Applications of Neutron Scattering - An Overview

Thomas Brückel

Jülich Centre for Neutron Science JCNS
and
Peter Grünberg Institut PGI
and
RWTH Aachen University

JCNS Neutron Lab Course 2014
Length- and Time Scales covered by Research with Neutrons
Outline

• Scattering and correlation functions
• Principle of a scattering experiment
• Diffraction – Where are the atoms?
  • Small angle neutron scattering
  • Reflectometry
  • Diffraction
• Spectroscopy – What are the atoms doing?
  • Time-of-flight spectroscopy
  • Spin echo spectroscopy
  • Triple axis spectroscopy
Scattering Triangle

Scattering vector

\[ \mathbf{Q} = \mathbf{k}' - \mathbf{k} \]

\[ k = \frac{2\pi}{\lambda} \]
Neutron Propagation: Wave Nature

Phase difference for scattering from 2 points:
\[ \Delta \Phi = 2\pi \cdot \frac{(\overline{AB} - \overline{CD})}{\lambda} = k' \cdot r - k \cdot r = Q \cdot r \]

Plane wave phase factor:
\[ e^{iQ \cdot r} = \cos(Q \cdot r) + i \sin(Q \cdot r) \]
De Broglie:
particle ↔ wave dualism:
momentum ↔ wavelength / propagation vector:

\[ p = \frac{h}{\lambda} = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \hbar k \ ; \quad p = \hbar k \]

change of momentum of radiation during scattering process
≡ - momentum transfer to scatterer:

\[ \Delta p = p' - p = \hbar k' - \hbar k = \hbar Q \]
Scattering vector $Q$:

- Phase factor $e^{iQ \cdot r}$
  $\rightarrow$ structure factor

- Momentum transfer $-\hbar Q$
Coherent Scattering

➢ Coherent:
  scattering from pairs of scatterers with definite phase relationship;
  adding up of scattered amplitudes with phase factor:

\[
\frac{d\sigma}{d\Omega}(Q) = \langle b \rangle^2 \left| \sum_i e^{iQ \cdot R_i} \right|^2
\]

- proportional to square $N^2$ of number $N$ of scatterers
- depends on average scattering length
- strong $Q$ dependence
Bragg Scattering

Laue condition: \[ Q = G^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \]

Bragg's law: \[ 2d \sin \theta = \lambda \]

\[ k \cdot \left( \frac{1}{2} G^* \right) = \left( \frac{1}{2} G^* \right)^2 \]

every wave vector from the origin to the boundary of the Brillouin zone satisfies the diffraction condition

with \[ \Delta p = p' - p = \hbar k' - \hbar k = \hbar Q \]
and \[ Q_{hkl} = \frac{2\pi}{d_{hkl}} \cdot \frac{d_{hkl}}{d_{hkl}} \]

we arrive at:

Born quantization condition: \[ \Delta p \cdot d_{hkl} = nh \]

action changes during quantum transition by multiples of \( h \)!
Incoherent Scattering

- **Incoherent:** individual scatterers without phase relationship; adding up of scattered intensity from individual scatterers:

\[ \sigma = -\frac{d}{d\Omega}(Q) = N \left\langle (b - \langle b \rangle)^2 \right\rangle \]

- proportional to number \( N \) of scatterers
- depends on statistical deviations from average
- no \( Q \) dependence
Scattering: Correlation Functions

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

\[ I \sim e^{-iQ \cdot r_i (0)} \cdot e^{iQ \cdot r_j (t)} \]
Elastic / Inelastic Scattering

- **elastic scattering:**
  particles at rest: “infinite time correlations”

- **inelastic scattering:**
  time dependent processes

\[
I \propto \frac{d^2 \sigma}{d \omega d \Omega} \propto S(Q, \omega) = \frac{1}{2\pi \hbar} \int_{-\infty}^{+\infty} dt \, e^{-i\omega t} \int d^3 r \, e^{iQ \cdot r} G(r, t)
\]

pair correlation function:

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

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

- **integral scattering:**
  snapshot: “instantaneous spatial correlations”
Cross Section & Scattering Functions

cross section: for nuclear scattering
\[
\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{k'}{k} \cdot N \cdot \left[ \left( |\bar{b}|^2 - |\bar{b}'|^2 \right) S_{inc}(Q, \omega) + |\bar{b}'|^2 S_{coh}(Q, \omega) \right]
\]
  phase space density factor
  "interaction strength"
  probe-sample interaction
  property of system studied

coherent scattering function:
\[
S_{coh}(Q, \omega) = \frac{1}{2\pi\hbar} \int G(r, t) e^{i(Q \cdot r - \omega t)} d^3 r dt
\]
  Fourier transform in space and time
  point like scatterers

pair correlation function:
\[
G(r, t) = \frac{1}{N} \sum_{ij} \int \langle \delta(r' - r_i(0)) \cdot \delta(r' + r - r_j(t)) \rangle d^3 r'
\]
  = \frac{1}{N} \int \langle \rho(r', 0) \cdot \rho(r' + r, t) \rangle d^3 r'

  particle density

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

self correlation function:
\[
G_s(r, t) = \frac{1}{N} \sum_{j} \int \langle \delta(r' - r_j(0)) \cdot \delta(r' + r - r_j(t)) \rangle d^3 r'
\]
Summary: Correlation Functions

- **coherent scattering:** pair correlation between different atoms at different times
  example: phonons

- **incoherent scattering:** one particle self correlation function at different times
  example: diffusion

- **magnetic scattering:** spin pair correlation function; vector quantity ↔ polarisation
  example: magnetic structure, magnons

- **elastic scattering:** infinite time correlation
  "time averaged structure,"
  example: Bragg scattering from x-tal

- **integral scattering in (quasi-) static approximation:** instantaneous correlations
  "snapshot,"
  example: liquids
Outline

• Scattering and correlation functions

• **Principle of a scattering experiment**

• Diffraction – Where are the atoms?
  • Small angle neutron scattering
  • Reflectometry
  • Diffraction

• Spectroscopy – What are the atoms doing?
  • Time-of-flight spectroscopy
  • Spin echo spectroscopy
  • Triple axis spectroscopy
• 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)
Collimation

- system of two slits:

- Soller collimator:

  e.g. Gd covered Mylar foils

radial collimator (PSI)
Monochromatization by Bragg Diffraction.

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

focussing monochromator:

Cu200; \( d = 1.807 \text{Å} \)

PG002; \( d = 3.35416 \text{Å} \)
Monochromatization by Time of Flight

- velocity selector:
  - moving channel with neutron absorbing walls

\[
\frac{\Delta \lambda}{\lambda} \approx 10 \ldots 20\%
\]
Monochromatization by Time of Flight

- Pair of choppers:

\[ v[m/s] \approx \frac{4000}{\lambda[\text{Å}]} \]

\[ s = v \Delta t \]

\[ \alpha = \omega \Delta t \]

Disk chopper

Chopper disk
Fermi chopper:

("rotating Soller collimator")

Fermi-Chopper

rotating collimator

$\Delta \alpha \approx 1^0$

$\Delta \tau \approx \Delta \alpha / \Omega$

$\Delta \tau \approx 10 \mu s$

$\Omega \approx 2\pi 200 \text{Hz}$
Gas counters:

principle: Geiger-Müller-counter:

\[ \text{neutron capture & conversion to charged particles:} \]

\[ ^3\text{He} + n \rightarrow ^4\text{He}^* \rightarrow p + ^3T + 0.76\text{MeV} \]

\[ \sigma [\text{barns}] = 5333 \frac{A}{1.8} \]

\[ \approx 25,000 \text{ ions and electrons per neutron} \]
Detection: Problem!

US homeland security: border control:

$^3$He detector banks
Detection

- scintillation counters:
  - neutron
  - scintillator crystal
  - emitted light
  - photo-multiplier

neutron capture & conversion to light:

\[ ^6\text{Li} + n \rightarrow ^7\text{Li}^* \rightarrow ^3\text{T} + ^4\text{He} + 4.79\text{MeV} \]

e.g. energetic charged particle in scintillator phosphor (e.g. CsI, ZnS(Ag))

neutron Anger camera:
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**Diffraction**

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

$$Q = \frac{4\pi}{\lambda} \sin \theta : \quad Q \approx \frac{2\pi}{d}$$

(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 $\rightarrow \lambda \approx 5\,\text{Å} \rightarrow 15\,\text{Å} \quad (! \text{ direct beam separation})$

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, \( \Delta \theta \)),
smaller wavelength spread \( \Delta \lambda \)), the smaller the intensity

\[
Q = \frac{4\pi}{\lambda} \sin \theta \\
\Delta Q^2 = \left( \frac{\partial Q}{\partial \theta} \right)^2 (\Delta \theta)^2 + \left( \frac{\partial Q}{\partial \lambda} \right)^2 (\Delta \lambda)^2 \\
= \left( \frac{4\pi}{\lambda} \right)^2 \cos^2 \theta (\Delta \theta)^2 + \left( \frac{4\pi \sin \theta}{\lambda^2} \right)^2 \Delta \lambda^2 \\
\approx \left( \frac{4\pi}{\lambda} \right)^2 \left[ (\Delta \theta)^2 + \theta^2 \left( \frac{\Delta \lambda}{\lambda} \right)^2 \right] \\
= \frac{k^2}{12} \left[ \left( \frac{d_D}{L_D} \right)^2 + \left( \frac{d_E}{L_C} \right)^2 + \left( \frac{d_s + d_s}{L_C} \right)^2 + \theta^2 \left( \frac{\Delta \lambda}{\lambda} \right)^2 \right]
\]

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

typical: \( L_D = L_C = 10 \text{ m} \); \( d_D = d_E = 3 \text{ cm} \)
Detector radius \( \sim 30 \text{ cm} =: r_D \)

\[
\Rightarrow \frac{\Delta \lambda}{\lambda} = \frac{d_E}{L_C} \cdot \frac{L_D}{r_D} \approx \frac{d_E}{r_D} \approx \frac{1}{10} = 10\% \Rightarrow \text{velocity selector}
\]
Example: Iron-oxide (Fe$_2$O$_3$ / Fe$_3$O$_4$) nanoparticles with organic ligand shell (oleic acid) in solution (toluene) scattering length density (continuum approximation!): 

x-ray: \[ \rho_{el} = \frac{r_e \sum_j Z_j}{V_m} \]

neutron: \[ \rho_n = \frac{\sum b_j}{V_m} \]
SAXS: Example - Nanoparticles

form factor:

\[
f(Q) \equiv \frac{\int_{V_0} d^3r' V(r') e^{i Q \cdot r'}}{\int_{V_0} d^3r' V(r')}
\]

sphere:

\[
\Rightarrow f(Q) = 3 \cdot \frac{\sin QR - QR \cdot \cos QR}{(QR)^3}
\]
SANS: Example - Nanoparticles

effects of

instrument resolution
and
particle size distribution

\( Q [\text{Å}^{-1}] \)
\( \mu [\text{cm}^{-1}] \)
\( \frac{d\sigma}{dQ} [\text{cm}^{-1}] \)

monodisperse
\( \sigma = 0.02 \)
\( \sigma = 0.05 \)
\( \sigma = 0.10 \)
\( \sigma = 0.20 \)
• 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
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
- Chopper
- Time-of-flight (TOF)
- Crystal monochromator

- PSD: position sensitive detector
- reflected beam
- thin film sample on goniometer
- primary collimation slits
- monitor
- monochromator
- white beam from source
- Velocity selector
Snell's law for refraction:

\[
\frac{\cos \alpha_i}{\cos \alpha_t} = \frac{k_t}{k_i} = n
\]

for x-rays and neutrons: in general \( n < 1 \)  
\( \Rightarrow \) external total reflection below critical angle \( \theta_c \): \( \cos \theta_c = n \)

**Example:** Reflectivity and Transmissivity of neutrons at a Ni surface:

\[ Q = 4\pi/\lambda \sin(\theta) \text{ (Å)} \]

\[ R, T \]
... by external total reflection \[ \cos \theta_c = n = 1 - \frac{\lambda^2}{2\pi} \sum_{j} b_j \rho_j \approx 1 - \frac{1}{2} \theta_c^2 \rightarrow \theta_c \propto \lambda \]

e.g. $^{58}\text{Ni}$ covered polished glass

natural Ni: \[ \theta_c [\text{degree}] \approx 0.1 \cdot \lambda [\text{Å}] \]
Beam Transport - Guide Hall @ FRM II
Path length difference:
\[ \Delta = (\overline{AB} + \overline{BC}) \cdot n_1 - \overline{AD} = 2dn_1 \sin \alpha_t \]

Distance of interference maxima (neglect refraction on top surface):
\[ \lambda = 2d \cdot (\Delta \alpha) \Rightarrow \Delta Q \approx \frac{2\pi}{d} \]

Example: Reflectivity of neutrons from a Ni layer on glass substrate (Neutron guide):
"Kiessig fringes"
• **Soft Matter:**
  Thin films, e.g. polymer films: polymer diffusion, self-organization of diblock copolymers; 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
Example: D9 at ILL:
Monochromator instrument:

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

Monochromatization by Bragg diffraction from a single crystal
Magnetic ordering in $\text{BaFe}_2\text{As}_2$

family of iron pnictide superconductors

Single-crystal neutron diffraction on $\text{BaFe}_2\text{As}_2$
saturated moment: $0.99(6)\mu_B$ along $a$ direction

Y. Su, et al.,
Antiferromagnetic ordering and structural phase transition in $\text{BaFe}_2\text{As}_2$ with Sn incorporated from the growth flux.
PRB 79, (2009), 064504
Example: D2B at ILL/Grenoble
Overlap of Reflections: Rietveld-Refinement

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

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

Resolution function:

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:

CMR Manganite
• 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
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Generic TOF Spectrometer

neutrons

histogrammic memory
incrementing

det. #
tof-channel
Path-Time Diagram

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

\[ v = \frac{d}{t} \] (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.)
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

\[ \Delta \lambda / \lambda = 10\% \]
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
\[ Q = k' - k = G_{hkl} + q \]

**Triple-Axis Spectroscopy**

... and in reciprocal space

\[ Q = k' - k = G_{hkl} + q \]

inelastic scattering!
TAS-Example: SV-30 / FZJ

- monochromator
- shielding
- sample table
- analyzer shielding
- detector shielding
- glass floor
- air pads
Lattice & Spin Dynamics

thermal motion

Ferromagnetic spin wave (magnon)

eigenmode (optical phonon)
Phonon Dispersion in FeAs- high $T_c$

R. Mittal et al.;
“Measurement of Anomalous Phonon Dispersion of CaFe$_2$As$_2$ Single Crystals Using Inelastic Neutron Scattering.”
PRL 102 (2009), 217001.

anomalous broadening zone boundary phonons involving only Fe
TAS-Applications

- Phonon dispersions → interatomic forces
- Spin wave dispersions → 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

Low dimensional magnets

Phonons in High $T_C$

Phase dynamics in frustrated systems

Energy (meV)

$S(Q)$ (willk"urliche Einheiten)
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
Why $X$ & $n$?

different cross sections!

\begin{align*}
\cdot 10^{-1} & \quad \sigma \, [\text{barn}] \\
\cdot & \quad 0.66 \quad \text{H} \\
\cdot & \quad 24 \quad \text{C} \\
\cdot & \quad 416 \quad \text{Mn} \\
\cdot & \quad 450 \quad \text{Fe} \\
\cdot & \quad 522 \quad \text{Ni} \\
\cdot & \quad 1408 \quad \text{Pd} \\
\cdot & \quad 2986 \quad \text{Ho} \\
\cdot & \quad 5631 \quad \text{U} \\
\cdot & \quad 0.1 \quad \text{U} \\
\cdot & \quad 1 \quad \text{U} \\
\cdot & \quad 2 \quad \text{U} \\
\cdot & \quad 58 \quad \text{U} \\
\cdot & \quad 60 \quad \text{U} \\
\cdot & \quad 62 \quad \text{U} \\
\cdot & \quad 8.90 \quad \text{U} \\
\cdot & \quad 8.90 \quad \text{U} \\
\cdot & \quad 8.90 \quad \text{U} \\
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\cdot & \quad 8.90 \quad \text{U} \\
\end{align*}

1 barn = $10^{-28} m^2$

\text{x-ray element} \quad \text{neutrons}
Neutrons and Society
"Wichtig ist, daß man nicht aufhört zu fragen."