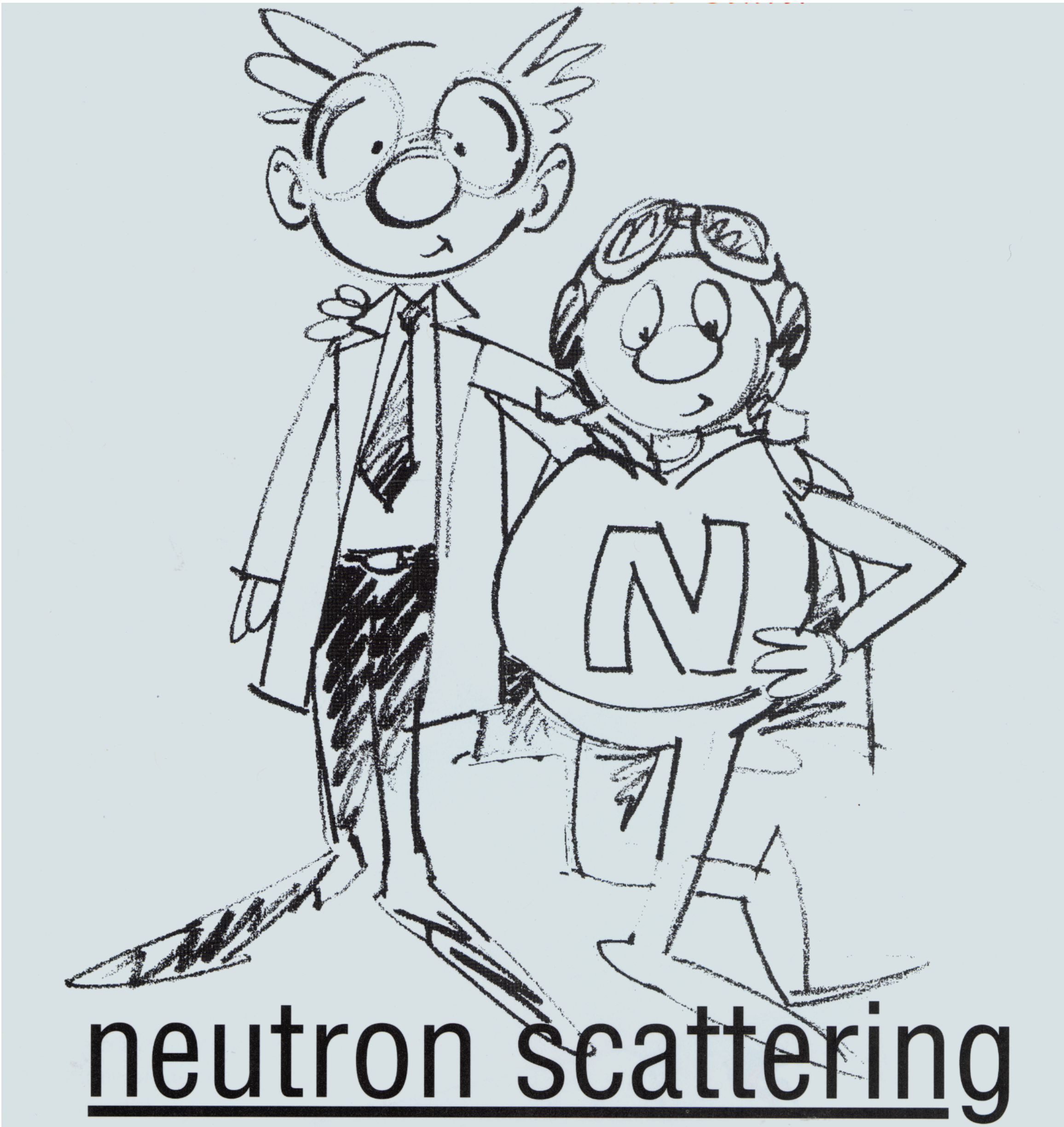

Surface Reflection

by

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This Lecture

- Reflection from layered films – the Parratt method
- The kinematic approximation
- Reflection from a graded interface
- Comparision of x-ray and neutron reflection
- The perils of fitting SLD profiles
- Exact determination of SLD profiles
- Polarized neutron reflectometry
- Science examples
  - Lipids at the liquid air interface
  - Shear alignment of worm-like micelles
- Rough surfaces and correlated roughness
- Grazing incidence diffraction

Multiple Layers – Parratt Iteration (1954)

- The 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

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

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

Then $\mathrm{R}(\alpha_\mathrm{i}) = |X_1|^2$

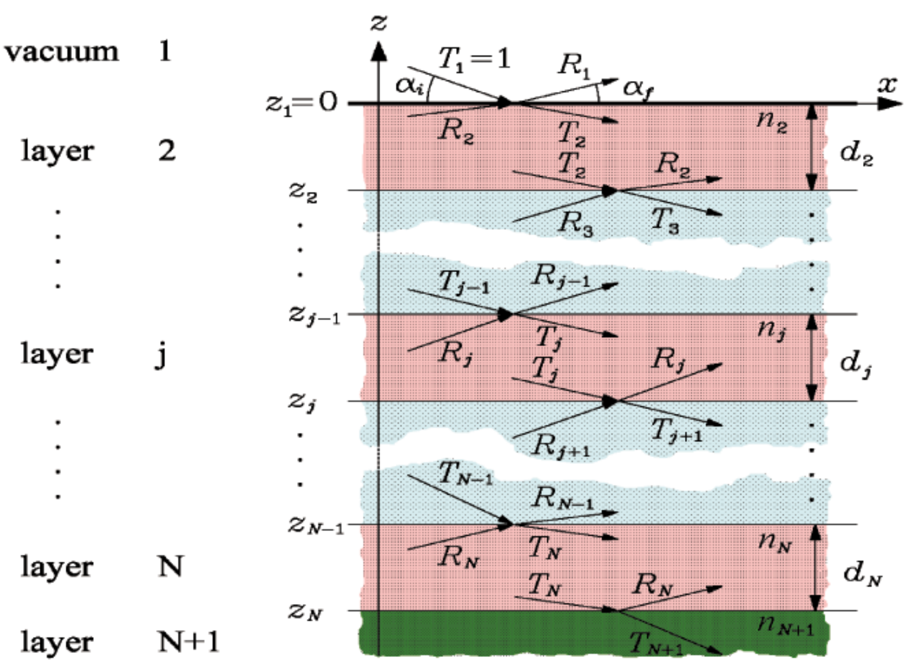


Image from M. Tolan

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!!

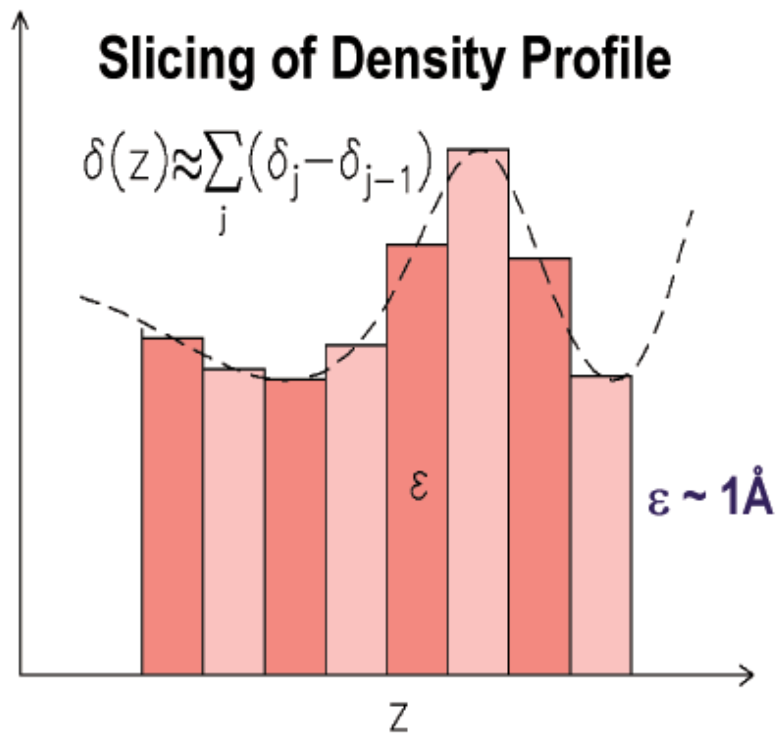


Image from M. Tolan

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:

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

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

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:

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

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

Reflection by a Graded Interface

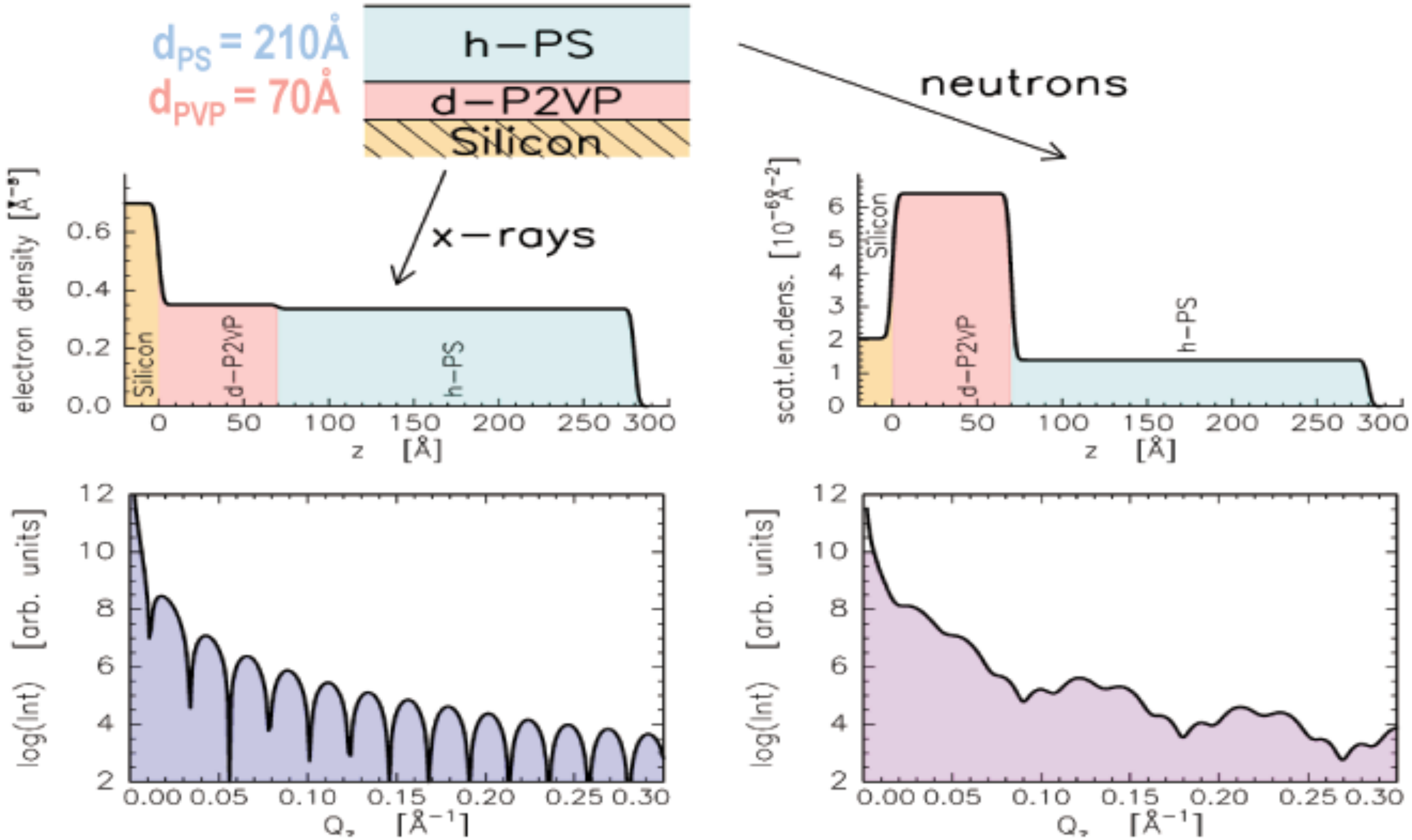
Repeating the bottom line of the previous viewgraph but keeping the z - dependence of ρ gives: $R = \frac{16\pi^2}{Q_z^2}\left|\int \rho(z) e^{iQ_z z} dz\right|^2 = \frac{16\pi^2}{Q_z^4}\left|\int \frac{d\rho(z)}{dz} e^{iQ_z z} dz\right|^2$ where the second equality follows after intergrating by parts.

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

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

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

Viewgraph courtesy of M. Tolan

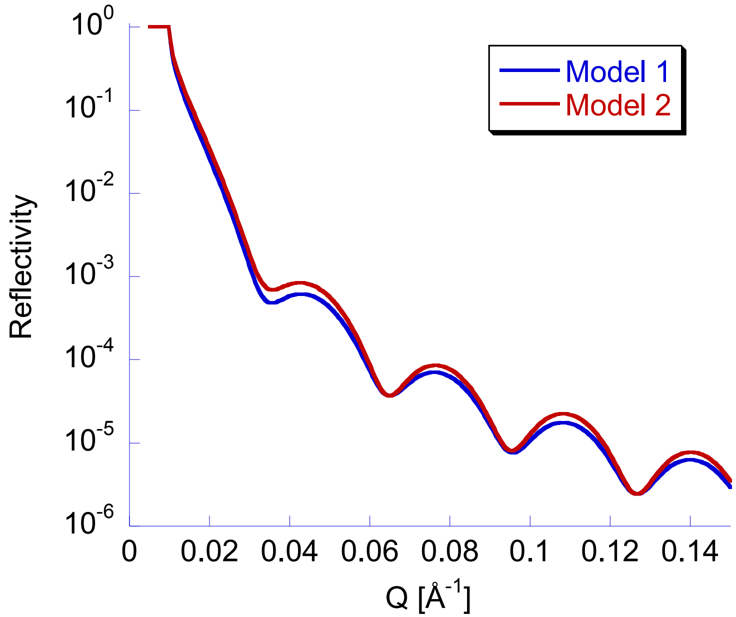
Analyzing Reflectivity Data

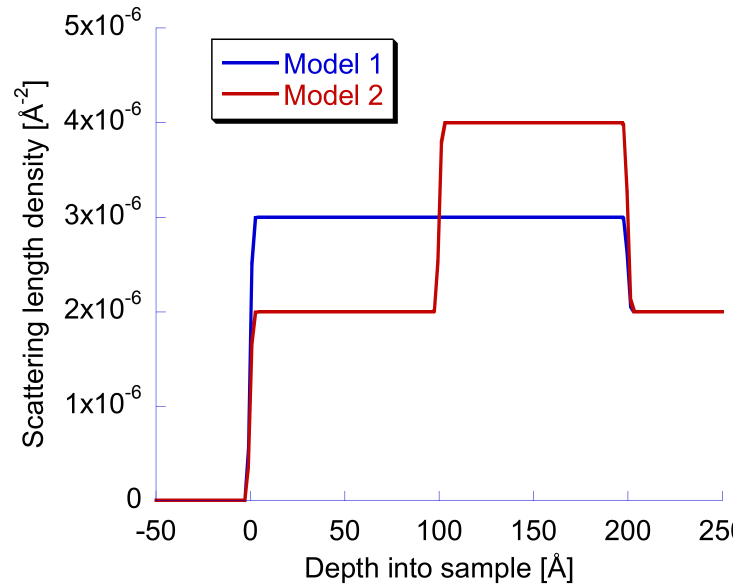
- We want to find $\rho(z)$ given a measurement of $R(Q_z)$
- This inverse problem is not generally solvable
- Two methods are used:

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





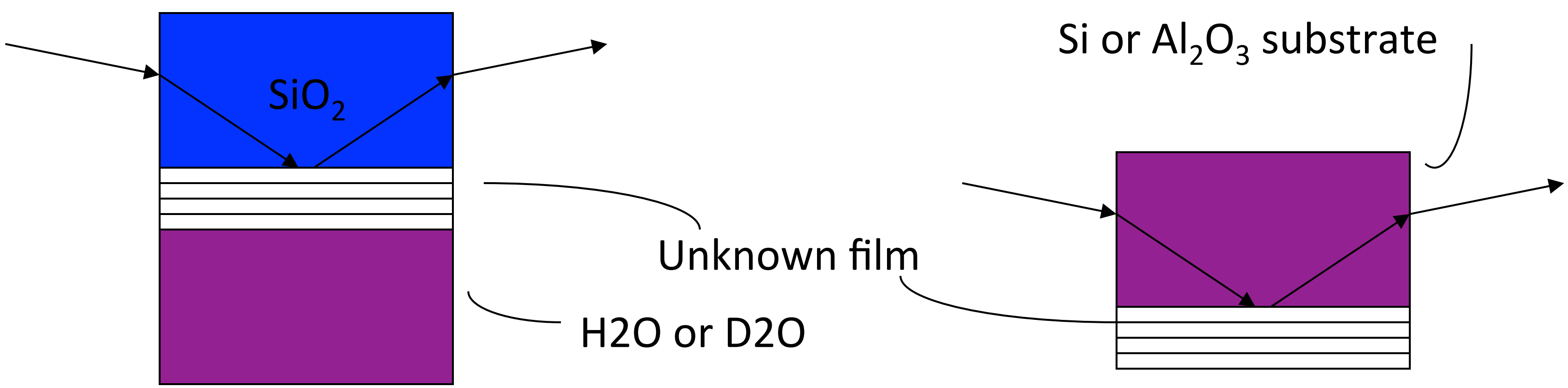
Lack of information about the phase of the reflected wave means that profoundly different scattering length density profiles can produce strikingly similar reflectivities.

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. 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)

Magnetic Properties of the Neutron

- The neutron has a magnetic moment of -9.649 x 10^{-27} JT^{-1}

  $$\vec{\mu}_n = -\gamma \mu_N \vec{\sigma}$$

  where $\mu_N = e\hbar / 2m_p$ is the nuclear magneton,

  $m_p =$ proton mass, $e =$ proton charge and $\gamma = 1.913$

  $\vec{\sigma}$ is the Pauli spin operator for the neutron. Its eignevalues are ± 1

- Note that the neutron's spin and magnetic moment are antiparallel
- Because of its magnetic moment, the neutron feels a potential given by:

$$V_m(\vec{r}) = -\vec{\mu}_n . \vec{B}(\vec{r}) \quad \text{where } \vec{B}(\vec{r}) = \mu_0 \mu \vec{H}(\vec{r}) = \mu_0 [\vec{H}(\vec{r}) + \vec{M}(\vec{r})]$$

- Thus the neutron senses the distribution of magnetization in a material

Magnetic Scattering of the Neutron

- For nuclear scattering, the matrix element that appears in the expression for the scattering cross section is: $\sum_j b_j e^{i\vec{Q}.\vec{R}_j}$

- The equivalent matrix element for magnetic scattering is:

$$\gamma r_0 \frac{1}{2\mu_B} \vec{\sigma}.\vec{M}_\perp(\vec{Q}) \quad \text{where } \mu_B = \frac{e\hbar}{2m_e} \text{ is the Bohr magneton } (9.27 \text{ x } 10^{-24} \text{ JT}^{-1})$$

$$\text{and } r_0 = \frac{\mu_0}{4\pi} \frac{e^2}{m_e} \text{ is classical radius of the electron } (2.818 \text{ x } 10^{-6} \text{ nm})$$

- Here $\vec{M}_\perp(\vec{Q})$ is the component of the Fourier transform of the magnetization that is perpendicular to the scattering vector $\vec{Q}$. This form arises directly from the dipolar nature of the magnetic interaction.

- Unlike the neutron-nucleus interaction, the magnetic interaction of the neutron with a scattering system specifically depends on neutron spin

A “first” PNR experiment

D.J. Hughes and M.T. Burgy, Phys. Rev., 81, 498 (1951).

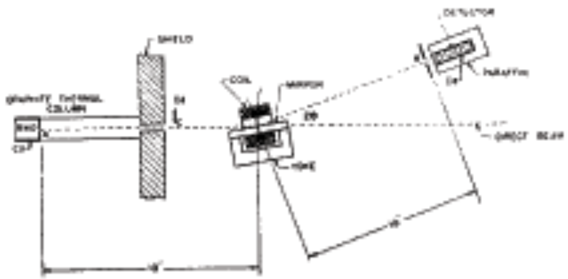


Fig. 1. Plan view of apparatus for reflection of neutrons from magnetized mirrors.

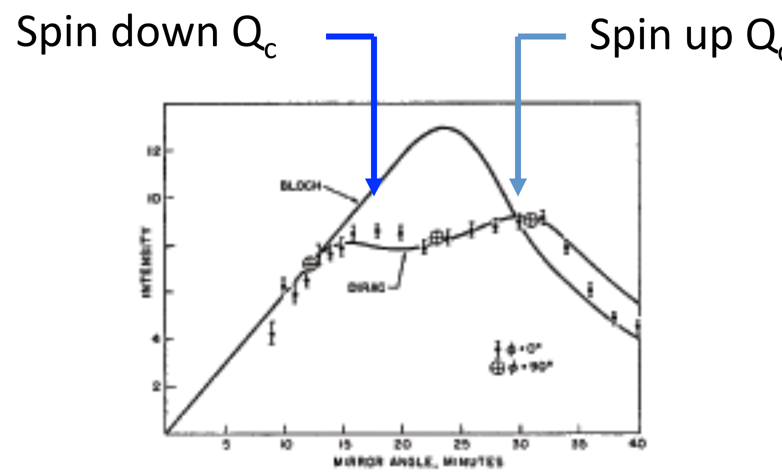


Fig. 4. Intensity of filtered neutrons reflected from a magnetized iron mirror. The theoretical curve labeled “Bloch” corresponds to Bloch's constant, C equal to zero, while “Dirac” corresponds to $C=1$. Experimental points for two directions of magnetization, $\phi=0°$ and 90°, are shown.

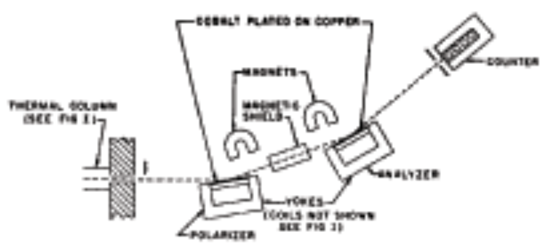


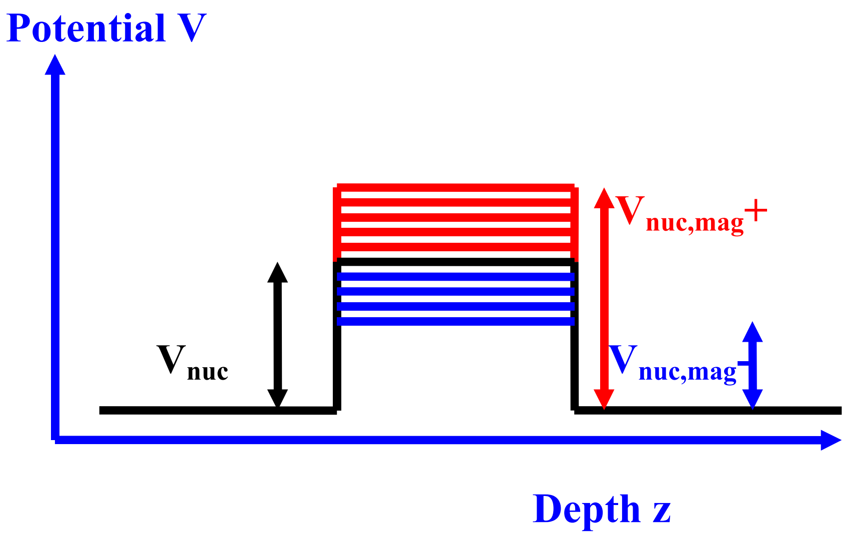
Fig. 8. Apparatus for the production of complete neutron polarization, and for measurement of polarization by the double reflection effect.

*Results supported Schwinger’s model of neutron moments as current loops and the predicted dependence on **B** not **H** (in contrast to Bloch’s model).*

Viewgraph courtesy of M. R. Fitzsimmons

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:

$$V = 2\pi \hbar^2 N (b_n +/- b_{mag})/m_N$$

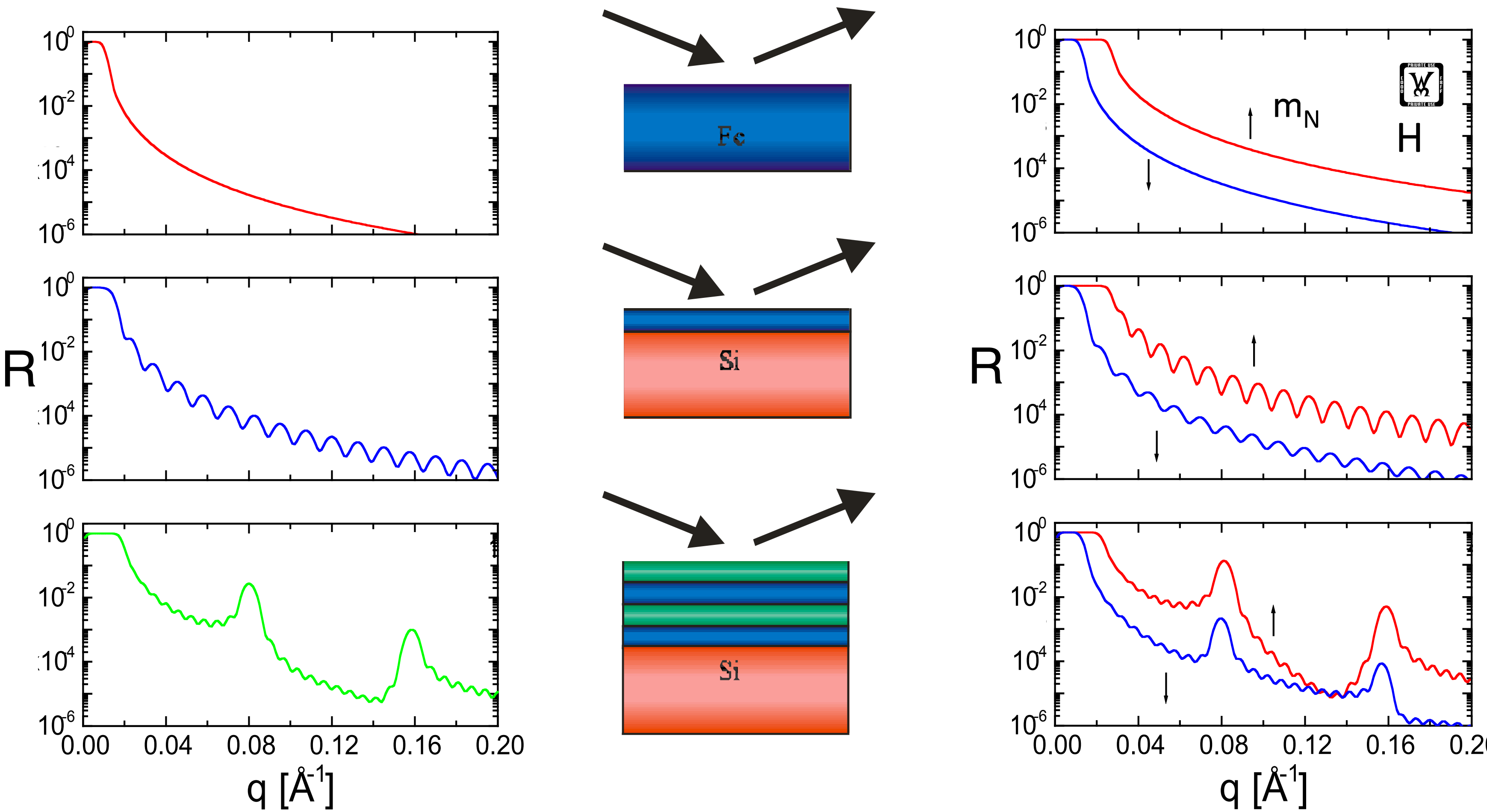
with	b_{nuc}:	**nuclear scattering length [fm]**
	b_{mag}:	**magnetic scattering length [fm]**
		(1 μ_B/Atom => 2.695 fm)
	N:	**number density [at/cm^3]**
	m_N:	**neutron mass**

Spin"up" neutrons see a high potential.
Spin"down" neutrons see a low potential.

Viewgraph courtesy of M. R. Fitzsimmons

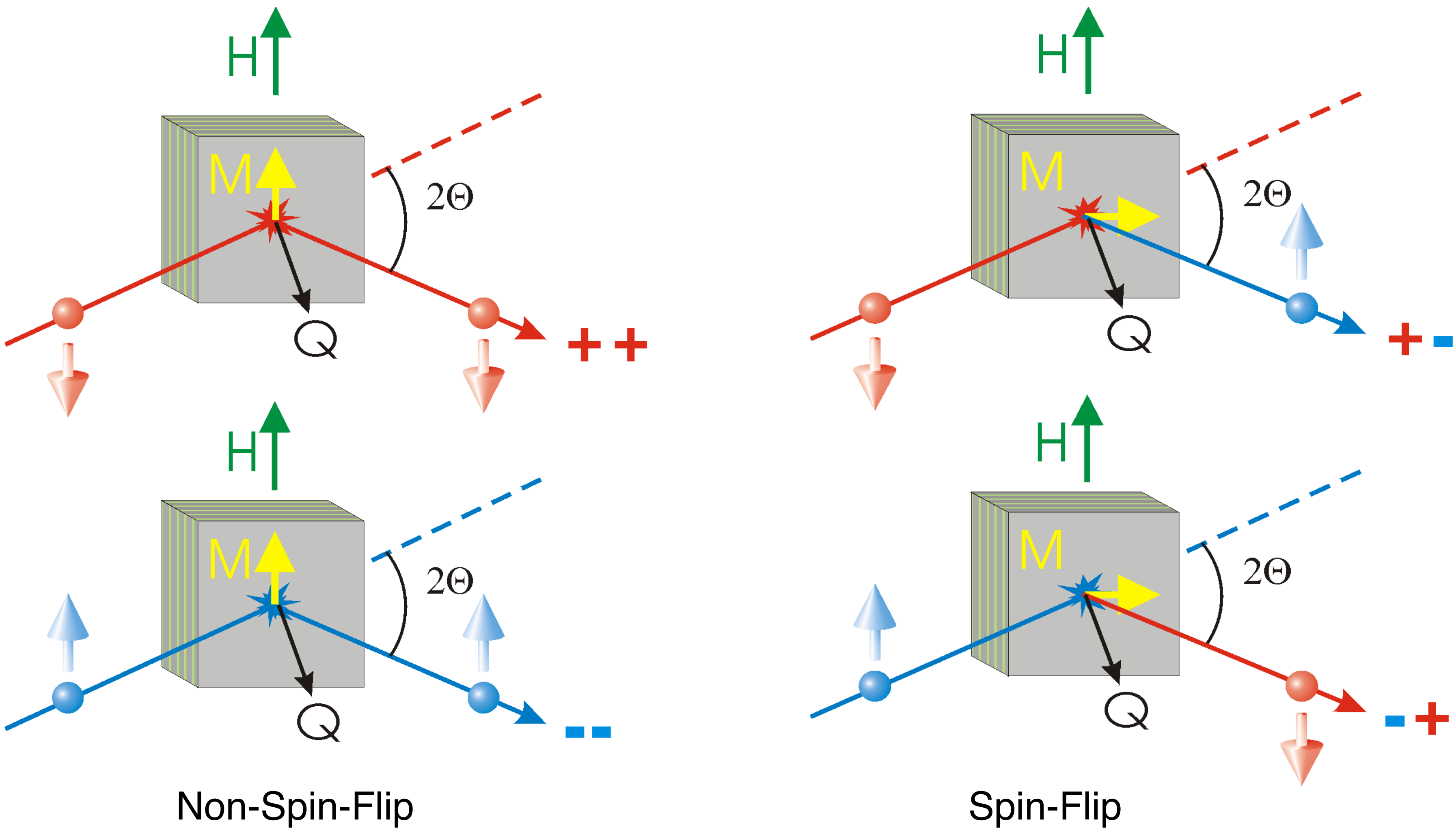
Typical Non-Spin-Flip Reflectivities

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



Courtesy of F. Klose

Polarized Neutron Reflection
Note: Arrows Represent Neutron Moments not Spins



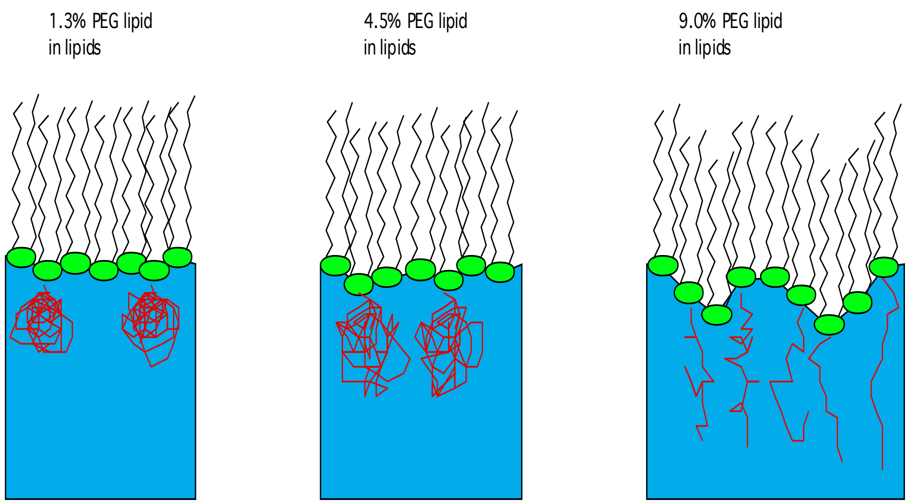
++ measures b + M_z
-- measures b - M_z

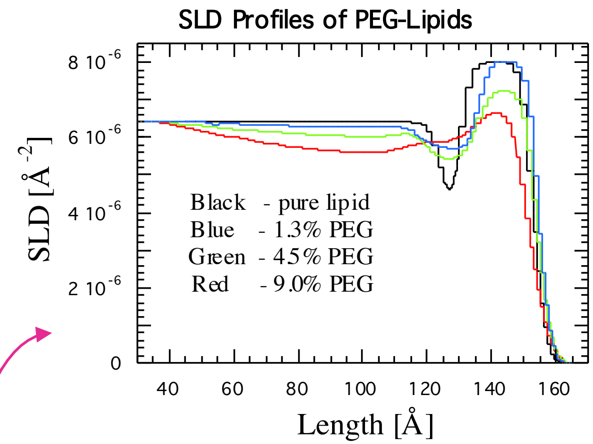
+- measures $M_x + i\, M_y$
-+ measures $M_x - i\, M_y$

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 (~10 cm^2) with good scattering contrast are needed

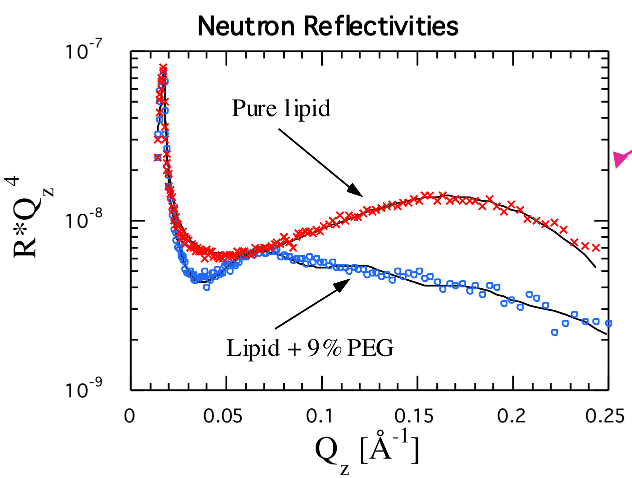
Polymer-Decorated Lipids at a Liquid-Air Interface*





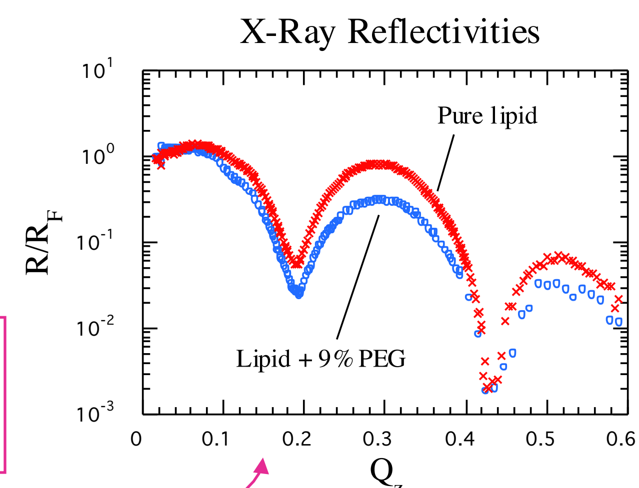
mushroom-to-brush transition

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



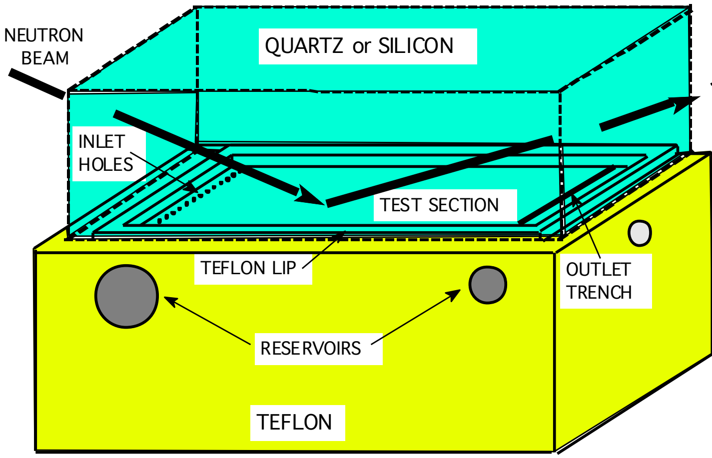
neutrons see contrast between heads (2.6), tails (-0.4), D_2O (6.4) & PEG (0.24)

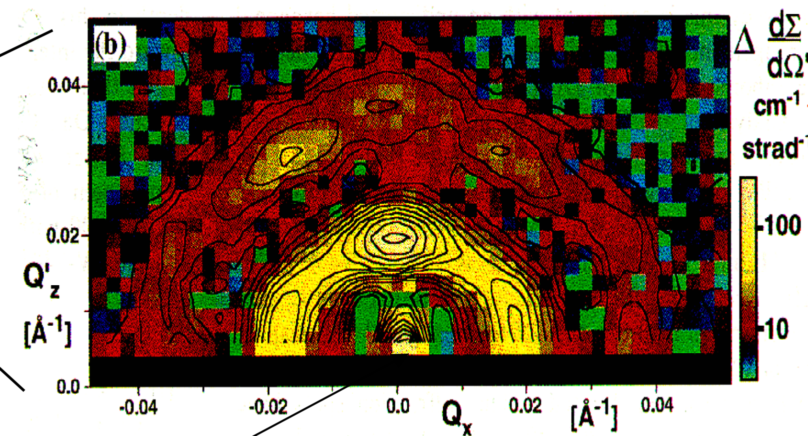
x-rays see heads (0.65), but all else has same electron density within 10% (-0.33)



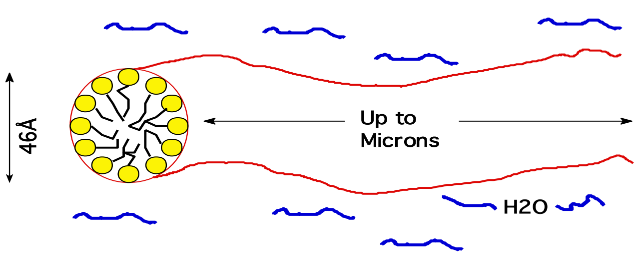
*Data courtesy of G. Smith (LANSCE)

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

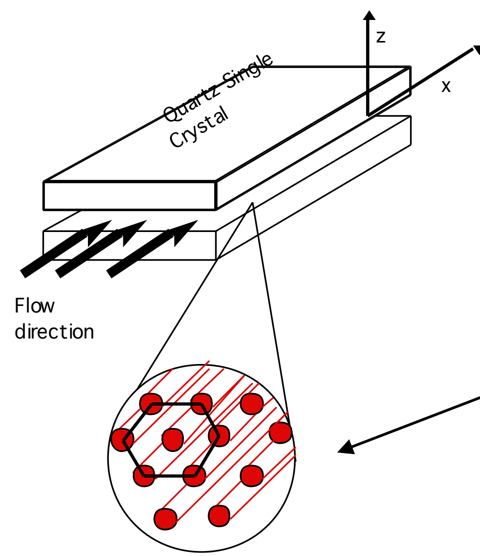




Specularly reflected beam



Thread-like micelle

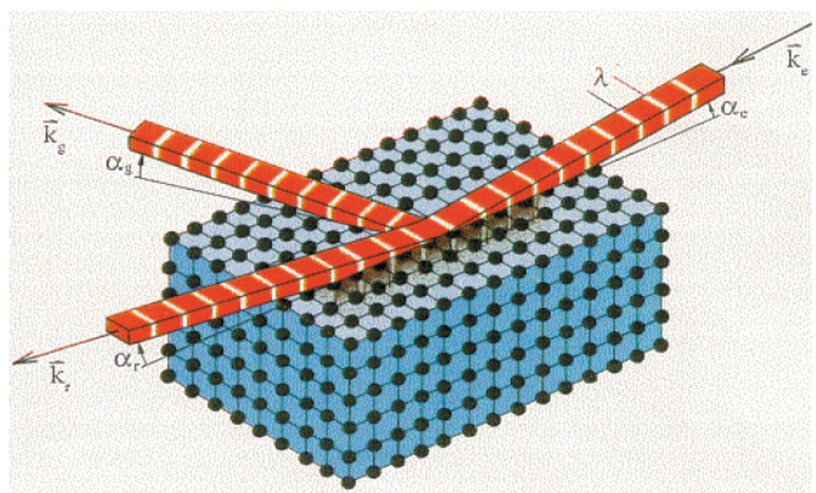


Scattering pattern implies hexagonal symmetry

W. A. Hamilton, P. D. Butler, S. M. Baker, G. S. Smith, John B. Hayter, L. J. Magid, and R. Pynn; Phys. Rev. Lett., 72, 2219 (1994)

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



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