STATISTICAL MOTIONS

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PRINCIPLE OF A NEUTRON EXPERIMENT

Two relevant quantities are measured:

i) **Momentum transfer**, $Q$, difference between final, $k$, and initial, $k_0$ neutron momentum

$$Q = k - k_0$$

ii) **Energy transfer**, $\hbar \omega$

difference between final, $E$, and initial, $E_0$, neutron energy,

$$\hbar \omega = E - E_0 = \frac{\hbar^2}{2m} (k^2 - k_0^2)$$
Differential scattering cross sections

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \frac{k}{k_0} \frac{1}{N} \sum_{\alpha} \sum_{\beta} \frac{1}{2\pi} \int_{-\infty}^{\infty} \left( b_\alpha b_\beta e^{-iQ.r_\alpha(0)} e^{iQ.r_\beta(t)} \right) e^{-i\omega t} dt
\]

Thermal average over the positions of the nuclei and over their spin states. In general, can be taken separately.

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \frac{k}{k_0} \frac{1}{N} \sum_{\alpha} \sum_{\beta} b_\alpha b_\beta \frac{1}{2\pi} \int_{-\infty}^{\infty} \left( e^{-iQ.r_\alpha(0)} e^{iQ.r_\beta(t)} \right) e^{-i\omega t} dt
\]

One component system

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \frac{k}{k_0} \frac{1}{N} \sum_{\alpha} \sum_{\beta} \frac{1}{2\pi} \int_{-\infty}^{\infty} \left( e^{-iQ.r_\alpha(0)} e^{iQ.r_\beta(t)} \right) e^{-i\omega t} dt
\]

\[
+ \frac{k}{k_0} \left( \frac{\bar{b}^2 - \bar{b}^2}{N} \right) \frac{1}{2\pi} \int_{-\infty}^{\infty} \left( e^{-iQ.r_\alpha(0)} e^{iQ.r_\alpha(t)} \right) e^{-i\omega t} dt
\]

Incoherent scattering length
\[
b^{\text{inc}} = \sqrt{\bar{b}^2 - \bar{b}^2}
\]

Coherent scattering length
\[
b^{\text{coh}} = \bar{b}
\]
SCATTERING FUNCTIONS

\[ \frac{d^2 \sigma}{d\Omega d\omega} = \left( \frac{d^2 \sigma}{d\Omega d\omega} \right)_{\text{coh}} + \left( \frac{d^2 \sigma}{d\Omega d\omega} \right)_{\text{inc}} \]

Coherent scattering  Incoherent scattering

Intermediate scattering function

\[ F(Q, t) = \frac{1}{N} \sum_\alpha \sum_\beta \left\langle e^{-iQ \cdot r_\alpha(0)} e^{iQ \cdot r_\beta(t)} \right\rangle \]

Spatial Fourier transform of time-dependent pair correlation function

\[ F(Q, t) = \int_{-\infty}^{\infty} G(r, t) e^{iQ \cdot r} dr \]

\[ G(r, t) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} F(Q, t) e^{-iQ \cdot r} dQ \]

Time Fourier transform: dynamical scattering function (scattering law, dynamical structure factor)

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

\[ F(Q, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} S(Q, \omega) e^{i\omega t} d\omega \]

\[ S(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G(r, t) e^{-i(\omega t - Q \cdot r)} dr dt \]

\[ G(r, t) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} S(Q, \omega) e^{i(\omega t - Q \cdot r)} dQ d\omega \]
**INCOHERENT SCATTERING**

Same scatterer interacts with neutron at times 0 and t

Intermediate incoherent scattering function

\[ F_{inc}(Q,t) = \frac{1}{N} \sum_{\alpha} e^{-iQ.r_{\alpha}(0)} e^{iQ.r_{\alpha}(t)} \]

Incoherent scattering function

\[ S_{inc}(Q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_{inc}(Q,t) e^{-i\omega t} dt \]

Space-time Fourier transform of **time dependent autocorrelation function**

\[ S_{inc}(Q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} G_s(r,t) e^{-i(\omega t-Q.r)} dr dt \]

\[ G_s(r,t) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} S_{inc}(Q,\omega) e^{i(\omega t-Q.r)} dQ d\omega \]

Finally

\[ \frac{d^2\sigma}{d\Omega d\omega} = \frac{1}{4\pi k_0} [\sigma_{coh} S(Q,\omega) + \sigma_{inc} S_{inc}(Q,\omega)] \]

Coherent scattering cross section \[ \sigma_{coh} = 4\pi (b_{coh})^2 \]

Incoherent scattering cross section \[ \sigma_{inc} = 4\pi (b_{inc})^2 \]
SEPARATION OF ATOMIC MOTIONS

Instantaneous position of a scattering nucleus
Belonging to a reorienting molecule or chemical group:

TWO CASES

No long-range motions (rotator phases in solids, liquid crystals...)

\[ r(t) = \mathbf{v}(t) + R(\Omega, t) + u(t) \]

- Lattice vibrations
- Equilibrium position within molecule with orientation \( \Omega \)
- Internal molecular vibrations

Existence of long-range displacements (liquid, intercalated species...)

\[ r(t) = T(t) + R(\Omega, t) + u(t) \]

- C.O.M translation
- Equilibrium position within molecule with orientation \( \Omega \)
- Internal molecular vibrations

Basic assumption: all the components of the atomic displacement are completely decoupled

Occur on different time scales:
- Lattice vibrations and internal molecular vibrations: \( 10^{-13} - 10^{-14} \) s
- Molecular reorientations: \( 10^{-11} - 10^{-12} \) s
- Translation of molecule C.O.M in liquids: \( 10^{-9} - 10^{-10} \) s
**Example:** molecular dynamic simulation of hexamethylethane \((CH_3)_3-C-C-(CH_3)_3\)

Intermediate scattering function:

No long-range displacements

\[
F_{inc}(Q, t) = \langle \exp(-iQ\cdot v(0))\cdot \exp(iQ\cdot v(t)) \rangle \\
\langle \exp(-iQ\cdot u(0))\cdot \exp(iQ\cdot u(t)) \rangle \\
\langle \exp(-iQ\cdot R(O,0))\cdot \exp(iQ\cdot R(O,t)) \rangle
\]

\[
F_{inc}(Q, t) = F_V(Q, t)\cdot F_U(Q, t)\cdot F_R(Q, t)
\]

Quantum mechanic

Classical mechanic

Incoherent scattering functions

\[
S_{inc}(Q, \omega) = S_V(Q, \omega) \otimes S_U(Q, \omega) \otimes S_R(Q, \omega)
\]

Long-range displacements

\[
F_{inc}(Q, t) = \langle \exp(-iQ\cdot T(0))\cdot \exp(iQ\cdot T(t)) \rangle \\
\langle \exp(-iQ\cdot u(0))\cdot \exp(iQ\cdot u(t)) \rangle \\
\langle \exp(-iQ\cdot R(O,0))\cdot \exp(iQ\cdot R(O,t)) \rangle
\]

\[
F_{inc}(Q, t) = F_T(Q, t)\cdot F_U(Q, t)\cdot F_R(Q, t)
\]

Quantum mechanic

Classical mechanic
LATTICE AND MOLECULAR VIBRATIONS

\[ F_{\text{inc}}(Q,t) = \left\langle e^{-iQ.u(0)} e^{iQ.u(t)} \right\rangle \]

\[ F(Q,t) = \left\langle \exp U_0 \exp U_t \right\rangle \]

\[ U_0 = -iQ.u(0) \quad U_t = iQ.u(t) \]

Operators \( U_0 \) and \( U_t \) do not commute, but each of them commute with their commutator \([U_0, U_t]\).

\[ \exp(U_0) \exp(U_t) = \exp(U_0 + U_t) \exp([U_0, U_t]) \]

\[ F(Q,t) = \exp \left\langle U_0^2 \right\rangle \exp \left\langle U_0 U_t \right\rangle \]

Expansion to second order of the second exponential term

\[ F(Q,t) = \exp \left( -\left\langle (Q.u(0))^2 \right\rangle \right) \exp \left\langle Q.u(0)Q.u(t) \right\rangle \]

\[ = \exp \left( -\left\langle (Q.u(0))^2 \right\rangle \right) \left[ 1 + \left\langle Q.u(0)Q.u(t) \right\rangle + \frac{1}{2} \left\langle Q.u(0)Q.u(t) \right\rangle^2 \ldots \right] \]

Debye-Waller term: interference between the neutronic wave scattered by atom at times 0 and \( t \) is attenuated by its own thermal vibrations

\[ \exp \left( -\left\langle (Q.u(0))^2 \right\rangle \right) = \exp(-Q^2 <u^2>) \]

\[ = \exp(-2W(Q)) \]

Purely inelastic term involving in its expansion the autocorrelation function of the atom displacement.
INTERNAL VIBRATIONS

\[ S_v(Q, \omega) = \exp\left(-2W_v(Q)\right)\left\{ \delta(\omega) + S_v^{\text{inel}}(Q, \omega) \right\} \]

Debye Waller term \[ 2W_v(Q) = \langle \nu^2 \rangle > Q^2 \]

Example:
Methyl torsion
30 meV

EXTERNAL VIBRATIONS

\[ S_u(Q, \omega) = \exp\left(-2W_u(Q)\right)\left\{ \delta(\omega) + S_u^{\text{inel}}(Q, \omega) \right\} \]

Debye Waller term \[ 2W_u(Q) = \langle u^2 \rangle > Q^2 \]

Optical modes:
Brillouin zone limits
Centre of Brillouin zone

Acoustic modes
Brillouin zone limits

Energy exchange
0

5 – 10 meV
CASE OF A MOLECULE

N atoms:

\[
\{ \begin{align*}
3N - 6 & \text{ harmonic oscillators} \\
3N - 6 & \text{ frequencies} \\
3N - 6 & \text{ Dirac peaks}
\end{align*} \]

Example 1: Cytidine \( T = 15 \, \text{K} \)
Gaigeot, M.-P., Leulliot, N., Ghomi, M., Jobic, H., Coulombeau, C., Bouloussa, O.,
Chemical Physics \textbf{261} (2000) 217

Example 2: camphor sulfonic acid

\( \theta = 25^\circ \)
\( \theta = 48^\circ \)
\( \theta = 95^\circ \)
Paraxylene liquide

\[ T = 290 \, K \]

\[ Q = 0.5 \, \text{A}^{-1} \]

Diffusion inélastique
(vibrations)

Diffusion quasiélastique
(réorientations, translations)
OVERVIEW OF SPECTROMETERS FOR QENS

**Time of flight**
(10^{-11}-10^{-12} s)

- **Multichoppers**
  - IN5, ILL Grenoble
  - Mibemol, LLB Saclay
  - NEAT, HMI Berlin
  - DCS, NIST USA

- **Crystal monochromator**
  - IN6, ILL Grenoble
  - FOCUS, PSI Switzerland
  - FCS, NIST USA

- **Inverted TOF geometry**
  - IRIS, RAL UK

**Backscattering**
(10^{-9}-10^{-10} s)

- **Doppler effect**
  - IN10, ILL Grenoble
  - BSS, KFA Jülich

- **Thermal expansion**
  - IN16, ILL Grenoble
  - HFBS, NIST USA
  - FRMII, (project) Munich

**Spin echo**
(10^{-8}-10^{-9} s)

- **Standard**
  - IN11, ILL Grenoble
  - MESS, LLB Saclay
  - IN15, ILL Grenoble

- **Zero field**
  - HMI Berlin
  - LLB Saclay
PROPERTIES OF TRANSLATIONAL AND ROTATIONAL SCATTERING FUNCTIONS

\[
F_{\text{inc}}(Q,t) = \int \int p(R(0); R(t)).p(R(0)).\exp(-iQ.R(0)).\exp(iQ.R(t)).dR(t).dR(0)
\]

\(p(R(0); R(t))\) Probability for a scattering atom, located at \(R(0)\) at initial time, to be at \(R(t)\) at time \(t\)

\(p(R(0))\) Distribution of probabilities at initial time

Return to equilibrium: \(p(R(0); R(\infty)) \rightarrow p(R(0))\) if \(t \rightarrow \infty\)

\[
F_{\text{inc}}(Q,\infty) = \int \int p(R(\infty))p(R(0))\exp(-iQ.R(0))\exp(iQ.R(\infty))dR(\infty)dR(0)
\]

\[= \int p(R(0))\exp(-iQ.R(0))dR(0)\int p(R(\infty))\exp(iQ.R(\infty))dR(\infty)\]

System in equilibrium \(p(R(\infty)) = p(R(0))\)

\[
F_{\text{inc}}(Q,\infty) = \left| \int p(R(0))\exp(-iQ.R(0))dR(0) \right|^2
\]

\[= \left| \int p(R(\infty))\exp(iQ.R(\infty))dR(\infty) \right|^2\]

\[
F_{\text{inc}}(Q,\infty) = \left| \langle \exp(iQ.R(0)) \rangle \right|^2
\]
At any arbitrary time, formal separation

\[ F_{\text{inc}}(Q,t) = F_{\text{inc}}(Q,\infty) + F'_{\text{inc}}(Q,t) \]

**Time-Fourier transformation**

\[
S(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_{\text{inc}}(Q,\infty) \exp(-i\omega t) dt + \frac{1}{2\pi} \int_{-\infty}^{\infty} F'_{\text{inc}}(Q,t) \exp(-i\omega t) dt
\]

\[ = F_{\text{inc}}(Q,\infty) \delta(\omega) + \frac{1}{2\pi} \int_{-\infty}^{\infty} F'_{\text{inc}}(Q,t) \exp(-i\omega t) dt \]

Purely elastic component

Inelastic component the shape and width of which depend on the nature and of the characteristic times associated to nucleus motions

**Very simple case:**

exponential decreasing, with a unique characteristic time, τ

\[ F'_{\text{inc}}(Q,t) = \left[ F_{\text{inc}}(Q,0) - F_{\text{inc}}(Q,\infty) \right] \exp \left( -\frac{t}{\tau} \right) \]

\[ S(Q, \omega) = F_{\text{inc}}(Q,\infty) \delta(\omega) + \left[ F_{\text{inc}}(Q,0) - F_{\text{inc}}(Q,\infty) \right] \frac{1}{\pi} \frac{\tau}{1 + \omega^2 \tau^2} \]
Immediate information about motion geometry.
Vanishing in the case of long-range diffusive motions (liquids).
For localised motions, the more the proton distribution is isotropic in space, the weaker is the elastic contribution to scattered intensity at large momentum transfer.

\[
EISF(Q) = F_{inc}(Q,\infty) = \left| \langle \exp(iQ\cdot R(\Omega)) \rangle \right|^2
\]

\[
= \frac{\text{Int}^{EL}(Q)}{\text{Int}^{EL}(Q) + \text{Int}^{QEL}(Q)}
\]
LONG RANGE DIFFUSION

Earlier QENS experiments (30 years ago) mainly devoted to studies of liquids

Phenomenological equation: second law of Fick (1855)
\[
\frac{\partial c(r, t)}{\partial t} = D \nabla^2 c(r, t) = D \left[ \frac{\partial^2 c(r, t)}{\partial x^2} + \frac{\partial^2 c(r, t)}{\partial y^2} + \frac{\partial^2 c(r, t)}{\partial z^2} \right]
\]

System at equilibrium: van Hove autocorrelation function,
\[
G_s(r, t) = \text{probability for an atom, initially located at origin, to be at } r \text{ at time } t:
\]
\[
G_s(r, t) = \frac{c(r, t)}{N}
\]

Fick's equation is also fulfilled by \( G_s(r, t) \). Solution: normalised gaussian function
\[
G_s(r, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp \left( -\frac{r^2}{4Dt} \right)
\]

Initial condition: \( G_s(r, t) = \delta(r) \).

Function isotropic in space (no driving force in any direction)
Mean square displacement of an atom proportional to time
\[
\left\langle r^2(t) \right\rangle = 6Dt
\]

Corresponds to the microscopic description of Einstein's random walk model
Einstein (1905), Smoluchowski
Second Fick’s law

\[ \frac{\partial c(r, t)}{\partial t} = D \nabla^2 c(r, t) = D \left[ \frac{\partial^2 c(r, t)}{\partial x^2} + \frac{\partial^2 c(r, t)}{\partial y^2} + \frac{\partial^2 c(r, t)}{\partial z^2} \right] \]

Spatial Fourier transform \[\rightarrow\] intermediate scattering function

\[ F(Q, t) = F(Q, t) = \exp(-DQ^2 t) \]

**Gaussian function isotropic with** \(Q\)

**Remark:**

\[ \lim_{t \to \infty} F(Q, t) = 0 \]

Any atom can move away from origin from an arbitrary distance, \[ \rightarrow \] the EISF is zero
SCATTERING LAW; DYNAMICAL STRUCTURE FACTOR

Spatial Fourier transform \( \rightarrow \) dynamical structure factor

\[
S_{\text{inc}}(Q, \omega) = \frac{1}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}
\]

Lorentzian function, isotropic with \( Q \)
Halfwidth at half maximum, \( \Gamma \), increases as a function of momentum transfer according to a parabolic law

\[
Q = \frac{\omega}{\pi} + \frac{DQ^2}{2Q^2}
\]
Earlier studies:
Liquid argon
Dasannacharya and Rao
Phys. Rev. 137 (1965) A417

Coherent scattering:
de Gennes narrowing

More recently observed
for liquid paraxylene
Jobic et al. (2001)
DQ2 law actually verified at small $Q$ values

Correspond to large distances (several tens of molecular diameters).

At large $Q$ values, systematic deviations: over small distances, microscopic mechanisms intervene.
**JUMP DIFFUSION**

Deviation with respect to Fick’s Discontinuous character of diffusion mechanism.

Different models: application to different systems

- Hydrogen in metals
- Molecules adsorbed inside porous media (zeolites)
- Molecular liquids (water)

The model of Chudley and Elliott

Initially developed for liquids with a short-range order. Numerous applications (e.g. diffusion of hydrogen atoms adsorbed in metals)

**Hypotheses:**

- Vibrations about an average position (site) during $\tau$,
- Displacement towards another site by instantaneous jumps,
- Jump distance, $l$, $>>$ vibrational displacements,
- Equilibrium sites on a Bravais lattice.
Diffusion equation (master equation)

Analogous to Fick’s equation
\[
\frac{\partial P(r, t)}{\partial t} = \frac{1}{n\tau} \sum_{i=1}^{n} [P(r + l_i, t) - P(r, t)]
\]

\(P(r, t)\): probability for one atom to occupy a given site
Sum over the \(n\) nearest neighbour sites located at distances \(l_i\).

**Fourier transformation:**

intermediate scattering function \(F(Q, t)\)

Differential equation
\[
\frac{\partial F(Q, t)}{\partial t} = \left[ \frac{1}{n\tau} \sum_{i=1}^{n} \{1 - \exp(-iQl_i)\} \right] F(Q, t)
\]

Solution
\[
F(Q, t) = \exp \left( -\frac{1}{n\tau} \sum_{i=1}^{n} \{1 - \exp(-iQl_i)\} t \right)
\]

Intermediate scattering function **non isotropic:**
depends on the orientation of scattering vector \(Q\) with respect to crystallographic directions.
Dynamical structure factor

\[ S_{inc}(Q, \omega) = \frac{1}{\pi} \frac{\Delta \omega(Q)}{\omega^2 + (\Delta \omega(Q))^2} \]

Halfwidth at half-maximum

\[ \Delta \omega(Q) = \frac{1}{n\tau} \sum_{i=1}^{n} \{1 - \exp(-iQl_i)\} \]

**DEPENDS ON THE DIRECTION OF THE SCATTERING VECTOR Q**

**Remarks:**
- Expressions more complicated in the case of jumps towards sites of different types involving several jump probabilities,
- Dependence with the direction of \( Q \) enables to discriminate between several hypotheses of dynamical models

**Case of powders**

Average over all the orientations of the crystallites with respect to \( Q \)

No analytical expression. Numerical average.

- Sum of Lorentzian functions with different widths.
- Low values of \( Q \): \( S_{inc}(Q, \omega) \) Lorentzian shape
- Large values of \( Q \): clear differences.
Jumps between octahedral sites
Distance 3 Å

Evaluated profile
Lorentzian

Energie

Intensité (u.a.)
Chudley and Elliott suggest an average of the halfwidth at half maximum over all directions of $Q$.

$$\Delta \omega(Q) = \frac{1}{\tau} \left\{ 1 - \frac{1}{2} \int_{0}^{\pi} \exp(-iQl \cos \theta) \sin \theta d\theta \right\}$$

$$= \frac{1}{\tau} \left\{ 1 - \frac{\sin(Ql)}{Ql} \right\}$$

Noticeably differs from the correct result (from the halfwidth of the average of the Lorentzian functions).
At small $Q$ values, development of the sine function

\[
\lim_{Q \to 0} \Delta \omega(Q) = \frac{1}{\tau} \left\{ 1 - \frac{Q^2 l^2}{3!} + \ldots \right\}
\]

\[
= \frac{Q^2 l^2}{6\tau}
\]

At low values of $Q$, Chudley-Elliott model

\[
\text{DQ}^2 \text{ law}
\]

Diffusion constant, $D$, related to residence time $\tau$,

\[
\text{Einstein relation} \quad D = \frac{l^2}{6\tau}
\]

At large $Q$ values, oscillatory term negligible

\[
\lim_{Q \to \infty} \Delta \omega(Q) = \frac{1}{\tau}
\]
Other models

Chudley-Elliott model can be generalised: distribution of jump distances, $g(l)$

$$\Delta \omega(Q) = \frac{1}{\tau} \left\{ 1 - \int \frac{\sin(Ql)}{Ql} g(l) dl \right\}$$

Hall and Ross:

$$g(l) = \frac{2l^2}{\sqrt{2\pi}l_0^3} \exp\left(-\frac{l^2}{2l_0^2}\right)$$

$$\Delta \omega(Q) = \frac{1}{\tau} \left\{ 1 - \exp\left(-\frac{Q^2l_0^2}{2}\right) \right\}$$

Singwi and Sjölander:

succession of vibratory and oscillatory states (water).

Jobic: delocalisation of the molecules around their sites.
Hydrogen diffusion

Dominant role within the past ($\sigma_{inc}(H) = 80 \times 10^{-24} \text{ cm}^{-2}$)

Still very active field

Hydrogen in $\text{TaV}_{5}$
A.V. Skripov et al. 1996

Proton diffusion in relation with protonic conductivity

Perovskites aliovalently doped or non with stochiometric composition:

At high temperature: Oxygen ionic conductors

In moist atmosphere can dissolve several mol% of water: proton conductivity

Grotthuss mechanism: proton exchange along an hydrogen bond + OH rotation

Yb-doped $\text{SrCeO}_3$ in the temperature range 400-1000°C
(Hempelmann et al., 1995; Karmonik et al., 1995)

Water-doped $\text{Ba[Ca}_{0.39}\text{Nb}_{0.61}]\text{O}_{2.91}$ between 460 and 700 K.
(Pionke et al., 1997)
Systems with hydrogen bonds in stoichiometric quantity
High conductivity in high temperature phases
Several energetically equivalent sites available for each proton
CsHSO₄ (Colomban et al. 1987; Belushkin et al. 1992; Belushkin et al. 1994)
CsOH.H₂O (Lechner et al. 1991; Lechner et al. 1993)
Solid ionic conductors

Activity has grown rapidly because of potential applications: batteries, fuel cells, electrochemical and photoelectrochemical devices

REQUIREMENTS FOR QENS
Favourable neutron cross sections,
Ions with high ionic mobility
small ionic radius
single charge (H\(^+\), Li\(^+\), Na\(^+\), Ag\(^+\) or OH\(^-\), F\(^-\) and Cl\(^-\))

Ag\(^+\) diffusivity in AgI, Ag\(_2\)Se, Ag2Se, and Rb\(_4\)Ag\(_4\)I\(_5\)

Na\(^+\) motions in the two-dimensional ionic conductor \(\beta\)-Al\(_2\)O\(_3\)
(Lucazeau et al. 1987)

Na\(^+\) motions sodium silicate glass, Na\(_2\)O.2 SiO\(_2\)
(Hempelmann et al. 1994)

Li\(^+\) cations in antifluorite Li\(_2\)S: diffusion via interstitial hopping
(Altorfer et al. 1994a)

Li\(^+\) in Li\(_{12}\)C\(_{60}\) fulleride (Cristofolini et al., 2000)

Cl\(^-\) diffusion in SrCl\(_2\) and yttrium doped single crystal (Sr,Y)Cl\(_{2.03}\) (Goff et al. 1992)
Intermetallic alloys

Applications for high-temperature environments (aerospace industry)
Diffusion of the constituents themselves
Knowledge of the kinetics on the atomic scale permits:
- to control industrial crucial processes
- to optimize macroscopic characteristics

CsCl structures: NiGa CoGa

Mechanism of self diffusion not yet fully understood
Structure can host a large amount of vacancies
Jump to vacant sites

1- Nearest Neighbour ?
   Disturbs local order
   Shorter jump distance

2- Next Nearest Neighbour ?
   Same sublattice
   Longer jump distance
Two distinct time-scales

Small width \rightarrow Long residence time on regular lattice

Large width \rightarrow Short residence time on antistructure sites
LONG RANGE DIFFUSION IN MICROPOROUS MATERIALS

Confined media: many effects can be observed: finite size effects, interface effects, dimensionality, liquid dynamics, thermodynamics

Challenge for the theoreticians

Important industrial processes:
- catalysis,
- separation of gases and liquids

Wide variety of experimental techniques:
Results can vary by up to six orders of magnitude
- Differences between microscopic and macroscopic
- QENS and pulsed-field gradient NMR complementary

Workshop
« Dynamics in confinement »
Jan 26-29, 2000 Grenoble
B. Brick, R. Zorn, H. Büttner
J.Physique IV, Vol 10 PR7-2000

Zeolite MFI structure (silicalite, ZSM-5)

Unit cell: \( a = 20.07 \, \text{Å}, \quad b = 19.92 \, \text{Å}, \quad c = 13.42 \, \text{Å} \)
- 96 tetrahedral units,
- Si or Al as central atom
- Oxygen as corner atoms
- 4 straight channels
- 4 zigzag channels
- 4 channel intersections
- 10-membered oxygen rings \( (\varnothing \sim 5.5 \, \text{Å}) \)
Kinetic separation of linear/branched alkanes in Zeolite MFI structure (silicalite, ZSM-5)

H. Jobic et al.

Deviations increase with the number of carbon atoms along the chain:

MD: infinite dilution, rigid framework, no thermalisation
Better agreement at higher loading
\( C_6D_6 / \text{ZSM-5 (Q = 0.4 Å}^{-1}) \)

**Benzene / ZSM5 (NSE)**

**Benzene / MFI**

**Time-scale extended to longer times**

**Flux: high loading**

**Analysis at low Q**

**Deuterated samples required**

**H. Jobic et al.**

Diffusion in 1D channel systems

**CH$_4$ molecules can cross each other**

\[ < x^2 > = 2 \, D \, t \]

**CH$_4$ molecules cannot cross each other**

\[ < x^2 > = 2 \, F \, \sqrt{t} \]

**Resolution: FWHM: 18 µeV ; Q = 0.3 Å$^{-1}$**

\[ D = 10^{-8} \text{ m}^2/\text{s} \]

\[ F = 10^{-11} \text{ m}^2/\text{s}^{1/2} \]
LOCALISED MOTIONS
Jump over two inequivalent sites

\[
\frac{dp(r_1, t)}{dt} = -\frac{1}{\tau_1} p(r_1, t) + \frac{1}{\tau_2} p(r_2, t)
\]
\[
\frac{dp(r_2, t)}{dt} = \frac{1}{\tau_1} p(r_1, t) - \frac{1}{\tau_2} p(r_2, t)
\]

**Equilibrium solution**

\[p(r_1, 0) = p(r_1, \infty) = \frac{\tau_1}{\tau_1 + \tau_2}\]
\[p(r_2, 0) = p(r_2, \infty) = \frac{\tau_2}{\tau_1 + \tau_2}\]

**Solutions:**

\[p(r_1, t) = A + B \exp(-t / \tau)\]
\[p(r_2, t) = \frac{\tau_2}{\tau_1} A - B \exp(-t / \tau)\]

**Characteristic time, \(\tau\) defined as**

\[\frac{1}{\tau} = \frac{1}{\tau_1} + \frac{1}{\tau_2}\]
Constant values $A$ and $B$ to be determined from initial conditions

Particle initially on site 1

\[ p(r_1,0;r_1,0) = 1 = A + B \]
\[ p(r_2,0;r_1,0) = 0 = \frac{\tau_2}{\tau_1} A - B \]

Particle initially on site 2

\[ p(r_1,0;r_2,0) = 0 = A + B \]
\[ p(r_2,0;r_1,0) = 1 = \frac{\tau_2}{\tau_1} A - B \]

Conditional probabilities

\[ p(r_1,t;r_1,0) = \frac{\tau_1}{\tau_1 + \tau_2} + \frac{\tau_2}{\tau_1 + \tau_2} \exp(-t/\tau) \]
\[ p(r_2,t;r_1,0) = \frac{\tau_2}{\tau_1 + \tau_2} - \frac{\tau_2}{\tau_1 + \tau_2} \exp(-t/\tau) \]
\[ p(r_1,t;r_2,0) = \frac{\tau_1}{\tau_1 + \tau_2} - \frac{\tau_1}{\tau_1 + \tau_2} \exp(-t/\tau) \]
\[ p(r_2,t;r_2,0) = \frac{\tau_2}{\tau_1 + \tau_2} + \frac{\tau_1}{\tau_1 + \tau_2} \exp(-t/\tau) \]

Normalisation

\[ p(r_1,t;r_1,0) + p(r_2,t;r_1,0) = 1 \]
\[ p(r_1,t;r_2,0) + p(r_2,t;r_2,0) = 1 \]

At infinite time, these solutions yield to equilibrium expressions:

\[ \lim_{t \to \infty} p(r_1,t;r_2,0) = \lim_{t \to \infty} p(r_1,t;r_1,0) = p(r_1,\infty) = \frac{\tau_1}{\tau_1 + \tau_2} \]
\[ \lim_{t \to \infty} p(r_2,t;r_1,0) = \lim_{t \to \infty} p(r_2,t;r_2,0) = p(r_2,\infty) = \frac{\tau_2}{\tau_1 + \tau_2} \]

Particle has forgotten its history.
At any arbitrary time

\[ p(r_1, t) = p(r_1, t; r_1, 0) p(r_1, 0) + p(r_1, t; r_2, 0) p(r_2, 0) \]
\[ p(r_2, t) = p(r_2, t; r_1, 0) p(r_1, 0) + p(r_2, t; r_2, 0) p(r_2, 0) \]

\[
\begin{align*}
 p(r_1, t) &= \frac{\tau_1}{\tau_1 + \tau_2} \left[ \frac{\tau_1}{\tau_1 + \tau_2} + \frac{\tau_2}{\tau_1 + \tau_2} \exp(-t/\tau) \right] + \frac{\tau_2}{\tau_1 + \tau_2} \left[ \frac{\tau_1}{\tau_1 + \tau_2} - \frac{\tau_1}{\tau_1 + \tau_2} \exp(-t/\tau) \right] \\
p(r_2, t) &= \frac{\tau_1}{\tau_1 + \tau_2} \left[ \frac{\tau_2}{\tau_1 + \tau_2} - \frac{\tau_2}{\tau_1 + \tau_2} \exp(-t/\tau) \right] + \frac{\tau_2}{\tau_1 + \tau_2} \left[ \frac{\tau_2}{\tau_1 + \tau_2} + \frac{\tau_1}{\tau_1 + \tau_2} \exp(-t/\tau) \right]
\end{align*}
\]

\[
\begin{align*}
 p(r_1, t) &= \frac{\tau_1}{\tau_1 + \tau_2} \\
p(r_2, t) &= \frac{\tau_2}{\tau_1 + \tau_2}
\end{align*}
\]

\[ p(r_1, t) + p(r_2, t) = 1 \]

The system is always in equilibrium.
Intermediate scattering function

\[
F(Q,t) = \left[ p(r_1,t;r_1,0) + p(r_2,t;r_1,0) \exp\{iQ.(r_2 - r_1)\} \right] p(r_1,0) \\
+ \left[ p(r_1,t;r_2,0) \exp\{iQ.(r_1 - r_2)\} + p(r_2,t;r_2,0) \right] p(r_2,0)
\]

\[
F(Q,t) = \left[ \frac{\tau_1}{\tau_1 + \tau_2} + \frac{\tau_2}{\tau_1 + \tau_2} \exp(-t/\tau) + \left( \frac{\tau_2}{\tau_1 + \tau_2} - \frac{\tau_2}{\tau_1 + \tau_2} \exp(-t/\tau) \right) \exp\{iQ.(r_2 - r_1)\} \right] \frac{\tau_1}{\tau_1 + \tau_2} \\
+ \left[ \left( \frac{\tau_1}{\tau_1 + \tau_2} - \frac{\tau_1}{\tau_1 + \tau_2} \exp(-t/\tau) \right) \exp\{iQ.(r_1 - r_2)\} + \frac{\tau_2}{\tau_1 + \tau_2} + \frac{\tau_1}{\tau_1 + \tau_2} \exp(-t/\tau) \right] \frac{\tau_2}{\tau_1 + \tau_2}
\]

\[
F(Q,t) = \frac{1}{(\tau_1 + \tau_2)^2} \left[ \tau_1^2 + \tau_2^2 + 2\tau_1\tau_2 \cos(Q.r) \right] + \frac{2\tau_1\tau_2}{(\tau_1 + \tau_2)^2} \left[ 1 - \cos(Q.r) \right] \exp(-t/\tau)
\]

Depends on the orientation of \( Q = Q(\theta, \phi) \) with respect to the jump vector \( r = r_1 - r_2 \)

Polycrystalline sample → Powder average \( F(Q,t) = \int \int F(Q,t) \sin \theta \ d\theta \ d\phi \)

At contrast with the case of long range jump diffusion over absorption sites of a lattice, the exponential term does not depend on the scattering vector \( Q \)

The powder average yields an analytical expression with a unique exponential function
\[ F(Q,t) = \frac{1}{(\tau_1 + \tau_2)^2} \left[ \tau_1^2 + \tau_2^2 + 2\tau_1\tau_2 \frac{\sin(Qr)}{Qr} \right] + \frac{2\tau_1\tau_2}{(\tau_1 + \tau_2)^2} \left[ 1 - \frac{\sin(Qr)}{Qr} \right] \exp\left(-\frac{t}{\tau}\right) \]

**Term independent on time:**
localisation of the particle in space

**Term dependent on time:**
Exponential decay of fluctuations

Limit at infinite time, of the intermediate scattering function

**ELASTIC INCOHERENT STRUCTURE FACTOR (EISF)**

\[ \lim_{t \to \infty} F(Q,t) = F(Q,\infty) \]

\[ = \frac{1}{(\tau_1 + \tau_2)^2} \left[ \tau_1^2 + \tau_2^2 + 2\tau_1\tau_2 \frac{\sin(Qr)}{Qr} \right] \]

Oscillatory, with pseudo-période \( Qr \)
Limit at high \( Q \)

\[ \lim_{Q \to \infty} F(Q,\infty) = \frac{\tau_1^2 + \tau_2^2}{(\tau_1 + \tau_2)^2} \]

\( \rho = \tau_1/\tau_2 \)
\( \rho = 1, \tau_1 = \tau_2 \)
Fourier transform  dynamical scattering function

\[
S(Q, \omega) = \frac{1}{\left(\tau_1 + \tau_2\right)^2} \left[\frac{\tau_1^2 + \tau_2^2 + 2\tau_1\tau_2}{Q.r} \sin(Q.r)\right] \delta(\omega) \\
+ \frac{2\tau_1\tau_2}{\left(\tau_1 + \tau_2\right)^2} \left[1 - \frac{\sin(Q.r)}{Q.r}\right] \frac{1}{\pi} \frac{\tau}{1 + \omega^2\tau^2}
\]

If the particle stays indefinitely over one of the sites whatever it is

\[
\lim_{\tau_1 \to \infty} \frac{\tau_1^2 + \tau_2^2}{\left(\tau_1 + \tau_2\right)^2} = \lim_{\tau_2 \to \infty} \frac{\tau_1^2 + \tau_2^2}{\left(\tau_1 + \tau_2\right)^2} = 1
\]

Two sites energetically equivalent

\[
F_{\text{min}}(Q, t) = \frac{1}{2} \left[1 + \frac{\sin(Q.r)}{Q.r}\right] + \frac{1}{2} \left[1 - \frac{\sin(Q.r)}{Q.r}\right] \exp(-t / \tau)
\]

\[
\lim_{t \to \infty} F_{\text{min}}(Q, t) = F_{\text{min}}(Q, \infty) = \frac{1}{2} \left[1 + \frac{\sin(Q.r)}{Q.r}\right]
\]

\[
\lim_{Q \to \infty} F_{\text{min}}(Q, \infty) = \frac{1}{2}
\]
JUMPS OVER 3 EQUIVALENT SITES
Polycrystalline sample

\[ S^{3-sites}(Q, \omega) = \frac{1}{3} \left\{ 1 + 2 \frac{\sin(Qr\sqrt{3})}{Qr\sqrt{3}} \right\} \delta(\omega) + \frac{2}{3} \left\{ 1 - \frac{\sin(Qr\sqrt{3})}{Qr\sqrt{3}} \right\} \frac{1}{\pi} \frac{\tau}{1 + \omega^2 \tau^2} \]

Example: methyl groups of monohydrated camphor sulfonic acid, \( C_{10}H_{15}O_4S^- - H_3O^+ \) (CSA)

\[ S(Q, \omega) = \frac{12}{18} \delta(\omega) + \frac{6}{18} S^{3-sites}(Q, \omega) \]
\[ = \frac{1}{9} \left\{ 7 + 2 \frac{\sin(Qr\sqrt{3})}{Qr\sqrt{3}} \right\} \delta(\omega) \]
\[ + \frac{2}{9} \left\{ 1 - \frac{\sin(Qr\sqrt{3})}{Qr\sqrt{3}} \right\} \frac{1}{\pi} \frac{\tau}{1 + \omega^2 \tau^2} \]

Analysis from 15 to 340 K, with backscattering and time of flight spectrometries.
Uncertainties over experimental points especially high.
Low neutron flux
Ratio mobile/total hydrogen atoms 6:18
Halfwidth at half maximum of quasielastic part of spectra:

HWHM is constant with \( Q \).

1 single lorentzian (2 or 3 sites)
CONTINUOUS ROTATIONAL DIFFUSION ON A CIRCLE

\[ \frac{\partial}{\partial t} P(\Phi, \Phi_0, t) = D_R \frac{\partial^2}{\partial \Phi^2} P(\Phi, \Phi_0, t) \]

rotational diffusion coefficient \( D_R \)

\[ P(\Phi, \Phi_0, t) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} \exp\left[ i n (\Phi - \Phi_0) t \right] \exp(-D_R n^2 | t |) \]

\[ I_{inc}^R (Q, t) = \int \int \exp\left\{ i Q [R(\Phi, t) - R(\Phi_0, 0)] \right\} P(\Phi, \Phi_0, t) P(\Phi_0) \, d\Phi \, d\Phi_0 \]

\[ I_{inc}^R (Q, t) = \sum_{m=-\infty}^{\infty} J_m^2 (Q R \sin \theta) \exp(-D_R m^2 | t |) \]

\[ S(Q, \omega) = A_0(Q) \delta(\omega) + \sum_{m=1}^{\infty} A_m(Q) \frac{1}{\pi} \frac{\tau_m}{1 + \omega^2 \tau_m^2} \]

with the EISF \( A_0(Q) = J_0^2 (QR \sin \theta) \) and quasilastic incoherent structure factors \( A_m(Q) = 2J_m^2 (QR \sin \theta) \) correlation times \( \tau_{m} \)

\[ \tau_m^{-1} = m^2 D_R \]
ISOTROPIC ROTATIONAL DIFFUSION OF AN ATOM ON A SPHERE

\[
\frac{\partial}{\partial t} P(\Omega, \Omega_0, t) = D_R \Delta_\Omega P(\Omega, \Omega_0, t)
\]

\[
I_{inc}^R(Q, t) = j_0^2(QR) + \sum_{l=1}^{\infty} (2l+1) j_l^2(QR) \exp[-l(l+1)D_Rt]
\]

\[
S(Q, \omega) = A_0(Q) \delta(\omega) + \sum_{l=1}^{\infty} A_l(Q) \frac{1}{\pi} \frac{\tau_l}{1 + \omega^2 \tau_l^2}
\]

\[
A_0(Q) = j_0^2(QR)
\]

Coefficients \(A_l(Q)\) with \(l \neq 0\) are the quasielastic incoherent structure factors

\[
A_l(Q) = (2l+1) j_l^2(QR)
\]

The hwhm of the successive Lorentzian functions in the expansion are directly related to the rotational diffusion coefficient \(D_R\) and increase with \(l\) according to

\[
\tau_l^{-1} = l(l+1)D_R
\]
The norbornane molecule

The OPCTS molecule
ELASTIC SCANS; THE FIXED-WINDOW METHOD

Backscattering spectrometers
Incident neutrons with exactly the same energy as selected by analyseurs.
Recording of elastic scattering
Variation of an external parameter (temperature, sometime pressure.)
Apparition of a motion in the experimental time-range

Quasielastic broadening
Decrease of the observed elastic intensity.

Rapid inspection of dynamics as a function of temperature.
To be completed by quasielastic measurements
Example: *camphor sulfonic acid*

Diffusive motions too slow
Harmonic vibrations
\[
\langle u^2(T) \rangle \text{ linear with } T
\]
\[
S(Q, \omega = 0) = C^{ste} \exp(-Q^2 \langle u^2 \rangle)
\]

\[ \theta = 29^\circ \]

\[ \theta = 93^\circ \]

\[ \theta = 156^\circ \]

Quasielastic broadening too large
Harmonic vibrations
\[
\langle u^2(T) \rangle \text{ linear with } T
\]
\[
S(Q, \omega = 0) = C^{ste} \exp(-Q^2 \langle u^2 \rangle)
\]

Possible extraction of EISF
Example of application: protein dynamics

Dynamical transition of myoglobin hydrated with D_2O. From 4 K to 180 K elastic intensity varies with Q according to a Gaussian law.

For an harmonic solid: Debye-Waller factor

\[ S(Q, \omega = 0) = \exp(-Q^2 \langle \nu^2 \rangle) \]

Mean square displacement \( \langle \nu^2 \rangle \) proportional to temperature.

Near 200 K apparition of new degrees of freedom. Deviation from Gaussian behaviour which increases with temperature

\[ S(Q, \omega = 0) = \frac{\exp(-Q^2 \langle \nu^2 \rangle)}{(\tau_1 + \tau_2)^2} \left[ \tau_1^2 + \tau_2^2 + 2\tau_1\tau_2 \frac{\sin(Qr)}{Qr} \right] \]

Initial slope of the curve.

\[ \left(-\frac{d \ln \{S(Q,0)\}}{d(Q^2)}\right)_{Q=0} = \langle \nu^2 \rangle + \frac{\tau_1\tau_2}{(\tau_1 + \tau_2)^2} \frac{r^2}{3} \]

From refinement to experimental data, \( \langle \nu^2 \rangle, \; r^2 \; \text{and} \; \tau_1/\tau_2 \).

Free energy \( \Delta G \)

\[ \frac{\tau_1}{\tau_2} = \exp\left(-\frac{\Delta G}{RT}\right) \]

Myoglobin (Doster et al.):

asymmetry of well DH = 12 kJ.mol\(^{-1}\)

Entropy \( DS/R = 3.0 \)

Jump distance \( r = 1.5 \text{ Å} \).
Mostly based on jump models

Earlier studies: SH reorientations in NaSH, CsSH
   Rowe et al., J. Chem. Phys. 58, 5463 (1973)
120° jumps of methyl groups in para-azoxy-anisole
   Hervet et al. (1976)
Rotations of aromatic rings
   Chhor et al. (1982)
Several axes: use of group theory
   Rigny Physica 59 707 (1972)
   Thibaudier and Volino Mol. Phys. 26 1281 (1973); ibid. 30 1159 (1975)

Some cases of rotational diffusion

Octaphenylcyclotetrasiloxane
Norbornane
Semi-oxydized, non conductive form: emeraldine base

\[
\begin{array}{c}
\text{Doping} \\
\text{AH}
\end{array}
\]

Insoluble powder, non conductive \(10^{-10} \text{ S/cm}\)

Conductive salt of emeraldine

\[
\begin{array}{c}
\text{Doping by HCl, H}_2\text{SO}_4\ldots \\
\text{Protonation with a functionalized organic acid: camphor sulfonic acid (CSA)}
\end{array}
\]

Insoluble powder, 1-20 S/cm

Brittle films 100-400 S/cm

Polar solvent: meta-cresol

Dynamics of counter-ions in conducting polyaniline.
Polyaniline chain

Camphor sulfonic acid

Chains are immobile
Motions of CSA

Whole CSA

Methyl groups

Electrical transition
Metallic regime

Semiconducting regime

Conductivity $\sigma$ (S/cm)

Temperature (K)

Normalized Elastic Intensity

Mean Square Displacement

$\langle U^2 \rangle (\text{Å}^2)$

Temperature (K)
New families of plastdopants: high conductivity, improved flexibility


DEHEPSA
1,2 di(2-ethylhexyl)ester of 4-sulphophtalic acid

DPEPSA
di-n-pentyl ester of 4-sulphophtalic acid
PANI / DEHEPSA : IN13 10^{-10} s time-scale

- \(2\theta = 24.5^\circ\)
  - \(Q = 1.2\) \(\text{Å}^{-1}\)

- \(2\theta = 45.6^\circ\)
  - \(Q = 2.8\) \(\text{Å}^{-1}\)

- \(2\theta = 66.8^\circ\)
  - \(Q = 3.1\) \(\text{Å}^{-1}\)

- \(2\theta = 88.0^\circ\)
  - \(Q = 3.9\) \(\text{Å}^{-1}\)
Elastic Incoherent Structure Factor

\[ Q \text{ (Å}^{-1}\text{)} \]

EISF is temperature dependent:
- Variation with T
- Of the region of space accessible to scatterers
- Of the fraction of mobile scatterers

Given T, DPEPSA more ordered than DEHEPSA
- Smaller chain
- Linear chain: packing favored

High values of EISF
Fraction of non mobile scatterers
Model: Diffusion inside a sphere
F. Volino and A.J. Dianoux; Molecular Physics 41 (1980) 271

\[ S(Q, \omega) = A_0^0 (Q) + \sum_{\{l,m\} \neq \{0,0\}} (2l+1) A_n^l (Q) \frac{1}{\pi} \frac{\lambda_n^l D}{(\lambda_n^l D)^2 + \omega^2} \]

**EISF**

\[ A_0^0 (Q) = \left[ 3 \frac{j_1(QR)}{QR} \right]^2 \]

**Structure factors**

\[ A_n^l (Q) = \frac{6R^2 \lambda_n^l}{R^2 \lambda_n^l - l(l+1)} \left[ \frac{QR j_{l+1}(QR) - l j_l(QR)}{R^2 (Q^2 - \lambda_n^l)} \right]^2 \quad \text{if} \quad Q^2 \neq \lambda_n^l \]

\[ A_n^l (Q) = \frac{3}{2} j_l^2(QR) \frac{Q^2 R^2 - l(l+1)}{Q^2 R^2} \quad \text{if} \quad Q^2 = \lambda_n^l \]
Distribution of radii along counter-ion tail

\[ R_m = R_\infty \cdot \Gamma(a, mp) \]

3 Parameters

Polymer chain  Counter-ion head  Counter-ion tail

\[ S(Q, \omega) = \alpha_1 \delta(\omega) + \alpha_2 \delta(\omega) + \sum_{m} \alpha_m S(Q, \omega; R_m) \]

Incomplete Gamma function

\[ \Gamma(a, x) \]
Proteins exhibit a complex structure: several thousand atoms fold into a unique 3-D structure.

Unfolding of biomolecules \iff Loose of biological activity
Biological function \iff Flexibility

Rich dynamical spectrum: $10^{-14}$ to $10^1$ s: many instruments concerned.

Nanosecond - picosecond regime: major role for intermolecular recognition and for enzymatic reactions: all QENS instruments are concerned.

Non exchangeable H atoms, distributed homogeneously within the sample give information on the overall dynamics and on those of the larger groups to which they are bound.

(J. C. Smith Quarterly Review of Biophys. J. 76, 1043 (1999))
Flexibility of DNA as a function of hydration

Dynamic transition at $T \sim 200 - 230$ K
Not clearly understood
Important for protein function

At high temperature a slow relaxation process appears:
Cooperative motion of many DNA’s monomers involving all parts of the molecule (backbone and base pairs)
Strongly depends on the level of hydration
Influence of the solvent in biopolymer dynamics

At low temperature
larger flexibility for low water content

Slow relaxation process
Fast relaxation process
Development of Theoretical Models

Long range diffusion
- Lattice model with gaussian statistics
- Single-file diffusion
- Extended Hall and Ross model
  H. Jobic J. de Physique IV 10 (2000) 77

Polymers
- Mode Coupling Theory
  Rotation-Rate Distribution Model
  A. Chahid et al.
  Macromolecules 17 3282 (1994)

Biology
- Force Constant Analysis
  D. Bicout and G. Zaccaï Biophys. J. 80, 1115 (2001)
- Combined dynamics: jump and diffusion inside a sphere
  D. Bicout, Proceedings ILL Millenium Symposium (2001)
- Diffusion inside two concentric spheres
- Influence of environment fluctuations
- Damped collective vibrations, diffusion in anharmonic potential
MOLECULAR DYNAMIC SIMULATIONS

Seem very promising for future
Still require long computing time.
Up to now application to QENS restricted to small molecules
Methods have been developed for larger molecules

Require a reliable interaction potential
  Can be a serious difficulty (delocalised charges)
  Can require long preliminary calculations calculations
  Need to be checked carefully by comparison with experimental results
  Necessary to evaluate QENS spectra (nMOLDYN)

Under that conditions, analysis of atoms trajectories can be of considerable help in understanding neutron results
Distribution of Potential barriers for methyl groups in glassy polyisoprene
MOLECULAR DYNAMIC SIMULATION OF NORBORNANE

Orientational distribution

Good agreement with earlier experimental neutron results

Dynamics more complex
Than an isotropic rotation
(preferential orientations).

HCP Phase    FCC Phase

J. Combet; Journées de la diffusion neutronique 2001
CONCLUSIONS AND PERSPECTIVES

Pioneer time is finished

“Simple” samples, geometrically well described, stimulated:
- numerous scattering models especially for rotation
- original theoretical approaches based on symmetry

They evidenced the existence and the importance of EISF.

Now

Most of samples are very complicated, involving
- many types of scatterers,
- many types of motions, no symmetry
- many time-scales

Models often offer a rather abstract form
They can not easily be connected with experimental data.

Molecular dynamic simulations are very long
Collaborations are required:
- between experimentalists and theoreticians
- between theoretical calculations and simulations

Multiply environment conditions:
- temperature, pressure, concentration, selective deuteration, illumination, ...

Multiply experimental conditions:
- analyse sample with different instruments and/or resolutions
- analyse sample with different energy ranges
  
  R.E. Lechner Physica B 301 (2001) 83

  use polarised neutrons to separate coherent from incoherent scattering

Improve software for data treatment:
- signal processing (intermediate scattering function)
- develop new analyses of data (memory function)

Collect maximum of information about the system:
- from other techniques
- from other scientific communities (chemistry, physics, biology, biophysics, ....)