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

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Outline

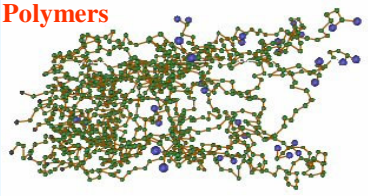
- Soft Matter and Neutron Spectroscopy
- Using elastic scattering and employing H/D contrast
- Quasielastic scattering spectra, susceptibility presentation
- Q-dependence: diffusive vs local processes Geometry of the motion from EISF
- Use of coherent scattering
- Spectrometers

Soft Matter

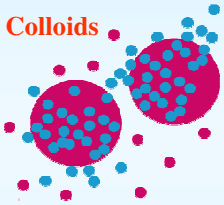
Characteristics of Soft Materials:

-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.

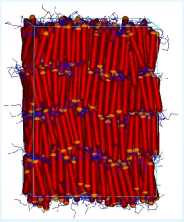
Polymers



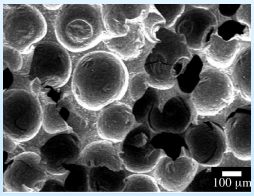
Colloids

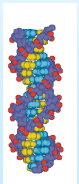


Liquid Crystals

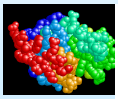


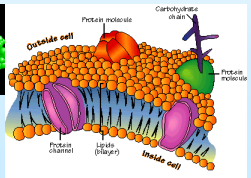
Foams and Gels

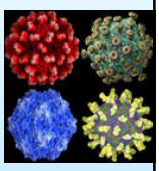




Biological Systems







Frequency map of polymer dynamics

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Chain dynamics: Rouse and terminal relaxation

Structural relaxation, α-process

Secondary relaxations — Fast relaxation — Vibrations

FREQUENCY, ν

10^{-2} 1 10^{2} 10^{4} 10^{6} 10^{8} 10^{10} 10^{12} 10^{14} Hz

Mechanical relaxation $G^*(\nu)$

Dielectric Spectroscopy, $\varepsilon^*(\nu)$

Quasi-optics,TDS

Traditional dielectric spectroscopy

IR-spectr.

Light Scattering, $I_{ij}(Q,\nu)$

Interferometry

Photon – Correlation Spectroscopy

Raman spectroscopy

Spin-Echo

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

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

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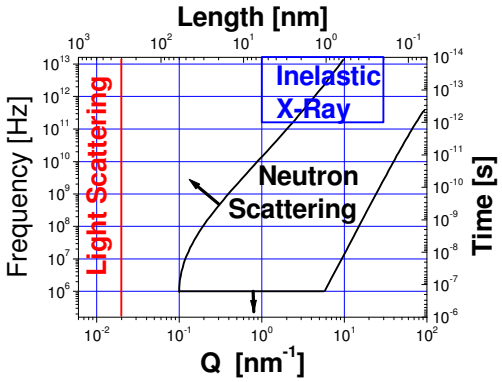
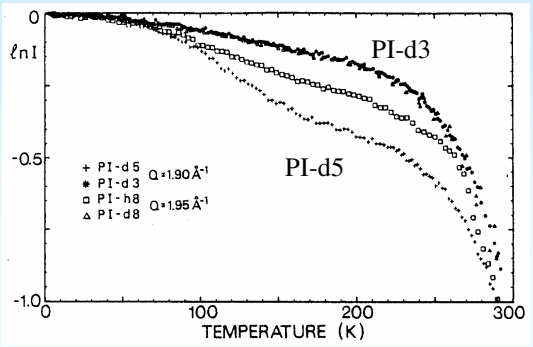


- Measures characteristic times (frequency) and geometry of the motions.
- Covers broad frequency and Q-range in the most important for microscopic dynamics region. *Current X-ray technology cannot compete!*
- Most of the soft materials contain hydrogen atoms, use of D/H contrast.
- Direct comparison to results of MD-simulations.

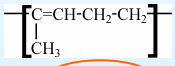
Using H/D Contrast

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.

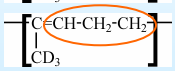
The onset of methyl groups rotation at temperatures below Tg is clearly seen.



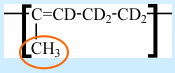
PI-h8 – all H,
PI-d8 with all D.

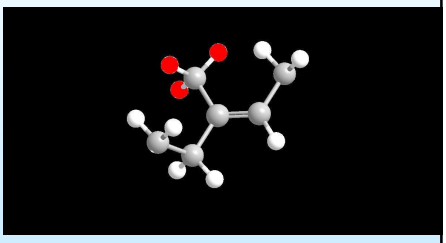


PI – d3



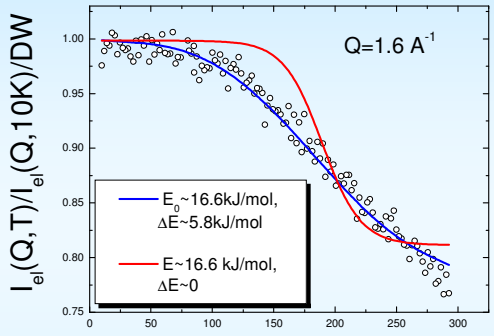
PI – d5

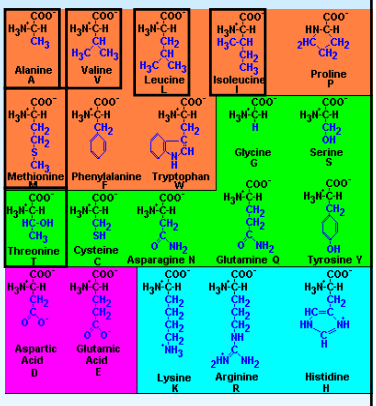




Methyl Group Dynamics in Proteins

Significant part of H-atoms in proteins are on methyl groups.





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

$$I_{el}(Q,T,\omega\sim 0) = DW(Q,T)\left[1 - p_m + p_m \int_{-\infty}^{\infty} S_{met}(Q,\omega')R(\omega-\omega')d\omega\Big|_{\omega=0}\right] \propto DW(Q,T)\left[const(Q) + \int_{-\infty}^{\infty} R(\omega-\omega')\int_{0}^{\infty} g(E_i)\frac{\tau_i}{1+\omega^2\tau_i^2}dE_i d\omega\Big|_{\omega=0}\right]$$

Here $\tau_i = \tau_0 exp(E_i/kT)$

Mean-squared Displacements $\langle r^2 \rangle$

In rough approximation, for an isotropic motion:

$$S_{inc}(Q,t) \propto \exp\left[-\frac{Q^2}{3} < r(t)^2 >\right]$$

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.

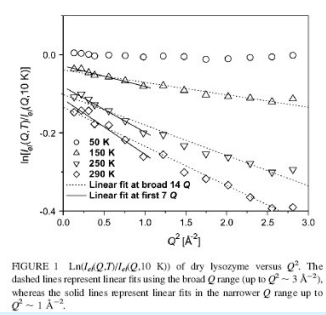
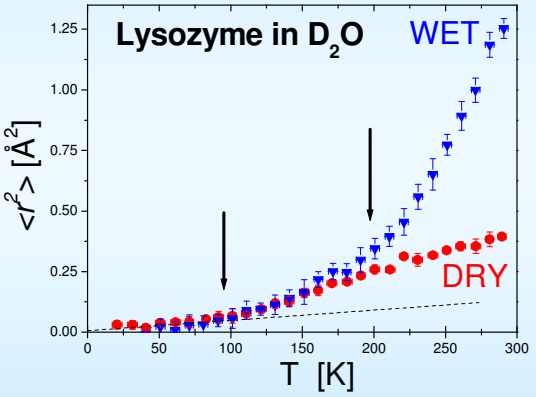


FIGURE 1 $\mathrm{Ln}(I_{el}(Q,T)/I_{el}(Q,10\ \mathrm{K}))$ of dry lysozyme versus Q^2. The dashed lines represent linear fits using the broad Q range (up to $Q^2 \sim 3$ Å^{-2}), whereas the solid lines represent linear fits in the narrower Q range up to $Q^2 \sim 1$ Å^{-2}.



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:

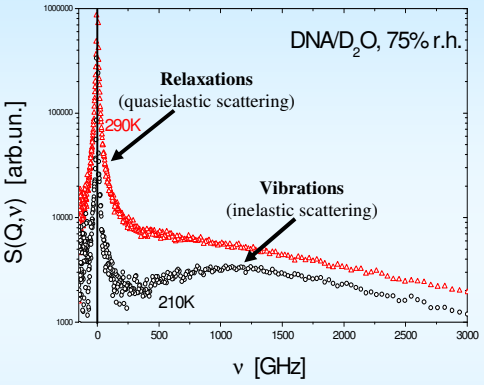
$$S(Q,E) \propto \frac{\Gamma(Q)}{E^2 + \Gamma(Q)^2}$$

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

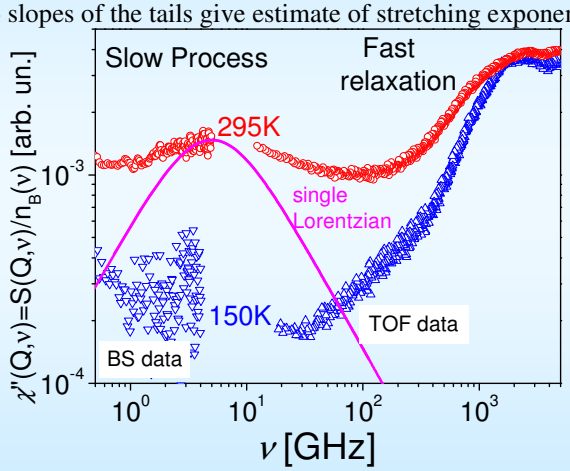
$$S(Q,t) \propto \exp\left[-(t/\tau)^{\beta}\right]$$



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 ε”(ν), G”(ν);
- each relaxation process appears as a maximum at $2\pi\nu\tau \sim 1$;
- slopes of the tails give estimate of stretching exponents.



Susceptibility spectra of wet lysozyme

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

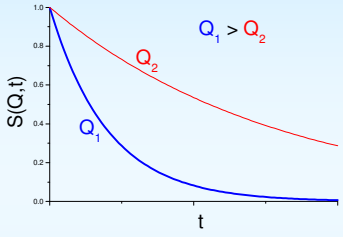
For regular diffusion: $\langle r(t)^2 \rangle \propto Dt$

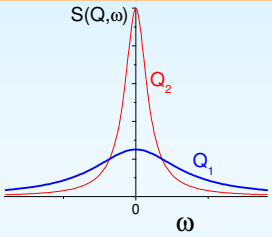
In that case:

$$S_{inc}(Q,t) \propto \exp(-Q^2 Dt) = \exp(-\Gamma t)$$

In frequency domain:

$$S_{inc}(\omega,t) = \frac{N}{2\pi}\int \exp(i\omega t)\exp(-\Gamma|t|)dt = \frac{N}{\pi}\frac{\Gamma}{\Gamma^2+\omega^2}$$





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

In the case of sub-diffusive regime: $\langle r(t)^2 \rangle \propto (Dt)^\beta \Rightarrow S(Q,t) \propto \exp\left[-Q^2(Dt)^\beta\right] \propto \exp\left[-(\Gamma t)^\beta\right]$ with $\Gamma \propto Q^{2/\beta}$.

Diffusion-like motions exhibit strong dependence of the decay rate Γ (or relaxation time $\tau \propto 1/\Gamma$) on Q.

Q-dependence: a Local Relaxation Process

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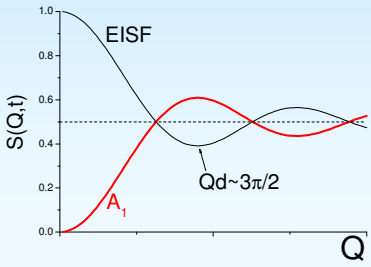
Let's assume that there are two equal positions and molecule makes jumps between r_1 and r_2 positions. In isotropic case:

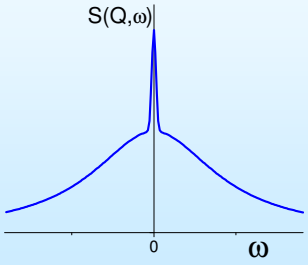
$$S_{inc}(Q,t) \propto [EISF(Q) + A_1(Q)\exp(-2t/\tau)]; d = r_2 - r_1$$

$$EISF(Q) = (1/2)\left\{1 + \frac{\sin Qd}{Qd}\right\}; A_1(q) = (1/2)\left\{1 - \frac{\sin Qd}{Qd}\right\}$$



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

$$S_{inc}(Q,\omega) = N\left[EISF(Q)\delta(\omega) + A_1(Q)\frac{1}{\pi}\frac{2\tau}{4+\omega^2\tau^2}\right]$$



For a local relaxation process:
✓S(Q,ω) has two component – elastic and quasielastic;
✓Characteristic time scale τ (or Γ) is independent of Q (at least, at large Q).

EISF in dry protein: Methyl Group Dynamics

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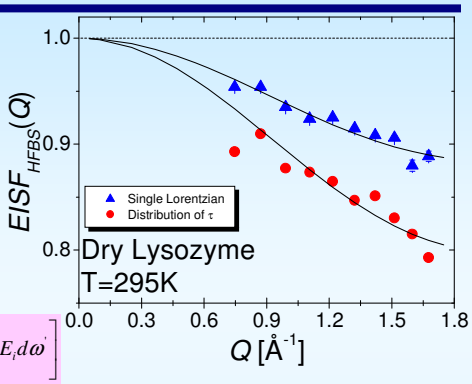
Analysis of elastic incoherent structure factor, $EISF(Q)=I_{el}(Q)/[I_{el}(Q)+I_{QES}(Q)]$, can be done:
(i) assuming a single exponential relaxation (single Lorentzian);
(ii) taking into account a distribution of τ_i or energy barriers $g(E_i)$:



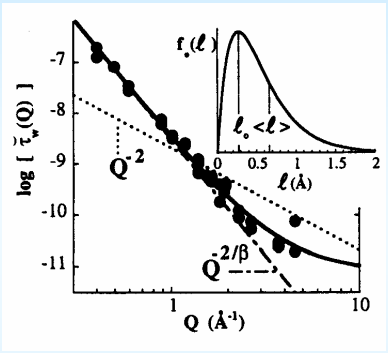
$$S(Q,\omega) \propto \left[const(Q) + \int_{-\infty}^{\infty} R(\omega-\omega')\int_0^{\infty} g(E_i)\frac{\tau_i}{1+\omega'^2\tau_i^2}dE_i d\omega'\right]$$

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)]:

$$EISF(Q) = 1 - p_m + \frac{p_m}{3}\left[1 + 2j_0(QR\sqrt{3})\right]$$

Analysis of the first data set (single Lorentzian) gives mobile fraction of H-atoms p_m=0.14 and radius R~1.3 A, while analysis of the second set gives p_m=0.25 and radius R~1.3 A. For methyl groups R~1.1 A 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 τ_S exhibits strong Q-dependence, $\tau_S \propto Q^{-2/\beta}$, indicating "stretched" diffusive-like process (β - KWW stretching parameter).

Homogeneous vs Heterogeneous Dynamics

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

$$S(Q,t) = \int_{-\infty}^{\infty} g(\ln D^{-1}) \exp\left(-Q^2 D t\right) d\left(\ln D^{-1}\right) \propto \exp\left[-\left(Q^2 D t\right)^{\beta}\right]$$

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

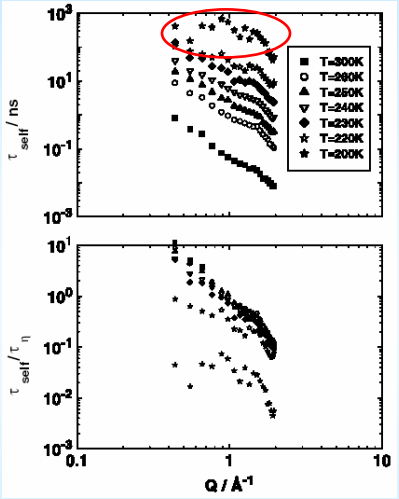
b) **Homogeneous**: Sublinear diffusion in time, $\langle r^2(t) \rangle \propto t^{\beta}$:

$$S(Q,t) = \exp\left(-Q^2 \left\langle r^2(t) \right\rangle / 6\right) \propto \exp\left[-Q^2 (Dt)^{\beta}\right]$$

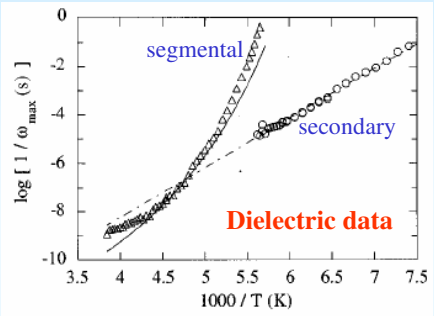
$$\tau \propto Q^{-2/\beta}$$

Colmenero, et al., **J.Phys.Con.Matter 11,** A363 (1999).

Polybutadiene (PB): Split of Segmental and Secondary Relaxations



Q dependence of τ_{self} change sharply when T approaches ~200 K. Also scaling with the viscosity time scale τ_η fails.



This behavior is ascribed to the split of segmental and secondary (local) relaxations.

S. Kahle, et al. **Appl.Phys. A 74**, S371 (2002)

Coherent Scattering

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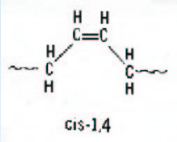
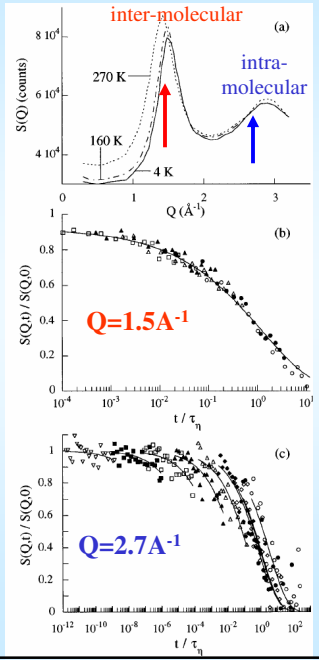
Polybutadiene



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

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

A. Arbe, et al. **PRE 54**, 3853 (1996).



Instruments: Back-Scattering Spectrometer HFBS

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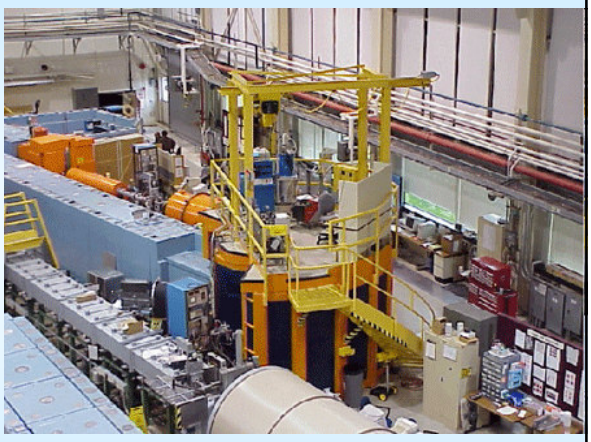
Wavelength	6.271 Å
Neutron Energy	2.08meV
Neutron Flux at Sample	3 x 10^5 n cm^{-2} s^{-1}
Energy range	± 36 μeV
Energy resolution at ± 36 μeV	About 1 μeV
Analyzer Span	165°
Q range	0.25 Å^{-1} – 1.75 Å^{-1}



Instruments: Back-Scattering Spectrometer HFBS

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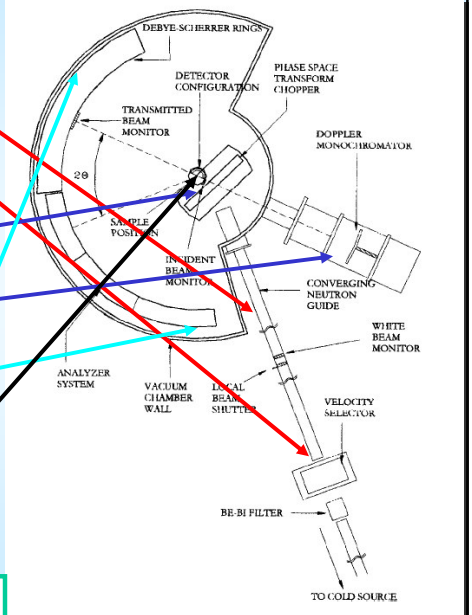
- Neutron Beam Guides.
- Neutron Velocity Selectors (NVS).
- Phase Space Transform (PST) Chopper.
- Monochromator/ Doppler.
- Analyzers.
- Detector Arrays.



Primary Reference: Meyer, A., Dimeo, R. M., Gehring, P. M., & Neumann, D. A. (2003). *Review of Scientific Instruments , 74* (5), 2759-2777.

Instruments: TOF Spectrometer DCS

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✓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.

Instruments: TOF Spectrometer DCS

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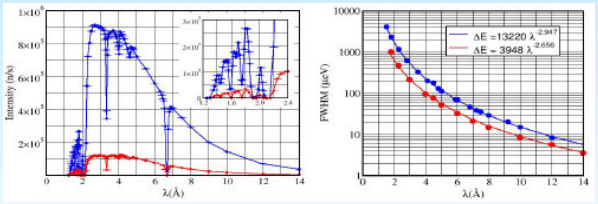
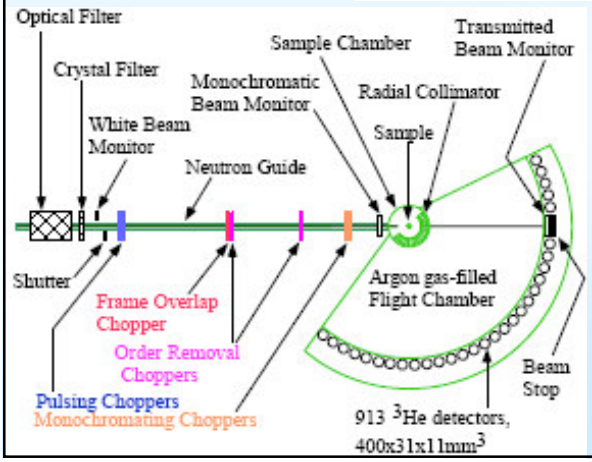
For any experiment try to optimize intensity vs resolution.





Conclusions

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- 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.

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).

❖**QENS spectrum of dry protein** (HFBS data from J.H.Roh, et al. **Biophys.J. 91**, 2573 (2006))**:**

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

-Analyze EISF(Q) (assuming Lorentzian spectrum).

❖**QENS spectrum of water of polypeptide hydration** (DCS data from D. Russo, et al. **J.Phys.Chem. B 109**, 12966 (2005))**:**

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