Diffraction <-> Structure

- **First Born Approximation**: (from quantum mechanics)
  - Scattering is weak, so scattered amplitude is Fourier Transform (F.T.) of structure (spatial distribution of neutron scattering length density).

- In 1-dimension across membrane:
  \[
  F(Q) = \text{F.T.} \{\rho(x)\} \quad \text{(scattering process)}
  \]
  \[
  \rho(x) = \text{F.T.} \{F(Q)\} \quad \text{(scientist’s job)}
  \]

\[
Q = \frac{4\pi \sin(\theta)}{\lambda} \quad \text{or} \quad Q = \frac{2\pi n}{d}
\]

Bragg Equation: \( n\lambda = 2d\sin(\theta) \)

d = repeat distance (across membrane).

Q = dimension in reciprocal space.
Fourier Transform for calculating
diffraction from Molecular Model

(Centrosymmetric case of bilayer. Need Sine part as well
if not centrosymmetric.)

\[ F_n = \sum_j b_j \cos(2\pi n x_j/d) \exp(-n^2 B_j/4d^2) \]

- \( b_j \) = neutron coherent scattering length of nucleus \( j \)
  - \( b(\text{hydrogen}) = -3.74 \times 10^{-13} \text{cm} \)
  - \( b(\text{deuterium}) = 6.67 \times 10^{-13} \text{cm} \)
  - \( b(\text{carbon}) = 6.65 \times 10^{-13} \text{cm} \)
  - \( b(\text{oxygen}) = 5.80 \times 10^{-13} \text{cm} \)
  - \( b(\text{nitrogen}) = 9.40 \times 10^{-13} \text{cm} \)
  (compare X-ray scattering by electron: s.i. = 2.8x10^{-13} \text{cm})

- \( B_j \) = Debye-Waller Temperature Factor: nucleus not
  fixed at \( x_j \) but has Gaussian distribution at \( x_j \).
- \( B_j \) includes dynamic and static disorder.
**Measured Intensities:** \( I_n \sim |F_n|^2 \)

Phase relations of \( F_n \) not included in measurement of intensity.
Must be recovered: “the phase problem”.

Geometric corrections:

\[
|F_n|^2 = I_n \sin(2\theta_n) C_{\text{abs}}(n)
\]

\( \sin(2\theta_n) = \text{Crystallographic Lorentz factor} \)
(for Bragg peaks integrated in \( \theta \)).
Lorentz factor is \( \sin(\theta_n) \) if integrated in \( Q \).

\( I_n \) are corrected for absorption. A small correction for thin samples.

\[
C_{\text{abs}}(n) = \frac{z}{1-\exp(-z)} \quad \text{where} \quad z = 2t/tosin\theta
\]

\( to = 1/e \) absorption length
Fourier Transform of 50A Model Bilayer. HC=30A, 2PG=10A
$|F.T.|^2$ of 50A Bilayer

Intensity (Reflectivity $\times 1000$)

$Q$

0 0.10 0.20 0.30 0.40 0.50
Reflectivity ($|F_T|^2/Q^2$) of Model Bilayer, free-standing.
Sampling of Transform in Bragg diffraction from multilayers

Sampling positions depend on repeat spacing, \( d \):  \( Q = \frac{2\pi n}{d} \).

Fourier Transform of 50A Model Bilayer. HC=30A, 2PG=10A

Amplitude

\( n=1 \) \( n=2 \) \( n=3 \) \( n=4 \)
Has a lot of information been lost compared to reflectivity curve?

\[ I_n \sim |F_n|^2 \]
The Shannon Sampling Theorem


If a function $\rho(x)$ is non-zero only for $-a/2 \leq x \leq a/2$, then its Fourier Transform $F(X)$ is completely specified by its values at $X = 0$, $\pm 1/a$, $\pm 2/a$, … etc.

The continuous $F(X)$ can be obtained as a sum of $\sin(\pi a X)/ \pi a X$, placed at each of the above points and weighted by the value of $F(X)$ at each point.

Note that amplitude and phase of $F(X)$ are needed.

Corollary: Data to $Q_{\text{max}}$ are completely specified by a small number of values, namely $a Q_{\text{max}} / \pi$. 
The Shannon Sampling Theorem can also apply to SANS.

Specifically, SANS data from solutions of objects of finite dimension. In this case, F.T. \{I(Q)\} yields the pair distribution function \(p(r)\). But since this is a truncated FT, better to generate \(p(r)\) as a series summation until its FT fits \(I(Q)\). The number of terms in the series is given by Shannon Theory.


Peter Moore’s program for generating \(p(r)\) from \(I(Q)\) is extensively used in SANS, especially in biology.
Calculate density of neutron scattering lengths:

\[ \rho(x) = \sum_n |F_n| \cos(2\pi nx/d - \phi_n) \]

Bilayer membrane is centrosymmetric, so use cosine F.T. and \( \phi_n = 0, \pi \).

Or, \( \rho(x) = \sum_n F_n \cos(2\pi nx/d) \)

\[ F_n = + |F_n| , \phi_n = 0 \]
\[ F_n = - |F_n| , \phi_n = \pi \]
Solving the Phase Problem

- Introduce heavy atom in the form of deuterium (D$_2$O) at $x = 0$, by diffusion from vapor.
- At low hydration (e.g. ~60%rh), D$_2$O should be narrow Gaussian at $x = 0$. F.T.$\{D_2\text{O}\} =$ **all positive values**.
  - Narrowest case: Dirac delta function. F.T.$\{\delta(0)\} =$ positive constant.
- Fourier Transforms are linear operations:
  \[
  \text{F.T.}\{\text{lipid+D}_2\text{O}\} = \text{F.T.}\{\text{lipid}\} + \text{F.T.}\{D_2\text{O}\}
  \]
- So, D$_2$O at $x = 0$ increases $|F_n|$ for positive $F_n$ and decreases $|F_n|$ for negative $F_n$. Can simply observe if $I_n$ increase or decrease : gives phases.
- $F_n$ can change from negative to positive, but 3 measurements will show this ($H_2O$, 50$\%D_2O$, D$_2$O) since $F_n$ is linear in $\%D_2O$.
- **This is the membrane version of the multiple isomorphous heavy atom method of protein X-ray crystallography.**
Fourier Transform of 50A Model Bilayer. HC=30A, 2PG=10A
Samples are multilayers on thin quartz or glass substrate, usually 3-12mg of lipid covering ~6cm², so ~5-20µm thick. This corresponds to ~1000 to 4000 bilayers.

Samples are hydrated from the vapor phase using saturated salt solutions.

Thin glass or quartz, e.g. microscope cover slip.
Neutron Scattering Length Density Profile.
DMPC + Cholesterol (2/1).  86%rh.