



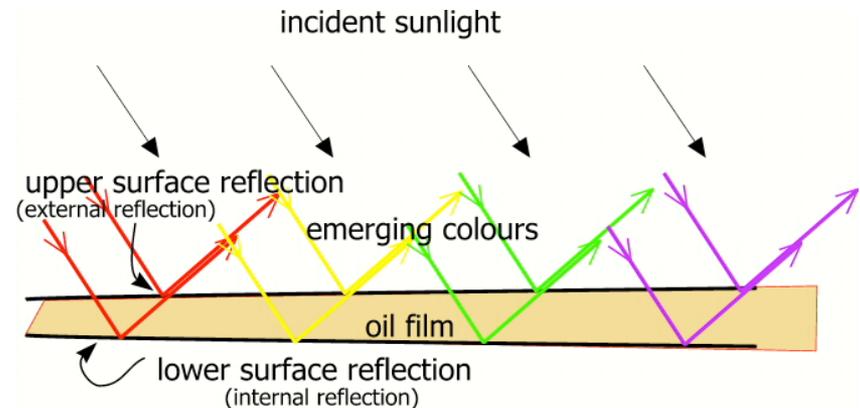
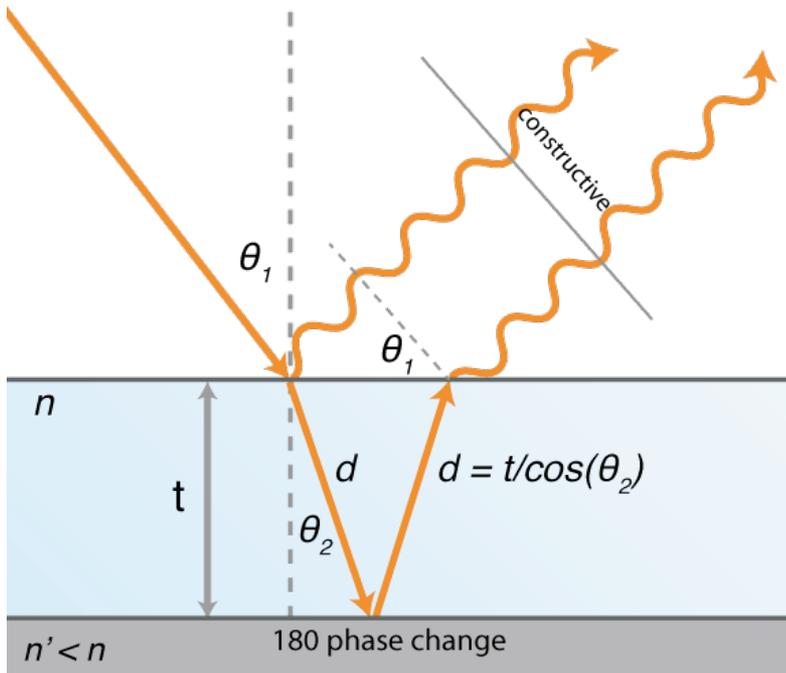
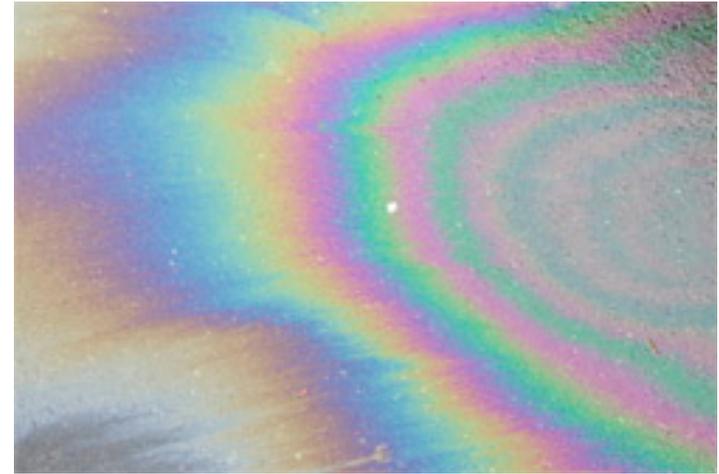
by

Roger Pynn

Erice 2016: Surface Reflection

You have all done reflectometry

- Light reflected from the top and bottom of the film interferes
- Certain wavelengths interfere constructively

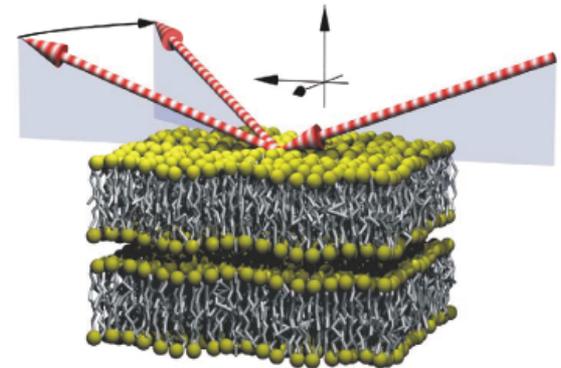


Surface Reflection Is Very Different From Most Neutron Scattering

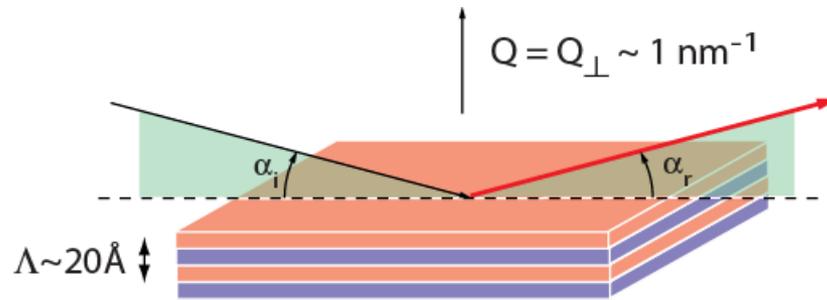
- Normally we work out the neutron cross section by adding scattering from different nuclei
 - We ignore double scattering processes because these are usually very weak
- This approximation is called the Born Approximation
- Below an angle of incidence called the critical angle, neutrons are perfectly reflected from a smooth surface
 - This is NOT weak scattering and the Born Approximation is not applicable to this case
- Specular reflection is used:
 - In neutron guides
 - In multilayer monochromators and polarizers
 - To probe surface and interface structure in layered systems

Why Use Neutron Reflectivity?

- Neutrons are reflected from most materials at grazing angles
- If the surface is flat and smooth the reflection is specular
 - Perfect reflection below a critical angle
 - Above the critical angle reflectivity is determined by the variation of scattering length density perpendicular to the surface
 - i.e. we can determine the “average” density profile normal to the surface of a film on the surface

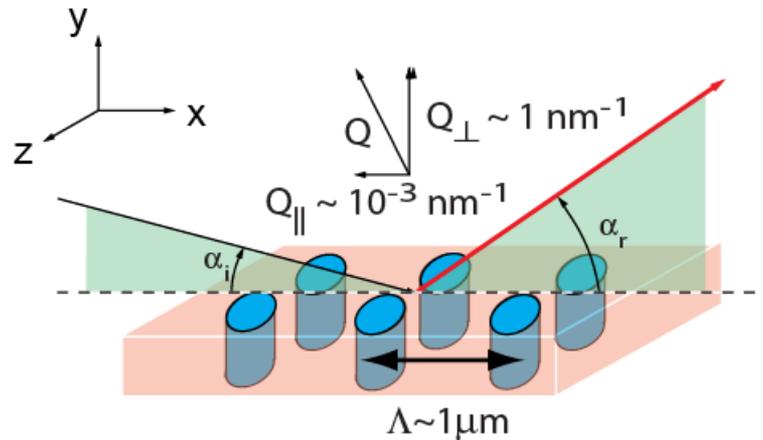


Various forms of small (glancing) angle neutron reflection



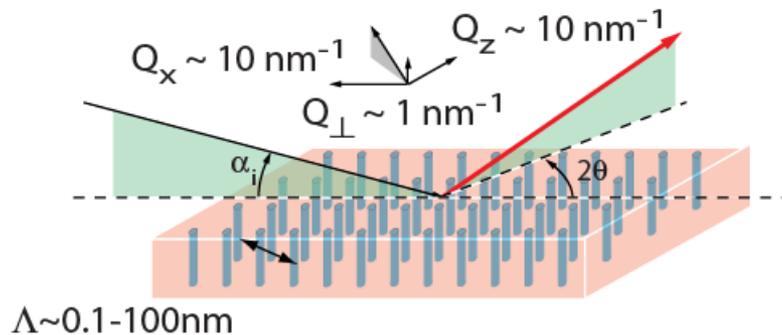
Specular reflectometry

Depth profiles
(nuclear and/or magnetic)



Off-specular (diffuse) scattering

In-plane correlated roughness
Magnetic stripes
Phase separation (polymers)

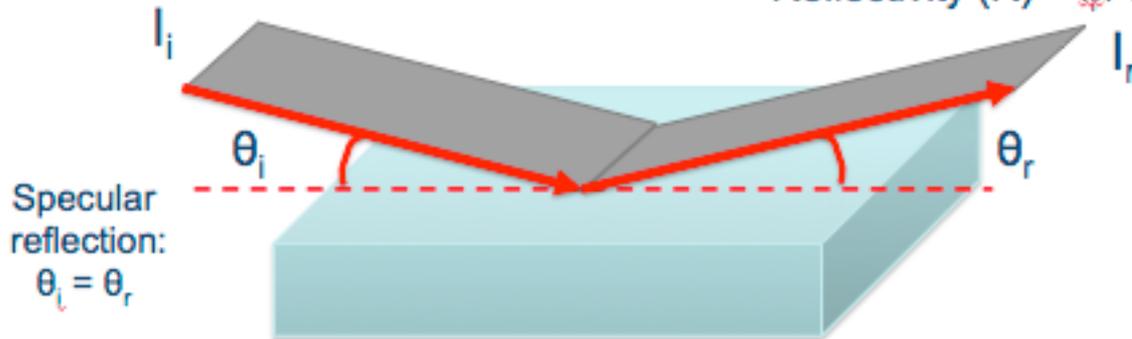
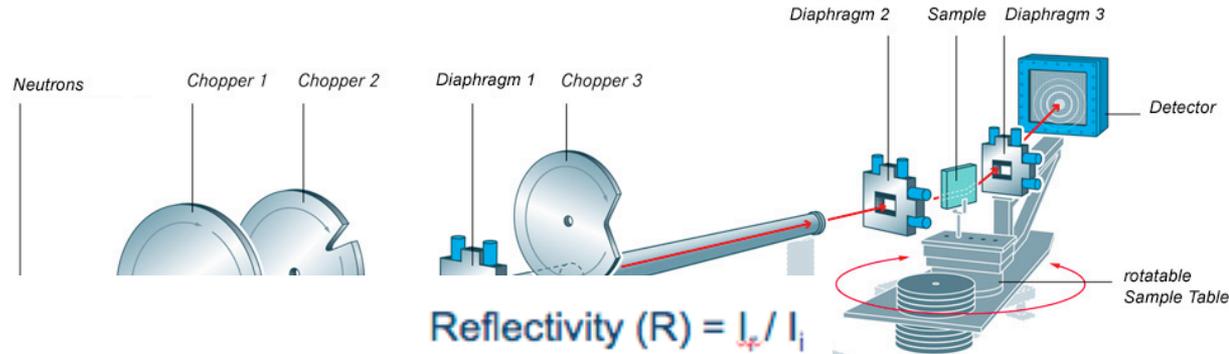


Glancing incidence diffraction

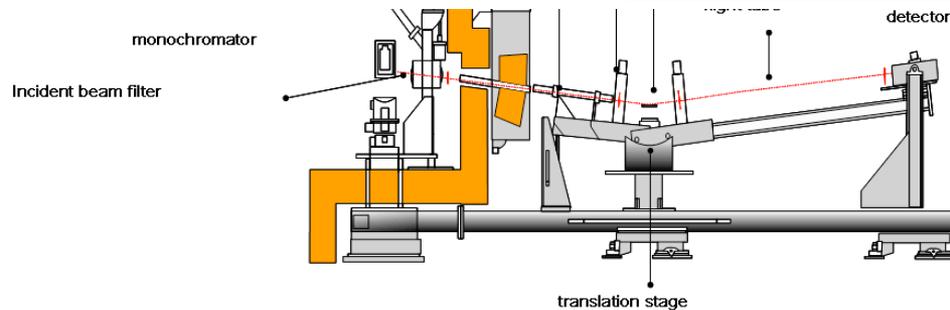
Ordering in liquid crystals
Atomic structures near surfaces
Interactions among nanodots

Neutron Reflectometers

Horizontal scattering plane; time of flight



Vertical scattering plane;
CW neutron source



Refractive Index for Neutrons

The nucleus - neutron potential is given by : $V(\vec{r}) = \frac{2\pi\hbar^2}{m} b\delta(\vec{r})$ for a single nucleus.

So the average potential inside the medium is : $\bar{V} = \frac{2\pi\hbar^2}{m} \rho$ where $\rho = \frac{1}{\text{volume}} \sum_i b_i$

ρ is called the nuclear Scattering Length Density (SLD) - the same one we used for SANS

The kinetic (and total) energy of neutron in vacuum is $E = \frac{\hbar^2 k_0^2}{2m}$

Inside the medium the total energy is $\frac{\hbar^2 k^2}{2m} + \bar{V}$

Conservation of energy gives $\frac{\hbar^2 k_0^2}{2m} = \frac{\hbar^2 k^2}{2m} + \bar{V} = \frac{\hbar^2 k^2}{2m} + \frac{2\pi\hbar^2}{m} \rho$ or $k_0^2 - k^2 = 4\pi\rho$

Since $k/k_0 = n = \text{refractive index (by definition)}$, and ρ is very small ($\sim 10^{-6} \text{ \AA}^{-2}$) we get :

$$n = 1 - \lambda^2 \rho / 2\pi$$

Since generally $n < 1$, neutrons are externally reflected from most materials.

Only Neutrons With Very Low Velocities Perpendicular to a Surface Are Reflected

$$k / k_0 = n$$

The surface cannot change the neutron velocity parallel to the surface so :

$$k_0 \cos \alpha = k \cos \alpha' = k_0 n \cos \alpha' \quad \text{i.e.} \quad n = \cos \alpha / \cos \alpha'$$

Neutrons obey Snell's Law

$$\text{Since } k^2 = k_0^2 - 4\pi\rho \quad k^2 (\cos^2 \alpha' + \sin^2 \alpha') = k_0^2 (\cos^2 \alpha + \sin^2 \alpha) - 4\pi\rho$$

$$\text{i.e. } k^2 \sin^2 \alpha' = k_0^2 \sin^2 \alpha - 4\pi\rho \quad \text{or } k_z^2 = k_{0z}^2 - 4\pi\rho$$

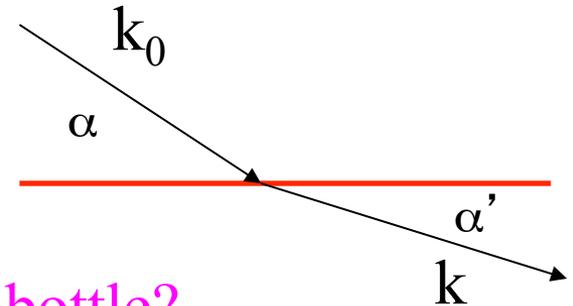
The critical value of k_{0z} for total external reflection is $k_{0z} = \sqrt{4\pi\rho}$

$$\text{For quartz } k_{0z}^{\text{critical}} = 2.05 \times 10^{-3} \text{ \AA}^{-1}$$

$$(2\pi / \lambda) \sin \alpha_{\text{critical}} = k_{0z}^{\text{critical}} \Rightarrow$$

$$\alpha_{\text{critical}} (^{\circ}) \approx 0.02 \lambda (\text{\AA}) \text{ for quartz}$$

$$\text{Note: } \alpha_{\text{critical}} (^{\circ}) \approx 0.1 \lambda (\text{\AA}) \text{ for nickel}$$



How do we make a neutron bottle?

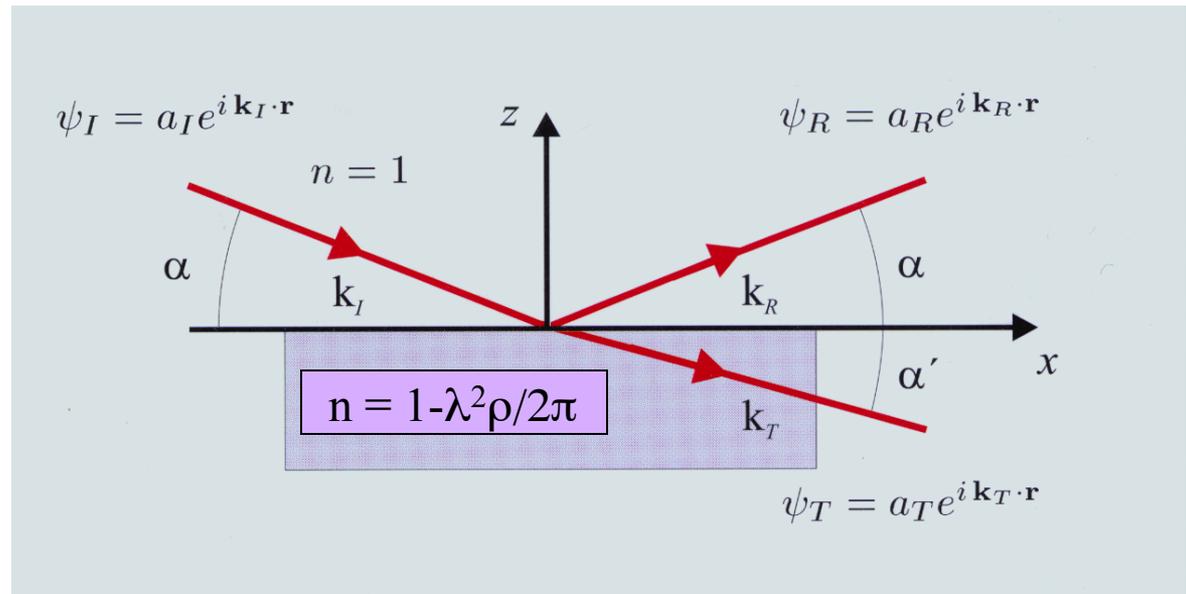
Reflection of Neutrons by a Smooth Surface: Fresnel's Law

continuity

of ψ & ψ' at $z = 0 \Rightarrow$

$$a_I + a_R = a_T \quad (1)$$

$$a_I \vec{k}_I + a_R \vec{k}_R = a_T \vec{k}_T$$



components perpendicular and parallel to the surface :

$$a_I k \cos \alpha + a_R k \cos \alpha = a_T n k \cos \alpha' \quad (2)$$

$$-(a_I - a_R) k \sin \alpha = -a_T n k \sin \alpha' \quad (3)$$

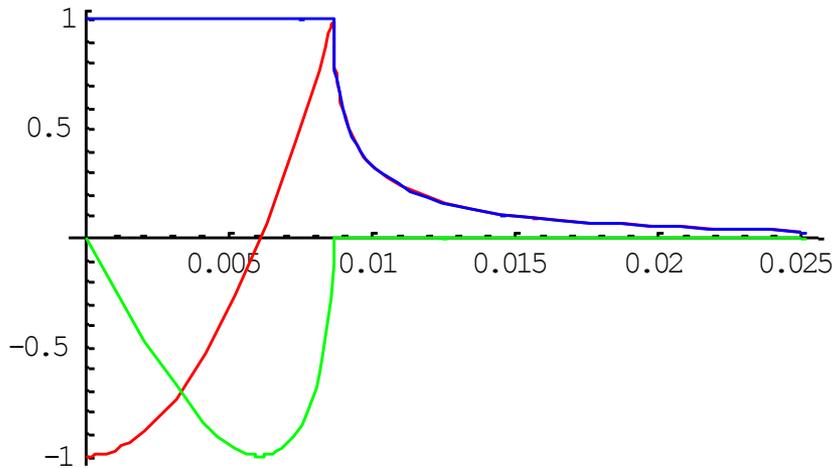
(1) & (2) \Rightarrow Snell's Law : $\cos \alpha = n \cos \alpha'$

$$(1) \text{ \& } (3) \Rightarrow \frac{(a_I - a_R)}{(a_I + a_R)} = n \frac{\sin \alpha'}{\sin \alpha} \approx \frac{\sin \alpha'}{\sin \alpha} = \frac{k_{Tz}}{k_{Iz}}$$

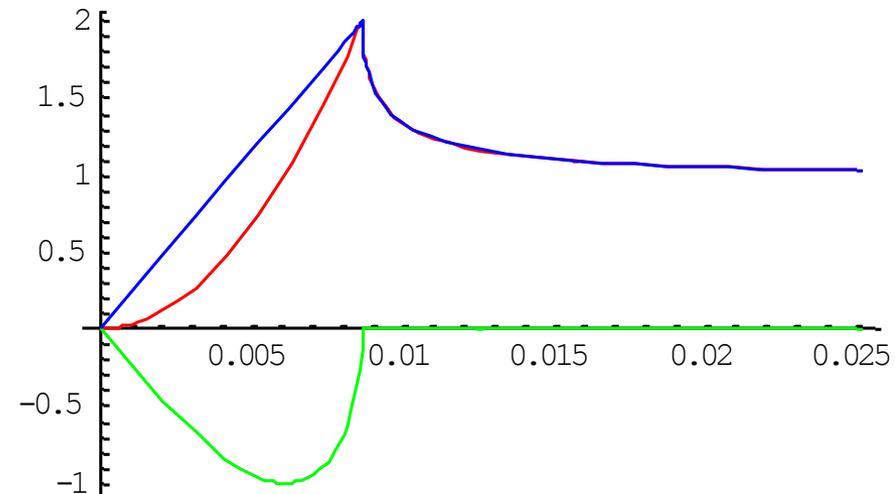
so reflectance is given by $r = a_R / a_I = (k_{Iz} - k_{Tz}) / (k_{Iz} + k_{Tz})$

What do the Amplitudes a_R and a_T Look Like?

- For reflection from a flat substrate, both a_R and a_T are complex when $k_0 < 4\pi\rho$ i.e. below the critical edge. For $a_i = 1$, we find:



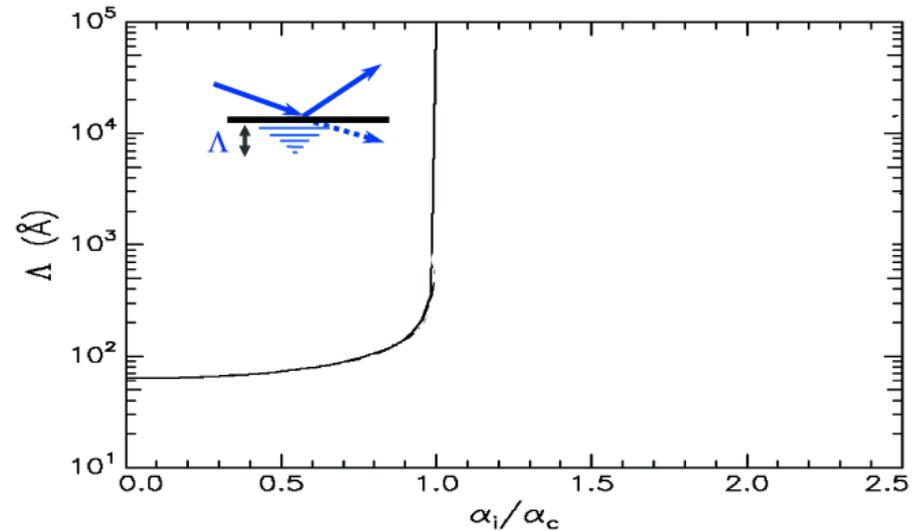
Real (red) & imaginary (green) parts of a_R plotted against k_0 . The modulus of a_R is plotted in blue. The critical edge is at $k_0 \sim 0.009 \text{ A}^{-1}$. Note that the reflected wave is completely out of phase with the incident wave at $k_0 = 0$



Real (red) and imaginary (green) parts of a_T . The modulus of a_T is plotted in blue. Note that a_T tends to unity at large values of k_0 as one would expect and that the transmitted intensity peaks at the critical edge.

Penetration Depth

- In the absence of absorption, the penetration depth becomes infinite at large enough angles
- Because k_z is imaginary below the critical edge (recall that $k_z^2 = k_{0z}^2 - 4\pi\rho$), the transmitted wave is evanescent
- The penetration depth $\Lambda = 1/\text{Im}(k)$
- Around the critical edge, one may tune the penetration depth to probe different depths in the sample



Measured Reflectivity

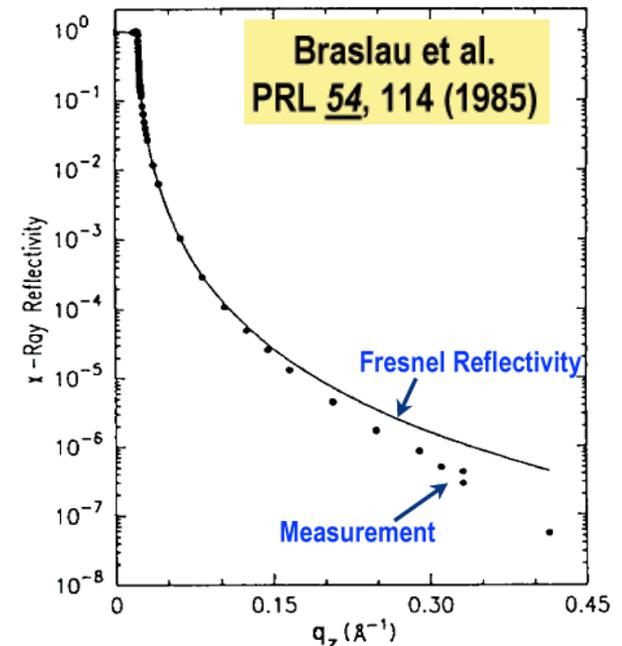
- We do not measure the reflectance, r , but the reflectivity, R given by:

$$R = \frac{\text{\# of neutrons reflected at } Qz}{\text{\# of incident neutrons}} = r \cdot r^*$$

i.e., just as in diffraction, we lose phase information

- Notice, also, that the measurement averages the reflectivity over the surface of the sample:
i.e. measured reflectivity depends on

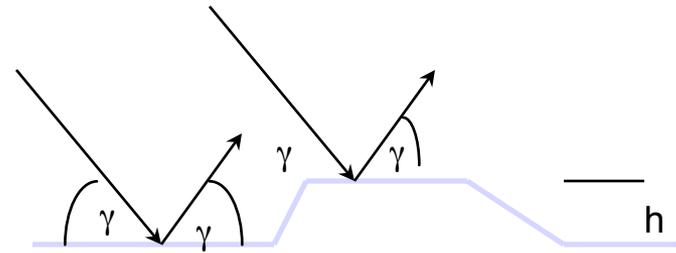
$$\bar{\rho}(z) = \frac{1}{S} \int dx \int dy \rho(x, y, z)$$



Measured and Fresnel reflectivities for water – difference is due to surface roughness

When Does a “Rough” Surface Scatter Diffusely?

- Rayleigh criterion

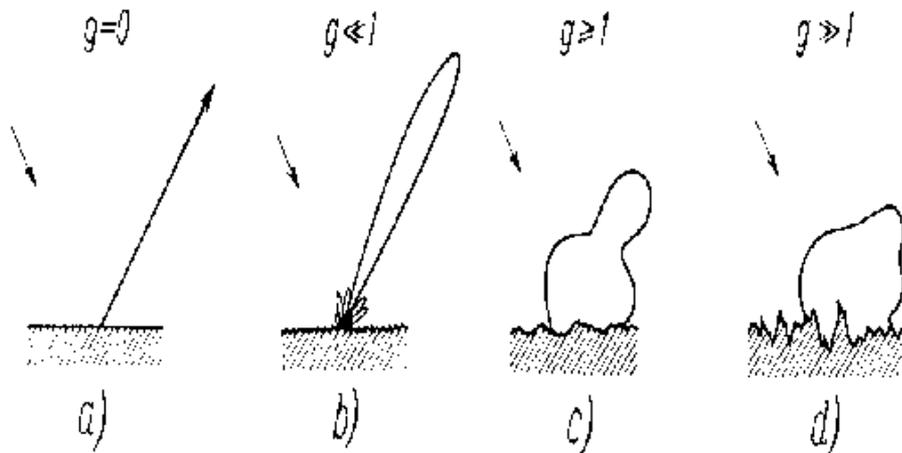


path difference: $\Delta r = 2 h \sin \gamma$

phase difference: $\Delta \phi = (4\pi h / \lambda) \sin \gamma$

boundary between rough and smooth: $\Delta \phi = \pi / 2$

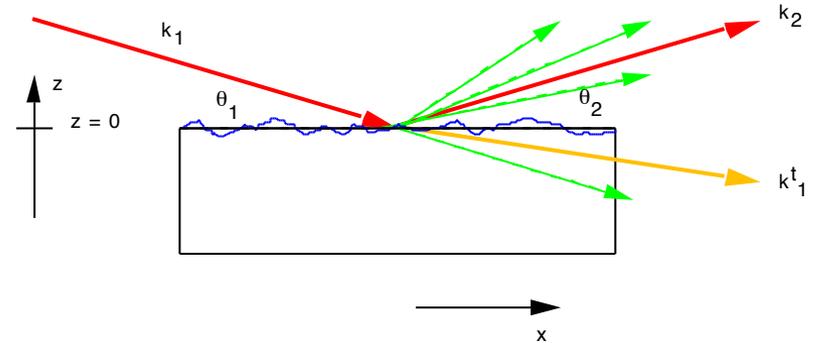
that is $h < \lambda / (8 \sin \gamma)$ for a smooth surface



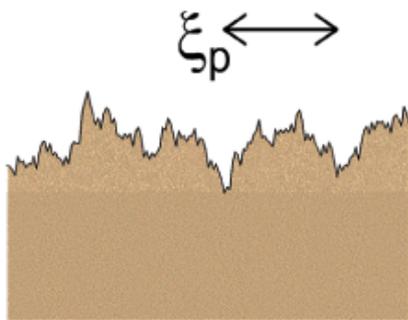
where $g = 4 \pi h \sin \gamma / \lambda = Q_z h$

Surface Roughness

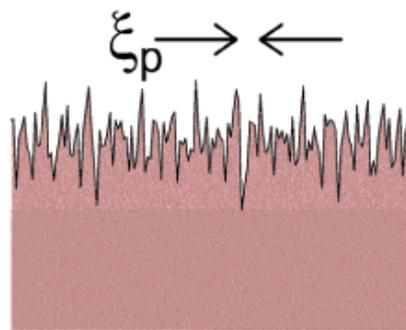
- Surface roughness causes diffuse (non-specular) scattering and so reduces the magnitude of the specular reflectivity



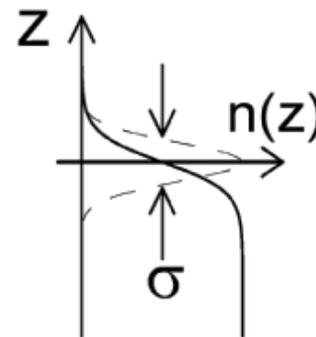
- The way in which the specular reflection is damped depends on the length scale of the roughness in the surface as well as on the magnitude and distribution of roughness



“sparkling sea” model
-- specular from many facets



each piece of surface scatters independently
-- Nevot Croce model



Note that roughness introduces a SLD profile averaged over the sample surface

$$\longrightarrow R = R_F e^{-2k_{Iz} k_{1z}^t \sigma^2}$$

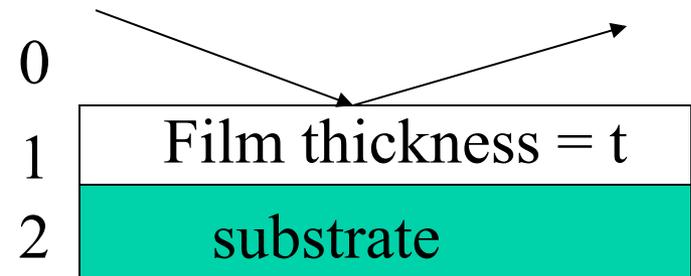
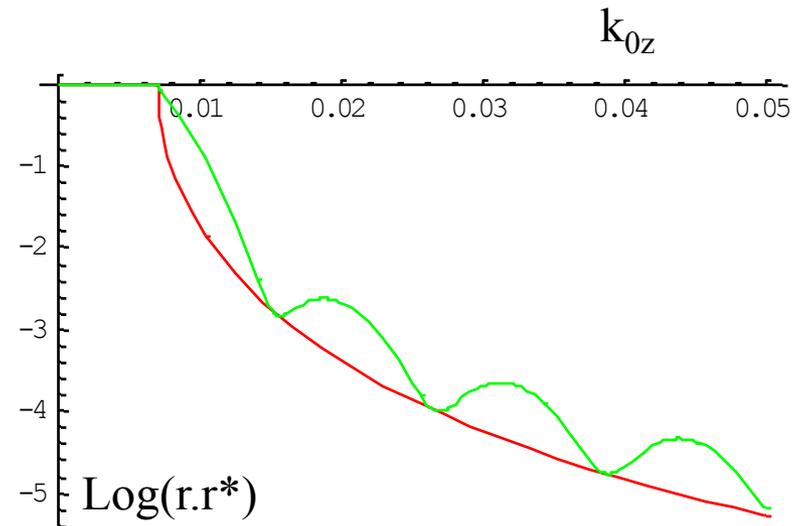
Fresnel's Law for a Thin Film

- $r = (k_{0z} - k_{1z}) / (k_{1z} + k_{0z})$ is Fresnel's law
- Evaluate with $\rho = 4 \cdot 10^{-6} \text{ A}^{-2}$ gives the red curve with critical wavevector given by $k_{0z} = (4\pi\rho)^{1/2}$
- If we add a thin layer on top of the substrate we get interference fringes & the reflectance is given by:

$$r = \frac{r_{01} + r_{12} e^{i2k_{1z}t}}{1 + r_{01}r_{12} e^{i2k_{1z}t}}$$

and we measure the reflectivity $R = r \cdot r^*$

- If the film has a higher scattering length density than the substrate we get the green curve (if the film scattering is weaker than the substance, the green curve is below the red one)
- The fringe spacing at large k_{0z} is $\sim \pi/t$ (a 250 Å film was used for the figure)



Multiple Layers – Parratt Iteration (1954)

- The same method of matching wavefunctions and derivatives at interfaces can be used to obtain an expression for the reflectivity of multiple layers

$$X_j = \frac{R_j}{T_j} = e^{-2ik_{z,j}z_j} \frac{r_{j,j+1} + X_{j+1}e^{2ik_{z,j+1}z_j}}{1 + r_{j,j+1}X_{j+1}e^{2ik_{z,j+1}z_j}}$$

where $r_{j,j+1} = \frac{k_{z,j} - k_{z,j+1}}{k_{z,j} + k_{z,j+1}}$

Start iteration with

$$R_{N+1} = X_{N+1} = 0 \text{ and } T_1 = 1$$

(i.e. nothing coming back from inside substrate & unit amplitude incident wave)

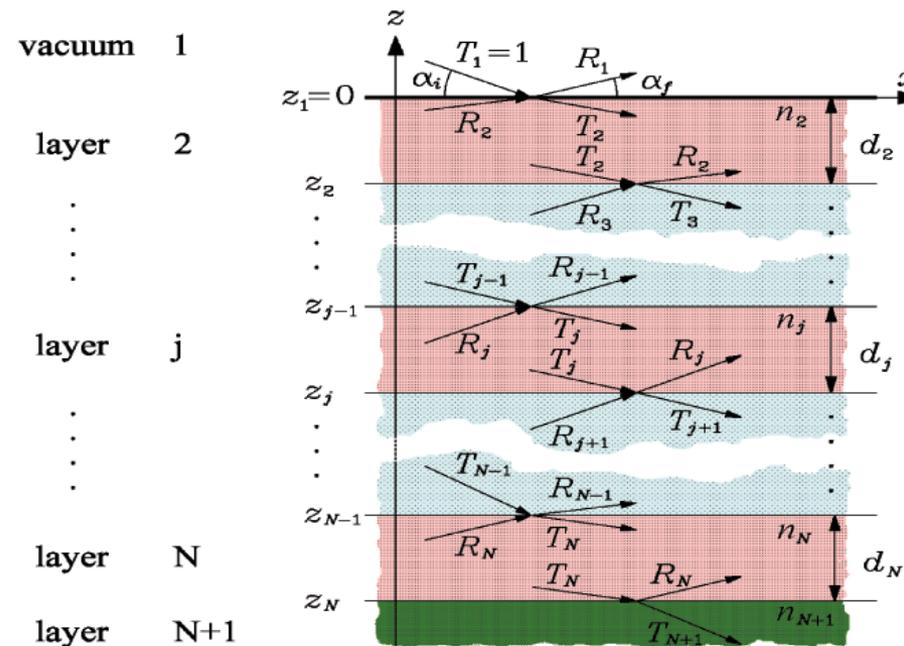
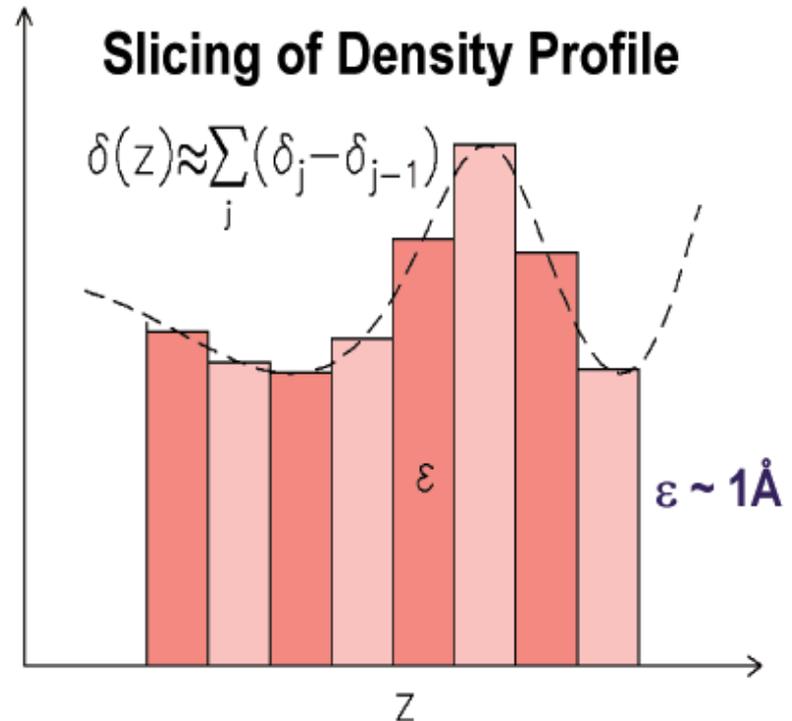


Image from M. Tolan

Dealing with Complex Density Profiles

- Any SLD depth profile can be “chopped” into slices
- The Parratt formalism allows the reflectivity to be calculated
- A thickness resolution of 1 Å is adequate – this corresponds to a value of Q_z where the reflectivity has dropped below what neutrons can normally measure
- Computationally intensive!!



Kinematic (Born) Approximation

- We defined the scattering cross section in terms of an incident plane wave & a **weakly** scattered spherical wave (called the Born Approximation)
- This picture is not correct for surface reflection, except at large values of Q_z
- For large Q_z , one may use the definition of the scattering cross section to calculate R for a flat surface (in the Born Approximation) as follows:

$$R = \frac{\text{number of neutrons reflected by a sample of size } L_x L_y}{\text{number of neutrons incident on sample } (= \Phi L_x L_y \sin \alpha)}$$

$$= \frac{\sigma}{L_x L_y \sin \alpha} = \frac{1}{L_x L_y \sin \alpha} \int \frac{d\sigma}{d\Omega} d\Omega = \frac{1}{L_x L_y \sin \alpha} \int \frac{d\sigma}{d\Omega} \frac{dk_x dk_y}{k_0^2 \sin \alpha}$$

because $k_x = k_0 \cos \alpha$ so $dk_x = -k_0 \sin \alpha d\alpha$.

From the definition of a cross section we get for a smooth substrate :

$$\frac{d\sigma}{d\Omega} = \rho^2 \int d\vec{r} \int d\vec{r}' e^{i\vec{Q} \cdot (\vec{r} - \vec{r}')} = \rho^2 \frac{4\pi^2}{Q_z^2} L_x L_y \delta(Q_x) \delta(Q_y) \text{ so } R = 16\pi^2 \rho^2 / Q_z^4$$

It is easy to show that this is the same as the Fresnel form at large Q_z

Reflection by a Graded Interface

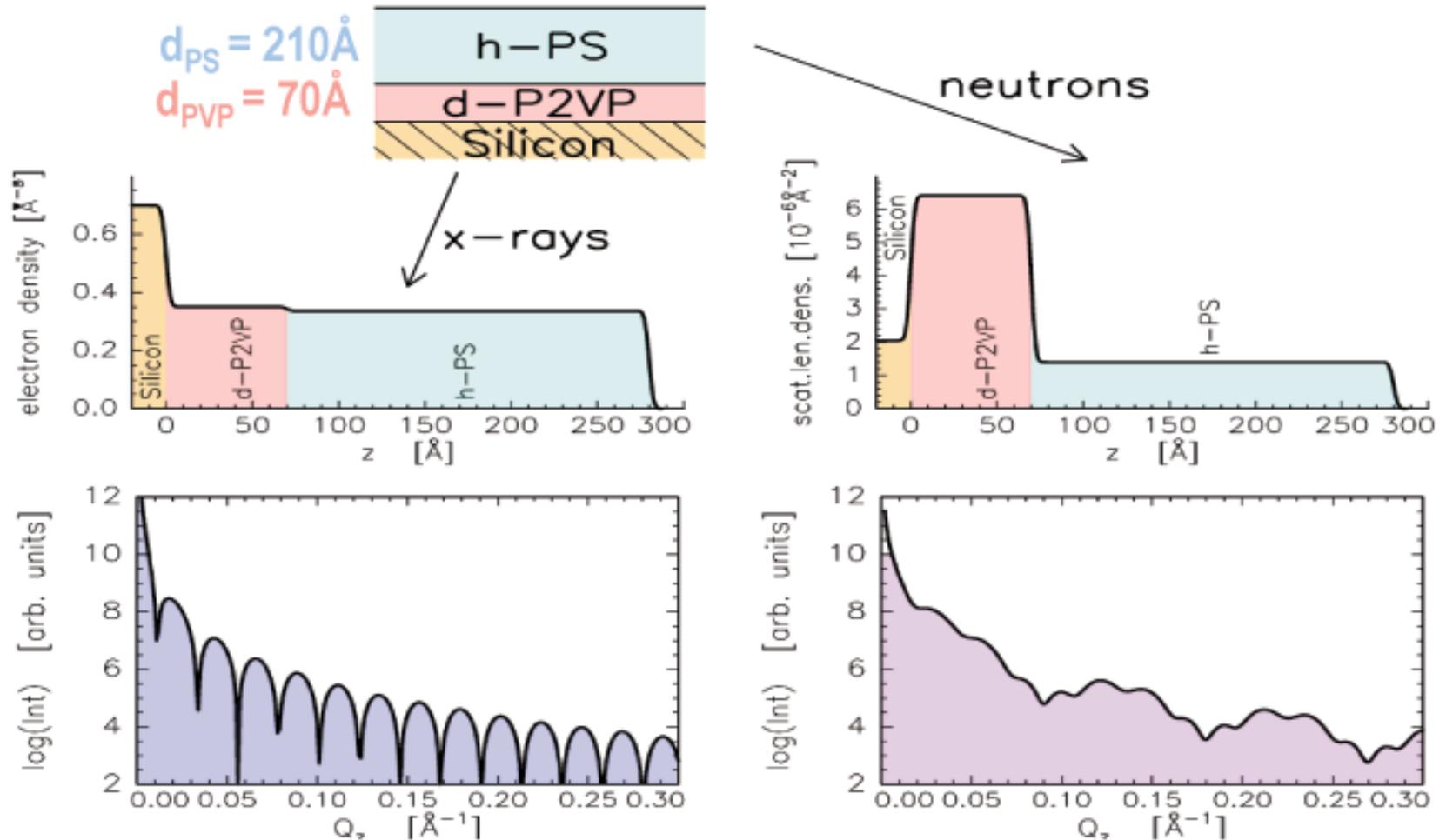
Repeating the bottom line of the previous viewgraph but keeping the z - dependence of ρ gives : $R = \frac{16\pi^2}{Q_z^2} \left| \int \rho(z) e^{iQ_z z} dz \right|^2 = \frac{16\pi^2}{Q_z^4} \left| \int \frac{d\rho(z)}{dz} e^{iQ_z z} dz \right|^2$ where the second equality follows after intergrating by parts.

If we replace the prefactor by the Fresnel reflectivity R_F , we get the right answer for a smooth interface, as well as the correct form at large Q_z

$$R = R_F \left| \int \frac{d\rho(z)}{dz} e^{iQ_z z} dz \right|^2$$

This can be solved analytically for several convenient forms of $d\rho/dz$ such as $1/\cosh^2(z)$. This approximate equation illustrates an important point : reflectivity data cannot be inverted uniquely to obtain $\rho(z)$, because we generally lack important phase information. This means that models refined to fit reflectivity data must have good physical justification.

Comparison of Neutron and X-Ray Reflectivity



Neutrons often provide better contrast and don't damage samples
X-rays provide better Q resolution and higher Q values

The Goal of Reflectivity Measurements Is to Infer a Density Profile Perpendicular to a Flat Interface

- In general the results are not unique, but independent knowledge of the system often makes them very reliable
- Frequently, layer models are used to fit the data
- Advantages of neutrons include:
 - Contrast variation (using H and D, for example)
 - Low absorption – probe buried interfaces, solid/liquid interfaces etc
 - Non-destructive
 - Sensitive to magnetism
 - Thickness length scale 10 – 5000 Å
- Issues include
 - Generally no unique solution for the SLD profile (use prior knowledge)
 - Large samples ($\sim 10 \text{ cm}^2$) with good scattering contrast are needed

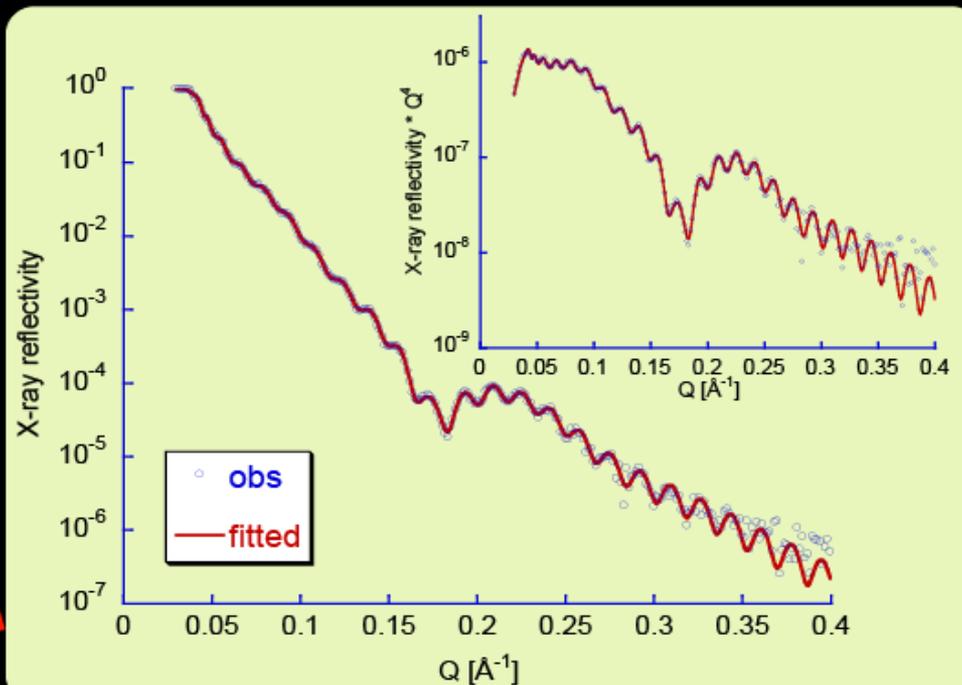
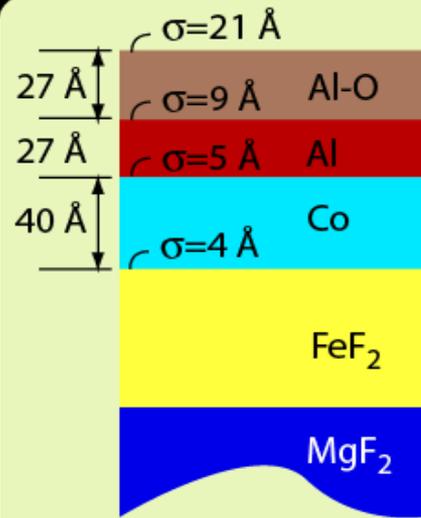
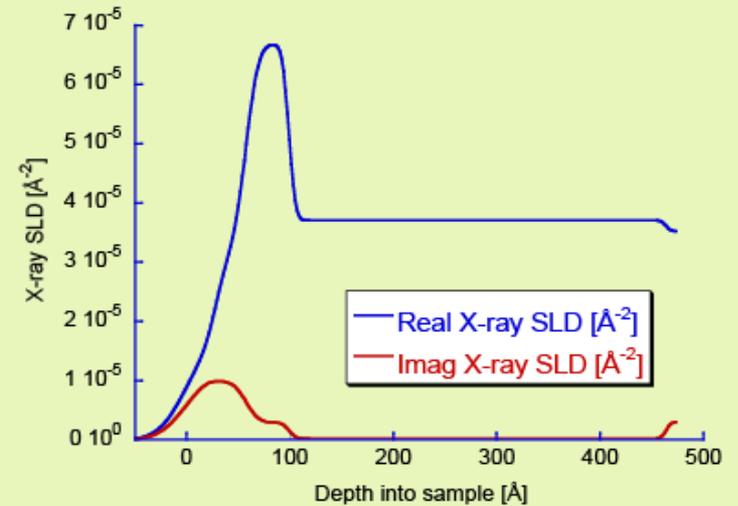
Analyzing Reflectivity Data

- We want to find $\rho(z)$ given a measurement of $R(Q_z)$
- This inverse problem is not generally solvable
- Two methods are used:
 1. Modelling
 - Parameterize $\rho(z)$ and use the Parratt method to calculate $R(Q_z)$
 - Refine the parameters of $\rho(z)$
 - BUT...there is a family of $\rho(z)$ that produce different $r(Q_z)$ but *exactly* the same $R(Q_z)$: many more $\rho(z)$ that produce similar $r(Q_z)$.
 - This non-uniqueness can often be satisfactorily overcome by using additional information about the sample (e.g. known order of layers)
 2. Multiple measurements on the same sample
 - Use two different “backings” or “frontings” for the unknown layers
 - Allows $r(Q_z)$ to be calculated
 - $R(Q_z)$ can be inverted to give $\rho(z)$ unless $\rho(z)$ has bound states (unusual)

Model of the chemical structure and refinement procedure.

Intelligent design

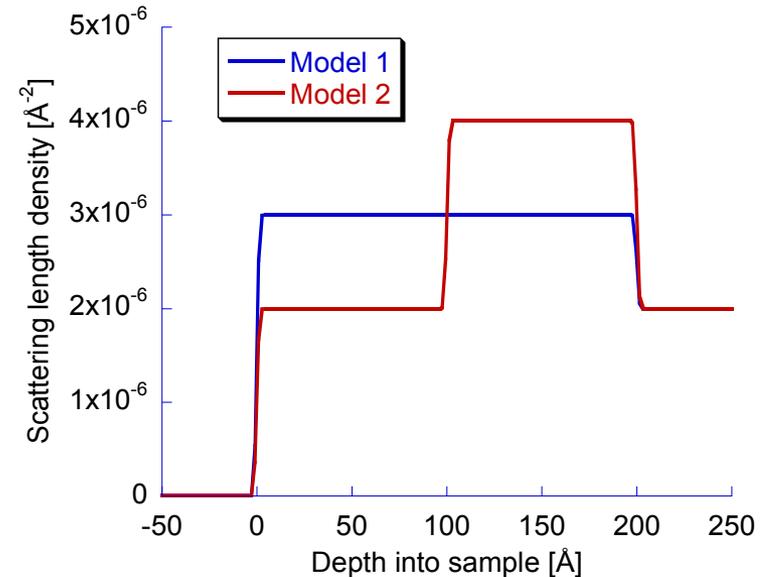
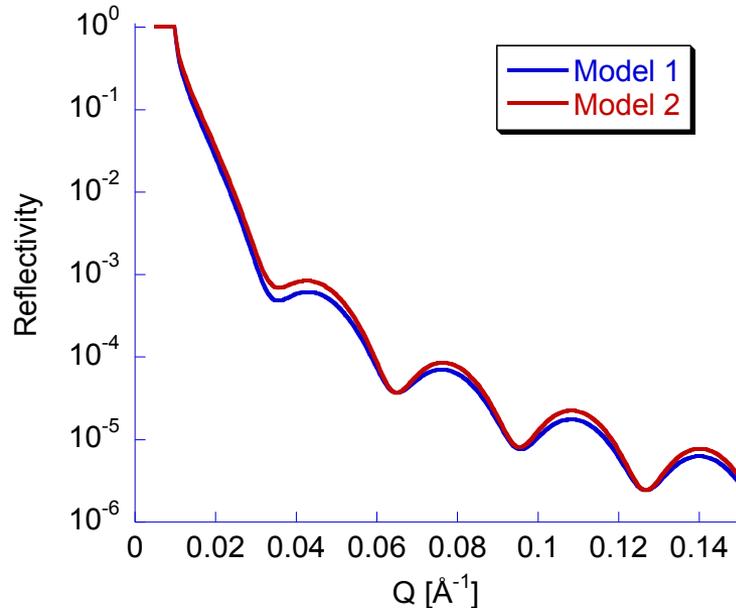
Calculate SLD profile



Compare and perturb

Calculate reflectivity

Perils of fitting



Lack of information about the phase of the reflected wave means that profoundly different scattering length density profiles can produce strikingly similar reflectivities.

Ambiguities may be resolved with additional information and physical intuition.

Sample growers

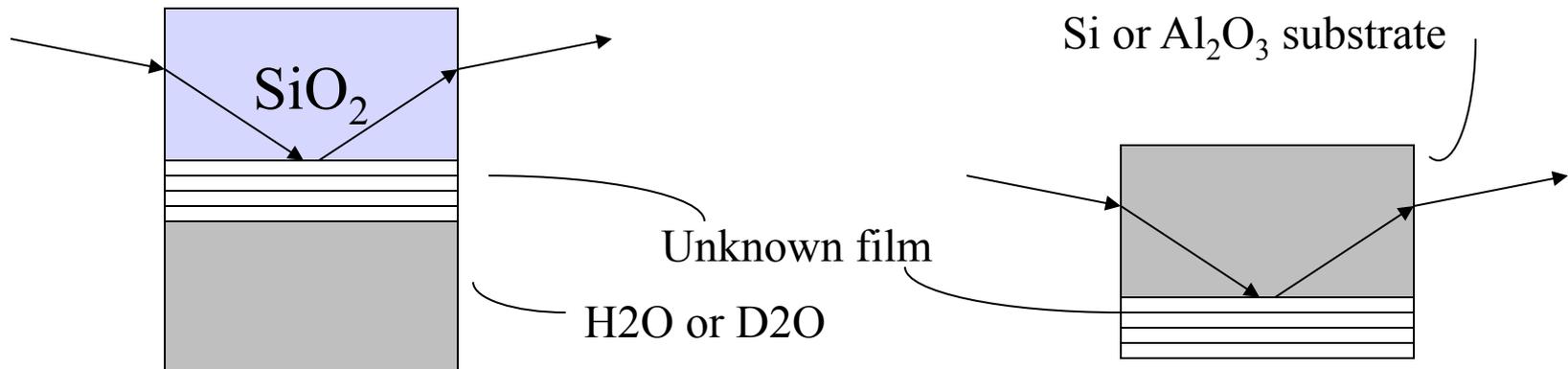
Other techniques, e.g., TEM, X-ray

Neutron data of very high quality

Well-designed experiments (simulation is a key tool)

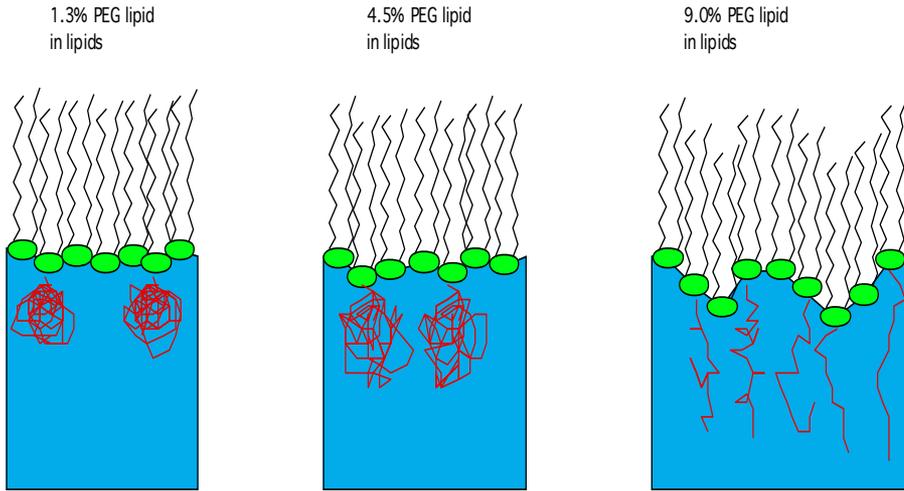
Direct Inversion of Reflectivity Data is Possible*

- Use different “fronting” or “backing” materials for two measurement of the same unknown film
 - E.g. D₂O and H₂O “backings” for an unknown film deposited on a quartz substrate or Si & Al₂O₃ as substrates for the same unknown sample
 - Allows Re(R) to be obtained from two simultaneous equations for $|R_1|^2$ and $|R_2|^2$
 - Re(R) can be inverted to yield a unique SLD profile
- Another possibility is to use a magnetic “backing” and polarized neutrons

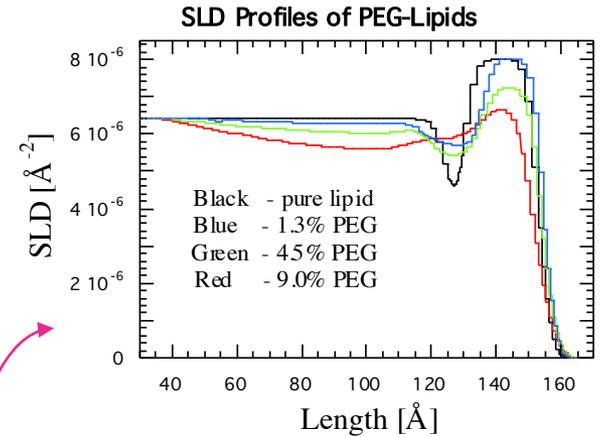


* Majkrzak et al Biophys Journal, 79,3330 (2000)

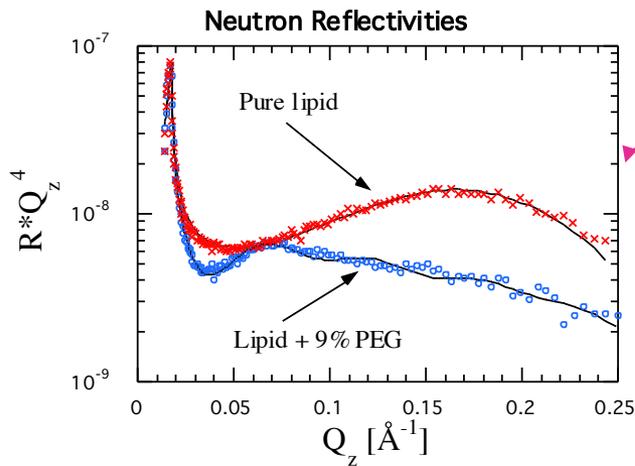
Polymer-Decorated Lipids at a Liquid-Air Interface*



mushroom-to-brush transition

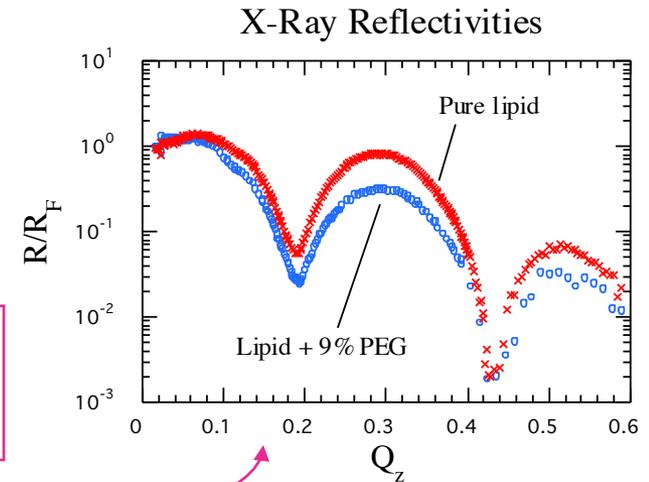


Interface broadens as PEG concentration increases - this is main effect seen with x-rays



neutrons see contrast between heads (2.6), tails (-0.4), D_2O (6.4) & PEG (0.24)

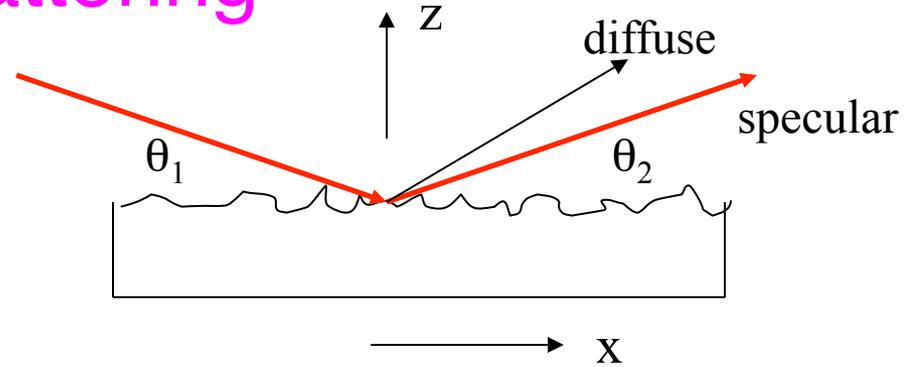
x-rays see heads (0.65), but all else has same electron density within 10% (-0.33)



*Data courtesy of G. Smith (LANSCE)

Diffuse Scattering

If an interface is rough it will scatter
both specularly and diffusely



$$Q_x = k(\cos\theta_2 - \cos\theta_1) \approx \frac{k}{2}(\theta_1^2 - \theta_2^2) = Q_z(\theta_1 - \theta_2)/4$$

If $\theta_1 - \theta_2 = 1^\circ \approx 0.02$ radians

$$Q_x \approx 0.005Q_z \approx 10^{-3} \text{ nm}^{-1}$$

i.e. the in - plane length scale
probed can be ~ 1 micron!!

If the roughness of neighboring interfaces is
correlated, the diffuse scattering will appear
as constant- Q_z ridges extended in Q_x

uncorrelated vs. correlated (conformal) fluctuations

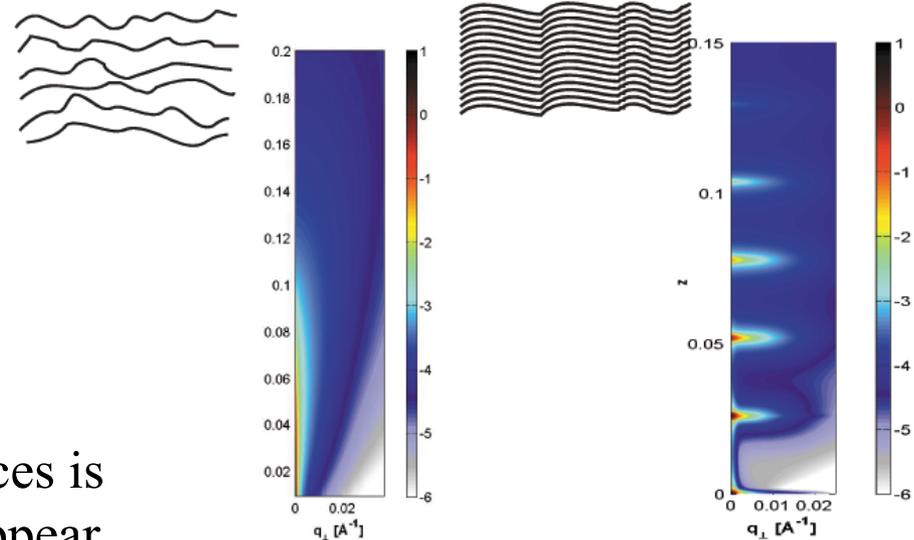
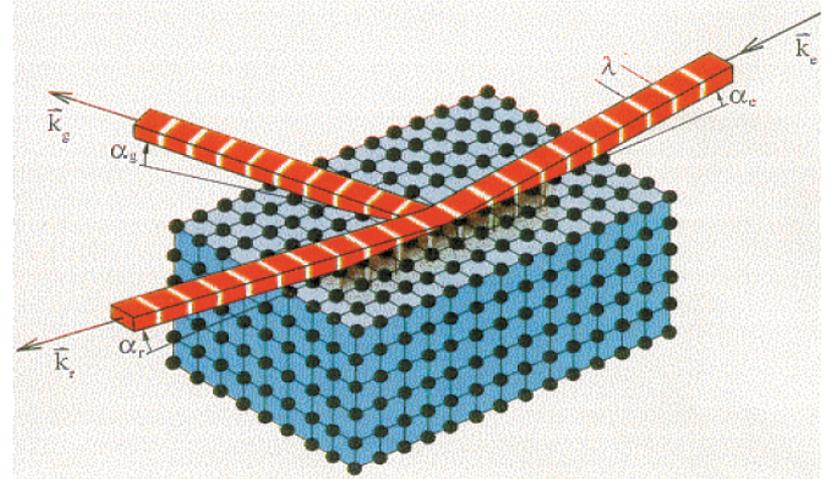


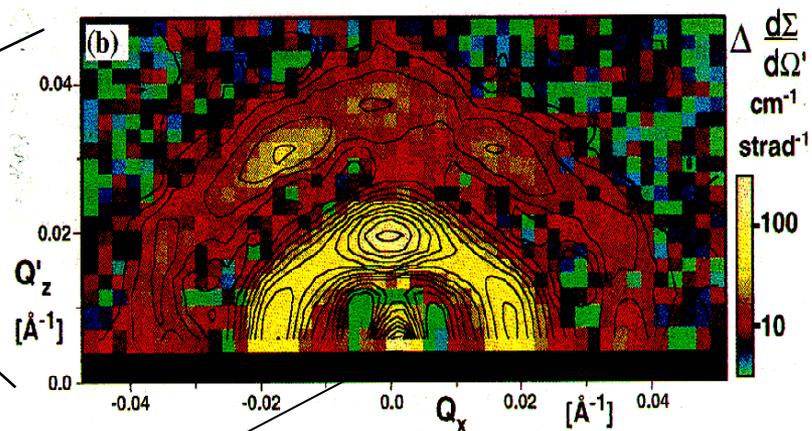
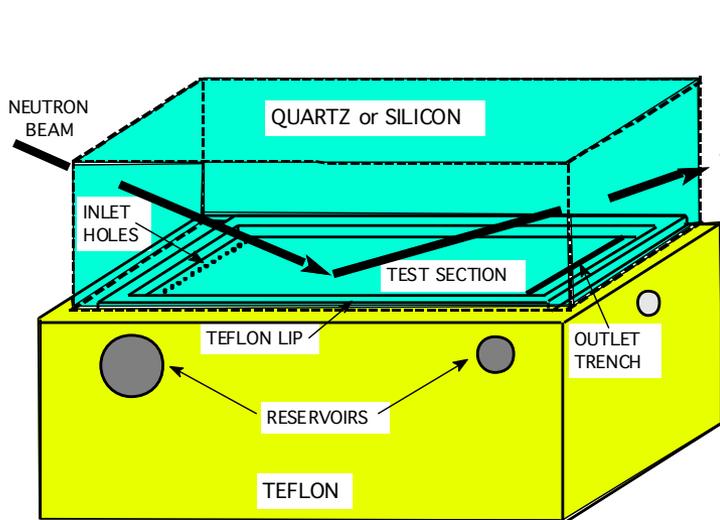
Image from G. Brotons & L. Belloni
(CEA/SACLAY).

Grazing Incidence Diffraction

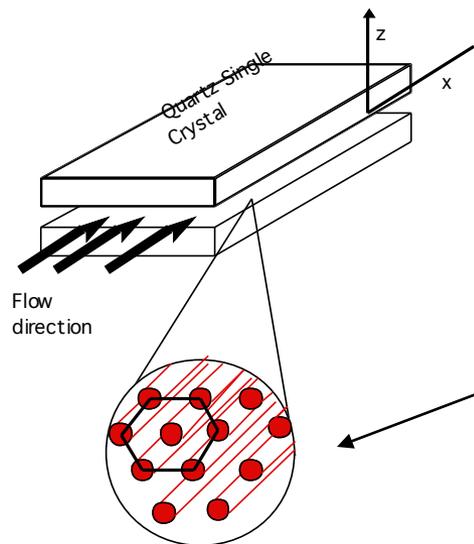
- In principal, grazing incidence diffraction can be used to probe lateral (in-plane) structure
- This is difficult with neutrons for several reasons:
 - Collimation in x-y plane is needed leading to low intensity
 - Hard to prevent the beam going in or out through the sample edge and picking up bulk order rather than surface order
- A few experiments have been done
- New techniques such as neutron spin echo may make this type of study easier



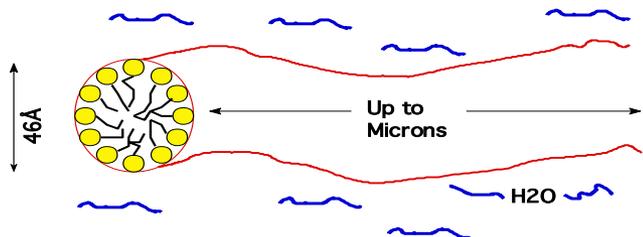
Observation of Hexagonal Packing of Thread-like Micelles Under Shear: Scattering From Lateral Inhomogeneities



Specularly reflected beam



Scattering pattern implies hexagonal symmetry



Thread-like micelle

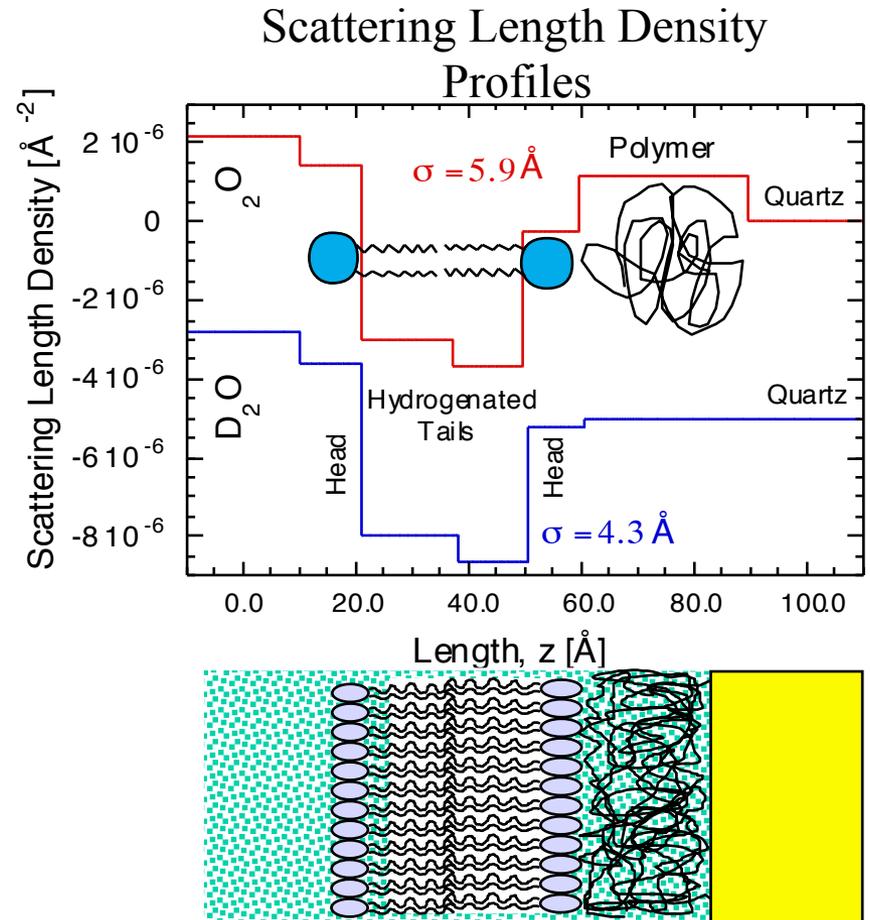
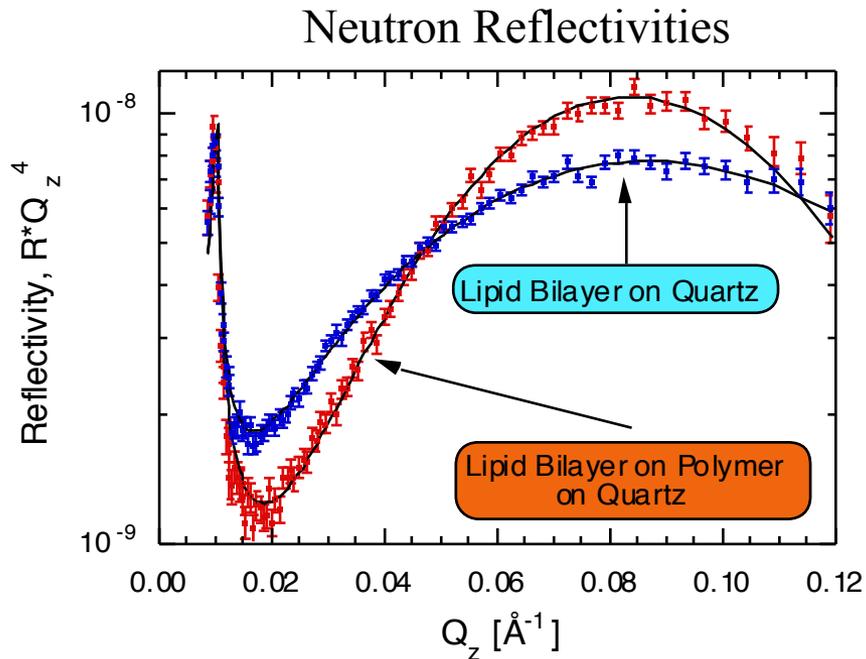
Planning a Reflectivity Measurement

- Simulation of reflectivity profiles using e.g. *Parratt* is essential
 - Can you see the effect you want to see?
 - What is the best substrate? Which materials should be deuterated?
- If your sample involves free liquid surface you will need to use a reflectometer with a vertical scattering plane
- Preparing good (i.e. low surface roughness) samples is key
 - Beware of large islands
- Layer thicknesses between 10 Å and 5000 Å
 - But don't mix extremes of thickness

END
Questions?

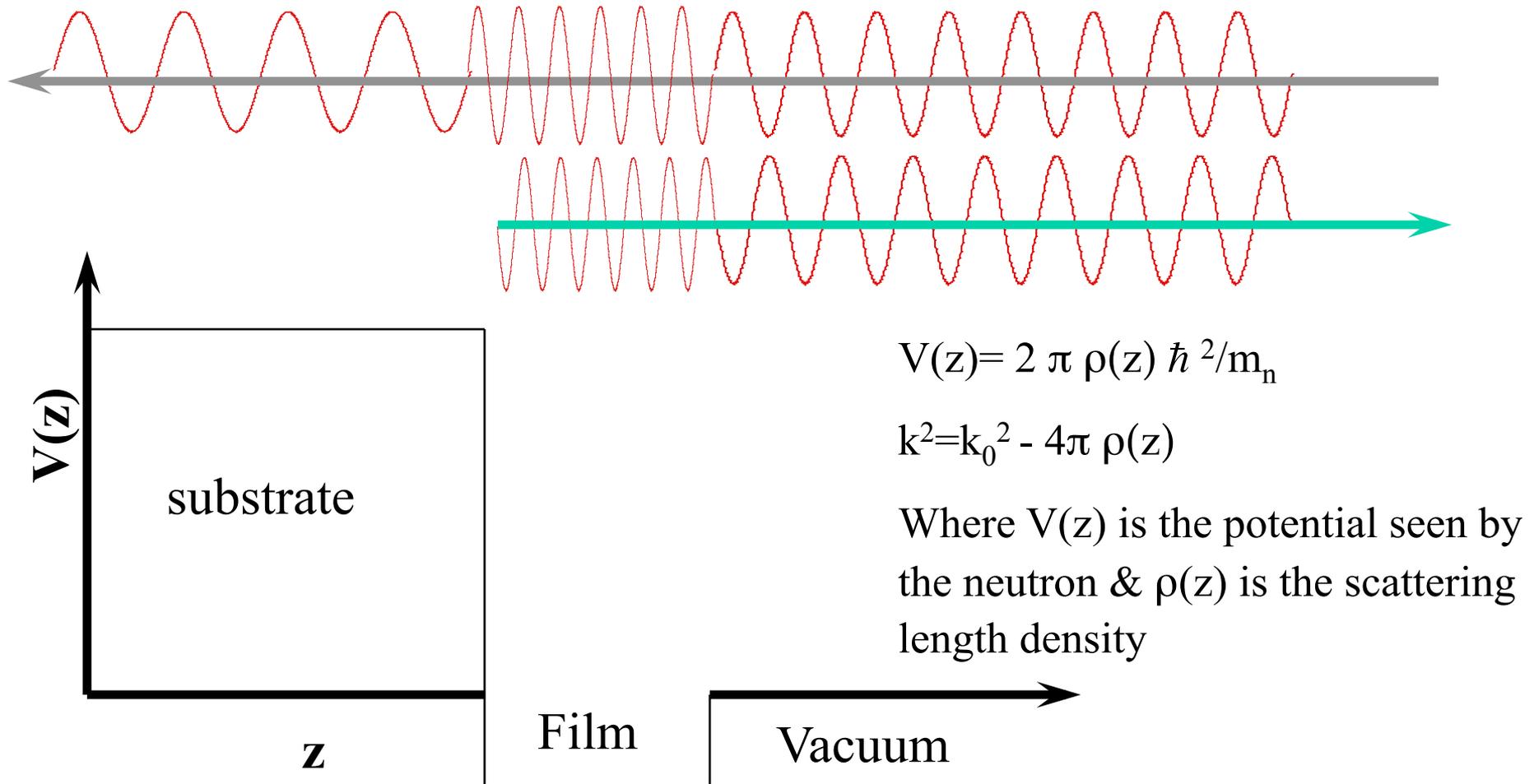
Vesicles composed of DMPC molecules fuse creating almost a perfect lipid bilayer when deposited on the pure, uncoated quartz block*
(blue curves)

When PEI polymer was added only after quartz was covered by the lipid bilayer, the PEI appeared to diffuse under the bilayer (red curves)



* Data courtesy of G. Smith (LANSCE)

One can also think about Neutron Reflection from a Surface as a 1-d Problem



This Lecture

- Why use neutron reflectivity?
- Refractive index for neutrons
- Neutron reflection by a smooth surface
- Neutron penetration depth
- Effect of surface roughness on specular reflection
- Reflection from a surface covered by a thin film
- Reflection from layered films – the Parratt method
- The kinematic approximation
- Reflection from a graded interface
- Comparison of x-ray and neutron reflection
- Exact determination of SLD profiles
- Science examples
 - Polymers & vesicles on a surface
 - Lipids at the liquid air interface
 - Boron self-diffusion
- Rough surfaces and correlated roughness
- Grazing incidence diffraction
- An example of GID: shear aligned worm-like micelles