First Elements of Thermal Neutron Scattering Theory (I)

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Talk outlines

- 0) Introduction.
- 1) Neutron scattering from nuclei.
- 2) Time-correlation functions.
- 3) Inelastic scattering from crystals.
- 4) Inelastic scattering from fluids (intro).
- 5) Vibrational spectroscopy from molecules.
- 6) Incoherent inelastic scattering from molecular crystals.
- 7) Some applications to soft matter.

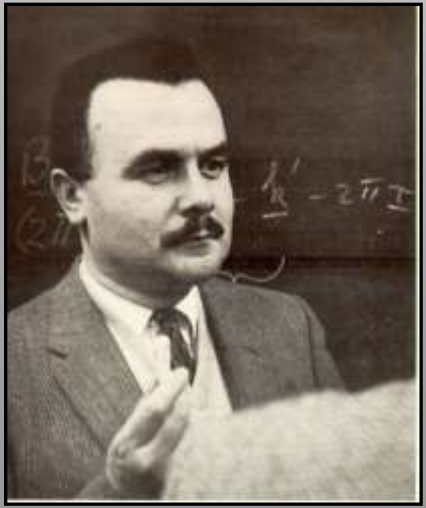
0) Introduction

Why neutron scattering (NS) from condensed matter?

Nowadays NS is relevant in physics, material science, chemistry, geology, biology, engineering etc., being highly complementary to X-ray scattering.

E. Fermi

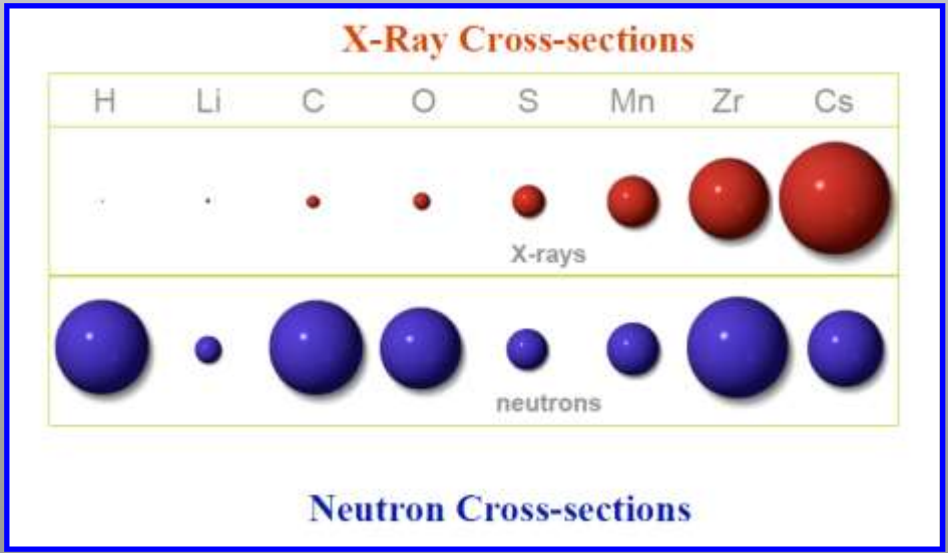
C. G. Shull



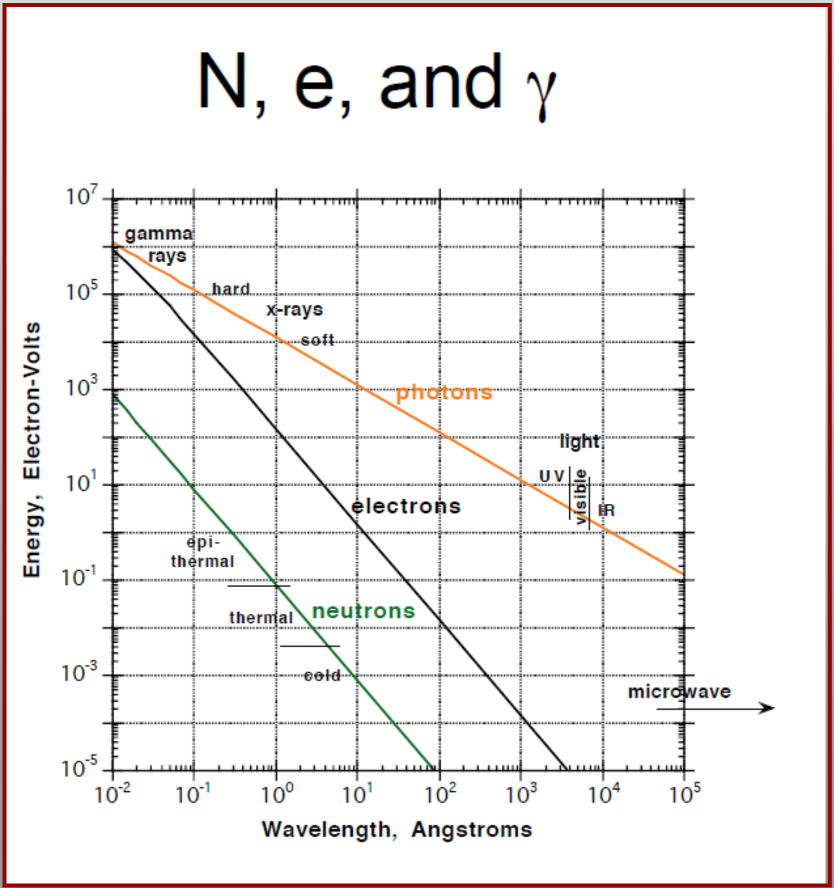
B. N. Brockhouse

What is special with NS?

1) Neutrons interact with nuclei and <u>not with their electrons</u> (neglecting magnetism). Ideal for light elements, isotopic studies, similar-Z elements, and lattice dynamics.



2) Neutrons have simultaneously the right λ and E, matching the typical distance and energy scales of condensed matter.



3) Weakly interacting with matter due to its neutrality, then: (a) small disturbance of the sample, so linear response theory always applies; (b) large penetration depth for bulky samples; (c) ideal for extreme condition studies; (d) little radiation damage.

4) The neutron has a magnetic moment, ideal for studying static and dynamic magnetic properties (not discussed in what follows).

Basic neutron properties

Mass: $1.67492729(28) \times 10^{-27}$ Kg

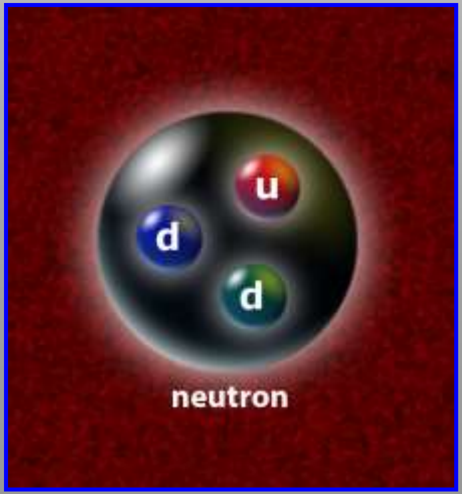
Mean lifetime: 885.7(8) s *(if free)*

Electric charge: 0 e

Electric dipole moment: $<2.9\times10^{-26}$ e·cm

Magnetic moment: $-1.9130427(5)\ \mu_N$

Spin: 1/2



Neutron wave-mechanical properties

Interested only in *<u>slow neutrons</u>* (E<1 KeV), *where:*

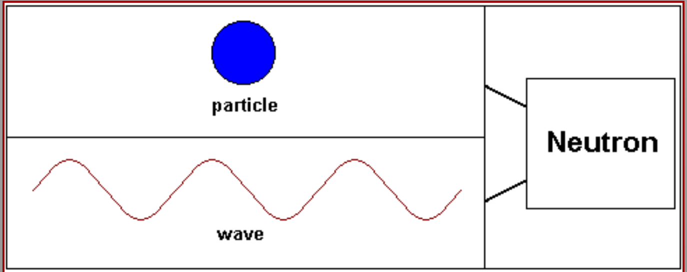
$E=mv^2/2$ (m=1.675·10^{-27} Kg) and

$\lambda=h/(mv)$

Using the wave-vector ($k=2\pi/\lambda$)*, one has:*

$$E(\text{meV})=81.81\,\lambda(\text{Å})^{-2}=2.072\,k(\text{Å}^{-1})^2$$

$$=5.227\,v(\text{Km/s})^2=0.08617\,T(\text{K})$$



How to imagine the wave-particle duality.

The slow neutron "zoology"

(a version of)

Name	Energy range (meV)
Very cold / Ultra-cold	<0.5
Cold	0.5 - 5
Thermal	5 - 100
Hot	100 - 10^3
Epithermal / Resonant	>10^3

1) Neutron scattering from nuclei

- **The neutron-Nucleus interaction**

1) <u>Short ranged</u> (i.e. ~10^{-15} m*).*

2) <u>Intense</u> (if compared to e.m.).

3) <u>Spin-dependent</u>.

4) <u>Complicated</u> (even containing non-central terms).

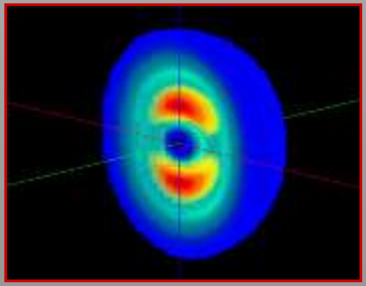
<u>Example</u>: **D=p+n**, *toy model (e.g. rectangular potential well)*

width: $r_0 = 2\cdot 10^{-15}$ m

depth: $V_r = 30$ MeV

binding energy: $E_b = 2.23$ MeV

Coulomb equivalent (p+p) *energy:* $E_C = 0.7$ MeV



The slow neutron-Nucleus system

<u>Good news</u>: *if* $\lambda_n >> r_0$ (*always true for **slow neutrons***) and $d >> r_0$ (d: *size of the nuclear delocalization*) *we do not need to know the detail of the* n-N *potential for describing the* n-N *system! Two quantities* (r_0 *and the so-called* ***scattering length***, a) *are enough.*

<u>Localized isotropic impact model</u>

$$\left[-\frac{\hbar^2\nabla_{\mathrm{n}}^2}{2m_{\mathrm{n}}}-\frac{\hbar^2\nabla_{\mathrm{N}}^2}{2m_{\mathrm{N}}}+U(\mathbf{r}_{\mathrm{N}})\right]\Psi(\mathbf{r}_{\mathrm{N}},\mathbf{r}_{\mathrm{n}})=H_0\Psi(\mathbf{r}_{\mathrm{N}},\mathbf{r}_{\mathrm{n}})=E\,\Psi(\mathbf{r}_{\mathrm{N}},\mathbf{r}_{\mathrm{n}})\quad(\text{for}\,|\mathbf{r}_{\mathrm{N}}-\mathbf{r}_{\mathrm{n}}|\equiv r\neq 0)$$

$$\Psi(\mathbf{r}_{\mathrm{N}},\mathbf{r}_{\mathrm{n}})_{r\to 0}\to\left(1-\frac{a}{r}\right)\varphi(\mathbf{r}_{\mathrm{N}})\quad(s\text{ wave})$$

The Schroedinger equation **plus** the boundary condition are **exactly** equivalent to:

$$H_0\Psi(\mathbf{r}_\mathrm{N},\mathbf{r}_\mathrm{n}) - E\,\Psi(\mathbf{r}_\mathrm{N},\mathbf{r}_\mathrm{n}) = -V(\mathbf{r}_\mathrm{n}-\mathbf{r}_\mathrm{N})\lim_{r\to 0}\frac{\partial}{\partial r}\left[r\,\Psi(\mathbf{r}_\mathrm{N},\mathbf{r}_\mathrm{n})\right]$$

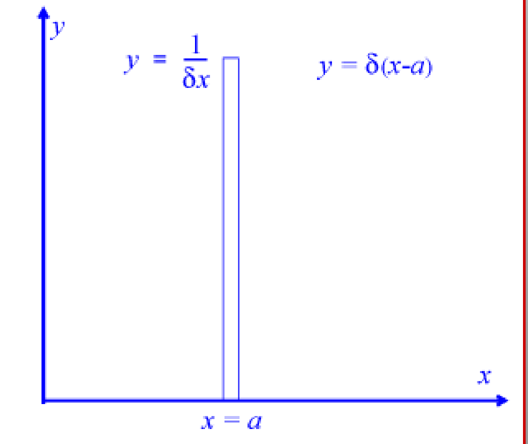
$$\text{where: } V(\mathbf{r}_\mathrm{n}-\mathbf{r}_\mathrm{N}) = \frac{2\pi\hbar^2}{\mu}a\,\delta(\mathbf{r}_\mathrm{n}-\mathbf{r}_\mathrm{N}) \equiv \frac{2\pi\hbar^2}{m_\mathrm{n}}b\,\delta(\mathbf{r}_\mathrm{n}-\mathbf{r}_\mathrm{N})$$

[Fermi pseudo-potential]

Tough equation… But it can be expanded in power series of V: $\Psi=\Psi_0+\Psi_1+\Psi_2+\ldots$ (if $\lambda_n \gg a$ and $d \gg a$), where:

$$H_0\Psi_0 - E\,\Psi_0 = 0$$

$$H_0\Psi_\mathrm{k} - E\,\Psi_\mathrm{k} = -V\lim_{r\to 0}\frac{\partial}{\partial r}\left[r\,\Psi_{\mathrm{k}-1}\right]$$

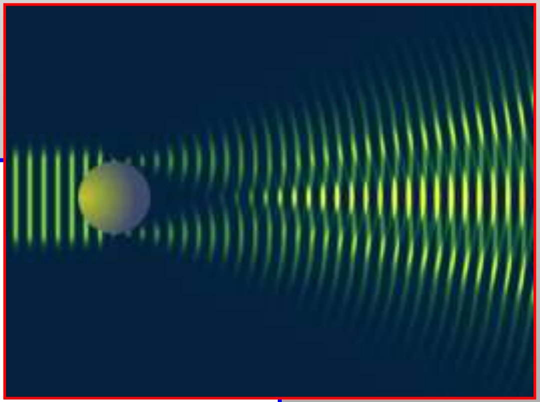


The Delta Function as a Narrow Spike

The *Fermi approximation* *is identical to the well-known* *first Born approximation*:

$$H_0\Psi_1 - E\,\Psi_1 \cong -V\lim_{r\to 0}\frac{\partial}{\partial r}\left[r\,\Psi_0\right] = -V\,\Psi_0\big|_{r=0} = -V\,\Psi_0$$

QM text-book solution:



$$\Psi_0 = \underbrace{\frac{1}{\sqrt{8\pi^3}}\exp\left(i\,\mathbf{k}\cdot\mathbf{r}_\mathrm{n}\right)}_{\text{neutron}}\underbrace{\varphi_0(\mathbf{r}_\mathrm{N})}_{\text{Nucleus}}\qquad \text{(unperturbed state)}$$

$$\Psi_1 \cong \underbrace{\frac{1}{\sqrt{8\pi^3}}\frac{\exp\left(i\,k'r_\mathrm{n}\right)}{r_\mathrm{n}}f(\mathbf{k}',F;\mathbf{k},0)}_{\text{neutron}}\underbrace{\varphi_\mathrm{F}(\mathbf{r}_\mathrm{N})}_{\text{Nucleus}}\qquad \text{(perturbation state)}$$

where a *spherical wave*, *modulated by the* *inelastic scattering amplitude* *$f(\mathbf{k}',F;\mathbf{k},0)$* *has been introduced:*

$$f(\mathbf{k}',F;\mathbf{k},0) = -\frac{1}{4\pi}\frac{2m_{\mathrm{n}}}{\hbar^2}\int d\mathbf{r}_{\mathrm{n}}\int d\mathbf{r}_{\mathrm{N}}\exp\left[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_{\mathrm{n}}\right]\varphi_{\mathrm{F}}^{*}(\mathbf{r}_{\mathrm{N}})V(\mathbf{r}_{\mathrm{n}},\mathbf{r}_{\mathrm{N}})\varphi_0(\mathbf{r}_{\mathrm{N}}) =$$

$$= -b\int d\mathbf{R}\exp\left[i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}\right]\varphi_{\mathrm{F}}^{*}(\mathbf{R})\varphi_0(\mathbf{R}) \equiv -b\left\langle\varphi_{\mathrm{F}}\middle|\exp(i\mathbf{Q}\cdot\mathbf{R})\middle|\varphi_0\right\rangle$$

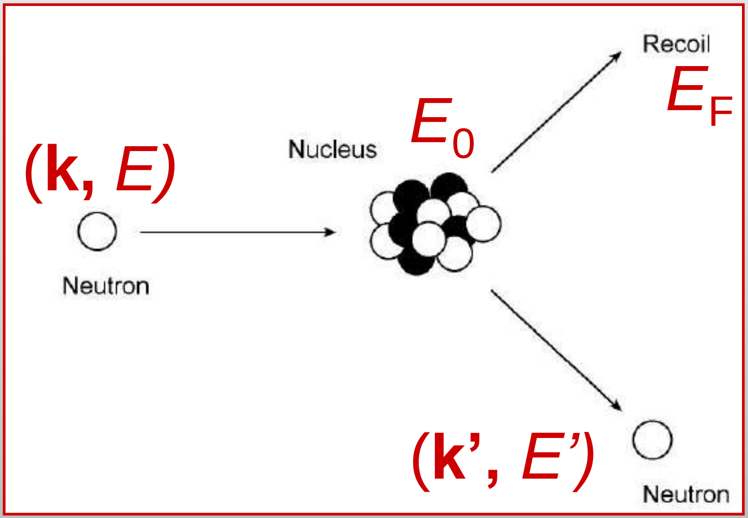
and the following energy conservation balance and useful definitions apply:

$$\frac{\hbar^2\mathbf{k}^2}{2m_{\mathrm{n}}} + E_0 = \frac{\hbar^2\mathbf{k}'^2}{2m_{\mathrm{n}}} + E_{\mathrm{F}} \Rightarrow \frac{\hbar^2\mathbf{k}^2}{2m_{\mathrm{n}}} - \frac{\hbar^2\mathbf{k}'^2}{2m_{\mathrm{n}}} \equiv \hbar\omega = E_{\mathrm{F}} - E_0 \ \text{(energy transfer)}$$

analogously one defines :

$$\hbar\mathbf{Q} \equiv \hbar\mathbf{k} - \hbar\mathbf{k}' \ \text{(momentum transfer)}$$

Slow neutron scattering from a nucleus



Q≡k-k'

$\hbar\omega \equiv E - E' = E_F - E_0$

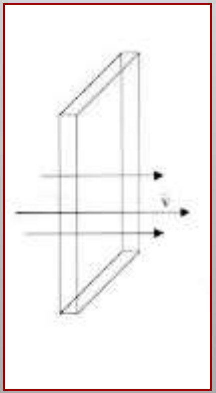
<u>Measurable quantity</u>: number of scattered neutrons, n detected in the time interval Δt, in the solid angle between θ and $\theta+\Delta\theta$, and between ϕ and $\phi+\Delta\phi$, having an energy ranging between E' and E'+ $\Delta E'$:

$$n = I(\theta, \phi, E')\Delta\theta\,\Delta\phi\,\Delta E'\,\Delta t$$

Scattering problem: how is $I(\theta,\phi,E')$ related to the intrinsic target properties [i.e. to $\varphi_i(\mathbf{R}_N)$]?

The concept of double differential scattering cross-section ($d^2\sigma/d\Omega/dE'$) has to be introduced:

$$\boxed{\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\theta,\varphi,E,E'} \equiv \frac{I(\theta,\phi,E')}{J_{in}} = \frac{r^2 J_{out}(\theta,\phi,E')}{J_{in}}}$$



where J_{in} is the current density of incoming neutrons (i.e. neutrons per m^2 *per* s*), all exhibiting energy E. Analogously, for the outgoing neutrons, one could write:* $J_{out}(\theta,\phi,E') = r^{-2}\, I(\theta,\phi,E')$ (spectral density current).

Going back to our QM text book, one finds the "recipe" for the <u>neutron density current</u>:

$$\boxed{\mathbf{J} = \frac{\hbar}{m_{\mathrm{n}}} \mathrm{Im}\left(\psi^{*} \vec{\nabla} \psi\right)}$$

which, applied to Ψ_0 and Ψ_1 *(box-normalized,* L^3*)*, gives:

$$J_{in} = \frac{\hbar}{L^3 m_n} k$$

$$J_{out}(\Omega) = \frac{\hbar}{L^3 m_n} \frac{k'}{r^2} \left| f(\mathbf{k}', F; \mathbf{k}, 0) \right|^2 = \frac{\hbar}{L^3 m_n} \frac{k'}{r^2} b^2 \left| \langle \varphi_{\mathrm{F}} | \exp(i\mathbf{Q} \cdot \mathbf{R}) | \varphi_0 \rangle \right|^2$$

$$J_{out}(\Omega) = \int_0^{\infty} d\varepsilon \, J_{out}(\varepsilon, \Omega) \Rightarrow J_{out}(E', \Omega) = J_{out}(\Omega) \delta\left(E - E' - E_{\mathrm{F}} + E_0\right)$$

and finally, the <u>neutron scattering fundamental equation</u>:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)^{0\to F}_{\theta,\varphi,E,E'} \equiv \frac{k'}{k} b^2 \left|\left\langle \varphi_F \left| \exp(i\mathbf{Q}\cdot\mathbf{R}) \right| \varphi_0 \right\rangle\right|^2 \delta\left(E - E' - E_F + E_0\right)$$

for the transition from the nuclear ground state 0 to the excited state F, with the constraint: $E-E'=E_F-E_0$.

Summing over all the possible nuclear excited states F, one has to explicitly add the energy conservation:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\theta,\varphi,E,E'} = \frac{k'}{k} b^2 \sum_F \left|\left\langle \varphi_F \left| \exp(i\mathbf{Q}\cdot\mathbf{R}) \right| \varphi_0 \right\rangle\right|^2 \delta\left(\hbar\omega - E_F + E_0\right)$$

Finally, if the target is not at $T=0$, one should also consider a statistical average (p_I) over the initial nuclear states, I:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\theta,\varphi,E,E'} = \frac{k'}{k} b^2 \sum_{I} p_I \sum_{F} \left|\langle \varphi_F | \exp(i\mathbf{Q}\cdot\mathbf{R}) | \varphi_I \rangle\right|^2 \delta(\hbar\omega - E_F + E_I)$$

$$\equiv \sqrt{\frac{E'}{E}}\, b^2\, \hbar^{-1} \underbrace{S(\mathbf{Q},\omega)}_{\text{Target property only}}$$

where the *inelastic structure factor* *or* *scattering law* *$S(\mathbf{Q},\omega)$ has been defined. Giving up to the neutron final energy (E') selection, one writes the* *single differential s. cross-section*:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\theta,\varphi,E} = \int_0^\infty dE' \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\theta,\varphi,E,E'} \qquad (\text{for } E_F - E_I < E)$$

$$= b^2 \sum_{I} p_I \sum_{F} \sqrt{\frac{E - E_F + E_I}{E}} \left|\langle \varphi_F | \exp(i\mathbf{Q}\cdot\mathbf{R}) | \varphi_I \rangle\right|^2$$

Giving up to the selection of the scattered neutron direction (Ω) too, one writes the s. cross-section:

$$\sigma(E) = \int d\Omega \left(\frac{d\sigma}{d\Omega}\right)_{\theta,\varphi,E} \begin{array}{ll} \to 4\pi b^2 & \text{for } E \to 0 \quad \text{(bound c.s.)} \\ \to 4\pi \dfrac{\mu^2}{m_n^2} b^2 & \text{for } E \to \infty \quad \text{(free c.s.)} \end{array}$$

- **Neutron scattering from an extended system**

$$\varphi_{I,F}(\mathbf{r}_N) \Rightarrow \varphi_{I,F}(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N) \quad \text{(many-body states)}$$

$$\frac{2\pi\hbar^2}{m_n} b\,\delta(\mathbf{r}_n - \mathbf{r}_N) \Rightarrow \frac{2\pi\hbar^2}{m_n} \sum_{j=1}^{N} b_j\,\delta(\mathbf{r}_n - \mathbf{R}_j) \text{ (comb-like potential)}$$

So, is everything so easy in **NS**? *No, not quite…*

Neutrons and incoherence

- "Real-life" neutron scattering *(from a set of nuclei with the same Z)*

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH}} + \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}}$$

where:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH}} = \sqrt{\frac{E'}{E}}\frac{\sigma_{\mathrm{COH}}}{4\pi}\hbar^{-1}S(\mathbf{Q},\omega)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}} = \sqrt{\frac{E'}{E}}\frac{\sigma_{\mathrm{INC}}}{4\pi}\hbar^{-1}S_{\mathrm{self}}(\mathbf{Q},\omega)$$

scattering laws defined for a many-body system (set of nuclei with the same Z) as:

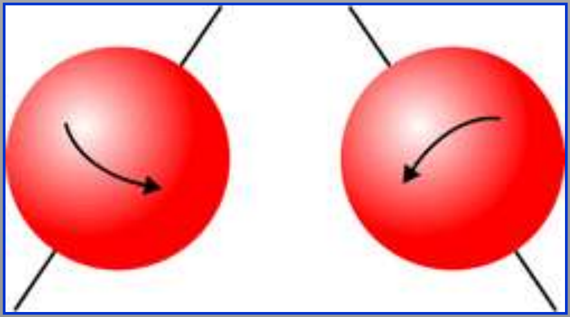
$$S(\mathbf{Q},\omega)=\frac{\hbar}{N}\sum_{\mathrm{I}} p_{\mathrm{I}}\sum_{\mathrm{F}}\left|\left\langle\varphi_{\mathrm{F}}\right|\sum_{\mathrm{j=1}}^{\mathrm{N}}\exp\left(i\mathbf{Q}\cdot\mathbf{R}_{\mathrm{j}}\right)\left|\varphi_{\mathrm{I}}\right\rangle\right|^{2}\delta\left(\hbar\omega-E_{\mathrm{F}}+E_{\mathrm{I}}\right)$$

$$S_{\mathrm{self}}(\mathbf{Q},\omega)=\frac{\hbar}{N}\sum_{\mathrm{I}} p_{\mathrm{I}}\sum_{\mathrm{F}}\sum_{\mathrm{j=1}}^{\mathrm{N}}\left|\left\langle\varphi_{\mathrm{F}}\right|\exp\left(i\mathbf{Q}\cdot\mathbf{R}_{\mathrm{j}}\right)\left|\varphi_{\mathrm{I}}\right\rangle\right|^{2}\delta\left(\hbar\omega-E_{\mathrm{F}}+E_{\mathrm{I}}\right)$$

$S(\mathbf{Q},\omega)$ is obvious, but where does $S_{self}(\mathbf{Q},\omega)$ come from? From the ***spins*** *of neutron (s_n,m_n) and nucleus (I_N,M_N), so far neglected! b depends on $\mathbf{I}_N+\mathbf{s}_n$*

- e.g. full quantum state for a neutron-nucleus pair:

$|\mathbf{k'}, s_n, m_n; F, I_N, M_N\rangle$



How does it work? Assuming <u>randomly distributed</u> neutron and nuclear spins, one can have a simple idea of the phenomenon:

$$\left|\left\langle \sum_{j=1}^{N} b_j \exp(i\mathbf{Q}\cdot\mathbf{R}_j) \right\rangle_{\text{spin+position}}\right|^2$$

$$= \left\langle \sum_{j=1}^{N} b_j \exp(i\mathbf{Q}\cdot\mathbf{R}_j) \right\rangle_{\text{spin+position}} \left\langle \sum_{j'=1}^{N} b_{j'} \exp(-i\mathbf{Q}\cdot\mathbf{R}'_{j'}) \right\rangle_{\text{spin+position}}$$

$$\Rightarrow \begin{cases} \text{for } j = j': & \langle b_j\, b_{j'} \rangle_{\text{spin}} = \langle b_j\, b_j \rangle_{\text{spin}} = \overline{b^2} \\ \text{for } j \neq j': & \langle b_j\, b_{j'} \rangle_{\text{spin}} = \langle b_j \rangle_{\text{spin}} \langle b_{j'} \rangle_{\text{spin}} = \left(\overline{b}\right)^2 \end{cases}$$

- The incoherence origin (rigorous theory):

$$\sigma_{\mathrm{TOT}} = 4\pi\left\langle \hat{b}^2 \right\rangle; \sigma_{\mathrm{COH}} = 4\pi\left\langle \hat{b} \right\rangle^2 \Rightarrow$$

$$\sigma_{\mathrm{INC}} = 4\pi\left[\left\langle \hat{b}^2 \right\rangle - \left\langle \hat{b} \right\rangle^2\right]$$

since b is actually not simply a number, but is the <u>scattering length operator</u> acting on $|i_{\mathrm{N}}, m_{\mathrm{N}}\rangle$ (nucleus) and on $|s_{\mathrm{n}}, m_{\mathrm{n}}\rangle$ (neutron) spin states:

$$\hat{b} = A + \frac{B}{2}\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{i}}_{\mathrm{N}}$$

This implies the existence of b^+ and b^- (if $i_N>0$) for any isotope (N, Z), respectively for $i_N \pm ½$:

$$A = \frac{1}{2i_N+1}\left\{(i_N+1)b^+ + i_N b^-\right\}$$

$$B = \frac{2}{2i_N+1}\left\{b^+ - b^-\right\}$$

After some algebra, <u>only</u> for <u>unpolarized</u> neutrons and nuclei, one can write:

$$\frac{1}{2(2i_N+1)}\sum_{M_N,m_n}\left\langle i_N, M_N; s_n, m_n \middle| \hat{b} \middle| i_N, M_N; s_n, m_n \right\rangle = A;$$

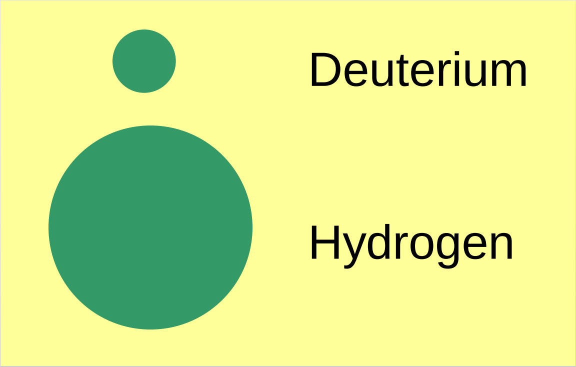
$$\frac{1}{2(2i_N+1)}\sum_{M_N,m_n}\left\langle i_N, M_N; s_n, m_n \middle| \hat{b}^2 \middle| i_N, M_N; s_n, m_n \right\rangle = |A|^2 + \frac{|B|^2}{4} i_N(i_N+1)$$

With various isotopes (c_j) one gets:

$$\left\langle \hat{b} \right\rangle = \sum_j c_j \frac{(i_{N,j}+1)b_j^+ + i_{N,j} b_j^-}{2i_{N,j}+1}$$

$$\left\langle \hat{b}^2 \right\rangle = \sum_j c_j \frac{(i_{N,j}+1)(b_j^+)^2 + i_{N,j} (b_j^-)^2}{2i_{N,j}+1}$$

σ_{TOT}:



Important case: hydrogen

(protium H, i_N=1/2*):* b^+=10.85 fm, b^-=-47.50 fm $\Rightarrow$

σ_{TOT}=82.03 b, σ_{COH}=1.7583 b

(deuterium D, i_N=1*):* b^+=9.53 fm, b^-=0.98 fm $\Rightarrow$

σ_{TOT}=7.64 b, σ_{COH}=5.592 b

High-*Q* spatial incoherence

(rearranging…)

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{DIS}} \equiv \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH}} - \frac{\sigma_{\mathrm{COH}}}{\sigma_{\mathrm{INC}}}\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}}$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) = \frac{\sigma_{\mathrm{TOT}}}{\sigma_{\mathrm{INC}}}\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}} + \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{DIS}}$$

Incoherent approximation

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right) \cong \frac{\sigma_{\mathrm{TOT}}}{\sigma_{\mathrm{INC}}}\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}} \quad \text{for } \hbar\omega \neq 0$$

$$\Updownarrow$$

$$S(\mathbf{Q},\omega) \cong S_{\mathrm{self}}(\mathbf{Q},\omega) \Leftrightarrow S_{\mathrm{dist}}(\mathbf{Q},\omega) \cong 0$$

When does it apply in a crystal?

$$|\mathbf{Q}| >> 2\pi \frac{\langle u^2 \rangle^{1/2}}{d^2}$$

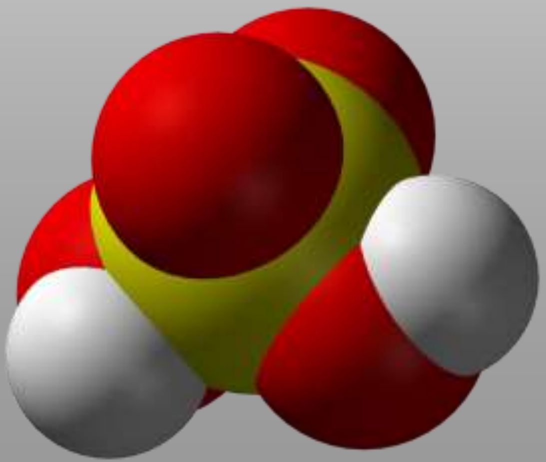
Practical example : D_2SO_4 (*T*=10 K)

d(DO)=*0.091* nm

$\langle u^2 \rangle^{1/2}$(D)=*0.0158* nm

$2\pi\langle u^2 \rangle^{1/2}/d^2$=*11.9* nm^{-1}

$|\mathbf{Q}_{inc}|$~*100* nm^{-1}



2) Time-correlation functions

$S(\mathbf{Q},\omega)$ and $S_{self}(\mathbf{Q},\omega)$ are <u>probe independent</u>, i.e. they are intrinsic sample properties. But what do they mean?

Fourier-transforming the two spectral functions, one defines $I(\mathbf{Q},t)$ and $I_{self}(\mathbf{Q},t)$, the so-called <u>intermediate scattering function</u> and <u>self intermediate scattering function</u>:

$$I(\mathbf{Q},t) \equiv \int_{-\infty}^{\infty} d\omega \exp\left(i\omega t\right) S(\mathbf{Q},\omega)$$

$$I_{\text{self}}(\mathbf{Q},t) \equiv \int_{-\infty}^{\infty} d\omega \exp\left(i\omega t\right) S_{\text{self}}(\mathbf{Q},\omega)$$

After some algebra (e.g. the Heisenberg representation), one writes $I(\mathbf{Q},t)$ and $I_{\mathrm{self}}(\mathbf{Q},t)$ as <u>time-correlation functions</u> (with a clearer physical meaning):

$$I(\mathbf{Q},t)=\frac{1}{N}\left\langle \sum_{\mathrm{j,k}} \exp\left\{-\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{j}}(0)\right\}\exp\left\{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{k}}(t)\right\}\right\rangle$$

$$I_{\mathrm{self}}(\mathbf{Q},t)=\frac{1}{N}\sum_{\mathrm{j}}\left\langle \exp\left\{-\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{j}}(0)\right\}\exp\left\{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{j}}(t)\right\}\right\rangle$$

$$I_{\mathrm{dist}}(\mathbf{Q},t)\equiv I(\mathbf{Q},t)-I_{\mathrm{self}}(\mathbf{Q},t)$$

So far we have dealt only with a pure <u>monatomic</u> system (set of nuclei with the same Z*).*

But what about “real-life” samples (e.g. chemical compounds)?

Sum over ”s” distinct species (concentration c[s]):

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH}} = \frac{k'}{k}\frac{1}{2\pi}\int_{-\infty}^{\infty} dt \exp(-\mathrm{i}\omega t)\sum_{\mathrm{s}}\sum_{\mathrm{z}} c[s]c[z]\bar{b}_{\mathrm{s}}\bar{b}_{\mathrm{z}}\, I^{(\mathrm{s,z})}(\mathbf{Q},t)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}} = \frac{k'}{k}\frac{1}{2\pi}\int_{-\infty}^{\infty} dt \exp(-\mathrm{i}\omega t)\sum_{s} c[s]\left(\overline{b_{\mathrm{s}}^2} - \bar{b}_{\mathrm{s}}^{\,2}\right) I_{\mathrm{self}}^{(\mathrm{s})}(\mathbf{Q},t)$$

where $I^{(s)}_{self}(\mathbf{Q},t)$ is the so-called <u>self intermediate scattering function</u> for the sth species:

$$I_{\mathrm{self}}^{(\mathrm{s})}(\mathbf{Q},t) = \frac{1}{N_{\mathrm{s}}}\sum_{\mathrm{j}=1}^{\mathrm{N_s}}\left\langle \exp\left\{-\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{j}}^{\mathrm{s}}(0)\right\}\exp\left\{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{j}}^{\mathrm{s}}(t)\right\}\right\rangle$$

and where $S^{(s)}_{self}(\mathbf{Q},\omega)$ *is the so-called* *<u>self inelastic structure factor</u>* *for the* s^{th} *species*. *Properties similar to those of* $S_{self}(\mathbf{Q},\omega)$:

$$S^{(s)}_{\mathrm{self}}(\mathbf{Q},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,\exp\left(-i\omega t\right)I^{(s)}_{\mathrm{self}}(\mathbf{Q},t)$$

The coherent part is slightly more complex

$I^{(s,z)}(\mathbf{Q},t)$ *is the so-called* *<u>total</u>* *intermediate scattering function for the* s^{th} *species (if* $s\equiv z$*), or the* *<u>cross</u>* *intermediate scattering function for the* s,z^{th} *pair of species* (if $s\neq z$):

$$I^{(s,z)}(\mathbf{Q},t) = \frac{N}{N_s N_z}\left\langle \sum_j^{N_s}\sum_k^{N_z} \exp\left\{-i\mathbf{Q}\cdot\mathbf{R}_j^s(0)\right\}\exp\left\{i\mathbf{Q}\cdot\mathbf{R}_k^z(t)\right\}\right\rangle$$

and $S^{(s,z)}(\mathbf{Q},\omega)$ *is the so-called* ***total*** *inelastic structure factor for the* s^{th} *species (if* $s\equiv z$*), or the* ***cross*** *inelastic structure factor for the* s,z^{th} *pair of species* (if $s\neq z$):

$$S^{(s,z)}(\mathbf{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\,\exp(-i\omega t)\,I^{(s,z)}(\mathbf{Q},t)$$

The ***total*** *contains a "distinct" plus a "self" terms, while the* ***cross*** *only a "distinct" term.*

Coherent sum rules

$$\text{from}: \int_{-\infty}^{\infty} d\omega\, \omega^{\mathrm{n}} S(\mathbf{Q},\omega) = (-i)^{\mathrm{n}} \frac{\partial^{\mathrm{n}}}{\partial t^{\mathrm{n}}} I(\mathbf{Q},t)\Big|_{t=0}$$

$$0^{\mathrm{th}})\int_{-\infty}^{\infty} d\omega\, S(\mathbf{Q},\omega) = S(\mathbf{Q}) \Rightarrow \text{Static structure factor}$$

where:

$$S(\mathbf{Q}) = \frac{1}{N}\sum_{\mathrm{I}} p_{\mathrm{I}} \langle \varphi_{\mathrm{I}} | \sum_{\mathrm{k,j}}^{\mathrm{N}} \exp(-i\mathbf{Q}\cdot\mathbf{R}_{\mathrm{k}}) \exp(i\mathbf{Q}\cdot\mathbf{R}_{\mathrm{j}}) | \varphi_{\mathrm{I}} \rangle$$

$$1^{\mathrm{st}})\int_{-\infty}^{\infty} d\omega\, \hbar\omega\, S(\mathbf{Q},\omega) = \frac{\hbar^2 |\mathbf{Q}|^2}{2M} = E_{\mathrm{R}} \Rightarrow \text{Recoil Energy}$$

Incoherent sum rules

$$\text{from}: \int_{-\infty}^{\infty} d\omega\, \omega^{n} S_{\text{self}}(\mathbf{Q},\omega) = (-i)^{n} \frac{\partial^{n}}{\partial t^{n}} I_{\text{self}}(\mathbf{Q},t)\Big|_{t=0}$$

$$0^{\text{th}})\int_{-\infty}^{\infty} d\omega\, S_{\text{self}}(\mathbf{Q},\omega) = 1 \Rightarrow \text{Normalization}$$

$$1^{\text{st}})\int_{-\infty}^{\infty} d\omega\, \hbar\omega\, S_{\text{self}}(\mathbf{Q},\omega) = \frac{\hbar^{2}|\mathbf{Q}|^{2}}{2M} = E_{\text{R}} \Rightarrow \text{Recoil Energy}$$

$$2^{\text{nd}})\int_{-\infty}^{\infty} d\omega \left(\hbar\omega - E_{\text{R}}\right)^{2} S_{\text{self}}(\mathbf{Q},\omega) = \hbar^{2}\left\langle \left(\mathbf{v}\cdot\mathbf{Q}\right)^{2}\right\rangle$$

$$\Rightarrow \text{Kinetic energy}: \left\langle E_{\text{k}}\right\rangle = \frac{M_{\text{N}}}{2}\left\langle \mathbf{v}^{2}\right\rangle$$

$$3^{\mathrm{rd}})\int_{-\infty}^{\infty} d\omega \left(\hbar\omega - E_{\mathrm{R}}\right)^3 S_{\mathrm{self}}(\mathbf{Q},\omega) = \frac{\hbar^4}{2M^2}\left\langle \sum_{\mathrm{i,j}} Q_{\mathrm{i}}\partial_{\mathrm{i}}\partial_{\mathrm{j}} U Q_{\mathrm{j}} \right\rangle$$

$\Rightarrow$ Laplacian of the potential U

$$4^{\mathrm{th}})\int_{-\infty}^{\infty} d\omega \left(\hbar\omega - E_{\mathrm{R}}\right)^4 S_{\mathrm{self}}(\mathbf{Q},\omega) = \hbar^4\left\langle \left(\mathbf{v}\cdot\mathbf{Q}\right)^4 \right\rangle$$

$$+\frac{\hbar^4}{M^2}\left\langle \left(\vec{\nabla} U\cdot\mathbf{Q}\right)^2 \right\rangle$$ $\Rightarrow$ Square gradient of the potential U

Detailed balance

$$S(-\mathbf{Q},-\omega) = \exp\left(-\tfrac{\hbar\omega}{k_B T}\right) S(\mathbf{Q},\omega)$$

$$S_{\mathrm{self}}(-\mathbf{Q},-\omega) = \exp\left(-\tfrac{\hbar\omega}{k_B T}\right) S_{\mathrm{self}}(\mathbf{Q},\omega)$$

from the ***microscopic reversibility*** *principle:*

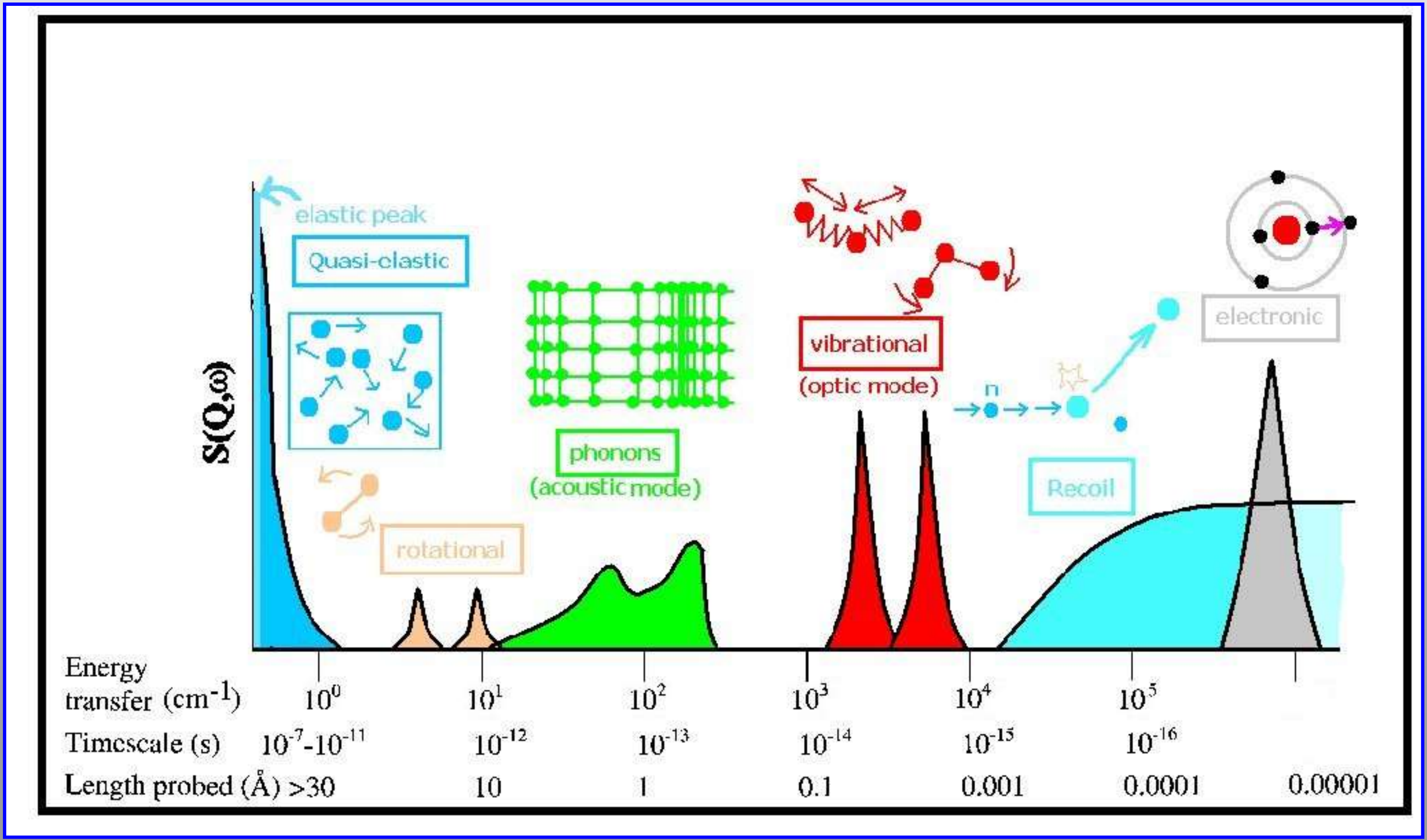
$$\sum_{\mathrm{m,n}} p_{\mathrm{n}} \left|\langle m|\exp(-i\mathbf{Q}\cdot\mathbf{R}_1)|n\rangle\right|^2 \delta(-\hbar\omega - E_{\mathrm{m}} + E_{\mathrm{n}}) =$$

$$\sum_{\mathrm{n,m}} p_{\mathrm{m}} \left|\langle n|\exp(-i\mathbf{Q}\cdot\mathbf{R}_1)|m\rangle\right|^2 \delta(-\hbar\omega - E_{\mathrm{n}} + E_{\mathrm{m}}) =$$

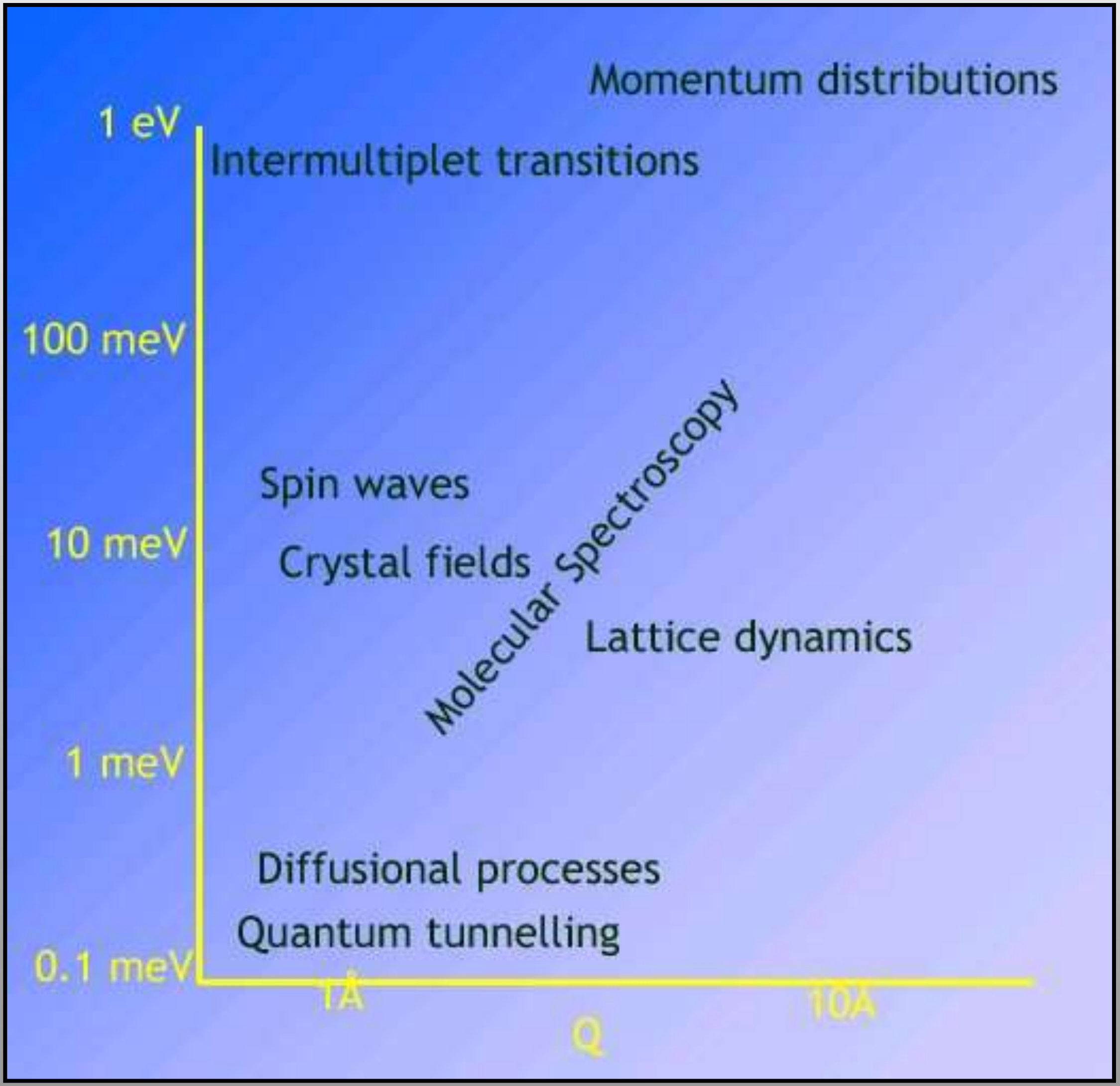
$$\sum_{\mathrm{m,n}} p_{\mathrm{n}} \frac{p_{\mathrm{m}}}{p_{\mathrm{n}}} \left|\langle m|\exp(i\mathbf{Q}\cdot\mathbf{R}_1)|n\rangle\right|^2 \delta(\hbar\omega - E_{\mathrm{m}} + E_{\mathrm{n}}) \quad \text{q.e.d.}$$

Analogous proof for the scattering law

The zoo of excitations…



…and their (|**Q**|-*E*) relationships



3) Inelastic scattering from crystals

Scattering law from a many-body system: analytically solved only in few cases (*e.g.* ideal gas, Brownian motion, and regular crystalline structures, with a purely harmonic dynamics.

Generalized scattering law (sometimes used for mixed systems)

$$\Sigma(\mathbf{Q},\omega) = \frac{1}{\sum_{\mathrm{m}} (\bar{b}_{\mathrm{m}})^2} \int_{-\infty}^{\infty} \frac{dt}{2\pi} \exp(-i\omega t)$$

$$\times \sum_{\mathrm{n,n'}} \bar{b}_{\mathrm{n}} \bar{b}_{\mathrm{n'}} \left\langle \exp\{-\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{n}}(0)\} \exp\{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{n'}}(t)\}\right\rangle$$

Generalized self scattering law (sometimes used for mixed systems)

$$\Sigma_{\text{self}}(\mathbf{Q},\omega) = \frac{1}{\sum_{\text{m}} \sigma_{\text{INC,m}}} \int_{-\infty}^{\infty} \frac{dt}{2\pi} \exp(-i\omega t)$$
$$\times \sum_{\text{n}} \sigma_{\text{INC,n}} \left\langle \exp\left\{-\text{i}\mathbf{Q}\cdot\mathbf{R}_{\text{n}}(0)\right\} \exp\left\{\text{i}\mathbf{Q}\cdot\mathbf{R}_{\text{n}}(t)\right\}\right\rangle$$

In a harmonic crystal the time correlation functions are exactly solvable in terms of phonons due to the Bloch theorem for a 1D harmonic oscillator (X is its adimensional coordinate):

$$\left\langle \exp X \right\rangle = \exp\left\{ \tfrac{1}{2} \left\langle X^2 \right\rangle \right\}$$

Three-dimensional crystalline lattice (*N* cells and *r* atoms in the elementary cell: *"l"* and *"d"* indexes):

$$\mathbf{R}_{\mathrm{l.d}}(t) = \underbrace{\mathbf{l}+\mathbf{d}}_{\text{equilibrium}} + \mathbf{u}_{\mathrm{l,d}}(t)$$

Harmonicity (expansion of $\mathbf{u}_{\mathrm{l,d}}(t)$ in normal modes; e.g. phonon *"s"*; quantized):

$$\mathbf{u}_{\mathrm{l,d}}(t) = \sqrt{\frac{\hbar}{2NM_{\mathrm{d}}}}\sum_{\mathrm{s}=1}^{3\mathrm{Nr}} \omega_{\mathrm{s}}^{-1/2}\left\{\mathbf{e}_{\mathrm{s,d}}\, a_{\mathrm{s}} \exp\left(i\,\mathbf{q}\cdot\mathbf{l} - i\omega_{\mathrm{s}} t\right) + \mathbf{e}^{*}_{\mathrm{s,d}}\, a^{+}_{\mathrm{s}} \exp\left(-i\,\mathbf{q}\cdot\mathbf{l} + i\omega_{\mathrm{s}} t\right)\right\}$$

with $\mathbf{e}_{s,d}$ *polarization versor,* $a^{\dagger}_{s}$ *(*a_s*) creation (annihilation) operator of the* s^{th} *phonon with* ω_s *frequency and* $2\pi|\mathbf{q}|^{-1}$ *wavelength*.

Collective index "s": $\{q_x,q_y,q_z,j\}$ *with* $\mathbf{q}\in 1BZ$ *(first Brillouin zone: N points). "j" labels the phonon branches (3 acoustic e 3r-3 optic).*

Polarizations: 2 transverse and 1 longitudinal.

Total: 3Nr d.o.f.

Dispersion curves: $\omega_s=\omega_j(\mathbf{q})$

Coherent scattering

Plugging the equations for $\mathbf{R}_{l,d}(t)$ *and* $\mathbf{u}_{l,d}(t)$ *(i.e. phonon quantization) into the coherent d. d. cross-section, one gets:*

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH}} = \frac{k'}{Nk}\sum_{\mathrm{d}}\sum_{\mathrm{l',d'}} \bar{b}_{\mathrm{d}}\bar{b}_{\mathrm{d'}} \exp\left[i\mathbf{Q}\cdot\left(\mathbf{d'}-\mathbf{d}+\mathbf{l'}\right)\right]$$

$$\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}\exp(-i\omega t)\left\langle \exp\left[-i\mathbf{Q}\cdot\mathbf{u}_{0,\mathrm{d}}(0)\right]\exp\left[i\mathbf{Q}\cdot\mathbf{u}_{\mathrm{l',d'}}(t)\right]\right\rangle$$

and using the Bloch theorem together with the commutation rules: $e^{A}e^{B}=e^{A+B}e^{[A,B]/2}$, one writes:

$$\left\langle \exp\left[-i\mathbf{Q}\cdot\mathbf{u}_{0,\mathrm{d}}(0)\right]\exp\left[i\mathbf{Q}\cdot\mathbf{u}_{\mathrm{l',d'}}(t)\right]\right\rangle$$
$$=\exp\left\langle -\frac{1}{2}\left\{\left[\mathbf{Q}\cdot\mathbf{u}_{0,\mathrm{d}}(0)\right]^2+\left[\mathbf{Q}\cdot\mathbf{u}_{0,\mathrm{d'}}(t)\right]^2\right\}\right\rangle$$
$$\times\exp\left\langle\left[\mathbf{Q}\cdot\mathbf{u}_{0,\mathrm{d}}(0)\right]\left[\mathbf{Q}\cdot\mathbf{u}_{\mathrm{l',d'}}(t)\right]\right\rangle$$

and then:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH}}=\frac{k'}{Nk}\sum_{\mathrm{d}}\sum_{\mathrm{l',d'}}\bar{b}_{\mathrm{d}}\bar{b}_{\mathrm{d'}}\exp\left[i\mathbf{Q}\cdot\left(\mathbf{d'}-\mathbf{d}+\mathbf{l'}\right)\right]$$
$$\exp\left[-B_{\mathrm{d}}(\mathbf{Q},0)/2-B_{\mathrm{d'}}(\mathbf{Q},0)/2\right]\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}\exp\left(-i\omega t\right)\exp\left[B_{\mathrm{d,l',d'}}(\mathbf{Q},t)\right]$$

where the static term is the Debye-Waller factor, whose exponent is:

$$B_{0,\mathrm{d}}(\mathbf{Q},0)=\frac{\hbar}{2NM_{\mathrm{d}}}\sum_{\mathrm{s}}\frac{\left|\mathbf{Q}\cdot\mathbf{e}_{\mathrm{d,s}}\right|^{2}}{\omega_{\mathrm{s}}}\left\langle 2n_{\mathrm{s}}+1\right\rangle\equiv 2W_{\mathrm{d}}(\mathbf{Q})$$

with $\langle n_s \rangle$ number of thermally activated phonons; while the dynamic term contains:

$$B_{\mathrm{d,l',d'}}(\mathbf{Q},t)=\frac{\hbar}{2N\sqrt{M_{\mathrm{d}}M_{\mathrm{d'}}}}\sum_{\mathrm{s}}\frac{(\mathbf{Q}\cdot\mathbf{e}_{\mathrm{d,s}})(\mathbf{Q}\cdot\mathbf{e}^{*}_{\mathrm{d',s}})}{\omega_{\mathrm{s}}}\left\{\left\langle n_{\mathrm{s}}+1\right\rangle\right.$$
$$\left.\exp[i\omega_{\mathrm{s}}t-i\mathbf{q}_{\mathrm{s}}\cdot(\mathbf{d'}-\mathbf{d}+\mathbf{l'})]+\left\langle n_{\mathrm{s}}\right\rangle\exp[-i\omega_{\mathrm{s}}t+i\mathbf{q}_{\mathrm{s}}\cdot(\mathbf{d'}-\mathbf{d}+\mathbf{l'})]\right\}$$

Coherent elastic scattering

Phonon expansion

Expanding $\exp[B_{d,d',l'}(\mathbf{Q},t)]$ *in power series, one gets a sum of terms with* n *phonons (created or annihilated):*

$$\exp\left[B_{d,d',l'}(\mathbf{Q},t)\right] = 1 + B_{d,d',l'}(\mathbf{Q},t) + \frac{1}{2}\left[B_{d,d',l'}(\mathbf{Q},t)\right]^2 + \ldots$$
$$+ \frac{1}{n!}\left[B_{d,d',l'}(\mathbf{Q},t)\right]^n + \ldots$$

one gets for the first term, 1, an <u>elastic</u> contribution:

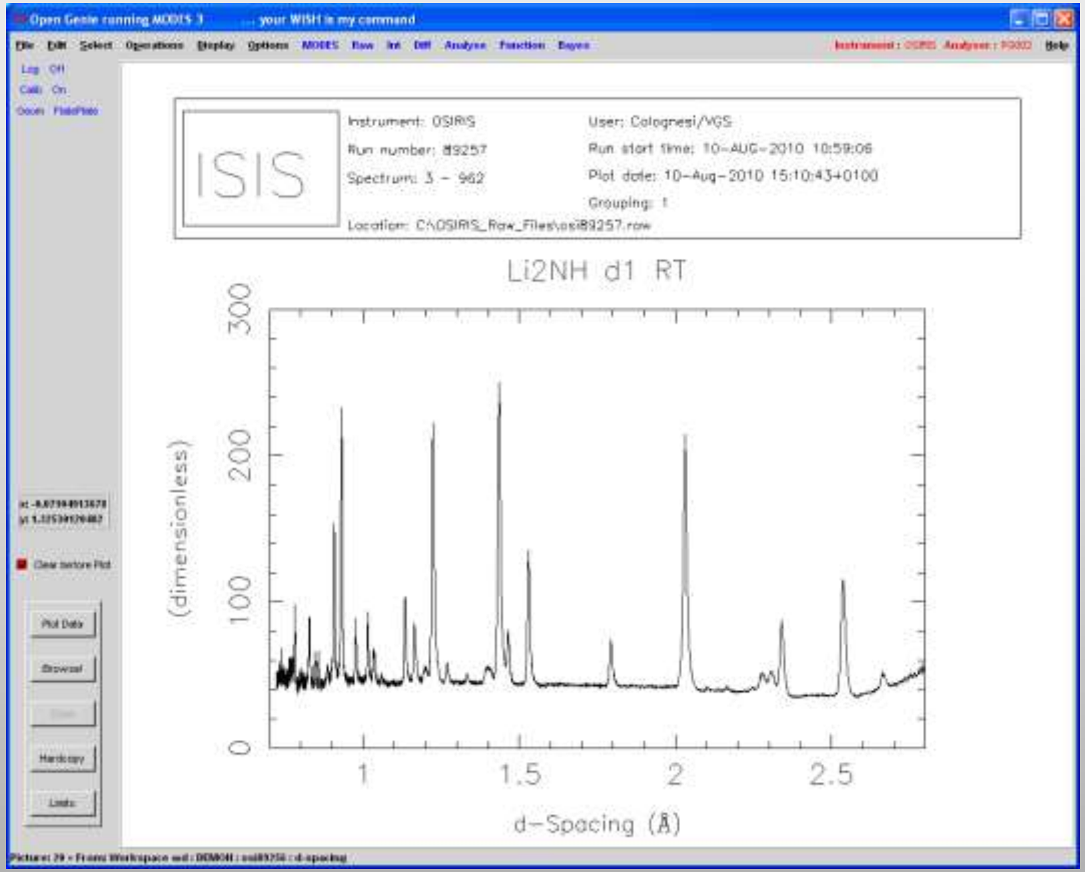
$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH,elast}} = N^{-1}\sum_{\mathrm{d}}\sum_{\mathrm{l',d'}} \bar{b}_{\mathrm{d}}\bar{b}_{\mathrm{d'}} \exp\left[i\mathbf{Q}\cdot\left(\mathbf{d'}-\mathbf{d}+\mathbf{l'}\right)\right]$$

$$\exp\left[-B_{\mathrm{d}}(\mathbf{Q},0)/2 - B_{\mathrm{d'}}(\mathbf{Q},0)/2\right]\delta\left(\hbar\omega\right)$$

Integrating over E' and making use of the reciprocal lattice (τ) sum rule: $\sum_{\mathbf{l}} \exp(i\mathbf{Q}\cdot\mathbf{l}) = 8\pi^3 v_{\mathrm{cell}}^{-1}\sum_{\boldsymbol{\tau}} \delta(\mathbf{Q}-\boldsymbol{\tau})$*, one obtains the well-known* ***Bragg law*** *:*

$$\left(\frac{d\sigma}{d\Omega}\right)_{\substack{\mathrm{COH,}\\ \mathrm{elast}}} = \frac{8\pi^3}{Nv_{\mathrm{cell}}} \underbrace{\sum_{\mathrm{d,d'}} \bar{b}_{\mathrm{d}}\bar{b}_{\mathrm{d'}} \exp\left[i\mathbf{Q}\cdot\left(\mathbf{d'}-\mathbf{d}\right)\right]\exp\left[-W_{\mathrm{d}}(\mathbf{Q})-W_{\mathrm{d'}}(\mathbf{Q})\right]}_{\left|F_{\mathrm{n}}(\mathbf{Q})\right|^2 :\ \text{nuclear unit-cell structure factor}}$$

$$\times \sum_{\boldsymbol{\tau}} \delta(\mathbf{Q}-\boldsymbol{\tau})\ \text{(Bragg peaks)}$$



Neutron powder diffraction pattern from Li_2NH *(plus* Al *container) at room temperature. Abscissa:* $d = 2\pi |\mathbf{Q}|^{-1}$

One-phonon coherent contribution

If $E_{R,d}(\mathbf{Q}) < \hbar / \langle \omega_s^{-1} \rangle$ [*the lightest* M_d] *then:*

$$\boxed{\exp\left[B_{\mathrm{d,d',l'}}(\mathbf{Q},t)\right] - 1 \cong B_{\mathrm{d,d',l'}}(\mathbf{Q},t)}$$

and one obtains the <u>single phonon</u> (created or annihilated) d. d. coherent cross section:

$$\boxed{\begin{aligned}\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH},\pm 1} &= \frac{k'}{Nk}\sum_{\mathrm{d}}\sum_{\mathrm{l',d'}}\bar{b}_{\mathrm{d}}\bar{b}_{\mathrm{d'}}\exp\left[i\mathbf{Q}\cdot\left(\mathbf{d'}-\mathbf{d}+\mathbf{l'}\right)\right]\\ &\exp\left[-W_{\mathrm{d}}(\mathbf{Q})-W_{\mathrm{d'}}(\mathbf{Q})\right]\int_{-\infty}^{\infty}\frac{dt}{2\pi\hbar}\exp\left(-i\omega t\right)B_{\mathrm{d,l',d'}}(\mathbf{Q},t)\end{aligned}}$$

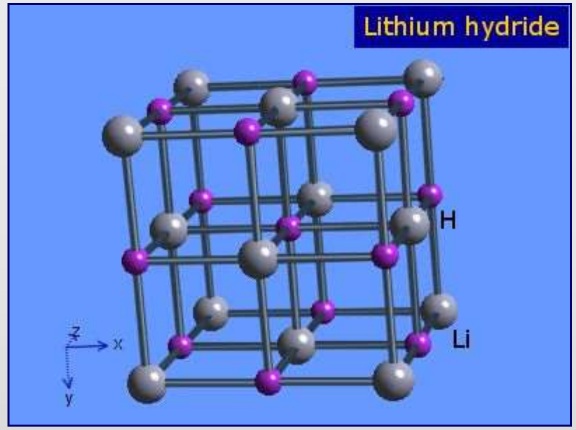
Plugging the equation for $B_{d,d',l'}(\mathbf{Q},t)$ into the <u>one-phonon coherent d. d. cross-section</u> and performing the Fourier transforms and the reciprocal lattice sums, one gets:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH},+1} = \frac{k'}{k}\frac{8\pi^3}{2Nv_{\mathrm{cell}}}\sum_{\mathrm{s}}\omega_{\mathrm{s}}^{-1}\left|\sum_{\mathrm{d}}\frac{\bar{b}_d}{\sqrt{M_{\mathrm{d}}}}\exp\left[i\mathbf{Q}\cdot\mathbf{d}-W_{\mathrm{d}}(\mathbf{Q})\right]\left(\mathbf{Q}\cdot\mathbf{e}_{\mathrm{d,s}}\right)\right|^2$$
$$\times\langle n_{\mathrm{s}}+1\rangle\delta(\omega-\omega_{\mathrm{s}})\sum_{\boldsymbol{\tau}}\delta(\mathbf{Q}\text{-}\mathbf{q}_{\mathrm{s}}\text{-}\boldsymbol{\tau})\ (1-\mathrm{phonon},\omega_{\mathrm{j}}(\mathbf{q}),\ \mathrm{creation}\ \omega>0)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{COH},-1} = \frac{k'}{k}\frac{8\pi^3}{2Nv_{\mathrm{cell}}}\sum_{\mathrm{s}}\omega_{\mathrm{s}}^{-1}\left|\sum_{\mathrm{d}}\frac{\bar{b}_d}{\sqrt{M_{\mathrm{d}}}}\exp\left[i\mathbf{Q}\cdot\mathbf{d}-W_{\mathrm{d}}(\mathbf{Q})\right]\left(\mathbf{Q}\cdot\mathbf{e}_{\mathrm{d,s}}\right)\right|^2$$
$$\times\langle n_{\mathrm{s}}\rangle\delta(\omega+\omega_{\mathrm{s}})\sum_{\boldsymbol{\tau}}\delta(\mathbf{Q}+\mathbf{q}_{\mathrm{s}}\text{-}\boldsymbol{\tau})\ (1-\mathrm{phonon},\omega_{\mathrm{j}}(\mathbf{q}),\mathrm{annihilation}\ \omega<0)$$

Dispersion Curve

practical example:
lithium hydride LiD
(cubic, Fm3m, *i.e.*
NaCl *type) with*
$r=2 \Rightarrow j=1,2,3$

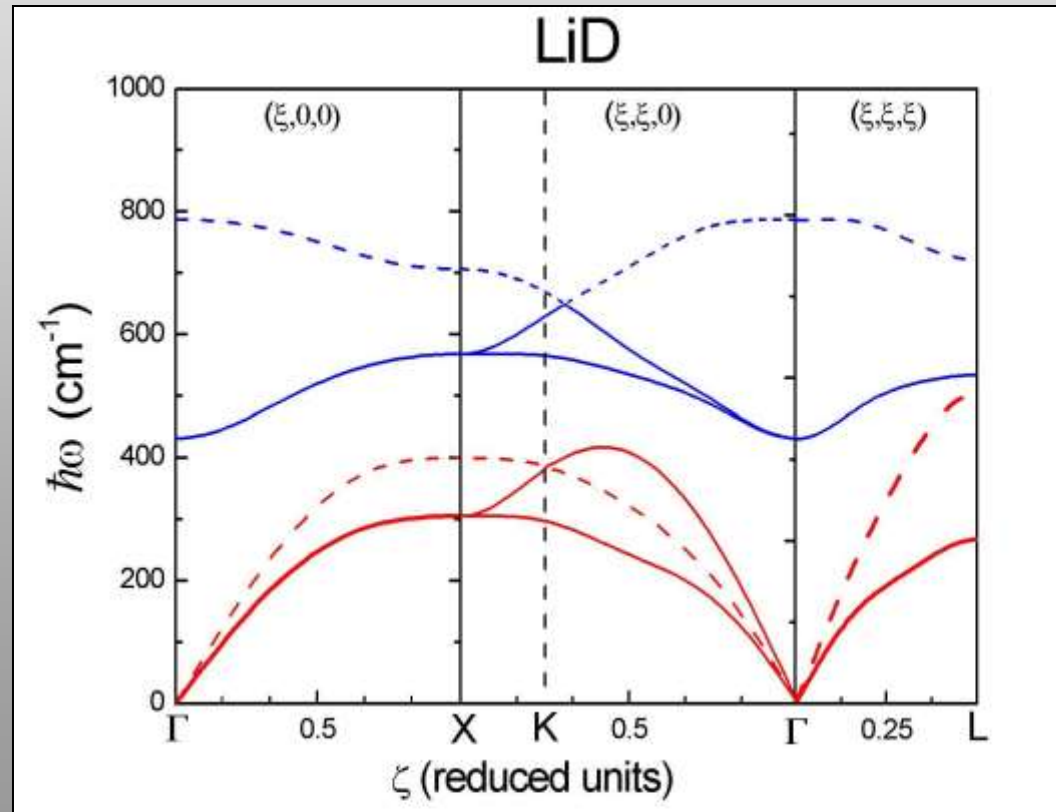


Red: *Acoustic*

Blue: *Optic*

Full: *Transverse*

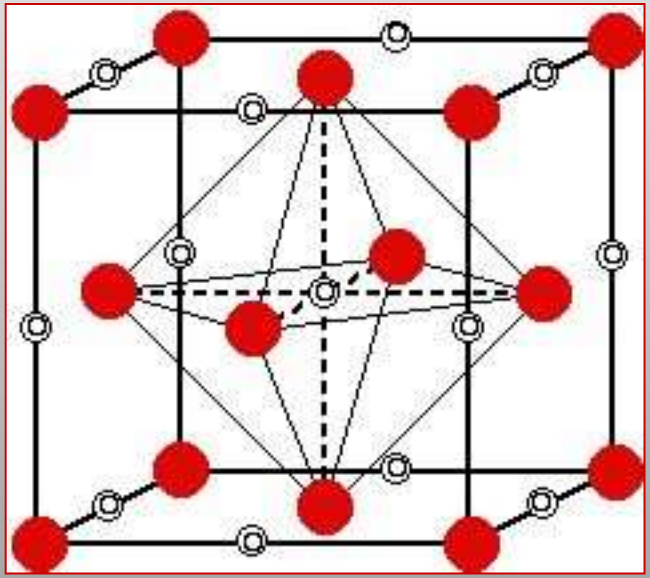
Dash: *Longitudinal*



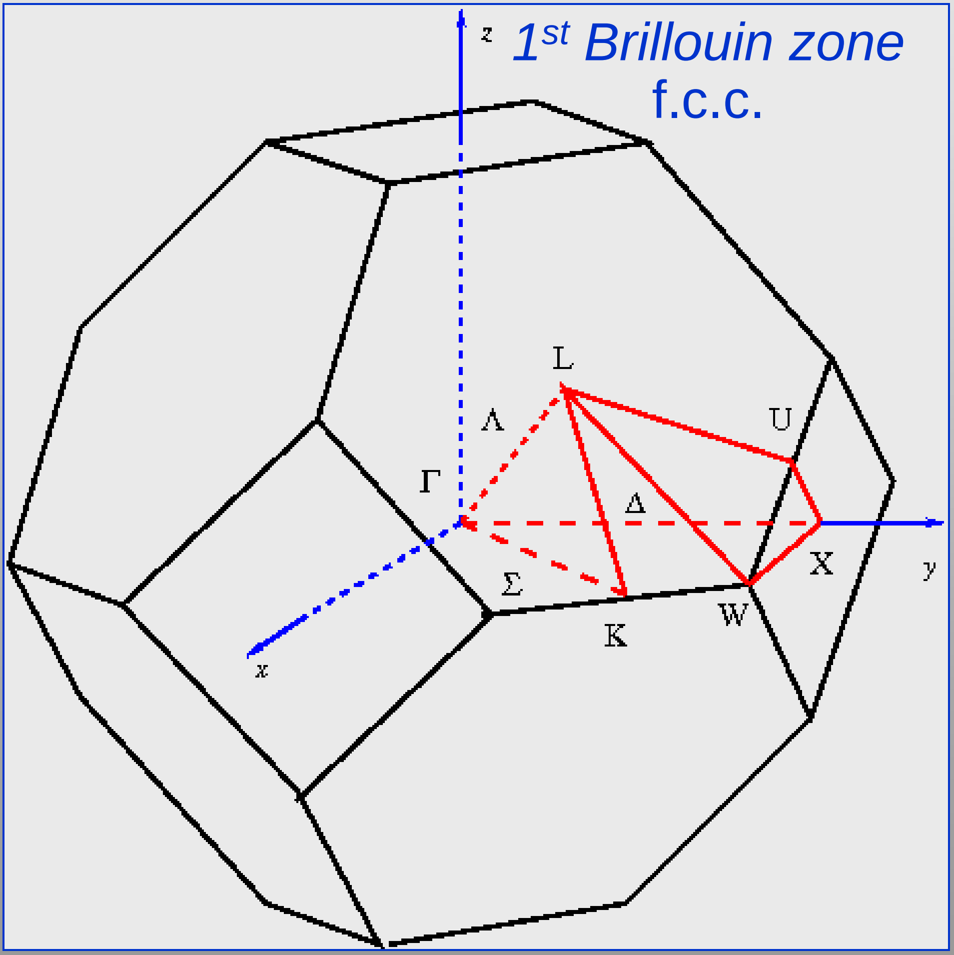
First Brillouin zone

in a face-centered cubic lattice

(f.c.c.)



face-centered cubic lattice



- One-phonon incoherent contribution

Bloch theorem:

$$\sum_{\mathrm{l,d}} \sigma_{\mathrm{INC}}^{(\mathrm{d})} \left\langle \exp\left\{-\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{l,d}}(0)\right\} \exp\left\{\mathrm{i}\mathbf{Q}\cdot\mathbf{R}_{\mathrm{l,d}}(t)\right\}\right\rangle =$$
$$= N \sum_{\mathrm{d}} \sigma_{\mathrm{INC}}^{(\mathrm{d})} \exp\left[-B_{\mathrm{d}}(\mathbf{Q},0)\right] \exp\left[B_{\mathrm{d}}(\mathbf{Q},t)\right]$$

where the static term is the <u>Debye-Waller factor</u>, whose exponent is:

$$B_{\mathrm{d}}(\mathbf{Q},0) = \frac{\hbar}{2NM_{\mathrm{d}}} \sum_{\mathrm{s}} \frac{\left|\mathbf{Q}\cdot\mathbf{e}_{\mathrm{d,s}}\right|^2}{\omega_{\mathrm{s}}} \left\langle 2n_{\mathrm{s}}+1\right\rangle$$

with $\langle n_s \rangle$ *number of thermally activated phonons;*
while the dynamic term contains:

$$B_d(\mathbf{Q},t) = \frac{\hbar}{2NM_d} \sum_s \frac{\left|\mathbf{Q}\cdot\mathbf{e}_{d,s}\right|^2}{\omega_s} \left\{ \langle n_s + 1 \rangle \exp\left(i\omega_s t\right) + \langle n_s \rangle \exp\left(-i\omega_s t\right) \right\}$$

Single phonon and density of states

Expanding $\exp[B_d(\mathbf{Q},t)]$ *in power series, one gets a sum of terms with* n *phonons (created or annihilated):*

$$\exp\left[B_{\mathrm{d}}(\mathbf{Q},t)\right]=1+B_{\mathrm{d}}(\mathbf{Q},t)+\frac{1}{2}\left[B_{\mathrm{d}}(\mathbf{Q},t)\right]^{2}+\ldots$$

$$+\frac{1}{n!}\left[B_{\mathrm{d}}(\mathbf{Q},t)\right]^{\mathrm{n}}+\ldots$$

if $E_{R,d}(\mathbf{Q})<\hbar/\langle\omega_s^{-1}\rangle$ *then:*

$$\exp\left[B_{\mathrm{d}}(\mathbf{Q},t)\right]\cong 1+B_{\mathrm{d}}(\mathbf{Q},t)$$

and one obtains the <u>single phonon</u> (creation or annihilation) d. d. incoherent cross section:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC},\pm1} = \frac{k'}{k}\sum_{\mathrm{d}}\frac{\sigma_{\mathrm{INC}}^{(\mathrm{d})}}{4\pi}\frac{1}{2NM_{\mathrm{d}}}\sum_{\mathrm{s}}\frac{\left|\mathbf{Q}\cdot\mathbf{e}_{\mathrm{d,s}}\right|^2}{\omega_{\mathrm{s}}}$$
$$\times\left\{\langle n_{\mathrm{s}}+1\rangle\delta(\omega-\omega_{\mathrm{s}})+\langle n_{\mathrm{s}}\rangle\delta(\omega+\omega_{\mathrm{s}})\right\}\exp\left[-B_{\mathrm{d}}(\mathbf{Q},0)\right]$$

Density of (phonon) states: density probability for a phonon of any kind with frequency between ω *and* $\omega+d\omega$:

$$g(\omega) = \frac{1}{3rN}\sum_{\mathrm{s}}^{3\mathrm{rN}}\delta(\omega-\omega_{\mathrm{s}})$$

The single-phonon incoherent d. d. cross section (creation or annihilation) becomes more simply:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC},\pm 1} \cong \frac{k'}{k}\sum_{\mathrm{d}} \frac{\sigma_{\mathrm{INC}}^{(\mathrm{d})}}{4\pi} \frac{Q^2}{2M_{\mathrm{d}}} \times \frac{r\left\langle \left|\mathbf{e}_{\mathrm{d}}(|\omega|)\right|^2\right\rangle g(|\omega|)}{\omega\{1-\exp[-\hbar\omega(k_B T)^{-1}]\}} \exp\left[-2W_{\mathrm{d}}(\mathbf{Q})\right]$$

where:

$$\left\{1-\exp\left[-\hbar\omega(k_{\mathrm{B}}T)^{-1}\right]\right\}^{-1} = \begin{cases} -\langle n(-\omega)\rangle \text{ for } \omega < 0 \,(\text{annih.}) \\ \langle n(\omega)+1\rangle \textit{ for } \omega > 0 \,(\text{creat.}) \end{cases}$$

weak point (“≅”), *i.e. the meaning of the averaged eigenvector:*

$$\left\langle \left| \mathbf{e}_{\mathrm{d}}(\omega) \right|^2 \right\rangle = \frac{1}{3rNg(\omega)\Delta\omega} \sum_{\omega<\omega_{\mathrm{s}}<\omega+\Delta\omega} \mathbf{e}_{\mathrm{d,s}}^2$$

The separation from **Q** *is rigorous only in cubic lattices:*

$$\left\langle \left[\mathbf{Q} \cdot \mathbf{e}_{\mathrm{d,s}} \right]^2 \right\rangle_{\mathrm{s}} = \frac{Q^2}{3} \left\langle \left| \mathbf{e}_{\mathrm{d}}(\omega) \right|^2 \right\rangle$$

otherwise one has the isotropic approximation.

In addition, using this approximation, one proves that:

$$\boxed{B_\mathrm{d}(\mathbf{Q},0) \equiv 2W_\mathrm{d}(\mathbf{Q}) \cong \frac{Q^2}{3}\left\langle \mathbf{u}_\mathrm{d}^2 \right\rangle}$$

link between the exponent of the <u>Debye-Waller factor</u>

and the mean square displacement of the d species.

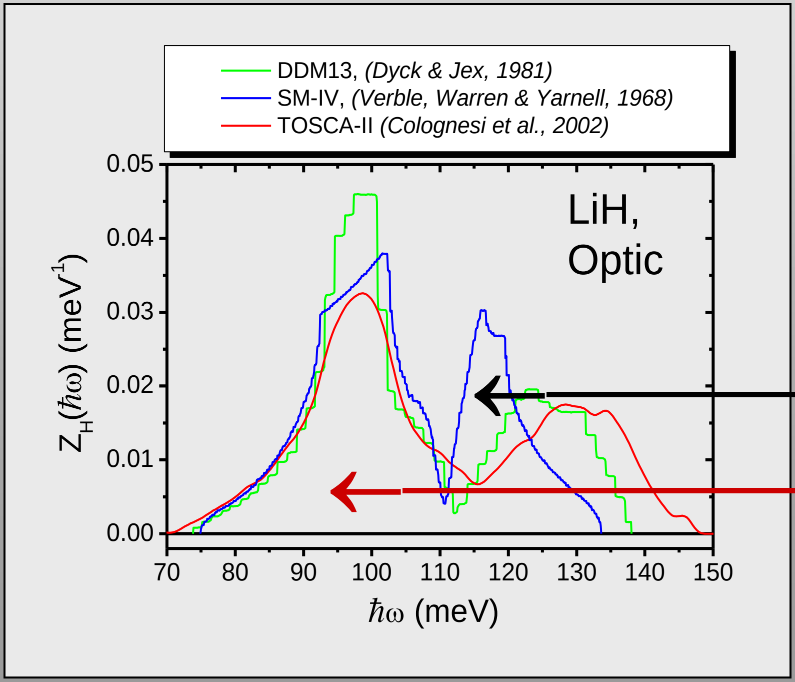
It is often used the <u>density of states projected</u> on d:

$$G_\mathrm{d}(|\omega|) = r\left\langle \left|\mathbf{e}_\mathrm{d}(|\omega|)\right|^2 \right\rangle g(|\omega|)$$

$$\left\langle \mathbf{u}_\mathrm{d}^2 \right\rangle = \frac{3\hbar}{2M_\mathrm{d}} \int_0^\infty \frac{G_\mathrm{d}(\omega)}{\omega} \coth\left(\frac{\hbar\omega}{2k_\mathrm{B}T}\right) d\omega$$

from which:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC},\pm1} \cong \frac{k'}{k}\sum_{\mathrm{d}} \frac{\sigma_{\mathrm{INC}}^{(\mathrm{d})}}{4\pi}\frac{Q^2}{2M_{\mathrm{d}}} \times \frac{G_{\mathrm{d}}(|\omega|)}{\omega\{1-\exp[-\hbar\omega(k_{\mathrm{B}}T)^{-1}]\}}\exp\left(-\frac{Q^2}{3}\left\langle \mathbf{u}_{\mathrm{d}}^2\right\rangle\right)$$



Density of states projected on H

practical example:
lithium hydride LiH

longitudinal

transverse

Multiphonon incoherent contributions

<u>Coherent</u> multiphonon terms are too complex and not very useful (*e.g.* for powders: Bredov approximation). Here only <u>incoherent</u> terms. Definition:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC,Mult}} = \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}} - \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC},\pm 1}$$

remembering that:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}} = \frac{k'}{\hbar k}\int_{-\infty}^{\infty}\frac{dt}{2\pi}\exp(-i\omega t)$$
$$\times\sum_{\mathrm{d}}\frac{\sigma_{\mathrm{INC}}^{(\mathrm{d})}}{4\pi}\exp\left[-B_{\mathrm{d}}(\mathbf{Q},0)\right]\exp\left[B_{\mathrm{d}}(\mathbf{Q},t)\right]$$

and that:

$$\exp\left[B_{\mathrm{d}}(\mathbf{Q},t)\right] = 1 + B_{\mathrm{d}}(\mathbf{Q},t) + \frac{1}{2}\left[B_{\mathrm{d}}(\mathbf{Q},t)\right]^{2} + \ldots + \frac{1}{n!}\left[B_{\mathrm{d}}(\mathbf{Q},t)\right]^{\mathrm{n}} + \ldots$$

one gets for the first term, 1, an elastic contribution:

$$\left(\frac{d^{2}\sigma}{d\Omega dE'}\right)_{\mathrm{INC,Elas}} = \frac{k'}{\hbar k}\int_{-\infty}^{\infty}\frac{dt}{2\pi}\exp\left(-i\omega t\right) \times \sum_{\mathrm{d}}\frac{\sigma_{\mathrm{INC}}^{(\mathrm{d})}}{4\pi}\exp\left[-2W_{\mathrm{d}}(\mathbf{Q})\right] = \frac{k'}{k}\sum_{\mathrm{d}}\frac{\sigma_{\mathrm{INC}}^{(\mathrm{d})}}{4\pi}\exp\left[-2W_{\mathrm{d}}(\mathbf{Q})\right]\delta\left(\hbar\omega\right)$$

not to be confused with the <u>incoherent</u> s. d. cross-section:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{INC}} = \int_0^{\infty} \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC}} dE'$$

For the second term one gets, ***B*(Q,*t*)**, *the <u>single phonon</u> contribution (±1, created or annihilated) already known:*

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC},\pm 1} \cong \frac{k'}{k} \sum_{\mathrm{d}} \frac{\sigma_{INC}^{(d)}}{4\pi} \frac{Q^2}{2M_{\mathrm{d}}}$$

$$\times \frac{G_{\mathrm{d}}(|\omega|)}{\omega\{1-\exp[-\hbar\omega(k_{\mathrm{B}}T)^{-1}]\}} \exp\left[-2W_{\mathrm{d}}(\mathbf{Q})\right]$$

While for the (n+1)th term, one gets $B^n(\mathbf{Q},t)$, a contribution with n <u>*phonons*</u> *(created and/or annihilated). Using the convolution theorem:*

$$\int_0^\infty \frac{dt}{2\pi}\exp\left(-i\omega t\right)B_{\mathrm{d}}^{\mathrm{n}}(Q,t)=\underbrace{\tilde{B}_{\mathrm{d}}(Q,\omega)\otimes\tilde{B}_{\mathrm{d}}(Q,\omega)\otimes\ldots\tilde{B}_{\mathrm{d}}(Q,\omega)}_{\text{n times}}$$

$$=\left[\tilde{B}_{\mathrm{d}}(Q,\omega)\right]^{\mathrm{n}}$$

where:

$$\tilde{B}_{\mathrm{d}}(Q,\omega)=\frac{\hbar Q^2}{2M_{\mathrm{d}}}\frac{G_{\mathrm{d}}(|\omega|)}{\omega\{1-\exp[-\hbar\omega/(k_{\mathrm{B}}T)]\}}\equiv\frac{\hbar Q^2}{2M_{\mathrm{d}}}f_{\mathrm{d}}(\omega)$$

we obtain:

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\mathrm{INC},\pm n} \cong \frac{k'}{\hbar k}\sum_{\mathrm{d}}\frac{\sigma_{\mathrm{INC}}^{(\mathrm{d})}}{4\pi}\left(\frac{\hbar Q^2}{2M_{\mathrm{d}}}\right)^{\mathrm{n}} \times \frac{\left[f_{\mathrm{d}}(\omega)\right]^{\mathrm{n}}}{n!}\exp\left[-2W_{\mathrm{d}}(\mathbf{Q})\right]$$

Self-convolution shifts and broadens $f_{\mathrm{d}}(\omega)$*, but blurs its details too…*

Sjölander approximation: $[f_{\mathrm{d}}(\omega)]^{\mathrm{n}}$ *is replaced by an appropriate Gaussian (same mean and variance):*

Properties of $f_d(\omega)$

for $f_{\mathrm{d}}(\omega)$:

$$A_{\mathrm{d}} = \frac{2M_{\mathrm{d}}\langle \mathbf{u}_{\mathrm{d}}^2\rangle}{3\hbar};$$

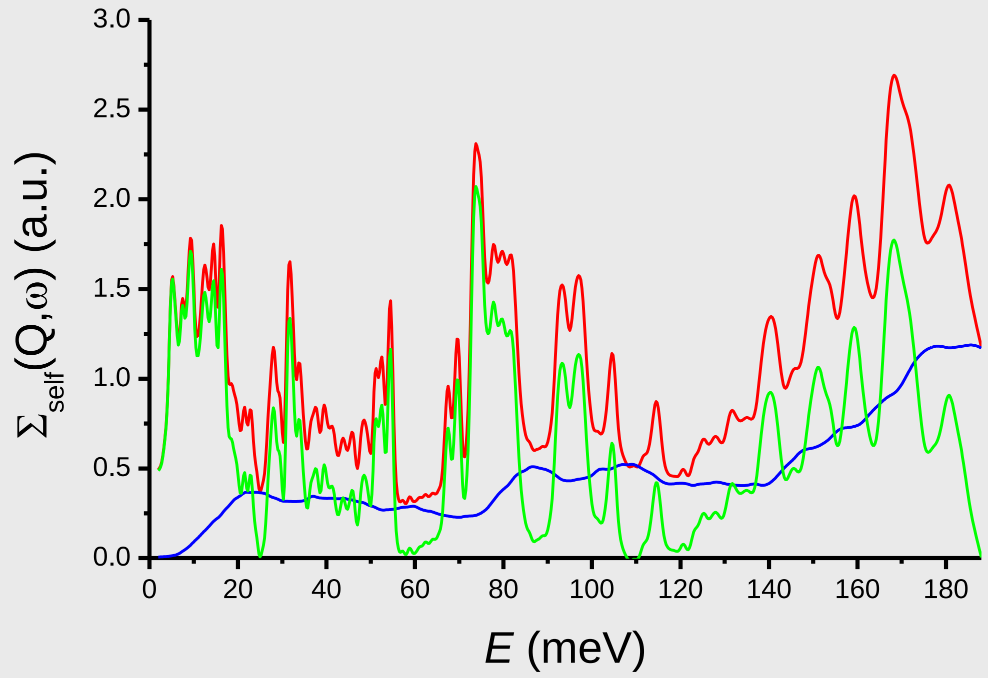
$$m_{\mathrm{d}} = \frac{3\hbar}{2M_{\mathrm{d}}\langle \mathbf{u}_{\mathrm{d}}^2\rangle} = A_{\mathrm{d}}^{-1};$$

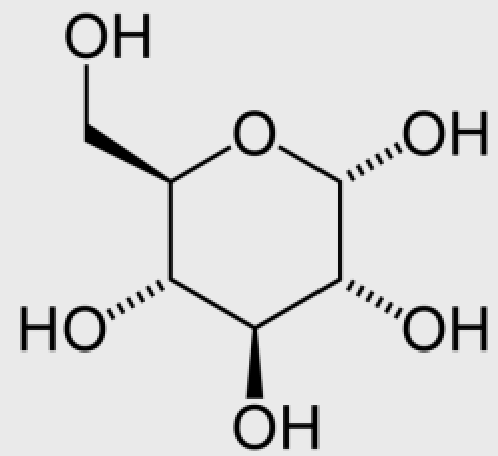
$$v_{\mathrm{d}} = \frac{2}{M_{\mathrm{d}}\langle \mathbf{u}_{\mathrm{d}}^2\rangle}\langle E_{\mathrm{k}}\rangle_{\mathrm{d}} - m_{\mathrm{d}}^2$$

Then we have:

$$\left[f_{\mathrm{d}}(\omega)\right]^{\mathrm{n}} \cong \frac{1}{\sqrt{2\pi n v_{\mathrm{d}}}}\left(\frac{1}{m_{\mathrm{d}}}\right)^{\mathrm{n}} \exp\left[-\frac{(\omega - n m_{\mathrm{d}})^2}{2 n v_{\mathrm{d}}}\right]$$

Not always appropriate…





α-D-glucose at *T*=19 K,
example from TOSCA