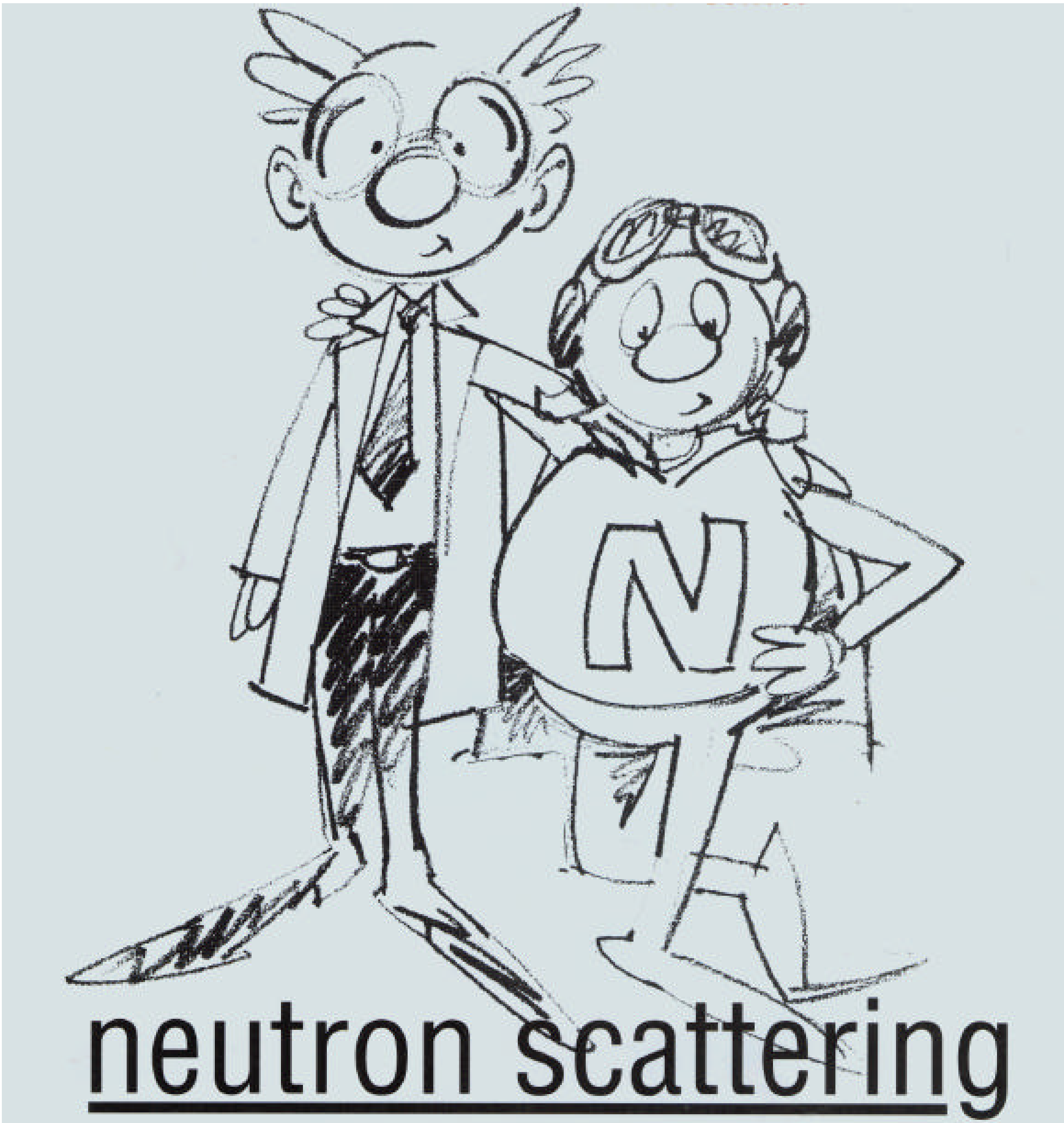


LECTURE 3: Surface Reflection

by

Roger Pynn

Los Alamos
National Laboratory

Surface Reflection Is Very Different From Most Neutron Scattering

- We worked out the neutron cross section by adding scattering from different nuclei
  - We ignored 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

This Lecture

- Reflectivity measurements
  - Neutron wavevector inside a medium
  - Reflection by a smooth surface
  - Reflection by a film
  - The kinematic approximation
  - Graded interface
  - Science examples
    - Polymers & vesicles on a surface
    - Lipids at the liquid air interface
    - Boron self-diffusion
    - Iron on MgO
  - Rough surfaces
    - Shear aligned worm-like micelles

What Is the Neutron Wavevector Inside a Medium?

Comparing our expression for S(Q) with that given by Fermi's Golden Rule, the nucleus - neutron potential is given by: $V(\vec{r}) = \frac{2p\hbar^2}{m} bd(\vec{r})$ for a single nucleus.

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

r is called the nuclear Scattering Length Density (SLD)

The neutron obeys Schrodinger's equation:

$$\left[\nabla^2 + 2m(E - \bar{V})/\hbar^2\right]y(r) = 0$$

in vacuo $y(r) = e^{i\vec{k}_o.\vec{r}}$ so $k_0^2 = 2mE/\hbar^2$. Simlarly $k^2 = 2m(E - \bar{V})/\hbar^2 = k_0^2 - 4pr$

where k_0 is neutron wavevector *in vacuo* and k is the wavevector in a material

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

$$n = 1 - l^2 r / 2p$$

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

Typical Values

- Let us calculate the scattering length density for quartz – SiO_2
- Density is 2.66 $gm.cm^{-3}$; Molecular weight is 60.08 gm. $mole^{-1}$
- Number of molecules per $Å^3$ = N = $10^{-24}(2.66/60.08)*N_{avagadro}$ = 0.0267 molecules per $Å^3$
- $\rho=\Sigma b/volume = N(b_{Si} + 2b_O) = 0.0267(4.15 + 11.6)\ 10^{-5}\ Å^{-2} = 4.21\ x10^{-6}\ Å^{-2}$
- This means that the refractive index $n = 1 – \lambda^2\ 2.13 \times 10^{-7}$ for quartz
- To make a neutron “bottle” out of quartz we require k= 0 I.e. $k_0{}^2 = 4\pi\rho$ or $\lambda=(\pi/\rho)^{1/2}$.
- Plugging in the numbers -- λ = 864 Å or a neutron velocity of 4.6 m/s (you could out-run it!)

Only Those Thermal or Cold 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 :

$k_0 \cos a = k \cos a' = k_0 n \cos a'$ i.e n = $\cos a / \cos a'$

Neutrons obey Snell's Law

Since $k^2 = k_0^2 - 4pr$ $k^2(\cos^2 a' + \sin^2 a') = k_0^2(\cos^2 a + \sin^2 a) - 4pr$

i.e. $k^2 \sin^2 a' = k_0^2 \sin^2 a - 4pr$ or $k_z^2 = k_{0z}^2 - 4pr$

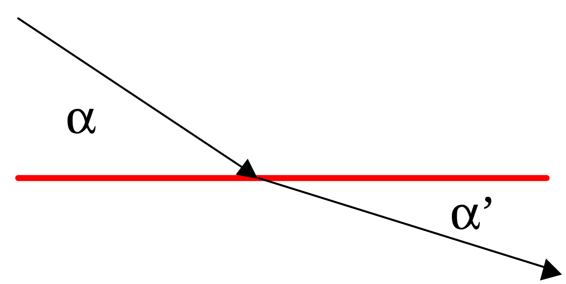
The critical value of k_{0z} for total external reflection is $k_{0z} = \sqrt{4pr}$

For quartz $k_{0zl}^{critical} = 2.05x10^{-3}$ A^{-1}

$(2p / l) \sin a_{\text{critical}} = k_{0zl}^{critical} \Rightarrow$

$a_{\text{critical}}(^o) \approx 0.02 l (A)$ for quartz

Note : $a_{\text{critical}}(^o) \approx 0.1 l (A)$ for nickel



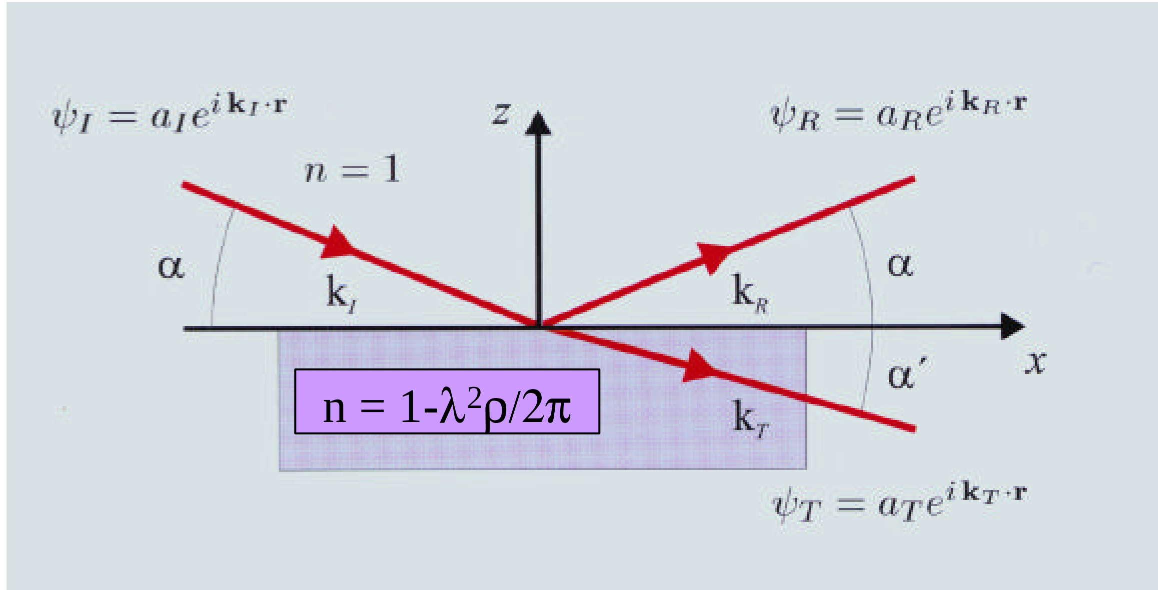
Reflection of Neutrons by a Smooth Surface: Fresnel's Law

continuity

of y & $\dot{y}$ at z = 0 ⇒

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

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



components perpendicular and parallel to the surface :

$$a_I k \cos a + a_R k \cos a = a_T nk \cos a' \qquad (2)$$

$$-(a_I - a_R) k \sin a = -a_T nk \sin a' \qquad (3)$$

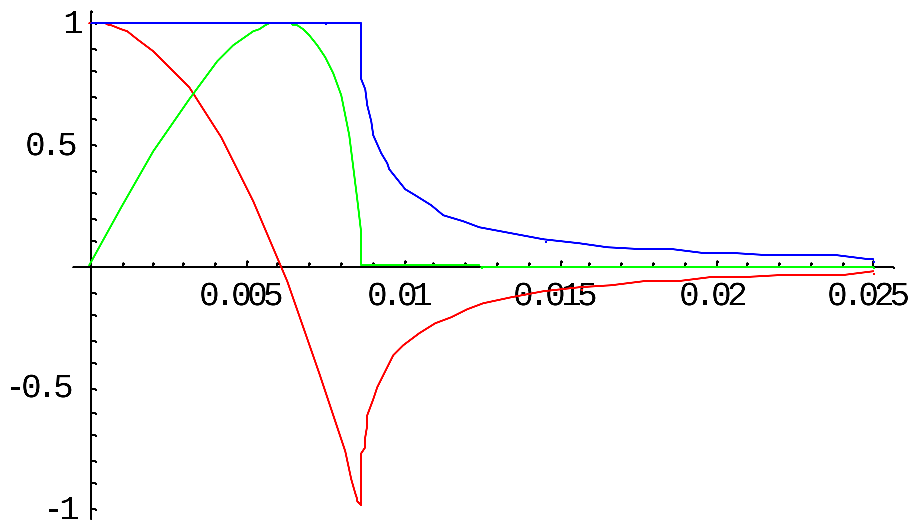
(1) & (2) => Snell's Law : $\boxed{\cos a = n \cos a'}$

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

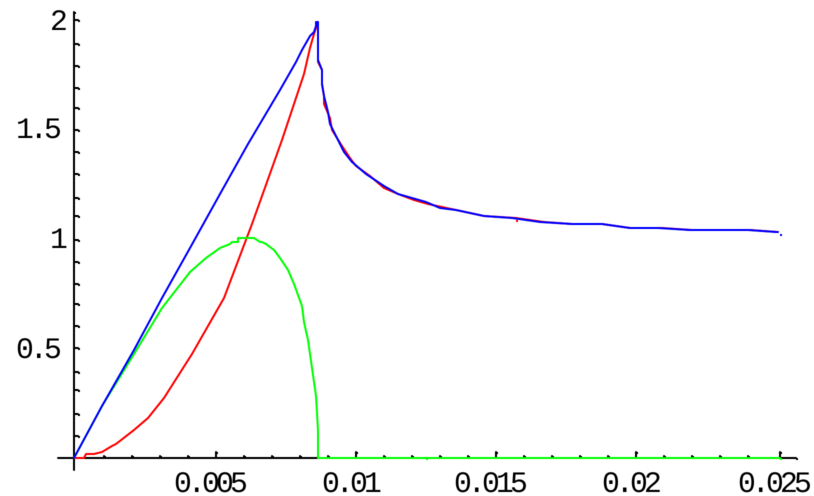
so reflectance is given by $\boxed{r = a_R / a_I = (k_{Iz} - k_{Tz})/(k_{Iz} + k_{Tz})}$

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:

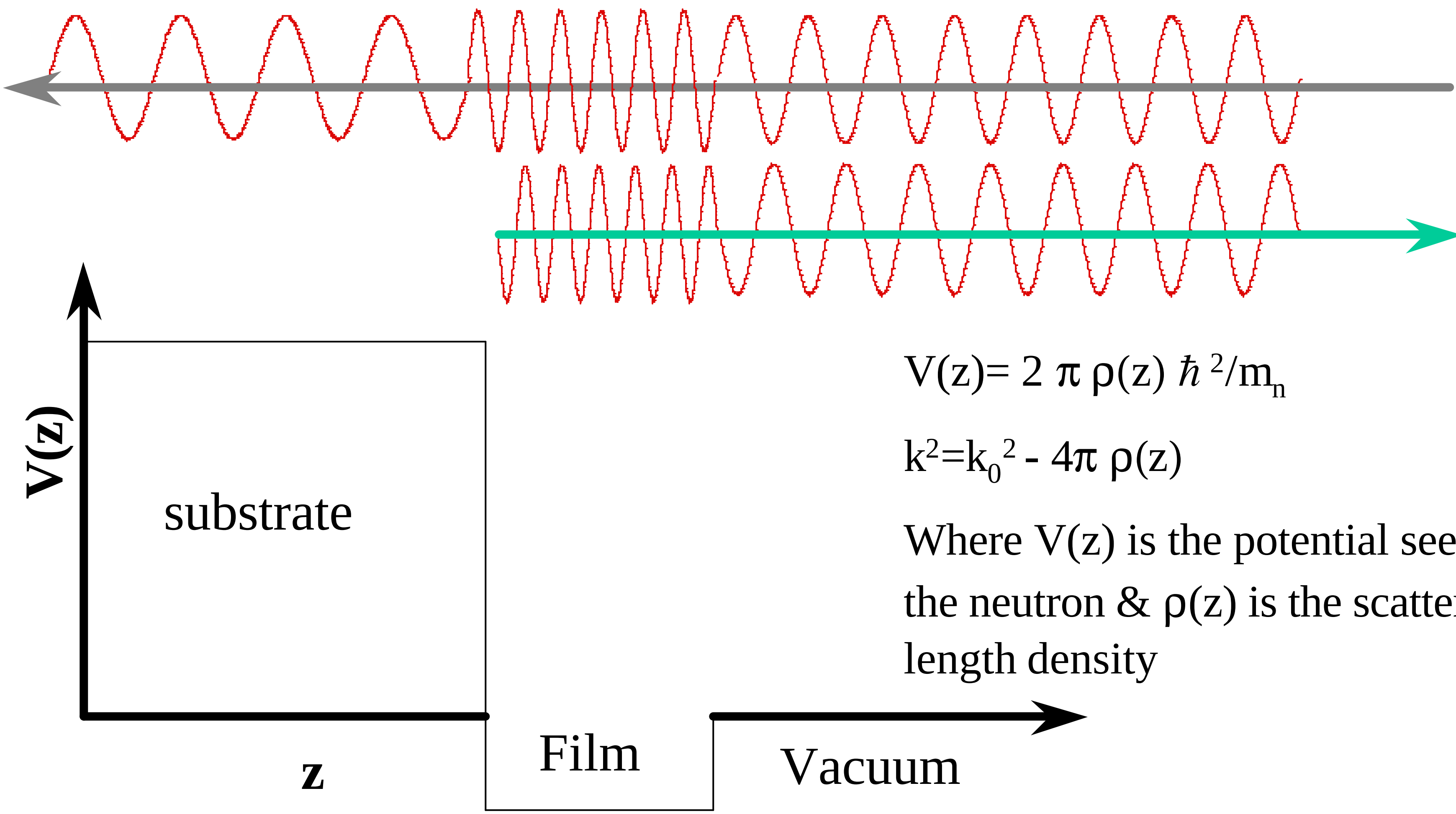


Real (red) & imaginary (green) parts of a_R plotted against k_0. The modulus of a_R is plotted in blue. The critical edge is at $k_0 \sim 0.09$ A^{-1} . Note that the reflected wave is completely out of phase with the incident wave at the critical edge



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

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



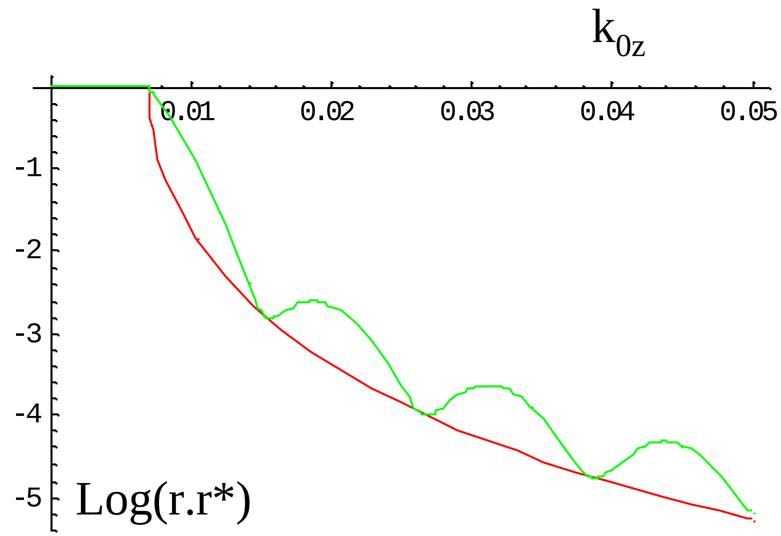
$V(z) = 2\pi\,\rho(z)\,\hbar^2/m_n$

$k^2 = k_0^2 - 4\pi\,\rho(z)$

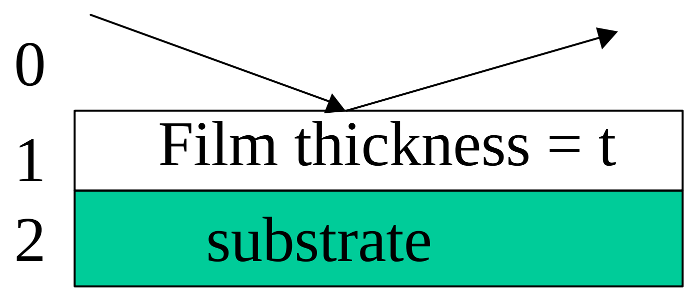
Where V(z) is the potential seen by the neutron & ρ(z) is the scattering length density

Fresnel's Law for a Thin Film

- $r=(k_{1z}-k_{0z})/(k_{1z}+k_{0z})$ is Fresnel's law
- Evaluate with $\rho=4.10^{-6}$ 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.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 ~ π/t (a 250 A film was used for the figure)

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:

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

$$= \frac{s}{L_x L_y \sin \boldsymbol{a}} = \frac{1}{L_x L_y \sin \boldsymbol{a}} \int \frac{ds}{d\Omega} d\Omega = \frac{1}{L_x L_y \sin \boldsymbol{a}} \int \frac{ds}{d\Omega} \frac{dk_x dk_y}{k_0^2 \sin \boldsymbol{a}}$$

because $k_x = k_0 \cos \boldsymbol{a}$ so $dk_x = -k_0 \sin \boldsymbol{a} \; d\boldsymbol{a}$.

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

$$\frac{ds}{d\Omega} = r^2 \int d\vec{r} \int d\vec{r}\,' e^{i\vec{Q}.(\vec{r}-\vec{r}\,')} = r^2 \frac{4p^2}{Q_z^2} L_x L_y d(Q_x) d(Q_y) \text{ so } \boxed{R = 16 p^2 r^2 / Q_z^4}$$

It is easy to show that this is the same as the Fresnel form at large $\mathrm{Q_z}$

Reflection by a Graded Interface

Repeating the bottom line of the previous viewgraph but keeping the z - dependence of r gives : $R = \frac{16p^2}{Q_z^2}\left|\int r(z)e^{iQ_z z}dz\right|^2 = \frac{16p^2}{Q_z^4}\left|\int \frac{dr(z)}{dz}e^{iQ_z z}dz\right|^2$ 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

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

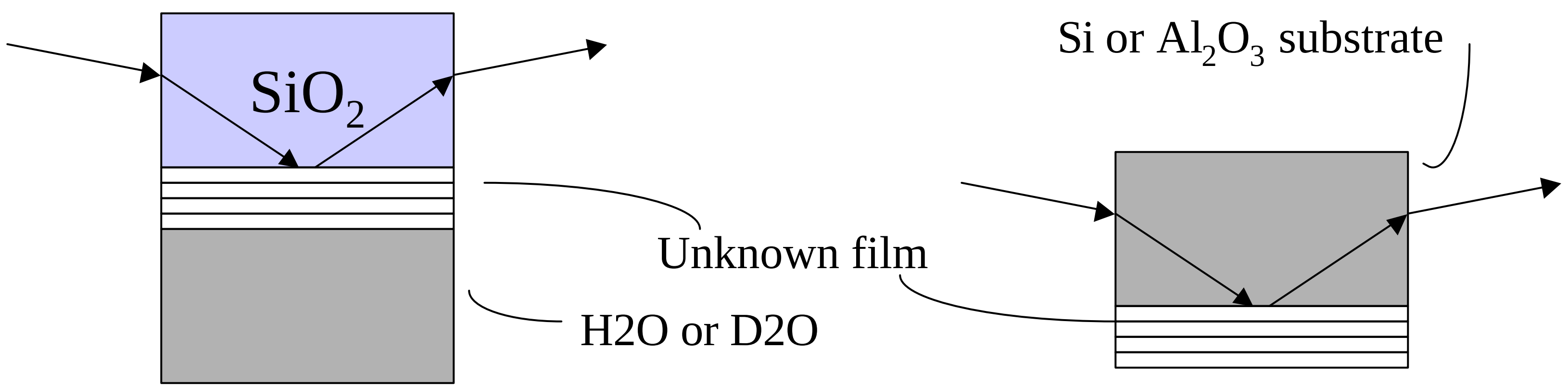
This can be solved analytically for several convenient forms of dr/dz such as $1/\cosh^2(z)$. This approximate equation illustrates an important point : reflectivity data cannot be inverted uniquely to obtain r(z), because we generally lack important phase information. This means that models refined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

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

Direct Inversion of Reflectivity Data is Possible*

- Use different "fronting" or "backing" materials for two measurement of the same unknown film
  - E.g. D_2O and H_2O "backings" for an unknown film deposited on a quartz substrate or Si & Al_2O_3 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 Fourier inverted to yield a unique SLD profile
- Another possibility is to use a magnetic "backing" and polarized neutrons

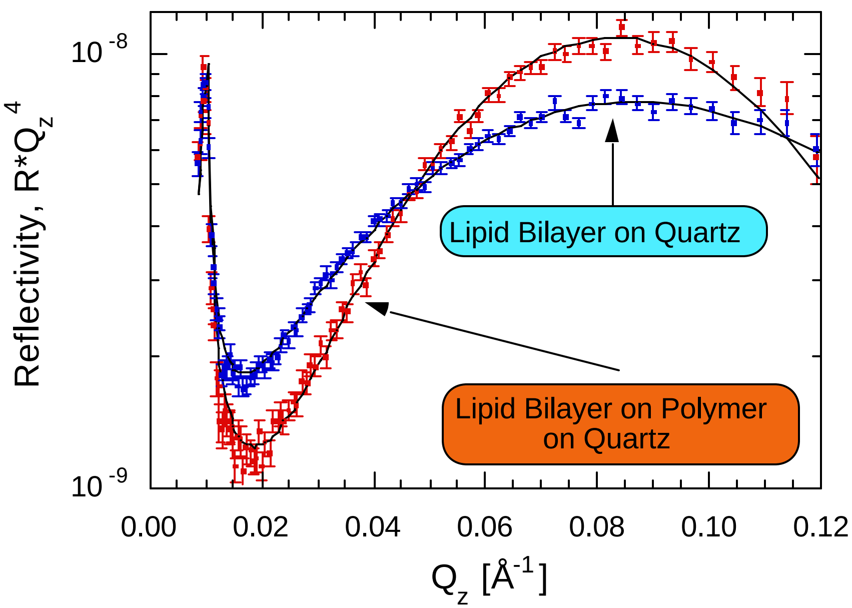


* Majkrzak et al Biophys Journal, 79,3330 (2000)

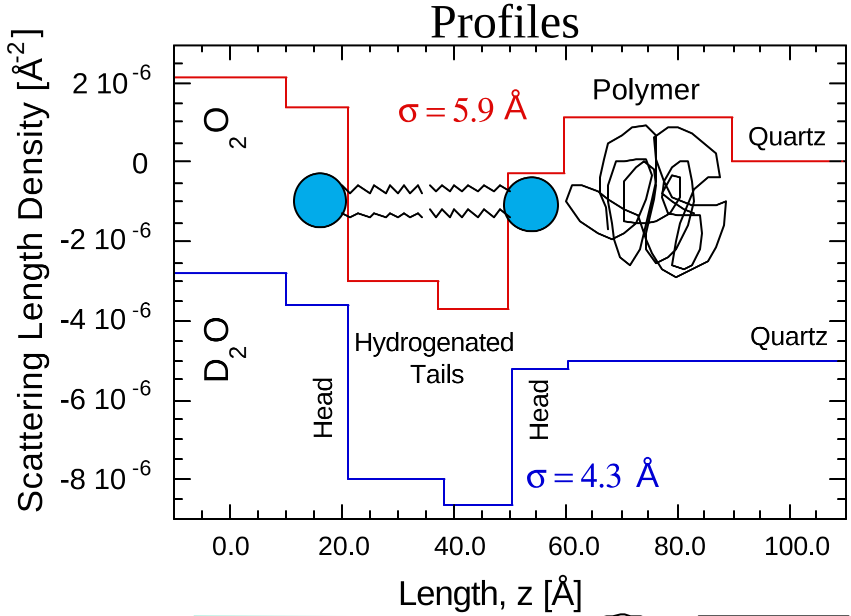
Vesicles composed of DMPC molecules fuse creating almost a perfect lipid bilayer when deposited on the pure, uncoated quartz block* (blue curves)

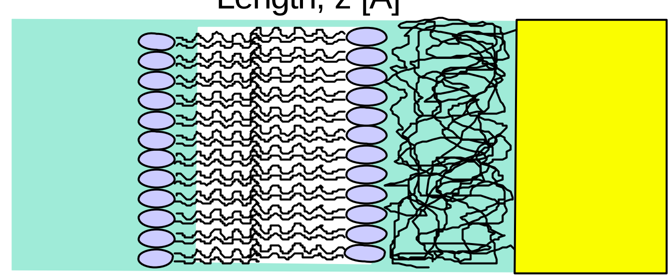
When PEI polymer was added only after quartz was covered by the lipid bilayer, the PEI appeared to diffuse under the bilayer (red curves)

Neutron Reflectivities



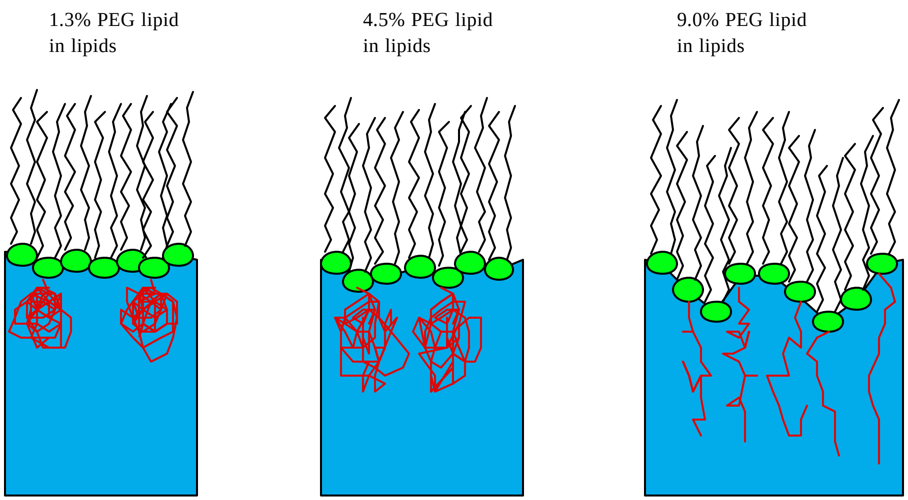
Scattering Length Density Profiles

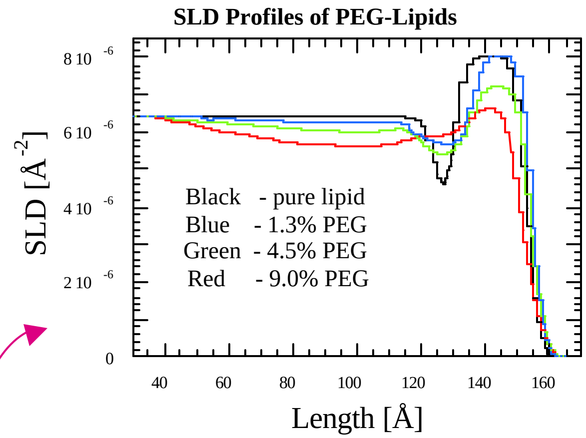




* Data courtesy of G. Smith (LANSCE)

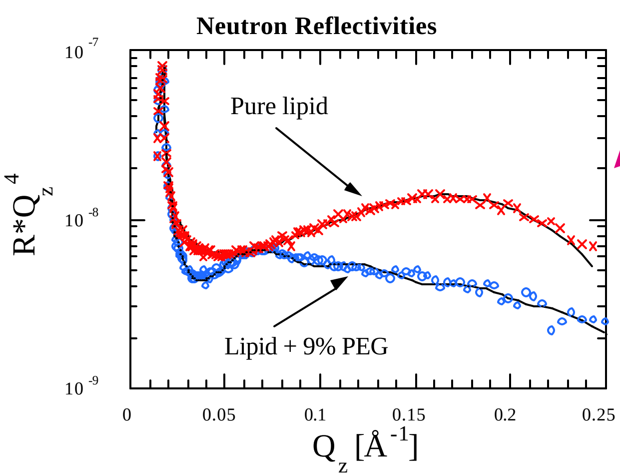
Polymer-Decorated Lipids at a Liquid-Air Interface*





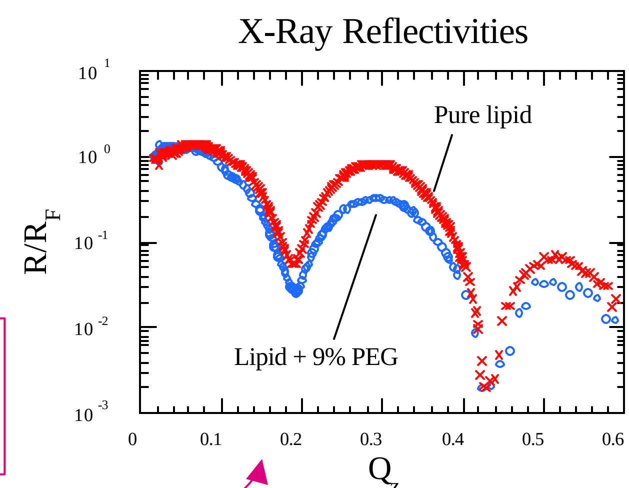
mushroom-to-brush transition

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



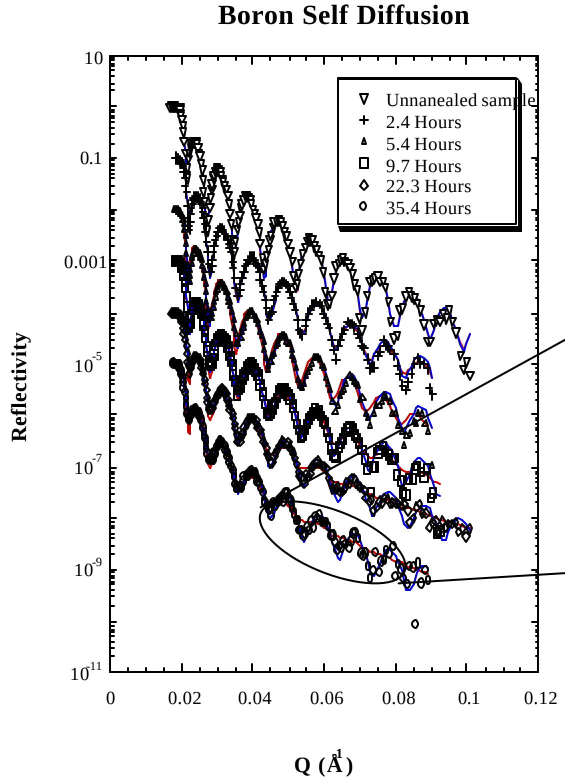
neutrons see contrast between heads (2.6), tails (-0.4), D_2O (6.4) & PEG (0.24)

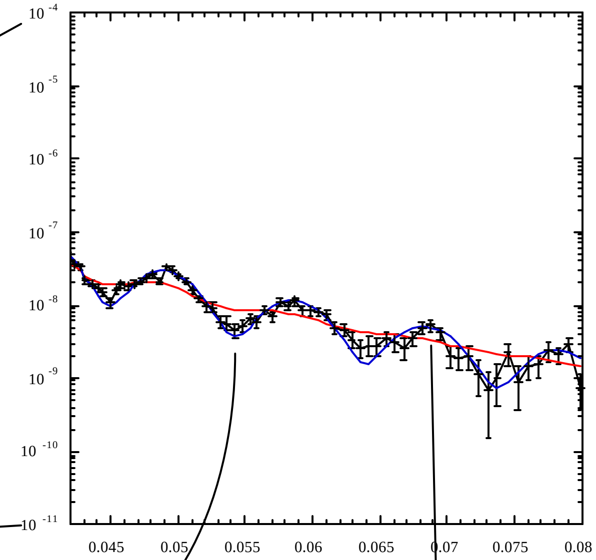
x-rays see heads (0.65), but all else has same electron density within 10% (-0.33)



*Data courtesy of G. Smith (LANSCE)

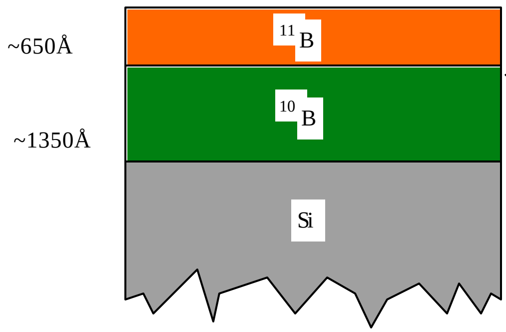
Non-Fickian Boron Self-Diffusion at an Interface*

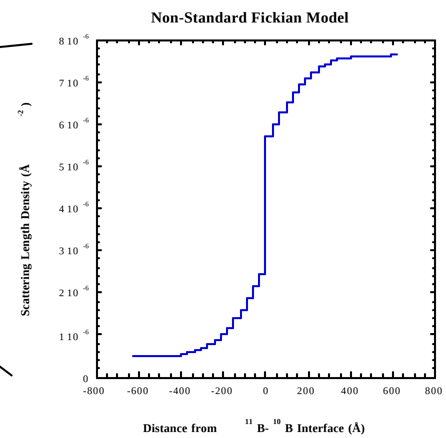


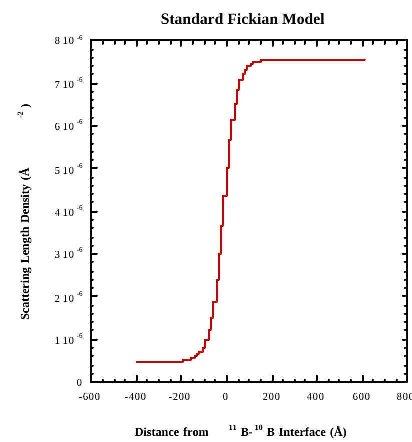


Data requires density step at interface

Fickian diffusion doesn't fit the data

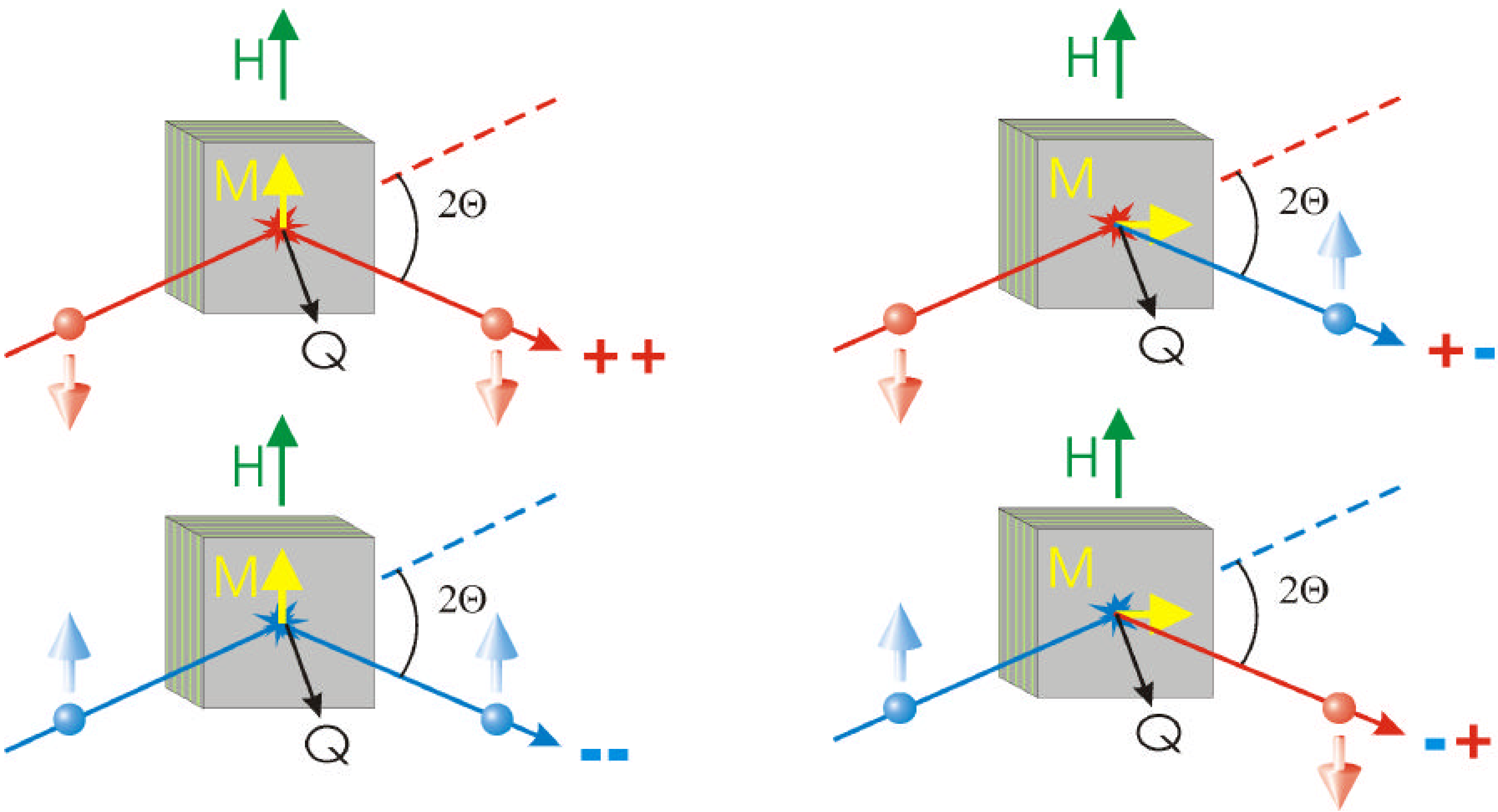






*Data courtesy of G. Smith (LANSCE)

Polarized Neutron Reflectometry (PNR)



Non-Spin-Flip

++ measures b + M_z

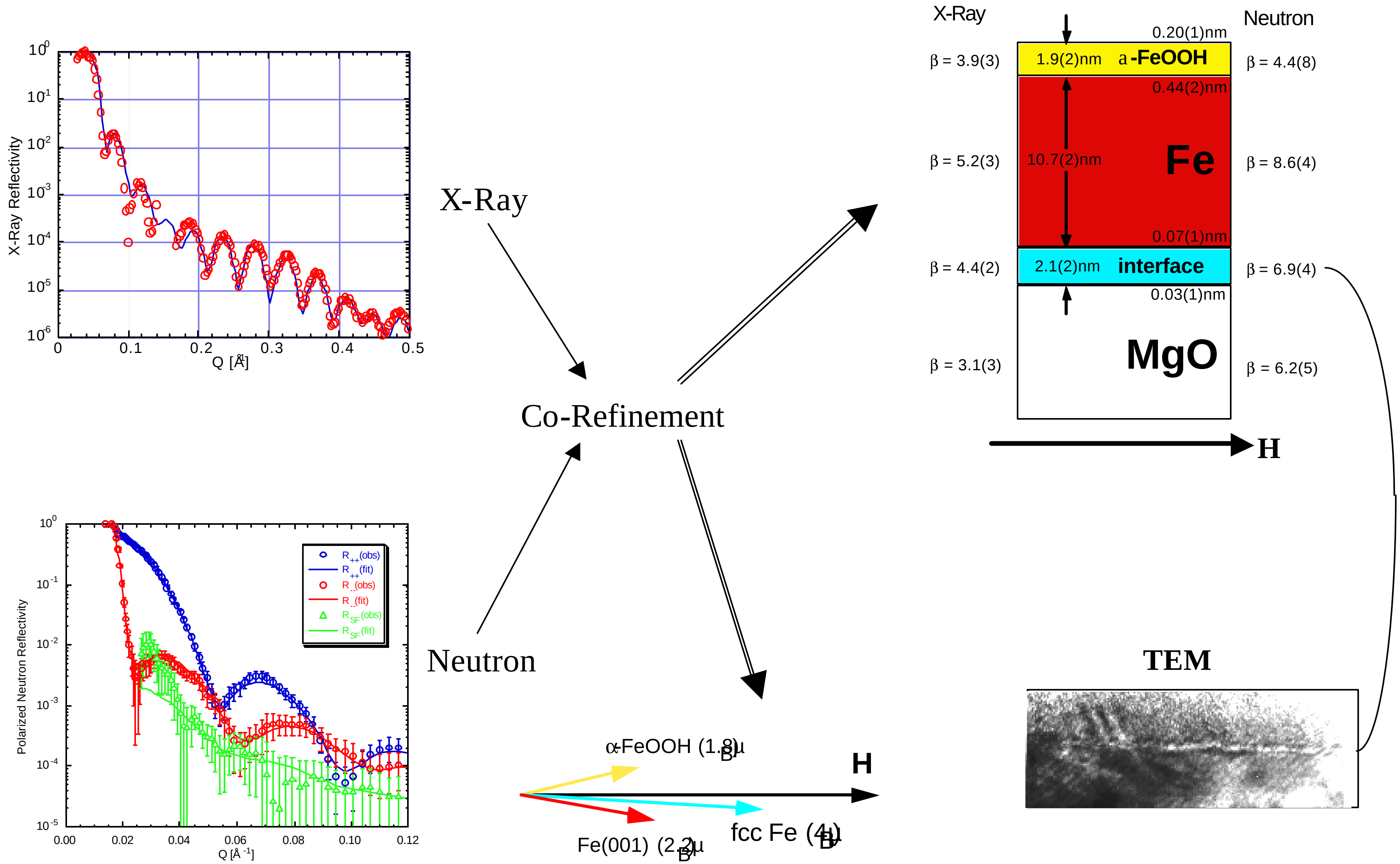
- - measures b - M_z

Spin-Flip

+- measures M_x + i M_y

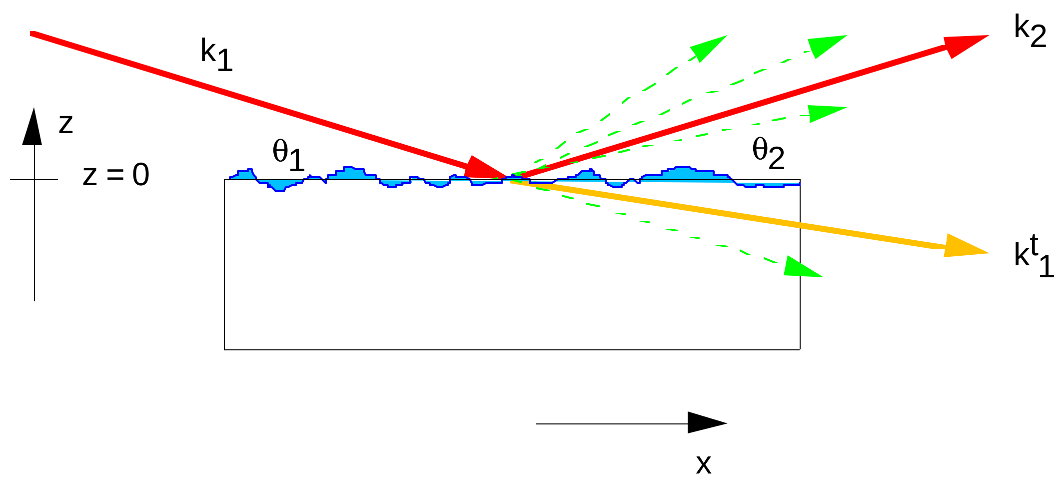
-+ measures M_x – i M_y

Structure, Chemistry & Magnetism of Fe(001) on MgO(001)*



*Data courtesy of M. Fitzsimmons (LANSCE)

Reflection from Rough Surfaces

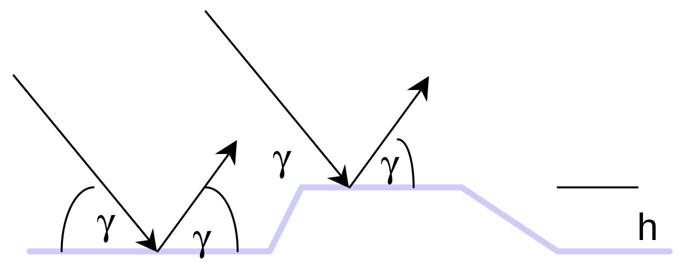


- diffuse scattering is caused by surface roughness or inhomogeneities in the reflecting medium
- a smooth surface reflects radiation in a single (specular) direction
- a rough surface scatters in various directions
- specular scattering is damped by surface roughness – treat as graded interface. For a single surface with r.m.s roughness σ:

$$R = R_F e^{-2 k_{Iz} k_{1z}^{t} s^{2}}$$

When Does a “Rough” Surface Scatter Diffusely?

- Rayleigh criterion

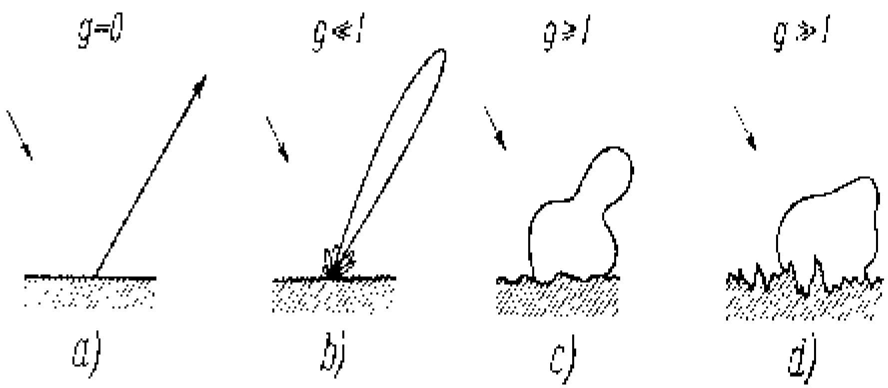


path difference: $\Delta r = 2 h \sin\gamma$

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

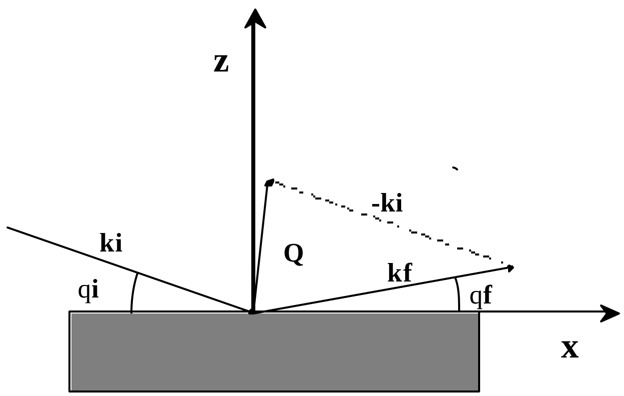
boundary between rough and smooth: $\Delta\phi = \pi/2$

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



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

Time-of-Flight, Energy-Dispersive Neutron Reflectometry

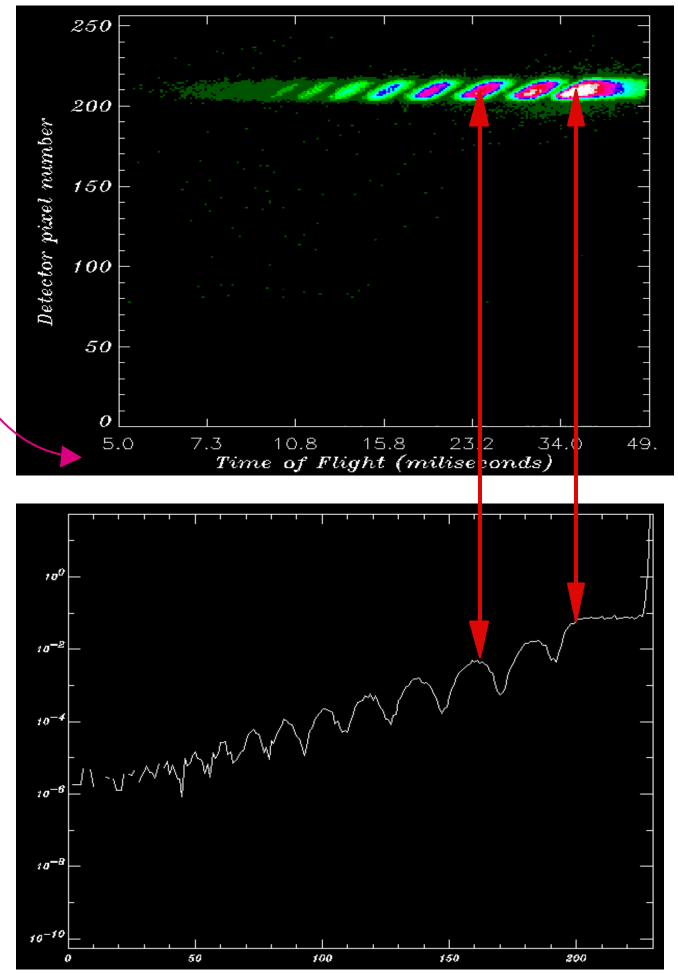


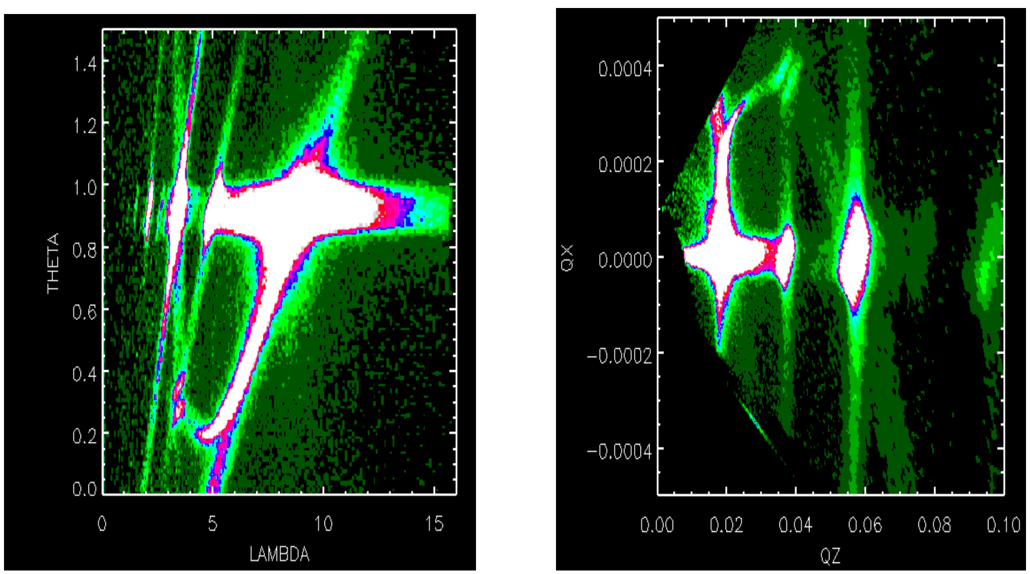
Q =kf -ki where $Q_x = \frac{2\,p}{l}*(\cos\ q_f - \cos\ q_i)$

$Q_z = \frac{2\,p}{l}*(\sin\ q_f + \sin\ q_i)$

Raw data in θ_f-TOF space for a single layer.
Note that large divergence does not imply poor Q_z resolution

TOF - l . L / 4



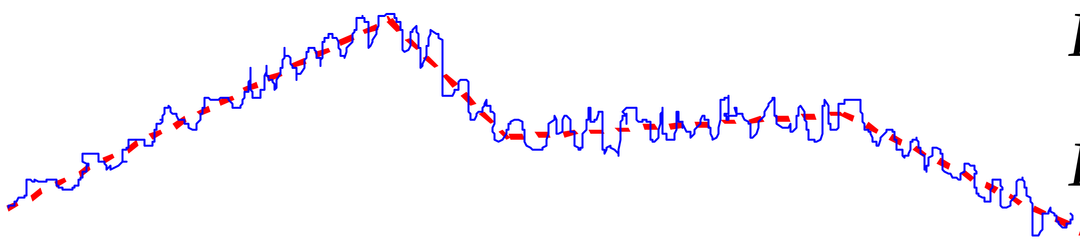


Vandium-Carbon Multilayer — specular & diffuse scattering
in θ_f-TOF space and transformed to Q_x-Q_z

The Study of Diffuse Scattering From Rough Surfaces Has Not Made Much Headway Because Interpretation Is Difficult

The theory (Distorted Wave Born Approximation) used to describe scattering from a rough surface, works in some cases but breaks down when $x k_z^2 / k^2 >> 1$, where x is the range of correlations in the surface

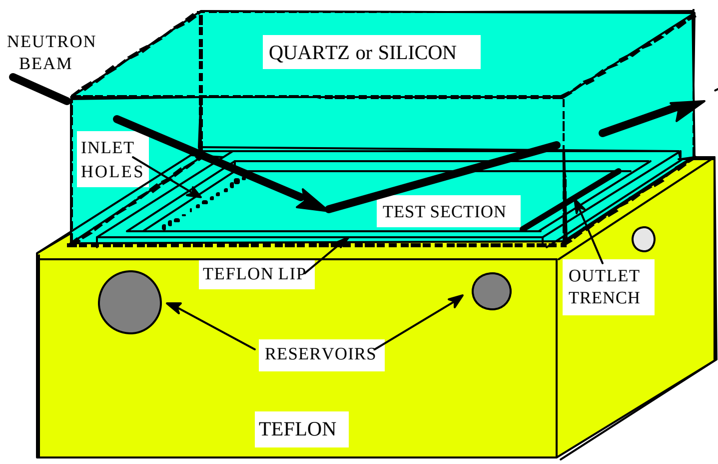
In some cases (e.g. faceted surfaces) one would also expect the approximation of a using an "average surface" wavefunction for perturbation theory to break down.

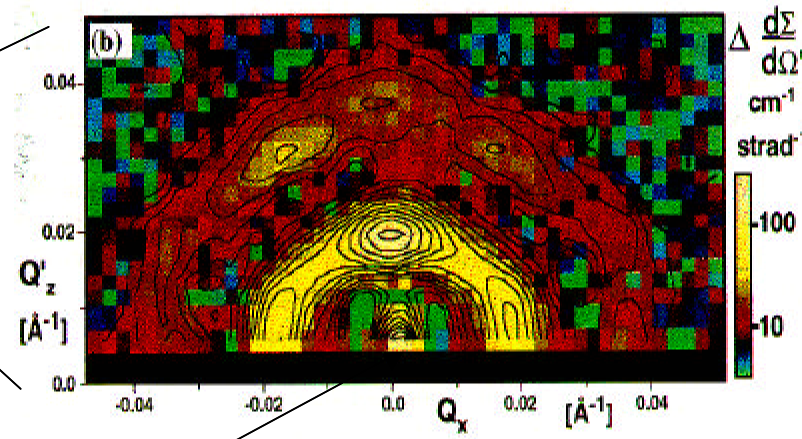


$$R_{micro-rough} = R_{smooth} e^{-2 k_0 k_1^t s^2}$$

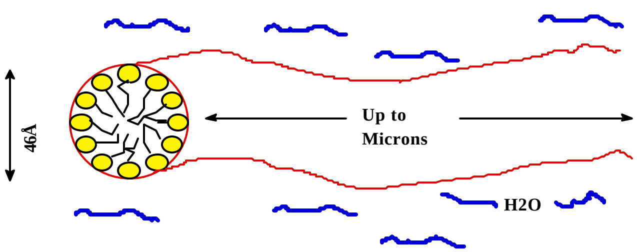
$$R_{facet} = R_{smooth} e^{-2 k_0^2 s^2}$$

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

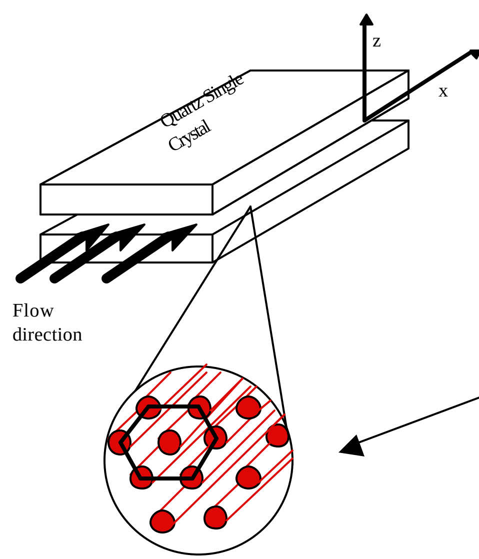




Specularly reflected beam



Thread-like micelle



Scattering pattern implies hexagonal symmetry