

Neutron Reflectometry

Roger Pynn

Indiana University and the Spallation Neutron Source



INDIANA UNIVERSITY

The next-generation neutron-scattering facility for the United States



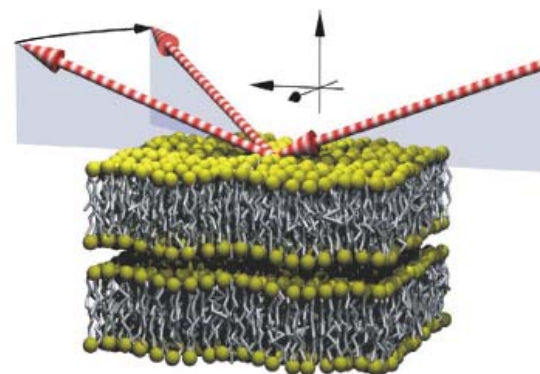
Surface Reflection Is Very Different From Most Neutron Scattering

- Normally, neutrons are very WEAKLY scattered
 - One can ignore doubly scattered neutrons
- 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
- Diffuse scattering gives information on surface & interface roughness



Images courtesy of M. Tolan & T. Salditt

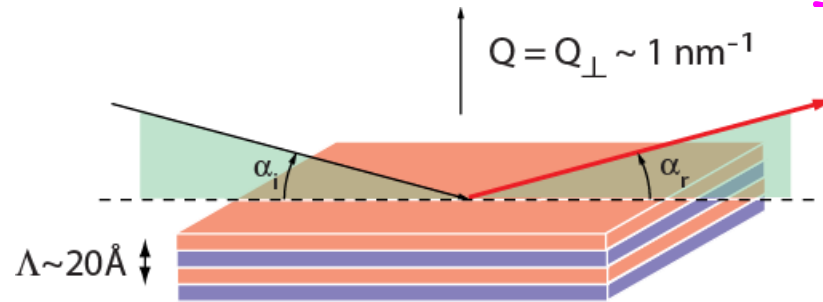


INDIANA UNIVERSITY

The next-generation neutron-scattering facility for the United States

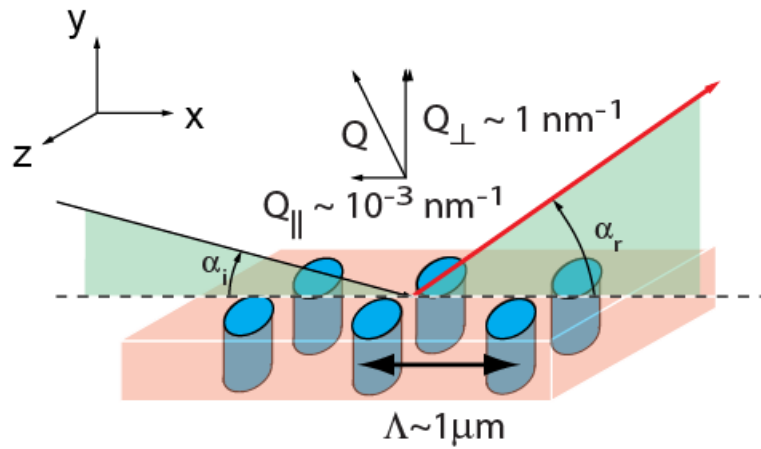


Various forms of small angle neutron reflection



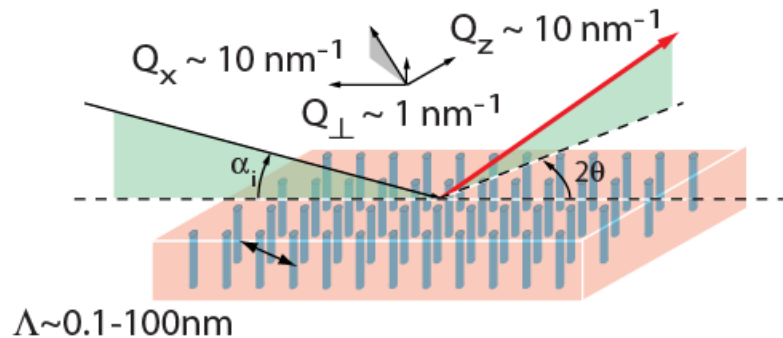
Specular reflectometry

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

Viewgraph from M. R. Fitzsimmons



Randomly Chosen Examples of Neutron Reflectometry Studies

- Inter-diffusion of polymers
- Phase separation in block copolymers
- Amphiphilic molecules at air-water interfaces
- Effect of shear on films of complex fluids
- Grafting of polymers to surfaces (mushrooms and brushes)
- Swelling of films exposed to vapor
- Magnetic structure of multilayers
- CMR/GMR films
- Exchange bias and exchange springs
- Nuclear polarization in spintronic materials



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

Refractive index : $k / k_0 = n$

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

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

i.e. Neutrons obey Snell's Law

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

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

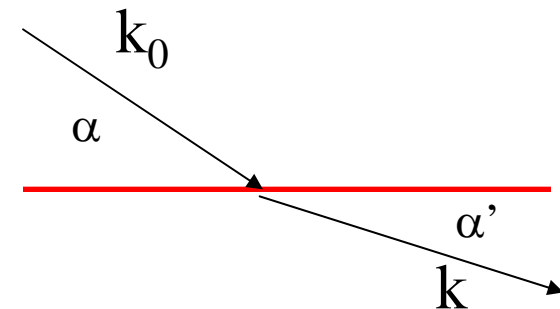
The critical value of k_{0z} for total external reflection is $k_{0z} = \sqrt{4\pi\rho}$

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

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

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

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



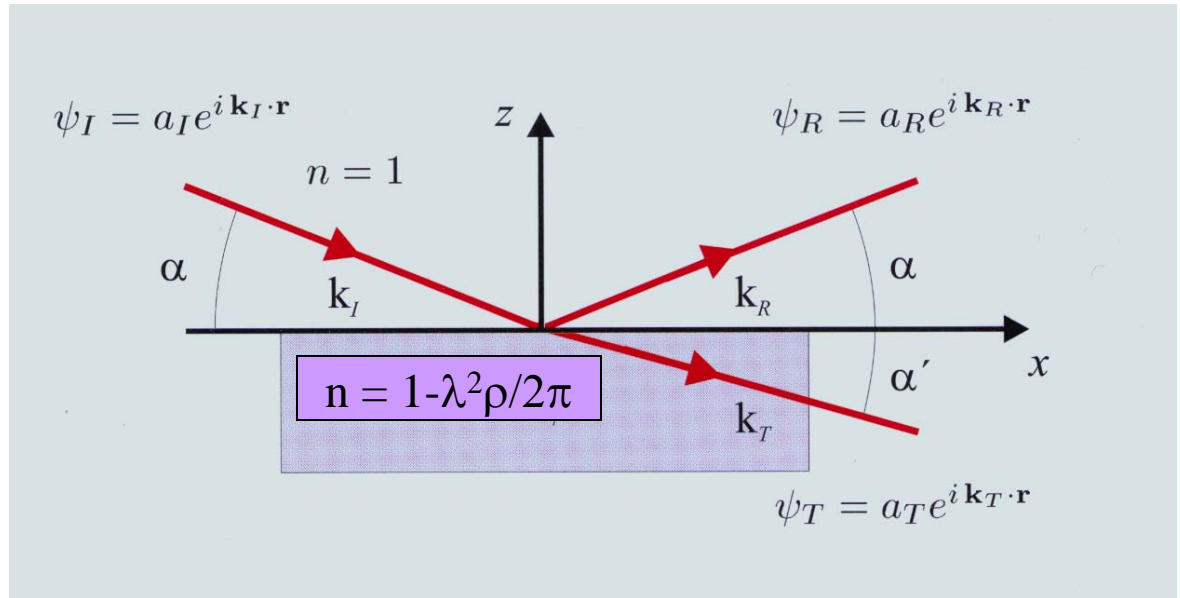
Reflection of Neutrons by a Smooth Surface: Fresnel's Law

continuity

of ψ & $\dot{\psi}$ at $z = 0 \Rightarrow$

$$a_I + a_R = a_T$$

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



reflectance: $r = \frac{a_R}{a_I} = \frac{(k_{Iz} - k_{Tz})}{(k_{Iz} + k_{Tz})}$

transmittance: $t = \frac{a_T}{a_I} = \frac{2k_{Iz}}{(k_{Iz} + k_{Tz})}$

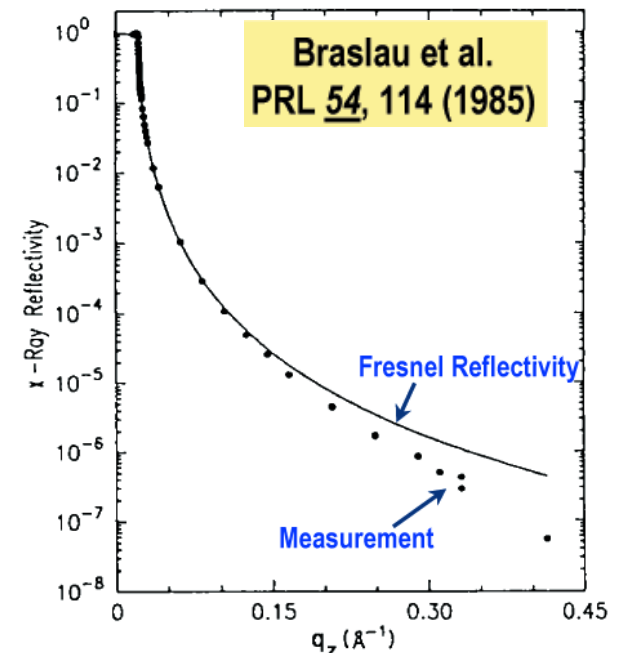
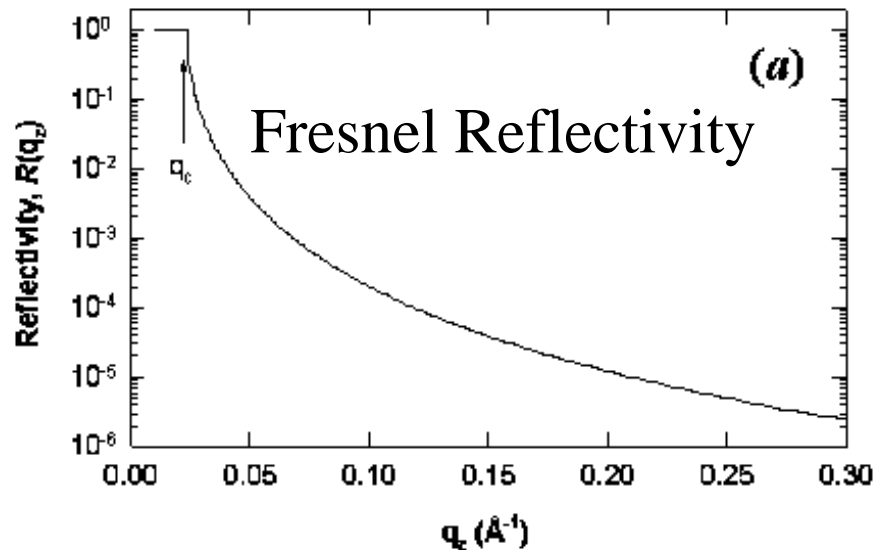


Reflectivity

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

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

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

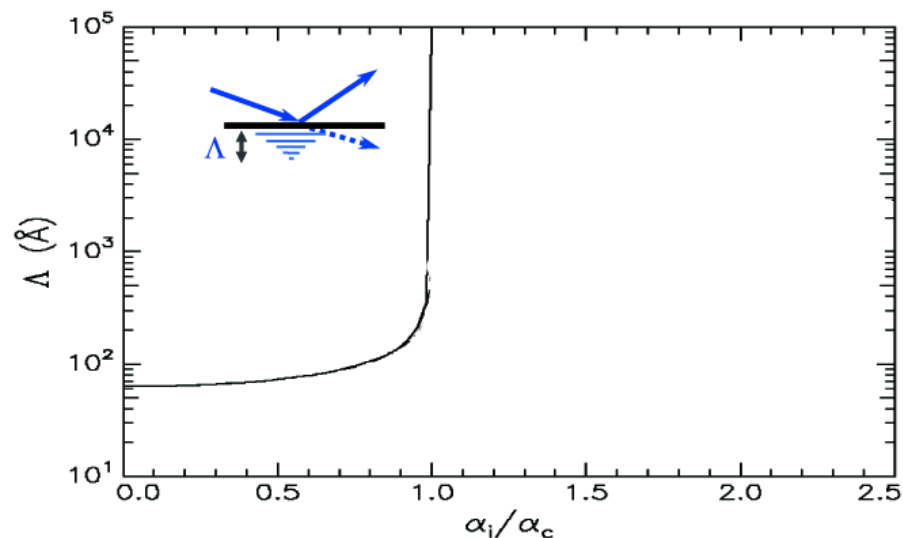


Measured and Fresnel reflectivities for water – difference is due to surface roughness



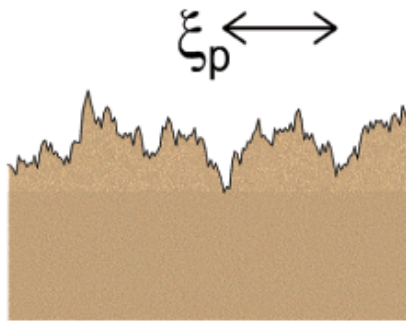
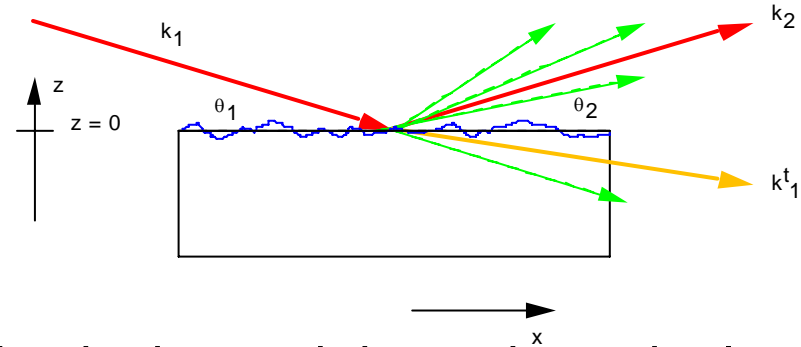
Penetration Depth

- 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

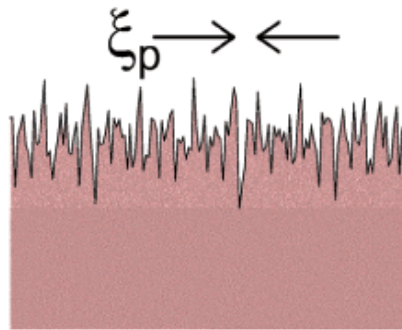


Surface Roughness

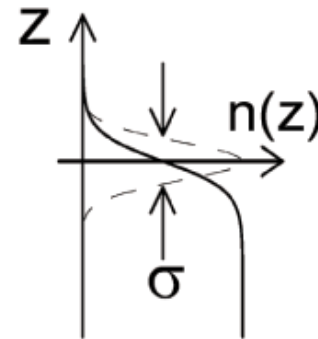
- Surface roughness causes diffuse (non-specular) scattering and so reduces the magnitude of the specular reflectivity
- The way in which the specular reflection is damped depends on the length scale of the roughness in the surface as well as on the magnitude and distribution of roughness



“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

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



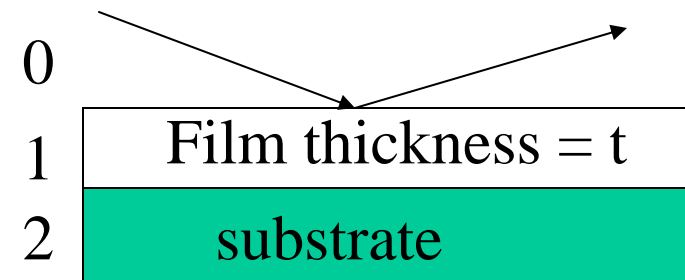
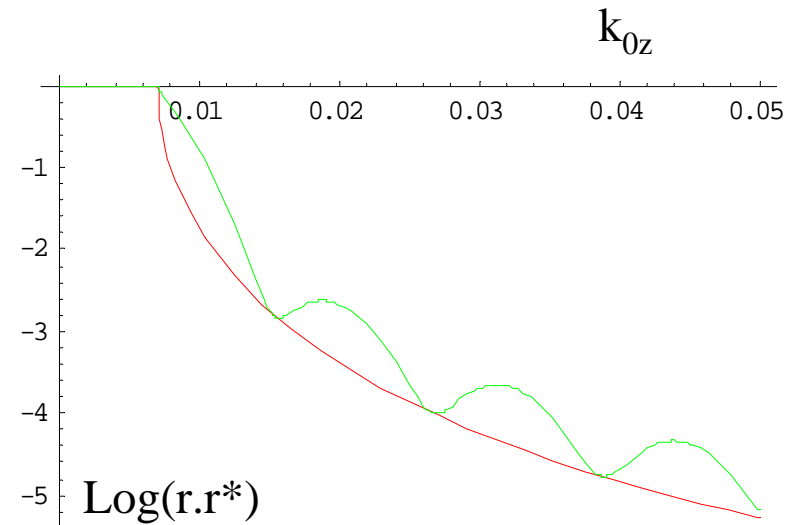
Fresnel's Law for a Thin Film

- $r = (k_{0z} - k_{1z}) / (k_{1z} + k_{0z})$ is Fresnel's law
- Evaluate with $\rho = 4.10^{-6} \text{ \AA}^{-2}$ 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:

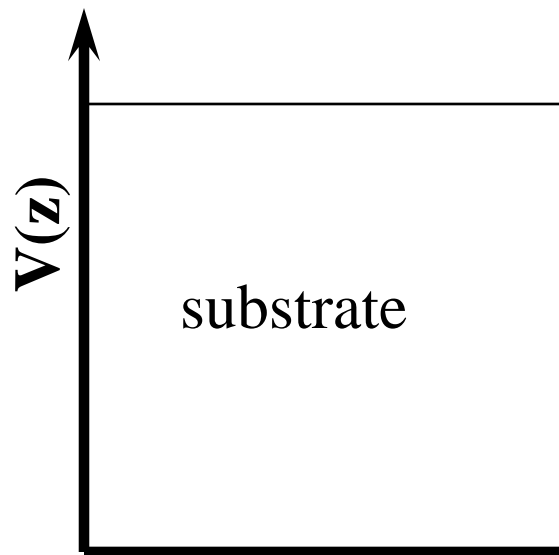
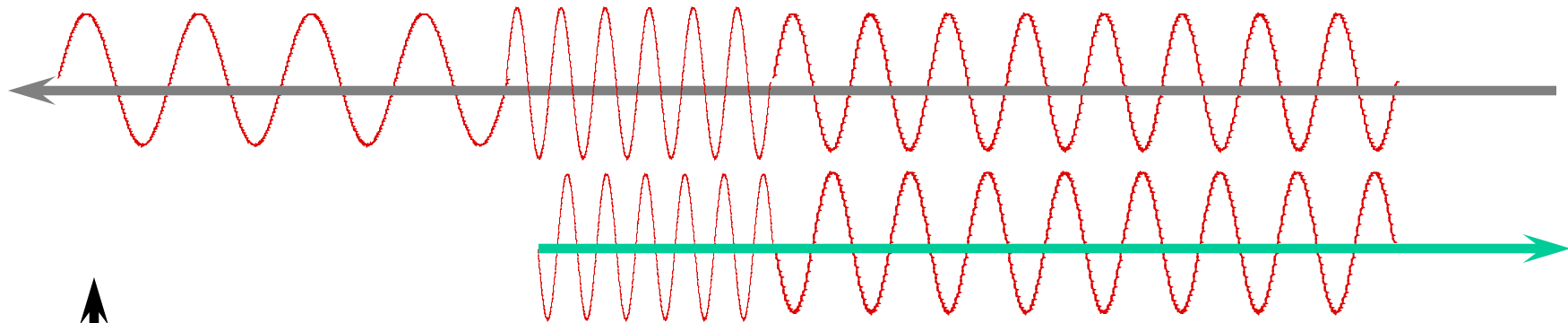
$$r = \frac{r_{01} + r_{12} e^{i2k_{1z}t}}{1 + r_{01}r_{12} e^{i2k_{1z}t}}$$

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 \text{ \AA} film was used for the figure)



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 & $\rho(z)$ is the scattering length density

Film

Vacuum



INDIANA UNIVERSITY

The next-generation neutron-scattering facility for the United States



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)

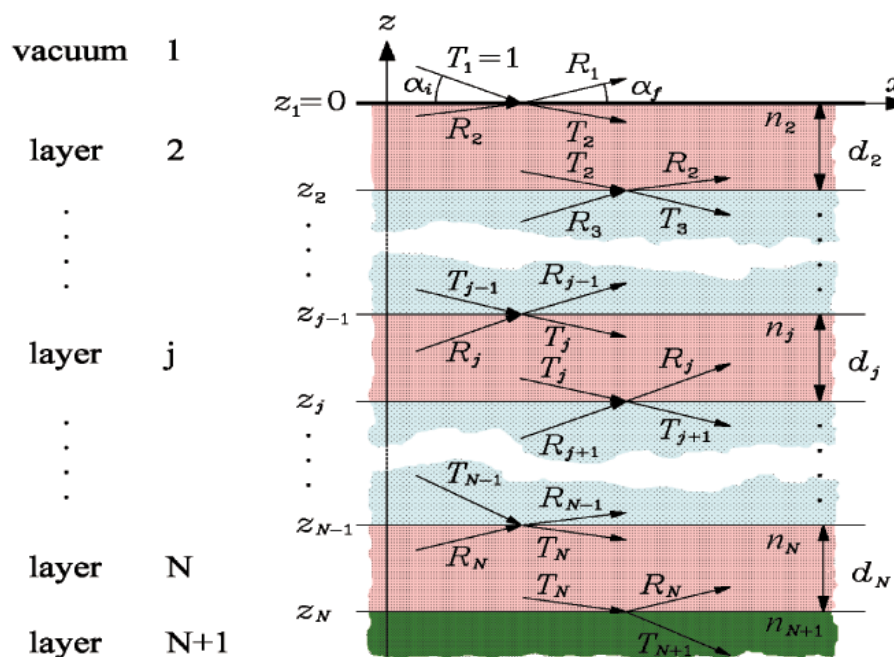


Image from M. Tolan



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!!

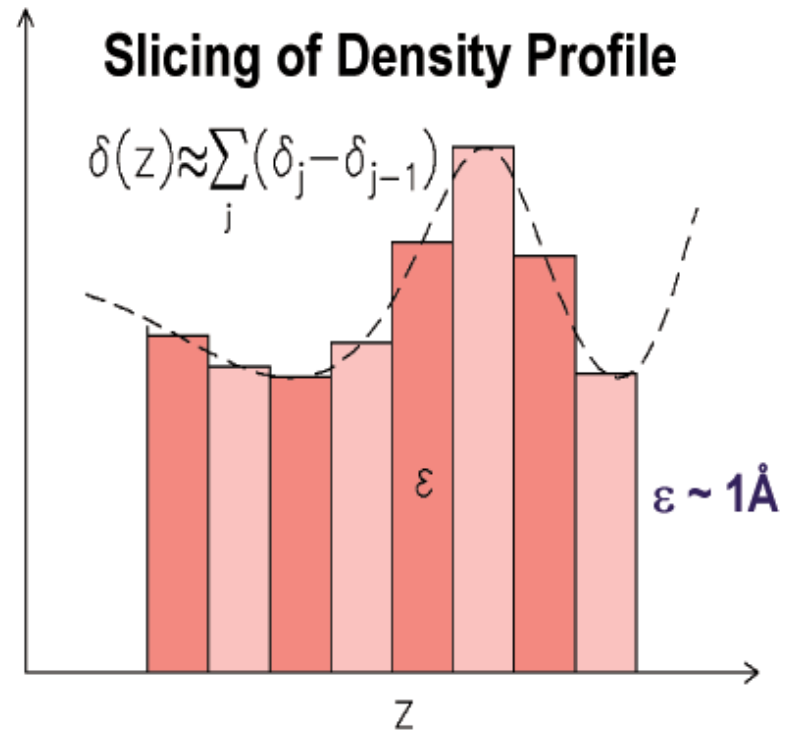
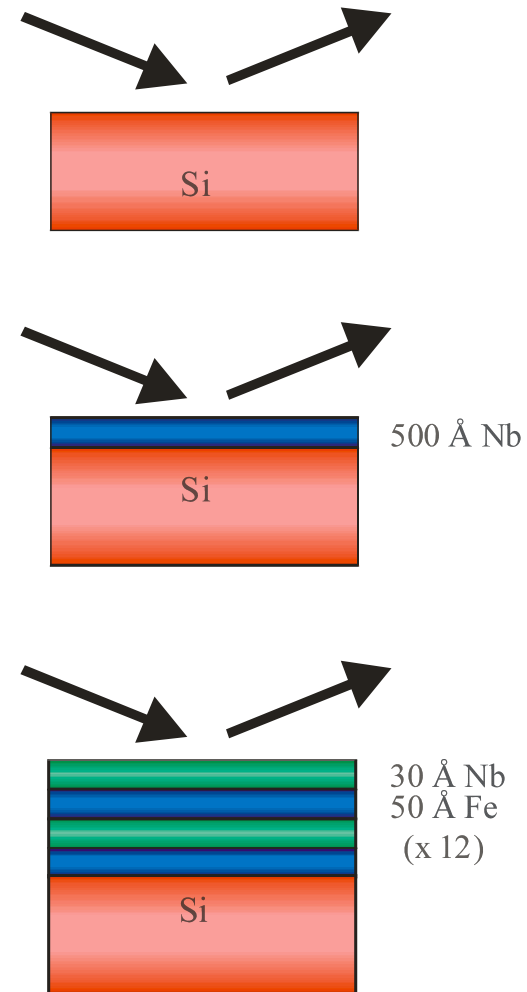
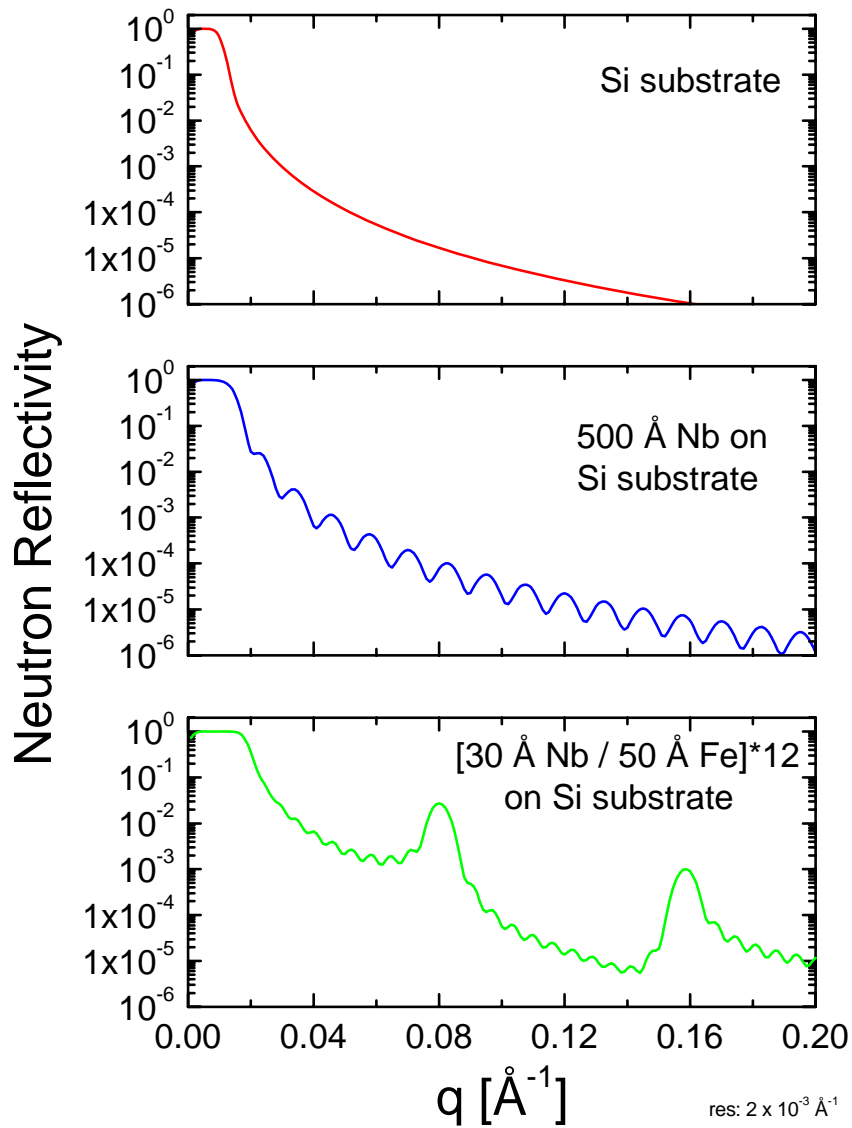


Image from M. Tolan



Typical Reflectivities

unpolarized



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

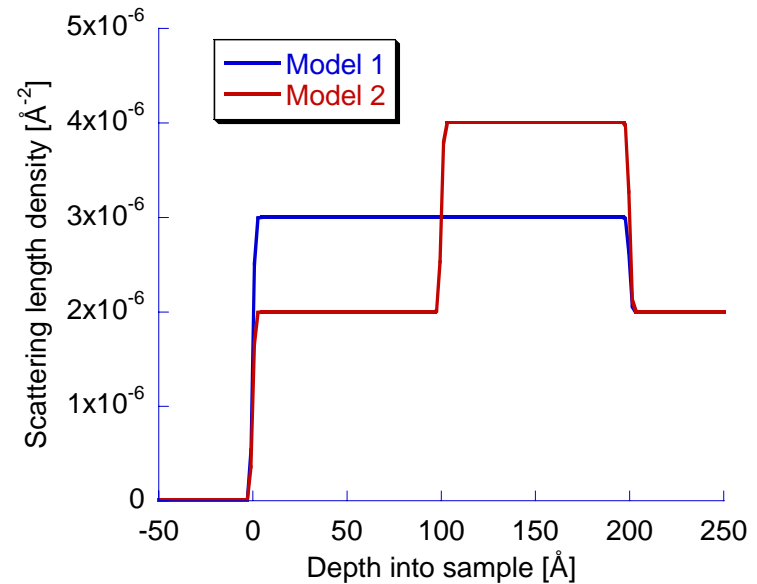
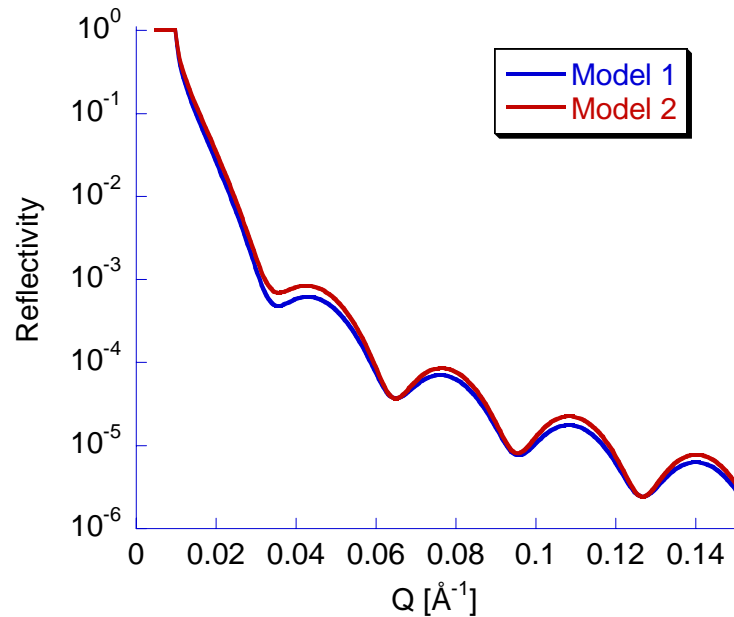


Analyzing Reflectivity Data

- 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)



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)

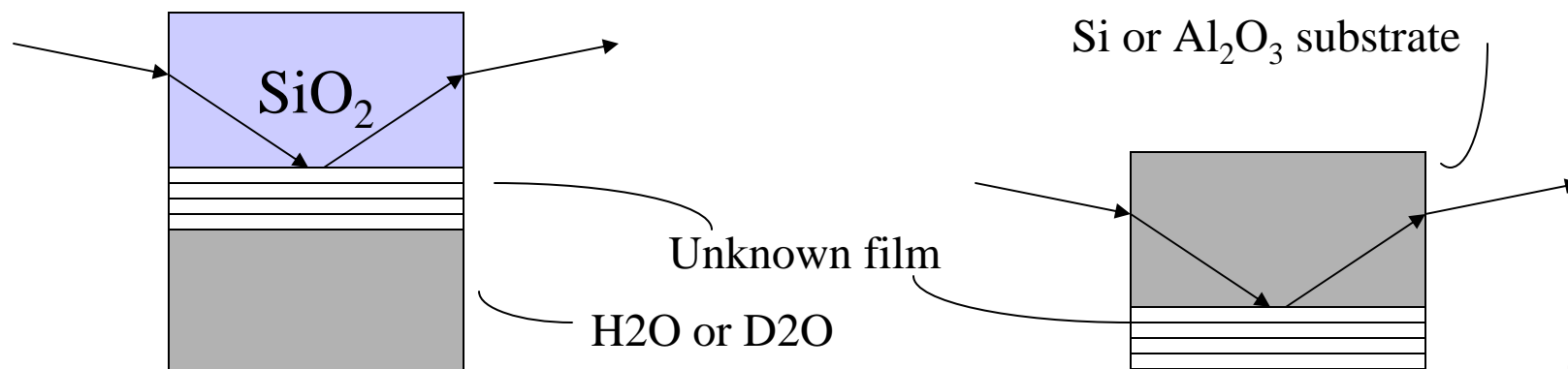
D. Sivia et al., J. Appl. Phys. **70**, 732 (1991).



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)



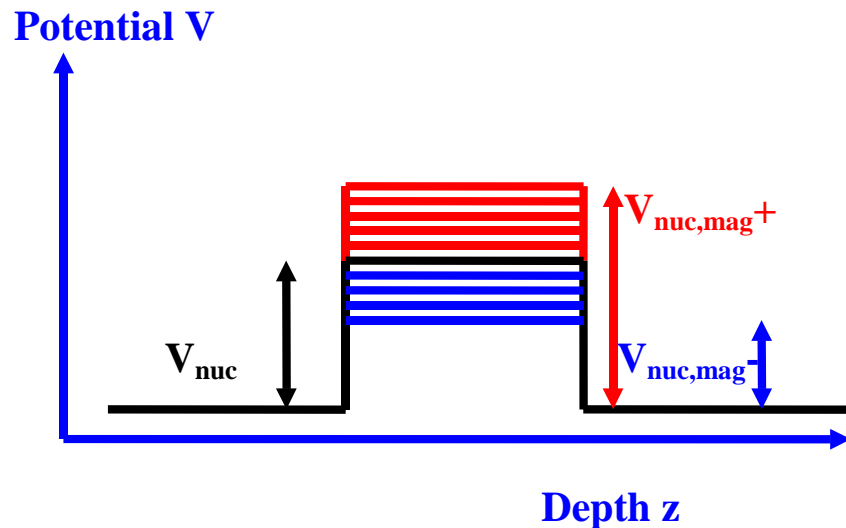
Planning a Reflectivity Measurement

- 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



Reflection of Polarized Neutrons

- Neutrons are also scattered by variations of B (magnetization)
- Only components of magnetization perpendicular to Q cause scattering
- If the magnetization fluctuation that causes the scattering is parallel to the magnetic moment (spin) of a polarized neutron, the neutron spin is not changed by the scattering (non-spin-flip scattering)



Fermi pseudo potential:

$$V = 2\pi \hbar^2 N (\mathbf{b}_{\text{n}} +/\!-\! \mathbf{b}_{\text{mag}}) / m_{\text{N}}$$

with \mathbf{b}_{nuc} : nuclear scattering length [fm]
 \mathbf{b}_{mag} : magnetic scattering length [fm]
($1 \mu_{\text{B}}/\text{Atom} \Rightarrow 2.695 \text{ fm}$)
 N : number density [at/cm^3]
 m_{N} : neutron mass

Spin“up” neutrons see a **high** potential.
Spin“down” neutrons see a **low** potential.

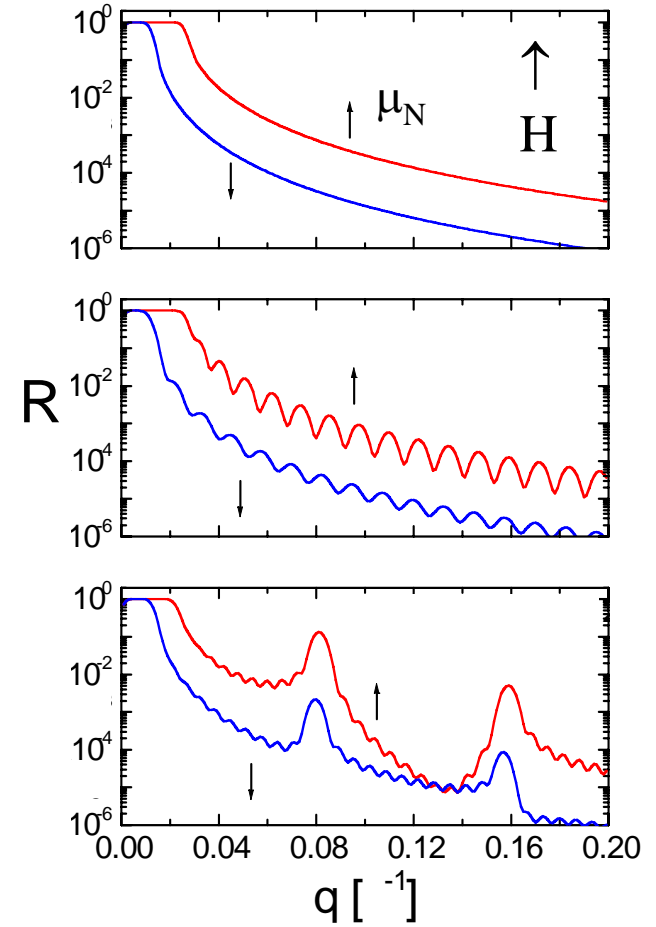
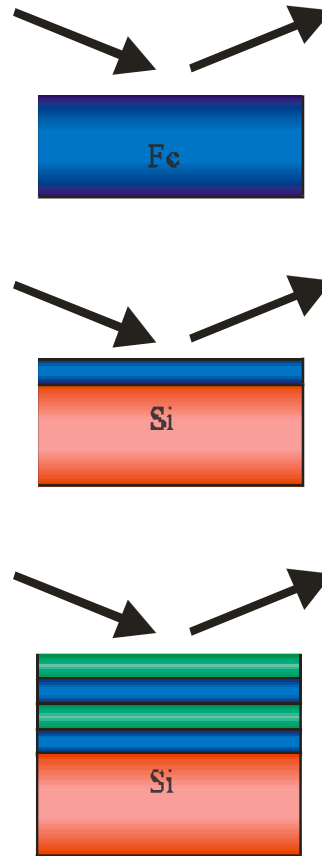
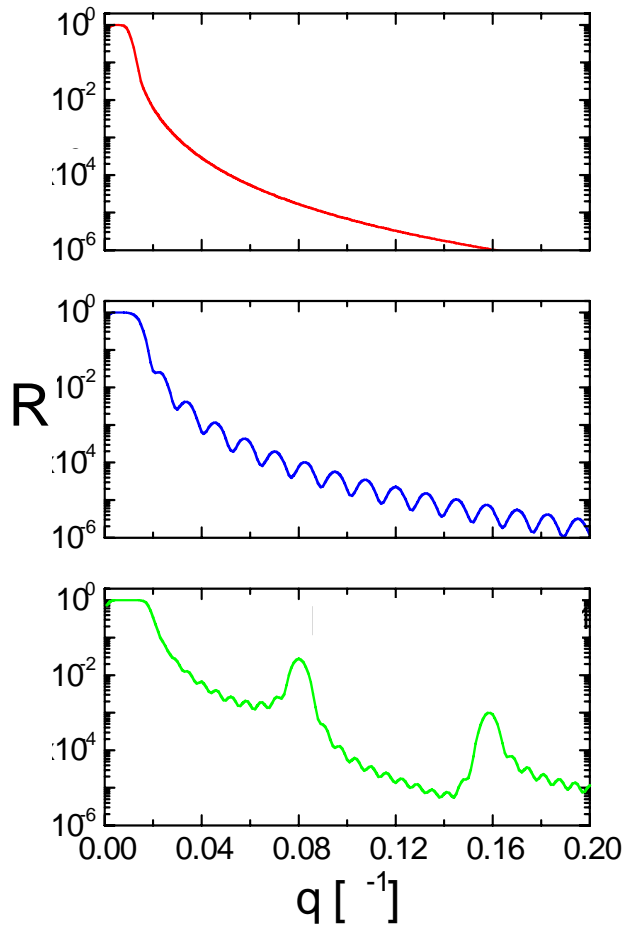


Typical Non-Spin-Flip Reflectivities

$$k_z = \sqrt{k_{z0}^2 - 4\pi(b/V)}$$

$$q_z = 2k_{z0}$$

$$k_z^\pm = \sqrt{k_{z0}^2 - 4\pi[(b/V) \pm cB]}$$



Courtesy of F. Klose

The next-generation neutron-scattering facility for the United States

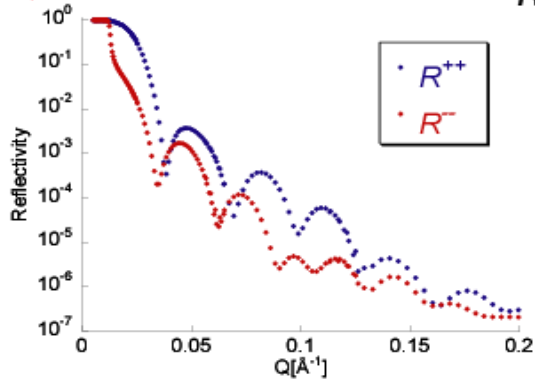
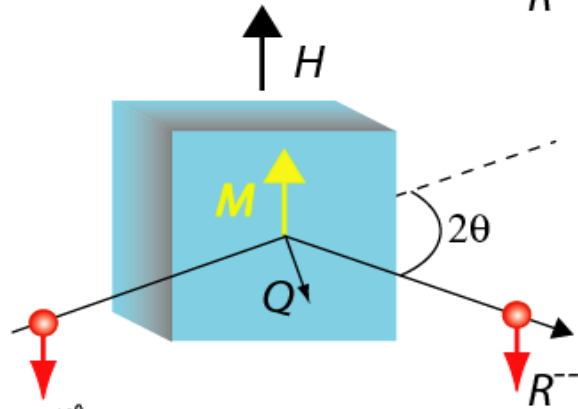
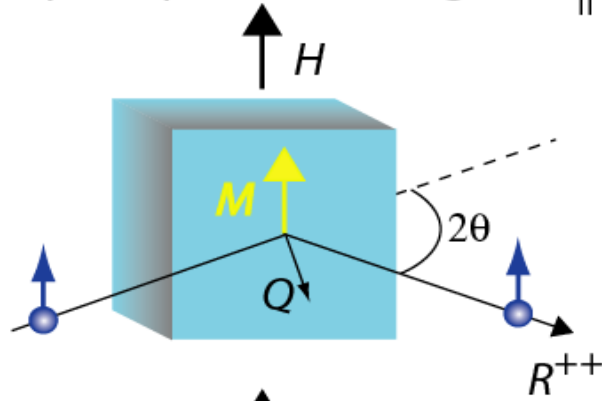


INDIANA UNIVERSITY

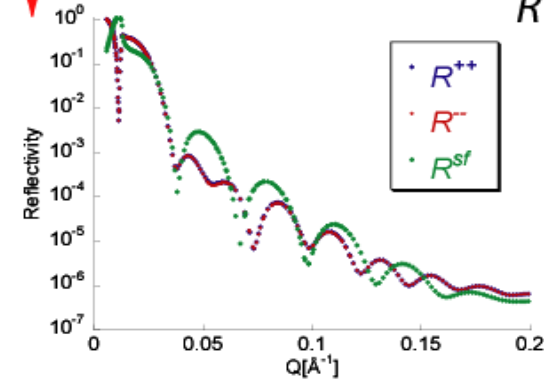
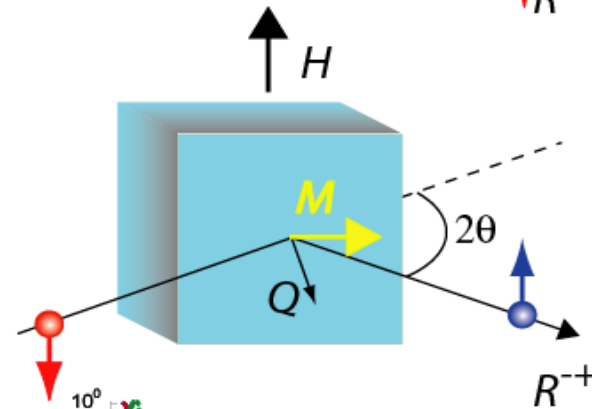
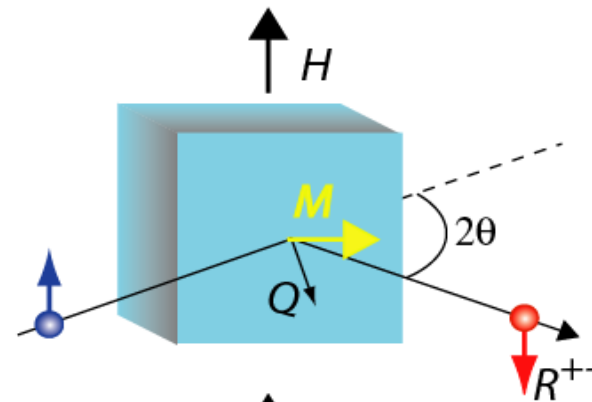


Polarized neutron reflectometry

non-spin-flip reflectivities give $\overline{M_{\parallel}}(Q)$



spin-flip reflectivities give $\overline{M_{\perp}^2}(Q)$



Summary so Far...

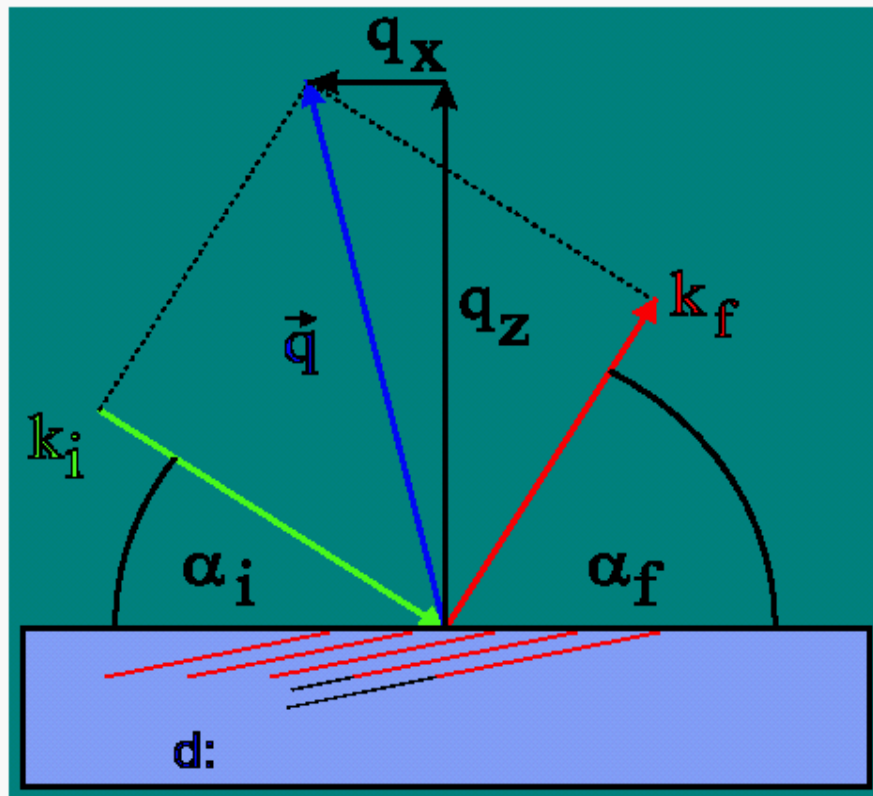
- Neutron reflectometry can be used to determine scattering length density profiles perpendicular to smooth, flat interfaces
- PNR (polarized neutron reflectometry) allows vector magnetic profiles to be determined
- Diffuse scattering gives information about surface roughness

What new things are we planning?

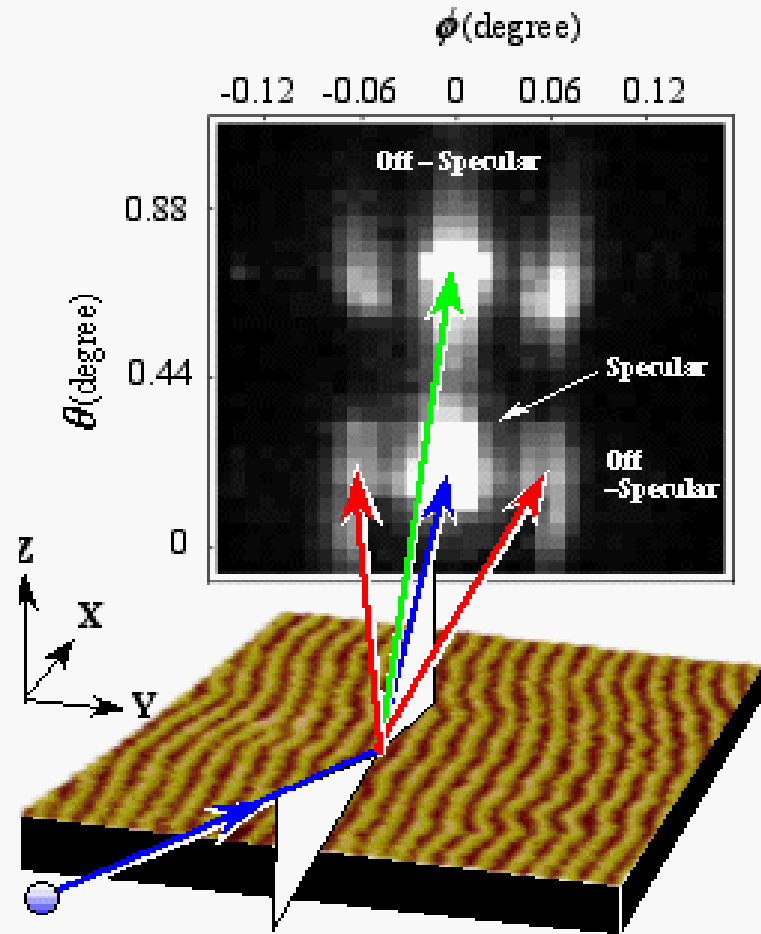


Components of the Scattering Vector in Grazing Incidence Geometry

Scattering Geometry & Notation



q_x is very small



Viewgraph courtesy of Gian Felcher



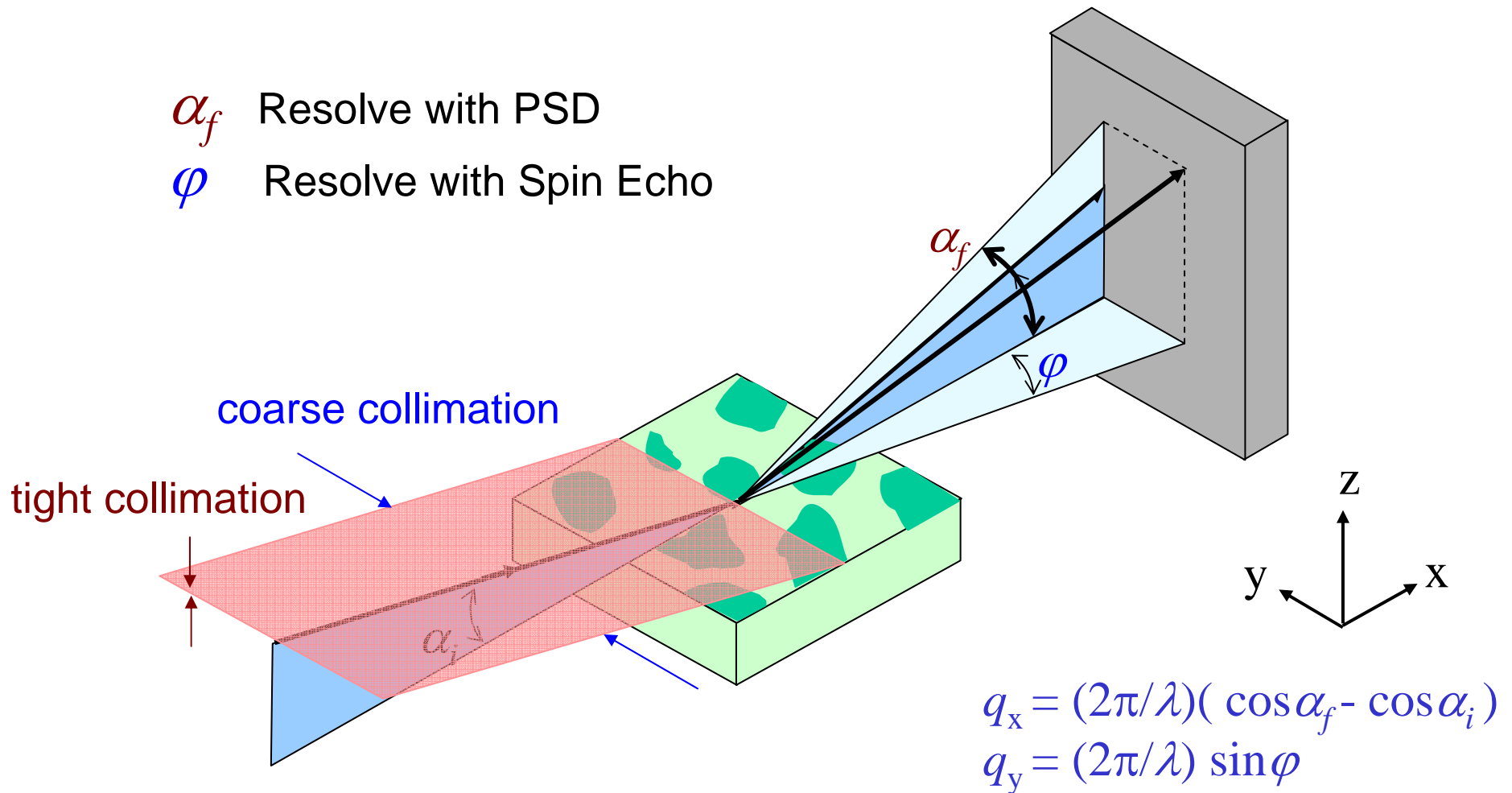
INDIANA UNIVERSITY

The next-generation neutron-scattering facility for the United States

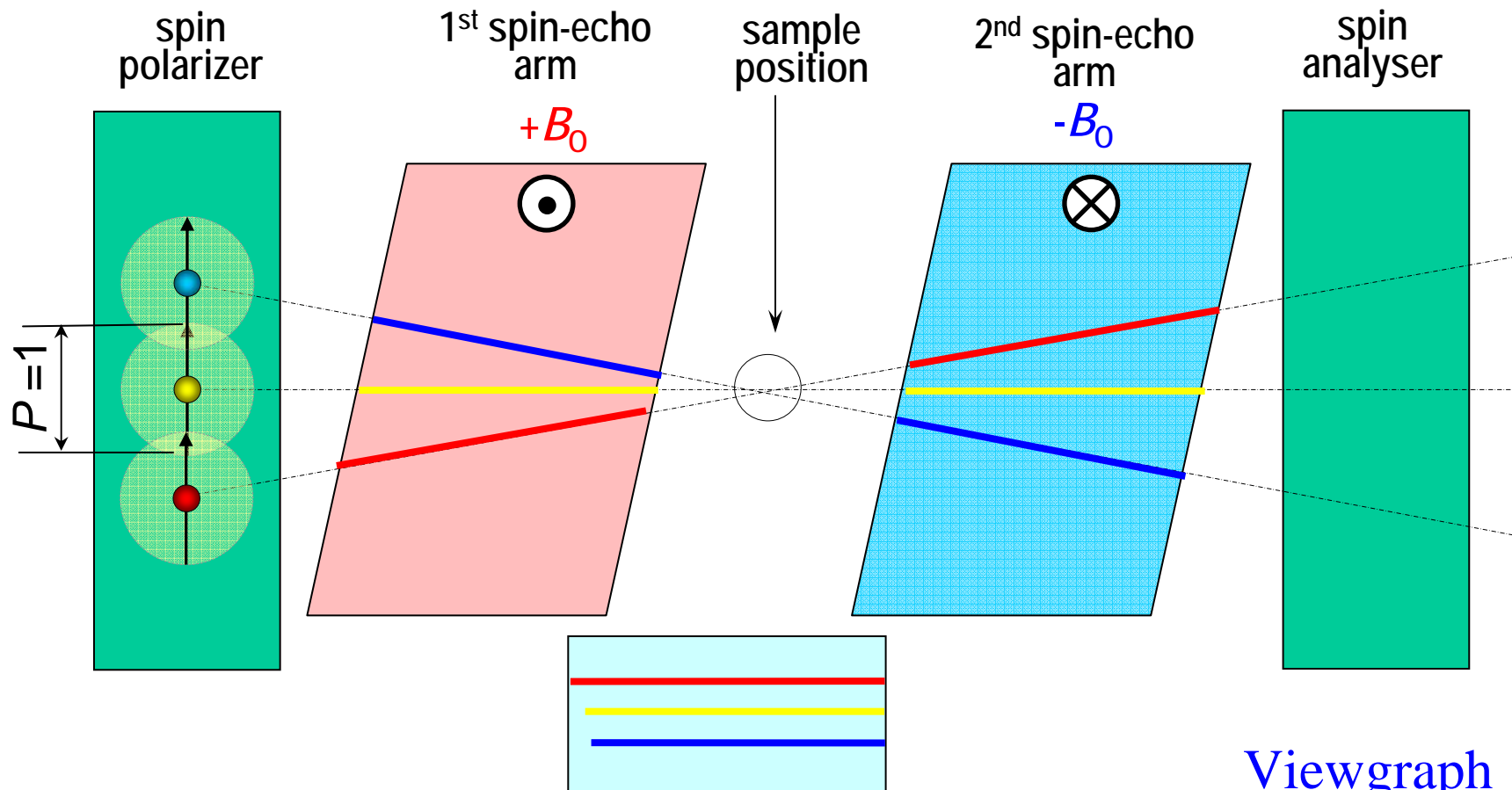


Geometry at grazing incidence

- α_f Resolve with PSD
- φ Resolve with Spin Echo



The Classical Picture of Spin Precession

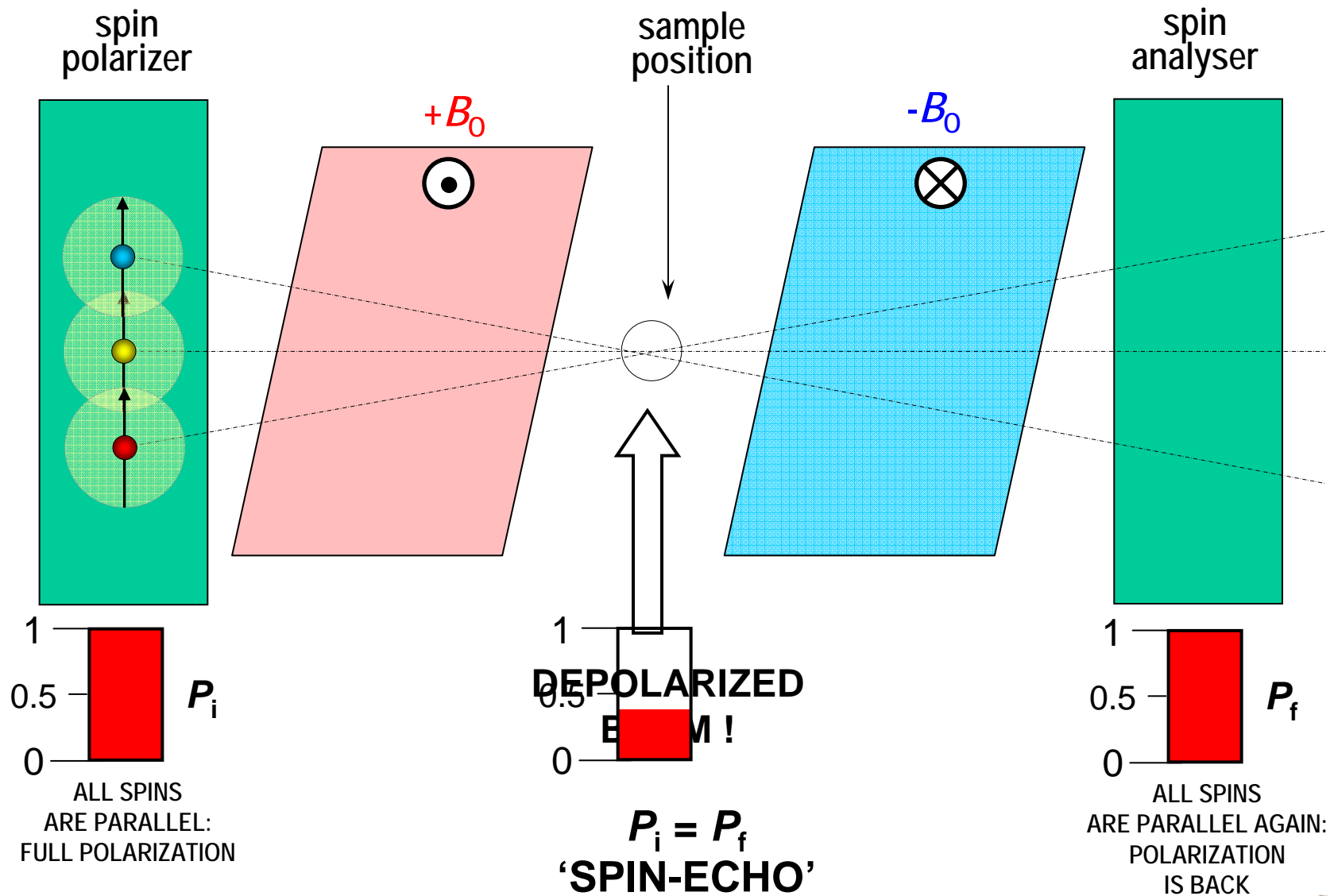


DIFFERENT PATH LENGTHS FOR THE DIFFERENT TRAJECTORIES !

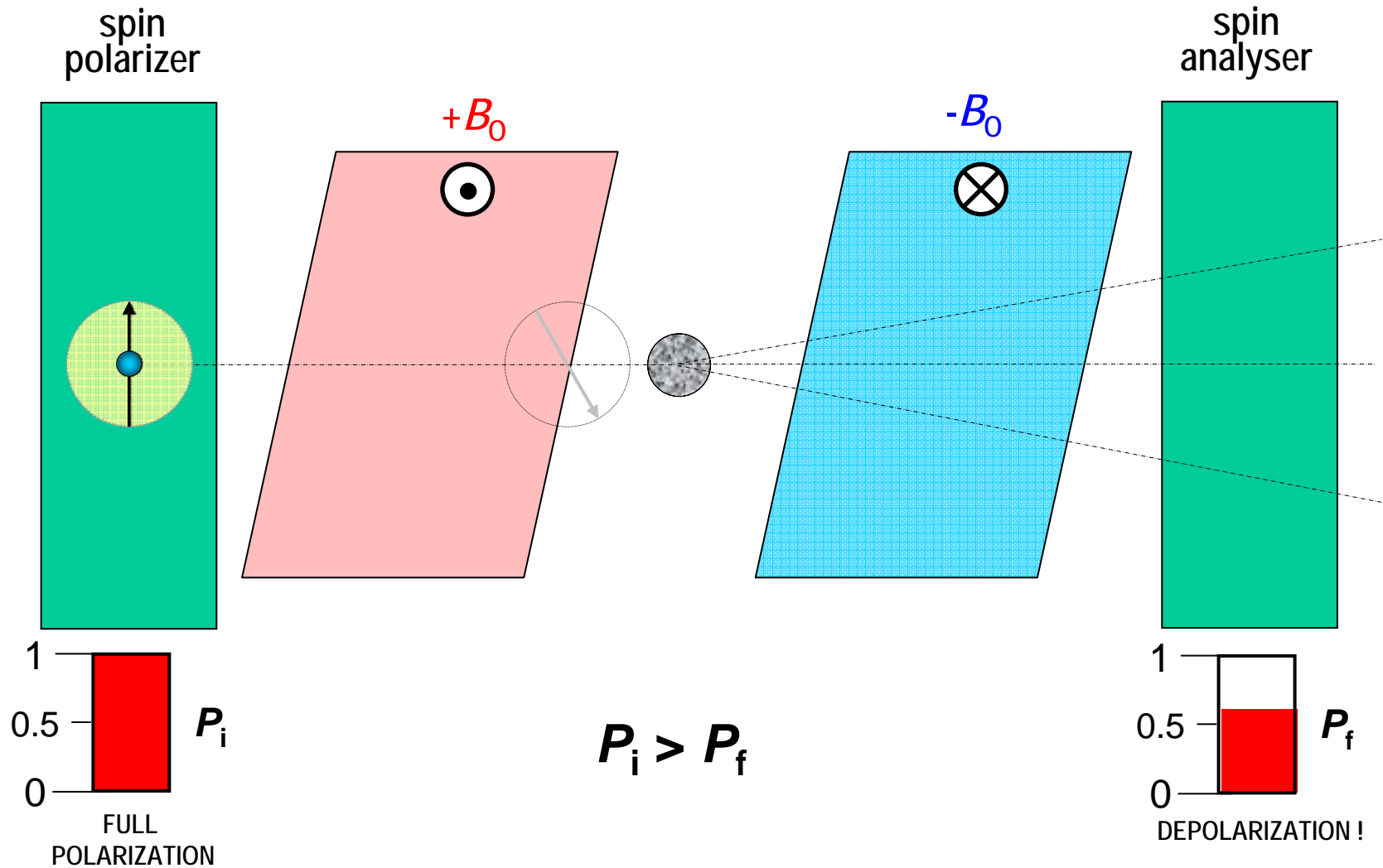
Viewgraph
sequence by
A. Vorobiev



Spin Echo Scattering Angle Measurement (SESAME) No Sample in Beam



Spin Echo Scattering Angle Measurement (SESAME) Scattering by the Sample



Spin Echo Scattering Angle Measurement (SESAME) Scattering of a Divergent Beam

