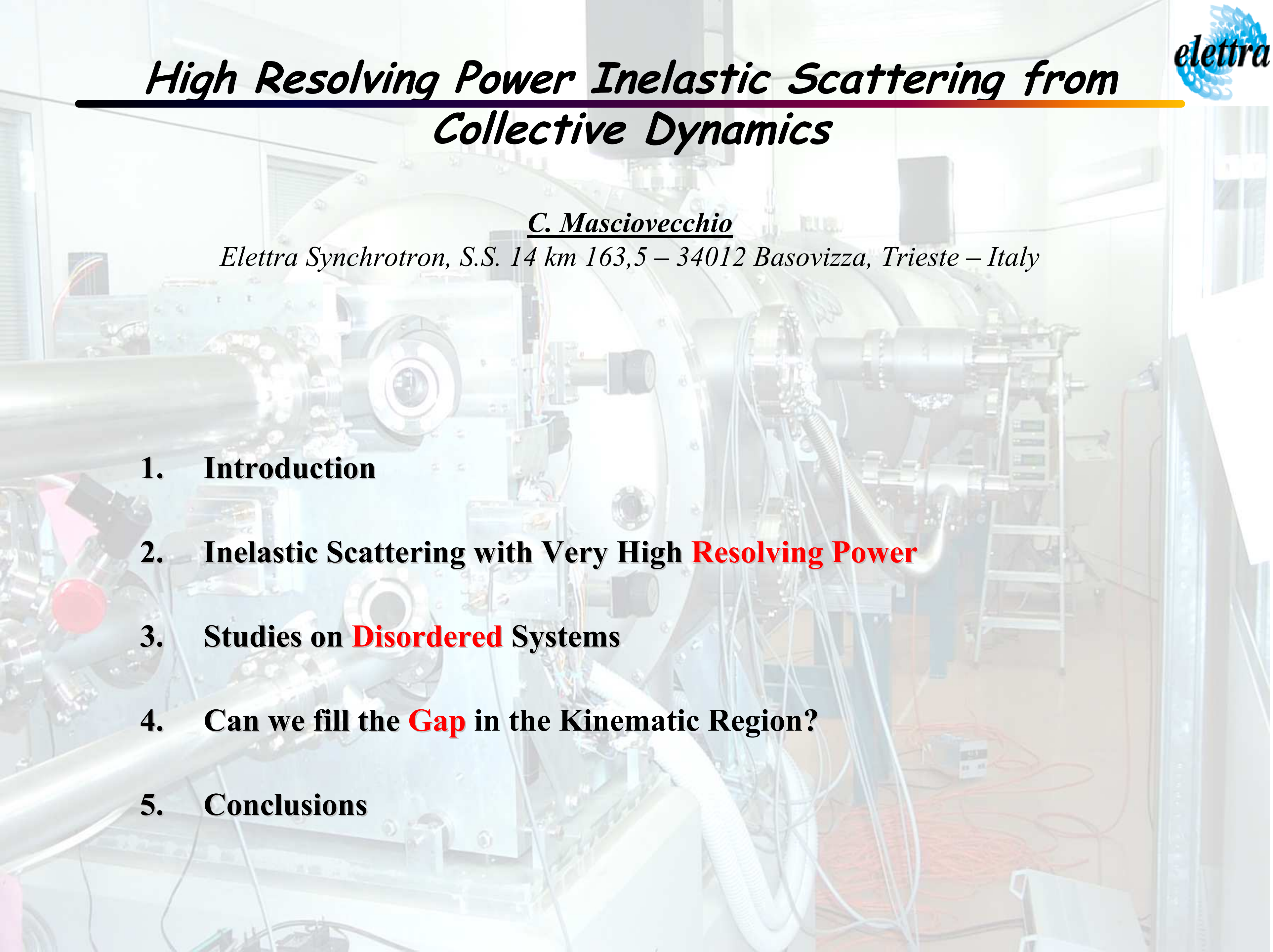

High Resolving Power Inelastic Scattering from Collective Dynamics

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1. **Introduction**
2. **Inelastic Scattering with Very High Resolving Power**
3. **Studies on Disordered Systems**
4. **Can we fill the Gap in the Kinematic Region?**
5. **Conclusions**

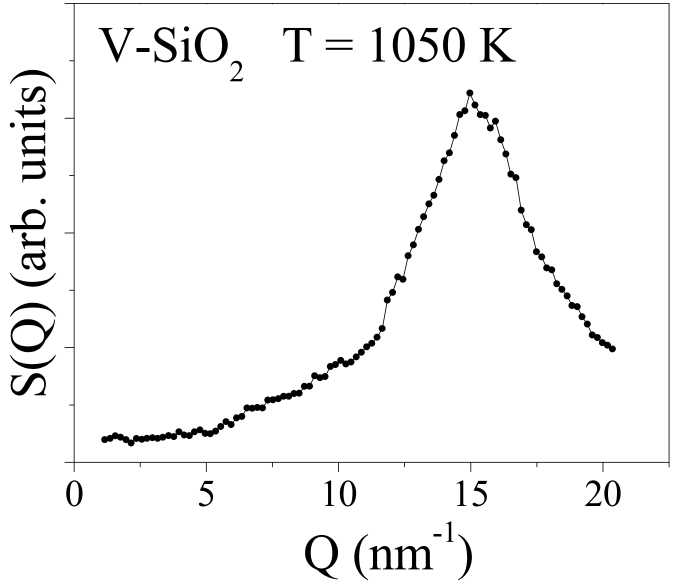
1. Introduction

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 on disordered systems in the **Mesoscopic** region

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



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

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**

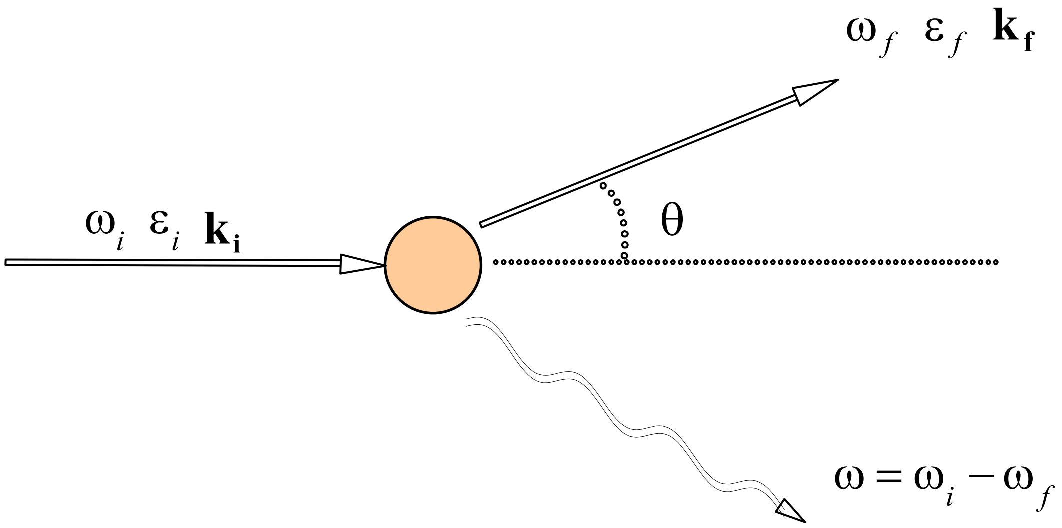
$$S(\mathbf{Q},\omega) = \int_{-\infty}^{\infty} dt \int d\mathbf{r} \langle (n(\mathbf{r},t) - n)(n(0,0) - n) \rangle e^{i(\omega t - \mathbf{Q}\cdot\mathbf{r})}$$

$n(\mathbf{r},t)$	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 Process



$$\omega = \omega_i - \omega_f$$

$$\mathbf{Q} = \mathbf{k_i} - \mathbf{k_f}$$

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

Visible → UV

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

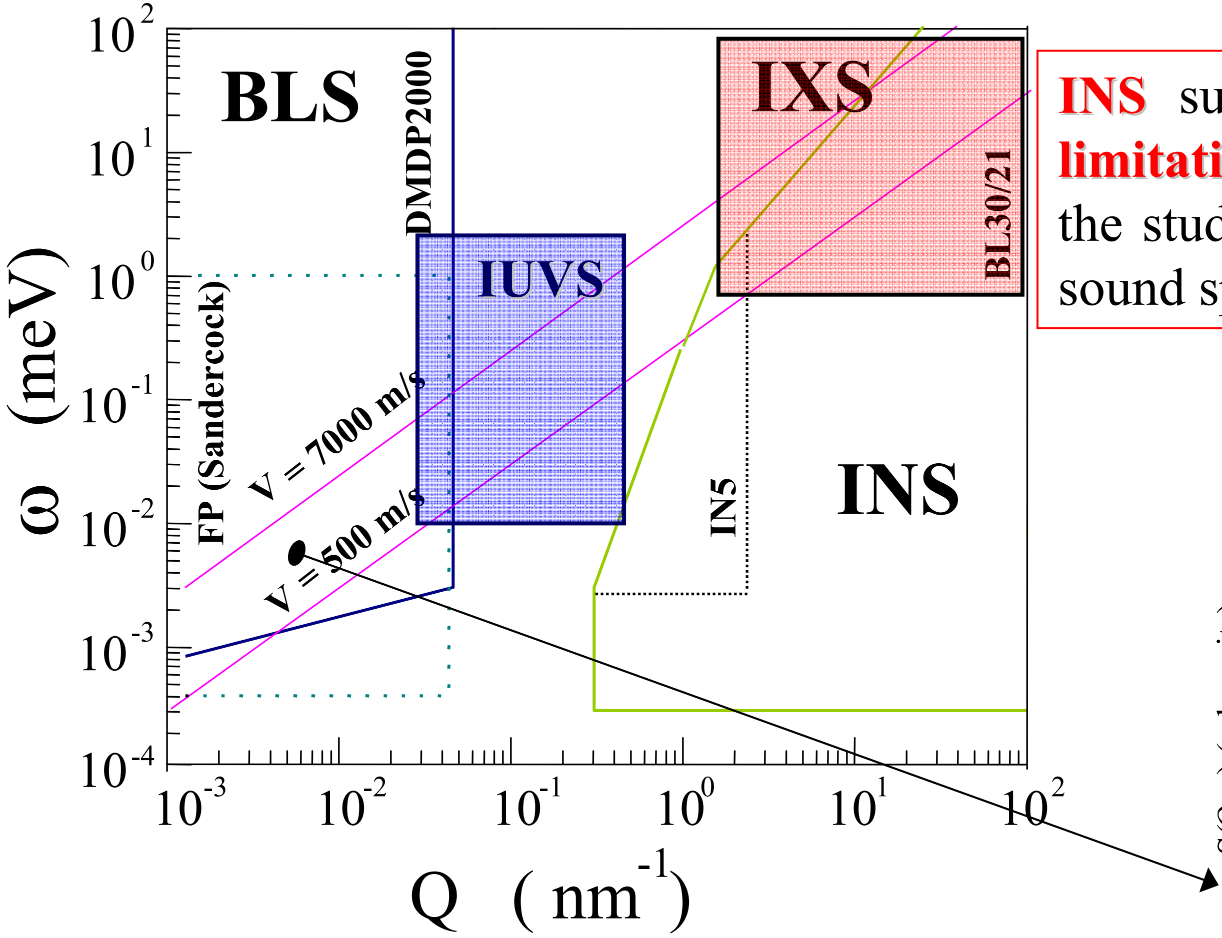
$$I_{if}(\mathbf{Q},\omega) \propto \frac{\omega_f}{\omega_i}(\varepsilon_o \cdot \varepsilon_1)\left|f(Q)^2\right| S(\mathbf{Q},\omega)$$

Density Fluctuation Spectrum

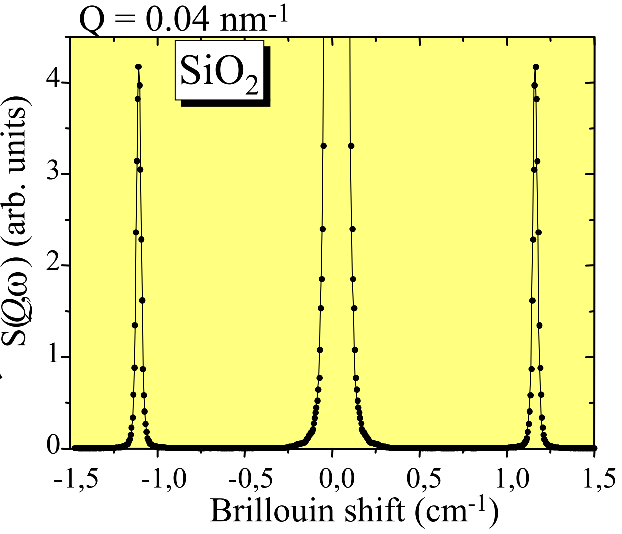
X

Our interest: Studying S(**Q**,ω) in **disordered** systems

Available probes to measure the S(Q,ω)



INS suffers of important kinematic **limitations** which make very difficult the study of sound-like modes with a sound speed larger than 1500 m/s



Investigations in these Regions 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)

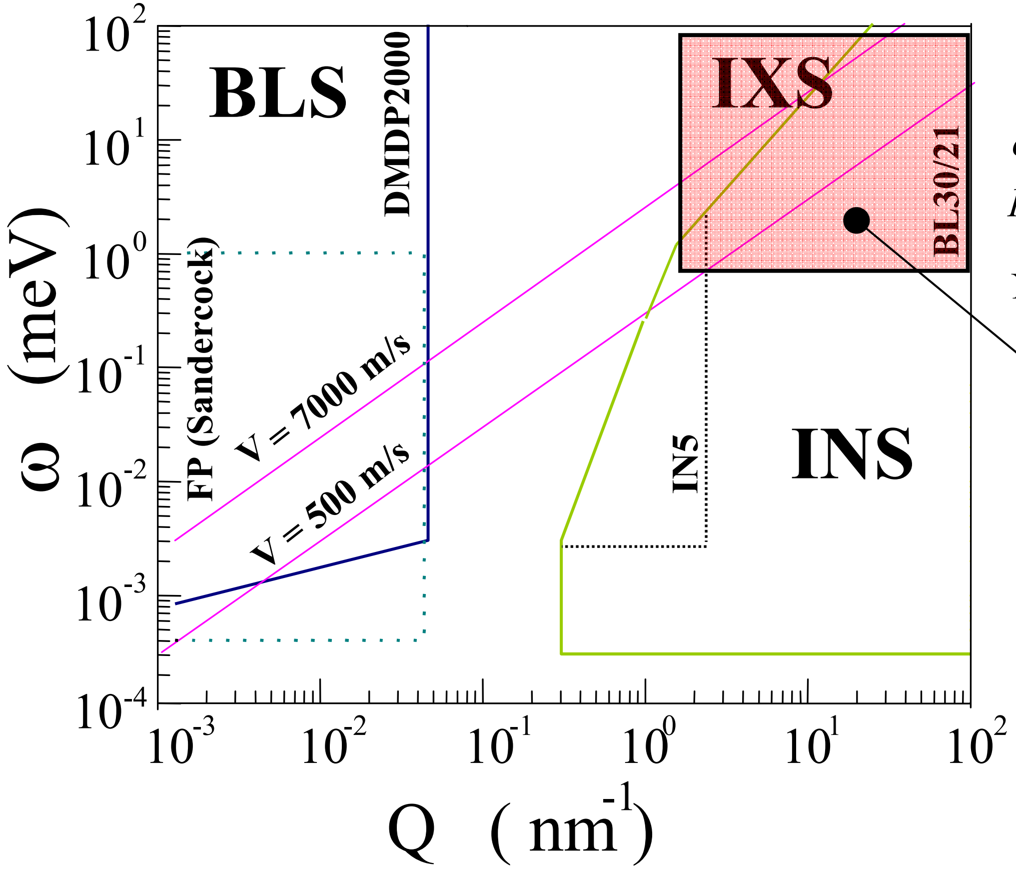
- Low count-rate experiments.
- Determination of Partial Dynamic Structure Factor in gas and fluid mixtures.
- Resonant Raman on Nanostructures.

2. Inelastic Scattering with Very High Resolving Power (E/ΔE)

Experimental requirements for **IXS**

- High incident photon **Flux** on the Sample (> 10^7 *photon/s*)
- High **Resolving Power** (≈ $10^7 - 10^8$)

~1 *count/s*



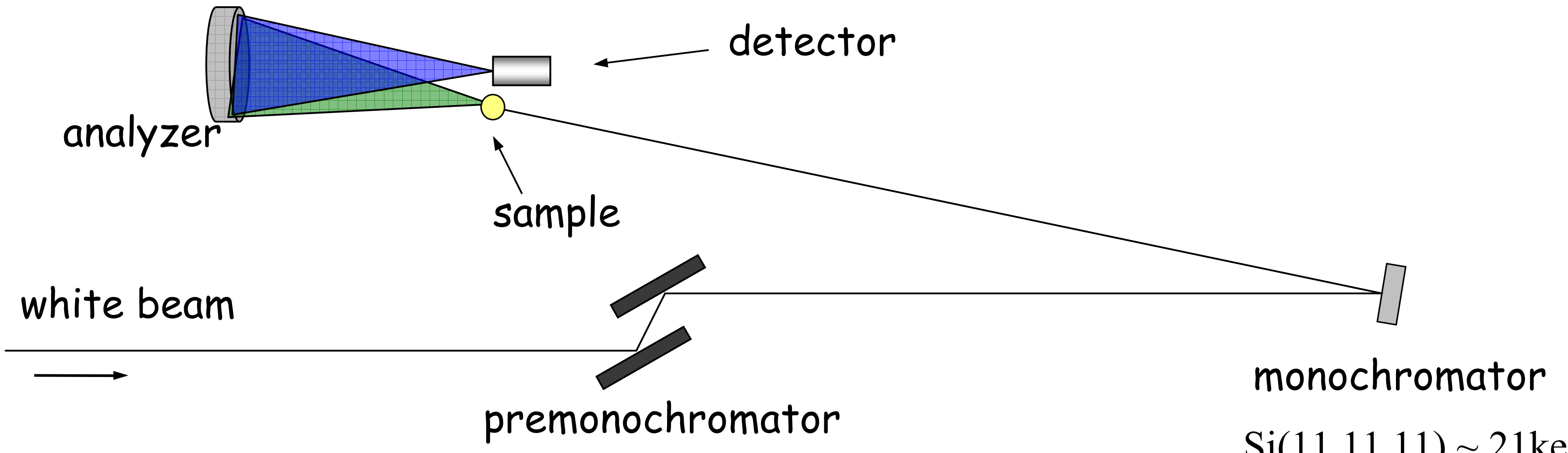
" Because of difficulty in energy resolution, the characteristic structure of the one-phonon process is lost and …… "

N. W. Ashcroft, N. D. Mermin, ***Solid State Physics***

$\omega \approx 1 - 10^2$ *meV*

$Q \approx 1 - 10^2$ nm^{-1}

BL21 & BL28 Triple Axis Spectrometers



Si(1,1,1) 10^{-4}

Si(11,11,11) ~ 21keV

Verbeni et al. J.of Sinc.Rad. (1996)

Flux

$$\omega_D > \Delta\theta \quad (\approx 20\,\mu rad)$$

$$\downarrow$$

$$\left(\frac{\Delta E}{E}\right)_h tg\,\theta_B$$

Resolution

$$\left(\frac{\Delta E}{E}\right)_h = \left(\frac{\Delta\lambda}{\lambda}\right)_h = \frac{4r_0}{\pi V}\frac{d_h^{\,2}}{\sqrt{b}}\,C\left|F_h\right|\,e^{-W} = \frac{2d_h}{L_P}$$

$$\left(\frac{\Delta E}{E}\right)_{11} = 3.6\ 10^{-8} \quad (10^8\ ph/s)$$

The Spherical Analyzer

In order to maximize the collected scattered intensity a
Spherical Analyzer
in a Rowland Geometry had to be used

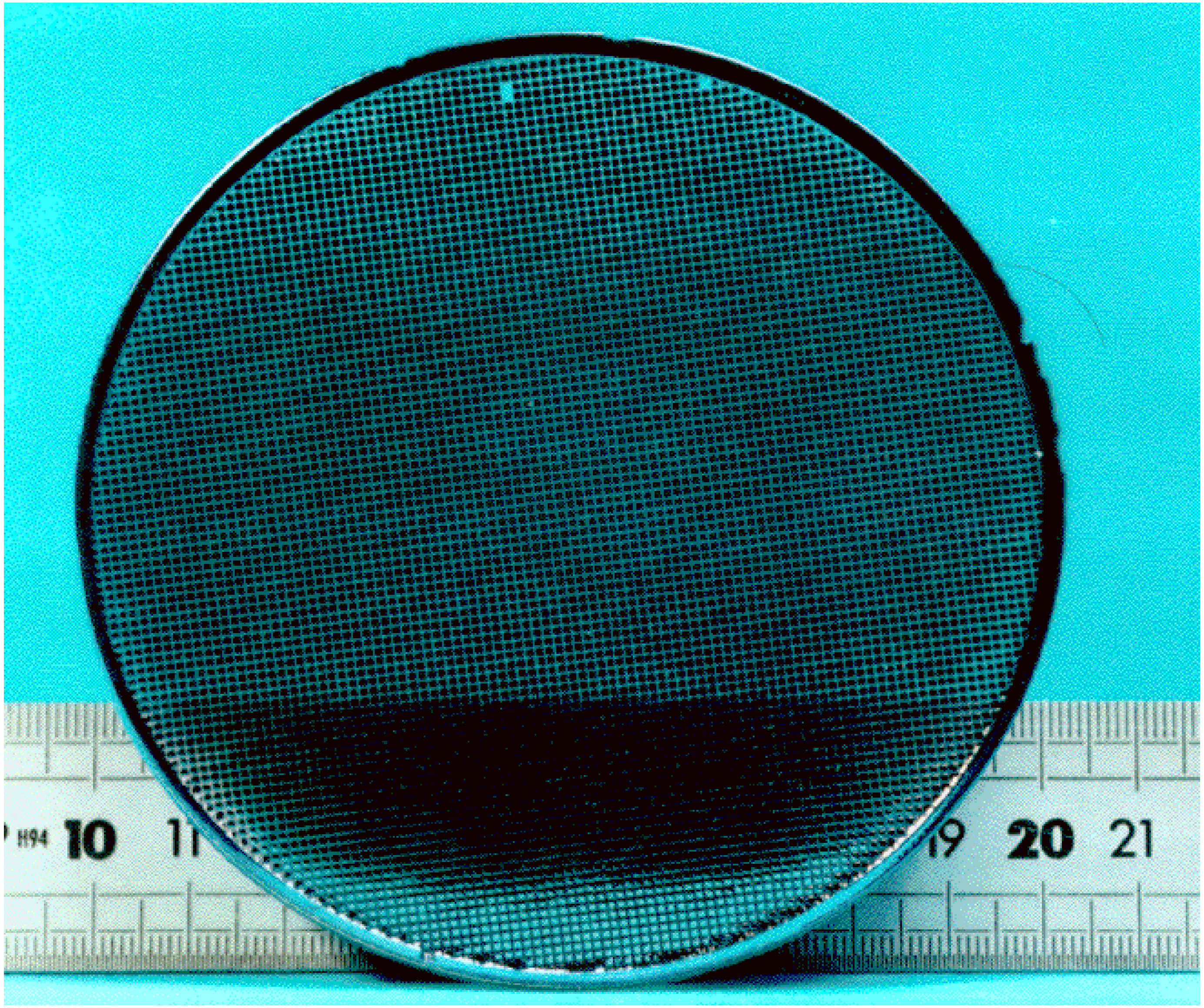
Bending a crystal introduce **important deformations** which can destroy the desired intrinsic energy resolution

$$\frac{\Delta d}{d} = \frac{\nu L_P}{R} << \frac{\Delta E}{E}$$

$$\left(\frac{\Delta E}{E}\right)_{11} = 3.6 \cdot 10^{-8} \Rightarrow R >> 1 \ km$$

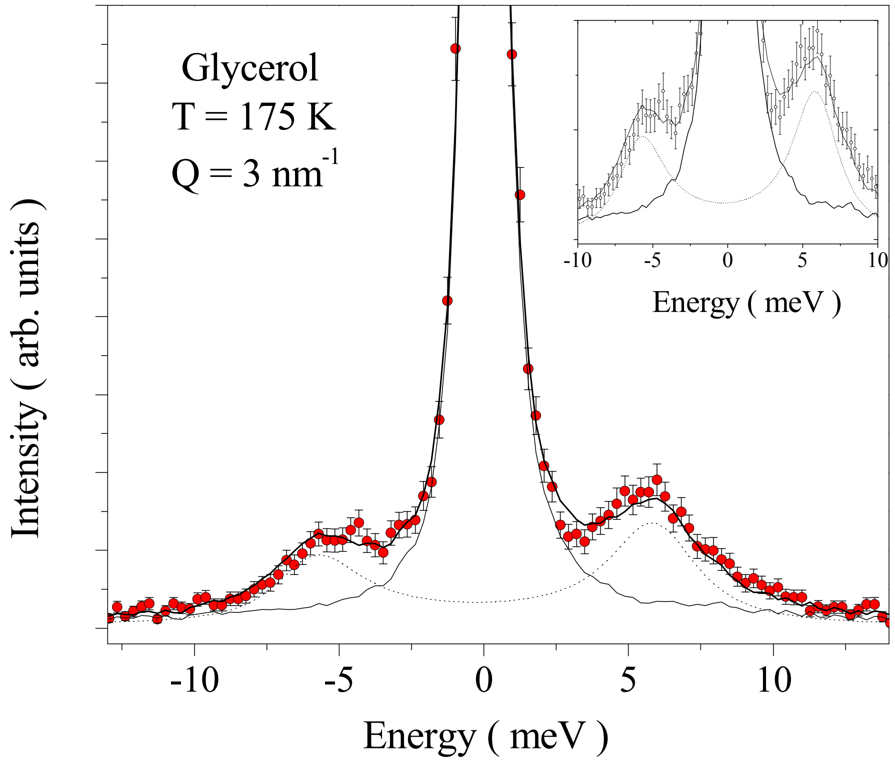
Solution: Glue small independent crystals on a spherical substrate maintaining ~ 10" relative alignment among them.

The Spherical Analyzer



Masciovecchio et al. Nucl. Inst. and Meth. (1996)

One Example



C. Masciovecchio et al., PRL (1996)
C. Masciovecchio et al., PRL (1998)
F. Sette et al., Science (1998)

Demonstration of the existence **at high frequencies** of acoustic-like excitations in the liquid and glass.

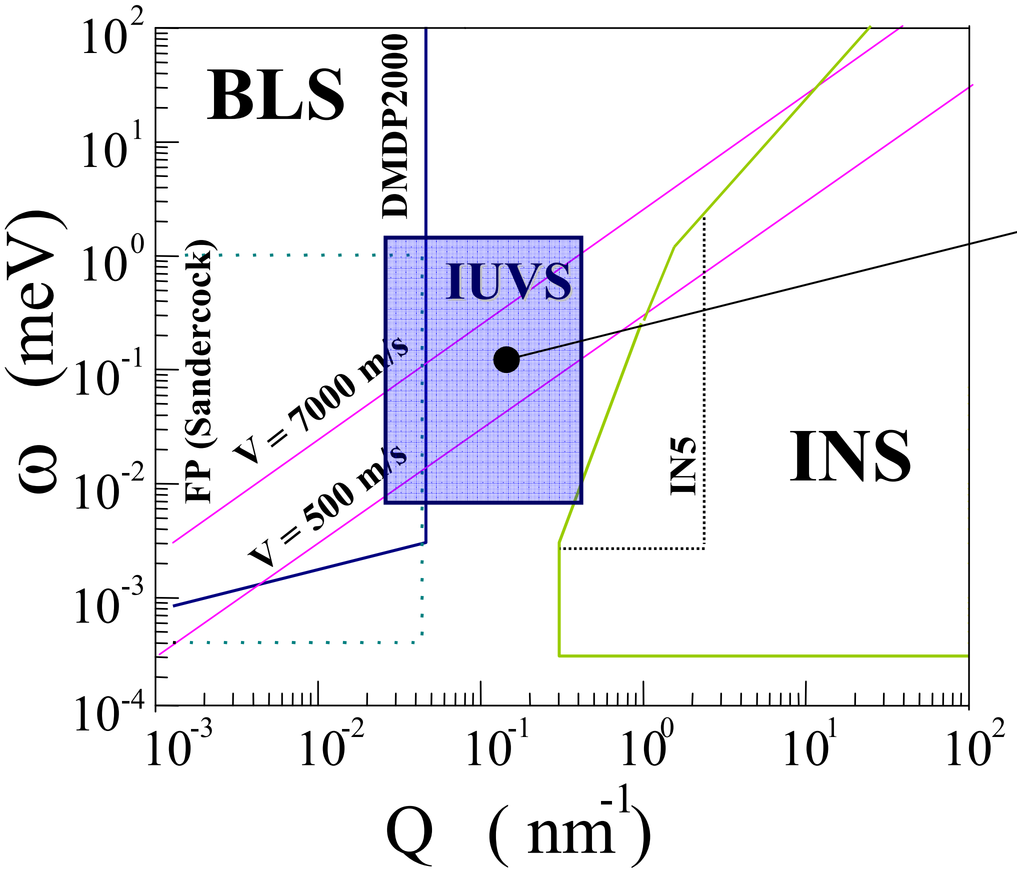
They propagate with the same sound speed found at low frequency.

The **eigenvectors** of a glass can be expressed as combination of acoustic-like plus a random component (possible explanation of the **excess** in the DOS).

Experimental requirements for IUVS

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

→ ~1 *count/s*



ω ≈ 10 - 10^3 *μeV*

Q ≈ 0.02 - 0.3 *nm*$^{-1}$

The Beamline Design and Construction

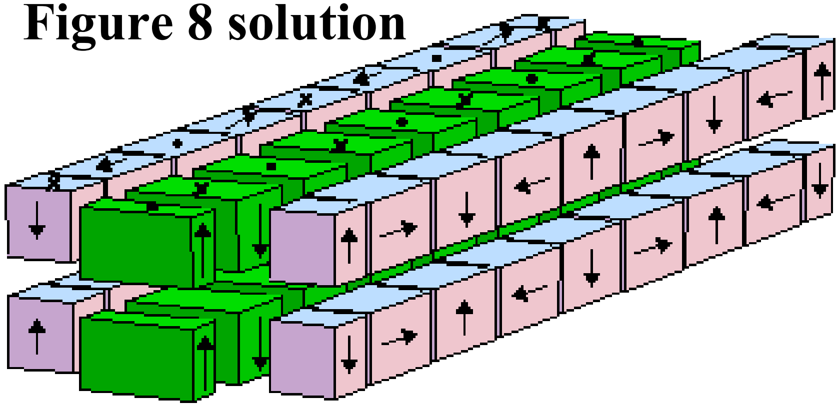
4.5 *m* length, 125 *mm* period, 400 *mA*

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

1.5 kW on the first mirror

Linear Undulator ?

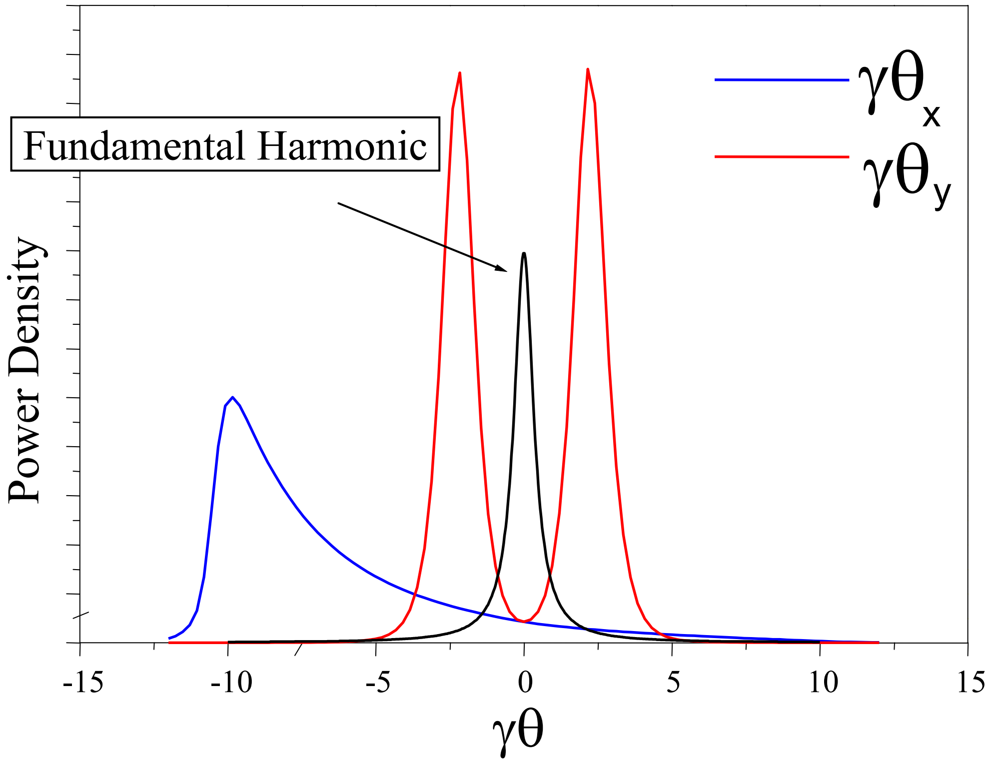
Figure 8 solution



$N_p = 32$
$\lambda = 140\ mm$
$K_x = 3.4$
$K_y = 9.4$

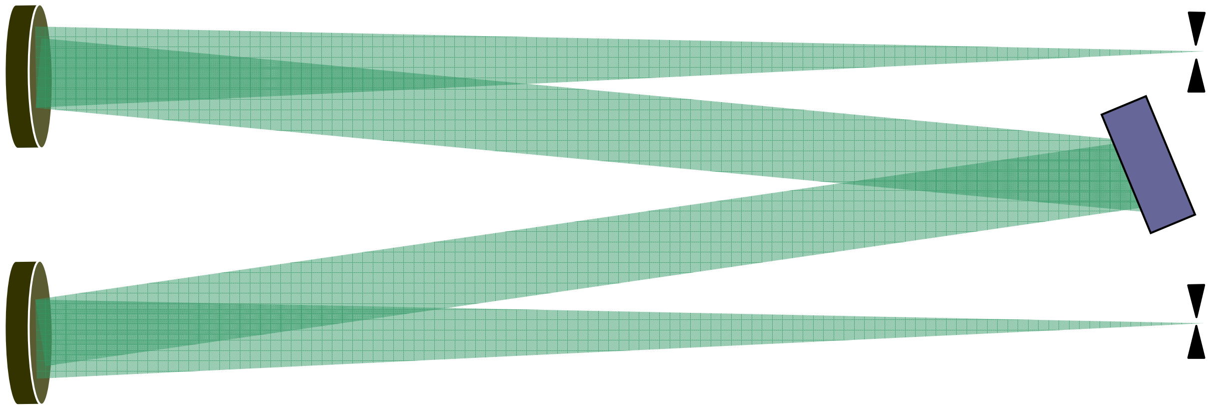
22 W on first mirror !!

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



The NIM Monochromator

Normal Incidence Monochromator (*Czerny-Turner* design)



Monochromator & Analyzer design

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

How to Scan?

The Beamline

Scanning Resolution: 80 *nrad*

Autocollimator Control: 50 *nrc*

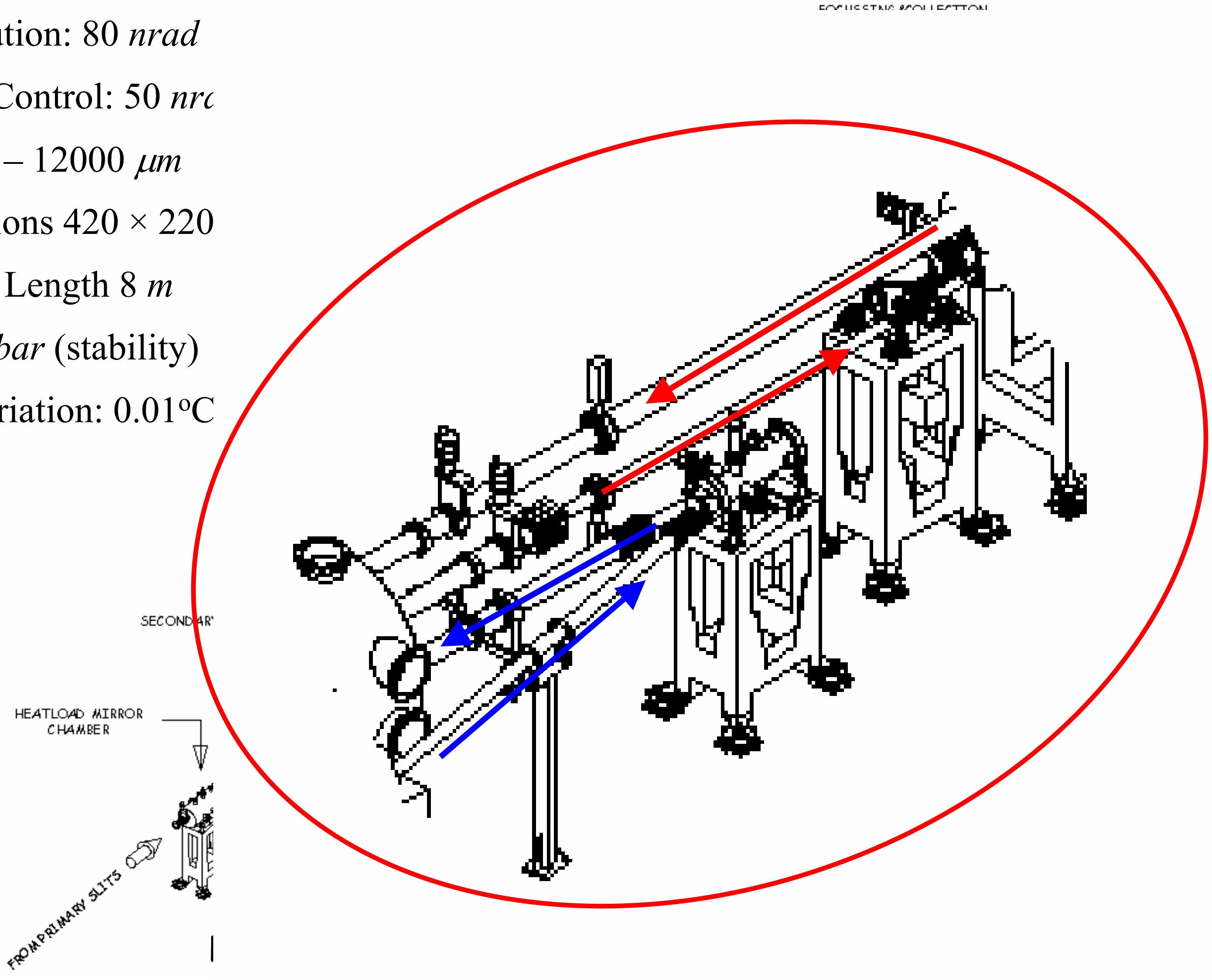
Slits Opening: 5 – 12000 *μm*

Grating Dimensions 420 × 220

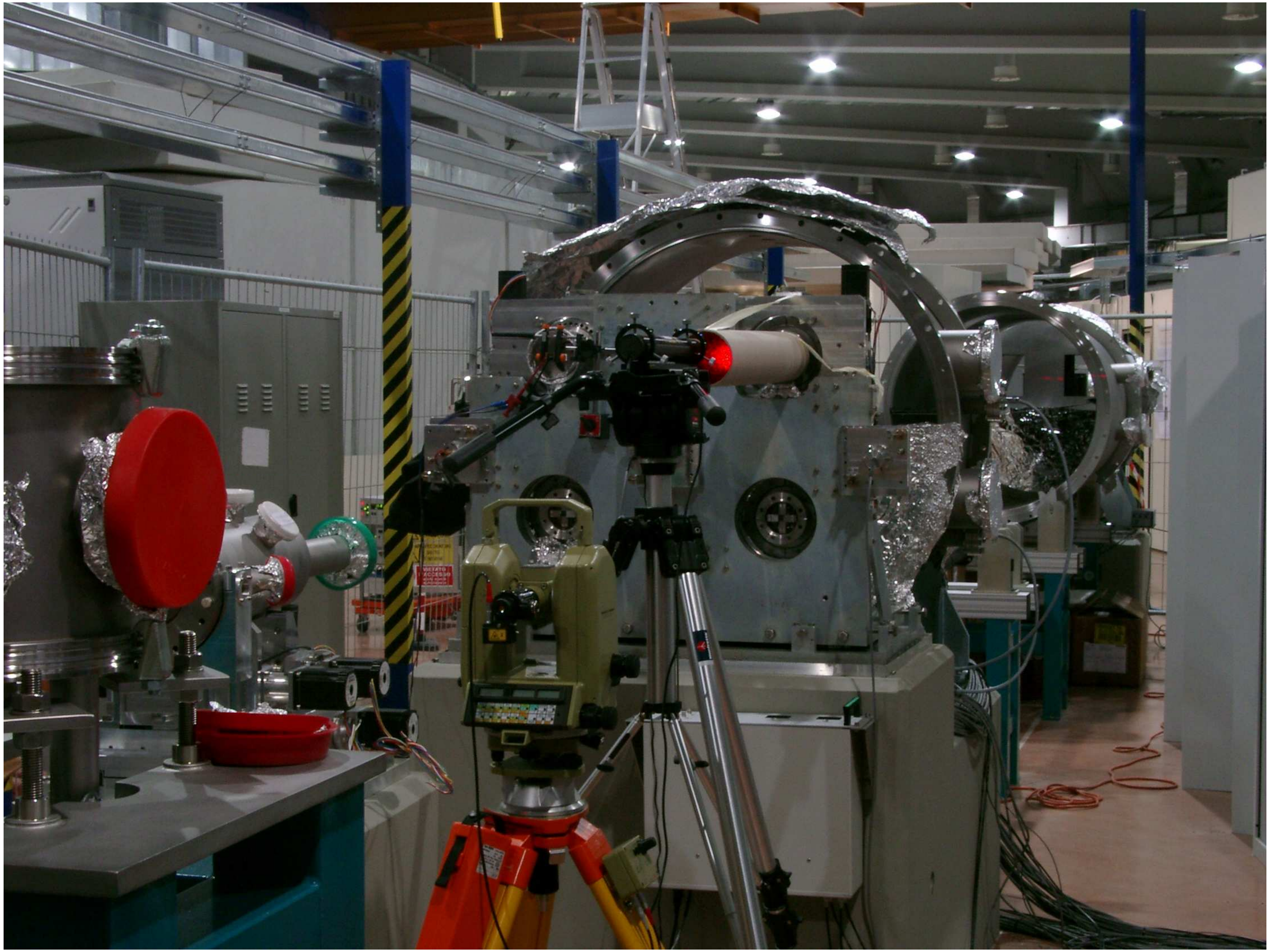
Monochromator Length 8 *m*

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

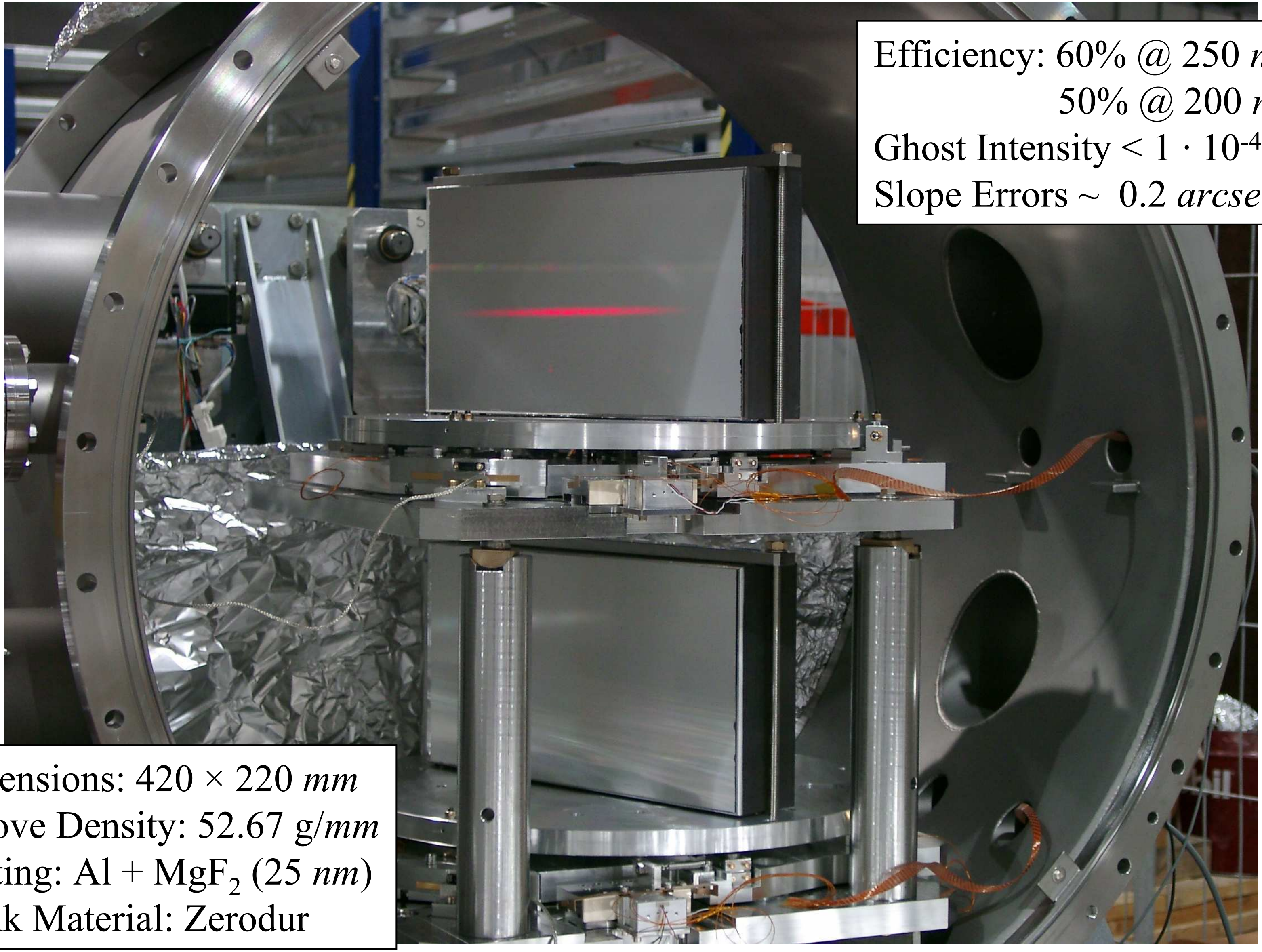
Temperature Variation: 0.01°C



The Construction



The Gratings



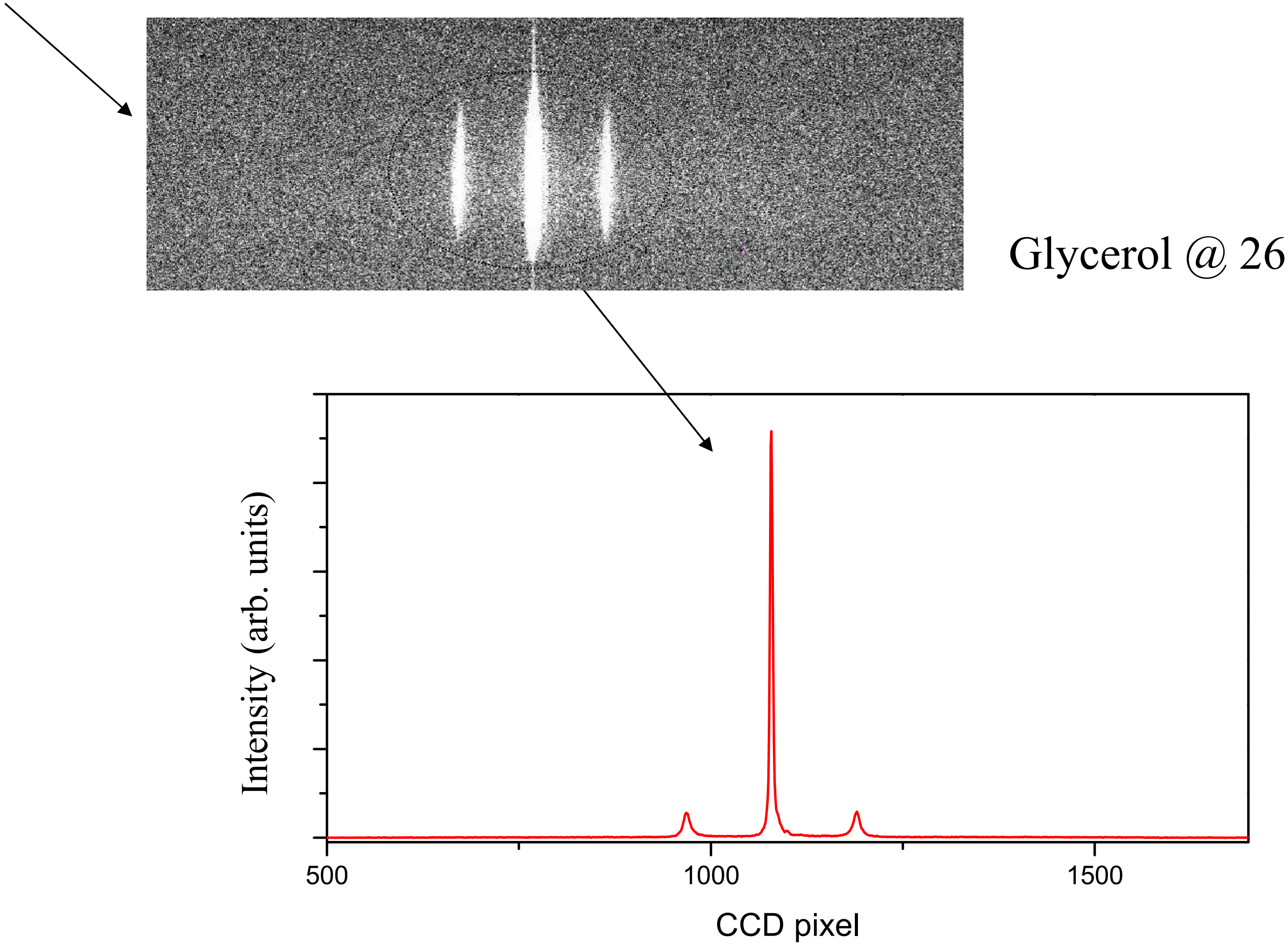
Efficiency: 60% @ 250 *nm*
50% @ 200 *nm*
Ghost Intensity < $1 \cdot 10^{-4}$ PL
Slope Errors ~ 0.2 *arcsec*

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

The Beamline

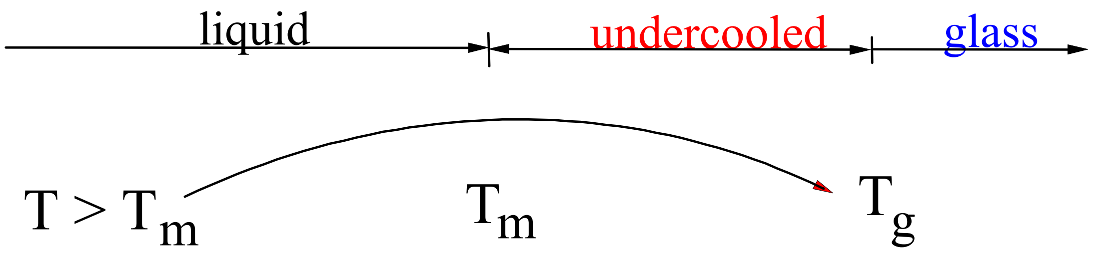
The Spectrum

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



Glycerol @ 260 K

3. Studies on Disordered Systems


liquid
undercooled
glass

$T > T_m$ T_m T_g

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*

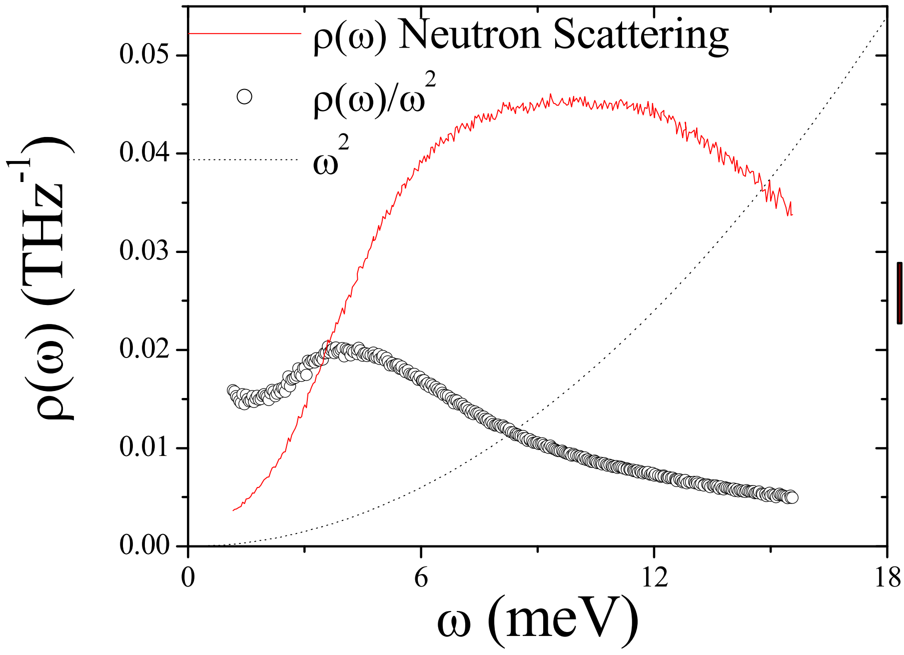
The **viscosity** η increases by lowering T and presents one of the **largest** changes of a physical measurable quantity of a material (14 orders of magnitude)

Glass-Forming Systems

Puzzling properties

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

The liquid to glass transition temperature T_g depends on the **quenching rate**. One cannot define an **order parameter** showing a critical behaviour at T_g.



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.

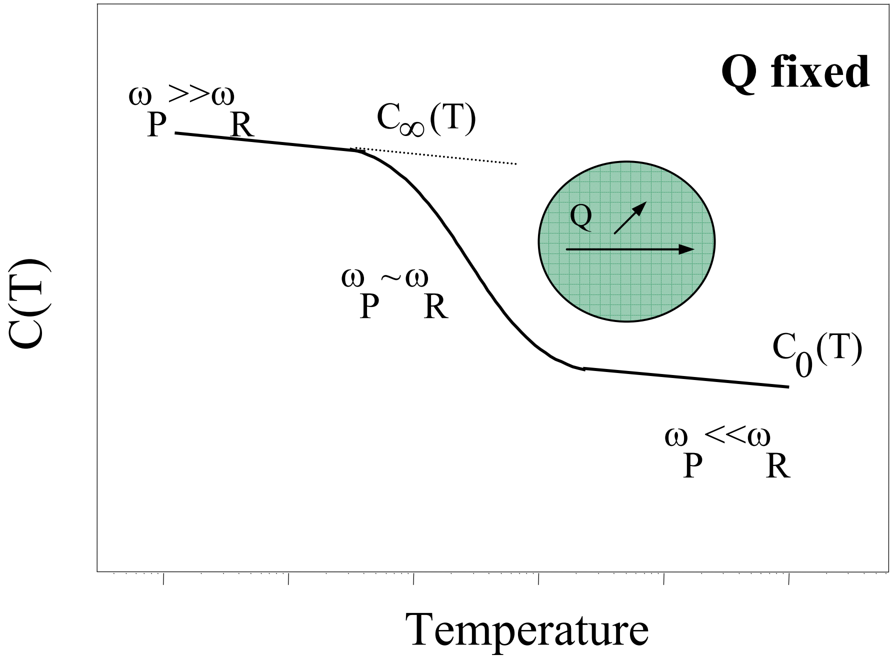
The Structural Relaxation

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

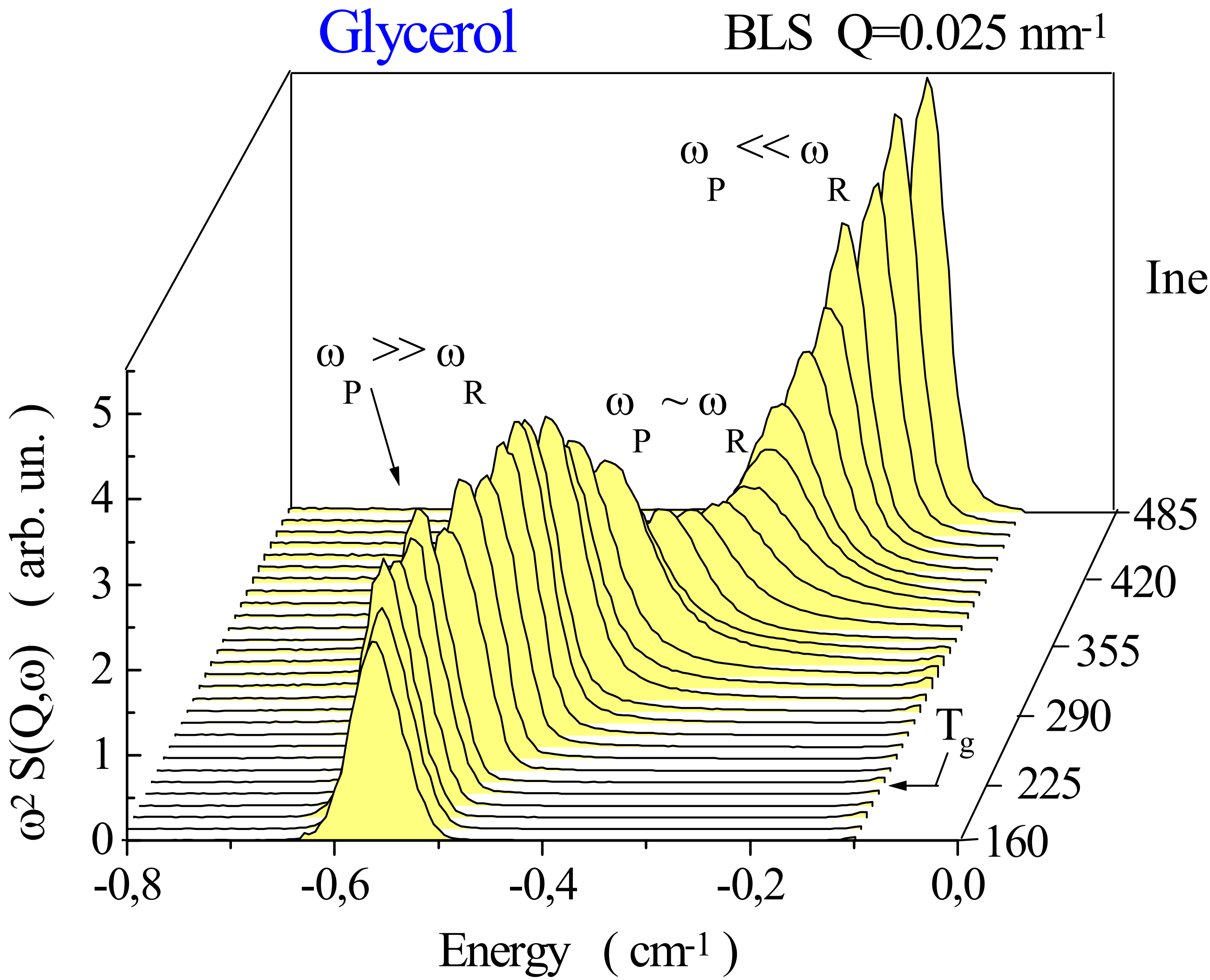
Mode Coupling Theory → a particle trapped in a the cage can migrate only through rearrangement of a large number of particle surrounding it



Knowledge of $C_o(T)$, C_∞ (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 normal liquid range
- Increasing liquid fluidity with increasing pressure

Liquid–Liquid Phase Transition

220 K – 100 MPa

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

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

in the undercooled liquid

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

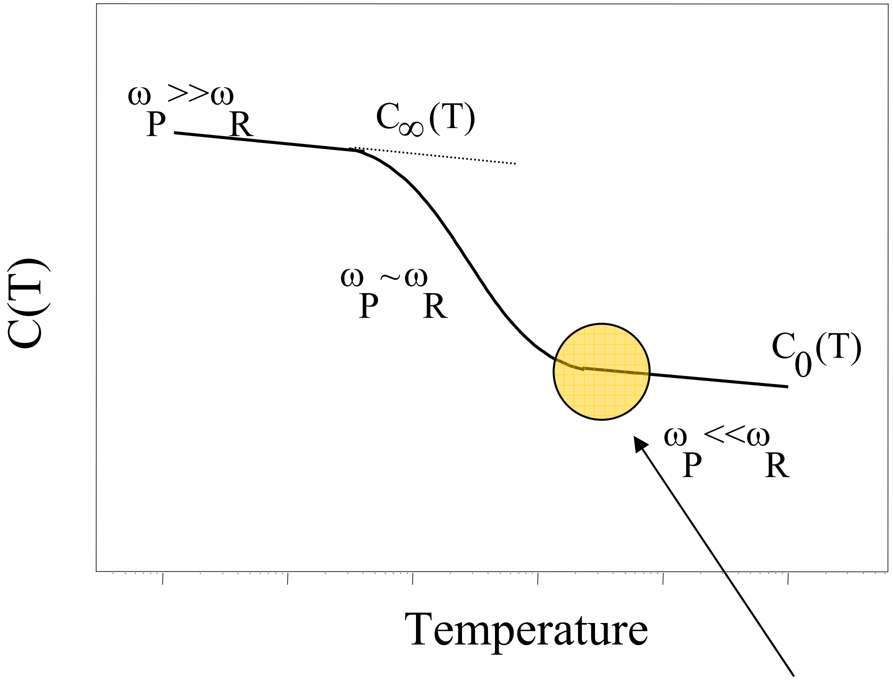
Mode Coupling Theory

transient caging of molecules

$$\mathbf{F(Q,t) \sim exp\text{-}(t/\tau(Q,T))^{\beta}}$$

MCT predicts
$$\begin{cases} \beta \text{ temperature independent and } < 1 \\ \tau \sim (T\text{-}T_c)^{-\gamma} \end{cases}$$

Study of Structural Relaxation in Supercooled Water



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

low frequency investigations: **Ultrasonic** and **BLS**

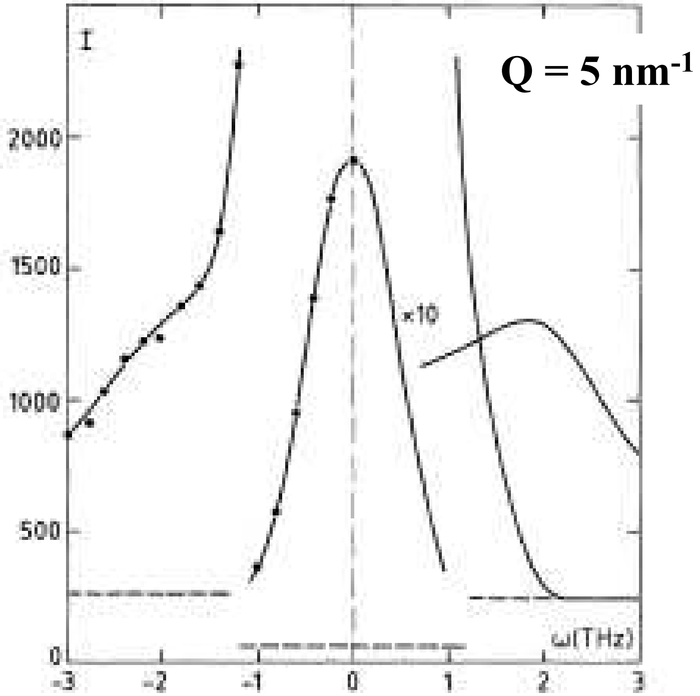
W. M. Slie et al., JCP (1966)
J. Rouch et al., JCP (1977)
G. Maisiano et al., PRL (1984)
S. Magazu' et al., JCP (1989)
A. Cunsolo et al., JCP (1996)

Line shape analysis is very difficult since measured linewidth is << resolution

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)



Q = 5 nm^{-1}

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

M. A. Ricci et al., PRL(1988)

………….

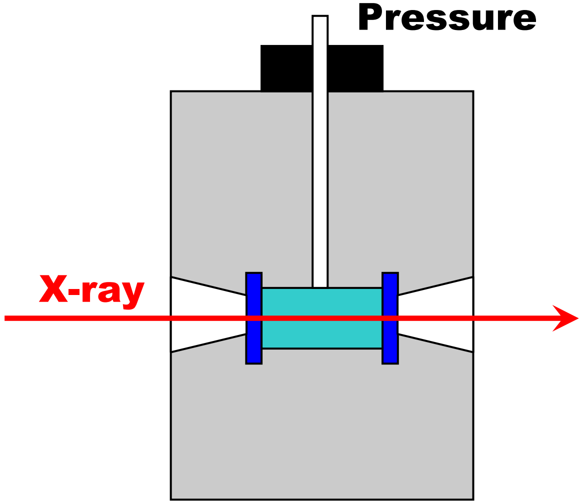
U. Balucani et al., PRE (1993)

Mode propagating through hydrogen atoms

IXS Investigations

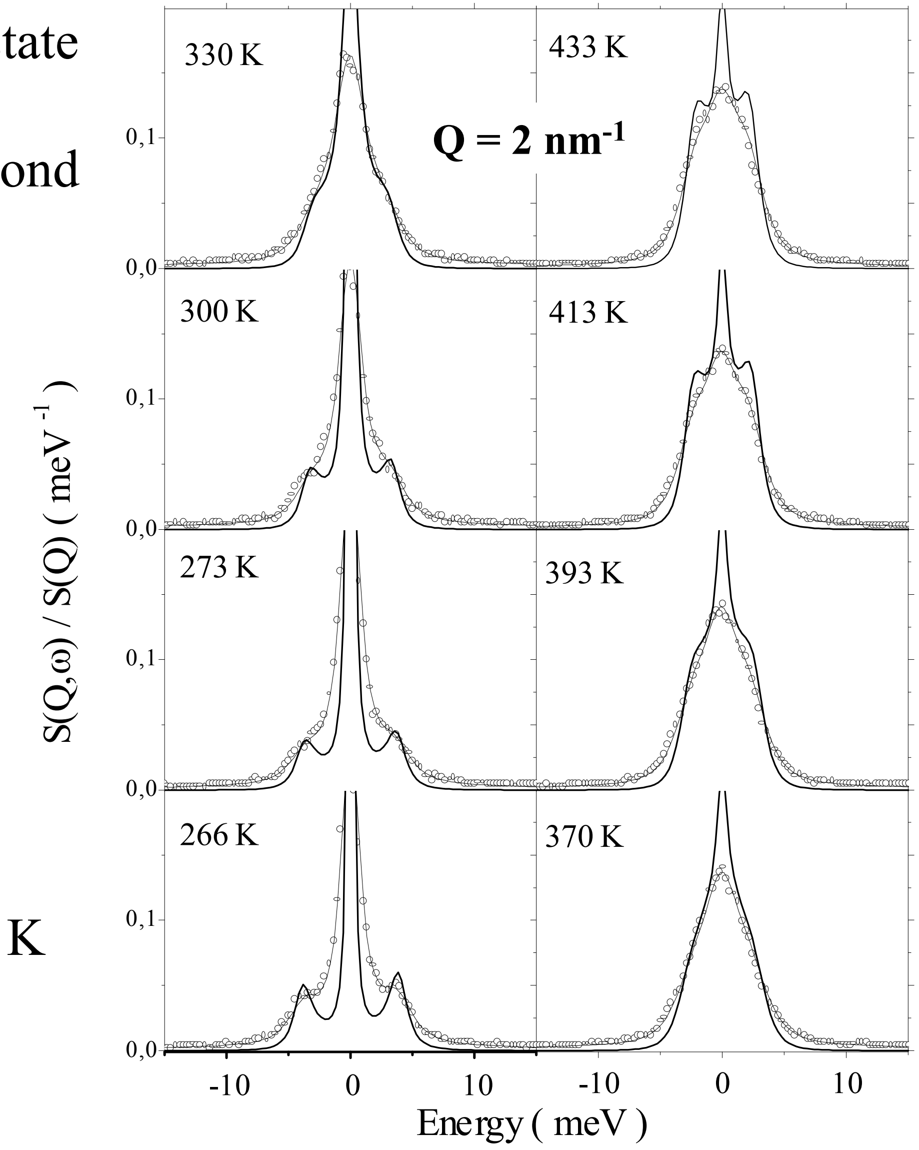
Water from liquid to undercooled state

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 $\Phi_Q(t) \longrightarrow n(\mathbf{r},t)$

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

Langevin equation

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

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

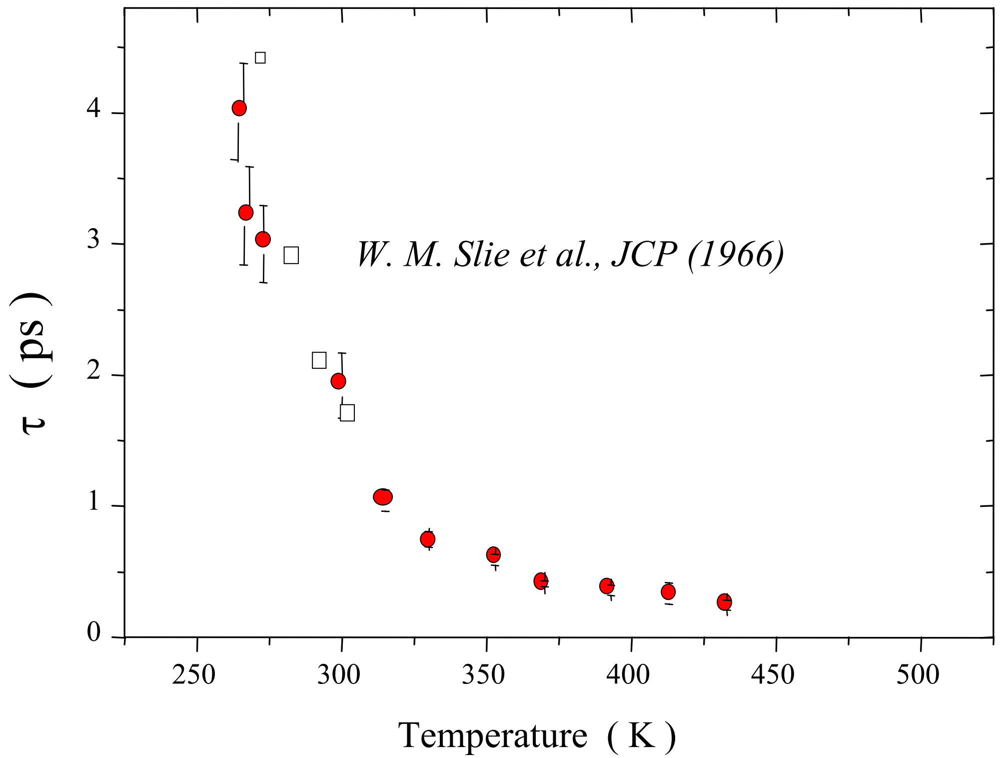
The **Viscoelastic** model

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

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

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

IXS Investigations



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

T ~ 350 K

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

$\omega_P\ \tau_R \sim 1$ **for IUVS** → **T ~ 250 K**

T_{NML} ~ 230 K

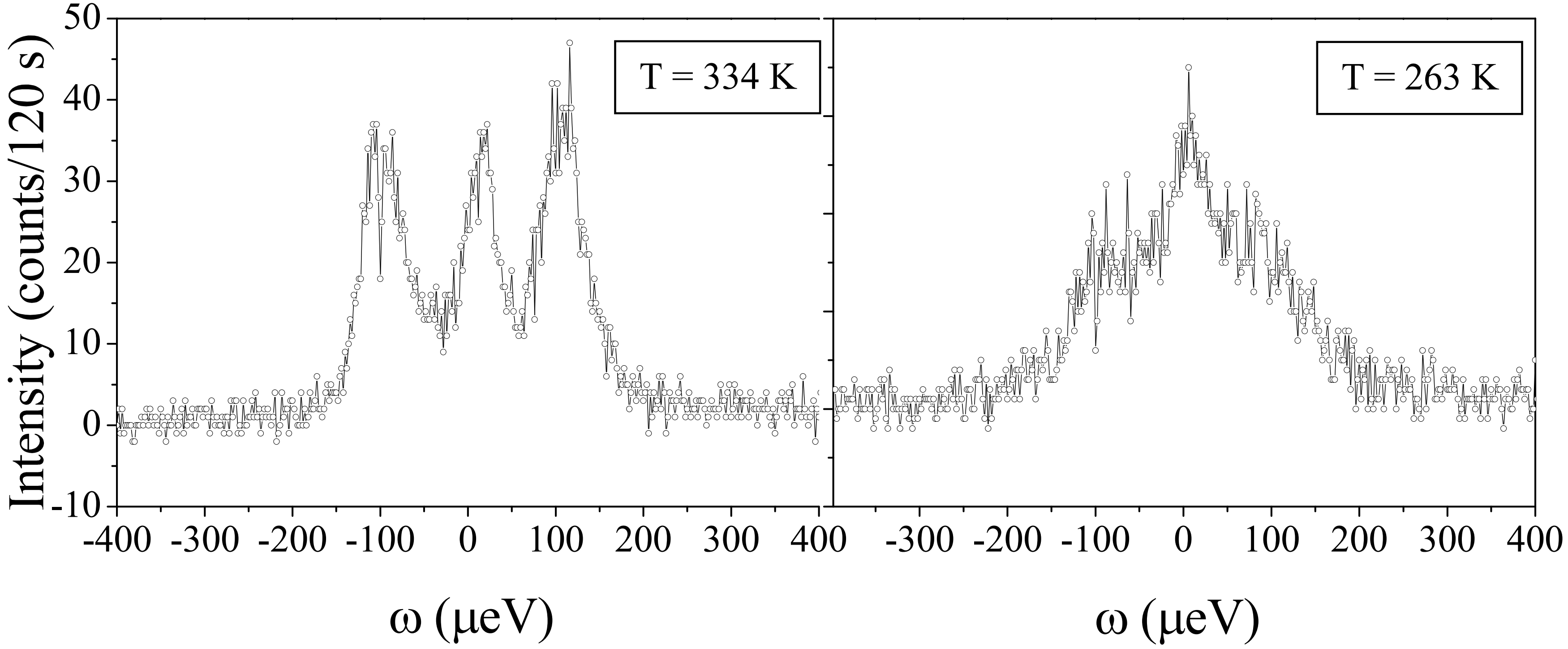
IUVS first measurements

Water from liquid to undercooled state

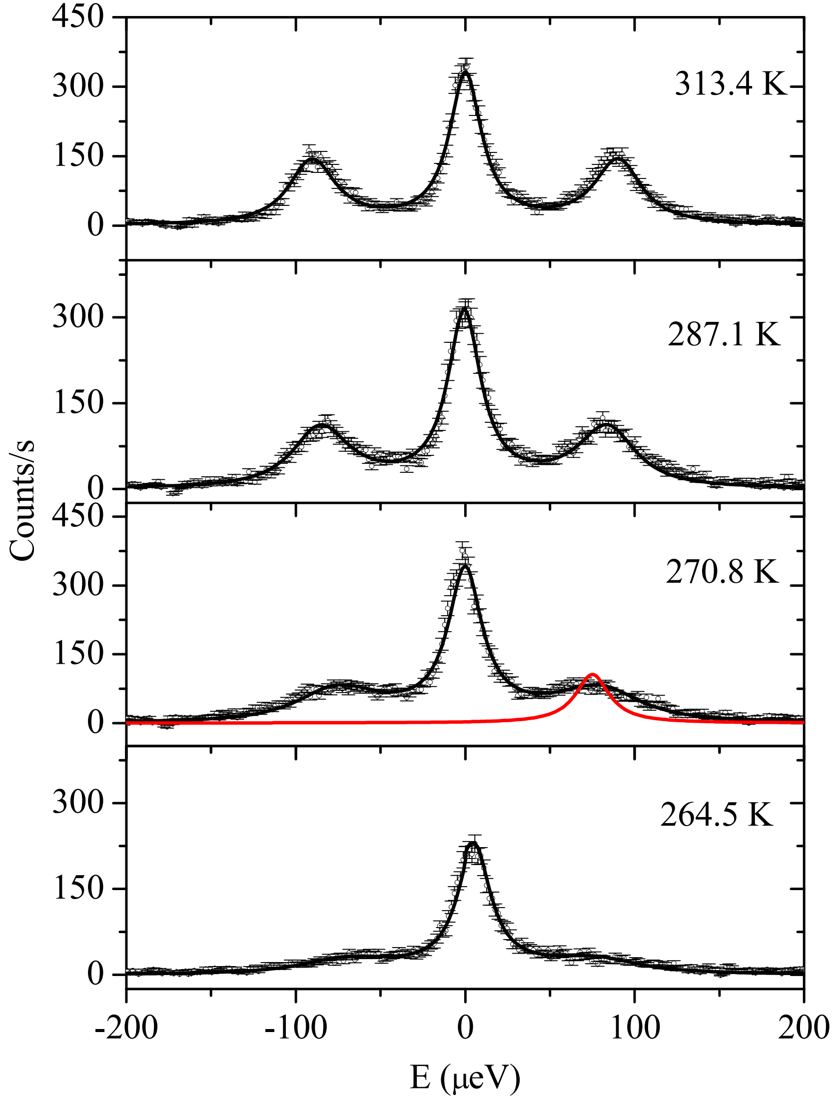
Cell: Fused Silica Fluorescence standard Cell

Momentum Transfer: 0.1 nm^{-1}

Temperature range: 343 → 248 K



The Modeling



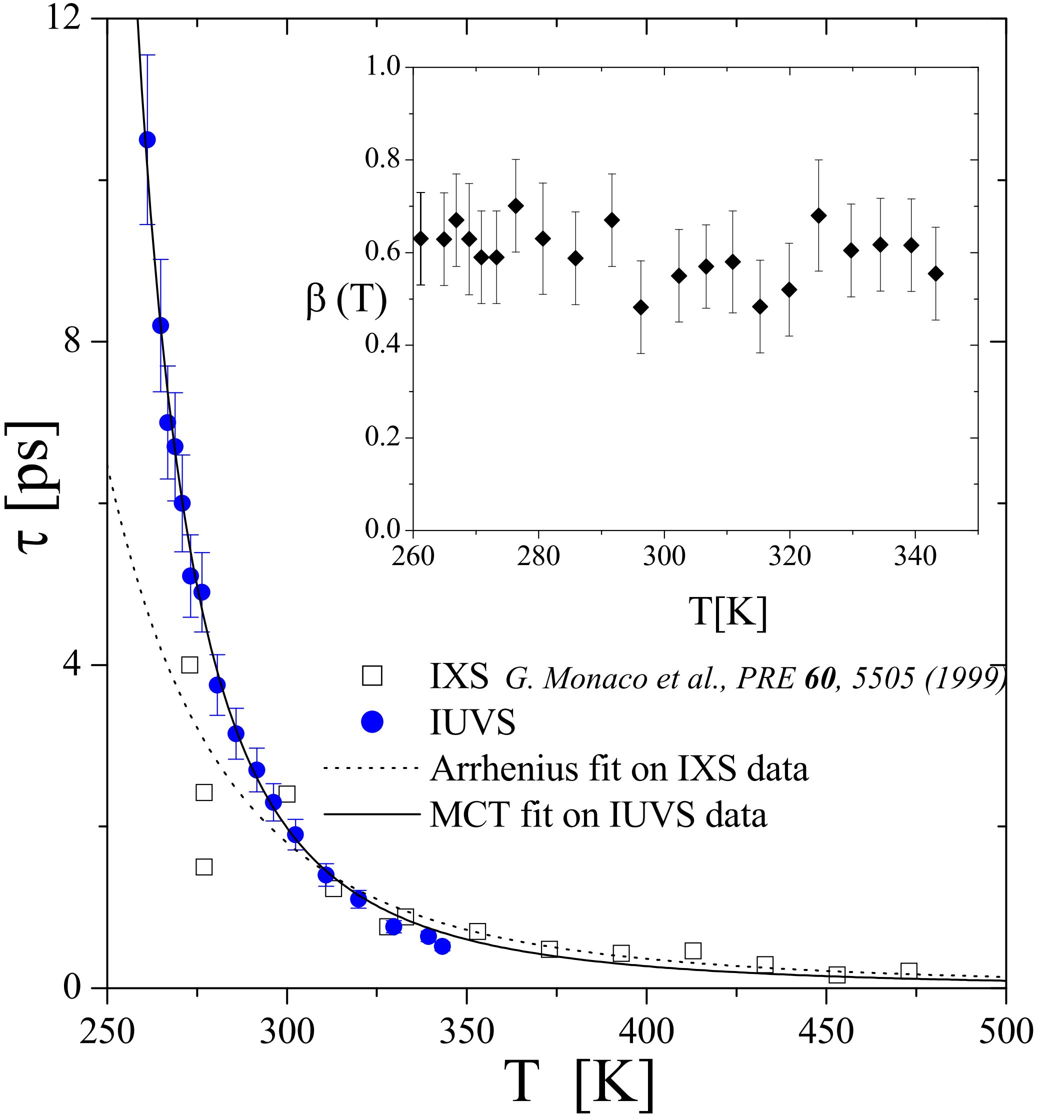
$$S(Q,\omega) = (2C_o^2Q^2/\omega)\mathrm{Im}[\omega^2 - \omega_o^2 - i\omega m_Q(\omega)]^{-1}$$

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

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

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

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

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
$\gamma = 2.3$

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

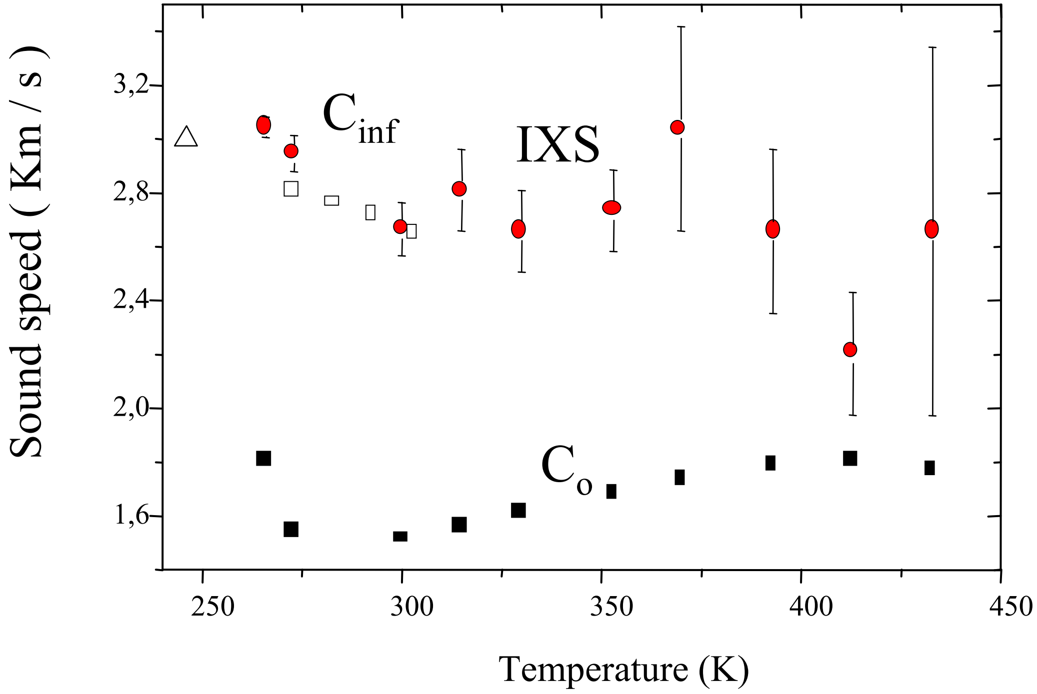
The observed anomalies in the transport properties, at **ambient pressure**,
do not need an underlying thermodynamic singularity

C. Masciovecchio et al., PRL (2004)

The Infinite Frequency Sound Speed

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

F. Sette et al., PRL (1999)

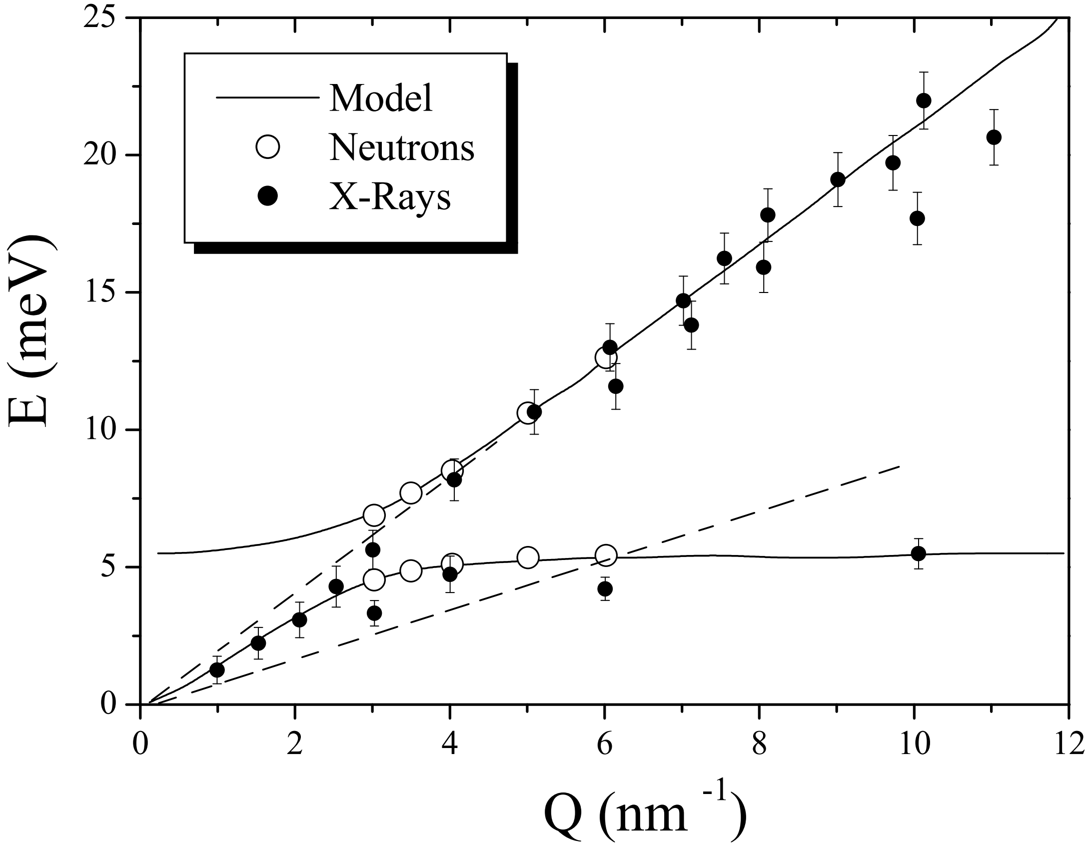


Fast Sound is the Relaxation Free Sound Speed C_∞

Most recent NS data and analysis

Back to **Neutron Scattering**

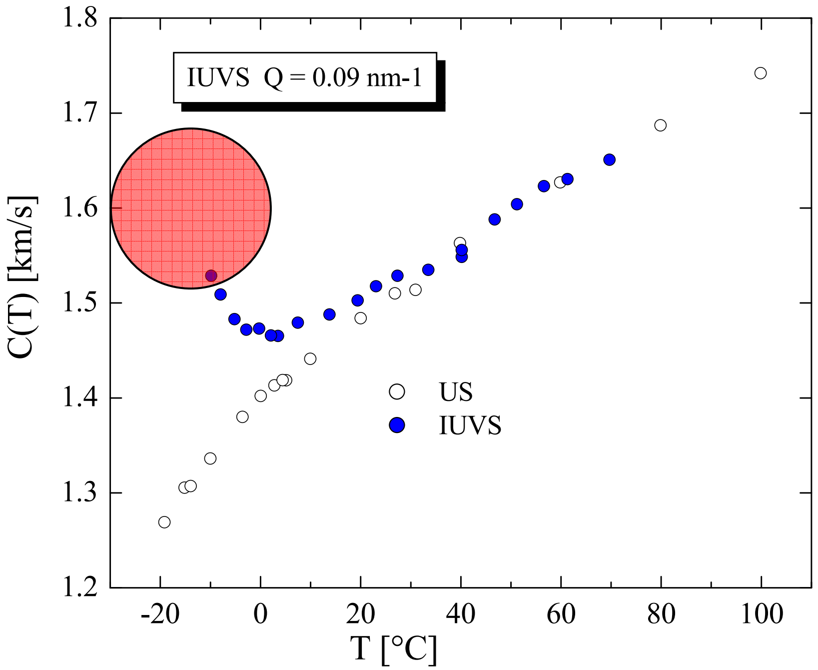
F. Sacchetti et al., PRE (2004)

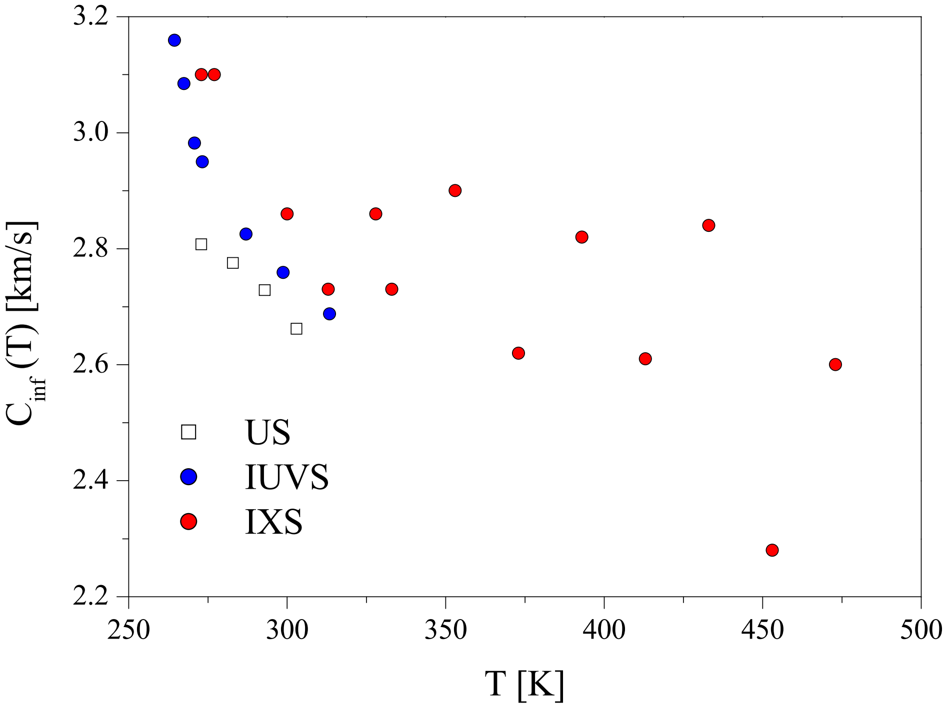


A phenomenological model of **interaction** between two vibrational branches

The Viscoelastic behavior of water

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



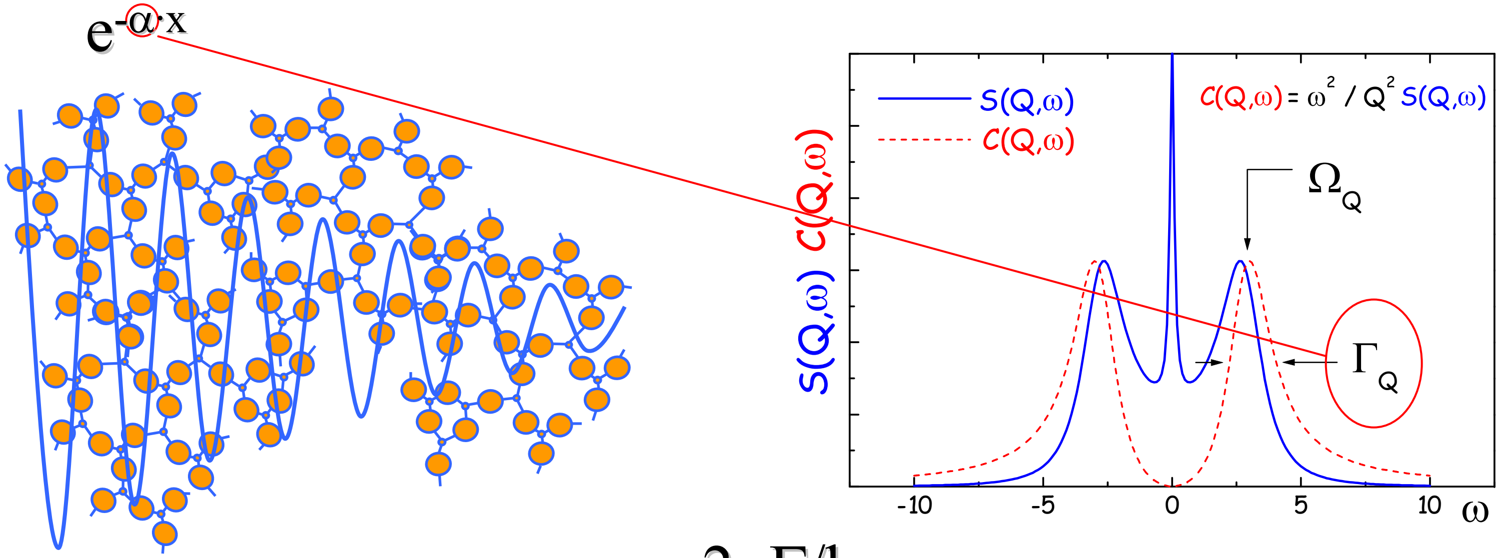


IUVS detects a clear departure from C_o

Fast Sound does not **exist** in water

S. C. Santucci et al., submitted

Acoustic Attenuation in Glasses



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

What is known:

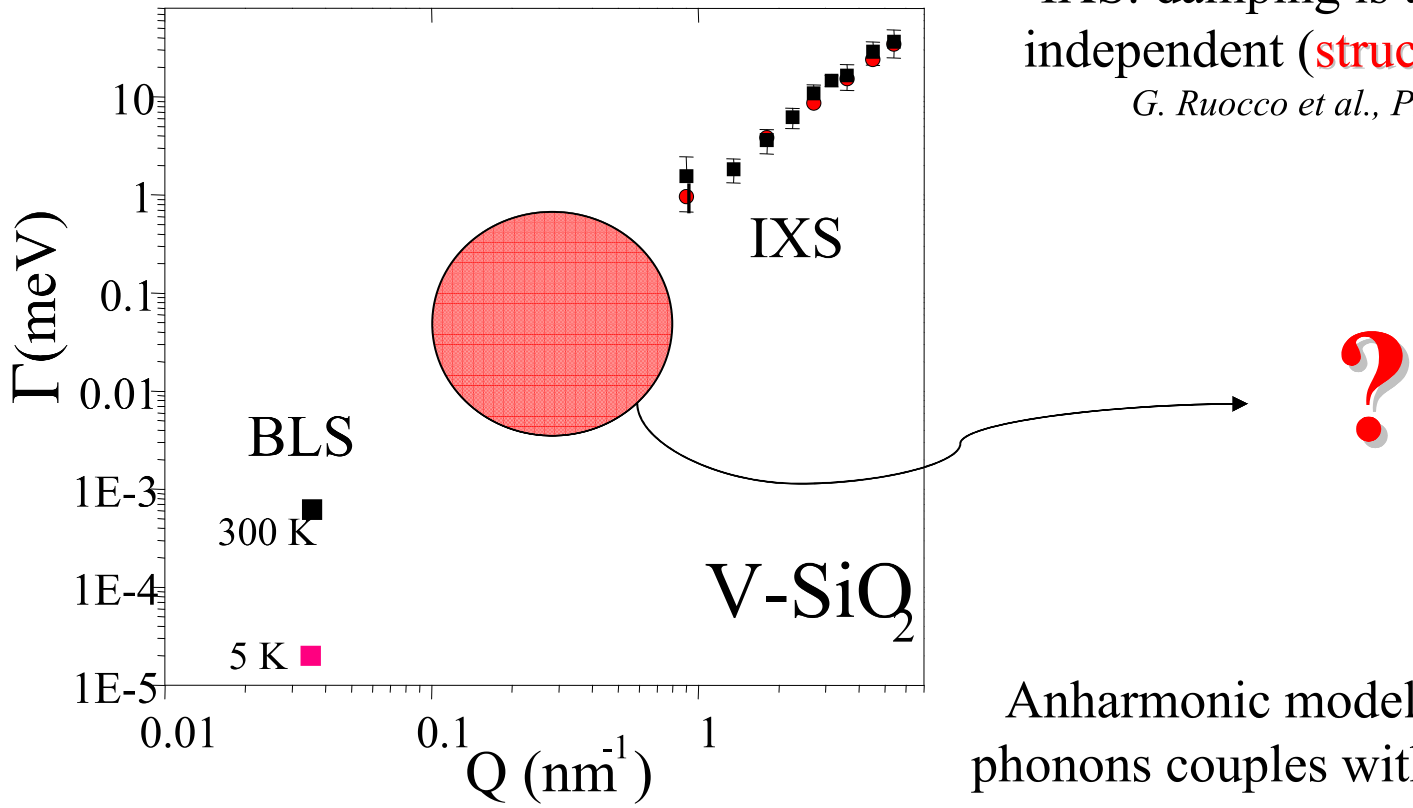
1) At T < 10 K US and BLS investigations **Γ(T)** exhibit a small, frequency dependent peak.

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).

Vitreous Silica

Study of the Q – T dependence of the attenuation mechanism in V- SiO_2



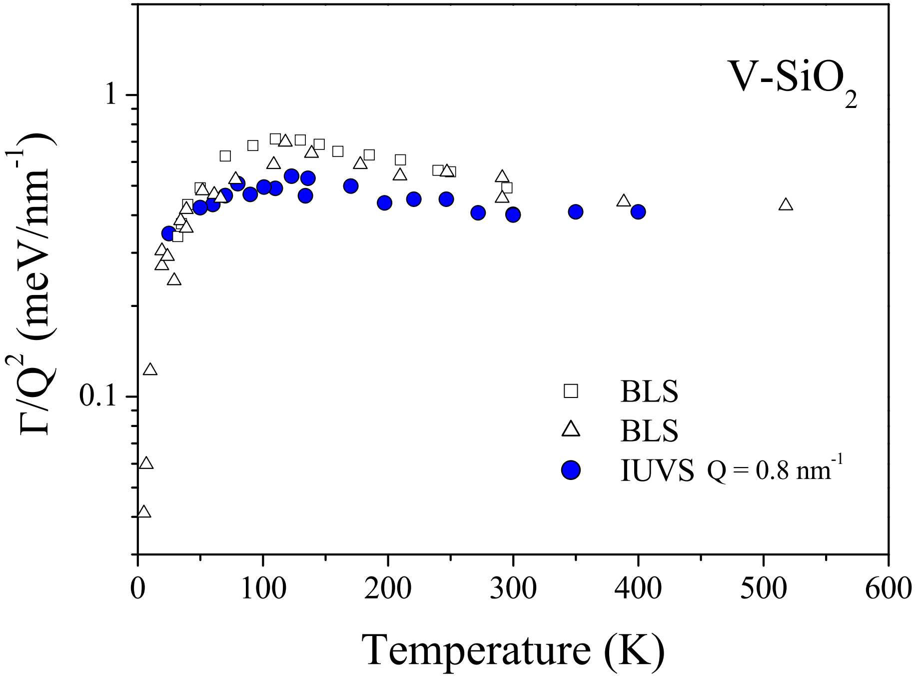
IXS: damping is temperature independent (structural origin)

G. Ruocco et al., PRL (1999)

Anharmonic model: acoustic phonons couples with thermally activated vibrations

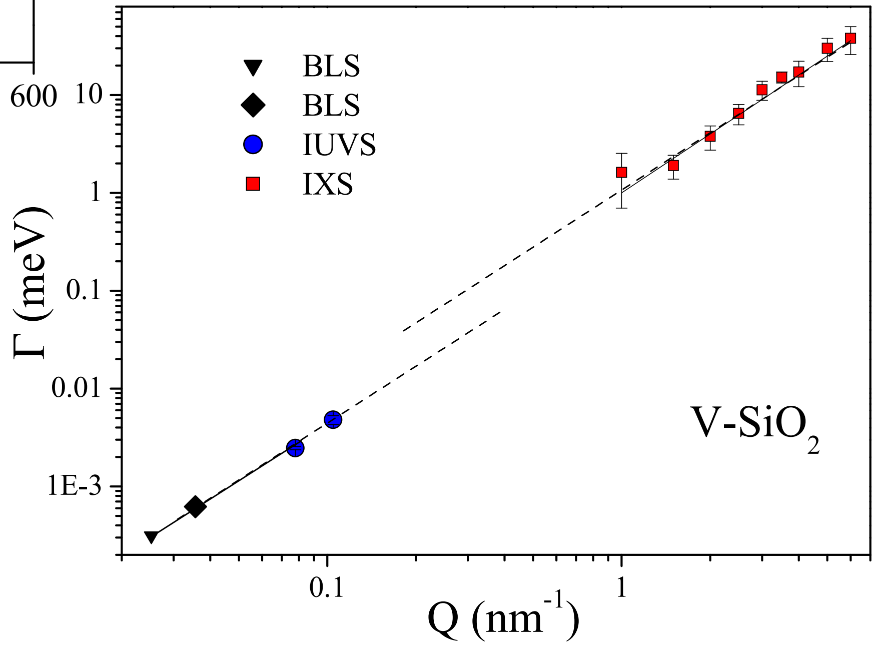
J. Fabian et al., PRL (1999)

IUVS measurements



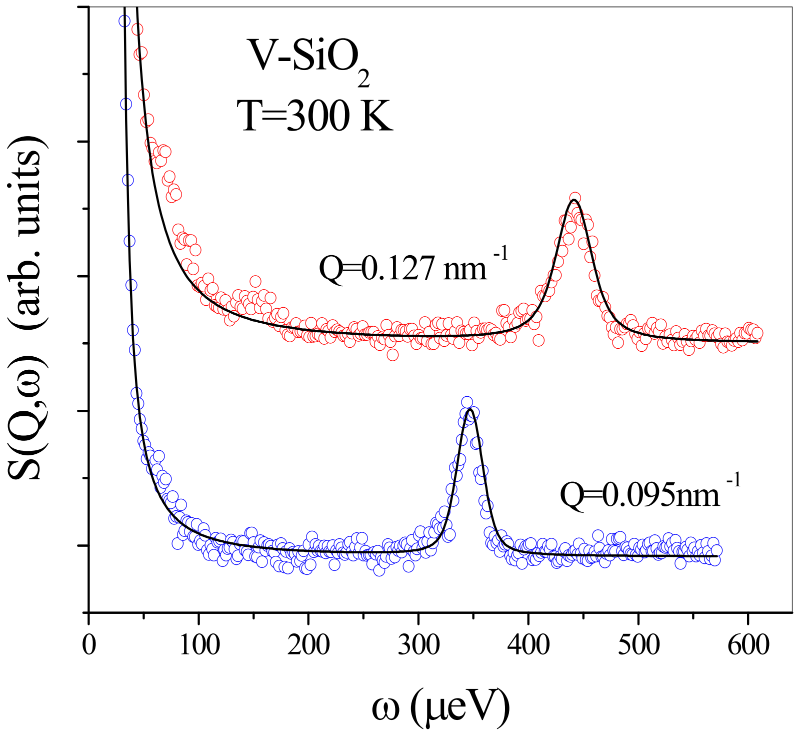
T-dependent measurements strongly **support** the anharmonic model presented by J. Fabian et al.,

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

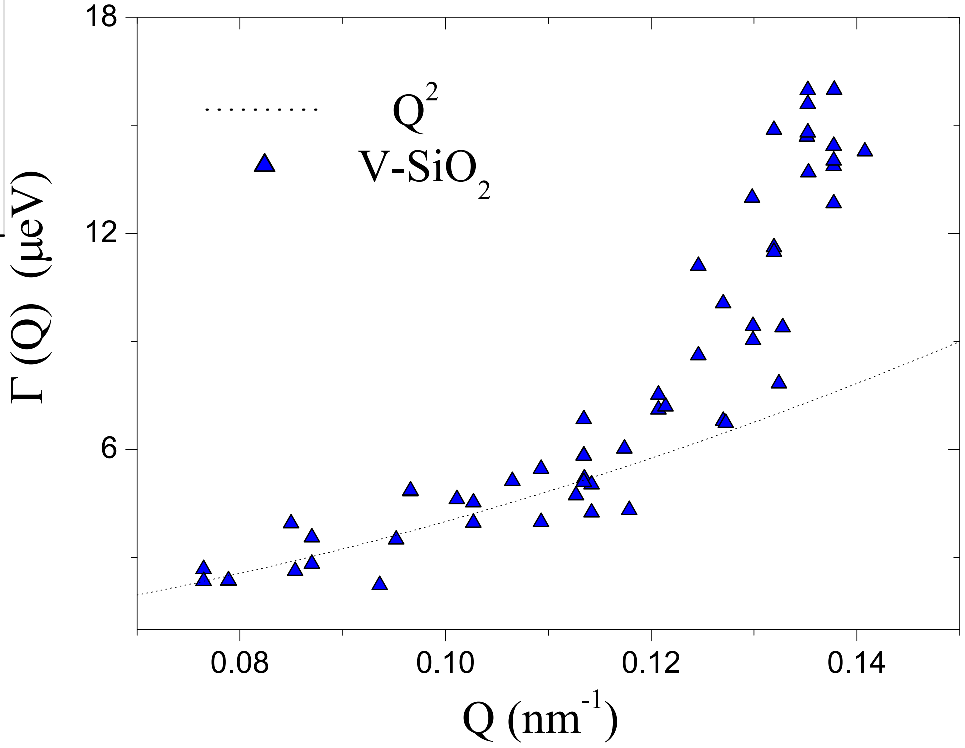


C. Masciovecchio et al., PRL (2004)

IUVS Spectra

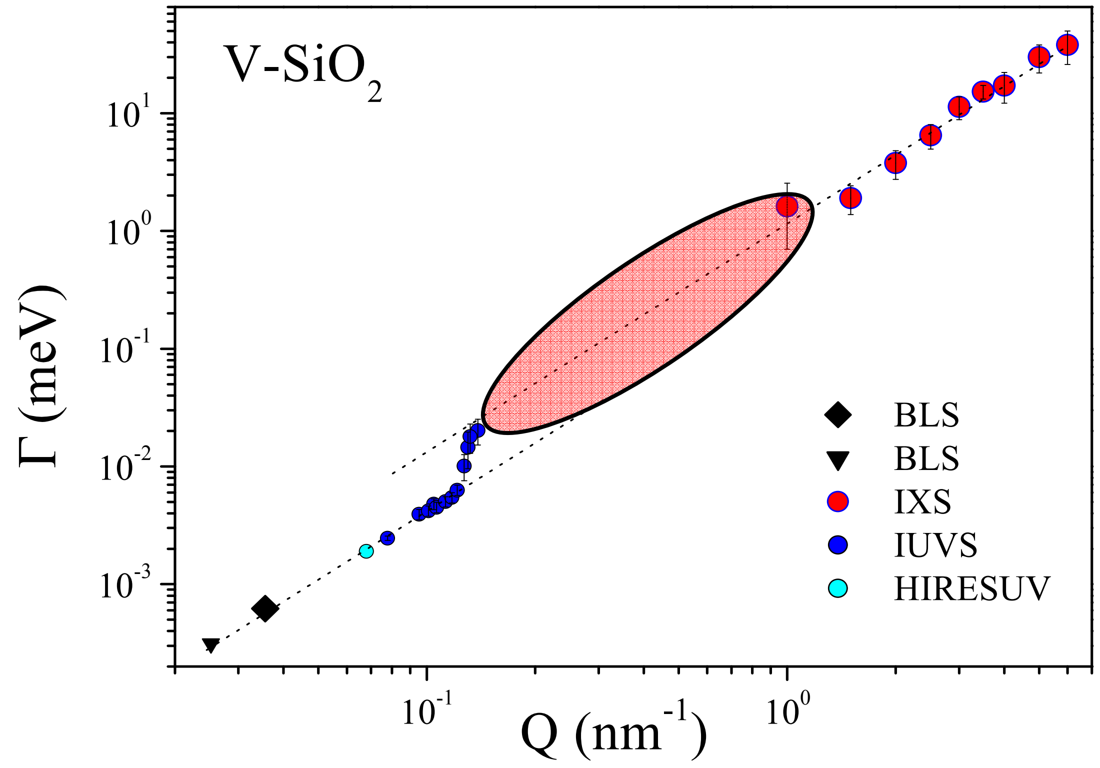


IUVS Spectra taken on vitreous silica as a function of momentum transfer Q



What about the **Attenuation?**

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

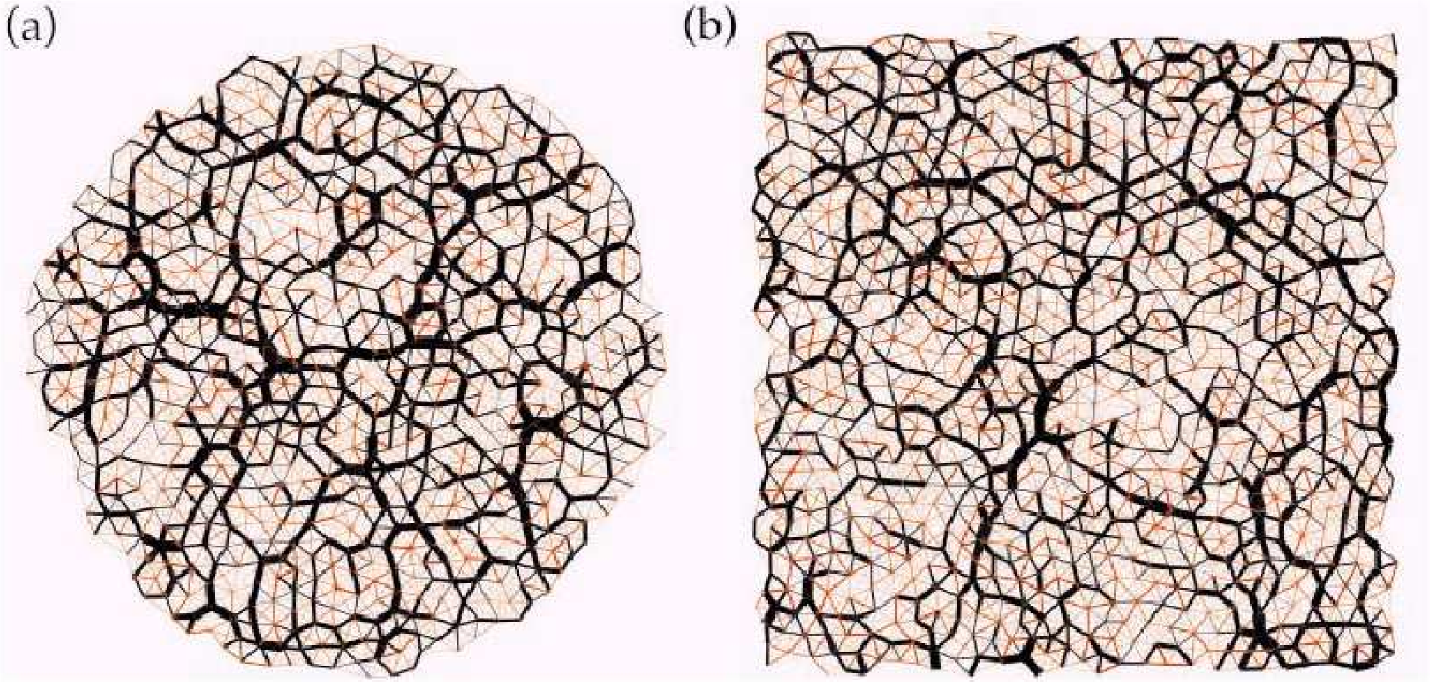


FIG. 1. (Color) Representation of the network of quenched stresses in two small quenched Lennard-Jones particle systems in two dimensions: (a) a disk-shaped aggregate of diameter $2R \approx 32a$ containing $N=732$ particles (protocol I) on the left and (b) a periodic bulk system with $L=32.9a$ and $N=1000$ (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.

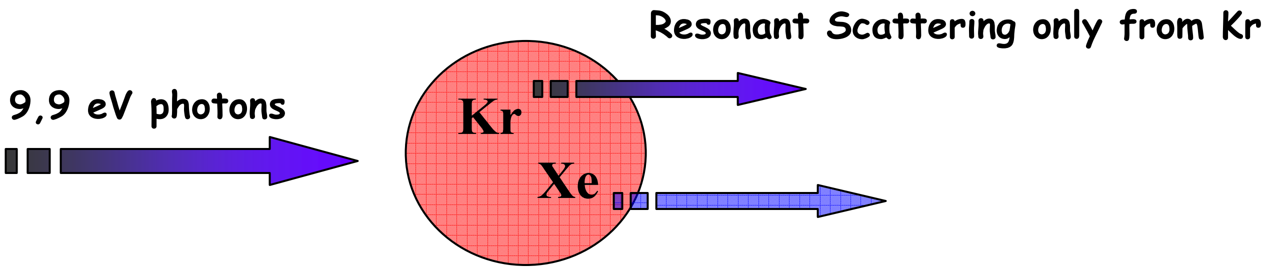
A. Tanguy et al., PRB (2002)

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

Resonant Brillouin UV Scattering

Noble Gases

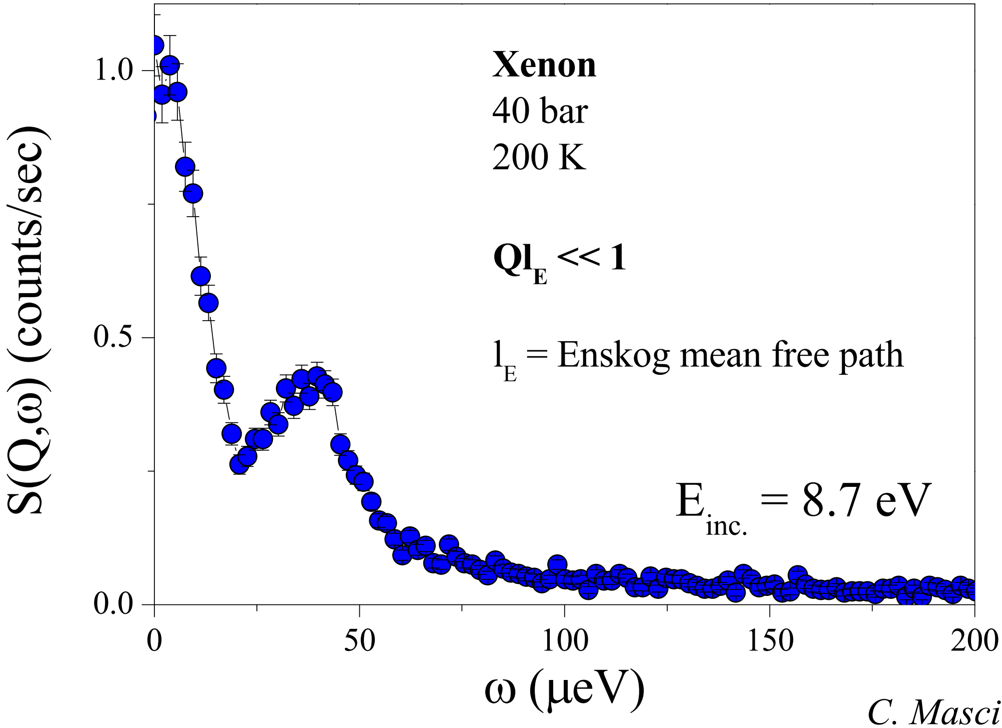
	E_1	λ (*nm*)
Helium	19.8	62
Neon	16.1	77
Argon	11.8	105
Krypton	9.9	125
Xenon	8.7	143



- Determination of **Partial** Dynamic Structure **Factors**
- Testing theoretical descriptions of Brillouin Scattering in a Mixture
- Shed Light on the Origin of **Fast** and **Slow** sound modes (H_2+Xe, CH_4+SF_6, ….)

Xenon

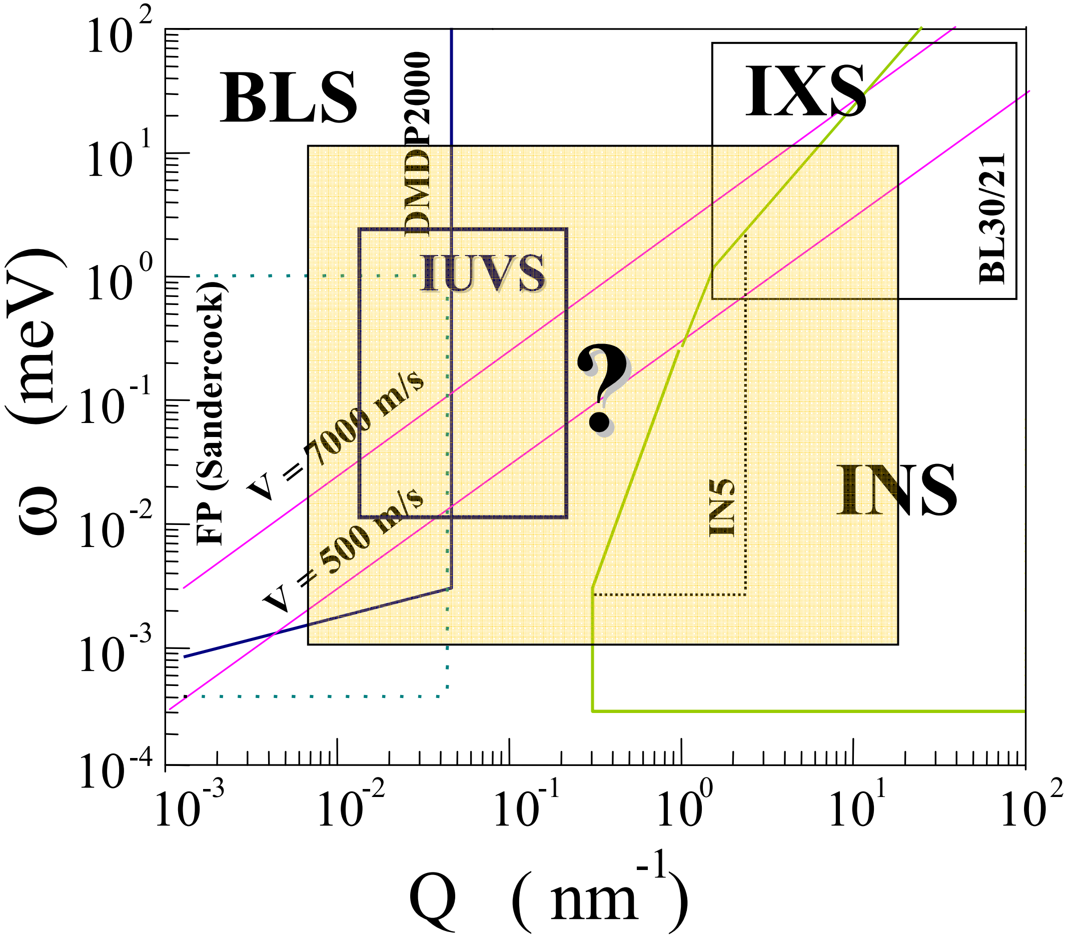
6s(3/2) → 1430 Å (8.7 eV)　　6s(1/2), 6p(5/2), 6p(3/2), …… above 9.4 eV



C. Masciovecchio et al., submitted

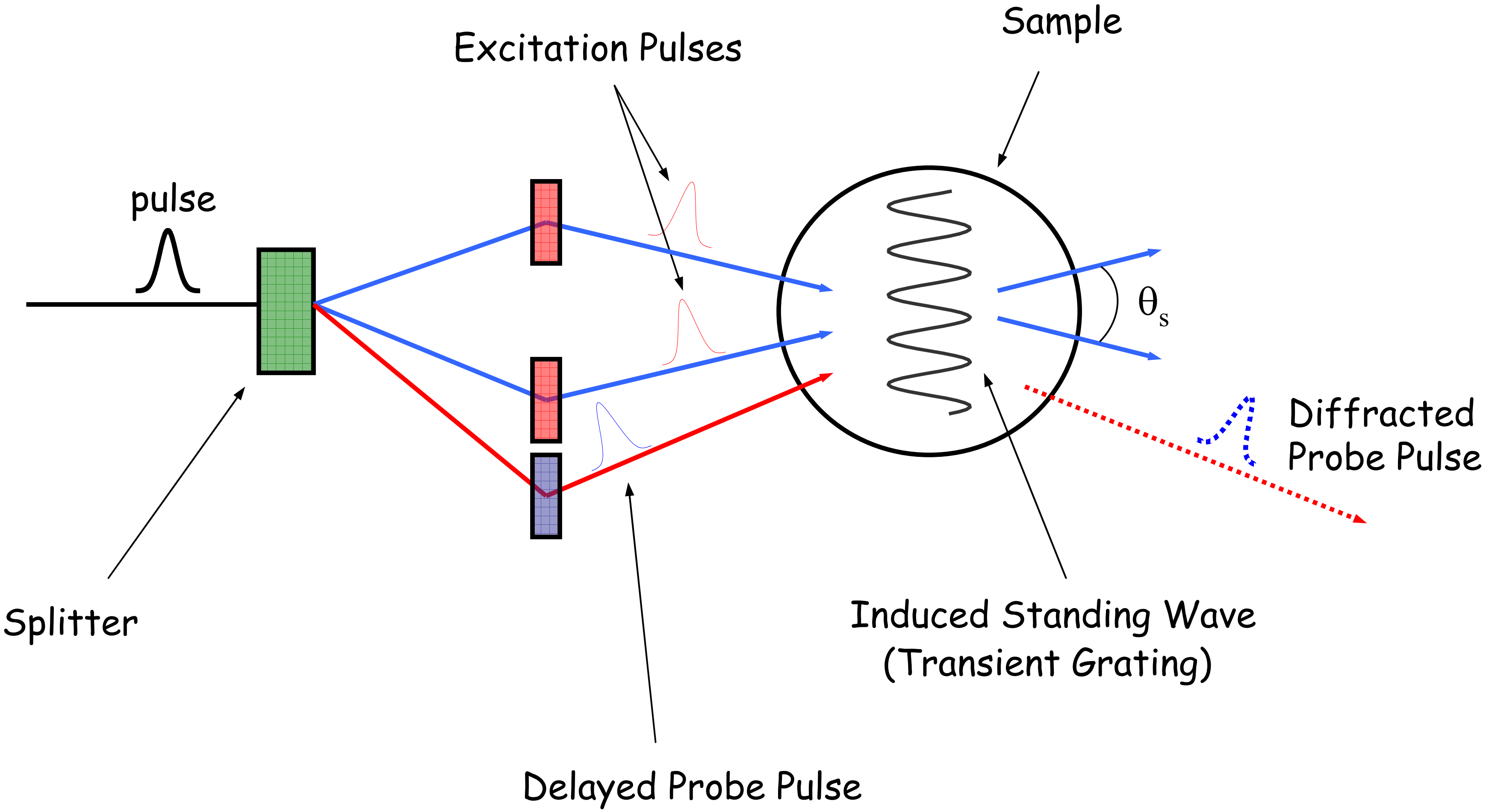
Modes **Bifurcation** in the dynamics of a Liquid Mixture → $Xe_{0.5}$ – $Freon_{0.5}$

4. Can we fill the Gap in the Kinematic Region?



YES ! with FEL based Transient Grating Spectroscopy

Transient Grating Spectroscopy



Standing Wave Periodicity ⇨ $\lambda = 2\pi/Q$ $Q = 2k_o \sin \theta_s/2$

Density Modulation Amplitude Monitored in Time by the Probe Pulse ⇨ $F(\mathbf{Q}, t)$

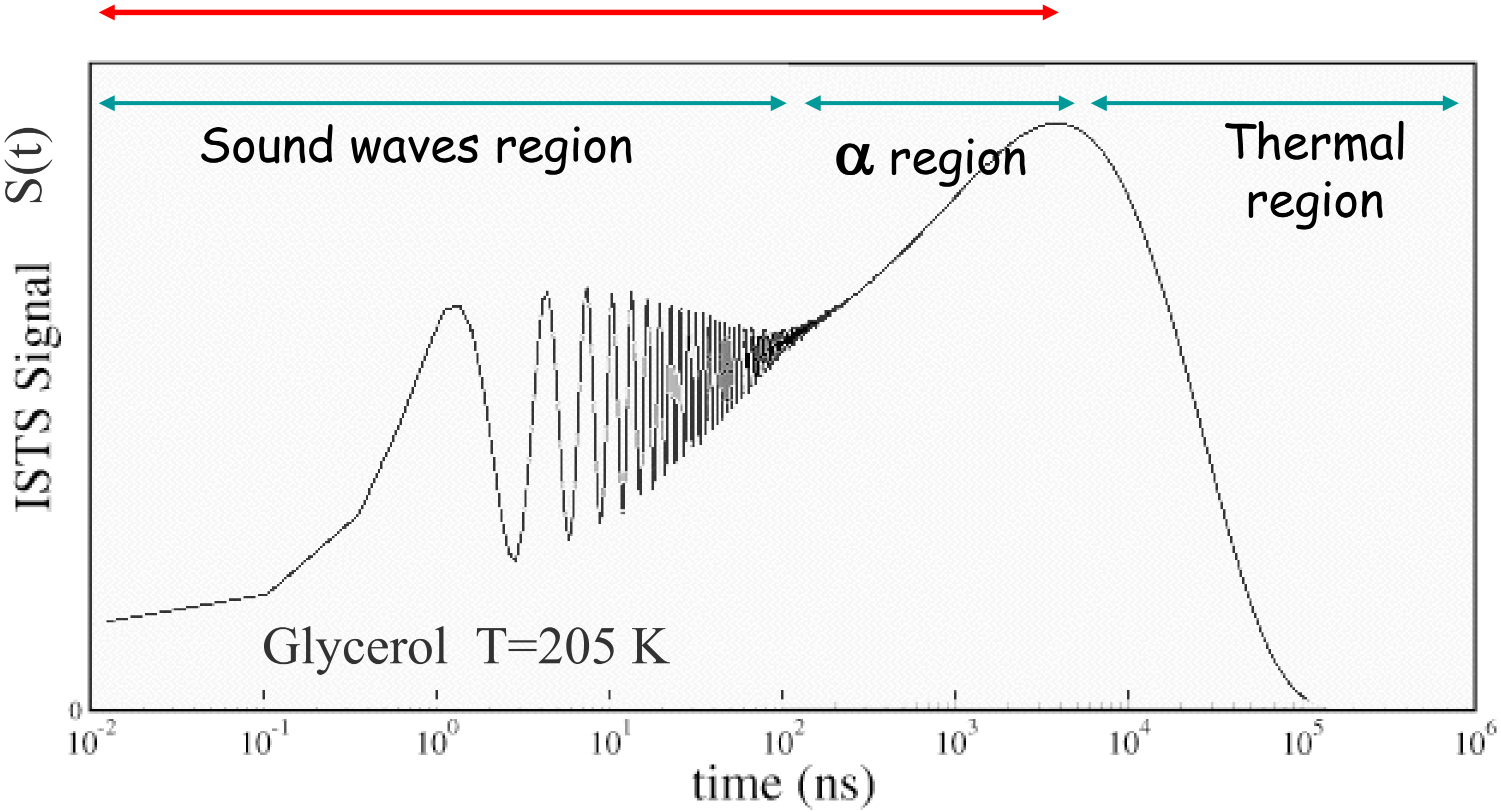
The Spectrum

ISTS = **Impulsive Stimulate Thermal Scattering**

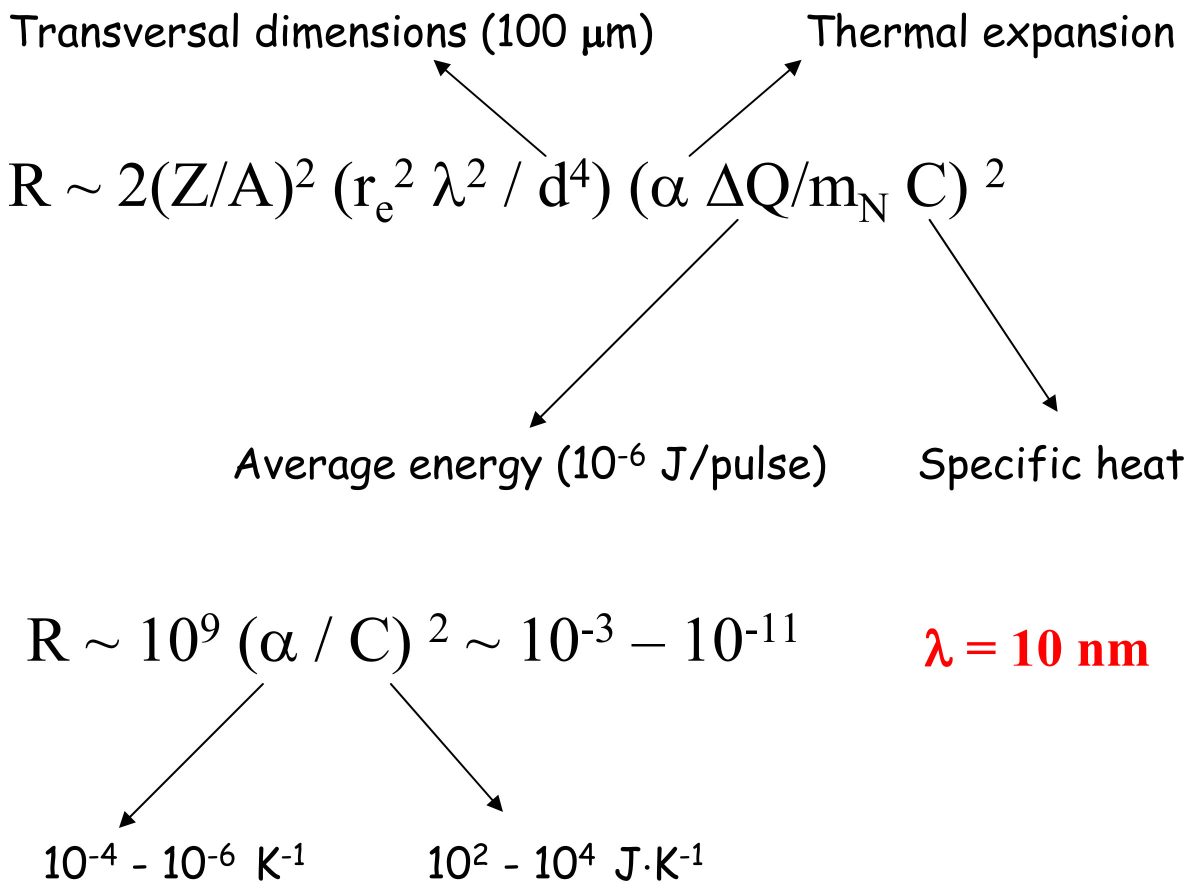
Optical absorption → Temperature Grating →Time-dependent Density Response

(driven by thermal expansion)

$S(t) \approx (\text{cost} - F(Q,t))$



Grating Reflectivity with FEL pulses



Transversal dimensions (100 μm)

Thermal expansion

$$R \sim 2(Z/A)^2\,(r_e^{2}\,\lambda^2 / d^4)\,(\alpha\,\Delta Q/m_N\,C)^{\,2}$$

Average energy (10^{-6} J/pulse)

Specific heat

$$R \sim 10^9\,(\alpha / C)^{\,2} \sim 10^{-3} - 10^{-11}$$

$\lambda = 10$ nm

10^{-4} - 10^{-6} K^{-1}

10^2 - 10^4 $J \cdot K^{-1}$

In the case of **Glass-Forming** systems $R \sim 10^{-4} - 10^{-9}$ ***(FEL pulses > 10^{10} ph)***

5. 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.