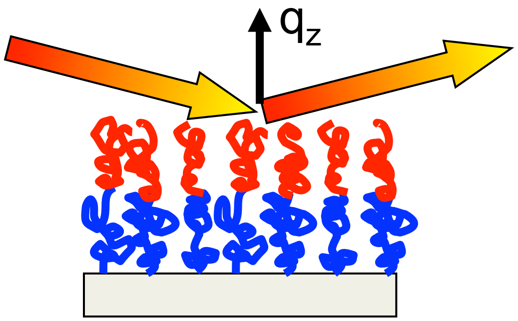
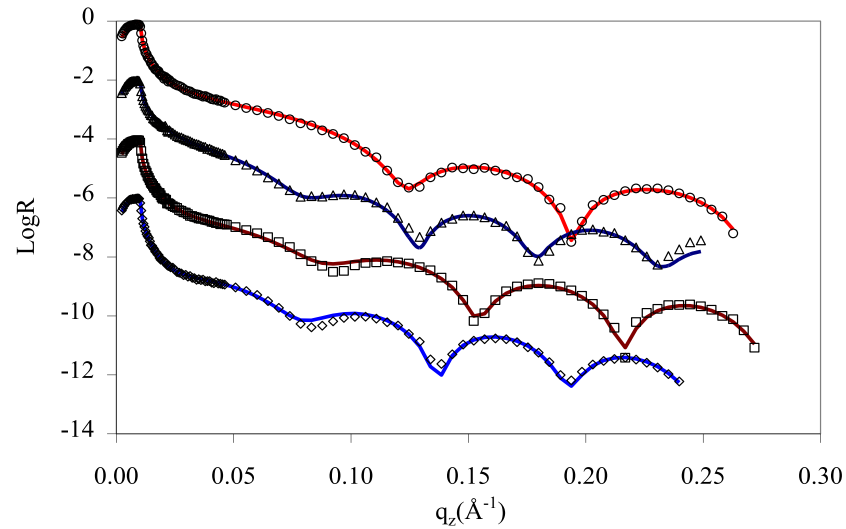
Neutron reflectivity and its applications in soft condensed matter





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June 19, 2012

NIST Center for Neutron Research

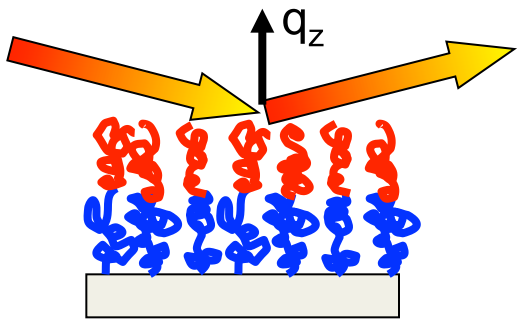
Outline

- Introduction
  - Specular reflectivity theory
  - Data analysis
  - Capabilities and the limitations of reflectivity techniques

- Examples
  - Conformation of membrane bound Nef
  - Controlled release of model polyelectrolyte (PE) chains from PE multilayer thin films
  - Surface dynamics of untethered chains on chemically identical polymer brushes

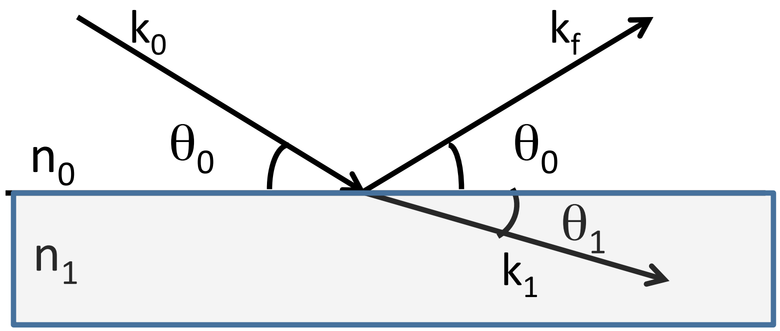
Specular reflection

- For a strictly planar interface in which composition is uniform in the parallel direction, the reflection will be entirely specular



- Below the critical angle neutrons are totally externally reflected and this is not a weak scattering.
- Born approximation is not valid in the proximity of the critical angle.

Reflection of Waves from Interfaces



$kz = k0\ sin\theta0$

$qz = 2kz = 4\pi/\lambda\ \sin\theta0$

$R = IR/I0$ = $number\ of\ reflected\ neutrons\ /\ = |r|^2$
$number\ of\ incident\ neutrons$

$n = k1/k0$ $\quad n = 1 - \lambda 2\rho/2\pi - i\lambda C$ $\quad$ where ρ is scattering length density

$C = n\sigma A/4\pi$

For polymers and biological molecules σA is negligible. It has to be accounted for materials which contain ^{6}B, ^{10}Li, ^{113}Cd and ^{157}Gd.

Scattering length density

It is a measure of how strongly material scatters the incoming radiation.

neutrons

$$\rho = b/V = N_A \rho m \sum b_i / MW$$

ρ_{dPS} = 6.48 x 10^{-6} Å^{-2}

ρ_{hPS} = 1.44 x 10^{-6} Å^{-2}

X-rays

$$\rho = N_A \rho m \sum Z_i r_e / MW$$

r_e =2.82 x 10^{-13} cm

$\rho_{dPS} = \rho_{hPS}$ = 9.6 x 10^{-6} Å^{-2}

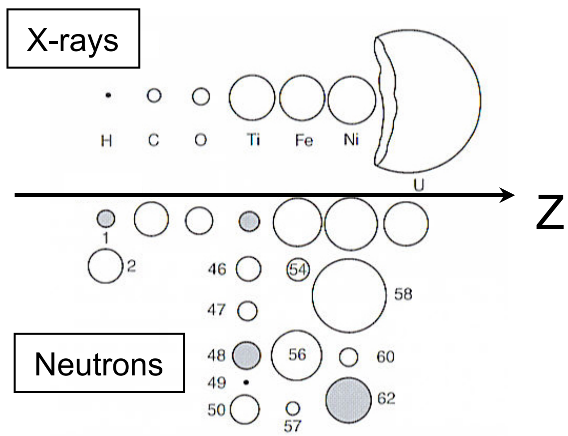


Figure from Peter Gehring

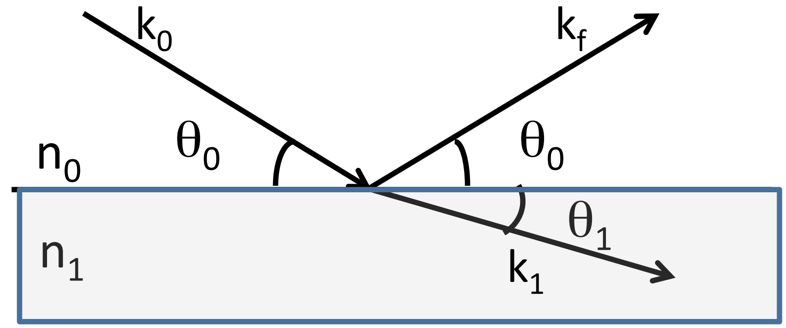
Fresnel reflection

Neutrons obey Snell's law

$n0\, cos\theta0 = n1\, cos\theta1$

$cos\theta c = n1$

$\theta c = \lambda\sqrt{}\rho/\pi$



If medium 0 is air, then n_0 is 1 and at the critical angle

$r = ar/ai = kz0 - kz1/kz0 + kz1$

Fresnel formula

$R = r01\, r01 \downarrow\uparrow *$

For $q < q_c$ $R = 1$

$kz_0 = 2\pi/\lambda\, sin\theta 0$

$kz1 = (k02 - 4\pi\rho)1/2 = (k02 - kc2)1/2$

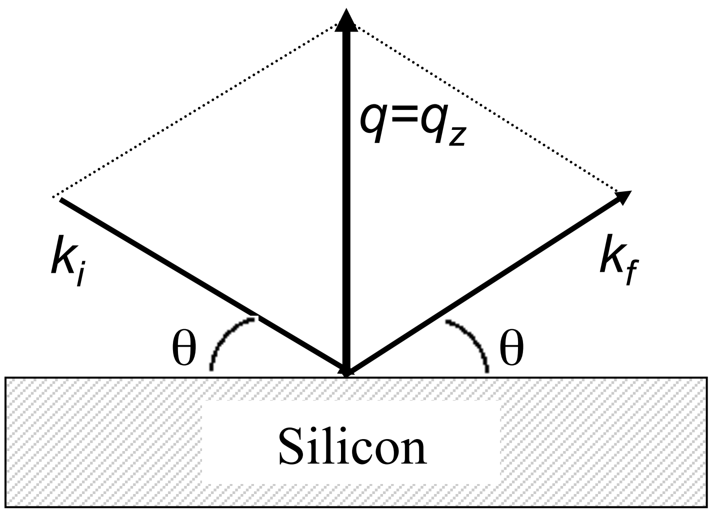
$qz = 2kz0 = 4\pi/\lambda\, sin\theta 0$

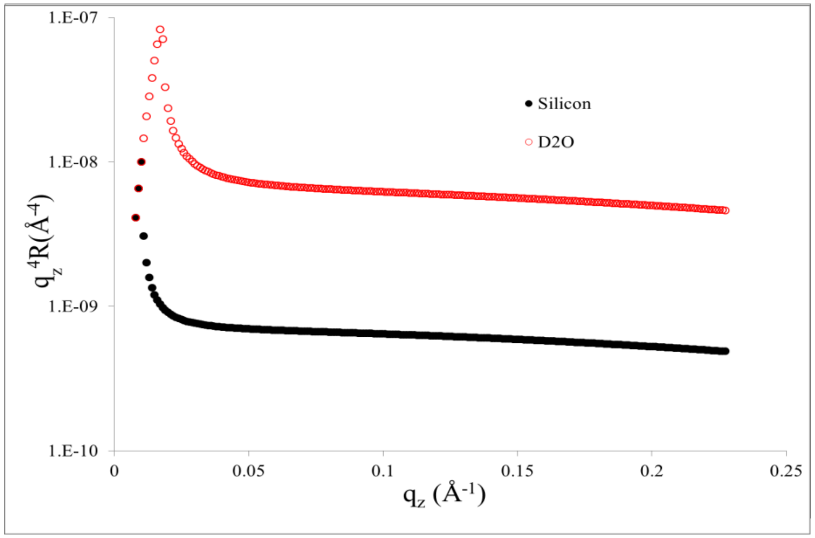
$qc = \sqrt{}16\pi\rho$

$RF = 16\pi 2\rho 2/q4$

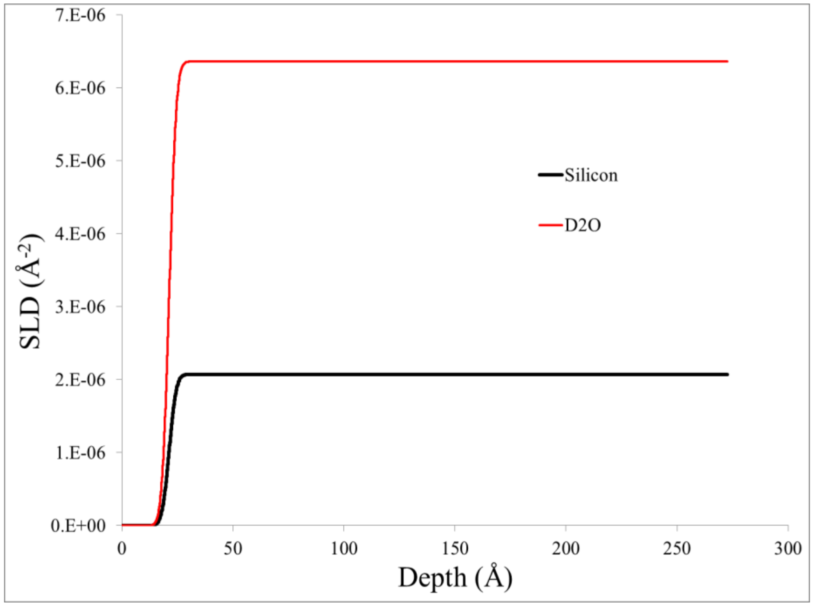
For $q \gg q_c$ *R decays with* q^4

Fresnel reflection visual examples

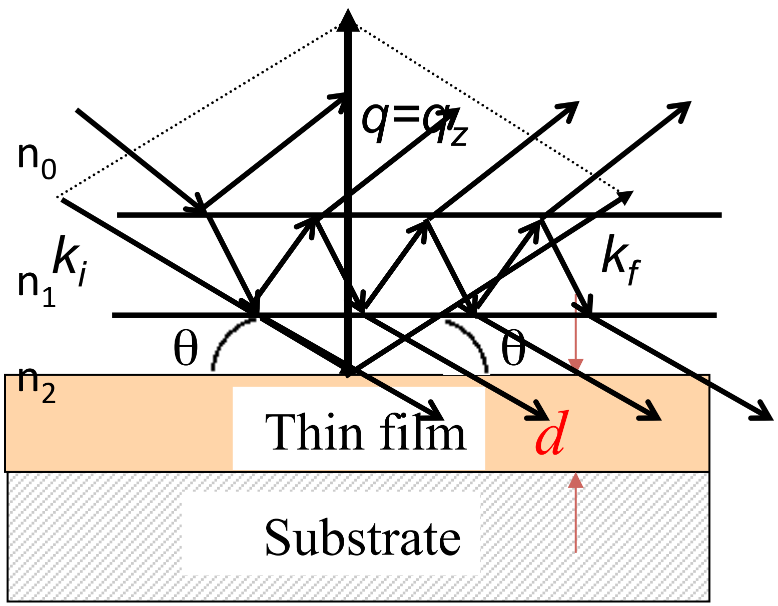




- $q_z = 4\pi \sin(\theta)/\lambda$
- $R_F = 16\pi^2\rho^2/ q^4$
- Integrated roughness
- $SLD = (b/V)_n = \Sigma(b_i/V_i) = (\rho_m N_A \Sigma b_i)/MW$



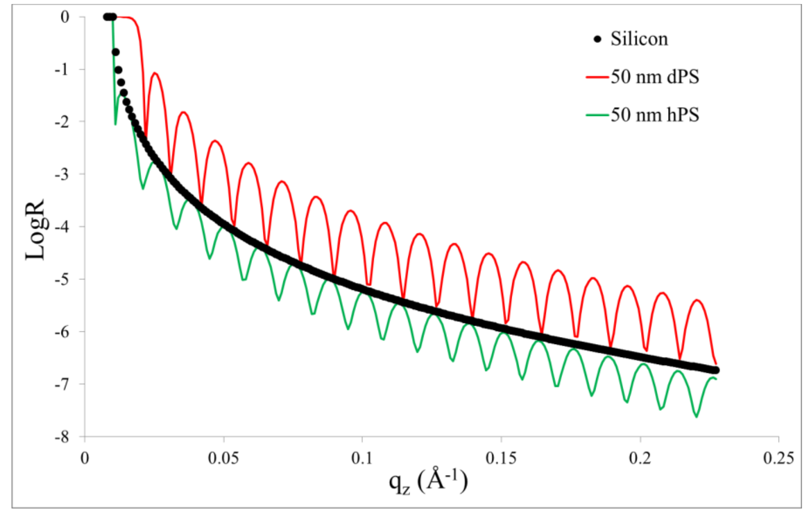
Fresnel calculation for a thin film on a substrate

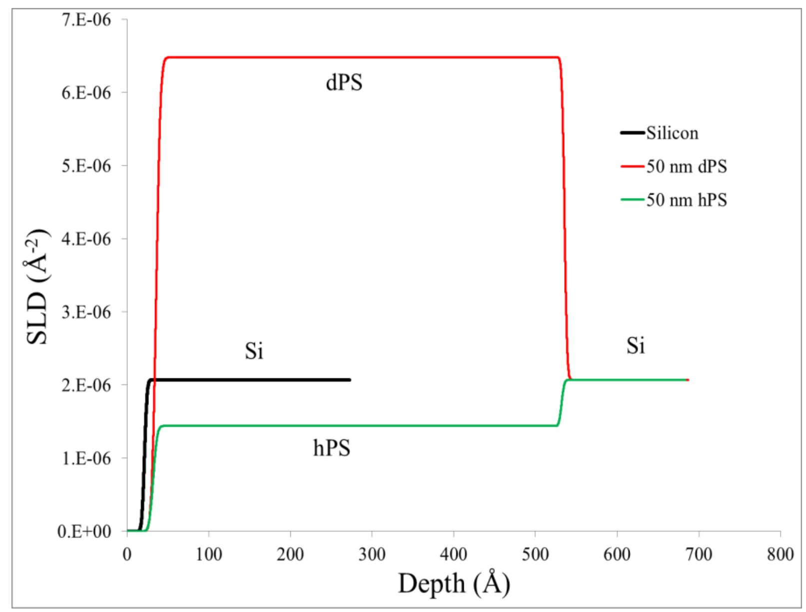


$RF=|r01+r12e\uparrow 2i\beta\ /1+r01r12e\uparrow 2i\beta\ |$

$\beta=2\pi/\lambda$ n1d sinθ1 Optical path length in medium 1

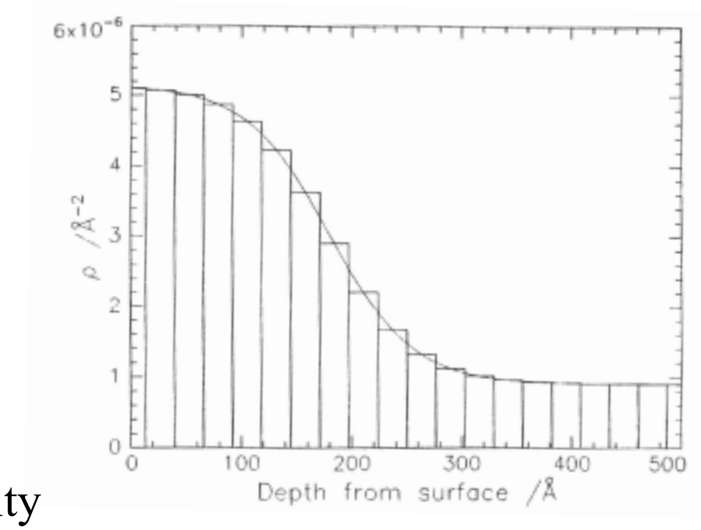
- Kiessig fringes, d=2π/Δq





Optical transfer matrix method

- Optical characteristics of any single layer in a multilayer can be accurately summarized in the transfer matrix $\boldsymbol{M_m}$
- Composition profile can be divided into series of discrete layers to approximate smooth decay
- Effect of roughness can be incorporated as a gaussian smoothing factor on the Fresnel reflectivity coefficients using Abeles method



$$M_m = \begin{bmatrix} e^{i\beta_{m-1}} & r_m e^{i\beta_{m-1}} \\ r_m e^{-i\beta_{m-1}} & e^{-i\beta_{m-1}} \end{bmatrix}$$

$$r_m = r_m^f \, e^{(-0.5 q_{m-1} q_m \langle\sigma\rangle^2)}$$

For a total of *n* layers

$$M_n = \prod_{i=1}^{n} M_i$$

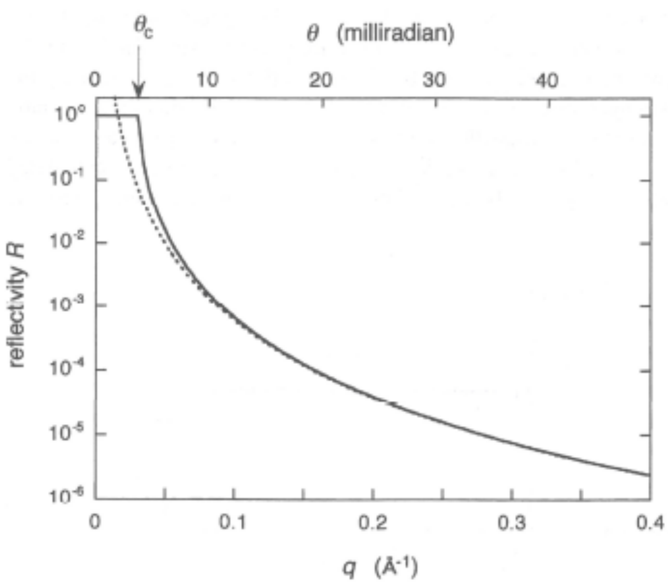
$$R(q) = M_{21} M_{21}^* / M_{11} M_{11}^*$$

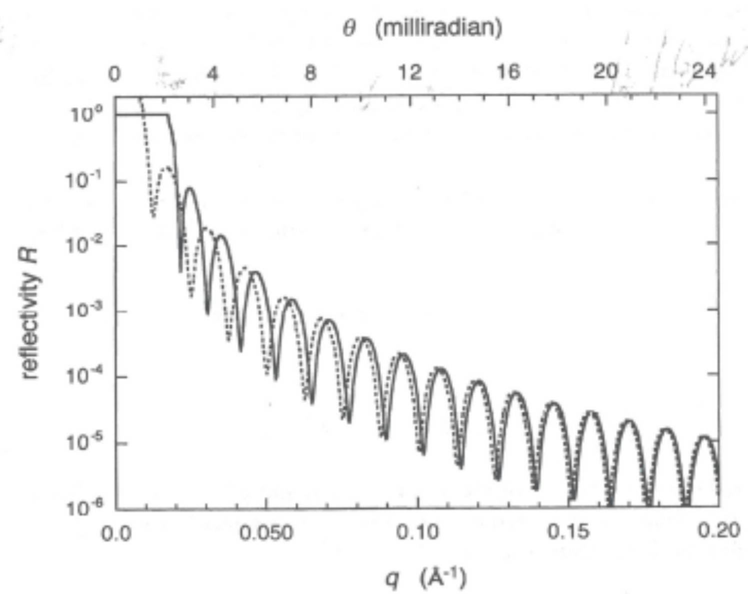
Born Approximation

- Born approximation is no longer valid around critical angle region since the scattering is not weak.

- Results of Born approximation is only valid for $q \gg q_c$.

$$R=16\pi^2/q^4\ |F\{d\rho(z)/dz\}|^2$$

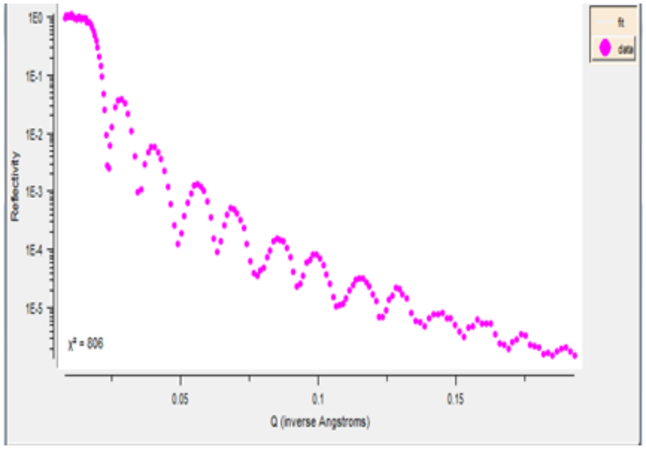




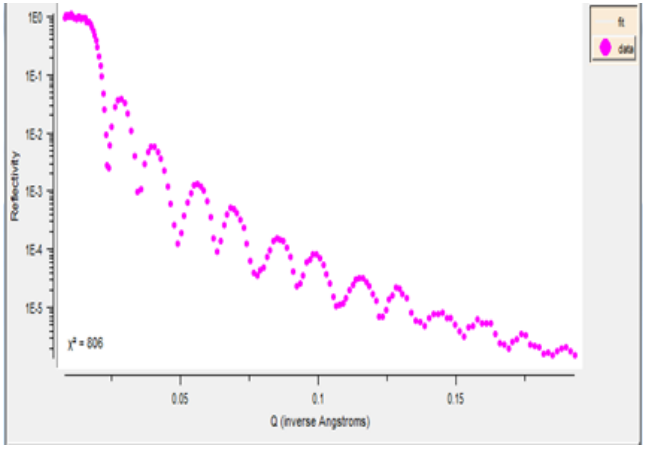
Ryong-Joon Roe, Methods of X-ray and Neutron Scattering in Polymer Science

Analyzing neutron reflectivity data

Real space SLD profile

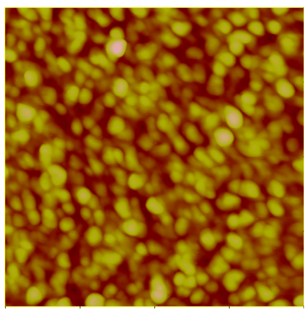


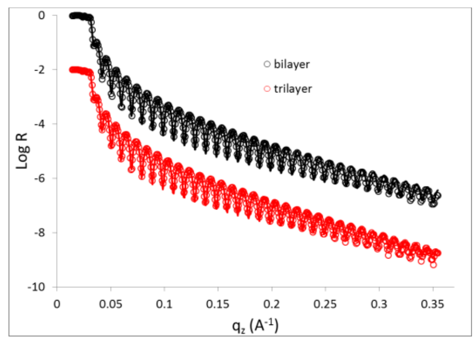
Model SLD profile



NR data analysis

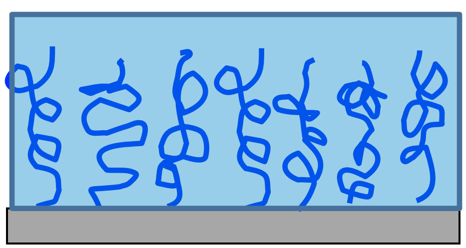
- Independent knowledge from other characterization techniques make the analysis reliable



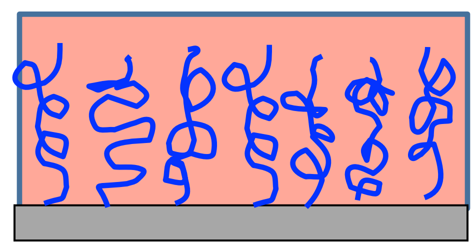


Ellipsometry, TEM, DSIMS

- Measuring the reflectivity using couple different contrast conditions and fitting the data simultaneously



dPS in h-toluene



dPS in d-toluene

- Depositing the sample on a magnetic reference layer and measuring reflectivity using different spin states

Advantages

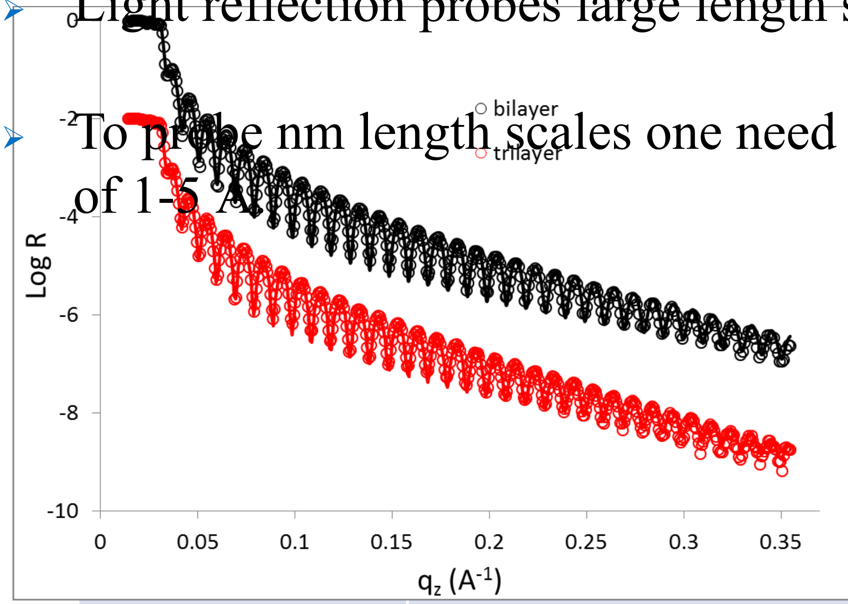
- Interact with nuclei not electrons
- Low absorption. Probes buried structure
  - vacuum chambers, liquid cells, high-pressure cells
- Simple interpretation – provides statistical averages
- Isotopic sensitivity and contrast variation (especially D and H) SLD_{H_2O}= -0.57x10^{-6} Å^{-2} SLD_{D_2O}= 6.36x10^{-6} Å^{-2}
- Non-destructive
- For multicomponent soft materials it is one of the best way to obtain information about the structure of individual components

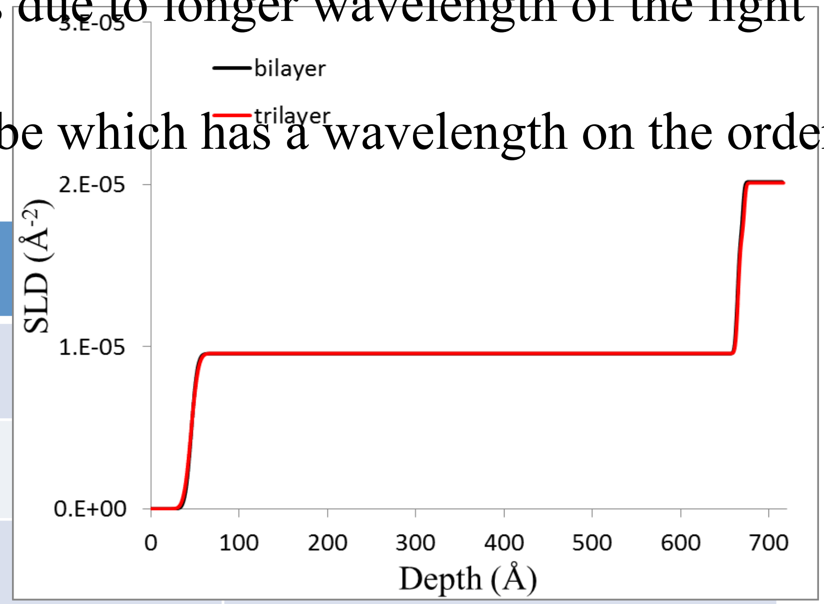
Disadvantages

- It requires relatively smooth surfaces ($\sigma_{rms} < 5$ nm)
- Sample uniformity over a large area is required
- Long measurement times due to lower flux of neutron sources
- Data analysis requires fitting and the results of fitting analysis may not be unique

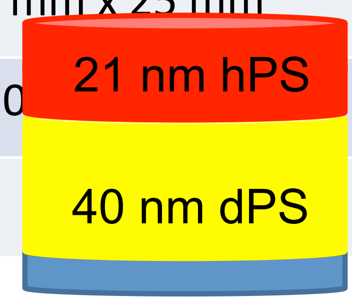
X-ray and Neutron Reflectivity comparison

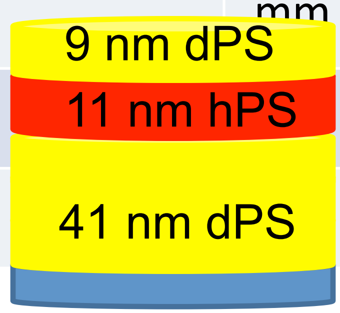
- Light reflection probes large length scales due to longer wavelength of the light
- To probe nm length scales one need a probe which has a wavelength on the order of 1-5 Å





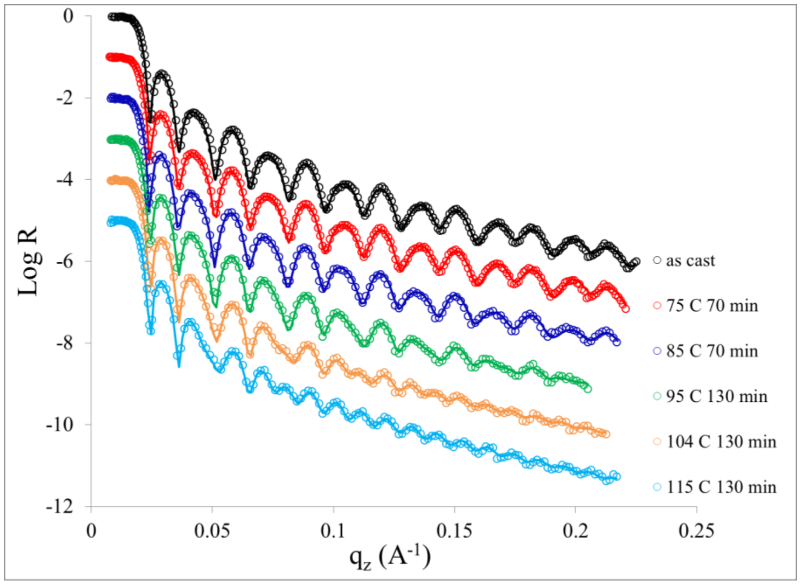
	…sity	
Sample size	25 mm x 25 mm	mm size samples
Time	1-10…	…nutes



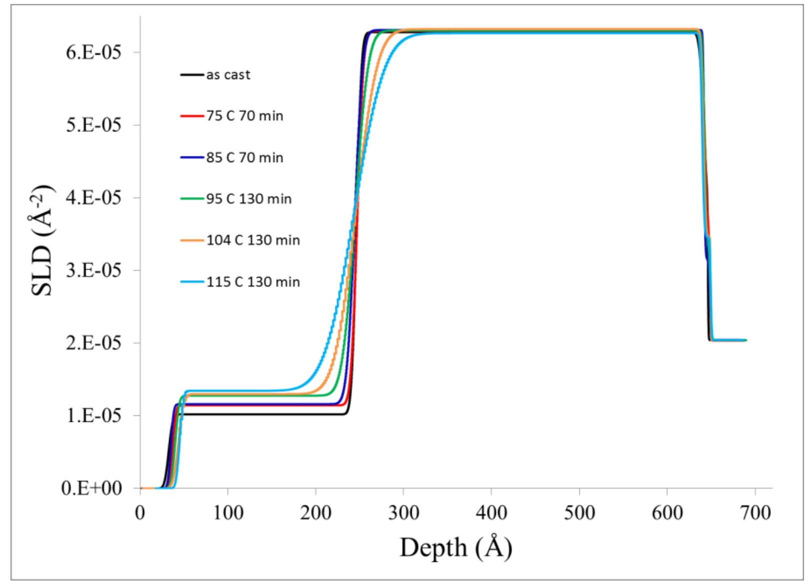


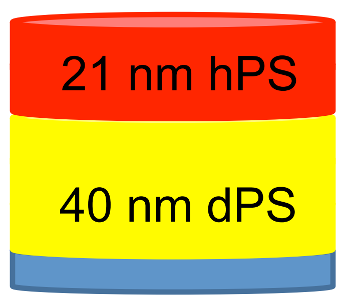
NR data and SLD profiles for Bilayer Sample

525k Bilayer Sample NR data



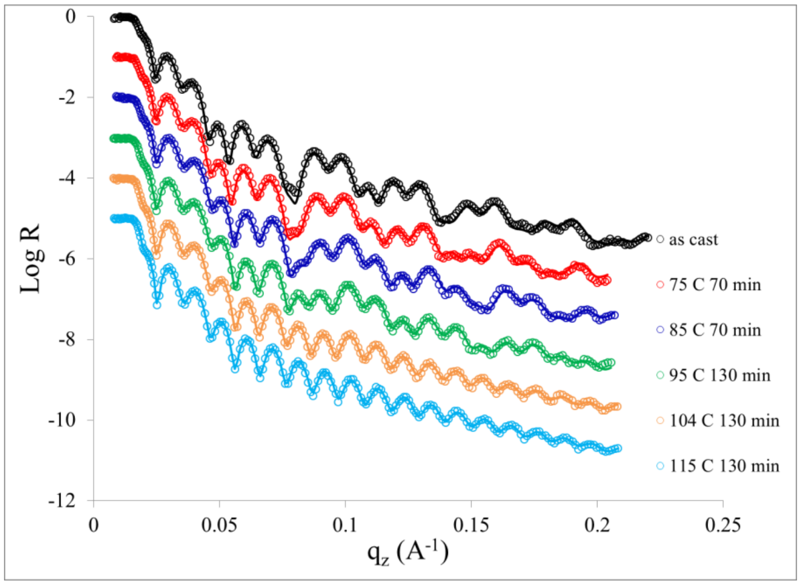
525k Bilayer SLD profile



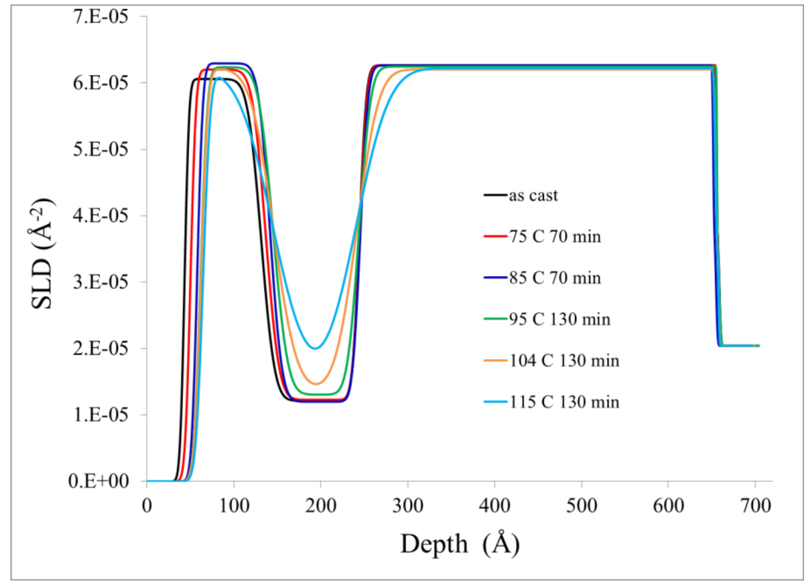


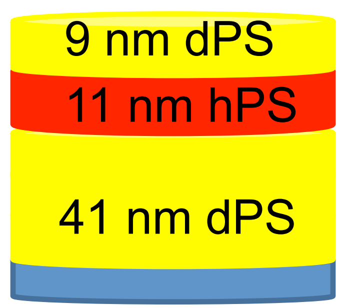
Reflectivity data and SLD profiles

525k Trilayer sample NR data



525k Trilayer sample SLD profile

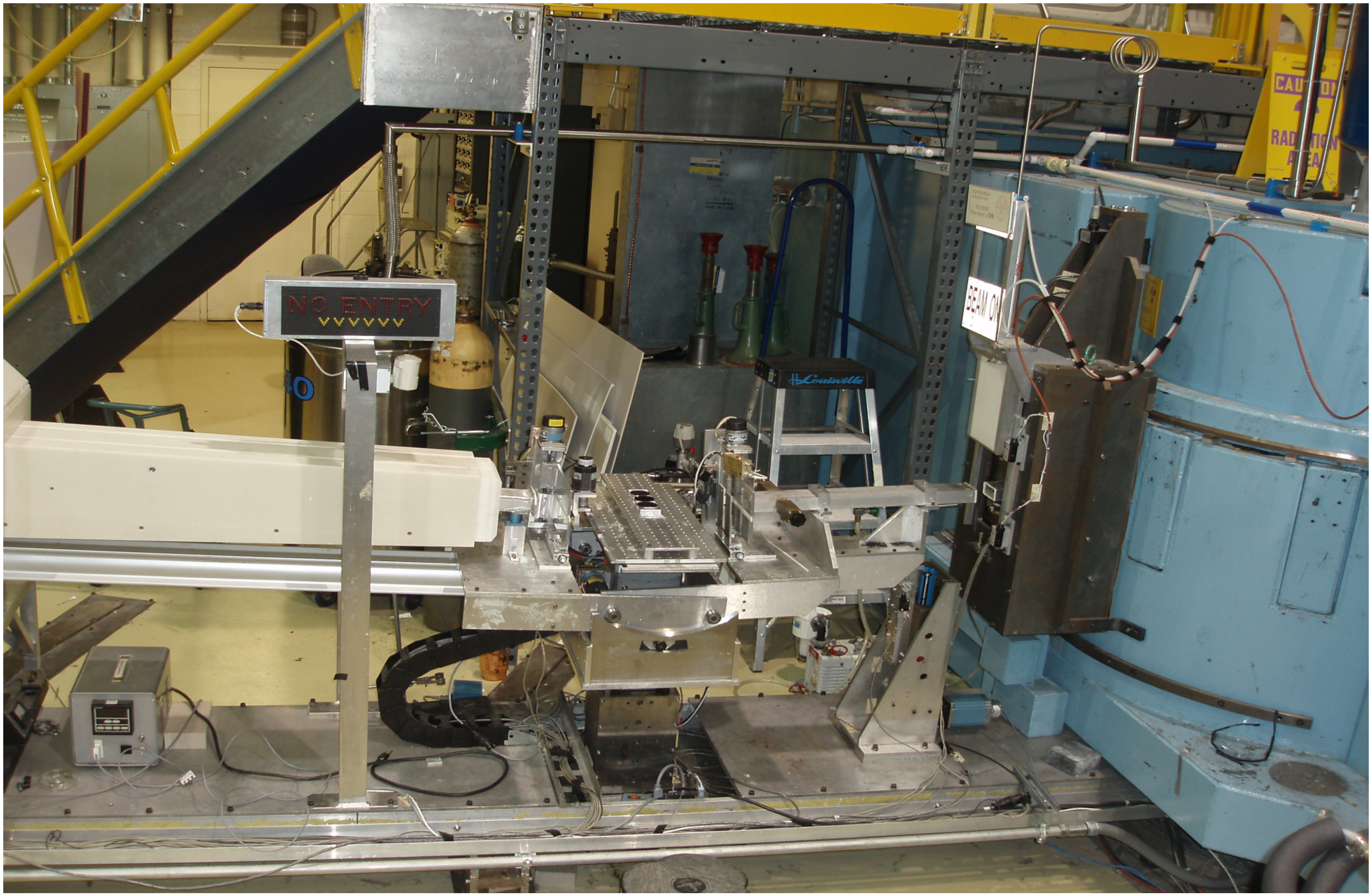




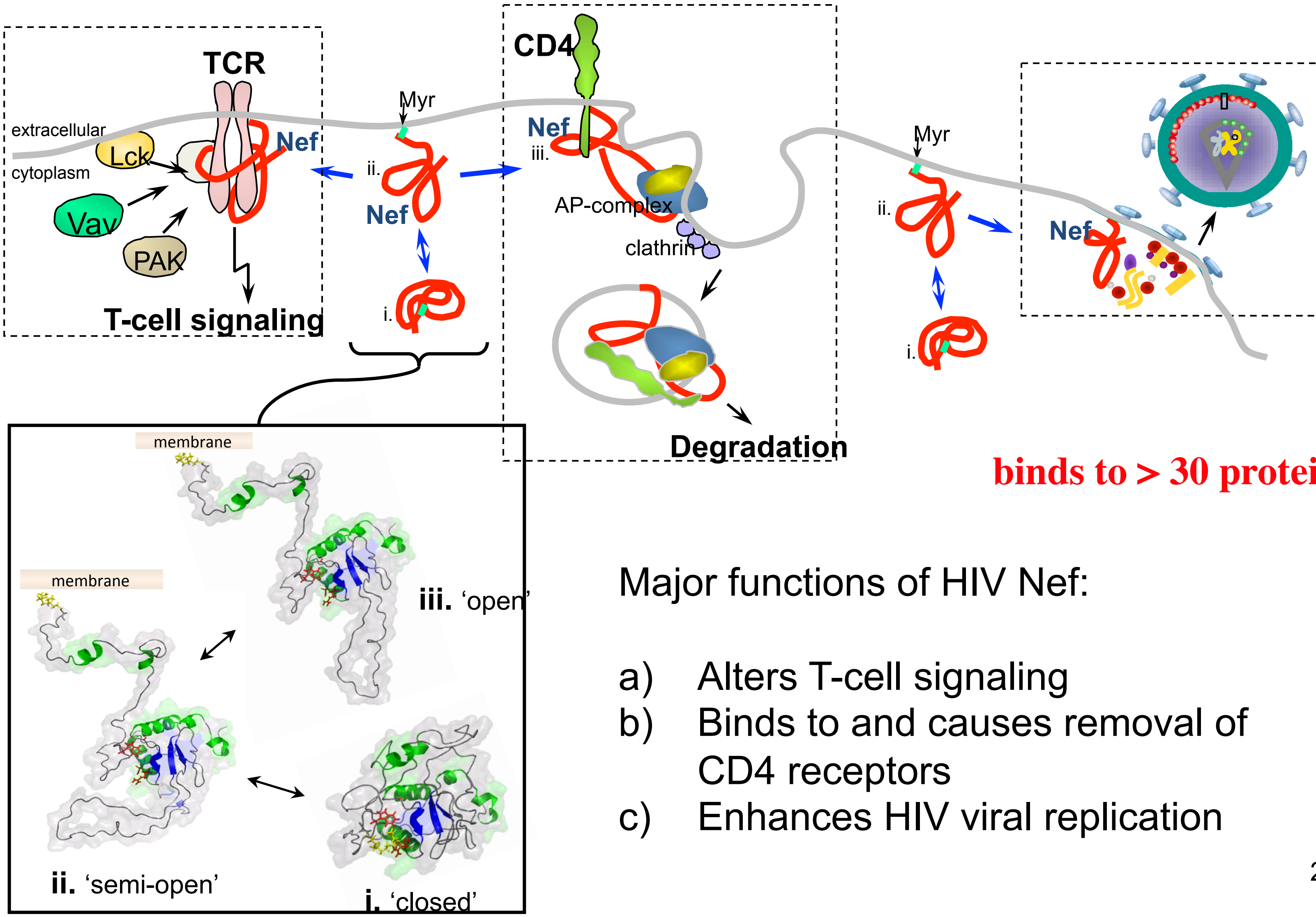
Commonly Studied Polymer and Biological Thin Film Cases with Neutron Reflectivity

- Surface adsorption of polymers
- Surface segregation in polymer blends
- Thin film swelling
- Block copolymer ordering
- Interdiffusion in polymer layers
- Interactions of proteins with lipid membranes
- Internal structure of polyelectrolyte multilayers

NG7 Horizontal Neutron Reflectometer



Nef is critical for the progression of HIV to AIDS

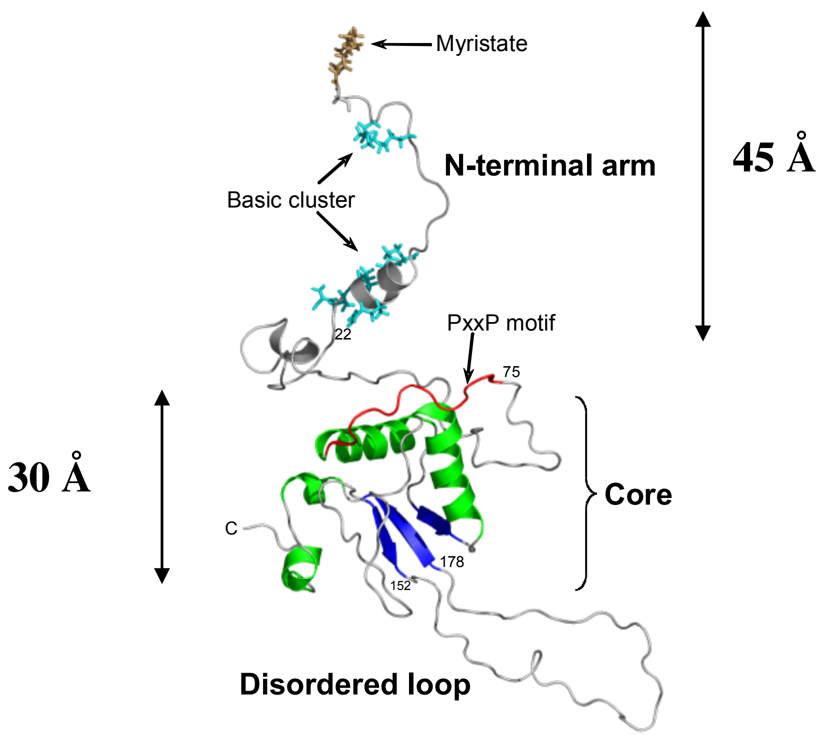


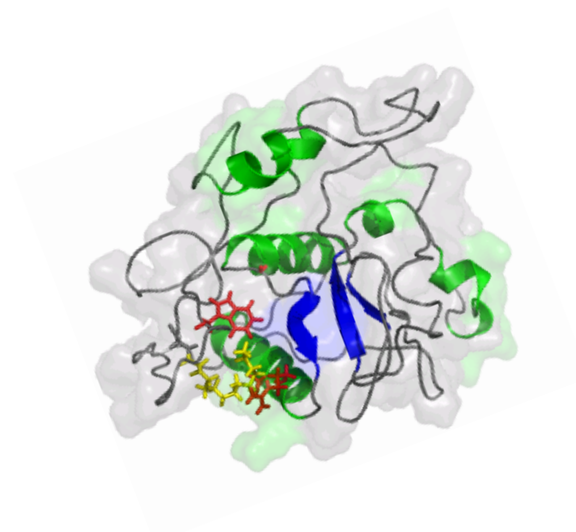
binds to > 30 proteins

Major functions of HIV Nef:

a) Alters T-cell signaling
b) Binds to and causes removal of CD4 receptors
c) Enhances HIV viral replication

Conformational changes are critical for Nef's activity





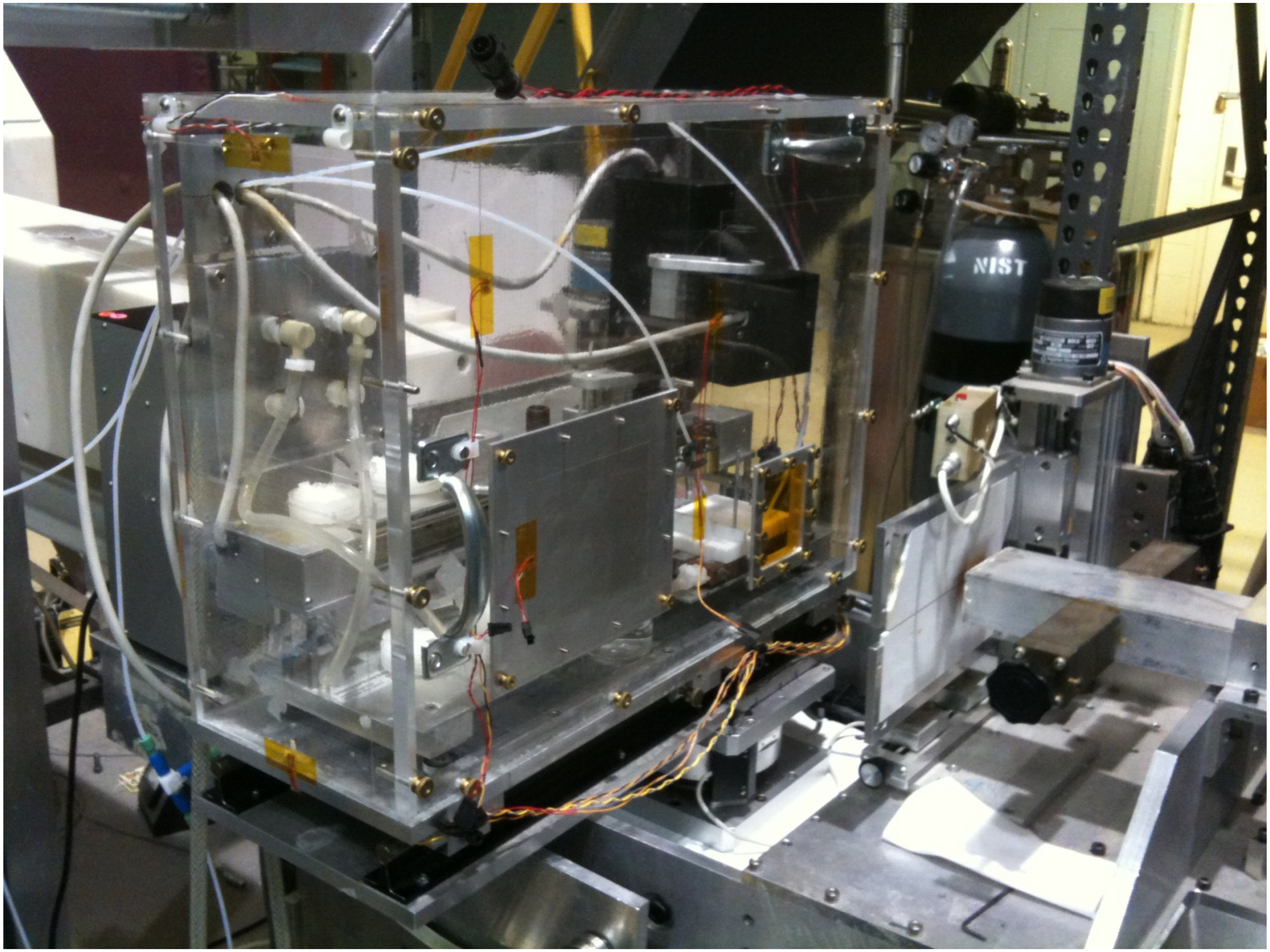
Open form

Closed form

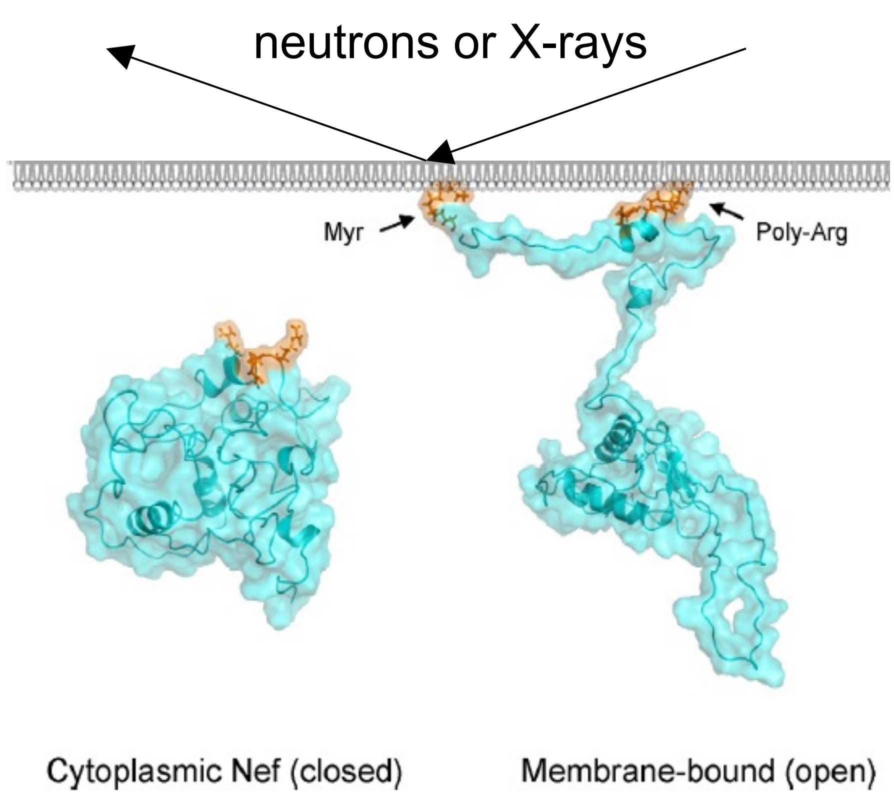
open form Model of Geyer and Peterlin

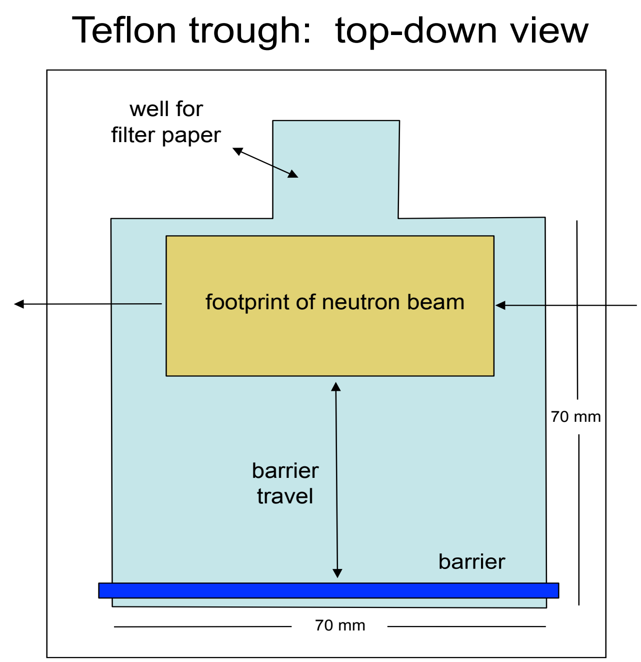
(NMR structures obtained for core domain)

Neutron Reflectivity Setup for Langmuir Trough



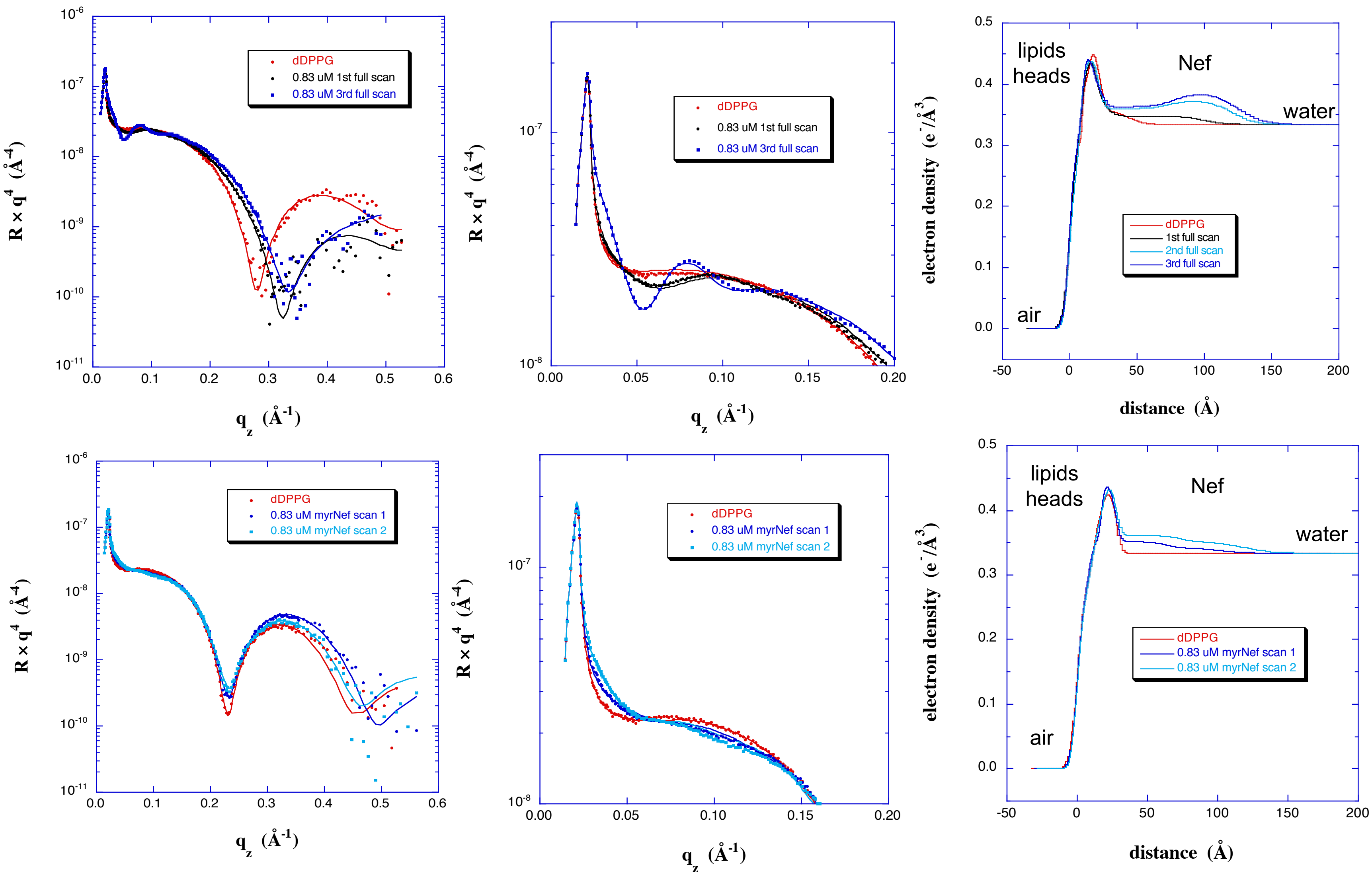
Neutron Reflectivity Setup for Langmuir Trough





Use neutron and X-ray reflection to test hypothesized transition from closed to open form upon membrane binding

X-ray reflectivity for myr-Nef



myr
inserted

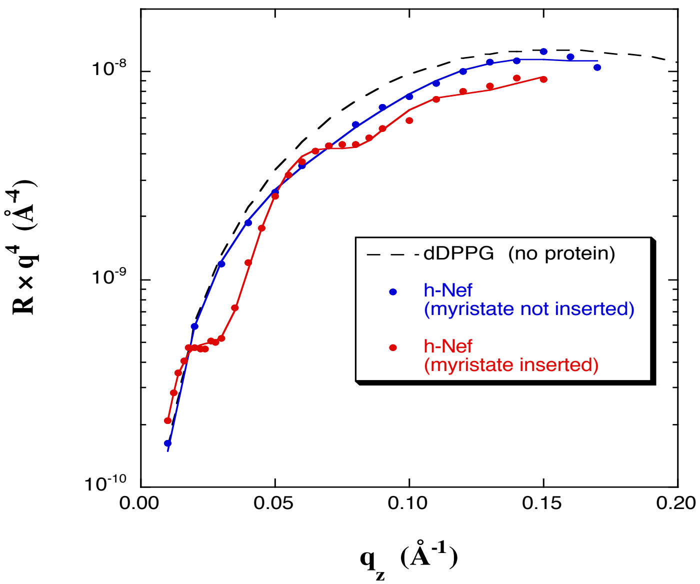
(low P)

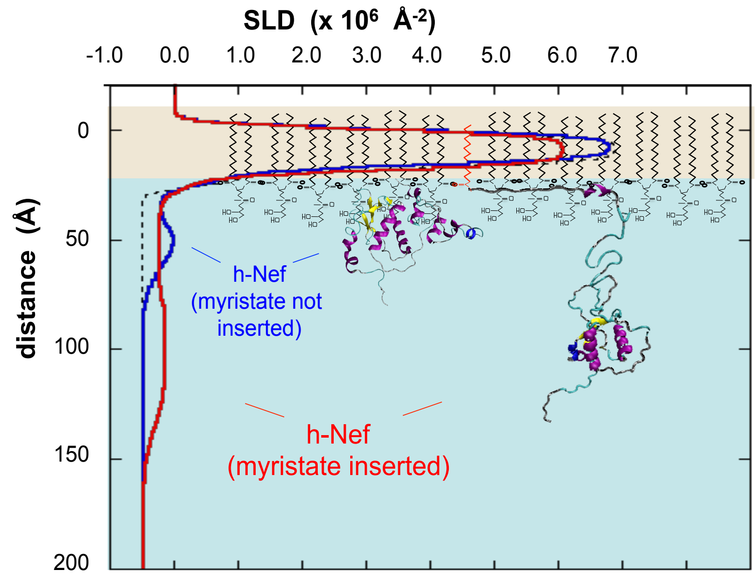
myr
not
Inserted

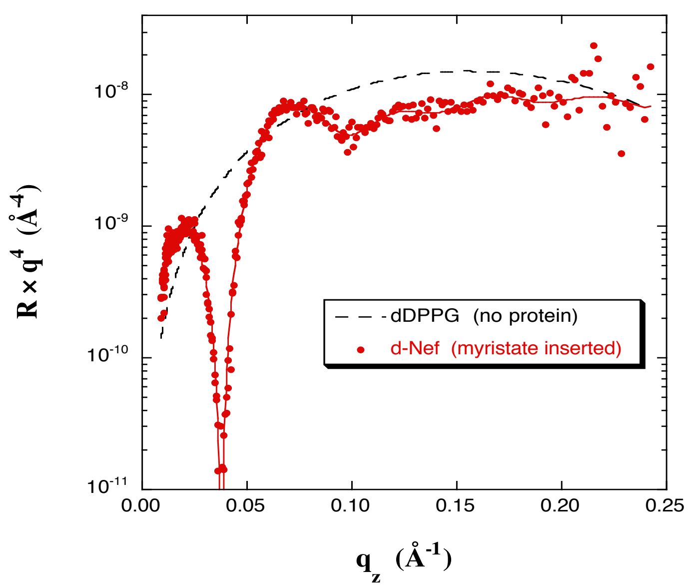
(high P)

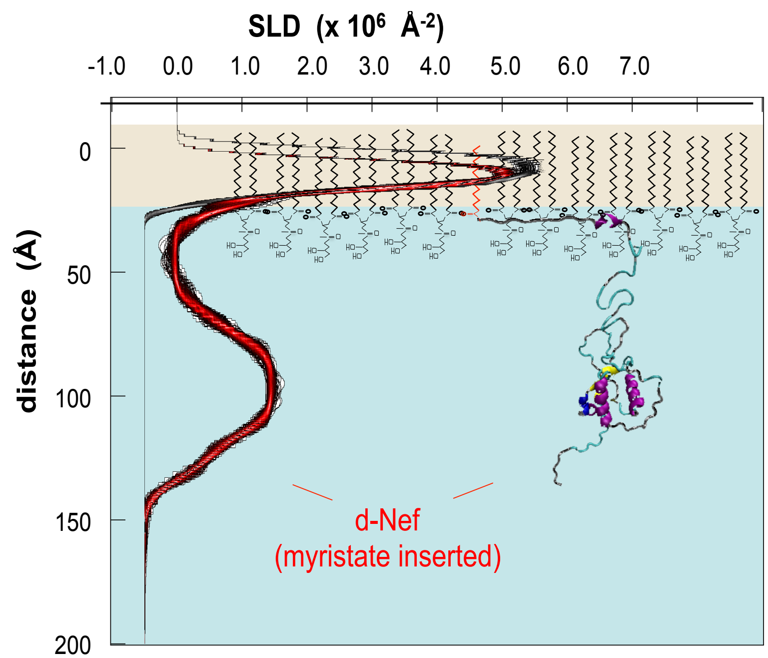
Insertion of myristate controlled through surface pressure

Neutron reflectivity for myr-Nef



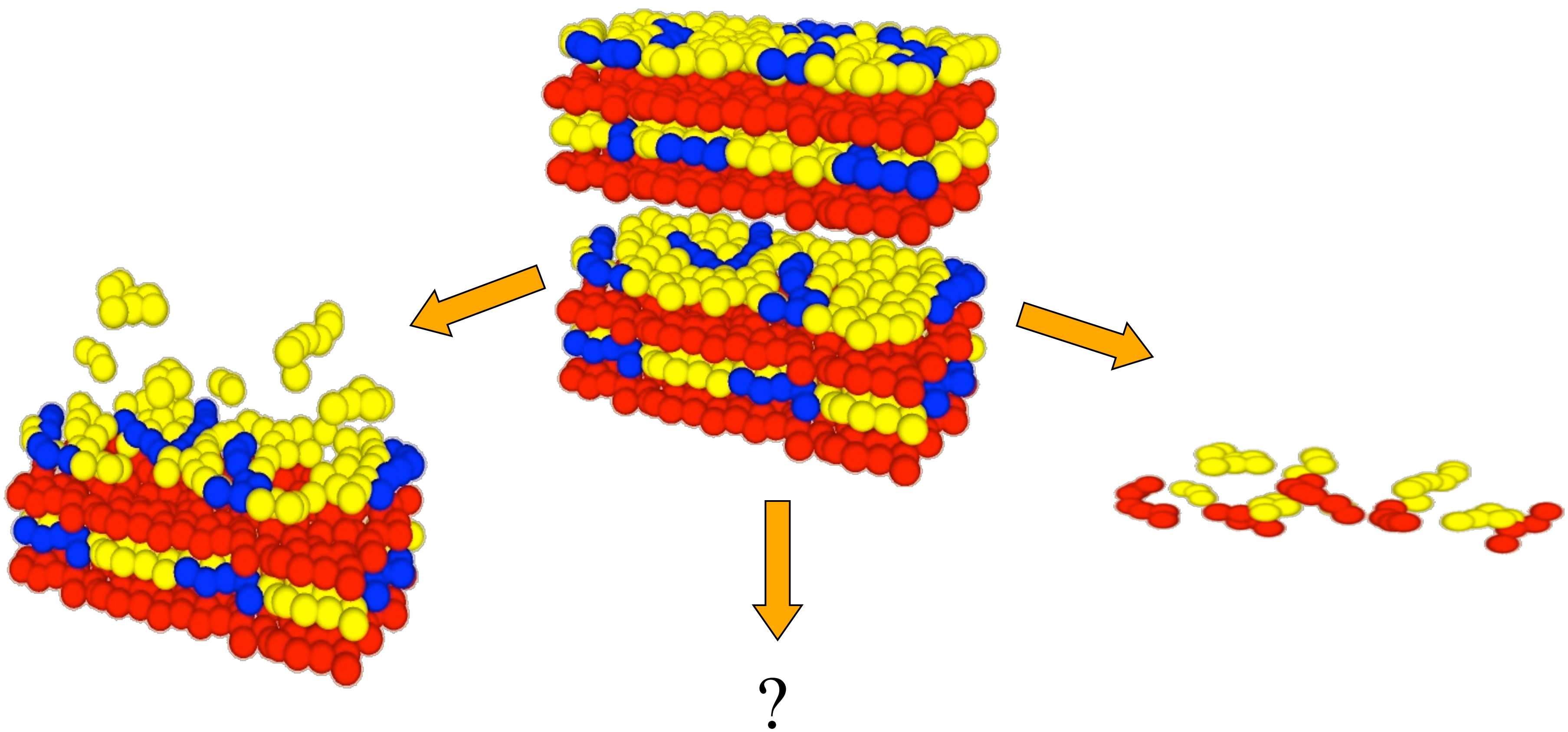






pH-driven Controlled Release from Model Blend Polyelectrolyte Multilayer Films

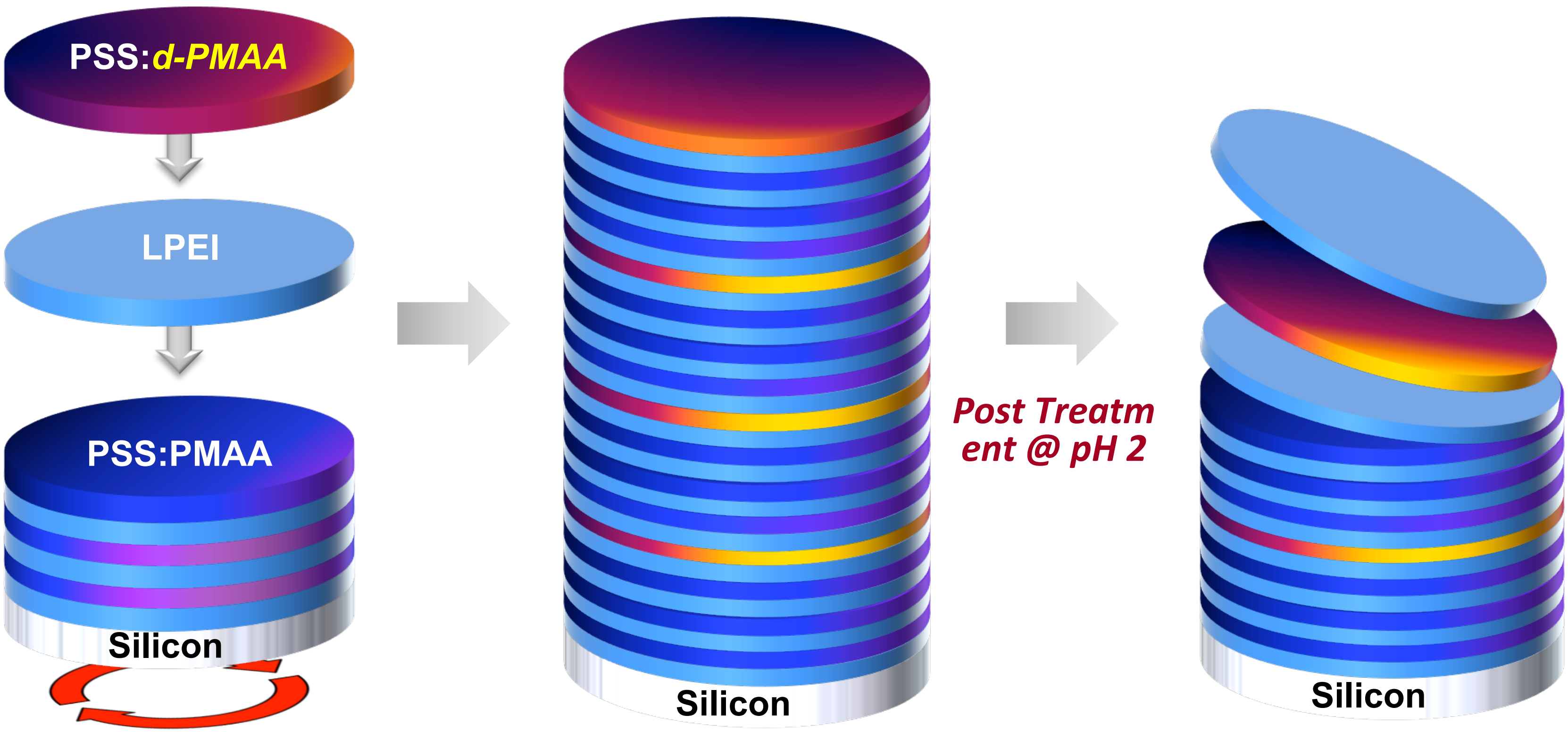
- To investigate the changes in the internal structure during the pH-driven release of polymer chains.



Model Blended Multilayer Films for Controlled Release

Architecture of Model Blended Multilayer Films♪

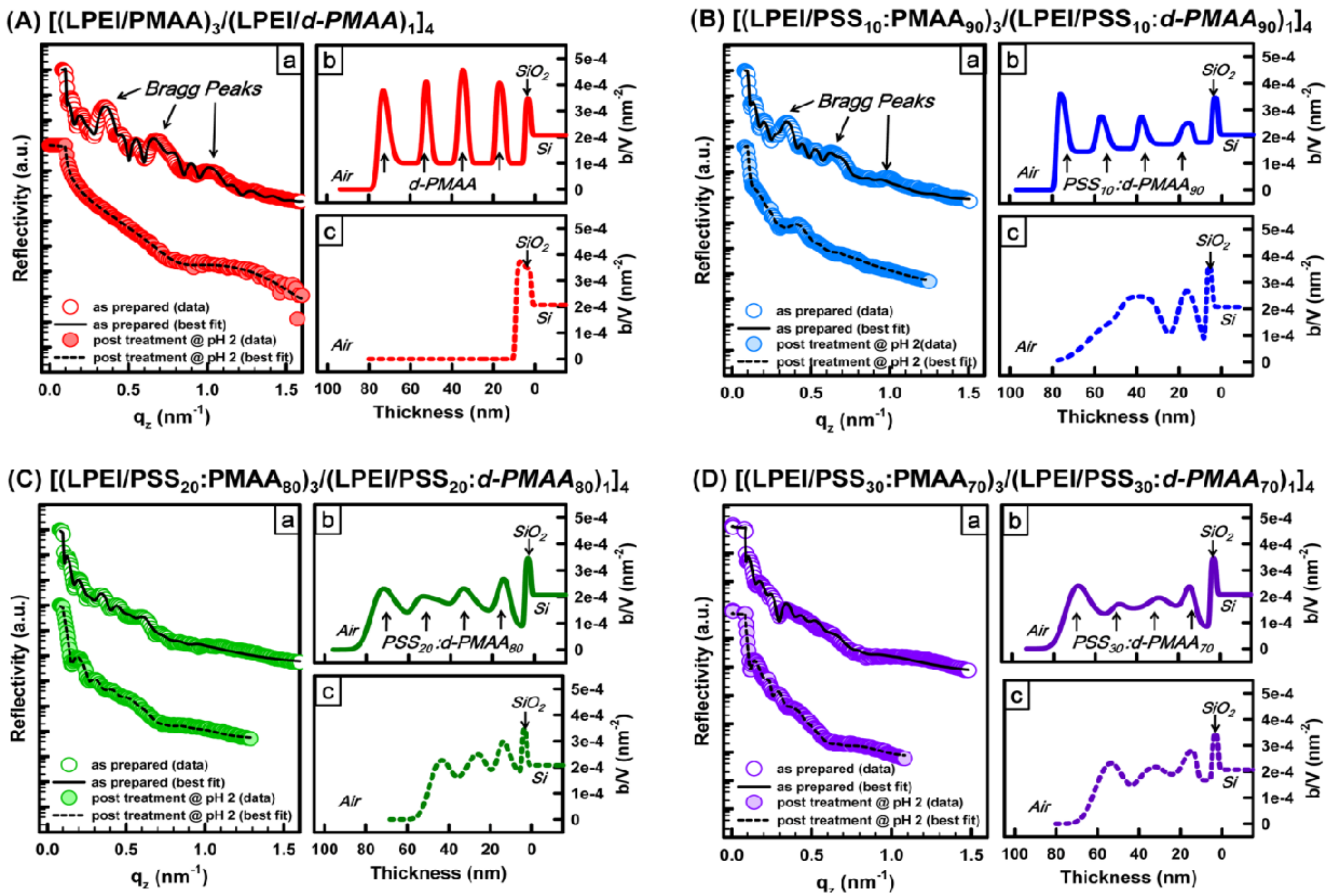
Monitoring the Changes of Internal Structure by NR



$(LPEI/PSS_x:PMAA_{100-x})_{16}$

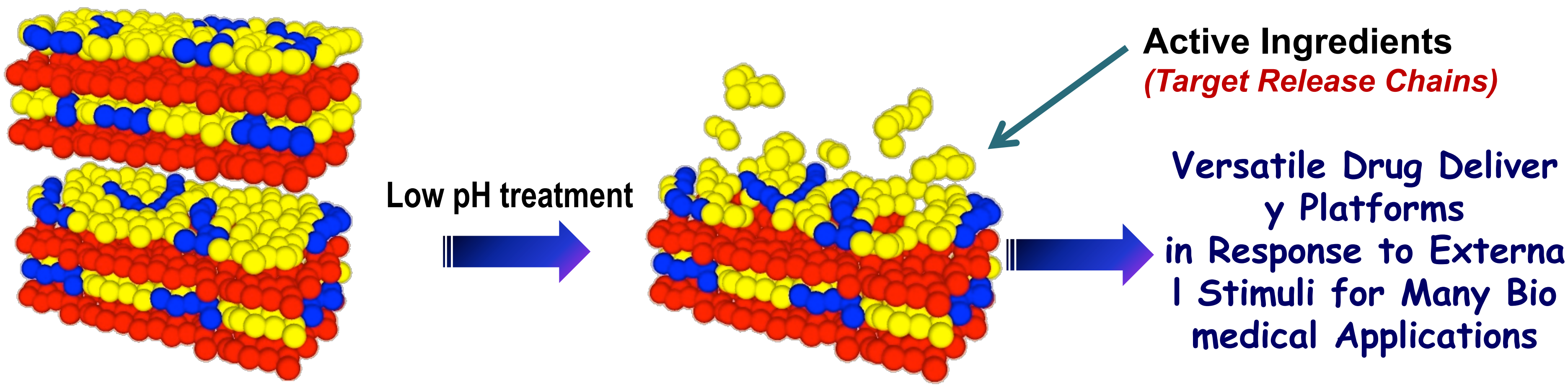
prepared @ pH 5.0/5.0 combination

Release behavior can be tuned by varying PSS content



Summary

from Model Study to Real Applications

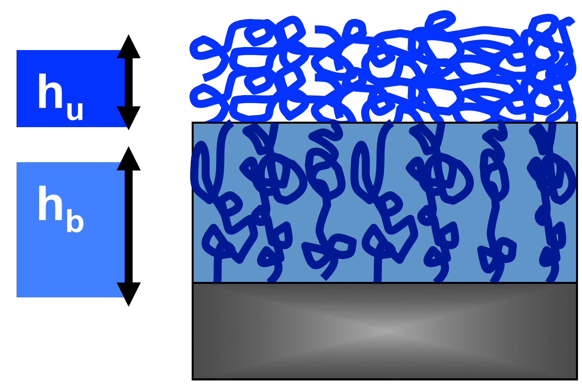


- *pH-triggered release* of polymer multilayer platforms could be ea sily tuned by the *blend ratio* between weak and strong PEs due to t heir *different degree of ionization* as a function of pH.

- Initial *burst erosion* of the films slowly transforms into surface er osion as the PSS content in the blend is increased.

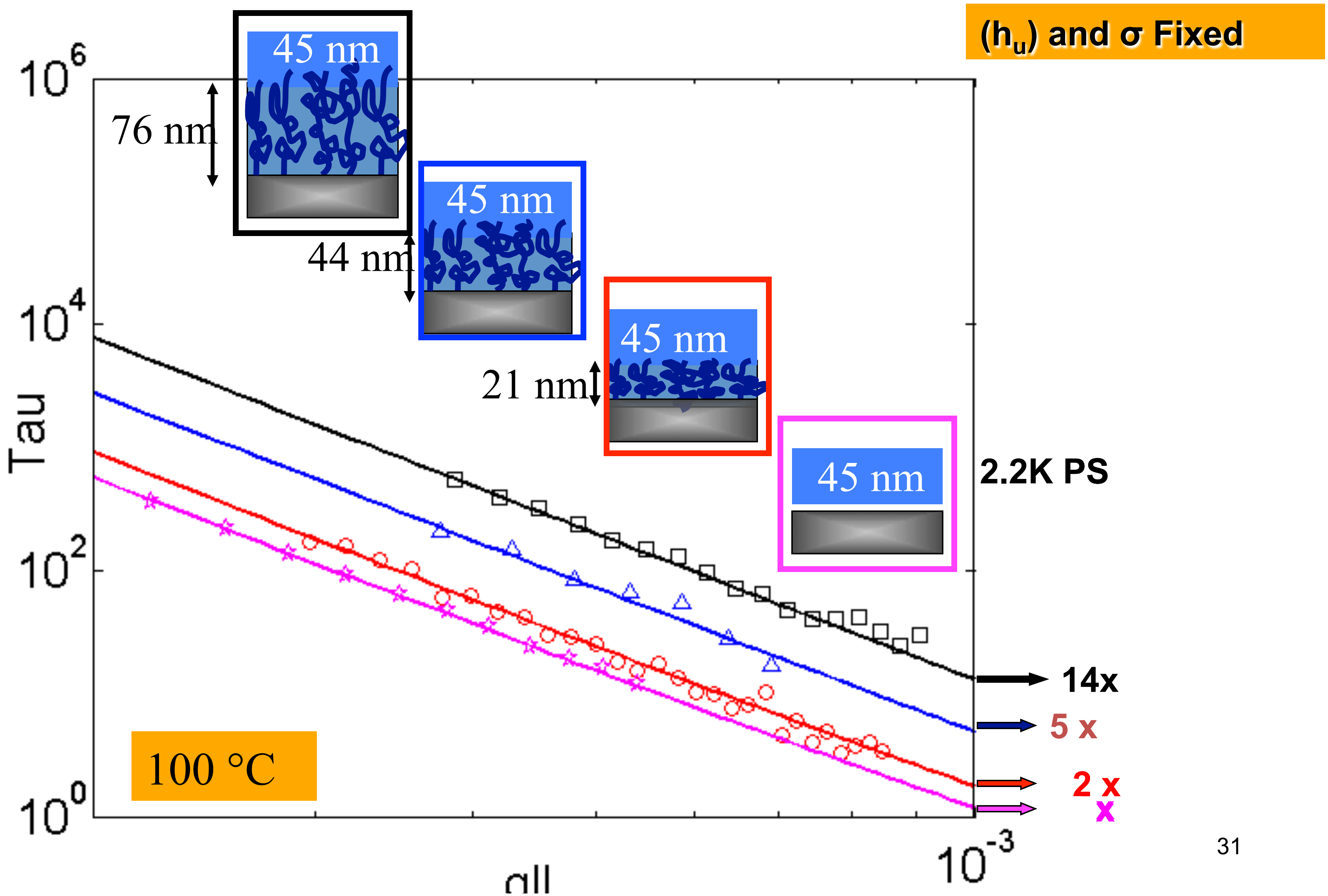
Objective

- Investigate the effect of underlying brushes on surface dynamics of spun-cast chains (Bilayer films)



- Brush thickness (h_b)
- Brush grafting density (σ)
- Untethered chain layer thickness (h_u)

τ Increases with Increasing Brush Thickness



Effective Thicknesses

Viscous model

from capillary wave theory

$$\tau(q_{\|}) \cong \frac{2\eta H}{\gamma q_{\|} F}$$

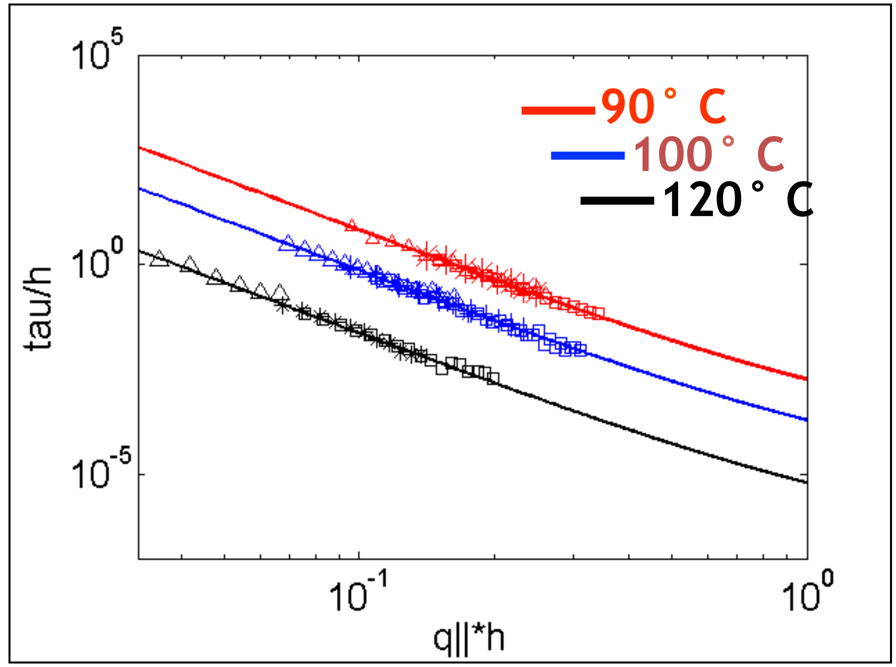
$$F = Sinh(q_{\|}h)Cosh(q_{\|}h) - (q_{\|}h)$$

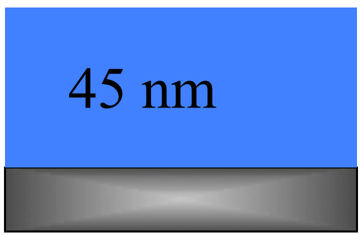
$$H = Cosh^2(q_{\|}h) + (q_{\|}h)^2$$

η = viscosity

γ = Surface tension

h = Film thickness



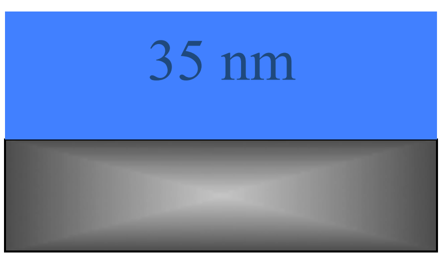


Taking

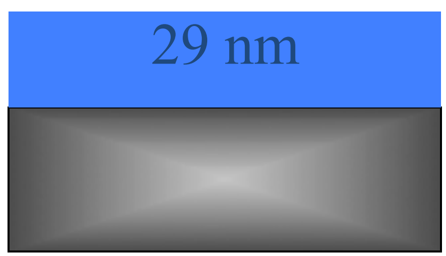
η=η(pure 2.2k)

On brushes

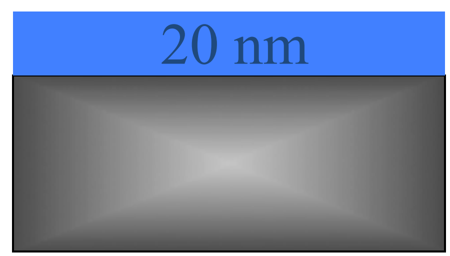
21 nm brush



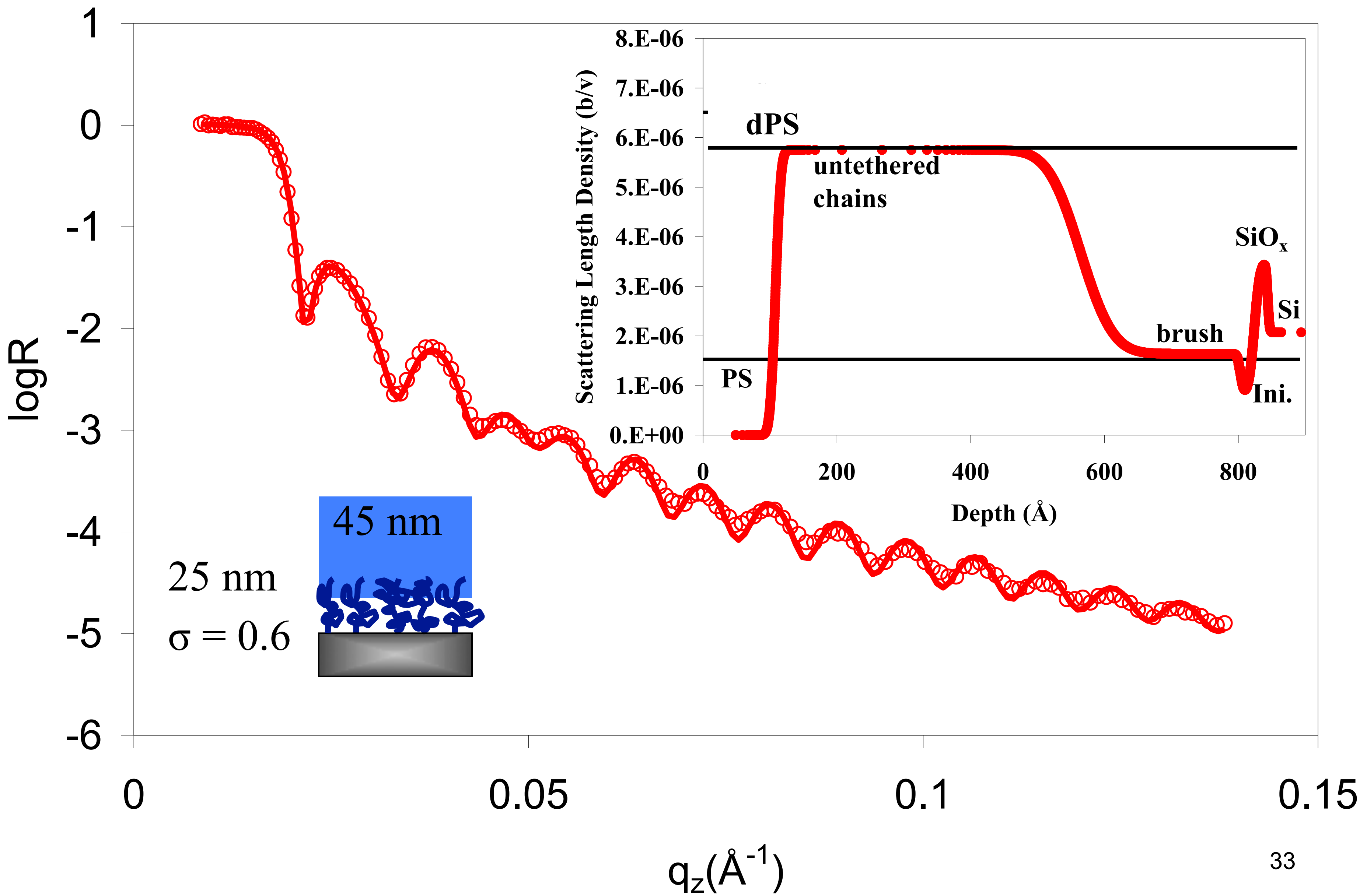
44 nm brush



76 nm brush

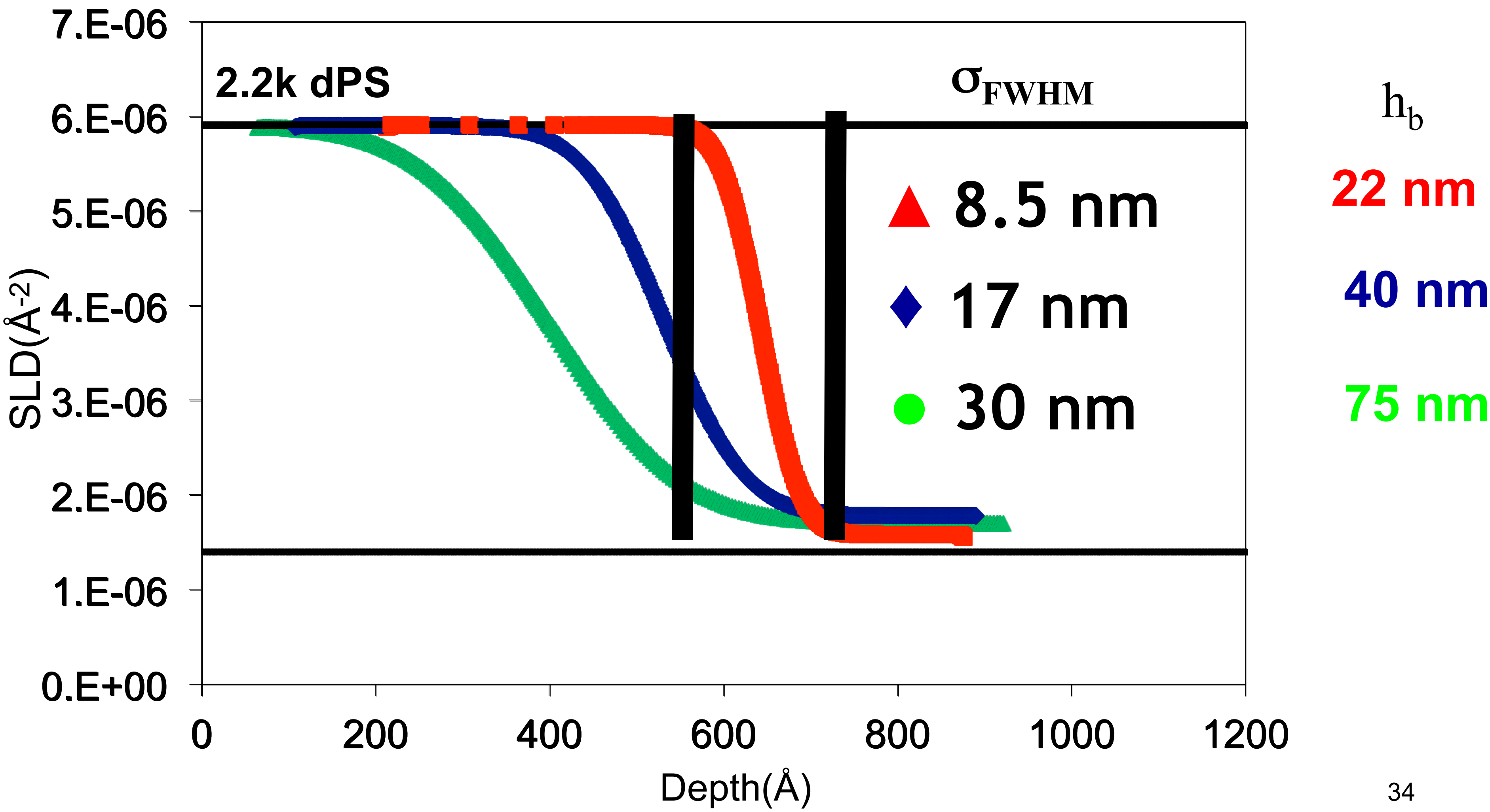


Representative NR and SLD

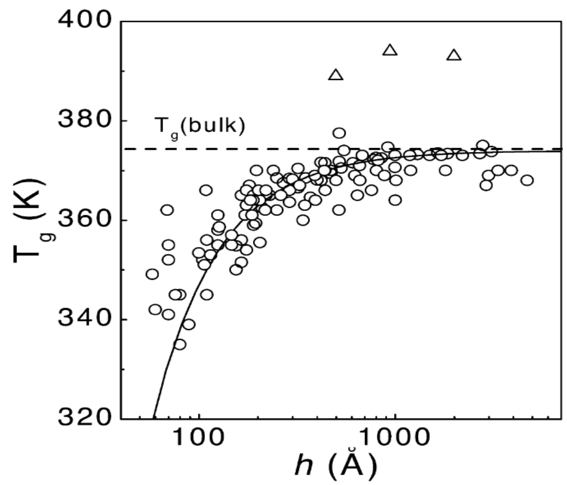


Interface Width Changes with h_b

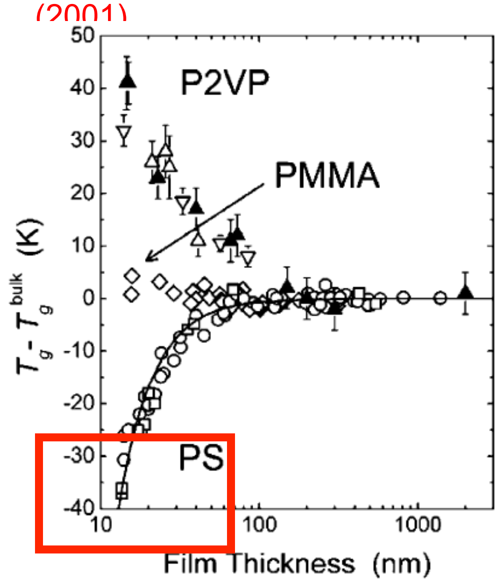
(h_u) fixed= 45 nm, 100 °C



Motivation

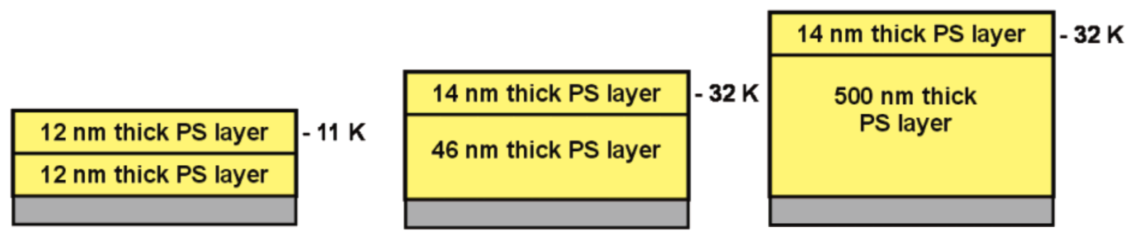


Forrest et al. *Adv. Coll. Interf. Sci.* 94, 167 (2001)



Roth et al. *Macromolecules* 40, 2568 (2007)

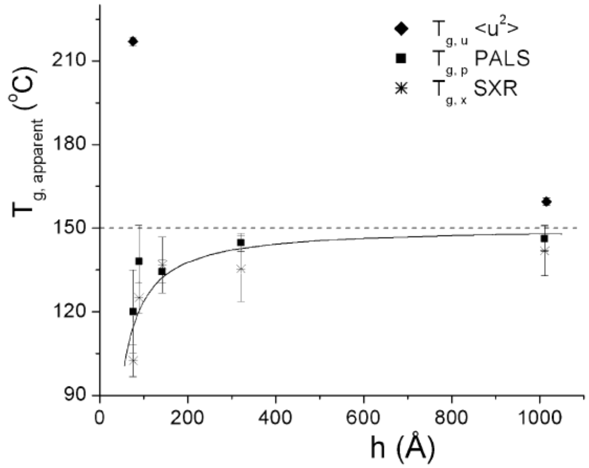
- Tg of PS thin films decreases as the film thickness decreases.
- If there is an attractive interaction between the film and the substrate then Tg of the film increases as the film thickness decreases.



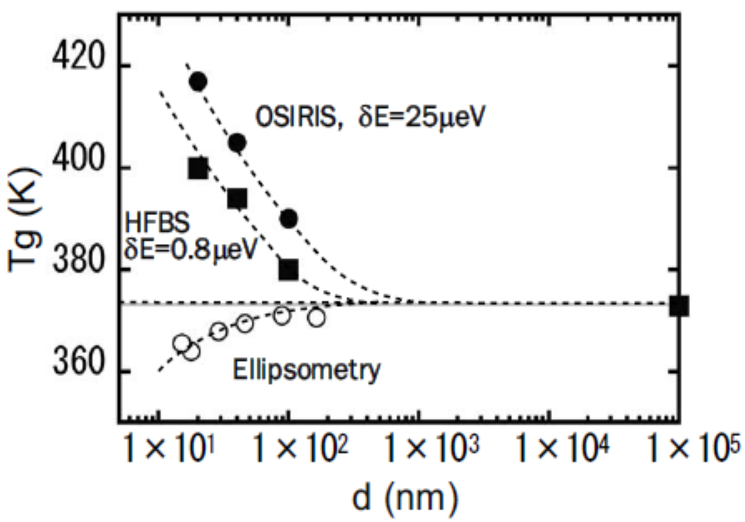
- Roth et al. showed that the Tg of 14 nm thick labeled PS layer decreases further if it is placed on top of 46 nm thick PS layer.

- Tg reduction in general is correlated with enhanced mobility in literature. Is this really true?

Motivation



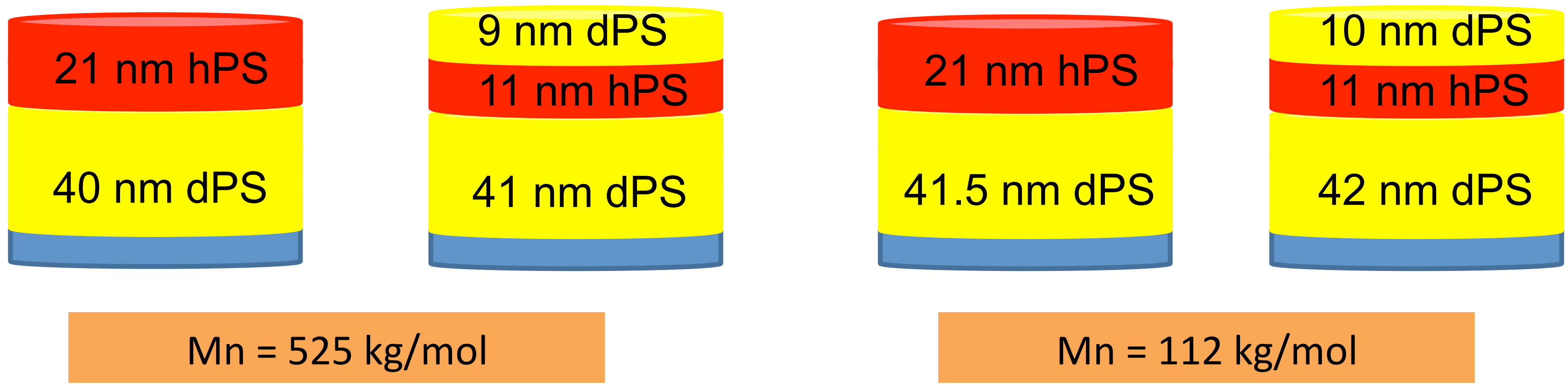
Soles, C. L. et al. *Macromolecules.* 37, 2890 (2004)



Inoue, R. et al. *Phys. Rev. E* 80, 031802 (2009)

- Determining Tg from specific volume, thermal expansion, heat capacity etc. is well established.
- It is not well established if the changes in these physical properties reflect the changes in molecular dynamics.
- For polycarbonate thin films apparent Tg decreases with film thickness (XR and PALS) but increases with film thickness obtained by INS measurements.

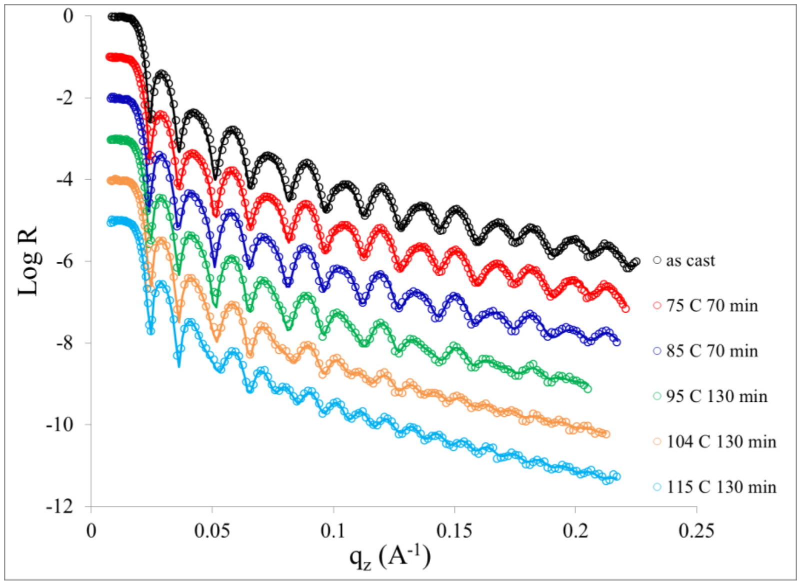
Bilayer and Trilayer Samples



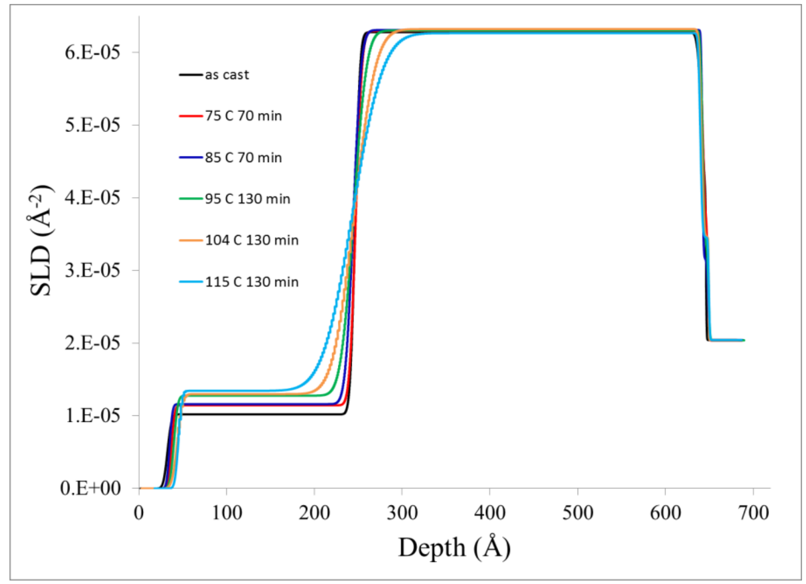
- Bottom layers are spun-cast onto HF-etched substrates and annealed at 150 C for 6 h.
- Top layers are floated onto water surface and picked up by bottom layers.
- Bilayer and trilayer samples dried overnight at 50 C.
- Samples are annealed between 68 C and 120 C for various times and quenched to RT before each neutron reflectivity (NR) measurements.
- Interdiffusion between the layers are monitored to elucidate if there is any depth dependent dynamics present.

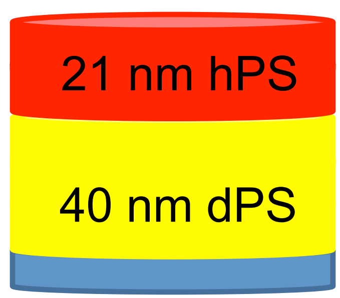
NR data and SLD profiles for Bilayer Sample

525k Bilayer Sample NR data



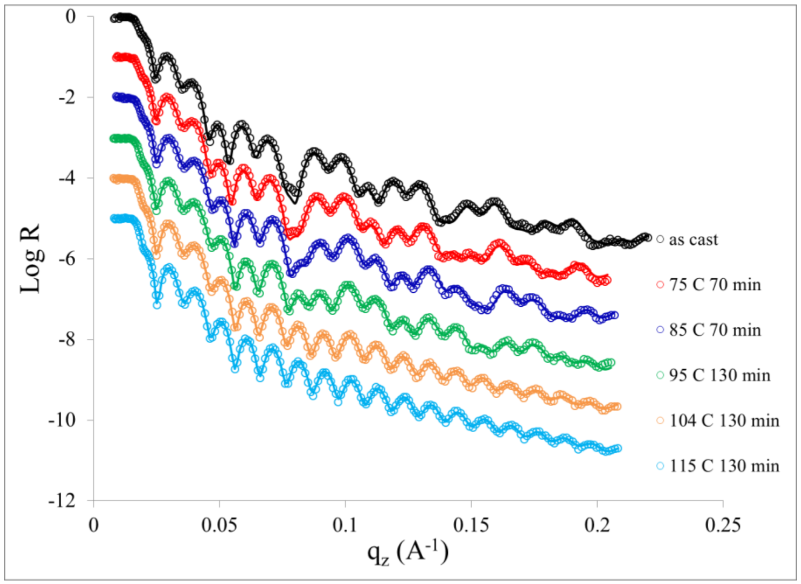
525k Bilayer SLD profile



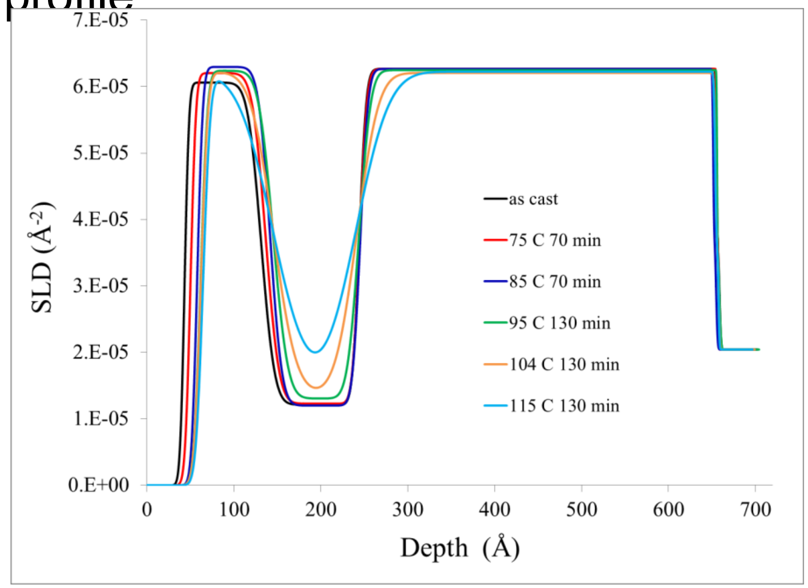


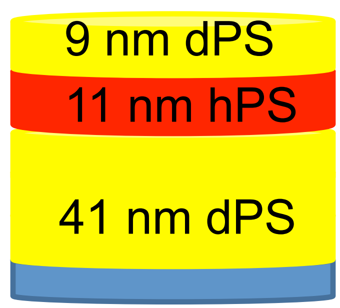
Reflectivity data and SLD profiles

525k Trilayer sample NR data



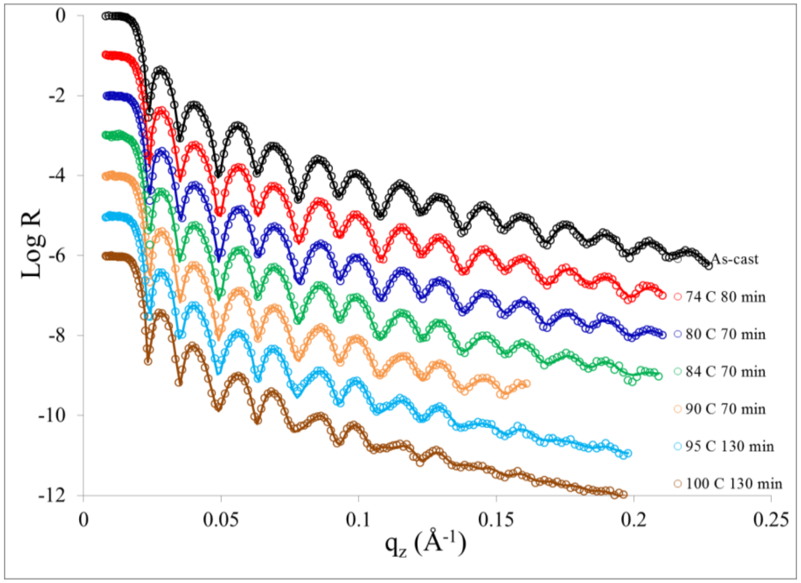
525k Trilayer sample SLD profile



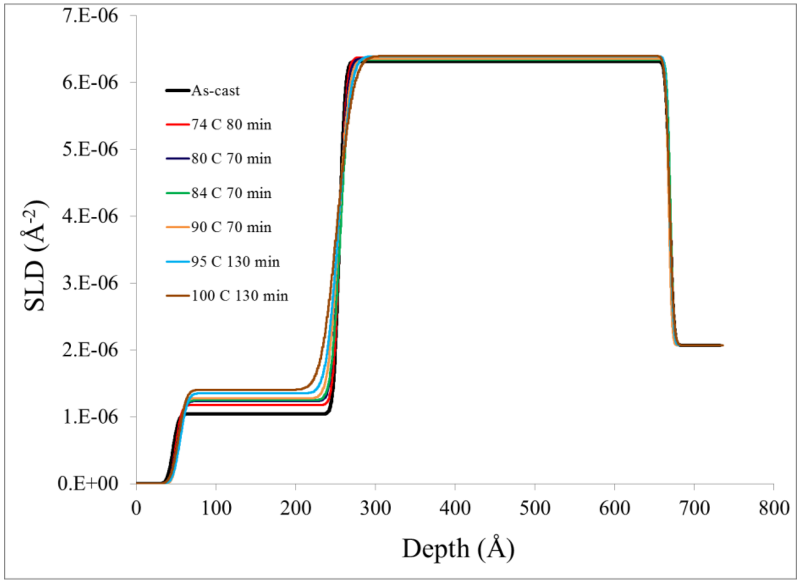


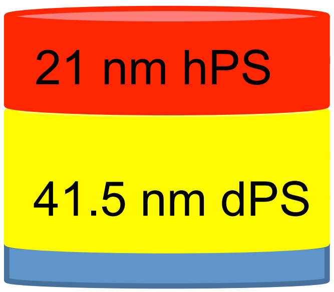
Reflectivity data and SLD profiles

112k Bilayer Sample NR data

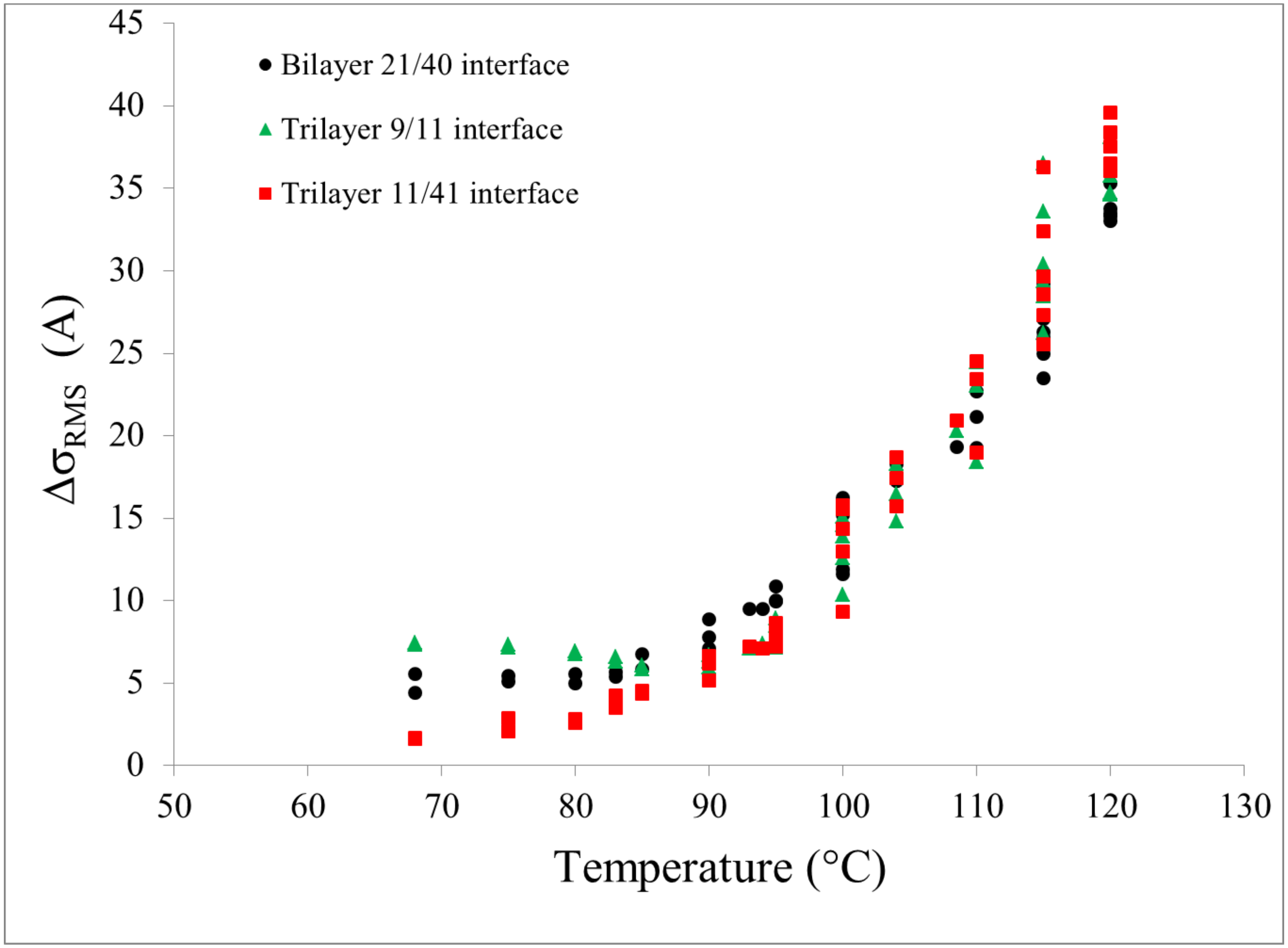


112k Bilayer SLD profile



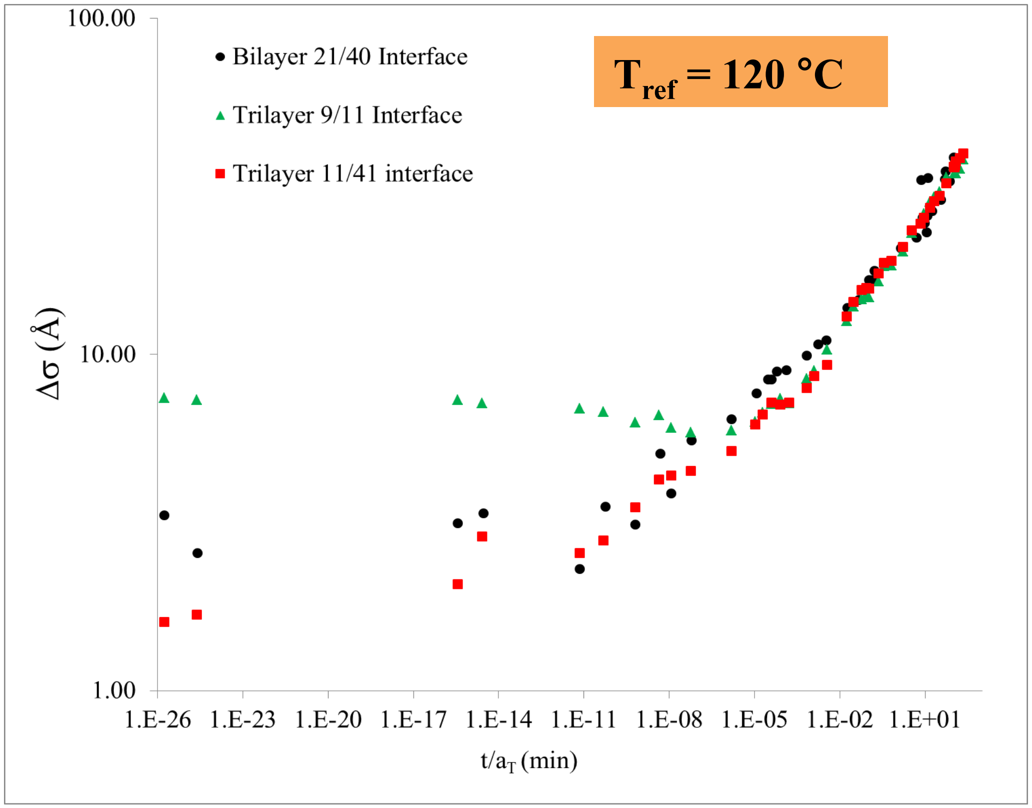


Interface broadening as a function of T



There is no detected molecular mobility till 90 -95 ° C

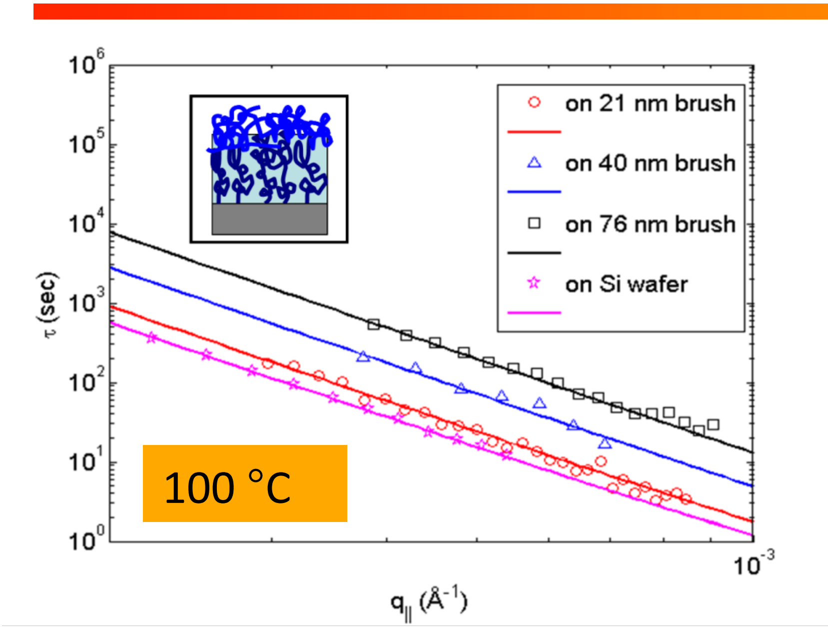
Molecular mobility is identical at both interfaces

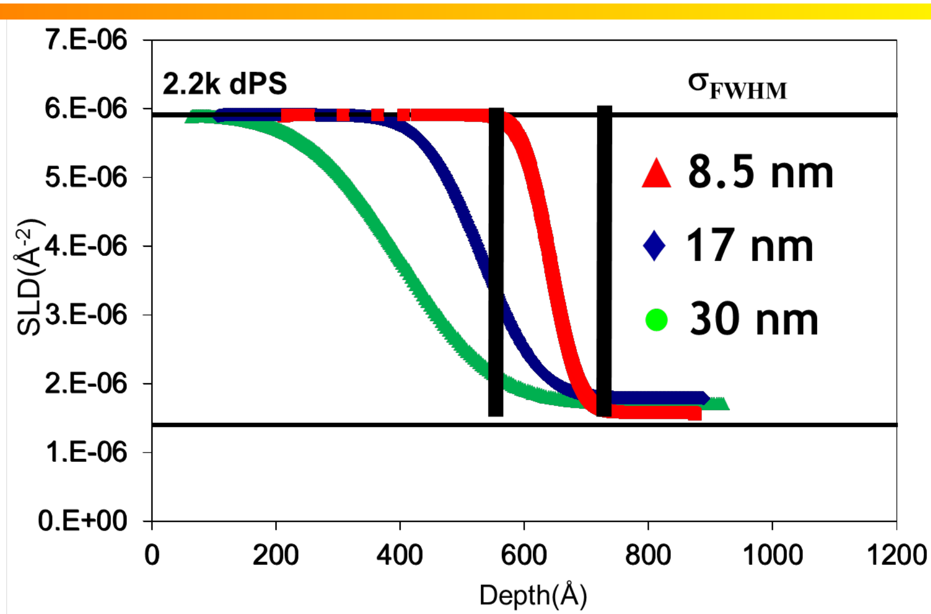


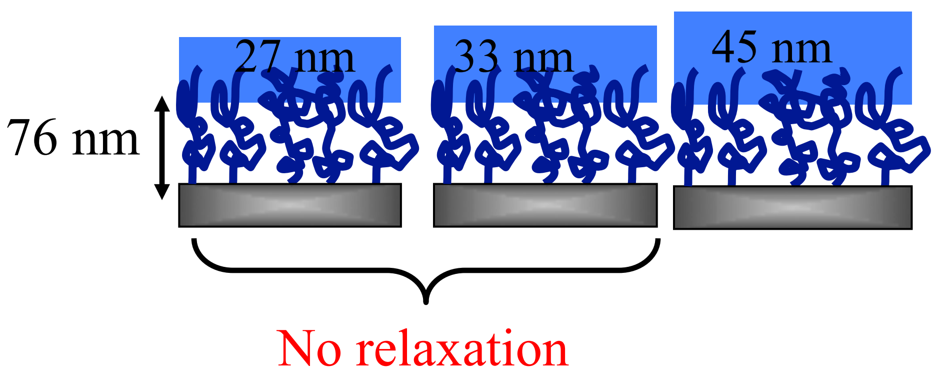
$$log a_T = \frac{-9.07\ (T\ - T_{ref})}{69.08 + (T - T_{ref})}$$

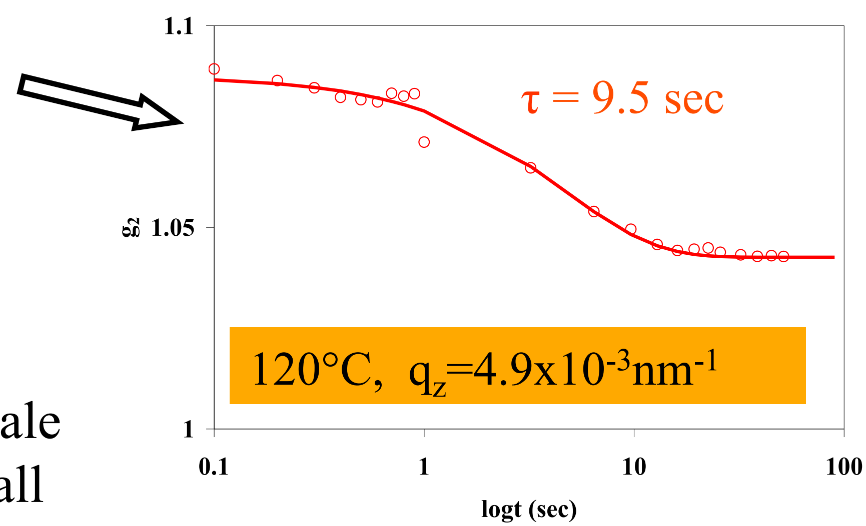
The molecular mobility at all three interfaces seems to be identical which argues against the reduced T_g.

XPCS and NR Results









No relaxation in XPCS length and time scale implies swollen brush is immobile since all of the 2.2k chains are inside the brush

Surface Dynamics of Polymer Brushes Swollen with Low Molecular Weight Chains

B. Akgün[1], G. Uğur[2], Z. Jiang[3], S. Narayanan[3], S. K. Satija[1], M. D. Foster[2]

1. NIST Center for Neutron Research, 2.Argonne National Lab, 3. Department of Polymer Science, University of Akron

- The objective is to elucidate the effect of underlying polymer brushes on the surface dynamics of spun cast chains and to determine whether swelling makes brush surface mobile.
- Thermally induced fluctuations are important for determining the surfaces' friction, wetting, and adhesion.
- The effect of tethering on surface dynamics is of scientific interest to elucidate how confinement of polymer chains changes their behavior near interfaces.
- Surface dynamics of 2.2k untethered polystyrene (PS) chains atop densely grafted PS brush are found to be equivalent to those of a layer of untethered chains on a rigid substrate when the layer thickness used fully excludes the region of interpenetration with the brush.
- Even when swollen with short chains to varying degrees the underlying brush plays the role of a rigid substrate in the experimentally accessible range of time and scattering vector.

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