Introduction to Neutron Spin Echo Spectroscopy

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1. Basic Principles of NSE
2. NSE Spectrometers and variations
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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

NSE can study:

- **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

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Received July 7, 1972

A simple method to change and keep track of neutron beam polarization parallel to the magnetic field is described. It makes possible the establishment of a focusing effect we call neutron spin echo. The technique developed and tested experimentally can be applied in several novel ways, e.g., for neutron spin flipper apertures. It might be the basis of a very high resolution spectrometer for direct determination of the Fourier transform of the scattering function, for generalised polarisation analysis and for the measurement of neutron particle properties with significantly improved precision.

THE IN11 NEUTRON SPIN ECHO SPECTROMETER

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INTRODUCTION

The first full-fledged Neutron Spin Echo spectrometer was built at the Institut Laue-Langevin on the H14 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

\[
\Delta E = \hbar \omega = \frac{1}{2} \left( m v_i^2 - m v_f^2 \right)
\]

\[
\vec{Q} = \vec{k}_i - \vec{k}_f
\]

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

\[ \varphi = \omega_L t = \gamma Bl \frac{1}{v} \]

or

\[ \varphi = \gamma \frac{m}{h} J\lambda \]

for example:

\[ \lambda = 8\text{Å}, \; Bl = 0.5 \text{Tm} \]

\[ \rightarrow \varphi/2\pi \approx 3 \times 10^4 \; [\text{nr. of turns}] \]

Notes: \( J \stackrel{\text{def}}{=} Bl \) or more precisely \( J \stackrel{\text{def}}{=} \int \vec{B} \cdot d\vec{l} \)
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 → spin rotation

\[ \pi/2 \rightarrow \pi \rightarrow \pi/2 \]

magnetic field

\[ \pi/2 \text{ flipper} \rightarrow \text{precession 1} \rightarrow \text{sample} \rightarrow \text{precession 2} \rightarrow \pi/2 \text{ detector analyzer} \]

spin-echo
Neutron Spin Echo (II)

neutron spin → spin rotation

$\pi/2$ → magnetic field → $\pi$ → $\pi/2$

flipper → precession 1 → sample → precession 2 → detector

$\pi/2$ → analyzer

Graph showing oscillatory data.
Neutron Spin Echo (inelastic)
Neutron Spin Manipulation
Mezei Flippers

\(\pi\)-flipper

\(\pi/2\)-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:** \( I \sim \langle \cos \phi \rangle = \langle \cos \omega \tau \rangle \)

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

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

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

\( \tau \approx 0.186 J \lambda^3 \) [ns]

\([J] = \text{Tm}, [\lambda] = \text{Å}\)
Coherent/Incoherent Scattering in NSE

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

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

$$I_{echo} = I_{coh} f_{coh}(\tau) - \frac{1}{3} I_{inc} f_{inc}(\tau)$$
Energy and Time Domain (QENS/INS ↔ NSE)

QENS: Dynamic Structure Factor

\[ S(Q, \omega) \]

NSE: Intermediate Scattering Function

\[ I(Q, \tau) \]

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

\[ I_D(Q, \omega) = S(Q, \omega) * R(Q, \omega) \]

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

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

- tilted magnetic field
- angle encoded in spin precession
Paramagnetic NSE

neutron spin

spin rotation

\( \pi/2 \)

\( \pi \)

\( \pi/2 \)

\( \pi/2 \) flipper

precession 1

sample is the \( \pi \)-flipper

precession 2

\( \pi/2 \) detector analyzer

\[ 3M/4 \]

\[ M/2 \]

\[ M/4 \]
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
**SNS-NSE is an IN11-Type NSE**

<table>
<thead>
<tr>
<th>Feature</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>main precession</strong></td>
<td>SC coils, actively shielded</td>
</tr>
<tr>
<td><strong>field integral</strong></td>
<td>$J = 0.56 , \text{Tm}$</td>
</tr>
<tr>
<td><strong>moderator</strong></td>
<td>cold-coupled hydrogen</td>
</tr>
<tr>
<td><strong>neutron guide h x b</strong></td>
<td>Ni coated $4 \times 8 , \text{cm}^2$</td>
</tr>
<tr>
<td><strong>wavelength selection</strong></td>
<td>system of 4 choppers</td>
</tr>
<tr>
<td><strong>wavelength frame</strong></td>
<td>$2 \AA &lt; \lambda &lt; 14 \AA$ BW $3.6 \AA - 2.4 \AA$</td>
</tr>
<tr>
<td><strong>max. scattering angle</strong></td>
<td>$29/42/56/79^\circ$ conf. dependent)</td>
</tr>
<tr>
<td><strong>sample size</strong></td>
<td>$30 \times 30 , \text{mm}^2$</td>
</tr>
<tr>
<td><strong>analyzer</strong></td>
<td>3 rotatable supermirrors</td>
</tr>
<tr>
<td><strong>temperature range</strong></td>
<td>TFS: -80+375C</td>
</tr>
<tr>
<td></td>
<td>Cryo: 5K to 650K</td>
</tr>
</tbody>
</table>

- **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)
  - $d\lambda \sim 0.07 \AA$ for @ 42 TOF
- **mu metal shielding, shielding factor 137**
  - echo phase stability
- **mu metal shielding, shielding factor 137**
  - echo phase stability
- **temperature range**
  - TFS: -80+375C
  - Cryo: 5K to 650K
SNS-NSE Instrument Layout

Instrument Cave & Magnetic Shielding

Choppers & Polarizers

Phase Stability \( \Delta \phi << 1^\circ \)
SNS-NSE Science Examples
SDS Micelles


\[ D_0 = kT / 6\pi\eta R \]  \hspace{1cm} \text{Stokes-Einstein}

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

\[ \frac{I(Q, t)}{I(Q, 0)} = e^{-D_{\text{eff}}(Q)Q^2t} \]
Reptation Model
(de Gennes/Doi/Edwards)


Coherent scattering, labeled chain

Melt of long chain linear PEP

\[
\frac{S(Q, \tau)}{S(Q, 0)} = \left[1 - F(Q)\right]S^{loc} + F(Q)S^{esc}
\]
Aspirin modulates the dynamical behavior of membranes


Zilman-Granek Model

\[
\frac{I(Q, t)}{I(Q, 0)} = \exp\left(-\left(\Gamma_{\text{Bend}} t\right)^{2/3}\right) \quad \Gamma_{\text{Bend}} = 0.025 \gamma_k \left(\frac{k_B T}{\kappa}\right)^{1/2} \left(\frac{k_B T}{\eta}\right) Q^3
\]
Mechanical Properties of Nanoscopic Lipid Domains


\[ \frac{S(q, \tau)}{S(q, 0)} = \exp\left(-\left(\Gamma(q)\tau\right)^{2/3}\right) \quad \Gamma(q) = 0.0058 \left(\frac{k_B T}{\kappa}\right)^{1/2} \frac{k_B T}{\eta} q^3 \]
Fast antibody domain motion

L.R. Stingaciu et al. Scientific Reports 2016

\[ F(Q, t) = F_{\text{trans}}(Q, t) \cdot F_{\text{rot}}(Q, t) \cdot F_{\text{int}}(Q, t) \]

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

\[ F_{\text{int}}(Q, t) = \left\{ \sum_{\alpha,\beta} b_{\alpha} b_{\beta} \exp(iQR^{\alpha\beta}_f) \exp(-iQR^{\alpha\beta}_f) \cdot f_{\alpha\beta}(Q, \infty) \cdot f_{\alpha\beta}(Q, t) \right\} \]
Example of Paramagnetic NSE

(a) \(Y_2\text{Mo}_2\text{O}_7\)

Order Parameter vs. Temperature (K)

(b) \(E(\mu\text{eV})\)

Ratio of Order Parameter vs. Frequency (Hz)

NXS 2019
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
6. M. Monkenbusch, D. Richter, High Resolution Neutron Spectroscopy
   http://doi.org/10.1016/j.crhy.2007.10.001
8. B.Farago, Basics of Neutron Spin-Echo, ILL Neutron Data Booklet,
Δλ/λ₀ up to ~50%

Echo Signals

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