2nd Lecture

Introduction to Dynamic Neutron Scattering

Antonio Faraone

Center for Neutron Research, National Institute of Standards and Technology

NSF NSE Workshop October 28th, 2021

University of Delaware

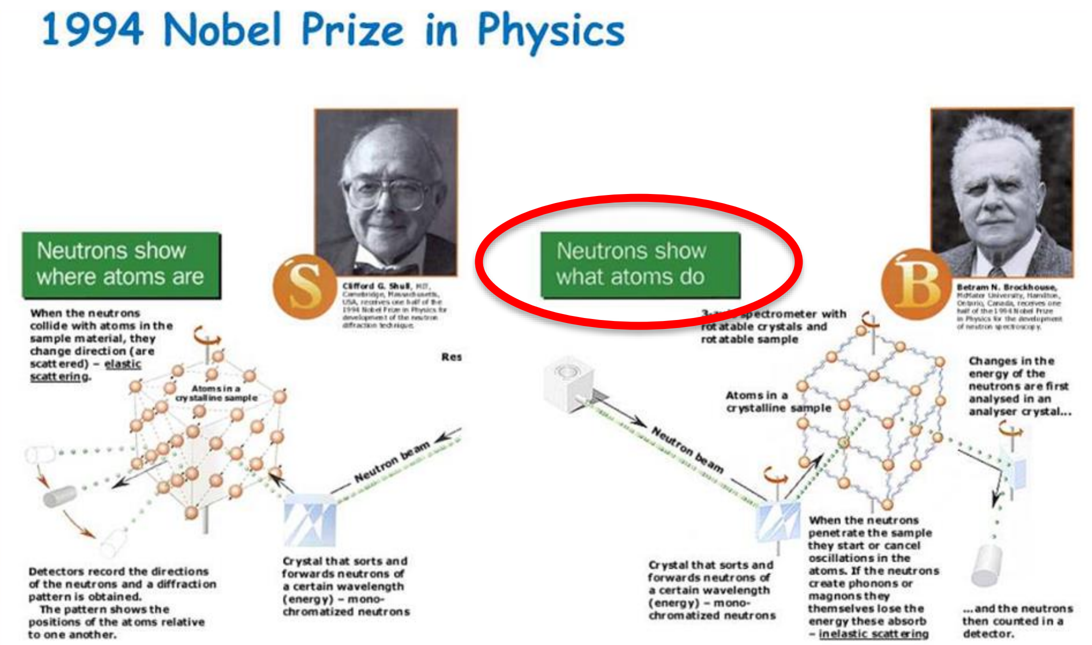
Learning Goal

- ✓ Understand the role of thermal fluctuations in dynamic scattering.
- ✓ Understand why neutrons are a good probe to study soft matter dynamics.
- ✓ Understand space-time correlation functions.
- ✓ Understand the concept of length/time scales in scattering measurement.
- ✓ Understand the meaning of static/dynamic and elastic/quasielastic/inelastic.
- ✓ Understand the concept of instrumental resolution and energy window

Outline

- Introduction
- Basic Equations of Dynamic Neutron Scattering
  - Dynamic Structure Factor, Intermediate Scattering Function, van Hove correlation functions
  - Coherent and Incoherent scattering
- Length- and Time- Scales
- General Features of Dynamic Neutron Scattering Spectra
  - Vibrations and relaxations: Inelastic, quasielastic, and elastic scattering
  - Resolution
- Conclusion

1994 Nobel Prize in Physics



http://www.nobelprize.org/nobel_prizes/physics/laureates/1994/illpres/neutrons.html (broken)
https://www.psi.ch/sites/default/files/import/sinq/hrpt/NeutronDiffractionPracticumEN/praktikum_talk.pdf

Microscopic Thermally Activated Motions

Is the water moving?

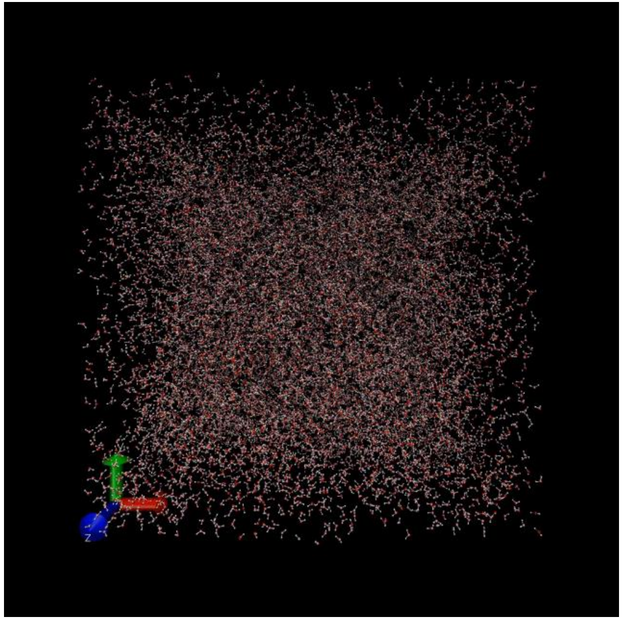
At the molecular scale water molecules diffuse, rotate, vibrate

A visual demonstration of molecular motion is the Brownian dynamics

https://www.youtube.com/watch?v=gPMVaAnij88
(Produced by the National STEM Learning Centre and Network and the Institute of Physics)

Visualizing motions at the molecular scale

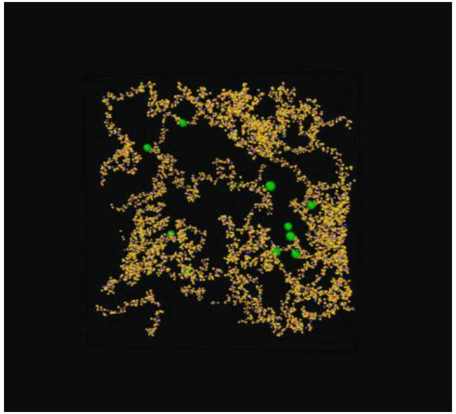
Visible light has a wavelength that does not allow nanoscale resolution. Computer simulations can provide visualization of molecular motions.



Water in methanol/water mixtures
Courtesy of Yanqin Zhai, UIUC

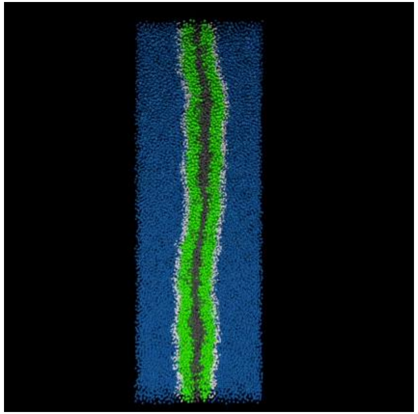
Nanoscale dynamics in soft matter

Computer simulations can also provide visualization of dynamics in soft matter systems:



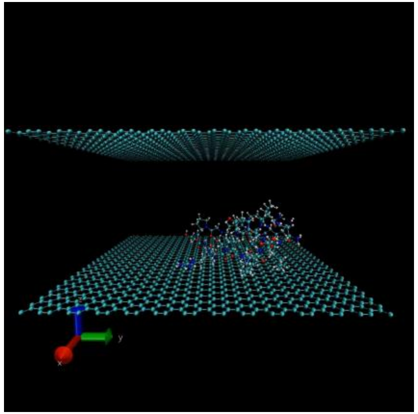
Courtesy of Michael Ohl, JCNS

Polymers



Courtesy of Takumi Hawa, OU

Membranes



Courtesy of Yanqin Zhai, UIUC

Proteins

Fluctuation examples

In a molecular liquid the energy associated with density fluctuation can be estimated as

$$E = \frac{1}{2}\delta P \delta V$$

Because of the equipartition theorem E≈ 1/2 k_BT.

Thus, the density fluctuations can be estimated as:

$$\frac{\langle \delta\rho^2 \rangle}{\rho^2} = \frac{k_B T}{V}\chi_T$$

χ_T the compressibility at constant temperature is of the order of 10^{-10} Pa-1. At room temperature over what length scale (volume) will fluctuations of the order of 10 % be observed?

Fluctuation examples II

In a macromolecular solution, the mean squared concentration fluctuation can be estimated as:

$$\frac{\langle \delta c^2 \rangle}{c^2} = \frac{k_B T}{M_W N} \frac{1}{\left(\frac{\partial \Pi}{\partial c}\right)}$$

Where M_W is the molecular mass of the particle, N is their number in the volume of interest and $\left(\frac{\partial \Pi}{\partial c}\right)$ is the osmotic compressibility.

Assume M_w=20 kg/mol, c=5 mg/cm^3 and $\left(\frac{\partial \Pi}{\partial c}\right)$=1 J/kg, over what length scale (volume) will fluctuations of the order of 10 % be observed?

Spectroscopic methods

Experimental information on the molecular motions is usually obtained through spectroscopic techniques:

- Dynamic scattering, dielectric spectroscopy, …

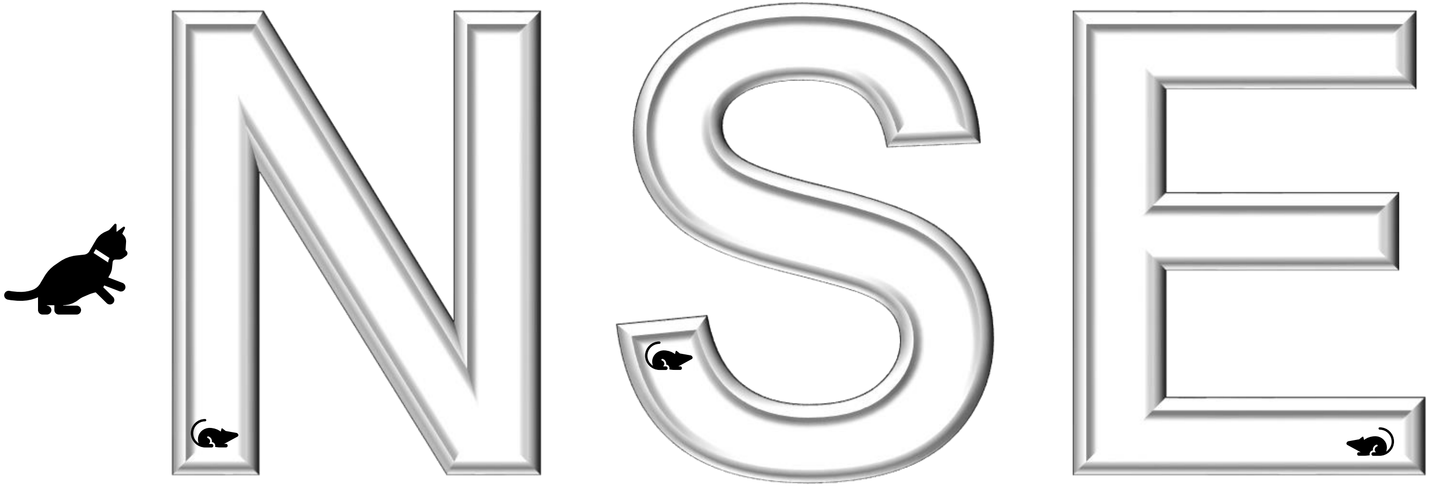
Generally speaking, spectroscopic method are based on spectral analysis of the data, i.e. as a function of frequency.

NB: These methods investigate thermally activated motions on samples at equilibrium: no stimuli, no pump-probe

Dynamic scattering

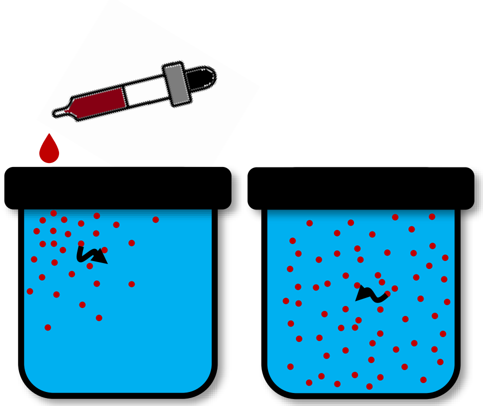
Scattering techniques determine both the time- and length scale of the motion

Gives information on the space explored as well as the time scale of the 'exploration'

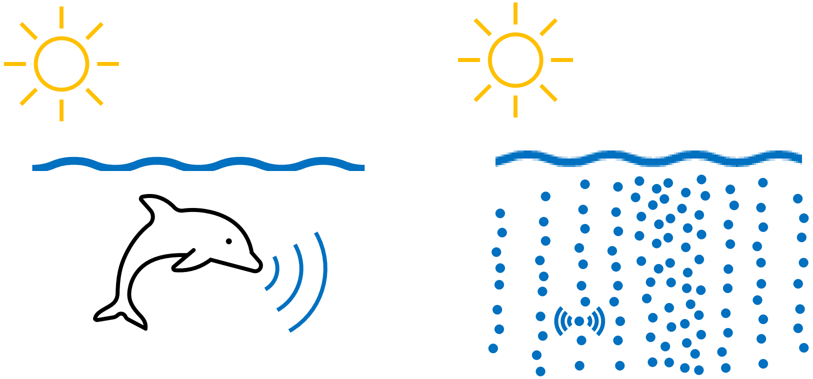


Fluctuation Dissipation Theorem

The parameters describing the microscopic thermally activated dynamics are related (the same) as the one describing the response to an external stimuli



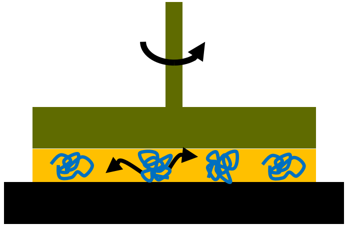
- E.g.: the diffusion coefficient of Brownian dynamics for a colloidal parti-cle is the same as the one describing transport in a concentration gradient
- E.g.: the behavior of collective density fluctuations (phonons) is governed by the same sound velocity and absor-ption coefficients as the macroscopic system

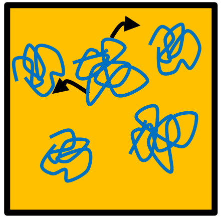


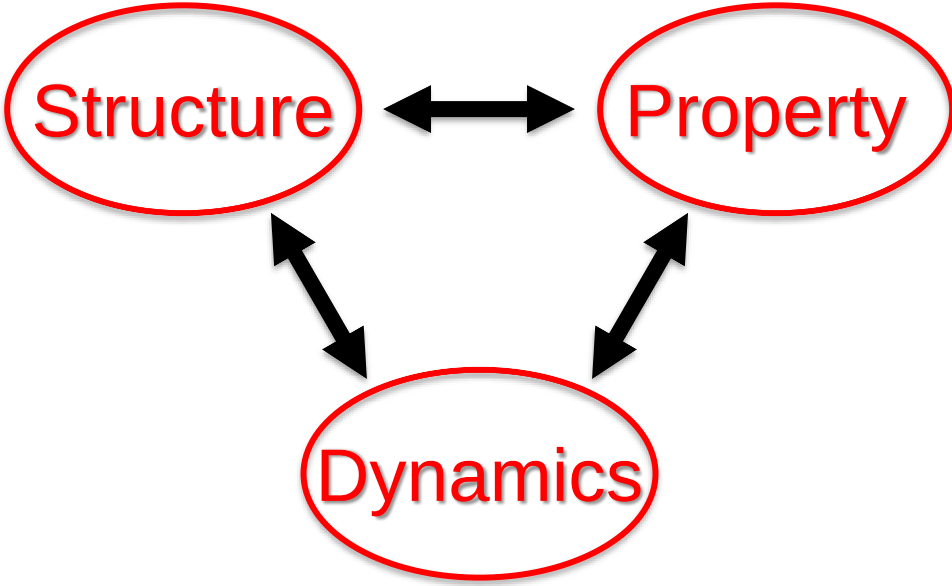
A new paradigm

In general, the microscopic dynamic properties contribute to determine the macroscopic behavior

E.g.: the conformational dynamics (Rouse motion) of polymer chains affects their viscoelastic behavior





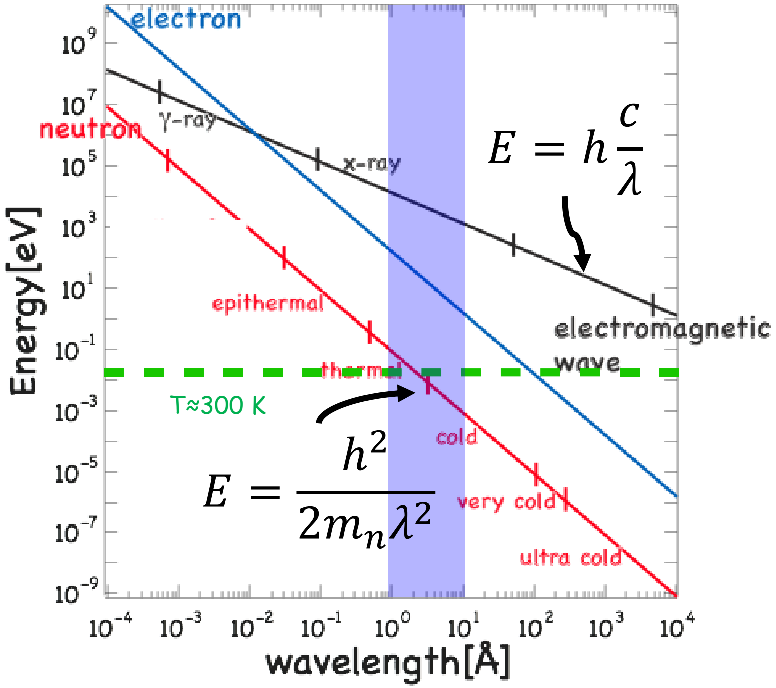


E.g.: new pharmaceuticals are prescreened by supercomputers considering both the structure and **dynamics** of the target. *Biophys. J.*, **114**, 2271 (2018).

Microscopic dynamics is important

In the rest of this presentation, it will be demonstrated how dynamic neutron scattering methods (and NSE in particular) are unique and powerful tool to investigate the nanoscopic dynamics of soft matter systems.

Why neutrons?



Typical wavelengths of beam neutrons range from ≈10 Å to ≈1 Å

comparable to interatomic and intermolecular distances

Typical energies of bem neutrons range from ≈1 meV up to ≈ 100 meV

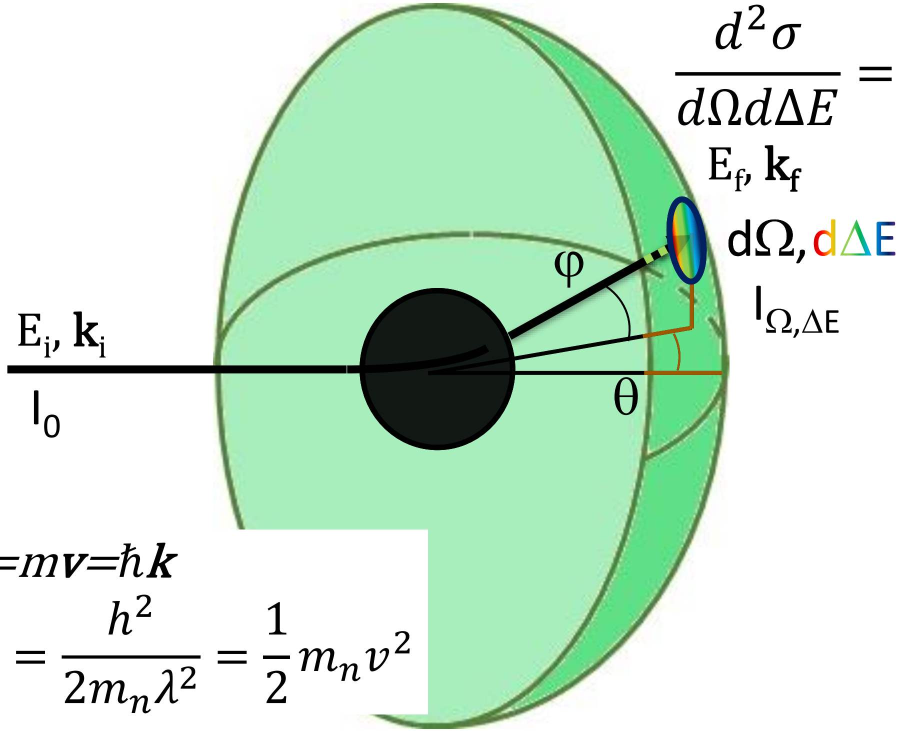
comparable to the energies of many motions in materials

Neutrons are suitable to study the dynamic properties at atomic and molecular scale.

Dynamic scattering

The relevant measured quantity is the double differential scattering cross section, $\frac{d^2\sigma}{d\Omega d\Delta E}$, defined as the probability that a probe particle is scattered in the solid angle between $\Omega(\theta,\varphi)$ and $\Omega+d\Omega$, having exchanged with the sample an energy between $\Delta E=E_i-E_f$ and $\Delta E+d\Delta E$.

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{I_{\Omega,\Delta E}}{I_0}$$



$$\boldsymbol{p}=m\boldsymbol{v}=\hbar\boldsymbol{k}$$

$$E = \frac{h^2}{2m_n\lambda^2} = \frac{1}{2}m_n v^2$$

Caveat

Often ΔE is simply indicated by E

Moreover, the frequency of the wave associated with a neutron of energy E is given by:

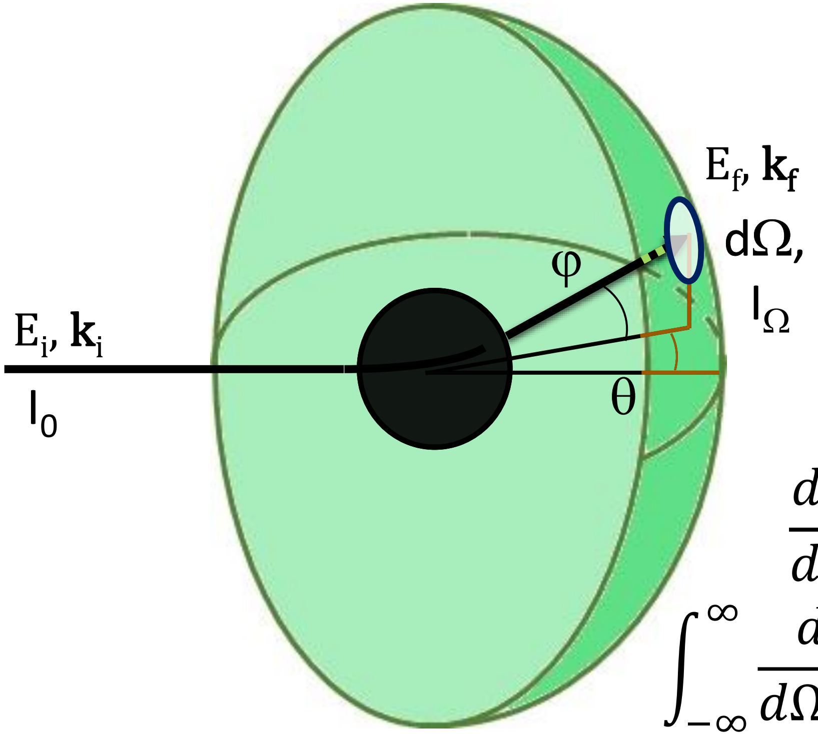
$$E=\hbar\omega$$

Often $\hbar\omega$ or simply ω, expressed in units of energy, are used instead of ΔE

Static *vs* Dynamic scattering

For static scattering, when the energy of the scattered probe particle is not analyzed, the relevant measured quantity is the differential scattering cross section,

$$\frac{d\sigma}{d\Omega} = \int_{-\infty}^{\infty} \frac{d^2\sigma}{d\Omega d\Delta E} d\Delta E$$



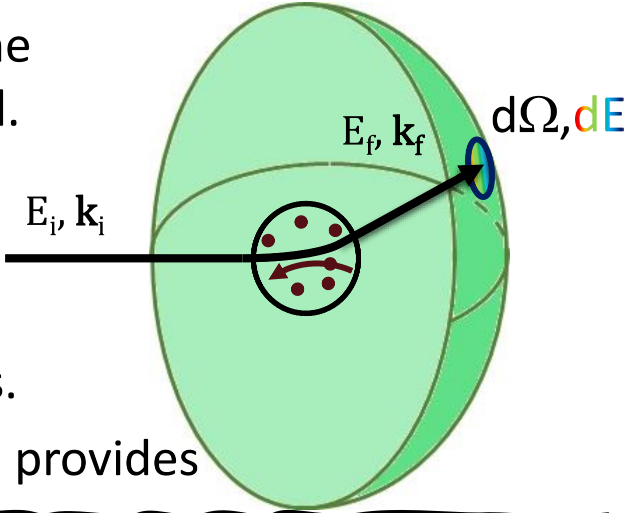
$$\frac{d\sigma}{d\Omega} = \frac{I_\Omega}{I_0} = \int_{-\infty}^{\infty} \frac{d^2\sigma}{d\Omega d\Delta E} d\Delta E$$

Connection with sample dynamics

Neutrons interact with the nuclei in the sample. The interaction is described by the Fermi pseudo potential.

$$V(\underline{r}) = \frac{2\pi\hbar^2}{m_n} b_i \delta\left(\underline{r} - \underline{r}_i\right)$$

b_i is the scattering length



The incoming and scattered neutrons are plane waves.

A little quantum-mechanics magic (Fermi golden rule) provides

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\left\langle b_n b_m \int_{-\infty}^{\infty} \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0) - \boldsymbol{r}_n(t)\}]\exp[-i\frac{\Delta E}{\hbar}t]dt\right\rangle$$

Key points on dynamic neutron scattering

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\left\langle b_n b_m \int_{-\infty}^{\infty} \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0) - \boldsymbol{r}_n(t)\}]\exp[-i\frac{\Delta E}{\hbar}t]dt\right\rangle$$

- Provides information on the spatial and time correlation between couple of atoms

Key points on dynamic neutron scattering

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\left\langle b_n b_m \int_{-\infty}^{\infty} \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0)-\boldsymbol{r}_n(t)\}]\exp[-i\frac{\Delta E}{\hbar}t]dt\right\rangle$$

- Provides information on the spatial and time correlation between couple of atoms
- Geometrical information on the motion is embedded in the data
  - The dynamics is probed over a length-scale determined by ***Q***

Key points on dynamic neutron scattering

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\left\langle b_n b_m \int_{-\infty}^{\infty}\exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0)-\boldsymbol{r}_n(t)\}]\exp[-i\frac{\Delta E}{\hbar}t]dt\right\rangle$$

- Provides information on the spatial and time correlation between couple of atoms
- Geometrical information on the motion is embedded in the data
  - The dynamics is probed over a length-scale determined by ***Q***
- Strength of scattering is determined by the nature of the nuclei

Key points on dynamic neutron scattering

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\left\langle b_n b_m \int_{-\infty}^{\infty} \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0) - \boldsymbol{r}_n(t)\}]\exp[-i\frac{\Delta E}{\hbar}t]dt\right\rangle$$

- Provides information on the spatial and time correlation between couple of atoms
- Geometrical information on the motion is embedded in the data
  - The dynamics is probed over a length-scale determined by ***Q***
- Strength of scattering is determined by the nature of the nuclei
- A Fourier transformation relates the correlation to the energy spectra

It's like an onion

$$\frac{d^2\sigma}{d\Omega d\Delta E} =$$

$$\frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\left\langle b_n b_m \int_{-\infty}^{\infty} \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0)-\boldsymbol{r}_n(t)\}]\exp[-i\frac{\Delta E}{\hbar}t]dt\right\rangle$$

$$= \frac{k_f}{k_i}\frac{N}{2\pi\hbar^2}\int_{-\infty}^{\infty}\left\{\int_V \left\langle \frac{1}{N}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta} b_n b_m \delta[r-(\boldsymbol{r}_m(0)-\boldsymbol{r}_n(t))]\right\rangle \exp[-i\boldsymbol{Q}\boldsymbol{r}t]d\boldsymbol{r}\right\}\exp[-i\frac{\Delta E}{\hbar}t]\,dt$$

Fourier transform in time

Fourier transform in space

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{N}{2\pi\hbar^2}\mathcal{F}_t\left\{\mathcal{F}_s\left\{\left\langle \frac{1}{N}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta} b_n b_m \delta[r-(\boldsymbol{r}_m(0)-\boldsymbol{r}_n(t))]\right\rangle\right\}\right\} = \frac{k_f}{k_i}\frac{N}{2\pi\hbar^2}\mathcal{F}_t\{\mathcal{F}_s\{G^n(\boldsymbol{r},t)\}\}$$

It's like an onion

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{N}{2\pi\hbar^2}\mathcal{F}_t\{\mathcal{F}_s\{G^n(\boldsymbol{r},t)\}\}$$

Prefactor related to experimental conditions

Contains the information on the atomic spatio temporal correlations

It's like an onion

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{N}{2\pi\hbar^2}\mathcal{F}_t\{\mathcal{F}_s\{G^n(\boldsymbol{r},t)\}\}$$

S(Q,ΔE)
Dynamic Structure Factor

$$S(Q,\Delta E) = \frac{1}{N}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\left\langle b_n b_m \int_{-\infty}^{\infty} \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0)-\boldsymbol{r}_n(t)\}]\exp[-i\frac{\Delta E}{\hbar}t]dt\right\rangle$$

It’s like an onion

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{N}{2\pi\hbar^2}\mathcal{F}_t\{\mathcal{F}_s\{G^n(\boldsymbol{r},t)\}\}$$

I(Q,t)
Intermediate Scattering Function (ISF)

$$\mathrm{I}(Q,t) = \frac{1}{N}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\langle b_n b_m \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0) - \boldsymbol{r}_n(t)\}]\,\rangle$$

Dynamic structure factor and ISF

- The dynamic structure factor and ISF describe 2-objects spatio-temporal correlations.
- They provide the same information.
- $S(Q,\Delta E)$ is defined in the energy domain, $I(Q,t)$ in the time domain.

The dynamic structure factor and ISF can be defined for any sample, e.g. it can be calculated for a simulated (or even imaginary sample).

NB: the sample is stationary, i.e. its ensemble properties do not change in time; the time 0 is arbitrary.

For an isotropic sample, the dynamic structure factor only depends on the modulus of the exchanged wave-vector: $S(\mathbf{Q},\Delta E)=S(|\mathbf{Q}|,\Delta E)=S(Q,\Delta E)$

Most dynamic scattering techniques work in the energy domain; however, dynamic light scattering, X-ray Photon Correlation Spectroscopy (XPCS), and NSE provide results in the time domain.

It's like an onion

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{N}{2\pi\hbar^2}\mathcal{F}_t\{\mathcal{F}_s\{G^n(\boldsymbol{r},t)\}\}$$

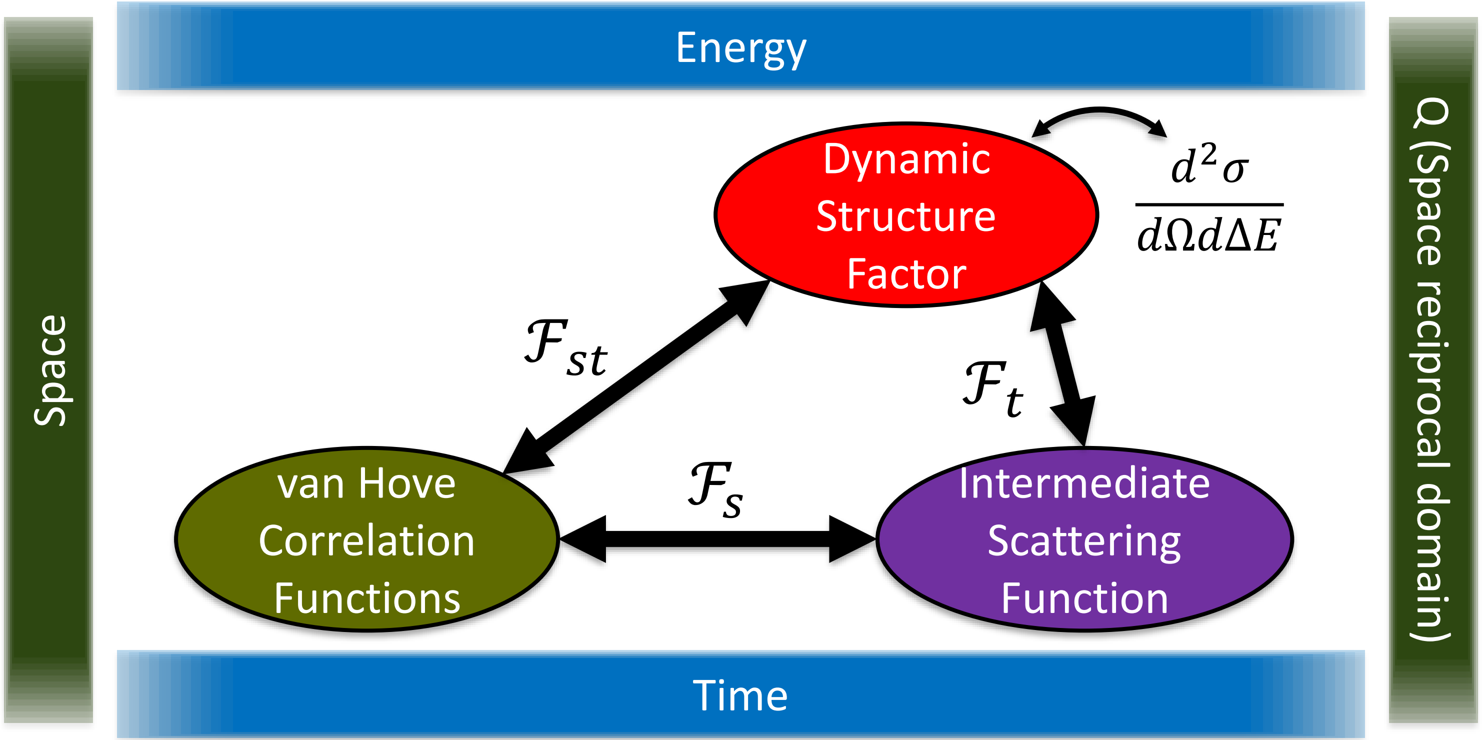
Van Hove correlation function

$$G^n(\boldsymbol{r},t) = \frac{1}{N}\sum_{\alpha\beta} b_{coh}^{\alpha} b_{coh}^{\beta} \sum_{nm}^{N_\alpha N_\beta} \langle \delta(\boldsymbol{r}-\boldsymbol{r}_n(t)+\boldsymbol{r}_m(0))\rangle$$

van Hove correlation function represents the probability of finding a particle at $\boldsymbol{r}_n$ at time t given that the same or another particle was at $\boldsymbol{r}_m$ at time 0.

It provides a framework to interpret dynamic neutron scattering data in terms of a spatio-temporal probability distribution, defined in real space and time.

Synoptic table



Isotopes and nuclear spins

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\left\langle b_n b_m \int_{-\infty}^{\infty} \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0)-\boldsymbol{r}_n(t)\}]\exp[-i\frac{\Delta E}{\hbar}t]dt\right\rangle$$

Even for the same type of atom α, the scattering length b_n might vary because of the presence of different

- Isotopes
- Nuclear spin states

Isotopes and nuclear spin states are independent of the atom position:

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta}\sum_{n,m}^{N_\alpha N_\beta}\langle b_n b_m\rangle \int_{-\infty}^{\infty} \langle\exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0)-\boldsymbol{r}_n(t)\}]\rangle\exp[-i\frac{\Delta E}{\hbar}t]dt$$

Coherent and Incoherent Scattering

For $\alpha \neq \beta \,|\, n \neq m$, $\langle b_n b_m \rangle = \langle b_n \rangle \langle b_m \rangle = \langle b_\alpha \rangle \langle b_\beta \rangle$; For $\alpha = \beta$ & $n = m$, $\langle b_n b_m \rangle = \langle b_\alpha^2 \rangle$

$$\langle b_n b_m \rangle = \langle b_\alpha \rangle \langle b_\beta \rangle (1 - \delta_{nm}\delta_{\alpha\beta}) + \langle b_\alpha^2 \rangle \delta_{nm}\delta_{\alpha\beta} =$$

$$\langle b_\alpha \rangle \langle b_\beta \rangle (1 - \delta_{nm}\delta_{\alpha\beta}) + \langle b_\alpha^2 \rangle \delta_{nm}\delta_{\alpha\beta} + \langle b_\alpha \rangle \langle b_\beta \rangle \delta_{nm}\delta_{\alpha\beta} - \langle b_\alpha \rangle \langle b_\beta \rangle \delta_{nm}\,\delta_{\alpha\beta} =$$

$$\langle b_\alpha \rangle \langle b_\beta \rangle + \left(\langle b_\alpha^2 \rangle - \langle b_\alpha \rangle \langle b_\beta \rangle \right) \delta_{nm}\delta_{\alpha\beta}$$

$$\frac{d^2\sigma}{d\Omega d\Delta E} = \frac{k_f}{k_i} \frac{1}{2\pi\hbar^2} \left\{ \sum_{\alpha\beta} \langle b_\alpha \rangle \langle b_\beta \rangle \sum_{n,m} \int_{-\infty}^{\infty} dt \exp\left[-i\frac{\Delta E}{\hbar}t\right] \langle \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0) - \boldsymbol{r}_n(t)\}] \rangle \right.$$

Coherent

$$\left. \sum_{\alpha} (\langle b_\alpha^2 \rangle - \langle b_\alpha \rangle^2) \sum_{n} \int_{-\infty}^{\infty} dt \exp\left[-i\frac{\Delta E}{\hbar}t\right] \langle \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_n(0) - \boldsymbol{r}_n(t)\}] \rangle \right\}$$

Incoherent

In summary

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

$$\left(\frac{d^2\sigma}{d\Omega d\Delta E}\right)_{coh} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha\beta} b^{\alpha}_{coh} b^{\beta}_{coh} \sum_{n,m}\int_{-\infty}^{\infty} dt \exp\left[-i\frac{\Delta E}{\hbar}t\right]\langle \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_m(0) - \boldsymbol{r}_n(t)\}]\rangle$$

$$\left(\frac{d^2\sigma}{d\Omega d\Delta E}\right)_{inc} = \frac{k_f}{k_i}\frac{1}{2\pi\hbar^2}\sum_{\alpha} \frac{\sigma^{\alpha}_{inc}}{4\pi} \sum_{n}\int_{-\infty}^{\infty} dt \exp\left[-i\frac{\Delta E}{\hbar}t\right]\langle \exp[-i\boldsymbol{Q}\{\boldsymbol{r}_n(0) - \boldsymbol{r}_n(t)\}]\rangle$$

Coherent scattering length of atom α: $b^{\alpha}_{coh} = \langle b_\alpha \rangle$

Coherent scattering cross section of atom α: $\sigma^{\alpha}_{coh} = 4\pi\langle b_\alpha \rangle^2$

Incoherent scattering cross section of atom α: $\sigma^{\alpha}_{inc} = 4\pi(\langle b^2_\alpha \rangle - \langle b_\alpha \rangle^2)$

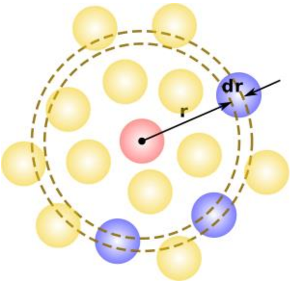
Coherent scattering provides information on relative positions and motions

Incoherent scattering yields information on the single particle dynamics

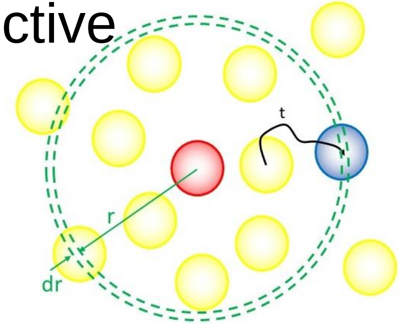
van Hove correlation functions

Coherent scattering yields the Fourier transform of the collective van Hove correlation function

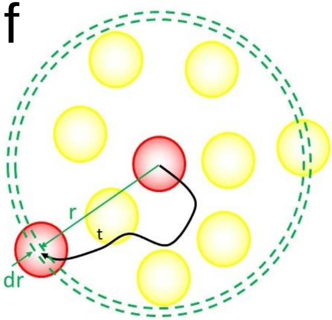
The pair correlation function is the limit for t→0 of the collective van Hove correlation function



Collective



Self



Incoherent scattering yields the Fourier transform of the self or single particle van Hove correlation function

Hydrogen

Nuclear spin incoherent element

	Nuclear Spin	σ_{coh} (barn)	σ_{inc} (barn)	b_{coh} (fm)	σ_A (barn)
H	½	1.75	80.22	-3.74	0.333
D	1	5.59	2.05	6.671	0

Knowledge Check

Calculate the total, incoherent, and coherent neutron scattering cross section per unit volume for H_2O and D_2O.

For both cases, consider a neutron scattering experiment in the Q range from 0.1 $Å^{-1}$ to 2.5 $Å^{-1}$, estimate which contribution is dominant (coherent or incoherent) as a function of the exchanged wave-vector.

Hint: Google neutron scattering lengths and follow the link:

https://www.ncnr.nist.gov/resources/n-lengths/

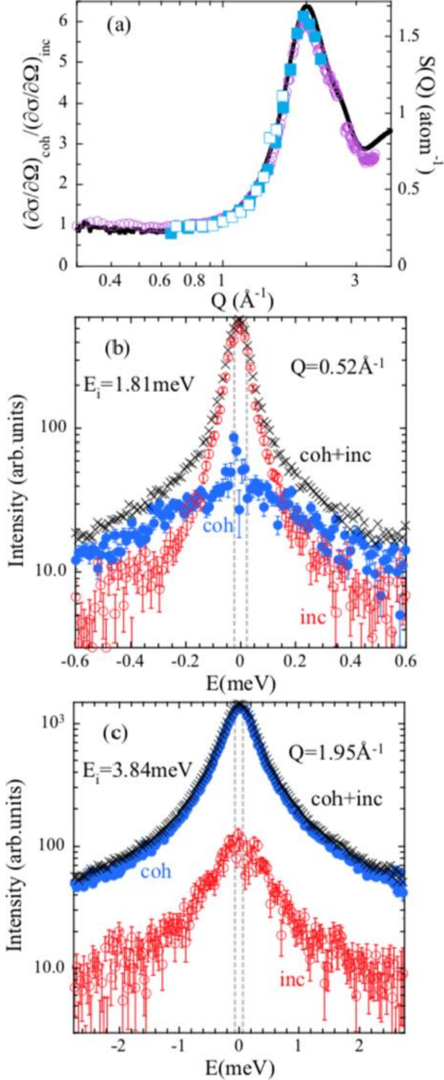
It's OK to cheat and use DAVE or any other available resource

	σ_{coh} (b)	σ_{inc} (b)	σ_{tot} (b)
H	1.757	80.26	82.02
O	4.232	0	4.232
D	5.592	2.05	7.64

Knowledge Check

Calculate the total, incoherent, and coherent neutron scattering cross section per unit volume for H_2O and D_2O.

For both cases, consider a neutron scattering experiment in the Q range from 0.1 Å^{-1} to 2.5 Å^{-1}, estimate which contribution is dominant (coherent or incoherent) as a function of the exchanged wave-vector.



A. Arbe, et al., Phys. Rev. Res., **2**, 022015(R) (2020)

Knowledge Check

Consider a mixture of 20 % (by mole) hydrogenated polymer chains dispersed in homologous (same chemistry same molecular mass) deuterated chains, can you make any reasoned guess as to which contribution is dominant (coherent or incoherent) as a function of the exchanged wave-vector.

In the SANS limit

For soft matter, an expression of the dynamic structure factor based on SANS approach is more useful.

Within a number of assumptions:

Centrosymmetry, monodispersity,

statistical decoupling

$$\frac{d^2\sigma}{d\Omega d\Delta E} \approx \left(\frac{d^2\sigma}{d\Omega d\Delta E}\right)_{coh}$$

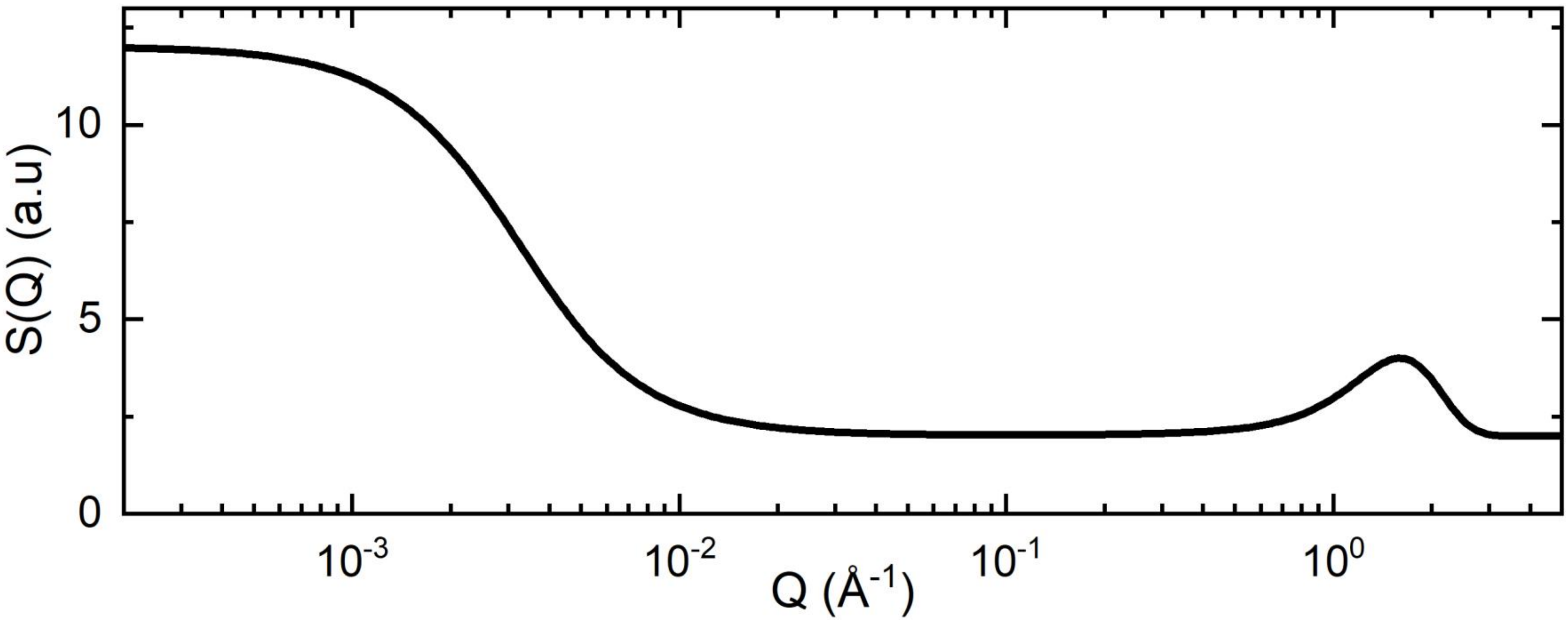
$$\left(\frac{d^2\sigma}{d\Omega d\Delta E}\right)_{coh} \approx \mathrm{n}P(Q,t)S(Q,t)$$

$$P(Q,t) = \langle F^*(Q,t)F(Q,0)\rangle$$

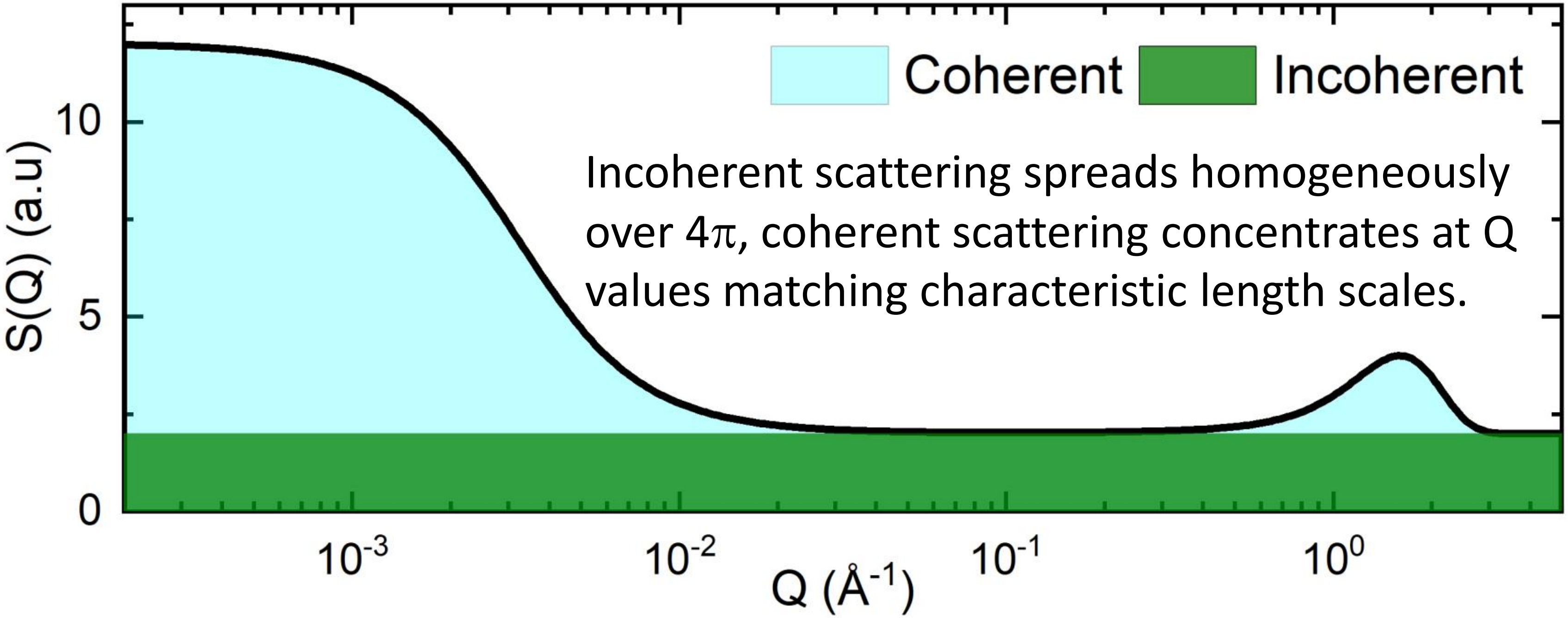
$$F(Q,t) = \sum b_m \exp[-i\boldsymbol{Q}\boldsymbol{r}_m(t)] = \int \rho(\boldsymbol{r},\boldsymbol{t})\exp[-i\boldsymbol{Q}\boldsymbol{r}]d\boldsymbol{r}$$

$$S(Q,t) = \left\langle \sum_{ij} \exp\{-i\boldsymbol{Q}[\boldsymbol{r}_i^R(t) - \boldsymbol{r}_j^R(0)]\} \right\rangle$$

In summary

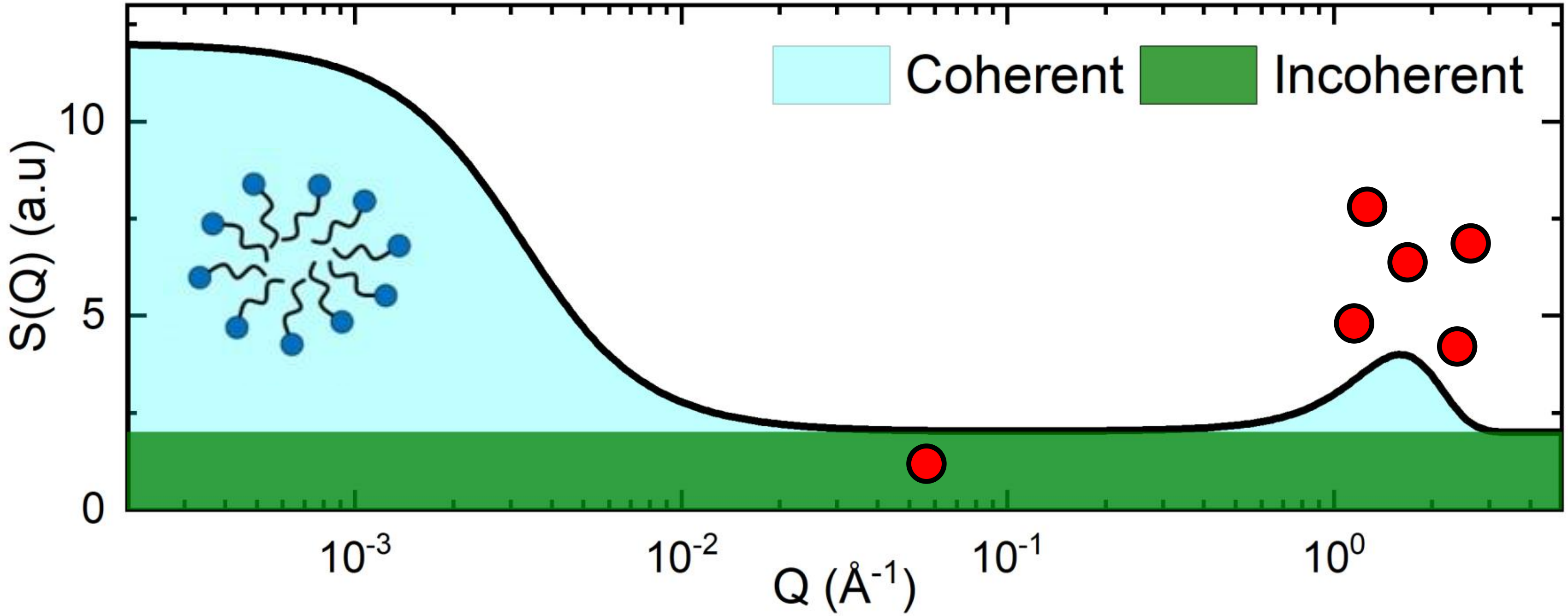


In summary

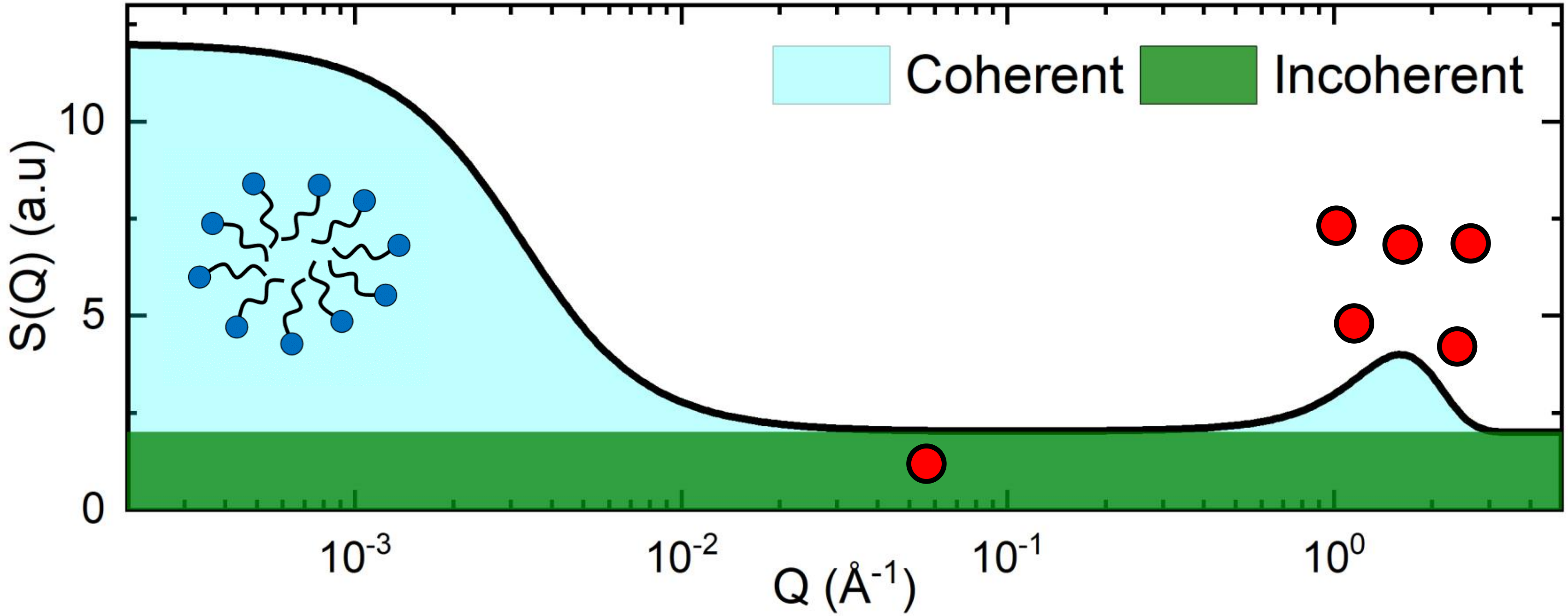


Incoherent scattering spreads homogeneously over 4π, coherent scattering concentrates at Q values matching characteristic length scales.

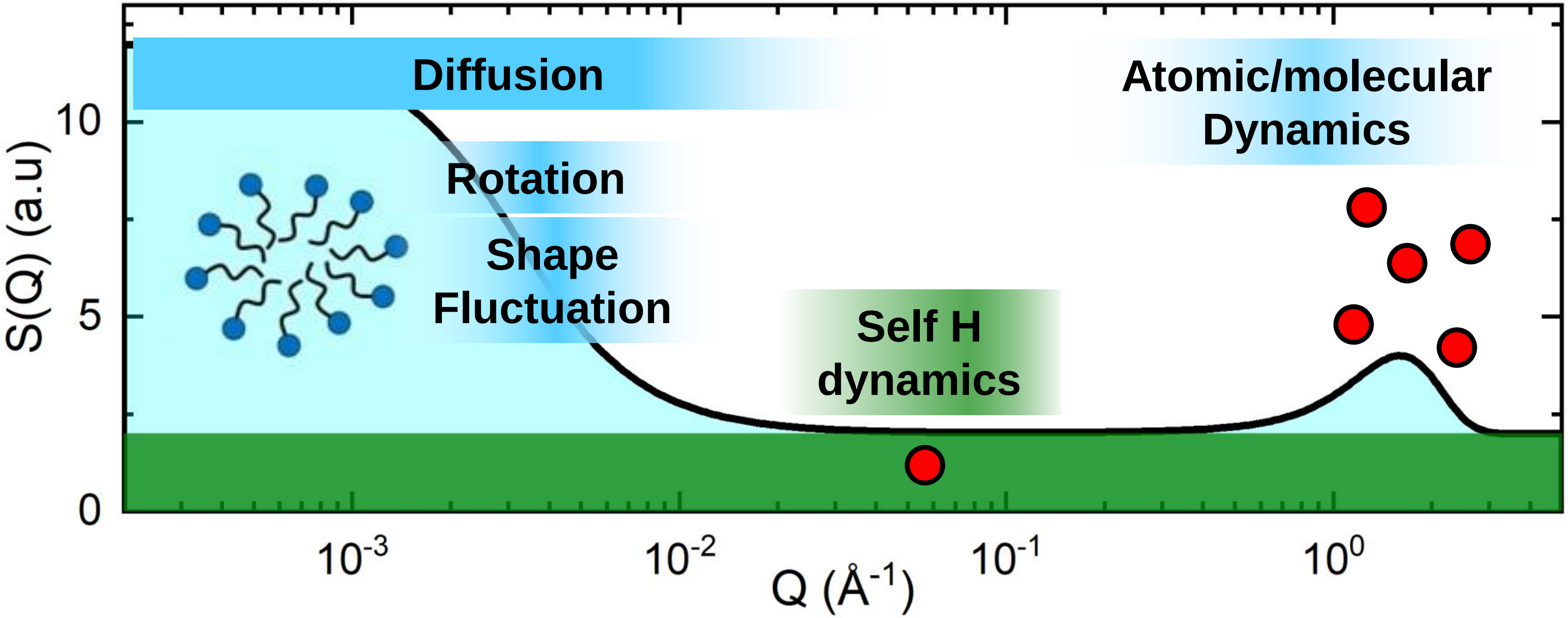
In summary



In summary

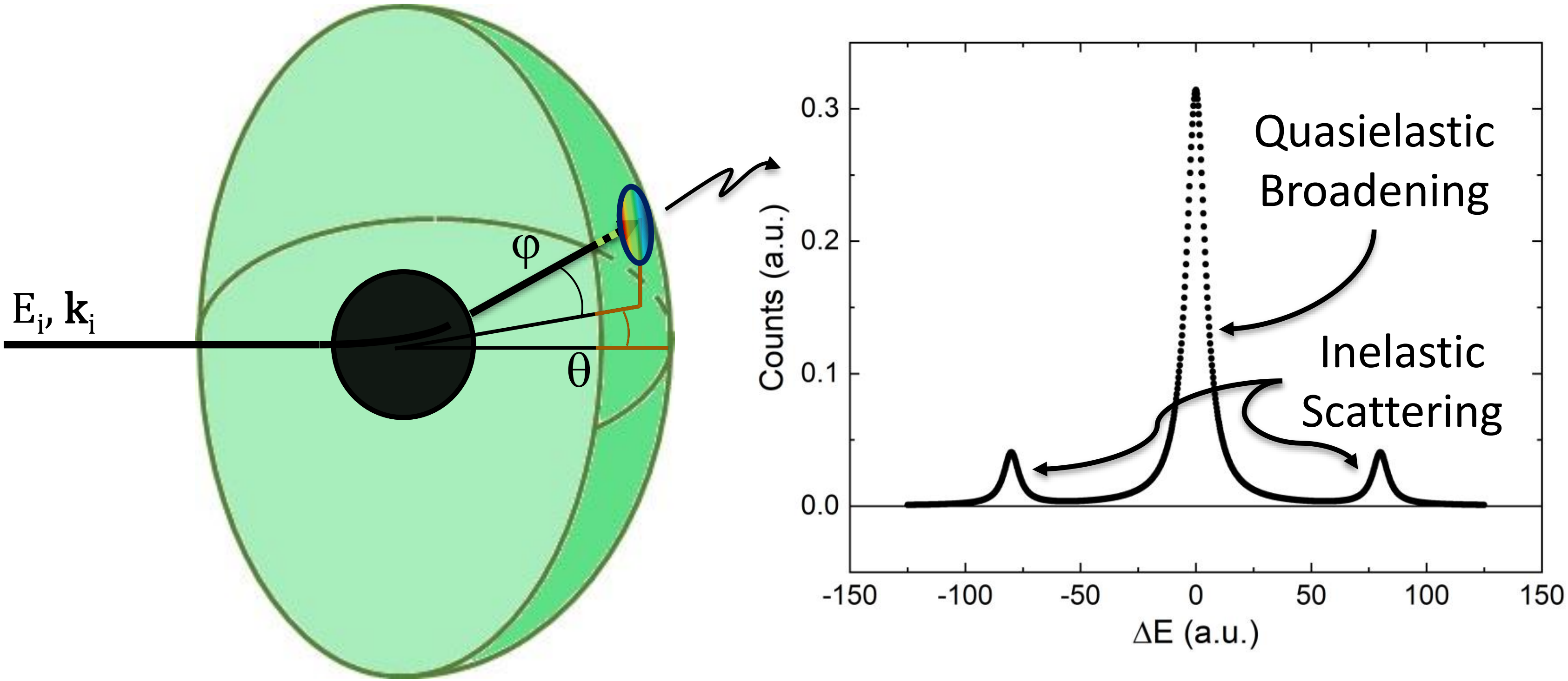


In summary

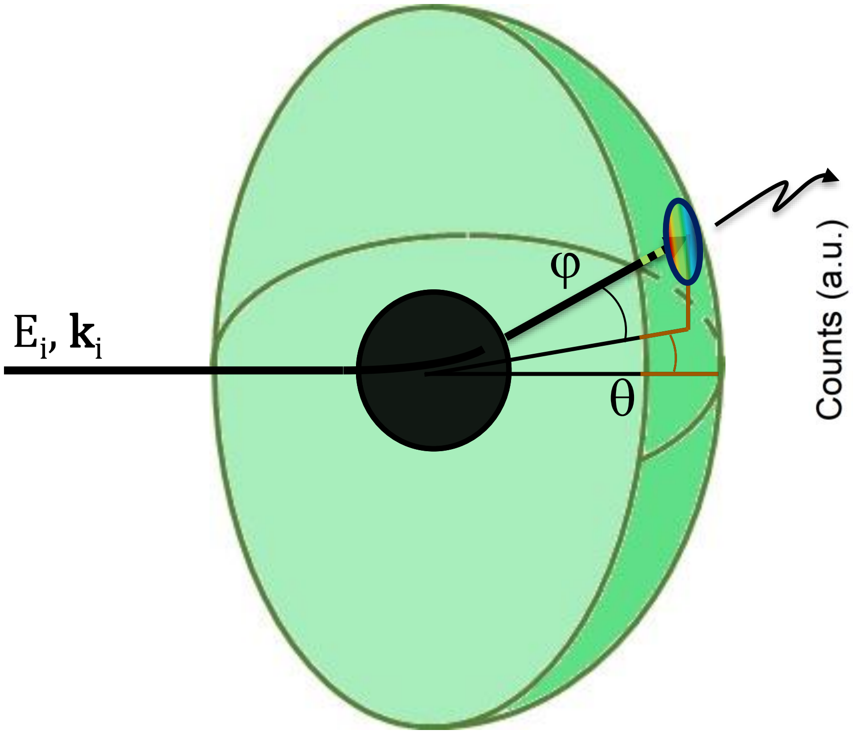


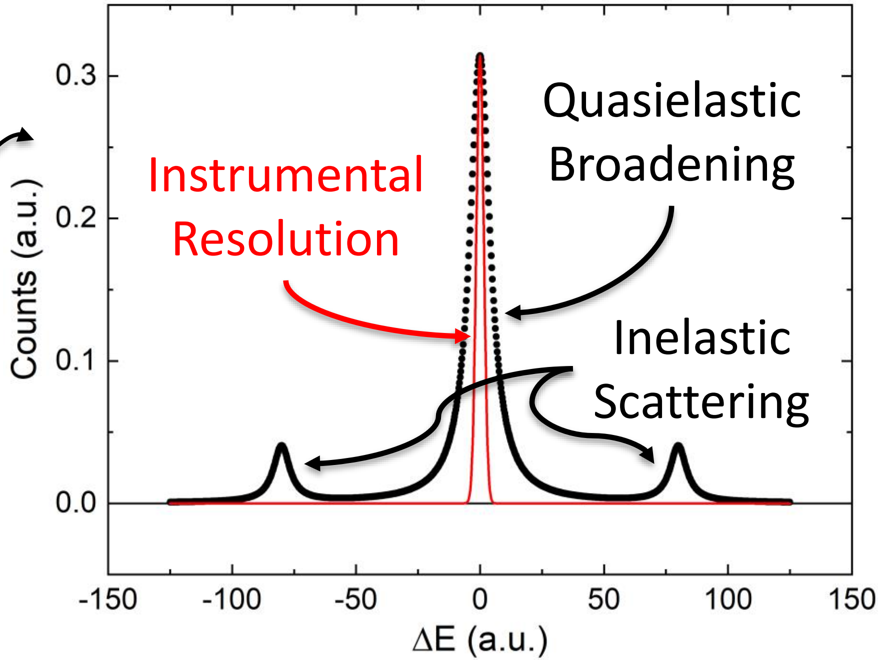
Diffusion
Rotation
Shape Fluctuation
Self H dynamics
Atomic/molecular Dynamics
S(Q) (a.u)
10
5
0
10^{-3}
10^{-2}
10^{-1}
10^{0}
Q (Å^{-1})

Dynamic scattering

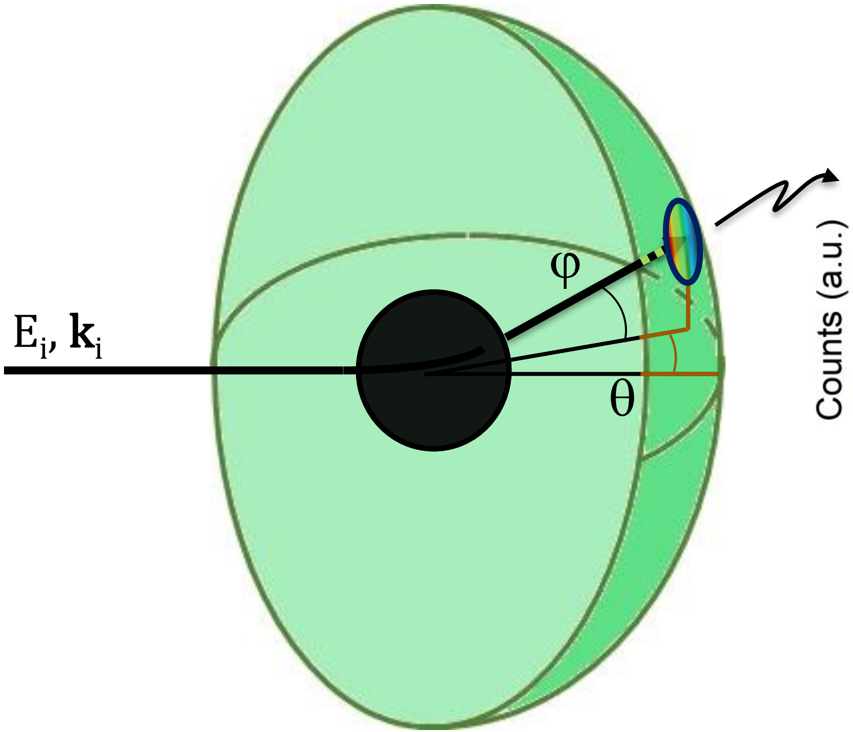


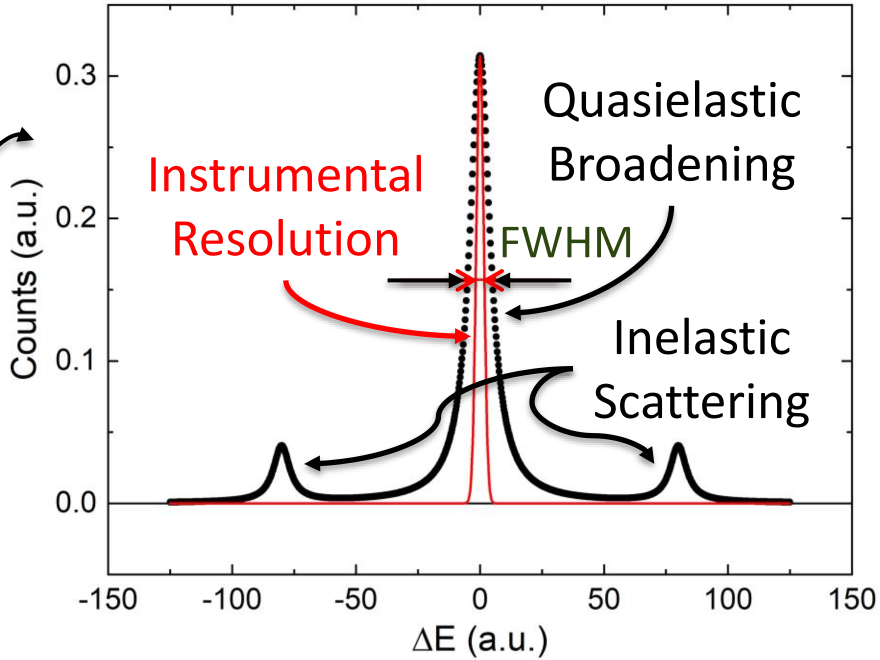
Dynamic scattering



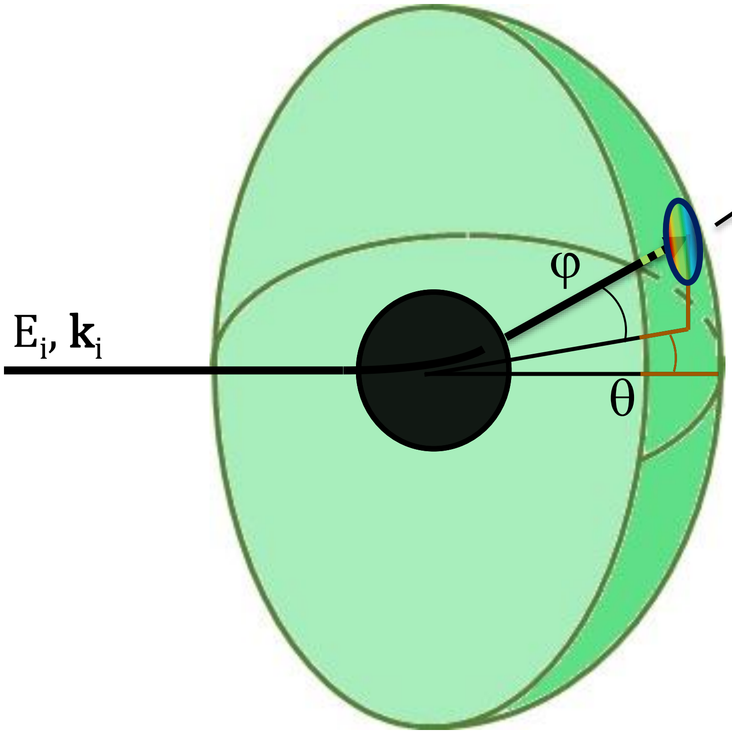


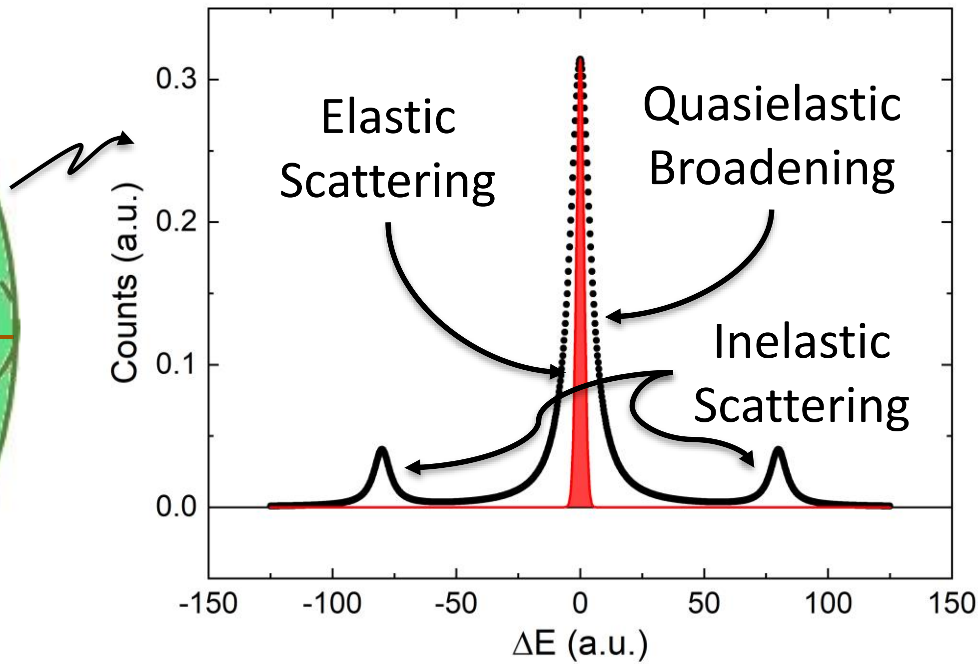
Dynamic scattering



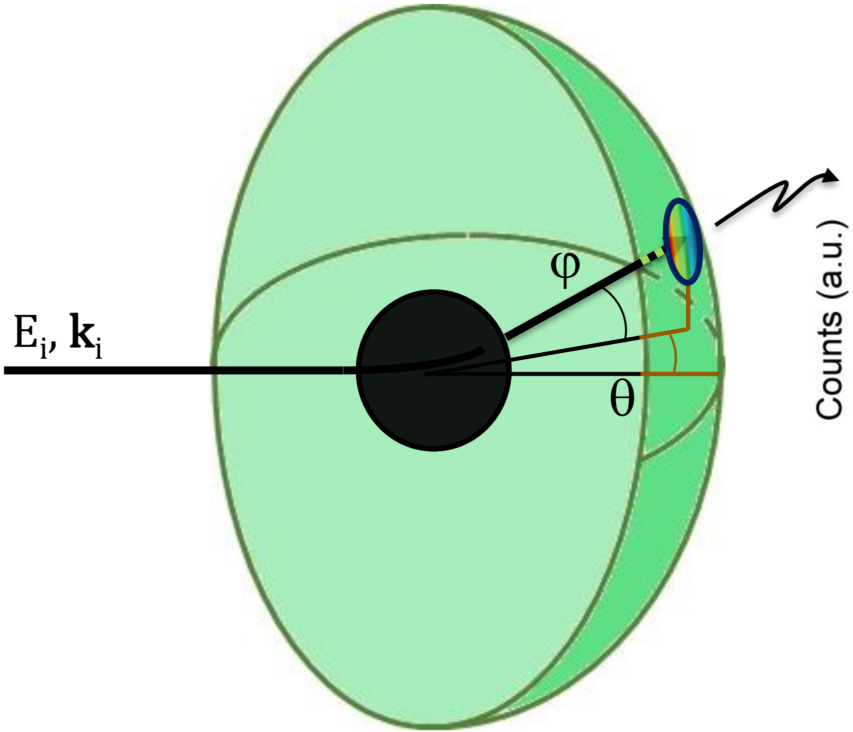


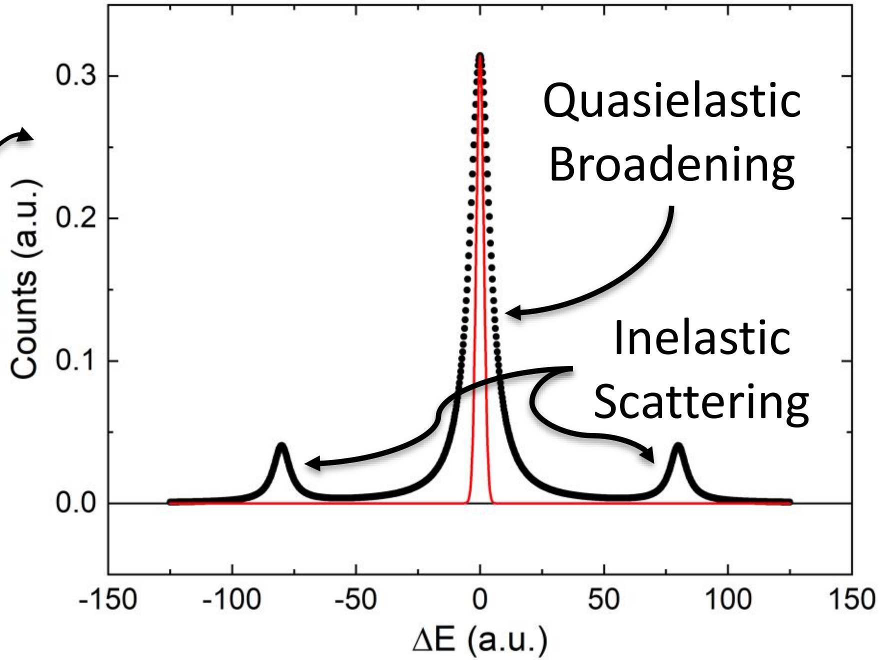
Dynamic scattering



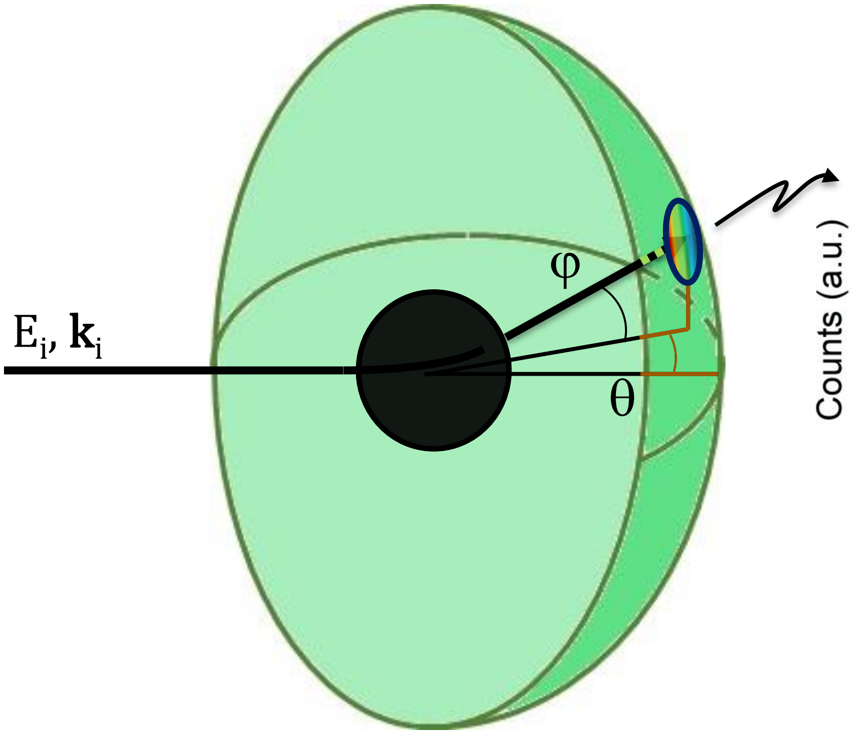


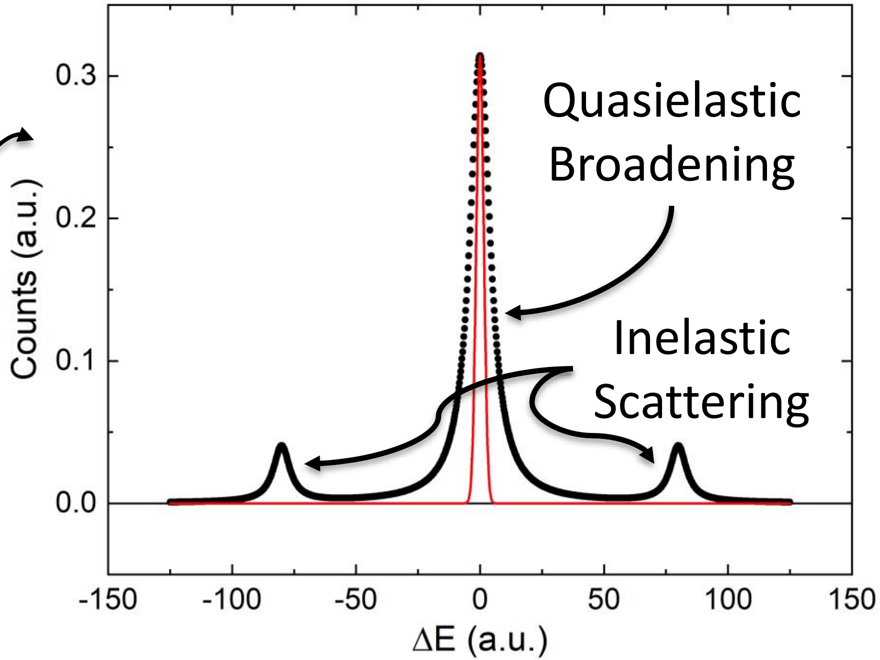
Dynamic scattering



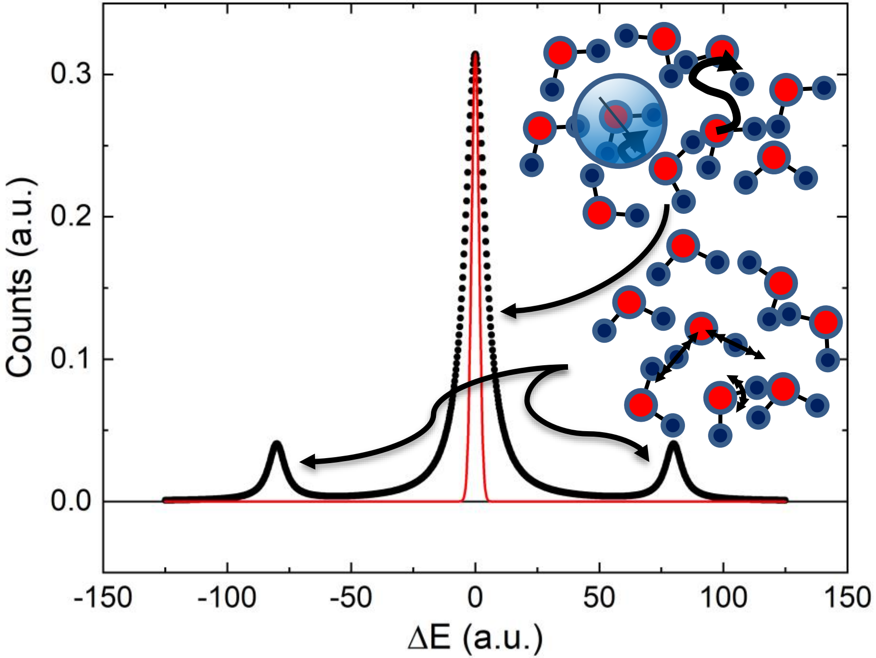


Dynamic scattering





Dynamic scattering



Thermally Activated Motions Take Place in the System.

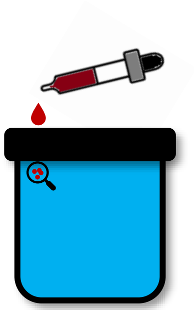
Inelastic Scattering

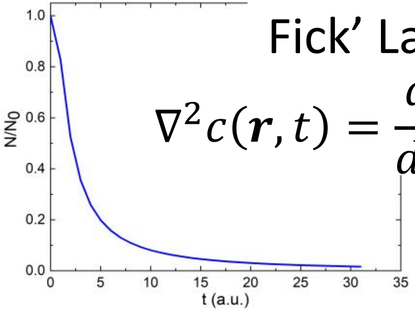
excitation: neutrons exchange energy with an oscillatory motion which has a finite energy transfer. E.g.: phonon, magnon, ...

Quasielastic Scattering

relaxation: neutrons exchange energy with random motion which makes another new equilibrium state (no typical finite energy transfer exists). E.g.: rotation, diffusion…

Vibrations and Relaxations

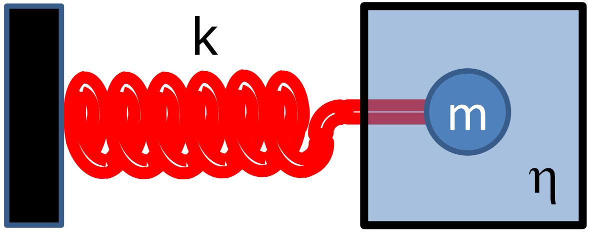




Fick' Law

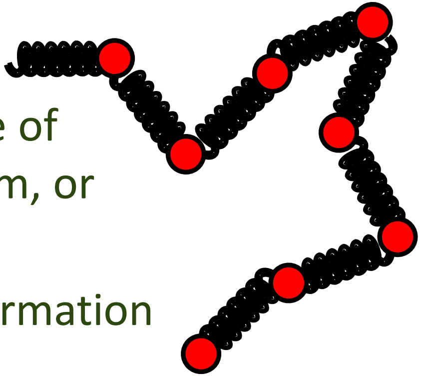
$$\nabla^2 c(\boldsymbol{r},t) = \frac{d}{dt} c(\boldsymbol{r},t)$$

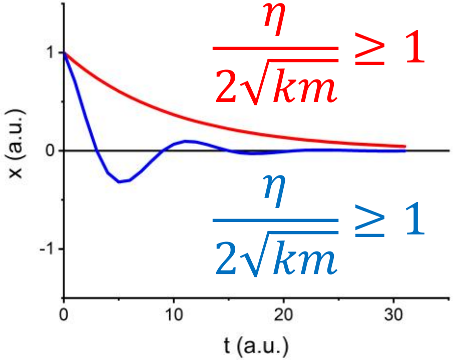
Damped Oscillator



NB Consider the presence of internal degree of freedom, or dissipation channels.

E.g. Polymer chains conformation

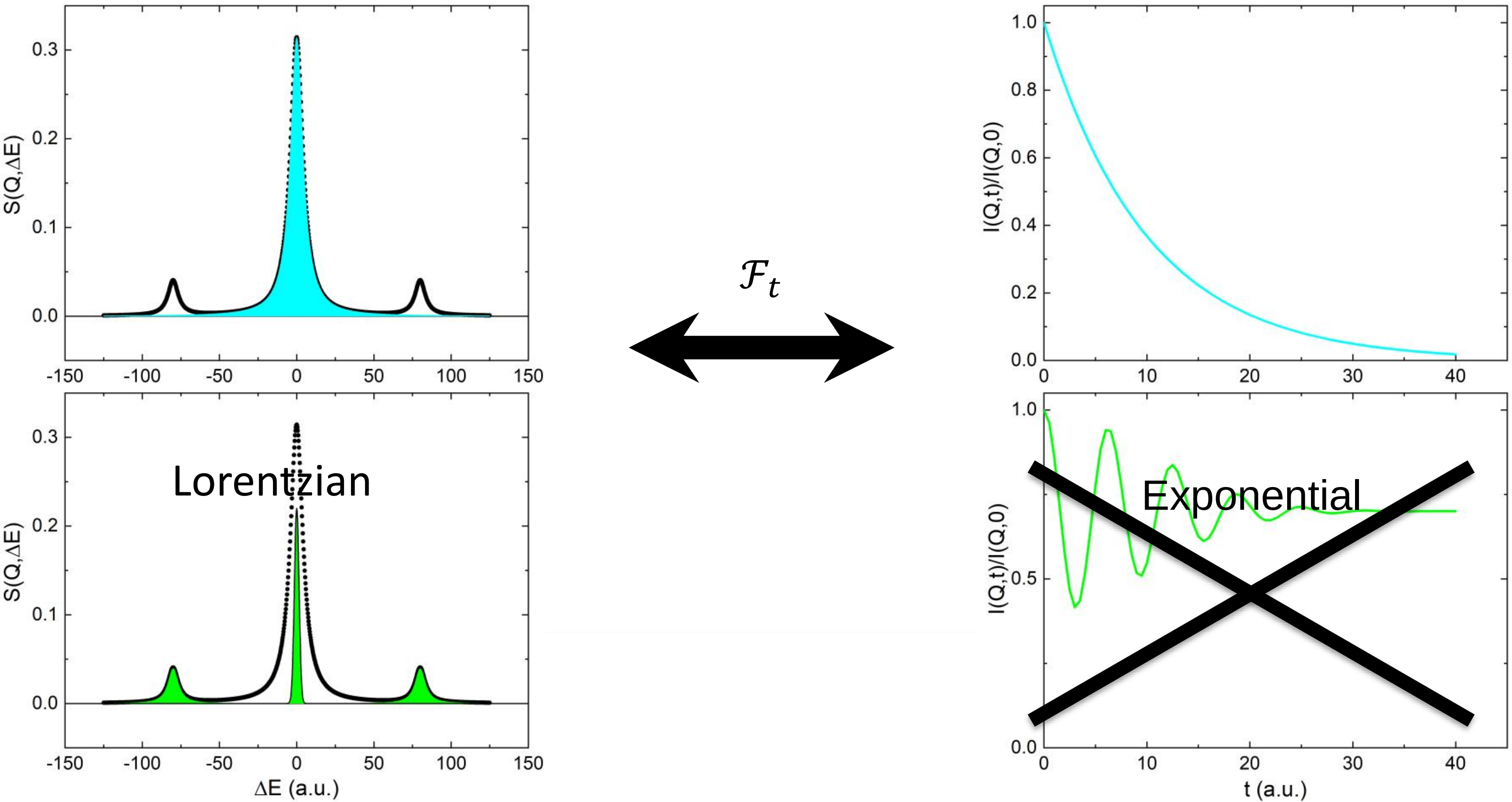




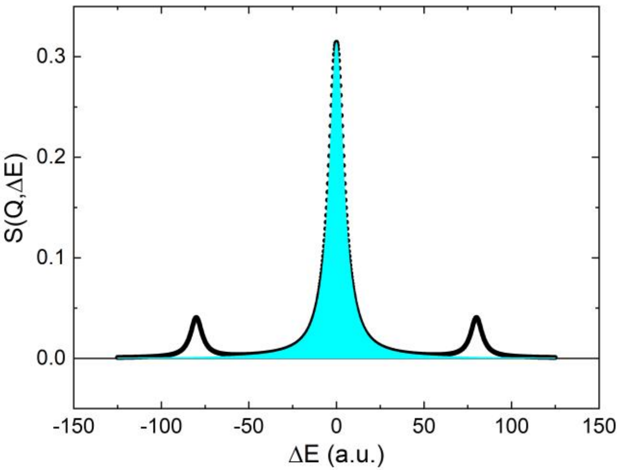
$$\frac{\eta}{2\sqrt{km}} \geq 1$$ Relaxation

$$\frac{\eta}{2\sqrt{km}} \geq 1$$ Vibration

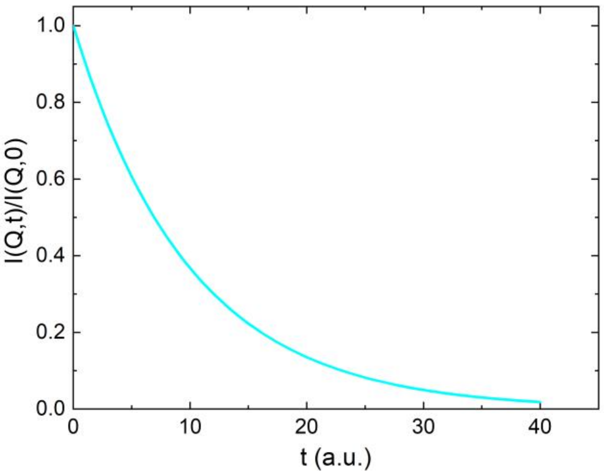
Elemental relaxation process form



Common fitting functions



$\mathcal{F}_t$



Lorentzian
$\mathcal{F}_t$ stretched exponential
Delta function
(immobile, i.e. too slow)
…
Sums…

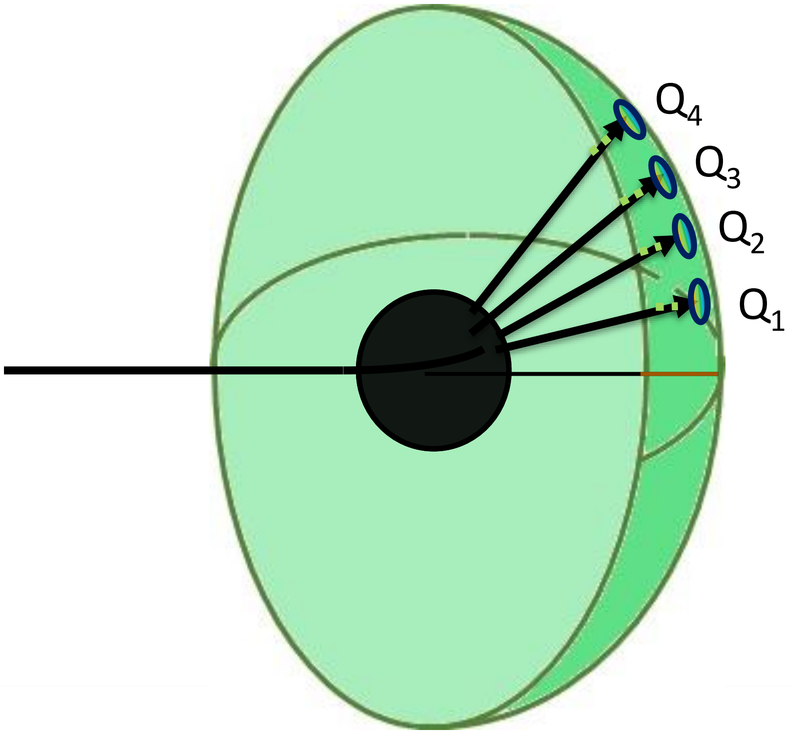
Exponential
Stretched exponential
constant
(immobile, i.e. too slow)
…
sums of…

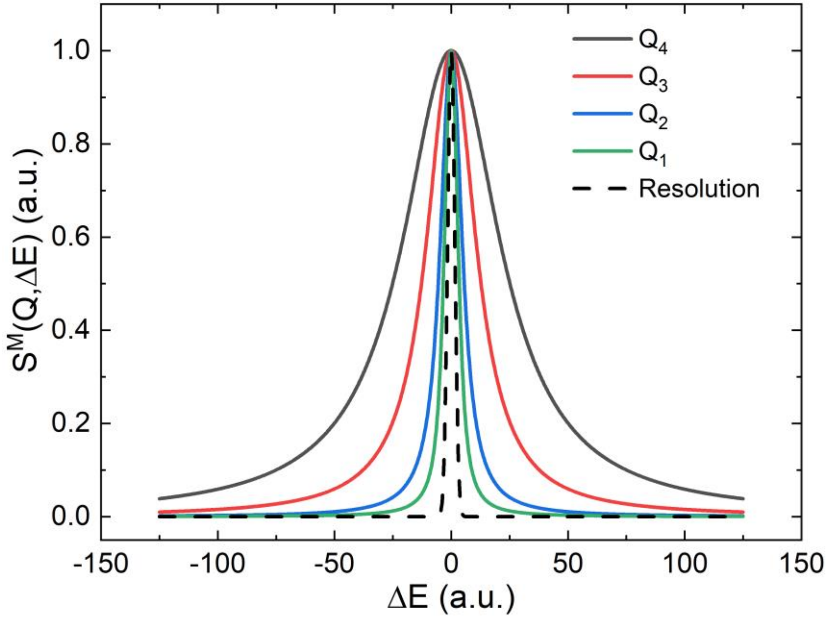
Checkpoint

Sketch any of the van Hove correlation functions at a couple of representative times for a crystal, i.e. a system of immobile particles, and for a fluid system of particles, i.e. just diffusing.

For the same systems sketch the ISF and the dynamic structure factor.

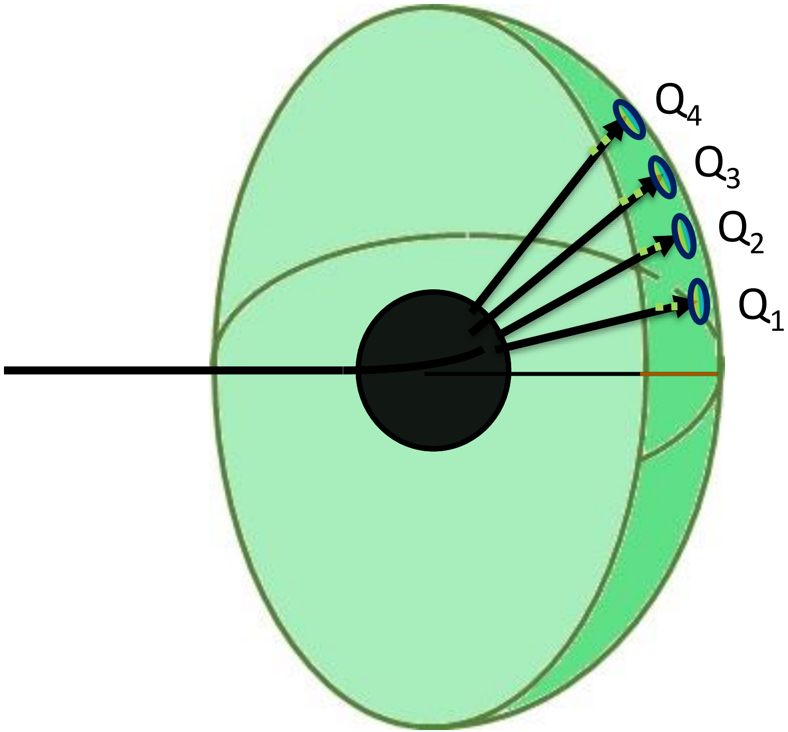
Qualitative depence on Q

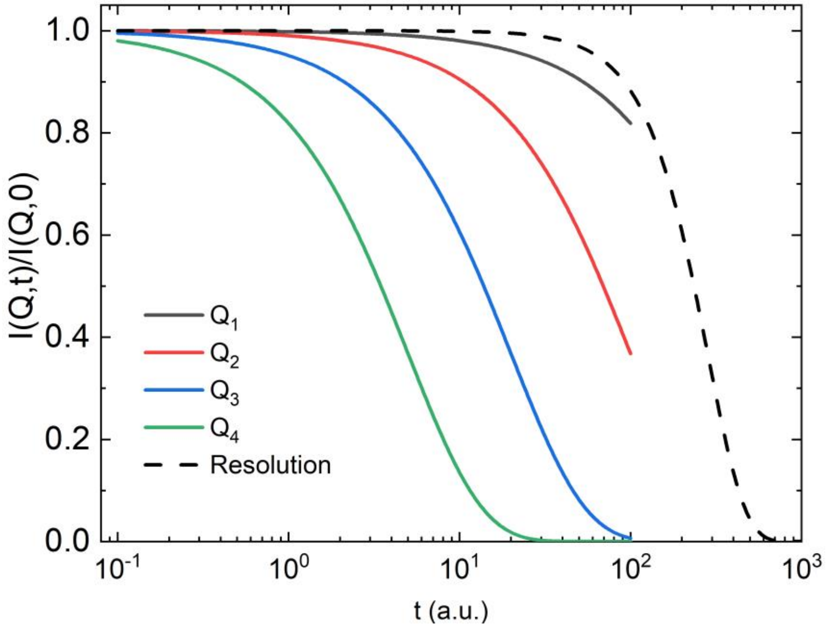




$$S^M(Q,E) = S(Q,E) \otimes R(Q,E) = \int_{-\infty}^{\infty} S(Q,E-E')R(Q,E')dE'$$

Qualitative depence on Q



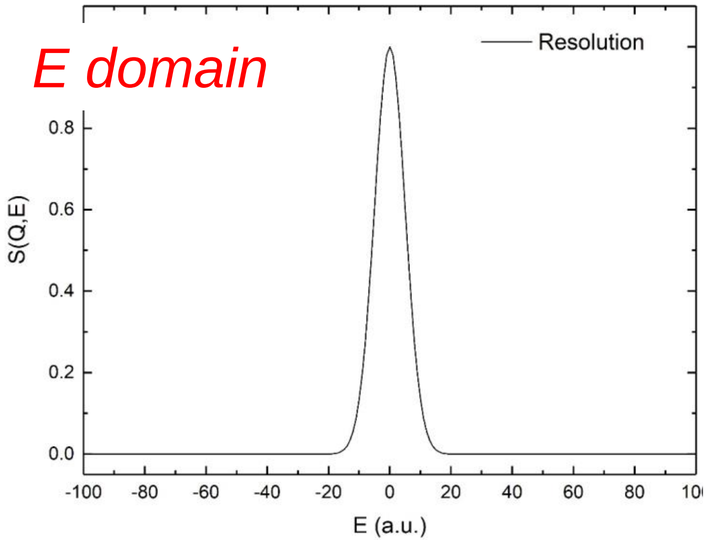


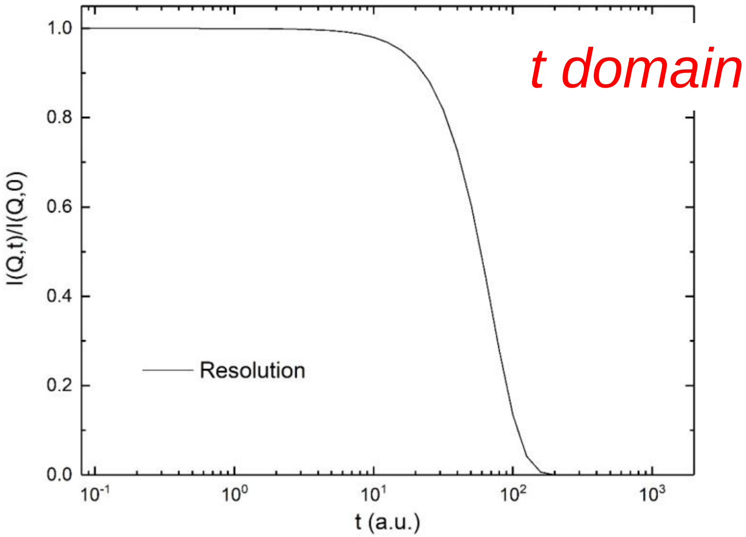
$$I^M(Q,t) = I(Q,t) \times R(Q,t)$$
$$I(Q,t) = I^M(Q,t)/R(Q,t)$$

Instrumental Resolution

Signal measured by the spectrometer on a static sample

Principle characteristic of a neutron spectrometer

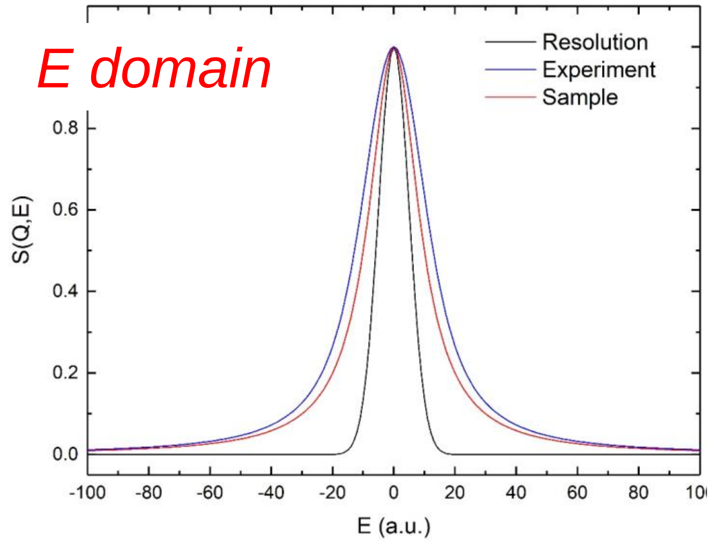


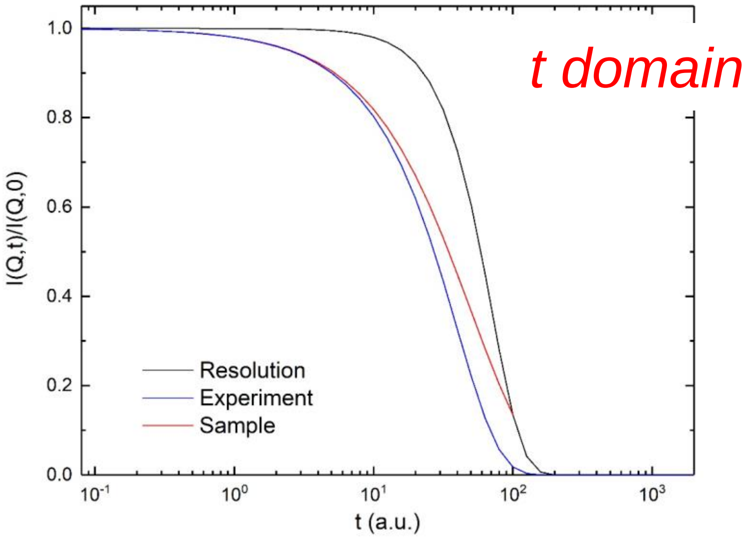


Instrumental Resolution

$$S^M(Q,E) = S(Q,E) \otimes R(Q,E)$$

$$I^M(Q,t) = I(Q,t) \times R(Q,t)$$
$$I(Q,t) = I^M(Q,t)/R(Q,t)$$

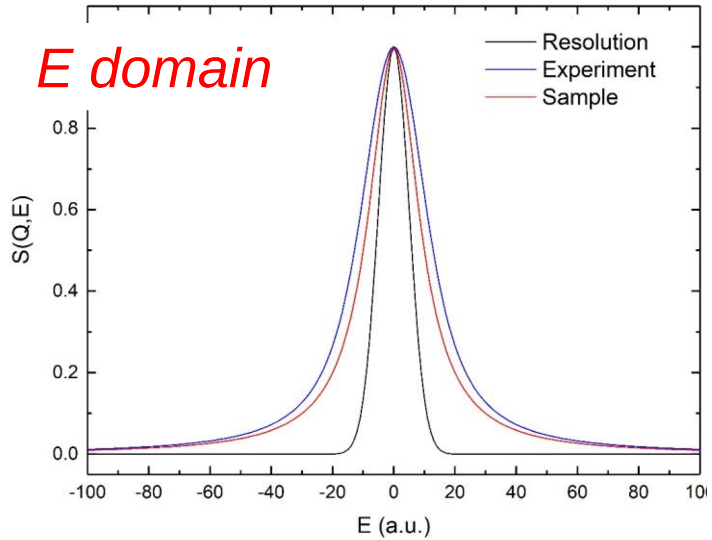


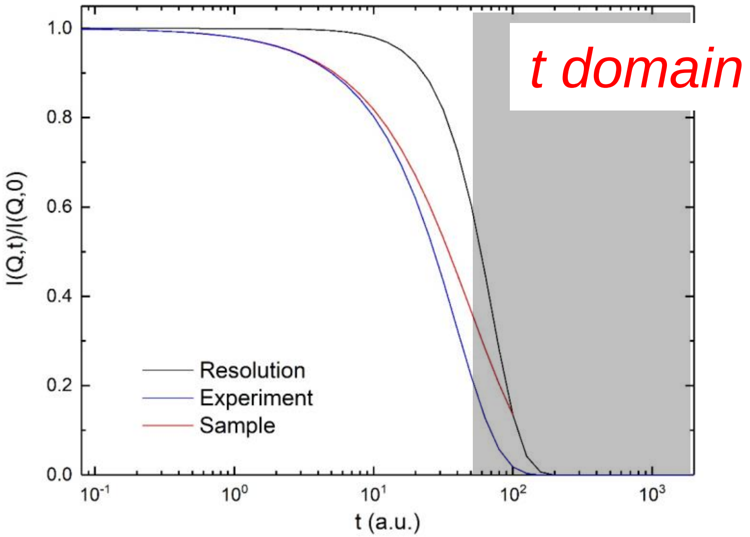


Instrumental Resolution

$$S^M(Q,E) = S(Q,E) \otimes R(Q,E)$$

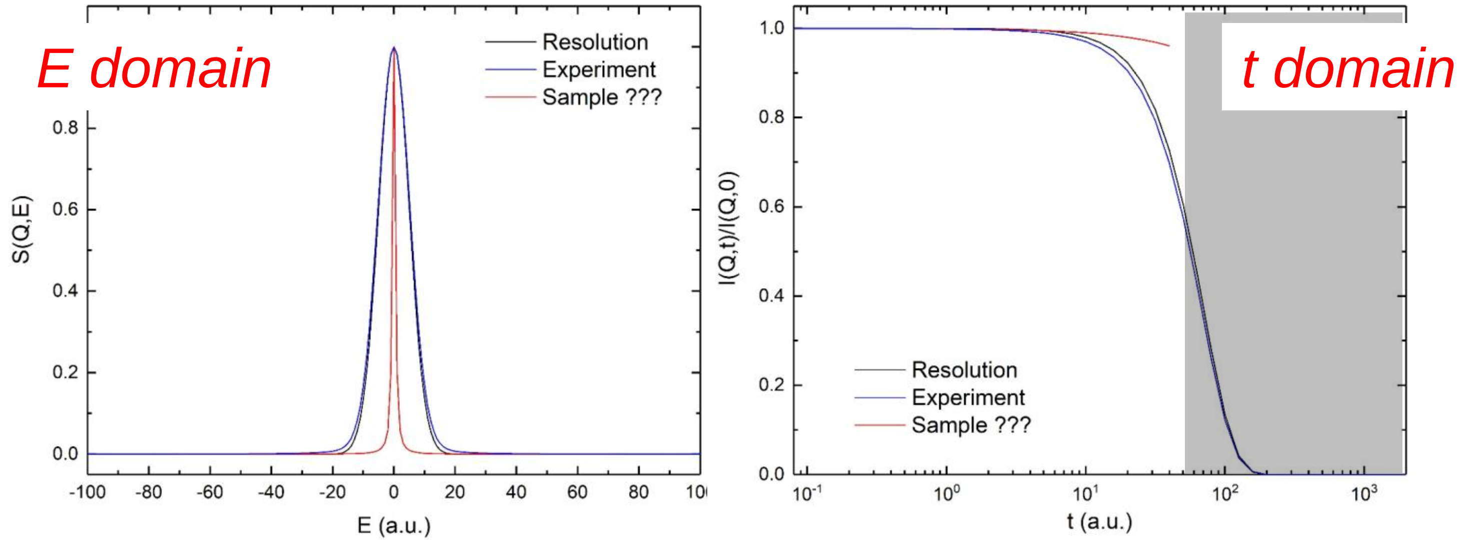
$$I^M(Q,t) = I(Q,t) \times R(Q,t)$$
$$I(Q,t) = I^M(Q,t)/R(Q,t)$$





Instrumental Resolution

When the measured signal approaches the resolution, it is practically impossible, considering experimental uncertainties, to get information on the sample



Knowledge Check

A QENS spectrometer has a resolution of $\approx$1 μeV and an energy window of $\pm$50 μeV.

An NSE spectrometer can probe times from 50 ps to 50 ns.

A 10 nm diameter nanoparticle is diffusing in water at room temperature.

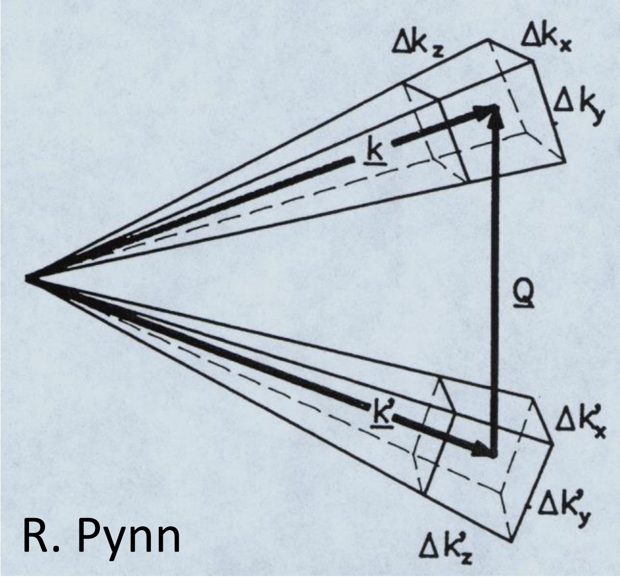
Just considering the timescale of its diffusion in what Q range would the two spectrometers be able to probe the diffusive motion.

Instrumental Resolution

Uncertainties in the neutron wavelength & direction of travel imply that *Q* and *E* can only be defined with a certain precision

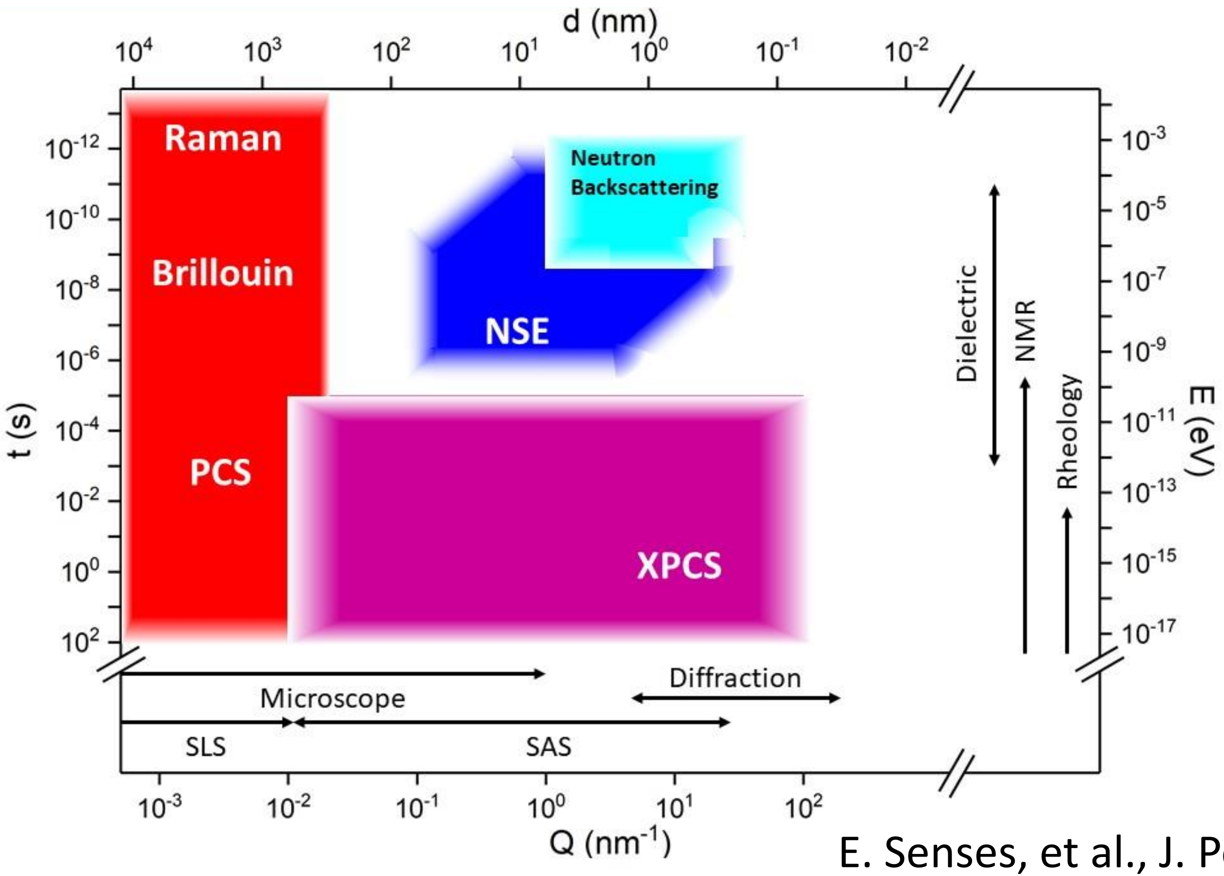
When the box-like resolution volumes in the figure are convolved, the overall resolution is Gaussian (central limit theorem) and has an elliptical shape in *(Q,E)* space

The total signal in a scattering experiment is proportional to the phase space volume within the elliptical resolution volume



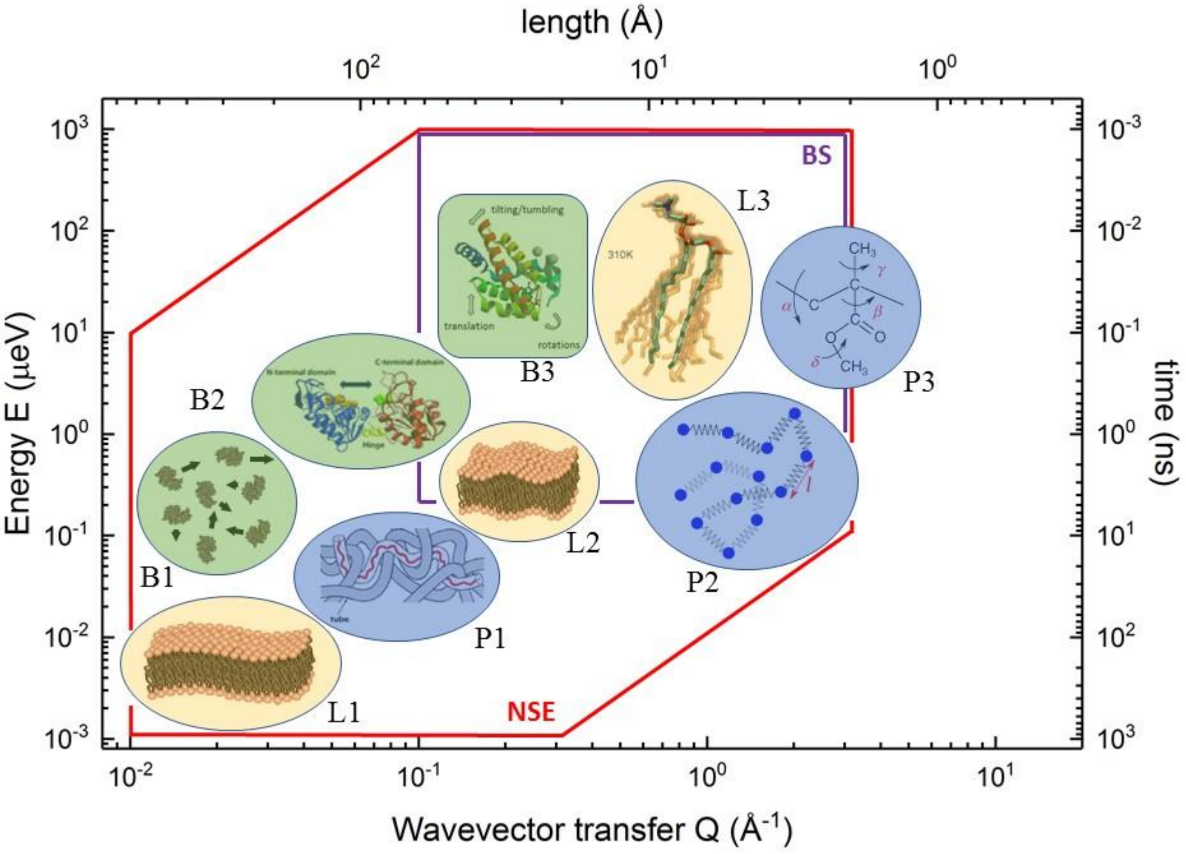
The better the resolution, the smaller the resolution volume and the lower the count rate

Dynamic Neutron Scattering length- and time- scale



E. Senses, et al., J. Polym. Sci. (2021)

Dynamic Neutron Scattering in Soft Matter



Conclusion

Dynamic neutron scattering techniques provide useful, often unique, insights in the motion occurring at equilibrium in soft matter systems.

Keep in mind:

- Length scale
- Time scale
- Coupling with the sample