Introduction to Neutron Spin Echo Spectroscopy

Laura-Roxana Stingaciu

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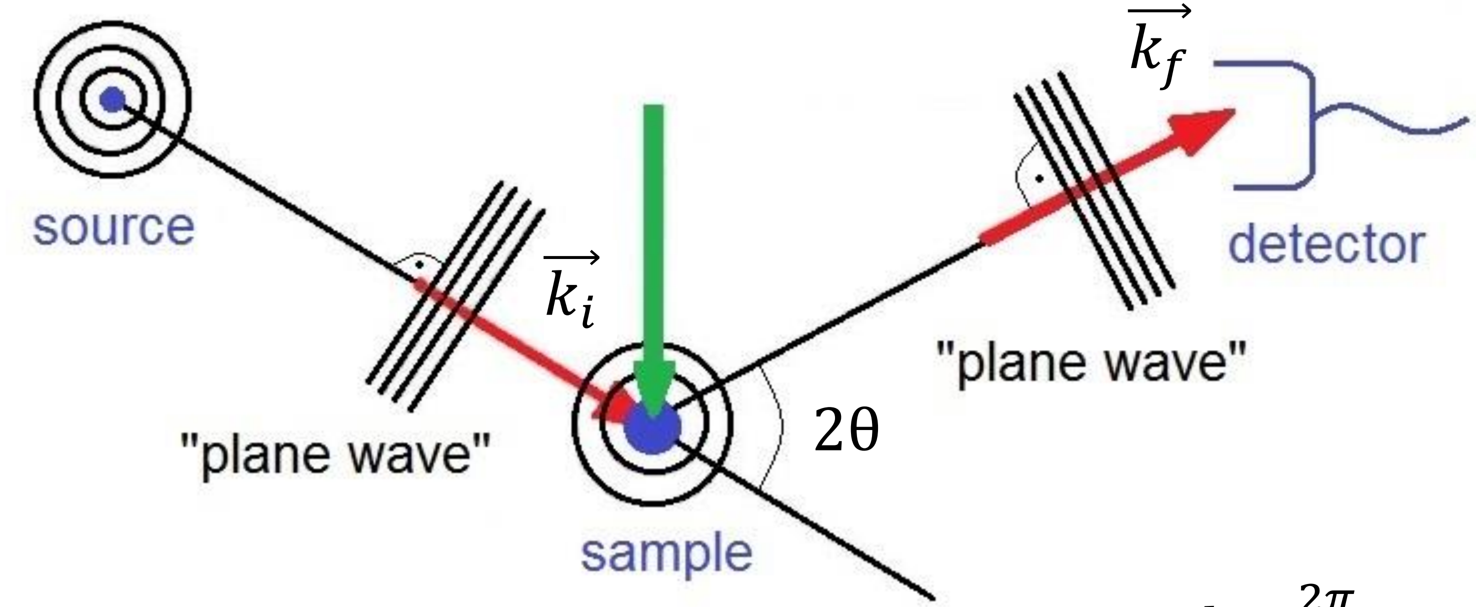
- ❑ Keith Taddei

A BIG ROUND OF APPLAUSE FOR THEM , PLEASE 🙏

The neutron scattering event
(in the Fraunhofer approximation)

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



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

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

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

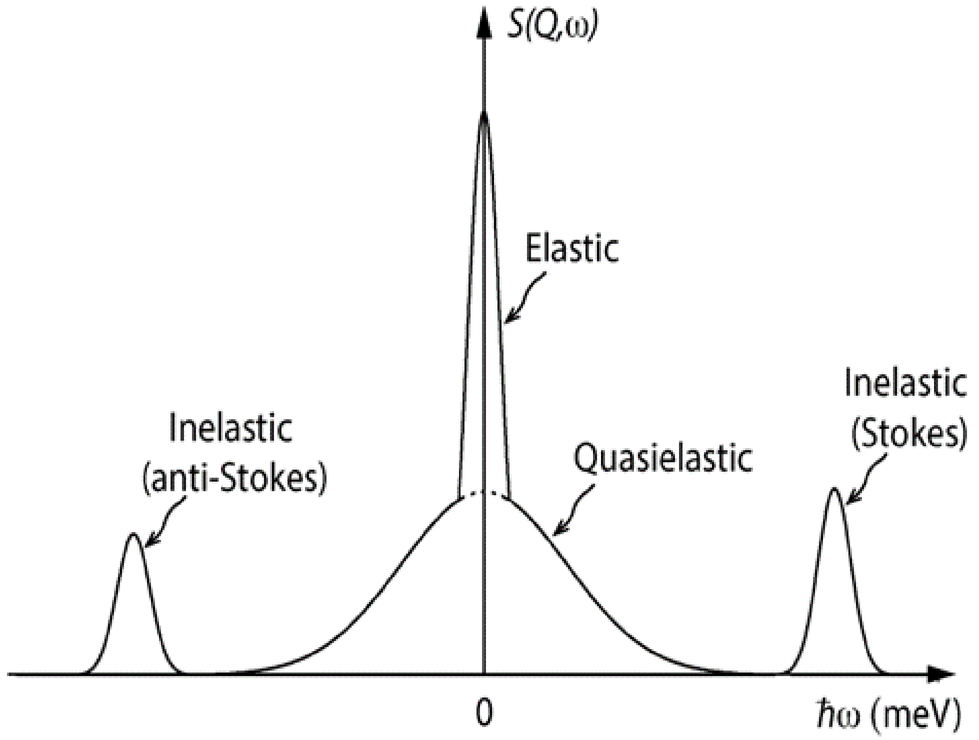
$$\Delta E = E_\mathrm{i} - E_\mathrm{f} = \hbar\omega = \text{energy transfer}$$

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

QENS: quasielastic neutron scattering

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

Energy spectra = structural and dynamical information
$S(Q, \omega)$ = dynamic structure factor



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

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

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

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

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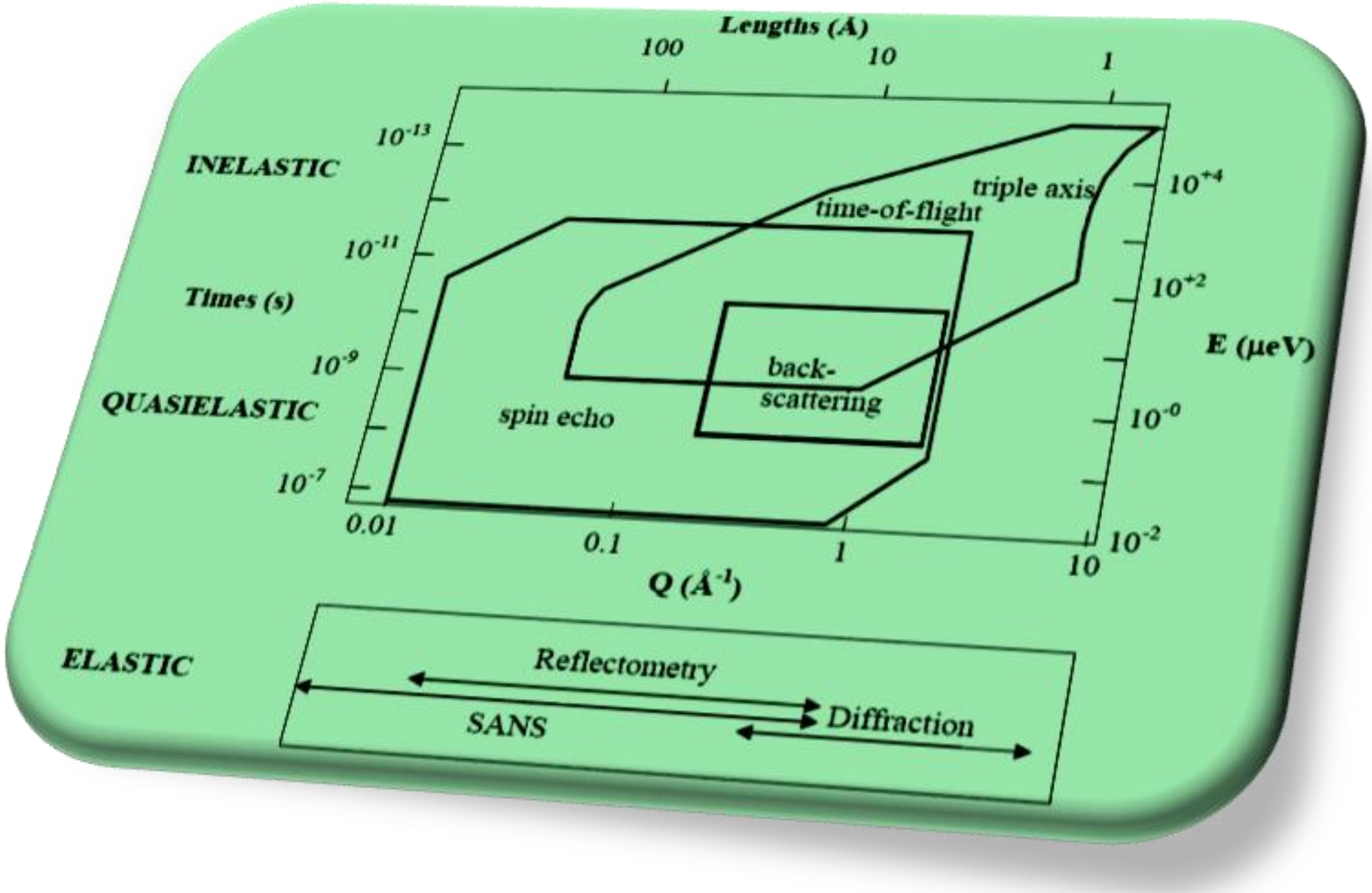
DOI: 10.1039/C4CP04112G (Perspective) Phys. Chem. Chem. Phys., 2015, 17, 26-38

Neutron spectroscopy landscape
(methods to measure dynamics)



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

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

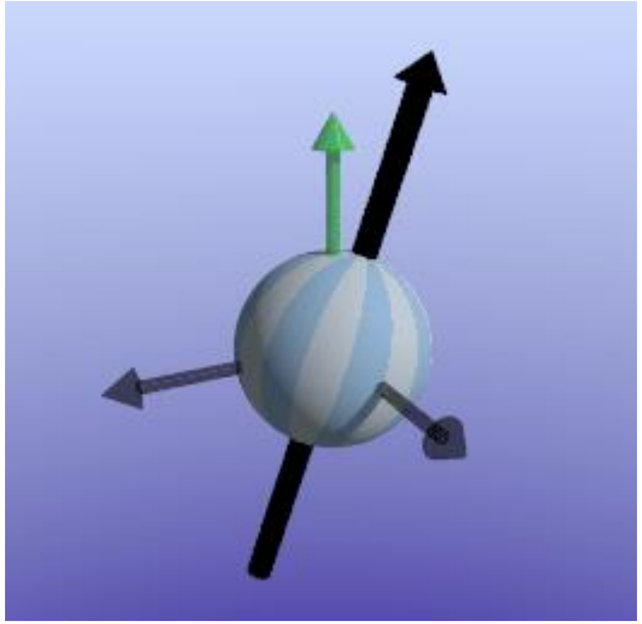
1µeV ~ 0.008cm^{-1} ~ 1ns

1neV ~ 8x10^{-6} cm^{-1} ~1µs

Figure design by L.R. Stingaciu, ORNL

Neutron Spin Echo (NSE) - principle 1

Larmor precession



http://xrayphysics.com/sequences.html

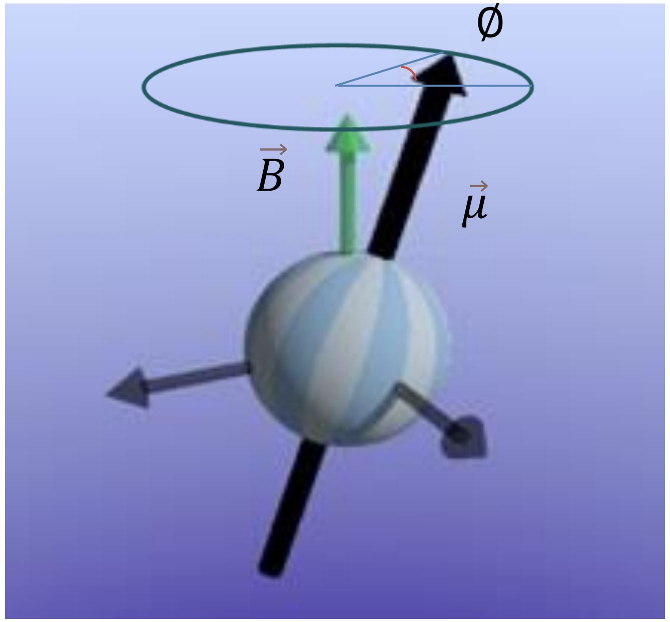


Figure by L.R. Stingaciu, ORNL

- Larmor Frequency

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

- Neutron Gyromagnetic Ratio

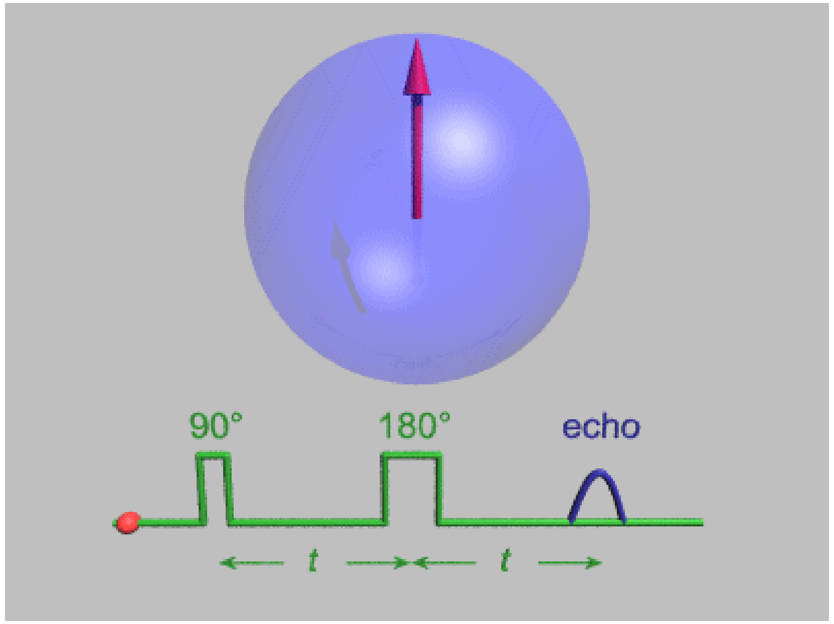
$$|\gamma/2\pi| \approx 30\ \mathrm{MHz/T}$$

- Accumulated phase

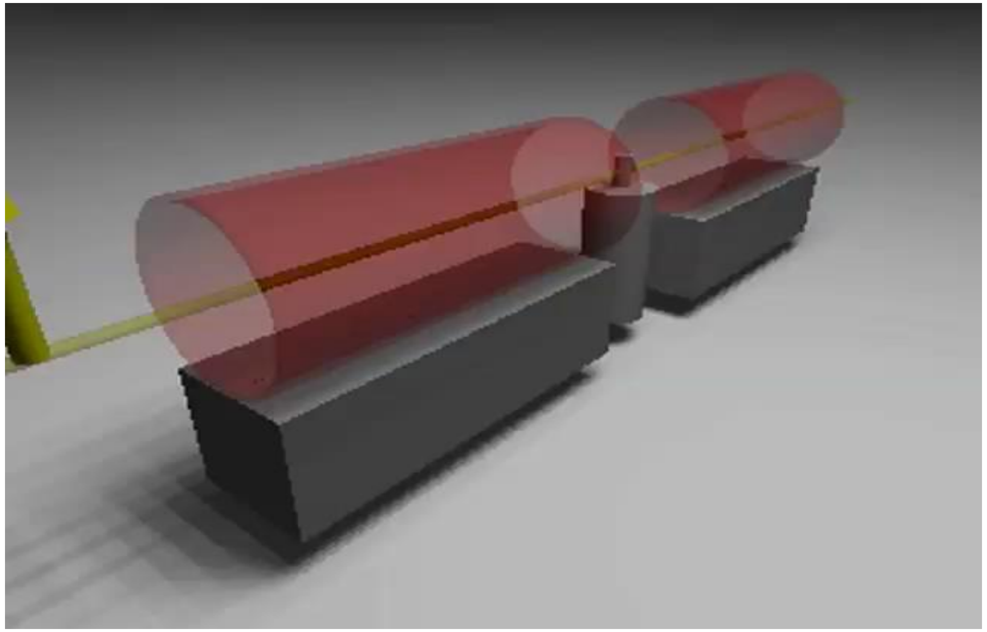
$$\emptyset = \omega_L t = \gamma_L B t = \gamma B l \frac{1}{v}$$

Neutron Spin Echo (NSE) - principle 2

Hann echo



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



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

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Neutron Spin Echo – a quasielastic process

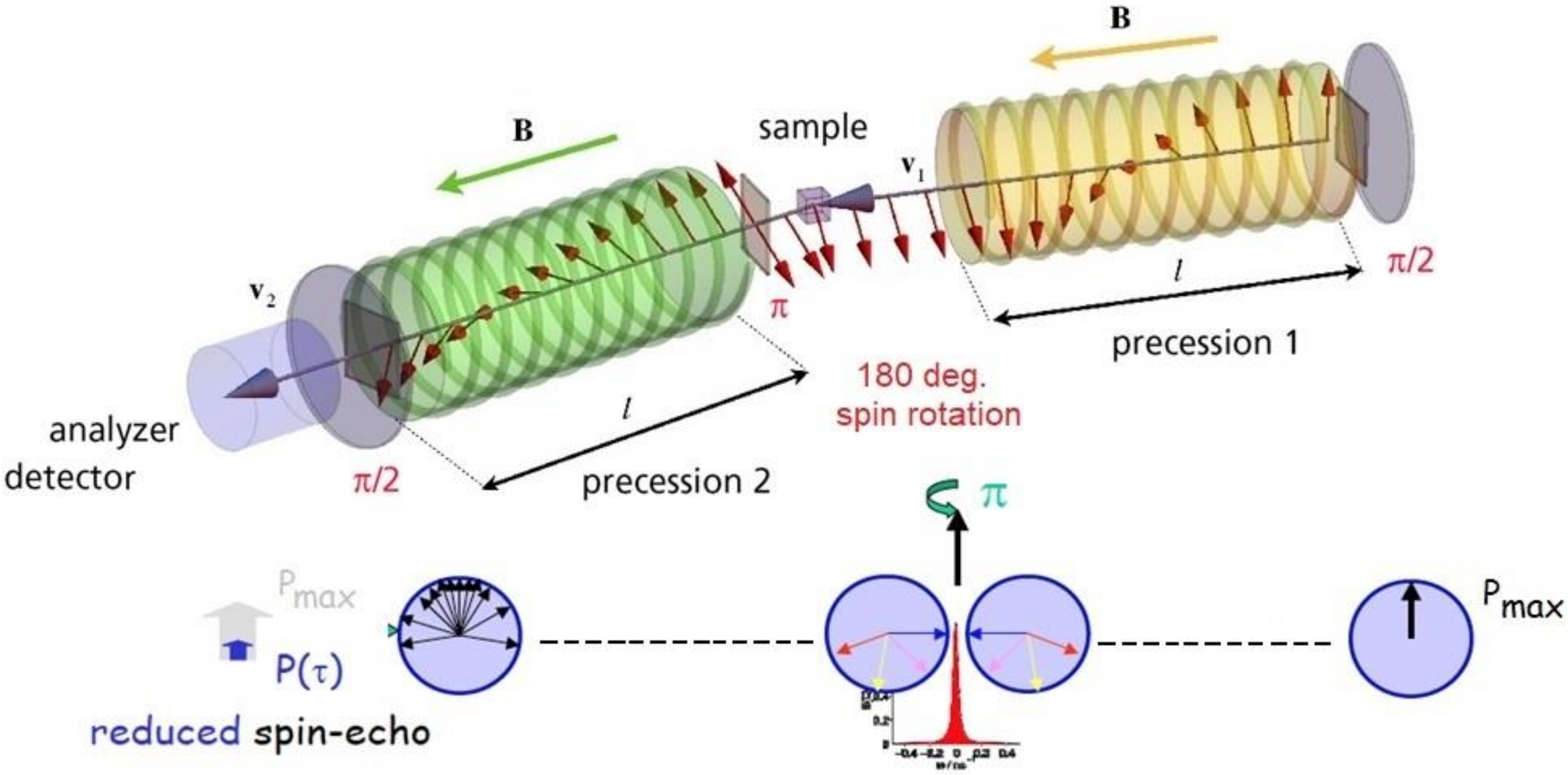


Figure design by L.R. Stingaciu, ORNL
inspired from Marcus Hennig: Dynamics of …Studied by Neutron Scattering, 2011, Corpus ID: 91625454 and [FZJ-2015-04876] Open Access Book, Brückel, T. ; Richter, D. ; Roth, G. ; et al, Laboratory Course Neutron Scattering Lectures.

Neutron Spin Echo signal

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

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

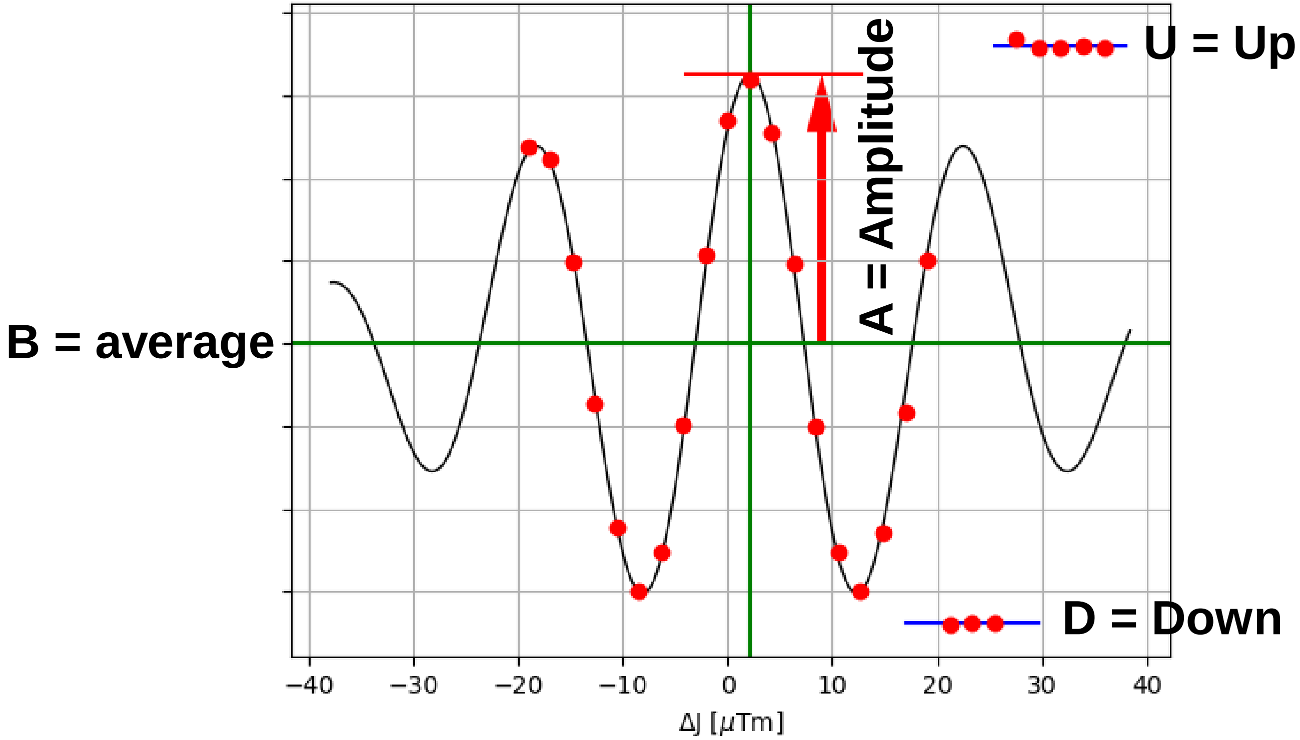
Fourier transform
(Real part)

- $\mathrm{B} \sim I(Q)$ = static = structure factor
- $\mathrm{A} \sim I(Q,\tau) = \mathcal{F}[S(Q,\omega)]$ = amplitude of oscillation
- $$\frac{I(Q,\tau)}{I(Q,0)} = \frac{2\,\mathrm{A}}{\mathrm{U-D}}$$

Fourier time

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

$$Example:\ \lambda = 8\text{Å}, \quad J = 0.56\, Tm \rightarrow \tau \cong 50ns$$
$$\rightarrow \Delta E \cong 0.01\, \mu eV = 10\, nanovolt$$



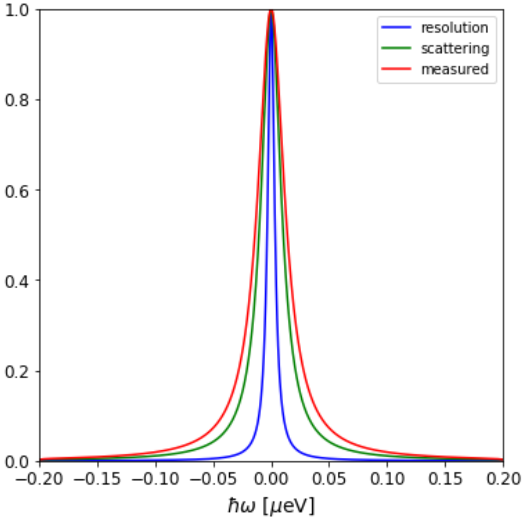
Neutron Spin Echo Spectroscopy by Piotr A. Zolnierczuk, NXS-2017: https://www.youtube.com/watch?v=tIFysL66PnM

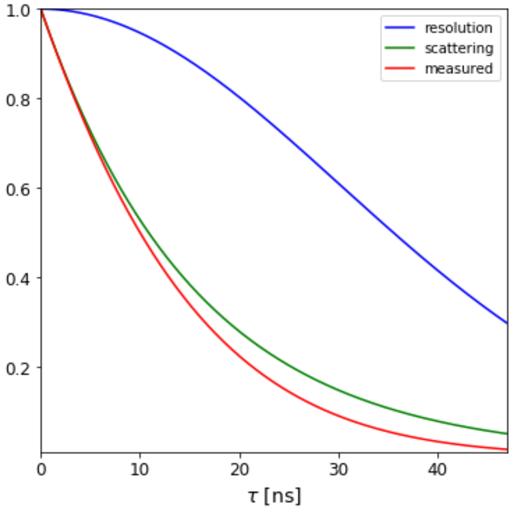
Energy and time domain QENS ↔ NSE

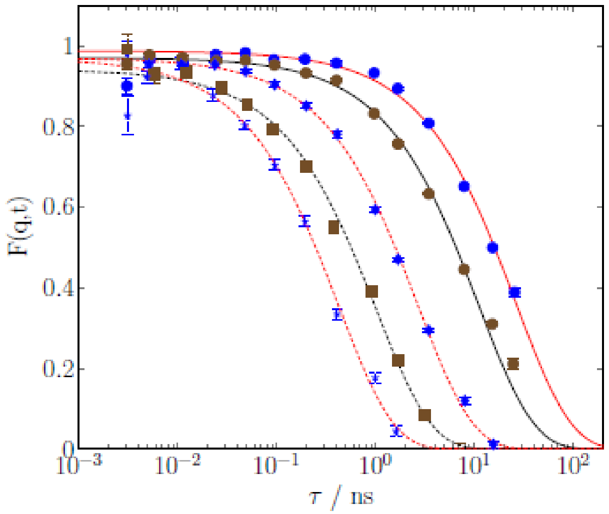
QENS: Dynamic Structure Factor

NSE: Intermediate Scattering Function

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





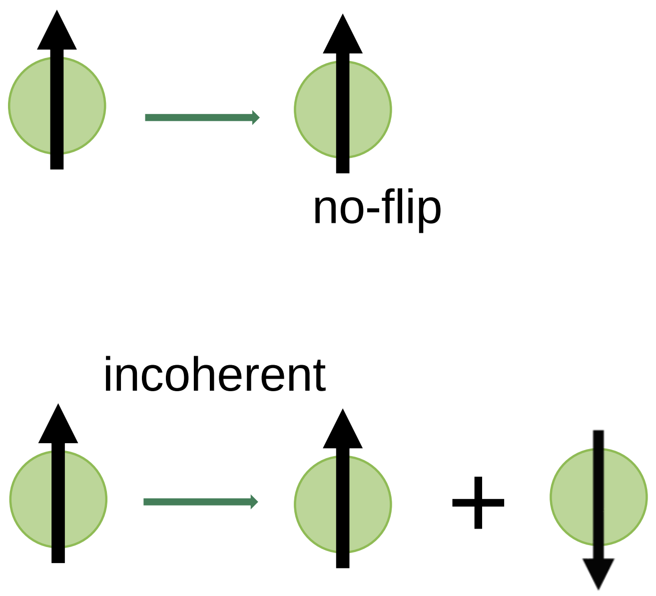


$I_D(Q,\omega) = S(Q,\omega) * R(Q,\omega)$

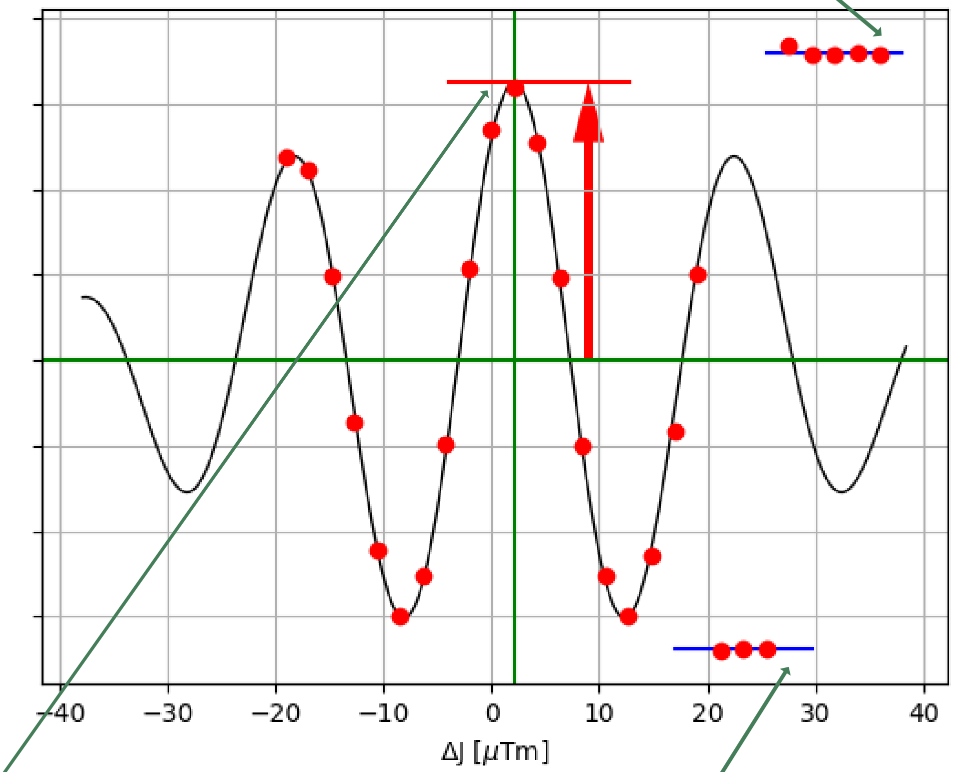
$I_D(Q,\tau) = I(Q,\tau)\ R(Q,\tau)$

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

Coherent and incoherent scattering in NSE



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



Flip Ratio

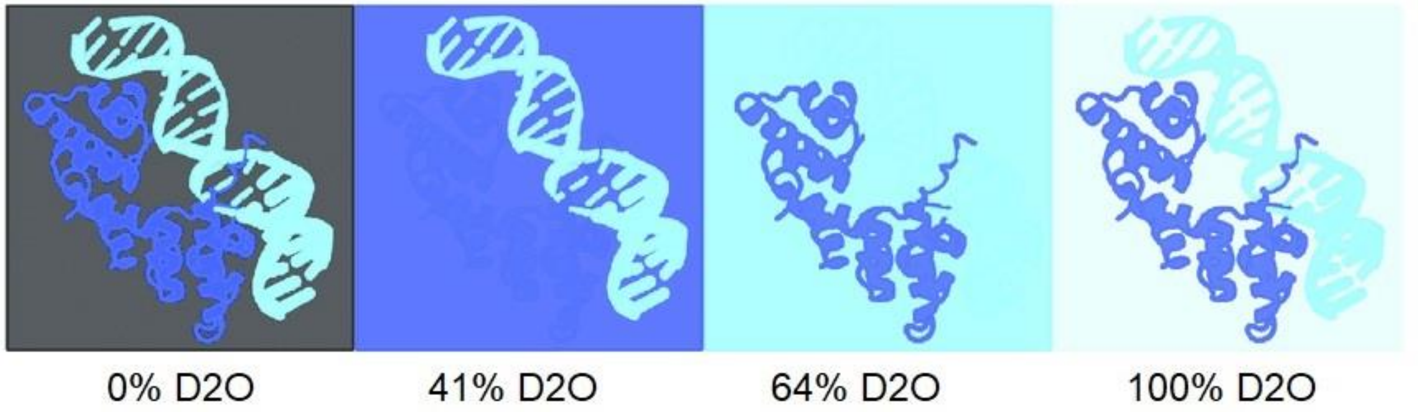
$$\mathrm{FR} = \frac{I_{\mathrm{up}}}{I_{\mathrm{down}}}$$

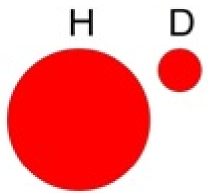
$$I_{\mathrm{echo}} = I_{\mathrm{coh}} f_{\mathrm{coh}}(\tau) - \frac{1}{3} I_{\mathrm{inc}} f_{\mathrm{inc}}(\tau)$$

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

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

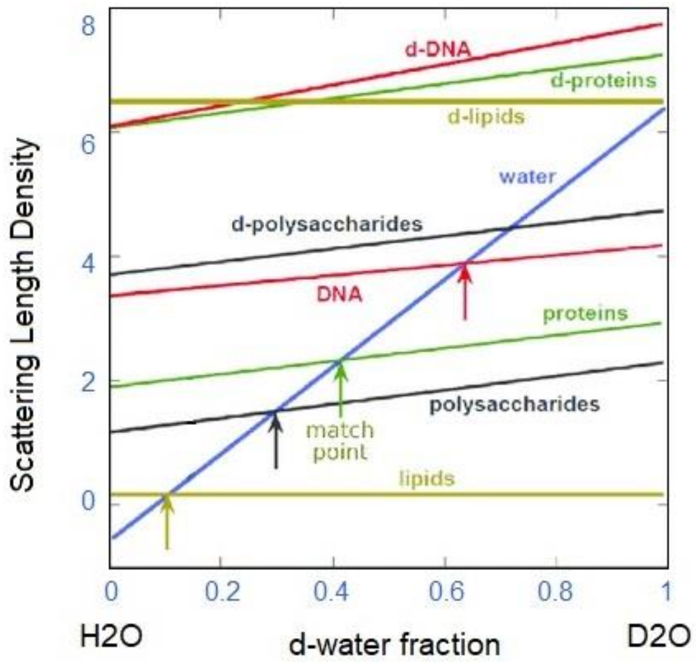
Deuterium labeling and contrast variation





Neutron cross section is isotope dependent

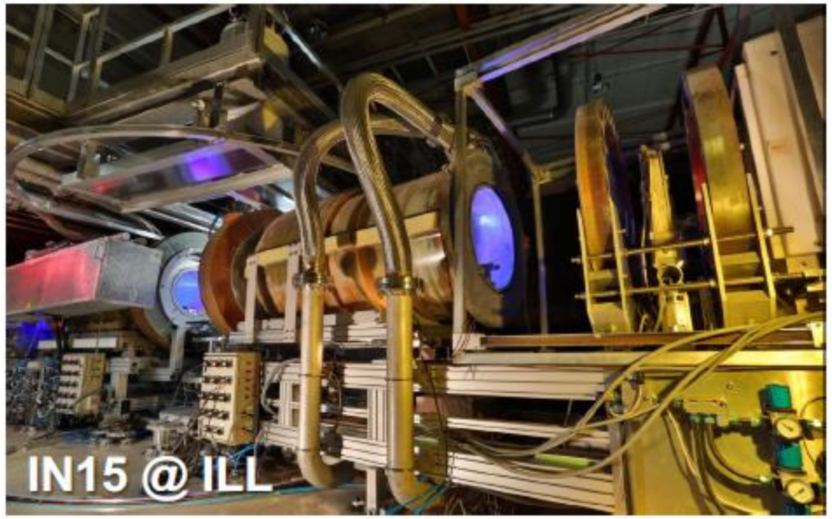
Isotope	b
^{1}H, Hydrogen	-3.7406(11)
^{2}H, Deuterium	6.671(4)
^{3}H, Tritium	4.792(27)



Controlled mixing of ^{1}H and ^{2}H allows contrast to be changed; very powerful for soft condensed matter.

Figure adapted by L. R. Stingaciu, ORNL, from DOI:10.1016/j.csbj.2016.12.004

NSE spectrometers around the world



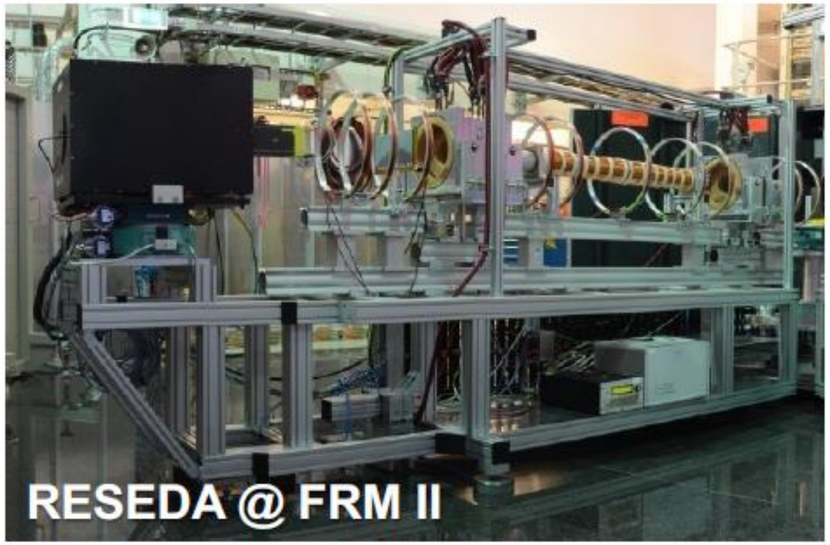
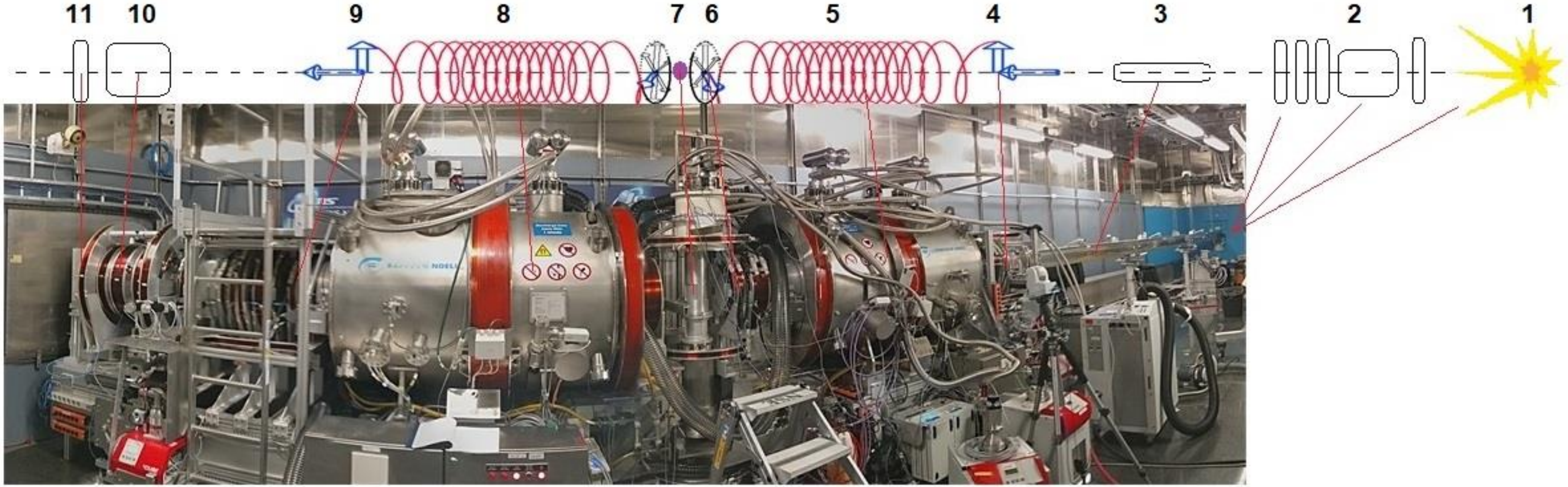


Image sources: Institute Laue-Langevin, Grenoble, France and Research Reactor (FRM II) Munich, Germany

SNS-NSE, the Neutron Spin Echo spectrometer @ SNS

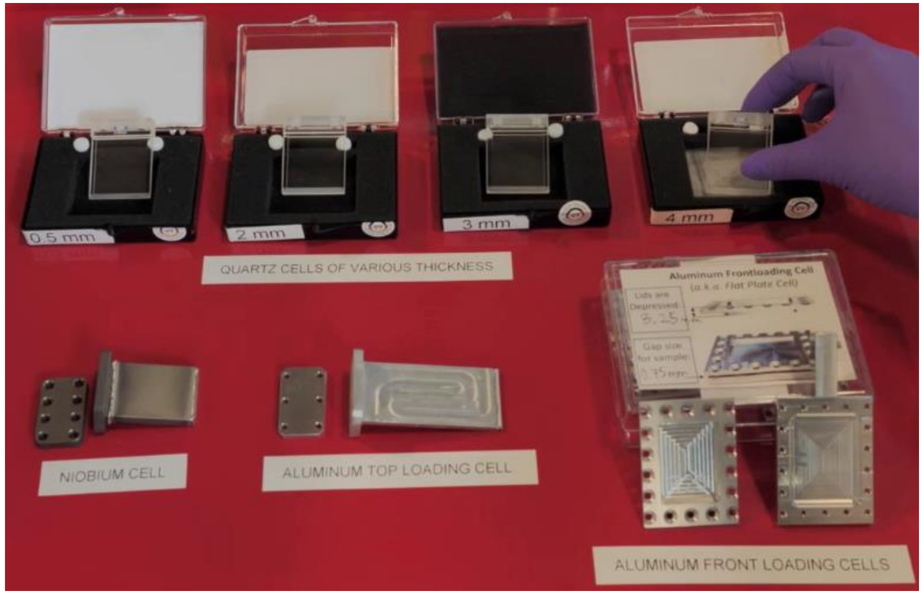


1 = neutron source; 2 = choppers-bender-polarizer-secondary shutter system; 3 = beam transport guides;
4 = pi/2 flipper for first 90° spin-turn; 5 = first precession zone; 6 = pi flipper for 180° spin-rotation;
7 = sample area and sample environment (cryo-furnace is shown here); 8 = second precession zone;
9 = pi/2 flipper for second 90° spin-turn; 10 = analyzer; 11 = detector.

Stingaciu L., "Study of Protein Dynamics via Neutron Spin Echo Spectroscopy", *JoVE,* **182,** e61862 (2022).

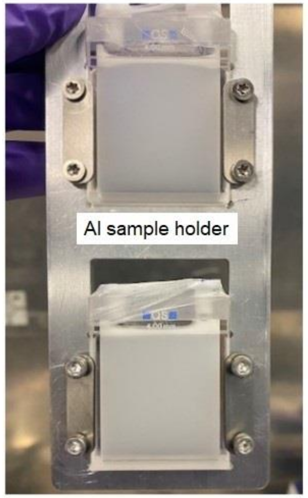
SNS-NSE sample environment & sample cells

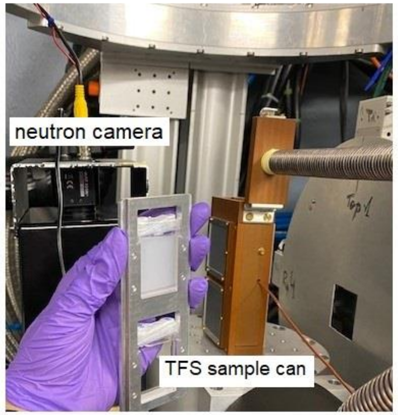
Temperature Forcing System (TFS), 275K - 400K

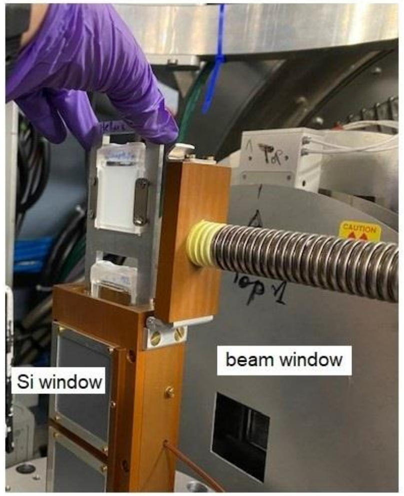


CCR , 5K - 700K

neutrons.ornl.gov/nse



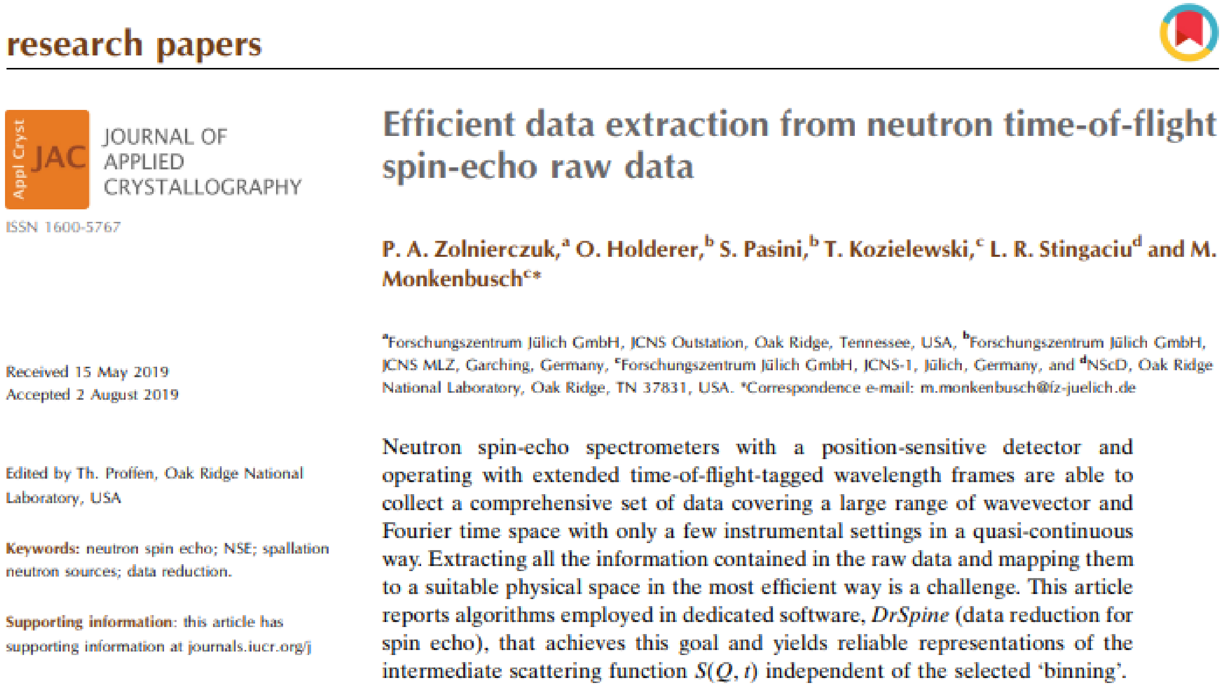




Stingaciu L., "Study of Protein Dynamics via Neutron Spin Echo Spectroscopy", *JoVE*, **182,** e61862 (2022).

SNS-NSE Data Reduction For Spin Echo Experiments

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



research papers

JOURNAL OF APPLIED CRYSTALLOGRAPHY

ISSN 1600-5767

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

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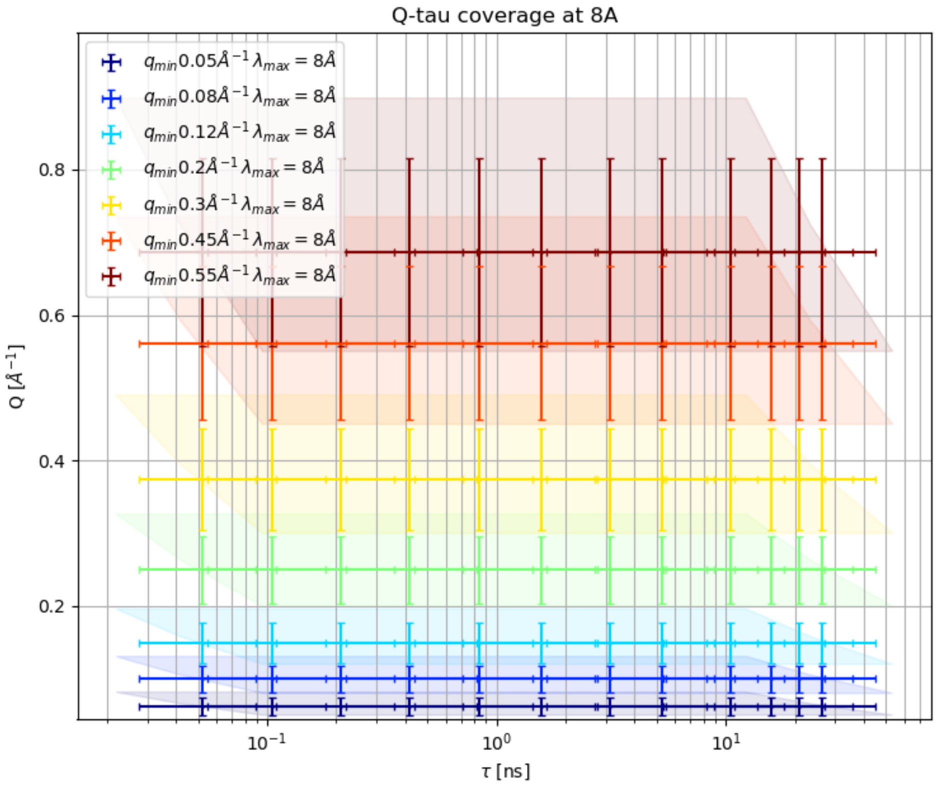
Supporting information: this article has supporting information at journals.iucr.org/j

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

SNS-NSE and TOF

- ❑ $\Delta\lambda$ = (5 - 8) Å
- ❑ $2\theta = 3.6^{\circ}$ Q = 0.02 − 0.15 $Å^{-1}$
- ❑ $2\theta = 37^{\circ}$ Q = 0.45 − 0.85 $Å^{-1}$



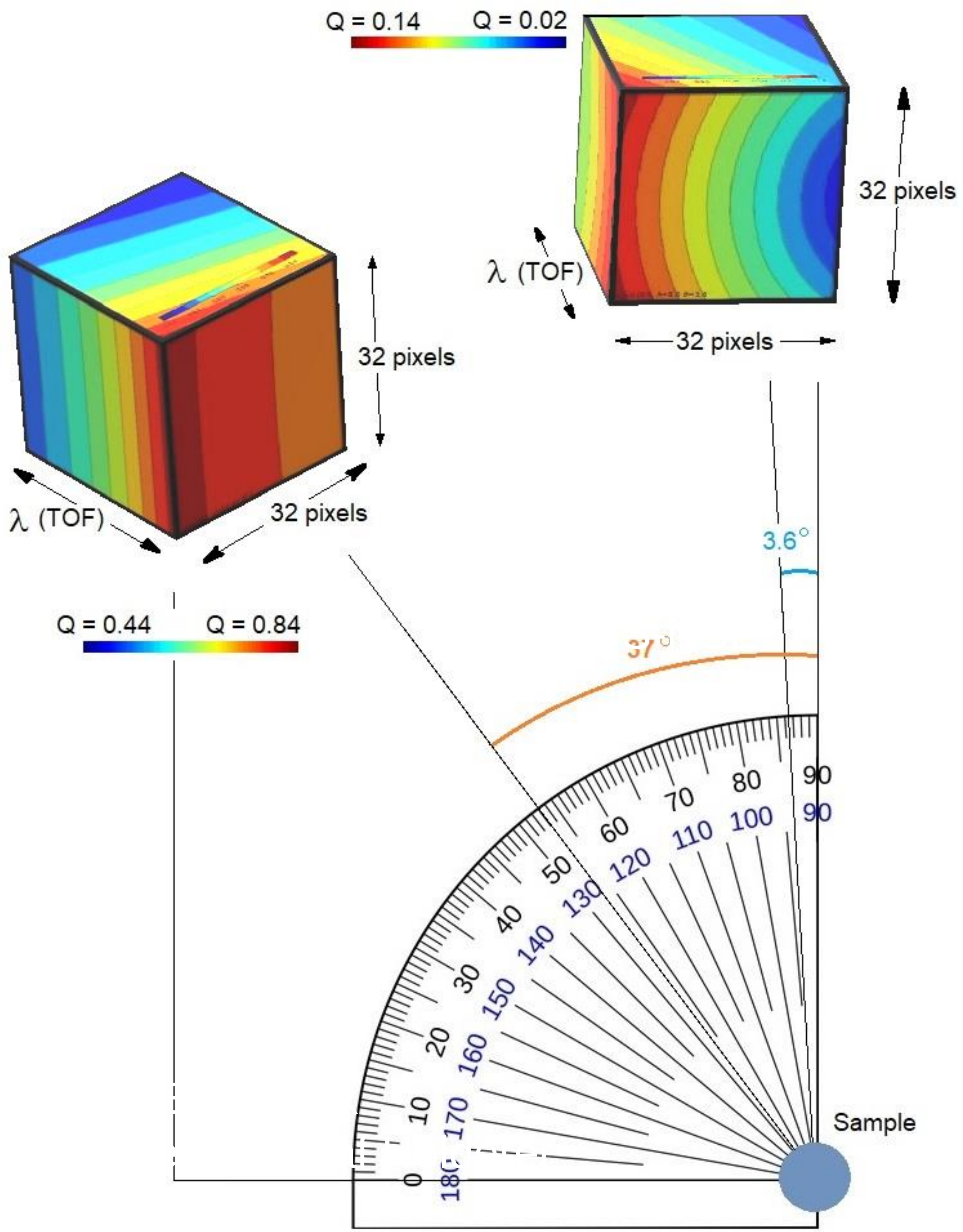
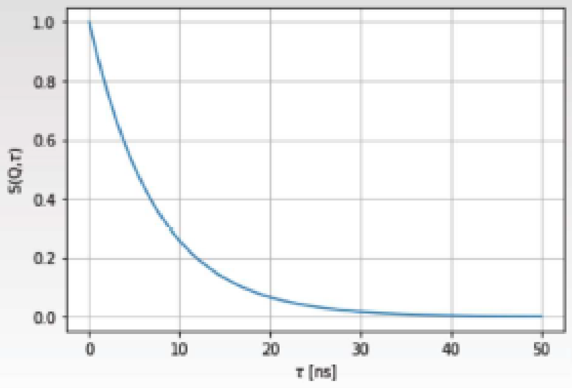


Figure idea and cubes design by Piotr A. Zolnierczuk, 3D rendering by L.R. Stingaciu

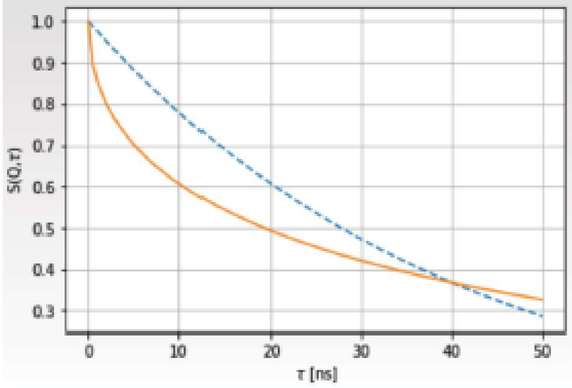
Typical SNS-NSE data models

Simple Diffusion



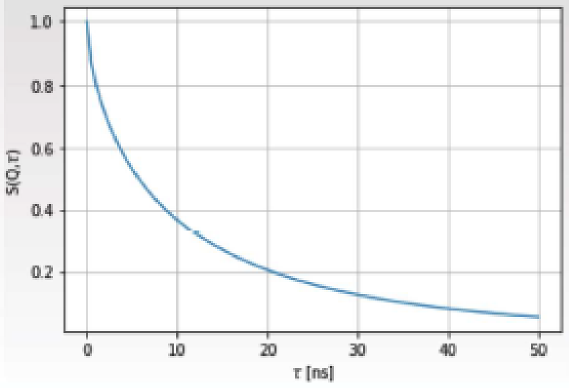
$$\frac{S(q,\tau)}{S(q,0)} = \exp(-DQ^2\tau)$$

KWW



$$\frac{S(q,\tau)}{S(q,0)} = \exp\left(-\left(\frac{\tau}{\tau_0}\right)^{\beta}\right)$$

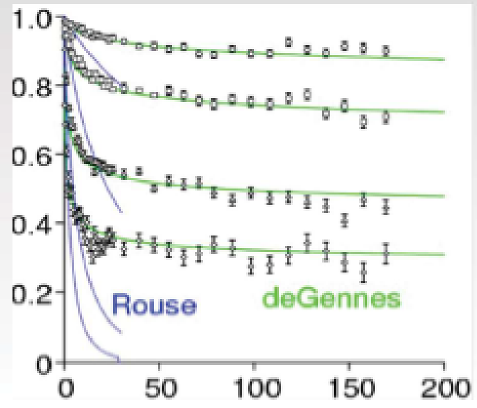
Zilman-Granek



$$\frac{S(q,\tau)}{S(q,0)} = \exp(-(\Gamma(q)\tau)^{2/3})$$

$$\Gamma(q) = \alpha\left(\frac{k_BT}{\kappa}\right)^{1/2}\frac{k_BT}{\eta}\, q^3$$

More complicated..



$$\frac{S(q,\tau)}{S(q,0)} = [1-\exp\left(-\left(\frac{\mathrm{qd}}{6}\right)^2\right)]\, S_{loc} + \exp\left(-\left(\frac{\mathrm{qd}}{6}\right)^2\right) S_{esc}$$

courtesy of Piotr A. Zolnierczuk, ORNL

SNS-NSE research highlights

dynamics of soft matter at nano- to meso-scale

Coherent dynamics in polymers, glassy systems, bio-macromolecules

Magnetic Dynamics, Spin glasses & spin fluids

Domain and allosteric motions in proteins

Shape fluctuations

Diffusion processes

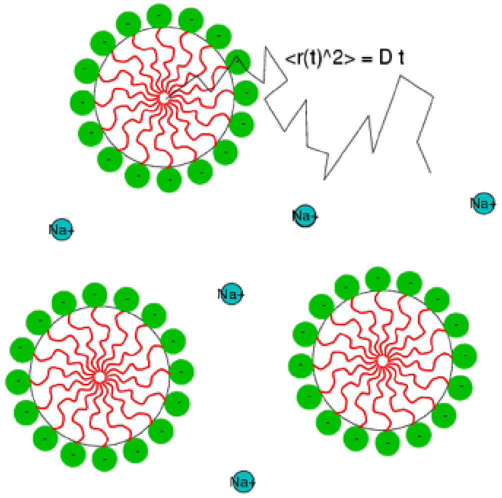
Hydrogen jump diffusion

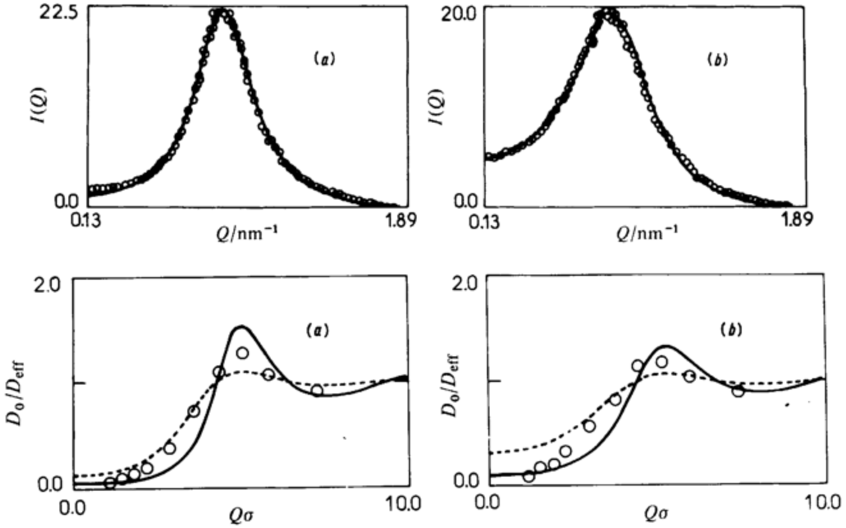
Interaction of solvent molecules with surfaces

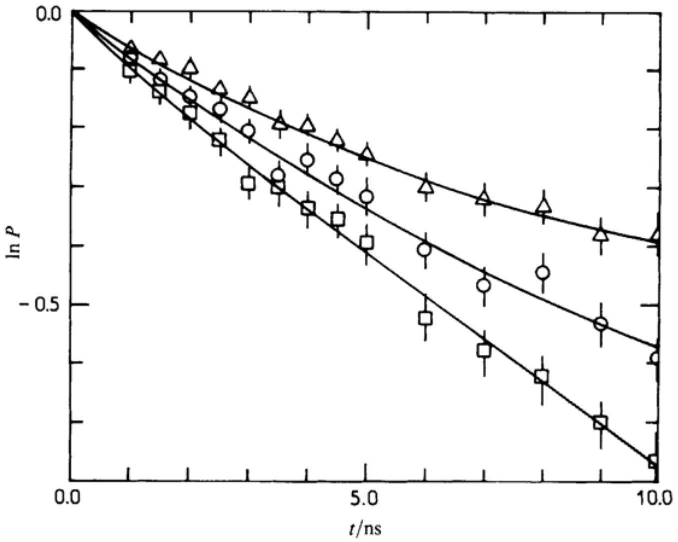
Short range translational, rotational and tumbling diffusive motions

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*







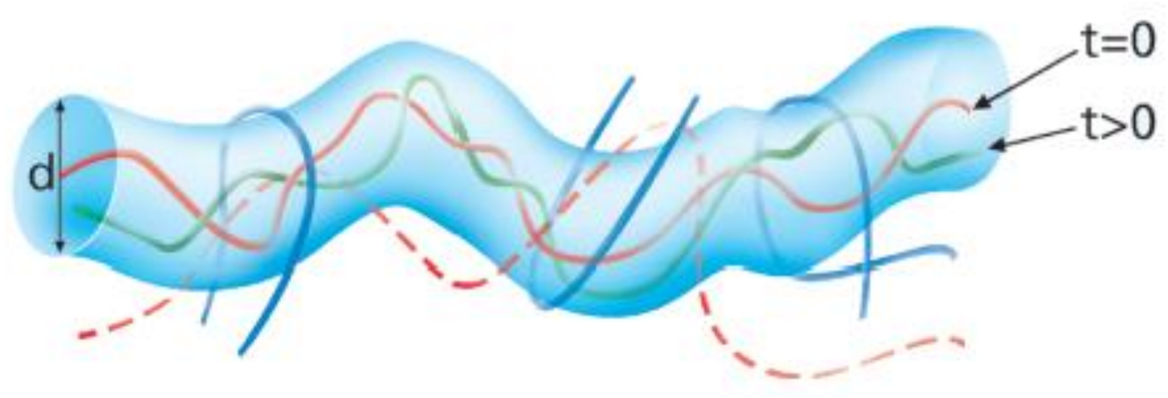
$$\frac{I(Q,t)}{I(Q,0)} = e^{-D_{\mathrm{eff}}(Q)Q^2 t}$$

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

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

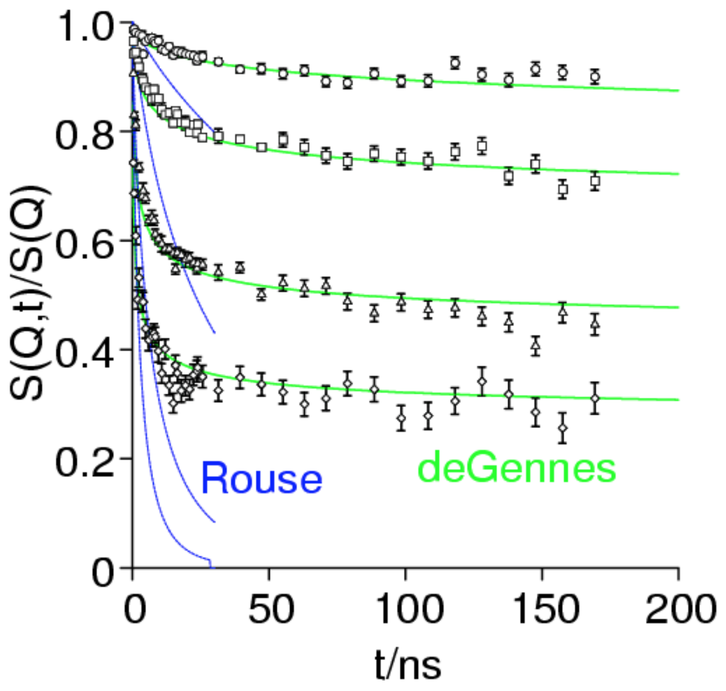
Motions in entangled polymer melts

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



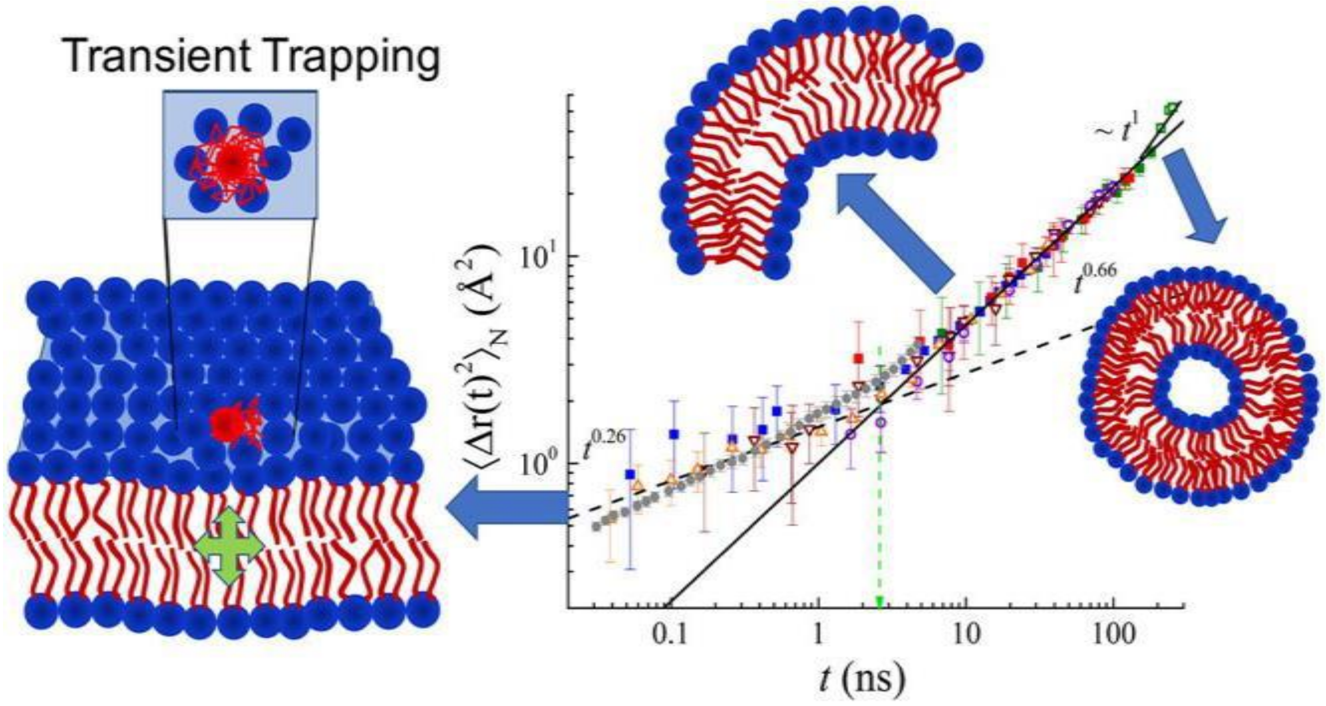
$$\frac{S(Q,\tau)}{S(Q,0)} = [1 - F(Q)]S^{loc} + \mathrm{F(Q)}\ S^{esc}$$

- 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



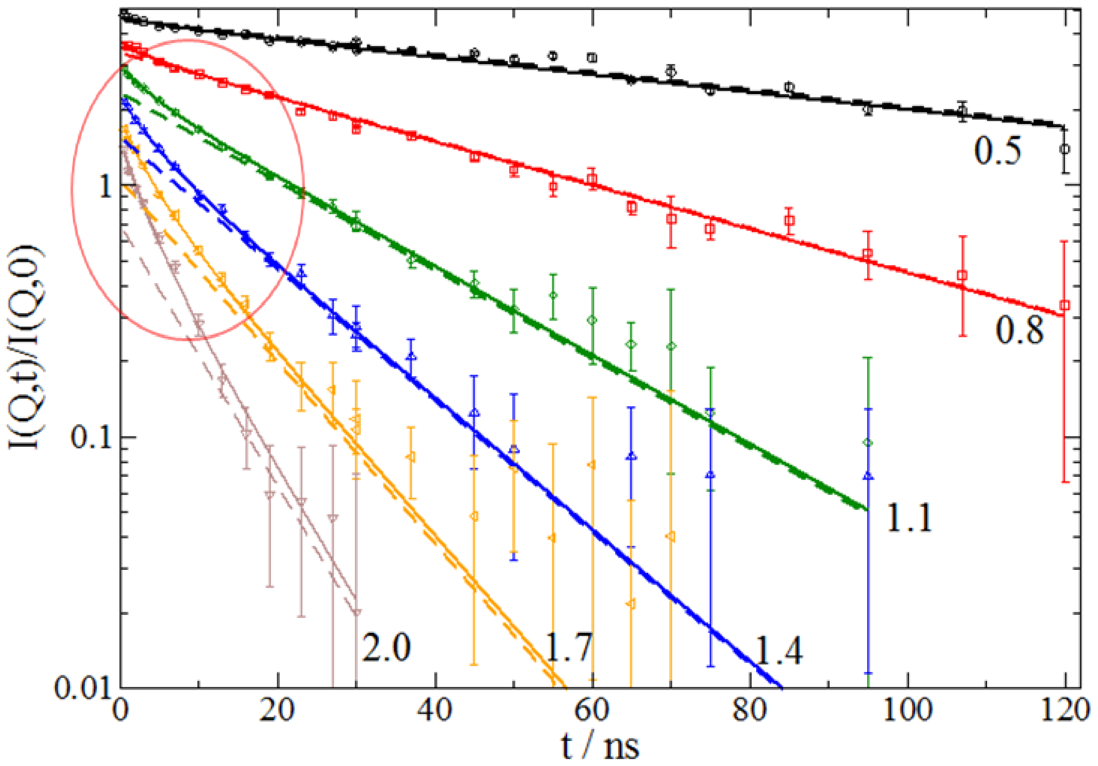
Proposed mechanism of transient trapping and mean square displacement ⟨Δr(t)^2 ⟩N as a function of Fourier time

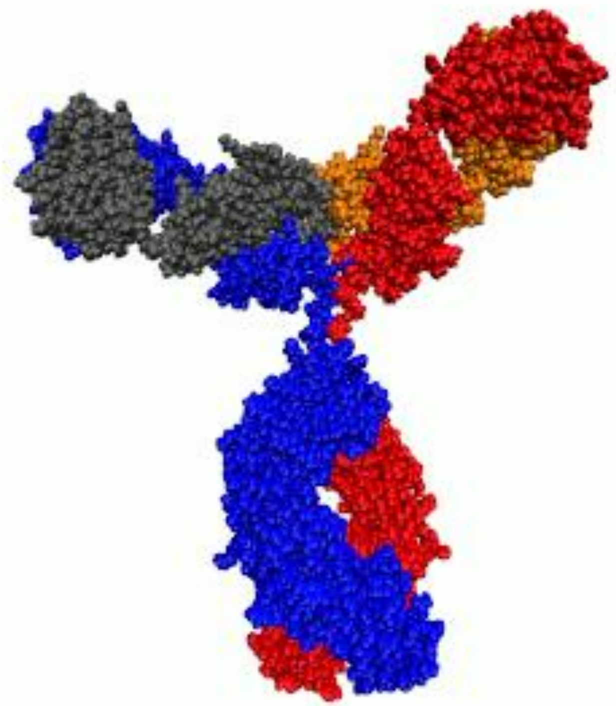
- ❑ Friction at the interface water - liposomes plays a minor role
- ❑ The center of mass diffusion of liposomes and the transient trapping of lipids define the range in which ZG model can be applied

Proteins domains dynamics

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

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

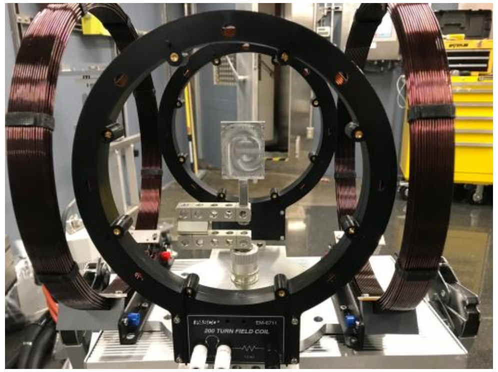




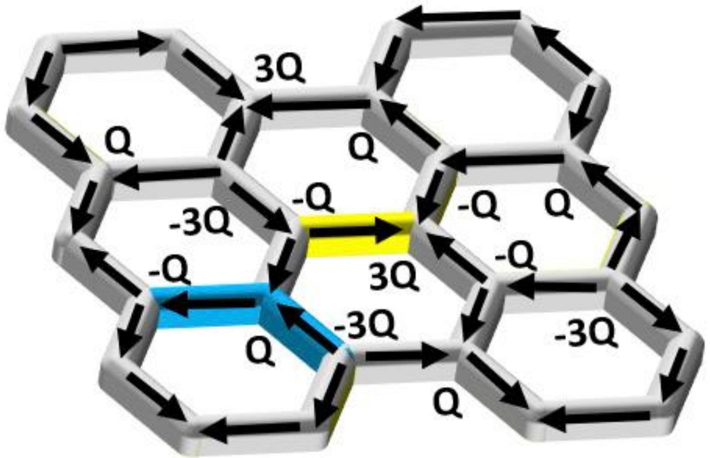
Three protein fragments in harmonic potential connected by flexible linkers

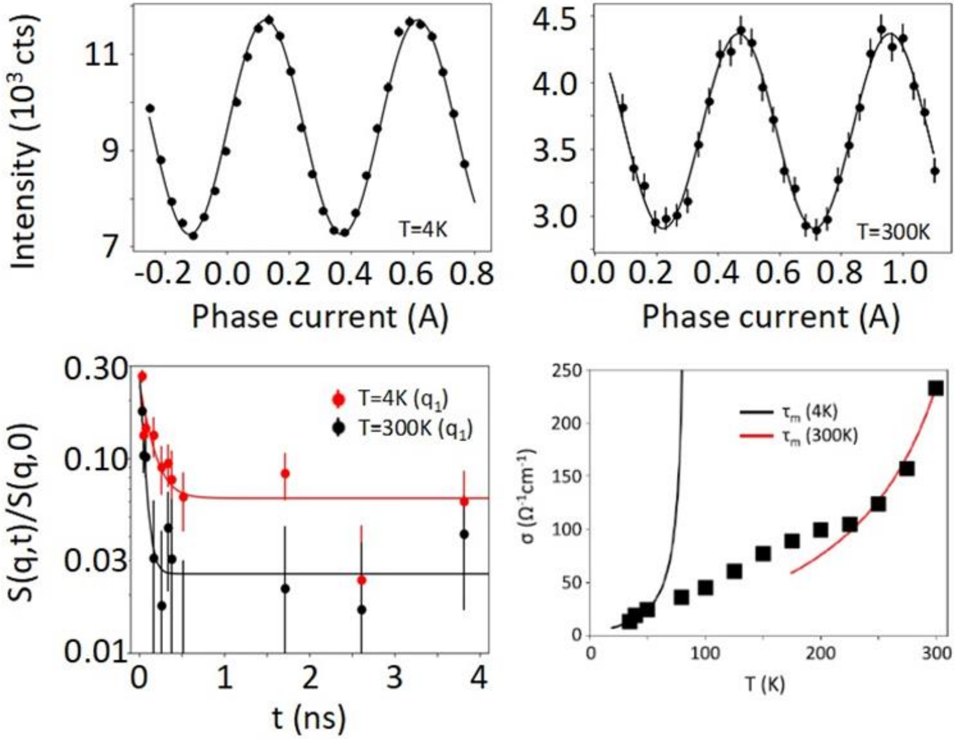
Spin dynamics in frustrated magnets

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



Polarization coils setup at SNS-NSE





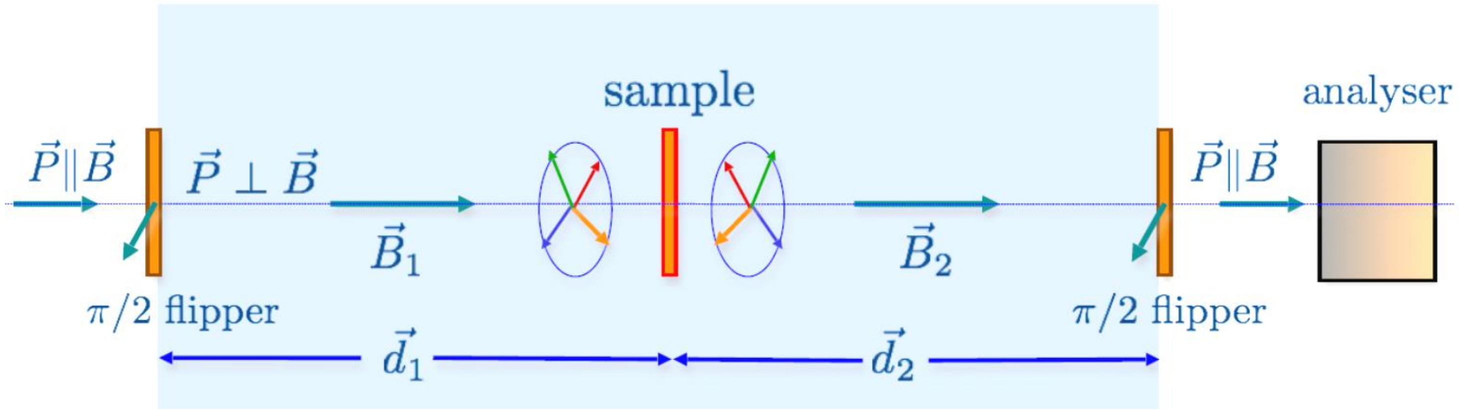
Magnetic charges of ±Q unit and ±3Q accumulate on the vertices of the honeycomb lattice

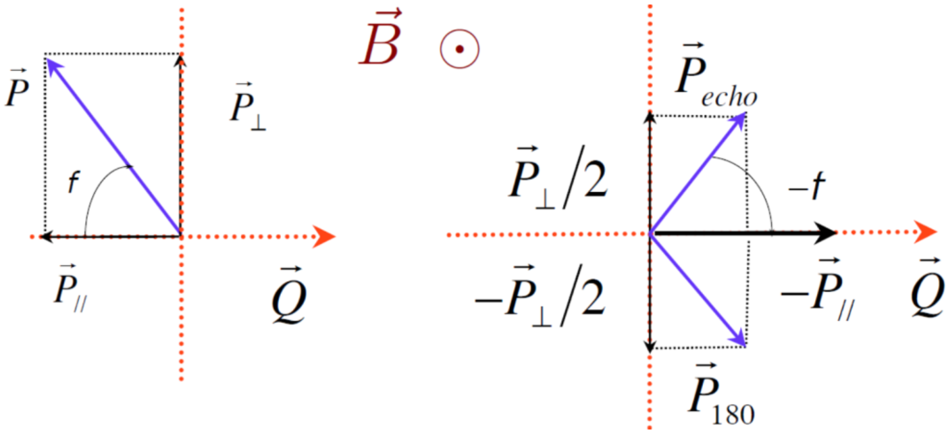
The charge defect relaxes between nearest neighbors

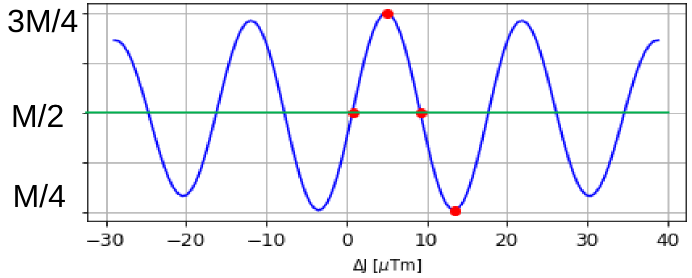
Neutron Spin Echo variations

Paramagnetic NSE

Sample is the π-flipper







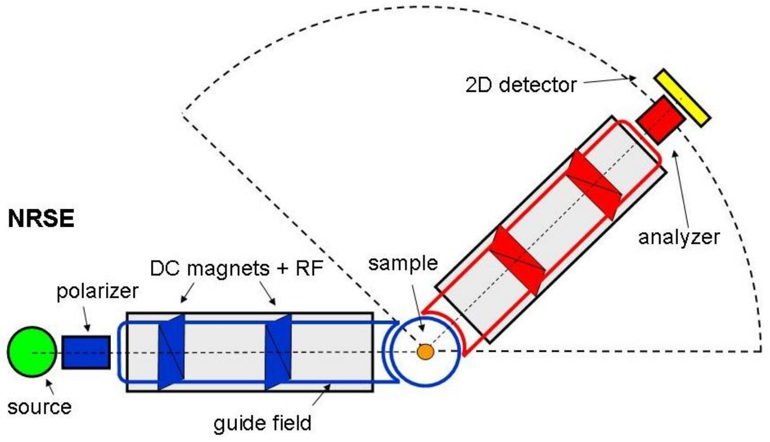
http://sons.uniroma2.it/ericeneutronschool/wp-content/uploads/2016/12/NSE_MAgnetism_Pappas.pdf

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



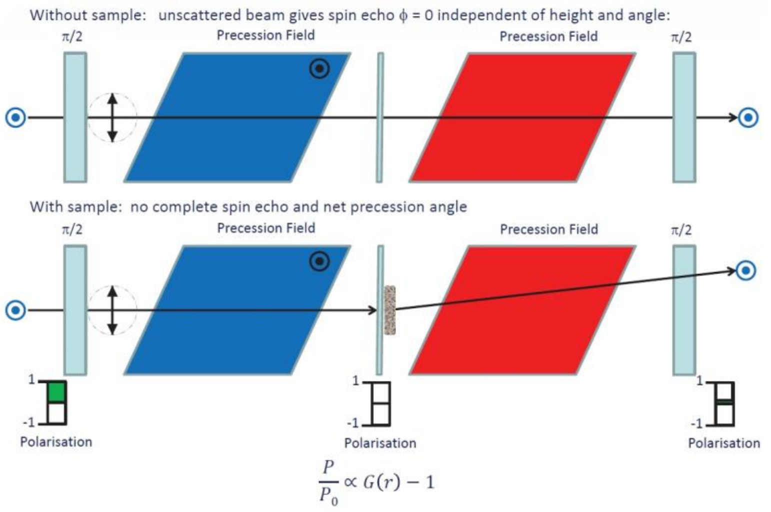
RF field instead of solenoid

- compact design
- shorter Fourier times

SESANS

Spin Echo SANS

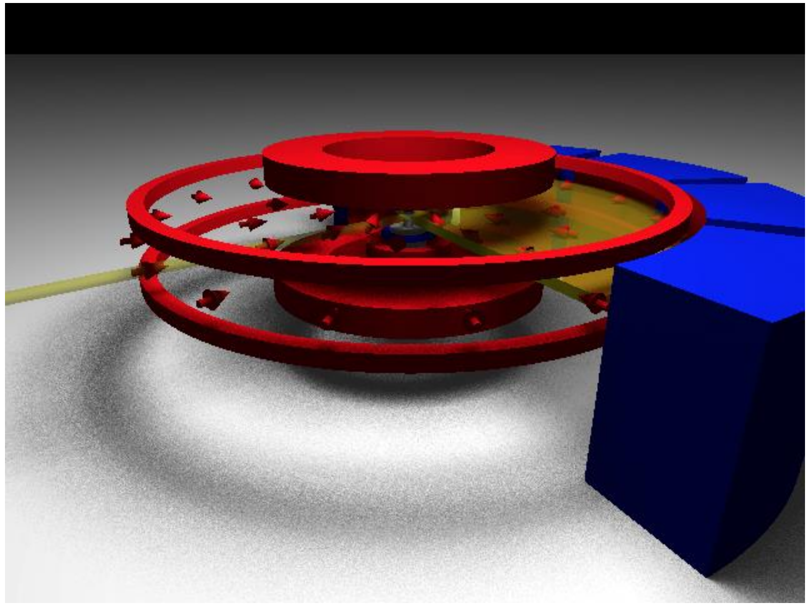
http://larmor.weblog.tudelft.nl/files/2013/07/S_Rogers_SANS_SESANS1.pdf

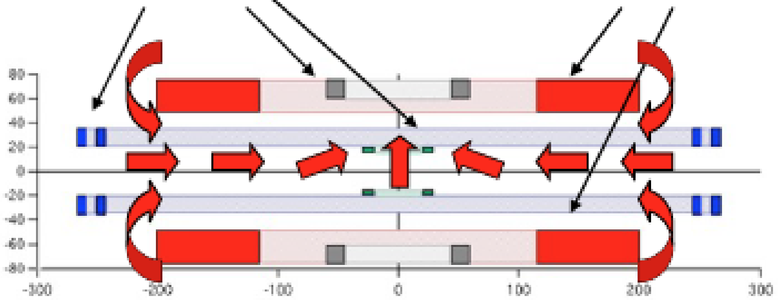


Spin Echo encoded SANS

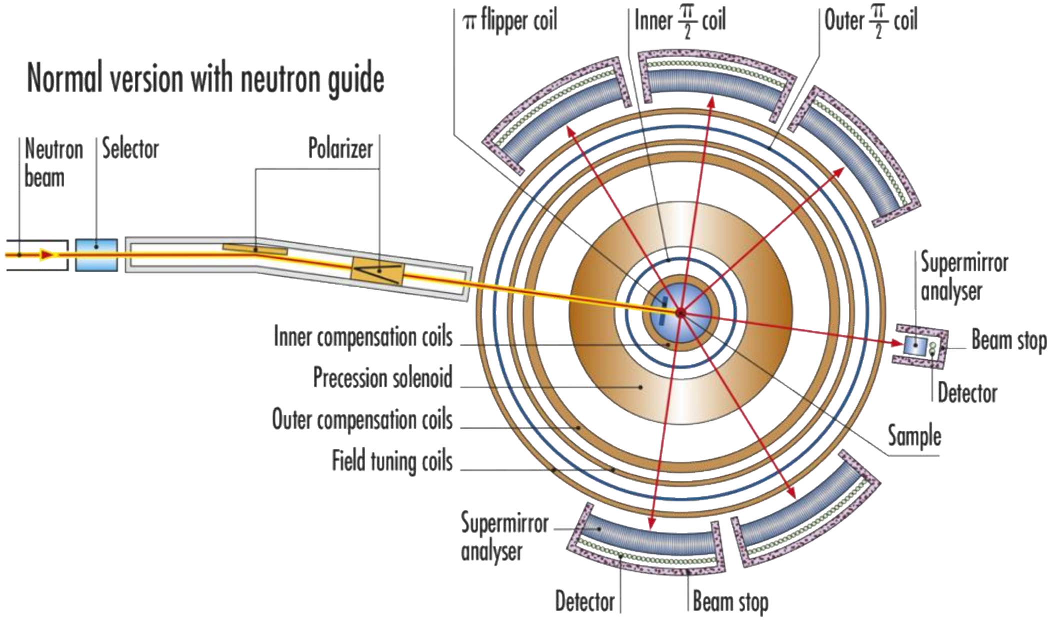
- tilted magnetic field
- angle encoded in spin precession

Wide angle spin echo





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

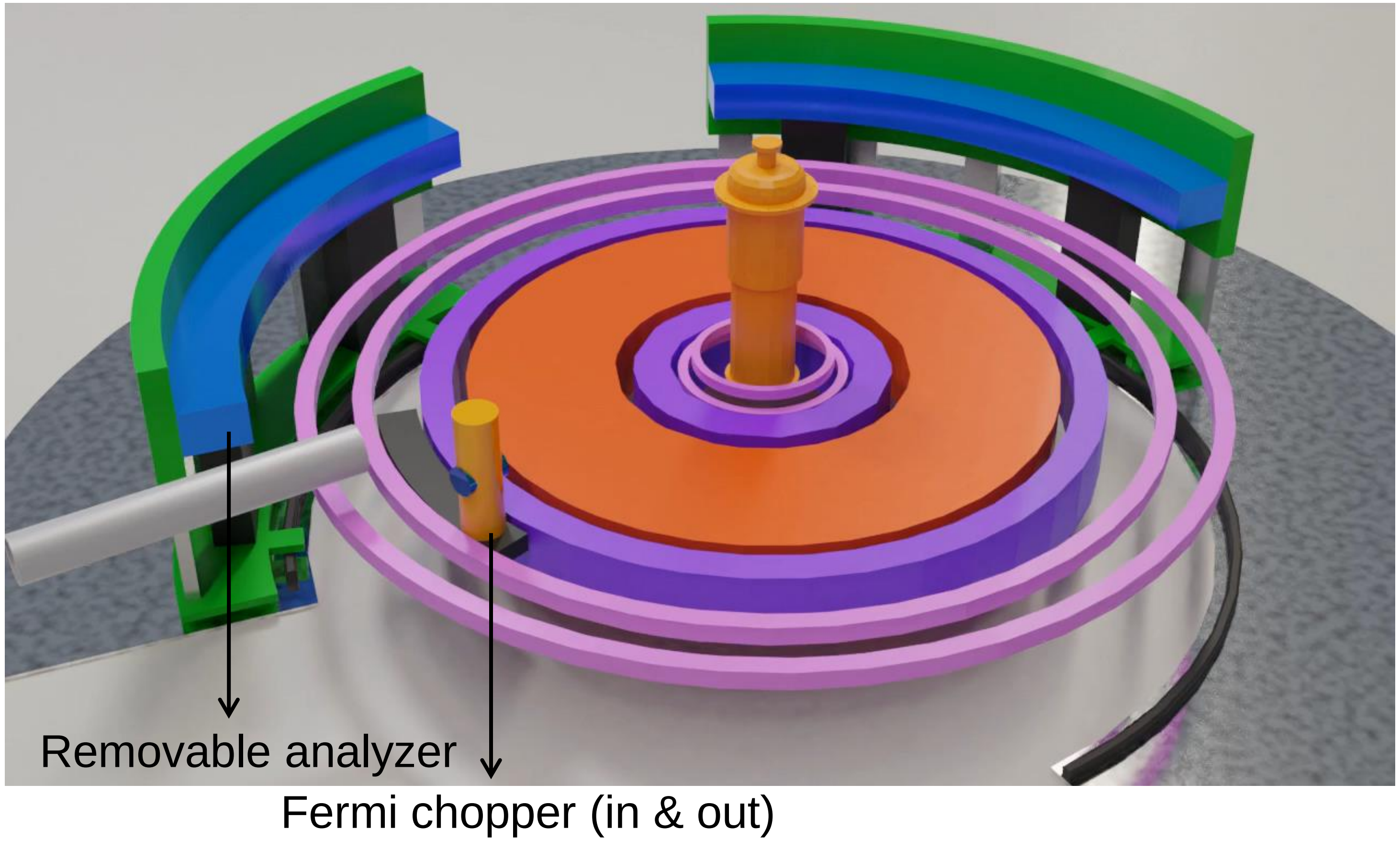


- Large angular coverage
- Higher Q (up to 3Å^{-1})

Oak Ridge National Laboratory

EXPANSE, the wide-angle spin echo spectrometer at STS

- Expand the capability by another level: dual-functional instrument
- With the high-speed Fermi chopper, instrument can be used as a direct-geometry inelastic neutron spectrometer measuring $S(Q,\omega)$



Available wavelength	4 - 16 Å
Wavelength band	~4Å (15 Hz)
Detector solid angle	180º x 2.5º array of He^3 tube detectors
Momentum transfer range	0.05 – 3.14 $Å^{-1}$
Fourier time range	30 ps – 90 ns (using 4 - 12Å)
Direct geometry mode	Energy resolution 10-300 μeV Incident energy range 0.5 – 9 meV (corresponds to 0.1 ps – 100 ps)

courtesy of Changwoo Do, ORNL

Summary – NSE technique 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 or highly concentrated samples

Reference reading

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

THANK YOU

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

NXS Lecture - Neutron Spin Echo - Laura Stingaciu

Neutron Spin Echo Spectrometer | Neutron Science at ORNL