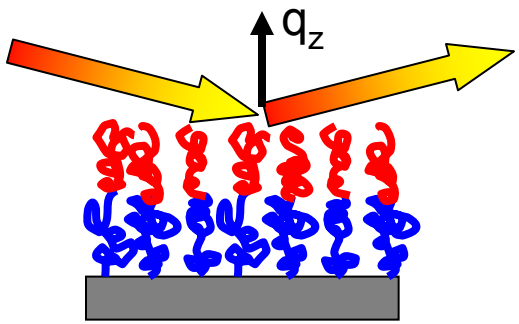
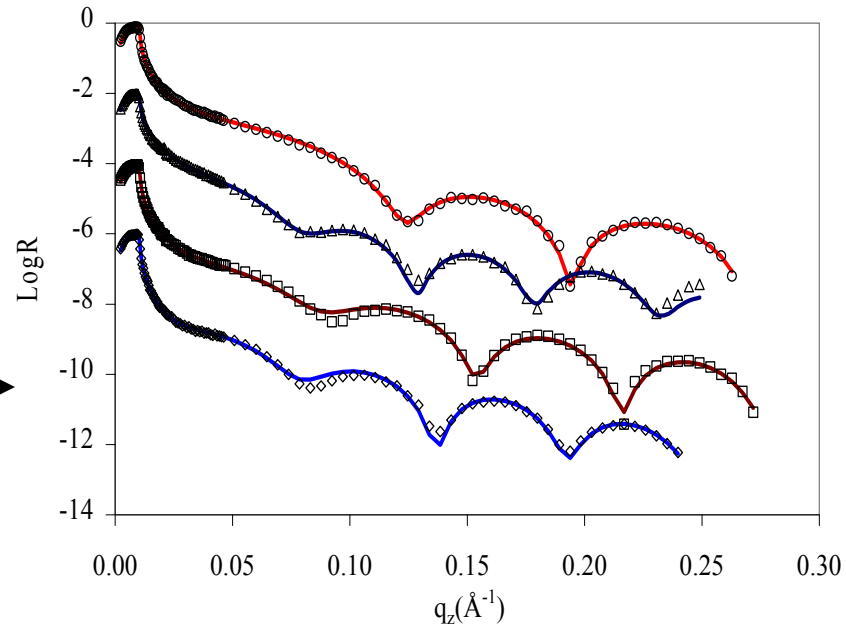
Polymers at Surfaces by Neutron Reflectivity





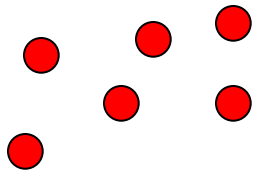
Bulent Akgun

NCNR Tutorial, April 22, 2009

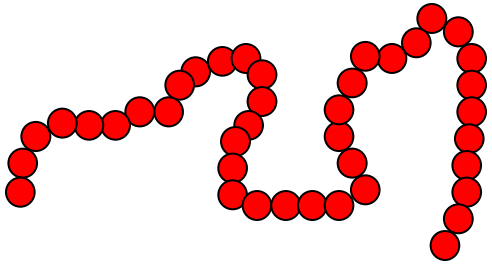
Outline

- Introduction
- Thin Polymer Films and Applications
- Why neutron reflectivity?
- Examples
  - Surface Dynamics of Untethered Chains on Chemically Identical Polymer Brushes
  - Supercritical CO_2 Swelling of Thin Polymer Films
  - Langmuir Study of Tethered Polymer Layers

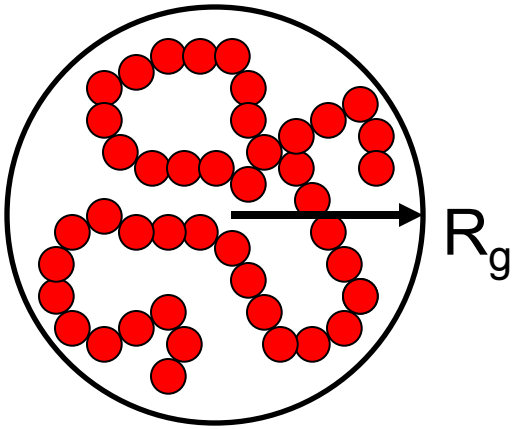
Polymers at Surfaces



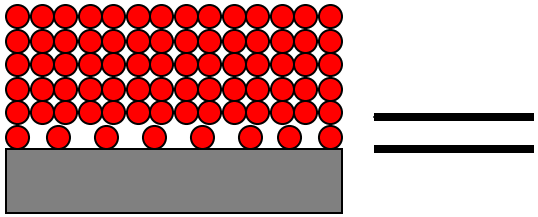
Monomers



Polymer

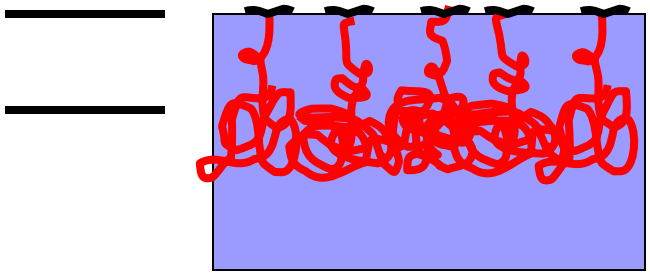


Molecular length scale



Small molecules at surfaces

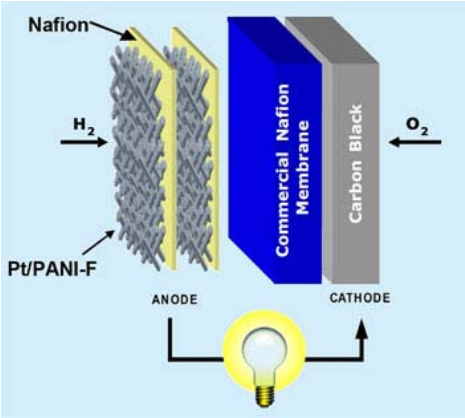
Length scale ~ Rg



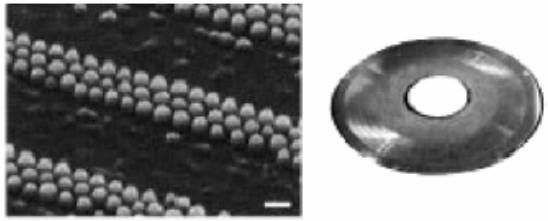
Polymers at surfaces

- Connectivity
- Configurational Entropy

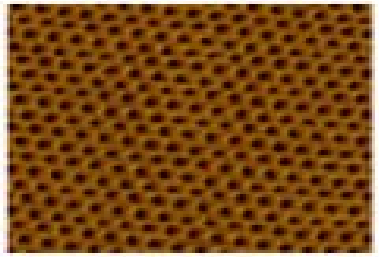
Applications of Polymer Thin Films



PEM for fuel cells

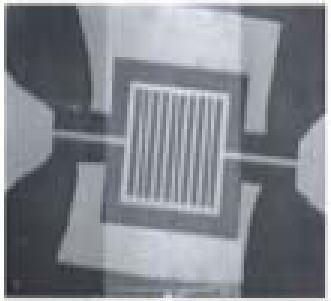


Nanotemplates for lithography

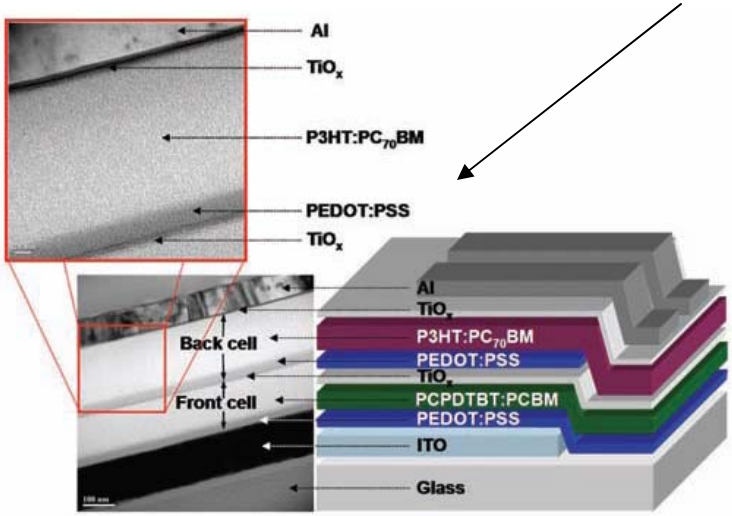


Sensors

Polymer film



Devices



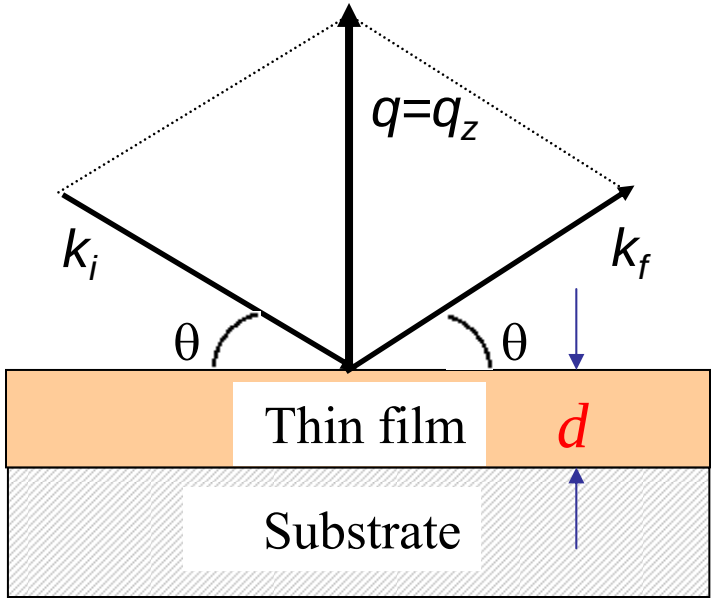
Polymer Solar Cells

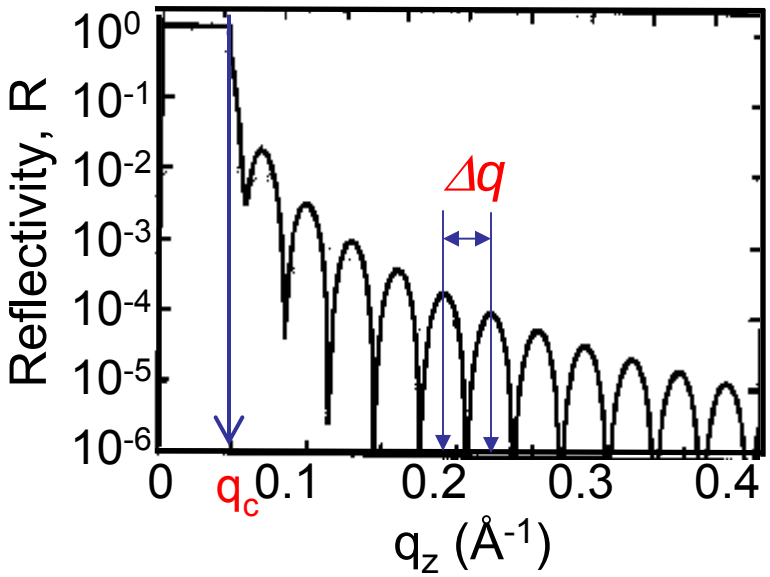
Coatings

Why Neutrons?

- Interact with nuclei not electrons
- Penetrates sample containment
- Sensitive to bulk and buried structure
- Simple interpretation – provides statistical averages
- Isotopic sensitivity (especially D and H)
- Non-destructive
- For multicomponent polymer systems it is the only way to obtain information about each component

Neutron reflectivity (NR)





- $q_z = 4\pi\sin(\theta)/\lambda$
- Kiessig fringes, $d=2\pi/\Delta q$
- Integrated roughness

Commonly Studied Scientific Polymer 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

Surface Dynamics of Free PS Chains on Chemically Identical Polymer Brushes: XPCS and NR Study

Gökçe Uğur, Bulent Akgun, Zhang Jiang, Suresh Narayanan, William J. Brittain, Sushil Satija, Mark D. Foster

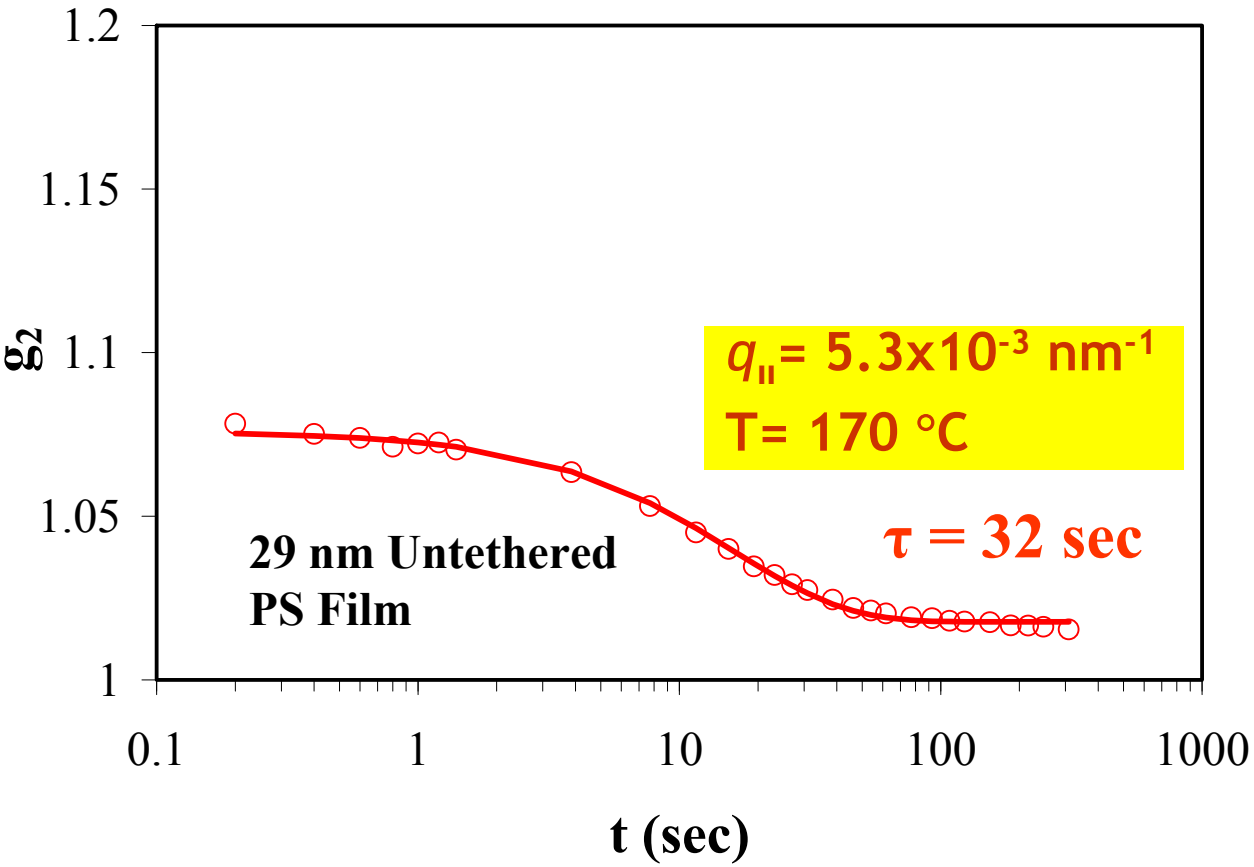
DEPARTMENT OF
POLYMER SCIENCE

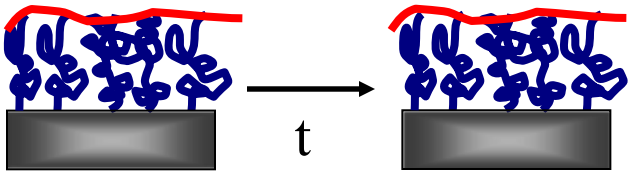
The University of Akron

Argonne NATIONAL LABORATORY

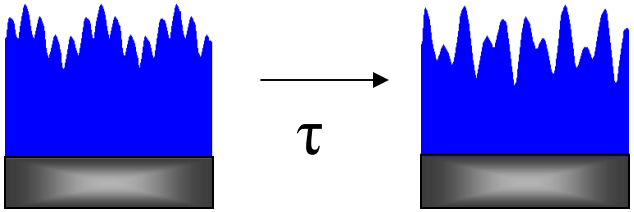
NIST Center for Neutron Research

Dynamics of PS Brushes are NOT Resolvable





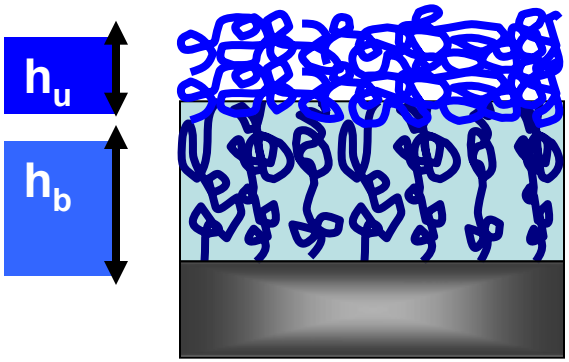
+1000 sec



- **thickness** (9 -100 nm)
- **wave-vector** (600nm - 3μm)
- **temperature** (T_g+ 130 ºC)
- **grafting density** (σ = 0.1 - 0.6 chains/nm^2)

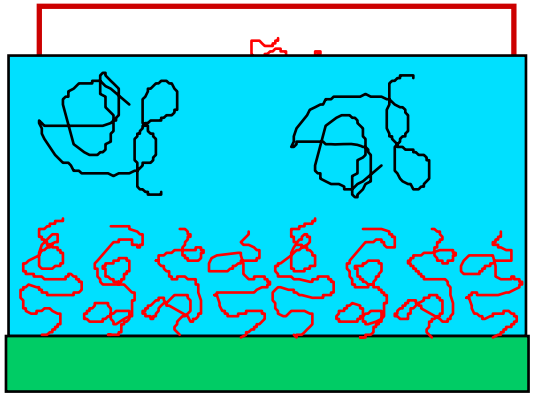
Objective

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

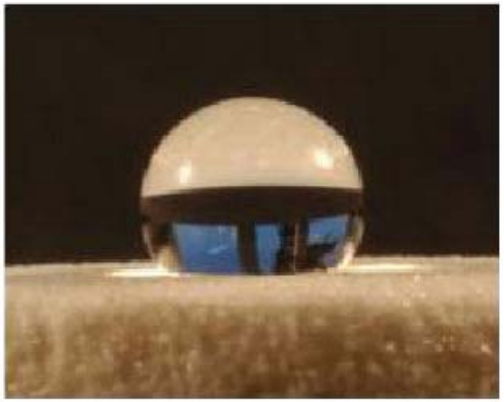


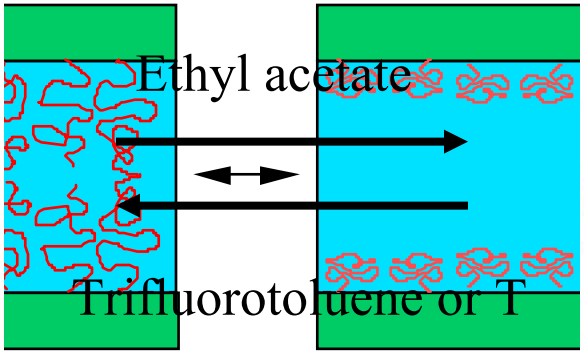
- ✓ **Brush thickness (h_b)**
- ✓ **Brush grafting density (σ)**
- ✓ **Untethered chain layer thickness (h_u)**

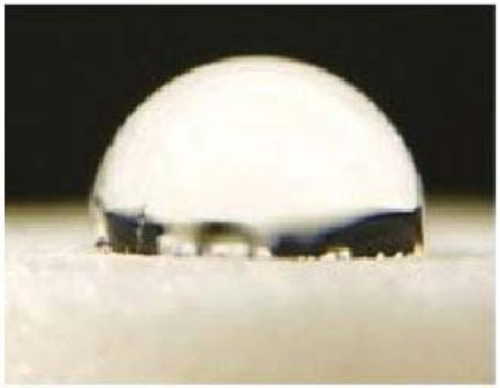
Applications of Polymer Brushes



- Stabilize colloids
- Create protein resistant surfaces
- Control solvent flow in microchannels
- Control adhesion, lubrication and wetting
- Create stimuli-responsive surfaces





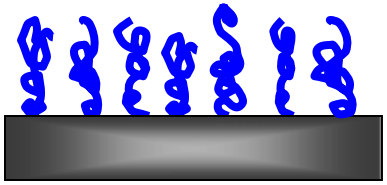


PMA-*b*-PPFA $\theta_S = 135^\circ$

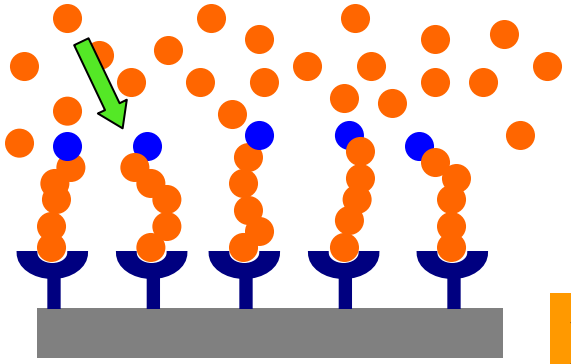
PMA-*b*-PPFA $\theta_S = 90^\circ$

Polymer Brush Synthesis

Homopolymer Brushes



d-PS, PS

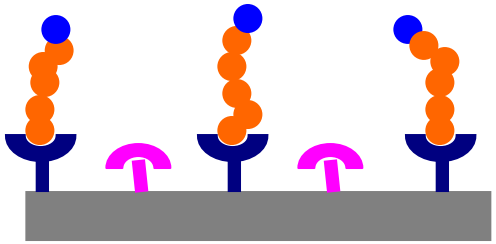


"Grafting from" technique is used

Atom transfer radical polymerization (ATRP)

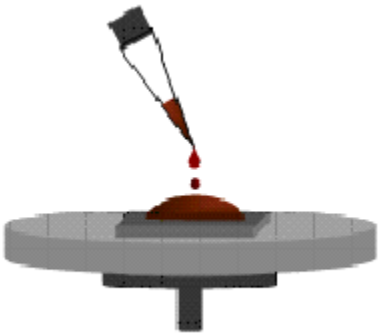
High grafting densities (~ 0.6 chains/nm^2)

For lower grafting densities (0.1-0.4 chains/nm^2) mixed monolayers are used.

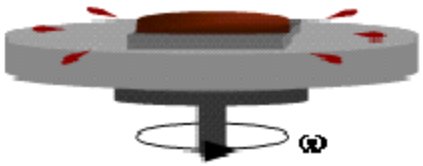


Preparation of Bilayer Samples

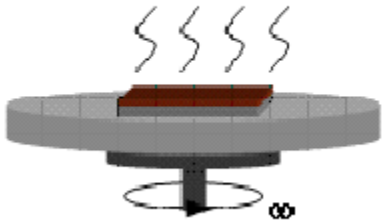
Spin-coating



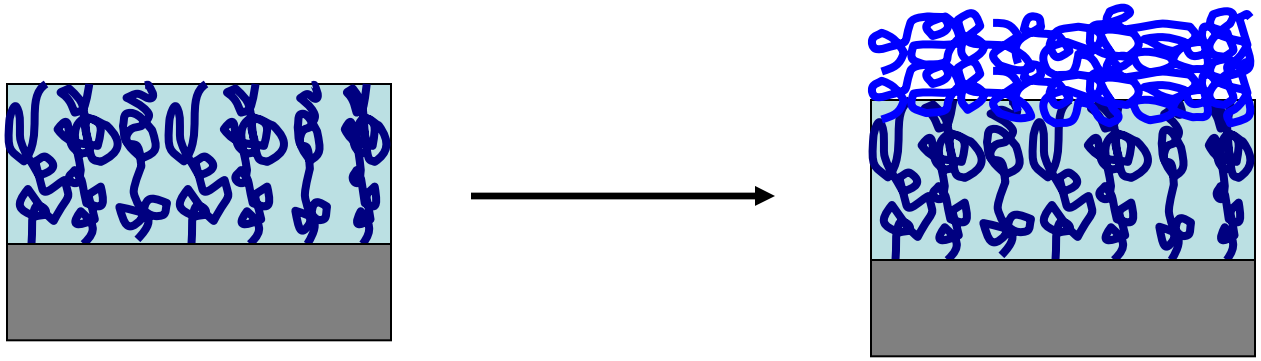
Dispense



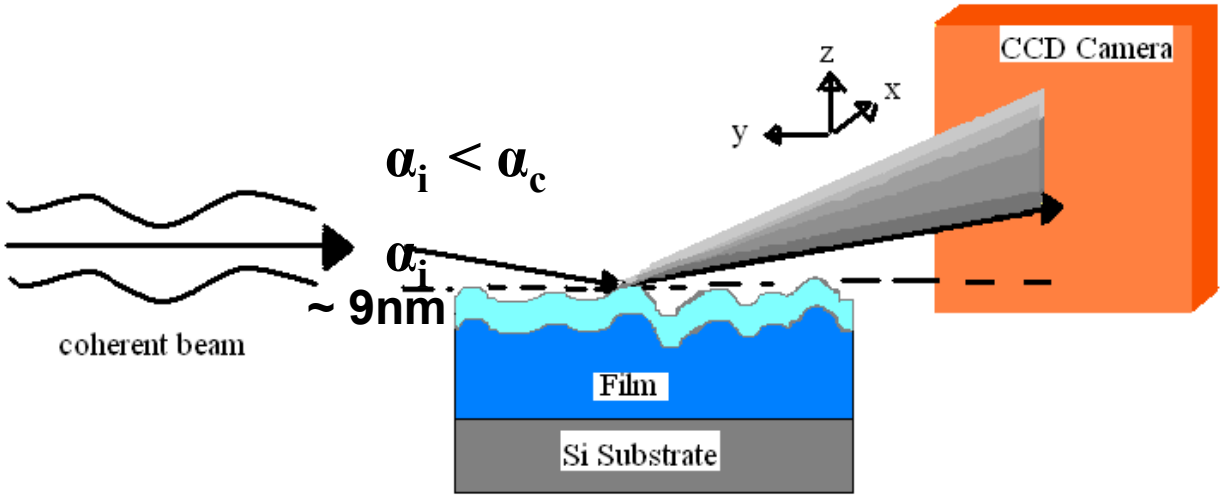
Ramp-up speeding

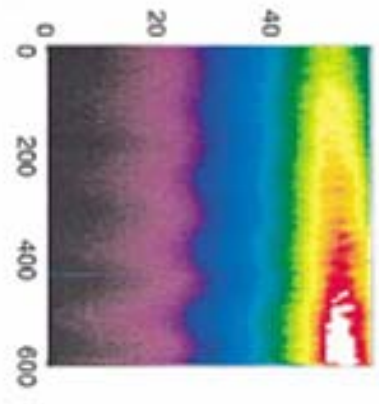


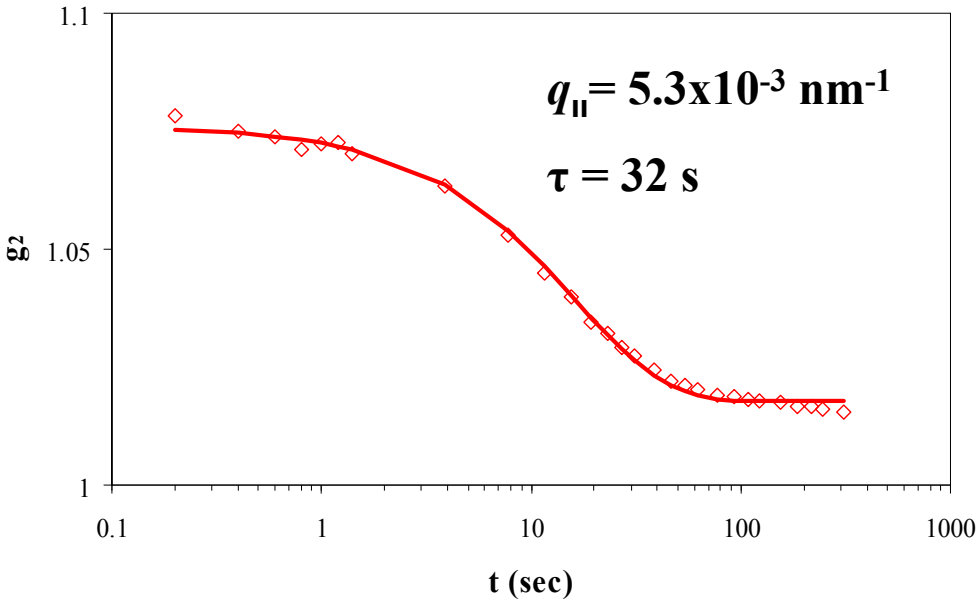
Constant drying



X-ray Photon Correlation Spectroscopy





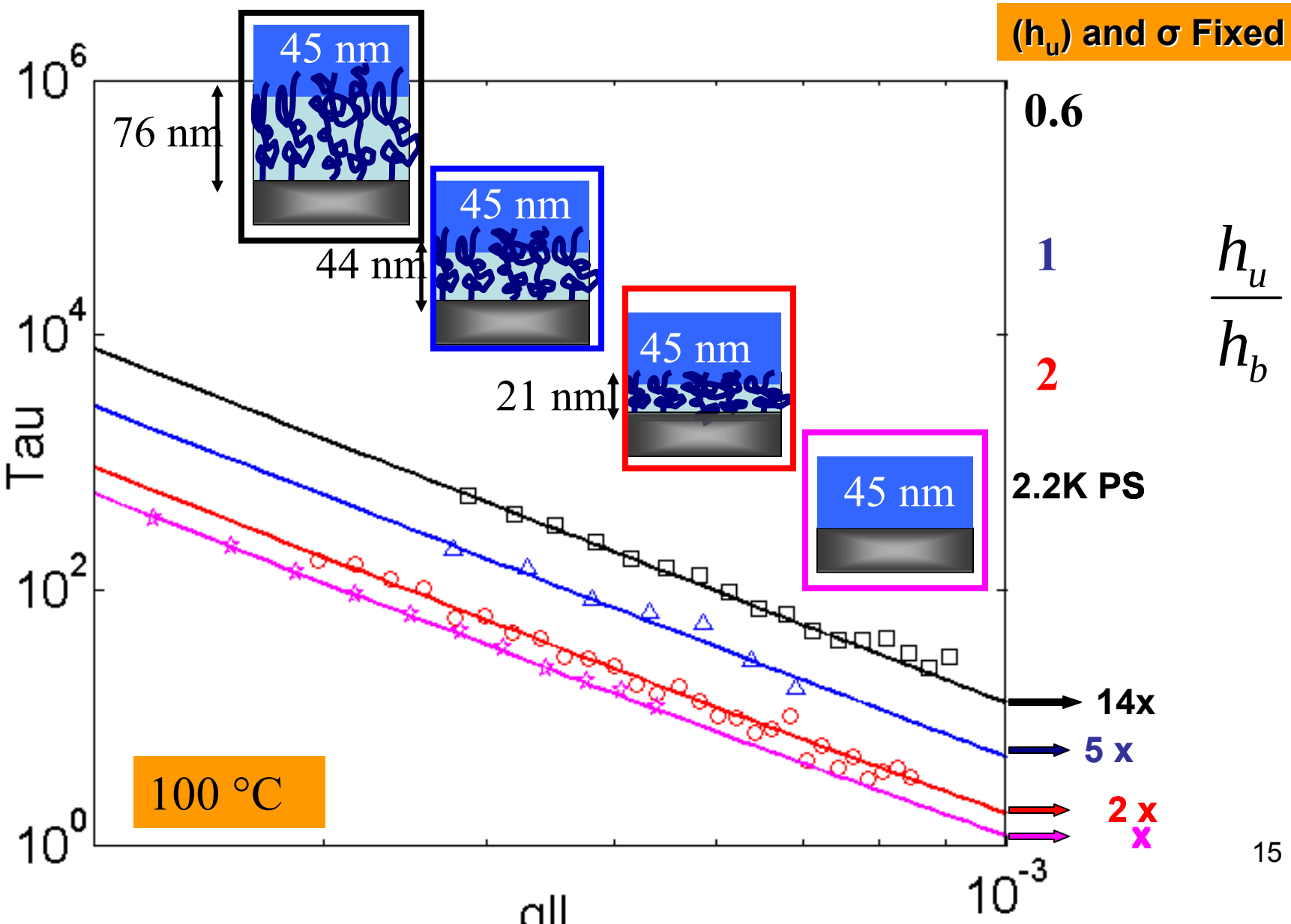


$$g_2(q,t) = \frac{< I(q,t')I(q,t'+t) >}{< I(q,t') >^2}$$

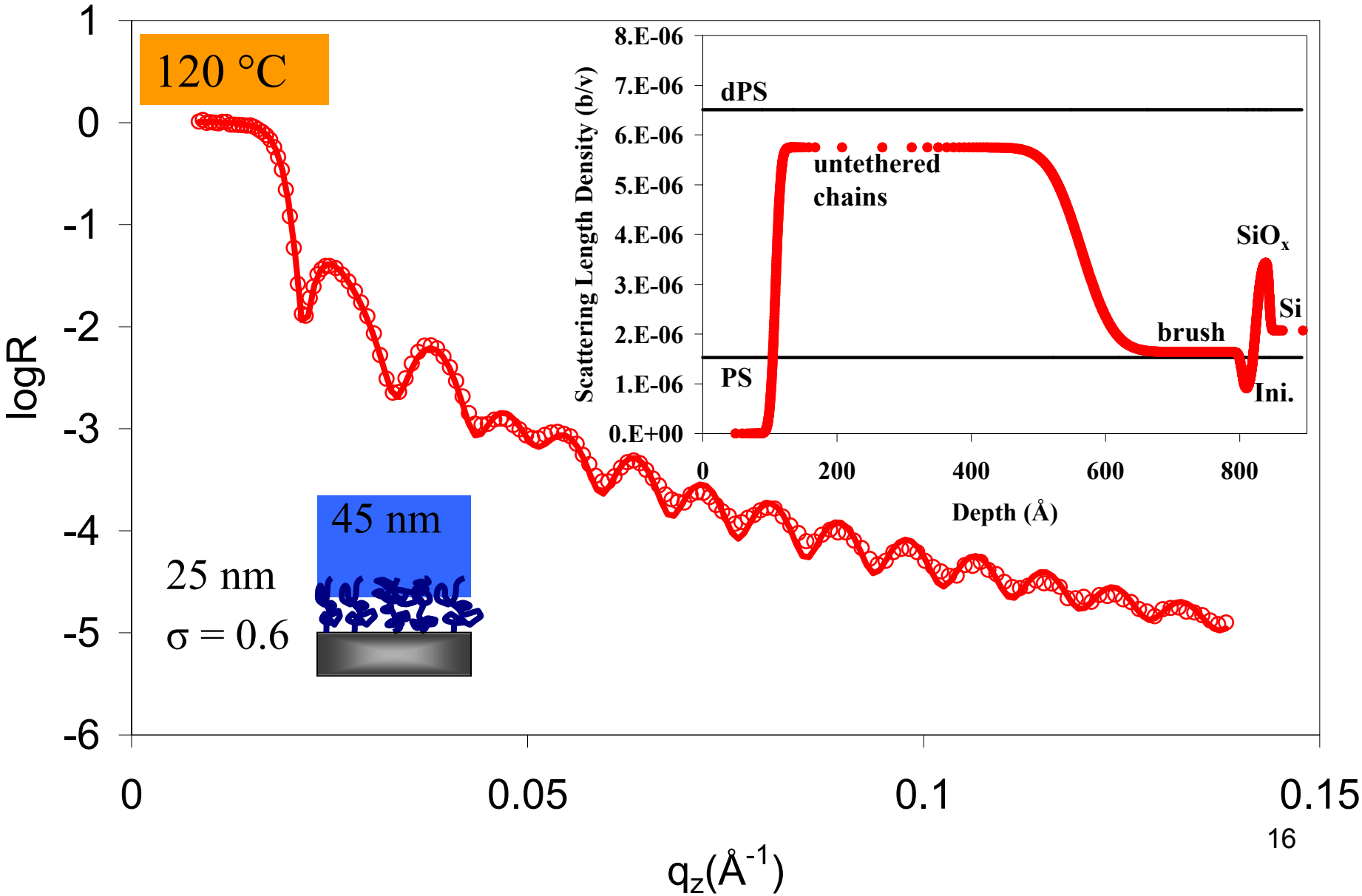
$$g_2 = 1 + \beta \exp(-2t/\tau)$$

$\beta =$ speckle contrast

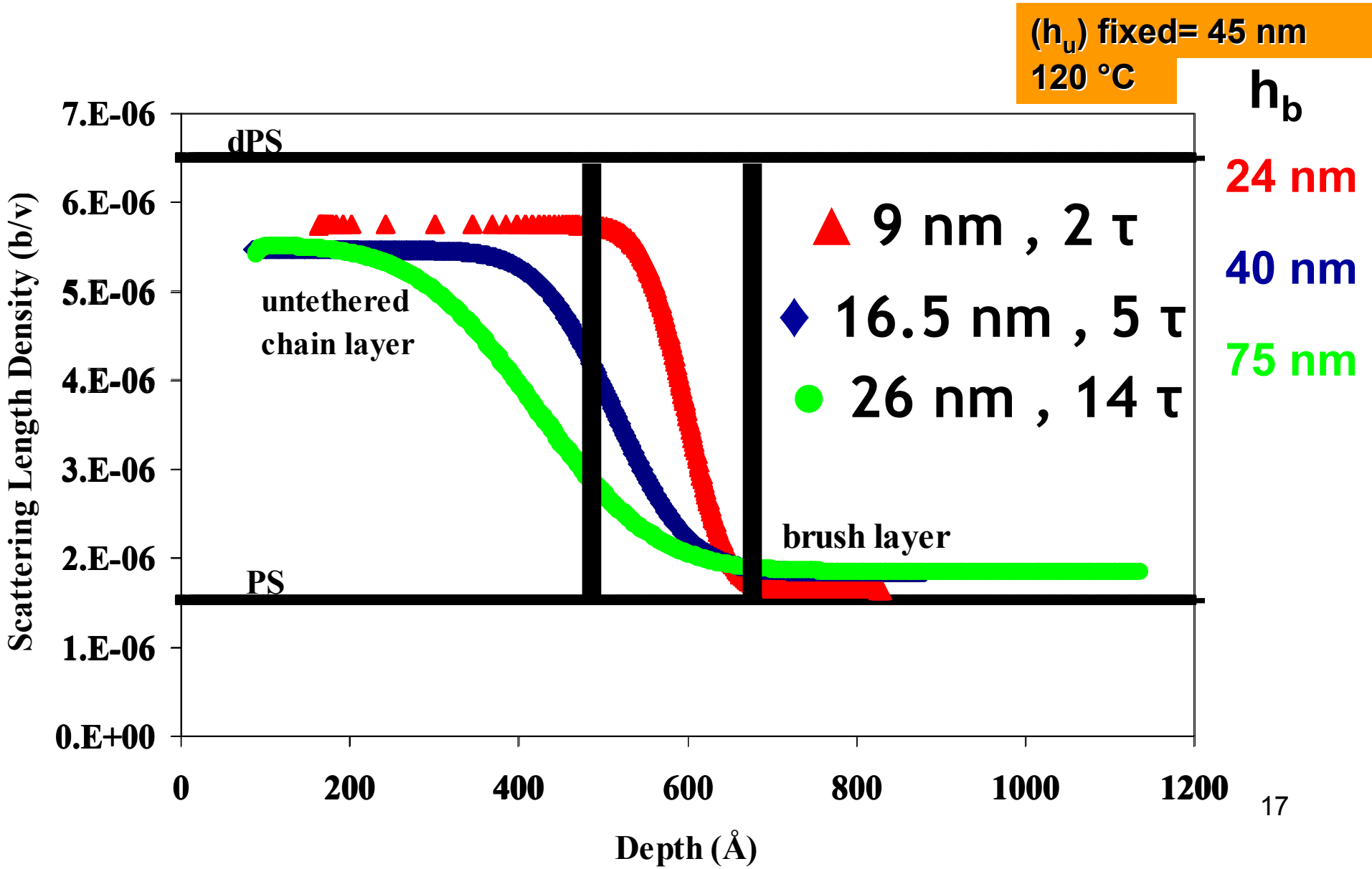
τ increases with increasing Brush Thickness



Representative NR and SLD profile

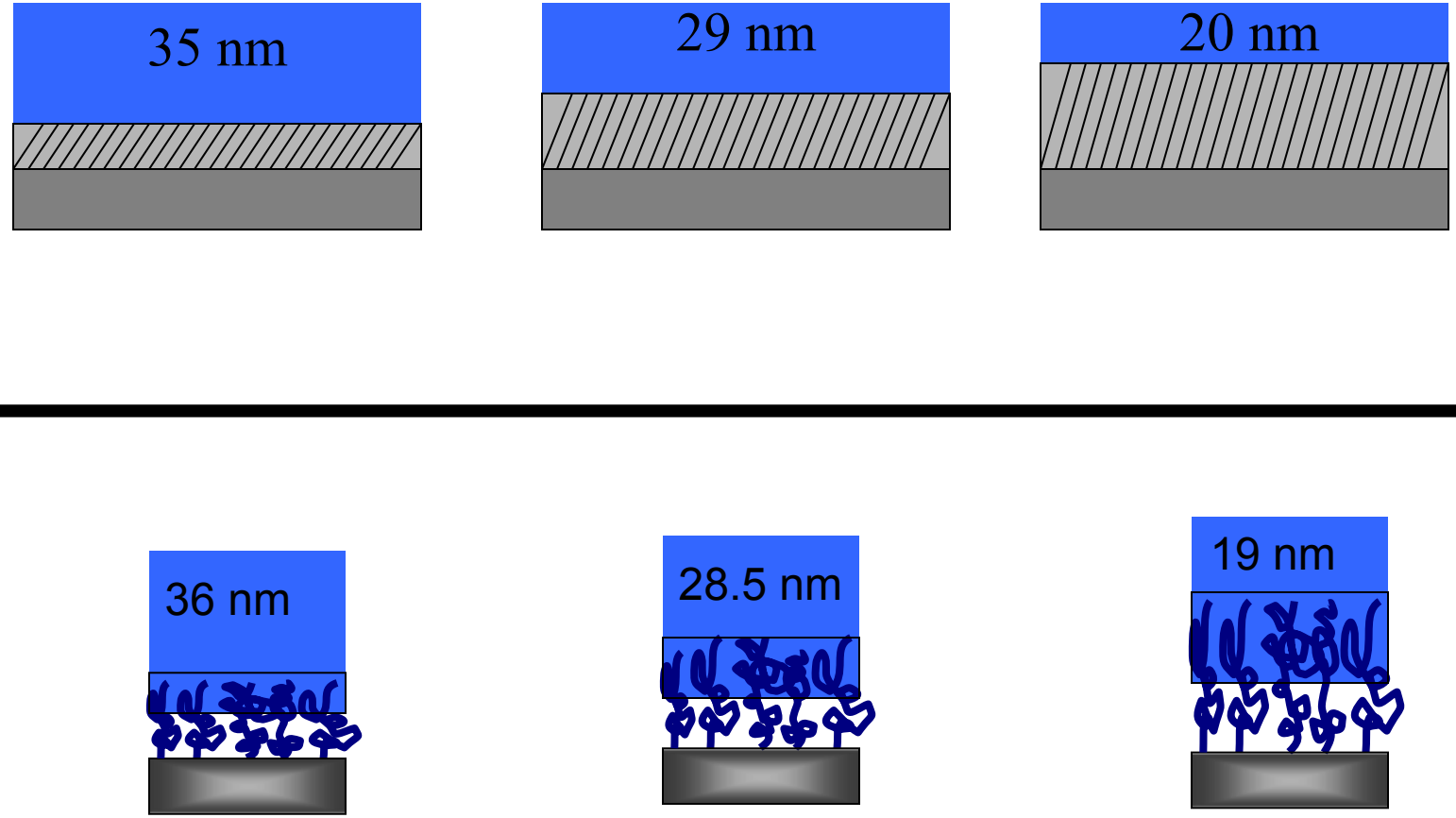


Interface Width Increases with h_b

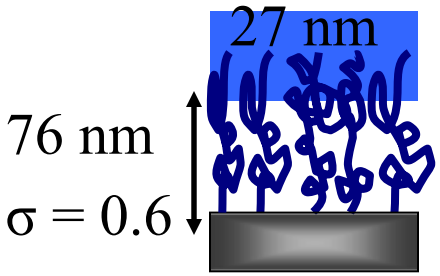


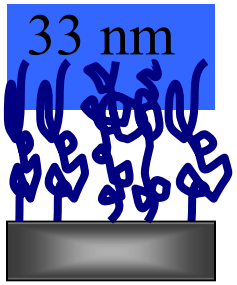
Effective Thicknesses

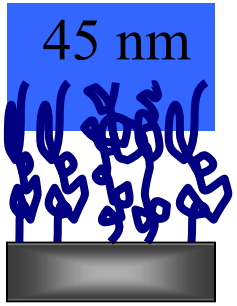
	21 nm brush	44 nm brush	76 nm brush
XPCS	35 nm	29 nm	20 nm
NR	36 nm	28.5 nm	19 nm



τ changes with h_u



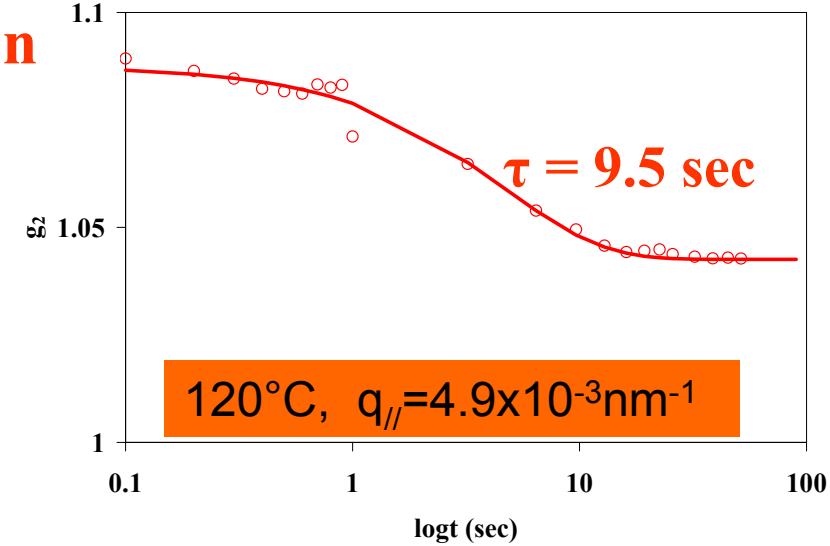




$$\frac{h_u}{h_b}$$

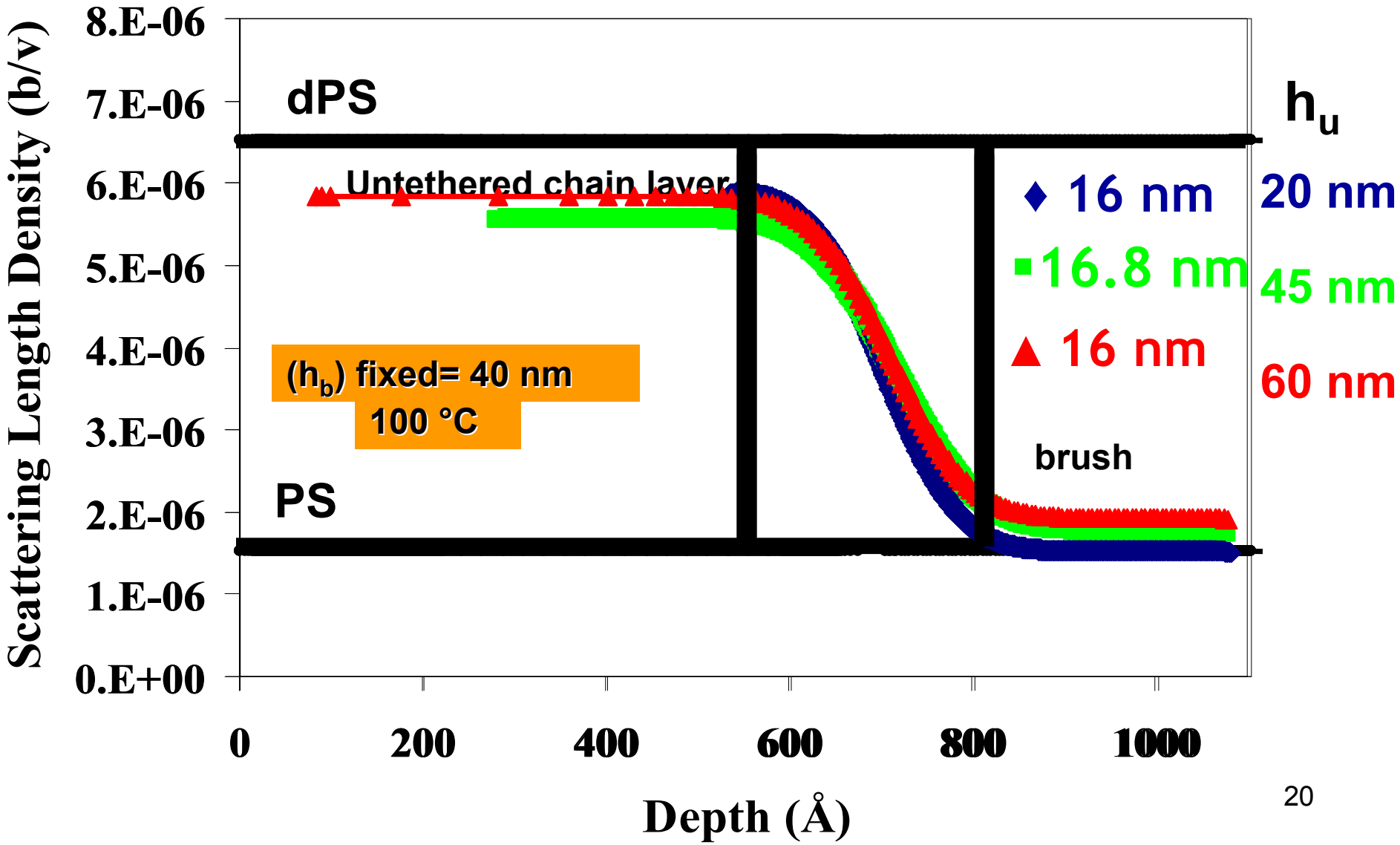
0.3 **0.4** **0.5**

No relaxation **No relaxation**

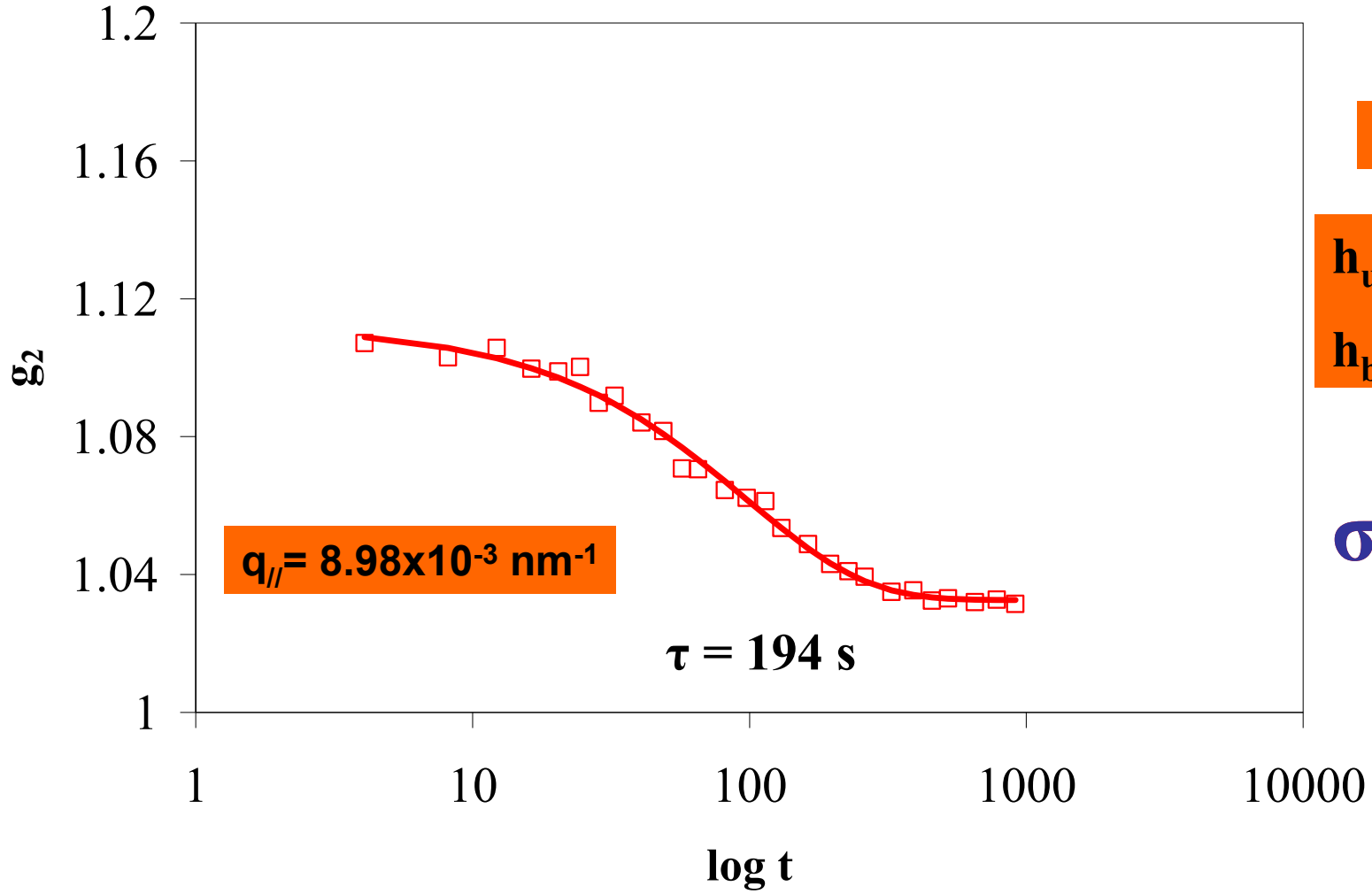


(h_b) and σ Fixed

Interface Width does NOT Change with h_u



τ increases with Decrease of σ



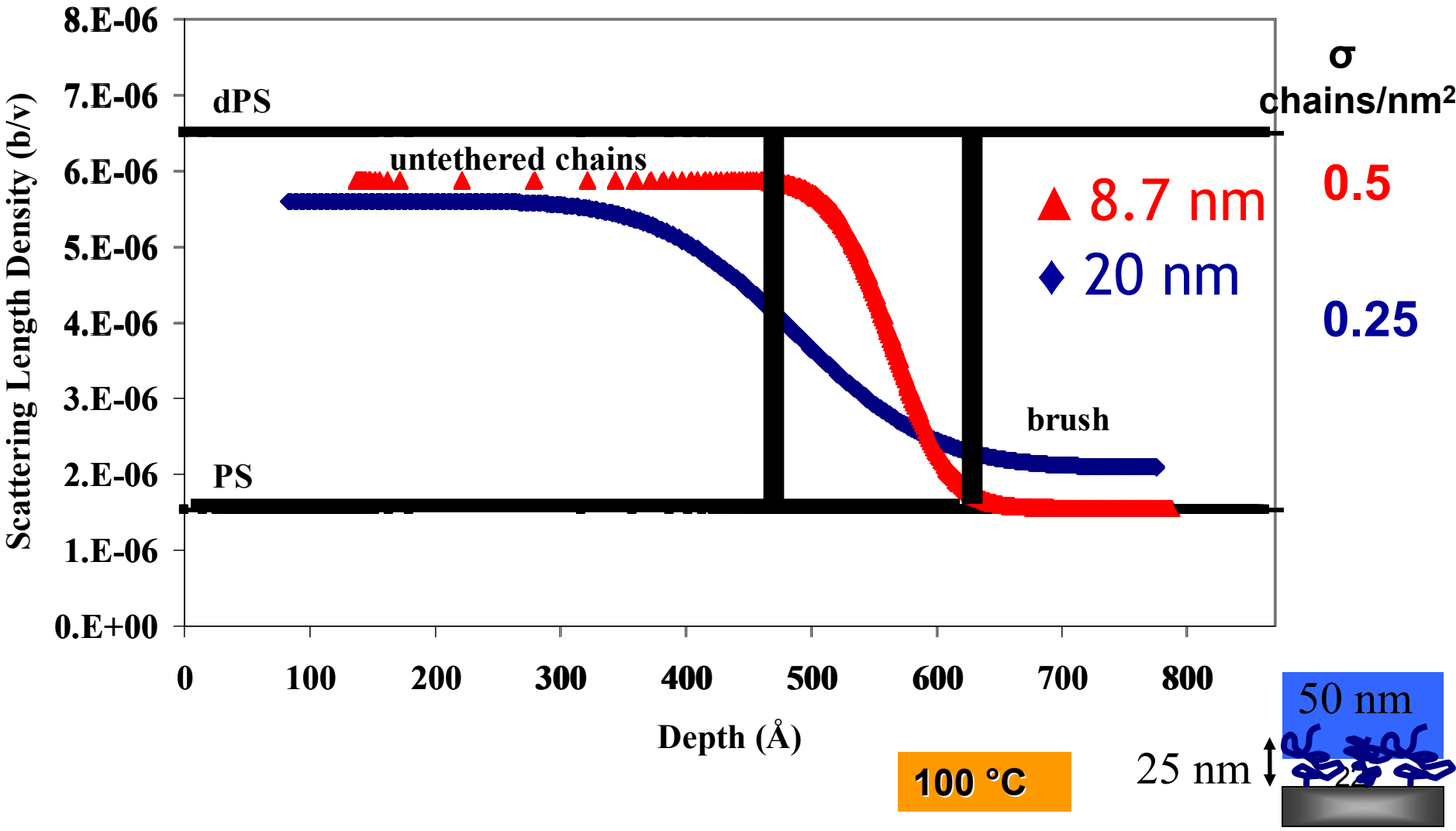
90°C

h_u = 46 nm

h_b = 45 nm

$\sigma = 0.2$

Interpenetration Depth for Lower σ



Summary

- **Brushes slows down dramatically surface dynamics of untethered chains. Untethered chain thickness, brush thickness and grafting density are important for bilayer films.**

- **Increase in brush thickness**
  decrease in grafting density,
  increases penetration depth of free chains and
  increases τ constants.

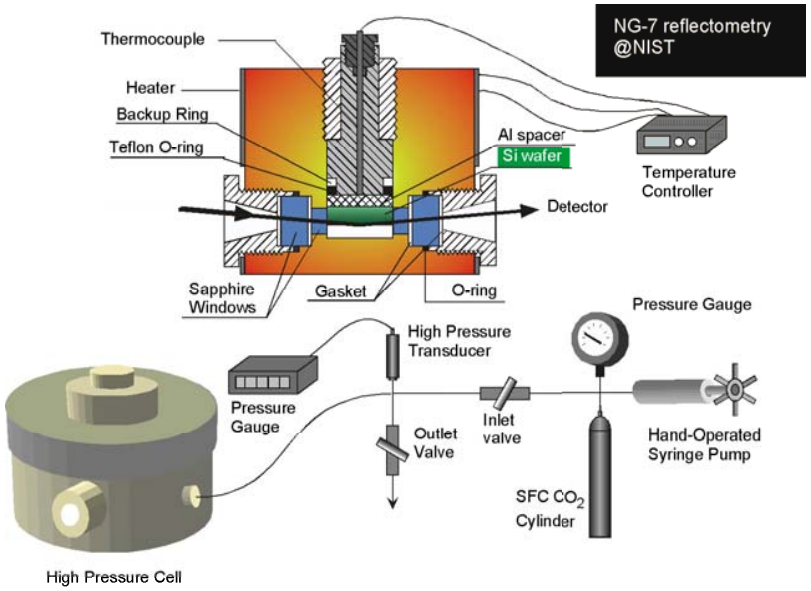
- **Surface dynamics of bilayers are determined by the characteristics of the brush layer.**

Density Fluctuation Induced Swelling of Polymer Thin Films in $scCO_2$

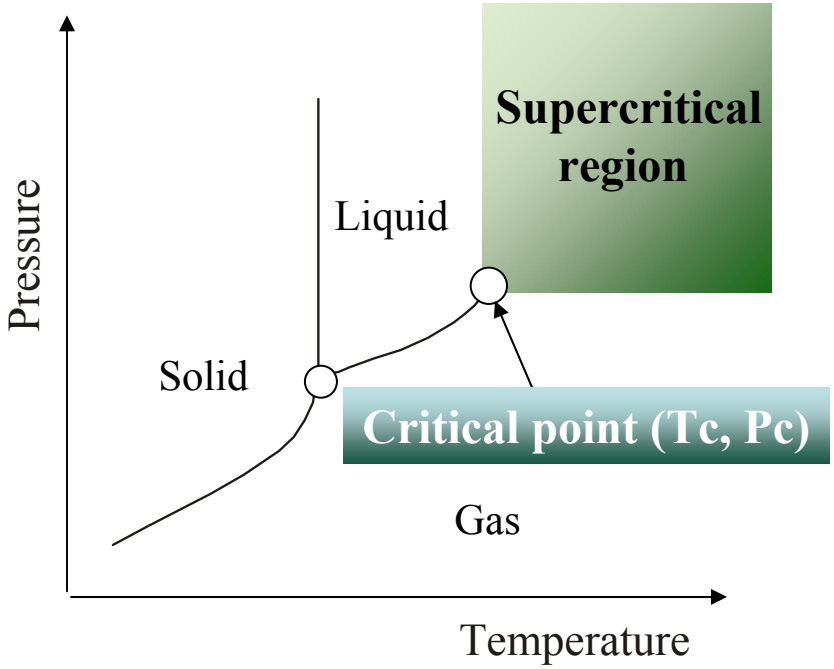
T. Koga, Y.S. Seo, K. Shin, M. H. Rafailovich, J. C. Sokolov, S. K. Satija

STONY BROOK UNIVERSITY

NIST Center for Neutron Research



Supercritical Fluids (SCFs)



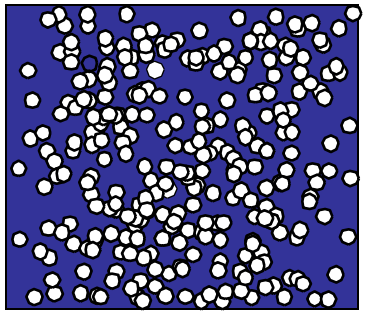
Tc: critical temperature
Pc: critical pressure

Substance	T_c(°C)	P_c(MPa)
CO_2	31.3	7.38
H_20	374.1	22.03
NH_3	132.5	11.39

Rayleigh scattering

T<Tc, P<Pc T≈Tc, P≈Pc T>>Tc, P>>Pc

<Two phases> <SCF region>



Inhomogeneous media with high and low-density region

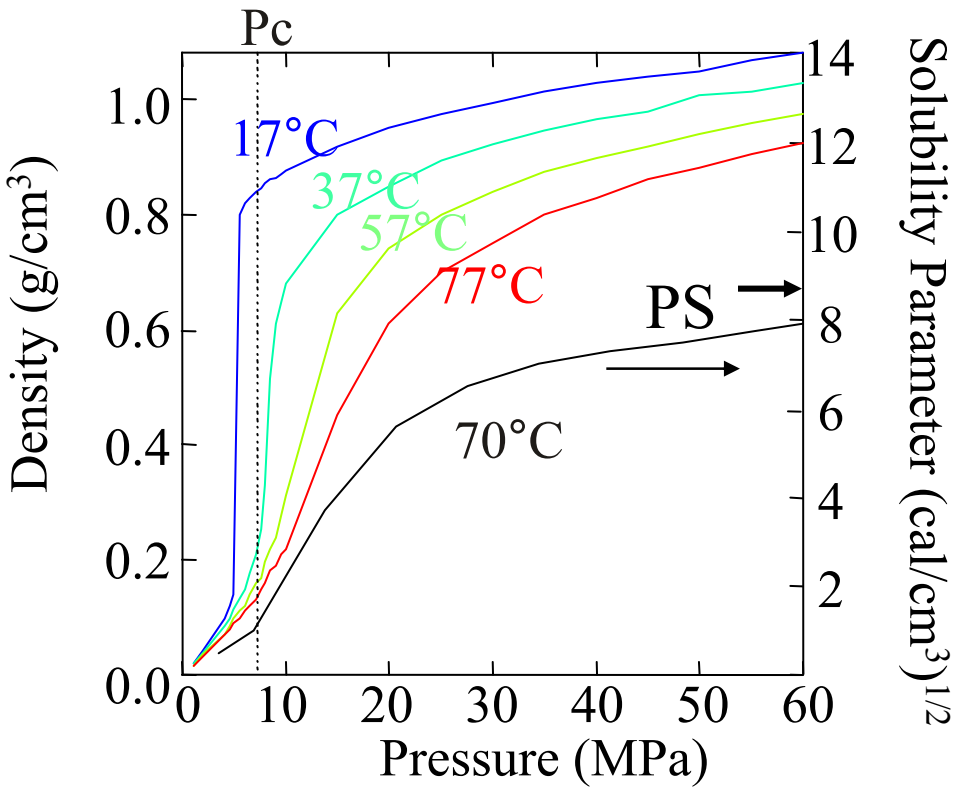
Why are supercritical fluids "super" ?

1. Environmental reasons

> 30 billion pounds of organic and halogenated solvents/year are used.

ScCO2 and water are developed to reduce the above

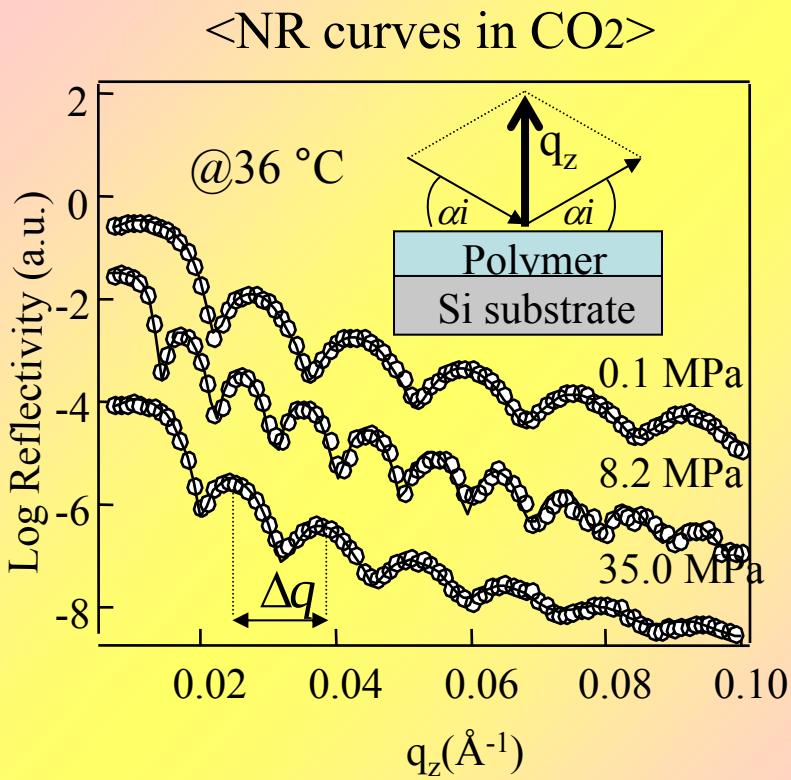
2. Unique physical properties : Density changes widely and drastically



Macroscopic features of SCFs, such as gaslike diffusivity and viscosity with liquid like density, originate from the microscopic structures in SCFs.

High Pressure Neutron Reflectivity (NR)

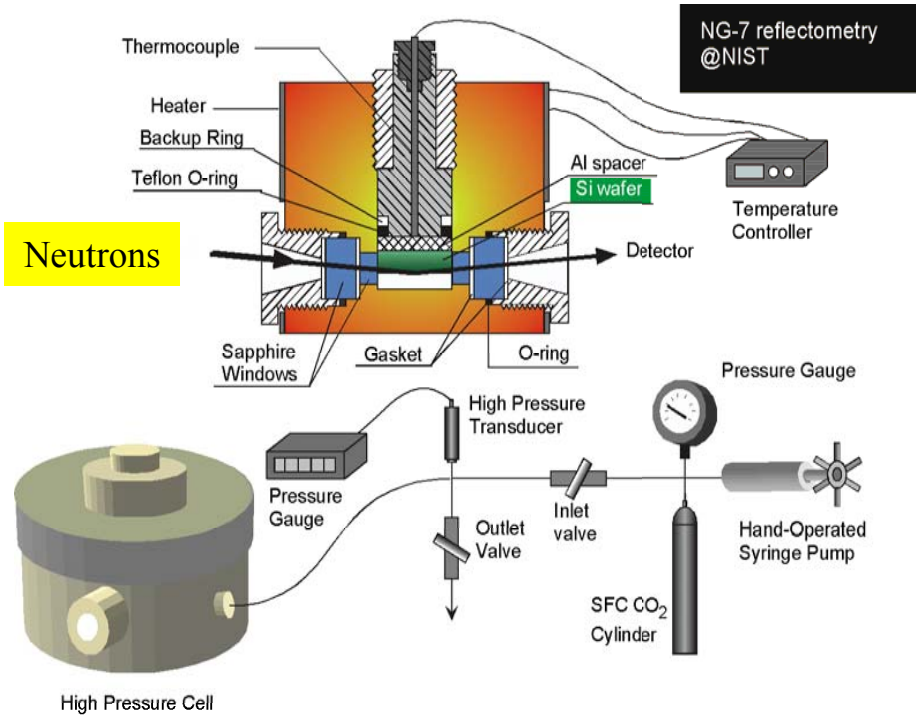
~Ideal tool to determine the in-situ film quality under compressed gases ~



$D = 2\pi/\Delta q$

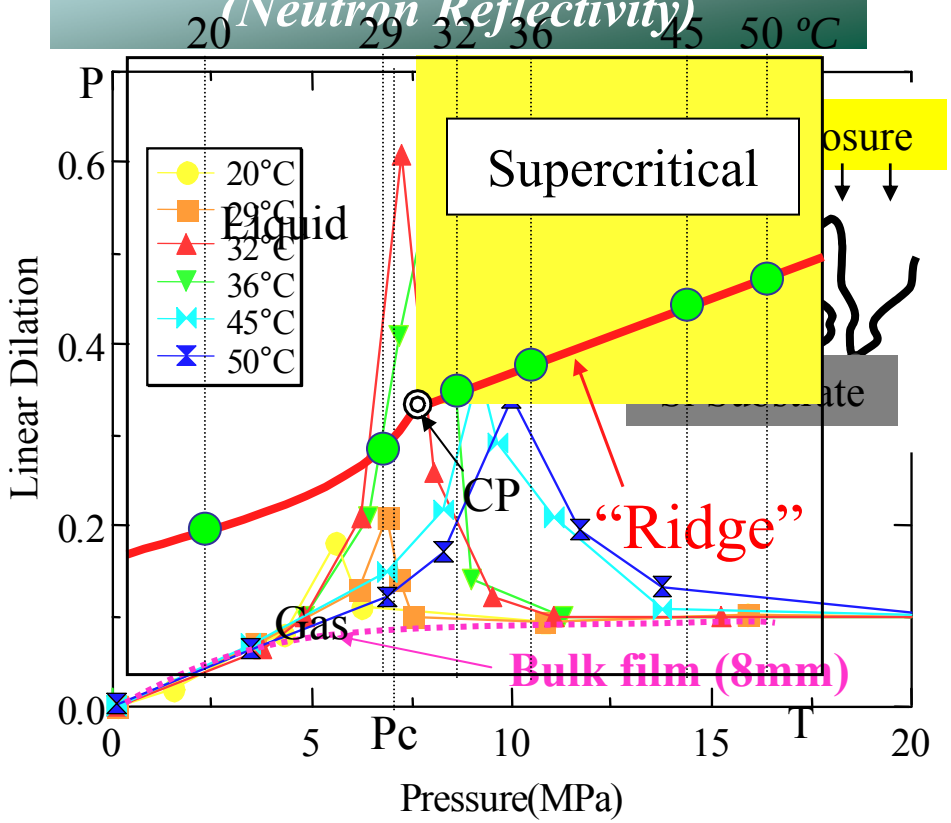
D: Film thickness

Schematic view of high pressure cell for NR experiments (NG7)



Density Fluctuations Induce Swelling

In situ Swelling Behavior (Neutron Reflectivity)



deuterated styrene-butadiene copolymer
(Mw=84k, **450 Å thickness**)

Linear dilation=$(L-L_0)/L_0$

L=Swollen film thickness

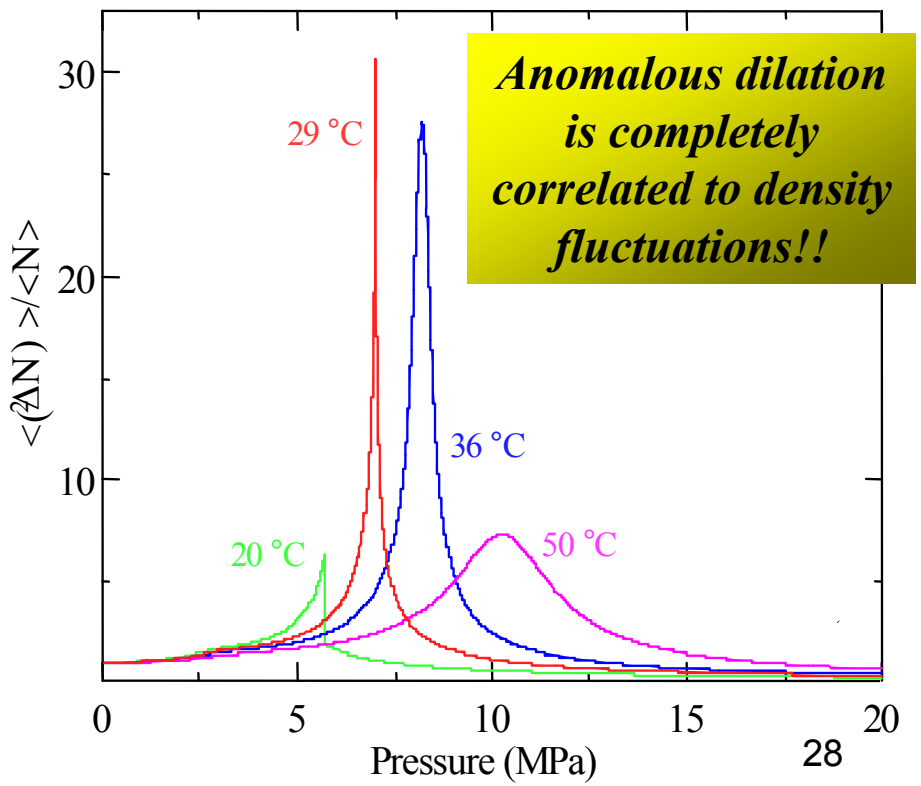
L_0=Unswollen thickness

Long-range Density Fluctuations

$$\langle(\Delta N)^2\rangle/\langle N\rangle=(N/V)\kappa_T k_B T$$

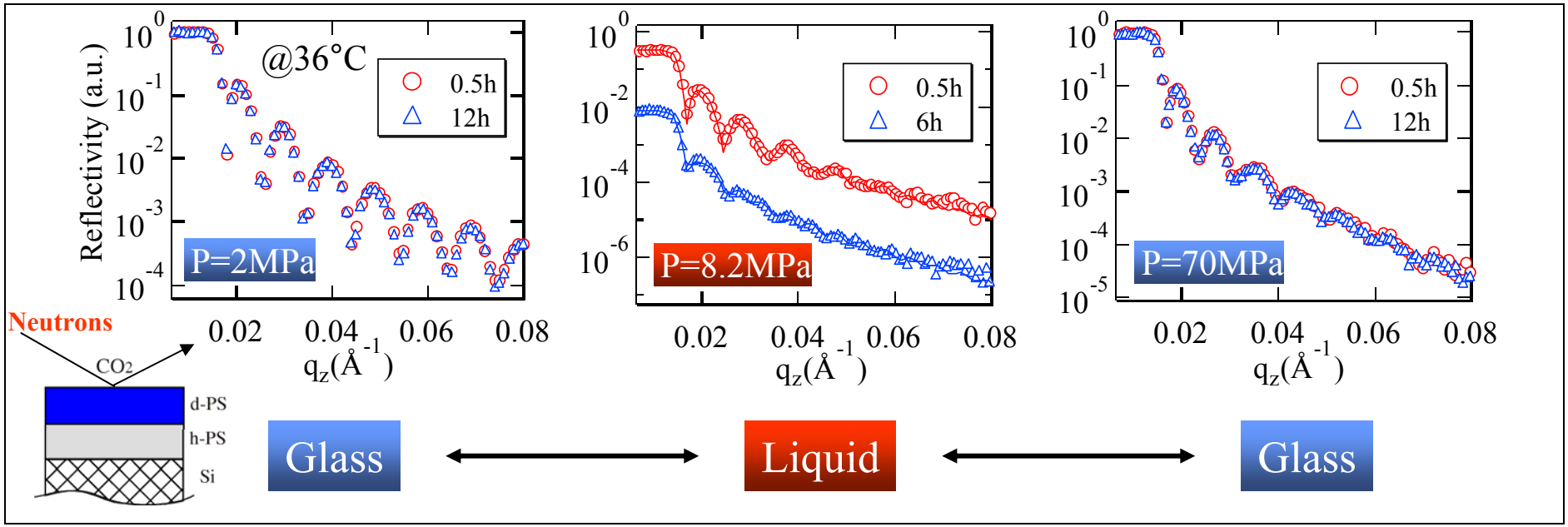
κ_T: Isothermal compressibility k_B: Boltzman constant

N: Number of molecules in the corresponding volume V

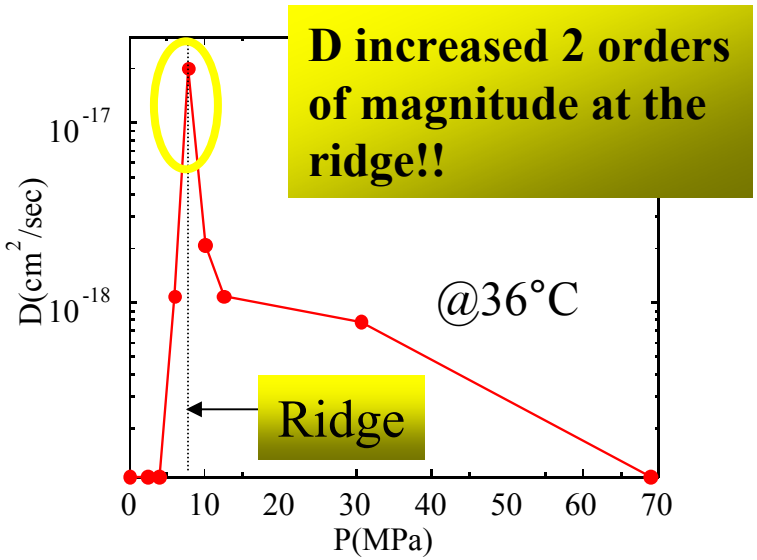


Anomalous dilation is completely correlated to density fluctuations!!

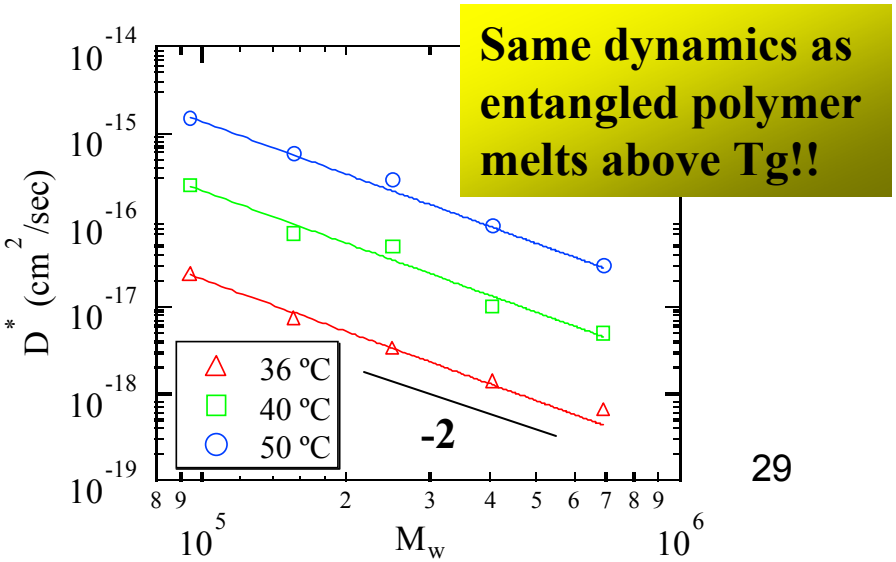
Plasticization Effect of Density Fluctuating scCO2



Diffusion coeff. vs. Pressure

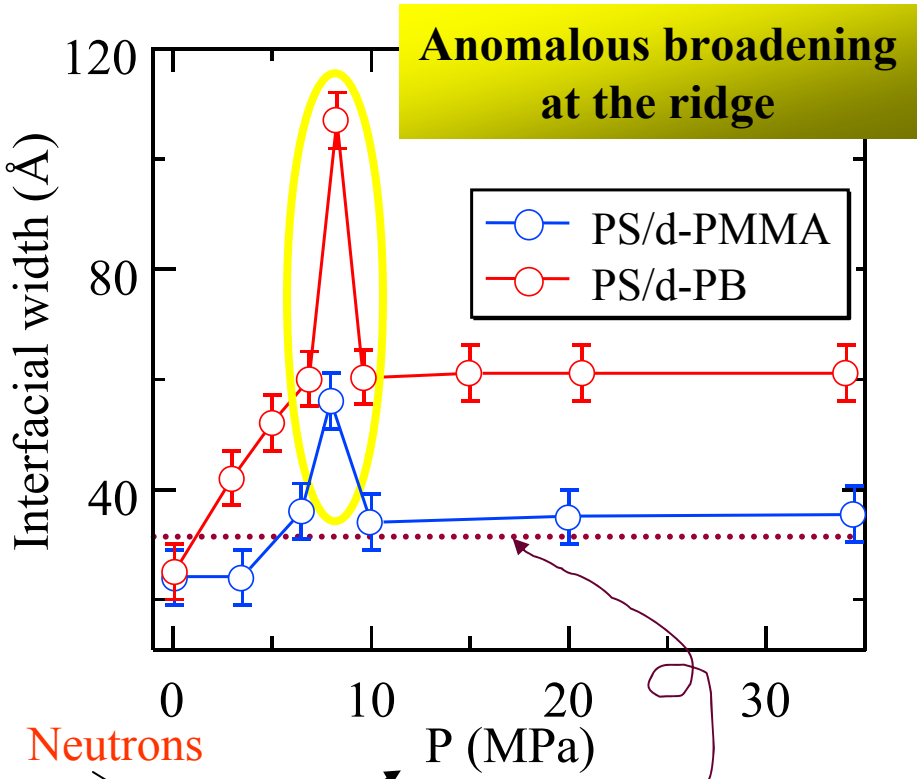


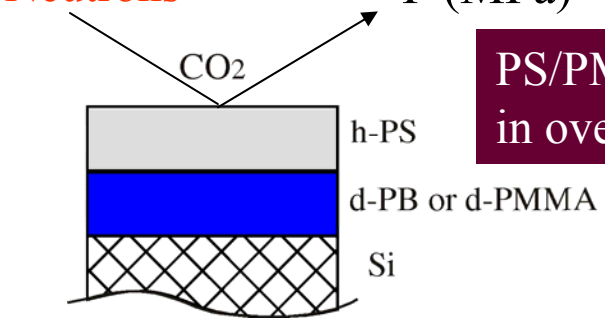
Diffusion coeff. at the ridge



Co-solvent effect for Immiscible Polymer Interfaces

In situ NR results @36 °C in $scCO_2$

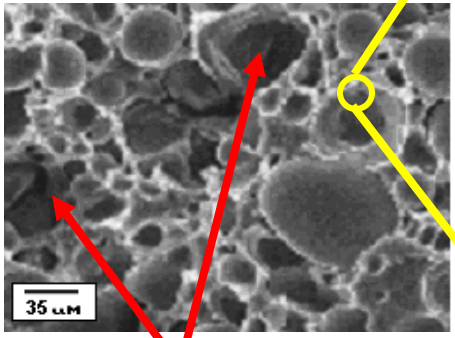




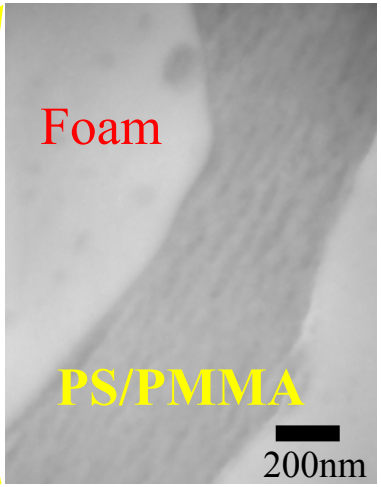
PS/PMMA(or PB) in oven (~170°C)

Application: Bulk PS/PMMA blend

After exposure <SEM image>



Foams



Homogenous !!

Density fluctuating $scCO_2$ enhanced the PS/PMMA compatibility near the surface of the foams.

Development of a novel material with a high degree of *flexibility* and *tensile strength* simultaneously

Tethered Chains in Theta Solvent Condition: Langmuir Diblock Copolymer Monolayer Study

M. S. Kent, S. Satija, J. Majewski, G. S. Smith, L. T. Lee

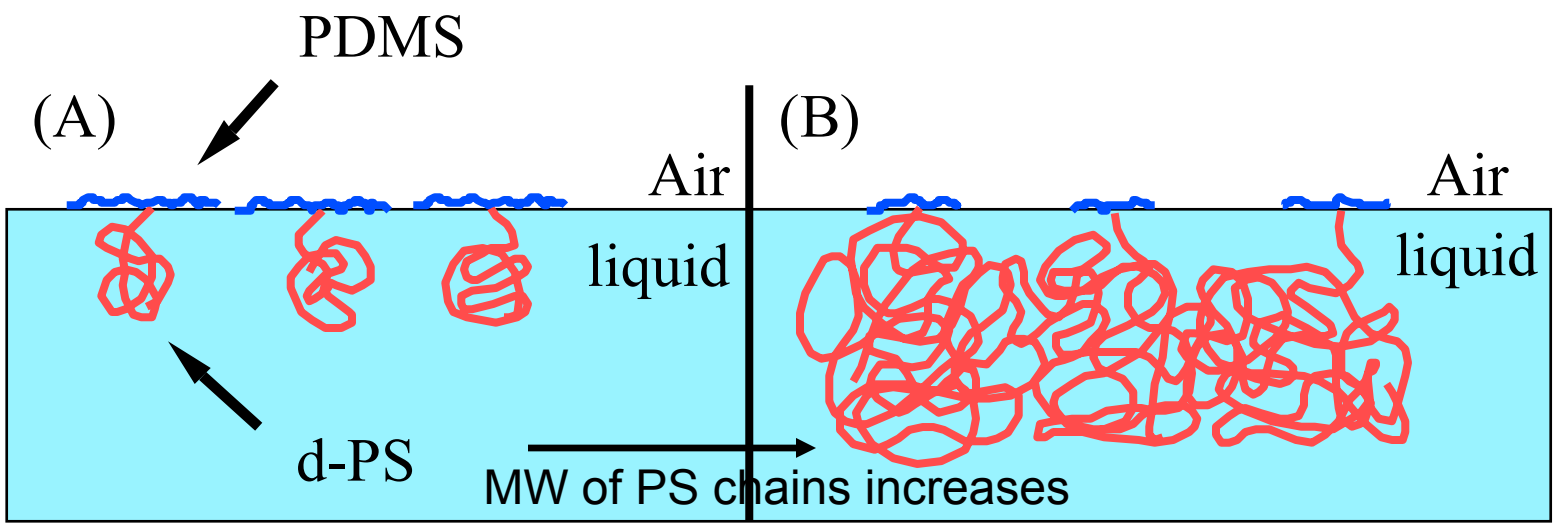
Objective

- To investigate the effect of molecular weight and surface coverage on the structure of tethered layers
- To examine the scaling laws and compare with the predictions for strong-stretching limit at infinite M

$h \sim \sigma^{1/3} M$ (good solvent)

$h \sim \sigma^{1/2} M$ (theta solvent)

Formation of tethered layer at air-liquid interface



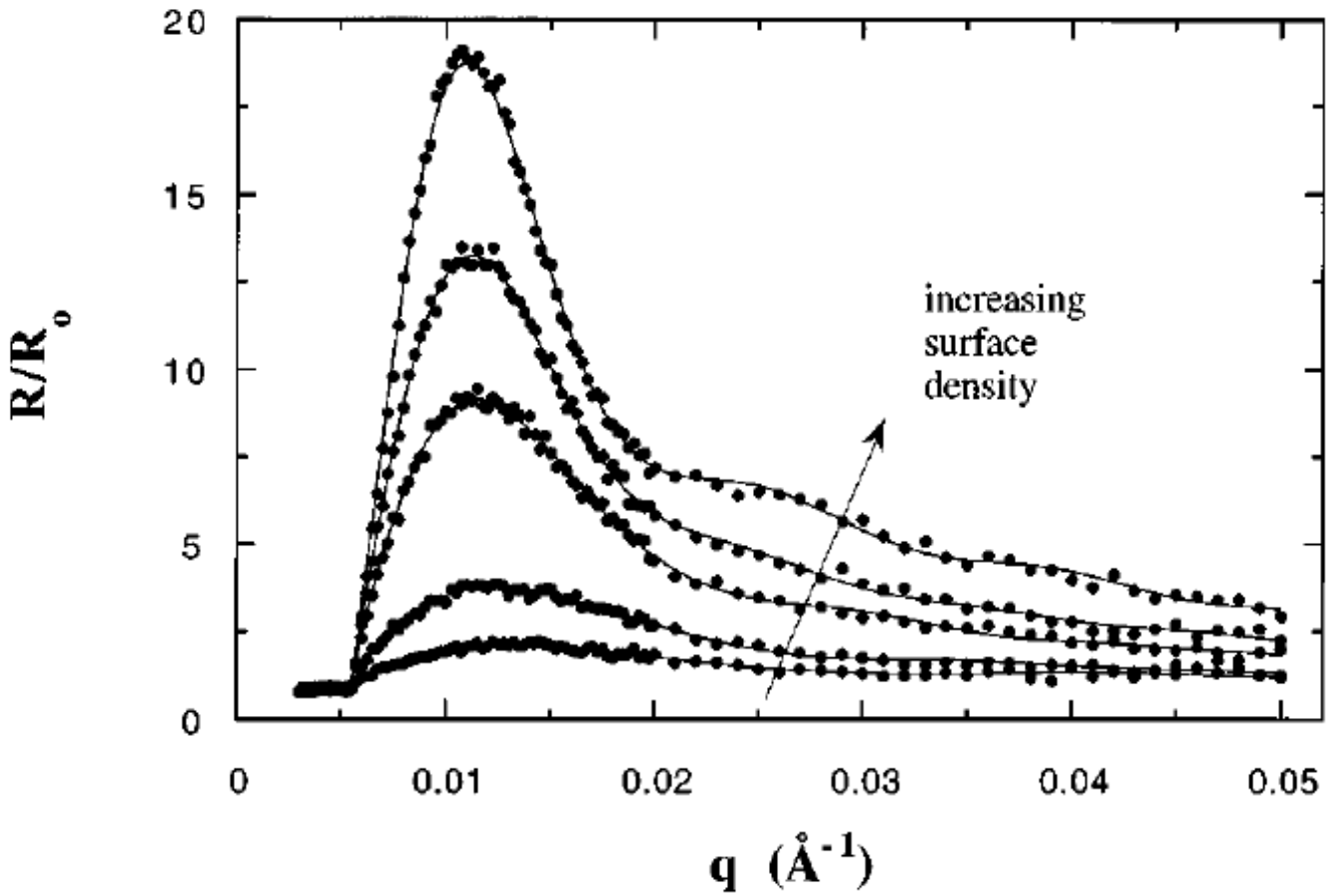
SLD Values

PDMS	7×10^{-8} Å^{-2}	(invisible to neutrons)
DOP	0.618×10^{-6} Å^{-2}	
DPS	6.4×10^{-6} Å^{-2}	
hPS	1.4×10^{-6} Å^{-2}	

Surface Tensions

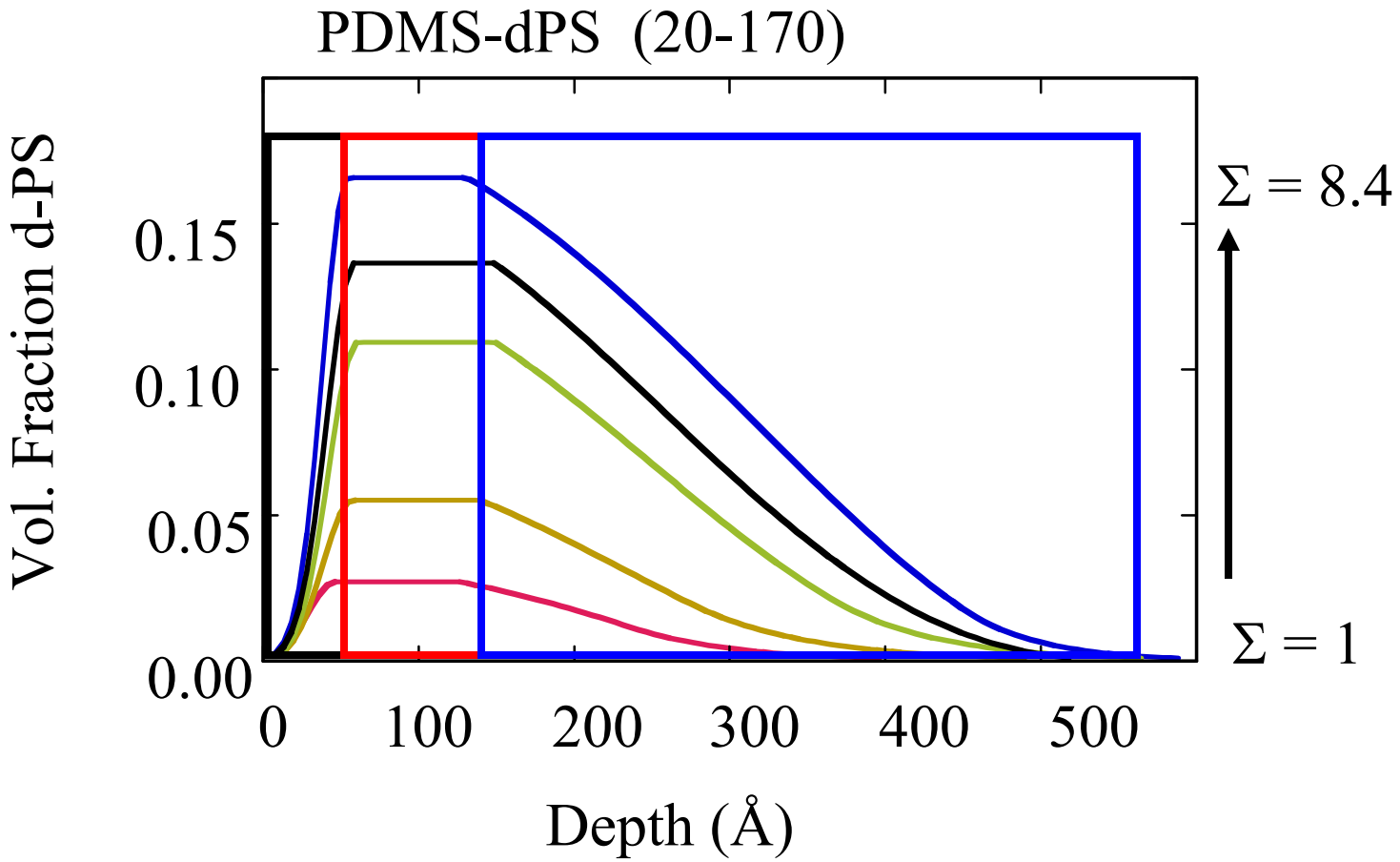
PDMS	20mN/m
PS	40 mN/m
DOP	31mN/m

Reflectivity for PDMS-dPS (20-170) at 22 °C for various reduced grafting densities



Reduced surface density, $\Sigma = \sigma\pi R_g^2$

d-PS Volume Fraction Profiles for PDMS-dPS

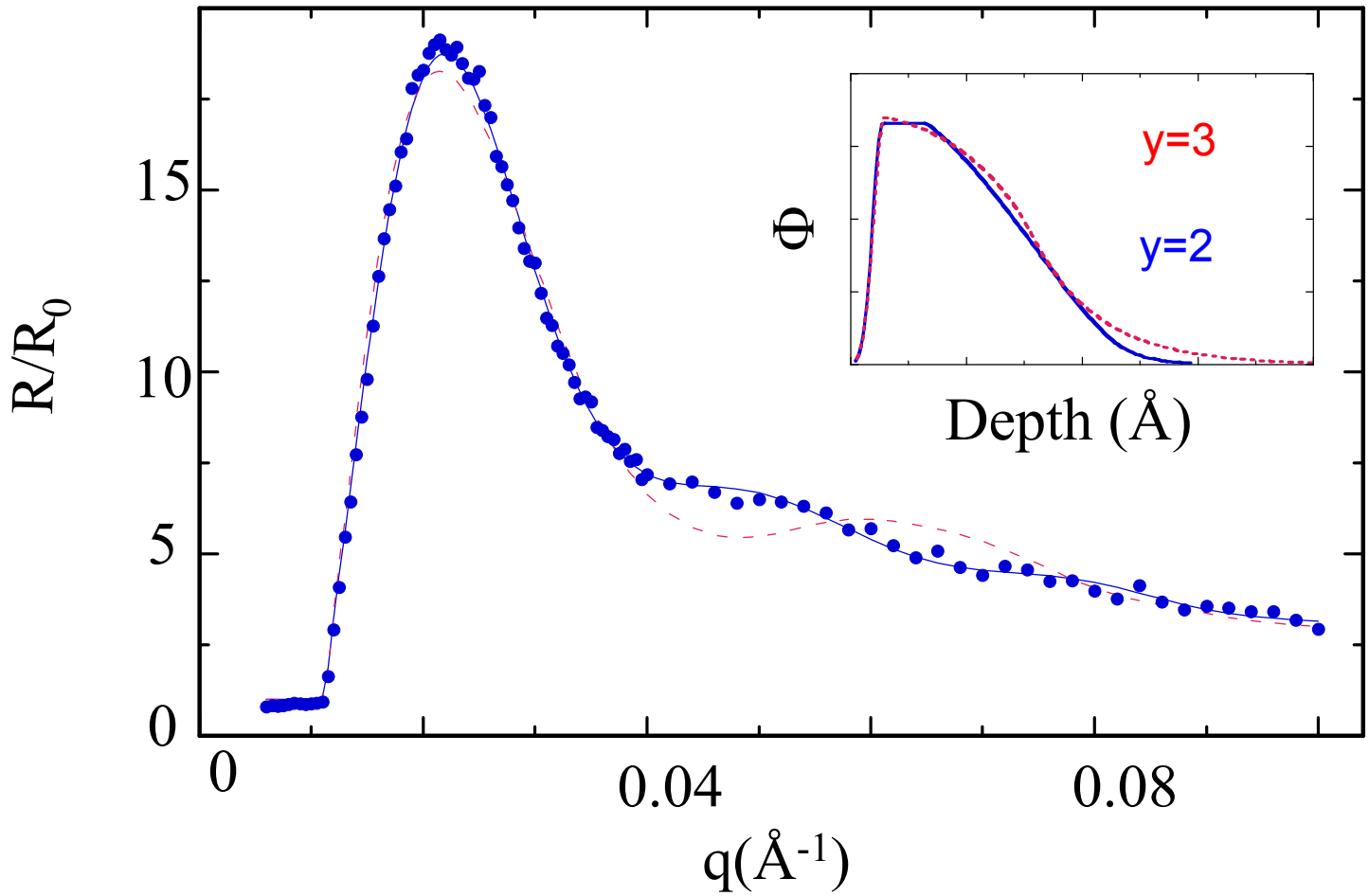


The shape of the density profile

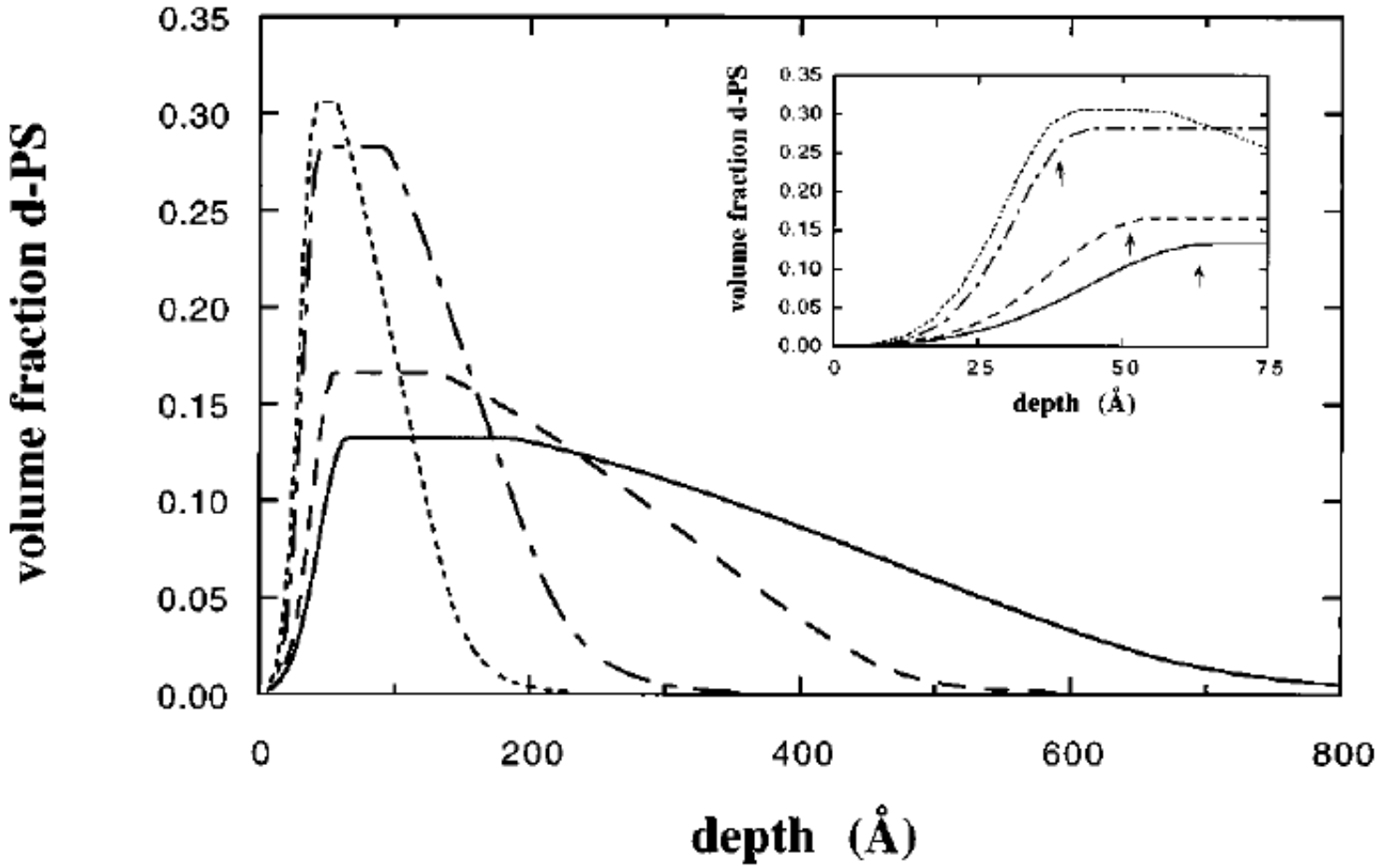
$\Phi = \Phi_0 [1 - (z / L_0)^2]^y$ SCF theory

Sensitivity of reflectivity to profile shape

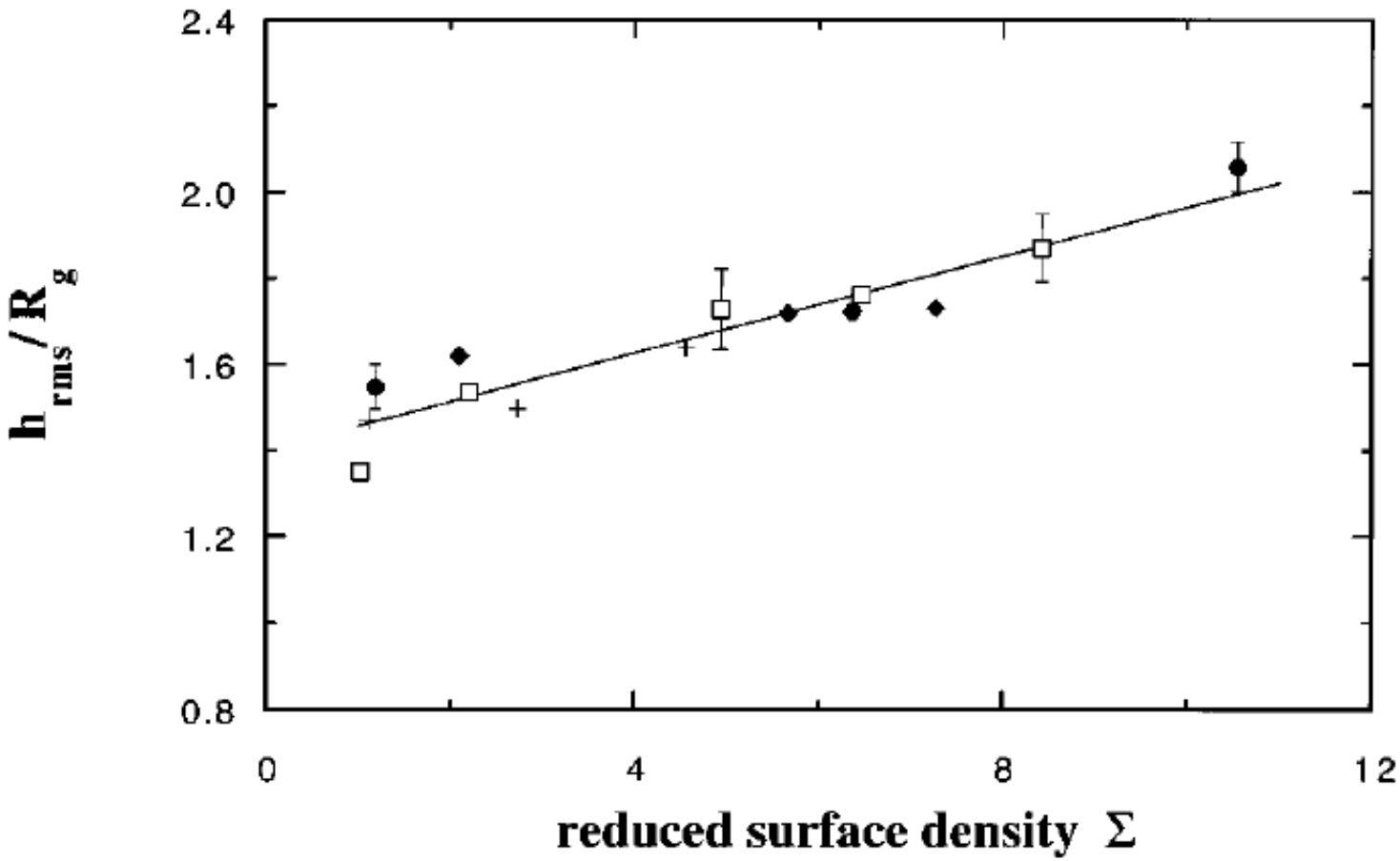
(PDMS-dPS 20-170 in DOP at 22 °C, theta solvent)



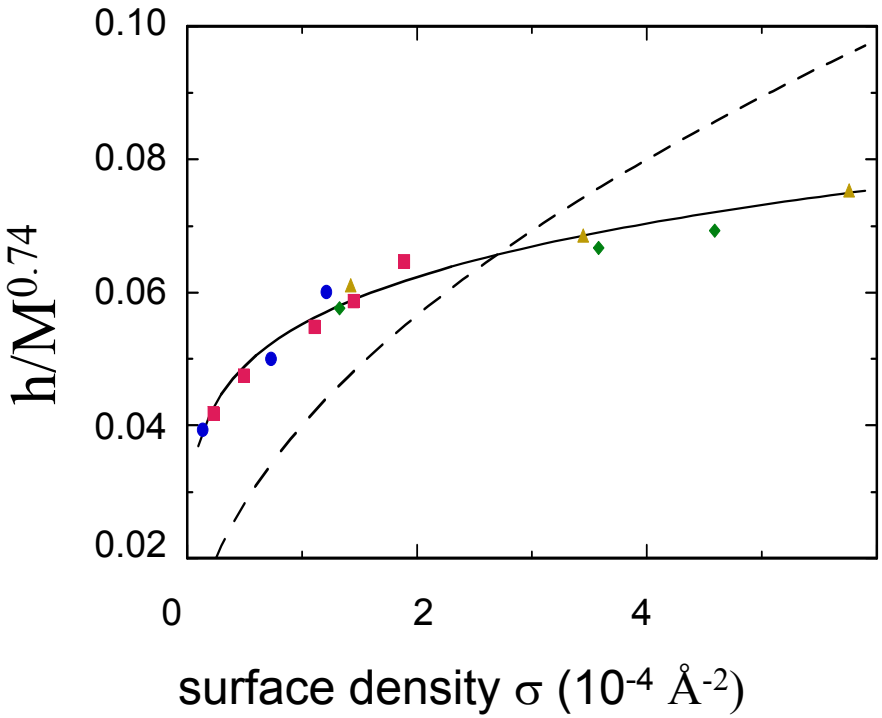
Effect of MW on the structure of Tethered Layer



Variation of Layer Height with Surface Density



Comparison of Scaling Laws with Theories



Data $h \sim \sigma^{0.18} M^{0.74}$

Theory $h \sim \sigma^{0.5} M^{1.0}$

$\phi(z) = (1-(h/z)^2)^{1/2}$ predicted by analytical SCF theory

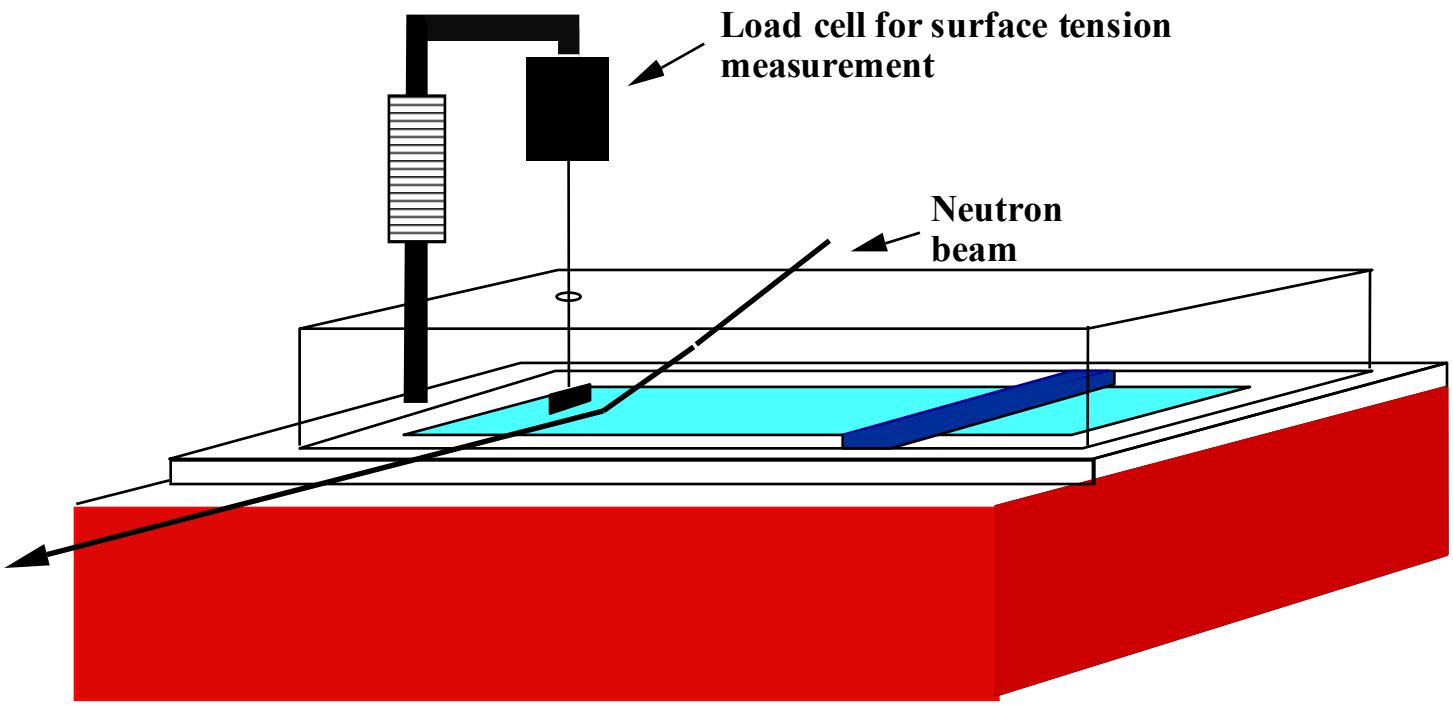
Summary

- Asymptotic limit not valid for $\Sigma < 12$ - need numerical SCF calculations for accurate description.

- Depletion layer present for repulsive surfaces. Nearly independent of σ, increases with M.

- Accessible range of surface density is limited when tethered layers are prepared from moderately dilute solutions.

- Higher surface densities achievable using concentrated solutions or with "grafting from" technique

Neutron Reflectivity Setup for Langmuir Trough

Langmuir Trough