Dynamics and Neutron Scattering

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Dynamics

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.

Dynamics
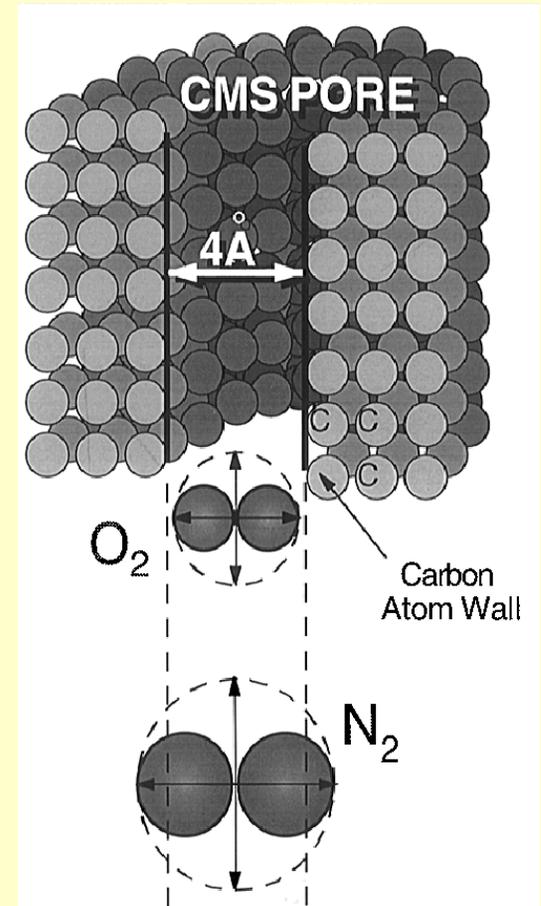
Batteries and Fuel Cells

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.

Negative current collector — Li_yC_6

Li ion conducting electrolyte

Positive current collector — $Li_{(1-x)}Mn_2O_4$
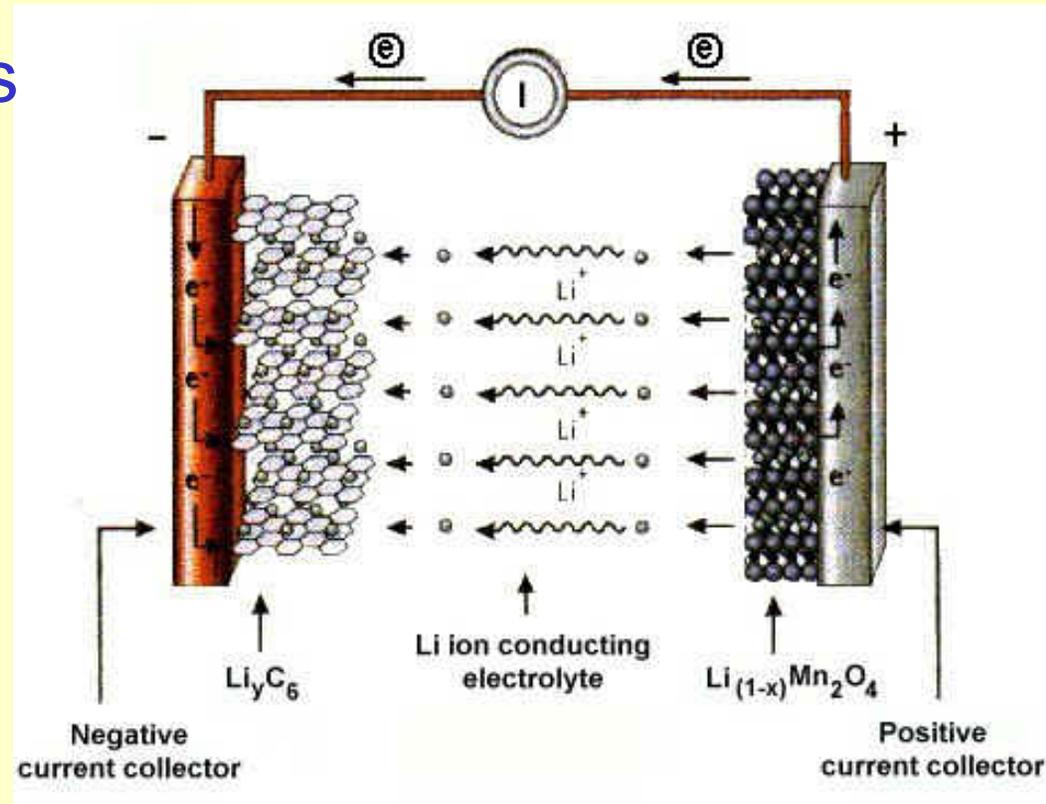
Dynamics

Protein Function

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.
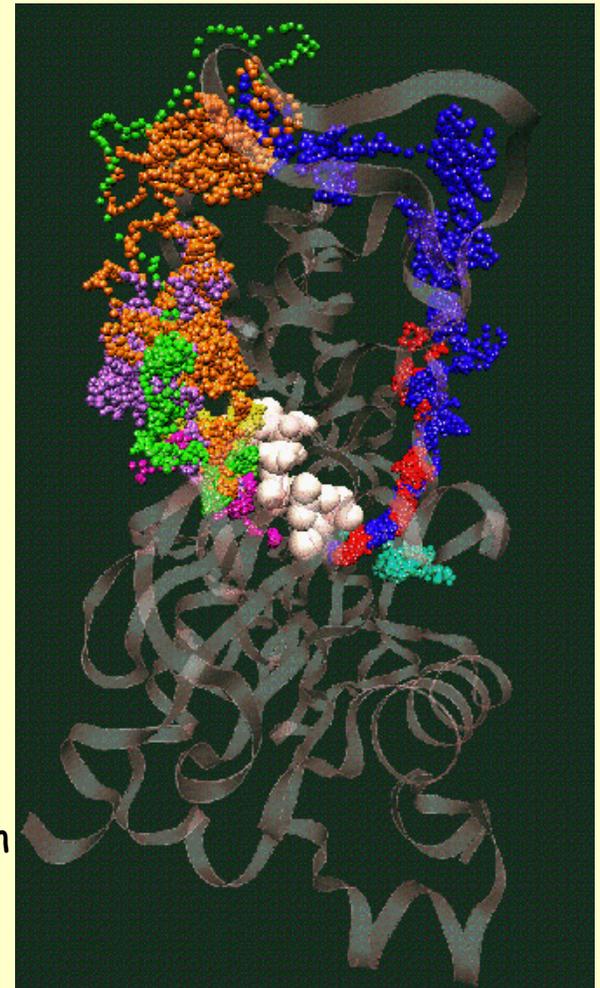
Dynamics

Fundamental Information on Interactions in Materials

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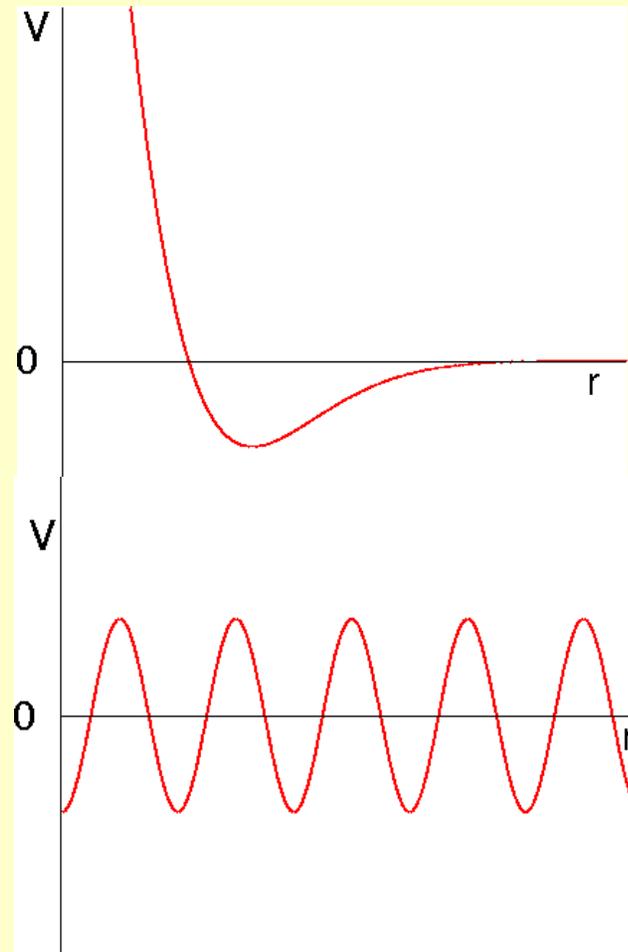
What is required to do an inelastic neutron scattering experiment

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

$$\text{momentum} = \hbar\vec{k} \qquad \text{energy} = (\hbar k)^2/(2m)$$
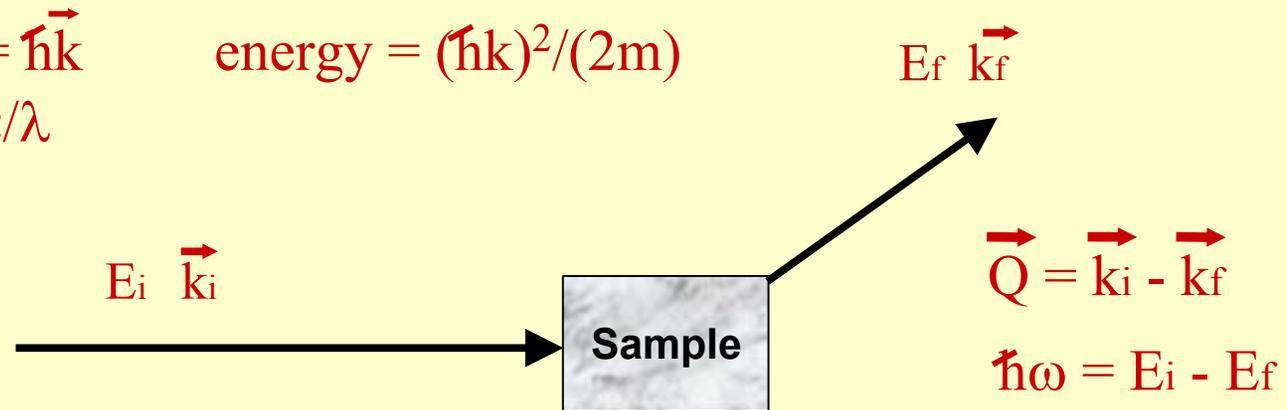
$$k = 2\pi/\lambda$$

$E_f \ \vec{k_f}$

$E_i \ \vec{k_i}$

Sample

$$\vec{Q} = \vec{k_i} - \vec{k_f}$$

$$\hbar\omega = E_i - E_f$$

Measure the number of scattered neutrons as a function of Q and ω

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

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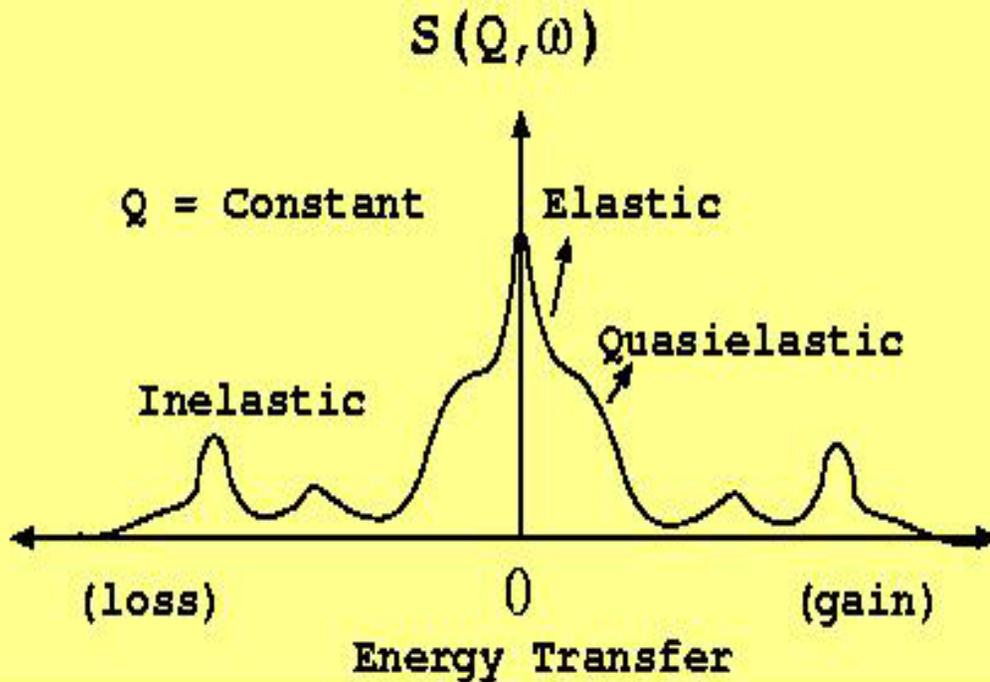
Inelastic neutron scattering peaks at non-zero energy transfer. This scattering reflects the vibrational modes of the system.

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 $\quad$ E ~ eV's $\quad$ λ ~ 1000 A's $\quad$ Q ~ 0 (selection rules)
- x-rays $\quad$ E ~ keV's $\quad$ λ ~ A's

cold neutrons - lower energies - longer time scales

1 meV $\cong$ 8 cm^{-1} $\cong$ 240 GHz $\cong$ 12 K $\cong$ 0.1 kJ/mol ~ ps

Why Neutrons

Wavelength ~ Å's   ⇔   Energy ~ meV's

=> geometry of the motion!

Why Neutrons

Magnetic Moment

- neutrons interact <u>directly</u> with magnetic materials

=> *magnetic structures*
=> *magnetic excitations*
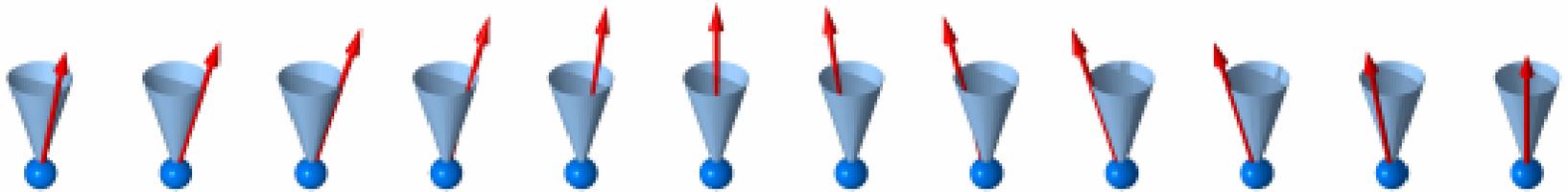
Spin Wave Animation courtesy of A. Zheludev (ORNL)

Why Neutrons

Nuclear Interaction

• scattering power varies "randomly" from isotope to isotope

=> isotopic labeling

=> scattering from light elements comparable to that from
heavy elements

Nuclear Interaction

scattering power varies "randomly" from isotope to isotope

Cross section (σ) - 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 $\sigma \sim 10^{-24}$ cm^2
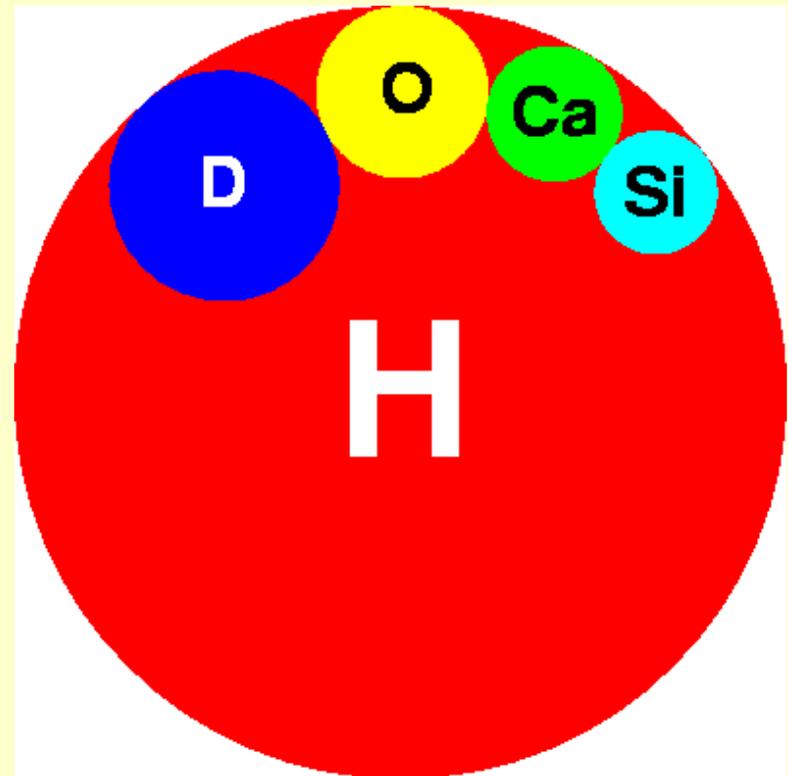
Relative total scattering cross sections for a few isotopes

Guanidinium Organodisulfonates (GDS)
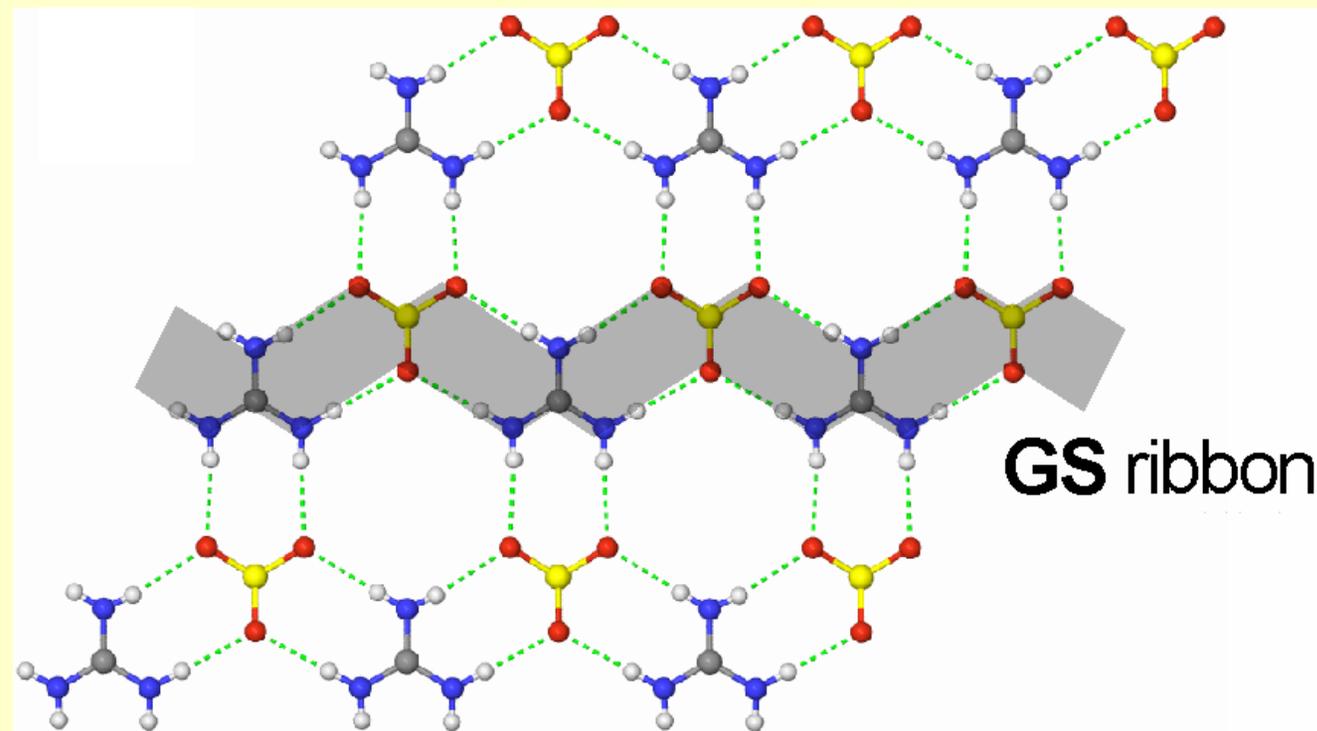
GS ribbon
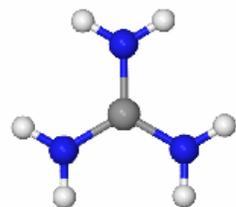
= **G**
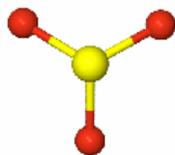
= -SO_3^-

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)

R =
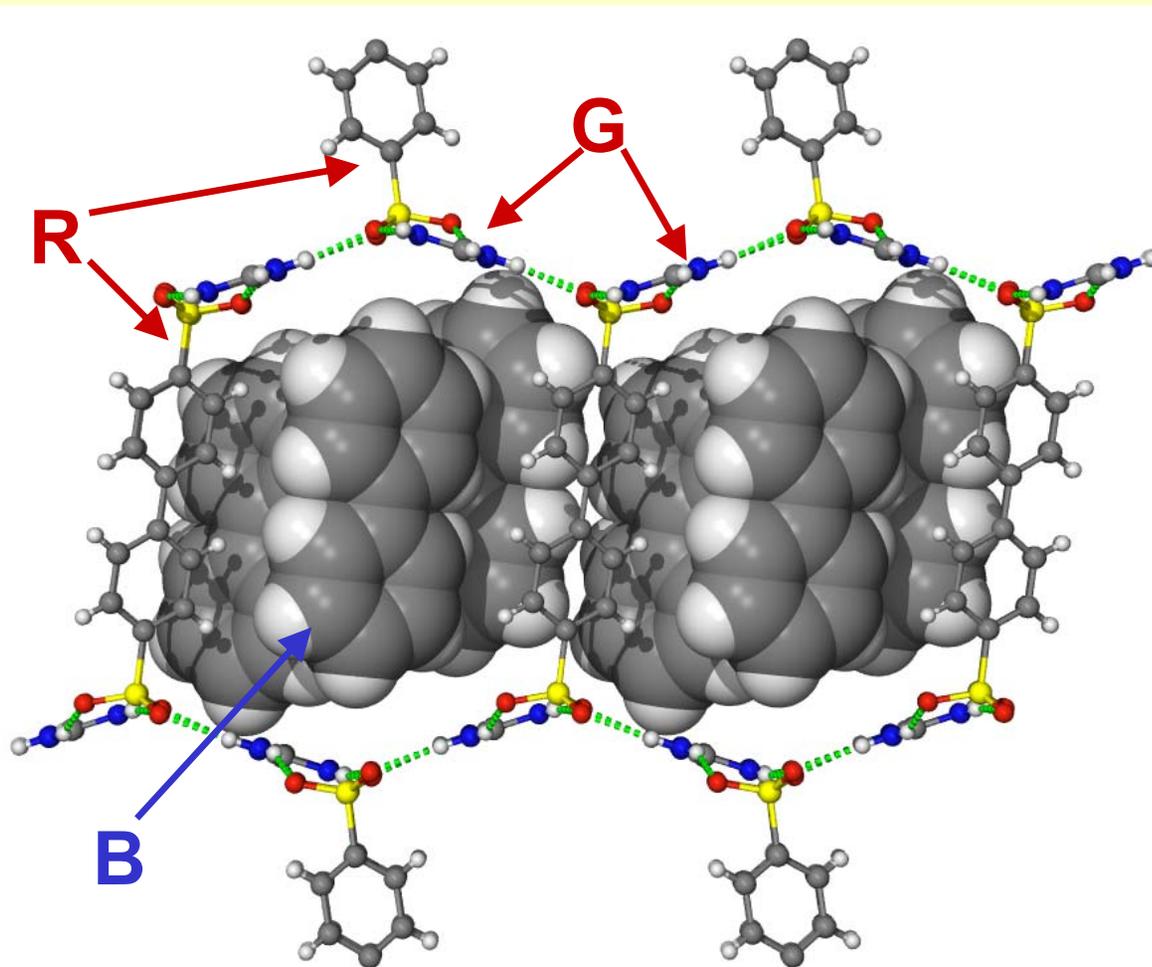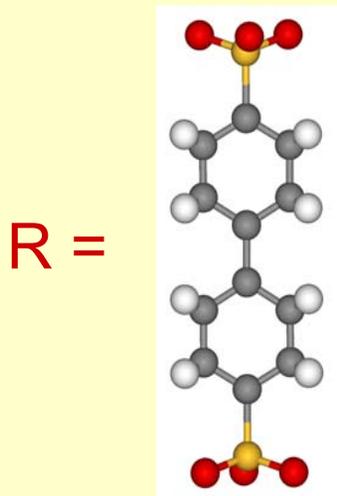
Three components

The host consists of G and R

The guests are biphenyl's - B

Isotopically substituted G$_2$[BPDS]*3(biphenyl)

A.M. Pivovar *et al.,* J. Phys. Chem. B **106**, 4916 (2002).
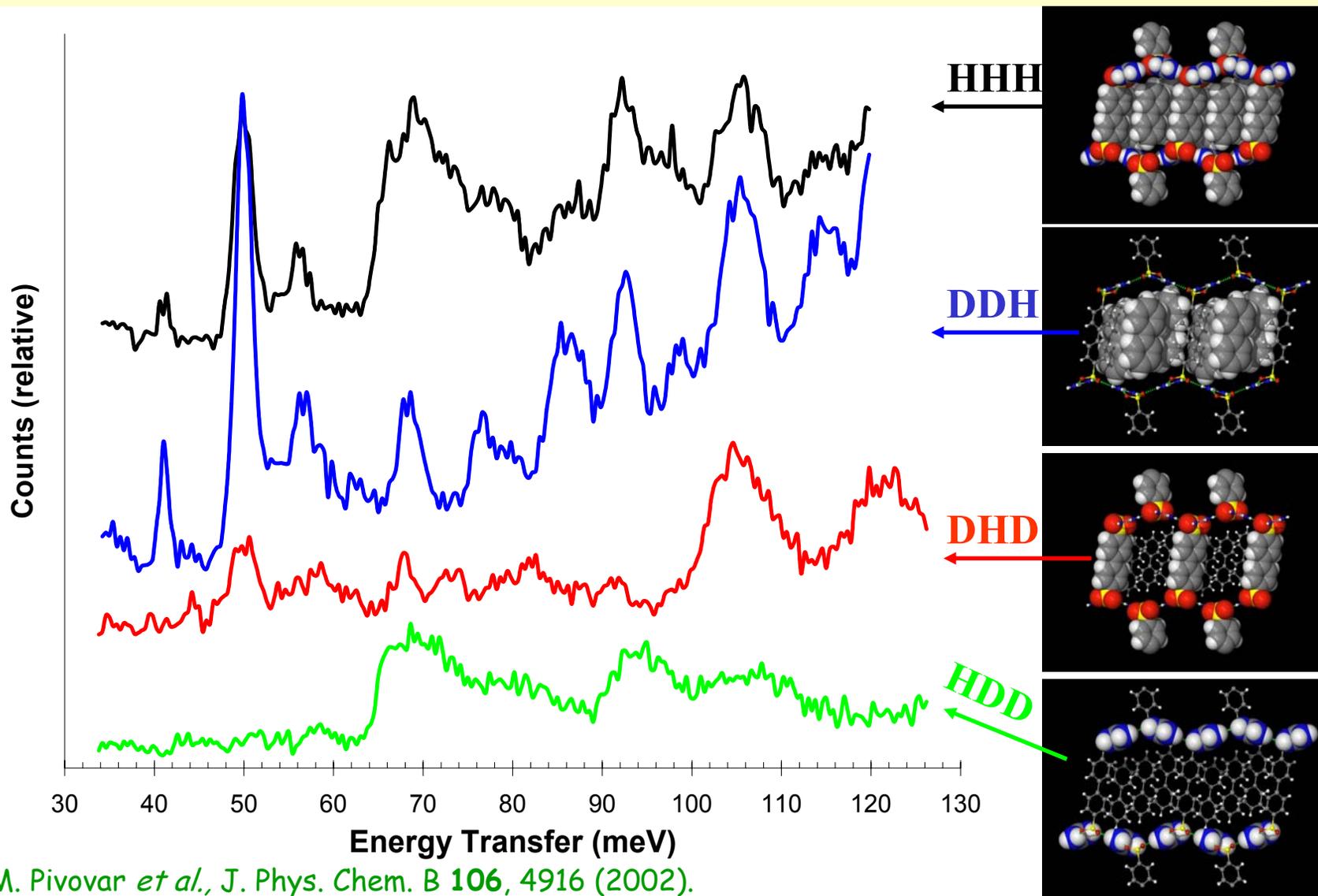
Nuclear Interaction

• 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 interefere
=> *IN*COHERENT SCATTERING

If the scattered neutron waves from the different nuclei have definite relative phases, they can interefere
=> **COHERENT SCATTERING**

Scattering function

Measure the number of scattered neutrons as a function of Q and ω

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

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

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

$S_{coh}(Q,\omega)$ 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

P(r) → **Fourier Transform** → S(Q)
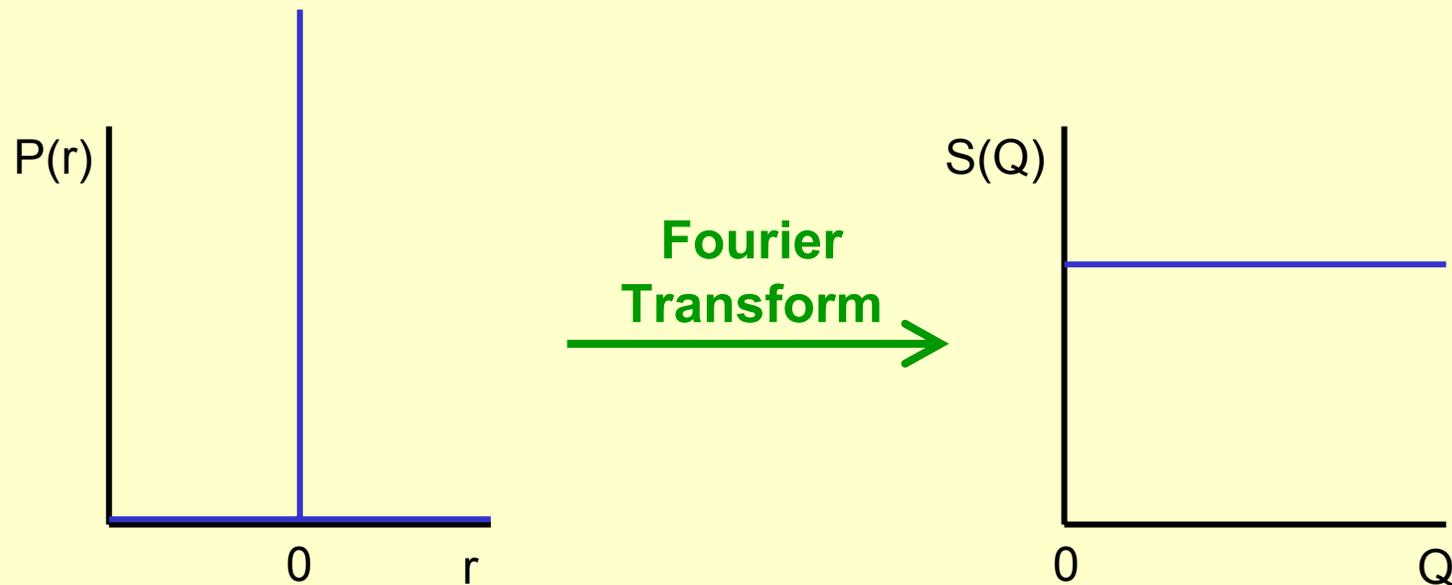
=> for diffraction experiments, incoherent scattering is **background**

Self-correlation function

Consider the time-dependence of the probability that a particle is
  correlated with itself for the case of a perfectly stationary particle

P(t)

**Fourier
Transform**

0   t

S(ω)

0   ω
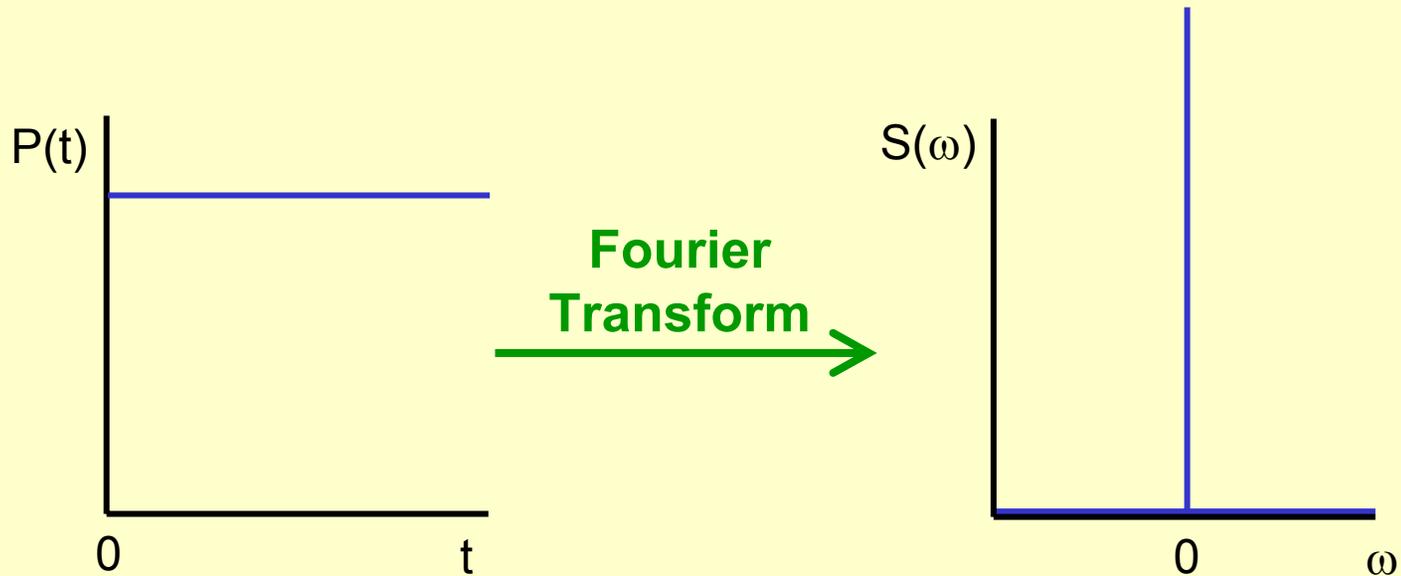
=> If there is no motion, the scattering is elastic *i.e.* it occurs only at ω=0

Self-correlation function

Consider the time-dependence of the probability that a particle is correlated with itself for the case of a randomly diffusing particle *i.e.* $P(t) = e^{-t/\tau}$

$$P(t) = e^{-t/\tau}$$

Fourier Transform

$$S(\omega) = \frac{1}{\pi} \frac{1}{1 + (\omega\tau)^2}$$
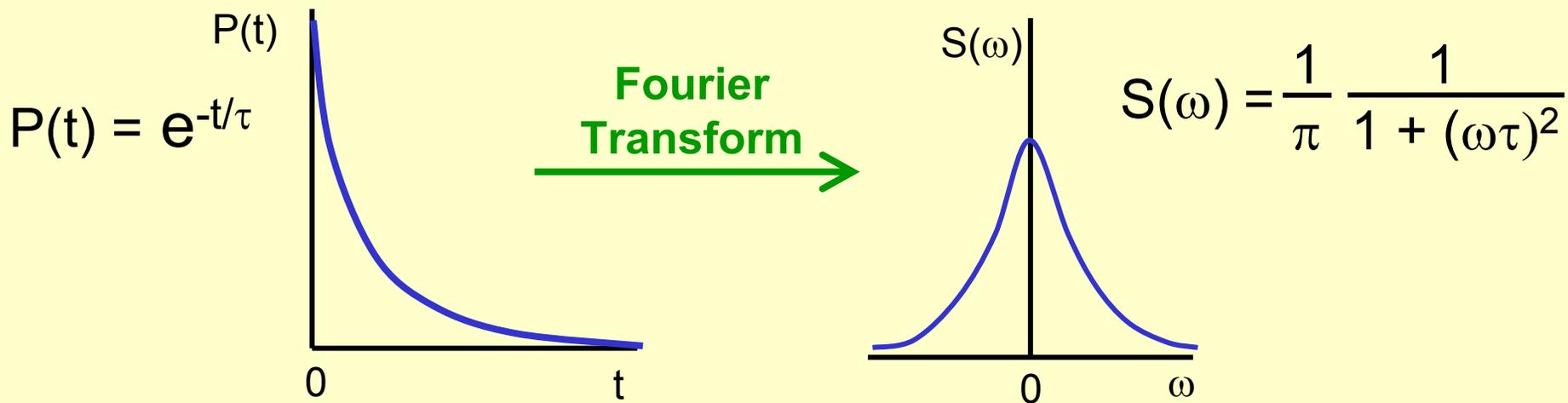
=> for quasielastic experiments, incoherent scattering is often the **signal**

Quasielastic Neutron Scattering

Inelastic neutron scattering centered at $\omega = 0$

=> Measures diffusion, molecular reorientations and relaxations
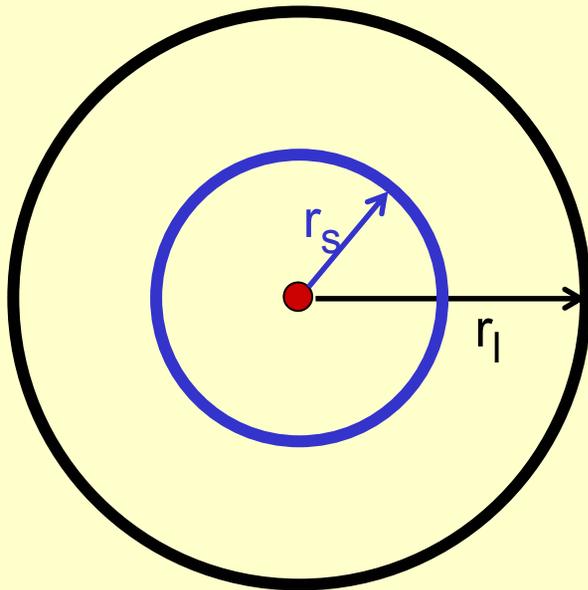
$$p = e^{-t/\tau} \qquad 1/\tau = DQ^2$$
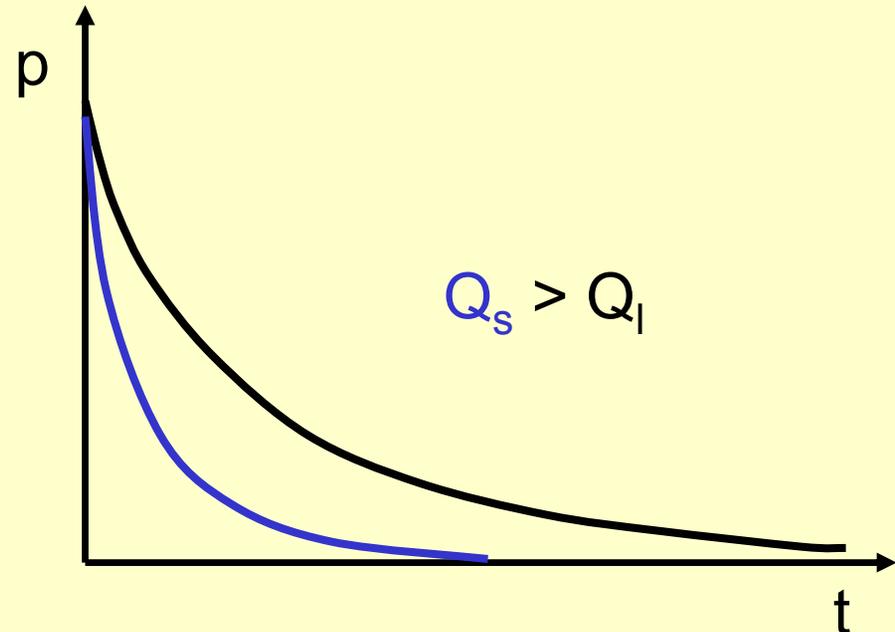
$Q_s > Q_l$

Quasielastic Neutron Scattering

S(Q,ω) is the time Fourier transform of I(Q,t)

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

$1/\tau = DQ^2$

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

r_s

r_l

$Q_s > Q_l$

Half Width = DQ^2

width

Q^2

0

E
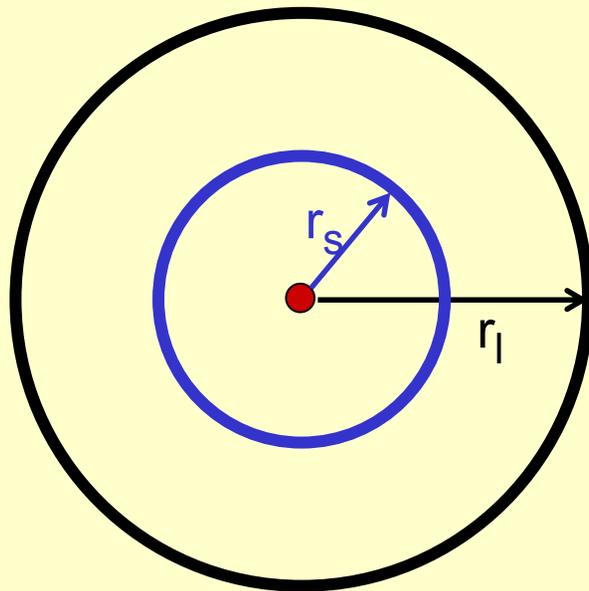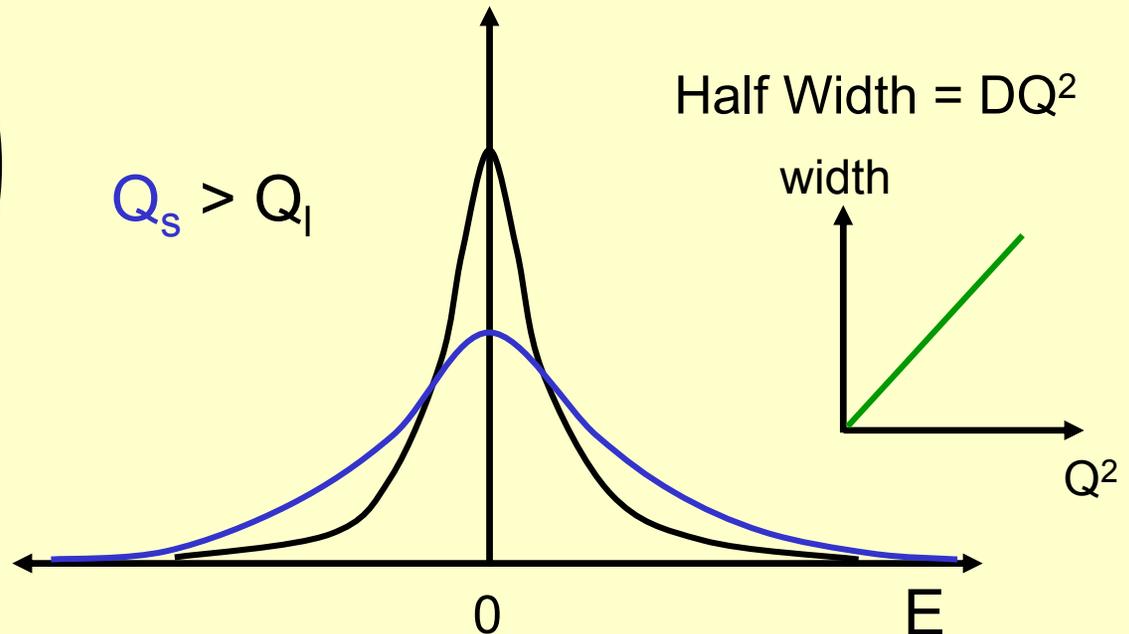
Time-Space Correlation Functions

The relevant correlation function for any neutron scattering experiment is typically written as

$$G(r,t) = \langle n(0,0)n(r,t) \rangle \qquad \text{where} \qquad n(r,t) = \sum_{j}^{N} \delta(r - r_j(t))$$

$G(r,t)$ 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
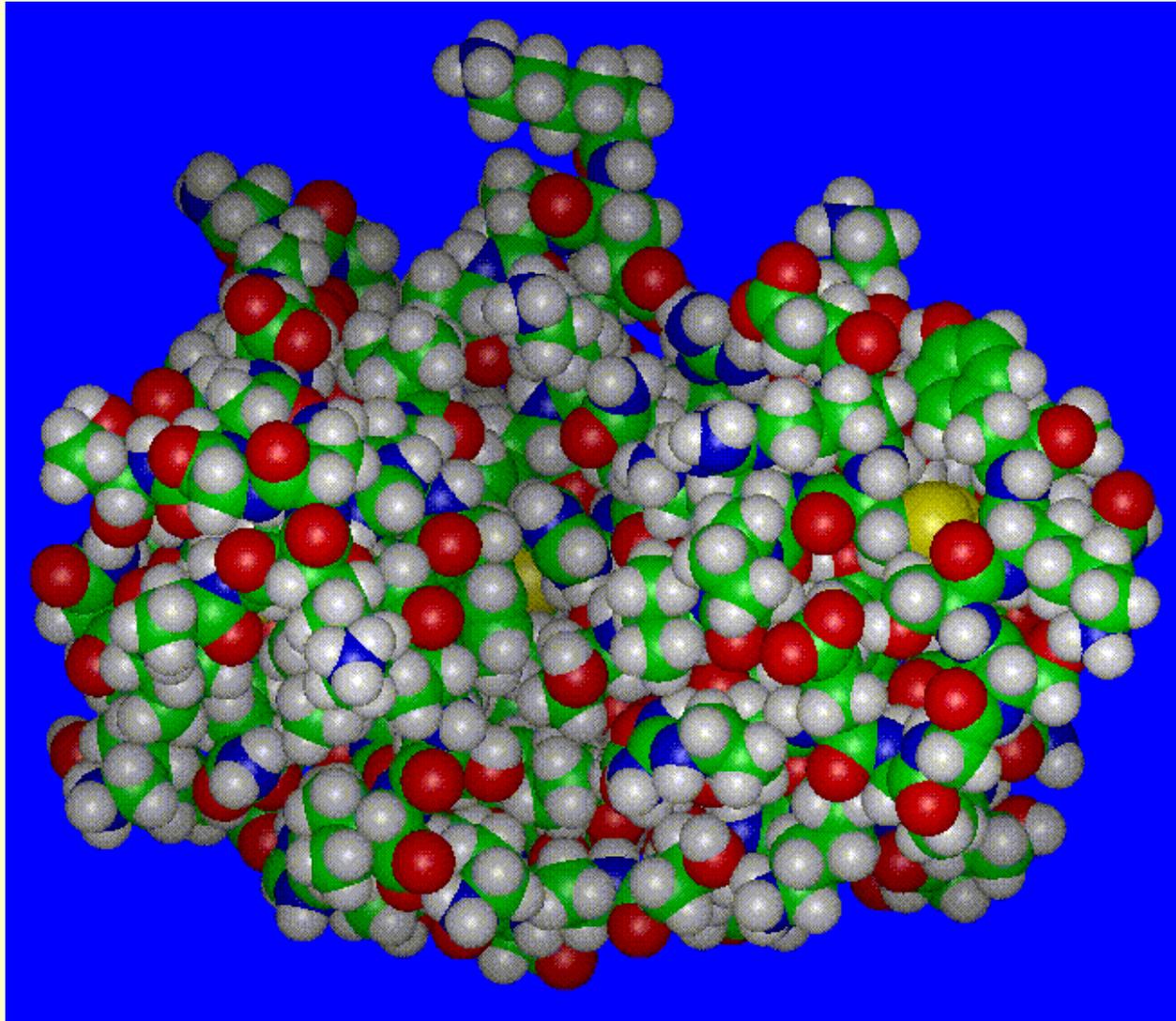
Time-Space Correlation Functions

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:

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

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

Coherent   **Incoherent**   **Coherent** **Incoherent**
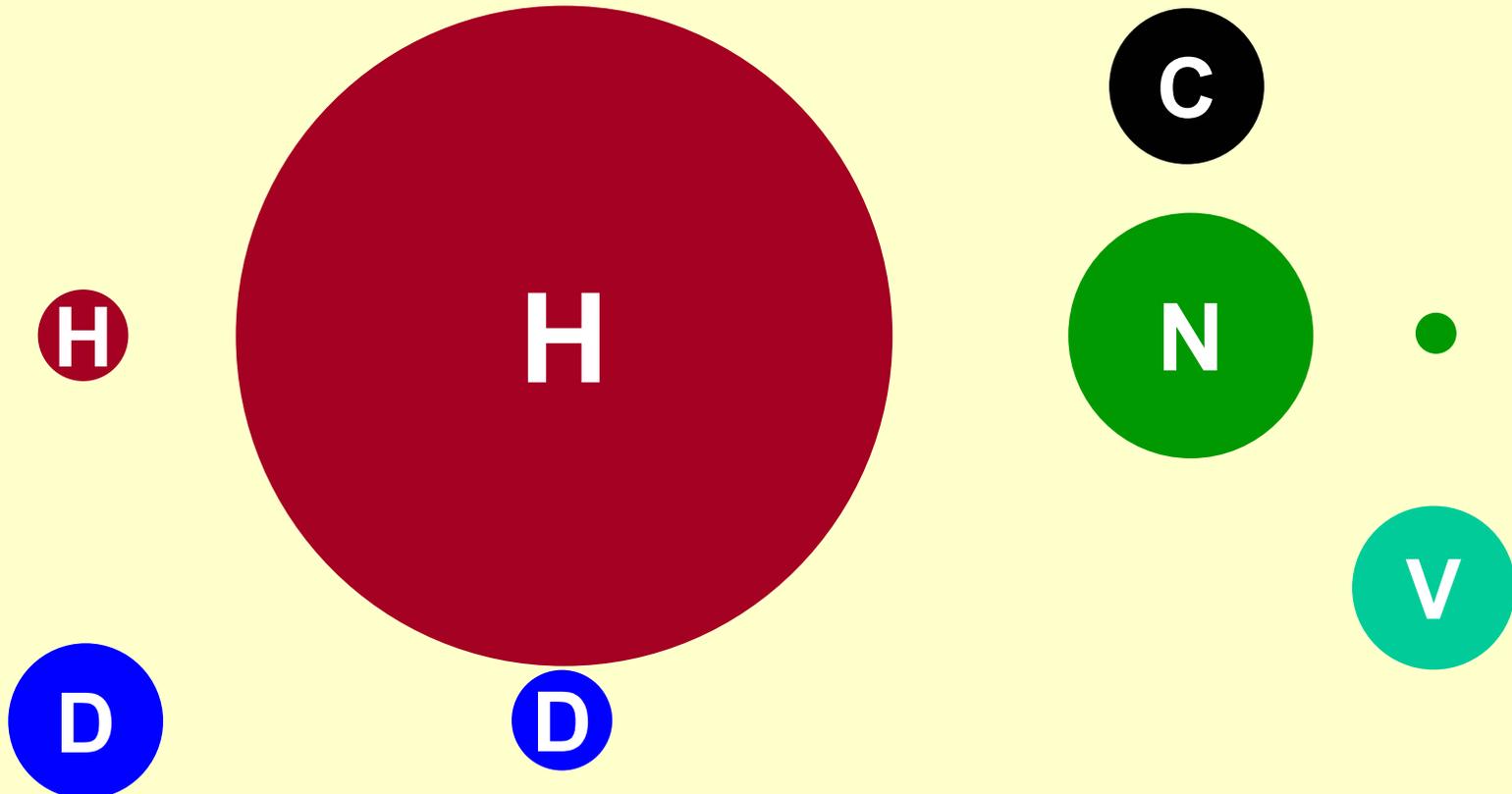
H

H

D   D

C

N

V

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

$$S_{inc}(Q,\omega) \propto \int_{-\infty}^{\infty} I_s(Q,t) e^{-i\omega t} dt \ , \quad I_s(Q,t) \propto \sum_j < e^{i\vec{Q}.\vec{r}_j(t)} e^{-i\vec{Q}.\vec{r}_j(0)} >$$

scattering function   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 α-lactalbumin

α-lactalbumin

native state
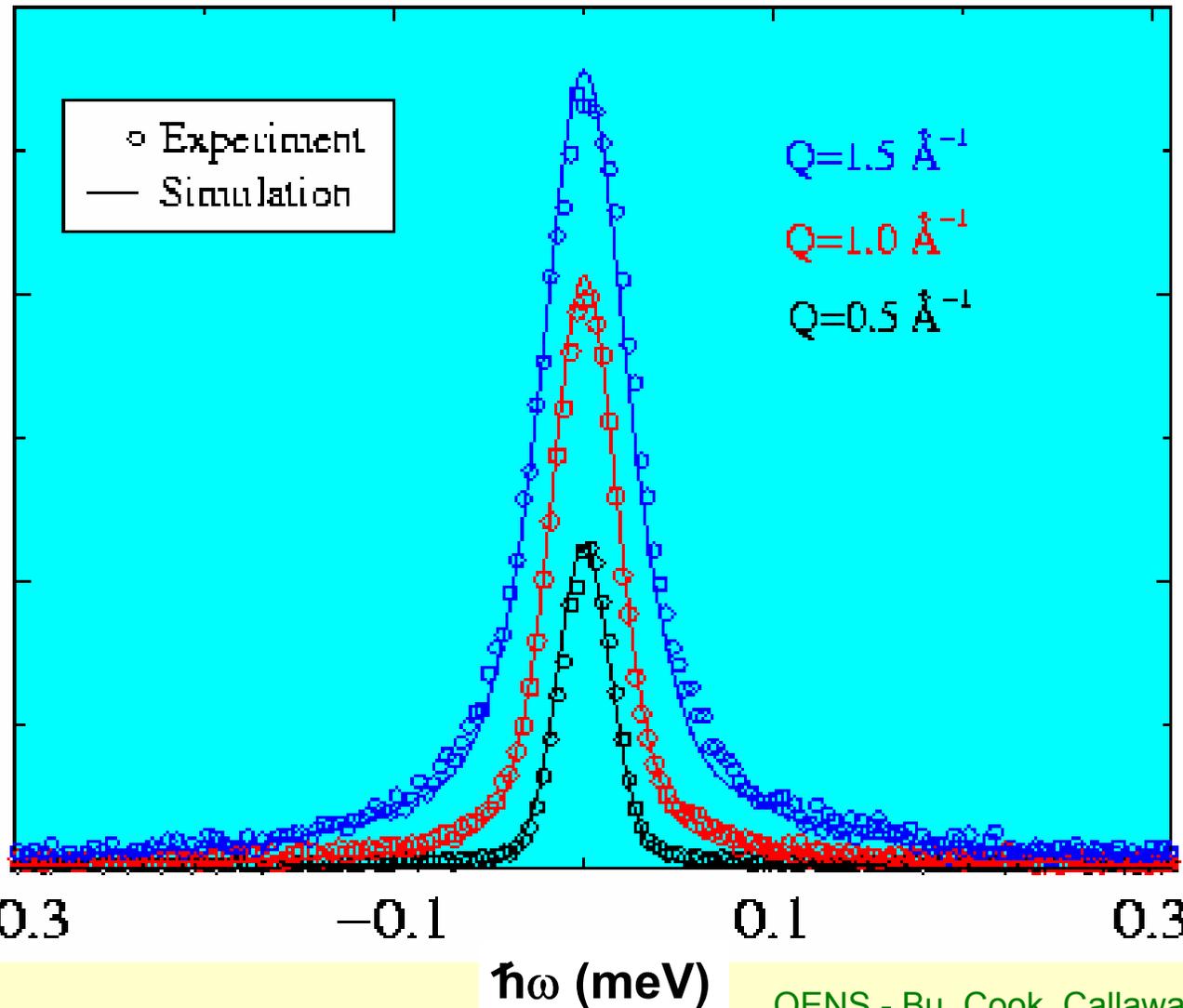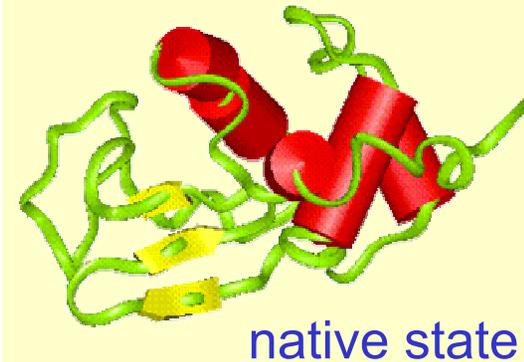
QENS - Bu, Cook, Callaway, Biophys. J. **312**, 865 (2001).

MD - Tarek, Neumann, Tobias, Chem. Phys. **292**, 435 (2003).

The NIST Center for Neutron Research

BT7 3-Axis Spec.

NG1 Vert. Refl.

BT8 Resid. Stress Diff.

BT6 Neutron Imaging Facil.

NG1 (future) 10 m SANS

NG2 Backscattering Spec.

NG1 AND/R

BT9 3-Axis Spec.

NG0 MACS

NG3 30 m SANS

Thermal Column

NG-5 SPINS

NG4 Disk Chopper TOF Spec.

BT1 Powd. Diff.

NG5 Spin-Echo Spec.

NG6 Fermi Chopper TOF Spec.

BT5 USANS

BT4 FANS

NG6 Fund. Physics

BT2 Polarized 3-axis Spec.

NG7 Hor. Refl.

NG7 Prompt γ, & (future) Neut. Depth Prof.

NG7 Interferometer

NG7 30 m SANS

Diffraction Instruments

Spectrometers

Other Neutron Methods

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
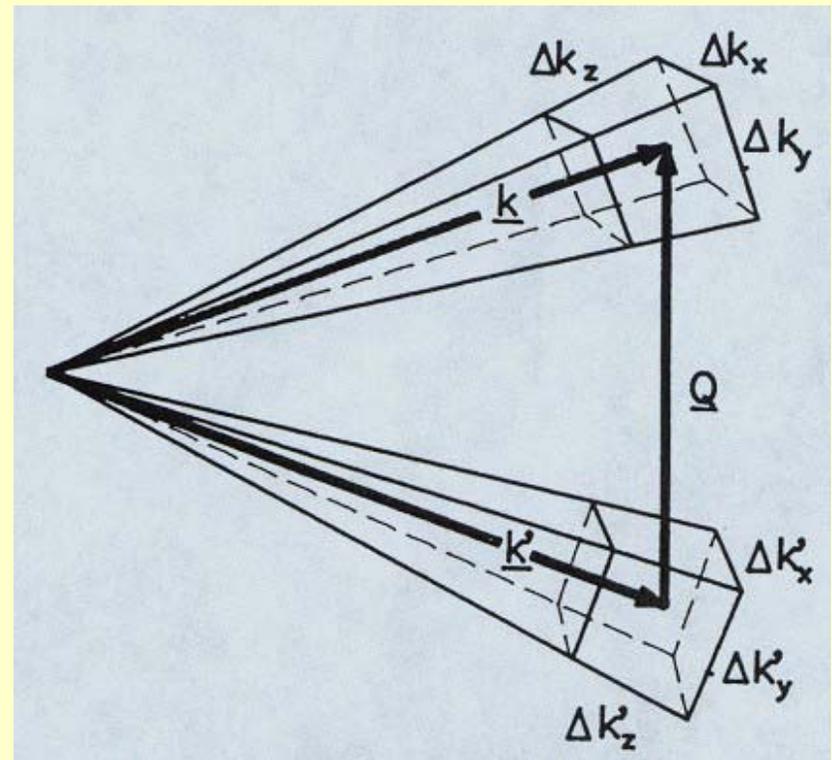
Courtesy of R. Pynn

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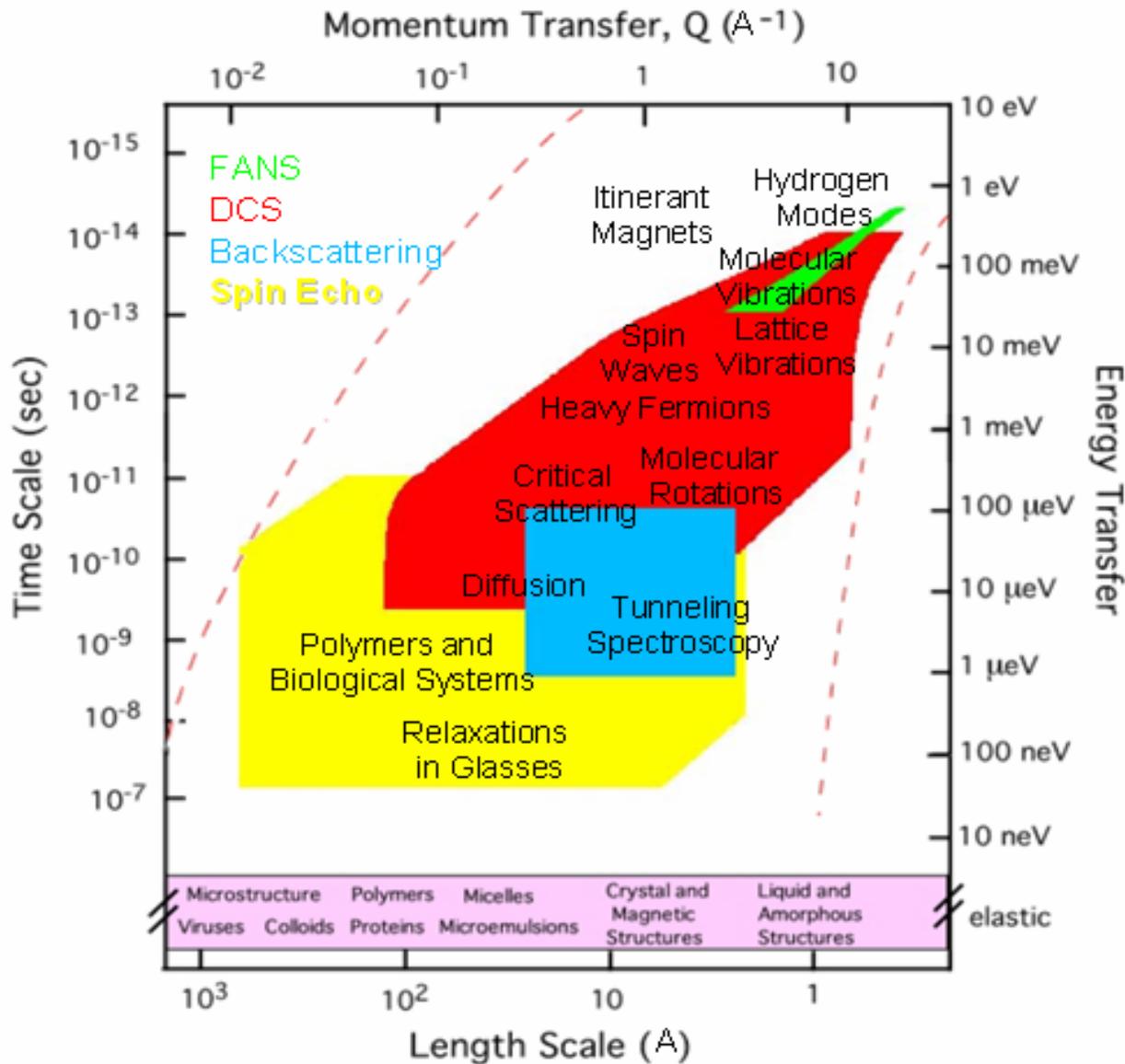
Neutron techniques available at the NCNR give researchers access to 7 orders of magnitude in time

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*