Neutron scattering presentation series

(1) Basic concepts and neutron diffraction

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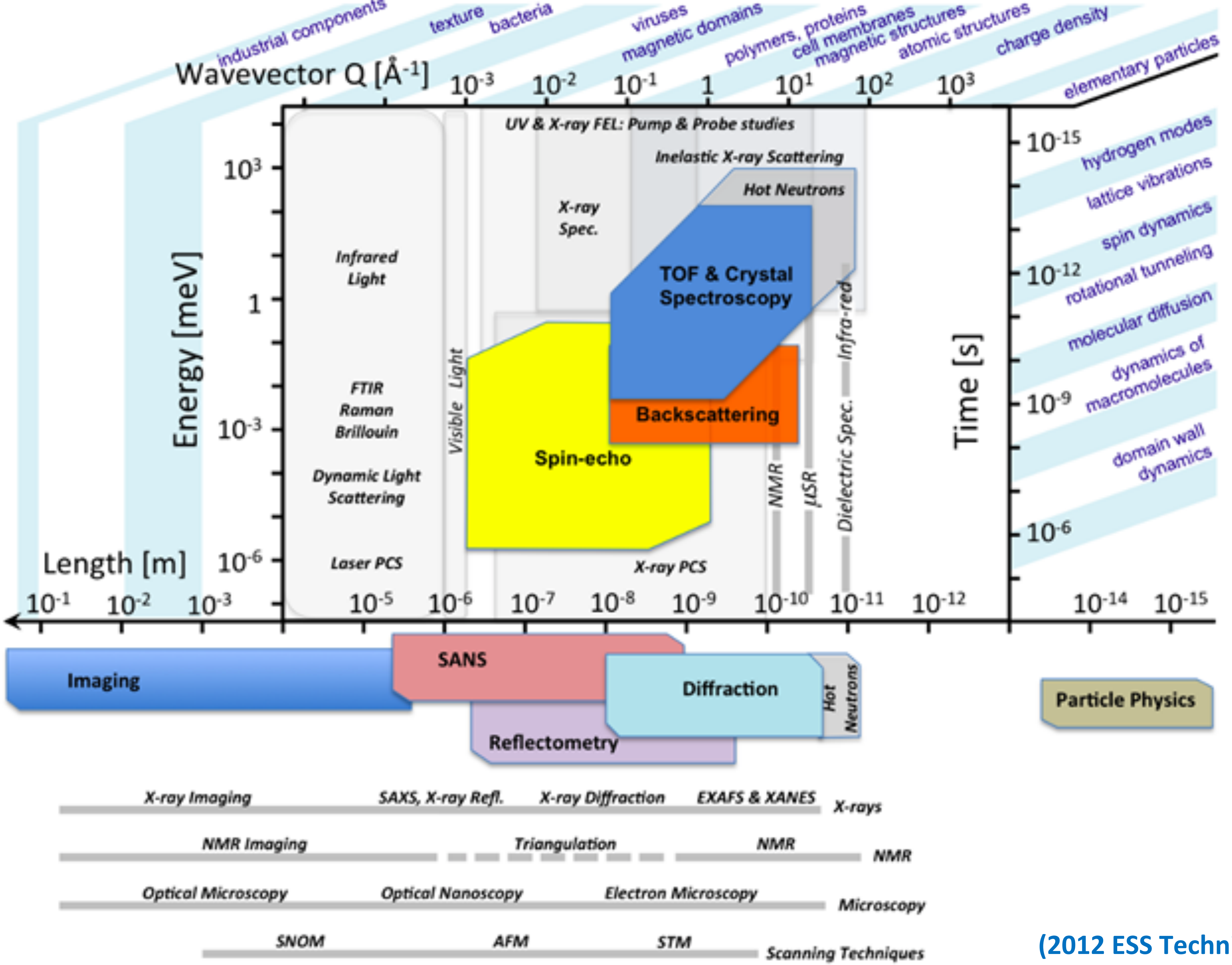
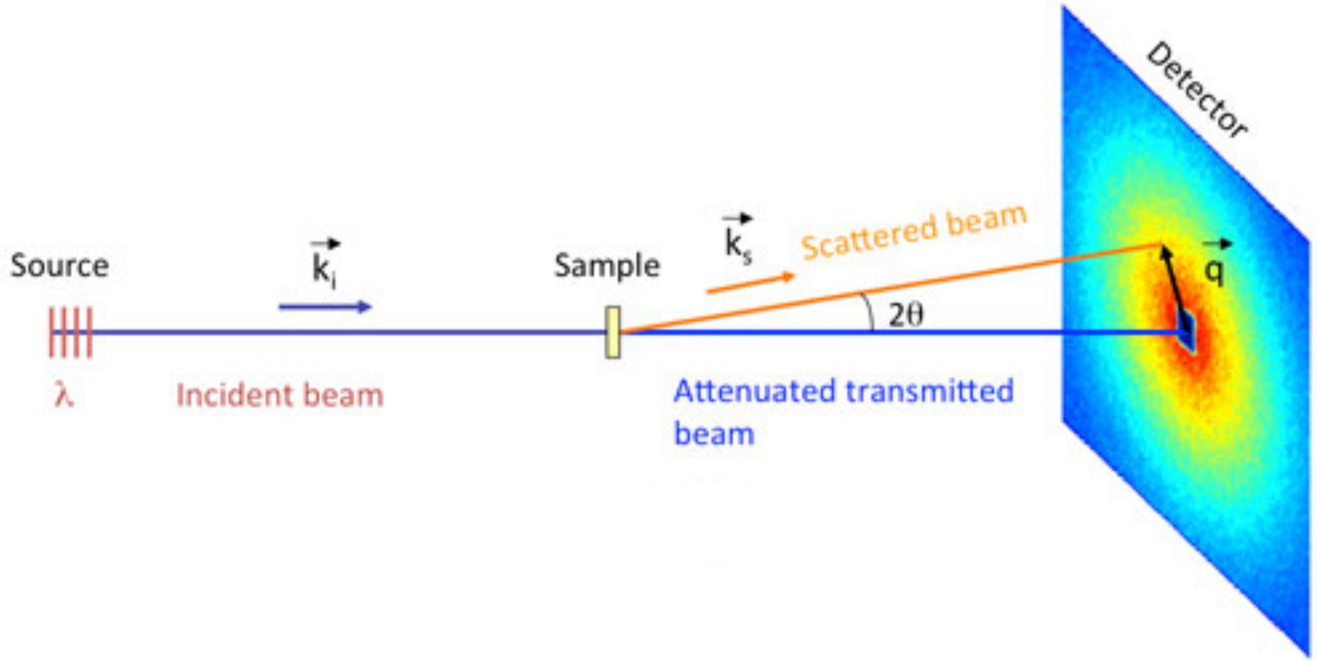
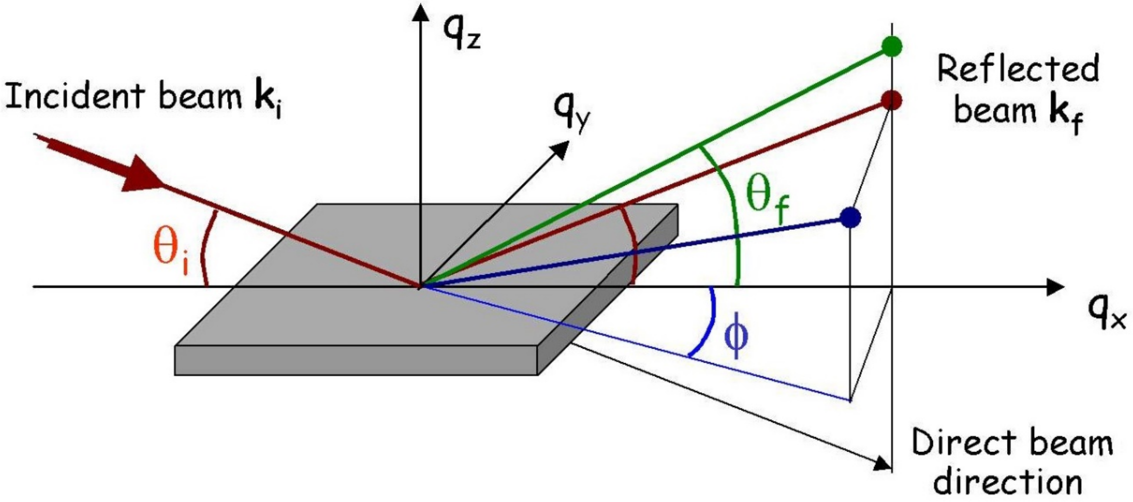


(2012 ESS Technical Design Report)

Type	Technique	Length scale		Time scale	
		Reciprocal space (Q/Å^{-1})	Real space (r/nm)	Energy space ($\Delta\omega$/μeV)	Time space (τ/ps)
Static scattering	Ultra-Small Angle Neutron Scattering (USANS)	5×10^{-6} ~ 0.005	100 ~ 10^5	N/A	
	Small Angle Neutron Scattering (SANS)	0.001 ~ 0.5	1 ~ 500		
	Neutron Diffraction	0.1 ~ 20	0.05 ~ 5		
	Neutron Reflectometry	0.001 ~ 0.5	1 ~ 500		
Dynamic scattering	Neutron Spin Echo (NSE)	0.01 ~ 0.5	1 ~ 50	0.01 ~ 100	10 ~ 10^5
	Quasi-Elastic Neutron Scattering (QENS)	0.1 ~ 10	0.05 ~ 5	1 ~ 100	0.1 ~ 10^3
	Inelastic Neutron Scattering (INS)	0.1 ~ 10	0.05 ~ 5	10 ~ 10^5	0.01 ~ 100





λ=0.1 ~ 10 Å	Source	Measurement time	Sample size	Incident energy
Neutron	Reactor Spallation source	min ~ hour	cm, mL	meV
X-ray	Synchrotron	μs ~ ms	mm, μL	keV
	In-house	min ~ hour		

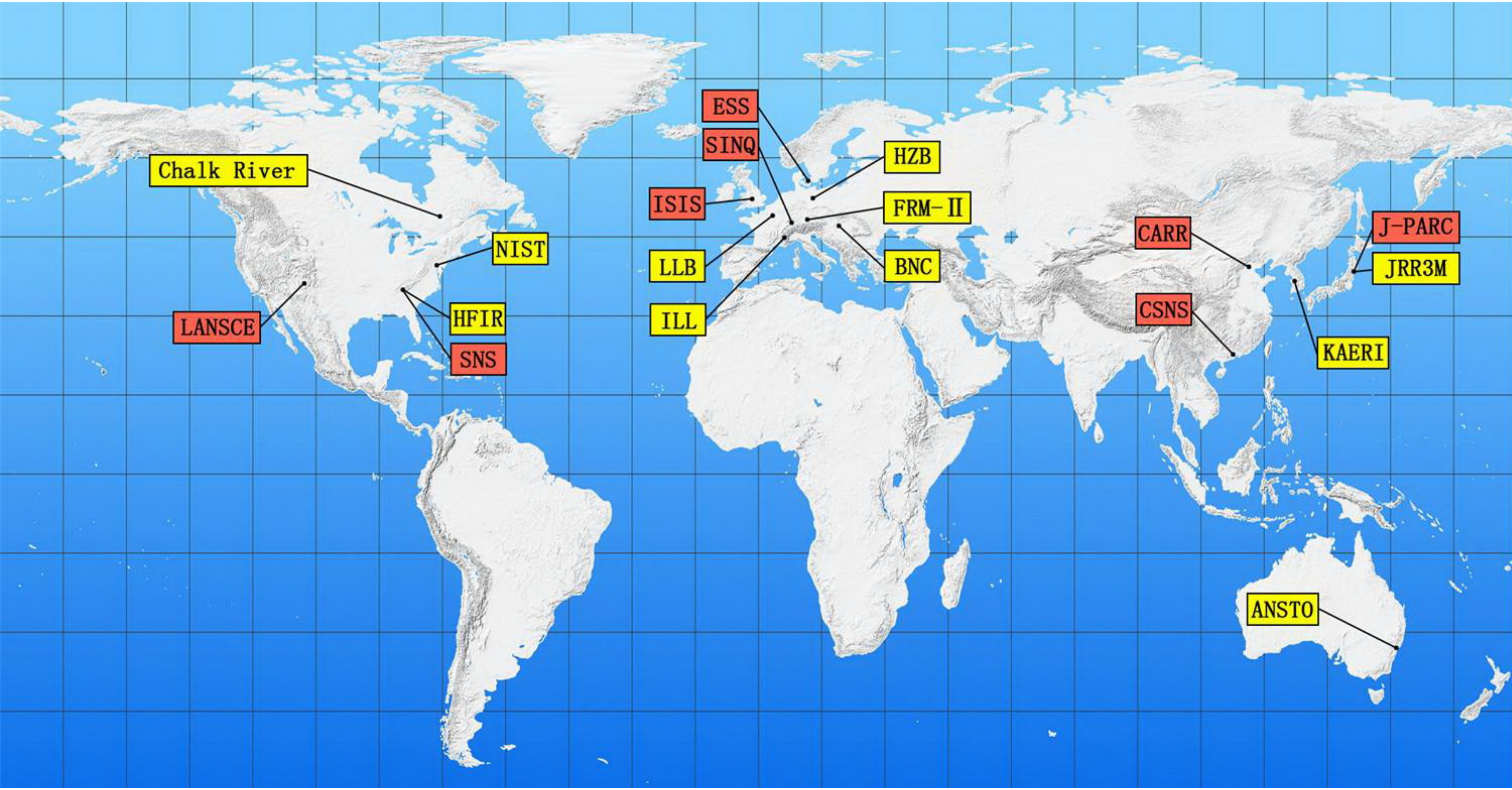
Advantages and Disadvantages of Scattering Techniques

Advantages:

1. Dynamical and structural information in several orders
2. Ensemble sampling
3. Non-destructive penetration
4. Contrast variation available
5. Sensitive to magnetic fields (neutron)

Disadvantages:

1. Inverse problem
2. Ensemble sampling
3. Radiation resistance (X-ray)
4. Sample amount
5. Beamtime accessibility (neutron)



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ILL
CSNS
SNS
KAERI
ANSTO

Outline

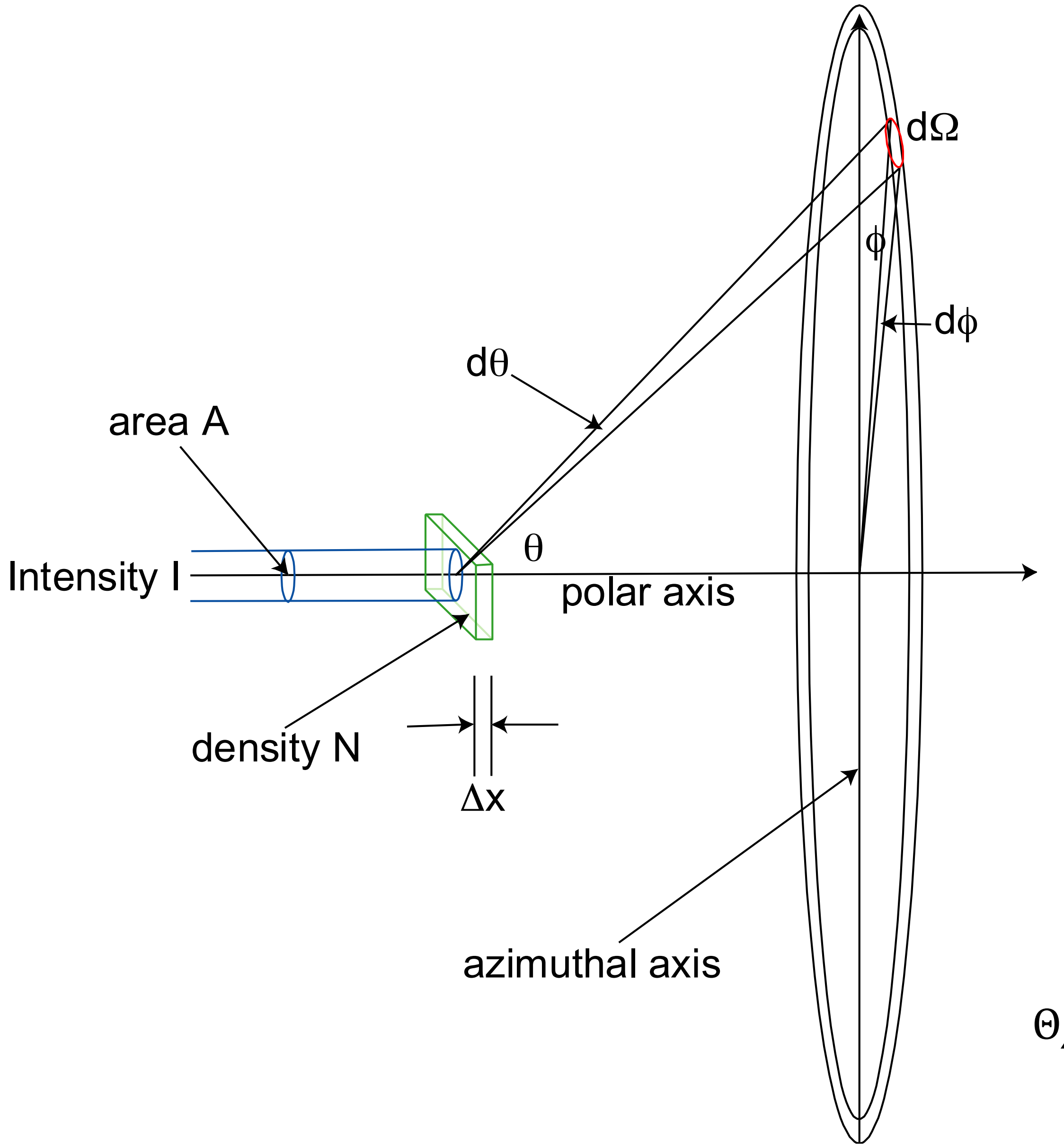
Basic concepts:

1. Scattering cross section
2. Scattering length and scattering length density
3. Coherent and incoherent scattering
4. Reciprocal space
5. Spatial and time correlation functions

Neutron diffraction:

1. Single crystal diffraction
2. Powder diffraction
3. Rietveld refinement method
4. Pair distribution function (PDF) method

Cross Section – Scattering Ability



Number of incident neutrons: *I*

Number of scattered neutrons: *Θ*

Number density of scatterers in the sample: *N* $[L^{-3}]$

Beam size: *A* $[L^2]$

Sample thickness: *Δx* [L]

Solid angle: *Ω*

Scattering probability:

$$\Theta/I \propto NA\Delta x/A = N\Delta x$$

$$\Theta/I = N\Delta x\boldsymbol{\sigma}$$

$$1/I\, d\Theta/d\Omega = N\Delta x\, \boldsymbol{d\sigma/d\Omega} = N\Delta x\boldsymbol{\sigma(\theta)}$$

Cross Section and Scattering Length

$\Theta / I = N \Delta x \boldsymbol{\sigma}$ $\quad\quad$ $1/I \, d\Theta / d\Omega = N \Delta x \boldsymbol{d\sigma / d\Omega} = N \Delta x \boldsymbol{\sigma(\theta)}$

σ [L^2] (microscopic cross section): describes the scattering ability of the material.

For neutrons scattered by the nuclei:

$\sigma(\theta) = d\sigma / d\Omega = b^2$

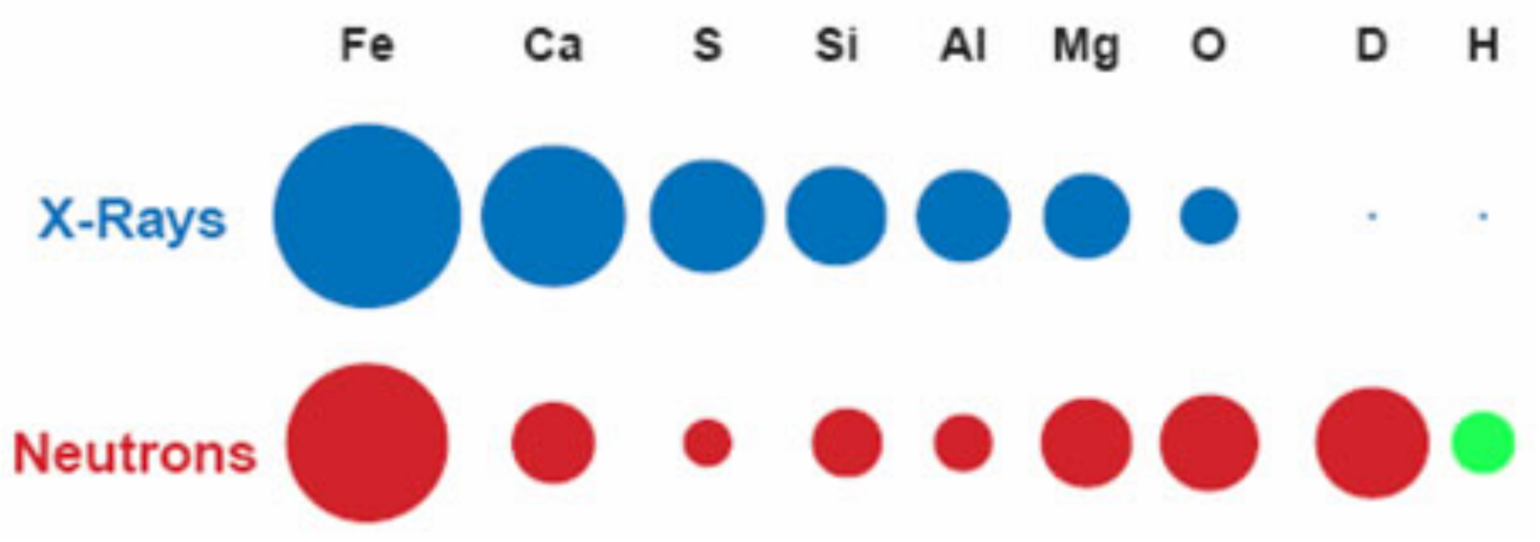
b [*L*]: constant, scattering length

$\sigma = \int_{\Omega} \sigma(\theta) d\Omega = 4\pi b^2$

Units: σ: 1 barn = 10^{-24} cm^2 = 10^{-28} m^2

b: 1 fm = 10^{-15} m = 10^{-5} Å

Cross Section and Scattering Length (cont'd)



1. X-ray sensitive to heavy atoms (high electron density)
2. Neutrons sensitive to light nuclei
3. Hydrogen: negative neutron scattering length (isotope substitution)
4. Chlorine and sulfur in the solvent strongly scatter X-ray
5. Boron: neutron absorption

Cross Section and Scattering Length (cont'd)

Example 1: scattering by 1mm thick water

Mass density: 0.99997 g/cm^3

Cross section: H: 82.02 barn, O: 4.232 barn

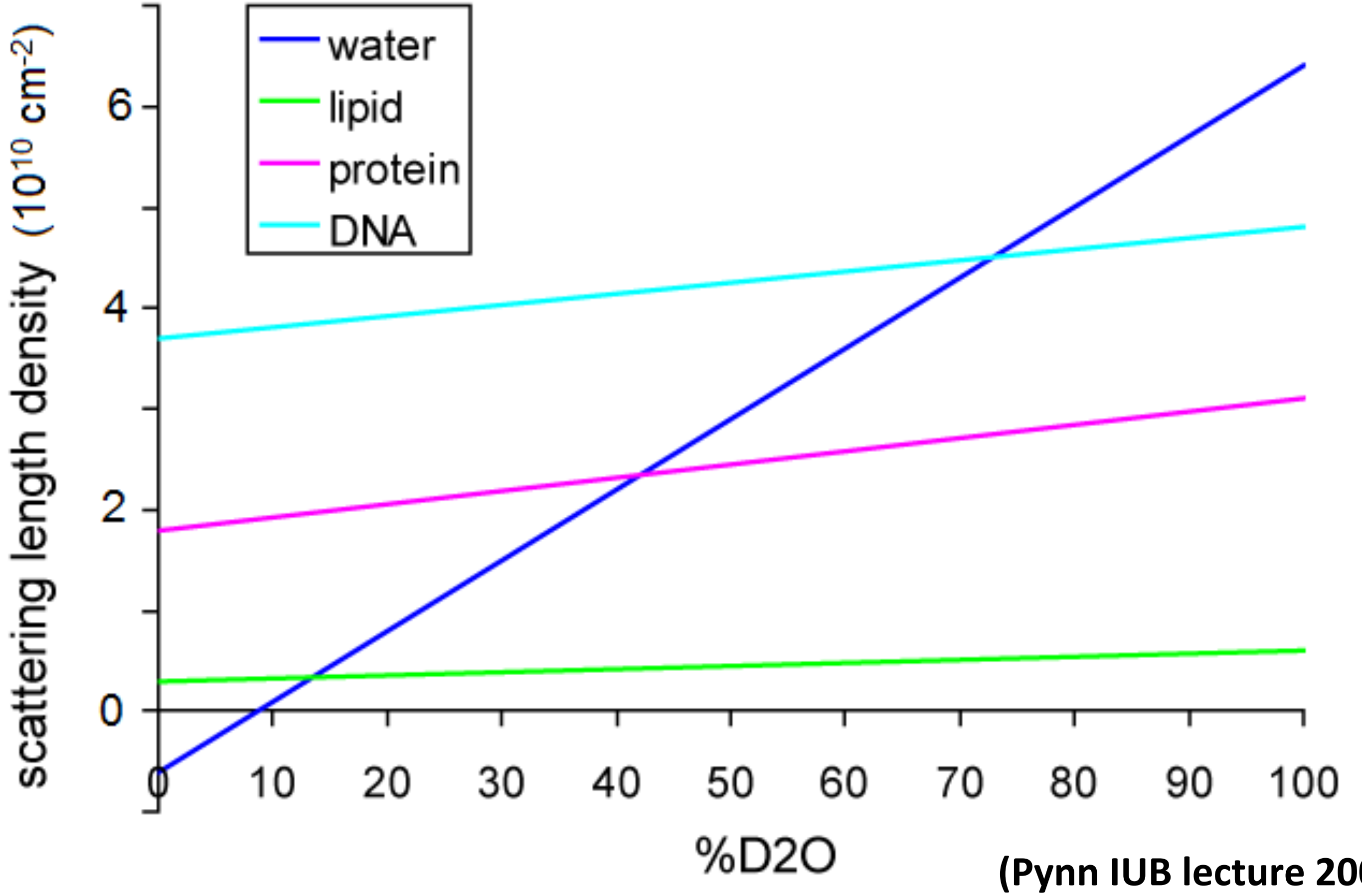
$$T_n = 1 - \Theta/I = 1 - N_{H_2O} \Delta x \sigma_{H_2O} = 1 - N_{H_2O} \Delta x (2\sigma_H + \sigma_O) = 1 - 0.99997/18.01528 \times 6.0221413 \times 10^{23} \times 0.1 \times (2 \times 82.02 + 4.232) \times 10^{-24} = \mathbf{0.4375}$$

Scattering Length Density

Contrast comes from the scattering length density.

$$\rho = \frac{1}{V}\sum_i b_i$$

Unit: 10^{-10} cm^{-2}=10^{-6} Å^{-2}



(Pynn IUB lecture 2006)

Scattering Length Density (cont'd)

Example 2: scattering length density of water

Mass density: 0.99997 g/cm^3

Scattering length: H: -3.7423 fm, O: 5.805 fm

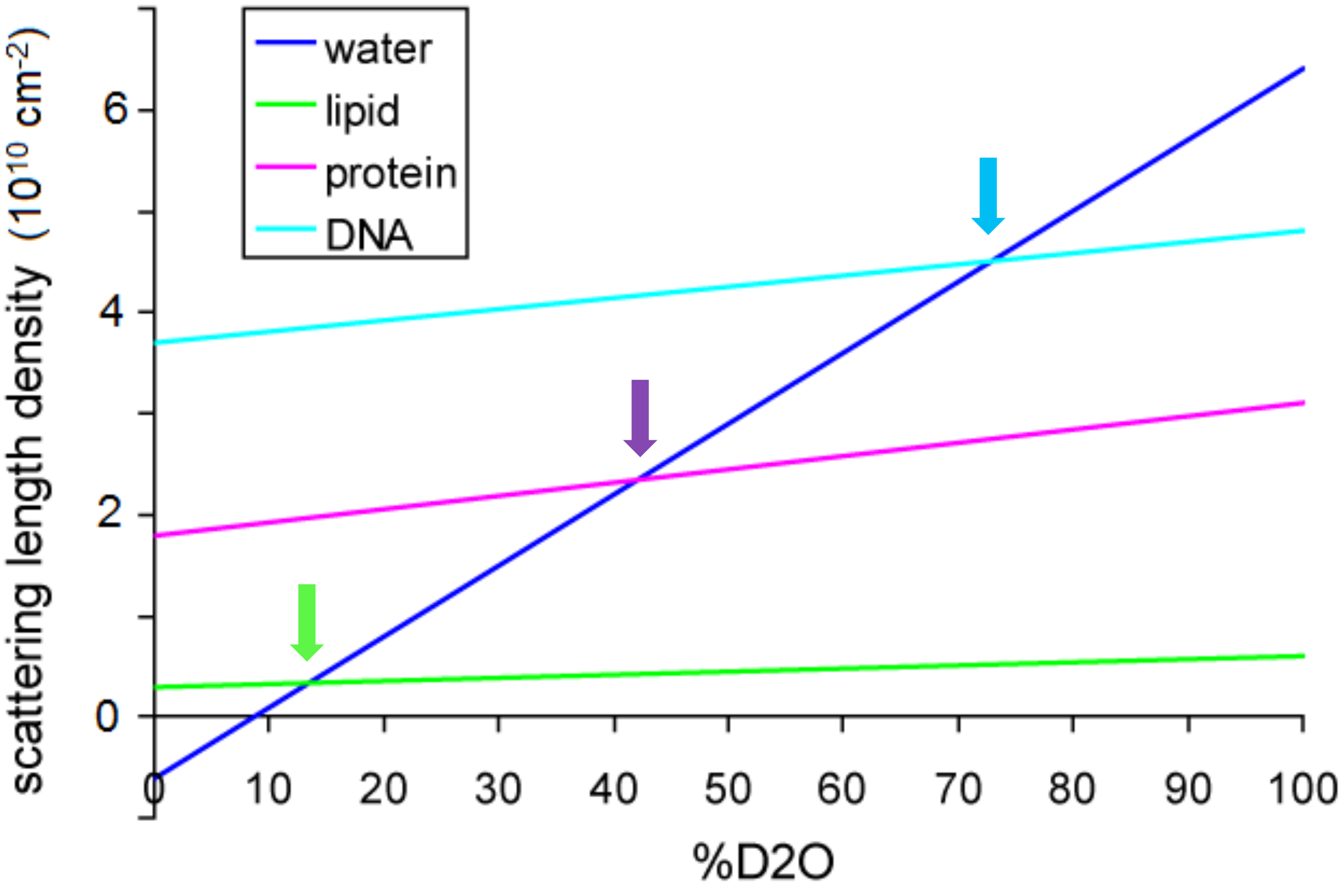
$$\rho_{H_2O} = \frac{\text{mass density}}{\text{molecular weight}} N_A \sum_i b_i = \frac{\text{mass density}}{\text{molecular weight}} N_A (2b_H + b_O) =$$

$$\frac{0.99997}{18.01528} \times 6.0221413\times10^{23} \times \frac{1}{10^{24}} \times (-2\times3.7423+5.805)\times10^{-5} = \mathbf{-0.5614\times10^{-6}}$$

(Å^{-2})

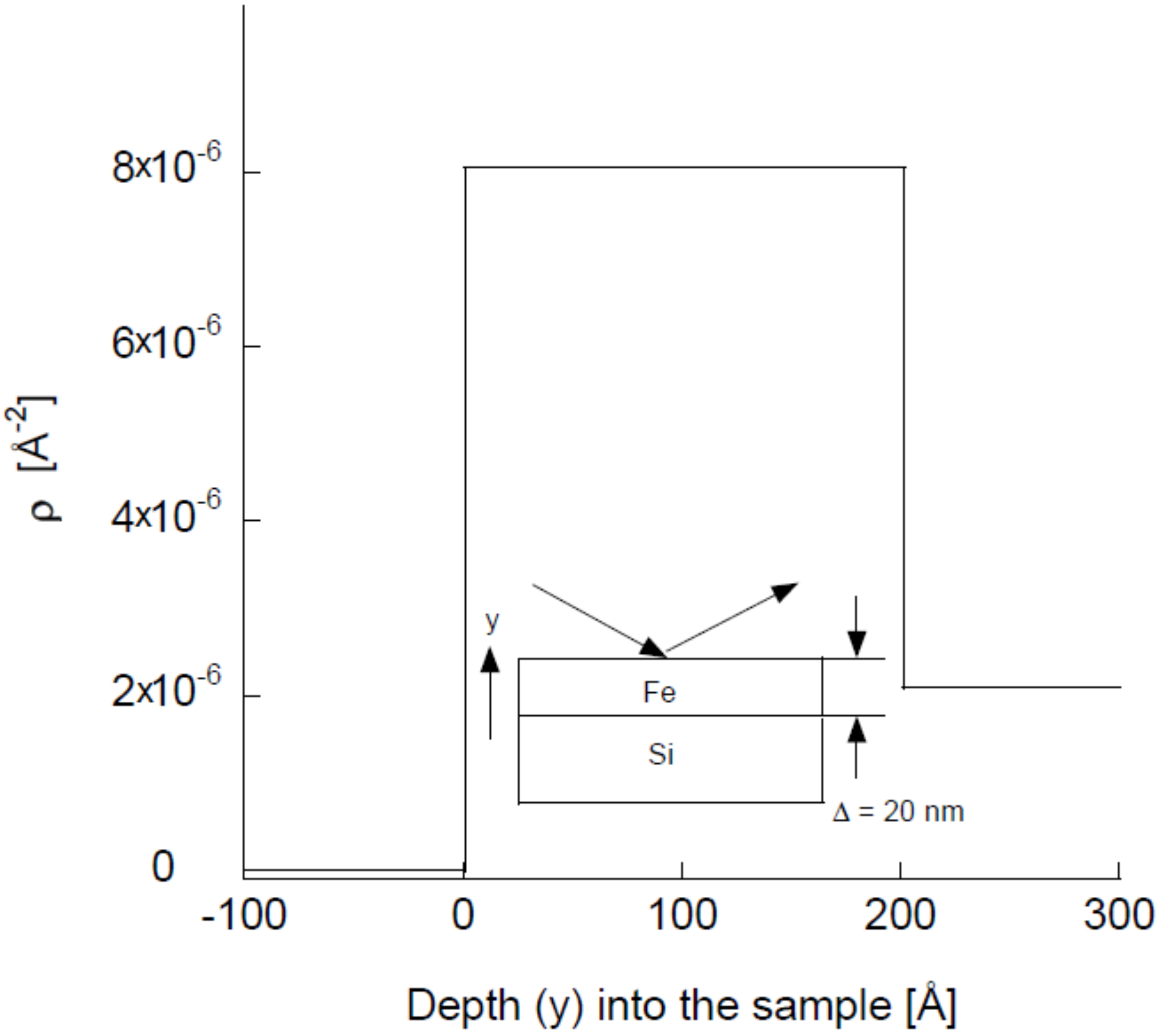
Scattering Length Density (cont'd)

materials	SLD (10^{-6} Å^{-2})
H_2O	-0.56
D_2O	6.39
h-styrene	1.413
d-styrene	6.5
h-cyclohexane	-0.24
d-cyclohexane	6.01
SiO_2	4.186

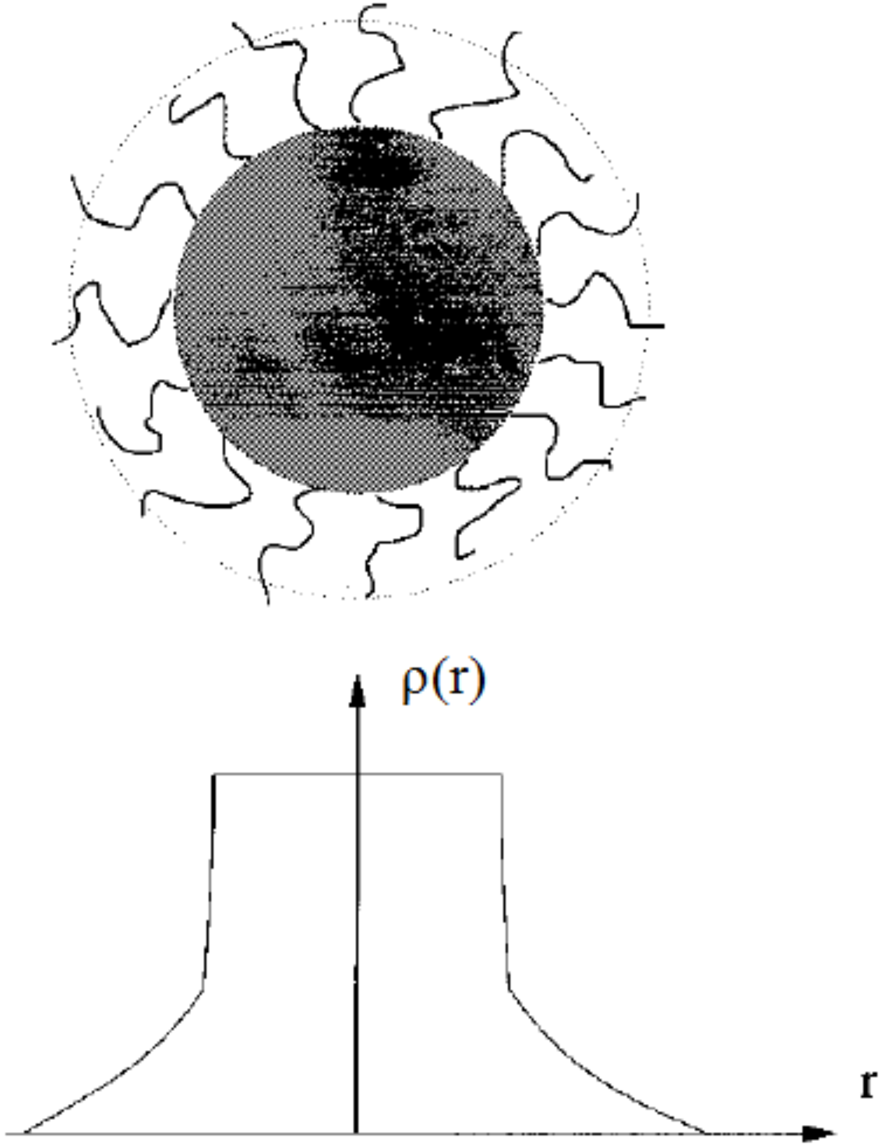


(Pynn IUB lecture 2006)

Scattering Length Density Profile



Fitzsimmons lecture 2005)



(S.-H. Chen Macromolecules 1998)

Coherent and Incoherent Scattering

The neutron scattering length depends on the nuclear isotope, spin relative to the neutron, and nuclear eigenstate.

For a single nucleus of a species,

$$b_i = \langle b \rangle + \delta b_i \qquad \text{where} \qquad \langle \delta b_i \rangle = 0$$

For the correlation between two nuclei,

$$b_i b_j = \langle b \rangle^2 + (\delta b_i + \delta b_j)\langle b \rangle + \delta b_i \delta b_j$$

Average over the whole group of nuclei,

$$\langle \delta b_i + \delta b_j \rangle = 0$$

$$\langle \delta b_i \delta b_j \rangle = \begin{cases} 0 & (i \neq j) \\ \langle (\delta b_i)^2 \rangle = \langle b^2 \rangle - \langle b \rangle^2 & (i = j) \end{cases}$$

Coherent and Incoherent Scattering (cont'd)

For the correlation between two nuclei,

$$b_i b_j = \langle b \rangle^2 + \delta b_i \, \delta b_j$$

Therefore, the correlation between all nuclei,

$$\frac{d\sigma}{d\Omega} = \sum_{i,j=1}^{N} b_i b_j e^{-i\mathbf{Q}\cdot(\mathbf{R}_i - \mathbf{R}_j)} = \langle \boldsymbol{b} \rangle^2 \sum_{i,j=1}^{N} \boldsymbol{b}_i \boldsymbol{b}_j e^{-i\boldsymbol{Q}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)} + \boldsymbol{N}(\langle \boldsymbol{b}^2 \rangle - \langle \boldsymbol{b} \rangle^2)$$

Coherent scattering → Correlation between relative spatial positions

Incoherent scattering → Individual scattering contribution

Coherent and Incoherent Scattering (cont'd)

$$\frac{d\sigma}{d\Omega} = \langle b\rangle^2 \sum_{i,j=1}^{N} b_i b_j e^{-i\mathbf{Q}\cdot(\mathbf{R}_i - \mathbf{R}_j)} + N\left(\langle b^2\rangle - \langle b\rangle^2\right)$$

Coherent scattering

Correlation between relative spatial positions

Incoherent scattering

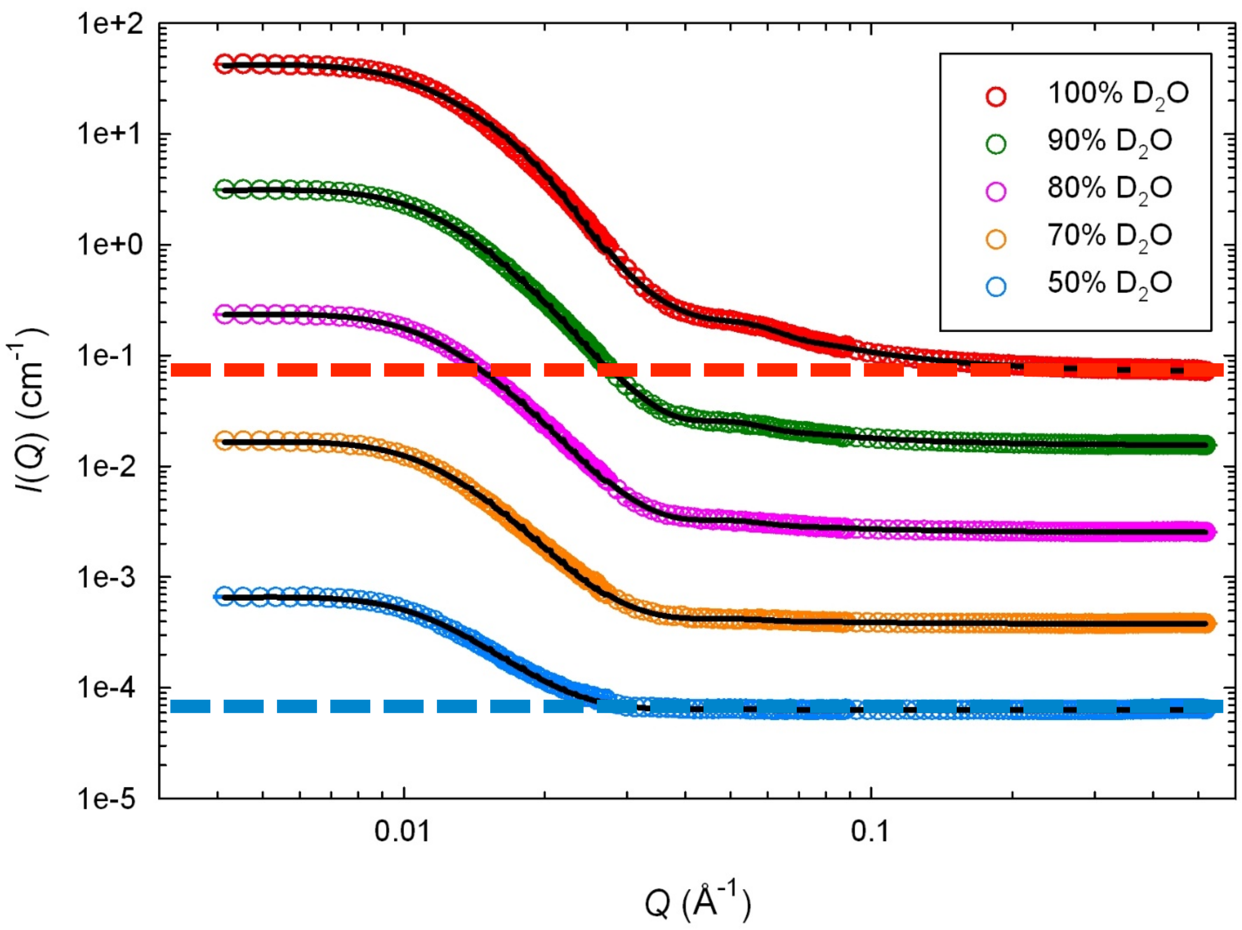
Individual scattering contribution

Coherent and Incoherent Scattering (cont'd)

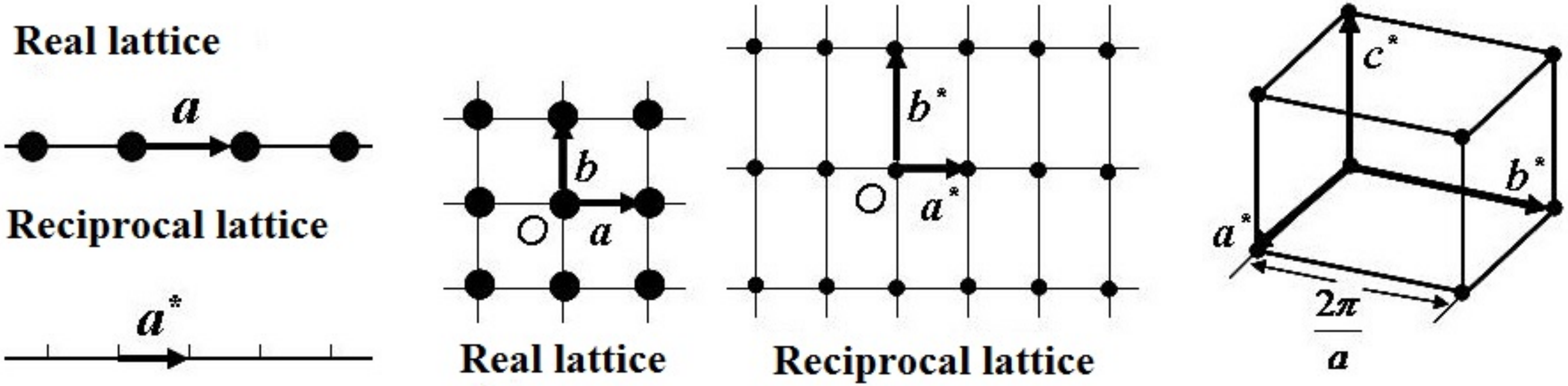
$\langle b \rangle^2$ Coherent scattering cross section

$\langle b^2 \rangle - \langle b \rangle^2$ Incoherent scattering cross section

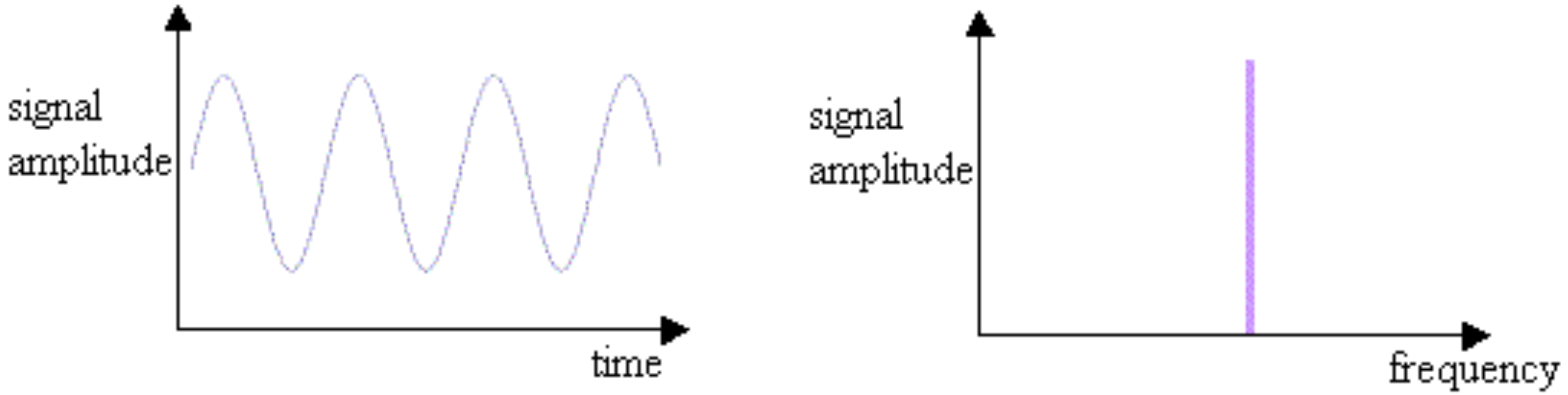
Nuclide	b_{coh} (fm)	σ_{coh} (barn)	σ_{inc} (barn)
H	-3.472	1.8	80.2
D	6.674	5.6	2
C	6.65	5.55	0.001
O	5.805	4.2	0.0008
V	-0.443	0.02	5



Reciprocal Space – Spatial Frequency

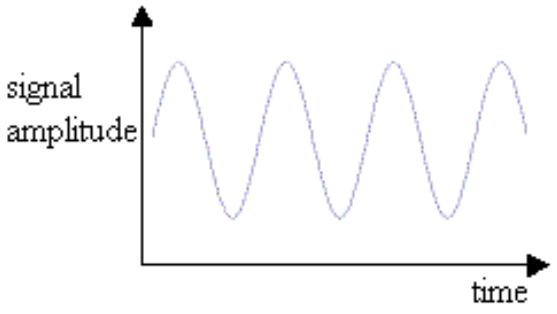


(a) 1D (b) 2D (c) 3D

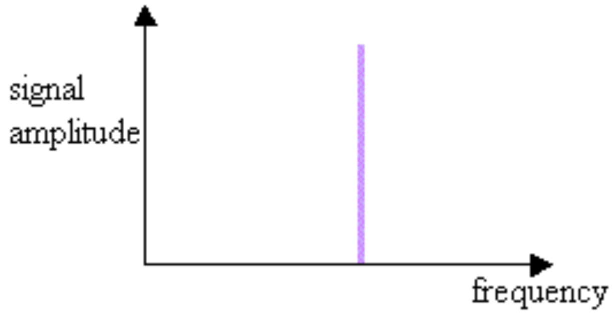


Time domain Frequency domain

Reciprocal Space – Spatial Frequency (cont'd)



Time domain



Frequency domain

Time space shape: $f(t)$

Frequency space shape: $F(\omega)$

$\mathcal{F}[f(t)] = F(\omega)$ $\qquad$ $\mathcal{F}^{-1}[F(\omega)] = f(t)$

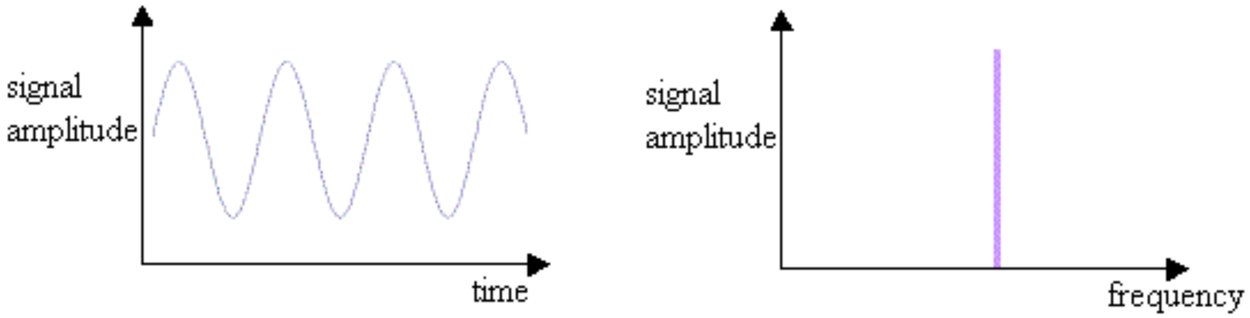
$\omega T = 2\pi$

Fourier transform:

$$\mathcal{F}[f(t)] = \int_{-\infty}^{+\infty} f(t) e^{-i\omega t}\, dt = F(\omega)$$

$$\mathcal{F}[f(\vec{r})] = \int_{V} f(\vec{r}) e^{-i\vec{r}\cdot\vec{Q}}\, d^3\vec{r} = F(\vec{Q})$$

Reciprocal Space – Spatial Frequency (cont'd)



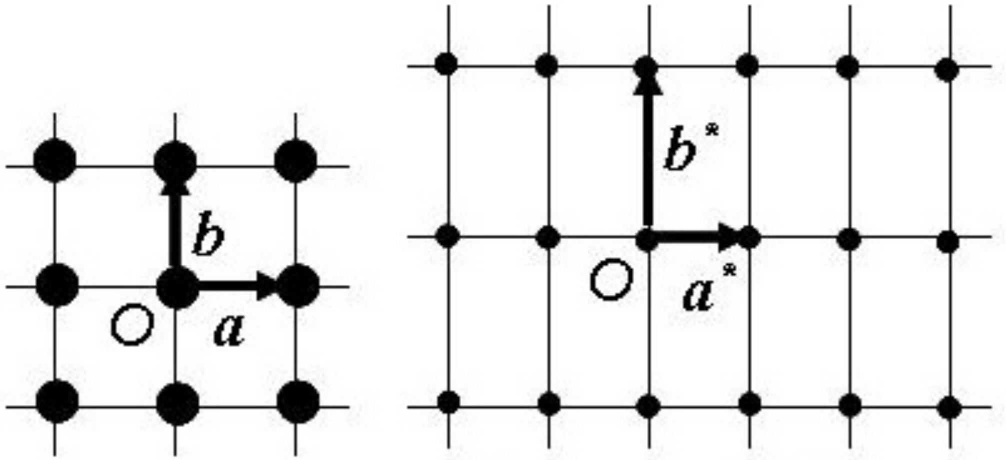
Time domain **Frequency domain**

Time space shape: $f(t)$

Frequency space spectrum: $F(\omega)$

$\mathcal{F}[f(t)]=F(\omega)$ $\mathcal{F}^{-1}[F(\omega)]=f(t)$

$\omega T=2\pi$



Real lattice **Reciprocal lattice**

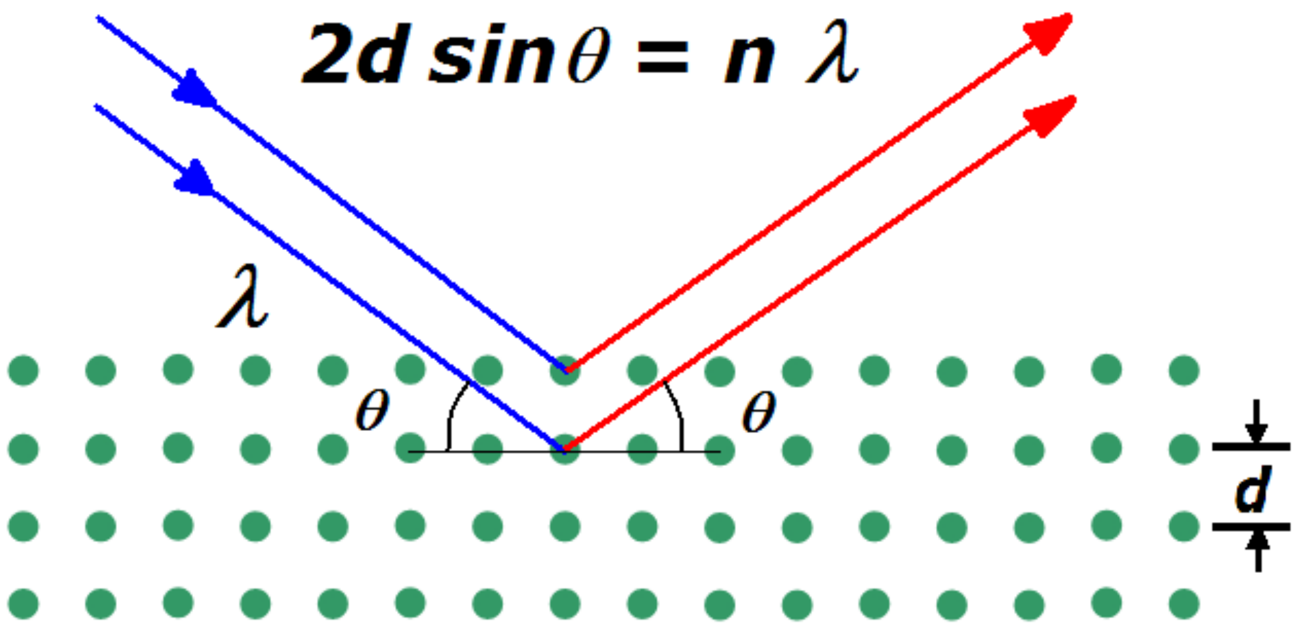
Real space distribution: $f(r)$

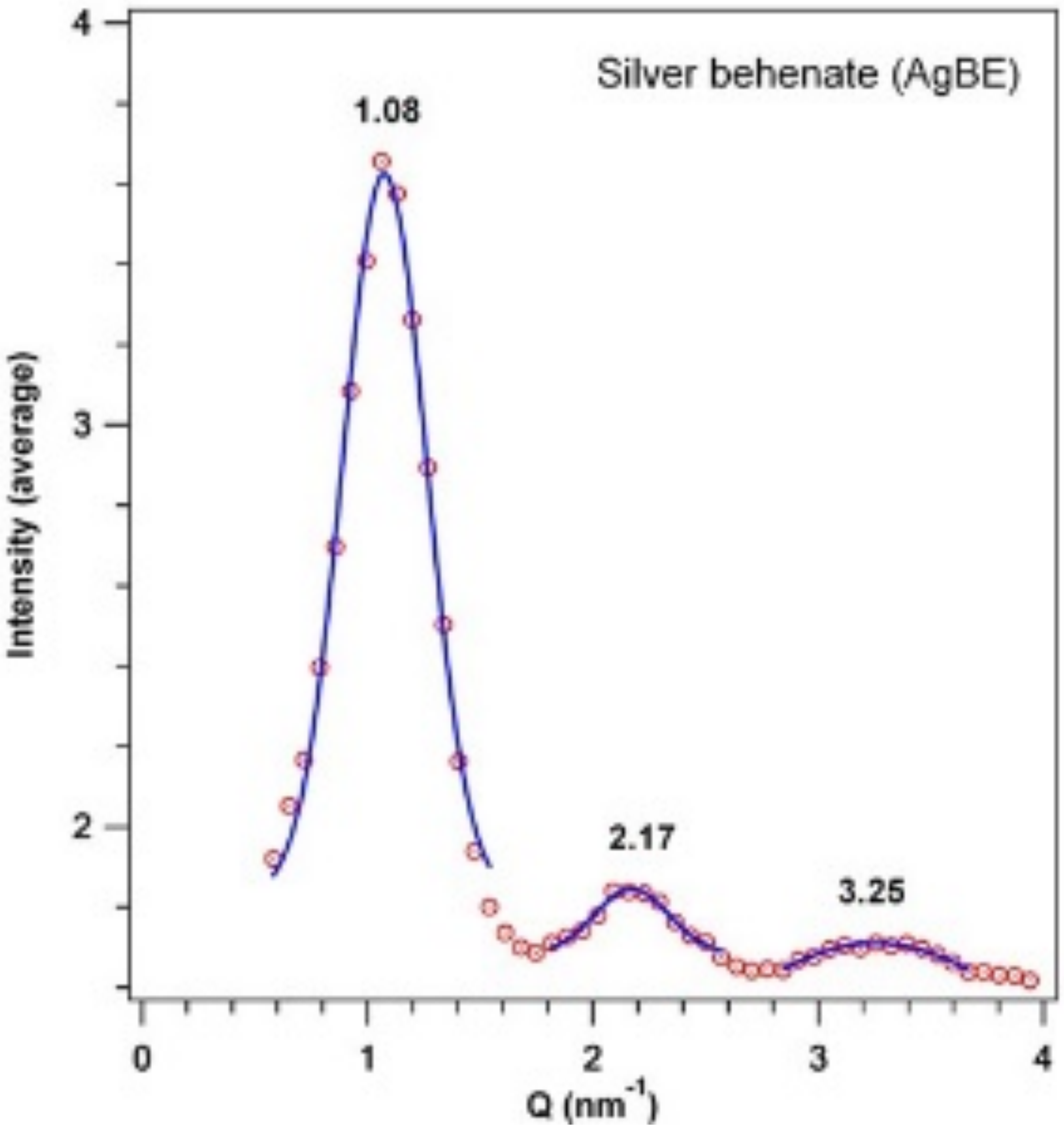
Reciprocal space spectrum: $F(Q)$

$\mathcal{F}[f(r)]=F(Q)$ $\mathcal{F}^{-1}[F(Q)]=f(r)$

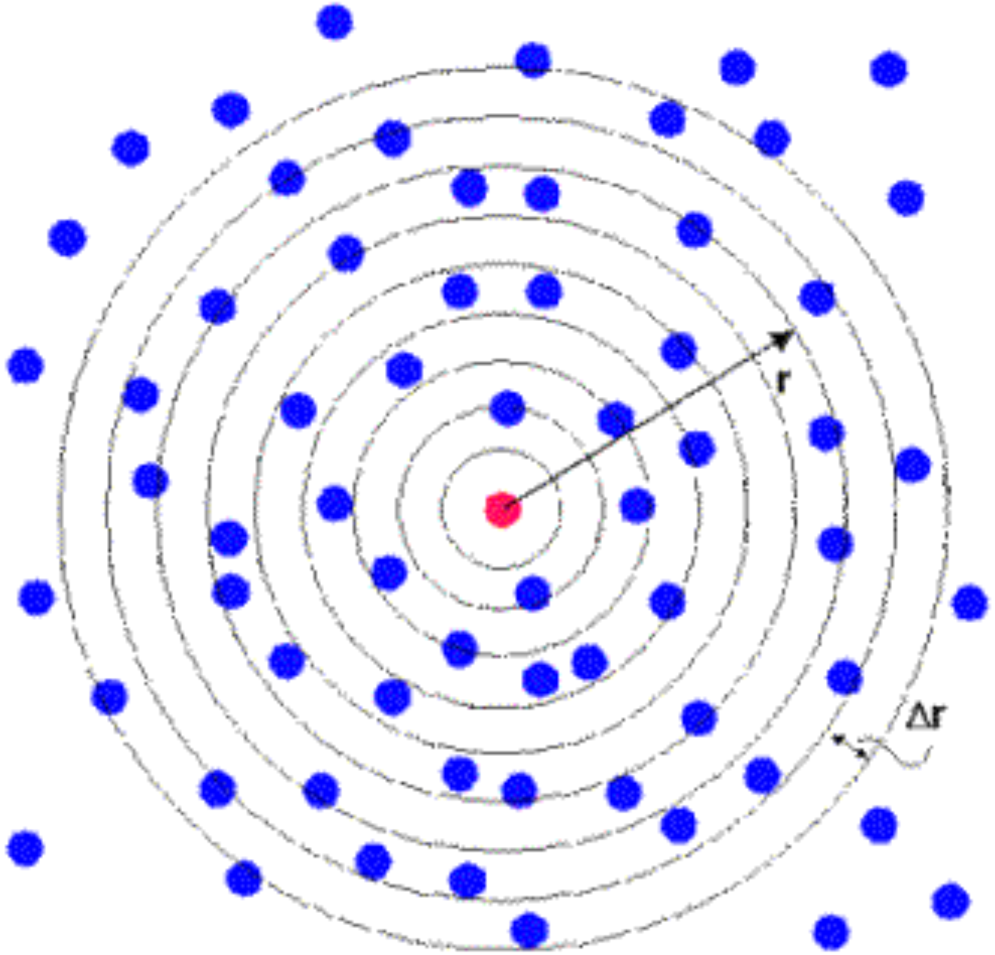
$Qd=2\pi$

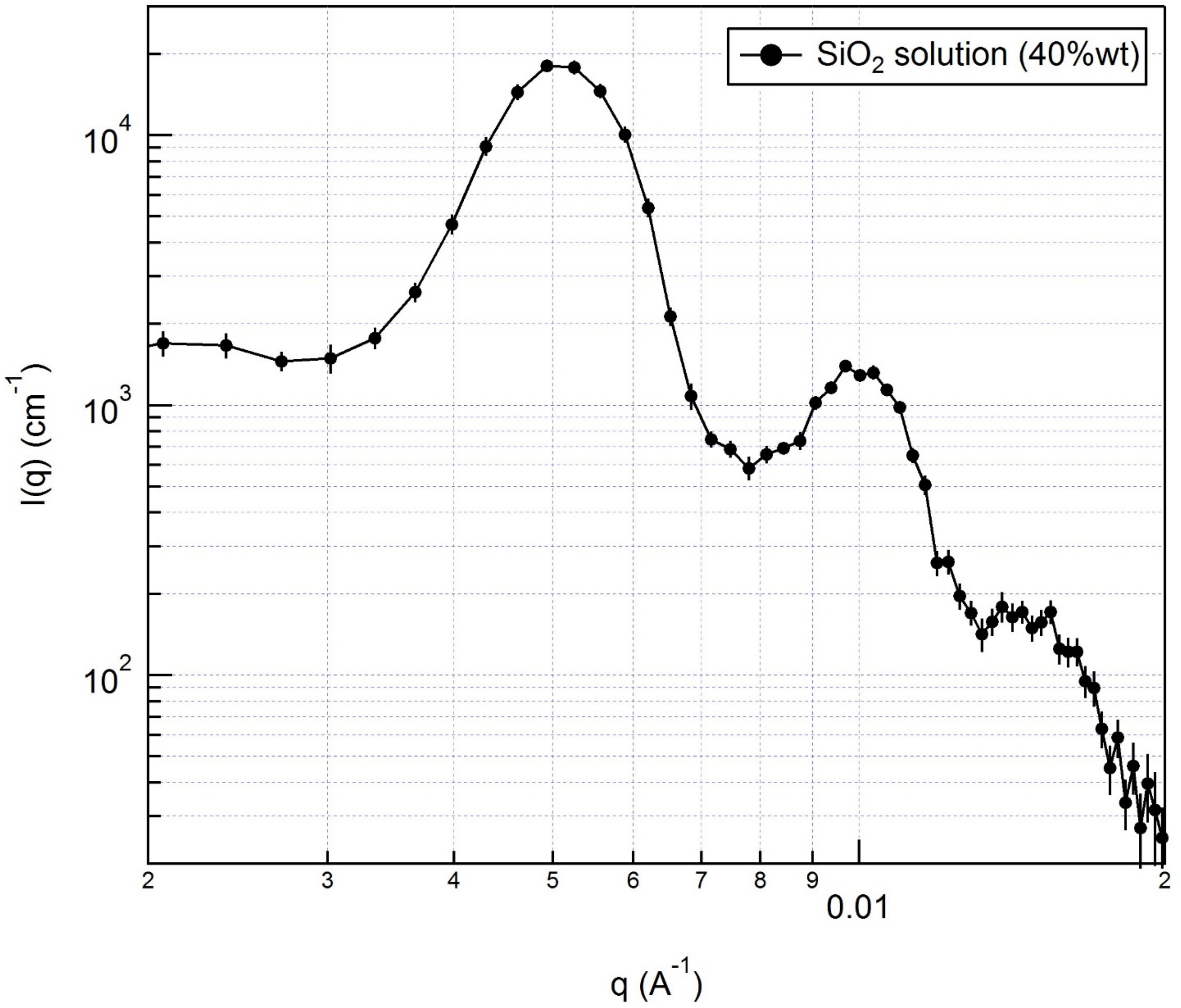
Reciprocal Space – Spatial Frequency (cont'd)



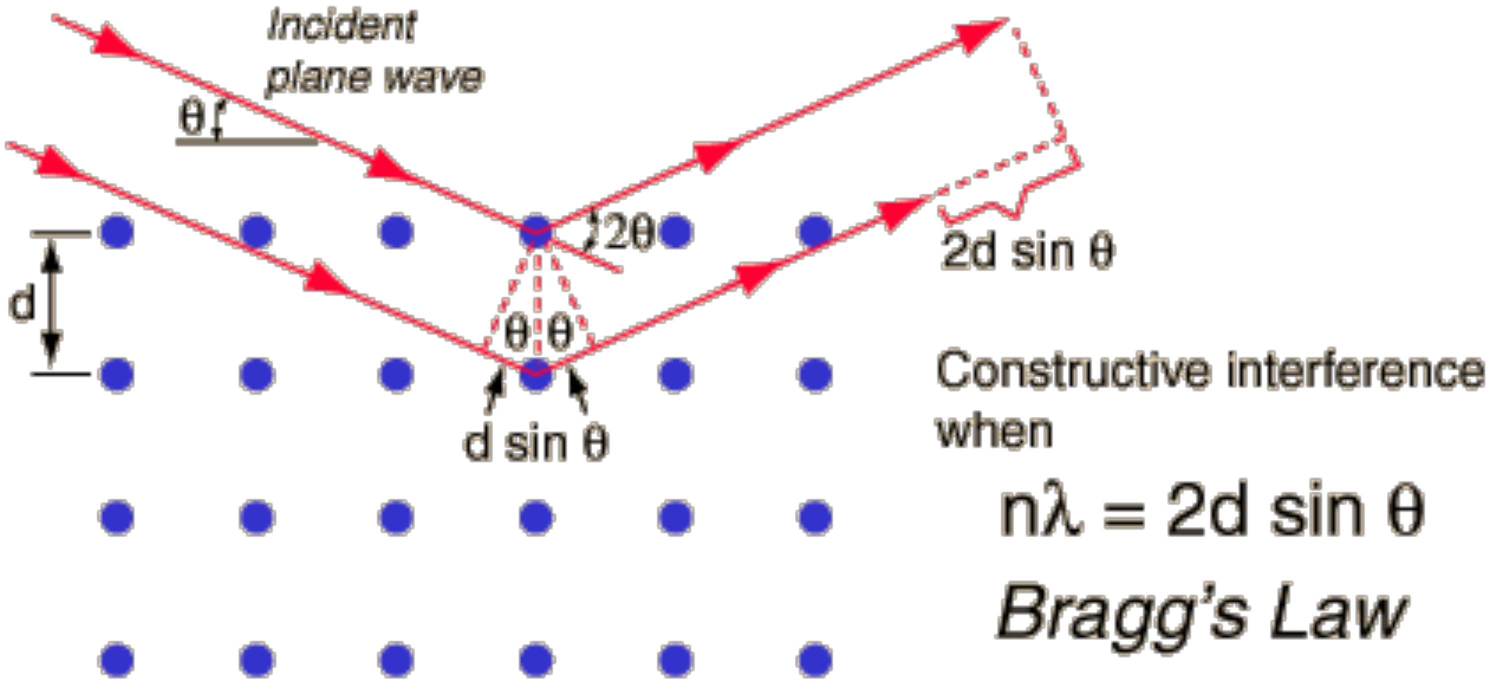


Reciprocal Space – Spatial Frequency (cont'd)



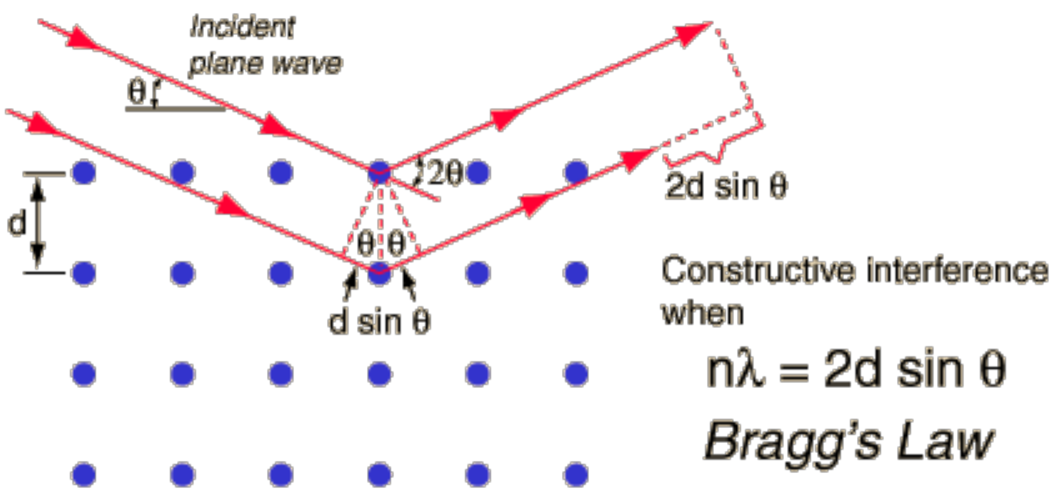


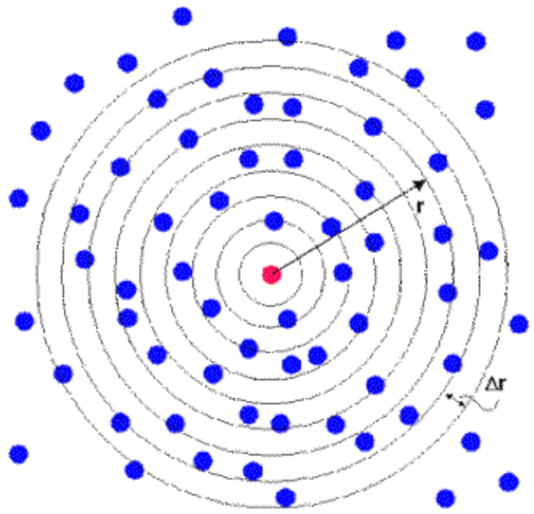
Correlation Functions



Neutron/X-ray/light scattering measures different **mathematical transforms** (Fourier, Abel) of **two-point correlation functions** (Debye, van Hove) in different **spaces** (r/Q, t/ω) and different **time or length scales** (λ, 2θ).

Correlation Functions (cont'd)





Interference between two scattered waves:

$$\Psi_i \Psi_j^* = b_i b_j e^{-iQ\cdot(R_i - R_j)}$$

Sum over all scatterers:

$$\frac{d\sigma}{d\Omega} = \sum_{i,j=1} \Psi_i \Psi_j^* = \sum_{i,j=1}^{N} b_i b_j e^{-iQ\cdot(R_i - R_j)}$$

Correlation Functions (cont'd)

$$\frac{d\sigma}{d\Omega} = \sum_{i,j=1} \Psi_i \Psi_j^* = \sum_{i,j=1}^{N} b_i b_j e^{-iQ\cdot(R_i - R_j)}$$

Debye correlation function (structure)

$$\gamma(r) = \int_V \rho(r')\rho(r' + r)\, d^3 r'$$

van Hove pair correlation function (dynamic)

$$G(r,t) = \frac{1}{N} \sum_{i,j=1}^{N} \delta(r - r_i(t) + r_j(0))$$

Pair distribution function (structure)

$$g(r) = \frac{V}{N^2} \sum_{i,j=1}^{N} \delta(r - r_i + r_j)$$

Self time correlation function (dynamic)

$$G_s(r,t) = \frac{1}{N} \sum_{i=1}^{N} \delta(r_i(0))\delta(r - r_i(t))$$

Correlation Functions (cont'd)

Debye correlation function (structure)

$$\gamma(r)=\int_V \rho(r')\rho(r'+r)\,d^3 r'$$

$$I(Q)=\mathcal{F}[\gamma(r)]$$ (SANS,USANS,ND,NR)

$$G(z)=\mathcal{A}[\gamma(r)]$$ (SESANS)

Pair distribution function (structure)

$$g(r)=\frac{V}{N^2}\sum_{i,j=1}^{N}\delta(r-r_i+r_j)$$

$$S(Q)=\mathcal{F}[g(r)]$$ (SANS,USANS)

van Hove pair correlation function (dynamic)

$$G(r,t)=\frac{1}{N}\sum_{i,j=1}^{N}\delta(r-r_i(t)+r_j(0))$$

$$I(Q,t)=\mathcal{F}_Q[G(r,t)]$$ (NSE)

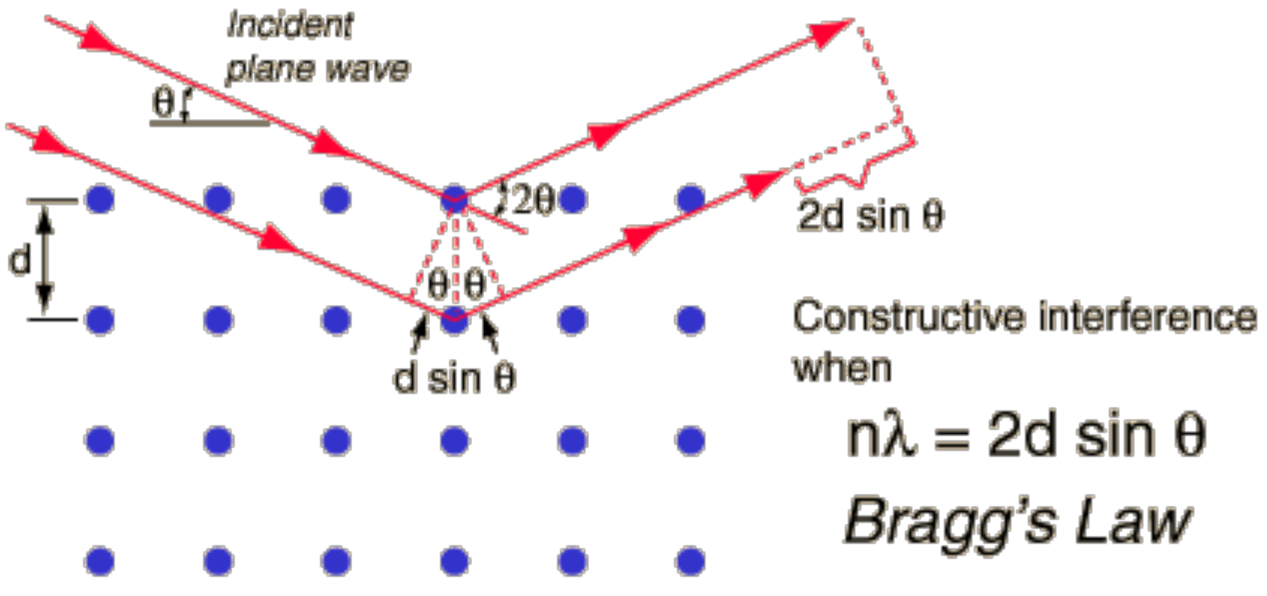
$$S(Q,\omega)=\mathcal{F}_{Q,\omega}[G(r,t)]$$ (INS)

Self time correlation function (dynamic)

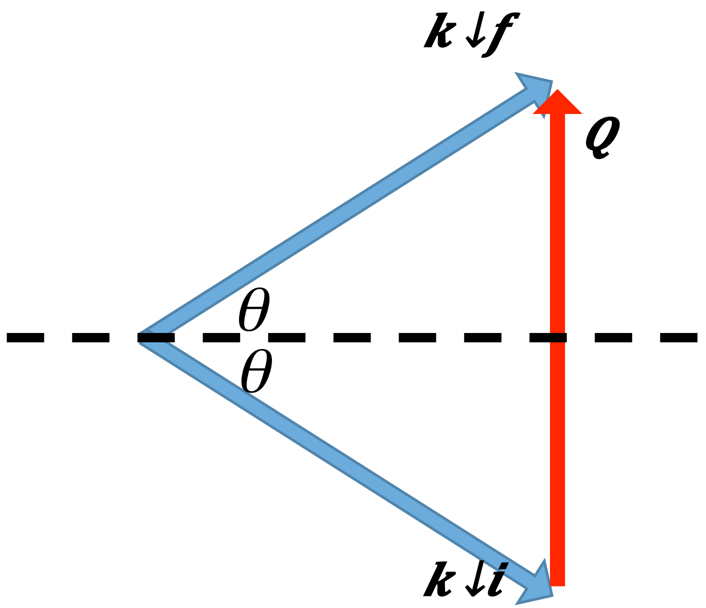
$$G_s(r,t)=\frac{1}{N}\sum_{i=1}^{N}\delta(r_i(0))\delta(r-r_i(t))$$

$$S_s(Q,\omega)=\mathcal{F}_{Q,\omega}[G_s(r,t)]$$ (QENS,incoh)

Neutron Diffraction



Scattering triangle



Q: Momentum transfer

$$Q = k_f - k_i$$

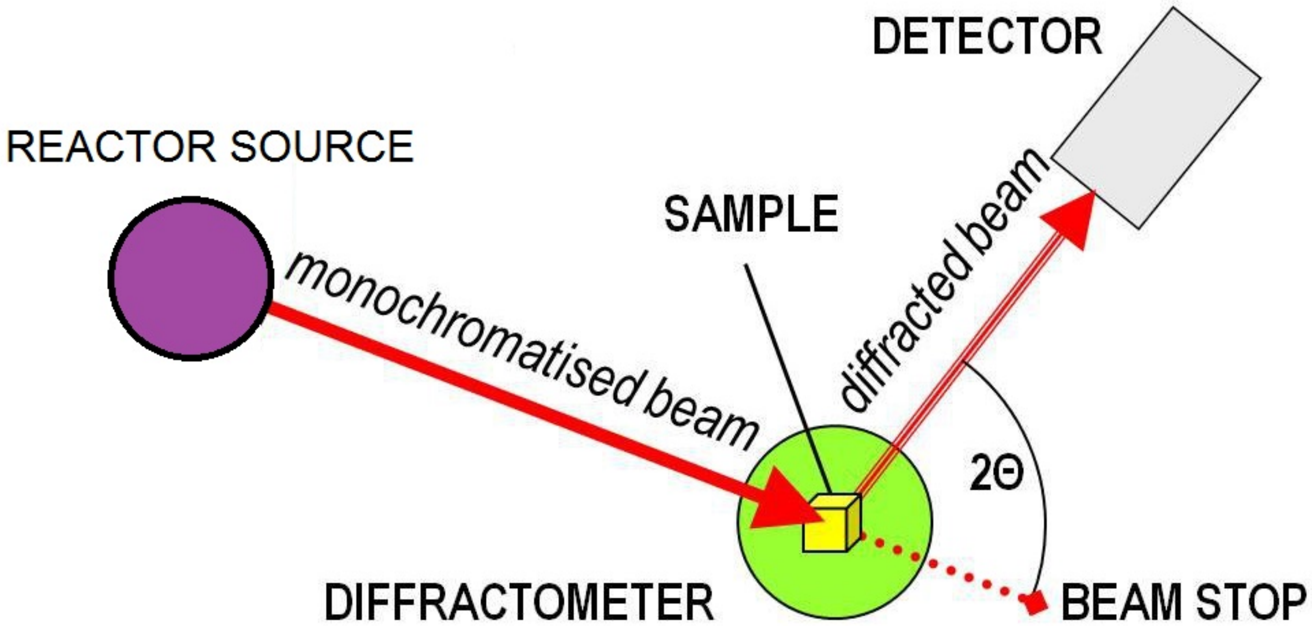
$$|k_f| = |k_i| = 2\pi/\lambda$$

$$\therefore Q = |Q| = 2|k_i|\sin\theta = 4\pi/\lambda \sin\theta$$

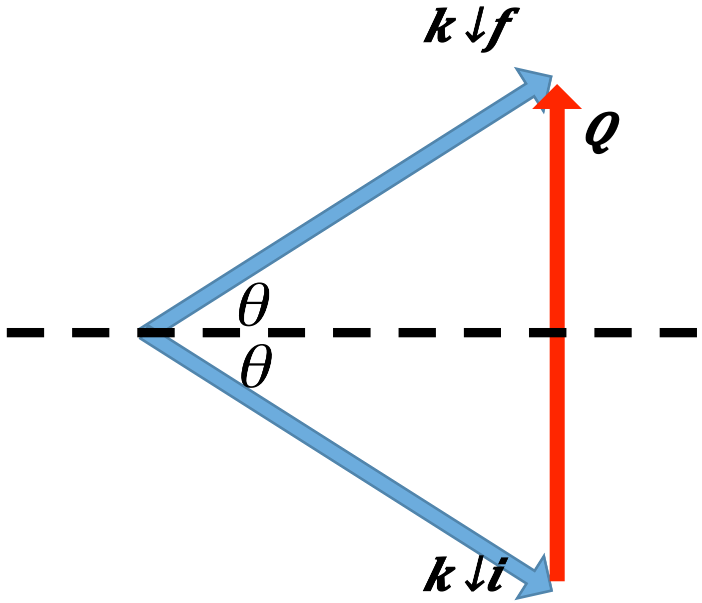
$$\boldsymbol{Qd = 2n\pi}$$

Neutron Diffraction (cont'd)

Two axis diffractometer



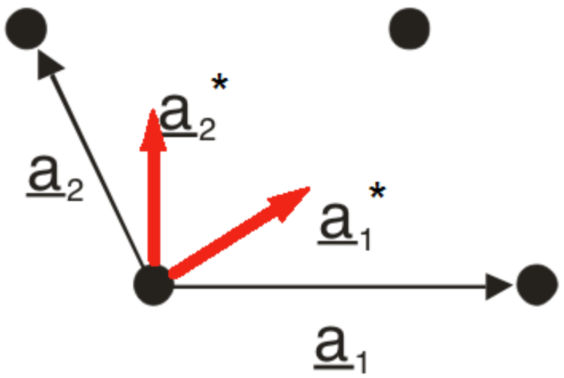
Scattering triangle



Diffraction – Where the atoms are:

Clifford Shull, 1994 Nobel Prize (1/2)

Notations



Crystal lattice

$$R = m_1 a_1 + m_2 a_2 + m_3 a_3$$

Reciprocal lattice

$$G_{hkl} = h a_1^* + k a_2^* + l a_3^*$$

Miller indices h,k,l

$$a_1^* = 2\pi/V \, a_2 \times a_3$$

$$a_2^* = 2\pi/V \, a_3 \times a_1$$

$$a_3^* = 2\pi/V \, a_1 \times a_2$$

$$V = a_1 \cdot (a_2 \times a_3)$$

$$a_i \cdot a_j^* = 2\pi \delta_{ij}$$

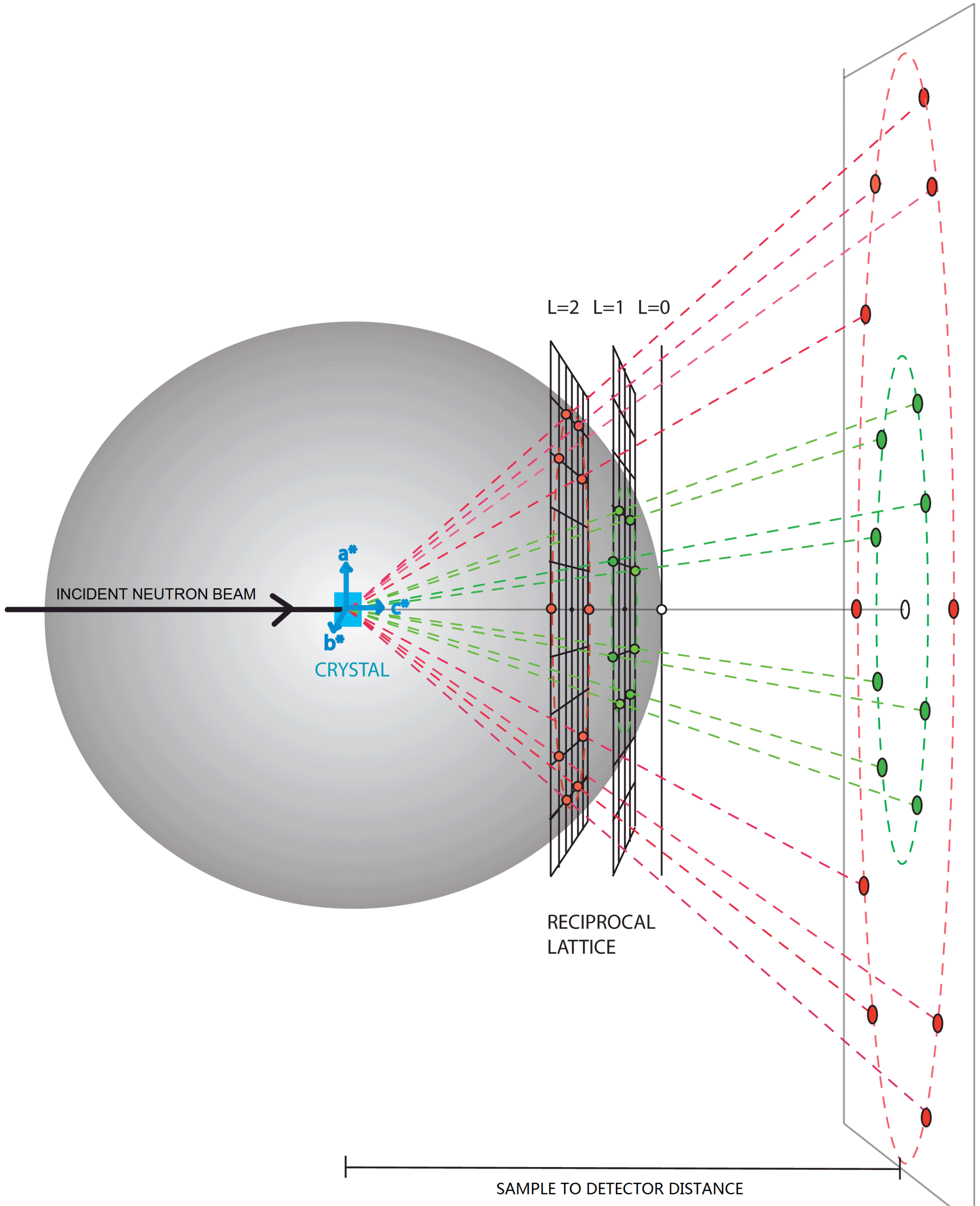
(hkl): a set of planes perpendicular to G_{hkl}, separated by $2\pi/|G_{hkl}|$

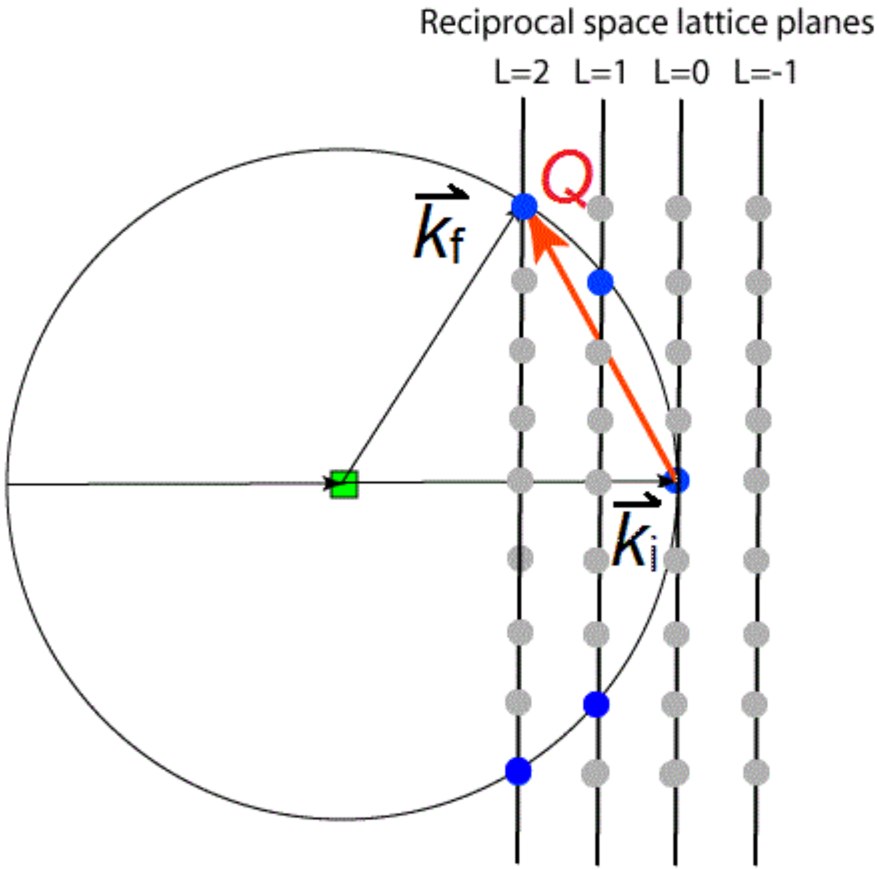
$[hkl]$: a specific crystallographic direction

$\{hkl\}$: a set of symmetry-related lattice planes

$\langle hkl \rangle$: a set of symmetry-equivalent crystallographic directions

Ewald Sphere

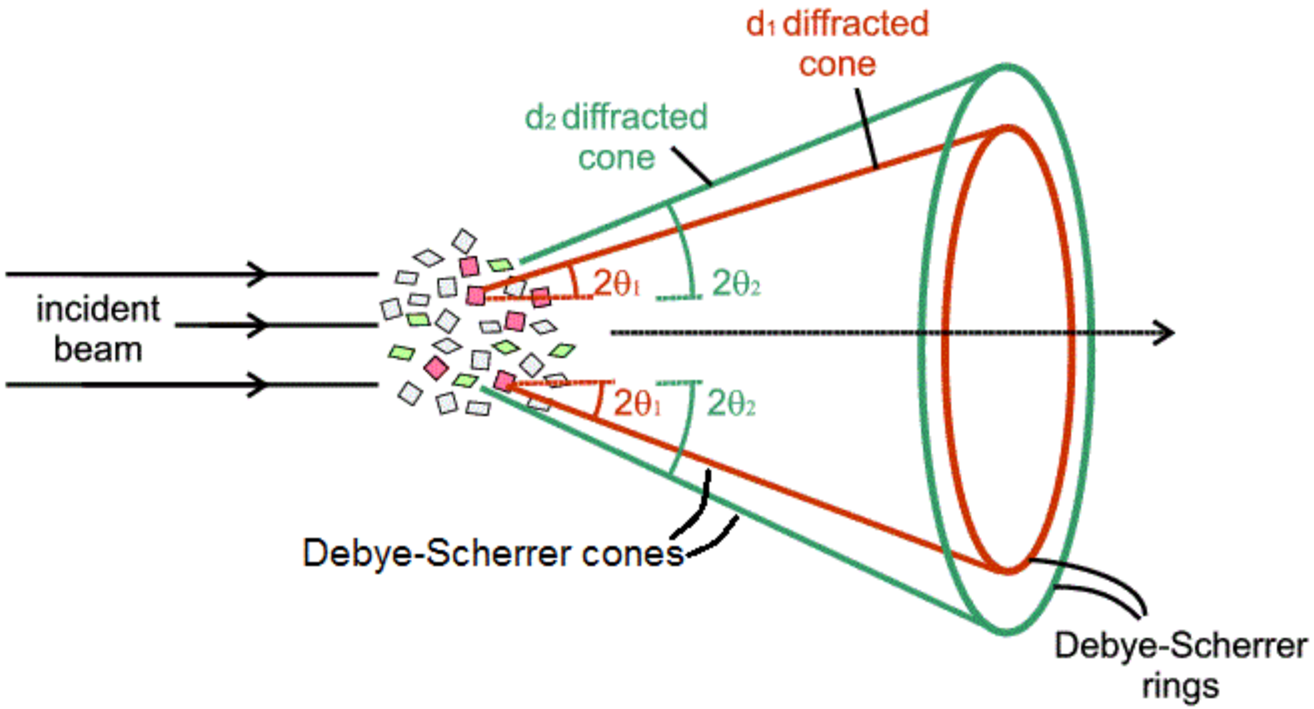


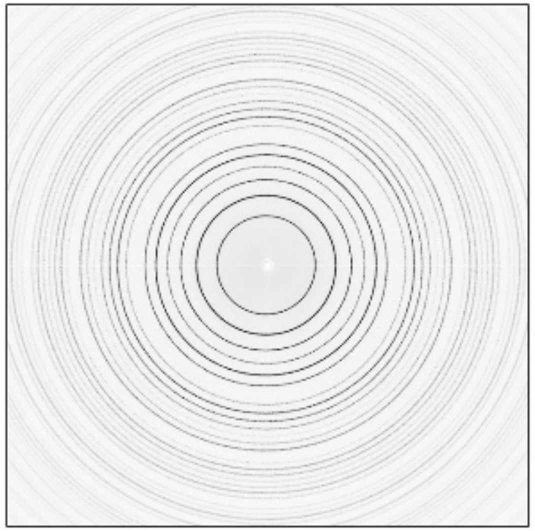


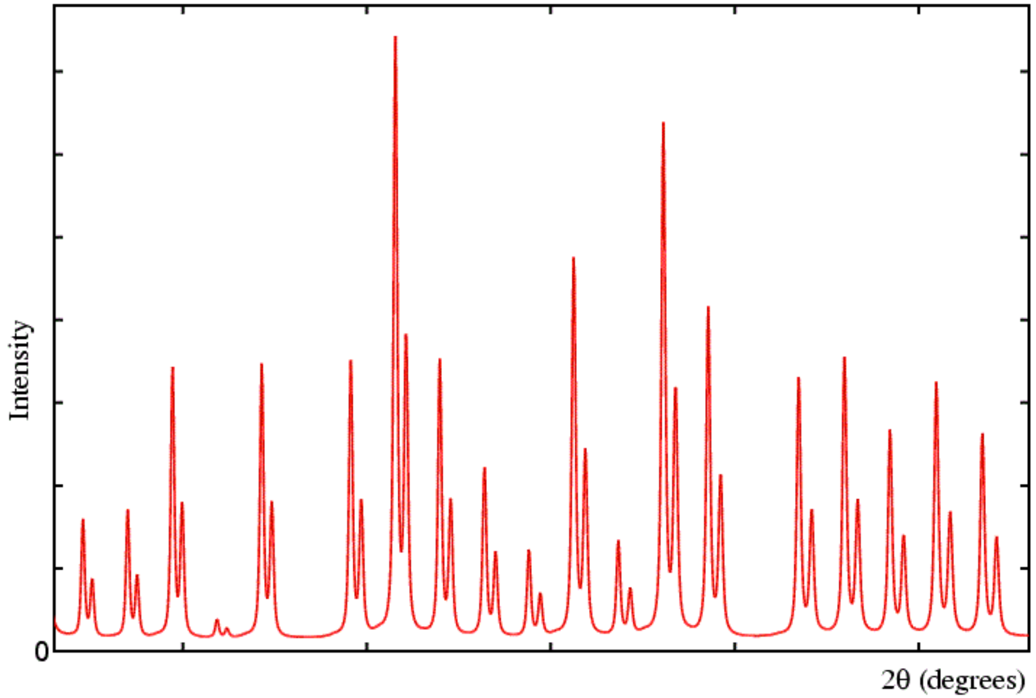
Laue's condition $Q = G_{hkl}$

$$Q \cdot a_1 = 2\pi h, Q \cdot a_2 = 2\pi k, \; Q \cdot a_3 = 2\pi l$$

Powder Diffraction







- Phase identification
- Crystallinity
- Lattice parameters
- Crystallite size
- Orientation

Rietveld Refinement Method

$$I = I_0 \sum_h k_h m_h L_h F_h^2 P(\Delta_h) + I_b$$

I_0 : incident intensity

k_h : scale factor for particular phase

m_h : reflection multiplicity

L_h : correction factors on intensity (texture…)

F_h : structure factor for a particular reflection $F_{hkl} = \sum_i b_i e^{-iQ\cdot R_i} e^{-W_i}$

$P(\Delta_h)$: peak shape function (instrument resolution function, crystallite size, strain, defects)

I_b : background intensity

Example: Polymer Diffraction

- Phase identification
- Crystallinity

$x_{cr} = A_{cr} / A_{cr} + KA_{am}$

- Lattice parameters

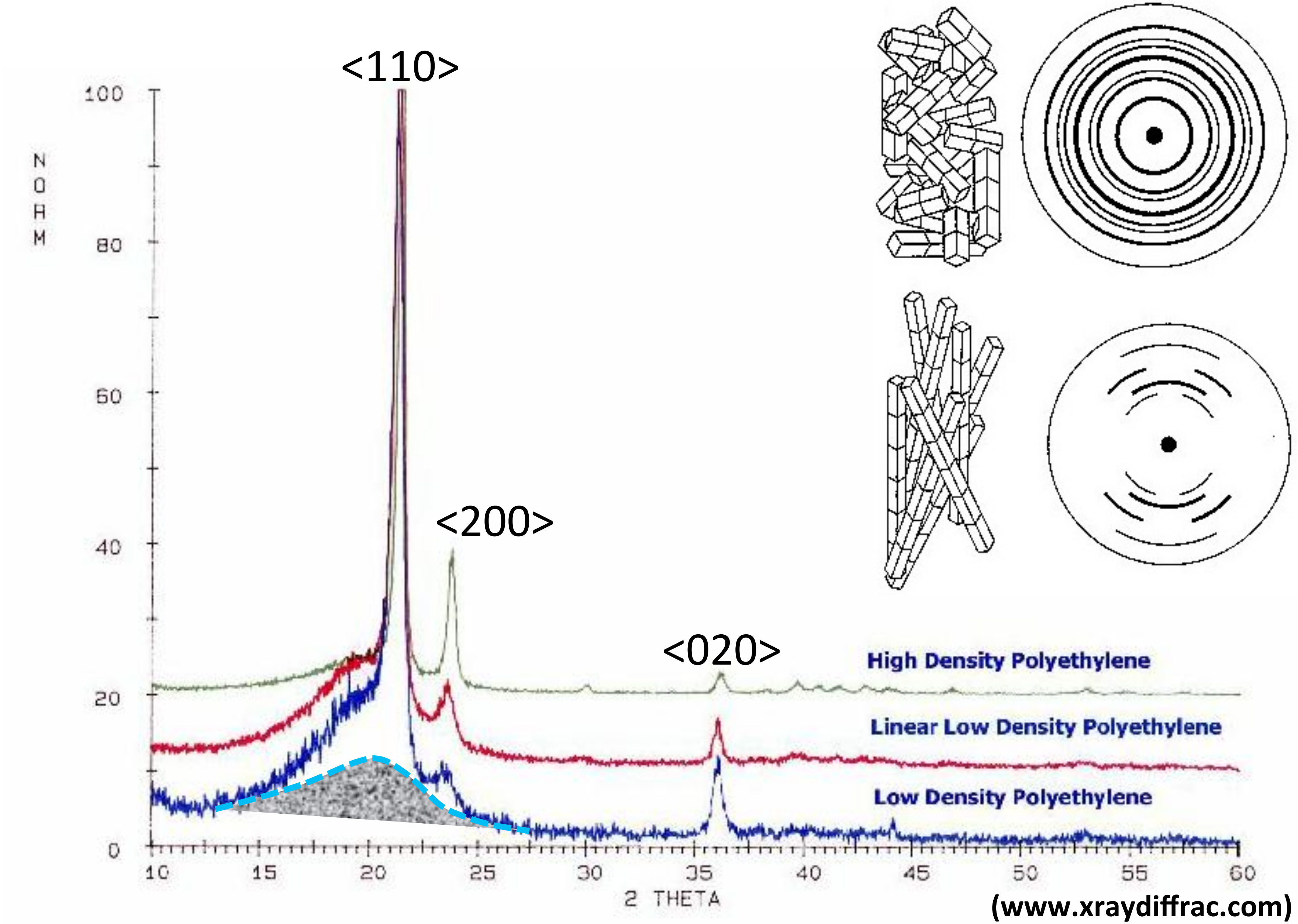
$d = 2\pi / Q$

- Crystallite size

$L_{hkl} = 0.89\lambda / (FWHM - \Delta\theta) \cos\theta$

- Orientation

$f_{\phi} = 1/2\ (3\langle \cos^{2}\phi \rangle - 1)$



(www.xraydiffrac.com)

Example: Polymer Diffraction (cont'd)

J|A|C|S
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Crystal Structure and Hydrogen Bonding System in Cellulose I$_\alpha$ from Synchrotron X-ray and Neutron Fiber Diffraction

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