Atomic motion in glasses studied with coherent X-rays

Beatrice Ruta
ESRF – Grenoble, France
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
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
HARD & SOFT GLASSES

Amorphous materials ...
HARD & SOFT GLASSES

... which can be driven in an arrested state ...

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

→ every physical observables spontaneously evolve with time
... where they display physical aging

→ every physical observables spontaneously evolve with time

**Temporal evolution**

![Temporal evolution graph](image)

... where they display physical aging

→ every physical observables spontaneously evolve with time

### Temporal evolution

![Temporal evolution graph](image)

### Thermal history dependence

![Thermal history dependence graph](image)


HARD & SOFT GLASSES

... where they display physical aging

→ every physical observables spontaneously evolve with time

**Temporal evolution**

**Thermal history dependence**


Understanding and controlling the physical properties requires information on the ongoing relaxation processes at the microscopic scale.
Information on the relaxation dynamics can be obtained from the decay of the intermediate scattering function on a scale $2\pi/Q$

$$f(q,t) = a \exp\left(-\left(\frac{t}{\tau}\right)\right)$$

$$F(Q,t) = \frac{S(Q,t)}{S(Q)} = \frac{\langle \delta \rho_Q^*(0) \delta \rho_Q(t) \rangle}{\langle \delta \rho_Q^*(0) \delta \rho_Q(0) \rangle}$$
Information on the relaxation dynamics can be obtained from the decay of the **intermediate scattering function** on a scale $2\pi/Q$.

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

- $f(q,t) = a \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]$ where $\tau$ is the time for structural rearrangements (on ~2/3 Å in the case of glasses).
How can we measure the relaxation dynamics in a glass?
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
X-ray Photon Correlation Spectroscopy is the **only technique** offering the potential to unravel the dynamics of glass formers around and below $T_g$ ($\tau \sim 1-10^4$ s, $Q \sim 0.3-4$ Å$^{-1}$).
XPCS uses the partial coherent properties of X-rays at 3rd generation synchrotrons

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.

Information on the microscopic dynamics

\[
I(Q,t) \propto \left| \sum_n f_n(Q) \cdot e^{iQ \cdot r_n(t)} \right|^2
\]
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
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, $\text{H}_2$ 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**

**Mg₆₅Cu₂₅Y₁₀**

- Decreasing T

- Liquid

**Fit model: KWW**

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

Fit model: KWW

\[ F(Q,t) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \]
**FIRST INVESTIGATION OF ATOMIC DYNAMICS IN MGs**

**Mg$_{65}$Cu$_{25}$Y$_{10}$**

- $\beta > 1$ (liquid)
- $\beta < 1$ (glass)

**Fit model: KWW**

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

**DYNAMICAL CROSSOVER AT $T_g$**

- $T > T_g$: stationary dynamics, $\beta < 1$, diffusive motion
- $T < T_g$: aging, $\beta > 1$, Anomalous stress-dominated dynamics

**Departure from the liquid curve**

Surprising hierarchy of “anomalous” dynamical regimes

- Mg\textsubscript{65}Cu\textsubscript{25}Y\textsubscript{10} ($T/T_g=0.99$)
- Pd\textsubscript{77}Si\textsubscript{16.5}Cu\textsubscript{6.5} ($T/T_g=0.73$)
- Zr\textsubscript{67}Ni\textsubscript{33} ($T/T_g=0.58$)

stationary well below $T_g$, …

fast initial aging
Surprising hierarchy of “anomalous” dynamical regimes

→ Contradiction with the continuous evolution of macroscopic measurements

Surprising hierarchy of “anomalous” dynamical regimes

Contradiction with the continuous evolution of macroscopic measurements


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


→ Universal stress-dominated dynamics?
What is the origin of the microscopic aging?
Combining XRD and XPCS → same thermal and temporal protocol

Pd$_{77}$Si$_{16.5}$Cu$_{6.5}$ ($T_g = 625$ K, $Q = 2.8$ Å$^{-1}$)

Heating rate 3K/min

2 XRD experiments:
   i) high resolution around the FSDP
   ii) large q range (up to 25Å$^{-1}$ to extract the pair distribution function $G(r)$)
Complementary dynamical (ID10) & structural (ID15) study

Dynamics at $Q_{\text{max}}$ of $S(Q)$ XPCS (ID10)

\[ \tau(T, t_w) = \tau_0(T) \exp\left(\frac{t_w}{\tau^*}\right) \]

\[ \tau^*(393\rightarrow493 \text{ K}) \approx 6000 \text{ s} \]

- Fast aging along isotherms, strong $\tau$ reduction at temperature jumps
- Frozen dynamics at the highest $T$ (513 K)
Complementary dynamical (ID10) & structural (ID15) study

**Evolution of the FSDP XRD (ID15)**

- Isothermal volume relaxation

\[
\frac{V}{V_0}(t, T) = \frac{V}{V_0}(0, T)\exp\left(-\frac{t}{\tau_V}\right)
\]

- Continuous FSDP sharpening

\[
\frac{\Gamma}{\Gamma_0}(t, T) = \frac{\Gamma}{\Gamma_0}(0, T)\exp\left(-\frac{t}{\tau_\Gamma}\right)
\]
Two main processes controlling the aging:
1) volume shrinking (density changes)
2) medium range ordering (constant density)
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)
2) medium range ordering (constant density)

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

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
MG MEMBRANES FOR H₂ SEPARATION FROM CO₂

Ni and Zr-based MGs:

→ better H₂ permeability than crystalline materials (high H₂ diffusivity due to the free volume)

→ high H₂ 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 H₂ ON THE DYNAMICS

Ni₆₀Nb₄₀, T=373 K, Qᵣ=2.7 Å⁻¹
H @ 0.6 bar

F(Q,t)

relaxation time (s)

1000 10 10000

annealing times:
0.4h 6.3h
1.3h 7.2h
3.5h 9.1h
4.6h 11 h
5.4h

V₁
H₂
V₂

Ni₆₀Nb₄₀
Ni$_{60}$Nb$_{40}$, T=373 K, $Q_p=2.7$ Å$^{-1}$
H @ 0.6 bar

Dramatic acceleration of the dynamics due to the hydrogen atmosphere
EFFECT OF H$_2$ ON THE DYNAMICS

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

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
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
SILICATE GLASSES: $0.8\text{SiO}_2-0.2\text{Na}_2\text{O}$ (NS4, $T_g=783$ K)

Stretched exponential decay of the correlation function as in the liquid phase ($\beta=0.67$) $\rightarrow$ diffusive motion

$Q_{\text{max}}=1.53\ \text{Å}^{-1}$; measurements in the glass transition region
Absence of physical aging on the experimental time scale

\( Q_{\text{max}} = 1.53 \, \text{Å}^{-1} \); measurements in the glass transition region

**Stretched exponential** decay of the correlation function as in the liquid phase \((\beta = 0.67) \rightarrow \text{diffusive motion}\)
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

\[
D_{\text{XPCS}} = \frac{1}{(\tau_{\text{incoh}}Q^2)} \\
\tau_{\text{incoh}} = \frac{\tau_{\text{XPCS}}}{S(Q)}
\]

Hempelmann et al., Z. Phys. B (1994)

B. Ruta et al., Nat. Commun. (2014)
WAVE VECTOR DEPENDENCE

\[ S(Q) \]

\[ Q (\text{Å}^{-1}) \]

\[ \tau(Q) \ (s) \]

\[ (S(\hat{Q}))^2 \]
QNS data of supercooled CKN

Mezei et al, Physica Scripta (1987)
WAVE VECTOR DEPENDENCE

Mezei et al, Physica Scripta (1987)


QNS data of supercooled CKN
What happens in oxide glasses?
IRRADIATION-DRIVEN DYNAMICS IN SiO$_2$ AT LOW TEMPERATURE

(a) $\frac{(g_2(t)-1)}{c}$ vs $t$ for increasing flux $F$.

(b) $\frac{(g_2(t)-1)}{c}$ vs $t \cdot F$.

- $F_0 \approx 1 \cdot 10^{11}$ ph/s
- $F_1 \approx 3 \cdot 10^{10}$ ph/s
- $F_2 \approx 1.2 \cdot 10^{10}$ ph/s
- $F_3 \approx 3.6 \cdot 10^9$ ph/s

The plots show the decay of $g_2(t)$ normalized by $c$ for different flux levels, with the flux increasing from $F_0$ to $F_3$. The data points are shown with different markers for each flux level.
The atomic motion at room temperature in SiO$_2$ is completely induced by the incoming X-rays.
IRRADIATION-DRIVEN DYNAMICS IN SiO$_2$ AT LOW TEMPERATURE

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), it is possible to tune “at will” the dynamics.
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.
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)*
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**

This effect is absent in metallic systems where electronic excitations are delocalized much faster on ~fs time scale

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

This effect is absent in metallic systems where electronic excitations are delocalized much faster on ~fs time scale

**Hard X-rays as pump and probe of the dynamics**

Similar to what observed with electron transmission microscopy on bi-dimensional SiO₂

*B. Ruta et al. arXiv (2016)*

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

*Huang et al. Science (2013)*
The wavevector dependence of the dynamics is independent on the flux

→ Typical increase as in supercooled liquids
The wavevector dependence of the dynamics is independent on the flux

→ Typical increase as in supercooled liquids

The shape of the curve is also independent on the flux

→ Compressed in SiO₂ and GeO₂, stretched in NS4 and lead-silicates. Stress-driven vs diffusive dynamics?
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
The EBS machine will lead to a 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
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
Thank you for your attention!!!
\[ \log[\tau(s)] = \frac{1000}{T(K^{-1})} \]

**Glass**

**Liquid**

- \( E_{a,\text{glass}} = 70 \text{ kJ/mol} \)
- \( E_{a,\text{liquid}} = 470 \text{ kJ/mol} \)

**Acknowledgments**

0.8\( \text{SiO}_2 \) - 0.2\( \text{Na}_2\text{O} \) (NS4, TG=783 K)

B. Ruta et al., Nat. Commun. (2014)
Threshold for structural damage at $\sim 10^4$ s of global irradiation at maximum flux

Occurrence of a real damage for longer exposure time
The dynamics is independent on the global accumulated dose.
POSSIBILITY TO GET INTRINSIC PROPERTIES OF THE SYSTEM

\( \beta \sim 1.5 \) for SiO\(_2\)

Different Q dependence

\( \beta \sim 0.67 \) for NS4

Stretched vs compressed mettere una figura del confronto curve
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**

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.
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.

\[ f(q,t) \]

- \( \tau_1 \) microscopic relaxation time related to the interactions between a particle and the cage of its nearest neighbors.
- \( \tau_2 \) structural relaxation time related to a structural rearrangement of the particles.

- \( t_w \) waiting time
- \( \Phi \) packing fraction
- \( 1/T \) temperature

**Fast relaxation**

**Slow relaxation**
EFFECT OF H$_2$ ON THE STRUCTURE

Reversible decreasing of the intensity of the FSDP
EFFECT OF H$_2$ ON THE STRUCTURE

Reversible decreasing of the intensity of the FSDP

Next step: high energy XRD & EFAFS