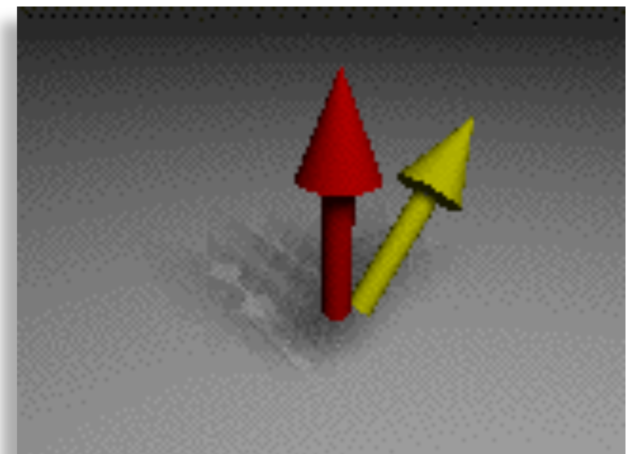
Neutron Spin Echo Spectroscopy



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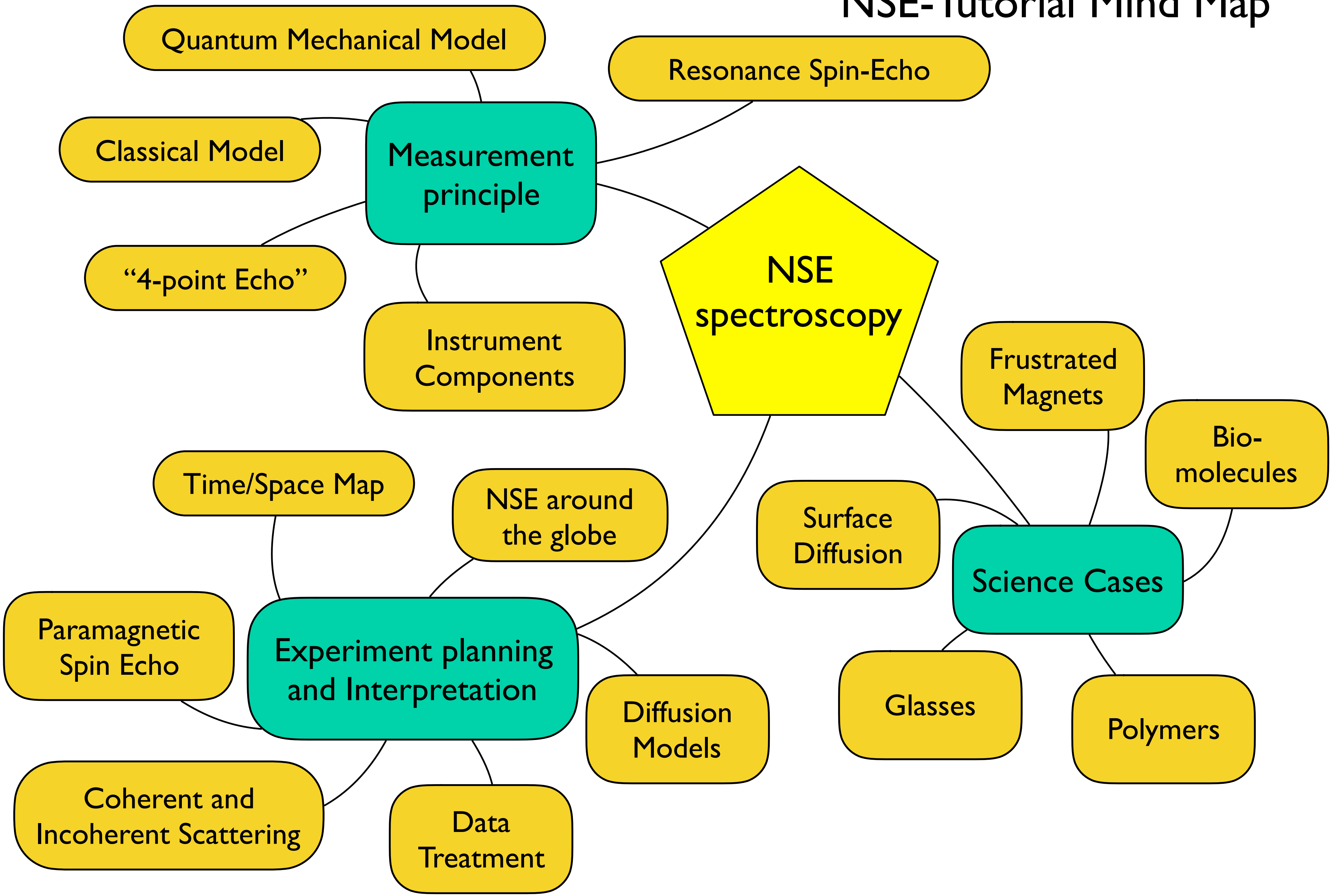
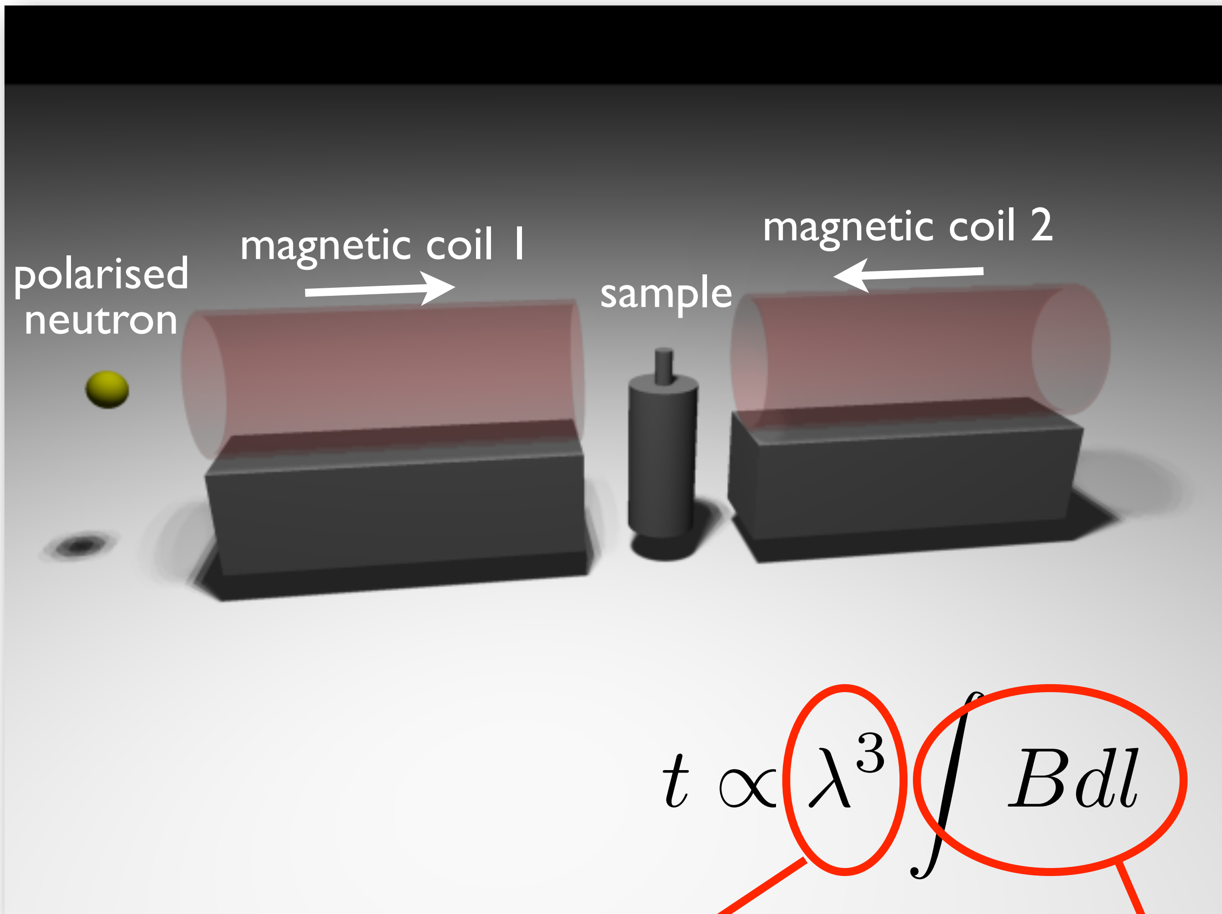
What you are supposed to learn in this tutorial

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?

NSE-Tutorial Mind Map



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



$$t \propto \lambda^3 \int B dl$$

strong wavelength dependence

field integral

- 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

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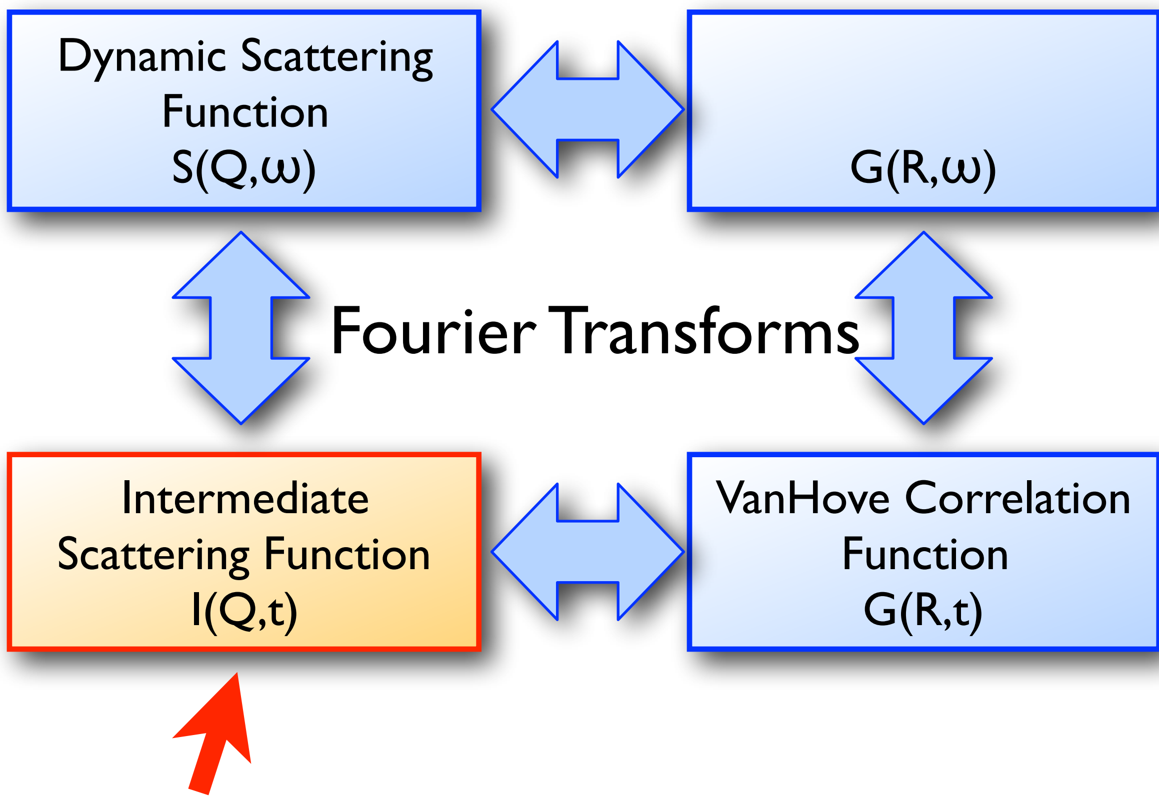
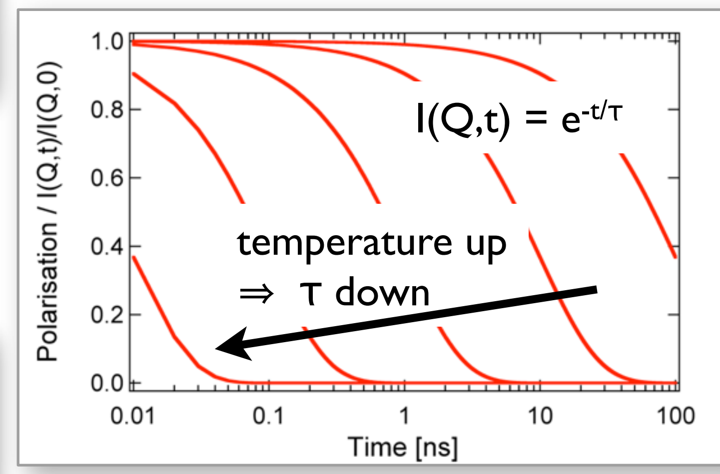
The measurement principle of neutron spin echo spectroscopy



NSE spectra for diffusive motion



Measured with Neutron Spin Echo (NSE) Spectroscopy

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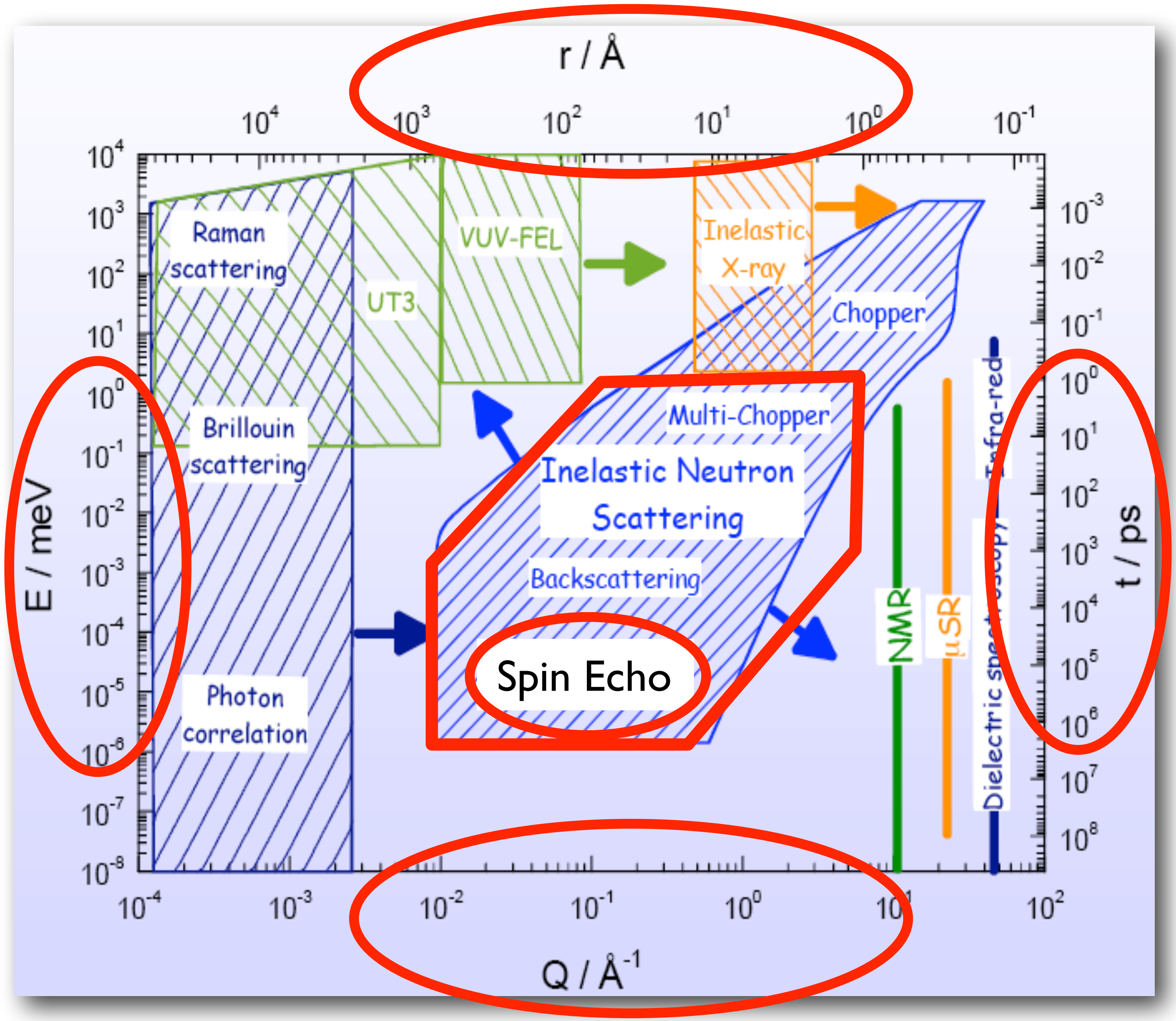
Neutron spin echo spectroscopy in the time/space landscape



- NSE is the neutron spectroscopy with the highest energy resolution
- The time range covered is 1 ps < t < 1 μs *(equivalent to neV energy resolution)*
- The momentum transfer range is 0.01 < Q < 4 Å^{-1}

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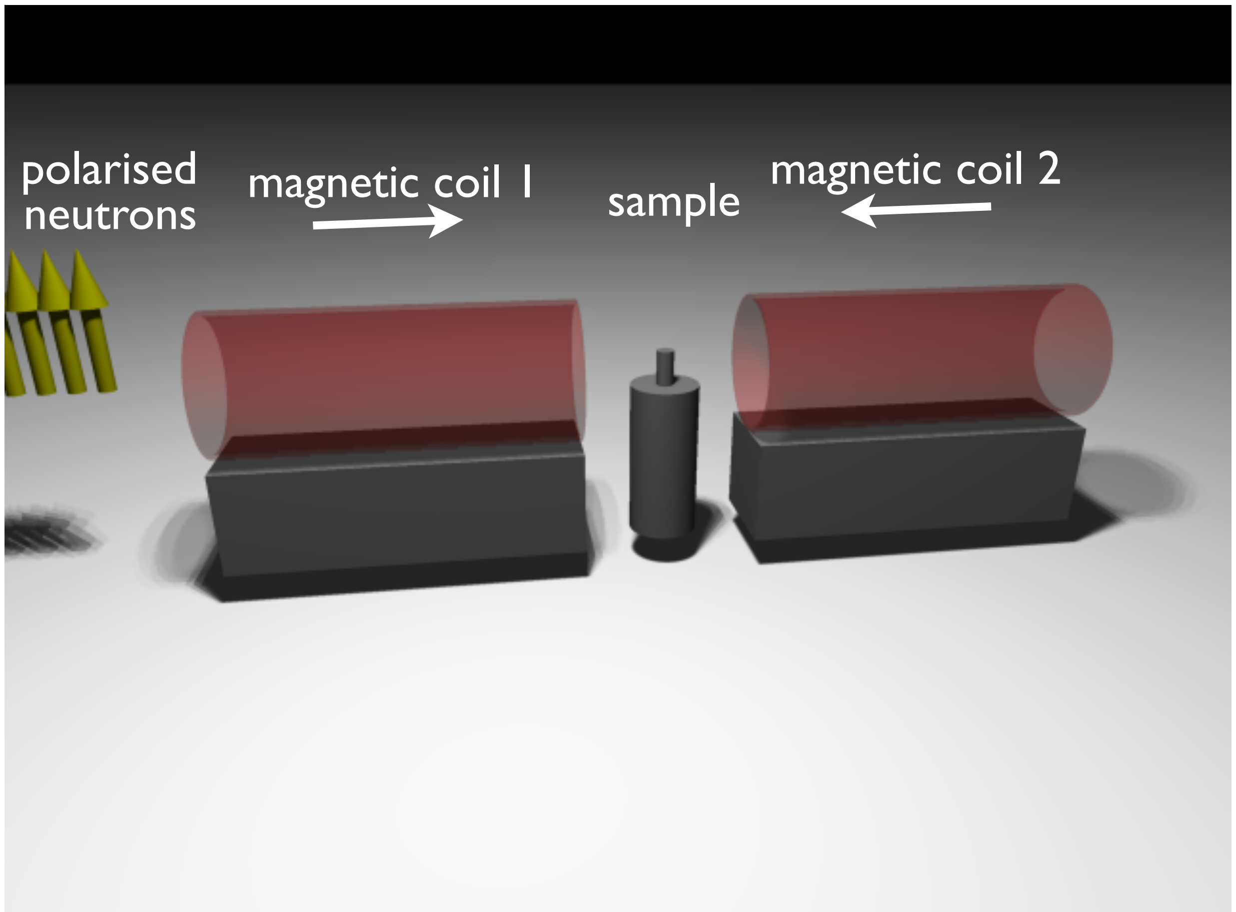
The measurement principle of neutron spin echo spectroscopy
Classical Description



- 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 monochroma-tisation needed**

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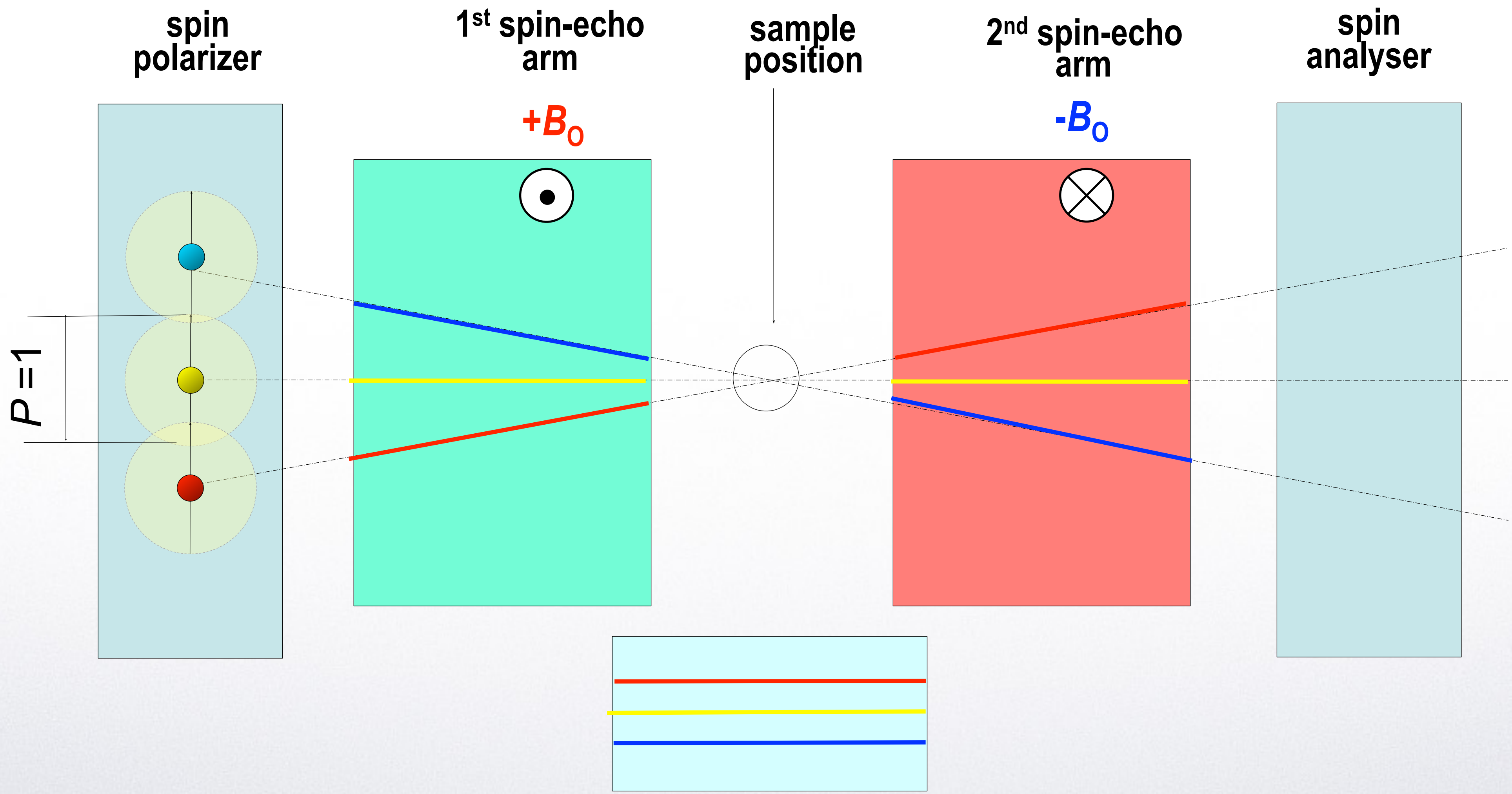
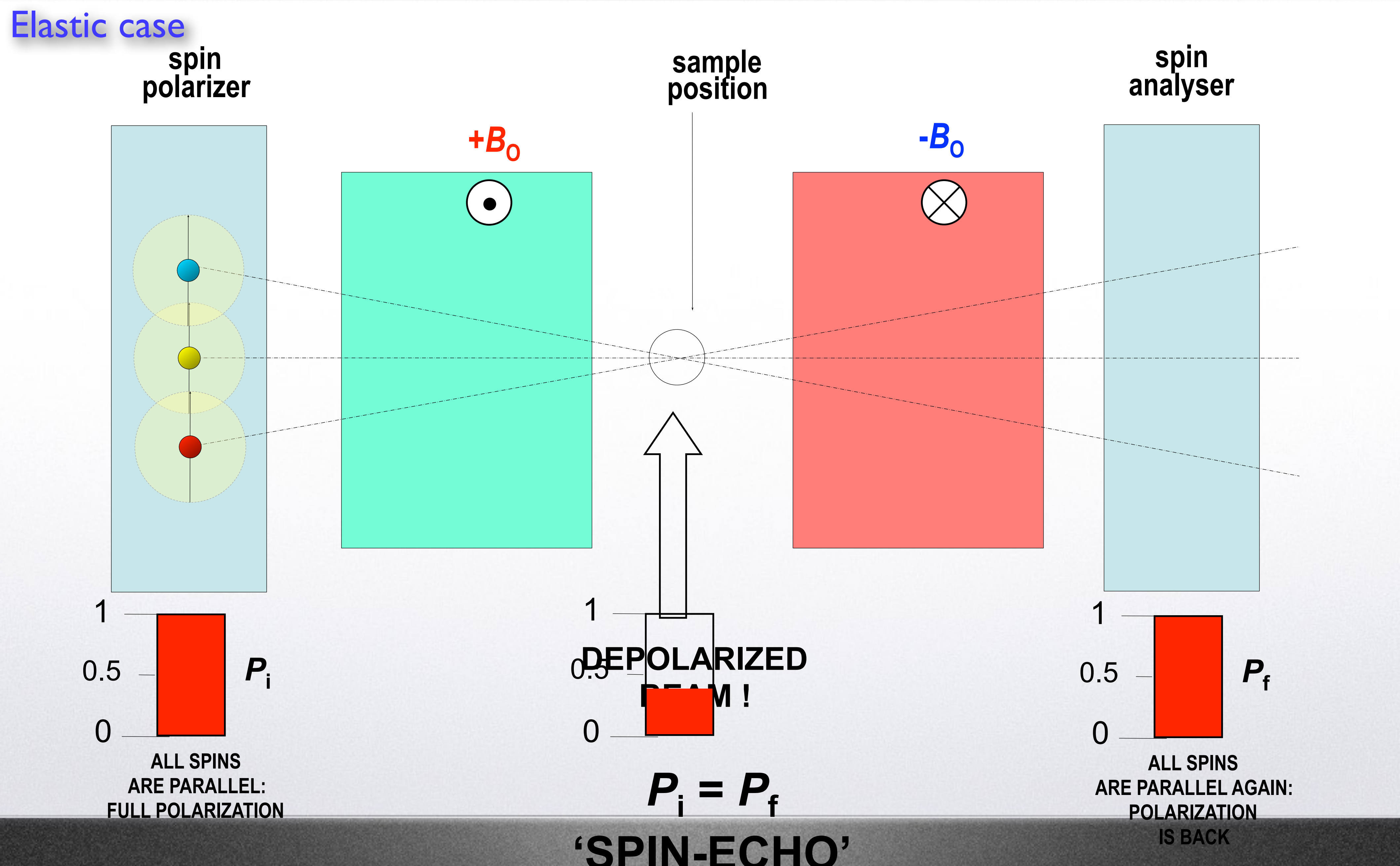
Fundamentals of NSE



No collimation no monochromatization necessary
The echo condition is fulfilled for all paths

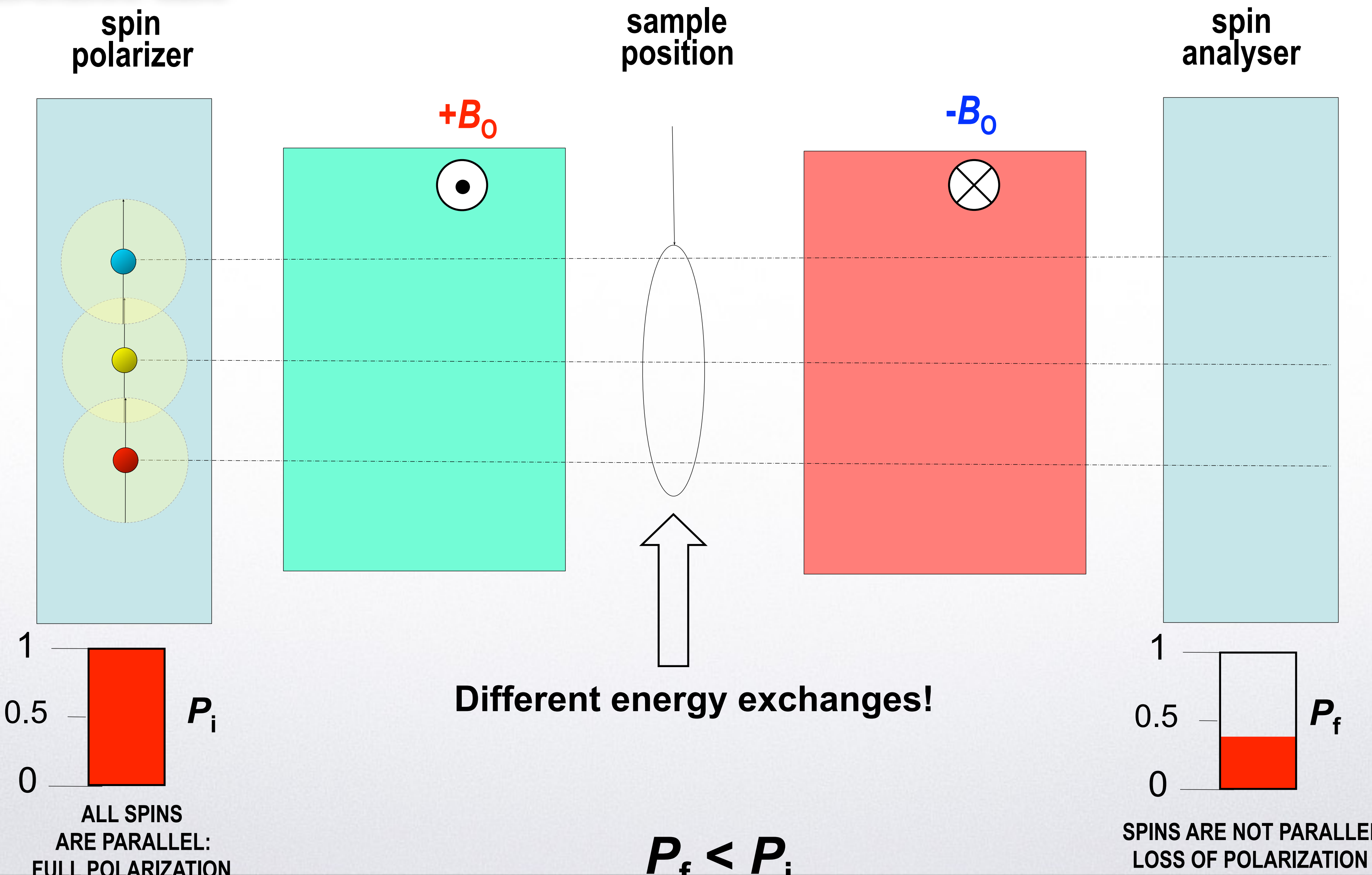
Courtesy: Orsolya Czakkel

How a NSE spectrometer is built up?



How a NSE spectrometer is built up?

Quasielastic case



$P_f < P_i$

'DECAYED ECHO'

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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.

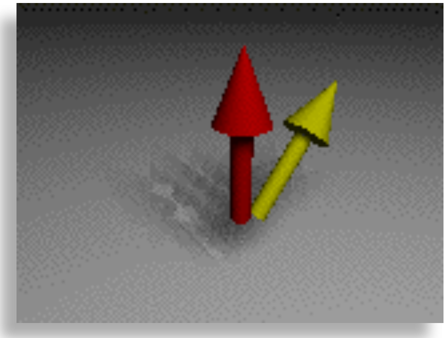
We start with the **classical equation of motion** for the **Larmor precession** of the neutron spin:

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

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 ⇒ 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 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:

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

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” φ=*t*ω and we will **calculate *t*** to first order by Taylor expansion.

Starting point is the energy transfer ω:

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

Taylor expansion to first order gives:

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

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:

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

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

The measurement principle of neutron spin echo spectroscopy
Classical Description

We consider the "fundamental equation" φ=*t*ω and we will **calculate *t*** to first order by Taylor expansion.

Starting point is the energy transfer ω:

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

Taylor expansion to first order gives:

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

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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,ω) 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,ω)***. 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 different is negligible, but this has to be kept in mind.

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The measurement principle of neutron spin echo spectroscopy
Example:

We consider a quasielastic **Lorentzian line**:

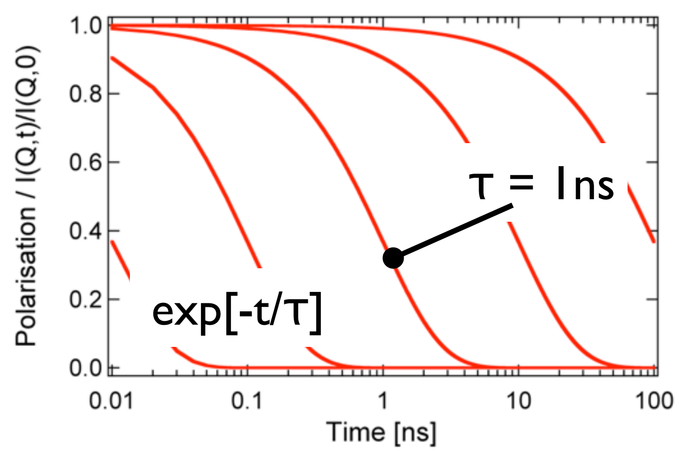
$$S(Q,\omega) \propto \frac{\Gamma}{\Gamma^2 + \omega^2}$$

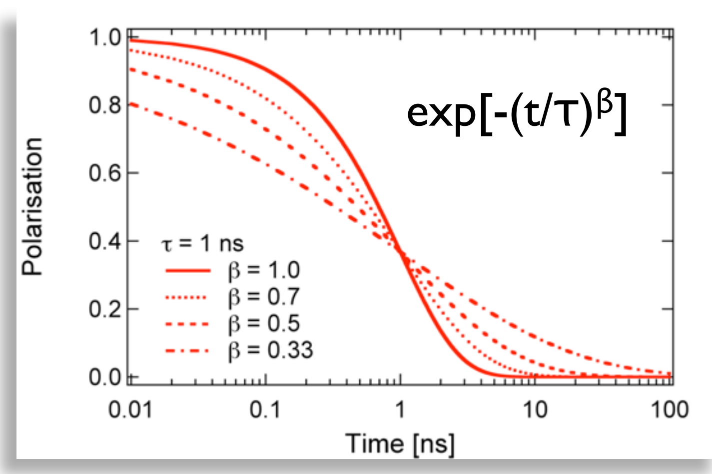
For a Lorentzian line, the **Fourier transform** is an **exponential decay function**:

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

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/τ)$^{\beta}$] (this is also called KWW Kohlrausch Williams Watt function).





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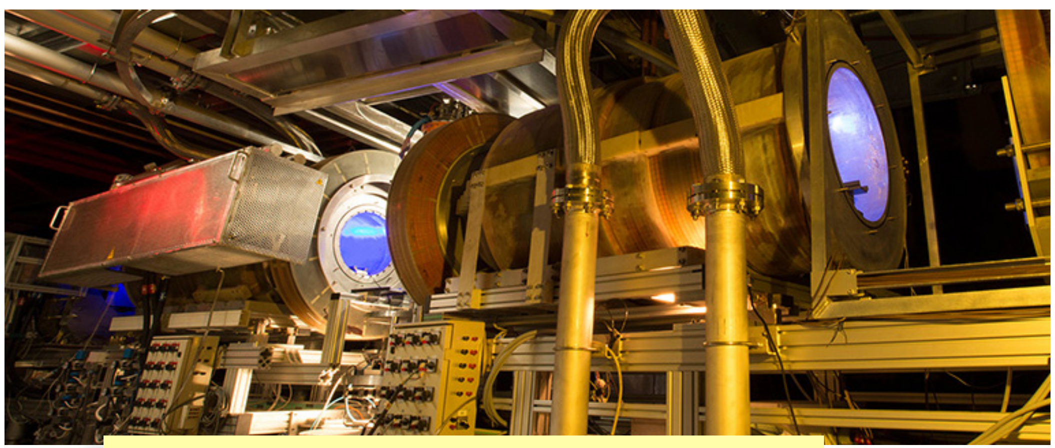
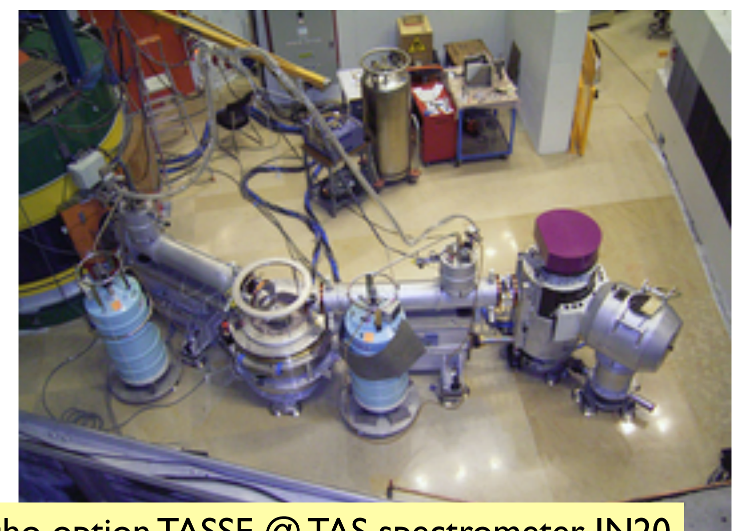
Spin Echo Spectrometers at ILL

Mezei's first spin echo
precession coils

Large angle NSE: IN11C for high signal



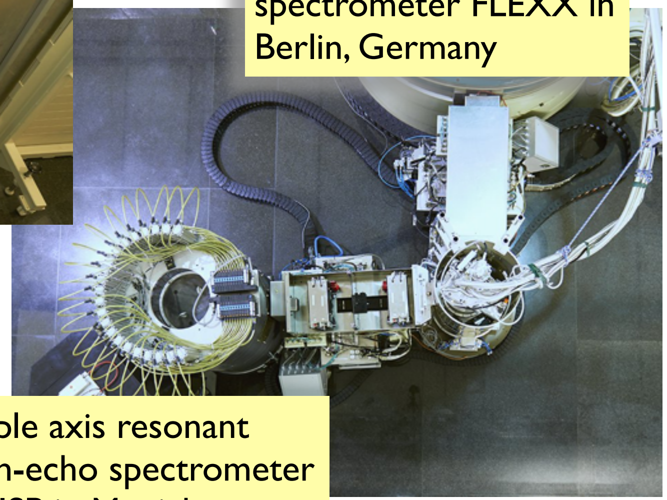
Today's IN15: measures up to 1 µs



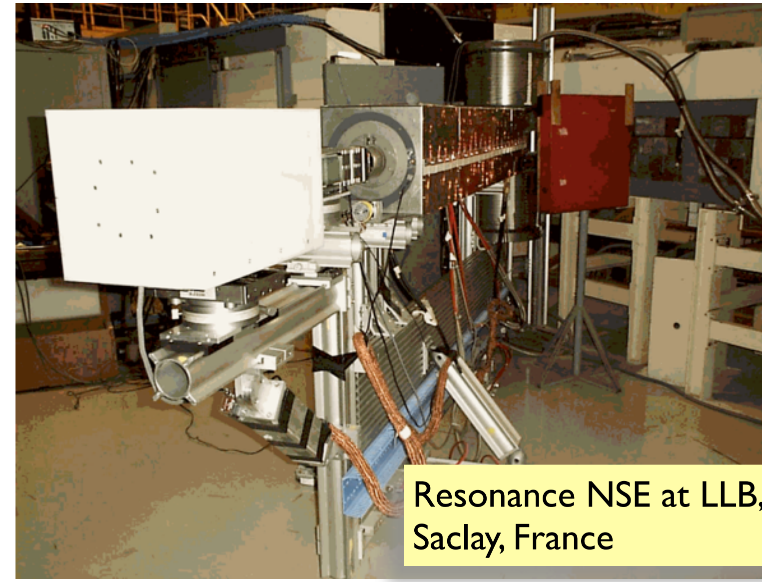
Spin-echo option TASSE @ TAS spectrometer IN20

Spin echo spectrometers in Europe


Resonant NSE RESEDA in Munich, Germany


RNSE option on TAS spectrometer FLEXX in Berlin, Germany

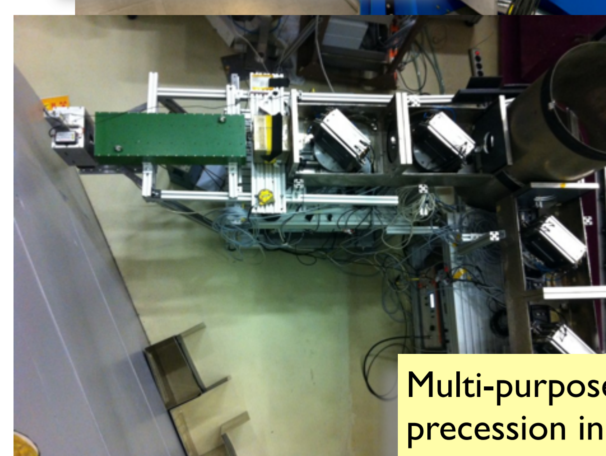
Triple axis resonant spin-echo spectrometer TRISP in Munich, Germany


Resonance NSE at LLB, Saclay, France


Spin-echo SANS with optional NSE OFFSEC at ISIS, UK

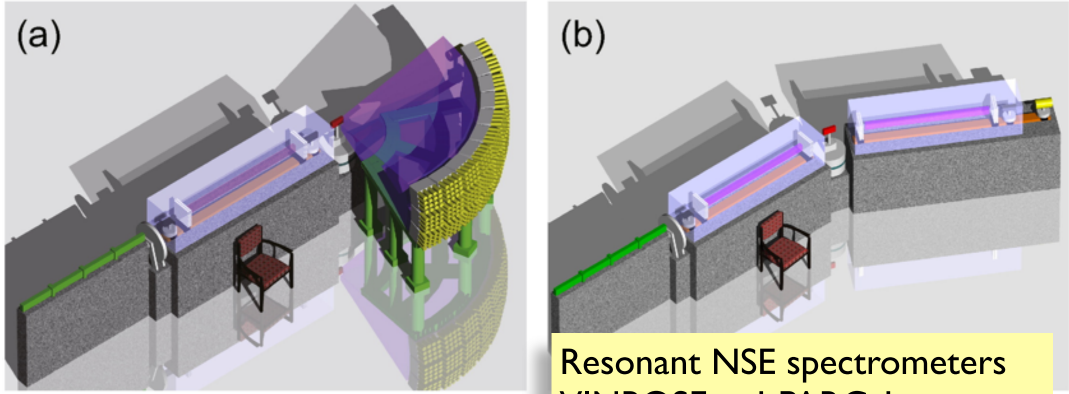

High resolution spectrometer J-NSE in Munich, Germany


two-/three-axis spectrometer with RNSE option MIRA in Munich, Germany

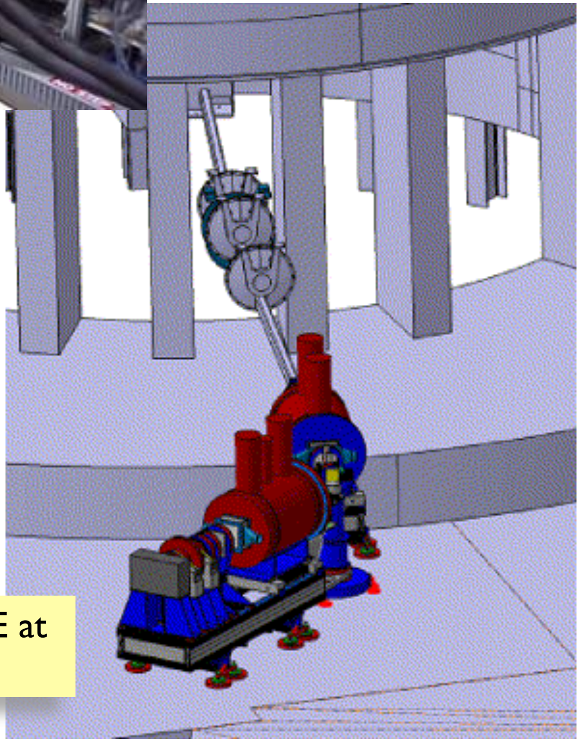

Multi-purpose spin precession instrument LARMOR at ISIS, UK

Spin echo spectrometers in the World

High resolution NSE at NIST, USA

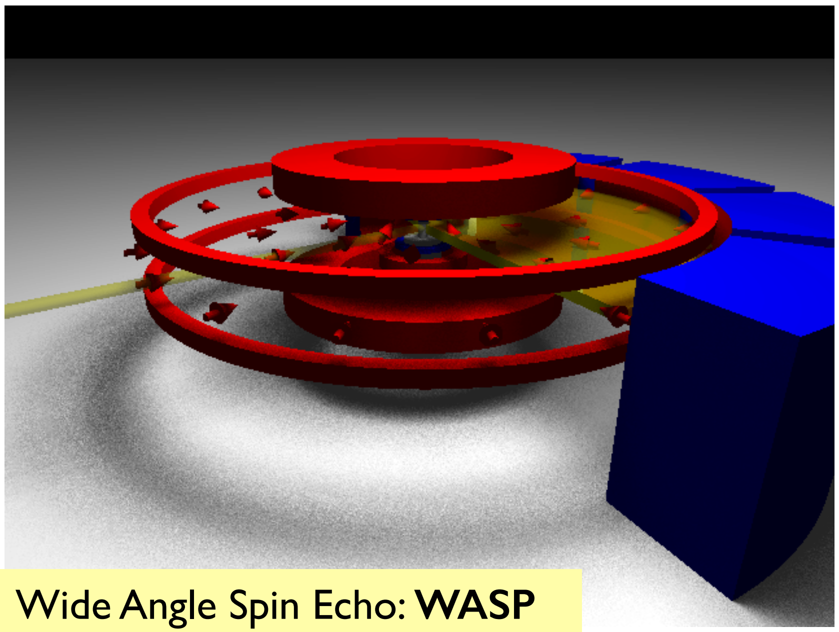


Resonant NSE spectrometers VINROSE at J-PARC, Japan

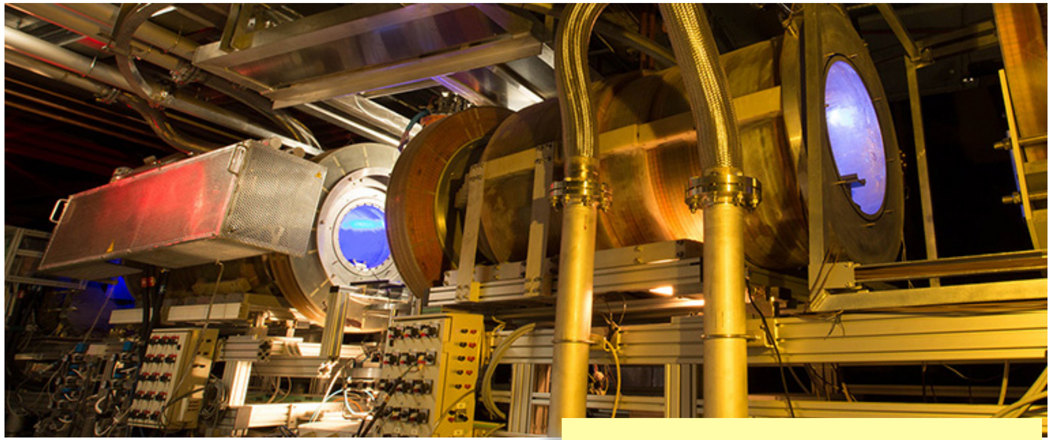


High resolution NSE at SNS, USA

Spin echo spectrometers around the world: Major trends in instrument development



Wide Angle Spin Echo: **WASP** (ILL, Millennium Programme)



Highest resolution spectrometer IN15 (ILL millennium update)

Large Signal/ High Q ⟷ High Resolution/ Small Q

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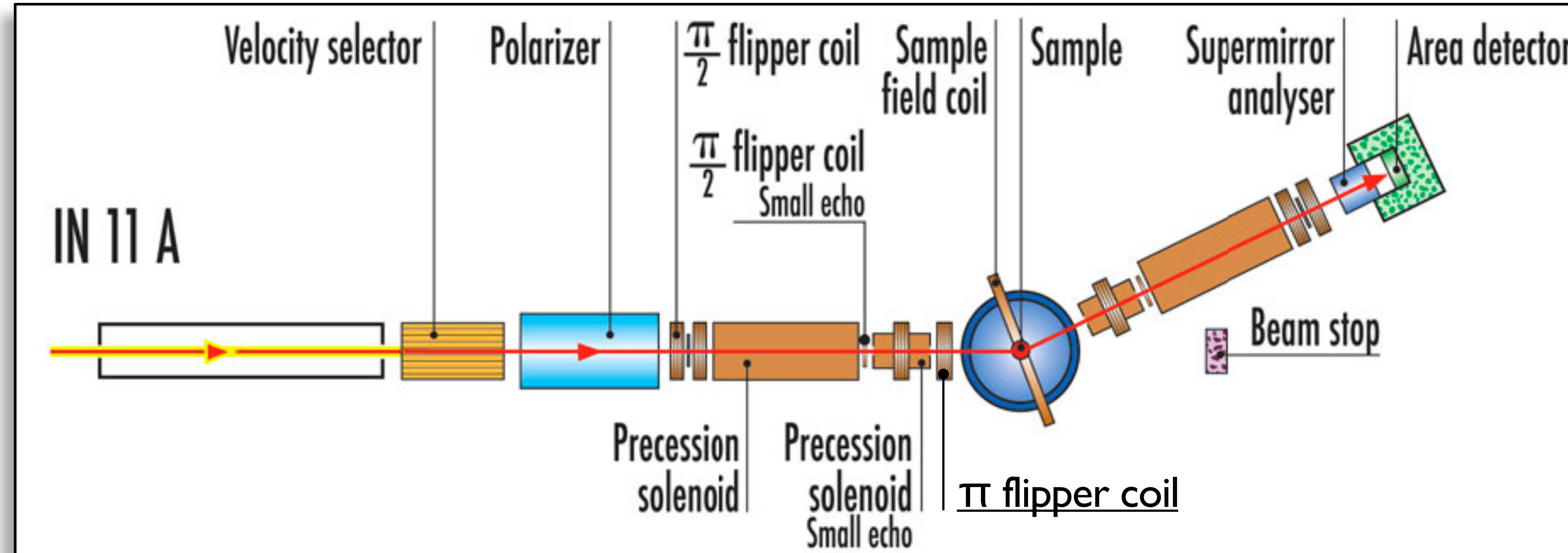
How a spin echo spectrometer works in practice



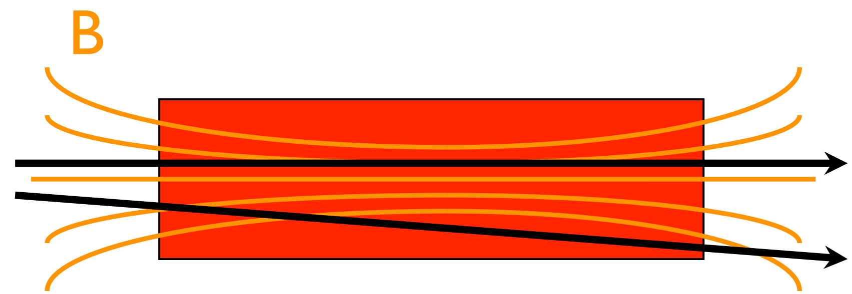
- The beam is monochromatised by a velocity selector to about dv/v = 15 %
- Spin polarization and analysis are performed by supermirrors
- Spin precession is started and stopped by π/2 (or 90°) spin flipper coils
- The fields B_{in} and B_{out} are parallel and, therefore, a 180° or π flipper coil is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

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

We consider again the precession angle:

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

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

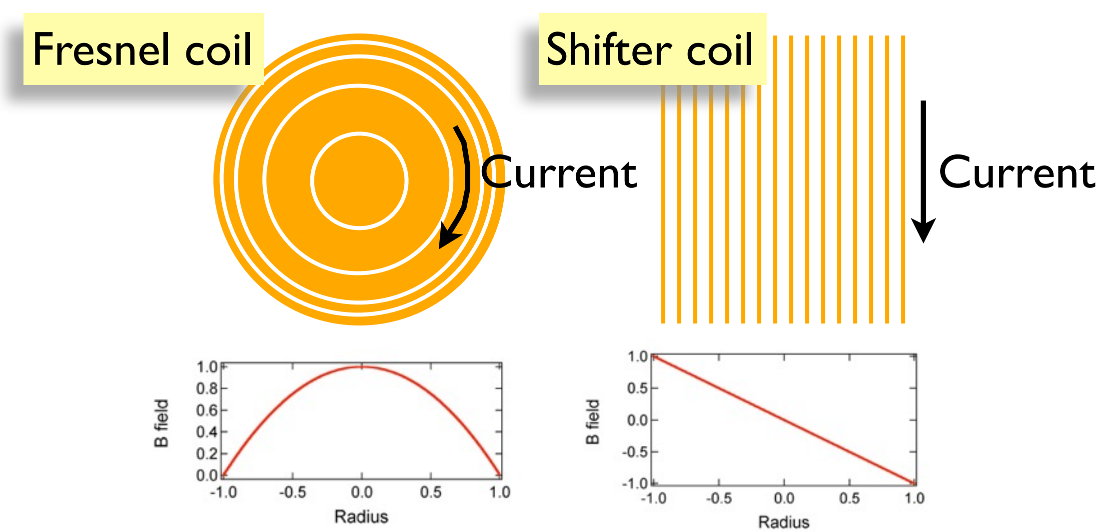


High number of precessions

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

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

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



quadratic

linear

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Discrimination methods for coherent, incoherent and magnetic dynamics

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 coil is not used.

The ratio of coherent/incoherent signal can be critical.

Type of scatterer	**Spin flip coils needed**	**Sample field**	**P_S**
Coherent and isotope-incoherent	π flipper	small	1
Spin-incoherent	π flipper	small	-1/3
Paramagnet	none	small	1/2
Ferromagnet	2 π/2 flippers	high	1/2
Antiferromagnet	none	small	1/2-1

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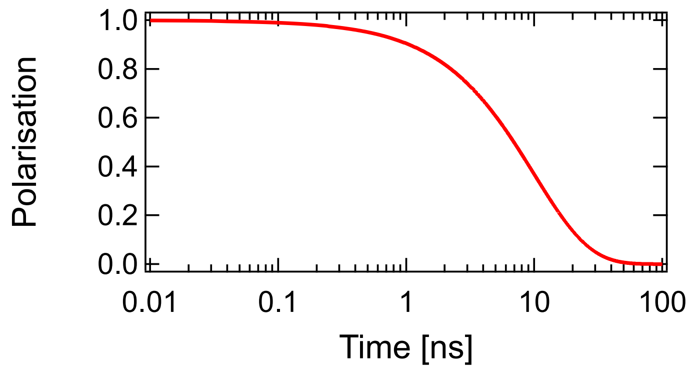
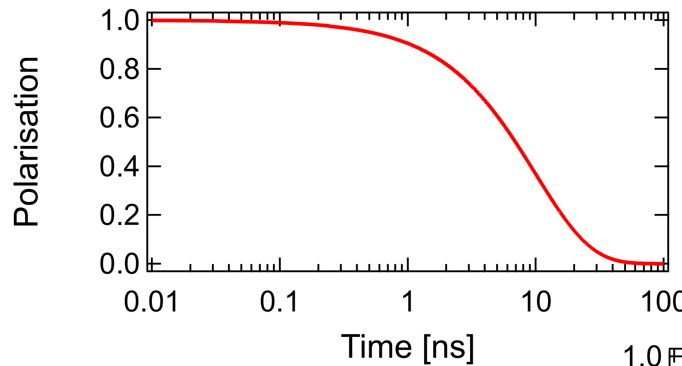
What happens if coherent and incoherent scattering co-exist

Coherent scattering: $P_S = 1$

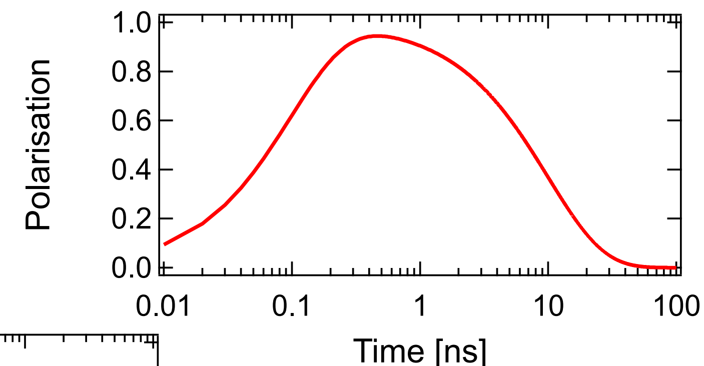
data



normalised

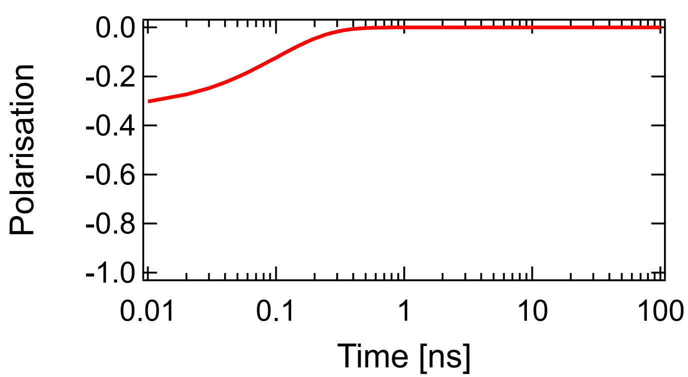


combined coherent and incoherent

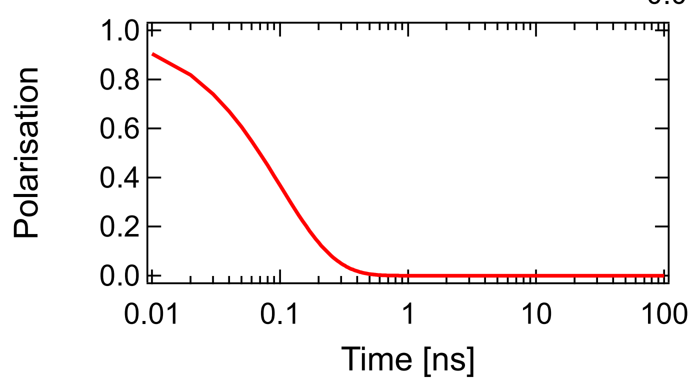


Incoherent scattering: $P_S = -1/3$

data



normalised



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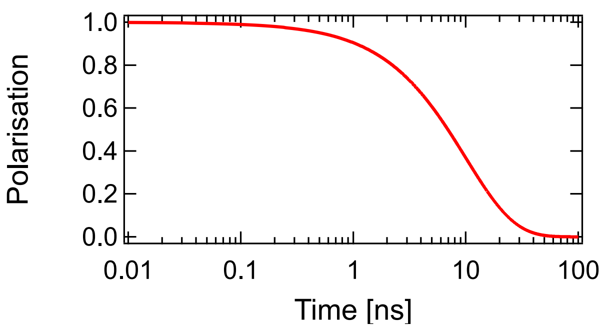
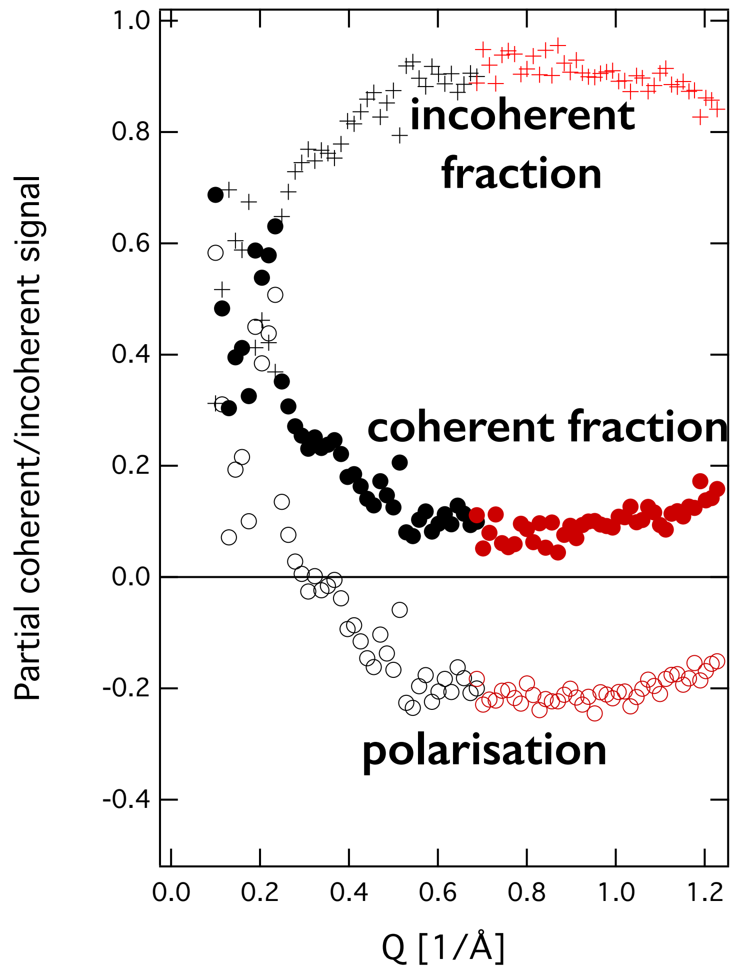
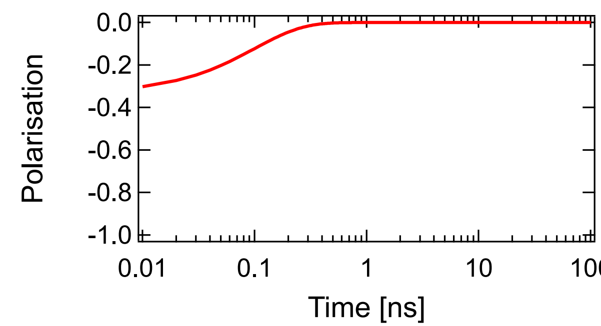
What happens if coherent and incoherent scattering co-exist

coherent scattering

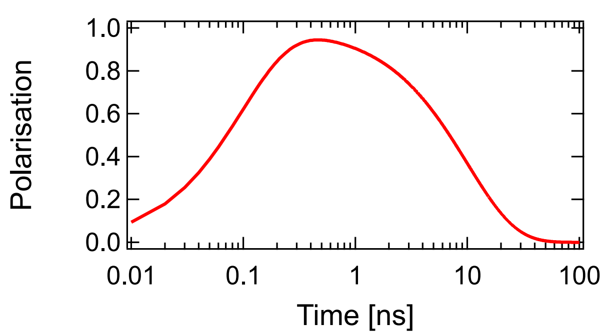




incoherent scattering



mixed signal



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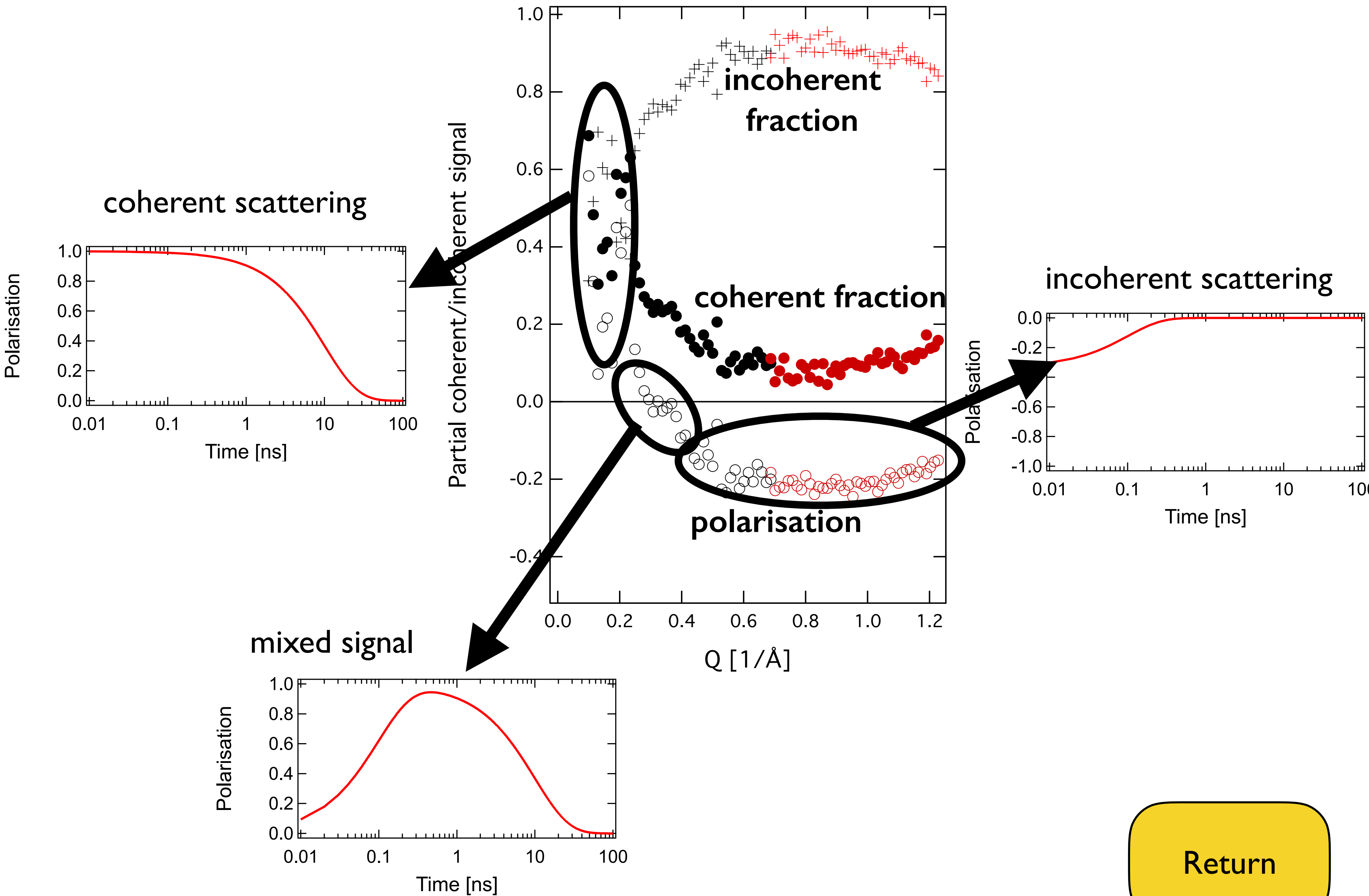
What happens if coherent and incoherent scattering co-exist



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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

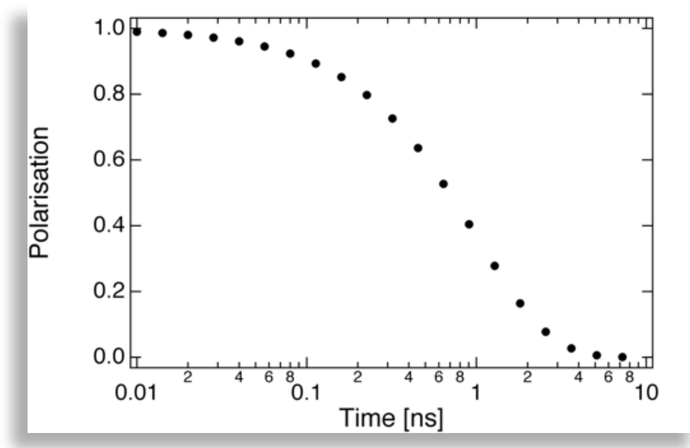
This gives us:

- average signal *A*, amplitude *I*, phase shift Δφ and frequency *f*

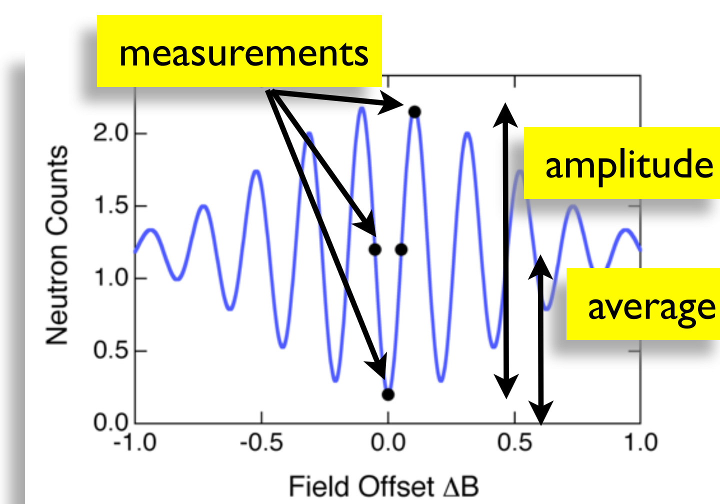
From these measurements we can extract:

- the polarization $P = I/A$

Typical NSE Spectrum



4-point measurement



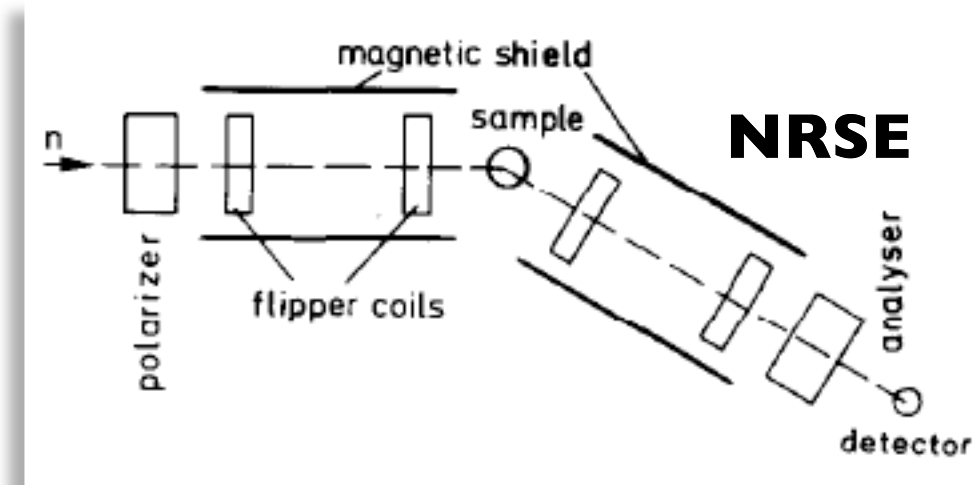
Neutron **Resonance** Spin Echo (NRSE)

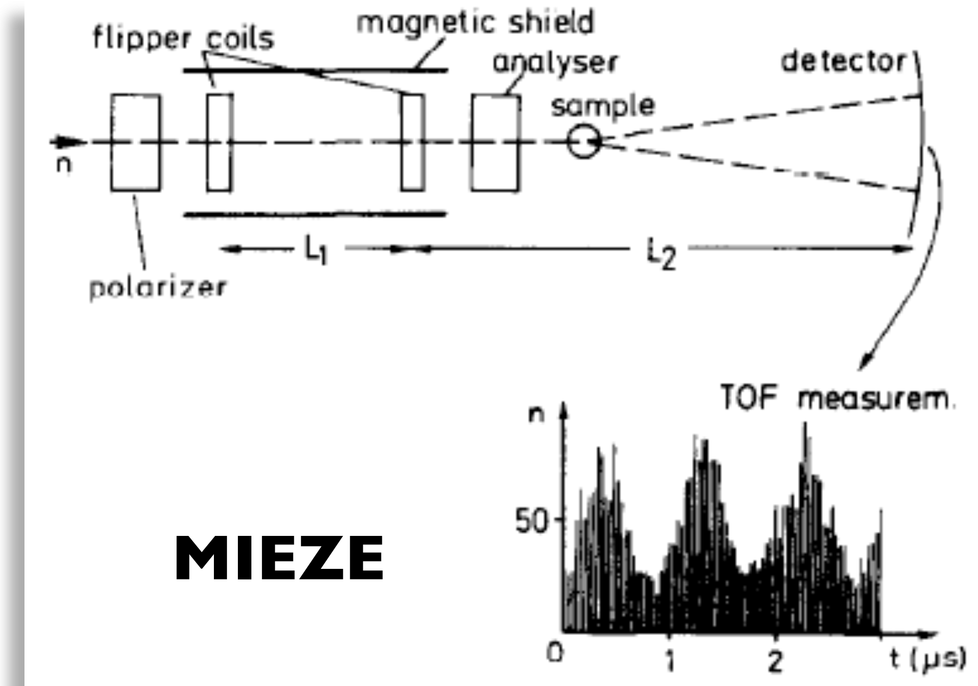
The principle of neutron resonance spin echo:

- 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)





R. Gähler et al., Physica B 180-181 (1992) 899

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Spin Echo Small Angle Neutron Scattering (SESANS)

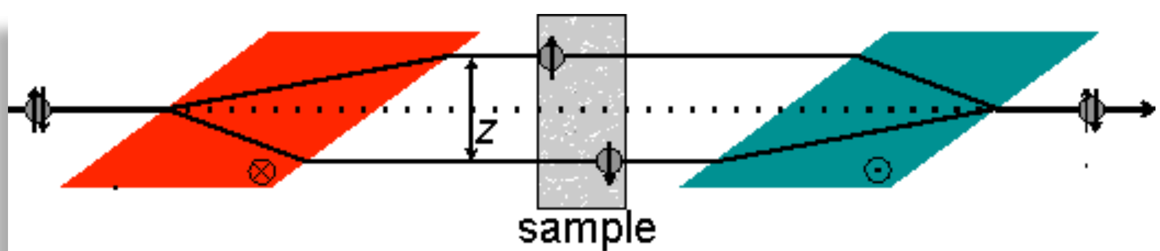
The aim of SESANS:

- Studying structure on very large scale

The basic principle:

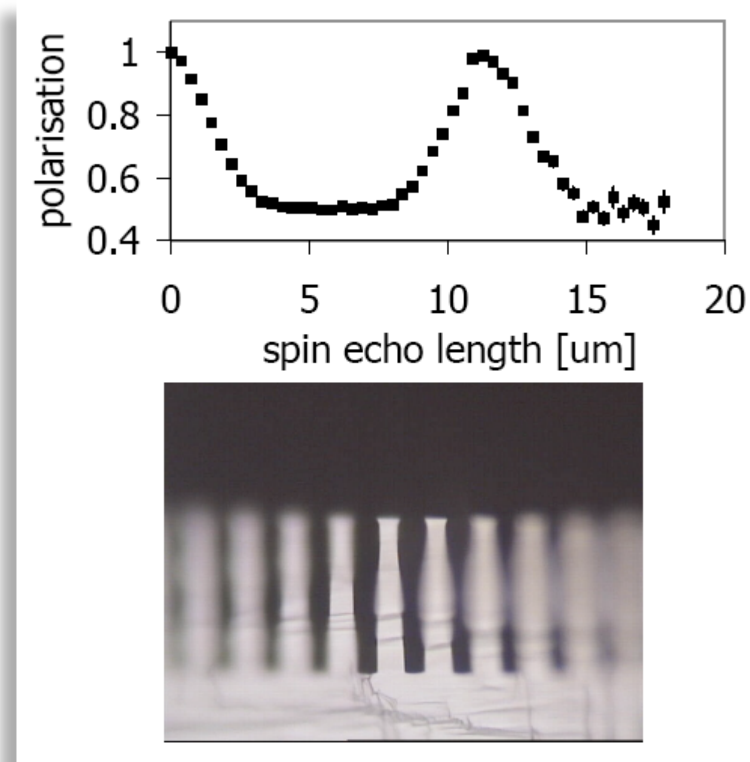
- Splitting neutron wave function *spatially* into two partial wave functions
- This is achieved by coils with inclined faces

SESANS Set-Up



W. Bouwman et al., TU Delft

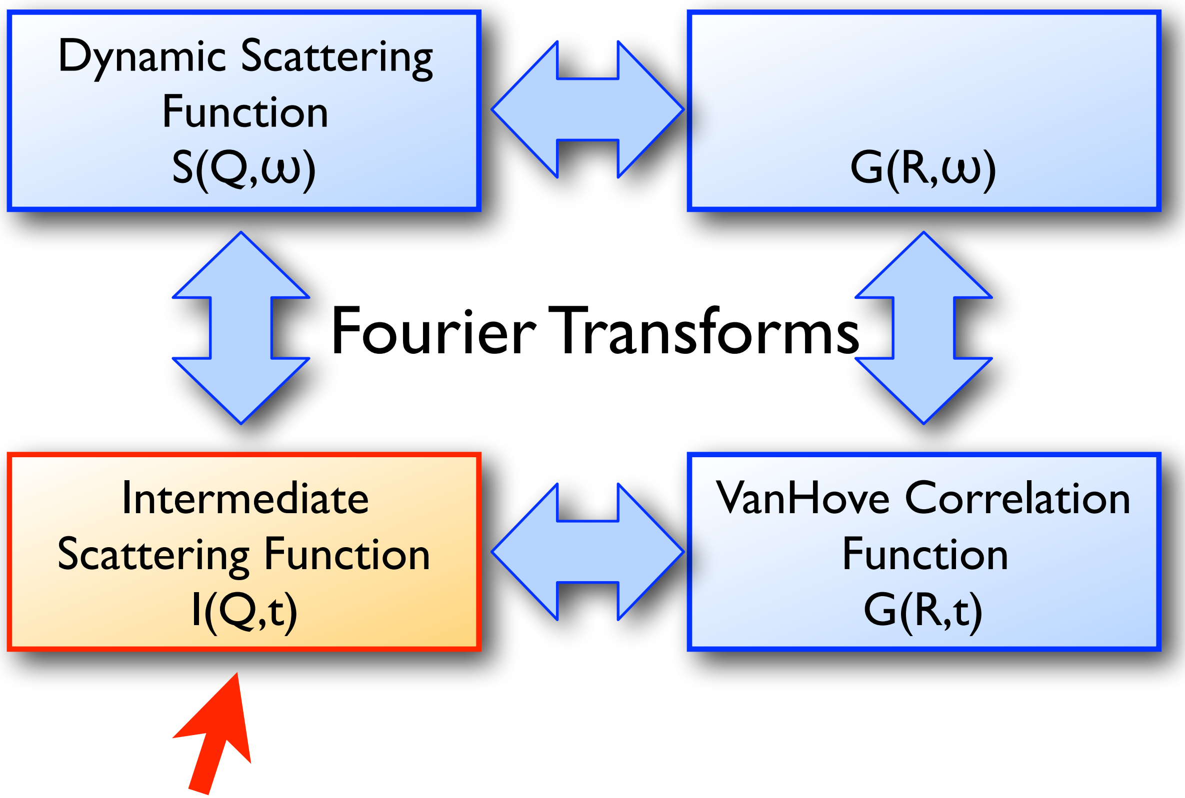
SESANS Example: Silicon Grating



M. Trinker et al. NIMA 579 (2007) 1081

How to do Science using NSE

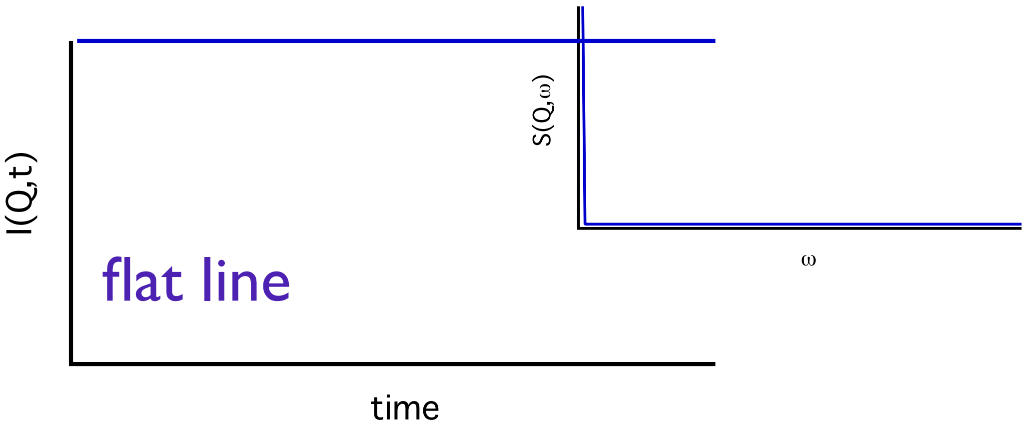
NSE measures I(Q,t), the intermediate scattering function



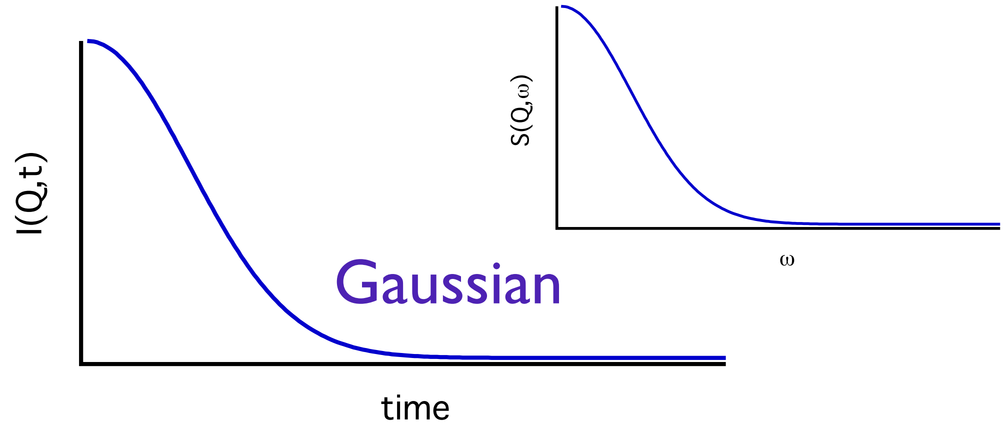
Measured with Neutron Spin Echo (NSE) Spectroscopy

The shape of the decay curve tells us already a story

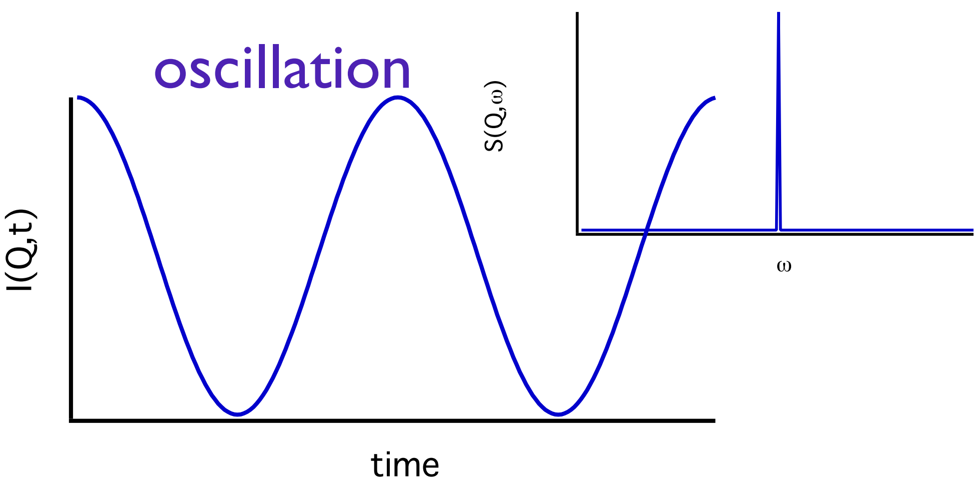
Static samples:



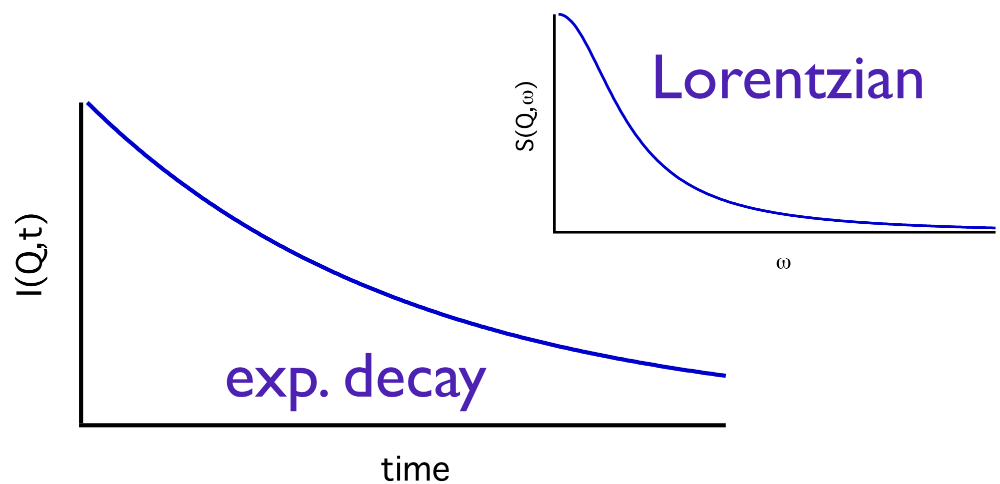
Ballistic motion:



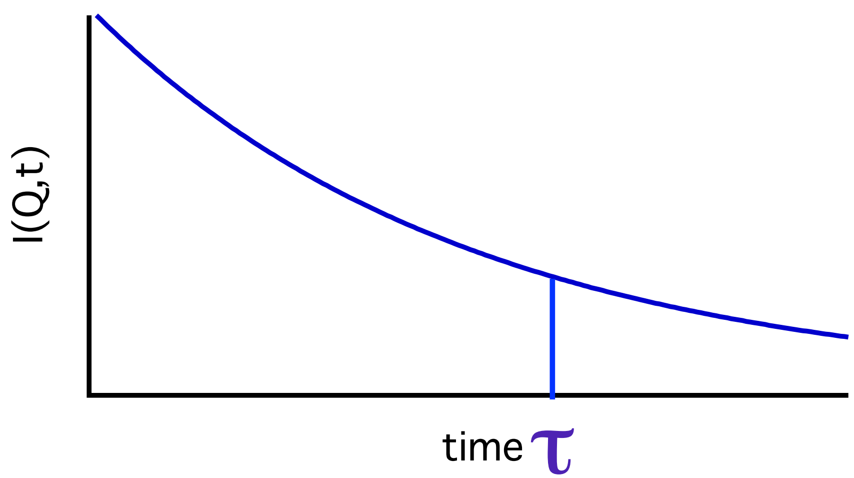
Vibrations:

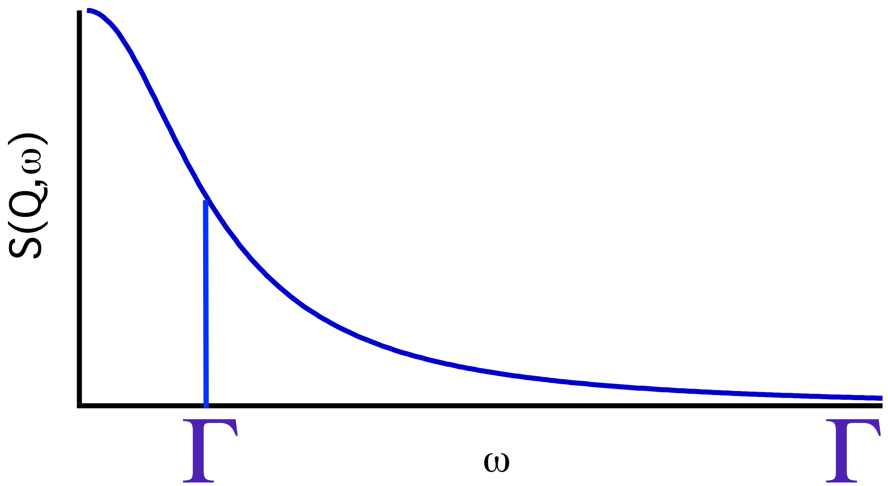


Diffusion:



The shape of the decay curve tells us already a story





$$\tau = h/\Gamma$$

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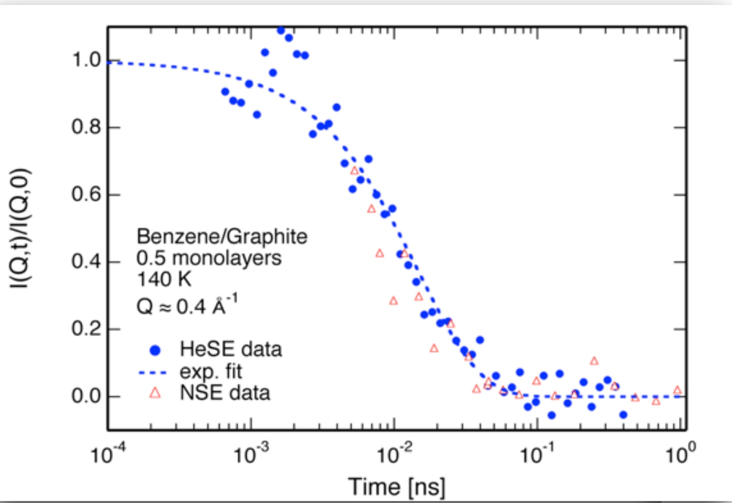
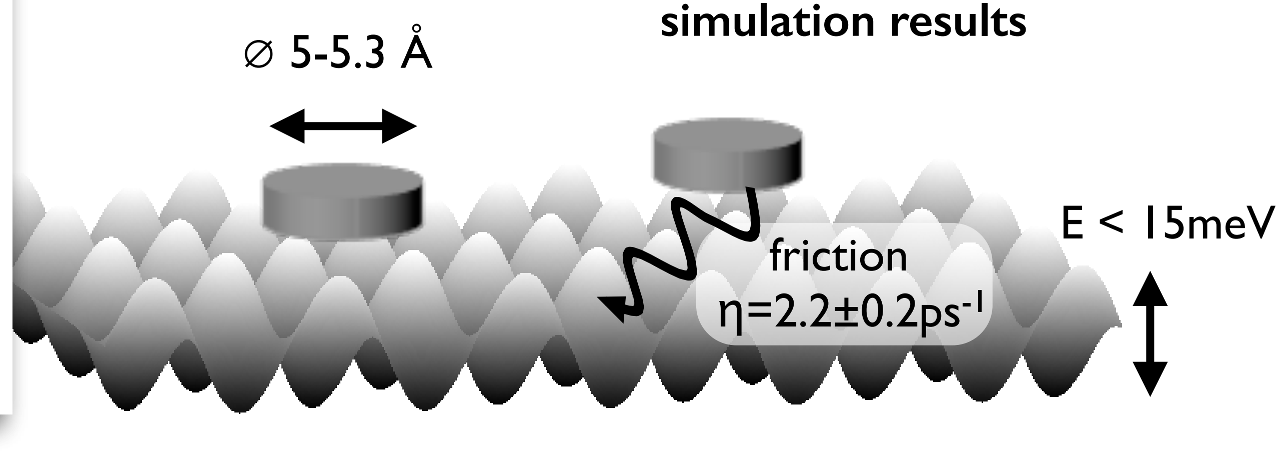
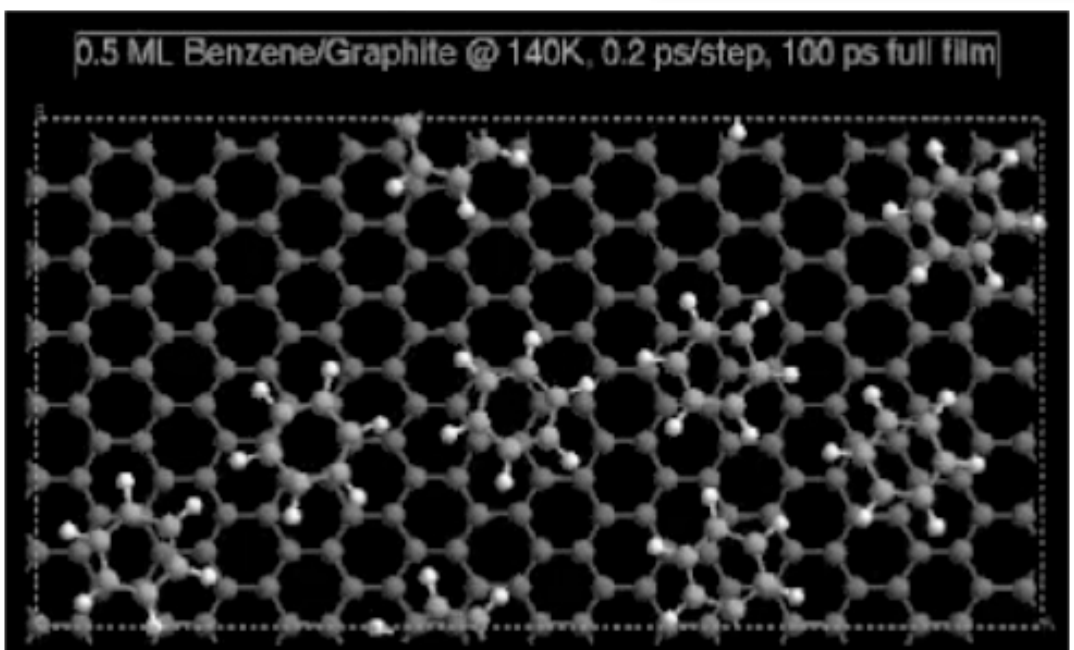
Science Examples

Aromatic molecules diffuse on graphite

H. Hedgeland, et al., Nature Phys. **5**, 561 (2009)
I. Calvo-Almazan, et al., Carbon **79**, 183 (2014)
I. Calvo-Almazan, et al., J. Chem. Phys. Lett. **7**, 5285 (2016)





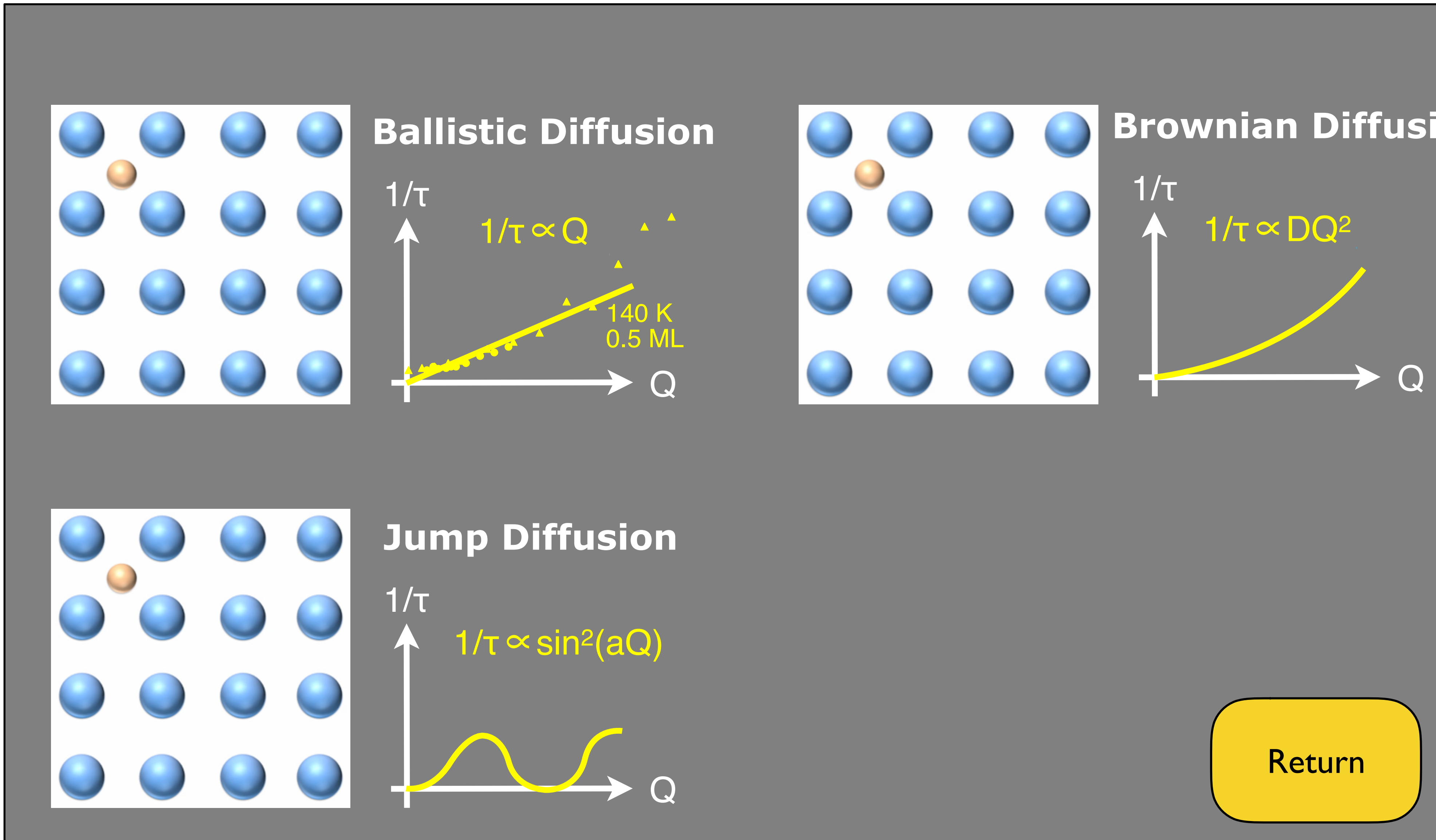


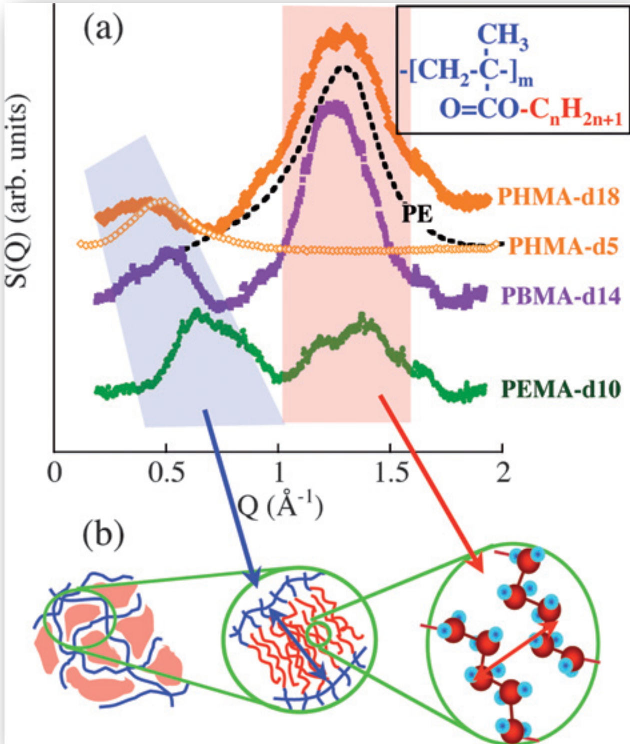
NSE - and its surface equivalent helium spin-echo - see “perfect” molecular Brownian diffusion.

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

Dynamic friction can be determined.

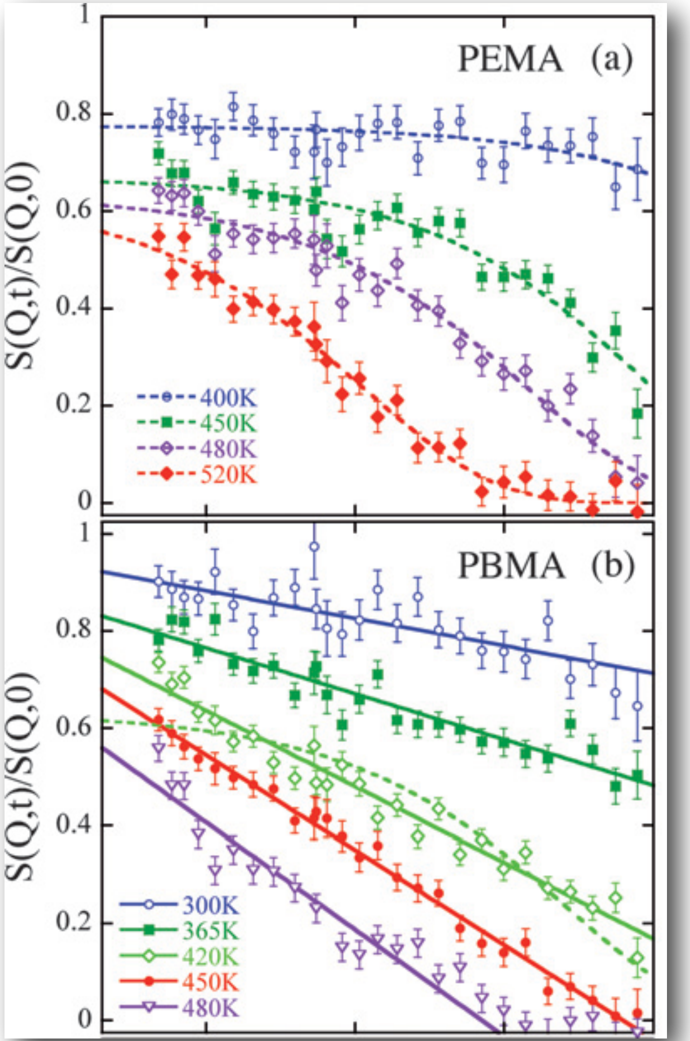
We can exploit the Q dependence of tau or Gamma





Science Examples

Dynamics of Polymers - Length Scales



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**

A. Arbe *et al.*, Soft Matter 4, 1792 (2008)

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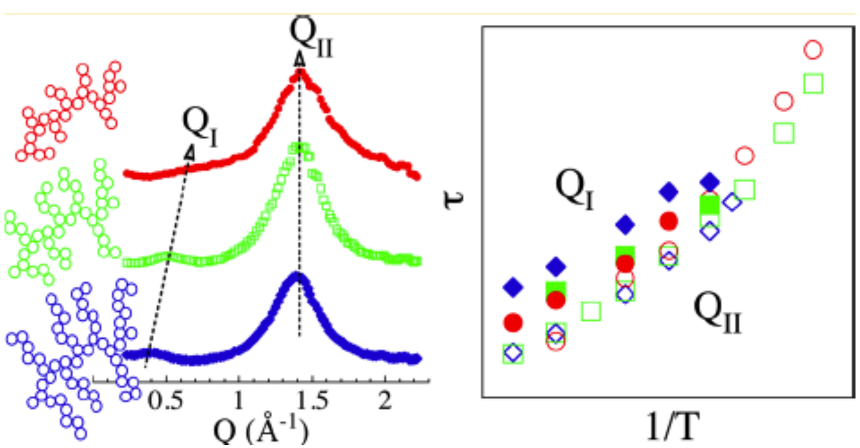
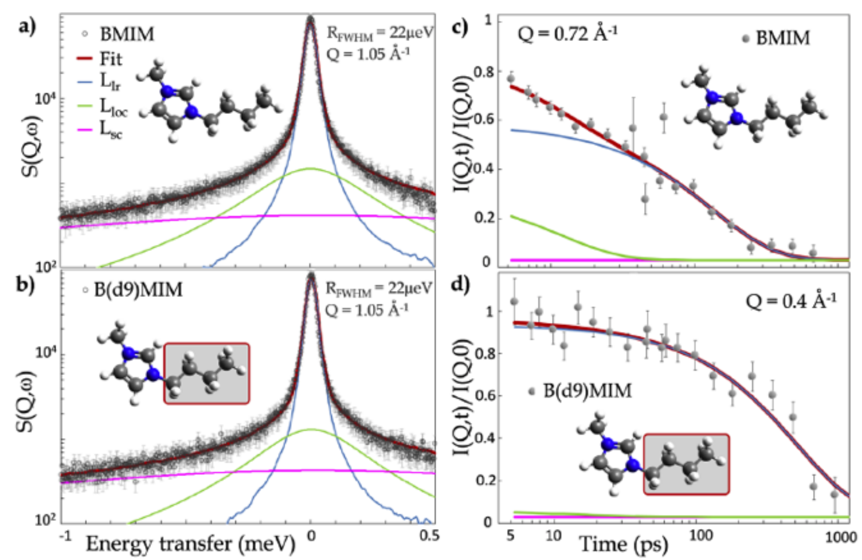
Science Examples

Dynamic differences of asymmetric comb-like polymers disappear at high T
A. Arbe et al.,
Macromolecules **49**, 4989 (2016)



Evidence for the scale-dependence of the viscosity of ionic liquids
Q. Berrod et al.,
Scientific Reports **7**, 2241 (2017)



Science Examples

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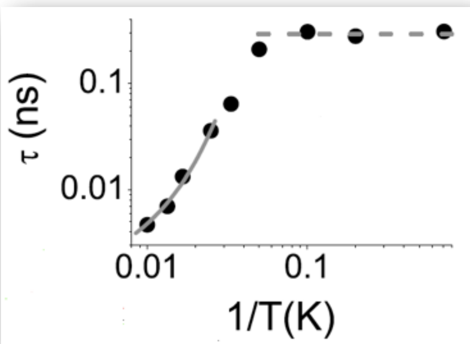
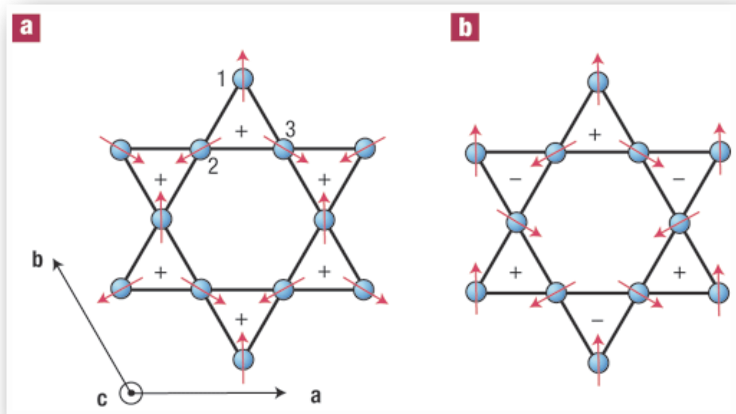
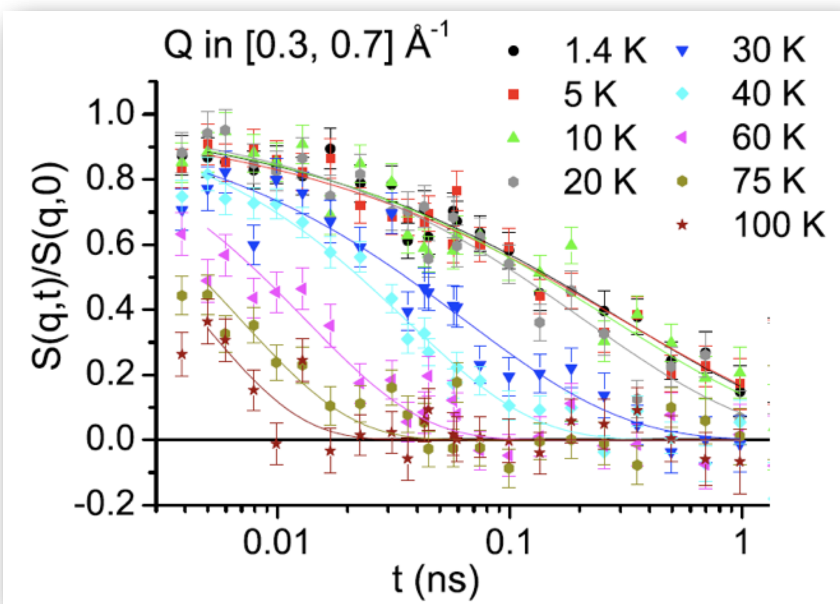
Dynamics of **Frustrated Magnets:** Nd langasite

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





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



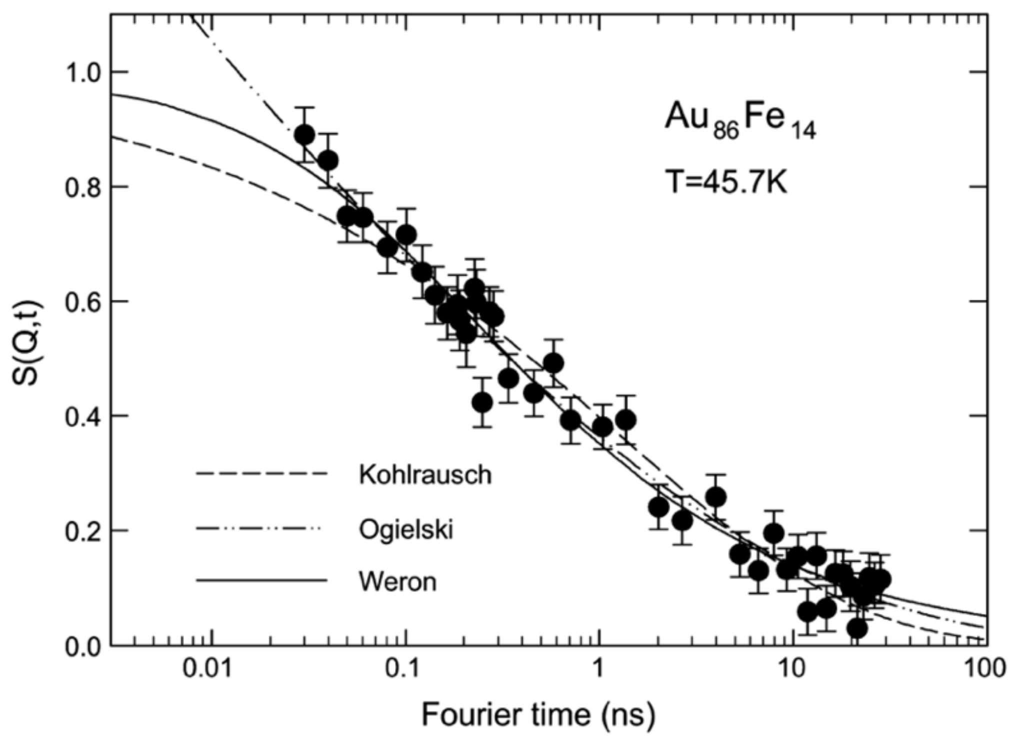
NSE is **strong in magnetism research** as it can distinguish between magnetic and non-magnetic dynamics.

$Nd_3Ga_5SiO_{14}$ 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.

Science Examples

Return



Cywinski, Pappas et al. PRL **102**, 097202 (2009)

Determination of line shape of relaxation

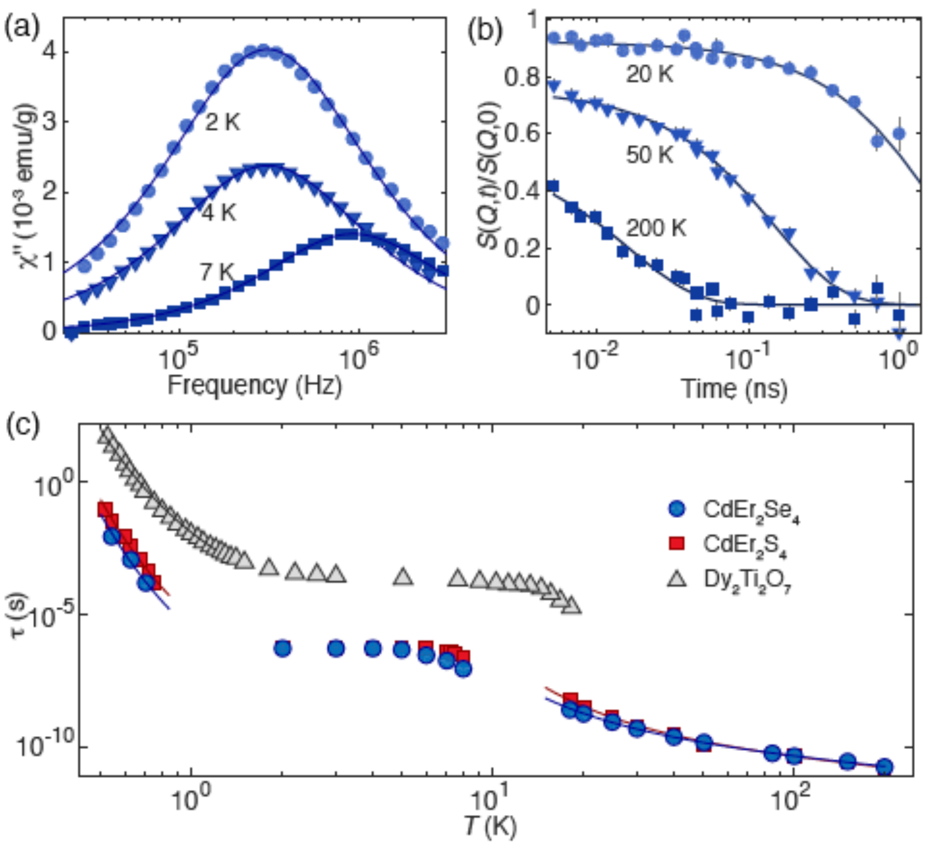
Limited by **statistics** and **spectroscopic range**

Science Examples

Return

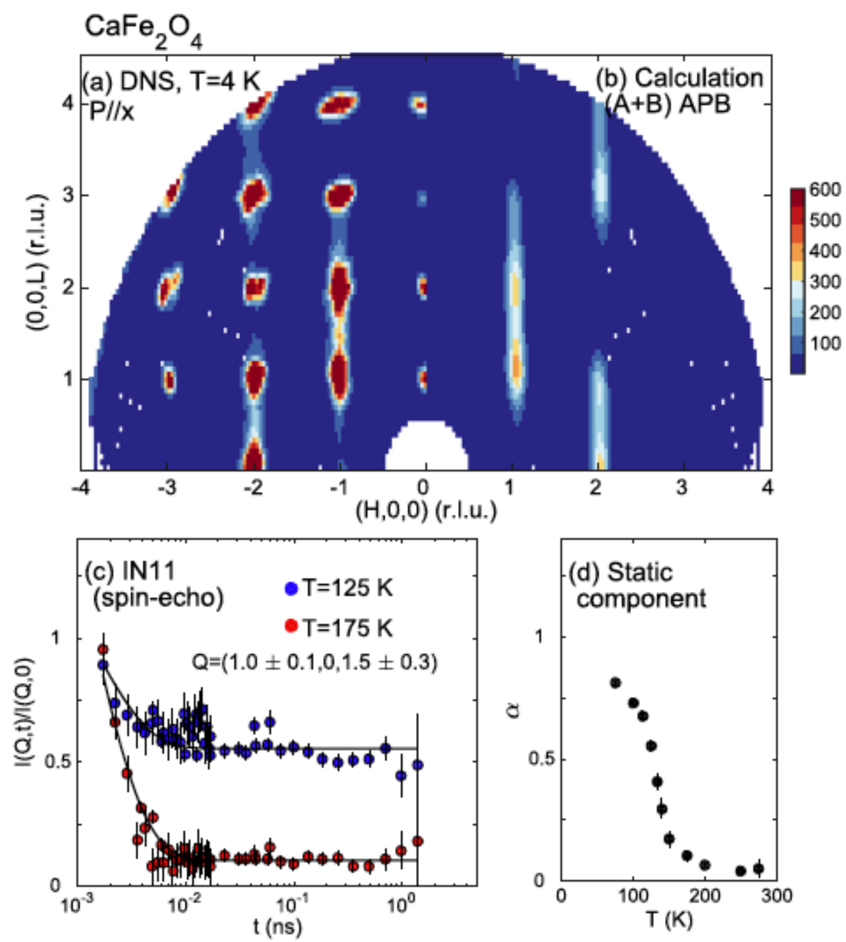
Dipolar spin ice states with fast monopole hopping rate in $CdEr_2X_4$ (X = Se, S)

S. Gao et al.,
PRL submitted



Solitary Magnons in CaFe2O4

C. Stock et al.,
PRL **117**, 017201 (2016)



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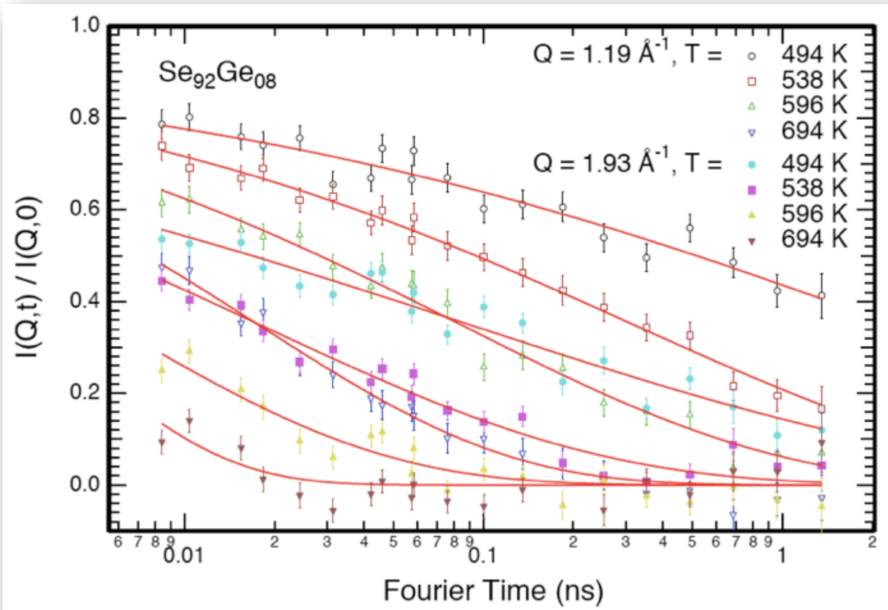
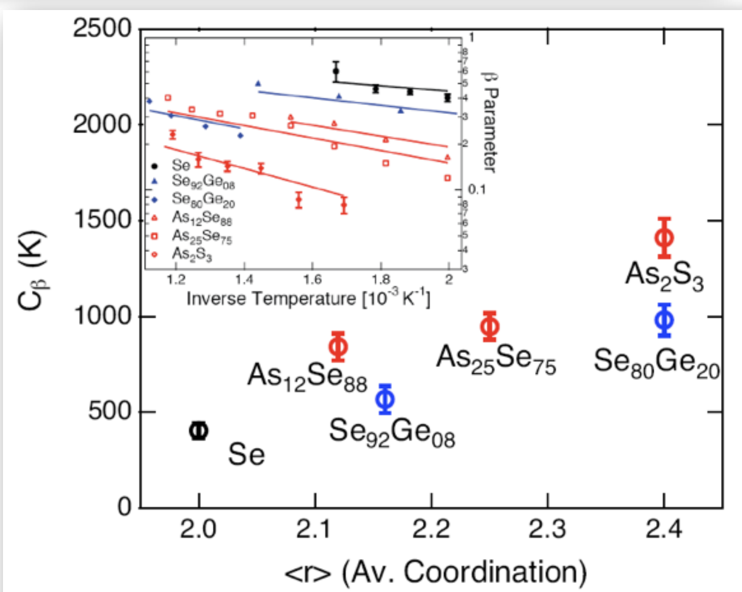
Science Examples

Dynamics of **Glasses**





$Ge_xAs_ySe_{1-x-y}$ alloy is a network glass

Normal liquid 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 co-ordination number <r>**:

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

J. Bermejo *et al.*, Phys. Rev. Lett. 100, 245902 (2008)

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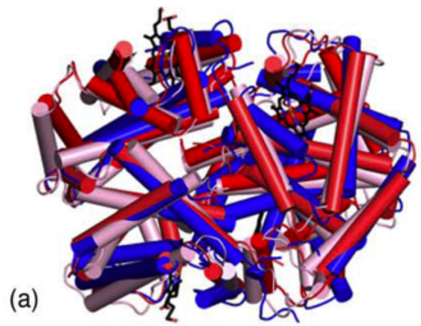
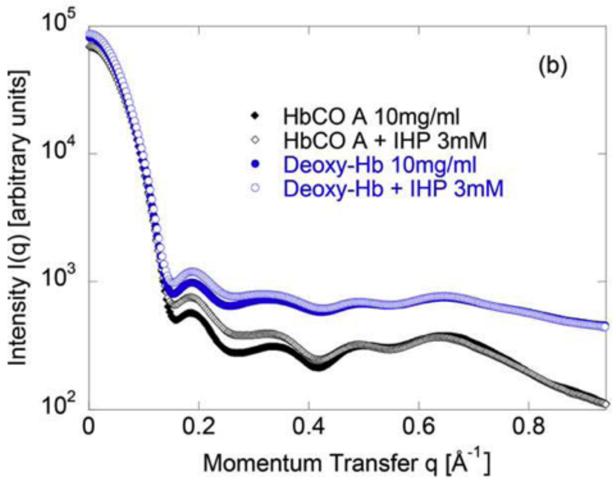
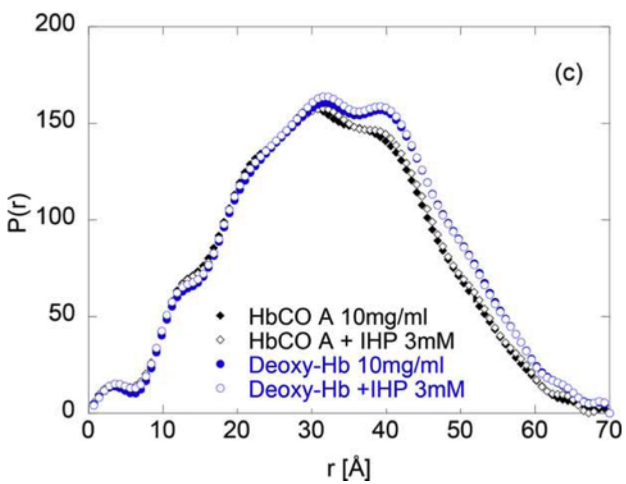
Science Examples

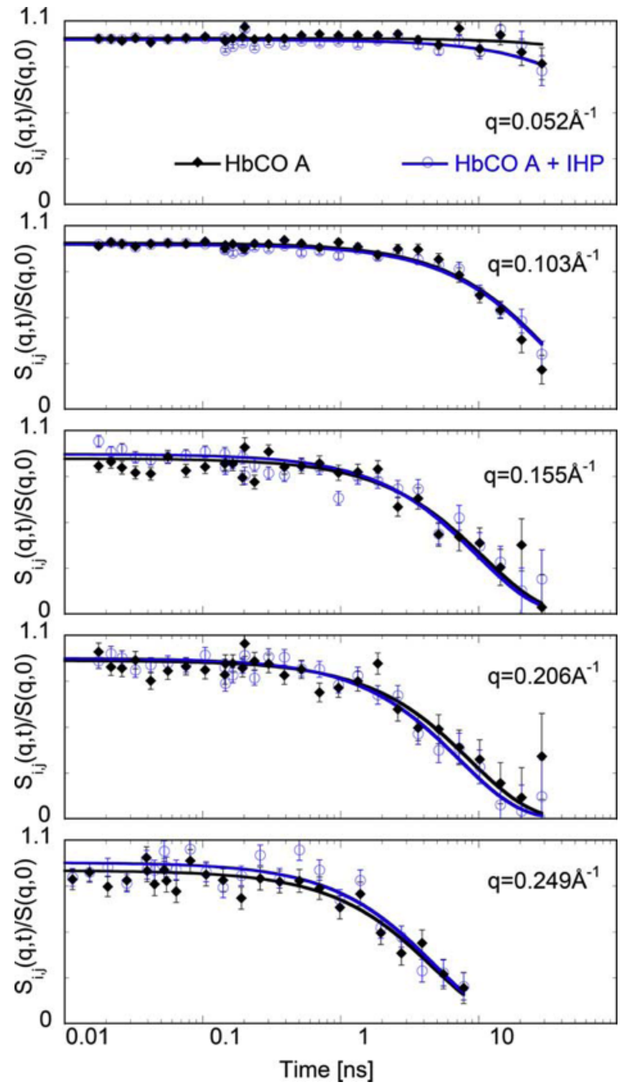
Dynamics of Biomolecules: Hemoglobin

J. Lal et al. Protein Science **26**, 505-514 (2017)

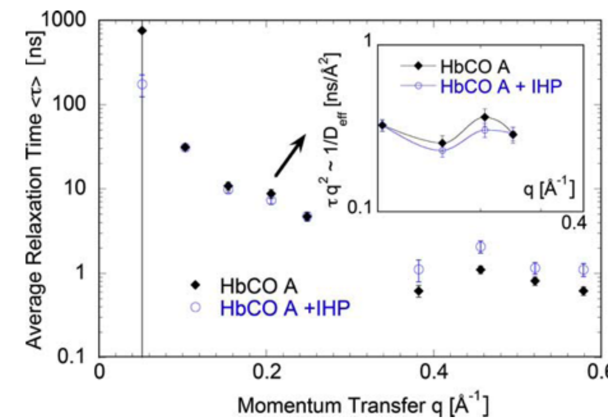








- Change of hemoglobin dynamics by an allosteric affector molecule
- Hemoglobin structure is different when IHP is attached (true for empty and CO-filled)
- Small dynamic changes are observed by NSE



Strengths and Weaknesses of Neutron Spin Echo

Strong Points

1. Highest energy resolution of all neutron scattering techniques
2. Large dynamic range
3. Relaxation is measured directly as function of time
4. Coherent, Incoherent and magnetic scattering can be discriminated
5. Sample signal high due to weak monochromatisation of incoming neutrons

Weak Points

1. Signal is often weak, because detector solid angles are, *generally*, small
2. Q resolution is, *generally*, not very high if velocity selector is used
3. Standard NSE spectrometers are sensitive to magnetic field environment
4. Incoherent scattering can lead to very bad signal-to-noise ratio

Literature

Ferenc Mezei (Ed.):
Neutron Spin-Echo, Lecture Notes in Physics **128**, Springer, Heidelberg, 1980.

Stephen Lovesey:
Theory of Neutron Scattering from Condensed Matter, Vol. 2, Clarendon Press, Oxford, 1986.

Marc Bee:
Quasielastic Neutron Scattering, Hilger, Bristol, 1988.

F. Mezei, C. Pappas, T. Gutberlet (Eds.):
Neutron Spin-Echo Spectroscopy (2nd workshop), Lecture Notes in Physics **601**, Springer, Heidelberg, 2003.

D. Richter, M. Monkenbusch, A. Arbe, J. Colmenero:
Neutron Spin Echo in Polymer Systems, Advances in Polymer Science **174**, Springer, Heidelberg, 2005.