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Inelastic UV Scattering

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Inelastic UV Scattering

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1. **Introduction (Disordered Systems)**
2. **Inelastic UV Scattering with Very High Resolving Power**
3. **Studies on Glass-Formers**
4. **Conclusions**

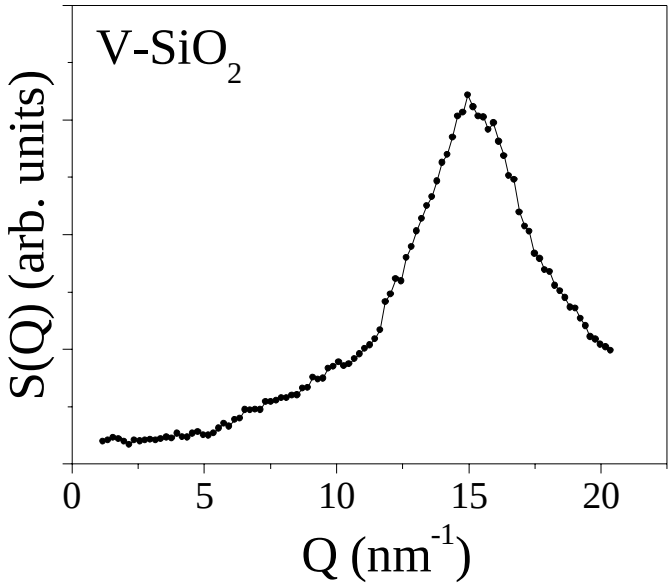
1. Introduction

The study of Atomic (Molecular) **Density Fluctuations** is of great importance to understand many physical properties of gases, liquids and solids

Crystals: Heat Capacity, Thermal Conductivity, Superconductivity

In **Disordered systems** the lack of translational invariance has delayed experimental studies in the **Mesoscopic** region

The presence of **Diffusional** and **Relaxational** processes strongly affects the collective dynamics making experiments even more difficult



$$n(\mathbf{r}) \xrightarrow{\text{FT}} S(\mathbf{Q})$$

Topological **Disorder**

Ill definition of Brillouin Zones

Why Disordered Systems

One Example: Glass-Formers

Glass is a **very general state** of condensed matter since a large variety of systems can be transformed from liquid to glass.

The liquid to glass transition cannot be described in the framework of classical phase transitions since the transition temperature Tg depends on the **quenching rate**, i. e. one cannot define an **order parameter** showing a critical behaviour at Tg.

Puzzling properties

Glass-transition: a theory describing the liquid-to-glass transition mechanism has not been formulated yet.

Relaxation processes (related to the huge increase of viscosity)

Thermal anomalies (In the Specific Heat or in the Thermal Conductivity)

Excess in the vibrational DOS as measured by Incoherent Neutron Scattering and Raman Spectroscopy

The Dynamic Structure Factor S(Q,ω)

The dynamical properties associated to atomic density fluctuations can be studied by means of scattering experiments which allow the determination of the **Dynamic Structure Factor**

$$S(\mathbf{Q},\omega) = \int_{-\infty}^{\infty} dt \int d\mathbf{r} \langle (n(\mathbf{r},t) - n)(n(0,0) - n) \rangle e^{i(\omega t - \mathbf{Q}\cdot\mathbf{r})}$$

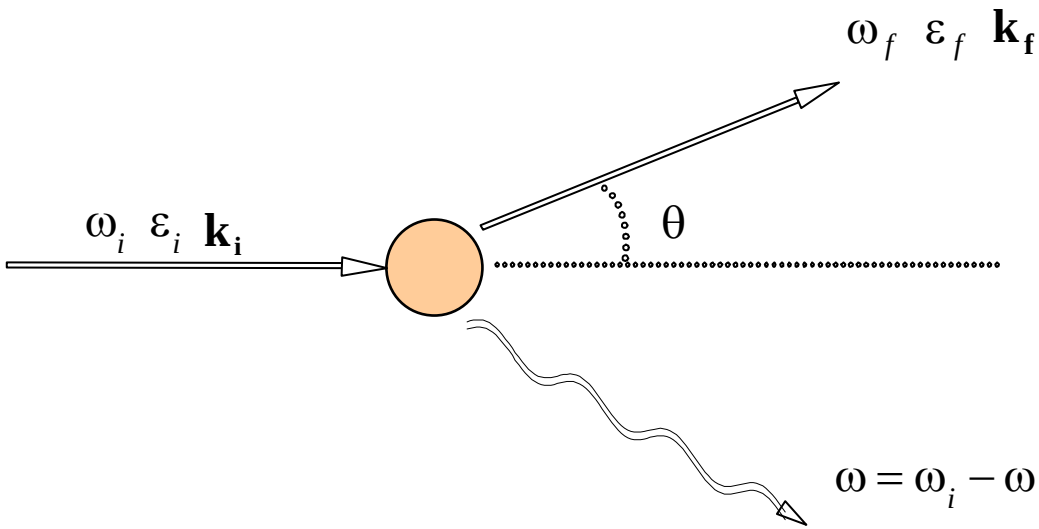
$n(\mathbf{r},t)$ Particle Density Operator

$\langle (n(\mathbf{r},t) \rangle$ Thermodynamical average of the Density

In Crystals one can study atomic (molecular) density fluctuations in any **Brillouin Zone** allowing measurements of density waves with a very high sound speed.

This is not the case for disordered systems were the **ill definition** of BZ makes impossible detecting phonon-like excitations out from the first **pseudo** BZ

Inelastic Scattering to measure S(Q,ω)



$$I_{if}(\mathbf{Q},\omega) \propto \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \delta\alpha_{if}(\mathbf{Q},0)\delta\alpha_{if}(\mathbf{Q},t) \rangle$$

$$I_{VV}(\mathbf{Q},\omega) \propto S(\mathbf{Q},\omega)$$

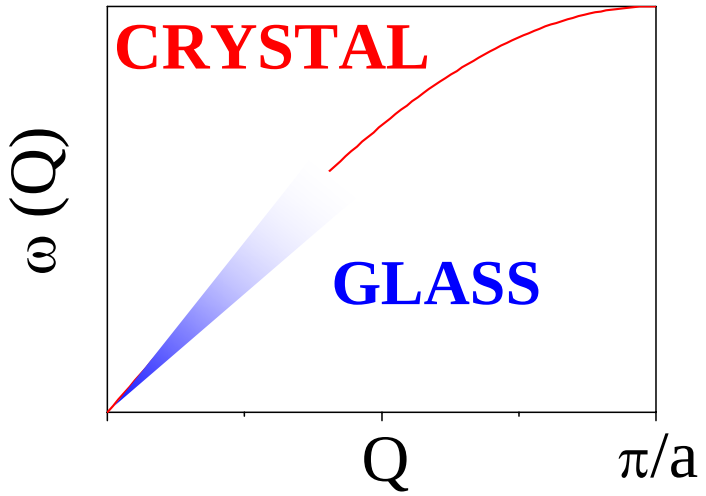
$$I_{if}(\mathbf{Q},\omega) \propto \frac{\omega_f}{\omega_i} (\varepsilon_o \cdot \varepsilon_1) \left| f(Q) \right|^2 S(\mathbf{Q},\omega)$$

Visible → UV

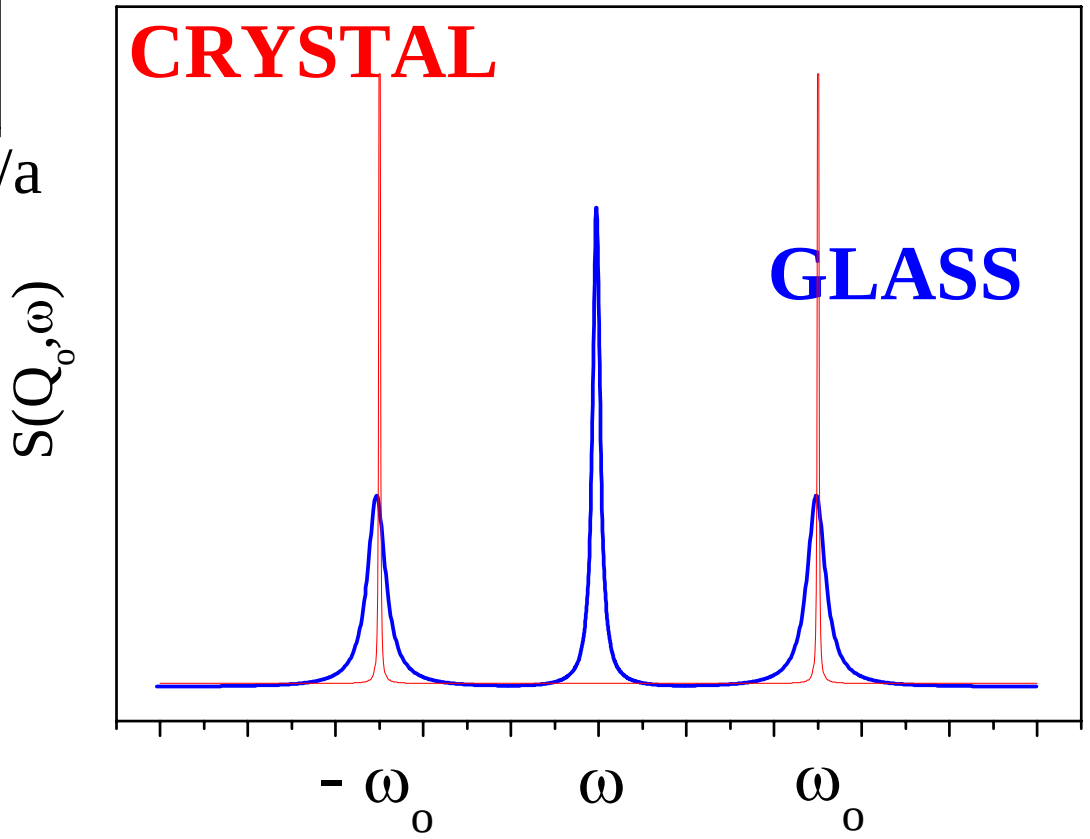
Density Fluctuation Spectrum

X

S(Q,ω) Crystal vs Glass

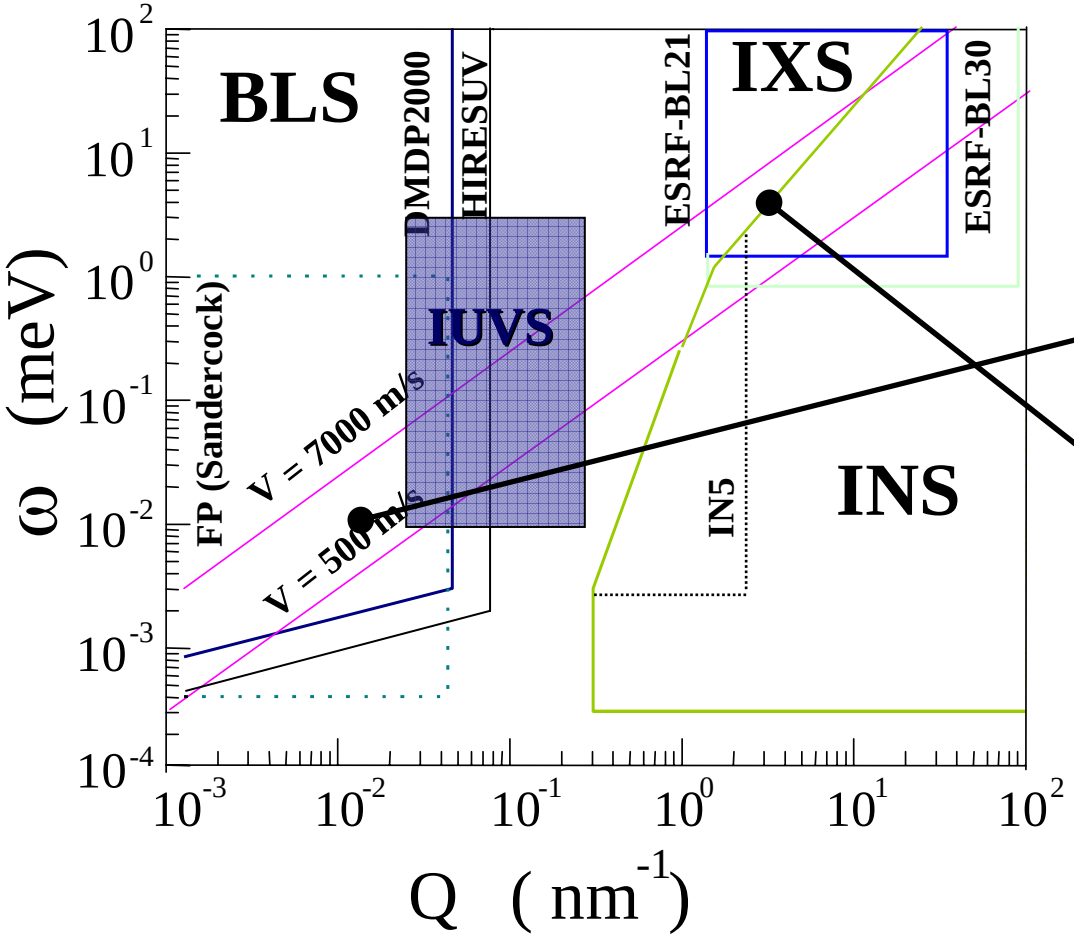


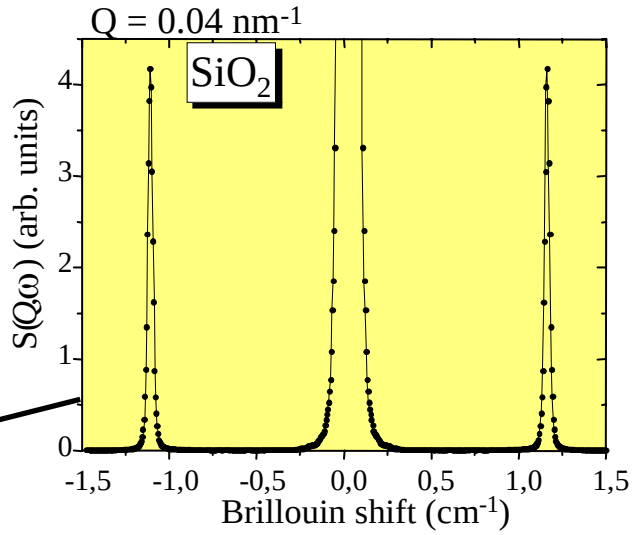
Dispersion Relation for an
Acoustic Vibrational Mode

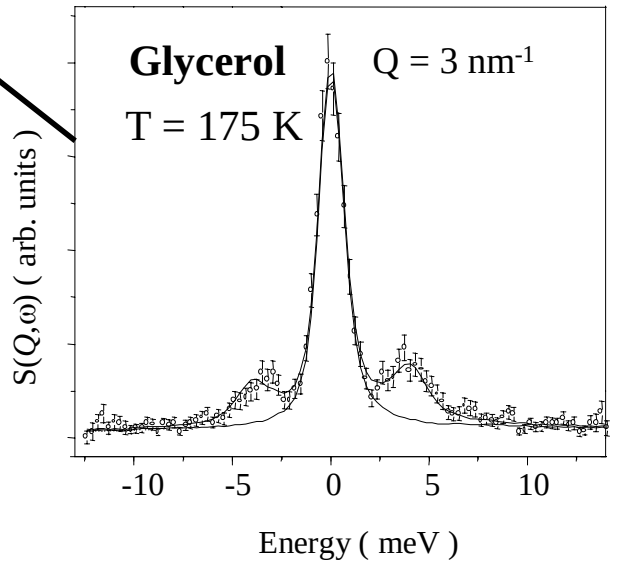


Available probes to measure the S(Q,ω)

Interest in measuring **S(Q,ω)** in Disordered Systems
in the largest possible **Kinematic** Region







Investigations at the nanoscale could Shed Light on:

Liquids - Fluids

- Transition from the Hydrodynamic to the Kinetic regime in Simple liquids and fluids.
- Effect of the Local Structure on the Collective Dynamics in Molecular liquids and H-bonded liquids.
- Liquid Metals.

Glasses

- Nature of the Vibrational Modes in the Mesoscopic space-time region.
- Relaxation Processes in Super-Cooled liquids and their relation to the Glass Transition.
- Vibrational and Relaxational Low Temperature Properties of Fragile and Strong glasses.

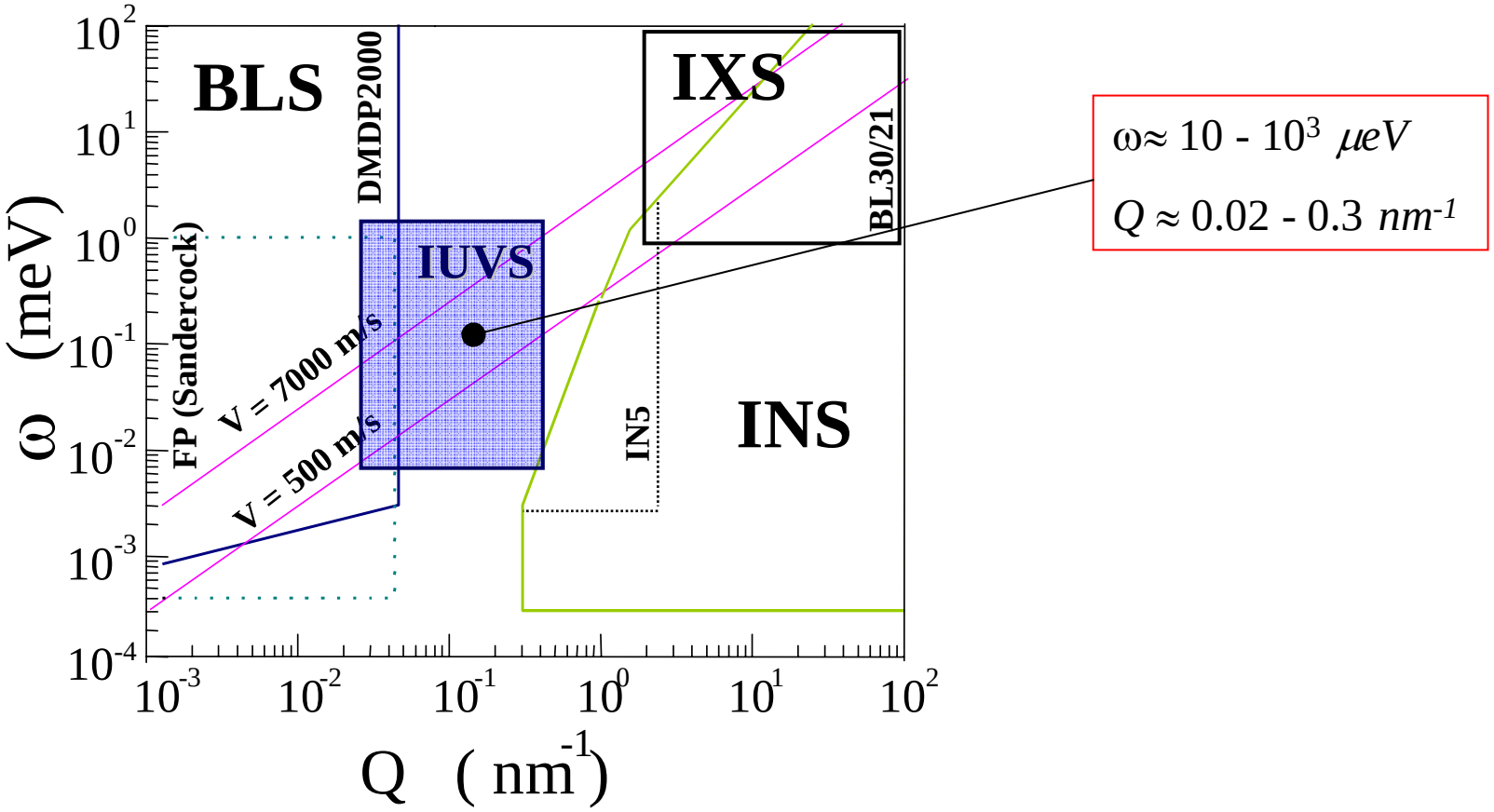
Resonant Scattering (Tunability)

- Low count-rate experiments.
- Determination of Partial Dynamic Structure Factor in gas and fluid mixtures.
- Resonant Raman on Nanostructures.

2. Inelastic UV Scattering (IUVS) with Very High Resolving Power

- Incident **Energy** in the 5 – 11(30) *eV* range ($\lambda \approx$ **240 – 110(40)*nm***)
- High incident photon **Flux** on the Sample ($> 10^{12}$ *photon/s*)
- High **Resolving Power** ($\approx 10^{5} - 10^{6}$)

→ ~1 *count/s*



ω≈ 10 - 10^3 μeV

$Q \approx 0.02 - 0.3$ nm^{-1}

The Beamline Design and Construction

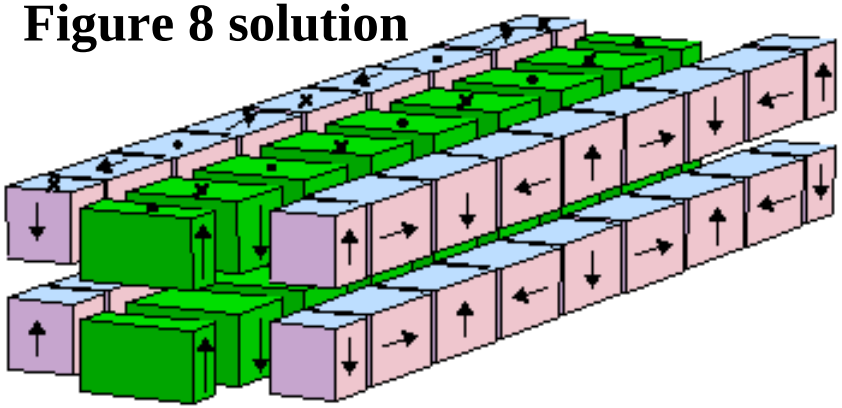
Linear Undulator ?

4.5 *m* length, 125 *mm* period, 400 *mA*

$2 \cdot 10^{15}$ *photons/s/0.1% bandwidth*

1.5 kW on the first mirror

Figure 8 solution

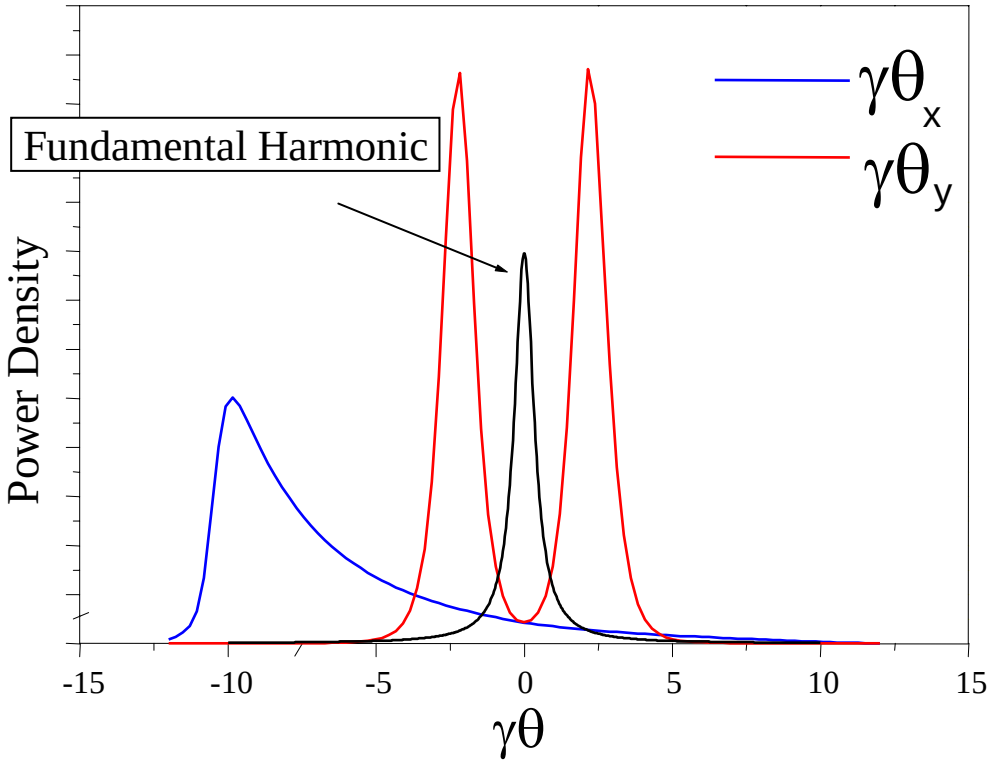


$N_p = 32$

$\lambda = 140$ *mm*

$K_x = 3.4$

$K_y = 9.4$

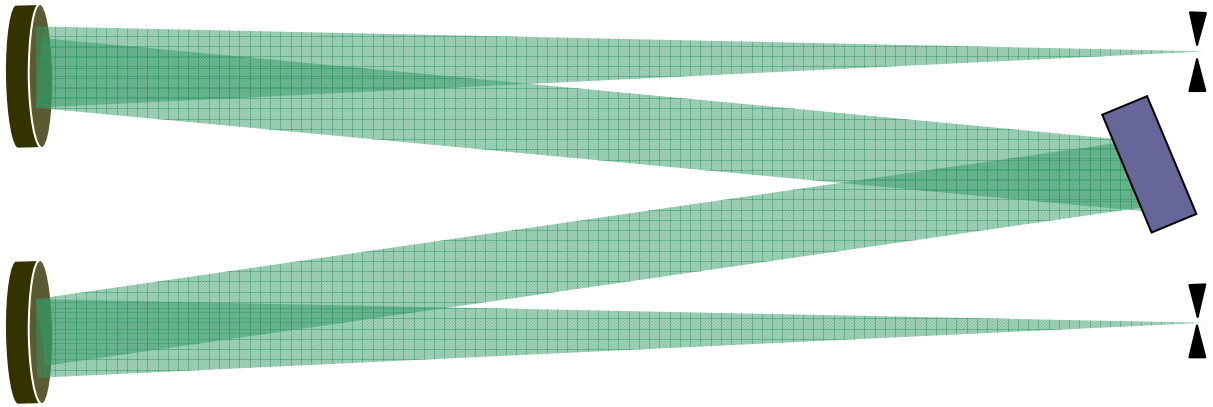


22 W on first mirror !!

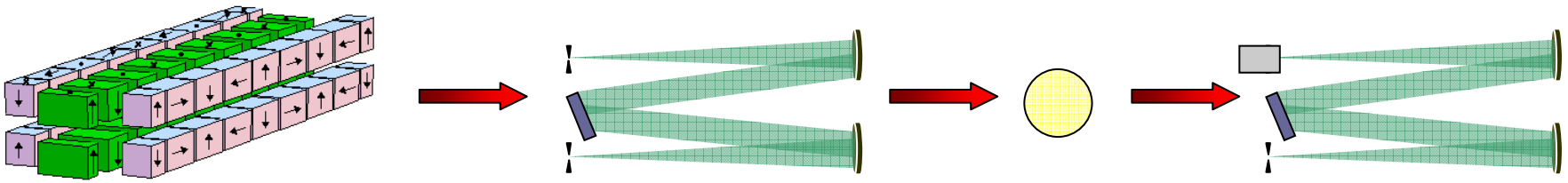
$2 \cdot 10^{15}$ *photons/s/0.1% BW* ($2 \cdot 10^{12}$ *photons/s*)

The NIM Monochromator

Normal Incidence Monochromator (**Czerny-Turner** design)



$$\frac{\Delta E}{E} = \frac{\delta \cdot ctg\theta}{2F} = \frac{50\mu m \cdot ctg(70^{o})}{16m} \approx 1 \cdot 10^{-6}$$



Source Monochromator Sample Analyzer

The Beamline

Scanning Resolution: 80 *nrad*

Autocollimator Control: 50 *nrad*

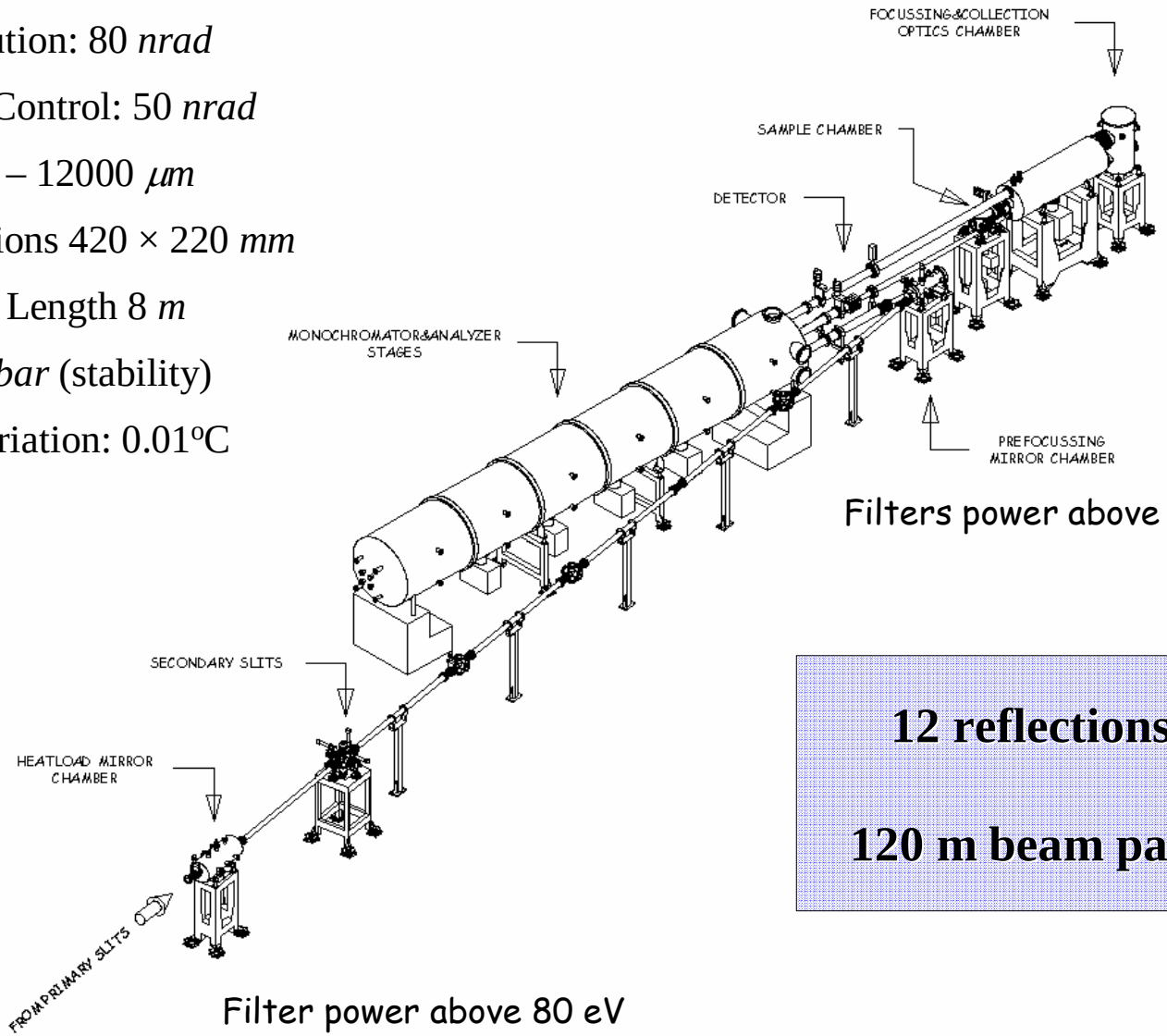
Slits Opening: 5 – 12000 μm

Grating Dimensions 420 × 220 *mm*

Monochromator Length 8 *m*

Vacuum: 10^{-8} *mbar* (stability)

Temperature Variation: 0.01ºC



Filters power above 15 eV

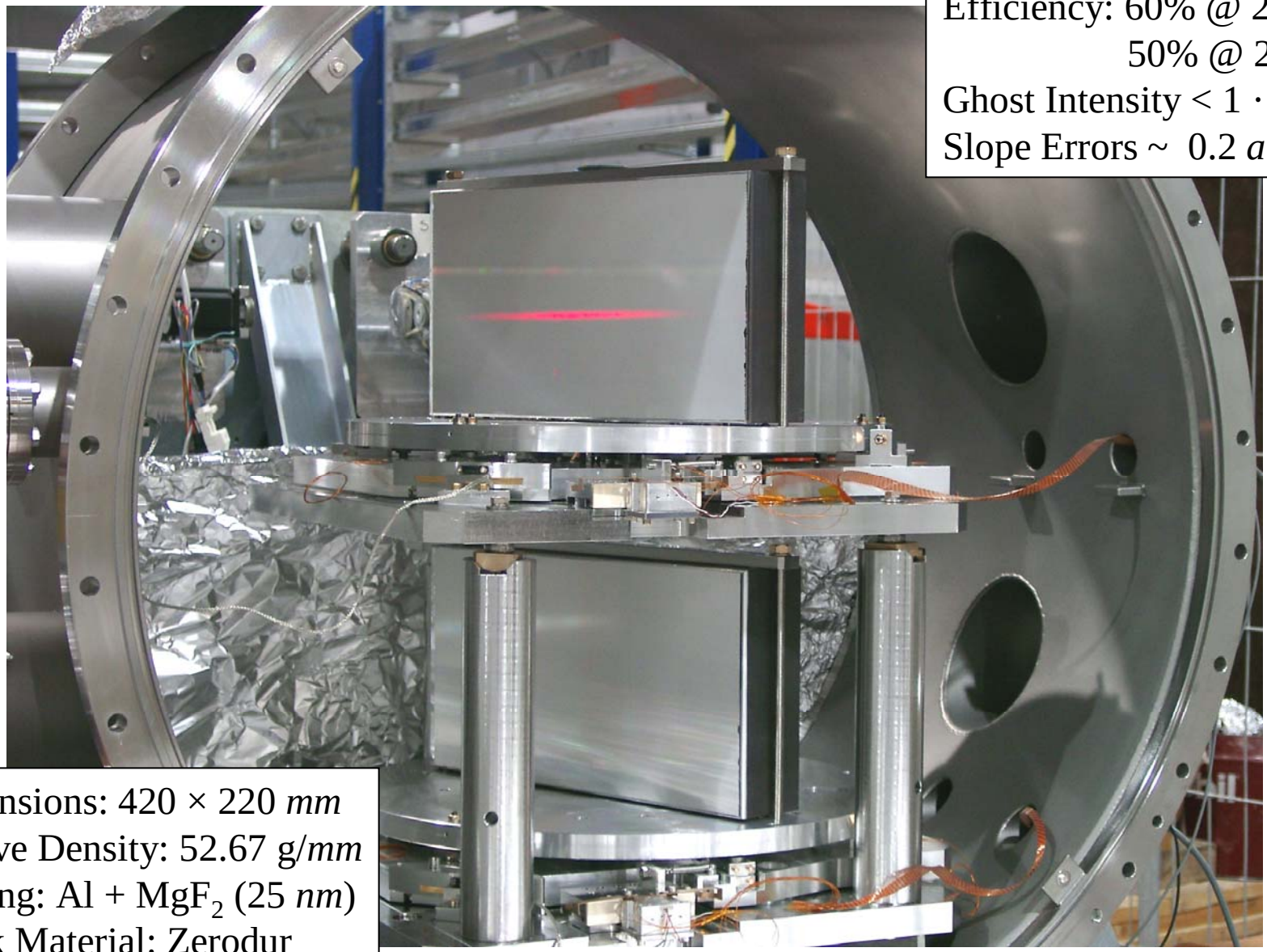
12 reflections

120 m beam path

Filter power above 80 eV

The Construction

The Gratings



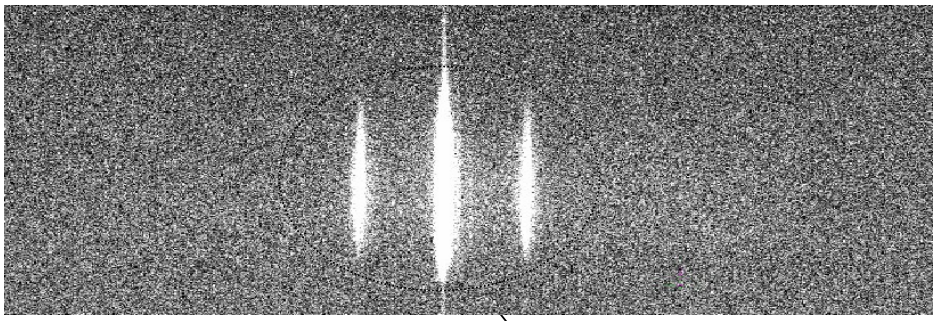
Efficiency: 60% @ 250 *nm*
50% @ 200 *nm*
Ghost Intensity < $1 \cdot 10^{-4}$ PL
Slope Errors ~ 0.2 *arcsec*

Dimensions: 420 × 220 *mm*
Groove Density: 52.67 g/*mm*
Coating: Al + MgF_2 (25 *nm*)
Blank Material: Zerodur

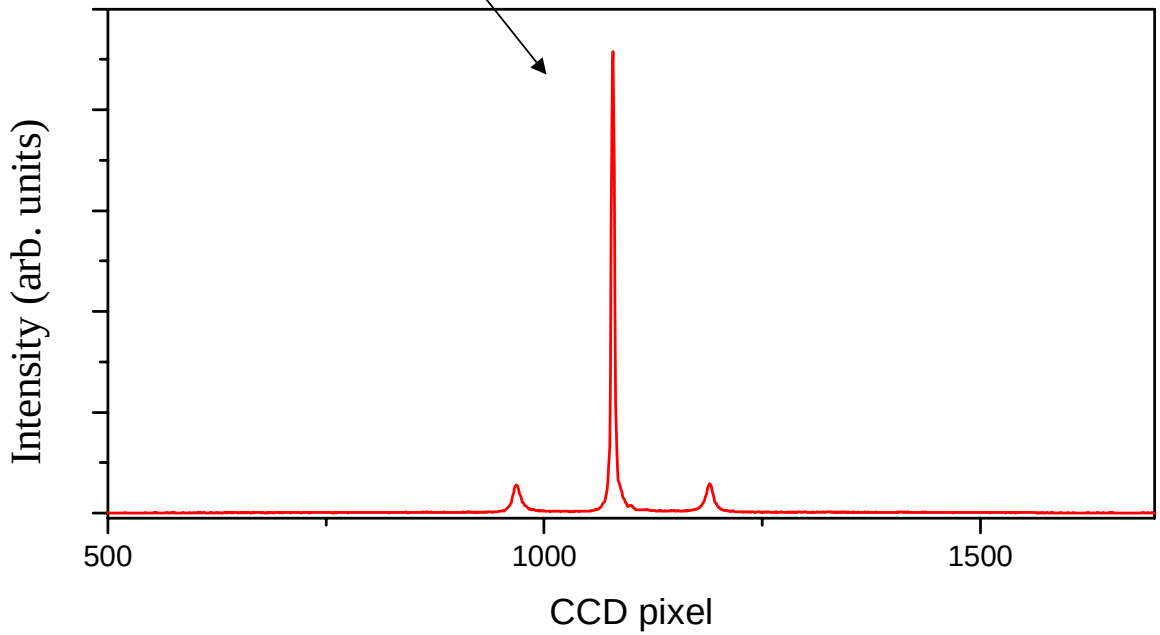
The Beamline

The Spectrum

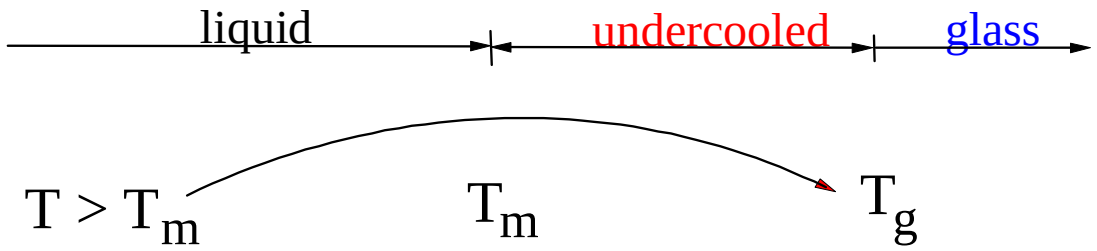
Image on CCD detector – Spectra can be collected in one single shot



Glycerol @ 260 K



3. Studies on Glass-Formers



Glass is a **very general state** of condensed matter

Elements (*Sulfur*, ...)
Oxides (SiO_2, ...)
Chalcogenides (As-S, ...)
Halides ($ZnCl_2$, ...)
Molten Salts ($KNO_3Ca(NO_3)_2$, ...)
Aqueous solutions (LiCl + RH_2O, ...)
Organic compounds (*Glycerol*, ...)

Quenching Rates

10^5 K/s *real*

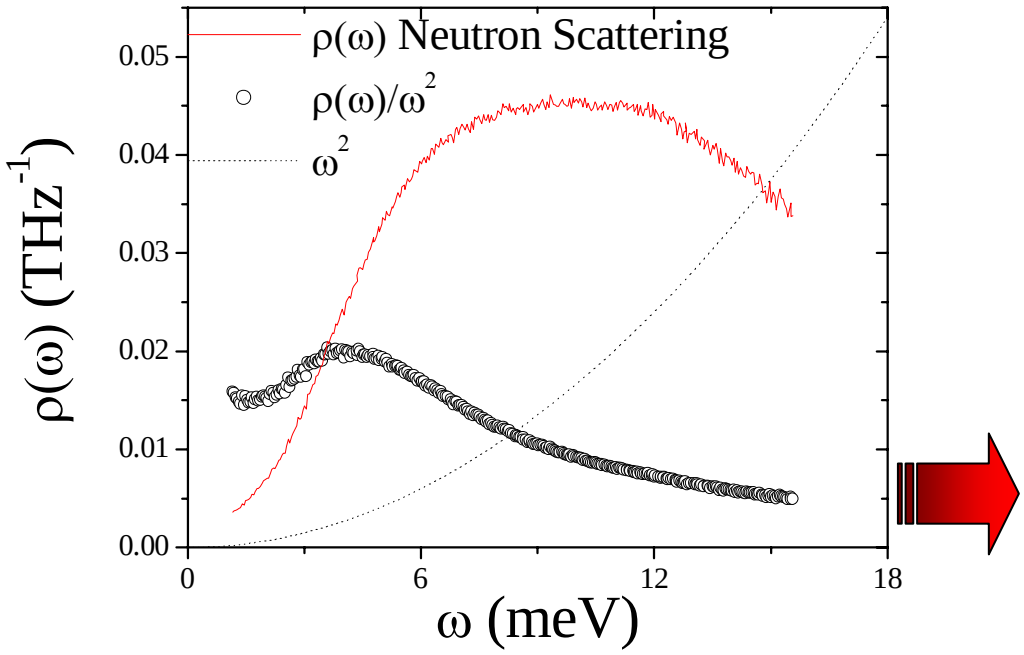
10^{12} K/s *simulations*

The **viscosity** η increases by lowering T and presents one of the **largest** changes of a physical measurable quantity of a material (14 orders of magnitude)

Glass-Forming Systems

Puzzling properties

- Glass-transition mechanism
- Relaxation processes
- Thermal anomalies
- **Excess in the vibrational DOS**



The **excess** in the vibrational density of states justifies the observed thermal anomalies (like the excess in the specific heat at low T) in glass-forming systems. Nevertheless the origin of this peak (usually called the **Boson peak**) in the V-DOS is still unclear.

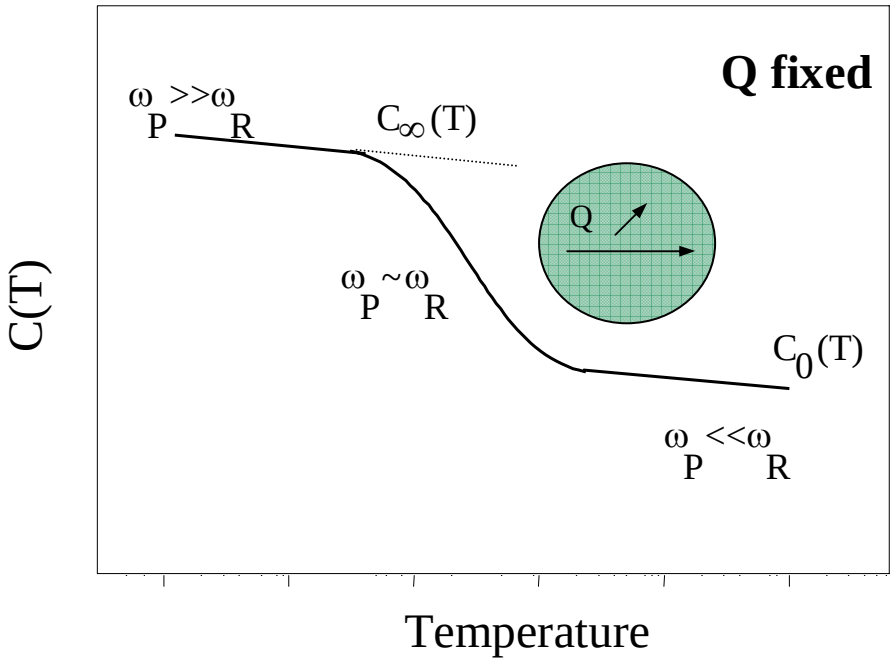
The Structural Relaxation

Puzzling properties

- Glass-transition mechanism
- **Relaxation processes**
- Thermal anomalies
- Excess in the vibrational DOS

Structural Relaxation → cooperative processes by which the local structure, after being perturbed by an external disturbance or by a spontaneous fluctuation, rearranges towards a new equilibrium position

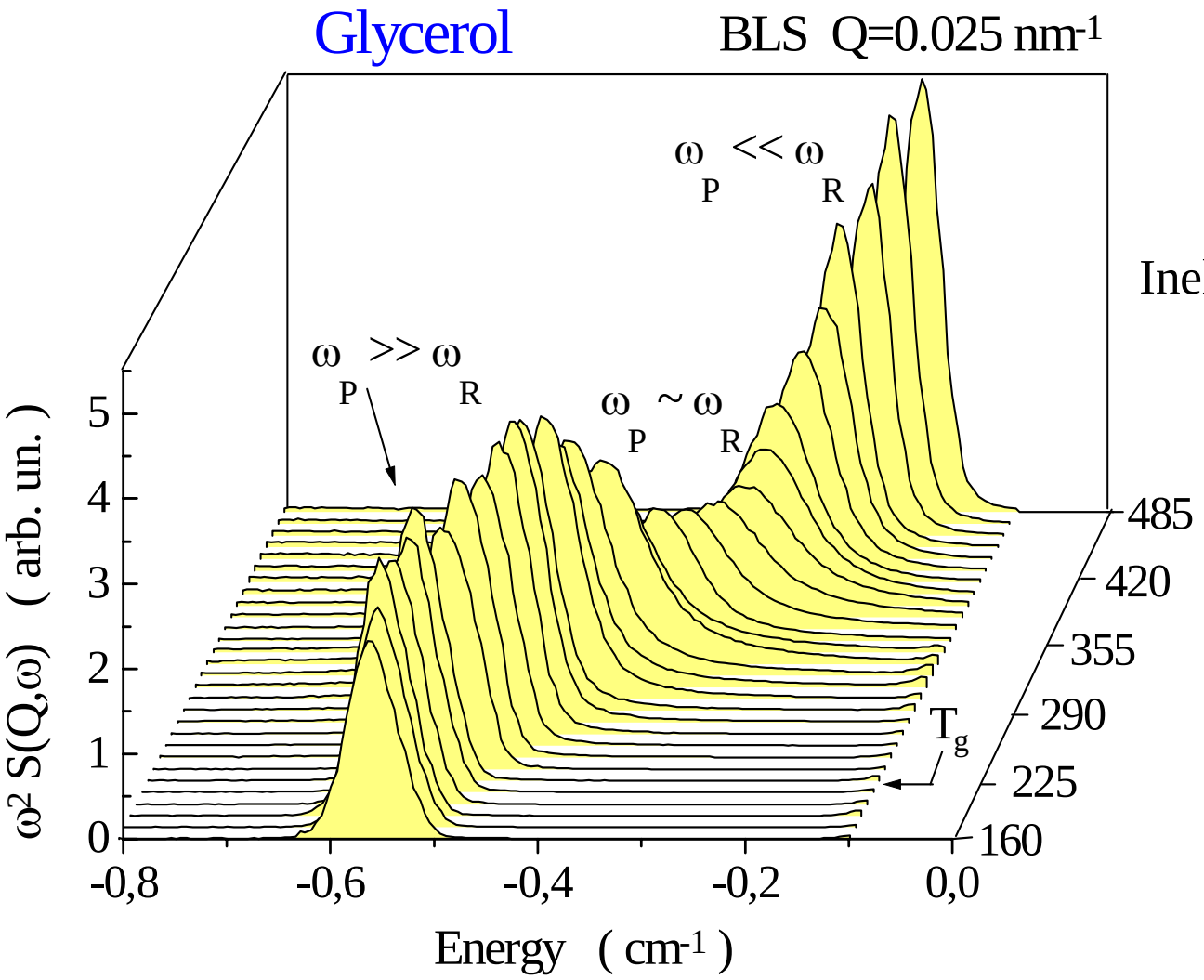
Mode Coupling Theory → a particle trapped in a the cage can migrate only through rearrangement of a large number of particle surrounding it



Knowledge of $C_0(T)$, $C_\infty(T)$, $\tau_R(Q)$, $C(Q,T)$

Formulation of Models describing the Glass Transition

The Structural Relaxation



Inelastic peak temperature dependence

Water

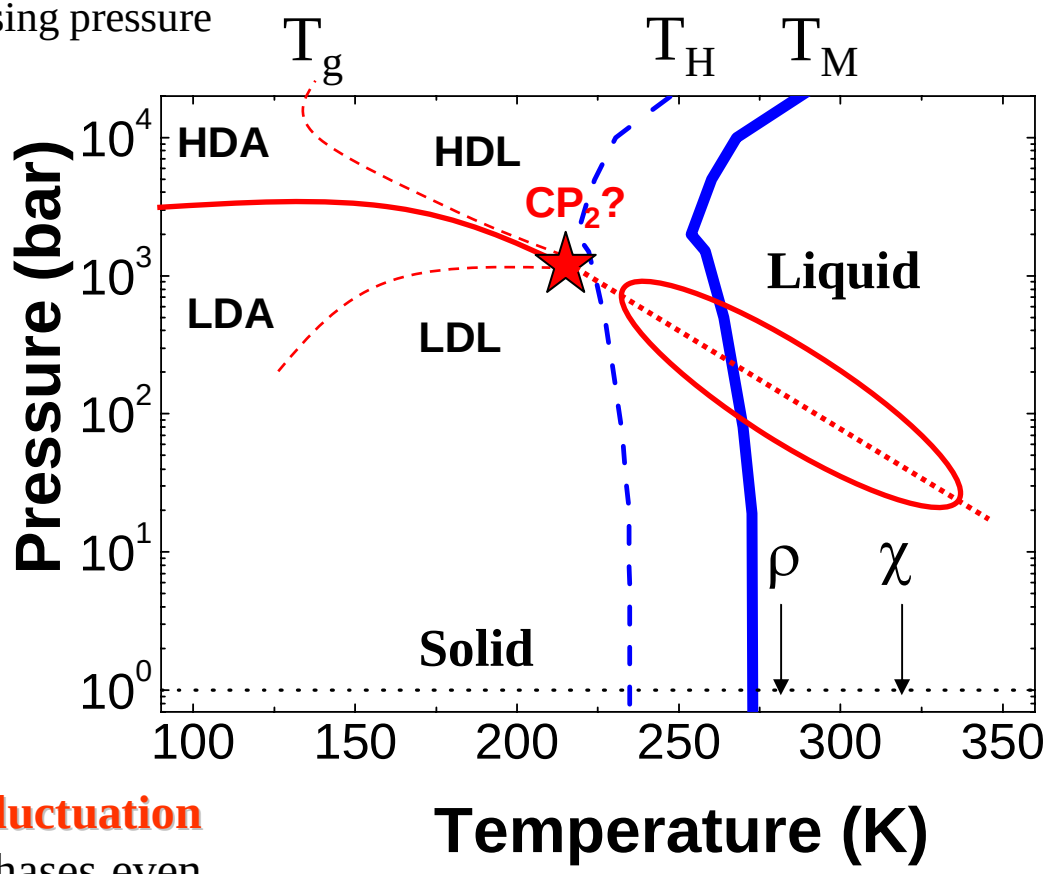
Water exhibits very **unusual** properties:

- Negative volume of melting
- Density maximum in the normal liquid range
- Isothermal compressibility minimum in the liquid
- Increasing liquid fluidity with increasing pressure

Liquid–Liquid Phase Transition

220 K – 100 MPa

P. H. Poole et al., Nature (1992)



The liquid will experience **spatial fluctuation** characteristic of the LDL and HDL phases even though the liquid has not yet **phase-separated**

Inelastic Scattering applied to Water

Anomalies in **Transport** Properties ← ? → **Thermodynamic** Singularity

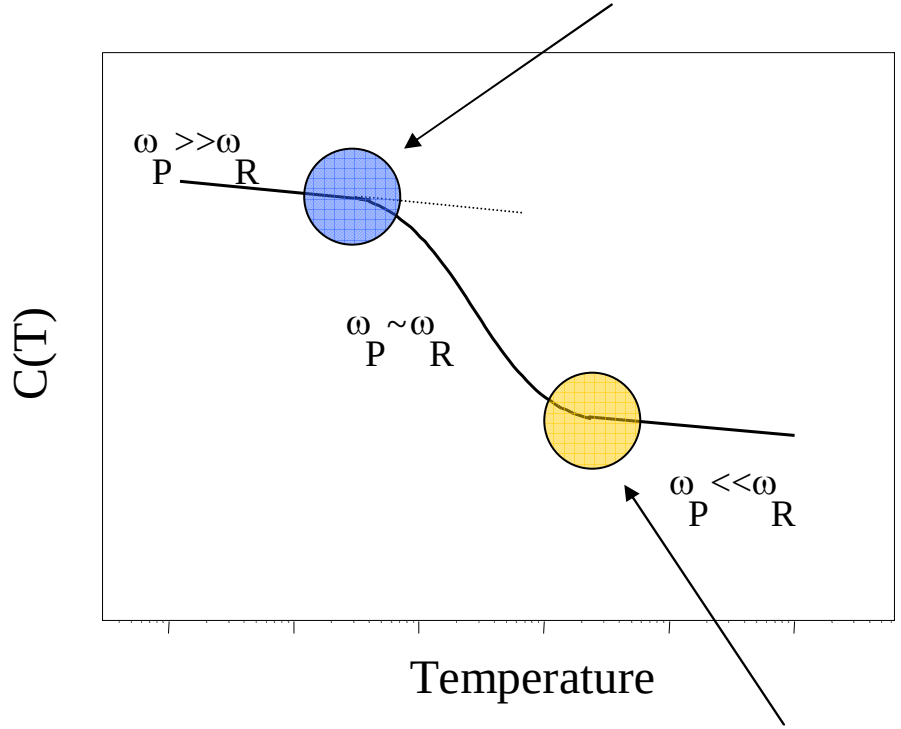
in the undercooled liquid

C. J. Roberts et al., PRL (1996)

Mode Coupling Theory $F(Q,t) \sim \exp-(t/\tau(Q,T))^{\beta}$

transient caging of molecules $\tau \sim (T-Tc)^{-\xi}$ $\beta \rightarrow$ T independent and < 1

high frequency investigations: **IXS** *F. Sette et al.*, PRL ***77***, *83 (1996)*



Best Sensitivity Condition $\omega_P \tau_R \sim 1$

For IUVS $T \sim 250$ K

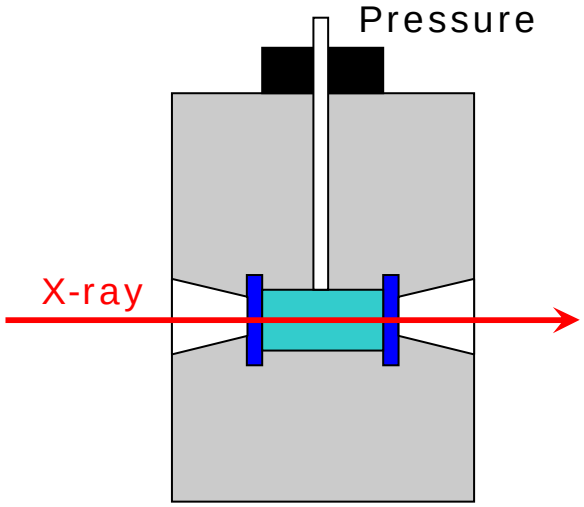
$T_{NML} \sim 230$ K

low frequency investigations: **Ultrasonic** and **BLS** *A. Cunsolo et al., JCP* ***105***, *3911 (1996)*

IXS Investigations

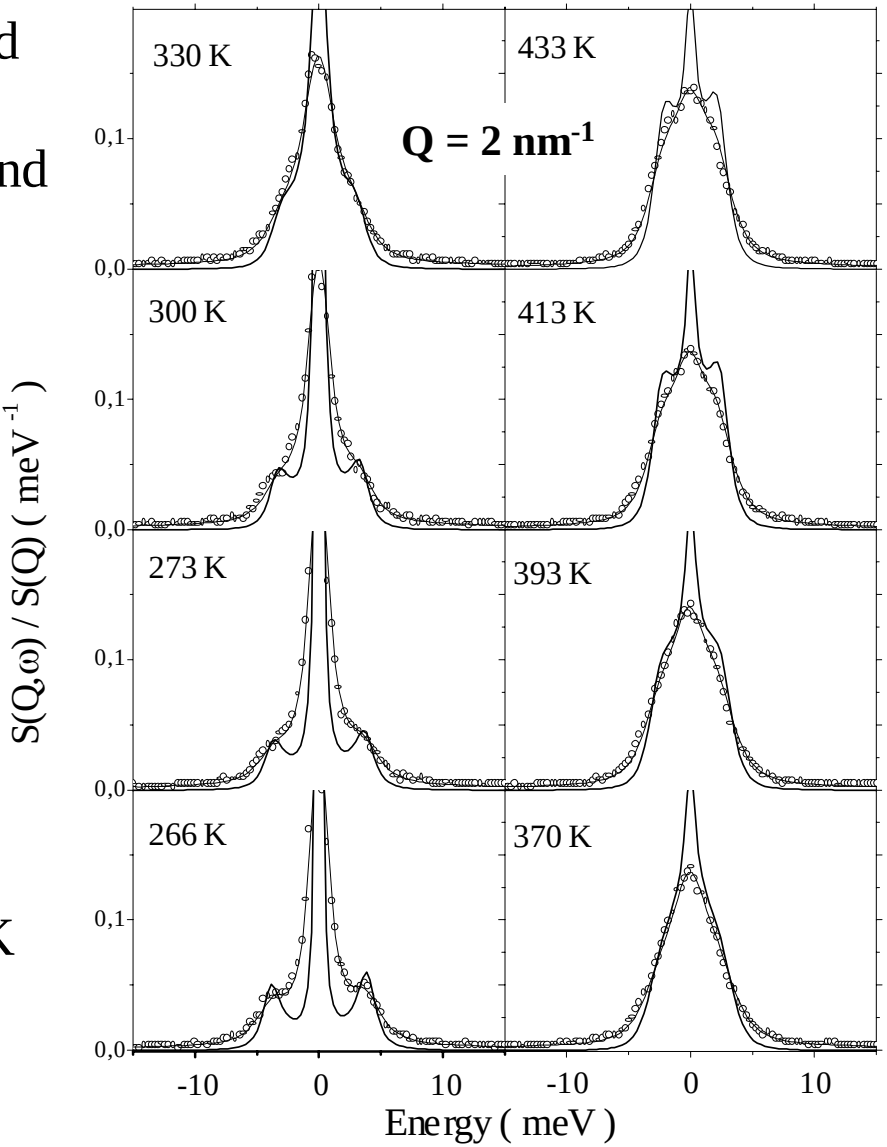
Water from hot liquid to undercooled

Cell: High pressure cell with Diamond windows (transparent to X-ray)



Momentum Transfer: 2 nm^{-1}

Temperature range: 433 → 266 K



F. Sette et al., PRL 1995, PRL 1996
A. Cunsolo et al., PRL 1999
Monaco et al., PRE 1999

Data Analysis – The Memory Function approach

Equation of motion for the **normalized correlation function** of density fluctuations $\Phi_Q(t) \rightarrow n(\mathbf{r},t)$

$$\frac{\partial^2 \Phi_Q(t)}{\partial t^2} + \Omega_Q{}^2 \Phi_Q(t) - \int_0^t m_Q(t-t') \frac{\partial}{\partial t} \Phi_Q(t') dt' = 0$$

Langevin equation

$$S(Q,\omega) = S(Q) \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \Phi_Q(t)$$

$$S(Q,\omega) = (2c_0^2 Q^2/\omega) \mathrm{Im}[\omega^2 - \omega_0^2 - i\omega\, m_Q(\omega)]^{-1}$$

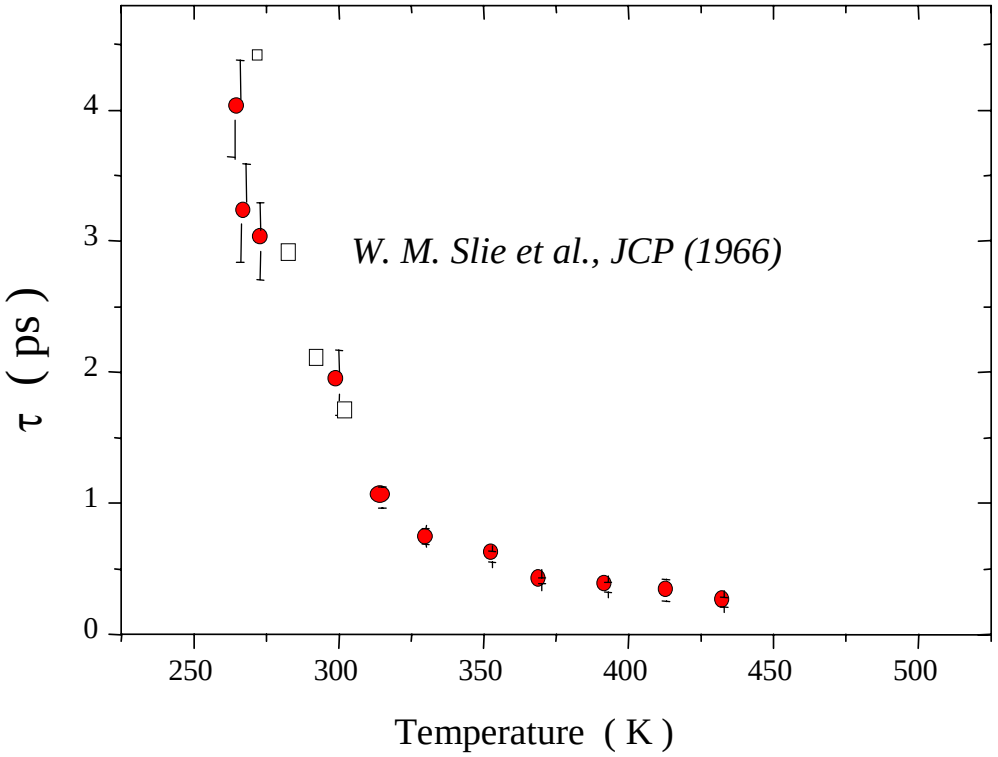
The **Viscoelastic** model

Two single exponential relaxations in the memory function of S(Q,ω)

$$m_Q(t) = \omega_o^2(\gamma-1)\exp(-D_T Q^2 t) + 2\,\gamma_o\,\delta(t) + (Q^2\Delta^2/\rho)\exp(-t/\tau)$$

$$\Delta^2 = \rho[C_\infty^2 - C_o^2]$$

IXS Investigations



$\omega_P \, \tau_R \sim 1$ **for IXS**

T ~ 350 K

MCT does not apply but we can estimate the **relaxation time**

For IXS **pressure** does not affect the structural relaxation of water

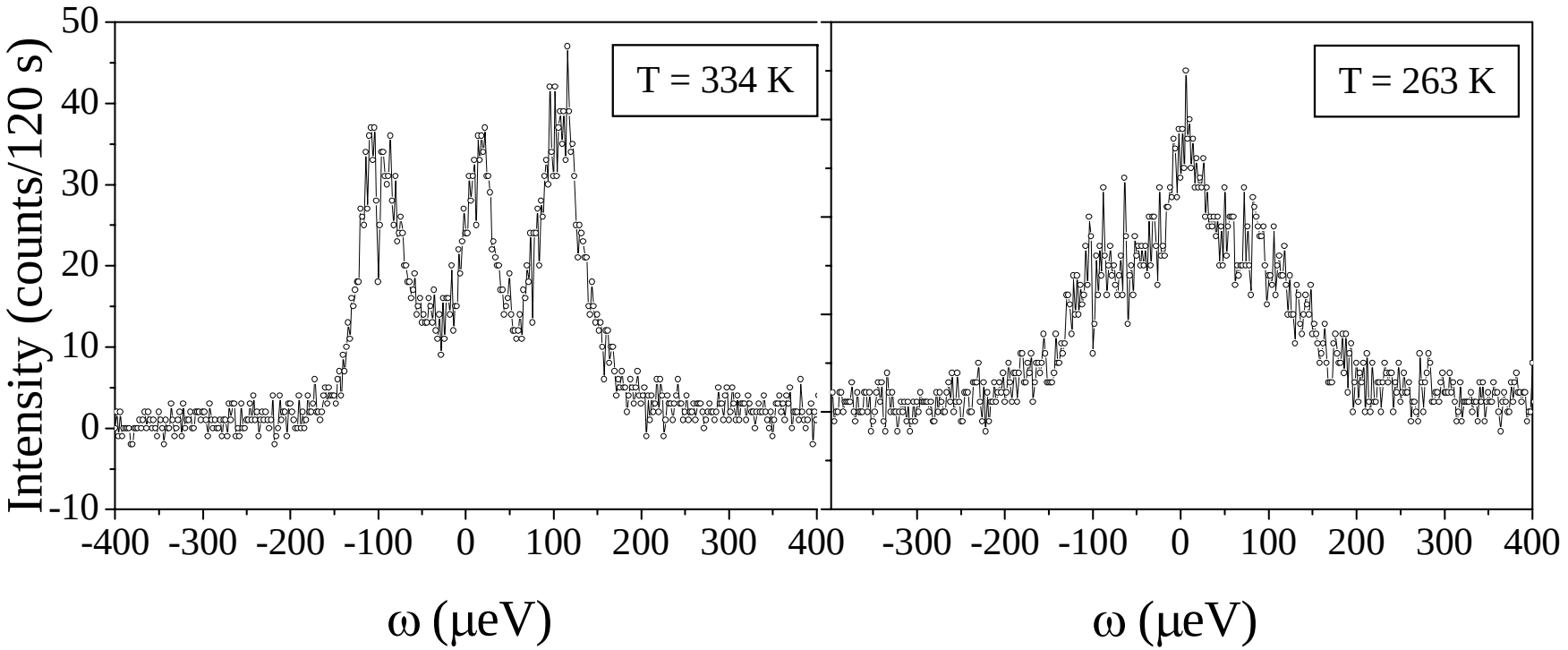
IUVS first measurements

Water from liquid to undercooled state

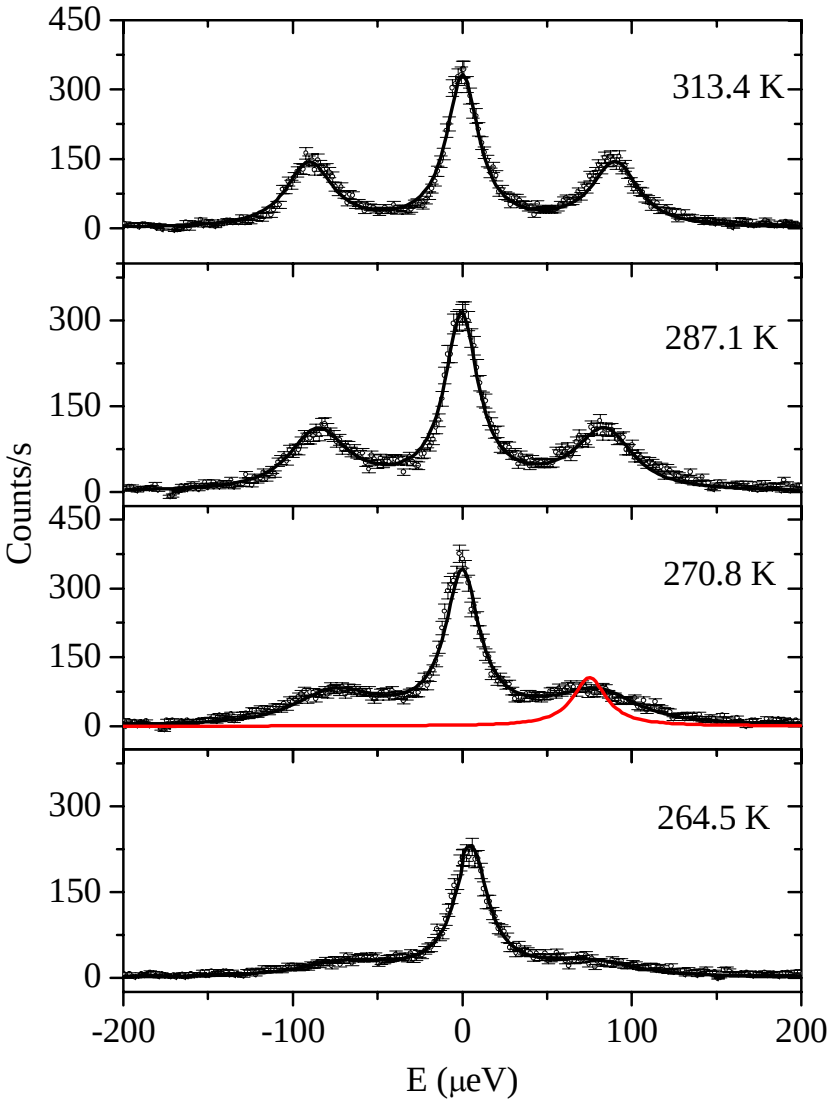
Cell: Fused Silica Fluorescence standard Cell

Momentum Transfer: 0.1 nm^{-1}

Temperature range: 343 → 248 K



The Modeling



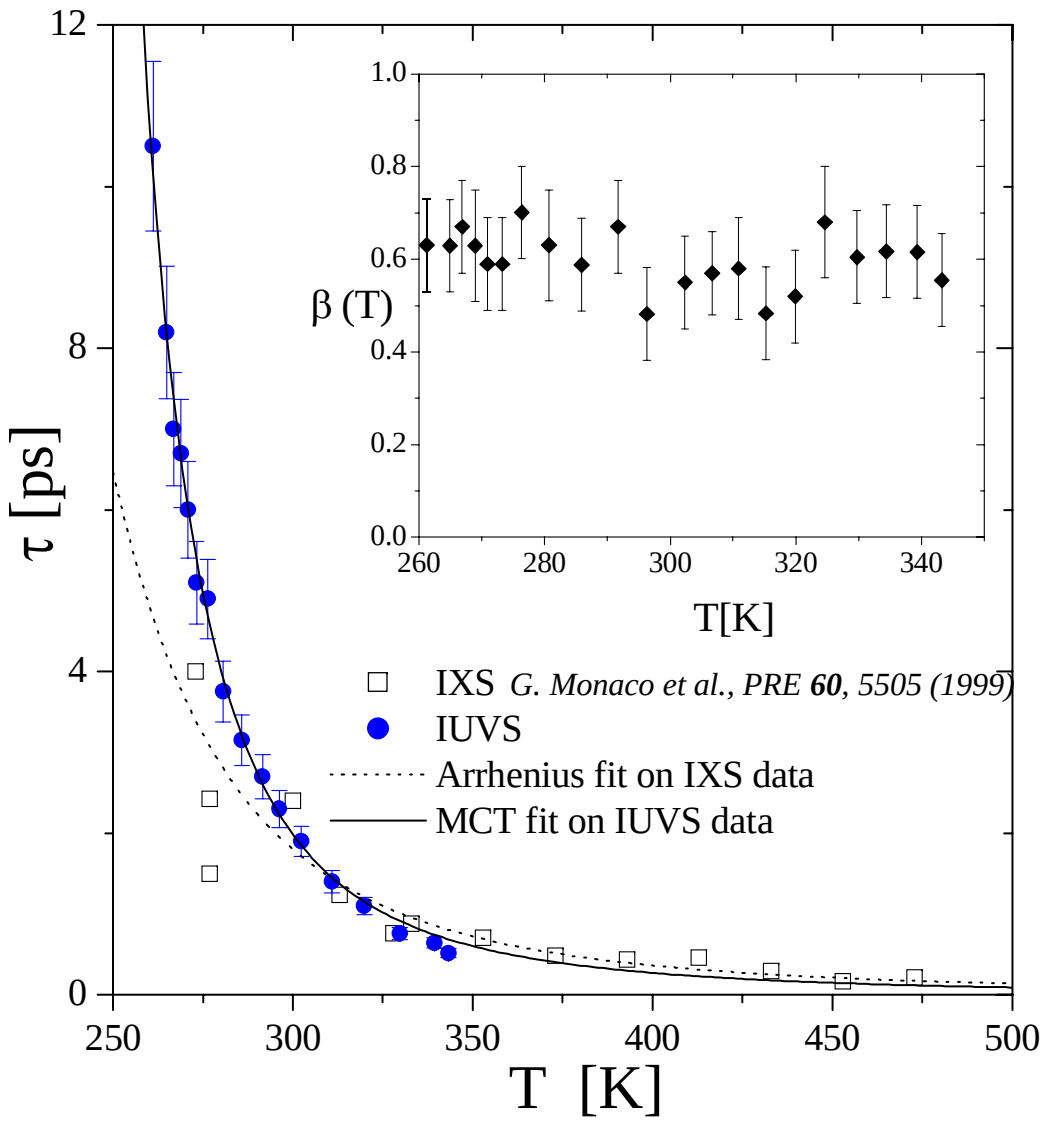
$$S(Q,\omega) = (2C_o^2Q^2/\omega)\mathrm{Im}[\omega^2 - \omega_o^2 - i\omega m_Q(\omega)]^{-1}$$

$$m_Q(t) = \omega_o^2(\gamma-1)\exp(-D_TQ^2t) + 2\,\gamma_o\,\delta(t) + \\ + (Q^2\Delta^2/\rho)\exp(-t/\tau)^\beta$$

$$\Delta^2 = \rho[C_\infty^2 - C_o^2]$$

We add the **stretching** parameter β in order to properly fit our data → MCT

The Relaxation Time T-dependence



IUVS finds:

β T-independent and < 1

$\tau \sim (T-T_c)^{-\xi}$

with $T_c = 220 \pm 10$ K
and $\gamma = 2.3 \pm 0.2$

The Relaxation Time T-dependence

Agreement with MCT *W. Götze et al., Rep. Prog. Phys. (1992)*

Simulation of **MCT** finds: *F. W Starr et al., PRL (1999)*

$T_c = 226$ K

$\xi = 2.3$

The critical slowing down can be described as a **purely dynamical** process

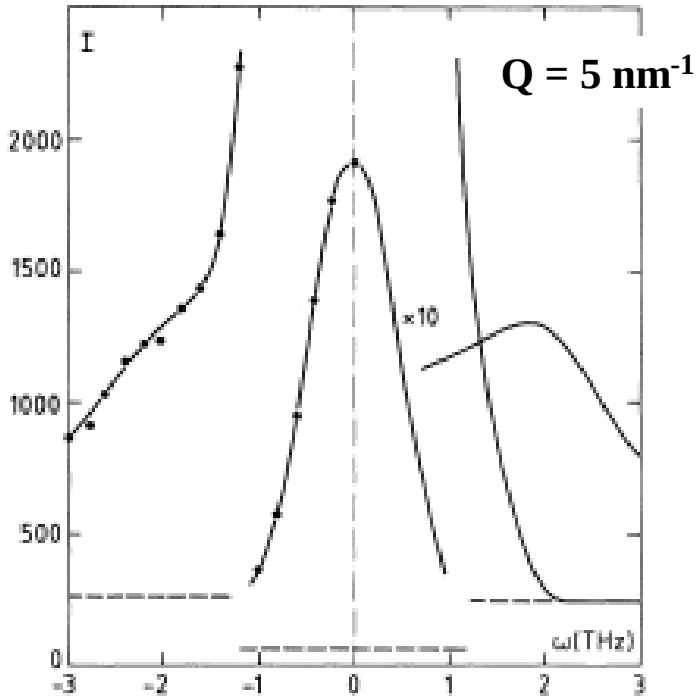
The observed anomalies in the transport properties, at **ambient pressure**, do not need an underlying thermodynamic singularity

C. Masciovecchio et al., PRL (2004)

Is There any "Fast Sound" in Water ?

High Frequency Sound @ Q > 1 nm^{-1} MD simulations (~ 3000 m/s)

A. Ramhan et al., PRL (1974)



Measured by NS (~ 3300 m/s)
in Heavy water D_2O

J. Teixeira et al., PRL (1985)

Fast Sound measured in gas mixtures *J. Bosse et al., PRL (1986)*

High Frequency Sound in water has a similar Origin of Fast Sound

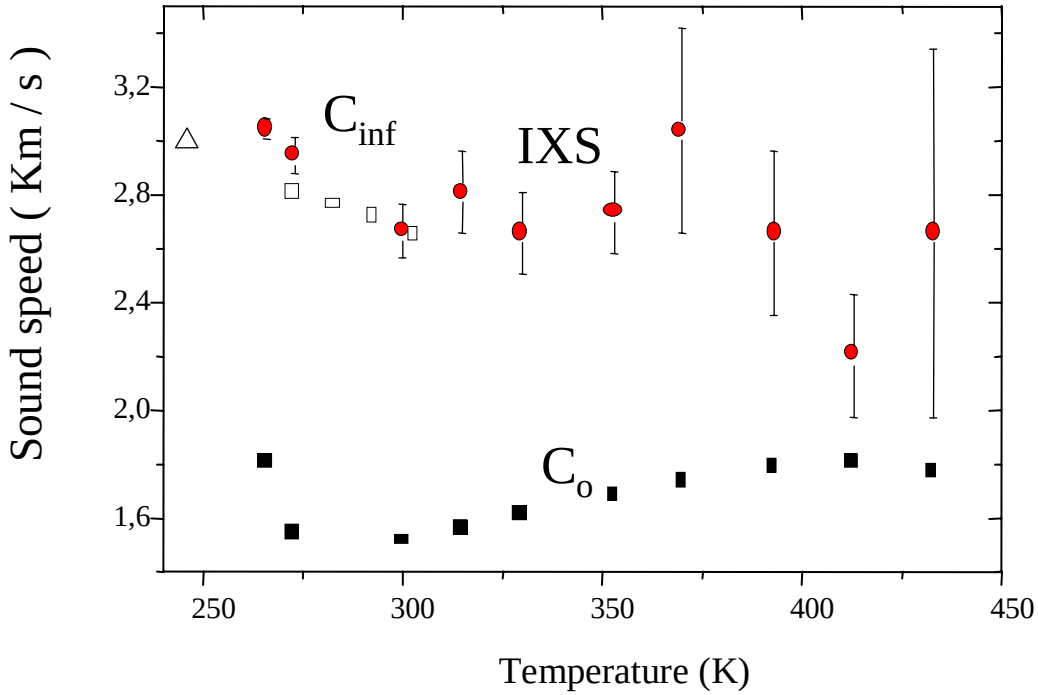
Mode propagating through hydrogen atoms

M. A. Ricci et al., PRL(1988)
……
U. Balucani et al., PRE (1993)

The Infinite Frequency Sound Speed

Transition from **Normal** to **Fast** Sound measured(?) by IXS

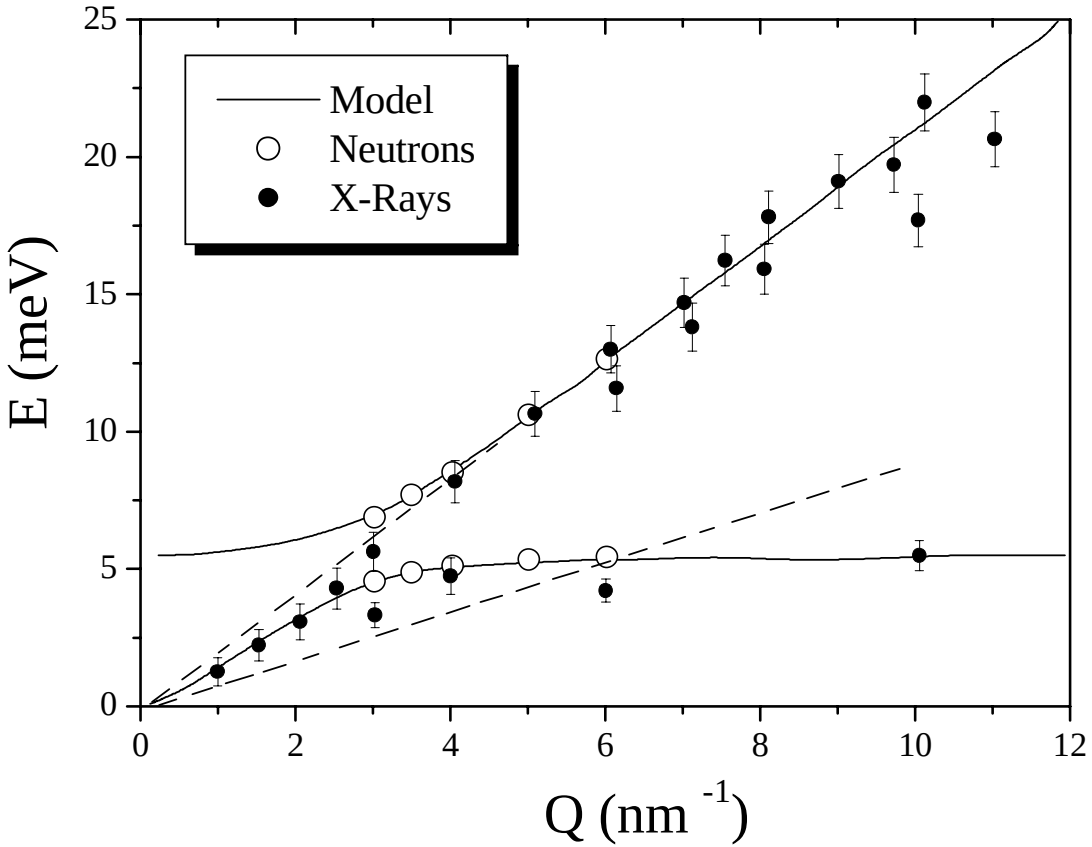
F. Sette et al., PRL (1999)



Fast Sound is the Relaxation Free Sound Speed C_∞

Most recent NS data and analysis

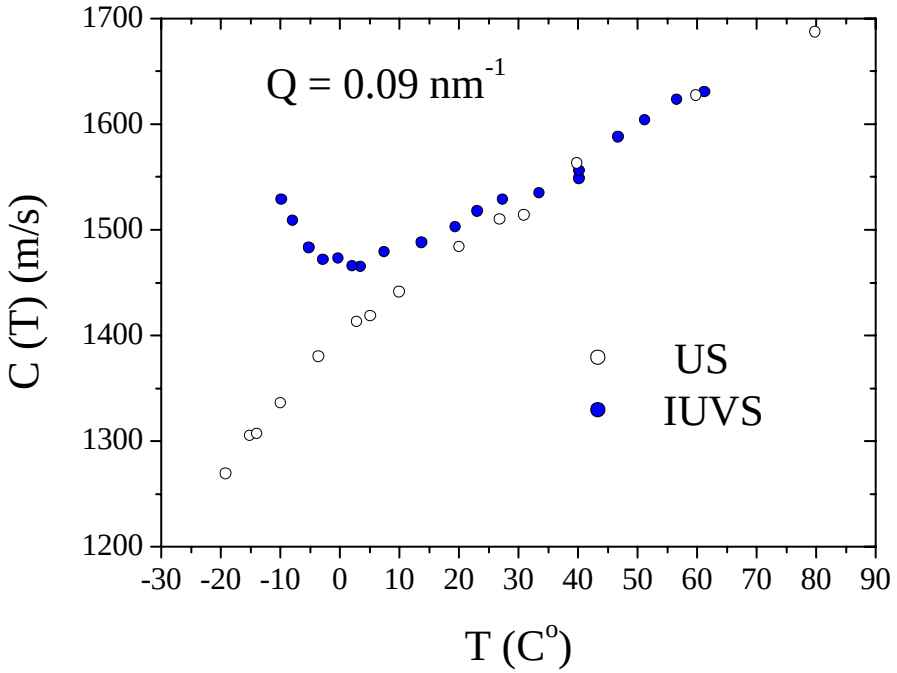
Back to **Neutron Scattering** *F. Sacchetti et al., PRE (2004)*

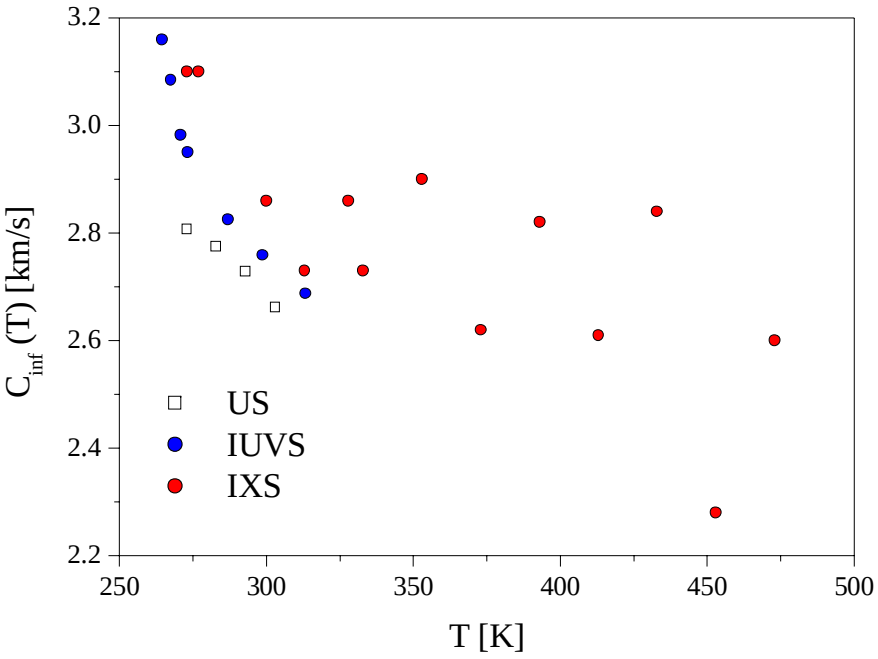


A phenomenological model of **interaction** between two vibrational branches

The Viscoelastic behavior of water

The Infinite Frequency Sound Speed as determined by **IUVS**





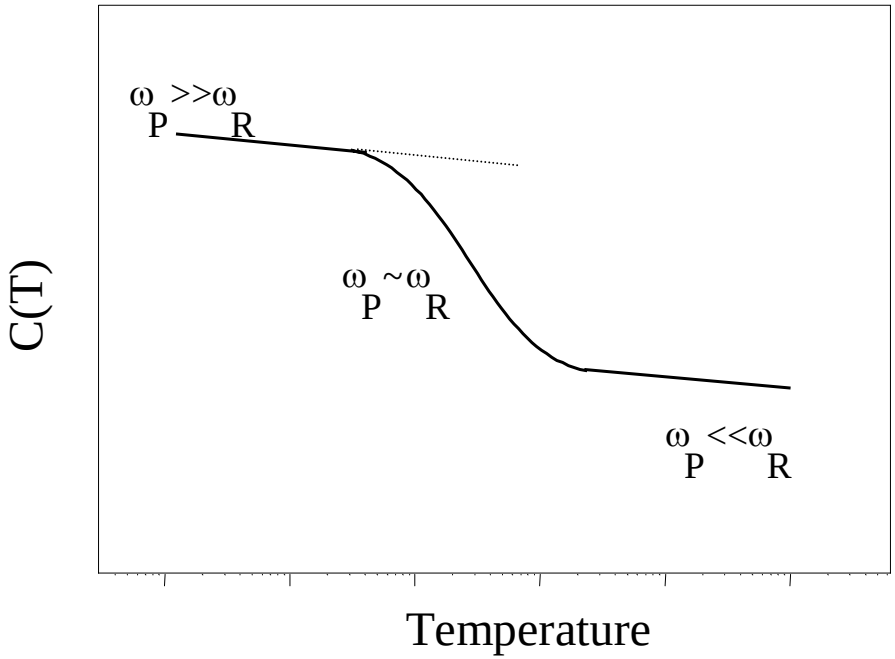
IUVS detects a clear departure from C_o

Fast Sound does not **exist** in water

S. C. Santucci et al., PRL (2006)

The "normal" behavior of water

Water behaves, at ambient pressure, as a **normal** glass-forming system:



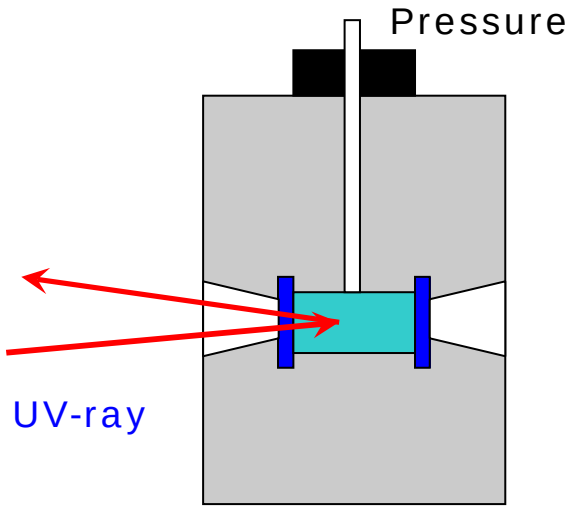
It shows a **viscoelastic** behavior

The infinity sound speed explains the origin of the **fast sound**

The structural relaxation follows the **MCT**

Let's apply Pressure to Water

High **Pressure** Set-up (Up to 4 kbar)



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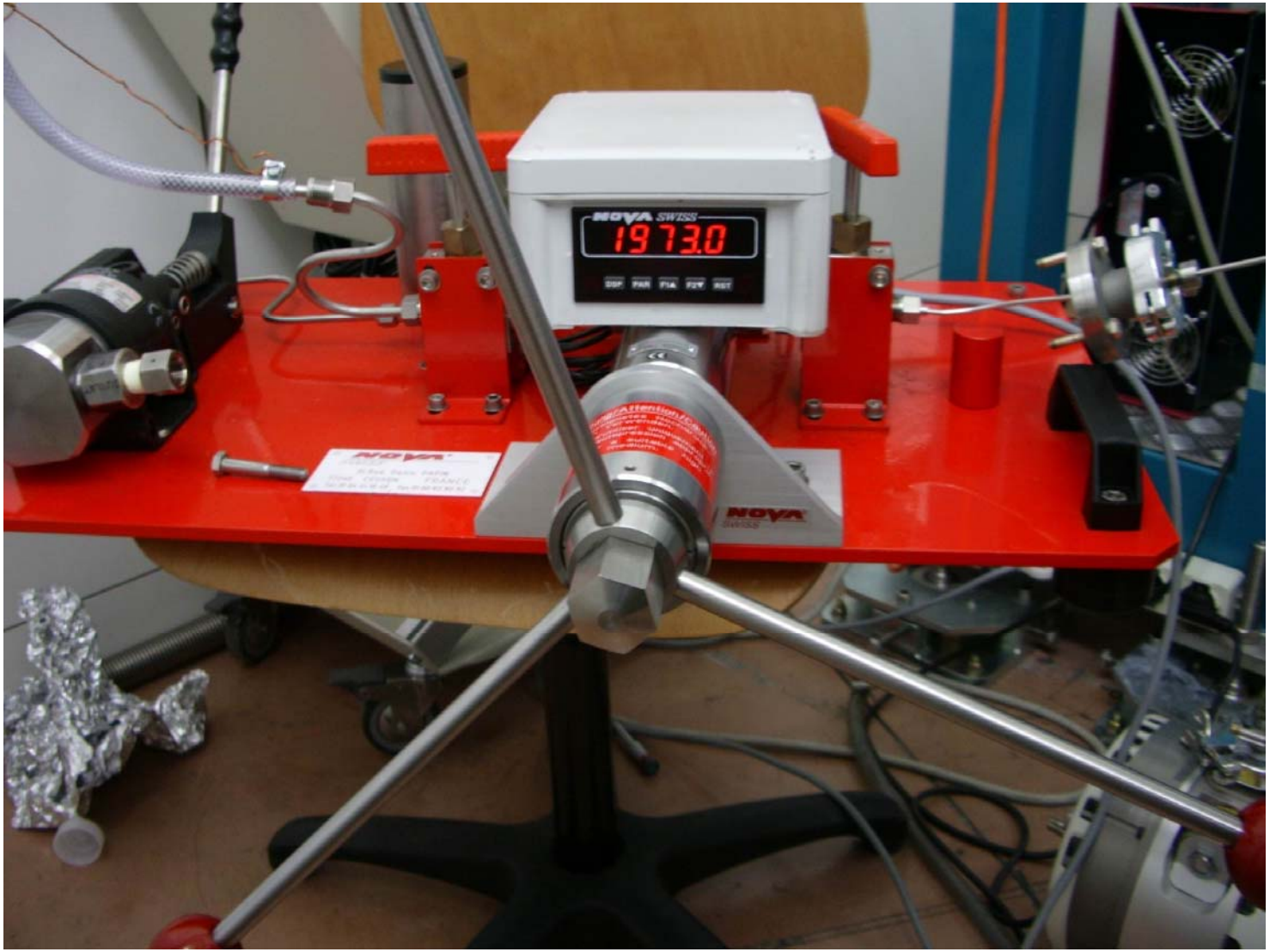
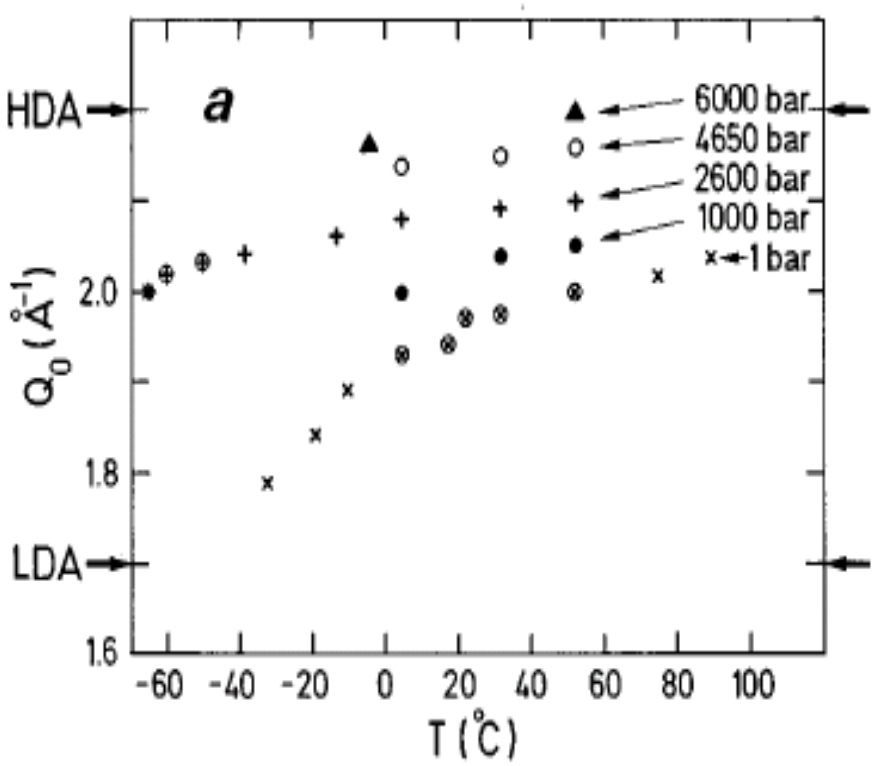


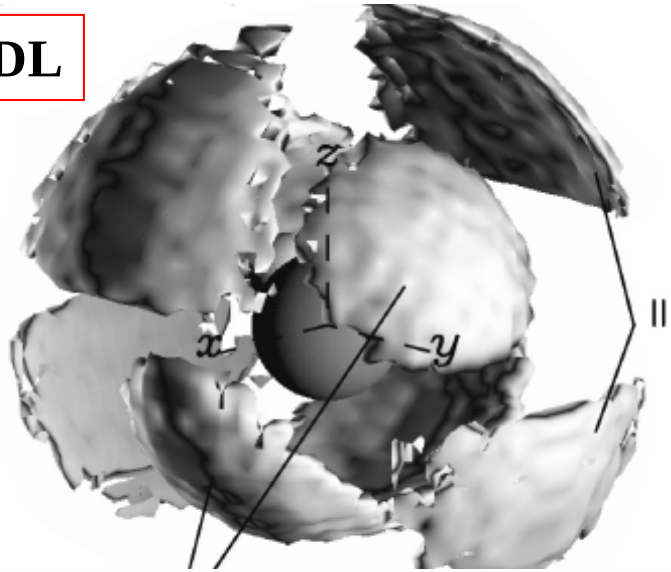
The Structure Behavior



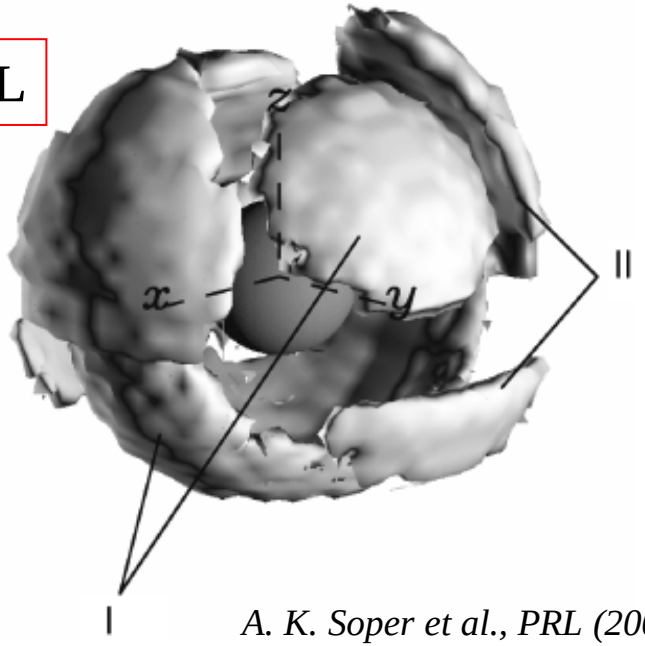
Water **Emulsions** with INS

M.-C. Bellissent-Funel et al., J. Chem. Phys. (1995)

LDL

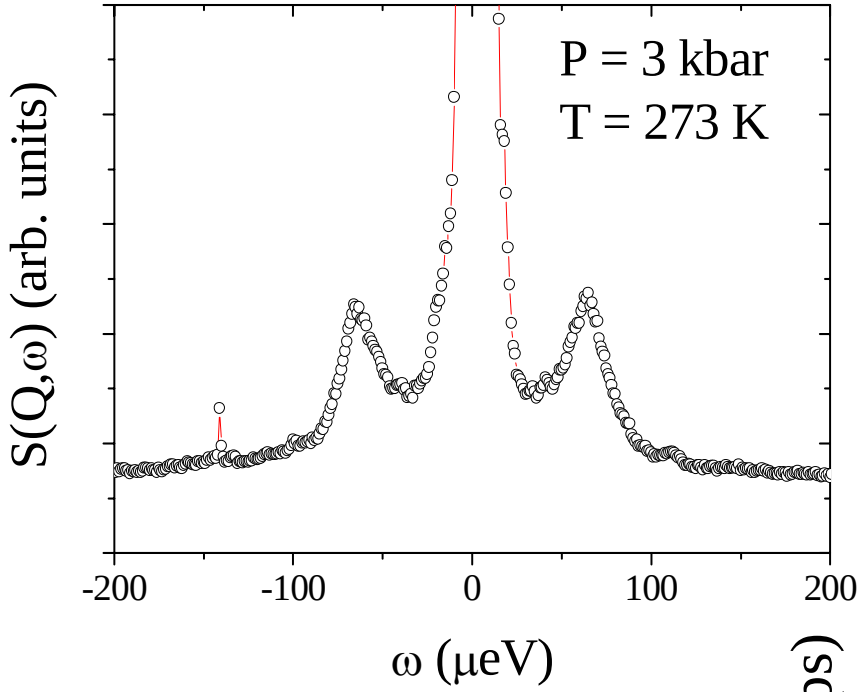


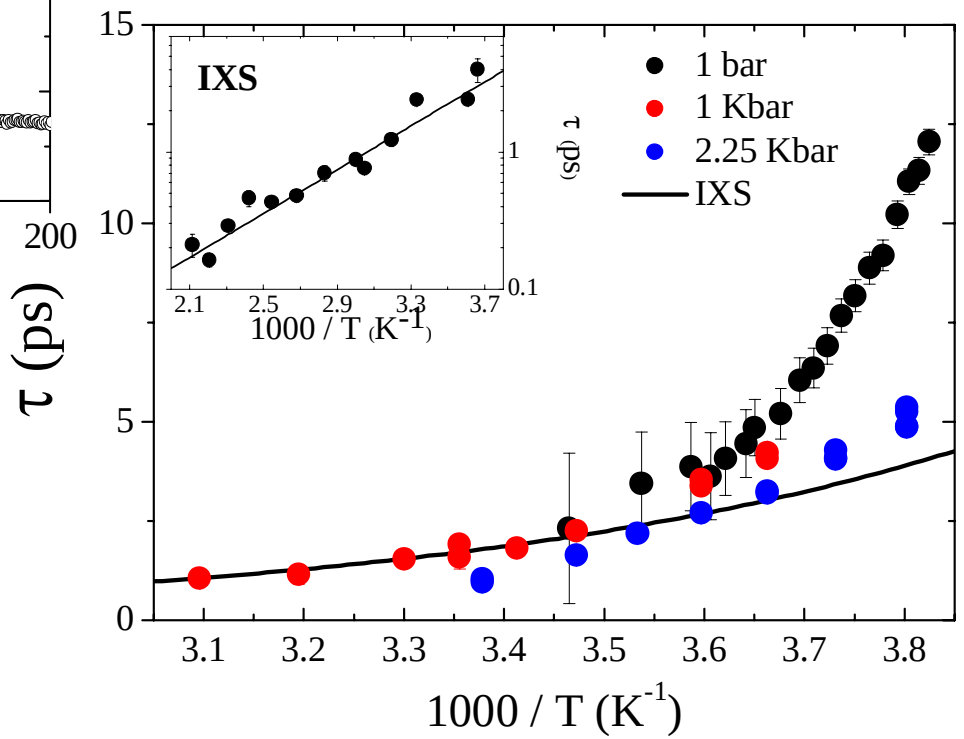
HDL



A. K. Soper et al., PRL (2000)

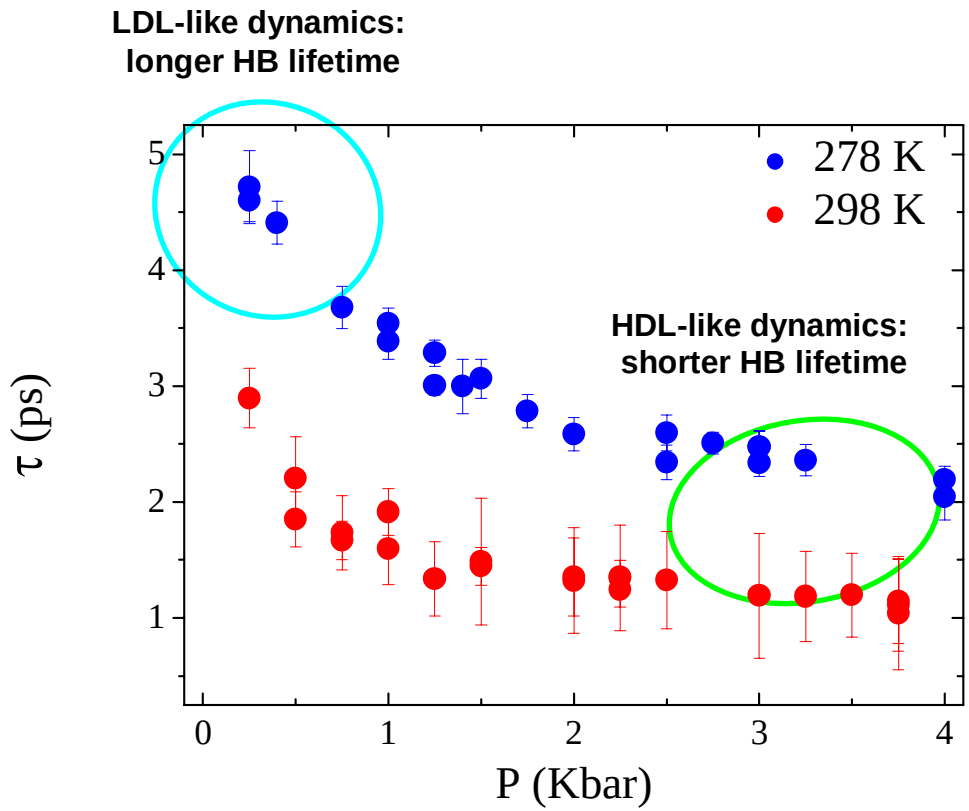
Relaxation Time





The anomalous behavior of τ could be related to **Structural Changes**
(reminiscence of LDL-HDL phase transition)

Relaxation Time vs. Pressure



Correlation beteween **Structure** and **Dynamics**

Viscosity – τ different behavior with **Pressure**

IUVS agrees with **Liquid-Liquid** phase transition Hypothesis

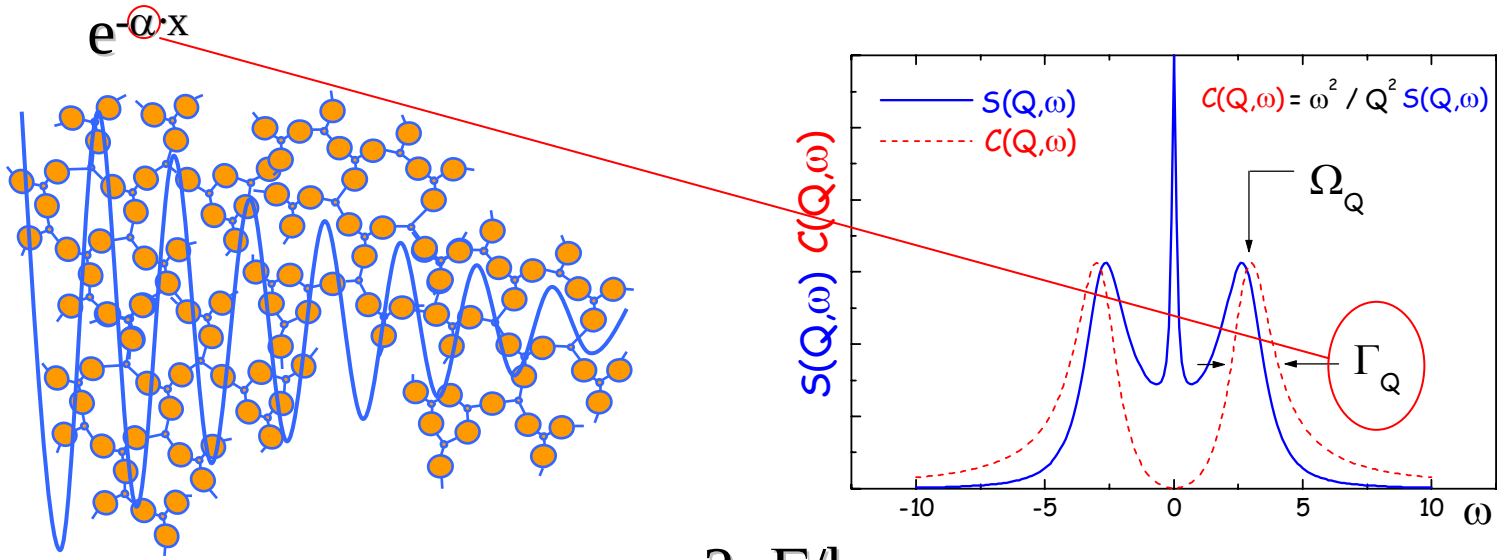
Activation Energy does change with pressure

Infinity frequency **Sound Speed** changes as function of pressure

→ Disagreement with previous IXS data

F. Bencivenga et al., submitted to Nature

Acoustic Attenuation in Glasses



$$\alpha = 2\pi\Gamma/hc_s$$

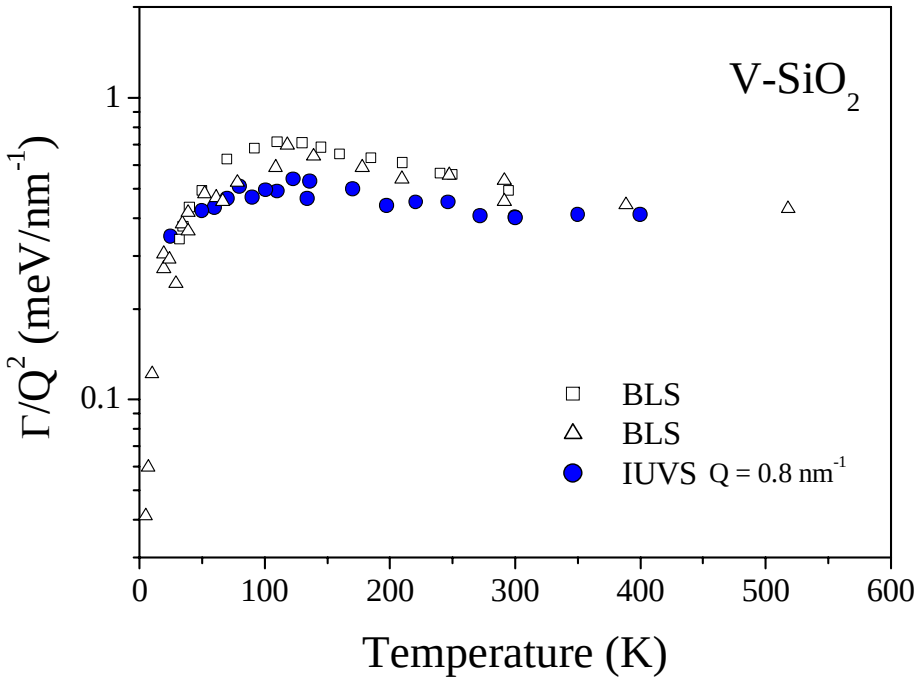
What is known:

1) At T < 10 K US and BLS investigations **Γ(T)** exhibit a small, frequency dependent peak.

2) Between 10 and 200 K **Γ(T)** shows a second peak.

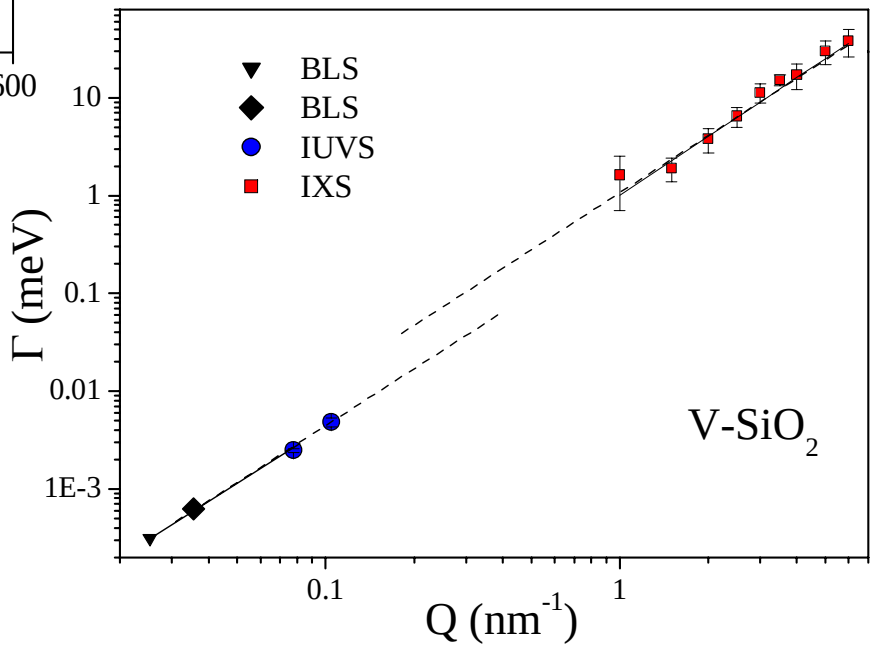
3) At room temperature **Γ(T)** scales as Q^2 and does not change at higher temperatures (plateau).

IUVS measurements on Vitreous Silica



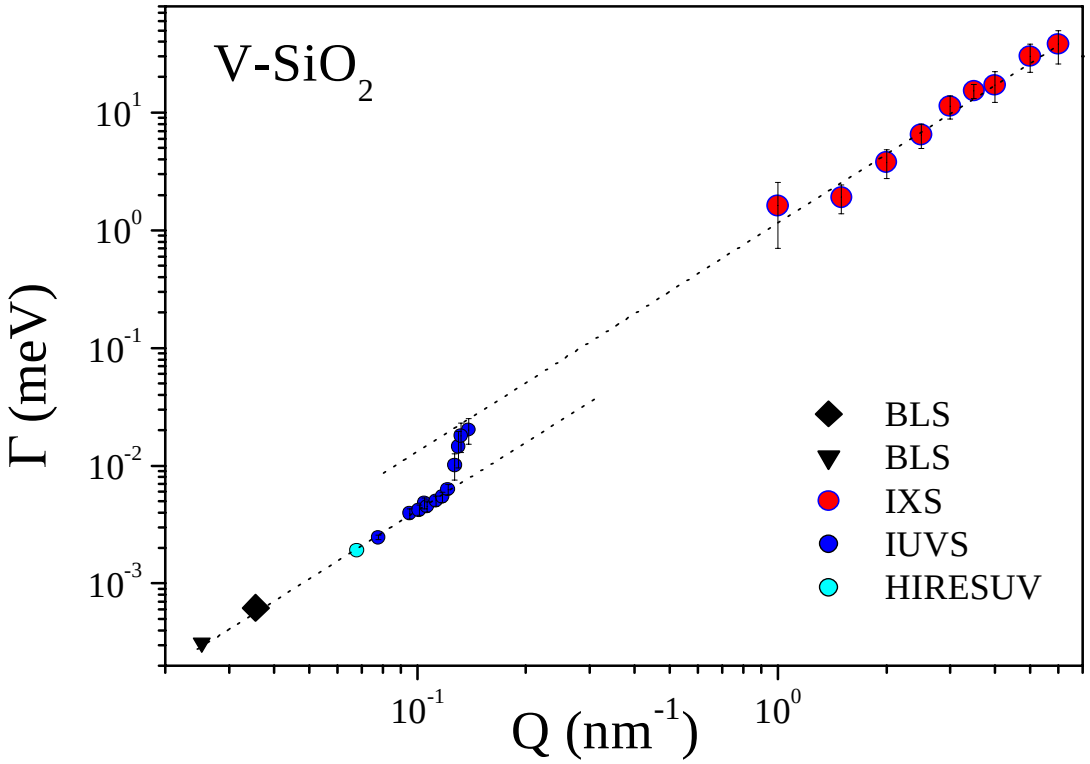
T-dependent measurements strongly **support** the anharmonic model presented by J. Fabian et al.,

Q-dependent measurements show the existence of a **change** of regime between 0.1 and 1 nm^{-1}



C. Masciovecchio et al., PRL (2004)

IUVS picture



C. Masciovecchio et al., PRL 2006

IUVS measurements demonstrate the existence of a ξ' of about 40 nm.

S(Q) maximum ~ 15 nm^{-1} → ξ' is in the range of 100 particle size

What could be the origin ?

Simulation of two-dimensional amorphous nanometric Lennard Jones systems

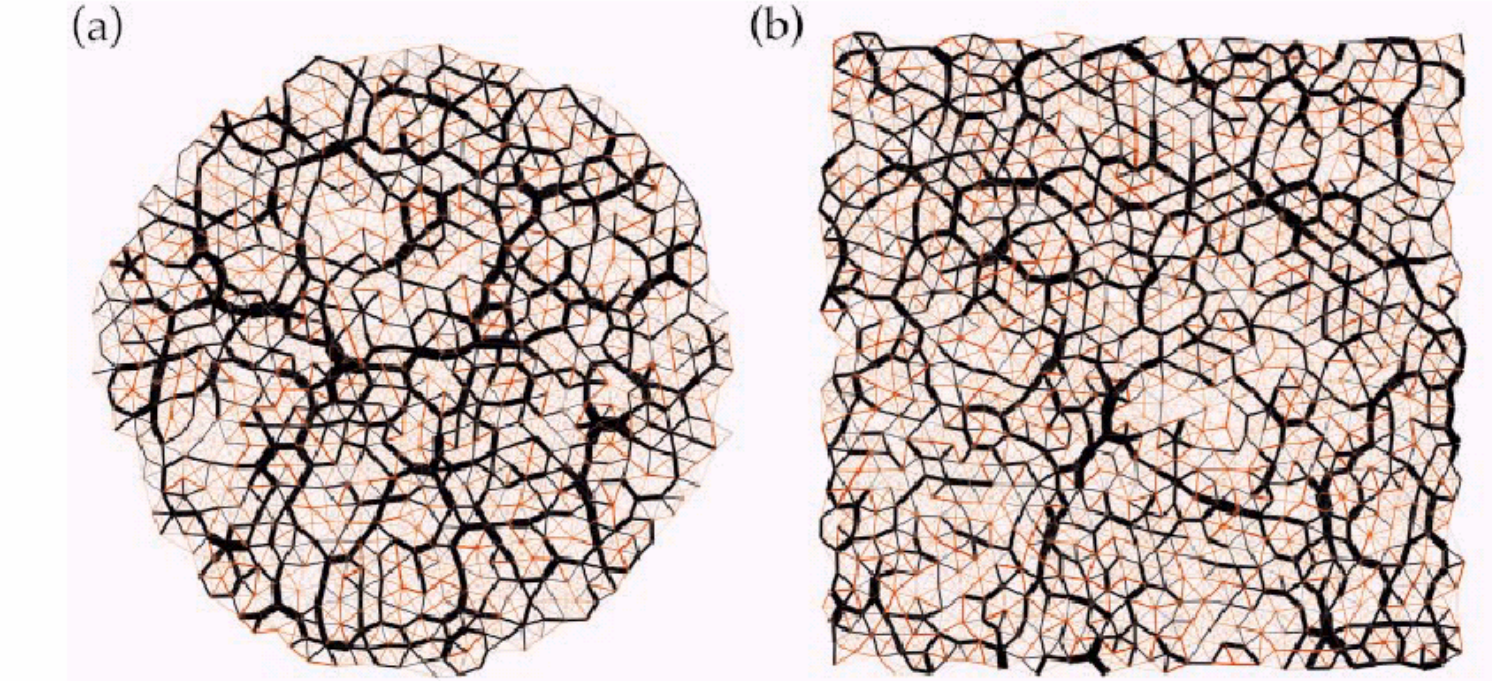


FIG. 1. (Color) Representation of the network of quenched stresses in two small quenched Lennard-Jones particle systems in two dimensions: (a) a disk-shaped aggregate of diameter $2R \approx 32a$ containing $N = 732$ particles (protocol I) on the left and (b) a periodic bulk system with $L = 32.9a$ and $N = 1000$ (protocol III) on the right-hand side. The line scale is proportional to the tension transmitted along the links between beads. The black lines indicate repulsive forces (negative tensions), while the red links represent tensile forces between the verticies. Both shown networks are very similar despite different symmetries and quench protocols. They are strongly inhomogeneous and resemble the pattern seen in granular materials. Zones of weak attractive links appear to be embedded within the strong skeleton of repulsive forces.

A. Tanguy et al., PRB (2002)

Existence of a characteristic length ξ below which the classical mechanical approach becomes inappropriate. ξ is about 30 particle sizes.

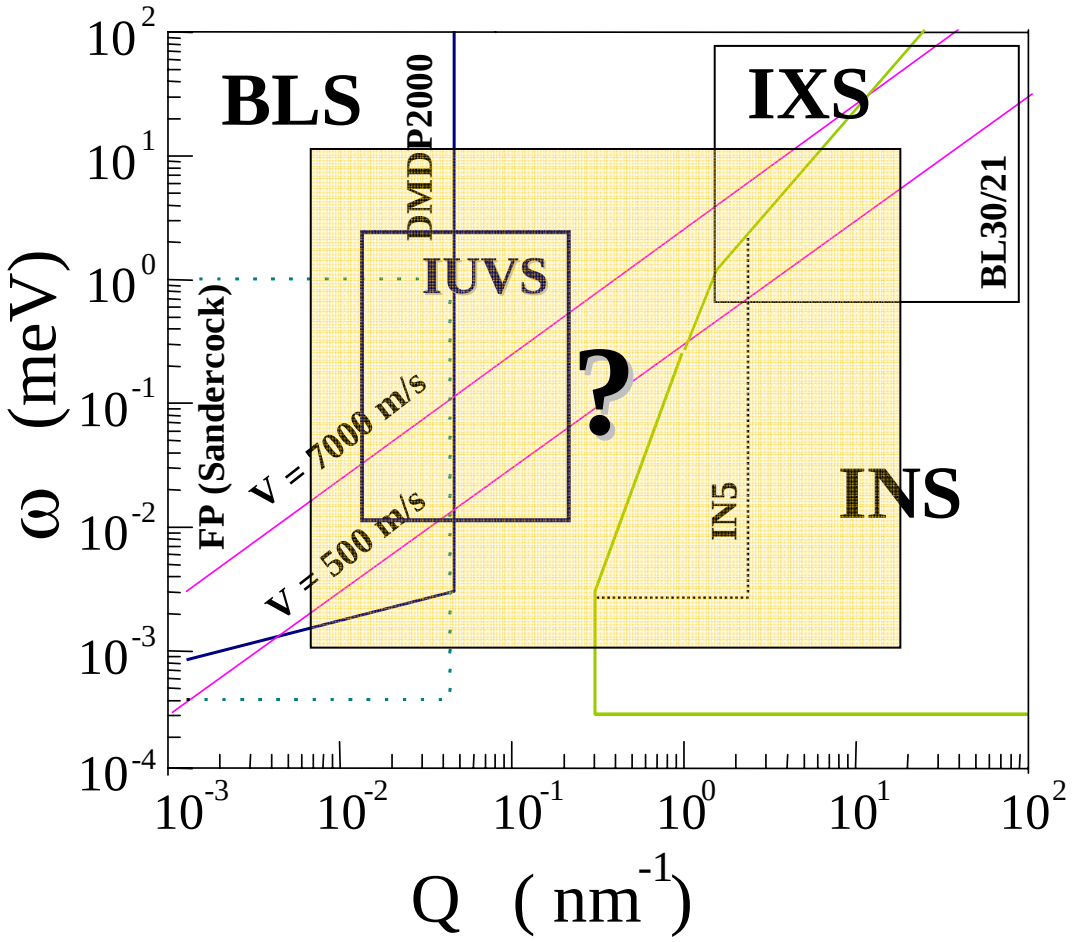
4. Conclusions

Inelastic Scattering seems to be a very useful technique for the study of collective excitations in disordered systems like **Liquids** and **Glasses**.

We've shown as in **water** as IXS and IUVS have experimentally demonstrated that the anomalies in the transport properties do not need an underlying thermodynamic singularity (used to explain properties as negative volume of melting, density maximum in normal liquid range, etc. ..).

In **vitreous silica** we have been finding an anomalous increase of the sound wave damping that we interpret as the existence of **inhomogeneous** regions (with different force constant) in the sample.

Can we fill the Gap in the Kinematic Region?



YES ! with FEL based Transient Grating Spectroscopy