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Modelling Data – Better Approaches
How to get useful information?

Adrian R. Rennie

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Monolayers – Simple Interpretation

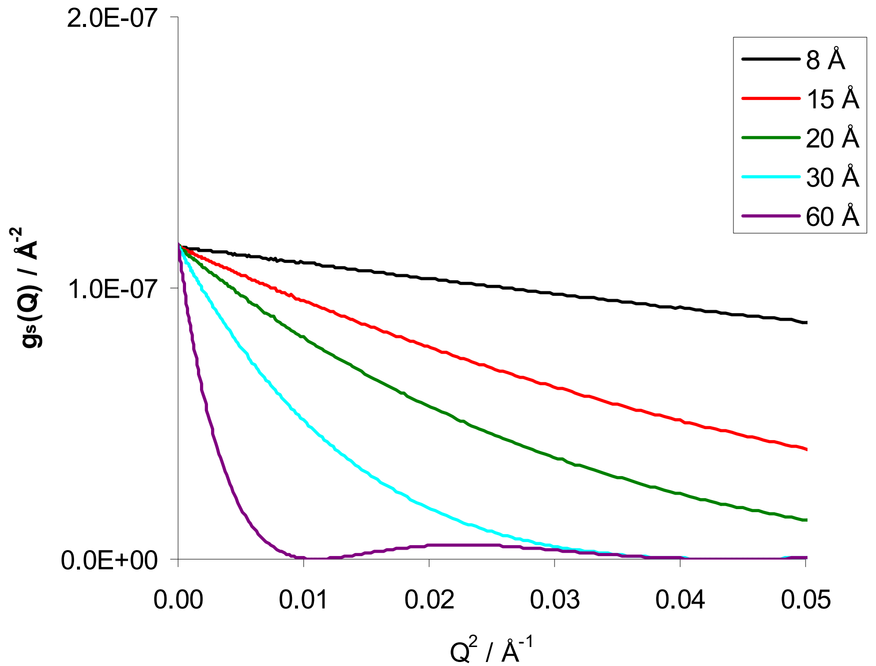
Define $g_s(Q_z)$ in terms of measured reflectivity and $R_F(Q_z)$ (the Fresnel reflectivity for perfectly sharp interface):

$$g_s(Q) = Q^2 (R - R_F) / (1 - R)$$

$$\ln g_s(Q) \approx -t^2 Q^2 / 12$$

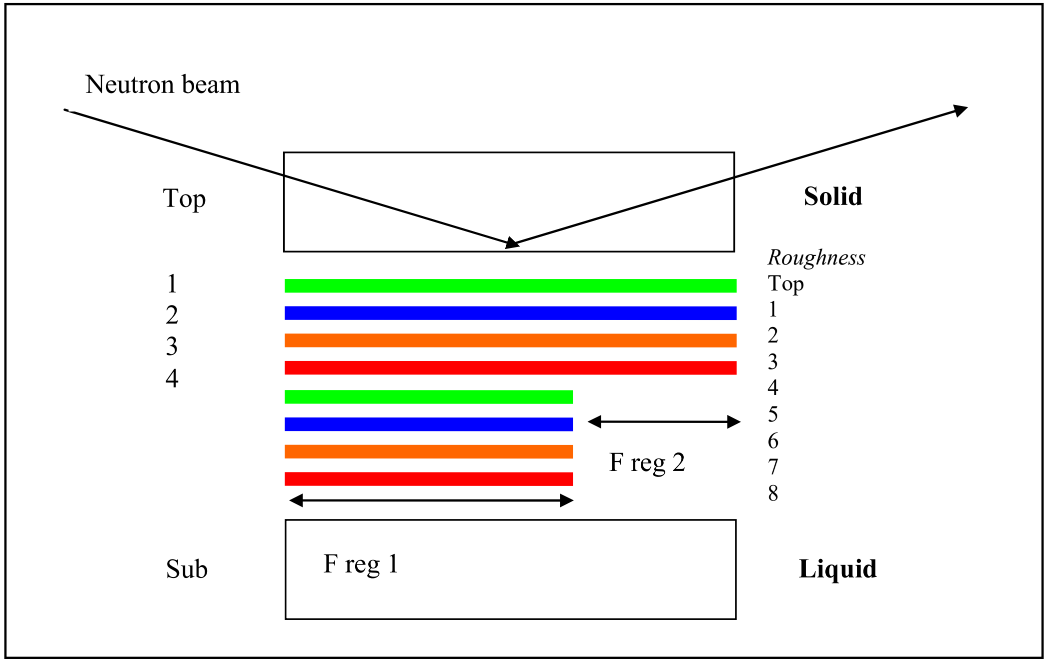
Roughly $\ln (Q^2 R) \approx -t^2 Q^2/12$

Contrast match of two bulk phases $R_F(Q) = 0$



Real Interfaces are not just layers

Slab models are easy to calculate but people are not very interested in just thickness and scattering length density



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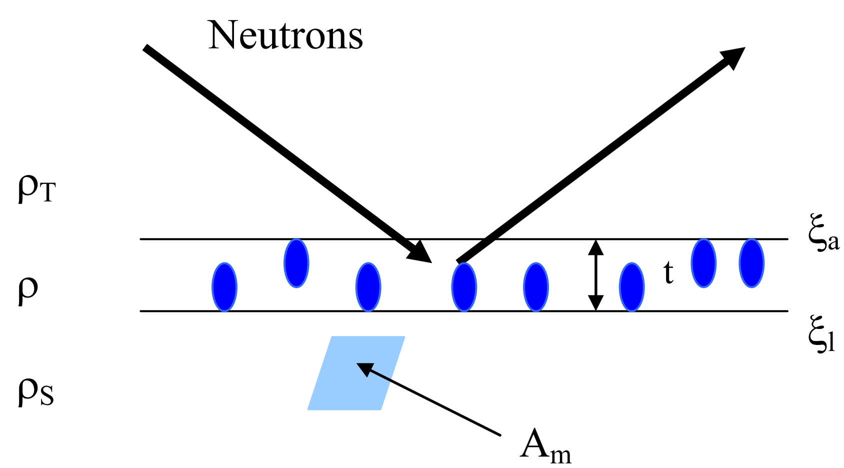
Surface Excess and Area per Molecule

Volume per molecule: V_m

Scattering length: b_m

Scattering length density:

$$\rho = b_m / V_m$$



Thickness of layer: t

Scattering length density ρ

Area per molecule: A_m

$$V_m = t\, A_m$$

Scattering length density:

$$\rho = (b_m / V_m) = b_m/(t\, A_m)$$

Area per molecule: $A_m = b_m / t\,\rho$

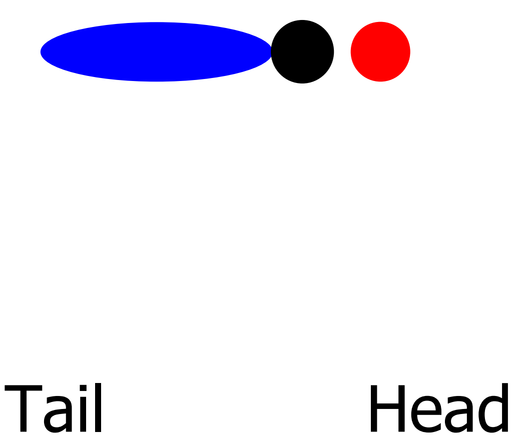
Adsorption of Surfactant

Surface active molecules

Amphiphilic

Bind to surface – how?

What are properties?



Hexadecyl trimethyl ammonium bromide

$C_{16}H_{33}N(CH_3)_3^+ Br^-$

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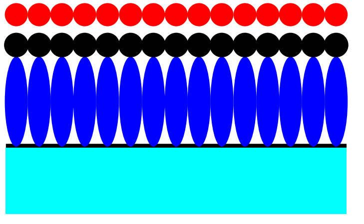
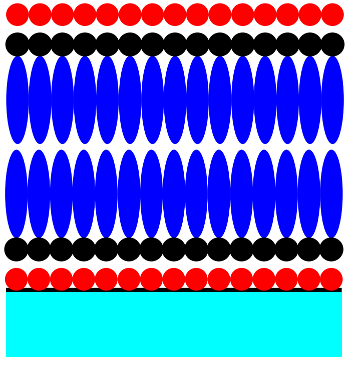
Some Possible Structures

- Monolayer



- Bilayer



Cationic Surfactant

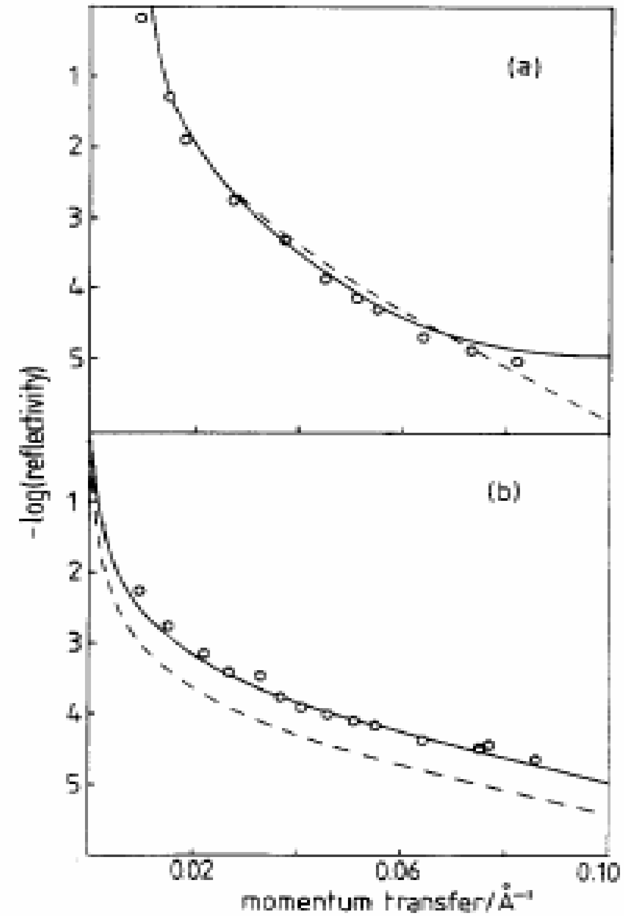
CTAB at 27° C on amorphous SiO_2

(a) D_2O (b) cmSiO_2 at 6×10^{-4} M

Models

Solid line – Bilayer

Dashed line - Monolayer



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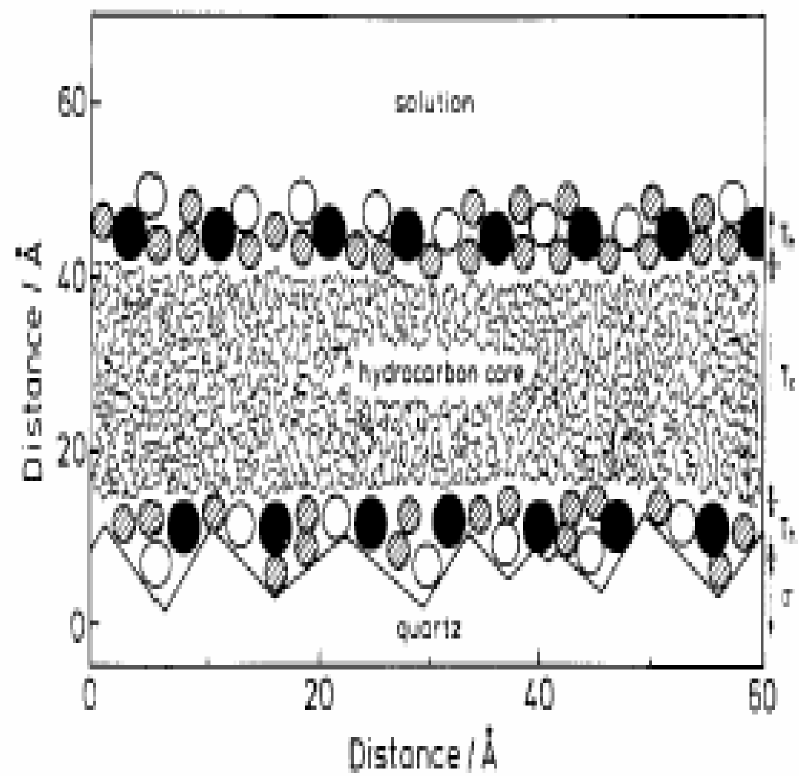
Cationic Surfactant

- **CTAB** 27 C on SiO_2
- Label heads & tails

Head 6 +/- 2 Å
Tail 28 +/- 4 Å
Roughness ~ 8 Å
Fractional Coverage
35% at 3 $\times 10^{-4}$ M
80% at 6 $\times 10^{-4}$ M



Langmuir **6**, 1031-1034 (1990).
J. Colloid Interf. Sci. **162**, 304-310 (1994).

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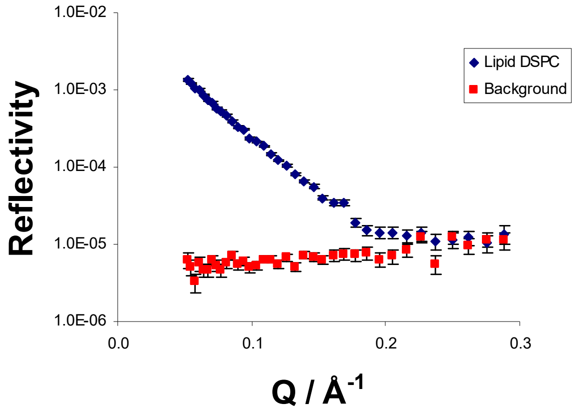
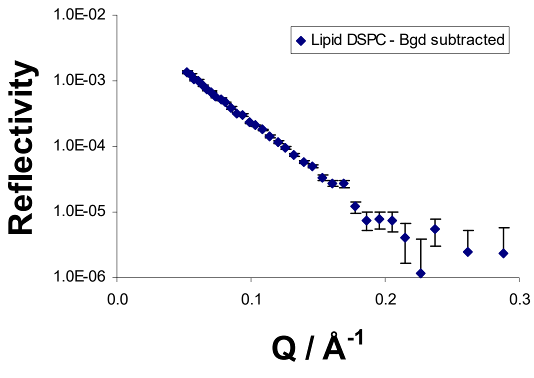
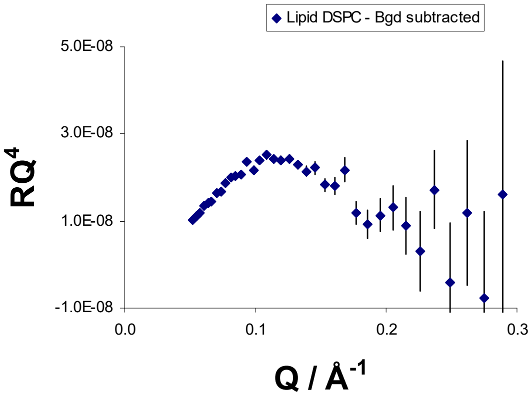
Plotting Data

Different representation is helpful







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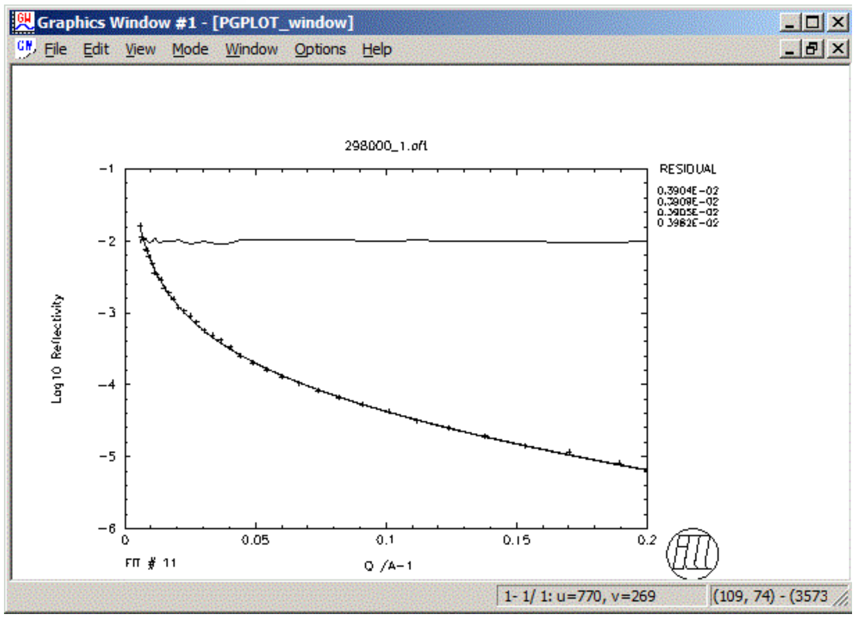
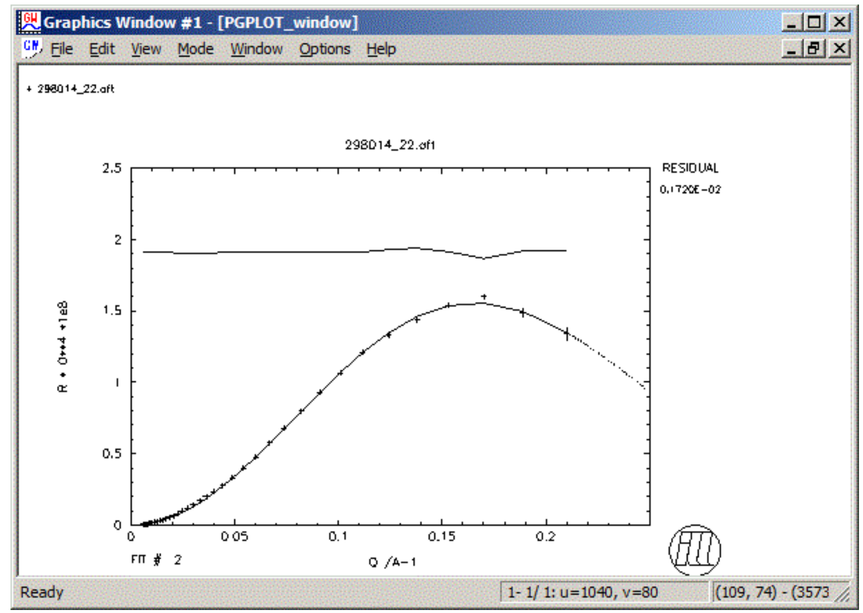
How to Look at Data?

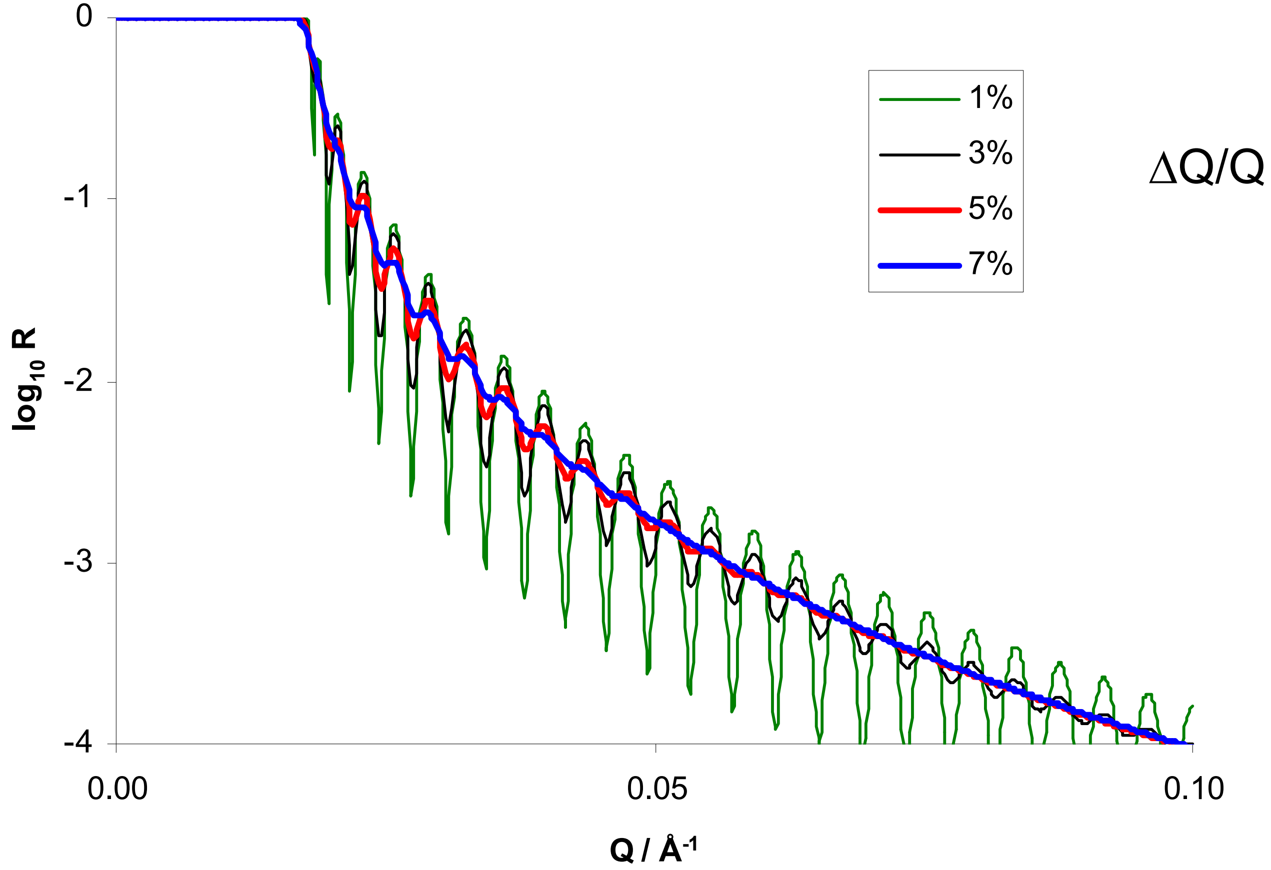


Log$_{10}$ R vs Q



RQ^4 vs Q

Effects of Resolution



Silicon substrate: film thickness 1500 Å
scattering length density 6.3×10^{-6} Å^{-2}

Non-Uniform Surfaces

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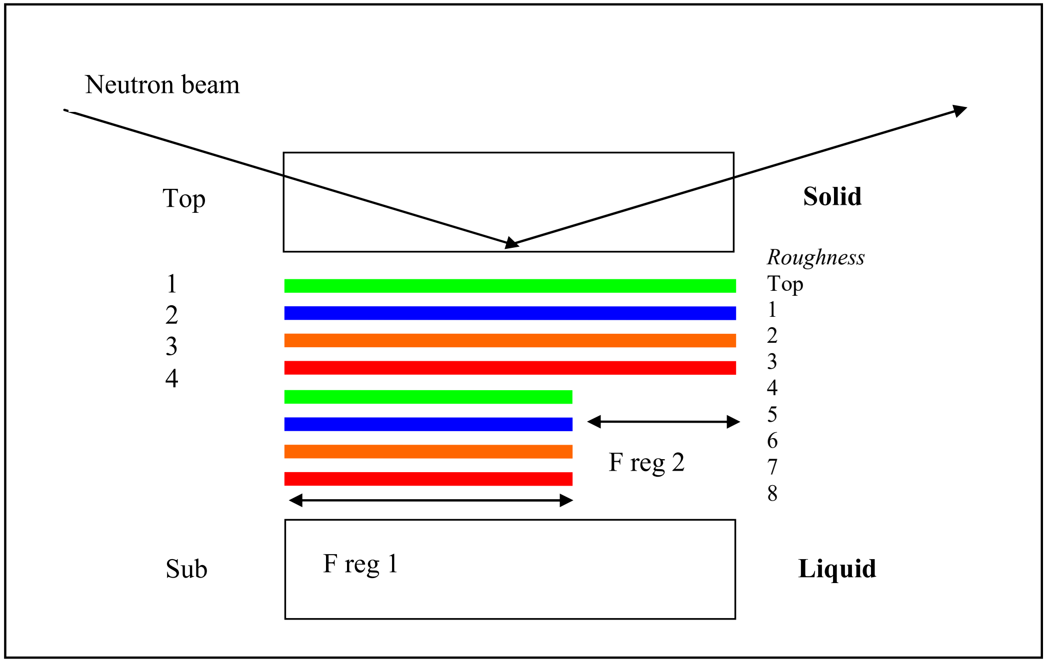
If you have patches of different layers at an interface do you average the density or average the reflectivity?



What is the coherence length of a neutron?

Describing Polymers

- Interdiffusion – is this roughness?
- Brushes – parabolic density profile

(E. P. K. Currie et al *Physica* B, **283** 17 – 21)

- Other scaling laws e.g. O. Guiselin *J. Phys.* **50**, 3407-3425 (1989).

We expect smooth profiles!

Thermoresponsive polymer brush

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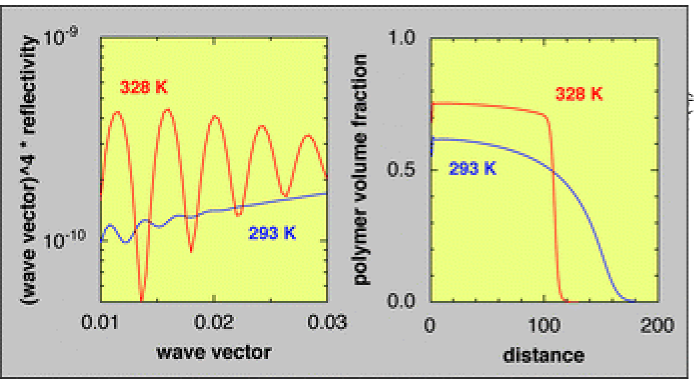

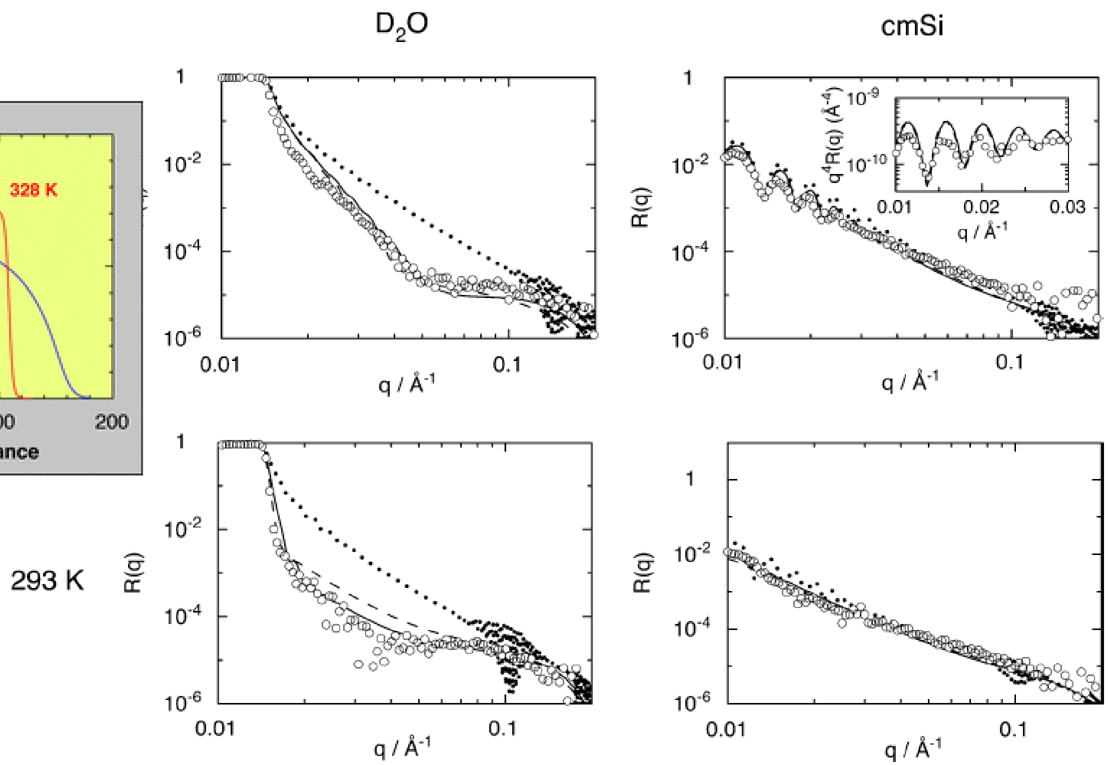

Fig. 6 Experimental reflectivity profiles obtained at ILL (circles) and fitted reflectivity profiles using a polymer layer model (dashed curves) and a lattice mean-field theory (solid curves) for polymers grafted on a Si/SiO_2/initiator surface at 328 K (top) and 293 K (bottom) in D_2O (left) and cmSi (right). Reflectivity profiles using a polymer layer model with zero roughness are also shown (dotted curves). The top right panel contains an inset displaying $q^4R(q)$ *versus* q for small q.

J. Zhang, et al., *Soft Matter*, 4, 500–509 (2008).

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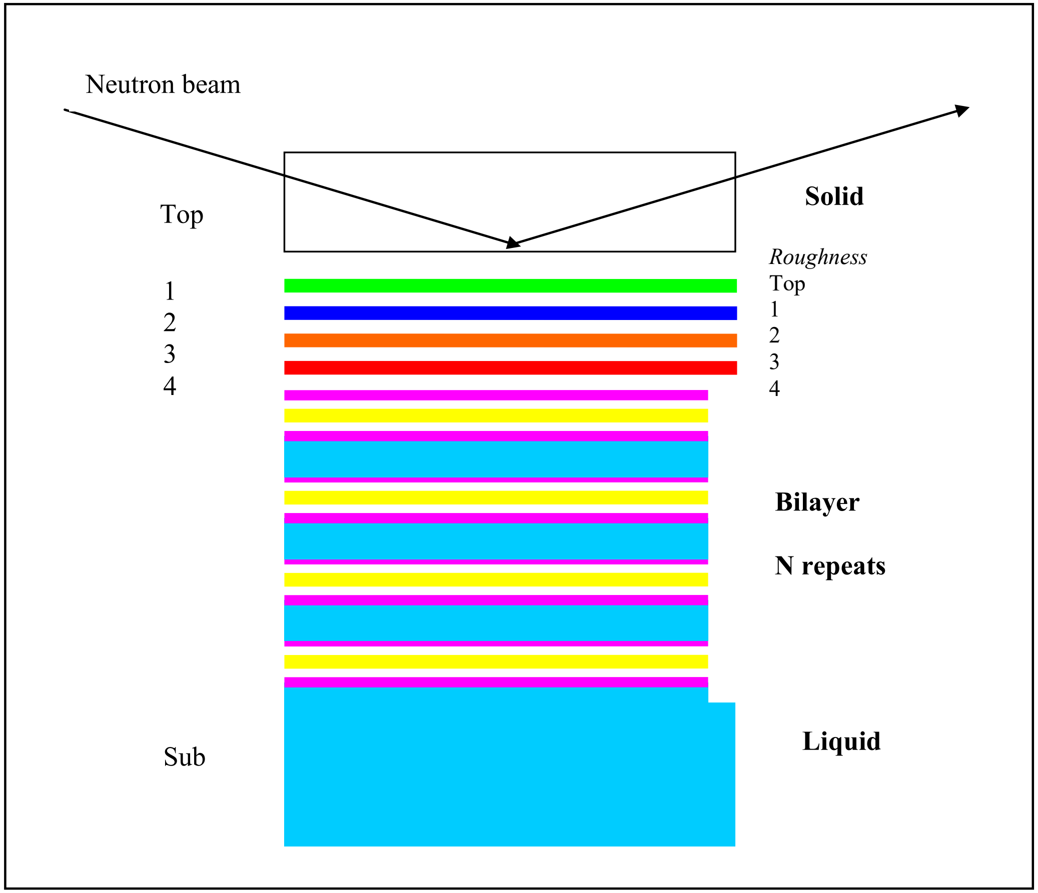
Repeating Layers

A one dimensional crystal

Bragg's law

Intensity of peaks may

Depend on size and disorder



Calculate reflectivity for a profile

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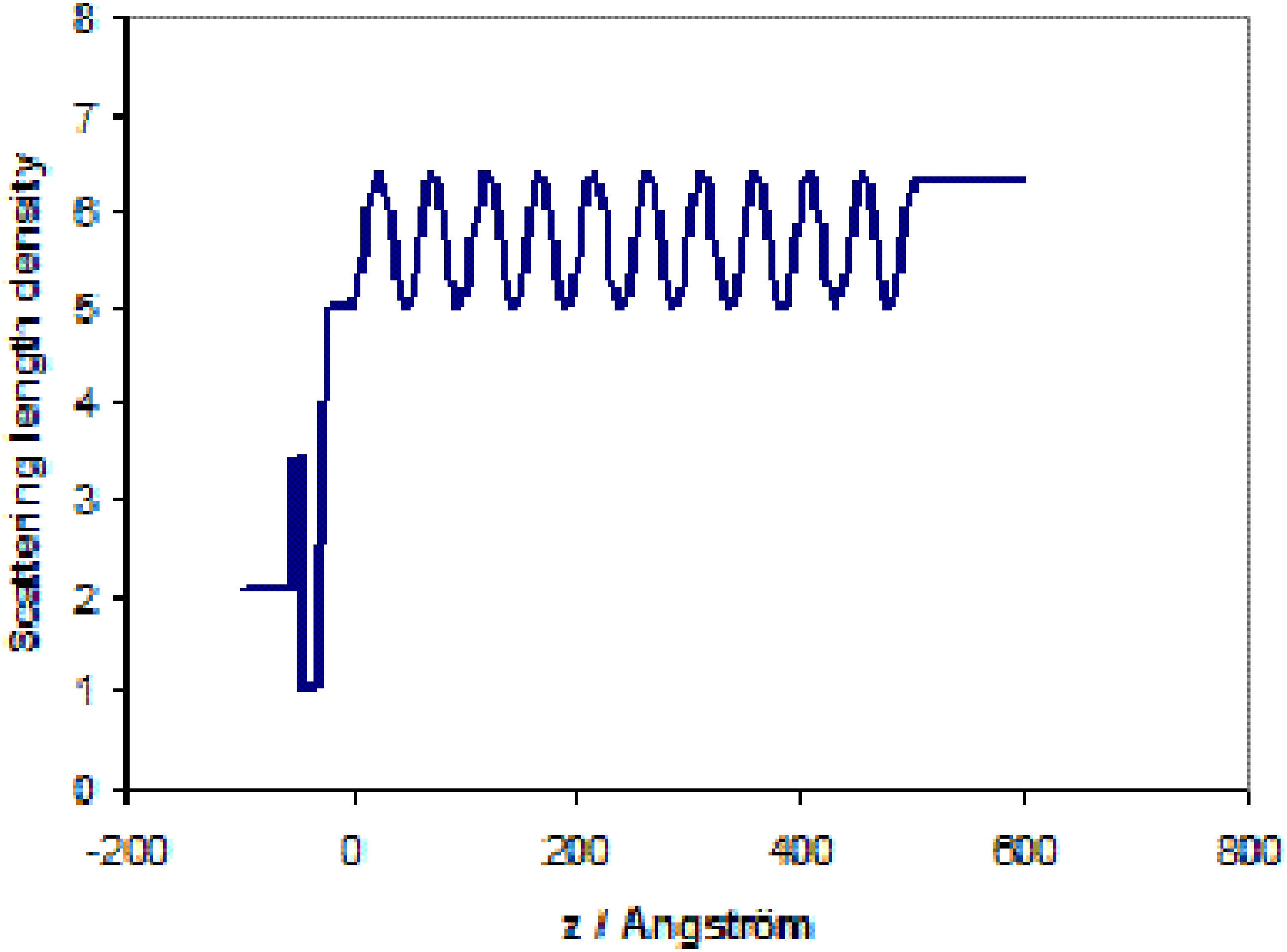

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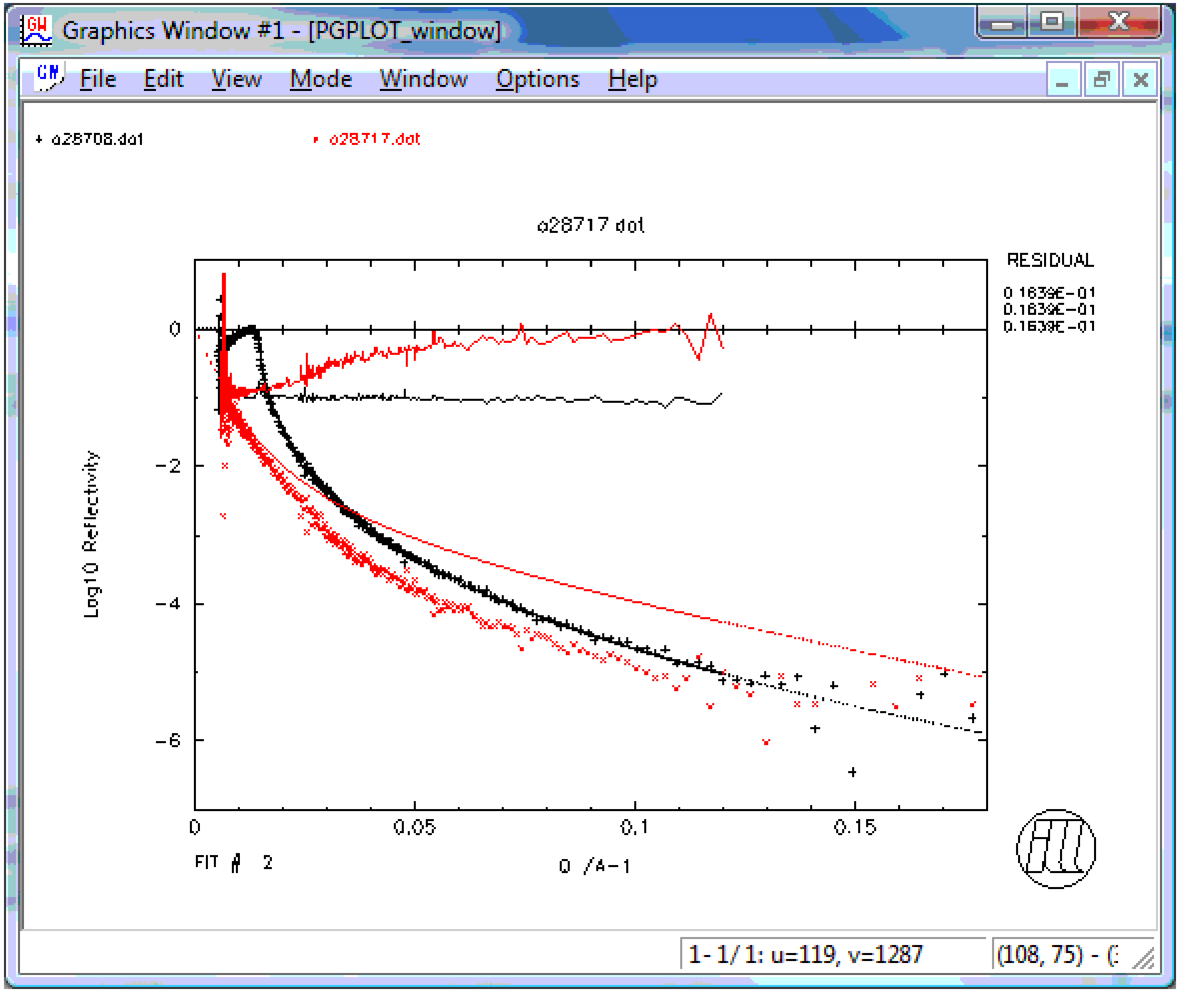
Using Multiple Contrasts



Simultaneous fits for multiple data sets

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Off-specular Scattering, GISANS, Near-surface SANS

Adrian R. Rennie

Interfaces are 3-dimensional

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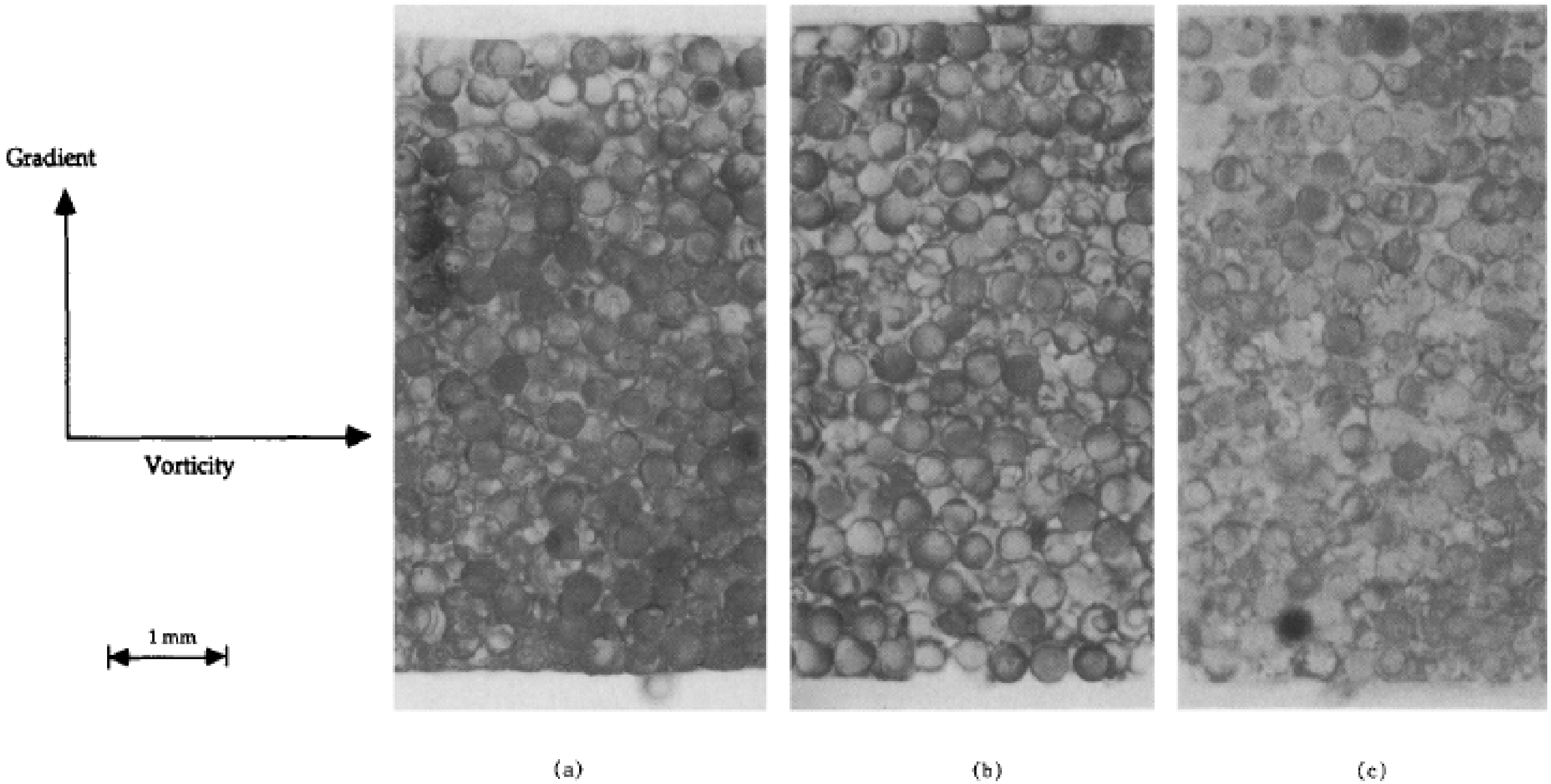

Understanding rheology – shear flow

Brown et al. *Progress in Colloid and Polymer Science* **98**, (1995) 99-102.

Fate of a Neutron at an Interface

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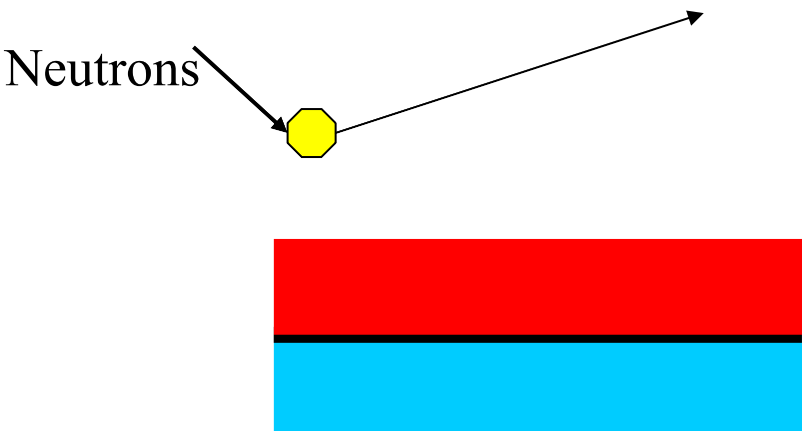
- Reflected
- Scattered/Diffracted from surface
- Absorbed
- Scattered from bulk (either side of surface)
- Other accidents



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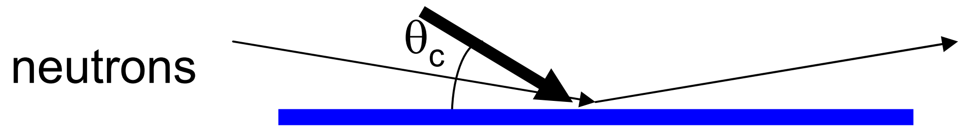
Evanescent Wave

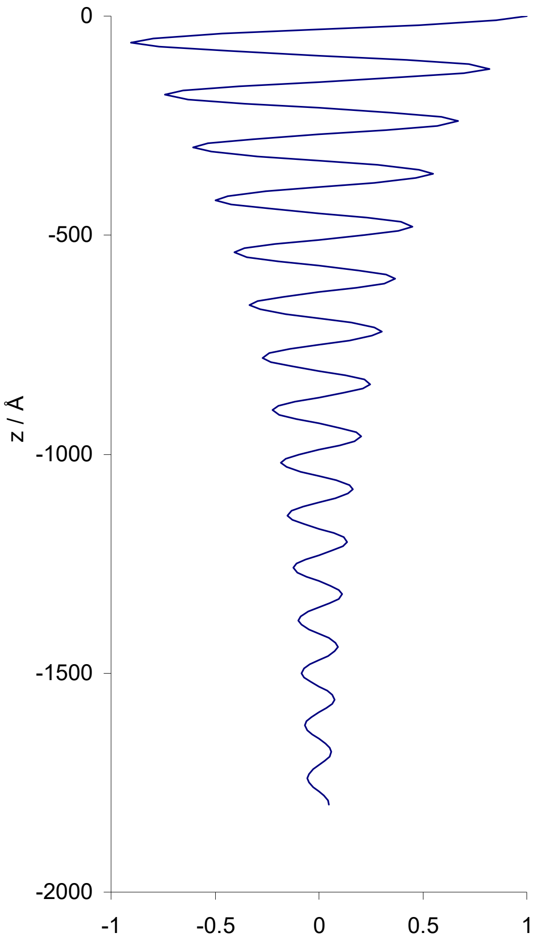


Below k_c no travelling wave enters the sample

Amplitude decays with depth in sample

Decay length depends on $(\theta_c - \theta)$

Evanescent wave can cause scattering



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Looking at Materials

Looking at Materials

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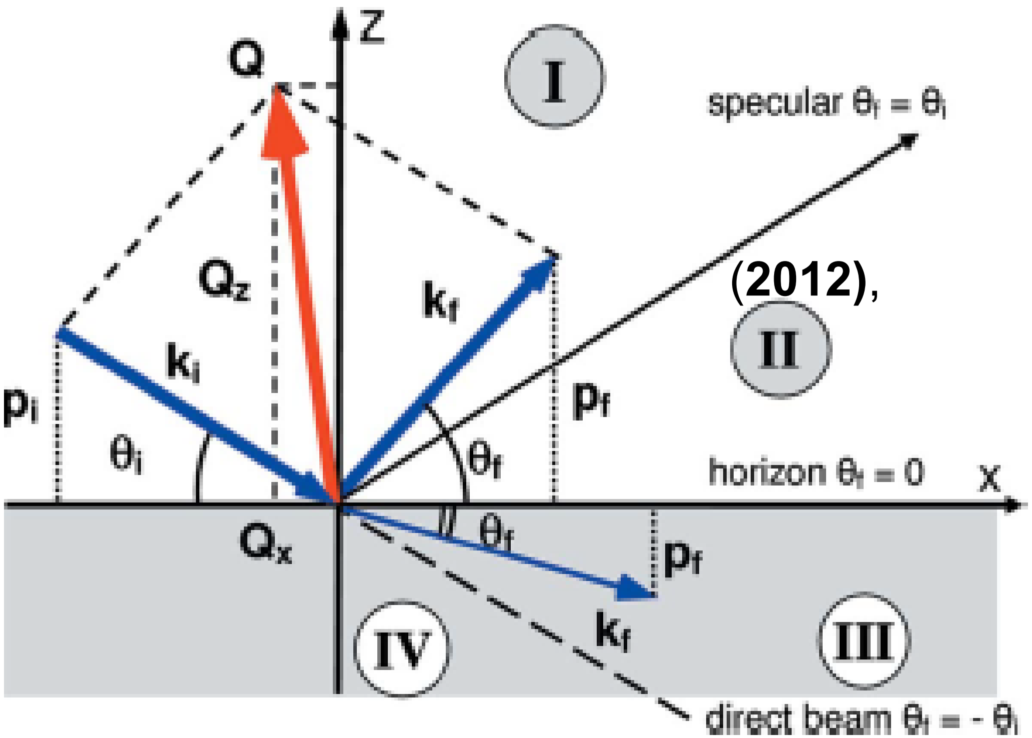
Off-specular & Reflection



$Q_z \approx (2\pi/\lambda)\ (\theta_i + \theta_f)$

$Q_x \approx (2\pi/\lambda)\ (\theta_i + \theta_f)\ (\theta_i - \theta_f)$

Frédéric Ott, Sergey Kozhevnikov ‘Off-specular data representations in neutron reflectivity’, J. Appl. Cryst. 44, (2011), 359-369.

Scattering from Surface Structures

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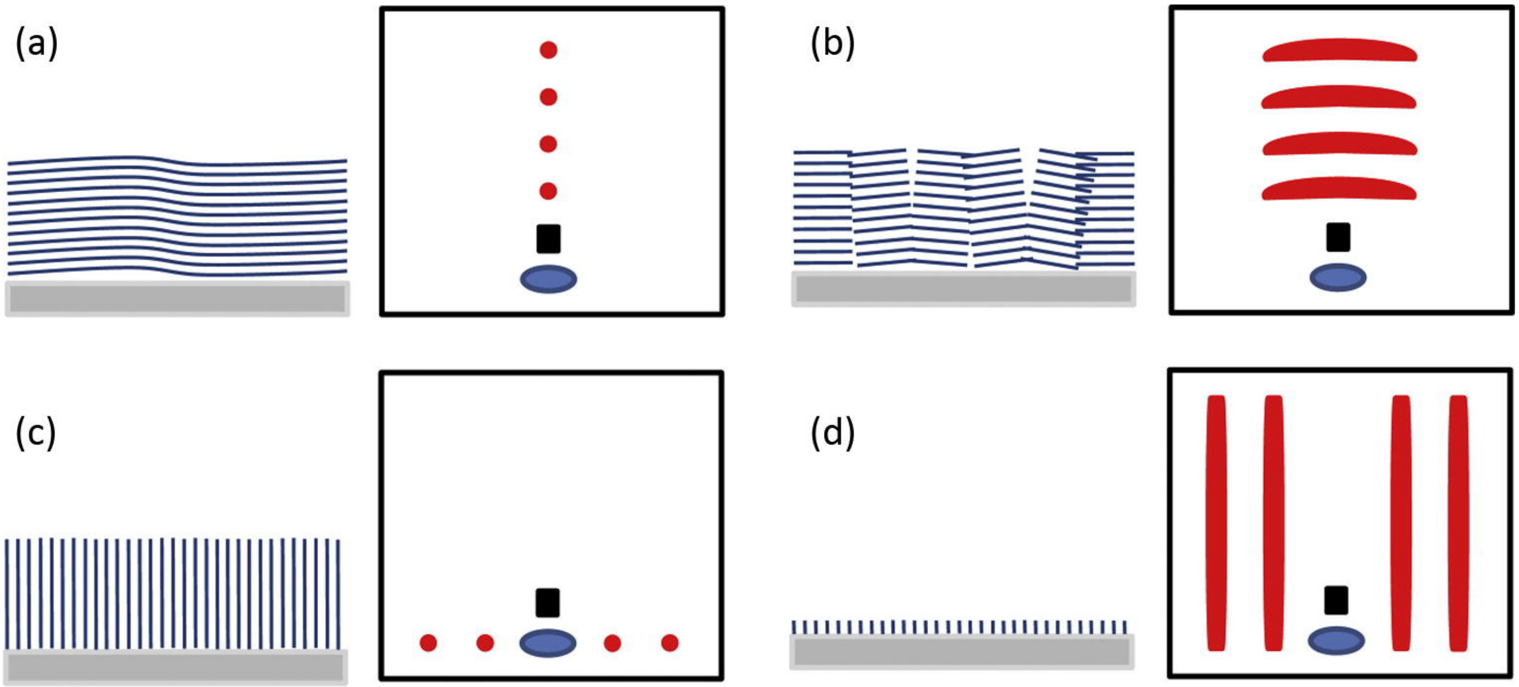
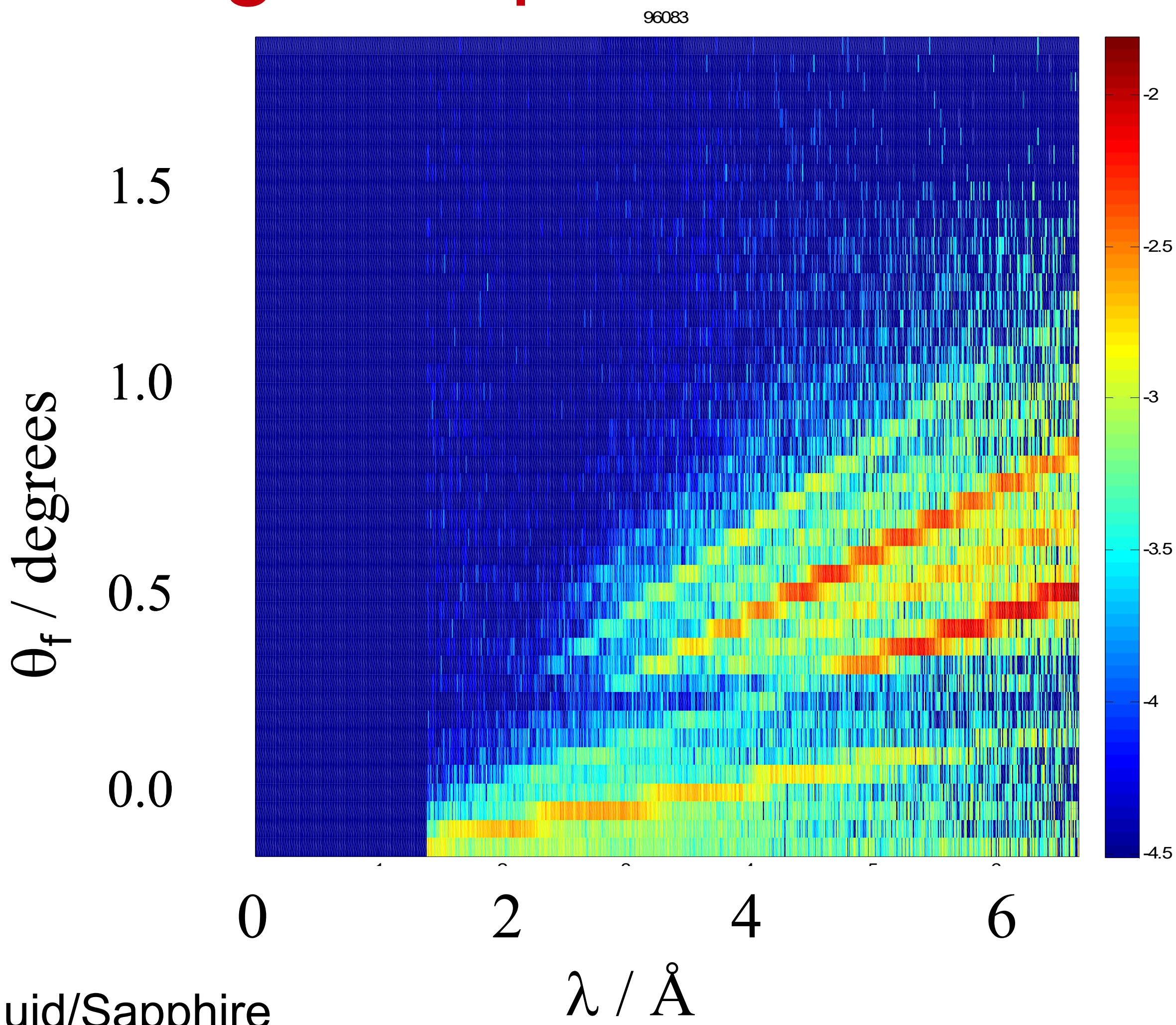


Peter Müller-Buschbaum 'GISAXS and GISANS as metrology technique for understanding the 3D morphology of block copolymer thin films' *European Polymer Journal* **81**, (2016), 470-493.

Strong Off-specular Scattering



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PS latex in D_2O Liquid/Sapphire

10% vol. dispersion, Radius ~350 Å. Sapphire substrate, θ_i = 0.35 deg

PS latex in D_2O Liquid/Sapphire

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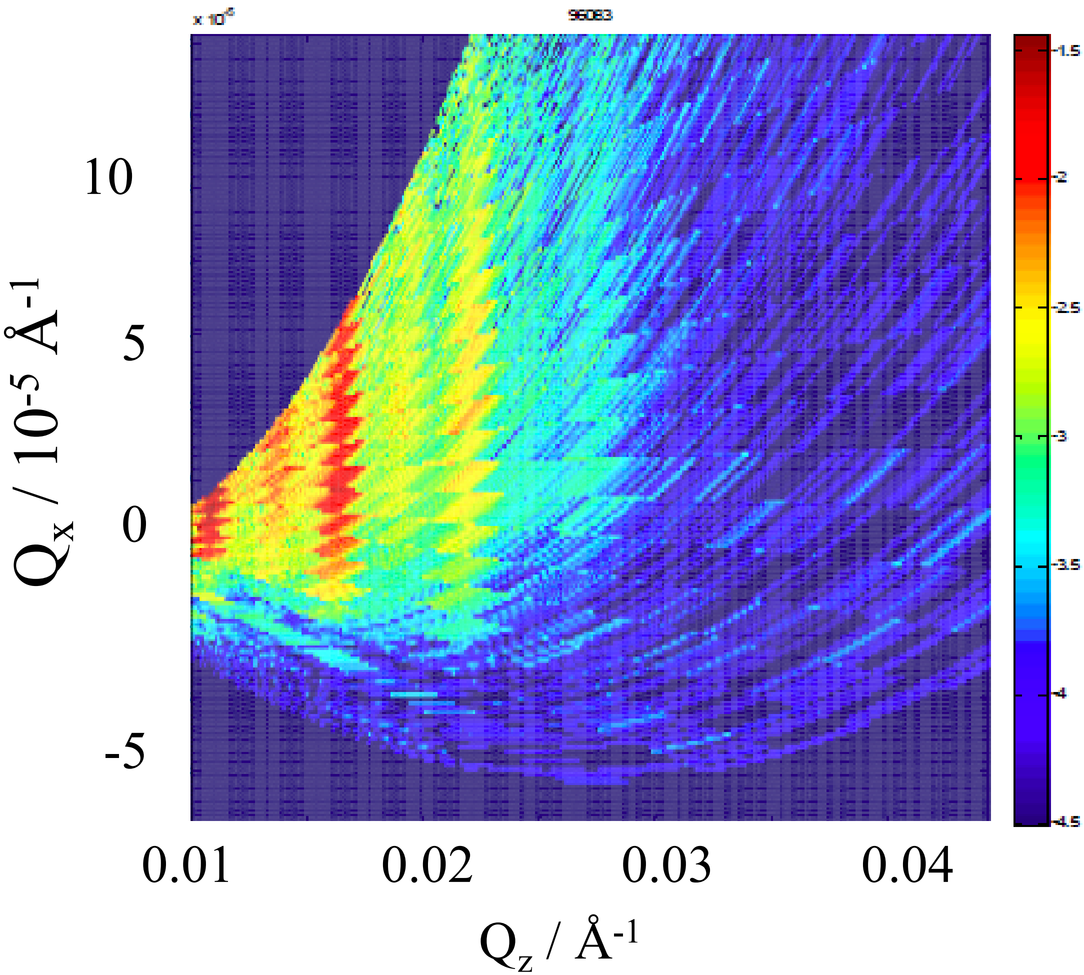
Transform to map of Q_zQ_x



10% vol. dispersion, Radius ~350 Å, sapphire substrate, $\theta_i = 0.35$ deg

Some Scattering at Interfaces

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X-ray scattering – glass

Sinha et al., *Phys. Rev. B.* **38**, 2297, 1988.

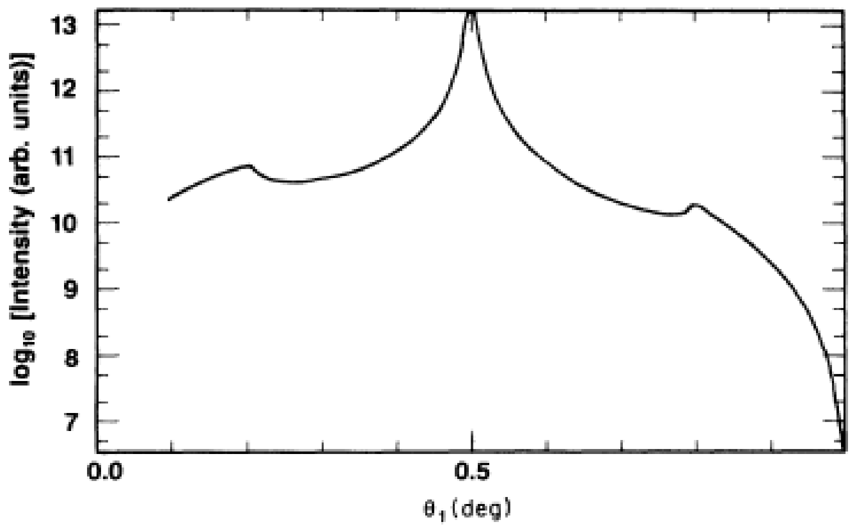

FIG. 6. Calculation of diffuse scattering in the distorted-wave Born approximation for rocking curve where θ_1 and θ_2 are varied such that 2θ is fixed at 1°. The asymmetry is due to the area of the illuminated surface decreasing as θ_1 is increased. The q_y direction has been integrated over. Parameters are $\sigma = 7$ Å, $h = 0.2$, $\xi = 7000$ Å, and the optical constants for Pyrex are given in Sec. V.

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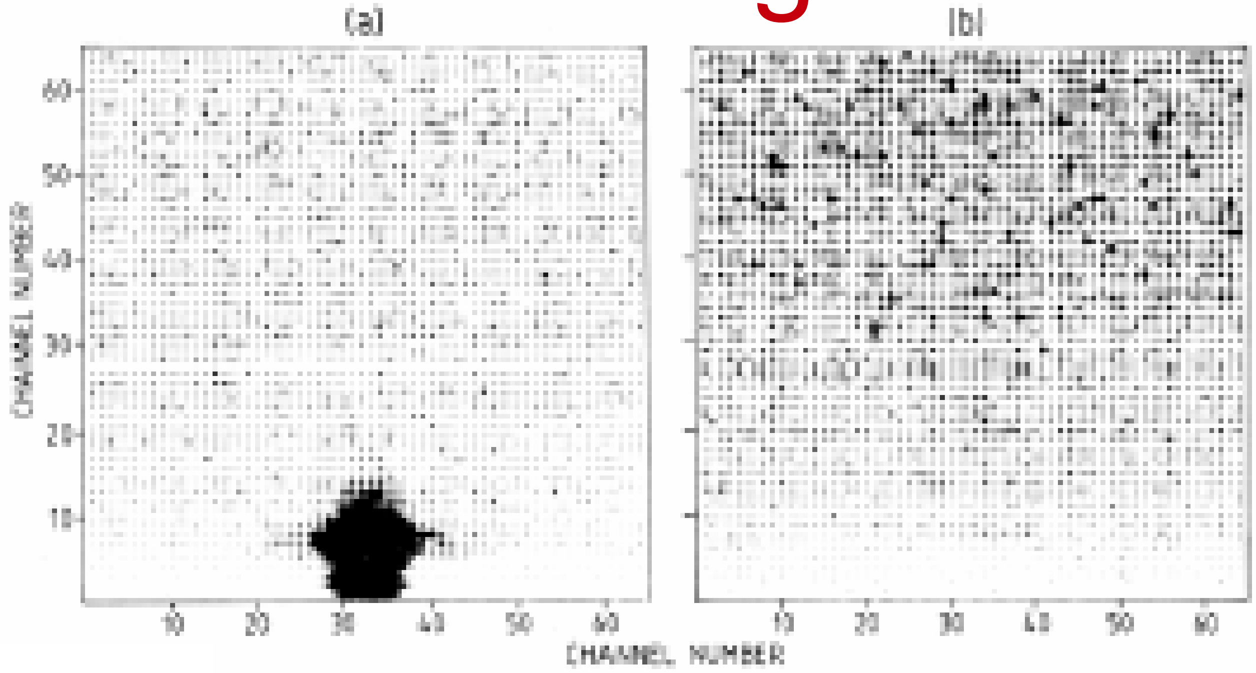
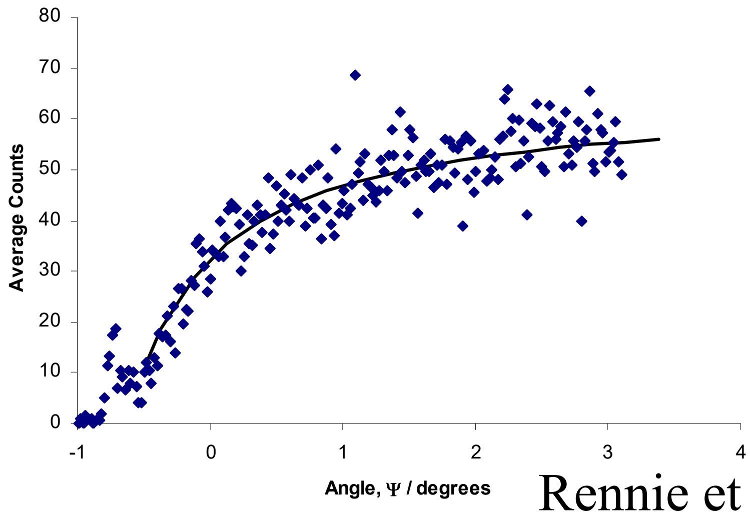
Incoherent background





Scattering from D_2O

and from null reflecting water

(8% D_2O)

Rennie et al., *Macromolecules* **22**, (1989), 3466-3475.

Interfacial structure: GISANS

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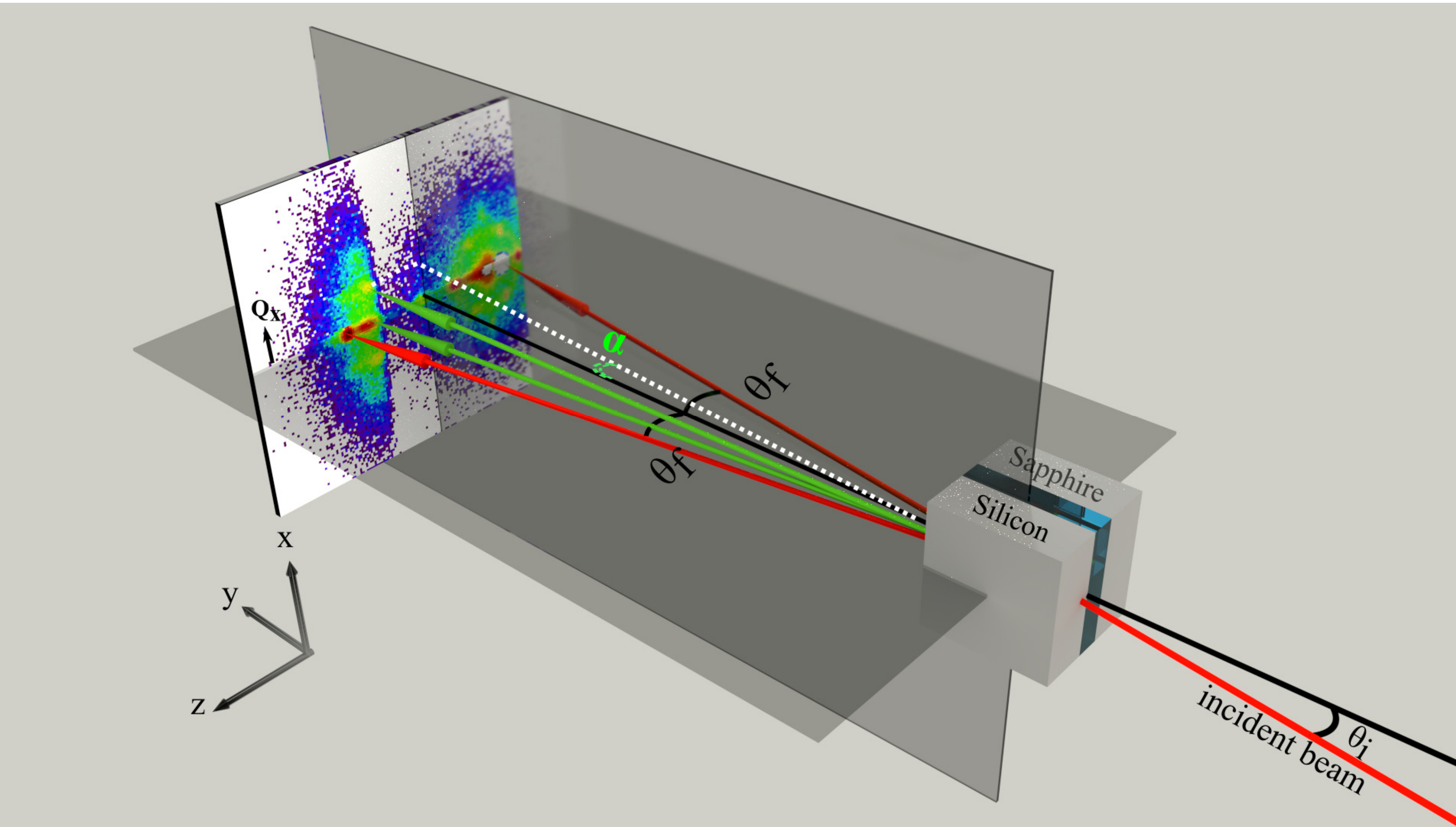


Nouhi et al. *Journal of Applied Crystallography* (2017)

Calculating Scattering

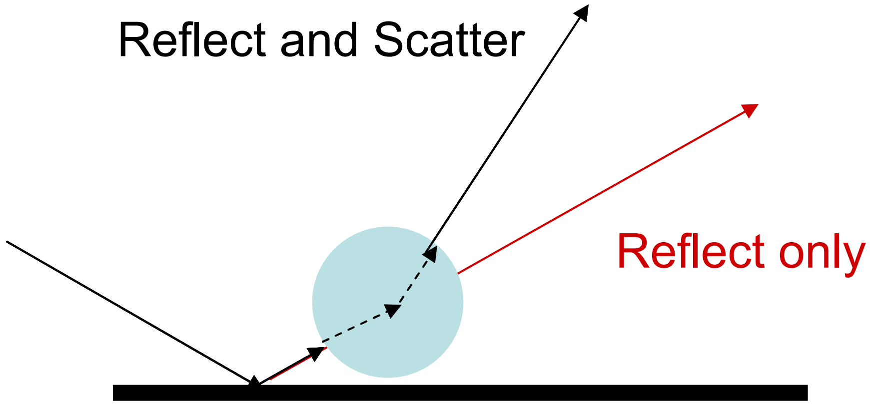
Distorted Wave Born Approximation (DWBA)

Simply allow for sequential events e.g.

Reflection then Scattering

Refraction then Scattering

Scattering then Reflection



Reflection followed by weak scattering.

(a) Optical Matrix Calculation

(b) Weak Scattering (Born approximation)

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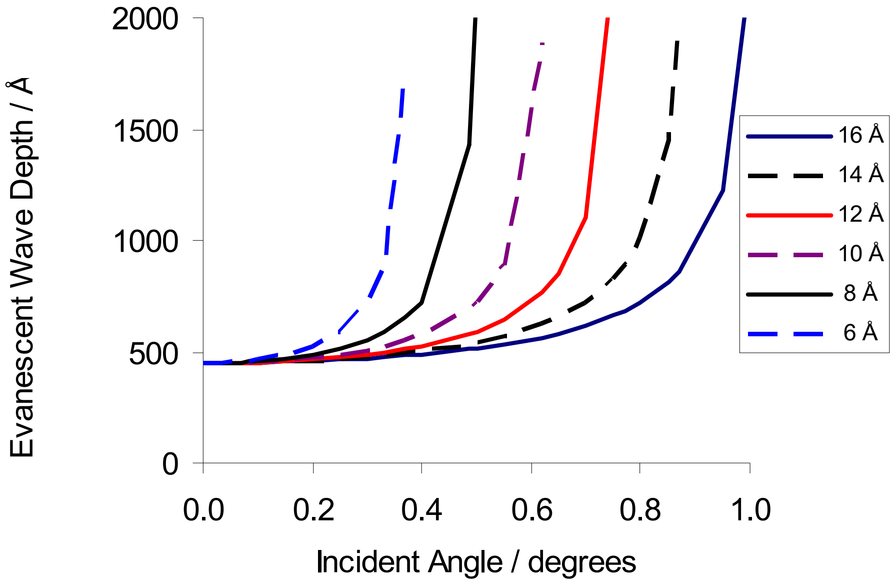
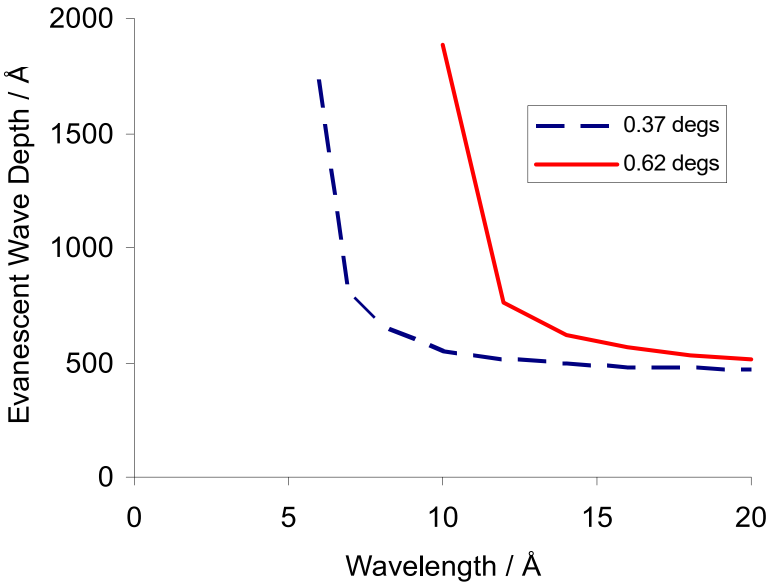
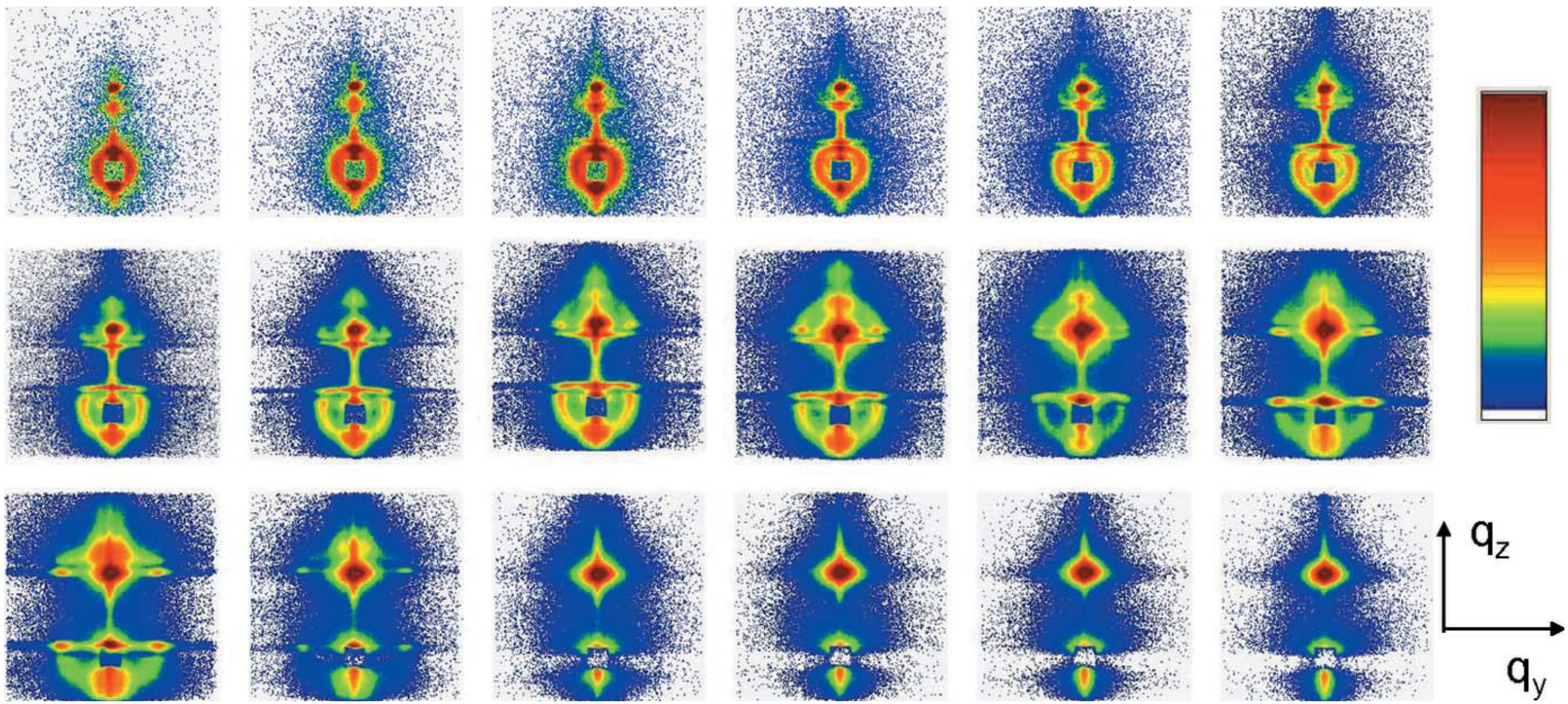
How deep is the evanescent wave?





Silicon/D_2O Interface

Copolymer films

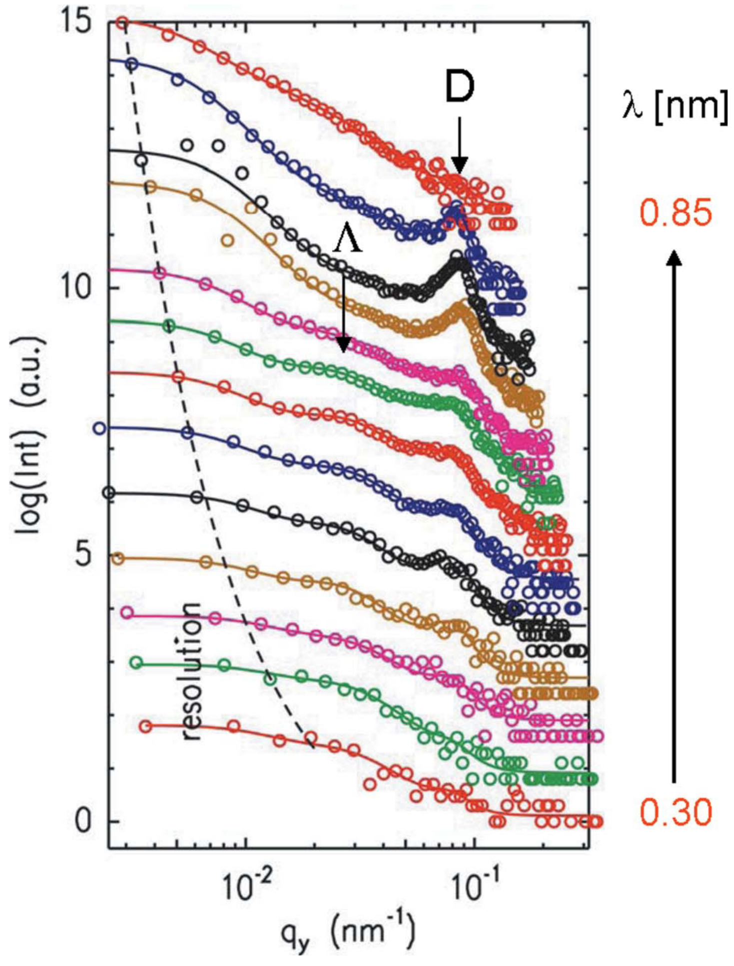


P. Müller Buschbaum *et al. J. Appl. Cryst*. **47**, (2014), 1228–1237

Changes with Depth

Horizontal cuts

- Used wavelength to probe different depths
- Longer wavelength looks neare the surface



J. Appl. Cryst. **47**, (2014), 1228–1237

Diffraction from Surface Layers

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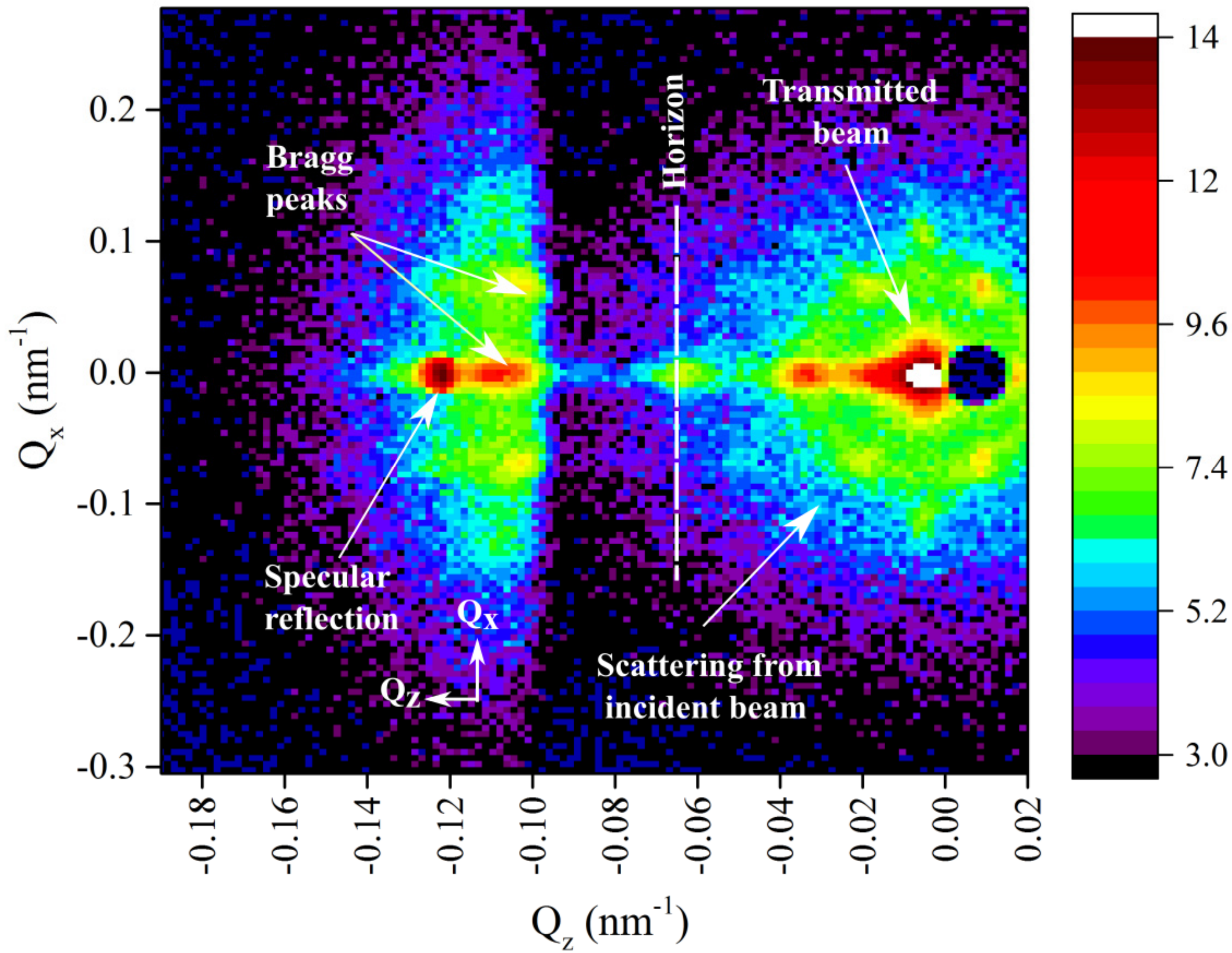

Nouhi et al. *Journal of Applied Crystallography* (2017)

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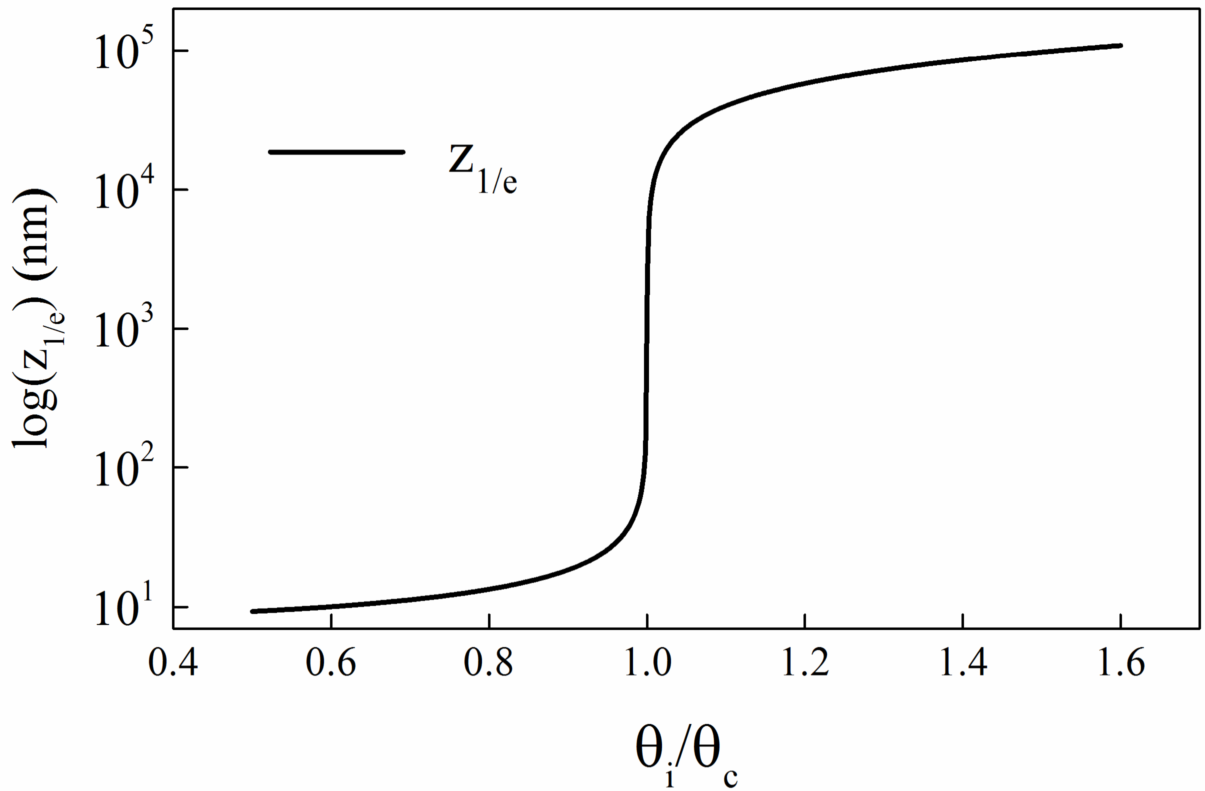
Penetration depth

$$z_{1/e} = \sqrt{2}\lambda \Big/ 4\pi \left[\sqrt{(\theta_i^2 - \theta_c^2)^2 + \left(\frac{\lambda}{2\pi}\mu\right)^2} - (\theta_i^2 - \theta_c^2) \right]^{1/2}$$

A depth sensitive technique:

Wavelength
Incident angle



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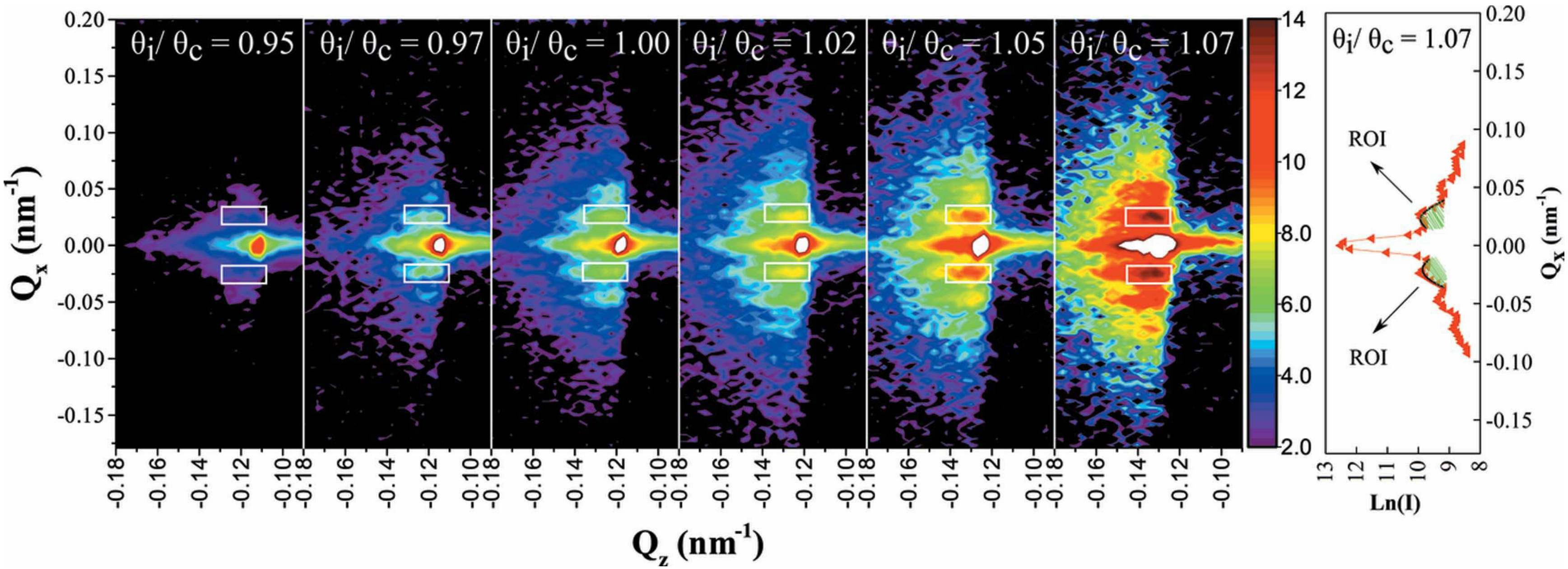
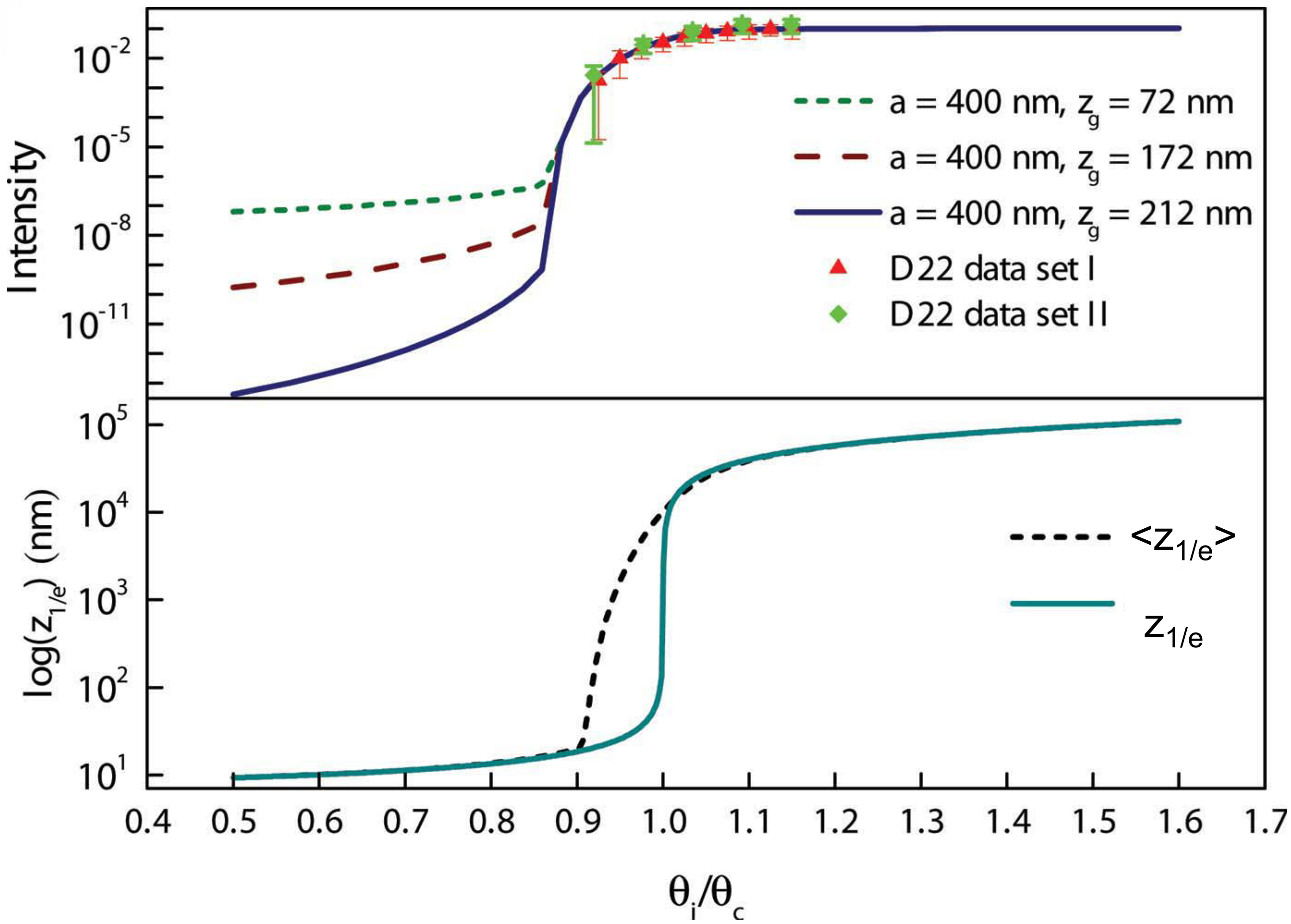
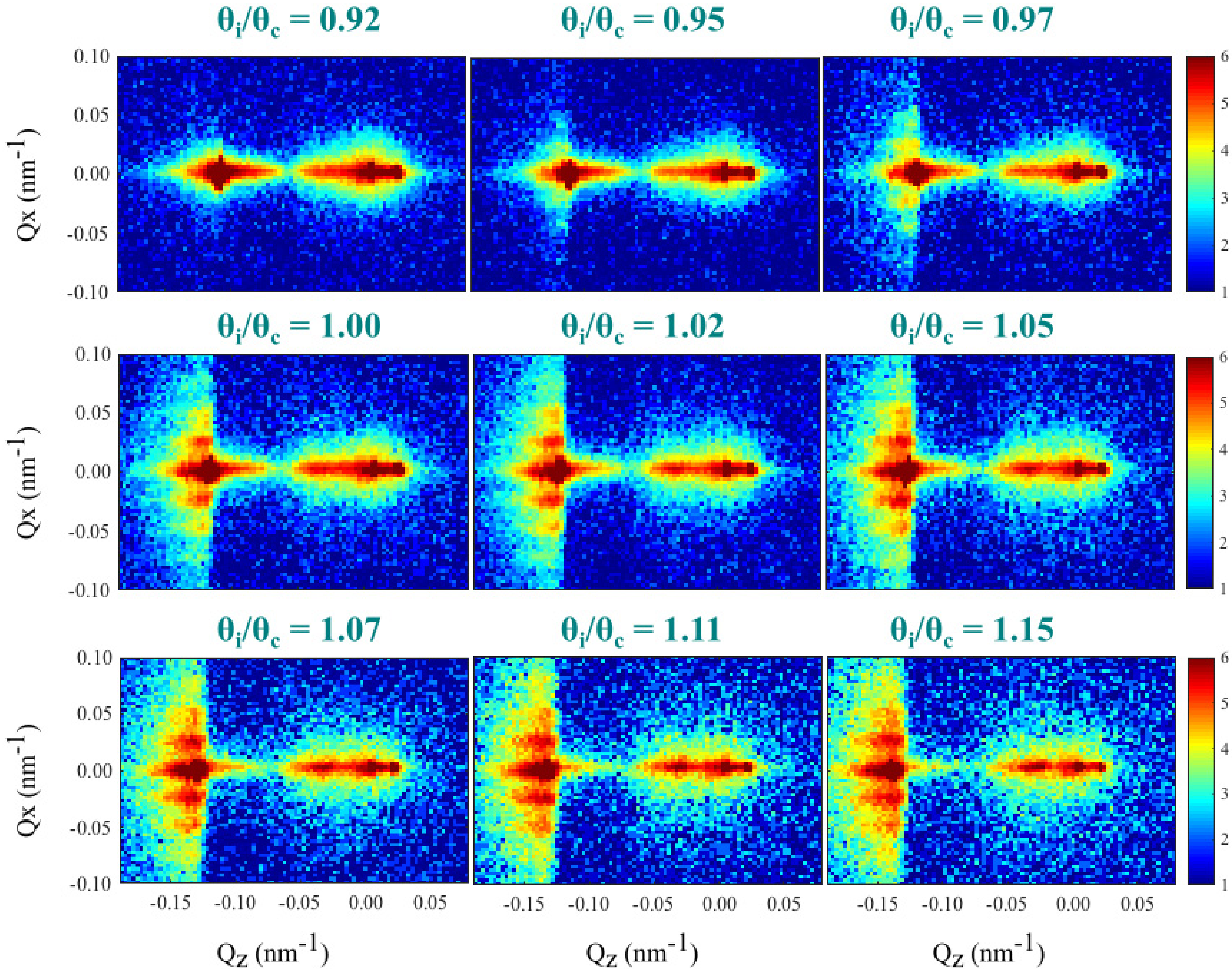
Data at different angles

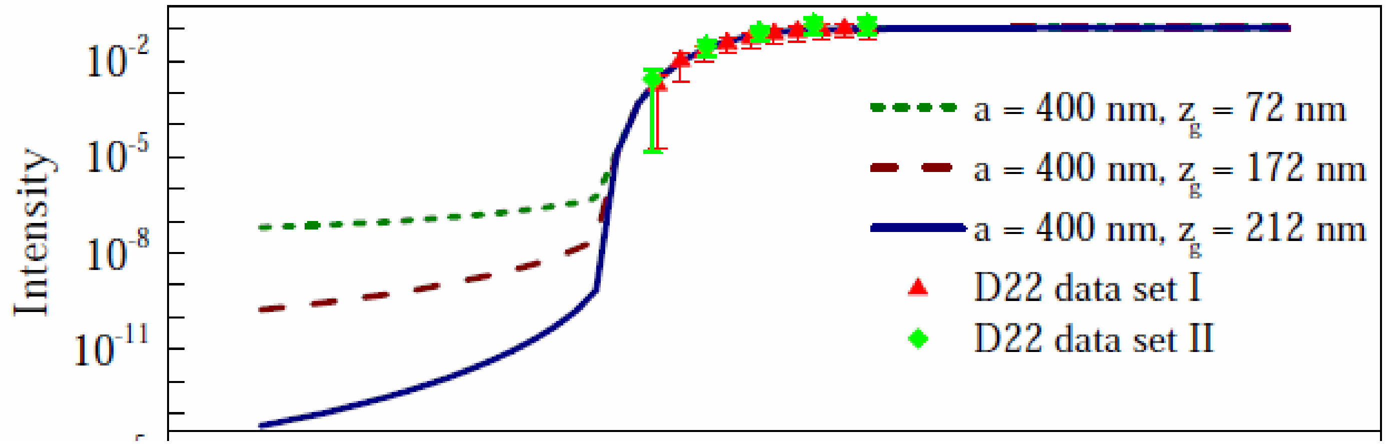


Data at different angles



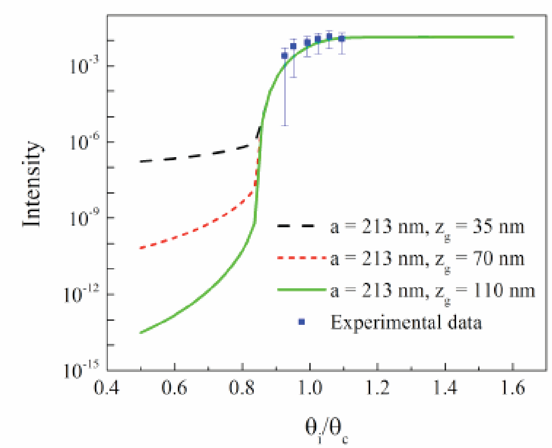

θi/θc = 0.92
θi/θc = 0.95
θi/θc = 0.97
θi/θc = 1.00
θi/θc = 1.02
θi/θc = 1.05
θi/θc = 1.07
θi/θc = 1.11
θi/θc = 1.15
Qx (nm-1)
Qz (nm-1)
0.10
0.05
0.00
-0.05
-0.10
-0.15
1
2
3
4
5
6

Calculations & Intensity Data



D22 - ILL

QCM-D data: structure forms with a separation from the interface [Hellsing et al. 2017, *manuscript*]



NG3 SANS - NCNR

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Scattering at Interfaces

- Off-specular scattering
- Near Surface SANS
- GISANS

What is the difference?

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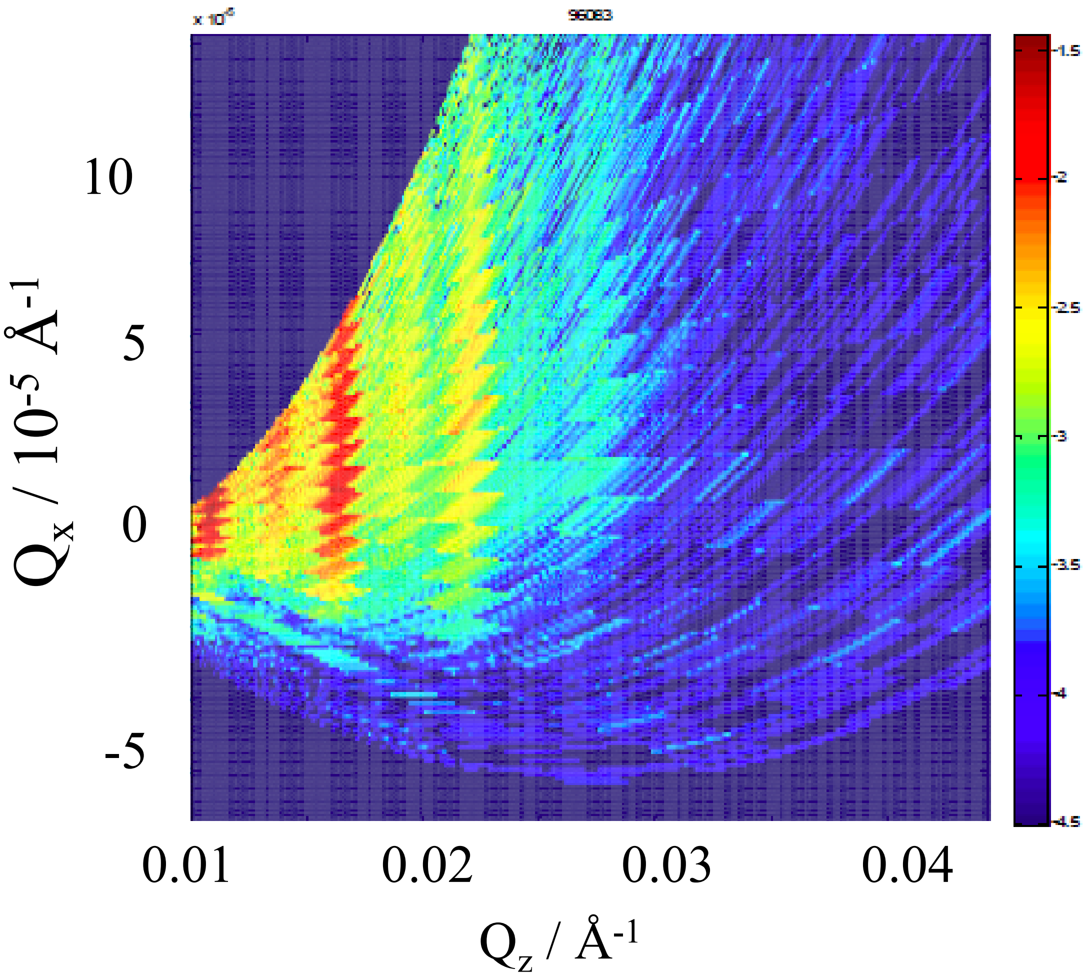
PS latex in D_2O Liquid/Sapphire

Transform to map of Q_zQ_x



10% vol. dispersion, Radius ~350 Å, sapphire substrate, $\theta_i = 0.35$ deg

PS latex in D_2O – sapphire surface

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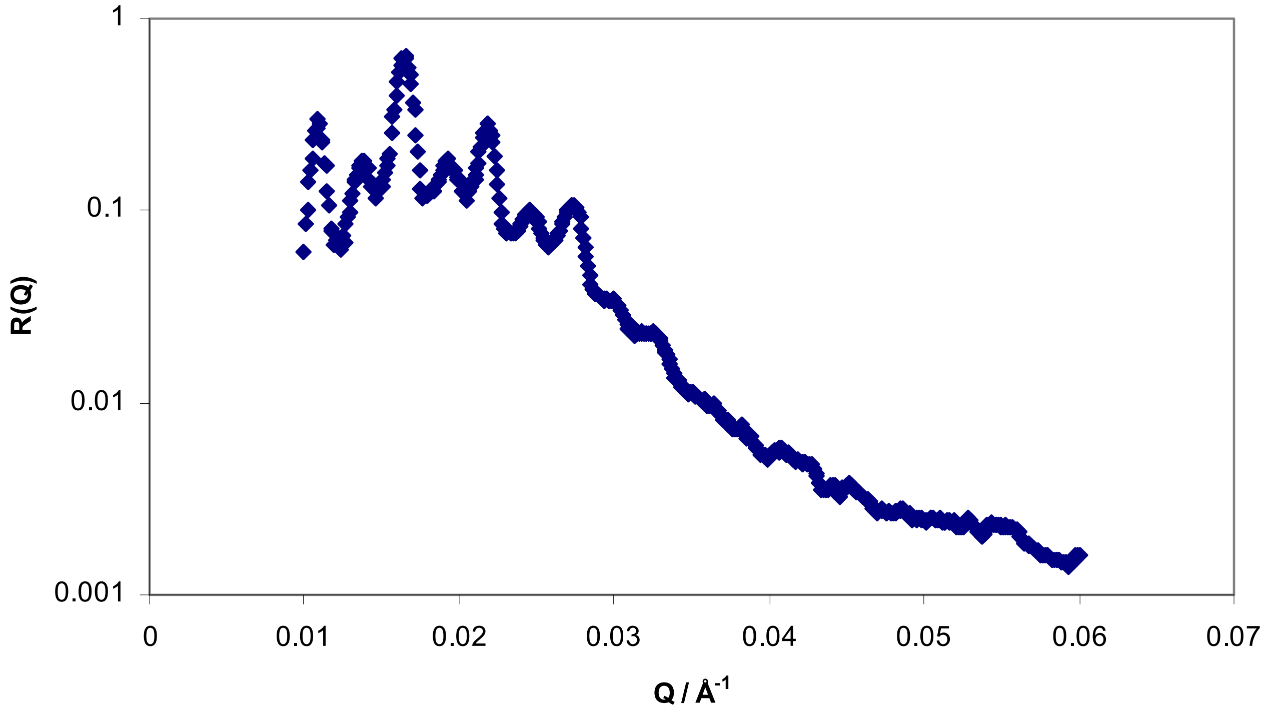
Sum along Q_x



10% vol dispersion, 0.35

PS latex in D_2O – sapphire surface

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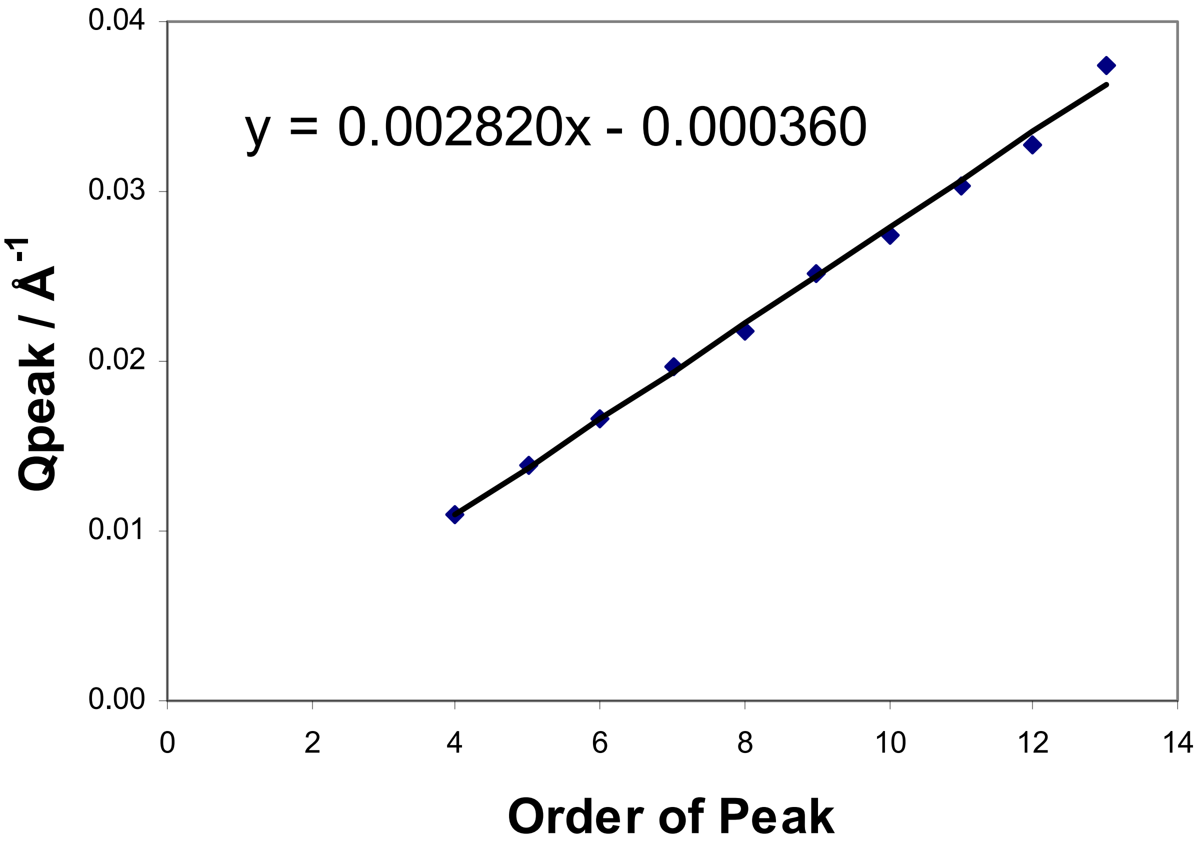
Assign Bragg peaks (index)

$Q_1 = 0.00282$ Å^{-1}

d = 2230 Å

3 first peaks outside range



10% vol dispersion, 0.35, 0.8 and1.5 deg

PS latex in D_2O – sapphire surface

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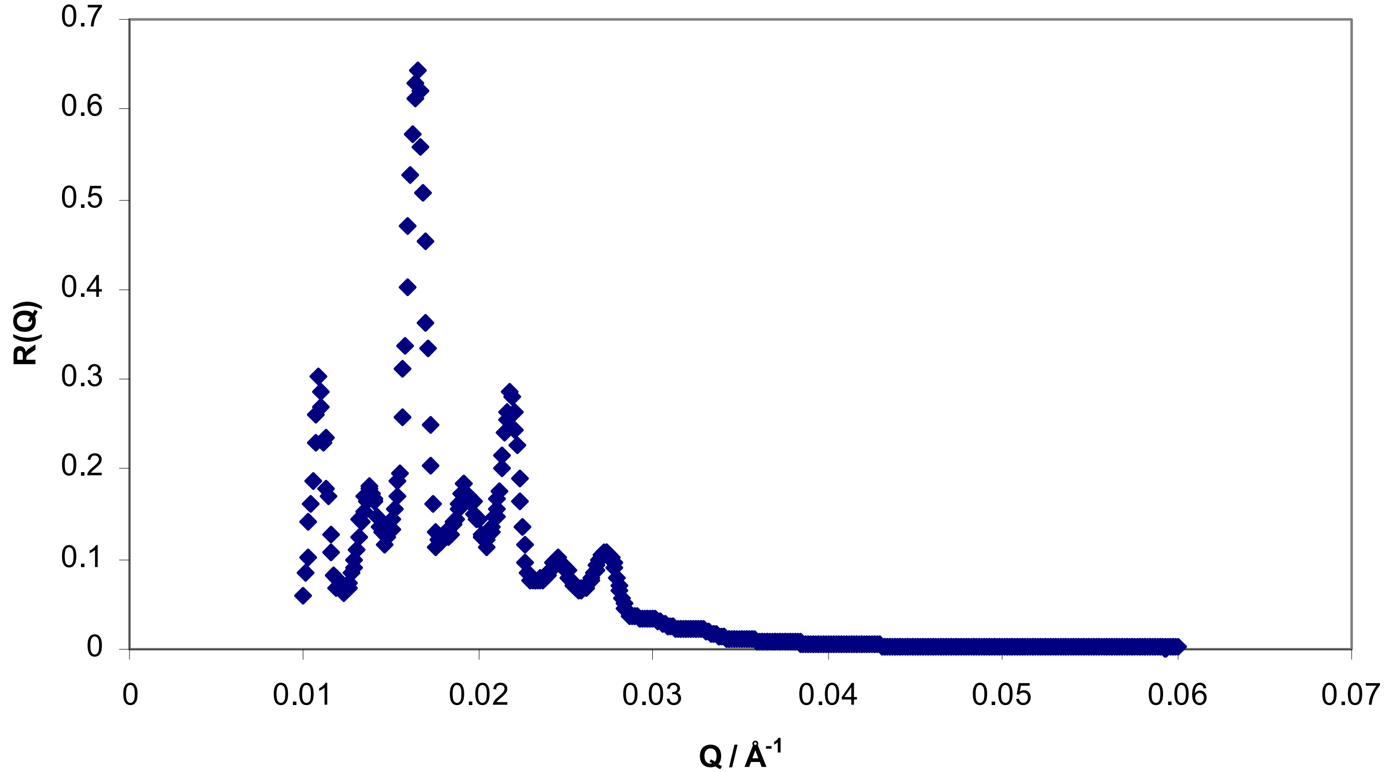
Sum along Q_x



10% vol dispersion, 0.35

Compare Qx and Qz

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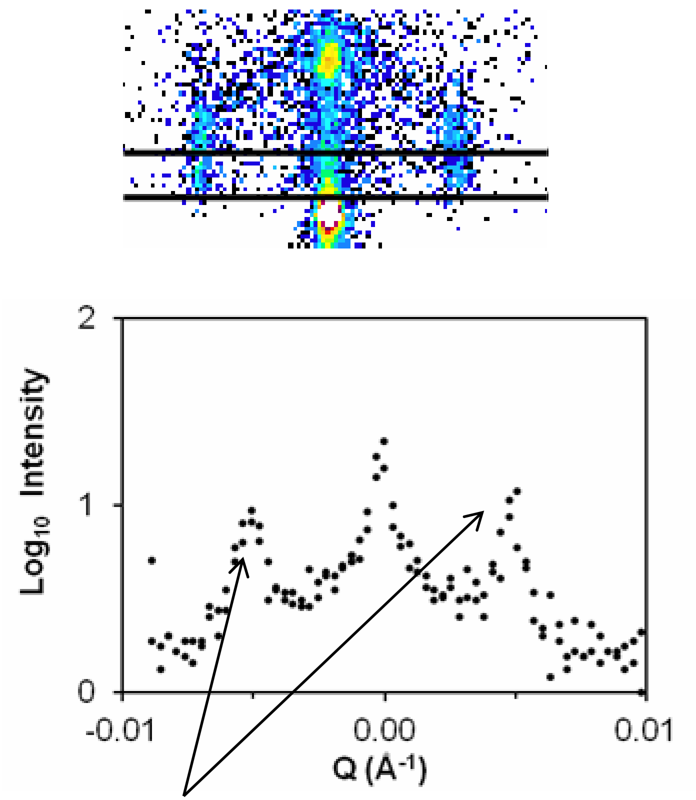

M. S. Hellsing, et al. *Applied Physics Letters*, **100**, (2012), 221601.