Neutron Spectroscopies

Quasi-Elastic Neutron Scattering

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Production of neutron beams

**Research reactors** by nuclear fission, example HFIR, ORNL, FRM II, Munich, Institute Laue Langevin (ILL) Grenoble, France, [www.ill.fr](http://www.ill.fr)

**Spallation sources** by using linear proton accelerators (for example at ISIS at the Rutherford Appleton Lab. Oxford, Great Britain, see [www.isis.rl.ac.uk](http://www.isis.rl.ac.uk) or at the US Spallation Neutron Source (SNS) [www.sns.gov](http://www.sns.gov), ESS-European Spallation Source.
Advances in the effective thermal flux for neutron

Today’s best sources typically $10^7$-$10^8$ neutrons cm$^{-2}$s$^{-1}$ on the sample

K. Anderson, Lectures
Energy Spectrum of neutrons

\[ E = \frac{p^2}{2m} = \frac{\hbar^2}{2m\lambda^2} \]

\[ E(\text{meV}) = \frac{81.8042}{(\lambda(A))^2} \]

Energy distribution of prompt neutrons from a reactor

Typical neutron energies and corresponding wavelengths used in experiments

i. "hot" neutrons \[ E = 100 - 500 \text{ meV} \] \[ \lambda = 0.5 - 1 \text{ Å} \]

ii. "thermal" neutrons \[ E = 10 - 100 \text{ meV} \] \[ \lambda = 1 - 3 \text{ Å} \]

iii. "cold" neutrons \[ E = 0.1 - 10 \text{ meV} \] \[ \lambda = 3 - 30 \text{ Å} \]
Going beyond the center of mass diffusion

< $10^9$ Hz slow motion
$\Delta E \sim \mu$eV
lowest available $E = 1\text{-}5\text{meV}$ neutrons
Thus, define neutron $E$ 1 part in $10^3$ or better

V. García Sakai, A. Arbe
Current Opinion in Colloid & Interface Science
Momentum Transfer $q$

**cross section** number of neutrons/time/$d\Omega$ with energy transfer in the interval $(h\omega, h\omega+d\omega)$ normalized by incident flux

Incident neutron along $z$, wave vector $k_i$ and energy $E_i$

$|k_i| = \sqrt{2mE_i}/h$

$2\theta$ and $\varphi$ define the direction of the scattered beam

$q = k_i - k_f$ wave vector or momentum transfer

$\Delta p = hq/2\pi = h(k_i - k_f)/2\pi$

$|k_i| = |k_f| = 2\pi/\lambda$ and $|q| = 4\pi \sin(\theta) / \lambda$
Energy transfer $\Delta E$ (TOF)

$$E = \frac{p^2}{2m}$$

$$p = \hbar k = mv$$

energy transfer $\Delta E = E_f - E_i = 0$

energy transfer $\Delta E = E_f - E_i \neq 0$
Exchange of energy and momentum with the sample

Scattering triangle (cosine rule)

\[ Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos 2\theta \]

Kinematic condition

\[ \frac{\hbar Q^2}{2m} = E_i + E_f - 2 \sqrt{E_i E_f} \cos 2\theta \]
Coherent and Incoherent Scattering

Interference of neutron waves emitted from different atoms

Coherent elastic scattering = diffraction

Interference of neutron waves emitted from same atom

Lecture: Gerald R. Kneller
Scattering Functions- Correlations

Remember that in the experiment we measure the total $S(Q, \omega)$ and that each term, coherent and incoherent is weighted by its respective cross-section $\sigma$

$$S(Q, \omega) = S_{\text{inc}}(Q, \omega) + S_{\text{coh}}(Q, \omega)$$

$$S_{\text{inc}}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \sum_i \langle \exp(-iQ \cdot R_i(0))\exp(-iQ \cdot R_i(t)) \rangle \exp(-i\omega t) \, dt$$

$$S_{\text{coh}}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \sum_{i,j} \langle \exp(-iQ \cdot R_i(0))\exp(-iQ \cdot R_j(t)) \rangle \exp(-i\omega t) \, dt$$

These expressions can also be re-written in terms of the self and collective intermediate scattering functions, $I(Q,t)$, such that:

$$S_{\text{inc}}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{self}}(Q,t) \exp(-i\omega t) \, dt$$

$$S_{\text{coh}}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{\text{coll}}(Q,t) \exp(-i\omega t) \, dt$$

Lecture: V. García Sakai
Neutron Scattering Spectrum

Elastic scattering – no energy exchange $\hbar \omega = 0$. In an ideal world this should be a **delta** function. Of course, this is not the case giving rise to an **instrumental resolution**.

$$S(Q, \omega) = S^*(Q, \omega) \otimes R(Q, \omega)$$

Inelastic scattering – there is energy exchange $\hbar \omega \neq 0$. Due to processes occurring **discrete energy steps** such as vibrational modes, stretching modes...

Quasi-elastic scattering (QENS) – there is **small** energy exchange $\hbar \omega \neq 0 \approx \text{neV or \textmu eV}$. High energy resolution. Due to processes occurring with a distribution of energies (rotations, translations...).

$$S(Q, \omega) = \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + \omega^2}$$

“A Lorentzian”

Half Width at Half Maximum = HWHM = $\Gamma = DQ^2$

V. G. Sakai, lecture
Map of the dynamical modes

V. G. Sakai, lecture
Quasi- and Inelastic Neutron Scattering

Propagating, Oscillating Mode

Relaxating (overdamped) Mode

Lecture notes: Maikel C. Rheinstädter
Exploring the dynamic phase space
Instrumentation: direct geometry

To determine $\Delta E$ we need to define either $E_i$ or $E_f$: Two methods

Measure: $S(Q, \omega)$
Define $E_i$

Send neutrons of known fixed $E_i$ ($v_i$) – neutron can lose as much energy as it has but can gain any (defines energy window)

Source-sample and sample-detector distances known

Time at which neutron is sent, known

Time at which neutron is detected tells us $E_f$; thus we know $\Delta E$

http://www.ill.eu/instruments-support/instruments-groups/instruments/in5/

V. G. Sakai, lecture
Instrumentation: indirect geometry

Measure: $S(Q, \omega)$

Define $E_f$

Send neutrons of a known band of wavelengths or $E_i (v_i)$s (defines your energy window)

In reactor source, use a Doppler drive; in a spallation source, use choppers

Analyser crystals reflect back only a fixed $E_f$ (Bragg’s Law)

Times & distances known, so detected neutron gives us $\Delta E$

V. G. Sakai, lecture
Backscattering Spectrometer BASIS at SNS
QENS Spectrometers – Which one?

**Direct geometry:**
Poor resolution, higher energies, wider E transfer window, small Q range.

**Indirect geometry:**
@ reactor, highest resolution with good intensity but limited E transfer range

@ spallation, medium resolution, high flux, wider E transfer range

V. G. Sakai, lecture
QENS scattering function

\[ S(Q, \omega) = S_{\text{inc}}(Q, \omega) + S_{\text{coh}}(Q, \omega) \]

- Incoherent scattering
  - Contains no information about structure
  - Describes the dynamics of individual particles

- Coherent scattering
  - Contaminates elastic signal arising from structure
  - Describes correlations between nuclei
  - Describes the collective dynamics of nuclei

V. G. Sakai, lecture
Scattering can be coherent – remembering spatial arrangement of molecules
Incoherent – sensitive only to energy changes induced by molecular motion in
the sample

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<th>Element</th>
<th>$\sigma_{\text{coh}}$ (b)</th>
<th>$\sigma_{\text{incoh}}$ (b)</th>
<th>$\sigma_{\text{abs}}$ (b)</th>
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<td>Silicon</td>
<td>2.17</td>
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Quasi-Elastic Scattering

Probes diffusion at a molecular scale

Is able to differentiate diffusion from confined dynamics

Analytical functions used to describe motions

Can be used as a systematic tool for comparisons

Time and spatial scale are directly comparable to results from Molecular Dynamics simulations

Complementarities with other experimental techniques

Unique view of motions (eg. contrast)

V. G. Sakai, lecture
Single-particle dynamics (incoherent)

For uncoupled motions

\[ S_{\text{inc}}(Q, \omega) = S_{\text{vib}}(Q, \omega) \otimes S_{\text{rot}}(Q, \omega) \otimes S_{\text{trans}}(Q, \omega) \]

\[ I_{\text{self}}(Q, t) = I_{\text{vib}}(Q, t) \times I_{\text{rot}}(Q, t) \times I_{\text{trans}}(Q, t) \]

motion decomposition

\[ I_{\text{self}}(Q, t) = \frac{1}{N} \sum_i \left< e^{iQ \cdot [V(t) - V(0)]} \right| \left< e^{iQ \cdot [T(t) - T(0)]} \right| \left< e^{iQ \cdot [R(t) - R(0)]} \right> \]

Vibrations:  Debye-Waller factor

\[ DWF = \left< \exp(iQ \cdot u) \right> = \exp(-\left< (Q \cdot u)^2 \right>) = \frac{1}{3} \exp(Q^2 \left< u^2(T) \right>) \]

Simple Translational Diffusion

\[ I(Q, t) = \exp(-Q^2 D t) \quad \text{relaxation rate } |\tau| = 1/(DQ^2) \]

\[ S_{\text{trans}}(Q, \omega) = \frac{\Gamma}{\pi \Gamma^2 + \omega^2} \quad \text{ie. a Lorentzian} \]
Models of translation diffusion-restricted diffusion

V. G. Sakai, lecture
More models including rotations

\[ S_{\text{inc}}(Q, \omega) = \exp(-Q^2 \langle u^2 \rangle) \left[ A_0(Q) \delta(\omega) + \left( 1 - A_0(Q) \right) L(Q, \omega) \right] \]

- Elastic stationary part, EISF
- Quasi-elastic decaying part

\[ EISF = \frac{S_{\text{el}}^{\text{inc}}(Q)}{S_{\text{inc}}^{\text{el}}(Q) + S_{\text{inc}}^{\text{qel}}(Q)} \]

The EISF is the area of the elastic curve divided by the total area, i.e. The fraction of elastic contribution.

For any given \( Q \)

\[ \int_{-\infty}^{+\infty} S_{\text{inc}}(Q, \omega) \, d\omega = 1 \]

V. G. Sakai, lecture
Structural dynamics of water by neutron spectrometry

Unambiguous statements to be made about the dynamical nature of liquids in general and of water in particular.

B. N. Brockhouse
General Physics Branch, Atomic Energy of Canada Limited - Chalk River, Ontario

Suppl. Nuovo Cimento
9, 45 (1958)

J. Copley, NIST
Improved measurements IN6, ILL

Random jump diffusion model

Why investigate dynamics?

By understanding microscopic dynamics
tune a materials bulk properties

By M. Telling
Quasi-elastic neutron Scattering measures \( S(q,\omega) \) (BASIS at SNS)

The line width of \( S(q,\omega) \) is related to diffusion of small molecules like water in confined nanometer channels (PHYSICAL REVIEW E 76, 021505 2007)

\[
\frac{S(q,\omega)}{S(q)} = \frac{\Delta \omega}{\Delta \omega^2 + \omega^2}
\]

http://neutrons.ornl.gov/research/highlights/BASIS/

Fast Proton Hopping Detection in Ice Ih by Quasi-Elastic Neutron Scattering

Energy-Time domains

\[ \tau = \frac{2\pi}{\Delta \omega} \]

\[ E = \frac{h}{et} \]

1 ps = \frac{4.14}{1 \text{meV}}

1 ns = \frac{4.14}{1 \text{µeV}}

1 µs = \frac{4.14}{1 \text{neV}}