VERRE
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GDR Verres
GDR 3338

Atomic motion in glasses studied with coherent X-rays

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Bordeaux, 18/11/2016

iLM INSTITUT LUMIÈRE MATIÈRE

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OUTLINE

- Glassy systems
- X-ray Photon Correlation Spectroscopy
- Aging in metallic glasses
- Measurements *in operando* conditions
- Atomic dynamics in network & oxide glasses
- Conclusions and future perspectives

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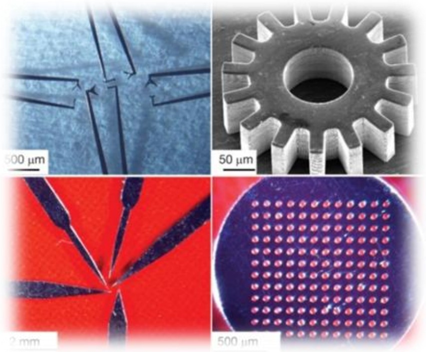
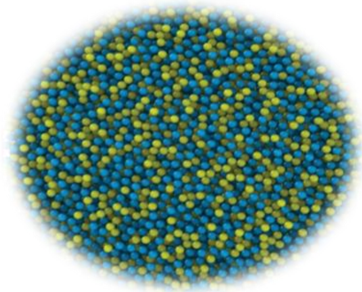
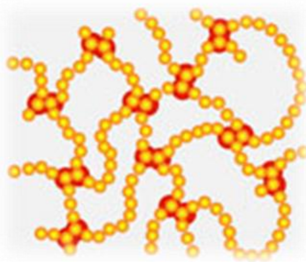
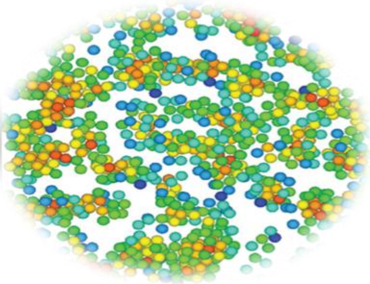
HARD & SOFT GLASSES

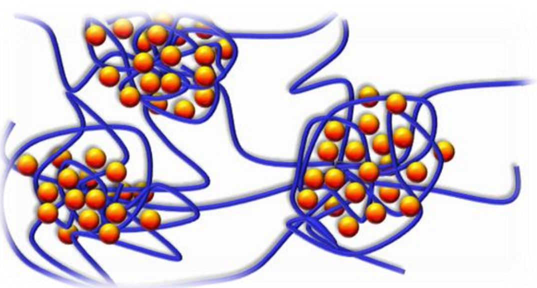
Amorphous materials …





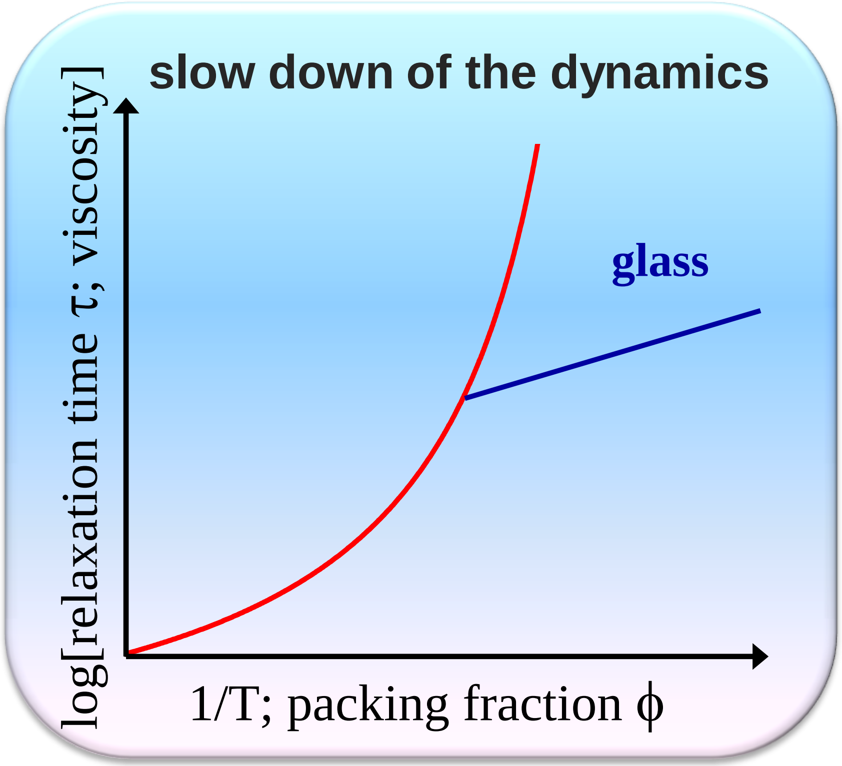






… which can be driven in an arrested state …

- **glasses** → by rapidly cooling the liquid
- **colloidal suspensions** → by increasing the packing fraction
- **granular materials** → by applying a shear
- **chemical gels** → spontaneously with time
- **physical gels** → by changing external parameters (i.e. temperature, pressure..)



… where they display physical aging

→ every physical observables spontaneously evolve with time

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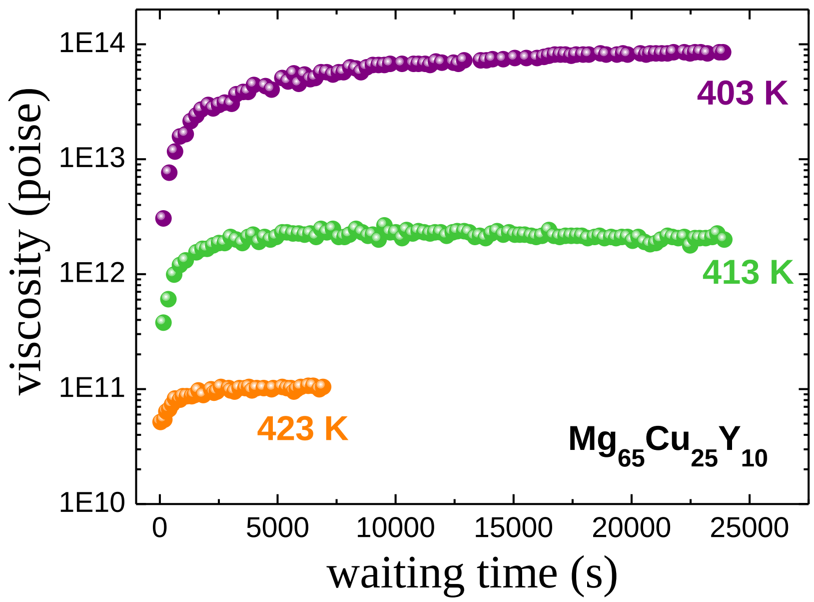
Temporal evolution



Busch et al. J. App. Phys. (1998)

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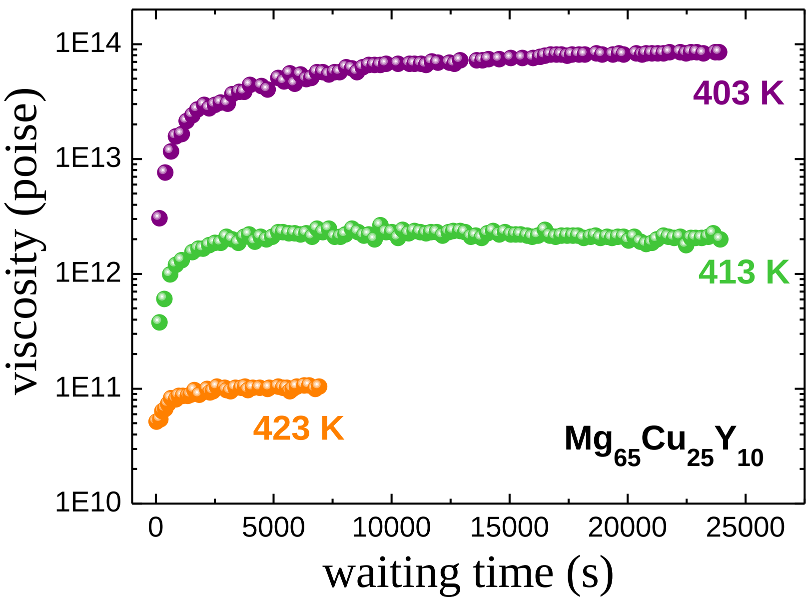

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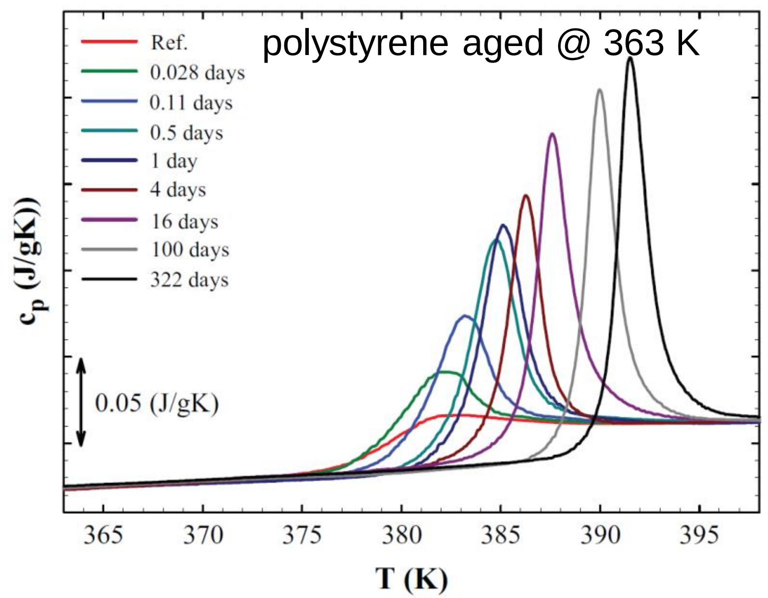
Thermal history dependence



Cangialosi et al. Phys. Rev. Lett. (2012)

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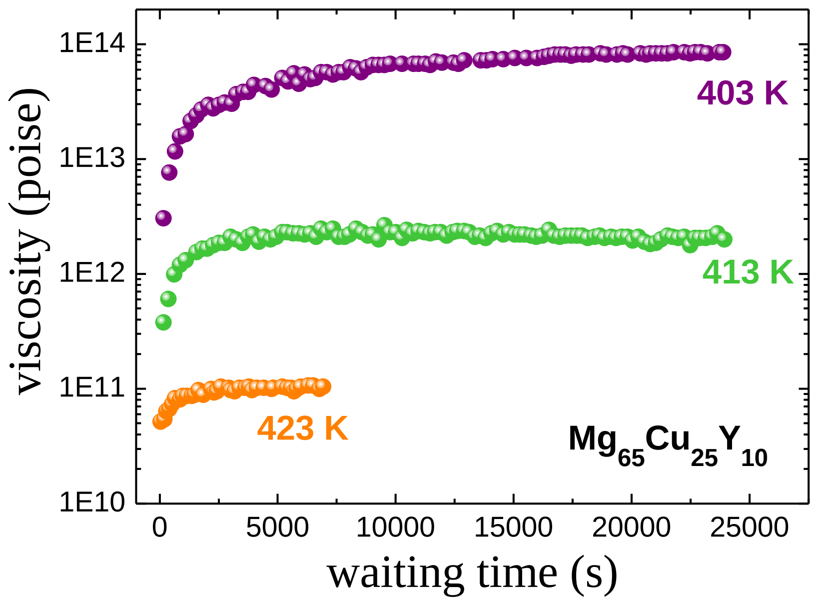

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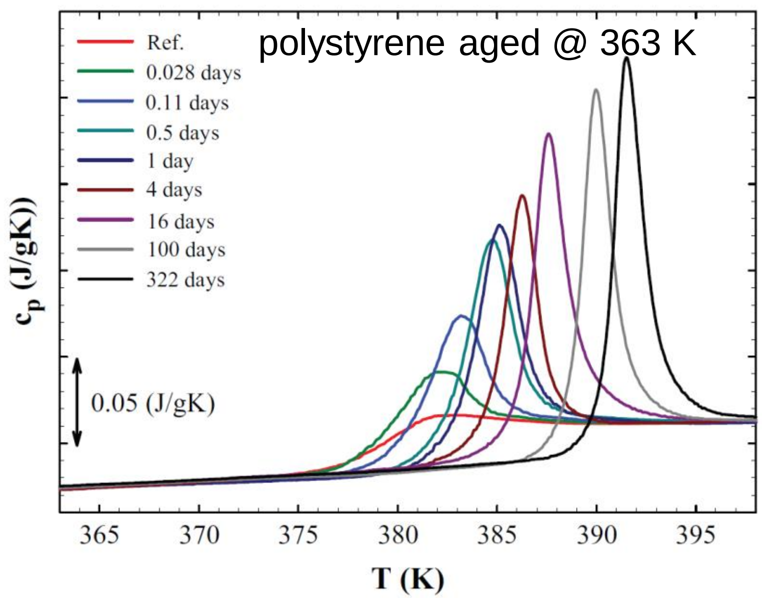


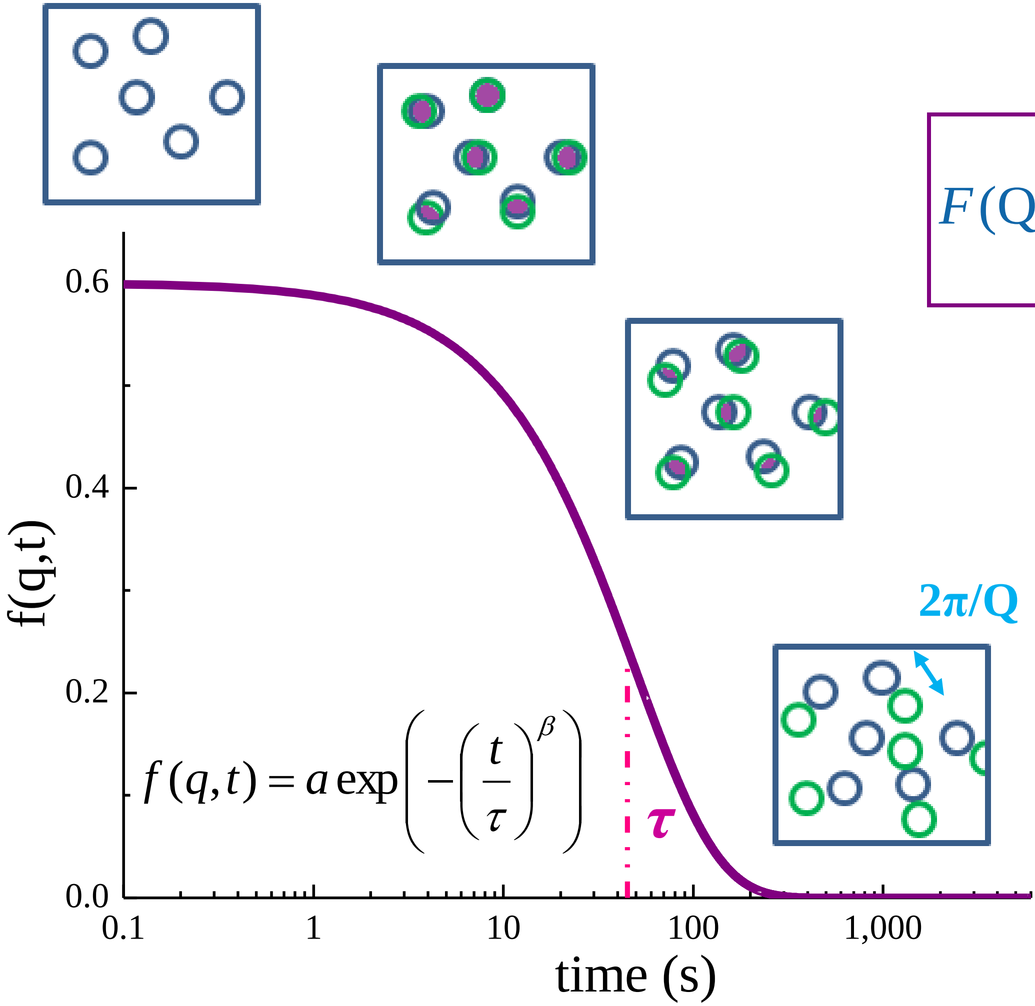
Cangialosi et al. Phys. Rev. Lett. (2012)

Understanding and controlling the physical properties requires information on the ongoing relaxation processes at the microscopic scale

RELAXATION DYNAMICS

Information on the relaxation dynamics can be obtained from the decay of the **intermediate scattering function** on a scale 2π/Q

$$F(\mathrm{Q,t}) = \frac{S(Q,t)}{S(Q)} = \frac{\left\langle \delta\rho_Q^*(0)\delta\rho_Q(t)\right\rangle}{\left\langle \delta\rho_Q^*(0)\delta\rho_Q(0)\right\rangle}$$



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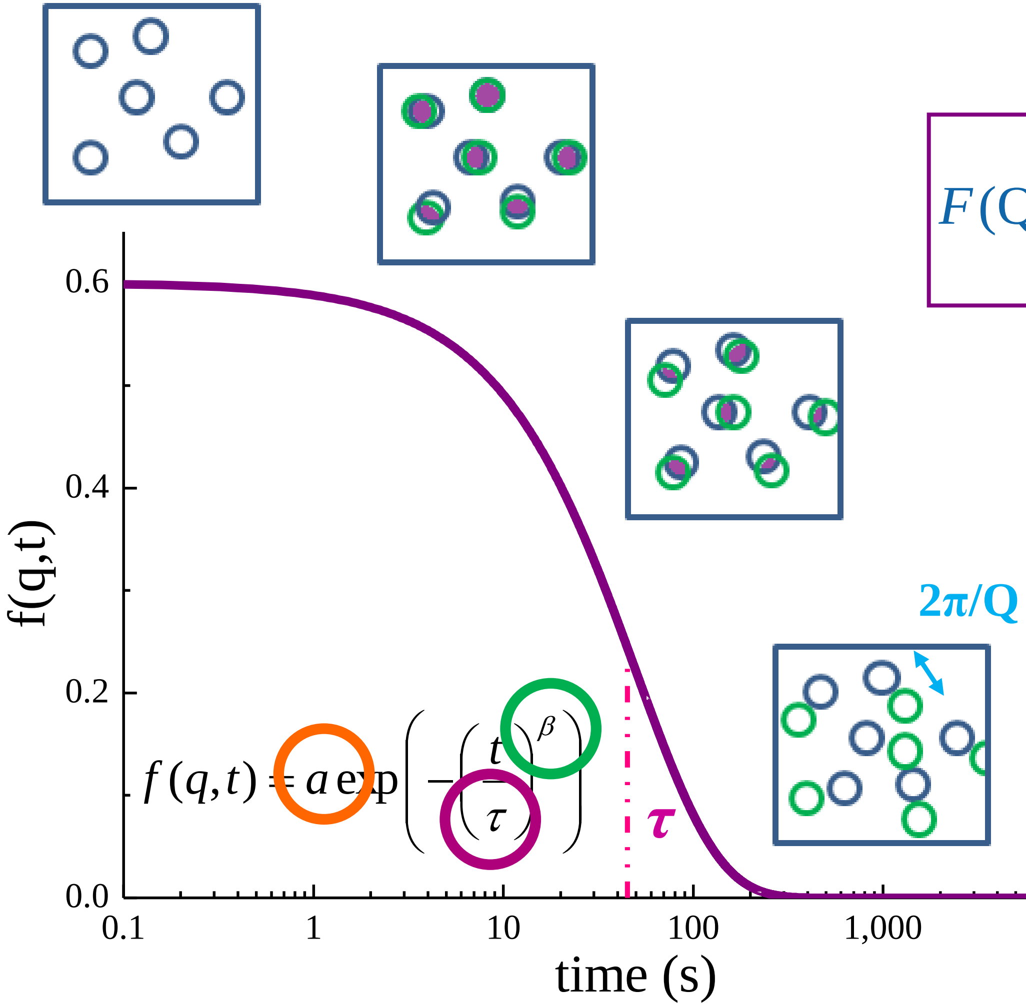

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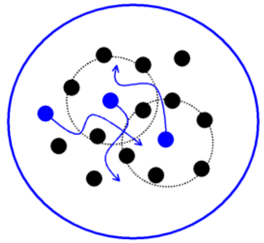

τ = time for structural rearrangements (on ~2/3 Å in the case of glasses)

How can we measure the relaxation dynamics in a glass?

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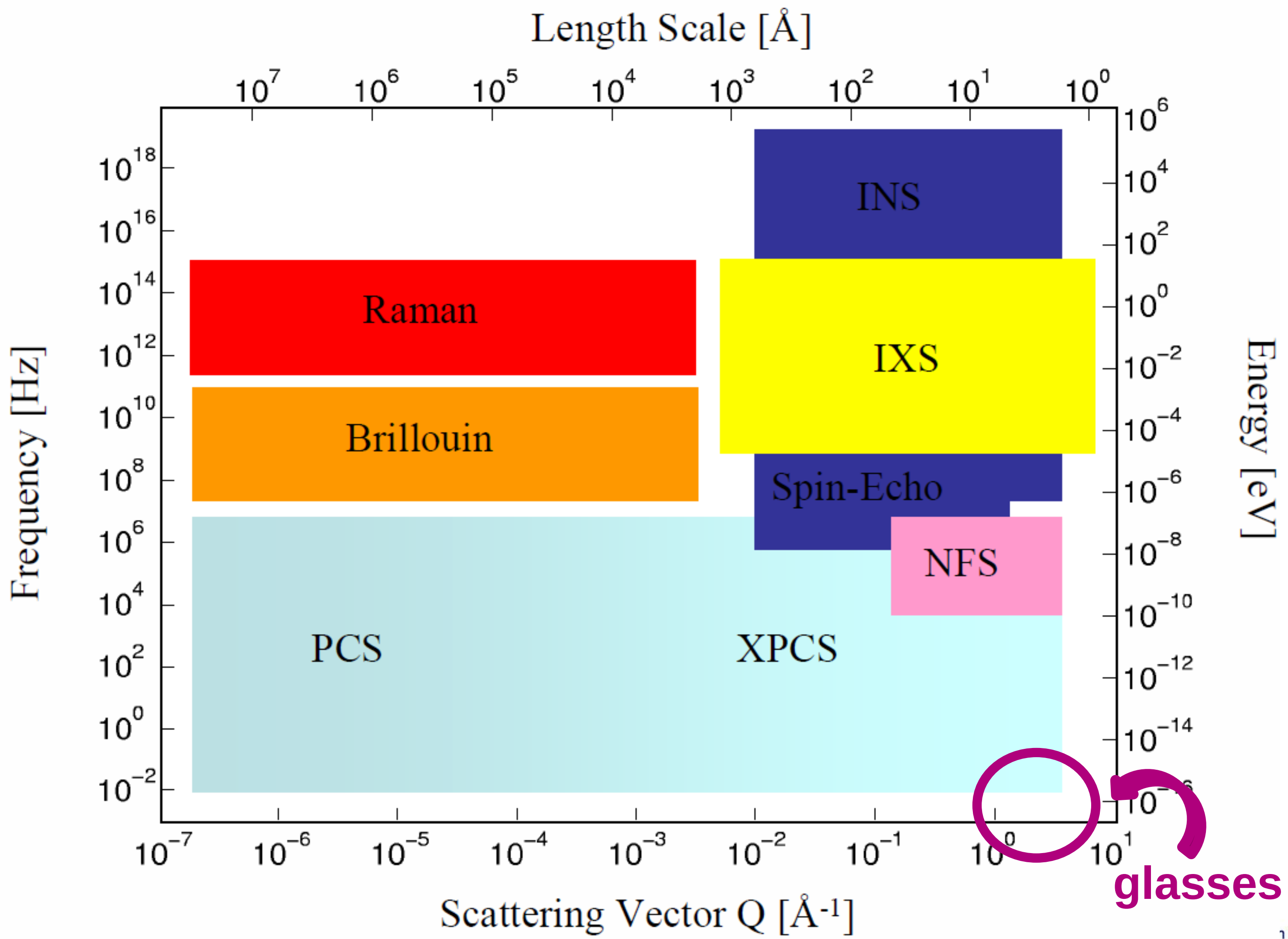
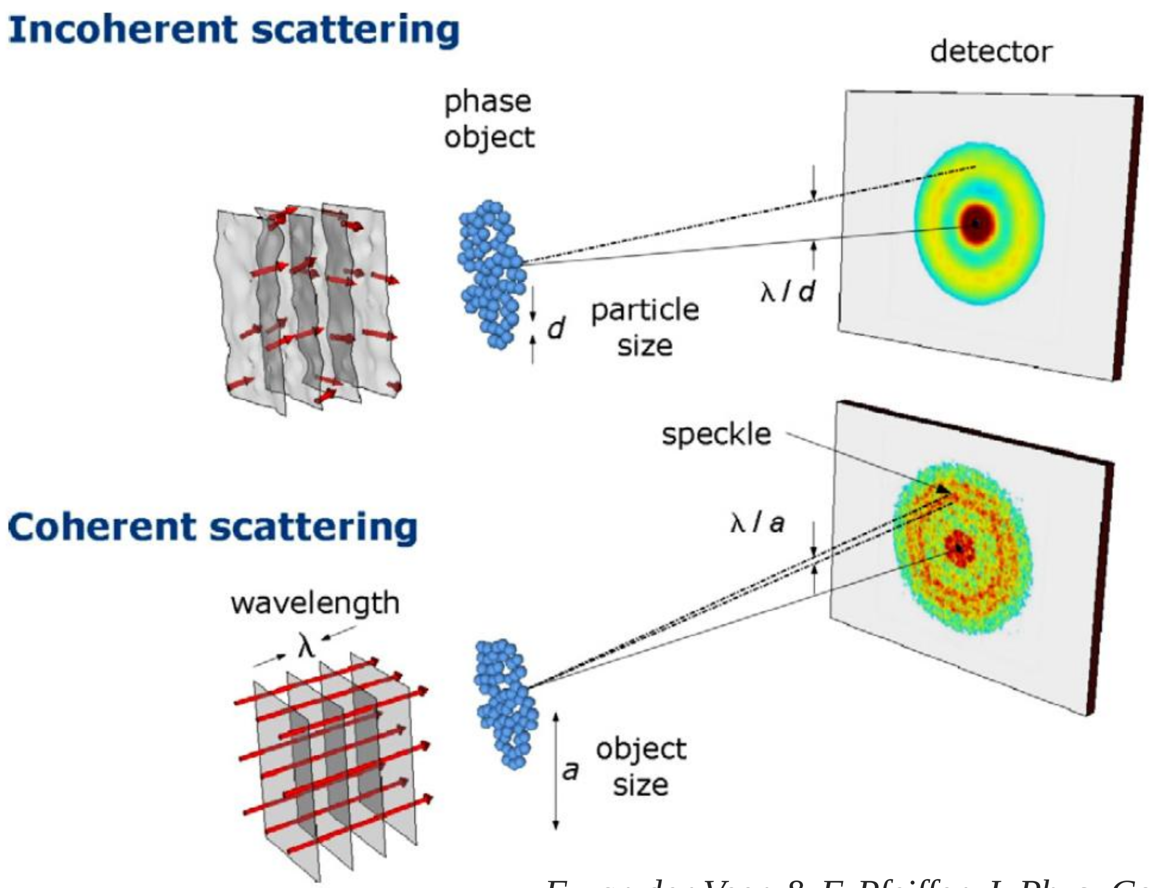
X-RAY PHOTON CORRELATION SPECTROSCOPY

X-ray Photon Correlation Spectroscopy is the **only technique** offering the potential to unravel the dynamics of glass formers around and below T_g **(τ~1-10^4 s, Q ~0.3-4 Å^{-1})**



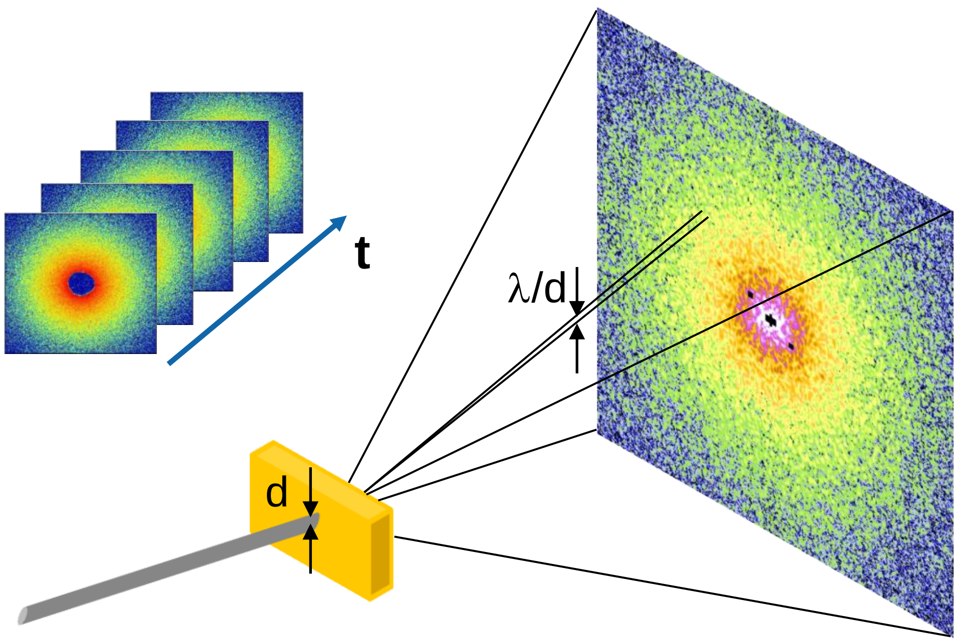
XPCS uses the partial coherent properties of X-rays at 3rd generation synchrotrons



F. van der Veen & F. Pfeiffer, J. Phys. Cond. Mat. (1998)

X-RAY PHOTON CORRELATION SPECTROSCOPY

Information on the dynamics can be obtained by measuring a series of speckles patterns and quantifying **temporal correlations of intensity fluctuations** at a given wave-vector q



The intensity of the speckles is related to the **exact spatial arrangement** of the scatters inside the system

$$I(Q,t) \propto \left| \sum_n f_n(Q) \cdot e^{iQ\cdot r_n(t)} \right|^2$$

Information on the microscopic dynamics

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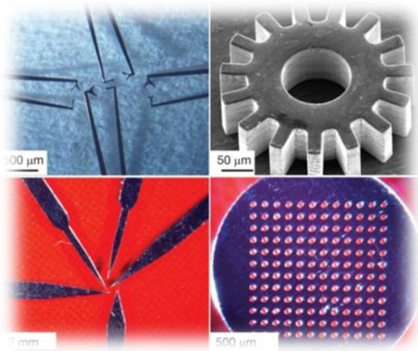
METALLIC GLASSES

MGs have outstanding properties and carry the promise of many applications.



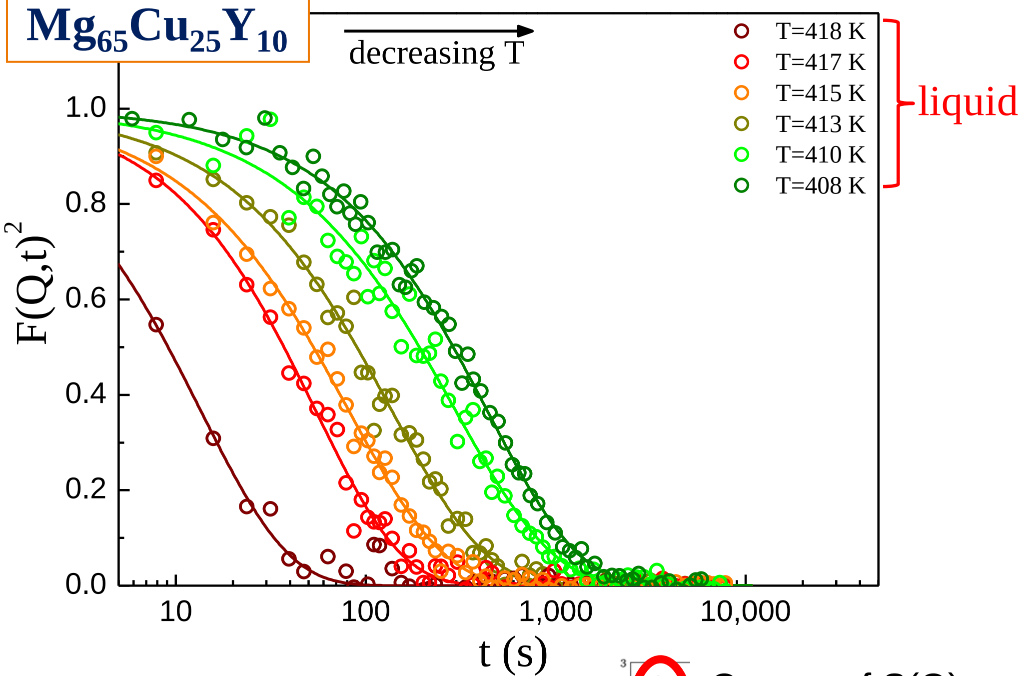
Applications of MGs

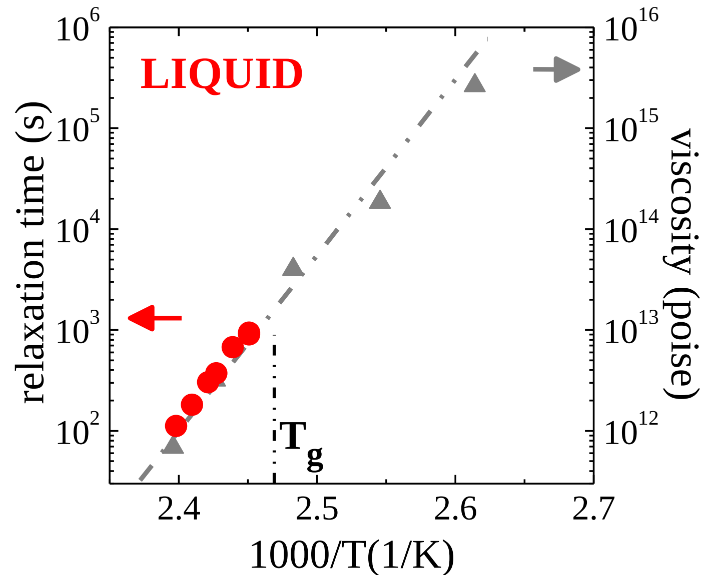
- Electronics and computers — Hard disks, sensors, CD, DVD
- Medicine and biology — Prosthesis, cell culture surfaces, surgery tools
- Tools and machine tools — Gears, micro-servo motors
- Environmental applications — Fuel cells, H_2 membranes

Their widespread use is **however** blocked by the **difficulty of avoiding aging and crystallization** during processing (particularly strong for MGs)

FIRST INVESTIGATION OF ATOMIC DYNAMICS IN MGs

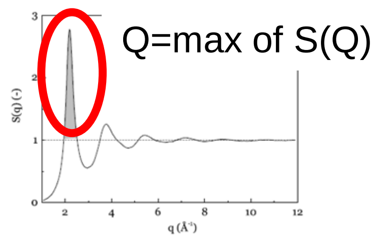
$Mg_{65}Cu_{25}Y_{10}$





Fit model: KWW

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



B. Ruta et al. Phys. Rev. Lett. 2012

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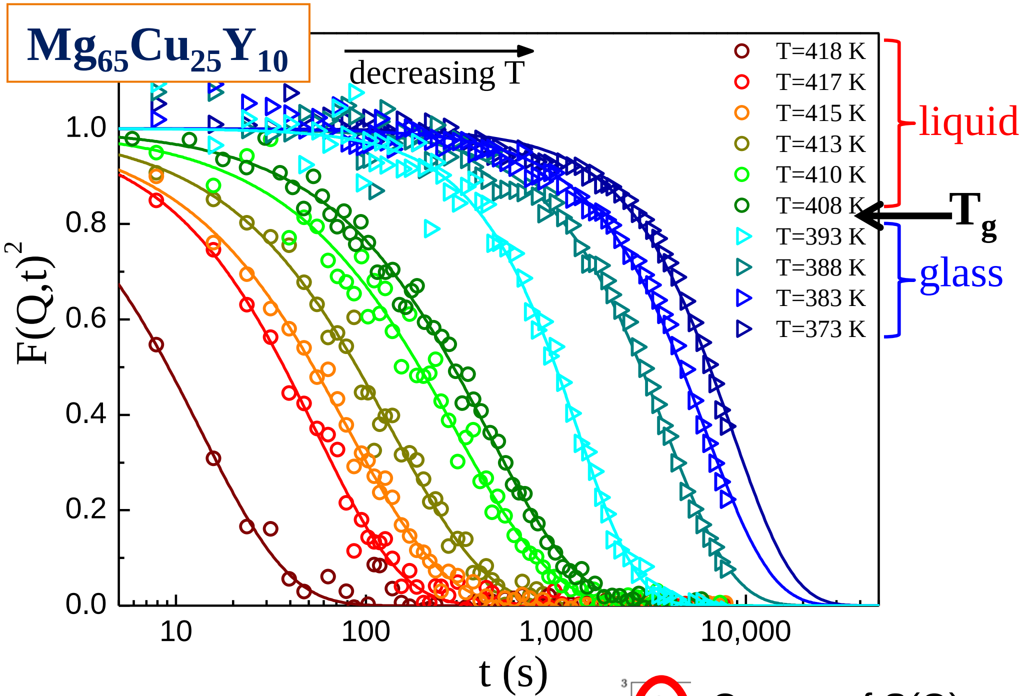

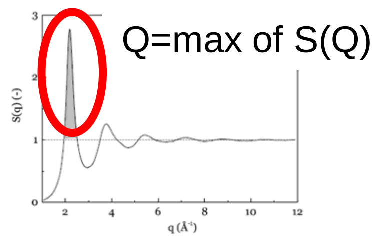

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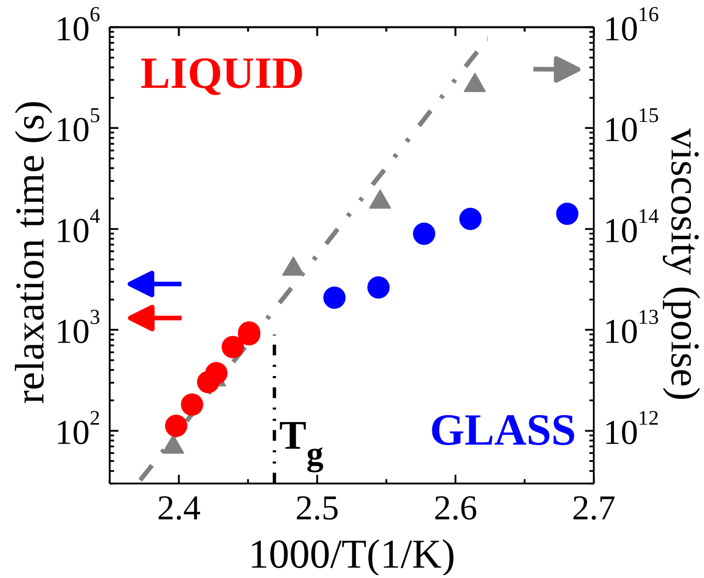

Departure from the liquid curve

B. Ruta et al. Phys. Rev. Lett. 2012

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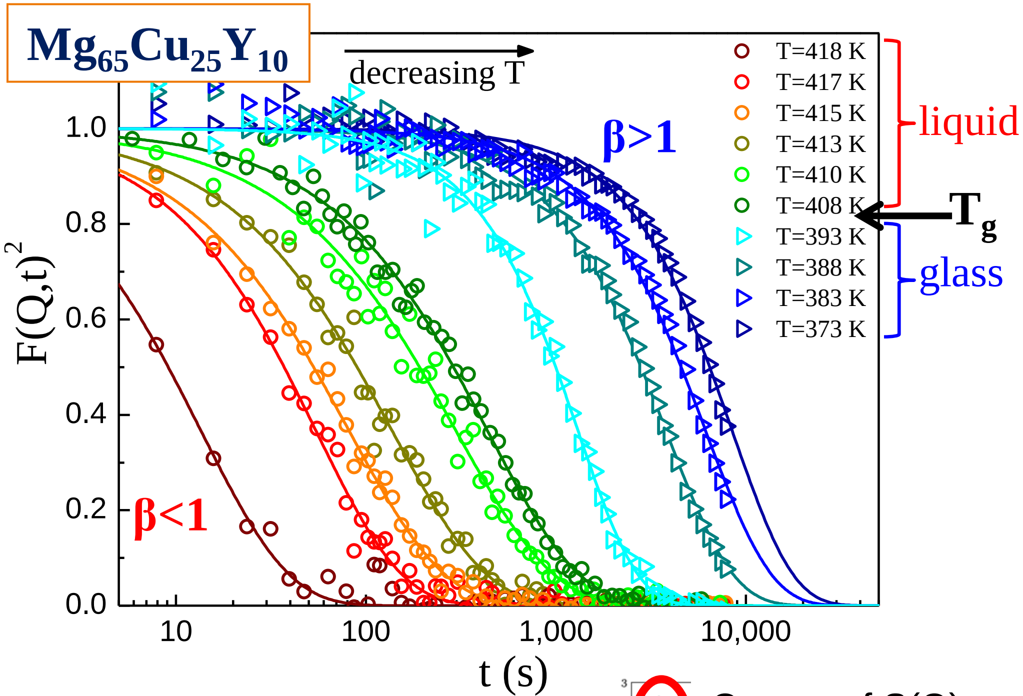

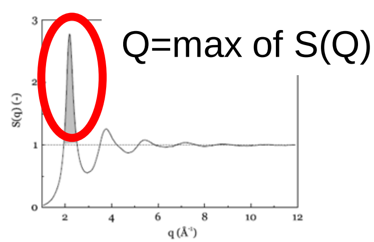

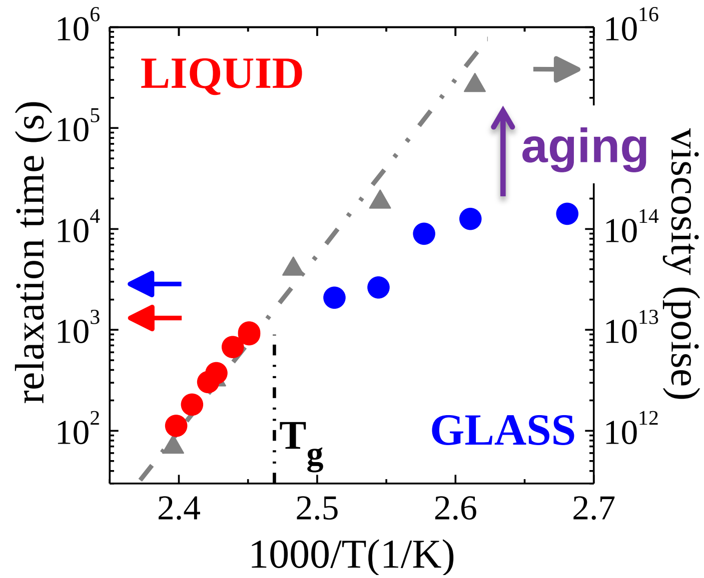

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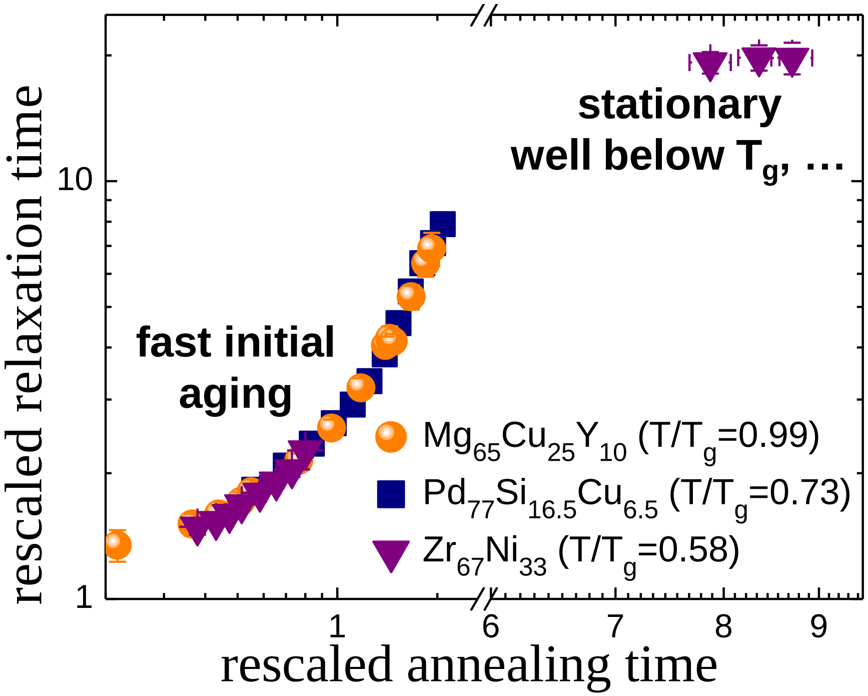
DYNAMICAL CROSSOVER AT T_G

$T>T_g$: stationary dynamics, β<1, diffusive motion

$T<T_g$: aging, β>1 , **Anomalous stress-dominated dynamics**

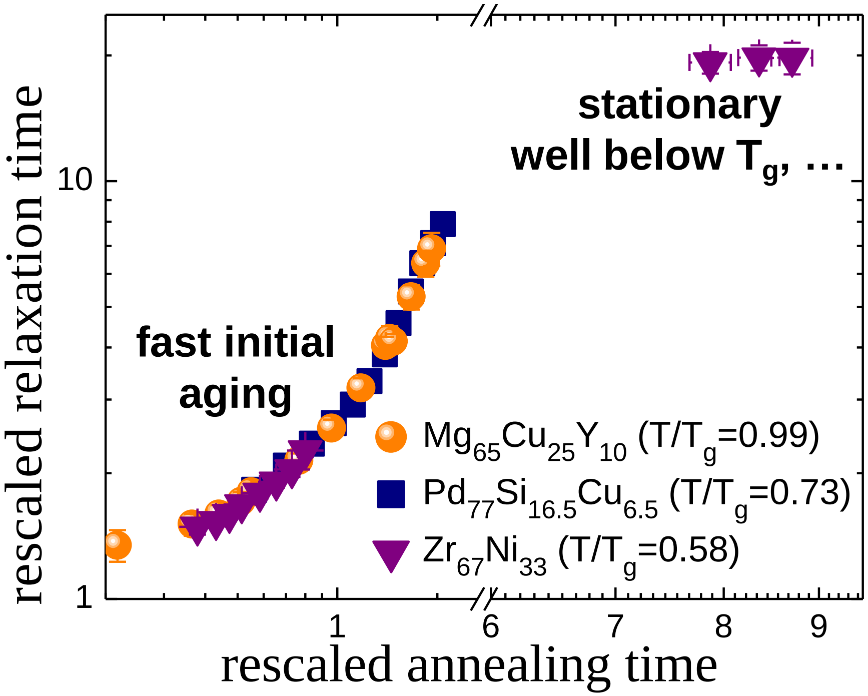
B. Ruta et al. Phys. Rev. Lett. 2012

MICROSCOPIC AGING IN MGs



Surprising hierarchy of “anomalous” dynamical regimes

MICROSCOPIC AGING IN MGs



Surprising hierarchy of "anomalous" dynamical regimes

→ Contradiction with the continuous evolution of macroscopic measurements

Ruta et al. Phys. Rev. Lett. (2012)
Ruta et al. J. Chem. Phys. (2013)
Evenson, Ruta et al. Phys. Rev. Lett. (2015)

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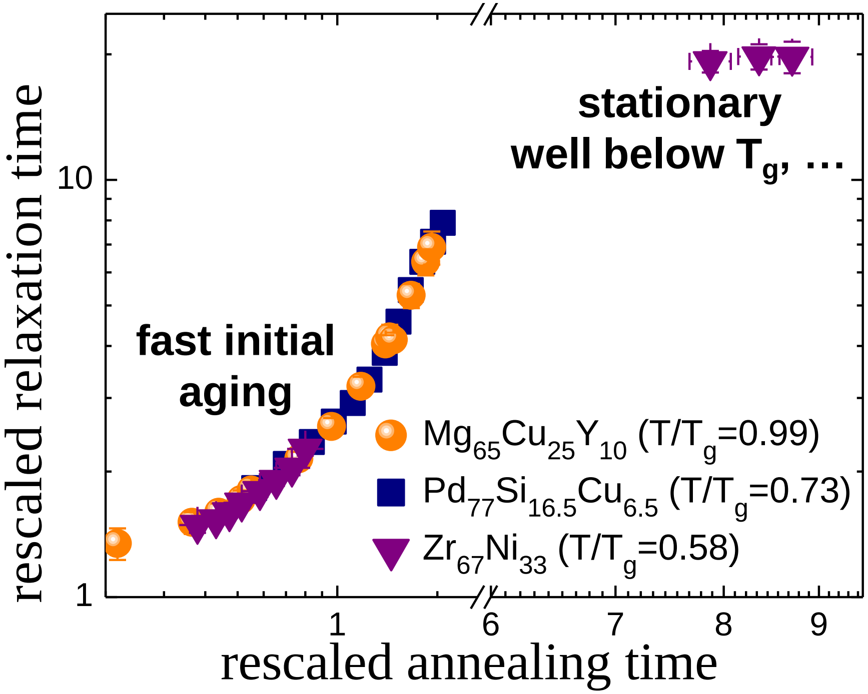

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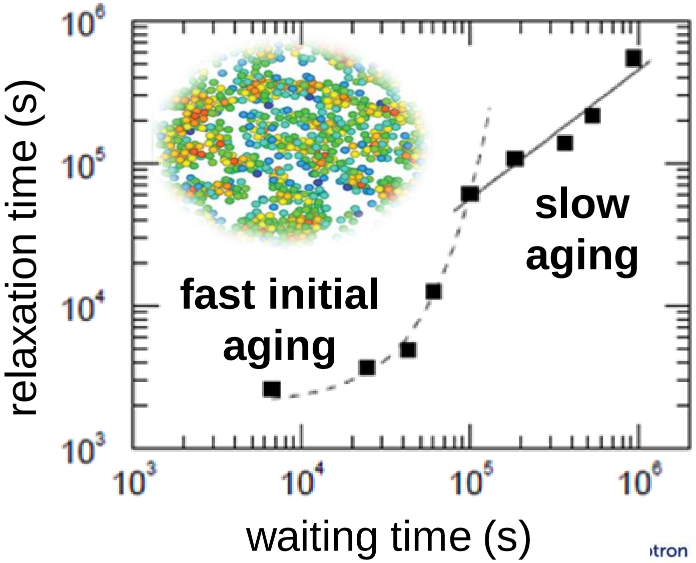
Ruta et al. Phys. Rev. Lett. (2012)
Ruta et al. J. Chem. Phys. (2013)
Evenson, Ruta et al. Phys. Rev. Lett. (2015)

Similar to what observed in soft materials (colloidal gels, emulsions, polymeric gels, …)

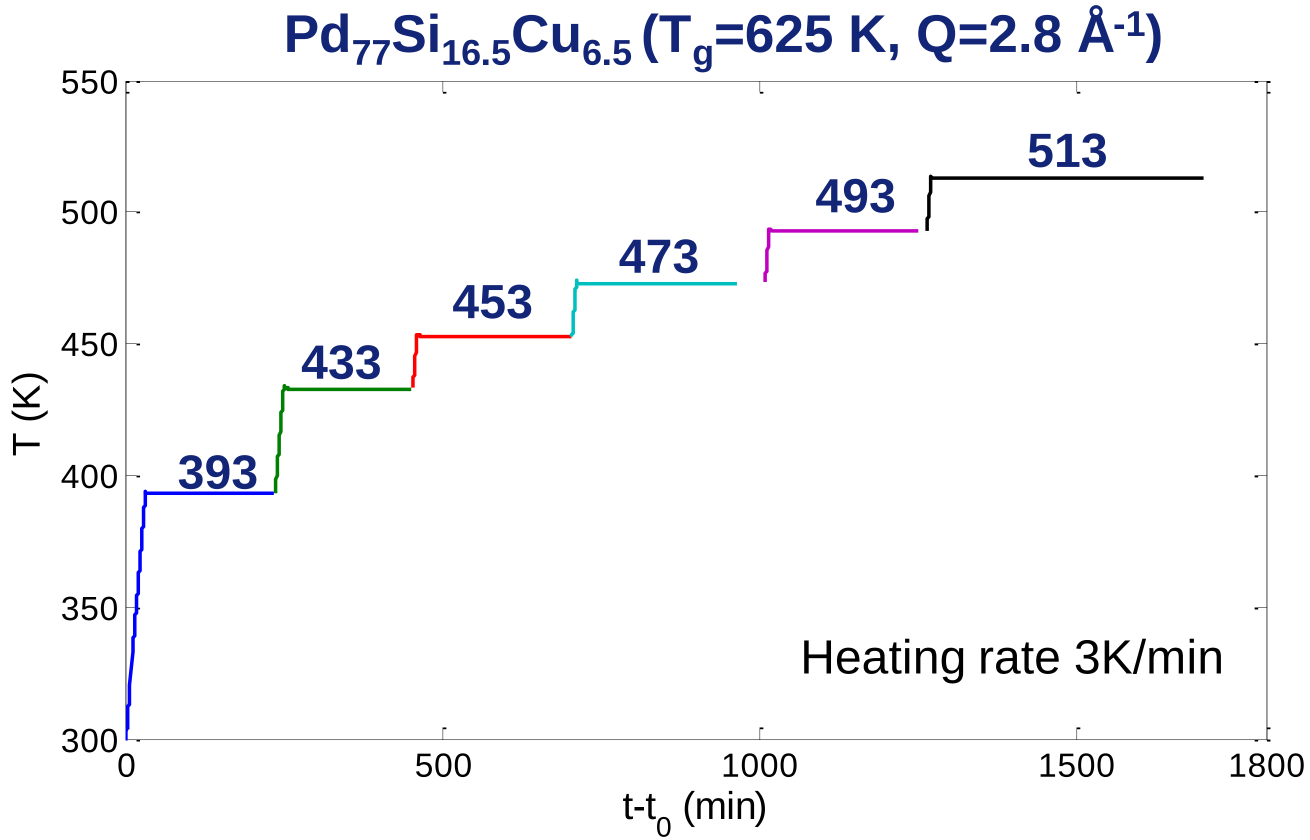
Cipelletti et al. Phys. Rev. Lett. (2000)

→ Universal stress-dominated dynamics?



What is the origin of the microscopic aging?

Combining XRD and XPCS → same thermal and temporal protocol

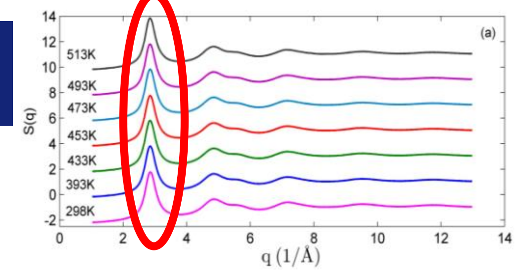


2 XRD experiments:

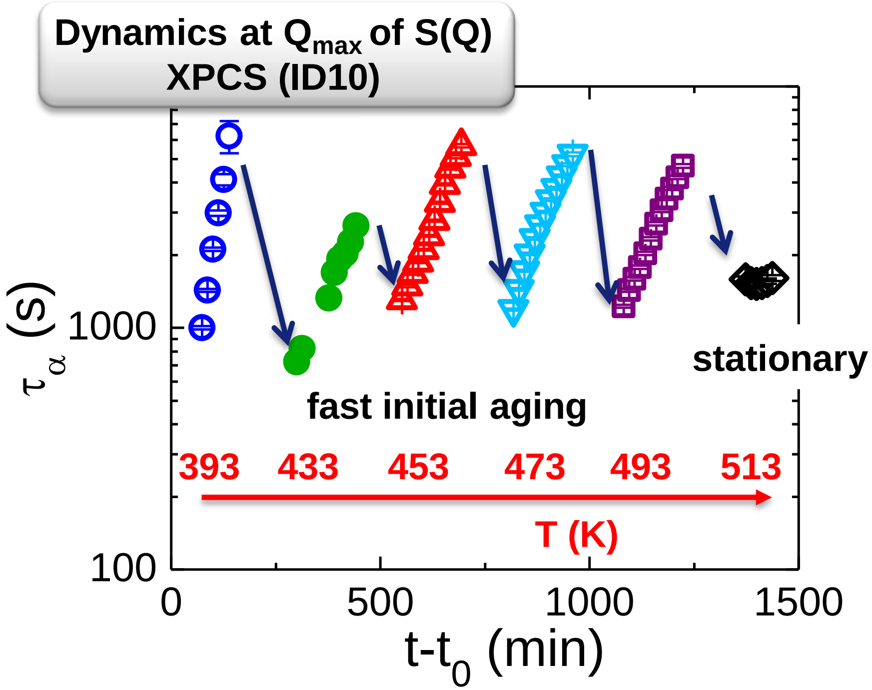
i) high resolution around the FSDP

ii) large q range (up to 25$Å^{-1}$ to extract the pair distribution function G(r))

STRUCTURE & DYNAMICS DURING AGING



Complementary dynamical (ID10) & structural (ID15) study

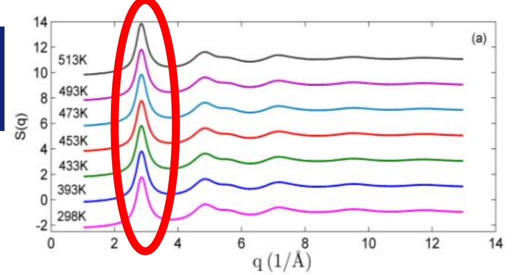


$$\tau(T, t_w) = \tau_0(T)\exp(t_w / \tau^*)$$

τ*(393→493 K) ~6000 s

- Fast aging along isotherms, strong τ reduction at temperature jumps
- Frozen dynamics at the highest T (513 K)

STRUCTURE & DYNAMICS DURING AGING



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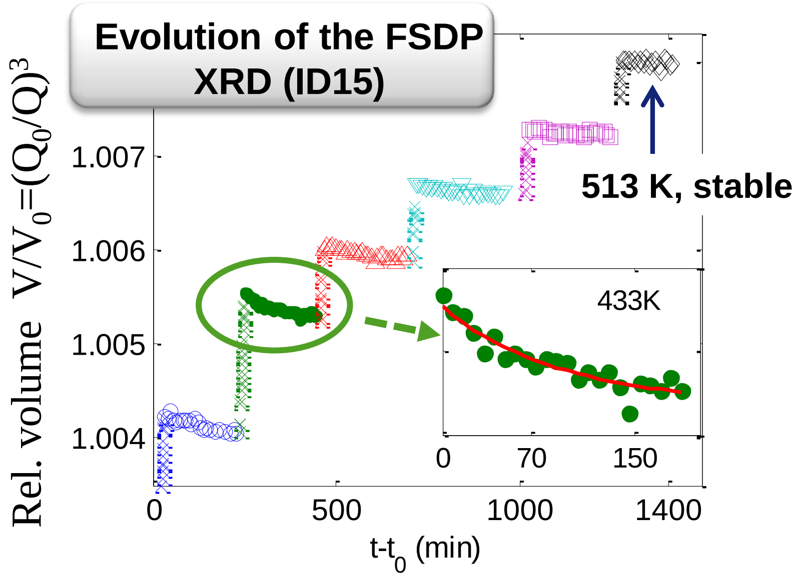
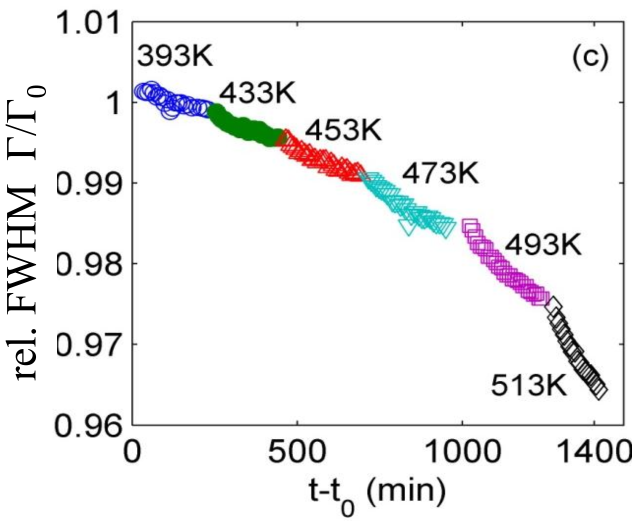




Isothermal volume relaxation

Continuous FSDP sharpening

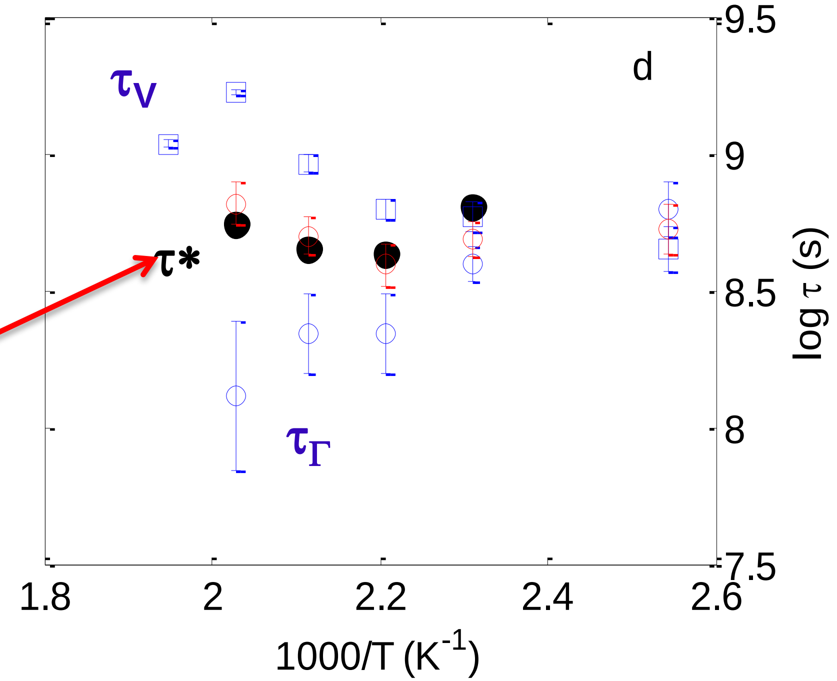
$$\frac{V}{V_0}(t,T) = \frac{V}{V_0}(0,T)\exp(-\frac{t}{\tau_V})$$

$$\frac{\Gamma}{\Gamma_0}(t,T) = \frac{\Gamma}{\Gamma_0}(0,T)\exp(-\frac{t}{\tau_\Gamma})$$

Three characteristic aging times:

Aging time from $V/V_0 \rightarrow \tau_V$
Aging time from $\Gamma/\Gamma_0 \rightarrow \tau_\Gamma$
Aging time from $\tau_\alpha \rightarrow \tau^*$

$$\tau^* = \frac{\tau_V + \tau_\Gamma}{2}$$



Two main processes controlling the aging:
1) volume shrinking (density changes) → **fast aging**

2) medium range ordering (constant density) → **stationary regime** (also → **fast aging**)

Giordano & Ruta, Nature Commun. 2016

STRUCTURE & DYNAMICS DURING AGING

Three characteristic aging times:

Aging time from $V/V_0 \rightarrow \tau_V$
Aging time from $\Gamma/\Gamma_0 \rightarrow \tau_\Gamma$
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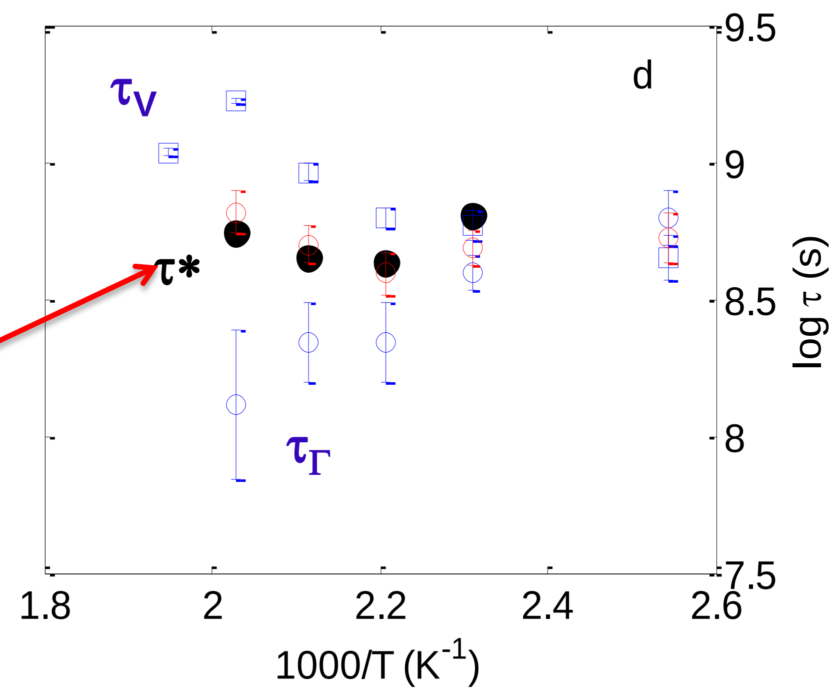

Two main processes controlling the aging:
1) volume shrinking (density changes) → **fast aging**

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the evolution between the two could be related to a **ductile to brittle transition**

Giordano & Ruta, Nature Commun. 2016

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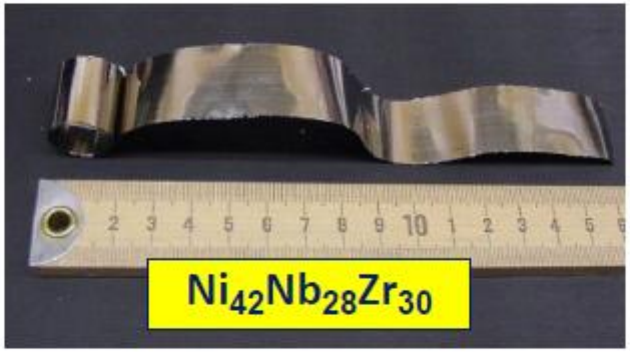
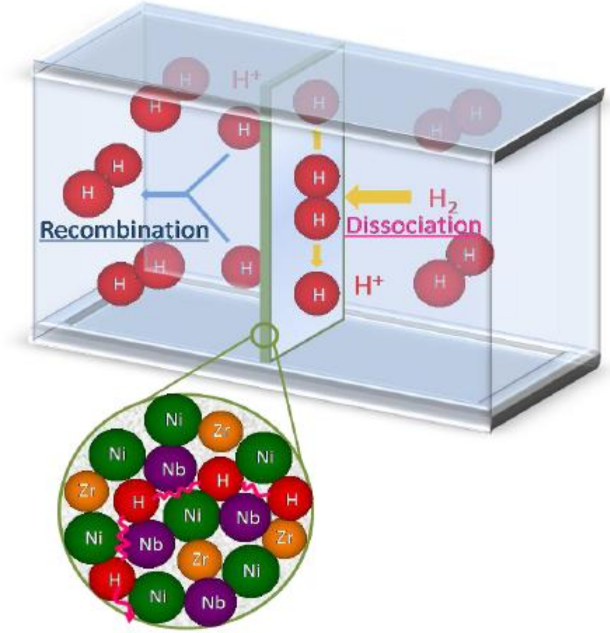
MG MEMBRANES FOR H_2 SEPARATION FROM CO_2





Ni and Zr-based MGs:

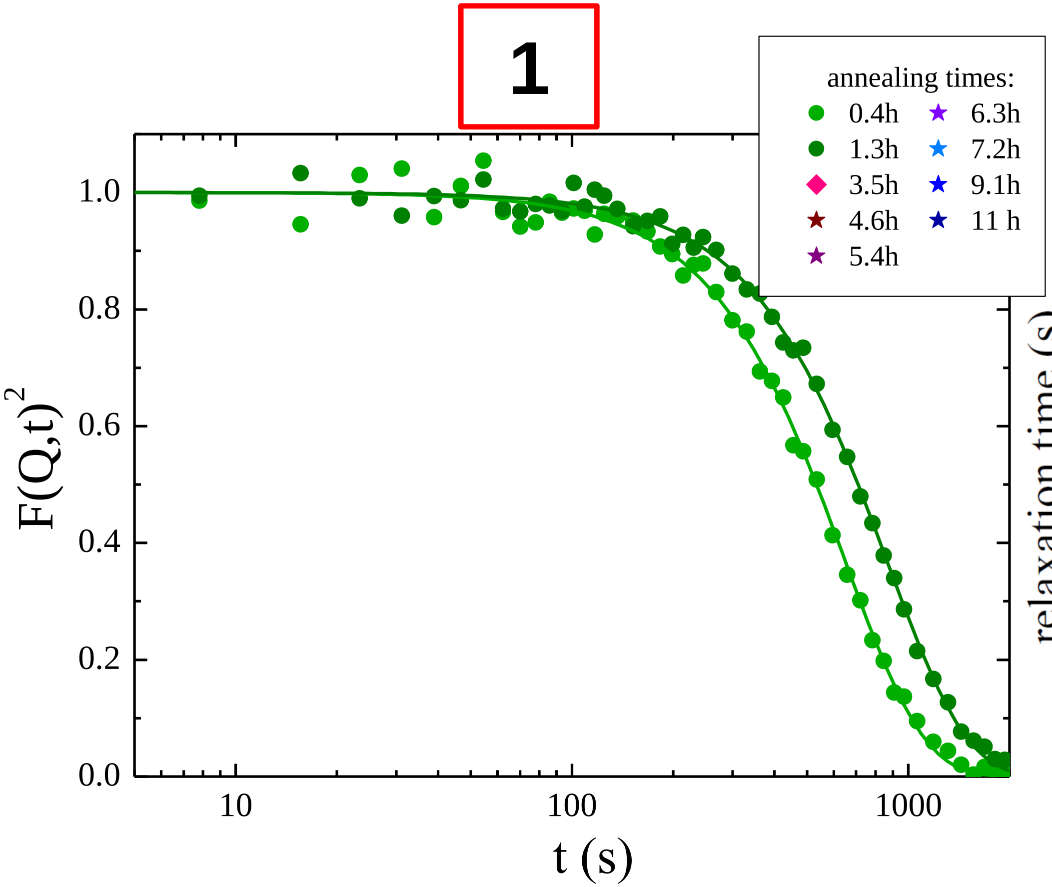
→ **better H_2 permeability** than crystalline materials (high H_2 diffusivity due to the free volume)

→ **high H_2 solubilities and diffusivities**

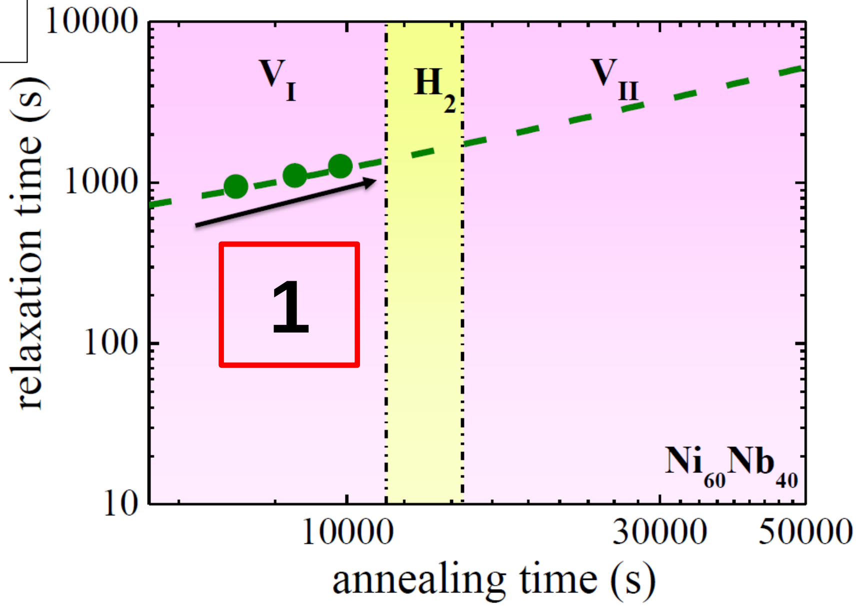
→ **non-precious metals/alloys**
Pd: ~20000 euro/Kg
Group IV and V metals ~10-200 euro/Kg

Collab. with Prof. D. Chandra (DOE - NNSA Grant, US)

EFFECT OF H_2 ON THE DYNAMICS



$Ni_{60}Nb_{40}$, T=373 K , Q_p=2.7 $Å^{-1}$
H @ 0.6 bar



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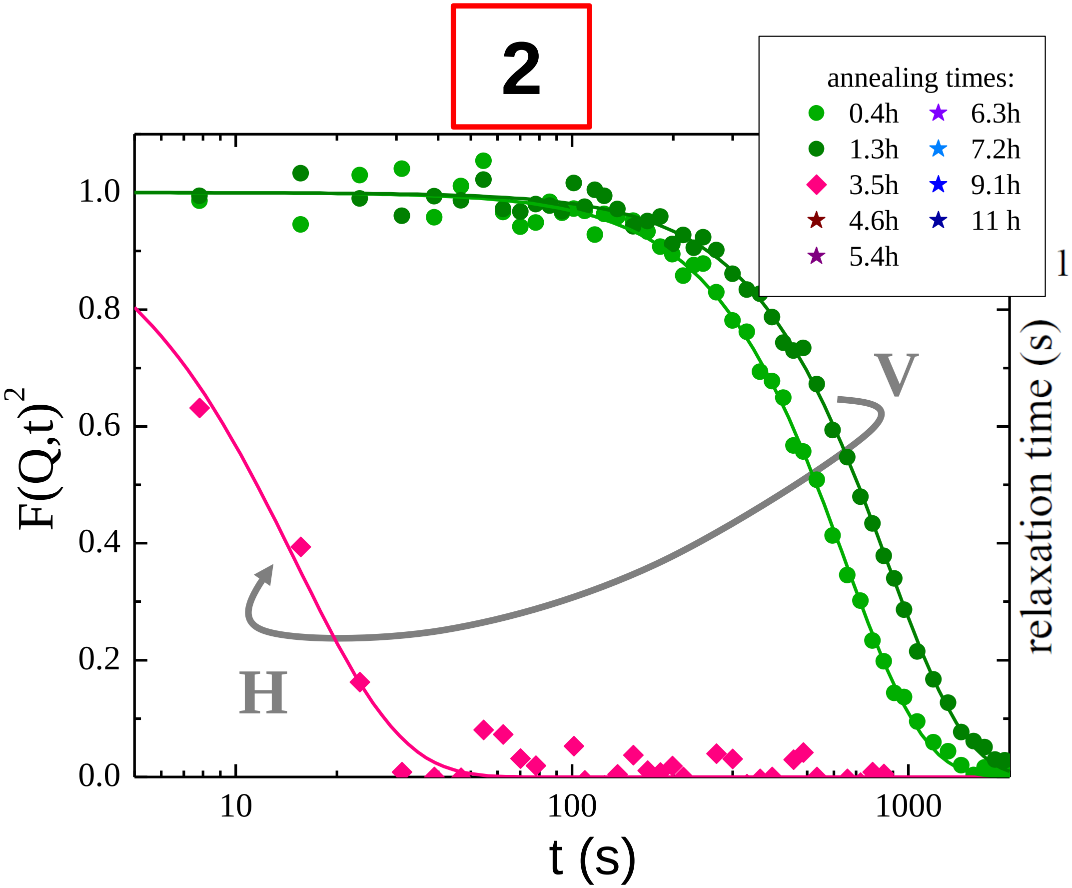

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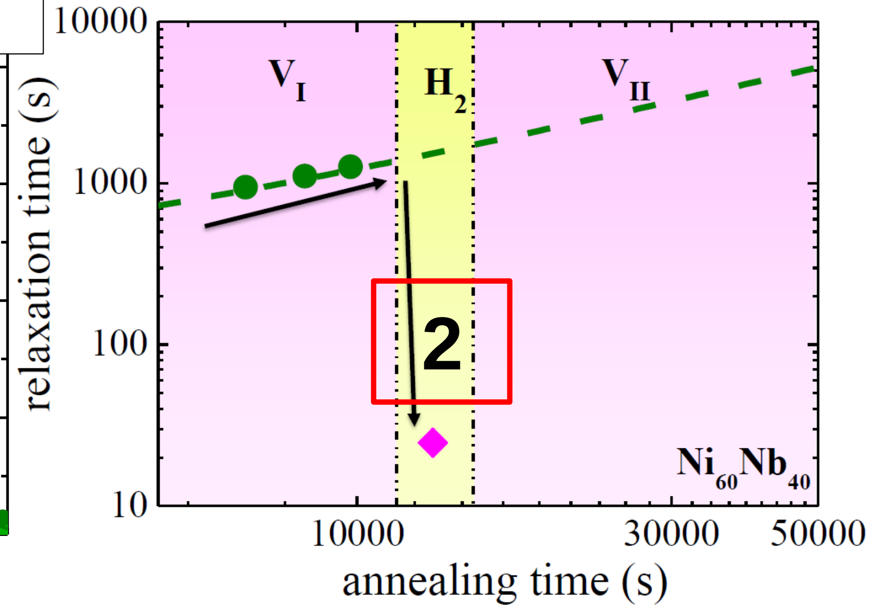
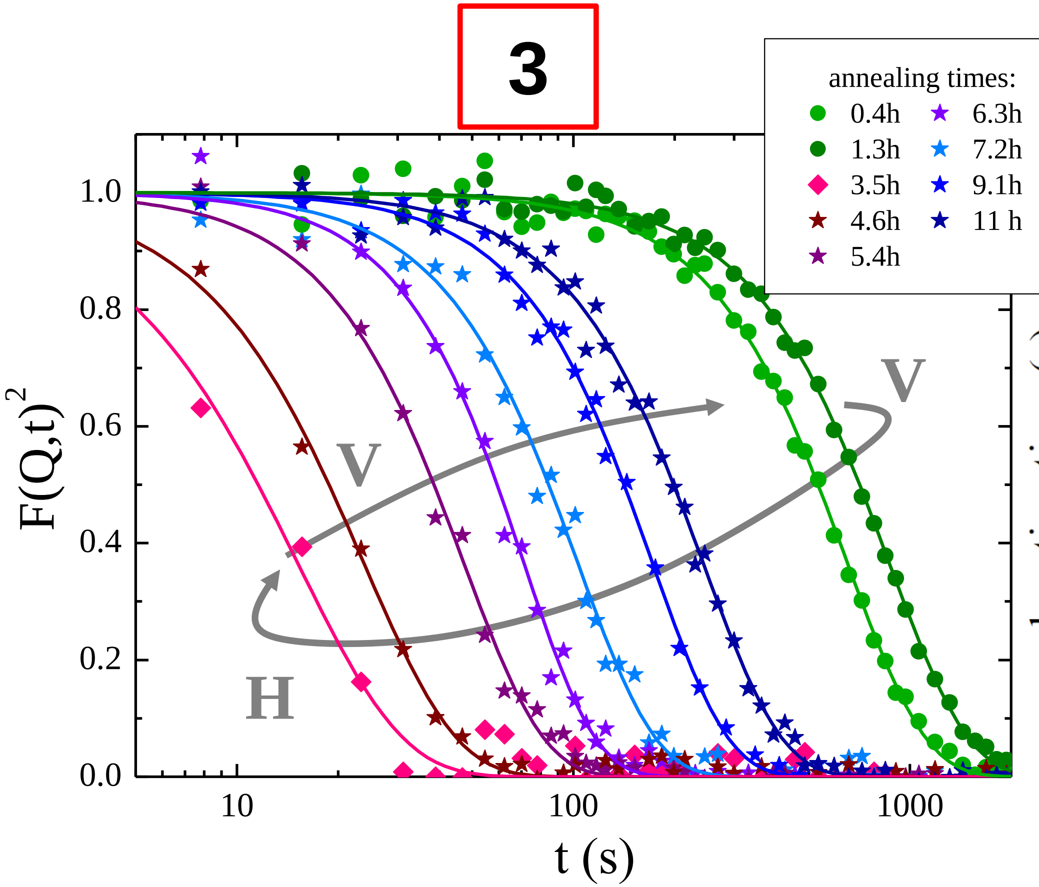


Dramatic acceleration of the dynamics due to the hydrogen atmosphere

EFFECT OF H_2 ON THE DYNAMICS



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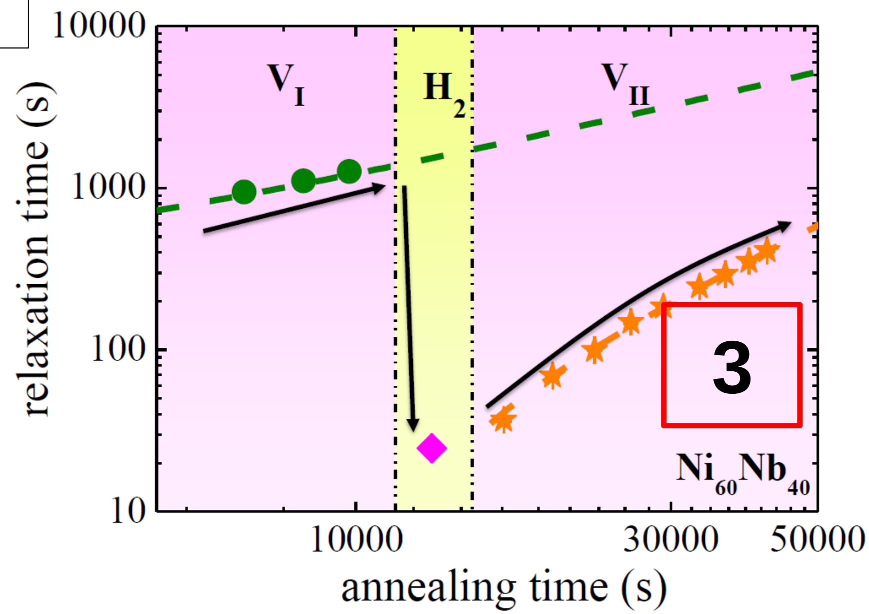

Dramatic acceleration of the dynamics due to the hydrogen atmosphere

Reversible transition: after removing the hydrogen, the dynamics slows down again but with a faster aging

B. Ruta et al. in progress

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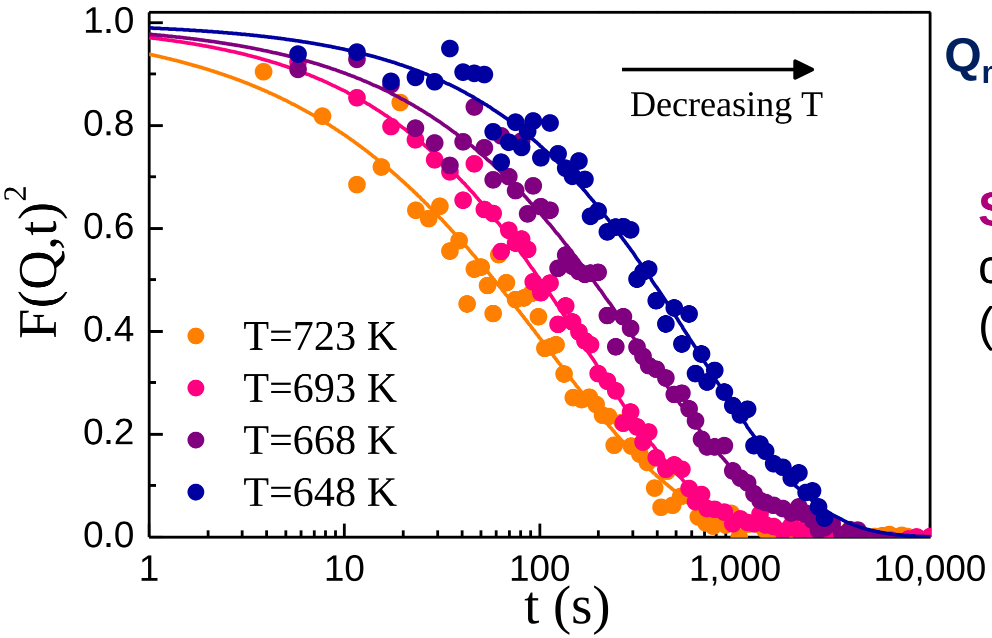
SILICATE GLASSES: $0.8SIO_2$-$0.2NA_2O$ (NS4, T_g=783 K)



Q_{max}=1.53 Å^{-1}; measurements in the glass transition region

Stretched exponential decay of the correlation function as in the liquid phase (β=0.67) → diffusive motion

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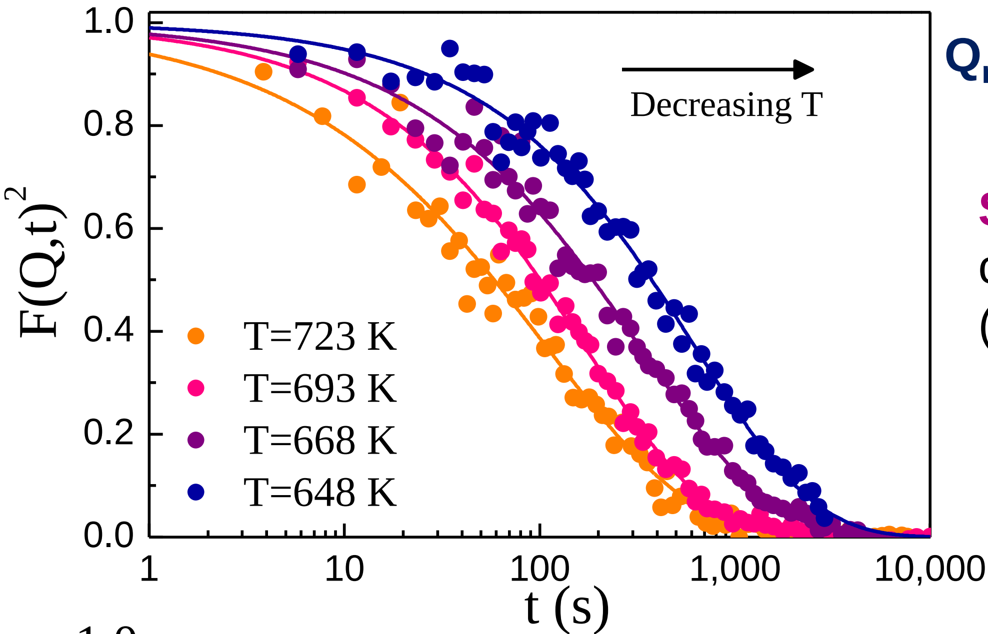
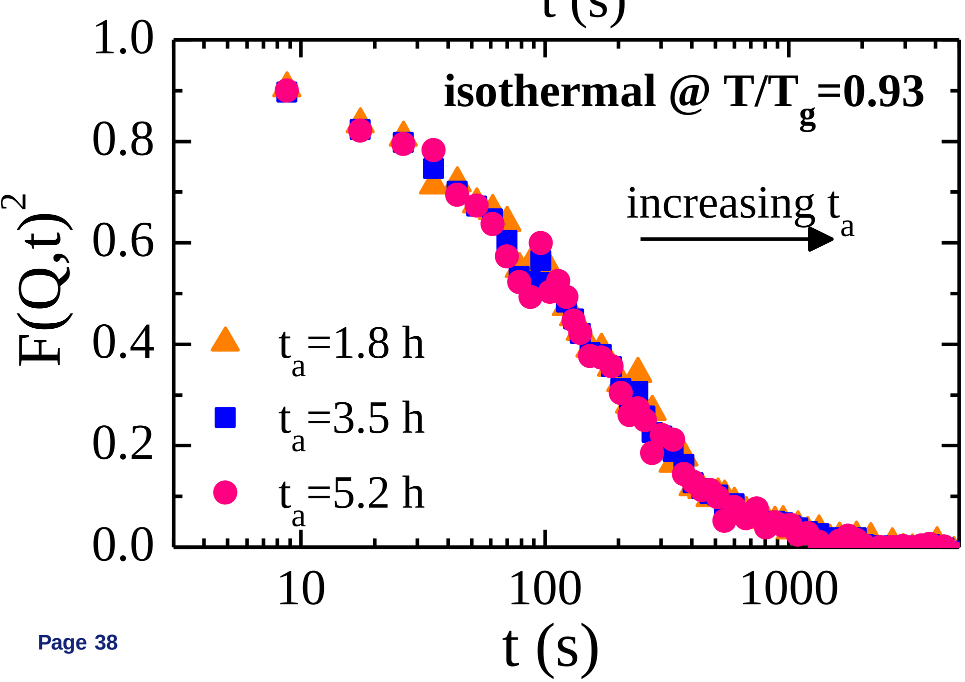


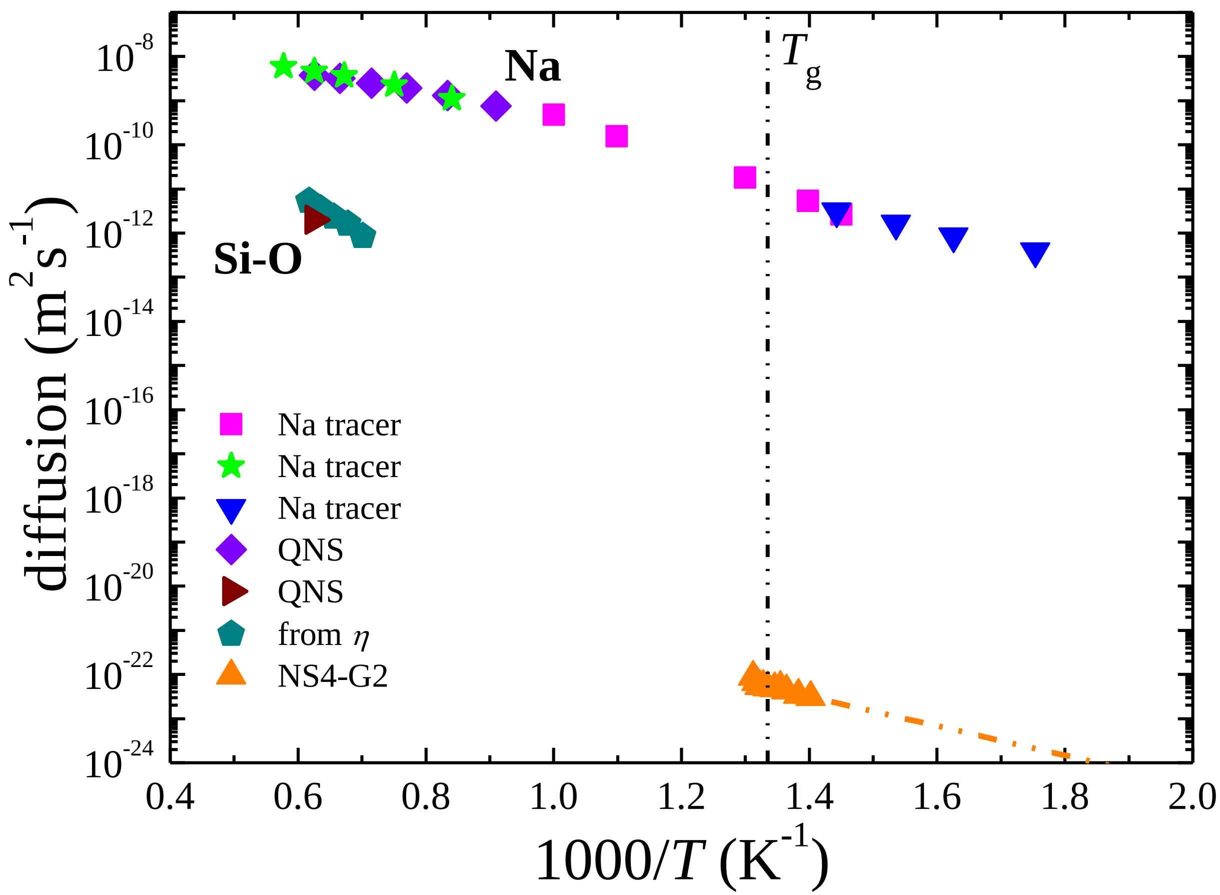
Q_{max}=1.53 Å^{-1}; measurements in the glass transition region

Stretched exponential decay of the correlation function as in the liquid phase (β=0.67) → diffusive motion



Absence of physical aging on the experimental time scale

COMPARISON WITH DIFFUSION DATA



XPCS data :

- ❑ ~10 orders of magnitude slower than the Na diffusion
- ❑ Closer to the low T extrapolation of the Si-O matrix

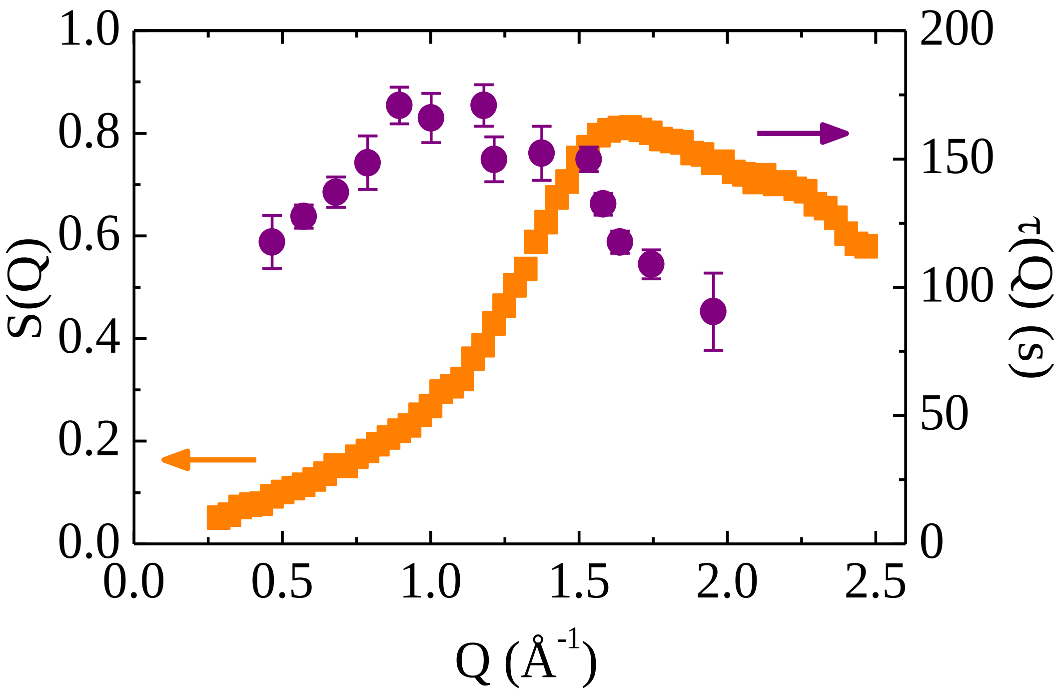
$$D_{XPCS} = 1/(\tau_{incoh} Q^2)$$

$$\tau_{incoh} = \tau_{XPCS} / S(Q)$$

Hempelmann et al, Z. Phys. B (1994)
Kargl et al. Phys. Rev. B. (2006)

B. Ruta et al., Nat. Commun. (2014)

WAVE VECTOR DEPENDENCE



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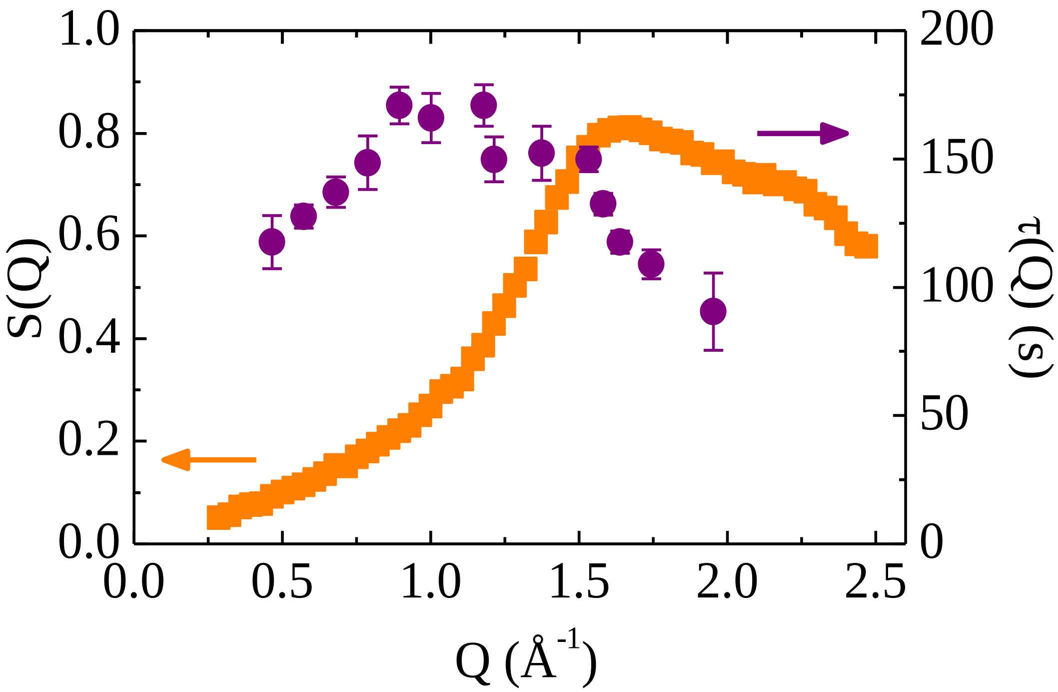
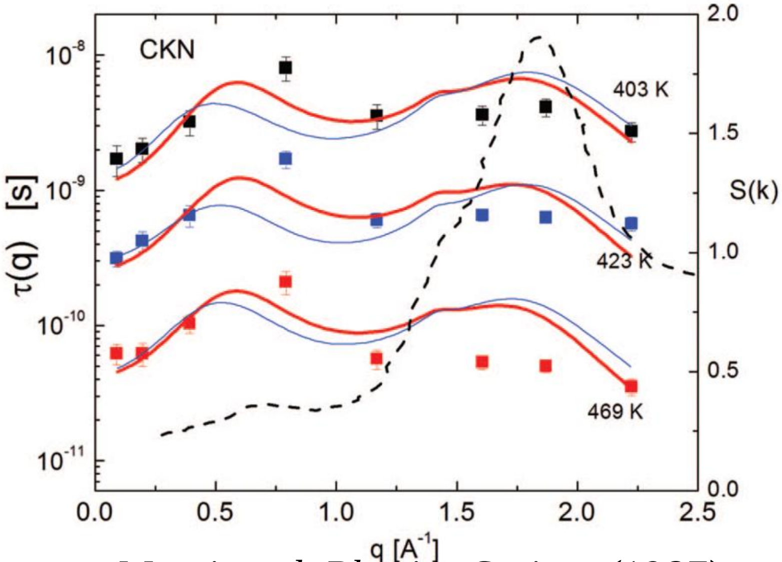


QNS data of supercooled CKN



Mezei et al, Physica Scripta (1987)

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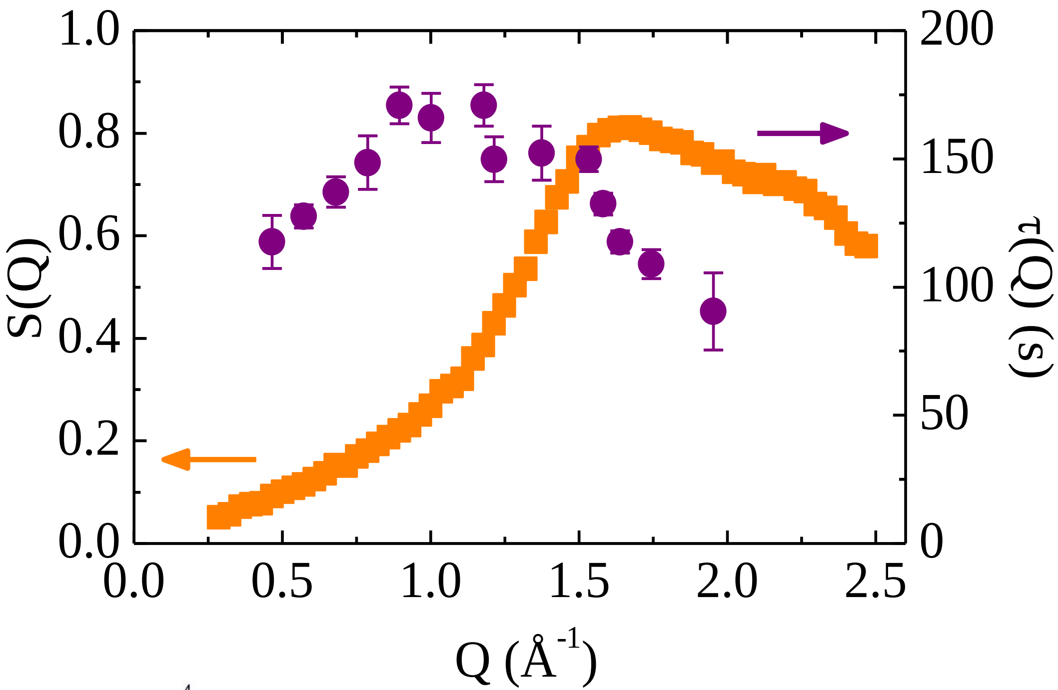

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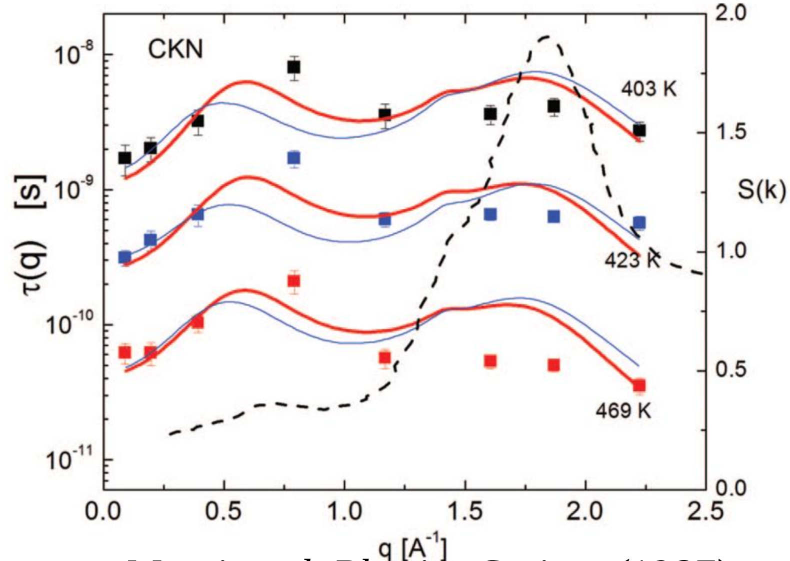
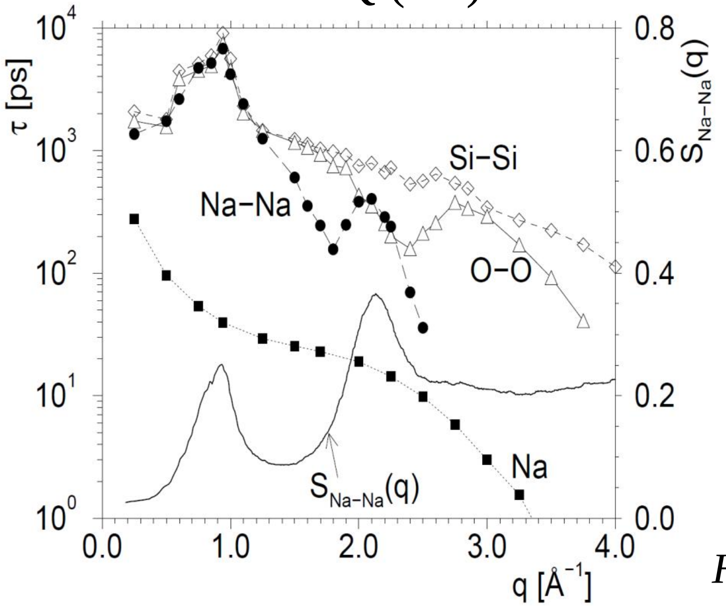
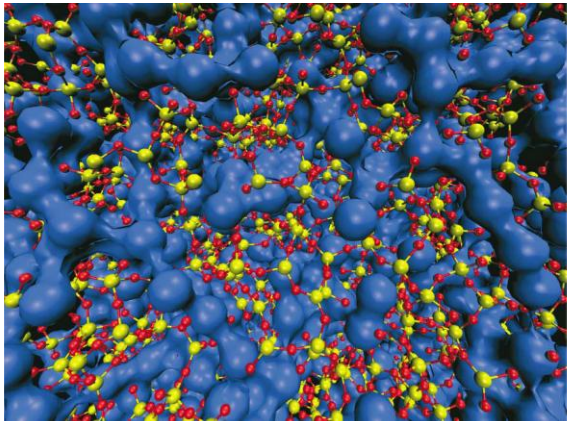


Mezei et al, Physica Scripta (1987)



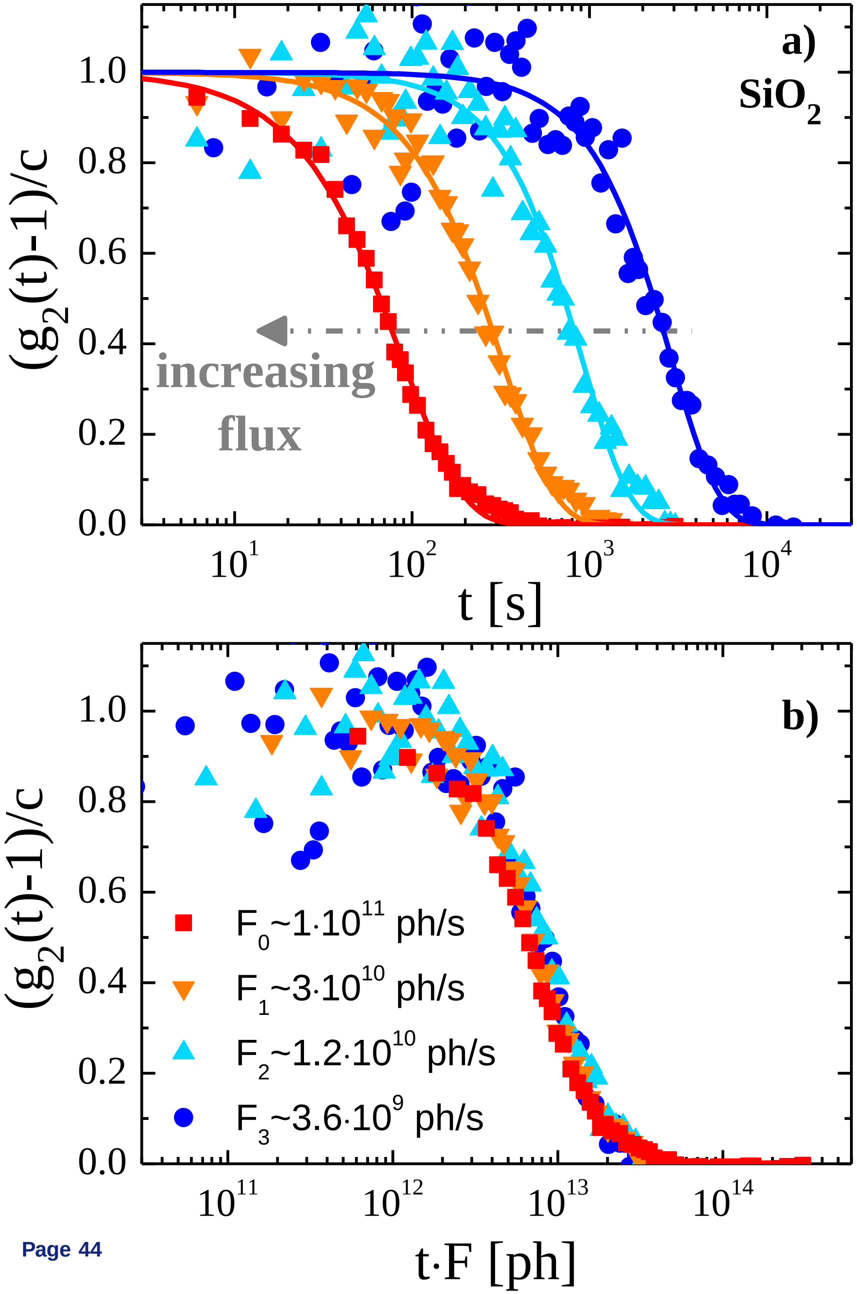
Horbach et al, Phys. Rev. Lett. (2002)



Meyer et al, Phys. Rev. Lett. (2004)

What happens in oxide glasses?

IRRADIATION-DRIVEN DYNAMICS IN SiO_2 AT LOW TEMPERATURE



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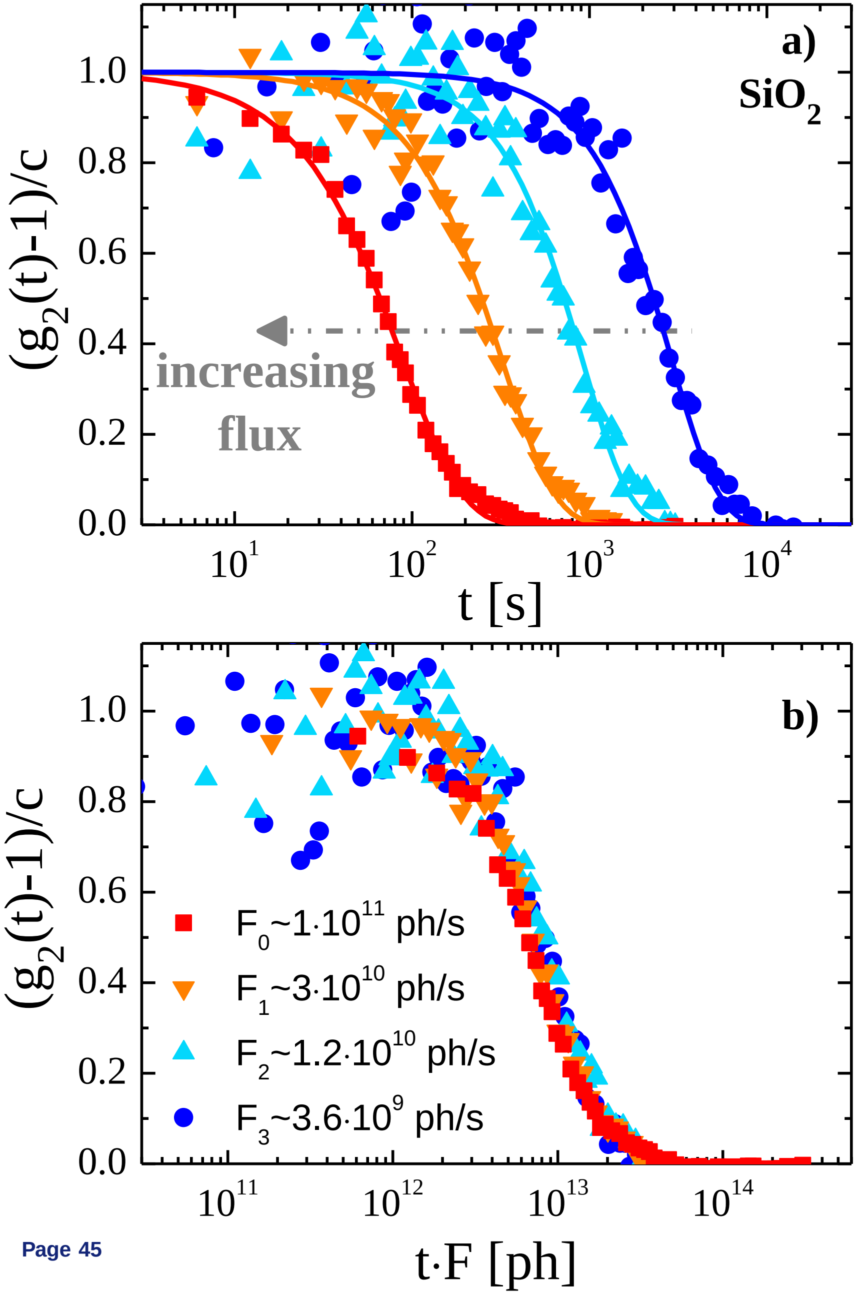

The atomic motion at room temperature in SiO_2 is completely induced by the incoming X-rays

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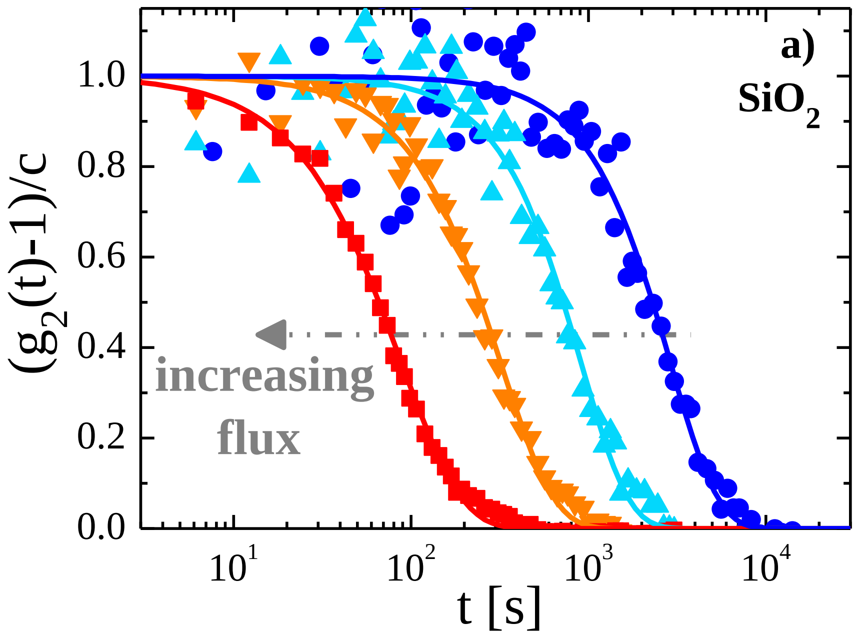
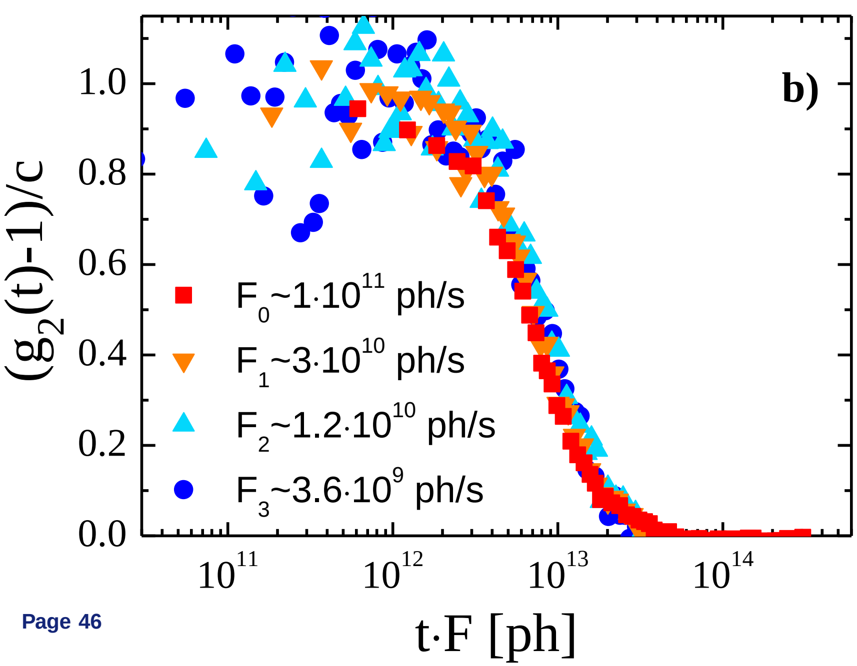
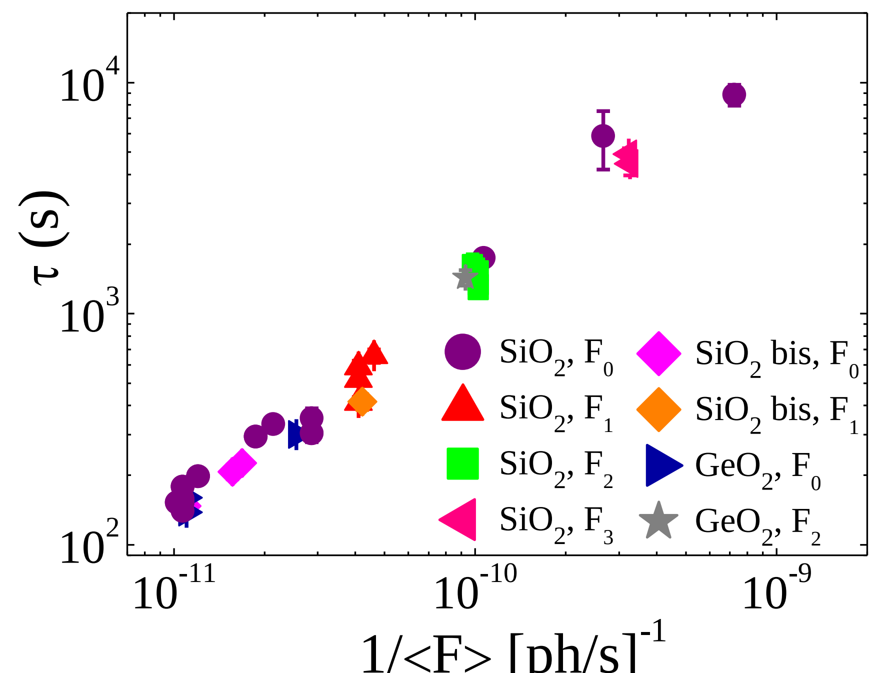




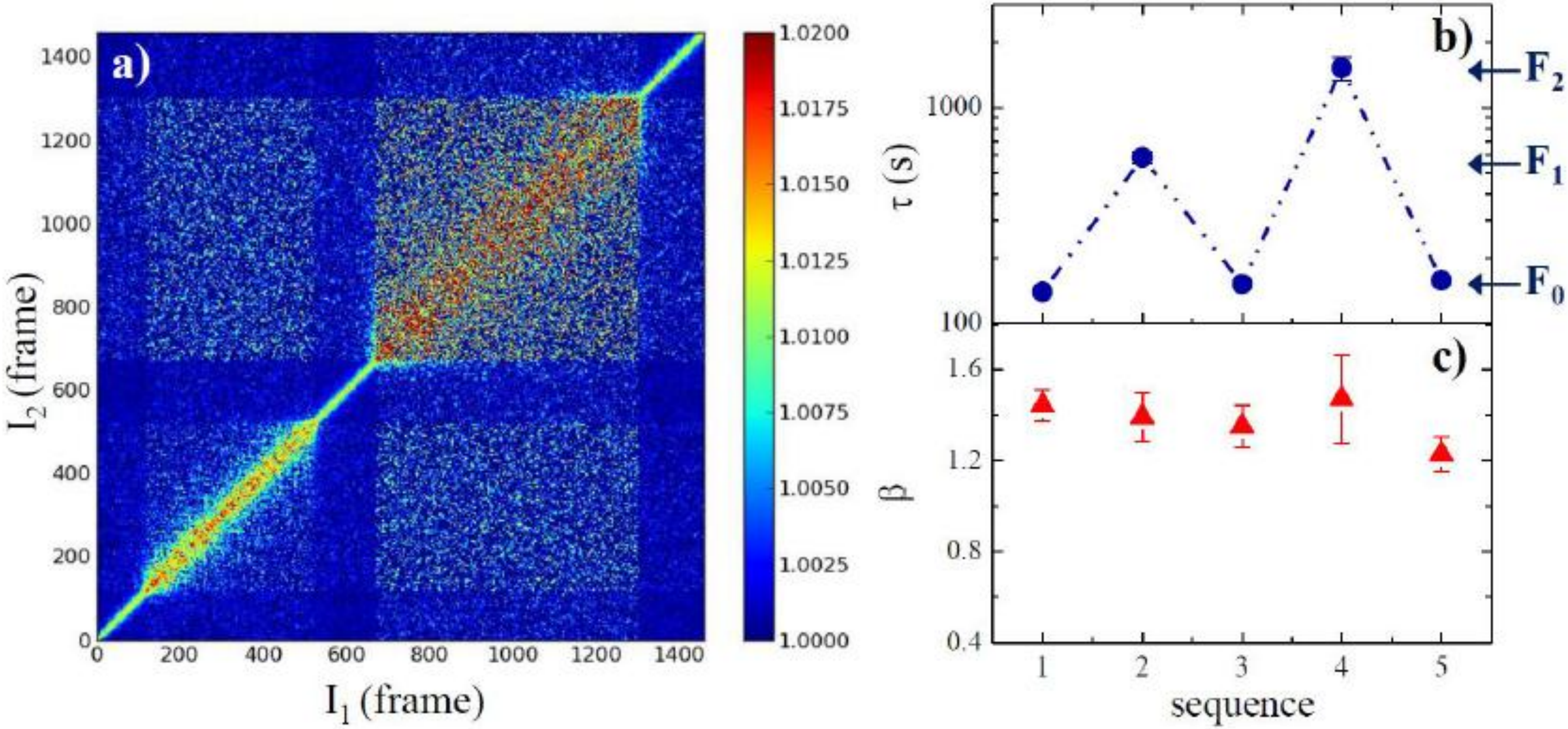
The atomic motion at room temperature in SiO_2 is completely induced by the incoming X-rays

By varying appropriately the average incoming flux (flux, exposure time, delay time) is possible to tune "at will" the dynamics



NO STANDARD RADIATION DAMAGE

The effect of the X-rays is almost instantaneous and leads to a reversible and stationary atomic motion, thus independent on the global accumulated dose within the experimental time



X-RAYS & HARD MATTER

Three main processes:

- **Knock-on events →** require high energy to break bonds
- **Electronic rearrangements →** require pre-existing defects
- **Radiolysis →** require lifetime of the excitation ~ vibrations ~1ps → **possible**

Hobbs et al. J. Nuclear Mat. (1994)

B. Ruta et al. arXiv (2016)

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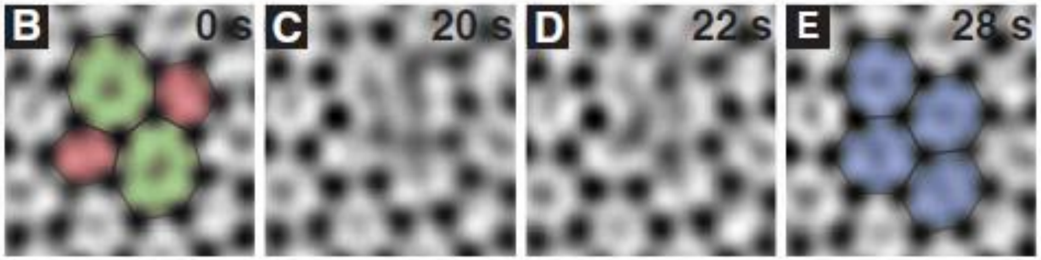
Hard X-rays as pump and probe of the dynamics

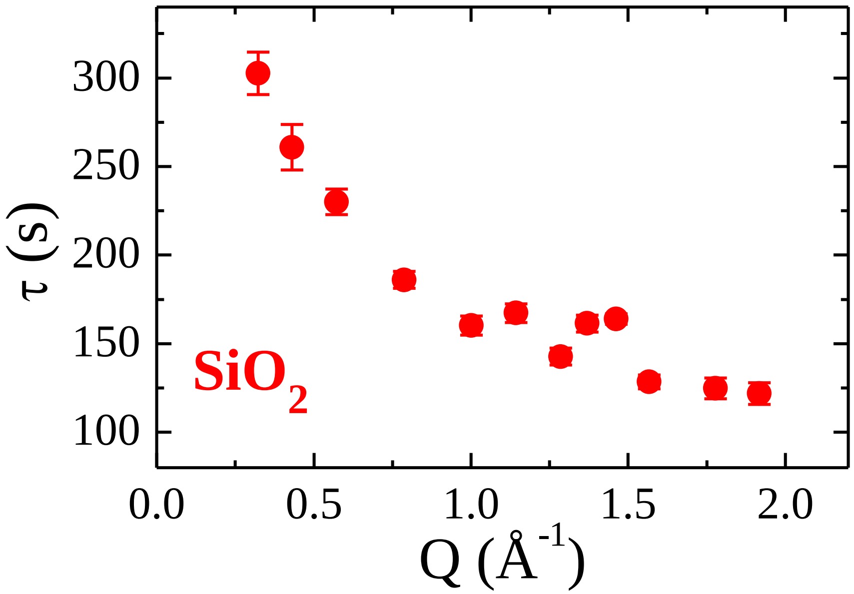
Similar to what observed with electron transmission microscopy on bi-dimensional SiO_2



Huang et al. Science (2013)

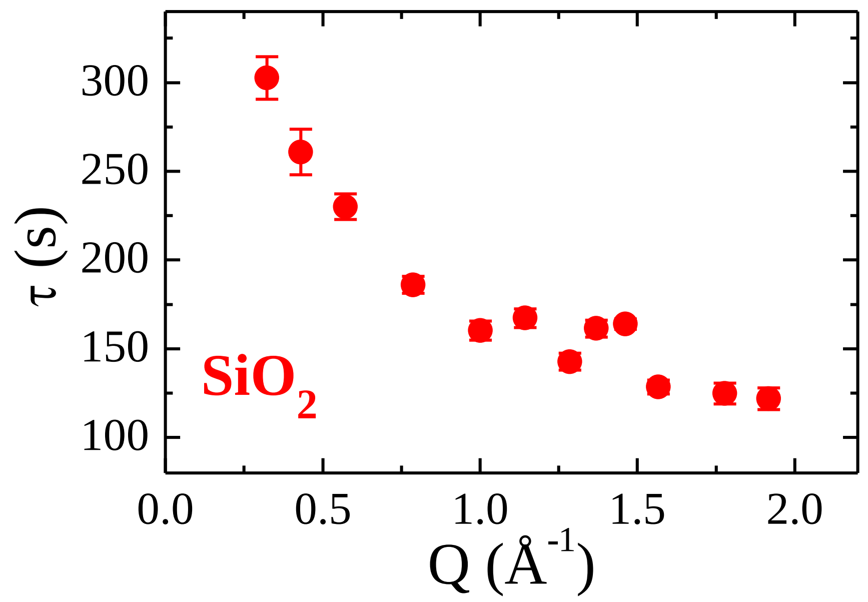
B. Ruta et al. arXiv (2016)

POSSIBILITY TO GET INTRINSIC PROPERTIES OF THE SYSTEM



The **wavevector dependence** of the dynamics is **independent on the flux**

→ Typical increase as in supercooled liquids



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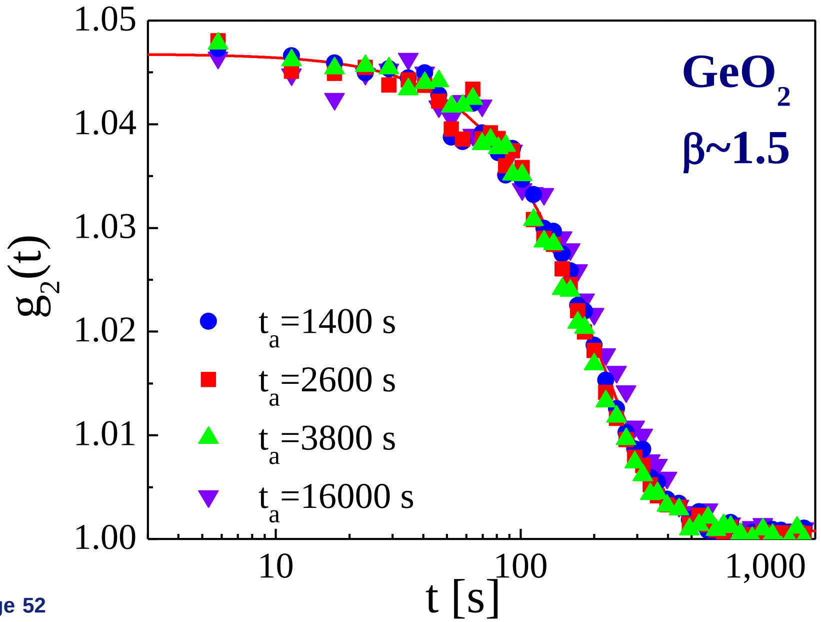


The **shape of the curve** is also **independent on the flux**

→ Compressed in SiO_2 and GeO_2, stretched in NS4 and lead-silicates. Stress-driven *vs* diffusive dynamics?

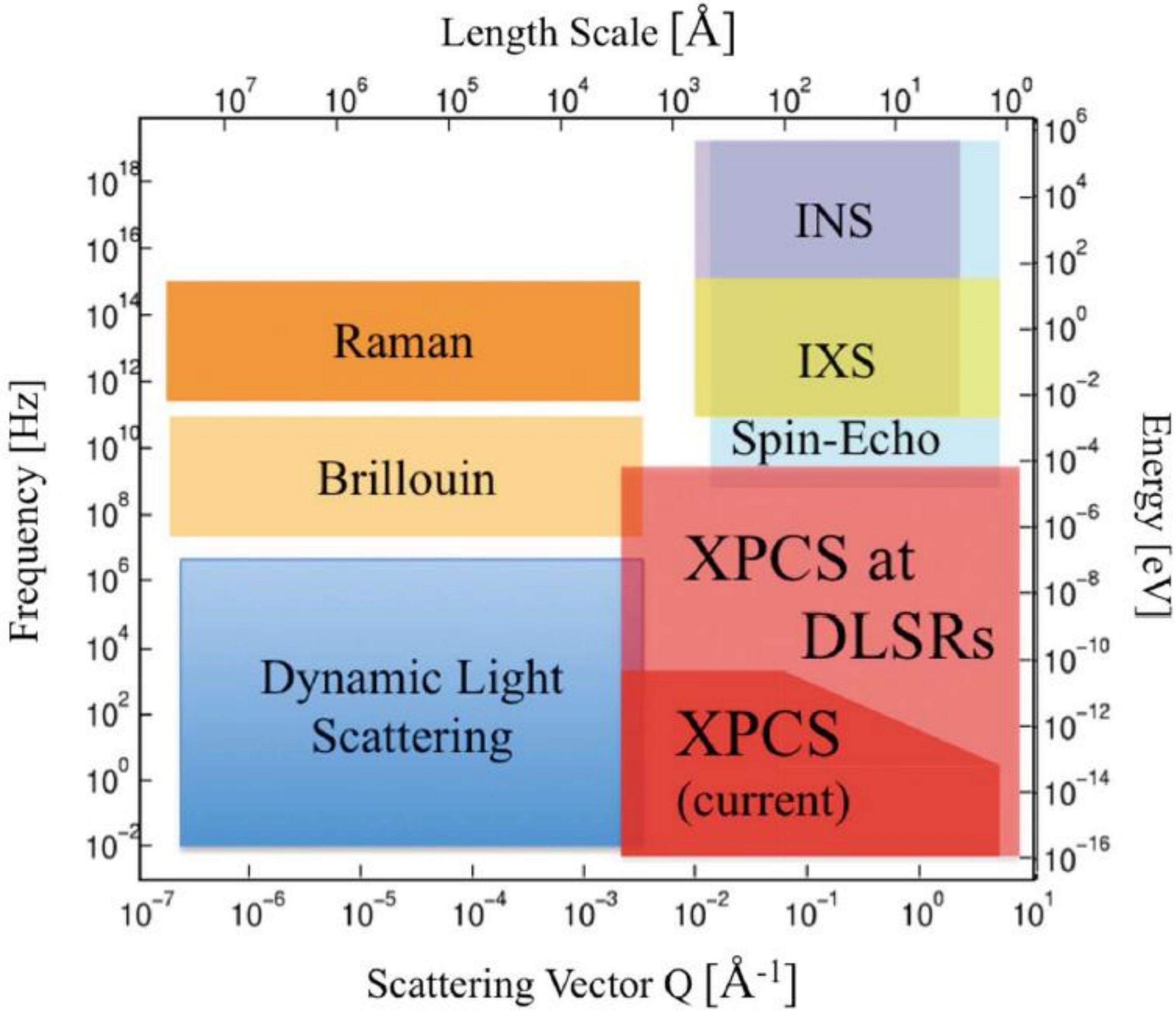
OUTLINE

- Glassy systems
- X-ray Photon Correlation Spectroscopy
- Aging in metallic glasses
- Measurements *in operando* conditions
- Atomic dynamics in network & oxide glasses
- Conclusions and future perspectives

ESRF UPGRADE: EXTREMELY BRILLIANT SOURCE (EBS)

XPCS AT EBS

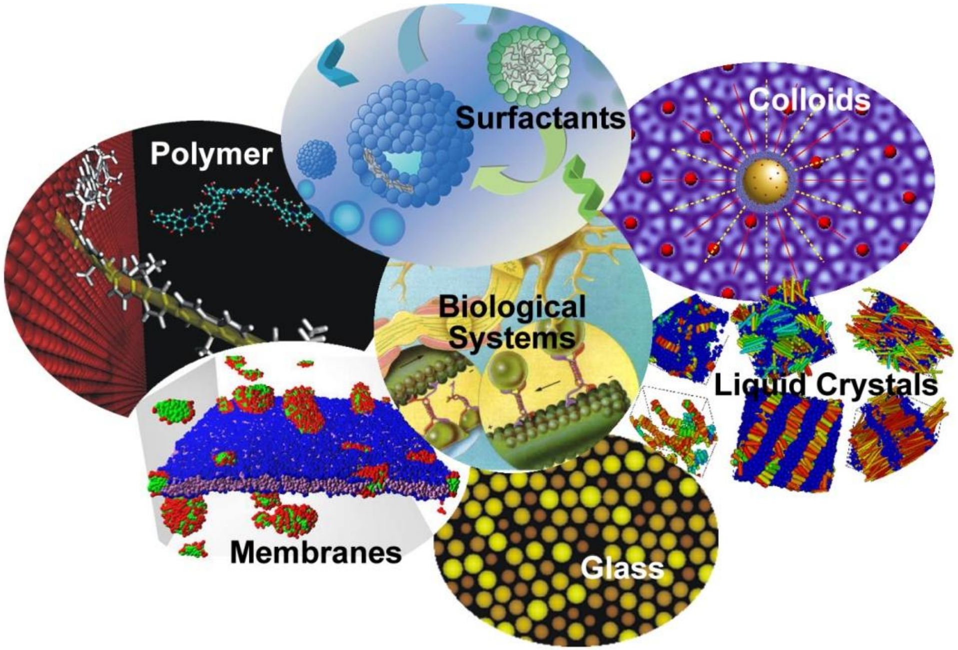
The EBS machine will lead to ~**100X increase in coherent flux** → possibility to measure **faster time scales** (from 0.1 ms to 0.01 μs) & to go at **higher energies** (up to 30 keV)



O. Shpyrko J. Synch, Rad. 2014

MANY NEW SCIENTIFIC OPPORTUNITIES

- protein dynamics in living cells
- dynamics under confinement
- dynamics of polymers, macromolecules, membranes, foams, …
- dynamics at buried interfaces
- polyamorphism (LL/GG phase transitions)
- dynamics at extreme conditions



® Pierre Gilles De Gennes

Presentation of 8 Conceptual Design Report (CDR) for new possible beamlines

CDR1 - **Beamline for coherence applications (XPCS)**
CDR2 - Beamline for hard X-ray diffraction microscope
CDR3 - High throughput large field phase-contrast tomography beamline
CDR4 - Surface science beamline
CDR5 - Advanced high-flux nano-XRD beamline for science under extreme conditions
CDR6 - Facility for dynamic compression studies
CDR7 - High brilliance XAS beamline
CDR8 - Serial crystallography beamline

http://www.esrf.eu/home/events/conferences/2016/ebs-science-workshop.html

TAKE HOME MESSAGE

Possibility to investigate the slow dynamics in glasses at the atomic length scale

Depending on the nature of the system and the competition between intrinsic and induced dynamics is possible to move from spontaneous density fluctuations to intensity-driven atomic motion

Many new scientific opportunities with XPCS @ EBS

ACKNOWLEDGMENTS


L. Cipelletti


B. Rufflé


W. Kob


M. Di Michiel


Y. Chushkin


F. Zontone

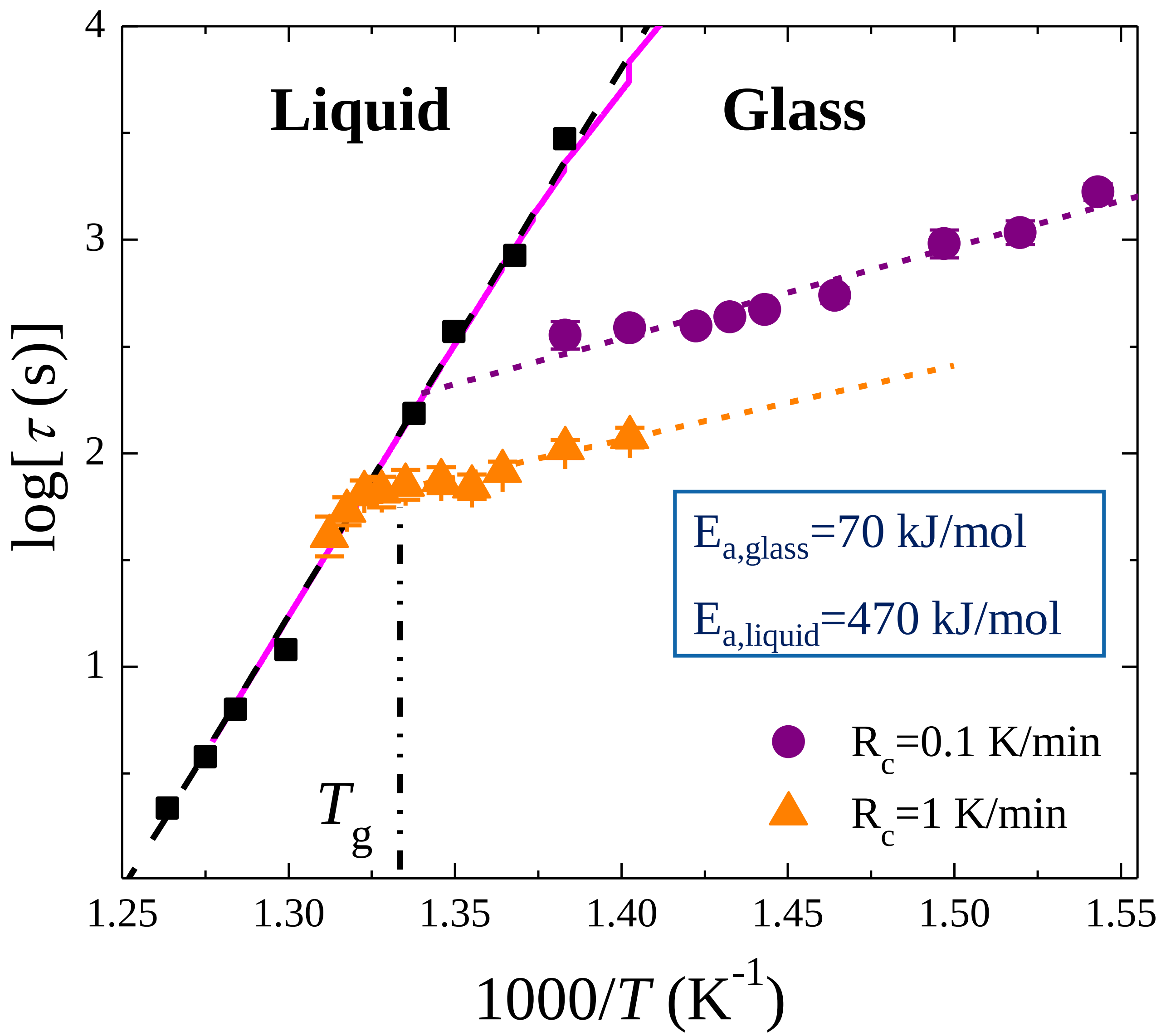

G. Baldi


G. Monaco

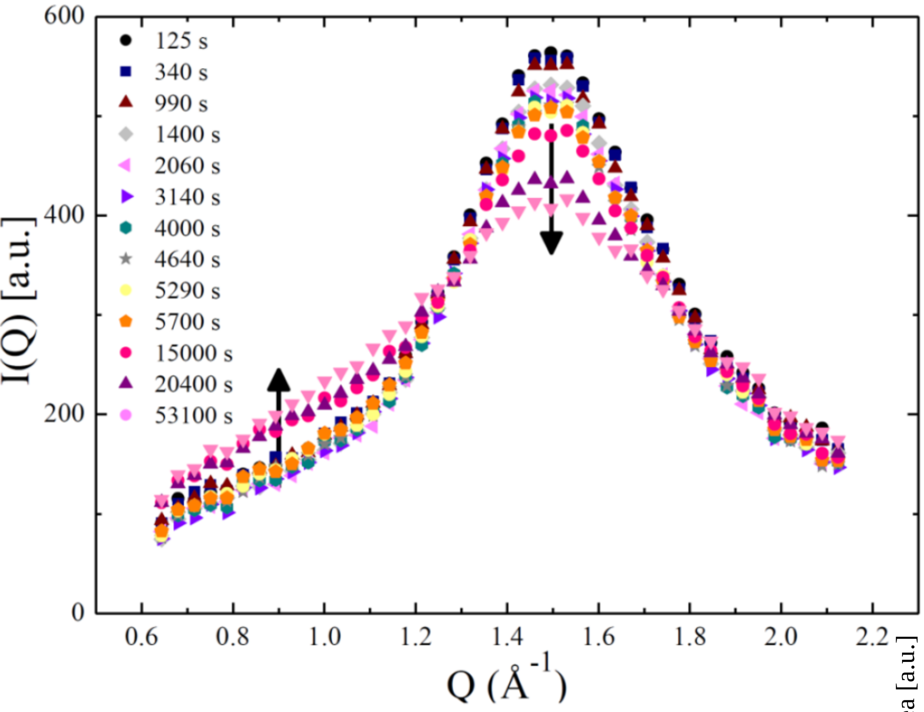
V.M. Giordano

Thank you for your attention!!!

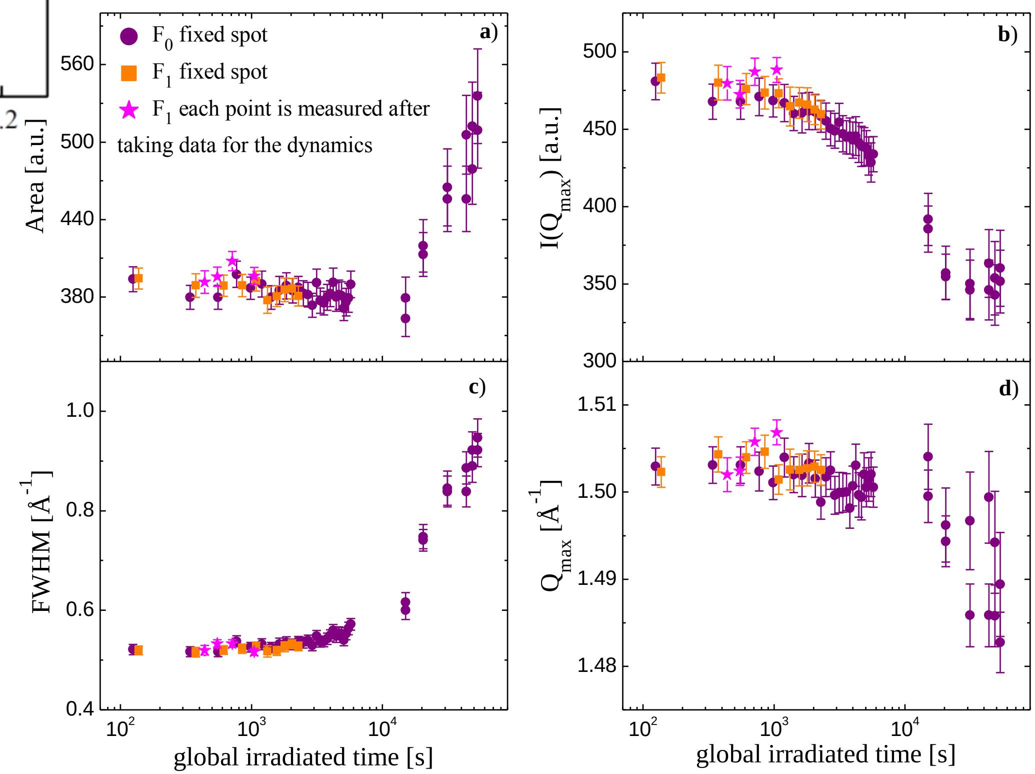
0.8SIO2-0.2NA2O (NS4, TG=783 K)



B. Ruta *et al.*, Nat. Commun. (2014)

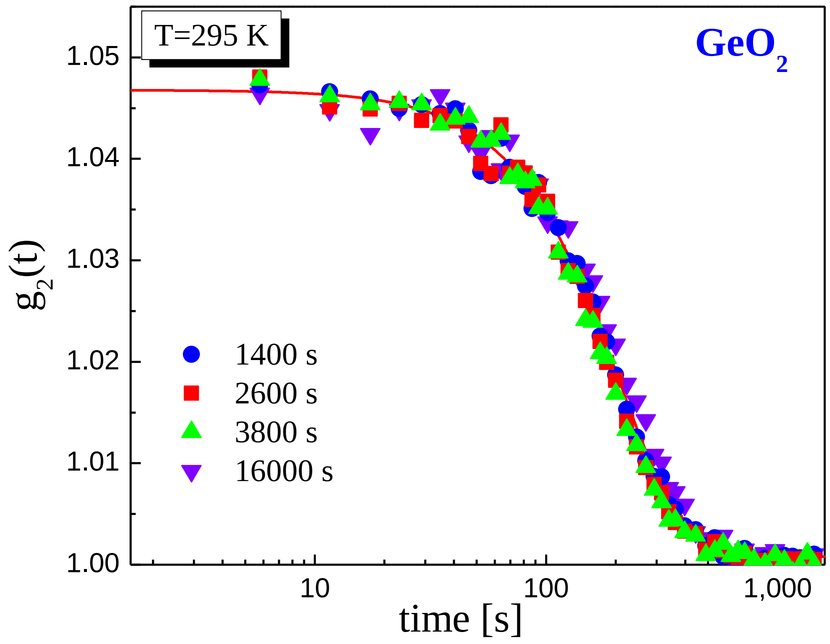


Occurrence of a real damage for longer exposure time



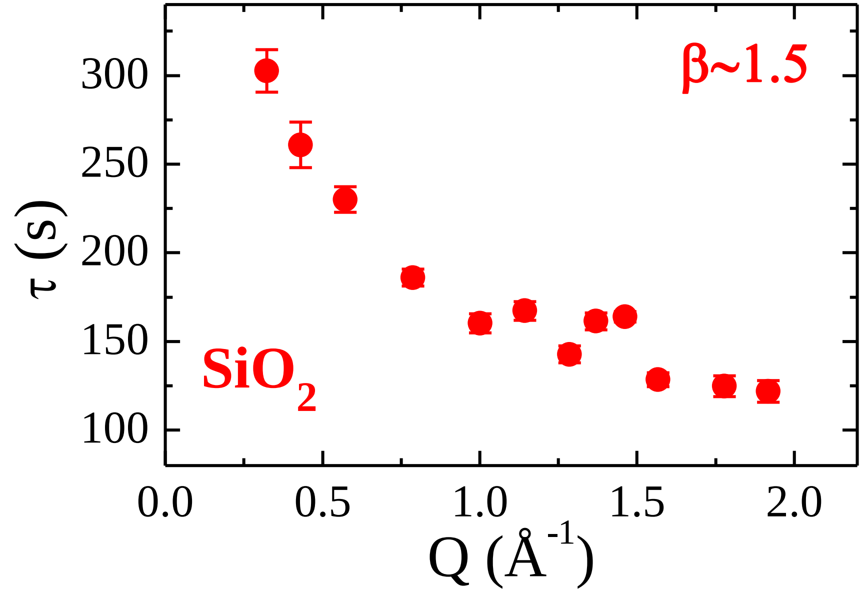
Threshold for structural damage at ~10^4 s of global irradiation at maximum flux

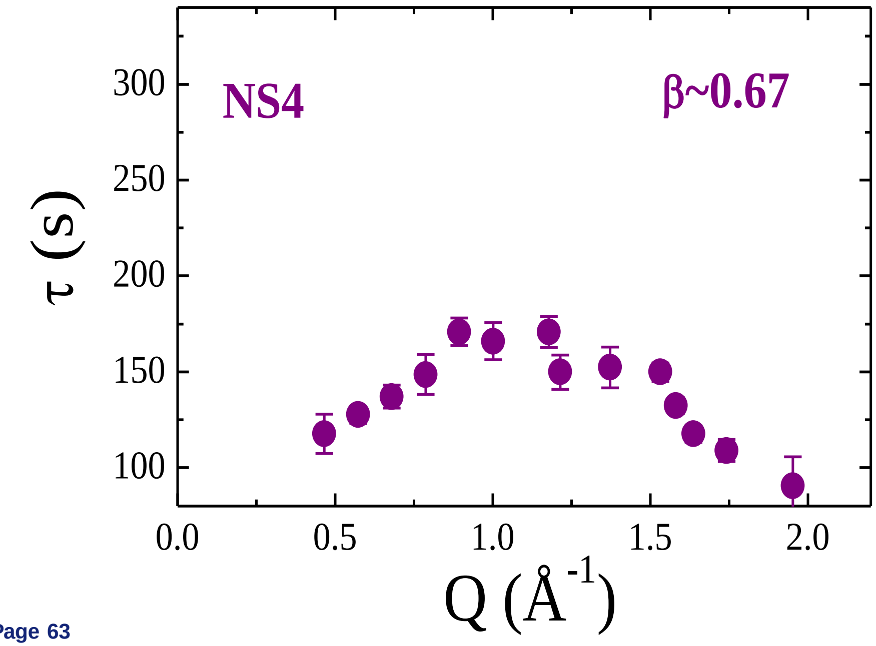
NO STANDARD RADIATION DAMAGE



The dynamics is independent on the global accumulated dose

POSSIBILITY TO GET INTRINSIC PROPERTIES OF THE SYSTEM





Stretched vs compressed mettere una figura del confronto curve

Different Q dependence

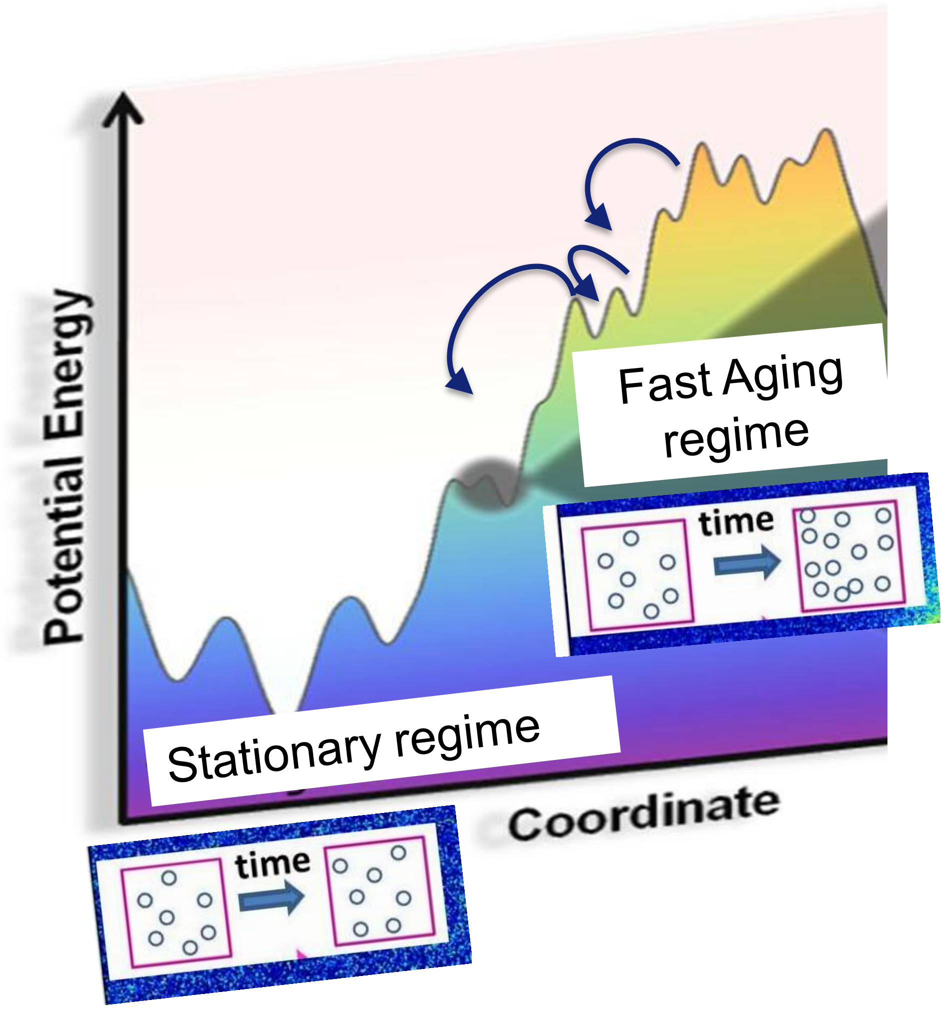
MICROSCOPIC AGING IN METALLIC GLASSES

Microscopic aging:

Fast aging: thermal activation of a cascade of jumps from a high-energy minimum with irreversible atomic rearrangements changing density

Stationary: more relaxed (low energy) minimum. Localized dynamics. no density change, MRO increase

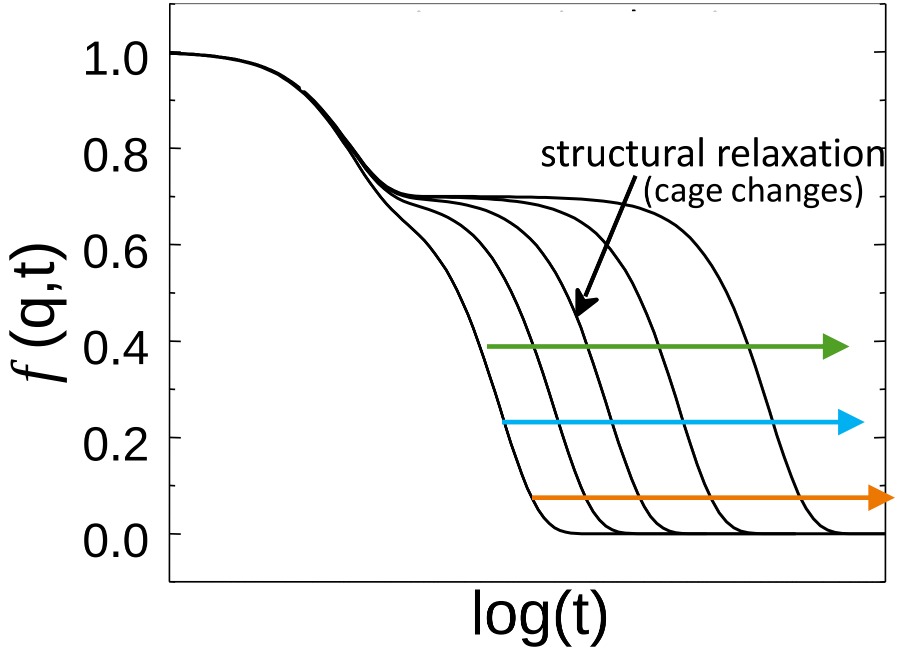
→ the evolution between the two could be related to a **ductile to brittle transition**



Fan et al. Phys. Rev. Lett. 2015

RELAXATION DYNAMICS

The slow down of the dynamics toward an arrested state corresponds to a continuous shift of the decay of the density fluctuations toward longer time scales



t_w waiting time

Φ packing fraction

1/T temperature

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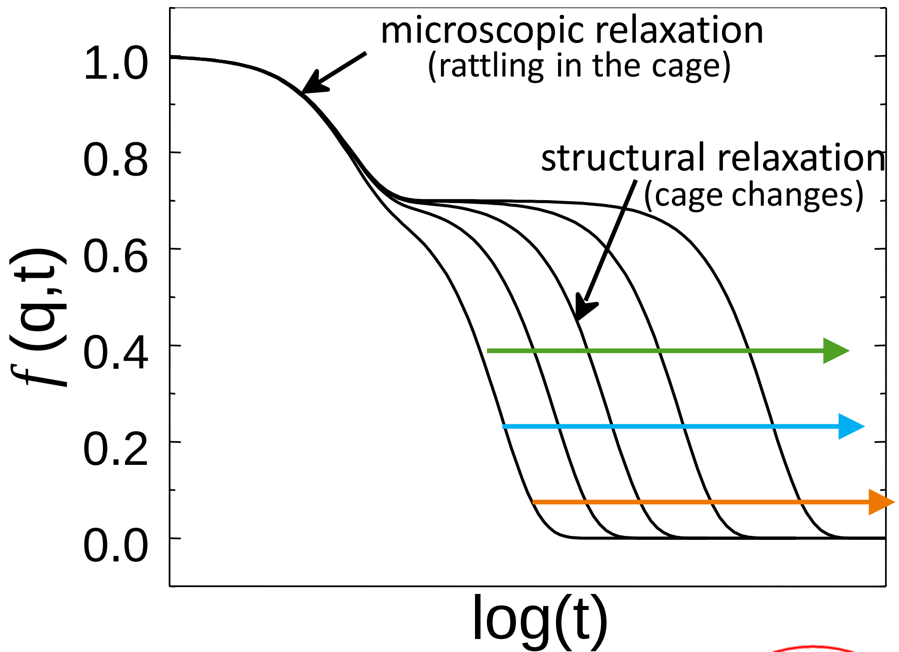

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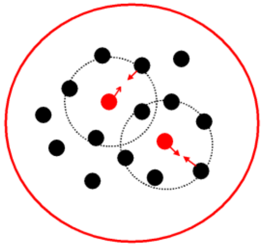
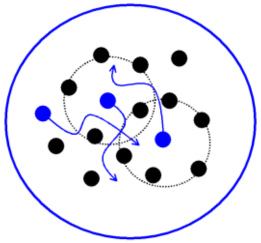
1/T temperature

τ_1 microscopic relaxation time related to the interactions between a particle and the cage of its nearest neighbors.



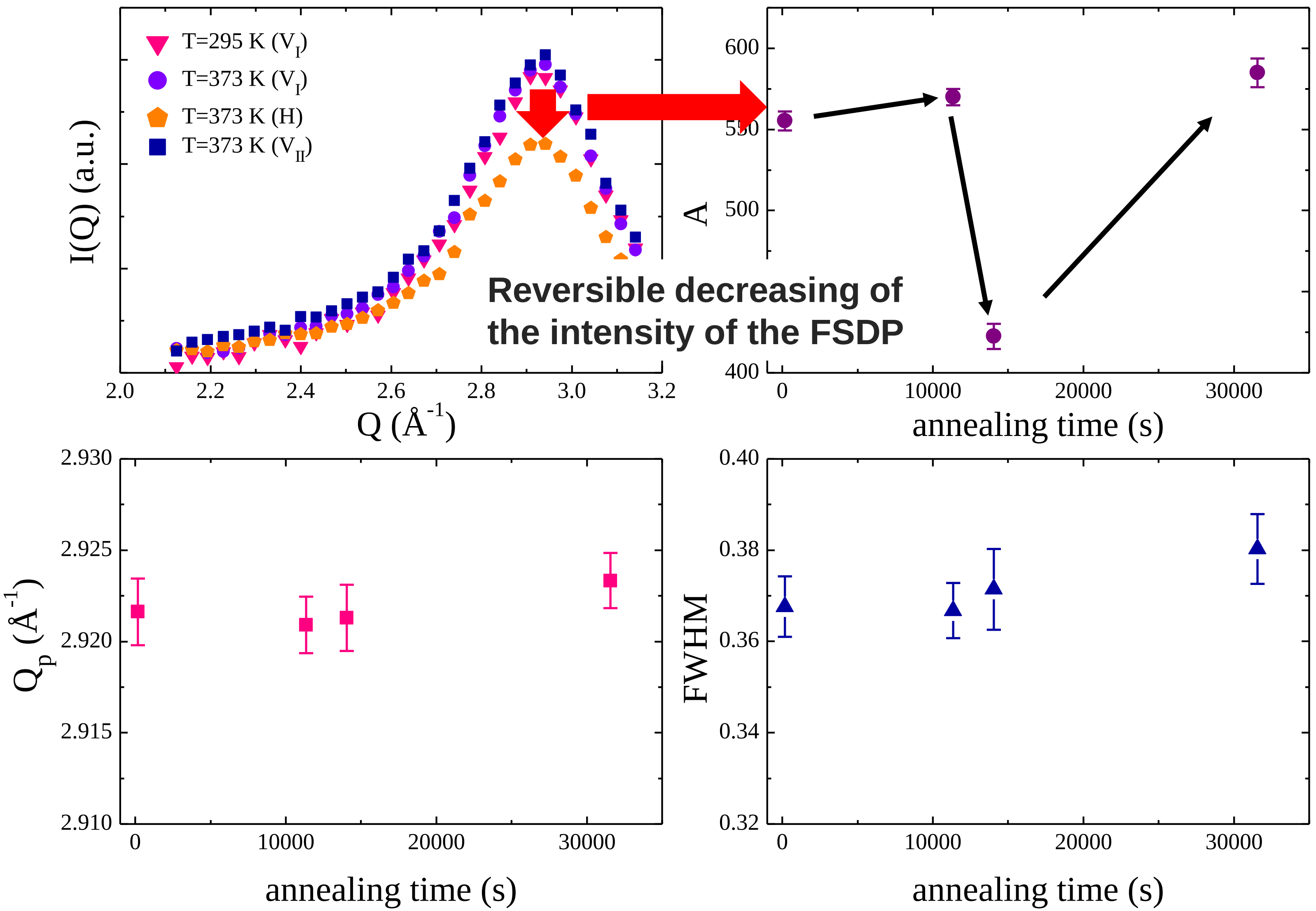
fast relaxation

τ_2 structural relaxation time related to a structural rearrangement of the particles.



slow relaxation

EFFECT OF H_2 ON THE STRUCTURE



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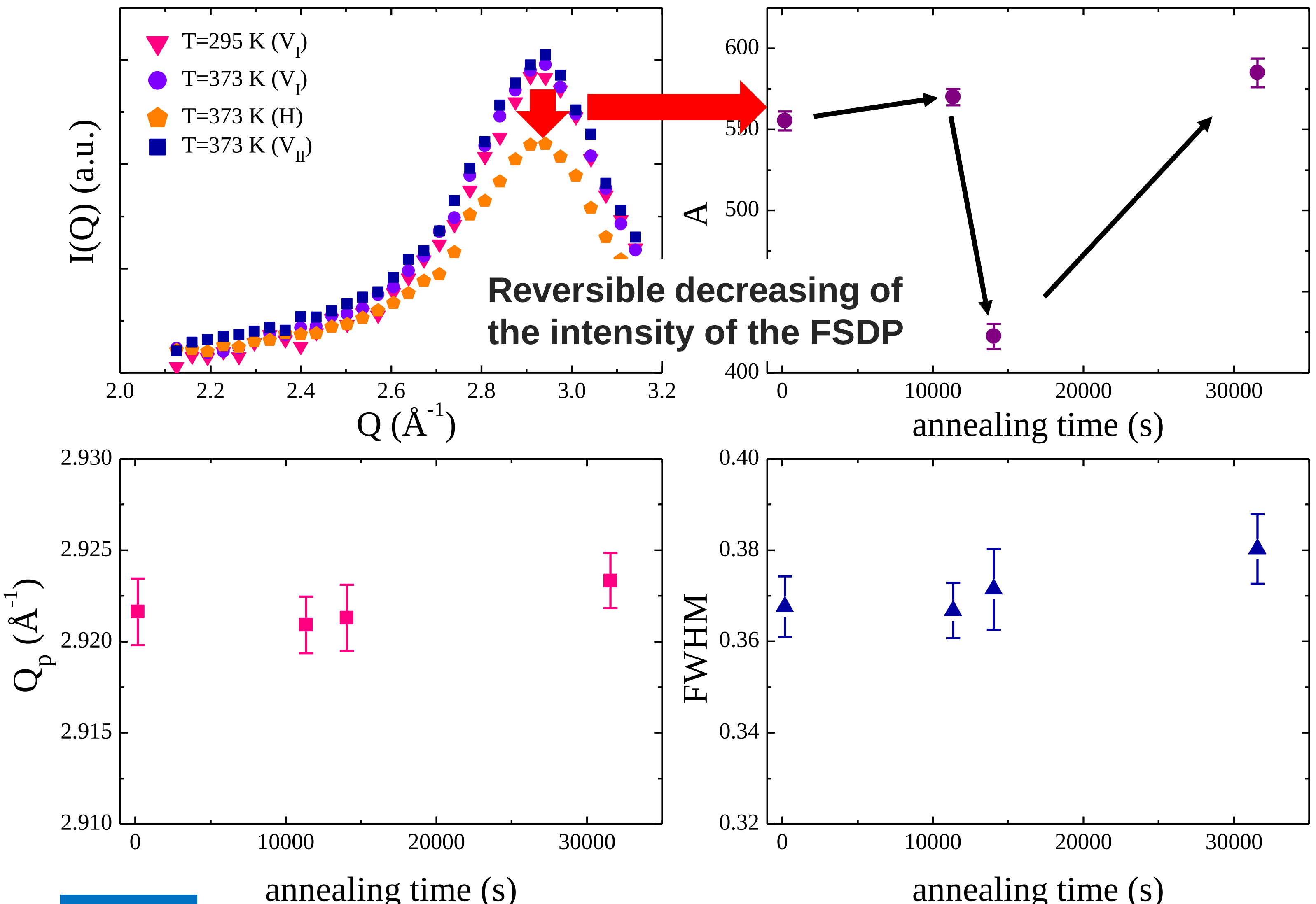

XRD ID10

Next step: high energy XRD & EFAFS