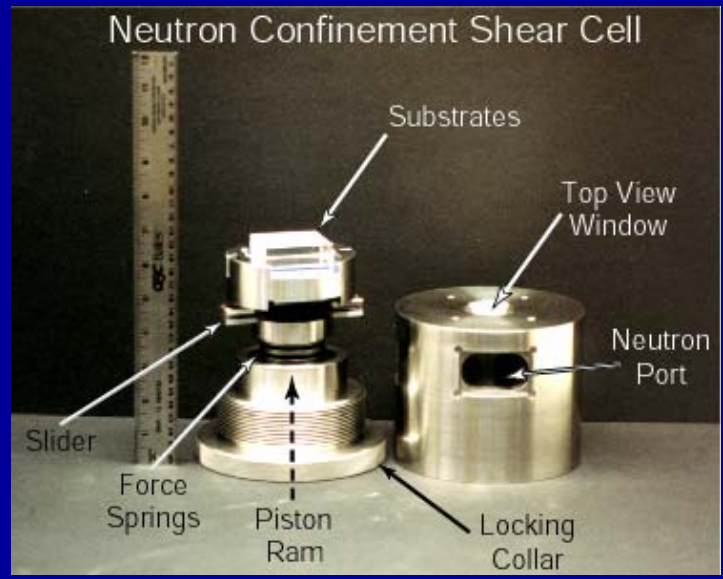
Challenges

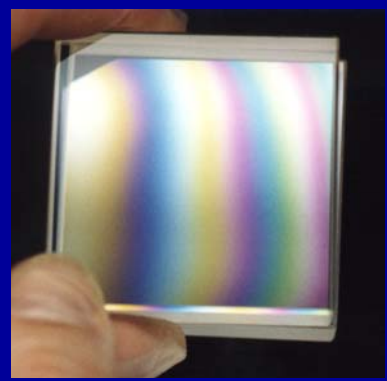
- Flux
- Films < 3000 Å
- Parallelism
- Sufficient contrast

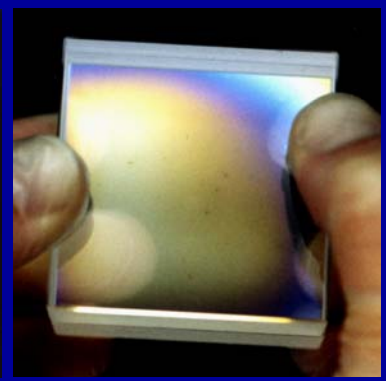
Neutron Reflectivity of Opposing Brushes

Neutron Confinement and Shear Cell





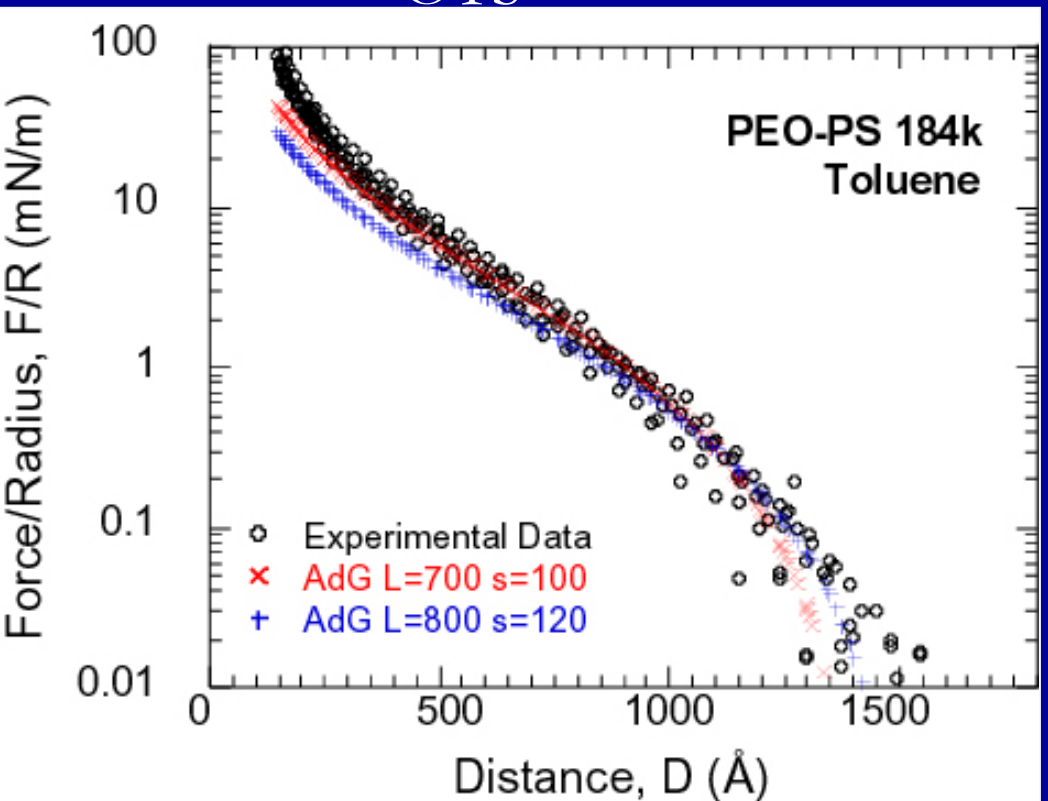


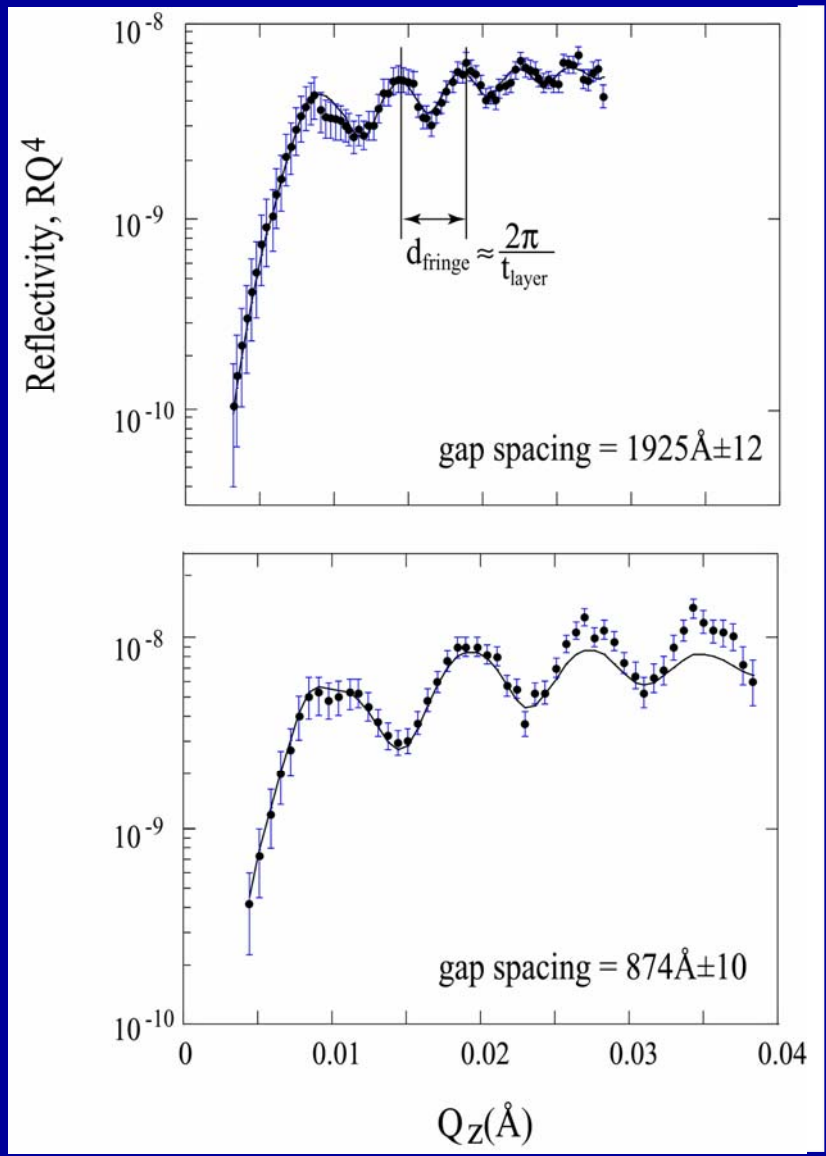


Demonstration – MIRROR Reflectometer

Substrates:

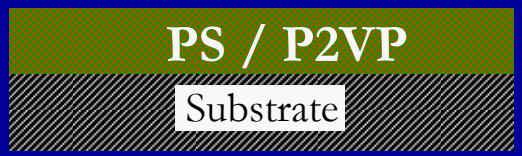
- Quartz
- Sapphire
- **Hydrophobic Coatings**
  - OTS





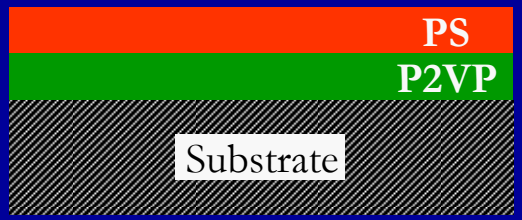
Dense Polymer Brush Layers

50:50 PS-P2VP

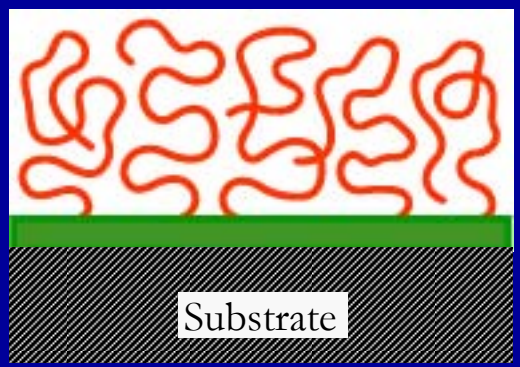


Contrast Variation

124k dPS-hP2VP
136k hPS-hP2VP

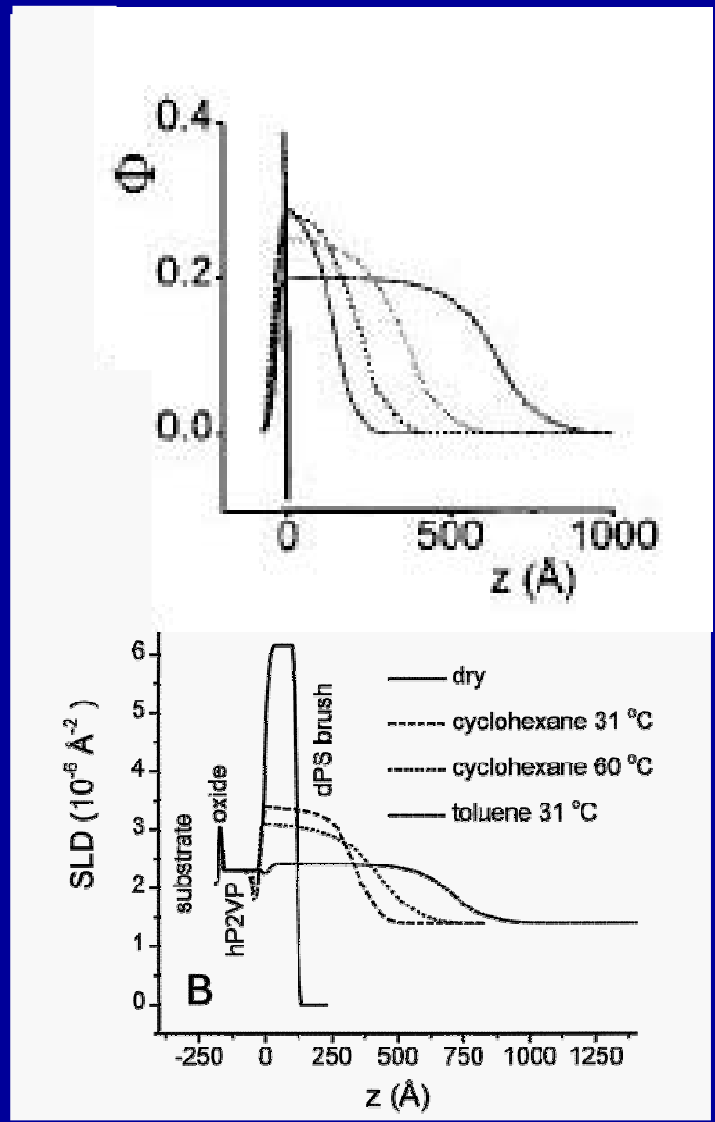


Anneal



Solvate

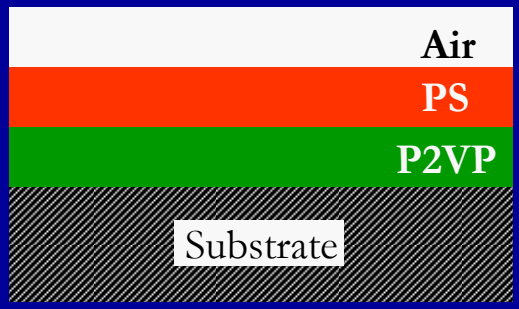
Contrast Variation

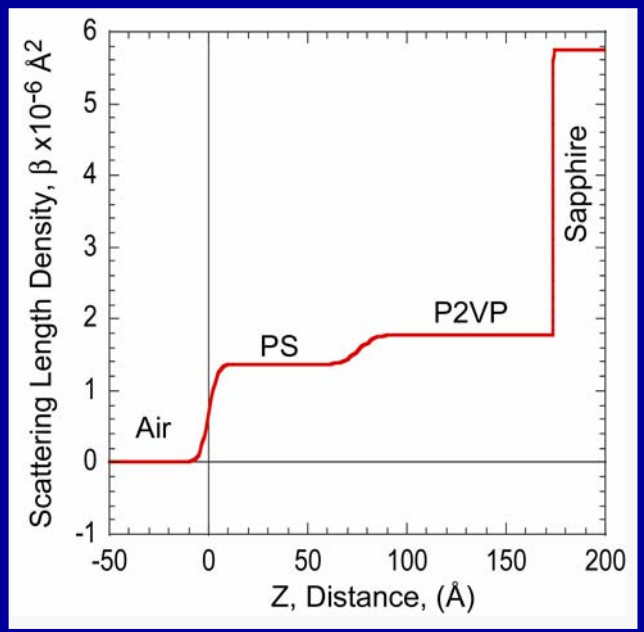


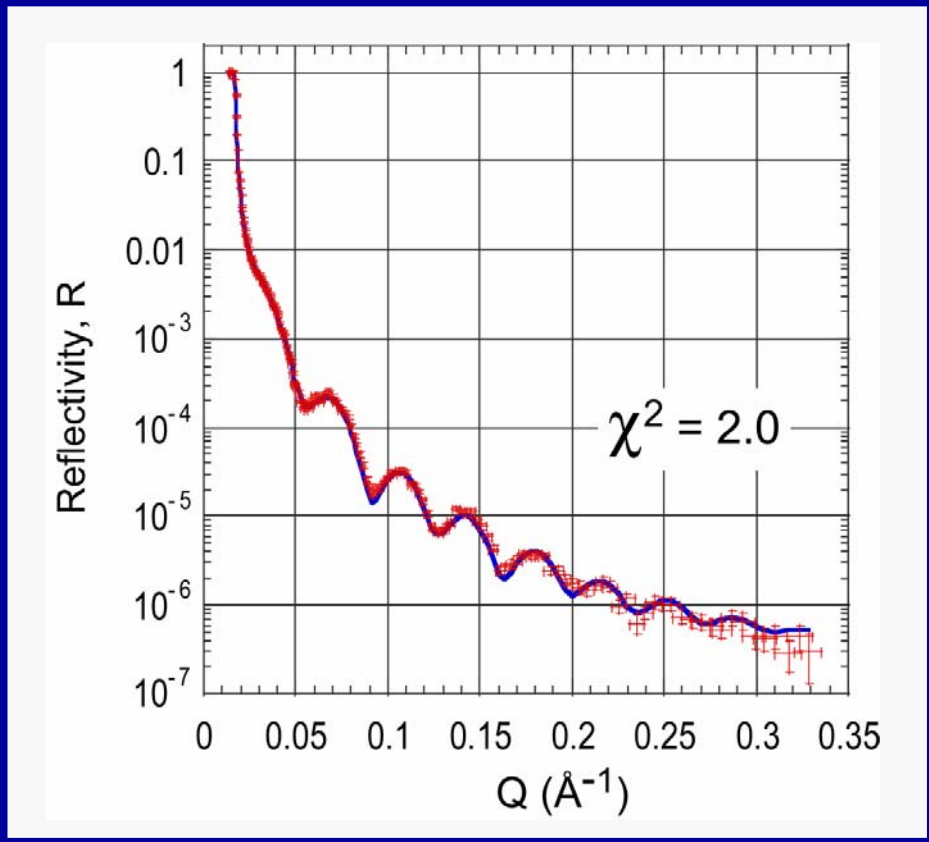
Levicky, et al Macromolecules 1998

Neutron Confinement Cell Experiments

124k dPS-hP2VP

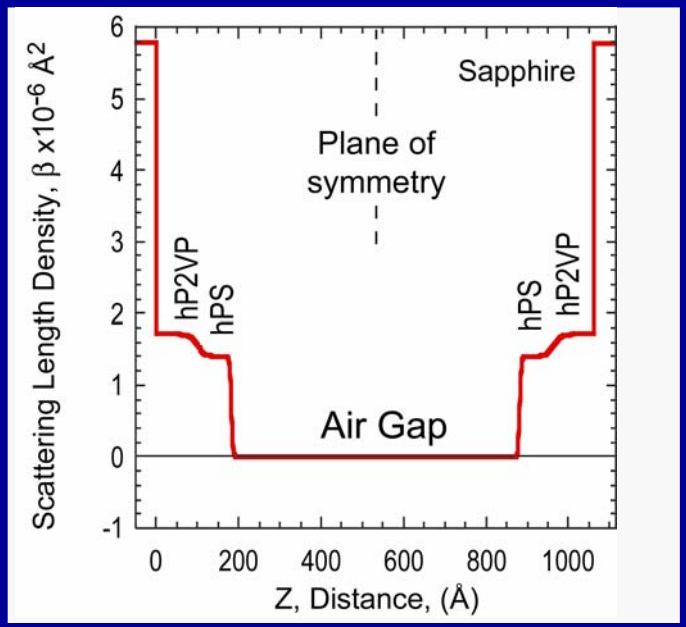


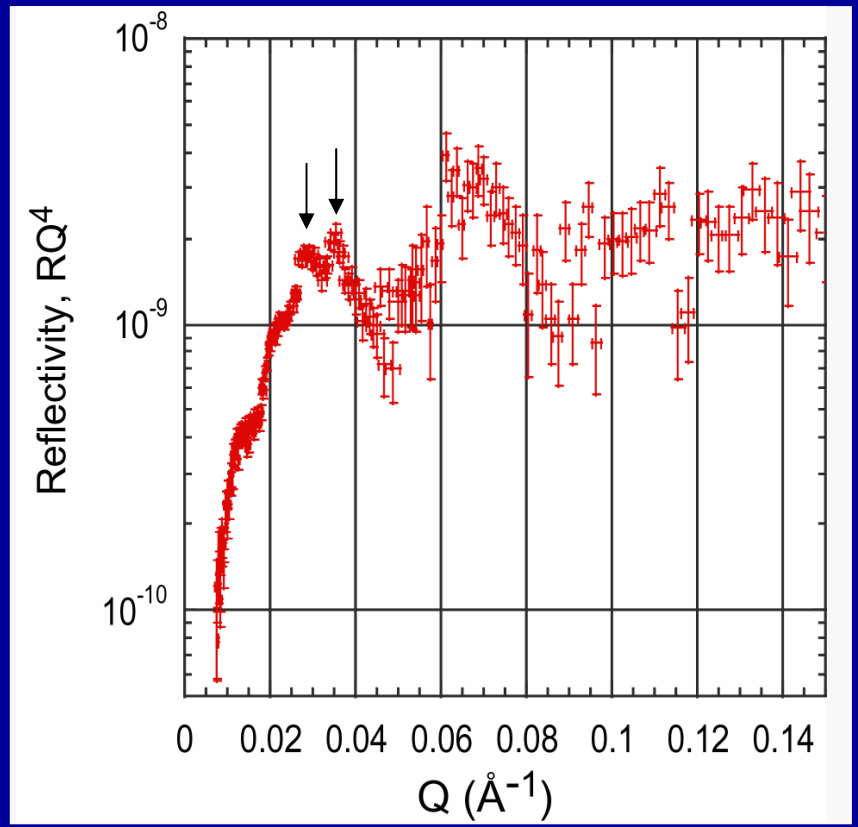




hPS	75 Å	β 1.42
hP2VP	100 Å	β 1.85

Air Gap





hPS	75 Å	β 1.42
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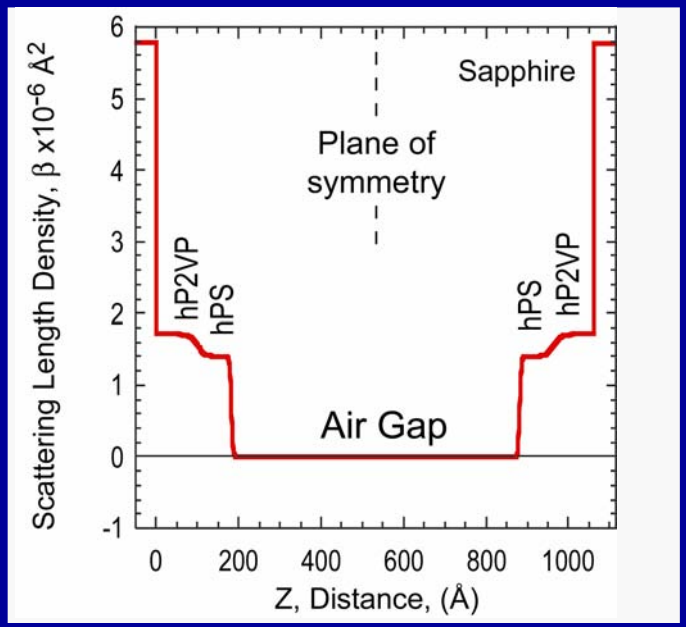
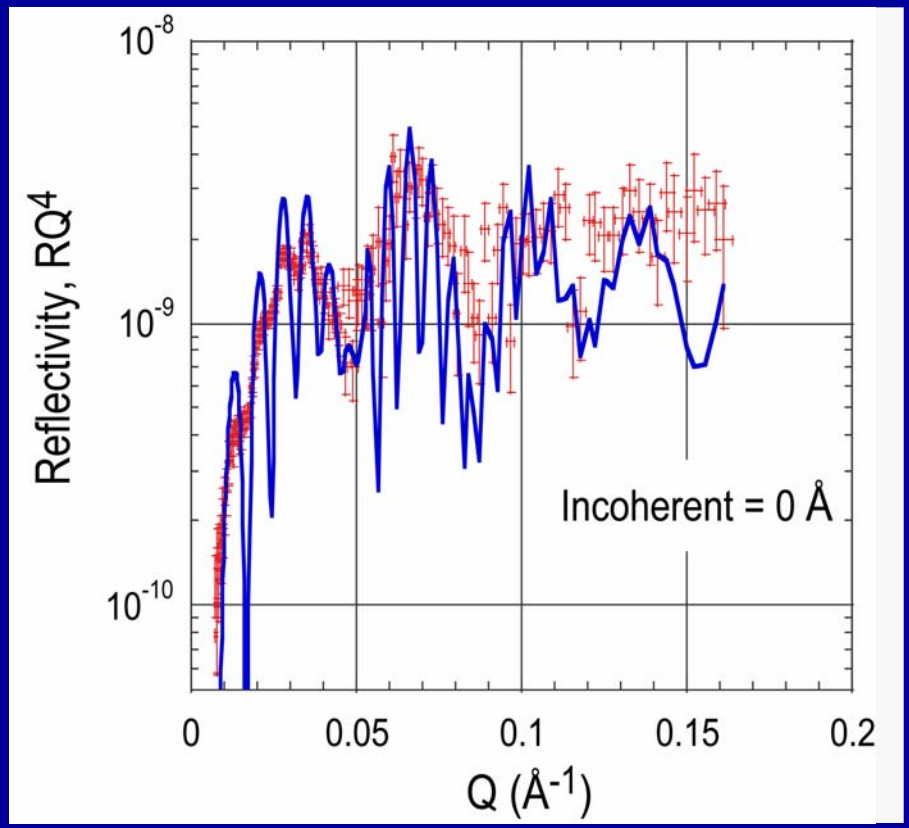
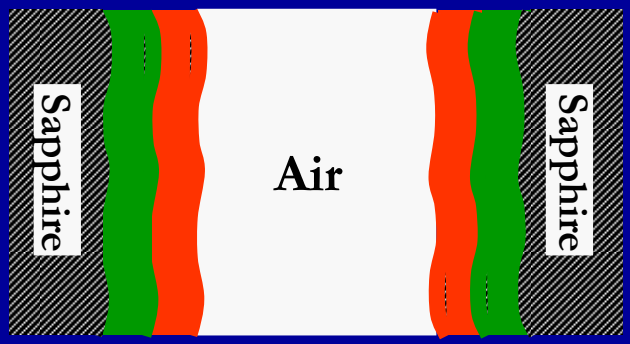
Air Gap

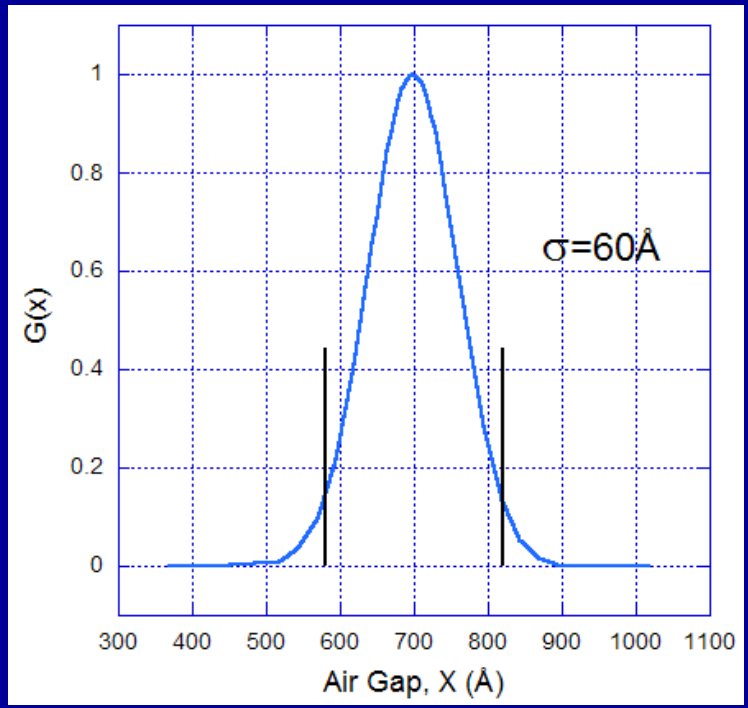




hPS	78 Å	β 1.42
hP2VP	104 Å	β 1.85
Air	697 Å	

Gaussian Distribution of Substrate Spacing



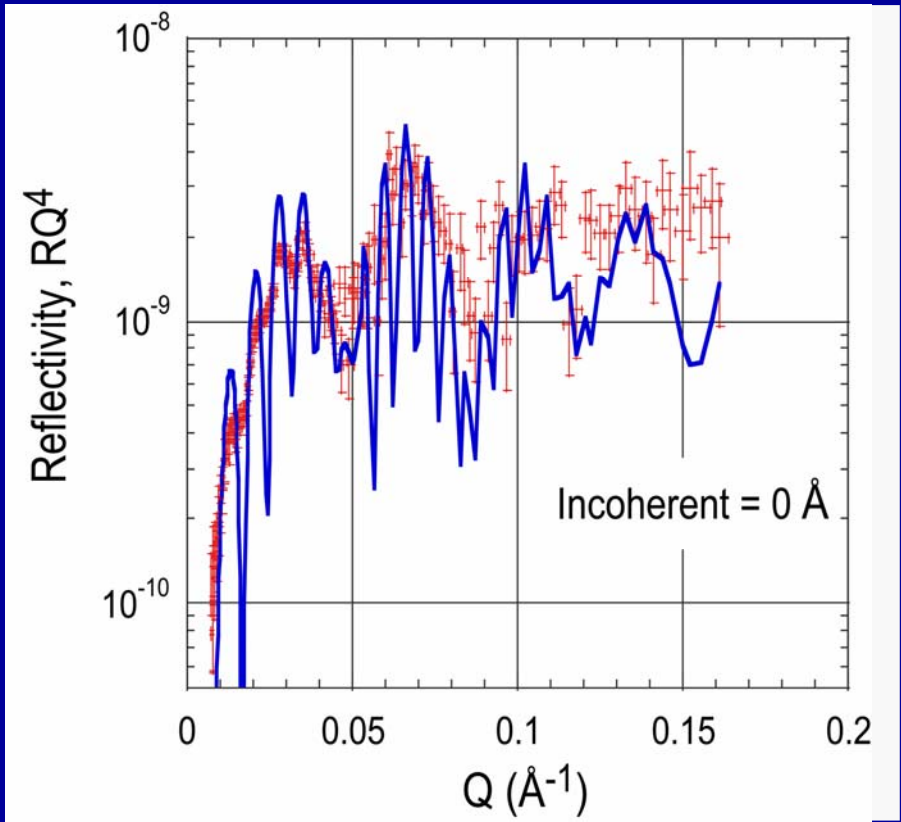


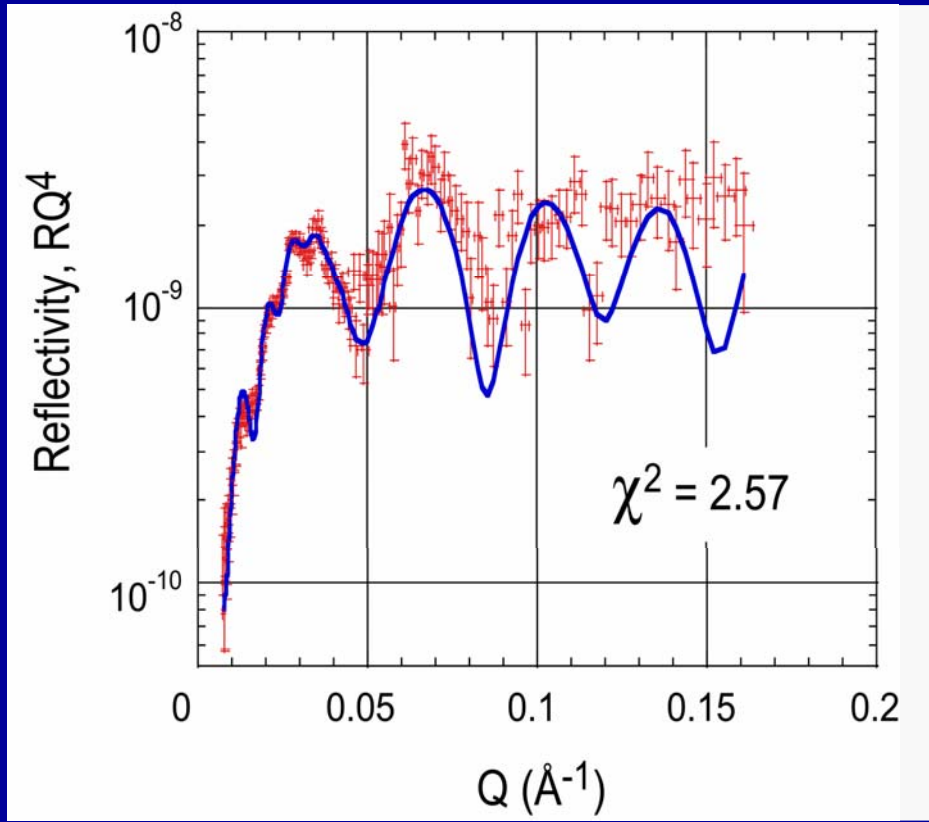
60Å variation over $1cm^2$
1m variation over $10km^2$

Variation in substrate spacing T from T_{avg}

$$R(q_z, T_{avg}) = \frac{1}{\sigma\sqrt{2\pi}} \int R(q_z, T)\ e^{-\frac{(T-T_{avg})^2}{2\sigma^2}}\ dT$$

Air Gap - Incoherrence

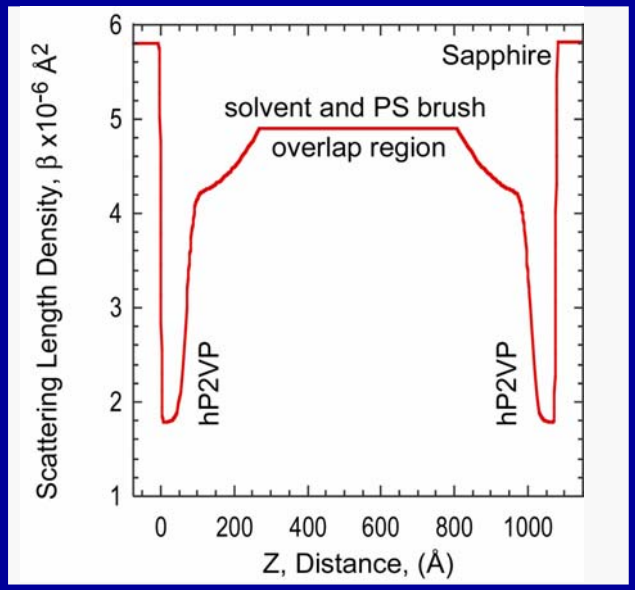


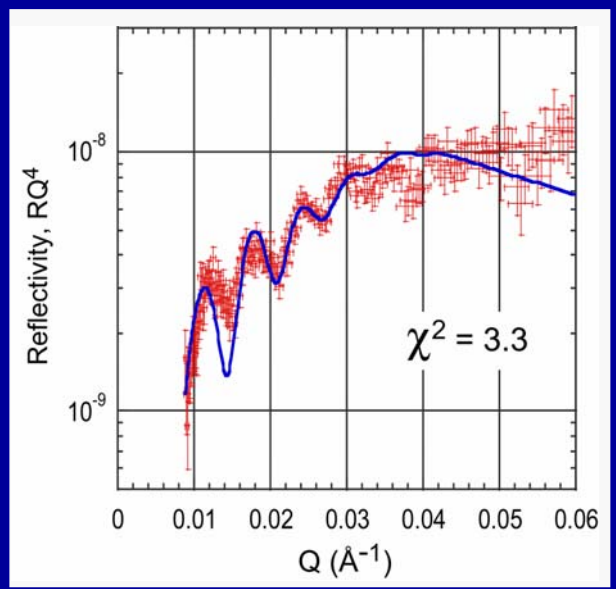


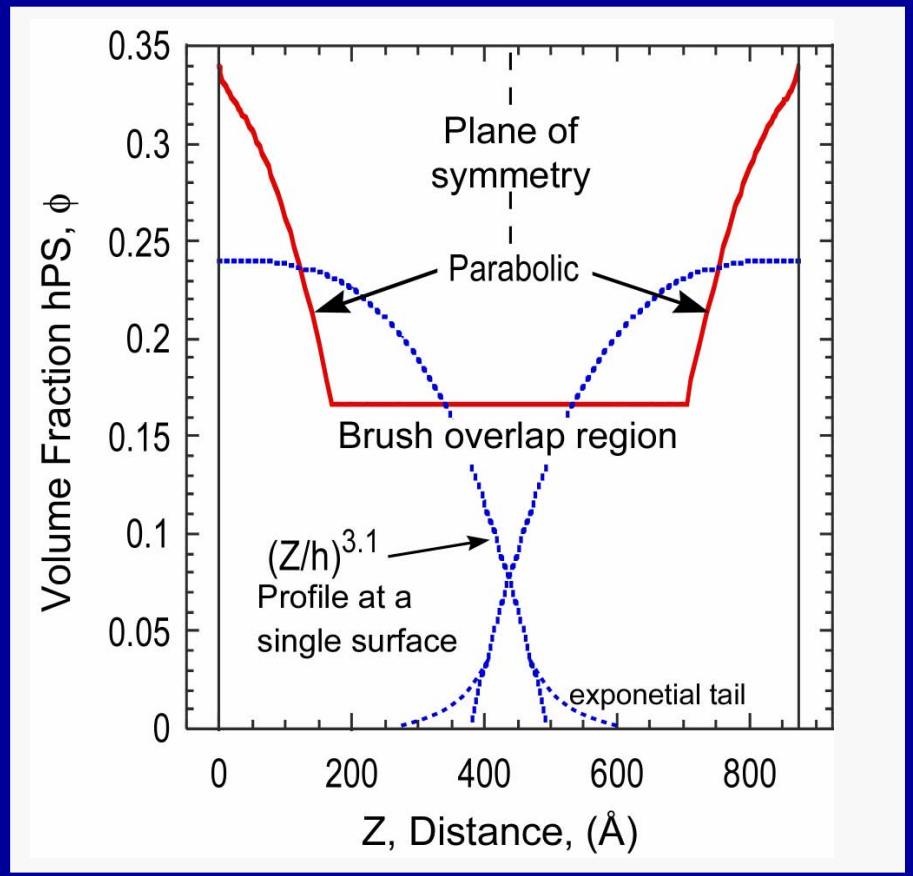
hPS	78 Å	β 1.42
hP2VP	104 Å	β 1.85
Air	697 Å	Inc 0Å

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

Solvated Polymer Brush – Large Gap 1100Å

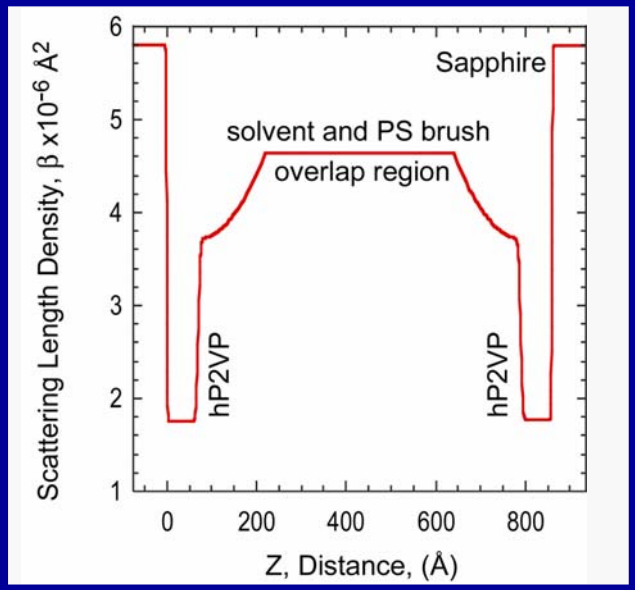


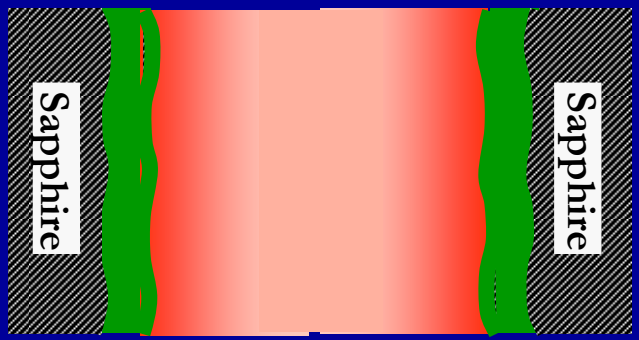


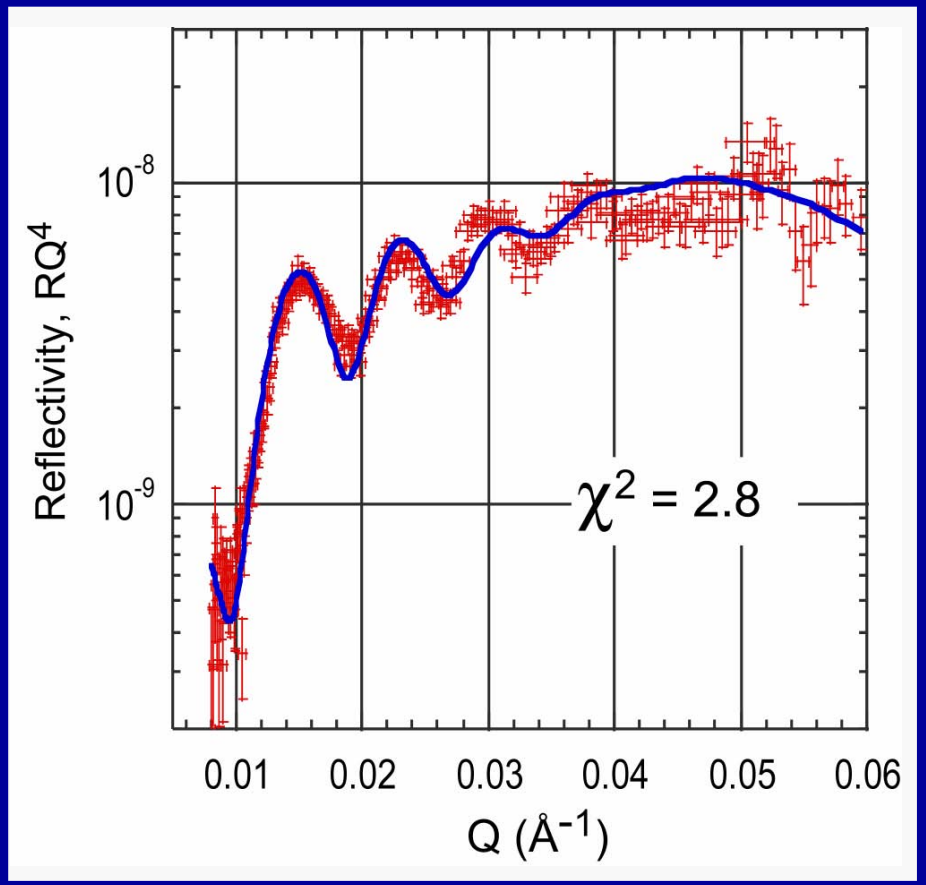


Parabola for brush, but power law similar

Solvated Polymer Brush – Smaller Gap 850Å



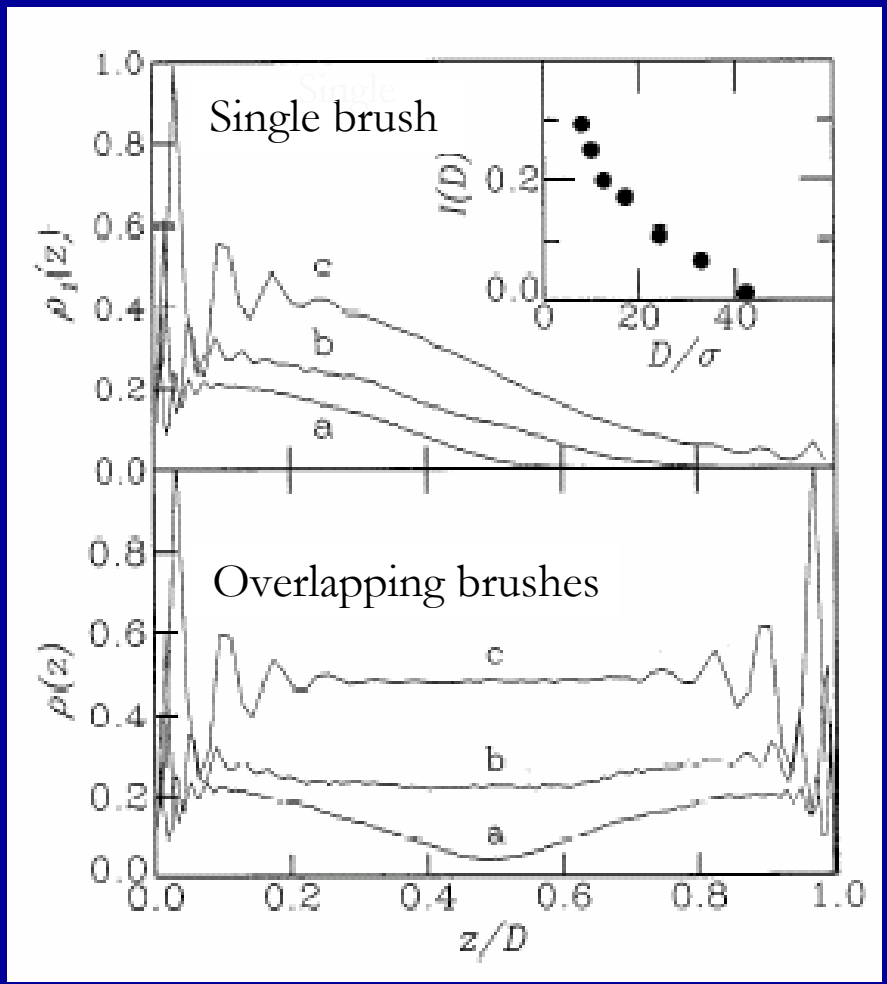




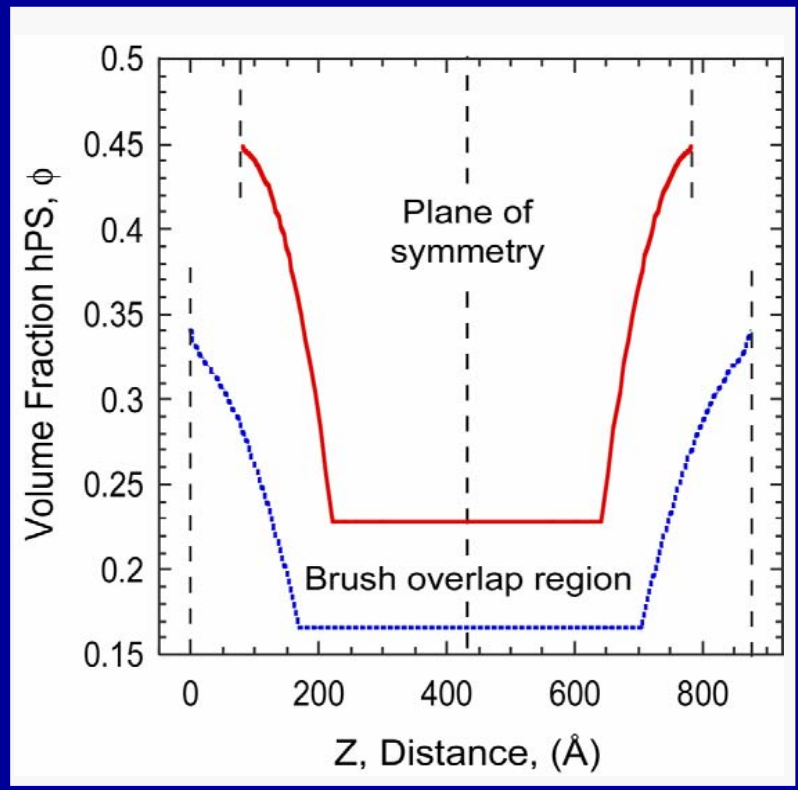
Smaller gap, same model fits

But is this the "right" model

Volume Fraction Profiles vs. Theory

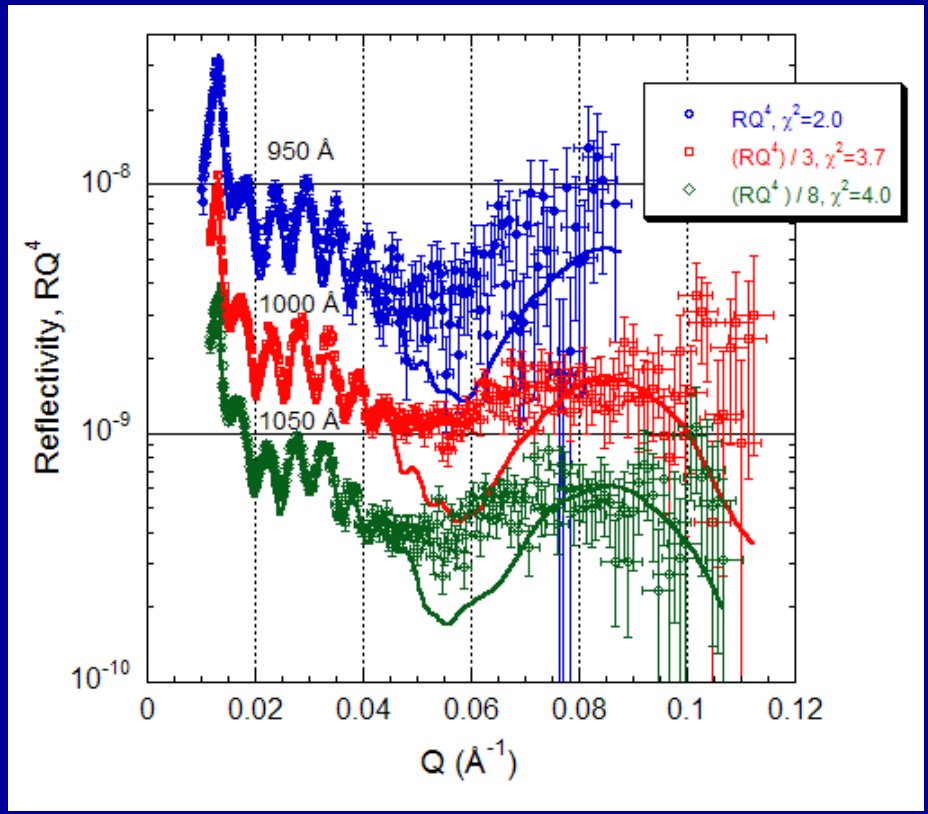


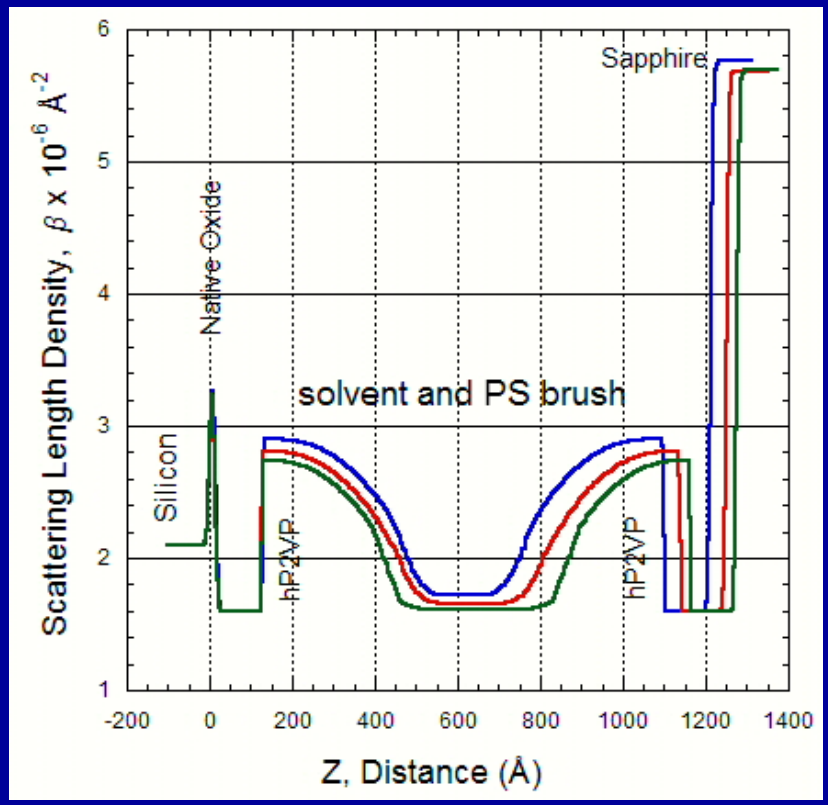
Grest, Adv Poly Sci, 1998



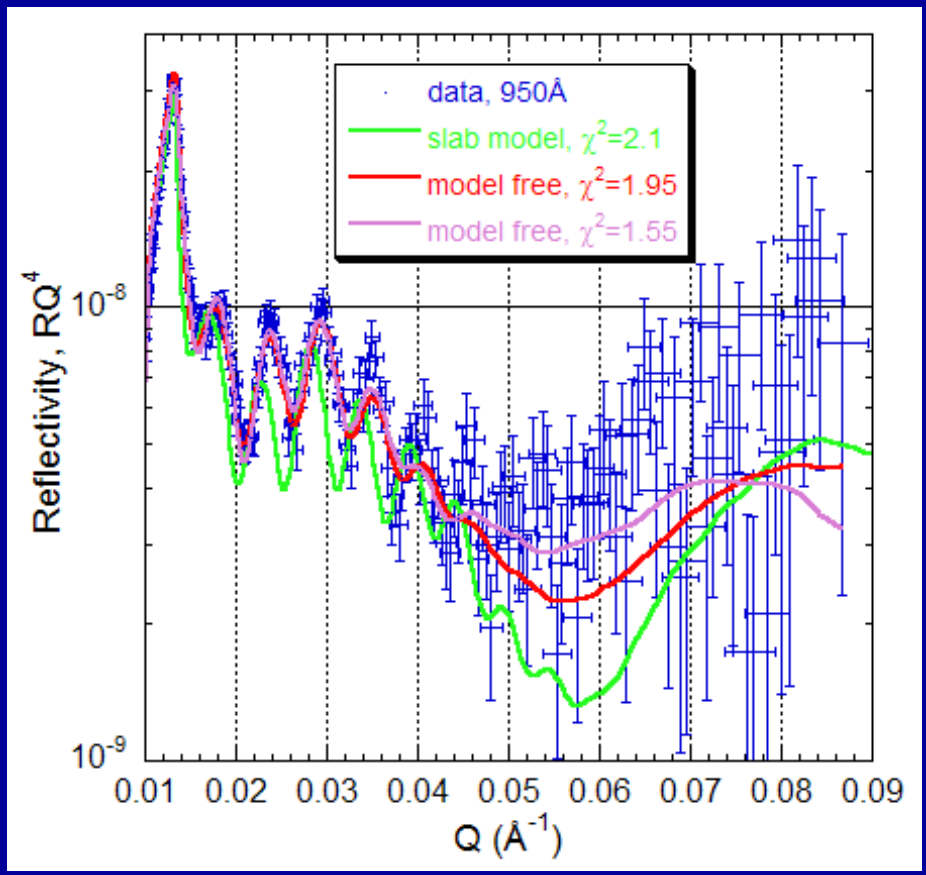
- Polymer compresses at middle and sides
- Density increases with gap
- Conservation of mass vs. normalization

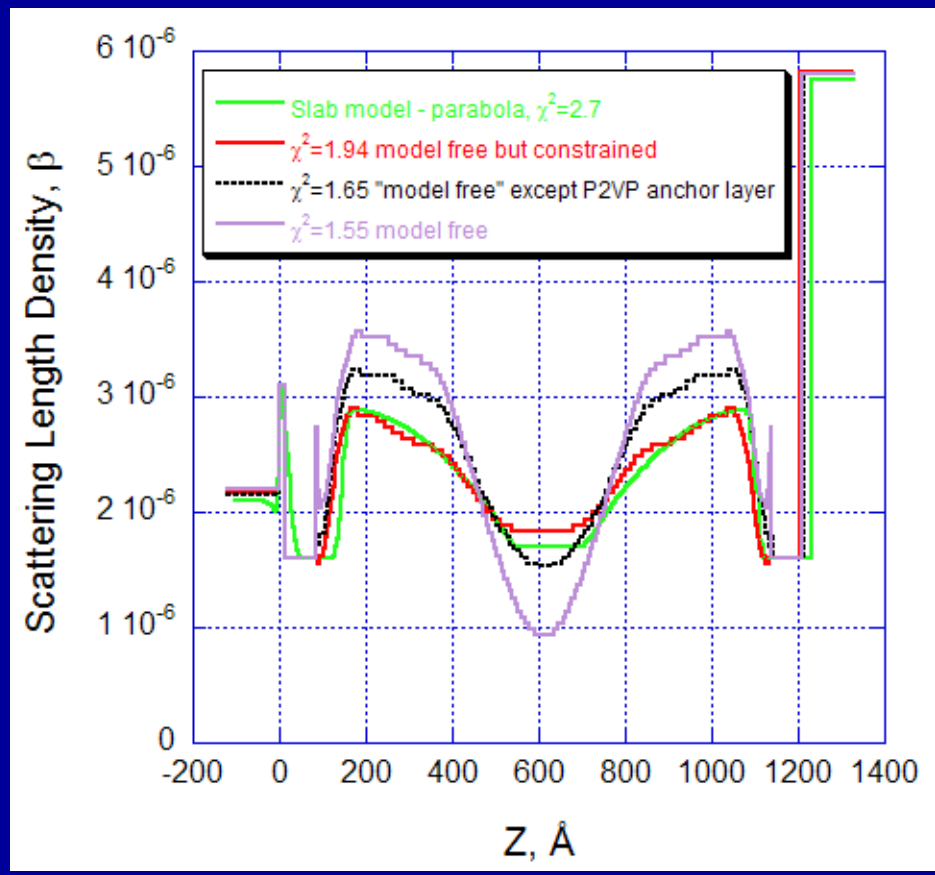
Deuterated PS Brushes





Model Free Fitting

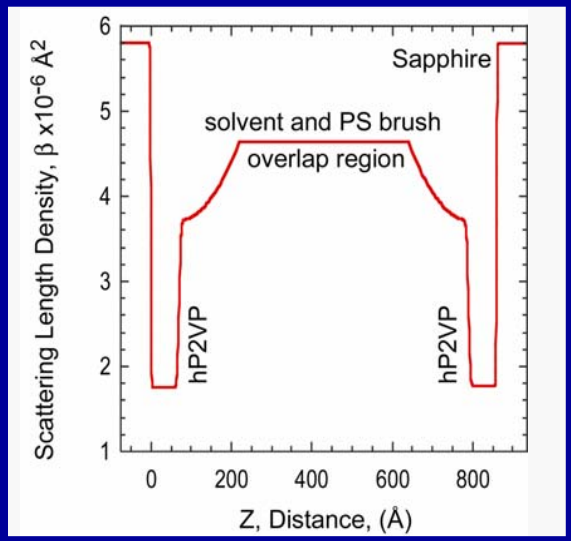


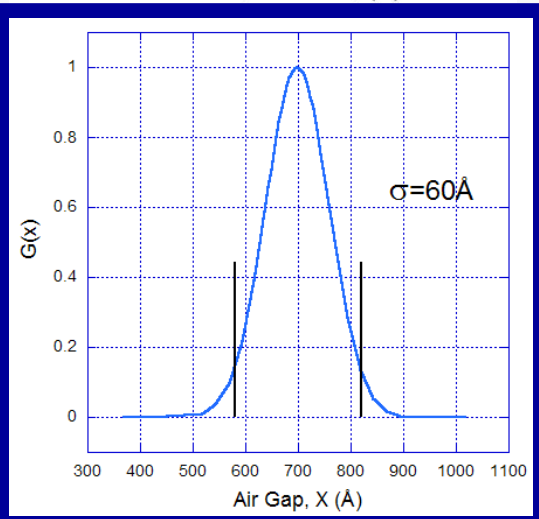


Slab Models vs. Model Free Fitting based on Chevyshev Polynomials

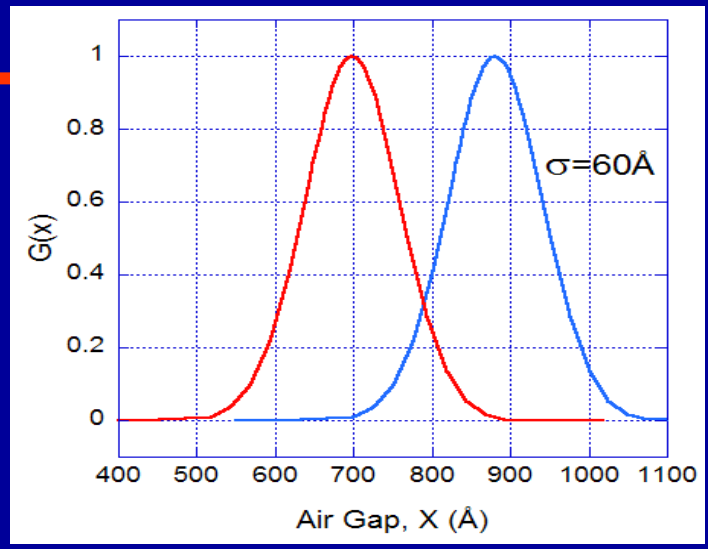
1D vs 2D Surface Profile

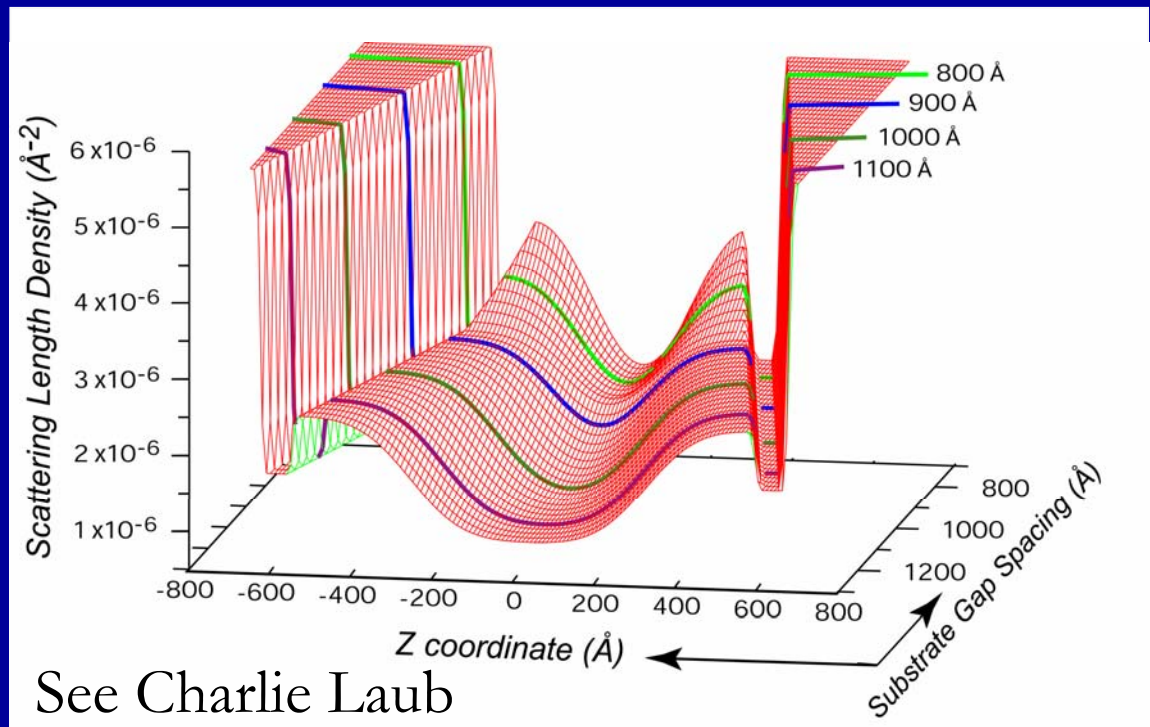
1D





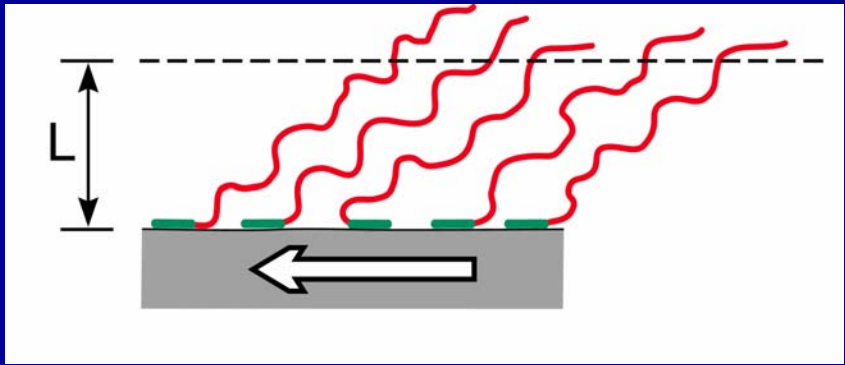
2D



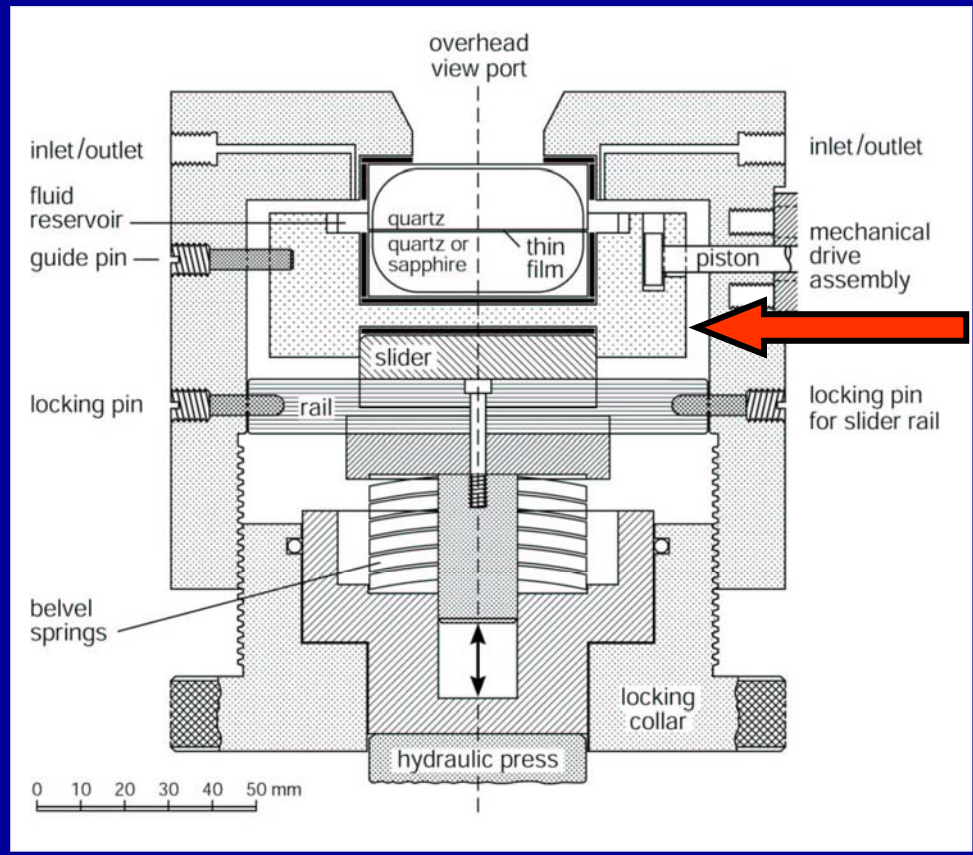


See Charlie Laub

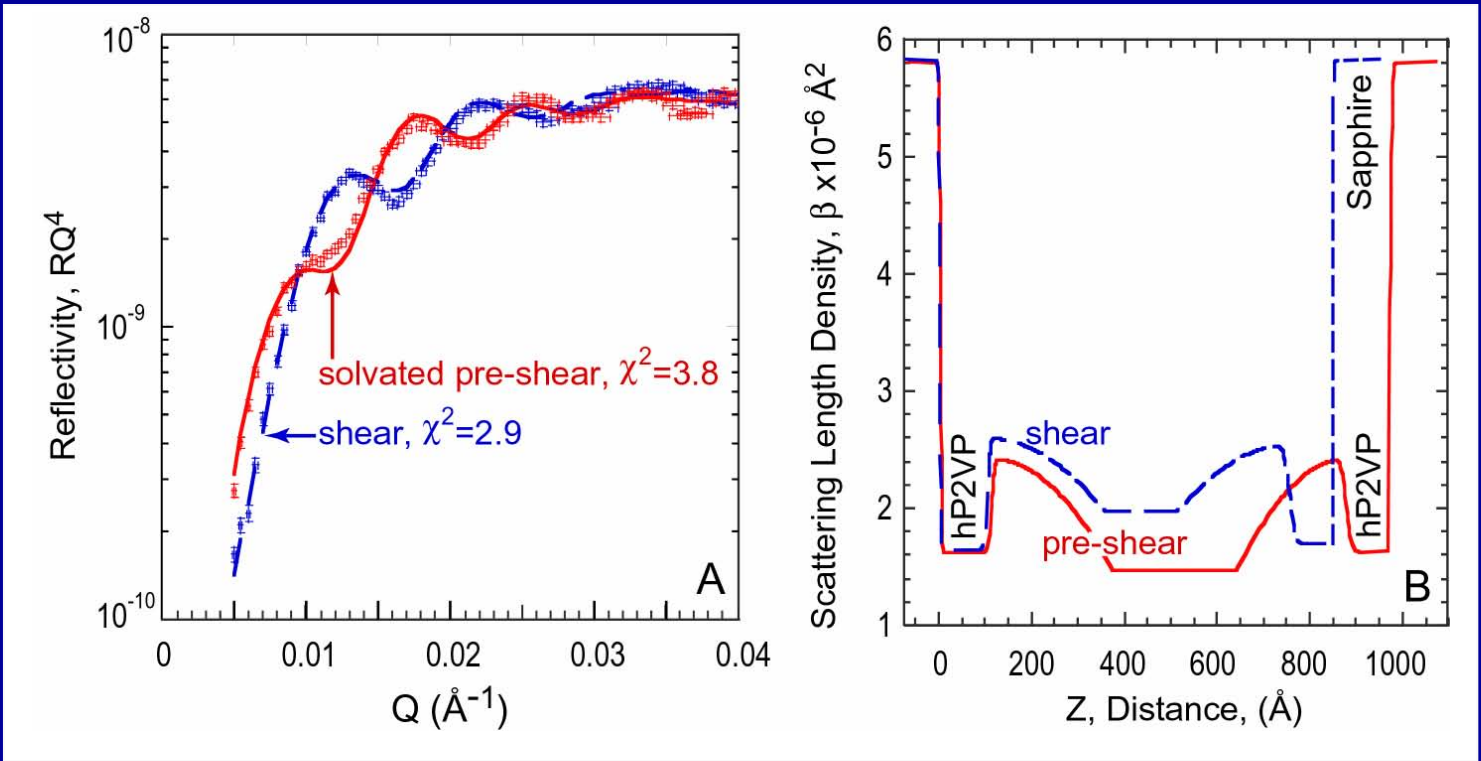
SHEAR



- Solvent flow does not penetrate the brush
- Laterally translate substrate
- steady $\gamma = .01 - 100 s^{-1}$
- non-steady $\gamma = 100 - 10^4 s^{-1}$



SHEAR



- non-steady $\gamma = 1000\ s^{-1}$
- substrate separation decreased
- improved alignment over time

More recent results – see Dennis Mulder Poster

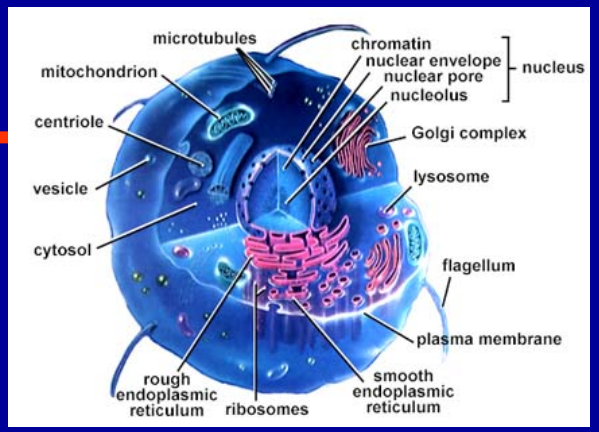
Summary

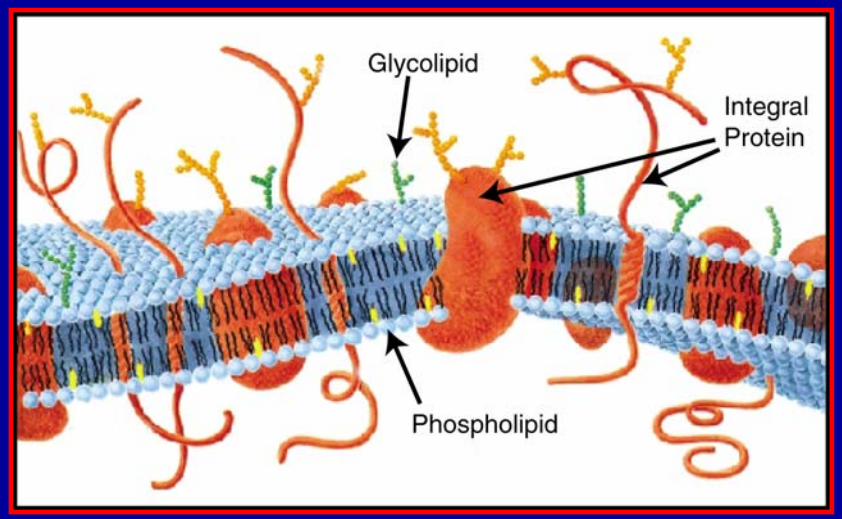
- High Density Polymer Brushes
- Confinement – YES
- 2D Surface Profiles
- Lateral Shear Looks Promising
- **Future needs**
  - **better modeling capabilities**
  - **enhanced shear capabilities = NCSCII**
  - **higher intensity – grazing incidence**
  - **off-specular**

Membranes

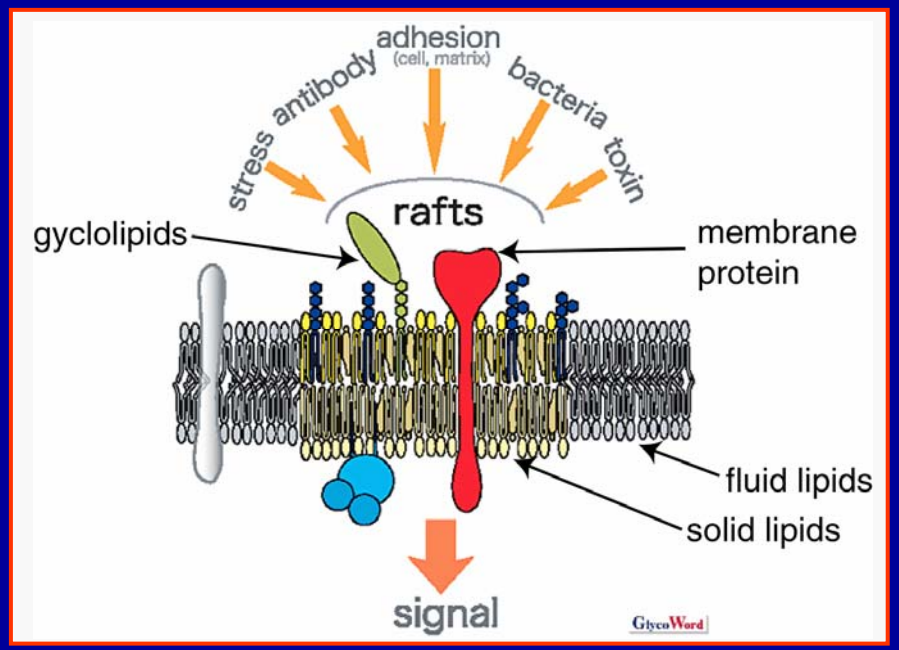
Membranes are where the *ACTION* takes place!

Mammalian cell





Cell membranes are no longer thought of as simply passive 2-D liquids.



cell polarity, protein trafficking, **signal transduction**