Introduction to
Neutron Spin Echo
Spectroscopy

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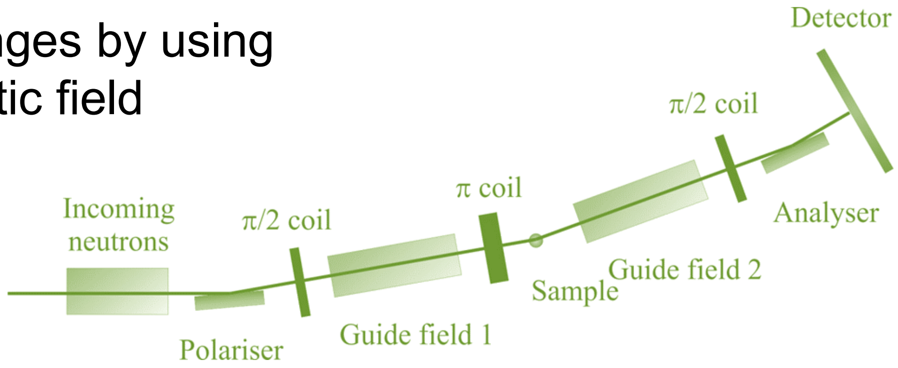
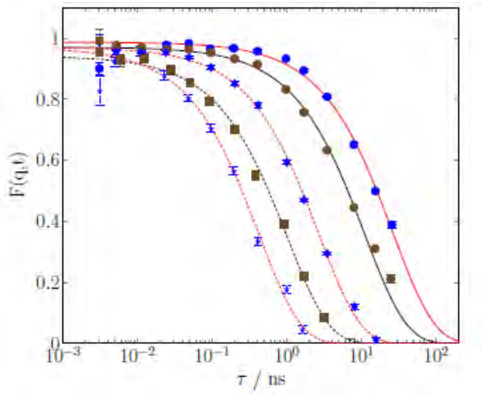
1. Basic Principles of NSE
2. NSE Spectrometers and variations
3. The NSE Spectrometer @ SNS
4. Science Examples
5. Summary and References

Neutron Spin Echo in a Nutshell

- Measures very small velocity changes by using neutron spin precession in magnetic field



- Broad $\Delta\lambda/\lambda$ and high resolution
- Intermediate Scattering Function: $I(Q,\tau)$
- Counting intensive and large samples
- Complementary to SANS/SAXS



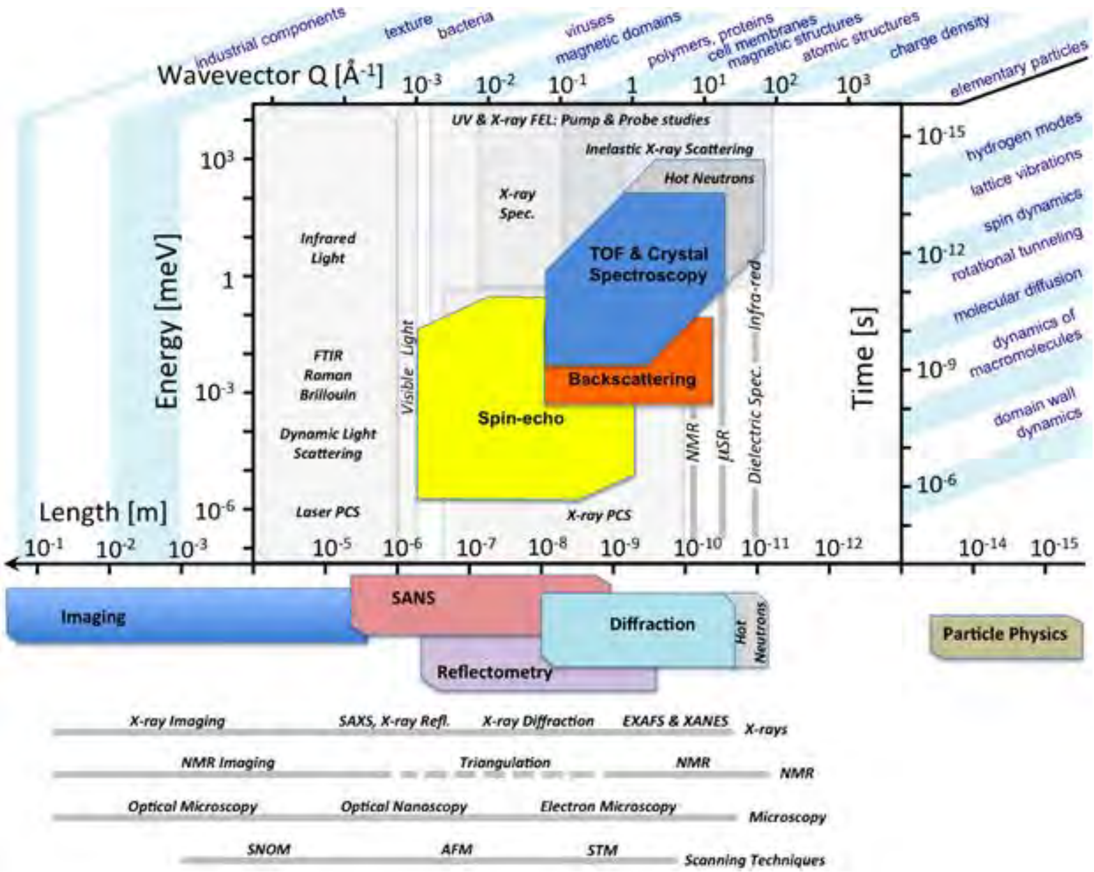
Neutron and X-Ray Instruments Landscape

<u>NSE can study:</u>

- Coherent Dynamics
  - Diffusion
  - Shape fluctuations
  - Polymer dynamics
  - Glassy systems

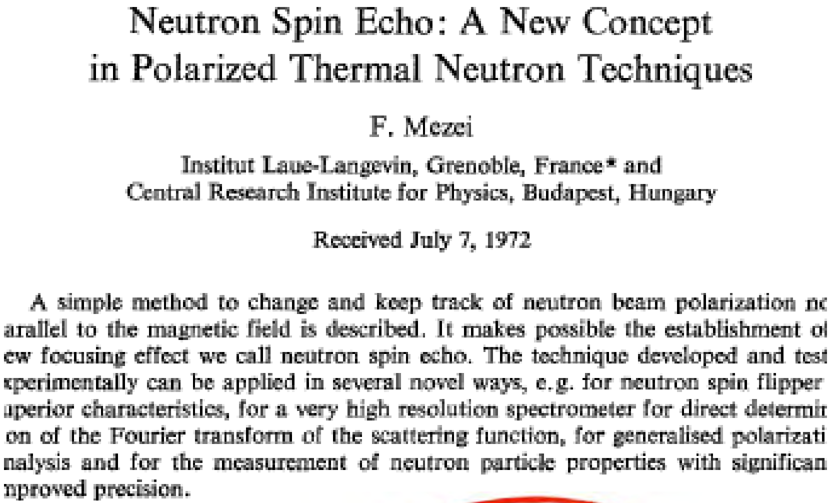
- Incoherent Dynamics
  - Hydrogen

- Magnetic Dynamics
  - Spin Glasses



NSE : From an Idea to a Instrument

1972 → 1978



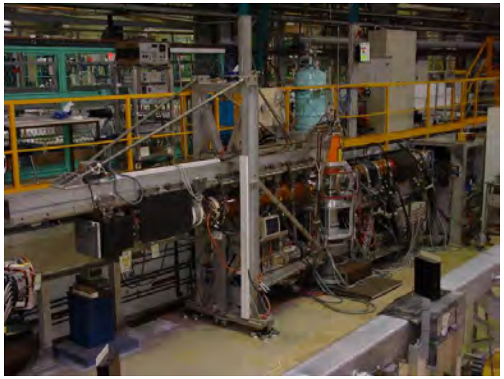
Neutron Spin Echo: A New Concept in Polarized Thermal Neutron Techniques

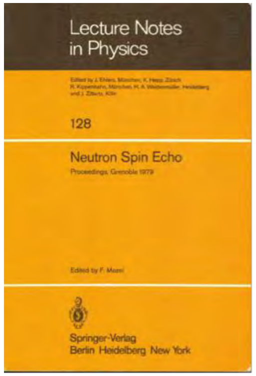
F. Mezei

Institut Laue-Langevin, Grenoble, France* and
Central Research Institute for Physics, Budapest, Hungary

Received July 7, 1972

A simple method to change and keep track of neutron beam polarization nc
arallel to the magnetic field is described. It makes possible the establishment of
ew focusing effect we call neutron spin echo. The technique developed and test
xperimentally can be applied in several novel ways, e.g. for neutron spin flipper
uperior characteristics, for a very high resolution spectrometer for direct determi
on of the Fourier transform of the scattering function, for generalised polarizati
nalysis and for the measurement of neutron particle properties with significan
nproved precision.





Lecture Notes in Physics

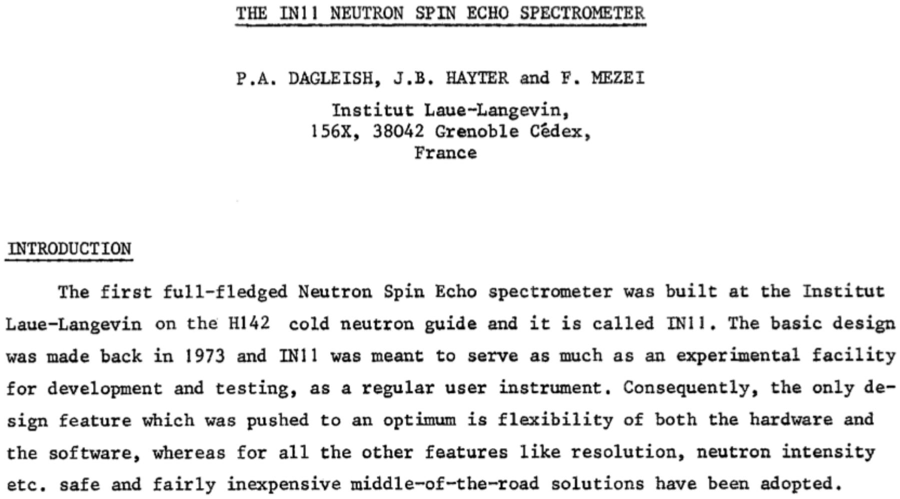
128

Neutron Spin Echo

Proceedings, Grenoble 1979

Edited by F. Mezei

Springer-Verlag
Berlin Heidelberg New York



THE IN11 NEUTRON SPIN ECHO SPECTROMETER

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156X, 38042 Grenoble Cêdex,
France

INTRODUCTION

The first full-fledged Neutron Spin Echo spectrometer was built at the Institut Laue-Langevin on the H142 cold neutron guide and it is called IN11. The basic design was made back in 1973 and IN11 was meant to serve as much as an experimental facility for development and testing, as a regular user instrument. Consequently, the only design feature which was pushed to an optimum is flexibility of both the hardware and the software, whereas for all the other features like resolution, neutron intensity etc. safe and fairly inexpensive middle-of-the-road solutions have been adopted.

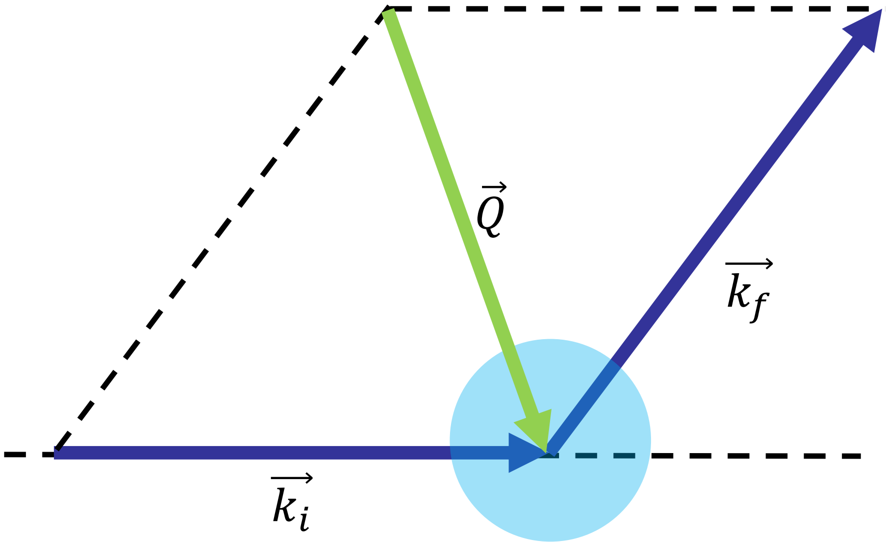
Basic Principles of Neutron Spin Echo

Inelastic Neutron Scattering

Neutron scattering kinematics

$$\Delta E = \hbar\omega = \frac{1}{2}\left(mv_i^2 - mv_f^2\right)$$

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



Dynamic Structure Factor

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\sigma}{4\pi}\frac{k_f}{k_i} N\, S(\vec{Q},\omega)$$

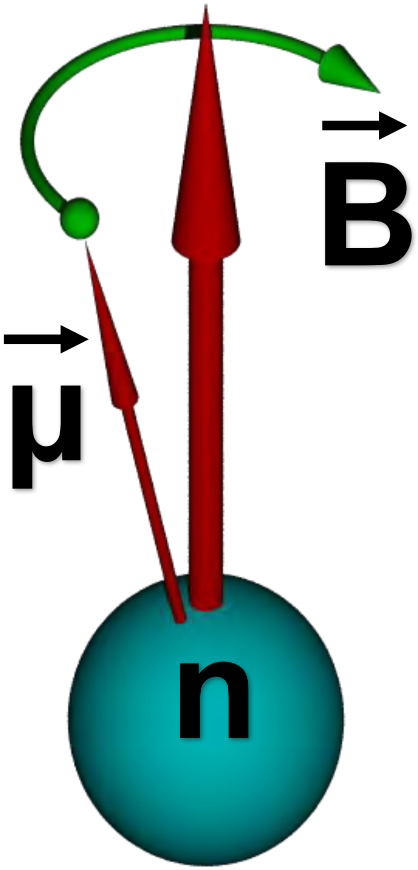
$$|\vec{k}| = \frac{2\pi}{\lambda}$$

$\lambda = \frac{h}{mv}$ (Louis de Broglie, 1924)

Larmor Precession (I)

Bloch Equation

$$\frac{d\vec{\mu}}{dt} = \gamma\vec{\mu} \times \vec{B}$$



Larmor Frequency

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

Neutron Gyromagnetic Ratio

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

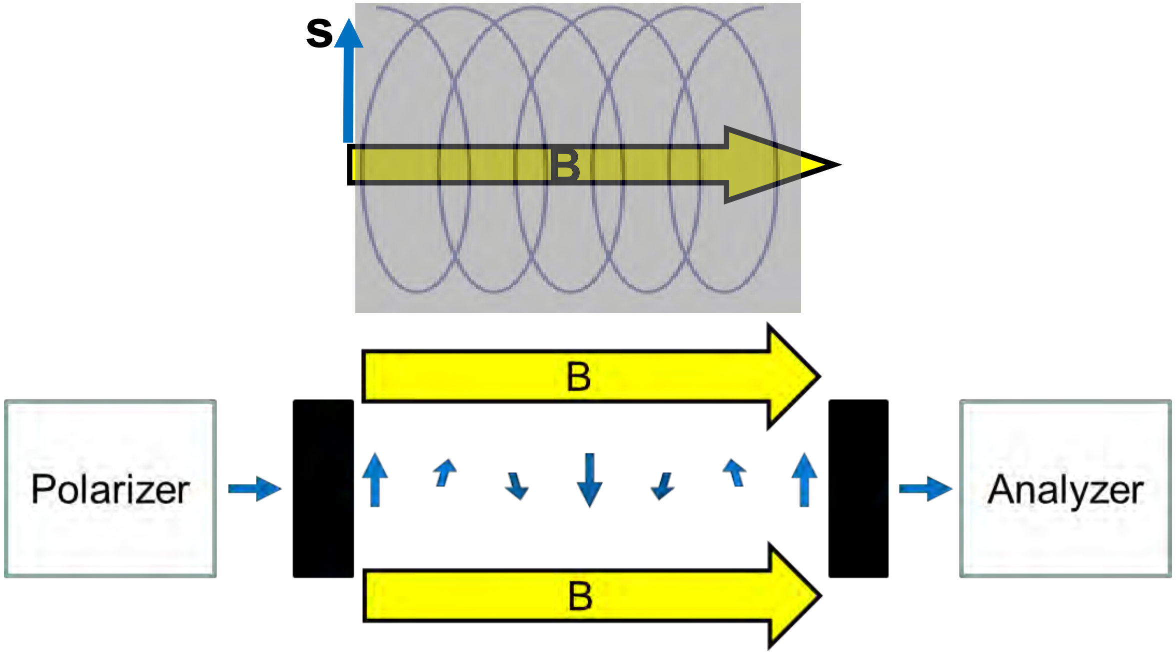
Larmor Precession (II)

Accumulated phase

$$\varphi = \omega_L t = \gamma B l \,\frac{1}{v}$$

or

$$\varphi = \gamma \frac{m}{h} J \lambda$$



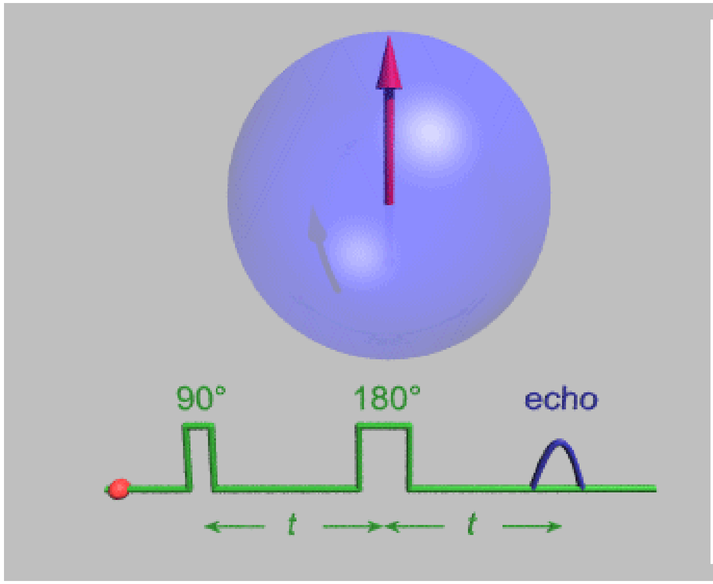
for example:

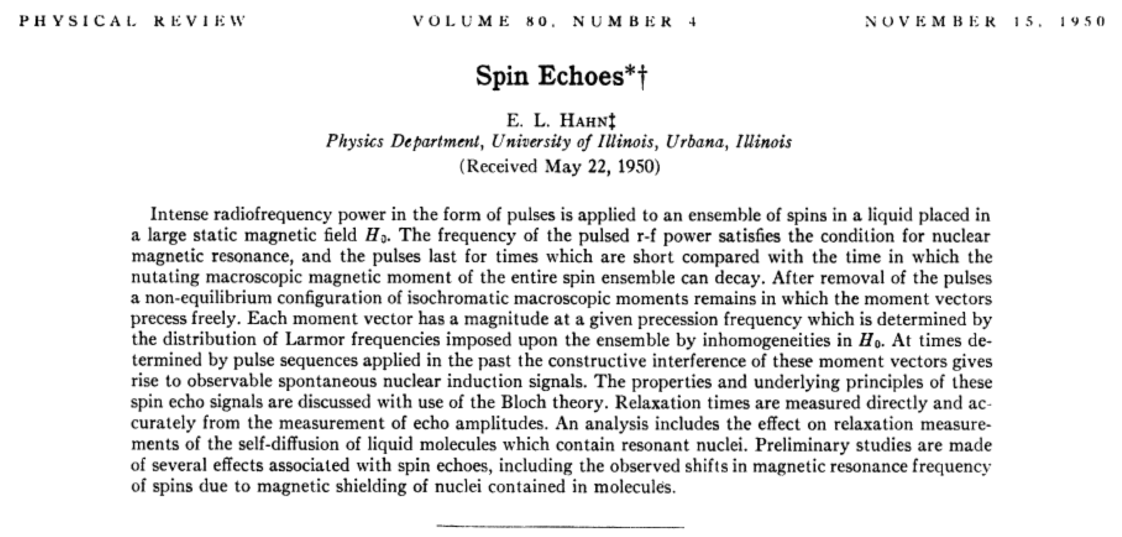
$\lambda = 8\text{Å},\ Bl = 0.5\ \text{Tm}$

$\rightarrow \varphi/2\pi \cong 3 \times 10^4$ [nr. of turns]

Notes: $J \stackrel{\text{def}}{=} Bl$ or more precisely $J \stackrel{\text{def}}{=} \int \vec{B} \cdot \vec{dl}$

HAHN Echo




PHYSICAL REVIEW VOLUME 80, NUMBER 4 NOVEMBER 15, 1950

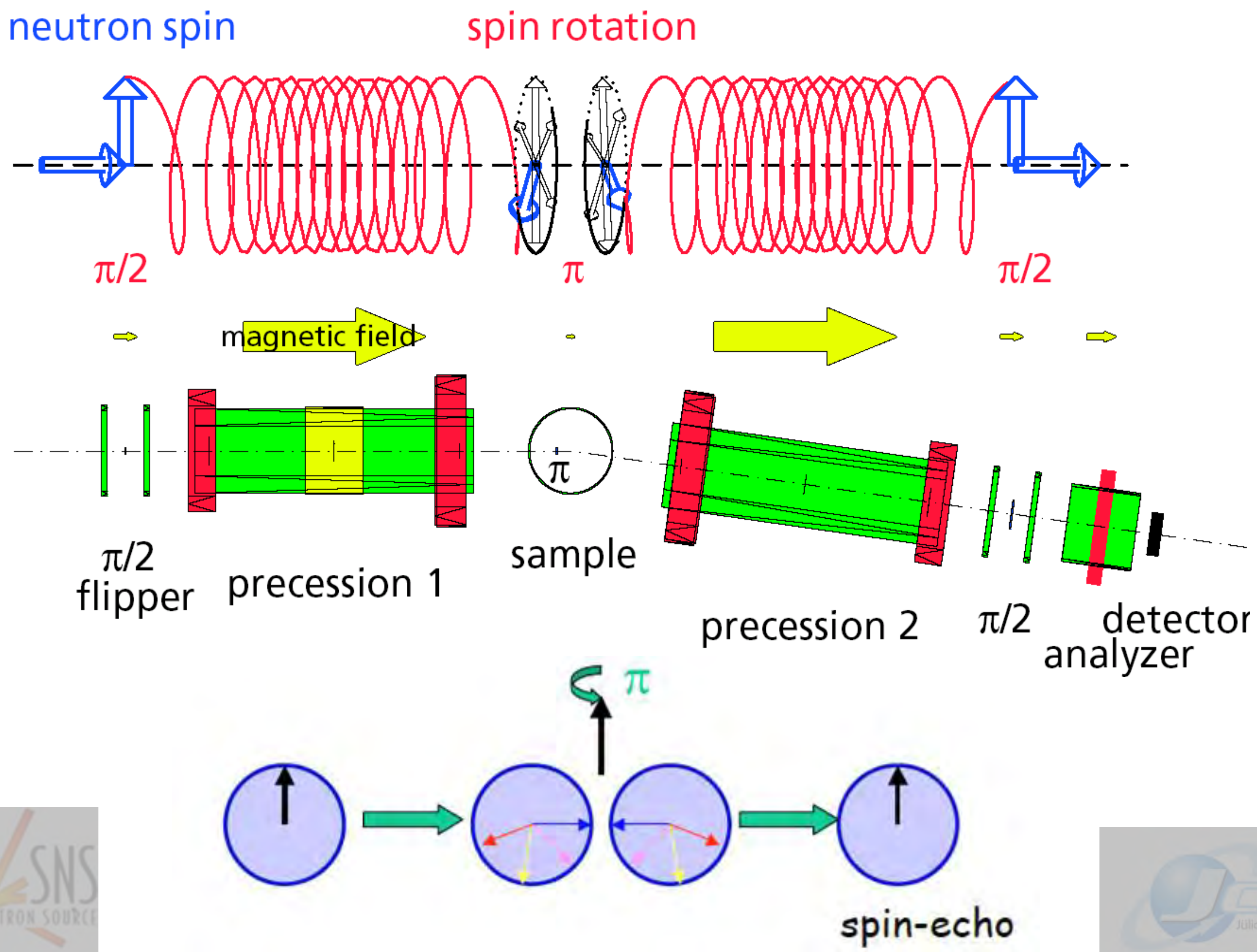
Spin Echoes*†

E. L. Hahn‡
Physics Department, University of Illinois, Urbana, Illinois

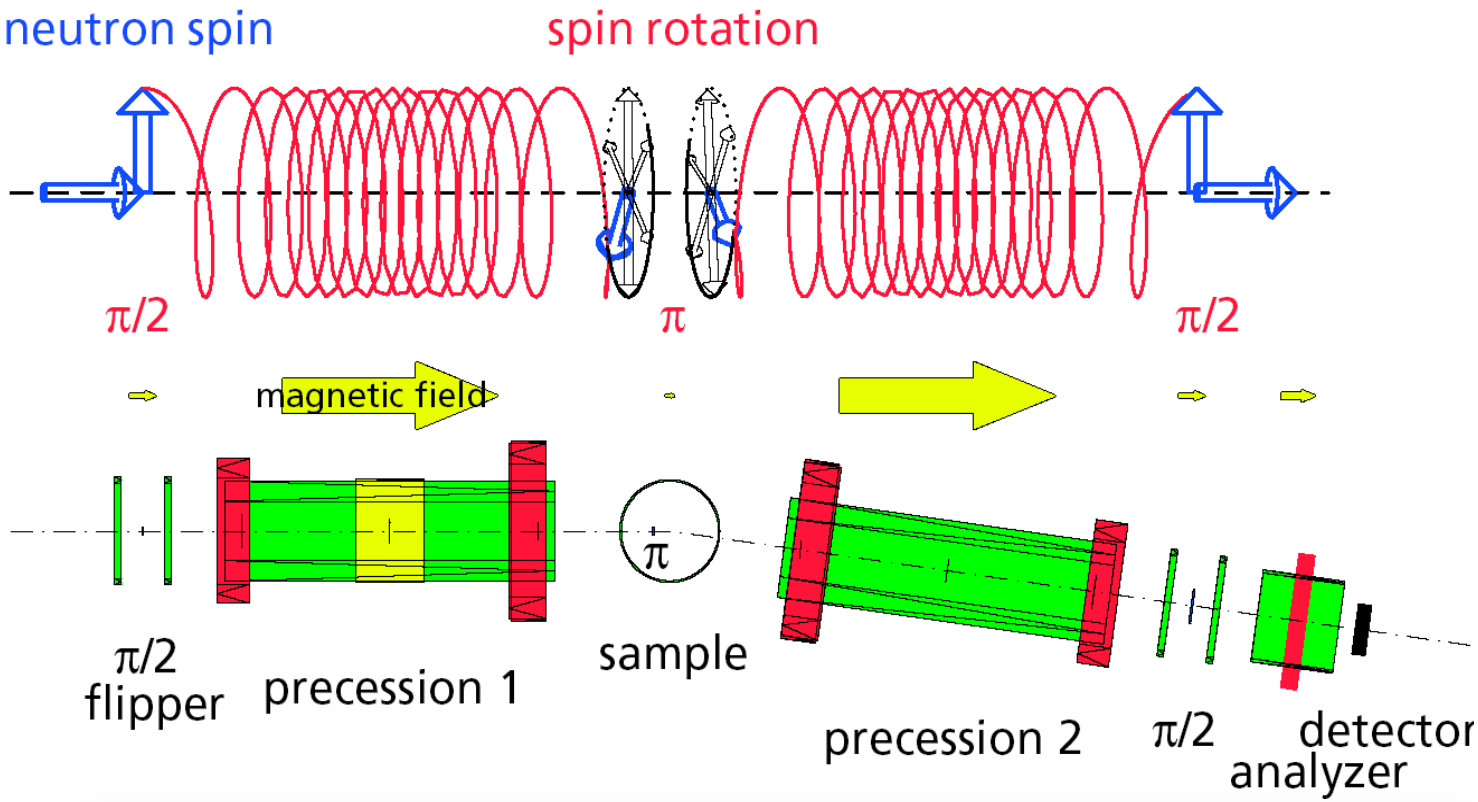
(Received May 22, 1950)

Intense radiofrequency power in the form of pulses is applied to an ensemble of spins in a liquid placed in a large static magnetic field H_0. The frequency of the pulsed r-f power satisfies the condition for nuclear magnetic resonance, and the pulses last for times which are short compared with the time in which the nutating macroscopic magnetic moment of the entire spin ensemble can decay. After removal of the pulses a non-equilibrium configuration of isochromatic macroscopic moments remains in which the moment vectors precess freely. Each moment vector has a magnitude at a given precession frequency which is determined by the distribution of Larmor frequencies imposed upon the ensemble by inhomogeneities in H_0. At times determined by pulse sequences applied in the past the constructive interference of these moment vectors gives rise to observable spontaneous nuclear induction signals. The properties and underlying principles of these spin echo signals are discussed with use of the Bloch theory. Relaxation times are measured directly and accurately from the measurement of echo amplitudes. An analysis includes the effect on relaxation measurements of the self-diffusion of liquid molecules which contain resonant nuclei. Preliminary studies are made of several effects associated with spin echoes, including the observed shifts in magnetic resonance frequency of spins due to magnetic shielding of nuclei contained in molecules.

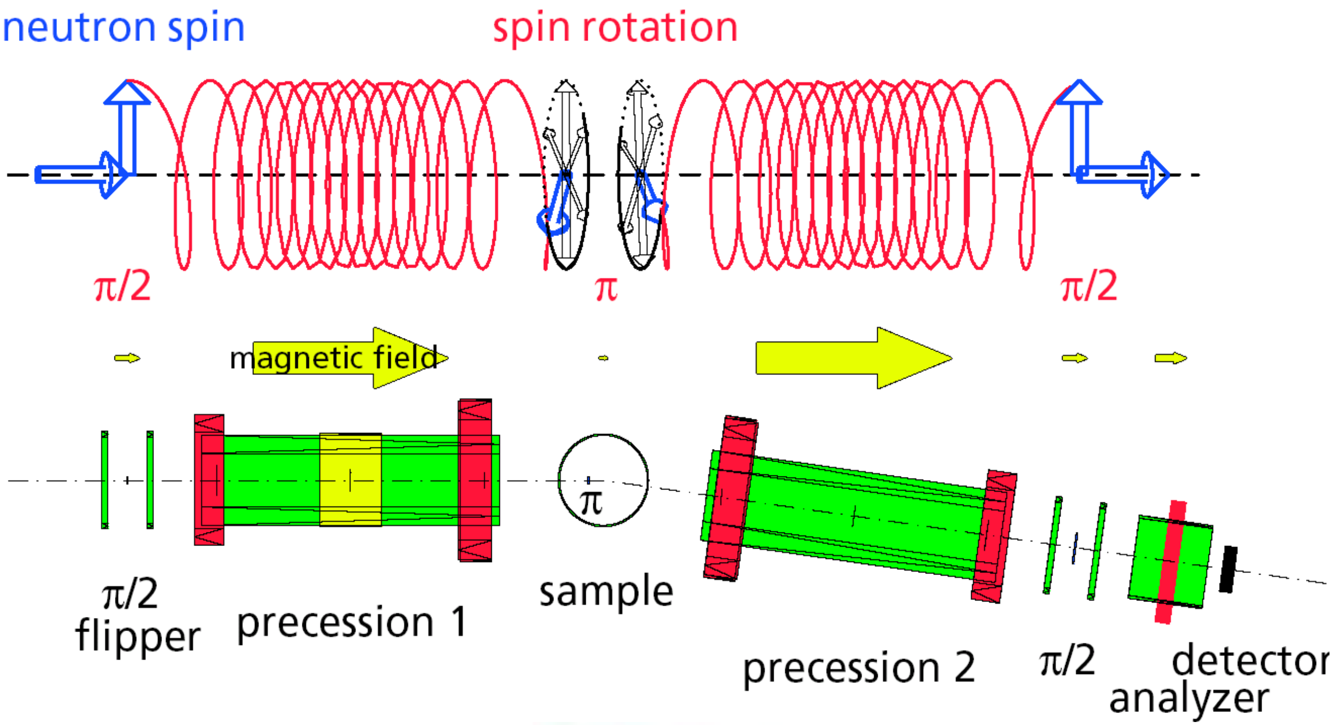
Neutron Spin Echo (I)



Neutron Spin Echo (II)



Neutron Spin Echo (inelastic)



neutron spin

spin rotation

π/2

π

π/2

magnetic field

π/2 flipper

precession 1

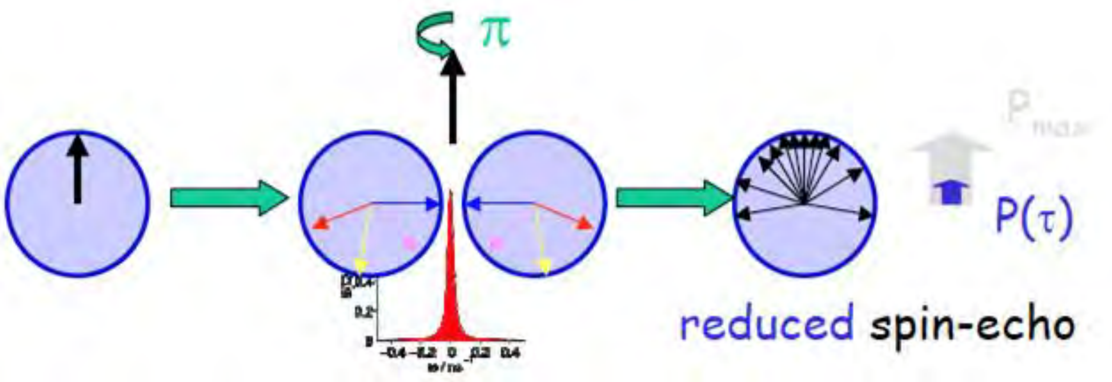
sample

precession 2

π/2

detector

analyzer



π

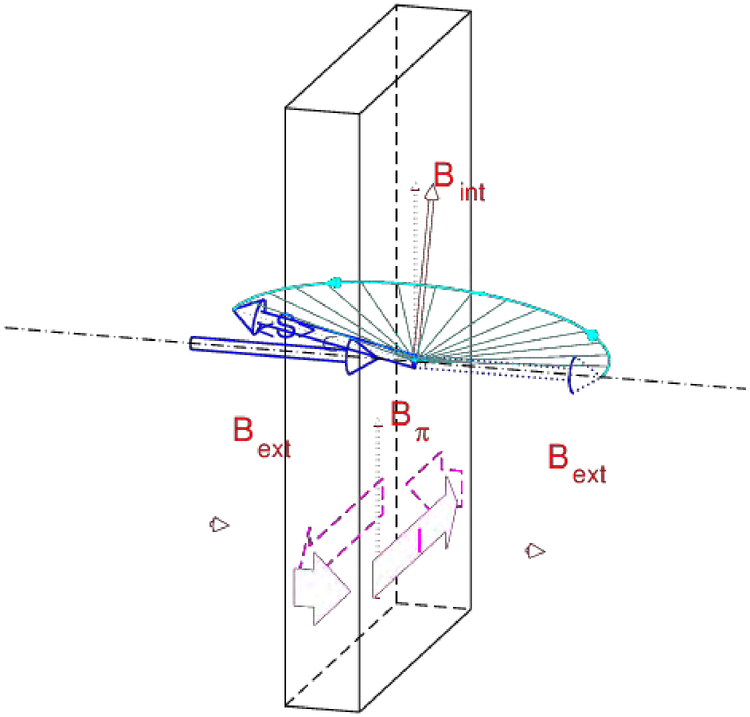
P(τ)

reduced spin-echo

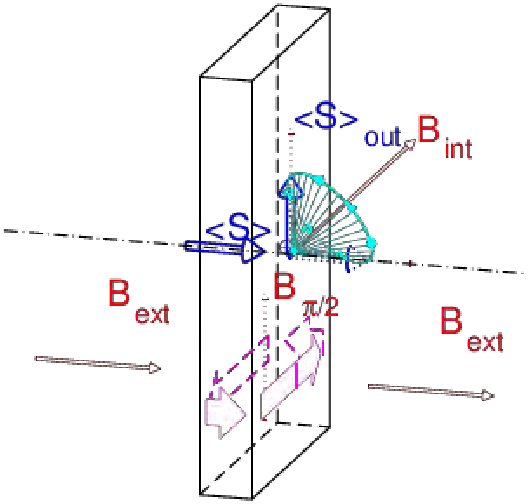
Neutron Spin Manipulation

Mezei Flippers

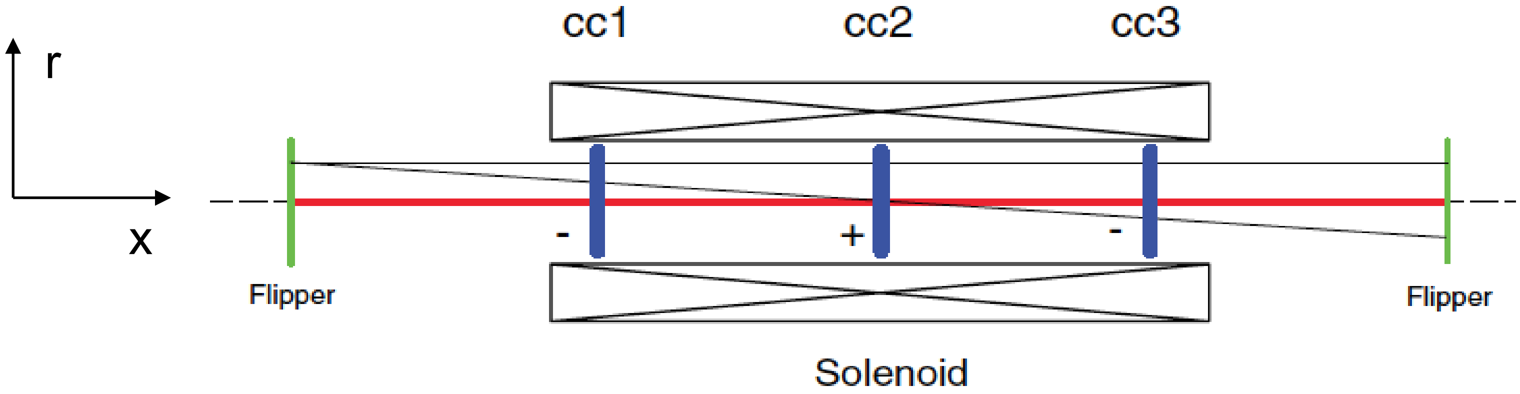
π-flipper

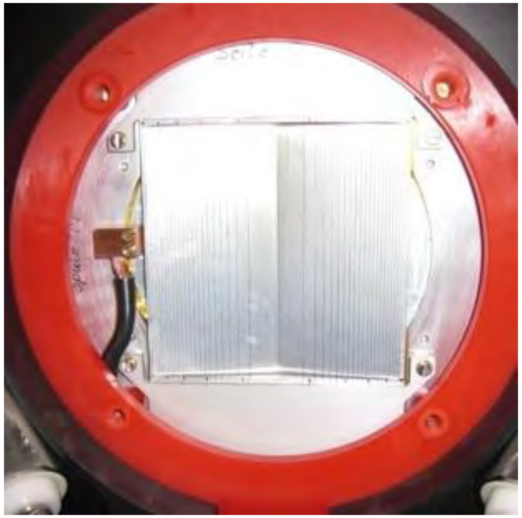


π/2-flipper



Correction Coils





- Problem:
    - $J = Bl$ the same for all trajectories
    - Solenoid field $B(r) \sim r^2$

- Solution:
    - correction coils

Neutron Spin Echo Signal

NSE Signal: $I \sim \langle \cos\phi \rangle = \langle \cos \omega\tau \rangle$

Fourier time

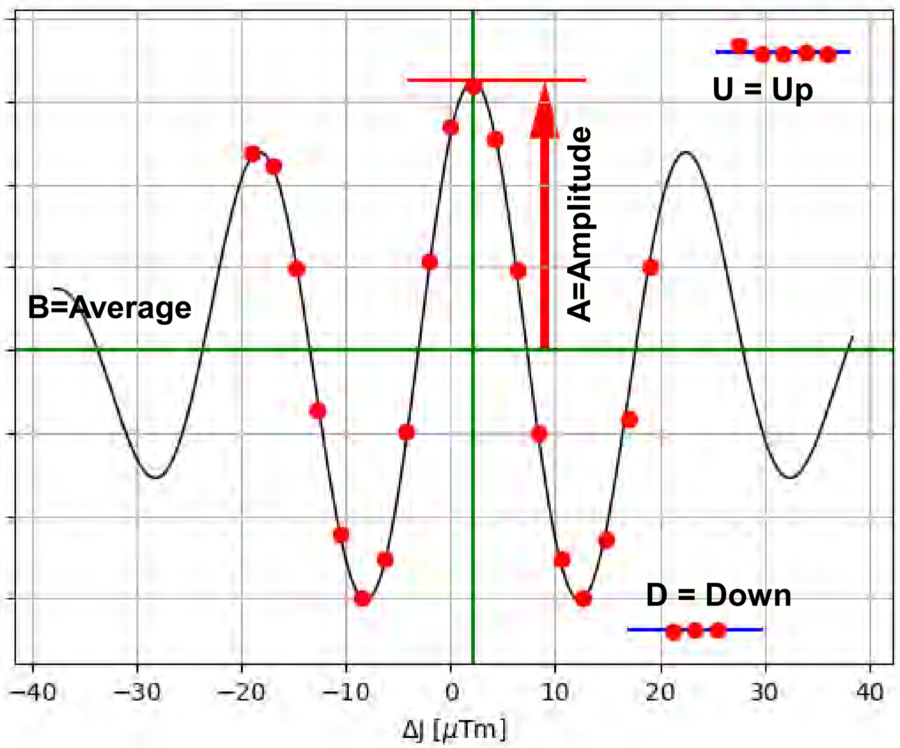
$\tau \cong 0.186\, J\, \lambda^3$ [ns]
$[\mathrm{J}] = \mathrm{Tm}, [\lambda] = \text{Å}$

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

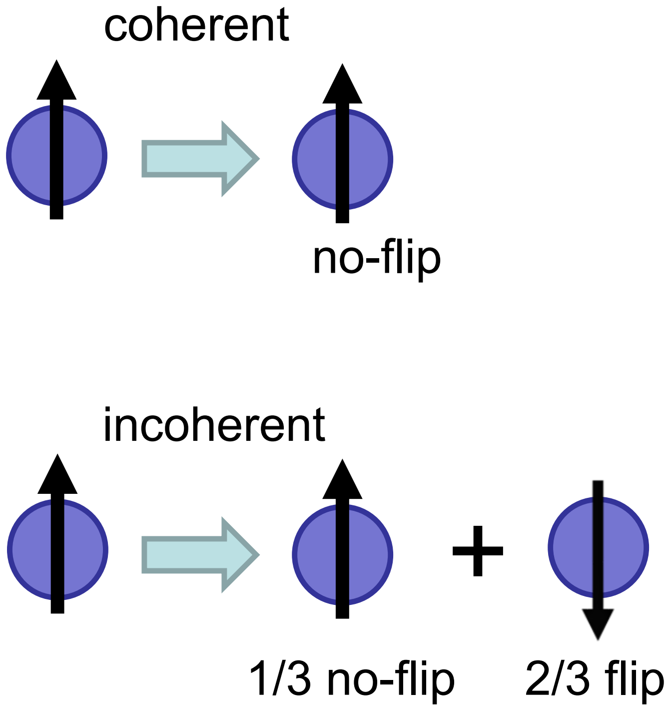
Fourier transform
(Real part)

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

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



Coherent/Incoherent Scattering in NSE



coherent

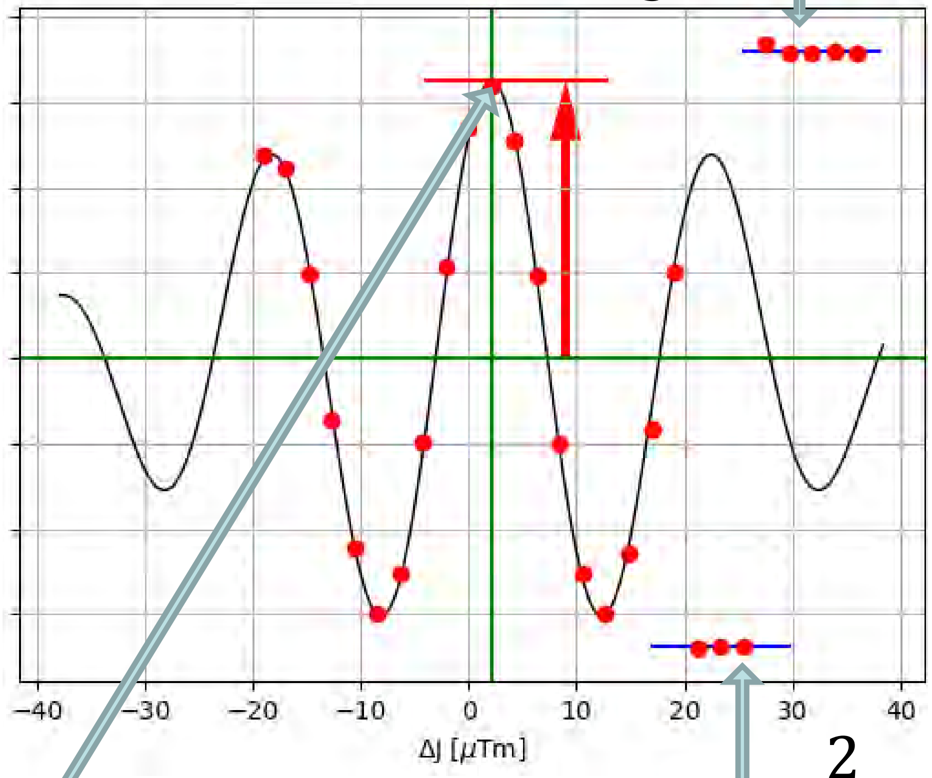
no-flip

incoherent

1/3 no-flip

2/3 flip

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



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

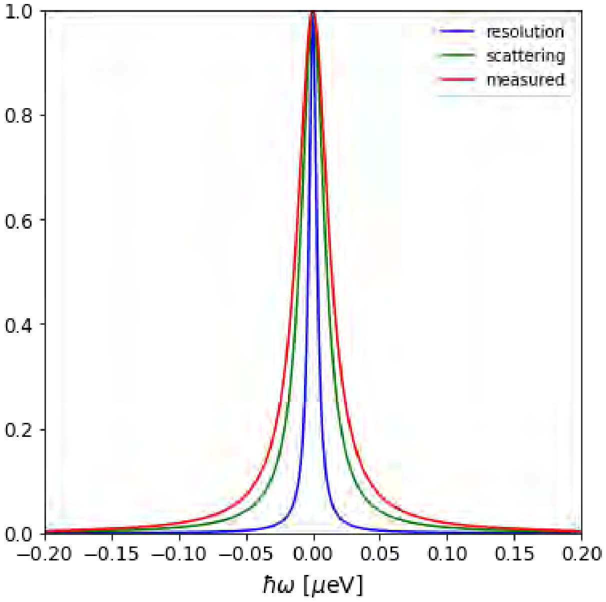
$$I_{\mathrm{echo}} = I_{\mathrm{coh}} f_{\mathrm{coh}}(\tau) - \frac{1}{3} I_{\mathrm{inc}} f_{\mathrm{inc}}(\tau)$$

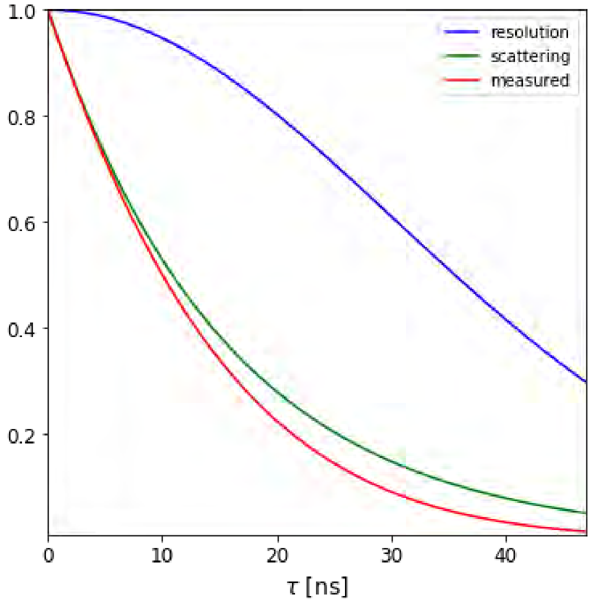
Energy and Time Domain (QENS/INS ↔ NSE)

QENS: Dynamic Structure Factor

NSE: Intermediate Scattering Function

$S(Q,\omega)$ ← *Fourier Transform* → $I(Q,\tau)$





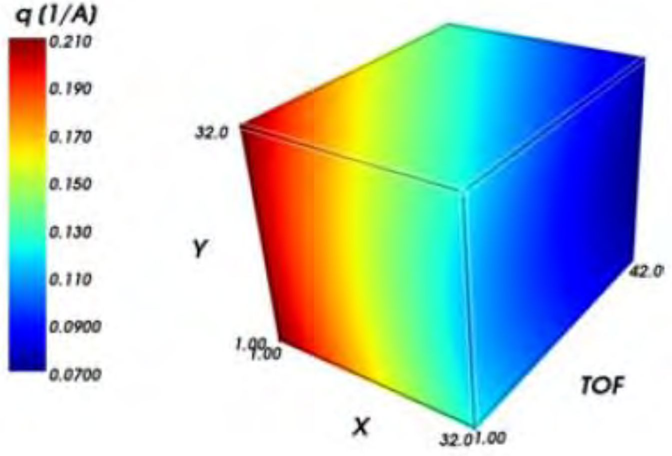
$$I_D(Q,\omega) = S(Q,\omega) * R(Q,\omega)$$

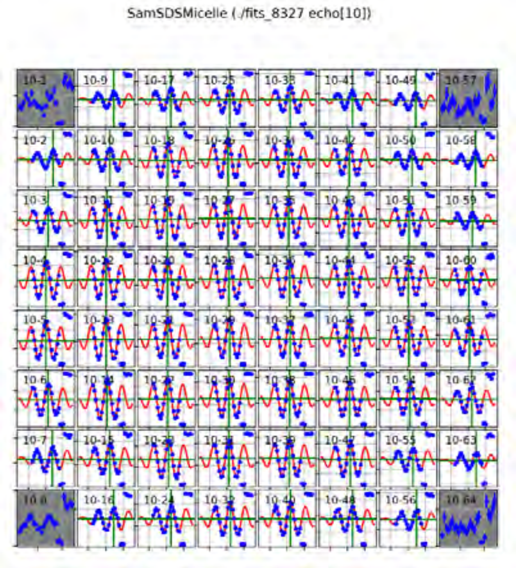
$$I_D(Q,\tau) = I(Q,\tau)\ R(Q,\tau)$$

To get $S(Q,\omega)$ we have to de-convolute instrument resolution

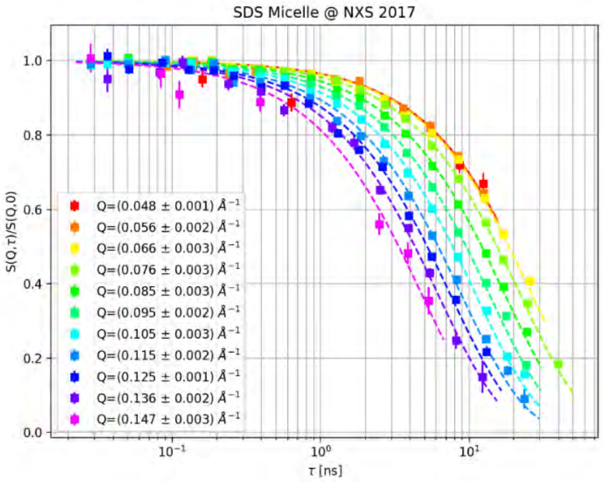
To get $I(Q,\tau)$ we just divide out instrument resolution

NSE Data Reduction





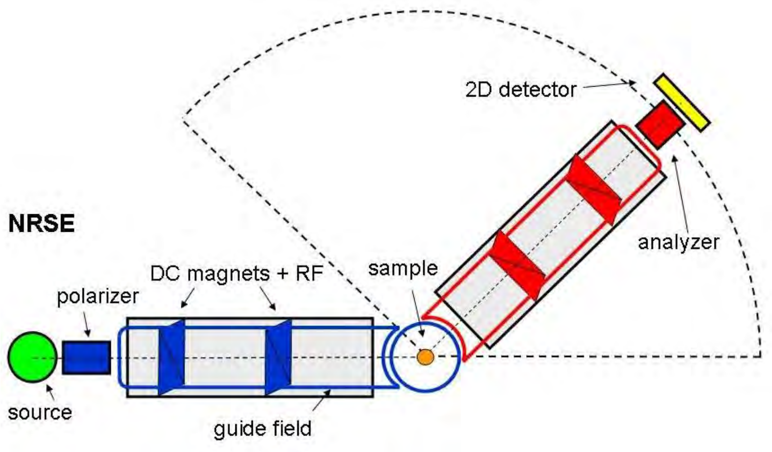
1. Resolution
   - symmetry phase (echo)
   - get $R(Q,\tau;\text{pixel})$
2. Sample: $I_{raw}(Q,\tau;\text{pixel})$
3. Background:
   - $I_{bgr}(Q,\tau;\text{pixel})$
   - correction → $I_{sig}(Q,\tau;\text{pixel})$
4. Compute $I(Q,\tau;\text{pixel}) = \frac{I_{sig}(Q,\tau)}{R(Q,\tau)}$



Some NSE Theme Variations

Resonance and SANS Spin Echo

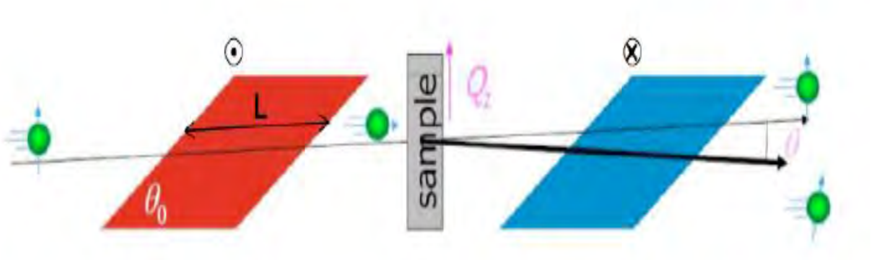
NRSE
Neutron Resonance Spin Echo



RF field instead of solenoid

- more compact design.
- shorter Fourier times

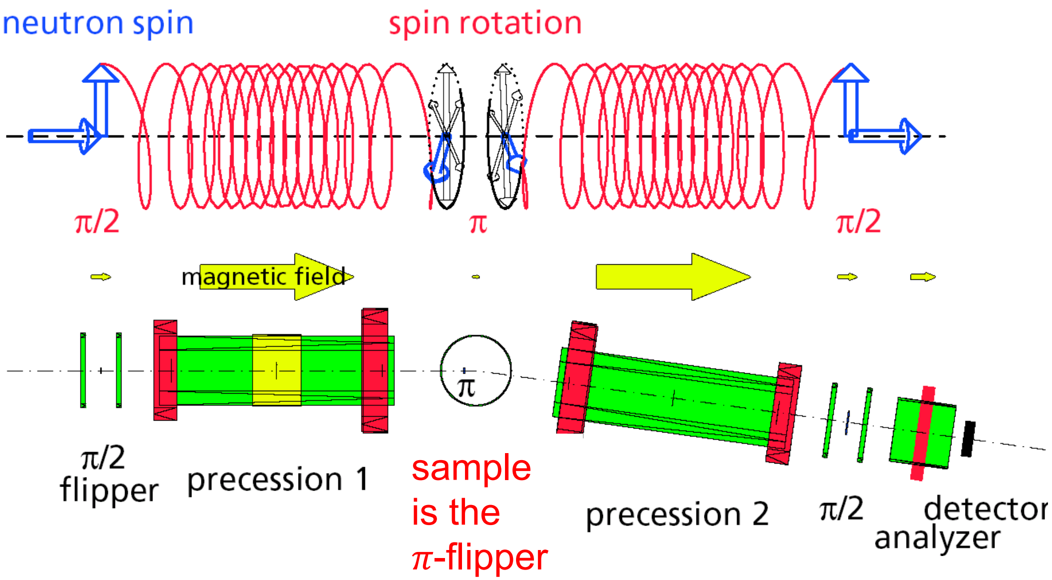
SESANS
Spin Echo SANS

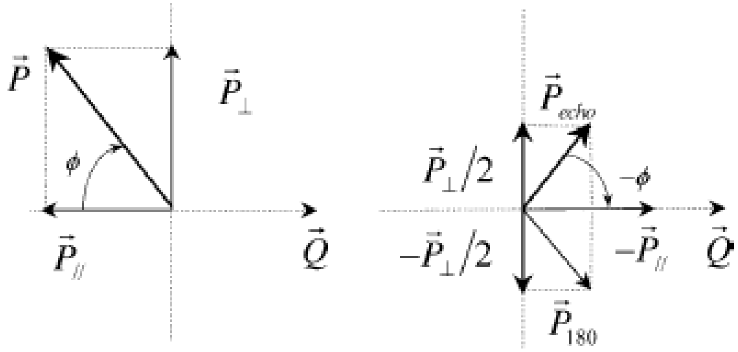


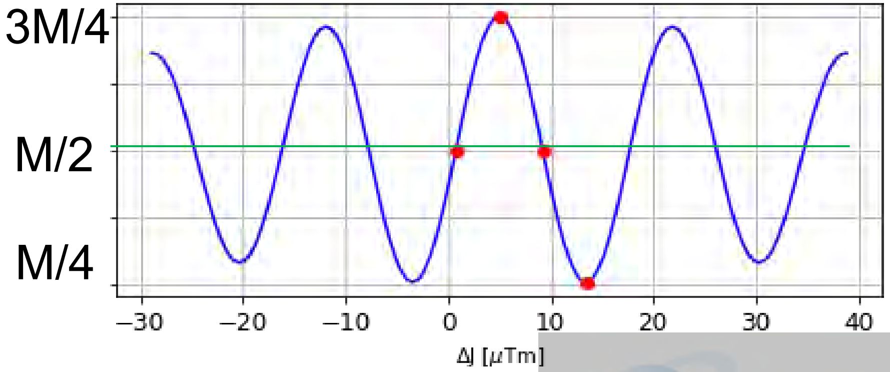
Spin Echo encoded SANS

- tilted magnetic field
- angle encoded in spin precession

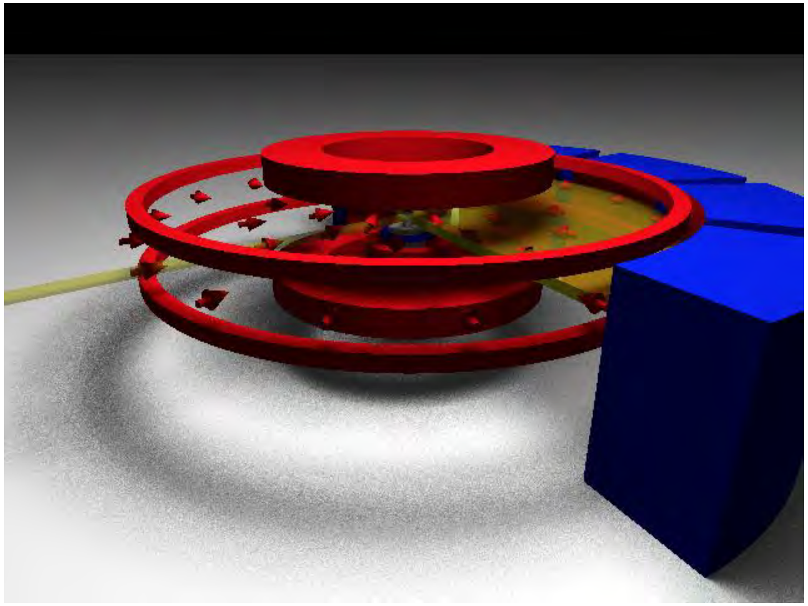
Paramagnetic NSE

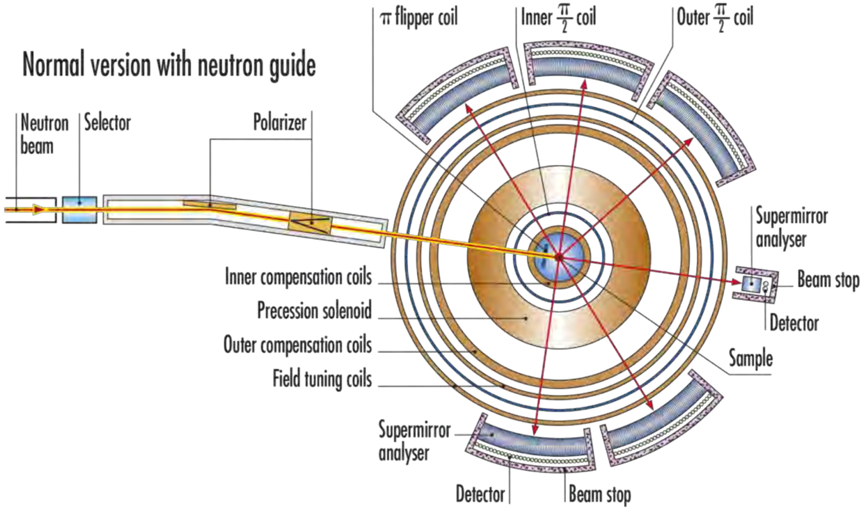


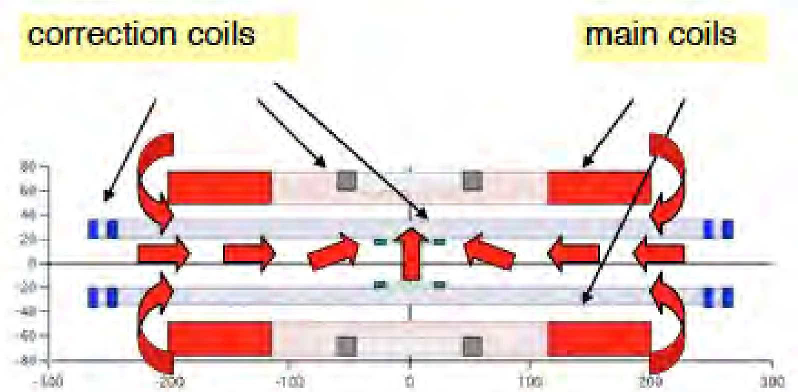




Wide Angle Neutron Spin Echo



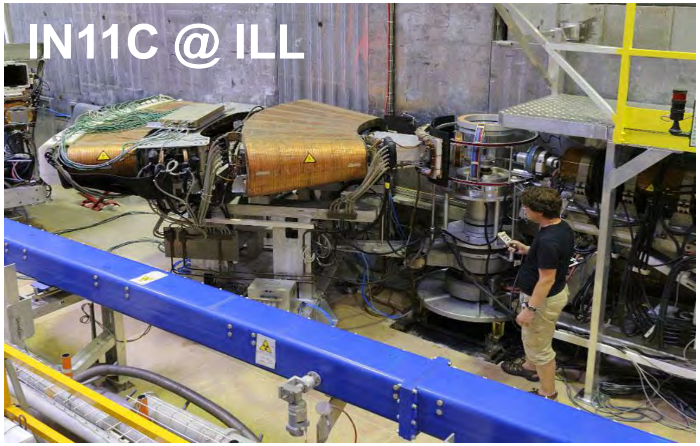


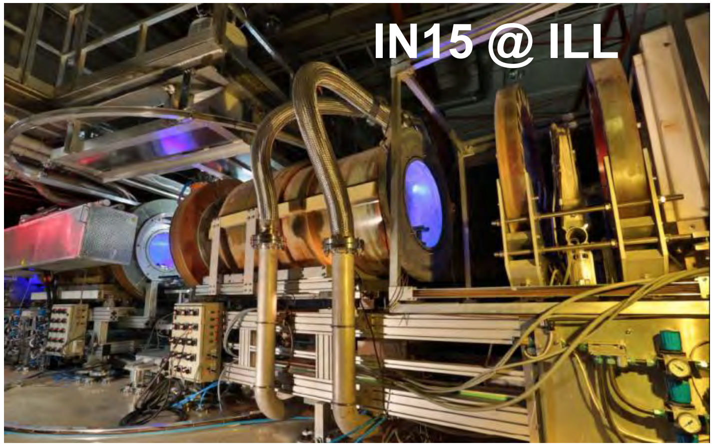


- Large angular coverage
- Higher Q (up to 3Å^{-1})

NSE Spectrometers in the World

NSE's around the World


IN11C @ ILL


IN15 @ ILL


J-NSE @ FRM II


RESEDA @ FRM II

All NSE Spectrometers

Classic “IN11-Type”

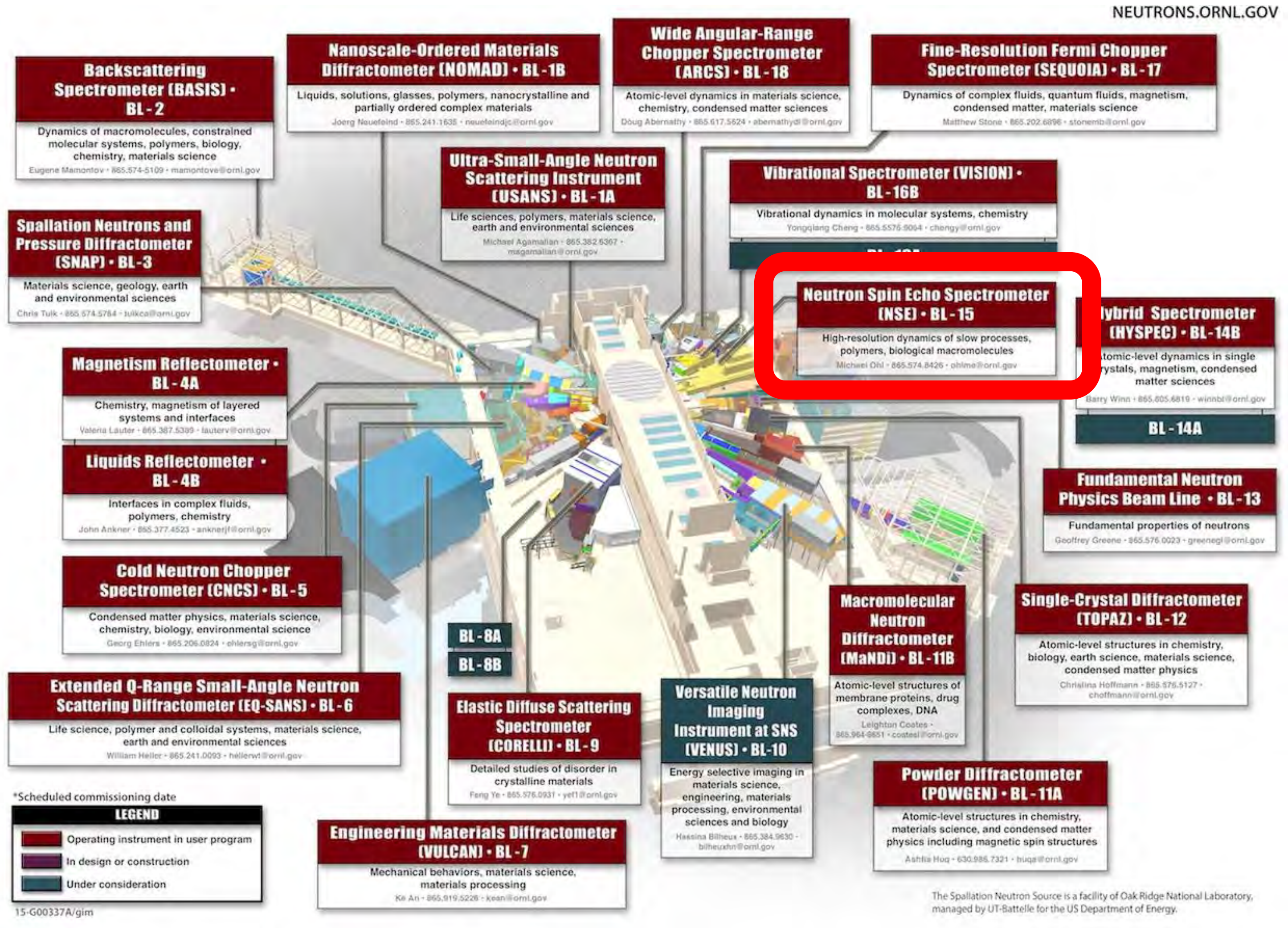
- IN11 - Institute Laue-Langevin, Grenoble, France
- IN15 - Institute Laue-Langevin, Grenoble, France
- J-NSE – JCNS hosted by FRM-II, Garching, Germany
- NG-A NSE – NIST, Gaithersburg, USA
- BL-15 SNS-NSE – FZJ & ORNL, Oak Ridge, USA
- C2-3-1 iNSE, ISSP JRR-3M, Tokai, Japan

Other

- MUSES [NRSE] – Laboratoire Léon Brillouin, Saclay, France
- RESEDA [NRSE] – FRM-II, Garching, Germany
- MIRA [TAS+MIEZE] – FRM-II, Garching, Germany
- FLEXX [TAS+NRSE] – HZB, Berlin, Germany
- Larmor [SE+SANS] – ISIS, Didcot, UK
- SESANS [SE+SANS] – TU Delft, Holland
- C2-3-1 iNSE, ISSP JRR-3M, Tokai, Japan

SNS-NSE: NSE Spectrometer at SNS

Spallation Neutron Source



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Backscattering Spectrometer (BASIS) • BL - 2
Dynamics of macromolecules, constrained molecular systems, polymers, biology, chemistry, materials science
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Atomic-level structures in chemistry, materials science, and condensed matter physics including magnetic spin structures
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Engineering Materials Diffractometer (VULCAN) • BL - 7
Mechanical behaviors, materials science, materials processing
Ke An • 865.919.5228 • kean@ornl.gov

*Scheduled commissioning date

LEGEND
- 🟥 Operating instrument in user program
- 🟪 In design or construction
- 🟦 Under consideration

15-G00337A/gim

The Spallation Neutron Source is a facility of Oak Ridge National Laboratory, managed by UT-Battelle for the US Department of Energy.

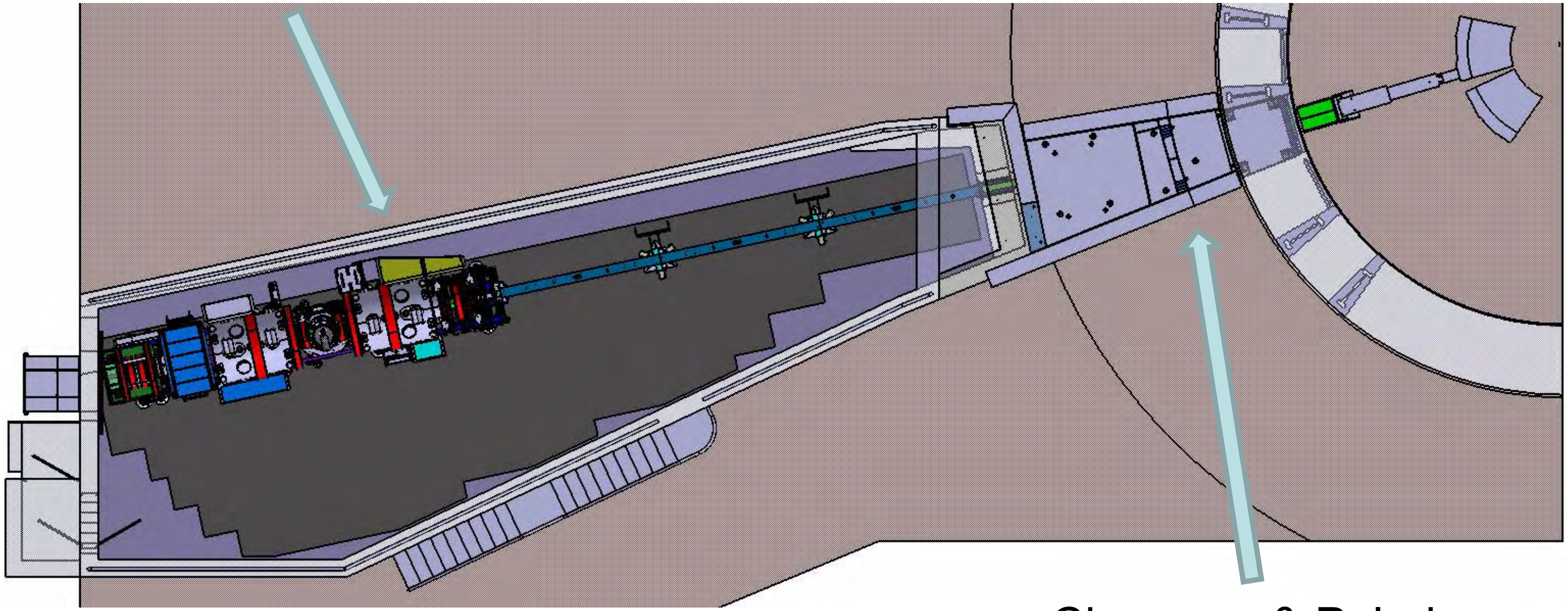
SNS-NSE is an IN11-Type NSE

main precession	SC coils, actively shielded
field integral	J = 0.56 Tm
moderator	cold-coupled hydrogen
neutron guide h x b	Ni coated 4 x 8 cm^2
wavelength selection	system of 4 choppers
wavelength frame	2Å < λ < 14Å BW 3.6Å – 2.4Å
max. scattering angle	29/42/56/79° conf. dependent)
sample size	30 x 30 mm^2
analyzer	3 rotatable supermirrors
temperature range	TFS: -80+375C Cryo: 5K to 650K

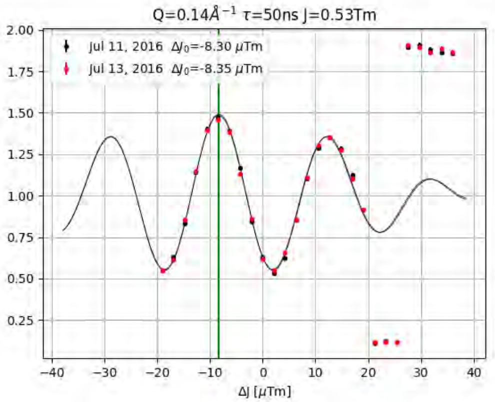
moderator - sample distance: → 18 m, 21 m, 24 m, 27 m sample - detector distance: → 4 m	30x30 cm^2 ^{3}He DENEX detector → 32x32 pixels TOF up to 99 channels (typical 42) → dλ ~ 0.07Å for @ 42 TOF	mu metal shielding, shielding factor 137 → echo phase stability

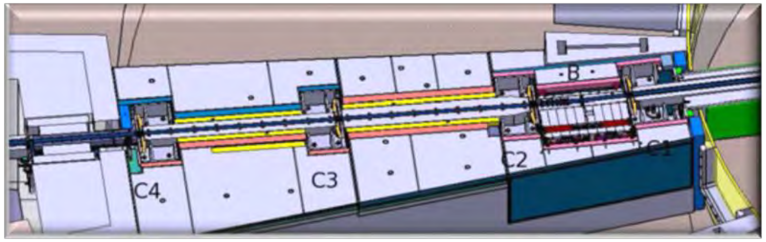
SNS-NSE Instrument Layout

Instrument Cave & Magnetic Shielding



Choppers & Polarizers



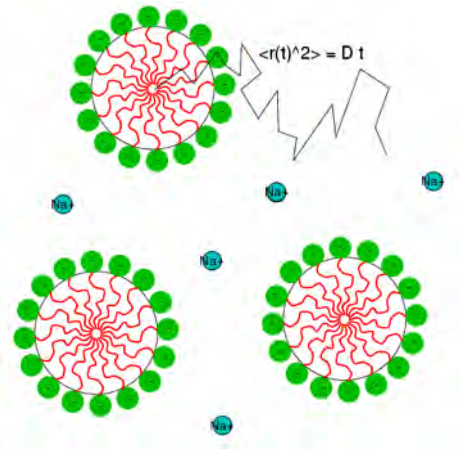


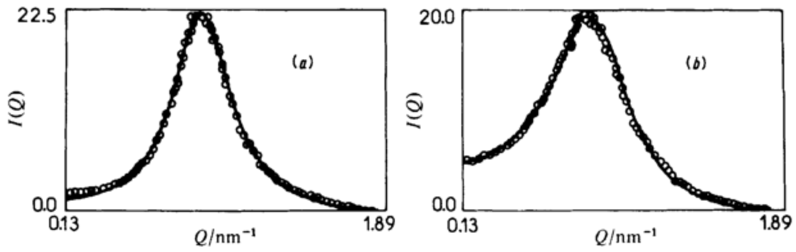
Phase Stability   Δϕ << 1°

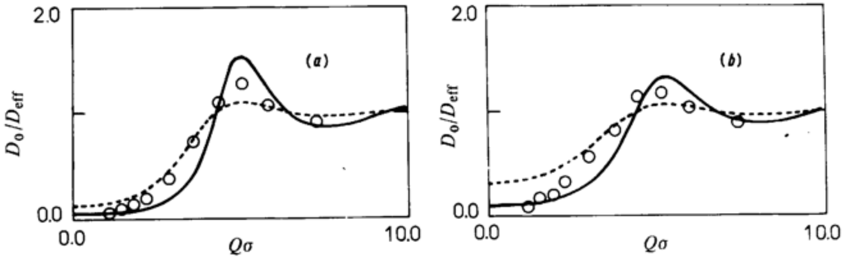
SNS-NSE Science Examples

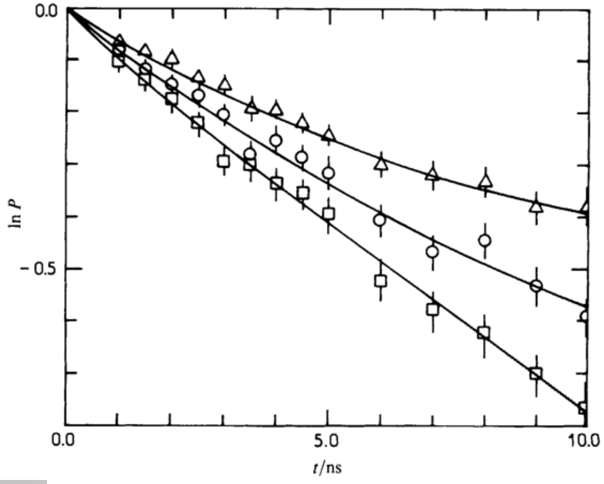
SDS Micelles

J. Hayter, J. Penfold, J. Chem. Soc., Faraday Trans. 1, 1981,77, 1851-1863









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

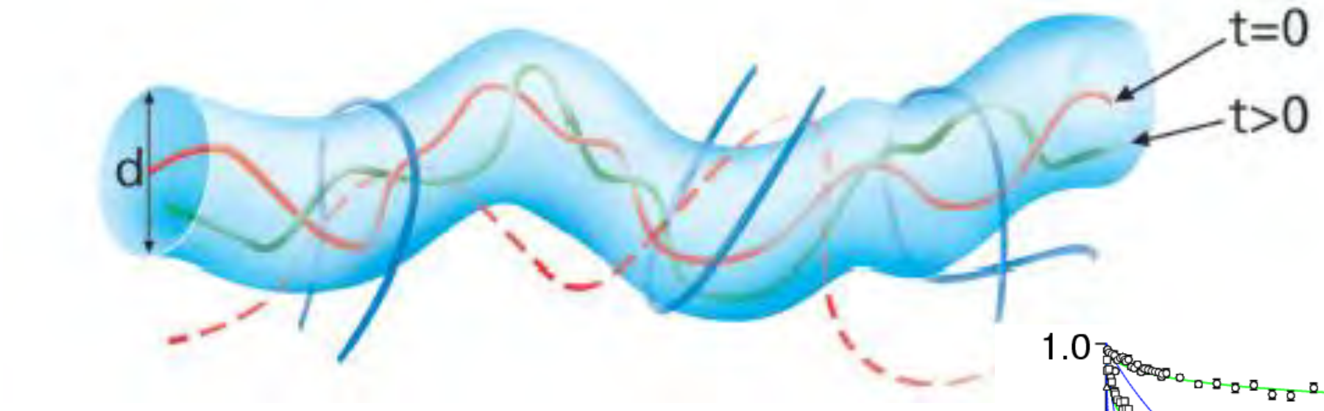
$$D_{\text{eff}} = D_0 H(Q)/S(Q)$$

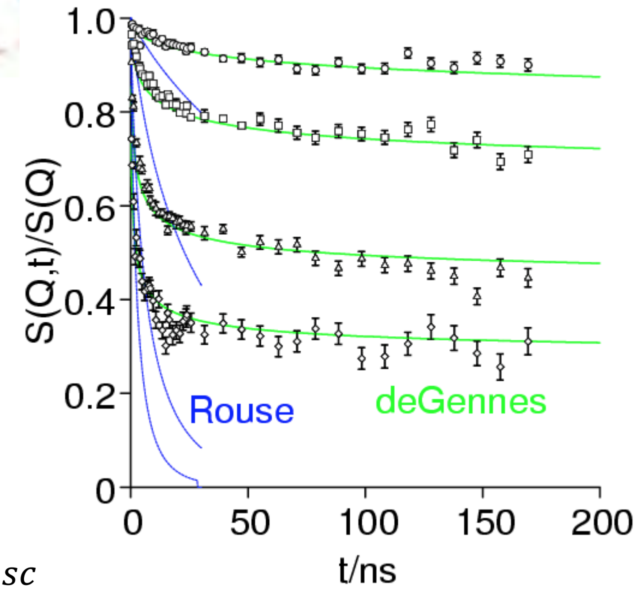
$$D_0 = \frac{kT}{6\pi\eta R}$$ Stokes-Einstein

Reptation Model

(de Gennes/Doi/Edwards)

A. Wischnewski et al., Phys. Rev. Lett. ***90*** *(2003), 058301*





Coherent scattering, labeled chain

Melt of long chain linear PEP

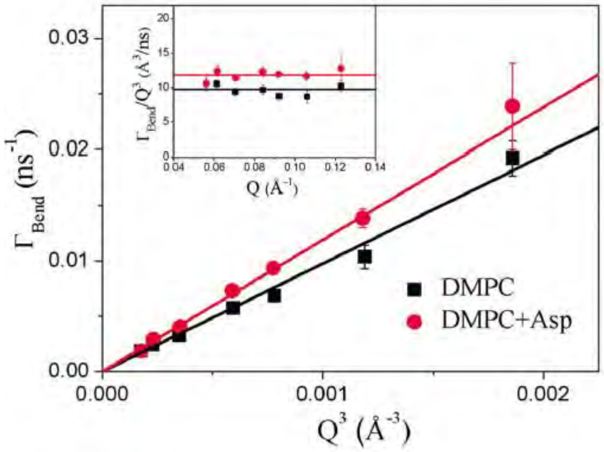
$$\frac{S(Q,\tau)}{S(Q,0)} = [1 - F(Q)]S^{loc} + \mathrm{F(Q)}\; S^{esc}$$

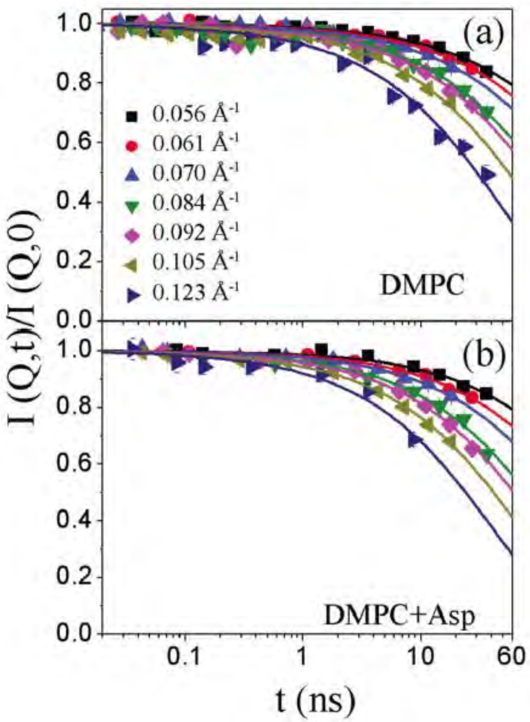
Aspirin modulates the dynamical behavior of membranes

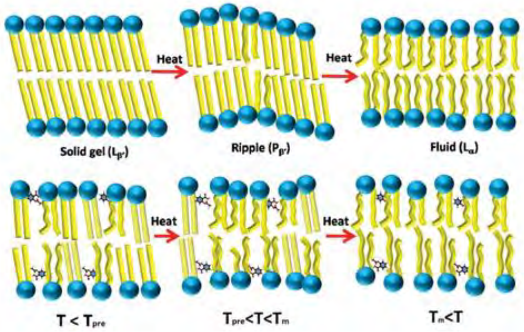
V. K. Sharma et al., Phys. Chem. Chem. Phys. 2017

Zilman-Granek Model

$$\frac{I(Q,t)}{I(Q,0)} = \exp(-(\Gamma_{\mathrm{Bend}}t)^{2/3}) \qquad \Gamma_{\mathrm{Bend}} = 0.025\,\gamma_k \left(\frac{k_B T}{\kappa}\right)^{1/2} \left(\frac{k_B T}{\eta}\right) Q^3$$

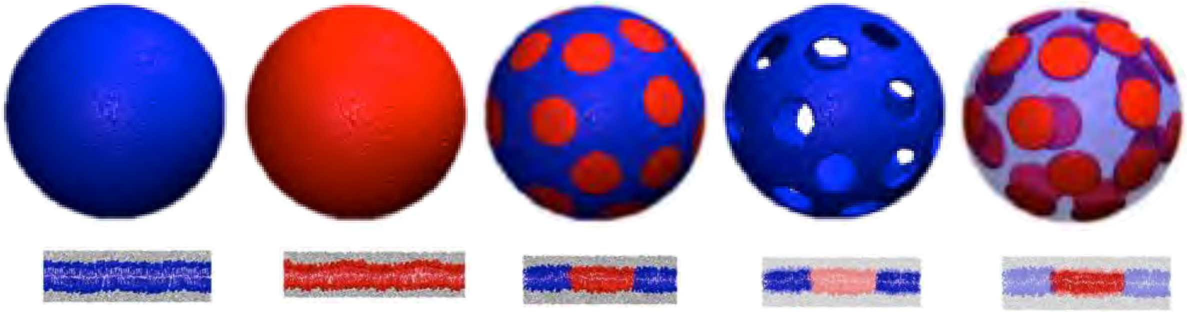


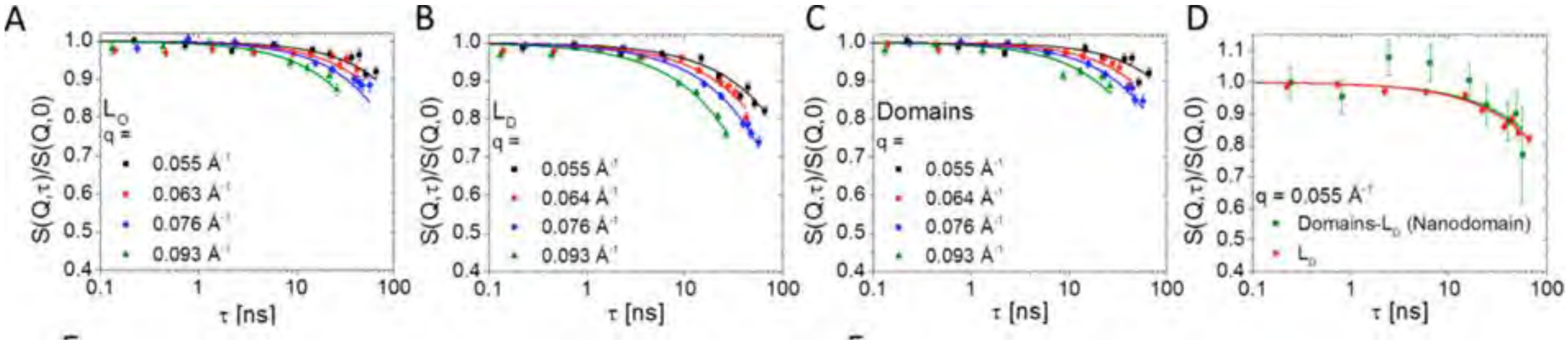




Mechanical Properties of Nanoscopic Lipid Domains

J. Nickels et al., J. Am. Chem. Soc., **2015**, *137* (50)





$$\frac{S(q,\tau)}{S(q,0)} = \exp\left(-(\Gamma(q)\tau)^{2/3}\right) \qquad \Gamma(q) = 0.0058\left(\frac{k_BT}{\kappa}\right)^{1/2}\frac{k_BT}{\eta}\,q^3$$

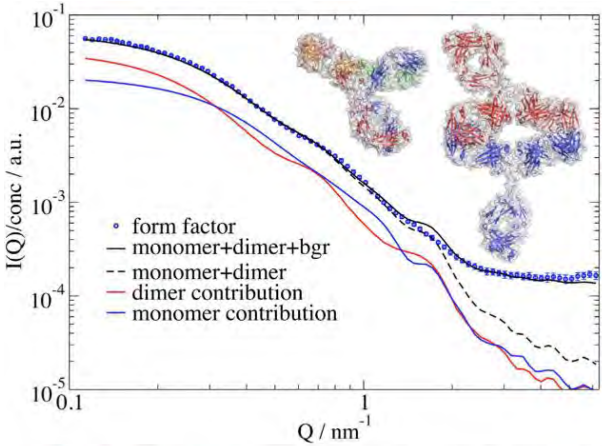
Fast antibody domain motion

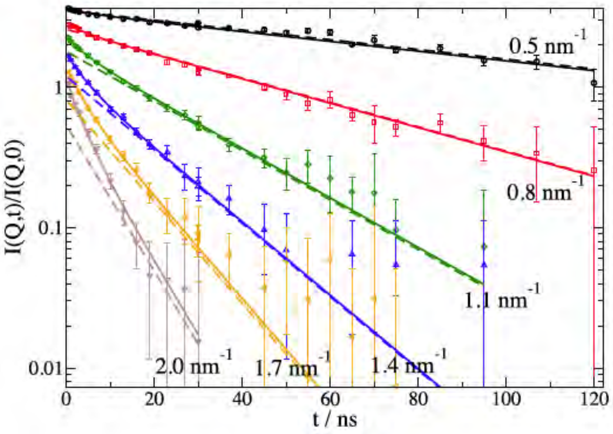
L.R. Stingaciu et al. Scientific Reports 2016

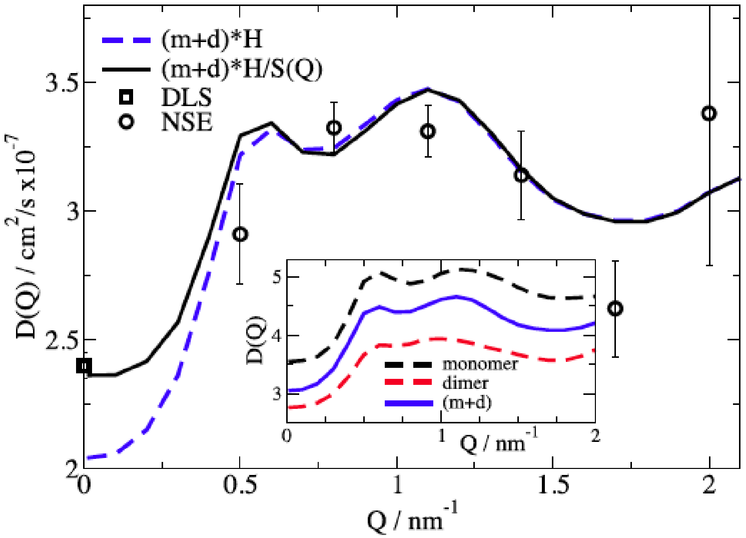
$$F(Q,t) = F_{trans}(Q,t)\cdot F_{rot}(Q,t)\cdot F_{int}(Q,t)$$

$$F_{trans}(Q,t) = \exp(-Q^2 D_T t)$$

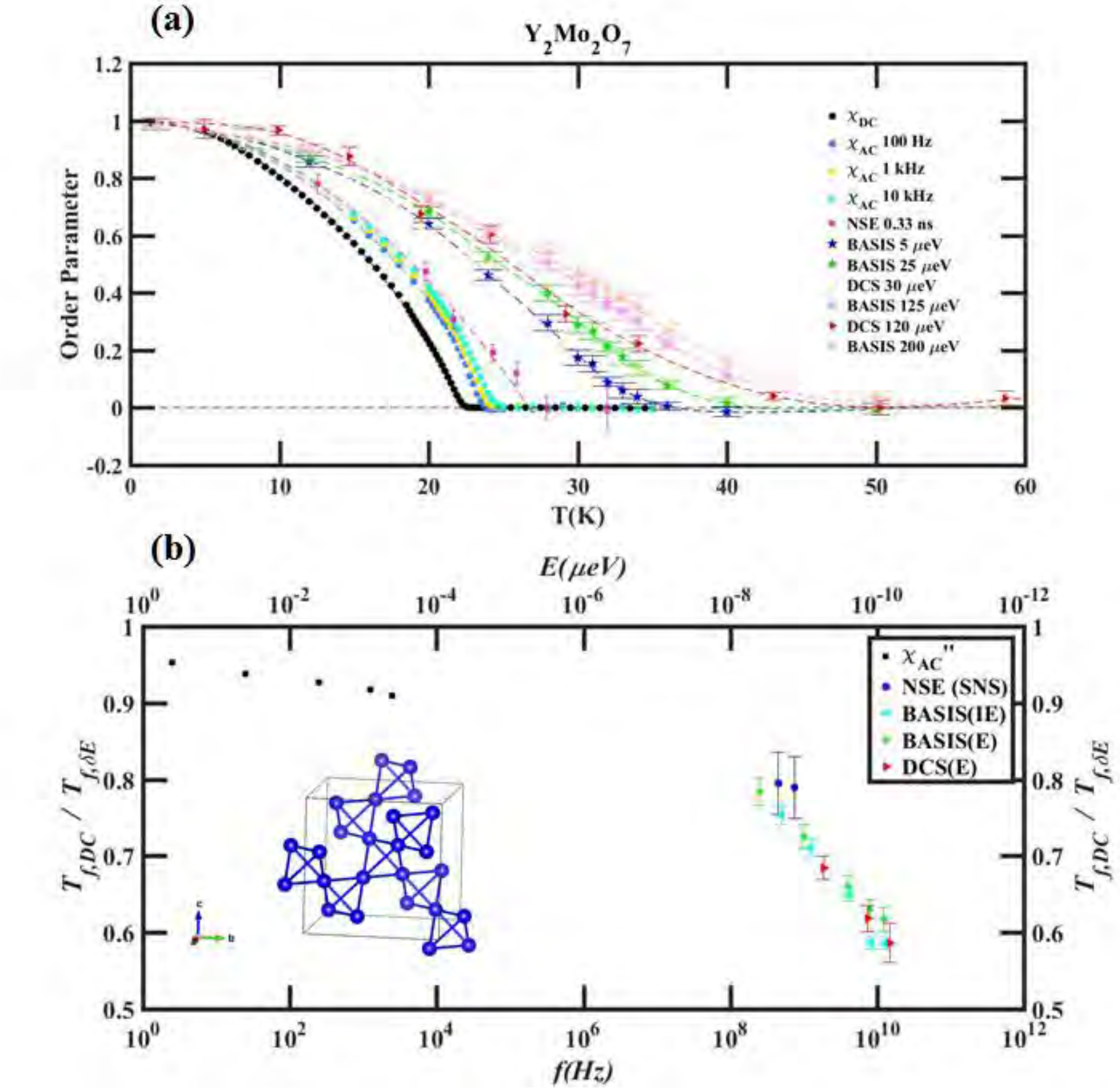
$$F_{int}(Q,t) = \left\langle \sum_{\alpha,\beta} b_\alpha b_\beta \exp(iQR_\beta^{eq})\exp(-iQR_\alpha^{eq})\cdot f_{\alpha\beta}(Q,\infty)\cdot f'_{\alpha\beta}(Q,t) \right\rangle$$







Example of Paramagnetic NSE



Summary

- NSE
  - high resolution neutron spectroscopy
  - complementary to SANS/SAXS
  - measures the intermediate scattering function $I(Q,\tau)$

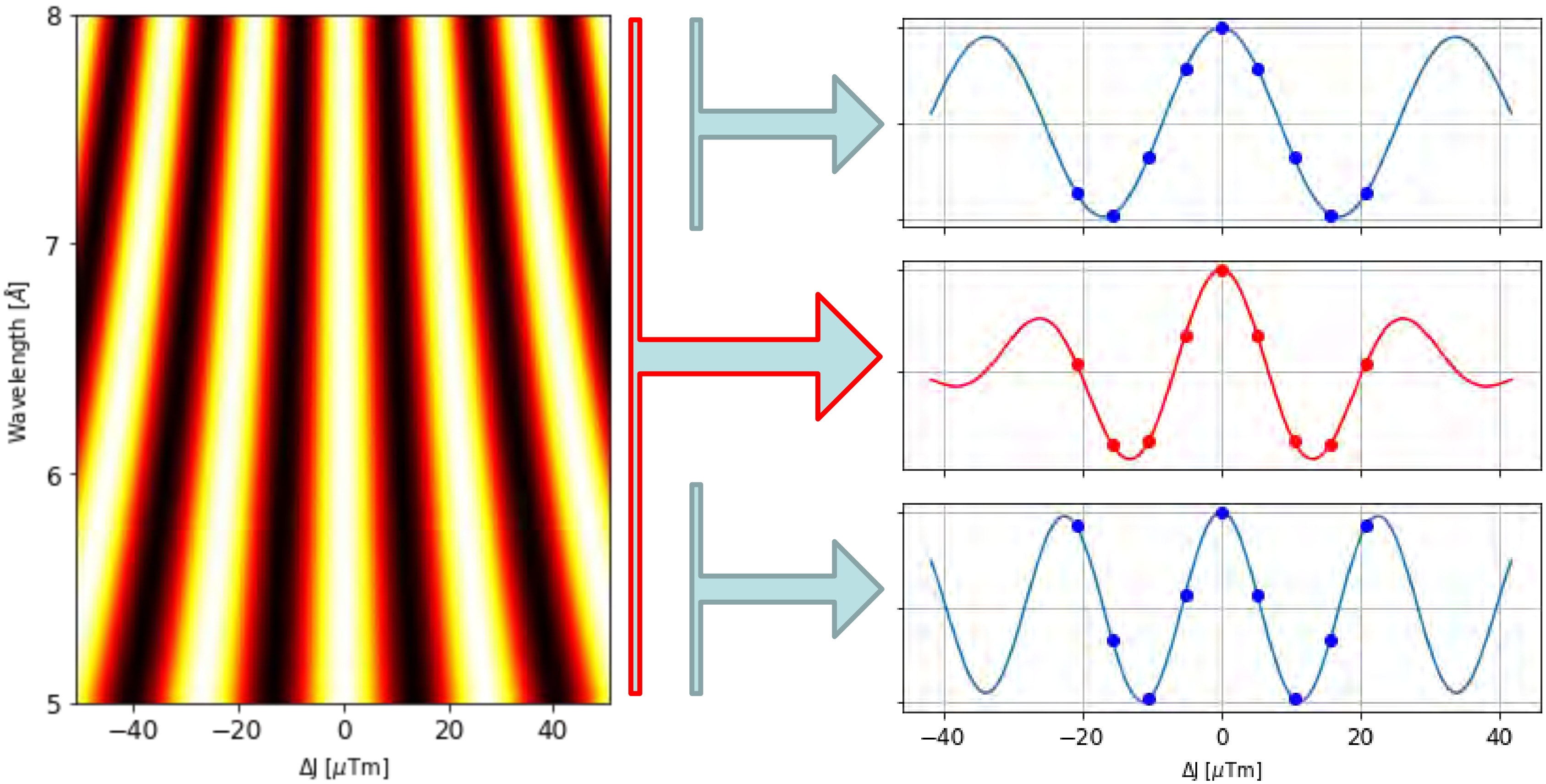
- SNS-NSE (BL-15)
  - the first NSE at a Spallation Source
  - the first one with superconducting coils
  - the only one with magnetic shielding
  - available in user program – write and submit proposals!
  - see http://neutrons.ornl.gov/nse

Suggested Literature

1. R. Pynn, Neutron Scattering, Neutron Spin Echo http://www.iub.edu/~neutron/notes/20061204_Pynn.pdf
2. F. Mezei, Z. Physik (1972) 255: 146.
3. F. Mezei (Ed.): Neutron Spin-Echo, Lecture Notes in Physics 128, Springer, 1980.
4. F. Mezei, C. Pappas, T. Gutberlet (Eds.): Neutron Spin-Echo Spectroscopy, Lecture Notes in Physics 601, Springer, 2003.
5. D. Richter, M. Monkenbusch, A. Arbe, J. Colmenero, Neutron Spin Echo in Polymer Systems, Adv. in Polymer Science 174, Springer, 2005
6. M. Monkenbusch, D. Richter, High Resolution Neutron Spectroscopy http://doi.org/10.1016/j.crhy.2007.10.001
7. C.Pappas, G. Ehlers, F. Mezei, Neutron Spin Echo and Magnetism in Neutron Scattering from Magnetic Materials, ed. T. Chatterji, Spinger 2006
8. B.Farago, Basics of Neutron Spin-Echo, ILL Neutron Data Booklet, https://www.ill.eu/fileadmin/users_files/documents/links/documentation/NeutronDataBooklet.pdf
9. G.L. Squires, Introduction to the Theory of Thermal Neutron Scattering, Cambridge Univ. Press, 3rd edition (2012)

$\Delta\lambda/\lambda_0$ up to ~50%

Echo Signals



Time-of-Flight and NSE why we don’t measure 4 points