Large Scale Structures

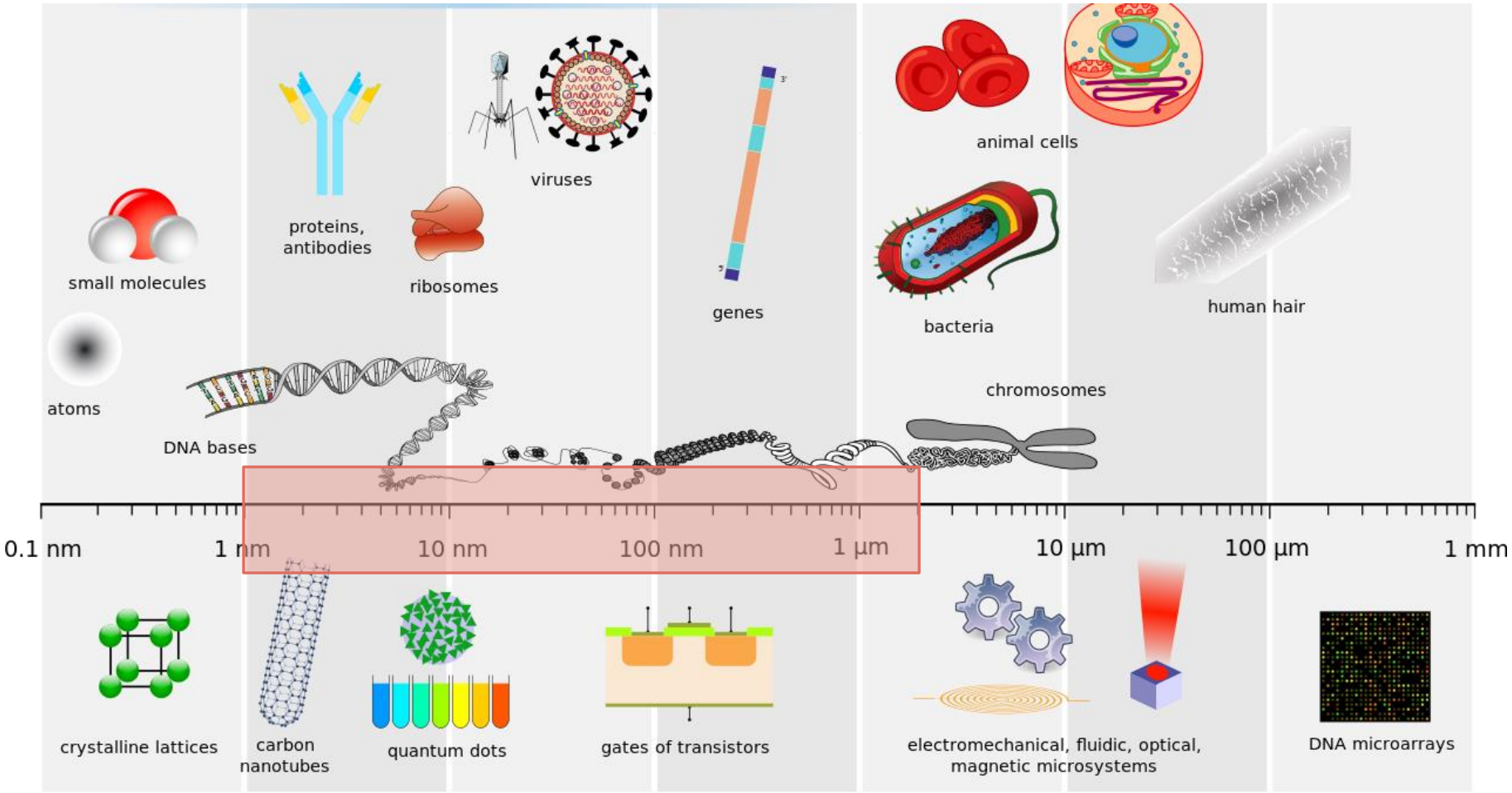
Small Angle Scattering & Reflectometry

Rana Ashkar

Assistant Professor, Physics Department, Virginia Tech

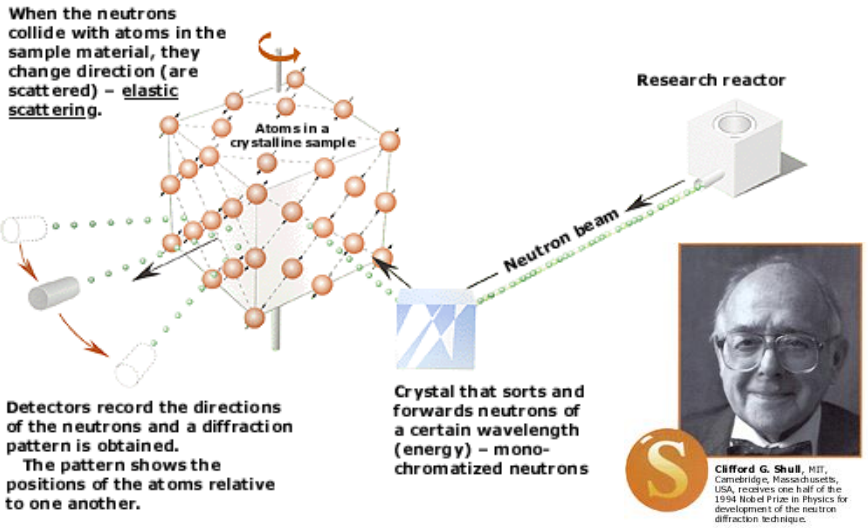
VIRGINIA TECH

Materials over Different Length Scales

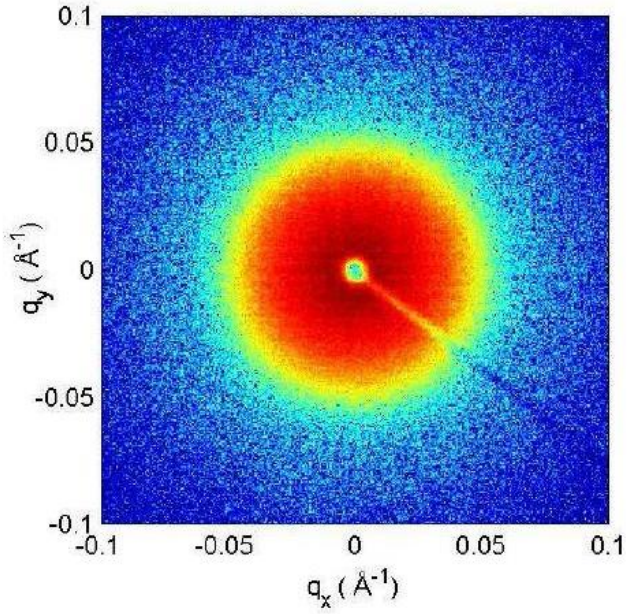


From Ordered to Disordered systems

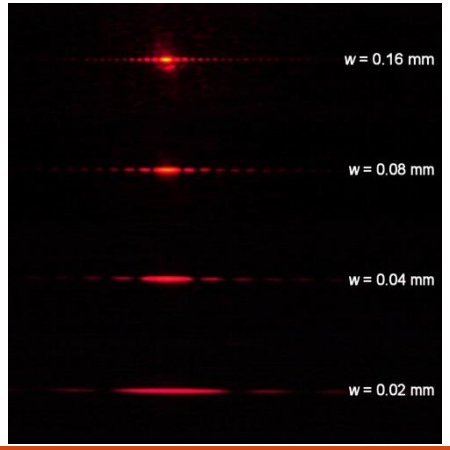
Neutrons show where atoms are…



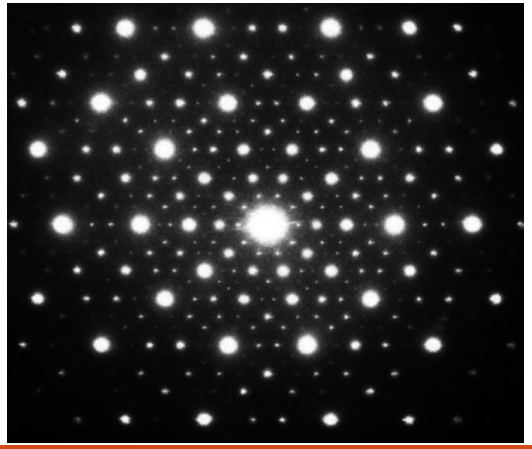
But what about soft materials and disordered systems??



Single Slit Diffraction

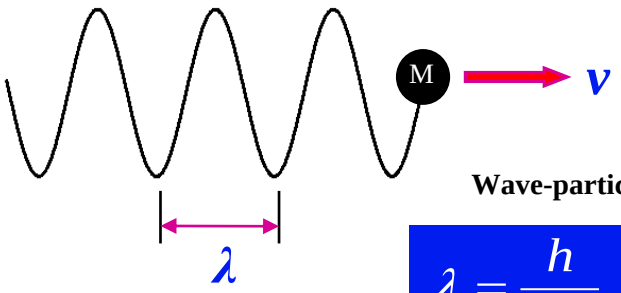


Crystal Diffraction



Scattering of Thermal Neutrons

$$E_0 = \frac{1}{2}Mv^2 \longleftrightarrow E = k_B T$$



Wave-particle duality

$$\lambda = \frac{h}{Mv}$$

de Broglie (1924)

At room temperature: $\lambda \sim 5$ A˚

Nuclear diameter ~ 10^{-5} A˚

Atomic spacing ~ A˚

Low-energy incident wave + Point-like scatterers

s-wave scattering

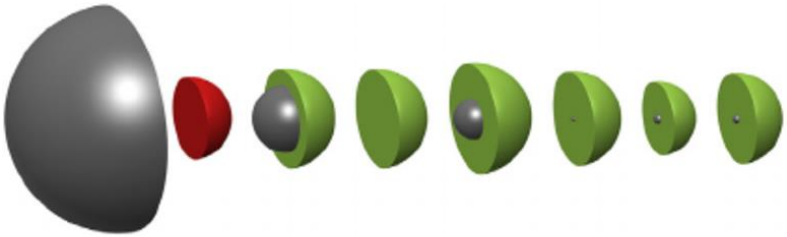
Fermi pseudopotential: $V(r) = \frac{2\pi\hbar^2 b}{M}\delta(r)$ $\xrightarrow{F.T.}$ $V = \frac{2\pi\hbar^2 b}{M}$

→ Coarse-graining: $V = \frac{2\pi\hbar^2 \rho}{M}$

Neutron Scattering Length Density

$$\rho = \frac{1}{volume}\sum_i b_i n_i$$

Neutron scattering lengths [fm]



	H	D	C	N	O	S	P
average:	**-3.74**	**6.67**	**6.65**	**9.36**	**5.81**	**2.85**	**5.13**

$$N_{b_{H_2O}} = \frac{2b_H + b_O}{V_{H_2O}} = \frac{(5.81 - 3.74 \cdot 2)\,fm}{30\,\mathring{A}^3}$$

$$N_{b_{H_2O}} = -0.56 \cdot 10^{10}\,cm^{-2}$$

$$V_{H_2O} = \frac{M_{H_2O}\bar{v}_{H_2O}}{N_A}$$

https://www.ncnr.nist.gov/resources/activation/

NIST Center for Neutron Research

D2O at 1.11 g/cm^3

Source neutrons: 1.000 Å = 81.80 meV = 3956 m/s
Source X-rays: 1.542 Å = 8.042 keV

1/e penetration depth (cm)		Scattering length density (10^{-6}/Å^2)		Scattering cross section (1/cm)		X-ray SLD (10^{-6}/Å^2)	
abs	43867.850	real	6.393	coh	0.513	real	9.455
abs+incoh	7.306	imag	-0.000	abs	0.000	imag	-0.032
abs+incoh+coh	1.535	incoh	3.302	incoh	0.137		

Neutron transmission is 87.21% for 1 cm of sample (after absorption and incoherent scattering).
Transmitted flux is 8.721e+7 n/cm^2/s for a 1e8 n/cm^2/s beam.

H2O at 1.00 g/cm^3

Source neutrons: 1.000 Å = 81.80 meV = 3956 m/s
Source X-rays: 1.542 Å = 8.042 keV

1/e penetration depth (cm)		Scattering length density (10^{-6}/Å^2)		Scattering cross section (1/cm)		X-ray SLD (10^{-6}/Å^2)	
abs	80.836	real	-0.561	coh	0.004	real	9.469
abs+incoh	0.186	imag	-0.000	abs	0.012	imag	-0.032
abs+incoh+coh	0.177	incoh	20.693	incoh	5.366		

Neutron transmission is 0.462% for 1 cm of sample (after absorption and incoherent scattering).
Transmitted flux is 4.616e+5 n/cm^2/s for a 1e8 n/cm^2/s beam.

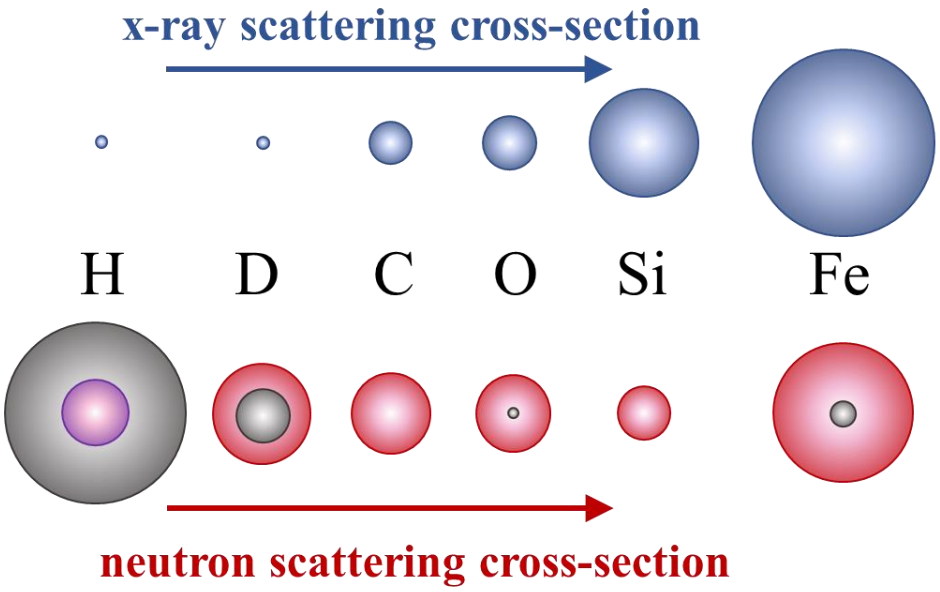
Si at 2.33 g/cm^3

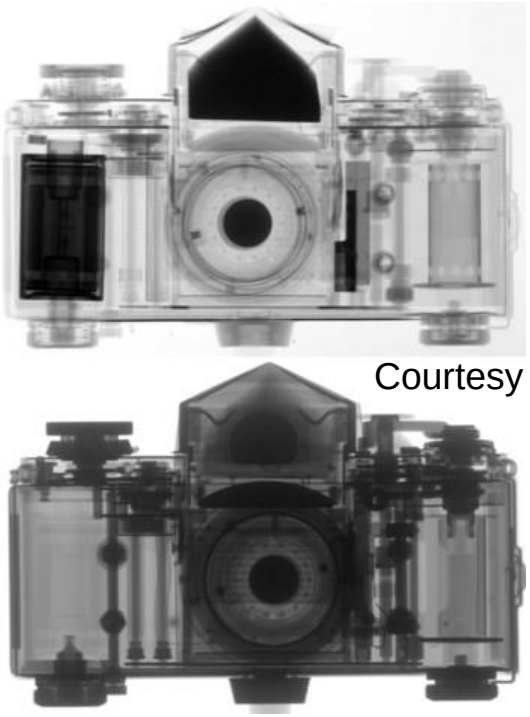
Source neutrons: 1.000 Å = 81.80 meV = 3956 m/s
Source X-rays: 1.542 Å = 8.042 keV

1/e penetration depth (cm)		Scattering length density (10^{-6}/Å^2)		Scattering cross section (1/cm)		X-ray SLD (10^{-6}/Å^2)	
abs	210.460	real	2.074	coh	0.108	real	20.071
abs+incoh	201.965	imag	-0.000	abs	0.005	imag	-0.458
abs+incoh+coh	8.848	incoh	0.089	incoh	0.000		

Neutron transmission is 99.51% for 1 cm of sample (after absorption and incoherent scattering).
Transmitted flux is 9.951e+7 n/cm^2/s for a 1e8 n/cm^2/s beam.

Neutron vs. X-rays



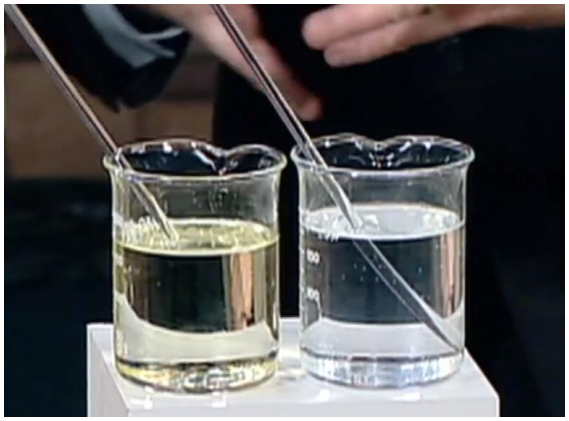


Courtesy of PSI

Remember that:

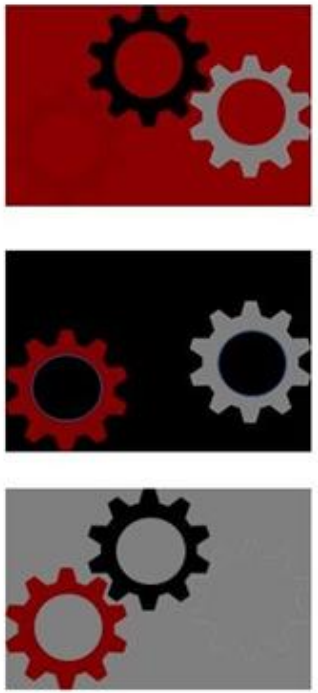
- ❑ Neutrons interact with matter through nuclear interactions while X-rays interact through electromagnetic interactions with the electron cloud of atoms.
- ❑ Neutron scattering is characterized by coherent and incoherent contributions to scattering. You will see later that coherent scattering depends on Q and thus informs about material structures, whereas incoherent scattering is Q independent.
- ❑ In structural measurements, incoherent scattering is undesirable and should be minimized.

The Power of Contrast Variation/Match



SLD is akin to the optical index of refraction. The ability to change contrast and selectively observe different components of a complex system is a powerful tool that can help solve key questions in advanced technologies and the machinery of life.

Machinery of Life is Complex
(Building a predictive understanding of life processes)



Small Angle Scattering

Used to measure large objects (few nm's to ~1μm)

Recall that :

$\vec{Q} = \vec{k}' - \vec{k}_0 = 2k_0 \sin\theta$ for elastic scattering

and that

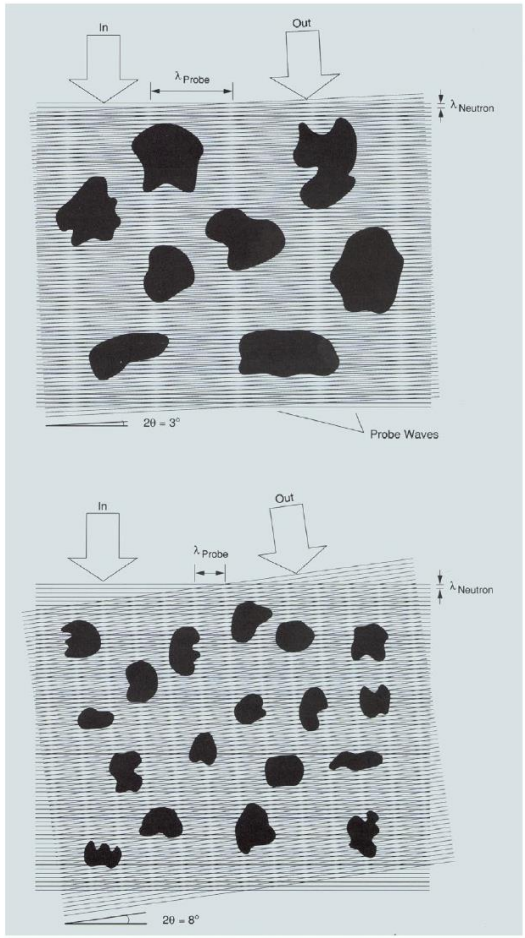
$\lambda = 2\pi / k = 2\pi / (Q / 2\sin\theta) = 4\pi \sin\theta / Q$

so we can rewrite Bragg's law $\lambda = 2d \sin\theta$ as

$d = 2\pi/Q$ or for small θ $d \approx \lambda/2\theta$

i.e. small Q => large length scales

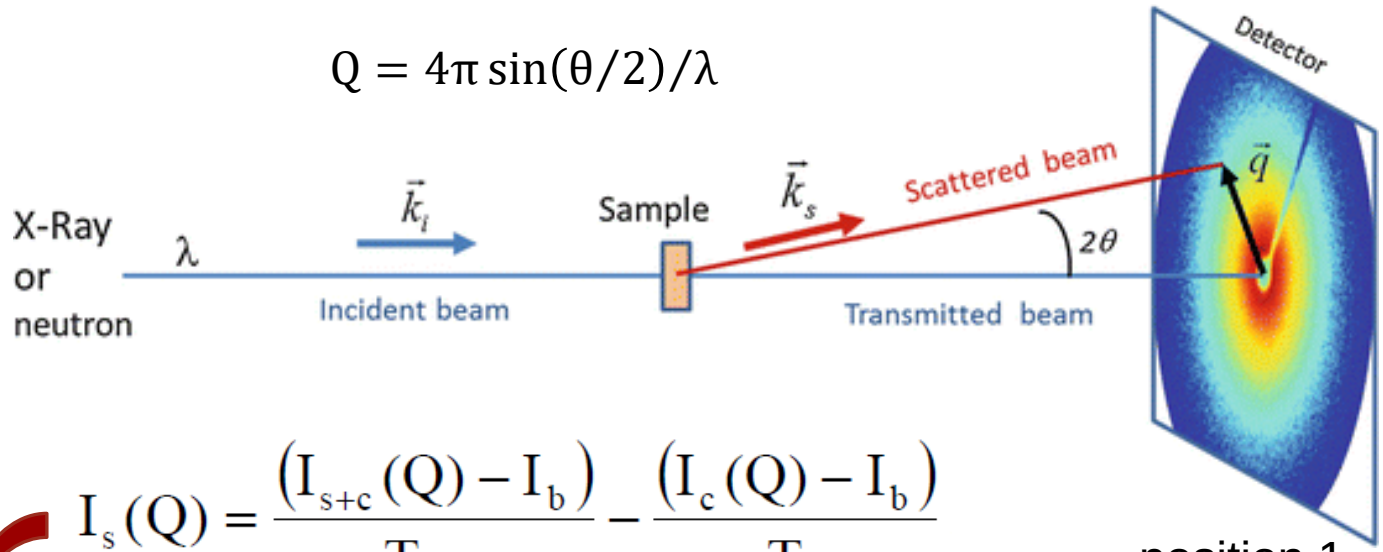
Scattering at small angles probes large length scales



Typical scattering angles for SANS are ~ 0.3° to 5°

The Concept of Small Angle Scattering

$$Q = 4\pi \sin(\theta/2)/\lambda$$

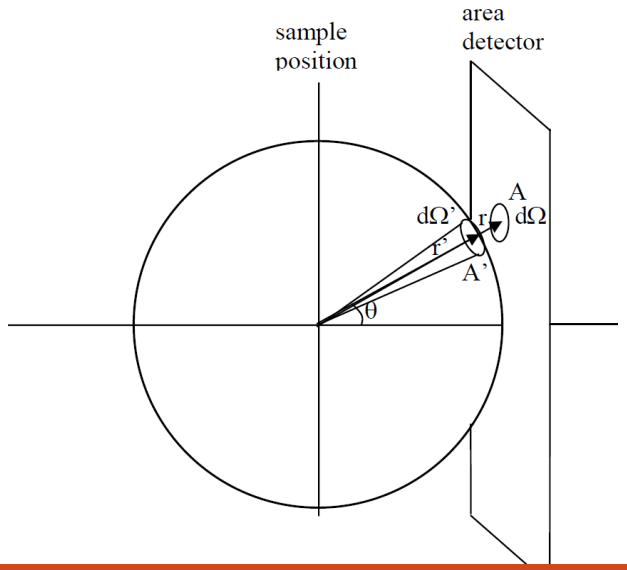


$$I_s(Q) = \frac{(I_{s+c}(Q) - I_b)}{T_{s+c}} - \frac{(I_c(Q) - I_b)}{T_c}$$

position 1

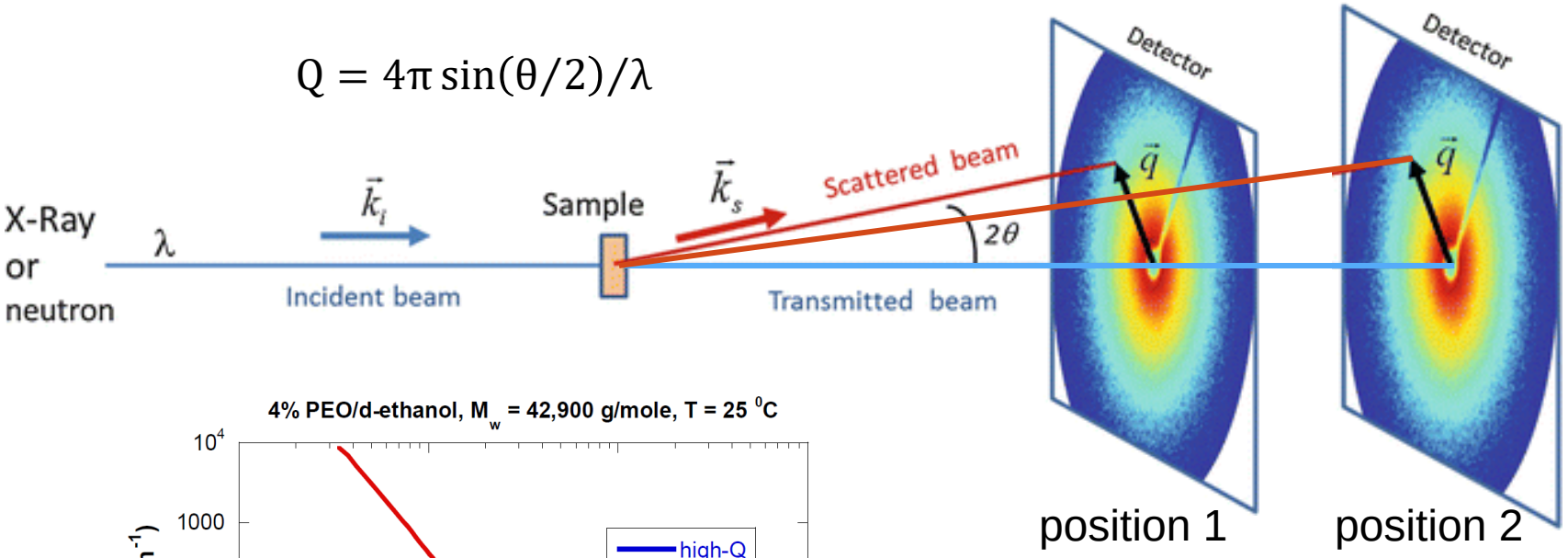
$$\frac{d\Sigma(Q)}{d\Omega} = \frac{I_s(Q)}{I_0(\lambda) T d\Delta\Omega}$$

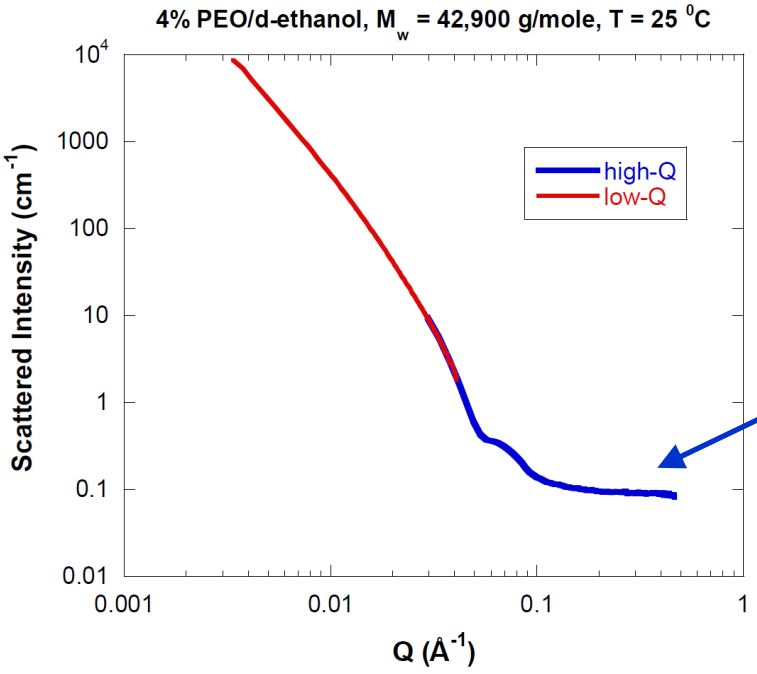
I_s (Q): reduced scattering intensity from sample
I_c (Q): scattering intensity from the empty cell
I_{s+c} (Q): scattering intensity from sample + cell
I_b (Q): background scattering intensity (with blocked beam
T_c (Q): transmission from the empty cell
T_{s+c} (Q): transmission from sample + cell



The Concept of Small Angle Scattering

$$Q = 4\pi \sin(\theta/2)/\lambda$$



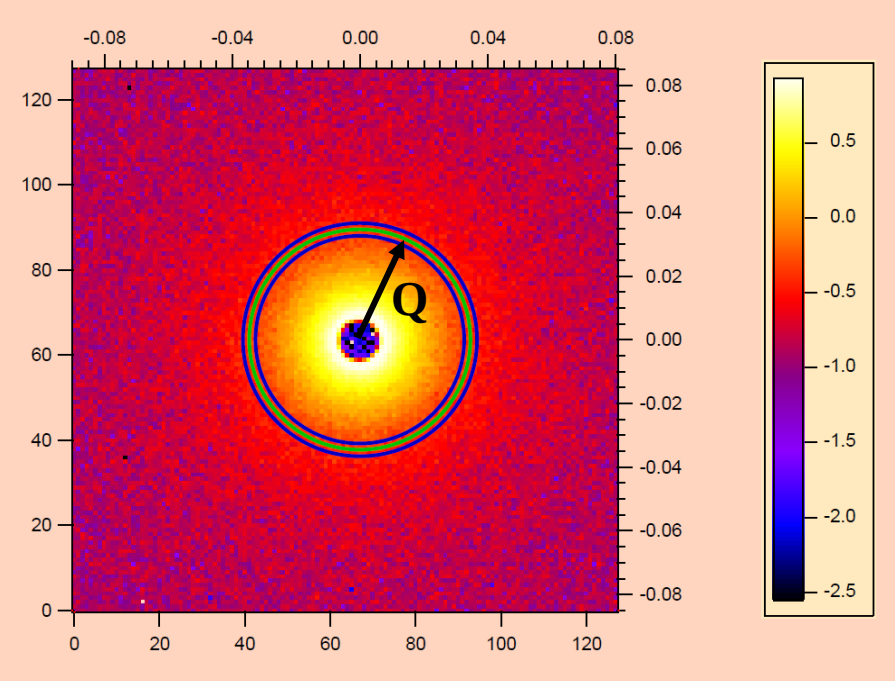


SANS toolbox, B. Hammouda

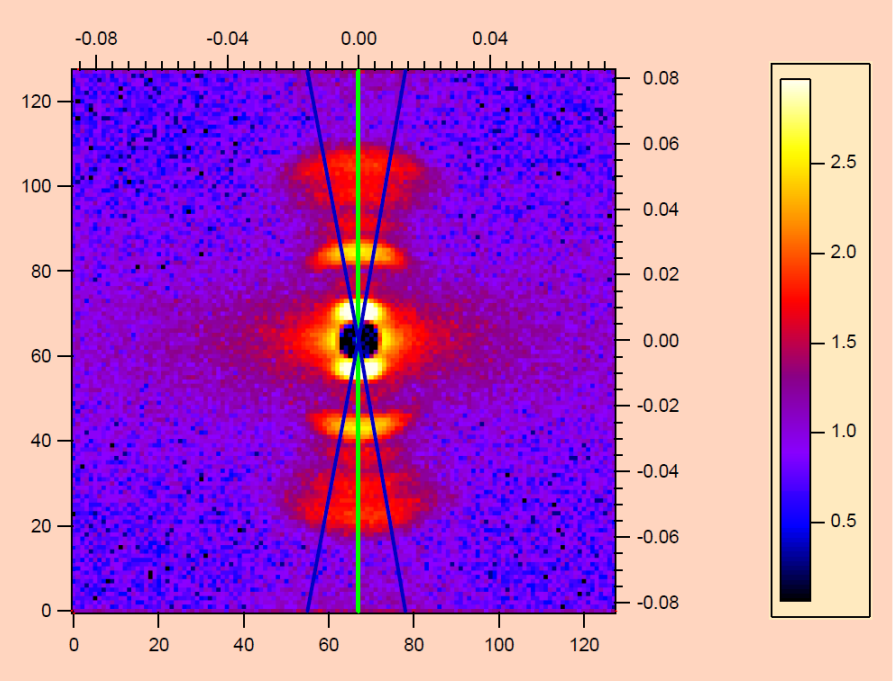
- Notice the flat featureless background (incoherent scattering)
- Also notice that the direct beam is always blocked in SANS/SAXS experiments (except when measuring transmission!)

Data Processing in Small Angle Scattering

Isotropic Scattering → Radial Averaging



Anisotropic Scattering → Sector Averaging



SANS toolbox, B. Hammouda

What do SANS instruments look like?

The NIST 30m SANS Instrument Under Construction

SAXS/SANS Measures Particle Shapes and Interparticle Correlations

$$\frac{d\sigma}{d\Omega} = \langle b \rangle^2 \int_{space} d^3r \int_{space} d^3r' n_N(\vec{r}) n_N(\vec{r}') . e^{i\vec{Q}.(\vec{r}-\vec{r}')}$$

$$= \int_{space} d^3R \int_{space} d^3R' \langle n_P(\vec{R}) n_P(\vec{R}') \rangle e^{i\vec{Q}.(\vec{R}-\vec{R}')} \left\langle \left| (\rho - \rho_0) \int_{particle} d^3x . e^{i\vec{Q}.\vec{x}} \right|^2 \right\rangle_{orientation}$$

$$\frac{d\sigma}{d\Omega} = (\rho - \rho_0)^2 \left| F(\vec{Q}) \right|^2 V_p^2 N_P \int_{space} d^3R . G_P(\vec{R}) . e^{i\vec{Q}.\vec{R}}$$

where G_P is the particle - particle correlation function (the probability that there is a particle at $\vec{R}$ if there's one at the origin) and $\left|F(\vec{Q})\right|^2$ is the particle form factor :

$$\left| F(\vec{Q}) \right|^2 = \frac{1}{V_p^2} \left\langle \left| \int_{particle} d^3x . e^{i\vec{Q}.\vec{x}} \right|^2 \right\rangle_{orientation}$$

These expressions are the same as those for nuclear scattering except for the addition of a form factor that arises because the scattering is no longer from point-like particles

Scattering from Dilute Particle Suspensions

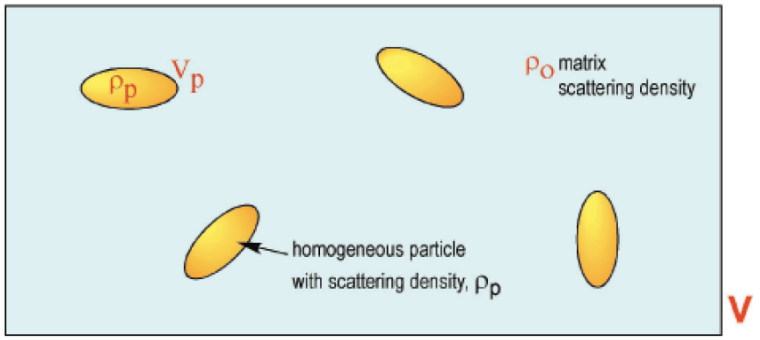
Scattered intensity per unit volume of sample = $I(\vec{Q}) = \frac{1}{V}\frac{d\sigma}{d\Omega} = \frac{1}{V}\left\langle \left| \int \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} d\vec{r} \right|^2 \right\rangle$

For identical particles

$$I(Q) = \frac{N}{V}(\rho_p - \rho_0)^2 V_p^2 \left\langle \left| \frac{1}{V_p} \int_{particle} e^{i\vec{Q}\cdot\vec{r}} d\vec{r} \right|^2 \right\rangle$$

contrast factor

particle form factor $|F(\vec{Q})|^2$



Note that $I(0) = \frac{N}{V}(\rho_p - \rho_0)^2 V_p^2$

Particle concentration $c = NV_p / V$ and particle molecular weight $M_w = \rho V_p N_A$

where ρ is the particle mass density and N_A is Avagadro's number

so $I(0) = \frac{cM_w}{\rho N_A}(\rho_p - \rho_0)^2$ provides a way to find the particle molecular weight

Scattering from Spherical Particles

The particle form factor $\left|F(\vec{Q})\right|^2 = \left|\int_V d\vec{r} e^{i\vec{Q}.\vec{r}}\right|^2$ is determined by the particle shape.

For a sphere of radius R, F(Q) only depends on the magnitude of Q :

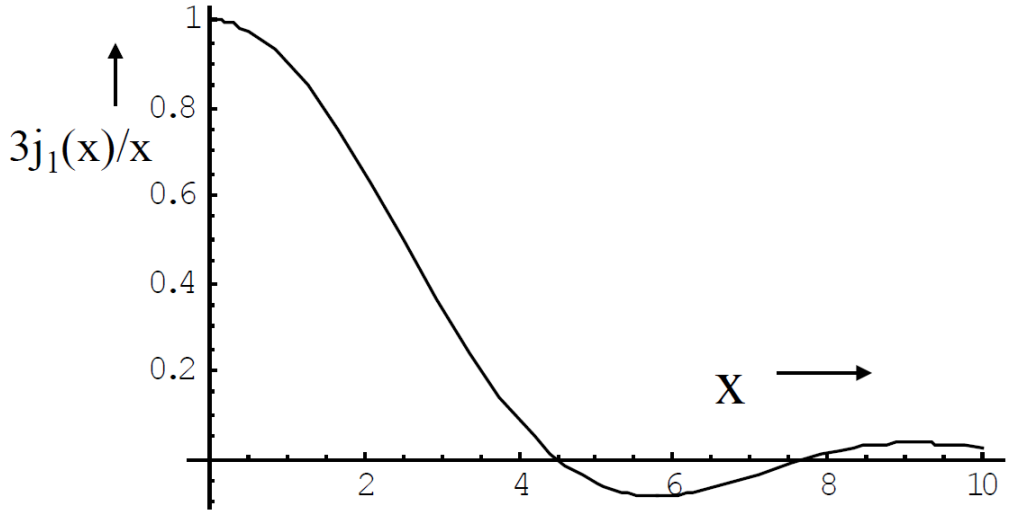
$$F_{sphere}(Q) = 3V_0\left[\frac{\sin QR - QR\cos QR}{(QR)^3}\right] \equiv \frac{3V_0}{QR} j_1(QR) \rightarrow V_0 \text{ at } Q = 0$$

Thus, as $Q \rightarrow 0$, the total scattering from an assembly of uncorrelated spherical particles [i.e. when $G(\vec{r}) \rightarrow \delta(\vec{r})$] is proportional to the square of the particle volume times the number of particles.

For elliptical particles replace R by :

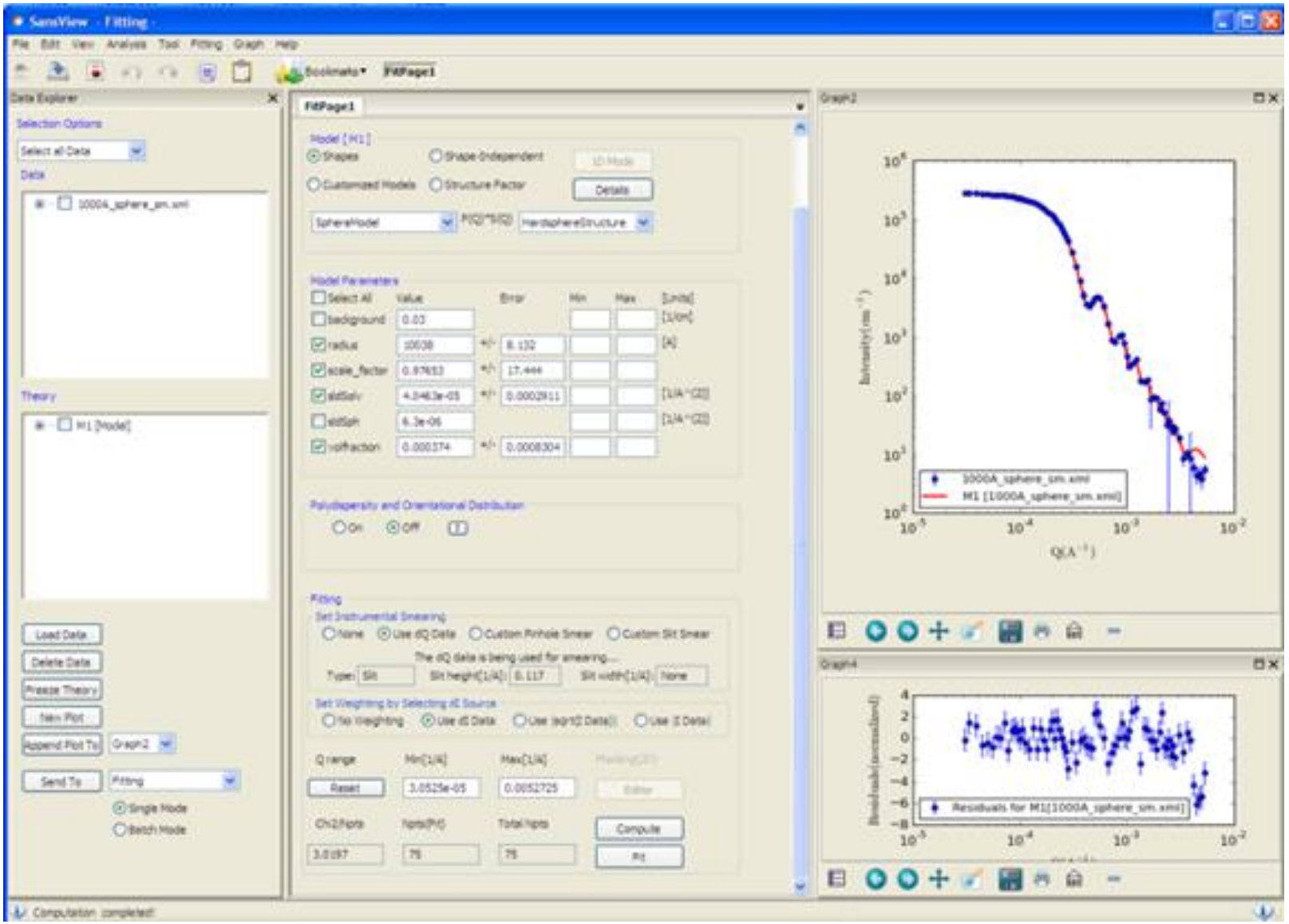
$R \rightarrow (a^2 \sin^2\vartheta + b^2 \cos^2\vartheta)^{1/2}$

where ϑ is the angle between the major axis (a) and $\vec{Q}$



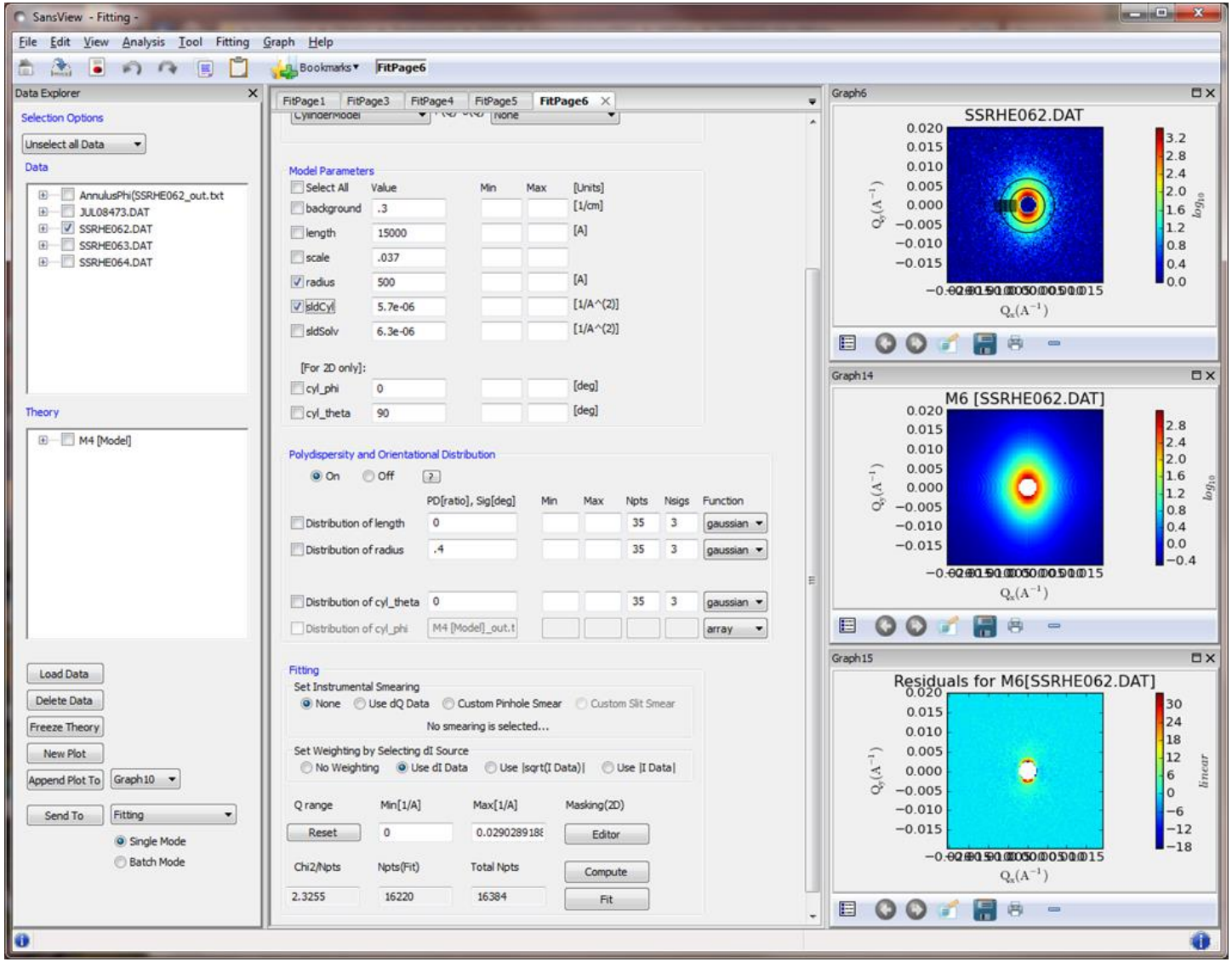
SANS/SAXS Data Fitting (1D)

www.sasview.org



SANS/SAXS Data Fitting (2D)

www.sasview.org



Tips for SANS/SAXS Measurements

- Simulate the reflectivity profiles that you expect to see
  - Make sure you can see the effect that you are looking for (Be mindful about layer thicknesses – extremes are challenging to resolve)
  - Choose the best substrate
  - Choose the right contrast conditions

- Make sure you have high quality samples
  - Low surface roughness
  - Beware of lateral imperfections (large islands, partial surface coverage)
  - If possible, try to do complimentary characterization (AFM, TEM, ...)

- Choose the right instrument & scattering geometry
  - For samples with rough surfaces or in fluid environments, consider incidence through substrate (beam attenuation, diffuse scattering, …)
  - For free surface or interface measurements of fluids, you need an instrument with a horizontal sample geometry
  - Check that the instrument has the right specs (resolution, q-range, ...)

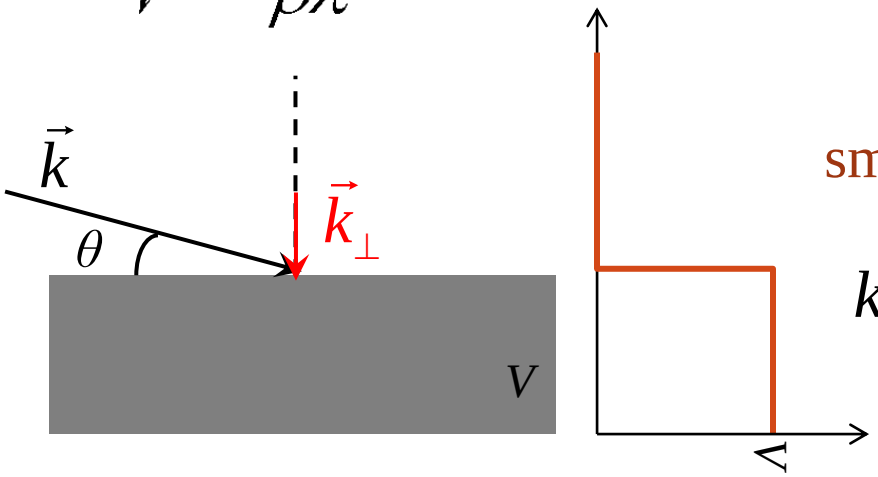
From Bulk Materials to Surfaces and Interfaces:

How do we study matter in thin films and buried structures?

Reflection from Surfaces and Interfaces

Consider neutrons of $\lambda = 5$ Å incident on silicon: $\rho_{Si} = 2.07 \times 10^{-6}$ Å^{-2}

$$\frac{E}{V} = \frac{\pi}{\rho\lambda^2} \sim 10^4$$ → Highly penetrating



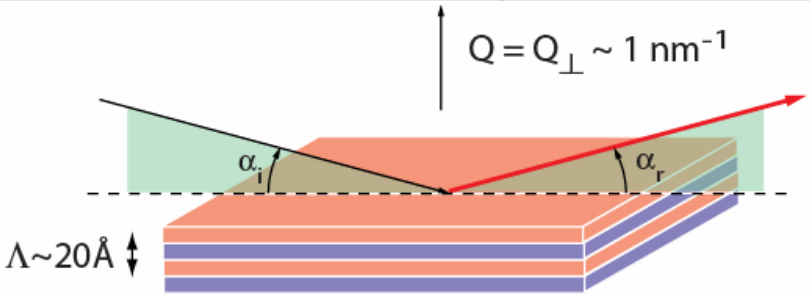
small angle approximation

$$k_\perp = \frac{2\pi}{\lambda}\sin\theta \sim \frac{2\pi}{\lambda}\theta$$

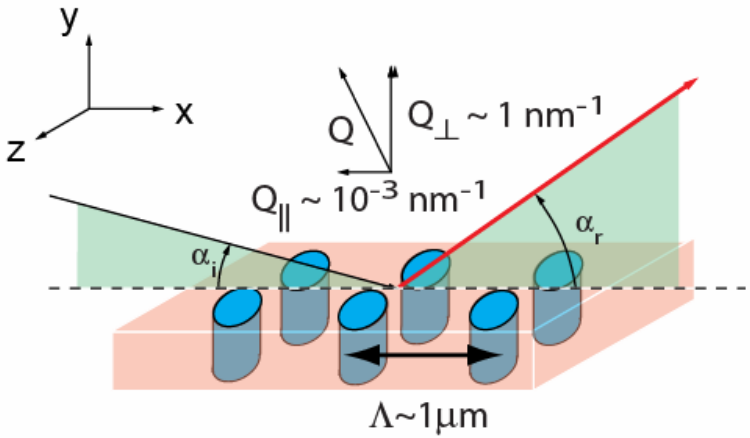
$$E_\perp = \frac{\hbar^2 k_\perp^{\,2}}{2M} = \frac{h^2}{2M\lambda^2}\theta^2 = V = \frac{2\pi\hbar^2\rho}{M} \rightarrow \theta_c = \lambda\sqrt{\frac{\rho}{\pi}}$$

Example: θ_c (Si @ 5Å) $= 0.23^\circ$ For $\theta = 0.2^\circ$ → $\frac{E_\perp}{V} = \frac{\pi}{\rho\lambda^2}\theta^2 \sim 10^{-1}$

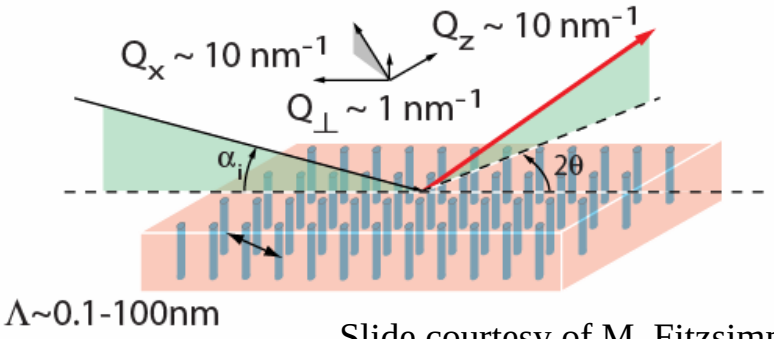
Types of Grazing Incidence Scattering



Specular reflectometry
Depth profiles
(nuclear and/or magnetic)



Off-specular (diffuse) scattering
In-plane correlated roughness
Magnetic stripes
Phase separation (polymers)

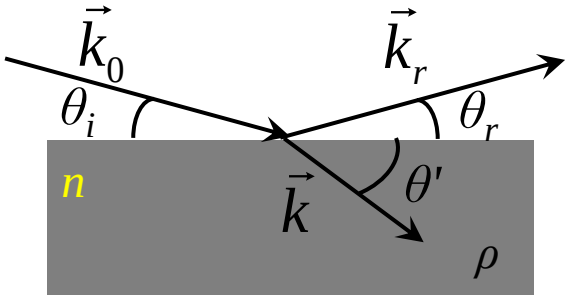


Glancing incidence diffraction
Ordering in liquid crystals
Atomic structures near surfaces
Interactions among nanodots

Slide courtesy of M. Fitzsimmons

Refractive Index

The kinetic (and total) energy of neutron in vaccuum is $E = \frac{\hbar^2 k_0^2}{2m}$



Inside the medium the total energy is $\frac{\hbar^2 k^2}{2m} + \bar{V}$

Conservation of energy gives $\frac{\hbar^2 k_0^2}{2m} = \frac{\hbar^2 k^2}{2m} + \bar{V} = \frac{\hbar^2 k^2}{2m} + \frac{2\pi\hbar^2}{m}\rho$ or $k_0^2 - k^2 = 4\pi\rho$

Since $k/k_0 = n =$ refractive index (by definition), and ρ is very small ($\sim 10^{-6}$ A^{-2}) we get :

$$n = 1 - \lambda^2 \rho / 2\pi$$

- Small difference in refractive index imply that critical angles are small (less than 1 degree)
- Since generally n < 1, neutrons are externally reflected from most materials
- Mixtures of isotopes can be used to match the index of refraction of different materials
- Absorption coefficient β is small for neutrons

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

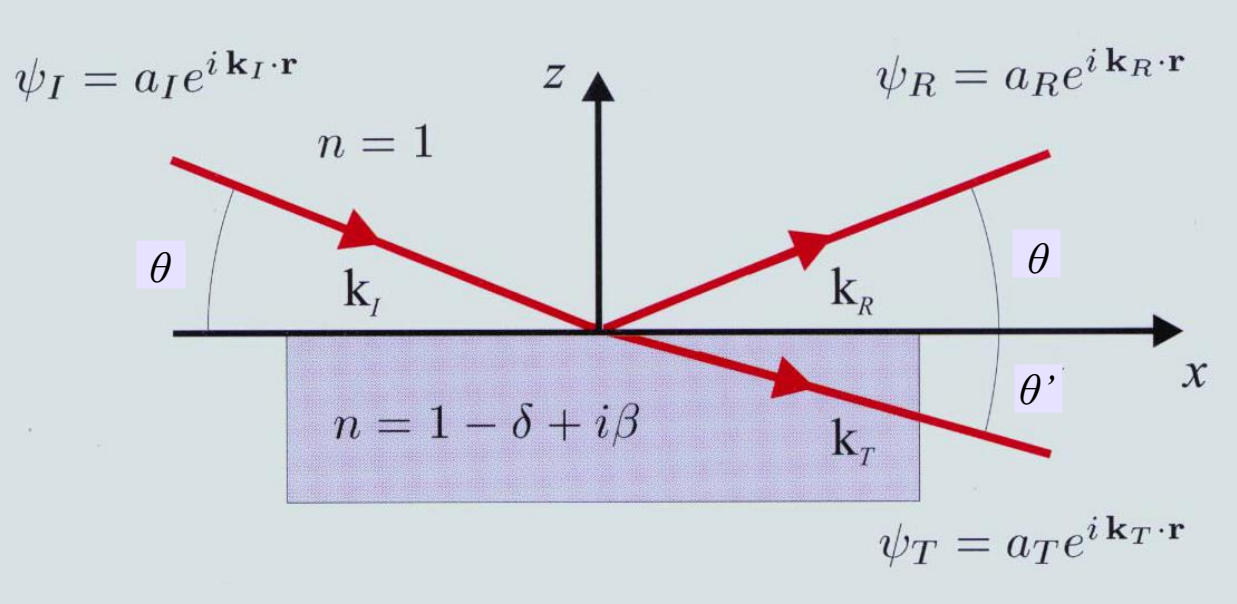
X-RAYS

$$\delta = \frac{\lambda^2}{2\pi} r_e \rho$$

NEUTRONS

$$\delta = \frac{\lambda^2}{2\pi} \rho_n$$

Quantum Description of Reflection



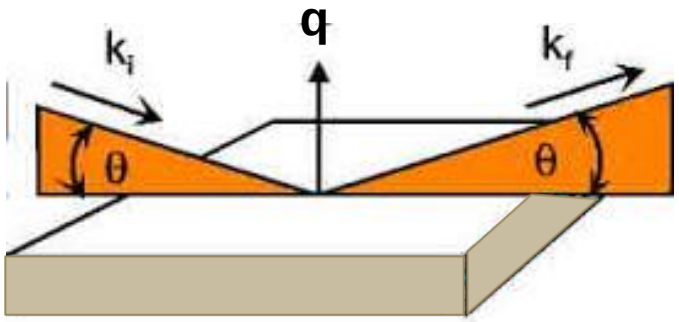
Schrödinger equation: $\nabla^2\psi(\vec{r}) + (k_0^2 - 4\pi\rho(\vec{r}))\psi(\vec{r}) = 0$

Continuity of the wavefunction and its derivative at the interface directly yields the classical Fresnel coefficients:

$$r = \frac{k_{i\perp} - k_{t\perp}}{k_{i\perp} + k_{t\perp}} \qquad \& \qquad t = \frac{2k_{i\perp}}{k_{i\perp} + k_{t\perp}}$$

Fresnel Reflection

The reflectivity, R, is usually measured or calculated as a function of the wave vector transfer $\vec{q} = \vec{k}_f - \vec{k}_i$



$$R_{\text{exp}} = \frac{\#\,\text{reflected neutrons at a given } q}{\#\,\text{incident neutrons}}$$

$$|k_i| = |k_r| = \frac{2\pi}{\lambda} \qquad q = \frac{4\pi}{\lambda}\sin\theta$$

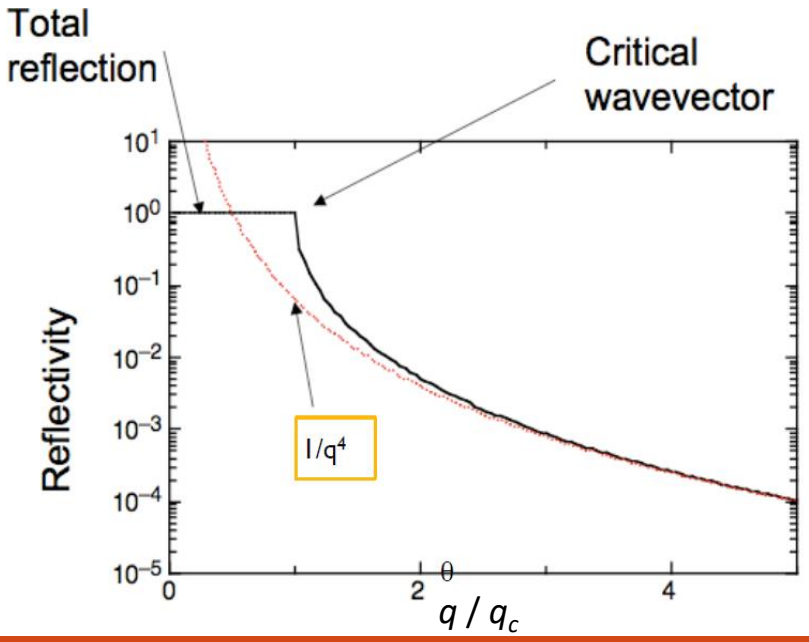
$$R_F = r.r^* = |r^2| = \left|\frac{q-(q^2-q_c^2)^{1/2}}{q-(q^2-q_c^2)^{1/2}}\right|^2$$

$$q_c = \sqrt{16\pi\rho}$$

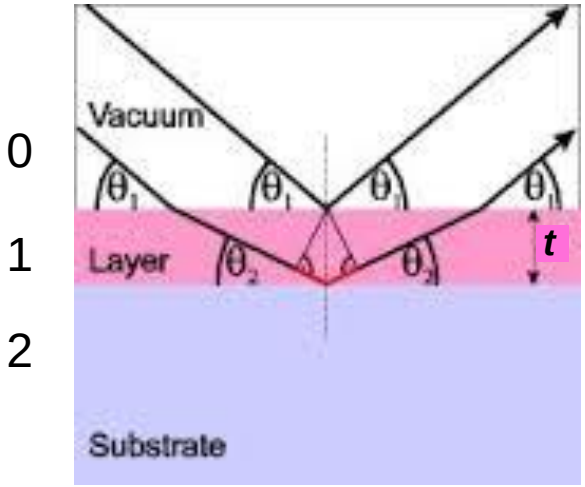
Born Approximation ($q >> q_c$)

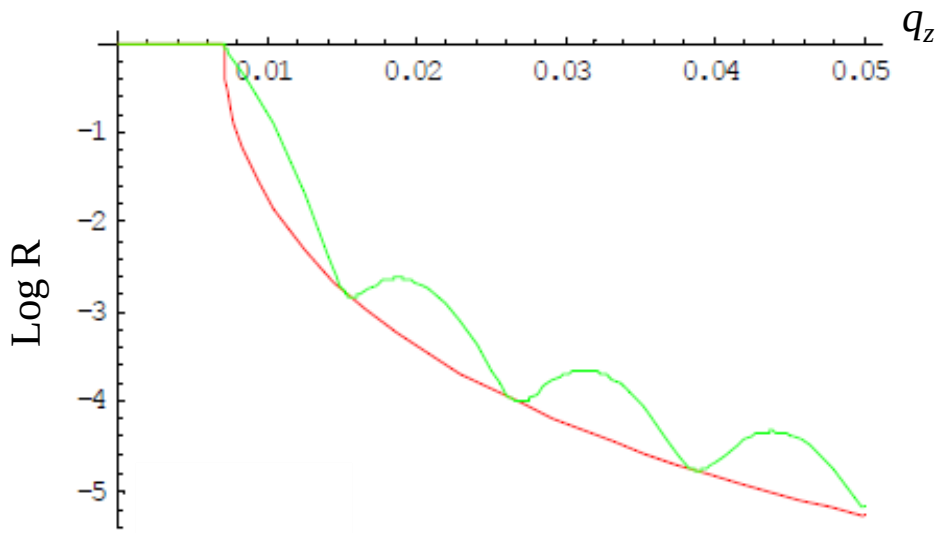
$$R_F = \frac{16\pi^2\rho^2}{q^4}$$

Ignoring double scattering processes because they are usually very weak



Fresnel Expression from a Thin Film



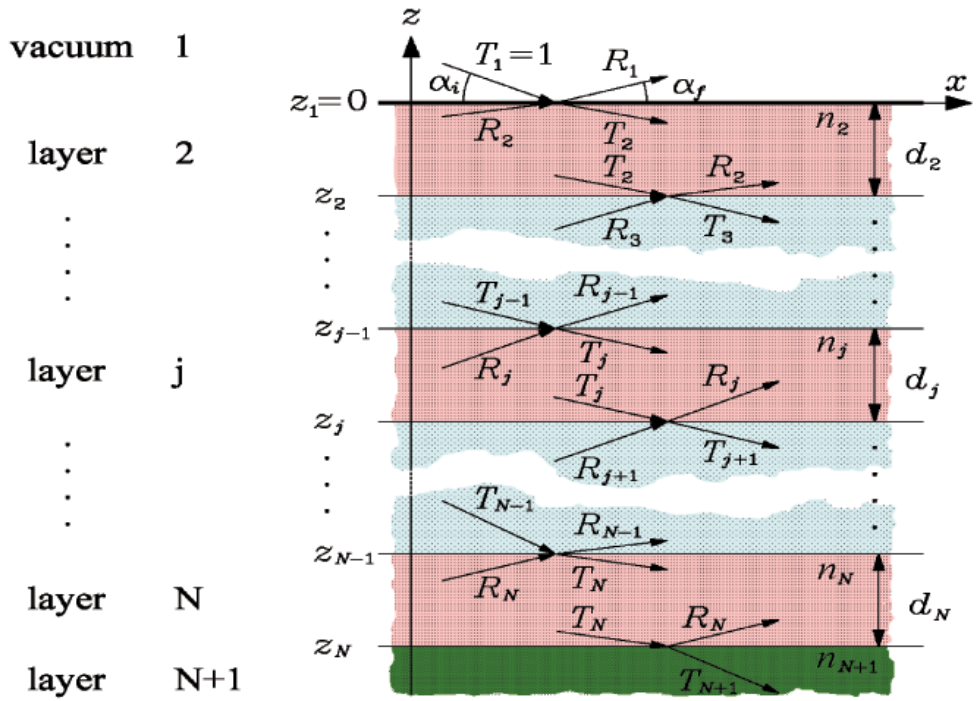


$$r = \frac{r_{01} + r_{12} e^{i2k_{1z}t}}{1 + r_{01} r_{12} e^{i2k_{1z}t}}$$

$$R_F = \left| r^2 \right|$$

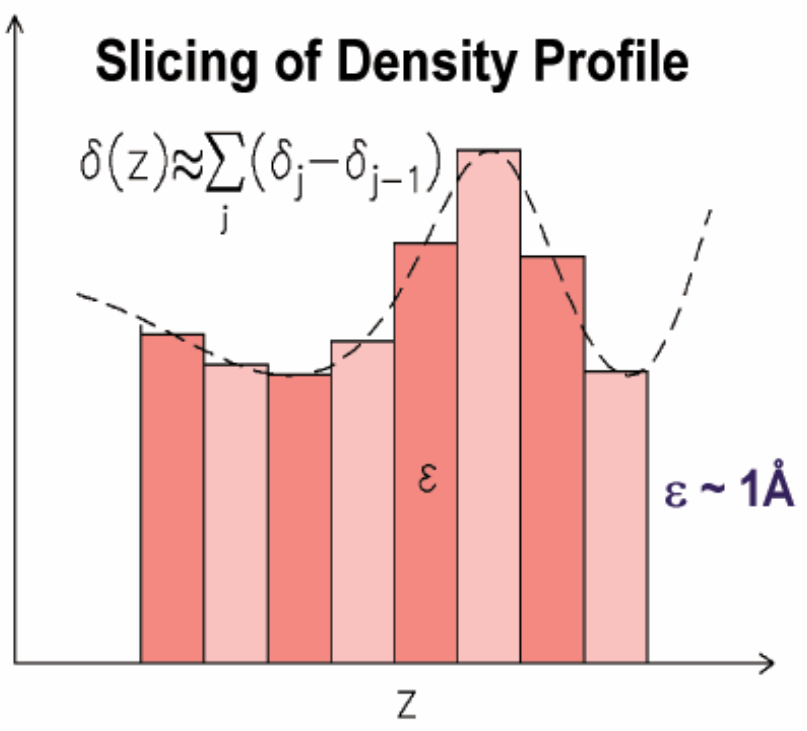
- If the film has a higher scattering length density than the substrate, the reflectivity pattern is above Fresnel prediction
- If the film scattering is weaker than that of the substrate, the green curve is below Fresnel prediction
- The fringe spacing at large q_z is ~ $2\pi/t$

Fresnel Expression for Multilayers (Parratt Formalism)



$$X_j = \frac{R_j}{T_j} = e^{-2ik_{z,j}z_j}\,\frac{r_{j,j+1} + X_{j+1}e^{2ik_{z,j+1}z_j}}{1 + r_{j,j+1}X_{j+1}e^{2ik_{z,j+1}z_j}}$$

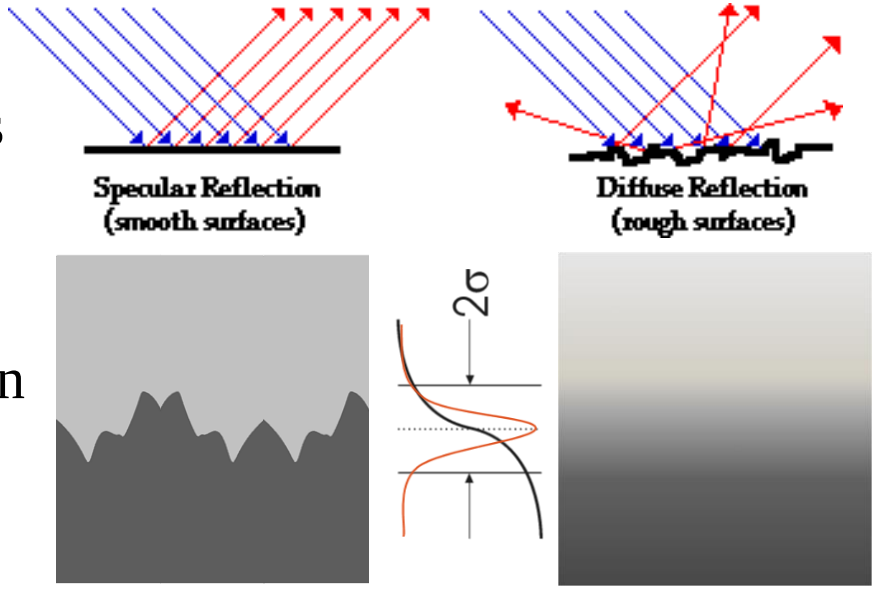
$$R_F = \left|R_1^{\,2}\right|$$



- Any complex SLD depth profile can be "sliced" into thin films
- The Parratt formalism allows calculation of reflectivity
- The computation is more intensive for thinner slices

Rough and Diffuse Interfaces

- Surface roughness causes diffuse (non-specular) scattering and reduces the magnitude of the specular reflectivity

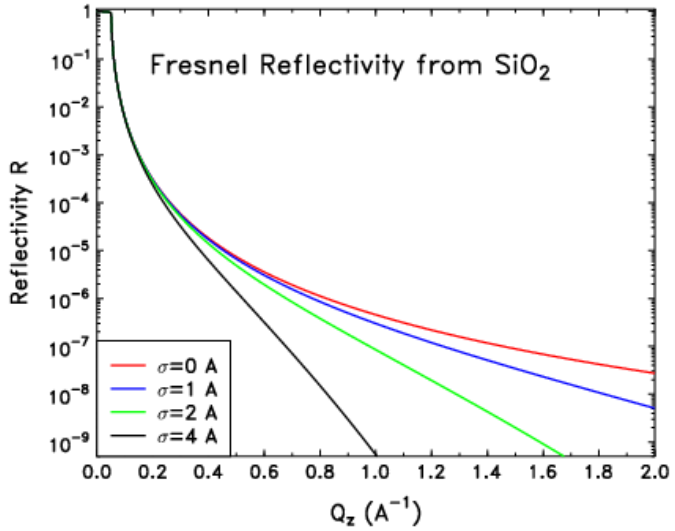


- The damping of the specular reflection depends on the length scale, magnitude, and distribution of roughness

- The signal is modified by the Nevot-Croce term:

$$R \approx R_F e^{-q_z^2 \sigma^2}$$

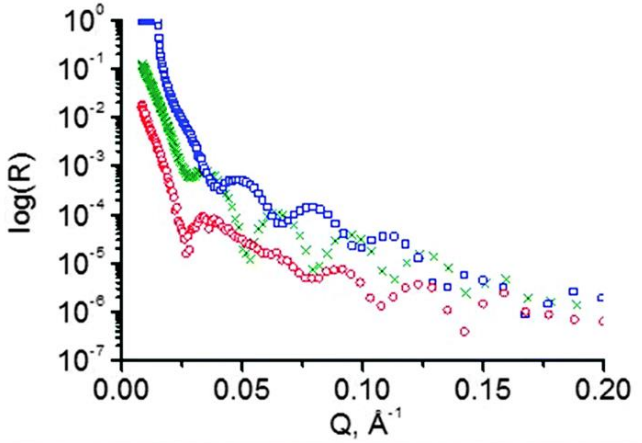
- This term applies equally well to diffuse interfaces

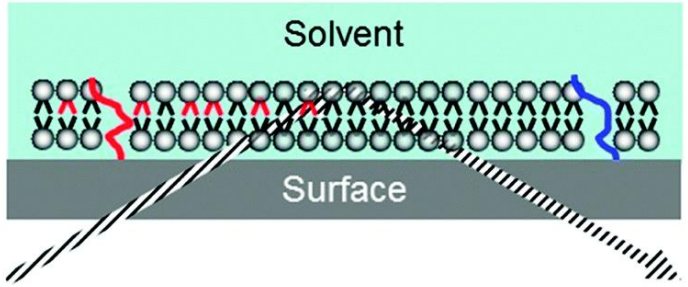


General Notes on Reflectivity Patterns

Specular reflection

Diffuse scattering



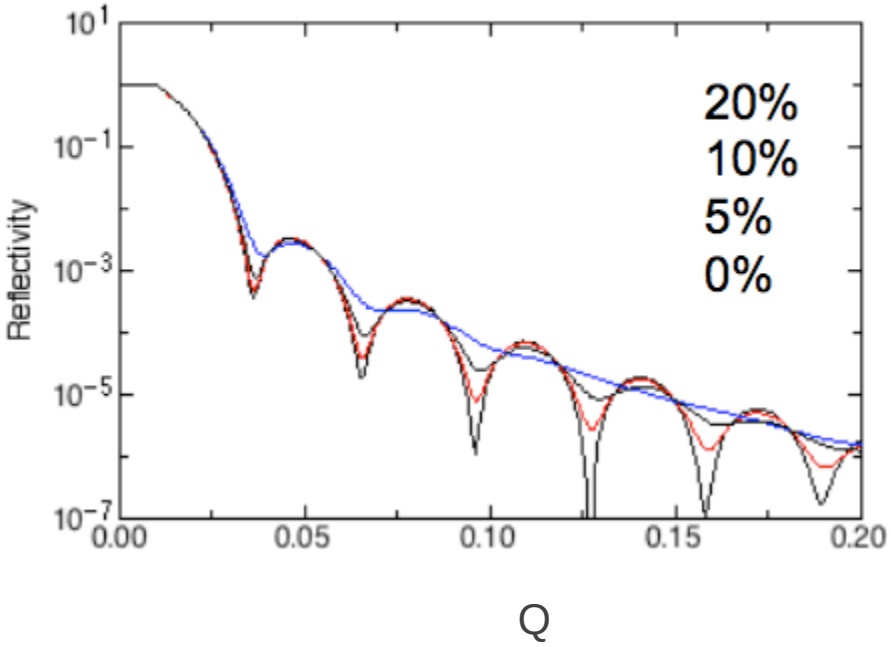


Mashaghi et al., Chem. Soc. Rev., 2014, 43, 887-900

- Rough or patterned surfaces can cause diffuse or offspecular scattering
- Flat, homogeneous, smooth surfaces result in specular reflection
  - Below the critical angle → total specular reflection
  - Above the critical angle → reflectivity patterns depend on the SLD profile normal to the surface

Effects of Instrumental Resolution

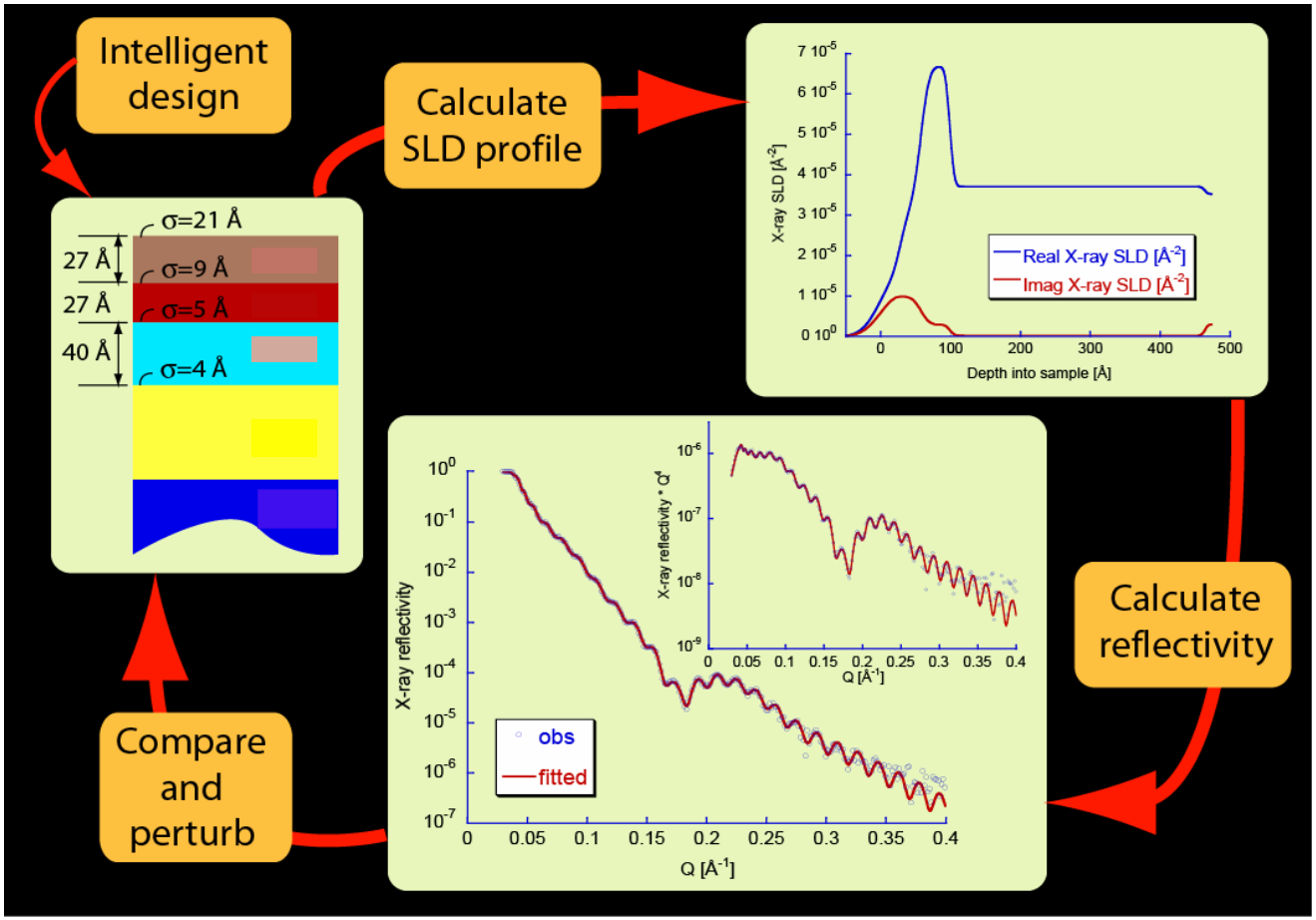
- Reflectivity drops quickly with increasing *Q* (or angle).
- Signal is easily 'lost' in background
- To observe fringes → measure over an appropriate range of Q and sufficient resolution (ΔQ small enough).
- Attenuation caused by scattering or absorption may be significant



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

$$\left(\frac{\Delta Q}{Q}\right)^2 = \left(\frac{\Delta\lambda}{\lambda}\right)^2 + \left(\frac{\Delta\theta}{\theta}\right)^2$$

Data Fitting and Fitting Software

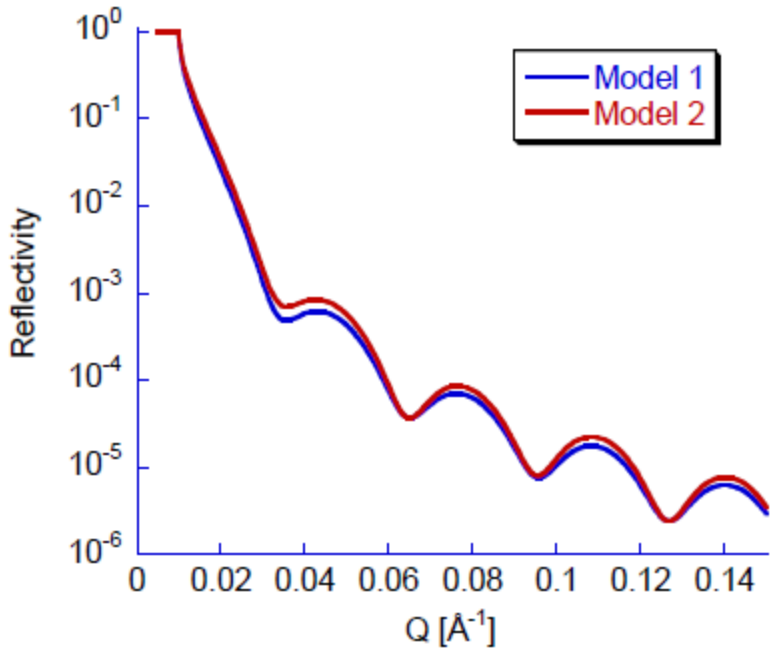


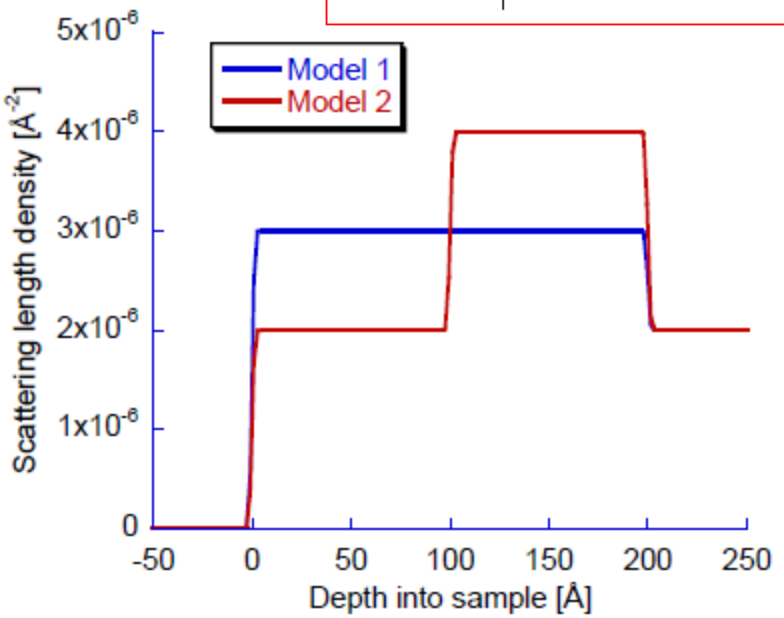
Courtesy of Roger Pynn

- Reflpak, Refl1D https://www.ncnr.nist.gov/reflpak/
- SasView Reflectometry package www.sasview.org
- Motofit https://sourceforge.net/projects/motofit/

Phase Problem & Perils of Data Fitting

$$R = R_F \left| \int \frac{d\rho(z)}{dz} e^{iQ_z z} dz \right|^2$$





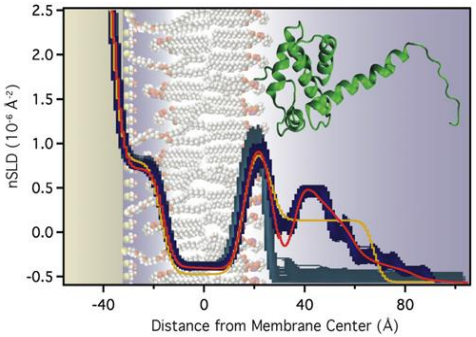
- Lack of phase information means that profoundly different scattering length density profiles can produce strikingly similar reflectivity patterns.

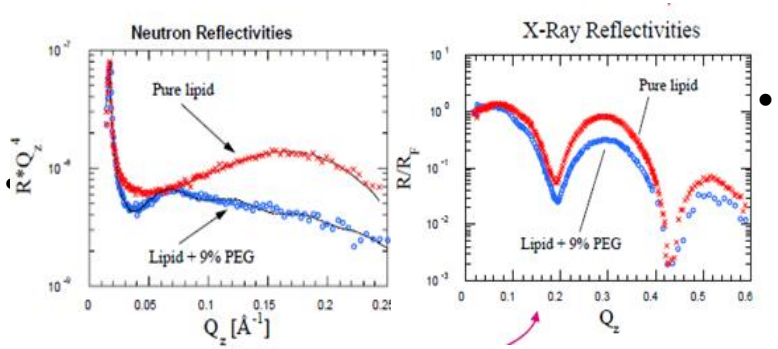
- Ambiguities **may** be resolved with additional information through the use of complementary characterization techniques (e.g. TEM, X-ray) or simulations, acquiring high-quality neutron data, and applying

D. Sivia et al., J. Appl. Phys. **70**, 732 (1991).

Ways around the Phase Problem

- Complementary characterization & model refinement; e.g. using NMR data and computer simulations – **Electrostatic Interactions and Binding Orientation of HIV-1 Matrix.** Nanda et al., *Biophys. J.* **2010** 99(8): 2516–2524.



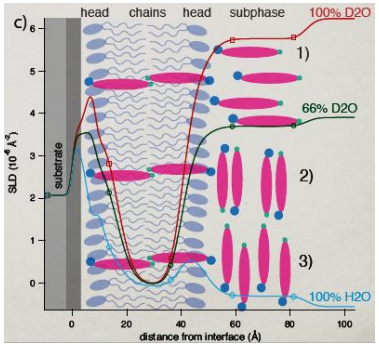


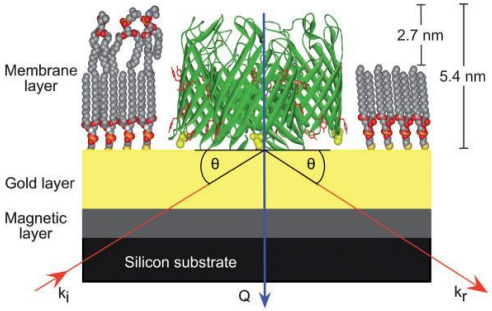
- Combine measurements using x-ray and neutron reflectometry and apply simultaneous model fits – **Structure of PEGylated lipid monolayers**

  Majewski et al., *J. Phys. Chem. B* **1997**, 101 (16), 3122–3129.

- Apply contrast variation using isotope labeling
  – **AmB effect on P. Pastoris yeast membranes**

  Ghellinck et al., *Biochim. Biophys. Acta* **2015**, 1848 (10), 2317–2325.





- Use polarized beams and magnetic reference layers; i.e. equivalent of nuclear and magnetic contrasts.
  – **High resolution protein adsorption profile with no labeling**

  Holt et al., Soft Matter. 2009, 5(13), 2576.

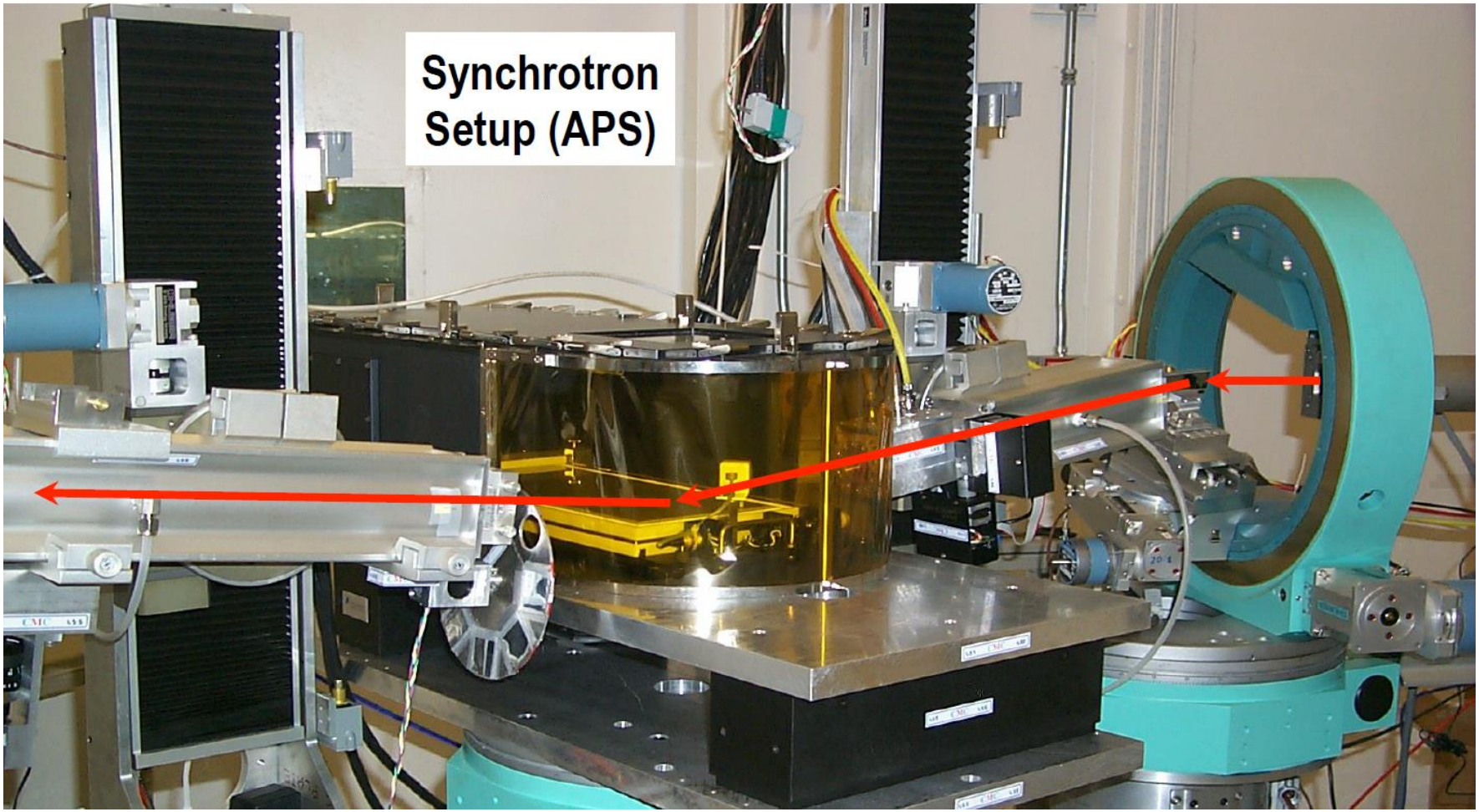
Tips for Reflectivity Measurements

- Simulate the reflectivity profiles that you expect to see
  - Make sure you can see the effect that you are looking for (Be mindful about layer thicknesses – extremes are challenging to resolve)
  - Choose the best substrate
  - Choose the right contrast conditions

- Make sure you have high quality samples
  - Low surface roughness
  - Beware of lateral imperfections (large islands, partial surface coverage)
  - If possible, try to do complimentary characterization (AFM, TEM, ...)

- Choose the right instrument & scattering geometry
  - For samples with rough surfaces or in fluid environments, consider incidence through substrate (beam attenuation, diffuse scattering, …)
  - For free surface or interface measurements of fluids, you need an instrument with a horizontal sample geometry
  - Check that the instrument has the right specs (resolution, q-range, ...)

Reflectometer Geometries

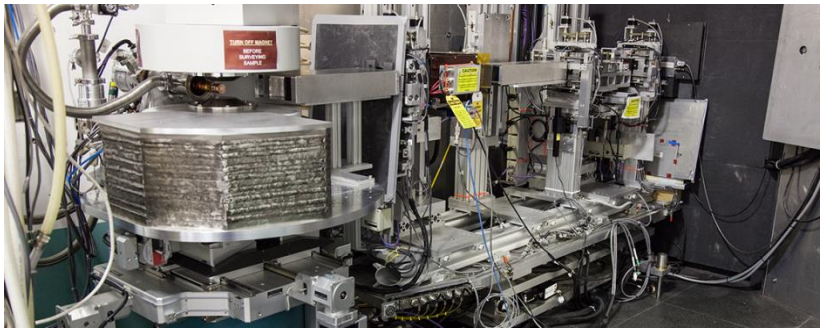


Neutron Reflectometers at SNS

Liquids Reflectometer (BL-4B)

- Vertical scattering plane (compatible with liquid-air and liquid-liquid interfaces)
- Langmuir trough
- Rheometer
- Fluid sample cells

Magnetism Reflectometer (BL-4A)



- Horizontal scattering plane
- Magnetic samples
- 1.15T electromagnet and temperature control (5K to 750K)
- Polarization capabilities

Useful References

- V. F. Sears 'Neutron Optics', Oxford Press, Oxford (1989)
- Lekner J (1987) in: *"Theory of Reflection"* Martinus Nijhoff Dordrecht
- Born M and Wolfe E (1989) in: *"Principles of Optics"* Pergamon Press Eds. Oxford
- Penfold J and Thomas R K (1990) *J. Phys. Condens. Matter* **2** 1369
- Russell T. P. (1990) *Mat. Sci. Rep.* **5** 171
- Felcher G P (1981) *Phys. Rev. B* **24** 1995
- Sinha S K, Sirota E B, Garoff S and Stanley H B (1998) *Phys. Rev. B* **38** 2297
- Pynn R (1992) *Phys. Rev. B* **45**, 602
- Pynn R, Baker S, Smith G, Fitzsimmons M (1999) *J. Neutron Res.* **7**, 139-158
- Zhou X-L and Chen S-H (1995) *Phys. Rep.* **257** 223
- Williams W "Polarized Neutrons", Oxford Press, Oxford (1989)
- Névot L and Croce P (1990) *Rev. de Phys. Appl.* **15** 761
- Daillant J and Gibaud A (1999) in: *"X-ray and Neutron Reflectivity: Principles and Applications"* Springer Eds.