Applications of Neutron Scattering

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Length- and Time Scales covered by Research with Neutrons

galaxy

1

motor

10^{-2}

texture

radiography / tomography

texture diffractometry

10^{-4}

cell

reflectometry and small-angle scattering

10^{-6}

domains

reflectometry

10^{-8}

diffractometry

10^{-10}

magnetic structure

charge density

10^{-14}

nucleus

nuclear and particle physics

10^{-15}

nucleon

1

particle hadrone physics

time-resolved

- radiography

- diffraction

- reflectometry

gelation

running motor

domain wall dynamics

spin echo spectroscopy

10^{-6}

viewing glass

dynamics of macromolecules

10^{-9}

backscattering spectroscopy

10^{-11}

rotation tunneling

time-of-flight and 3-axis spectroscopy

time [s]

10^{-12}

spin waves

10^{-13}

lattice vibrations

10^{-14}

Stoner excitations

10^{-15}

nuclear Compton scattering
Sword Swallower

Radiography / Tomography
Neutron Radiography and Tomography

running car engine
Scattering: Correlation Functions

\[ S_{\text{coh}}(Q, \omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} e^{-i\omega t} \sum_{i,j} \left\langle e^{-iQ \cdot r_i(0)} \cdot e^{iQ \cdot r_j(t)} \right\rangle dt \]
Cross Section & Scattering Functions

**Cross Section: for Nuclear Scattering**

\[
\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{k'}{k} \cdot N \cdot \left[ \left( |\vec{b}|^2 - |\vec{b}'|^2 \right) S_{\text{inc}} (Q, \omega) + |\vec{b}'|^2 S_{\text{coh}} (Q, \omega) \right]
\]

- Phase space density factor
- "Interaction strength" property of system studied
- "Incoherent scattering function" depends only on time dependent positions of atoms in sample!

**Coherent Scattering Function**

\[
S_{\text{coh}} (Q, \omega) = \frac{1}{2\pi \hbar} \int G(r, t) e^{i(Q \cdot r - \omega t)} \, d^3 r \, dt
\]

- Fourier transform in space and time
- Point like scatterers

**Pair Correlation Function**

\[
G(r, t) = \frac{1}{N} \sum_{ij} \left\langle \delta (r' - r_i(0)) \cdot \delta (r' + r - r_j(t)) \right\rangle \, d^3 r'
\]

\[
= \frac{1}{N} \int \left\langle \rho (r', 0) \cdot \rho (r' + r, t) \right\rangle \, d^3 r'
\]

- Particle density

**Incoherent Scattering Function**

\[
S_{\text{inc}} (Q, \omega) = \frac{1}{2\pi \hbar} \int G_s (r, t) e^{i(Q \cdot r - \omega t)} \, d^3 r \, dt
\]

**Self Correlation Function**

\[
G_s (r, t) = \frac{1}{N} \sum_j \left\langle \delta (r' - r_j(0)) \cdot \delta (r' + r - r_j(t)) \right\rangle \, d^3 r'
\]
Elastic Scattering

intermediate scattering function: \( S(Q, t) := \int G(r, t)e^{iQr}d^3r \)

\[ = S(Q, \infty) + S'(Q, t) \]

where \( S(Q, \infty) = \lim_{t \to \infty} S(Q, t) \)

\[ \Rightarrow S(Q, \omega) = \frac{1}{2\pi \hbar} \int_{-\infty}^{+\infty} S(Q, t)e^{-i\omega t}dt \]

\[ = \frac{1}{2\pi \hbar} \int_{-\infty}^{+\infty} \left[ S(Q, \infty) + S'(Q, t) \right]e^{-i\omega t}dt \]

\[ = \frac{1}{\hbar} \delta(\omega)S(Q, \infty) + \frac{1}{2\pi \hbar} \int_{-\infty}^{+\infty} S'(Q, t)e^{-i\omega t}dt \]

Elastic scattering: infinite time correlation function

\[ e.g. \ "particles \ at \ rest" \]

(compare tennis ball reflected from wall!)

Examples: - Bragg scattering from crystal: elastic
- scattering from liquids: purely inelastic
If the detection does not discriminate the final neutron energy, we measure an integral cross section for fixed direction $\hat{k}'$ of $k'$:

$$
\left( \frac{d\sigma}{d\Omega} \right)_{coh,\text{int}} = \int \frac{\partial^2 \sigma}{\partial \Omega' \partial \omega} \bigg|_{\hat{k}'=\text{const}} \cdot d\omega
$$

Since $Q = k - k'$ and $\hbar \omega = E - E' = \frac{\hbar^2}{2m} \left( k^2 - k'^2 \right)$, $Q$ will vary with $E'$ or $\omega$ as this integral is performed ($m \neq 0 \Rightarrow$ neutron parabola!).

The (quasi-) static approximation neglects this variation, uses $Q_0$ for $\omega = 0$, and is valid only, if the energy transfer is small compared to the initial energy (or if the movement of the atoms is negligible during the propagation of the radiation wave from one atom to another):

$$
\left( \frac{d\sigma}{d\Omega} \right)_{coh,\text{QSa}} = \frac{k'}{k} \frac{N}{2\pi \hbar} \int \left( \int G(r,t) e^{iQ_0 \cdot r} \delta(t) d^3 r \right) d\omega
$$

$$
= \frac{k'}{k} \frac{N}{2\pi \hbar} \int G(r,t) e^{iQ_0 \cdot r} \delta(t) d^3 r = \frac{k'}{k} \frac{N}{2\pi \hbar} \int G(r,0) e^{iQ_0 \cdot r} d^3 r
$$

Integral scattering in quasistatic approximation: instantaneous spatial correlations; "snapshot".
Summary: Correlation Functions

- **coherent scattering**: pair correlation between different atoms at different times
- **incoherent scattering**: one particle self correlation function at different times
- **magnetic scattering**: spin pair correlation function; vector quantity ↔ polarisation
- **elastic scattering**: infinite time correlation "time averaged structure"
- **integral scattering** in (quasi-) static approximation: instantaneous correlations "snapshot,"
**Principle of Scattering Experiment**

- define \( k_i \) \((k_i = 2\pi/\lambda_i)\) and \( k_f \) with collimators and “monochromatizers”
- inelastic scattering (spectroscopy): determine change of neutron energy \( E = \frac{\hbar^2 k^2}{2m} \) during scattering process
- two possibilities to define neutron energy \( E \):
  - diffraction from single crystal (Neutron as wave)
  - time-of-flight (Neutron as particle)
Diffraction: scattering without energy analysis

either true elastic scattering (e.g. Bragg scattering from crystals)
or quasistatic scattering (e.g. slow dynamics in polymer melts)

⇒ determination of the position of the scatterers

the movement is neglected!

Relation between characteristic real space distance $d$ and magnitude of scattering vector

$Q = \frac{4\pi}{\lambda} \sin \theta$:

$Q \approx \frac{2\pi}{d}$

(compare Laue function: distance between maxima $Q \cdot d = 2\pi$)

<table>
<thead>
<tr>
<th>example</th>
<th>$d$</th>
<th>$Q$</th>
<th>$2\theta$ ($\lambda=1$ Å)</th>
<th>$2\theta$ ($\lambda=10$ Å)</th>
<th>technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom-atom distance in crystals</td>
<td>2 Å</td>
<td>3.14 Å$^{-1}$</td>
<td>29°</td>
<td>&quot;cut-off&quot;</td>
<td>wide angle diffraction</td>
</tr>
<tr>
<td>Co precipitates in Cu matrix</td>
<td>400 Å</td>
<td>0.016 Å$^{-1}$</td>
<td>0.14°</td>
<td>1.46°</td>
<td>small angle scattering</td>
</tr>
</tbody>
</table>
Small Angle Neutron Scattering SANS

SANS: large scale structures

wavelength: reasonable scattering angles → \( \lambda \approx 5\text{Å} \rightarrow 15\text{Å} \) (! direct beam separation)

Pin-hole SANS: definition of \( k_i \) through distant apertures

Focussing SANS: focus entrance aperture onto detector
Resolution: "Smearing of signal due to finite performance of instrument"

Optimisation: the better the resolution (better angular collimation, Δθ, smaller wavelength spread Δλ), the smaller the intensity

\[ Q = \frac{4\pi}{\lambda} \sin \theta \implies \]

\[ \Delta Q^2 = \left( \frac{\partial Q}{\partial \theta} \right)^2 (\Delta \theta)^2 + \left( \frac{\partial Q}{\partial \lambda} \right)^2 (\Delta \lambda)^2 \]

\[ = \left( \frac{4\pi}{\lambda} \right)^2 \cos^2 \theta (\Delta \theta)^2 + \left( \frac{4\pi \sin \theta}{\lambda^2} \right)^2 \Delta \lambda^2 \]

\[ \approx \left( \frac{4\pi}{\lambda} \right)^2 \left[ (\Delta \theta)^2 + \theta^2 \left( \frac{\Delta \lambda}{\lambda} \right)^2 \right] \]

\[ \approx \frac{k^2}{12} \left[ \left( \frac{d_E}{L_D} \right)^2 + \left( \frac{d_S}{L_C} \right)^2 + \left( \frac{d_S}{L_C} + \frac{d_S}{L_D} \right)^2 + \theta^2 \left( \frac{\Delta \lambda}{\lambda} \right)^2 \right] \]

Optimised → all terms have similar values
→ \( L_D = L_C; \) \( d_E = d_D = 2d_S \)

typical: \( L_D = L_C = 10 \) m; \( d_D = d_E = 3 \) cm

Detector radius ~ 30 cm = \( r_D \)

\[ \frac{\Delta \lambda}{\lambda} \approx \frac{d_E}{L_C} \frac{L_D}{r_D} \approx \frac{d_E}{r_D} \approx \frac{1}{10} = 0.1 \implies \] velocity selector

"screw thread – principle"
Selforganisation of crystalline-amorphous diblock-copolymer

Networks of bundles with mass-fractal aspect: “snow flake”

Rods on medium length scale

Rods organize as bundles

2-d structure on shortest length scale

A. Radulescu et al., Neutron News 16 (2005), 18
SANS: Applications

- Polymers and colloids, e.g.
  - Micelles
  - Dendrimers
  - Liquid crystals
  - Gels
  - Reaction kinetics of mixed systems
- Materials Science
  - Phase separation in alloys and glasses
  - Morphologies of superalloys
  - Microporosity in ceramics
  - Interfaces and surfaces of catalysts
- Biological macromolecules
  - Size and shape of proteins, nucleic acids and of macromolecular complexes
  - Biomembranes
  - Drug vectors
- Magnetism
  - Ferromagnetic correlations
  - Flux line lattices in superconductors
  - Magnetic nanoparticles
Large Scale Structures: Reflectometry

soap-bubbles:

colours due to interference:

- destructive (here: blue)
- constructive (here: red)

⇒ determination of film thickness (soap bubble ~ µm)
Large Scale Structures: Reflectometry

Schematics of a neutron reflectometer:

Monochromatization

Velocity selector

Chopper

Time-of-flight TOF

Crystal monochromator
\[
\Delta = (\overline{AB} + \overline{BC}) \cdot n_1 - \overline{AD} = 2dn_1 \sin \alpha_t
\]

Distance of interference maxima (neglect refraction on top surface):

\[
\lambda = 2d \cdot (\Delta \alpha) \Rightarrow \Delta Q \approx \frac{2\pi}{d}
\]
• **Soft Matter:**
  Thin films, e.g. polymer films: polymer diffusion, selforganization of diblockcopolymers; surfactants; liquid-liquid interfaces,…

• **Life science:**
  Structure of biomembranes;

• **Materials Science:**
  Surfaces of catalysts; Kinetic studies of interface evolution; structure of buried interfaces

• **Magnetism:**
  Thin film magnetism, e.g. exchange bias, laterally structured systems for magnetic data storage, multilayers of highly correlated electron systems

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Reflectometry: Applications

- **Biomembranes**
- **Spin valve**
- **Magnetic Random Access Memory (MRAM)**
- **Catalyst surfaces**
- **Buried interfaces**
Example: D9 at ILL:
Monochromator instrument:

\[ 2d \sin \theta = \lambda \]

Monochromatization by Bragg diffraction from a single crystal
Atomic Structures: Powder Diffraction

Example: D2B at ILL/Grenoble
Overlap of Reflections: Rietveld-Refinement

- Bragg reflections overlap for larger unit cells e. g. due to finite peak width.

Resolution function:

\[
(\Delta 2\theta)^2 = U \tan^2 \theta + V \tan \theta + W
\]

How to determine structural parameters?

Solutions:
Rietveld-Refinement (profile refinement)
- refine structural parameters (unit cell metric, atom positions and site occupations, Debye-Waller-factors, …) together with instrument parameters \((2\theta_0, U, V, W, \ldots)\)

Pair Distribution Function analysis (PDF)

Example:
Life science:
Structure of biological macromolecules, e.g. water in protein structures

Chemistry:
Structure determination of new compounds, position of light atoms; Time resolved reaction kinetics

Materials science:
Stress / Strain in structure materials; texture

Geoscience:
Phase and texture analysis

Solid state physics:
Structure-function relations, e.g. in high-Tc superconductors; magnetic structures and spin densities e.g. in molecular magnets
neutrons

Generic TOF Spectrometer
Path-Time Diagram

\[
p = \frac{h}{\lambda} = m \cdot v \quad \text{and} \quad v = \frac{d}{t} = \frac{m \cdot d \cdot \lambda}{h}
\]

(typically 1 ms/m)
Example for an Application

Molecular structure

Excitation spectrum
Measured with TOF

Energy level diagram

Neutron spectroscopy from the molecular magnet Mn$_{12}$ acetat:
determination of magnetic interaction parameters (Güdel et al.)
Applications TOF Spectroscopy

- **Soft Matter and Biology:**
  dynamics of gels, proteins and biological membranes; diffusion of liquids, polymers; dynamics in confinement
- **Chemistry:**
  vibrational states in solids and adsorbed molecules on surfaces; rotational tunnelling in molecular crystals
- **Materials Science:**
  molecular excitations in materials of technological interest (e.g. zeolites) and especially in diluted systems (matrix isolation); local and long-range diffusion in superionic glasses, hydrogen-metal systems, ionic conductors.
- **Solid State Physics:**
  quantum liquids; crystal field splitting in magnetic systems; spin dynamics in high-$T_C$ superconductors; phase transitions and quantum critical phenomena; phonon density of states
Neutron Spin Echo Spectroscopy

Problem: Conventional TOF: high resolution requires good monochromatization → low intensity

Solution: Neutron Spin Echo NSE: each individual neutron carries its own clock to measure its individual time of flight

\[ \Delta \lambda / \lambda = 10\% \]

\[ \frac{ds}{dt} = \gamma_S \times B \]

\[ \pi/2 \] flipper \quad \text{precession 1} \quad \pi \quad \text{sample} \quad \text{precession 2} \quad \pi/2 \] detector analyzer
Example NSE: Polymer Dynamics
Triple-Axis Spectroscopy

... and in reciprocal space

\[ Q = k_f - k_i = G_{hkl} + q \]

inelastic scattering!
TAS-Example: SV-30 / FZJ
Lattice & Spin Dynamics

- Thermal motion
- Eigenmode (optical phonon)

- Ferromagnetic spin wave (magnon)
- Antiferromagnetic spin wave (magnon)
Determination of Spin Wave Dispersions

Dispersion relations for the garnet $\text{Fe}_2\text{Ca}_3\text{Ge}_3\text{O}_{12}$:

<table>
<thead>
<tr>
<th>Mode</th>
<th>$E$ [THz]</th>
<th>$\sigma_{\text{Fe}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.030</td>
<td>-</td>
</tr>
<tr>
<td>1'</td>
<td>0.091</td>
<td>+</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>atom no.</th>
<th>1</th>
<th>5</th>
<th>9</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td>coordinates $q_{\text{Fe}}$, $\sigma_{\text{Fe}}$</td>
<td>(0 0 0)</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
</tr>
</tbody>
</table>

Th. Brückel et al

magnetic structure

eigenmodes

constant Q-scans

Brillouin zone

Determination of interaction (exchange) parameters

Counts per 10 min

$E$ [THz]
• Phonon dispersions $\rightarrow$ interatomic forces

• Spin wave dispersions $\rightarrow$ exchange and anisotropy parameters

• Dynamics of biological model membranes

• Lattice and spin excitations: Quantum magnets, superconductors, …

• Phase transitions: critical behaviour

Chiral phase transitions
Spin dynamics in frustrated systems
Phonons in High $T_C$
Low dimensional magnets
Experimental techniques with spatial resolution:
Neutron Diffraction compared to other experimental techniques

Experimental techniques with time / energy resolution:
Neutron spectroscopy compared to other experimental techniques
Neutrons and Society