New Opportunities to Unveil Glass Dynamics with X-ray Photo Correlation Spectroscopy at ESRF-EBS

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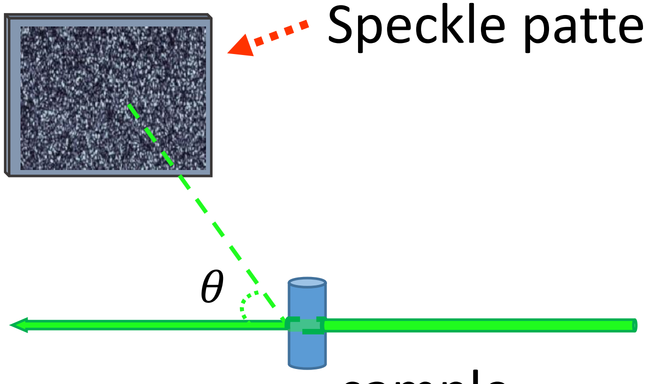
UNIVERSITY OF TRENTO

Outline

- WA XPCS – Introduction
- Dynamics of the glassy state
- Beam-induced dynamics
- New opportunities at ESRF-EBS

Wide Angle - XPCS

Unique method to measure the Q-resolved dynamics of glasses and supercooled liquids



Speckle pattern

sample

Energy = 8 KeV

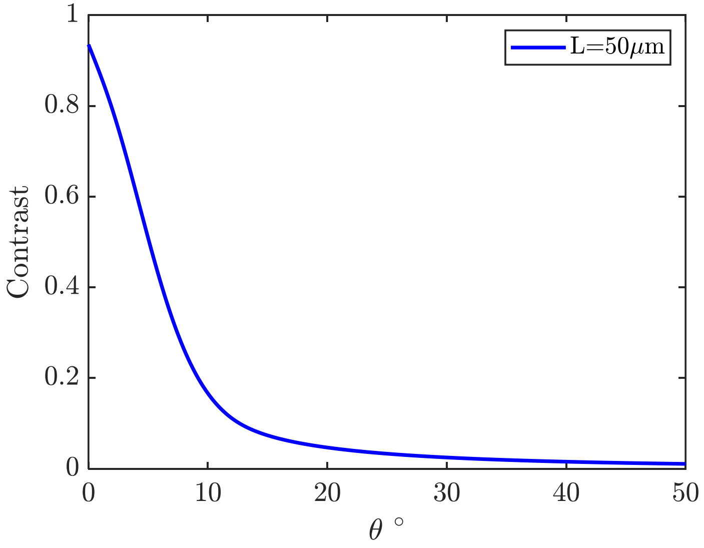
↓

Peak of the S(Q) for $\theta \sim 20 - 40°$

Limited longitudinal coherence length

↓

Low contrast at wide angles



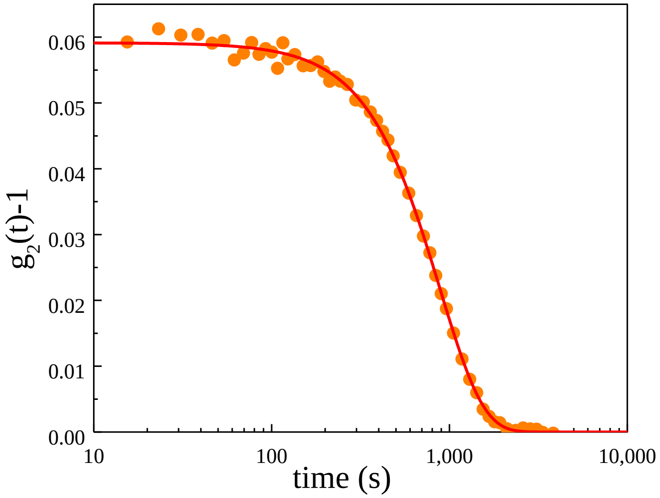
Wide Angle - XPCS

$$g_2(Q,t) = \frac{\langle I(Q,0)I(Q,t)\rangle}{\langle I(Q)\rangle^2} = 1 + A(Q)\left|F(Q,t)\right|^2$$

Contrast:

$$A(Q_{FSDP}) \sim 1-5\ \%$$

Typical correlation curve at wide angles



Signal to noise ratio:

$$SNR \sim A \cdot \bar{I} \cdot \sqrt{T \cdot dt \cdot N_p}$$

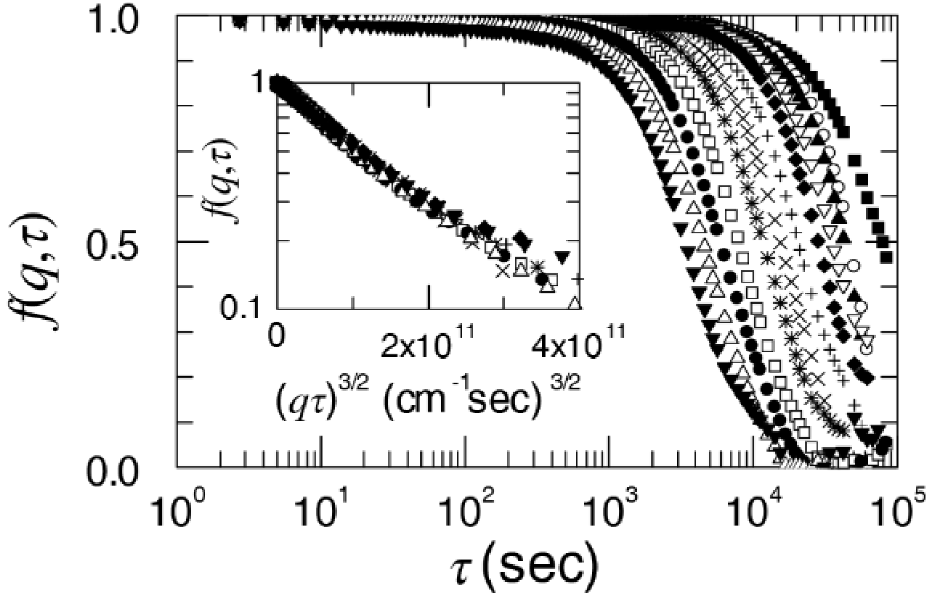
$\bar{I}$: count rate per pixel
T: total duration of the measurement
dt: accumulation time per frame
N_p: number of detector pixels

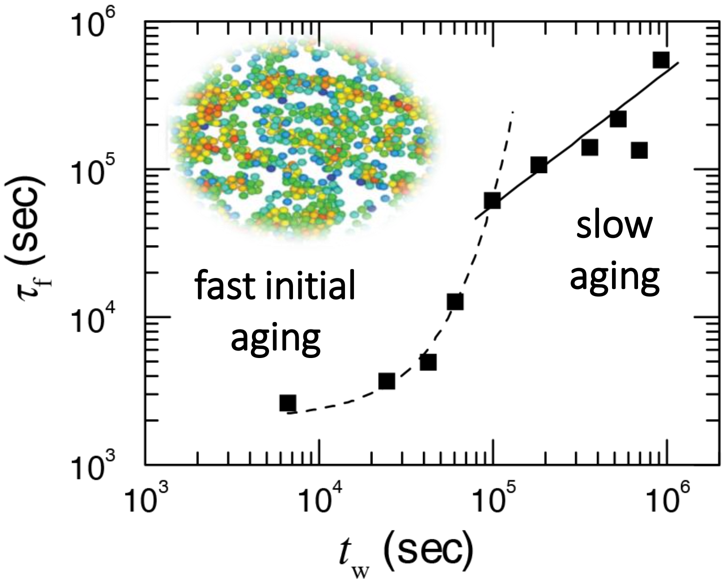
Outline

- WA XPCS – Introduction
- Dynamics of the glassy state
  - Metallic glasses
  - Oxide glasses
- Beam-induced dynamics
- New opportunities at ESRF-EBS

Physical aging in colloidal glasses

Aggregating polystyrene colloids





- Faster than exponential decay
- Ballistic-like motion (super-diffusive)
- Fast aging regime

$\beta \sim 1.5$

$\tau_\alpha \sim q^{-1}$

$$F(q,\tau) = e^{-\left(\frac{\tau}{\tau_\alpha}\right)^\beta}$$

While in normal diffusion:

$\tau \sim q^{-2} \quad \beta = 1$

Cipelletti, Manley, Ball, Weitz, *Phys. Rev. Lett.* 2000.

Physical aging in colloidal glasses - II

Theoretical insight

Eur. Phys. J. E **9**, 287–291 (2002)
DOI 10.1140/epje/i2002-10075-3

THE EUROPEAN
PHYSICAL JOURNAL E

Anomalous dynamical light scattering in soft glassy gels

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[2] Laboratoire de Physique Mathématique et Théorique, Université Montpellier II, UMR 5825, France

Received 15 April 2002 /

Abstract. We compute the dynamical structure factor $S(q,\tau)$ of an elastic medium where force dipoles appear at random in space and in time, due to "micro-collapses" of the structure. Various regimes are found, depending on the wave vector q and the collapse time θ. In an early time regime, the logarithm of the structure factor behaves as $(q\tau)^{3/2}$, as predicted in (L. Cipelletti *et al.*, Phys. Rev Lett. **84**, 2275 (2000)) using heuristic arguments. However, in an intermediate-time regime we rather obtain a $(q\tau)^{5/4}$ behaviour. Finally, the asymptotic long-time regime is found to behave as $q^{3/2}\tau$. We also give a plausible scenario for aging, in terms of a strain-dependent energy barrier for micro-collapses. The relaxation time is found to grow with the age t_w, quasi-exponentially at first, and then as $t_w^{4/5}$ with logarithmic corrections.

PACS. 82.70.Gg Gels and sols – 81.40.Cd Solid solution hardening, precipitation hardening, and dispersion hardening; aging

J.-P. Bouchaud and E. Pitard, 2002

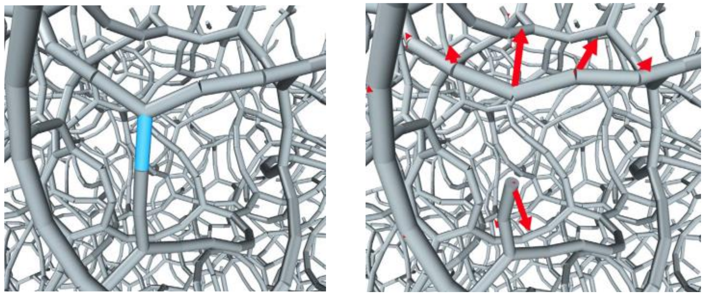
Appearance of **random collapses** in the glassy gel, with a rate which is thermally activated

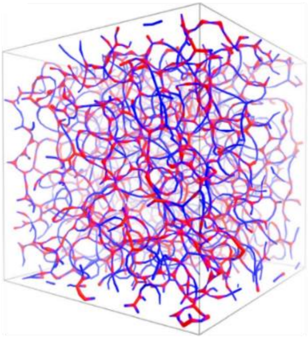
Agreement with experiment if the **measuring time is small** compared to the collapse-time

Physical aging in colloidal glasses - III

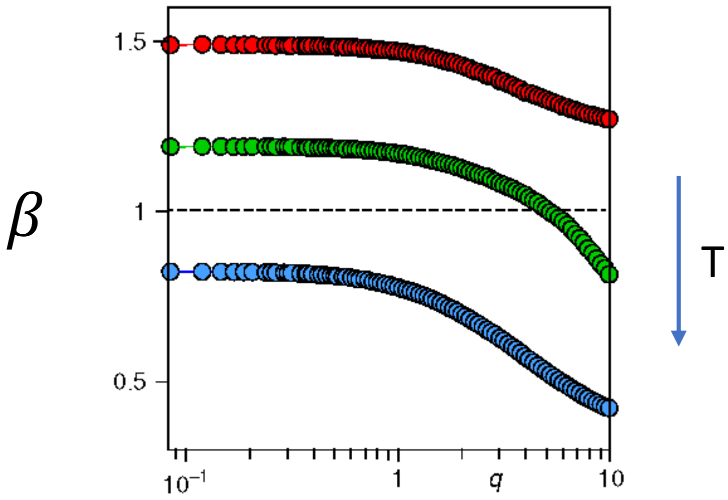
Numerical simulations:

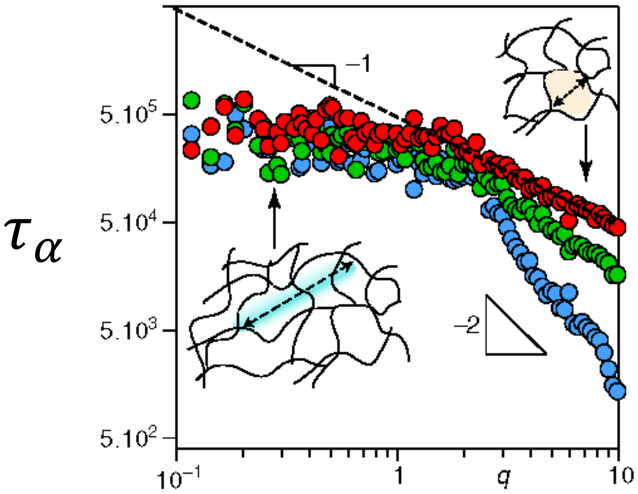
structural changes by means of
rupture of particle connections





Local stresses

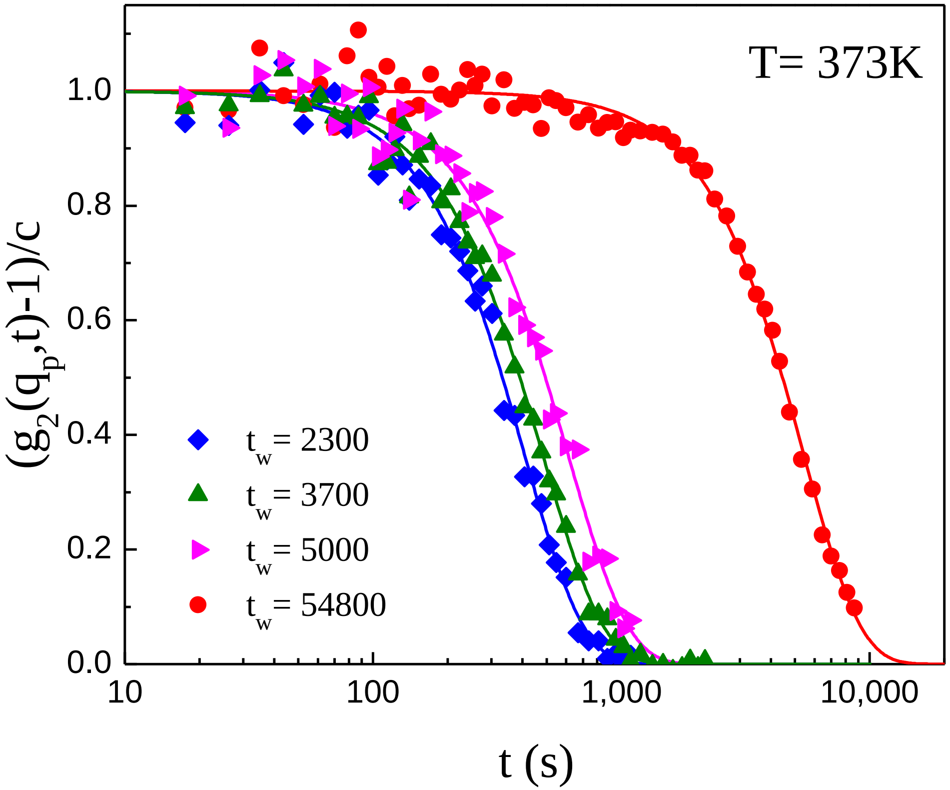


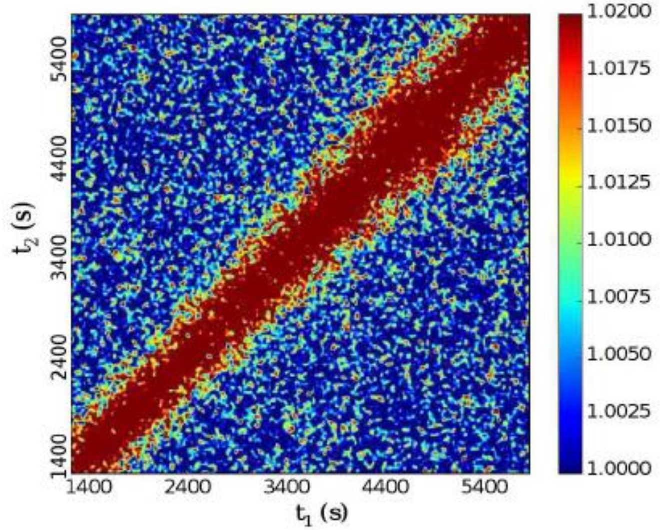


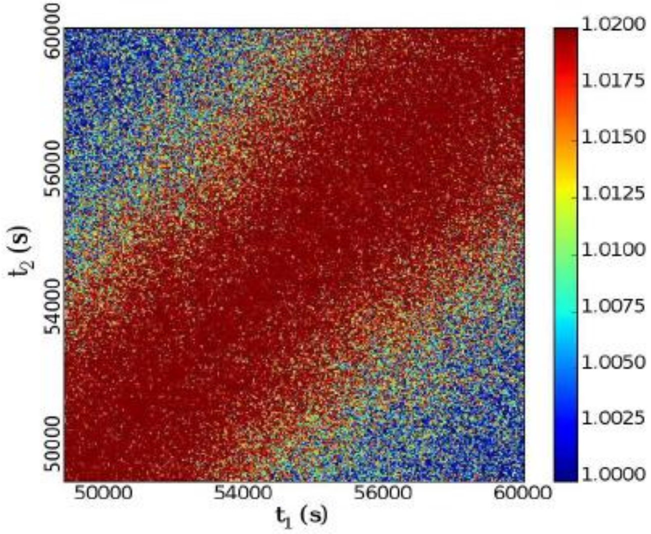
Bouzid, Colombo, Barbosa, Del Gado, *Nat. Commun.* 2017.
Chaudhuri, Berthier, *Phys. Rev. E* 2017.

XPCS of metallic glasses

$Zr_{67}Ni_{33}$ (T_g=647 K)





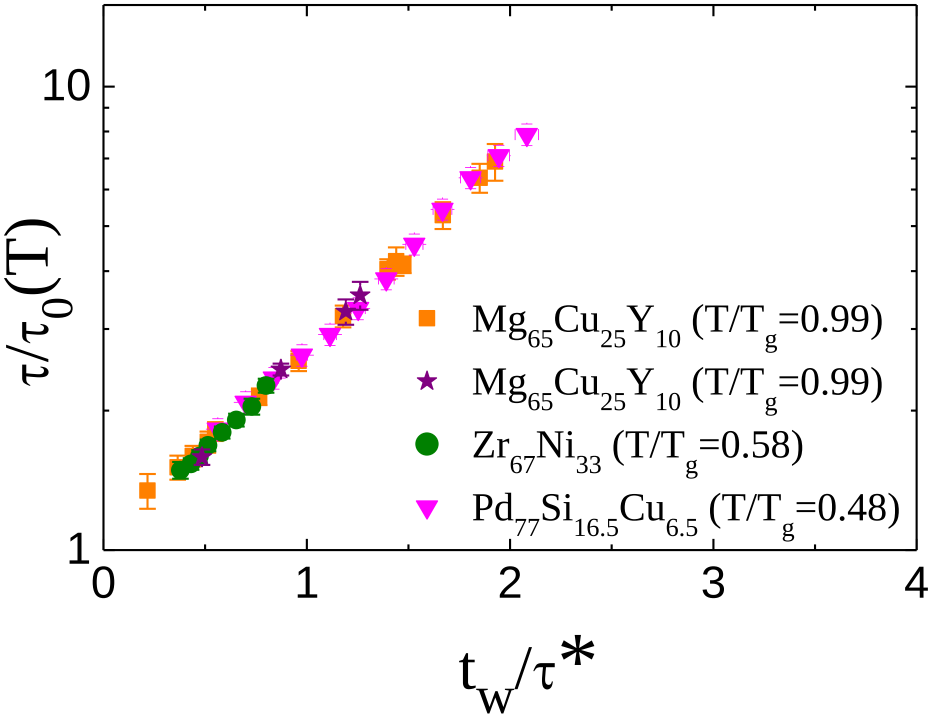


B. Ruta, G. Baldi, G. Monaco, and Y. Chushkin, J. Chem. Phys. **138**, 054508 (2013)

XPCS of metallic glasses

Metallic glasses produced by a fast quench: ~ 10^6 K/s

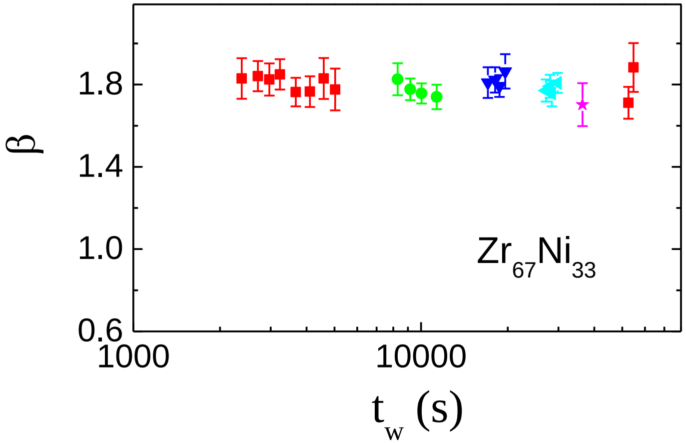
Fast aging regime:



For $t_w \lesssim 12$ h the relaxation time grows exponentially:

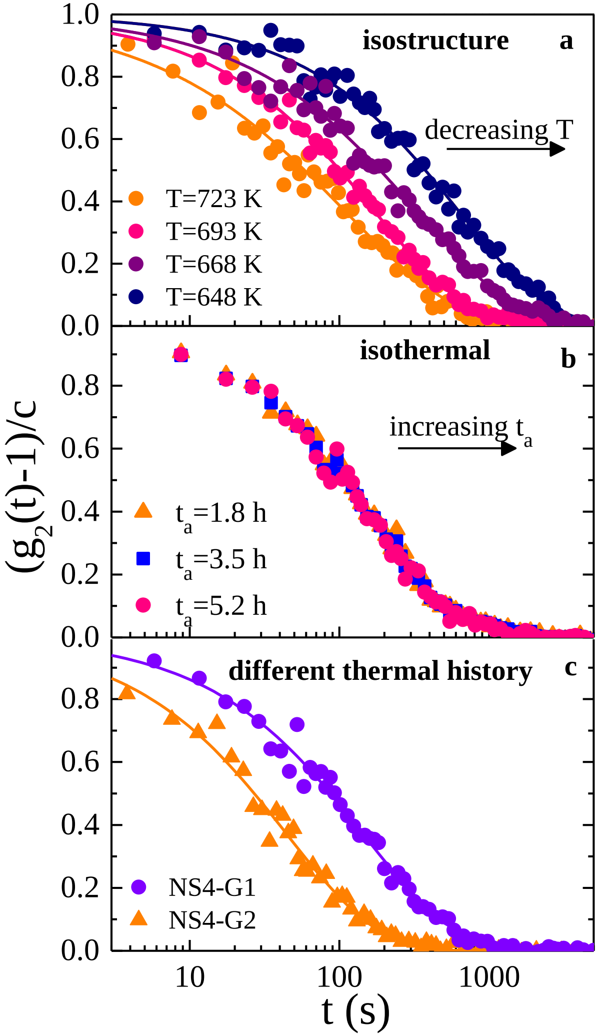
$$\tau(T, t_w) = \tau_0(T)\exp(t_w/\tau^*)$$

Relaxation almost Gaussian

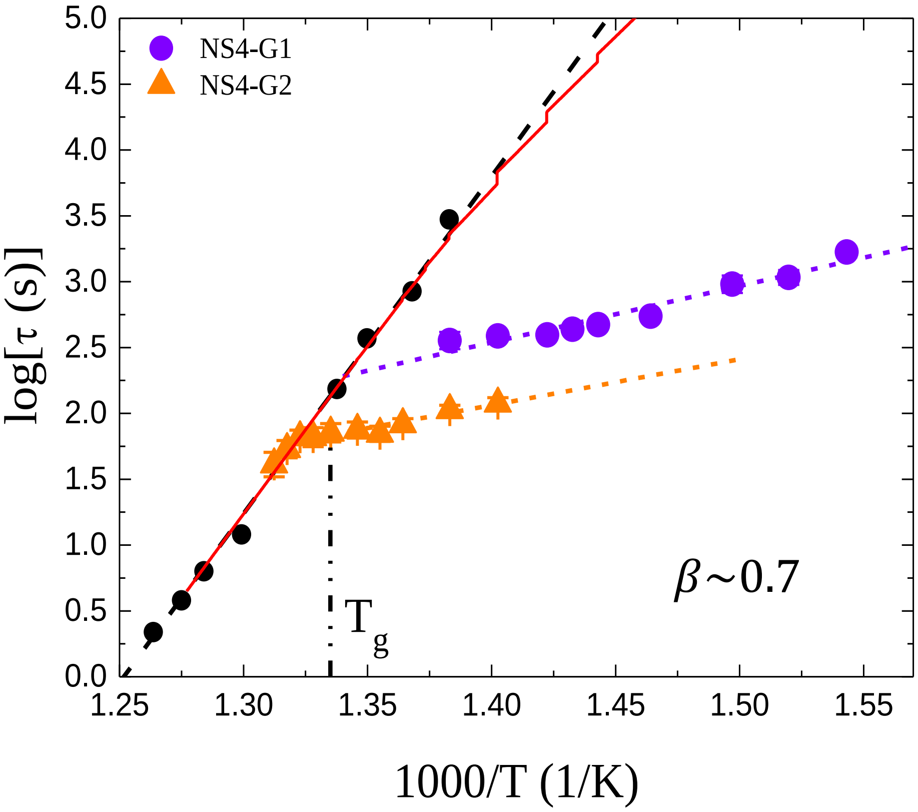


B. Ruta, G. Baldi, G. Monaco, and Y. Chushkin, J. Chem. Phys. **138**, 054508 (2013)

XPCS of oxide glasses



Sodium silicate, NS4



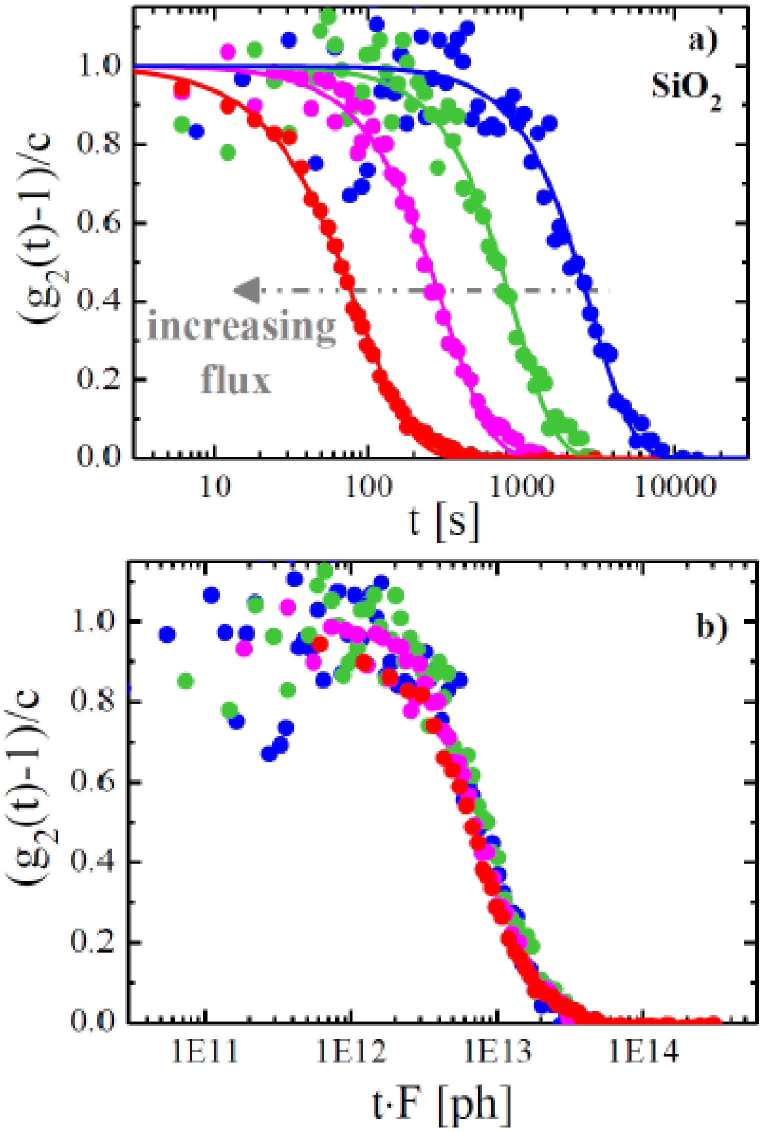
$Q = 1.5$ Å^{-1}

B. Ruta, G. Baldi *et al.*, Nat. Commun. **5**, 3939 (2014)

Outline

- WA XPCS – Introduction
- Dynamics of the glassy state
- Beam-induced dynamics
  - Vitreous silica
  - Vitreous boron oxide
- New opportunities at ESRF-EBS

XPCS of oxide glasses – beam effect



Vitreous silica

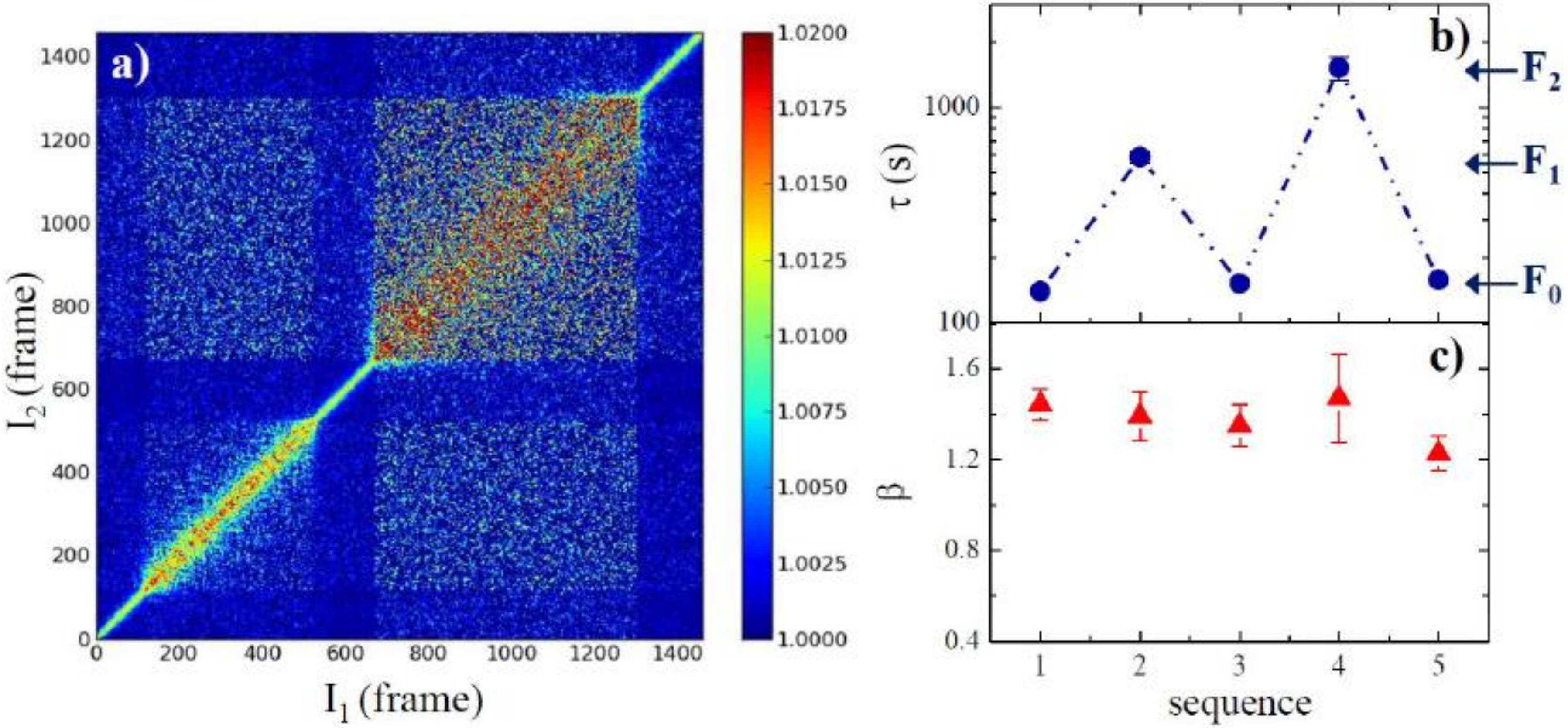
Room temperature, Q = 1.5 Å^{-1}

$F_0 \approx 1\cdot10^{11}$ ph/s (red)
$F_1 \approx 3\cdot10^{10}$ ph/s (orange)
$F_2 \approx 1.2\cdot10^{10}$ ph/s (cyan)
$F_3 \approx 3.6\cdot10^{9}$ ph/s (blue)

Ruta *et al.*, Sci. Rep. **7**, 3962 (2017)

Beam induced dynamics - I

The observed beam-induced effect is reversible

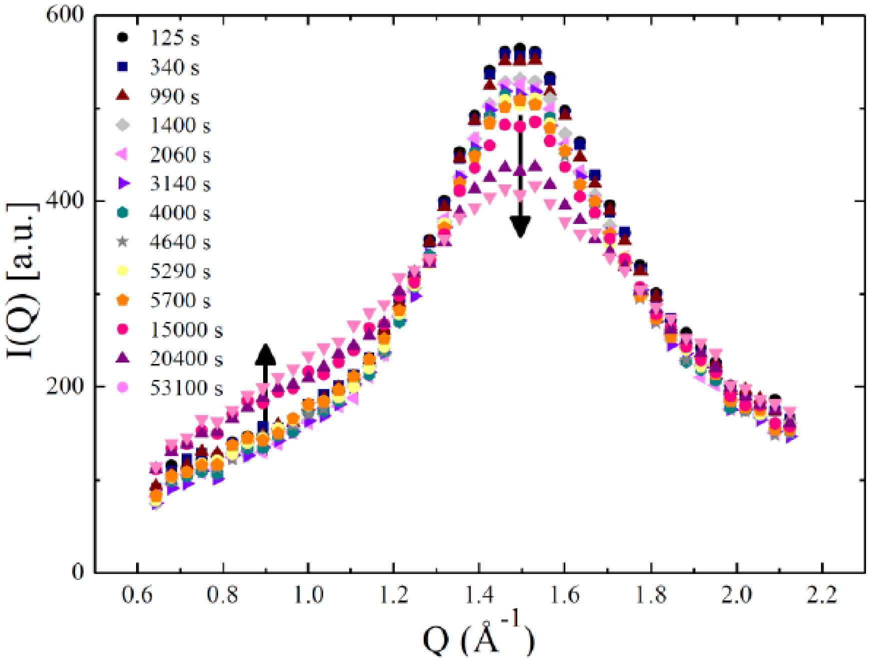


v-SiO_2

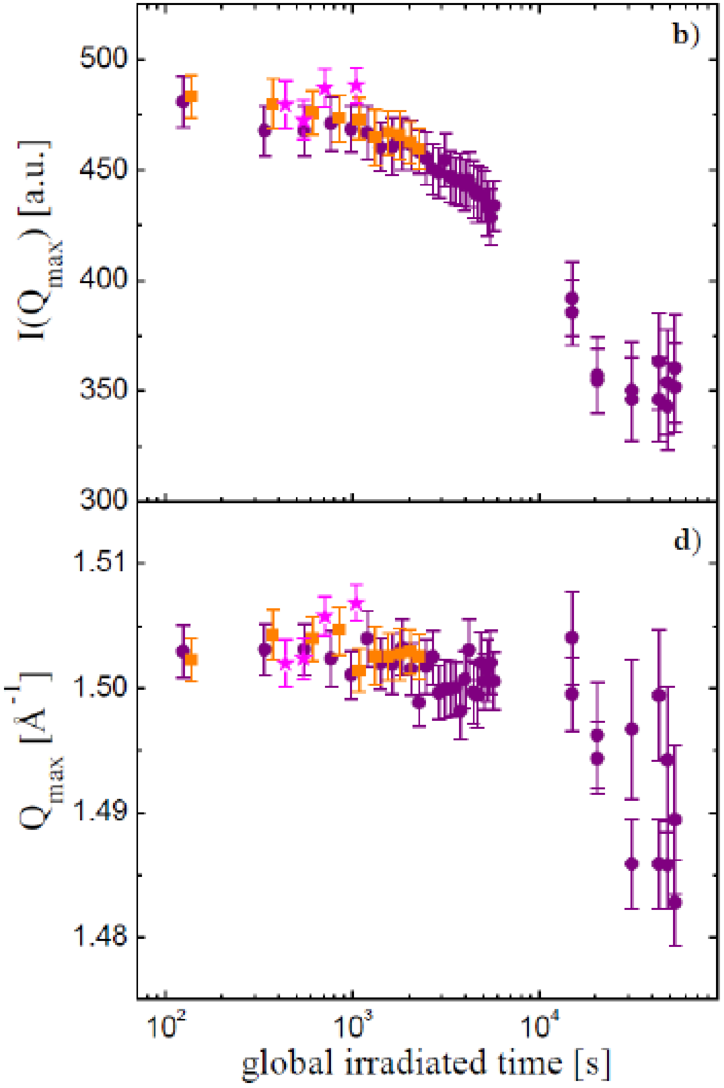
Ruta *et al.*, Sci. Rep. **7**, 3962 (2017)

Beam induced dynamics - II

This beam-induced effect appears when radiation damage is negligible



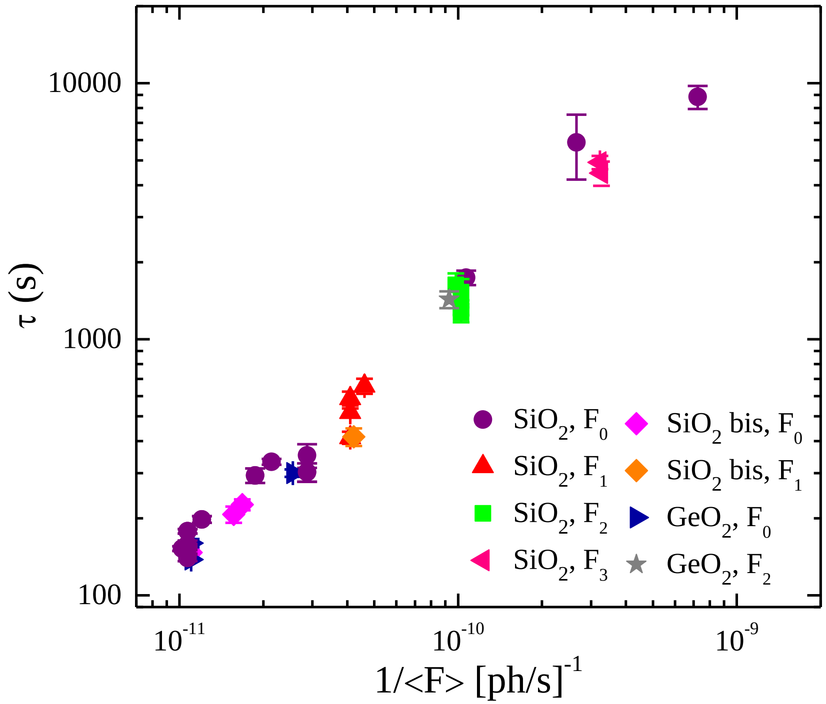
v-SiO$_2$



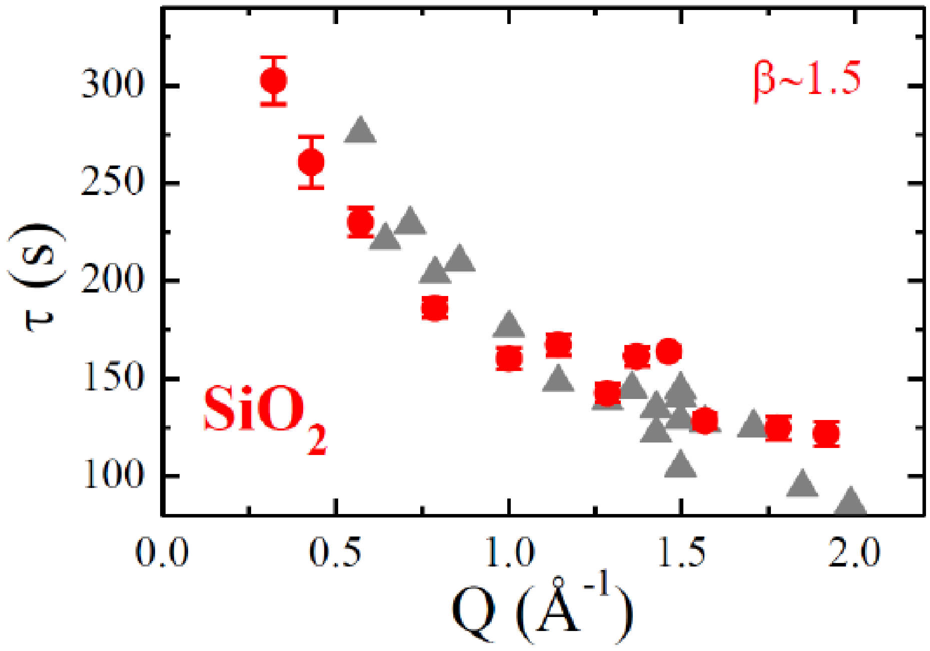
Ruta *et al.*, Sci. Rep. **7**, 3962 (2017)

Beam induced dynamics - III

The decorrelation time scales with the inverse flux over two decades in flux



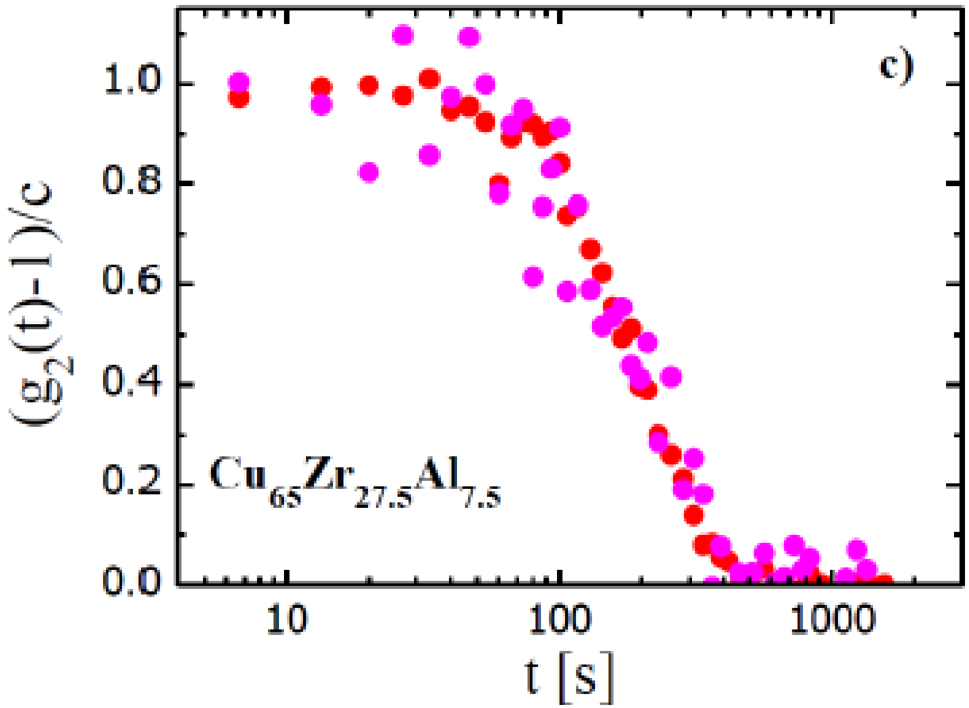
The decorrelation time shows a clear Q-dependence



Ruta *et al.*, Sci. Rep. **7**, 3962 (2017)

Beam induced dynamics - IV

Metallic glasses appear to be immune to beam-induced effects.
Radiolysis?

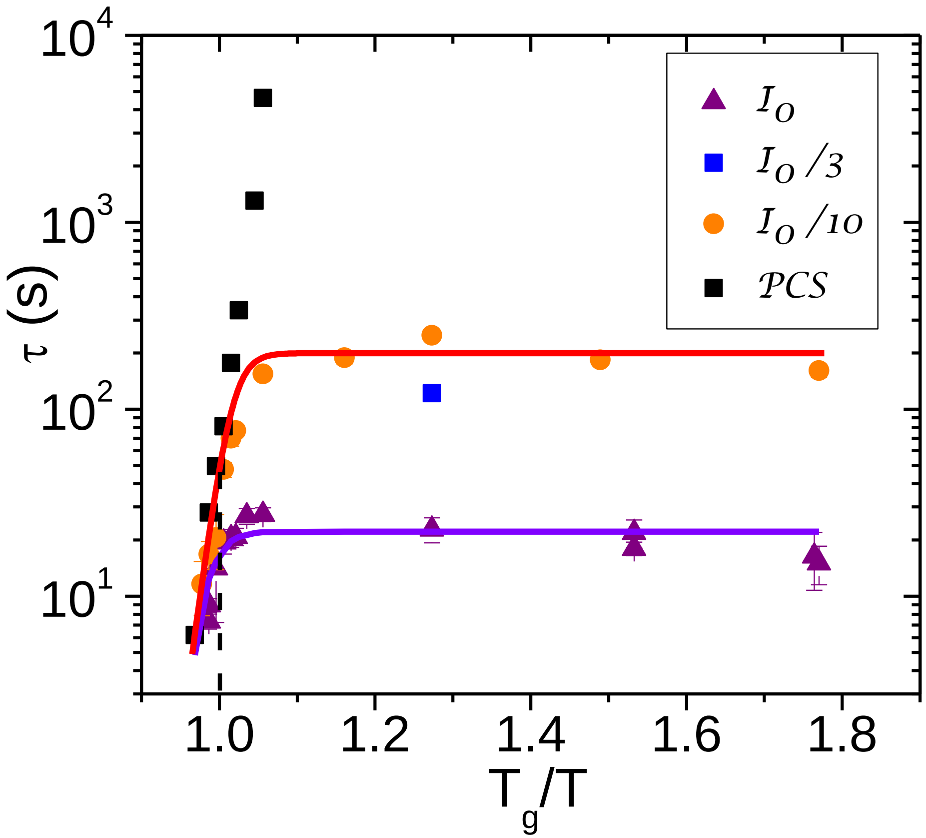


T = 416 K, Q = 2.5 Å^{-1}

Ruta *et al.*, Sci. Rep. **7**, 3962 (2017)

Beam induced dynamics – v-B_2O_3

v-B_2O_3



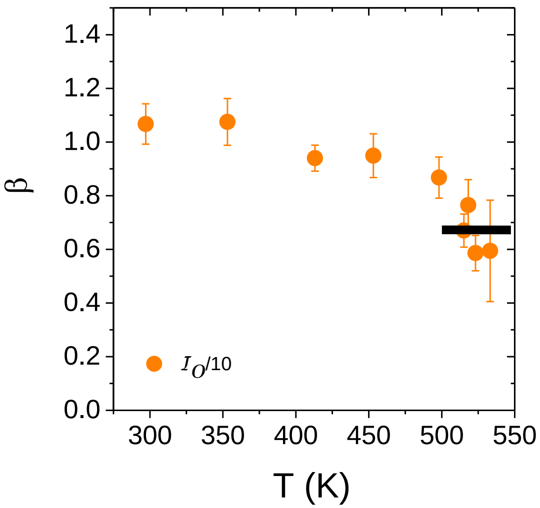
T_g = 526 K

The τ_α and τ_X seem independent:

$$\frac{1}{\tau} = \frac{1}{\tau_\alpha} + \frac{1}{\tau_X}$$

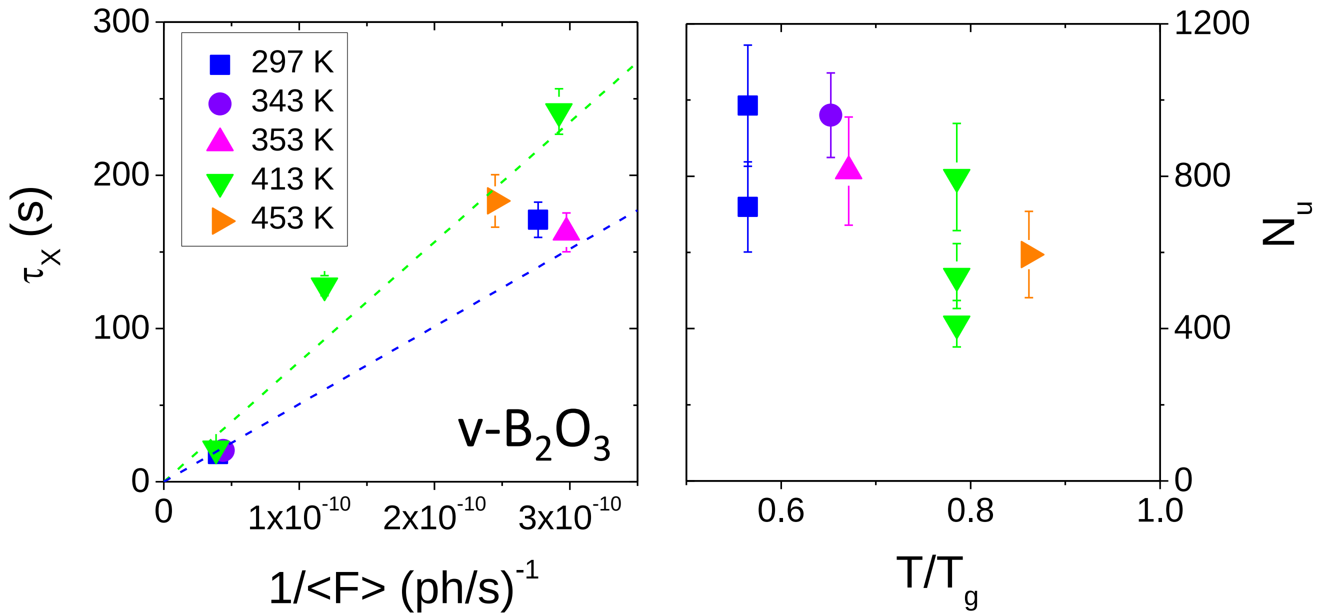
Structural rel. time

Beam induced decorrelation



G. Pintori, G. Baldi, B. Ruta, G. Monaco, Phys. Rev. B **99**, 224206 (2019)

Beam induced dynamics – v-B_2O_3



N_{tot}= number of B_2O_3 units in the scattering volume

A number $\sim \frac{N_{tot}}{e}$ of B_2O_3 units move in a time τ_X

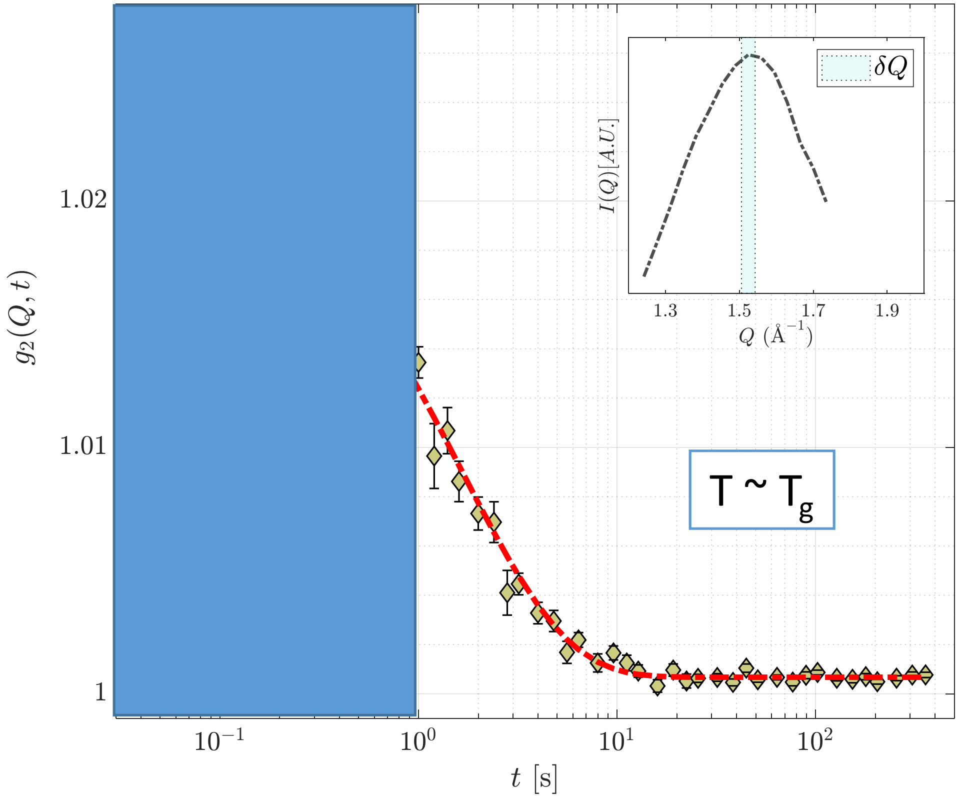
$$N_u = \frac{\#\, units\ that\ move\ in\ \tau_X}{\#\, photons\ absorbed\ in\ \tau_X} = \frac{1}{e}\frac{N_{tot}}{\tau_X < F >_a}$$

Number of B_2O_3 units that move after the absorption of 1 X-ray photon

G. Pintori, G. Baldi, B. Ruta, G. Monaco, Phys. Rev. B **99**, 224206 (2019)

Recent improvements

Vitreous B_2O_3



CCD detector:

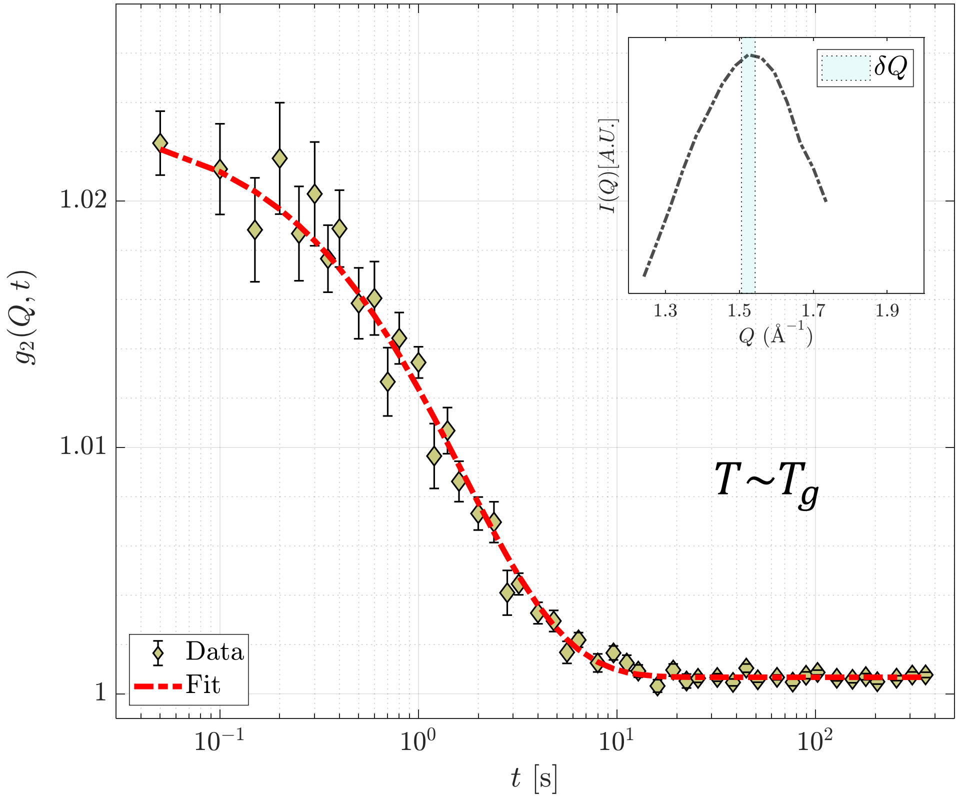
$dt > 1$ s

Time between frames

Recent improvements

Vitreous B_2O_3

Eiger detector at ESRF-ID10



$T \sim T_g$

$$\tau = (3.9 \pm 0.1)\ \text{s}$$
$$\beta = 0.81 \pm 0.03$$

Parameters of the measurement:

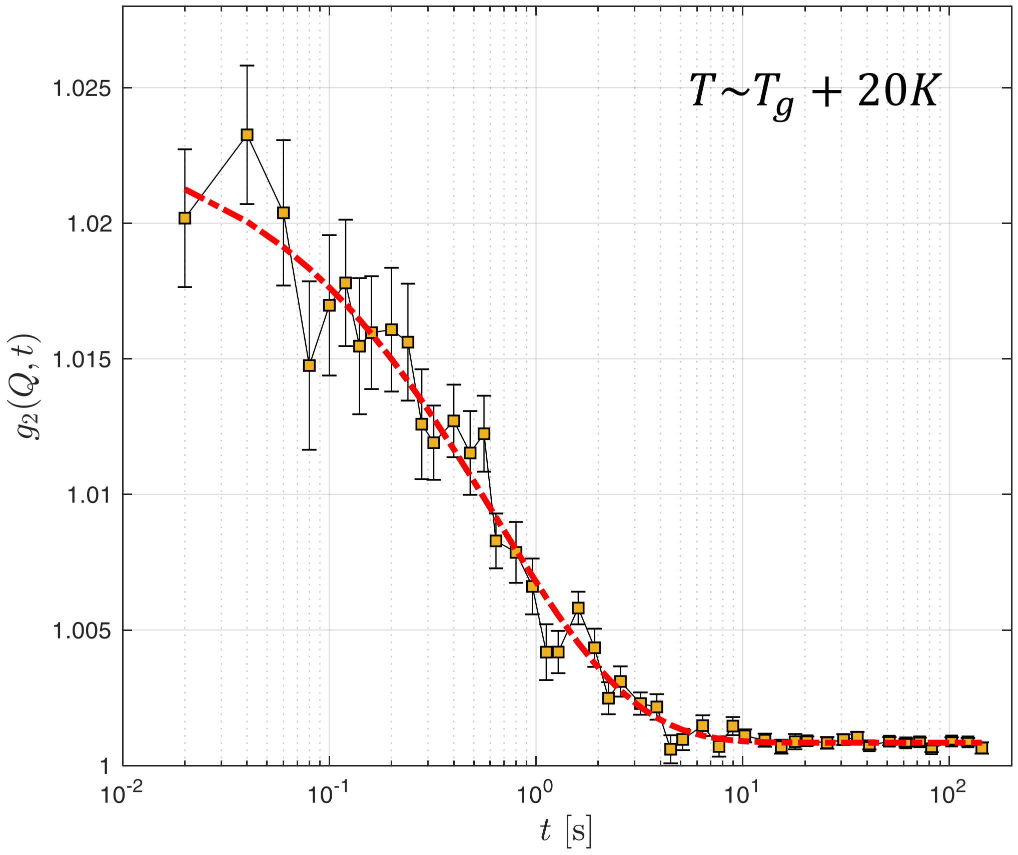
$\mathrm{dt} = \mathbf{50\ ms}$
20 x 10000 images
Total duration ~ 3 hours

A. Martinelli *et al.*, in preparation

Recent improvements

B_2O_3
Supercooled liquid

Eiger detector at ESRF-ID10



$\tau = (1.8 \pm 0.1)$ s
$\beta = 0.65 \pm 0.04$

Parameters of the measurement:

dt = **20 ms**
70 x 10000 images
Total duration ~ 4h

Difficult to measure $\tau < 1$ s

A. Martinelli *et al.*, in preparation

Outline

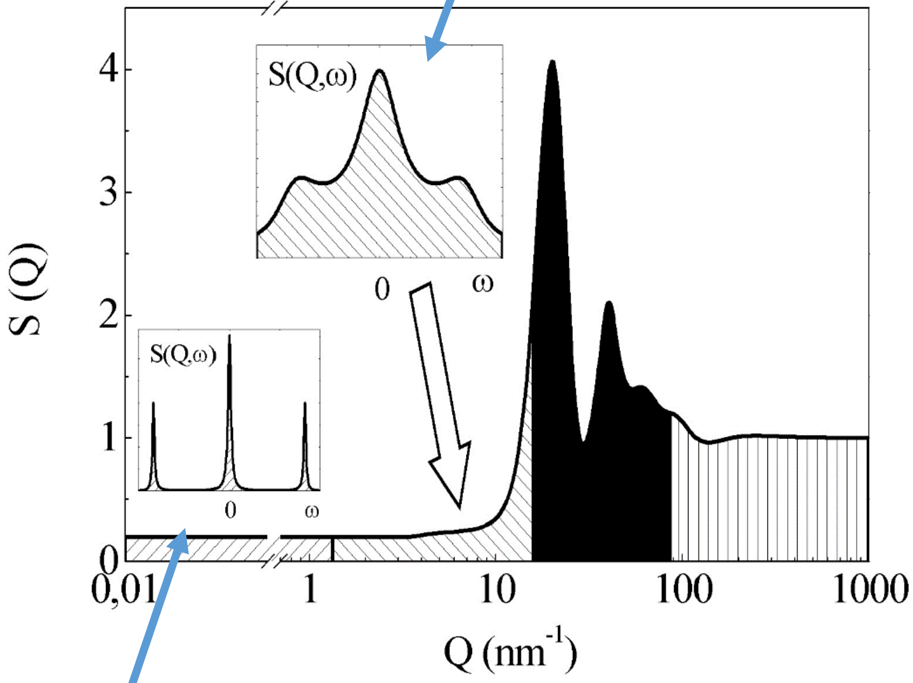
- WA XPCS – Introduction
- Dynamics of the glassy state
- Beam-induced dynamics
- New opportunities at ESRF-EBS
    - From microscopic to macroscopic
    - Dynamics of supercooled liquids
    - Link with vibrational dynamics
    - Nano-focusing
        - Dynamical heterogeneities
        - Stress relaxation
    - Extreme conditions (HP – HT)

Connecting the microscopic and macroscopic dynamics

Bridge the gap between WAXS and SAXS XPCS

Microscopic regime: not well understood

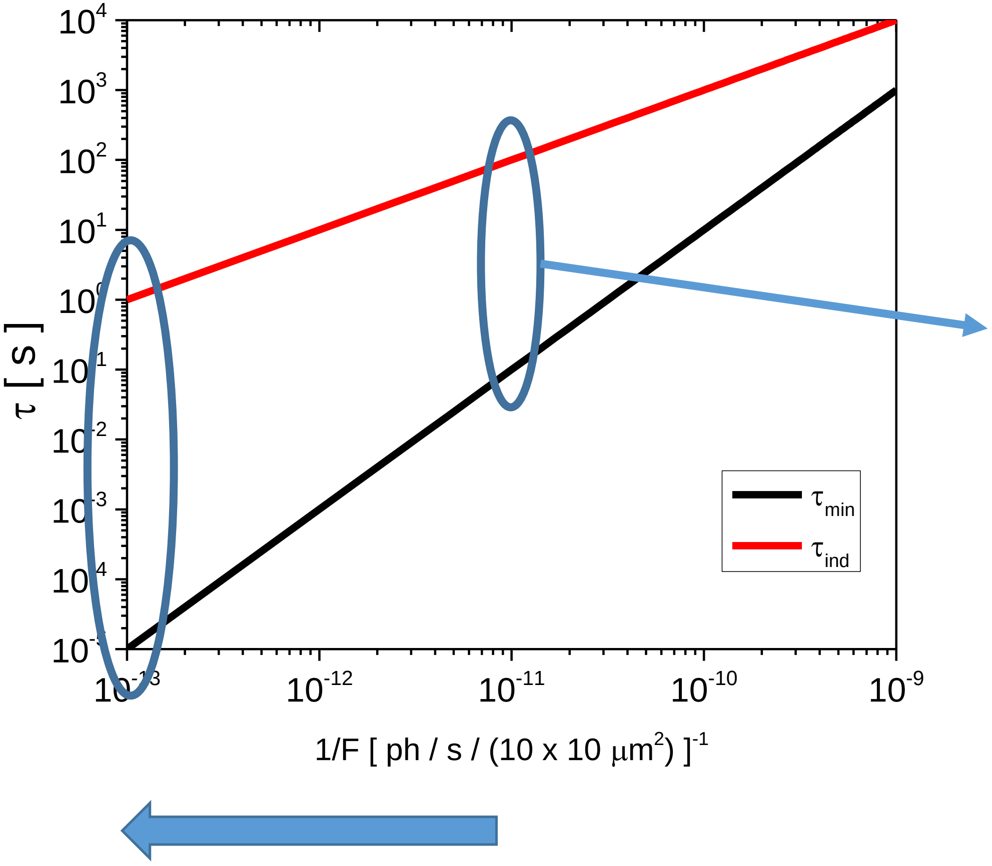
x100 Intensity variation



Microscopic regime: hydrodynamics

Probing the liquid dynamics

How to “win” over the beam induced decorrelation



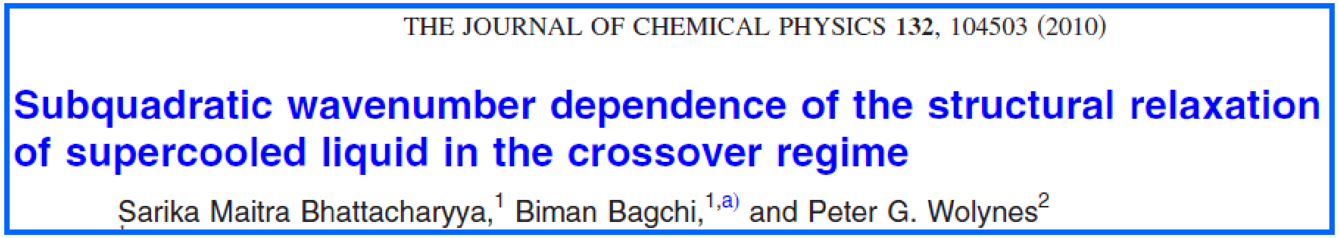
Now at ID10:
$F \sim 10^{11}$ ph/s

Assuming:
$\tau_{ind} \sim 100$ s
$\tau_{min} \sim 0.1$ s

x100 Intensity:

$\tau_{ind} \sim 1$ s
$\tau_{min} \sim 0.01$ ms

Dynamics of supercooled liquids



THE JOURNAL OF CHEMICAL PHYSICS **132**, 104503 (2010)

Subquadratic wavenumber dependence of the structural relaxation of supercooled liquid in the crossover regime

Sarika Maitra Bhattacharyya,[1] Biman Bagchi,[1,a)] and Peter G. Wolynes[2]

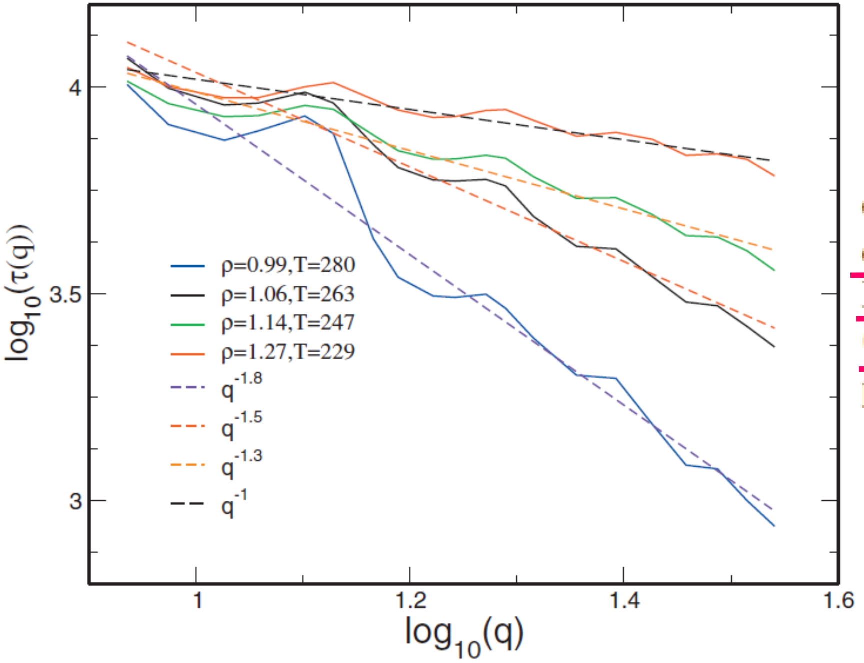
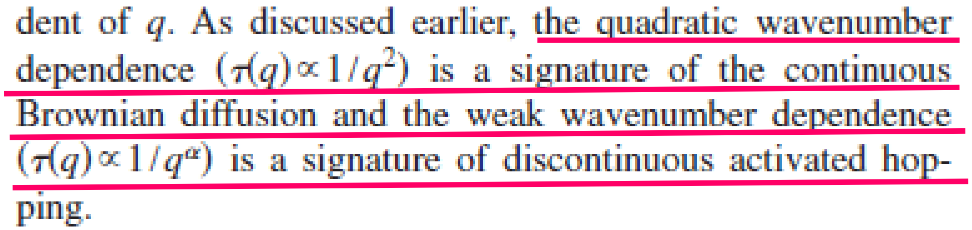


FIG. 1. The α relaxation timescale $\tau(q)$ plotted as a function of q at different densities and temperatures. The $\tau(q)$ values are scaled such that at $q=8.6$ they have similar values. $\tau(q)$ shows a weaker q dependence as the temperature is lowered.

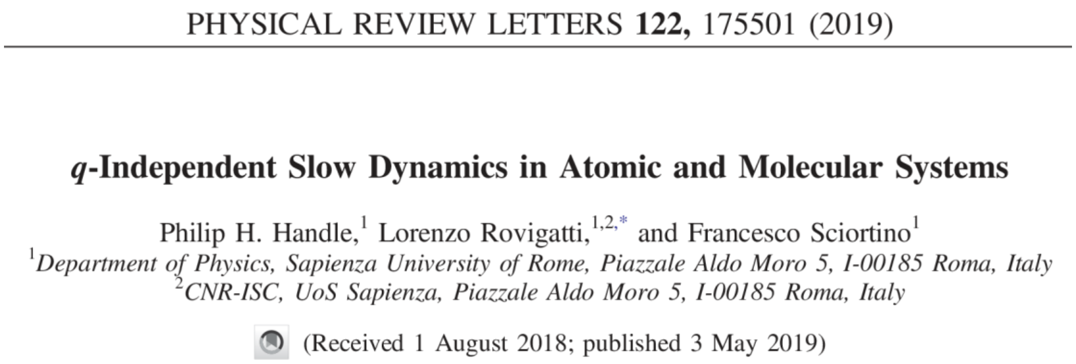


dent of q. As discussed earlier, the quadratic wavenumber dependence ($\tau(q) \propto 1/q^2$) is a signature of the continuous Brownian diffusion and the weak wavenumber dependence ($\tau(q) \propto 1/q^{\alpha}$) is a signature of discontinuous activated hopping.

Theoretical model

Dynamics of supercooled liquids

MD simulations



PHYSICAL REVIEW LETTERS **122,** 175501 (2019)

q-Independent Slow Dynamics in Atomic and Molecular Systems

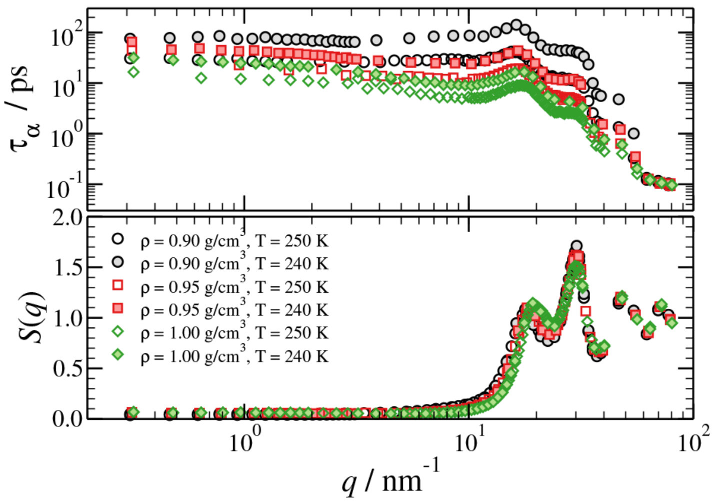
Philip H. Handle,[1] Lorenzo Rovigatti,[1,2,*] and Francesco Sciortino[1]

[1]*Department of Physics, Sapienza University of Rome, Piazzale Aldo Moro 5, I-00185 Roma, Italy*

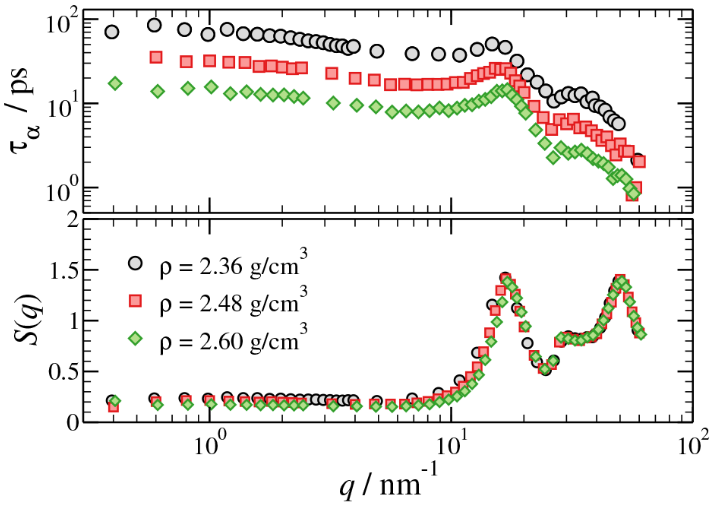
[2]*CNR-ISC, UoS Sapienza, Piazzale Aldo Moro 5, I-00185 Roma, Italy*

(Received 1 August 2018; published 3 May 2019)

Investigating million-atom systems for very long simulation times, we demonstrate that the collective density-density correlation time (τ_α) in simulated supercooled water and silica becomes wave-vector independent (q^0) when the probing wavelength is several times larger than the interparticle distance.



Water (TIP4P/2005)



BKS Silica

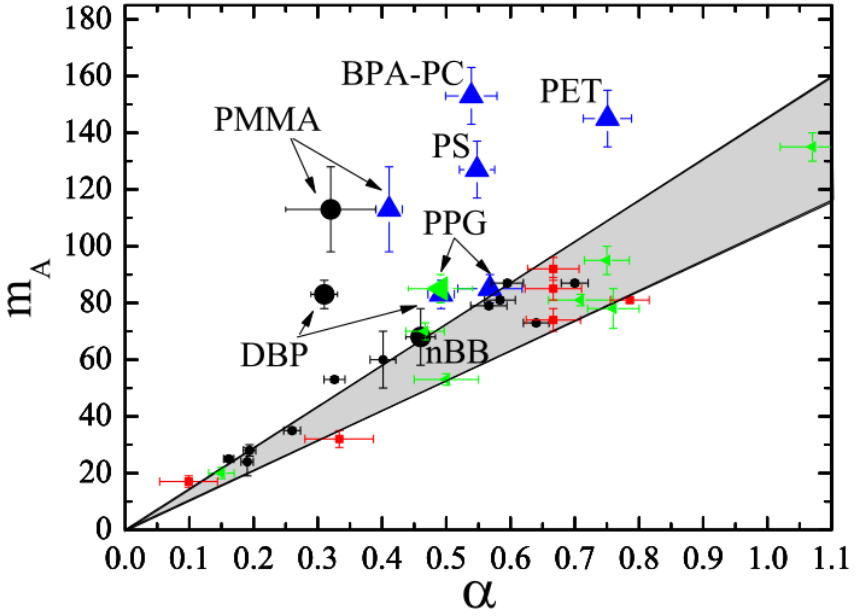
Link with vibrational dynamics

Non-ergodicity parameter in the harmonic approximation:

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

$$m\sim\alpha(Q\rightarrow 0)$$

Glass fragility



T. Scopigno *et al.*, Science **302**, 849 (2003)
T. Scopigno *et al.*, Phys. Rev. B **81**, 100202 (2010)

Link with vibrational dynamics

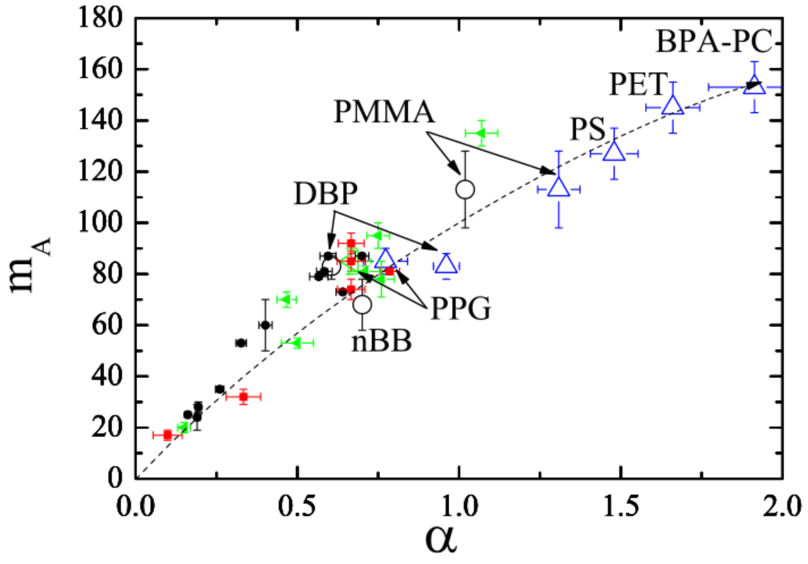
Non-ergodicity parameter in the harmonic approximation:

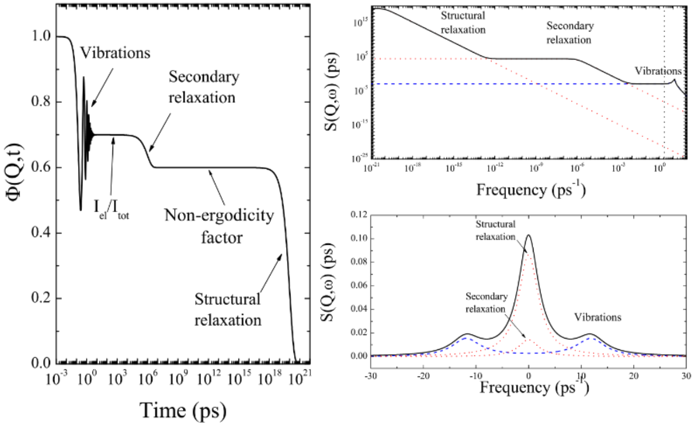
$$f(Q,T) = \frac{1}{1+\alpha(Q)\frac{T}{T_g}}$$

$$m \sim \alpha(Q \to 0)$$

Glass fragility

α parameter corrected for the presence of secondary relaxations



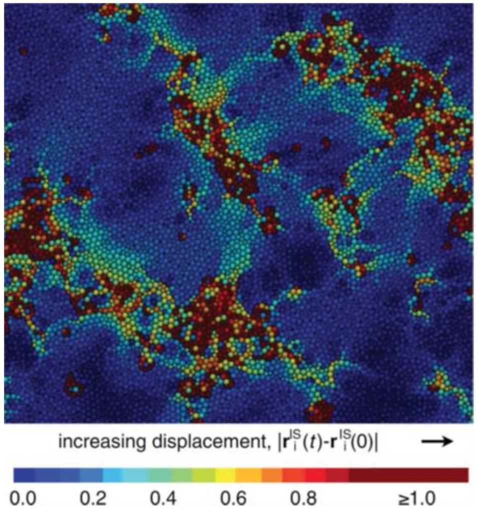


T. Scopigno *et al.*, Science **302**, 849 (2003)
T. Scopigno *et al.*, Phys. Rev. B **81**, 100202 (2010)

Growing length scales approaching T_g?

Numerical **simulations**

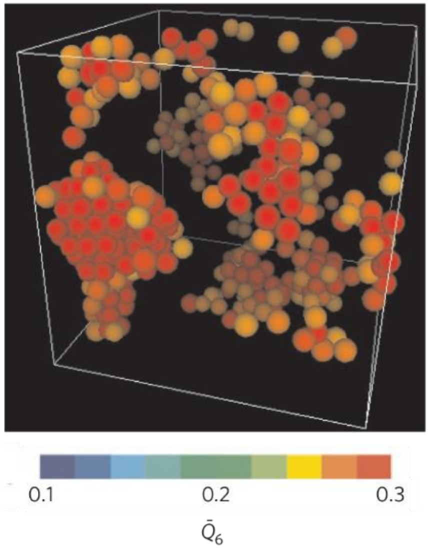
$T \gtrsim T_g$



Regions of high and low mobility

Dynamical correlation length

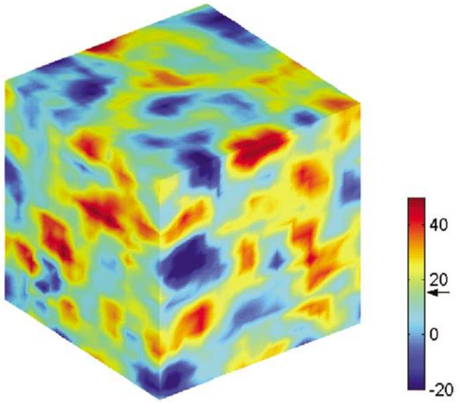
$T \gtrsim T_g$



Static length scale

Clustering of the bond orientational order parameter

$T < T_g$



Elastic heterogeneities

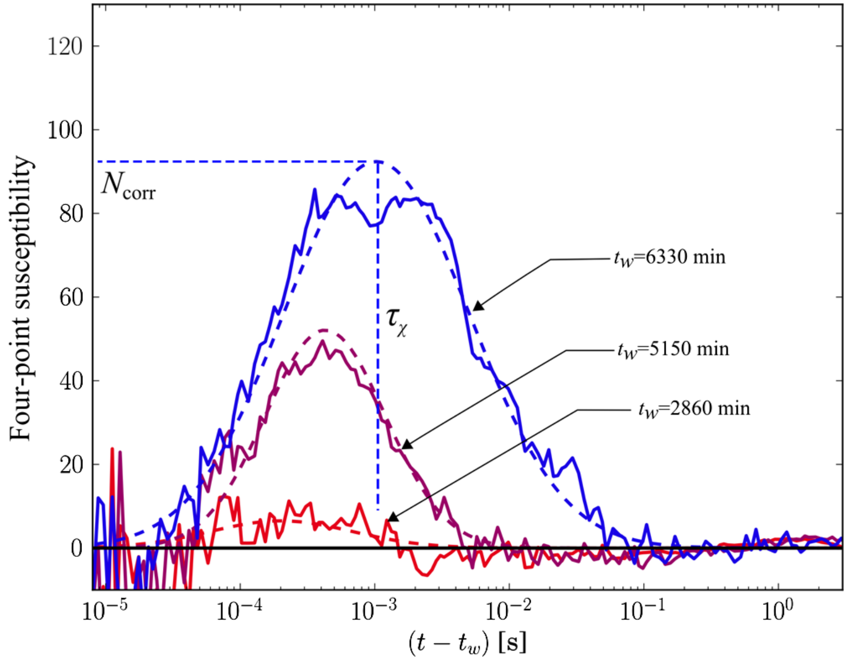
Local shear modulus

A. S. Keys *et al.*, Phys. Rev. X **1**, 021013 (2011).
H. Tanaka *et al.*, Nat. Mater., **9**, 324 (2010).
K. Yoshimoto *et al*., Phys. Rev. Lett. **93**, 175501 (2004).

Nanofocusing -> dynamical heterogeneities

Aging Laponite colloidal solution, DLS setup

Scattering volume ~ 1 μm^3,
with ~10^4 particles



The four-point susceptibility shows a peak when N_{corr} ~ 10 - 100

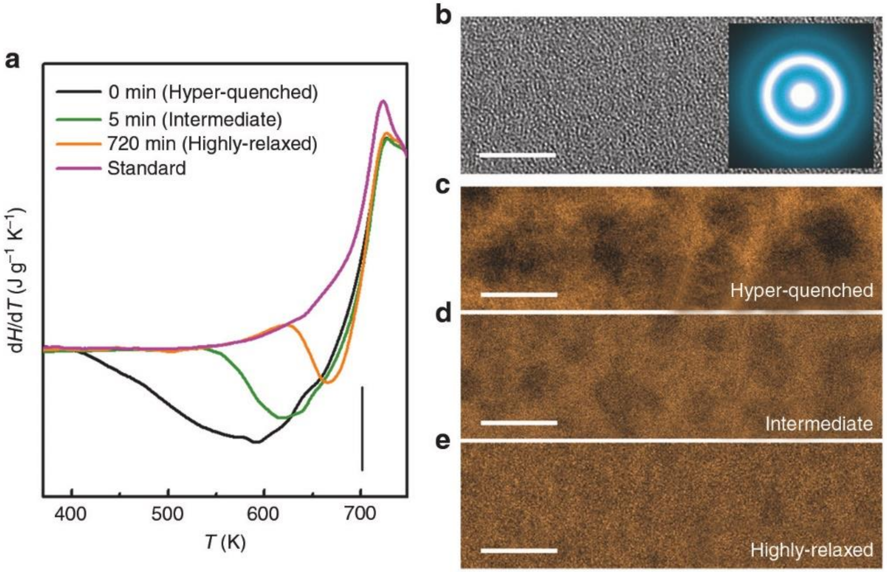
$\lesssim 1000$ independent regions in the scattering volume

$\sim 10 - 50$ nm focus

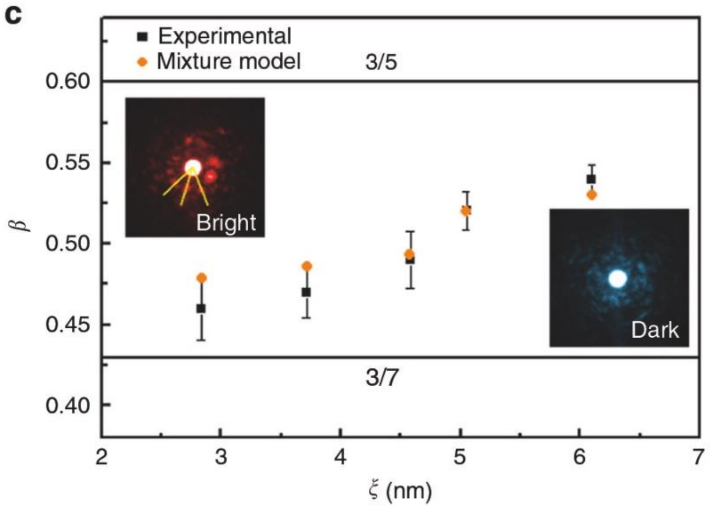
C. Maggi *et al.*, Phys. Rev. Lett. **109**, 097401 (2012)

Nanofocusing -> stress relaxation

$Zr_{53}Cu_{36}Al_{11}$ hyper-quenched metallic glass



Scale bar, 5 nm

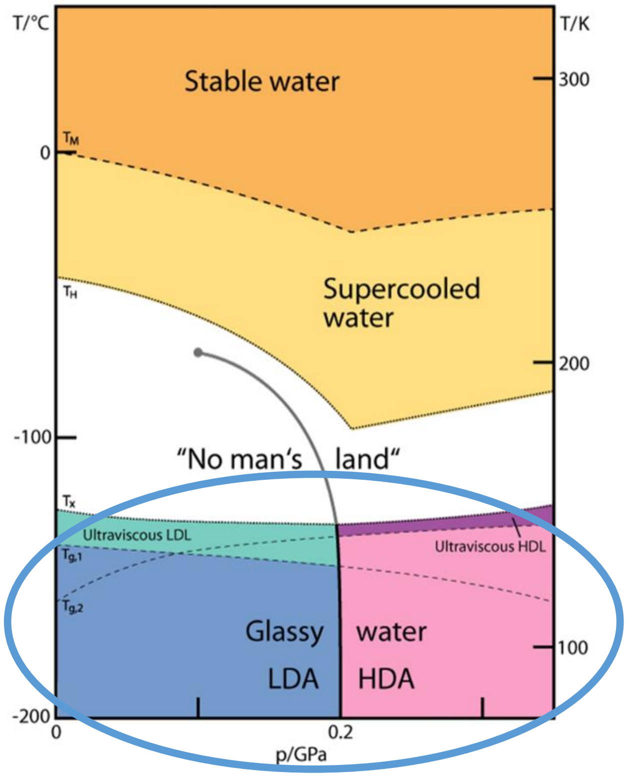


Nanoscale spatial heterogeneity observed by HRTEM.
The typical size evolve during annealing

F. Zhu *et al.*, Nat. Commun. **9**, 3965 (2018)

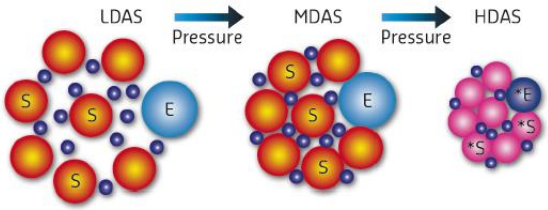
Dynamics at Extreme Conditions

Dynamical evolutions during polyamorphic transitions



P. Gallo et al. Chem. Rev. 2016
Mischima et al. Nature 1985

Hierarchical densifications in metallic glasses



Q. Luo et al. Nat. Commun. 2015
H. W. Sheng et al. Nat. Materials 2007

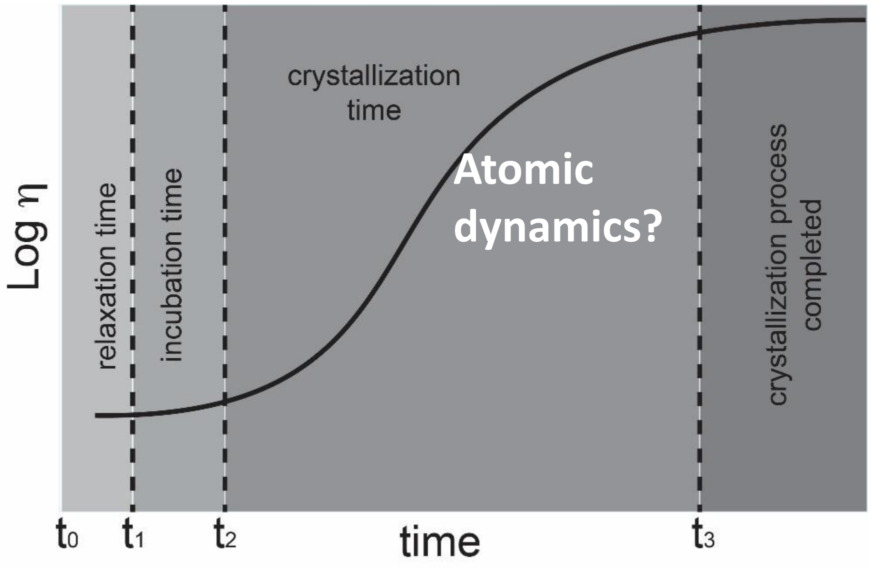
Nucleation in magmas

F. Vetere et al. Earth-Sci. Rev. 2015

XPCS of nucleation in magmas

Crystallization in magmas strongly affects viscosity, and thus magma flow.

Determining the microscopic mechanism of crystallization can lead to an *a priori* assessment of the volcanic risk.



XPCS can clarify the microscopic atomic dynamics in crystallizing magmas

High incident energy → Edge selective XPCS , sensitivity to impurities.

Improved brillance → High temperature studies (HT, about 1000°C).

→ High pressure studies (HP, 1 - 100 kbar).

→ Realistic conditions (HT-HP, chaotic mixing,…).

Conclusions

- Fast **aging** regime and compressed corr. functions in fast quenched metallic glasses
- **Structural** relaxation of oxides accessible only if faster than the beam induced decorrelation
- Many new exciting possibilities exploiting the improved coherent flux of ESRF-EBS

Thank you!

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