

Neutron Spin Echo Spectroscopy

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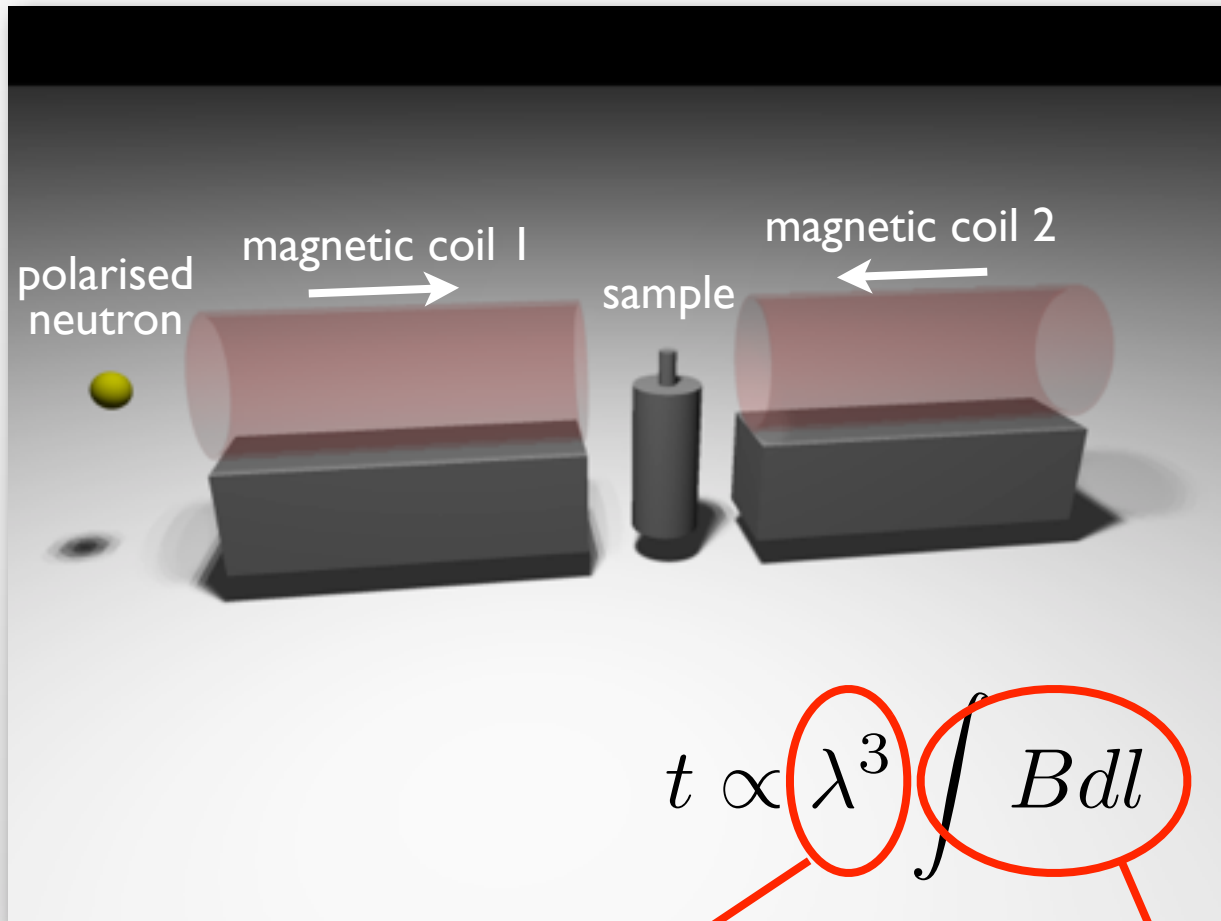
September 2014

Hercules Specialized Course 17 - Grenoble

What you are supposed to learn in this lecture

1. The **length and time scales** that can be studied using NSE spectroscopy
2. The **measurement principle** of NSE spectroscopy
3. **Discrimination** techniques for **coherent, incoherent** and **magnetic** dynamics
4. To **which scientific problems** can I apply NSE spectroscopy?

The measurement principle of neutron spin echo spectroscopy (quantum mechanical model)

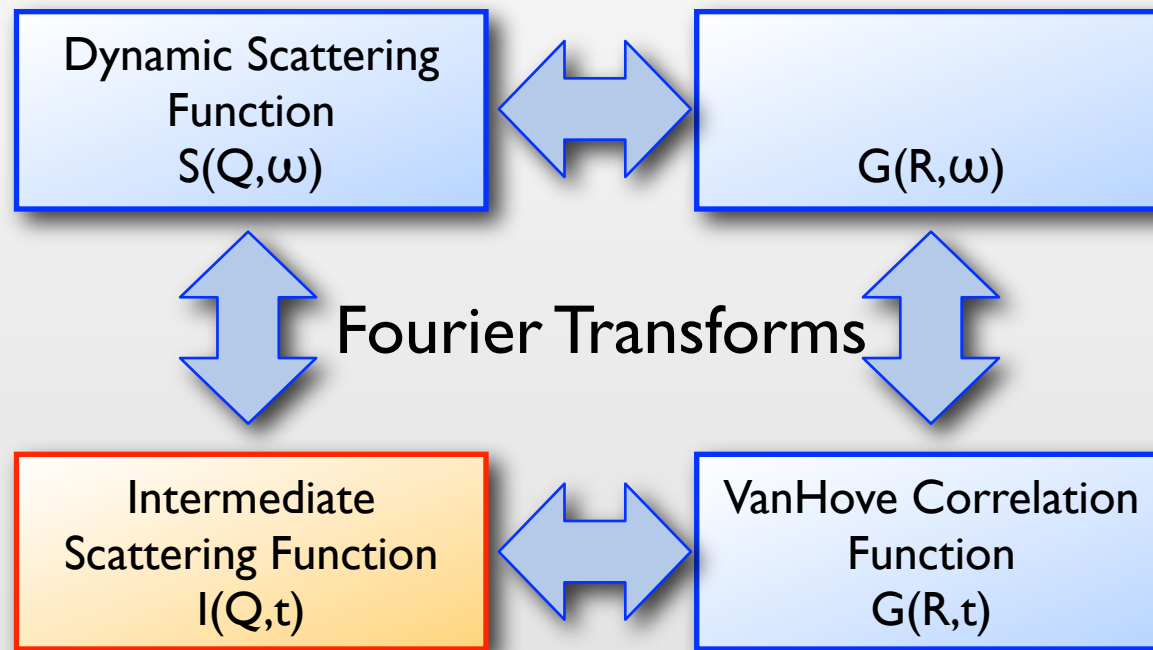


- The **neutron wave function** is split by **magnetic fields**
- The 2 wave packets arrive at the sample with a **time difference t**
- If the **molecules move** between the arrival of the first and second wave packet then **coherence is lost**
- The **intermediate scattering function $I(Q,t)$** reflects this loss in coherence

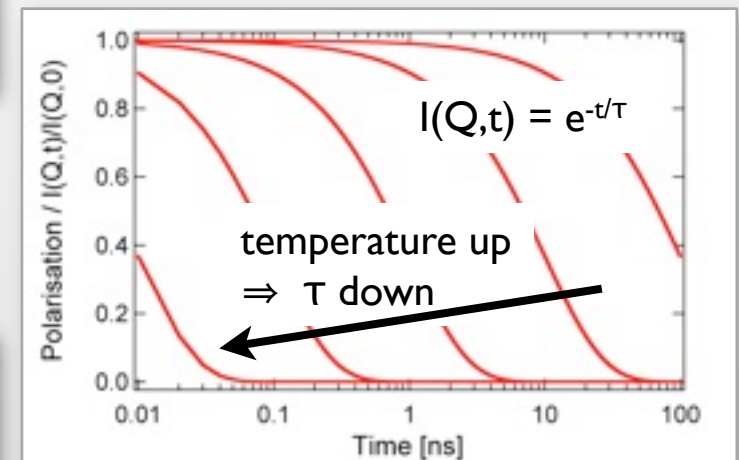
strong wavelength
dependence

field integral

The measurement principle of neutron spin echo spectroscopy

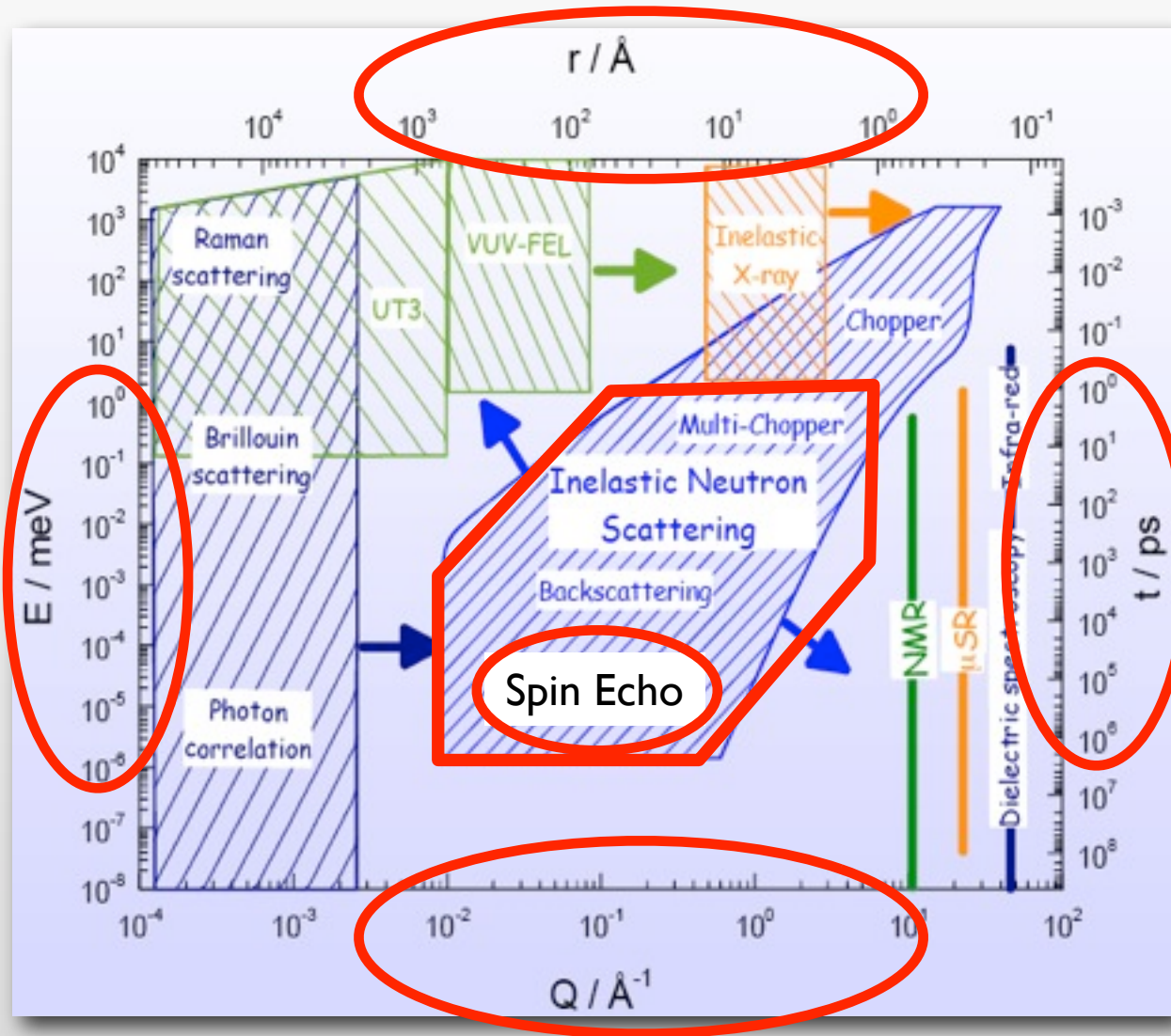


NSE spectra for diffusive motion



Measured with Neutron Spin Echo (NSE) Spectroscopy

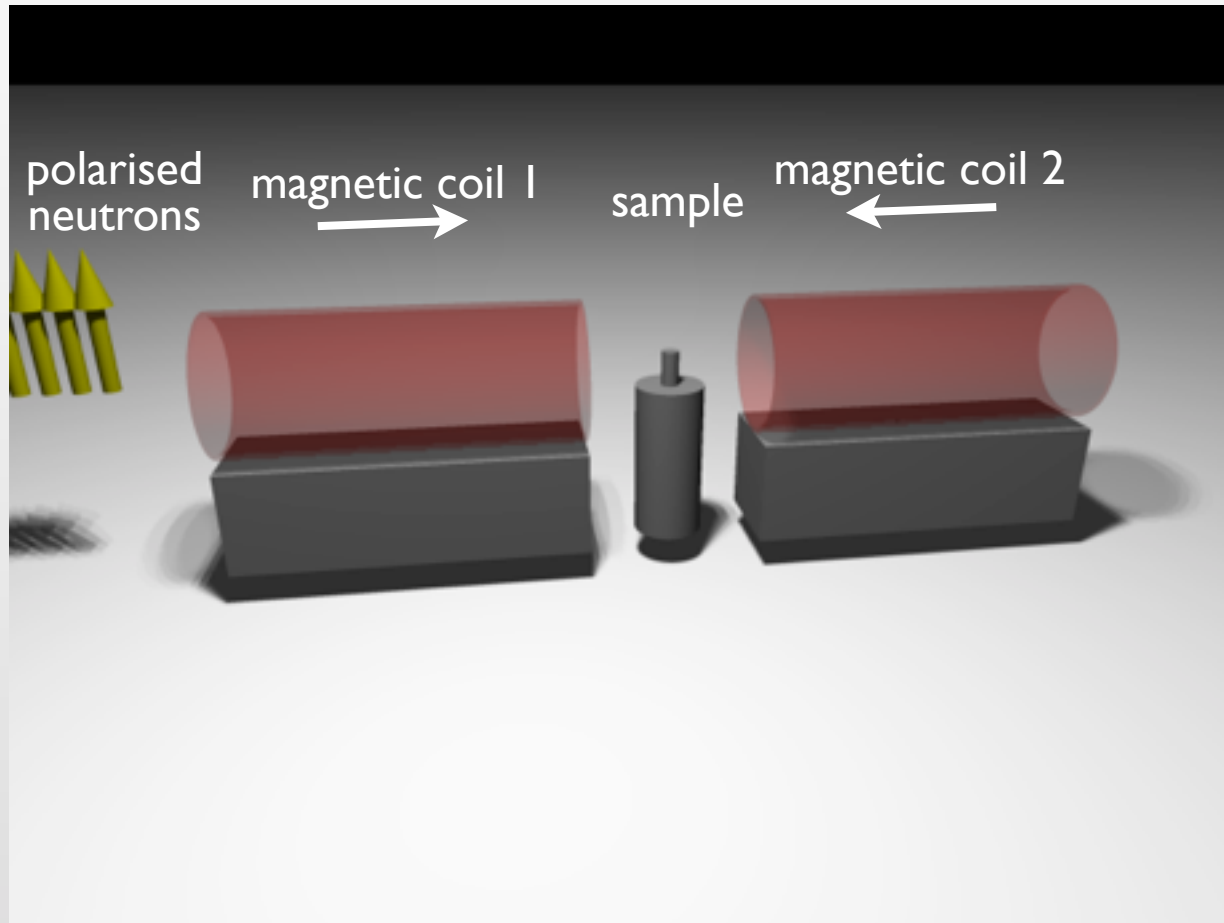
Neutron spin echo spectroscopy in the time/space landscape



- NSE is the neutron spectroscopy with the highest energy resolution
- The time range covered is $1 \text{ ps} < t < 1 \text{ }\mu\text{s}$ (equivalent to neV energy resolution)
- The momentum transfer range is $0.01 < Q < 4 \text{ }\text{\AA}^{-1}$

The measurement principle of neutron spin echo spectroscopy

Classical Description



- Neutrons are polarised perpendicular to magnetic fields
- **Elastic Case:** Neutrons perform the same number of spin rotations in both coils and exit with the original polarisation (*spin echo condition*)
- **Quasielastic Case:** Time spent in the second coil will be slightly different, i.e., the original polarisation angle is not recovered (loss in polarisation)
- **No strong monochromatisation needed**

The measurement principle of neutron spin echo spectroscopy

Classical Description

The description of NSE in a classical framework helps to understand the spectrometer operation and its limits.

We start with the **classical equation of motion** for the **Larmor precession** of the neutron spin:

$$\frac{d\vec{S}}{dt} = \gamma_L [\vec{S} \times \vec{B}]$$

with the **neutron gyromagnetic ratio** γ_L :

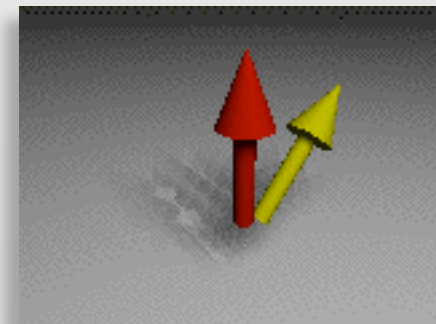
$$\gamma_L = 1.832 \times 10^8 \text{ rad s}^{-1} \text{T}^{-1}$$

The **field B** from a magnetic coil of length l will create a **precession angle φ**

$$\varphi = \gamma_L \frac{\int \vec{B} \cdot d\vec{l}}{v}$$

“Field Integral”

speed of neutrons \Rightarrow time spent in the B field



The measurement principle of neutron spin echo spectroscopy

Classical Description

Now we will consider how to link the precession to the dynamics in the sample.

Performing a **spin echo experiment** we measure the **polarisation \mathbf{P}** with respect to an arbitrarily chosen coordinate x . P_x is the projection on this axis and we have to take the average over all precession angles:

$$P_x = \langle \cos \varphi \rangle = \langle \cos(\varphi_{in} - \varphi_{out}) \rangle$$

The precession angles φ_{in} and φ_{out} for the neutrons before and after scattering from the sample are given by the respective speeds of the neutrons:

$$P_x = \langle \cos[\gamma_L (\frac{\int \vec{B}_{in} \cdot d\vec{l}}{v_{in}} - \frac{\int \vec{B}_{out} \cdot d\vec{l}}{v_{out}})] \rangle$$

To first order φ is proportional to the energy transfer at the sample ω with the proportionality constant t (spin echo time).

$$\varphi = t\omega$$

This is the **“fundamental equation”** of classical neutron spin echo.

The measurement principle of neutron spin echo spectroscopy

Classical Description

We consider the “fundamental equation” $\varphi = t\omega$ and we will **calculate t** to first order by Taylor expansion.

Starting point is the energy transfer ω :

$$\hbar\omega = \frac{m}{2} [(\bar{v} + \Delta v_{out})^2 - (\bar{v} + \Delta v_{in})^2]$$

Taylor expansion to first order gives:

$$\omega = \frac{m}{\hbar} [\bar{v}\Delta v_{out} - \bar{v}\Delta v_{in}]$$

Now we turn to the phase φ :

$$\varphi = \gamma_L \left[\frac{\int \vec{B} \cdot d\vec{l}}{\bar{v} + \Delta v_{in}} - \frac{\int \vec{B} \cdot d\vec{l}}{\bar{v} + \Delta v_{out}} \right]$$

Here, Taylor expansion to first order gives:

$$\varphi = \gamma_L \left[\frac{\int \vec{B} \cdot d\vec{l}}{\bar{v}^2} \Delta v_{out} - \frac{\int \vec{B} \cdot d\vec{l}}{\bar{v}^2} \Delta v_{in} \right]$$

Combining the equations for ω and φ , we get:

$$t = \frac{\varphi}{\omega} = \frac{\hbar}{m} \frac{\gamma_L \int \vec{B} \cdot d\vec{l}}{\bar{v}^3} = \frac{m^2 \gamma_L \int \vec{B} \cdot d\vec{l}}{2\pi \hbar^2} \lambda^3$$

using de Broglie $p = mv = \frac{h}{\lambda}$

The measurement principle of neutron spin echo spectroscopy

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The measurement principle of neutron spin echo spectroscopy

Classical Description

We return to the equation for the **polarization P_x**

$$P_x = \langle \cos \varphi \rangle = \langle \cos(\omega t) \rangle$$

and use it to prove that we measure the intermediate scattering function.

In a first step we **write down the average as an integral**

$$P_x(Q, t) = \frac{\int S(Q, \omega) \cos(\omega t) d\omega}{\int S(Q, \omega) d\omega}$$

Here, we exploit that the scattering function $S(Q, \omega)$ *is the probability for scattering a neutron with a given momentum and energy transfer.*

It turns out that **P_x is the cosine transform of the $S(Q, \omega)$** . Thus, P_x is not strictly equal to the intermediate scattering function, but to the real part only.

$$P_x(Q, t) = \frac{\Re(I(Q, t))}{I(Q, 0)}$$

For most cases this difference is negligible, but this has to be kept in mind.

The measurement principle of neutron spin echo spectroscopy

Example:

We consider a quasielastic **Lorentzian line**:

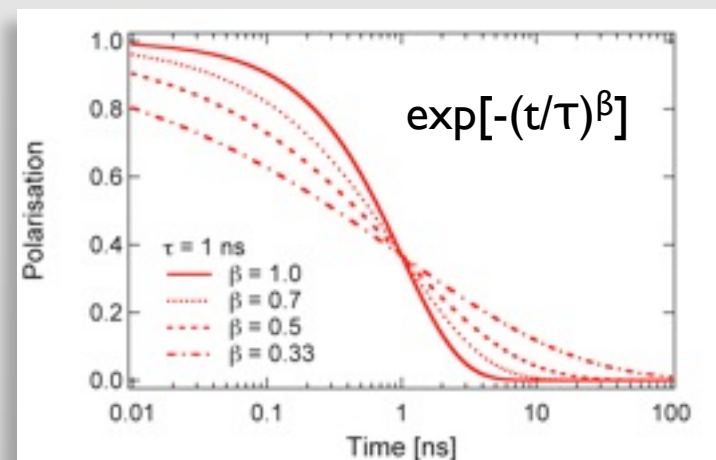
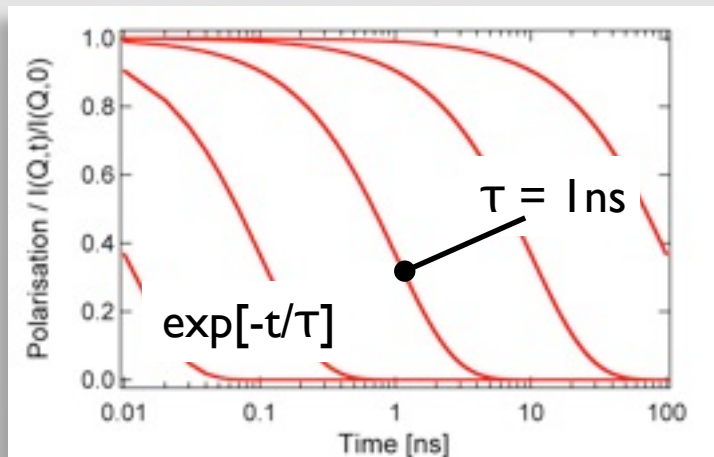
$$S(Q, \omega) \propto \frac{\Gamma}{\Gamma^2 + \omega^2}$$

For a Lorentzian line, the **Fourier transform** is an **exponential decay function**:

$$P_x(Q, t) = \frac{\int [\Gamma^2 + \omega^2]^{-1} \cos(\omega t) d\omega}{\int [\Gamma^2 + \omega^2]^{-1} d\omega} = e^{-\Gamma t} = e^{-t/\tau}$$

Γ is the quasi-elastic line broadening and τ is the decay/relaxation time.

For a mixture of relaxation times we often get a good description by a **stretched exponential** function $\exp[-(t/\tau)^\beta]$ (this is also called KWW Kohlrausch Williams Watt function).



Spin Echo Spectrometers at ILL



Mezei's first spin echo precession coils

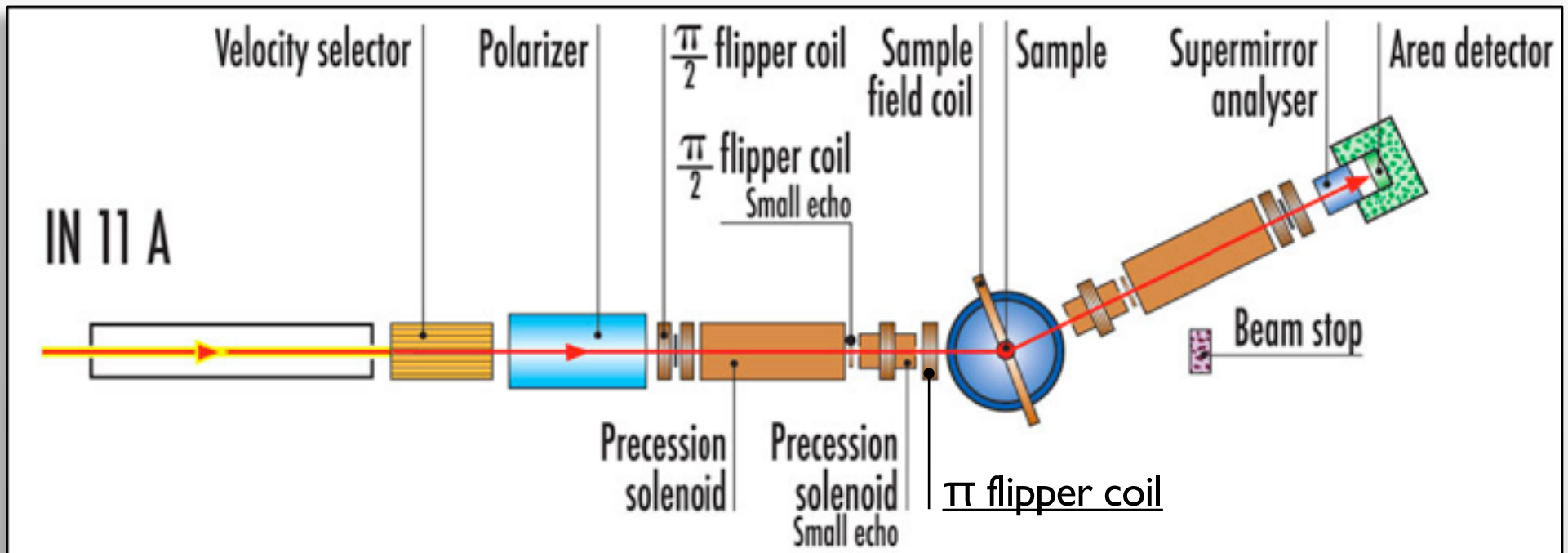


Today's IN15: measures up to 1000 ns



Large angle NSE: IN11C for high signal

How a spin echo spectrometer works



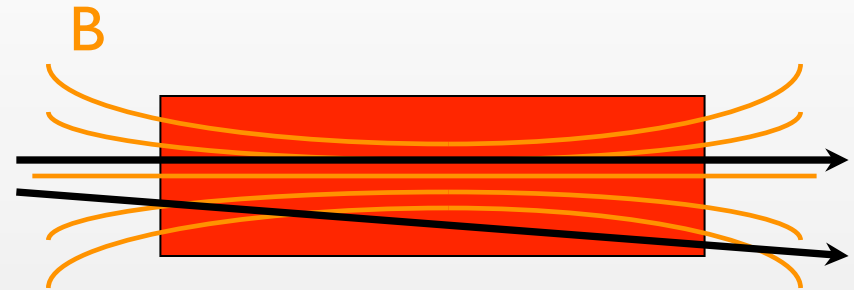
- The beam is monochromatised by a velocity selector to about $dv/v = 15\%$
- Spin polarization and analysis are performed by supermirrors
- Spin precession is started and stopped by $\pi/2$ (or 90°) spin flipper coils
- The fields B_{in} and B_{out} are parallel and, therefore, a 180° or π flipper coil is necessary
- Small times are reached by “Small Echo” coils

How a spin echo spectrometer works: **Correction elements**

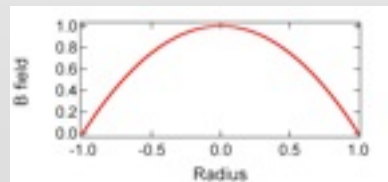
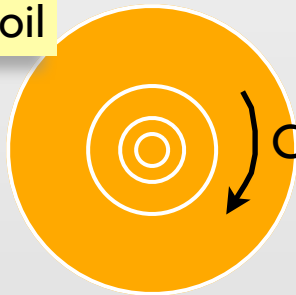
We consider again the precession angle:

$$\varphi(v) = \gamma \frac{\int \mathbf{B} \cdot d\mathbf{l}}{v}$$

This angle should be the same for all neutrons with the same velocity - **irrespective of their trajectories!**

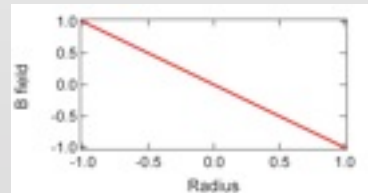
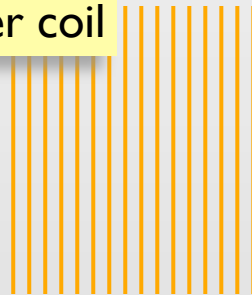


Fresnel coil



quadratic

Shifter coil



linear

High number of precessions

$$\varphi(v) = \gamma \frac{0.25 \text{ Tm}}{v} \approx 10,000 \times 2\pi$$

means that we need an error in the field integral of about:

$$\frac{\Delta \int \mathbf{B} \cdot d\mathbf{l}}{\int \mathbf{B} \cdot d\mathbf{l}} \leq 10^{-6}$$

Discrimination methods for coherent, incoherent and magnetic dynamics

Classical Description

Up to now, we have neglected spin interactions with the sample, but they are important!
We include this effect by introducing a **pre-factor P_s** to the calculation of P_x :

$$P_x(Q, t) = P_s \frac{\Re(I(Q, t))}{I(Q, 0)}$$

In addition, spin interactions with the sample can lead to an apparent π flip by the sample - for paramagnetic samples a π flipper coils is not used.

The ratio of coherent/incoherent signal can be critical.

Type of scatterer	Spin flip coils needed	Sample field	P_s
Coherent nuclear	π flipper	small	1
Incoherent nuclear	π flipper	small	-1/3
Paramagnet	none	small	1/2
Ferromagnet	2 $\pi/2$ flippers	high	1/2
Antiferromagnet	none	small	1/2-1

Measuring an NSE Spectrum and the “4-point method”

- An NSE spectrum is measured **step-wise and not “continually”**
- A spin echo time is set by sending the same current $I \propto B$ through both coils
- For each spin echo time, the signal is measured as the phase φ is scanned by applying a small offset current
- In the **“4-point method”** we measure the projection of the polarization as we change φ in steps of 90° around the spin-echo point

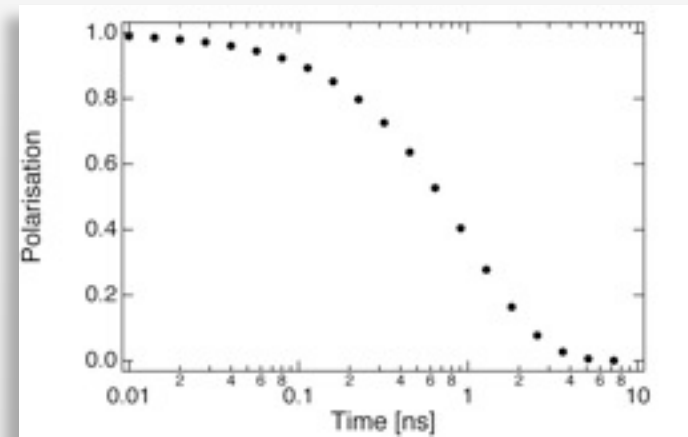
This gives us:

- average signal A , amplitude I , phase shift $\Delta\varphi$ and frequency f

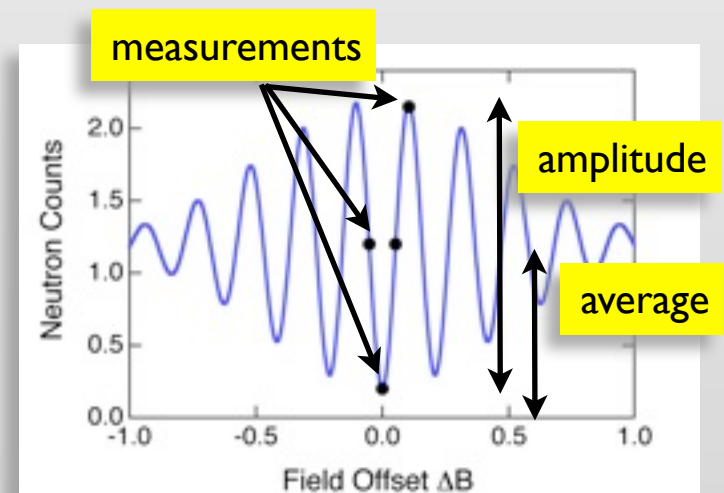
From these measurements we can extract:

- the polarization $P = I/A$

Typical NSE Spectrum



4-point measurement



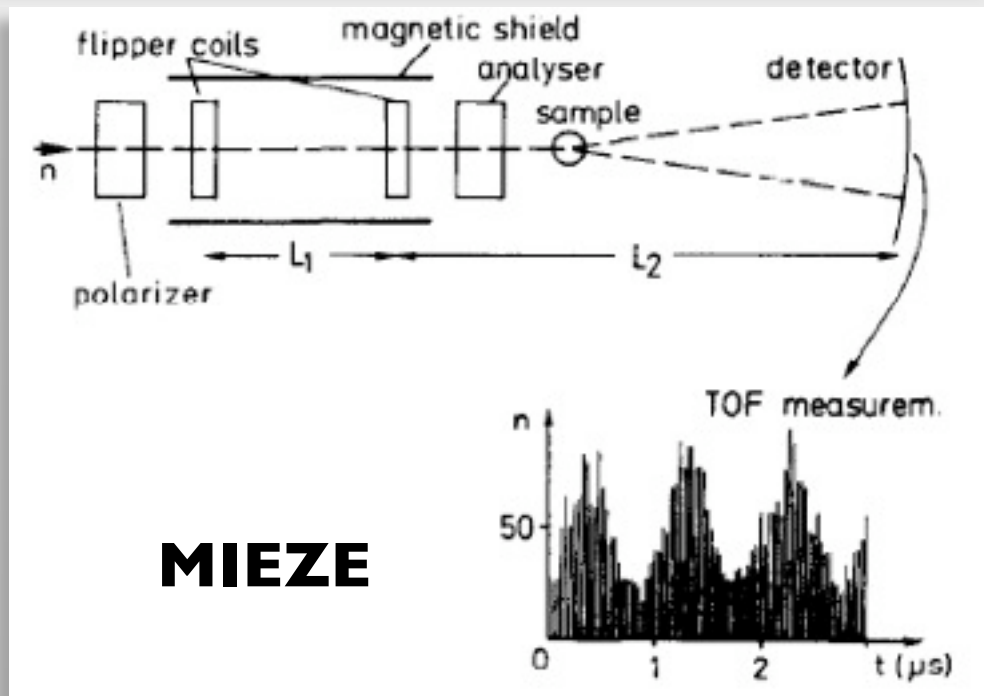
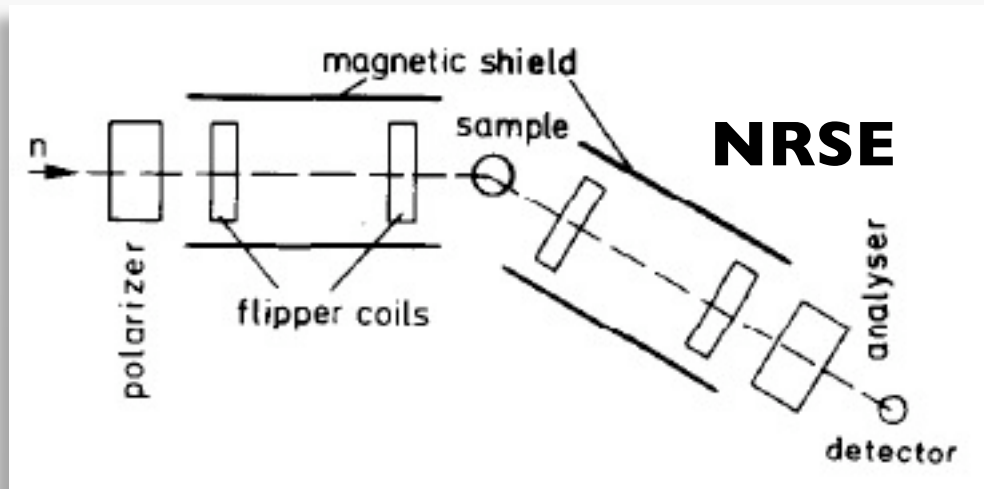
Neutron **Resonance** Spin Echo (NRSE)

The principle of neutron resonance spin echo:

- Instead of rotation of neutron spins, NRSE uses **rotation of fields**

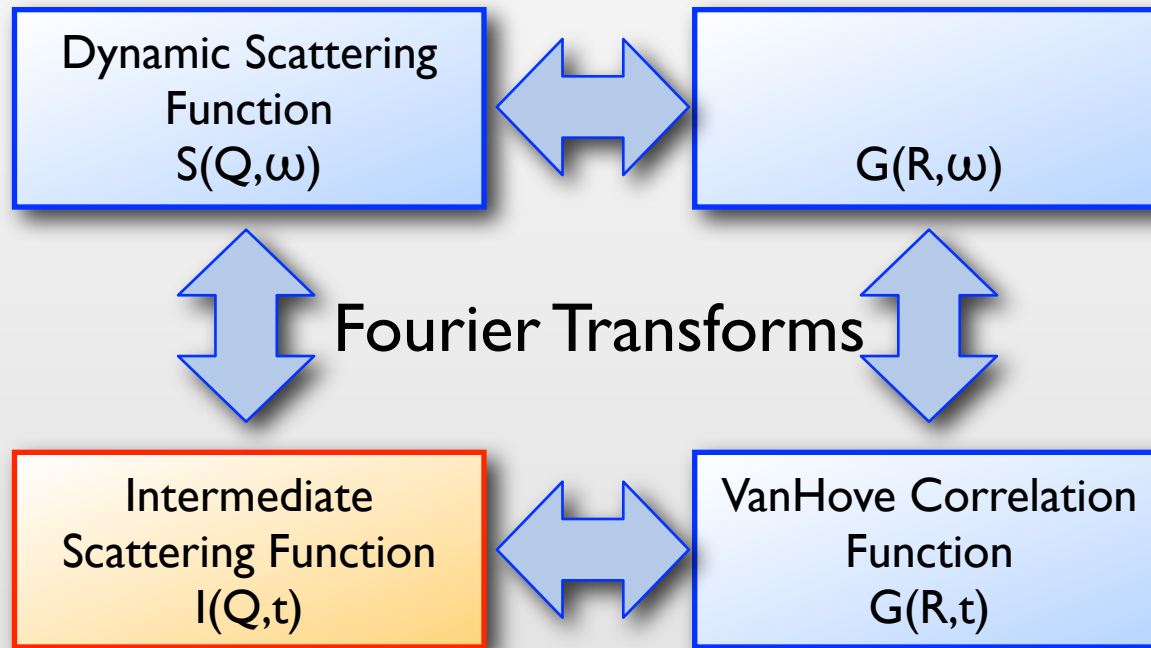
Technical realisation:

- NRSE uses spin flipper coils with rotating field directions
- Between flipper coils the B field is 0
- Flipper coils can be inclined for inelastic line width measurements
- Ideal for combination with TAS
- NRSE can be extended to MIEZE technique (second arm flippers replaced by ToF detection scheme)



How to do Science using NSE

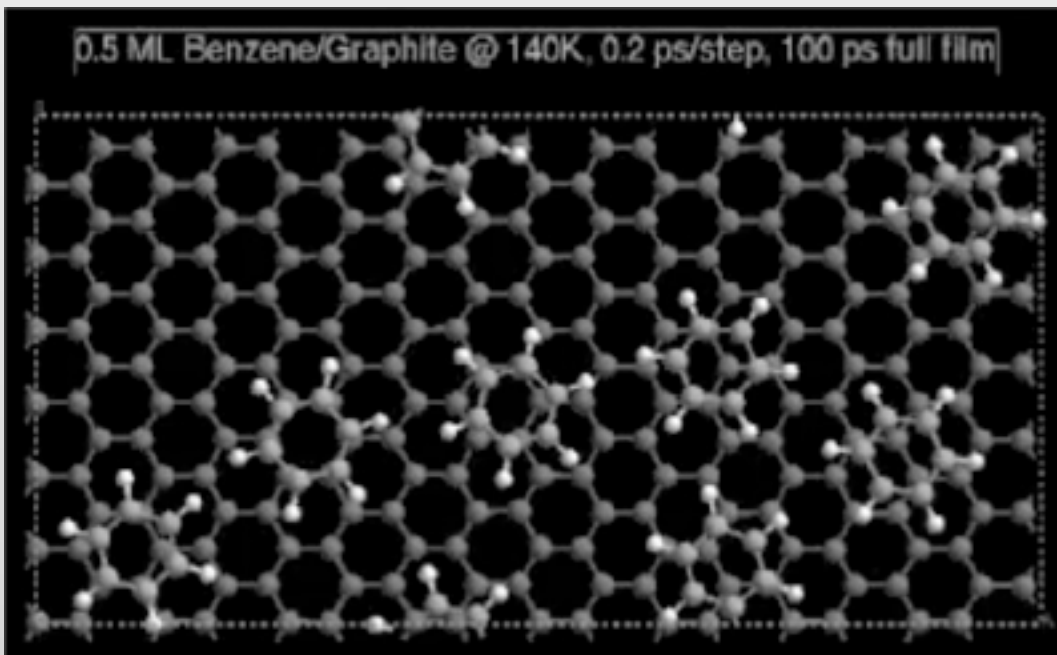
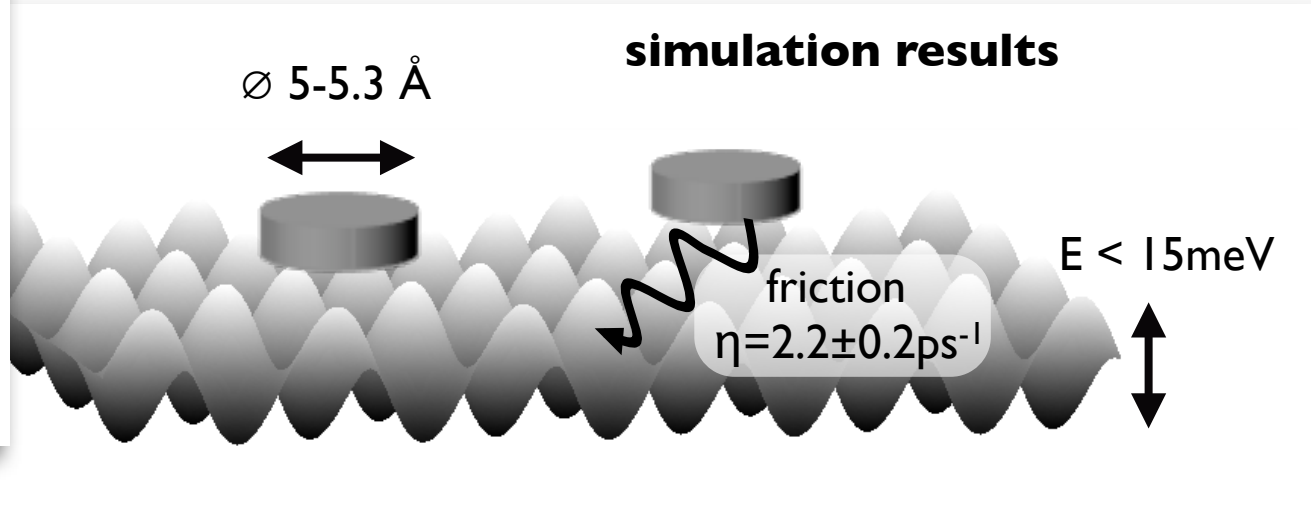
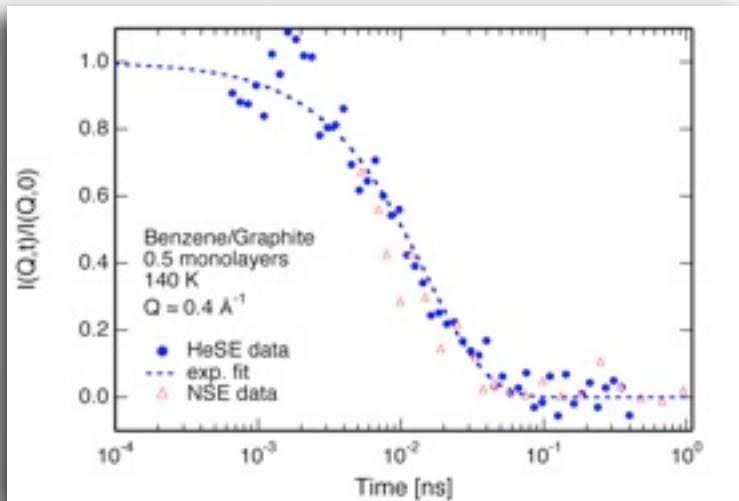
NSE measures $I(Q,t)$, the intermediate scattering function



Measured with Neutron Spin Echo (NSE) Spectroscopy

Science Examples

Case I: Molecular Ice Hockey: Benzene on Graphite

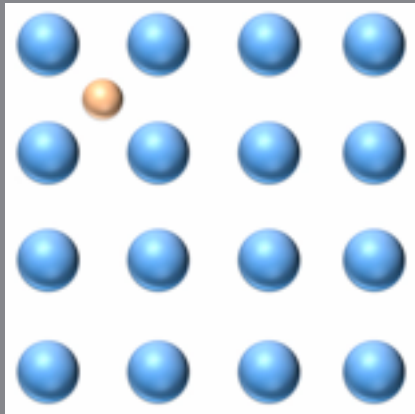


NSE - and its surface equivalent helium spin-echo - see “perfect” molecular Brownian diffusion.

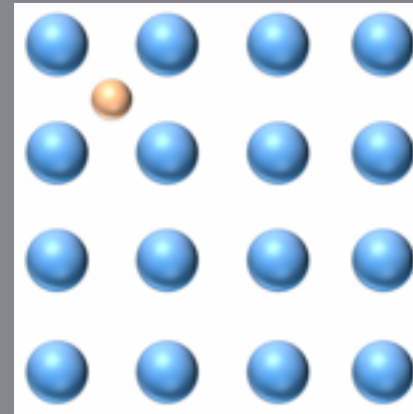
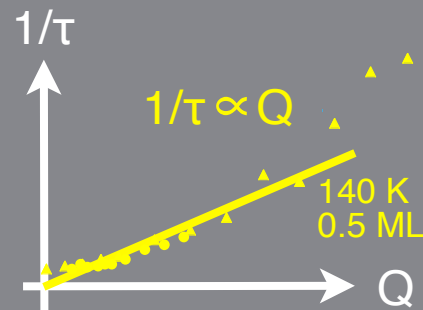
Data can be reproduced with molecular dynamics (MD) simulations.

Dynamic friction can be determined.

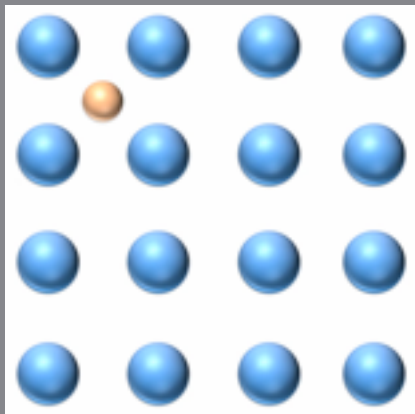
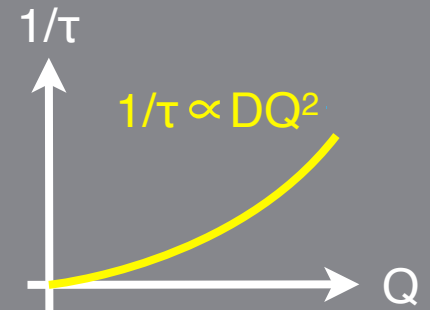
We can exploit the Q dependence of τ or Γ



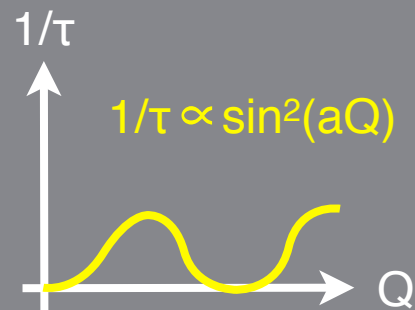
Ballistic Diffusion



Brownian Diffusion

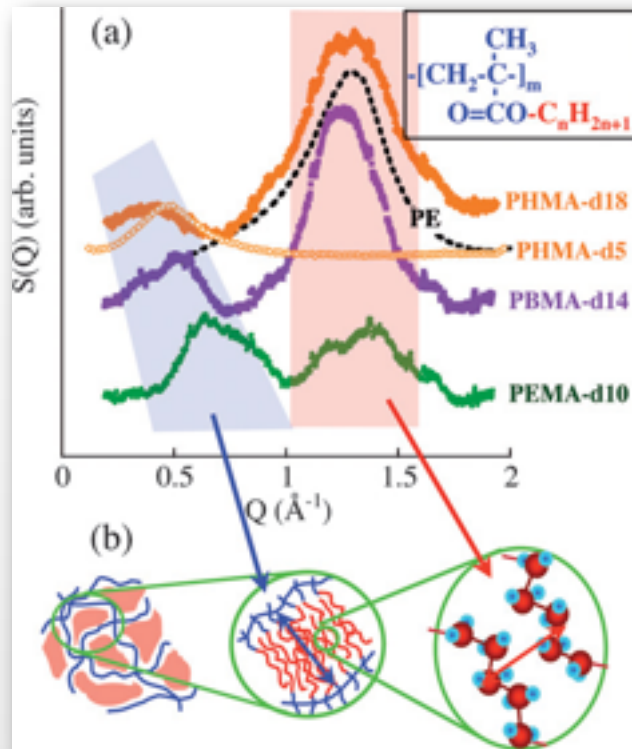


Jump Diffusion



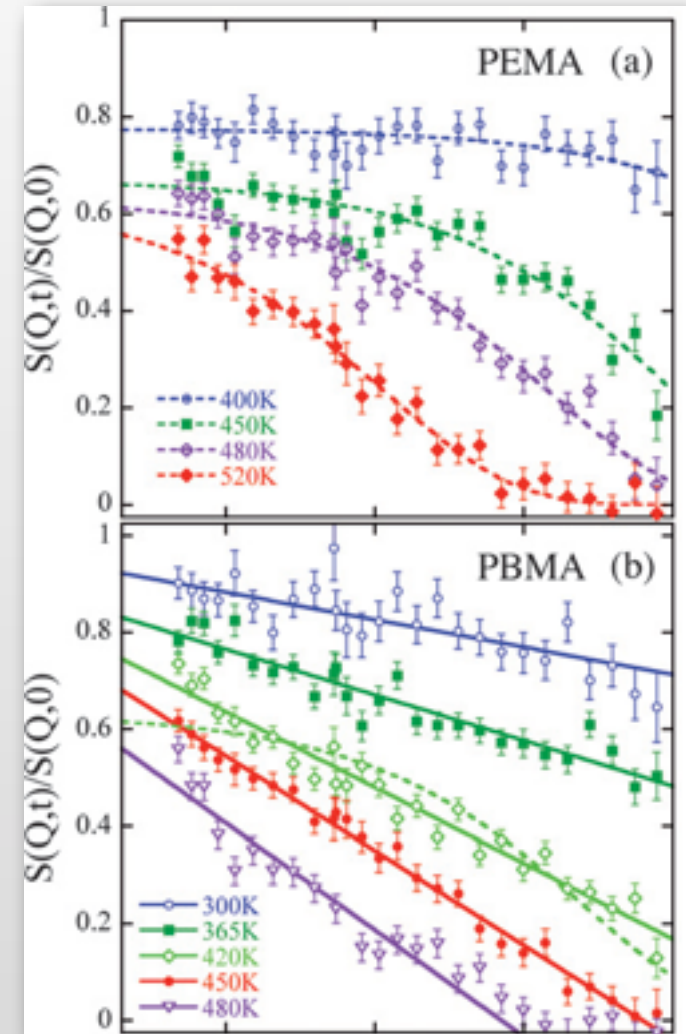
Science Examples

Case 2: Dynamics of Polymers



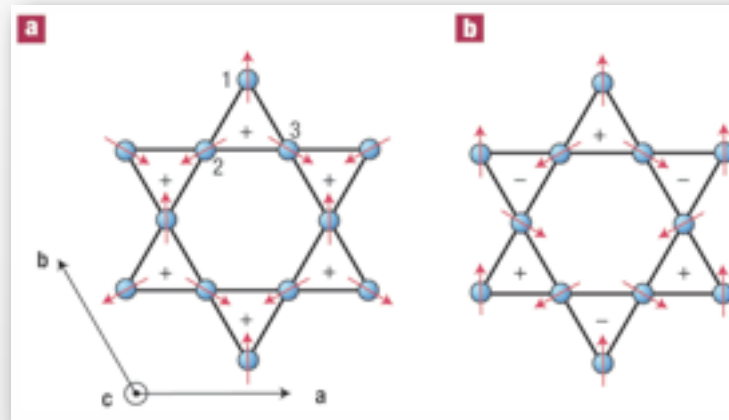
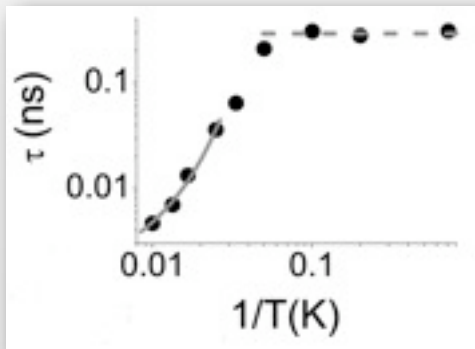
In different Q regions, dynamics can be profoundly different:

PnMA polymers, show **standard KWW** decay on the **low Q range** and **logarithmic decay** in the region of the **nano domains**

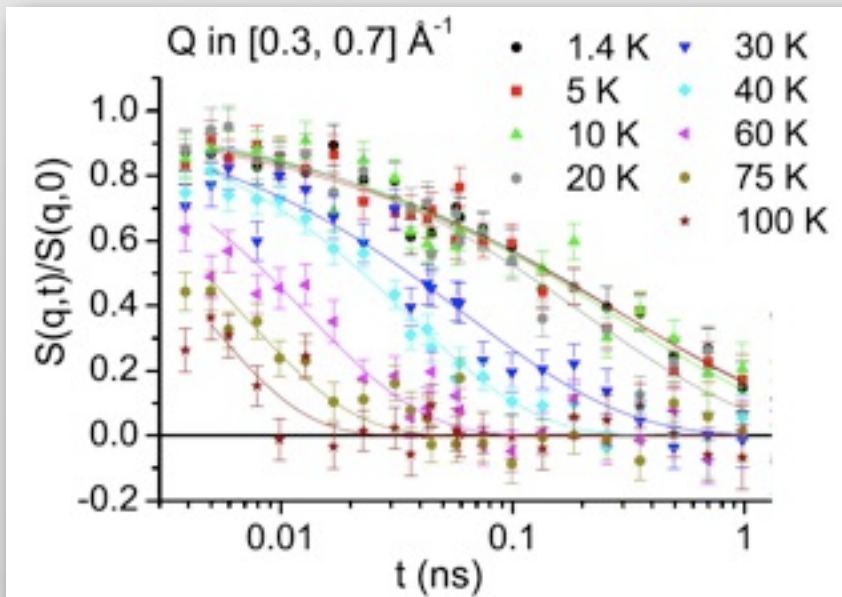


Science Examples

Case 3: Dynamics of **Frustrated Magnets**: Nd langasite



D. Grohol *et al.*, Nature Materials **4**, 323 (2005)



NSE is **strong** in magnetism research as it can distinguish between magnetic and non-magnetic dynamics.

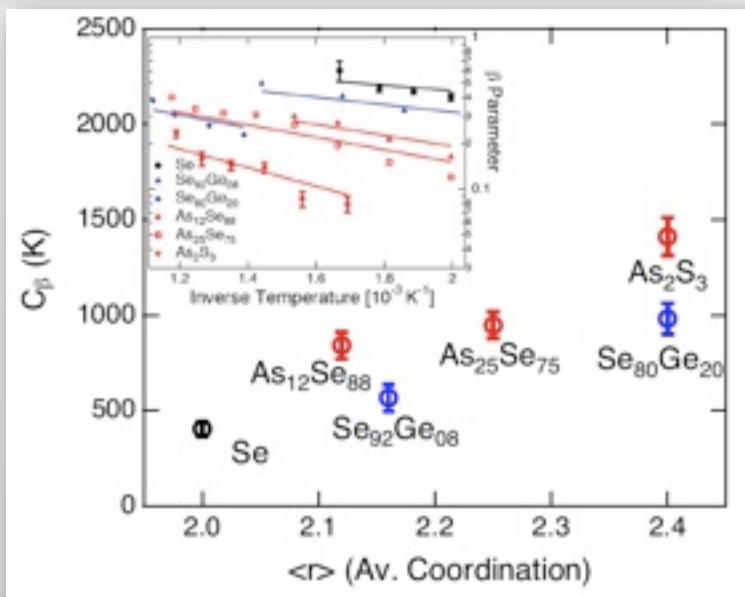
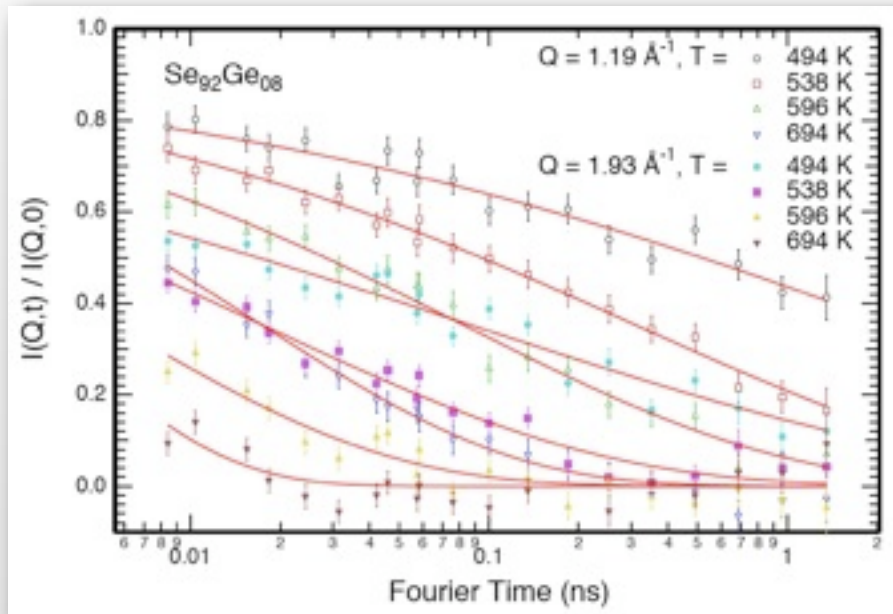
$\text{Nd}_3\text{Ga}_5\text{SiO}_{14}$ is a **frustrated magnet** with a 2 dim. “**Kagome**” lattice. Such systems have no fixed spin orientation and are highly dynamic.

Here, a **quantum relaxation** hides the effects of frustration.

V. Simonet *et al.*, Phys. Rev. Lett. **100**, 237204 (2008)

Science Examples

Case 4: Dynamics of **Glasses**



$\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ is a prime example of a network glass

Normal liquids dynamics show a thermal activation according to $\exp[-kT/E_a]$

Dynamics of **glasses** close to the transition temperature, however, show sometimes **strong deviations from exponential behaviour**

With measurements on IN11 it was possible to see this effect even far away from the glass transition and the dynamics were linked to the **average coordination number $\langle r \rangle$** :

$$\langle r \rangle = 4x + 3y + 2(1-x-y)$$

Literature

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