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

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References

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Whittaker D A J et al. *Phys. Rev. B* 98 (2018) 064205

Squires G L *Introduction to the Theory of Thermal Neutron Scattering* CUP, Cambridge, 1978)

Champeney D C *Fourier Transforms and their Physical Applications* (Academic, London, 1973)

DIFFRACTION

- **Fraunhoffer 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)**

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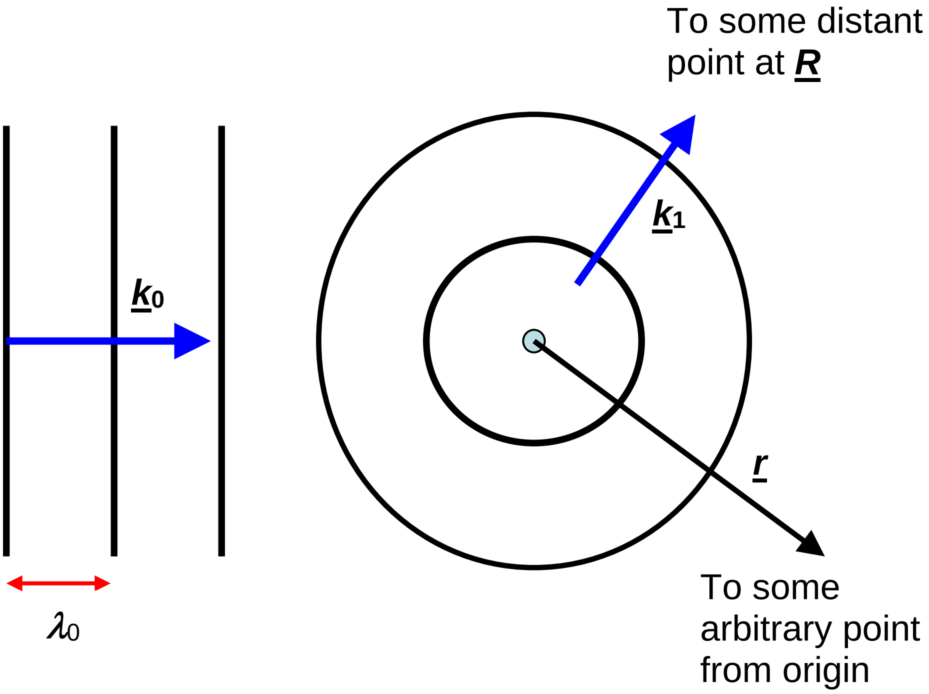
SCATTERING BY A SINGLE PARTICLE

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



Incident plane wave:

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

Scattered spherical wave (∵ λ_0 >> particle diameter)

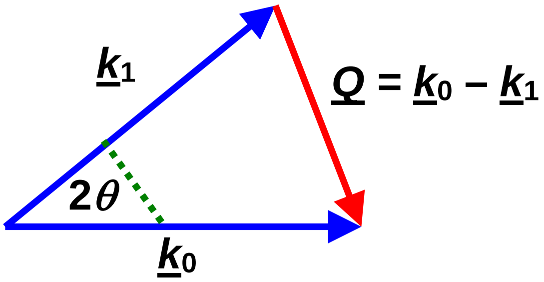
$$\Phi_{sc} = \frac{\phi_0 A}{R} \exp i\left(k_1 R - \omega_0 t + \alpha\right) \equiv \frac{\phi_0 a}{R} e^{ik_1 R} e^{-i\omega_0 t}$$

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



2θ = 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

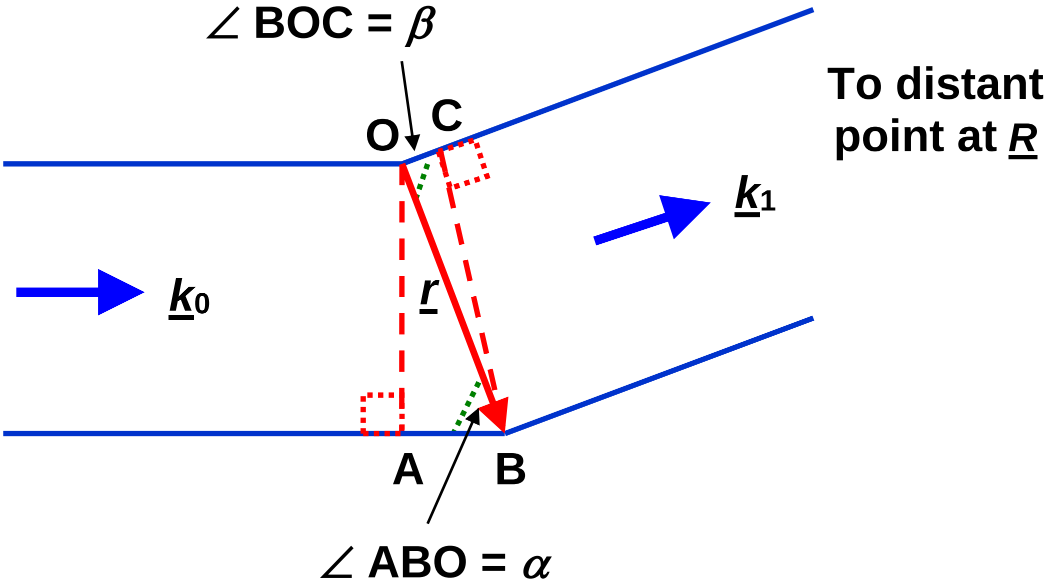
By the cosine rule $Q^2 = k_0^2 + k_1^2 - 2k_0k_1\cos 2\theta$

For elastic scattering $|\underline{k}_0| = |\underline{k}_1| = 2\pi/\lambda_0$. So

$$Q^2 = 2k_0^2(1-\cos 2\theta)$$
$$= 4k_0^2 \sin^2\theta$$

or $$\boxed{Q = \frac{4\pi}{\lambda_0}\sin\theta}$$

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



$$AB = r\cos\alpha = \underline{r} \bullet \hat{\underline{k}}_0 \qquad \hat{\underline{k}}_0 = \frac{\underline{k}_0}{|\underline{k}_0|}$$

$$OC = r\cos\beta = \underline{r} \bullet \hat{\underline{k}}_1 \qquad \hat{\underline{k}}_1 = \frac{\underline{k}_1}{|\underline{k}_1|}$$

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

$$= \frac{\lambda_0}{2\pi} \underline{r} \bullet \underline{Q} \qquad \text{for elastic scattering}$$

(phase difference) = (path difference) x $2\pi/\lambda_0 = \underline{r} \bullet \underline{Q} = \underline{Q} \bullet \underline{r}$

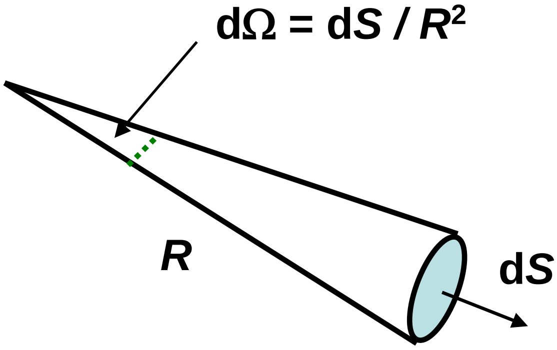
$$\therefore \Phi_{sc} = \frac{\phi_0 a}{R} e^{i(k_1 R + \underline{Q} \bullet \underline{r})} e^{-i\omega_0 t}$$

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

DIFFRACTION FROM AN ASSEMBLY OF PARTICLES

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

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



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

$$\frac{d\sigma}{d\Omega} \equiv \text{(intensity of rad}^{n}\text{ scattered into small solid angle } d\Omega \text{ in direction of } R) \,/\, \text{(intensity of incident radiation x } d\Omega)$$

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

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

Note: a depends on the nature of the interaction between the rad^n and the scattering centre

DENSITY FUNCTIONS & FOURIER TRANSFORMS

Define the density function

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

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

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

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

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = aa^* \left| \sum_{i=1}^{N} e^{i\underline{Q}\bullet\underline{r}_i} \right|^2 = aa^* \left| \int \mathrm{d}^3\underline{r}\; \rho(\underline{r}) e^{i\underline{Q}\bullet\underline{r}} \right|^2$$

$$\equiv aa^* N S(\underline{Q})$$

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

Note: The derivation of $\mathrm{d}\sigma/\mathrm{d}\Omega$ 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

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = aa^* \left| \int \mathrm{d}^3\underline{r}\, \rho_{\text{at}}(\underline{r}) e^{i\underline{Q}\bullet\underline{r}} \right|^2$$

$$\equiv aa^* \left| f(\underline{Q}) \right|^2$$

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: -

$$\mathrm{d}^3\underline{r} = r^2 \sin\theta\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\phi$$

$$\underline{Q} \bullet \underline{r} = Q\, r \cos\theta$$

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

Using $x = \cos\theta$

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

Hence

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

Limits: $Q \to 0,\ f(Q \to 0) = 4\pi \int_0^\infty \mathrm{d}r\, r^2 \rho_{at}(r) = Z$

$$Q \to \infty,\ f(Q \to \infty) = 0$$

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

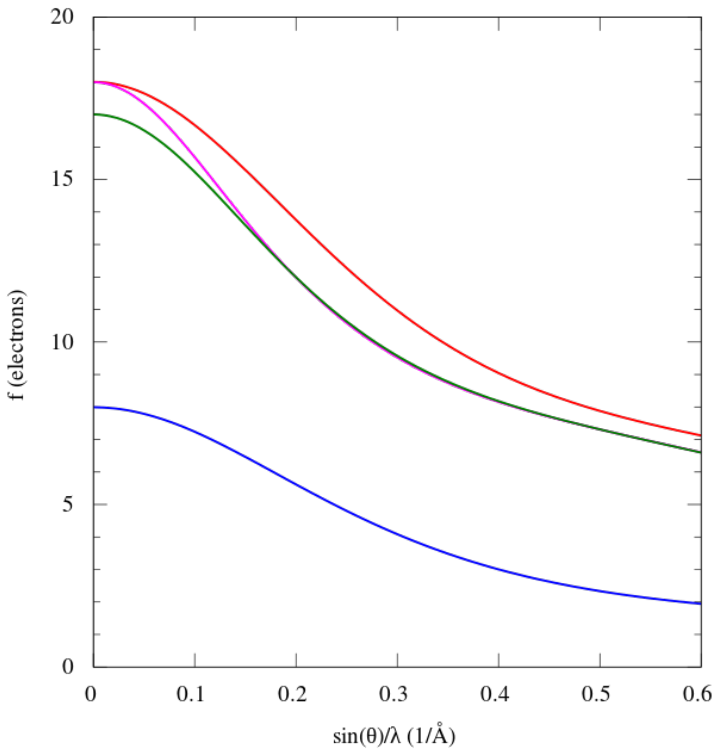
E.g. for x-ray scattering from a single atom or ion

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

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

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

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

$$\rho\left(\underline{r}\right) = \rho_{\mathrm{at}}\left(\underline{r}\right) \otimes \rho_{\mathrm{st}}\left(\underline{r}\right)$$

By using the convolution theorem, it follows that

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

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

For an isotropic liquid or glass, $\underline{Q} \rightarrow \left|\underline{Q}\right|$

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

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 $\hbar Q$ and energy transfer $E = \hbar\omega$ for a scattering event and can be written in terms of the double differential scattering cross-section $\mathrm{d}^2\sigma/\mathrm{d}\Omega\mathrm{d}E_1$, i.e.,

$$I(Q,E) \propto \frac{1}{N}\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E_1} = \frac{\sigma}{4\pi}\frac{k_1}{k_0}S(Q,E)$$

Incident energy of quantum: E_0

Final energy of quantum: E_1

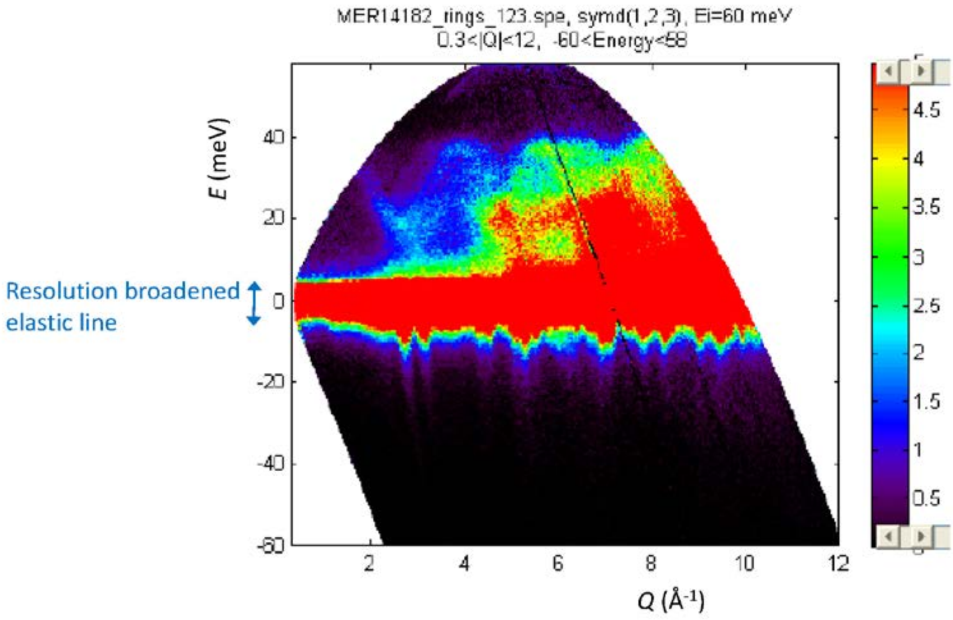
Energy transfer: $E = E_0 - E_1$

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

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

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

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



Resolution broadened elastic line

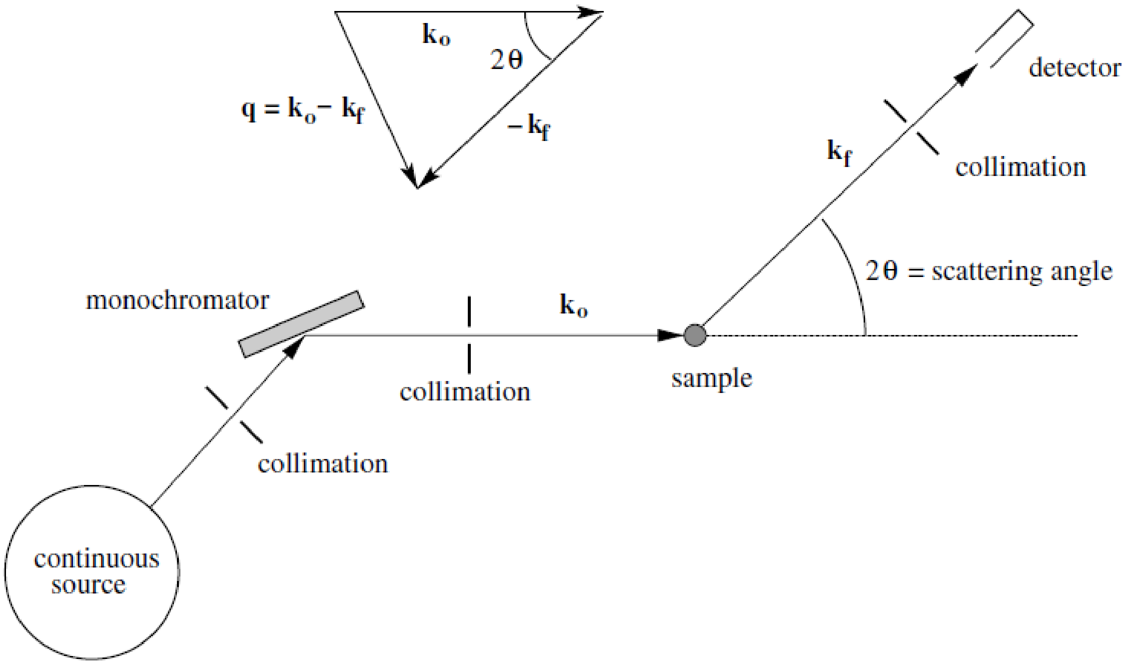
$I(Q,E)$ ~ 0 for $E < 0$: Quanta do not gain energy from the scattering system (it's too cold!)

$I(Q,E)$ 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: there is always some recoil in the scattering event

POWDER DIFFRACTOMETER



Monochromator uses Bragg diffraction to select an incident wavelength λ_0

$|\underline{k}_0| = 2\pi/\lambda_0$, and the incident energy E_0 is fixed

Detector has an efficiency $\varepsilon(E_1)$

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

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

The upper limit could be extended to infinity provided $E_0 >> E \Rightarrow$ incident energy of a quantum is large compared to the max^{m} energy of an excitation in the system

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 $E_0 >> E$ or $E/E_0 = 1 - E_1/E_0 << 1$ which requires $E_0 \approx E_1$

In neutron scattering, $E_0 = \hbar^2 k_0^2 / 2m_n$ and $E_1 = \hbar^2 k_1^2 / 2m_n$ (m_n is the neutron mass), so $k_0 \approx k_1$

In x-ray scattering, $E_0 = hc/\lambda_0 = \hbar k_0 c$ and $E_1 = hc/\lambda_1 = \hbar k_1 c$ (c is the speed of light), so $k_0 \approx k_1$

Hence,

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

$$= \varepsilon(E_0)\frac{\sigma}{4\pi}S(Q)$$

The approximation requires $E_0 >> \hbar\omega_{\text{max}}$ where $\hbar\omega_{\text{max}}$ is the maximum energy of an excitation. The energy corresponds to a characteristic timescale for atomic motion: $\omega_{\text{max}} = 2\pi f_{max} \approx \tau_{\text{min}}^{-1}$ where τ_{min} is the shortest period of atomic vibration in a solid or the shortest relaxation time for a disturbance in a liquid

We are considering the scattering from pairs of particles, which will occur on a characteristic "snapshot" timescale τ_{snapshot} given by the time for an incident quantum of velocity v_0 to travel one interatomic distance *a*, i.e., $\tau_{\text{snapshot}} \approx a/v_0 \approx (a/\lambda_0)\omega_0^{-1}$ where $a \approx 10^{-10}$ m

$[E_0 = \hbar\omega_0 = mv_0^2/2 = \hbar k_0 v_0/2 = \pi\hbar v_0/\lambda_0]$

In diffraction experiments λ_0 is generally of the order *a*, so $\omega_0 \approx \tau_{\text{snapshot}}^{-1}$

The condition $E_0 = \hbar\omega_0 >> \hbar\omega_{\max}$ for validity of the static approximation can therefore be re-written as $\tau_{\text{snapshot}} \ll \tau_{\min}$. Typically, $\tau_{\min} \approx 10^{-13} - 10^{-12}$ 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

The measured differential scattering cross-section $d\sigma/d\Omega|_{SA}$ gives the average of more-or-less instantaneous or snapshot pictures of the structure

In x-ray diffraction, the photons travel at the speed of light

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

So, the static approximation is valid

In neutron diffraction, $v_0 \approx 10^3\ \mathrm{m\,s^{-1}}$

$$\tau_{\text{snapshot}} \approx a/v_0 \approx 10^{-13}\,\mathrm{s}$$

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

For a liquid the scattering is inelastic and it is necessary to employ the static approximation to extract *S*(*Q*) from the measured intensity

For a solid both elastic and inelastic scattering will occur and the detector will sum both contributions.

Note: In the absence of diffusion, the atoms in a solid will vibrate about fixed positions. For a glass, the cross-section for elastic scattering $d\sigma/d\Omega|_{\text{elastic}}$ differs from $d\sigma/d\Omega|_{\text{SA}}$ by the appearance of Debye-Waller factors in the self-scattering terms [Whittaker et al. 2018]

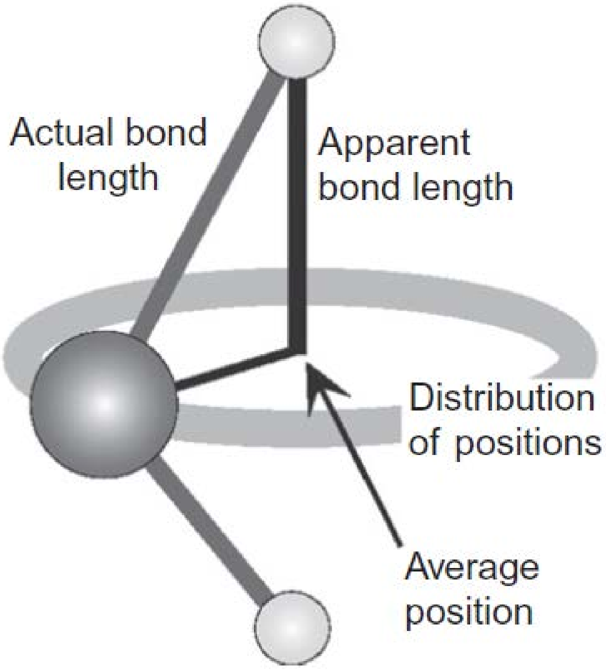
TOTAL VERSUS ELASTIC SCATTERING

In Bragg scattering from a crystal, only elastic scattering is observed

From the Heisenberg Uncertainty principle $\Delta E\tau_{\text{elastic}} \geq \hbar/2$, the characteristic timescale τ_{elastic} is expected to be infinite. So, $d\sigma/d\Omega|_{\text{elastic}}$ will give a time averaged picture of the atomic positions

In total scattering experiments, the measured differential cross section will contain information from a series of "instantaneous" snapshots

The bond lengths measured by Bragg and total scattering can be different as in the case of α-quartz



Tucker et al. 2000 J Phys: Condens Matter **12** L425

Rotation leads to an apparent Si-O bond length from Bragg scattering that is shorter than the actual Si-O bond length measured by total scattering

STRUCTURE FACTOR

Neutron diffraction: -

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

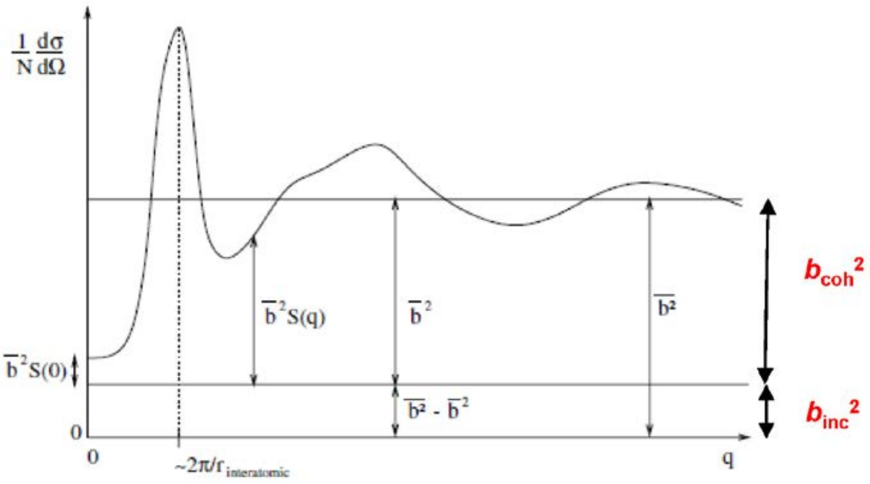
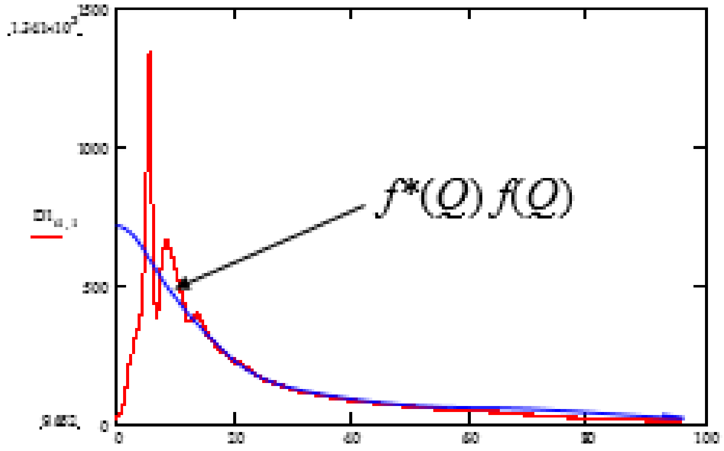


Figure 2. Differential scattering cross-section per atom $(1/N)d\sigma/d\Omega = \bar{b}^2 S(q) + (\overline{b^2} - \bar{b}^2)$ for a monatomic liquid or glass. The position of the first peak is inversely proportional to the interatomic distance, $r_{\text{interatomic}}$.

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

X-ray diffraction: -

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

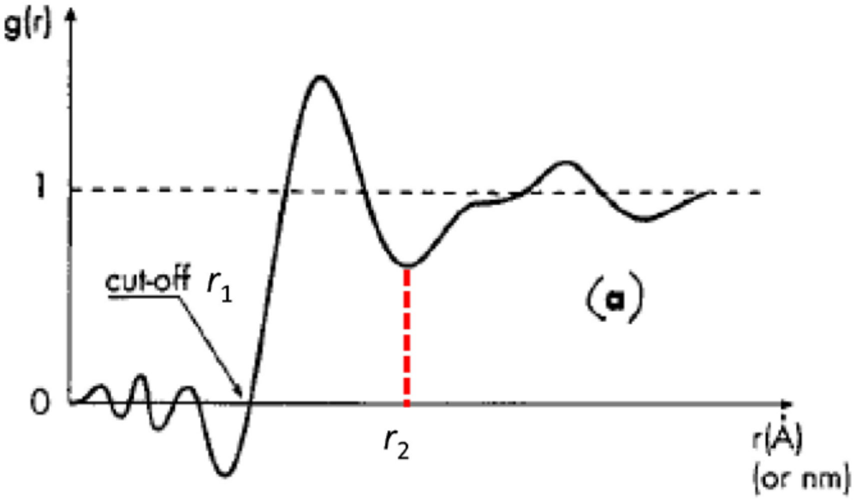


REAL-SPACE STRUCTURE

Subtract the forward scattering.
Fourier transform → the pair-distribution function

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

where ρ is the atomic number density



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

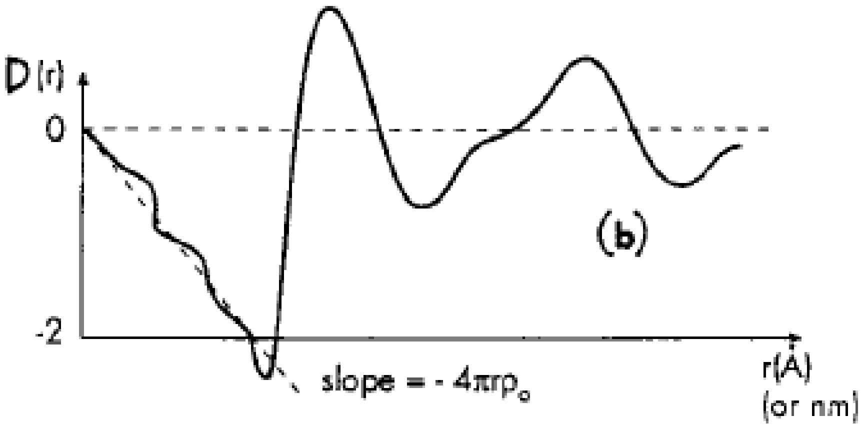
The coordination number $\bar{n}$ for the distance range $r_1 \le r \le r_2$ is obtained by integration

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

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

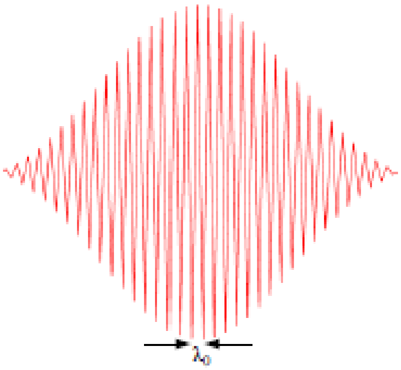
The real-space information can also be expressed in terms of the density function $D(r)$ [often denoted by $G(r)$], which is used in pair-distribution function (PDF) analyses: -

$$\mathbf{PDF}(r) = D(r) = G(r) = 4\pi\rho r\left[g(r)-1\right] \\ = \frac{2}{\pi}\int_0^\infty dQ\,Q\left[S(Q)-1\right]\sin(Qr)$$



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 $\Delta\lambda/\lambda_0$ 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. In general, each quantum will therefore 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
$f_\alpha(Q)$ = atomic form factor

For x-ray diffraction: -

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

For neutron diffraction: -

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

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

There are $n(n+1)/2$ different $S_{\alpha\beta}(Q)$ 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

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

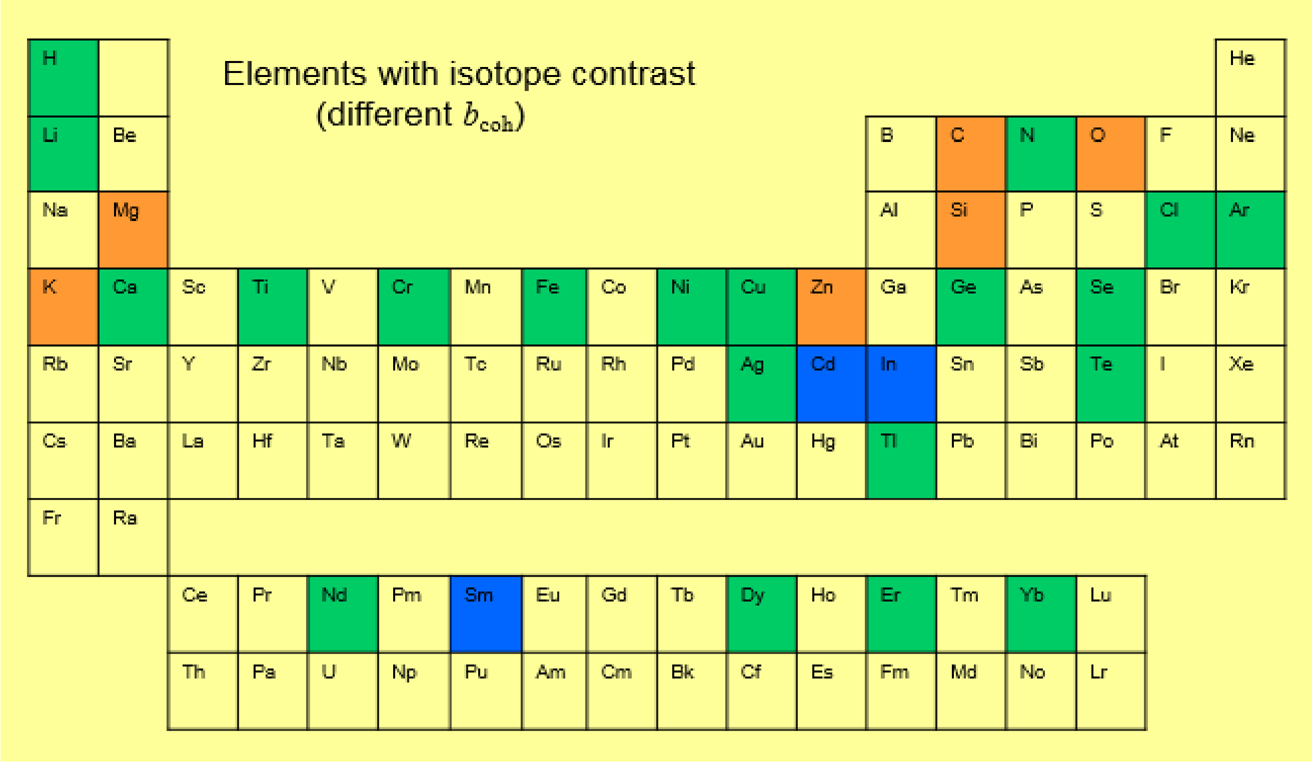
The weighting factors for the $S_{\alpha\beta}(Q)$ functions can be changed by altering either b_α or $f_\alpha(Q)$. The diffraction pattern will change, but the structure will remain unaltered

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
^{58}Ni (b_{coh} = 14.4 fm) for ^{62}Ni (b_{coh} = -8.7 fm)
Can then eliminate all the partial structure factors apart from those of the targeted element → 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

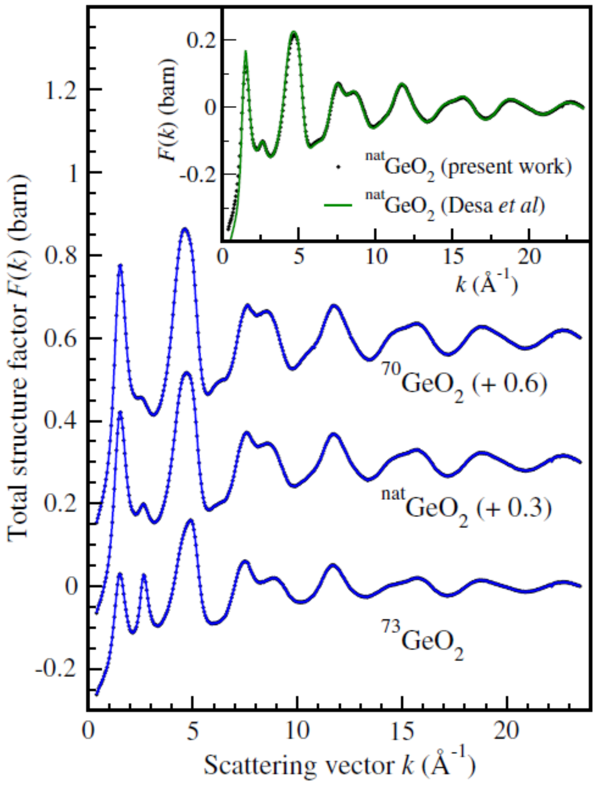
CASE STUDY: Glassy GeO_2

For details see Salmon et al. 2007
J. Phys.: Condens. Matter **19** 415110

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

Scattering matrix

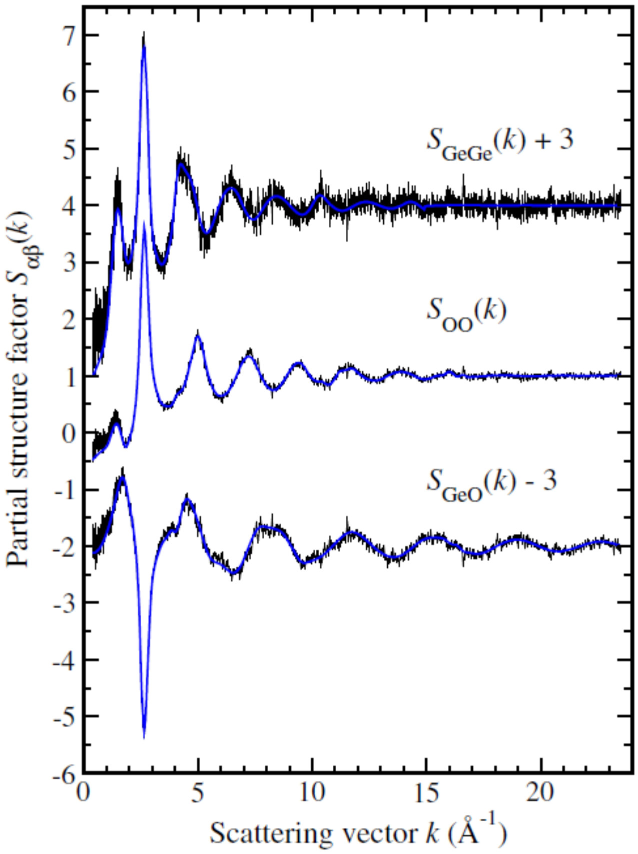
$$\begin{pmatrix} {}^{\text{nat}}_{\text{nat}}F(k) \\ {}^{70}_{\text{nat}}F(k) \\ {}^{73}_{\text{nat}}F(k) \end{pmatrix} = \begin{pmatrix} 0.074 & 0.150 & 0.211 \\ 0.110 & 0.150 & 0.256 \\ 0.030 & 0.150 & 0.133 \end{pmatrix} \begin{pmatrix} S_{\text{GeGe}}(k) \\ S_{\text{OO}}(k) \\ S_{\text{GeO}}(k)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



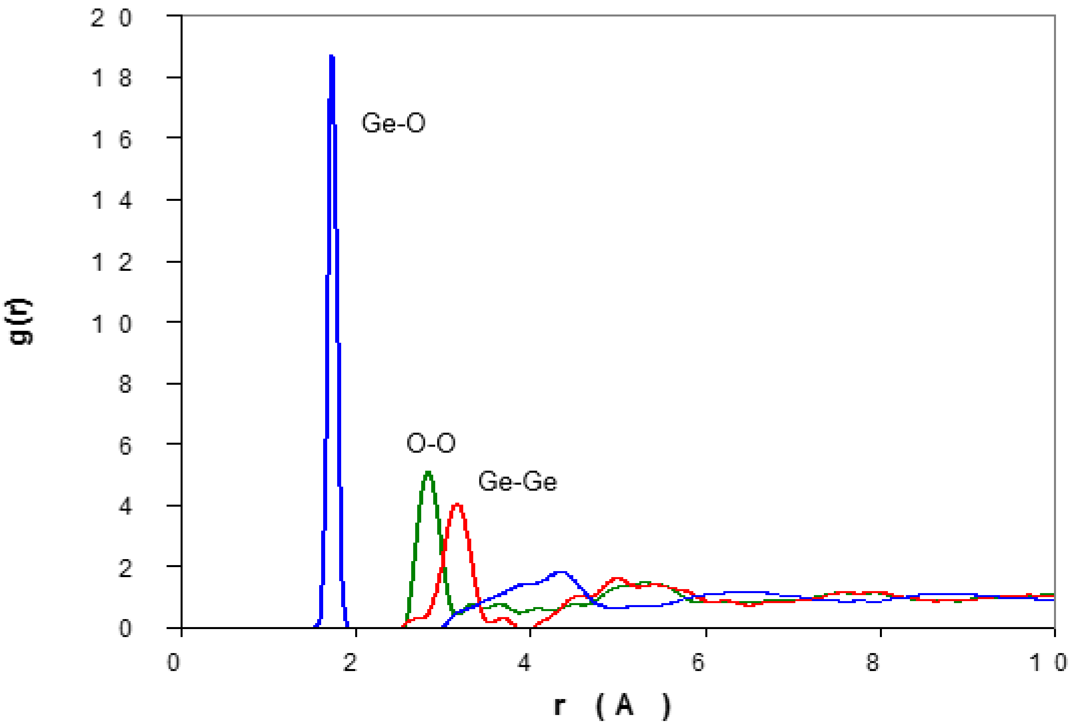
Note the change in notation: *k* is now the scattering vector

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

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



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)

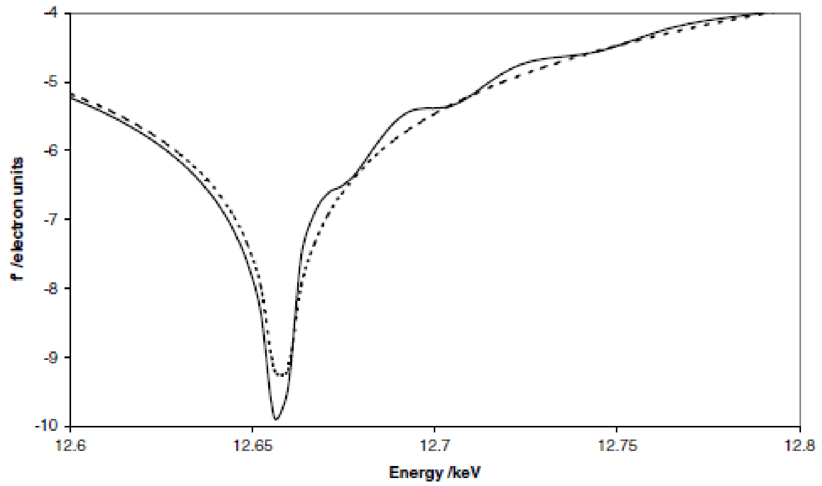
In general, the form factor depends on the scattering vector Q *and* the incident photon energy E_0

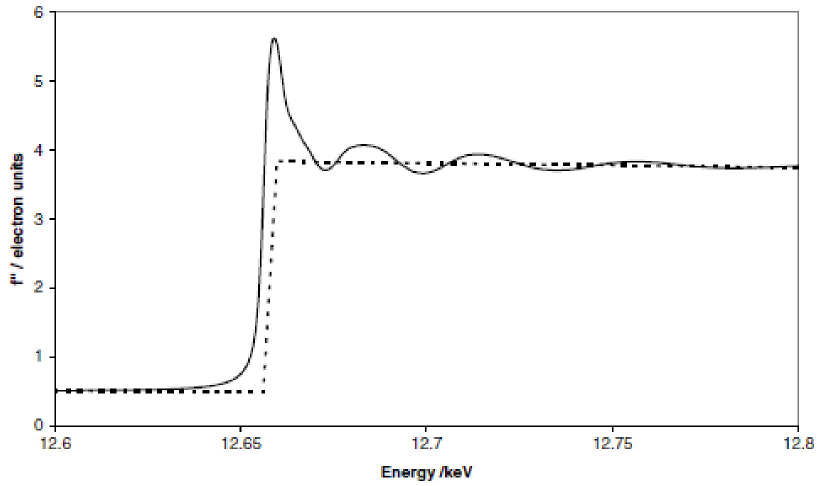
$$f_\alpha(Q,E_0) = f_\alpha(Q) + f'_\alpha(E_0) + if''_\alpha(E_0)$$

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

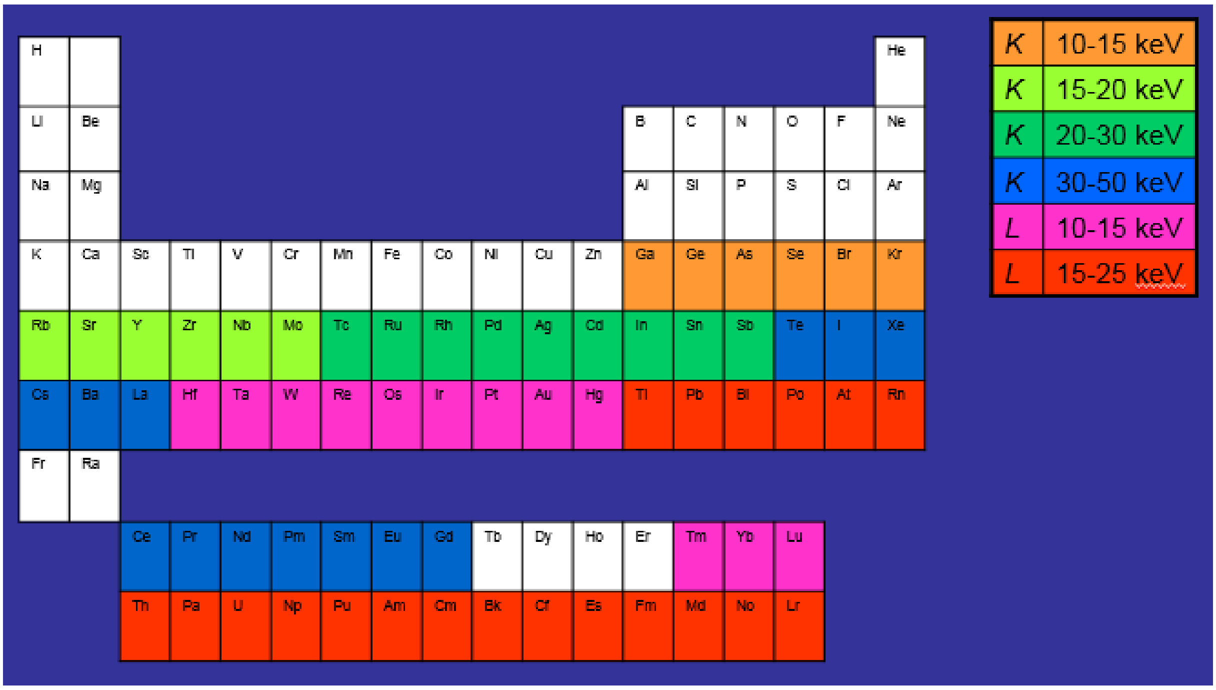
Near an absorption edge, $f'_\alpha(E_0)$ and $f''_\alpha(E_0)$ change with E_0, the detail of which depends on the chemical environment of the absorbing species

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



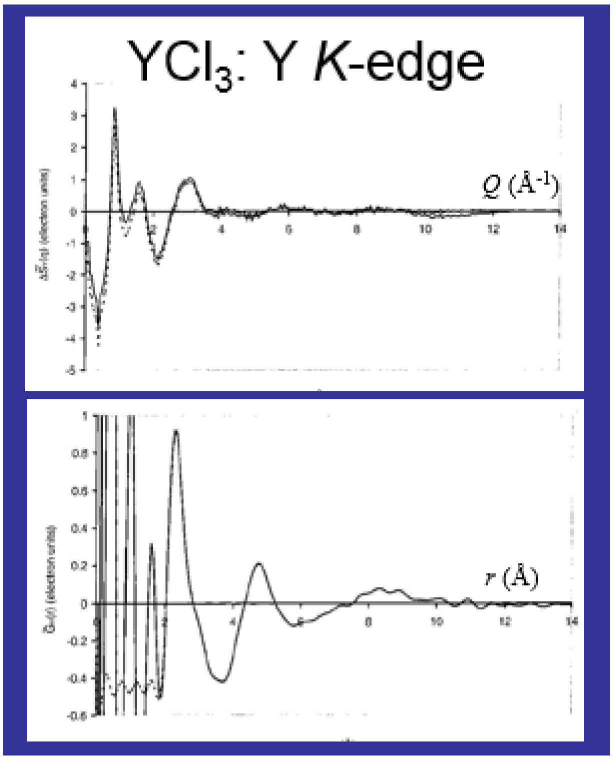


Energy ranges for absorption edges of the elements



K	10-15 keV
K	15-20 keV
K	20-30 keV
K	30-50 keV
L	10-15 keV
L	15-25 keV

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]

NO ELASTIC SCATTERING FROM A LIQUID

For coherent elastic scattering (Squires 1978)

$$\frac{1}{N}\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E_1}\right)_{\mathrm{cohel}} = \frac{\sigma_{\mathrm{coh}}}{4\pi}\frac{k_1}{k_0}\delta(E)I(Q,t\to\infty)$$

where N is the number of atoms, σ_{coh} is the coherent scattering cross-section, the intermediate scattering function in the limit as time $t\to\infty$ is given by the Fourier transform

$$I(Q,t\to\infty)=\int \mathrm{d}\underline{r}\; G(r,t\to\infty)\exp\left(i\underline{Q}\bullet\underline{r}\right)$$

and the van Hove correlation function in this limit is given by

$$G(r,t\to\infty)=\frac{1}{N}\int \mathrm{d}\underline{r}'\left\langle\rho\left(\underline{r}'\right)\right\rangle\left\langle\rho\left(\underline{r}'+\underline{r}\right)\right\rangle$$

The average density of a liquid is uniform, i.e.,

$$\left\langle\rho\left(\underline{r}\right)\right\rangle=\rho=\frac{N}{V}$$

where V is the volume. Hence

$$G(r,t\to\infty)=\frac{1}{N}\rho^2V=\rho$$

So,

$$I(Q,t\to\infty)=\rho\int \mathrm{d}\underline{r}\;\exp\left(i\underline{Q}\bullet\underline{r}\right)\propto\delta\left(\underline{Q}\right)$$

The Dirac delta function ensures that elastic scattering only occurs for $\underline{Q} = 0$. This corresponds to incident neutrons transmitted in the forward direction and does not, therefore, correspond to scattering at all

The same result applies to incoherent neutron scattering

So, there is no elastic scattering, coherent or incoherent, from a liquid!

Note: In the static approximation, the coherent differential scattering cross section is proportional to the Fourier transform of the van Hove correlation function $G(r, t = 0)$

NOTE: ENERGY OF RADIATION FOR DIFFRACTION STUDIES

1) X-rays

For an x-ray photon $E_0 = hf_0 = \dfrac{hc}{\lambda_0}$

Exercise: express E_0 in eV and λ_0 in Å (1 Å ≡ 10^{-10} m). Hence show that

$$E_0(\text{eV}) = 12.4\text{x}10^3/\ \lambda_0(\text{Å})$$

2) Neutrons

For a thermal neutron $E_0 = \dfrac{p_0^2}{2m_n}$

de Broglie wavelength $\lambda_0 = \dfrac{h}{p_0}$

$$\therefore\ E_0 = \frac{h^2}{2m_n\lambda_0^2} = \frac{\hbar^2 k_0^2}{2m_n} \text{ where } k_0 \equiv \frac{2\pi}{\lambda_0}.$$

Exercise: Show that $E_0(\text{eV}) = 81.81\text{x}10^{-3}/[\lambda_0(\text{Å})]^2$

3) Electrons

For a non-relativistic electron

$$E_0 = \frac{h^2}{2m_e\lambda_0^2} = \frac{\hbar^2 k_0^2}{2m_e}$$

Exercise: Show that $E_0(\text{eV}) = 150.4/[\lambda_0(\text{Å})]^2$

Note: If λ_0 = 1 Å energy of neutron is 81.81 meV cf. 12.4 keV for an x-ray

Energy of neutrons released in nuclear fission ≈ 1 MeV. ∴ to make diffraction experiments require a reduction in energy of ≈ 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 ≈ $k_B T$

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, λ_0 >> nuclear dimensions (10^{-15} m) we have point-like scattering centres ⇒ isotropic scattering.