QENS in the Energy Domain: Backscattering and Time-of-Flight

Alexei Sokolov
Department of Polymer Science, The University of Akron

Outline

- Soft Matter and Neutron Spectroscopy
- Using elastic scattering and employing H/D contrast
- Quasielastic scattering spectra, susceptibility presentation
- Q-dependence: diffusive vs local processes
- Geometry of the motion from EISF
- Use of coherent scattering
- Spectrometers

Soft Matter

Characteristics of Soft Materials:
- Variety of states and large degree of freedom, metastable states;
- Delicate balance between Entropic and Enthalpic contributions to the Free Energy;
- Large thermal fluctuations and high sensitivity to external conditions;
- Macroscopic softness.

Polymers  Colloids  Liquid Crystals

Foams and Gels  Biological Systems
**Frequency map of polymer dynamics**

Chain dynamics: Rouse and terminal relaxation

Structural relaxation, α-process

Secondary relaxations

Fast relaxation

Vibrations

FREQUENCY, \( \nu \)

Mechanical relaxation \( G'(\nu) \)

Dielectric Spectroscopy, \( \varepsilon'(\nu) \)

Quasi-optics, TDS

Traditional dielectric spectroscopy

IR-spectr.

Light Scattering, \( I(Q, \nu) \)

Interferometry

Photon – Correlation Spectroscopy

Raman spectroscopy

Neutron Scattering, \( S(Q, \nu) \)

Spin-Echo

Back-sc.

Time-of-Flight

Inelastic X-ray Scattering, \( S(Q, \nu) \)

High-Resolution IXS

Scattering techniques have an advantage due to additional variable – wave-vector \( Q \)

**Beauty of Neutron Spectroscopy**

- Measures characteristic times (frequency) and geometry of the motions.
- Covers broad frequency and Q-range in the most important for microscopic dynamics region. *Current X-ray technology cannot compete!*
- Most of the soft materials contain hydrogen atoms, use of D/H contrast.
- Direct comparison to results of MD-simulations.
An example of elastic scan measurements of PI [Frick, Fetters, Macromol. 27, 1994]. Decrease of elastic intensity marks onset of a relaxation process. Various deuteration of the polymer allows separate methyl group and main-chain motion.

The onset of methyl groups rotation at temperatures below $T_g$ is clearly seen.

Using H/D Contrast

PI-h8 – all H,
PI-d8 with all D.
PI – d3
PI – d5

Decrease of the elastic intensity in dry lysozyme can be described assuming a Gaussian distribution of energy barriers, $g(E_i) \propto \exp\left(-\frac{(E_i - E_0)^2}{2\Delta E^2}\right)$, with $E_0 \approx 16.6$ kJ/mol and $\Delta E \approx 5.8$ kJ/mol in good agreement with earlier NMR data [J.H.Roh, et al. Biophys.J. 91, 2573 (2006)].

Here $\tau = \tau_0 \exp(E/kT)$
### Mean-squared Displacements $\langle r^2 \rangle$

In rough approximation, for an isotropic motion:

$$S_{\text{iso}}(Q, t) = \exp \left( -\frac{Q^2}{3} \langle r(t)^2 \rangle \right)$$

This approximation works well only at low $Q$.

The estimated $\langle r^2 \rangle$ depends on the selected $Q$-range and the resolution function of the spectrometer.

Analysis of $\langle r^2 \rangle$ helps to identify interesting temperature ranges. However, $\langle r^2 \rangle$ is an integrated quantity (includes vibrations, rotation, diffusion, etc.) and analysis of spectra is required for understanding the dynamics.

### Quasielastic Scattering Spectrum

Usual approximation is a Lorentzian function:

$$S(Q, E) \propto \frac{\Gamma(Q)}{E^2 + \Gamma(Q)^2}$$

In most cases 2 or more Lorentzians are used for the fit of the spectra. This approximation assumes single exponential relaxation:

$$S(Q, t) \propto \exp(-t/\tau)$$

However, many relaxation processes in soft matter are strongly stretched

$$S(Q, t) \propto \exp\left[-\left(t/\tau\right)^\beta\right]$$

So, approximation by Lorentzians can give misleading quantitative results.
Susceptibility presentation

Susceptibility presentation of scattering spectra has a few advantages:
- can be directly compared to \( \varepsilon''(\nu) \), \( G''(\nu) \);
- each relaxation process appears as a maximum at \( 2\pi\nu\tau \sim 1 \);
- slopes of the tails give estimate of stretching exponents.

The spectra of proteins show two relaxation processes. Both processes are strongly stretched (can not be described by a single exponential relaxation).

Q-dependence: Diffusion

For regular diffusion: \( \langle (r(t)^2) \rangle = Dt \)

In that case:
\[
S_{inc}(Q,t) = \exp(-Q^2Dt) = \exp(-\Gamma t)
\]

In frequency domain:
\[
S_{inc}(\omega,t) = \frac{N}{2\pi} \exp(i\omega t) \exp(-\Gamma|\omega|dt) = \frac{N}{\pi} \frac{\Gamma}{\Gamma^2 + \omega^2}
\]

An exponential decay for \( S(Q,t) \), with decay rate \( \Gamma \propto Q^2 \)

In the case of sub-diffusive regime: \( \langle (r(t)^2) \rangle \propto (Dt)^\beta \Rightarrow S(Q,t) \propto \exp[-Q^2(Dt)^\beta] \propto \exp[-(\Gamma t)^\beta] \)

with \( \Gamma \propto Q^{-2\beta} \).

Diffusion-like motions exhibit strong dependence of the decay rate \( \Gamma \) (or relaxation time \( \tau \propto 1/\Gamma \)) on \( Q \).
Let’s assume that there are two equal positions and molecule makes jumps between \( r_1 \) and \( r_2 \) positions. In isotropic case:

\[
S_m(Q,t) \propto \left[ \text{EISF}(Q) + A_i(Q) \exp(-2\tau / \tau_i) \right] d = r_2 - r_1
\]

\[
\text{EISF}(Q) = (1/2) \left[ 1 + \frac{\sin Qd}{Qd} \right] \delta(Q) + (1/2) \left[ 1 - \frac{\sin Qd}{Qd} \right] \delta(Q)
\]

EISF(Q) is the Elastic Incoherent Structure Factor. It contains information on geometry of the motion. In the frequency domain:

\[
S_m(Q,\omega) = N \left[ \text{EISF}(Q)\delta(\omega) + A_i(Q) \frac{2\tau}{\pi \left( 4 + \omega^2 \tau_i^2 \right) } \right]
\]

For a local relaxation process:
- \( S(Q,\omega) \) has two component – elastic and quasielastic;
- Characteristic time scale \( \tau \) (or \( \Gamma \)) is independent of \( Q \) (at least, at large \( Q \)).

---

**EISF in dry protein: Methyl Group Dynamics**

Analysis of elastic incoherent structure factor, \( \text{EISF}(Q) = I_{el}(Q)/[I_{el}(Q)+I_Q(EISF)(Q)] \), can be done:

(i) assuming a single exponential relaxation (single Lorentzian);

(ii) taking into account a distribution of \( \tau_i \) or energy barriers \( g(E_i) \):

\[
S(Q,\omega) = \left[ \text{const}(Q) + \int R(\omega - \omega') \delta(\omega') g(E_i) \frac{\tau_i}{1 + \omega^2 \tau_i^2} d\omega' \right]
\]

The first approximation overestimates EISF.

Fit of the EISF to a 3-site jump model [J.H.Roh, et al. Biophys.J. 91, 2573 (2006)]:

\[
\text{EISF}(Q) = 1 - p_m \frac{P^2}{3} \left[ 1 + 2[Q \cdot R \cdot \sqrt{3}] \right]
\]

Analysis of the first data set (single Lorentzian) gives mobile fraction of H-atoms \( p_m = 0.14 \) and radius R~1.3 Å, while analysis of the second set gives \( p_m = 0.25 \) and radius R~1.3 Å. For methyl groups R~1.1 Å and \( p_m = 0.26 \) in lysozyme [J.H.Roh, et al. Biophys.J. 91, 2573 (2006)].
Segmental and Secondary Relaxations in Polymers

Segmental relaxation time $\tau_s$ exhibits strong $Q$-dependence, $\tau_s \sim Q^{-2}$, indicating “stretched” diffusive-like process ($\beta$ - KWW stretching parameter).

Homogeneous vs Heterogeneous Dynamics

a) **Heterogeneous**: Normal diffusion with distribution of diffusion coefficient $D$:

$$S(Q,t) = \int g((ln D)^{1/2}) \exp[-Q^2(Dt)]/(ln D) \approx \exp[-(Q^2Dt)^{2/3}]$$

$$\tau \sim Q^{-2}$$

b) **Homogeneous**: Sublinear diffusion in time, $<r^2(t)> \approx t^\beta$:

$$S(Q,t) = \exp[-Q^2<r^2(t)>/\eta] \approx \exp[-Q^2(Dt)^{2/3}]$$

$$\tau \sim Q^{-2/\beta}$$


Polybutadiene (PB): Split of Segmental and Secondary Relaxations

$Q$ dependence of $\tau_{self}$ change sharply when $T$ approaches ~200 K. Also scaling with the viscosity time scale $\tau_\eta$ fails.

Coherent Scattering

Polybutadiene

NSE data measured at different T for deuterated PB scaled with the viscosity time scale $\tau_0$:
- Master curve for the data measured at $Q \sim 1.5\text{A}^{-1}$;
- No master curve for the data at $Q \sim 2.7\text{A}^{-1}$.

Conclusions:
✓ Segmental relaxation involves inter-molecular motions;
✓ Secondary relaxation involves intra-molecular motion, rotation about the double-bond.


Instruments: Back-Scattering Spectrometer HFBS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>6.271 Å</td>
</tr>
<tr>
<td>Neutron Energy</td>
<td>2.08 meV</td>
</tr>
<tr>
<td>Neutron Flux at Sample</td>
<td>$3 \times 10^7$ n cm$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>Energy range</td>
<td>± 36 μeV</td>
</tr>
<tr>
<td>Energy resolution at ± 36 μeV</td>
<td>About 1 μeV</td>
</tr>
<tr>
<td>Analyzer Span</td>
<td>165°</td>
</tr>
<tr>
<td>Q range</td>
<td>0.25 Å$^{-1}$ – 1.75 Å$^{-1}$</td>
</tr>
</tbody>
</table>
The DCS is a direct geometry time-of-flight spectrometer, the only instrument of its kind in North America. The DCS is primarily used for studies of low energy excitations and diffusive motions in a wide variety of materials. The DCS is an extremely versatile instrument. Useful incident wavelengths range from < 2Å to at least 9Å; correspondingly the elastic energy resolution (FWHM) varies from ~1500 to ~15 µeV.

For any experiment try to optimize intensity vs resolution.

**Conclusions**

- Neutron Spectroscopy is well positioned for analysis of dynamics of Soft Materials.
- Analysis of elastic scattering and use of H/D contrast allows to identify molecular units involved in the motion, geometry of the motion and interesting temperature ranges.
- Analysis of the Q-dependence differentiate diffusive and local processes and provide additional information on geometry of molecular motions.
- Analysis of the energy-resolved spectra provides information on characteristic relaxation times and vibrational frequencies, their distribution and temperature dependence.
- Coherent scattering provides additional information on cooperativity and geometry of molecular motion. However, analysis of the coherent scattering is more complex than analysis of incoherent scattering.
Hands-on Exercises
Santa Fe, May 2008

Using DAVE program and provided experimental data (3 sets of data) perform the following tasks:

- **Mean-squared displacement \( \langle r^2 \rangle \) in dry protein** (HFBS data from J.H. Roh, et al. Biophys. J. 91, 2573 (2006)):
  - Analyze temperature dependence of \( \langle r^2 \rangle \) using HFBS data from elastic scan (Doppler stopped).

  - Analyze Q-dependence of the characteristic relaxation time (decay rate);
  - Analyze EISF(Q) (assuming Lorentzian spectrum).

  - Analyze Q-dependence of characteristic relaxation time (decay rate)