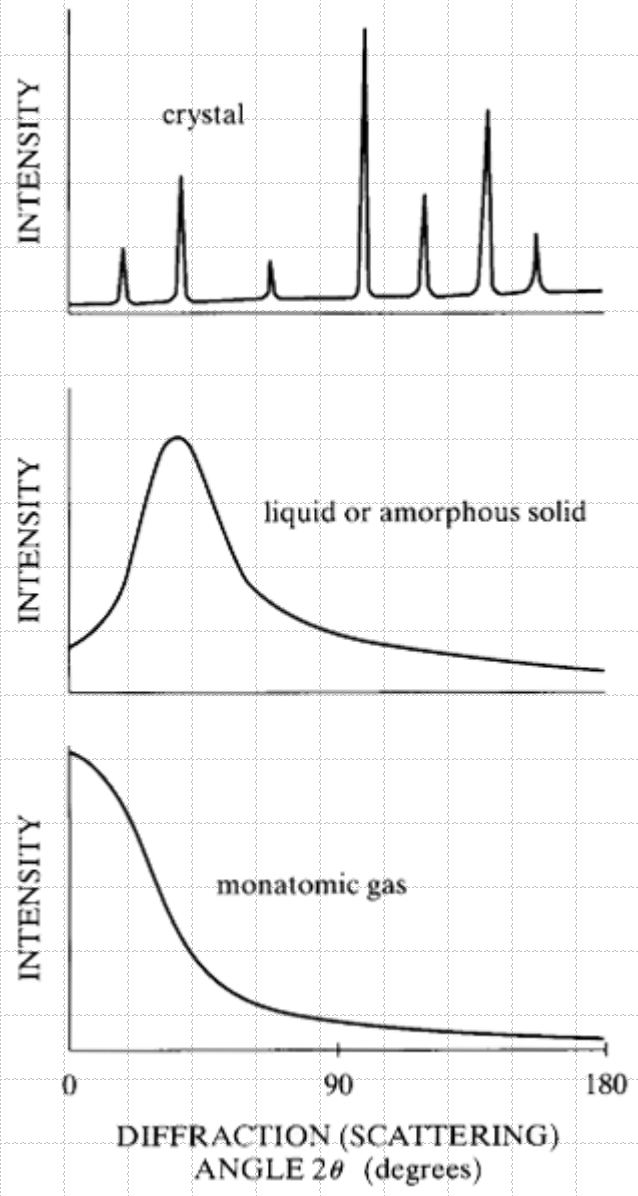
Reflectivity & Amorphous

Amorphous Materials

- Periodic arrangement of atoms causes destructive interference in all directions except those predicted by Bragg's law.
- The measurable diffraction occurs at non-Bragg angles only when crystal imperfections are present.
- Amorphous materials do not show long-range order. They exhibit short-range order: statistical preference of a particular interatomic distance.



Amorphous Materials

- Consider our sample as any form of matter in which there is random orientation.
- This includes gases, liquids, amorphous solids, and crystalline powders.

$$I = \sum_m f_m e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{r}_m} \sum_n f_n e^{-(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{r}_n},$$

- The scattered intensity from such sample:

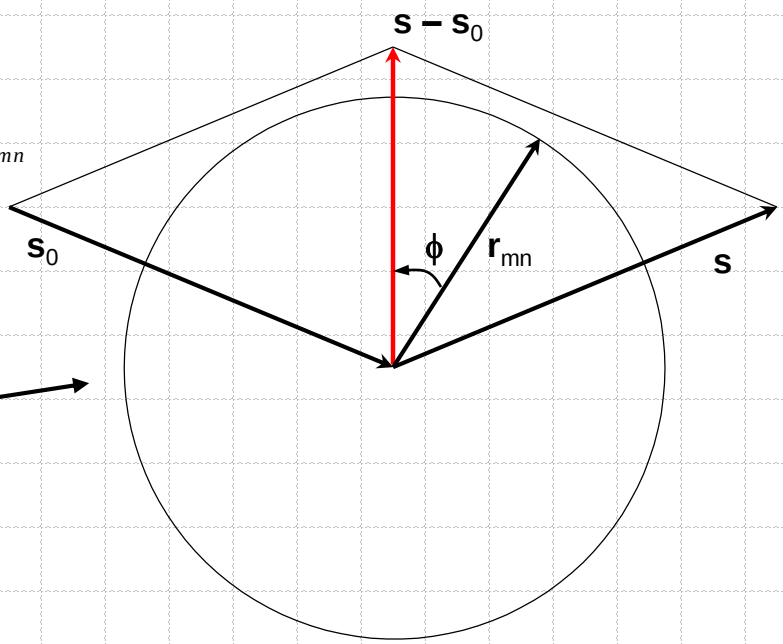
$$I = \sum_m \sum_n f_m f_n e^{(2\pi i/\lambda)(\mathbf{s}-\mathbf{s}_0)\cdot\mathbf{r}_{mn}} = \sum_m \sum_n f_m f_n e^{i\mathbf{q}\cdot\mathbf{r}_{mn}}$$

where

$$\mathbf{r}_{mn} = \mathbf{r}_m - \mathbf{r}_n$$

takes all orientations

$$\mathbf{q} = \frac{2\pi}{\lambda}(\mathbf{s}-\mathbf{s}_0)$$



Amorphous Materials

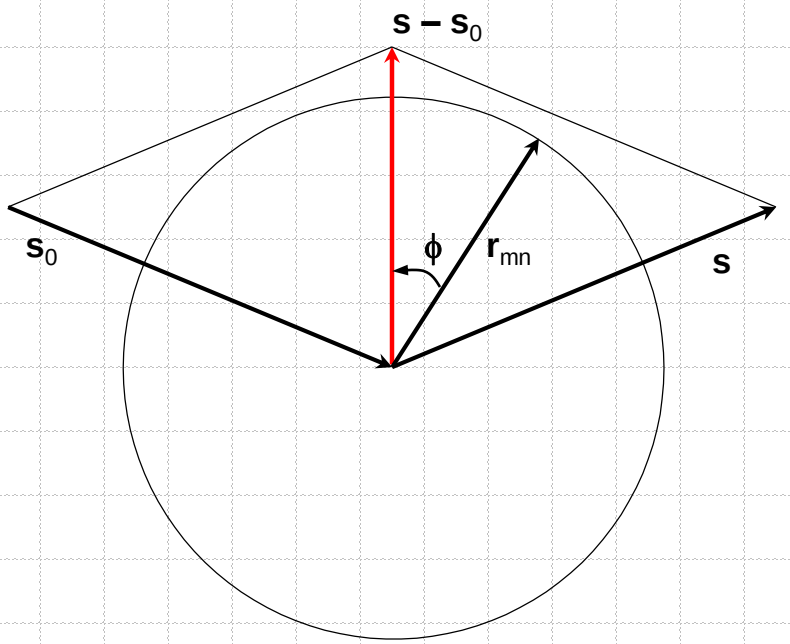
- Average intensity from an array of atoms which takes all orientations in space:

$$I = \sum_m \sum_n f_m f_n \frac{\sin qr_{mn}}{qr_{mn}},$$

where $q = \dfrac{4\pi \sin\theta}{\lambda}$ Bragg's law

Debye scattering equation

It involves only the magnitudes of the distances r_{mn} of each atom from every other atom



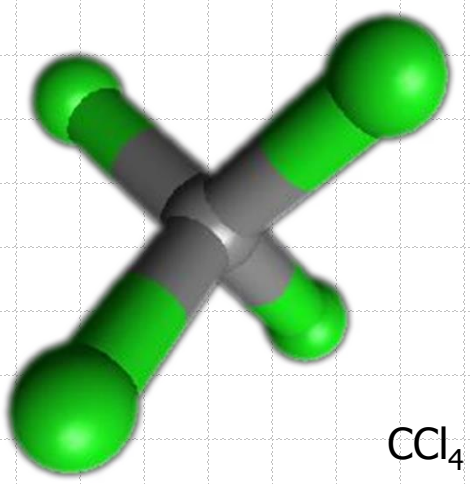
Polyatomic Molecules

- Consider gas of polyatomic molecules.
- Gas is not too dense – there is complete incoherency between the scattering by different molecules.

- Intensity per molecule:

$$I/N = \sum_m \sum_n f_m f_n \frac{\sin qr_{mn}}{qr_{mn}} + R$$

← correction factor



CCl_4

- Lets take a carbon tetrachloride as example.
  It is composed of tetrahedral molecules CCl_4.
- Then:

$$I/N = f_C \left\{ f_C + 4 f_{Cl} \frac{\sin qr(C-Cl)}{qr(C-Cl)} \right\}$$

$$+ 4 f_{Cl} \left\{ f_{Cl} + f_C \frac{\sin qr(C-Cl)}{qr(C-Cl)} + 3 f_{Cl} \frac{\sin qr(C-Cl)}{qr(C-Cl)} \right\}$$

Polyatomic Molecules

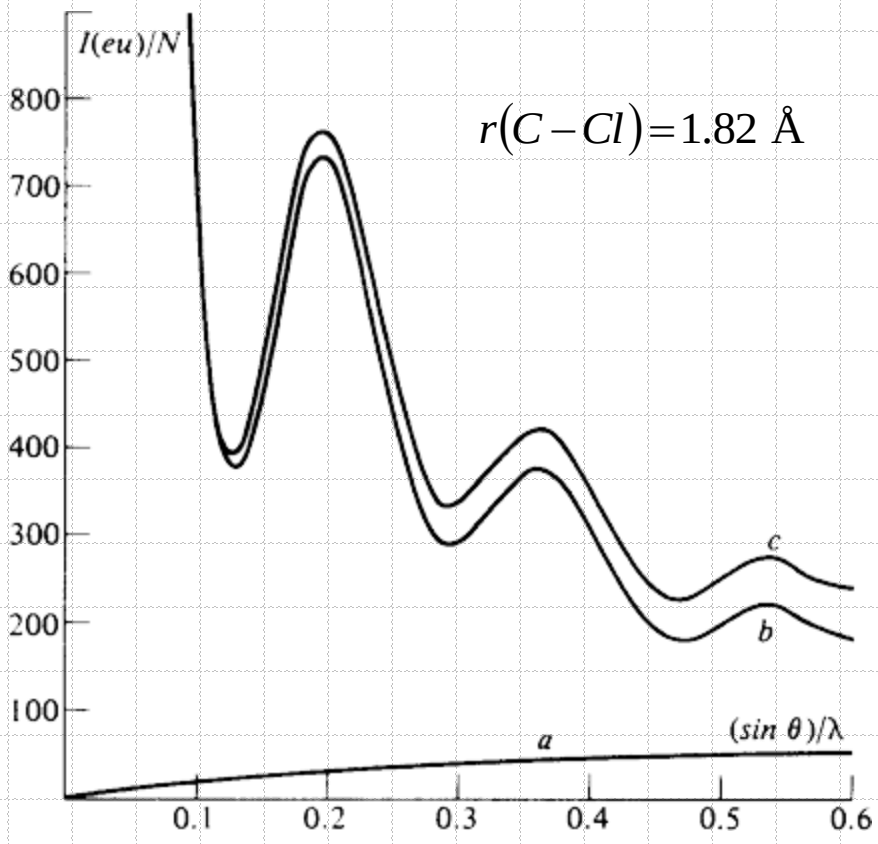
$$I/N = f_C^2 + 4f_{Cl}^2 + 8f_C f_{Cl}\frac{\sin qr(C-Cl)}{qr(C-Cl)} + 12f_{Cl}^2\frac{\sin qr(C-Cl)}{qr(C-Cl)} + R$$

- For tetrahedral CCl_4 molecule:

$$r(Cl-Cl) = \sqrt{\frac{8}{3}}\, r(C-Cl)$$

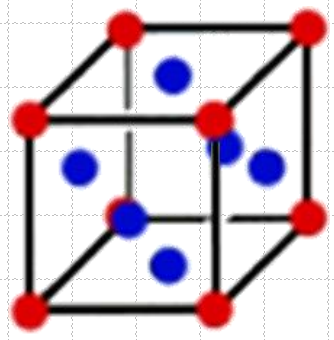
- The intensity depends on just one distance r(C – Cl).
- Peaks and dips do not require the existence of a crystalline structure.
- Certain interatomic distances that are more probable than others are enough to get peaks and dips on the scattering curve.

$$r(C-Cl) = 1.82 \text{ Å}$$



Intensity (in e.u. per molecule) for a CCl_4 gas in which the C – Cl distance is r = 1.82 Å. (*Warren*)

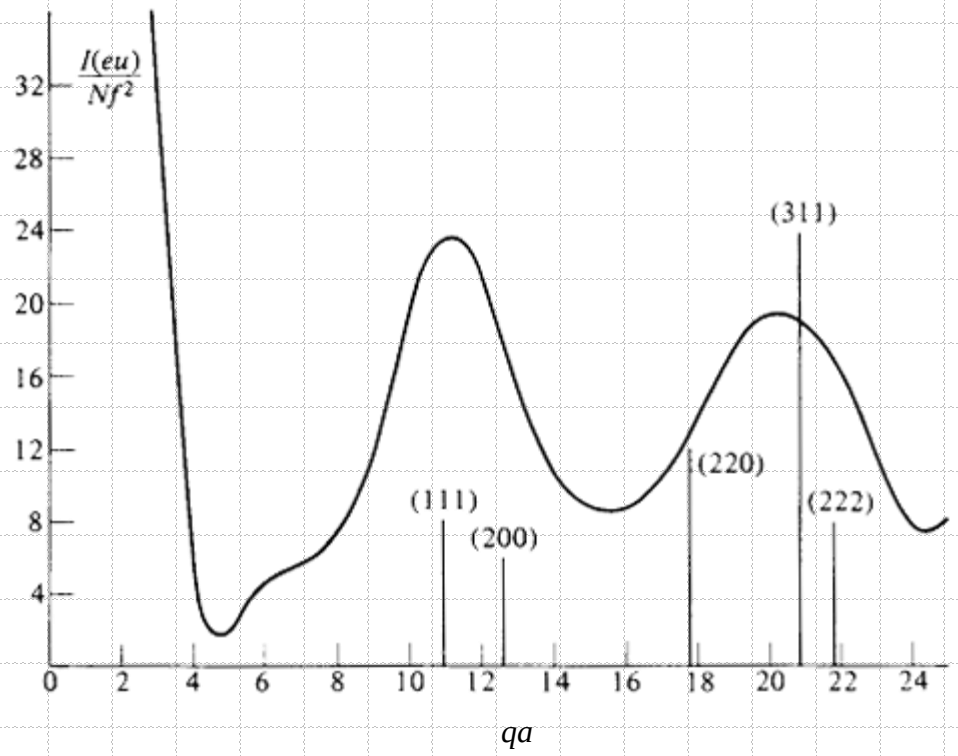
Crystal as Molecule



- Lets treat crystal as a molecule
- FCC has 14 atoms:
  - 8 at corners of a cube
  - 6 at face center positions
- *a* is the edge of a cube

$$I/N = \sum_m \sum_n f_m f_n \frac{\sin qr_{mn}}{qr_{mn}} + R$$

$$I/Nf^2 = 14 + 72\frac{\sin q\,a/\sqrt{2}}{q\,a/\sqrt{2}} + \frac{30\sin qa}{qa} + \frac{48\sin qa\sqrt{1.5}}{qa\sqrt{1.5}} + \frac{24\sin qa\sqrt{2}}{qa\sqrt{2}} + \frac{8\sin qa\sqrt{3}}{qa\sqrt{3}}$$



Amorphous Materials

- Atoms in liquids and amorphous solids have definite structures relative to an origin at the center of an average atom.
- This type of structure is expressed by a radial distribution function:

$$4\pi r^2 \rho(r)$$

$4\pi r^2 \rho(r)\, dr$ – average number of atom centers between distances r and $r + dr$ from the center of an average atom

- We use the equation: $I = \sum_m \sum_n f_m f_n \frac{\sin qr_{mn}}{qr_{mn}}$

Assumption: Sample takes with equal probability all orientations in space

- It can be shown that the scattered intensity can be written as:

$$I = Nf^2 + Nf^2 \int_0^\infty 4\pi r^2 [\rho(r) - \rho_0] \frac{\sin qr}{qr} dr + f^2 \rho_0^2 \int e^{-ikz} A(z) dz \int e^{ikz} A(z) dz$$

interaction between near neighbors

interaction between distant neighbors

not negligible only for very small angles

Amorphous Materials

- We obtain very important and much used equation:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty q\left(\frac{I}{Nf^2} - 1\right) \sin rq \; dq$$

ρ_0 – average atom density per sample

can be obtained experimentally from the scattering curve

- For solids:
  - $4\pi r^2 \rho(r)dr$ – average number of atom centers between distances r and $r + dr$ from the center of an average atom.
- For liquids:
  - $4\pi r^2 \rho(r)dr$ – average over surroundings of each atom in the sample and also an average over the time of measurement.

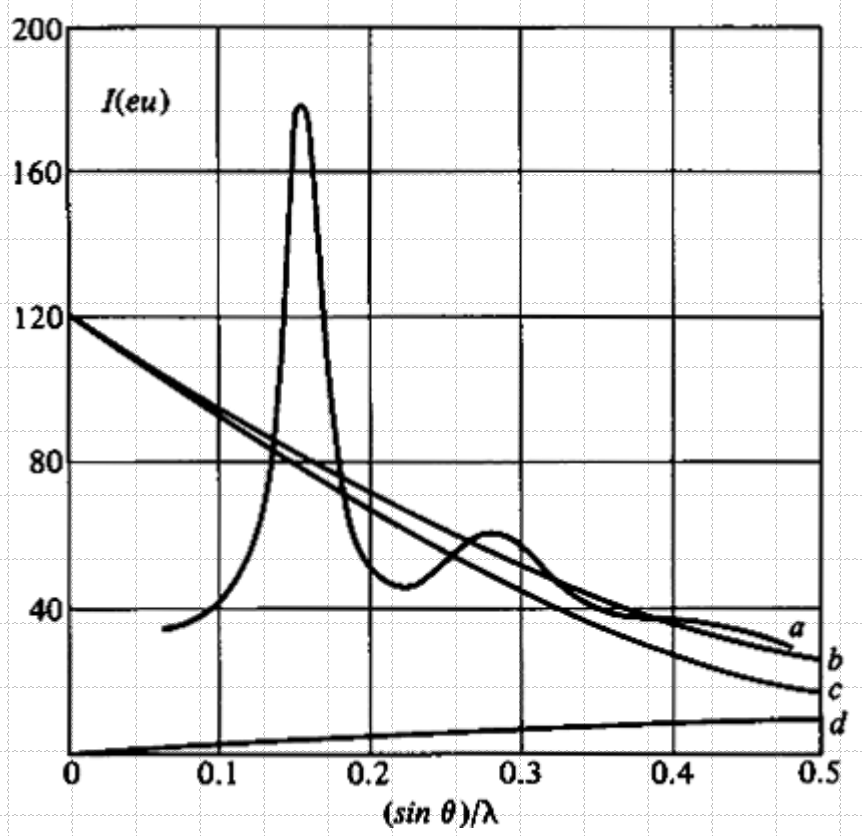
Experimental determination of $4\pi r^2\rho(r)$

- Previous expressions apply only to coherent (unmodified) scattering.
- Many corrections are required:
  - correct for air scatter
  - correct for absorption by sample
  - correct for polarization
  - correct for incoherent (Compton-modified) scattering – requires conversion to absolute (electron) units
- RDF determination requires high-quality data at large q (small r).

Example: Liquid Sodium

- We obtain $i(q) = \frac{I}{Nf^2} - 1$:

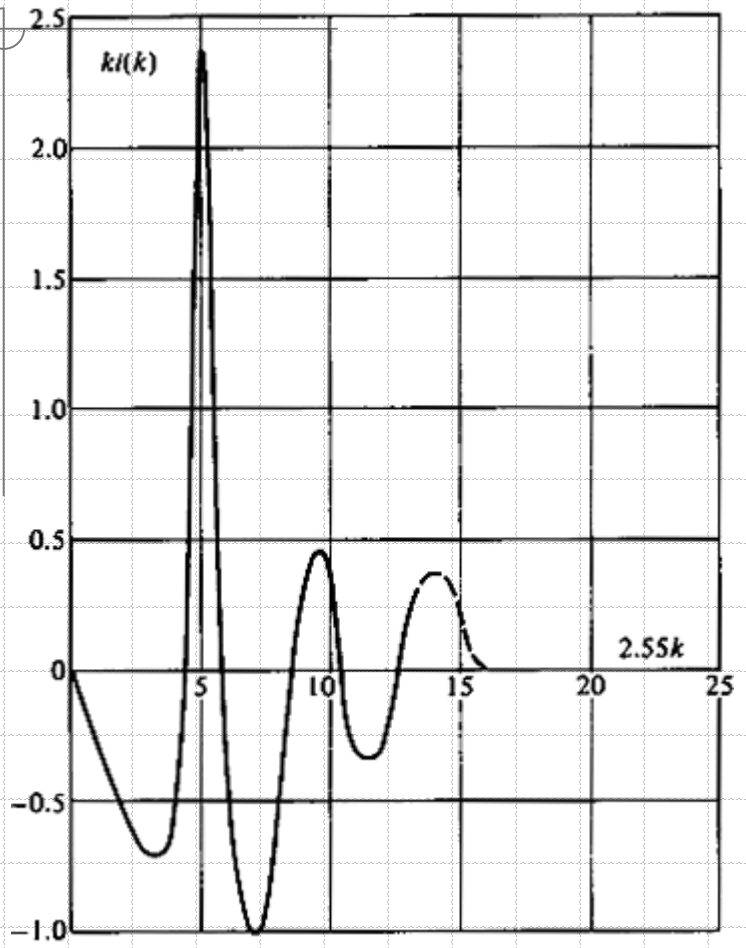
$$i(q) = \frac{I}{Nf^2} - 1 = \frac{I - f^2}{Nf^2}$$
$$= \frac{(a-d)-c}{c} = \frac{a-b}{c}$$



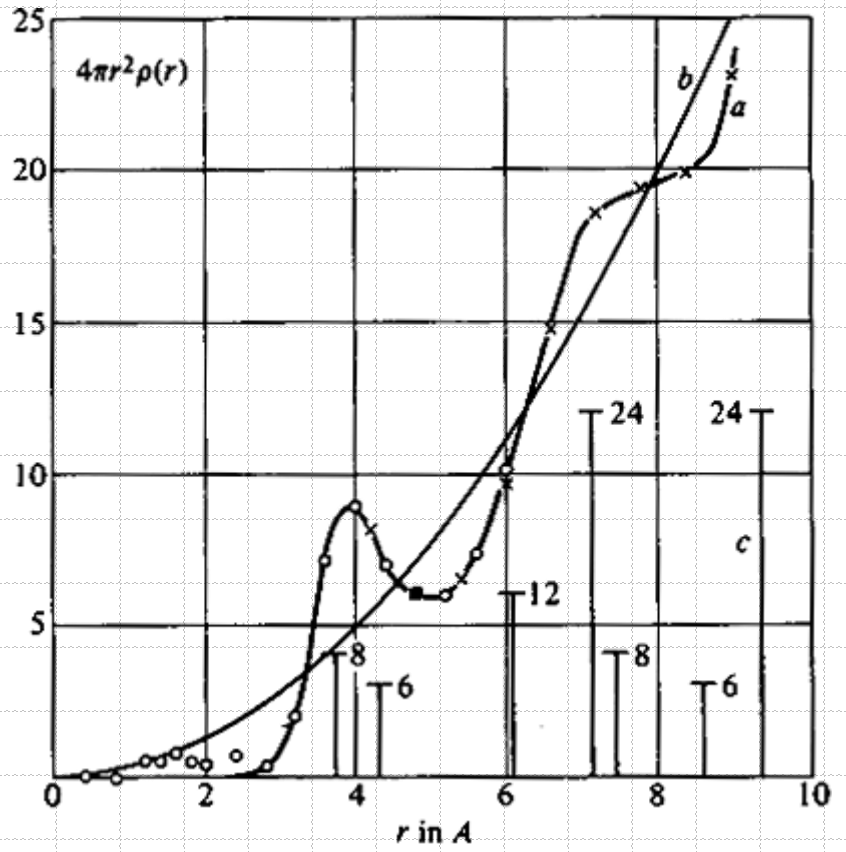
(a) Total intensity curve for liquid Na unmodified + modified, (b) total independent scattering per atom, (c) independet unmodified scattering per atom f^2, (d) modified scattering per atom $i(M)$. (*Warren*)

Example: Liquid Sodium

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty q\, i(q) \sin rq \; dq$$



Experimental curve qi(q) for liquid Na. (*Warren*)



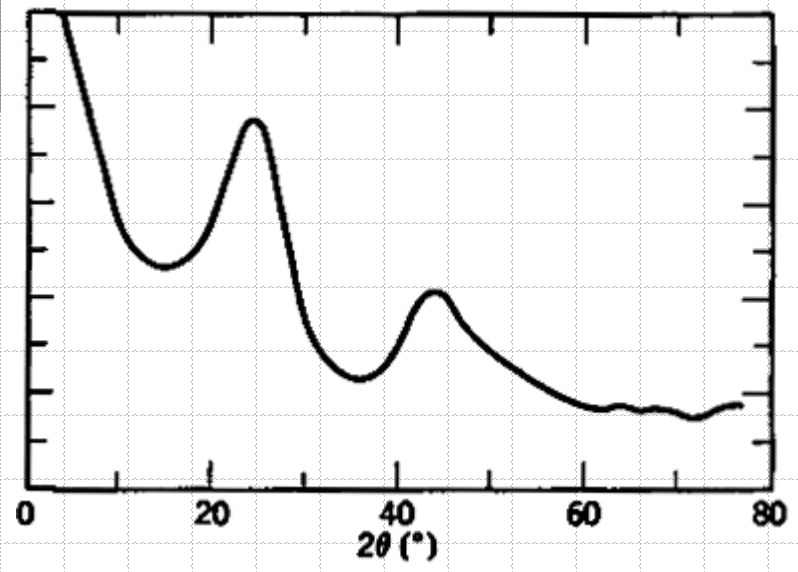
(a) RDF $4\pi r^2\rho(r)$ for liquid Na, (b) average density curve $4\pi r^2\rho_0(r)$, (c) distribution of neighbors in crystalline Na. (*Warren*)

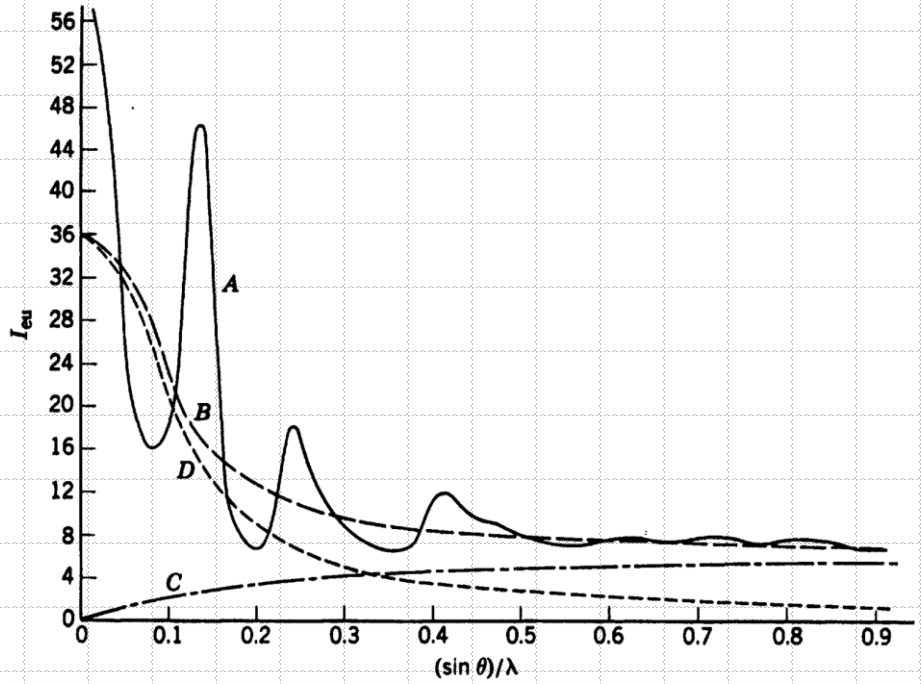
Example: Carbon black

What is Carbon Black?

Carbon black is made primarily from a petroleum-based feedstock. The oil is pumped into a specially designed furnace, where it is heated above 2,000° F. This process "cracks" the oil to produce a gas stream laden with carbon black powder. The gas stream passes through a series of filters, where the carbon black is separated from the gases. The carbon black powder then is bound with water to create larger beads or granules, which are passed through a dryer and packaged for delivery to customers in every part of the world.

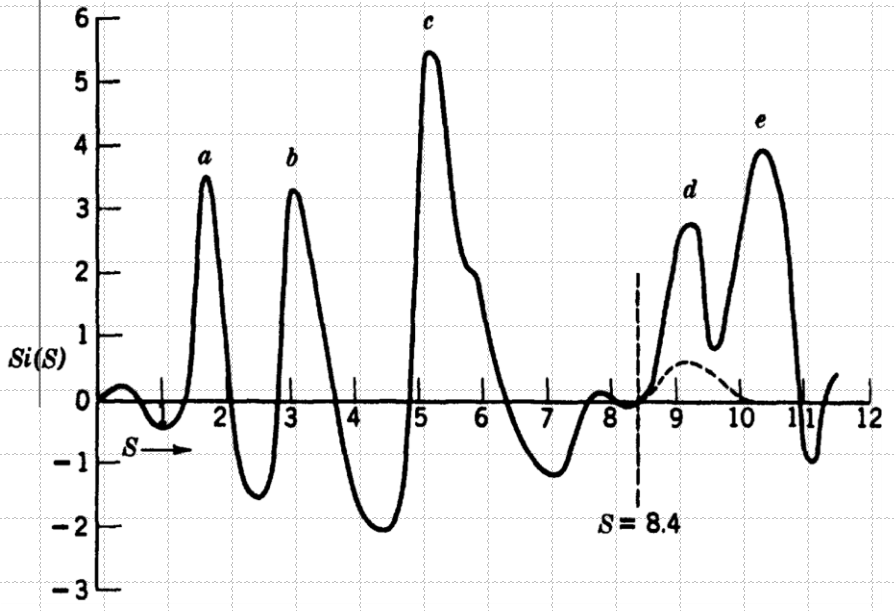
Actual measurement



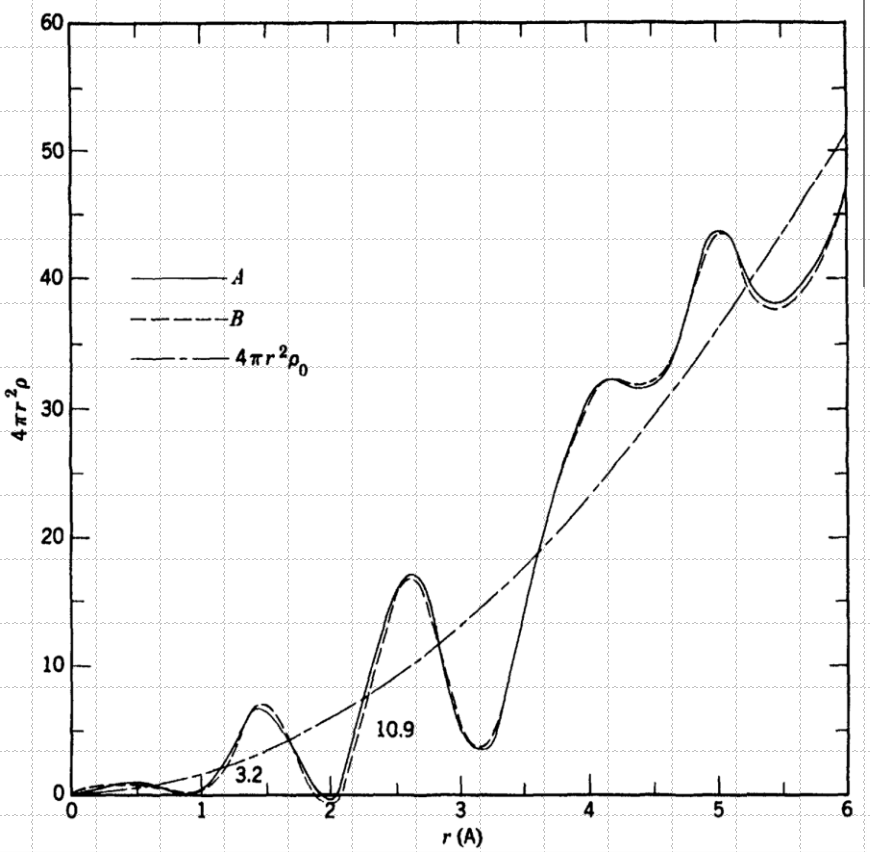


(a) Final scattering curve of carbon black, theoretical independent scattering curves: (d) coherent, (c) incoherent, and (b) total independent scattering.

Example: Carbon black



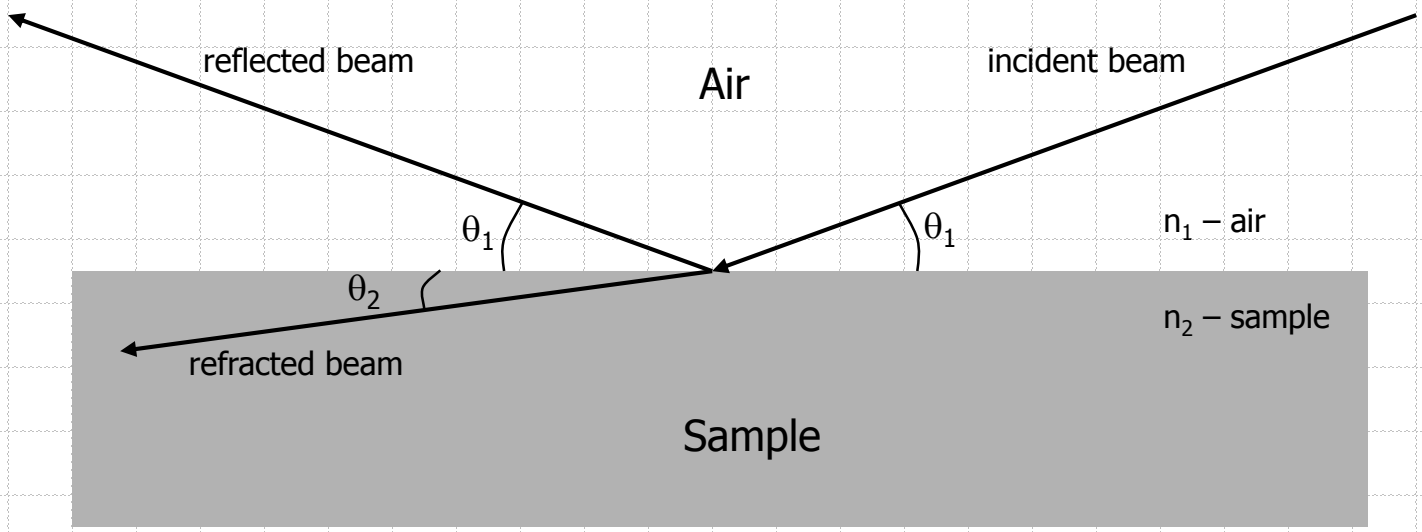
Plot of the experimental amplitude function S i(S) for carbon black



RDF of carbon black

X-ray Reflectivity

- X-ray reflectivity is a precise and non-destructive method used to determine the layer thickness, density and roughness of a layer on a substrate.



X-ray Reflectivity

- An X-ray-beam that strikes a solid-surface at a small angle (0-2°) is totally reflected.
- Above the critical angle of total reflectance θ_c the beam penetrates the sample, whereby the angle of refraction θ_2 is smaller than the angle of incidence θ_1 (the refractive index of X-rays in solids is smaller than that in air).
- The refractive index for X-ray radiation is given by the formula:

$$n = 1 - \delta$$

n – refractive index,
δ – term, that specifies the dispersion of the x-ray beam.

- According to Snell´s law of refraction:

$$n_1 \cos\theta_1 = n_2 \cos\theta_2 \rightarrow \cos\theta_2 = \frac{n_1}{n_2}\cos\theta_1$$

if n_1 – index of refraction of air ~ 1
n_2 – index of refraction in solid < 1

then $\theta_2 < \theta_1$

X-ray Reflectivity

- Below critical angle total reflection occurs:

$$\theta_2 = 0^o$$

$$n_1 \cos\theta_C = n_2 \cos 0^o \rightarrow \cos\theta_C = n_2 = 1-\delta_2 \qquad \text{since} \quad n_1 \approx 1$$

then

$$\arccos(1-\delta_2) \approx \sqrt{2\delta_2} \rightarrow \boxed{\theta_C = \sqrt{2\delta_2}}$$

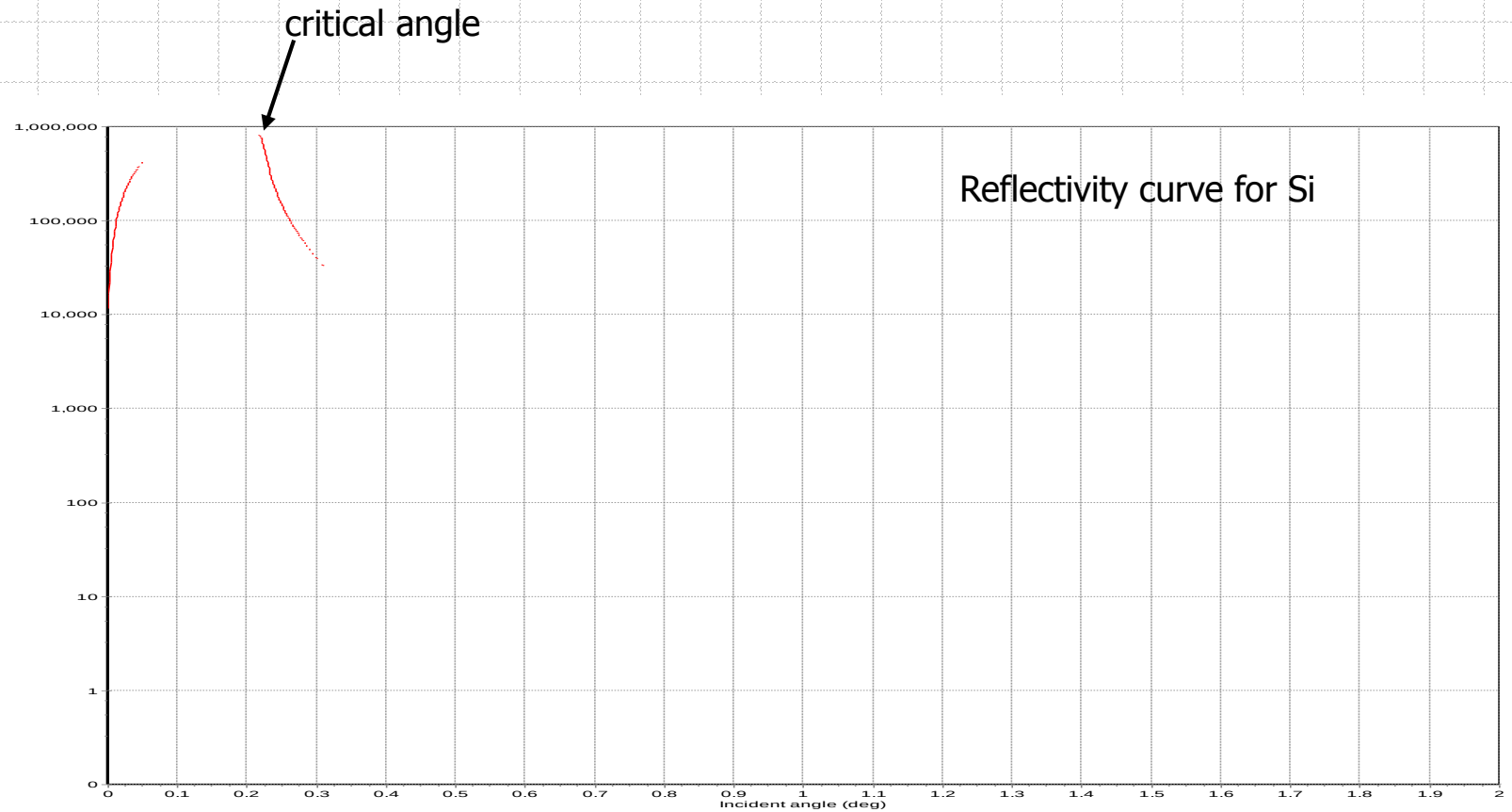
- The density of the sample can be calculated from the critical angle and using the following equation:

$$\delta_2 = \frac{N_A r_0 \lambda^2}{2\pi} \sum_j \frac{\rho_j}{A_j} \left(Z_j + f_j'\right)$$

N_A – Avogadro-Number
r_0 – classical radius of an electron
λ – wavelength
ρ_j – density of the atom j in the compound
A_j – atomic mass of the atom j
Z_j – atomic number of the atom j
f'_j – correction factor for the dispersion for the atom j

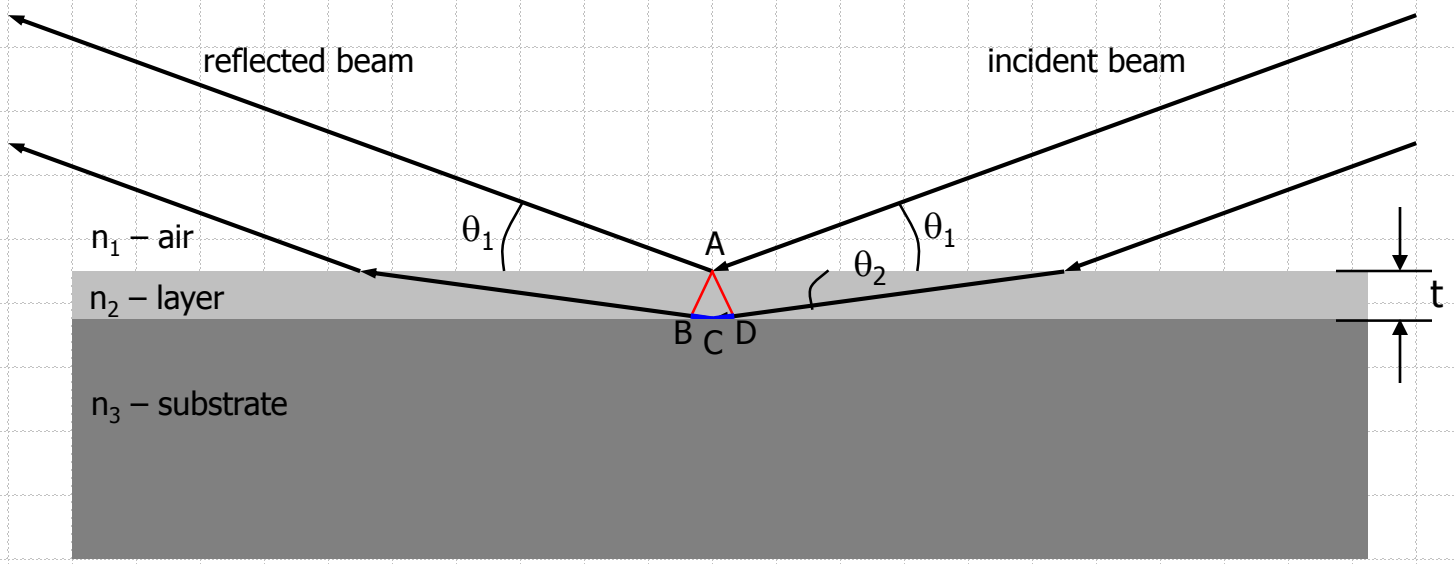
X-ray Reflectivity

$$\text{Reflectivity } R = \frac{Intensity\ of\ the\ reflected\ beam}{Intensity\ of\ the\ primary\ beam}$$



X-ray Reflectivity from Thin Layers

- If the sample contains a thin layer, x-rays are reflected from the air/layer as well as from the layer/substrate interfaces.

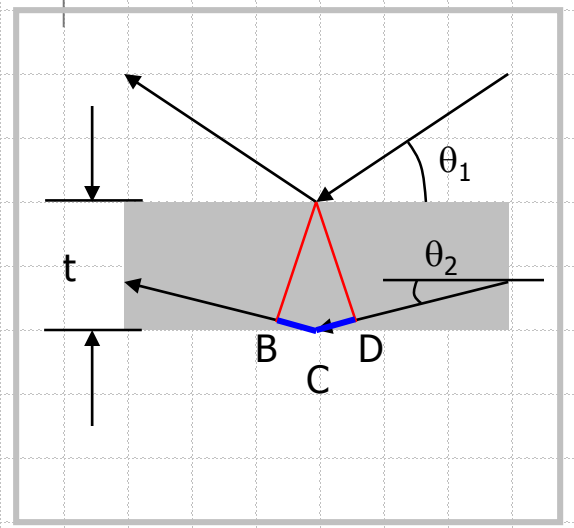


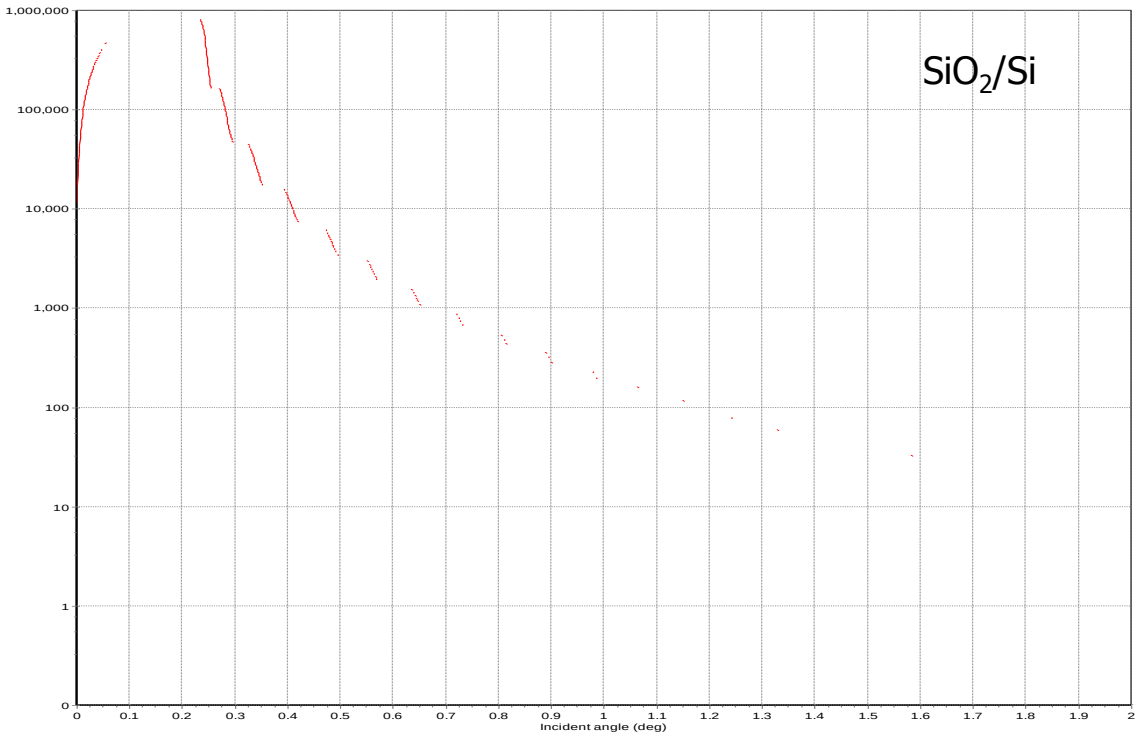
path difference: BCD

X-ray Reflectivity from Thin Layers

- Positions of the maxima can be calculated using Bragg's law:

$$L = n\lambda = BC + CD = t\sin\theta_2 + t\sin\theta_2 = 2t\sin\theta_2$$





X-ray Reflectivity from Thin Layers

- Some simplifications and approximations:

$$BC = CD = t\sin\theta_2$$

if θ is small $\sin\theta \approx \theta$

using Snell's law of refraction ($n_1 \sim 1$):

$$\cos\theta_1 = n_2\cos\theta_2 \rightarrow \cos\theta_1 = (1-\delta_2)\cos\theta_2$$

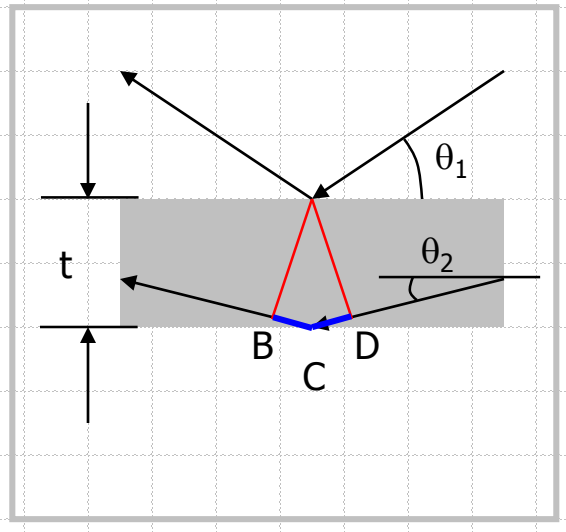
$$\cos\theta_2 = \frac{\cos\theta_1}{1-\delta_2} \rightarrow \theta_2 = \arccos\left(\frac{\cos\theta_1}{1-\delta_2}\right) \approx \sqrt{\theta_1^2 - 2\delta_2}$$

$$\theta_2 \approx \sqrt{\theta_1^2 - 2\delta_2}$$

$$L = n\lambda = 2t\sin\theta_2 \approx 2t\sqrt{\theta_1^2 - 2\delta_2}$$

$$\theta_1 = \frac{\lambda^2}{4t^2}n^2 + 2\delta_2$$

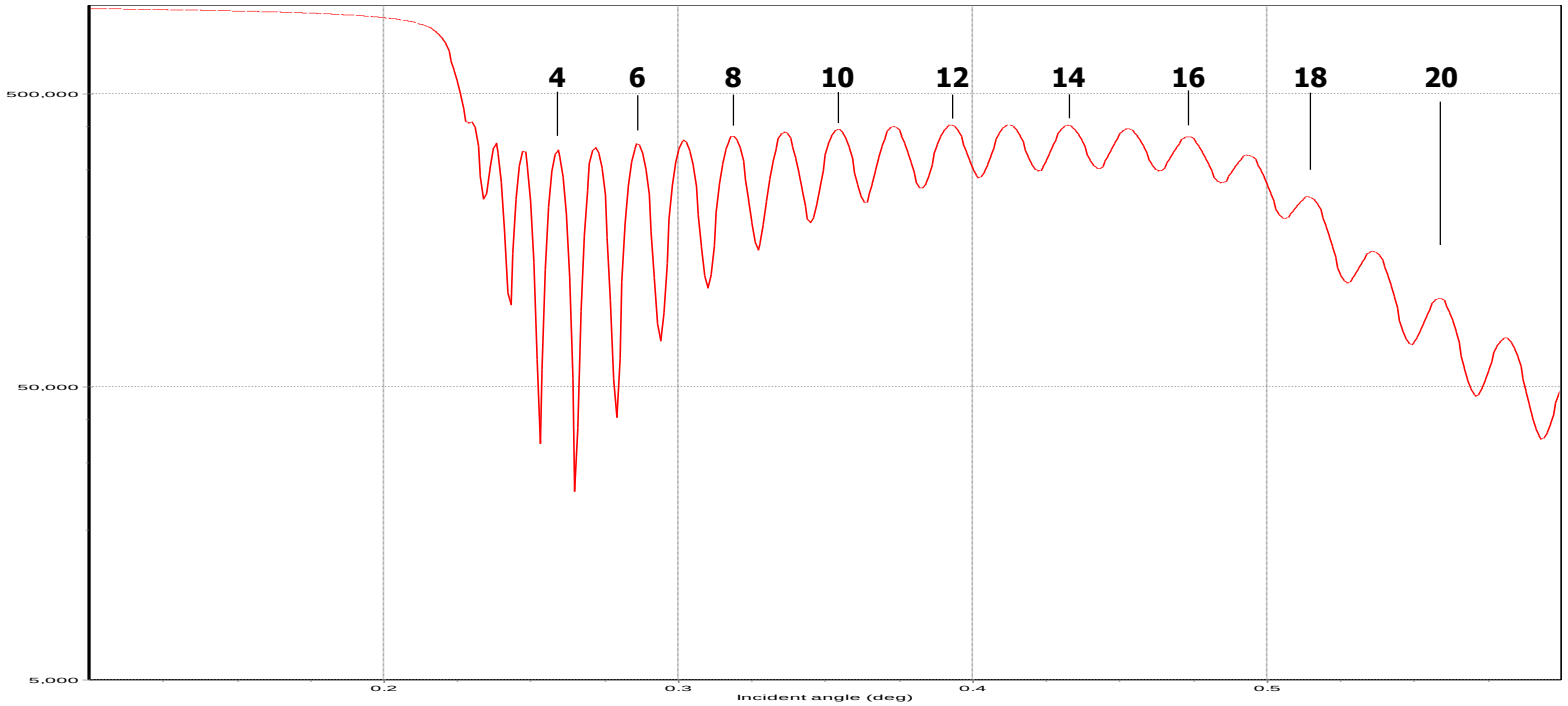
y = a · x + b



Example: Si on Ta

$$\theta_1 = \frac{\lambda^2}{4t^2} n^2 + 2\delta_2$$

y = a · x + b



Example: Si on Ta

$$\theta_1 = \frac{\lambda^2}{4t^2} n^2 + 2\delta_2$$

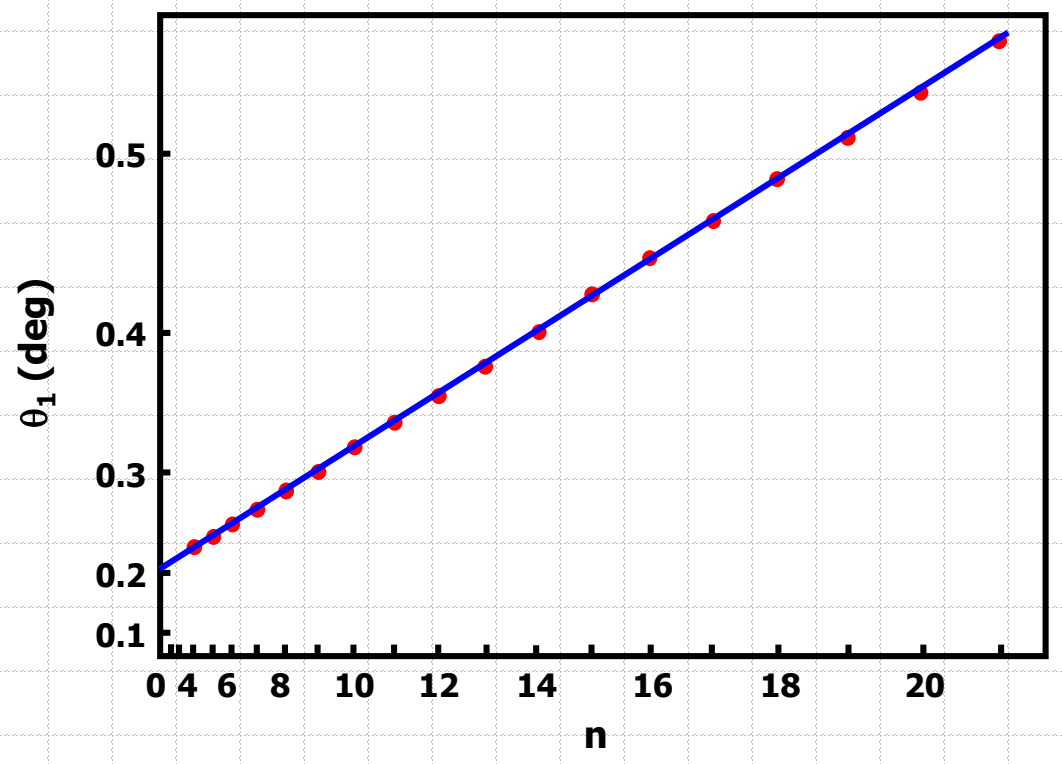
y = a · x + b

$$b = 2\delta_2 = 2\frac{N_A r_0 \lambda^2}{2\pi}\frac{\rho}{A}(Z + f')$$

$$a = \frac{\lambda^2}{4t^2}$$

$$\rho = \frac{b\pi A}{N_A r_0 (Z + f')\lambda^2}$$

$$t = \frac{\lambda}{2\sqrt{a}}$$

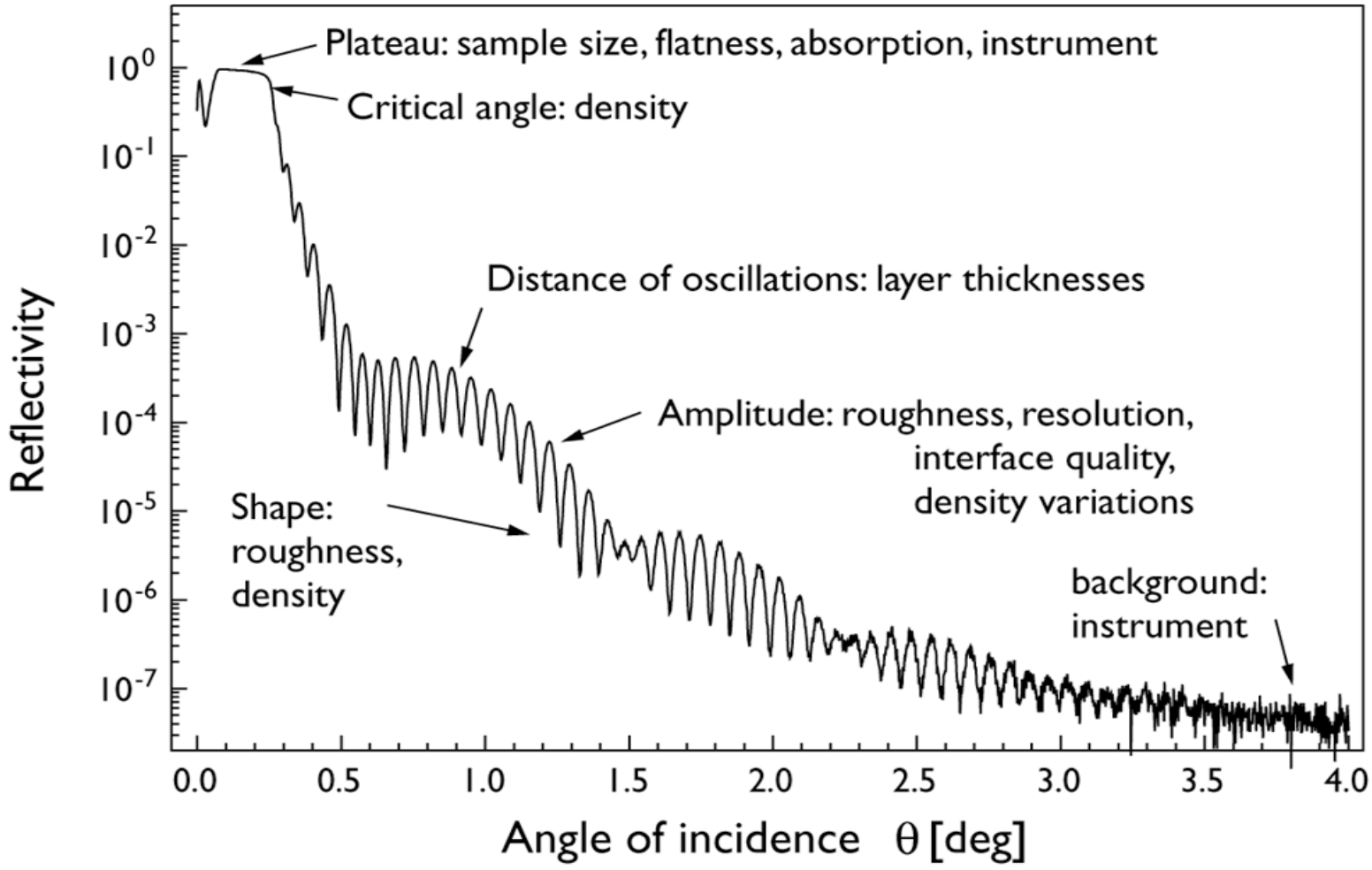


N_A – Avogadro-Number
r_0 – classical radius of an electron
λ – wavelength
ρ_j – density of the atom j in the compound
A_j – atomic mass of the atom j
Z_j – atomic number of the atom j
f'_j – correction factor for the dispersion for the atom j

We get:

t = 181 nm
ρ = 2.2 g/cm³

X-ray Reflectivity from Thin Layers



X-ray Reflectivity: Simulation

- Reflectivity can be calculated completely using Fresnell equations

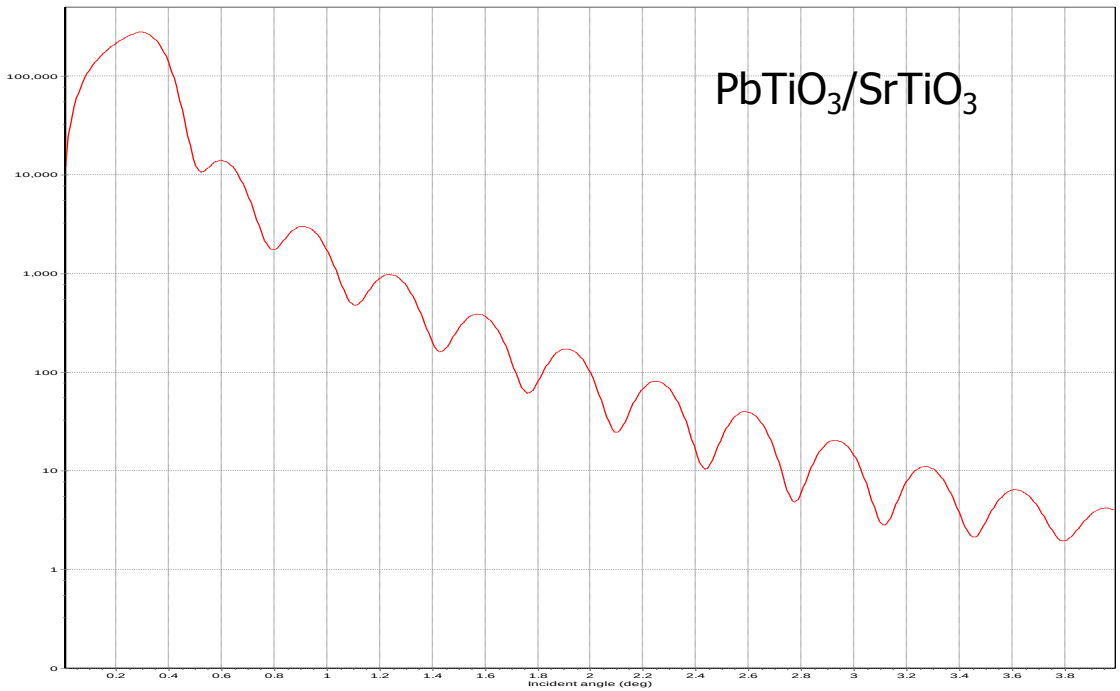
Simple version for substrate + one layer

$$R = \left(\frac{R_1 + R_2 e^{\frac{4\pi i \theta_2 t_2}{\lambda}}}{1 + R_1 R_2 e^{\frac{4\pi i \theta_2 t_2}{\lambda}}} \right)^2$$

R_1 and R_2 reflectivities of air/layer and layer/substrate interfaces:

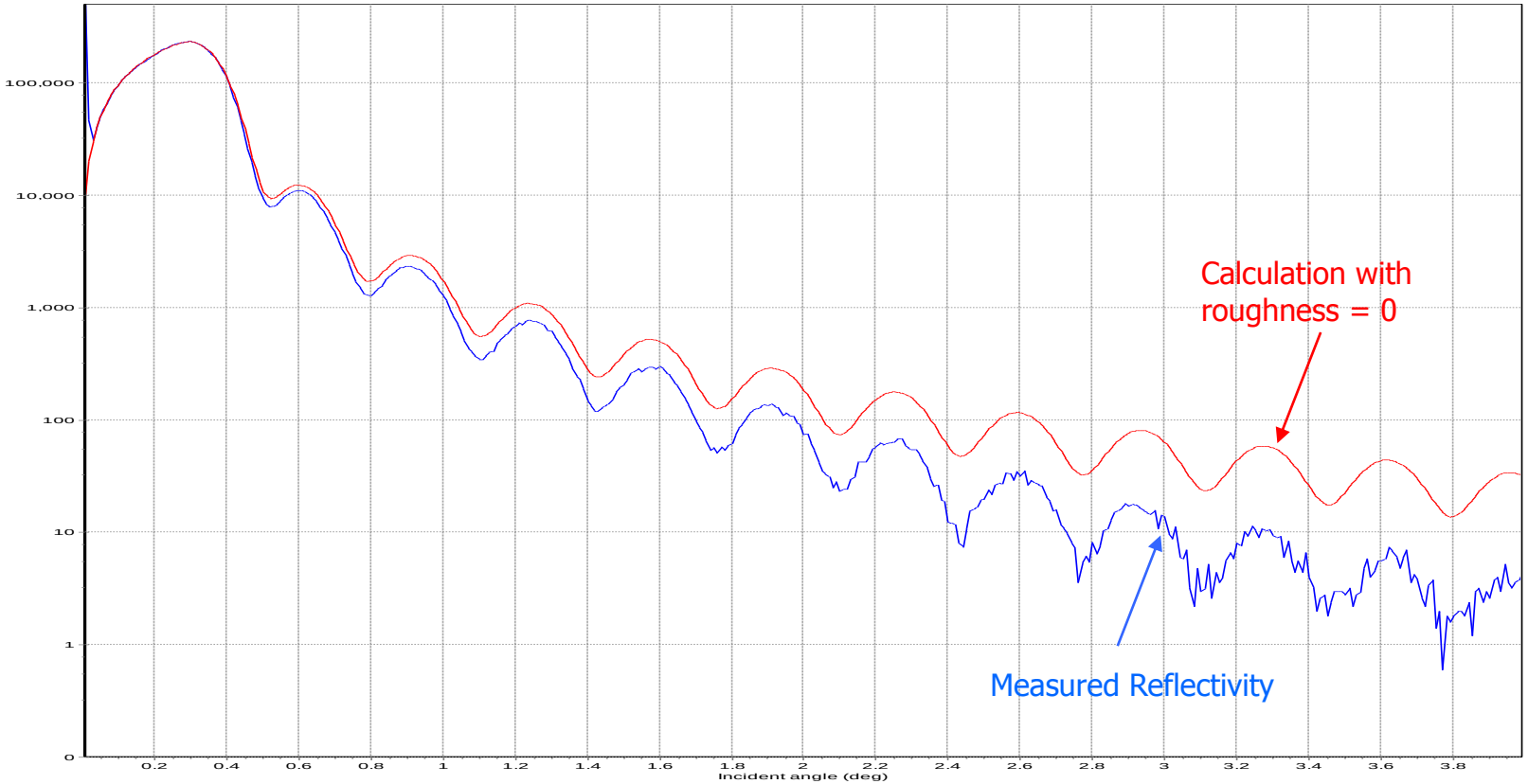
$$R = \frac{\theta_1 - \theta_2}{\theta_1 + \theta_2} e^{\frac{-4\pi^2 \theta_1 \theta_2 \sigma^2}{\lambda^2}}$$

σ – surface roughness



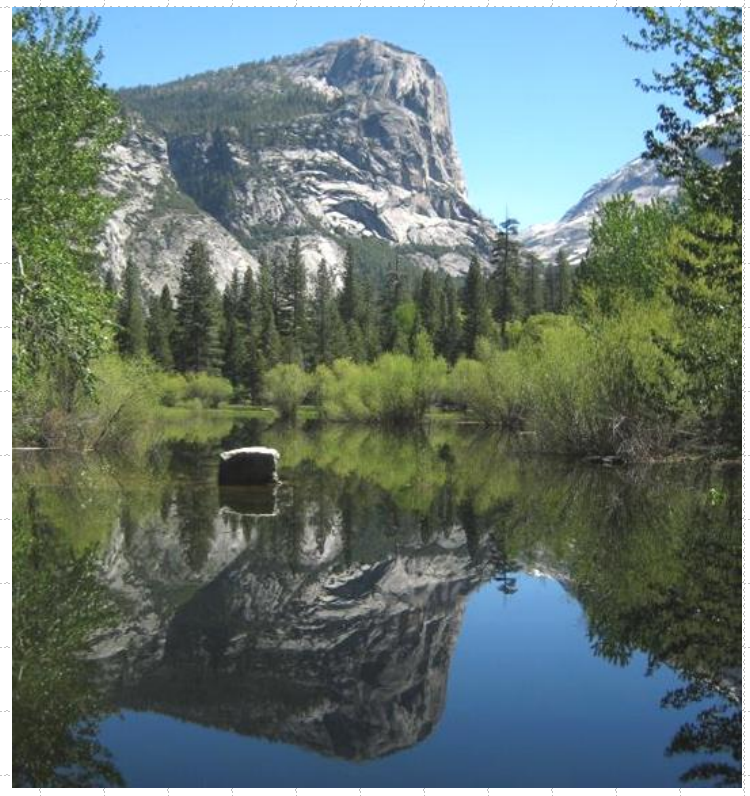
X-ray Reflectivity: Roughness

- $PbTiO_3$ on $SrTiO_3$



X-ray Reflectivity: Roughness

Smooth surface

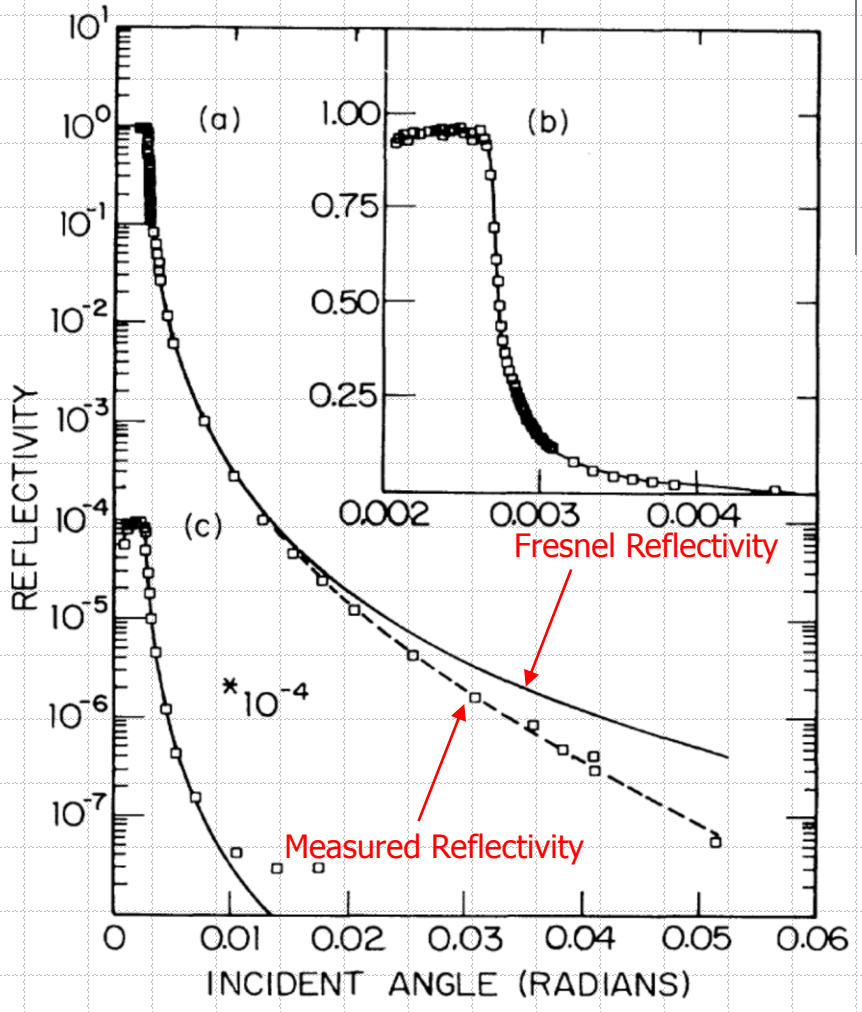


Rough surface

X-ray Reflectivity: Roughness

- **Reflectivity of water**

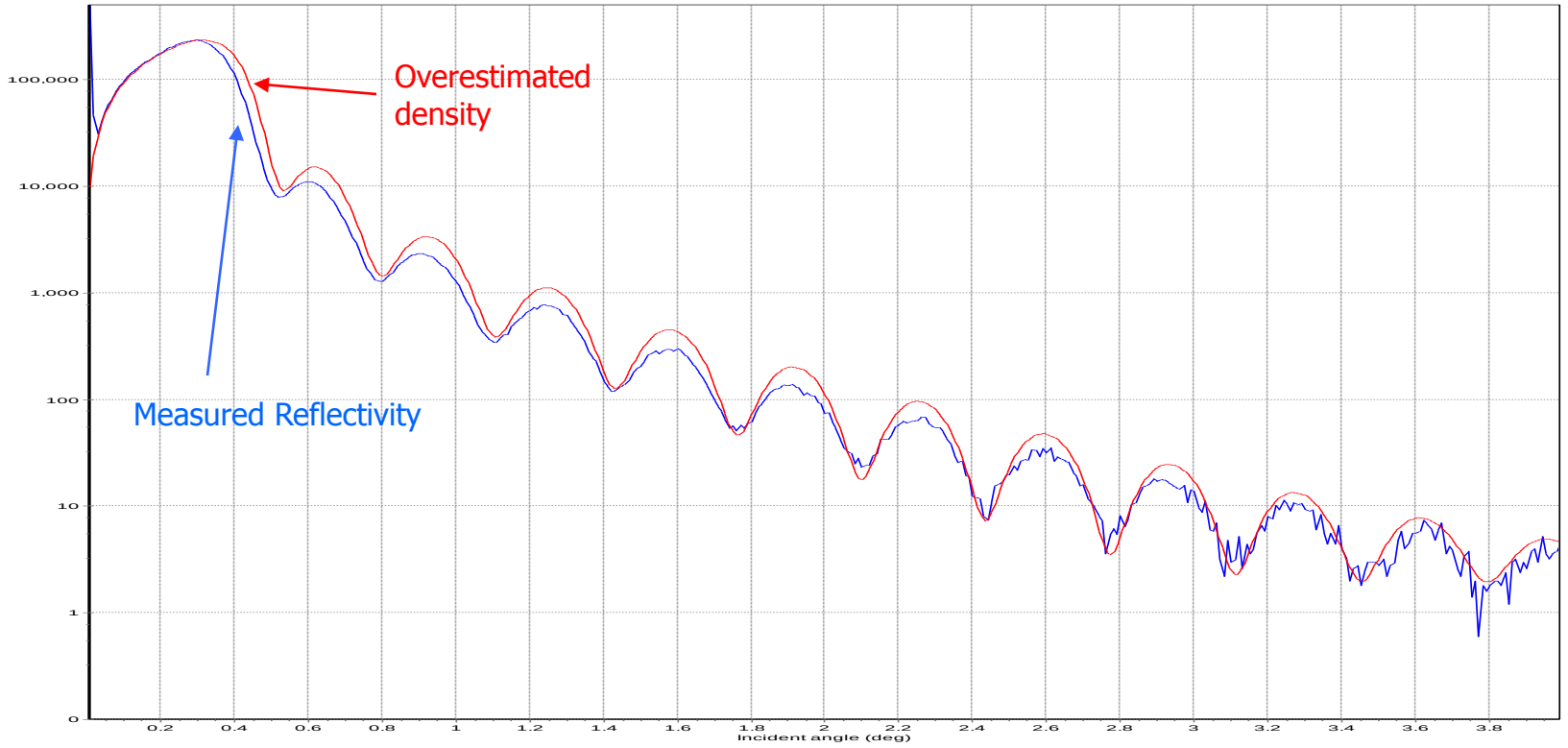
Difference between experiment and theory due to **roughness**



Braslau et al. Phys. Rev. Lett. **54** 114 (1985)

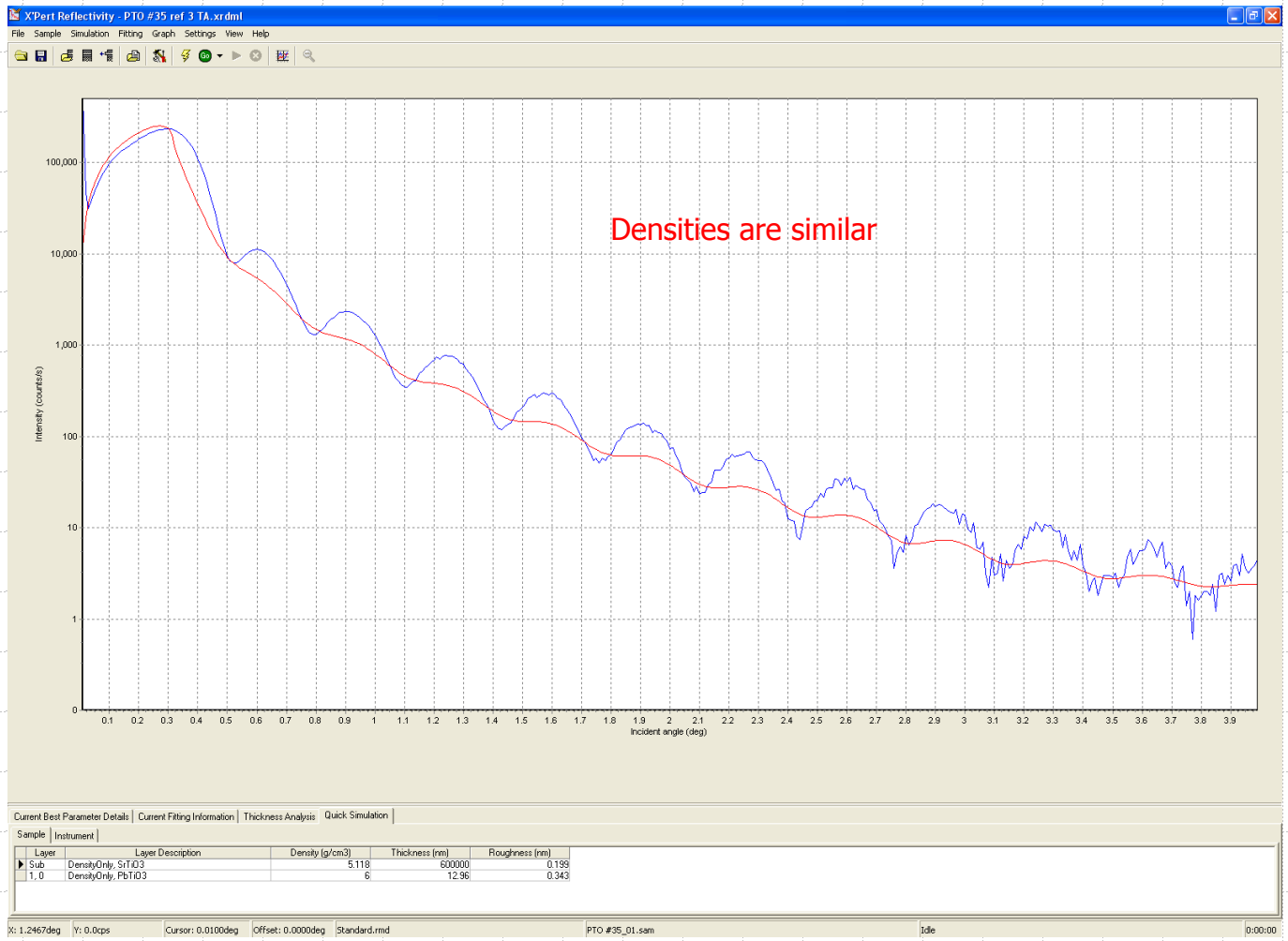
X-ray Reflectivity: Density

- $PbTiO_3$ on $SrTiO_3$



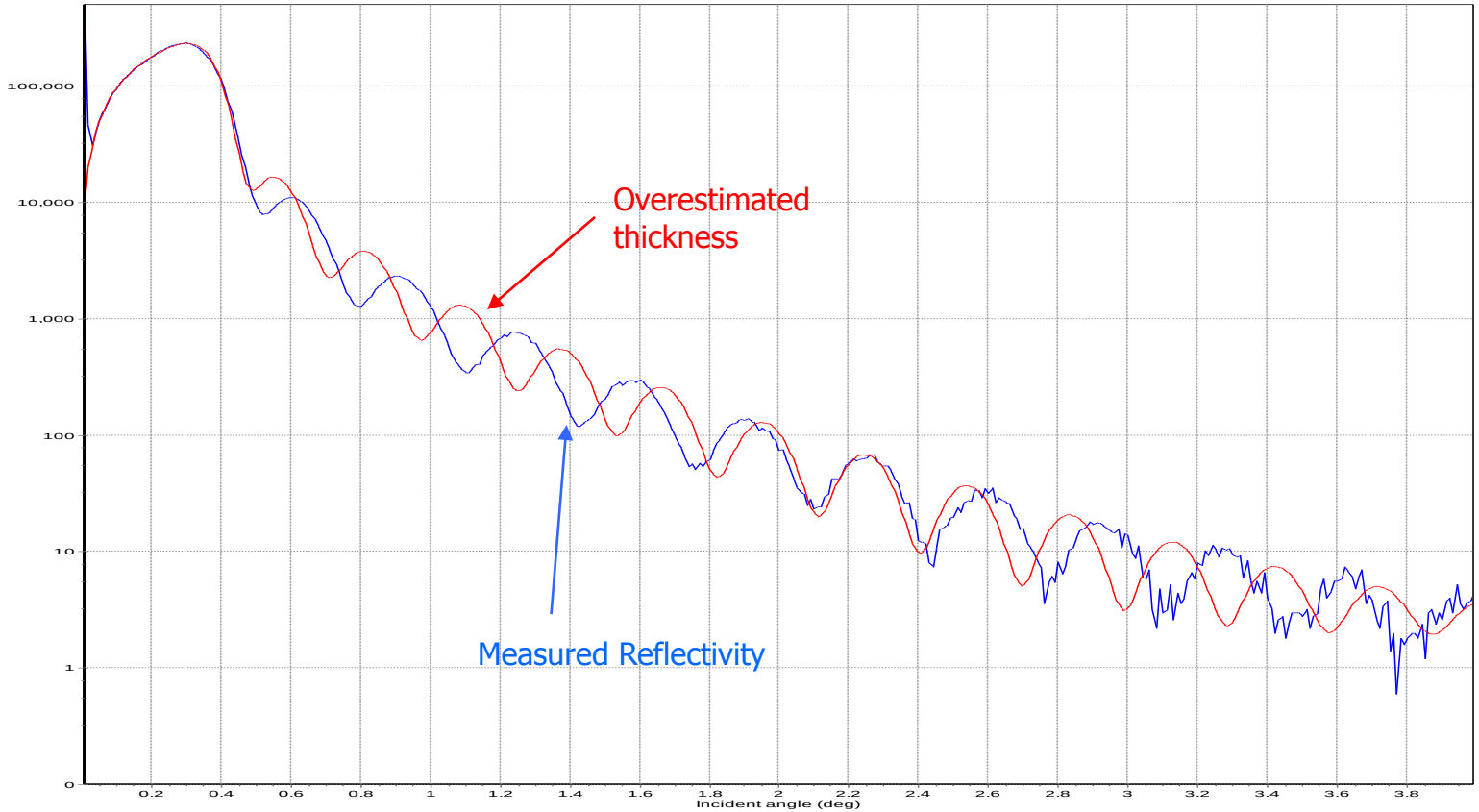
X-ray Reflectivity: Density

- $PbTiO_3$ on $SrTiO_3$



X-ray Reflectivity: Thickness

- $PbTiO_3$ on $SrTiO_3$



X-ray Reflectivity: Fitting

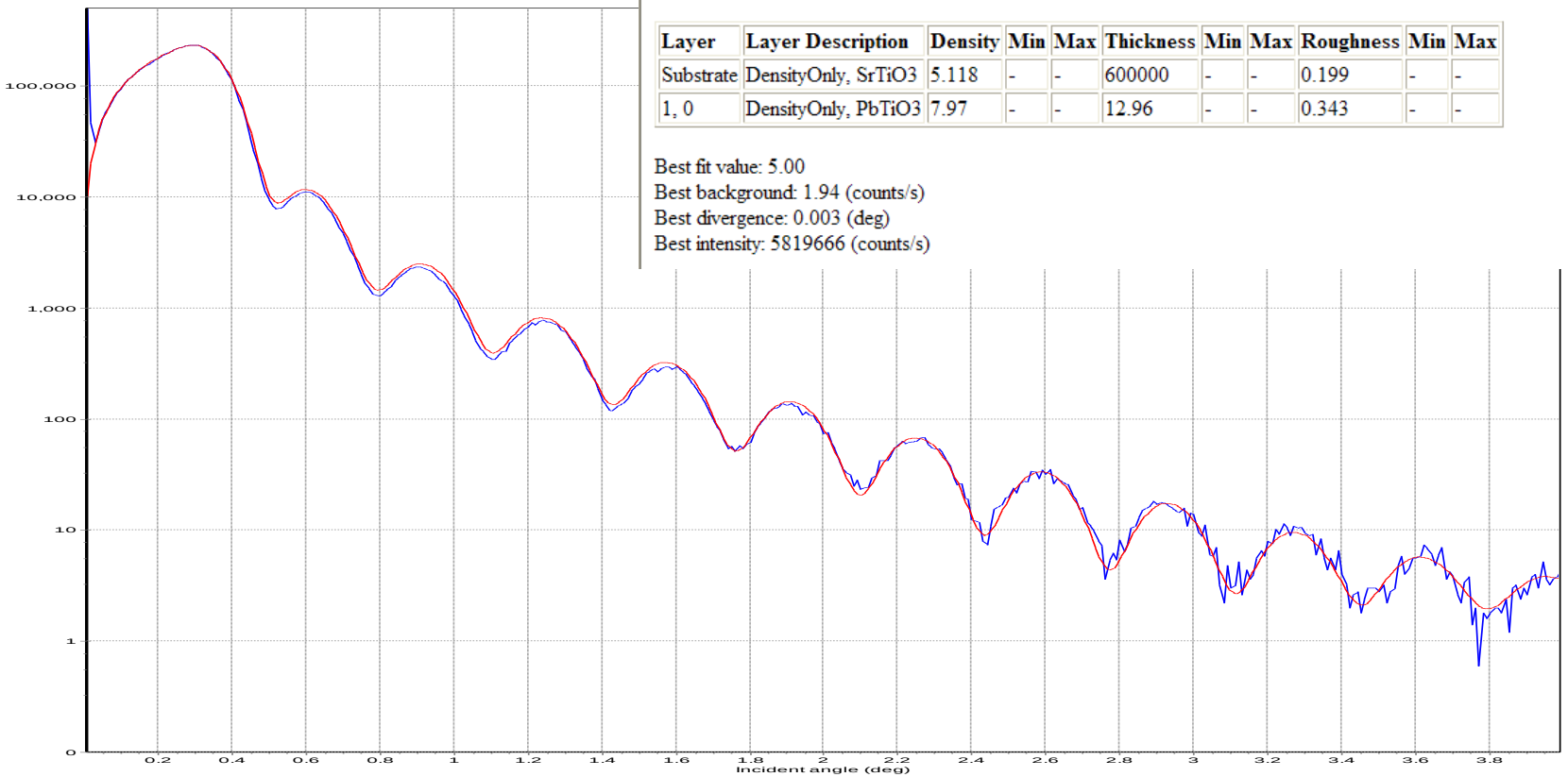
- $PbTiO_3$ on $SrTiO_3$

Input file: C:/Documents and Settings/Arturas/My Documents/Xray Lab/PTO/PTO #35/PTO #35 ref 3 TA.xrdml
Sample file: C:/Documents and Settings/Arturas/My Documents/Xray Lab/PTO/PTO #35/PTO #35_01.sam
Date fitted: 05 - Mar - 2008
Fitting mode used: Genetic Algorithm
Difference scheme used: Abs Log Difference

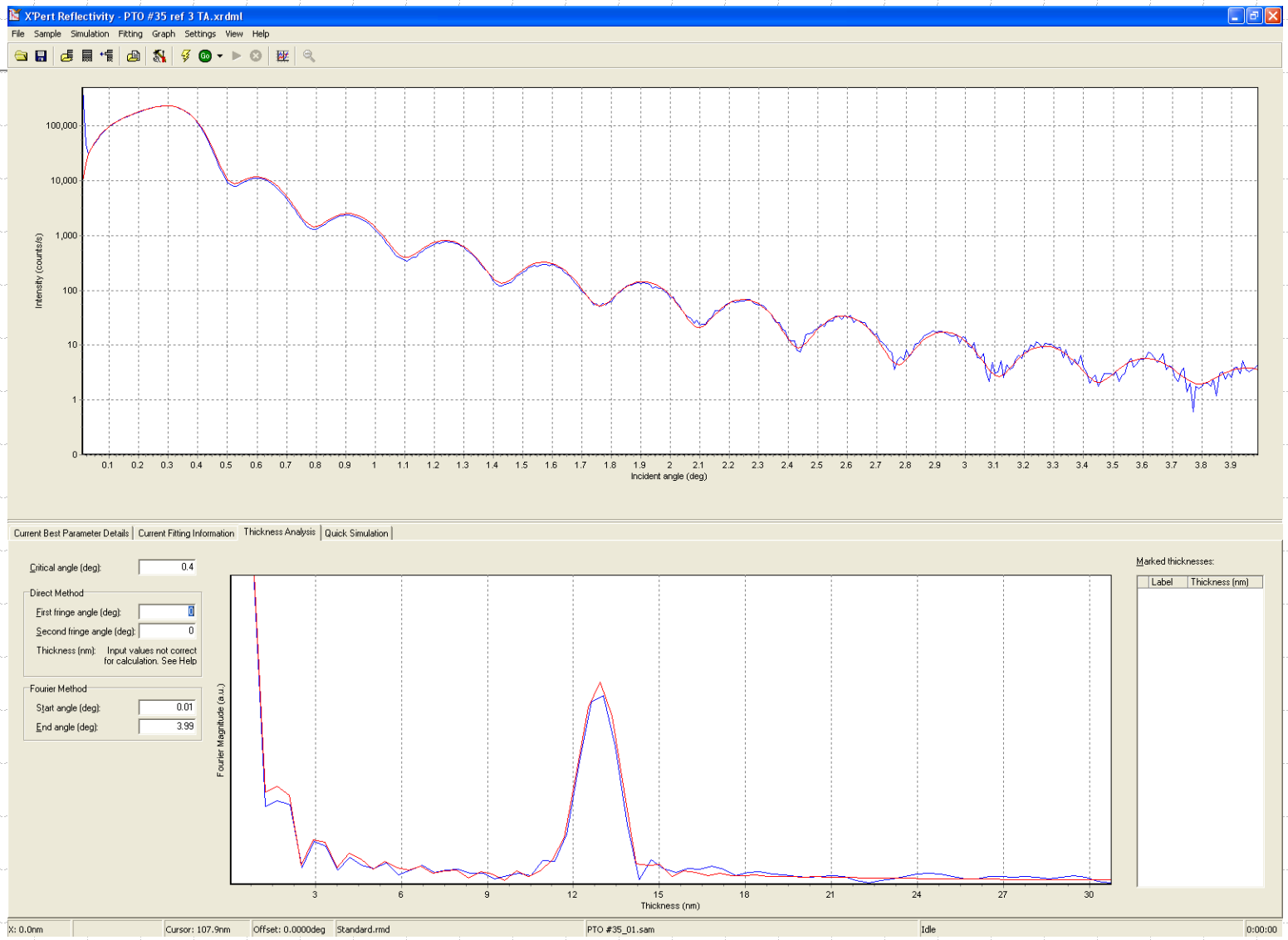
Measured data corrected with offset: 0 (deg)

Layer	Layer Description	Density	Min	Max	Thickness	Min	Max	Roughness	Min	Max
Substrate	DensityOnly, SrTiO3	5.118	-	-	600000	-	-	0.199	-	-
1, 0	DensityOnly, PbTiO3	7.97	-	-	12.96	-	-	0.343	-	-

Best fit value: 5.00
Best background: 1.94 (counts/s)
Best divergence: 0.003 (deg)
Best intensity: 5819666 (counts/s)

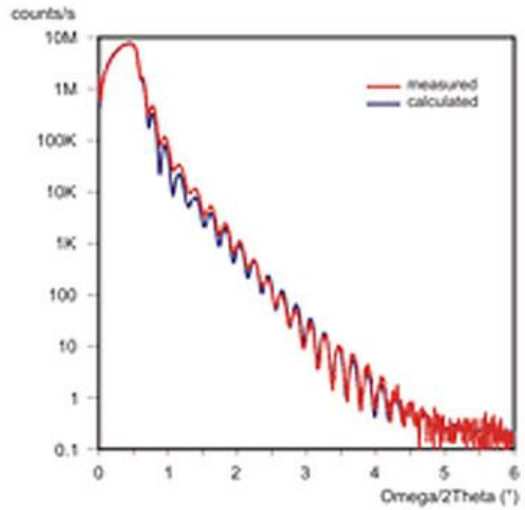


X-ray Reflectivity: Simulation

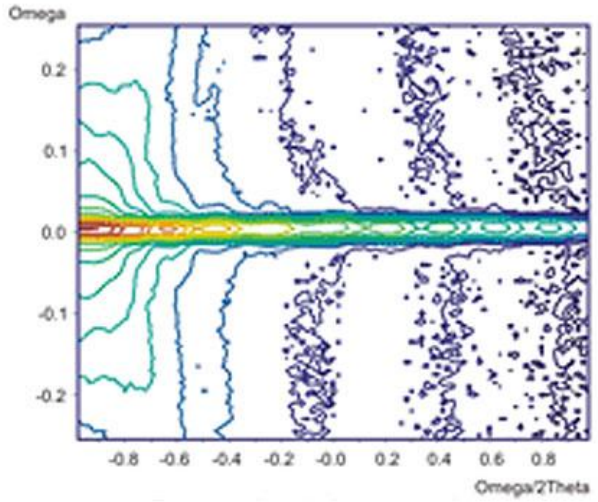


Self-Assembled Monolayers $C_{18}H_{37}SH$ on Au

Specular Reflectivity Curve



Reflectivity Map, Diffuse Scattering



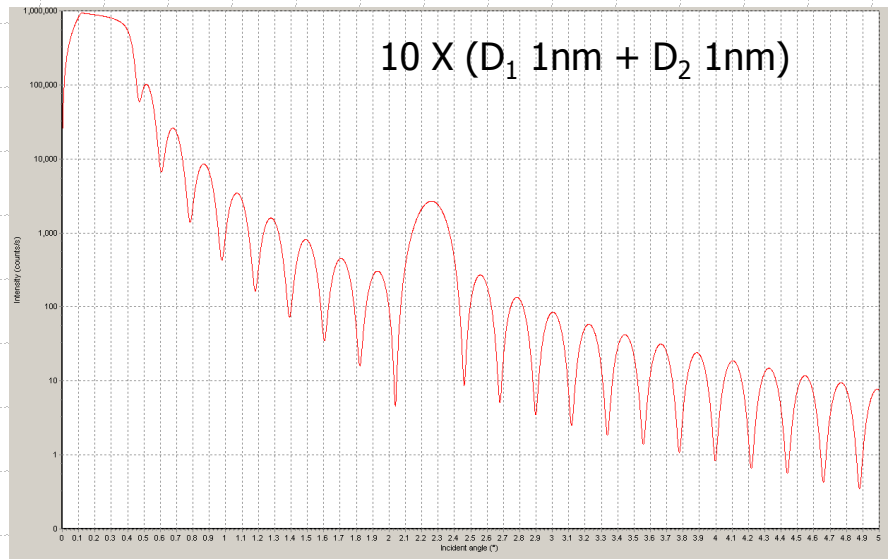
Determined thickness of the layers:

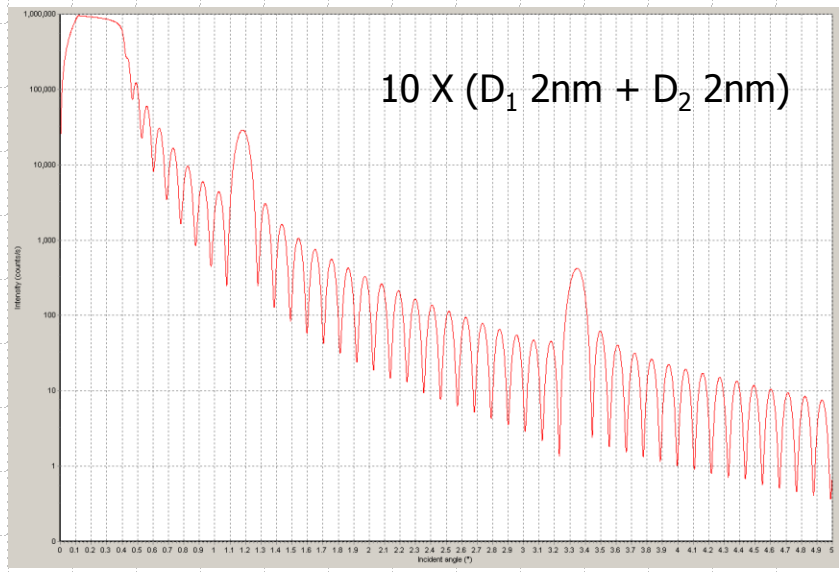
$C_{18}H_{37}SH$	- 1.6nm
Au1	- 0.6nm
Au2	- 19.0nm
Si	> 100,000nm

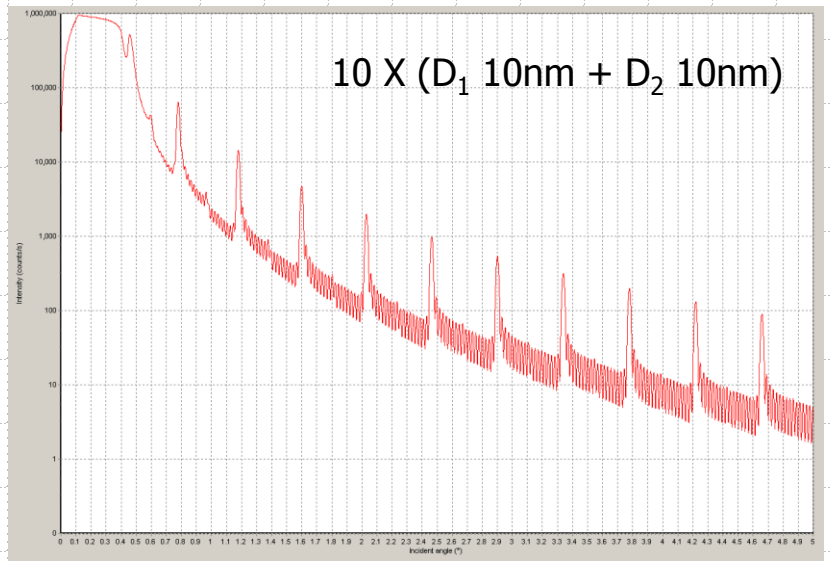
Determined:
Average Lateral Correlation Length: 2.5nm

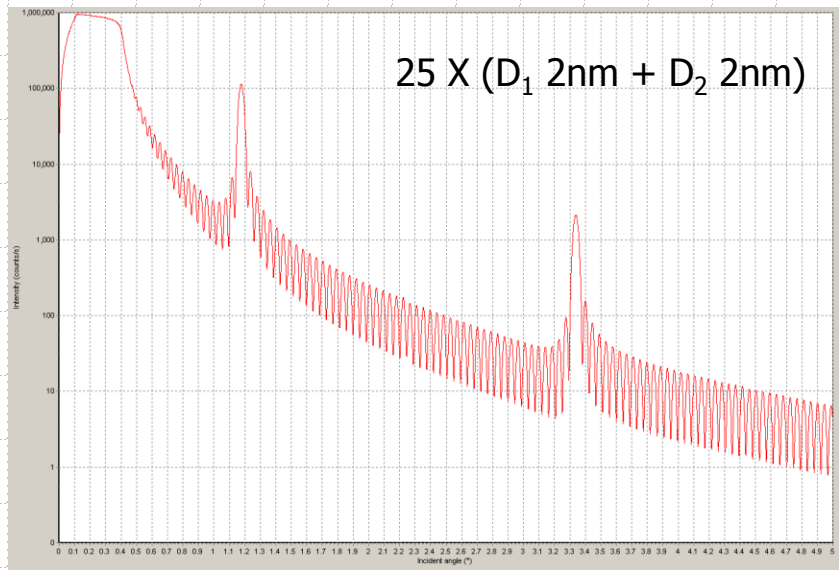
Vladimir Kogan, PANalytical

X-ray Reflectivity

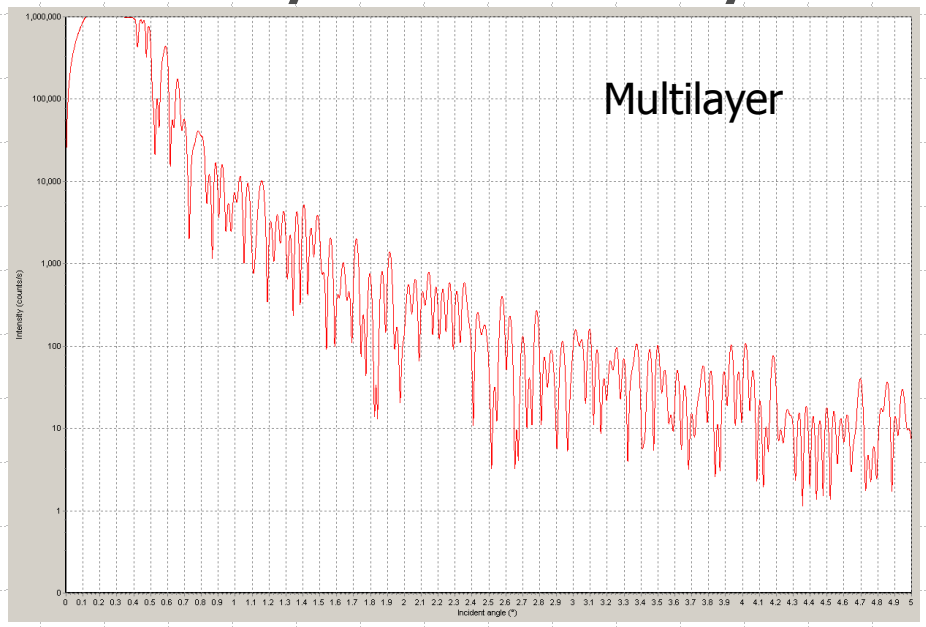




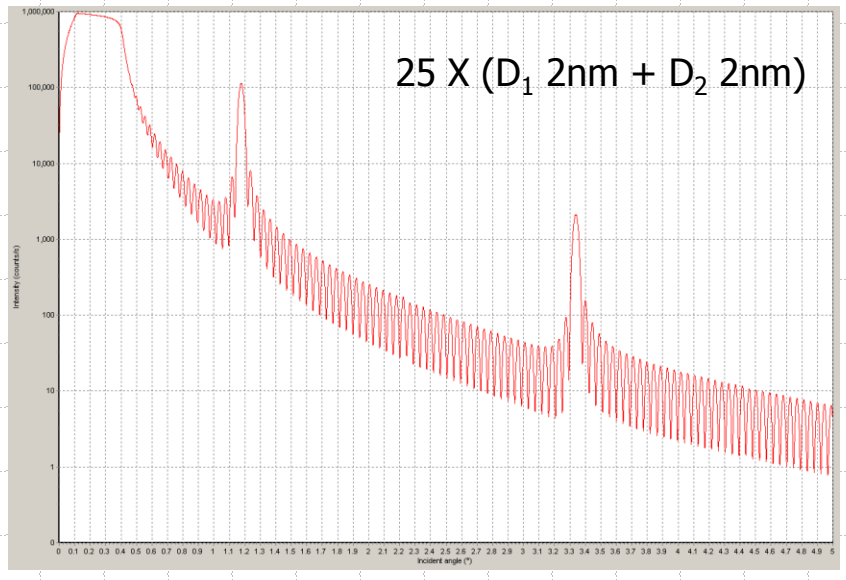


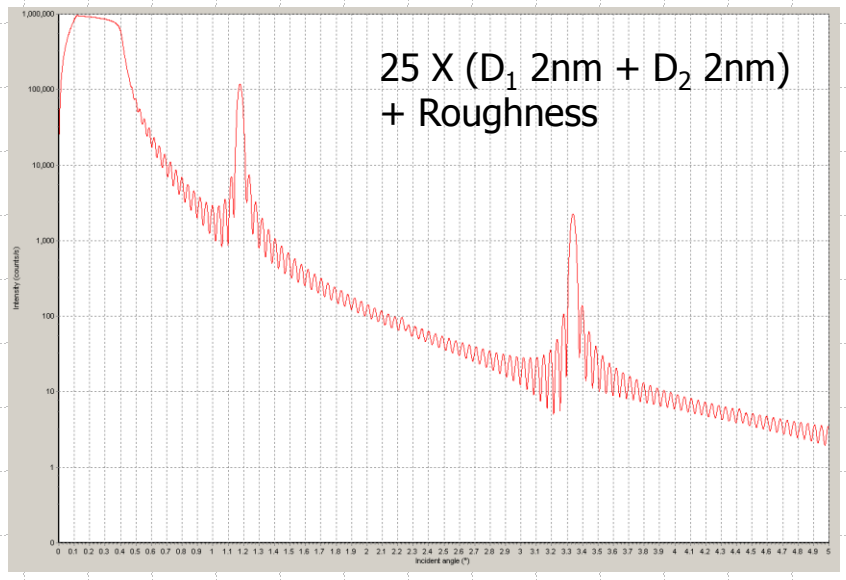


X-ray Reflectivity

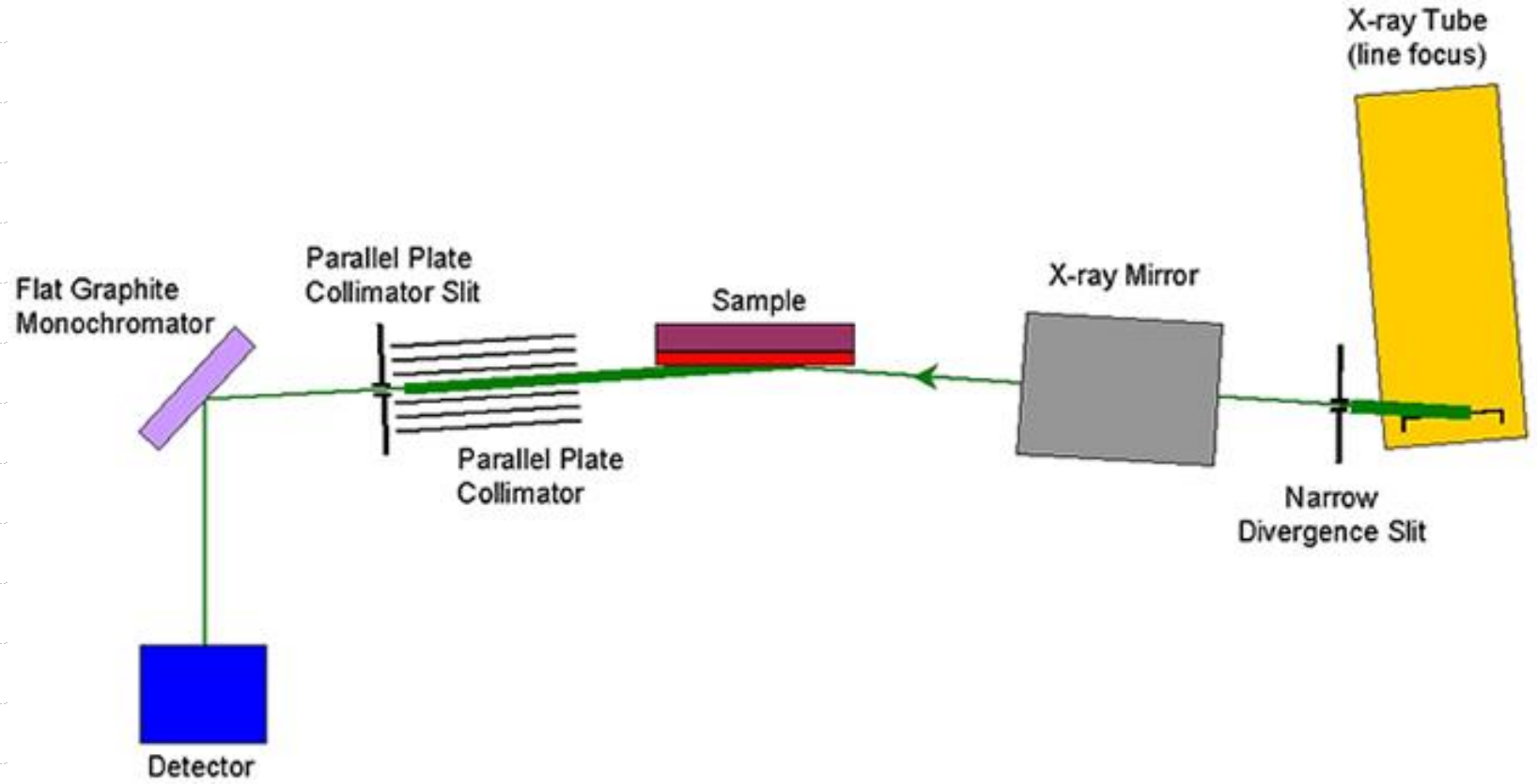


1 – D_1 2nm
2 – D_2 5nm
3 – D_1 3nm
4 – D_2 15nm
5 – D_1 25nm
6 – D_2 7nm
7 – D_1 14nm
8 – D_2 6nm
9 – D_1 3nm
10 – D_2 11nm
11 – D_1 14nm
12 – D_2 5nm



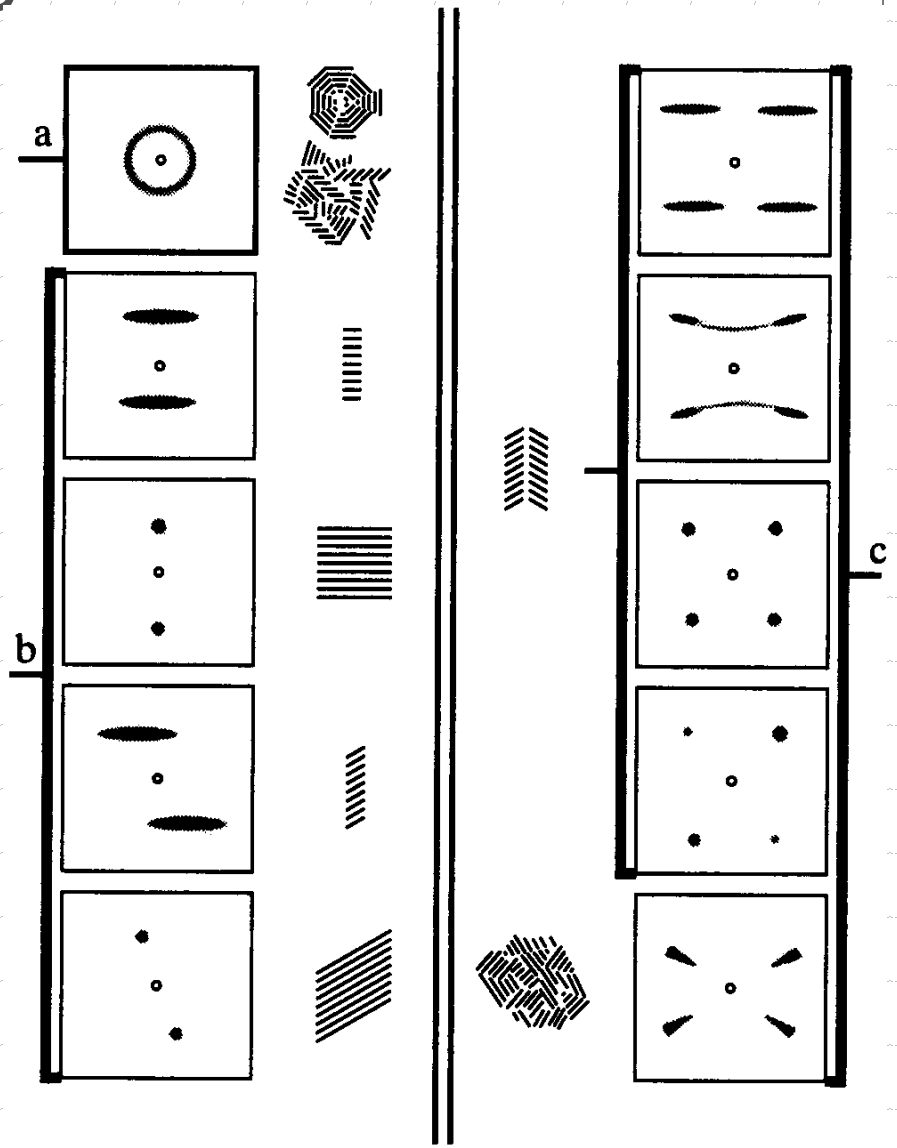


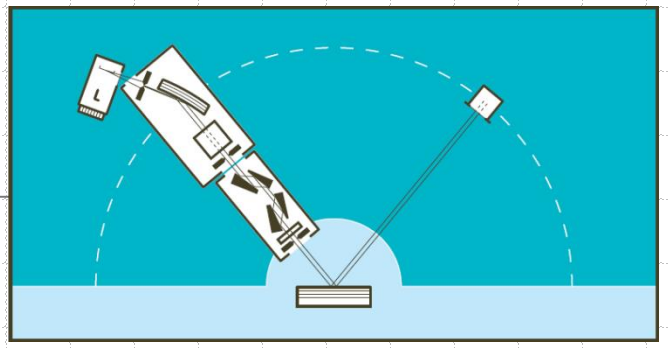
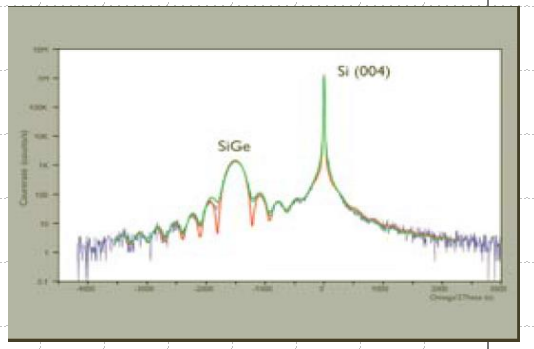
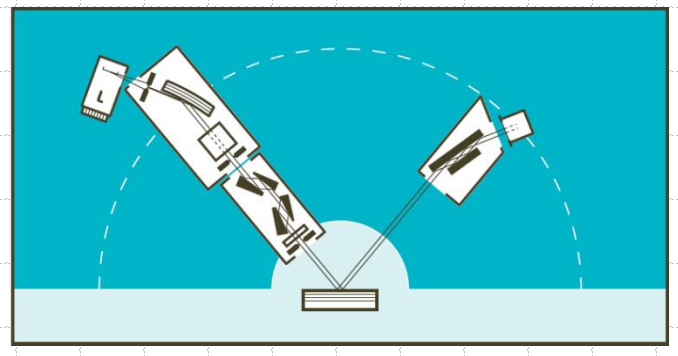
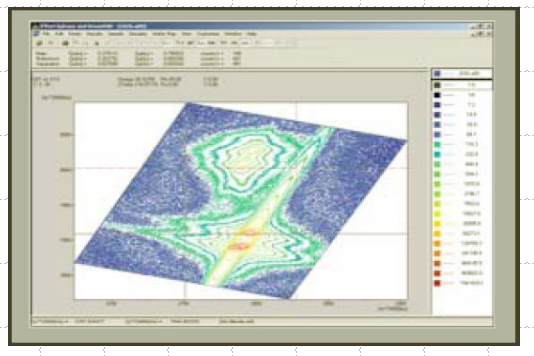
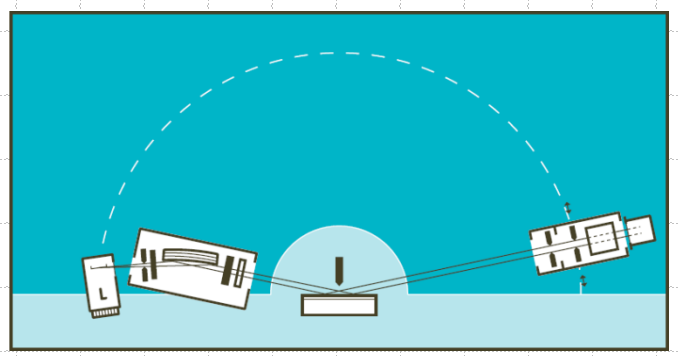
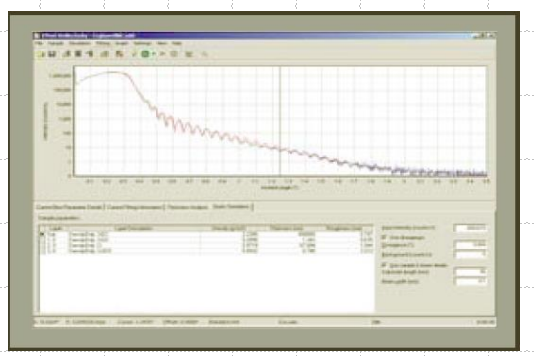
X-ray Reflectivity

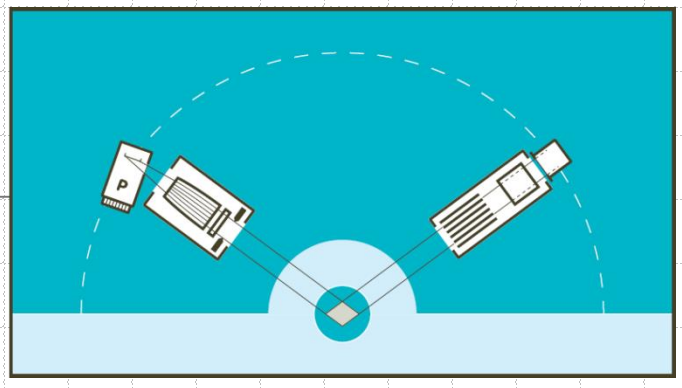
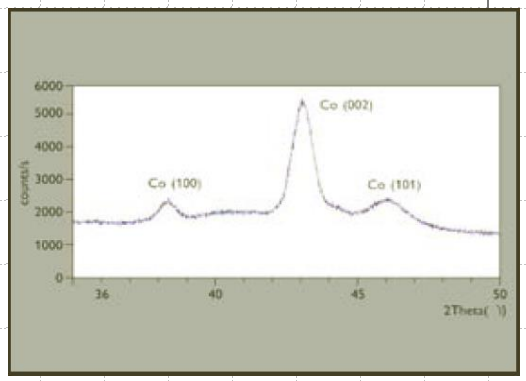
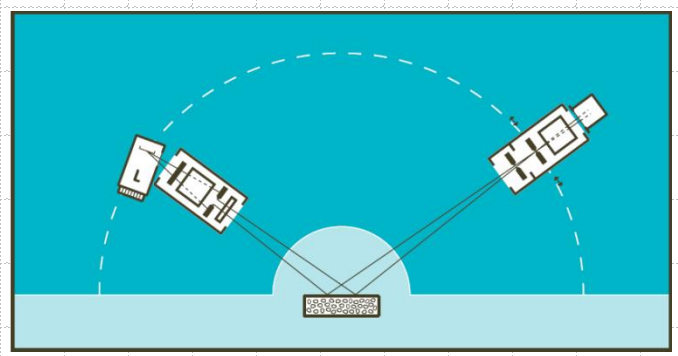
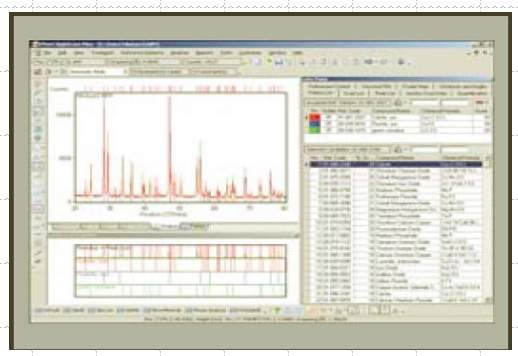
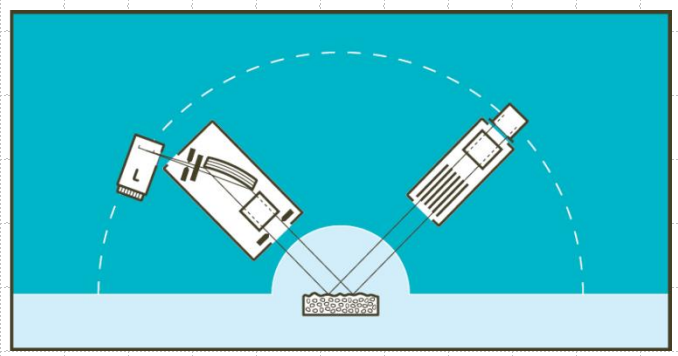
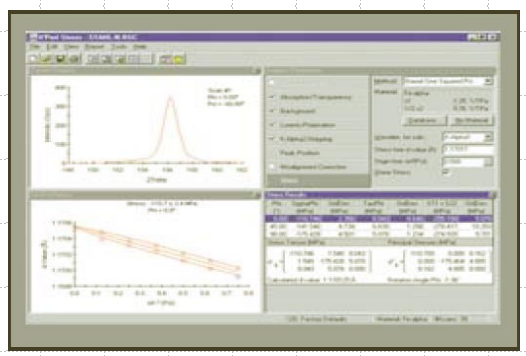


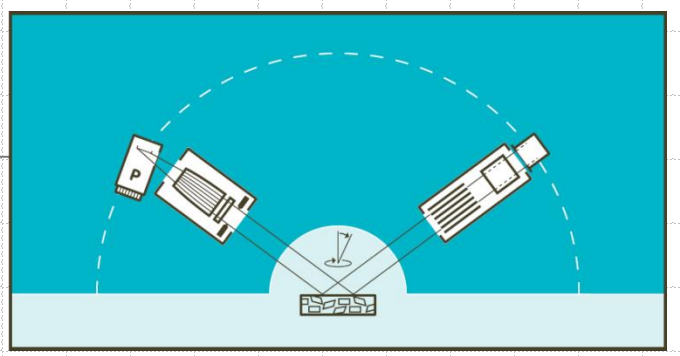
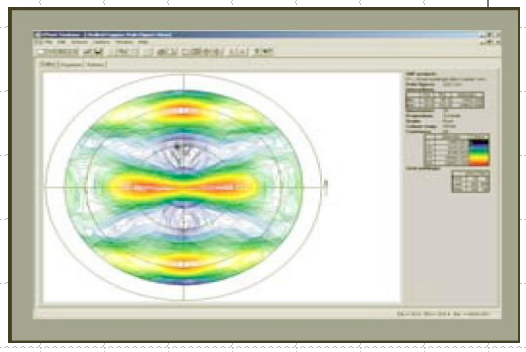
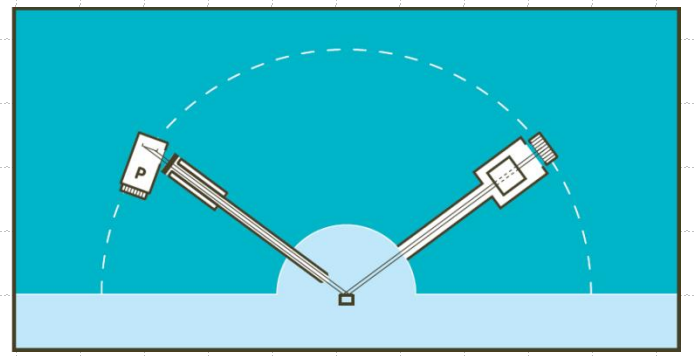
Small Angle Scattering

- Using 2D detector



Schematic Sample	Schematic Beam Path	Applications	Example
 Epitaxial Layer Structure		**Rocking Curve Analysis** with high resolution optics	
 Epitaxial Layer Structure		**Reciprocal Space Maps** using triple-axis analyzer	
 Thin Films epitaxial polycrystalline amorphous		**Reflectometry and thin film phase analysis** composition, layer thickness and interface quality	

Schematic Sample	Schematic Beam Path	Applications	Example
Very thin films		**In-plane diffraction** from very thin films. Depth sensitivity	
Polycrystalline material. Flat surface		**Phase analysis and Omega-stress** with Bragg-Brentano geometry	
Polycrystalline material. Rough surface		**Phase analysis and Omega-stress** with parallel beam optics	

Schematic Sample	Schematic Beam Path	Applications	Example
 Solid sample		**Psi-stress and texture analysis** using point focus with lens and parallel plate collimator optics	
 Very small sample. Spot on a sample		**Spot analysis on small and inhomogeneous samples** using mono-capillary optics