Introduction to Neutron Spin Echo Spectroscopy

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and

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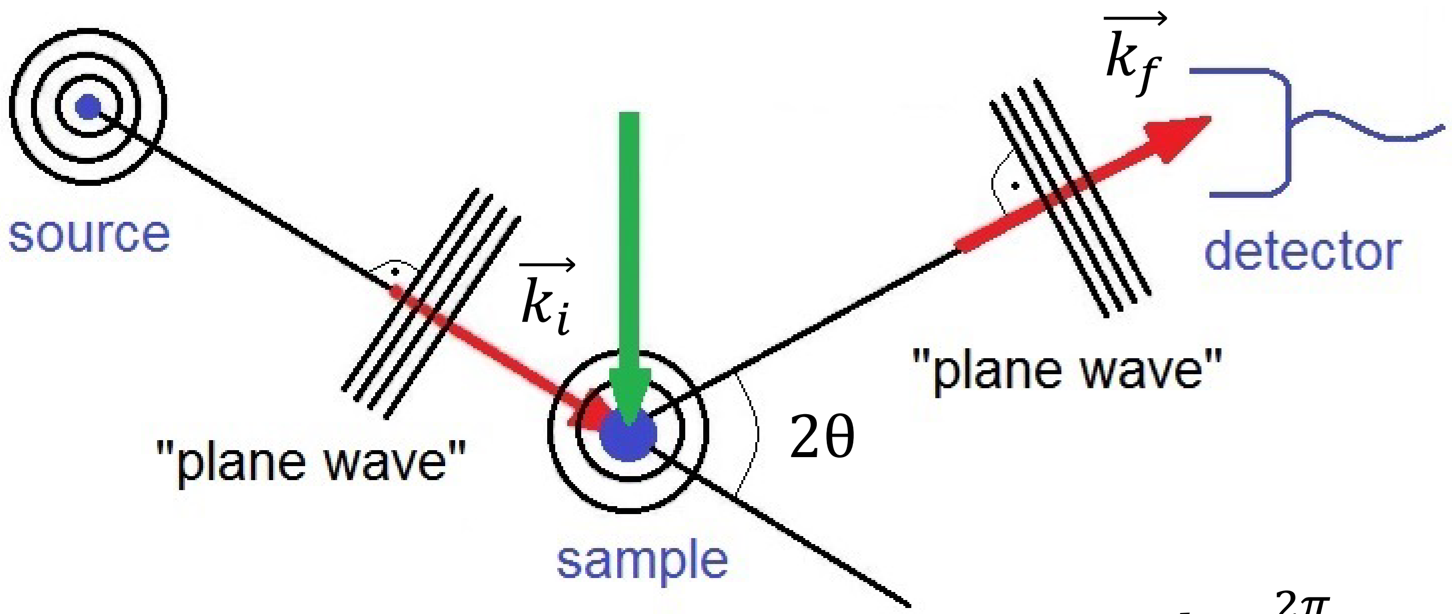
ORNL is managed by UT-Battelle, LLC for the US Department of Energy

This research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory.

1. The neutron scattering event

(in the Fraunhofer approximation)

$$\vec{Q} = \overrightarrow{k_i} - \overrightarrow{k_f}$$



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

$$\vec{Q} = \overrightarrow{k_i} - \overrightarrow{k_f} \qquad = \text{momentum transfer}$$

$$\Delta E = E_\mathrm{i} - E_\mathrm{f} = \hbar\omega = \text{energy transfer}$$

$$E = \frac{(\hbar k)^2}{2m_n}$$ neutron energy

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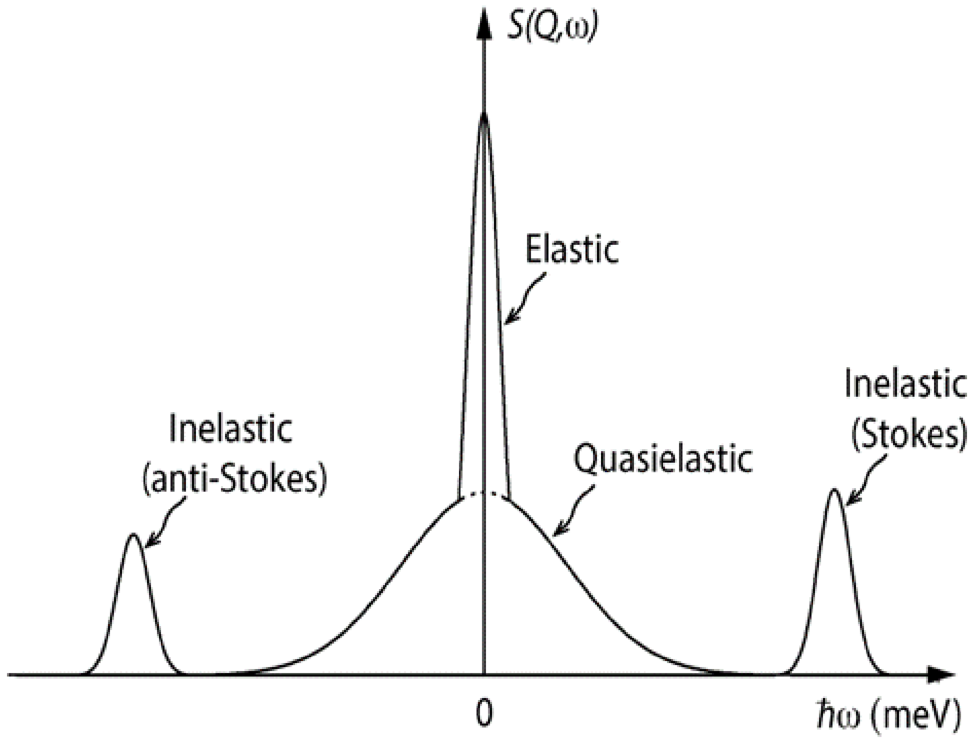
[FZJ-2015-04876] Open Access Book, Brückel, T. ; Richter, D. ; Roth, G. ; et al, Laboratory Course Neutron Scattering: Lectures

2. QENS: quasielastic neutron scattering

A limiting case of inelastic scattering, centered at ω = 0 characterized by small energy transfers

Energy spectra = structural and dynamical information
S(Q, ω) = dynamic structure factor



$\omega < 0\ (gain)$ $\omega = 0$ $\omega > 0 (loss)$

$$\Delta E = E_{\rm i} - E_{\rm f}$$

$$\Delta E \ll E_{\rm i}$$

- ❑ elastic peak
- ❑ quasielastic line
- ❑ inelastic peaks

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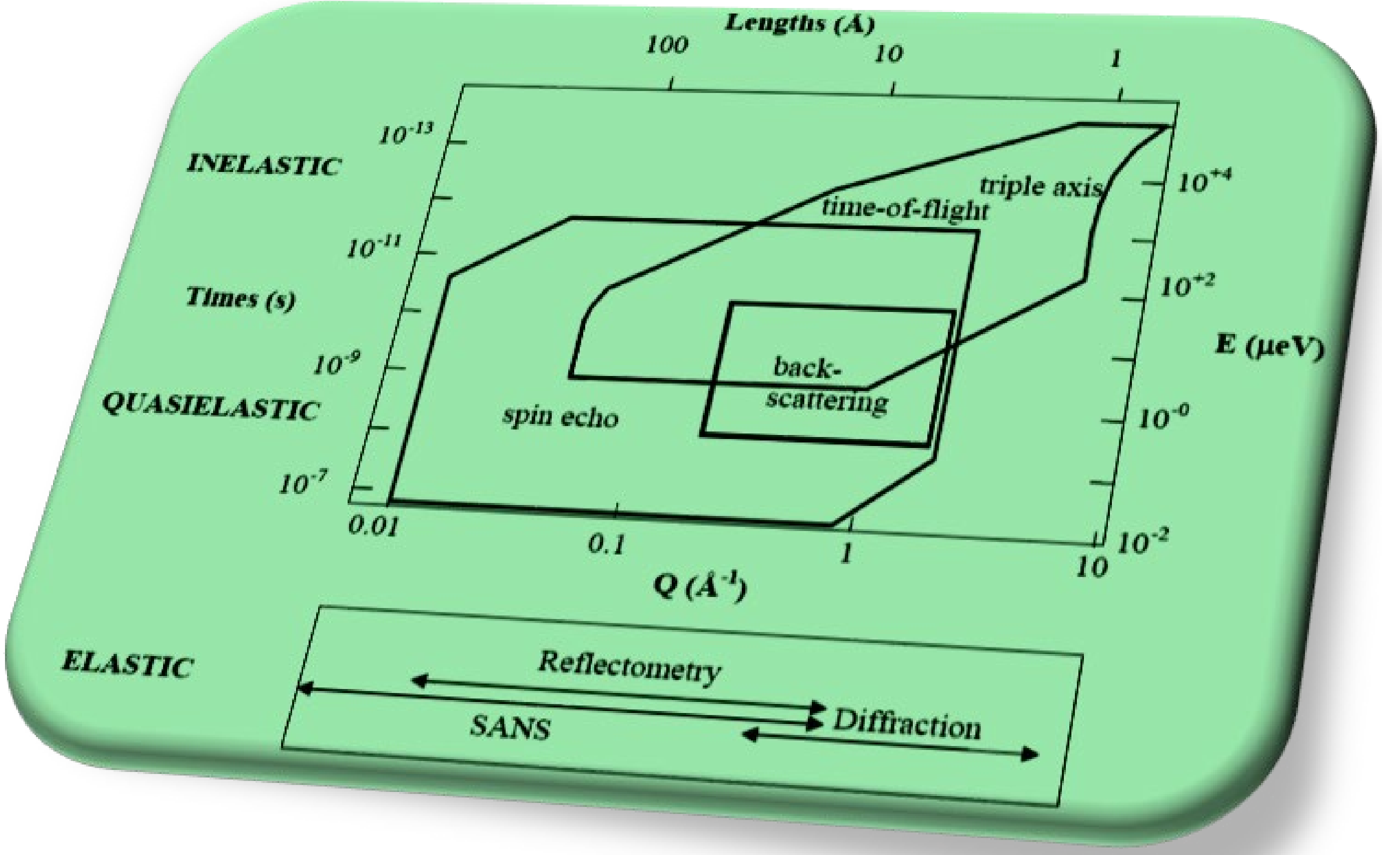
DOI: 10.1039/C4CP04112G (Perspective) Phys. Chem. Chem. Phys., 2015, 17, 26-38

3. Neutron spectroscopy landscape

(methods to measure dynamics)



XTL, TOF, XTL-TOF, TOF-TOF, **XTL-XTL**, **TOF-XTL, NSE**

1meV ~ 8cm^{-1} ~ 1ps

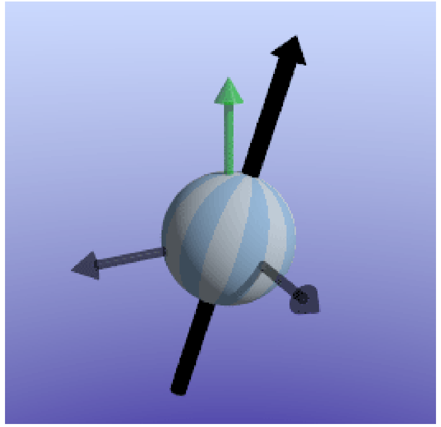
1μeV ~ 0.008cm^{-1} ~ 1ns

1neV ~ 8x10^{-6} cm^{-1} ~1μs

Figure design by Laura R. Stingaciu, ORNL

4. Neutron Spin Echo = NSE - two principles

4.1. Larmor precession



http://xrayphysics.com/sequences.html

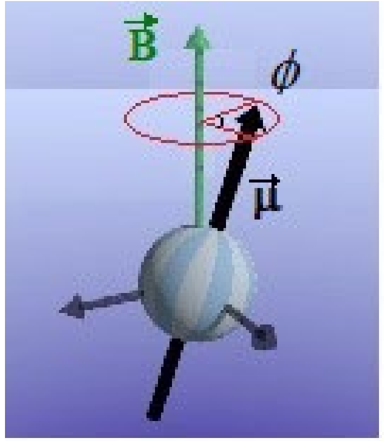


Figure by Laura R. Stingaciu, ORNL

- Larmor Frequency

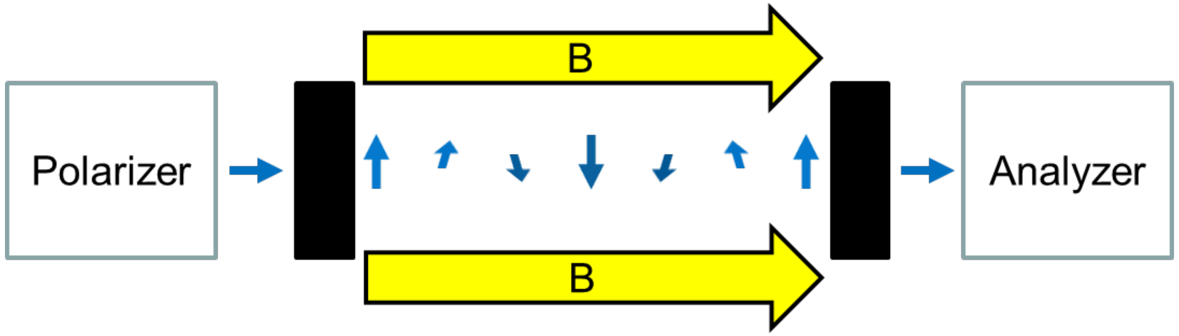
$$\omega_L = |\gamma B|$$

- Accumulated phase

$$\emptyset = \omega_L t = \gamma_L B t = \gamma B l \frac{1}{v}$$

- Neutron Gyromagnetic Ratio

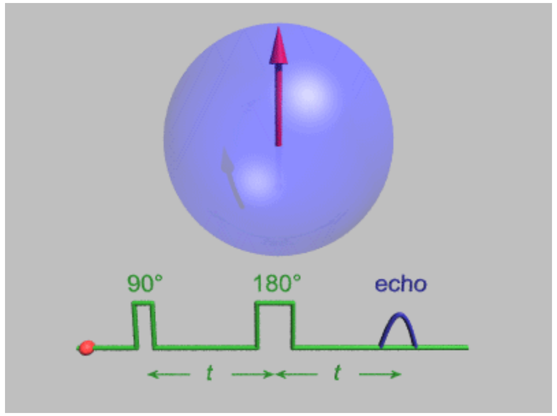
$$|\gamma/2\pi| \approx 30 \text{ MHz/T}$$



Neutron Spin Echo Spectroscopy by Piotr A. Zolnierczuk, NXS-2017: https://www.youtube.com/watch?v=tIFysL66PnM

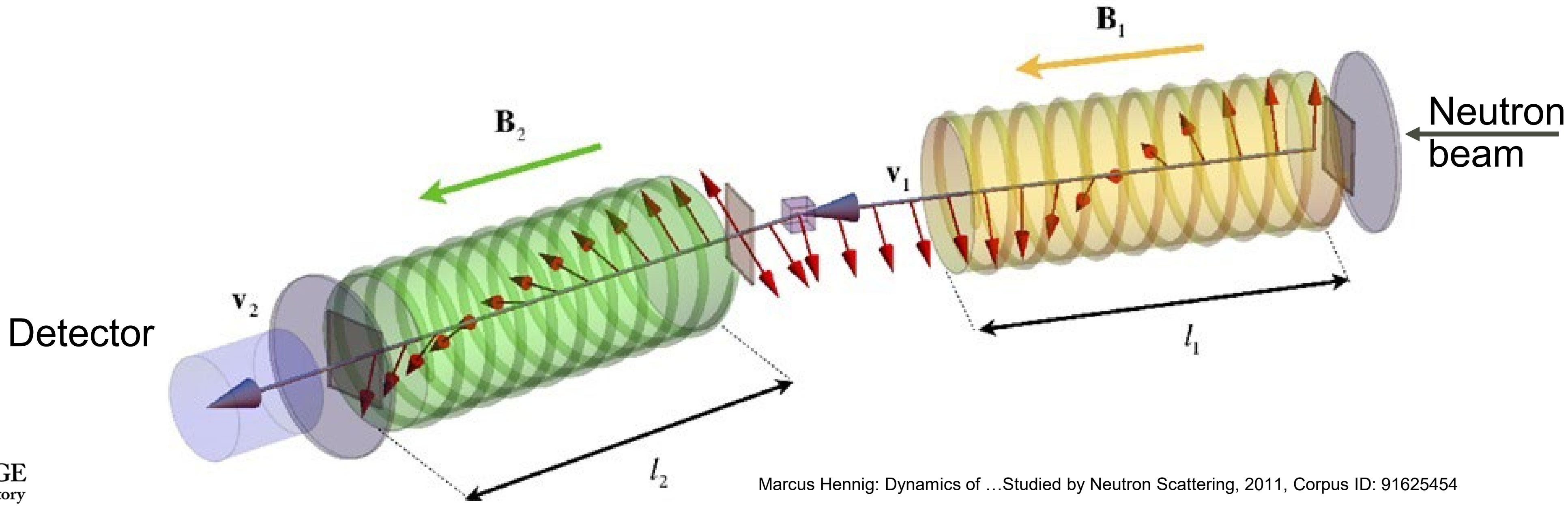
Neutron Spin Echo = NSE - two principles

4.2. Hann echo



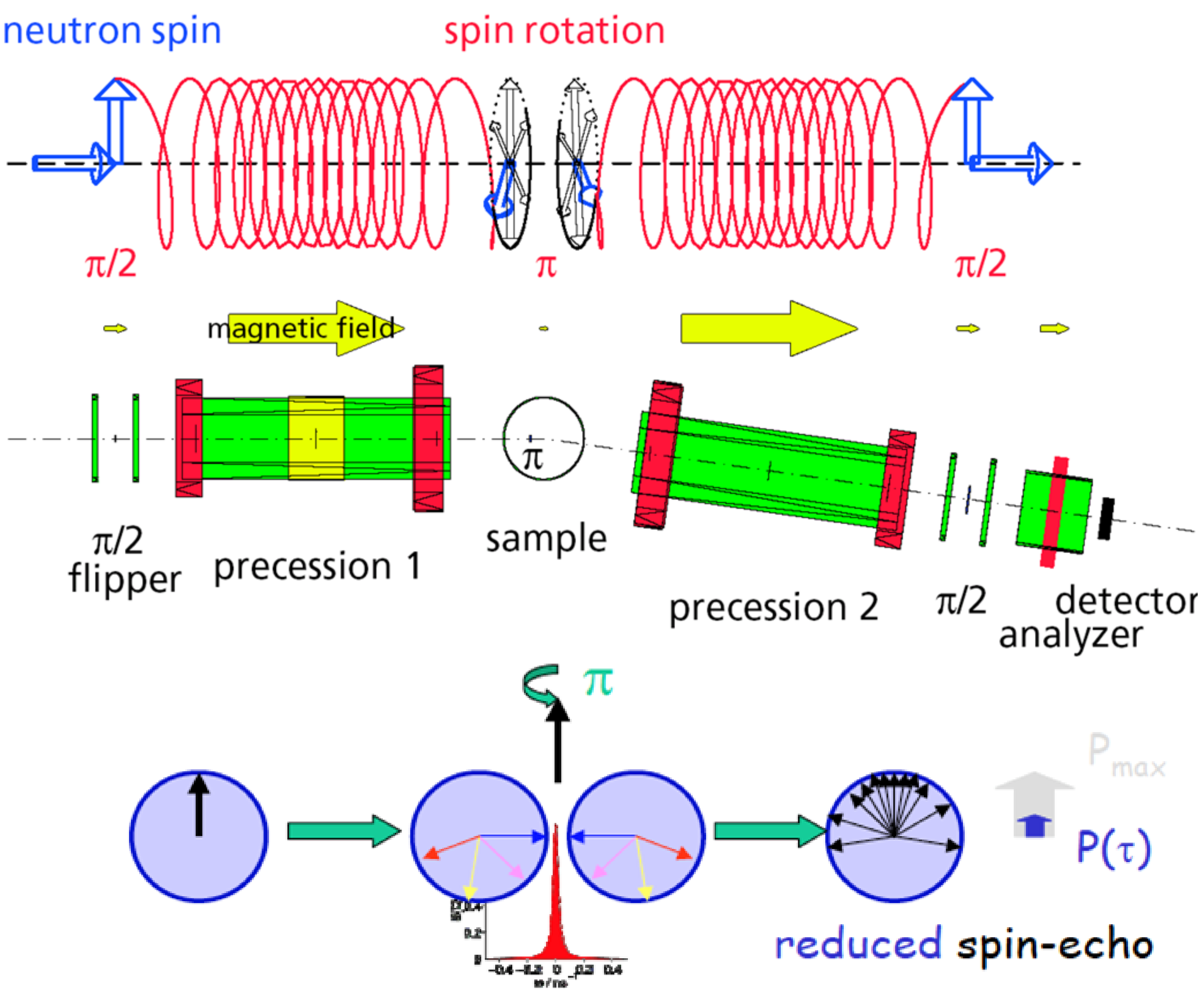
https://en.wikipedia.org/wiki/Neutron_spin_echo

https://www.oxfordneutronschool.org/2017/Lectures/Fouquet%20-%20Neutron%20Spin%20Echo.pdf



Marcus Hennig: Dynamics of …Studied by Neutron Scattering, 2011, Corpus ID: 91625454

Neutron Spin Echo – a quasielastic process



[FZJ-2015-04876] Open Access Book, Brückel, T. ; Richter, D. ; Roth, G. ; et al, Laboratory Course Neutron Scattering: Lectures

Neutron Spin Echo signal

$$I \sim \langle \cos\phi \rangle = \langle \cos \omega\tau \rangle$$

$$I \sim I(Q) \pm \int S(Q,\omega)\cos(\omega\tau)\, d\omega$$

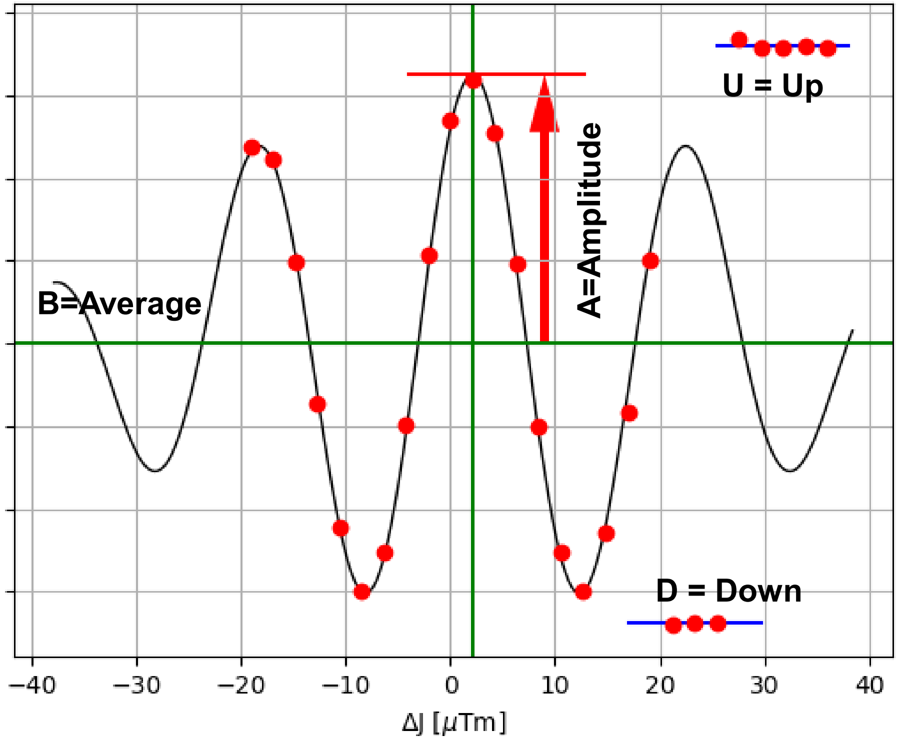
Fourier transform
(Real part)

- $\mathrm{B} \sim I(Q)$
- $\mathrm{A} \sim I(Q,\tau) = \mathcal{F}[S(Q,\omega)]$

- $\frac{I(Q,\tau)}{I(Q,0)} = \frac{2\,\mathrm{A}}{\mathrm{U-D}}$

Fourier time

$\tau \cong 0.186\, J\, \lambda^3$ [ns]
$[\mathrm{J}] = \mathrm{Tm}$, $[\lambda]$=Å



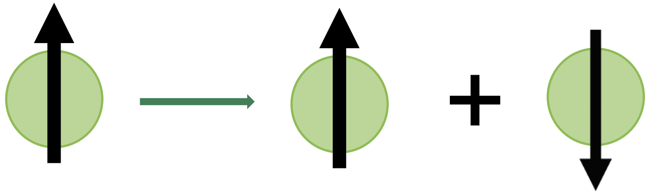
Neutron Spin Echo Spectroscopy by Piotr A. Zolnierczuk, NXS-2017: https://www.youtube.com/watch?v=tIFysL66PnM

Coherent and incoherent scattering in NSE

coherent

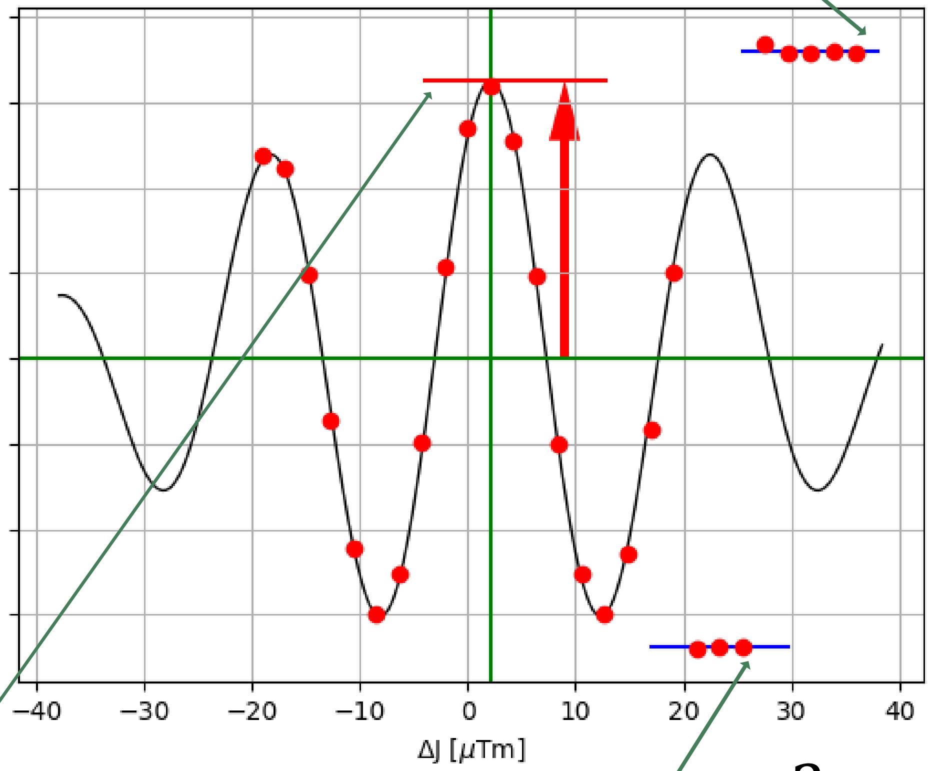
no-flip

incoherent



1/3 no-flip 2/3 flip

$$I_{\text{up}} = I_{\text{coh}} + \frac{1}{3} I_{\text{inc}}$$



$$I_{\text{down}} = \frac{2}{3} I_{\text{inc}}$$

$$I_{\text{echo}} = I_{\text{coh}} f_{\text{coh}}(\tau) - \frac{1}{3} I_{\text{inc}} f_{\text{inc}}(\tau)$$

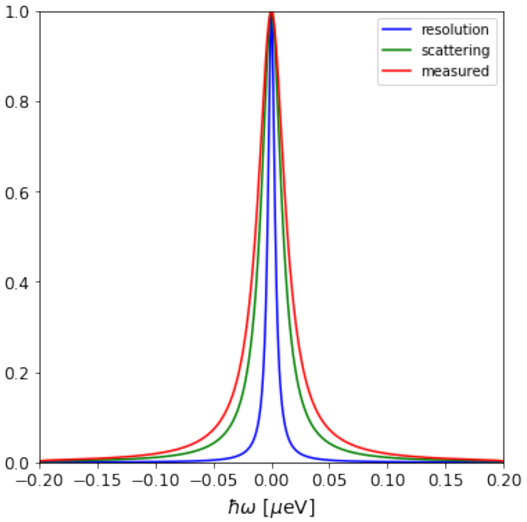
Neutron Spin Echo Spectroscopy by Piotr A. Zolnierczuk, NXS-2017: https://www.youtube.com/watch?v=tIFysL66PnM

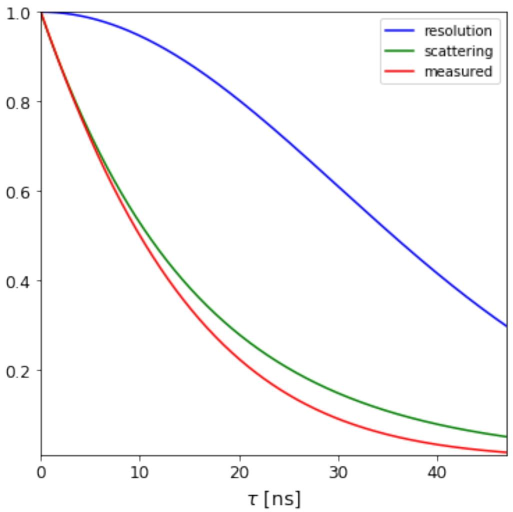
Energy and time domain QENS ↔ NSE

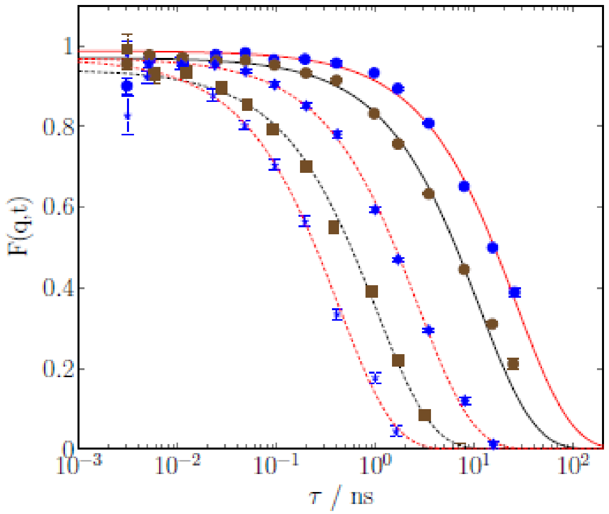
QENS: Dynamic Structure Factor

NSE: Intermediate Scattering Function

$S(Q,\omega)$ ⟵ Fourier Transform ⟶ $I(Q,\tau)$







$$I_D(Q,\omega) = S(Q,\omega) * R(Q,\omega)$$

$$I_D(Q,\tau) = I(Q,\tau)\ R(Q,\tau)$$

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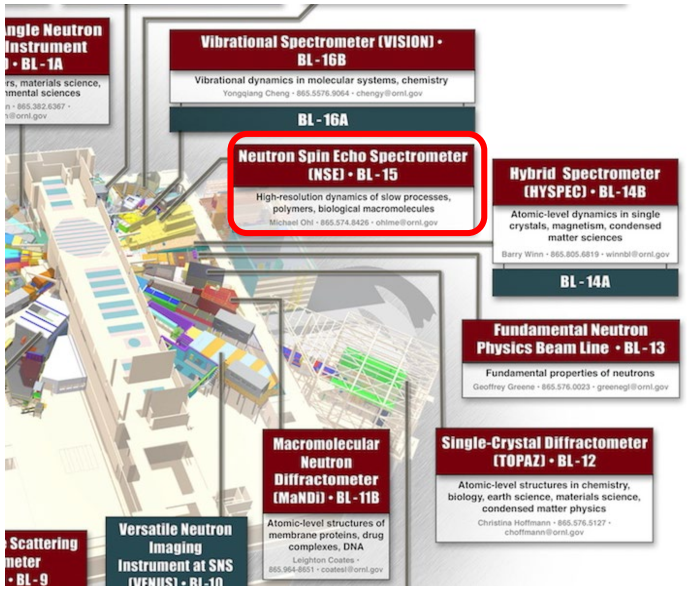
Neutron Spin Echo Spectroscopy by Piotr A. Zolnierczuk, NXS-2017: https://www.youtube.com/watch?v=tIFysL66PnM

NSE spectrometers world map

Neutron Spin Echo Spectroscopy by Piotr A. Zolnierczuk, NXS-2017: https://www.youtube.com/watch?v=tIFysL66PnM

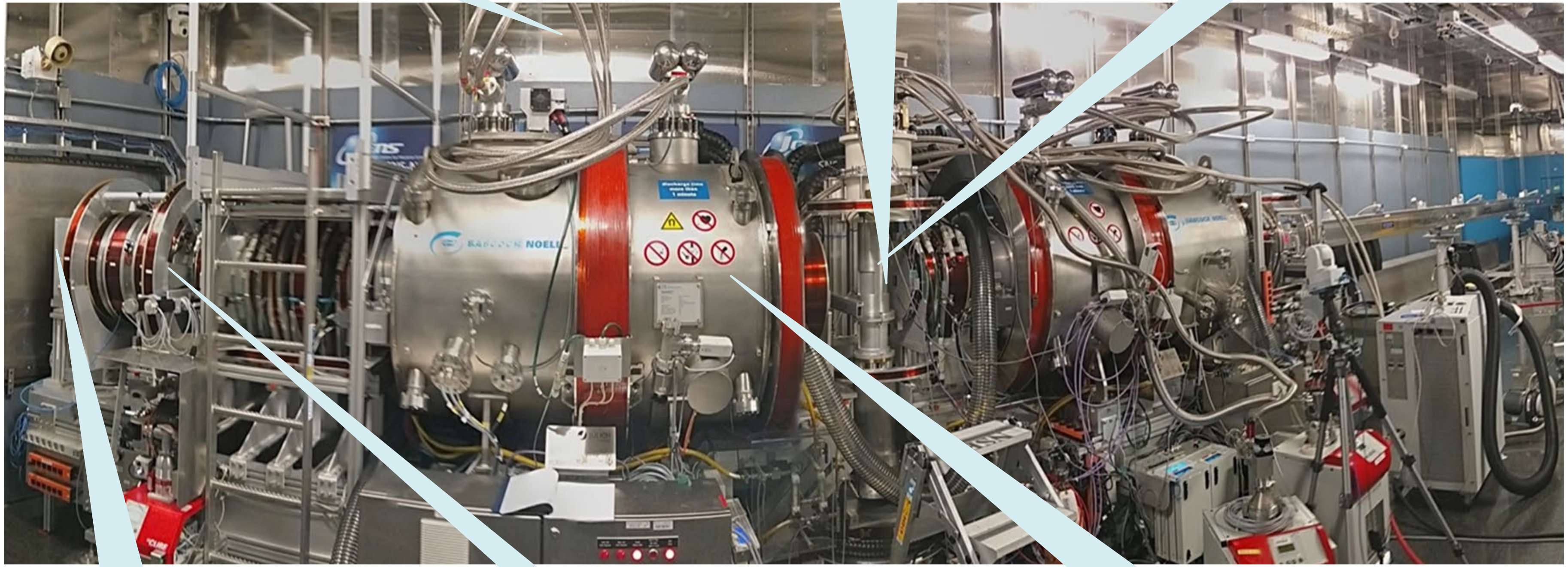
SNS-NSE overview

- Ultrahigh resolution spectrometer for characterizing slow dynamics of soft condensed matter @ nanoscopic and mesoscopic scale
- Detects neutron velocity changes < 10^{-5}
- The only NSE spectrometer at a pulse source
- The first NSE spectroscopic design based on superconducting technology
- The only NSE spectrometer with complete magnetic shielding



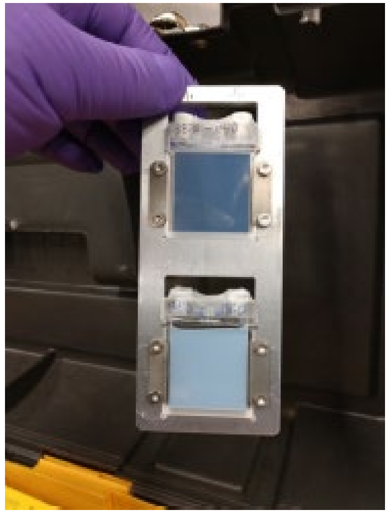
neutrons.ornl.gov/nse

SNS-NSE, the Neutron Spin Echo spectrometer @ SNS



SNS-NSE Sample Environments

ThermoJET Temperature Forcing System (TFS), 275K - 400K



Janis cryostat , 5K - 700K

SNS-NSE Data Reduction For Spin Echo Experiments *DrSPINE*

DrSPINE is a unified reactor - pulse source NSE data reduction software

research papers

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Efficient data extraction from neutron time-of-flight spin-echo raw data

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Neutron spin-echo spectrometers with a position-sensitive detector and operating with extended time-of-flight-tagged wavelength frames are able to collect a comprehensive set of data covering a large range of wavevector and Fourier time space with only a few instrumental settings in a quasi-continuous way. Extracting all the information contained in the raw data and mapping them to a suitable physical space in the most efficient way is a challenge. This article reports algorithms employed in dedicated software, *DrSpine* (data reduction for spin echo), that achieves this goal and yields reliable representations of the intermediate scattering function $S(Q, t)$ independent of the selected 'binning'.

J-NSE Phoenix courtesy of Olaf Holderer, FRMII

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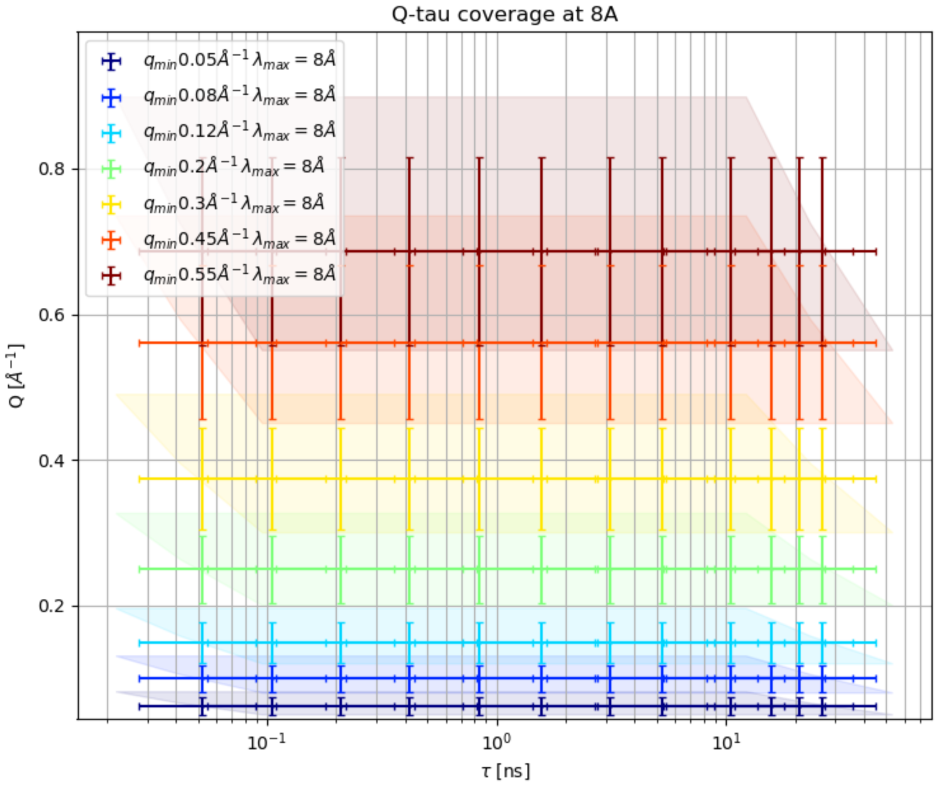
SNS-NSE and TOF

- ❑ Δλ = (5 - 8) Å
- ❑ 2θ = 3.6˚ Q = 0.02 − 0.15 $Å^{-1}$
- ❑ 2θ = 37˚ Q = 0.45 − 0.85 $Å^{-1}$



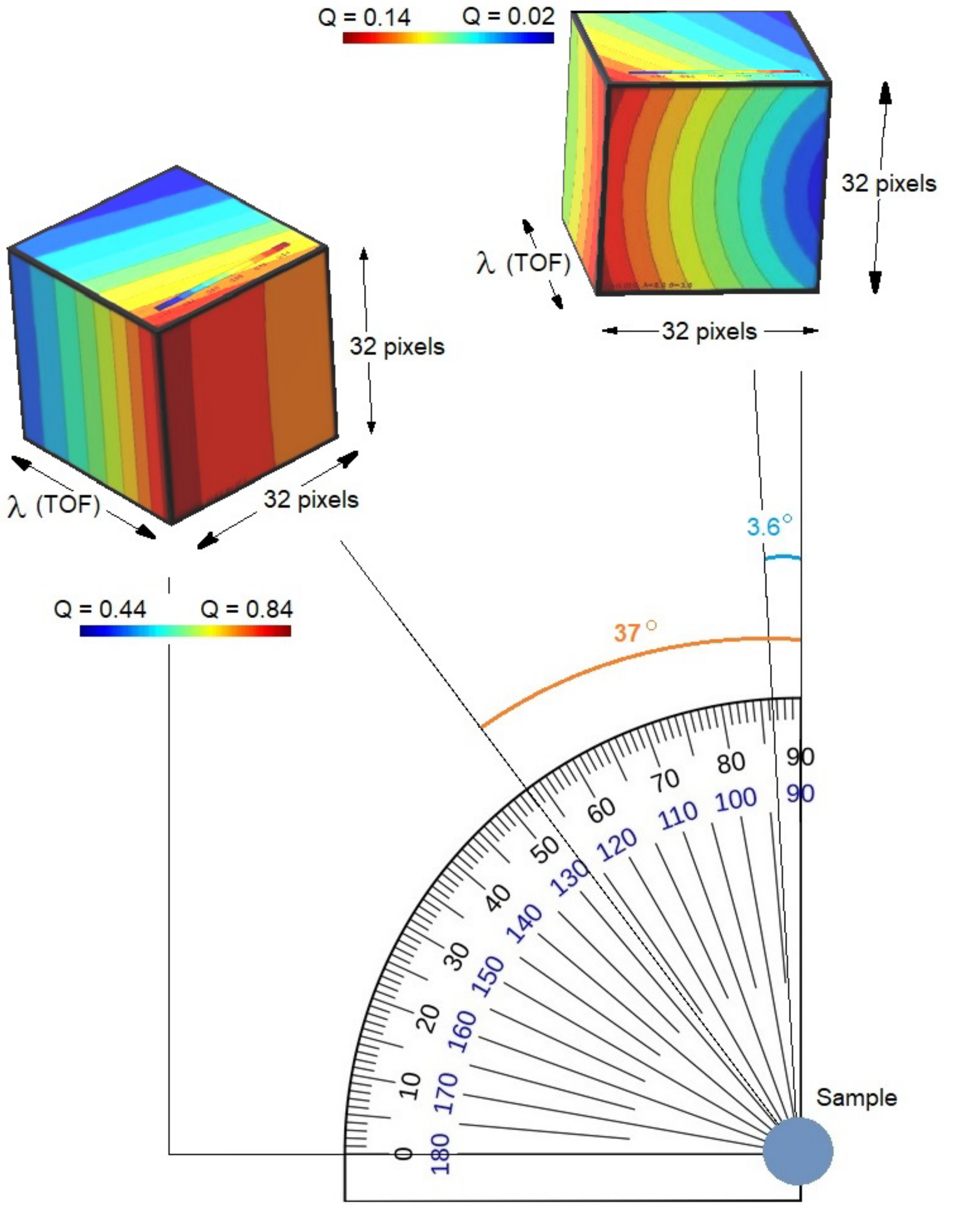


Figure idea and cubes design by Piotr A. Zolnierczuk, 3D rendering by L.R. Stingaciu

Coherent dynamics in polymers, glassy systems, bio-macromolecules

Magnetic Dynamics, Spin glasses & spin fluids

Domain and allosteric motions in proteins

Shape fluctuations

SNS-NSE research highlights

dynamics of soft matter at nano- to meso-scale

Diffusion processes

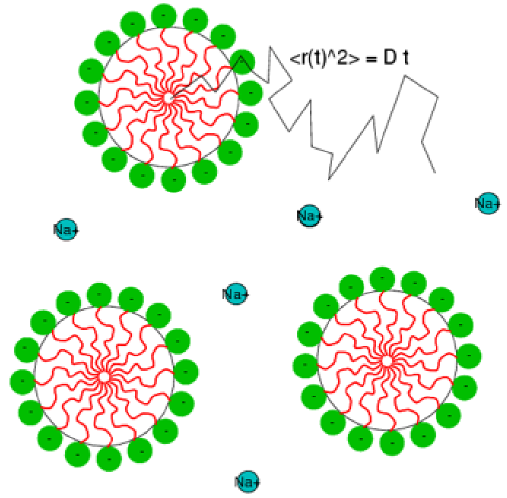
Hydrogen jump diffusion

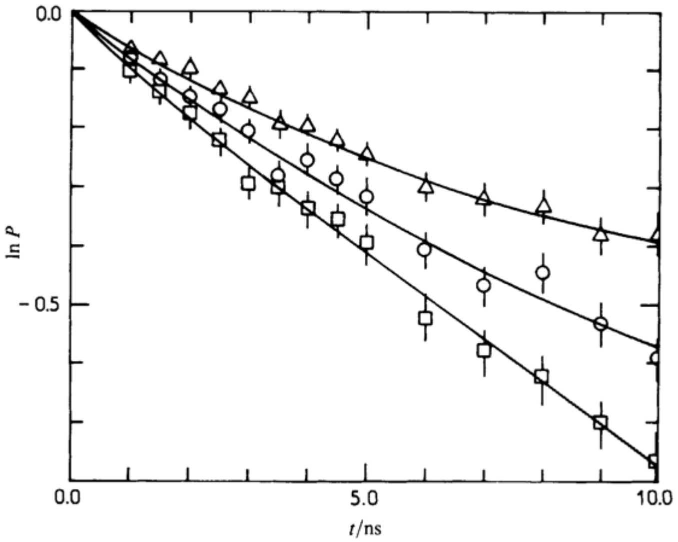
Interaction of solvent molecules with surfaces

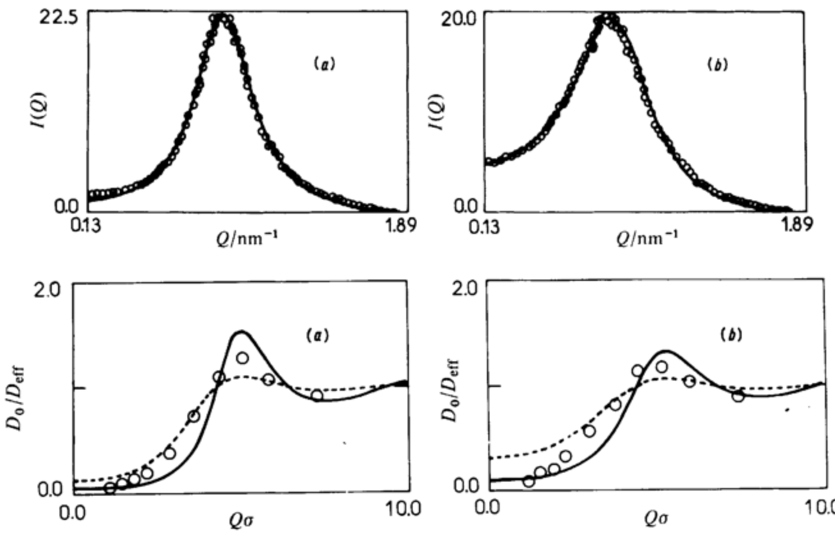
Short range translational, rotational and tumbling diffusive motions

SDS micelles in aqueous solution

J. Hayter, J. Penfold, J. Chem. Soc., Faraday Trans. 1, 1981,77, 1851-1863, *https://doi.org/10.1039/F19817701851*







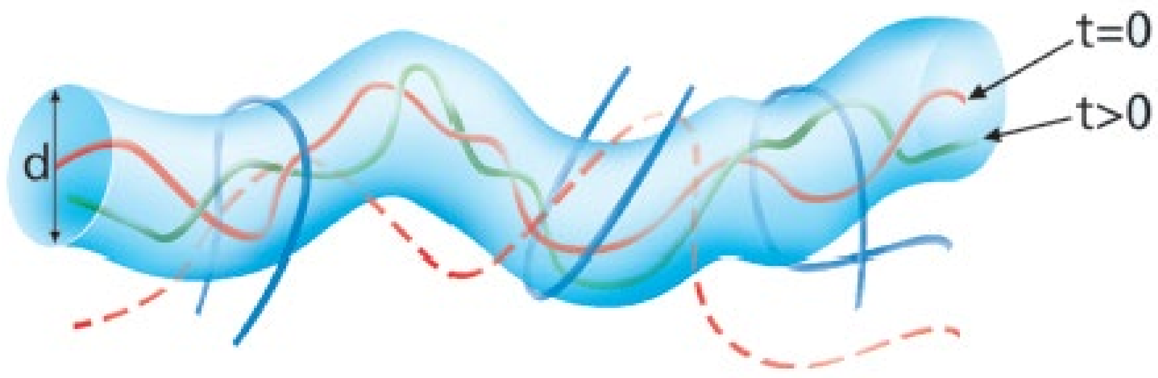
$$\frac{I(Q,t)}{I(Q,0)} = e^{-D_{\text{eff}}(Q)Q^2 t}$$

$$D_{\text{eff}} = D_0 H(Q)/S(Q)$$

$$D_0 = \frac{kT}{6\pi\eta R}$$ Stokes-Einstein

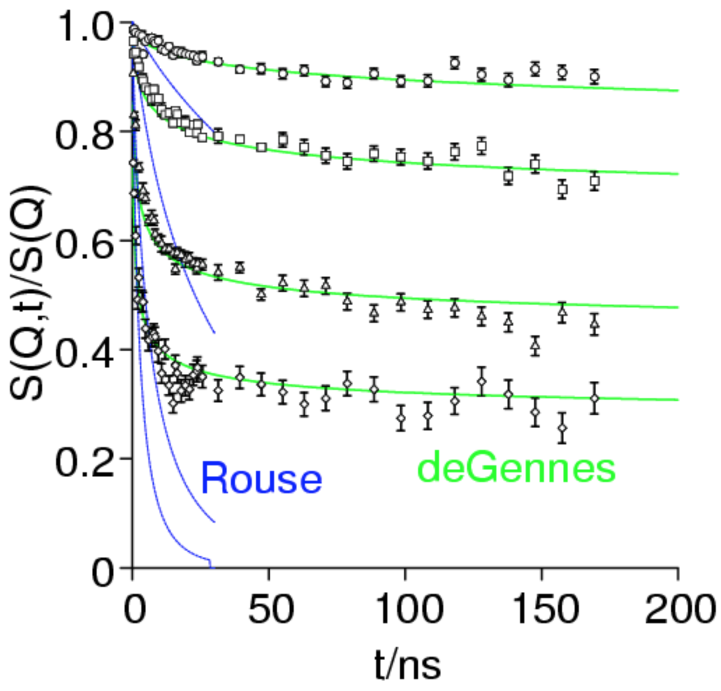
Motion in entangled polymer melts

*A. Wischnewski, M. Monkenbusch, L. Willner,... and D. Richter, Phys. Rev. Lett. **90** (2003), DOI: 10.1103/PhysRevLett.90.058302*



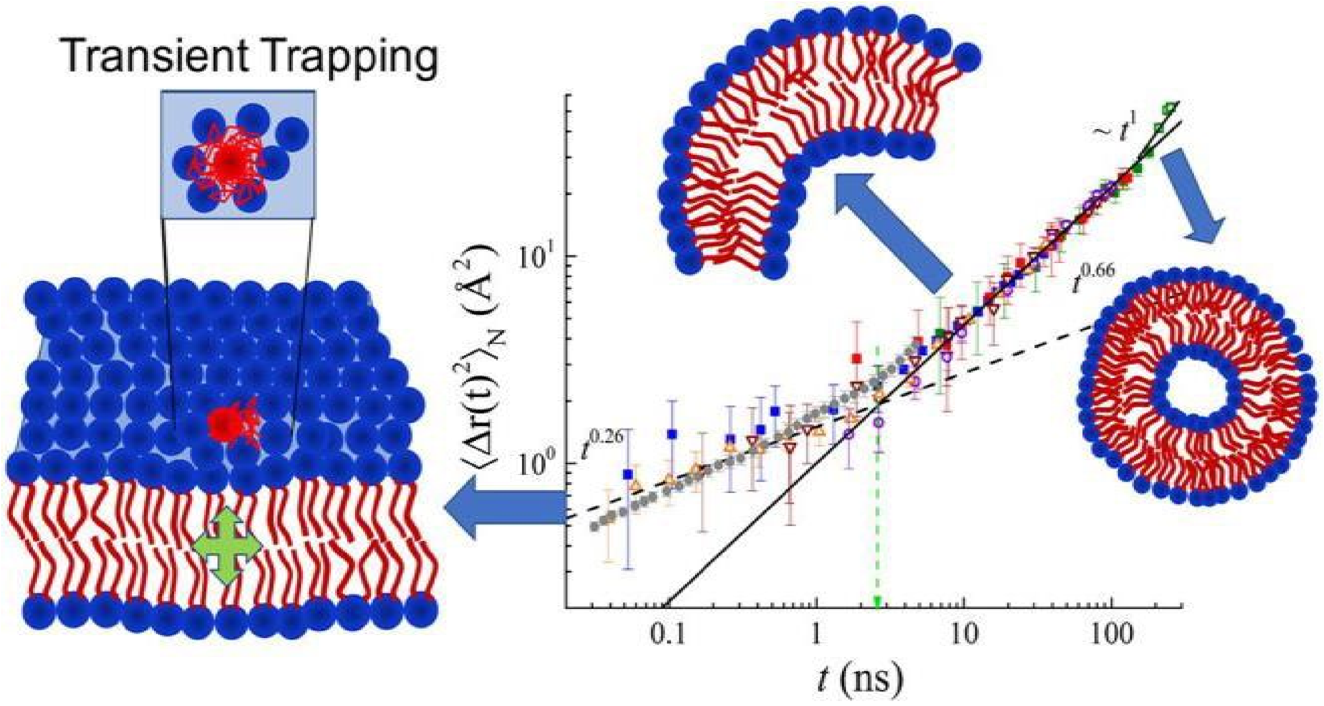
$$\frac{S(Q,\tau)}{S(Q,0)} = [1 - F(Q)]S^{loc} + \mathrm{F(Q)}\ S^{esc}$$

- ❑ NSE Spin-Incoherent scattering measures proton self-correlation function
- ❑ Labeled long linear PEP polymer chain
- ❑ Segmental dynamics



Dynamics of phospholipid membranes

Sudipta Gupta, Piotr Zolnierczuk, Gerald J. Schneider, et al., J. Phys. Chem. Lett. 9, 2956 (2018), DOI: 10.1021/acs.jpclett.8b01008



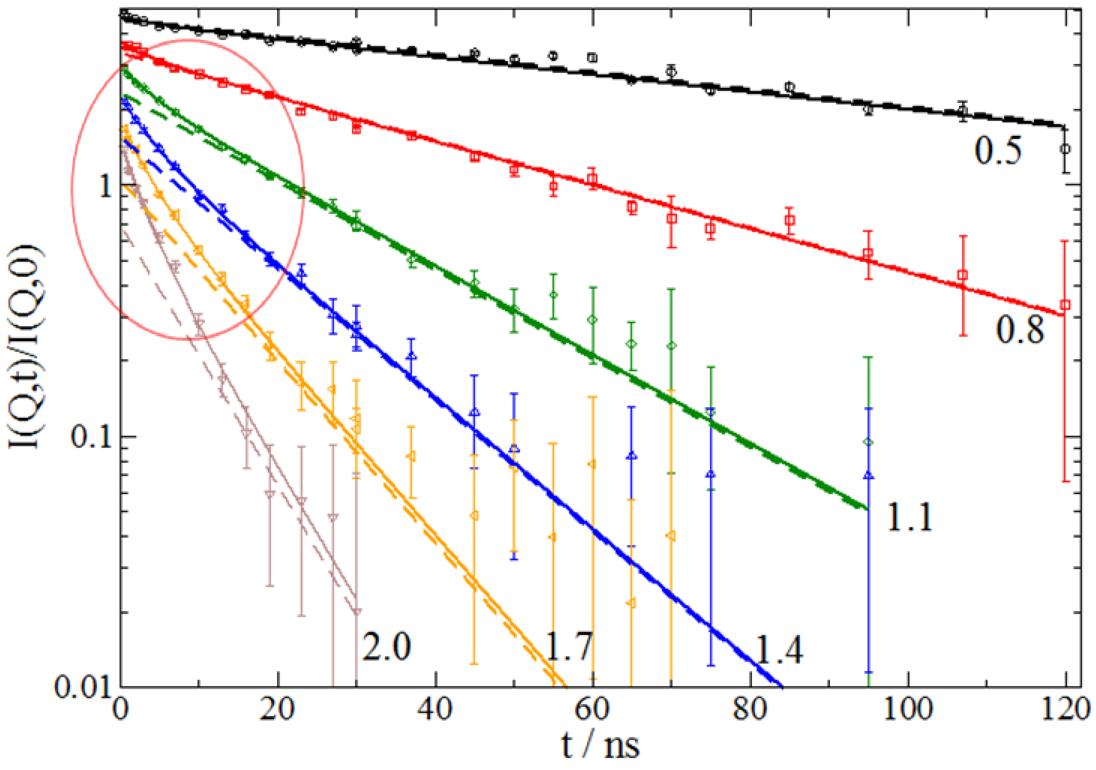
Proposed mechanism of transient trapping and mean square displacement ⟨Δr(t)^2 ⟩N as a function of Fourier time

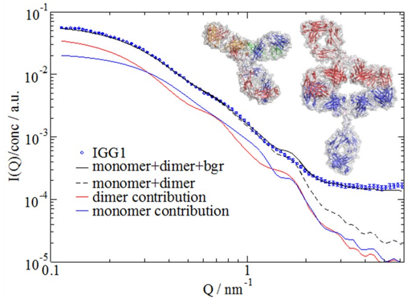
- ❑ Friction at the interface water - liposomes plays a minor role
- ❑ The center of mass diffusion of liposomes and the transient trapping of lipids define the range in which ZG model can be applied

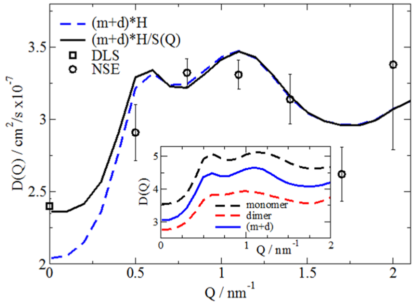
Proteins domains dynamics

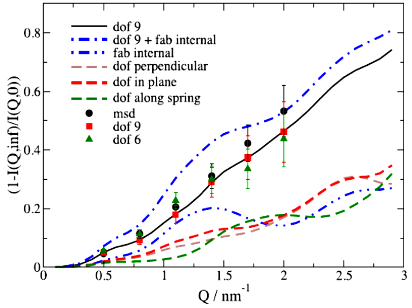
L.R. Stingaciu et al., Sci Rep 6, 22148 (2016) https://doi.org/10.1038/srep22148

$$F(Q,t) = F_{trans}(Q,t) \cdot F_{rot}(Q,t) \cdot F_{int}(Q,t)$$





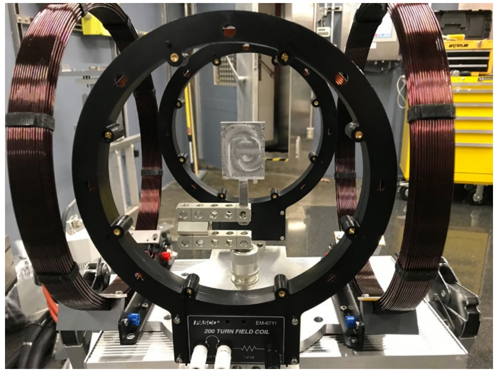




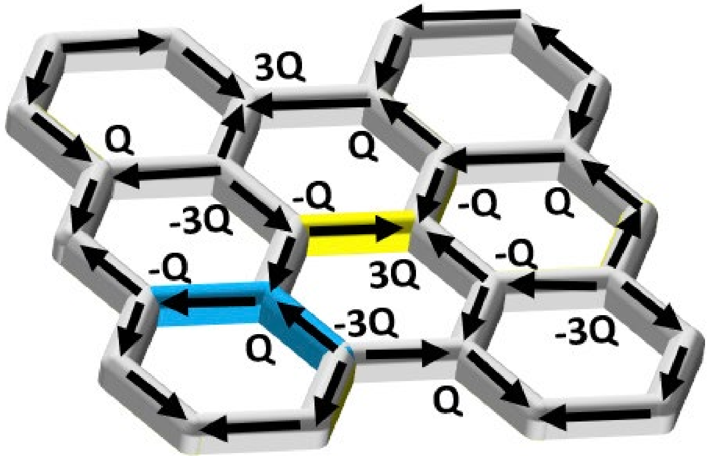
Three protein fragments in harmonic potential connected by flexible linkers

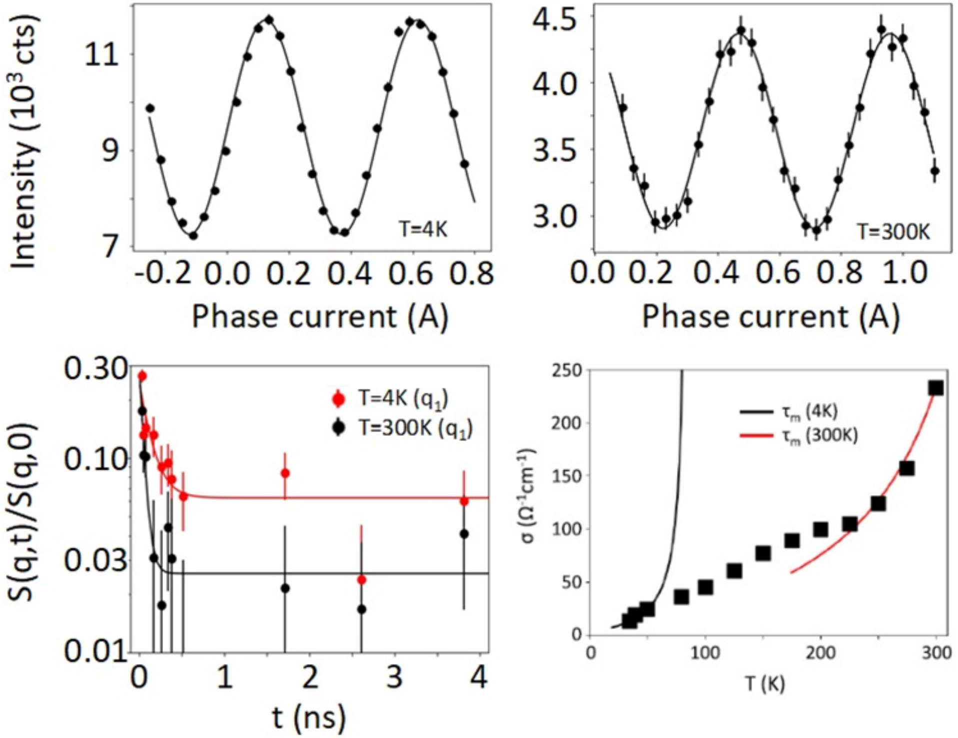
Spin dynamics in frustrated magnets

Yiyao Chen et al., iScience 24, https://doi.org/10.1016/j.isci.2021.102206



Polarization coils setup at SNS-NSE





Magnetic charges of ±Q unit and ±3Q accumulate on the vertices of the honeycomb lattice

The charge defect relaxes between nearest neighbors

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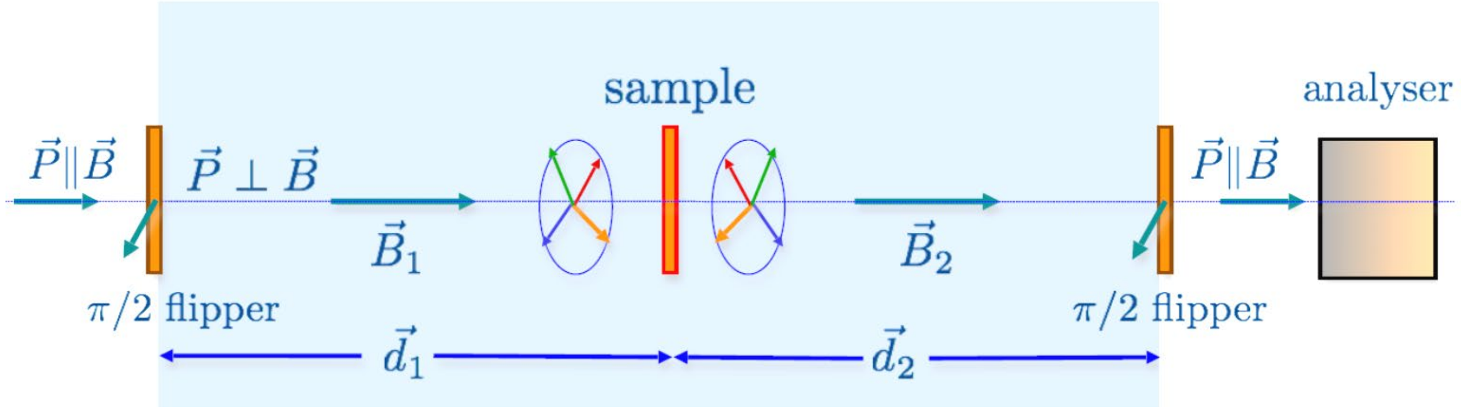
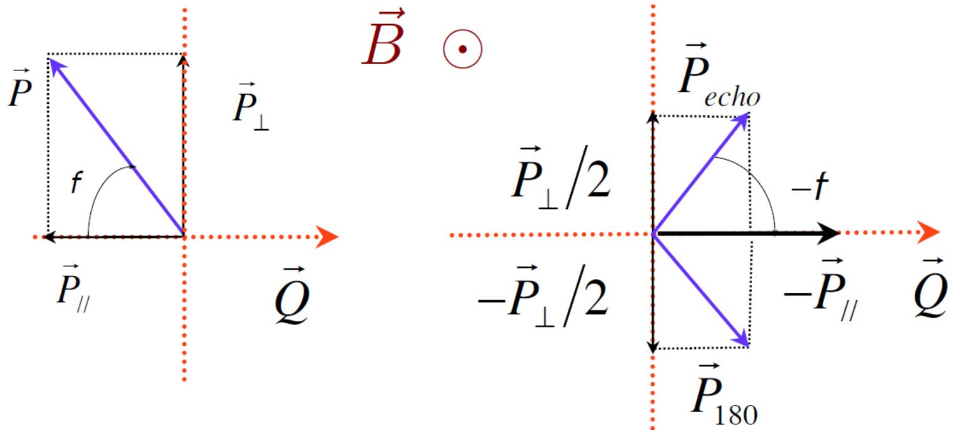
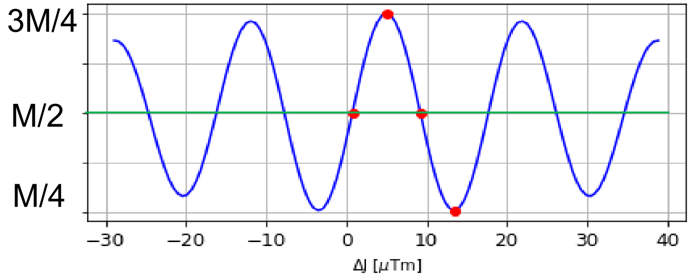
Neutron Spin Echo
Variations

Paramagnetic NSE

Sample is the π-flipper







http://sons.uniroma2.it/ericeneutronschool/wp-content/uploads/2016/12/NSE_MAgnetism_Pappas.pdf

Resonance, MIEZE, and SANS - spin echo

NRSE (Neutron Resonance Spin Echo)

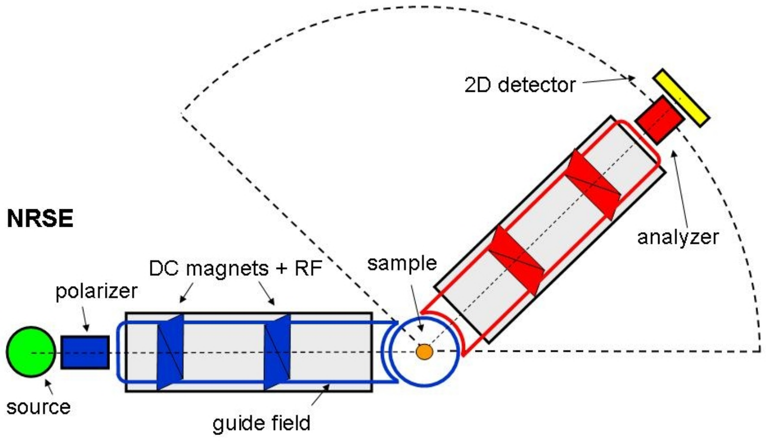
T-NRSE or L-NRSE

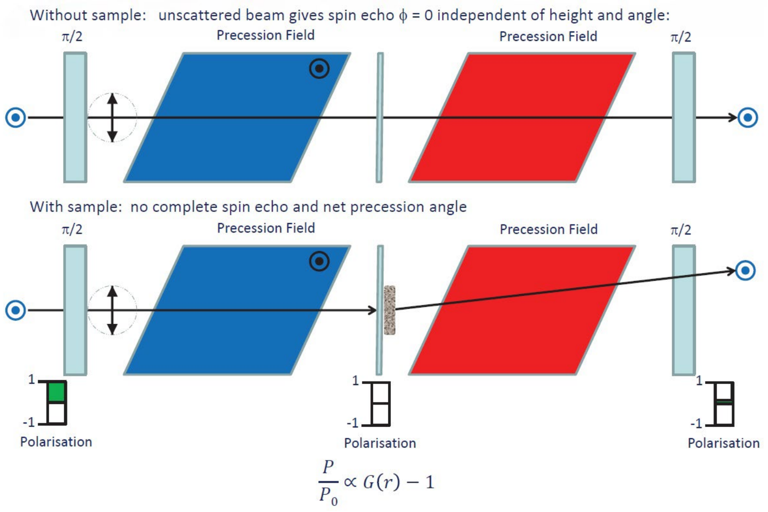
https://www-llb.cea.fr/fr-en/pdf/muses-llb.pdf

SESANS

Spin Echo SANS

http://larmor.weblog.tudelft.nl/files/2013/07/S_Rogers_SANS_SESANS1.pdf

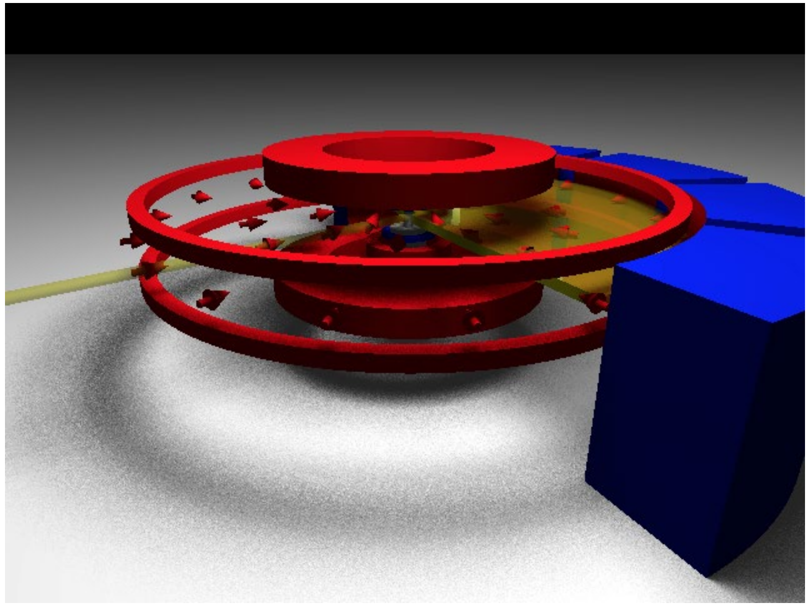


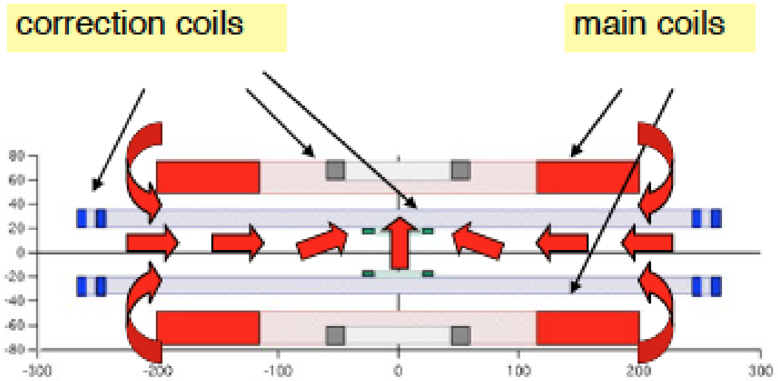


RF field instead of solenoid
- compact design
- shorter Fourier times

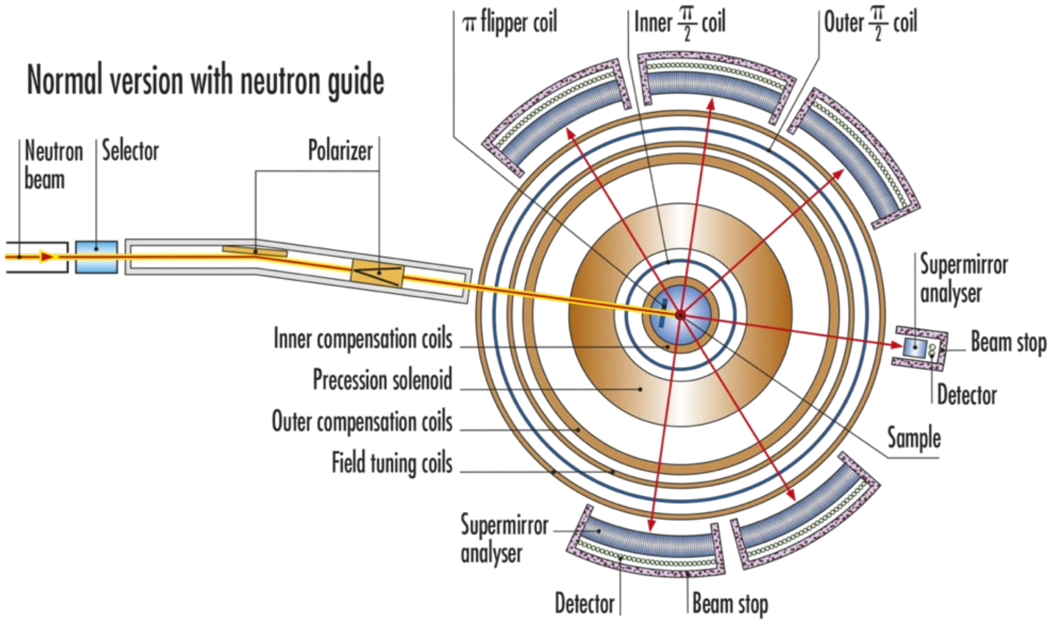
Spin Echo encoded SANS
- tilted magnetic field
- angle encoded in spin precession

Wide angle spin echo





https://www.ill.eu/users/instruments/instruments-list/wasp/description/instrument-layout



- ❑ Large angular coverage
- ❑ Higher Q (up to 3Å^{-1})

Summary - NSE in a nutshell

- NSE measures very small velocity changes using neutron spin precession in magnetic field
- Broad $\Delta\lambda/\lambda$ and high resolution
- Intermediate Scattering Function: $I(Q,\tau)$
- Complementary to SANS/SAXS
- Counting intensive and large samples

Reference reading

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  https://www.ill.eu/fileadmin/users_files/documents/links/documentation/NeutronDataBooklet.pdf

Questions about NSE?

https://neutrons.ornl.gov/instruments

Neutron Spin Echo Spectrometer | Neutron Science at ORNL

Acknowledgements

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- SNS and HFIR facility support groups
- SNS and HFIR user labs
- SNS and HFIR User Office
- US taxpayers

THANK YOU