Dynamics and Neutron Scattering

Dan Neumann
NIST Center for Neutron Research

dan@nist.gov www.ncnr.nist.gov
Chemical Separation

Molecular sieves separate chemical species via different rates of diffusion.

*Carbogenic molecular sieves are used to separate oxygen and nitrogen. The ratio of diffusivities is ~ 20:1.*
Solid state batteries and fuel cells depend on the rapid diffusion of ions both in the electrodes and through the electrolyte.

Li ions move from a transition metal oxide to a carbon electrode by traversing a polymer electrolyte in response to a flow of electrons supplied by an external circuit.
The biological activity of a protein depends on its ability to fold into its own native state. Protein function relies on structure and dynamics.

Dynamic actin based structures are important in cell shape changes and motility, cytokinesis and other processes. Here we see the diffusion pathways for water to reach the active site. These are believed to be relevant for the dissociation of phosphate after hydrolysis.
Dynamics

Fundamental Information on Interactions in Materials

Structural probes yield indirect information on interactions in materials by locating the minimum of the potential. Dynamical probes, including neutron scattering, reveal information on the shape of the potential.
What is required to do an inelastic neutron scattering experiment

1. A source of neutrons
2. A method to prescribe the wavevector ($k_i$) of the neutrons incident on the sample
3. A well-chosen sample
4. A method to determine the wavevector ($k_f$) of the scattered neutrons
5. A detector

$$\text{momentum} = \frac{\hbar \mathbf{k}}{2\pi/\lambda}$$
$$\text{energy} = \frac{(\hbar k)^2}{2m}$$
$$E_f \mathbf{k_f}$$

Measure the number of scattered neutrons as a function of $Q$ and $\omega$

$$S(Q, \omega) \text{ (the scattering function)}$$

depends ONLY on the sample
Quasielastic and Inelastic Neutron Scattering

Inelastic neutron scattering peaks at non-zero energy transfer. This scattering reflects the vibrational modes of the system.

Quasielastic neutron scattering peaks at zero energy transfer, but is broadened compared to the instrumental resolution. It arises from diffusive processes.

Elastic neutron scattering is the scattering for which the energy transfer is identically zero.
Why Neutrons

Wavelength ~ Å’s

• comparable to interatomic and intermolecular distances
• comparable to x-rays

=> interference effects

cold neutrons - long wavelengths - longer length scales
Why Neutrons

Energy ~ meV’s

• comparable to the time scale of many motions in materials
  => inelastic scattering from vibrations, diffusion, reorientations,
      and relaxational processes can be observed

• light \( E \sim \text{eV’s} \quad \lambda \sim 1000 \text{Å’s} \quad Q \sim 0 \) (selection rules)
• x-rays \( E \sim \text{keV’s} \quad \lambda \sim \text{Å’s} \)

cold neutrons - lower energies - longer time scales

\[ 1 \text{ meV} \approx 8 \text{ cm}^{-1} \approx 240 \text{ GHz} \approx 12 \text{ K} \approx 0.1 \text{ kJ/mol} \sim \text{ps} \]
Why Neutrons

Wavelength ~ Å’s ⇔ Energy ~ meV’s

=> geometry of the motion!
Why Neutrons

Magnetic Moment

- neutrons interact \textit{directly} with magnetic materials

=> \textit{magnetic structures}

=> \textit{magnetic excitations}

Spin Wave Animation courtesy of A. Zheludev (ORNL)
Why Neutrons

Nuclear Interaction

• scattering power varies “randomly” from isotope to isotope
  => isotopic labeling
  => scattering from light elements comparable to that from heavy elements
scattering power varies “randomly” from isotope to isotope

**Cross section (\(\sigma\))** - Area related to the probability that a neutron will interact with a nucleus in a particular way (e.g. scattering or absorption)

For systems containing a reasonable proportion of H atoms, scattering from H tends to dominate

For a single nucleus \(\sigma \sim 10^{-24} \text{ cm}^2\)

Relative total scattering cross sections for a few isotopes
Guanidinium Organodisulfonates (GDS)

Class of guest-host materials developed by Mike Ward’s group at the University of Minnesota.

Basic bonding motif is through hydrogen bonds between the H’s on guanidinium ions and the O’s on sulfonate groups.
Guanidinium Organodisulfonates (GDS)

Three components
The host consists of G and R
The guests are biphenyl’s - B
Isotopically substituted $G_2[BPDS]^3$(biphenyl)

Nuclear Interaction

- scattering power varies “randomly” from isotope to isotope
- nuclear spin dependence of the interaction

Not all nuclei in a sample consisting of only one element or even only isotope necessarily scatter identically

=> RANDOMNESS

If the scattered neutron waves from the different nuclei have RANDOM relative phases, they don’t interfere

=> INCOHERENT SCATTERING

If the scattered neutron waves from the different nuclei have definite relative phases, they can interfere

=> COHERENT SCATTERING
Scattering function

Measure the number of scattered neutrons as a function of $Q$ and $\omega$

$$\Rightarrow S(Q,\omega) \text{ (the scattering function)} \quad \text{depends ONLY on the sample}$$

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

$S_{\text{inc}}(Q,\omega)$ is the time and space Fourier transform of the SELF correlation function

$S_{\text{coh}}(Q,\omega)$ is the time and space Fourier transform of the PAIR correlation function

* Spin Echo measures the INTERMEDIATE scattering function $I(Q,t)$
Self-correlation function

Consider the instantaneous probability that a particle is correlated with itself.

This corresponds to a typical “diffraction” measurement which integrates over energy.

=> for diffraction experiments, incoherent scattering is **background**
Consider the time-dependence of the probability that a particle is correlated with itself for the case of a perfectly stationary particle.

\[ P(t) \]

\[ S(\omega) \]

\[ \omega = 0 \]

=> If there is no motion, the scattering is elastic i.e. it occurs only at \( \omega = 0 \)
Consider the time-dependence of the probability that a particle is correlated with itself for the case of a randomly diffusing particle i.e. \( P(t) = e^{-t/\tau} \)

\[
S(\omega) = \frac{1}{\pi} \frac{1}{1 + (\omega \tau)^2}
\]

=> for quasielastic experiments, incoherent scattering is often the **signal**
Inelastic neutron scattering centered at $\omega = 0$

$=>$ Measures diffusion, molecular reorientations and relaxations

$$p = e^{-t/\tau}$$

$1/\tau = DQ^2$

$Q_s > Q_l$
Quasielastic Neutron Scattering

$S(Q, \omega)$ is the time Fourier transform of $I(Q,t)$

$I(Q,t) = e^{-t/\tau}$

$\frac{1}{\tau} = DQ^2$

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

Half Width = $DQ^2$

$Q_s > Q_l$
The relevant correlation function for any neutron scattering experiment is typically written as

$$G(r,t) = \langle n(0,0) n(r,t) \rangle$$

where

$$n(r,t) = \sum_{j}^{N} \delta(r - r_j(t))$$

$G(r,t)$ is the sum of:
- the self correlation function $G_S(r,t)$ and
- the pair correlation function $G_p(r,t)$.

$G_S(r,t)$ is the probability of finding a particle at position $r$ at time $t$ if that same particle was at position 0 at time 0.

$G_p(r,t)$ is the probability of finding a particle at position $r$ at time $t$ if there was a particle at position 0 at time 0.
Motions in a protein

Simulation of RNase-A

Courtesy of M. Tarek
Intermediate scattering function is a space-Fourier transform of $G(r,t)$:

$$I(Q,t) = \int_V G(r,t) \exp(iQr) d^3r$$

Van Hove [Phys.Rev. 95, 249 (1954)] showed that the intermediate scattering function can also be written as:

$$I(Q,t) = \sum_i \sum_j \langle \exp[-iQr_i(0)]\exp[iQr_j(t)] \rangle = \sum_i \sum_j \langle \exp[-iQ\{r_i(0) - r_j(t)\}] \rangle$$

The scattering function is the time-Fourier transform of $I(q,t)$:

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

$$S_{coh}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I_{coh}(Q, t) \exp(-i\omega t) dt$$
Coherent vs. Incoherent Scattering

Most isotopes and elements scatter mostly coherently. The most important exception is hydrogen.
Why Neutrons

Nuclear Interaction

- scattering power varies “randomly” from isotope to isotope
  => isotopic labeling
  => scattering from light elements comparable to that from heavy elements
- nuclear spin dependence of the interaction
- strong but very short ranged
- no electrostatic interaction (overall interaction is weak)
  => neutrons easily penetrate experimental apparatus
  => easy to compare with theory and models
  e.g. First-principles calculations, Molecular dynamics simulations
Molecular dynamics simulations and neutron scattering

\[ S_{inc}(Q, \omega) \propto \int_{-\infty}^{\infty} I_s(Q, t)e^{-i\omega t} dt, \quad I_s(Q, t) \propto \sum_j \langle e^{i\tilde{Q}\cdot\tilde{r}_j(t)} e^{-i\tilde{Q}\cdot\tilde{r}_j(0)} \rangle \]

scattering function \quad intermediate scattering function

\( I(Q, t) \) can be calculated from MD simulations

 Typical instruments and MD time and length scale overlap

check validity of inter-atomic interactions
interpret INS data, describe motions in real space
guide additional neutron measurements
QENS vs. MD for $\alpha$-lactalbumin native state

The NIST Center for Neutron Research
Why are there so many different spectrometers?

Neutron scattering is an intensity limited technique. Thus the detector coverage and resolution MUST be tailored to the science.

Uncertainties in the neutron wavelength and direction imply that $\mathbf{Q}$ and $\hbar\omega$ can only be defined with a certain precision.

The total signal in a scattering experiment is proportional to the resolution volume i.e. better resolution leads to lower count rates

Courtesy of R. Pynn
Inelastic Neutron Scattering

Neutron techniques available at the NCNR give researchers access to 7 orders of magnitude in time.

Future sources (the SNS under construction at ORNL) should provide 9
Dynamics and Neutron Scattering

The *dynamics* of a system reflect the interatomic and intermolecular interactions which are responsible for the properties of materials.

Neutron Scattering is an excellent way to study *dynamics*.