UT-BATTELLE

An Introduction to Neutron Reflectivity

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HFIR

SNS
SPALLATION NEUTRON SOURCE

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U. S. DEPARTMENT OF ENERGY

Section I: Neutron Scattering and Neutron Reflectometry Theory

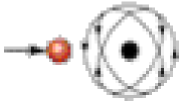
Why Use Elastically Scattered Neutrons to Probe Thin Films?

Neutron WAVELENGTH ~ atomic/molecular dimensions:

- interference
- reflection
- refraction

Neutrons are NEUTRAL particles:

- highly penetrating
- nondestructive probe
- sample environments

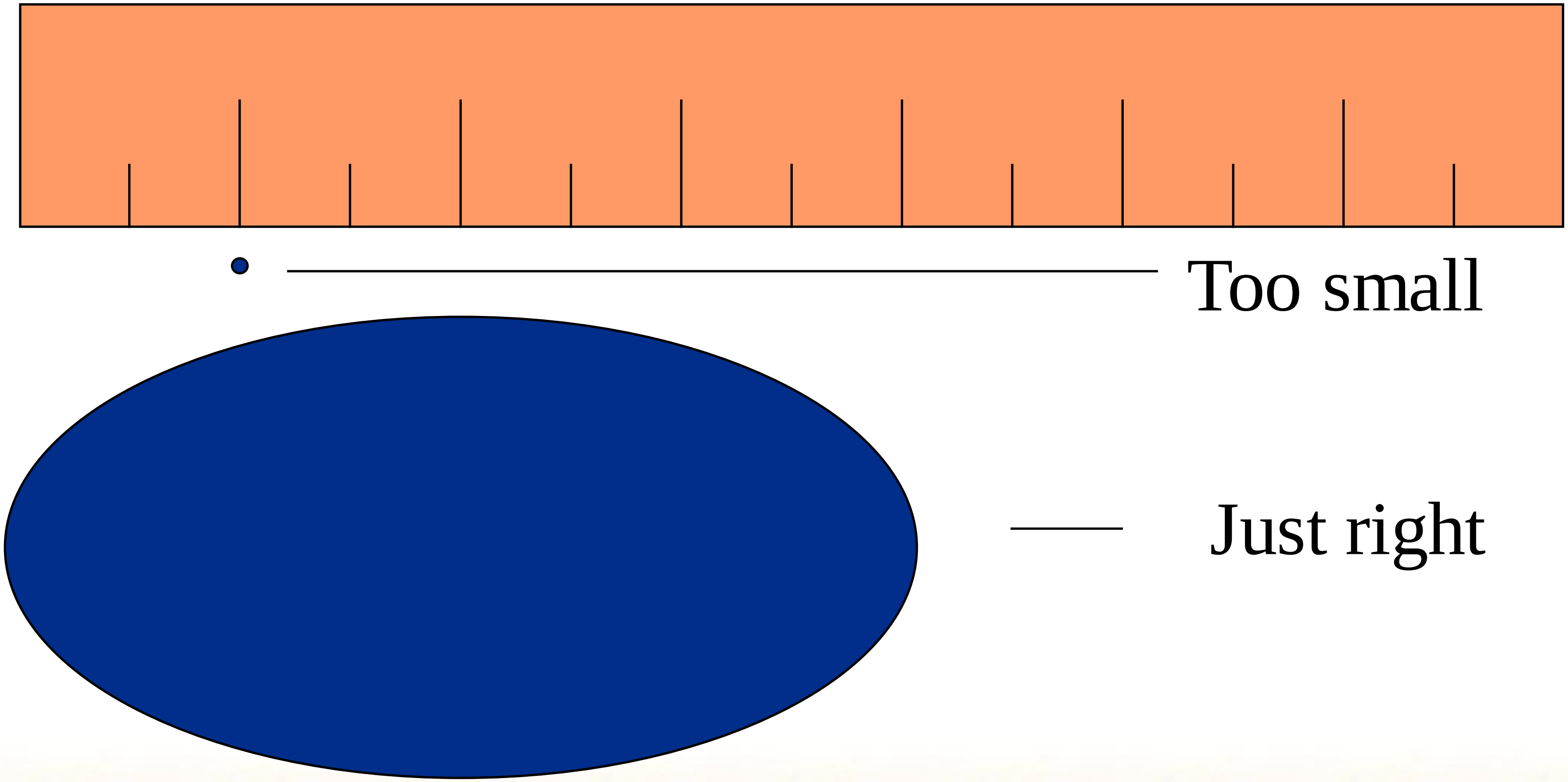


Neutrons interact with atomic NUCLEI:

- sensitive to light atoms
- can exploit isotopic substitution
- contrast matching

To Measure a Length:

Find the Proper Ruler



Too small

Just right

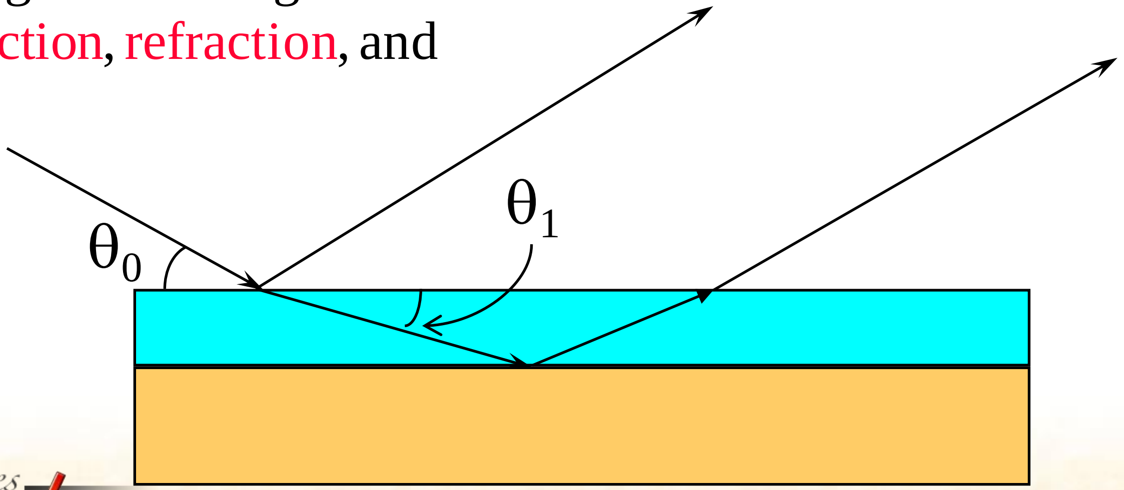
The Wave Nature of the neutron

- Neutrons can be treated as a plane waves with wavevectors **k**, where $|\mathbf{k}|=2\pi/\lambda$ and λ is the neutron wavelength.
- Momentum = $m_n\mathbf{v}=\hbar\mathbf{k}$
- Energy= $\hbar^2k^2/2m_n$
- Because of their wave nature, much of the effects seen in light scattering are also seen in neutron-reflection, refraction, and interference.

Schrödinger Equation:

$$-\frac{\hbar^2}{2m_n}\nabla^2\psi+\cancelto{0}{V}\psi=E\psi$$

$$\psi=e^{i\vec{k}\cdot\vec{r}}$$



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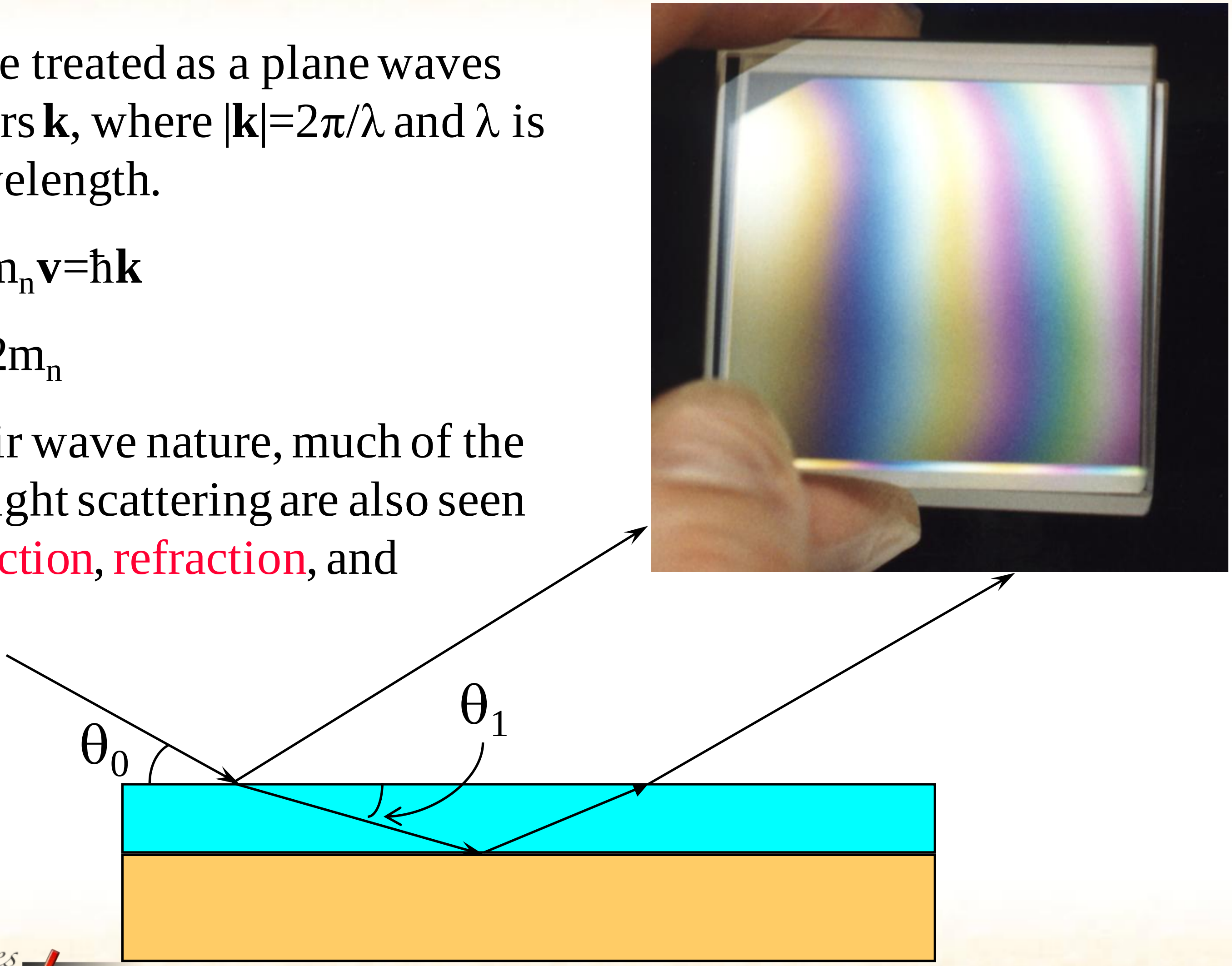
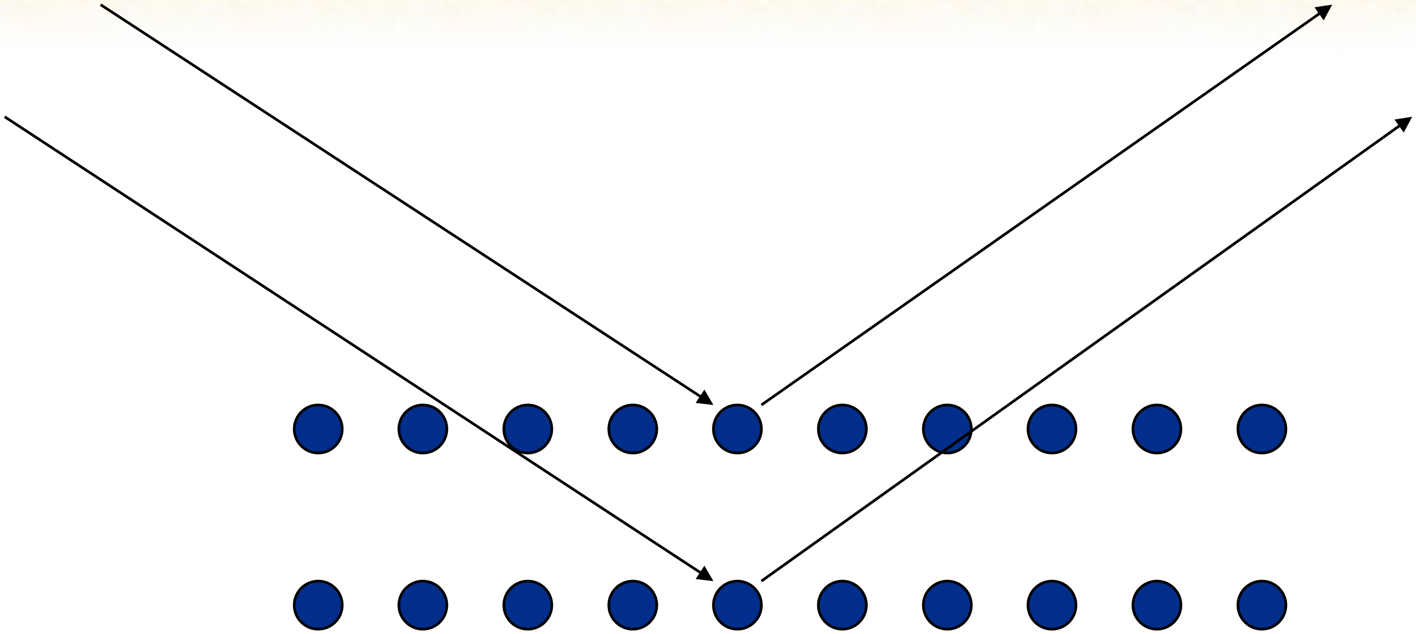
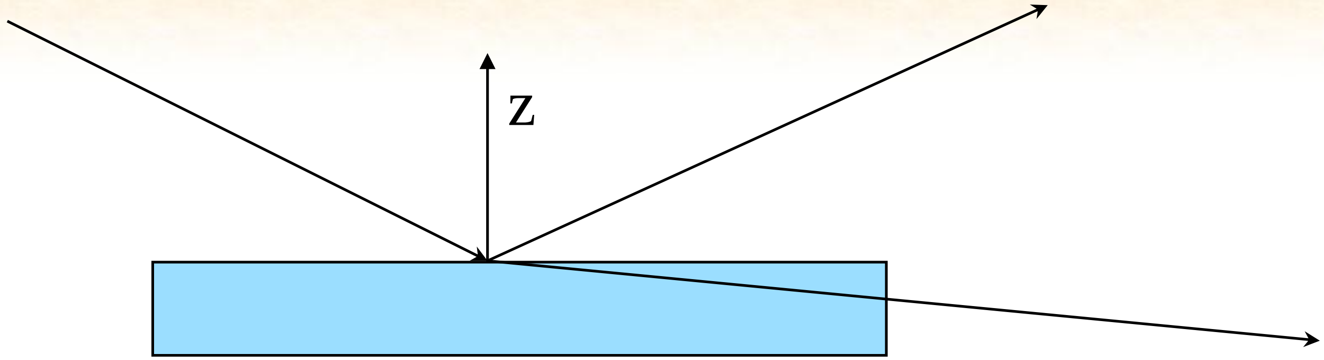


Low angles / long wavelengths



- Don’t satisfy Bragg law [$n\lambda=2d \sin(\theta)$]
- Still have coherent scattering
- Can average over the coherent scattering

Neutron Interaction



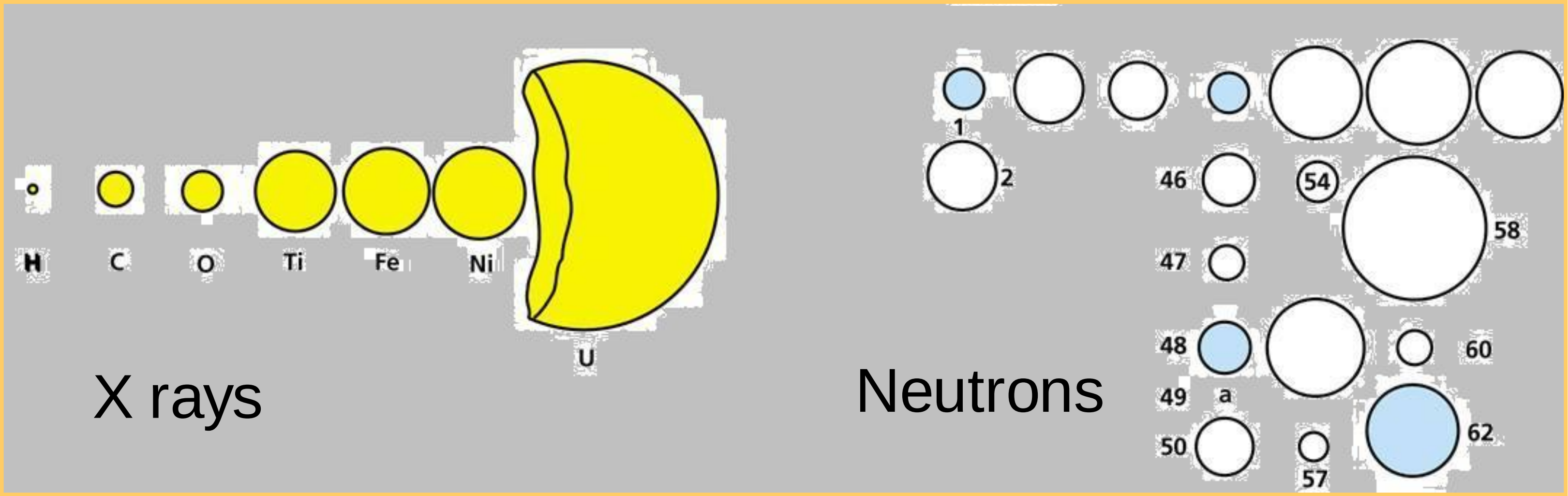
- The potential seen by the neutron is the Fermi pseudopotential; $V_F = \hbar^2 k_F^2 / 2m_n$
- $k_F^2 = 4\pi\beta$, where the *scattering length density,* $\beta = \Sigma N_i b_i$, N_i=nuclear number density of atom i, b_i=the coherent scattering length of atom i
- Since the potential only changes in z, this reduces to a 1-dimensional problem

Neutrons Scatter from Nuclei

X rays see electrons
Neutrons see nuclei

=>

Isotopic substitution



H C O Ti Fe Ni U

Radii of balls = *b* = scattering amplitude

Example 1: Calculating the scattering length density of quartz

$$\beta = \sum_i N_i b_i$$

Quartz is SiO_2. The density is $\rho_{SiO2}=2.66\ gm/cm^3$. The molecular weight is $(MW)_{SiO2}=60.08gm/mole$. The number of molecules (or nuclei) per unit volume is:

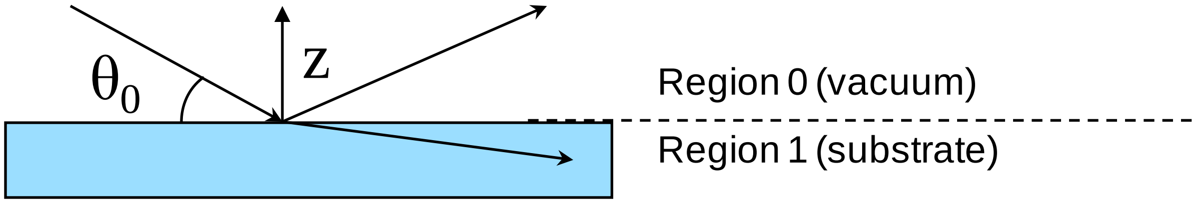
$N=\rho_{SiO2}/(MW)_{SiO2}\ A_{avagadro}\ 10^{-24}cm^3/Å^3= .0267$ molecules/ $Å^3$

$\beta=\Sigma N_i b_i= N\ (b_{Si}+2b_O)$

from the tables of coherent neutron scattering lengths of the elements: $b_{Si}=4.149 X 10^{-5}$ Å and $b_O=5.805 X 10^{-5}$ Å,

then $\beta_{Si}=4.21 X 10^{-6}\ Å^{-2}$.

Example 2:Scattering from a bare substrate and Fresnel's Law



Apply 1-d Schrödinger Equation:

$$-\frac{\hbar^2}{2m_n}\frac{\partial^2\psi(z)}{\partial z^2}+V(z)\psi(Z)=E\psi(z)$$

using the trial wave functions:

$$\psi(z)=e^{ik_0 z}+re^{-ik_0 z} \qquad z>0$$

$$\psi(z)=Ce^{ik_1 z} \qquad z<0$$

$$where,\ k_0=\frac{2\pi\sin(\theta_0)}{\lambda}$$

We find that since

$$k_F^2=4\pi\sum_i N_i b_i \qquad in\ \ the\ \ substrate$$

then

$$k_1^2=k_0^2-k_F^2$$

Example 2:Scattering from a bare substrate and Fresnel’s Law (cont.)

Match the wave-functions and their derivatives at the boundary (z=0):

$$1+r=C \qquad and \qquad ik_0(1-r)=ik_1(C)$$

Then, $$r=\frac{(k_0-k_1)}{(k_0+k_1)}$$

The current density is:

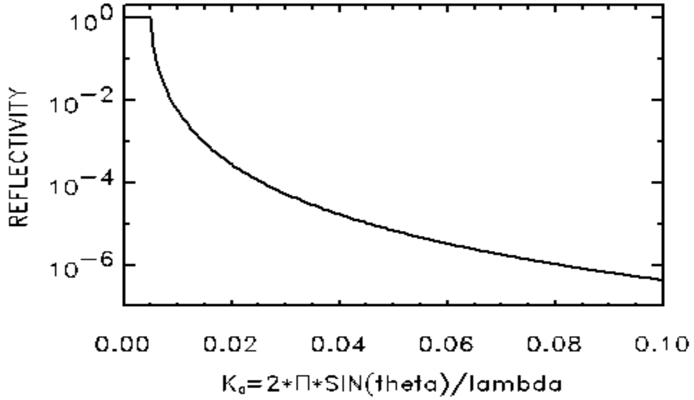
$$j=\frac{\hbar}{2m_n i}[\psi^*\nabla\psi-(\nabla\psi^*)\psi]$$

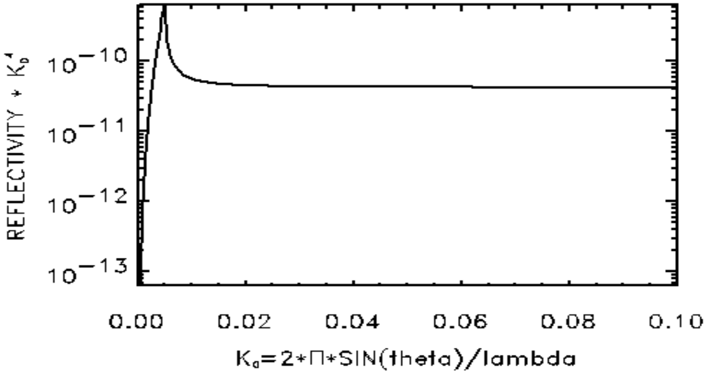
So,

$$R\equiv\frac{j_{outgoing}}{j_{incoming}}=\frac{|r|^2\hbar k_0/m_n}{\hbar k_0/m_n}=|r|^2=\left|\frac{k_0-k_1}{k_0+k_1}\right|^2$$

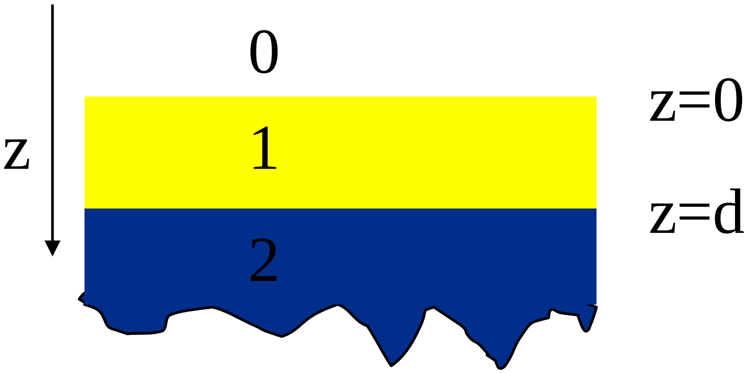
k_{crit} when $k_0=k_F=(4\pi\beta)^{1/2}$

$$R_{Fresnel}\approx(k_F/k_0)^4$$





Example 3: Reflection from a single layer on a substrate



$$\psi_0 = e^{ik_0 z} + re^{-ik_0 z}$$

$$\psi_1 = Ae^{ik_1 z} + Be^{-ik_1 z}$$

$$\psi_2 = te^{ik_2 z}$$

$$@ z = 0 \qquad (1+r) = A + B \quad \text{and} \quad (1-r)\frac{k_0}{k_1} = (A - B)$$

$$@ z = d \qquad te^{ik_2 d} = Ae^{ik_1 d} + Be^{-ik_1 d} \quad \text{and} \quad \frac{k_2}{k_1} te^{ik_2 d} = Ae^{ik_1 d} - Be^{-ik_1 d}$$

Example 3: Reflection from a single layer on a substrate (cont.)

After some algebra:

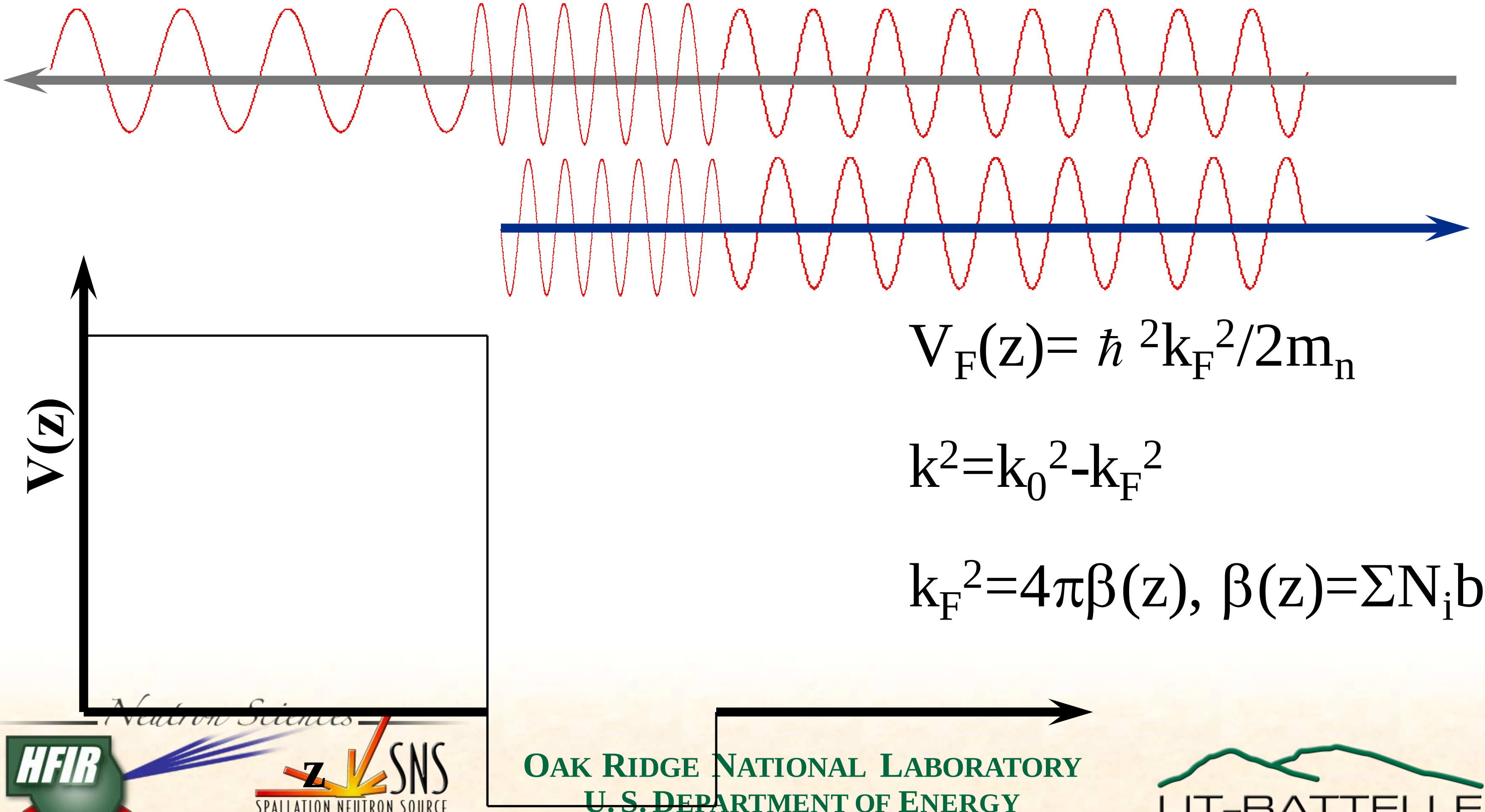
$$[(k_1+k_0)+r(k_1-k_0)]e^{2idk_1}=[(k_1-k_0)+r(k_1+k_0)]\left(\frac{k_1+k_2}{k_1-k_2}\right)$$

$$or \qquad [1-r(r_{01})]e^{2idk_1}=[-r_{01}+r]\frac{1}{r_{12}}$$

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

$$\boxed{r=\frac{r_{12}e^{2idk_1}+r_{01}}{1+r_{01}r_{12}e^{2idk_1}} \qquad and \qquad R=\left|r\right|^2}$$

1-d Reflection at Interfaces



$V_F(z) = \hbar^2 k_F^2/2m_n$

$k^2 = k_0^2 - k_F^2$

$k_F^2 = 4\pi\beta(z),\ \beta(z) = \Sigma N_i b_i$

Kinematic Approximation

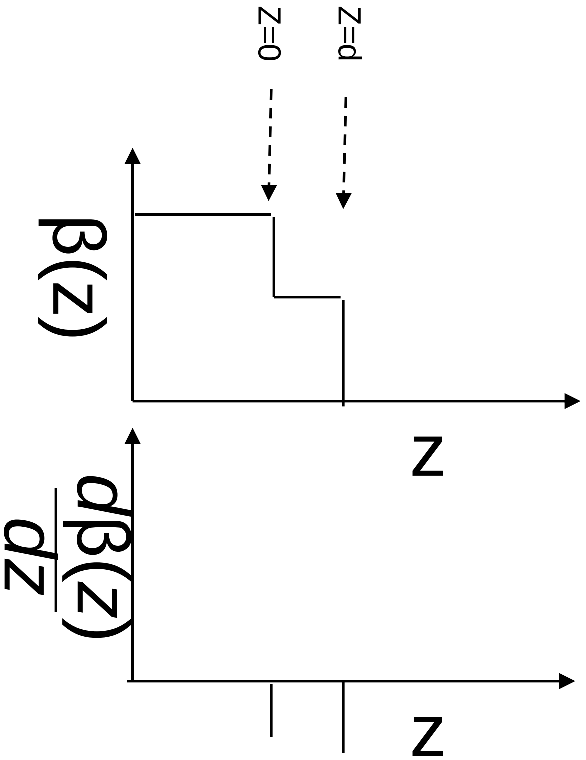
- When the scattering is weak (ie $k_0 > k_F$)

$$R(k_0) \approx \frac{1}{k_0^4}\left|\int \frac{d\beta(z)}{dz} e^{2ik_0 z} dz\right|^2$$

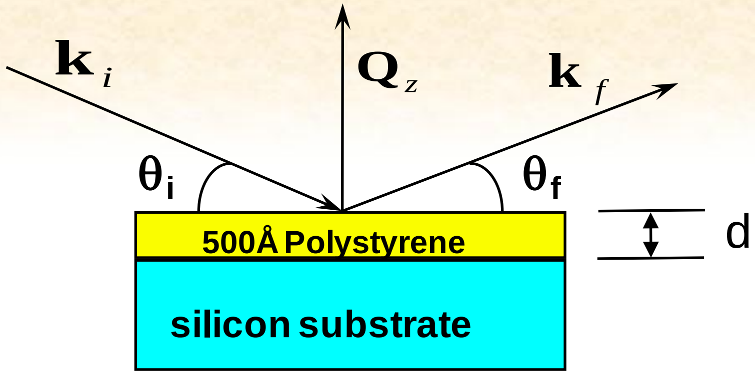
- For a single layer this reduces to

$$R(k_0) \propto [const + \cos(2k_0 d)]$$

- Goes as k_0^{-4}
- Fourier Transform of <u>derivative</u> of SLD

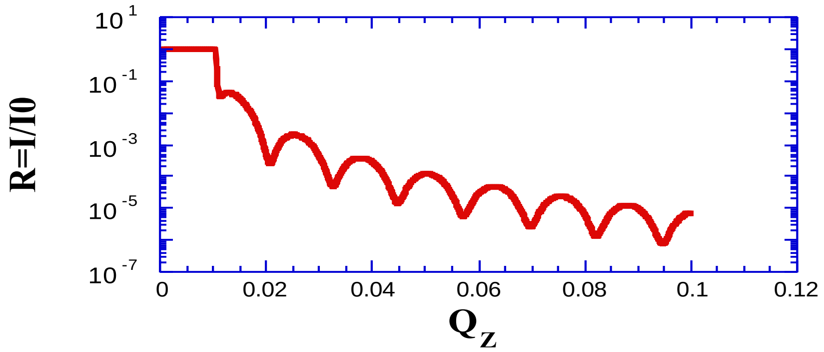


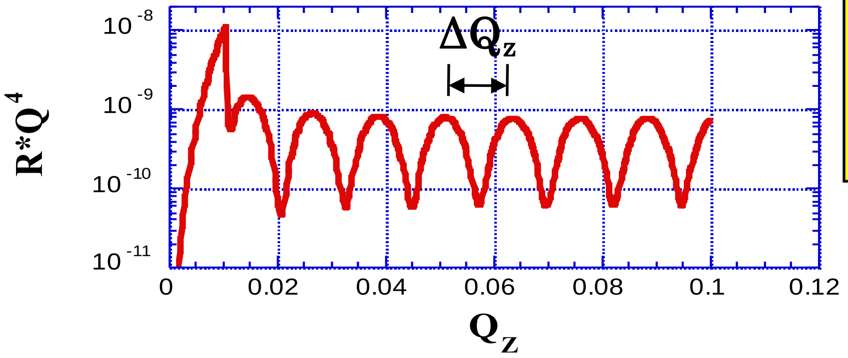
Neutron Reflection from a single layer on a substrate



$$|\mathbf{k}_i| = |\mathbf{k}_f| = \frac{2\pi}{\lambda}, \qquad m\mathbf{v} = \hbar\mathbf{k}$$

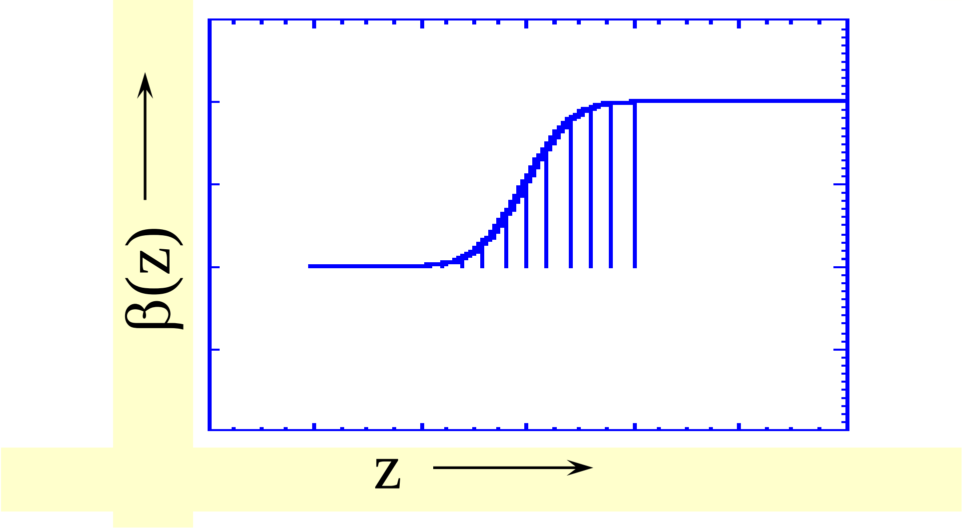
$$\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i, \qquad Q_z = \frac{4\pi\sin(\theta)}{\lambda}$$





- Incident neutron has velocity, v
- Snell’s Law, $\theta_i=\theta_f$
- Momentum transfer Q along z-axis
- Reflectivity defined as I/I_0
- Interference fringes with spacing $\Delta Q_z=2\pi/d$
- Interfacial roughness reduces reflectance

Multilayers



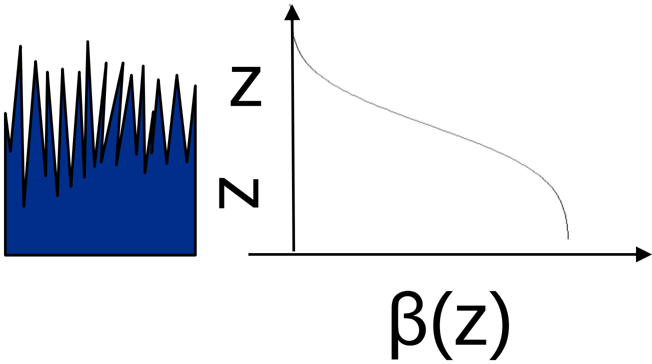
- For complex potentials approximate by multilayers
- For each layer

$$r_{n-1,n} = \frac{r'_{n-1,n} + r'_{n,n+1} e^{2id_n k_n}}{1 + r'_{n-1,n} r'_{n,n+1} e^{2id_n k_n}} \quad \text{, where} \quad r'_{n-1,n} = \frac{k_{n-1} - k_n}{k_{n-1} + k_n}$$

Roughness

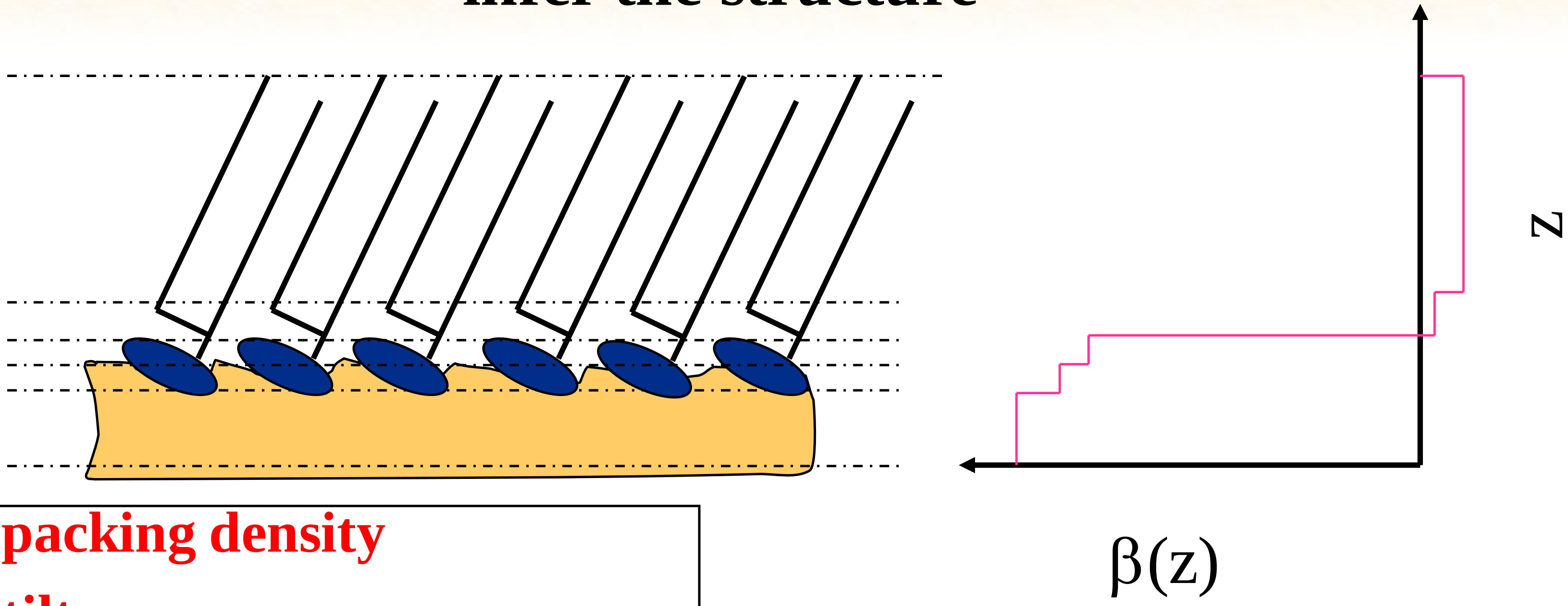
- Specular Reflectivity
  - Gaussian roughness at a substrate. In this case, the deviations of the surface from an average value are described by Gaussian function such that:

$$\beta'(z) = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-z^2}{2\sigma^2}}$$



  - If we plug this into the approximate expression derived above we get: $R(k_0) = R_F(k_0) e^{-4k_0^2\sigma^2}$
  - At each interface that is rough is modified by a damping factor.
- Off specular
  - Use a full 3 dimensional approach. Neutrons scattered in directions other than the specular direction. This is called diffuse scattering.

Goal: To measure the density profile and constituents ⇒ infer the structure



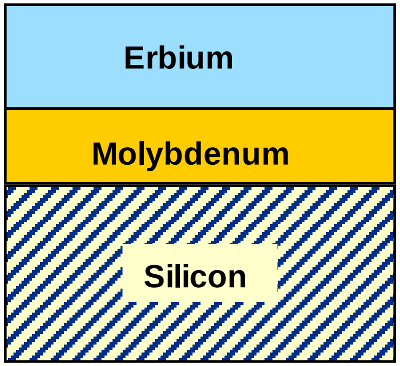
- •packing density
- •tilt
- •interpenetration
- •thickness
- •roughness

Section II: Example of neutron reflectivity measurement

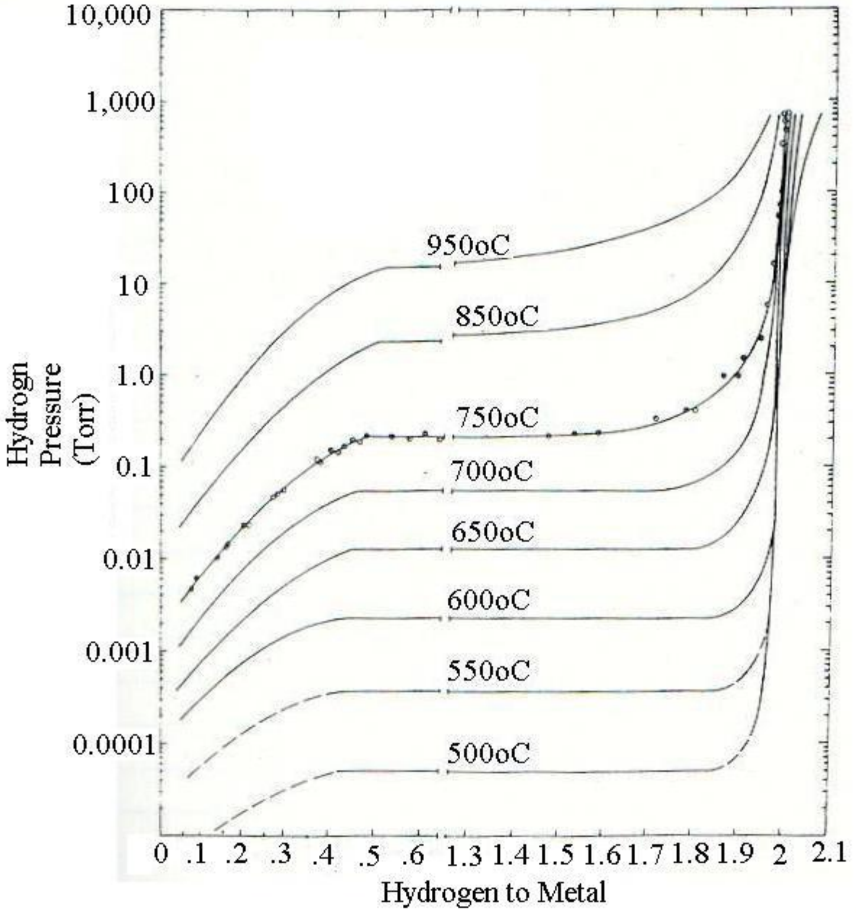
Example: Erbium Hydride Films

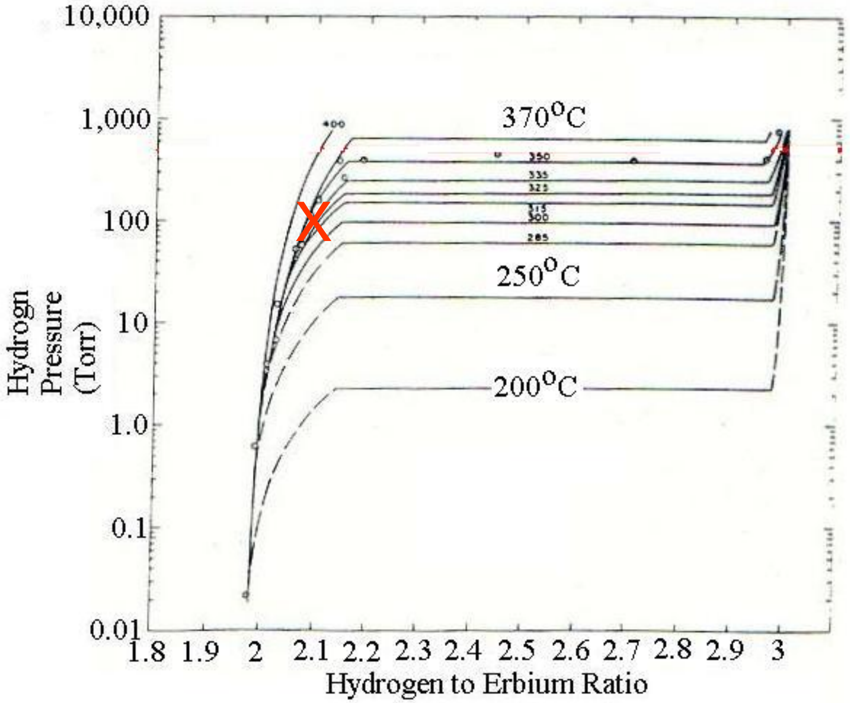
- We are interested in gaining an understanding of how Er film architecture changes during the hydriding process
  - This includes surface chemistry and structure
  - A description of any interfacial regions
  - Hydride layer chemistry and layer expansion resulting from hydrogen incorporation into the Er film

- Sample configuration
  - Si <111> substrate
  - Deposition
    - 1000 Å Mo (to prevent formation of Er-Si compounds) deposited by e-beam PVD (preconditioned Mo)
    - 1500 Å of Er deposited by e-beam PVD
    - Mo & Er deposition rate of 10 Å/s
    - Substrate temperature held at 450^{o}C



Erbium-Hydrogen Isotherms





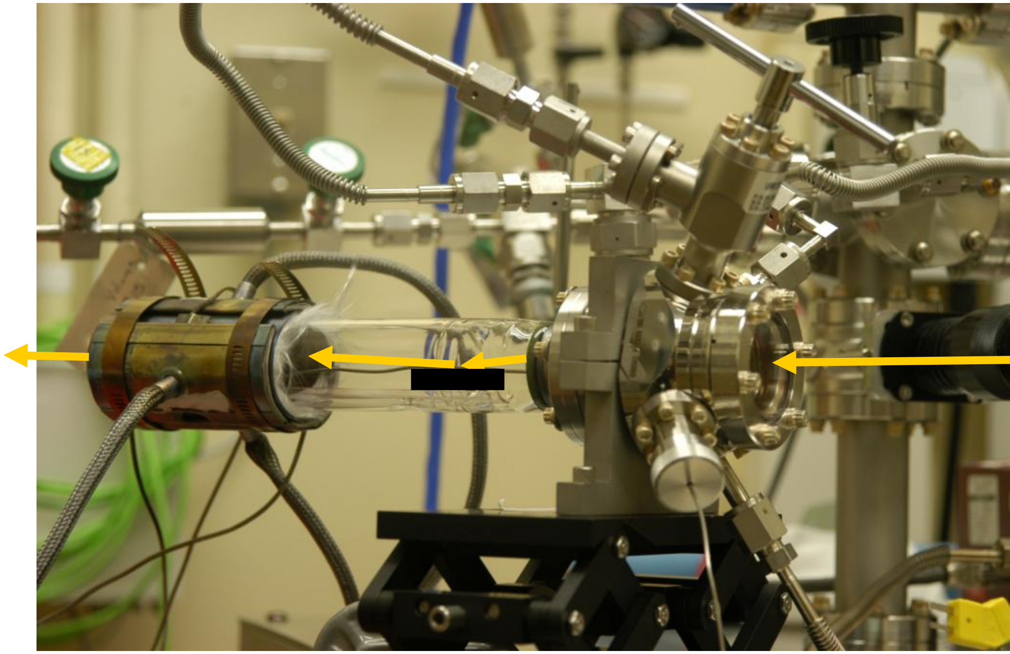
Lundin, C. E. (1968). "The erbium-hydrogen system." Transactions of the Metallurgical Society of AIME 242: 903-907

Hydriding Parameters

350C at ~ 100 Torr

Sample chamber for neutron reflectivity experiments

- **Hydriding and Scattering Chamber:**
  - **12” GE 214 Quartz (pyrex transition to SS)**
  - **Kimball Physics Multiplexer**
    - **Sapphire window**
    - **Blown glass window**
  - **Chamber evacuated ~10^{-8} Torr at beginning of experiment**
  - **Watlow Band Heater with series 96/97 controllers**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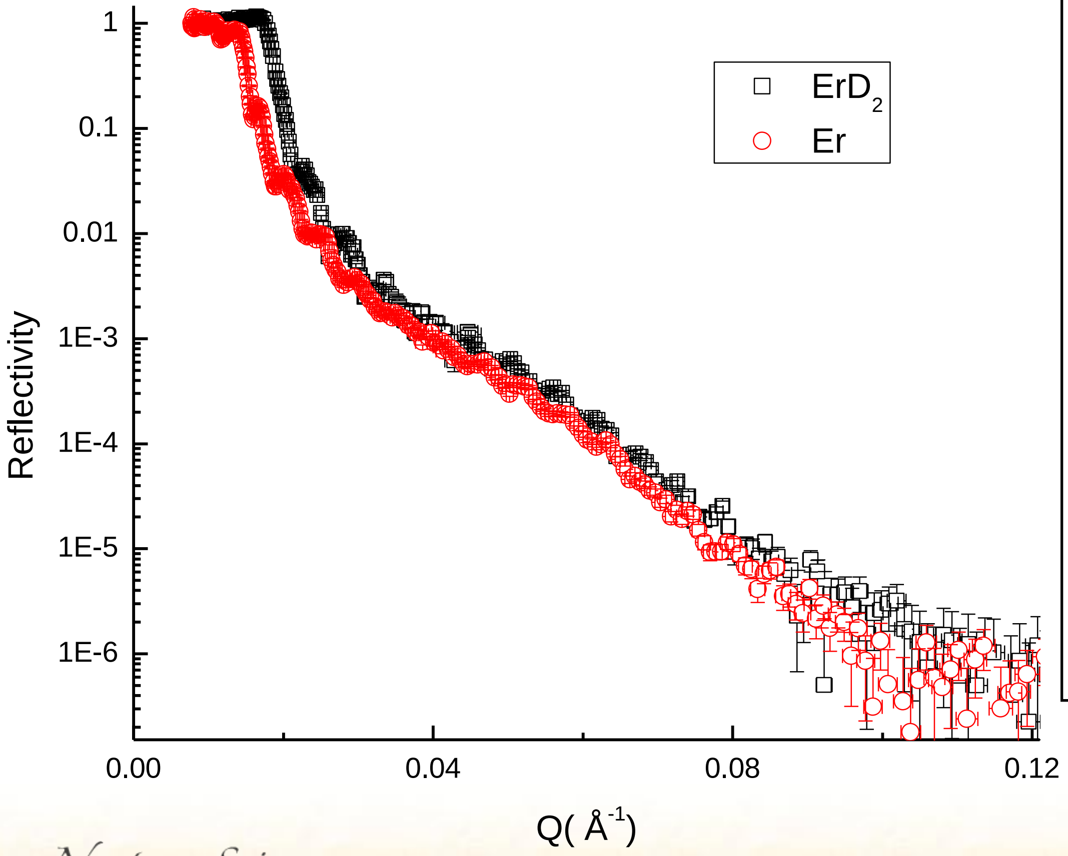
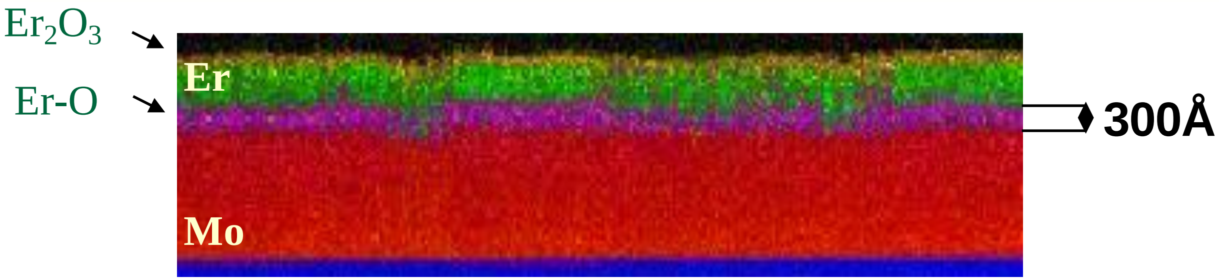
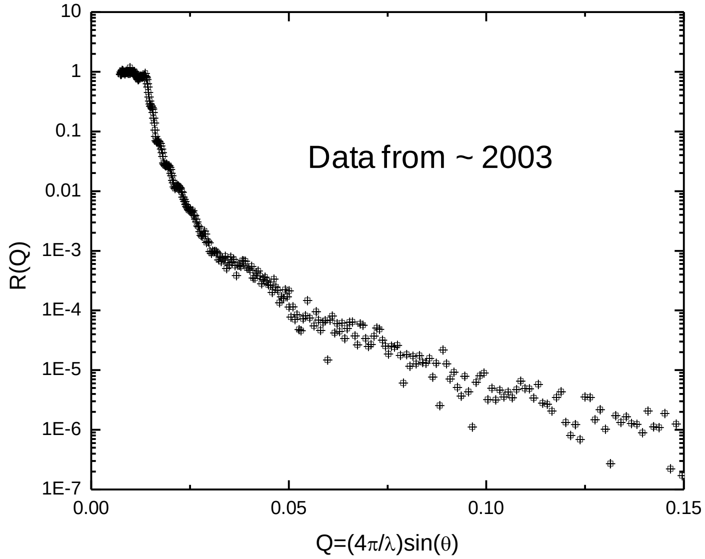
ErMoA before and after hydriding

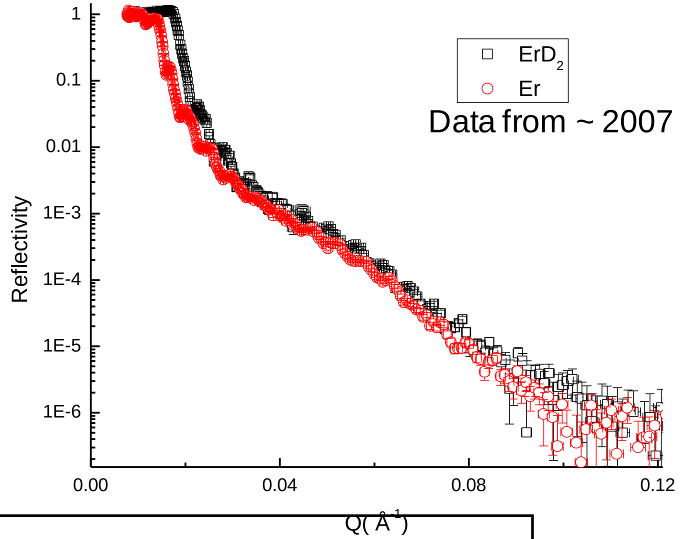


- •Er/Mo film on silicon substrate
- •Measured in-situ @ 350 C before and after introducing D2 gas
- •Clear change in neutron reflectivity
- •Measured the reflectivity at several times after hydriding to ensure no more changes in the curve
- •Better samples than past!

Latest samples – Molybdenum preconditioned

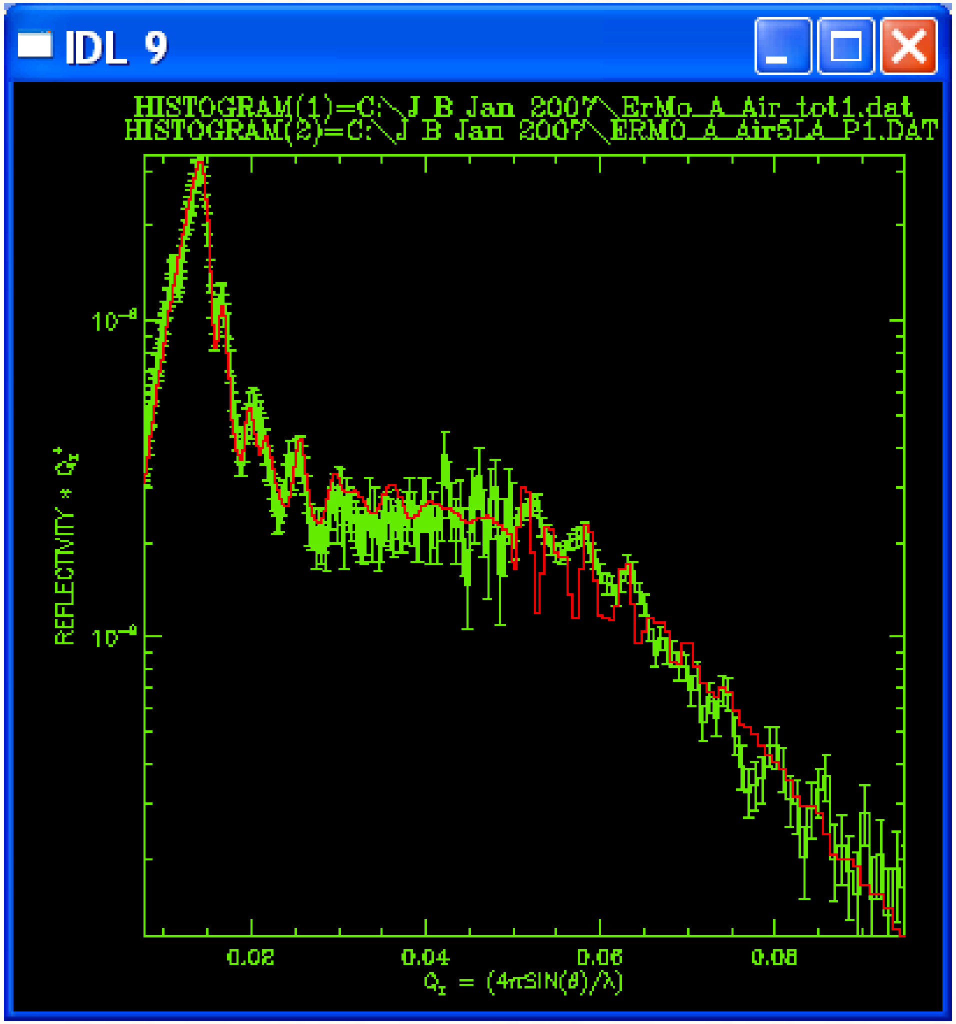




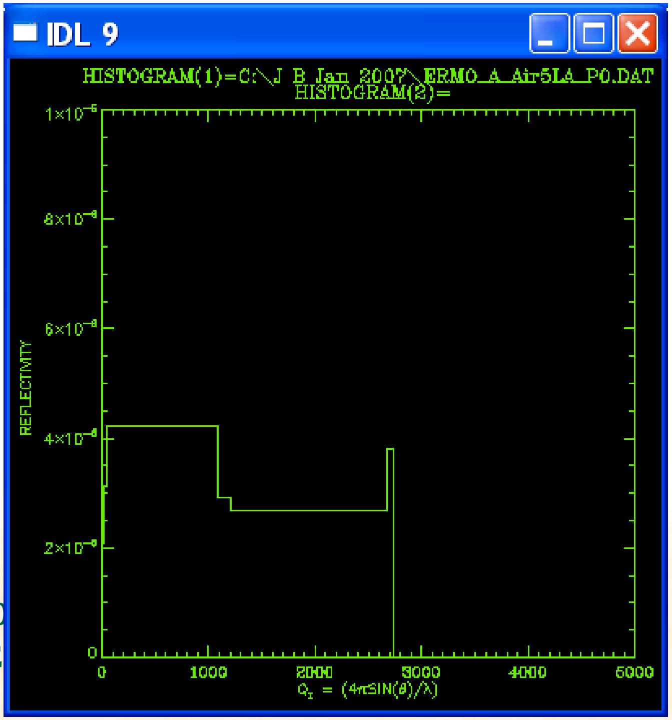


Better visibility fringes= less diffuse/rough interfaces

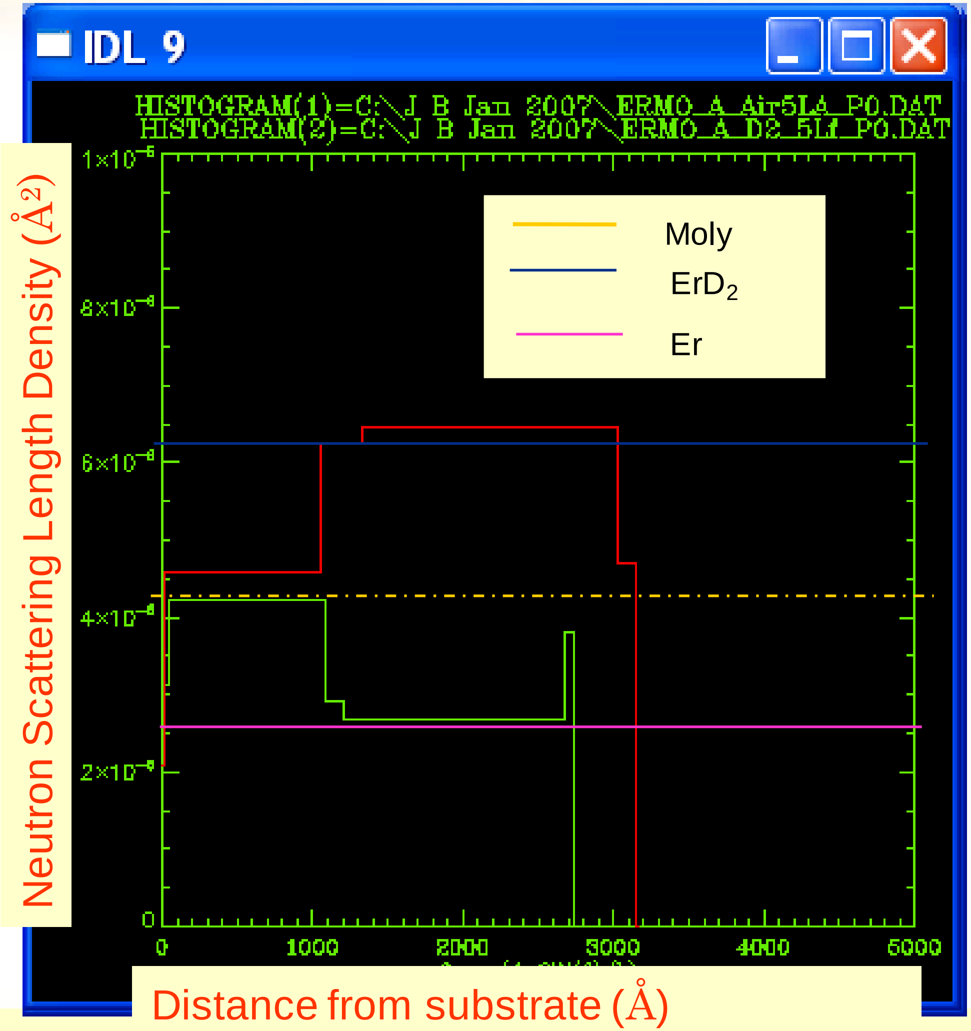
5 Layer model fit- Sample A



- Five layers on silicon substrate
  - Silicon oxide
  - Moly
  - Intermediate layer
  - Er
  - Surface layer
- Roughness at each interface 10-20Å



5 Layer model fit- Sample A



- Sample heated in vacuum $1X10^{-8}$ Torr
- 100 Torr D_2 introduced
- Five layer fit on silicon substrate
  - Silicon oxide
  - Moly
  - Intermediate layer
  - ErD_2
  - Surface layer
- Roughness increases slightly at each interface
- ~ 20% increase in film thickness

Before hydriding

Layer number	1	2	3	4	5
β	3.1	4.2	2.9	2.7	3.8
T	39	1022	121	1463	57

After hydriding

Layer number	1	2	3	4	5
β	3.4	4.6	6.28	6.44	4.7
T	.2	1048	274	1697	115

Summary

- Pre annealing important to remove oxygen from Mo
- Early analysis implies intermediate layer between the Mo and Er layers- several more samples various pressures
- After hydriding the RT film structure same as the HT structure
- Also need a layer on the surface (Er2O3)
- After hydriding Er layer consistent with ErD2

Types of Interfaces Studied Using Neutron Reflectometry

- Solid/solid interfaces
- Solid/air interfaces
- Solid/liquid interfaces
- Liquid/air interfaces
- Magnetization density profile

Collaborators

Jim Browning, Sandia National Laboratories

Clark Snow, Sandia National Laboratories

Erik B Watkins, University of California (Formally LANL)

Jarek Majewski, LANL

Gillian M Bond, New Mexico Institute of Mining and Technology

Loren Espada, Sandia National Laboratories

Ryan Wixom, Sandia National Laboratories

Example I

Structural Studies of Polymer-Cushioned Lipid Bilayers

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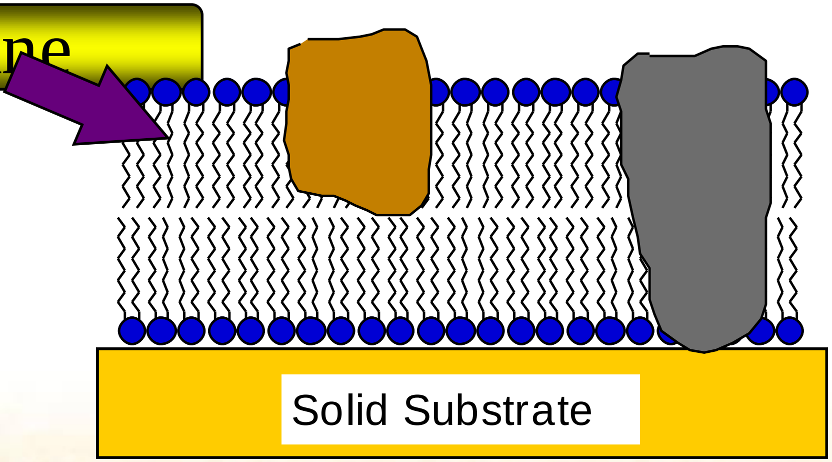
J. Wong, C. K. Park, M. Seitz, and J. Israelachvili, University of California at Santa Barbara

Motivation

To create supported lipid membrane on solid substrate (mica, quartz, silicon, glass) which will:

(i) allow incorporation of functional transmembrane proteins,
(ii) increase lipid and protein fluidity,
(iii) allow transport of ions, water, and solutes across the membrane

Supported planar bilayer membrane

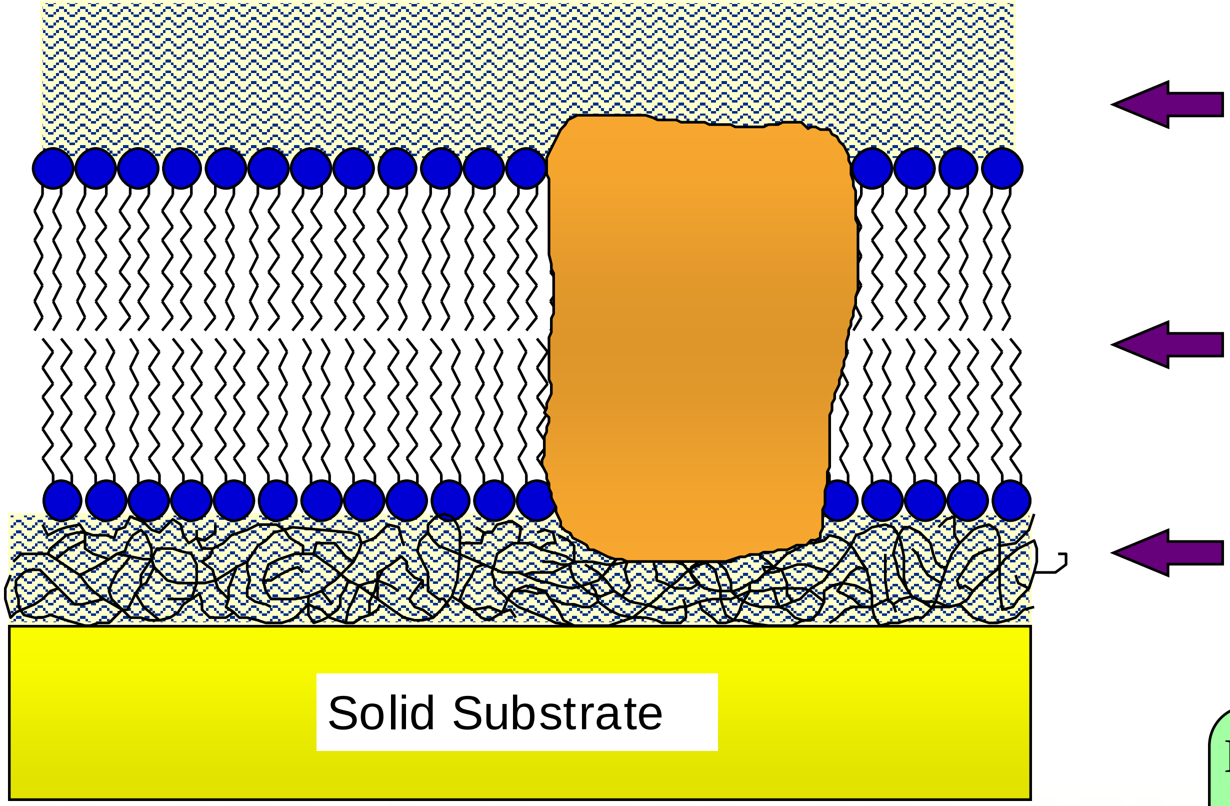


works for partially *inserted* or membrane *surface bound* proteins

not for *transmembrane* proteins

Gel-supported lipid bilayer

A soft, water swollen polymer gel can decouple the membrane from the solid substrate

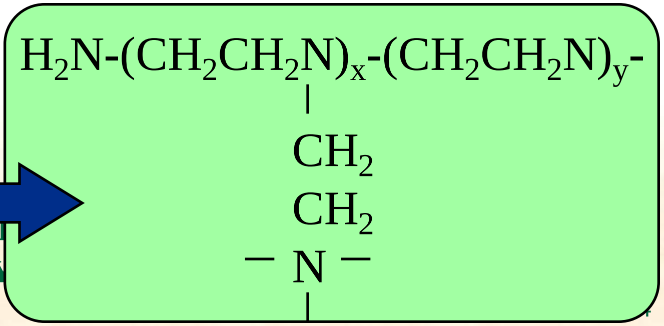


outer aqueous space

lipid bilayer with trans-membrane proteins

water-swollen polymer gel

Polymer: PEI (polyethyleneimine)
1.8K, 100ppm



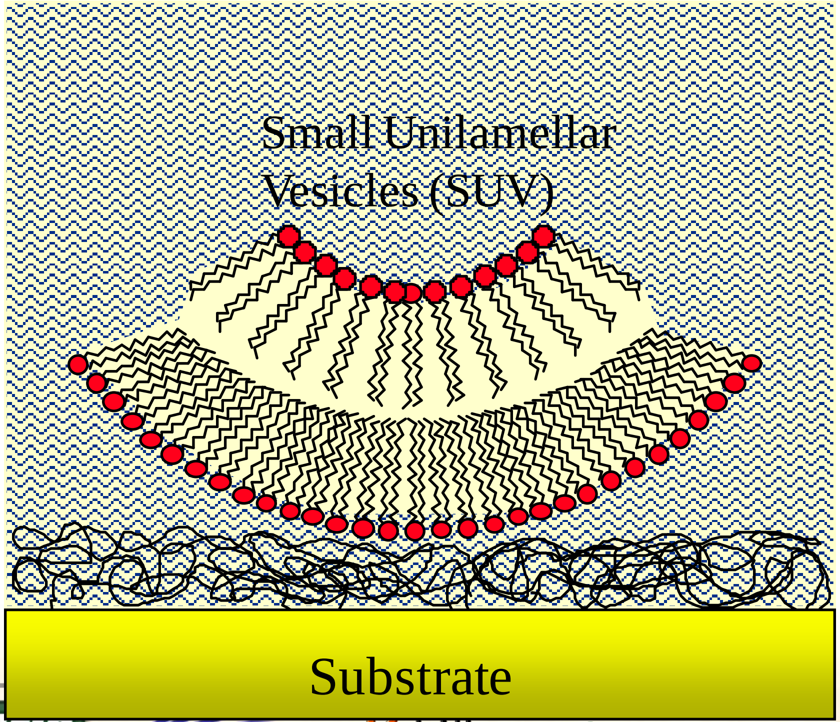
$$\begin{array}{l} H_2N\text{-}(CH_2CH_2\underset{|}{N})_x\text{-}(CH_2CH_2N)_y\text{-} \\ \qquad\qquad\quad CH_2 \\ \qquad\qquad\quad CH_2 \\ \qquad\qquad\; -\underset{|}{N}- \end{array}$$

Approaches

Vesicle adsorption

i) immerse solid substrate in PEI solution (100 ppm, 0.5 mM KNO_3) overnight

ii) inject SUV's of DMPC (T = 24^{o}C)



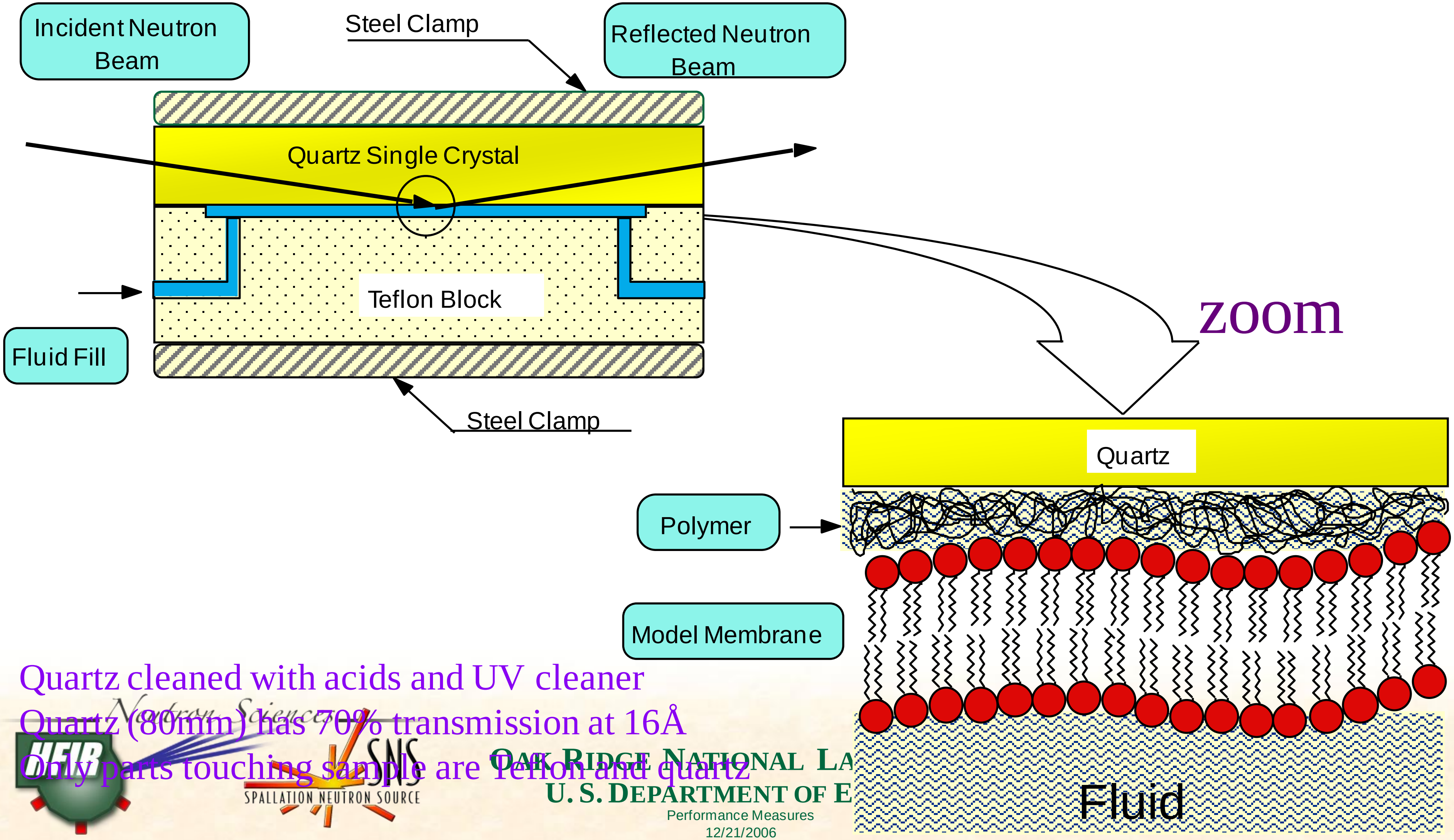
Advantages:

Ease of preparation,
Incorporation of *transmembrane* proteins possible

Disadvantages:

Control of lipid density and of surface structure is difficult, unsure of micro-inhomogeneity, such as defects and multilayers

Liquid/Solid Interface Cell for Neutron Reflection



Quartz cleaned with acids and UV cleaner

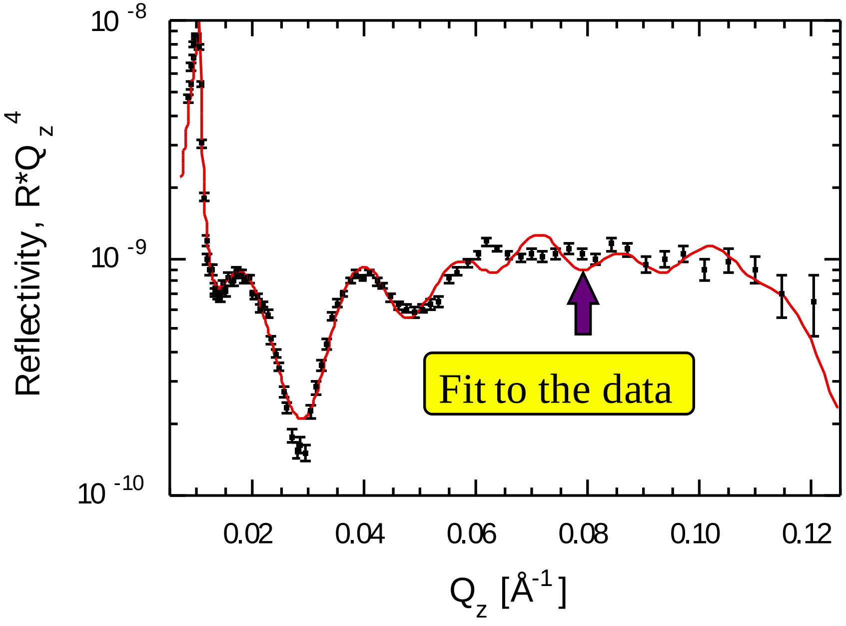
Quartz (80mm) has 70% transmission at 16Å

Only parts touching sample are Teflon and quartz

Contrary to mica surface, the unilamellar vesicles composed of DMPC molecules, do not totally fuse to create bilayer on the PEI polymer deposited on quartz.

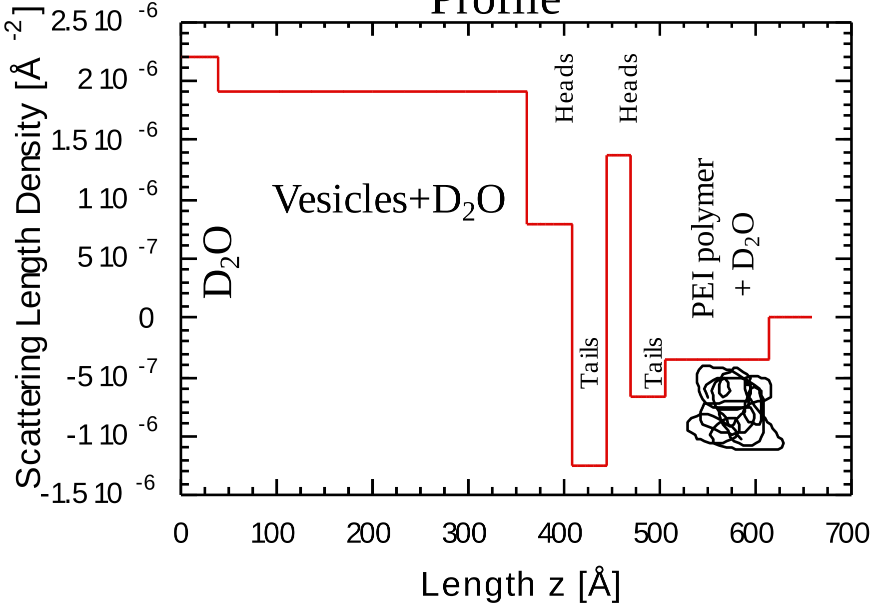
Some of them stay attached intact at the quartz/PEI/DMPC-multilayer (?) surface!!

Neutron reflectivity data



Fit to the data

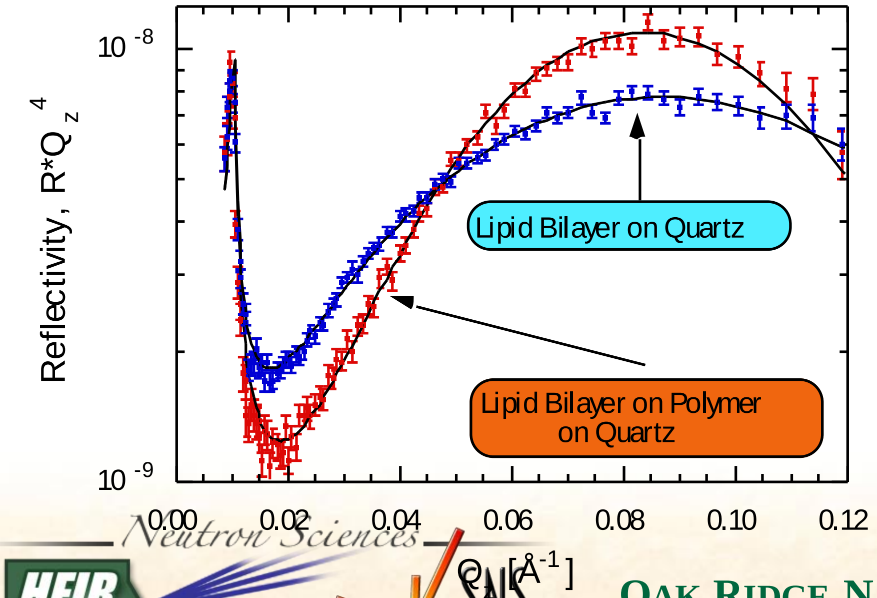
Scattering Length Density Profile



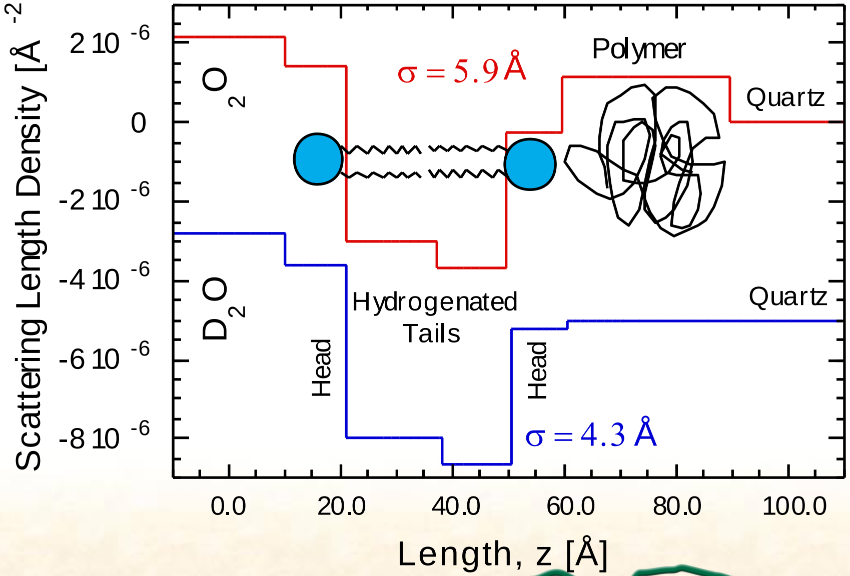
Vesicles composed of DMPC molecules fuse creating almost a perfect lipid bilayer when deposited on the pure, uncoated quartz block (blue curves)

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

Neutron Reflectivities



Scattering Length Density Profiles



Conclusions

- Neutron reflectivity allows us to investigate complex biologically relevant structures at the solid-liquid interface.
- Fusion of DMPC vesicles on the quartz substrate covered with PEI polymer does not work well! Vesicles form complicated multilayerstructures. Some of them stay attached intact.
- PEI diffuses between bilayer of DMPC and the quartz substrateforming the desired structure.This might be the simplest way to prepare *gel-supported* lipid bilayers!