Introduction to Neutron Reflectometry (NR)

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Outline

• Principles of Neutron Reflectometry

• Reflectometry of Non-Polarized and Polarized Neutrons from Solid Interfaces

• Neutron Reflectometry from Interfaces with Liquids

• Experimental Aspects of Neutron Reflectometry
• **Principles of Neutron Reflectometry**

• Reflectometry of Non-Polarized and Polarized Neutrons from Solid Interfaces

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• Experimental Aspects of Neutron Reflectometry
NR modes

\[ \vec{q} = \vec{k} - \vec{k}_0 \]

Specular reflection
NR modes

\[ \mathbf{q} = \mathbf{k} - \mathbf{k}_0 \]

- Specular reflection
- Off-specular scattering

incident beam: \(\mathbf{k}_0\)
reflected beam: \(\mathbf{k}\)
transmitted beam: \(\mathbf{k}_0\)
NR modes

\[ \vec{q} = \vec{k} - \vec{k}_0 \]

- Specular reflection
- Off-specular scattering
- GISANS (Grazing Incidence Small-Angle Neutron Scattering)

incident beam \( \vec{k}_0 \)

transmitted beam \( \vec{k}_0 \)

reflected beam \( \vec{k}_0 \)

\( q_x \) Off-specular scattering

\( q_z \) Specular reflection

\( q_y \) GISANS

(Grazing Incidence Small-Angle Neutron Scattering)
3D Reflectometry

Complete reflectometry \( q_x q_y q_z \)

\[ \bar{q} = \bar{k} - \bar{k}_0 \]

\( q_x \) Off-specular scattering

\( q_z \) Specular reflection

GISANS (Grazing Incidence Small-Angle Neutron Scattering)

\( u_z(x,y) \) - vertical surface displacement

\( \xi_x, \xi_y \) - correlation lengths
**Specular reflection**

**Tight collimation of incident beam over Z-direction**

**Optical approach**

\[ R(q_z) = \frac{I_f}{I_0} \]

**Reflectivity**

\[ \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \]

\[ \theta = 2\alpha_i \]

\[ \alpha_i \sim 1 - 10 \text{ mrad} \]

**Total external reflection**

\[ R = 1 \quad \text{at} \quad \alpha_i < \alpha_c \quad \cos \alpha_c = n \]

\[ \alpha_c^2 \approx 1 - n^2 \quad \Rightarrow \quad \alpha_c = \lambda \sqrt{\frac{N}{\pi} \bar{b}} \]

for $^{58}\text{Ni}$ \( (\alpha_c/\lambda) \approx 0.0017 \text{ rad/Å} \)

**Fresnel law**

\[ q_z \approx 4 \sin \frac{\theta}{2} \]

\[ q_z \approx 4 \left( \frac{\pi \rho}{\lambda} \right)^{1/2} \]

\[ q_{zc} \approx 4(\pi \rho)^{1/2} \]

At \( q_z \to \infty \) \[ R(q_z) \approx \left( \frac{1}{16} \right) \left( \frac{q_{zc}^4}{q_z^4} \right) \]
Specular reflection

Tight collimation of incident beam over Z-direction

Quantum-mechanical approach

\[ q_{zc} = 2\sqrt{2mU_{opt}/\hbar^2} \]

\[ r = (k_{0z} - k_{1z})/(k_{0z} + k_{1z}) \]

\[ t = 1 + r = 2k_{0z}/(k_{0z} + k_{1z}) \]

\[ k_{0z} = \sqrt{2mE_\perp/\hbar^2} \]

\[ k_{1z} = \sqrt{2m(E_\perp - U_{opt})/\hbar^2} \]

\[ R = |r|^2 = \left| \frac{k_{0z} - k_{1z}}{k_{0z} + k_{1z}} \right|^2 = \frac{1 - \sqrt{1 - U_{opt}/E_\perp}}{1 + \sqrt{1 - U_{opt}/E_\perp}}^2 \]

\[ E_\perp > U_{opt}, \text{ or } q_z > q_{zc} \]
Off-specular scattering

Rough interface

\[ G(z) = \left(\frac{1}{\sqrt{2\pi}\sigma}\right) \exp\left[-\frac{z^2}{2\sigma^2}\right] \]

\[ R(q_z) = \exp\left(-4z^2 k_0^2 k_{1z}^2 / \sigma^2\right) R_F(q_z) \]

Roughness should be as minimal as possible!
Off-specular scattering

Correlated roughness

\[ <U_j(x, y)U_j(x', y')> = \sigma^2 e^{-\frac{r^{2H}}{\xi}} \tau = \left[ (x - x')^2 + (y - y')^2 \right]^{\frac{1}{2}} \]

- The Hurst parameter, \( H = 3 - D \) (\( D \) is the surface fractal dimension) is varied between 0 and 1.
- The lateral correlation length \( \xi \) acts as a cut-off for the lateral length scale on which an interface begins to look smooth. If \( \xi \gg \tau \) the surface is smooth.

Distorted-wave Born approximation (DWBA)

non-distorted

\[
\begin{align*}
[D_0 - 4\pi \hat{v}(r)]\Psi(r) &= 0 \\
D_0 &= \nabla^2 + K^2 \\
v(r) &= \frac{m}{2\pi\hbar^2} V(r) = \sum_j \langle b_j \delta[r - r_j(t)] \rangle
\end{align*}
\]

distorted

\[
\hat{v}(r) = \tilde{v}(z) + \hat{u}(r)
\]

In-plane function

\[
\frac{d\sigma}{d\Omega} = \left| \int d^3r \Psi_i(r)\hat{u}(r)\Psi^*_f(r) \right|^2
\]

BornAgain program software

Calculated 2D patterns of NR diffuse scattering from semi-infinite medium of Cu, interface roughness $\sigma = 2$ nm, in-plane roughness correlation length $\xi_\parallel = 100$ nm (a), $\xi_\parallel = 1000$ nm (b).

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Calculations have been made in the Distorted Wave Born approximation (DWBA) using Program BornAgain; https://www.bornagainproject.org/
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Grazing incidence small-angle scattering

Tight collimation of incident beam over Z- and Y- directions

\( R = 10 \text{ nm}, \text{hexagonal lattice (orientation \{11\}, along } x). \)
\( \xi_\parallel = 400 \text{ nm}; n = 1 - \delta; \delta = 6 \times 10^{-4}; \text{substrate } \delta = 6 \times 10^{-6}; \)
\( \lambda = 1 \text{ A }^\circ, \alpha_i = 0.2^\circ. \)
Steady-state and TOF modes

Steady-state (SS) mode

- $\lambda$ is fixed (monochromatization)
- $\theta$-scan (grazing angle)

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

Time-of-flight (TOF) mode

- $\theta$ is fixed
- $\lambda$-scan

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

$$\lambda = \frac{h \, \text{TOF}}{mL}$$

time-of-flight
flight path

monochromatic beam

TOF
Neutron reflectometry experiment is aimed at determining the scattering length density distribution at planar interfaces. Two equivalent approaches to treat specular neutron reflectivity from planar interfaces exist. Optical approach is an extension of the laws of the geometrical optics of light to the case of neutrons. In quantum mechanical approach, the reflectivity is derived by considering neutron wave functions meeting barriers of the optical potential. Off-specular scattering occurs for rough interfaces. It reduces the specular reflectivity. The distribution of off-specular scattering is sensitive to in-plane (lateral) correlations. Lateral ordering of nanoscaled objects at interfaces produces 2D diffraction patterns (widened Bragg rods) in GISANS plane.
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Reflectivity of arbitrary interface

\[ R(q_z) = \frac{16\pi^2}{q_z^4} \left| \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \rho(z) e^{-iq_z z} dz \right|^2 \]

- contrast \( \Delta \rho \)
- thickness of thin layer
- period of superlattice
Small-angle Scattering and Reflectometry

Small-angle scattering (SAXS, SANS)
- bulk structure

Reflectometry (XRR, NR)
- structure at interface
Block copolymer (PS-d-b-PBMA) multilayers mixed with nanoparticles (Fe$_3$O$_4$, D ~ 5 nm) on Si substrate.

Off-specular scattering from multilayers

Ideal interfaces

Scattering from a non-magnetic multilayer

\[ \sigma = 0.5 \text{ nm}, \]
\[ \xi_{\|} = 30 \text{ nm}, \]
\[ \xi_{\perp} = \infty \]

\[ \text{d} = 80 \text{ Å}, \]
\[ D = 960 \text{ Å}, \]
\[ N = 12 \text{ layers} \]

\[ 2n\pi/D \]
\text{total thickness oscillations}

\[ 2n\pi/d \]
\text{bilayer thickness Bragg peaks}

Rough interfaces

Conf = \infty

Bragg-sheet scattering

Off-specular scattering in TOF mode

Molecular mixing at a conjugated polymer interface

F8 [100 nm]/ d-PMMA [48 nm] / Si


Initial film

After annealing (Yoneda wing is marked by white line)

D17, ILL
Polymer P(S-b-MMAd) film (thickness 800 nm) on Si.

Penetration depth depends on neutron wavelength

\[
z_{1/e} = \frac{\lambda}{2^{1/2} \pi (l_i + l_f)^2}
\]

\[
l_{i,f} = \left( (\alpha_i^2 - \alpha_c^2) + \sqrt{(\alpha_i^2 - \alpha_c^2)^2 + (\lambda \mu / 2\pi)^2} \right)^{1/2}
\]

\[\mu = \Sigma_{\text{tot}}\] - volume adsorption coefficient

Both reflected and refracted beams are measured!

Polarized neutrons


Refraction index

\[
(n^\pm)^2 = 1 - \left[ \frac{\lambda^2 N_B}{\pi} \pm \left( \frac{m}{2\pi\hbar^2} \right) \mu_B \right]
\]

Nuclear SLD \( \rho_n = N_B \)

Magnetic SLD \( \rho_m = \left( \frac{m\mu_B}{2\pi\hbar^2} \right) \)

\[
q_{zc}^\pm = \left( q_{zcn}^2 \pm q_{zcm}^2 \right)^{1/2}
\]

\[
q_{zcn, zcm} = 4(\pi\rho_{n,m})^{1/2}
\]

\[
R^\pm (q_z) = \left| \frac{1 - \sqrt{1 - (q_{zc}^\pm)^2 / q_z^2}}{1 + \sqrt{1 - (q_{zc}^\pm)^2 / q_z^2}} \right|^2
\]
Reflectivity of arbitrary interface. Polarized neutrons

\[ R^\pm (q_z) = \frac{16\pi^2}{q_z^4} \left| \int_{-\infty}^{+\infty} \frac{d}{dz} \left[ \rho_n(z) \pm \rho_m(z) \right] e^{-iq_z z} \right|^2 \]
Polarization of neutron beams

\[ P = \frac{N_+ - N_-}{N_+ + N_-} \]

\[ P = \frac{R_+(k) - R_-(k)}{R_+(k) + R_-(k)} \]
Off-specular scattering of polarized neutrons

\[ \psi_{\perp i}(z) = \exp(ik_{0z}z) \begin{pmatrix} \psi_{+}^{(i)} \\ \psi_{-}^{(i)} \end{pmatrix}; \quad - \text{Incident beam} \]

Mixed states

\[ \psi_{\perp f}(z) = \exp(-ik_{0z}z) \begin{pmatrix} \psi_{+}^{(f)} \\ \psi_{-}^{(f)} \end{pmatrix}. \quad - \text{Reflected beam} \]

Coefficient of reflection

\[ \hat{r} = \begin{pmatrix} r_{++} & r_{+-} \\ r_{-+} & r_{--} \end{pmatrix} \begin{pmatrix} \psi_{+}^{(f)} \\ \psi_{-}^{(f)} \end{pmatrix} = \hat{r} \begin{pmatrix} \psi_{+}^{(i)} \\ \psi_{-}^{(i)} \end{pmatrix} \]

Solutions of the system of Schrödinger equations!

\[
\begin{align*}
R_{++} = R_{+} &= |r_{++}|^2 \\
R_{--} = R_{-} &= |r_{--}|^2 \\
R_{-+} &= |r_{-+}|^2 \\
R_{+} &= |r_{+}|^2
\end{align*}
\]

Reflectivity matrix

\[
\begin{align*}
\text{reflection from in-plane } M\text{-component} \\
\text{reflection from out-of-plane } M\text{-component (e.g. magnetic roughness)}
\end{align*}
\]
Full polarization analysis

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

spin-flip reflectivities give $M_{\perp}(Q)$
Magnetic multilayers

\[ q_i = 2k_0 \sin \alpha_i \quad \text{and} \quad q_f = 2k_0 \sin \alpha_f \]


Software: FitSuite

L. Deák et al, PRB 76 224420 (2007)
Neutron reflectometer

PBR polarized beam reflectometer (NIST)

Main units

- **Polarizer** (spin polarization of neutron beam)
- **Spin-flippers** (change of beam polarization at given polarization after polarizer or sample)
- **Analyzer** (analysis of polarization after sample)
- **Detector** (detection of scattered and transmitted beams)
Neutron reflectometer

GINA reflectometer (BNC, Budapest)

http://mffo.rmki.kfki.hu/gina
Domain structure in thin films with perpendicular anisotropy

CoCrPt films

SuperADAM, ILL

Micromagnetic simulations

- $M_z > 0$
- $M_z < 0$

NR

D. Navas, PRB 90, 054425 (2014)
Magnetic bilayer with exchange bias

CoO [2 nm] / Co [20 nm]

HZB

GISANS. Polarized neutrons

KWS-2, FRJ-2

FeCoV/TiN$_x$
polarizing supermirror

Roughness: $\zeta_R \approx 15$ nm

Magnetic correlations: $\zeta_M \approx 200$ nm

Summary to ‘Reflectometry of non-polarized and polarized neutrons from solid interfaces’

- Three neutron reflectometry modes are efficient in the characterization of the multilayered interface structures at interfaces. In addition to the structure, modulation along the depth profile, the characteristic of the distributions in in-plane and out-of-plane correlations are well determined using specific features in off-specular scattering and GISANS patterns.

- Polarized neutron reflectometry is very efficient in the study of magnetic layered interface structures. The characteristics of the magnetic scattering length density distribution at interfaces are related to the magnetization distribution. Thus, the method represents a spatial magnetometry.
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Horizontal reflectometers

Time-Of-Flight setup - GRAINS, IBR-2

Steady-State setup - N-REX, MLZ

Horizontal sample plane → studies of interfaces with liquids:

- Solid – Liquid;
- Air – Liquid;
- Liquid – Liquid
NR from Solid-Liquid interfaces

Sample volume
5-10 ml

Si crystal block
(5 \times 7.5 \times 1.5 \text{ cm}^3)
Simplest interface: Silicon - Water

Specular reflectivity: contrast variation

Diffuse scattering: long-period non-homogeneities of substrate

TOF mode (GRAINS, Dubna)

Interface Assembling of Magnetic Nanoparticle from Ferrofluids Induced by Non-Homogeneous Magnetic Field

Nanomagnetite (⌀ 2-200 nm) in transformer oil, $\varphi_m \sim 6\%$

GRAINS, IBR-2, Dubna

Adsorption of nanoparticles from aqueous magnetic fluids on silicon substrate

Effect of polymer (PEG) modification

PEG – poly(ethylene glycol)


Amyloidβ Peptides in interaction with raft-mime model membranes

Vertical geometry

D17, ILL, Grenoble

Study of Electrolyte-Electrode Interfaces by NR

counter electrode (CE)

Li

LiClO$_4$/d-PC

electrolyte

SEI

working electrode (WE)

Ti

Si

n

propylene carbonate (PC)

h-PC
d-PC

$Z$, nm

$S LD_x \times 10^{-6} \text{Å}^{-2}$
Study of Electrolyte-Electrode Interfaces by NR

counter electrode (CE)

LiClO₄/d-PC

electrolyte

SEI

propylene carbonate (PC)

working electrode (WE)

Ti

n

θ

k

q

θ

k

h-PC
d-PC

Z, nm

SLD, x 10⁻⁶ Å⁻²

Ti  Si  Au  Cu  Ni

-20

0

20

40

60

80
Study of Electrolyte-Electrode Interfaces by NR

Formation of Solid Electrolyte Interphase (SEI) on plane metal anodes

GRAINS TOF Reflectometer, IBR-2, Dubna
Effect of TBAP: neutron reflectometry

tetra-n-butylammonium perchlorate (TBAP)

Effect of TBAP: neutron reflectometry

- SLD: 10^{-6} \text{Å}^{-2}
- distance from interface, nm

**Thickness**
- No additive
- With TBAP

**Roughness**
- No additive
- With TBAP

**SLD**
- No additive
- With TBAP

**Dense Li**

**+0.5M TBAP**

**Crystalline Li**
Smoothening of polyelectrolyte multilayers with molecular additive (glutamic acid)

Adsorption of polyelectrolytes on Si from D₂O sample ML:
PEI/((PSS/PAH)₂/(dPSS/PAH))

Sample ML + GA:
PEI/((PSS/PAH)₂/(dPSS/PAH/GA))₃

TREFF, MLZ

Neutron reflectometry from free surfaces

Surfactants at air-water interface

MODELS 1-3

FIGARO, ILL

Neutron reflectometry experiments for interfaces with liquids require special cells and sample environment. The active development of such kind of experiments for soft matter research is due to high penetrating power of neutrons and possibilities for enhancing reflectivity by varying the contrast (using deuteration).

The behavior of colloidal liquid solutions at interfaces with solids is an important area of research with the practical impact.

Off specular scattering is sensitive to fine structural effects in liquid-solid interfaces with colloidal solutions.

Study of structural organization of free surfaces of air-liquid interfaces is of current interest.
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Resolution function: vertical sample geometry

Wavelength resolution:
- Graphite monochromator \[ \Delta \lambda / \lambda \sim 1\% \]
- Multilayered monochromator \[ 5\% < \Delta \lambda / \lambda < 20\% \]
- TOF-mode \[ 1\% < \Delta \lambda / \lambda < 20\% \]

Angular resolution:
- Determined by aperture sizes

\[ \delta \theta = (s_1 + s_2) / L \]

For analytical representation see
Additional gravity effect is important for $\lambda > 1$ nm

Model monolayer
$d = 150$ nm ; $\theta = 15$ mrad

Resolution function: horizontal sample geometry

For analytical representation see
Representation of NR data: specular scattering

\[
Q_x = (\pi/\lambda)(\theta_i + \theta_f)(\theta_i - \theta_f)
\]
\[
Q_z = (2\pi/\lambda)(\theta_i + \theta_f).
\]

Steady state mode

TOF mode
Representation of NR data: diffuse scattering

Analysis of NR data: matrix formalism for specular reflectivity

For $j$-th layer

$$M_j = \begin{bmatrix} \cos \beta_j & -(i/p_j)\sin \beta_j \\ -ip_j \sin \beta_j & \cos \beta_j \end{bmatrix}$$

$$p_j = n_j \sin \theta_j \quad \beta_j = (2\pi/\lambda)n_jd_j \sin \theta_j$$

Total reflectivity matrix

$$M = [M_1][M_2] - - - - - [M_n]$$

Reflectivity

$$R^2 = \left| \frac{(M_{11} + M_{12}p_s)p_0 - (M_{21} + M_{22})p_s}{(M_{11} + M_{12}p_s)p_0 + (M_{21} + M_{22})p_s} \right|^2$$

Software: Parrat32, Motofit / IGOR PRO, EFFI, SansView, MAUD …
Resolution function of neutron reflectometer contains wavelength and angular components which in optimum should be close. For reflectometers with horizontal sample plane gravitational effect for long-wave neutrons should be taken into account;

- Off-specular scattering patterns can be represented in different systems of coordinates depending on the mode of experiment and specific scattering features;

- Matrix formalism is one of the mostly used approaches for calculating specular reflectivity and fitting it to experimental curves.