National School on Neutron and X-ray Scattering
Argonne and Oak Ridge National Laboratories
X-ray and Neutron Reflectometry
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(Figure courtesy of Norm Berk)

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photons, electrons, neutrons, atom and ion beams, miniature mechanical devices

* DIRECT IMAGING (REAL SPACE)
  e.g.:
  - optical microscopy (~ 1000 x magnification)
  - scanning electron microscopy (SEM) (orders of magnitude higher magnification than possible with light)
  - transmission electron microscopy (TEM)
  - atomic force microscopy (AFM)

* DIFFRACTION (RECIPIROCAL SPACE)
  e.g.:
  - low energy electron diffraction (LEED)
  - spin polarized LEED (SPEEED)
  - reflection high energy electron diffraction (RHEED)
  - ellipsometry (optical polarimetry)
    - x-ray reflectometry
    - neutron reflectometry

For quantitative measurements of depth profiles along a normal to the surface, x-ray and neutron reflectometry are particularly useful because of their relatively weak interactions with condensed matter and the fact that these interactions can be described accurately by a comparatively simple theory. In the case of electron diffraction, on the other hand, the potential is non-local and the scattering is non-spherical, relatively strong and highly energy-dependent. For atom diffraction, the description of the interaction potential can be even more complicated.
Principal Uses and Advantages of Neutron Reflectometry:

* For the specular condition, provides the chemical (isotopic) scattering length density (SLD) depth profile along the surface normal with a spatial resolution approaching half a nanometer.

* With polarized neutrons, provides the vector magnetization depth profile of a ferromagnetic material.

* Isotopic contrast, particularly applicable to hydrogen and deuterium.

* A non-destructive probe which can penetrate macroscopic distances through single crystalline substrates, making possible reflection studies of films in contact with liquids within a closed cell.

* As a consequence of the relatively weak interaction between the neutron and material, a remarkably accurate theoretical description of the reflection process and quantitative analysis of the data is possible, although the Born approximation is often not valid and an “exact” or “dynamical” formulation is required.
The great success in using neutron reflection/diffraction to study thin film systems of hard condensed matter, in particular the structures and fundamental interactions in magnetic materials, is largely due to the ability to tailor, with atomic-layer accuracy and precision, single-crystalline, layered sandwiches and superlattices (using vapor deposition techniques such as molecular beam epitaxy in ultra-high vacuum). Advances in film deposition techniques and lithography continue at a remarkable rate.

Similarly, neutron reflectometry in principle can be applied as a probe to further our understanding of the structure and function of molecules in lipid membranes, of relevance in biology and bioengineering, when comparable control over the fabrication of model systems is achieved. Great progress has been made toward realizing this goal in practice. However, we are still at a relatively early stage of development in our ability to engineer soft condensed matter films on atomic and nanometer scales. Progress can be expected as efforts in creating and manipulating membrane / molecular systems accelerates.

Employing phase-sensitive methods in reflectivity measurements ensures a unique scattering length density (SLD) depth profile. Additional application of hydrogen / deuterium substitution techniques and comparison with molecular dynamics calculations assures a correspondingly high degree of certainty of obtaining an unambiguous chemical composition depth profile.
"Specular" or "Mirror" Reflection of a Wave

Angle of Incidence $\theta_i$ = Angle of Reflection $\theta_r$
REFRACTION OF A LIGHT WAVE

\[ \eta_1 = 1 \] (FOR VACUUM)

\[ \eta_1 \sin \theta_1 = \eta_2 \sin \theta_2 \]

\[ \eta_2 = 1.581 \] (CERTAIN GLASS)

\[ C = \frac{c_0}{\eta} \] (VACUUM)

\[ \lambda = \frac{\lambda_0}{\eta} \]

\[ k = \eta k_o = \frac{2\pi \nu}{c} \]

REFRACTIVE INDEX \( \eta \) DEPENDS ON MATERIAL AND WAVELENGTH OF THE LIGHT
Atomic resolution micrograph of multiply-twinned nanocrystalline film of Si. (C. Song)
Figure 2.5-6  Interference of two spherical waves of equal intensities originating at the points $P_1$ and $P_2$. The two waves can be obtained by permitting a plane wave to impinge on two pinholes in a screen. The light intensity at an observation plane a distance $d$ away takes the form of a sinusoidal pattern with period $\approx \lambda/\theta$.

Diffraction pattern which results from the coherent superposition of two waves (amplitudes of the two waves add together at any given point in space)

A characteristic reciprocal relationship exists between the positions of the intensity maxima in the diffraction pattern and the distance separating the objects causing the scattering.
Wave interference patterns produced by monochromatic laser light diffracting through a triple slit aperture for various intensities – L. Page (www.vias.org/physics). This is a dramatic illustration of wave-particle duality.
Reflectivity = \frac{\text{Number of reflected neutrons}}{\text{Number of incident neutrons}} = |r|^2

Specular reflection: \bar{\rho}(z) = \langle \rho(x,y,z) \rangle_{xy}

Non-Specular reflection: \Delta\rho(x,y,z) = \rho(x,y,z) - \bar{\rho}(z)

(AFTER N.F. BERK ET AL.)
$Q = \frac{4\pi r \sin \theta}{\chi}$

$\rho = N \bar{b}$

$\text{SLD} = \left( \frac{\text{# Atoms}}{\text{u. vol.}} \right)$

$\sim -2 \rightarrow 10$
single-crystal quartz block and reflected from the quartz-solution interface were recorded as a function of angle of incidence. The off-specular background, including any signal due to scattering from the bulk solution [15], was subtracted to give the reflection coefficient of the surfactant-coated interface. All solutions used were above their critical micelle or aggregation concentration, a condition which leads to a saturated adsorbed film at the solid-solution interface.

The cationic surfactant tetradecyltrimethylammonium bromide (TTAB) forms nearly spherical micellar aggregates consisting of approximately 80 molecules in bulk solution. Small angle neutron-scattering measurements [16] give mi-
THE NEUTRON AS A PLANE WAVE PROPAGATING IN FREE SPACE

\[ \Psi \propto e^{i \mathbf{k}_0 \cdot \mathbf{r}} \]

For \( \mathbf{k}_0 \) along \( \hat{z} \), for example,

\[ \Psi \propto \cos(k_0 z x) + i \sin(k_0 z x) \]

\[ \left( \frac{2\pi}{\lambda} \right) \]

\[ |\Psi|^2 \propto \text{PROBABILITY OF THE NEUTRON BEING THERE} \]
FOR ELASTIC INTERACTIONS
TOTAL ENERGY OF THE NEUTRON IS CONSTANT

TOTAL ENERGY = KINETIC ENERGY + POTENTIAL ENERGY = CONSTANT

WAVE EQUATION OF MOTION (SCHROEDINGER EQUATION)

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right) \psi = E \psi
\]

\[\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\]

IN VACUUM
K.E. \_\_\_\_ \_\_\_\_ T.E.

K.E. = \frac{\hbar^2 k_0}{2m}
IN THE CONTINUUM LIMIT

\[ V(\mathbf{r}) = \frac{2\pi^2 \hbar^2}{m} \sum_{j=1}^{N} N_j b_j = \frac{2\pi^2 \hbar^2}{m} \rho \]

(b = Re b + i Im b)

\[ \rho = \text{"scattering length density" (SLD)} \]

IN VACUUM:

\[ E_0 = \frac{\hbar^2 k_0^2}{2m} + 0 \]

IN A MATERIAL MEDIUM:

\[ E = \frac{\hbar^2 k^2}{2m} + \frac{2\pi^2 \hbar^2}{m} \rho \]

CONSERVATION OF ENERGY Requires \( E_0 = E \)

\[ \therefore \quad k^2 = k_0^2 - 4\pi \rho \]
Thus

$\left[ \nabla^2 + k^2 \right] \psi = 0$

Note refractive index $n = \frac{k}{k_0}$:

$n^2 = 1 - \frac{4\pi\rho}{k_0^2}$
Reflection from an ideal film or slab of material

Wavevector transfer $\vec{Q} = \vec{k}_f - \vec{k}_i$

$\rho = \rho(z)$ only
Expanding \( k^2 = k_0^2 - 4\pi \rho \),
\[ k_x^2 + k_y^2 + k_z^2 + 4\pi \rho = k_{0x}^2 + k_{0y}^2 + k_{0z}^2. \]

Now if \( \rho = \rho(z) \) only, then
\[ \frac{\partial \rho}{\partial x} \text{ and } \frac{\partial \rho}{\partial y}, \] which are proportional to the gradients of the potential or forces in the respective directions, are equal to zero. Thus, no force acts along these directions to change \( k_x \) and \( k_y \). Then
\[ k_x = k_{0x} \text{ and } k_y = k_{0y} \]
is "constants of the motion".

Substituting \( \psi(x) = e^{ik_0x^2}e^{-ik_0z} \psi(z) \)
into \( [\nabla^2 + k^2] \psi = 0 \) gives
\[ \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} \right] \psi(z) = 0. \]
AND: \[ k_z^2 = k_0^2 - 4\pi \rho(z) \].

Because there is no change in the potential in the \( x \)- or \( y \)-directions, there can be no momentum change in these directions either.

The ideal slab geometry with \( \rho = \rho(z) \) only gives rise to the coherent "specular" reflection of a plane wave which is described by a one-dimensional wave equation:

\[
\left[ \frac{\partial^2}{\partial z^2} + k_0^2 - 4\pi \rho(z) \right] \Psi(z) = 0
\]

In this case \( \theta_i = \theta_f = \theta \), \( |\vec{k}_i| = |\vec{k}_f| \) and \( Q = 2k \sin \theta \)

Also, \( \eta_z^2 = 1 - \frac{4\pi \rho(z)}{k_0^2} \).
\[ Q = Z k_0 z \]

From the wave equation, it is possible to find a solution for the reflection amplitude in integral form (see article pages):

\[ r(Q) = \frac{4\pi}{iQ} \int_{-\infty}^{+\infty} \psi(z) \rho(z) e^{i k_0 z z} \, dz \]

What is localized at \( z \) in the SLD profile \( \rho(z) \) in "real" space, is distributed over the reflection amplitude \( r(Q) \) in the related scattering or "reciprocal" space.
\[ M_j = \begin{bmatrix} \cos \delta_j & \frac{1}{n_{x_j}} \sin \delta_j \\ -n_{x_j} \sin \delta_j & \frac{n_{x_j}}{\cos \delta_j} \end{bmatrix} \]  

with \( \delta_j = k_{ox} n_{xj} \Delta_j \), with \( n_{ox} \) and \( n_{ox} \) corresponding to the substrate and incident medium, respectively. The \( j \)th matrix \( M_j \) corresponds to the \( j \)th slab of thickness \( \Delta_j \) wherein the scattering density is assumed to be constant and equal to \( \rho_j \). The amplitude of the incident wave is assumed to be unity. The transmission and reflectivity are \( T^*T = |T|^2 \) and \( R^*R = |R|^2 \), respectively, and can be obtained directly from Equation (9).

Thus, for a given model potential, it is straightforward to calculate the expected reflectivity. Unfortunately, the converse of this statement is not necessarily true, as will be discussed in more detail in Section 4.

At this point it is useful to consider an alternate derivation of the reflectivity from which the Born approximation (corresponding to the kinematic limit which is discussed below) and other useful results can be directly obtained. Suppose that there exist two arbitrary but different density profiles \( \rho_1(x) \) and \( \rho_2(x) \) for which the corresponding, separate reflectivities are to be calculated. In each case we take the incident wave to propagate from left to right. We then have to solve the following pair of equations (derived from equations 6 and 7):

\[ \psi_j''(x) + [k_{ox}^2 - 4\pi \rho_j(x)] \psi_j(x) = 0 \quad j = 1,2 \]  

for \(-\infty < x < \infty\) where \( \psi_1(x) \) and \( \psi_2(x) \) are the exact solutions in each case. From these we can construct the Wronskian function

\[ W(x) = W[\psi_1(x), \psi_2(x)] = \psi_1(x)\psi_2'(x) - \psi_1'(x)\psi_2(x). \]  

Differentiating both sides of eq. (13) and using eq. (12) we obtain

\[ W'(x) = -\psi_1(x)4\pi \rho_{12}(x)\psi_2(x) \]  

where

\[ \rho_{12}(x) = \rho_1(x) - \rho_2(x). \]  

Equation (14) tells us that \( W(x) \) is a constant over intervals where the two density profiles coincide, \( \rho_1(x) = \rho_2(x) \), which is a property we will exploit to obtain a formula relating the reflectivities for each profile. First, assume that \( \rho_1 \neq \rho_2(x) \) only within an interval \( \ell_1 < x < \ell_2 \). We allow subintervals of \( (\ell_1, \ell_2) \) where \( \rho_1(x) = \rho_2(x) \), but we demand finite \( \ell_1 \) and \( \ell_2 \) such that \( \rho_1(x) = \rho_2(x) \) for all \( x < \ell_1 \) and for all \( x > \ell_2 \). We also assume that the wave is incident in vacuum so for \( x < \ell_1 \), \( \rho_1(x) = \rho_2(x) = 0 \). The wavefunctions for \( x < \ell_1 \) are then

\[ \psi_j(x) = e^{ik_{ox}x} + R_j e^{-ik_{ox}x} \]  

where \( R_j \) and \( R_2 \) are the reflection amplitudes for each problem. Similarly, we assume that each density profile has a common substrate so that for \( x > \ell_2 \), \( \rho_1(x) = \rho_2(x) = \rho(\infty) \). The wavefunctions for \( x > \ell_2 \) are then

\[ \psi_j(x) = T_j e^{ikx} \]  

where
\[ R = \sqrt{k_{0x}^2 - 4\pi \rho(\infty)} \]  

(18)

and \( T_1 \) and \( T_2 \) are the transmission amplitudes in each problem. Now we see that for the given pair of profile functions \( \rho_1(x) \) and \( \rho_2(x) \), \( W(x) \) is uniquely determined everywhere and varies with \( x \) only in \( (\ell_1, \ell_2) \), where \( \rho_1(x) \) and \( \rho_2(x) \) can differ. Substituting (17) into (13) we obtain

\[ W(x) = 0 \]  

(19)

for all \( x \geq \ell_2 \), since \( \psi_1(x) \) and \( \psi_2(x) \) are proportional to one another (linearly dependent) in this region. However, substituting (16) into (13) we get

\[ W(x) = 2ik_{0x}(R_1 - R_2) \]  

(20)

for all \( x \leq \ell_1 \), which is a complex constant. Finally, for \( \ell_1 < x < \ell_2 \) we integrate both sides of equation (14) to obtain

\[ \int_{\ell_1}^{\ell_2} W(x)dx = W(\ell_2) - W(\ell_1) = -\alpha_{12} \]  

(21)

where

\[ \alpha_{12} = \int_{\ell_1}^{\ell_2} \psi_1(x)4\pi\rho_{12}(x)\psi_2(x)dx \]  

(22)

Now \( W(x) \) is continuous everywhere since \( \psi_1(x) \) and \( \psi_2(x) \) are. Thus, evaluating (19) and (20) at \( x = \ell_2 \) and \( x = \ell_1 \), respectively, we find \( W(\ell_2) = 0 \) and \( W(\ell_1) = 2ik_{0x}(R_1 - R_2) \). Thus, from equation (21) we get

\[ R_1 = R_2 + \frac{\alpha_{12}}{iQ} \]  

(23)

where again \( Q = 2k_{0x} \) is the wavevector transfer. Equation (23) is the general formula we set out to derive and is a handy starting point for exact treatments as well as approximation schemes.

For example, consider any \( \rho(x) \) which vanishes identically for \( x < \ell_1 \) and for \( x > \ell_2 \). Then, in equation (23) we can set \( \rho_1(x) = \rho(x) \), \( \psi_1(x) = \psi(x) \), and \( R_1 = R \) whereas for the "other" density profile we take \( \rho_2(x) = 0 \) everywhere so that \( \psi_2(x) = \exp(ik_{0x}x) \) and \( R_2 = 0 \). Combining equations (22) and (23) then gives the exact solution of the reflectivity for an arbitrary scattering density profile \( \rho(x) \):

\[ R = \frac{4\pi}{iQ} \int_{-\infty}^{+\infty} \psi(x)\rho(x)e^{ik_{0x}x}dx \]  

(24)

where we have formally extended the integration over all \( x \), though only the region where \( \rho(x) \neq 0 \) contributes. Although it may not be obvious from the derivation, equation (24) also holds if we allow \( \rho(x) \) to be nonzero as \( x \to \infty \), as long as the integral exists. Note that (24) requires, to be exact, the exact wavefunction \( \psi(x) \) wherever \( \rho(x) \neq 0 \). The corresponding expression for the reflectivity \( |R|^2 \), is
\( \psi(z) \) inside the medium is generally unknown:

**Born approximation replaces** \( \psi(z) \) **with the incident wave function** \( e^{i k_0 z} \) **based on the assumption that** \( \psi(z) \) **is not significantly distorted from the free space form (weak interaction):**

\[
\rho(Q) \approx \frac{4\pi i}{iQ} \int_{-\infty}^{\infty} \rho(z) e^{iQz} \, dz
\]

**Fourier transform**

For a real potential \( \rho(z) \)

\[
\text{Re} \, \rho(Q) \approx \frac{4\pi}{Q} \int_{-\infty}^{\infty} \rho(z) \sin(Qz) \, dz
\]
ARBITRARY POTENTIAL DIVIDED INTO RECTANGULAR SLABS OF WIDTH \( d \) AND CONSTANT \( p \)

THEN

\[
\text{Re} \, r(Q) = \frac{4\pi}{Q} \int_0^L p(z) \sin(Qz) \, dz
\]

BECOMES

\[
\text{Re} \, r(Q, \gamma) = \frac{4\pi}{Q \gamma} \sum_{l=1}^{N} \frac{l \, d}{(l-1) \, d} \int_0^L p_2 \sin(Q_l \gamma z) \, dz
\]

\[
= -\frac{4\pi}{Q^2} \sum_{l=1}^{N} \frac{l \, d}{(l-1) \, d} \sum_{j=1}^{N} p_2 \left[ \cos(Q_l \gamma z) \right]_0^L
\]

\[
\text{Re} \, r_1 = C_{11} p_1 + C_{12} p_2 + \ldots + C_{1N} p_N
\]

\[
\text{Re} \, r_2 = C_{21} p_1 + C_{22} p_2 + \ldots + C_{2N} p_N
\]

\[ \vdots \]

\[
\text{Re} \, r_N = C_{N1} p_1 + C_{N2} p_2 + \ldots + C_{NN} p_N
\]

SOLVE SIMULTANEOUS EQUATIONS FOR \( p_2 \) GIVEN \( \text{Re} \, r_\text{'s} \)

E.g., SVD, EIGENVALUE PROBLEM FORMULATION, ...
\[
\text{Re } r_{BA}(Q) \left[ \frac{Q^2}{8\pi \sin(Qd/2)} \right] = \sum_{j=1}^{N} p_j \sin \left[ \frac{(2j-1)Qd}{2} \right]
\]

\[
\equiv f(Q)
\]

\[
\int_{0}^{\pi} \sin m\theta \sin n\theta d\theta = \begin{cases} 
0 & m, n \text{ integers, } m \neq n \\
\frac{\pi}{2} & m, n \text{ integers, } m = n
\end{cases}
\]

ORTHOGONALITY

\[
p_j = \frac{d}{4\pi^2} \int_{0}^{\pi} Q^2 \text{Re } r_{BA}(Q) \frac{\sin \left[ \frac{(2j-1)Qd}{2} \right]}{\sin \left( \frac{Qd}{2} \right)} dQ
\]
Solid, long-dash, and short-dash neutron reflectivity curves corresponding to their respective scattering length density profiles shown in the inset. This series of curves and profiles illustrates the sensitivity of the reflectivity to the overall film thickness at reflectivities approaching 10^-7 whereas detailed features such as the oscillation in the long-dash profile can only be accurately discerned at reflectivities an order of magnitude or so lower, at Q-values corresponding to 2 \pi/ width of the feature.
"Reflectivity" Regime

Low Q: Higher Sensitivity for Composition Profile

Log Intensity (arb. units)

\[ N = 20 \]
\[ d = 2 \text{ Å} \]
\[ \Delta = 60 \text{ Å} \]

High Q: Higher Sensitivity for Strain Lattice or Spacing Profile

\[ |R|^2 = \left( \frac{4\pi T}{Q} \right)^2 \sum_{m=1}^{N} \sum_{n=1}^{M} \left( \frac{\sin (md + n\Delta)}{\sin (Qd/2)} \right)^2 \]

\[ = \left( \frac{4\pi T}{Q} \right)^2 \left( \frac{\sin (NGd/2)}{\sin (Qd/2)} \right)^2 \left( \frac{\sin (MQd/2)}{\sin (Qd/2)} \right)^2 \]
**Problem:** Born approximation fails at sufficiently small $Q$ — must then use exact theory.

Comparison between kinematic (line) and dynamic (triangle + line) plus-state reflectivities for a density profile similar to that of Fig. 2 as described in the text.
\[
\frac{\partial^2 \psi(z)}{\partial z^2} + k_z^2 \psi(z) = 0
\]

Conservation of momentum and particle number require that \( \frac{\partial \psi(z)}{\partial z} \) and \( \psi(z) \) be continuous at the boundaries \( z=0 \) and \( z=L \).

\[
\begin{pmatrix}
  t \\
  i t
\end{pmatrix}
\]

\[
e^{-i k_0 z L} = \begin{pmatrix} A & B \\ C & D \end{pmatrix} \begin{pmatrix} 1+r \\ i(1-r) \end{pmatrix}
\]
\[
\begin{align*}
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix}
&= 
\begin{pmatrix}
a_n & b_n \\
c_n & d_n
\end{pmatrix}
\begin{pmatrix}
a_{n-1} & b_{n-1} \\
c_{n-1} & d_{n-1}
\end{pmatrix}
\cdots
\begin{pmatrix}
a_2 & b_2 \\
c_2 & d_2
\end{pmatrix}
\begin{pmatrix}
a_1 & b_1 \\
c_1 & d_1
\end{pmatrix} \\
\begin{pmatrix}
a_j & b_j \\
c_j & d_j
\end{pmatrix}
&= 
\begin{pmatrix}
\cos S_j & \frac{1}{m_j} \sin S_j \\
-m_j \sin S_j & \cos S_j
\end{pmatrix} \\
S_j &= k_{0z} m_{zj} \Delta_j \\
&= k_{zj} \Delta_j
\end{align*}
\]
Then, once we know \( M_k(L) \):

\[
\begin{align*}
\begin{pmatrix} 1 \\ i \end{pmatrix} t(k) e^{ikL} &= \begin{pmatrix} A_k(L) & B_k(L) \\ C_k(L) & D_k(L) \end{pmatrix} \begin{pmatrix} 1 + r(k) \\ i[1 - r(k)] \end{pmatrix} \\

r &= \frac{B + C + i(D - A)}{B - C + i(D + A)} \\
t &= \frac{2ie^{-ikL}}{B - C + i(D + A)} \\
R &= |r|^2 = \frac{\Sigma - 2}{\Sigma + 2}, \quad \Sigma = A^2 + B^2 + C^2 + D^2
\end{align*}
\]
Fresnel Reflectivity

For $Q_z < Q_{zc}$, $R_F = 1$.

$$|r_F|^2 = \frac{1 - \sqrt{1 - \frac{Q_{zc}^2}{Q^2}}}{1 + \sqrt{1 - \frac{Q_{zc}^2}{Q^2}}}$$

Analogue of SANS Porod's Law: effect of sharp edges.

$Q_c^2 = 16 \pi \rho$

(N.F. Berk)
"Soft" substrate

Smooth transition:
interlayer diffusion
roughness

\[ \frac{p}{p_{Si}} \]

rms width = 3.5Å

\[ Q_z \]

\[ \log_{10} R \]
Uniform slab

\[ \rho = 2.07 \times 10^{-6} \, \text{Å}^{-2} \]

\[ z = 0 \quad z = 200 \, \text{Å} \]

\[ R(0) = 1 \]

\[ \sqrt{Q_z^2 - 16\pi \rho} = \frac{2\pi m}{L} \quad \frac{2\pi m}{L} = 1, 2, \ldots \]

(Kinematical)

Kiessig Fringes

Si Fresnel
Multilayer on Si

\[ D = 200\text{Å} \quad \text{and} \quad L = 9 \times 200\text{Å} \]

Pseudo Bragg peaks:
\[ \frac{2\pi m}{D} = 1, 2, \ldots \]

\[ \frac{2\pi m}{L} = 1, 2, \ldots \]

\[ L = 18 \times 200\text{Å} \]
IF $\rho$ IS NOT EXACTLY $\rho(z)$, I.E., SOME VARIATIONS EXIST IN THE $(x,y)$-PLANE, THEN

$$r_{\text{Born}} = \frac{4\pi}{iQ} \int_{-\infty}^{+\infty} \langle \rho(x,y,z) \rangle_{x,y} e^{iQz} \, dz$$

ON SPECULAR "RIDGE" WHERE $\vec{q} = Q \hat{z}$

WHERE

$$\langle \rho(x,y,z) \rangle_{x,y} = \frac{1}{A} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho(x,y,z) \, dx \, dy$$

$A = \text{NORMALIZING AREA OF THE }(x,y)$-PLANE

$= \bar{\rho}(z)$ ONLY
Possible microstructures corresponding to interfacial roughness.
\[ \mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i \]

**In-Plane Correlation (\( ? \))**

**Simultaneous and/or Multiple Scattering**

**Specular and/or Diffuse**

\[ \log_10 R \]

\[ Q_L (\text{Å}^{-1}) \]

\[ Q_T \]
Fig 2. Diagram of expected orientation of lamellae. Silicon substrate with etched channels is displayed in grey, with lighter and darker regions corresponding to the two polymer components.
Diblock copolymer lamellar nanostructures – R.Jones, B.Berry, and K.Yager (NIST Polymer Division) and S.Satija, J.Dura, B.Maranville et al. (NCNR).

Fig 1. Side-view scanning-electron micrograph of laser-interferometry-produced silicon substrate with 400 nm channels, spaced by 400 nm for a total repeat distance of 800 nm.
Neutron diffraction from silicon with channels but without polymer.
Neutron diffraction from Si channels filled with ordered diblock copolymer.
small-scale *heterogeneity* laterally averages SLD profile

large-scale *heterogeneity* laterally averages reflectivity
\[ Q = \frac{4\pi \sin \theta}{\lambda} \]

\[ \Delta Q \approx \frac{\Delta \lambda}{\lambda} Q + \sqrt{\left(\frac{4\pi}{\lambda}\right)^2 - Q^2} \Delta \theta \]

Typical values:
\[
\begin{align*}
\frac{\Delta \lambda}{\lambda} &\approx 0.01 \\
\Delta \theta &\approx 1 \text{ min of arc}
\end{align*}
\]

Keep \( \frac{\Delta Q}{Q} \approx \text{constant} \)

\[
R_{\text{obs}}(Q_0) \sim \left(\frac{0.9394}{n}\right)^{t_1} R_{\text{act}}(Q) e^{-\left(\frac{2.7725}{n^2}\right)(Q-Q_0)^2} \, dQ
\]

(Assuming a Gaussian distribution of Q-values)
\[
\frac{1}{\lambda} \approx \frac{4\pi \sin \theta}{\lambda}
\]

**Incident Neutron Beam**

**Si Single Crystal**

**Solution**

**Cell**

**E electrode**

**Specularly Reflected Beam**
Structure of symmetric polyolefin block copolymer thin films

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The microstructure of thin films of nearly symmetric poly(ethylene-propylene)–poly(ethylene) (PEP-PEE) diblock copolymers (f = 0.55, where f is the volume fraction of PEP) was characterized by neutron reflectometry (NR). A symmetric film structure in which the PEE block segregates preferentially to both interfaces is observed above and below the bulk order-disorder transition (ODT). Measurements at room temperature for several chain lengths, N, provide a real-space picture of the change in interdomain interfacial profiles associated with the crossover between the strong and weak segregation limits. The polymer/air and substrate/polymer interfaces are observed to induce an ordered microstructure even when the center of the film is disordered. The characteristic dimension of this near surface microstructure is larger than the corresponding bulk value for values of χN lying between those of the bulk Gaussian-to-stretched-coil and order-disorder transitions, where χ is the segment–segment interaction parameter. This behavior is attributed to the correlation of large amplitude composition fluctuations in the film with the interfaces. A mean-field behavior prevails for χN < χN_{ODT,thick}, where some preferential segregation occurs at the interfaces, but the characteristic dimension once again matches that in the bulk.

I. INTRODUCTION

In recent years interest has grown rapidly in understanding how the presence of symmetry breaking interfaces affects the microstructure and transitions of systems that undergo order–order and order–disorder transitions. Two types of systems where considerable study has already proved linked at one point. The overall degree of polymerization, N, the fraction of block A in the chain, f, the A–B segment–segment (Flory–Huggins) interaction parameter χ, are generally assumed to dictate the phase behavior of bulk block copolymers. At equilibrium the melt microstructure is that which minimizes the overall free energy and the transition...
FIG. 5. Thin film morphologies for symmetric PEP–PEE diblock copolymers. (a) Interfacial segregation of PEE occurs for $\chi N < (\chi N)_{GST}$. The center of the film is spatially homogeneous. (b) For $(\chi N)_{GST} < (\chi N) < (\chi N)_{ODT}$ the film contains a microstructured morphology that is oriented at the film interfaces. The range of the orientational correlation increases with increasing $(\chi N)$. (c) A lamellar microstructure that is highly oriented with the film interfaces exists when $(\chi N) > (\chi N)_{ODT}$. 

No. 11, 1 June 1992
Neutron Reflectivity Studies of Surfactants at Electrode Surfaces

Knowledge of the forces that control the assembly of surfactant molecules at the solid-liquid interface is vital for traditional fields such as detergency, flotation, oil recovery and tribology [1]. Thin organic films deposited at solid surfaces also find application in the fabrication of optoelectronic devices, sensors, biosensors, and chemically modified electrodes [2]. It has long been established that the assembly of surfactants at the solid-liquid interface depends on the charge at the solid surface [3, 4]. For example, the spreading of vesicles into a phospholipid bilayer requires that the surface of the solid be negatively charged and hydrophilic.

However, the present understanding of the role played by charge on the interaction of a surfactant molecule with the electrified solid surface is far from being complete. Electrochemistry provides a unique opportunity to study the effect of the charge on the properties of amphiphilic and ionic surfactants at the charged solid-liquid interface [5]. When an organic film is deposited on a gold electrode, the charge density at the metal surface may be varied from about 30 $\mu$C/cm$^2$ to about 40 $\mu$C/cm$^2$. This magnitude of charge generates electric fields on the order of $10^8$ V/m. Such a field interacts with polar molecules in the membrane. By changing the sign of the charge one can use attractive or repulsive forces. In this manner, by turning a knob on a control instrument one can force phase transitions in the film of organic molecules or force surfactants to desorb or re-adsorb on the surface.

We have recently employed electrochemical techniques, atomic force microscopy, and neutron reflectivity to study the field driven transformations of thin films formed by a model anionic surfactant, sodium dodecyl sulfate (SDS), at the surface of a gold electrode [6]. Figure 1 shows how the surface concentration of SDS at the Au electrode surface changes with the electrode potential. A convenient way to interpret these data is to look at the electrode potential as an operational variable that can be easily adjusted using a control instrument.

Figure 1 shows that the character of SDS adsorption is strongly influenced by the charge on the metal. At sufficiently negative potentials SDS molecules are totally desorbed from the electrode surface. At moderate negative charge densities SDS forms a film characterized by a limiting surface concentration $4.0 \times 10^{-12}$ mol cm$^{-2}$. When the metal surface is positively charged the surface concentration of SDS increases to $8.1 \times 10^{-12}$ mol cm$^{-2}$.

Neutron reflectivity experiments carried out on the NG-7 reflectometer were employed to determine the structure of the film formed by SDS at different charge densities at the gold surface. Thin layers of chromium ($\approx 20 \AA$) and gold ($\approx 80 \AA$) were sputtered onto the crystal quartz substrate. After cleaning, the crystal was mounted on a specially constructed Teflon® cell [7]. The cell had ports for the counter (gold foil) and reference electrodes (Ag/AgCl, $E = -40$ mV versus SCE). D$_2$O (99.9 % molecular fraction) was used as a solvent in reflectivity studies.

Figure 2a shows the neutron reflectivity data determined for SDS adsorption at various electrode potentials, and Fig. 2b shows the scattering length density profiles calculated from the reflectivity curves. The neutron reflectivity data are consistent with electrochemical measurements. They show that at very negative potentials the gold solution interface is free from hydrogenated species. When
the potential increases, the film of hydrogenated species appears at the electrode surface. The thickness of this film increases, and the scattering length density progressively decreases, with increasing potential. When combined with the results of electrochemical measurements and atomic force imaging, the neutron reflectivity data allow the determination of the structure of the film formed at different charge densities. At small or moderate negative charge densities SDS molecules form a hemimicellar film that consists of hemicylindrical stripes, as first observed by Mane [4]. The packing of SDS molecules in a cross section of that hemicylinder is shown schematically in Fig. 3 (top). At positive charge densities the hemimicellar state is transformed into the interdigitated bilayer schematically shown in Fig. 3 (bottom).

The results of this study demonstrate the need for the use of neutron reflectometry to study adsorption and phase transitions in films of surfactants adsorbed at the solid-solution interface. Specifically, they show that when neutron reflectivity measurements are combined with electrochemical studies and atomic force microscopy, they provide unique opportunities to study different stages involved in the interaction of surfactants with solid surfaces.

FIGURE 2. (a) Normalized neutron reflectivity curves for a Au/Cr-coated quartz substrate in 0.016 mol/L SDS in D$_2$O. (b) Scattering length density profiles of the interface as determined from the fitting procedure.

References

Phase Sensitive Neutron Reflectometry on a Water-Cushioned Biomembrane-Mimic

Biomimetic membranes have been developed as models of living cell membranes, and this has applications in the quest for biocompatibility of inorganic materials in biologically active mediums, such as coatings for artificial organs. A membrane consists of a lipid bilayer (two lipid layers) where hydrophobic carbon chains form the inside of the membrane and their polar head groups the interface with the aqueous surrounding medium. A supported membrane-mimic consists of a lipid-like bilayer, typically attached to a single-crystal substrate, with access to water only at the top surface [1, 2]. Here we use neutron reflectometry to study a system in which water has access to both sides of a membrane-mimic attached to such a substrate, thus making the system a closer mimic to a real cell membrane.

The system devised by Liu et al. [3] consists of a water-swellable polyelectrolyte that electrostatically binds to the substrate and acts as a "cushion" for the membrane, not unlike the cytoskeletal support found in actual mammalian cell membranes. The lower half of the membrane-mimic is a terpolymer that attaches to the polyelectrolyte. A phospholipid layer forms on top of the terpolymer and the bilayer is finally chemically crosslinked for added stability. The system is shown schematically in Fig. 1.

Neutron reflectivity measurements were performed at the NG-1 vertical stage reflectometer to obtain the compositional profile at every step of the assembling process of the membrane-mimic which consisted of three stages: a) polyelectrolyte multilayer (PE), b) polyelectrolyte multilayer plus terpolymer (PE+TER), and c) polyelectrolyte multilayer plus terpolymer plus phospholipid layer (PE+TER+PC) [4]. The spatial resolution attained was approximately 10 Å, about half the thickness of a membrane bilayer, making it possible to distinguish the two layers of a membrane but not the structure of a single layer.

A unique compositional profile of the biomimetic film with no a priori knowledge of the sample's composition is obtained by measuring the reflectivity of equivalent samples made onto two substrates [5]. The substrates used were single crystal silicon (Si) and sapphire (Al$_2$O$_3$) coated with chromium (Cr) and then a gold (Au) layer to allow the polyelectrolytes to bond to a similar surface on both wafers.

Figure 2 shows the compositional profiles for the PE, PE+TER, and PE+TER+PC assemblies in a D$_2$O atmosphere at 92 % relative humidity. The figures shows that the hydration of the PE layer is almost unaffected by the addition of the terpolymer and the phospholipid layer. Also, upon the addition of the phospholipid layer to the PE+TER assembly, the composite PE+TER+PC assembly shows an increase in thickness of approximately 30 Å, consistent with the formation of a single phospholipid layer at the surface. It is also clear that the addition of a phospholipid layer onto the terpolymer layer rearranges this region.

Fig. 1. Schematic diagram of a biomimetic membrane. The phospholipid layer at the top combines with the terpolymer layer to form a membrane-mimic that in turn resides on the water (blue dots) permeable "cushion" polyelectrolyte multilayer. The latter attaches electrostatically to the Au-capped substrate.

Fig. 2. Compositional profile of biomimetic membrane in a D$_2$O atmosphere at 92 % relative humidity at various stages of assembly on Au-capped substrate: only polyelectrolyte (PE), polyelectrolyte and terpolymer (PE+TER), polyelectrolyte, terpolymer and phospholipid (PE+TER+PC). The compositional profile is given by the scattering length density, SLD, profile when using neutrons.
significantly, since the terpolymer layer only becomes apparent after the phospholipid layer is added. It is possible to verify with an independent technique (contact angle) that the terpolymer was in fact deposited because it forms a hydrophobic outer layer. The outer surface becomes hydrophilic once the phospholipid layer is deposited onto the terpolymer layer.

Figure 3 (top) shows the profile for the PE-TER+PC assembly under 92% relative humidity in 100% D₂O and in 50/50 D₂O/H₂O. The overall thickness change due to the intake of water, in going from dry (not shown) to 92% relative humidity, was found to be 20 Å. Figure 3 (bottom) shows the water fraction in the assembly under 92% relative humidity. This is obtained by assuming that the distribution of each component in the layers is unaffected by having either D₂O or 50/50 D₂O/H₂O. From the figure it can be seen that the polyelectrolyte multilayer has a 40% water uptake. This is a significant amount of water, which suggests that the polyelectrolyte multilayer can work as a “cushion” for membrane-mimetic systems. The terpolymer and the phospholipid layers contain an average of 10% water, which is also significant, suggesting that these layers are not tightly packed.

The method of making equivalent samples on two substrates to obtain a unique compositional profile has a built-in congruency test, particularly useful in checking the reproducibility of the samples as well as the quality of the films. The test is to compare the calculated imaginary part of the complex reflectivity from the obtained profile with the corresponding data, as is shown in Fig. 4 for the PE-TER and PE-TER+PC assemblies. From Fig. 4 it is concluded that the PE-TER samples are homogenous and essentially identical while for the PE-TER+PC assembly, the absence of true zeros, as indicated by the calculated curve, is suggestive of a small degree of sample inhomogeneity.

The system from Liu et al. has many characteristics desirable in a biomimetic membrane. It is a single membrane-mimic attached to a significantly hydrated soft “cushion” support that allows some membrane proteins to function. Thrombomodulin, a membrane protein relevant to blood-clotting, is being studied in this membrane-mimic environment to further develop biocompatible coatings for artificial organs [6].

References

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Figure 1:

1 Schematic representation the terpolymer (TER)-acrylate phospholipid (PC) membrane mimic supported on a polyelectrolyte multilayer (PE) "cushion". 

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Fig. 3. Scattering length density profiles (top) and water fraction (bottom) for PE+TER+PC under indicated conditions.
A computer simulation of a 0.8-nm slab of a phospholipid bilayer in water. Phosphorus atoms are shown in green, nitrogen atoms in dark blue, lipid oxygen atoms in red, terminal-chain groups in magenta, and other carbon atoms in gray; the carbon hydrogen atoms are omitted. The water molecules are shown in yellow (oxygen) and white (hydrogen).
(From R.M. Venable, Y. Zhang, B.J. Hardy, and R.W. Pastor, Science 262, 223–228, 1993.)
Lipid Phase Transitions

$L'_B$ Crystalline
"Gel" State

$L_\alpha$ Liquid Crystalline
Fluid State (thinner)

Transition State $P_\alpha$
Surface Effect?

Increasing Temperature

<table>
<thead>
<tr>
<th>Lipid</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMPC</td>
<td>24 (14) °C</td>
</tr>
<tr>
<td>DPPC</td>
<td>42 (35) °C</td>
</tr>
<tr>
<td>DSPC</td>
<td>54 (49) °C</td>
</tr>
</tbody>
</table>

(S. Krueger et al.)
Effect of Temperature on the Neutron Reflectivity of DPPC in Si-Matched H$_2$O/D$_2$O

![Graph showing the effect of temperature on neutron reflectivity](image)

- 60 °C
- 20 °C

S. Krueger et al.
Supported Lipid Bilayers
A model system to mimic the structure and dynamics of cell membranes.

Proteins in Lipid Bilayers

- Difficult to characterize by traditional x-ray crystallography.

- Play a crucial role in cell function
  - regulate ion and nutrient transport
  - engage in binding, signalling and cell recognition
  - participate in cell fusion events.

Biosensors (Anne Plant & coworkers)
Melittin in Hybrid Bilayer Membranes

- pore-forming toxin
- used as model membrane peptide
- active in HBMs

- depth of penetration into bilayer
- nature of pore (water-filled?)
- conformational changes
- random or ordered distribution?
- influence on surrounding lipids (location, conformation)

S. Krueger, A. Plant, et al., NIST (Langmuir)
FIGURE 1. Family of scattering length density profiles obtained by model-independent fitting of the reflectivity data in the inset. The profile represented by the blue dashed line is unphysical for this Ti/TiO film system yet generates a reflectivity curve that fits the data with essentially equivalent goodness-of-fit (all the reflectivity curves corresponding to the SLD’s shown are plotted in the inset but are practically indistinguishable from one another).
**Inverting reflectivity**

**Phase determination**
A.A. van Well, S. Adenwalla, & G.P. Felcher

**Logarithmic dispersion**

**Tunneling times**

**Pseudo-inversion**
Phase Determination with 3 References

Prepare
\[ \rho + \rho_{\text{ref}} \]
\[ \rho + \rho_{\text{ref}} \]
\[ \rho + \rho_{\text{ref}} \]

Measure
\[ |r|^2 \]
\[ |r|^2 \]
\[ |r|^2 \]

Invert

(Unique) \( r \)

Reduce (algebraically)

Majkrzak & Berk, 1995
de Haan, et al., 1995
**UNIQUE DETERMINATION OF BIOMIMETIC MEMBRANE PROFILES BY NEUTRON REFLECTIVITY**

New biomimetic membrane materials, of fundamental importance in understanding such key biological processes as molecular recognition, conformational changes, and molecular self-assembly, can be characterized using neutron reflectometry. In particular, scattering length density (SLD) depth profiles along the normal to the surface of a model biological bilayer, which mimics the structure and function of a genuine cell membrane, can be deduced from specular neutron reflectivity data collected as a function of wavevector transfer $Q$. Specifically, this depth profile can be obtained by numerically fitting a computed to a measured reflectivity. The profile generating the best fitting reflectivity curve can then be compared to cross-sectional slices of the film's chemical composition predicted, for example, by molecular dynamics simulations [1]. However, the uniqueness of a profile obtained by conventional analysis of the film's reflectivity alone cannot be established definitively without additional information. In practice, significantly different SLD profiles have been shown to yield calculated reflectivity curves with essentially equivalent goodness-of-fit to measured data [2], as illustrated in Fig. 1.

The existence of multiple solutions, only one of which can be physical, is especially problematic in cases where a key additional piece of structural or compositional information is lacking as can happen in the investigation of these biological membrane systems.

Why this inherent uncertainty? The neutron specular reflection amplitude for a model SLD can be computed exactly from first principles; the square of its modulus gives the measurable reflectivity. It is firmly established, however, that the complex amplitude is necessary and sufficient for a unique solution of the inverse problem, that of recovering the SLD from reflection measurements. Unambiguous inversion requires both the magnitude and phase of reflection. Once these are known, practical methods [3] exist for extracting the desired SLD.

In fact, considerable efforts were made about a quarter century ago to solve the analogous "phase problem" in X-ray crystallography using known constraints on the scattering electron density [4] and by the technique of isomorphic substitution [5]. Variations of the latter approach have been applied to reflectivity, using a known reference layer in a composite film in place of atomic substitutions. These

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**FIGURE 1.** Family of scattering length density profiles obtained by model-independent fitting of the reflectivity data in the inset. The profile represented by the blue dashed line is unphysical for this Ti/TiO film system yet generates a reflectivity curve that fits the data with essentially equivalent goodness-of-fit (all the reflectivity curves corresponding to the SLD's shown are plotted in the inset but are practically indistinguishable from one another).

**FIGURE 2.** Reflectivity curves for the thin film system depicted schematically in the inset, one for a Si fronting (red triangles), the other for Al$_2$O$_3$ (black circles). The curve in the lower part of the figure (blue squares) is the real part of the complex reflection amplitude for the films obtained from the reflectivity curves by the method described in the text.
solution methods, however, were tied to the Born approximation, which generally is valid in crystal structure determination but which fails catastrophically at low Q (low glancing angles) in reflection from slab-shaped samples such as thin films. Exact inversion requires accurate knowledge of the reflection amplitude over the entire Q-range, especially at low Q.

In this decade the reflection phase problem has been exactly solved using a protocol of three reflectivity measurements on composite films consisting of the film of interest in intimate contact with each of three known reference layers [6, 7]. Subsequently, variations using only two measurements have been shown to partially solve the phase problem, an additional procedure being required to choose between two solution branches, only one of which is physical [8, 9]. In the past year [10], an exact solution has been found for a two measurement strategy in which the film surround, either the fronting (incident) or backing (transmitting) medium, is varied. This new approach is simpler to apply than reference layer methods and is adaptable to many experiments. Surround variation neutron reflectometry has been successfully applied to the challenging type of biological membrane depth profiling described earlier.

In Fig. 2 are plotted a pair of neutron reflectivity curves measured for the layered film structure schematically depicted in the upper right inset, one with Si and the other with Al₂O₃ as the fronting medium. The lower part of Fig. 2 shows the real part of the complex reflection amplitude for the multilayer as extracted from the reflectivity data, according to the method described above, and which was subsequently used to perform the inversion to obtain the SLD shown in Fig. 3. For comparison, the SLD predicted by a molecular dynamics simulation is also shown in Fig. 3, in a slightly distorted version, corresponding to a truncated reflectivity data set, which indicates the spatial resolution of an SLD obtainable in practice. This latter SLD was obtained by inversion of the reflection amplitude computed for the exact model SLD, but using values only up to the same maximum Q value (0.3 Å⁻¹) over which the actual reflectivity data sets were collected. Overall, agreement between the experimentally determined profile and the theoretical prediction is remarkable, essentially limited only by the Q-range of the measurement. Surround variation neutron reflectivity thus makes it possible to measure complicated thin film structures without the ambiguity associated with curve fitting. The veridical SLD profile is obtained directly by a first principles inversion.

REFERENCES:
FIGURE 2. Reflectivity curves for the thin film system depicted schematically in the inset, one for a Si fronting (red triangles), the other for Al₂O₃ (black circles). The curve in the lower part of the figure (blue squares) is the real part of the complex reflection amplitude for the films obtained from the reflectivity curves by the method described in the text.
FIGURE 3. SLD profile (red line) resulting from a direct inversion of the Re r of Fig. 2 compared with that predicted by a molecular dynamics simulation (white line) as discussed in the text. The headgroup for the Self-Assembled-Monolayer (SAM) at the Au surface in the actual experiment was ethylene oxide and was not included in the simulation but, rather, modelled separately as part of the Au. Also, the Cr-Au layer used in the model happened to be 20 Å thicker than that actually measured in the experiment.
\[
F = \sum_{j=1}^{N} \left[ \frac{b_{sj}}{p_{sj}} \cos \phi \right] e^{iQu_j}
\]
\[
F = \sum_{j=1}^{N} p_{sj} \sin \phi e^{iQu_j}
\]

\[
Q = |k_f - k_i|
\]
Crystallographic Direction

[0 0 l]

Magnetic Atom Layer

Interdiffusion

Strain

hydrogen

electron

Intervening Layer
(e.g., insulating, normal, semi-, or super-conducting)

Magnetic Atom Layer

Epitaxial Growth of Superlattices
(Andreas Schreyer et al. - polarized neutron reflection/diffraction)
REFERENCES


* Neutron Reflectometry Studies of Thin Films and Multilayered Materials, C.F. Majkrzak, Acta Physica Polonica A 96, 81(1999) -- this article can also be found at the website: http://www.ncnr.nist.gov -- along with some additional information on analysing neutron reflectivity data (click on "Summer School Course Materials")
