How Neutrons Help to Study the Dynamics of Soft Materials

Alexei Sokolov

Department of Polymer Science, The University of Akron

Outline

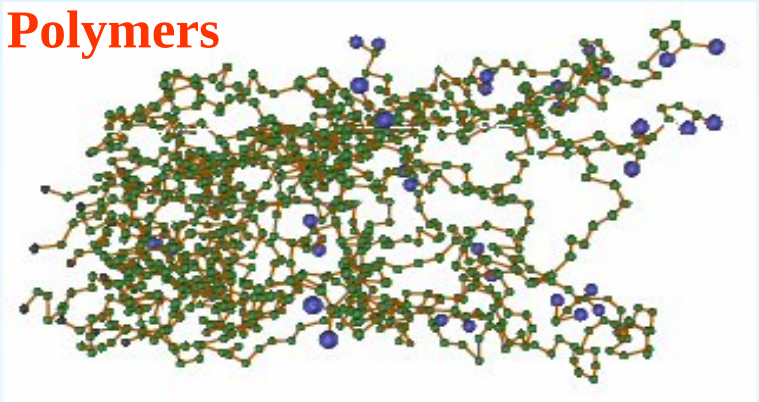
- Soft Matter and Neutron Spectroscopy
- Polymer Dynamics: *Chain, Segmental and Secondary Relaxations*
- Dynamics of Biomolecules: *Dynamic Transition and Structural Relaxation*
- Conclusions

Soft Matter

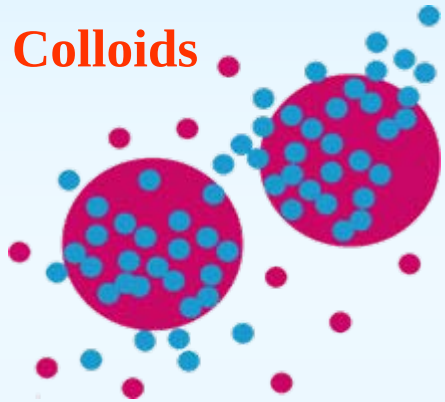
Characteristics of Soft Materials:

-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.

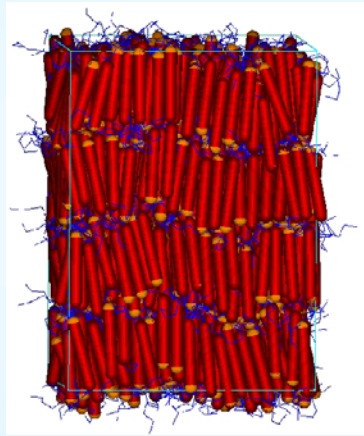
Polymers



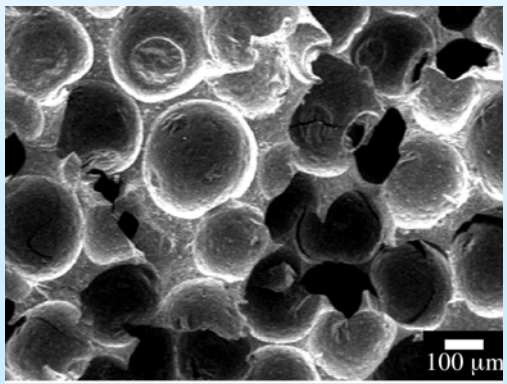
Colloids

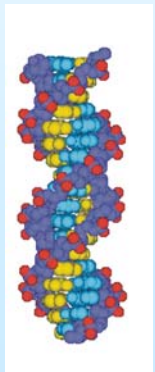


Liquid Crystals

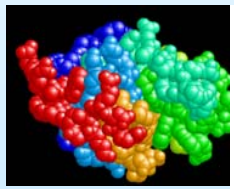


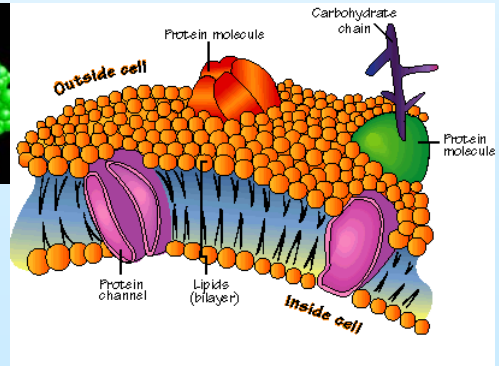
Foams and Gels

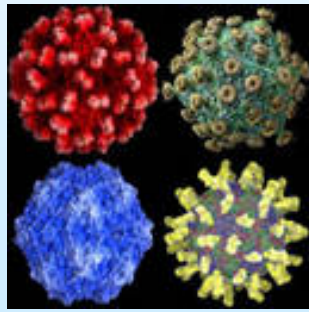




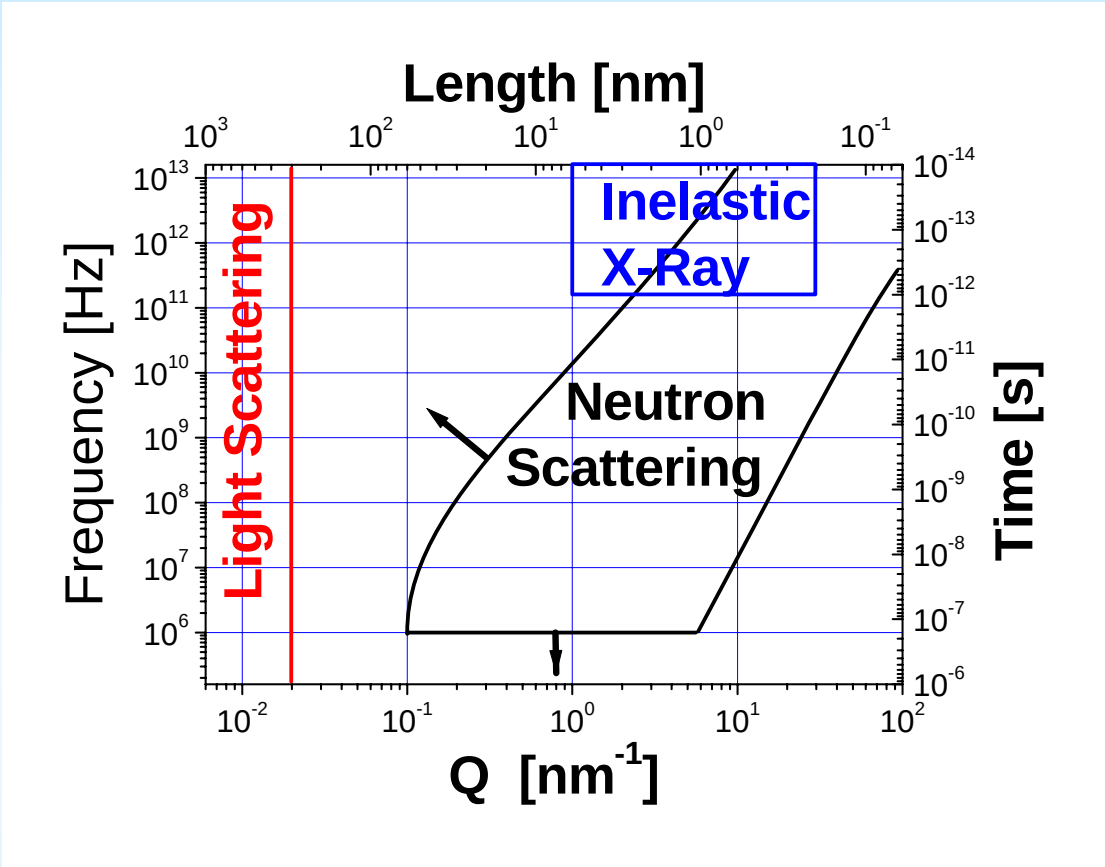
Biological Systems







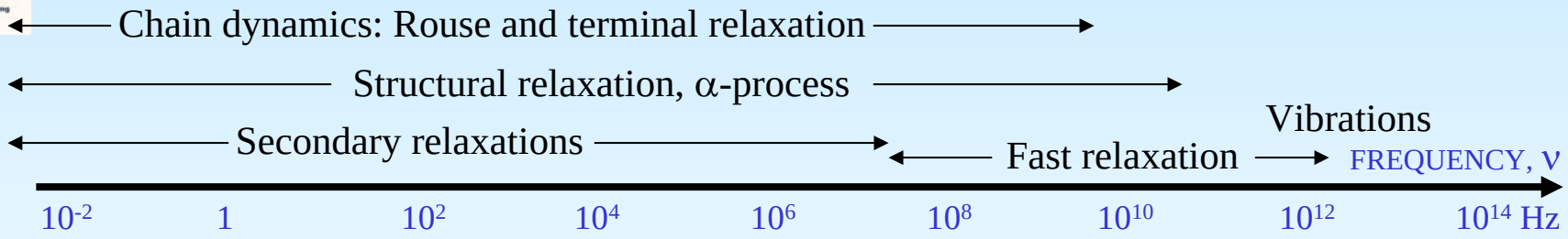
Beauty of Neutron Spectroscopy

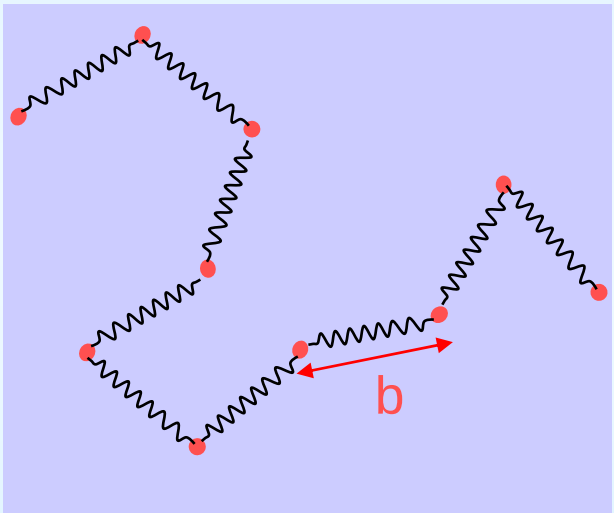


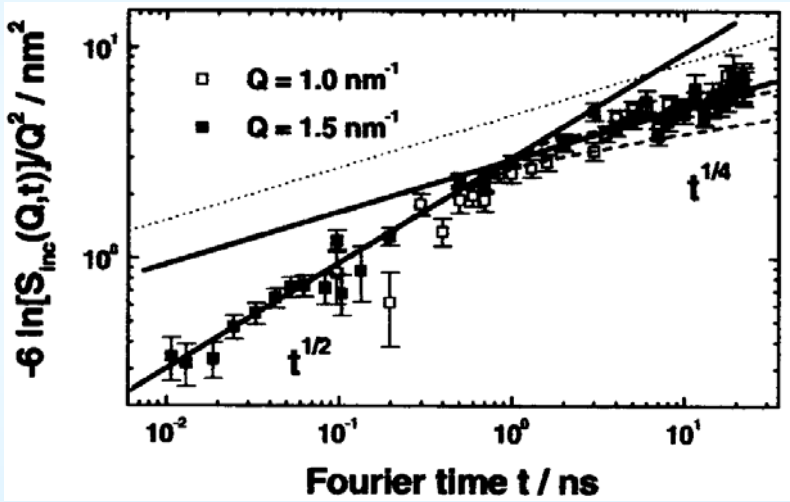
- Measures characteristic times (frequency) and geometry of the motions.
- Covers broad frequency and Q-range in the most important for microscopic dynamics region. *Current X-ray technology cannot compete!*
- Most of the soft materials contain hydrogen atoms, use of D/H contrast.
- Direct comparison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

Example 1: Chain Relaxation in Polymers

Frequency map of polymer dynamics







Bead and spring model is traditional approximation. Rouse and reptation models provide clear quantitative predictions for the chain motion:

✓$\langle x^2 \rangle \propto t^{1/2}$ predicted for Rouse (non-entangled) chain;

✓$\langle x^2 \rangle \propto t^{1/4}$ predicted for reptation (entangled chain).

Predicted behavior has been observed in [Wischnewski, et al. **PRL 90**, 058302 (2003)].

Comparison of two polymers: *PDMS vs PIB*

	PIB	PDMS
C_∞	6.7	6.3
b_K(Å)	18	14

S(Q,t) in PDMS follows well the Rouse predictions up to rather high Q~0.4A^{-1}, while strong deviations are observed in PIB already at Q~0.15A^{-1} [Arbe, et al. **Macromol. 34**, 1281 (2001)].

The deviation at higher Q appears because of the probed length becomes smaller than $\mathbf{b_K}$. In that case the observed difference between PDMS and PIB reflects a significant difference in the length of their $\mathbf{b_K}$.

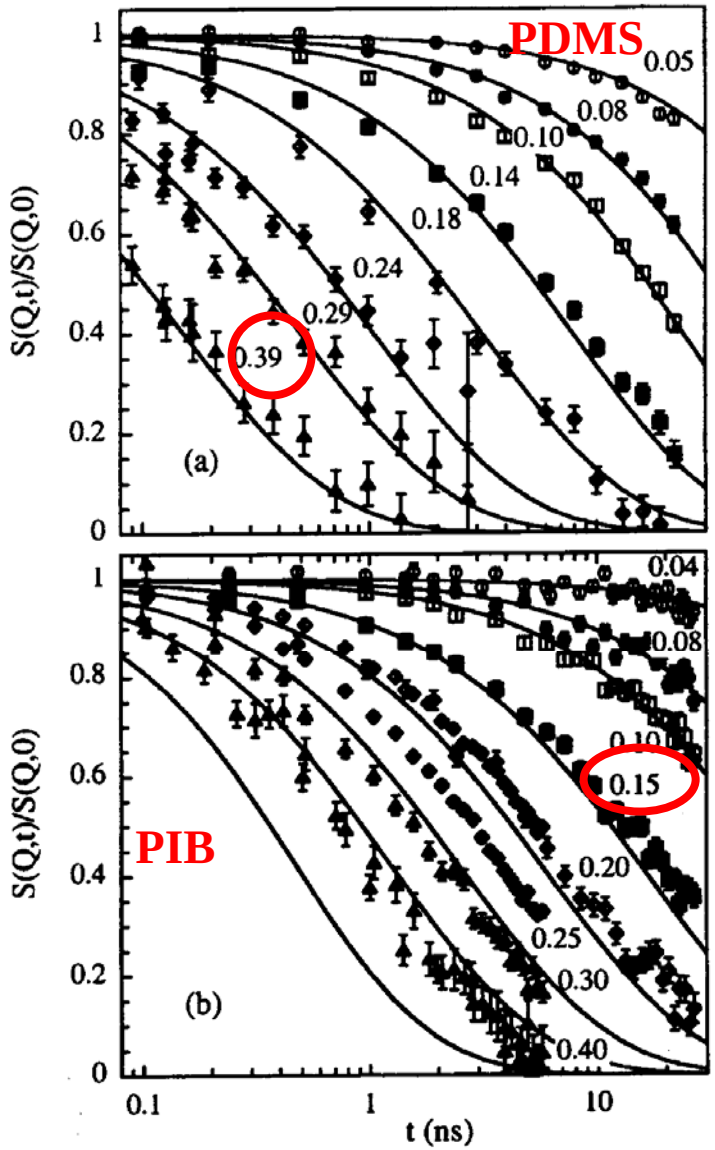
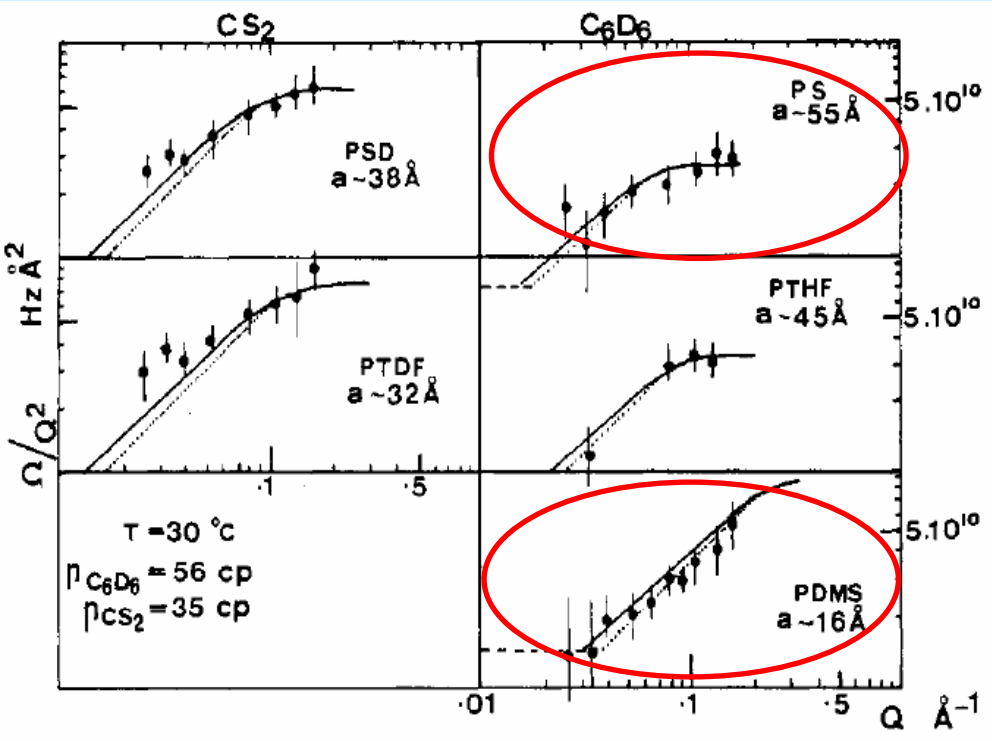
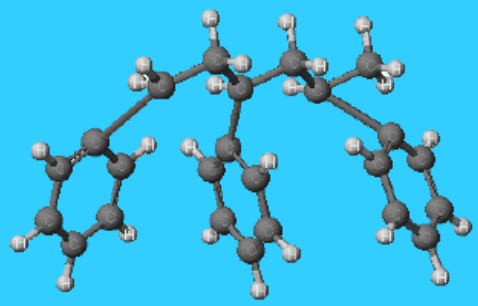


Figure 5. Chain dynamic structure factor of (a) PDMS at 373 K and (b) PIB at 417 K measured in the melt. Each symbol corresponds to the same or very close values of *Q* for both polymers, which are indicated in the figures. Solid lines show the Rouse prediction.

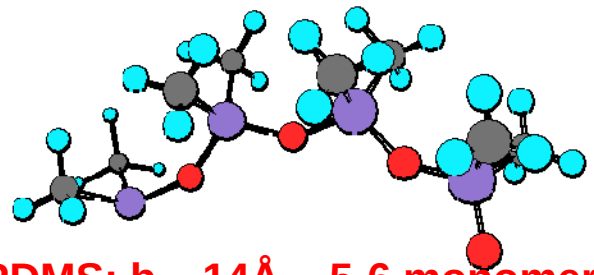
Polymers in θ–Solution

[Nicolson, et al. *Macrom.* 1981]





PS: b_K~20Å, ~8-9 monomers



PDMS: b_K~14Å, ~5-6 monomers

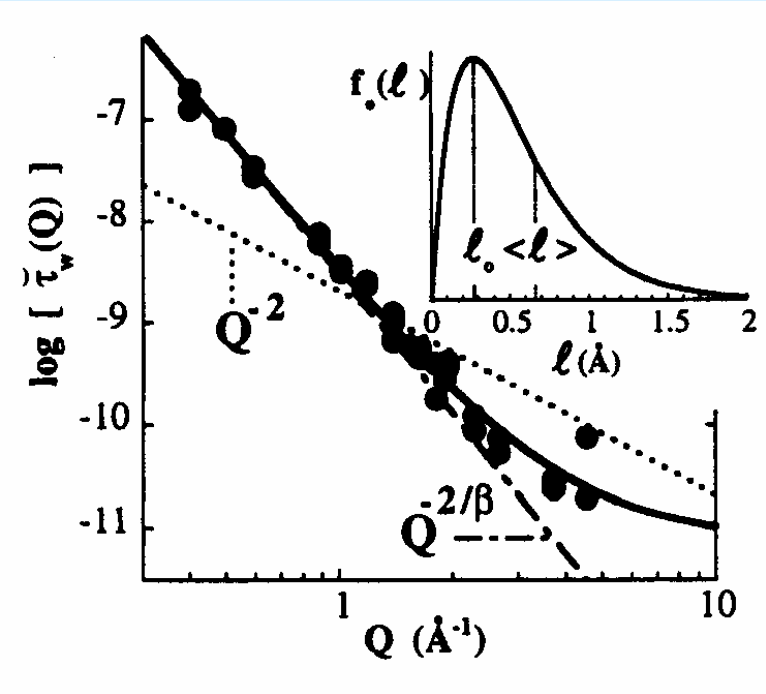
Neutron spectroscopy provides estimates of the characteristic length of the moving beads. Analysis of the chain dynamics in solution reveals:

✓PDMS **b_K**~16A, ~6-7 monomers in good agreement with expectations

✓PS **b_K**~55A, ~50 monomers, significantly large than expected values

These results emphasize deficiency of our understanding of chain dynamics

Example 2: Segmental and Secondary Relaxations



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:

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

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

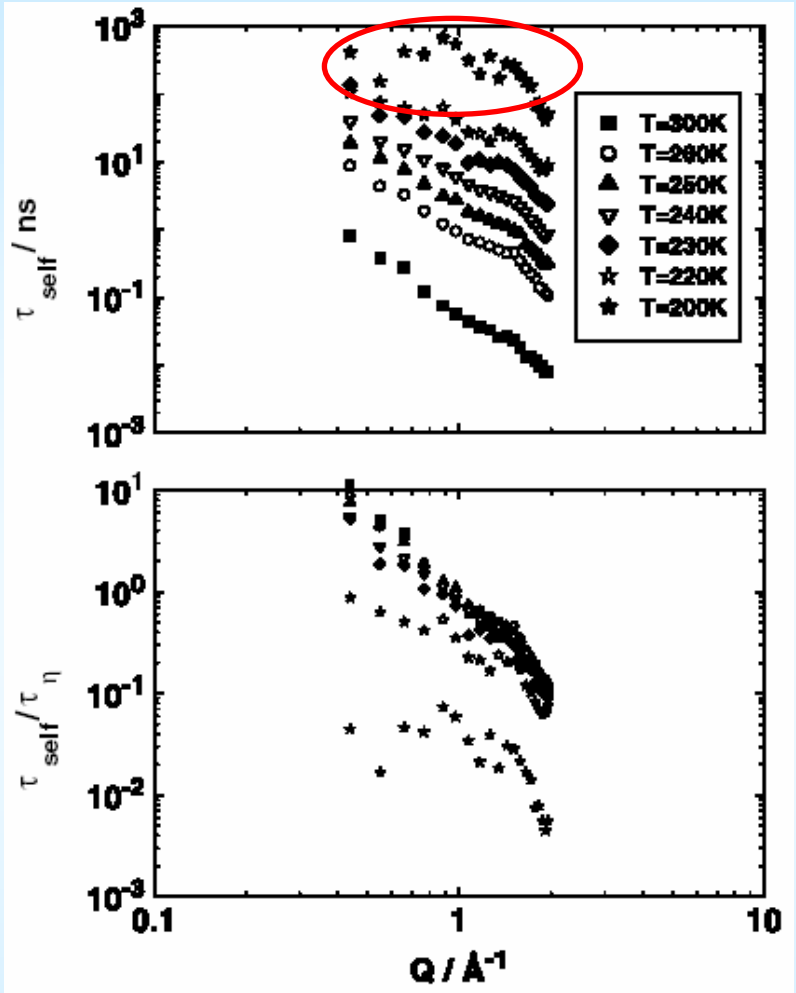
b) **Homogeneous**: Sublinear diffusion in time, $\langle r^2(t) \rangle \propto t^{\beta}$:

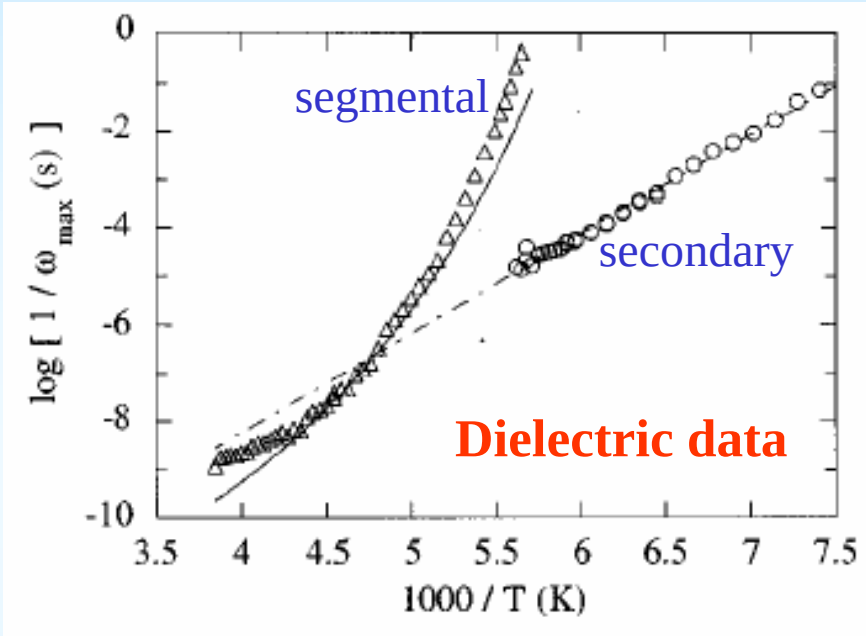
$$S(Q,t) = \exp\left(-Q^2 \left\langle r^2(t) \right\rangle / 6\right) \propto \exp\left[-Q^2 (Dt)^{\beta}\right]$$

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

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

Polybutadiene (PB): Split of Segmental and Secondary Relaxations





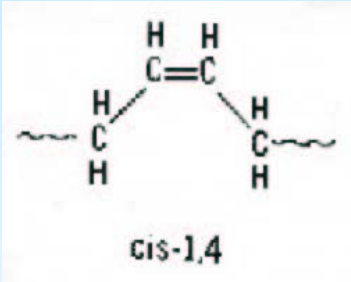
This behavior is ascribed to the split of segmental and secondary (local) relaxations.

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

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

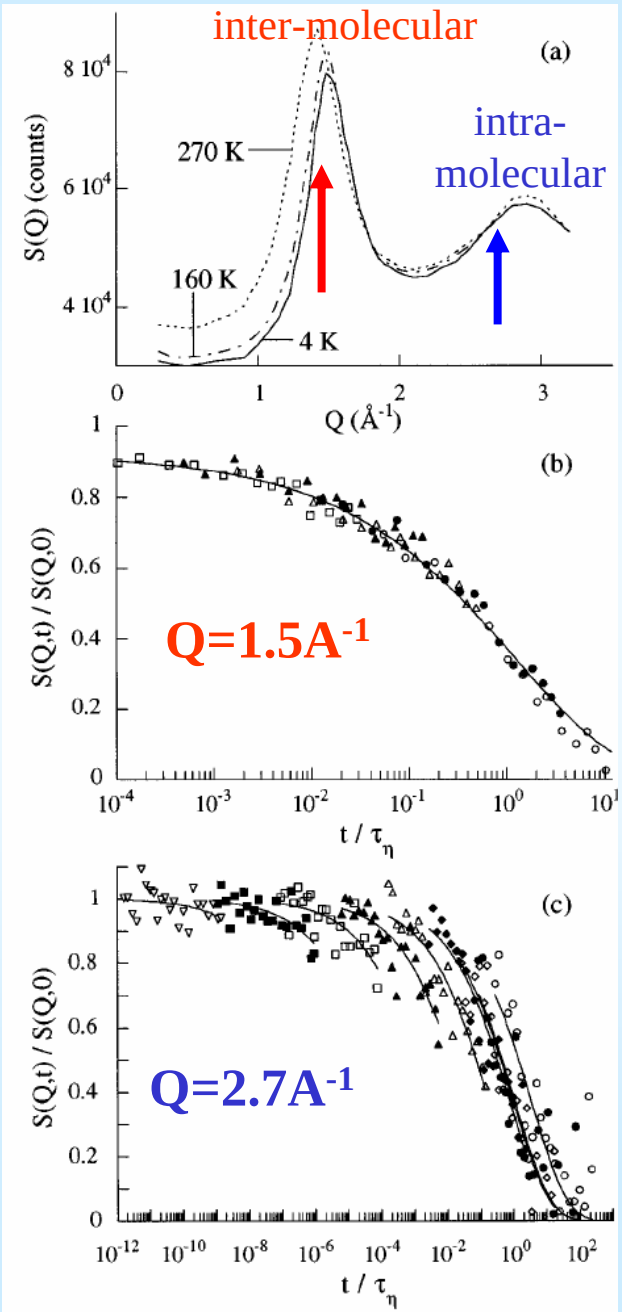
Segmental vs Secondary Relaxations: Coherent Scattering

Polybutadiene



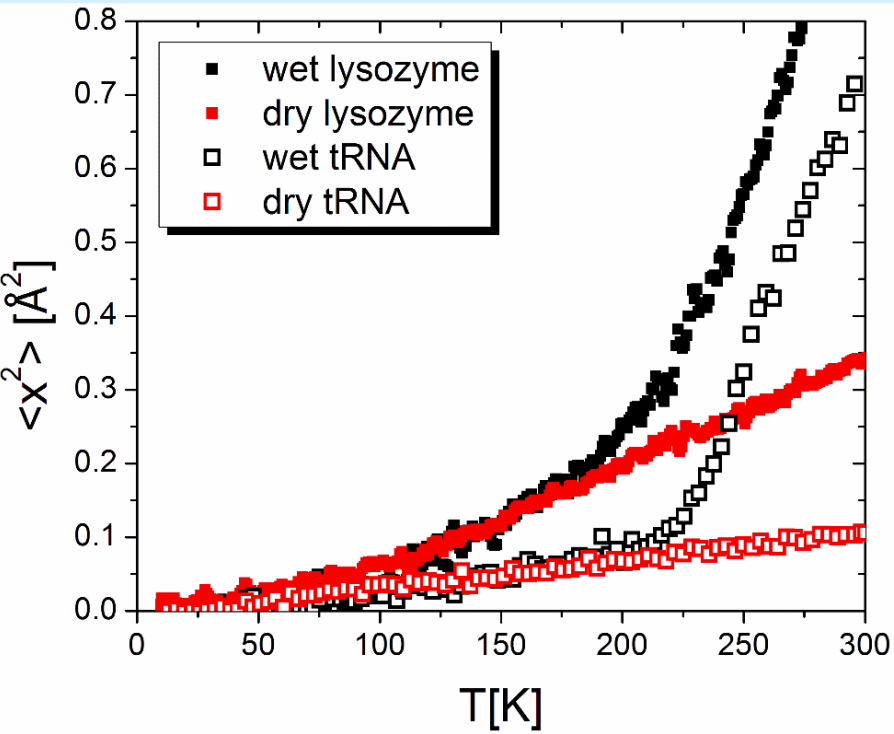
NSE data measured at different T for deuterated PB scaled with the viscosity time scale τ_η:
-Master curve for the data measured at Q~1.5A^{-1};
-No master curve for the data at Q~2.7A^{-1}.

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).

Example 3: Dynamic Transition in Biomolecules

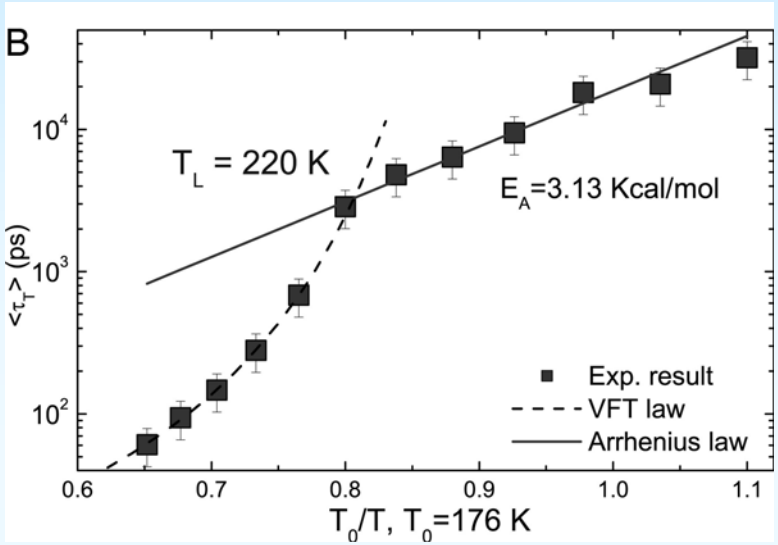


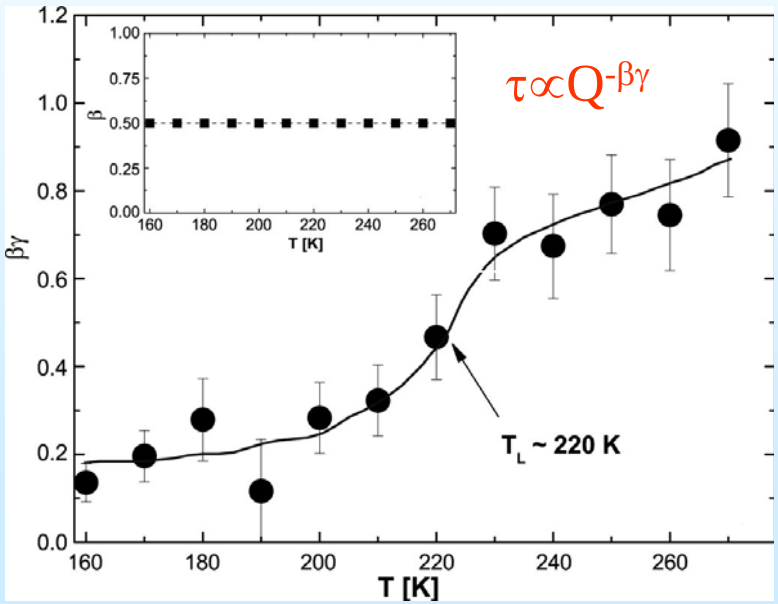
Dynamic transition appears in all hydrated proteins, DNA and RNA around the same T_D~200-230K and is not observed in dry biomolecules.

- Dynamic crossover *a la MCT* [Doster, et al., **Nature 337,** 754 (1989)]
- Sudden change of "effective" elasticity of the protein [Zaccai, **Science 288,** 1604 (2000)]
- Protein structural relaxation enters the experimental frequency range [Daniel, et al., **Biophys. J. 77,** 2184 (1999)]
- Activation of some side group motions, e.g. methyl groups [Lee and Wand, **Nature 411,** 501 (2001)]
- Fragile-to-Strong crossover in dynamics of water of hydration [Chen, et al., **PNAS 103**, 9012 (2006)]

Caliskan, et al. **JACS 128,** 32 (2006)

Fragile-to-Strong Crossover in Water of Hydration





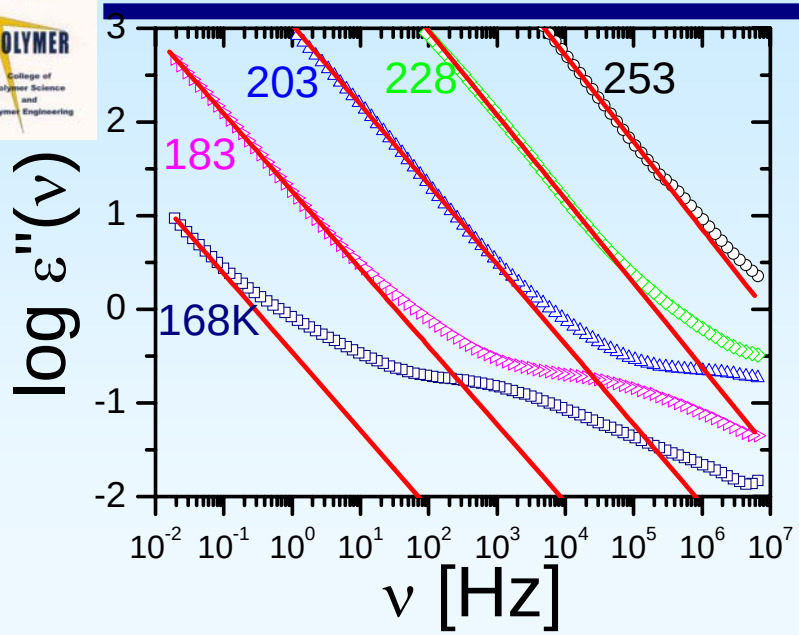
Using H/D contrast, Chen and co-workers analyzed dynamics of water of protein's hydration and observed sharp cusp-like change in the temperature dependence of the relaxation time at T~220K.

The change is ascribed to fragile-to-strong crossover (FSC) in dynamics of water. A connection between the protein's dynamic transition and the FSC in water of hydration is suggested.

Strong change in the Q-dependence of τ has been observed at the same T:
-subdiffusive regime $\tau \propto Q^{-1}$ at high T;
-essentially local motion $\tau \propto Q^{-0.2}$ at low T.

S.H.Chen, et al., **PNAS 103**, 9012(2006).

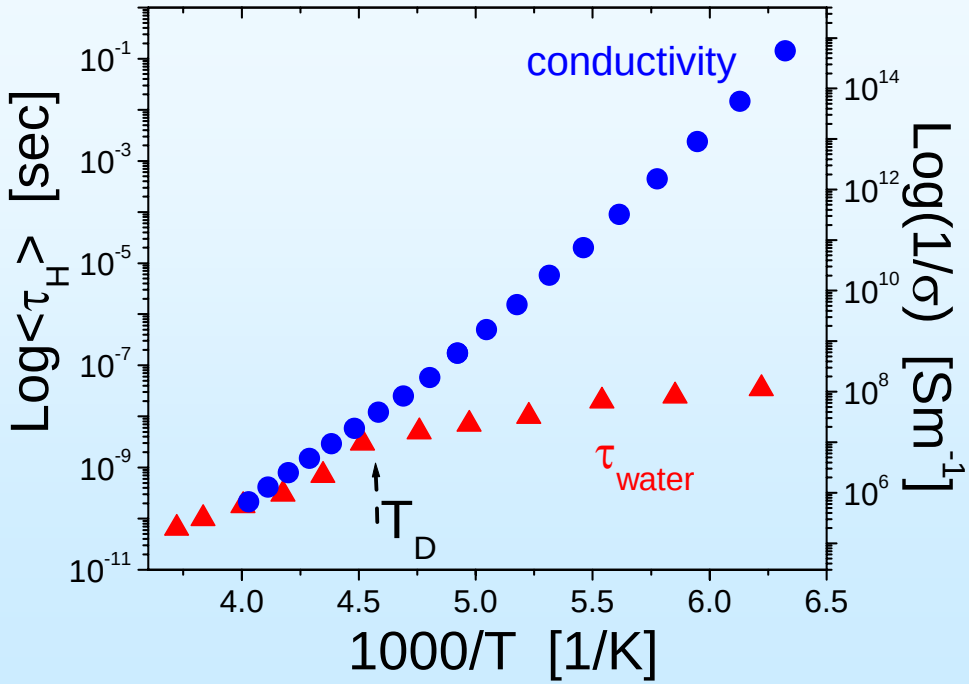
Conductivity in Hydrated Lysozyme Powder



Using dielectric spectroscopy we measured conductivity in hydrated lysozyme powder.

According to DSE-relationship:

$$\sigma \propto \frac{D}{T} \propto \frac{1}{\tau T}$$

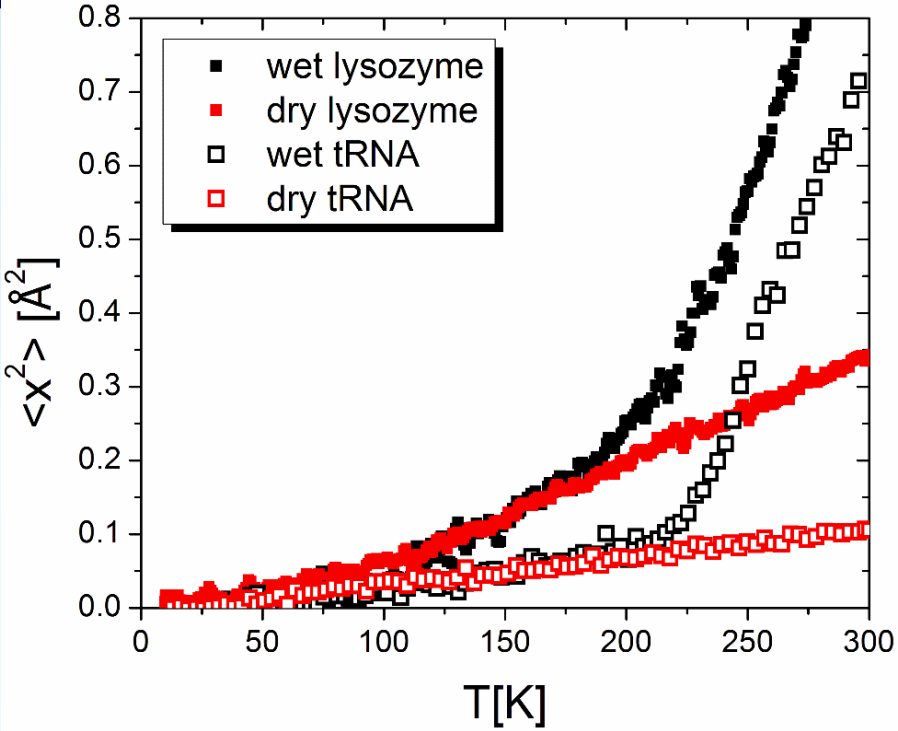


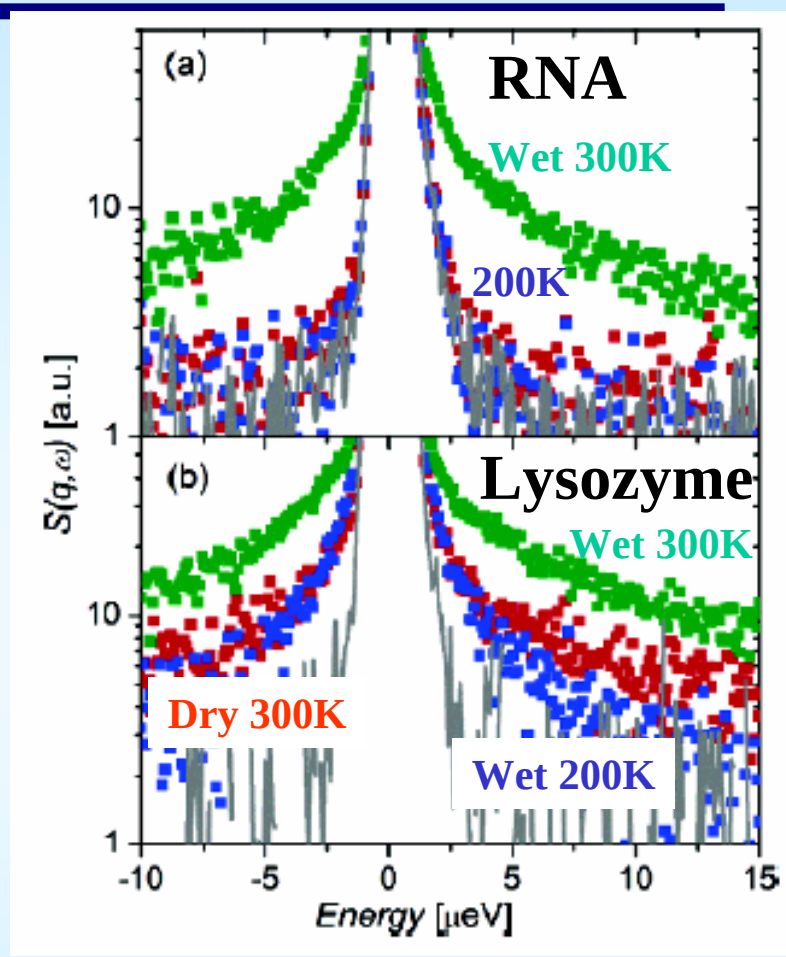
Inverse conductivity shows smooth temperature variations around T~220-200K.

The results suggest no cusp-like behavior in the structural relaxation of hydration water.

The observed in neutron scattering behavior can be ascribed to split of the α- and β- processes.

Additional Relaxation Process





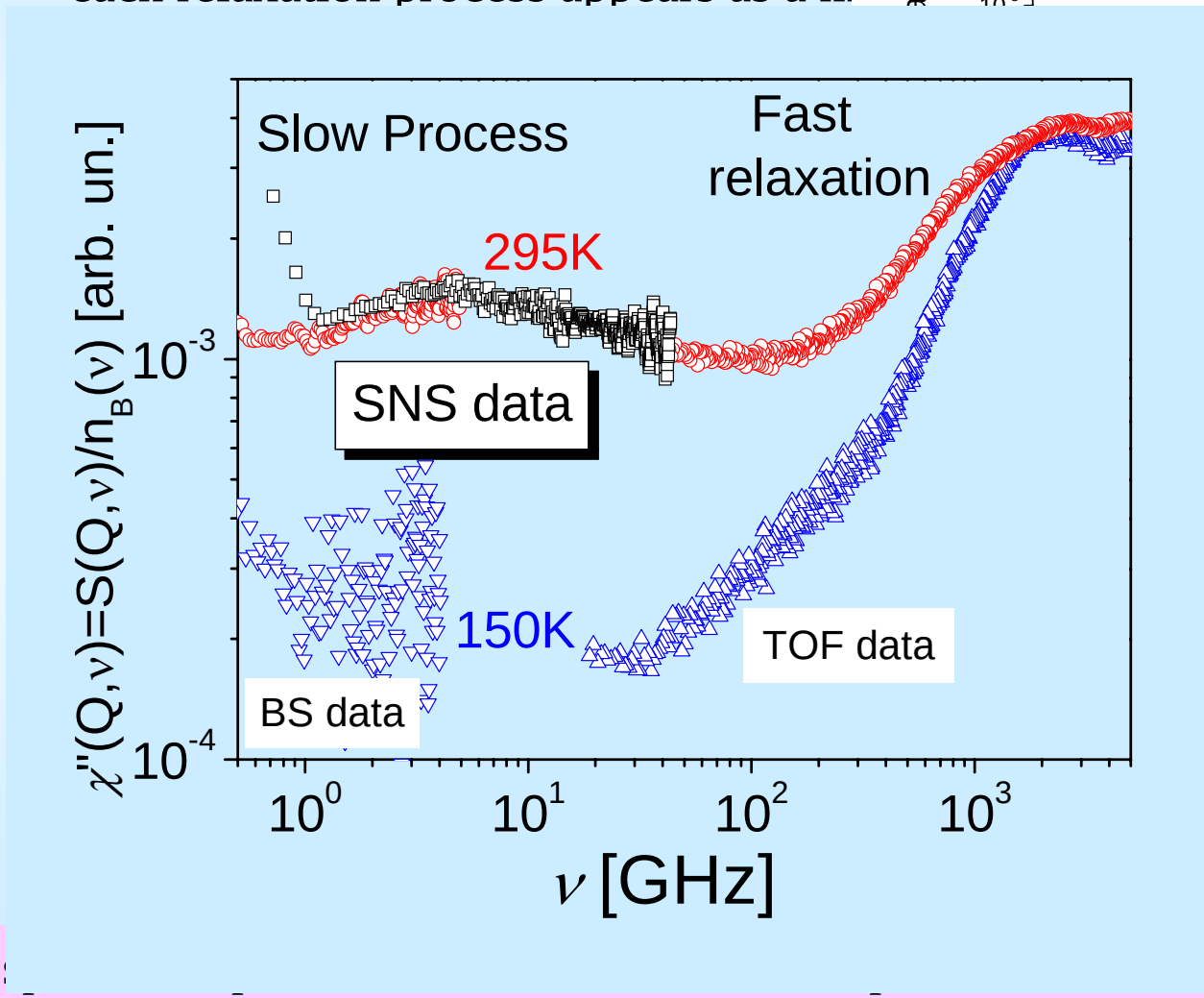
Hydrated proteins, RNA and DNA exhibit the dynamic transition around the same T. Thus chemical and 3-D structure of the biological molecules does not affect significantly the dynamic transition.

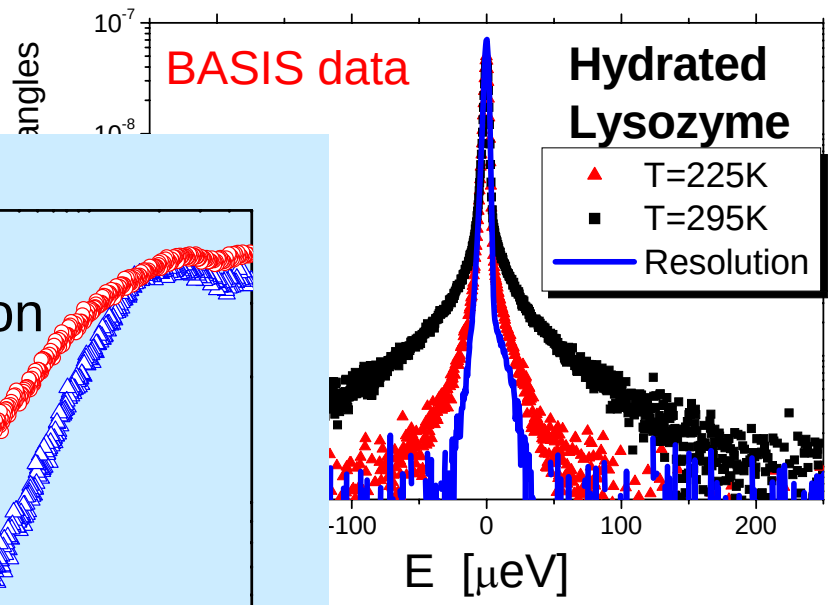
Caliskan, et al. **JACS 128,** 32 (2006)

Strong relaxation process appears in the spectra of hydrated biomolecules above T_D.

Susceptibility presentation

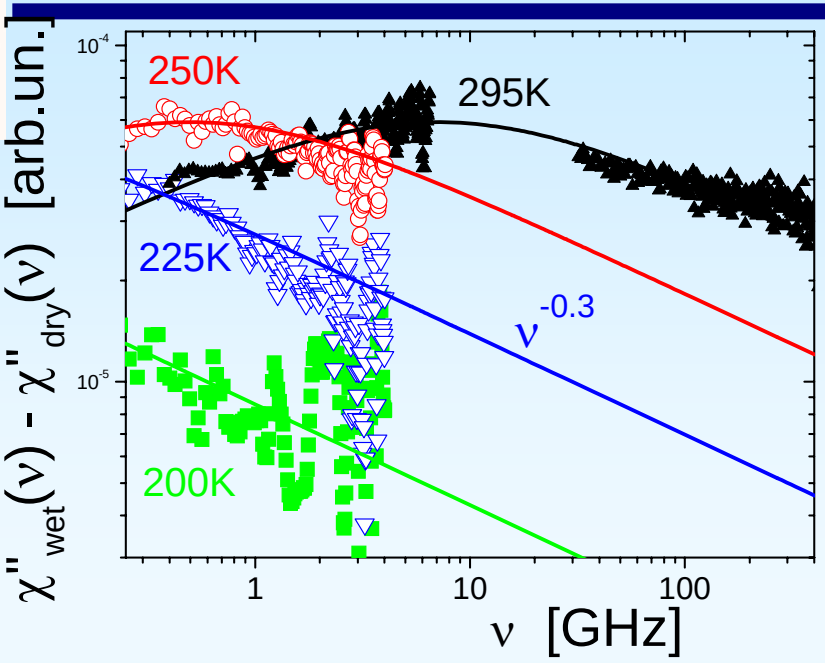
Susceptibility presentation of scattering
- can be directly compared to ε”(ν), G”(
- each relaxation process appears as a m



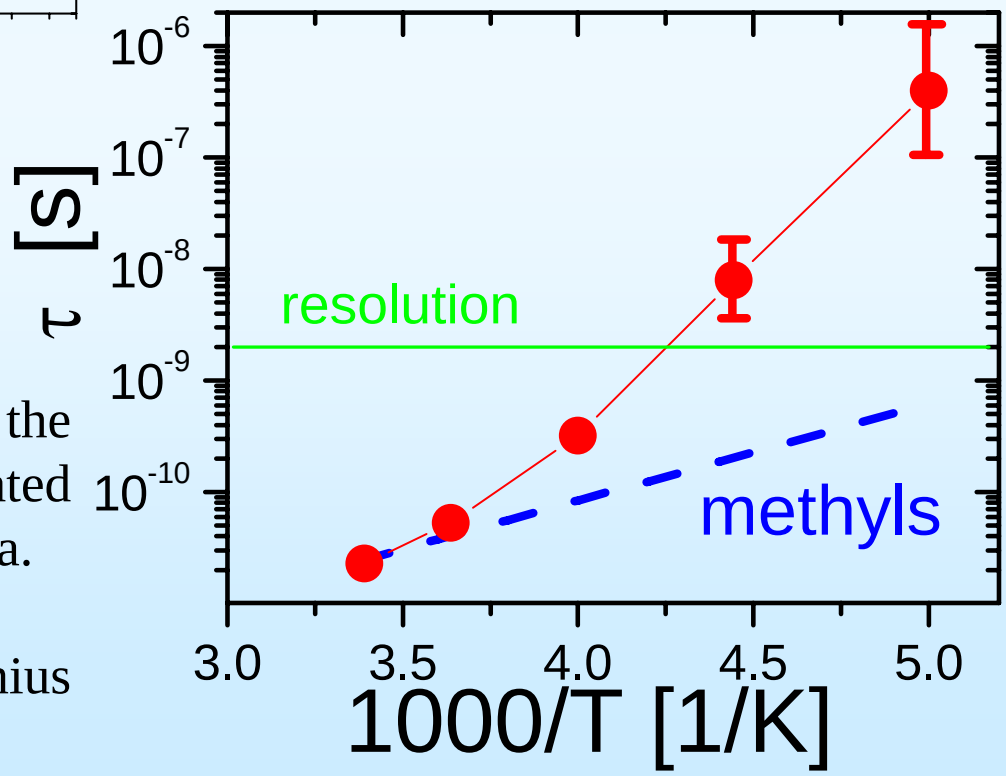


The s n processes are strongly stretched (can not be described by a single exponential relaxation).

Structural Relaxation Time in Lysozyme



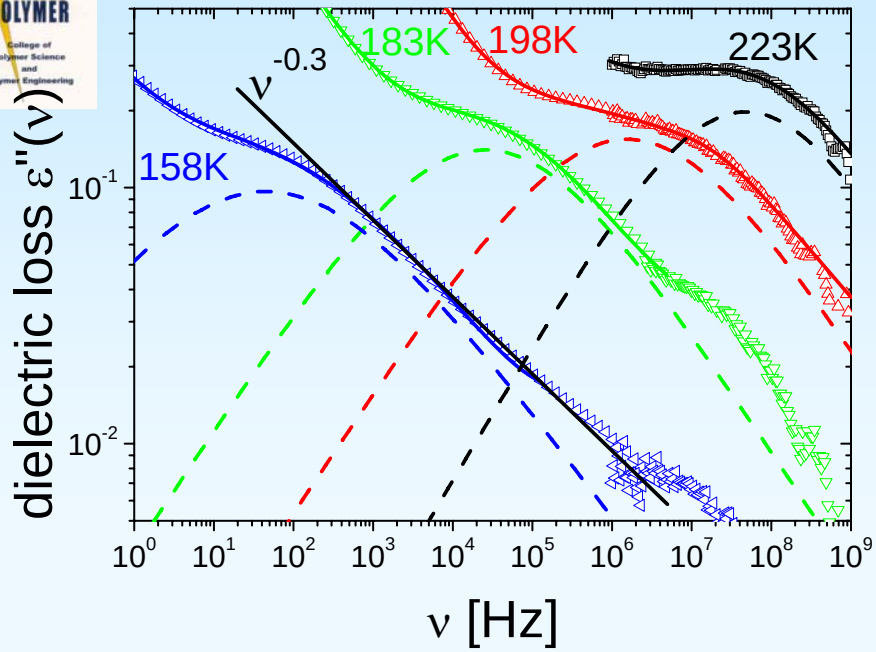
QES spectra of wet protein at different temperatures were analyzed in the susceptibility presentation *after correction for the methyl group dynamics*.



Characteristic relaxation time of the protein's structural relaxation estimated from the corrected susceptibility spectra.

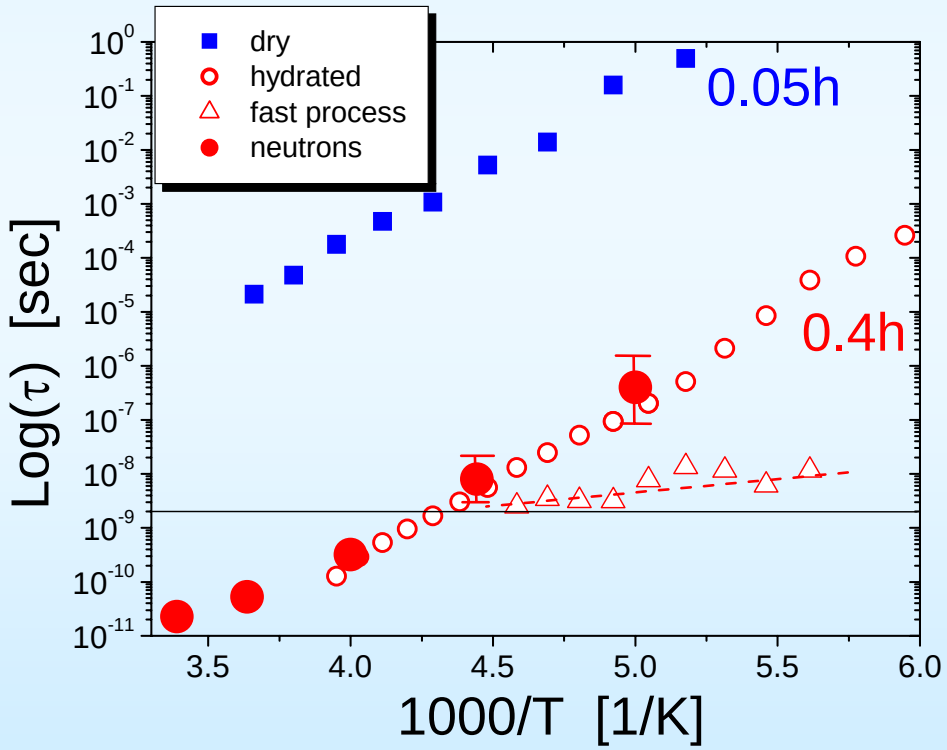
It shows slightly non-Arrhenius temperature dependence.

Dielectric Relaxation Spectra



Dielectric relaxation spectra of hydrated lysozyme show relaxation process with stretching similar to the one observed in neutron scattering.

Faster process splits from the main process at lower T.

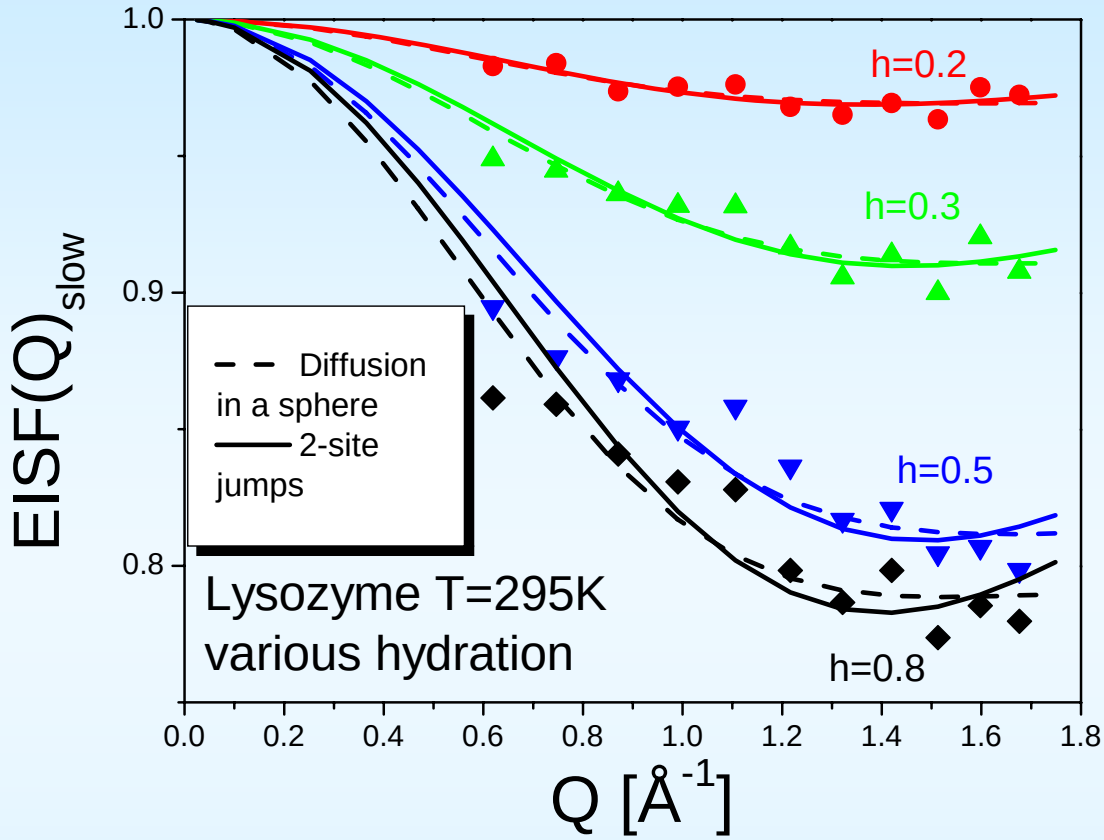


We ascribe the main process to the structural relaxation of proteins. The process exhibits smooth temperature variations at T~200-220K.

The faster process seems to be related to the process observed for water of hydration by Chen, et al.

The sharp rise in $\langle r^2 \rangle$ is caused by the protein's structural relaxation that enters the resolution window of the spectrometer. Proteins exhibit no particular transition.

Example 4: Structural Relaxation in Proteins

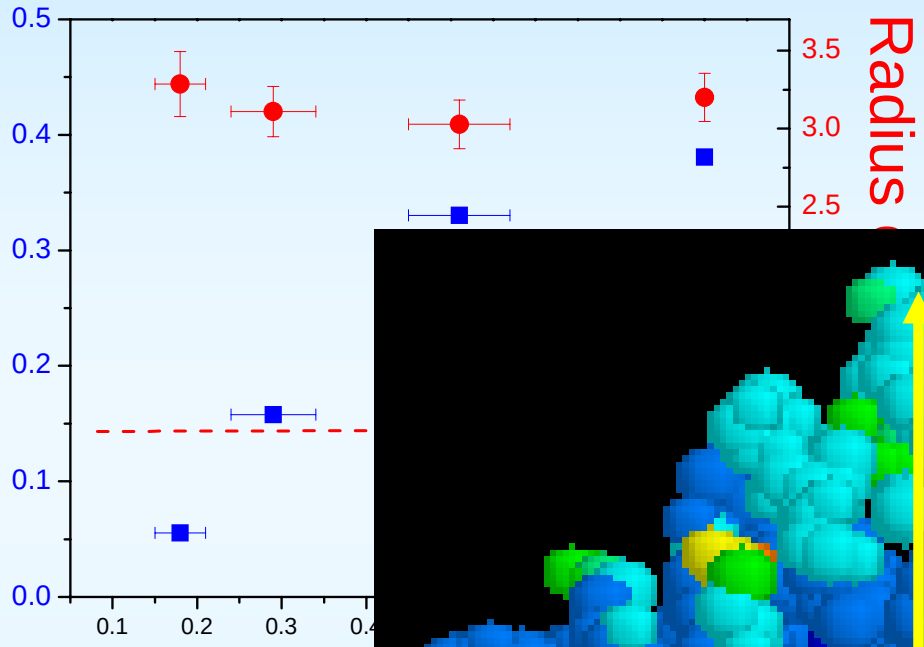


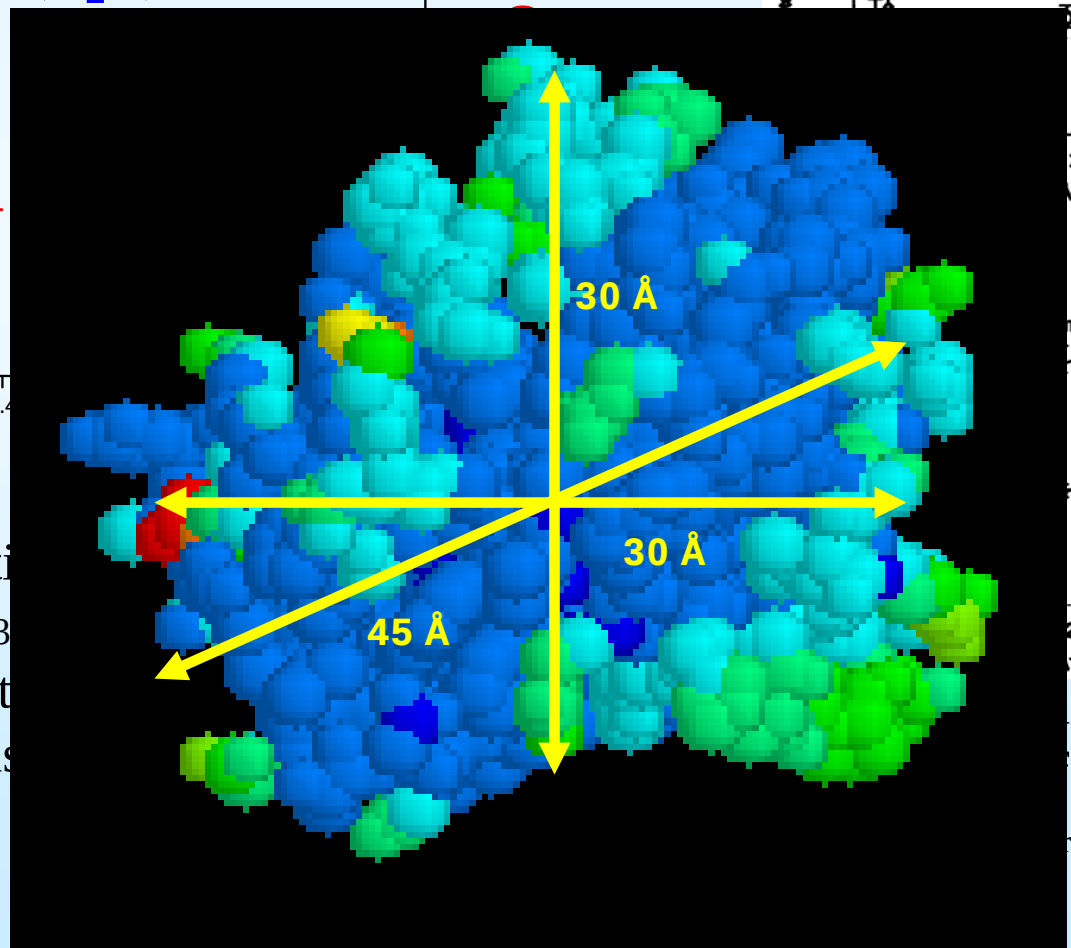
We calculate EISF(Q) at various hydrations after corrections for the methyl group contribution:

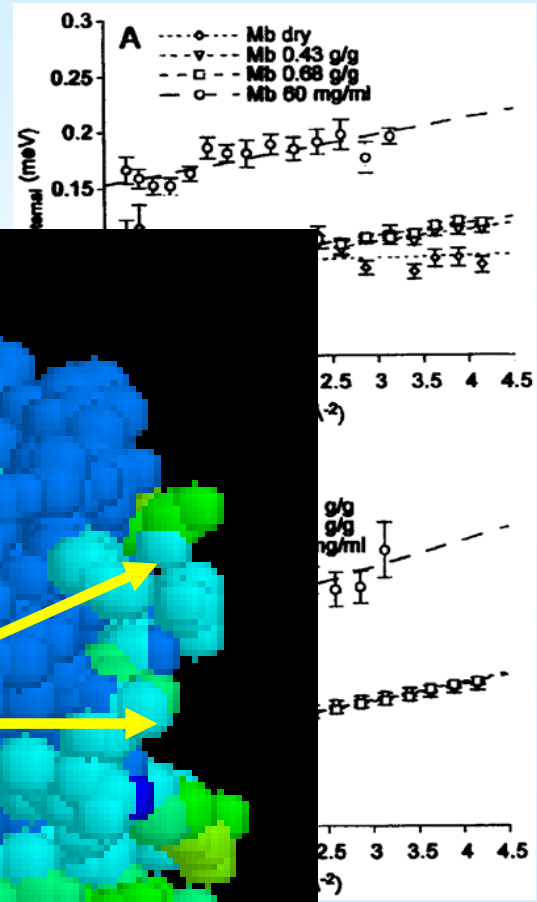
$$EISF(Q,h)_{slow}=EISF(Q,h)_{total}-EISF(Q,dry)+1$$

The fit of $EISF(Q,h)_{slow}$ has been done by two models: two-site jumps and diffusion in a sphere.

Although the structural relaxation in proteins seems to be similar to segmental relaxation in polymers, there is an important difference in the Q-dependence.







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[Roh, et al., **PRL 95**, 03

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rez, et al. **Biophys.J. 77**,

Conclusions

- Neutron Spectroscopy is well positioned for analysis of dynamics of Soft Materials.

- It already helped to unravel many microscopic details of molecular motions in polymers, glass forming and some biological systems. However, it faces many more challenges, especially in application to Life Sciences.

Acknowledgments

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Gus Carri	Akron U.	Eugene Mamontov	ORNL
Vicky Garcia Sakai	NIST		
Joseph Curtis	NIST		

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WHERE DISCOVERIES BEGIN

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