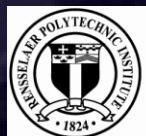


Quasi-elastic Neutron Scattering

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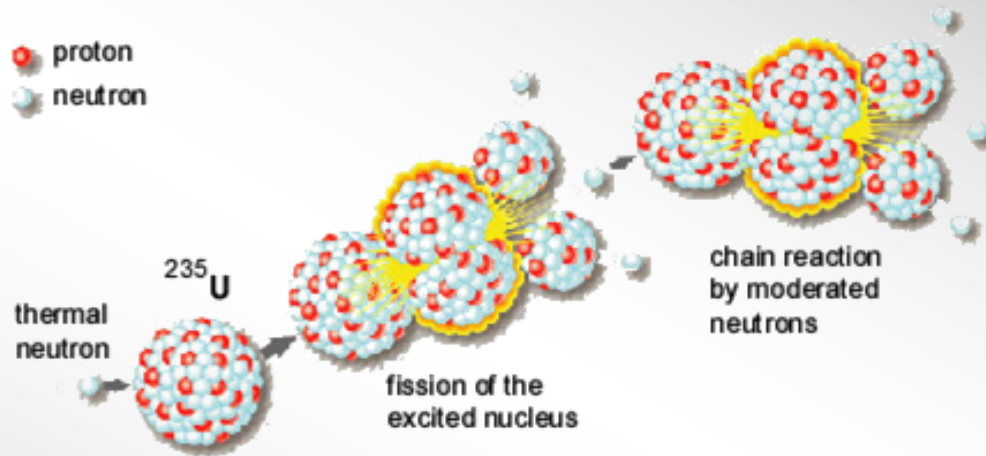
Rensselaer



ENGINEERING PHYSICS
IN CHARACTERIZATION

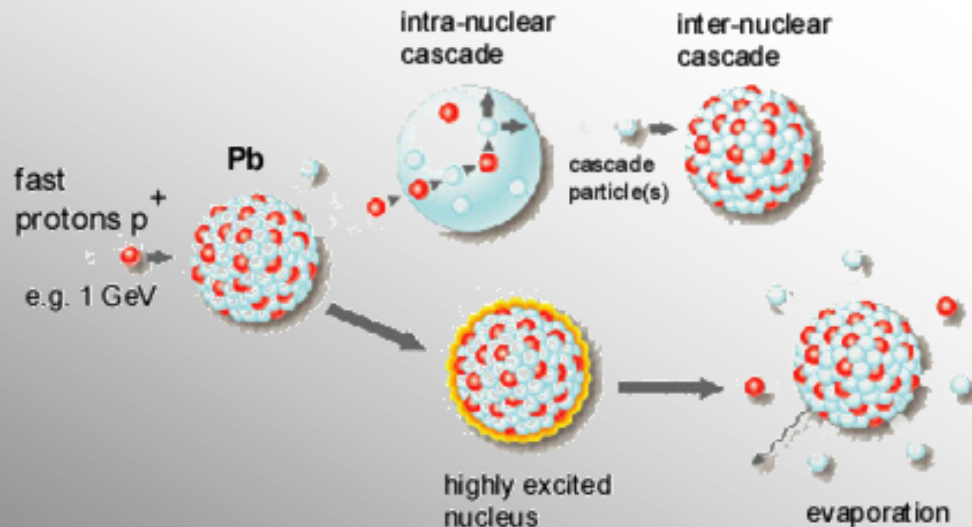
Croucher Summer Course on Neutron Scattering
10-16 August 2025, City University of Hong Kong

How Do We Produce Neutrons?



Fission

- chain reaction
- continuous flow
- 1 neutron/fission
- 180 MeV/neutron



Spallation

- no chain reaction
- pulsed operation
- 40 neutrons/proton
- 30 MeV/neutron



Why Neutrons

Energy $\sim$ meV's (thermal and cold neutrons)

- comparable to the time scale of many motions in materials
=> inelastic scattering from vibrations, diffusion, reorientations, and relaxational processes can be observed
- light $E \sim$ eV's $\lambda \sim 1000$ Å's $Q \sim 0$ (selection rules)
- x-rays $E \sim$ keV's $\lambda \sim$ Å's

cold neutrons - lower energies - longer time scales

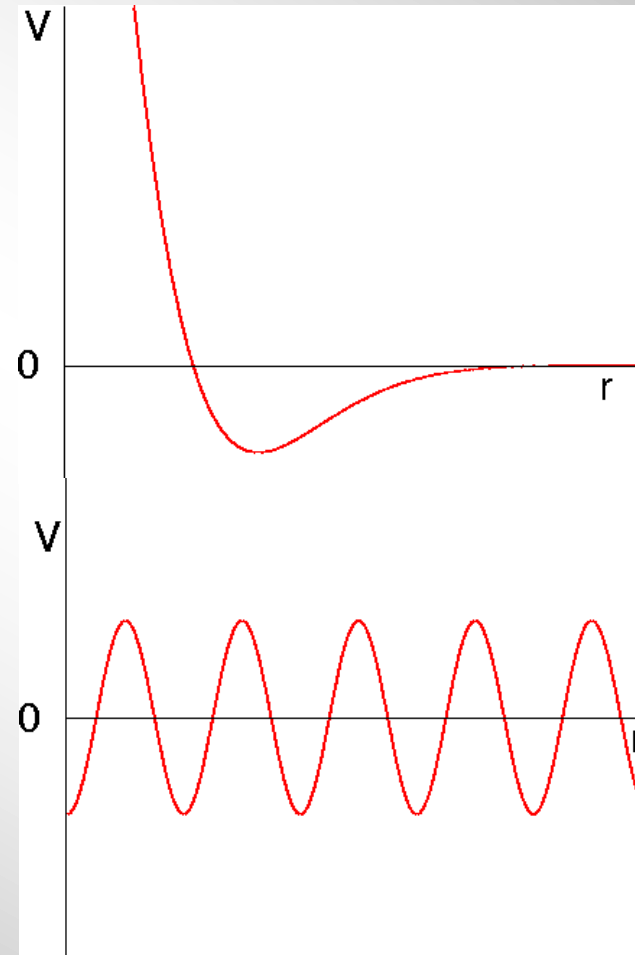
$$1 \text{ meV} \cong 8 \text{ cm}^{-1} \cong 240 \text{ GHz} \cong 12 \text{ K} \cong 0.1 \text{ kJ/mol} \sim \text{ps} = 10^{-12} \text{ second}$$

$\lambda = 1.8 \text{ Å}$ for $E \cong k_B T$ and $T = 300 \text{ K}$. Neutrons probe structure *and* dynamics of condensed matter on the atomic scale.

Structure vs. Dynamics

Fundamental Information on Interactions in Materials

Structural probes yield indirect information on interactions in materials by locating the minimum of the potential. Dynamical probes, including neutron scattering, reveal information on the shape of the potential.

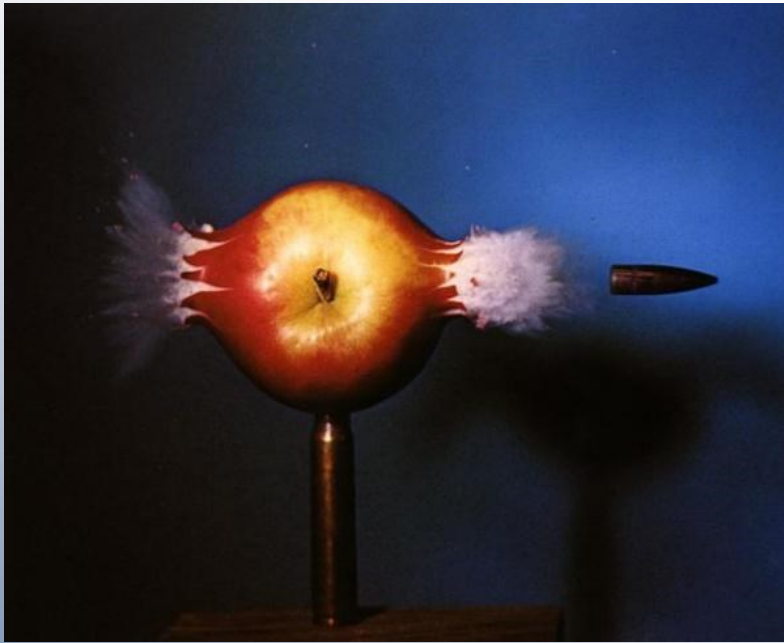


An aerial photograph of a university campus, likely the University of Illinois at Urbana-Champaign, featuring a large, historic building with a prominent dome in the foreground. The campus is surrounded by greenery and modern buildings, with a city skyline visible in the background. The entire image is overlaid with a dark blue tint.

Neutrons for Dynamics

Different time scales

High speed camera
(tracing bullet's movement)

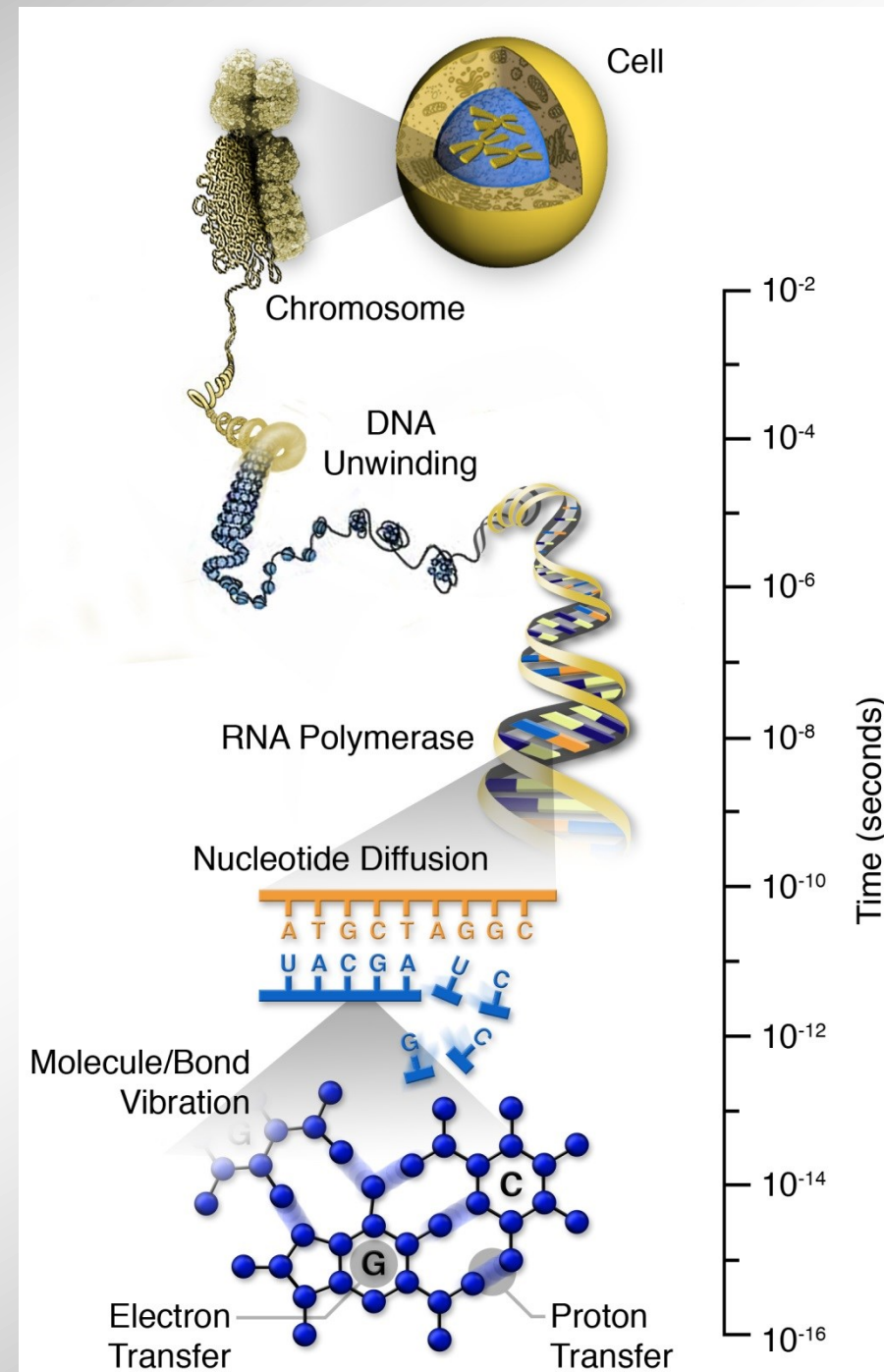


Continental drift
(a very slow process)



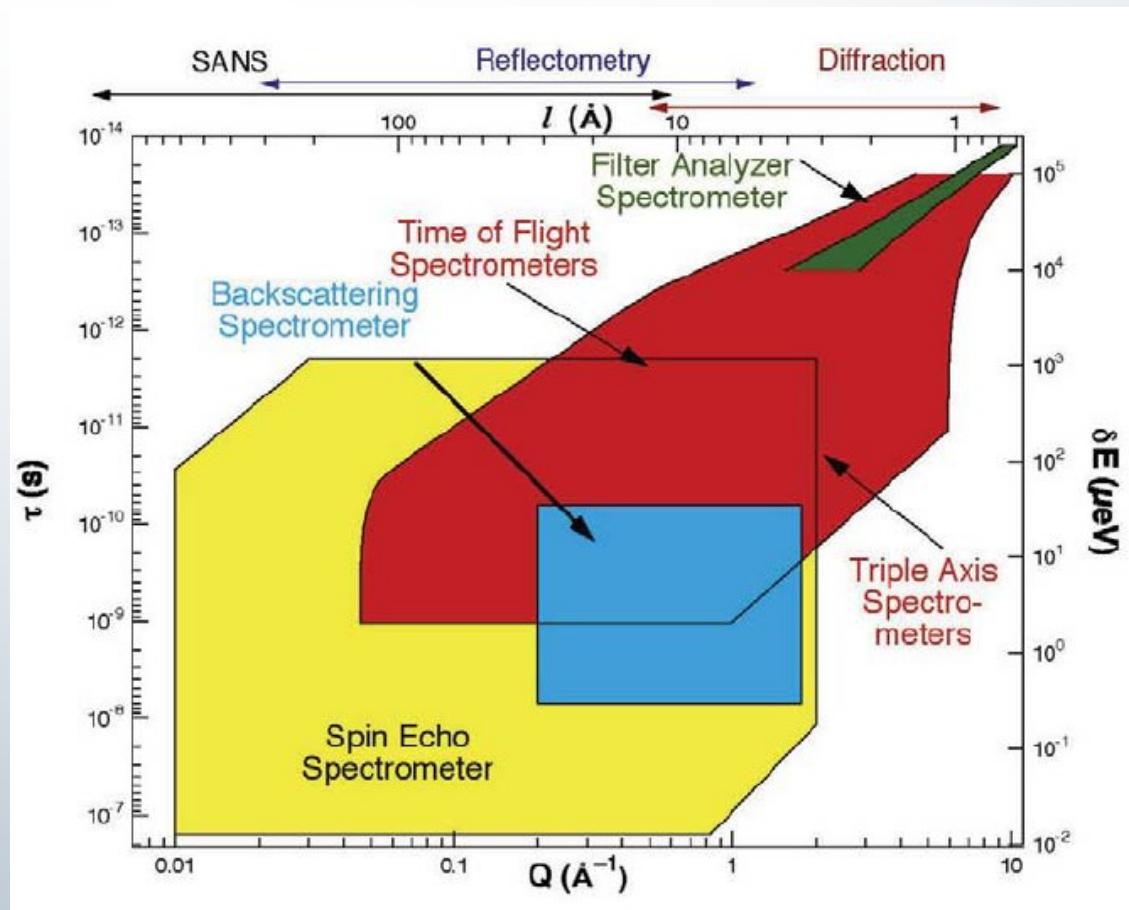
- **We can also measure how things move!**
- **No one length scale, or time scale is more fundamental than any other!**

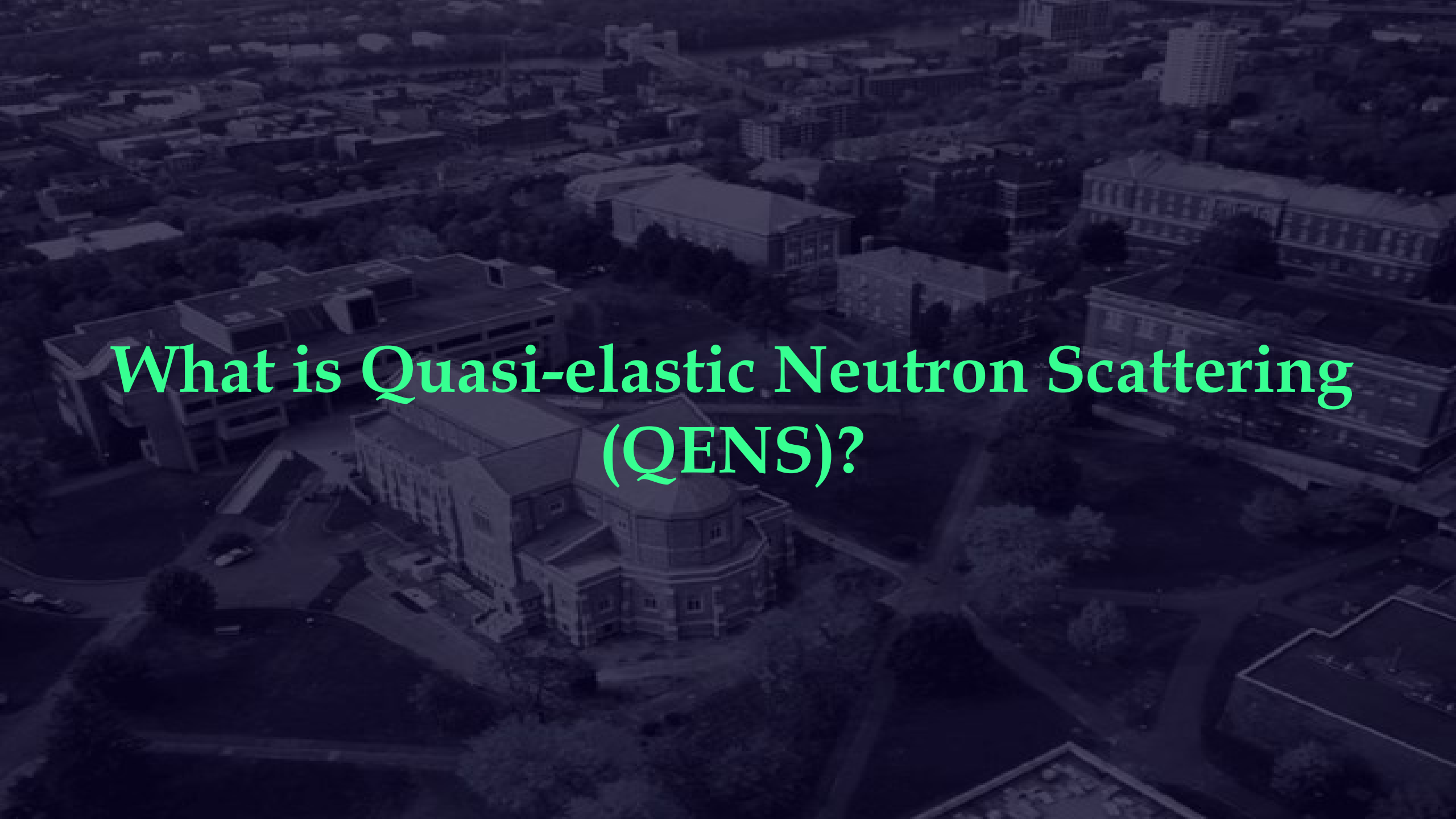
The *dynamics* of a system reflect the interatomic and intermolecular interactions which are responsible for the properties of materials



How to choose appropriate neutron spectrometer (length scale, time scale, and neutron wave length)

Length scale: several μm $\sim$ 0.01 nm; time scale: $1\mu\text{s}$ $\sim$ 0.01 ps

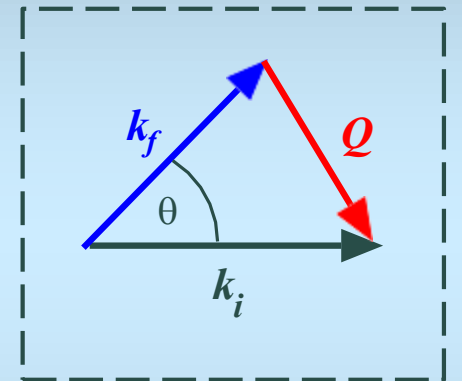
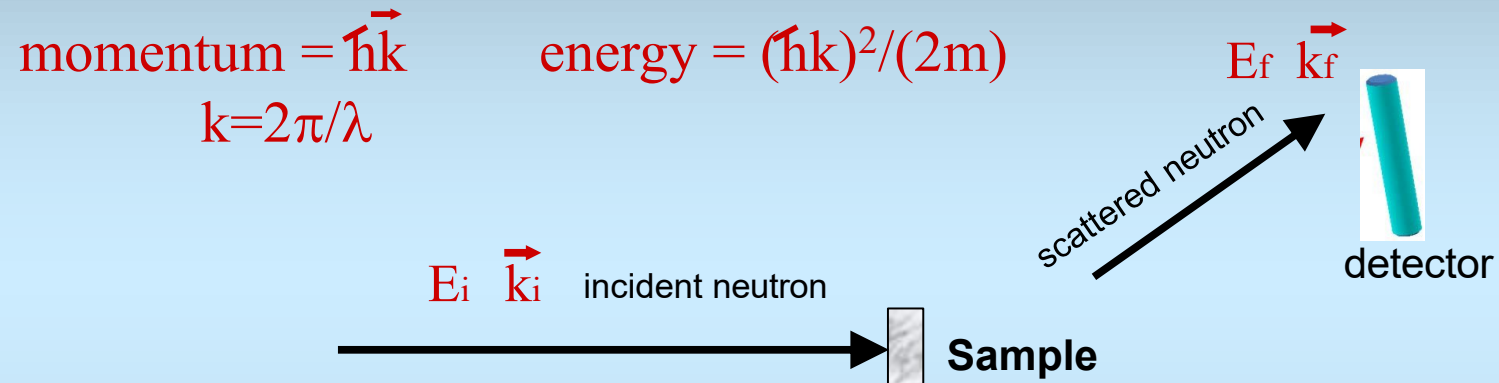


An aerial photograph of a city, likely Cambridge, Massachusetts, featuring a large, historic building with a prominent dome in the foreground. The image is overlaid with a semi-transparent blue filter. The text "What is Quasi-elastic Neutron Scattering (QENS)?" is centered over the image in a bright green, serif font.

What is Quasi-elastic Neutron Scattering (QENS)?

Scattering Process and Geometry

Interaction of neutron with nuclei – there can be an exchange of **momentum** and of **energy** (**non-relativistic**)



Wave vector

$$k = \frac{2\pi}{\lambda}$$

$$\text{Energy} = E = \frac{(\hbar k)^2}{2m_n}$$

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

$$\text{Energy Transfer } \Delta E = \hbar \omega = E_i - E_f$$

$$\text{Momentum Transfer } \Delta \vec{p} = \hbar \vec{Q} = \hbar(\vec{k}_i - \vec{k}_f)$$

$$Q \propto \frac{1}{\text{Length}}$$

$$\omega \propto \frac{1}{\text{Time}}$$

$$\text{Here } \hbar = \frac{h}{2\pi}, \text{ and } h = 6.626176 \cdot 10^{-34} \text{ J} \cdot \text{s}.$$

Quasi-elastic Neutron Scattering

Measure scattered neutrons (double differential scattering cross section $\frac{d^2\sigma_H}{d\Omega d\omega}$) as a function of $\mathbf{Q}$ and $\omega \Rightarrow S(\mathbf{Q}, \omega)$
(*Dynamic Structure Factor*: the scattering function for quasi-elastic and inelastic scattering)

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \frac{k_f}{k_i} \frac{\sigma}{4\pi} S(\mathbf{Q}, \omega)$$

The double differential cross section is related to the dynamic structure factor $S(\mathbf{Q}, \omega)$, which is proportional to the probability that a neutron is scattered with a momentum transfer $\hbar\mathbf{Q}$ and an energy transfer $\hbar\omega$ to the sample. $S(\mathbf{Q}, \omega)$ contains all the physics of the system (in space and time) and **depends only on the system**.

Elastic Scattering, $E_i = E_f$,

Inelastic Scattering, $E_i \neq E_f$

Quasi-elastic Scattering, $E_i - E_f \text{ near } 0$

$$\omega = 0$$

$$\omega \neq 0$$

$$\omega \text{ near } 0$$



Elastic Scattering Intensity $I(\mathbf{Q})$



Dynamic Structure Factor $S(\mathbf{Q}, \omega)$

Scattering function

$$S(Q,\omega) = S_{\text{inc}}(Q,\omega) + S_{\text{coh}}(Q,\omega)$$

$S_{\text{inc}}(Q,\omega)$ is the time and space Fourier transform of the **SELF** correlation function

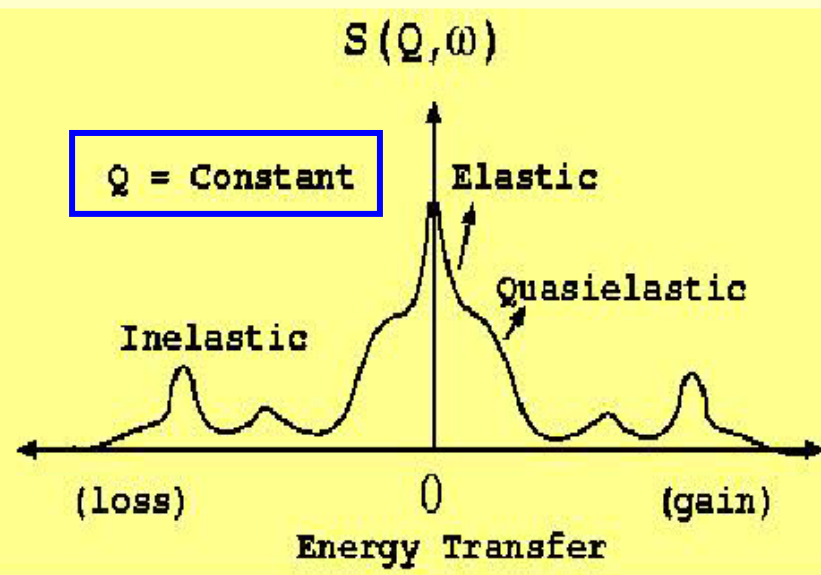
$S_{\text{coh}}(Q,\omega)$ is the time and space Fourier transform of the **PAIR** correlation function

* Spin Echo measures the INTERMEDIATE scattering function $I(Q,t)$

An aerial photograph of a city, likely New York City, showing a dense urban landscape. In the foreground, a large, ornate church with a prominent dome and multiple spires is visible. The church is surrounded by greenery and a few smaller buildings. In the background, a variety of city buildings, including skyscrapers and residential structures, are visible under a clear sky. The overall scene is captured from a high angle, providing a comprehensive view of the urban environment.

Spectra and Motions

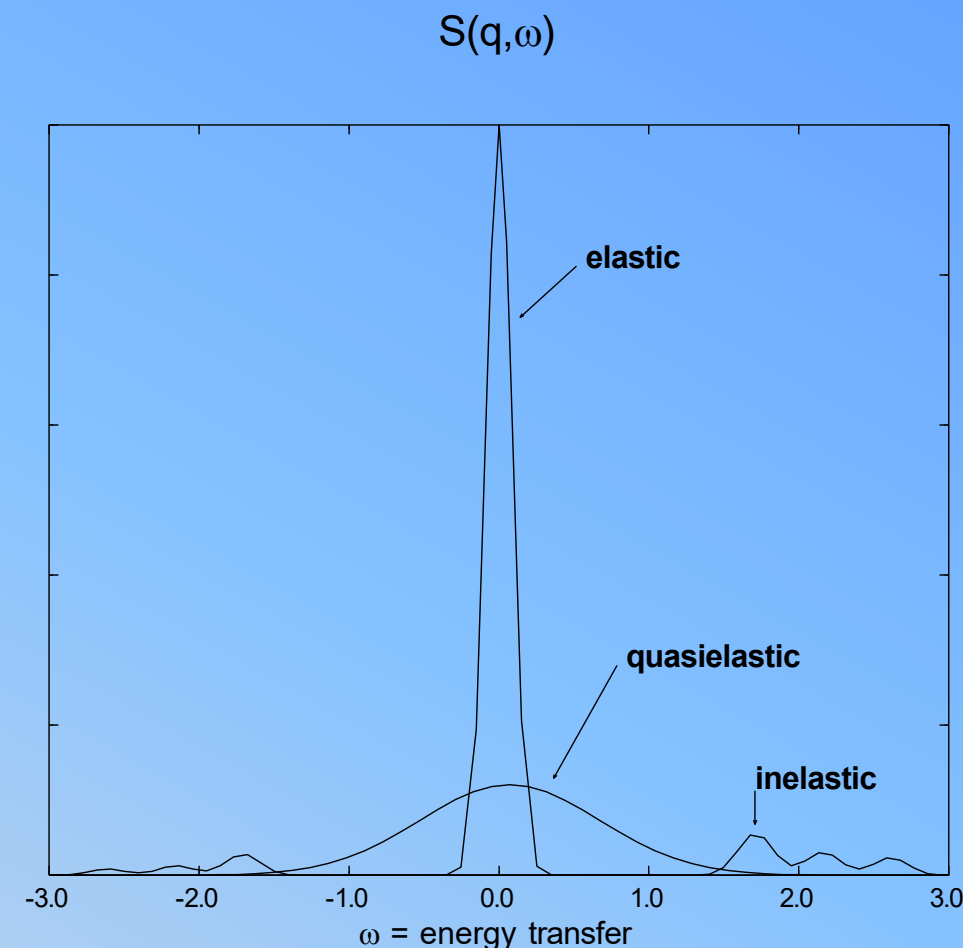
Quasielastic and Inelastic Neutron Scattering



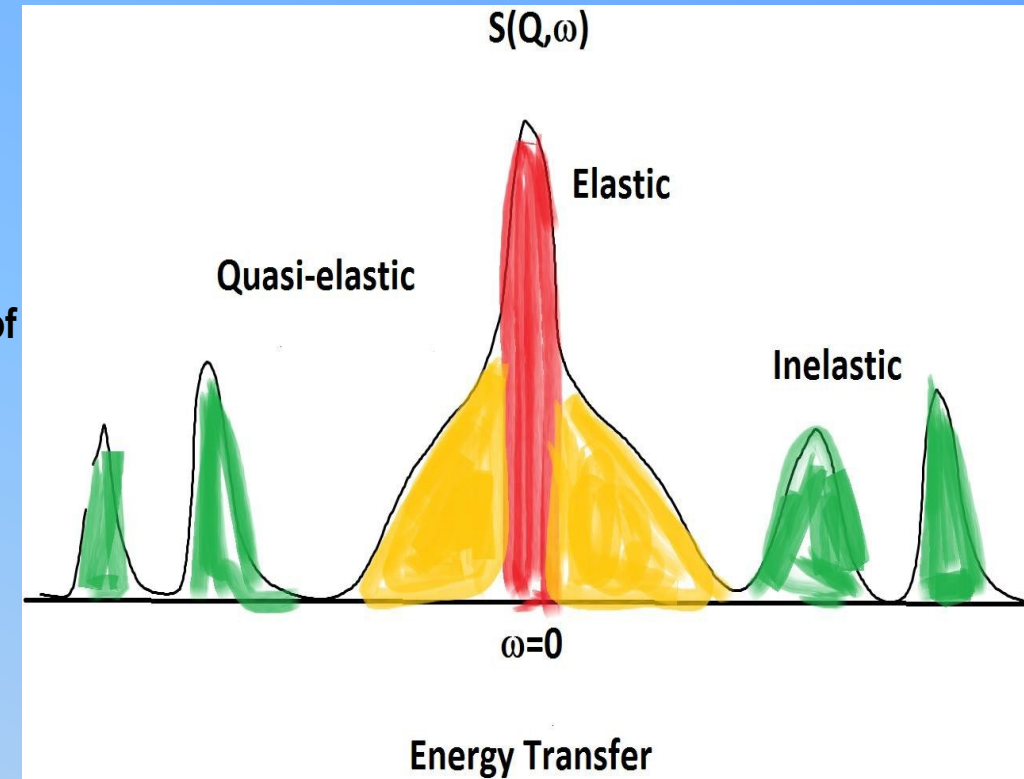
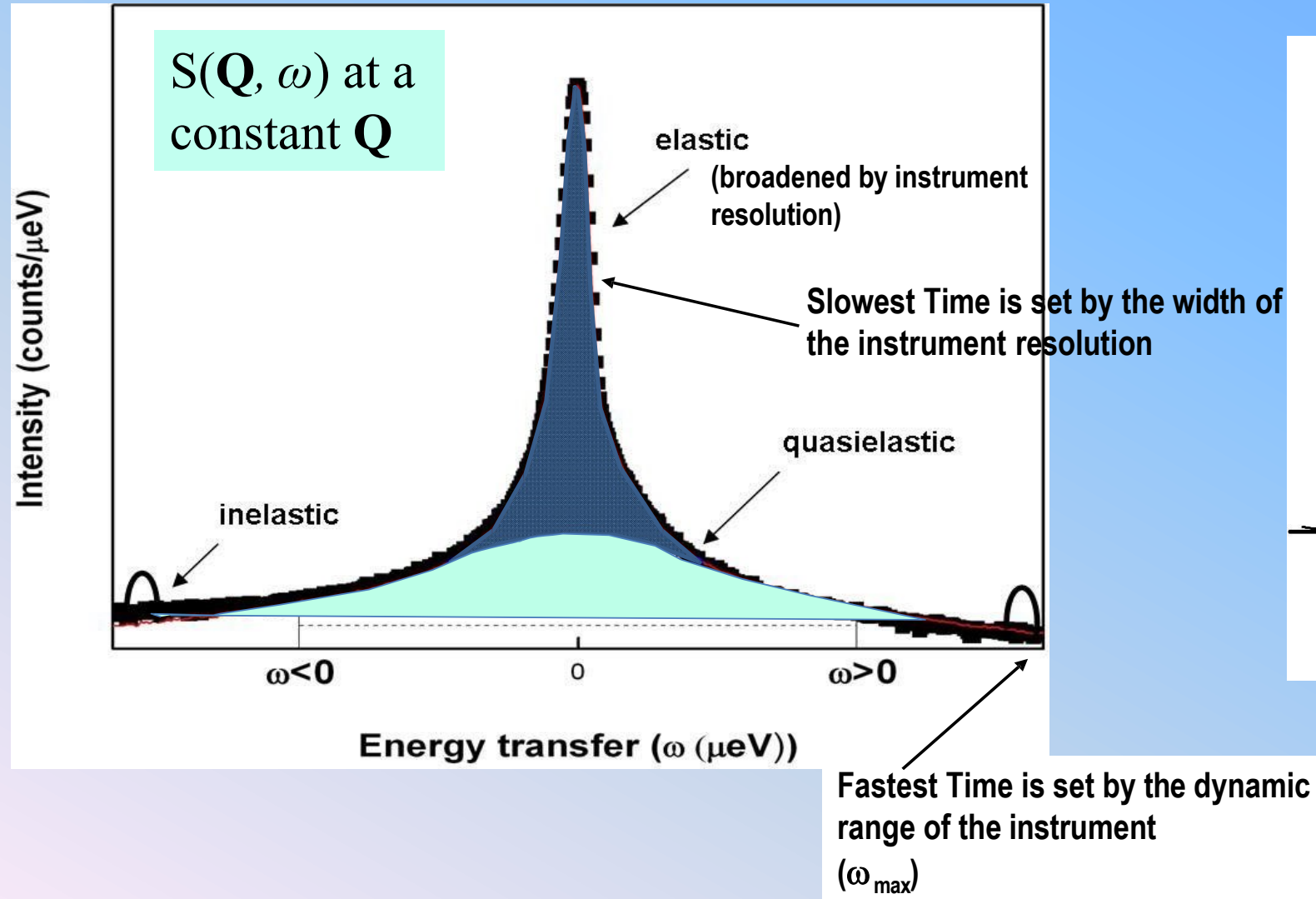
Inelastic neutron scattering peaks at non-zero energy transfer. This scattering reflects the vibrational modes of the system.

Quasielastic neutron scattering peaks at zero energy transfer, but is broadened compared to the instrumental resolution. It arises from diffusive processes.

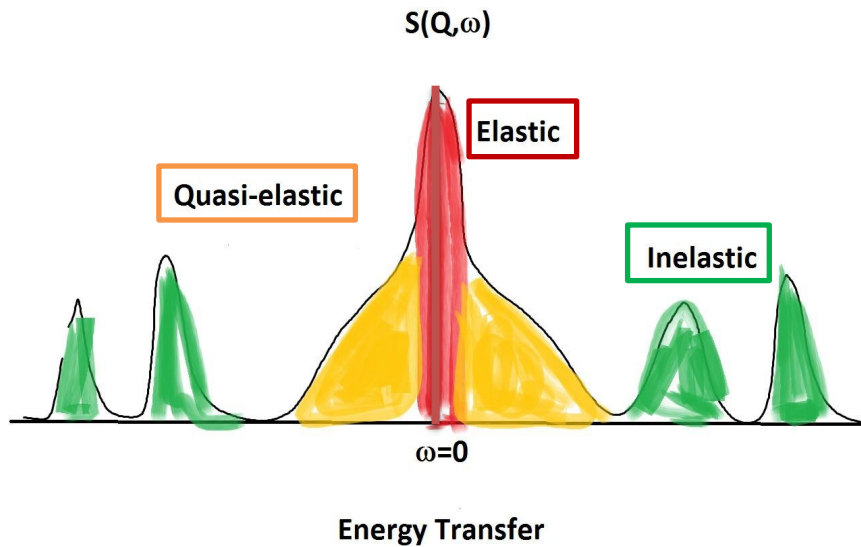
Elastic neutron scattering is the scattering for which the energy transfer is identically zero.



QENS Spectra



Quasi-Elastic Scattering



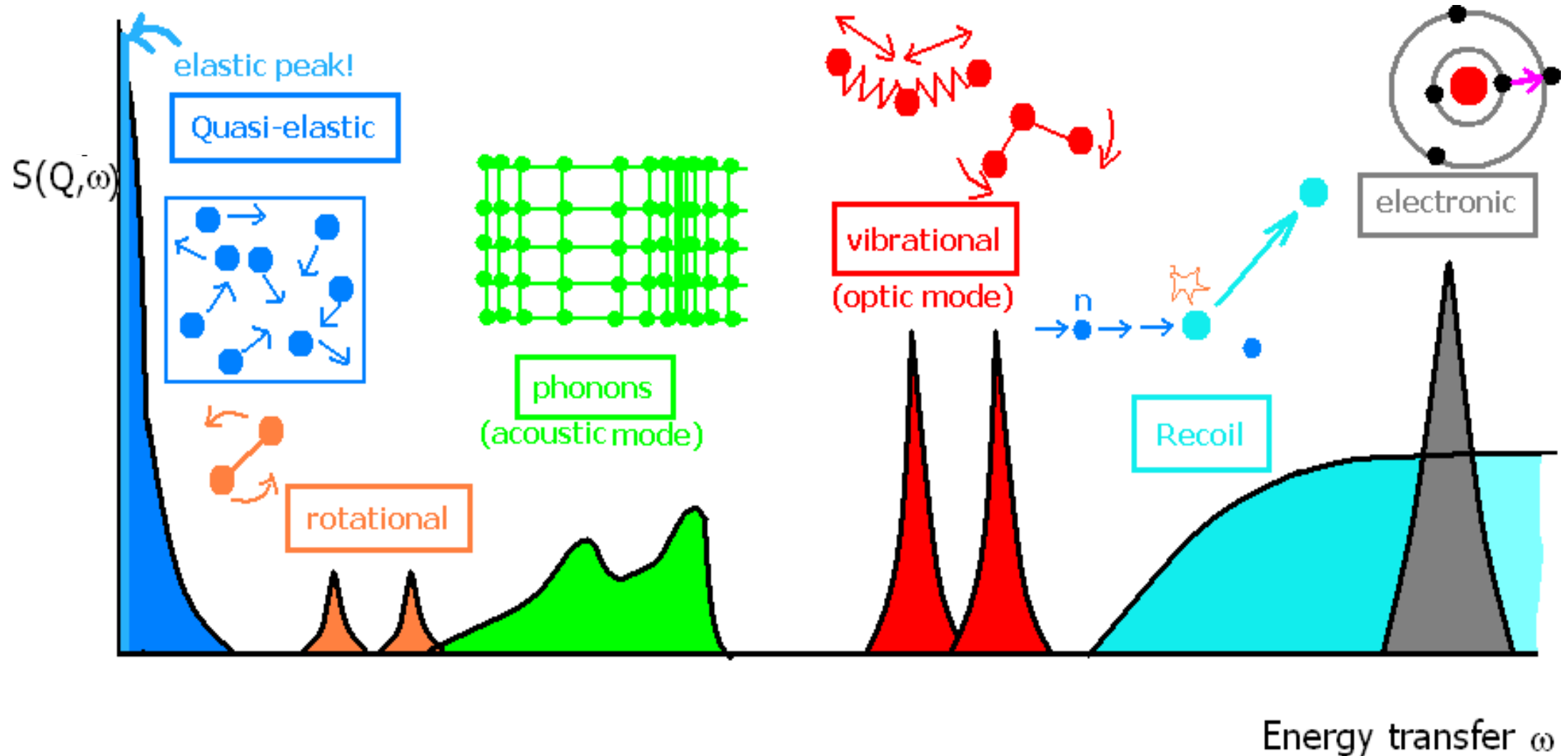
Elastic scattering – no energy exchange $\hbar\omega=0$. In an ideal world this should be a delta function. Of course, this is not the case giving rise to an instrumental resolution.

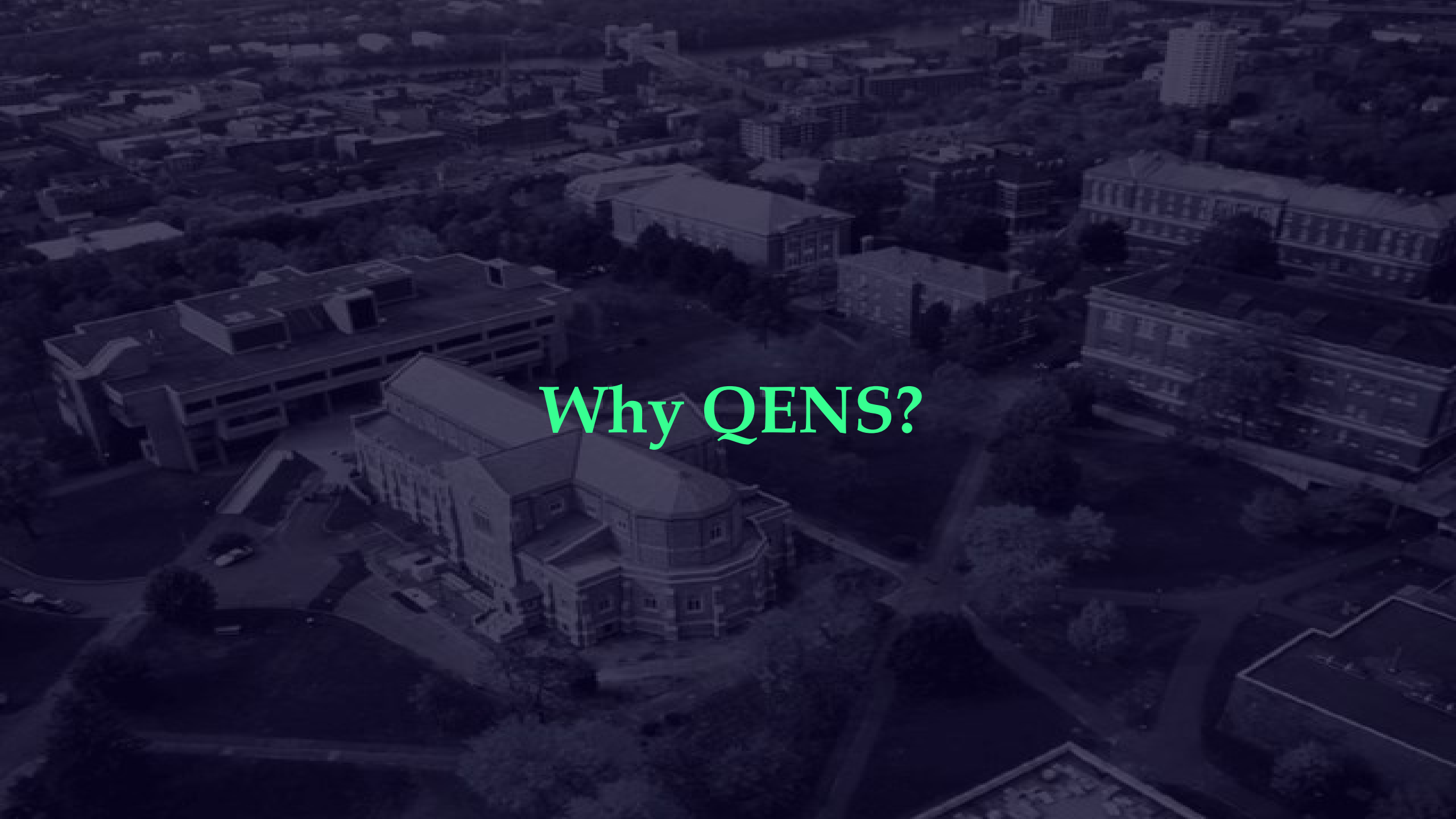
$$S(\mathbf{Q}, \omega) = S^*(\mathbf{Q}, \omega) \otimes R(\mathbf{Q}, \omega)$$

Inelastic scattering – there is energy exchange $\hbar\omega \neq 0$. Due to processes occurring discrete energy steps such as vibrational modes, stretching modes...

Quasi-elastic scattering (QENS) – there is small energy exchange $\hbar\omega \neq 0 \approx \text{neV}$ or μeV . **High energy resolution**. Due to processes occurring with a distribution of energies (rotations, translations...).

Map of dynamical modes



An aerial photograph of a city, likely New York City, with a large, ornate church building in the foreground. The church has a prominent dome and is surrounded by other buildings and greenery. The text "Why QENS?" is overlaid in the center of the image.

Why QENS?

Quasi-Elastic Scattering – Why care?

- Probes dynamics in a wide **range of science** areas
 - *Materials science*: hydrogen storage, surface science, fuel cells
 - *Soft Matter*: polymer nanocomposites and blends, organic photovoltaics, polymer electrolytes
 - *Biology*: hydration water, protein structure-dynamics-function relationships, cell membrane-protein/small molecules interactions, drug delivery, protein binding
 - *Chemistry*: ionic liquids, clays, porous media, complex fluids

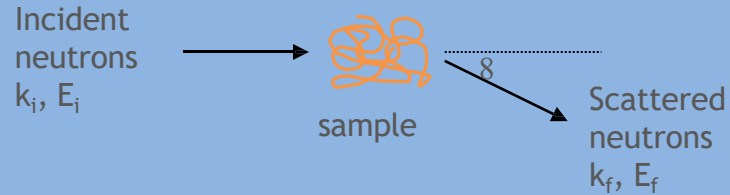
Quasi-Elastic Scattering – Why care?

- Probes diffusion at a molecular scale
- Is able to differentiate bulk from confined dynamics
- Analytical functions used to describe motions
- Can be used as a systematic tool for comparisons
- Time and spatial scale are directly comparable to results from Molecular Dynamics simulations
- Complementarities with other experimental techniques
- Unique view of motions (eg. contrast)

An aerial photograph of a university campus, featuring various academic buildings, green spaces, and parking areas. The image is overlaid with a semi-transparent dark blue filter. The word "Instruments" is centered in a bright green, serif font.

Instruments

QENS Summary

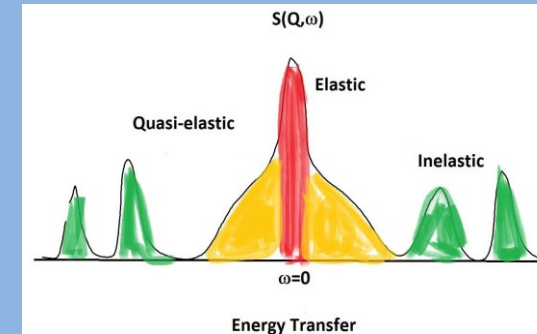


We measure $S(Q, \omega)$, the number of scattered neutrons as a function of Q and ω .
What information does $S(Q, \omega)$ give us?

Q gives information about structure

ω gives information about dynamics (motion)

- Elastic
- Quasi-elastic
- Inelastic



Elastic Scattering

Quasi-elastic/Inelastic Scattering

Structure

$$[r_i(0) - r_j(0)]$$



- SANS, reflectometry, diffraction
- Coherent scattering
- Contrast due to differences in scattering length densities

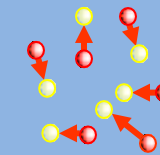
Relative motion

$$[r_i(t) - r_j(0)]$$

- Neutron spin-echo
- Coherent scattering
- Contrast due to differences in scattering length densities

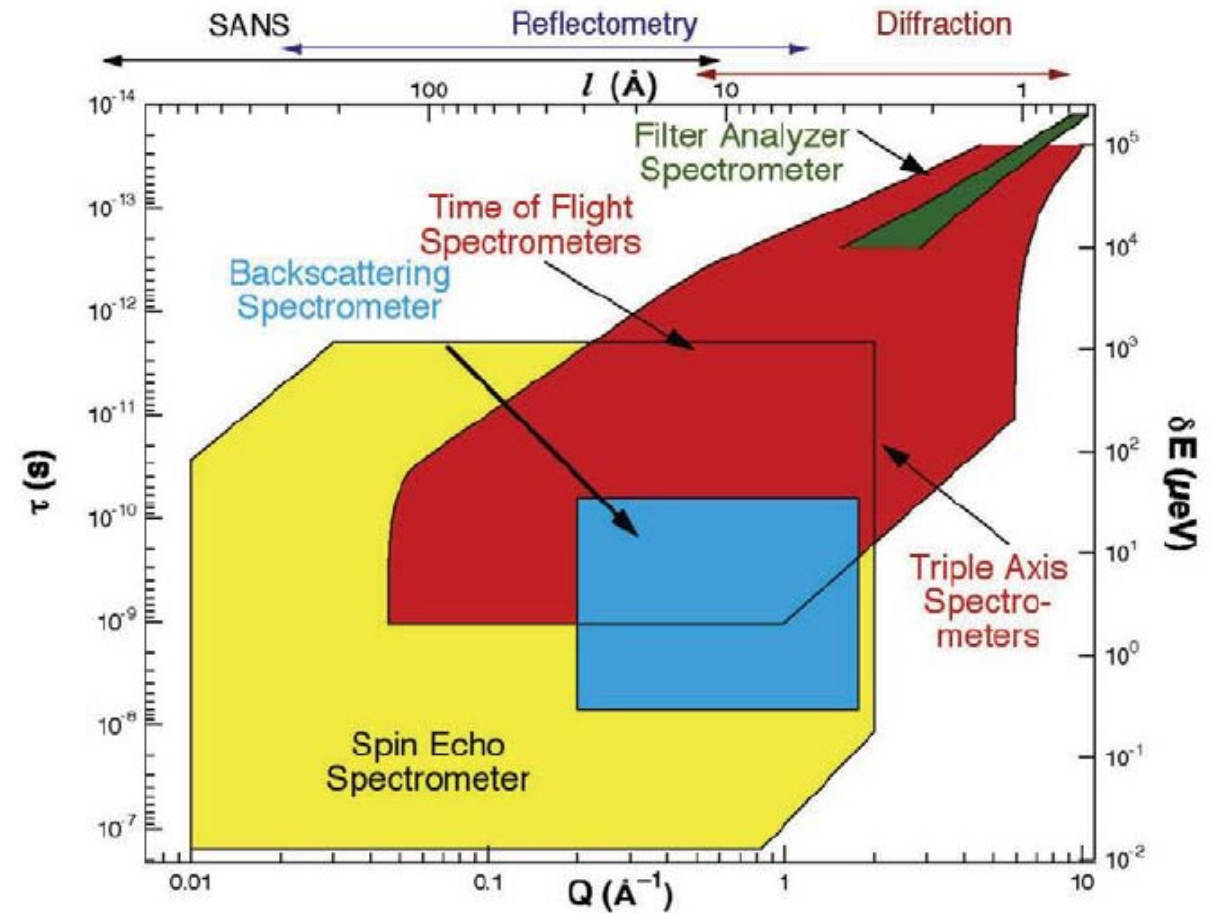
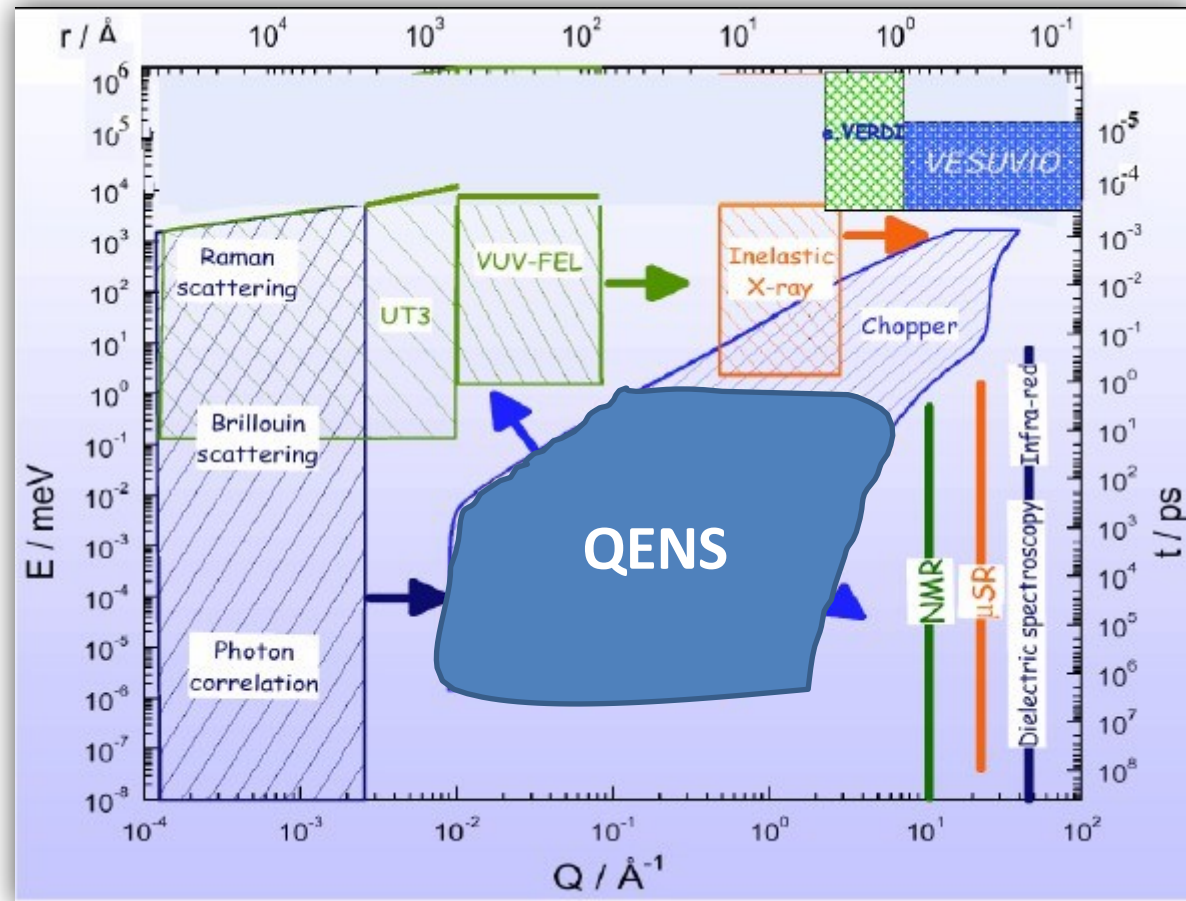
Self motion

$$[r_i(t) - r_i(0)]$$

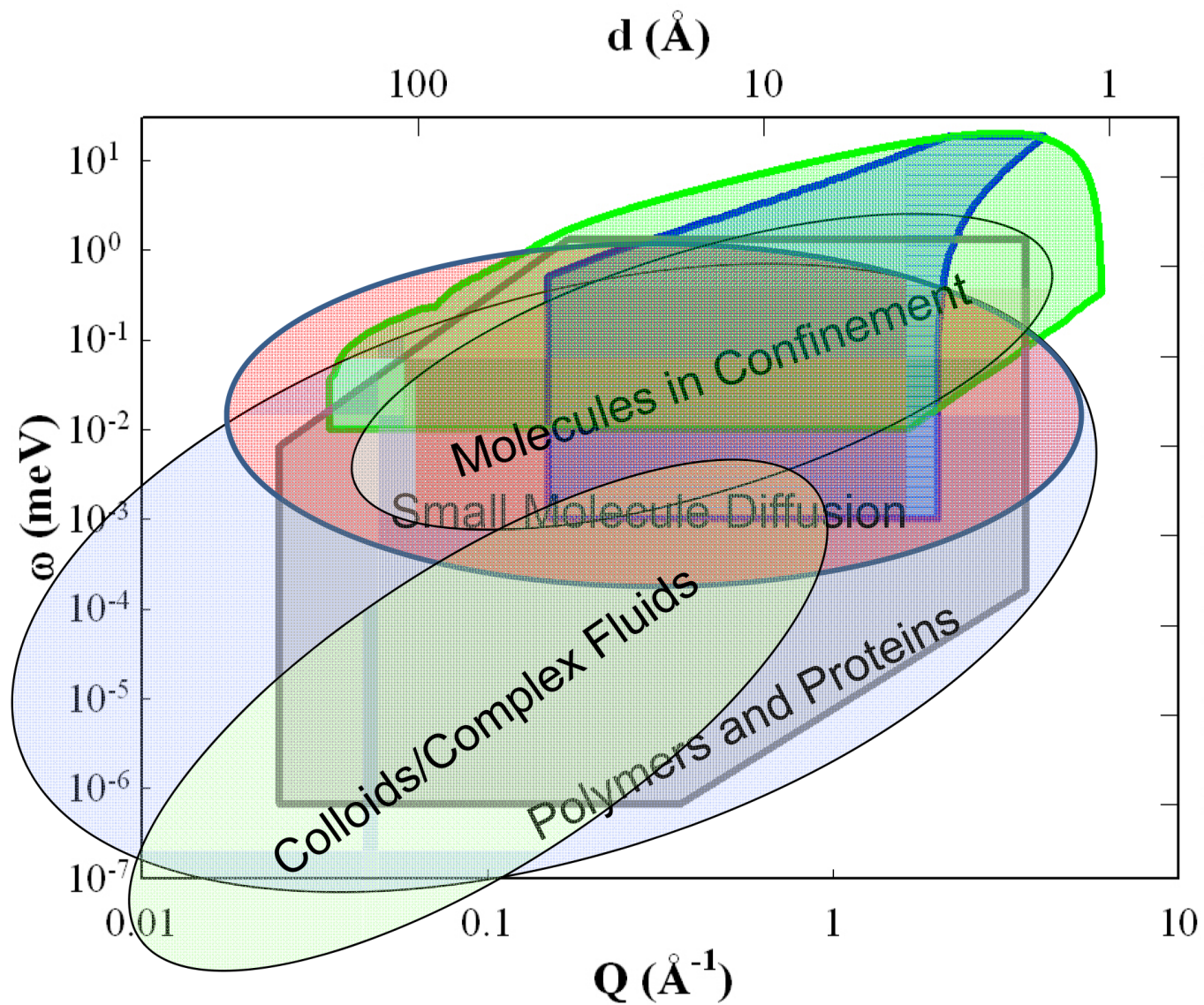


- Backscattering, time-of-flight
- Incoherent scattering
- Contrast provided by large incoherent x-section of H atoms

Map of dynamical modes



The High-Resolution Neutron Spectrometer Landscape



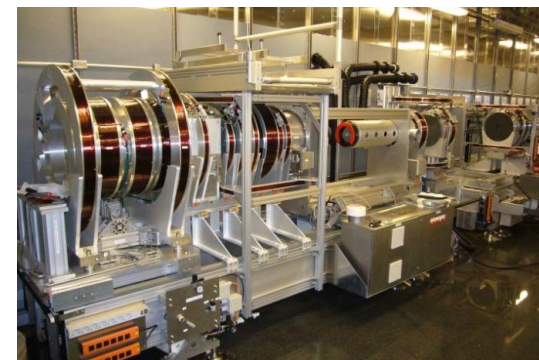
● Backscattering



● Cold Neutron Chopper



● Neutron Spin Echo



Disc-Chopper Spectrometer at NIST

DCS at NIST

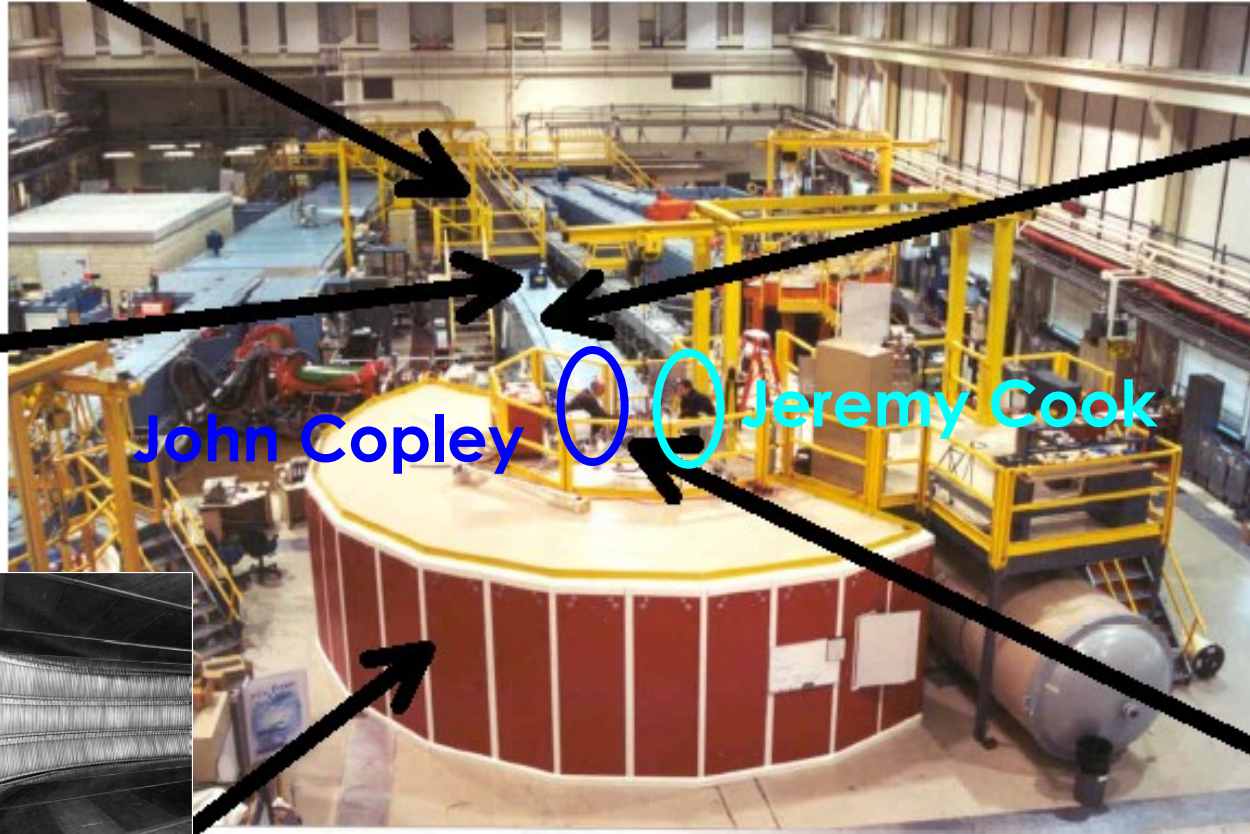
(1) The neutron guide

(2) The
crystal
filter

(3) The
choppers

(4) The
sample area

(5) The flight chamber and the detectors



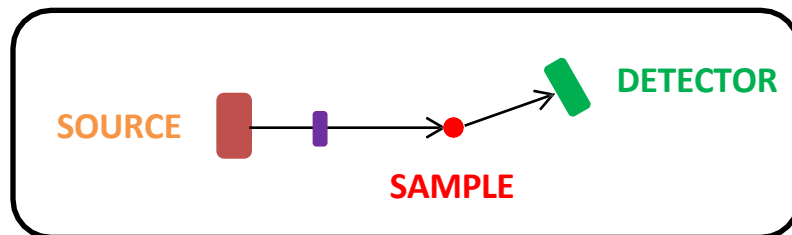
John Copley

Jeremy Cook

Instrumentation

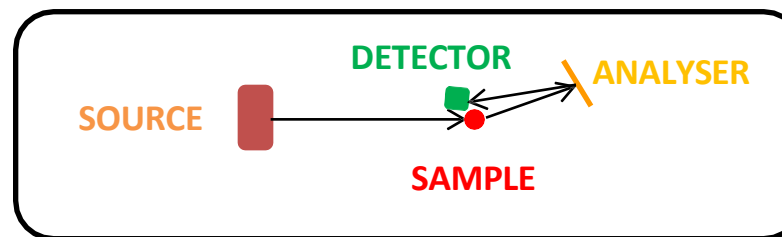
Frequency domain $S(Q, \omega)$

Direct geometry



- Lower energy resolution
- Larger ΔE and Q range
- Flexible in choosing Q-E space
- Repetition Rate Multiplication
- Picosecond
- Self-correlation function (H)
- IN5, LET, CNCS ...

Indirect geometry or Backscattering

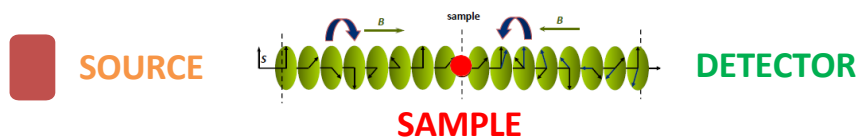


- Higher energy resolution
- Smaller ΔE and Q range
- Fixed Q-E space
- Picosecond-nanosecond
- Self-correlation function (H)
- DNA, IRIS, IN16B, HFBS

Instrumentation

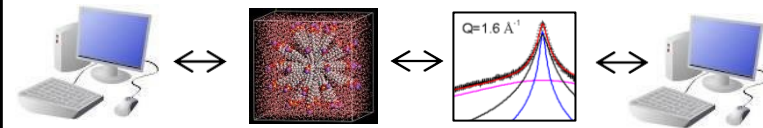
Time domain $I(Q,t)$

Neutron Spin Echo



- Highest energy resolution
- Typically lower Q range
- Nanosecond
- Collective dynamics (H/D)
- IN15, NIST-NSE

Molecular Dynamics Simulations



- Flexible parameter space
- Large parameter space
- Need to optimize and choose FF
- Directly comparable with neutron data

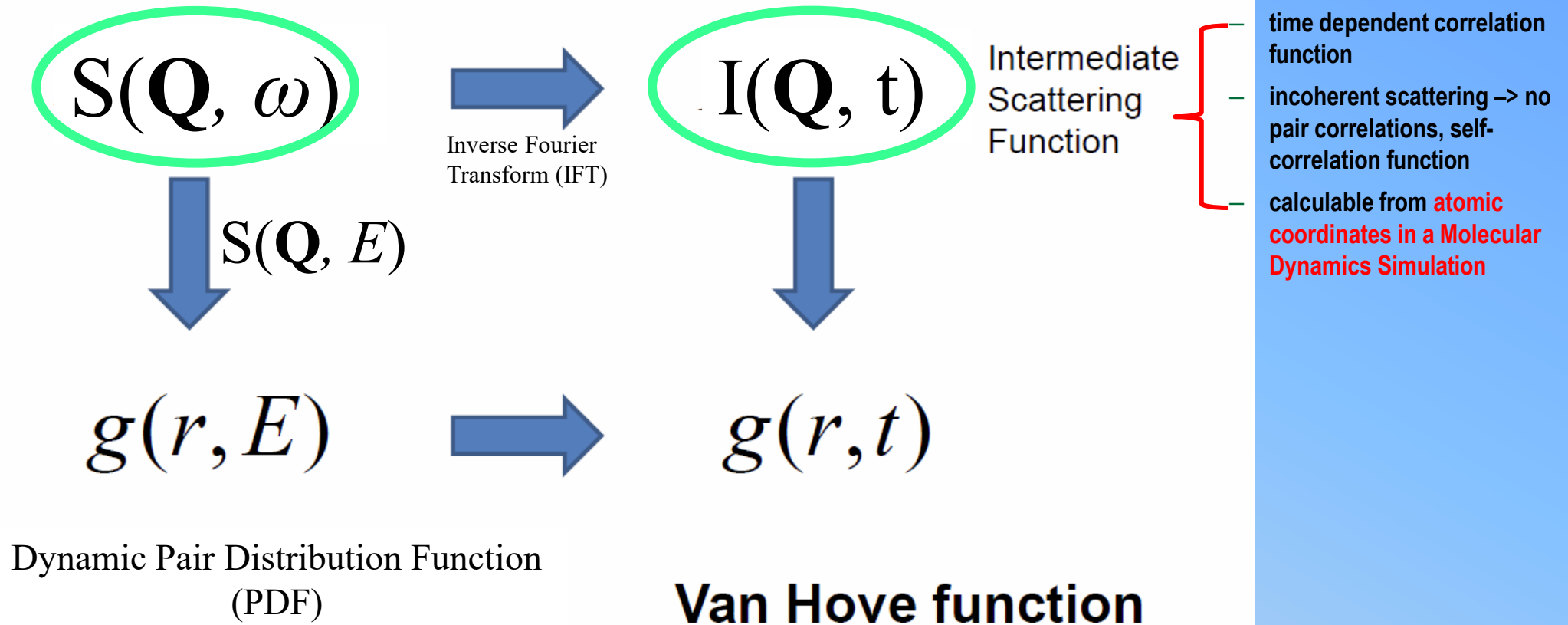
An aerial photograph of a city, likely New York City, showing a dense urban landscape. In the foreground, a large, ornate church with a prominent dome and classical architectural features is visible. The church is surrounded by greenery and a parking lot. In the background, a variety of city buildings, including residential and commercial structures, are visible, interspersed with trees. The overall scene is captured from a high angle, providing a comprehensive view of the urban environment.

How to Analyze and Understand QENS?

Real Space and Reciprocal Space: Dynamics

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I(\mathbf{Q}, t) \exp(-i\omega t) dt; \quad F(\mathbf{Q}, t) = \int_{-\infty}^{\infty} S(\mathbf{Q}, \omega) e^{i\omega t} d\omega$$

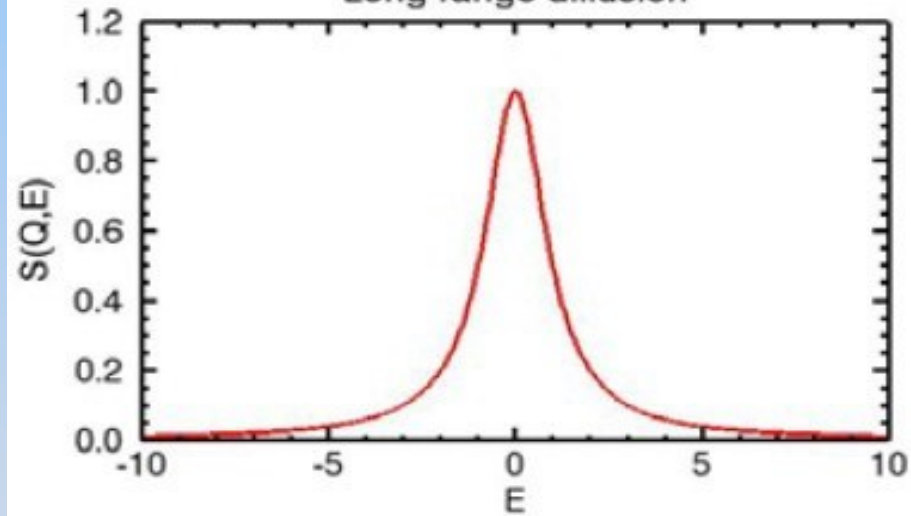
Dynamic Structure Factor $S(\mathbf{Q}, \omega)$ is sensitive to structural and dynamical correlations of atomic positions.



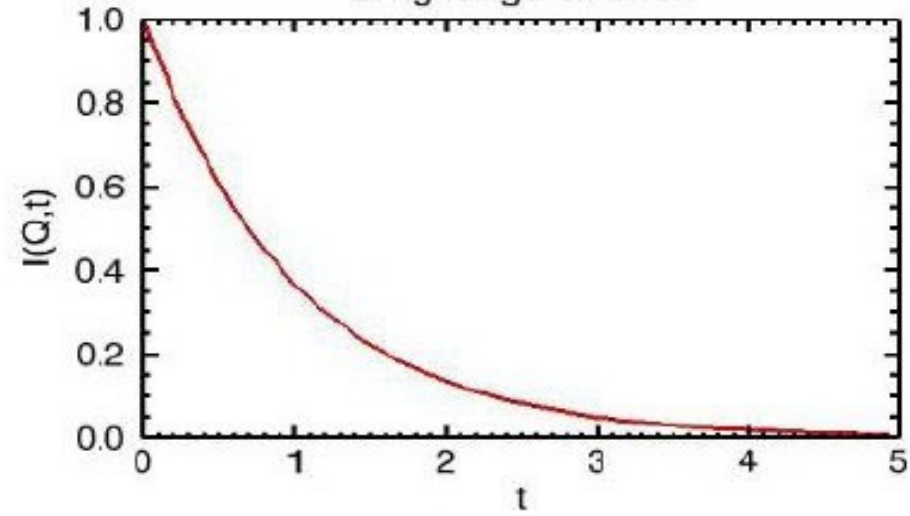
Van Hove function

Typical $S(Q,\omega)$ and $I(Q,t)$

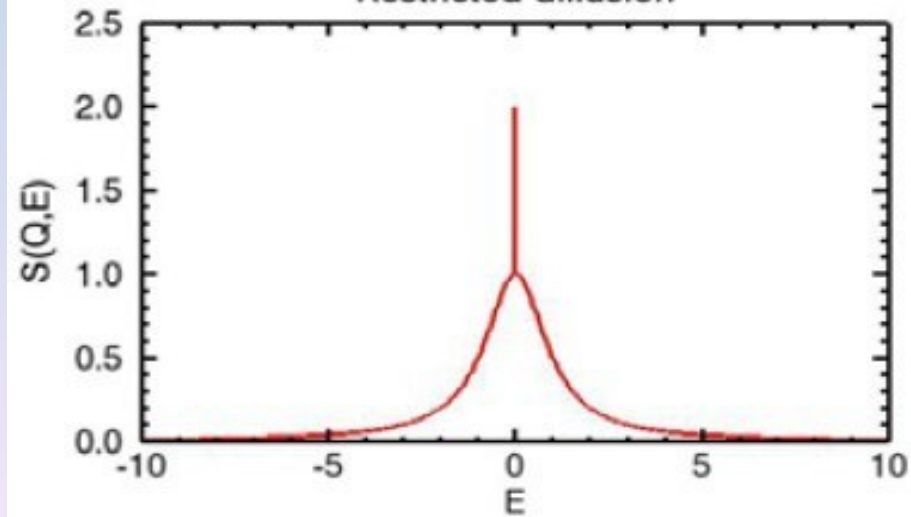
Long range diffusion



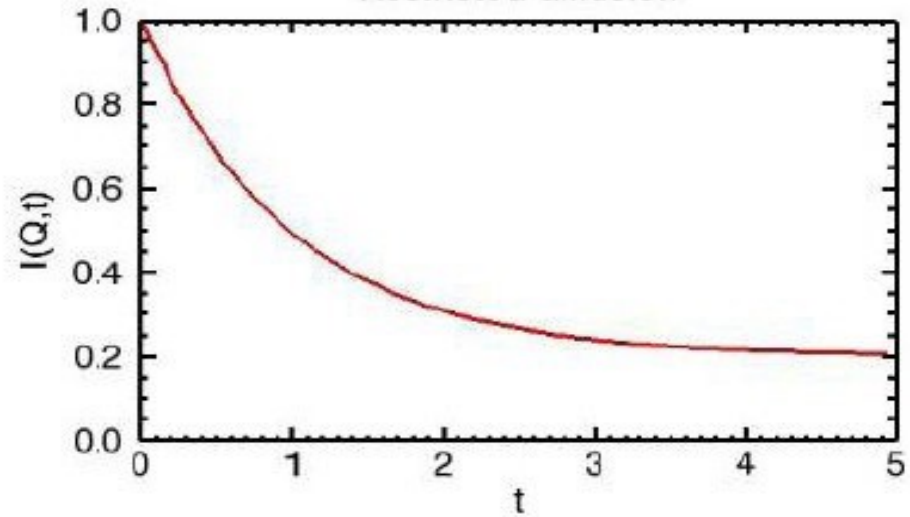
Long range diffusion



Restricted diffusion

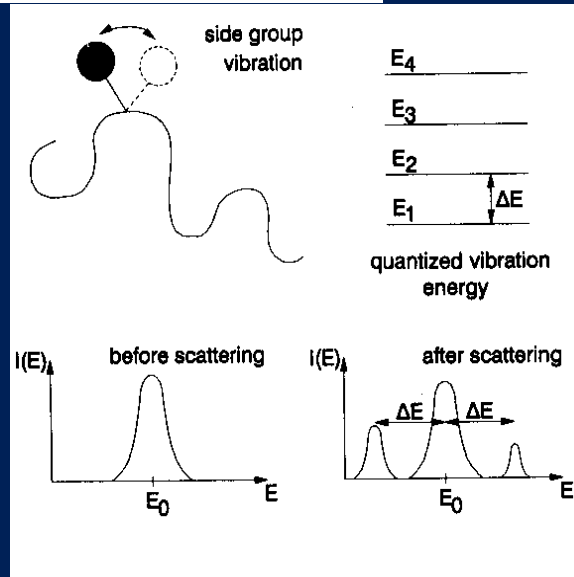


Restricted diffusion



$$S(Q, \omega) = FT[I(Q, t)]$$

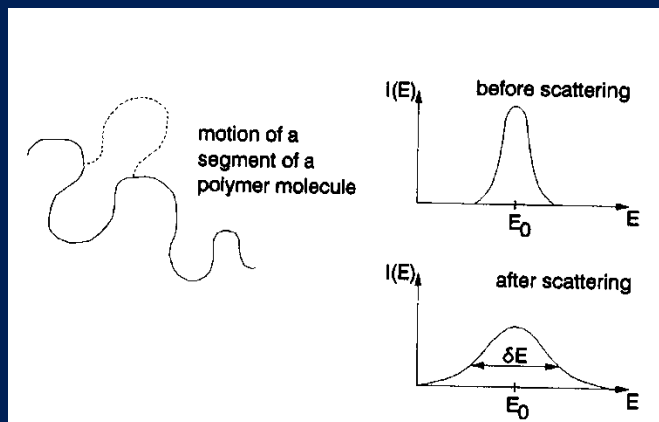
Inelastic Scattering from molecular vibrations



If atoms oscillate around fixed positions:

- intermediate scattering function $I(Q, t)$ has oscillating component;
- the dynamic structure factor $S(Q, \omega)$ has an **inelastic component** shifted in energy $\Delta E = \hbar\omega$. Also significant elastic component is present.

Quasi-elastic Scattering from translation, rotation and conformation-jump motions



If atoms change their position:

- $I(q, t)$ decays with a rate that is inversely proportional to characteristic relaxation time of the motion τ ;
- $S(q, \omega)$ has **quasielastic component** (broadening of the elastic line) with the width inversely proportional to τ . Depending on type of motion, elastic component can be present.

QENS scattering function

$$S(\mathbf{Q}, \omega) = S_{\text{inc}}(\mathbf{Q}, \omega) + S_{\text{coh}}(\mathbf{Q}, \omega)$$

- **Incoherent** scattering
 - Contains no information about structure
 - Describes the **dynamics of individual** particles
- **Coherent** scattering
 - Contaminates elastic signal arising from **structure**
 - Describes **correlations between nuclei**
 - Describes the **collective dynamics** of nuclei

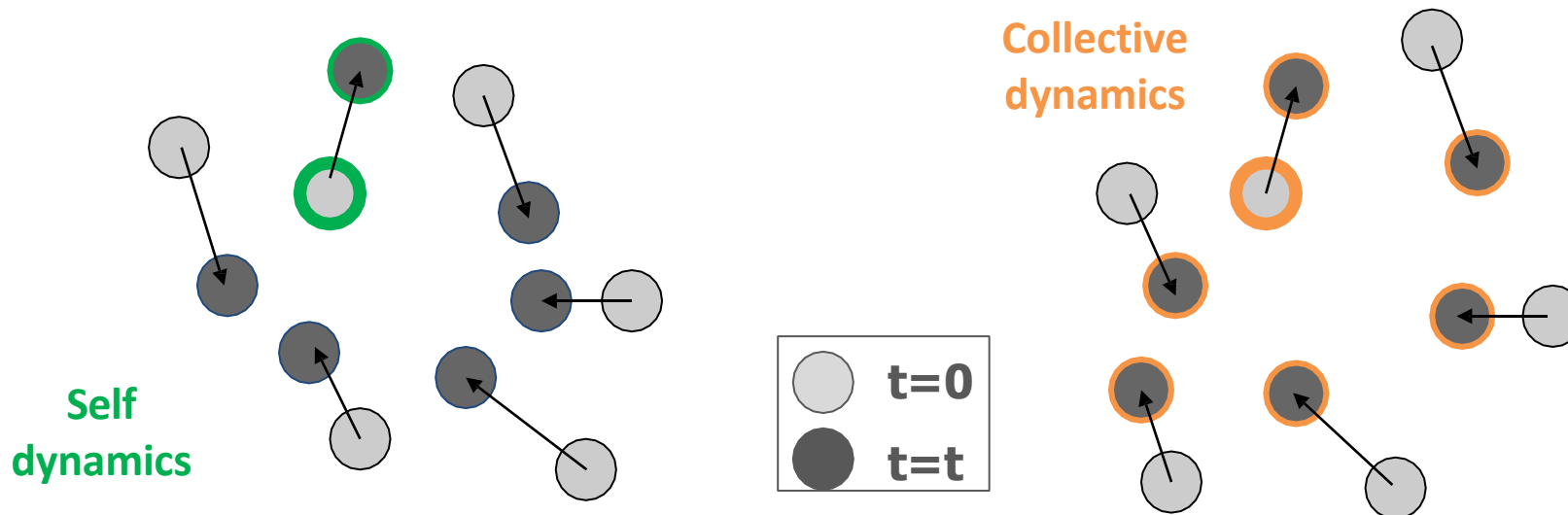
Scattering Functions- Correlations

Remember that in the experiment we measure the total $S(\mathbf{Q}, \omega)$ and that each term, coherent and incoherent is weighted by its respective cross-section α

$$S(\mathbf{Q}, \omega) = S_{\text{inc}}(\mathbf{Q}, \omega) + S_{\text{coh}}(\mathbf{Q}, \omega)$$

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \sum_i \langle \exp(-i\mathbf{Q} \cdot \mathbf{R}_i(0)) \exp(-i\mathbf{Q} \cdot \mathbf{R}_i(t)) \rangle \exp(-i\omega t) dt$$

$$S_{\text{coh}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \sum_{i,j} \langle \exp(-i\mathbf{Q} \cdot \mathbf{R}_i(0)) \exp(-i\mathbf{Q} \cdot \mathbf{R}_j(t)) \rangle \exp(-i\omega t) dt$$



Scattering Functions- Correlations

Remember that in the experiment we measure the total $S(\mathbf{Q}, \omega)$ and that each term, coherent and incoherent is weighted by its respective cross-section α

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$$S_{\text{coh}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \sum_{i,j} \langle \exp(-i\mathbf{Q} \cdot \mathbf{R}_i(0)) \exp(-i\mathbf{Q} \cdot \mathbf{R}_j(t)) \rangle \exp(-i\omega t) dt$$

These expressions can also be re-written in terms of the self and collective **intermediate scattering functions, $I(\mathbf{Q}, t)$** , such that:

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{self}}(\mathbf{Q}, t) \exp(-i\omega t) dt$$

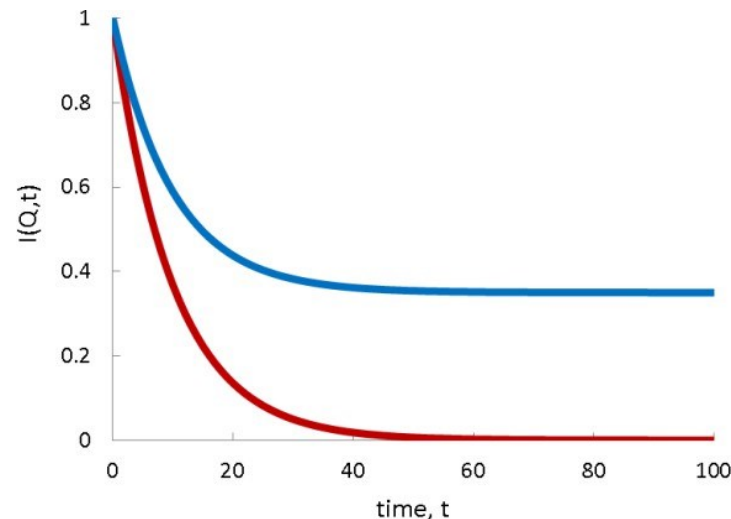
$$S_{\text{coh}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{coll}}(\mathbf{Q}, t) \exp(-i\omega t) dt$$

Intermediate Scattering Function

The intermediate scattering functions are **the time and space Fourier transform of the self autocorrelation function** and the **pair correlation function** (incoherent and coherent scattering functions respectively).

They describe the position of particle i in space as a function of time.

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{self}}(\mathbf{Q}, t) \exp(-i\omega t) dt$$
$$S_{\text{coh}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{coll}}(\mathbf{Q}, t) \exp(-i\omega t) dt$$



In most elements the coherent cross section dominates.

Hydrogen is a very important exception:

Its huge incoherent cross section enables studies of hydrogen diffusion in a variety of materials (quasi-elastic and inelastic scattering).

Summary of Self Scattering Function

$$S(Q, \omega) = S_{vib}(Q, \omega) \otimes S_{trans}(Q, \omega) \otimes S_{rot}(Q, \omega) \otimes \dots$$

EISF (elastic incoherent structure factor)- motion geometry

Translation diffusion

Vibrations [Debye-Waller]

Elastic contribution

Rotations

$$S(Q, \omega) = e^{-Q^2 u^2} \left\{ \frac{1}{\pi} \frac{\Gamma(Q)}{\Gamma^2(Q) + \omega^2} + j_0^2(Qa) \delta(\omega) + \sum_{l=1}^{\infty} A_l(Q) \frac{1}{\pi} \frac{l(l+1)D_R}{(l(l+1)D_R)^2 + \omega^2} \right\} + \dots$$

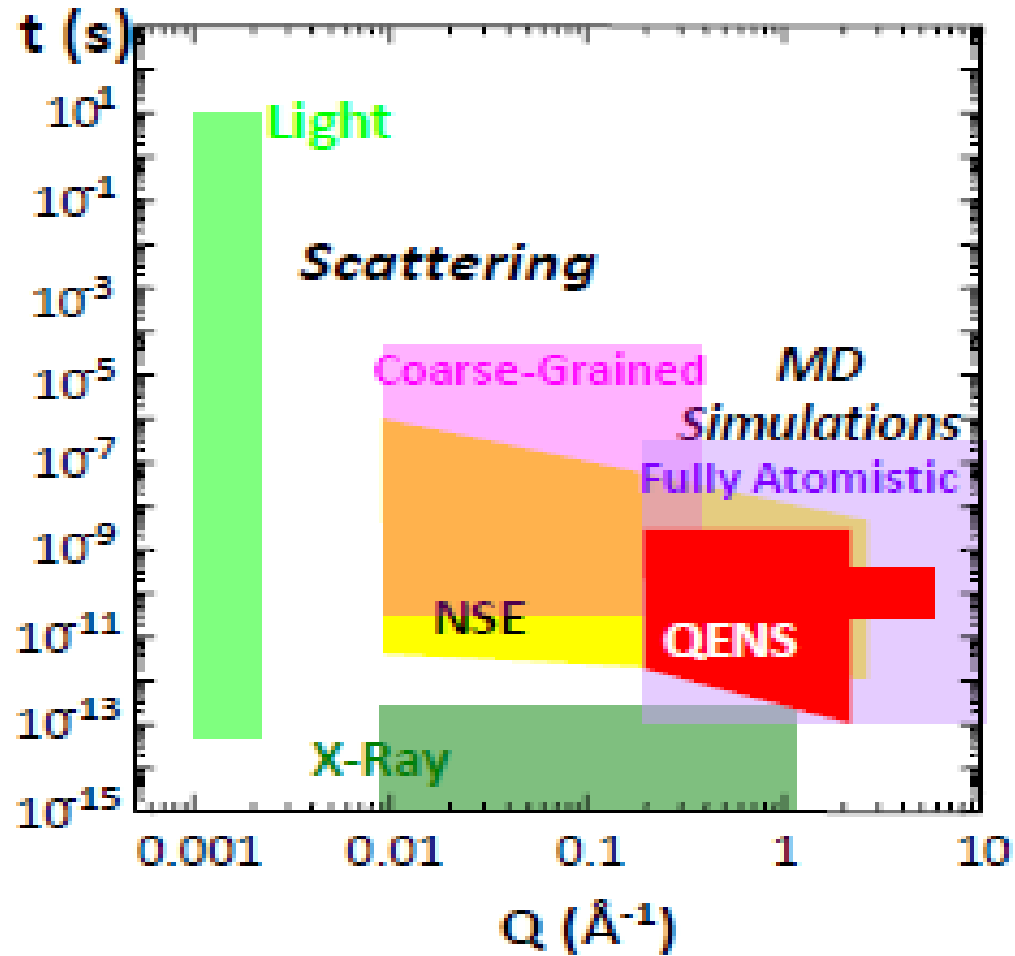
Can't forget the instrumental resolution:

$$S'(Q, \omega) = S(Q, \omega) \otimes R(Q, \omega)$$

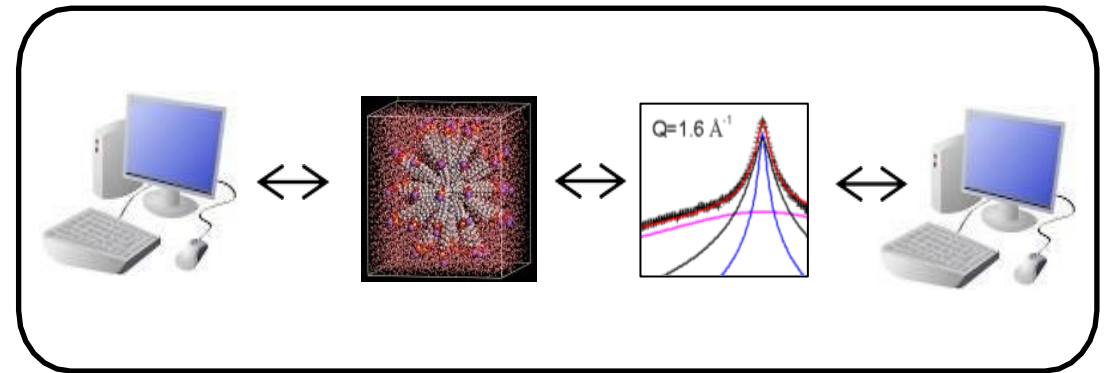
An aerial photograph of a city, likely Baltimore, Maryland, featuring a large, historic church with a prominent dome in the foreground. The church is surrounded by greenery and parking areas. In the background, a dense urban landscape with various buildings and streets is visible. The entire image is overlaid with a semi-transparent dark blue filter.

QENS and MD

Map of dynamical modes



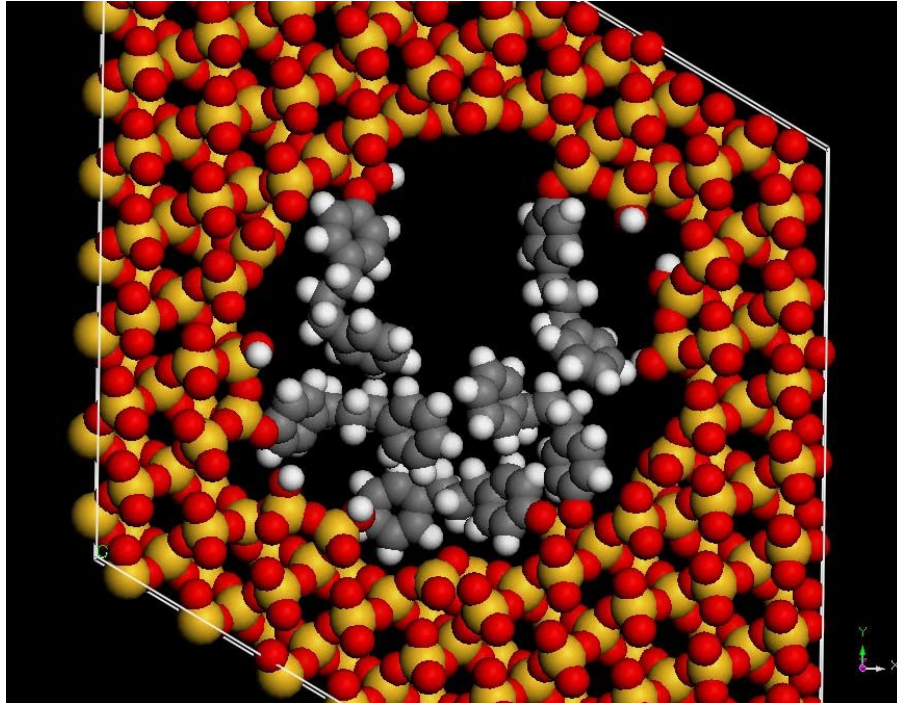
Molecular Dynamics Simulations



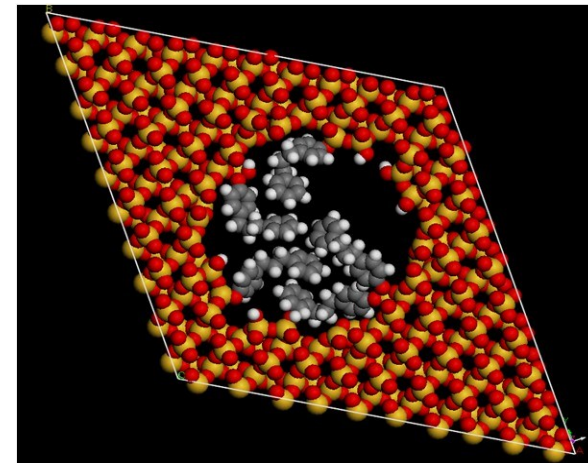
- Flexible parameter space
- Large parameter space
- Need to optimize and choose FF (Force Fields)
- Directly comparable with neutron data

QENS and Molecular Dynamics Simulations

- Same atomic coordinates used in classical MD are all that is needed to calculate $I_{inc}(Q,t)$

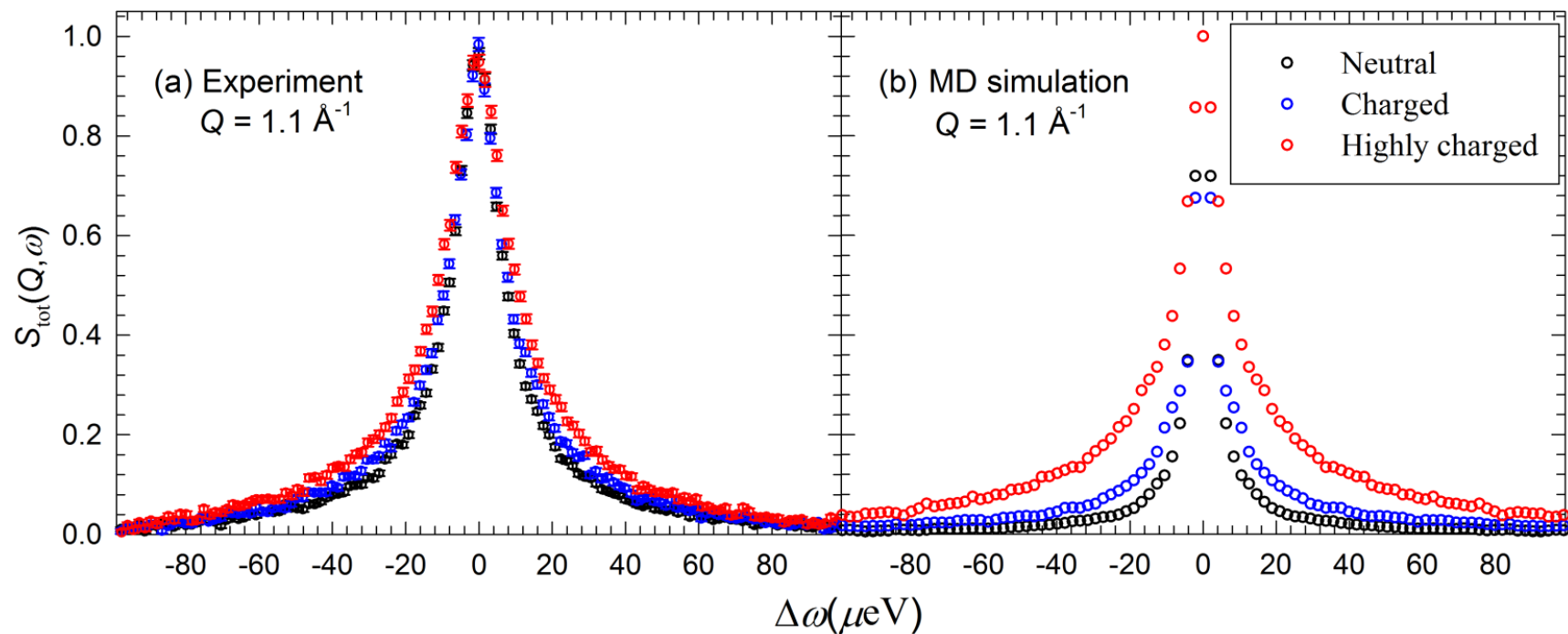


1,3 diphenylpropane
tethered to the pore
surface of MCM-41



MD benchmark

•Direct comparison for measured $S(Q,\omega)$ for Dendrimer



•Qualitative agreement

•Gradual broadening suggests dynamical enhancement

•Dominant by ^1H dynamics

An aerial photograph of a city, likely New York City, showing a dense urban landscape. In the foreground, a large, ornate church with a prominent dome and multiple spires is visible. The church is surrounded by greenery and a few smaller buildings. In the background, a variety of city buildings, including skyscrapers and residential structures, are visible under a clear sky. The overall scene is captured from a high angle, providing a comprehensive view of the urban environment.

Quick Examples

Model for the Translational Motion of Hydration Water

$$\frac{d^2\sigma_H}{d\Omega d\omega} = 2N \frac{\sigma_H}{4\pi} \frac{k_f}{k_i} S_{inc}(Q, \omega) \otimes R(\omega) \quad F_S(Q, t) = \int_{-\infty}^{\infty} S_{inc}(Q, \omega) e^{i\omega t} d\omega$$

Model for the Translational Motion of Hydration Water

$$F_H(Q, t) = p + (1 - p)F_v(Q, t)\exp[-(t / \tau)^\beta]$$

(Intermediate Scattering Function)

Fitting parameters:

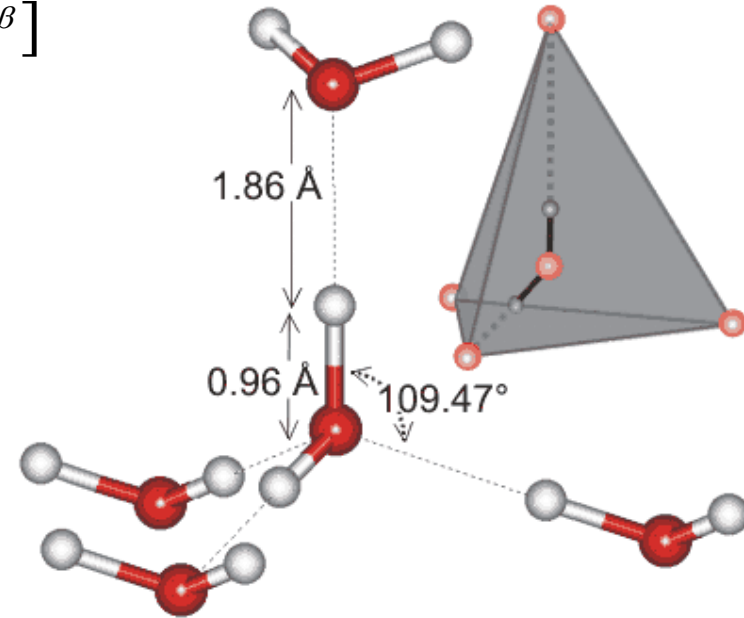
p = fraction of immobile water

β = stretched exponent (*α*-relaxation)

τ = *α*-relaxation time

$$S_H(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_H(Q, t) e^{-i\omega t} dt$$

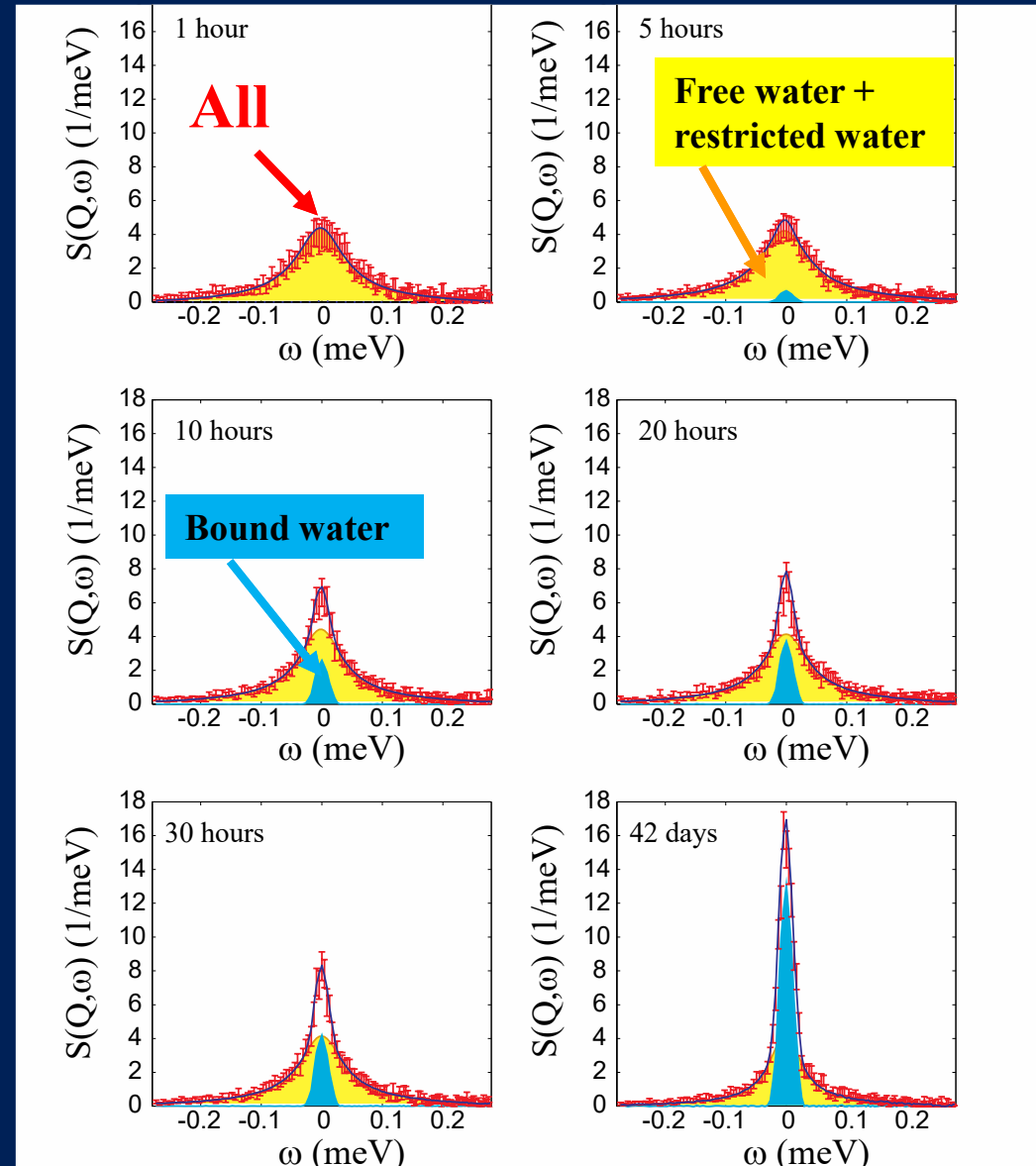
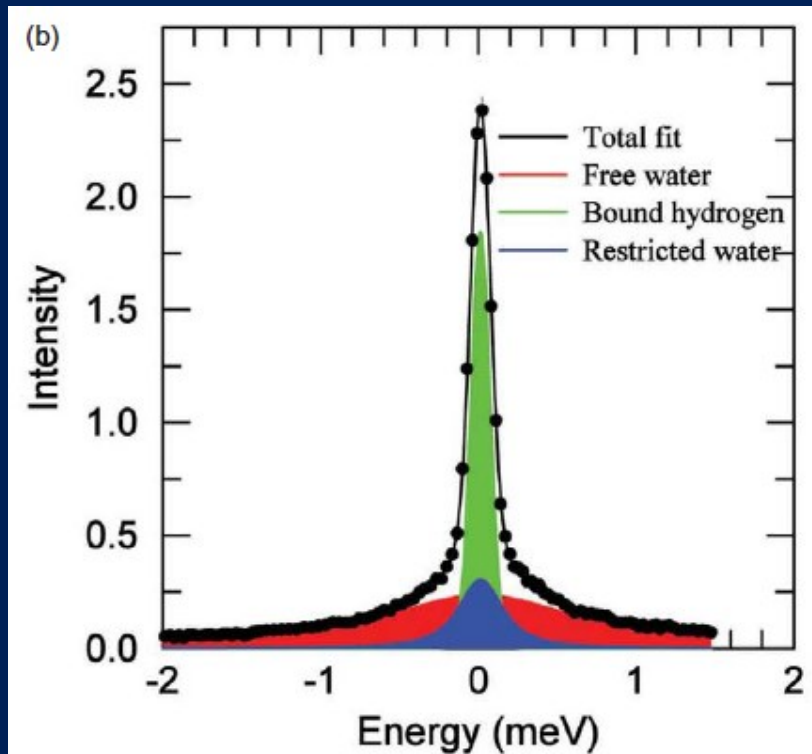
(Dynamic Structure Factor)



Typical water molecule in the hydrogen bond cage

Fitting the spectra: $S(Q, \omega) = S_H(Q, \omega) \otimes R(\omega)$

There are three types of water in a curing cement paste (concrete): **free water**, a **glassy, pseudo-bound (restricted) water**, and a **bound, crystalline water**.



Experiment Measures Double Differential Cross Section $\Rightarrow$ Dynamic Structure Factor

$$\frac{d^2\sigma_H}{d\Omega d\omega} = 2N \frac{\sigma_H}{4\pi} \frac{k_f}{k_i} S_H(Q, \omega)$$

Dynamics Structure Factor $S_H(Q, \omega) = \text{FT} [\text{Intermediate Scattering Function } F_H(Q, t)]$

$$S(Q, \omega) = pR(Q_0, \omega) + (1-p)\text{FT} \{F_H(Q, t)R(Q_0, t)\}$$

For $Q < 1.1 \text{ \AA}^{-1}$, $F_H(Q, t) \approx F_T(Q, t)$.

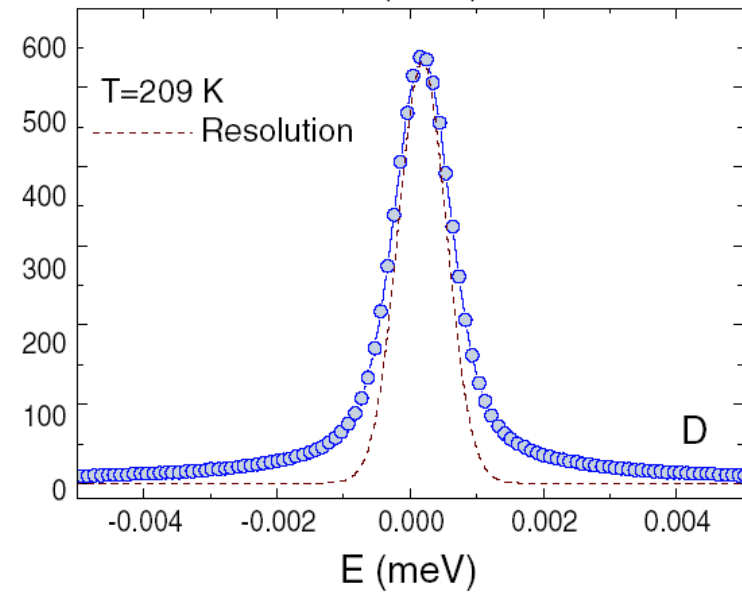
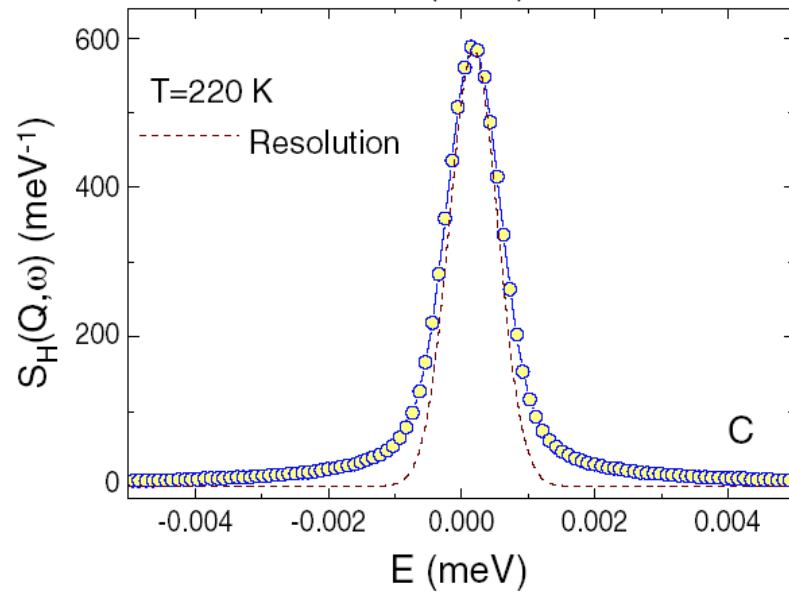
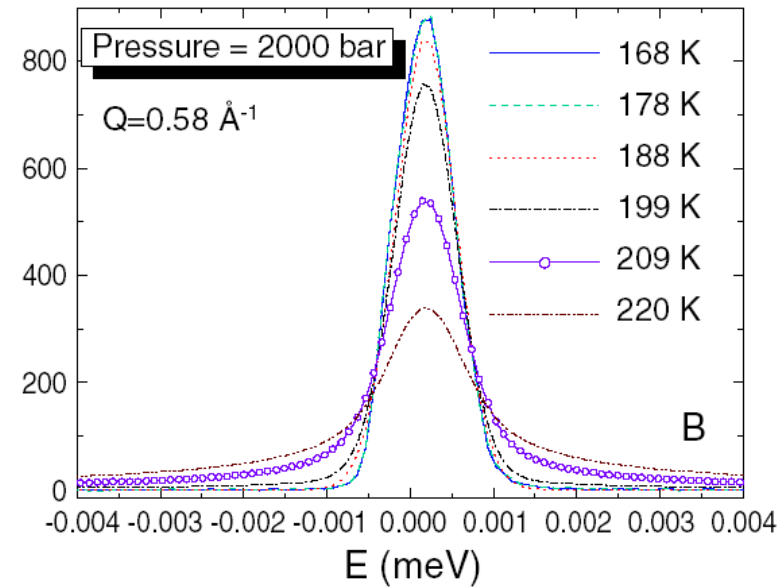
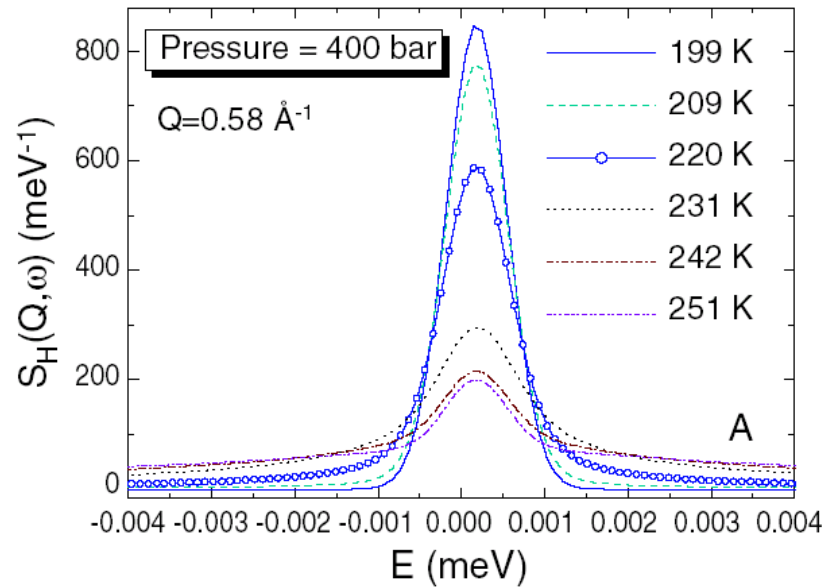
$$F_T(Q, t) = F_T^s(Q, t) \exp[- (t/\tau_T)^\beta], \quad \tau_T = \tau_0 (aQ)^{-\gamma};$$

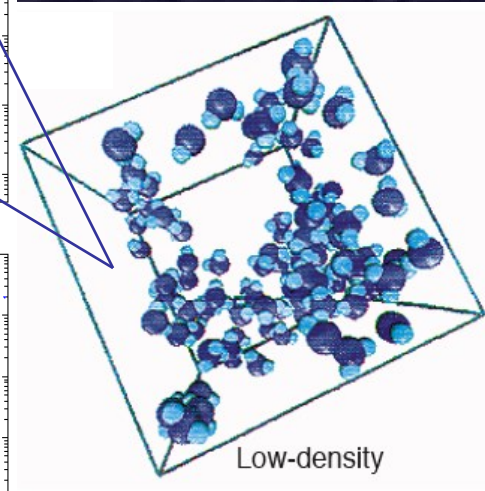
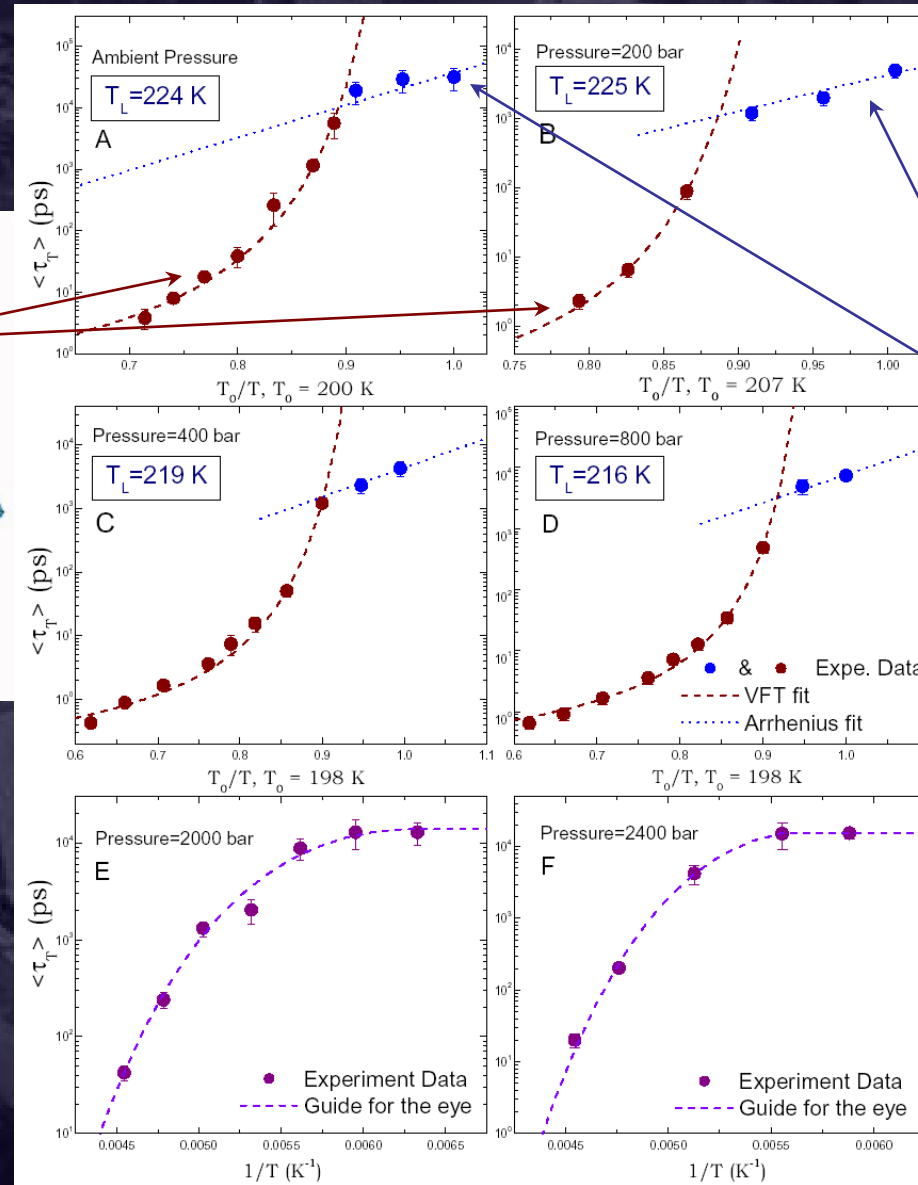
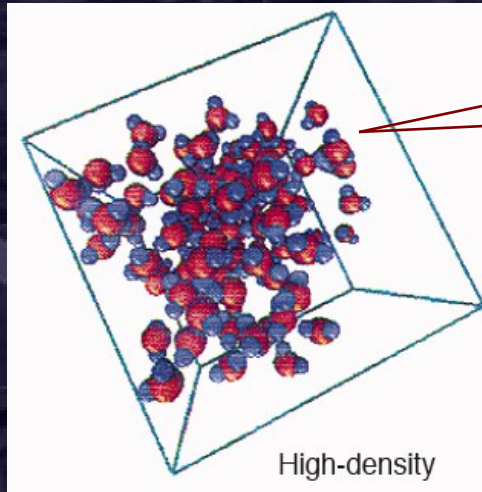
$F_T^s(Q, t)$ is calculated from known proton density of states.

Fitting parameters: p, β, γ, τ_0 , from which we calculate the average translational relaxation time:

$$\langle \tau_T \rangle = \frac{\tau_0}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

QENS Spectra of the Supercooled Confined Water Under Pressure





[L Liu, SH Chen, *et al*,
“Pressure Dependence of
Fragile-to-Strong Transition
and a Possible Second Critical
Point in Supercooled Confined
Water” *Phys. Rev. Lett.* **95**,
117802 (2005)]

Arrhenius plot of the structural relaxation time, $\langle \tau_T \rangle$, shows a cusp below the critical pressure. Therefore, the critical temperature and pressure can be determined from the phase point where the cusp begins to be rounded off.

Summary

- 💧 QENS is an excellent technique to measure diffusive dynamics
 - ❑ Length scales/geometry accessible through Q-dependence
 - ❑ Many analytic models form a framework for comparison and parametric studies
 - ❑ Large range of time scales (sub-picosecond $< t <$ nanosecond (100's nsec for NSE)
 - ❑ H-atom sensitivity
- 💧 Instrument selection is a critical decision – the resolution must match the time scale of the expected motion
- 💧 Natural connection to theory (Molecular Dynamics Simulations)
- 💧 Analysis software and theory development with the help of Instrument Scientists are important

An aerial photograph of a university campus, featuring various academic buildings, a large central hall with a dome, and surrounding greenery. The image is overlaid with a semi-transparent dark blue filter. The text "Any Questions?" is centered in a bright green, serif font.

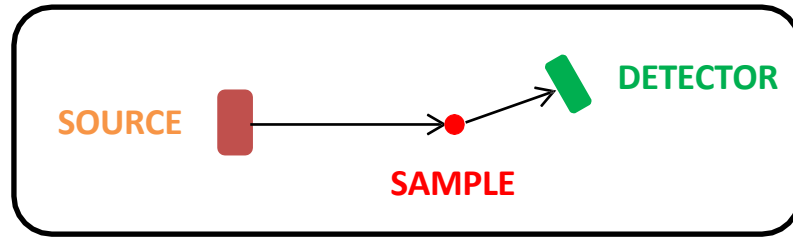
Any Questions?

An aerial photograph of a university campus, featuring a large, prominent building with a dome in the foreground, surrounded by other academic buildings and green spaces. The image is overlaid with a dark blue filter.

Additional Instruments

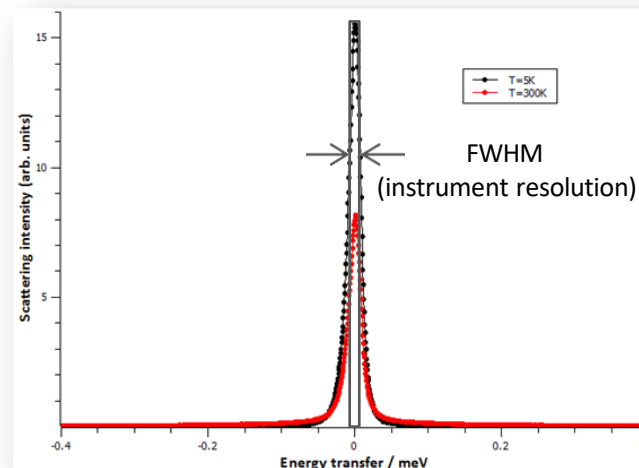
QENS Spectrometers - Direct

Direct geometry



LET on ISIS-TS2

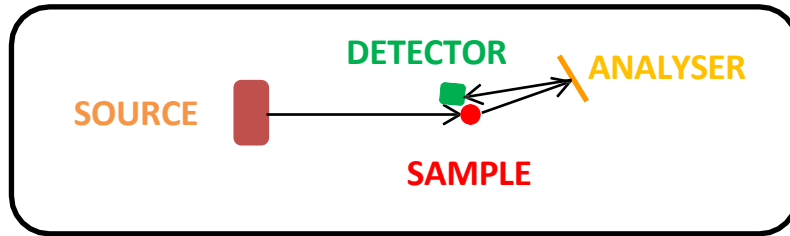
- Send neutrons of known **fixed** E_i (v_i) – neutron can lose as much energy as it has but can gain any (defines energy window)
- Source-sample and sample-detector distances known
- Time at which neutron is sent, known
- Time at which neutron is detected tells us E_f ; thus we know ΔE



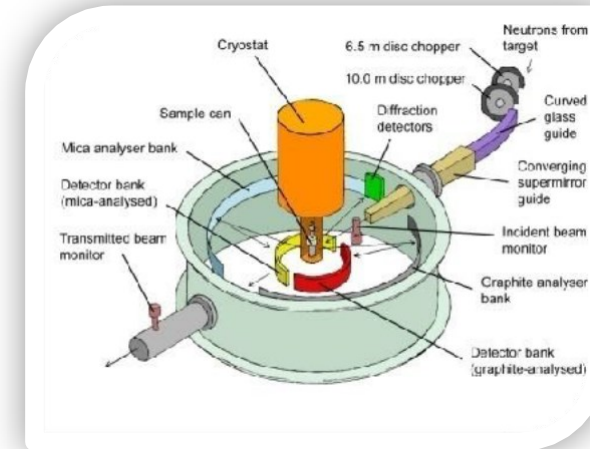
Elastic intensity is the integral of the line around $E=0$ as given by the instrumental resolution.

QENS Spectrometers - Indirect

Indirect geometry or Backscattering

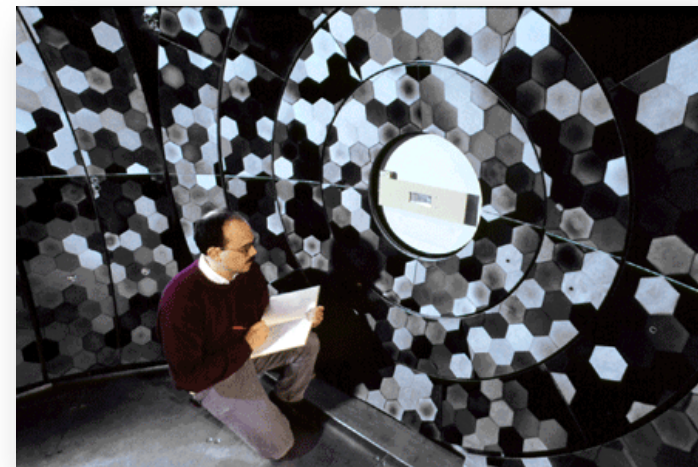


- Send neutrons of a known band of wavelengths or E_i (v_i)s (defines your energy window)
- In reactor source, use a Doppler drive; in a spallation source, use choppers
- Analyser crystals reflect back only a **fixed** E_f (Bragg's Law)
- Times & distances known, so detected neutron gives us ΔE

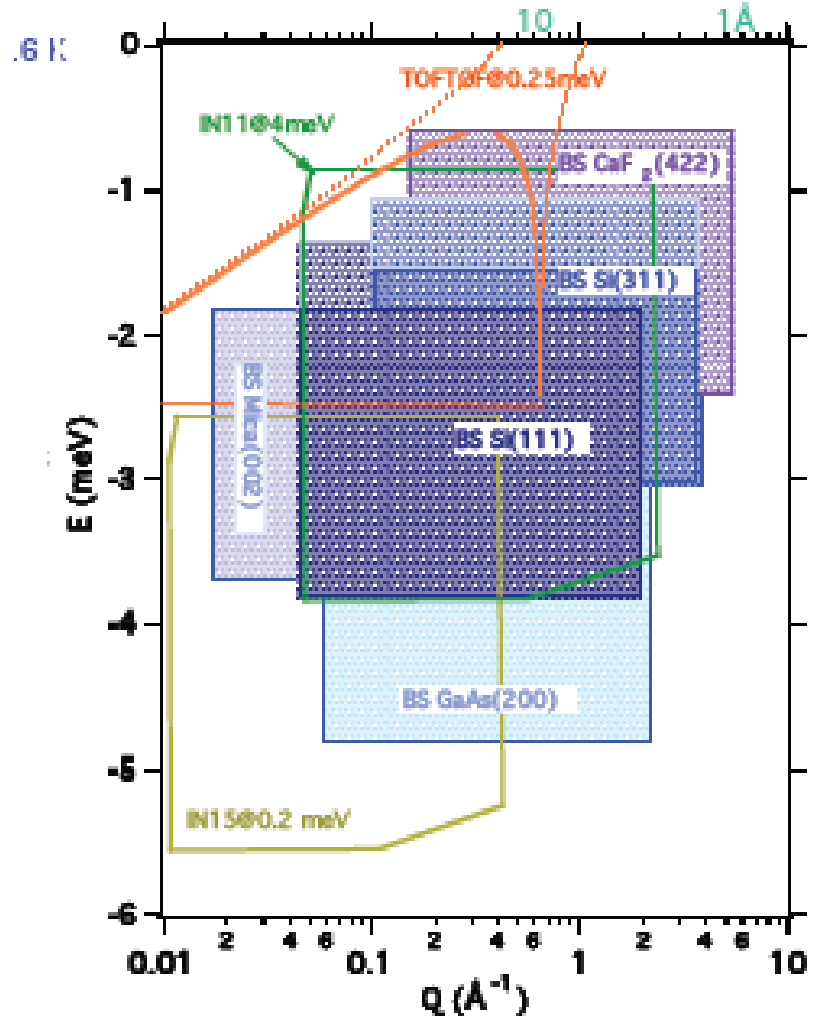


IRIS on ISIS-TS1

HFBS at the NCNR, USA



QENS Spectrometers – Which one?



4.1 ps

4.1 ns

time

4.1 μs



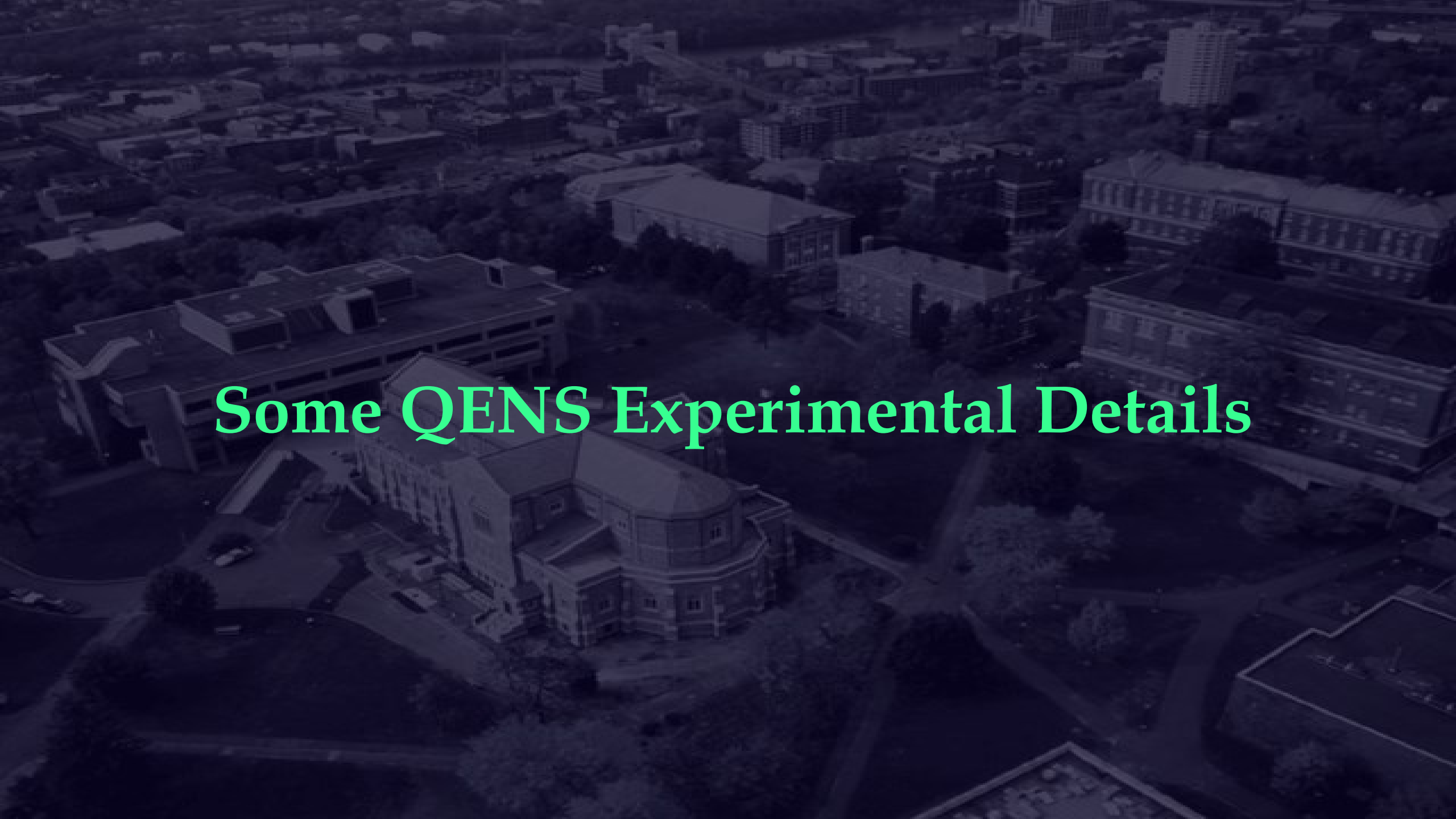
- Direct geometry:
 - Poorer resolution, higher energies, wider E transfer window, small Q range.
- Indirect geometry:
 - @ reactor, highest resolution with good intensity but limited E transfer range
 - @ spallation, medium resolution, high flux, wider E transfer range

QENS and Neutron Scattering Instruments

- **Probe Diffusive Motions**
 - Length scales set by Q , $0.1 \text{ \AA}^{-1} < Q < 3.7 \text{ \AA}^{-1}$, $60 \text{ \AA} > d > 1.7 \text{ \AA}$.
 - **Time scales set by the width of instrument energy resolution**, typically at least 0.1 meV (fwhm) but higher resolution -> longer times/slower motion
- **Energy transfers $\sim \pm 2 \text{ meV}$ (or less)**
 - High resolution requirements emphasizes use of cold neutrons (but long λ limits Q)
 - Incident neutron wavelengths typically 4 $\text{\AA}$ to 12 $\text{\AA}$ (5.1 meV to 0.6 meV)
- **Why a variety of instruments? (Resolutions vary from 1 μeV to 100 μeV)**
 - Terms in the resolution add in quadrature – typically primary spectrometer (before sample), secondary spectrometer (after the sample)
 - Improvement in each resolution term cost linearly in neutron flux (ideally)
 - Optimized instrument has primary and secondary spectrometer contributions approximately equal
 - **Factor of 2 gain in resolution costs at a minimum a factor of 4 in flux**

Role of Instrumentation

- Currently about 25 neutron scattering instruments in the world useful for QNS (6 in the U.S., including NSE)
- U.S. instruments – Opportunity is Good- Competition is High
 - NIST Center for Neutron Research
 - Disc Chopper Spectrometer
 - High Flux Backscattering Spectrometer
 - Neutron Spin Echo
 - Spallation Neutron Source
 - BaSiS – near backscattering spectrometer (3 μeV)
 - Cold Neutron Chopper Spectrometer (CNCS) (10 – 100 μeV)
 - Neutron Spin Echo (f to 400 nsec)
- Trade-offs
 - Resolution/count rate
 - Flexibility
 - Dynamic range
 - Neutron λ vs Q
 - large λ $\rightarrow$ high resolution $\rightarrow$ long times/slow motions
 - large λ $\rightarrow$ limited Q-range, limited length scales

An aerial photograph of a city, likely New York City, showing a dense urban landscape. In the foreground, a large, multi-story building complex with a prominent circular structure is visible. The image is overlaid with a dark blue filter. The text "Some QENS Experimental Details" is centered in the image in a bright green, serif font.

Some QENS Experimental Details

Single Particle Motion

Similarly there is a second contribution to the double differential scattering cross section. In the simplest case we have:

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{\sigma_{coh}}{4\pi\hbar} \frac{k_f}{k_i} S(\mathbf{Q}, \omega) + \frac{\sigma_{inc}}{4\pi\hbar} \frac{k_f}{k_i} S_S(\mathbf{Q}, \omega)$$

Where:

- $S(\mathbf{Q}, \omega)$ reflects the collective behavior of the particles (e.g. phonons)
- $S_S(\mathbf{Q}, \omega)$ reflects the individual (self) behavior (e.g. diffusion), Self Scattering Function
- σ_{coh} and σ_{inc} are **coherent** and **incoherent** scattering cross sections respectively

Coherent and incoherent scattering

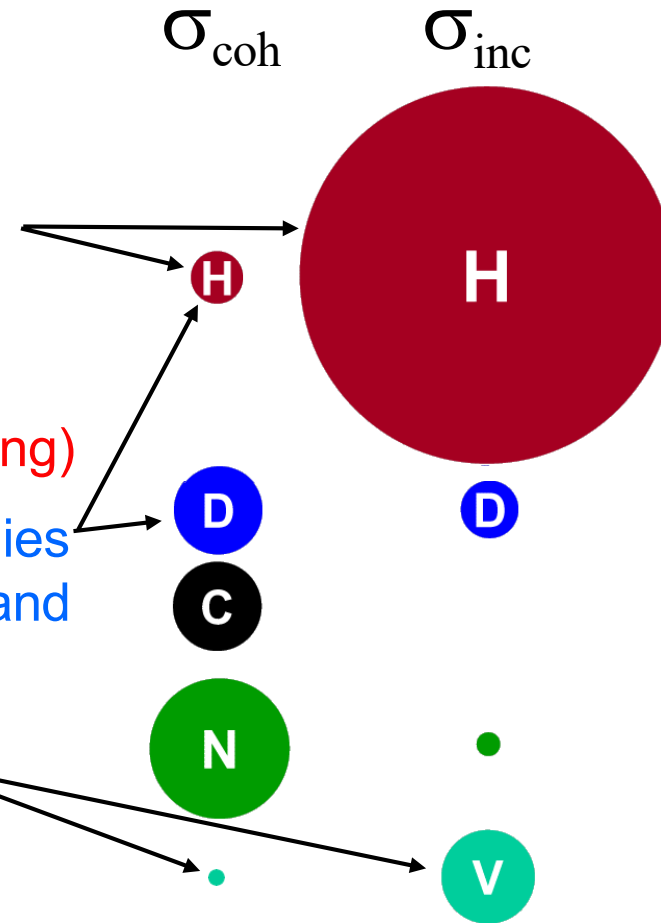
In most elements the coherent cross section dominates.

Hydrogen is a very important exception:

Its huge incoherent cross section enables studies of hydrogen diffusion in a variety of materials (quasielastic and inelastic scattering)

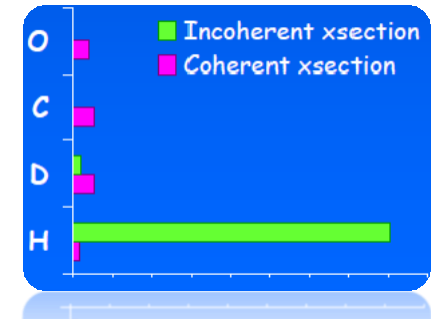
Selective deuteration enables detailed studies of the structure and dynamics of polymers and biomolecules.

Vanadium has a significant incoherent cross section and a very small coherent cross section. It is used for instrument calibration (and for sample cans).



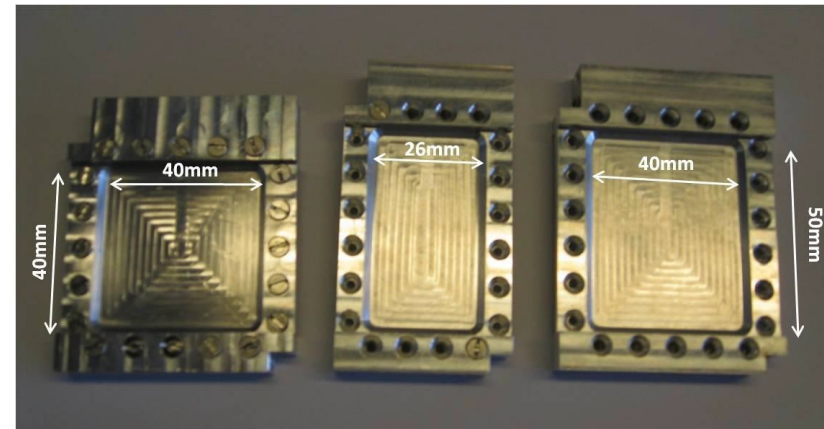
... for QENS ...

	σ_{coh} (b)	σ_{inc} (b)	σ_{abs} (b)
Hydrogen	1.76	80.2	0.33
Deuterium	5.59	2.05	0.00
Carbon	5.56	0.00	0.00
Nitrogen	11.0	0.50	1.90
Oxygen	4.23	0.00	0.00
Phosphorus	3.31	0.01	0.17
Aluminium	1.50	0.01	0.23
Silicon	2.17	0.00	0.17



The QENS experiment

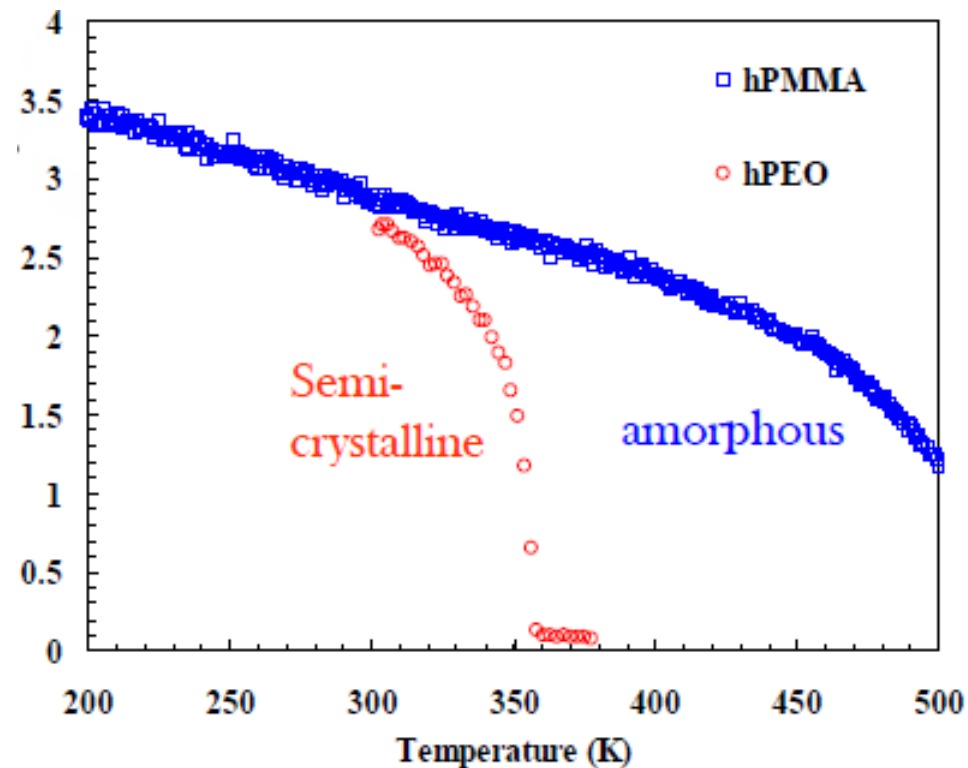
- Minimise possibility of multiple scattering
=> Keep transmission at 90 %
- Use annular or flat aluminium cans



Elastic Window Scan

Measurement of the elastic **intensity** as a function of **temperature** is a typical technique in QENS spectrometers. It resembles a DSC scan and is very good for locating **transitions** – at what temperatures do the dynamics enter the time window of the neutron spectrometer?

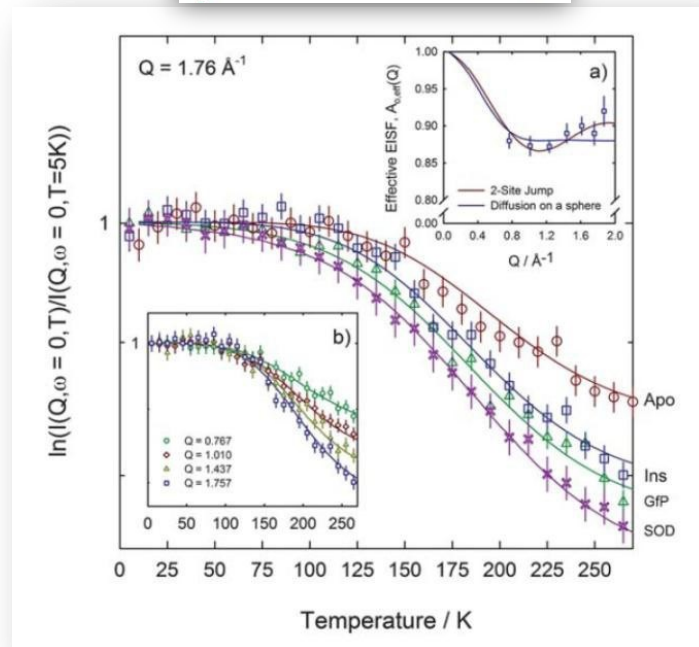
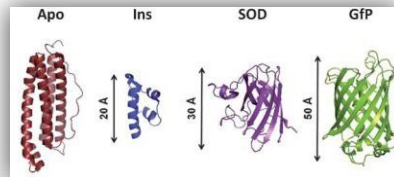
A lot of **biology and soft matter** experiments start with this type of measurement.



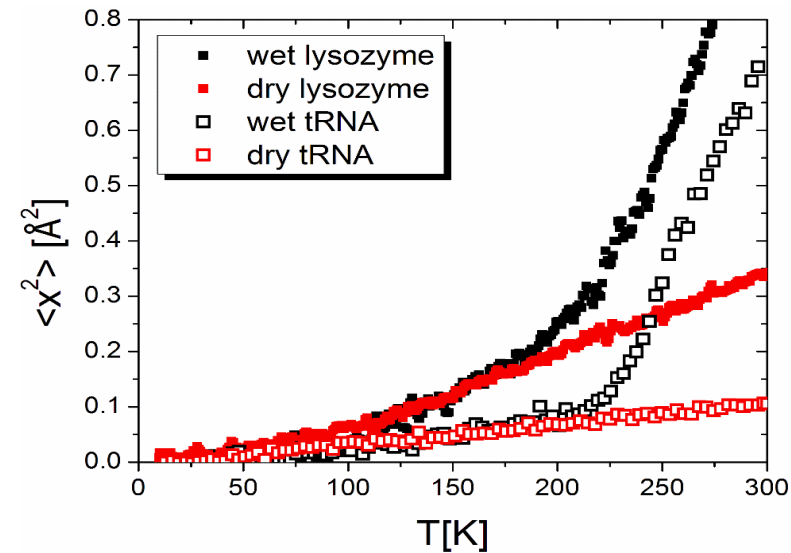
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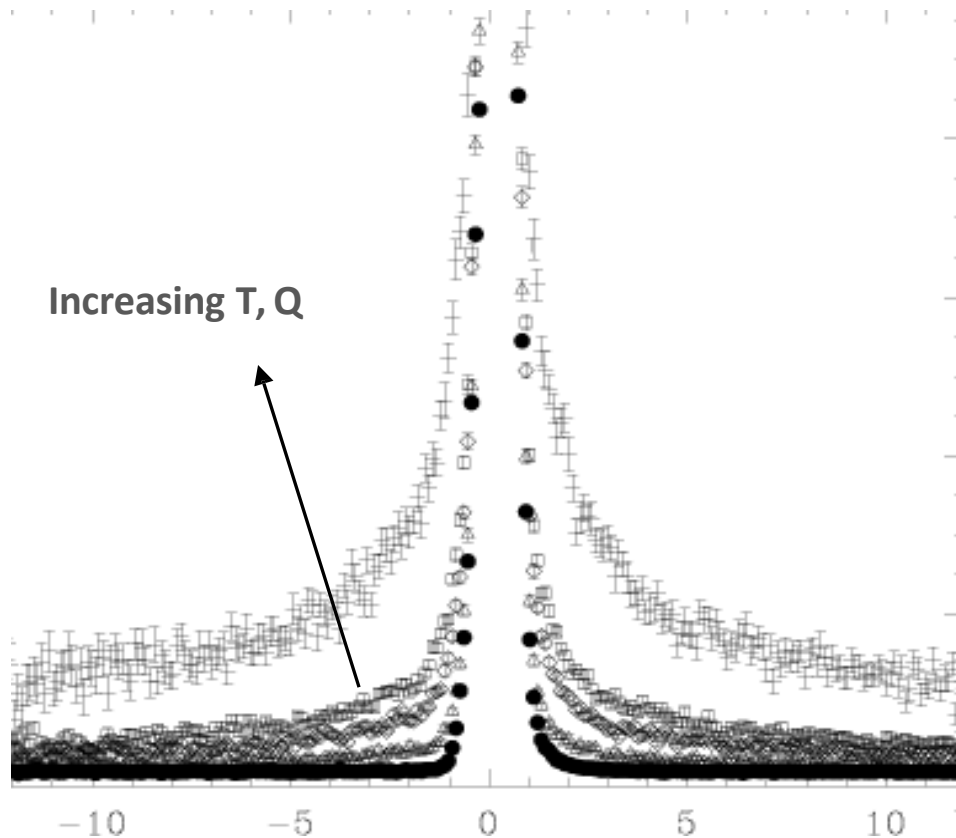


Fingerprinting as a $f(c, P, ..)$



QENS Measurement

In elastic mode we only look at no change in energy, but QENS is all about measuring changes in energy which tells us about the **timescale of motion of the atoms as a function of T, P, c...** The initial scan allows us to pick temperatures where the dynamics will fall in our instrumental time window. Each spectrometer is different.



1. Elastic line - If motions are too slow for the spectrometer
2. Flat background – if motions are too fast for the spectrometer & all atoms are moving
3. Combo of 1 & 2 if not all atoms are moving or some are moving in a confined geometry
4. **Elastic line plus QENS broadening if motions are in the spectrometer's time window**

Self (incoherent) scattering function

Let's consider **the self correlation function**, ie. how particles move as a function of time. This corresponds as we have seen before to the incoherent signal. In general terms, the incoherent scattering function is written as:

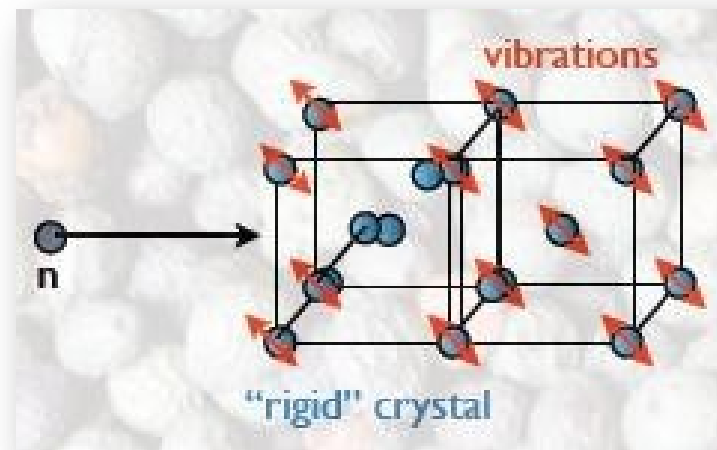
$$S_{\text{inc}}(\mathbf{Q}, \omega) = S_{\text{vib}}(\mathbf{Q}, \omega) \otimes S_{\text{rot}}(\mathbf{Q}, \omega) \otimes S_{\text{trans}}(\mathbf{Q}, \omega)$$

$$I_{\text{self}}(\mathbf{Q}, t) = I_{\text{vib}}(\mathbf{Q}, t) \times I_{\text{rot}}(\mathbf{Q}, t) \times I_{\text{trans}}(\mathbf{Q}, t)$$

the **convolution of components**, in its simplest case we can consider vibrations, rotations and translations. Note that for simplicity we assume that they are **independent** motions. Note that in the time domain we multiply the terms (easier!)

Vibrations: Debye-Waller factor

In reality, nuclei (even in a rigid crystal) are **not stationary**, causing a decrease in the intensity of a diffracted beam (remember Bragg's law) because waves are not so well in phase. In addition, this smearing is a function of temperature. Assuming that **vibrations** are **harmonic** and **isotropic**:



$$DWF = \langle \exp(i\mathbf{Q} \cdot \mathbf{u}) \rangle = \exp(-\langle (\mathbf{Q} \cdot \mathbf{u})^2 \rangle) = \frac{1}{3} \exp(Q^2 \langle u^2(T) \rangle)$$

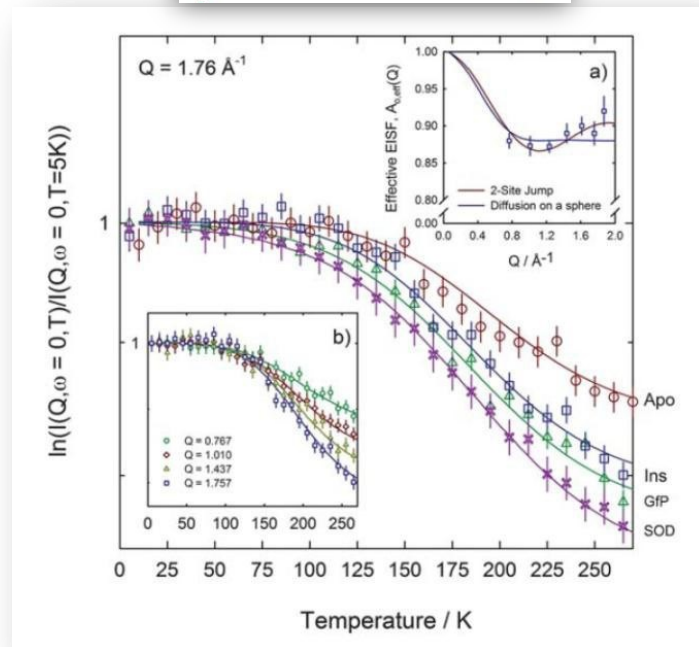
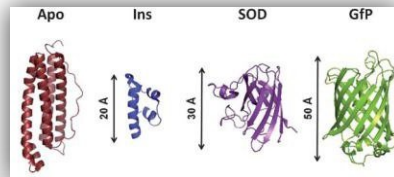
Mean-square displacement of atoms, $\langle u^2 \rangle$, is measured as a function of temperature. Assuming particles are harmonic, we can think of them as springs and we can obtain an **effective force constant** – measurement of **flexibility** (used for proteins).

$$\langle k' \rangle = 2k_B \left(\frac{d\langle u^2 \rangle}{dT} \right)^{-1}$$

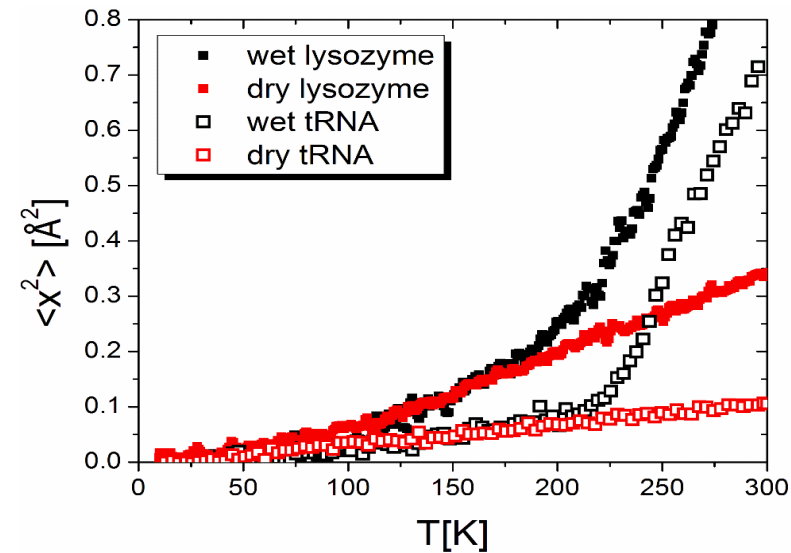
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Fingerprinting as a $f(c, P, ..)$

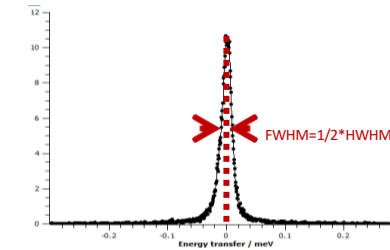


Simple Translational Diffusion

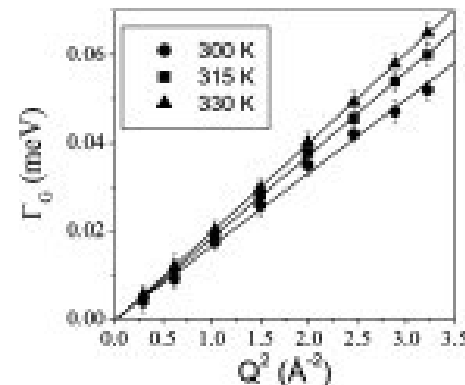
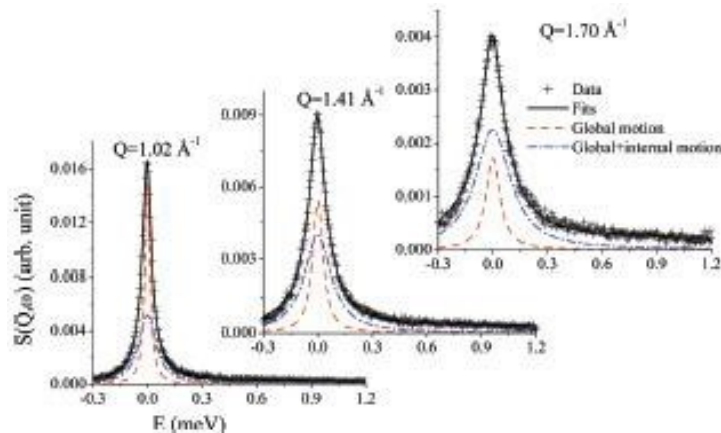
Let's go back to the incoherent scattering law and how to fit the data – in the energy space we typically fit with Lorentzians. Let's look at **continuous long-range isotropic translational diffusion**. In this case particles follow Fick's Law .

$$I(Q, t) = \exp(-Q^2 Dt) \quad \text{relaxation rate } |\tau| = 1/(DQ^2)$$

$$S_{\text{trans}}(\mathbf{Q}, \omega) = \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + \omega^2} \quad \text{ie. a Lorentzian}$$



D (m^2/s) is the diffusion coefficient and ρ is the **half width at half maximum** (HWHM) which in this case $= DQ^2$. Leads to a broadening of the elastic line following a given Q -dependence. Diffusion coefficient follows Arrhenius Law



$$D \approx \exp(-E_a/kT)$$

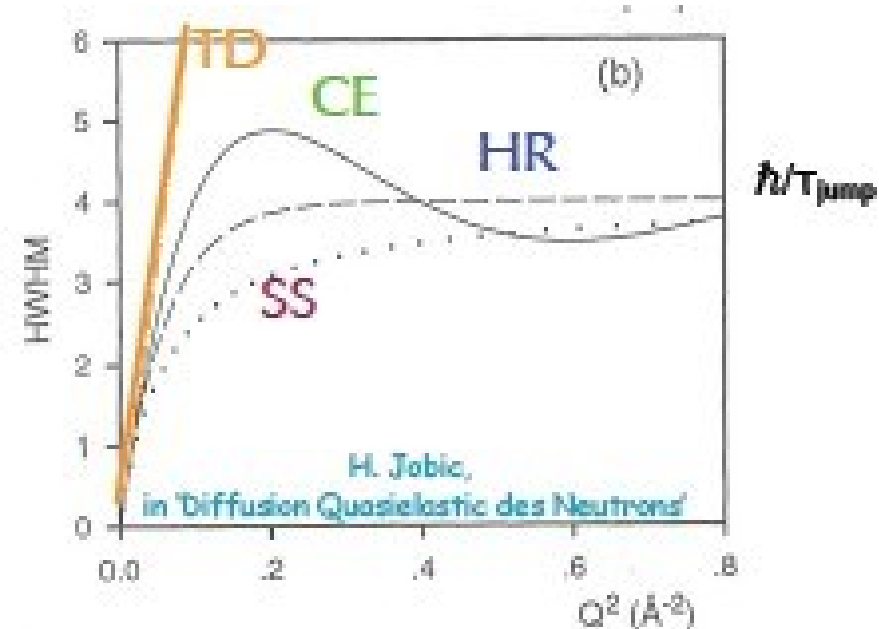
Models for Translational Diffusion

Not all is simple of course, and in many cases **diffusion is restricted** due to confinement (hard or soft), strong interactions, bonding restrictions, or diffusion happens in jumps; ie. deviations from Fick's Law. So we need other models. Here are some examples:

Chudley-Elloitt (CE) – jumps on a lattice

Singwi-Sjölander (SS)- alternation between oscillatory motion and directed motion

Hall-Ross (HR) – jump diffusion within a restricted volume



Residence time in jump and jump length

DQ^2 at low Q and then approaches $1/\tau''_{\text{jump}}$ at high Q

More models including rotations

$$S_{\text{inc}}(\mathbf{Q}, \omega) = S_{\text{vib}}(\mathbf{Q}, \omega) \otimes S_{\text{rot}}(\mathbf{Q}, \omega) \otimes S_{\text{trans}}(\mathbf{Q}, \omega)$$

The final part is the case of localised motions such as rotations. In this case we have a stationary part plus a decaying part giving rise to some elastic contribution. This gives rise to a Q-independent line-width and an EISF.

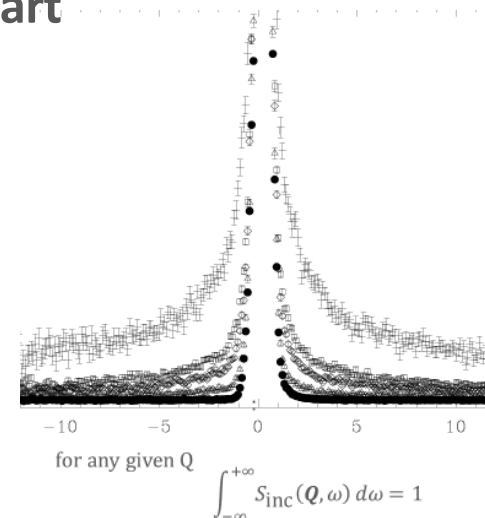
$$S_{\text{inc}}(\mathbf{Q}, \omega) = \exp(-Q^2 \langle u^2 \rangle) [A_0(\mathbf{Q}) \delta(\omega) + (1 - A_0(\mathbf{Q})) L(\mathbf{Q}, \omega)]$$

**Elastic stationary
part, EISF**

**Quasi-elastic
decaying part**

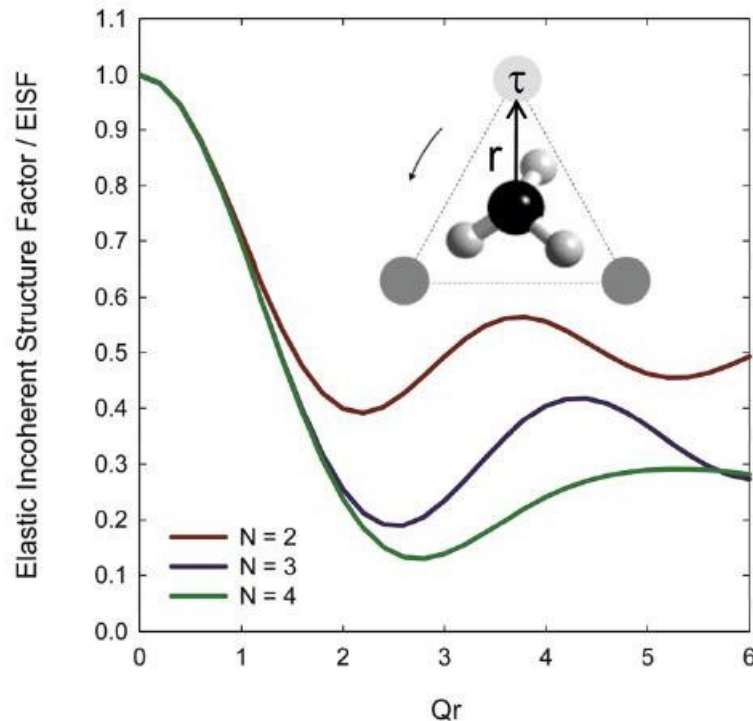
$$EISF = \frac{S_{\text{inc}}^{\text{el}}(\mathbf{Q})}{S_{\text{inc}}^{\text{el}}(\mathbf{Q}) + S_{\text{inc}}^{\text{qel}}(\mathbf{Q})}$$

The **EISF** is the area of the elastic curve divided by the total area, ie. the fraction of elastic contribution.



EISF – Geometry of Motion

Particles move in a restricted space having a specific **geometry of motion**



For a CH_3 group – site site jumps

$$EISF = \frac{1}{3} [1 + 2j_0(\sqrt{3} Qr)]$$

Jumps between 2 sites

$$EISF = \frac{1}{2} \left[1 + \frac{\sin(2Qd)}{2Qd} \right]$$

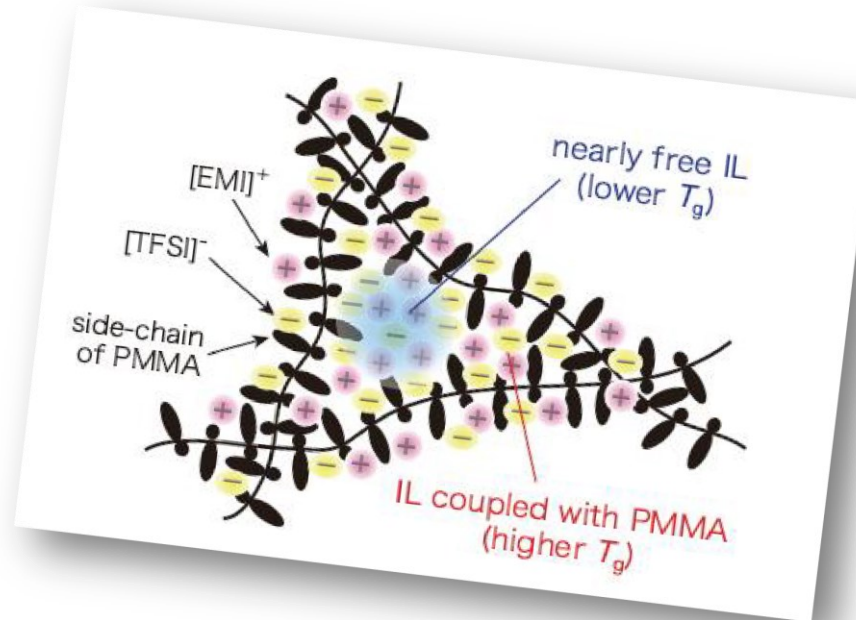
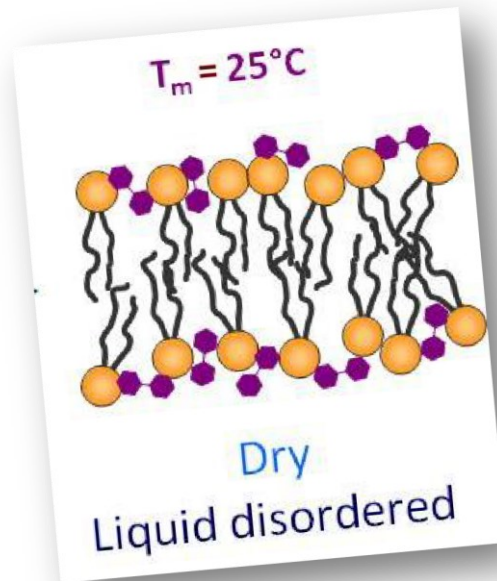
Free diffusion inside a sphere

$$EISF = \left(\frac{3j_1(Qr)}{Qr} \right)^2$$

- Jumps between 2, 3, ... n sites
- Rotational diffusion on a circle
- Diffusion on a sphere
- Diffusion inside a sphere, cylinder...

A different way to analyse QENS data

Unfortunately things are not quite as easy for some soft matter systems due to their **complexity** (*environments*) and extra **degrees of freedom**. What we are faced with is a distribution of relaxation times (FWHM's), jump lengths, mixture of components, activation energies...

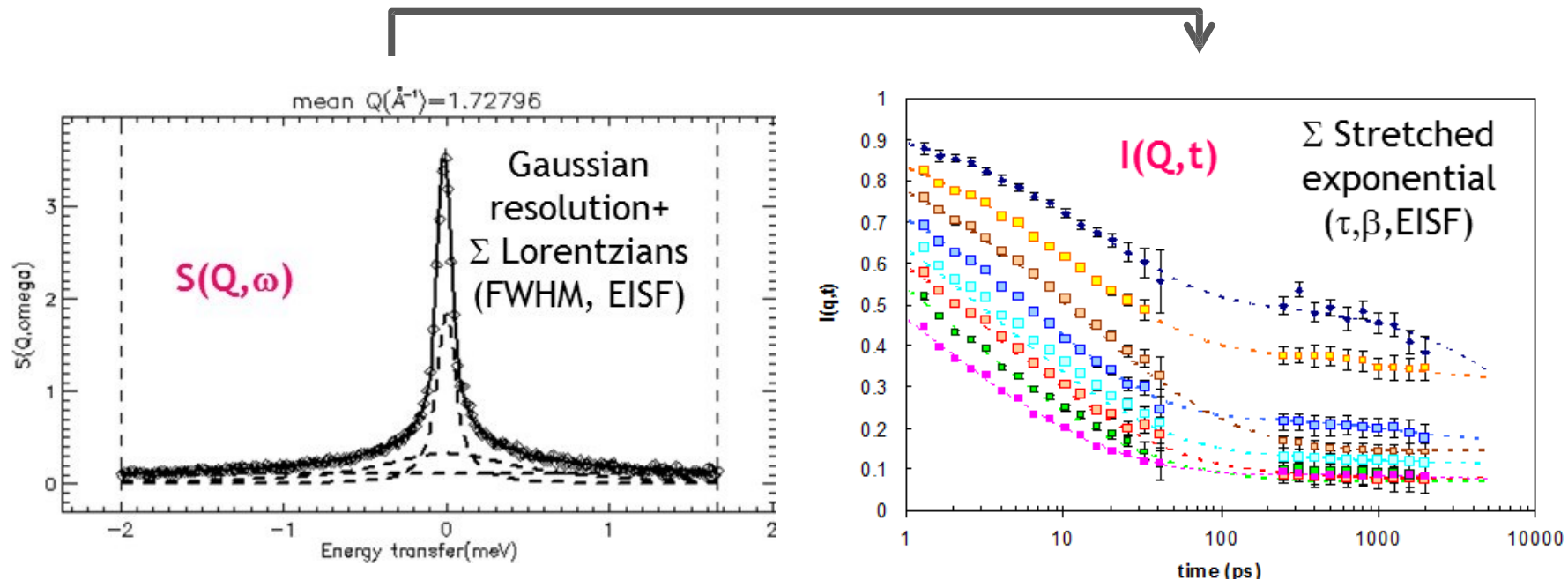


So, many times we cannot simply fit QENS spectra with 1, 2 or even 3 Lorentzians, in fact we need a **distribution of Lorentzians** and since it is easier we move from thinking in the energy space to the time space!

The Stretched Exponential (KWW)

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{self}}(\mathbf{Q}, t) \exp(-i\omega t) dt$$

Let's take the Fourier Transform



and fit in the time domain

$$I(\mathbf{Q}, t) = A \exp \left[- \left(\frac{t}{\tau_{\text{KWW}}} \right)^\beta \right] = \int_{-\infty}^{+\infty} f(\ln \tau) \exp \left(- \frac{t}{\tau} \right) d(\ln \tau) \quad \langle \tau \rangle = \frac{\Gamma(1/\beta)}{\beta} \tau_{\text{KWW}}$$

Heterogeneity in Some Systems

$$I(Q, t) = A \exp \left[- \left(\frac{t}{\tau_{\text{KWW}}} \right)^{\beta} \right] + (1 - A)$$

What do the parameters mean?

$\langle \tau \rangle$ = average **relaxation time** = $f(T, Q)$

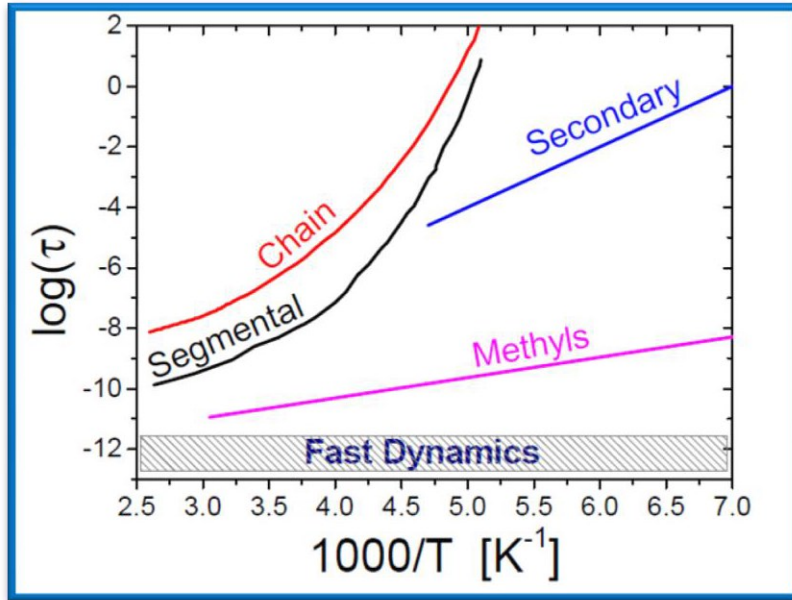
β = **stretching exponent** = $f(T, Q)$ If $\beta = 1$, all particles move alike

If $\beta < 1$, there is heterogeneity in the system.
For pure macromolecules $0.4 < \beta < 0.6$ is typical. For polymer blends, confined systems, biological molecules, it can be lower

A = fraction of moving (or **relaxing molecules**) = $f(T, Q)$

It is the **Q and T dependence of these parameters** that give us information about the homogeneity or heterogeneity in the system.

Dynamics: Activation energy & Geometry

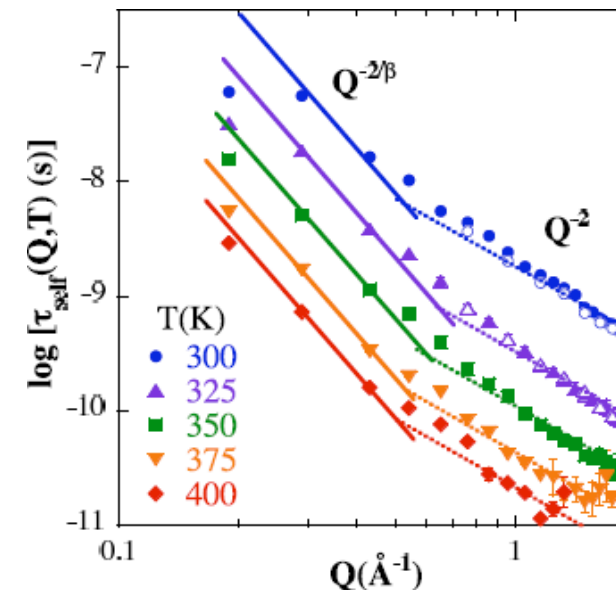


Spatial (Q) dependence of the relaxation time

- if $I'' \propto Q^{-2}$ then heterogeneous
- if $I'' \propto Q^{-2/\beta}$ then homogeneous

Temperature dependence of the relaxation time

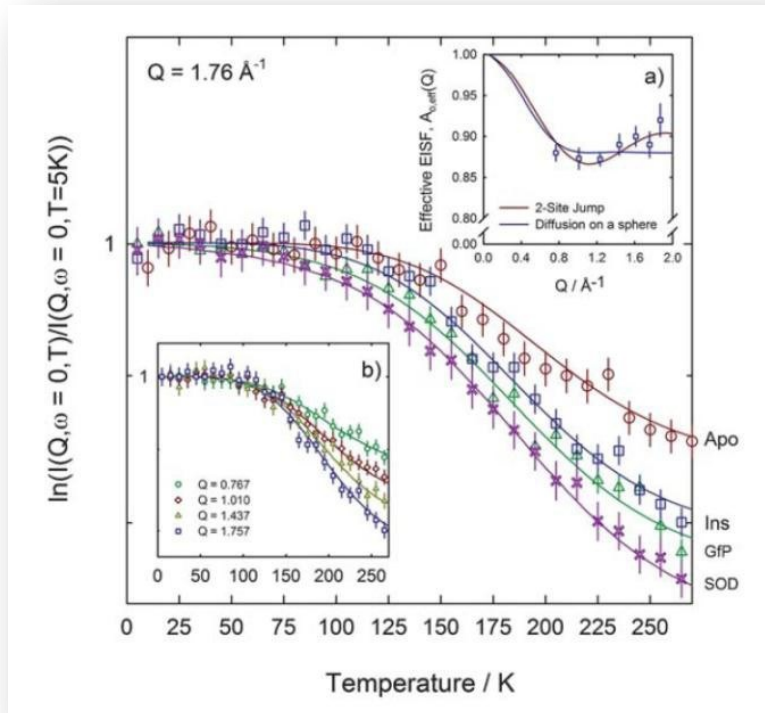
- α -relaxation in polymers (related to T_g) follows a so-called VFT curve
- β -relaxation and other localised modes follow Arrhenius dependence



Dynamics in Soft Matter Systems

$$I(\mathbf{Q}, t \approx 0, T) = DWF \times (EISF(Q) + \frac{2}{\pi} (1 - EISF(Q)) \arctan\left(\frac{\Gamma_{\text{res}}}{\Gamma}\right))$$

where ρ_{res} is the energy resolution of the spectrometer, and ρ is the width of the Lorentzian line characterising the QENS broadening.



In this model we assume that the QENS broadening follows an Arrhenius relationship:

$$\frac{\Gamma}{\Gamma_0} = \exp\left(-\frac{E_a}{kT}\right)$$

For a distribution of E_a 's with weighting g_i

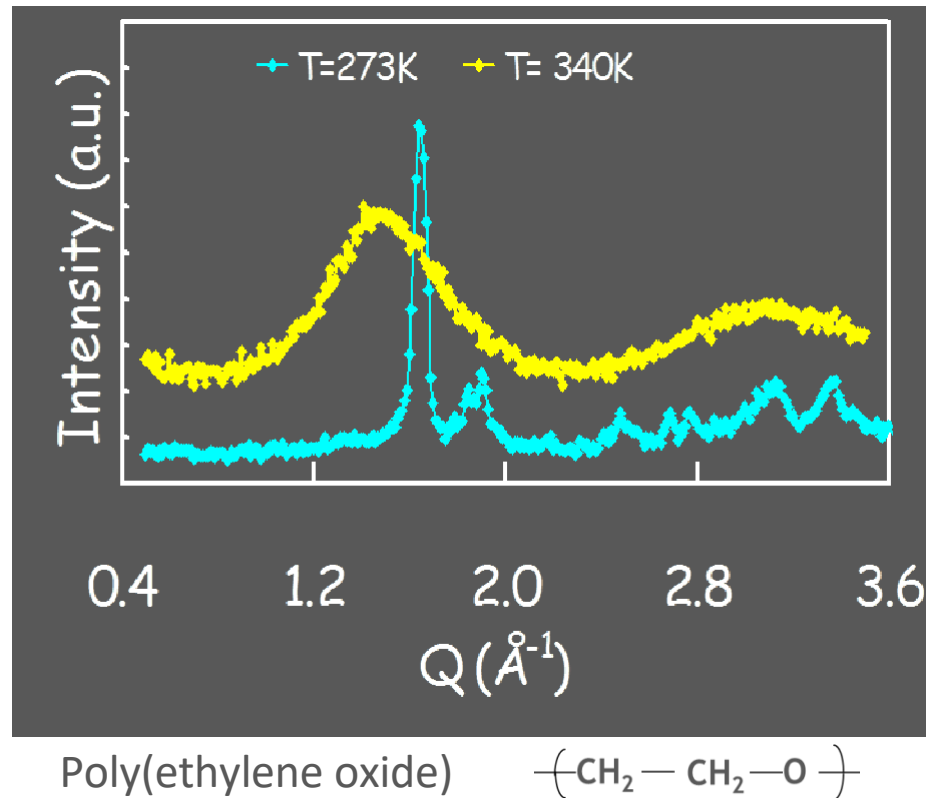
$$\sum g_i \arctan\left(\frac{\Gamma_{\text{res}}}{\Gamma_i}\right)$$

In addition, not all atoms might be mobile and contribute to the fall of elastic intensity:

$$EISF' = p_f + p_m EISF \text{ where } p_f + p_m = 1$$

Collective Dynamics (at structure peaks)

Up to now we have only been talking of the self dynamic structure factor and have said nothing about collective modes, the **coherent part of the correlation function**. This is because QENS is mostly used for measurements where the incoherent signal dominates. Also they are trickier to interpret and you need to take into account the **structure factor**, $S(Q)$, ie. how atoms are distributed in space.

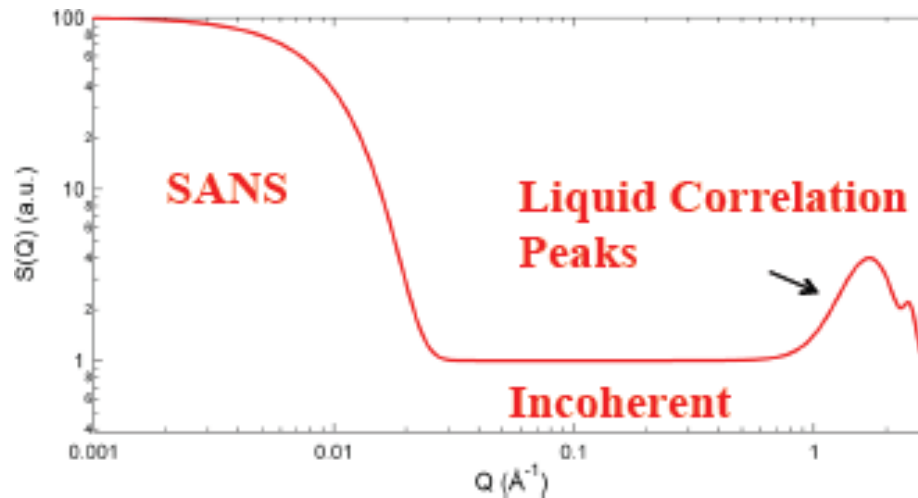


$$I_{\text{coll}}(Q, t) \approx I_{\text{self}}(Q, t) \left(\frac{Q}{\sqrt{S(Q)}}, t \right)$$

$$\tau_{\text{coll}}(Q, T) \approx a(T) \tau_{\text{self}}(Q, T) S(Q)^{1/\beta}$$

Neutron Spin-Echo

Although we can measure collective dynamics on any QENS machine, the timescale of motions for soft matter systems are more suited to doing this at a type of neutron spectrometer called **Neutron Spin Echo (NSE)**. One advantage is that it gives us the intermediate scattering function, **$I(Q,t)$** , **directly** and there is no need to FT the data, but the technique is a little trickier!



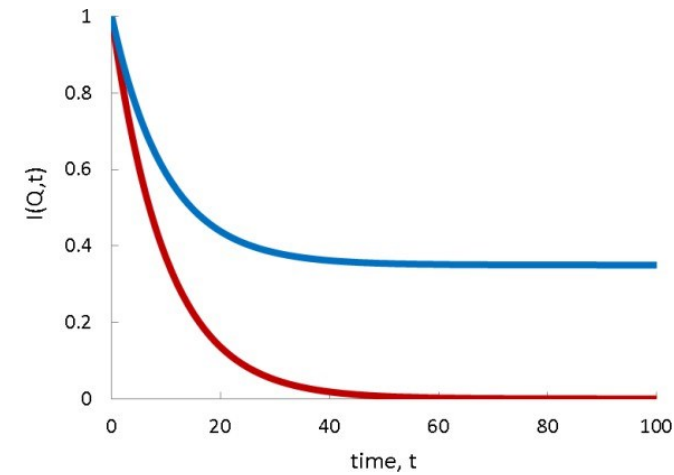
The best signal in NSE is at the peaks and is very complementary to the SANS structural information.

$$I_{\text{NSE}}(Q, t) = \frac{I_{\text{coh}}(Q, t) - \frac{1}{3}I_{\text{inc}}(Q, t)}{I_{\text{coh}}(Q, 0) - \frac{1}{3}I_{\text{inc}}(Q, 0)}$$

Neutron Spin-Echo

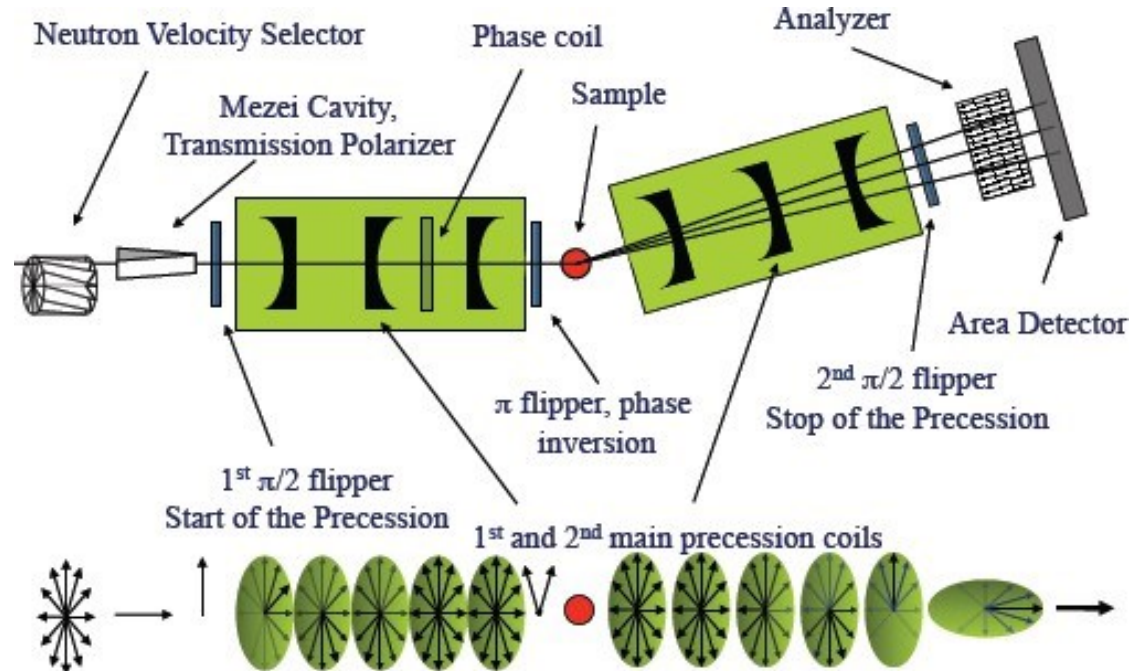
- NSE measures in the time domain – intermediate scattering function
- Primarily use to look at the coherent signal, i.e. collective dynamics
- Incoherent dynamics are possible but still rather slow
- Best NSE in the world is IN15 @ ILL that can measure Fourier times of between 1ps and 1usec

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{self}}(\mathbf{Q}, t) \exp(-i\omega t) dt$$
$$S_{\text{coh}}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{coll}}(\mathbf{Q}, t) \exp(-i\omega t) dt$$



Neutron Spin-Echo

- NSE uses the neutron's **spin polarisation** to encode the difference in energies between incident and scattered beams. Very high energy resolution.
- Neutrons perform **Larmor precessions** in two antiparallel magnetic fields, before and after the sample, resulting in polarization of the neutrons.
- Precession angles are equal and opposite and the difference is analysed at the detector. Small energy transfers lead to a change in the precession angle and thus a decrease in measured polarization.



Further Reading

General QENS books

- M. Bée, “Quasi-elastic Neutron Scattering Principles and Application in Solid State Chemistry, Biology and Materials Science”, Adam Hilger, Bristol (1988)
- R. Hempelmann, “Quasi-elastic neutron scattering and solid state diffusion”, Oxford Series on Neutron Scattering in Condensed Matter 13, Clarendon Press, Oxford (2000)
- T. Springer, “Quasi-elastic neutron scattering for the diffusive motions in solids and liquids”, Springer Tracts in Modern Physics 64, 197, Springer Verlag (1972)
- V. Garcia Sakai and M. T. F. Telling, “A Practical Guide to QENS”, in prep. (tbp 2019)

Specific for Soft Matter

- V. Garcia Sakai, C. Alba-Simionesco, S.-H. Chen, “Dynamics in Soft Matter”, Springer (2012)
- V. Garcia Sakai and A. Arbe, “Quasielastic neutron scattering in soft matter”, Current Opinion in Colloid and Interface Science 14, 381-390 (2009)
- J. S. Higgins and H. C. Benoît, “Polymers and Neutron Scattering”, Oxford Science Publications (1994)
- J. Fitter, T. Gutberlet, J. Katsaras (Eds.), “Neutron Scattering in Biology”, Springer (2006)