Chapter 3: Neutron and X-ray Reflectometry

3.1 Reflectometry at a glance

X-Ray and Neutron Reflectometry are based on the principle of reflection of x-ray or neutrons from the surface of a thin film. The reflected beam bears signature of the structure of the thin film at mesoscopic length scales [52]. Reflection is an optical phenomenon where electromagnetic radiation (e.g. visible light, x-rays) or matter waves (e.g. neutrons) are reflected from an interface between two media of different indices of refraction. For x-rays and neutrons, however, most materials have indices of refraction marginally less than one. This means that neutrons or x-rays impinging on a surface will undergo total external reflection up to a certain angle of incidence with respect to the reflecting surface. The real part of the refractive index of a medium for neutrons or x-rays can be represented as 1- δ, where δ is typically ~ 10⁻⁶ for neutrons and ~ 10⁻⁵ for x-rays. This entails that total reflection of x-rays/neutrons can occur only when they impinge on a surface at a glancing angle. Reflectivity of the surface is unity up to the critical angle for total external reflection (similar to total internal reflection for visible light) and falls sharply when the incident angle is larger than the critical angle due to penetration of the radiation in the film. This reflected intensity as a function of angle carries information regarding structure of...
the film at mesoscopic length scale in terms of its density, thickness, surface roughness from
where it is reflected.

There are two possible types of reflections from a surface: (a) specular
reflection, which obeys Snell’s law, when the angle of reflection is equal to the angle of
incidence ((θi=θr in Fig. 3(b)) and (b) off-specular reflection, where the above equality is not
maintained. Fig 3.1(a) gives a sketch of specular and off-specular (or diffuse) reflection from
a rough surface. Specifically, specular reflectivity can be used to reconstruct laterally
averaged compositional depth profile along the normal to the surface of the film [53]. Specular neutron reflectivity in un-polarized mode can be used to determine the structural
parameters of thin films in terms of individual layer thickness, interface roughness and the
density of the layers (similar parameters are also given by x-ray reflectivity). In polarized
mode neutron beam is spin-polarized with respect to sample magnetization, either parallel
(reflectivity R+) or anti parallel (reflectivity R–) with a possibility of polarization analysis of
the reflected beam (R++, R+, R–, R–+). From R+ and R– we can obtain additional information
of magnetic moment density profile of a magnetic layer along with the structural parameters
[54,55]. If one carries out polarization analysis of the reflected beam then one can also obtain
in-plane magnetic structure of the thin film [56]. In the present thesis we have used specular
polarized neutron reflectivity (PNR) and x-ray reflectivity (XRR) only for characterizing thin
samples. Specular reflectivity from a sample surface is measured as a function of the wave
vector transfer $Q = \frac{4\pi \sin(\theta)}{\lambda}$ along a direction perpendicular to the sample surface as
shown in Fig.3.1(a), where ‘θ’ is the incident angle on the film and ‘λ’ is the wavelength of
the incident radiation. Off-specular reflectivity introduces a component of wave vector along
the surface of the sample providing information about the lateral in-homogeneties in the
sample. Hence it can be used to obtain the height-height correlation function on a surface,
which provides detail morphology of the surfaces and buried interfaces (in-plane structure) [56].

Figure 3.1: (a) Geometry of specular and off-specular (diffuse) reflectivity (b) Wave function at the interface

3.2 Neutron and X-ray Reflectometry at an interface

Treatment of neutron reflectometry considers the neutron beam as a particle wave and uses quantum mechanics to calculate reflection \((r)\) and transmission \((t)\) amplitudes at the interfaces [56]. For X-ray reflectometry (XRR) one uses Maxwell’s equations leading to continuity of electric field and its derivative, to evaluate the transmission and reflectivity amplitudes [57]. Here we consider an one dimensional potential that varies along the depth of the sample. Considering \(\Psi_0\) and \(\Psi_1\), representing the neutron wave function outside (medium 0) and inside (medium 1) the reflecting sample (Fig. 3.1) we can write:

\[
\psi_0(z) = e^{iK_0z} + re^{-iK_0z} \\
\psi_1(z) = te^{ik_1z} 
\]

Where \(K_0\) and \(K_1\) are the wave vectors in medium 0 and 1 respectively considering ‘Q’, the momentum transfer vector measured along \(z\) direction, normal to the sample surface. The
wave function $\Psi_0(z)$ comprises the incident and the reflected amplitudes. The Schrödinger equation for the wave function in a medium can be written as [56]:

$$\left[ -\frac{\hbar^2}{2m_n}\frac{\partial^2}{\partial z^2} + V(z) \right] \psi(z) = E\psi(z) \quad \text{..........................(3.2)}$$

Where $\hbar$ is Planck’s constant divided by $2\pi$, The potential $V(Z)$ is given by

$$V = \frac{2\pi \hbar^2}{m} N_b, \quad N = \frac{dN_A}{M}$$

is the neutron-nucleus potential seen by the neutron in a medium, $m_n$ is the mass of the neutron, and $E = \frac{\hbar^2 k_0^2}{2m_n}$ is the neutron energy in vacuum and $k = 2\pi/\lambda$, is its wave vector [58]. Where $N, d, N_a, M, b$ are the atomic number density, atomic density, Avogadro’s number, atomic (molecular) weight, and the coherent neutron scattering length respectively.

The intensity of the specularly reflected signal from an ideally flat surface can be calculated by considering continuity of the neutron wave function $\Psi(z)$ and its derivative (electric field $E(z)$ and its derivative for x-rays) at the interface. The result is known as Fresnel relationships, which gives the amplitude of specular reflection and the transmission coefficient of the beam.

Schrodinger’s equation for the neutron wave function in a medium can be given by:

$$\left[ \frac{\partial^2}{\partial z^2} + k_0^2 - 4\pi \rho(z) \right] \psi(z) = 0 \quad \text{..........................(3.3)}$$

From continuity of $\psi$ and $d\psi/dz$ we can get: $1+r = t ; q_1(1-r) = q_2 t$ ; where $q_1$ and $q_2$ are the normal components of the wave vector in vacuum and in the medium respectively and $r, t$ are the reflection and transmission amplitudes. Solving these two equations for $r$ and $t$, we can get:

$$r = \frac{q_1 - q_2}{q_1 + q_2} , \quad t = \frac{2q_1}{q_1 + q_2} \quad \text{..........................(3.4)}$$
Where, \( q_1 = \frac{2\pi}{\lambda} \sin \theta \) and \( q_2 = \sqrt{q_1^2 - 4\pi\rho b} \) and \( \theta \) is the glancing angle. The Fresnel reflectivity for an ideally flat surface, is defined as:

\[
|r_f|^2 = \frac{q_1 - q_2}{q_1 + q_2} = \left| \frac{\sin \theta - \sqrt{n^2 - \cos^2 \theta}}{\sin \theta + \sqrt{n^2 - \cos^2 \theta}} \right|^2
\]  

……(3.5)

From eqn. (3.5), when \( \cos \theta > n \) then \( r \) is a complex number and the Fresnel reflectivity is unity, i.e. for \( \theta < \theta_c \) there will be total external reflection of neutrons. Above the critical angle when \( \theta >> \theta_c \) the reflectivity drops off as \( \theta^{-4} \). Then \( r_f \) can be written as:

\[
r_f = \frac{16\pi^2 \rho^2 \langle b \rangle^2}{Q^4}
\]  

………………(3.6)

This rapid drop in intensity beyond critical angle makes reflectivity experiment intensity limited at larger angles.

### 3.2.1 Refractive Index and Critical Angle

From equation (3.3), it can be shown:

\[
k_i = n k_0 = \sqrt{1 - \frac{4\pi\rho}{k_0} k_0}
\]  

………………(3.7)

Where \( n \) is the index of refraction of the medium (R.I.) for neutrons [59].

According to Snell’s law, at the interface between two media the R.I is defined as:

\[
n = \frac{\cos \theta_i}{\cos \theta_t}
\]  

………………..(3.8)

Where \( \theta_i \) and \( \theta_t \) are angle of incidence and transmission respectively (Fig.3.1 (b)). For total external reflection, at critical angle \( \theta_c \) we have, \( \theta_t = 0 \),

Then,

\[
n = \cos \theta_i = \cos \theta_c = 1 - \frac{\theta_c^2}{2}
\]  

…………………..(3.9)
Under the assumption that $\theta_c \to 0$. Comparing with (3.7) and putting value of $k_0$ for neutrons,

$$n = \sqrt{1 - \frac{4\pi \rho}{k_0^2}} = \left(1 - \frac{\lambda^2}{\pi} \sum_i N_i b_i\right)^{1/2} = \left(1 - \frac{\lambda^2}{2\pi} \sum_i N_i b_i\right)$$

This implies,

$$\theta_c = \lambda \sqrt{N_i b_i / \pi} \quad \text{..................(3.10)}$$

This expression illustrates that the critical angle is dictated by the scattering length density of the medium ($N_i b_i$) for the $i^{th}$ species. The refractive index for neutron is, in most cases, smaller than one except a few materials with negative scattering lengths (e.g. Ti and Mn). This means the neutrons will undergo total external reflection from most of the material surfaces.

Refractive index for neutron as well as for x-rays can be given by a general expression:

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

Where ‘$\delta$’ is the deviation from unity given by $\frac{\lambda^2}{2\pi} \sum_i N_i b_i$ and ‘$\beta$’ contains the absorption term. For most of the materials studied, the absorption coefficient ‘$\beta$’ is very small for neutrons and hence usually neglected. Similar treatment for x-rays yields:

$$n = 1 - \frac{\lambda^2 r_0}{2\pi} \sum_i N_i (Z_i + f_i) \quad \text{..........(3.11)}$$

Where $r_0$ is the classical electron radius $= 2.81\text{fm}$, $N_i$ is the number density, $Z_i$ is the atomic number and ‘$f_i$’ is the energy dependent anomalous dispersion factor for the $i^{th}$ species.

Now comparing with (3.9) critical angle for x-ray can be written as:

$$\theta_c = \lambda \sqrt{\frac{r_0}{\pi} N_i (Z_i + f_i)} \quad \text{..........................(3.12)}$$
For most of the materials the critical angles are about few arc minute per Å wavelength. For x-ray the critical angle are somewhat larger compared to neutrons due to the larger value of δ for x-rays.

3.2.2 Reflectivity from a rough surface

Reflectivity from an ideal surface is given by equation 3.5. But perfectly flat interface or surface can’t be achieved in reality and the modulation of the actual interface between the layers are modified by undulations with respect to the ideal interface (shown as inset in Fig.3.2) and termed as physical roughness.

![Figure 3.2 Effect of roughness on specular reflectivity from Si substrate with σ = 0 Å (solid line) and σ = 10 Å (dashed line). Inset (a) shows image of rough interface with Gaussian profile of height. The standard deviation of the Gaussian function describing the roughness represents the root mean square roughness, σ.](image)

Another kind of in-homogeneity, which arises at the interface, is mixing of two materials due to inter-diffusion. These two components constitute the roughness at an interface. The
influence of the physical roughness and of the inter-diffusion is indistinguishable in specular reflectivity and both are categorized as the root mean square roughness to give a convoluted roughness parameter. For specular reflectivity calculations, they (the physical roughness and mixing due to inter-diffusion) to give an average $\sigma$. It is necessary to incorporate the roughness, i.e., the width of the interface for determining reflected intensity from a sample. Roughness has the effect of reducing the specular intensity at any given momentum transfer value. Inset (a) of Fig 3.2 shows a typical rough interface with the profile of the random height distribution, which is a Gaussian, centered on an average interface. The standard deviation of the Gaussian function describing the roughness represents the root mean square roughness, $\sigma$. The reflectance for a Gaussian rough surface after including the effect of roughness is defined as [60]:

$$r(Q) = r_f e^{-\frac{Q^2 \sigma^2}{2}} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3.13)$$

Where, $Q$ is the momentum transfer vector, given by $Q = \frac{4\pi}{\lambda} \sin \theta$ and $r_f$ is Fresnel reflectance of the ideal surface given in Eqn. (3.5). Roughness adds an exponential damping factor ($e^{-\frac{Q^2 \sigma^2}{2}}$) to the reflectivity, similar to Debye-Waller factor in diffraction [60]. Above equation shows, reflectivity is very sensitive to the roughness of the sample at larger momentum transfer values. Even small roughness will cause a substantial deviation of the reflectivity from the ideal Fresnel case. Fig 3.2 shows the reflectivity of a Si substrate without any roughness (shown by continuous line) and with a roughness of 10 Å (shown by dashed line). Fig. 3.2 shows clearly how the reflectivity from a rough interface deviates from the reflectivity from an ideal smooth surface as a function of $Q$.

Equation 3.13 gives the reflected intensity from the surface of an infinitely thick layer. The reflectivity for a multiple layer or multilayer structure can be obtained by using Parrat’s
formalism [15]. This formalism allows one to calculate the reflected intensity from an idealized stratified medium of known layer thickness and density.

Consider a neutron beam incident on a multilayer stack, i.e., a series of \( N \) layers \((N+1\) interfaces), where the \( i^{th} \) layer has thickness \( d_i \), interfacial roughness \( \sigma_i \), and refractive index \( n_i \) (defined in Eqns. (3.7) as shown in Fig. 3.3 The semi-infinite region below the film, the substrate, has refractive index \( n_s \).

![Diagram of a multilayer stack containing \( N \) layers, where the refractive index, thickness, propagation angle, and interface roughness parameter of the \( i^{th} \) layer are \( n_i, d_i, \theta_i \), and \( \sigma_i \), respectively.](image)

Figure 3.3: Diagram of a multilayer stack containing \( N \) layers, where the refractive index, thickness, propagation angle, and interface roughness parameter of the \( i^{th} \) layer are \( n_i, d_i, \theta_i \), and \( \sigma_i \), respectively.

To find the reflectance for a multilayer, the boundary conditions must be fulfilled at each interface. One needs to start from the bottom layer, which is the substrate (Fig. 3.3) and build the reflectivity upwards to the air-film interface by applying the continuity conditions at every interface. The ultimate goal is to find the reflectance on the top of the multilayer.
Parratt’s formalism is used extensively to generate reflectivity pattern (both for x-ray and neutrons) from multilayer samples theoretically [15].

Consider a sample consisting of \( N \) layers \( j = 1 \ldots N \) as shown in Fig. 3.3. The Fresnel reflectance and transmittance between \( j^{th} \) layer and \( j+1^{th} \) layer can be calculated from the continuity of wave function and its derivative at the interface. For smooth interface the Fresnel reflectance and transmission amplitude are

\[
\begin{align*}
 r_{j-1,j} &= (k_{z,j-1} - k_{z,j}) / (k_{z,j-1} + k_{z,j}) \\
t_{j-1,j} &= 2k_{z,j-1} / (k_{z,j-1} - k_{z,j})
\end{align*}
\]

respectively [57], with \( k_{z,j} \) the \( z \) component of the wave vector in medium \( j \), which is determined by the law of refraction:

\[
k_{z,j} = k(n_j^2 - \cos^2 \theta) \frac{\lambda}{2}.
\]

The glancing angle of incidence is \( \theta \) and \( k = 2\pi / \lambda \) is the modulus of the incoming wave vector (\( \lambda \) is the wavelength of neutron/x-ray). The phase factor that is defined in the middle of two surfaces of \( j^{th} \) medium is

\[
A_j = e^{ik_zd_j/2},
\]

with \( d_j \) = thickness of \( j^{th} \) layer. We first consider a film on a substrate having a thickness \( d \) and uniform scattering length density. The film will have two-step changes in the refractive index, at the air/film and film/substrate interfaces, separated by a distance \( d \). The reflection coefficient of the sample, in terms of the Fresnel reflection coefficients at the substrate/sample interface, \( r_{1,2} \), and at the sample/air interface, \( r_{0,1} \), can be written as:

\[
r = \frac{r_{0,1} + r_{1,2} \exp(2ik_zd)}{1 + r_{0,1}r_{1,2} \exp(2ik_zd)} \quad \text{........................(3.14)}
\]

We can easily extend the above calculation to the case of reflectivity for a system having \( N \) such thin layers (stratified homogeneous media), having smooth interfaces. A set of simultaneous equations similar to Eqn. (3.14) can be solved and one can arrive at a recursive formula [15] given by:
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\[ R_{j-1,j} = \exp(-2ik_{z,j-1}d_{j-1}) \frac{R_{j,j+1} + r_{j-3,j}}{1 + R_{j,j+1}r_{j-1,j}} \]  

\[ \text{.........}(3.15) \]

Where \( r_{j-1,j} \) and \( k_{z,j-1} \) are defined in the above paragraph. To obtain the reflectivity of this system, one solves this recursive relation given by Eqn. (3.15) from the bottom layer with the knowledge that \( R_{n,n+1} = 0 \) since the thickness of this medium (normally the substrate) can be taken as infinite. So the reflectivity of the system (smooth interfaces) is given by \( I = |R_{0,1}|^2 \).

The reflectivity for rough multilayer can be calculated by considering a static ‘Debye – Waller’ like factor (Eqn. 3.13) for reflectance at each interface in multilayer and using above recurrence relation. The Fresnel reflectance from \( j^{-1} \)th layer and \( j^n \)th layer for rough interface is given by:  

\[ r_{j-1,j} = \exp(-2k_{z,j-1}k_{z,j}^{2}) \frac{k_{z,j-1} - k_{z,j}}{k_{z,j-1} + k_{z,j}} \]

The Parratt formalism has the advantage of providing the correct expression for all regions of scattering since no approximation is applied, and any density profile can be modeled by slicing the material in an arbitrary number of thin layers.

3.3 Polarized Neutron Reflectometry (PNR)

Polarized Neutron Reflectometry (PNR) is a tool to investigate the physical as well as magnetization depth profile in thin films and multilayers [61]. This technique is highly sensitive, being able to measure the absolute magnetization of a monolayer of iron (~10\(^{-4}\) emu) with 10% precision [62], and magnetization density as small as 30 emu/cm\(^3\) with comparable precision. Detection of small moments (from samples with surfaces measuring ~ few cm\(^2\) in area) is possible combined with excellent depth resolution of fractions of a nanometer even for films as thick as several hundreds of nanometer.
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Neutrons have a spin $\bar{\sigma}$, related to the magnetic moment $\vec{\mu}_n$ of the neutron by the vector operator:

$$\vec{\mu}_n = \mu_n \bar{\sigma} \quad \text{………………………………… (3.16)}$$

With $\mu_n = -1.913 \beta_N$ [63] and $\beta_N$ the nuclear magnetron equal to $e\hbar / 2m_p c$, where, $e$ is the elementary charge, $m_p$ is the proton mass and ‘c’ is the speed of light in vacuum. From quantum mechanics it follows that the magnitude of the spin of a neutron is always $\hbar / 2$, and only one component of the spin can be quantized along a chosen direction giving the values $\hbar / 2$ or $-\hbar / 2$. For convenience, however, in this thesis “spin up” and “spin down” convention has been used for the magnetic moment of the neutron beam parallel and anti-parallel to the applied field. The spin up component increases the neutron-nucleus scattering potential whereas the spin down component decreases it. Because of the magnetic moment, corresponding to the spin, the potential energy of a neutron in a magnetic medium contains a nuclear and a magnetic term

$$V = V_n + V_m \quad \text{…………………………(3.17)}$$

The nuclear part of $V$ is defined in Eqn. (3.2). The magnetic part of the potential may be written as [64]:

$$V_m = \pm \mu_n B \quad \text{…………………………(3.18)}$$

Where, $B$ is the magnitude of magnetic induction and the $+(-)$ applies for the spin component parallel (anti parallel) [i.e. spin up (spin down)] to the induction. In reflectivity the difference in potential energy $\Delta V$ (i.e. change in refractive index at interface) at an interface, rather than potential energy itself is of importance.

In the experiments described in this thesis, the magnetic field is usually applied in the $y$-direction (see Fig. 3.4 for direction conventions used in this thesis). Further, if it is assumed
that the in-plane magnetization in the sample is parallel to the applied field direction, the magnitude of the magnetic potential can be written as [64].

\[ |\Delta V_m| = \mu_n |B_y - B_0| = \mu_0 n |M_y| \]

Where \( B_0 \) is the magnetic induction outside the sample and \( \mu_0 \) is the magnetic permeability of vacuum.

Analogous to the nuclear scattering length \( b \), a magnetic scattering length \( p \) can be defined. This magnetic scattering length is related to \( \mu_S \) the magnetic moment per atom expressed in units of Bohr magnetrons, by the relation:

\[ p = \frac{m_n \mu_S}{2\pi\hbar^2} \mu_S \]

So the magnitude of magnetic potential difference when entering a sample (which is saturated along in-plane direction, i.e. y-axis in Fig. 3.4) can now be written in terms of \( p \), the magnetic scattering length:

\[ |\Delta V_m| = \frac{2\pi\hbar^2}{m_n} Np \]
Where, \( N \) is same as defined in Eqn. (3.3). So, the total interaction potential for neutron in a magnetic medium can be written in the form

\[
V = V_n + V_m = \frac{\pi h^2}{m_n} N(b \pm p) \quad \ldots \ldots \ldots (3.22)
\]

Where (+) and (-) signs corresponds to the spin up and spin down neutrons with respect to sample magnetization. Now using Eqn. (3.4) and (3.8) the refractive index and critical angle for a neutron in magnetic medium can be written as:

\[
n = 1 - \frac{\lambda^2}{2\pi} N(b \pm p); \quad \theta_c = \lambda \sqrt{\frac{N(b \pm p)}{\pi}} \quad \ldots \ldots \ldots (3.23)
\]

Magnetizing the sample to saturation in the direction perpendicular to the surface of the sample (i.e. along \( z \)-axis, which is also the direction of momentum transfer (\( Q \)) makes \( B_x \) and \( B_y \) vanish. Because \( \nabla \cdot \vec{B} = 0 \), \( B_z \) is the same inside and outside the sample. Therefore, in this case, neutrons hitting the sample experience changes only in nuclear part of potential and one gets pure nuclear contribution to neutron reflectivity.

Fig. 3.5 (a) and (b) shows simulated un-polarized and polarized neutron reflectivity pattern respectively, for a Ni/Al multilayer as a function of wave vector transfer \( Q \) generated using Parrat’s formalism explained above. For simulating polarized reflectivity pattern we have used the bulk magnetic moment (0.60\( \mu_B \)) for Ni atom.

The difference in the reflectivity pattern of the sample for spin up and spin down neutrons is due to the difference in the step potential due to magnetic part of the Ni layers for the spin up and spins down neutrons. The change in critical angle (Eqn. 3.23) for the two spins is also evident in Fig. 3.5.
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3.4 Polarized Neutron Reflectometer at DHURUVA

In case of polarized neutron reflectometry one measures the specularly reflected intensity as a function of wave vector transfer \( Q \). The wave vector transfer \( Q \) is scanned either by collecting the data by varying \( \theta \) with a fixed \( \lambda \) (monochromatic beam reflectometer) or by using a white beam with varying \( \lambda \) and collecting the data at a fixed angle \( \theta \) (time of flight (TOF) reflectometer). In the present case we used a monochromatic beam reflectometer at DHURUVA reactor, BARC, INDIA. In this type of reflectometer it is desirable to use neutrons of longer wavelength, preferably in the range of 2-5 Å. A monochromator with a large mosaic spread (0.5° corresponding to \( \delta \lambda / \lambda \sim 1\% \)) and high reflectivity should be chosen. For specular reflectivity measurements the sample and the detector are moved in 0–20 mode to cover the desired \( Q \) range. This can also be achieved by using a linear position sensitive detector (PSD), where only sample table is rotated to cover the desired \( Q \) range and the
reflected beam is detected on the PSD without moving the detector. This rotation stage needs to have resolution in the range of tens of arc seconds. A constant wavelength instrument is the simplest and probably the cheapest type of reflectometer that can be built.

3.4.1 Description of the instrument

The schematic diagram of the PNR set up is shown in Fig. 3.6 (a). Neutron beam from a reactor beam tube is carried to an adjacent laboratory using a curved neutron guide tube (GT) which can transport neutrons out from the reactor hall. The reflectometer is located on a thermal neutron guide tube with a radius of curvature of 3.3 km (critical wavelength 2.2 Å). The [119] reflection from a cylindrical Si single crystal monochromator gives a monochromatic neutron beam of 2.5 Å reflected at approximately 99 degree angle with respect to the guide tube axis. The chosen reflection [Si(113)] does not have any second order contamination and comes out nearly normal to the guide axis, which is desirable. The beam from the monochromator enters a collimator, consisting of two vertical cadmium slits located at a distance of 800 mm from each other, that gives the initial collimation of the beam. The Cd slits have heights of 40 mm and horizontal width varying from 0.1 to 1 mm. Following the collimator there is a non-polarizer/polarizer mirror assembly on a translation and rotation stage combination. Two such non-polarizer/polarizer super mirror assemblies along with their rotation and translation stages had been procured from PNPI, St Petersburg, Russia. The assembly consists of two neutron mirrors, a non-polarizing supermirror and a polarizing neutron supermirror in a permanent magnetic field with their reflecting planes vertical, placed nearly parallel to each other at a distance of approximately 10 mm. One can switch from un-polarized to polarized beam mode quite easily by predetermined rotation and translation to bring the required mirror in the neutron beam.
A D.C. (Mezei) flipper [65] for flipping the spin of the polarized neutron beam is located after the polarizer. Following the flipper there is a third Cd-slit, close to the sample stage for final collimation. A neutron beam of horizontal divergence in the range of 0.8–5 arc min can be delivered on the sample using several combinations of Cd-slits. The sample is placed on a translation stage which itself is located on top of a high precision rotation stage. The smallest step size of the rotation 0.001° with an accuracy of 15 arc min. There is also an absolute encoder at the bottom of the rotation stage to provide true rotation. The sample is placed between the pole pieces of a permanent magnet of 2 kG strength (vertical) for in-plane magnetization of the samples during polarized runs. A Position Sensitive Detector (PSD) allows one to collect specular as well as off-specular (or diffuse) data simultaneously around any specular peak. This configuration overcomes the intensity problem for collecting off-specular (diffuse scattering) reflectivity data in a medium-flux reactor. Data collected on the PSD, beyond specular peak, correspond to conventional detector scan for diffuse scattering.
The entire spectrometer assembly, surrounded by shielding blocks, is located on a stainless steel table made from 8mm thick stainless steel plate. Fig. 3.6 (b) shows the photograph of the spectrometer. The total weight of the table along with the shielding blocks and parts of the spectrometer is about six metric tons, which makes the spectrometer table nearly vibration free. The specifications of the instrument are given in table 3.1.

### 3.4.2 Control and data acquisition system

A stepper motor-based control system has been designed for the high precision translation and rotation stages. The monochromator is mounted on a tilt and rotation stage assembly. The spectrometer table can rotate around the monochromator to facilitate $\theta - 2\theta$ coupling between the monochromator and the table. This allows changing the incident wavelength, if required.

**Table 3.1:** Specification of PNR instrument
The collimator is mounted on a high precision linear stage, which can move the collimator in steps of 10 microns across the beam. A similar linear stage to move the second slit in the collimator across the first slit is present. These two stages were used initially to align the neutron beam on the sample table centre. The sample and the magnet are mounted on a linear stage with one-micron step size on top of a rotation stage. Sample surface is brought to the centre of the rotation stage with the help of this linear stage. In the high precision rotation stage an optical encoder is located at the bottom of the rotation table that allows one to monitor true rotation of the table with a resolution of 0.001 °. The control system for all the stepper motors is an integral unit with the drivers and the power supplies located in it. It is operated from the instrument’s PC through a serial port communication. Options exist for
collecting data either for a fixed number of monitor counts or for a fixed time. The data acquisition software allows one to select the number of steps in the reflectivity scan and the angular step size. Once a run starts, the system collects data for fixed monitor counts (or time), saves the data channel wise in a file, moves to the new reflection angle and restarts the run [66].

3.4.3 Resolution of the instrument

In the present reflectometer, a Si single crystal (113) monochromator delivers 2.5Å neutrons. There is no second order contamination for the chosen reflecting plane. The monochromator crystal has a mosaic spread of about 15 arc min. For the chosen wavelength the Bragg angle is nearly 49 degrees, giving (0.1%), where λ is the spread in wavelength. The coherence length is 625Å for the neutron wave packet. Lateral inhomogeneities in a film are averaged over this length scale in a reflectivity measurement. The resolution of the instrument for small angles of scattering, as in case of reflectometry, is given by:

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

(3.24)

Where, \(\Delta \theta\) is the angular divergence of the beam, which can be varied from 0.8 to 5 arc min with various combinations of Cd slits, in our instrument. The values of \(\Delta Q\) are typically in the range of 0.001–0.006 Å\(^{-1}\) [66]. The reflectivity patterns is usually taken with nearly same \(\Delta Q/Q\) by changing the slit combination, as the angle of incidence increases. The reflectometer works in a unique configuration of step scan mode coupled to a linear PSD. While the sample stage rotates to scan various angles of incidence (or \(Qz\) values), the detector is fixed, causing the reflected beam “walk” on the PSD. At each angle of incidence, the reflected beam is a Gaussian profile on the detector. This Gaussian is a convolution of the angular divergence of the beam with the position resolution of the detector. To get the
reflected intensity at one particular angle, we integrate over the Gaussian profile and subtract the background counts below it. This allows us to remove the off-specular background under the specular peak and gives true specular intensity.

3.4.4 Analysis of Specular Reflectometry data

Analysis of specular neutron reflectivity data has two major obstacles. Firstly, the phase of the scattered wave, which is required to reconstruct the scattering potential in a unique way, cannot be measured directly. Secondly, once the phase is known, the scattering potential must be recovered from the complex reflection coefficient by solving the inverse problem for 1D quantum scattering. But we can usually measure the reflected intensity only over a limited range of scattering angles. Hence we must usually opt for an indirect method, to postulate a model and then to calculate the amplitude of the reflection coefficient and compare its modulus square with the measured intensity. Using the model, we simulate the neutron reflectivity profile and calculate the difference between experimental and simulated data using some error function $E_r$ (e.g. $\chi^2$ minimization) [67,68]. The model can accordingly be adjusted by some optimization method to get closer agreement with the experimental data. A variety of data fitting and parameter optimization strategies exist. These techniques include Direct search, Downhill simplex, Levenberg-Marquardt method, Simulated annealing and Genetic algorithm [69].

All of the above methods run into difficulties when fitting x-ray and neutron reflectivity data. The downhill simplex and Levenberg-Marquardt methods work well for nonlinear problems because they are guided by the geometry of the error function in parameter space. However, the initial estimate of parameter values need to be very close to the optimum values. If local minima are present, the error function will be trapped in the first local minimum that it encounters. The Monte Carlo based simulated annealing methods do
not get trapped in local minima. However, they are very inefficient at searching the parameter space, since they search it randomly without taking into account the geometry of the error function. Genetic algorithms are efficient and robust technique, since they start from a large set of parameters (population) to find the global minima in parameter space. We have implemented a Genetic algorithm technique based program that has been used to analyze the neutron reflectivity data in this thesis [67].

Genetic Algorithms (GA) are the heuristic search and optimization techniques that mimic the process of natural evolution. It is based on the principle of selecting the best and discarding the poorer solutions, similar to survival of the fittest in Darwinian theory of evolution and hence draws its name from the similarity. It implements the optimization strategies by simulating evolution of species through various selection processes such as natural selection, crossover and mutation. GA is the most efficient and robust technique to find the global minima in a large parameter space [67]. A GA based optimization technique has been used to analyze the neutron and x-ray reflectivity data in this thesis.

Initially a fitness function is defined that quantifies the quality of a solution corresponding to a model with adjustable parameters. The value of this fitness function is used to rank a particular solution against all other possible solutions within a physically reasonable range of the physical parameters. The GA process determines which solutions are to be preserved and allowed to reproduce a next generation of solutions and which ones deserve to die out. The primary objective of the selection operator is to emphasize the good solutions and improve on them after eliminating the bad solutions in a population (set of solutions) while keeping the population size constant. The crossover operator is used to create new solutions from the existing solutions available in the mating pool after applying selection operator. Mutation is the occasional introduction of new features into the solution strings of the population pool to maintain diversity in the population. Though crossover has
the main responsibility to search for the optimal solution, mutation is also used for this purpose. The mutation probability is generally kept low for steady convergence. The steps involved in working of GA is given in Fig.3.7.

For, fitting the neutron and x-ray reflectivity data, the error function should have some desirable properties like: (a) there should be a single deep global minimum and local minima, which are much less deep then the global minimum (b) It should be fast and simple to calculate (c) It should have relative insensitivity to the absolute magnitude of the data, since reflectivity data often spans many orders of magnitude.

![Flowchart showing the steps involved in working of GA.](image)

**Figure 3.7: Steps involved in working of GA. (I is the number of iteration).**

There are number of error functions [70] that have been applied successfully to fitting problems. Following are the functions, which we have adopted in our analysis program.

\[
E_r = \frac{1}{N-1} \sum_{j=1}^{N} \left[ R_{\text{exp}} - R_{\text{cal}} \right]^2
\]

\[\text{......... (3.25)}\]
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And

\[ E_r = \frac{1}{N-1} \sum_{j=1}^{N} \left[ \log R_{\text{exp}} - \log R_{\text{cal}} \right]^2 \]  

……………… (3.26)

With \( R_{\text{exp}} \) and \( R_{\text{cal}} \) are the measured and calculated intensity, respectively. \( N \) is the number of measured data points. The logarithmic function, Eqn. (3.26), could cope with large “Q” (momentum transfer) adequately, since the intensity of reflected neutrons falls rapidly at large \( Q \).

The actual reflected intensity detected in an experiment is convoluted with instrumental resolution function. Therefore, for obtaining the error function, (comparing the experimental data with theatrical profile for a model) defined above, we have to either convolute the theoretical profile with instrument resolution or to de-convolute the experimental data for instrument resolution. For comparing the experimental specular reflectivity data with calculated intensity for a model, we have convoluted the theoretical intensity, \( R_{\text{th}}(Q_r) \) with an appropriate instrumental resolution function [71]:

\[
R_{\text{cal}}(Q) = \left[ \frac{\int_{-\infty}^{\infty} R_{\text{th}}(Q_r) \exp\left\{ -4(\ln 2)(Q - Q_r)^2 / \beta^2 \right\} dQ_r}{\int_{-\infty}^{\infty} \exp\left\{ -4(\ln 2)(Q - Q_r)^2 / \beta^2 \right\} dQ_r} \right] 
\]

……………… (3.27)

Where, \( \beta \) and \( Q \) are the FWHM of the Gaussian resolution function and the wave vector transfer defined as \( Q = (4\pi/\lambda) \sin \theta \), where \( \theta \) is the incident angle on the film and \( \lambda \) is the wavelength of the neutron. We compare \( R_{\text{con}}(Q_r) \) with the background-corrected and normalized experimental data in the \( \chi^2 \) minimization program.

**3.4.5 Estimation of errors in fitted parameter**

It is essential to assess the accuracy and reliability of best-fit parameter values resulted from data fitting procedure and it is an important part of the data analysis. It is difficult and computationally intensive problem to calculate the errors in each parameter with
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respect to all other parameters. In the present case we have adapted technique known as “Bootstrap method” [69]. In this technique we generate a number of “synthetic data set ” \{D_i\} from the experimental data by randomly changing the data points within the experimental error bars in the data. The sets of synthetic data are fitted using the same optimization techniques discussed above and sets of physical parameters \{a_i, b_i……\} are generated. Now one can estimate average values of physical parameters \{a_{av}, b_{av}……\} from the sets of parameters and the fluctuation around them. The fluctuation is an estimate of the error on a particular parameter. This method is especially successful for counting experiments like reflectometry that are inherently statistical in nature.

3.5 Determining stoichiometry of interface alloy layer by XRR and PNR

The present thesis has dealt extensively in characterization of interface alloy formed at mesoscopic length scale. Often these alloy layers, though crystalline, being typically few nanometers thick may not produce any diffraction peaks or the diffraction peaks are too broad to characterize the alloy phase uniquely. We have used a technique where simultaneous measurement of XRR and PNR allows one to obtain exact composition of the alloy layer [10,14].

Consider a binary system consisting of elements A and B as shown in Fig. 3.8. When we anneal the system, solid state reaction occurs between the consecutive layers and an alloy layer forms at the interface, which is a mixture of both A and B. The alloy layer is of composition mA+nB, where values of m, n can vary from 0 to 1 and decides the stoichiometry of the alloy layer (Fig 3.8).

An XRR data reveals the electron scattering length density or ESLD as it interacts with the atomic electrons only. PNR gives the nuclear as well as magnetic scattering length density (NSLD and MSLD) for the same sample. But both the SLDs (NSLD and ESLD)
originates from the same number density (no. of scatterers per unit volume) in a medium. Hence for the binary system forming an alloy layer (A: B as $m:n$) due to inter diffusion (schematic shown below), we can have the set of equations for the alloy layer as:

$$
\rho_{\text{neutron}} = mN_A b_A + nN_B b_B \\
\rho_{\text{x-ray}} = mr_0 N_A Z_A + nr_0 N_B Z_B 
$$

(3.28)

Where ‘$\rho$’ is the respective SLD values for x-ray and neutrons. $N, b, Z$ are the number density, coherence scattering length for neutrons and atomic no. of reacting elements and ‘$r_0$’ is the classical electron radius. Once ‘$\rho_{\text{x-ray/neutrons}}$’ values are known, above set of linear equations can be solved for ‘$m$’ and ‘$n$’ giving the ratio of A atoms vs B to form the alloy at the interface. Neutron reflectometry together with XRR on a sample gives the stoichiometry of the alloy layer. PNR also gives the additional information of magnetization depth profile in the sample in terms of MSLD.

Figure 3.8: Schematic of alloy layer formation in a bilayer