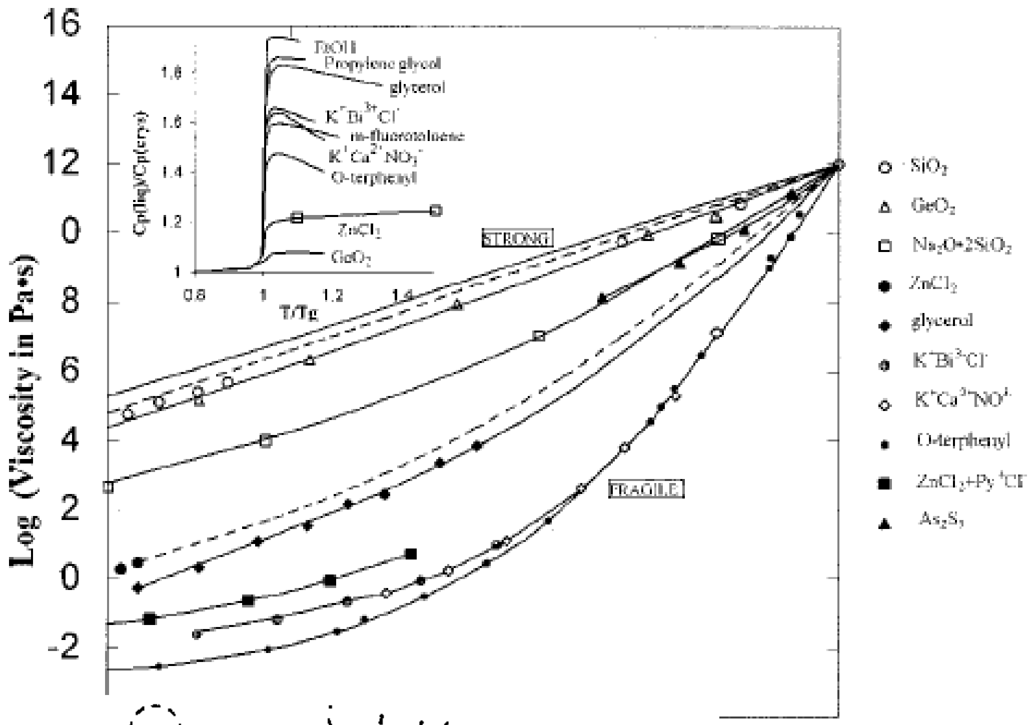
IXS for studies of Collective Dynamics: From Glass-forming Systems to Proteins

Alexei Sokolov

ORNL / UT Knoxville

Glass Transition: The Key Question



Non-Arrhenius temperature dependence of structural relaxation.

Fragility Index

$$m = \left. \frac{\partial \log \tau(T)}{\partial (T_g / T)} \right|_{T=T_g}$$

m characterizes the deviation of temperature dependence from Arrhenius behavior.

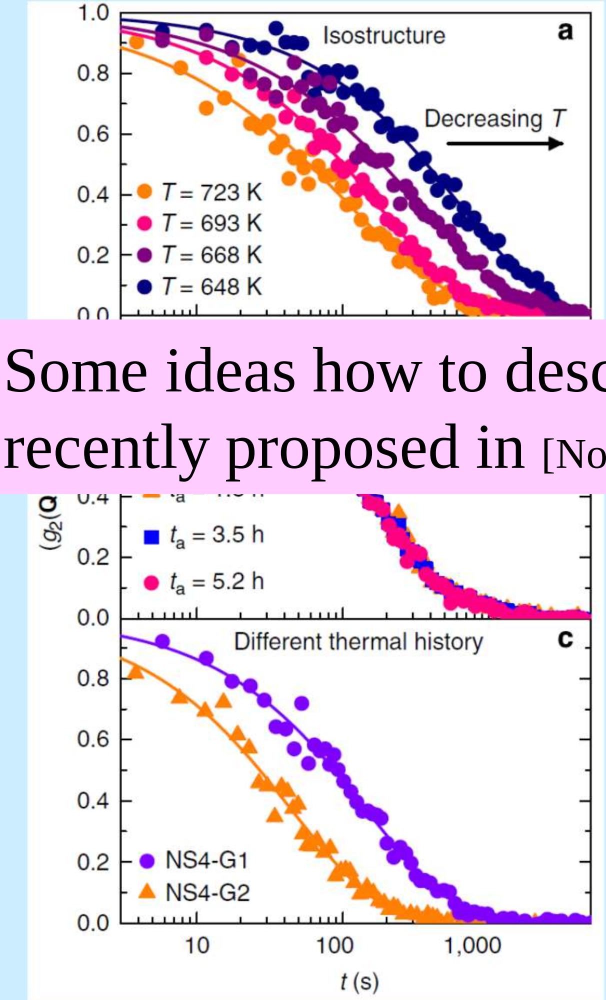
Adam-Gibbs Picture

Traditional view:

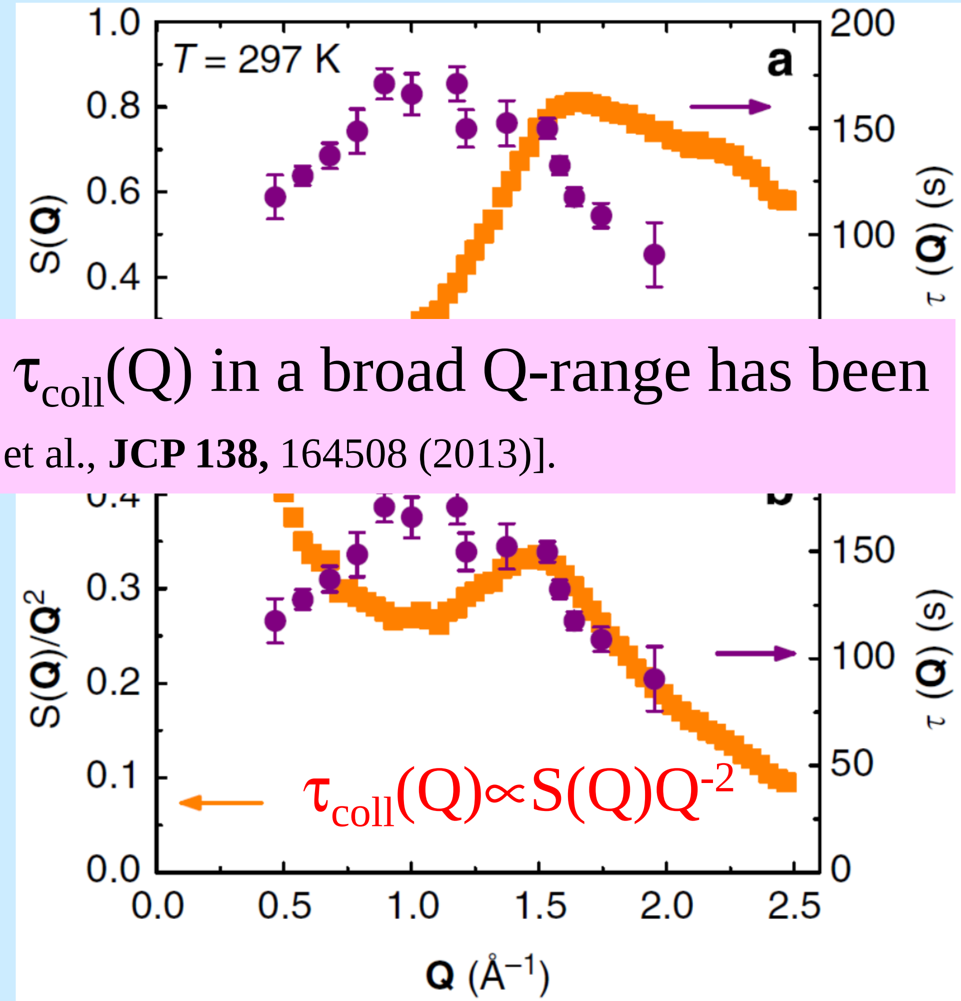
Sharp increase in apparent activation energy is caused by increase in cooperativity.

Implicit assumption: **Fragility ➔ Cooperativity**

The main focus – Slow Dynamics



X-PCS correlation function for sodium silicate glasses.



The studies revealed unexpected Q-dependence for collective $\tau(Q)$.

Some ideas how to describe $\tau_{coll}(Q)$ in a broad Q-range has been recently proposed in [Novikov, et al., **JCP 138,** 164508 (2013)].

X-PCS can measure the slow relaxation (if it doe not burn the sample).

Ruta, et al., **Nat. Comm.** 4939 (2014)

Can IXS help?

Frequency map of polymer dynamics

← Chain dynamics: Rouse and terminal relaxation →

← Structural relaxation, α-process →

← Secondary relaxations →

Vibrations

← Fast relaxation →

FREQUENCY, ν

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

<u>Inelastic X-ray Scattering, *S(Q,ν)*</u>

High-Resolution IXS

<u>Neutron Scattering, *S(Q,ν)*</u>

Spin-Echo

Back-sc.

Time-of-Flight

<u>Mechanical relaxation G*(ν)</u>

<u>Dielectric Spectroscopy, *ε*(ν)*</u>

Quasi-optics,TDS

Traditional dielectric spectroscopy

IR-spectr.

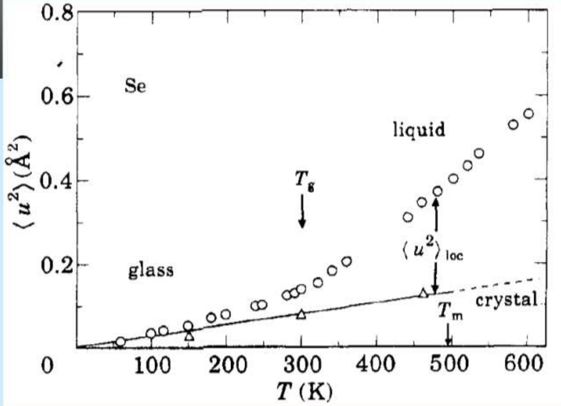
<u>Light Scattering, $I_{ij}(Q,\nu)$</u>

Interferometry

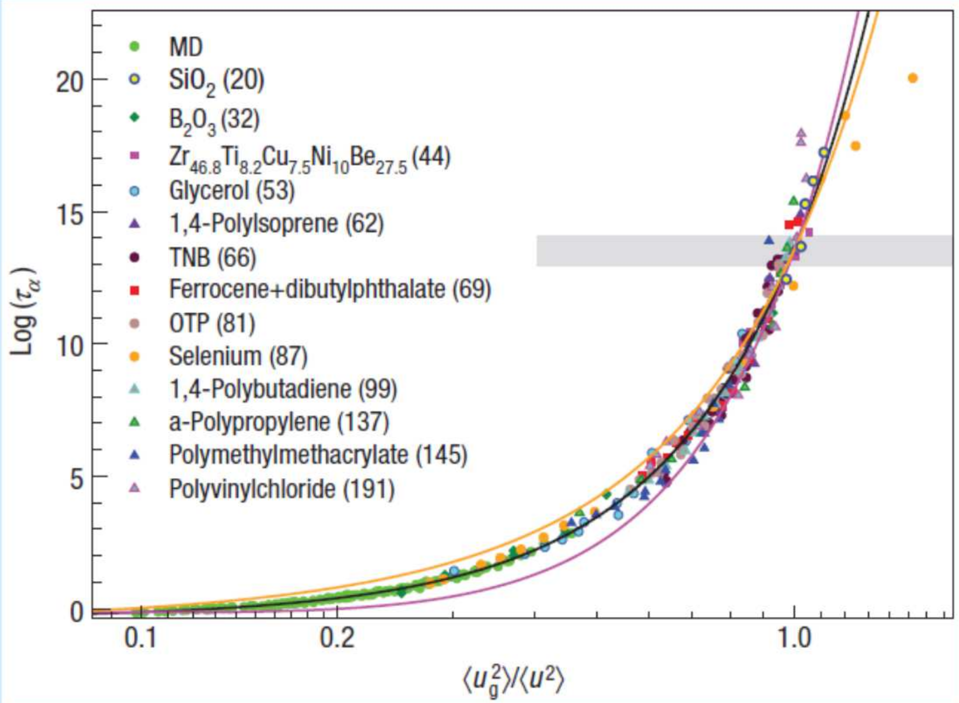
Photon – Correlation Spectroscopy

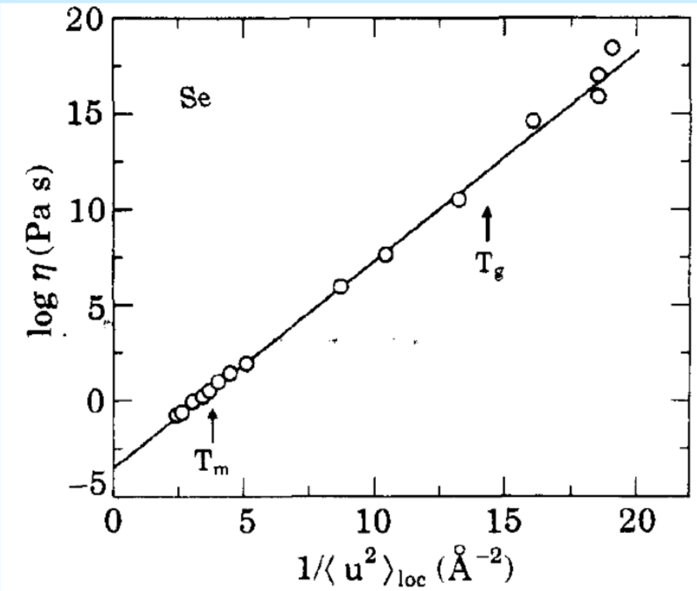
Raman spectroscopy

<u²> on ps-time scale and Fragility



Analysis of mean-squared atomic displacements (MSD), <u^2>, for Se revealed a good correlations between inverse MSD (1/<u^2>) and viscosity [Buchenau, Zorn, **Europhys. Lett. 18**, 523 (1992)]





Recent analysis demonstrated a strong relationship between log(τ) and 1/<u^2> for various kinds of glass-forming systems, from rather 'strong' (SiO_2) to very fragile (polyvinylchloride) [Larini, et al. **Nat.Mat. 4,** 42 (2008)].

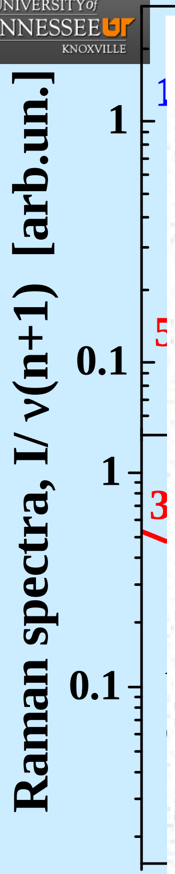
These results suggest a strong connection between the fast and the slow dynamics

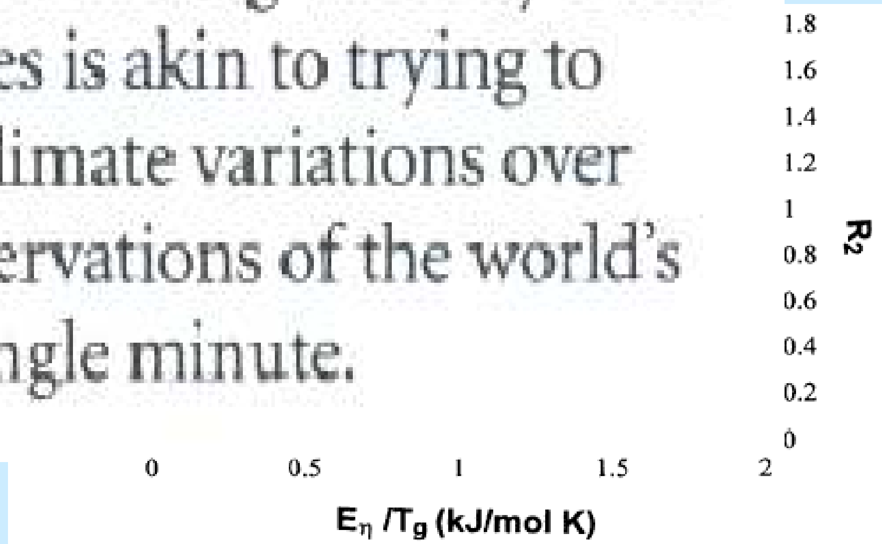
Fragility and Fast Dynamics

Jeppe Dyre recently commented [**Nature Mat. 3**, 749 (2004)]:

enormously. Indeed, the characteristic timescales over which processes in these two regimes occur can easily differ by more than 12 orders of magnitude, with short-timescale processes lasting less than one nanosecond and long-timescale processes occurring over seconds, minutes, hours and longer. Consequently, the task of predicting viscosity from short-time liquid properties is akin to trying to predict the rate of global climate variations over millions of years from observations of the world's weather collected over a single minute.

ow-
ond
two
the
tive
tem





IXS and Neutron Spectroscopy

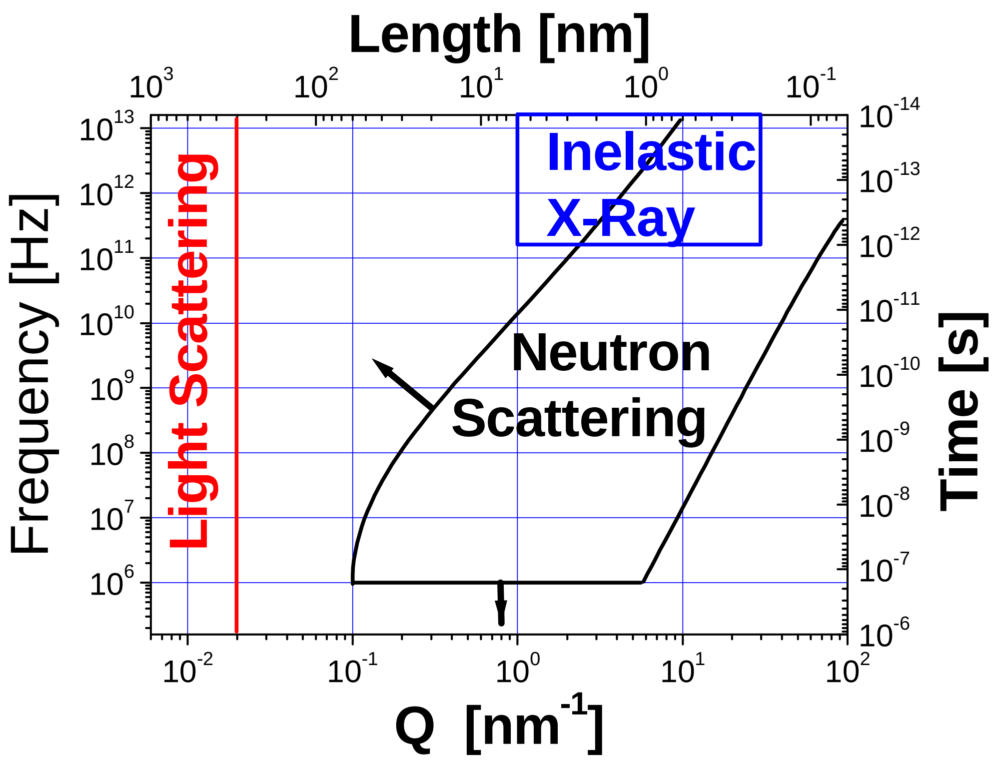


Table 3.1 Scattering lengths and cross section for some common isotopes

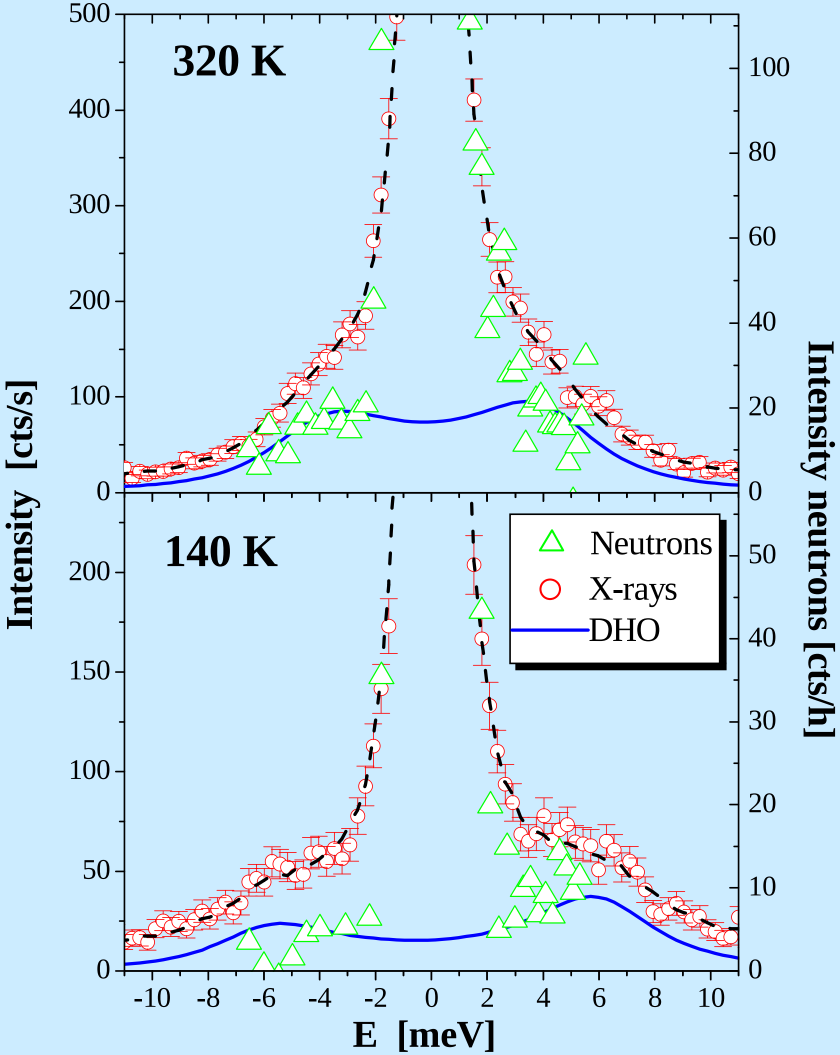
	$b \times 10^{12}$ (cm)	$\sigma_{coh} \times 10^{24}$ (cm^2)	$\sigma_{inc} \times 10^{24}$ (cm^2)	$\sigma_{abs} \times 10^{24}$ (cm^2 at 1.798 Å)
^{1}H	−0.374	1.76	79.7	0.33
^{2}D	0.667	5.59	2	0.0005
^{12}C	0.665	5.55	0	0.003
^{14}N	0.94	11.01	0.5	1.9
^{16}O	0.58	4.23	0	0.0001
^{19}F	0.57	4.02	0	0.0096
$^{ave\,28.06}Si$	0.415	2.16	0	0.17
^{32}S	0.28	1.02	0	0.53
$^{ave\,35.5}Cl$	0.96	11.53	5.3	33.5

Current IXS has several disadvantages relative to neutron scattering, including limited energy range and resolution

Advantage of IXS

A comparison of inelastic X-ray and neutron scattering [Sokolov, et al. **PRE 60**, R2464 (1999)] clearly demonstrates much higher (~10^5) count rate in the case of X-ray.

Brillouin X-ray and neutron scattering in PB



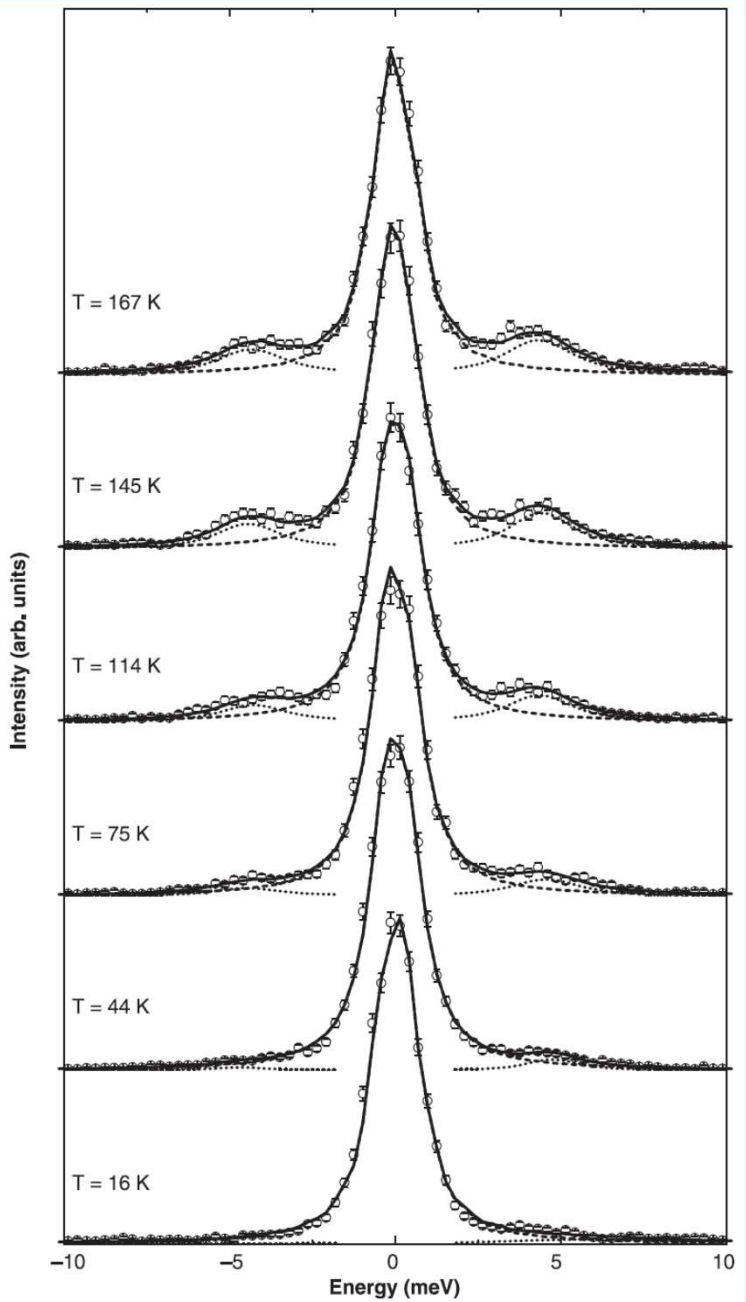
The absolute intensities were scaled at the first maximum Q=1.5A^{-1}.

The comparison demonstrates a reasonable agreement.

Non-ergodicity parameter measured by IXS

IXS provides measure of the non-ergodicity parameter through ratio of integrated intensity of the Brillouin modes, $S_{inel}(Q,T)$, to the elastic scattering $S_{IS}(Q,T)$:

$$f(Q,T) = \frac{1}{1 + S_{inel}(Q,T)/S_{IS}(Q,T)}$$



Scopigno, et al. **Science 302**, 849 (2003)

Non-ergodicity below Tg and Fragility

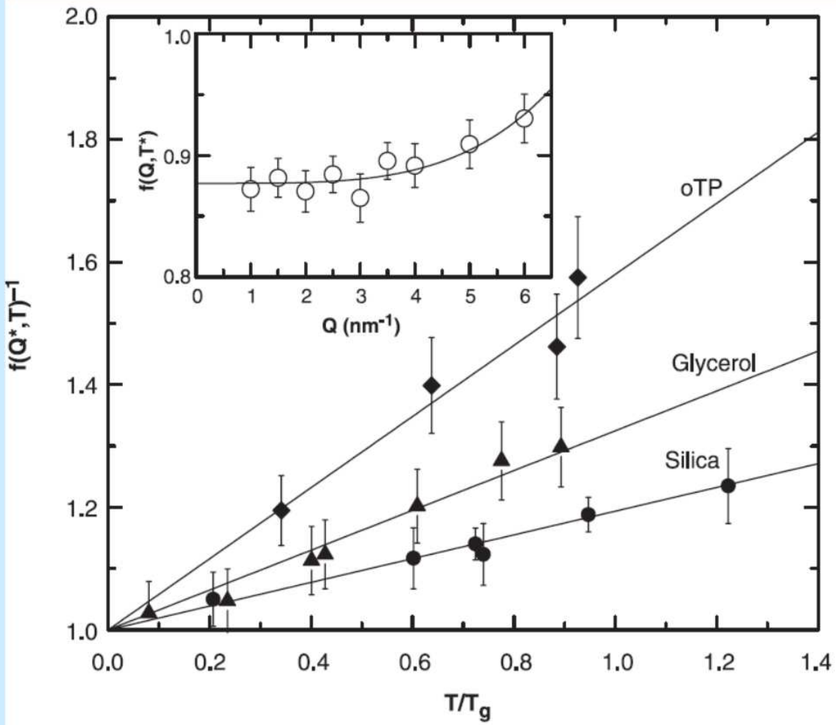
Approximating the ratio by linear temperature dependence the authors of [Scopigno, et al. **Science 302**, 849 (2003)] expressed f(Q,T) at lower Q as:

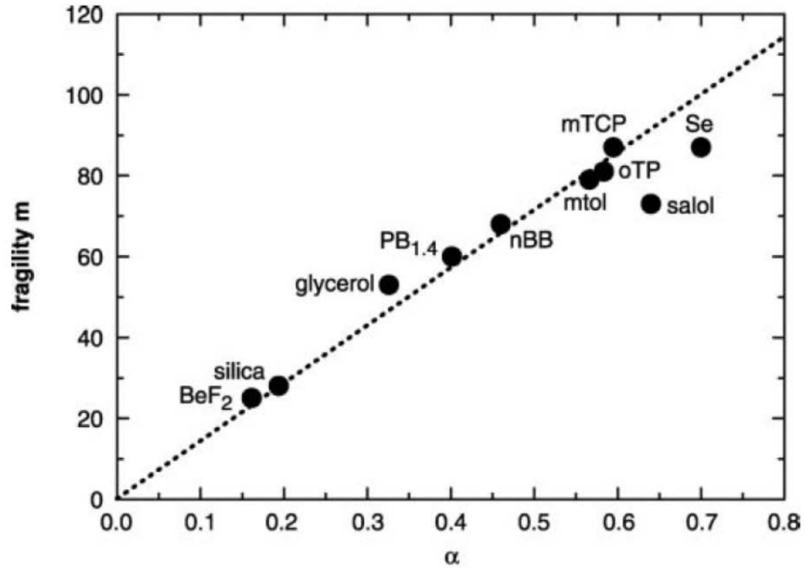
$$f(Q\to 0,T)=\frac{1}{1+\alpha\frac{T}{T_g}}$$

The analysis reveals that the coefficient α correlates to fragility.

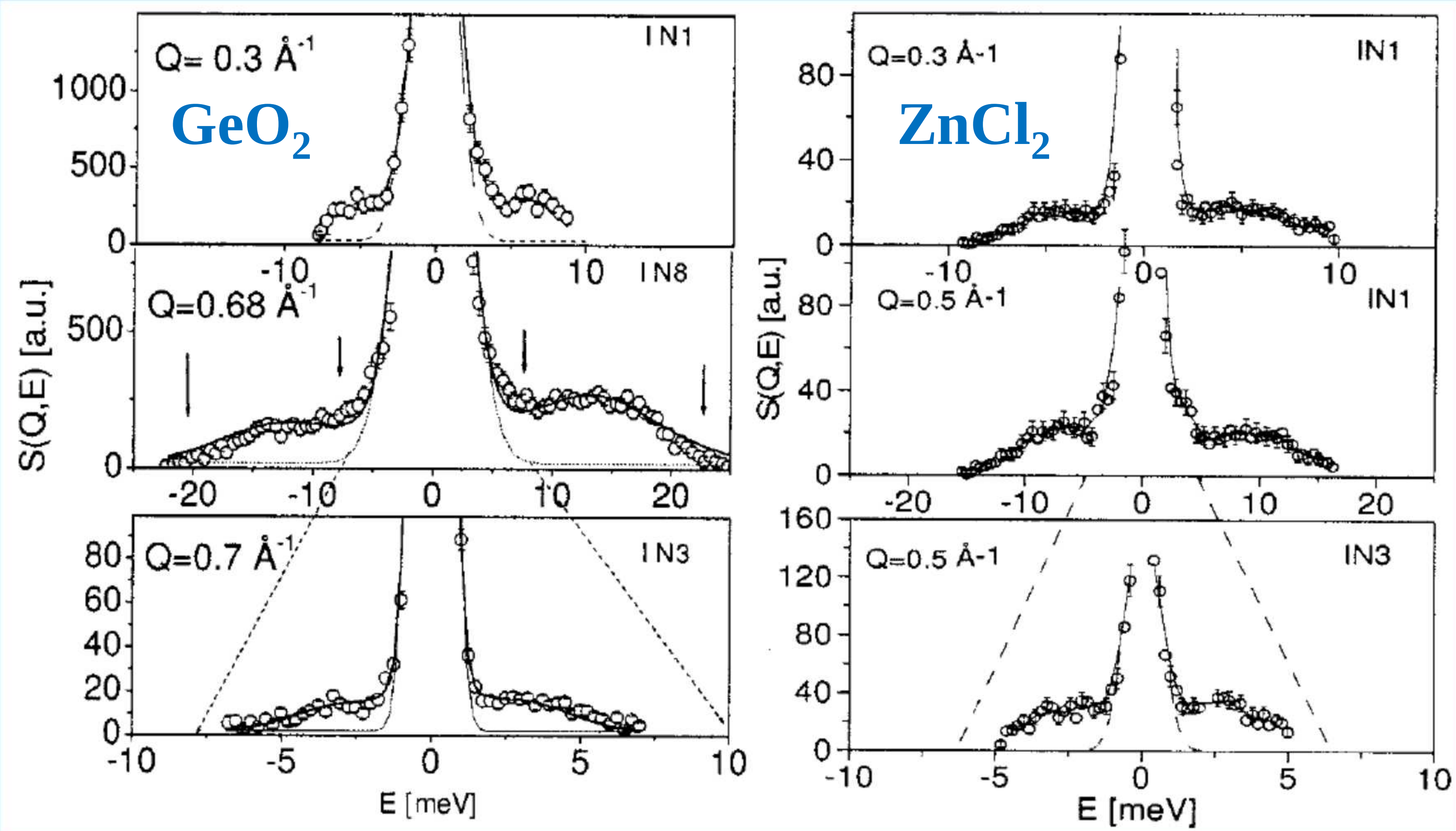
It presents another sign of strong connection between the fast and slow dynamics.

Scopigno, et al. **Science 302**, 849 (2003)





If we will have IXS with better resolution

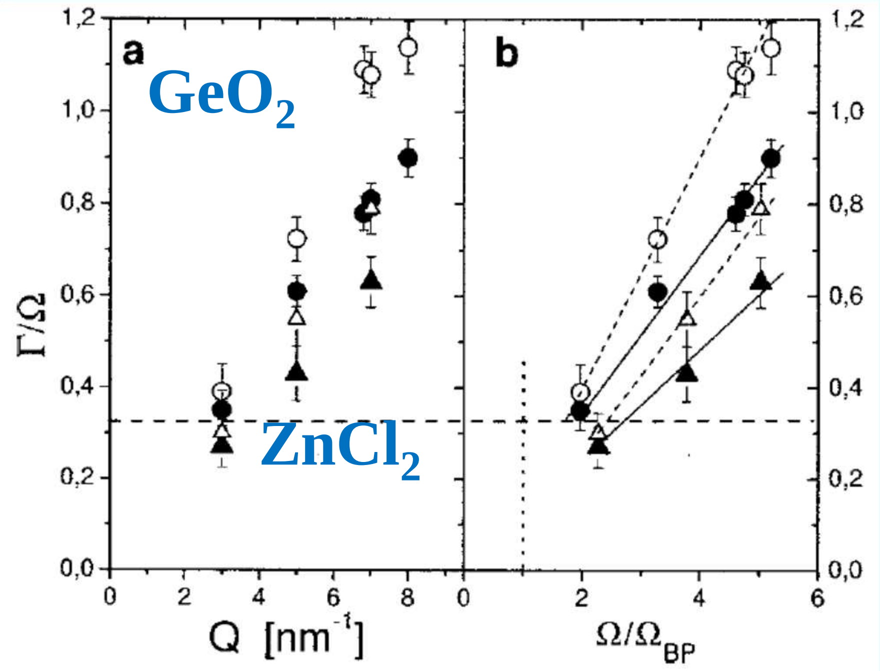


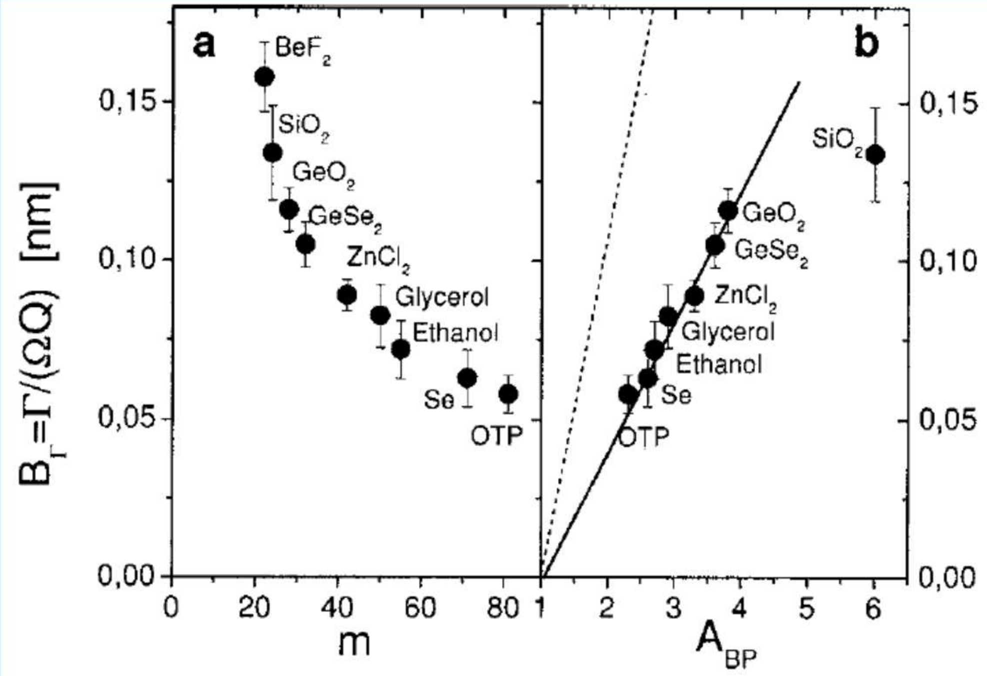
Detailed INS studies using several spectrometers revealed that there are two peaks in the inelastic scattering spectra, longitudinal with strong Q-dependence and a Q-independent mode.

Analysis of the width Γ of the longitudinal mode should take the second mode into accounts.

Bove, et al. **J.Chem.Phys. 128,** 184502 (2008)

Inelastic Scattering and Phonon Damping

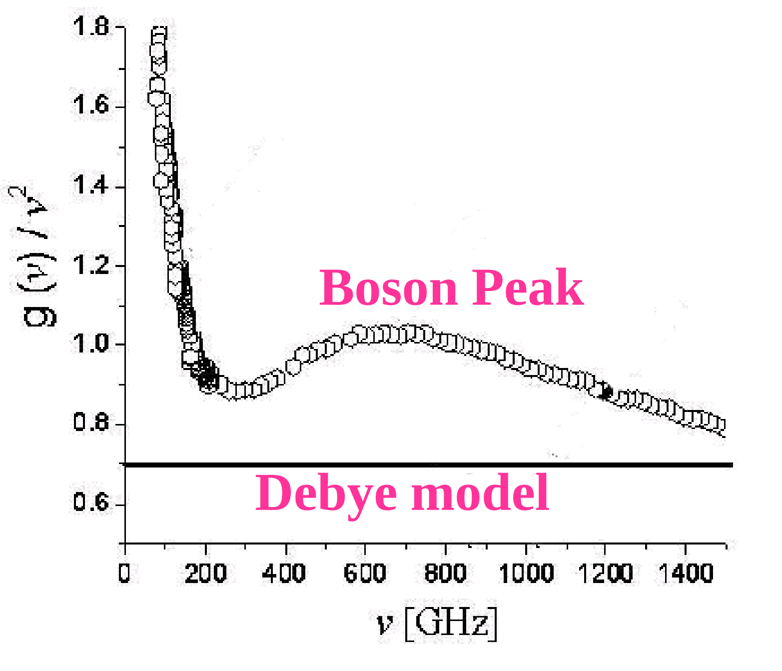




Analysis of internal friction Γ/Ω reveals its linear variation with Q or Ω of the modes. The slope of this dependence characterizes ‘effective damping’ of the modes and is different for different materials.

It appears that the effective damping correlates with fragility and the amplitude of the boson peak.
The latter is consistent with the idea ascribing the boson peak to fluctuations in elastic constants.

Collective excitations in glasses: The Boson Peak

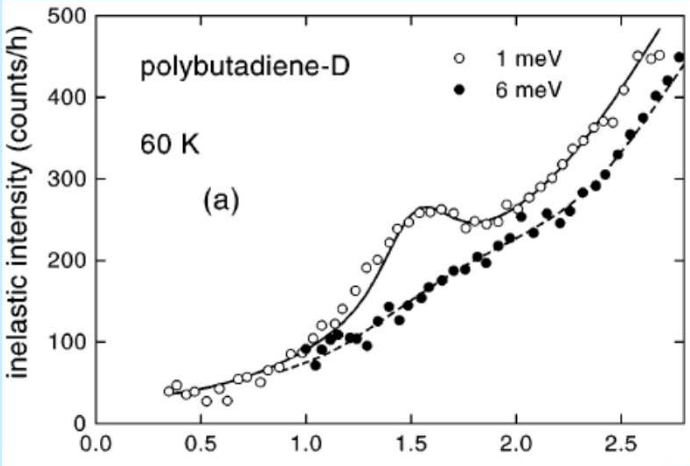


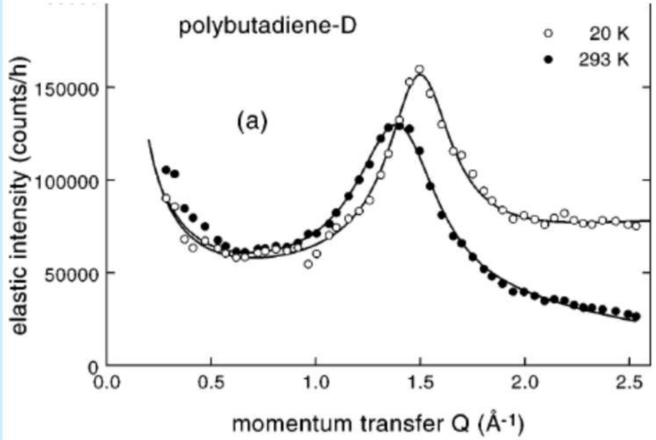
Coherent Neutron Scattering and Cooperativity

$S(Q,E) \sim Q^2$ *random motions*

$S(Q,E) \sim S(Q)Q^2$ *cooperative motions*

Carpenter, Pelizzari, **PRB 12**, 2391 (1975)



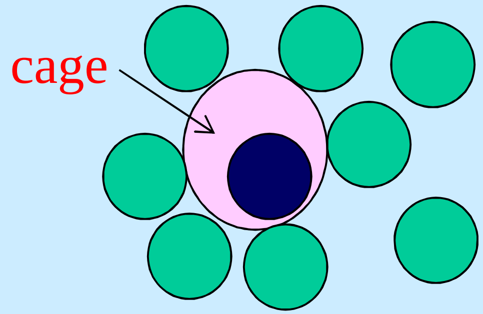


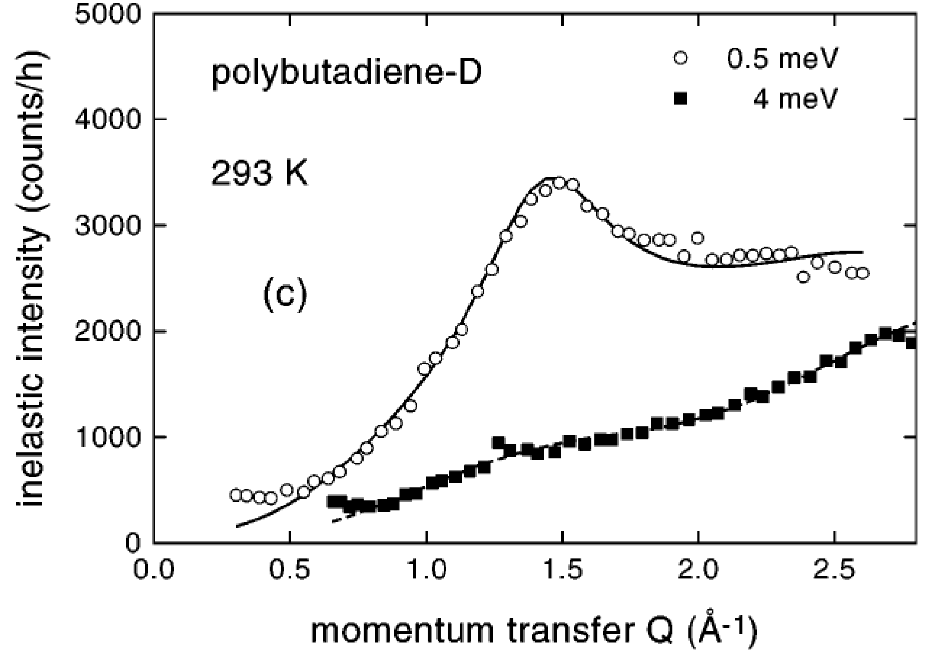
Vibrational spectra of all glass-forming systems exhibit the boson peak. **g(ν)** is the vibrational density of states measured by neutron scattering.

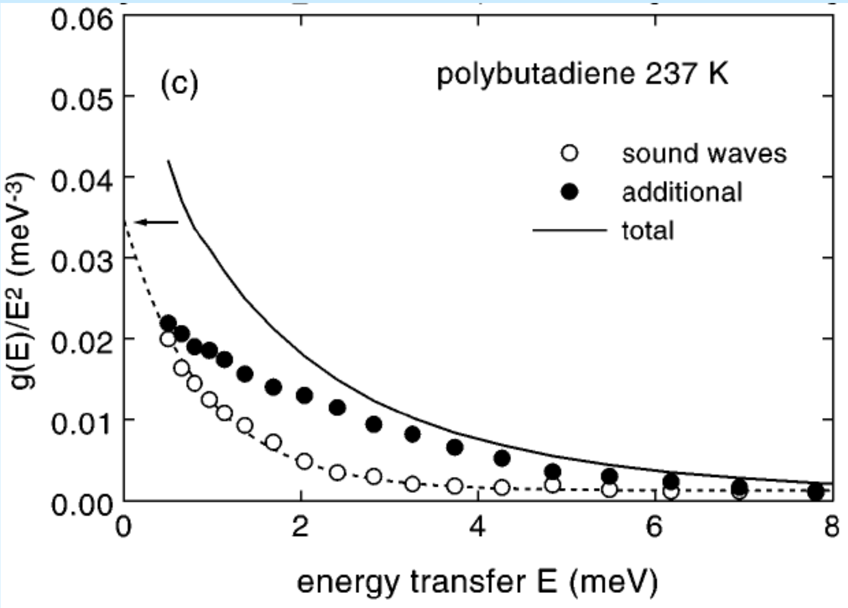
Analysis of coherent S(Q,E) reveals cooperative intermolecular motions around the boson peak [Buchenau, et al., **PRL 77**, 4035 (1996)].

Collective Dynamics in Fast Relaxation

Fast picosecond relaxation is usually ascribed to a 'rattling in a cage' formed by neighbor particles.







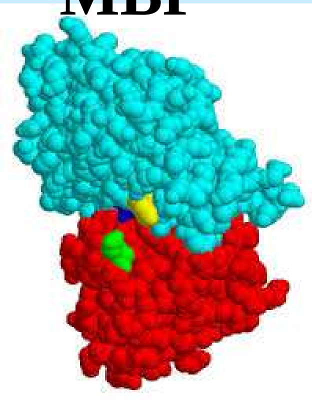
Buchenau, et al., **PRL 77**, 4035 (1996)

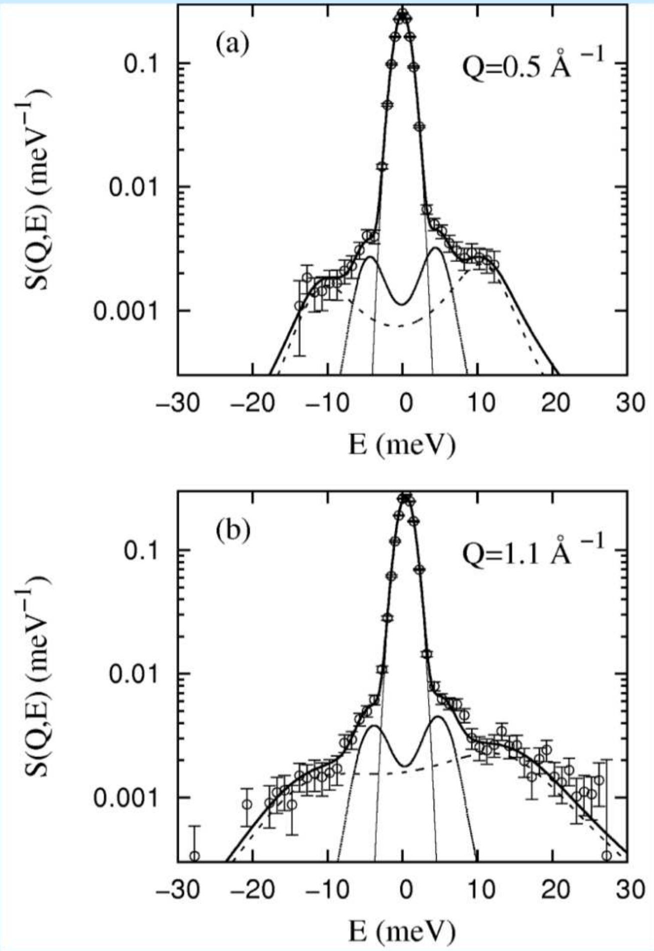
S(Q,E) in the region of fast relaxation in PB (E~0.5meV) exhibit clear peak at the first Q_{max}.

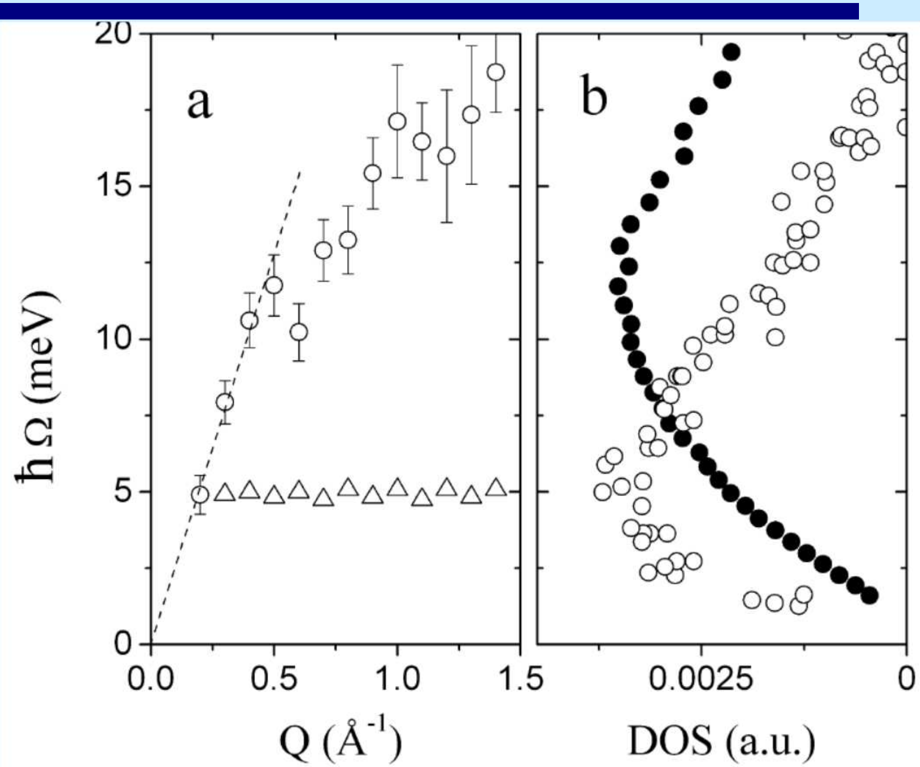
This result suggests coherent motion of neighbor chains on the ps-time scale.

Collective Dynamics in Proteins

MBP





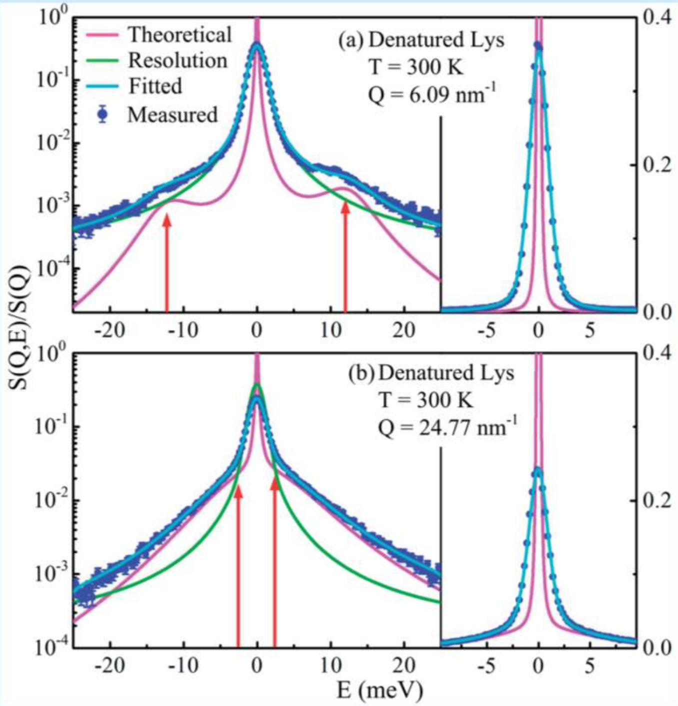


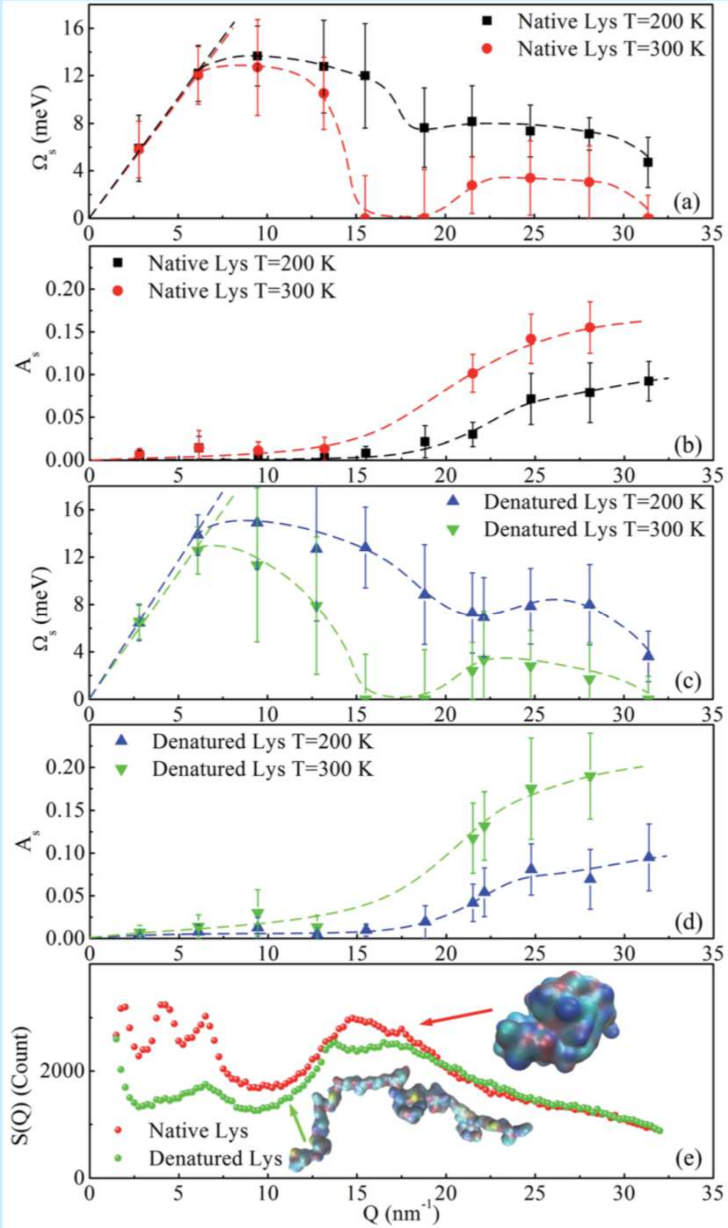
INS detects propagating and localized modes in deuterated maltose binding protein (MBP).

Despite small size of the protein and existence of secondary structure, its collective dynamics look rather similar to collective dynamics in glass-forming systems.

Paciaroni, et al. **JPC B 116**, 3861(2012)

IXS studies of Proteins



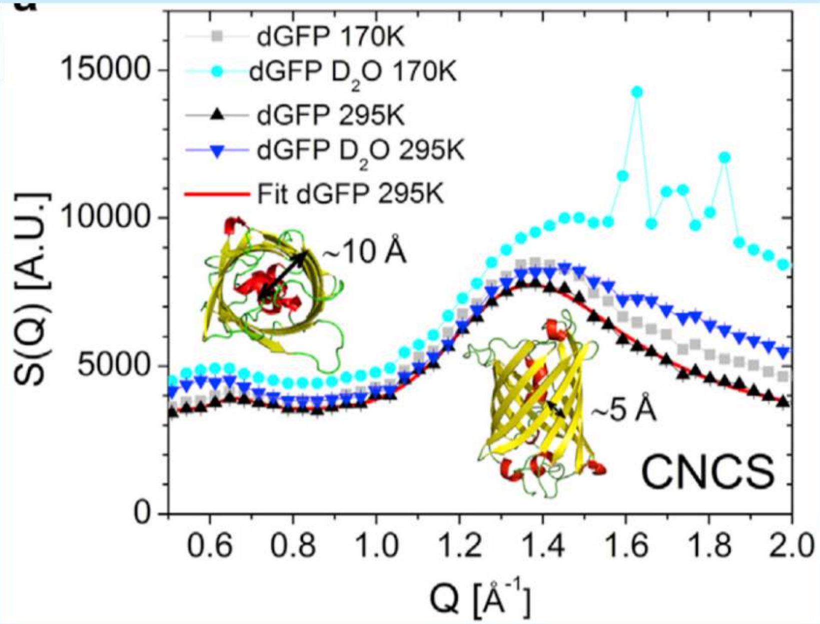


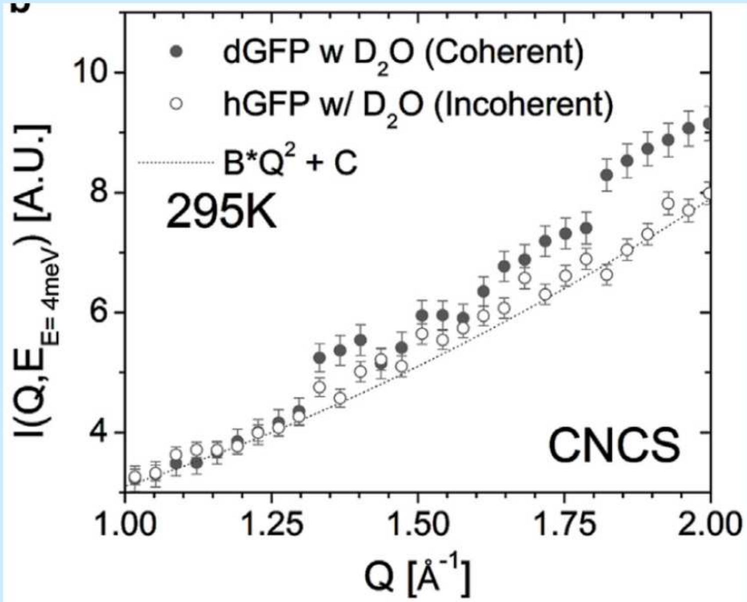
Using IXS Chen with co-workers discovered strong softening of the modes at Q>15 nm^{-1} with T. First they relate the softening to protein activity.

However, the same effect is observed in denatured protein. Thus the softening has no direct connection to the protein activity.

Wang, et al. **Soft Matter 10**, 4298(2014)

Coherency of the low-frequency vibrations in proteins

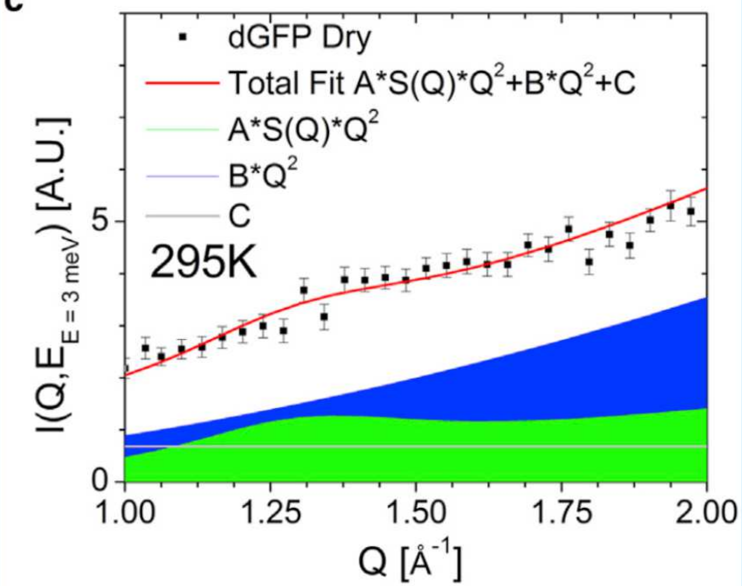




Green fluorescence protein (GFP) has a rigid barrel-like structure.
So, we expected high coherency in motion of neighbor structural units.

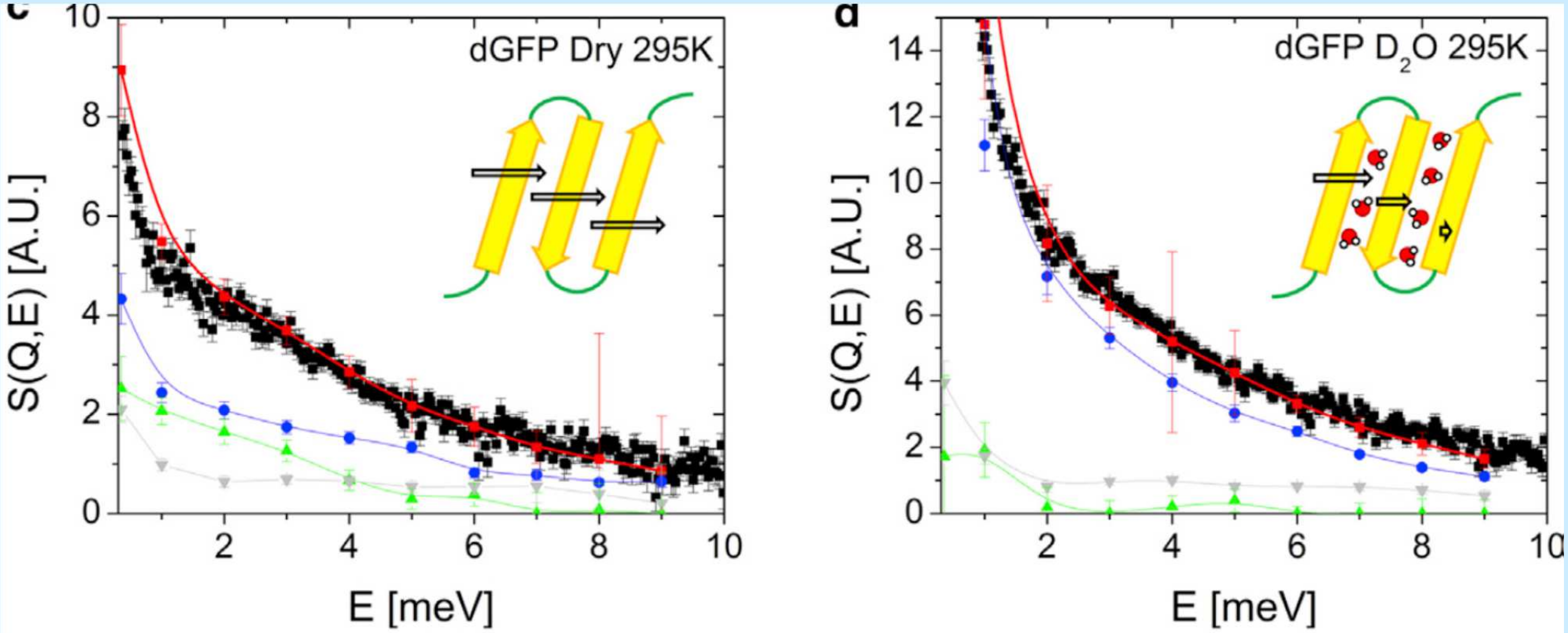
However, the difference between coherent and incoherent scattering is minor, and the peak at Q_{max}~1.4 A^{-1} is barely visible in the dynamic structure factor S(Q,E).

c



Nickels, et al. **Biophys.J. 105**, 2182(2013)

Coherency in dry and hydrated GFP



Decomposition of the S(Q,E) on random (blue symbols, S(Q,E)~Q^2) and cooperative (green symbols, S(Q,E)~S(Q)*Q^2) motions revealed rather low cooperativity in dry GFP which farther reduced upon hydration.

These unexpected results remain unexplained. It is not obvious whether this is specific for GFP or will be also observed in any other globular protein.

Nickels, et al. **Biophys.J. 105**, 2182(2013)

Conclusions

- There are strong correlations between fast (picosecond) and slow (structural) dynamics in glass-forming systems. The nature of these correlations remains a puzzle.
- IXS might help to understand microscopic details of the fast dynamics and in this way might contribute towards understanding of the glass transition phenomena and also protein dynamics.
- Significant improvement of IXS resolution is required for the technique to have stronger impact on the field of Soft Matter Dynamics.

Acknowledgments

Vladimir Novikov	University of Tennessee, USA
Alexander Kisliuk	Oak Ridge National Lab, USA
Uli Buchenau	Juelich, Germany
Cristiane Alba-Simionesco	Sacley, France
Livia Bove	U. Paris 6, France

Funding:

U.S. Department of Energy, Office of Science
National Science Foundation — Where Discoveries Begin