

Introduction to Neutron reflectometry

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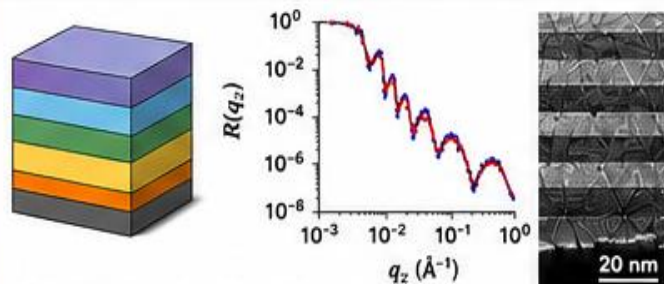
HUN-REN Wigner Research Centre for Physics



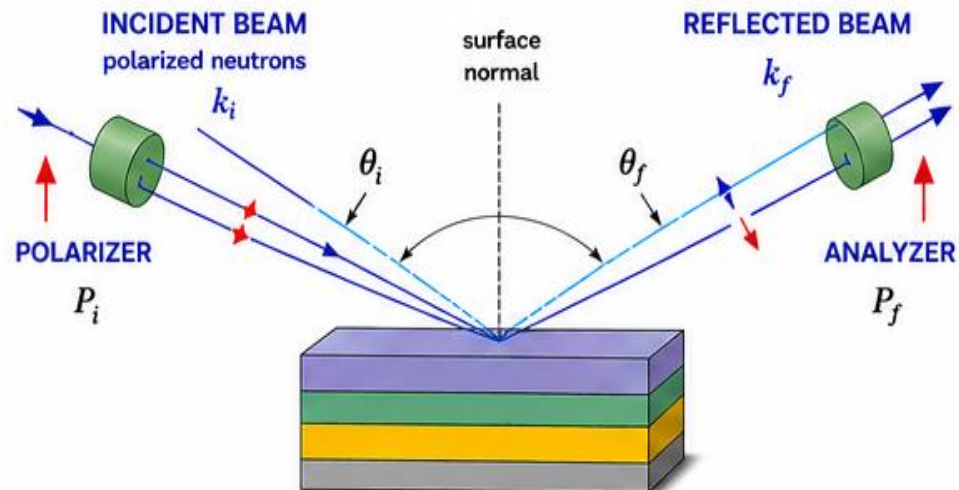
NEUTRON REFLECTOMETRY – APPLICATIONS

Atomic-scale structure and magnetic characterization of interfaces and thin films

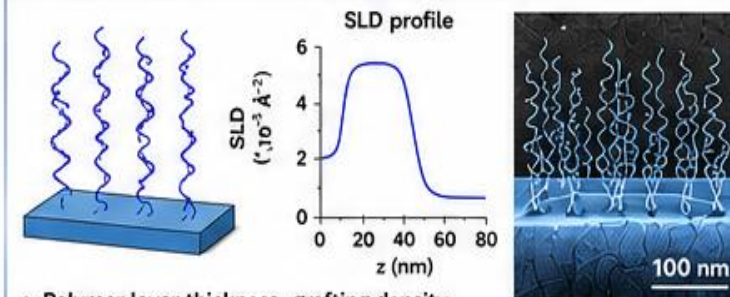
1. THIN FILMS & MULTILAYERS



- Film thickness, density, roughness
- Interdiffusion and buried layers
- Oxides and interface characterization

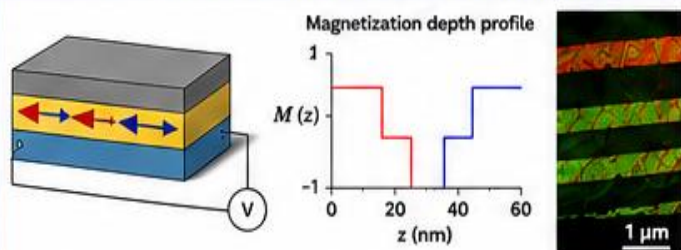


2. POLYMERS & SOFT MATTER



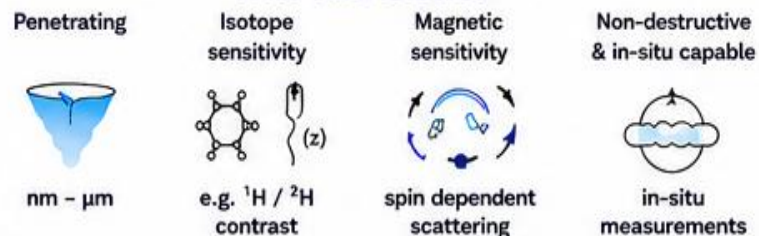
- Polymer layer thickness, grafting density
- Conformation changes, swelling, hydration
- Temperature, pH, solvent and ion effects

3. MAGNETIC LAYERS & SPINTRONICS

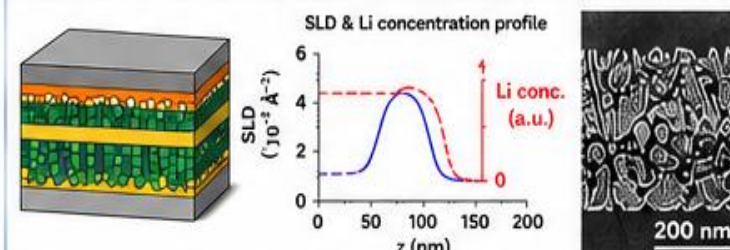


- Depth-resolved magnetization (longitudinal & transverse)
- Magnetic dead layers, interdiffusion, anisotropy
- Exchange coupling and spin-dependent phenomena

WHY NEUTRONS?

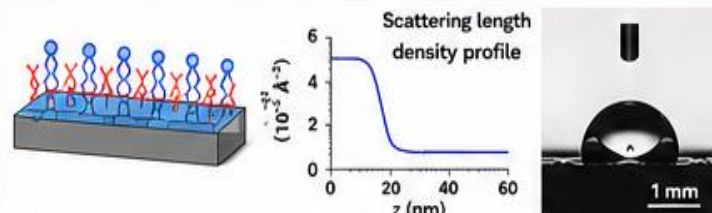


4. ENERGY & FUNCTIONAL MATERIALS



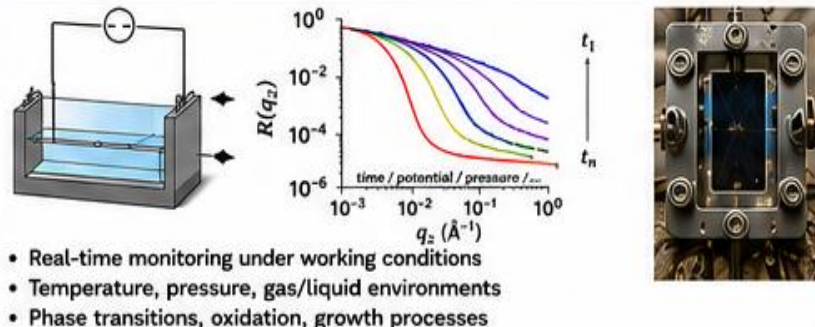
- Battery electrodes (charge/discharge, SEI layers)
- Fuel cells, catalysts, supercapacitors
- Chemical and structural changes during operation

5. SOFT MATTER / SURFACES & INTERFACES



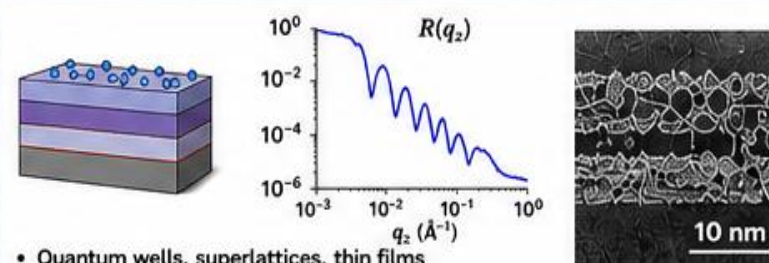
- Surfactants, lipid monolayers and bilayers
- Adsorption, wetting, swelling, self-assembly
- Corrosion inhibitors and surface treatments

6. IN-SITU & OPERANDO STUDIES



- Real-time monitoring under working conditions
- Temperature, pressure, gas/liquid environments
- Phase transitions, oxidation, growth processes

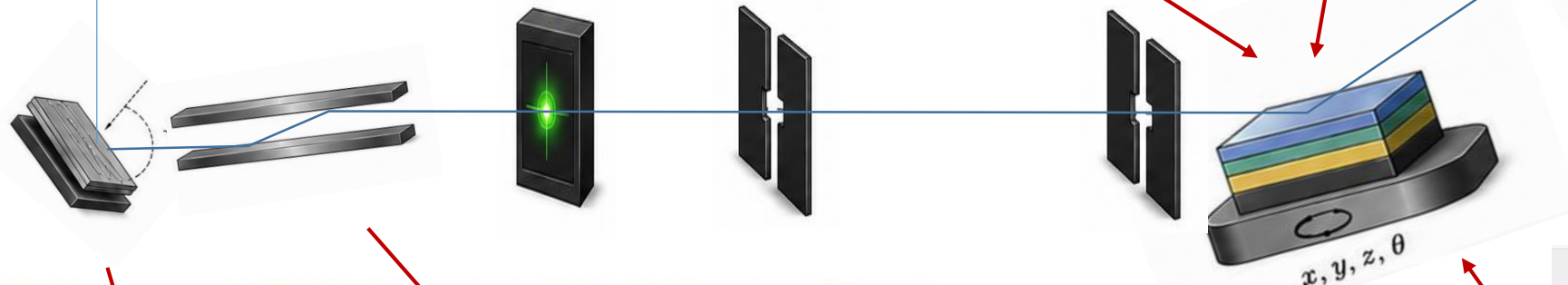
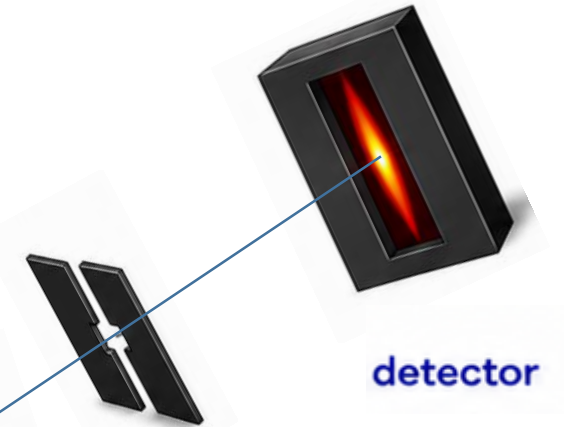
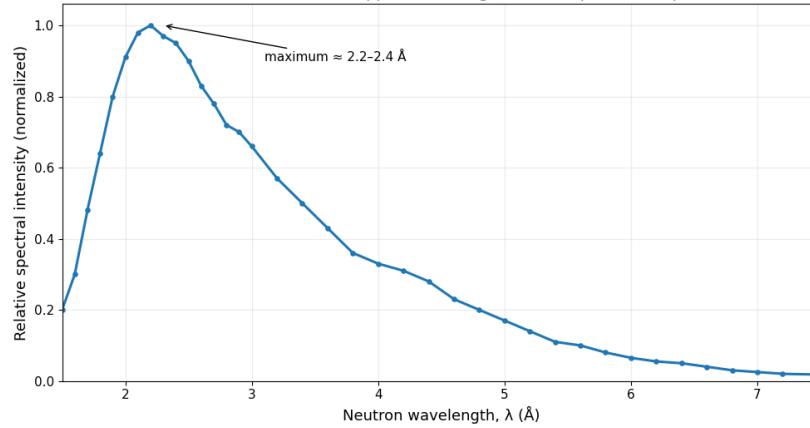
7. NANOSTRUCTURES & QUANTUM SYSTEMS



- Quantum wells, superlattices, thin films
- Magnetic multilayers, topological materials
- Interface roughness and electronic confinement

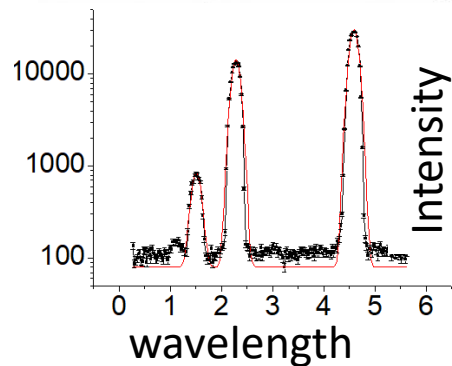
Unpolarized neutron reflectometer

Budapest Research Reactor cold-neutron spectrum
BNC cold beamline 10/3 - approximate digitization of published spectrum



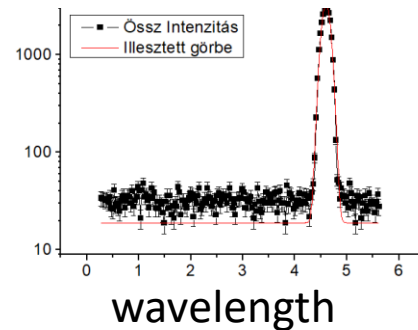
Monochromator

Pyrolytic graphite (PG) crystal
Bragg reflection selects wavelength λ



Non magnetic supermirror

Two flat mirrors (multi-layer coating)
Maintains polarization and controls divergence



Beam monitor

Measures incident beam intensity

Slit

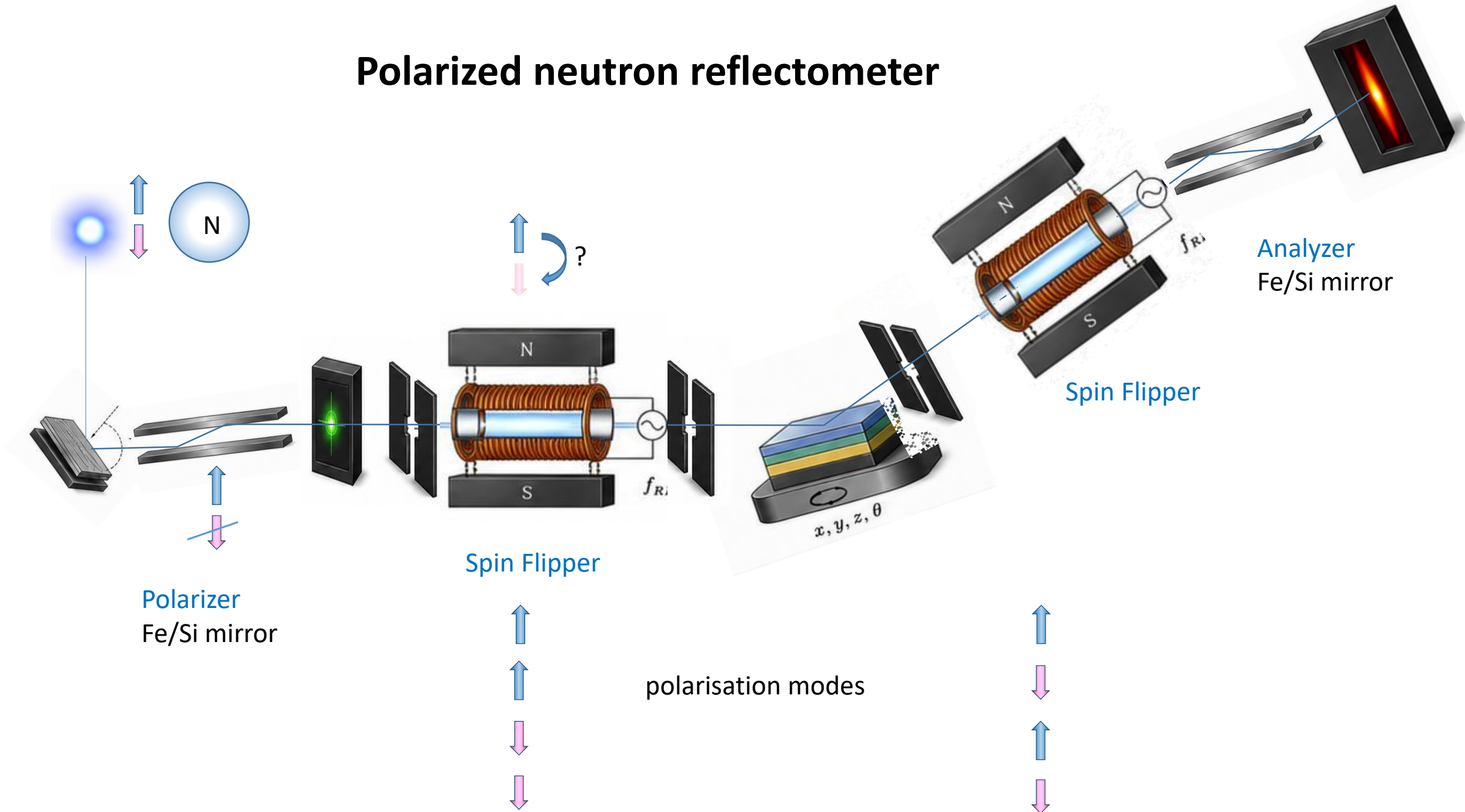
Defines beam height

Sample

Mounted on high precision stage

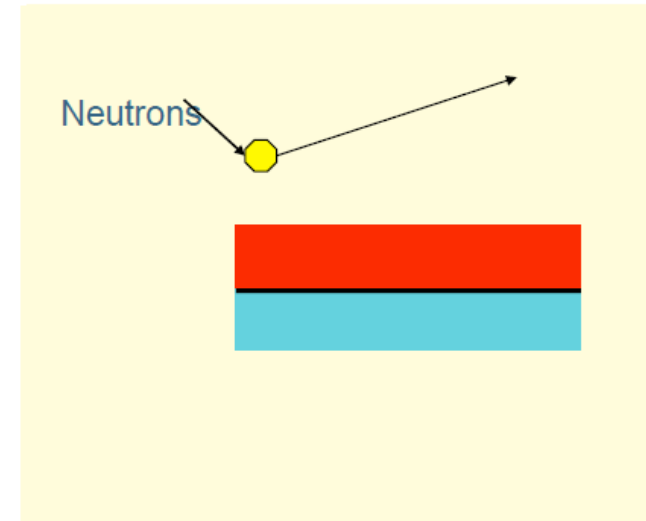


Polarized neutron reflectometer

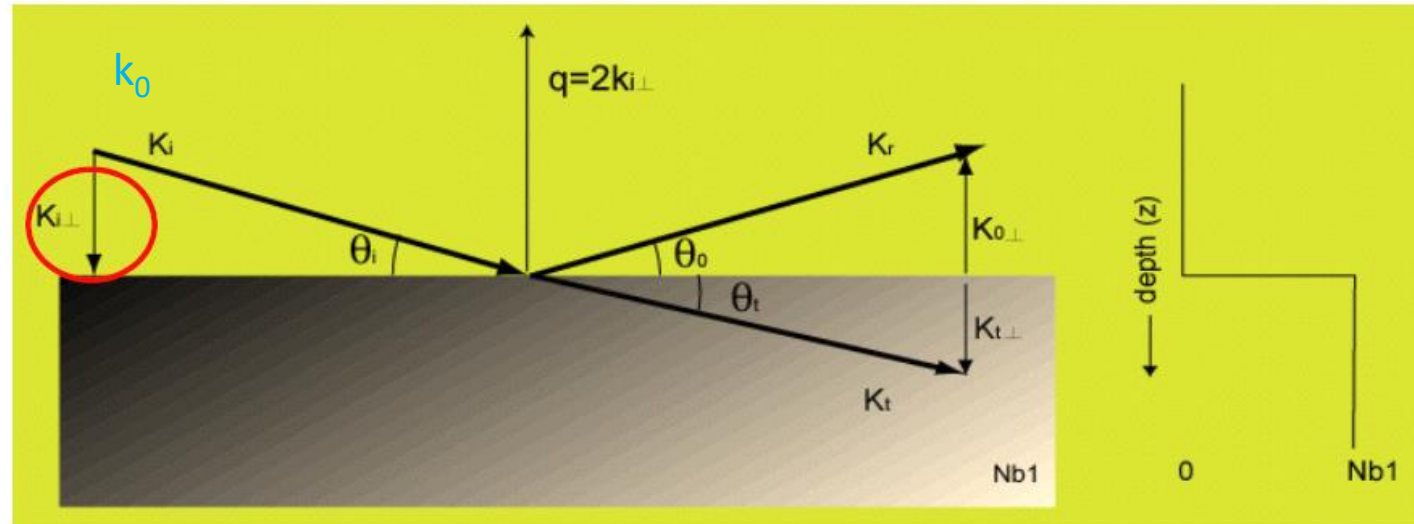


Fate of a Neutron at an Interface

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



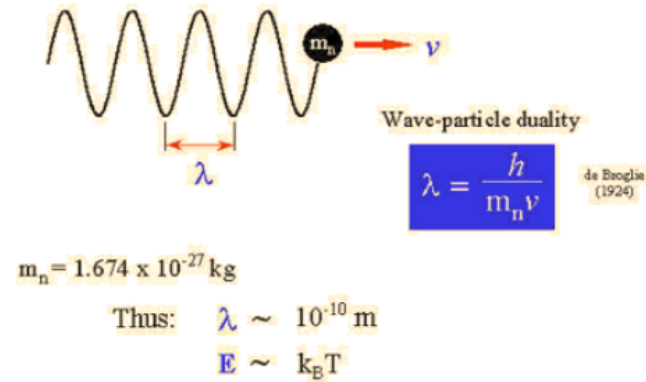
Let us consider a beam approaching a surface with a bulk potential V , infinitely deep



With no structure within the surface the only potential gradient and hence force is perpendicular to the surface.

Only the normal component of the incoming wave vector, k_i is altered by the barrier potential and it is the normal component of the kinetic energy $E_{i\perp}$ which determines whether the neutron is totally reflected from the barrier or not.

Neutrons can be treated as a wave:



Wave-particle duality

$$\lambda = \frac{h}{m_n v}$$

de Broglie (1924)

$m_n = 1.674 \times 10^{-27} \text{ kg}$

Thus: $\lambda \sim 10^{-10} \text{ m}$

$E \sim k_B T$

The Schroedinger equation is analogous to the wave equation for light and leads to neutrons showing characteristic optical behaviour such as total reflection and refraction.

The Schroedinger equation may be written as:

$$-\frac{\hbar^2}{8\pi^2 m_n} \nabla^2 \Psi + V\Psi = E\Psi$$

Where V is the potential to which the neutron is subject and E its energy

Refractive Index for Neutrons

Fermi pseudopotential

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

Sometimes it is denoted by N_b

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 $E = \frac{\hbar^2 k_0^2}{2m}$

Here, k_0 is the incident, k is the wave vector of the refracted beam

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

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

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

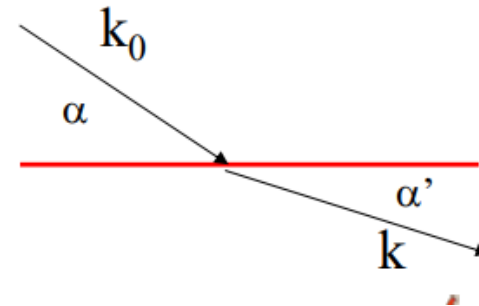
The critical value of k_{0z} for total external reflection is $k_{0z} = \sqrt{4\pi\rho}$

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

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

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

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



Values of Refractive Index

$$n = 1 - \delta - i\beta$$

X-RAYS

$$\delta = \frac{\lambda^2}{2\pi} r_e \rho$$

NEUTRONS

$$\delta = \frac{\lambda^2}{2\pi} N_b$$

- Small difference in refractive index mean that critical angles are small (less than 1 degree)
- As most $n < 1$, total external reflection is common. In optics $n > 1$
- Mixtures of isotopes can be used to match values of different materials
- β absorption coefficient small with neutrons

Quantum mechanical approach

The wavefunction describing the probability amplitude of a neutron near to the surface is:

$$\frac{\partial^2 \Psi_z}{\partial z^2} + k_{\perp}^2 = 0 \quad \text{where} \quad k_{\perp}^2 = \frac{2m_n}{\hbar^2} (E_i - V) - k_{\parallel}^2$$

Solutions for this above and below the surface are:

$$\Psi_z = e^{ik_{i\perp} z} + re^{-ik_{i\perp} z} \quad \& \quad \Psi_z = te^{ik_{t\perp} z}$$

where r and t are the probability amplitudes for reflection and transmission.

Continuity of the wavefunction and its derivative gives the expressions:

$$1 + r = t \qquad k_{i\perp} (1 - r) = t k_{t\perp}$$

where the second relation only holds for $E_{i\perp} > V$;

this leads directly to the classical **Fresnel coefficients** found in optics:

$$r = \frac{k_{i\perp} - k_{t\perp}}{k_{i\perp} + k_{t\perp}} \qquad \& \qquad t = \frac{2k_{i\perp}}{k_{i\perp} + k_{t\perp}}$$

Reflectivity is measured as a function of wavevector transfer or q

Note that what is measured is an intensity and thus is a function of the quantum mechanical probability amplitude squared.

$$R = r^2 = \left[\frac{q - (q^2 - q_c^2)^{1/2}}{q + (q^2 - q_c^2)^{1/2}} \right]^2$$

Fresnel reflectivity

$$q = \frac{4\pi}{\lambda} \sin \theta$$

Born Approximation

$$q \gg q_c$$

Ignored double scattering processes because these are usually very weak

$$q_c = \sqrt{16\pi N_b}$$

$$R(q) = \frac{16\pi^2}{q^4} |N'_b(q)|^2$$

$$N'_b(q) = \int_{-\infty}^{+\infty} \exp(iqz) \frac{dN_b}{dz} dz$$

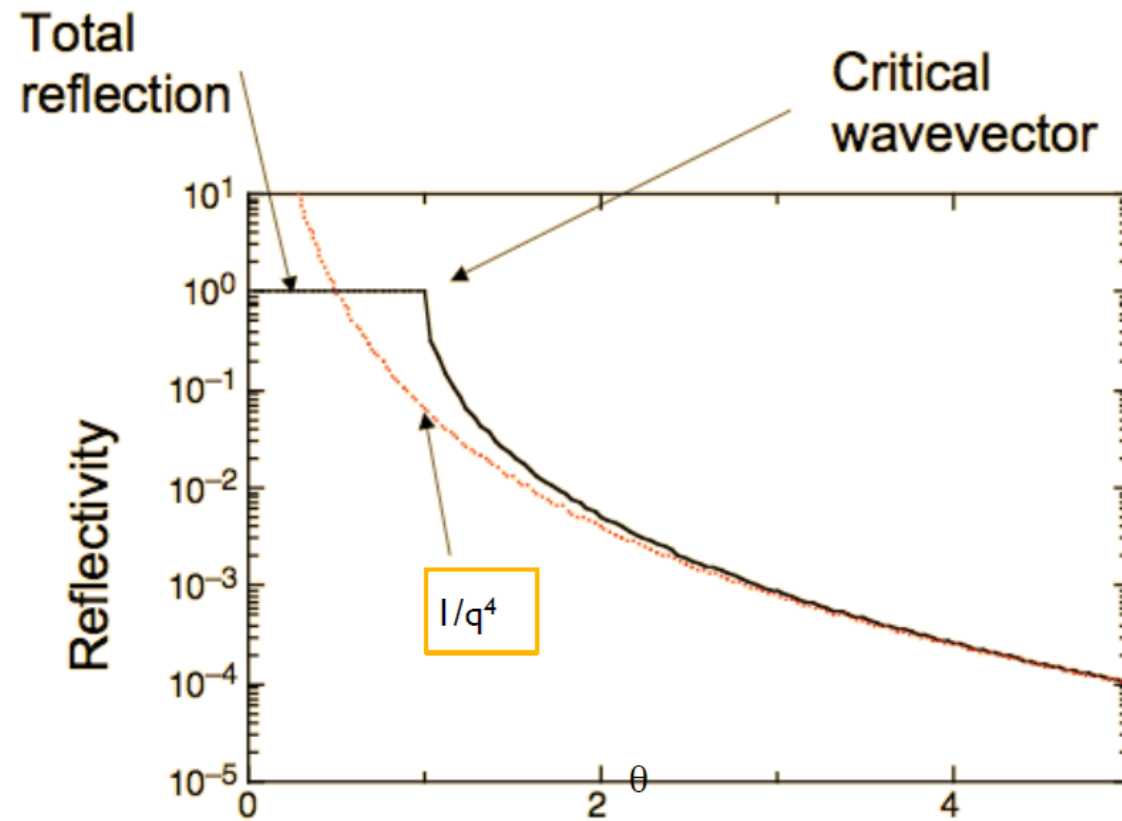
Scattering length density

$$N_b = \frac{\sum n_i b_i}{V}$$

$$R = 1 \text{ below } q_{\text{crit}}$$

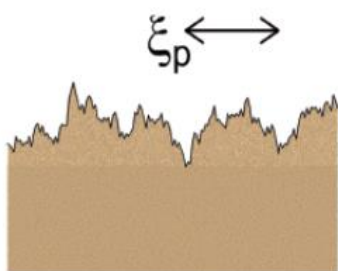
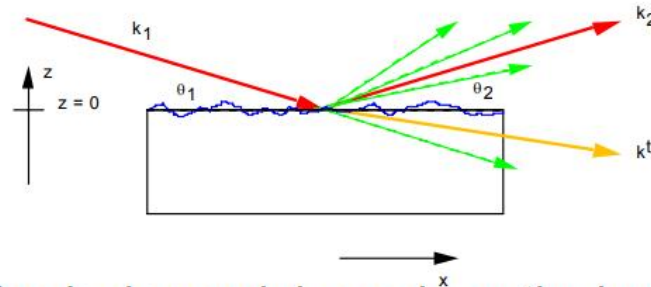
$$\theta_c = \arccos(n_1/n_2)$$

Fresnel law

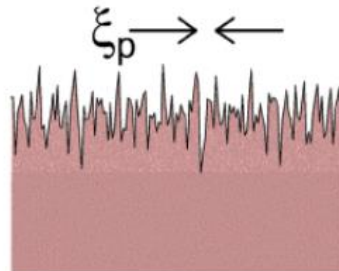


Surface Roughness

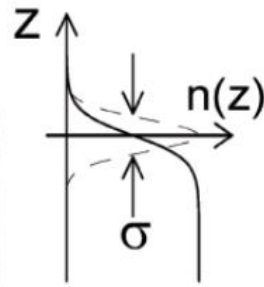
- Surface roughness causes diffuse (non-specular) scattering and so reduces the magnitude of the specular reflectivity
- The way in which the specular reflection is damped depends on the length scale of the roughness in the surface as well as on the magnitude and distribution of roughness



"sparkling sea" model
-- specular from many facets

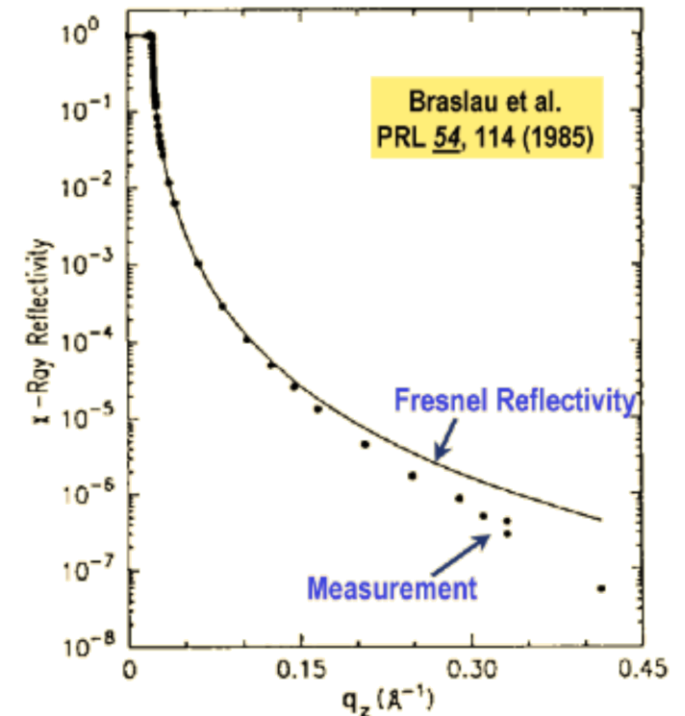


each piece of surface scatters independently
-- Nevot-Croce model

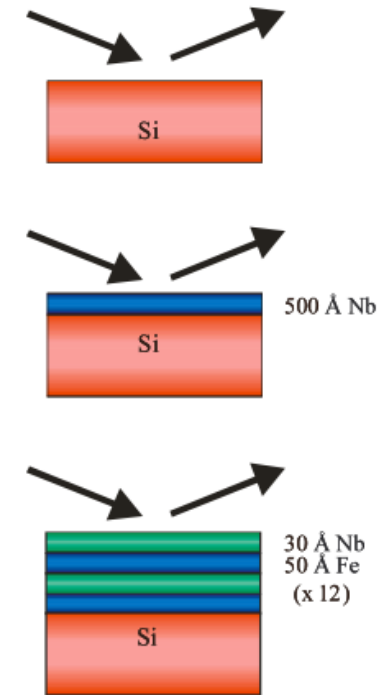
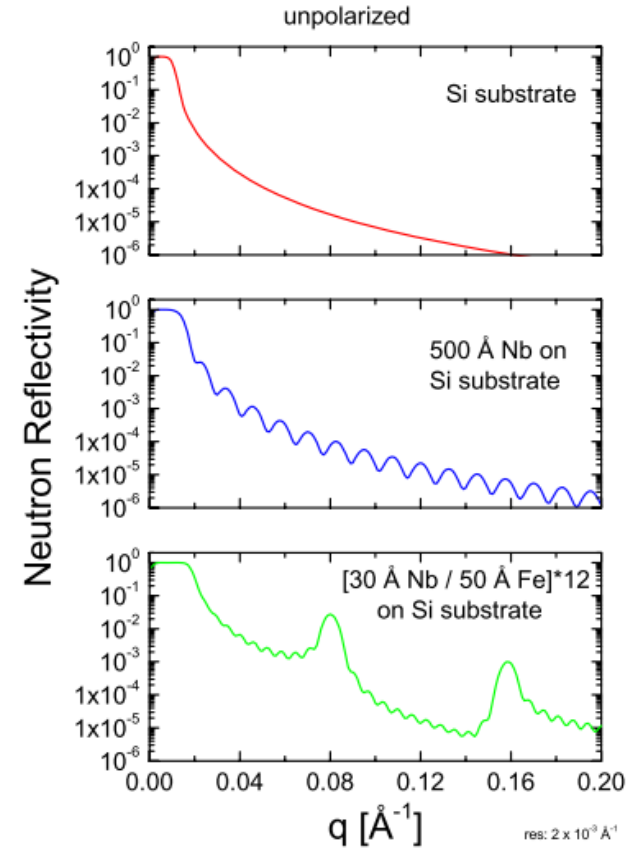
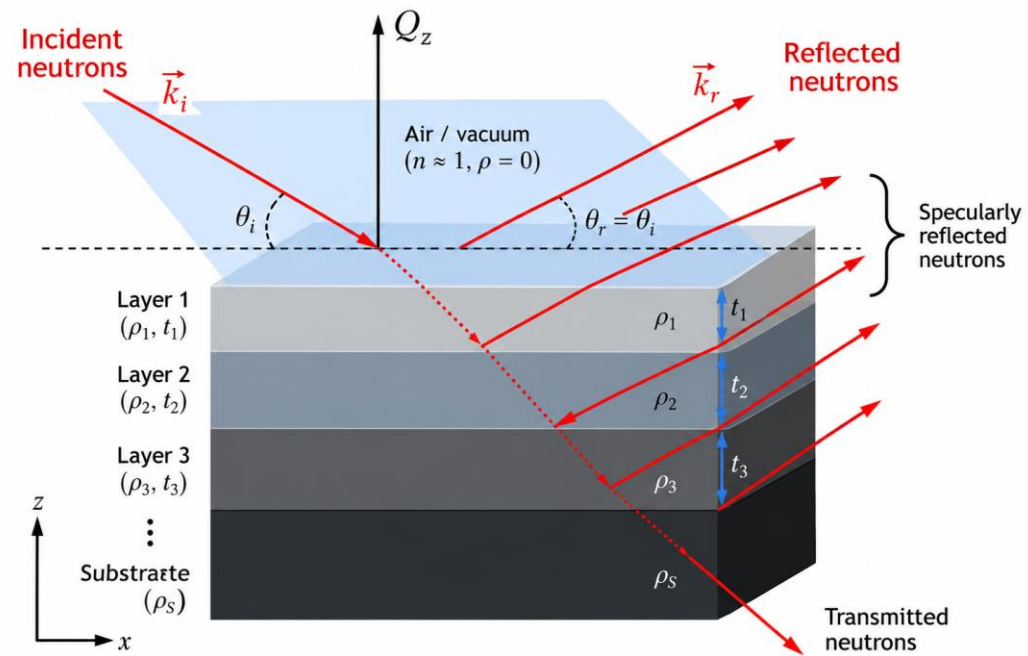


Note that roughness introduces a SLD profile averaged over the sample surface

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



Reflectivity from m layers



Multiple Layers – Parratt Iteration (1954)

- Matching wavefunctions and derivatives at interfaces can be used to obtain an expression for the reflectivity of multiple layers

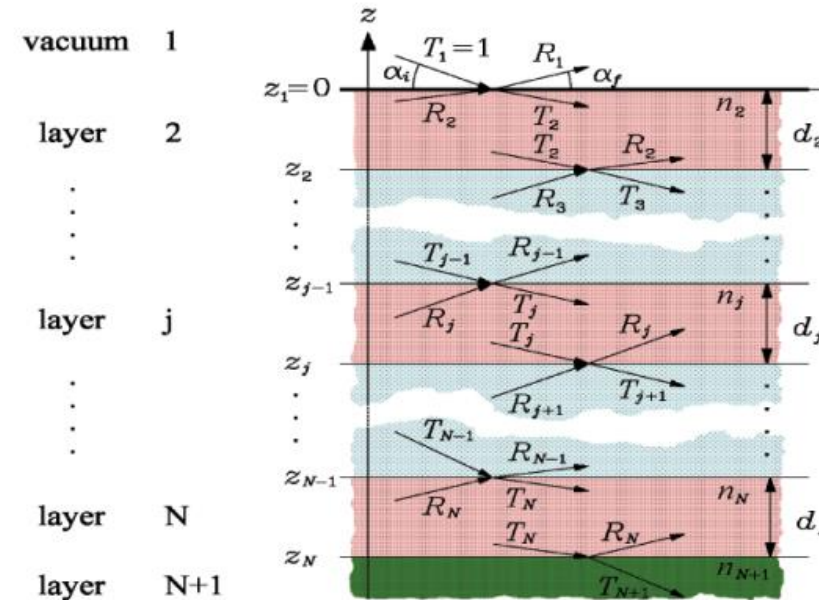
$$X_j = \frac{R_j}{T_j} = e^{-2ik_{z,j}z_j} \frac{r_{j,j+1} + X_{j+1}e^{2ik_{z,j+1}z_j}}{1 + r_{j,j+1}X_{j+1}e^{2ik_{z,j+1}z_j}}$$

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

Start iteration with

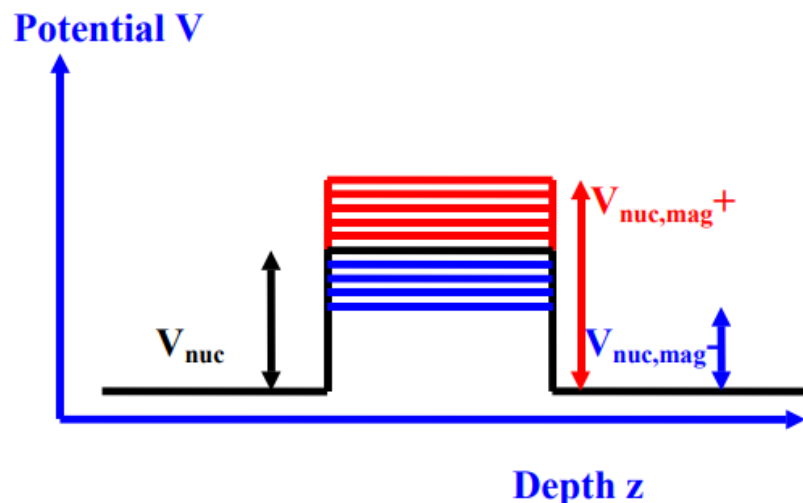
$$R_{N+1} = X_{N+1} = 0 \text{ and } T_1 = 1$$

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



Reflection of Polarized Neutrons

- Neutrons are also scattered by variations of B (magnetization)
- Only components of magnetization perpendicular to Q cause spin flip 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)



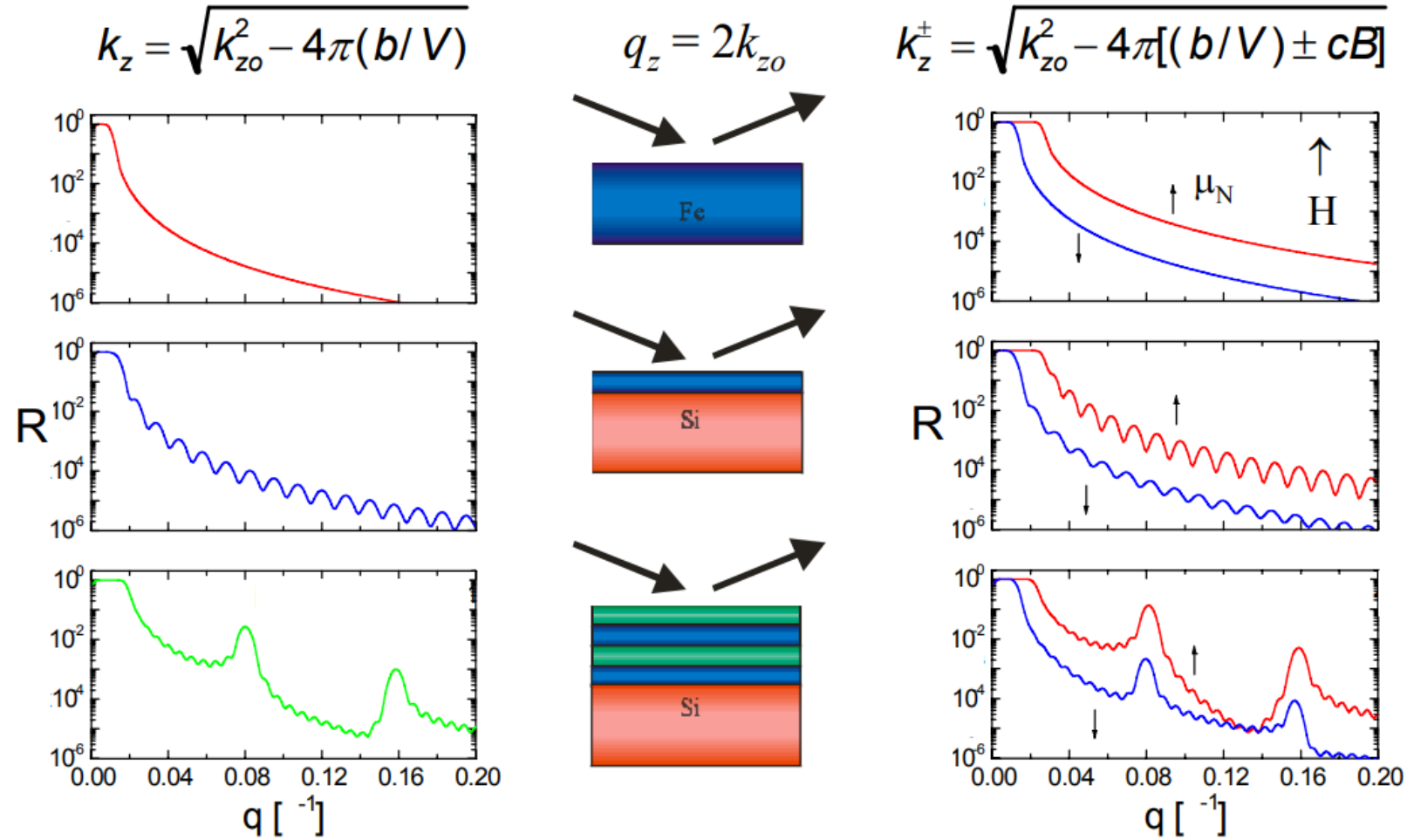
Fermi pseudo potential:

$$V = 2\pi \hbar^2 N (\mathbf{b}_n +/\mathbf{b}_{\text{mag}})/m_N$$

with $\mathbf{b}_{\text{nuc}}$: nuclear scattering length [fm]
 $\mathbf{b}_{\text{mag}}$: magnetic scattering length [fm]
($1 \mu_B/\text{Atom} \Rightarrow 2.695 \text{ fm}$)
 N : number density [at/cm³]
 m_N : neutron mass

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

Typical Non-Spin-Flip Reflectivities



Used materials:

- T.E. Mason
 - Experimental Facilities Division
 - Spallation Neutron Source
- Kent Crawford & Ron Cooper
- Ettore Fiorini
 - Laureato presso l' Università di Milano
- Giovanna Fragneto
 - Institut Laue-Langevin
- Roger Pynn
 - Indiana University and the Spallation Neutron Source

Thank you for your attention!

Neutrons reveal the structure and magnetism
beneath the surface

