Langmuir Monolayer Study of Tethered Polymer Brushes

NG7 Reflectometer Experiment

NG7 Reflectometer is a horizontal reflectometer on which we can study free liquid surfaces. This experiment involves the study of spread monolayers of highly asymmetric PDMS-PS(polydimethyl-siloxane-polystyrene) diblock copolymers on the surface of an organic liquid ,DOP (dioctyl phthalate). DOP is a theta solvent for the PS block and a non solvent for the PDMS block.

Thus PDMS block is anchored at the air-solvent interface and PS block is in the solvent forming a brush.

Scattering Length Densities of Polymers and DOP

PDMS 7×10^{-8} Å^{-2} (invisible to neutrons)

DOP $.61 \times 10^{-6}$ Å^{-2}

DPS 6.4×10^{-6} Å^{-2}

hPS 1.4×10^{-6} Å^{-2}

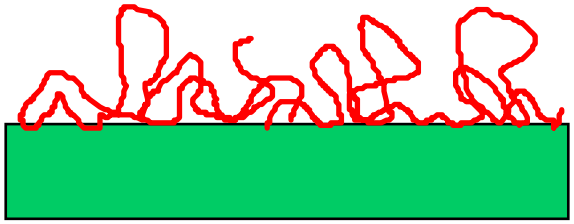
Surface Tensions

PDMS 20mN/m PS 40 mN/m

DOP 31mN/m

I. Introduction

tethered chains



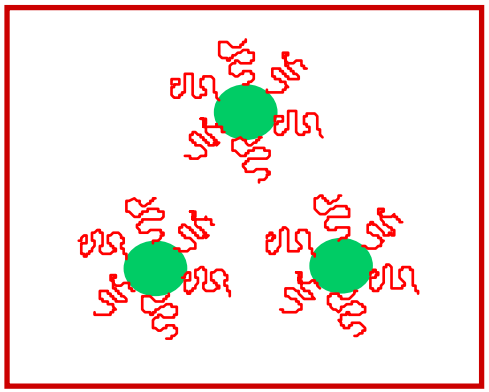
adsorbing chains

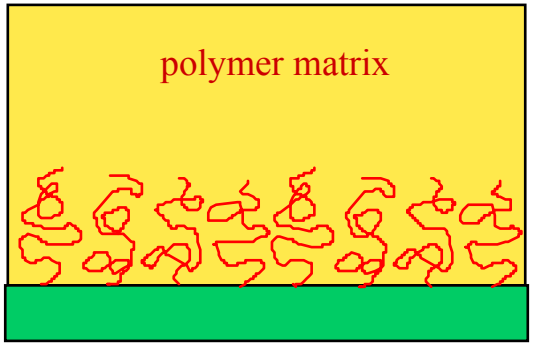
tethered chains - chains fixed by one end to a point or an interface

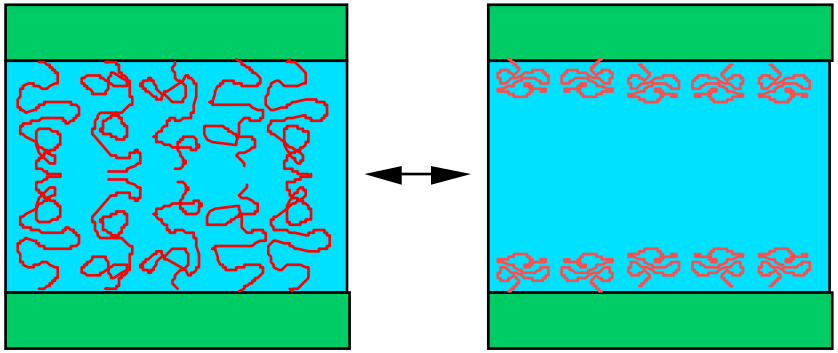
different from adsorbing chains - segmental concentration profile more extended from surface

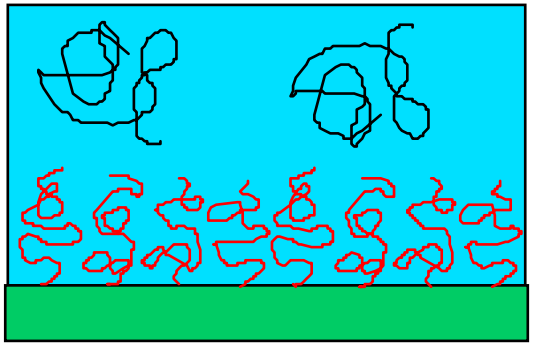
Why study tethered chains?

a) control flocculation
b) compatibility of bio-implants
c) chromatography
d) adhesion
e) lubricants
f) drug delivery
g) prevent protein adsorption
h) wetting
i) valves

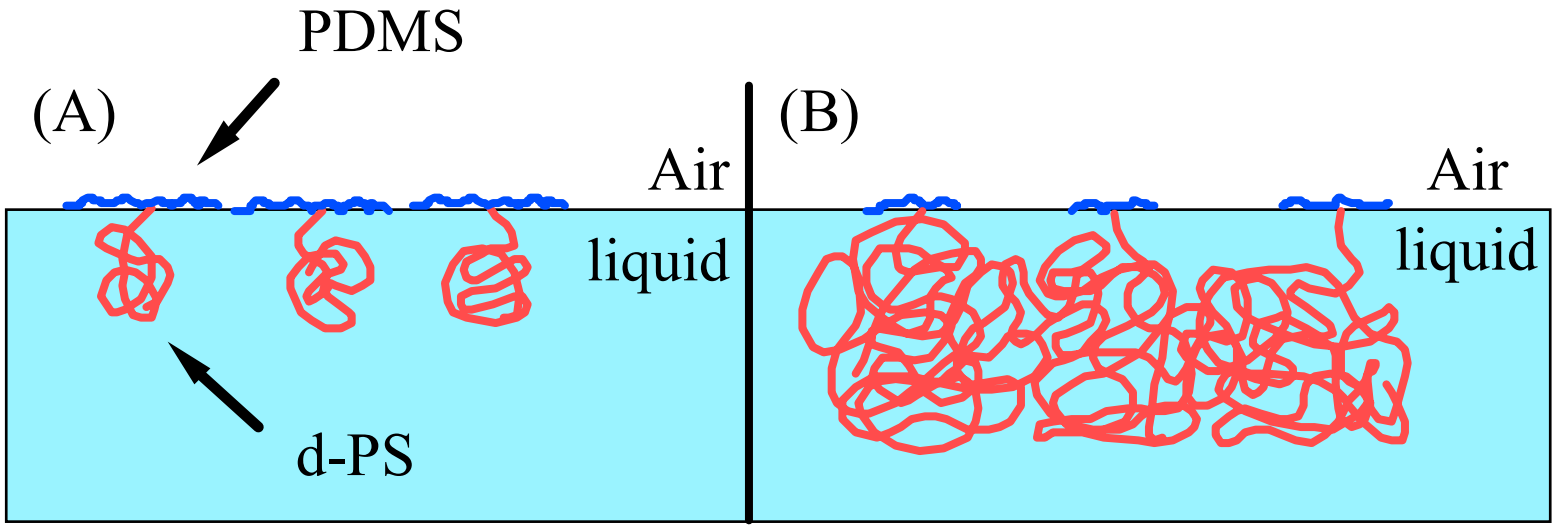






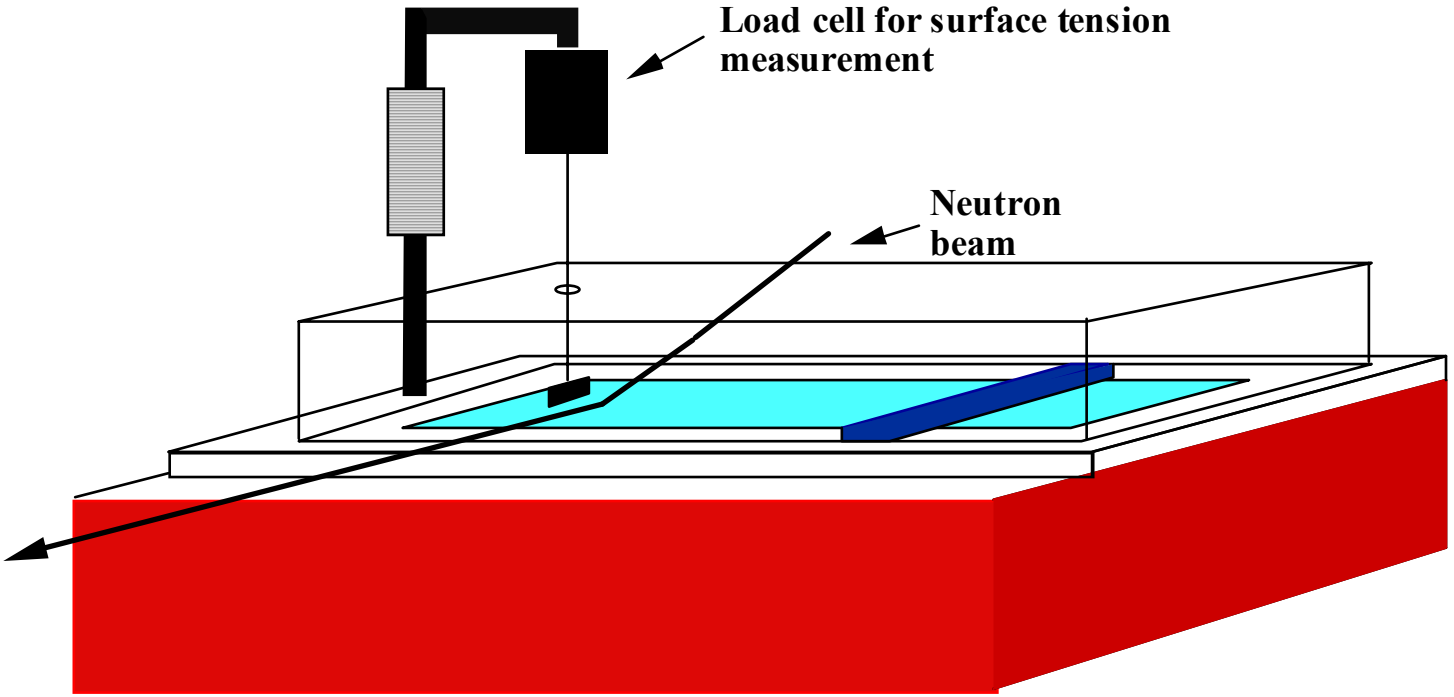


II. Our approach - tether chains to liquid-air interface



Technique - Neutron Reflectivity

Langmuir trough



A. Surface density and molecular weight

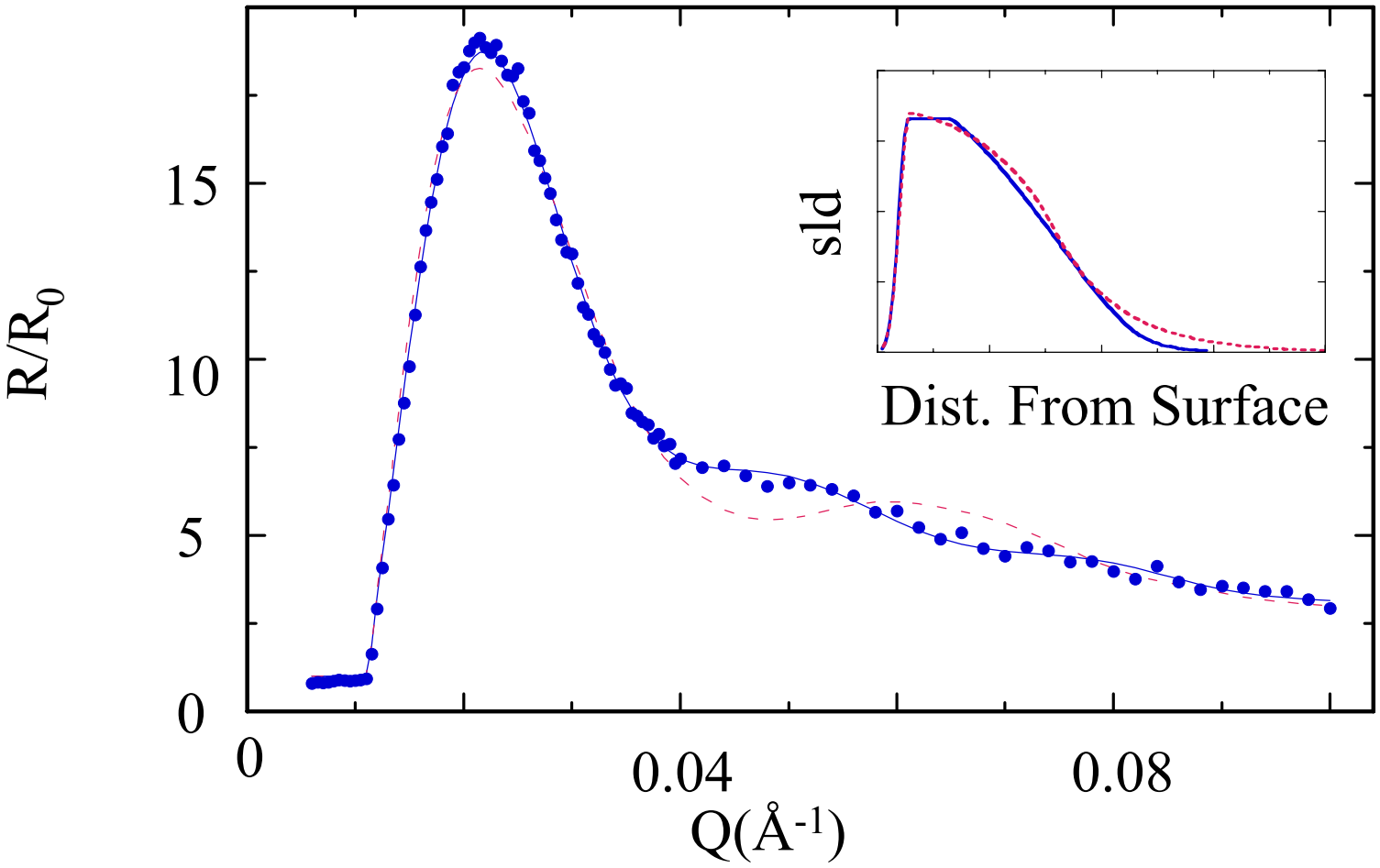
Examine scaling laws, compare to strong-stretching, infinite M limit

$$\mathbf{h \sim \sigma^{1/3} M^{1.0}} \quad \textbf{(good solvent)}$$

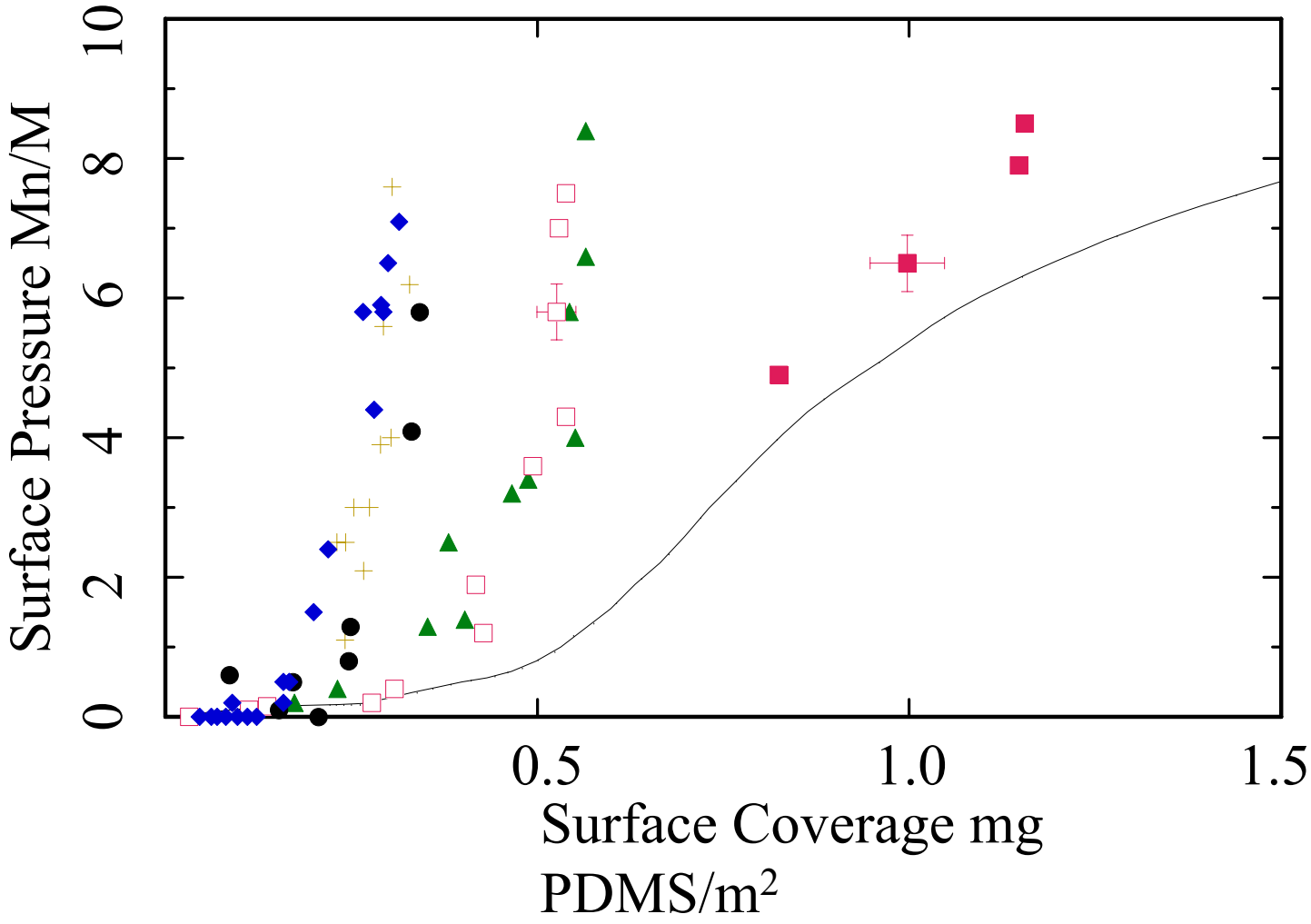
$$\mathbf{h \sim \sigma^{1/2} M^{1.0}} \quad \textbf{(theta solvent)}$$

Sensitivity of reflectivity to profile shape

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

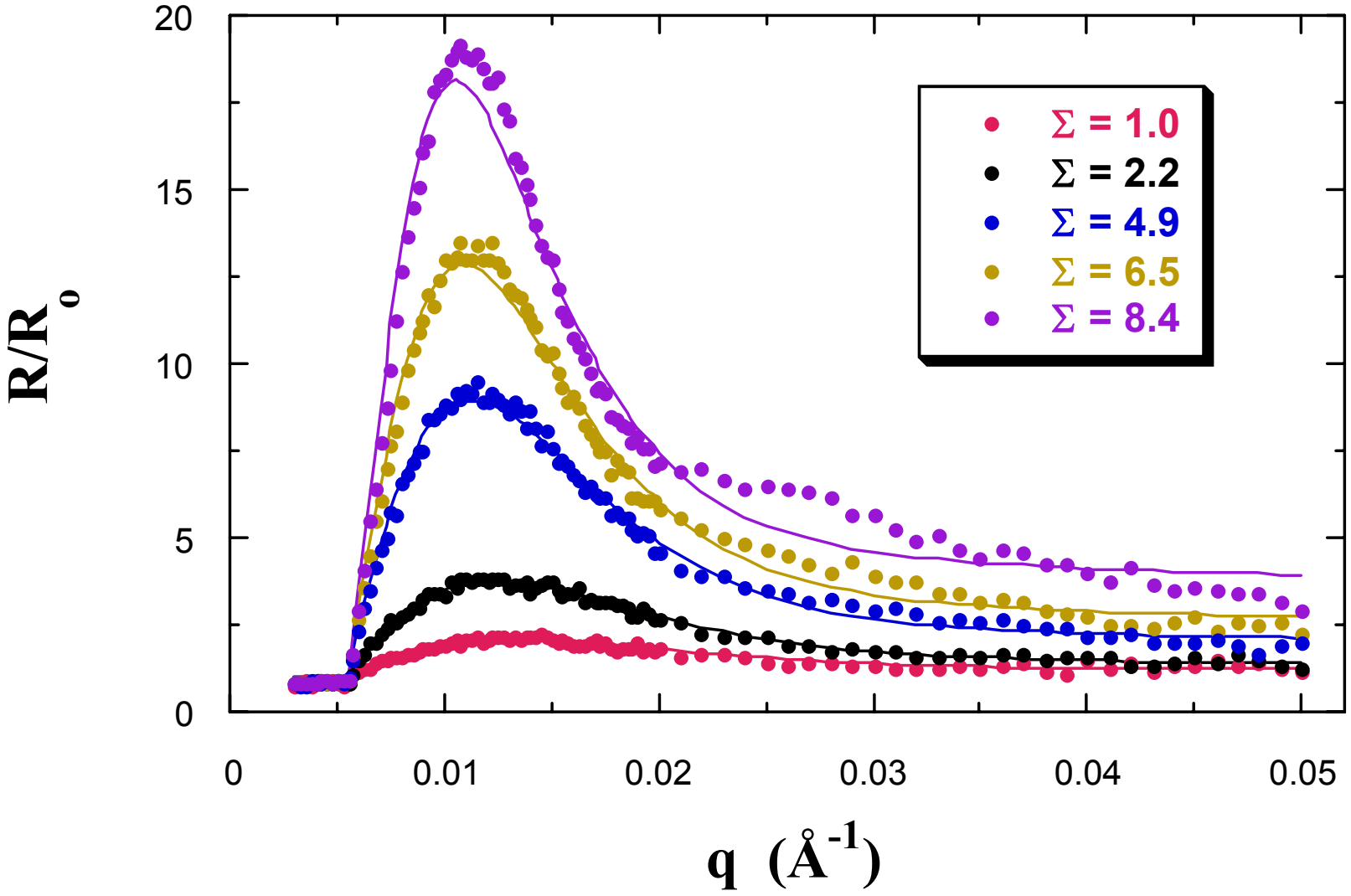


Surface Pressure Change as a function of surface coverage for different Mw.



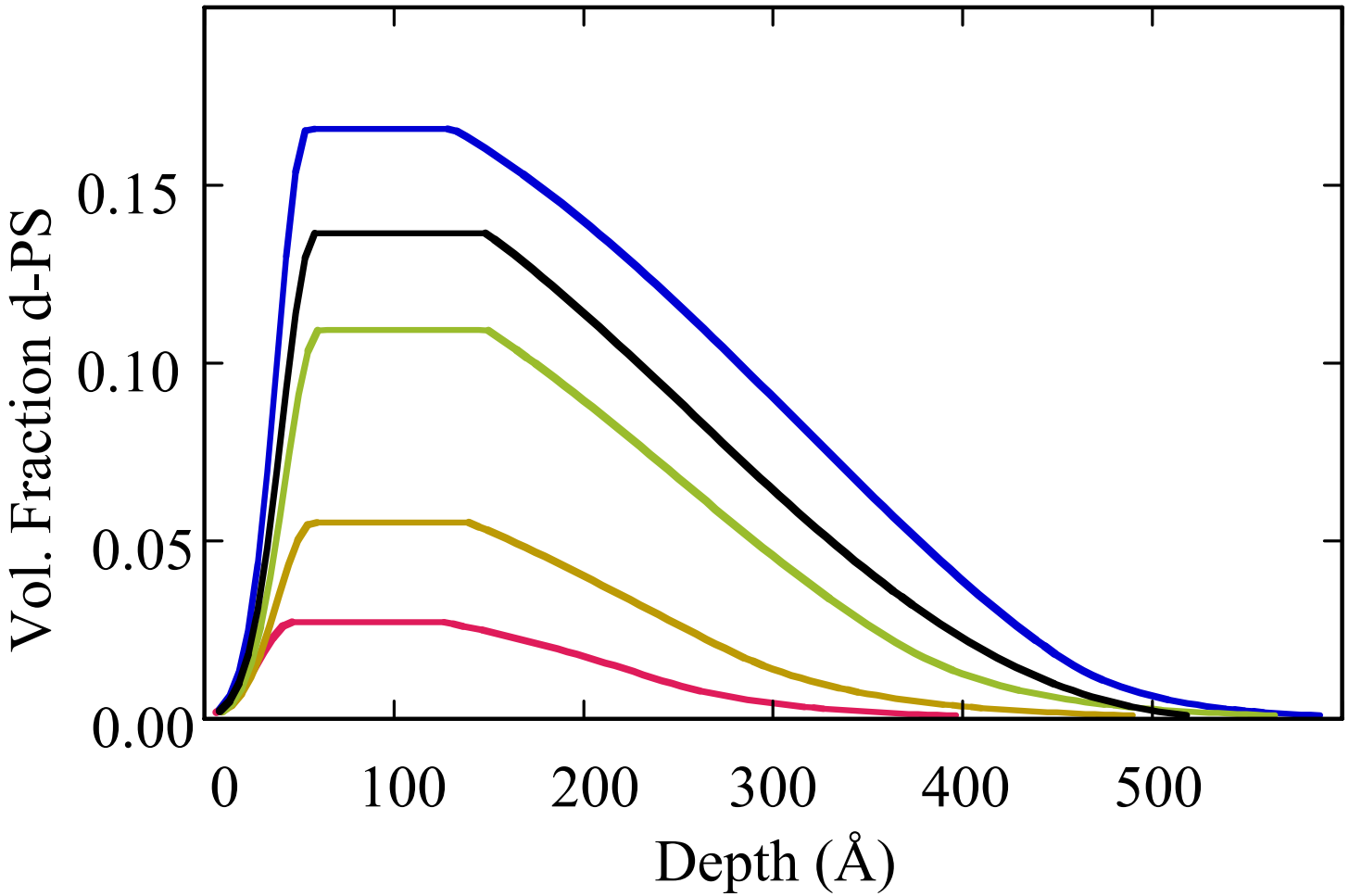
PDMS-PS (20-170) on DOP, (22 ^{O}C = T_{Θ})

(Fits using Renorm. Group profile of Adamuti-Trache, et al, J. Chem. Phys. '96)

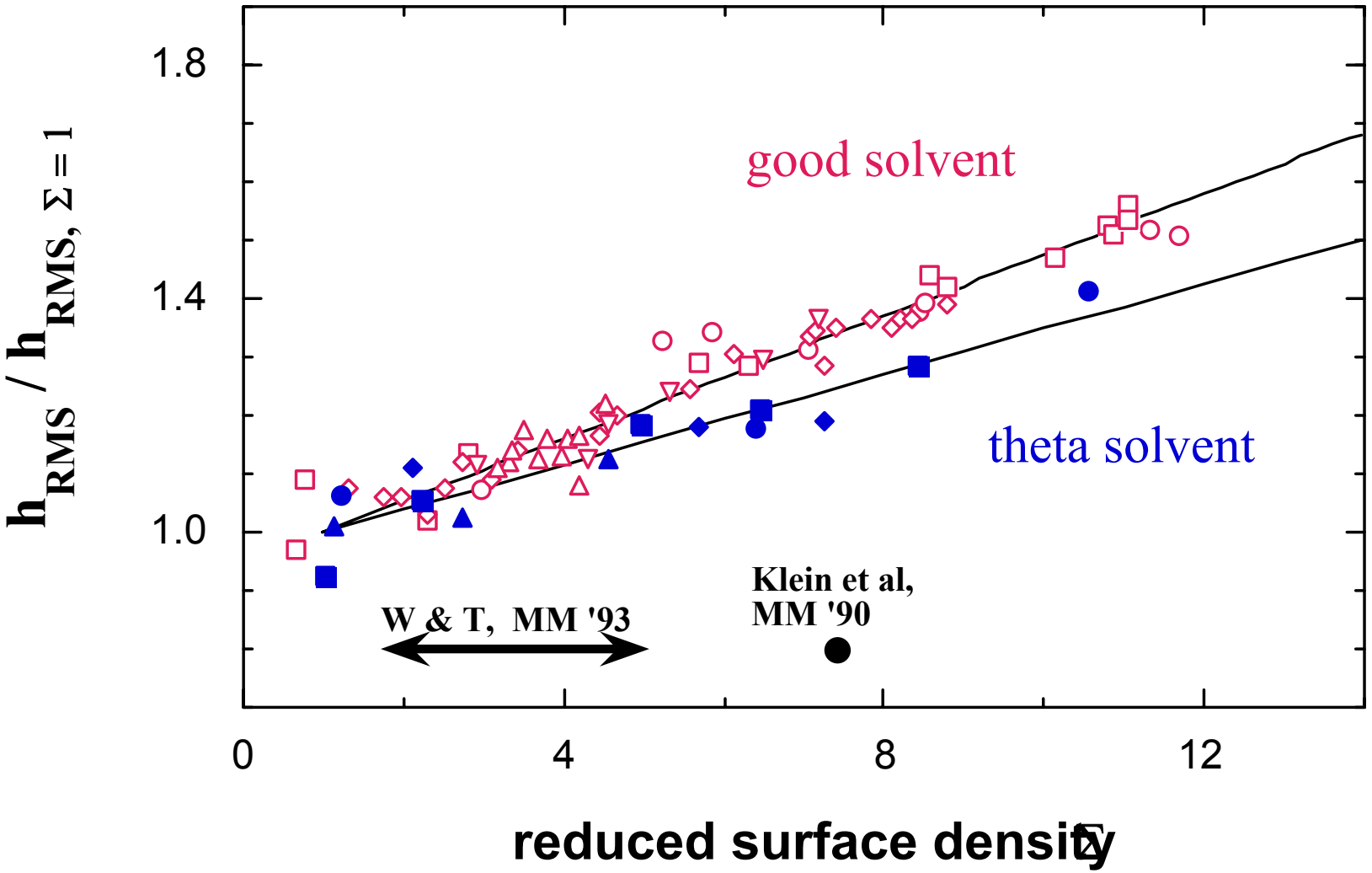


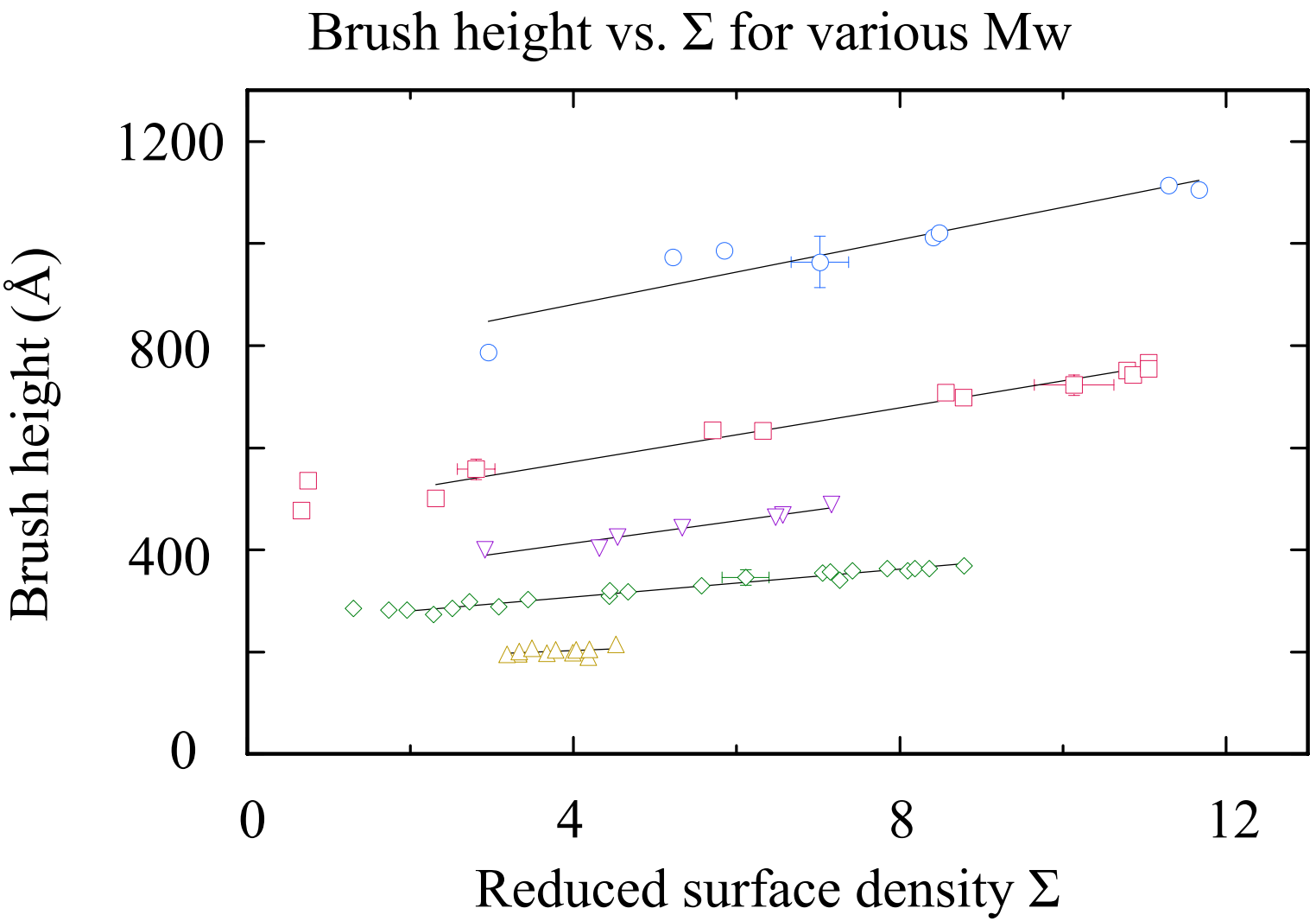
Σ is reduced surface density

Volume Fraction of d-PS for the fits shown in previous slide



Brush height h as a function of reduced surface density Σ




Brush height vs. Σ for various Mw
Brush height (Å)
1200
800
400
0
0
4
8
12
Reduced surface density Σ

Experimental Procedure

1) Dissolve Copolymer of a given MW in $CHCl_3$.

2) Spread Monolayer on DOP and measure surface tension.

3) Remove tensiometer and align sample in neutron beam.

4) Take data overnight

5) Data reduction and analysis.

A) Parametric B-spline fitting (PBS)

B) Mlayer fitting (Multiple layers)

C) Fitting with specific functions

Shape of Density Profile

$$\Phi = \Phi_0 [\ 1 - (z / L_0)^2]^{1/2}$$

(Zhulina et. Al. 1991 SCF theory)

a) Depletion Layer

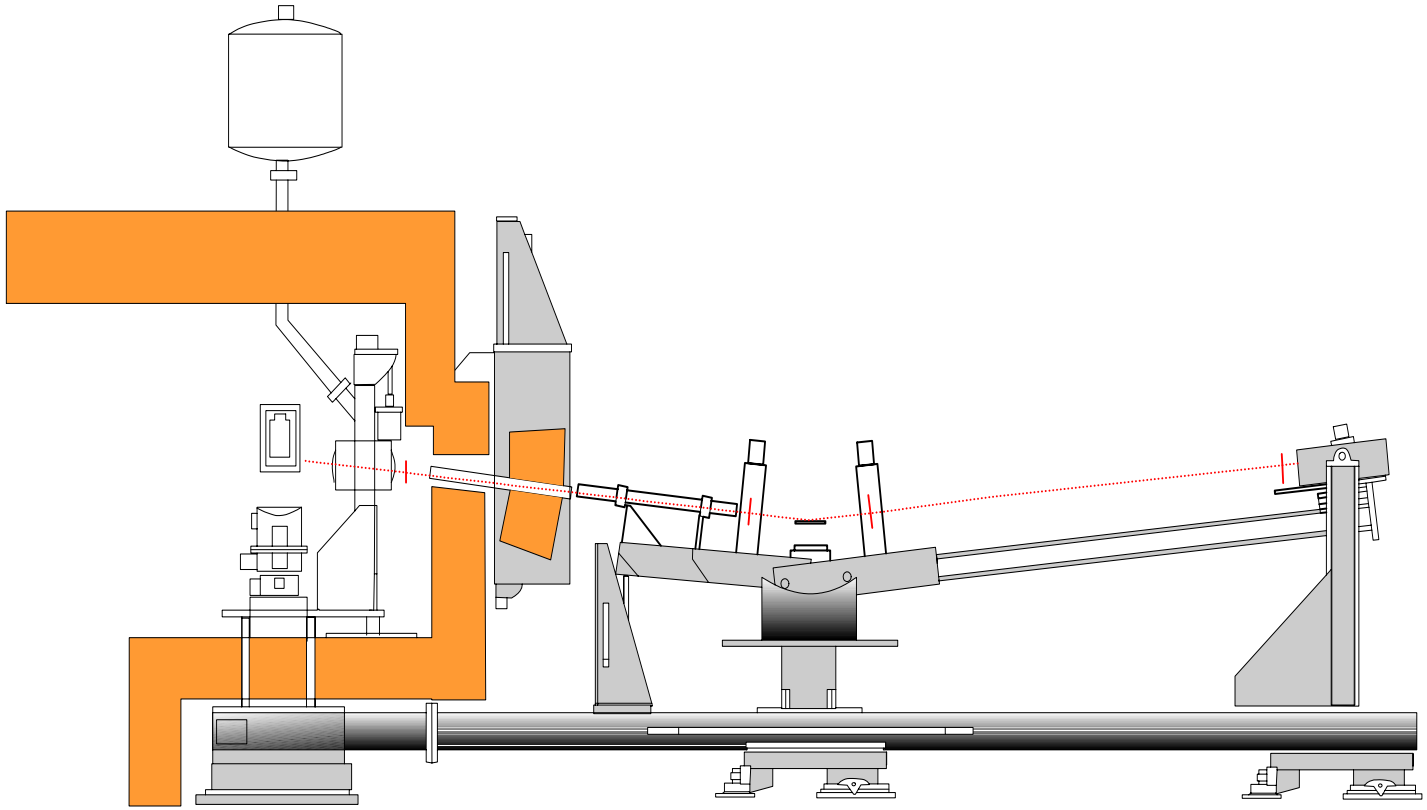
b) Exponential tail

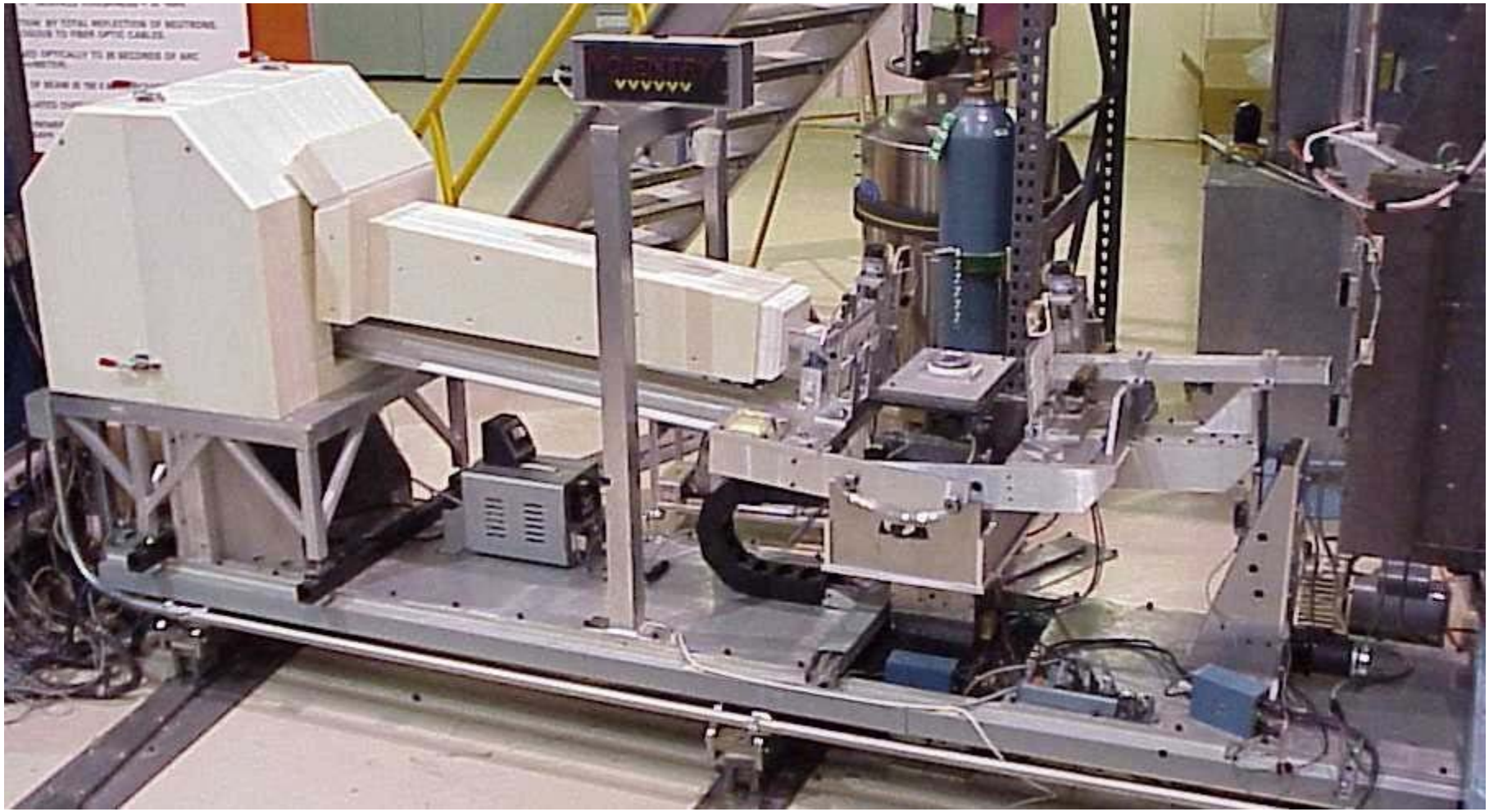
c) Step of variable width

d) $\Phi = \Phi_0 [\ 1 - (z / L_0)^2]^y$ where y is a fitting parameter

All groups will do experiments with different Mw polymers at highest surface density and compare the brush heights.

NG7 Reflectometer





Selected Refrences

1) M.S. Kent, J. Majewski, G. Smith, L.T. Lee and S.K. Satija Journal of Chem. Phys. **108,** 5635 (1998)

2) S.T. Milner, T.A. Witten, M.E. Cates, Macromolecules **21**, 2610 (1988)

3) S.T. Milner, Science **251**, 905 (1991)

4) A. Karim, S.K. Satija, J.F. Douglas, J.F. Ankner, L.J. Fetters, Phys. Rev. Lett. **73**, 3407 (1994)

5) M.S. Kent, *Macromol. Rapid Commun.* **21**, 243 (2000)

6) E.B. Zhulina et.al. Macromolecules **24,** 140 (1991)