Laboratoire Léon Brillouin

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Dynamics (diffusion) in solids and liquids

C. ALBA-SIMIONESCO

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+ S. Longeville, JM Zanotti, R. Pynn…

17th Oxford School on Neutron Scattering

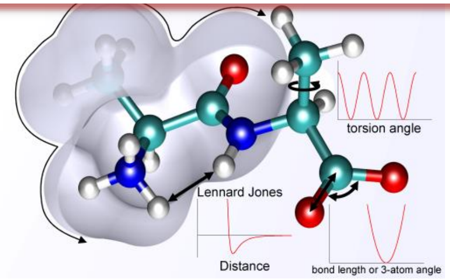
UNIVERSITY OF OXFORD

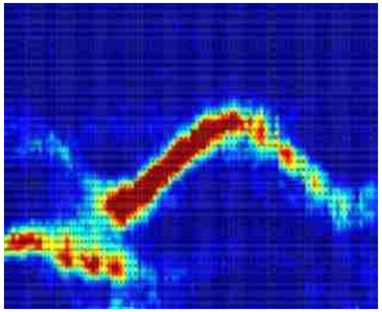
Application to solid state physics, chemistry, biophysics, material sciences (Quantum), geology, food sciences, cultural heritage etc ..

The key observable :
is the dynamic structure factor S(Q,ω)
the space and time Fourier transform of the density-density correlation function

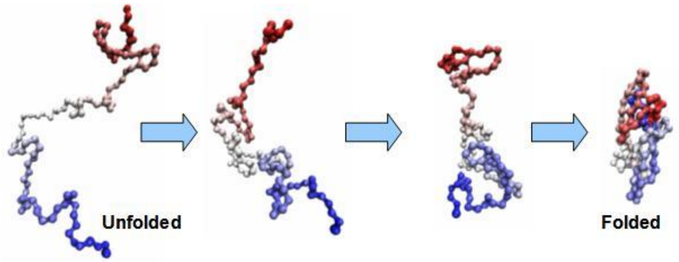
atomic and molecular motions

Understand molecular interactions

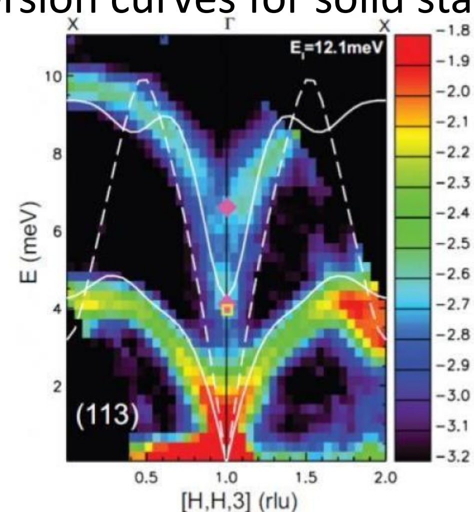




Understand macromolecular conformations changes



Dispersion curves for solid state physics



magnetic excitations in unconventional superconductors, various quantum phenomena, magneto-elastic or multiferroic materials, ….

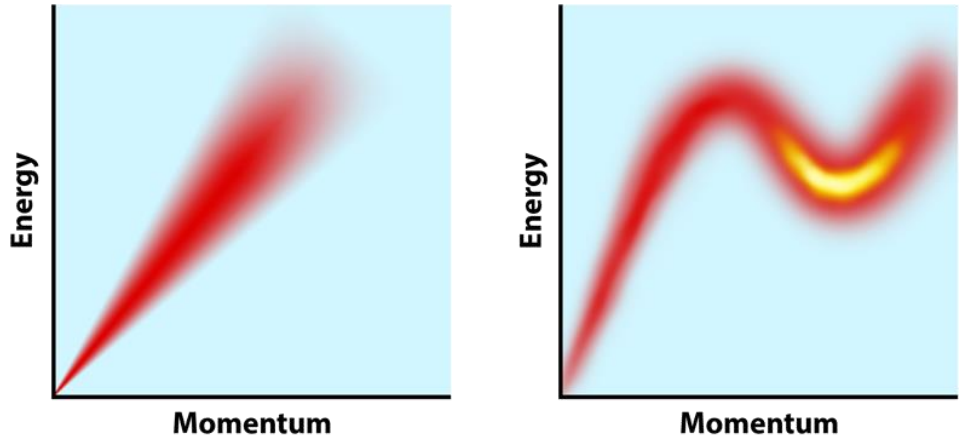
Domain: Condensed Matter Physics

H. Godfrin, et al, Dispersion relation of Landau elementary excitations and thermodynamic properties of superfluid ^4He, Phys. Rev. B 103, 104516 (2021)

Excitations in the Ultimate Quantum Fluid : Researchers have measured superfluid helium's full dispersion spectrum, explaining discrepancies in previous studies and constraining theories of superfluidity.

Says Professor Elizabeth Blackburn

Schematic energy-momentum dispersion relations for (left) a normal fluid and (right) superfluid helium. In the linear part of the spectrum, excitations take the form of phonons in both cases. The minimum of the superfluid spectrum (yellow) corresponds to roton excitations



Domain: Planetary Physics

Ranieri, U.,. et al. **Diffusion in dense supercritical methane from quasi-elastic neutron scattering measurements**. Nat Commun 12, 1958 (2021). https://doi.org/10.1038/s41467-021-22182-4

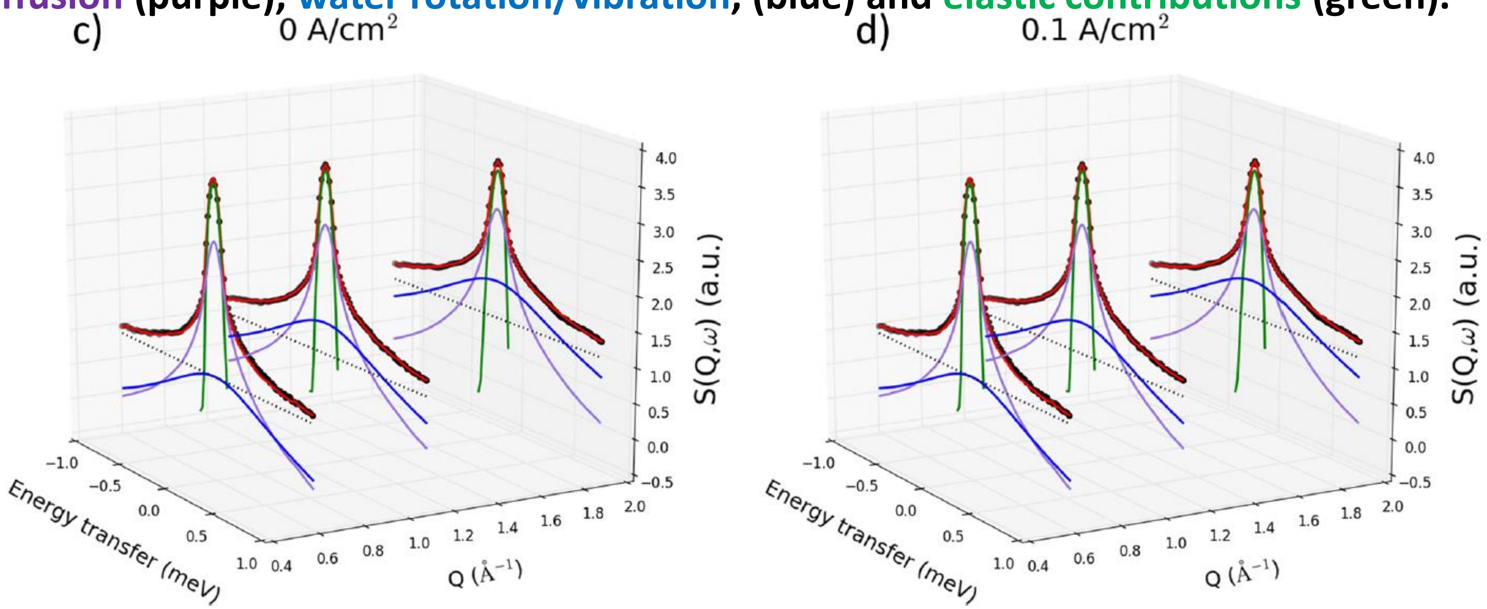
Domain : sustainable energy production/conversion and separations technologies

Fabrizia Foglia et al, Progress in neutron techniques: towards improved polymer electrolyte membranes for energy devices, 2021 J. Phys.: Condens. Matter 33 264005

research in advanced polymer electrolyte membranes (PEM) by QENS

quasielastic signal due to hydrogen atoms motions in the ps and ns time scales: it demonstrates the applicability of operando QENS to provide in situ characterization of the molecular dynamics **in the operating system**

water diffusion (purple), water rotation/vibration, (blue) and elastic contributions (green).



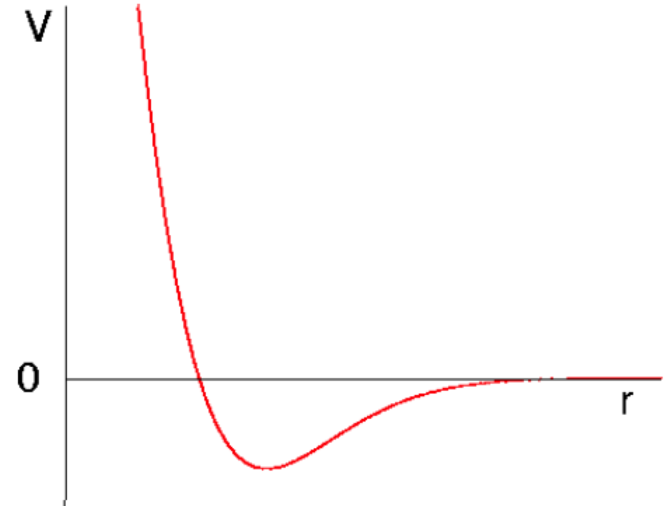
Mohamed Zbiri et al. Probing Dynamics of Water Mass Transfer in Organic Porous Photocatalyst Water-Splitting Materials by Neutron Spectroscopy (2021). https://doi.org/10.1021/acs.chemmater.0c04425

How to get fundamental information on Interactions in condensed phases ?

Structural probes

information by locating

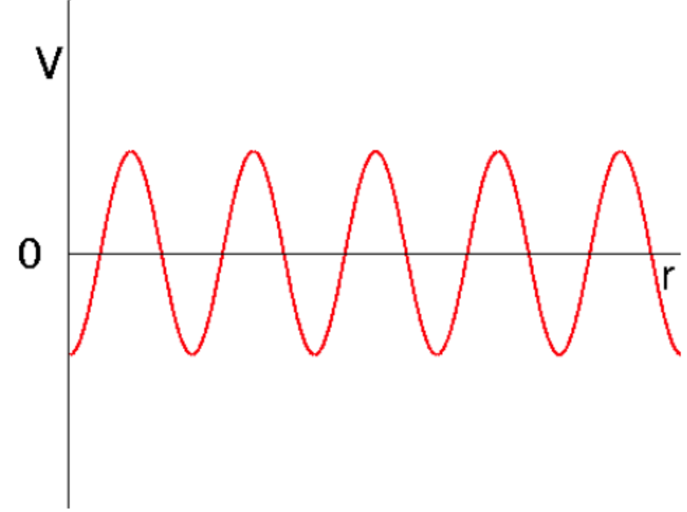
the minimum of the potential



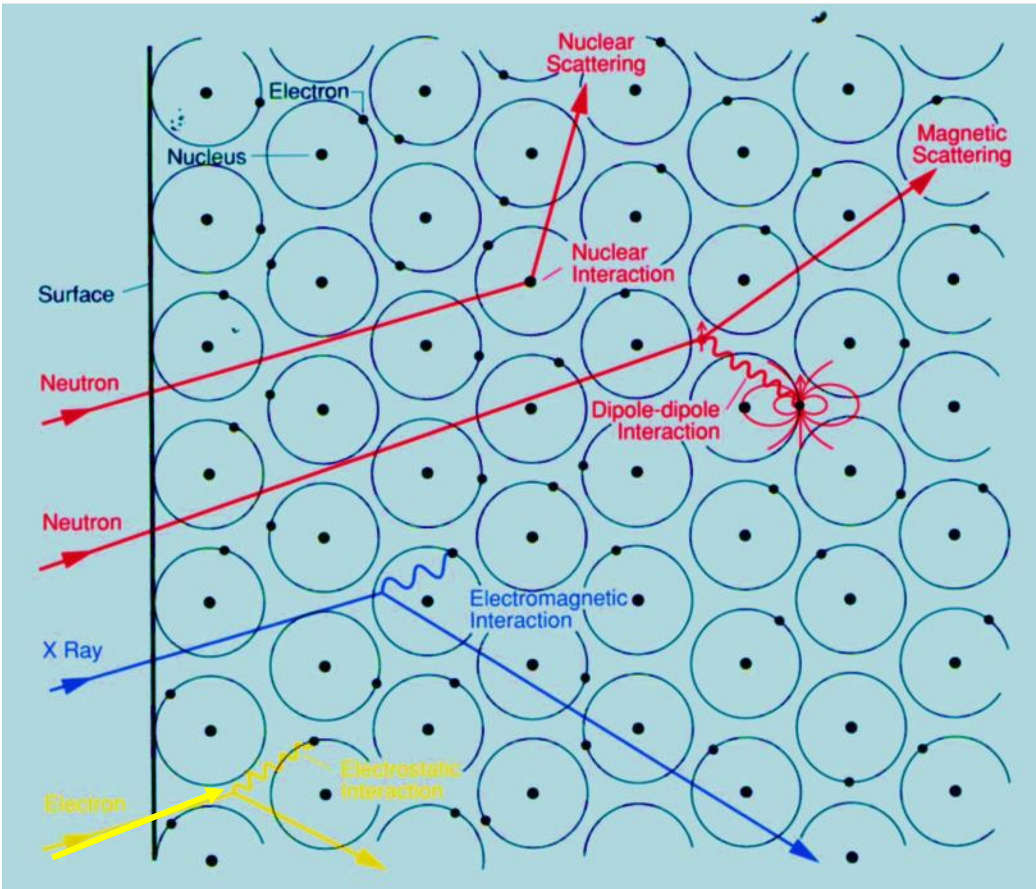
Dynamical probes

information on

the shape of the potential



Probes and Matter : Interactions Mechanisms

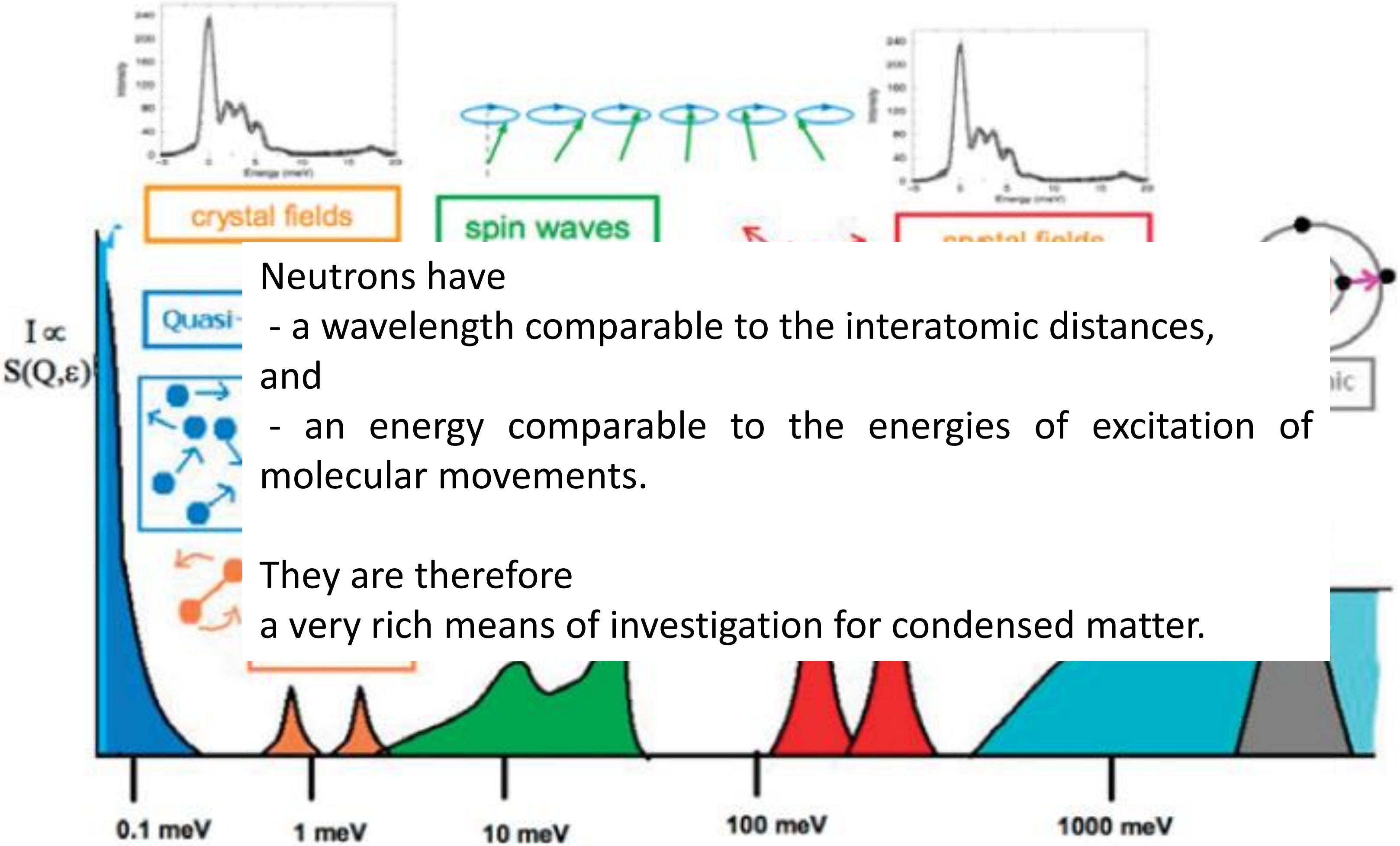


- Neutrons interact with atomic nuclei via very short range (~fm) forces.
- Neutrons interact with unpaired electrons via magnetic dipole interaction.
- X-rays interact with electrons via an electromagnetic interaction

Probes (Waves) ➡ observables via interactions ➡ property

its response to a perburbation ➡ specific phenomenon or application

EXPLORING VARIOUS TYPES OF MOTIONS -INS (from T. Perring)



Neutrons have

- a wavelength comparable to the interatomic distances,

and

- an energy comparable to the energies of excitation of molecular movements.

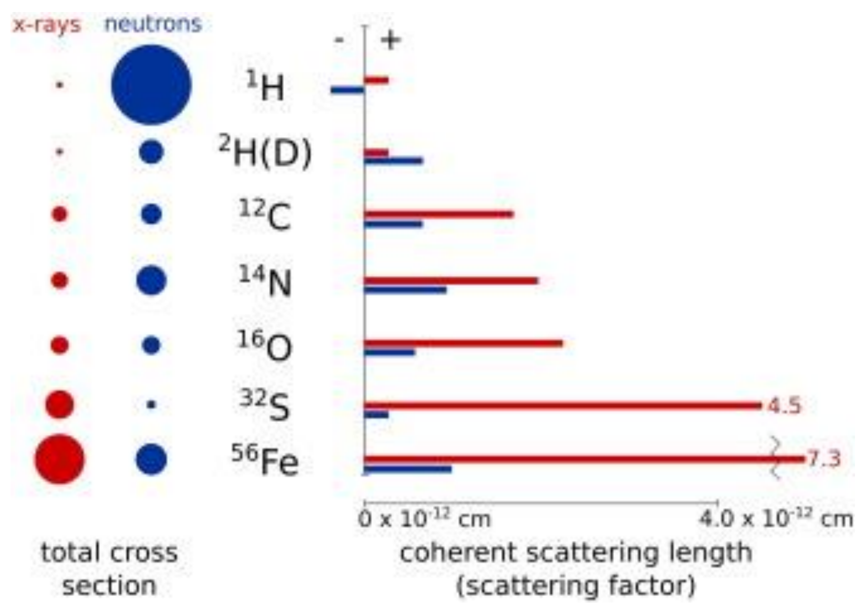
They are therefore
a very rich means of investigation for condensed matter.

Inelastic **neutron** Scattering : interaction neutron-nucleus

Neutrons: waves of particules

$$\mathcal{V}(\vec{r}) = \frac{2\pi\hbar^2}{m_n} b\delta(\vec{r} - \vec{R})$$

Fermi pseudopotential



Inelastic **X-ray** Scattering : interaction X-ray-electron

$$\mathcal{V}(\vec{r}) = \frac{q}{m_e c}\vec{p}.\vec{A}(\vec{r}) + \frac{q^2}{m_e c^2}\vec{A}^2$$

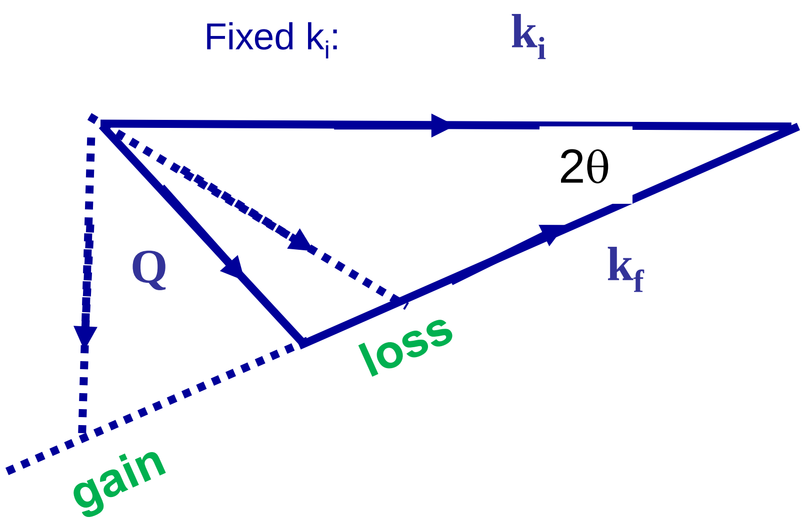
electromagnetic waves

with

the scattering triangle

exchange of energy & momentum

between the incident beam and moving particles



$$Q^2 = (\mathbf{k_i} - \mathbf{k_f}).(\mathbf{k_i} - \mathbf{k_f})$$
$$= k_i^2 + k_f^2 - 2k_i k_f \cos 2\theta$$

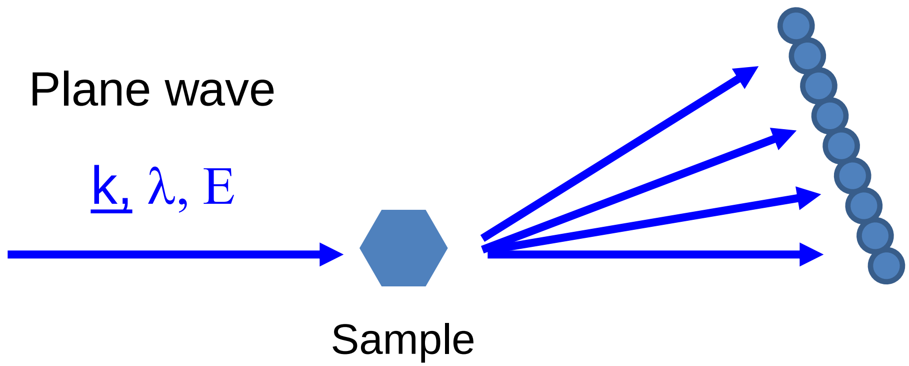
Elastic scattering

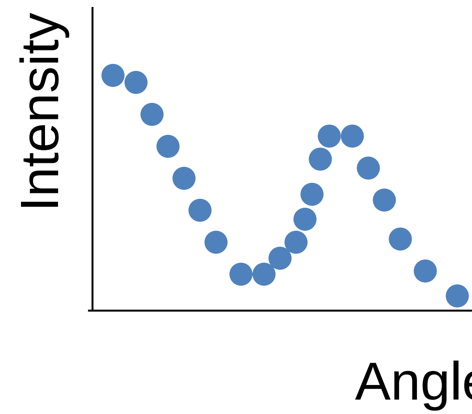
Quasielastic scattering is characterized by energy transfer peaks centered at zero energy (with finite widths).

Inelastic scattering is characterized by energy transfer peaks centered at finite energy (μev to meV)

What do we measure?

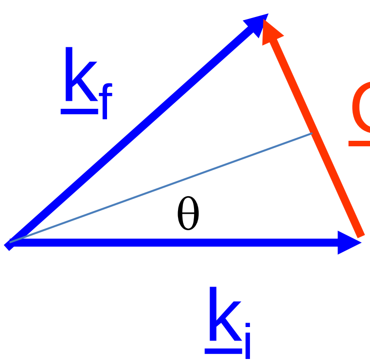
Elastic case





λ Wave length of the particule,

$\vec{k}$ = wavevector of magnitude $2\pi/\lambda$ that points along the trajectory of the particule, magnitude of the wavevector, k, is related to the neutron velocity, v, by the equation $|k| = 2\pi vm/h$, momentum $mv = hk/2\pi$.



$\underline{Q} = \underline{k}_f - \underline{k}_i$

momentum transfer at the collision

$$h\vec{Q}/2\pi = h(\vec{k} - \vec{k'})/2\pi$$

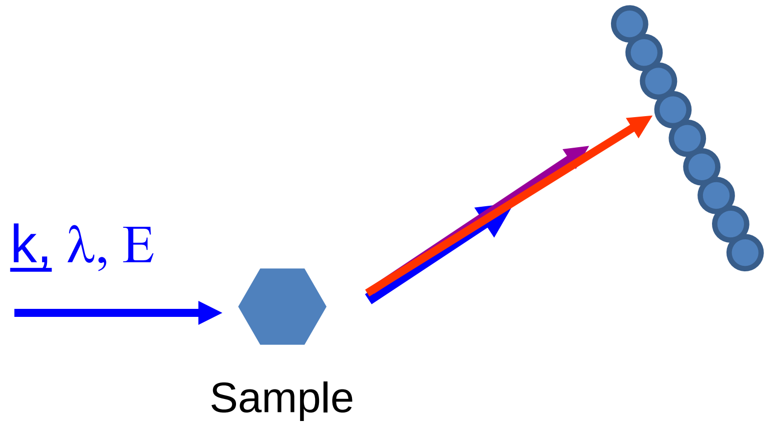
scattering vector $\vec{Q}$

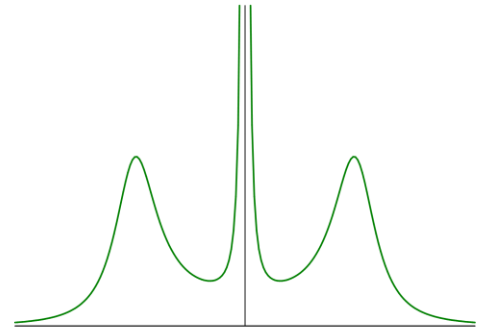
$$Q = 4\pi \sin\theta/\lambda$$

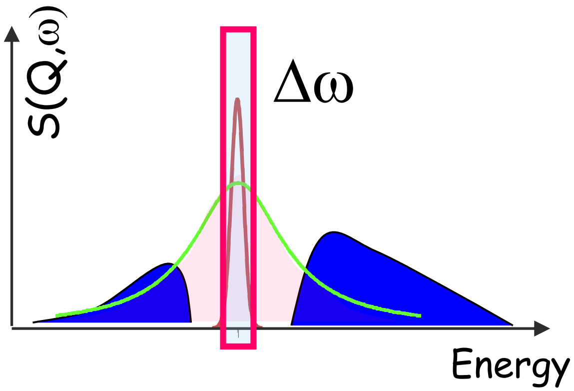
$|k_f| = |k_i|$ "Elastic" scattering $I(\underline{Q})$

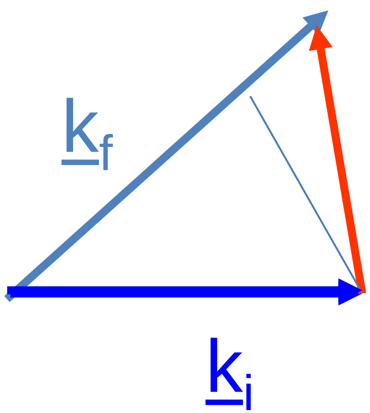
Quasi-Inelastic case

What do we measure?







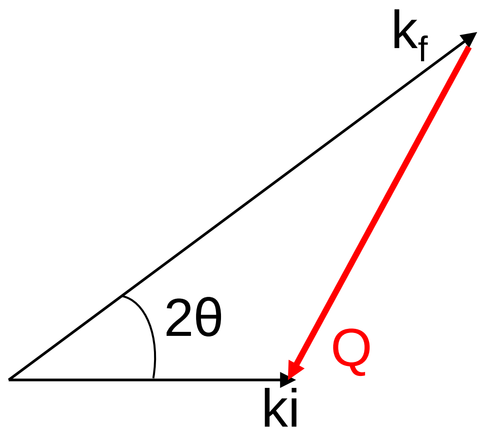


$\underline{Q} = \underline{k}_f - \underline{k}_i$ momentum transfer

$\hbar\omega = \underline{E}_f - \underline{E}_i$ Energy transfer

$|k_f| \neq |k_i|$ "Inelastic" scattering $I(\underline{Q}, \omega)$

Comparison neutrons, X rays and light



$\mathbf{Q} \equiv \mathbf{k_f} - \mathbf{k_i}$

$Q^2 = k_f^2 + k_i^2 - 2|\mathbf{kf}||\mathbf{ki}| \cos 2\theta$

$\hbar\omega \equiv E_f - E_i$

$Q_{el} = 2|\mathbf{kf}| \sin (2\theta/2)$
$= (4\pi/\lambda) \sin 2(\theta/2)$

Neutrons:

$$E = \frac{h^2}{2m_n}\left(\frac{1}{\lambda}\right)^2$$

E (meV) = 81.81/ λ^2

X Rays and Light scattering:

$$E = hc\left(\frac{1}{\lambda}\right)$$

E(keV) = 12.4 / λ

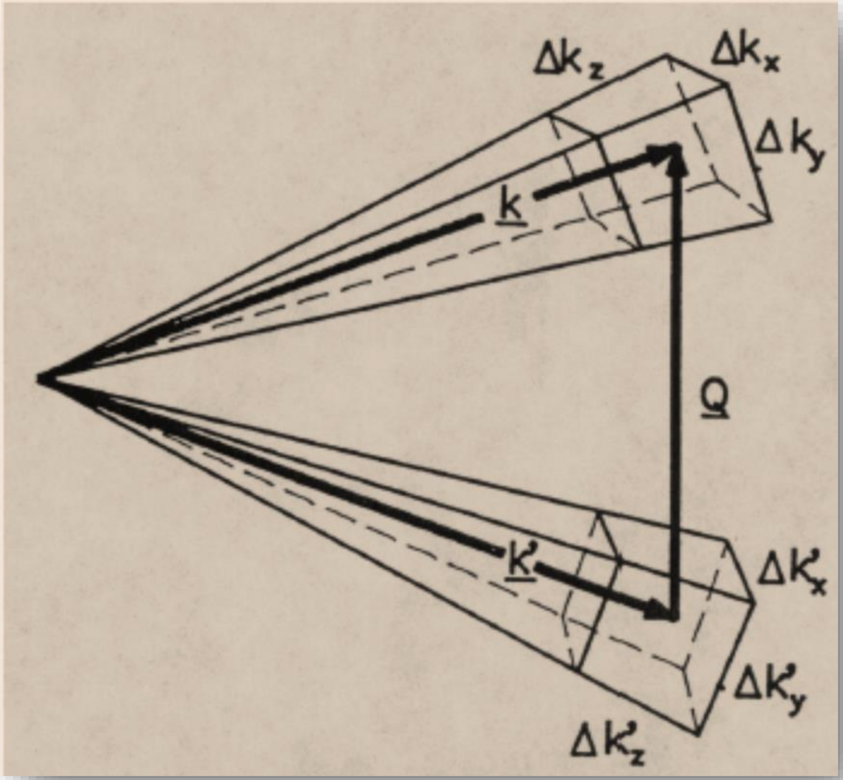
Energy conservation

(λ in Å)

1meV= 8.1 cm^{-1}=11.6 K

Instrumental resolution :
The better the resolution, the lower the count rate

Uncertainties in the neutron/X-ray wavelength and direction of travel imply that Q and w (or E) can only be defined with a certain precision



When the box-like resolution volumes in the figure are convoluted, the overall resolution width is the quadrature sum of the box sizes
Small 'boxes' =good resolution

The total signal in a scattering experiment is proportional to the product of the 'box' sizes

A part of the neutron flux is **transmitted** (the largest) with a probability Pt

A part of the neutron flux is **absorbed with a probability Pa**

A part of the neutron flux is scattered (the smallest) with a probability Ps

$$Pt + Pa + Ps = 1$$

Transmission = ratio between the emerging neutron flux /incident flux
need at least T=80% to neglect multiple scattering.

Different kinematic limitation

For **neutrons** :

$$E_{neutron} = \frac{\hbar^2 Q^2_{neutron}}{2m_{neutron}}$$

Neutron cannot lose more than its initial kinetic energy & momentum must be conserved !
Energy and momentum transfer are interdependent

Note :
For **photons** :
c = speed of light.

$$E_{photon} = \hbar \; c \; Q_{photon}$$

Intermolecular energy meV, while Xray energy is keV
No kinematic limitation for inelastic X-ray scattering
Inelastic X-ray scattering has therefore given access to a domain in energy-Q-space which where not accessible by neutrons.

Inelastic Neutron scattering Specific Methods
quasi-elastic and inelastic

motions { **0.1psec to 500nsec**
.5meV à 20meV
1000Å à 1 Å } Several instruments

Triple axis Spectrometer

Time of Flight Spectrometer
Backscattering Spectrometer

Neutron spin Echo Spectrometer (NSE and NRSE)
Based on the Fourier time analysis of the scattered intensity (time domain)

High energy spectrometer (DINS, up to 20eV, 200$Å^{-1}$)
Deep Inelastic Neutron Scattering or Neutron Compton Scattering
in analogy with Compton scattering of photons

New opportunities with ESS 2025

How/What do we measure ?
Cross Sections

probability that a neutron (E_0, k_0) is scattered ($E_0+\hbar\omega$, k)

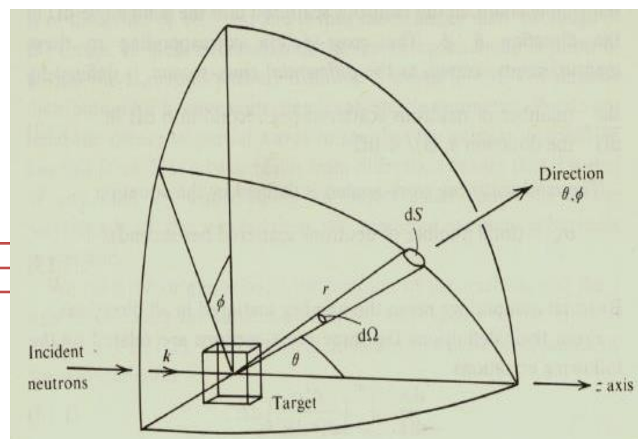
$$\frac{d^2\sigma}{d\Omega\, dE} = \frac{1}{\Phi_0} \frac{\text{Nb of Neutrons scattered per sec in } d\Omega \text{ and } dE}{d\Omega\, dE}$$

Incident Neutron flux =
Nb of neutrons per second and surface unit

in barns per steradian and unit of energy

1 barn = 10^{-24} cm^2

Φ_0 $\vec{k}_0$ E_0



Momentum Transfert

$$\vec{Q} = \vec{k} - \vec{k}_0$$

Energy Transfert

$$\hbar\omega = E - E_0$$

σ =total number of neutrons scattered per second/ Φ_0

Convention

ħω > 0 if the neutron gives energy to the system

Doble differential cross sections and *Dynamic Structure Factor*

INS

$$\frac{\partial^2 \sigma}{\partial E \partial \Omega} = b^2 \frac{k_1}{k_2} S(\vec{Q}, E)$$

- **strong correlation between momentum- and energy transfer**
- Δ E/E = 10^{-1} to 10^{-2}
- Cross section ~ b^2
- Weak absorption => multiple scattering
- incoherent scattering contributions
- **large beams: several cm**

E or ω

N.B. In an alternative notation the energy transfer is written $\hbar\omega = E$ and the scattering function $S(Q,\omega) = \hbar S(Q,E)$

Dynamic Structure Factor

$$I(\vec{Q},\omega) = b_{coh}^2 \frac{k'}{k} NS(\vec{Q},\omega)$$

$$S(\vec{Q},\omega) = \frac{1}{h} \iint G(\vec{r},t) e^{i(\vec{Q}.\vec{r}-\omega t)} d\vec{r} dt$$

$$S_i(\vec{Q},\omega) = \frac{1}{h} \iint G_s(\vec{r},t) e^{i(\vec{Q}.\vec{r}-\omega t)} d\vec{r} dt$$

Inelastic coherent scattering measures correlated motions of atoms

Inelastic incoherent scattering measures self-correlations, e.g., diffusion, VDOS

Related to density-density fluctuations; easily calculated by molecular simulations

Correlation functions and Scattering functions

For a given number density of atoms at r $\rho(\vec{r},t) = \sum_j \delta\left(\vec{r} - \vec{R}_j(t)\right)$

pair correlation function

Probability to find a particule at $(\vec{r}, t)$
Knowing that there was one at $(\vec{O}, O)$

N scatterers

$$G(\vec{r},t) = \frac{1}{N} \int \left\langle \rho(\vec{r}',0)\, \rho(\vec{r}'+\vec{r},t) \right\rangle d\vec{r}'$$

$$= \frac{1}{N} \sum_{jj'} \int \left\langle \delta\left[\vec{r}' - \vec{R}_j(0)\right] \delta\left[\vec{r}' + \vec{r} - \vec{R}_{j'}(t)\right] \right\rangle d\vec{r}'$$

autocorrelation function (self)

$$G_s(\vec{r},t) = \frac{1}{N} \sum_{j} \int \left\langle \delta\left[\vec{r}' - \vec{R}_j(0)\right] \delta\left[\vec{r}' + \vec{r} - \vec{R}_{j}(t)\right] \right\rangle d\vec{r}'$$

dim : 1/volume

What are the observables?

Dynamical structure factor
S(q,w)

$$\frac{d^2\sigma}{d\Omega d\omega} \equiv \frac{b^2}{\hbar}\frac{k}{k_0} S(q,\omega)$$

Pair correlation function
time dependent
(Van Hove)

$$G(r,t) = \frac{1}{2\pi^2}\int_0^\infty F(q,t)\cdot\frac{\sin qr}{qr}\cdot q^2 \cdot dq$$

Intermediate Scattering function

$$F(q,t) = \int_{-\infty}^{\infty} S(q,\omega)\cdot\cos\omega t \cdot d\omega$$

Scattered intensity can be split in 2 terms
coherent and incoherent

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right) = \left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{coh} + \left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{inc}$$

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{coh} = \frac{1}{2\pi\hbar}\frac{k}{k_0}\frac{\sigma_c}{4\pi}\sum_{jj'}\int_{-\infty}^{+\infty}\left\langle e^{-i\vec{Q}\vec{R}_j(0)}\, e^{i\vec{Q}\vec{R}_{j'}(t)}\right\rangle e^{-i\omega t}\, dt \qquad j\neq j'$$

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{inc} = \frac{1}{2\pi\hbar}\frac{k}{k_0}\frac{\sigma_i}{4\pi}\sum_{j}\int_{-\infty}^{+\infty}\left\langle e^{-i\vec{Q}\vec{R}_j(0)}\, e^{i\vec{Q}\vec{R}_{j}(t)}\right\rangle e^{-i\omega t}\, dt$$

Neutrons : Coherent and Incoherent scattering

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

$$\overline{b} = f_+ b_+ + f_- b_-$$

$$\overline{b^2} = f_+ b_+^2 + f_- b_-^2$$

$$\sigma_{coh} = 4\pi \left(\overline{b}\right)^2$$

$$\sigma_{inc} = 4\pi \left[\overline{b^2} - \left(\overline{b}\right)^2\right]$$

$$\sigma_S = \sigma_{coh} + \sigma_{inc}$$

σ's are Q independant

	H	**D**
I	1/2	1
I+½	1	3/2
I-½	0	1/2
b_+ (10^{-12}cm)	1.085	0.953
b_- (10^{-12}cm)	-4.750	0.098
f_+	3/4	2/3
f_-	1/4	1/3
$b = \overline{b}$ (10^{-12}cm)	-0.374	0.668
$\overline{b^2}$ (barn)	6.523	0.609
σ_{coh} (barn)	1.758	5.607
σ_{inc} (barn)	79.81	2.04
σ_s (barn)	81.67	7.65

Local vibrations and phonons

VDOS vibrationnal density of states

$$\left(\frac{d^2\sigma}{dE_f d\Omega}\right)_{\text{inc}} = \frac{N\sigma_{\text{i}}}{8\pi m}\frac{k_f}{k_i}Q^2 e^{-2W(\vec{Q})}\frac{G(\omega)}{\omega}(n(\omega)+1)$$

$$\int_{Q_{\min}}^{Q_{\max}} \left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}(\hbar\omega)\mathrm{d}\Omega}\right)_{\text{coh}} Q\mathrm{d}Q \approx \int_{Q_{\min}}^{Q_{\max}} \left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}(\hbar\omega)\mathrm{d}\Omega}\right)_{\text{inc}} Q\mathrm{d}Q$$

Incoherent approximation

Heat capacity at low T

$$c_{\text{p}}(T) \simeq c_{\text{V}}(T) = N_{at}R\int d\omega g(\omega)\frac{(\beta/2)^2}{\sinh^2(\beta/2)}, \beta = \hbar\omega/k_{\text{B}}T$$

Neutrons Inelastic Scattering
Why ?

excitations

(Q,w) space Dispersion curves
Vibrational Density of states
Limitations and complementarity

diffusion and relaxations

dynamic structure factor
Pair correlation functions
Coherent and incoherent scattering

excitations

INS :A direct measure of the dispersion relation of acoustic and optical phonons

- crystalline solids, glasses, amorphous, liquids, gazes

a reflection of forces acting upon atoms and leads to

- sound velocity: V_s, V_p
- vibrational entropy, S_v
- specific heat, C_p
- force constant, **<F>**
- compression tensor, c_{11}, c_{12}, c_{44}
- Young's modulus, **E**
- Shear modulus, **G**
- stiffness and resilience
- Gruneisen constant, **γ**
- viscosity, **η**

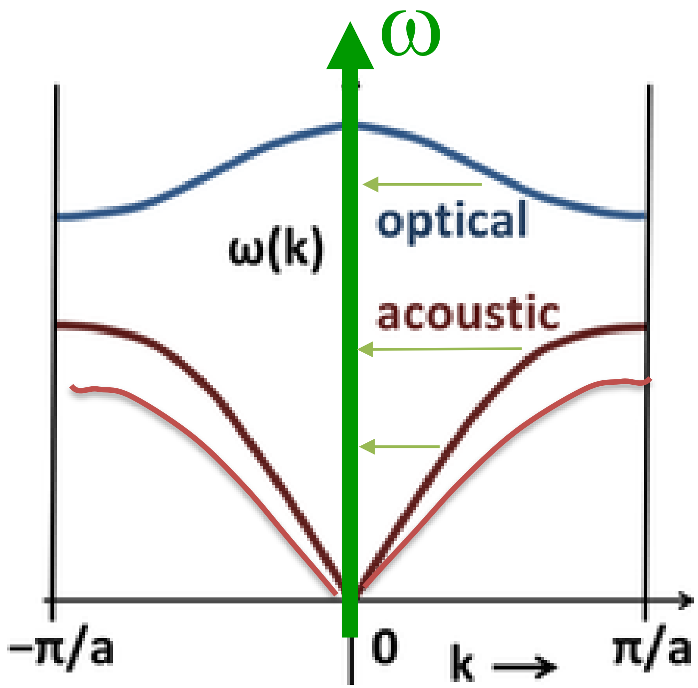
and Phase transition and critical phenomena (soft mode …)

Many complementary techniques exist • sound velocity, deformation, thermal expansion, heat capacity….

spectroscopic methods using light DLS, x-rays and neutrons, and electrons

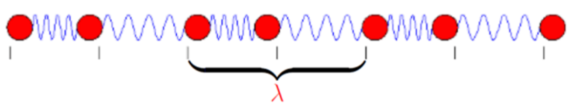
Energy and Momentum are connected through dispersion relation :

$$\omega(\vec{q})$$

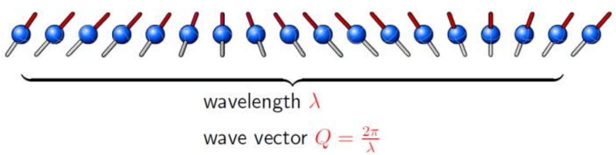


collective modes :

Phonons,



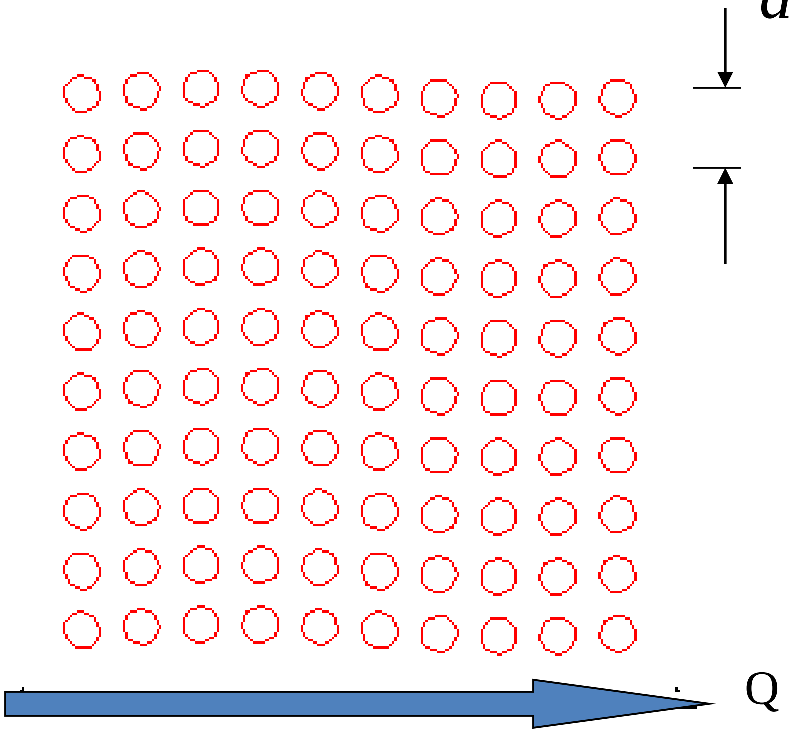
Magnons, …



Excitation	Crystal Field	Magnon	Phonon
Energy	~ 1 meV	~ 10 meV	10-100 meV

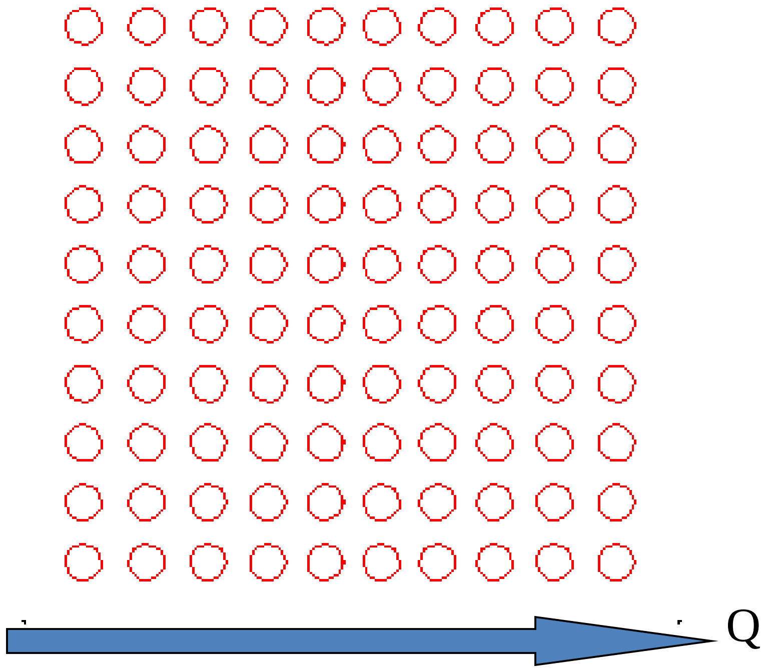
Atomic Motions for Longitudinal & Transverse Phonons

$$\vec{Q} = \frac{2\pi}{a}(0.1,0,0)$$



Transverse phonon

$$\vec{e}_T = (0,0.1,0)a$$



Longitudinal phonon

$$\vec{e}_L = (0.1,0,0)a$$

$$\vec{R}_l = \vec{R}_{l0} + \vec{e}_s e^{i(\vec{Q}.\vec{R}_l - \omega t)}$$

A Phonon is a Quantized Lattice Vibration

- Consider linear chain of particles of mass M coupled by springs. Force on n' th particle is

$$F_n = \alpha_0 u_n + \alpha_1(u_{n-1} + u_{n+1}) + \alpha_2(u_{n-2} + u_{n+2}) + \ldots$$

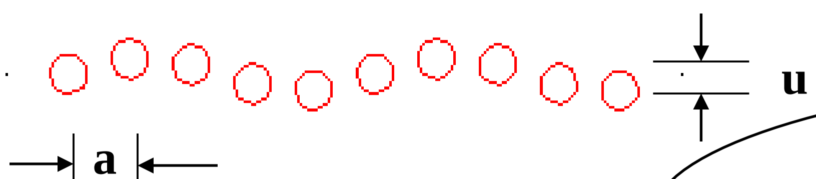
First neighbor force constant — displacements

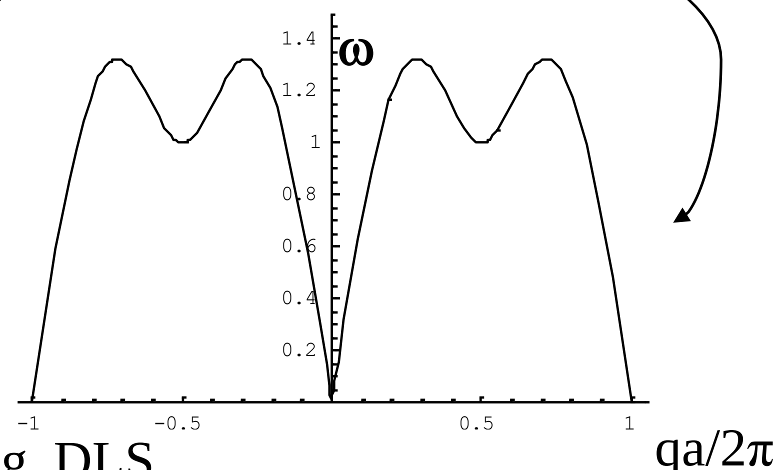
- Equation of motion is

$$F_n = M\ddot{u}_n$$

- Solution is: $u_n(t) = A_q e^{i(qna-\omega t)}$ with $\omega_q^2 = \frac{4}{M}\sum_\nu \alpha_\nu \sin^2(\frac{1}{2}\nu qa)$

$$q = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots\ldots \pm\frac{N}{2}\frac{2\pi}{L}$$

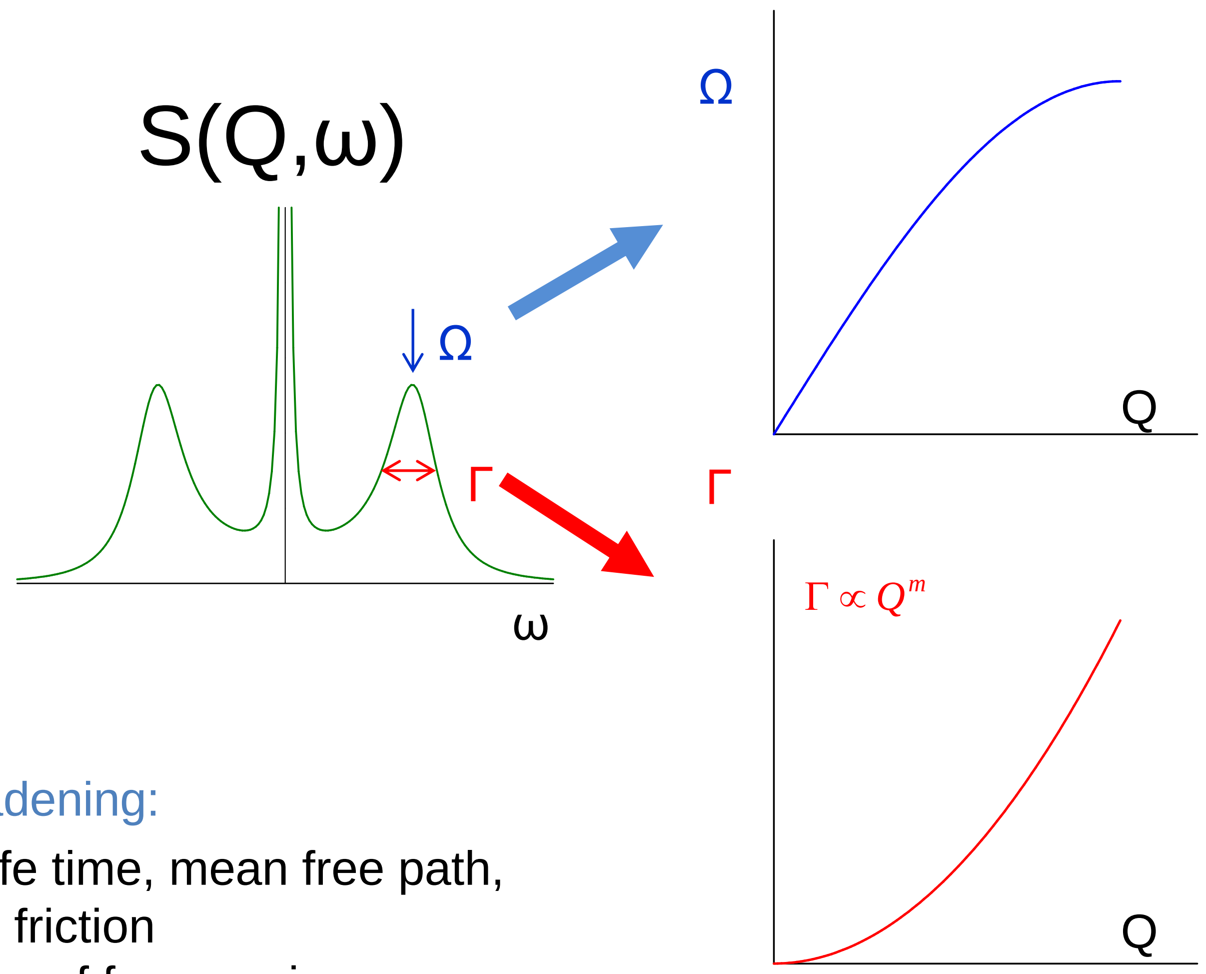




Phonon Dispersion Relation:
Measurable by inelastic neutron and Xray scattering, DLS

How / What do we measure ?

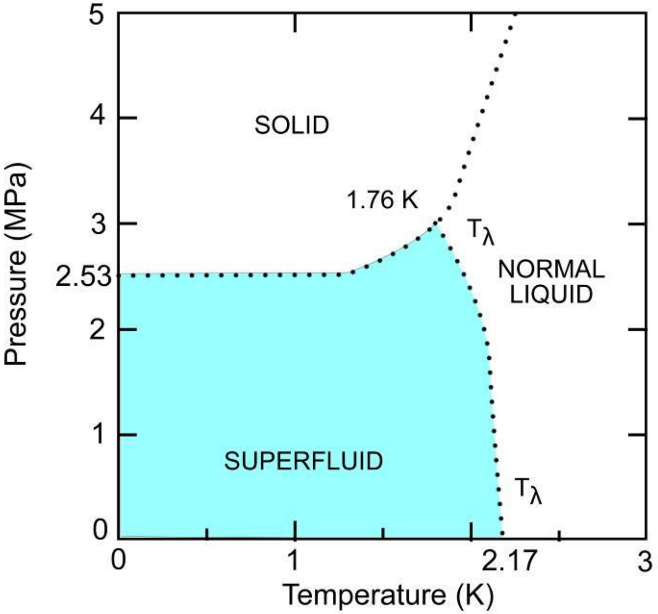
Brillouin line broadening (DLS low Q's, IXS, INS, coherent), acoustic lines

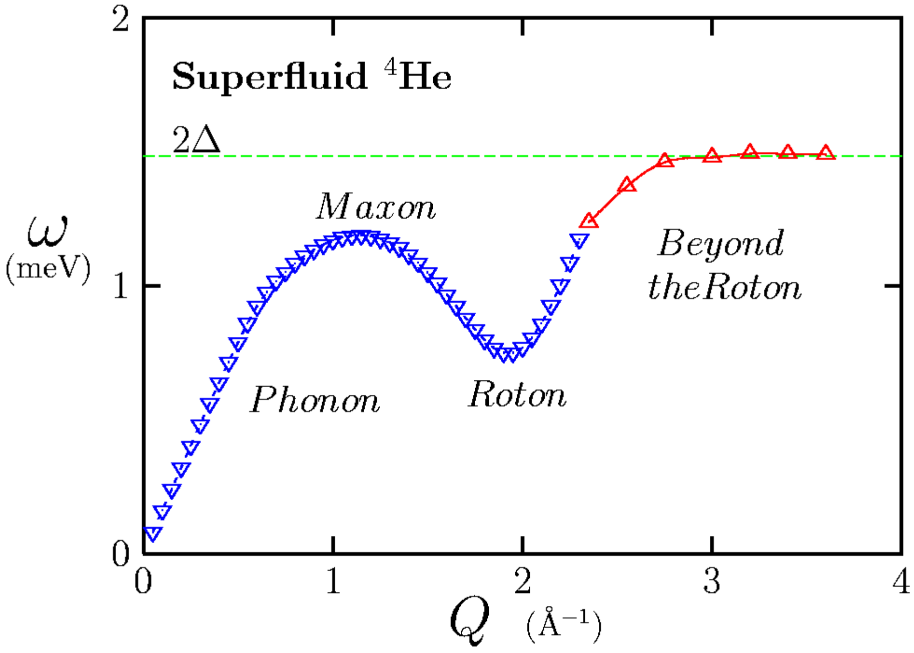


Line broadening:

phonon life time, mean free path,
damping, friction
distribution of frequencies

Roton Minimum in Superfluid ^{4}He was Predicted by Landau

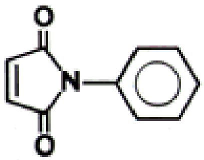


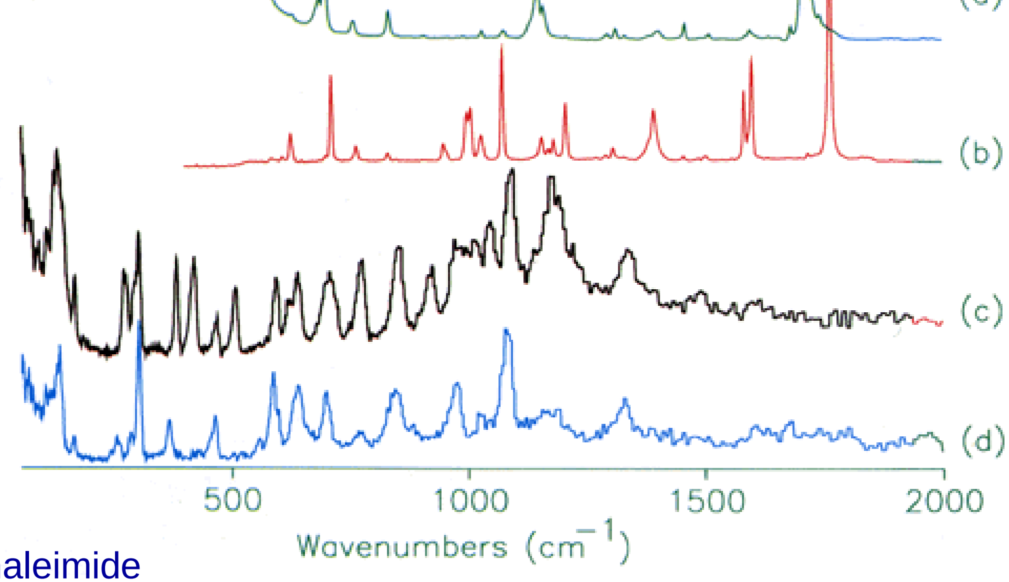


Indirect geometry – high energy

Gives similar information to Raman and infra-red

- No selection rules
- Simple interpretation of cross-section
- Element and isotope dependent





a) Infrared
b) Raman
c) INS spectra of N-phenylmaleimide
d) INS spectrum of N-(perdeuterophenyl)maleimide

TOSCA spectrometer (ISIS)

Vibrational and lattice excitations

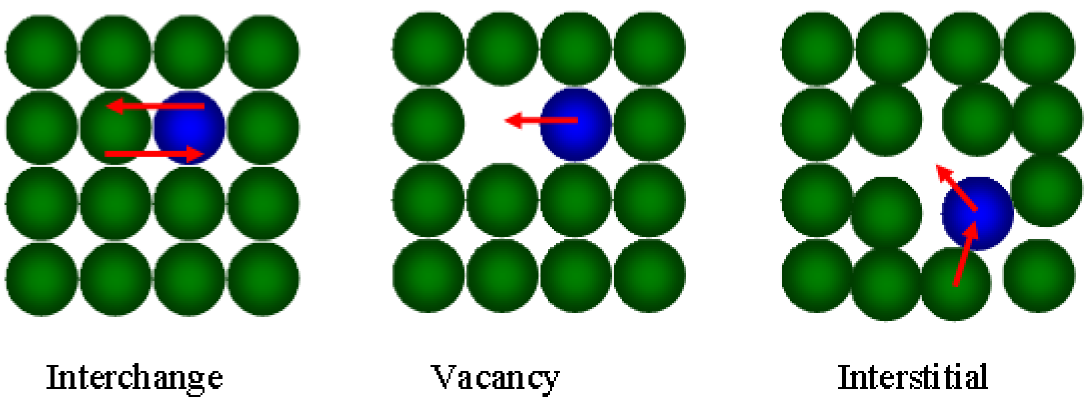
and

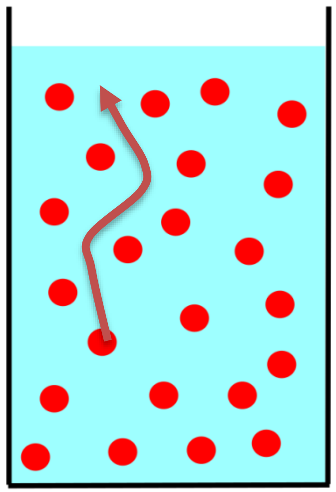
Diffusion, relaxation processes

In crystals and amorphous solids

In liquids, solutions, polymers, gels….

Various diffusion mechanisms

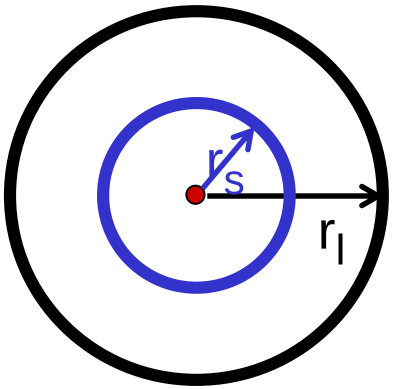




$$\mathbf{D} = \lim_{t\to\infty} \frac{1}{6t} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$$

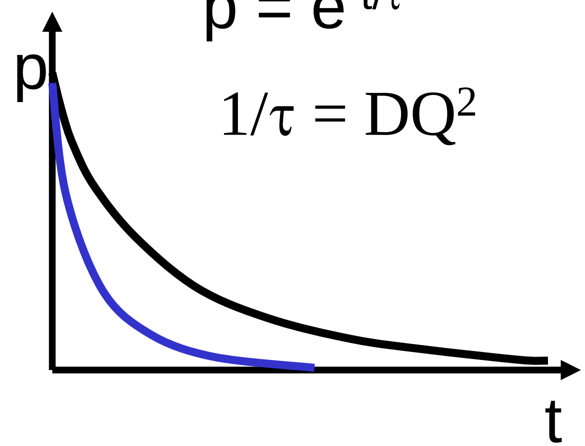
What do we measure ?

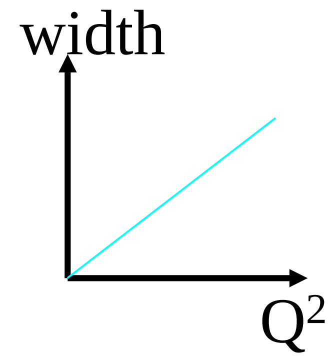
- For a single diffusing particle, the probability, p, of finding it within a sphere around its starting position looks like….



$p = e^{-t/\tau}$

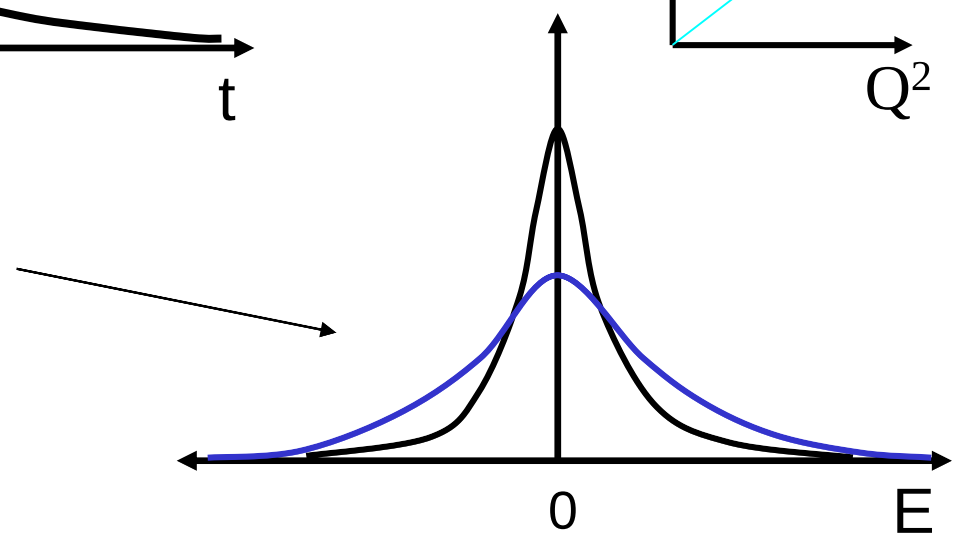
$1/\tau = DQ^2$





- $S_{inc}(Q,E)$ is the time Fourier transform of this probability

$$S_{inc}(Q,E) = \frac{\hbar}{\pi}\frac{DQ^2}{(\hbar DQ^2)^2 + E^2}$$



Jump Diffusion at large Q (M.Bée book)

τ_0 residence time in a given site

$$S_{inc}(Q,\omega) = \frac{1}{\pi}\frac{f(Q)}{\left(f(Q)\right)^2+\omega^2} \qquad \text{with} \quad f(Q) = \frac{DQ^2}{DQ^2\tau_0+1}$$

Elastic Incoherent Structure Factor

Rotational Diffusion

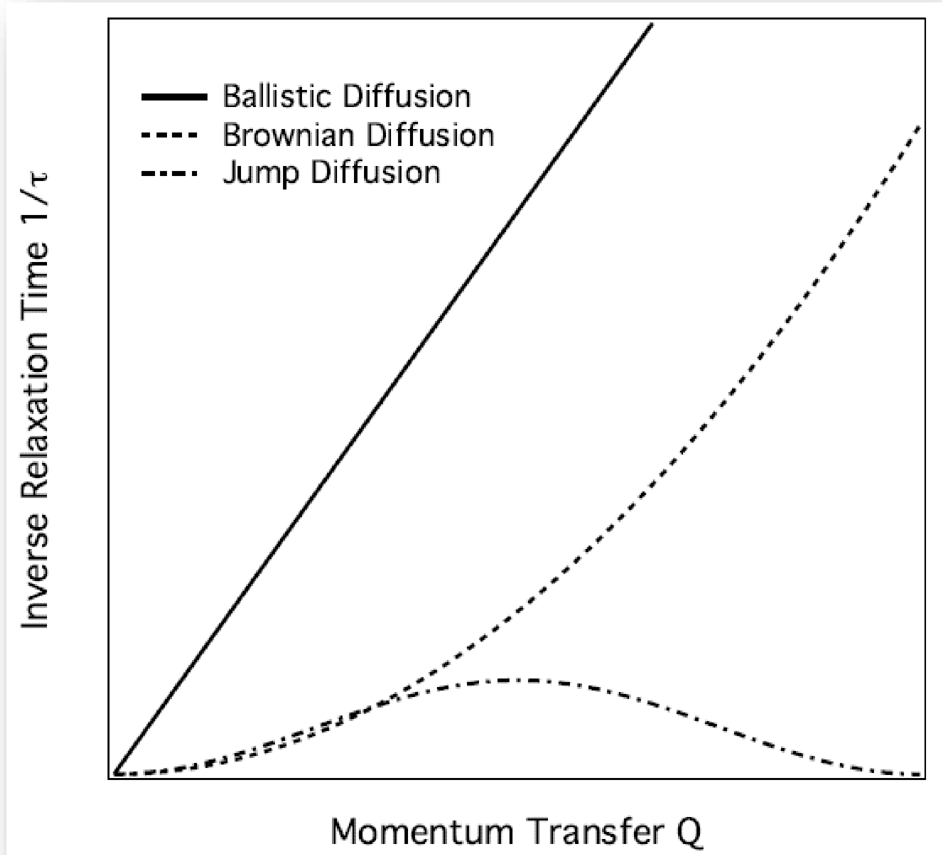
Uni dimensional Diffusion

molecules in channels, membranes

$$\boldsymbol{S_{1D}(Q,\omega) = \tfrac{1}{2\pi}\int_0^{\pi}\frac{DQ^2\cos^2\theta\sin\theta}{\left(DQ^2\cos^2\theta\right)^2+\omega^2}d\theta}$$

For d~σ, single file diffusion

An exemple on metallic liquids



diffusion processes (self) in quasi-elastic spectra :
broadening or inverse relaxation times versus momentum transfer

diffusion : translational dynamics
jumps or continous

Fick' s Law 1855 $$\frac{\partial c(r,t)}{\partial t} = D\nabla^2 c(r,t)$$ D = diffusion coefficeint

macroscopic quantity

N = total nbof atoms

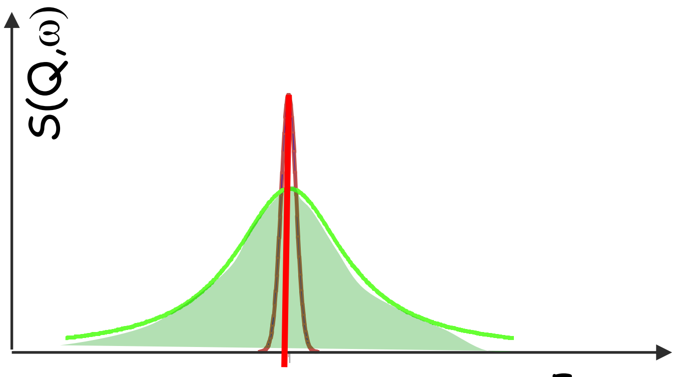
$$G_S(r,t) = c(r,t)/N$$

$$G_S(r,t) = \frac{1}{(4\pi Dt)^{3/2}}\exp\left(\frac{-r^2}{4Dt}\right)$$

microscopic

of neutrons

With Gs(r,0)=δr and Gs(r, t=∞)=0



$$F(Q,t) = \exp\left(-DQ^2 t\right)$$

$$S_{inc}(Q,\omega) = \frac{1}{\pi}\frac{DQ^2}{\left(DQ^2\right)^2 + \omega^2}$$

At large Q → jump **diffusion**

Case of liquid water

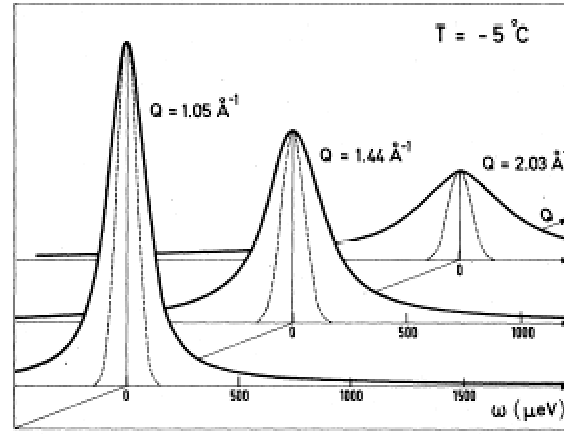


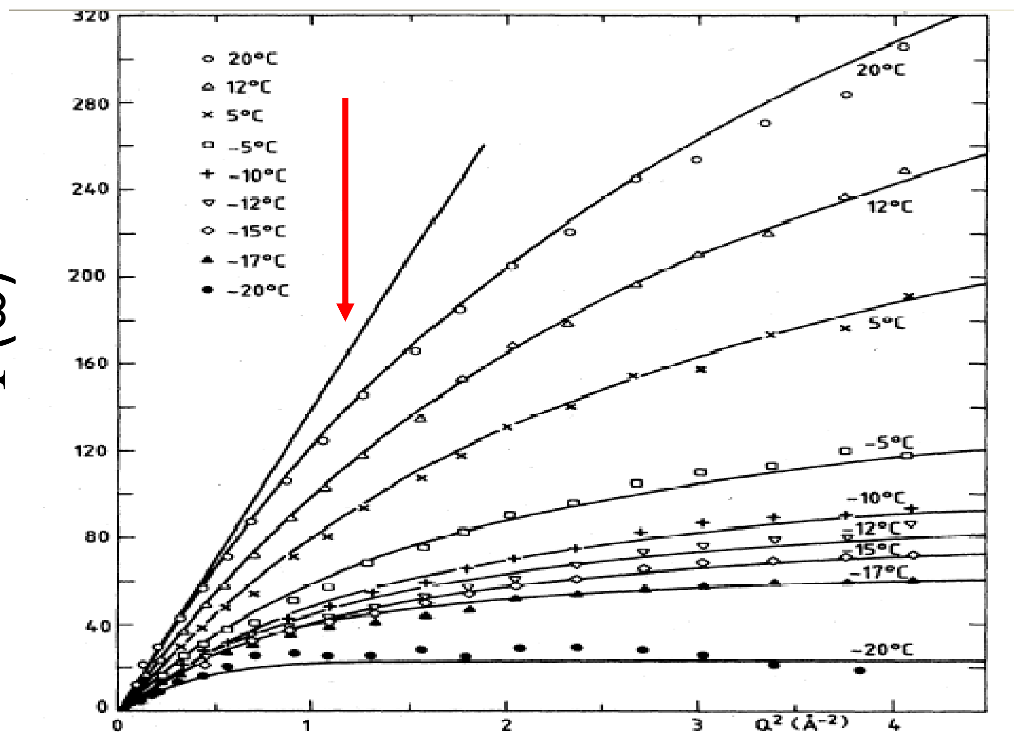
FIG. 1. Quasi-elastic incoherent neutron spectra from water at −5 °C for three different values of Q. ——: best fit. – – –: resolution function. Experimental points are within the thickness of the solid line.

Small Q:

« Macroscopic » → Fick's Law

Self Diffusion coef. D=2.5 10^{-5} cm^2/s at 298 K

$\Gamma(\omega)$



Q^2

High Q:

« Microscopic » →

residence time: t_0=1 ps

at 298 K

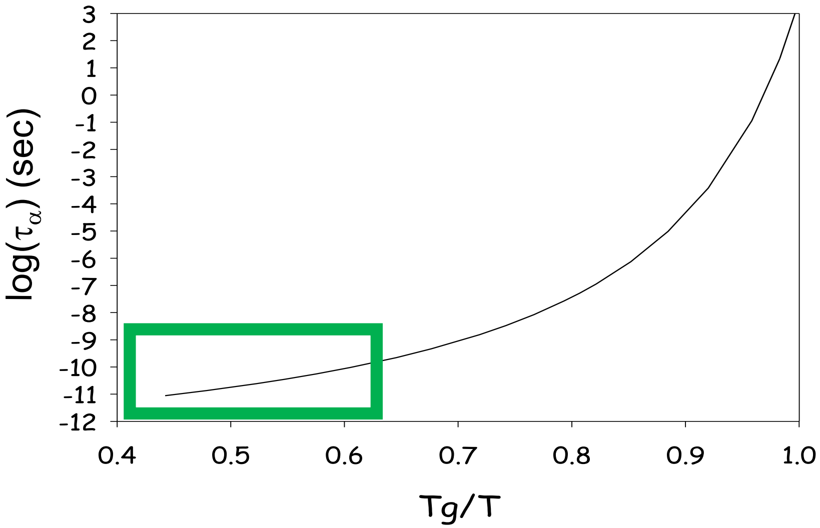
$1/t_0$

At each Q:

Data fitting by a Lorenzian

Teixeira, Bellissent-Funel & Dianoux, Phys.Rev. A, 31,1915,(1985)

Looking at relaxation time of a molecular liquid



Dynamics at pico-nano sec.

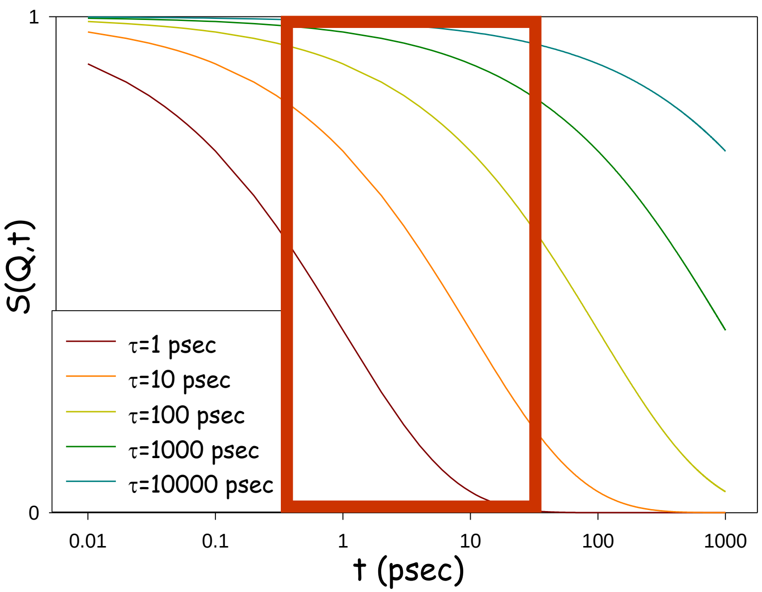
Many diffusional and relaxation processes are characterised by a Lorentzian dynamical correlation function:

$$S(\mathbf{Q},\omega) \propto \frac{1}{\Gamma^2 + (\omega - \omega_0)^2}$$

Fourier transform:

$$F(Q,t) = a * \exp(-\frac{t}{\tau})$$

Leading to a exponential decay with time



Experimental time window

However , another function is commonly used
Stretched exponential

$$S(Q,t) = \exp\left(-\left(\frac{t}{\tau_\alpha}\right)^{\beta_{KWW}}\right)$$

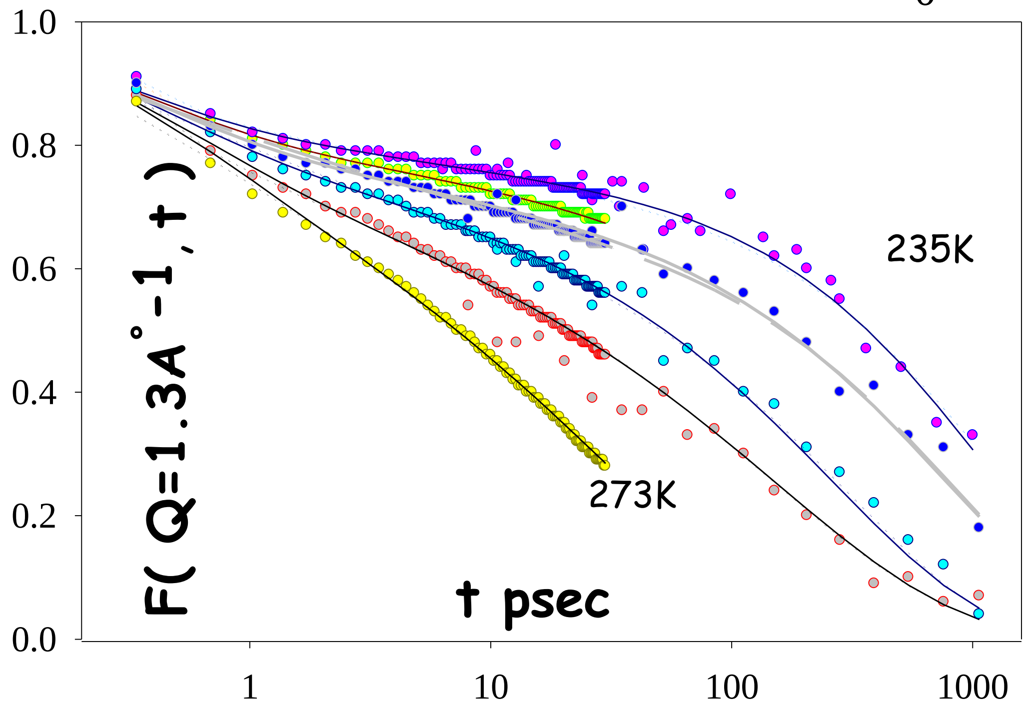
$\tau_\alpha(Q)$, $\beta_{KWW}(Q)$

a larger dynamical range for glassforming liquids

Combining ToF and NSE experiments

Fitting the generalized Langevin equations (on the basis on the Mode Coupling Theory)

$$\ddot{\phi}_i(t)+\Gamma_i\Omega_i\dot{\phi}_i(t)+\Omega_i^2\phi_i(t)+\Omega_i^2\int_0^t m_i(\mathrm{V};\phi(t-t'))\dot{\phi}_i(t')dt'=0$$



$\lambda_{sch}^{critique} < \lambda_{fit}$ asymp. laws

$T_{sch}c$ precise,
but accuracy ~Tc± 10K

Coherent Diffusion
Of a molecular liquid

Lines = schematic mode coupling theory analysis

ToF(mibemol) + NSE (IN11A)

Polymer melt Physics in « bulk »

- Segmental relaxation : short, few monomers (Tg) (Q~1A°-1, ps to s)

Long chains ($M_W > M_e$) :

- Short time & medium scale:
  Rouse Model
- Long time & large scale:
  Reptation

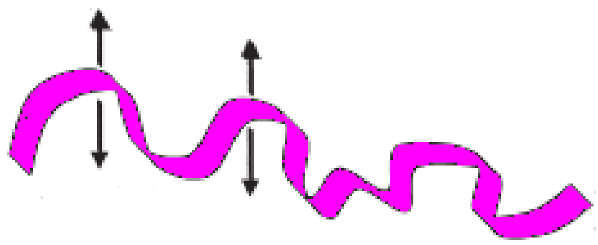
Kuhn length: ***b***
Tube diameter : ***d***

Macroscopic properties:

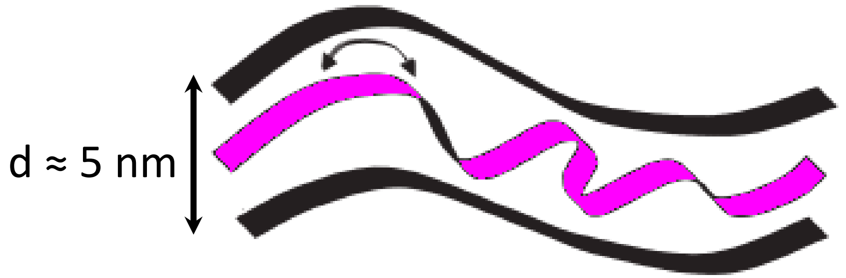
Rheology:

$$G_e \approx \frac{b^3 kT}{d^2 b}$$

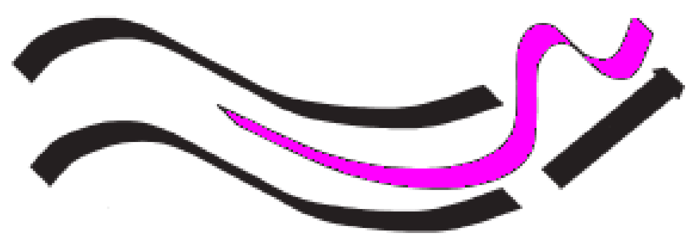
Rouse regime
(Q< .1 Å^{-1}, t ≈ 1 ns)



Local reptation
(Q< .01 Å^{-1}, t ≈ 100 ns)



Pure reptation

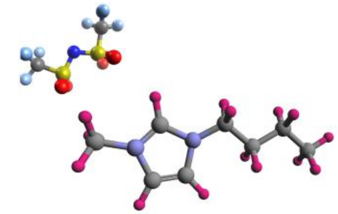


D. Richter, M.Monkenbusch, A. Arbe and J. Colmenero, *Adv Polym Sci* 174(2005) 1–

multiscale scale analysis of transport properties

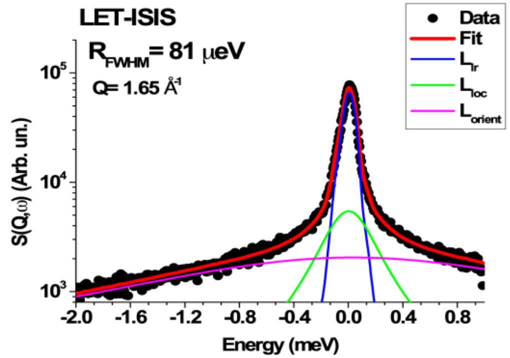
multiscale analysis : QENS + NSE + PFG NMR (BMIMTFSI)

limited to the study of cation (incoherent neutron, ^{1}H NMR)

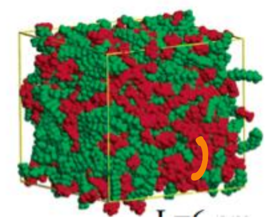


Quasi Elastic Neutron Scattering :

1-100 ps / 1-20 Å

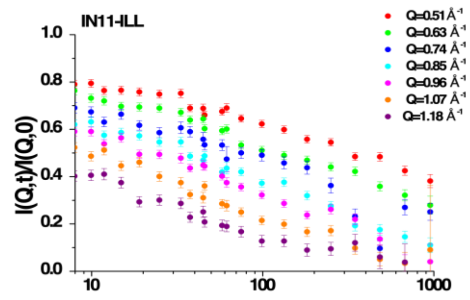


$D_{loc} = 4.8\ 10^{-9}\ m^2s^{-1}$



Neutron Spin Echo :

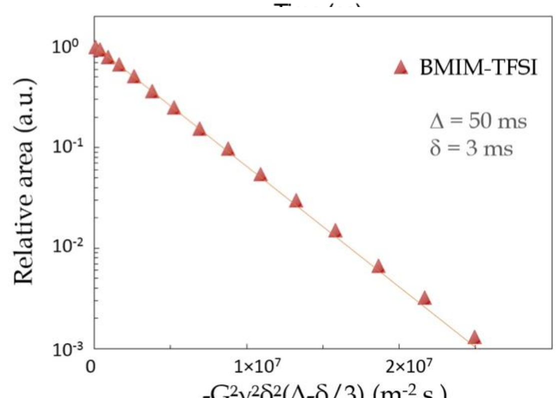
50ps-1ns / 1-50 Å



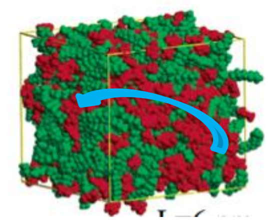
$D_{lr} = 0.16\ 10^{-9}\ m^2s^{-1}$

Pulsed Field Gradient-NMR :

1ms-1000ms / 0.5-10 μm



$D_{sd} = 0.022\ 10^{-9}\ m^2s^{-1}$



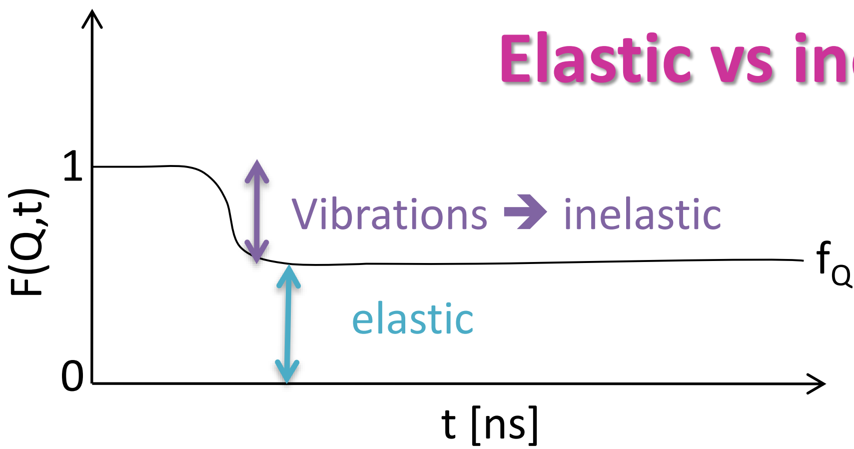
Other complementary techniques :
fluorescence, EPR, 2D-IR …

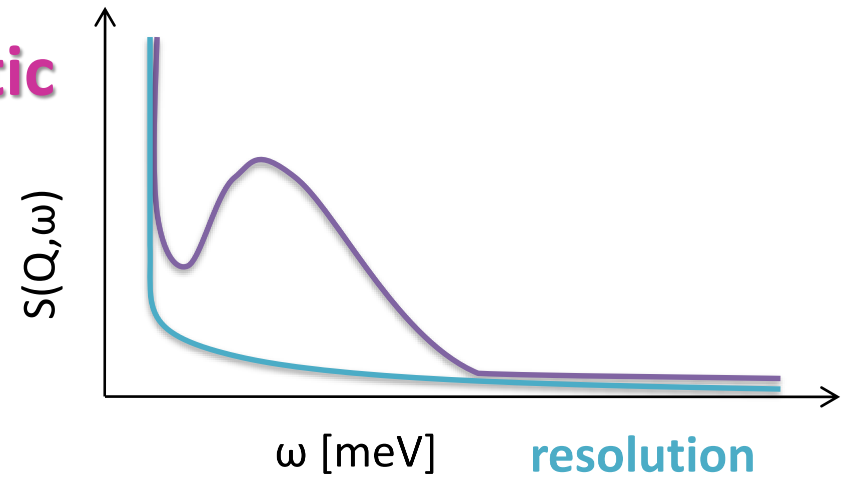
F. Ferdeghini, et al, *Nanoscale*, (9), **2017**, 1901-1908.

Q. Berrod,et al , *Scientific Reports*, (7) **2017**, (2017), 2241.

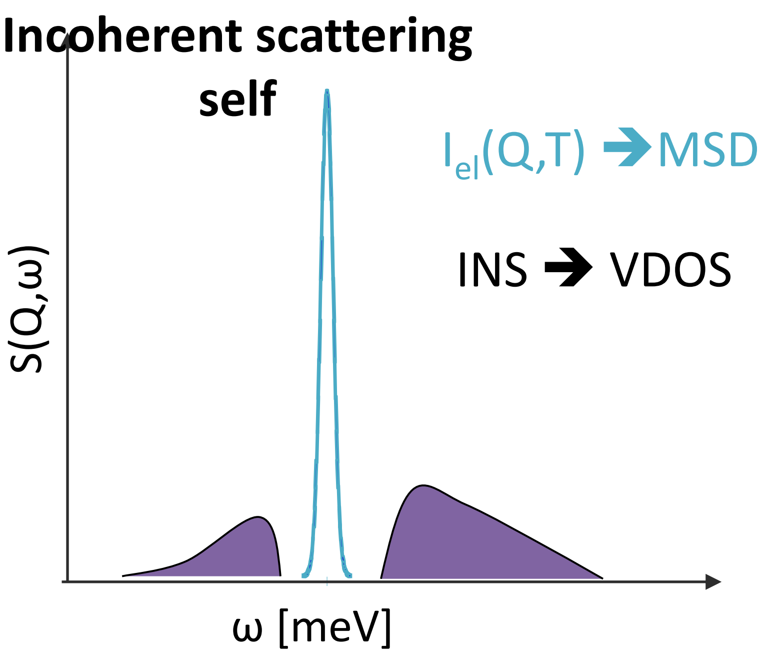
Short summary

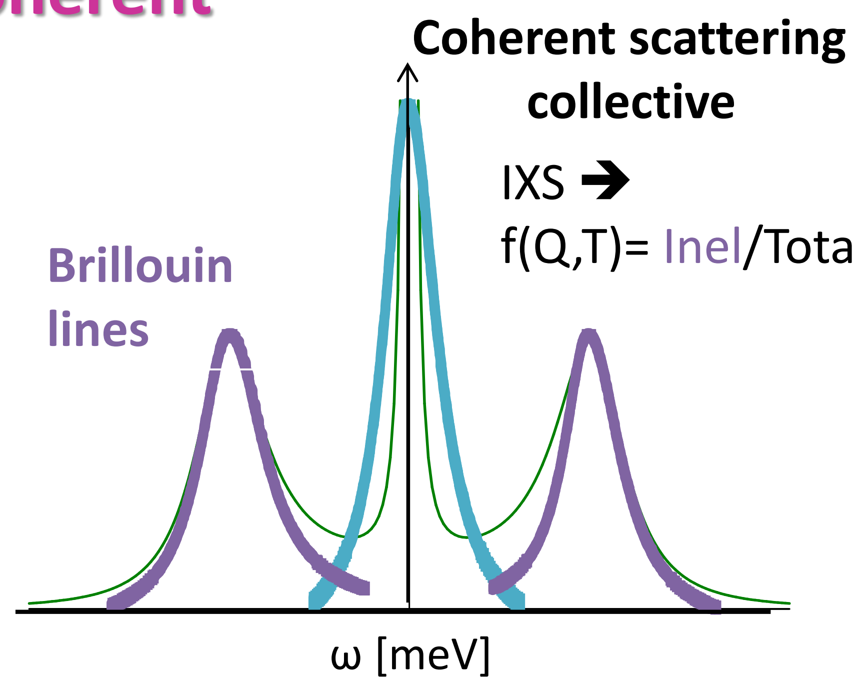
Elastic vs inelastic





coherent vs incoherent





The Elastic & Inelastic Scattering Cross Sections Have an Intuitive Similarity What are the correlation functions behind ?

- The intensity of **elastic, coherent scattering** is proportional to the spatial Fourier Transform of the **Pair Correlation Function**, **G(r)** *i.e.* the probability of finding a particle at position r if there is simultaneously a particle at r=0.
- The intensity of inelastic *coherent* **scattering** is proportional to the space *and time* Fourier Transforms of the *time-dependent* pair correlation function function, **G(r,t)** = probability of finding a particle at position r *at time t* when there is a particle at r=0 and *t=0*.

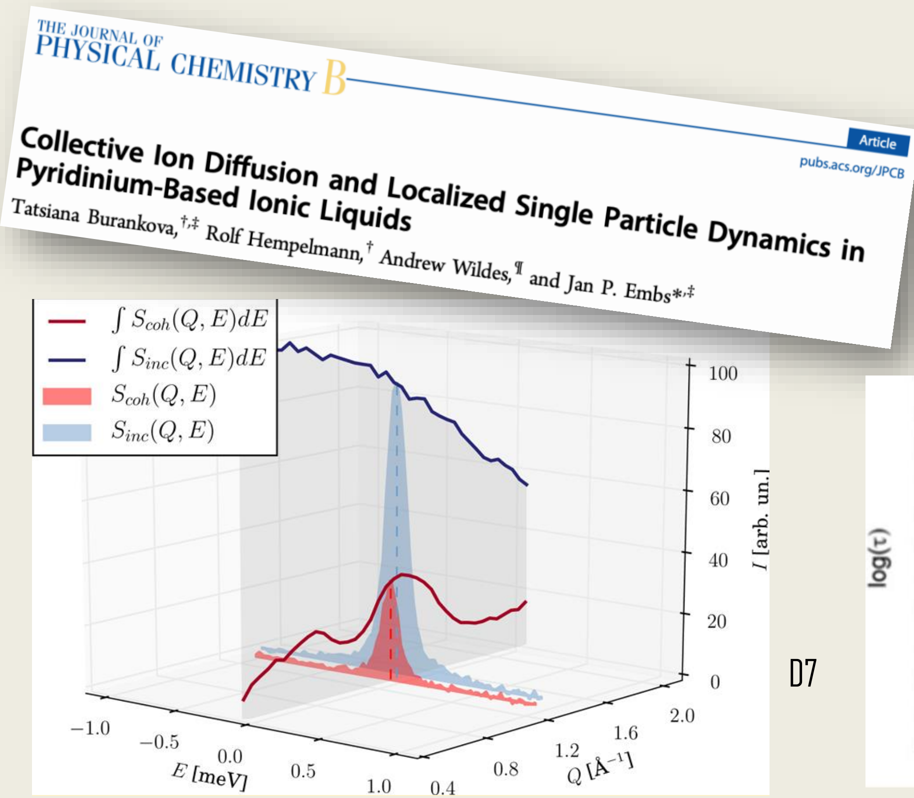
Neutrons case

For **inelastic** *incoherent* scattering, the intensity is proportional to the space and time Fourier Transforms of the ***self-correlation*** **function**, **G_s(r,t)** *i.e.* the probability of finding a particle at position r at time t when *the same* particle was at r=0 at t=0

Coherent scattering – scattering from different nuclei add in phase
Incoherent scattering – random phases between scattering from different nuclei

A solution / Cf Ross Stewart

separation of coherent and incoherent scattering, polarization analysis



D7

Burankova, *et al., J. Phys. Chem. B* **118,** 14452 (2014)

DNS

Gambino, *et al., Macromolecules* **51,** 6692 (2018)

D7 at the ILL

Take-Home Message
Be aware of each method strength and weakness is crucial

- to choose the appropriate method for the system / property of interest
- not to over-interpret the (non exact) results
- be aware on corrections and specific sample environment :

If we have a multi atomic system :
many nuclear species with different scattering lengths,
Randomly distributed scattered waves
that could destroy the interference or enhance them if they are in phase.

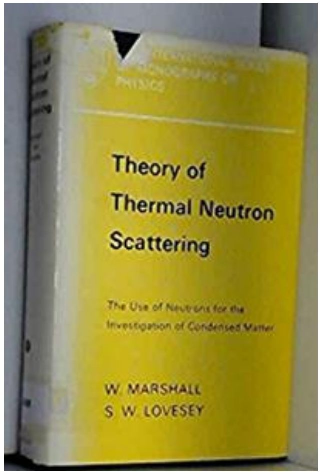
Depends on the **relative orientation**
of the spin of the neutron and the spin of the nucleus, b+ and b-
If the spins are **unpolarised** $\rightarrow$ this randomness detroys again part
of the interference

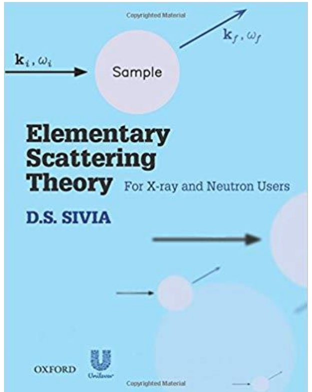
Neutron inelastic scattering : kinematics limit

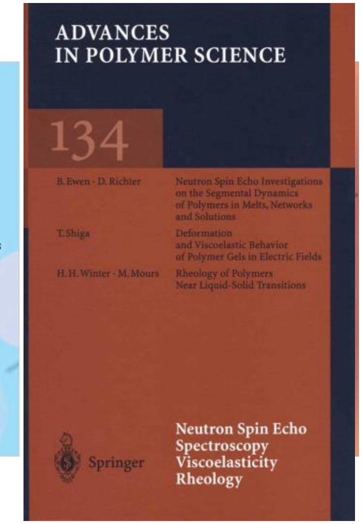
INS large Q and low energy

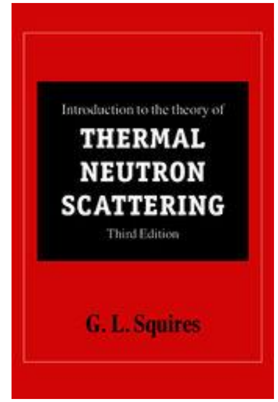
X ray inelastic scattering : no kinematics limitation IXS large w and small Q
however because of the high energy (keV) of an X-ray with λ =1A° compared to the energies of excitations (meV), experiments by IXS require very good relative energy resolution $\Delta E/E$ of 10-8

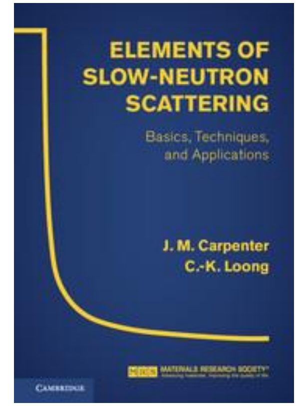
some reference books

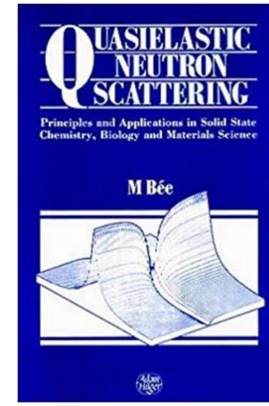


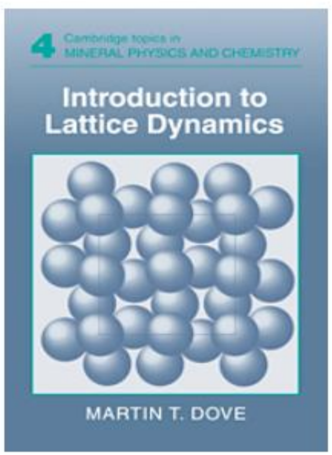


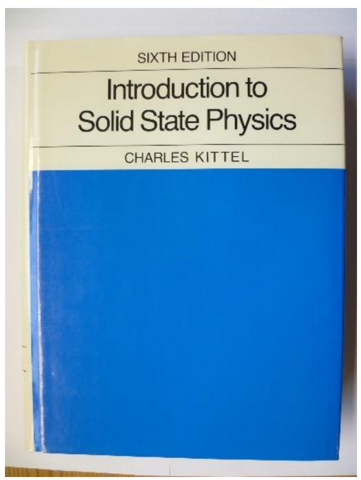


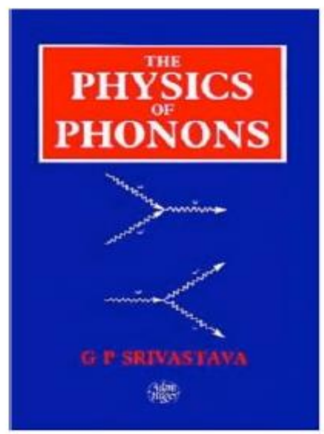


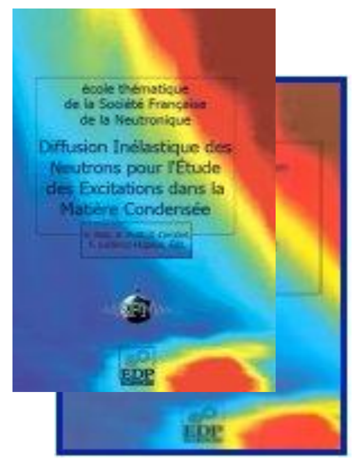


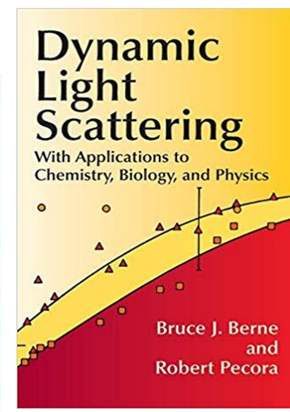












http://www.sfn.asso.fr/ecoles-thematiques/

Neutron Scattering: A Non-Destructive Microscope for Seeing Inside Matter by Roger Pynn
Available on-line at http://www.springerlink.com/content/978-0-387-09415-1

From scattering angle to Q

$$Q(\hbar\omega) = \left(\frac{2m_n}{\hbar^2} \left[2E_i - \hbar\omega - 2cos(2\theta)\sqrt{{E_i}^2 - \hbar\omega E_i} \right] \right)^{1/2}$$

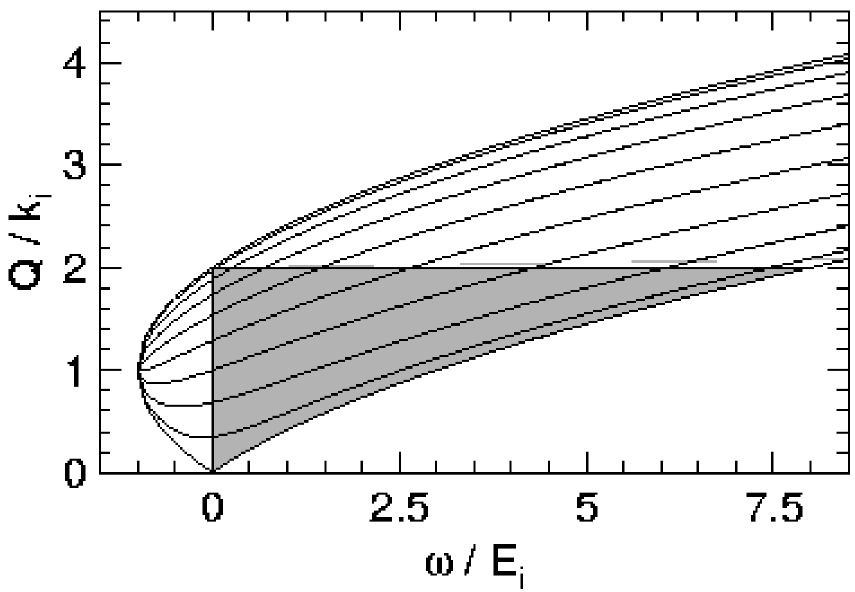
After first corrections

- Efficiency
- Normalisation with vanadium (or quartz)
- Background, empty can, cryostat..

- Absorption,selon la géométrie de la cellule
- Multiple scattering

•2θ → Q, interpolation (TOF)

(how to group detectors ? Consequences on the Q value !!)



Each detector has a parabolic trajectory through (Q, ω) space

Not necessary for
- Backscattering (low energy)
- and NSE , Q defined.

Coherent and Incoherent Scattering of Neutrons

The scattering length, b_i , depends on the nuclear isotope, spin relative to the neutron & nuclear eigenstate. For a single nucleus:

$$b_i = \langle b \rangle + \delta b_i \quad \text{where } \delta b_i \text{ averages to zero}$$

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

$$\text{but } \langle \delta b \rangle = 0 \text{ and } \langle \delta b_i \delta b_j \rangle \text{ vanishes unless i = j}$$

$$\langle \delta b_i^2 \rangle = \langle b_i - \langle b \rangle \rangle^2 = \langle b^2 \rangle - \langle b \rangle^2$$

$$\therefore \frac{d\sigma}{d\Omega} = \langle b \rangle^2 \sum_{i,j} e^{-i\vec{Q}.(\vec{R}_i - \vec{R}_j)} + (\langle b^2 \rangle - \langle b \rangle^2) N$$

Coherent Scattering
(scattering depends on the direction & magnitude of **Q**)

Incoherent Scattering
(scattering is uniform in all directions)

Note: N = number of atoms in scattering system

Same formalism for Neutrons and Xrays, but

Neutrons : $\hbar\omega_i = \frac{p_i^2}{2m} = \frac{\hbar^2 k_i^2}{2m}$

Transfered energy : $\hbar\omega = \hbar\omega_i - \hbar\omega_f = \frac{\hbar^2}{2m}(k_i^2 - k_f^2)$

Photons : $\hbar\omega_i = p_i c = \hbar c k_i$

Transfered energy : $\hbar\omega = \hbar\omega_i - \hbar\omega_f = \hbar c(k_i - k_f)$

method	**RIXS**	**IXS**	**Raman**	**Brillouin**	**InfraRed**	**Q-I Neutrons scattering**	DINS
probe	X-Ray photon	X-Ray photon	Photon	Photon	Photon	Neutron	Neutron
Incident Energy	0.5-100 keV	~10 keV	~1 eV	~1 eV	1-100 meV	1-150 meV	≤ eV
Energy transfert		1-400 meV	1-1000 meV	0.01-1 meV	1-100 meV	0.1-250 meV	Up to 200 eV

The strength of the interactions depends on the energy (initial, transferred) of the particle.
Incident energy restrains (limits) the resolution.