

STRUCTURE OF LIQUIDS & GLASSES BY NEUTRON & X-RAY DIFFRACTION

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References

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DIFFRACTION

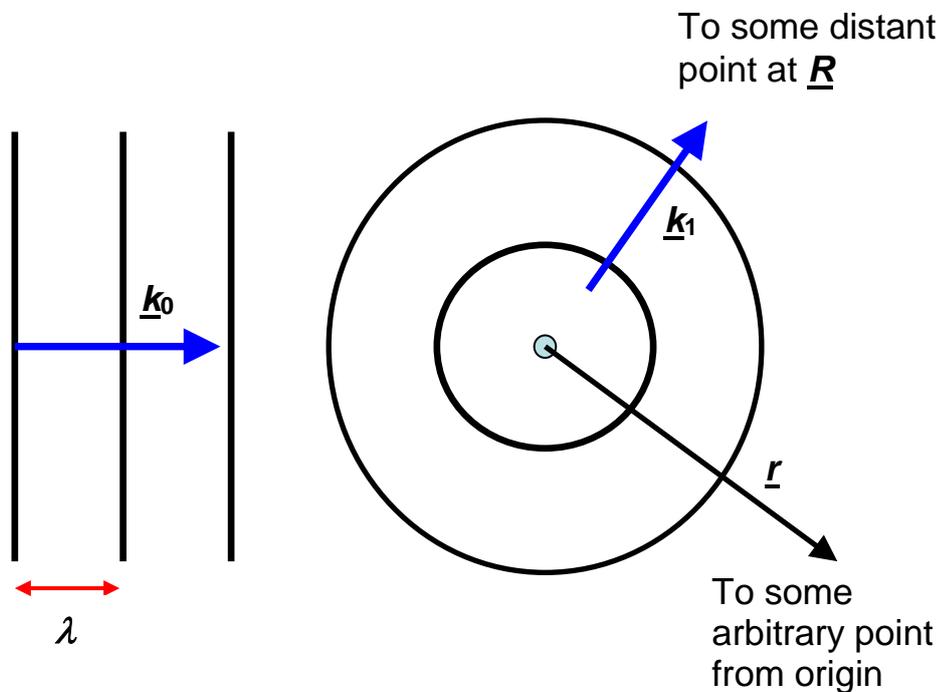
- Fraunhofer diffraction: (i) point-like single particle and (ii) assembly of point-like scattering centres (weak scattering limit)
- Density functions and Fourier transforms
- Diffraction from an assembly of finite-sized scattering centres
- Differential scattering cross-section: The static approximation
- Real-space structure
- Multicomponent systems
- Neutron diffraction with isotope substitution (NDIS)
- Anomalous X-ray scattering (AXS)



The Institut Laue-Langevin (ILL) (www.ill.fr) and the European Synchrotron Radiation Facility (ESRF) (www.esrf.fr) in Grenoble

SCATTERING BY A SINGLE PARTICLE

Consider a single **point-like** particle at the origin and an incident **plane** wave



Incident plane wave:

$$\Phi_{\text{inc}} = \phi_0 \exp i(\underline{k}_0 \cdot \underline{r} - \omega_0 t)$$

Scattered spherical wave ($\because \lambda \gg$ particle diameter)

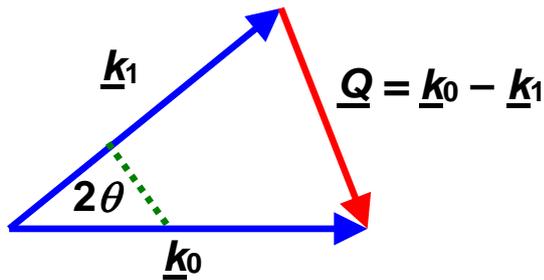
$$\Phi_{\text{sc}} = \frac{\phi_0 A}{R} \exp i(k_1 R - \omega_0 t + \alpha) \equiv \frac{\phi_0 a}{R} e^{ik_1 R} e^{-i\omega_0 t}$$

where $a = Ae^{i\alpha}$ depends on the nature of the **interaction** between the incident wave and the scattering centre

(α determines the **phase** of the scattered wave relative to that incident)

Note: For Schrödinger waves Φ_{inc} and Φ_{sc} are complex. For other waves only the real parts have physical significance.

Scattering triangle



$2\theta =$ scattering angle

$\hbar \underline{k}_0 =$ incident mom^m

$\hbar \underline{k}_1 =$ scattered mom^m

Change in particle's mom^m $\hbar(\underline{k}_0 - \underline{k}_1) = \hbar \underline{Q}$

\underline{Q} is called the **scattering vector**

By the cosine rule $Q^2 = k_0^2 + k_1^2 - 2k_0k_1 \cos 2\theta$

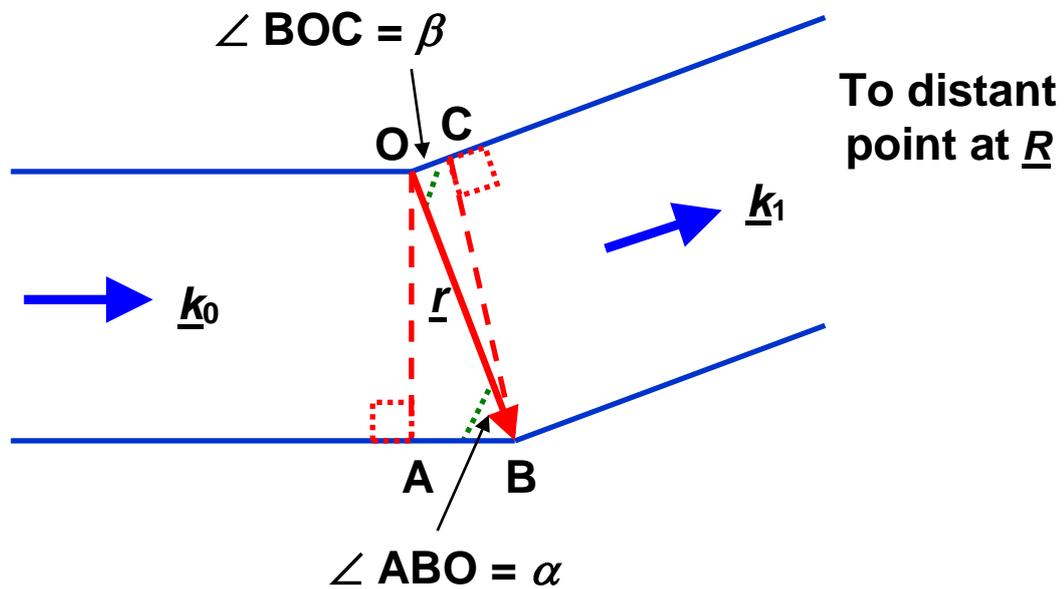
For elastic scattering $|\underline{k}_0| = |\underline{k}_1| = 2\pi/\lambda$. So

$$\begin{aligned} Q^2 &= 2k_0^2(1 - \cos 2\theta) \\ &= 4k_0^2 \sin^2 \theta \end{aligned}$$

or

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

If a **second** particle is at some position \underline{r} : -



$$AB = r \cos \alpha = \underline{r} \cdot \hat{\underline{k}}_0 \quad \hat{\underline{k}}_0 = \frac{\underline{k}_0}{|\underline{k}_0|}$$

$$OC = r \cos \beta = \underline{r} \cdot \hat{\underline{k}}_1 \quad \hat{\underline{k}}_1 = \frac{\underline{k}_1}{|\underline{k}_1|}$$

$$\therefore \text{path difference } AB - OC = \frac{\underline{r} \cdot \underline{k}_0}{|\underline{k}_0|} - \frac{\underline{r} \cdot \underline{k}_1}{|\underline{k}_1|}$$

$$= \frac{\lambda}{2\pi} \underline{r} \cdot \underline{Q} \quad \text{for elastic scattering}$$

$$(\text{phase difference}) = (\text{path difference}) \times 2\pi/\lambda = \underline{r} \cdot \underline{Q} = \underline{Q} \cdot \underline{r}$$

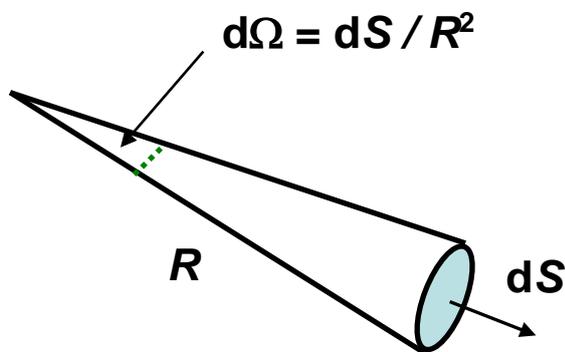
$$\therefore \Phi_{sc} = \frac{\phi_0 a}{R} e^{i(k_1 R + \underline{Q} \cdot \underline{r})} e^{-i\omega_0 t}$$

i.e. **second** particle gives an **additional phase shift** of $\underline{Q} \cdot \underline{r}$

DIFFRACTION FROM AN ASSEMBLY OF PARTICLES

For an **assembly** of point-like scattering centres at positions \underline{r}_i ($i = 1, 2, \dots, N$)

$$\Phi_{sc} = \frac{\phi_0 \mathbf{a}}{R} e^{ik_1 R} e^{-i\omega_0 t} \sum_{i=1}^N e^{i\mathbf{Q} \cdot \underline{r}_i}$$



Hence **intensity** of scattered radiation in detector of area dS at R

$$\propto |\Phi_{sc}|^2 dS = |\Phi_{sc}|^2 R^2 d\Omega$$

Define the **differential scattering cross-section**

$\frac{d\sigma}{d\Omega} \equiv$ (intensity of radⁿ scattered into small solid angle $d\Omega$ in direction of R) /
(intensity of incident radiation $\times d\Omega$)

$$= \frac{|\Phi_{sc}|^2 R^2 d\Omega}{|\Phi_{inc}|^2 d\Omega} = \mathbf{a} \mathbf{a}^* \left| \sum_{i=1}^N e^{i\mathbf{Q} \cdot \underline{r}_i} \right|^2$$

So for a **single** point-like scattering centre at the origin $d\sigma / d\Omega = \mathbf{a} \mathbf{a}^*$: $\sigma = \int d\Omega (d\sigma / d\Omega) = 4\pi |\mathbf{a}|^2$

Note: \mathbf{a} depends on the **nature** of the interaction between the radⁿ and the scattering centre

DENSITY FUNCTIONS & FOURIER TRANSFORMS

Define the **density function**

$$\rho(\underline{r}) \equiv \sum_{i=1}^N \delta(\underline{r} - \underline{r}_i)$$

This eqn describes a set of point delta functions at the positions of the N scattering centres s.t.

$$\int \rho(\underline{r}) d^3 \underline{r} \equiv N$$

Then $d\sigma/d\Omega$ can be re-written in terms of the Fourier transform of $\rho(\underline{r})$

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= aa^* \left| \sum_{i=1}^N e^{i\mathbf{Q} \cdot \underline{r}_i} \right|^2 = aa^* \left| \int d^3 \underline{r} \rho(\underline{r}) e^{i\mathbf{Q} \cdot \underline{r}} \right|^2 \\ &\equiv aa^* NS(\underline{Q}) \end{aligned}$$

The **structure factor** $S(\underline{Q})$ accounts for the effects of interference and depends on the **structure** of the system

Note: The derivation of $d\sigma/d\Omega$ assumes that the scattered wave is not attenuated (**small sample limit**), i.e. there is no beam attenuation and there are no multiple scattering events

SCATTERING CENTRES OF FINITE SIZE

Consider a **single** atom with Z electrons distributed according to the density function $\rho_{\text{at}}(\underline{r})$ about the charge centre as origin. Then

$$\begin{aligned}\frac{d\sigma}{d\Omega} &= aa^* \left| \int d^3\underline{r} \rho_{\text{at}}(\underline{r}) e^{i\underline{Q}\cdot\underline{r}} \right|^2 \\ &\equiv aa^* \left| f(\underline{Q}) \right|^2\end{aligned}$$

which defines the **atomic form factor** $f(\underline{Q})$ as the Fourier transform of $\rho_{\text{at}}(\underline{r})$

If the electron distribution is **spherically symmetric** then $f(\underline{Q}) = f(Q)$ and the integral can be made using spherical polar coordinates: -

$$\begin{aligned}d^3\underline{r} &= r^2 \sin\theta \, dr \, d\theta \, d\phi \\ \underline{Q}\cdot\underline{r} &= Qr \cos\theta\end{aligned}$$

$$\therefore f(Q) = \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi \, e^{iQr \cos\theta} \rho_{\text{at}}(r) r^2 \sin\theta$$

Using $x = \cos\theta$

$$f(Q) = 2\pi \int_0^\infty dr \rho_{\text{at}}(r) r^2 \int_{-1}^1 dx [\cos Qrx + i \sin Qrx]$$

Hence

$$f(Q) = 4\pi \int_0^\infty dr r^2 \rho_{\text{at}}(r) \frac{\sin Qr}{Qr}$$

Limits: $Q \rightarrow 0, f(Q \rightarrow 0) = 4\pi \int_0^\infty dr r^2 \rho_{\text{at}}(r) = Z$
 $Q \rightarrow \infty, f(Q \rightarrow \infty) = 0$

So for a single centre of **finite** size the scattering is **not isotropic**: it is Q -dependent

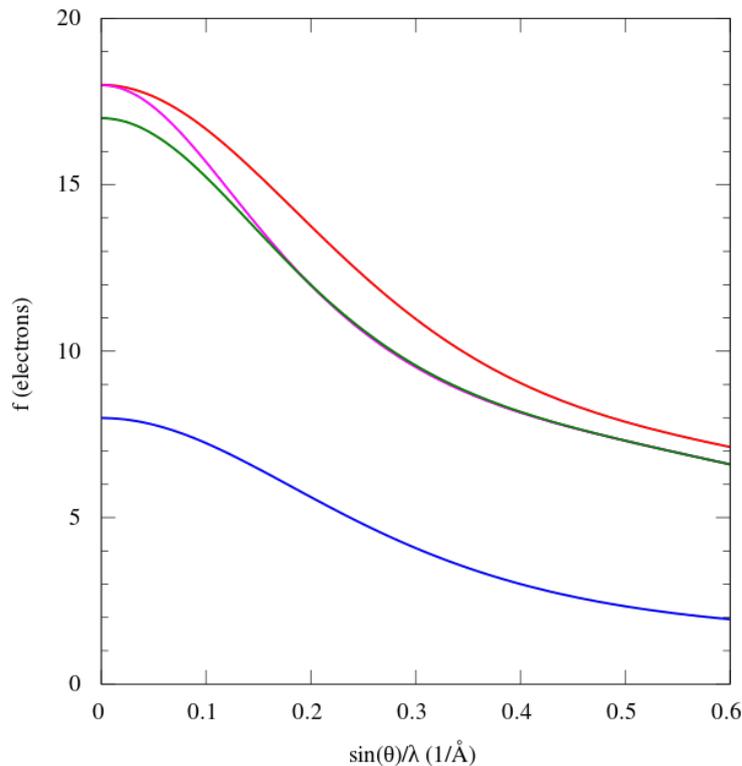
E.g. for X-ray scattering from a single atom or ion

$$\frac{d\sigma}{d\Omega} = r_e^2 |f(Q)|^2$$

r_e = classical radius of an electron

(= 2.8179×10^{-15} m),

and the form factor $f(Q)$ for some selected atoms and ions (in electron units) is given by: -



O: blue (Z = 8)

Cl: green (Z = 17)

Cl⁻: magenta (Z = 18)

K⁺: red (Z = 18)

DIFFRACTION FOR AN ASSEMBLY OF FINITE-SIZED SCATTERING CENTRES

Let the N atoms in the scattering system be arranged with their centres distributed according to the structural density function

$$\rho_{\text{st}}(\underline{r}) \equiv \sum_{i=1}^N \delta(\underline{r} - \underline{r}_i)$$

If the charge-density distribution associated with each atom is $\rho_{\text{at}}(\underline{r})$ then the overall charge density is given by the convolution relation

$$\rho(\underline{r}) = \rho_{\text{at}}(\underline{r}) \otimes \rho_{\text{st}}(\underline{r})$$

By using the convolution theorem it follows that

$$\begin{aligned} \frac{d\sigma}{d\Omega} &= aa^* \left| \int d^3\underline{r} [\rho_{\text{at}}(\underline{r}) \otimes \rho_{\text{st}}(\underline{r})] e^{i\underline{Q} \cdot \underline{r}} \right|^2 \\ &= aa^* f(\underline{Q}) f(\underline{Q})^* N S_{\text{st}}(\underline{Q}) \end{aligned}$$

where $S_{\text{st}}(\underline{Q})$ is the structure factor associated with $\rho_{\text{st}}(\underline{r})$ and does **not** depend on the nature of the scattering process

For an **isotopic** liquid or glass, $\underline{Q} \rightarrow |\underline{Q}|$

Henceforth, we will write $S_{\text{st}}(\underline{Q})$ as $S(Q)$

ELASTIC & INELASTIC SCATTERING

So far we have considered elastic scattering. But scattering events can be either elastic or inelastic

More generally, the measured intensity will depend on both the momentum transfer $\hbar\mathbf{Q}$ and energy transfer $E = \hbar\omega$ for a scattering event. This intensity depends on the **double differential scattering cross-section**

$$I(\mathbf{Q}, E) \propto \frac{1}{N} \frac{d^2\sigma}{d\Omega dE_1} = \frac{\sigma}{4\pi} \frac{k_1}{k_0} S(\mathbf{Q}, E)$$

Incident energy of quantum: E_0

Final energy of quantum: E_1

Energy transfer: $E = E_0 - E_1$

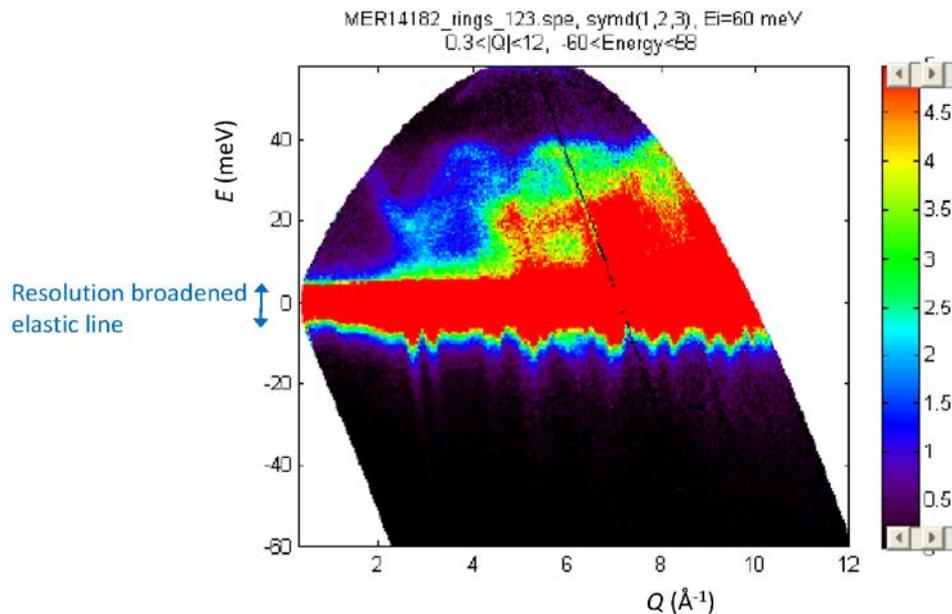
Scattering cross section: σ

(e.g., $\sigma = 4\pi |a|^2$ for point-like scattering centres)

For a **glass**, the **dynamical structure factor** $S(\mathbf{Q}, E)$ will have contributions from both elastic and inelastic (phonon and multi-phonon) scattering

$$S(\mathbf{Q}, E) = S_{\text{el}}(\mathbf{Q})\delta(E) + S_{\text{phonon}}(\mathbf{Q}, E)$$

For example, $I(Q, E)$ for a glass at **low** temperature T



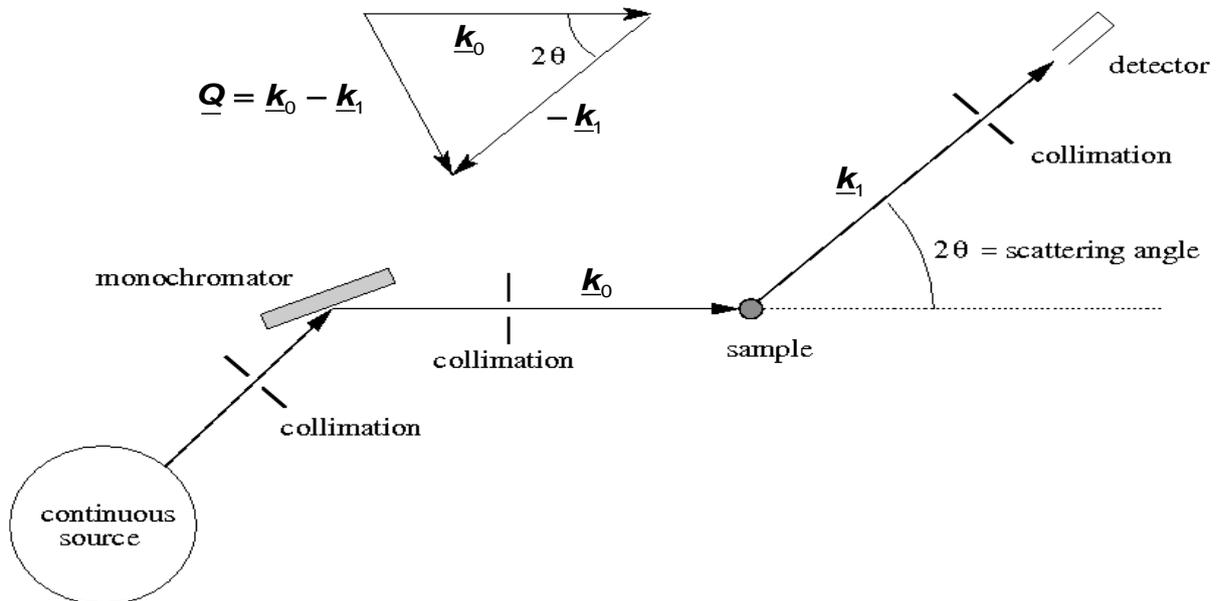
$I(Q, E) \sim 0$ for $E < 0$: Quanta do **not** gain energy from the scattering system (it's too cold!)

$I(Q, E)$ for $E = 0$: Elastic line broadened by resolution function of spectrometer. Signal related to **equilibrium** positions of pairs of scattering centres

$I(Q, E)$ for $E > 0$: finite intensity because quanta can **excite** system states (phonons)

Note: For a **liquid or gas**, there is **no** truly elastic scattering (i.e., there is always some recoil in the scattering event)

POWDER DIFFRACTOMETER



Monochromator uses **Bragg diffraction** to select an incident wavelength λ .

$|\underline{k}_0| = 2\pi/\lambda$, and the incident energy E_0 is fixed

Detector has an **efficiency** $\varepsilon(E_1)$

In the diffraction experiment, the detector integrates $I(Q, E)$ over all energy exchanges E at constant scattering angle 2θ

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{meas}} = \int_{-\infty}^{E_0} dE \varepsilon(E_1) I(Q, E)$$

DIFFERENTIAL SCATTERING CROSS-SECTION: THE STATIC APPROXIMATION

The **static approximation** is usually made to obtain the differential cross-section for the **total** scattering. Here, it is assumed that $E/E_0 \ll 1$ such that $k_0 \simeq k_1$. Then,

$$\begin{aligned} \left. \frac{d\sigma}{d\Omega} \right|_{SA} &= \frac{\sigma}{4\pi} \int_{-\infty}^{E_0} dE \varepsilon(E_1) \frac{k_1}{k_0} S(Q, E) \\ &= \varepsilon(E_0) \frac{\sigma}{4\pi} S(Q) \end{aligned}$$

We can define an **observation timescale** τ_{snapshot} by the time taken for an incident quantum of velocity v to travel one interatomic distance a , i.e.,

$$\tau_{\text{snapshot}} \sim a/v \text{ where } a \sim 10^{-10} \text{ m}$$

The condition $E/E_0 \ll 1$ for validity of the static approximation can be re-written as $\tau_{\text{snapshot}} \ll \tau_{\text{min}}$, where τ_{min} is a **characteristic time** for atomic motion, e.g., the period of atomic vibration in a solid, or the relaxation time in a liquid. Typically

$$\tau_{\text{min}} \sim 10^{-13} - 10^{-12} \text{ s}$$

Hence, the static approximation corresponds to a structure that is relatively **static** on the timescale for a quantum wavepacket to pass from one atom to the next

For X-ray diffraction, the photons travel at the speed of light

$$\tau_{\text{snapshot}} \sim a/c \sim 10^{-18} \text{ s}$$

So the static approximation is **valid**

For neutron diffraction, $v \sim 10^3 \text{ ms}^{-1}$

$$\tau_{\text{snapshot}} \sim a/v \sim 10^{-13} \text{ s}$$

So the static approximation is **not valid**, and **inelasticity** (or **Placzek**) corrections must be applied to the results obtained from neutron diffraction experiments

Within the static approximation, the **measured differential cross-section gives a more-or-less instantaneous or snapshot picture of the structure**

STRUCTURE FACTOR

Neutron diffraction: -

$$\left. \frac{1}{N} \frac{d\sigma}{d\Omega} \right|_{SA} = b_{coh}^2 S(Q) + b_{inc}^2$$

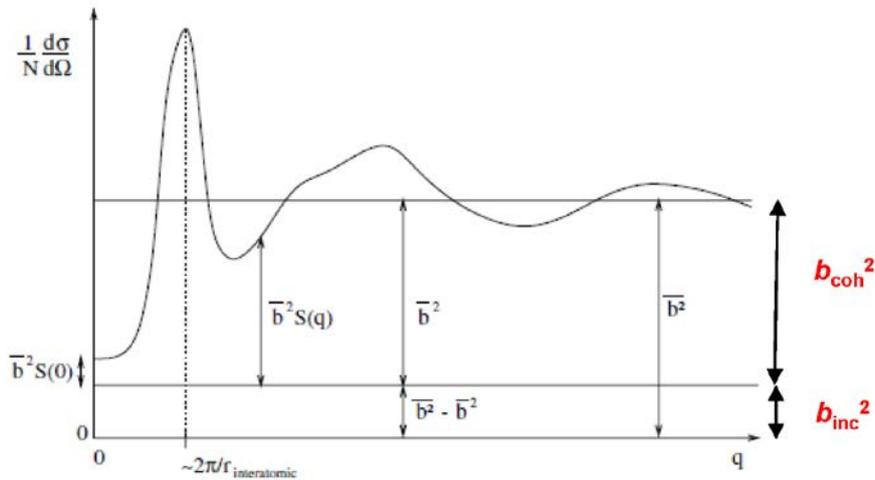
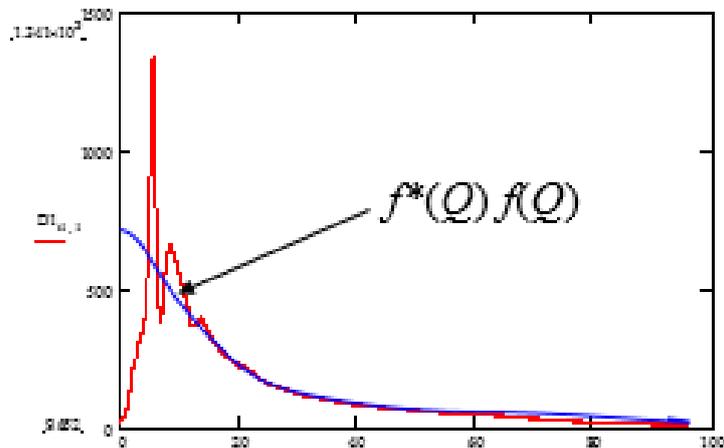


Figure 2. Differential scattering cross-section per atom $(1/N)d\sigma/d\Omega = \bar{b}^2 S(q) + (\bar{b}^2 - \bar{b}^2)$ for a monatomic liquid or glass. The position of the first peak is inversely proportional to the interatomic distance, $r_{interatomic}$.

Spin and isotope incoherence → additional term that does not depend on Q

X-ray diffraction: -

$$\left. \frac{1}{N} \frac{d\sigma}{d\Omega} \right|_{SA} = r_e^2 |f(Q)|^2 S(Q)$$



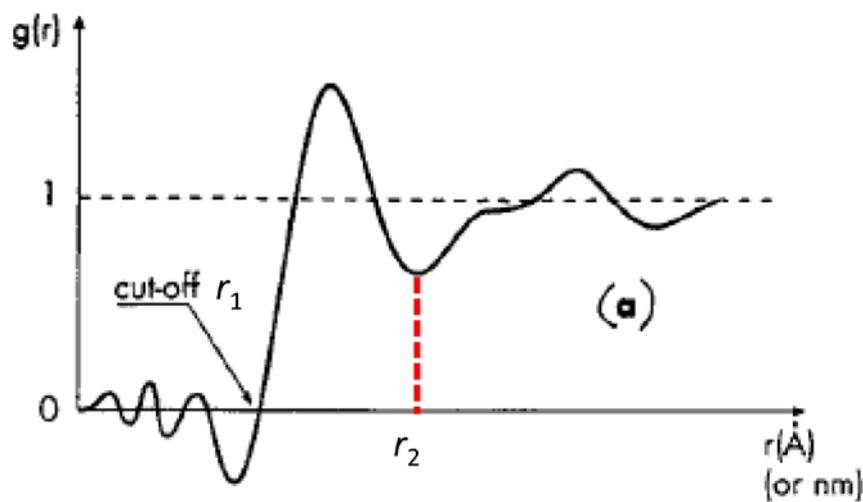
REAL-SPACE STRUCTURE

Subtract the forward scattering.

Fourier transform → the **pair-distribution function**

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho} \int_0^\infty dQ Q [S(Q) - 1] \sin(Qr)$$

where ρ is the atomic number density



$g(r)$ is a measure of the probability of finding two atoms a distance r apart

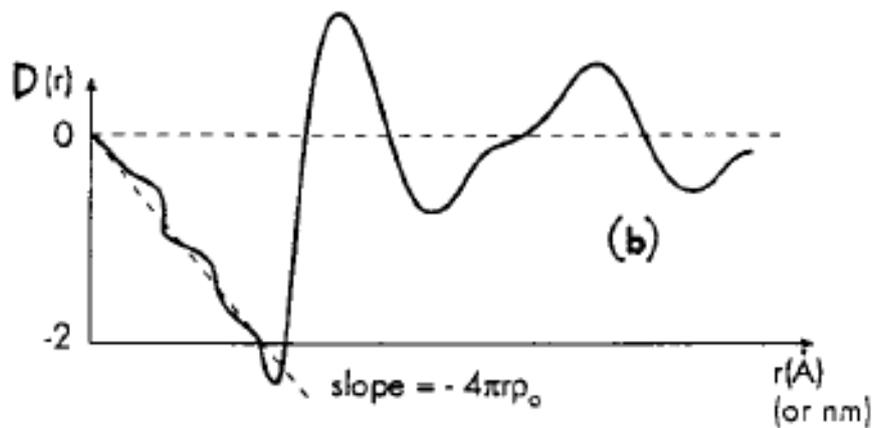
The **coordination number** \bar{n} for the distance range $r_1 \leq r \leq r_2$ is obtained by integration

$$\bar{n} = 4\pi \rho \int_{r_1}^{r_2} dr r^2 g(r)$$

and gives the **average** number of nearest-neighbours about a particle at the origin of coordinates

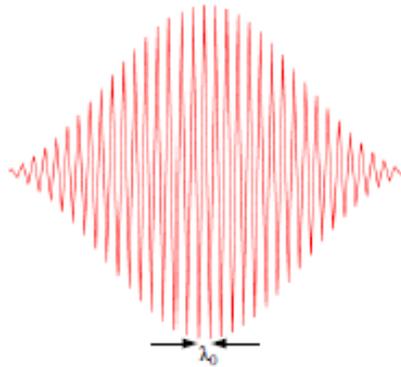
The real-space information can also be expressed in terms of the density function $D(r)$ [often represented as $G(r)$], which is used in **pair-distribution function (PDF)** analyses: -

$$\begin{aligned} \text{PDF}(r) = D(r) = G(r) &= 4\pi \rho r [g(r) - 1] \\ &= \frac{2}{\pi} \int_0^{\infty} dQ Q [S(Q) - 1] \sin(Qr) \end{aligned}$$



HOW IS A DIFFRACTION PATTERN BUILT-UP?

Each incident quantum is not described by a perfect plane wave, but by a wavepacket that is coherent over a finite extent of space, which defines its **coherence volume**



The **size** of the coherence volume is dependent on spread in wavelengths $\Delta\lambda/\lambda$ selected by the monochromator, and by the collimation of the incident and scattered beams, i.e., it depends on the **Q-space resolution** of the diffractometer

The **maximum** real-space structure that can be probed will depend on the size of the coherence volume. Hence, each quantum will probe only **part** of the structure (that within its coherence volume) of a system of **finite** size

A complete diffraction pattern is built-up from a set of scattered quanta, i.e., it represents an **ensemble average** of the snapshot pictures of the structure taken by the quanta over the duration of the diffraction experiment

DATA CORRECTIONS

To obtain an accurate representation of the structure, the differential cross-sections must be placed on an **absolute scale**

Corrections must also be performed carefully: -

Neutrons

- Attenuation
- Multiple scattering
- Placzek (inelasticity)
- Incoherence
- Resolution
- Background
- Furnace/container/pressure cell
- Normalisation (vanadium)
- Dead time

X-rays

- Attenuation
- Multiple scattering
- Compton scattering
- Fluorescence/Resonance Raman
- Resolution
- Background
- Polarization
- Furnace/container/pressure cell
- Normalisation (?)
- Dead time

MULTICOMPONENT SYSTEMS

System of n different chemical species α

c_α = atomic fraction

b_α = coherent scattering length

$b_{\text{inc},\alpha}$ = incoherent scattering length

$f_\alpha(\mathbf{Q})$ = atomic form factor

For **X-ray** diffraction: -

$$\begin{aligned} \left. \frac{1}{r_e^2} \frac{1}{N} \frac{d\sigma}{d\Omega} \right|_{\text{SA}} &= \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} f_{\alpha}(\mathbf{Q}) f_{\beta}^*(\mathbf{Q}) [S_{\alpha\beta}(\mathbf{Q}) - 1] + \sum_{\alpha} c_{\alpha} f_{\alpha}(\mathbf{Q}) f_{\alpha}^*(\mathbf{Q}) \\ &= F_X(\mathbf{Q}) + \sum_{\alpha} c_{\alpha} |f_{\alpha}(\mathbf{Q})|^2 \end{aligned}$$

For **neutron** diffraction: -

$$\begin{aligned} \left. \frac{1}{N} \frac{d\sigma}{d\Omega} \right|_{\text{SA}} &= \sum_{\alpha} \sum_{\beta} c_{\alpha} c_{\beta} b_{\alpha} b_{\beta} [S_{\alpha\beta}(\mathbf{Q}) - 1] + \sum_{\alpha} c_{\alpha} (b_{\alpha}^2 + b_{\text{inc},\alpha}^2) \\ &= F_N(\mathbf{Q}) + \sum_{\alpha} c_{\alpha} (b_{\alpha}^2 + b_{\text{inc},\alpha}^2) \end{aligned}$$

Each **partial structure factor** $S_{\alpha\beta}(\mathbf{Q})$ describes the pair-correlations between atomic species α and β

There are $n(n+1)/2$ different $S_{\alpha\beta}(\mathbf{Q})$ functions, which overlap

For a given material, we want to measure these $S_{\alpha\beta}(Q)$ functions, and Fourier transform to get the **partial pair-distribution functions**

$$g_{\alpha\beta}(r) = 1 + \frac{1}{2\pi^2 r \rho} \int_0^{\infty} dQ Q [S_{\alpha\beta}(Q) - 1] \sin(Qr)$$

The weighting factors for the $S_{\alpha\beta}(Q)$ functions can be changed by altering either b_{α} or $f_{\alpha}(Q)$. The diffraction pattern will **change**, but the structure will remain **unaltered**

Then combine these diffraction patterns to reduce the complexity of correlations associated with a single diffraction pattern

Can change the b_{α} values by using isotope substitution → **neutron diffraction with isotope substitution (NDIS)**

Can change the $f_{\alpha}(Q)$ values by working near to an absorption edge → **anomalous X-ray scattering (AXS)**

NEUTRON DIFFRACTION WITH ISOTOPE SUBSTITUTION (NDIS)

Elements with isotope contrast
(different b_{coh})

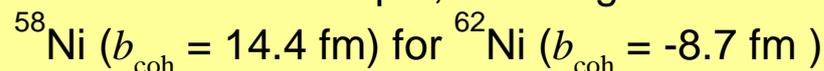
H																		He					
Li	Be																	B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
Fr	Ra																						
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu								
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr								

Green: Good scattering length contrast
Orange: Marginal scattering length contrast
[Blue: anomalous neutron diffraction]

First-difference method

Prepare two samples that are **chemically identical**, but change the isotopic content of one of the elements X.

For example, exchange



Can then eliminate all of the partial structure factors apart from those of the targeted element \rightarrow weighted sum of the $S_{X\beta}(Q)$

Second-difference method

Prepare three or more samples that are chemically identical, but change the isotopic enrichment of one of the elements X.

Can then isolate $S_{XX}(Q)$ for the targeted element

Full partial structure factor analysis

Realistically, only feasible for binary systems.

Prepare $n(n+1)/2$ samples with identical chemical compositions but with different isotopic mixtures.

Solve the scattering matrix to isolate each of the individual partial structure factors.

We will use this method as a case study

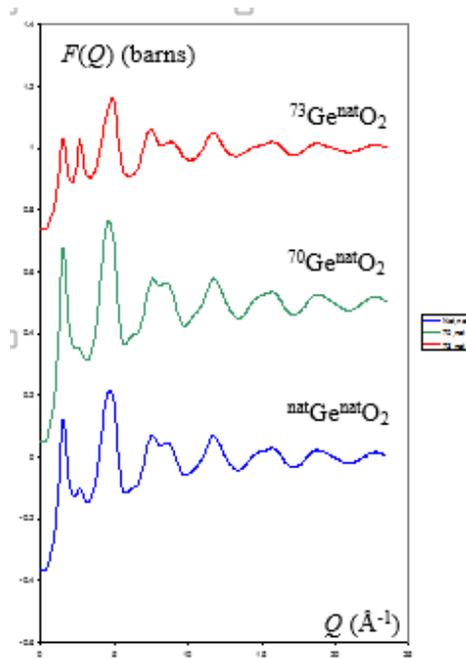
CASE STUDY: GeO₂

For details see Salmon et al. (2007)
J. Phys. Condens. Matter 19 (2007) 415110

Isotope	b (fm)
^{nat} Ge	8.185
⁷⁰ Ge	10.00
⁷³ Ge	5.02
^{nat} O	5.805

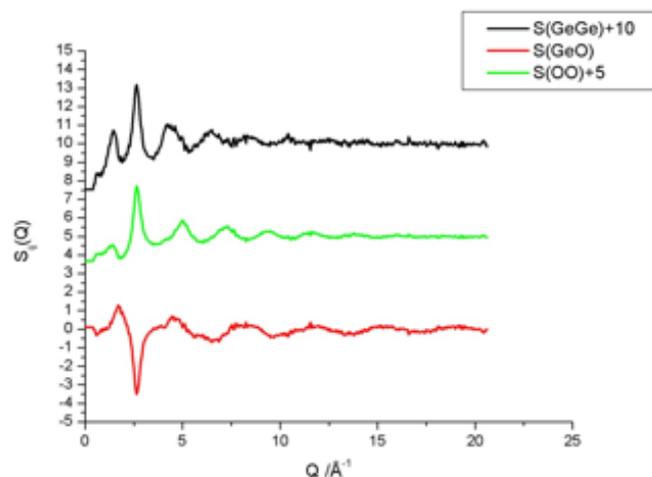
Scattering matrix

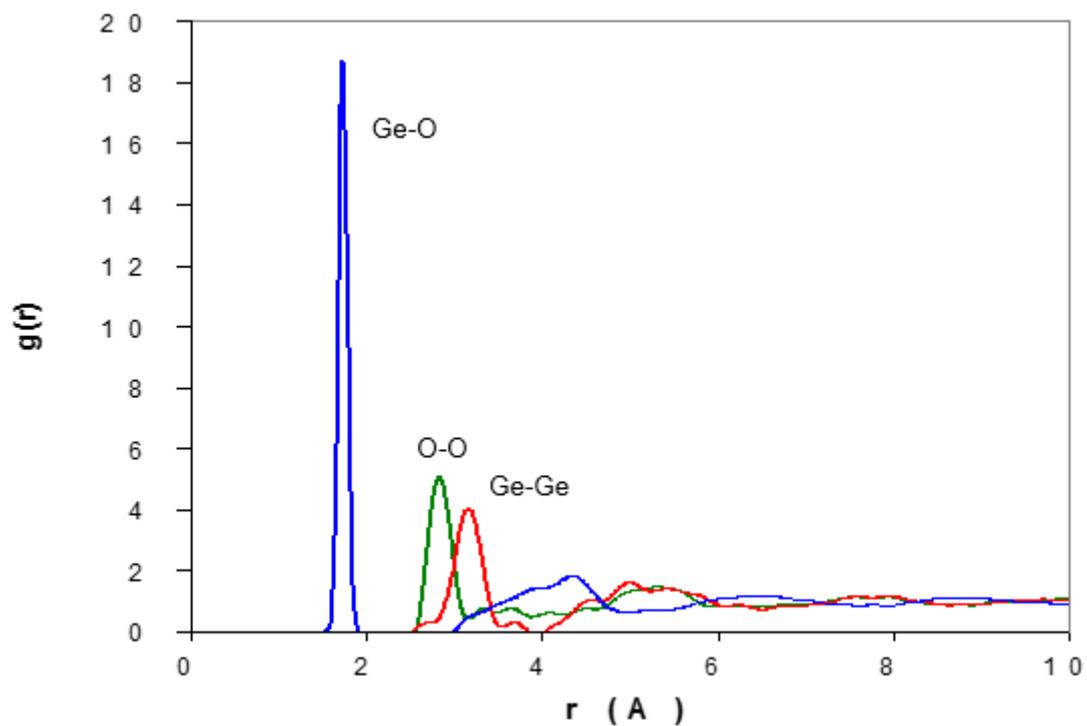
$$\begin{pmatrix} {}^{\text{nat}}F(Q) \\ {}^{\text{nat}}F(Q) \\ {}^{70}\text{nat}F(Q) \\ {}^{73}\text{nat}F(Q) \end{pmatrix} = \begin{pmatrix} 0.074 & 0.150 & 0.211 \\ 0.110 & 0.150 & 0.256 \\ 0.030 & 0.150 & 0.133 \end{pmatrix} \begin{pmatrix} S_{\text{GeGe}}(Q) \\ S_{\text{OO}}(Q) \\ S_{\text{GeO}}(Q) \end{pmatrix}$$



Invert matrix to obtain $S_{\alpha\beta}(Q)$

$$\begin{pmatrix} S_{\text{GeGe}}(Q) \\ S_{\text{GeO}}(Q) \\ S_{\text{OO}}(Q) \end{pmatrix} = \begin{pmatrix} -171 & 108 & 63 \\ -65 & 34 & 38 \\ 111 & -62 & -49 \end{pmatrix} \begin{pmatrix} {}^{\text{nat}}F(Q) \\ {}^{70}\text{nat}F(Q) \\ {}^{73}\text{nat}F(Q) \end{pmatrix}$$



Fourier transform to obtain the $g_{\alpha\beta}(r)$ **Notes**

The multiplicative factors in the inverse matrix are large. So small statistical errors in the data are inflated in the inversion process – most scattering matrices are poorly conditioned

High statistical precision is needed for the total structure factors

Small systematic errors on one or more of the measured total structure factors (e.g. poor normalisation, steps, poor attenuation and/or multiple scattering corrections) will produce large errors in the partial structure factors

High accuracy for the measured total structure factors is essential. Data should be carefully checked for self-consistency using the known density and scattering lengths

ANOMALOUS X-RAY SCATTERING (AXS)

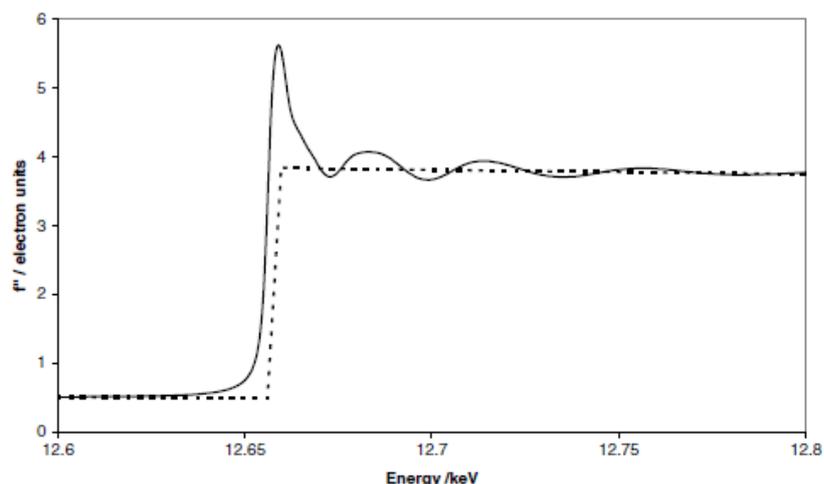
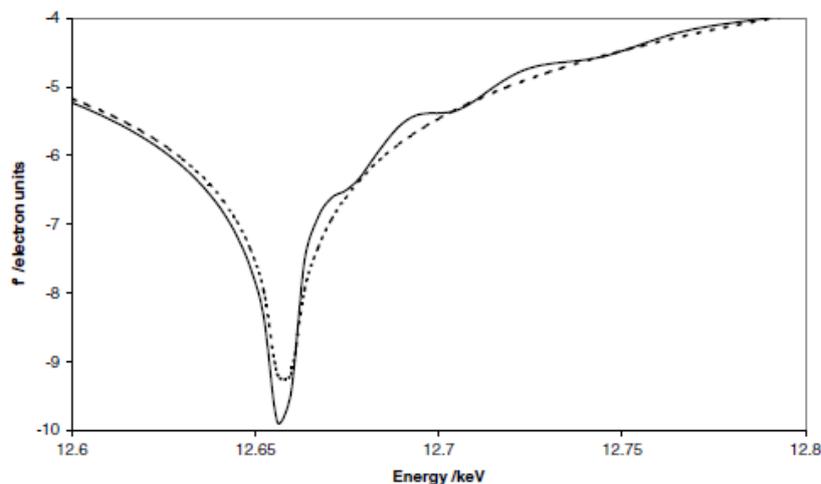
In general, the form factor depends on the scattering vector Q **and** the incident photon energy E_0

$$f_{\alpha}(\mathbf{Q}, E_0) = f_{\alpha}(\mathbf{Q}) + f'_{\alpha}(E_0) + if''_{\alpha}(E_0)$$

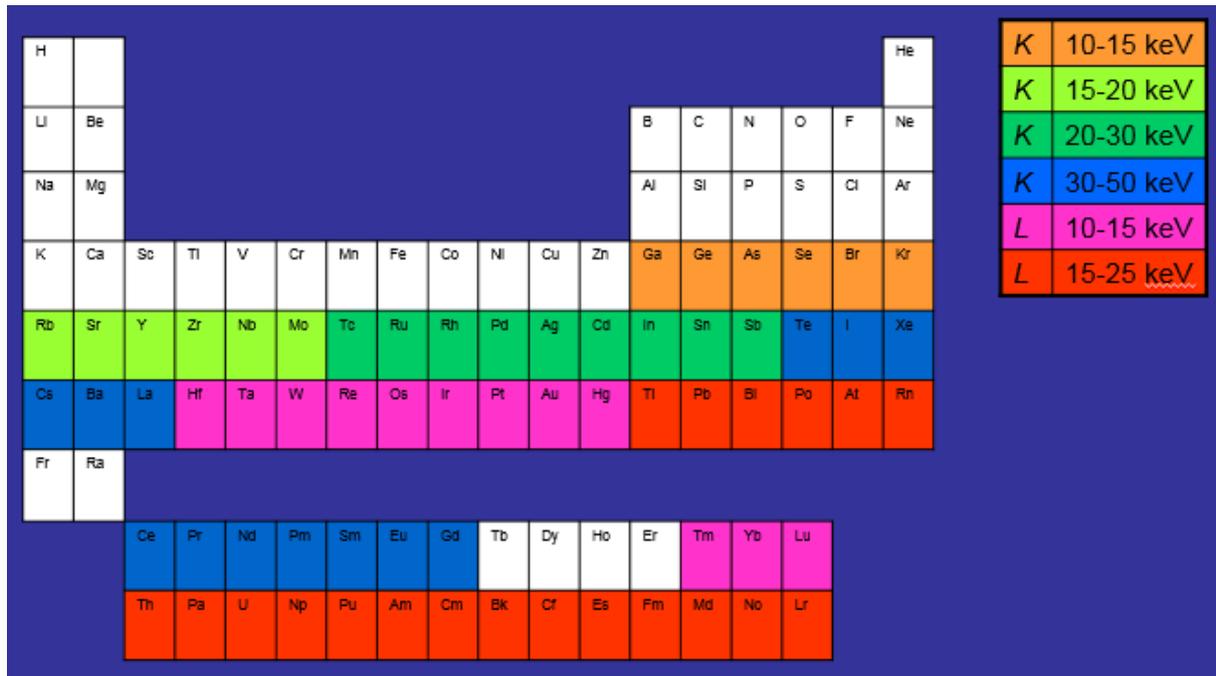
where $f'_{\alpha}(E_0)$ and $f''_{\alpha}(E_0)$ are the real and imaginary parts of the so-called **anomalous dispersion term**

Near an **absorption edge**, $f'_{\alpha}(E_0)$ and $f''_{\alpha}(E_0)$ change with E_0 , the detail of which depends on the chemical environment of the absorbing species

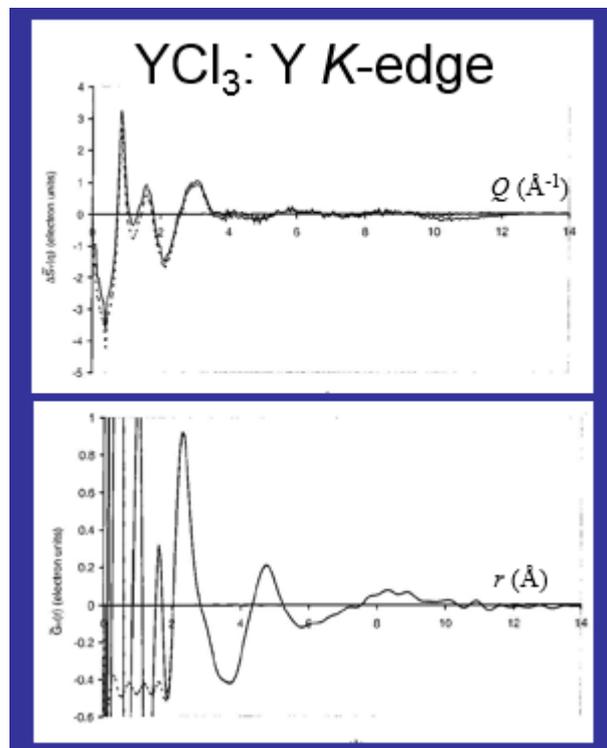
For example, for the *K*-edge of Se: -



Energy ranges for **absorption edges** of the elements



E.g., can probe the coordination environment of Y^{3+} in aqueous solution by using the Y K-edge



The method is challenging: -

- Excellent incident energy resolution (< 1 eV)
- Excellent scattered energy resolution (<100 eV?)
- Need to measure the absorption cross-section to get $f'_\alpha(E_0)$
- Difficulties associated with resonance Raman and subsequent absorption
- Contrast limited to ~10%

SUMMARY AND CONCLUSIONS

Neutron and X-ray diffraction are important tools for elucidating the structure of disordered materials

Experiments require great care, and high counting statistics

Information at the **partial** structure factor level is important for revealing the detail of the structure on a local and intermediate length scale

Methods for obtaining this information include **NDIS** and **AXS** (can also combine x-ray and neutron diffraction)

Results can be used to test the reliability of, e.g., the theoretical scheme used in **molecular dynamics simulations**

Can also use the diffraction results to help build structural models via, e.g., (i) the **reverse Monte Carlo (RMC)** method [McGreevy, J. Phys.: Condens. Matter 13 (2001) R877] or (ii) the **Empirical Potential Structure Refinement (EPSR)** method [Soper, Phys Rev B 72 (2005) 104204]

NOTE: ENERGY OF RADIATION FOR DIFFRACTION STUDIES

1) X-rays

For an x-ray photon $E = h\nu = \frac{hc}{\lambda}$

Exercise: express E in eV and λ in Å (1 Å $\equiv 10^{-10}$ m). Hence show that

$$E(\text{eV}) = 12.4 \times 10^3 / \lambda(\text{Å})$$

2) Neutrons

For a thermal neutron $E = \frac{p^2}{2m_n}$

de Broglie wavelength $\lambda = \frac{h}{p}$

$$\therefore E = \frac{h^2}{2m_n \lambda^2} = \frac{\hbar^2 k^2}{2m_n} \text{ where } k \equiv \frac{2\pi}{\lambda}.$$

Exercise: Show that $E(\text{eV}) = 81.81 \times 10^{-3} / [\lambda(\text{Å})]^2$

3) Electrons

For a non-relativistic electron

$$E = \frac{h^2}{2m_e \lambda^2} = \frac{\hbar^2 k^2}{2m_e}$$

Exercise: Show that $E(\text{eV}) = 150.4 / [\lambda(\text{Å})]^2$

Note: If $\lambda = 1 \text{ \AA}$ energy of neutron is 81.81 meV
cf. 12.4 keV for an x-ray

Energy of neutrons released in nuclear fission $\approx 1 \text{ MeV}$. \therefore to make diffraction experiments require a **reduction** in energy of $\approx 10^7$. This is achieved via inelastic collisions in a moderator material, e.g., a block of graphite at 2000 K. The resultant neutrons have **thermal** energies $\approx k_B T$

Note: X-rays and electrons are scattered by the **electrons** of an atom. Neutrons are scattered by the **nucleus** of an atom, and also by the unpaired electrons of a magnetic atom.

Note: For a thermal neutron, $\lambda \gg$ nuclear dimensions (10^{-15} m) we have **point-like scattering centres** \Rightarrow **isotropic** scattering.