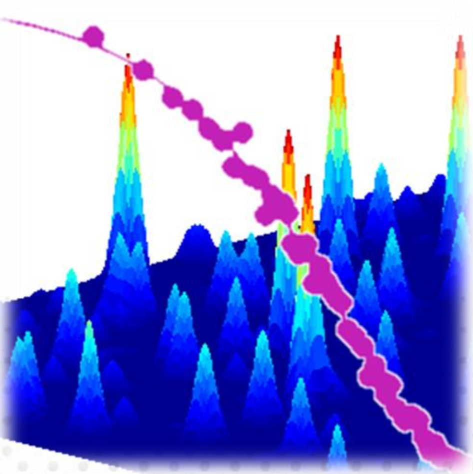
Dynamical properties of glass formers probed with coherent X-rays

Beatrice Ruta



Grenoble 21/11/2019

Outline

- ☐ Coherent X-rays and X-ray Photon Correlation Spectroscopy
- ☐ Glassy systems
  - ☐ Atomic motion in metallic glass formers
  - ☐ Dynamics in oxide and silicates glasses
- ☐ The EBS-ESRF upgrade
- ☐ New scientific opportunities

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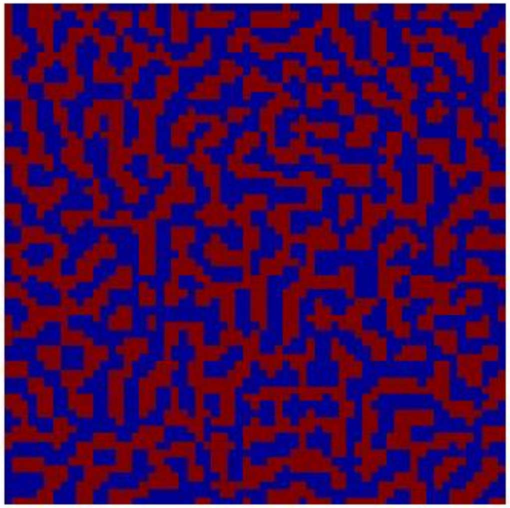
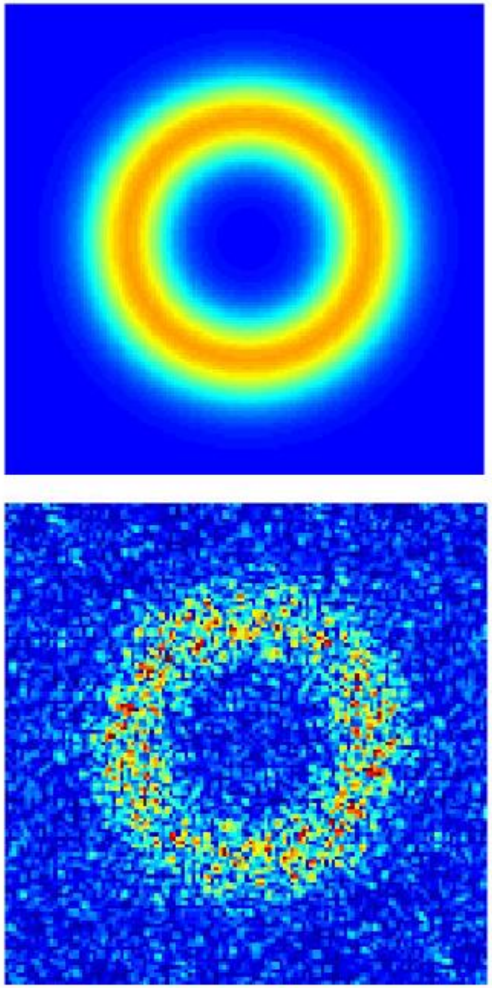
Coherent X-rays

sample with disorder
(e.g. domains)



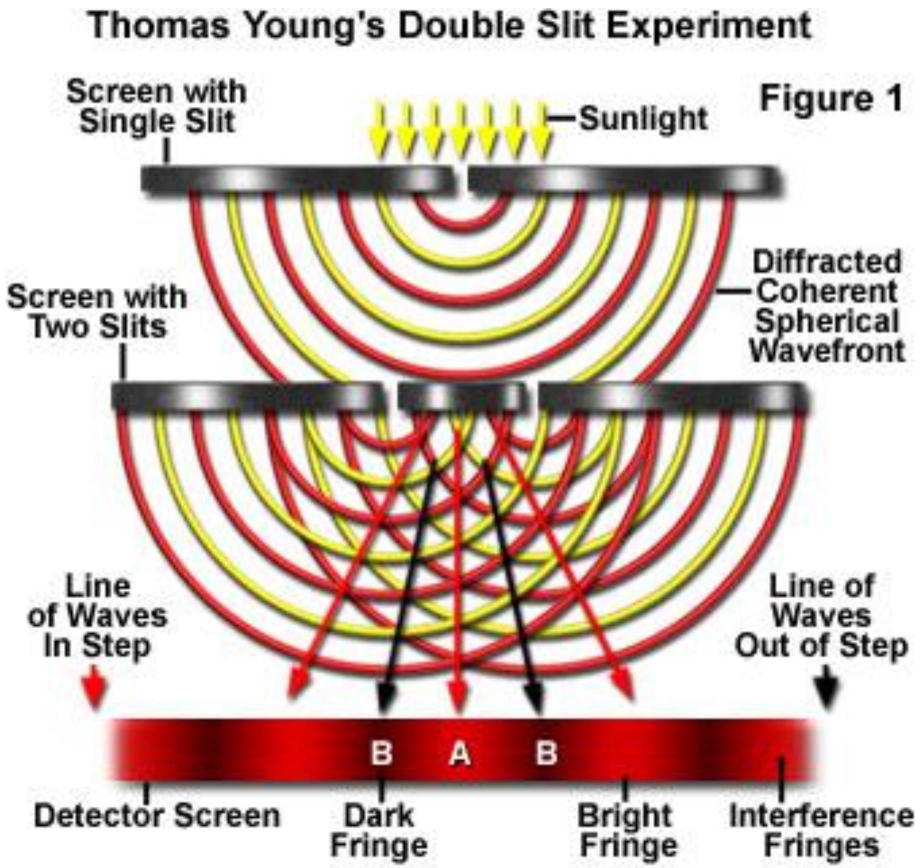
- ***Incoherent Beam: Diffuse Scattering***
  - **Measures averages, e.g. size, correlations**
- ***Coherent Beam: Speckle***
  - **Speckle depends on exact arrangement**

scattering



Courtesy of C. Gutt

Coherent Radiation



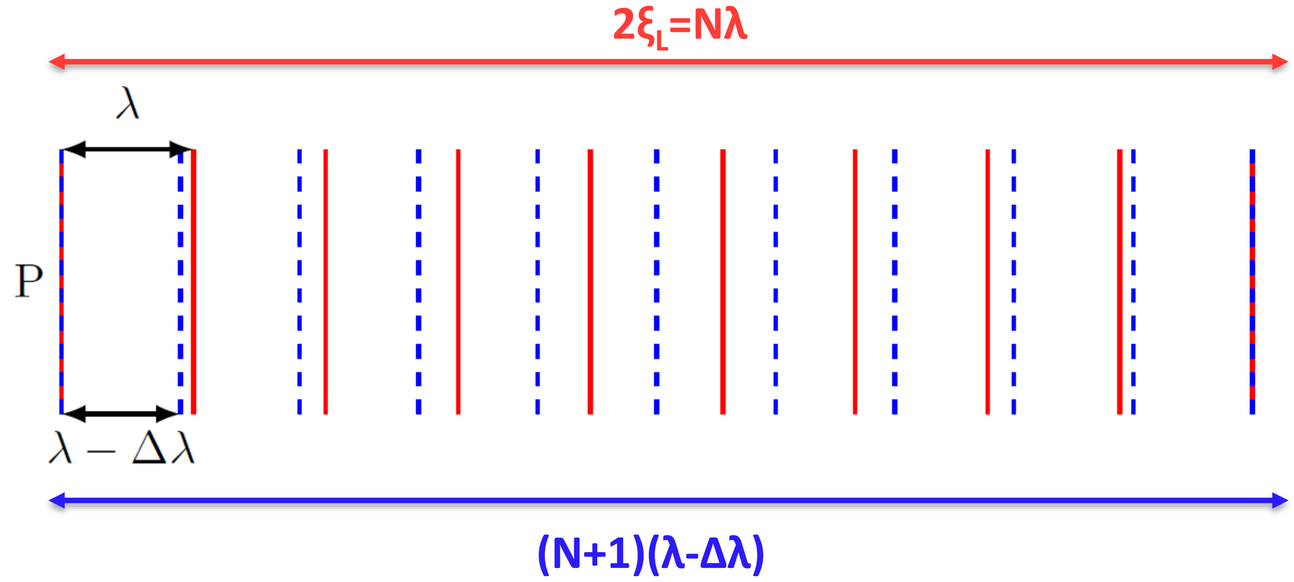
The intensity fluctuations are related to the constructive and destructive interference between the two waves

Coherence is observed when phases stay correlated (constant phase difference between pairs of points) in time and space → two types of coherent lengths.

http://micro.magnet.fsu.edu/primer/java/interference/doubleslit/

Longitudinal coherent length

Determined by monochromaticity: distance over which two waves with slightly different λ are out of phase ($\Delta\phi=\pi$)



$$N\lambda = (N+1)(\lambda-\Delta\lambda)$$

$$\lambda = (N+1)\Delta\lambda \text{ and } N\sim\frac{\lambda}{\Delta\lambda}$$

$$\Rightarrow \boxed{\xi_L = \frac{N\lambda}{2} = \frac{1}{2}\frac{\lambda^2}{\Delta\lambda}}$$

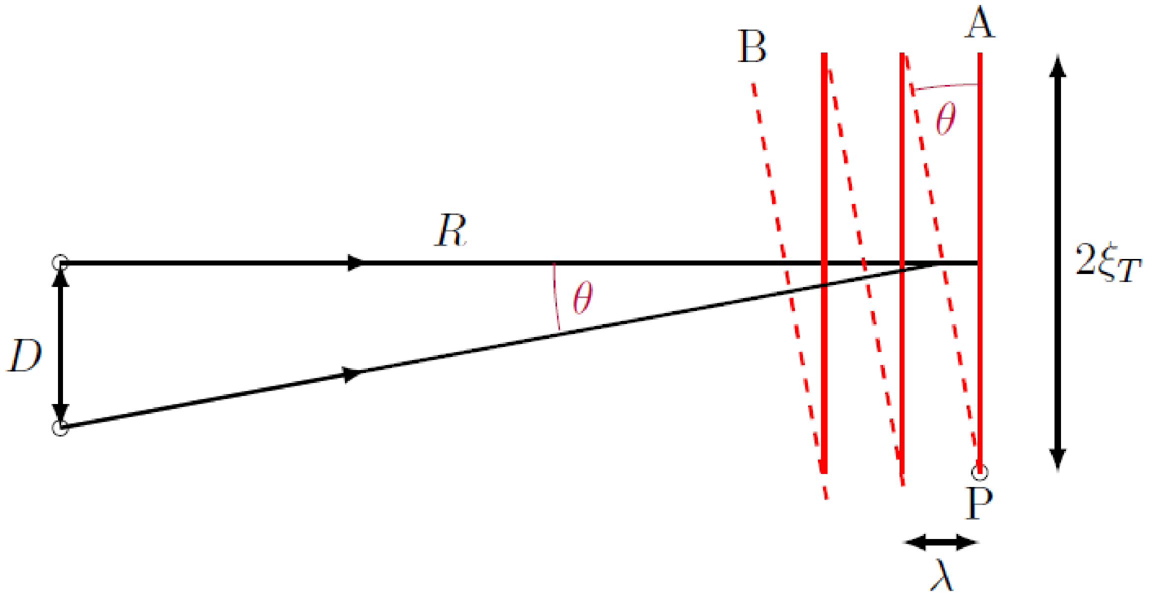
$\lambda \approx 1.5$Å

$\Delta\lambda/\lambda = 1.4\text{x}10^{-4}$ Si (1,1,1)

$\xi_L \approx 0.5$ µm

Transverse coherent lengths

Determined by beam size D and distance R: distance over which two waves slightly tilted of an angle θ are out of phase (Δϕ=π)



$$\frac{\lambda}{2\xi_T} = \sin\theta \approx \theta$$

$$\frac{D}{R} = \tan\theta \approx \theta$$

$$\boxed{\xi_{T\,h,v} \approx \frac{\lambda}{2}\frac{R}{D_{h,v}}}$$

Transverse coherent lengths

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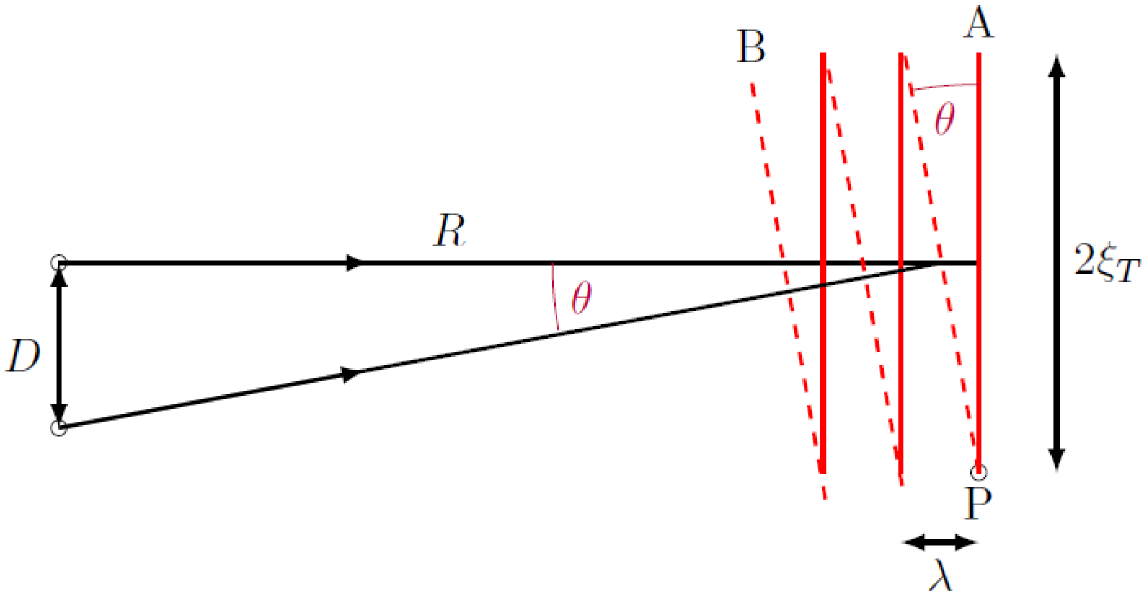

$$\frac{\lambda}{2\xi_T} = \sin\theta \approx \theta$$

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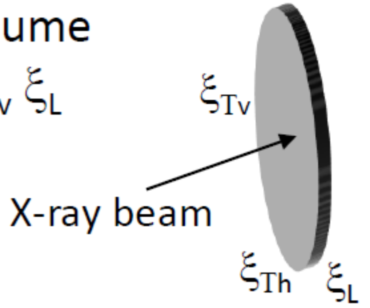
$$\boxed{\xi_{T\,h,v} \approx \frac{\lambda}{2}\frac{R}{D_{h,v}}}$$

To use coherence, the scattering volume V_S should be smaller than the coherent volume V_c

This condition is difficult to achieve with X-rays

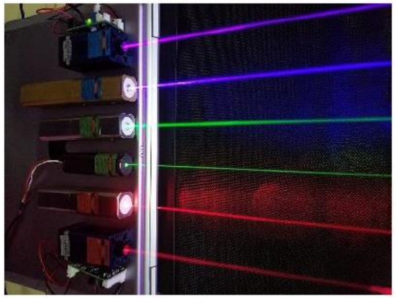
Coherence volume

$V_C = \pi/4\ \xi_{Th}\ \xi_{Tv}\ \xi_L$



Coherent X-rays

- ☐ The ideal photon source would be a one-mode source (stimulated emission), e.g. unimodal lasers

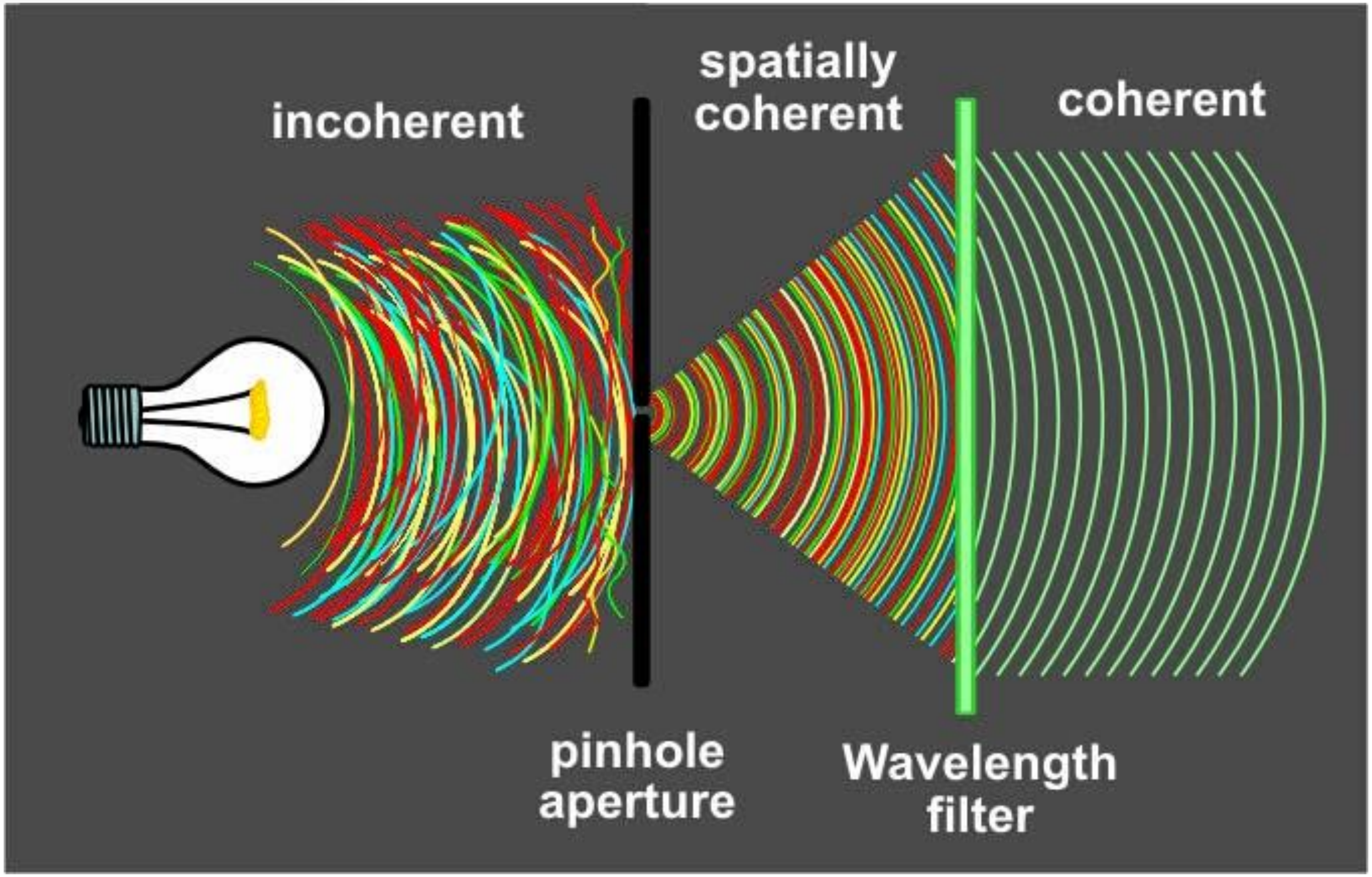


- ☐ X-ray sources are **chaotic**, because photons are generated by spontaneous emission like e.g. light bulbs, radioactive sources …

The **key parameter** quantifying the coherence properties of the photon source is the degeneracy parameter n_c, i.e. the **number of photons contained in the coherent volume V_c**

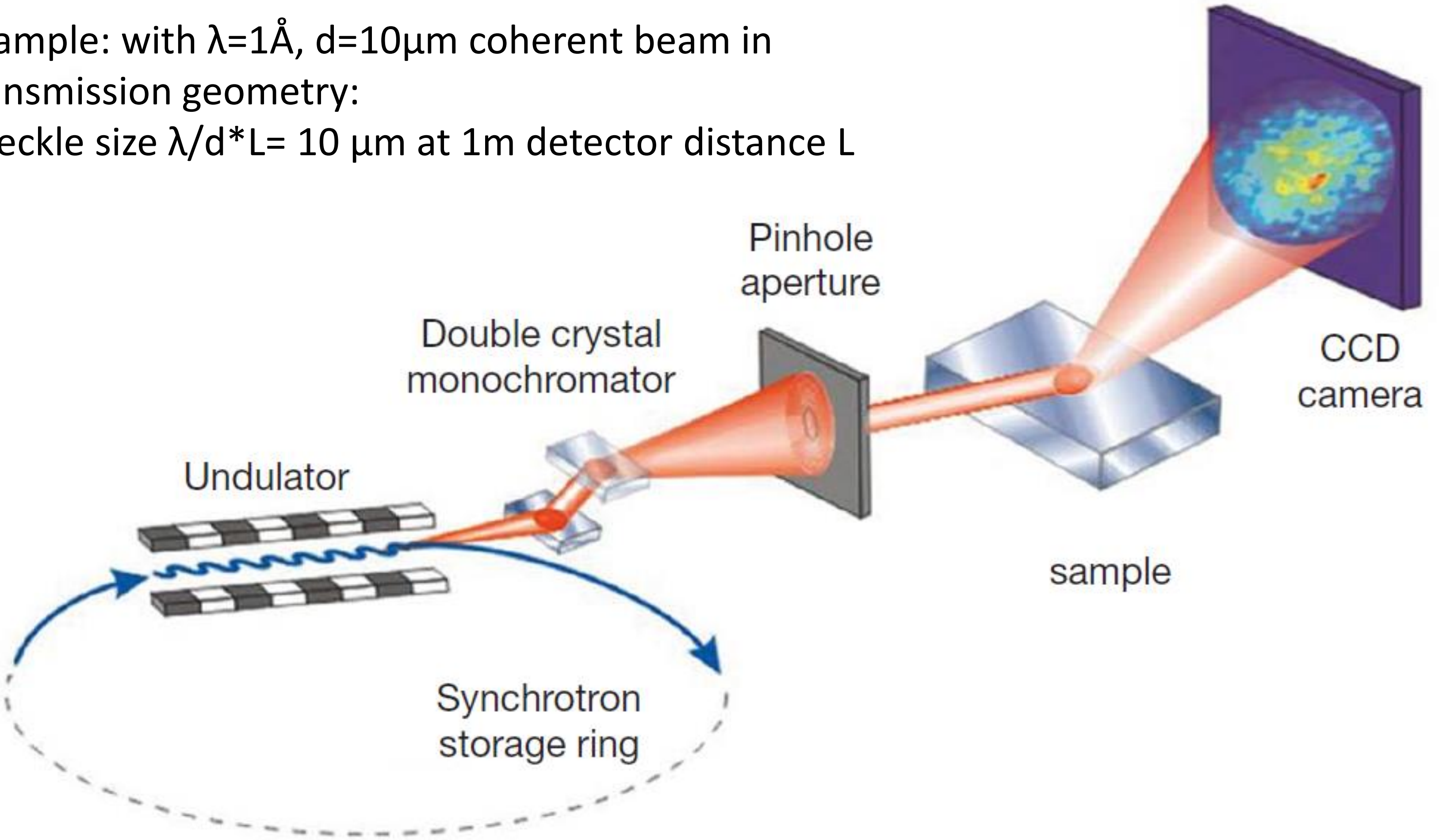
$n_c \approx 10^7$ for a typical optical laser
$n_c \approx 10^{-3}$ for a typical (old) ESRF undulator

Coherent X-rays



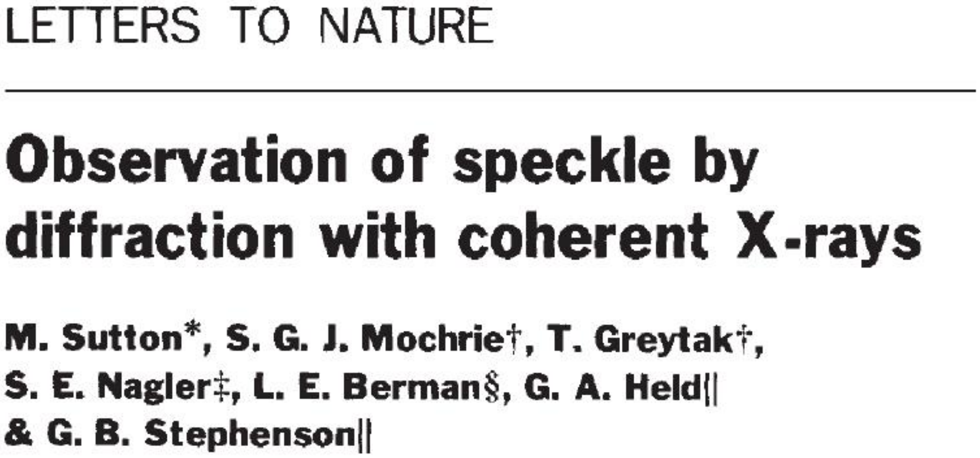
X-Ray Photon Correlation Spectroscopy

Example: with λ=1Å, d=10µm coherent beam in transmission geometry:
Speckle size λ/d*L= 10 µm at 1m detector distance L



O. Shpyrko et al, Nature 2007

Speckle pattern with X-rays



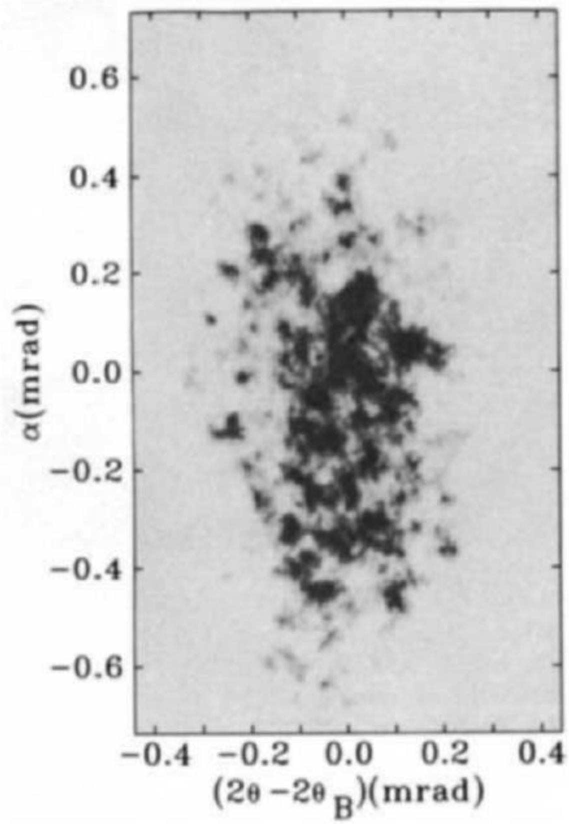
LETTERS TO NATURE

Observation of speckle by diffraction with coherent X-rays

M. Sutton[*], S. G. J. Mochrie[†], T. Greytak[†], S. E. Nagler[‡], L. E. Berman[§], G. A. Held[||] & G. B. Stephenson[||]

X-ray wiggler source
B=10^{15} photons s^{-1} $mrad^{-2}$ mm^{-2} per 0.1% bandwidth
Si(111) monochromator $\Delta\lambda/\lambda \approx 1.4\times10^{-4}$
5 μm pinhole 28 from the source ~3×10^{5} photons
Speckle size ~λ/L

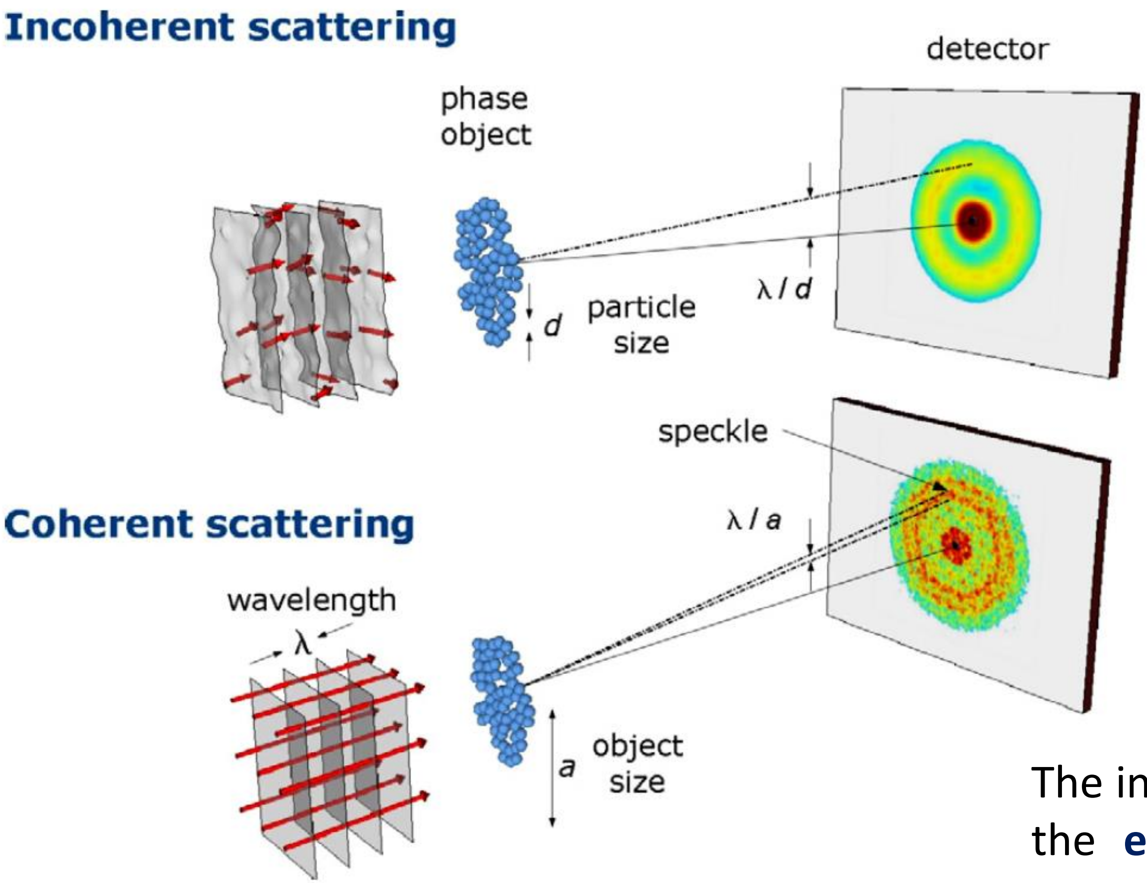
(001) Cu_3Au peak



M. Sutton et al. Nature 1991

How do we measure the dynamics?

X-Ray Photon Correlation Spectroscopy



Averaged quantities

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

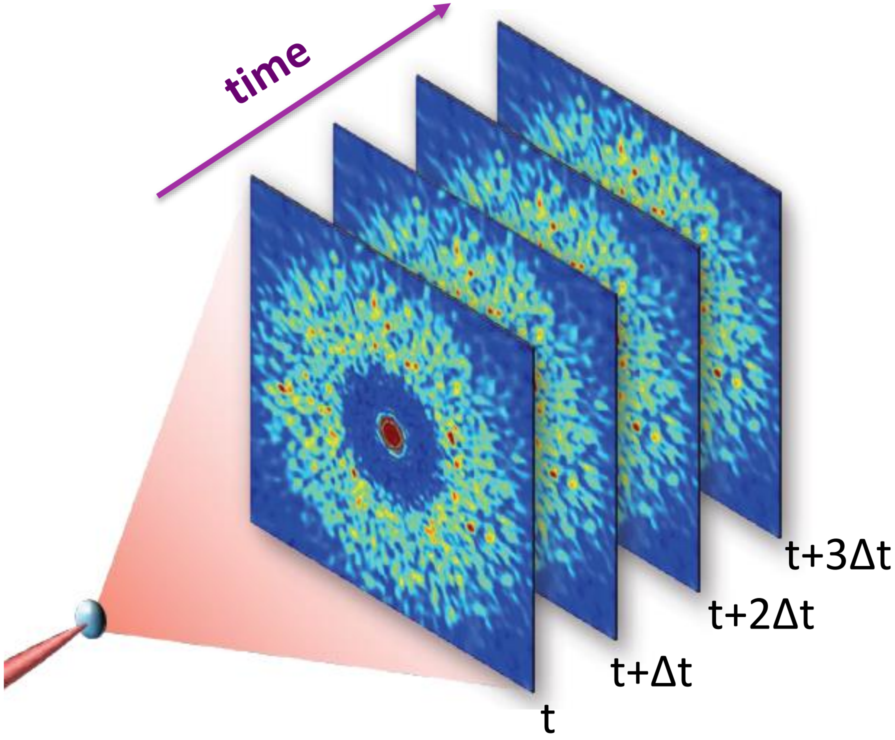
$$I(Q,t) \propto \left| \sum_n f_n(Q) \cdot e^{iQ\cdot r_n(t)} \right|^2$$

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

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



Siegert relation

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

experimental contrast

Intermediate scattering function

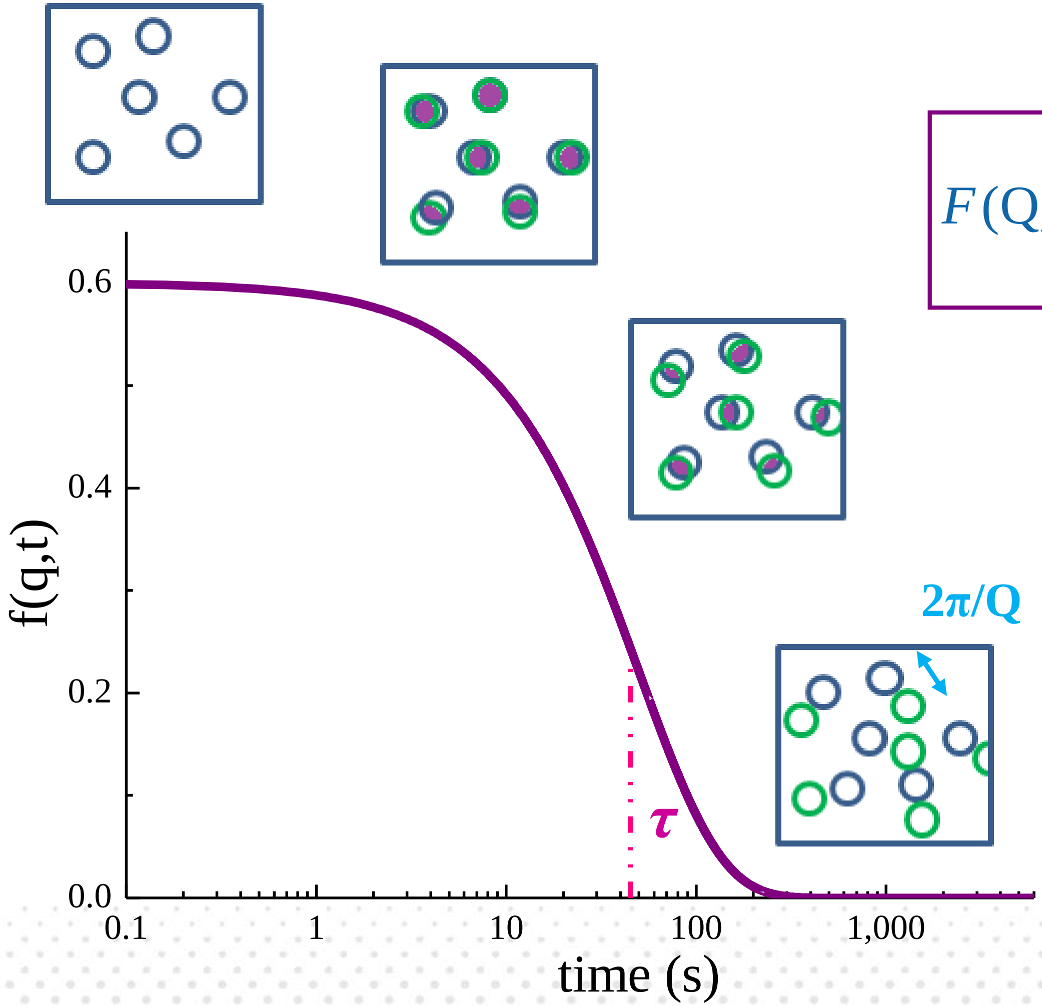
$$F(Q,t) = \frac{1}{S(Q)}\frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N}\langle exp\left[i\boldsymbol{Q}\left(\boldsymbol{r_i}(0) - \boldsymbol{r_j}(t)\right)\right]\rangle$$

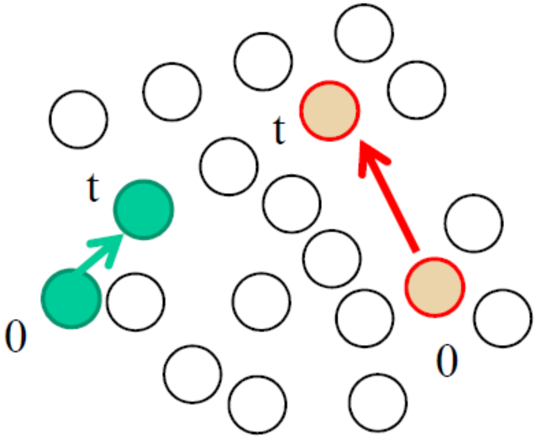
A. Madsen, A. Fluerasu and B. Ruta, XPCS, Springer, 2015

The intermediate scattering function

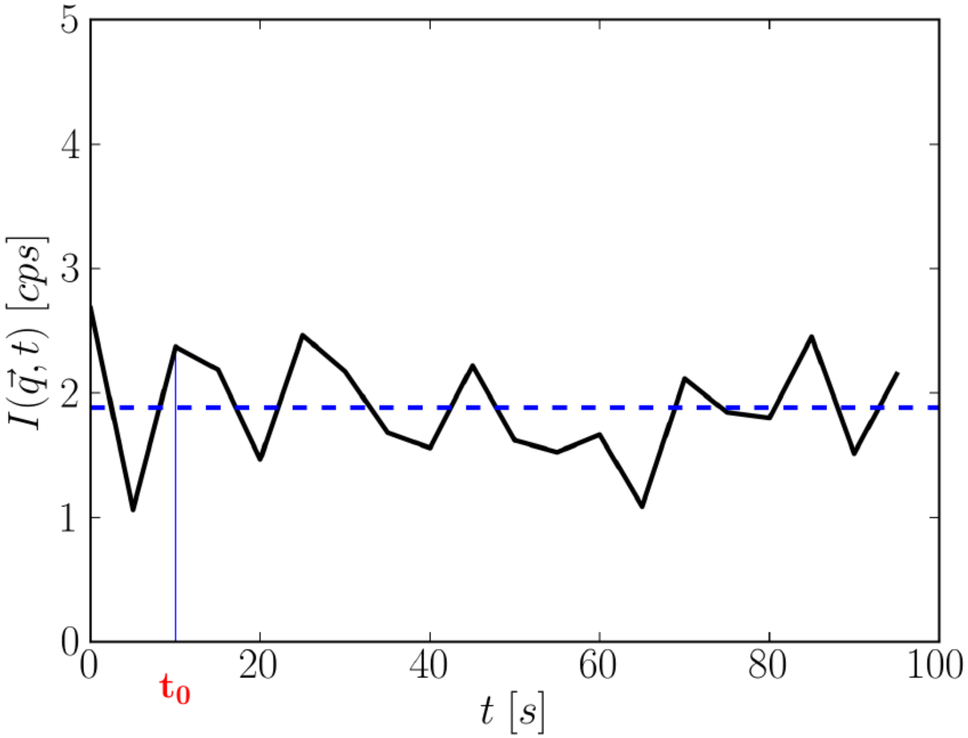
The intermediate scattering function monitors the decay of the **density fluctuations** on a scale 2π/Q

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



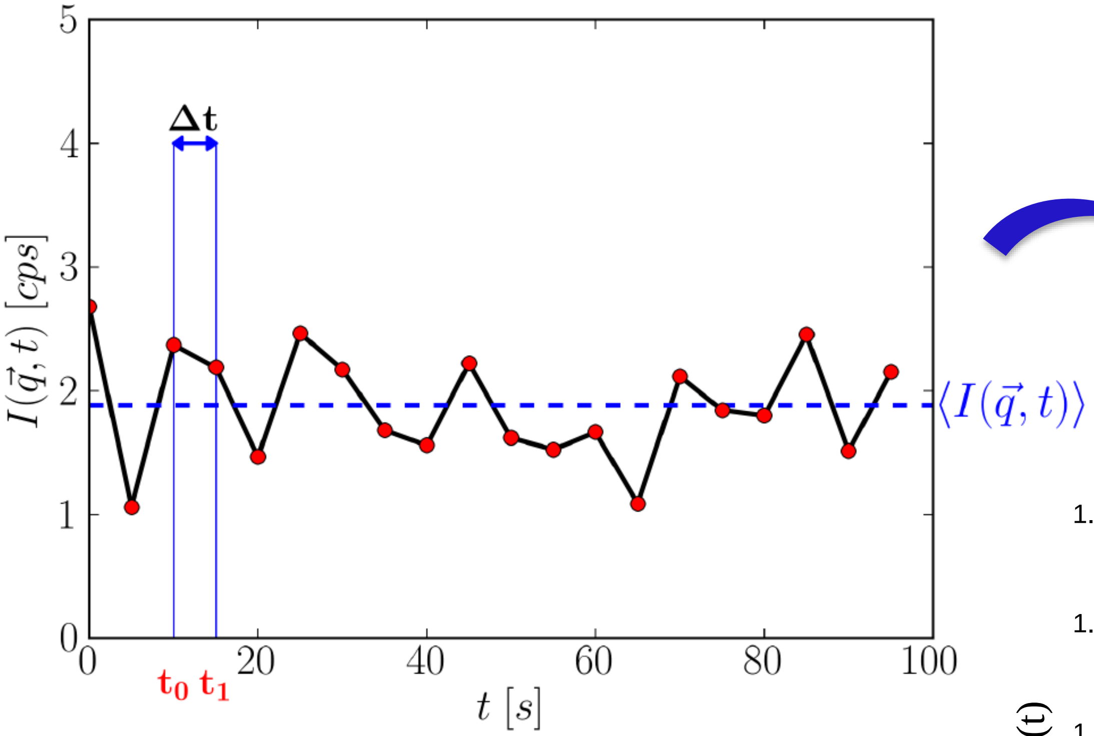


Intensity auto-correlation functions

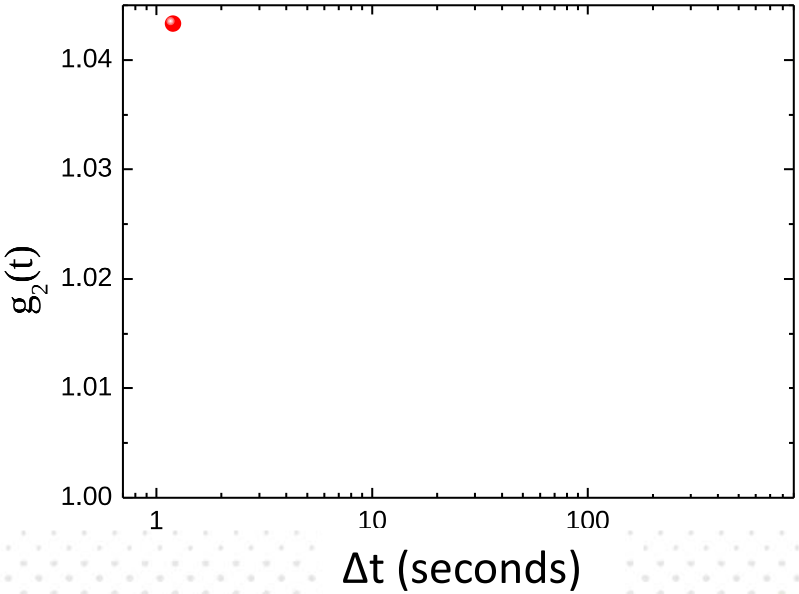


$$\frac{I(\vec{q},t_0)}{}$$

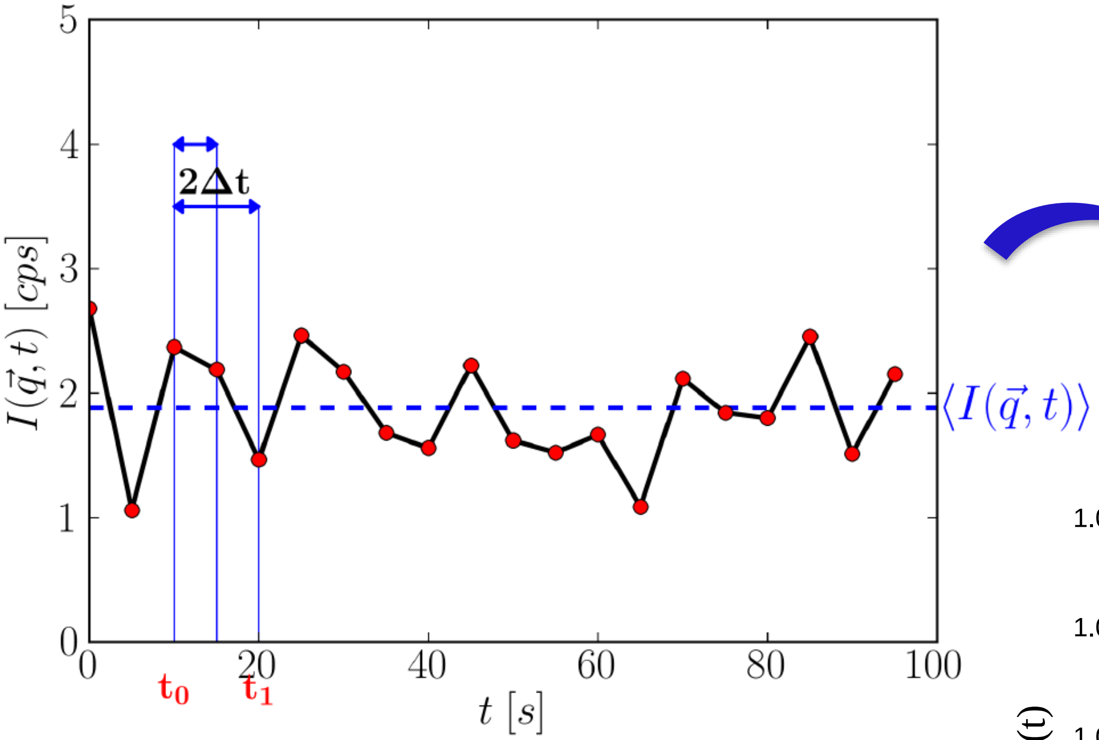
Intensity auto-correlation functions



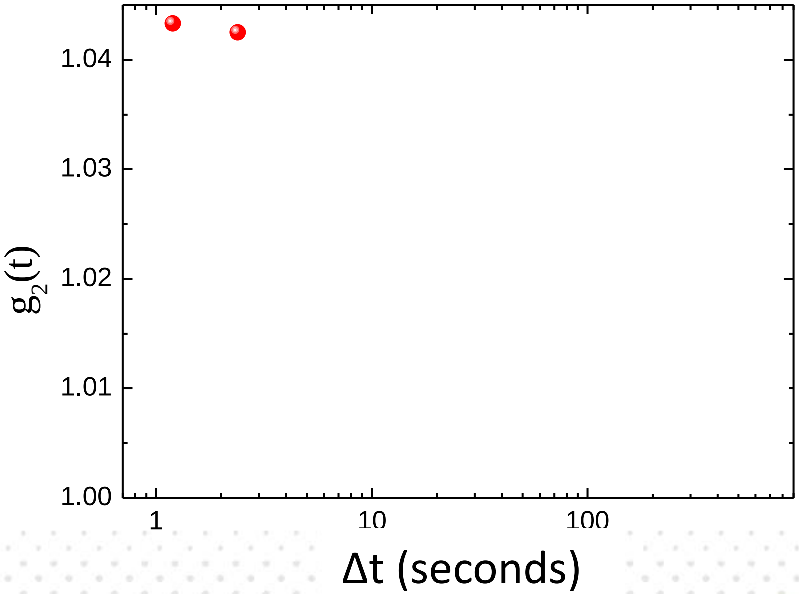
$$\frac{\langle I(\vec{q},t_0)\,I(\vec{q},t_0+\Delta t)\rangle}{\langle I(\vec{q},t)\rangle^2}$$



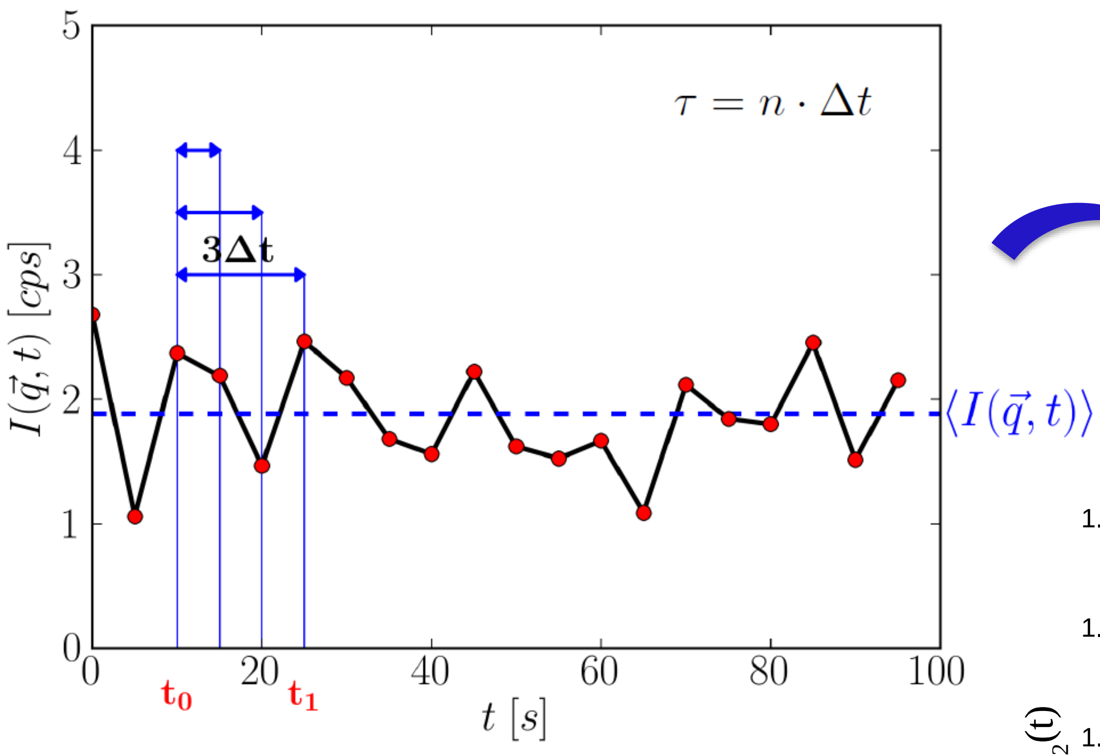
Intensity auto-correlation functions



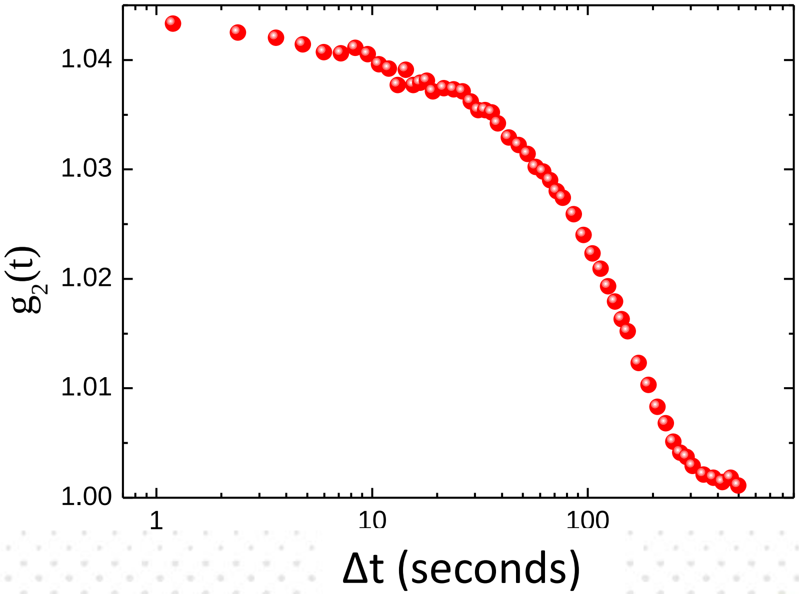
$$\frac{\langle I(\vec{q},t_0)I(\vec{q},t_0+2\Delta t)\rangle}{\langle I(\vec{q},t)\rangle^2}$$



Intensity auto-correlation functions



$$g_2(\vec{q},\tau) = \frac{\langle I(\vec{q},t_0) I(\vec{q},t_0+\tau) \rangle}{\langle I(\vec{q},t) \rangle^2}$$



Scientific activity with XPCS at ID10, ESRF

Energy range: 7,8,10 & 21 keV

Time resolution [2D det.]: ≈ ms - 10^4 s

Probed length scales: $8 \cdot 10^{-4}$ - 3 $Å^{-1}$

XPCS: (saxs, waxs, gi-xpcs)

- Supercooled liquids and glasses
- Soft materials (gels, colloids, …)
- Fluctuations at ordering phase transitions
- Driven dynamics by external fields T, E, B
- Interface dynamics in soft matter systems
- Atomic diffusion in alloys
- …

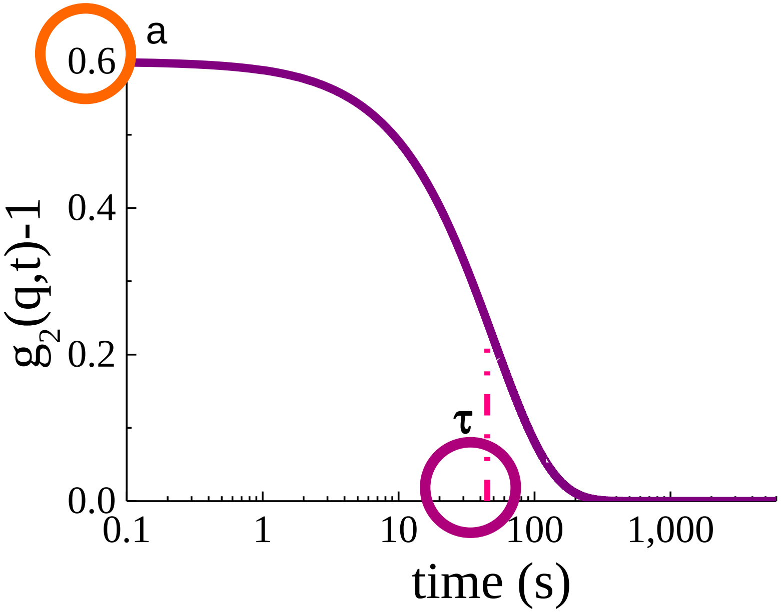
Y. Chushkin

F. Zontone

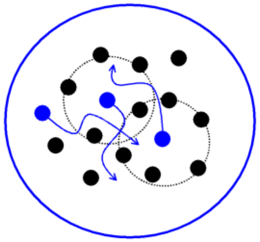
Interpretation of a correlation function

Kohlrausch-Williams-Watts (KWW) function

$$g_2(q,t) = 1 + a\exp\left(-2\left(\frac{t}{\tau}\right)^{\beta}\right)$$



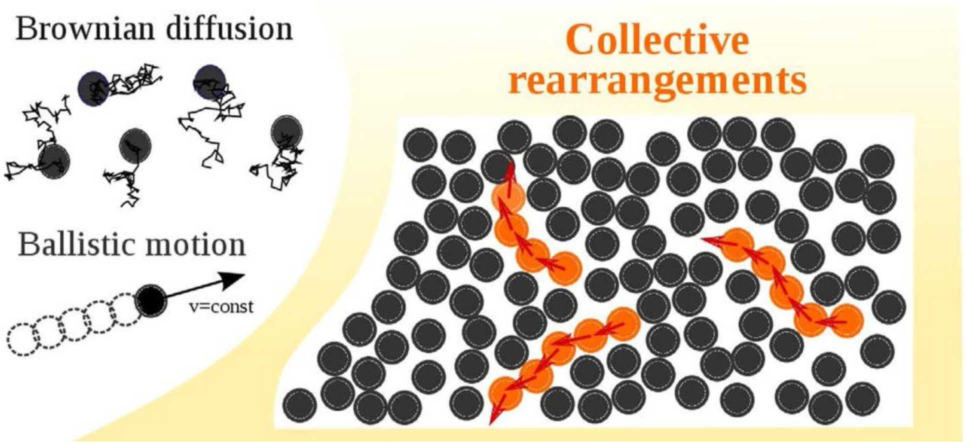
- ☐ $a(q,t)=A*f_q^2(t)$. Experimental contrast*nonergodicity parameter of glasses → info on secondary relaxation processes or elasticity in the material
- ☐ β(q,t) = shape parameter → info on the distribution of microscopic relaxation processes
- ☐ τ(q,t) = structural relaxation time → info on the mechanism of particle motion on a scale 2π/q

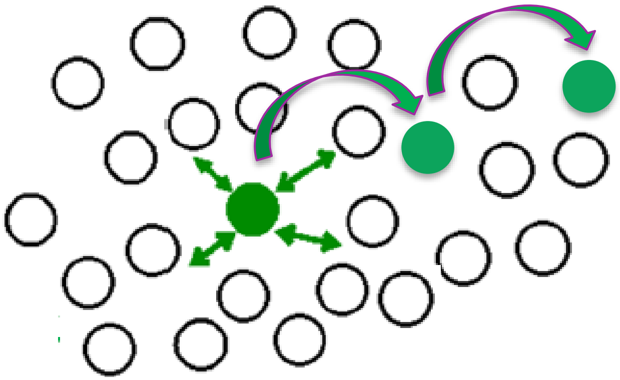


Interpretation of a correlation function

Depending on the value and dependence of the different parameters, it is possible to distinguish different particle motions

- ☐ $\beta=1$ and $\tau=1/Q^2$ Brownian motion
- ☐ $\beta<1$ and $\tau=1/Q$ Hopping of caged particles
- ☐ $\beta>1$ and $\tau=1/Q$ Super diffusion, ballistic like motion and stress relaxation





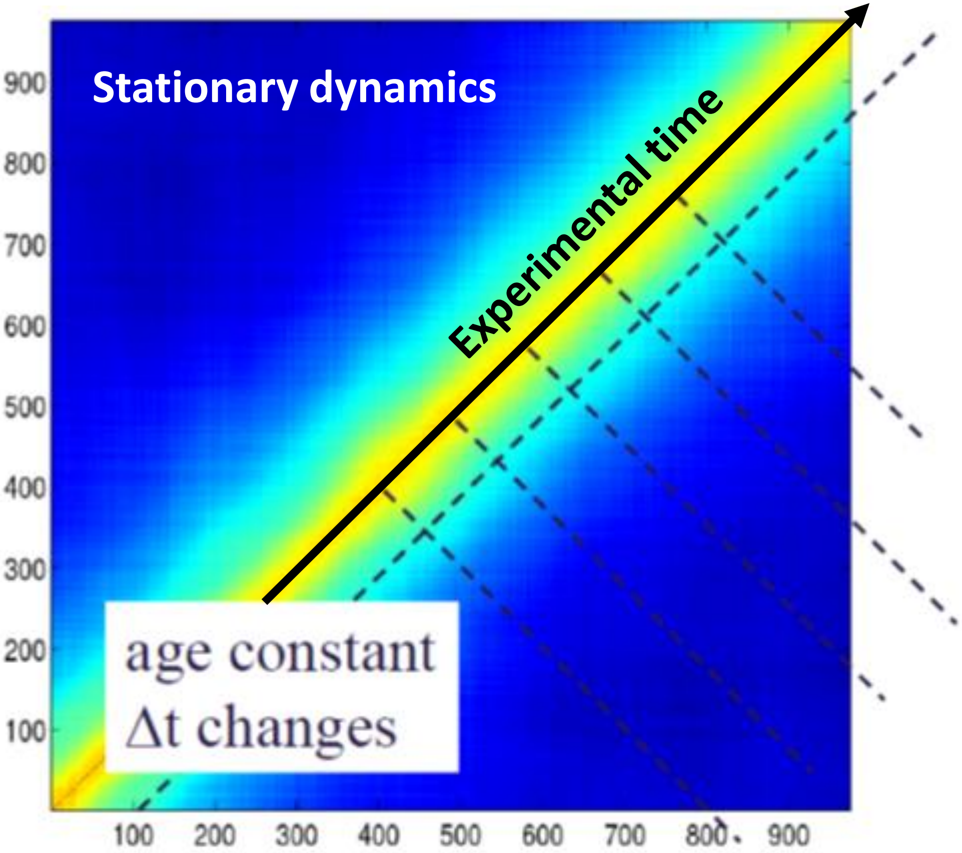
hopping of caged particles

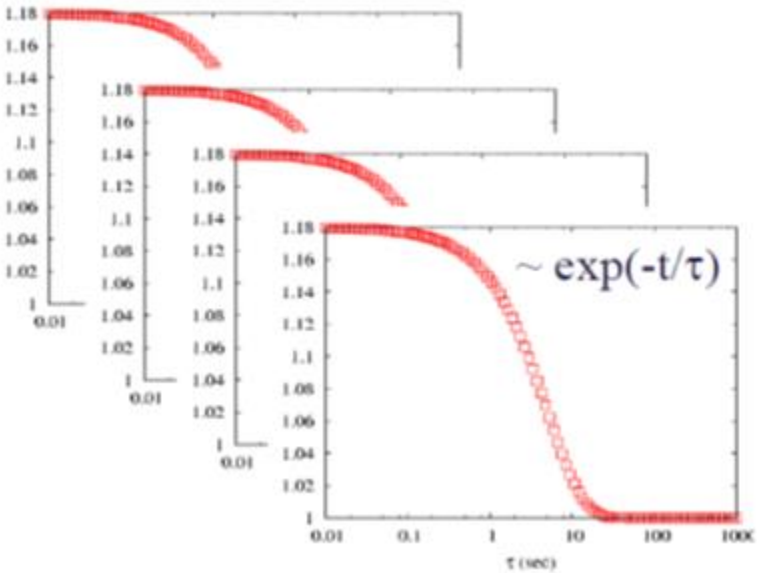
Two times correlation functions (TTCF)

Direct measurements of temporal evolution of the dynamics: time-resolved version of $g_2(q,t)$

$$G(Q,t_1,t_2)=\frac{\langle I(Q,t_1)I(Q,t_2)\rangle_P}{\langle I(Q,t_1)\rangle_P\langle I(Q,t_2)\rangle_P}$$

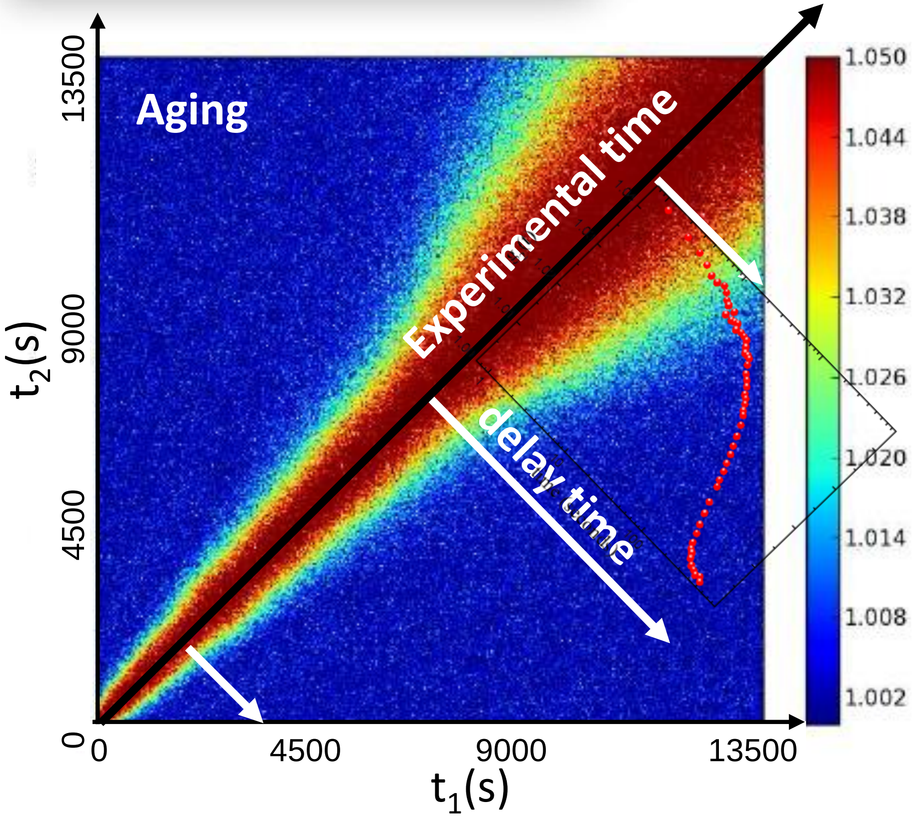
$$g_2(Q,t)=\langle G(Q,t_1,t)\rangle_{t_1}$$





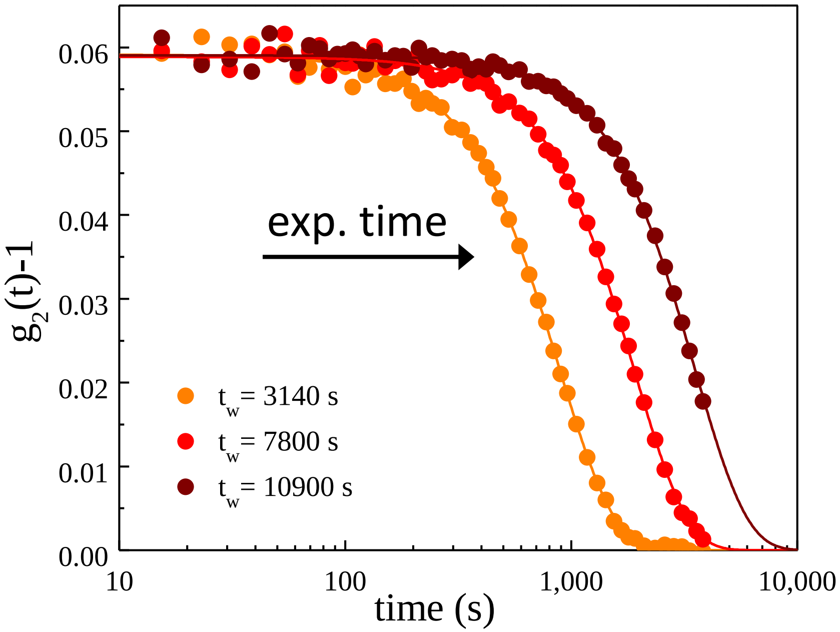
Courtesy of A. Madsen

Two times correlation functions (TTCF)



Broadening of two-time correlation function
→ slowing down of the dynamics

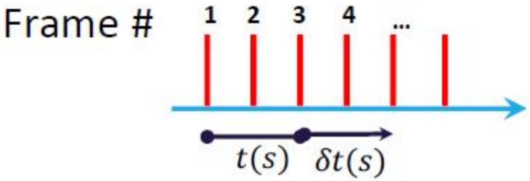
$$g_2(Q,t) = \left\langle G(Q,t_1,t) \right\rangle_{t_1}$$



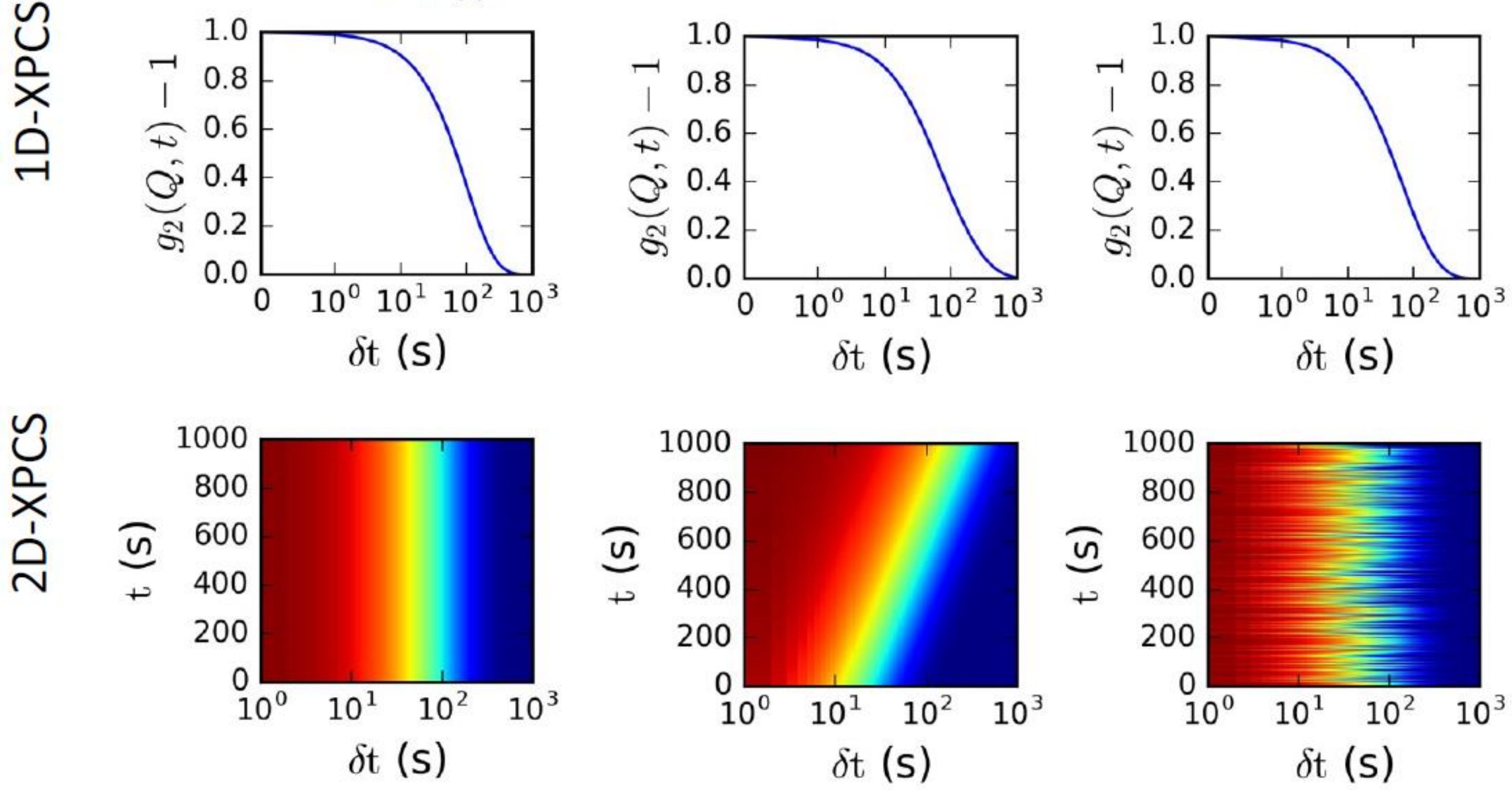
TTCF important also to check the reliability of the measurements

Two times correlation functions (TTCF)

TTCF are important also for the data interpretation

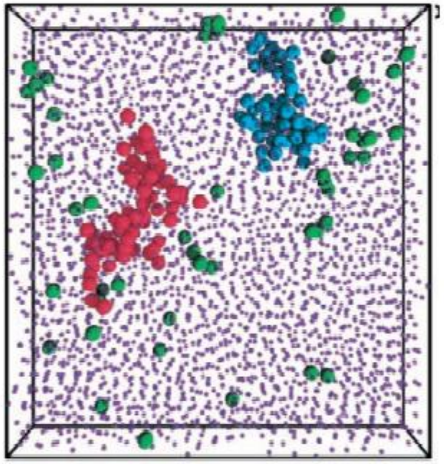


$$\boxed{g_2(Q,\delta t) = \frac{1}{N}\langle I(Q,t)\cdot I(Q,t+\delta t)\rangle}$$



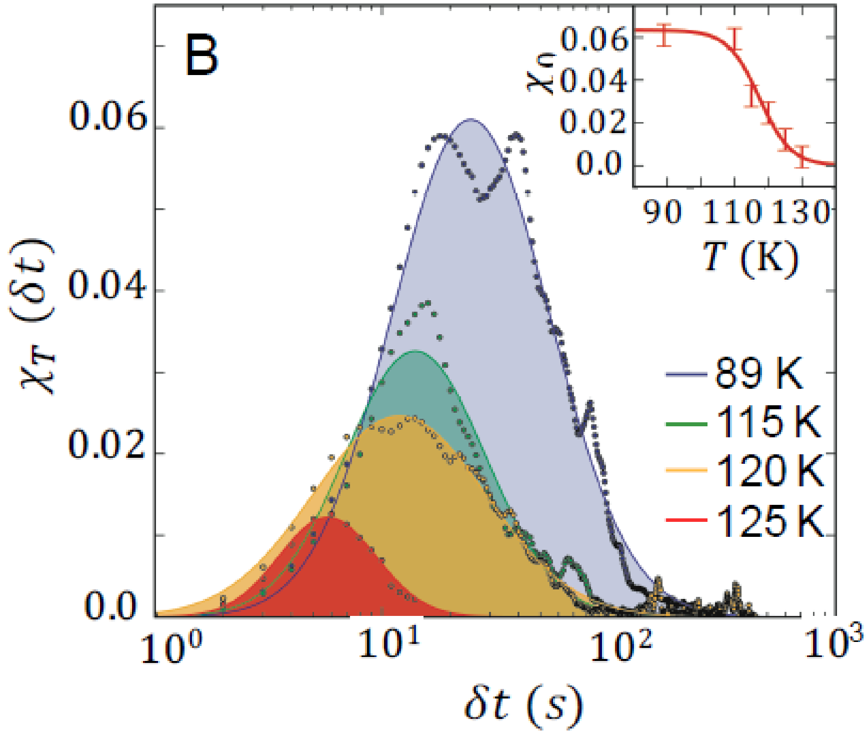
Courtesy of F. Perakis

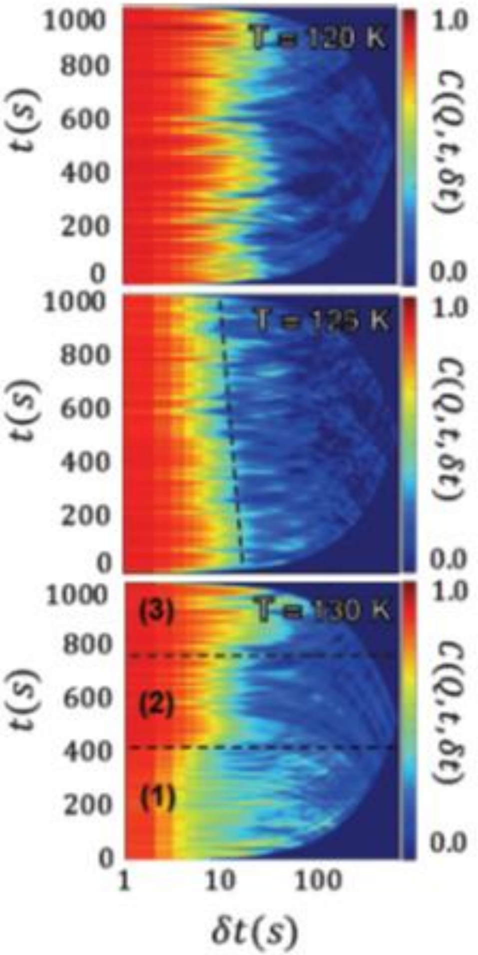
Dynamical heterogeneities



E. Weeks et al. Science 2000

normalized variance

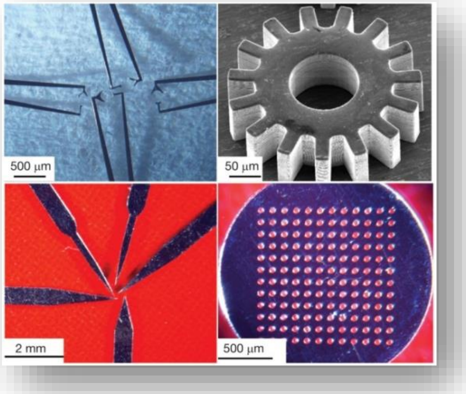




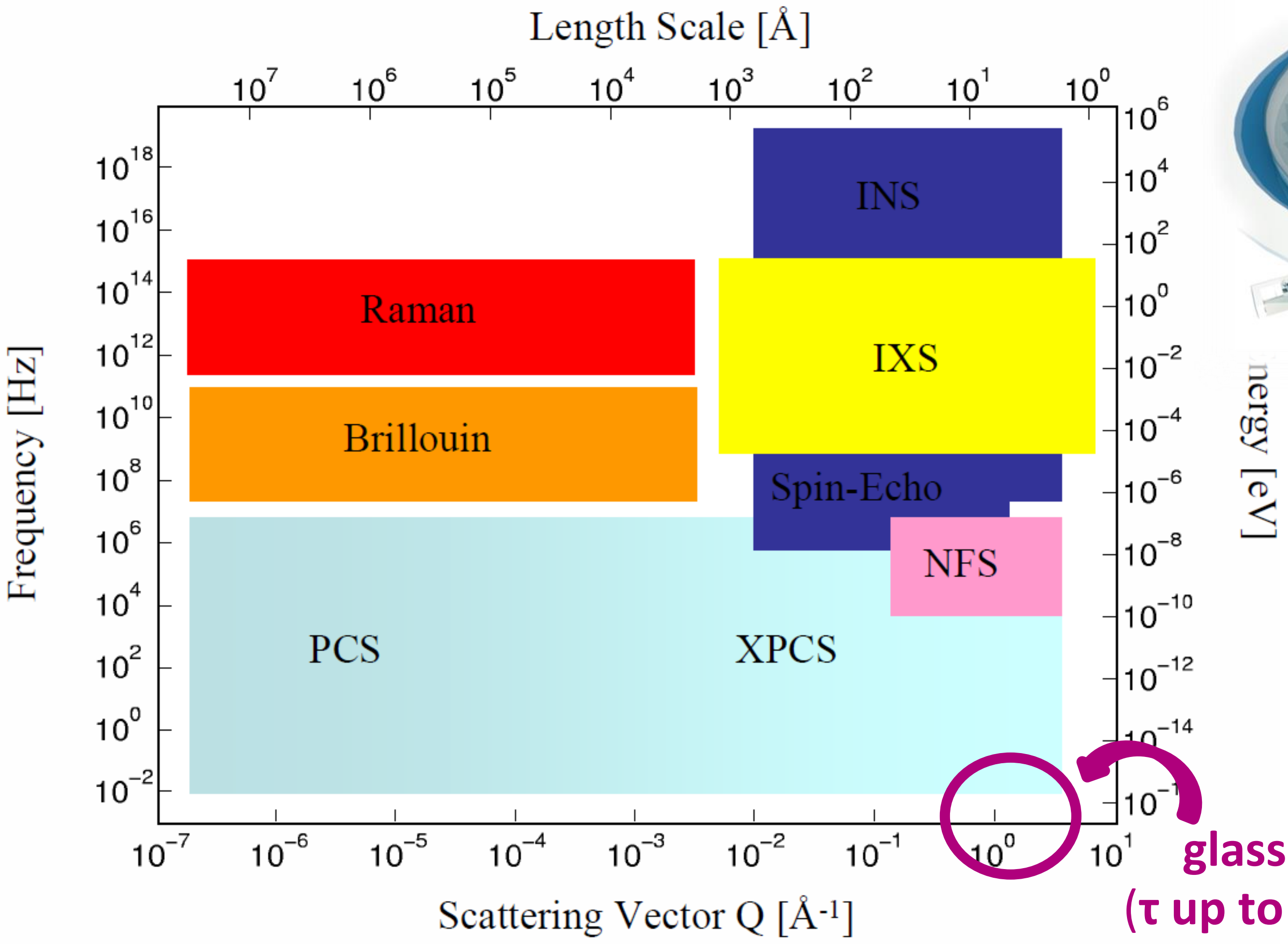
$$\chi_T(Q,\delta t) = \frac{1}{N}\left[\langle C^2(t,\delta t)\rangle_t - \langle C(t,\delta t)\rangle_t^{\ 2}\right]$$

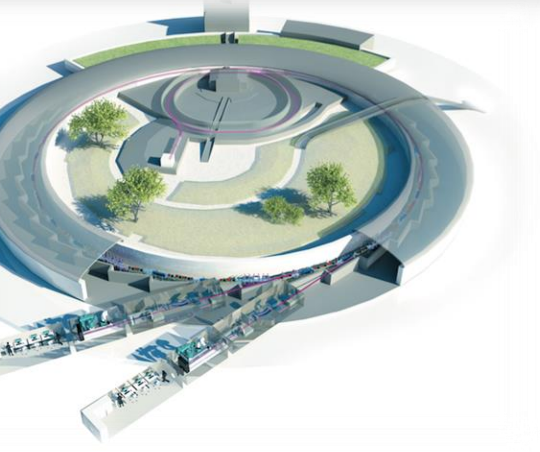
F. Perakis et al. PNAS 2017

XPCS on Glasses



XPCS in Glasses





glasses

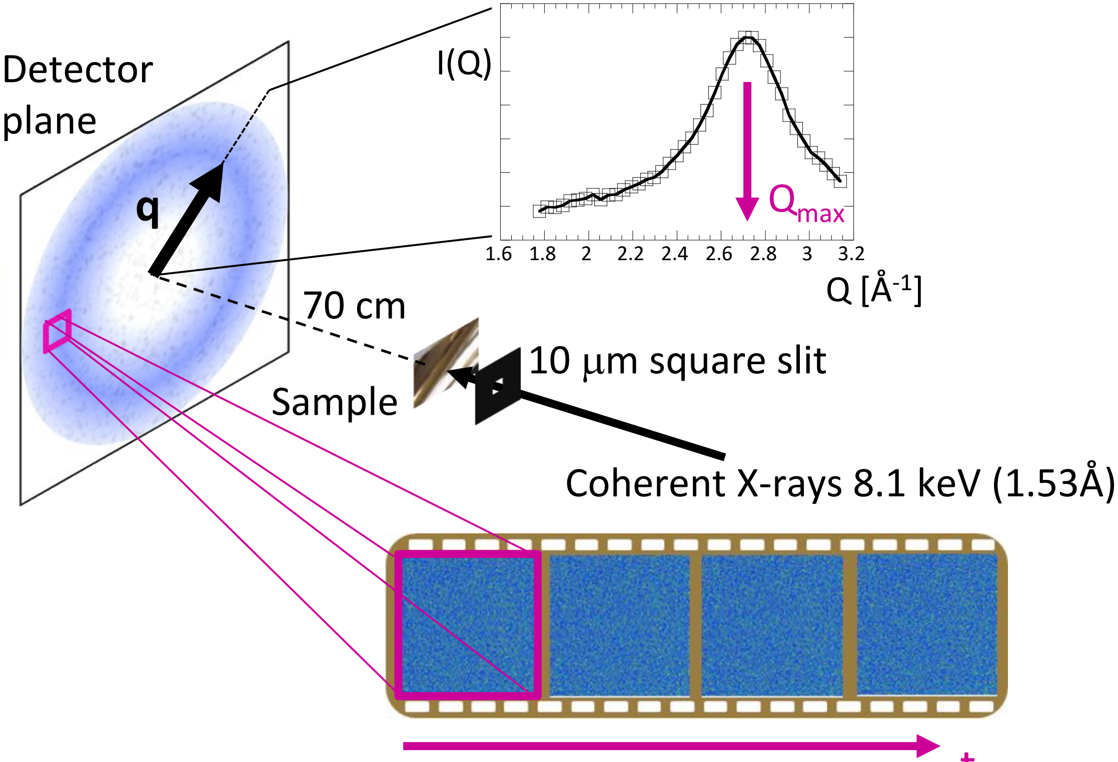
(τ up to 10^4 s, Q up to 4 Å^{-1})

XPCS in Glasses

WAXS geometry

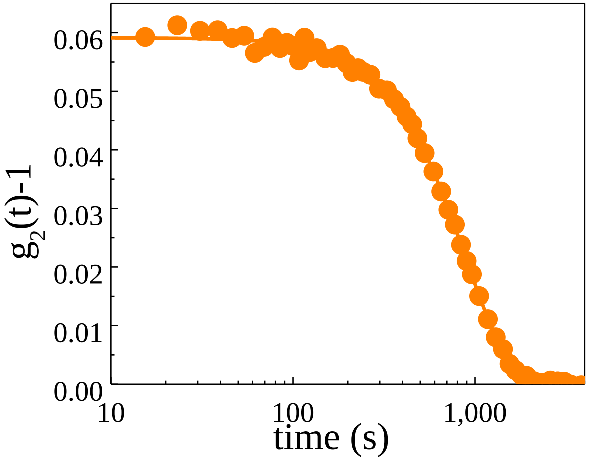
8 keV: peak at 20°- 45° deg.

ANDOR CCD



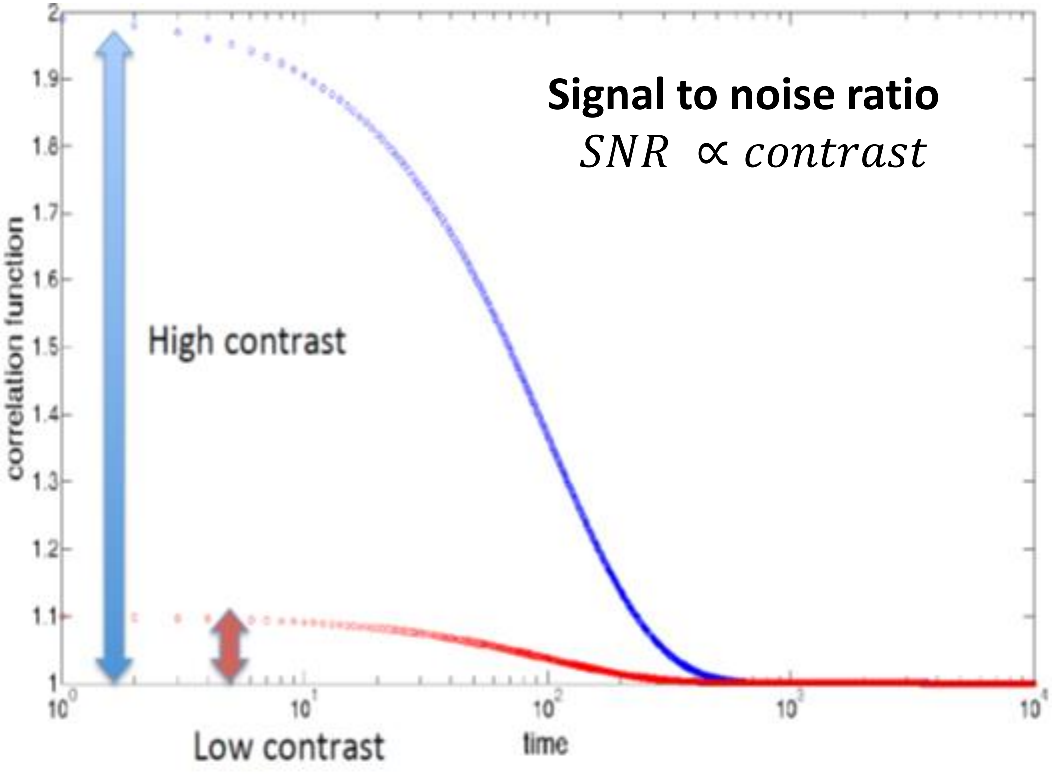
0.04 ph/pixel/frame

One q per measurement



XPCS in practise

The problem of the contrast

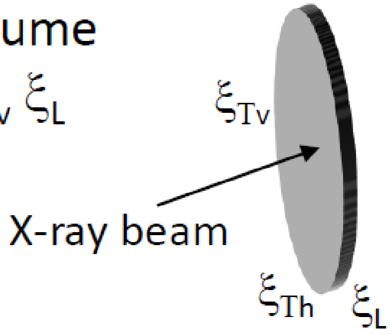


Signal to noise ratio

$$SNR \propto contrast$$

Coherence volume

$V_C = \pi/4\ \xi_{Th}\ \xi_{Tv}\ \xi_L$



Ideal condition : $V_S < V_c$

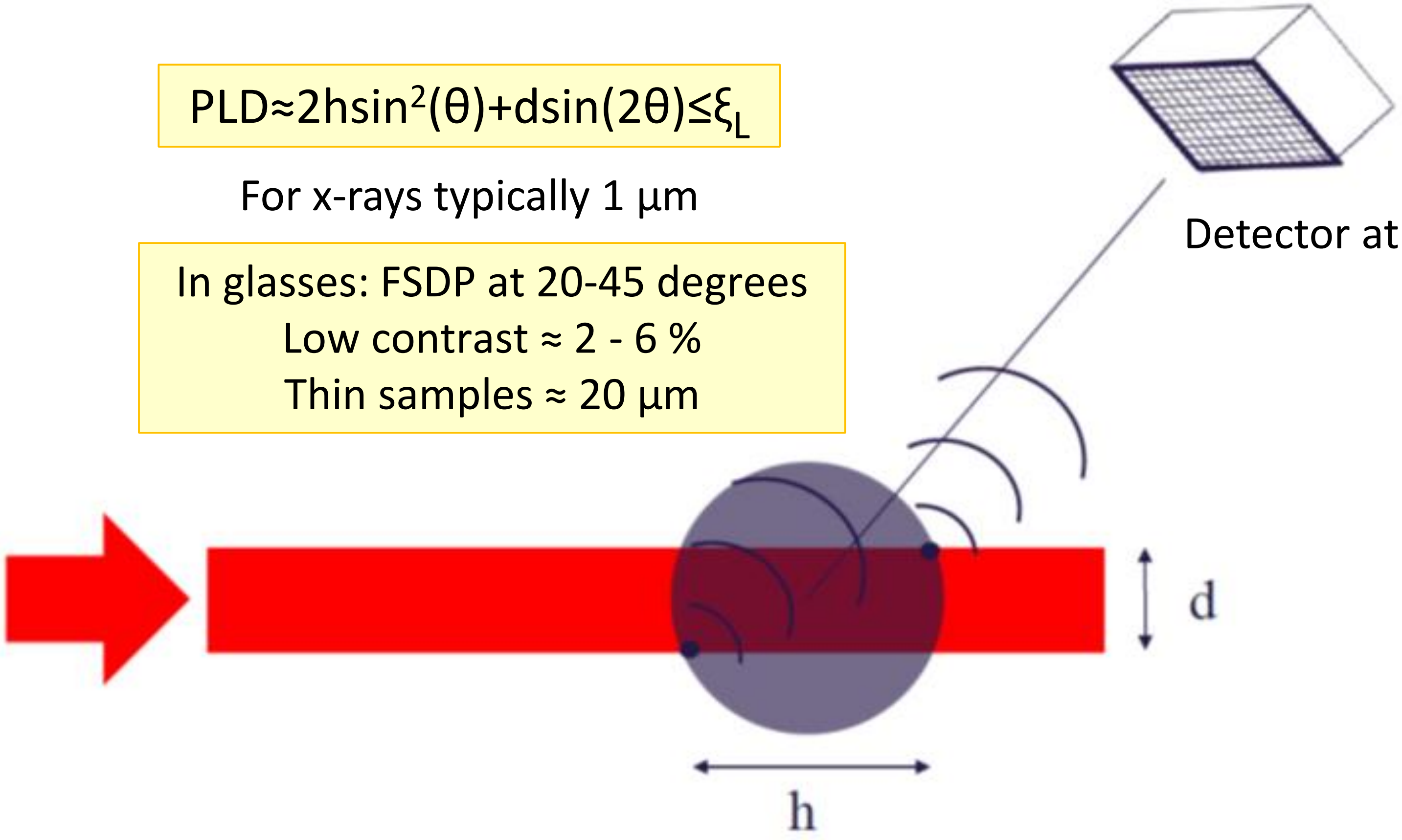
Contrast $A = V_c/V_s$

With X-rays contrast<1

Courtesy of C. Gutt

Path length difference and coherence

Contrast decreases at large angles due to increase in path length difference between scattered waves:



$\mathrm{PLD} \approx 2h\sin^2(\theta) + d\sin(2\theta) \leq \xi_L$

For x-rays typically 1 µm

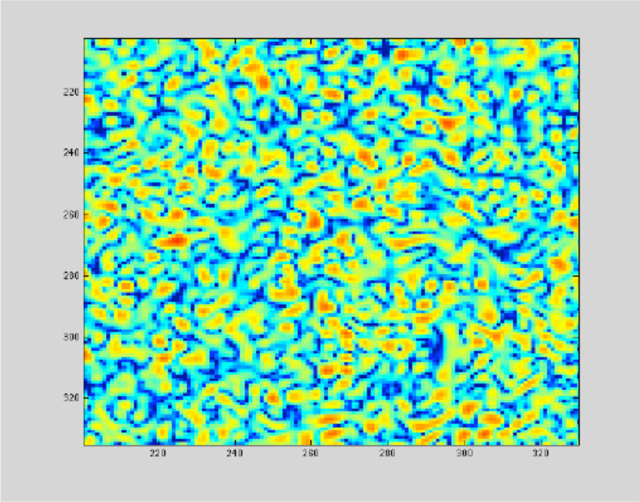
In glasses: FSDP at 20-45 degrees
Low contrast ≈ 2 - 6 %
Thin samples ≈ 20 µm

Courtesy of A. Madsen

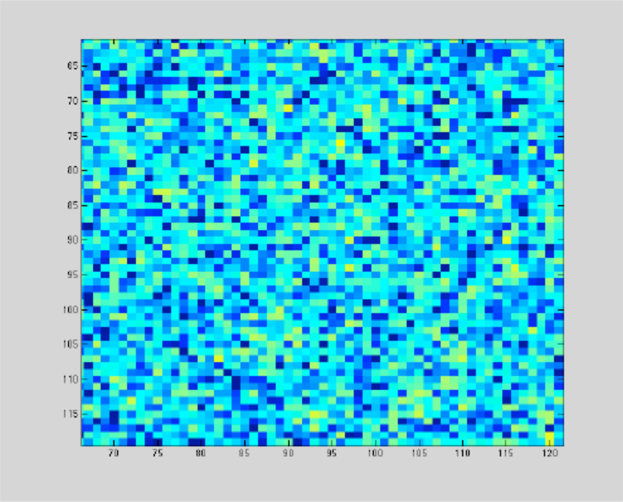
XPCS in practise

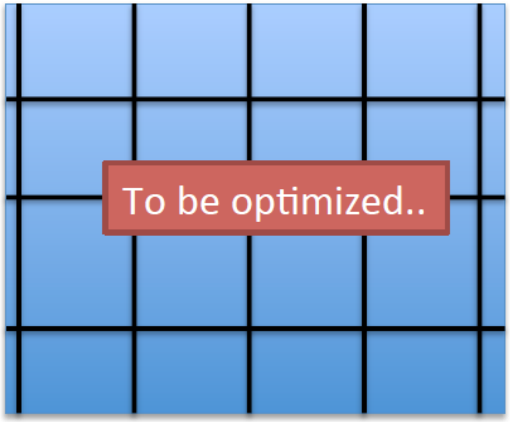
Contrast decreases if the speckles are not resolved

Large speckles



Small speckles





Courtesy of C. Gutt

XPCS in practise

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= exposure time per frame

N_p= number of pixel per detector

A= contrast

If the dynamics is stationary, SNR can be improved averaging different data sets

Other practical rules:

- ☐ Thickness of the sample (depends on absorption and contrast/q)
- ☐ Detector optimization (speckles and dynamics)
- ☐ Check sample-X-ray interaction
- ☐ Check always TTCF

Outline

☐ Coherent X-rays and X-ray Photon Correlation Spectroscopy

☐ Glassy systems

  ☐ Atomic motion in metallic glass formers

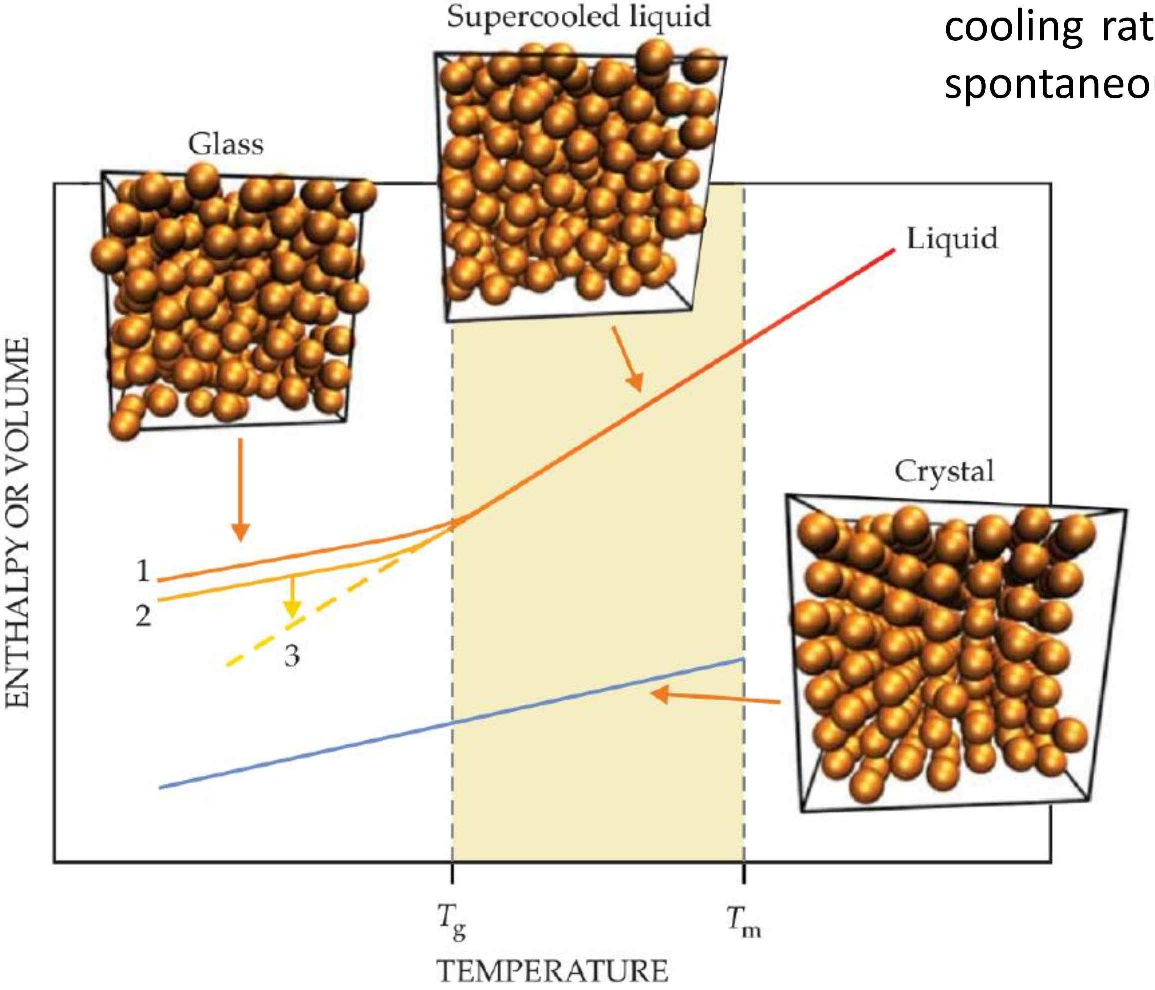
  ☐ Dynamics in oxide and silicates glasses

☐ The EBS-ESRF upgrade

☐ New scientific opportunities

The glass transition: a dynamical process

The final structure depends on the cooling rate (Glass 1 & 2) and evolves spontaneously with time (Glass 3)

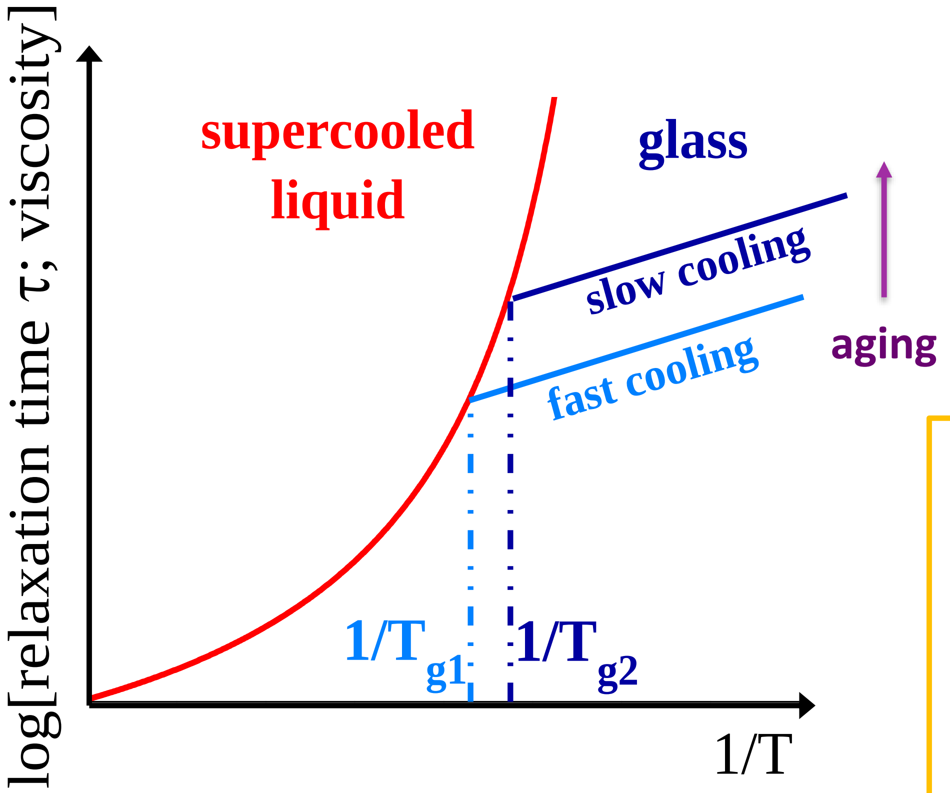


L. Berthier & M. Ediger, Phys. Today 2016

The glass transition: a dynamical process

A liquid that has lost its ability to flow, being trapped in a metastable state

C. A. Angell, Science, 1995



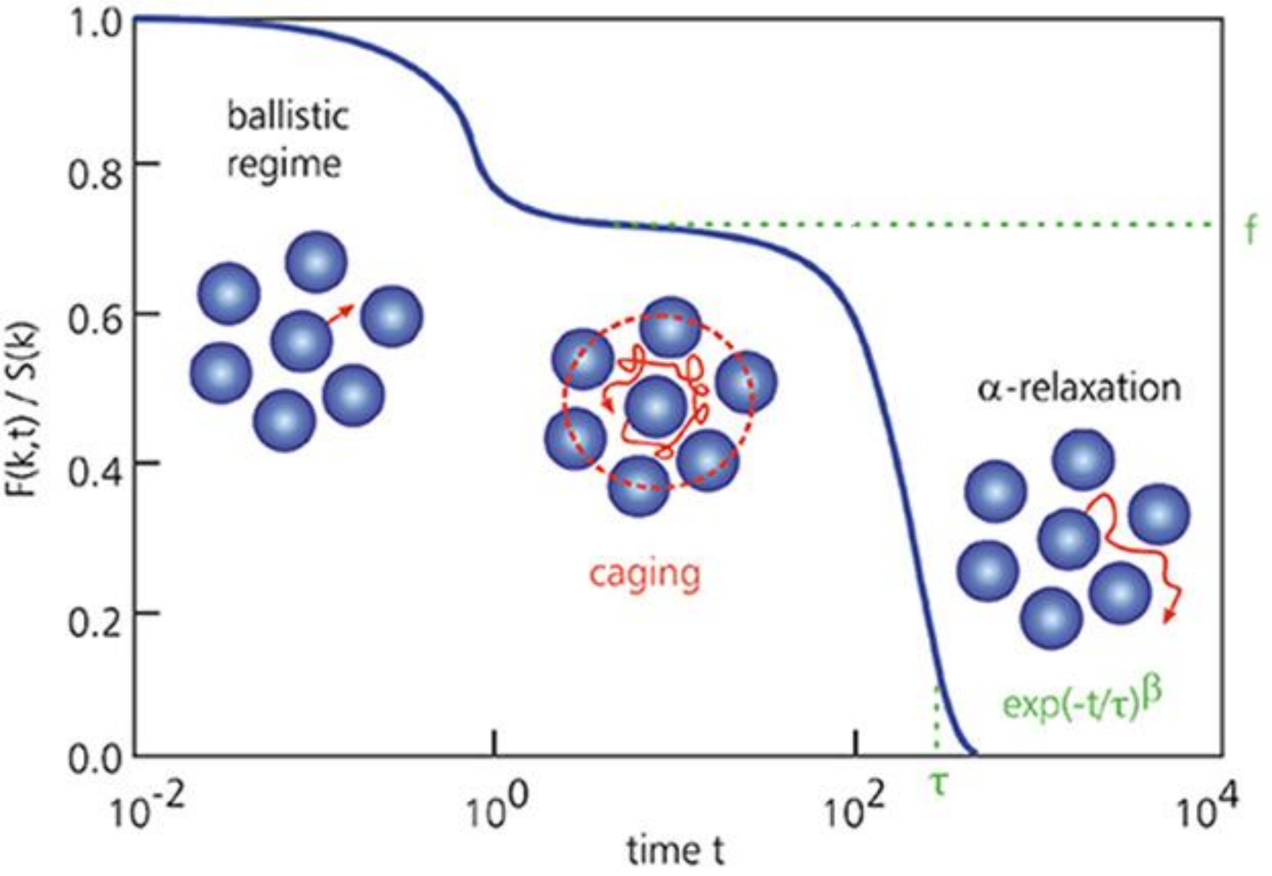
Out-of-equilibrium state → aging

☐ Temporal evolution: Every observable evolves with time

☐ Memory effects: strong dependence on the sample preparation and history

F(q,t) in supercooled liquids

The slow down of the dynamics toward the glassy state corresponds to a continuous shift of the decay time toward longer time scales and the emerging of different relaxation processes.

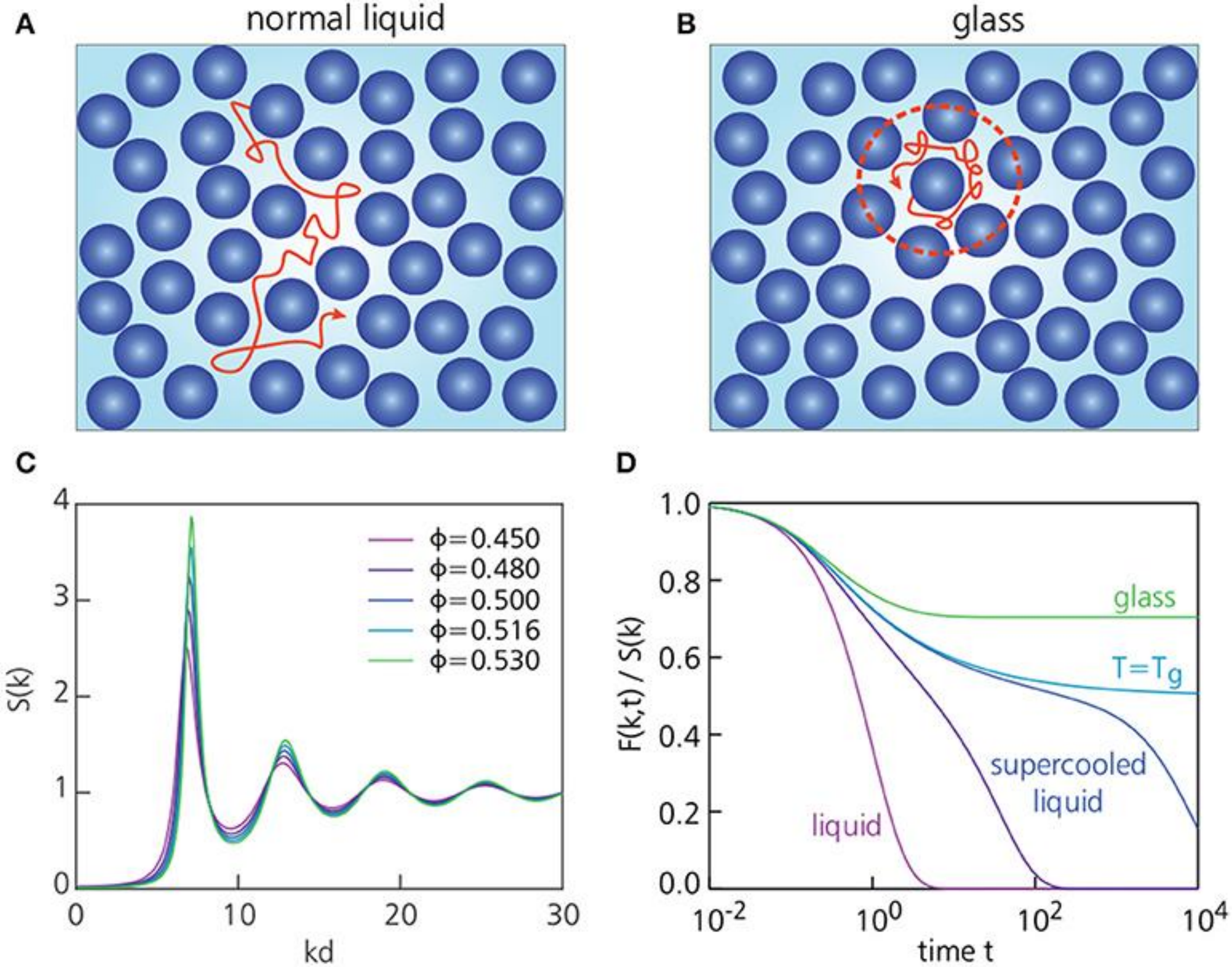


L.M.C. Janssen Front. Phys. 2018

F(q,t) in glasses

The intermediate scattering function of a glass should not decorrelate

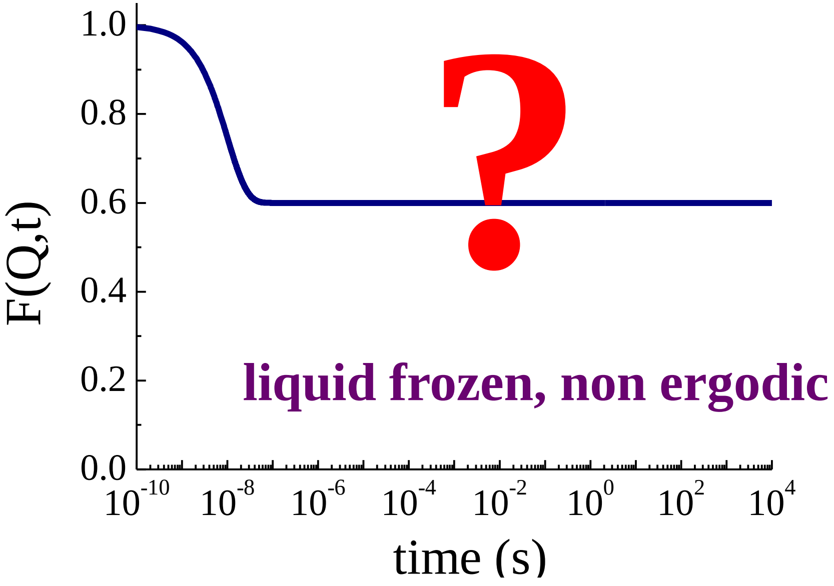
Liquid:
$t_{exp} \gg \tau$



Glass:
$t_{exp} \gg \tau$

L.M.C. Janssen Front. Phys. 2018

F(q,t) in glasses

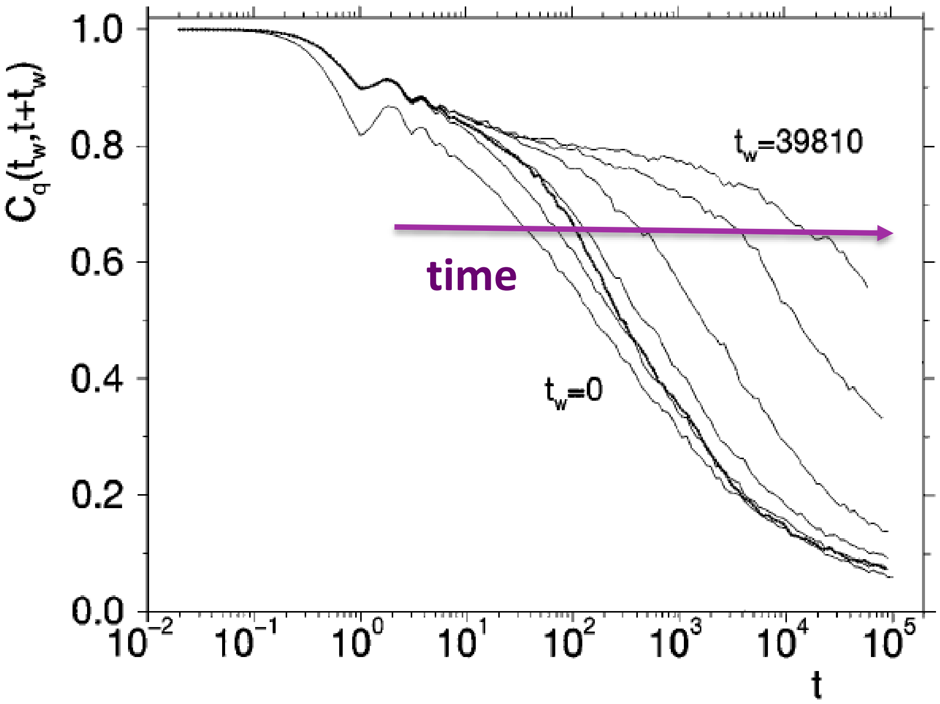


Glassy state ($T<T_g$):

No information due to limitation in experiments

MD simulations in a Lennard-Jones glass

A the microscopic scale there are structural rearrangements that evolve with time



W. Kob and J-L. Barrat Phys. Rev. Lett. 1997

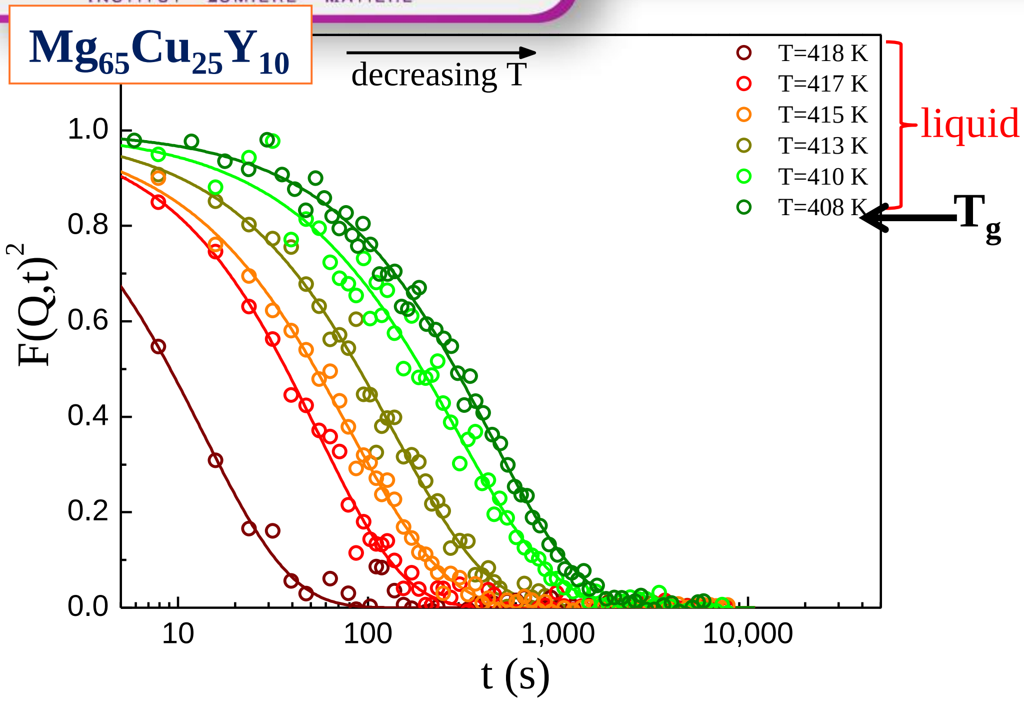
Outline

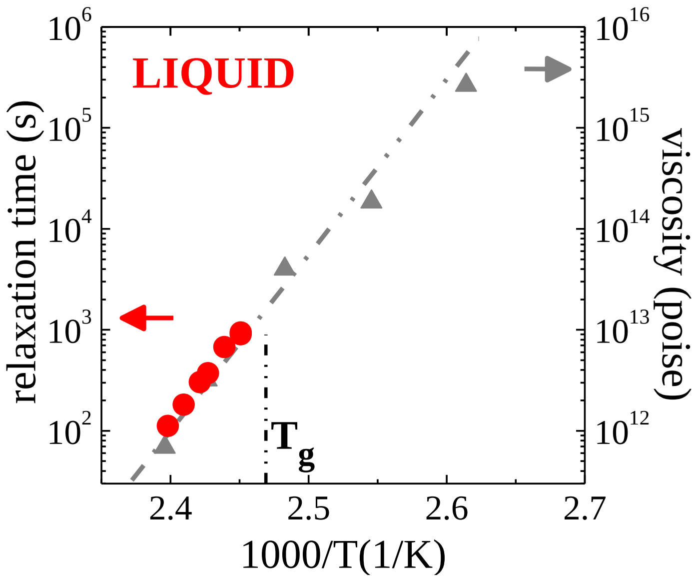
- ☐ Coherent X-rays and X-ray Photon Correlation Spectroscopy
- ☐ Glassy systems
  - ☐ Atomic motion in metallic glass formers
  - ☐ Dynamics in oxide and silicates glasses
- ☐ The EBS-ESRF upgrade
- ☐ New scientific opportunities

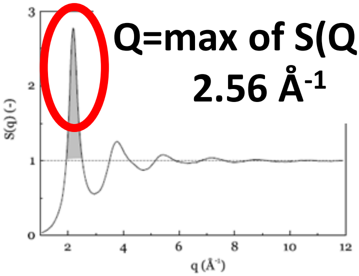
Anomalous dynamics in metallic glasses:
1. The dynamical crossover

The dynamical crossover

XPCS measurements (ID10 - ESRF)







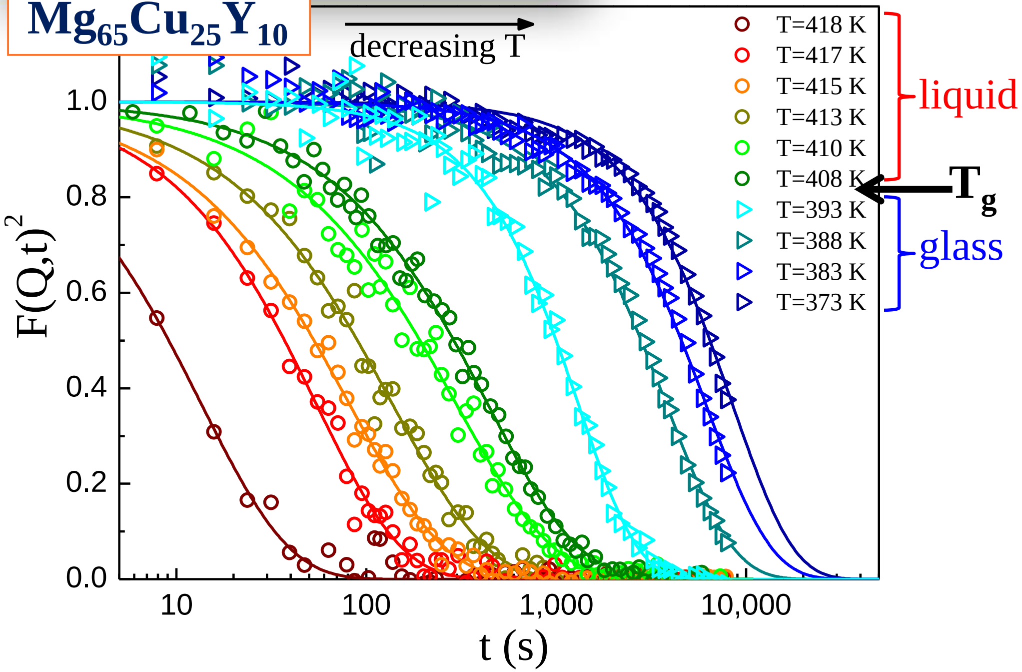
Q=max of S(Q)
2.56 Å^{-1}

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

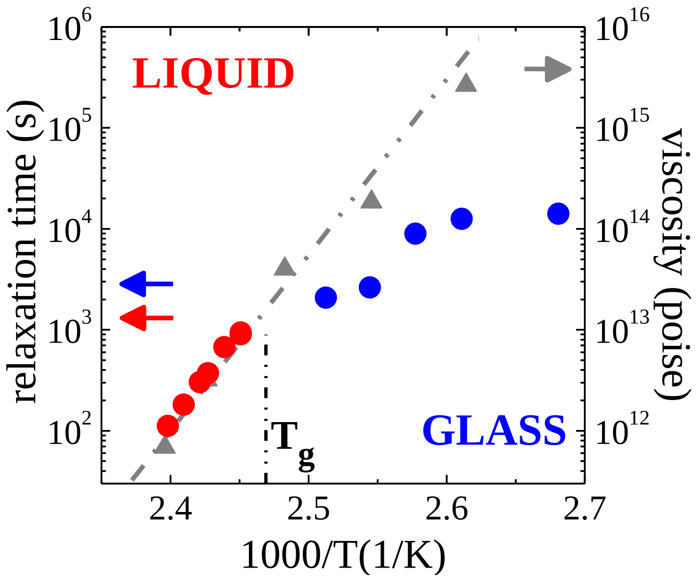
Ruta *et al.* Phys. Rev. Lett. 2012
Ruta *et al.* Topical Review J. Phys. Cond. Matt. 2017

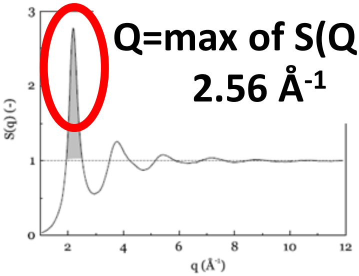
The dynamical crossover

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



XPCS measurements (ID10 - ESRF)





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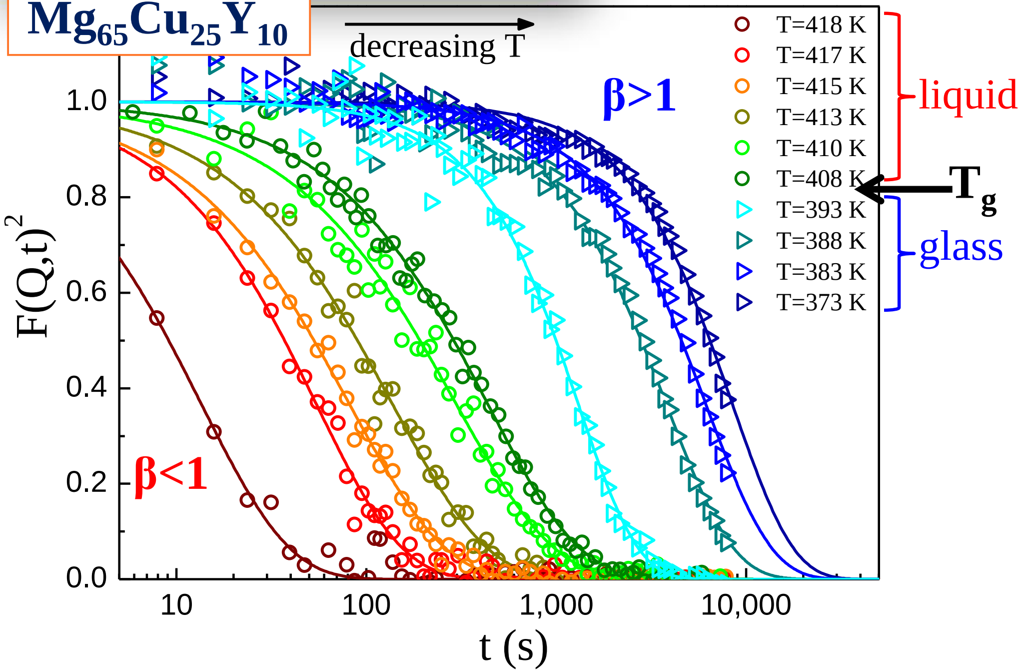
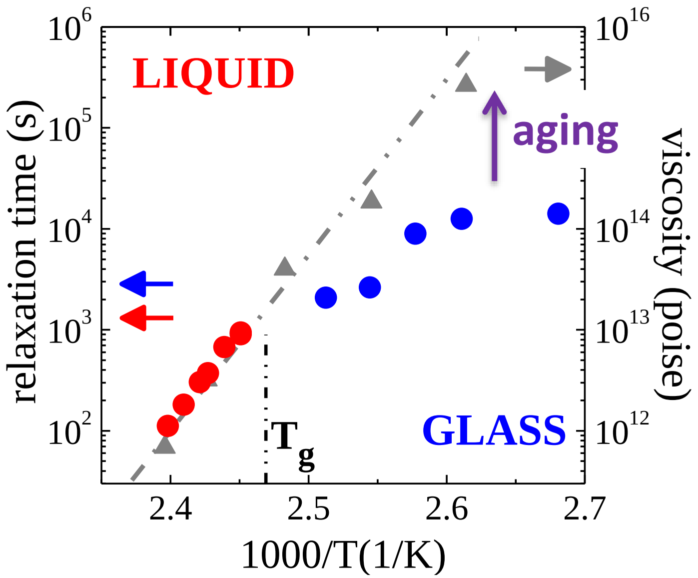
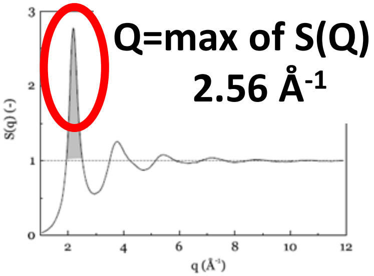


XPCS measurements (ID10 - ESRF)





Q=max of S(Q)

2.56 Å^{-1}

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

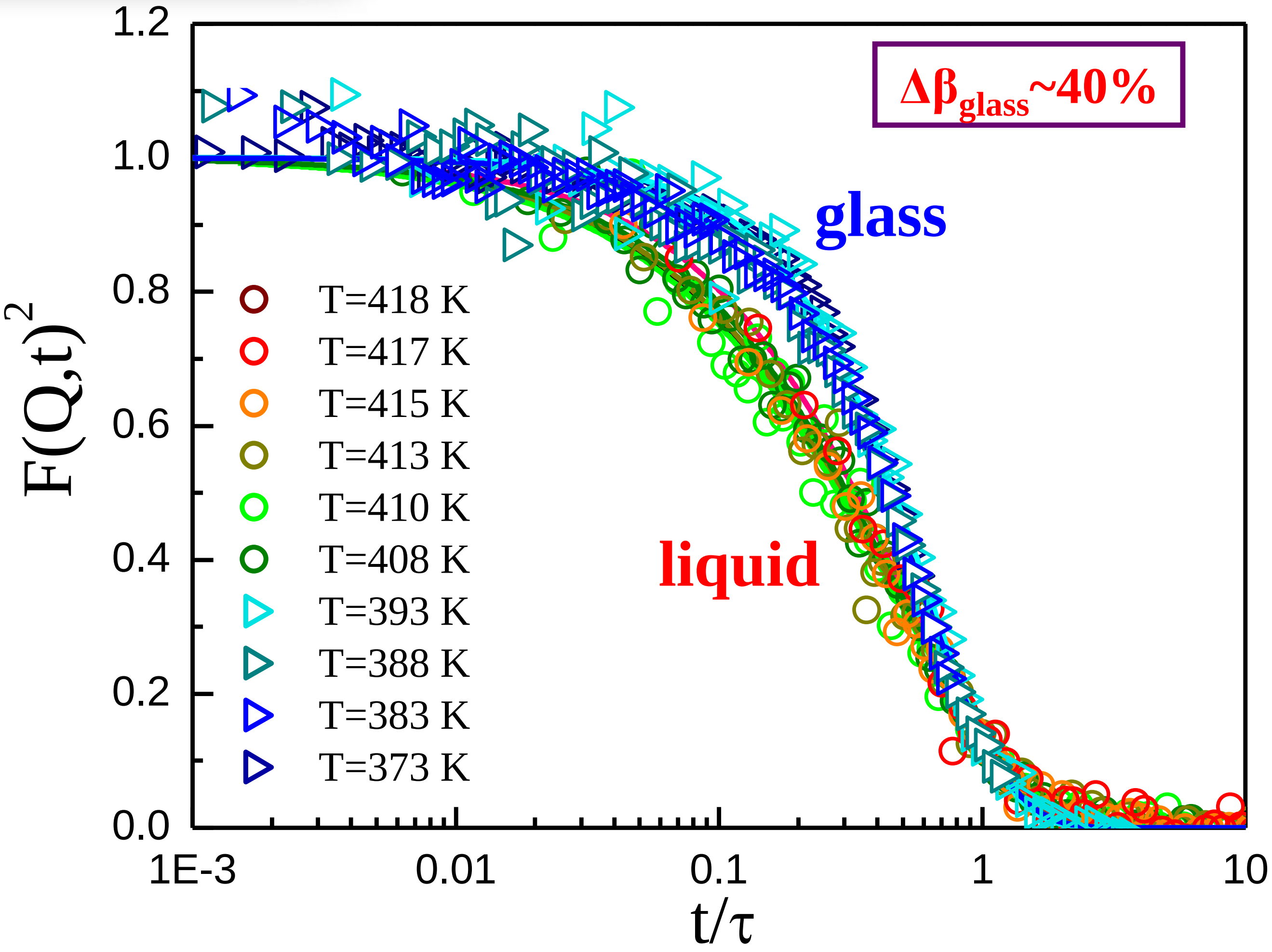
$T>T_g$: stationary dynamics, β<1, diffusive motion

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

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

Ruta *et al.* Topical Review J. Phys. Cond. Matt. 2017

The dynamical crossover at T_g



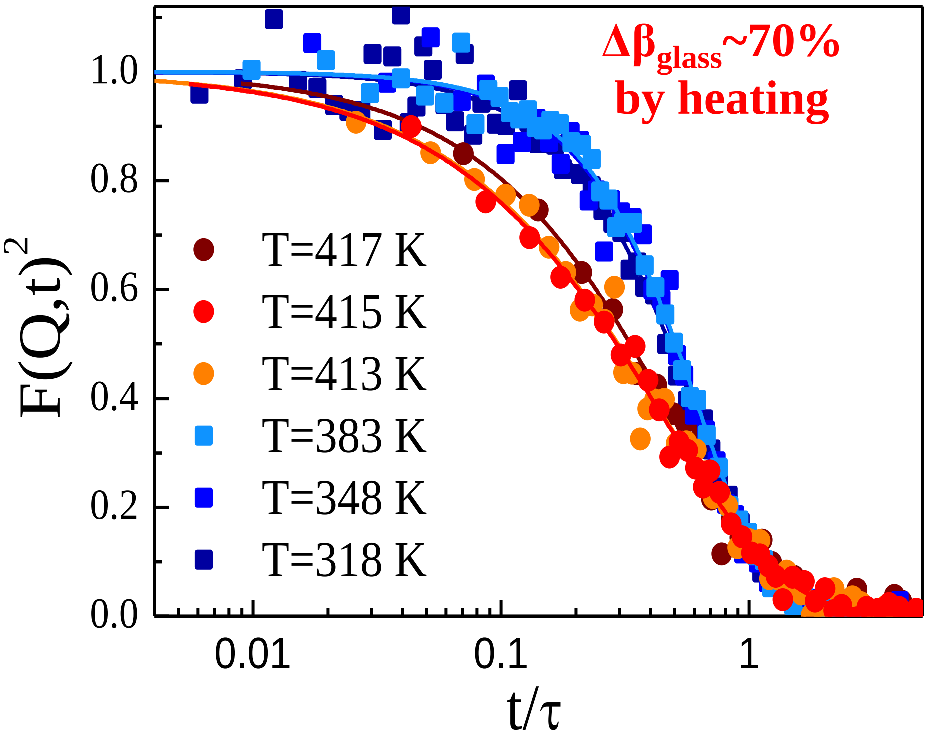
$Q=2.56$ Å^{-1}

$T_g=405$ K

B. Ruta et al. Topical review, J. Phys. Cond. Matt. 2017

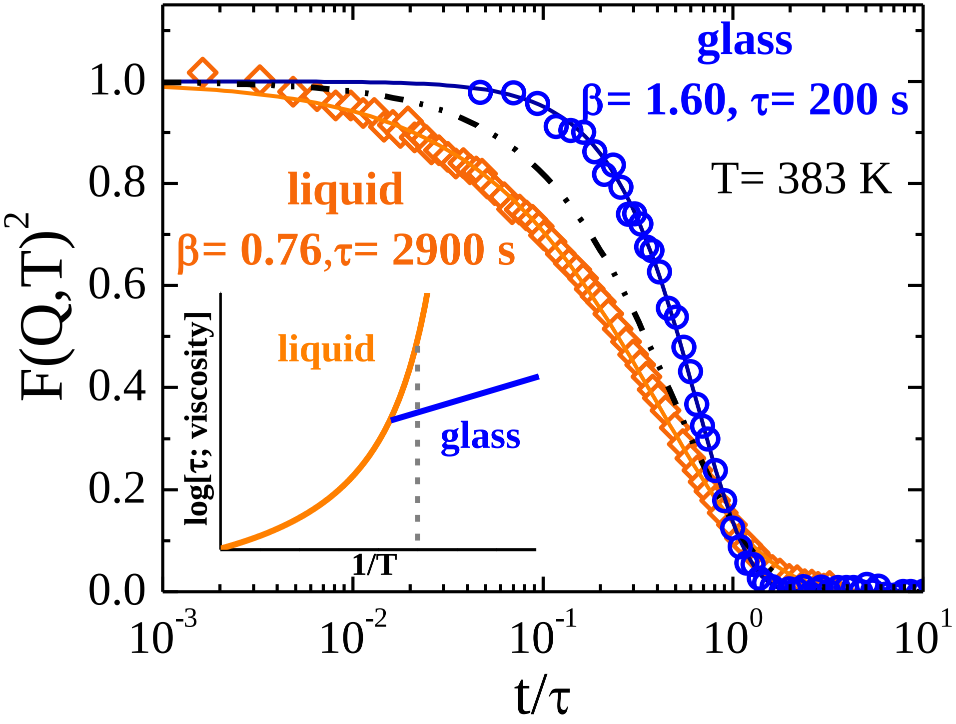
The dynamical crossover

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



B. Ruta et al., AIP Conf. Proc. 2013

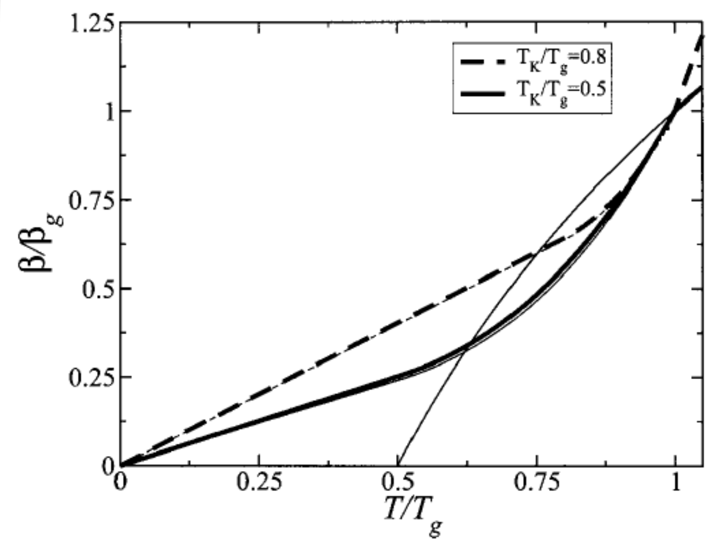
$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$



S. Hechler et al., Phys. Rev. Mat. 2018

The dynamical crossover

strange in hard glasses …



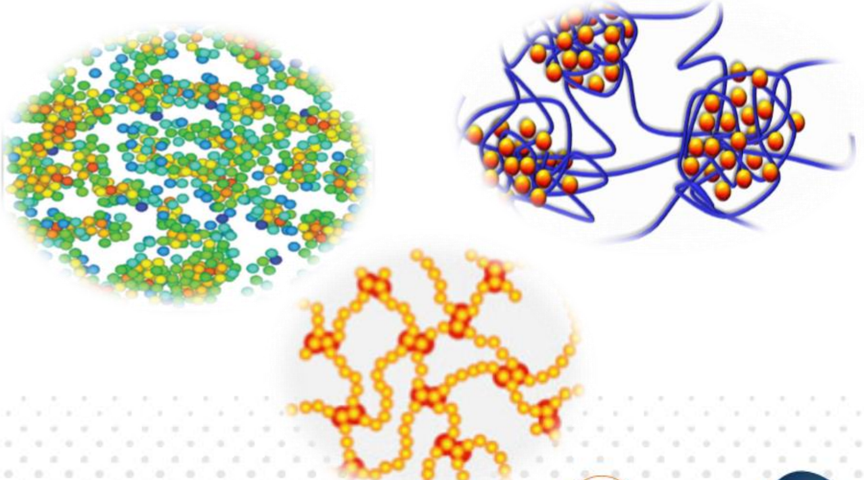
theories for aging predict a continuous decreasing of β below T_g

V. Lubchenko & P. G. Wolynes J. Chem. Phys. 2004

… similar to soft glasses (colloidal gels, clay suspensions, polymeric gels, …)

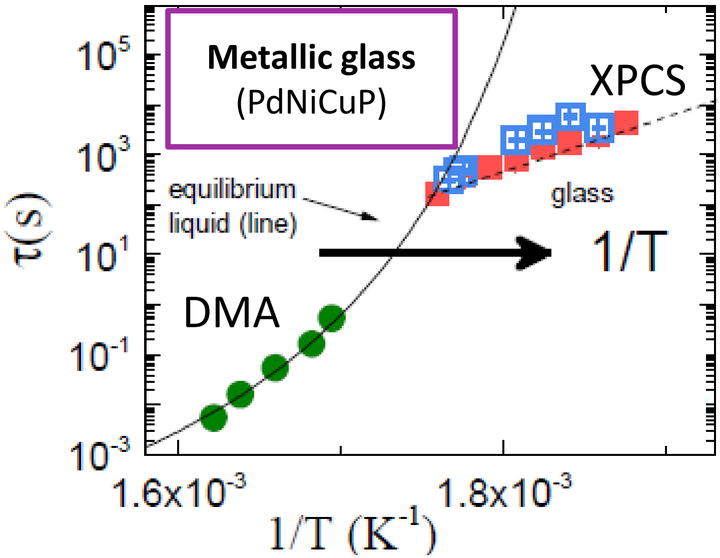
attributed to rearrangement events induced by internal stresses

L. Cipelletti et al. Phys. Rev. Lett. 2000
J.-P. Bouchaud & E. Pitard ,Eur. Phys. J. E, 2001
E. Ferrero et al. Phys. Rev. Lett. 2014
M. Bouzid et al. Nat. Commun. 2017
P. Chaduri & L. Berthier, Phys. Rev. E, 2017

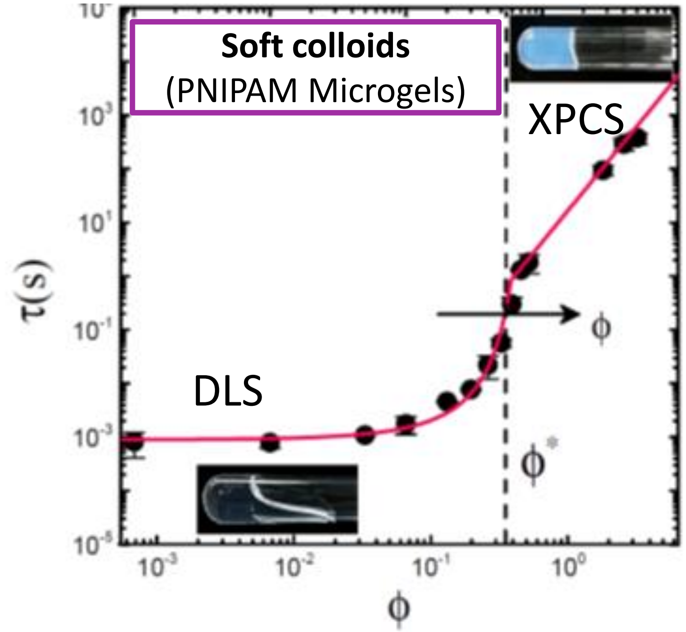


Common to different glassy systems

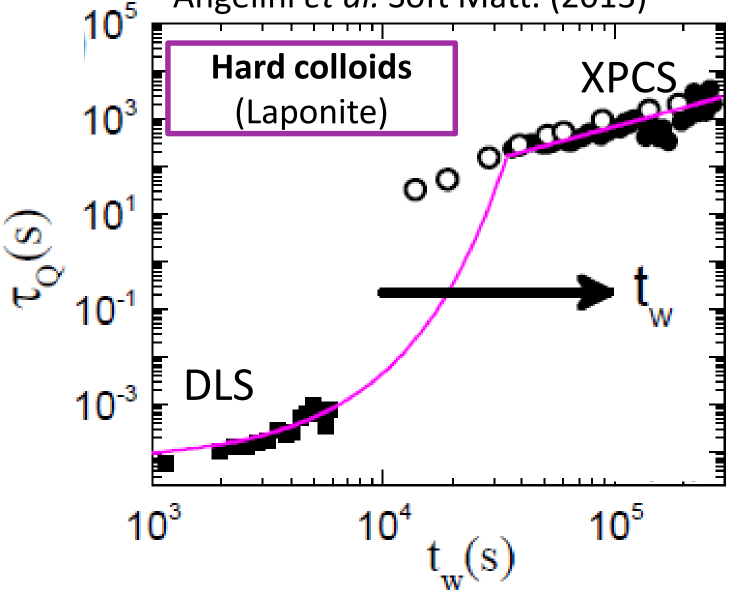
Evenson, Ruta *et al.* PRL (2015)



Nigro/ Ruta *et al.* submitted



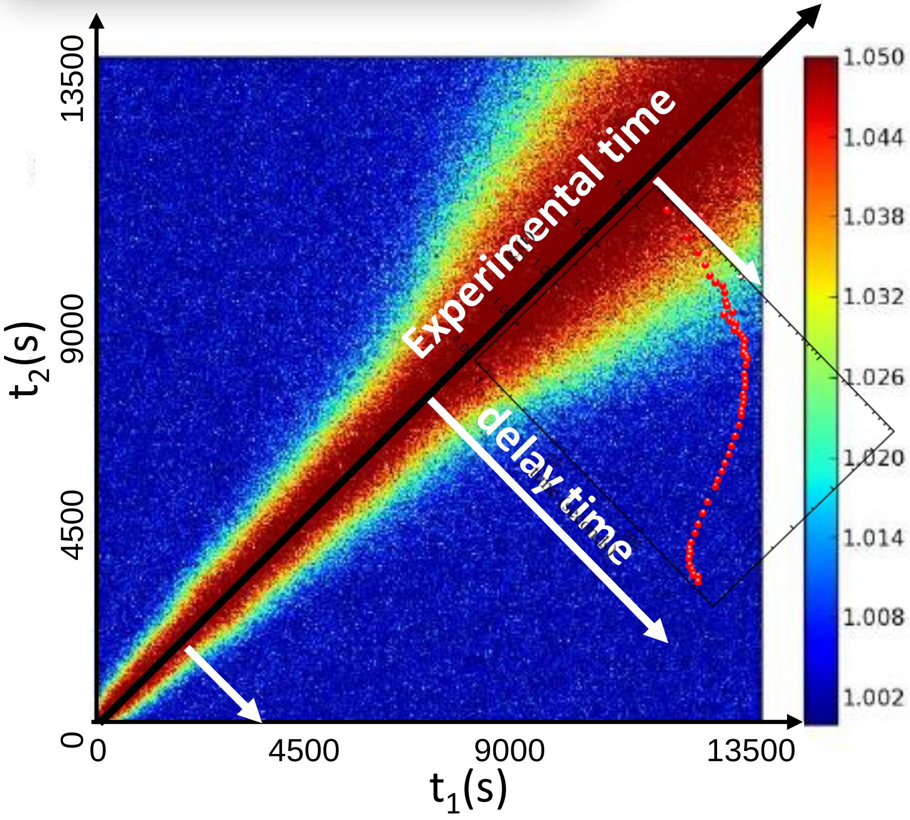
Angelini *et al.* Soft Matt. (2013)



Common dynamical crossover from diffusive to **stress-driven microscopic dynamics** and compressed correlation functions.

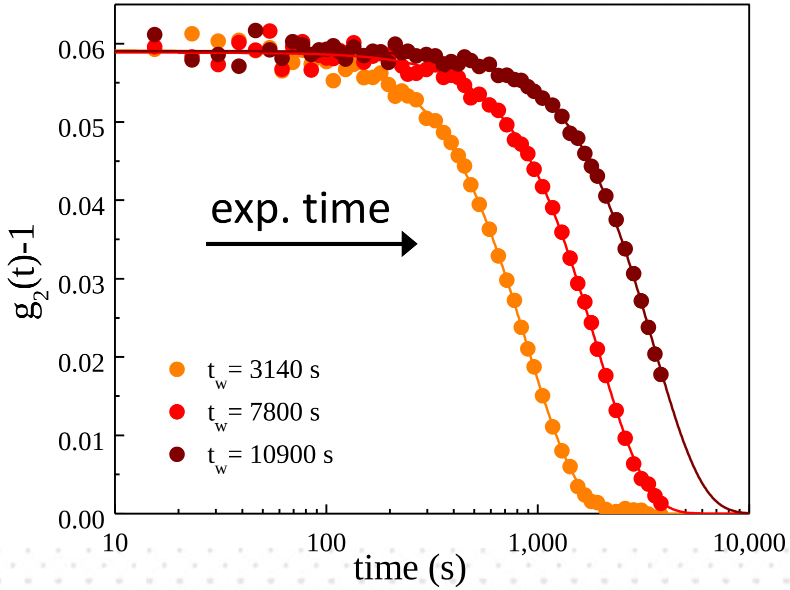
Anomalous dynamics in metallic glasses:
2. The hierarchical aging

Two times correlation functions



Direct measurements of the temporal evolution of the dynamics

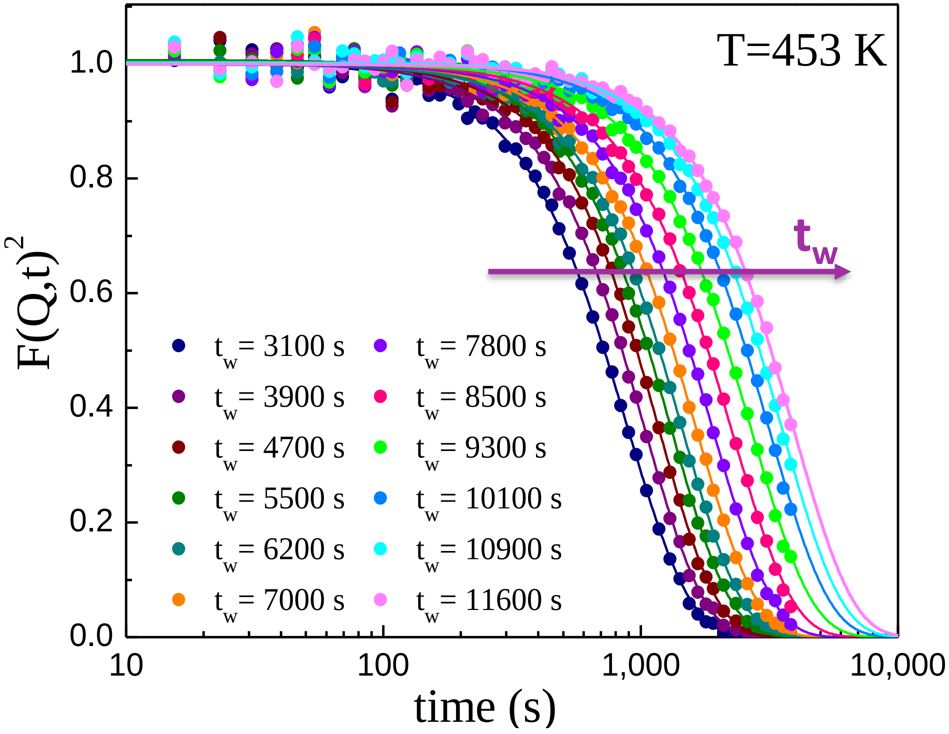
$$g_2(Q,t) = \langle G(Q,t_1,t) \rangle_{t_1}$$



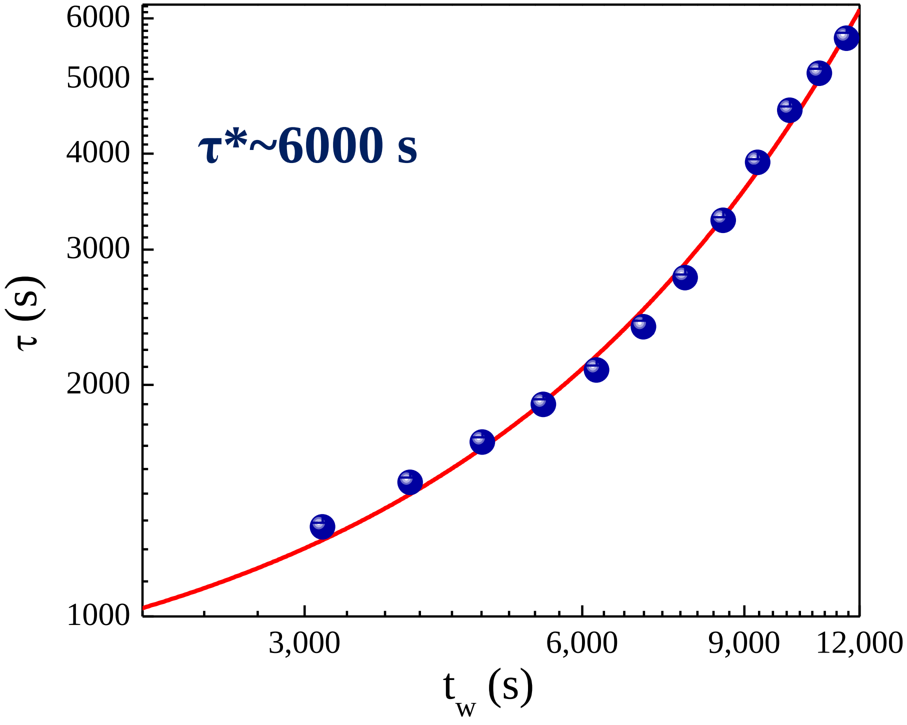
$$G(Q,t_1,t_2) = \frac{\langle I(Q,t_1) I(Q,t_2) \rangle_P}{\langle I(Q,t_1) \rangle_P \langle I(Q,t_2) \rangle_P}$$

Microscopic Aging in Metallic Glasses

$Pd_{77}Si_{16.5}Cu_{6.5}$ (T_g=625 K, Q=2.8 Å^{-1})



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

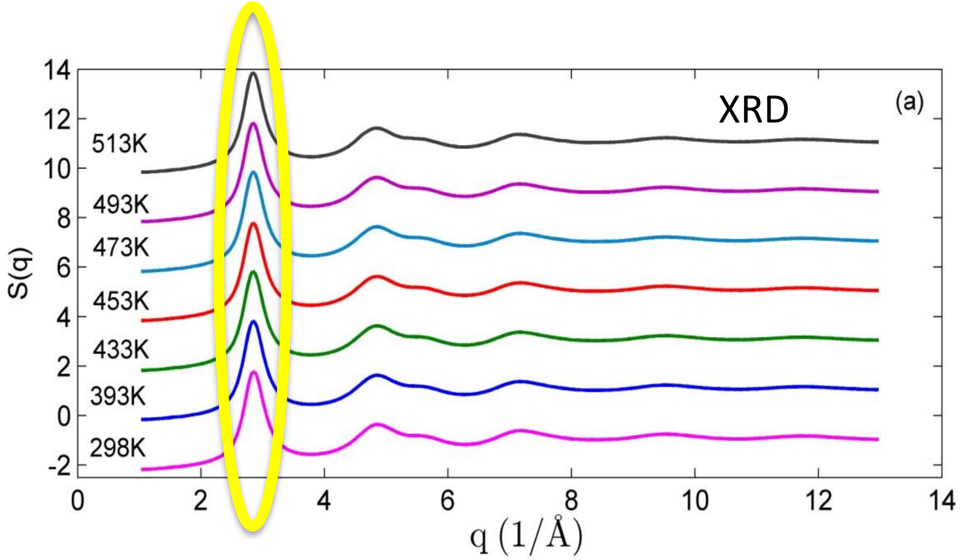


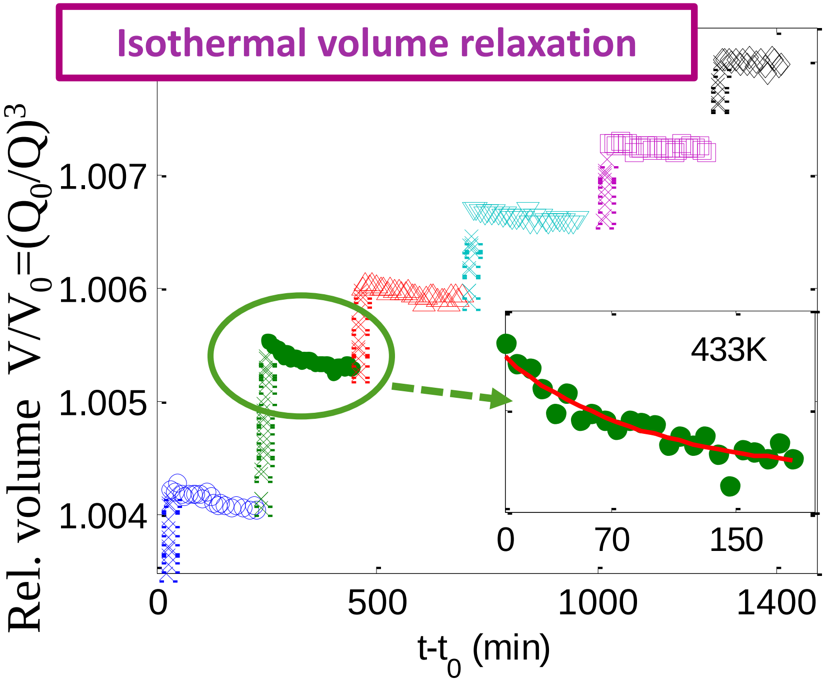
$$f(q,t) = a\exp\left(-\left(\frac{t}{\tau}\right)^{\beta}\right)$$

V.M. Giordano & B. Ruta, Nat. Commun. 2016

Structural origin of the fast aging

$Pd_{77}Si_{16.5}Cu_{6.5}$ (T_g=625 K, Q=2.8 Å^{-1})



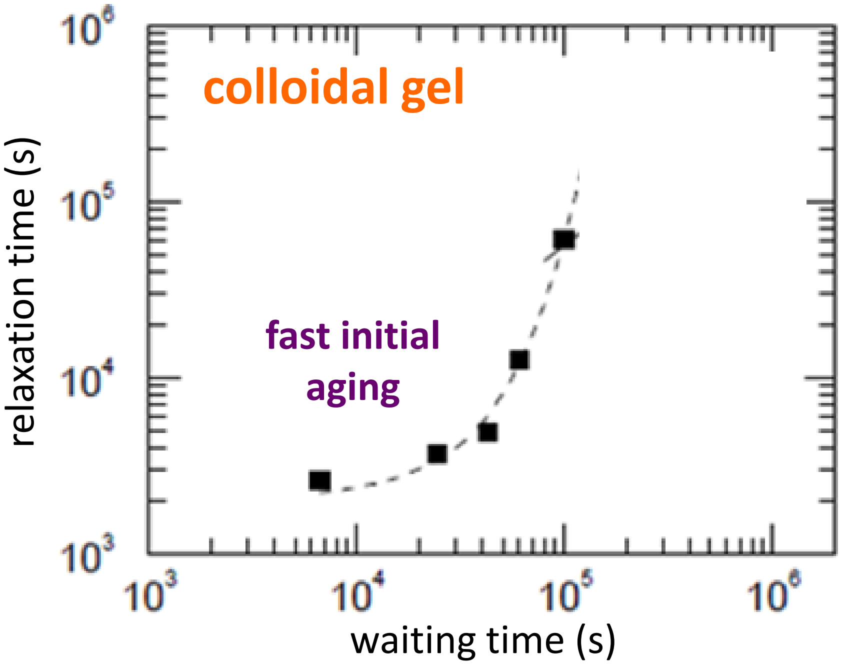

Isothermal volume relaxation

Fast aging due to density changes (structural defects annihilation)

Hierarchical aging in complex systems

Similarities with jammed soft materials

L. Cipelletti et al. Phys. Rev. Lett. 2000



Hierarchical aging in complex systems

Similarities with jammed soft materials

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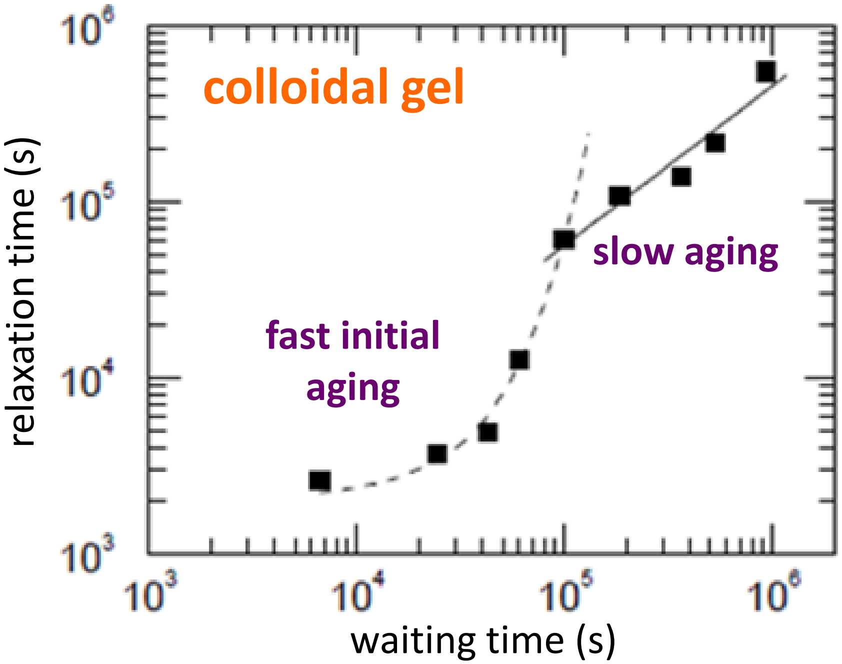
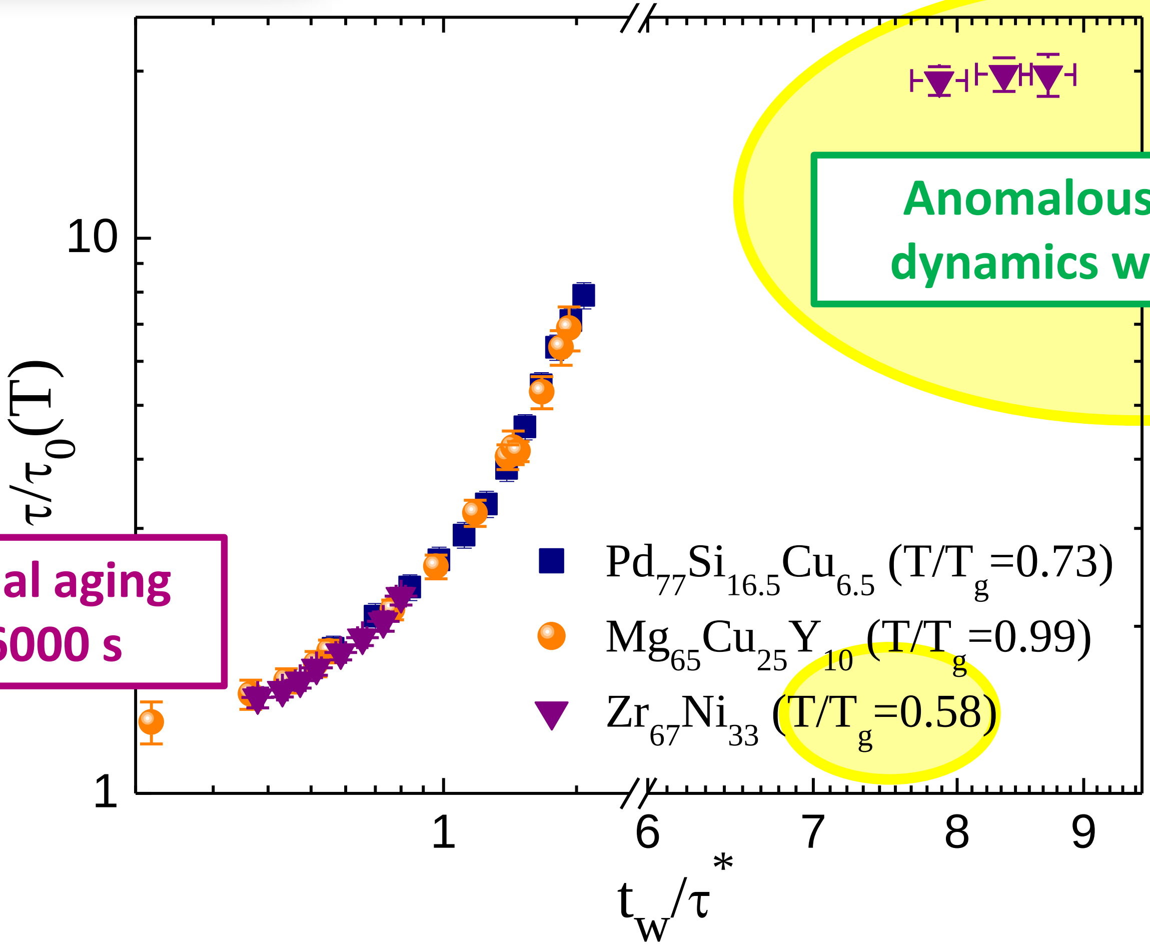


Universal behavior?

Hierarchical aging below T_g

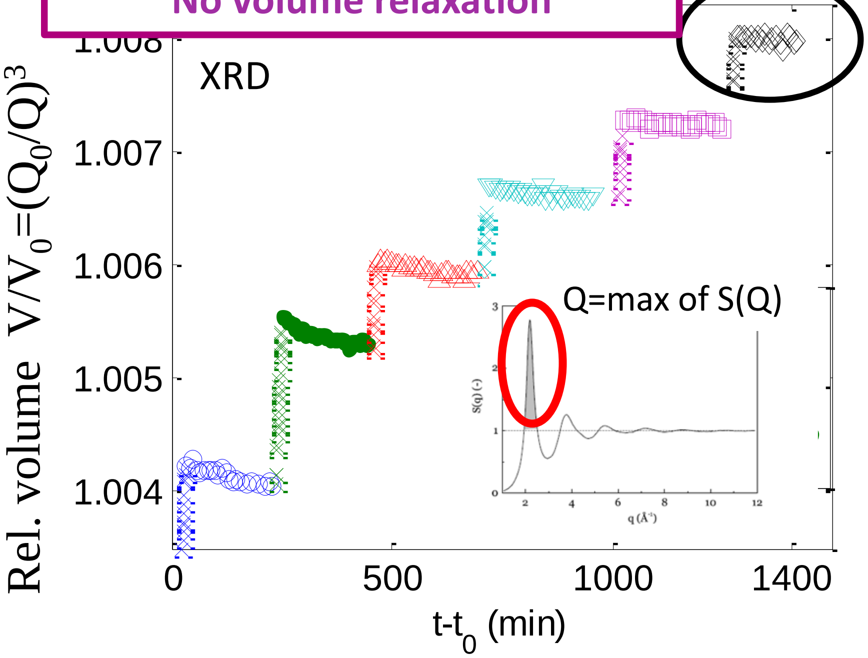


Anomalous stationary dynamics well below T_g

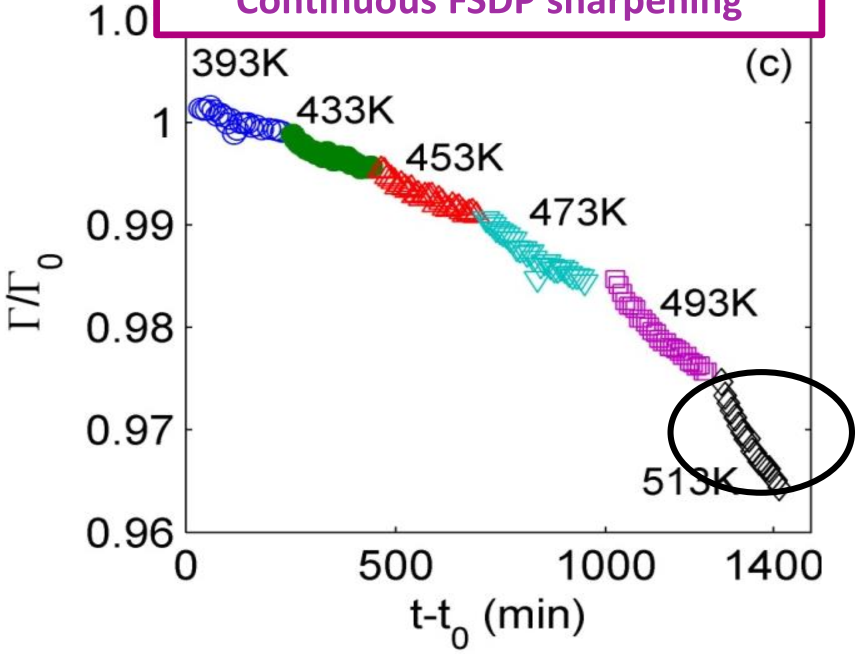
fast initial aging
τ^* ~ 6000 s

Structural origin of the stationary regime

No volume relaxation



Continuous FSDP sharpening



Structural origin of the stationary regime

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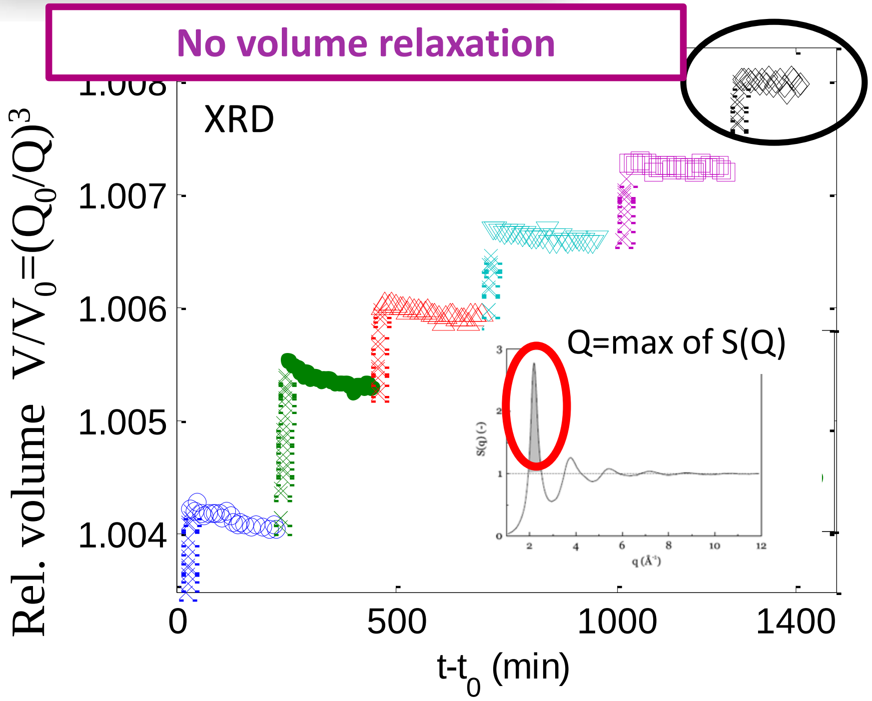
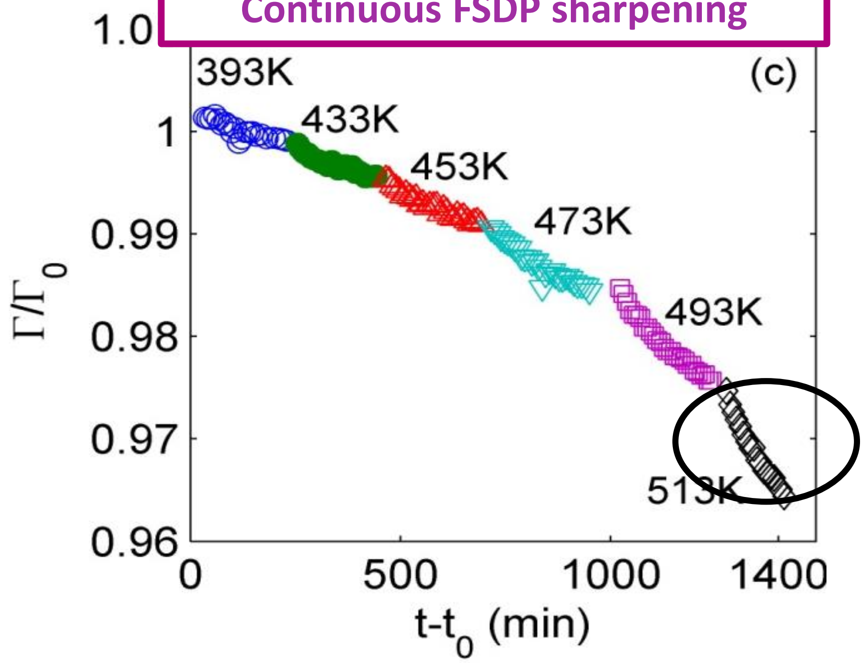


Continuous FSDP sharpening



Two main processes controlling the aging:

1) volume shrinking (density changes) → **fast aging**

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

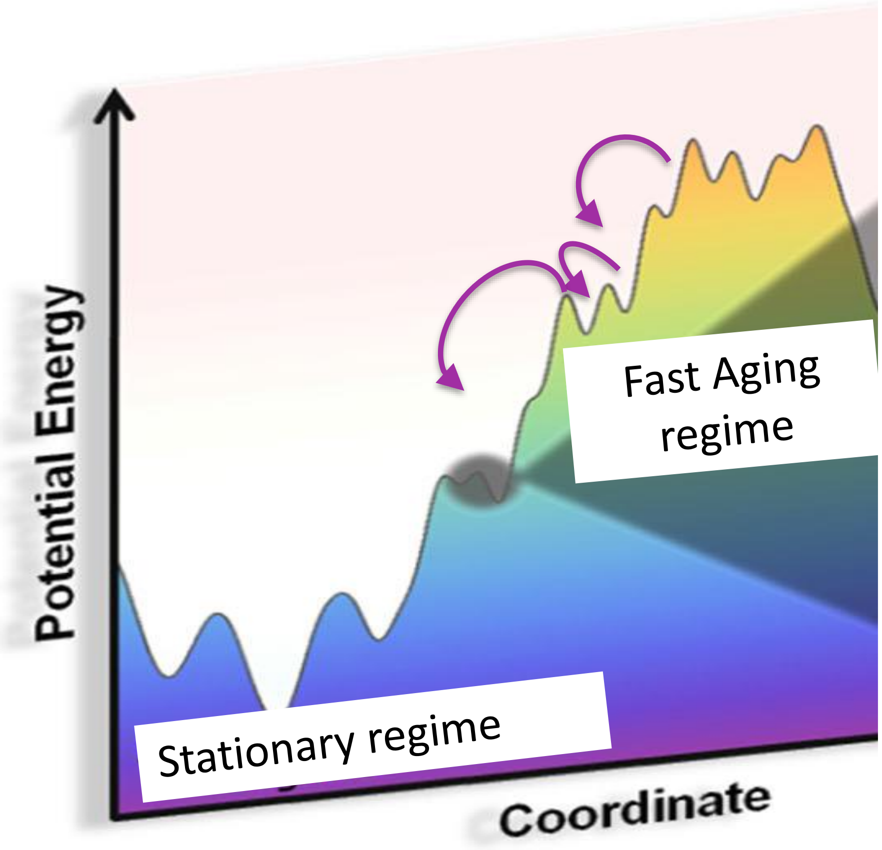
V.M. Giordano & B. Ruta, Nat. Commun. 2016

From cascade relaxation to localized motion

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

Stationary: **Localized dynamics** in a more relaxed minimum → constant density but increasing MRO

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



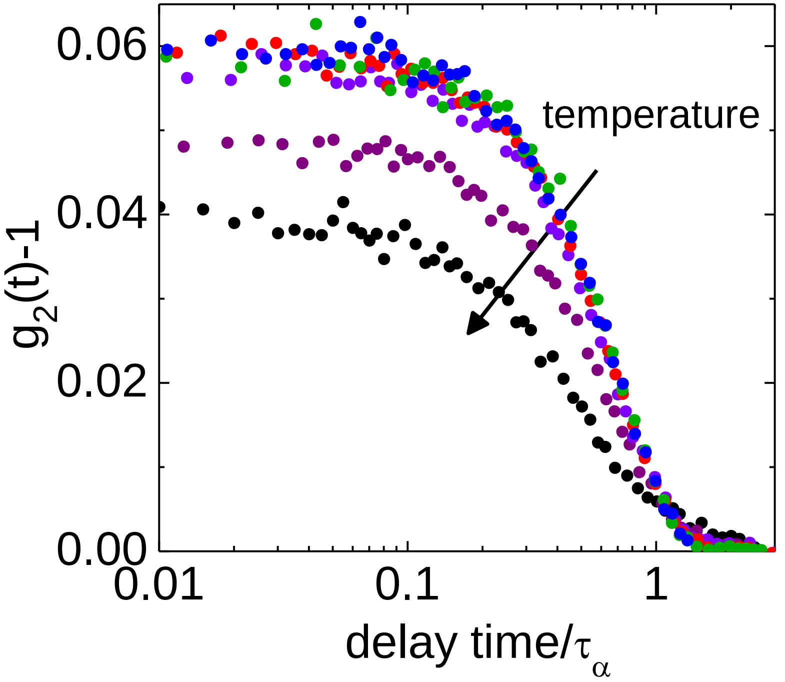
Fan et al. Phys. Rev. Lett. 2015

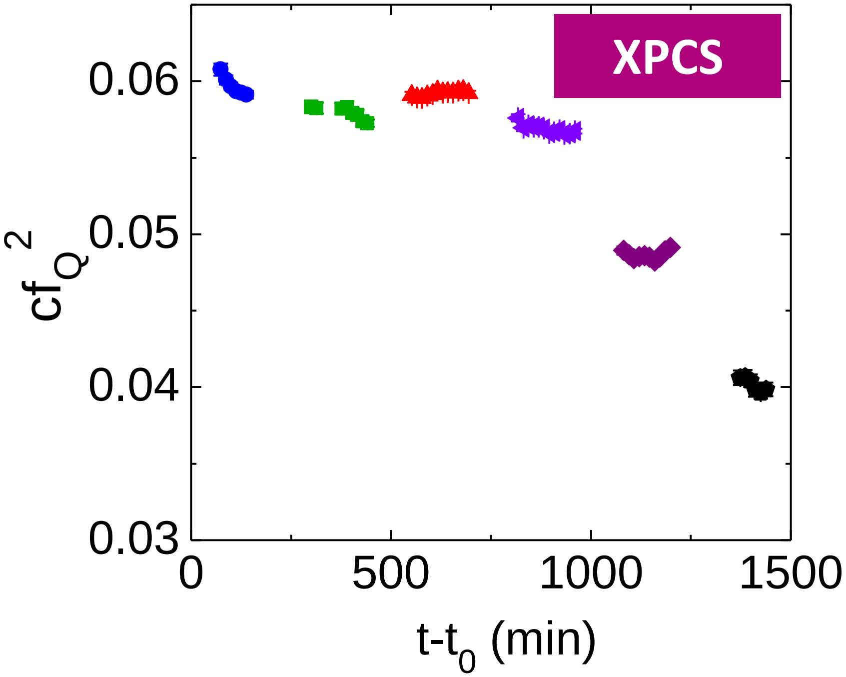
Anomalous dynamics in metallic glasses: 4. Secondary relaxation processes and crystallization

Temperature induced secondary processes

Temperature activation of an additional relaxation process

$$g_2(q,t)_{XPCS} = (cf_Q^{\,2})\exp\left(-2\left(\frac{t}{\tau}\right)^{\beta}\right)$$





Contrast decreases at the two highest temperatures

V.M. Giordano & B. Ruta, Nature Commun. 2016

Temperature induced secondary processes

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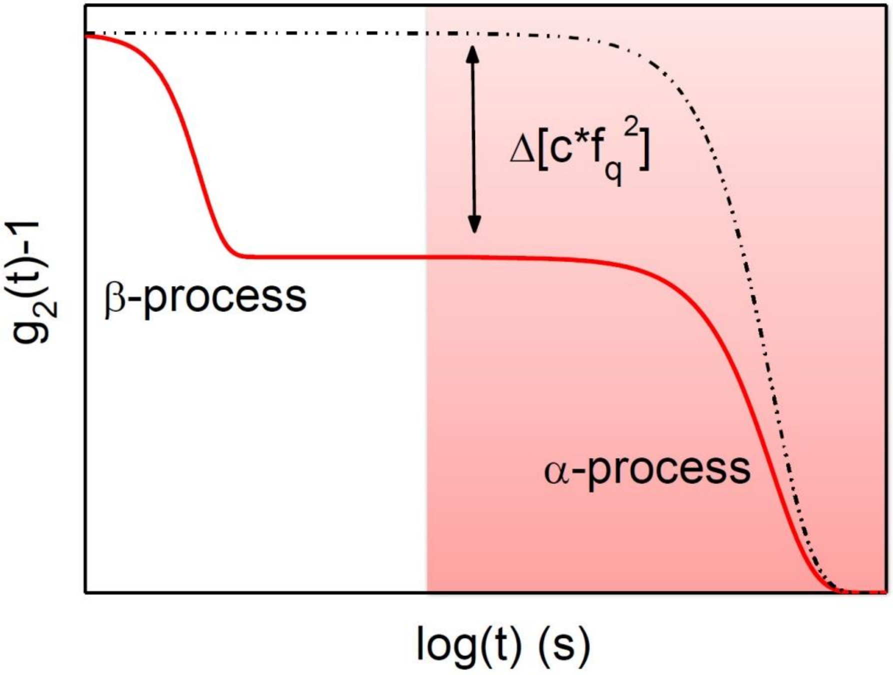
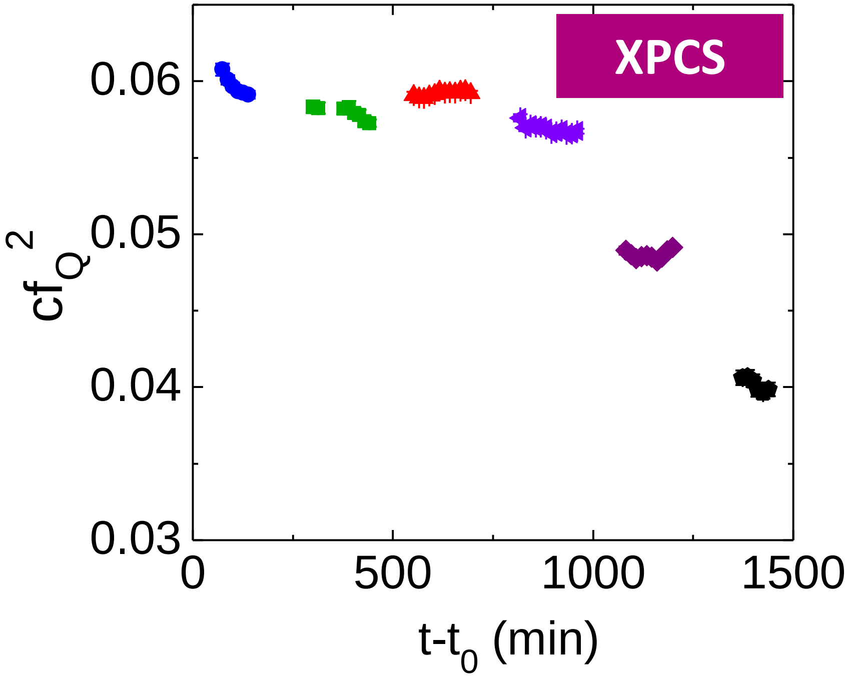


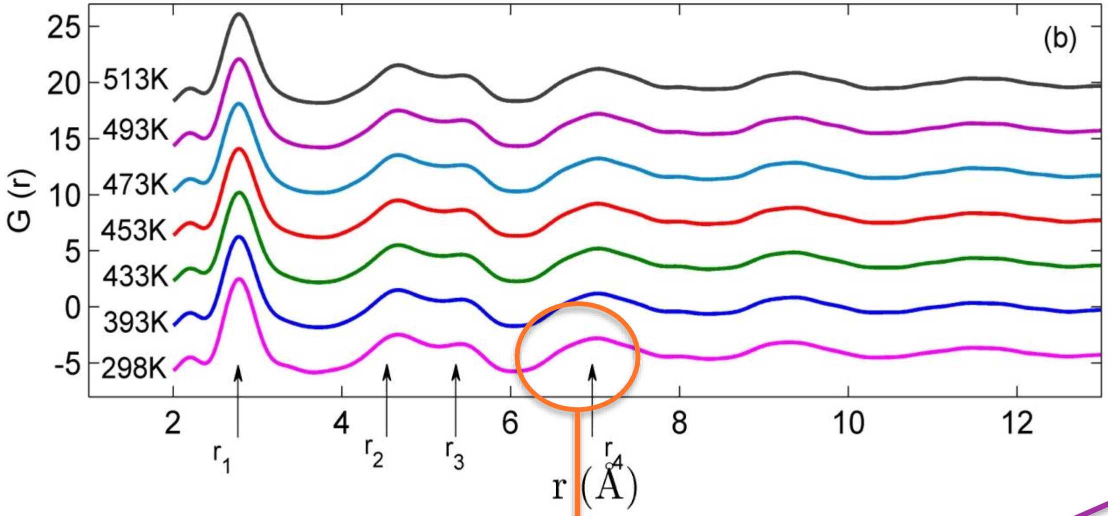


Contrast decreases at the two highest temperatures

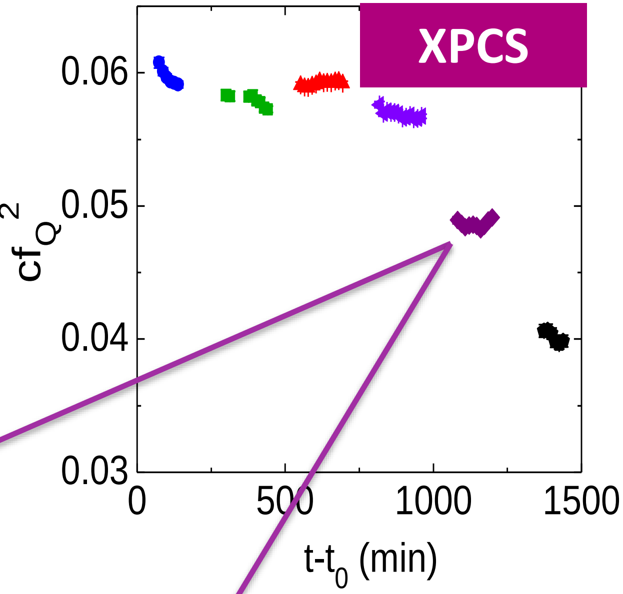
→high temperature activation of a secondary relaxation with τ_β<3s (experimental temporal resolution)

V.M. Giordano & B. Ruta, Nature Commun. 2016

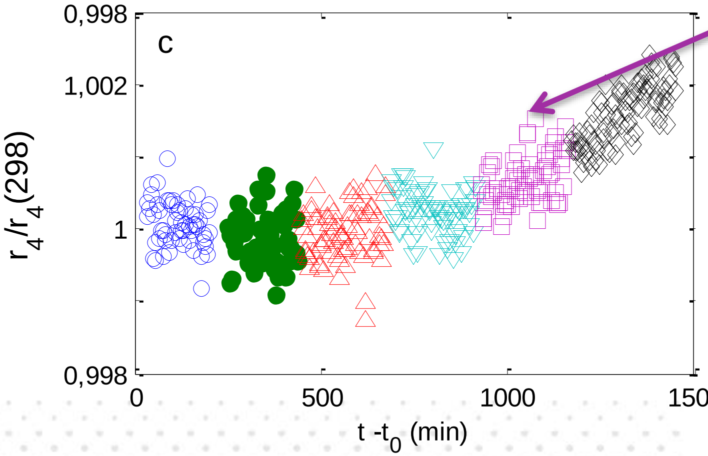
Temperature induced secondary processes

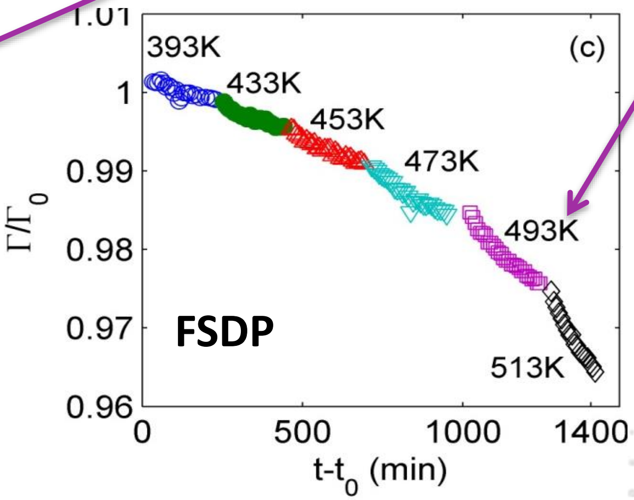


XPCS



XRD





→ stronger ordering at the medium range and 3rd shell expansion

V.M. Giordano & B. Ruta, Nature Commun. 2016

Temperature induced secondary processes

The fast secondary relaxation starts at 493K and implies a stronger ordering.

Precursor to crystallization?

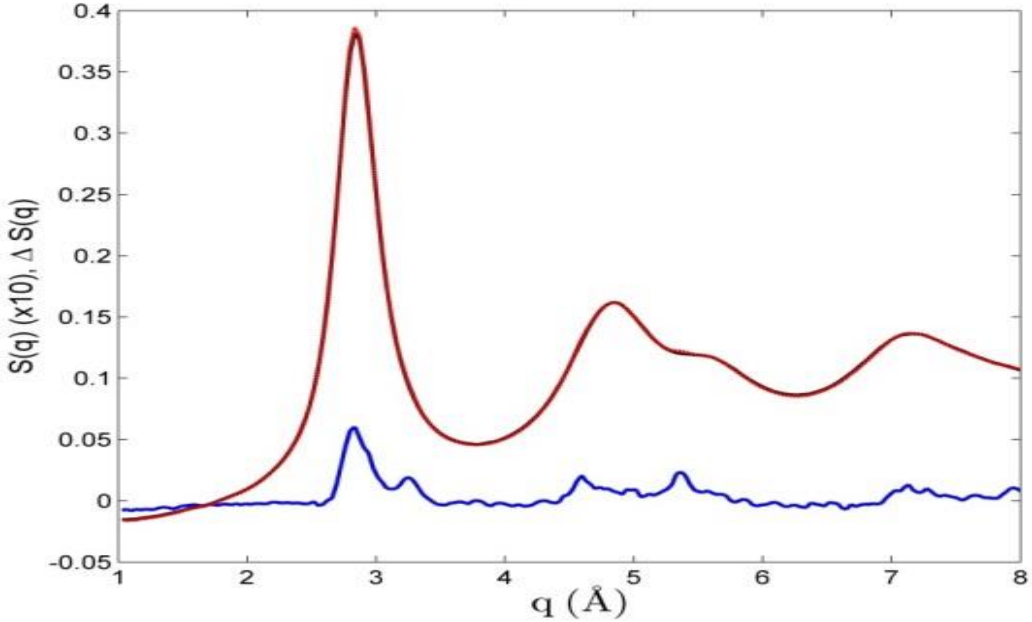
V.M. Giordano & B. Ruta, Nature Commun. 2016

Temperature induced secondary processes

The fast secondary relaxation starts at 493K and implies a stronger ordering

Precursor to crystallization?

- 493K: no evidence of crystallization in XRD spectra
- However at 513K: 0.8% crystallization after 7h

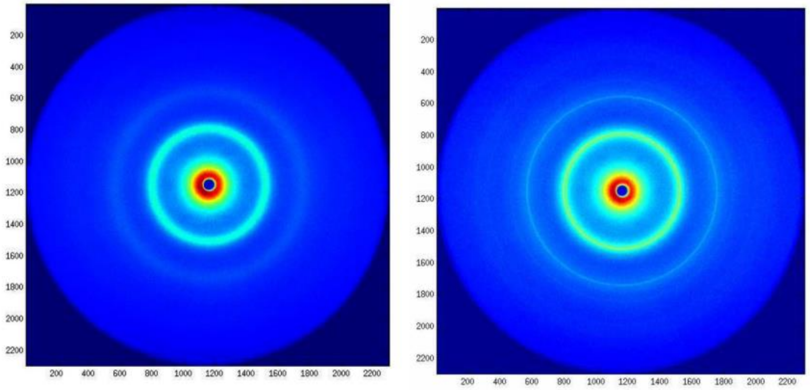


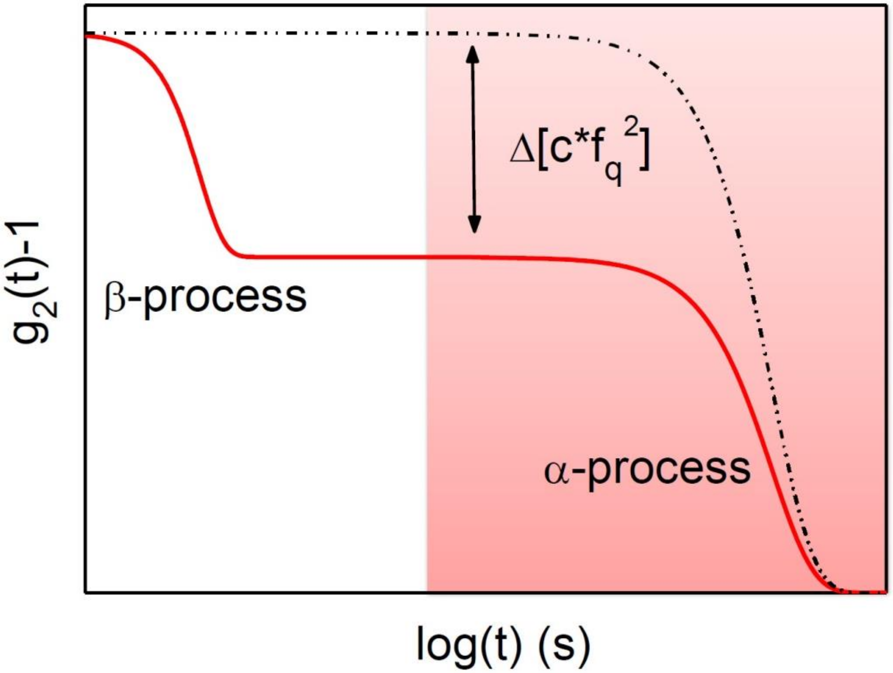
→ Strong support to the interpretation of this process as precursor to crystallization

V.M. Giordano & B. Ruta, Nature Commun. 2016

How can we go further?

Structural & dynamical measurements during crystallization





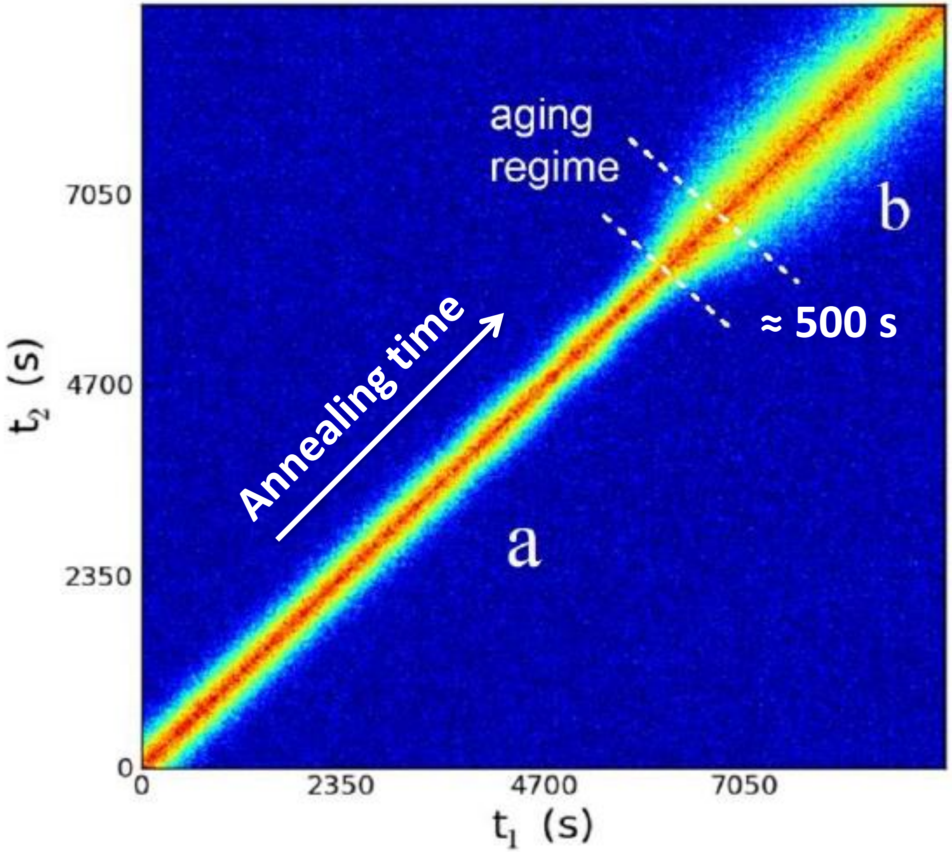
What do we need for these studies?
Better contrast (now ≈ 4%)
More Flux + Faster detectors!

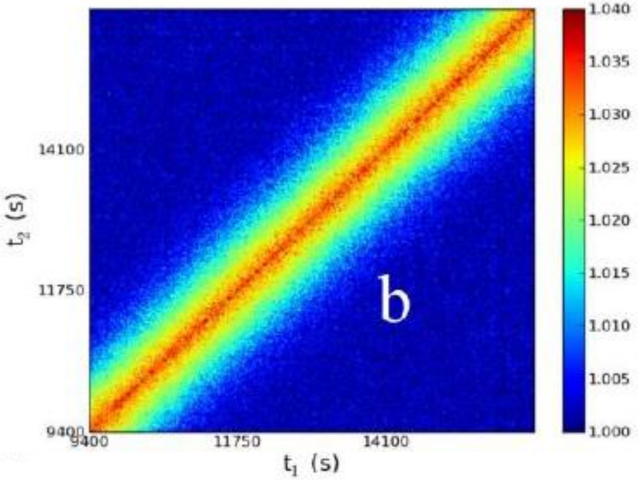
Anomalous dynamics in metallic glasses:

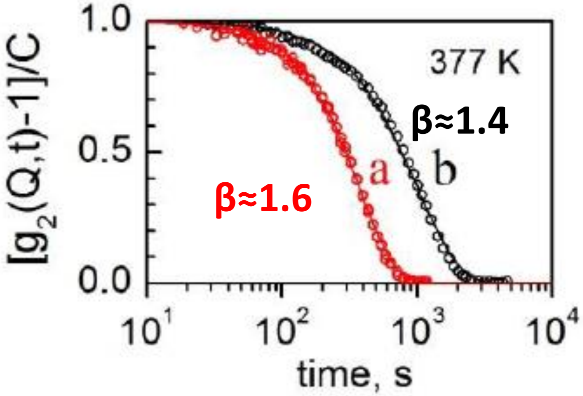
3. The intermittent aging

Aging triggered by “discrete events”

$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$



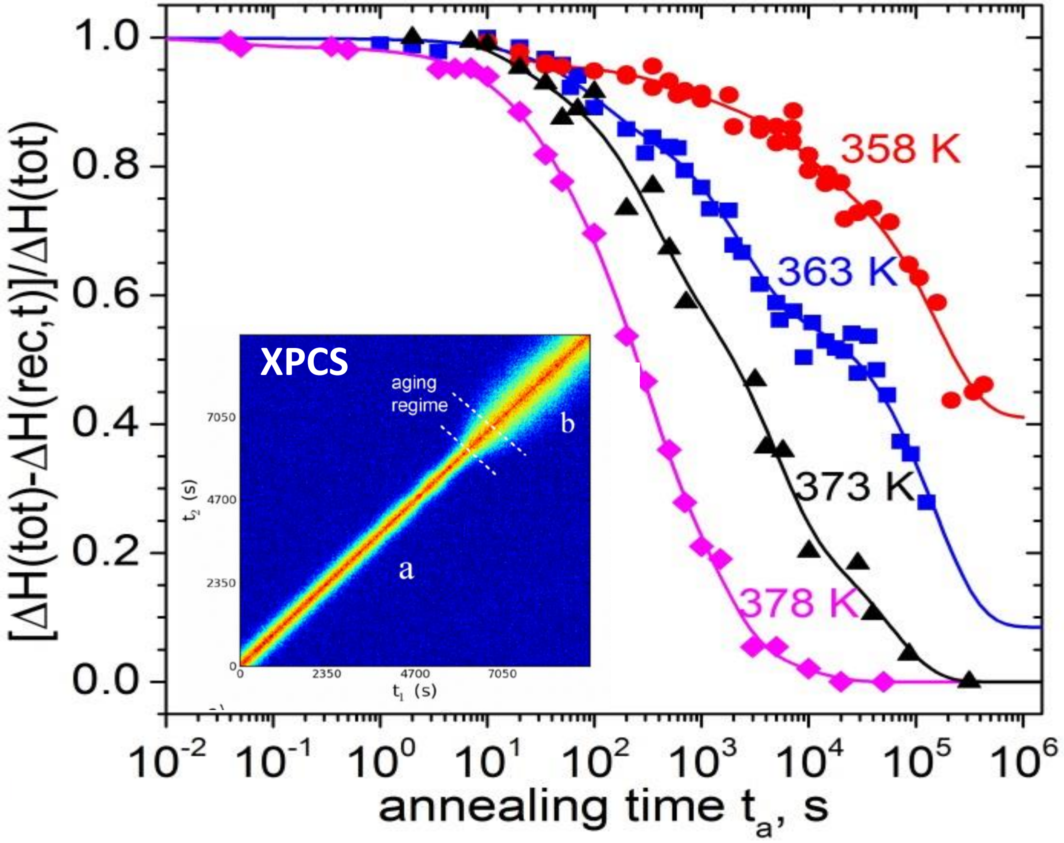


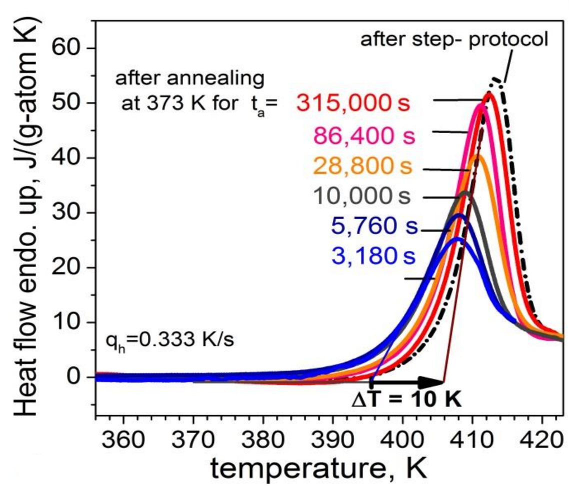


I. Gallino/ B. Ruta Acta Mat. 2018

Anomalous enthalpy recovery

$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$

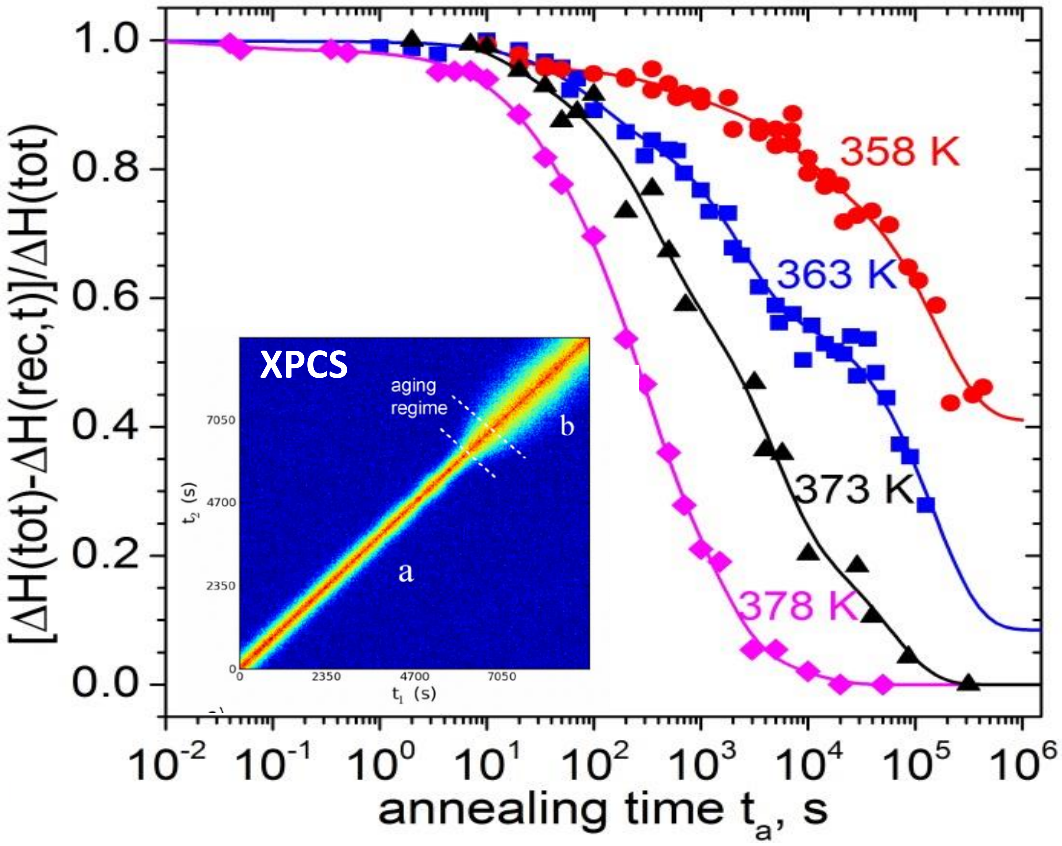


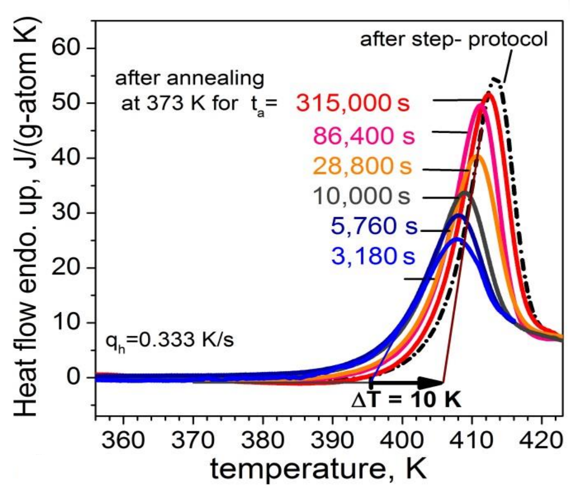


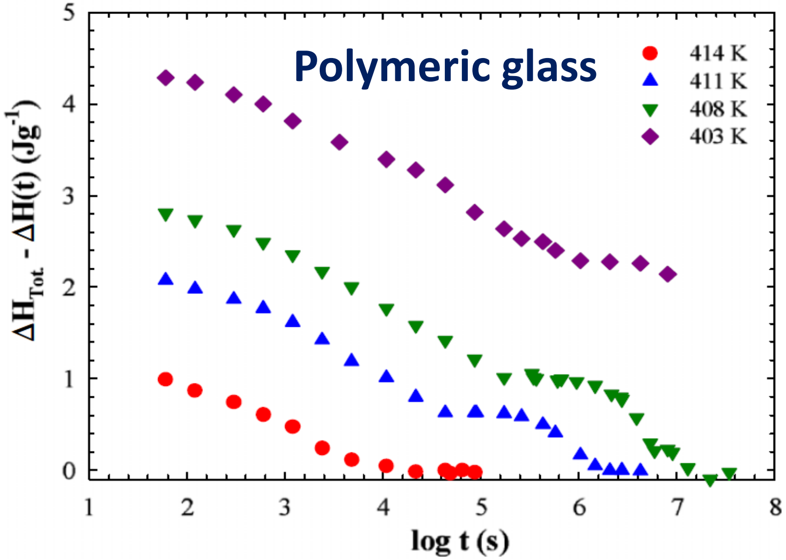
I. Gallino/ B. Ruta Acta Mat. 2018

Anomalous enthalpy recovery

$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$







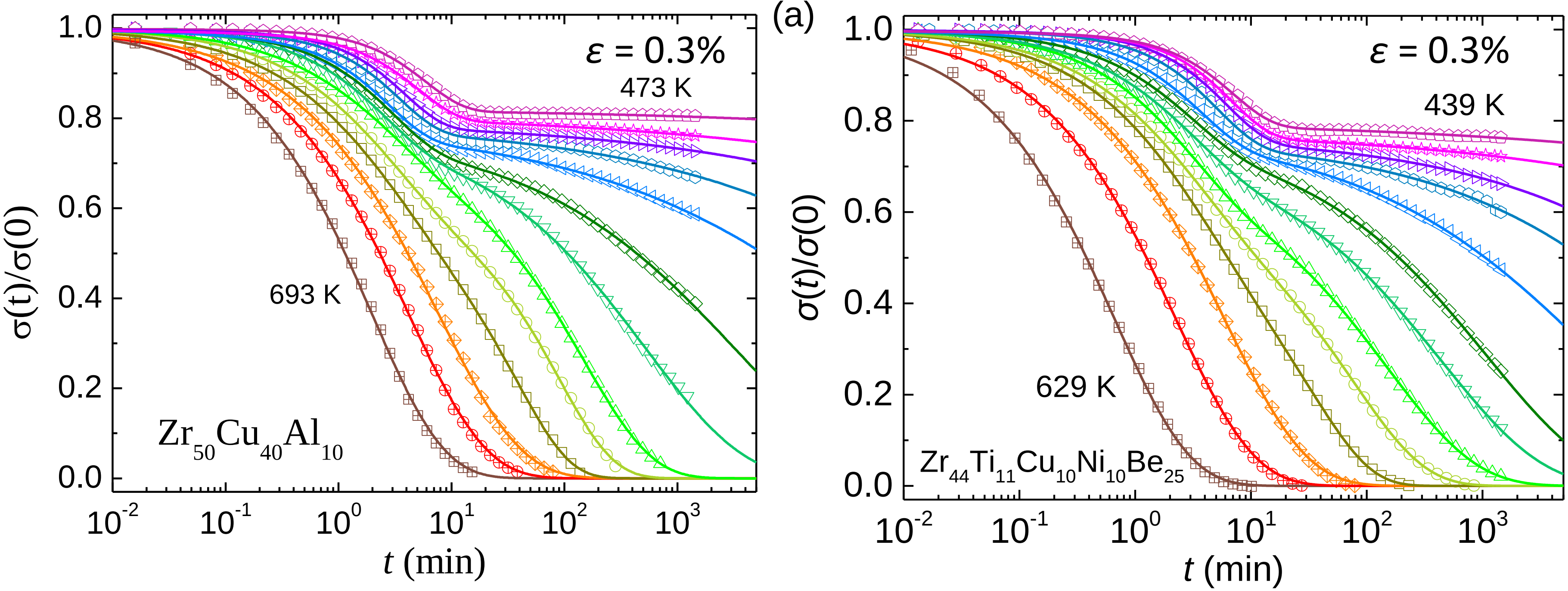
Cangialosi et al. Phys. Rev. Lett. (2012)

I. Gallino/ B. Ruta Acta Mat. 2018

Multiple relaxations in the elastic response

Dynamic Mechanical Analyser under constant tensile strain

samples pre-annealed at 0.9 T_g for 48 h



$$\sigma(t)/\sigma(0) = A\exp[-(\Gamma_1 t)^{\gamma_1}] + (1-A)\exp[-(\Gamma_2 t)^{\gamma_2}]$$

Fast process: $\gamma_1 > 1$ and almost no thermal contribution

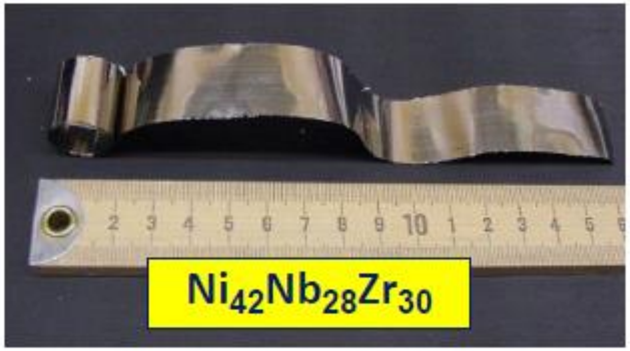
Slow process: $\gamma_2 < 1$, strong T dependence

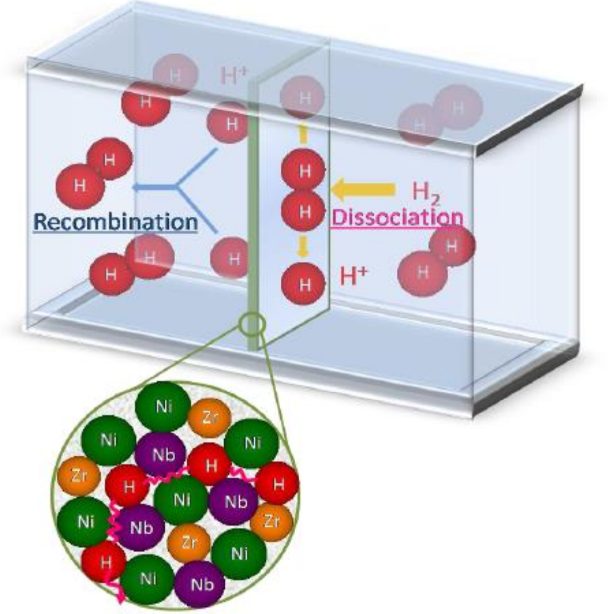
P. Luo/ B. Ruta, W.H. Wang. Phys. Rev. Lett. 2017

Measurements *in operando* conditions

INSTITUT LUMIÈRE MATIÈRE

MG membranes for H_2 separation from CO_2





Ni and Zr-based MGs:

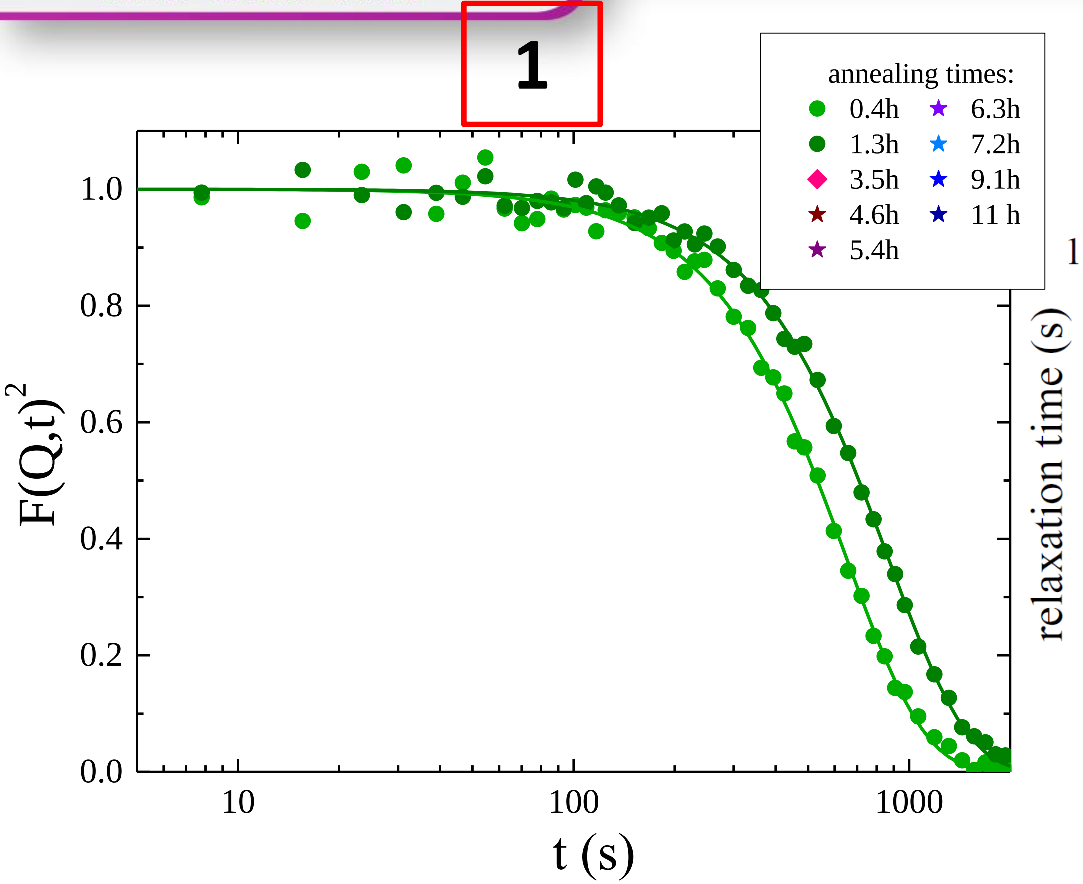
→ **better H_2 permeability** than crystalline materials (high H_2 diffusivity due to the free volume)

→ **high H_2 solubilities and diffusivities**

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

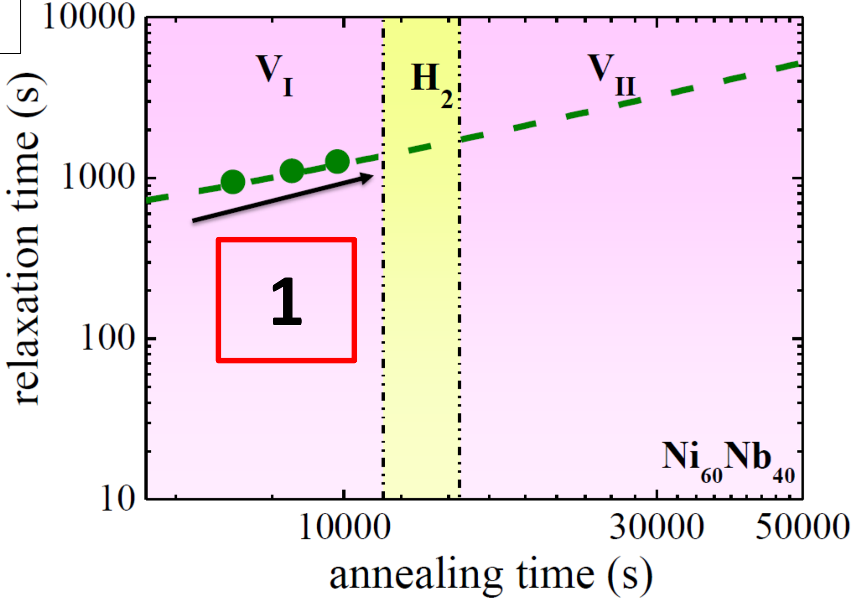
Collab. with Prof. D. Chandra
Reno University

Effect of H_2 on the dynamics



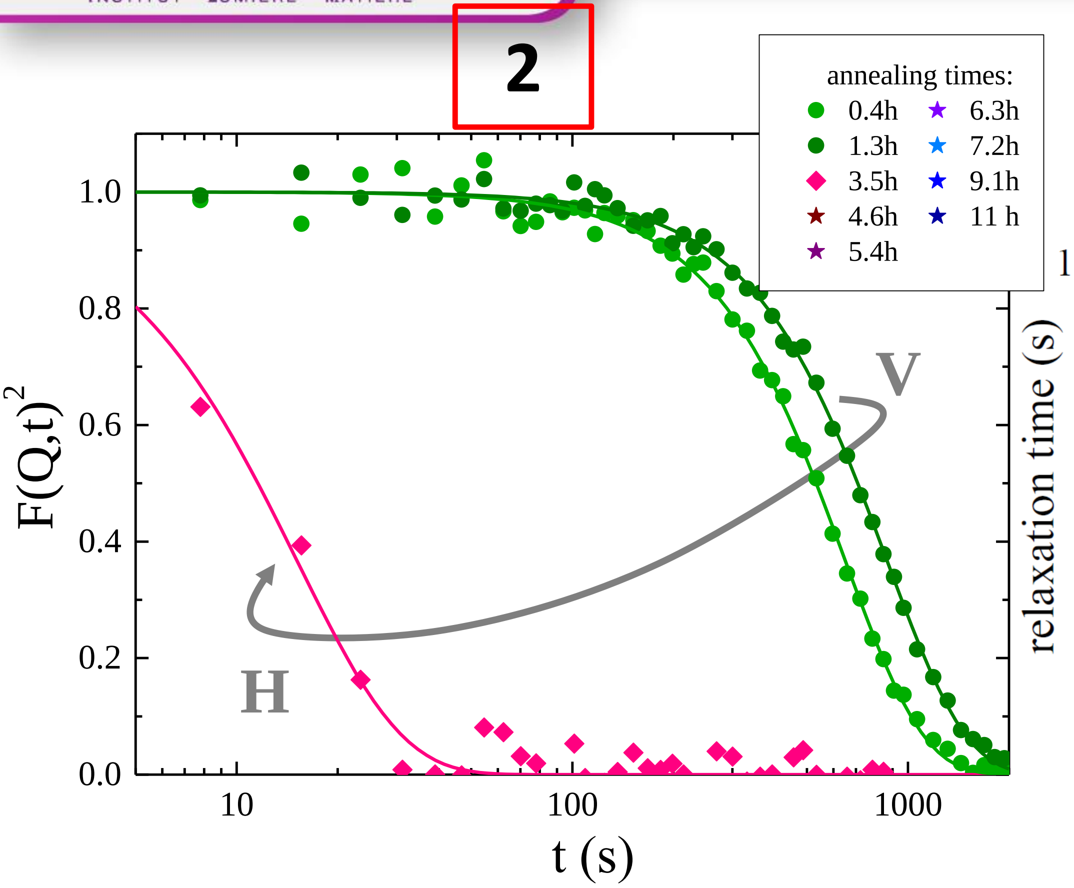
$Ni_{60}Nb_{40}$, T=373 K , Q_p=2.7 $Å^{-1}$

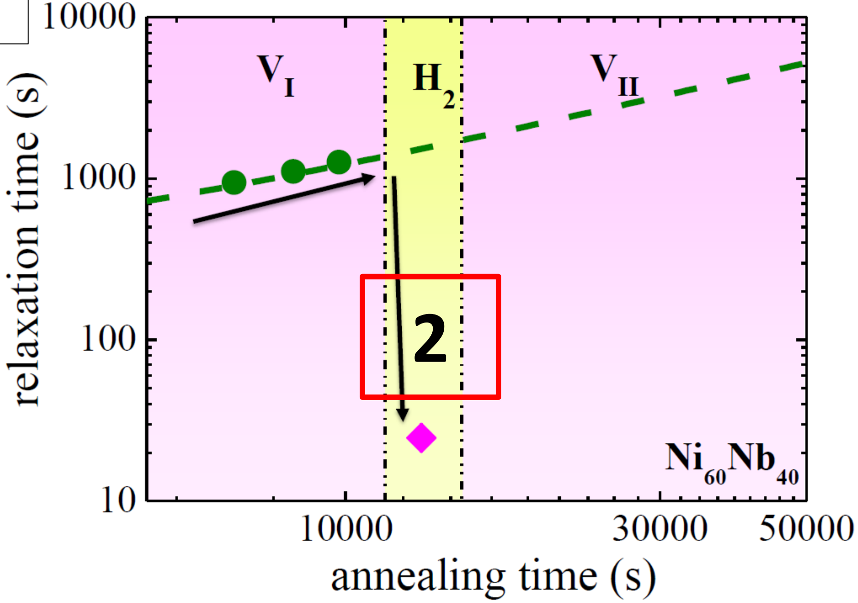
H_2 @ 0.6 bar



Effect of H_2 on the dynamics

$Ni_{60}Nb_{40}$, T=373 K , Q_p=2.7 Å^{-1}
H_2@ 0.6 bar

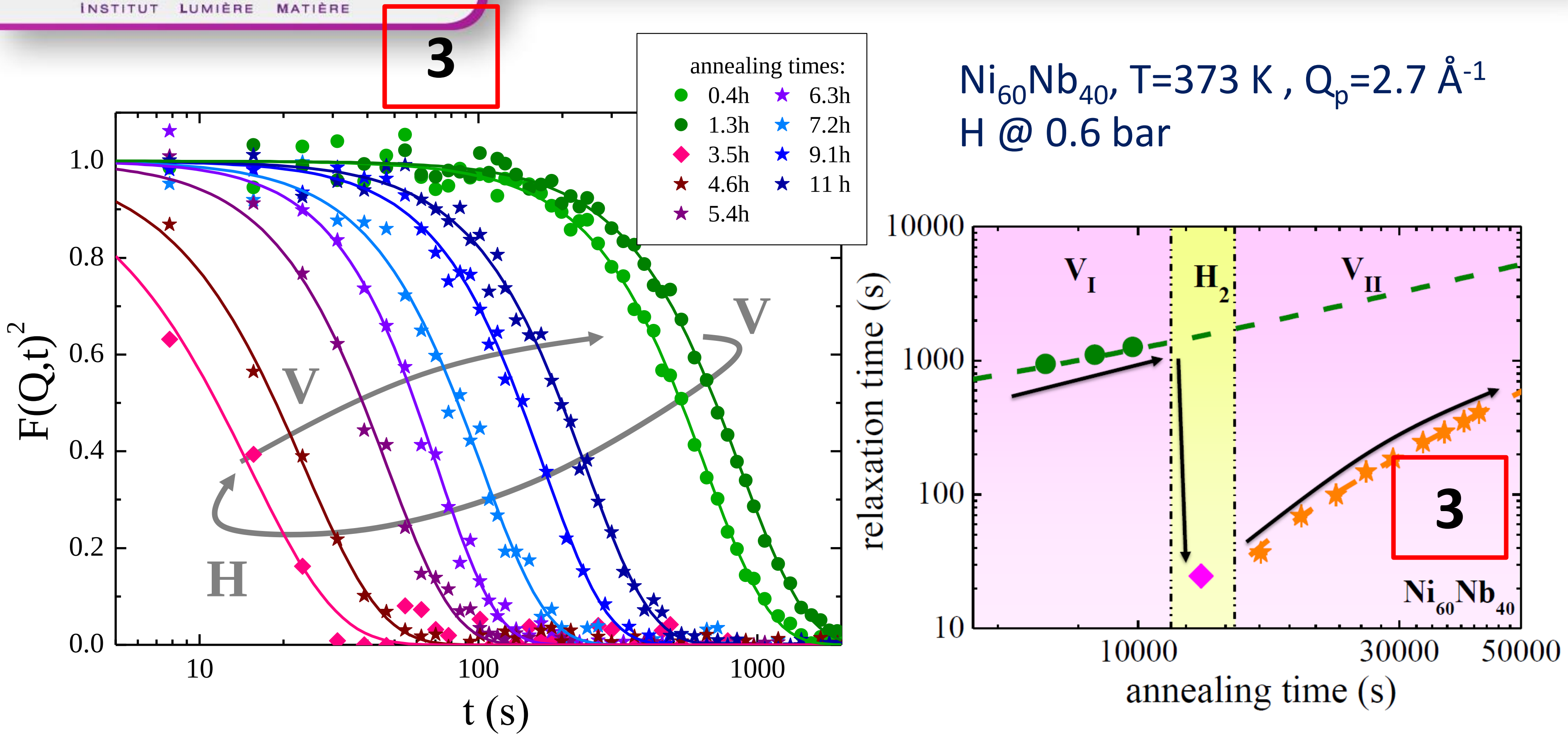




Dramatic acceleration of the dynamics due to the hydrogen atmosphere

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

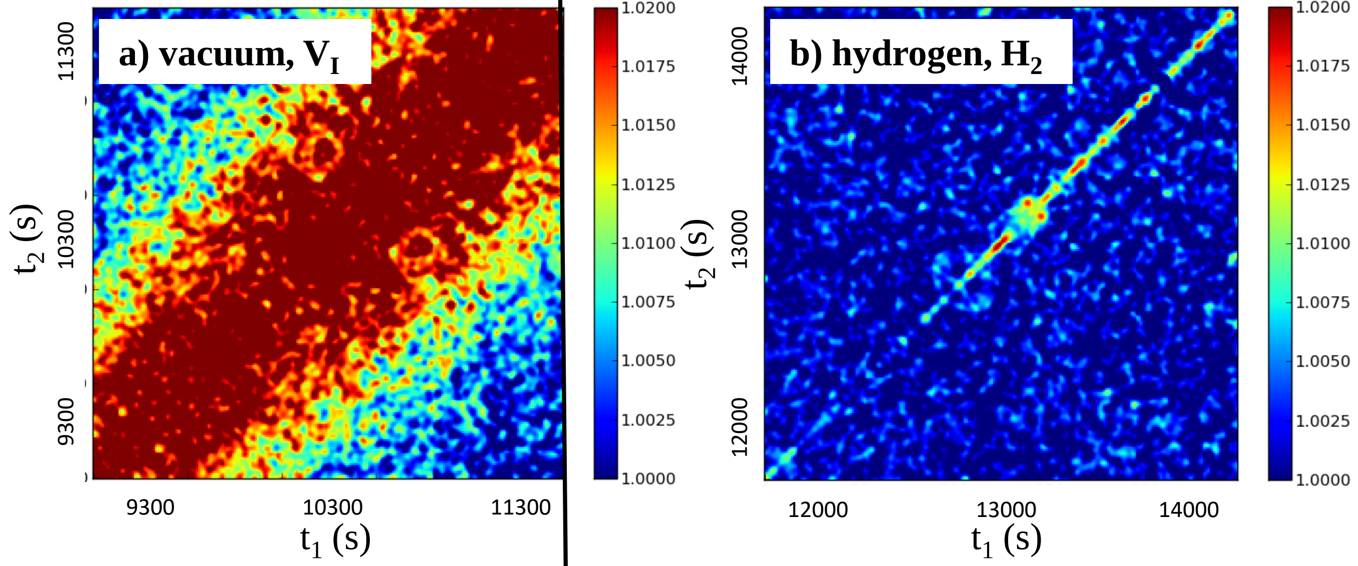
Reversible transition: after removing the hydrogen, the dynamics slows down again but with a faster aging

B. Ruta et al. in preparation

Effect of H_2 on the dynamics

In vacuum

In H_2 atmosphere



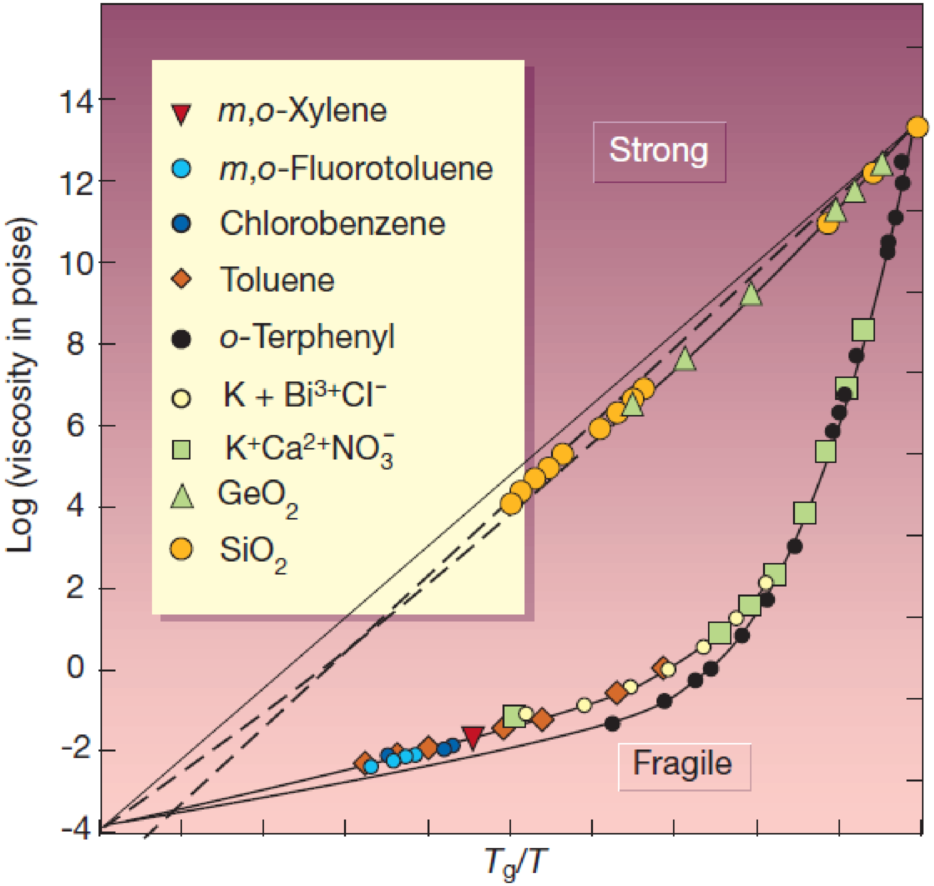
Experimental time t_1(s)

Measurements at 60 kPa and 373 K

B. Ruta et al. in preparation

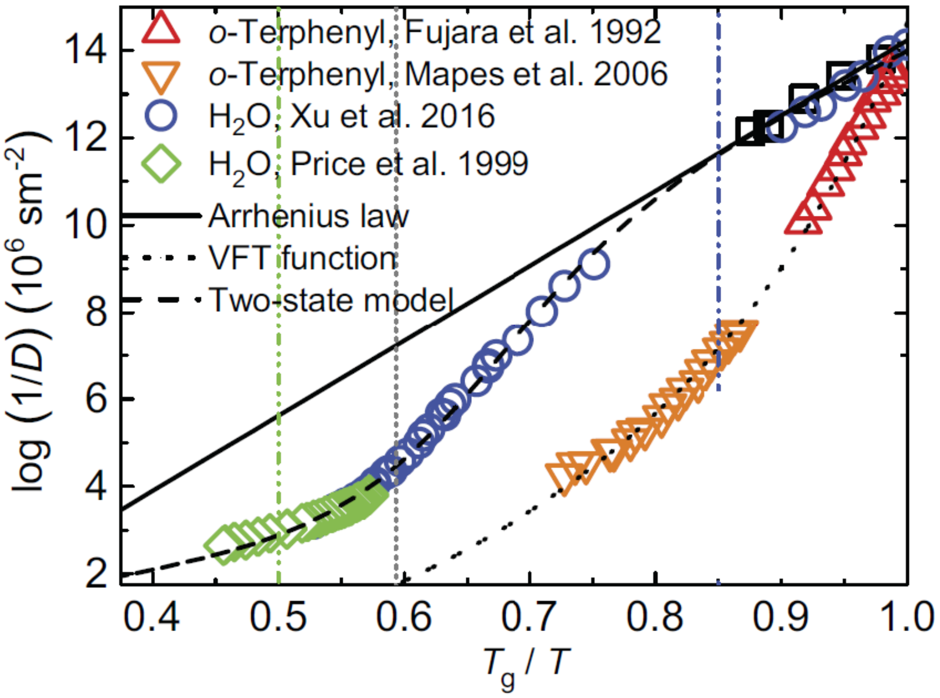
Dynamical crossovers

Angell's classification of glass-formers



Debenedetti & Stillinger Nature, 2001

Fragile to strong dynamical crossover



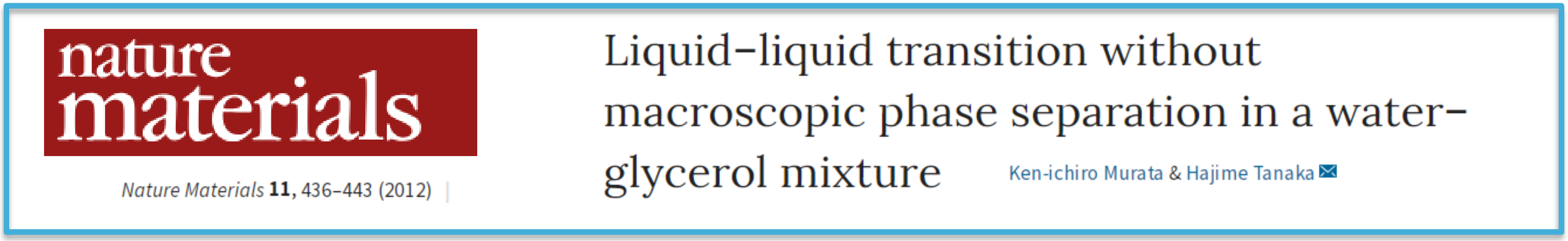
Shi, Russo & Tanaka PNAS, 2018

Fragile-to-strong-crossover and LLTs

Fragile-to-strong transition and polyamorphism in the energy landscape of liquid silica

Ivan Saika-Voivod, Peter H. Poole & Francesco Sciortino

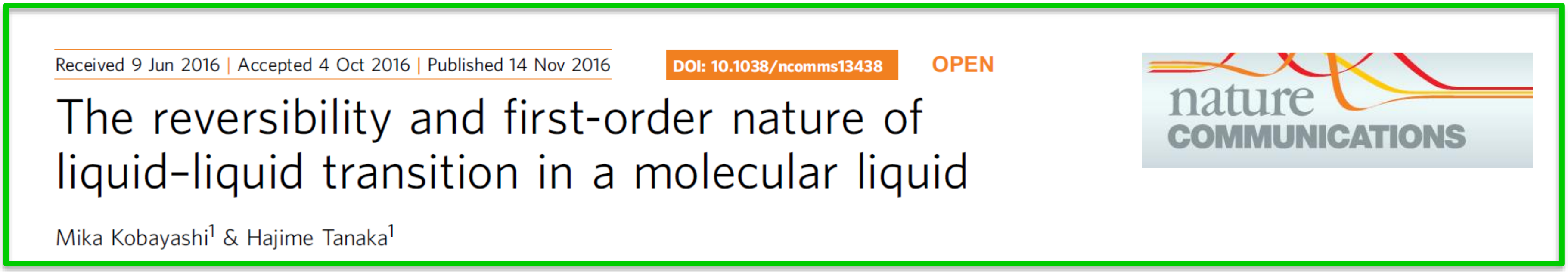
nature
International journal of science
Nature **412**, 514–517 (02 August 2001)



nature materials
Nature Materials **11**, 436–443 (2012)

Liquid–liquid transition without macroscopic phase separation in a water–glycerol mixture

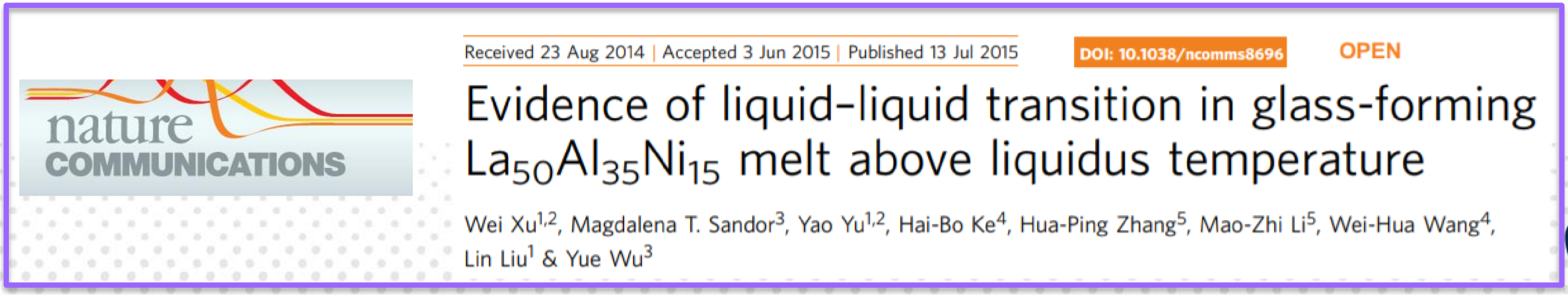
Ken-ichiro Murata & Hajime Tanaka



Received 9 Jun 2016 | Accepted 4 Oct 2016 | Published 14 Nov 2016
DOI: 10.1038/ncomms13438
OPEN
nature COMMUNICATIONS

The reversibility and first-order nature of liquid–liquid transition in a molecular liquid

Mika Kobayashi[1] & Hajime Tanaka[1]



nature COMMUNICATIONS
Received 23 Aug 2014 | Accepted 3 Jun 2015 | Published 13 Jul 2015
DOI: 10.1038/ncomms8696
OPEN

Evidence of liquid–liquid transition in glass-forming $La_{50}Al_{35}Ni_{15}$ melt above liquidus temperature

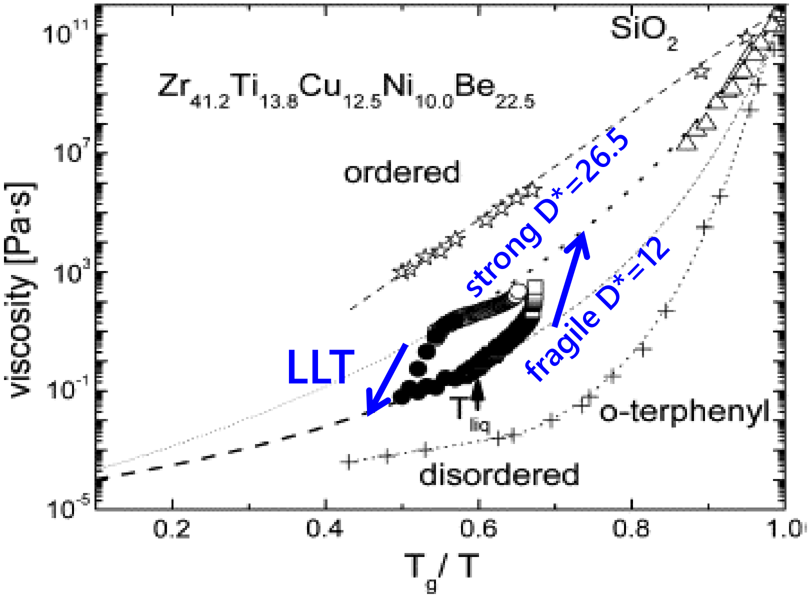
Wei Xu[1,2], Magdalena T. Sandor[3], Yao Yu[1,2], Hai-Bo Ke[4], Hua-Ping Zhang[5], Mao-Zhi Li[5], Wei-Hua Wang[4], Lin Liu[1] & Yue Wu[3]

Fragile-to-strong-crossover and Liquid-Liquid transition

kinetics

2-order of magnitude hysteresis in viscosity

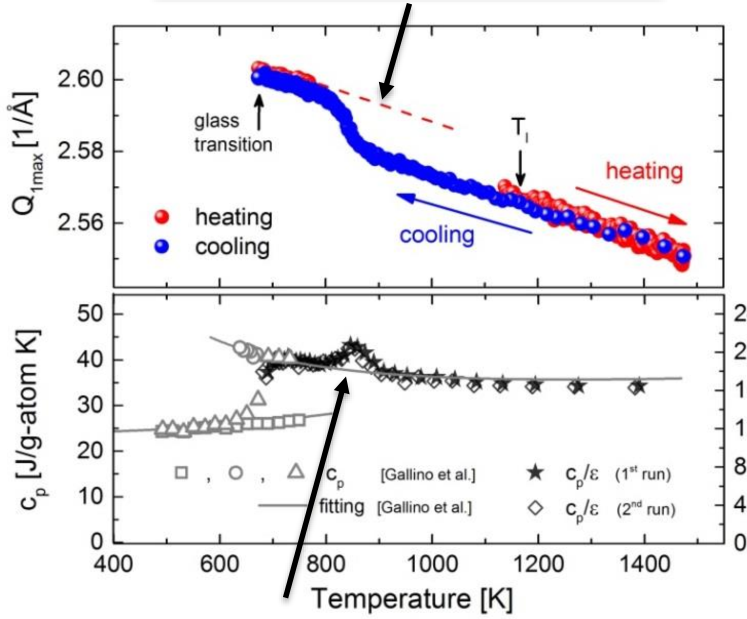
change in fragility: D* = 12 ←→ D* = 26.5



C. Way, P. Wadhwa, R. Busch, Acta Mater. 2007

structure

Discontinuities in total structure factor S(Q)



thermodynamics

Peak-like anomalies in heat capacity

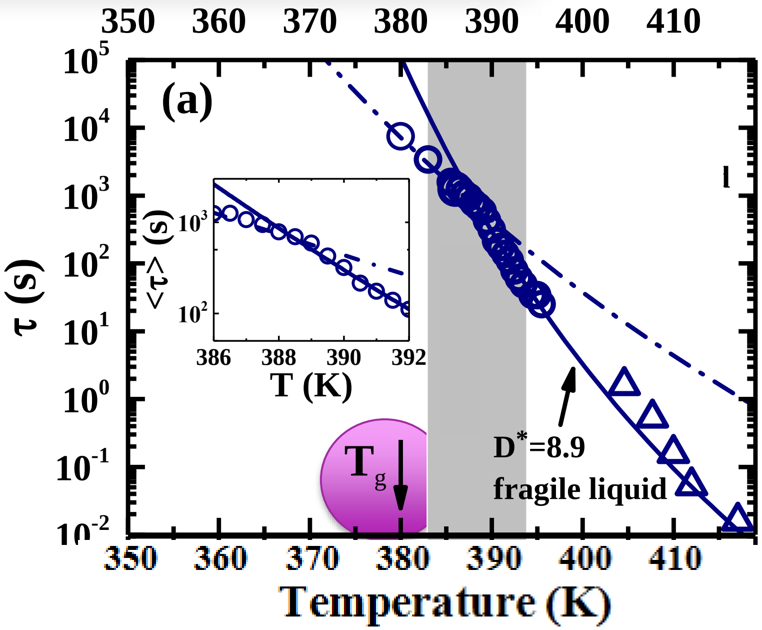
Stolpe/ Busch Phys. Rev. B 2016

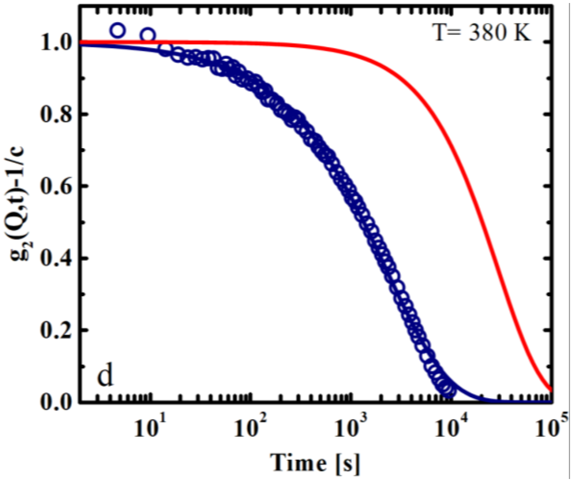
Courtesy of R. Busch

The supercooled liquid phase (XPCS+DMA)

$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$

$Q=2.78$ Å^{-1}





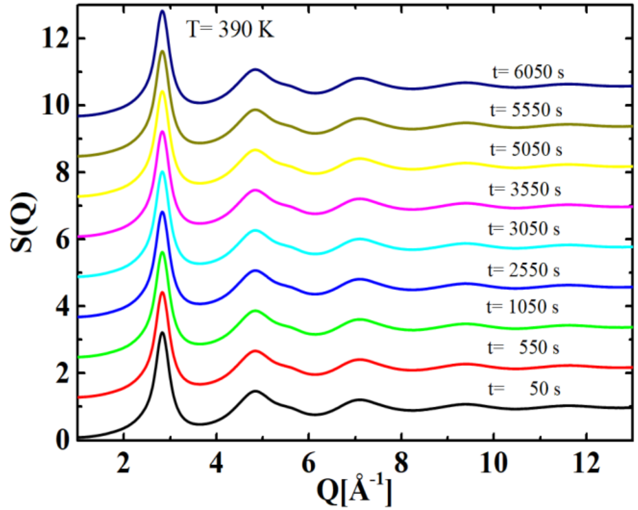
Glass transition?

- Expected T_g is 10 K lower
- Aging only at expected T_g
- Stretched correl. functions
- Steep temperature dependence

S. Hechler, et al. Phys. Rev. Mat. (2018)

The supercooled liquid phase (XRD)

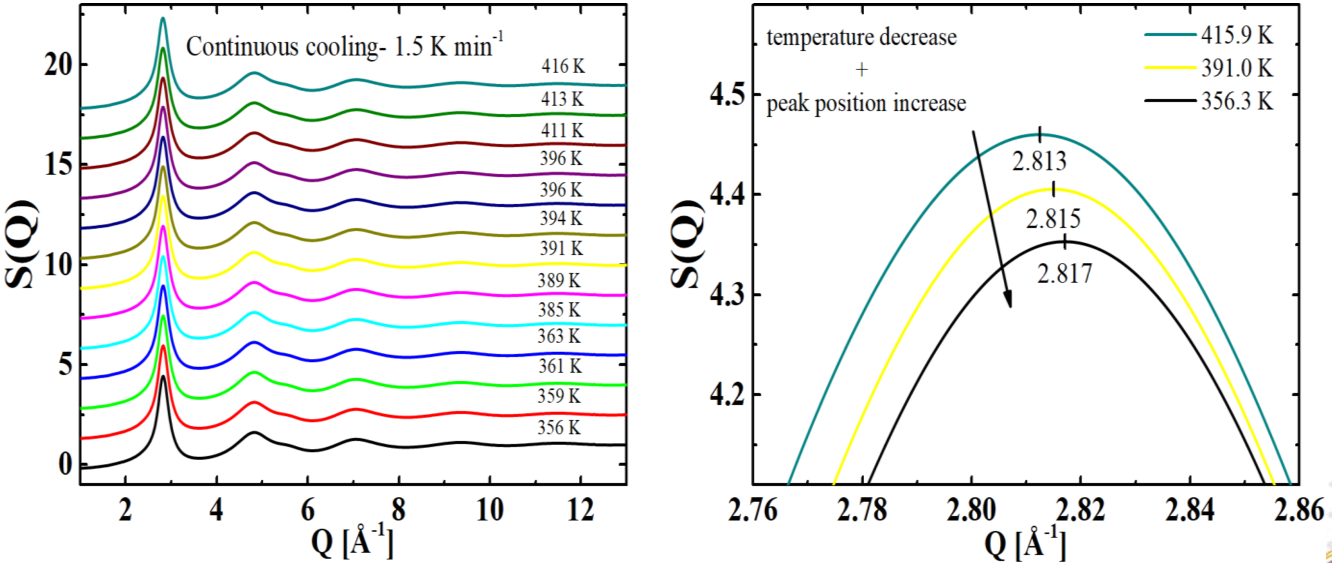
T-step with long isotherms



2 XRD experiments

- Same thermal protocol as XPCS
- Continuous cooling with 1.5 K/min

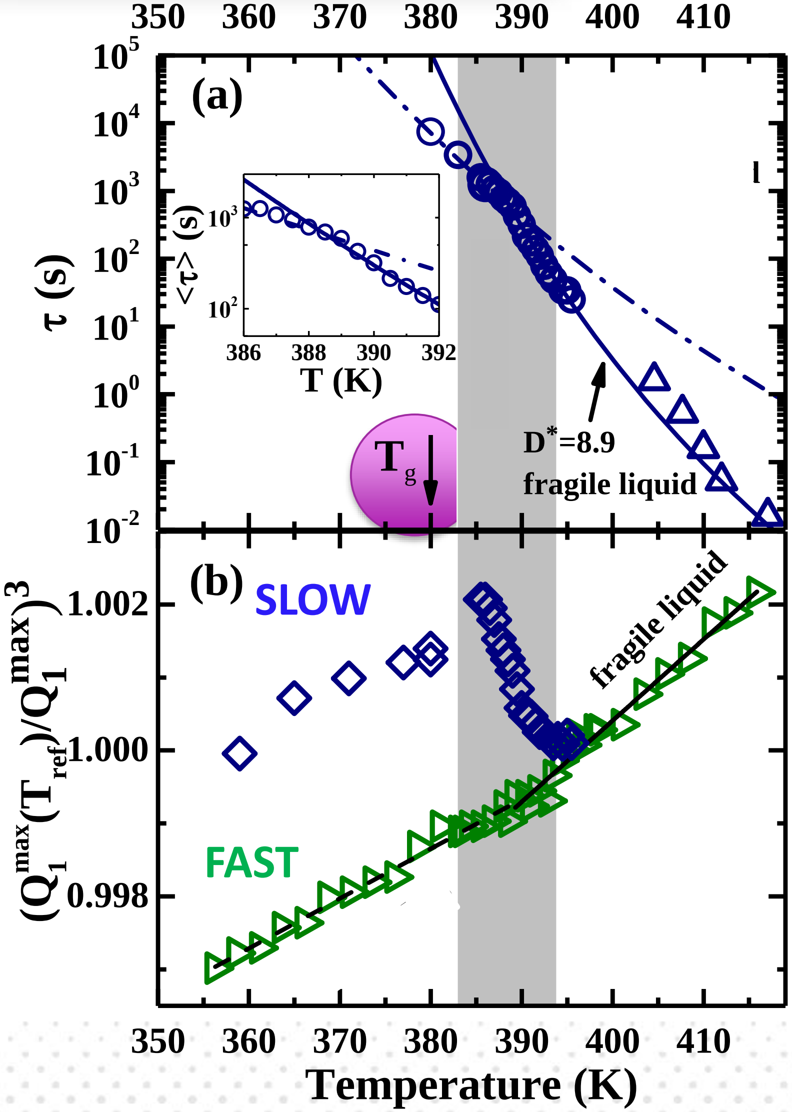
Continuous cooling



S. Hechler, et al. Phys. Rev. Mat. (2018)

The supercooled liquid phase (XPCS+DMA+XRD)

$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$

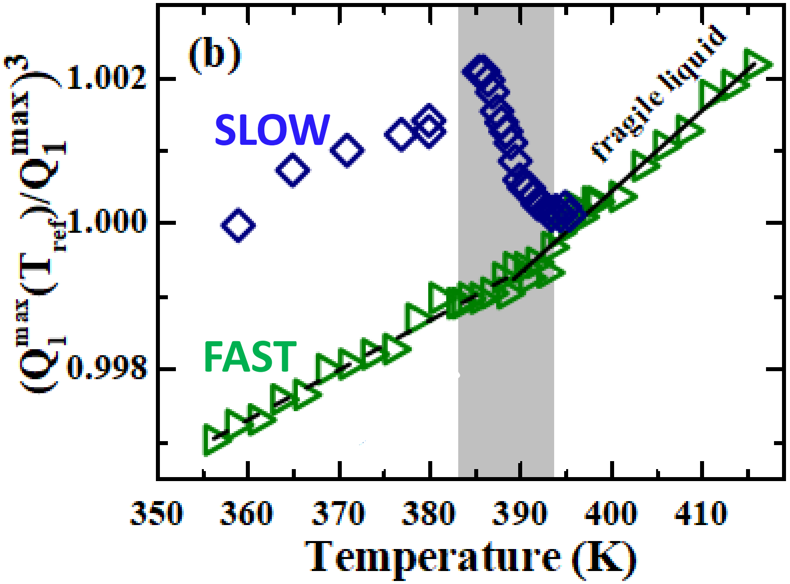


Occurrence of important structural rearrangements which cannot be associated to the glass transition

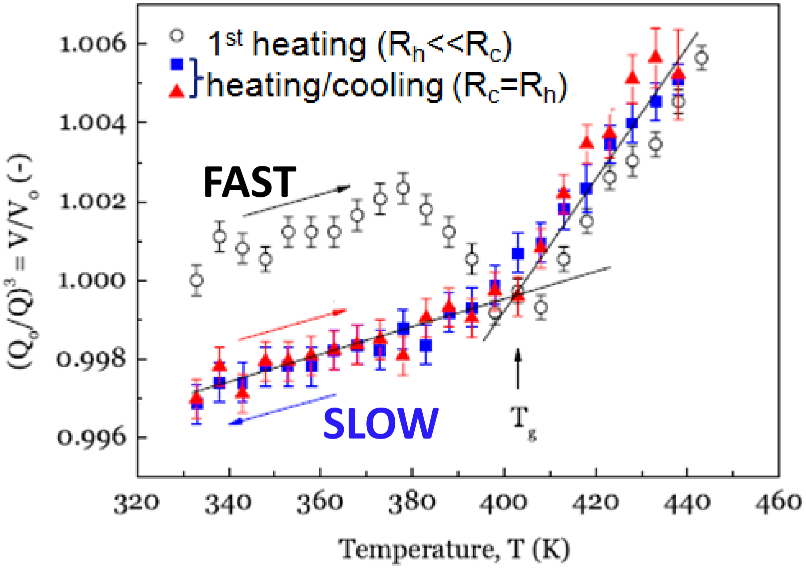
S. Hechler, et al. Phys. Rev. Mat. (2018)

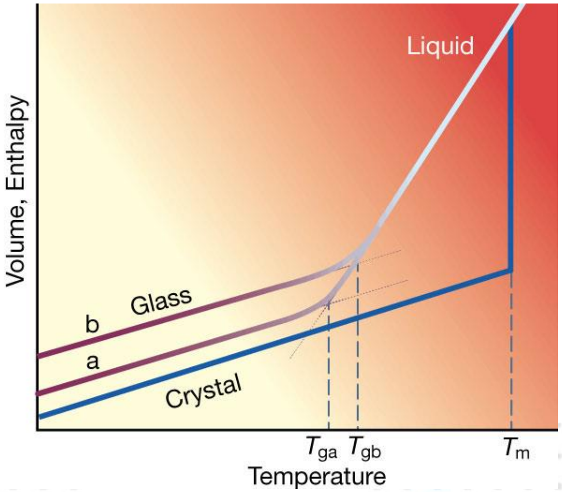
The liquid-liquid transition

$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$



J. Bednarcik et al, J. All. Compd. 2010





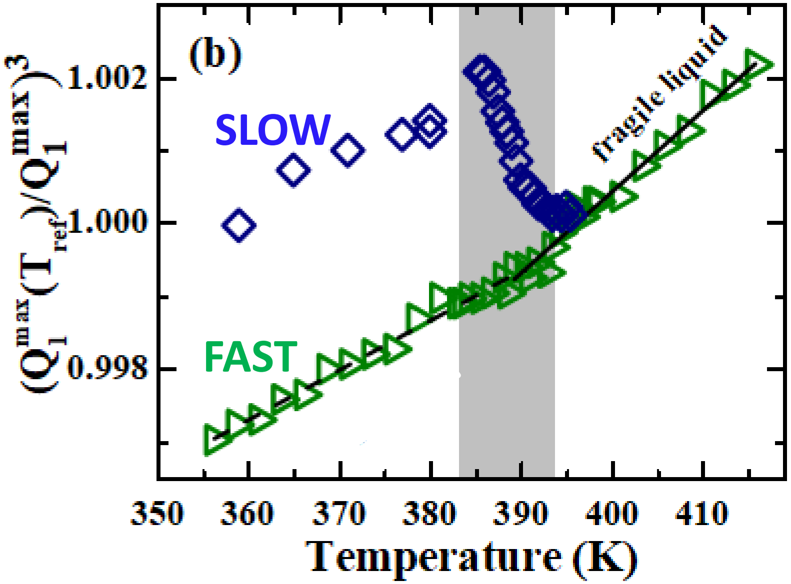
$Q = 0.1$ K/min: $1/Q^3 \neq V$

$Q = 1.5$ K/min: $1/Q^3 \approx V$

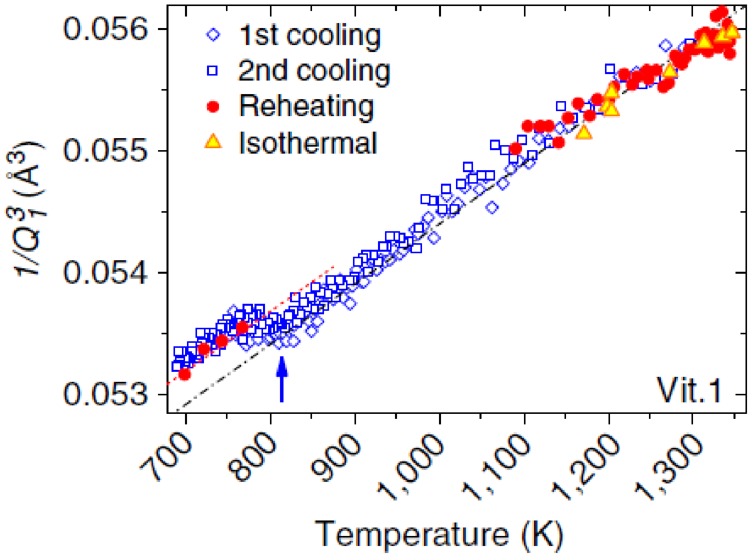
S. Hechler, et al. Phys. Rev. Mat. (2018)

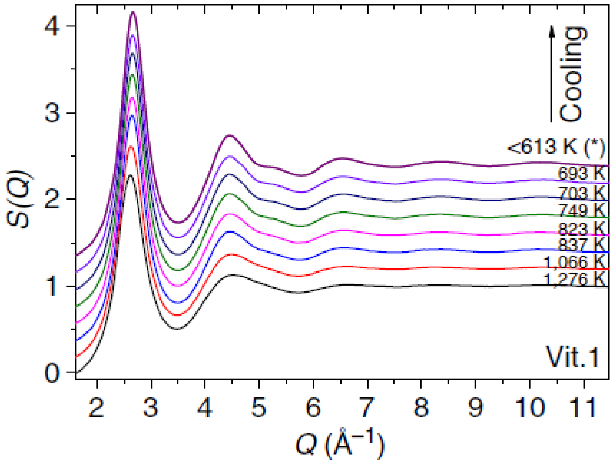
The liquid-liquid transition

$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$



S. Wei et al, Nat. Commun. 2013





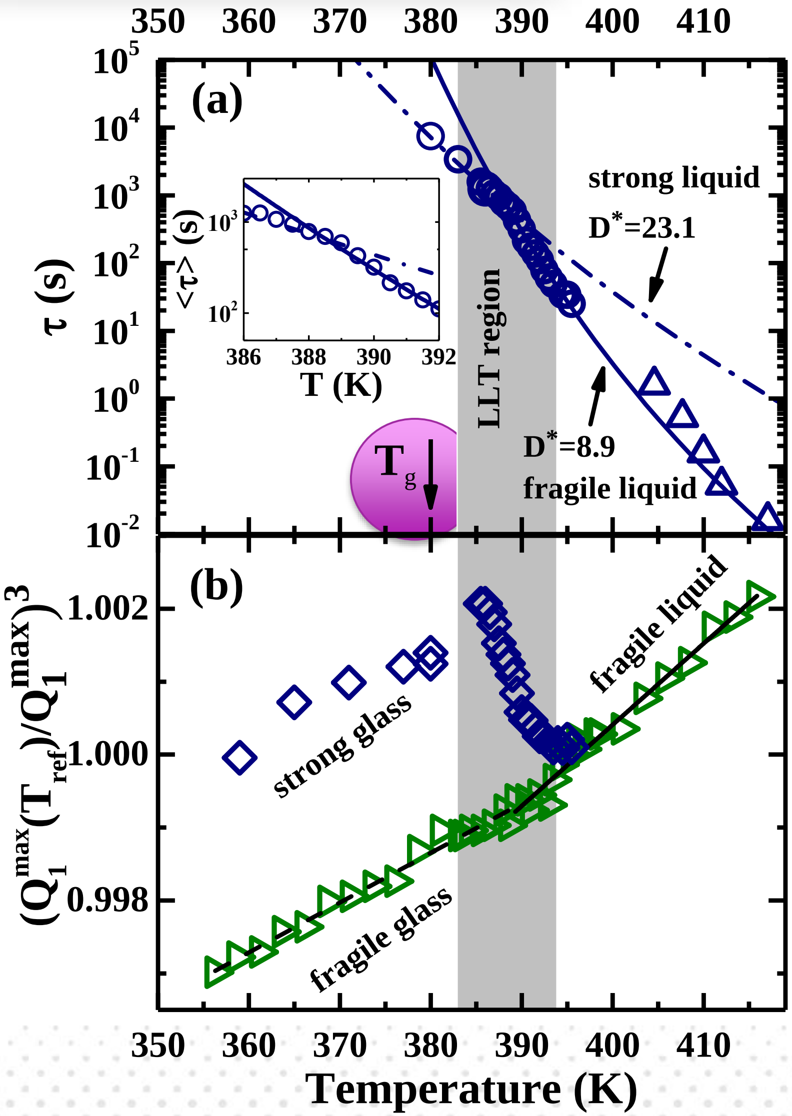
Q= 0.1 K/min: $1/Q^3 \neq V$

Q= 1.5 K/min: $1/Q^3 \approx V$

S. Hechler, et al. Phys. Rev. Mat. (2018)

Fragile-to-strong liquid-liquid transition

$Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$



The LLT is accompanied by a **fragile-to-strong dynamical crossover** and a surprising shifting of the main peak of the S(Q) to lower Qs (increasing 1/Q)

The glass transition is the dominant process at faster cooling rates

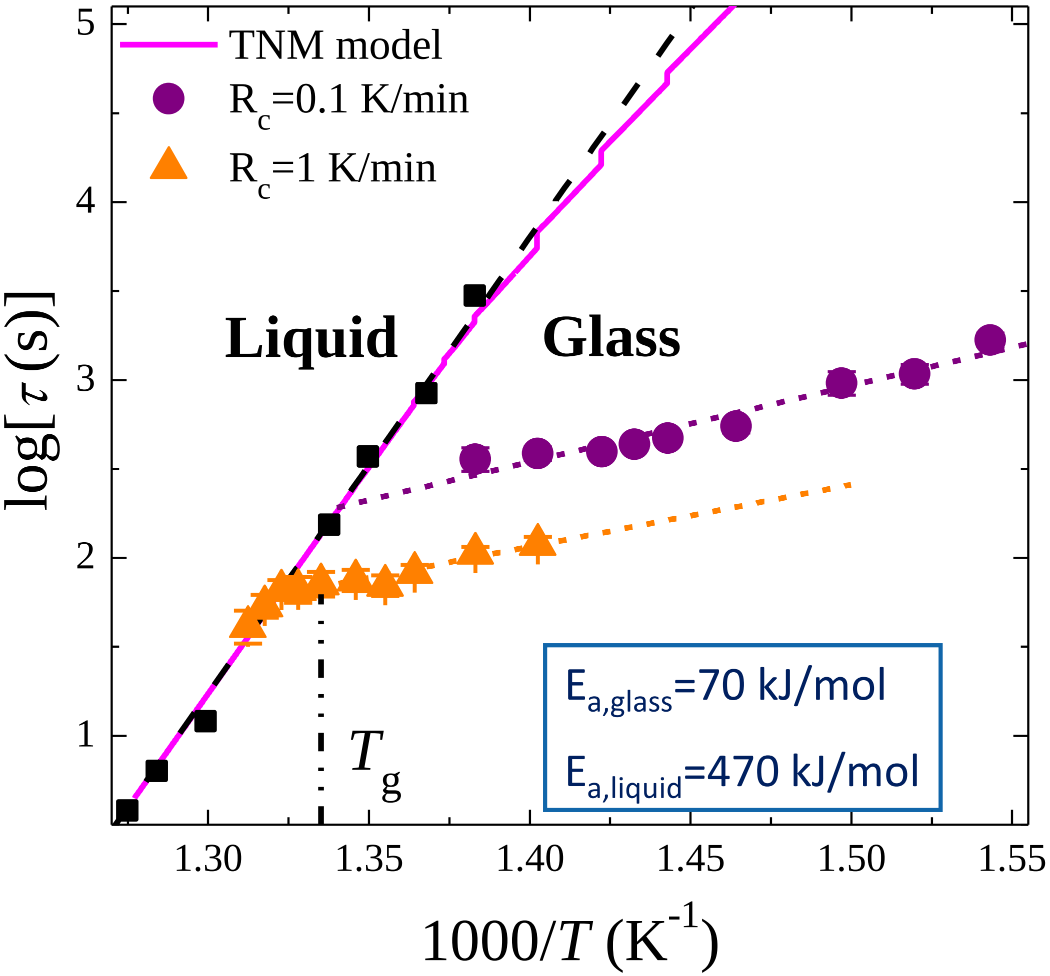
S. Hechler, et al. Phys. Rev. Mat. (2018)

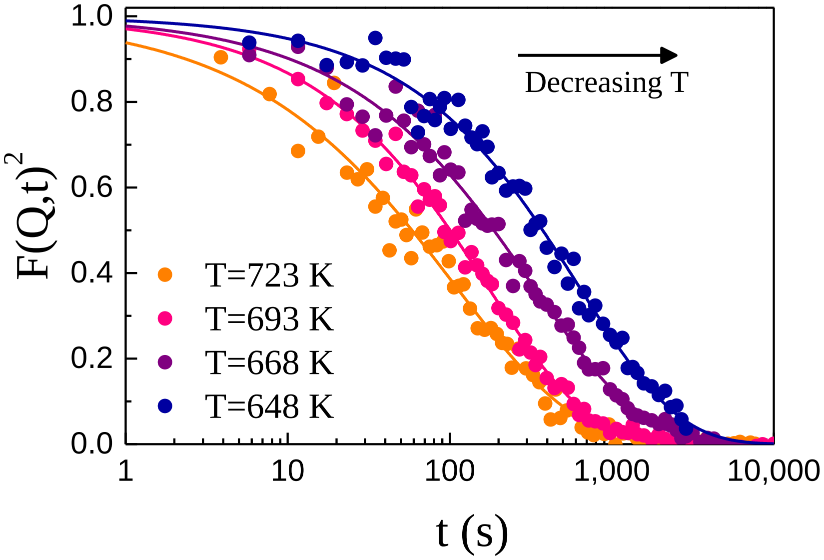
Outline

- ☐ Coherent X-rays and X-ray Photon Correlation Spectroscopy
- ☐ Glassy systems
  - ☐ Atomic motion in metallic glass formers
  - ☐ Dynamics in oxide and silicates glasses
- ☐ The EBS-ESRF upgrade
- ☐ New scientific opportunities

$0.8SiO_2$-$0.2Na_2O$ (NS4, T_g=783 K)

Q_{max}=1.53 Å^{-1}

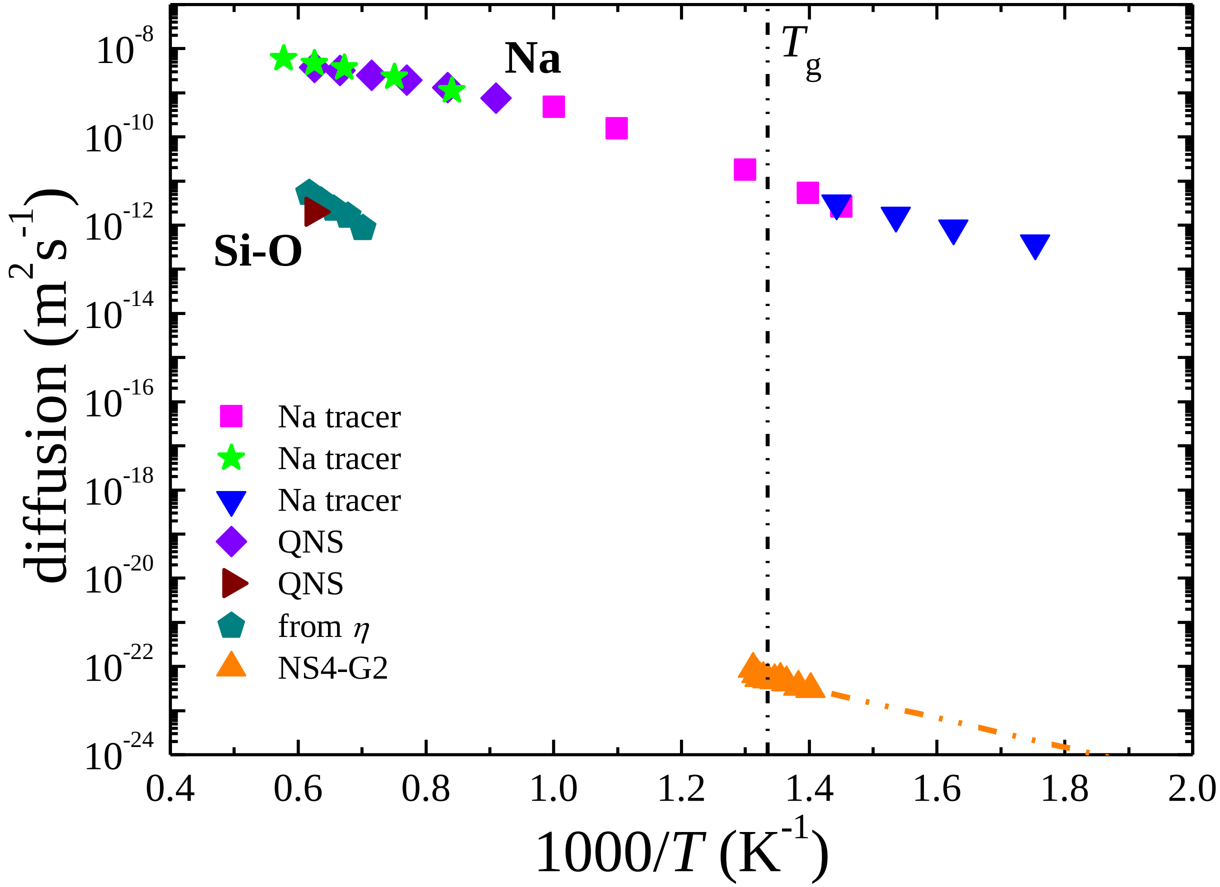




The correlation functions decay in a stretched exponential way as in the liquid phase (β=0.67)

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

Comparison with diffusion data



XPCS data :

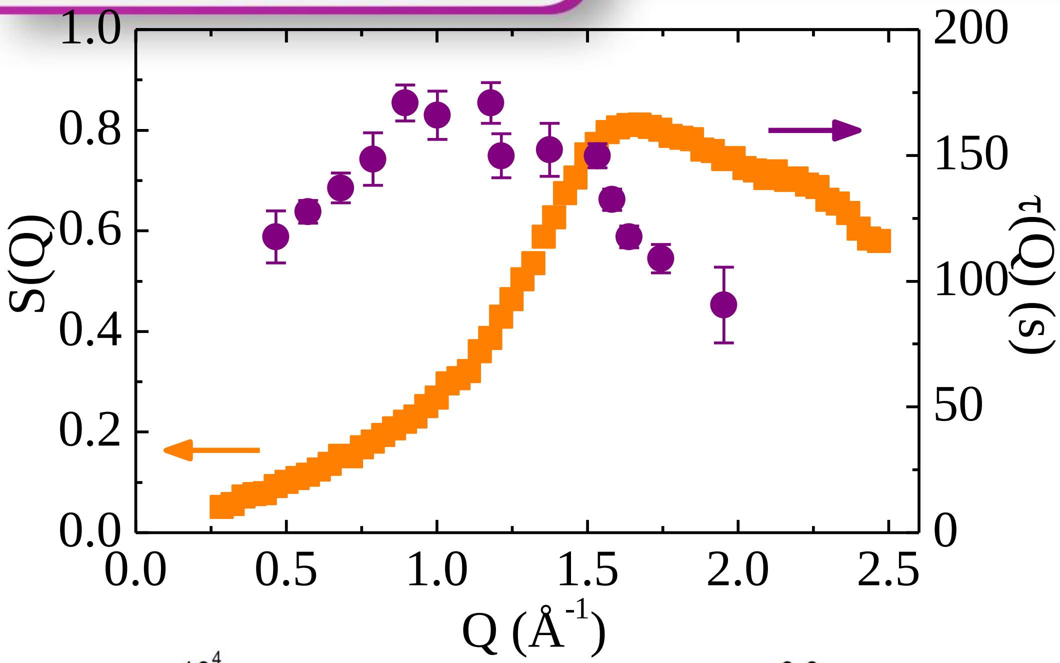
- ❑ ~10 orders of magnitude slower than the Na diffusion
- ❑ Closer to the low T extrapolation of the Si-O matrix

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

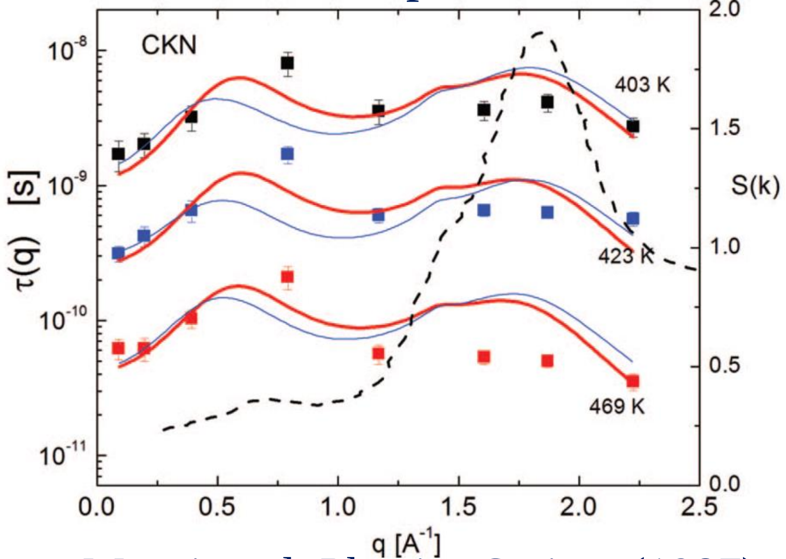
$$\tau_{incoh} = \tau_{XPCS} / S(Q)$$

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

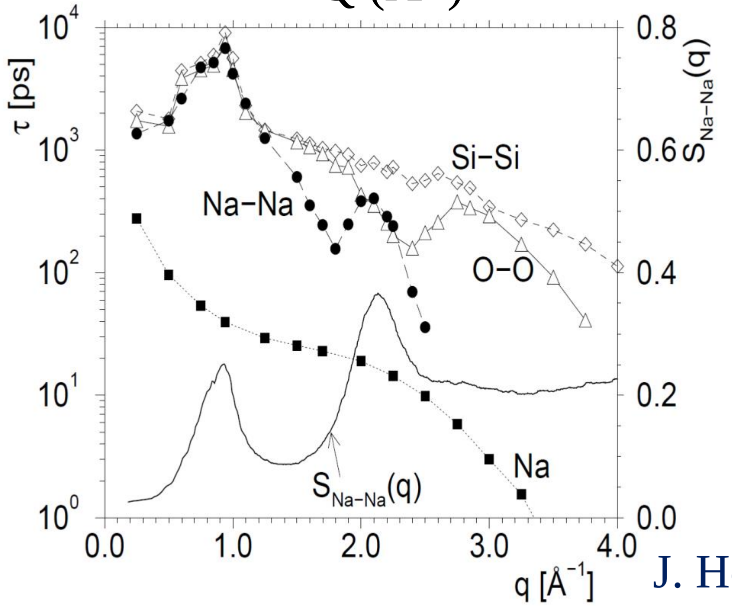
Wave vector dependence



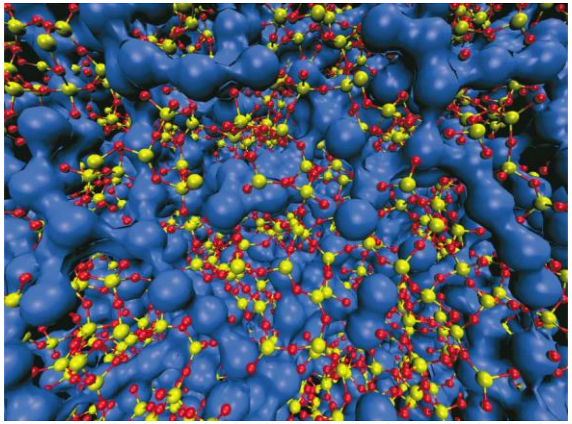
QNS data of supercooled CKN



Mezei et al, Physica Scripta (1987)



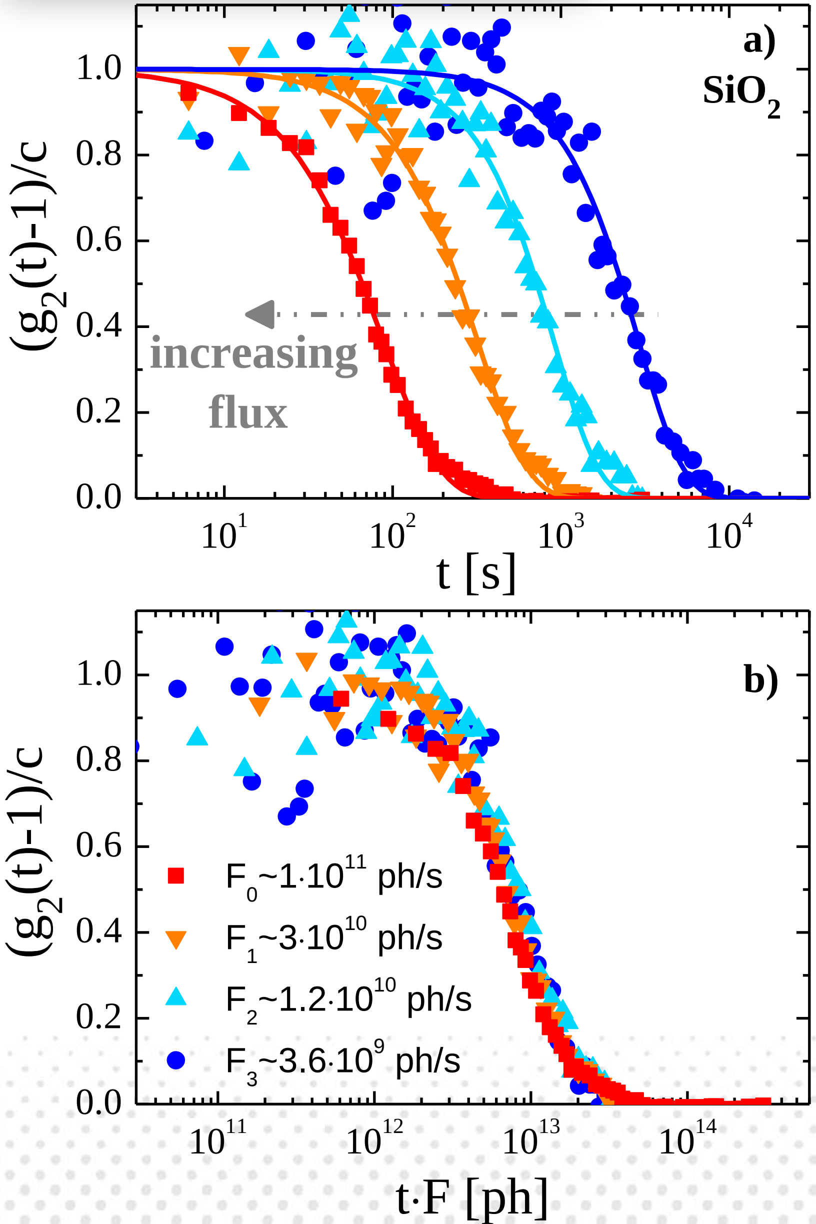
J. Horbach et al, Phys. Rev. Lett. (2002)



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

Dynamics of oxide glasses

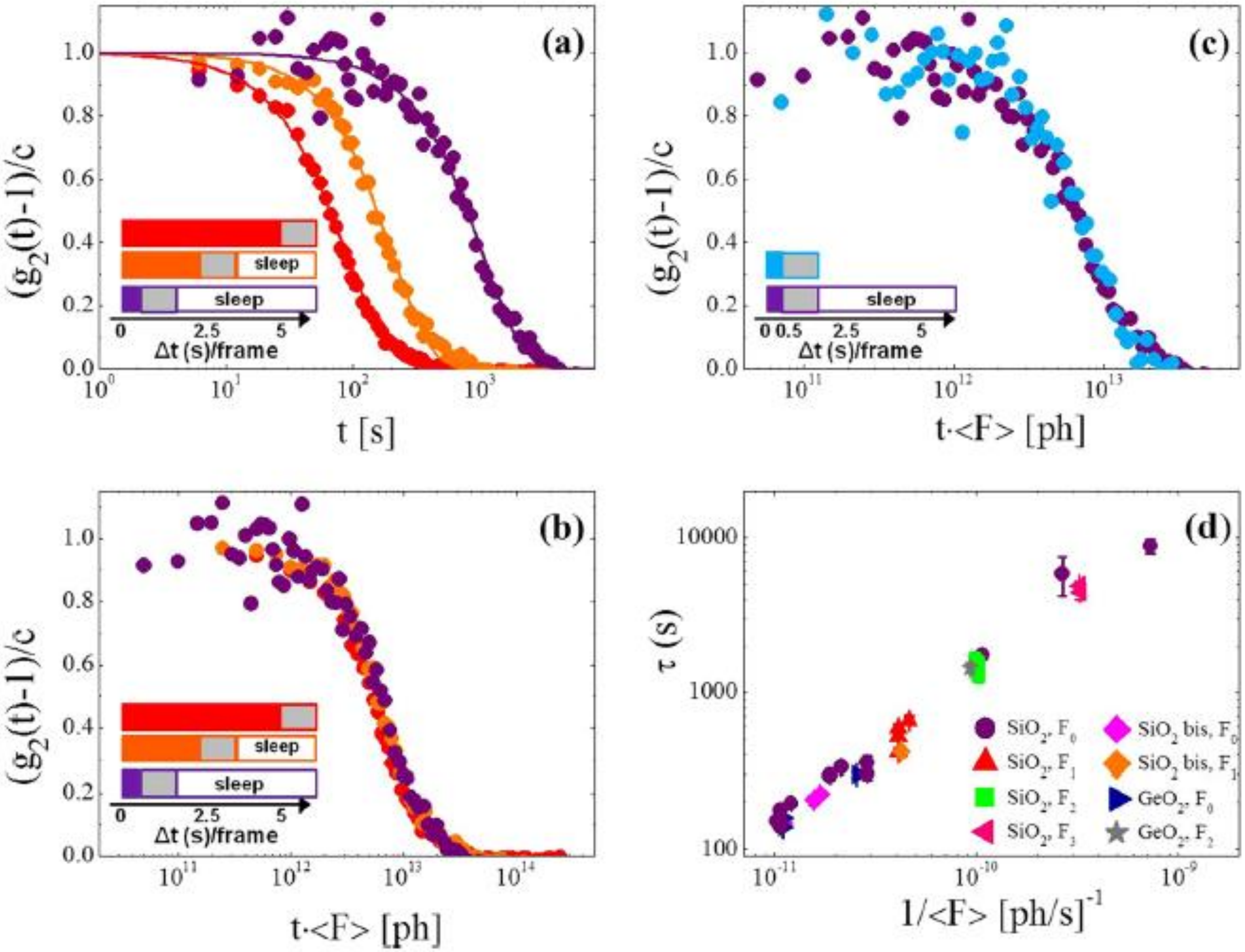
Irradiation-driven dynamics in SiO_2 at low temperature



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

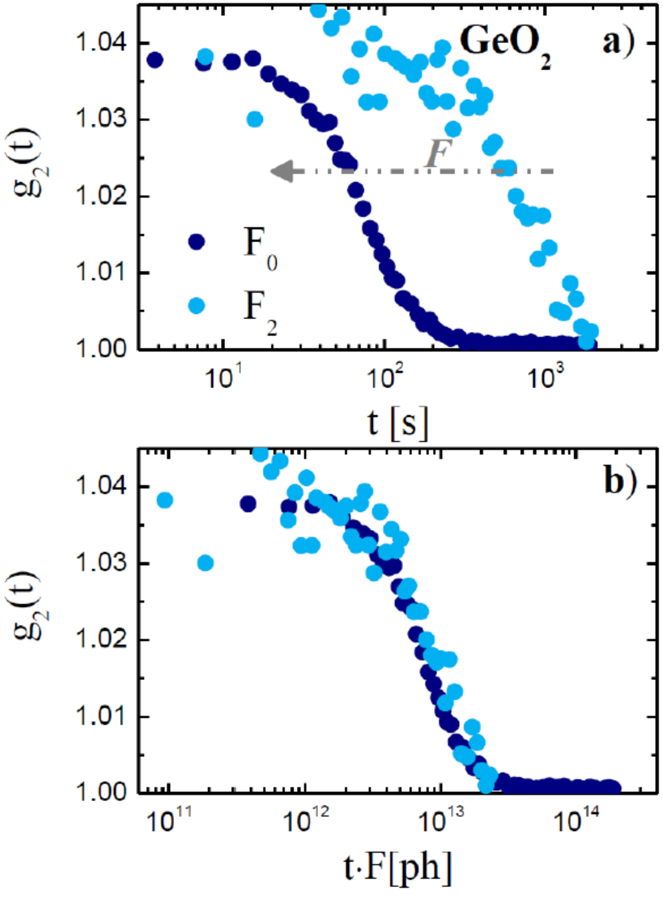
By varying appropriately the average incoming flux (flux, exposure time, delay time) is possible to tune “at will” the dynamics

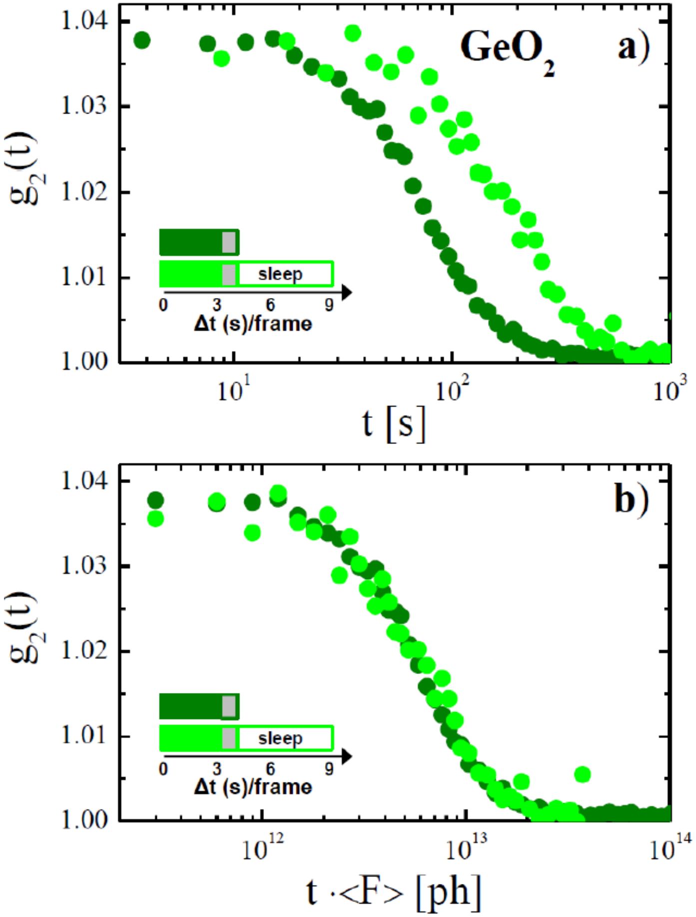
Irradiation-driven dynamics in SiO_2 at low temperature



B. Ruta et al. Scient. Report (2017)

Same induced dynamics in GeO$_2$ at low temperature

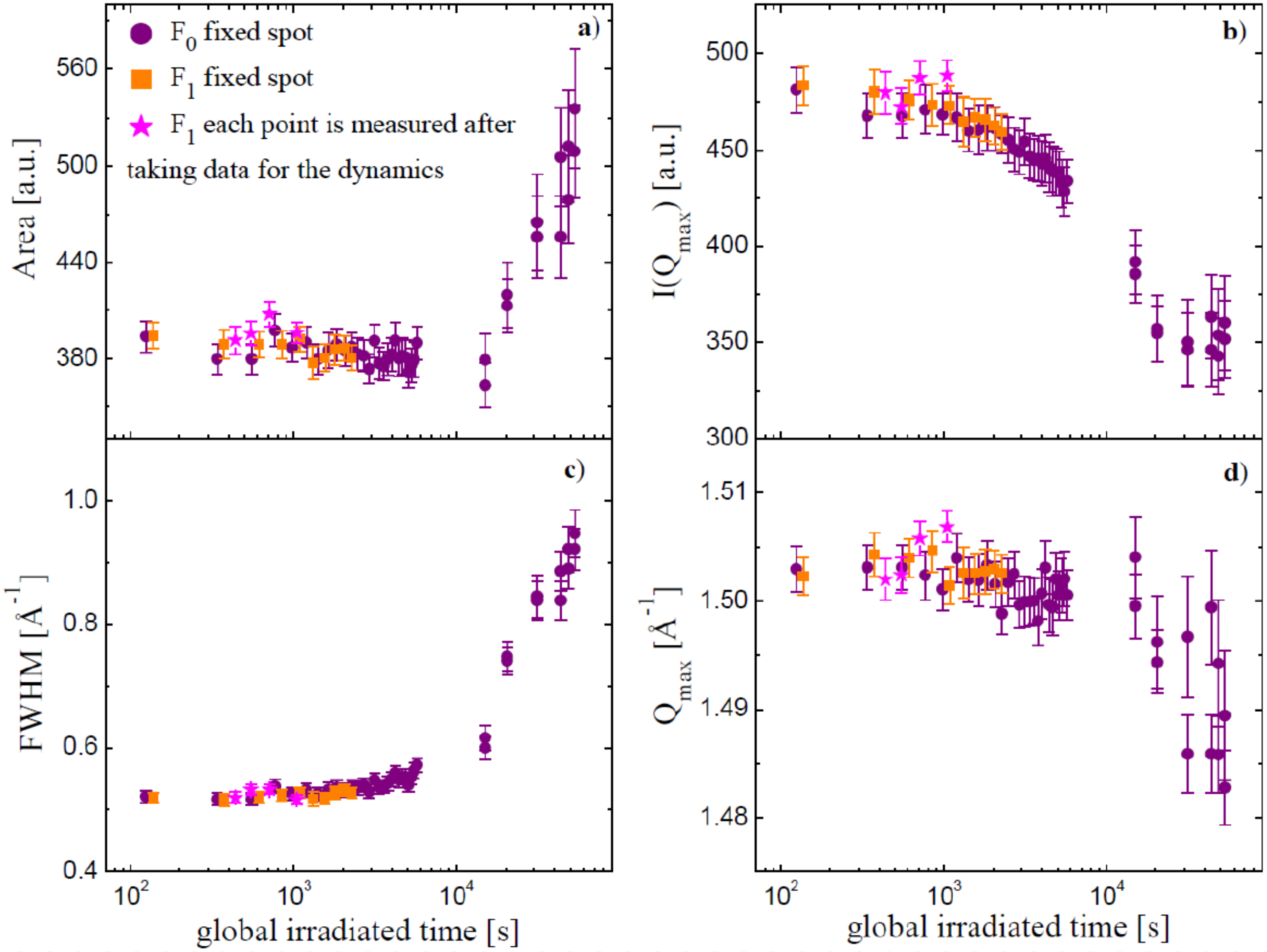




B. Ruta et al. Scient. Report (2017)

No radiation damage

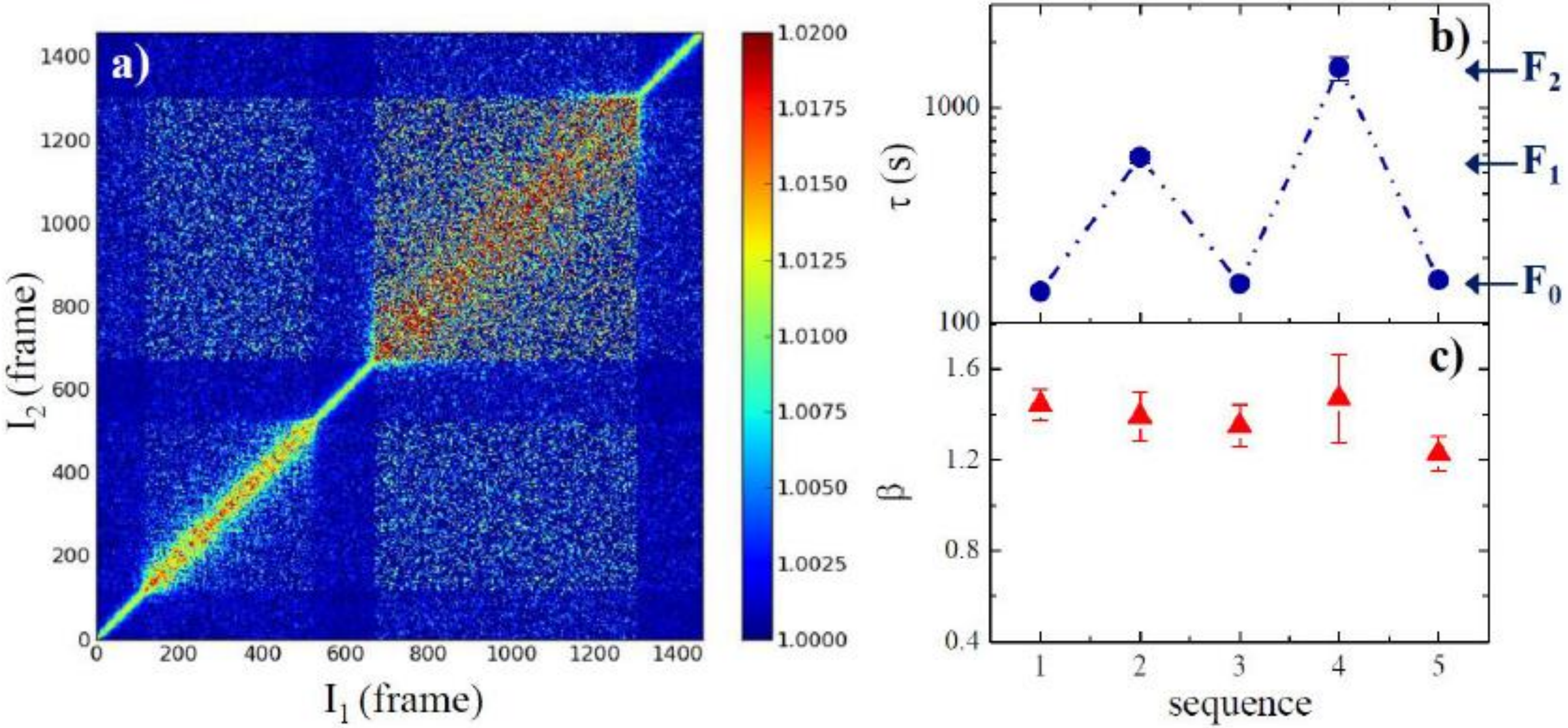
SiO_2



B. Ruta et al. Scient. Report (2017)

Reversible process

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



B. Ruta et al. Scient. Report (2017)

X-rays & Hard matter

Three main processes:

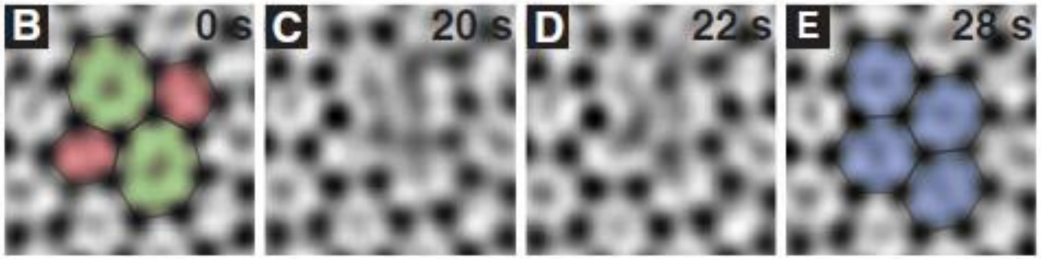
- **Knock-on events** → require high energy to break bonds
- **Electronic rearrangements** → require pre-existing defects
- **Radiolysis** → require lifetime of the excitation ~ vibrations ~1ps → **possible**

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

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 SiO_2

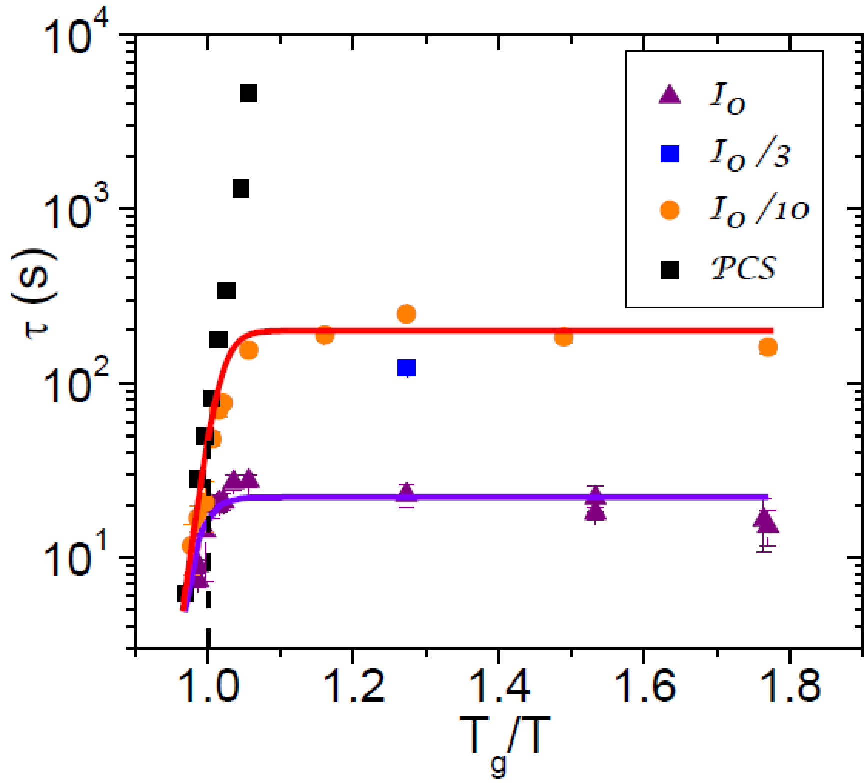


Huang et al. Science (2013)

B. Ruta et al. Scient. Report (2017)

Temperature dependence of the induced dynamics

v-B_2O_3



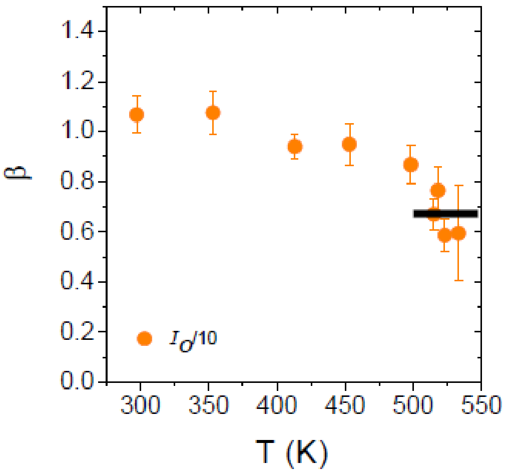
T_g = 526 K

The τ_α and τ_X seem independent:

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

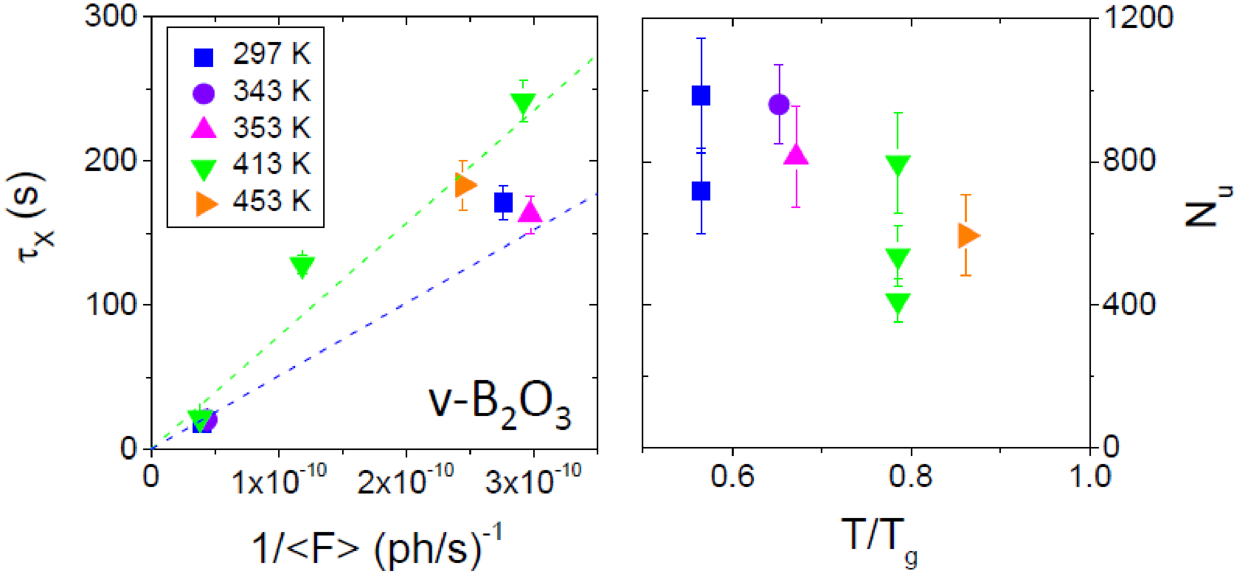
Structural rel. time

Beam induced decorrelation



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

Temperature dependence of the induced dynamics



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 et al. Phys. Rev. B (2019)

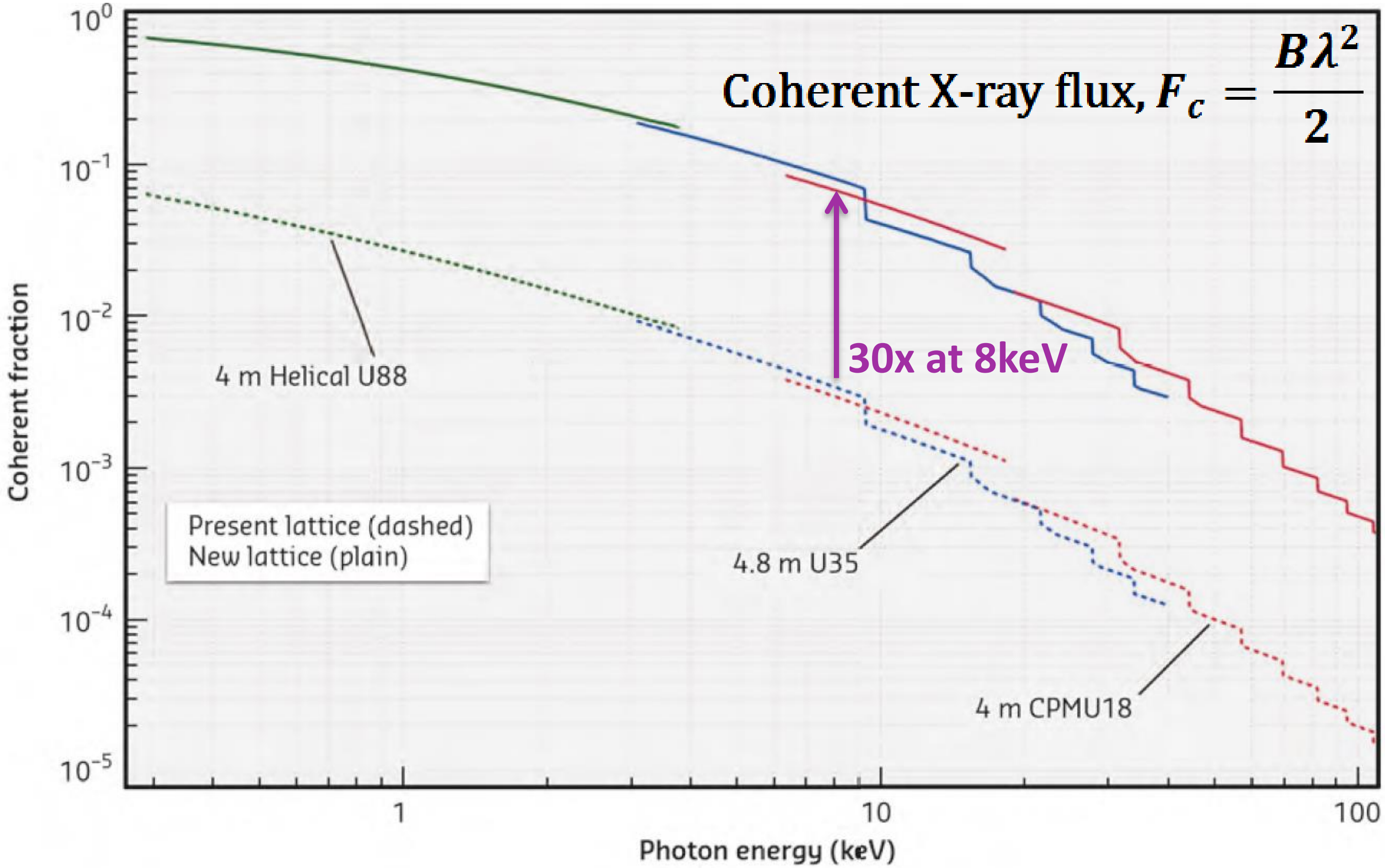
Outline

- ☐ Coherent X-rays and X-ray Photon Correlation Spectroscopy
- ☐ Glassy systems
  - ☐ Atomic motion in metallic glass formers
  - ☐ Dynamics in oxide and silicates glasses
- ☐ The EBS-ESRF upgrade
- ☐ New scientific opportunities

The Extremely Brilliant Source upgrade

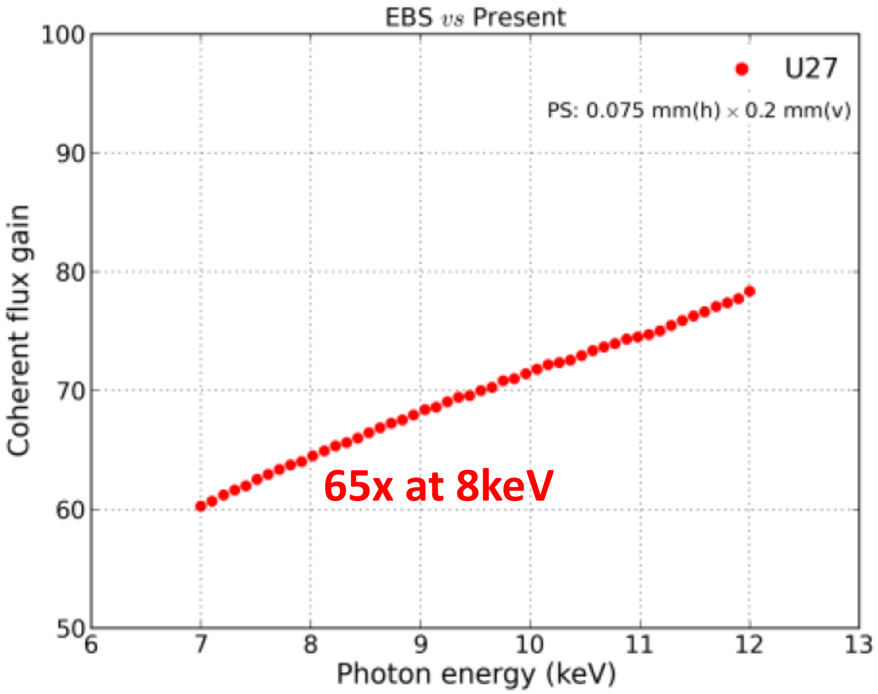
The Extremely Brilliant Source upgrade

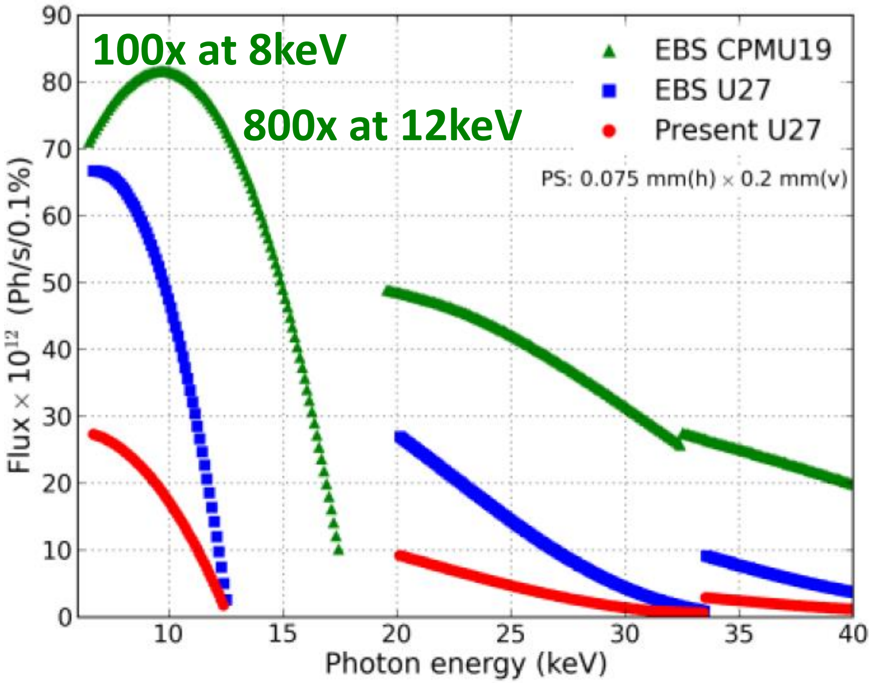
Coherence: a key feature of the EBS-ESRF upgrade



The Extremely Brilliant Source upgrade

The real gain at an undulator beamline as ID10





Huge gain for coherence-based techniques!

Courtesy of J. Chavanne, group head "Insertion Device & Magnets", ESRF

Main parameters for XPCS

Coherent X-ray flux $F_c = \frac{B\lambda^2}{2}$

Fastest time scale $\tau_{min} \propto \frac{1}{B^2}$

Signal to noise ratio $\propto B$

$$SNR \propto \langle I \rangle C \sqrt{\tau_{min} T N_{pix}}$$

XPCS at ESRF - EBS

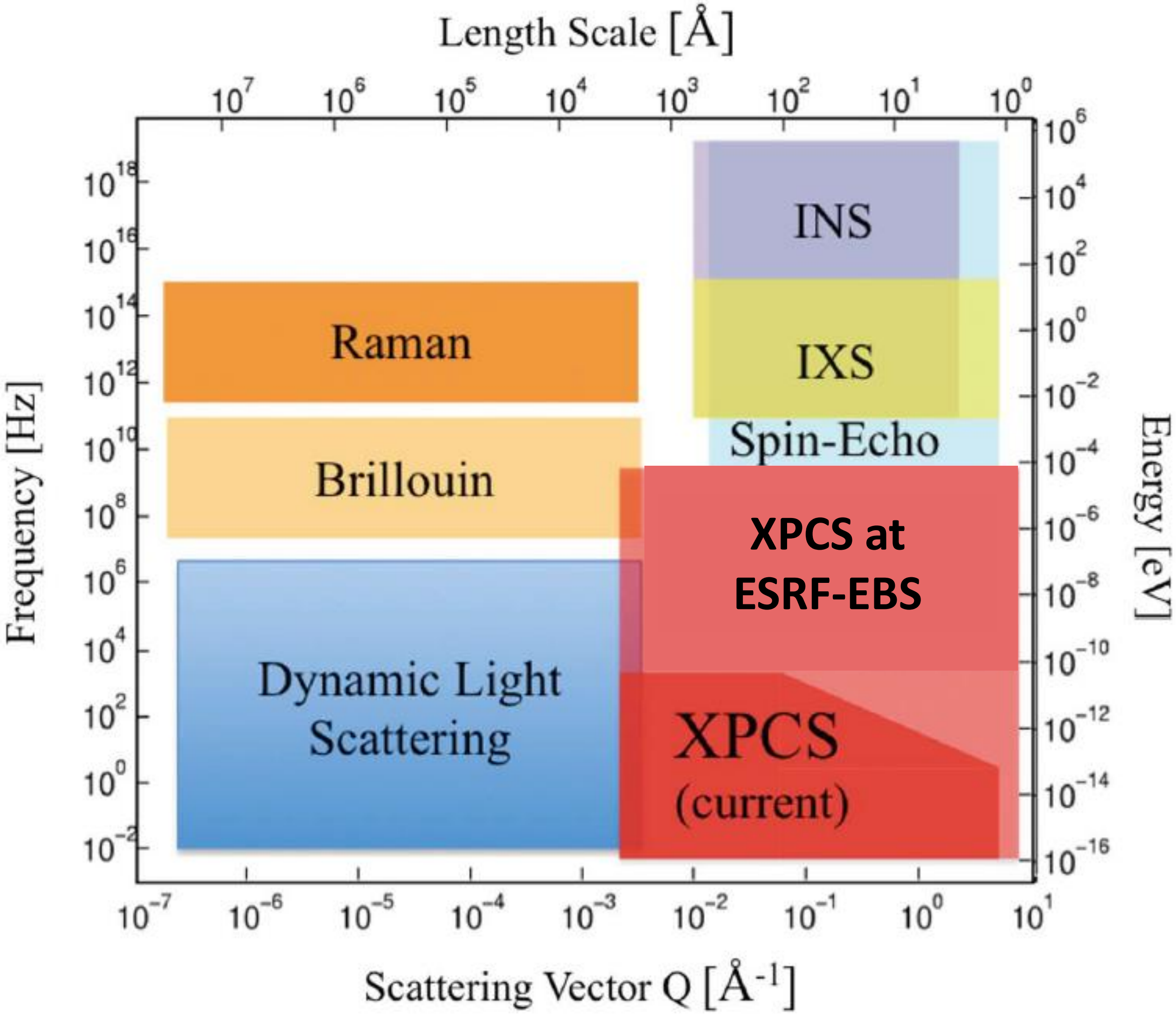
EBS-ESRF will break new ground for XPCS

- **Up to 10.000 times faster time scales**
- Up to 100 times larger signal to noise ratio
- Extension into hard x-rays beyond 10 keV

XPCS at ESRF - EBS

$\tau_{min} \approx 100$ ns
(now only ≈ ms)

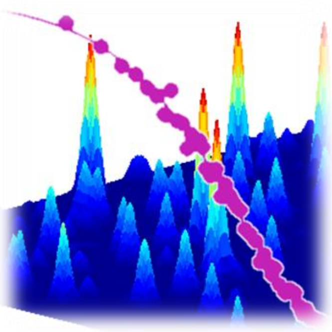
Energy: 6.5 - 35 keV
(now mainly at 8 keV)

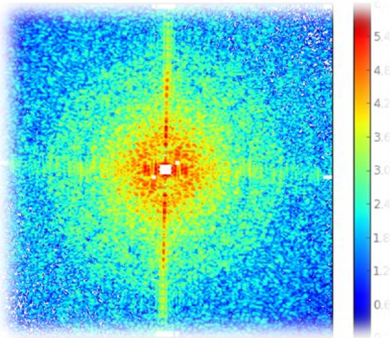


Adapted from O. Shpyrko J. Synch, Rad. 2014

EBS-L1: A new beamline for coherence based structural & dynamical studies

Approved by SAC in June 2017





Outline

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Dynamics of supercooled liquids

Theoretical models:
Discontinuous hopping of caged particles : β<1 & $\tau \approx q^{-1}$

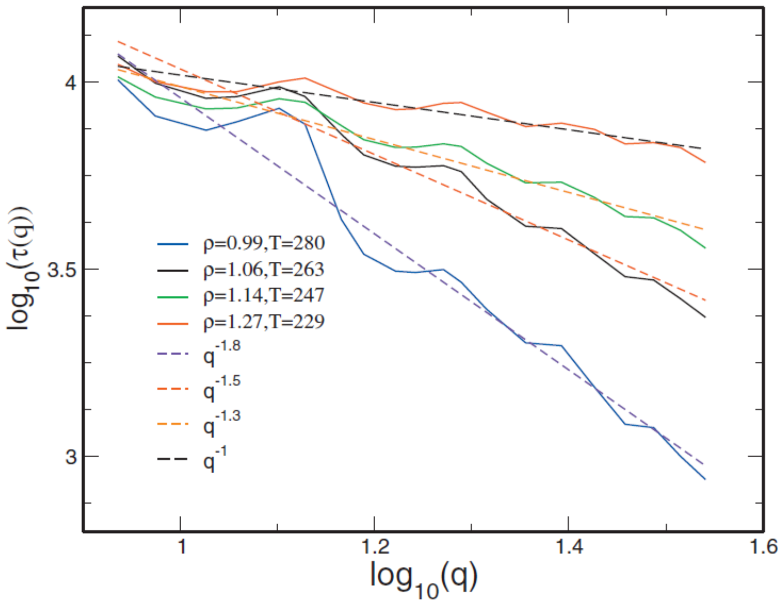
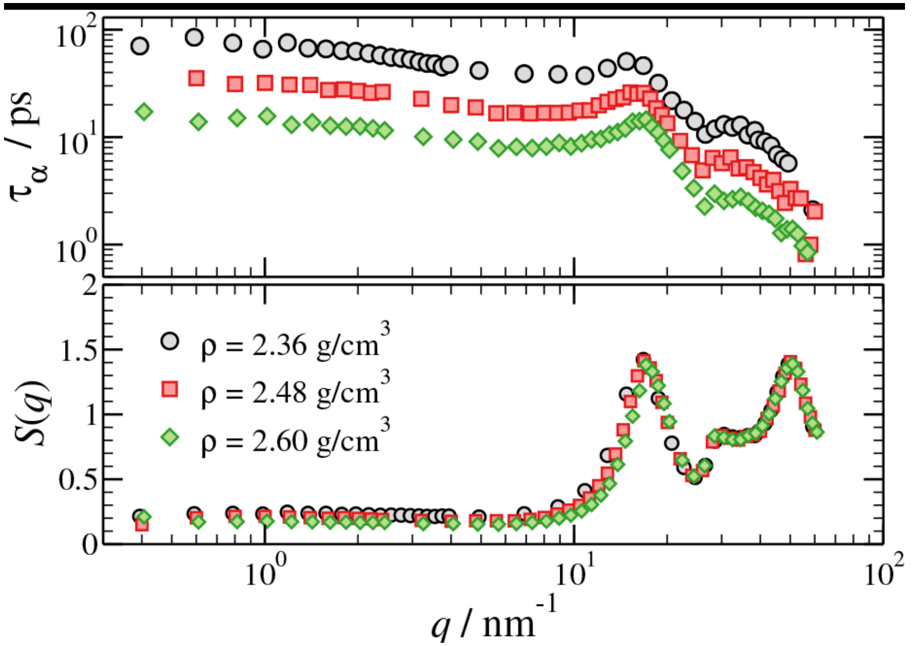


FIG. 1. The α relaxation timescale $\tau(q)$ plotted as a function of q at different densities and temperatures. The $\tau(q)$ values are scaled such that at q =8.6 they have similar values. $\tau(q)$ shows a weaker q dependence as the temperature is lowered.

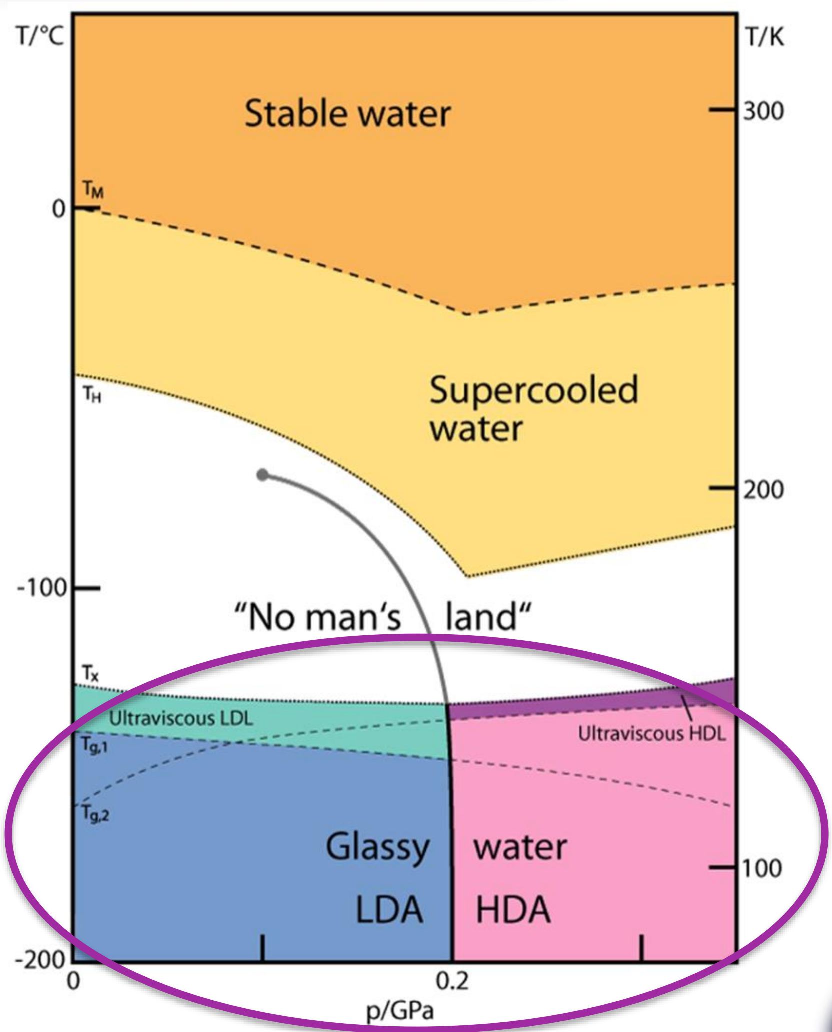
Batthacharryya et al. J. Chem. Phys. 2010

MD simulations of SiO_2:
No q-dependence <u>at low Qs</u> :
β<1 & τ constant



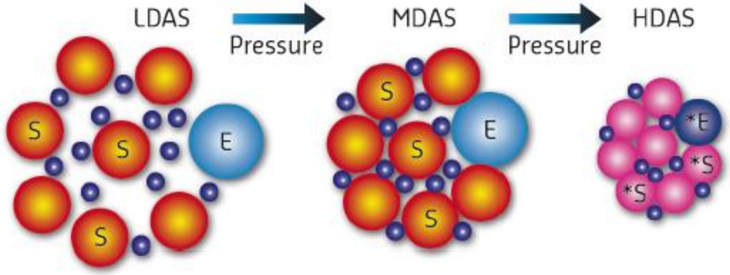
Handle et al. Phys. Rev. Lett. 2019

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

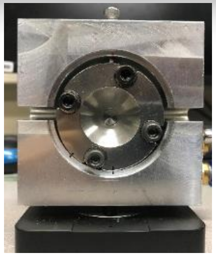
Nucleation in magmas

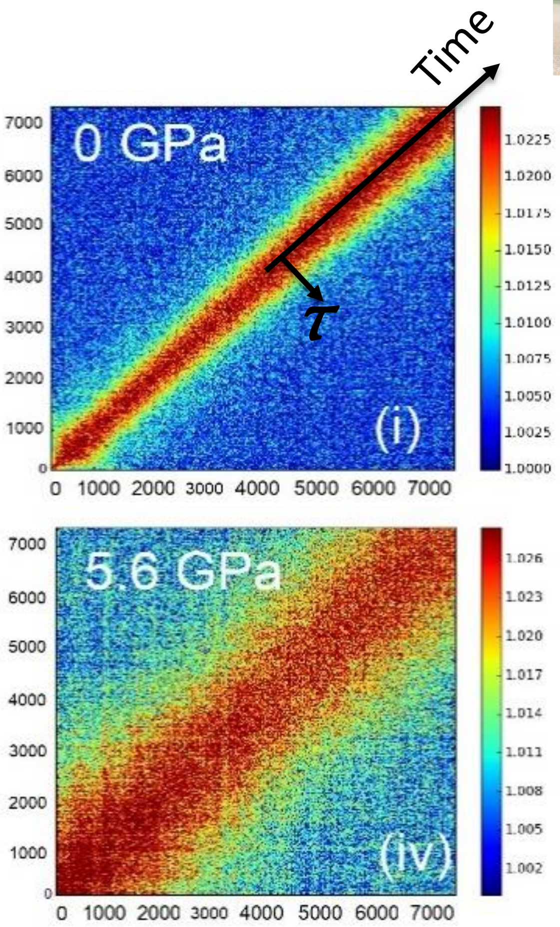
F. Vetere et al. Earth-Sci. Rev. 2015

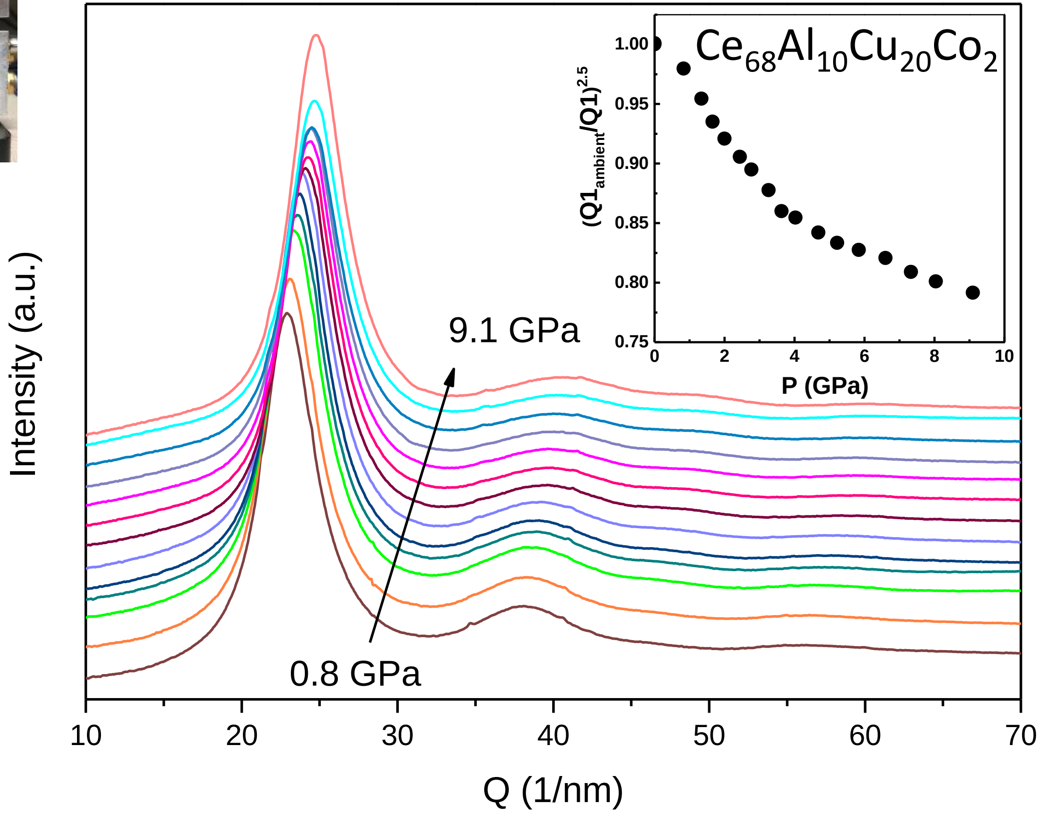
INSTITUT LUMIÈRE MATIÈRE

Dynamics of the polyamorphous Ce-based MG

XPCS @ 21 keV with a DAC







北京高压科学研究中心
HPSTAR
Center for High Pressure Science
& Technology Advanced Research

Lyon 1
CNRS

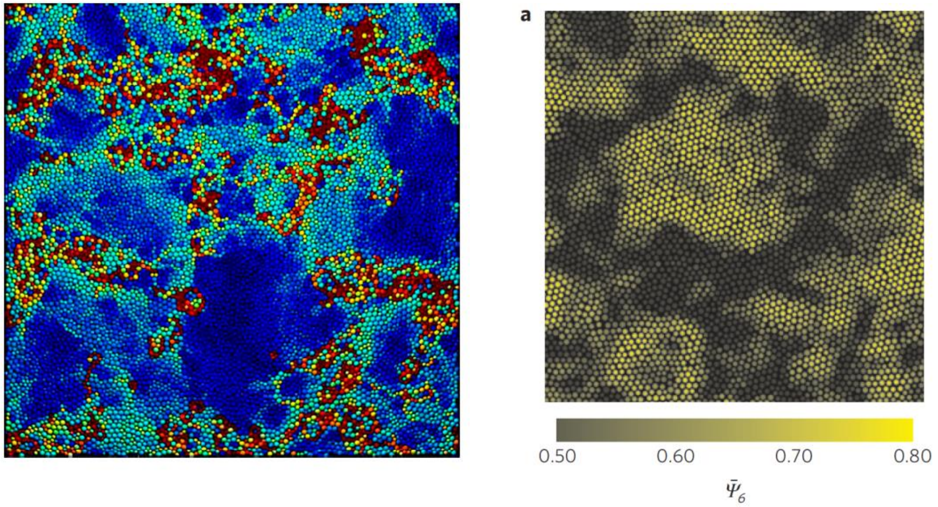
Intermittent correlations

- ***Dynamical heterogeneity*** are ubiquitous in nature
  - *Supercooled liquids and glasses*
  - *Domain fluctuations and avalanches in high-Tc superconductors and magnetic systems*
  - *Polymers and biomaterials*

ESRF - EBS:

1. *Dynamics from (sub-)µs to s*
2. *Length scales: from single particles to particle clusters*

J.P. Garrahan, PNAS (2011) H. Tanaka et al. Nat. Mat. 2010



Dynamical (left) and spatial (right) heterogeneity in simulations of 2D glass transitions

Courtesy of F. Lehmkühler, Desy, Hamburg, Germany

Take home message

- ☐ Coherent X-rays are a perfect tool to investigate the dynamics in supercooled liquids and glasses
- ☐ Dynamical crossover and anomalous stress-driven microscopic dynamics in metallic and several soft glasses
- ☐ Larger sensitivity of XPCS than structural techniques
- ☐ Perfect tool for measurements in operando conditions
- ☐ Tricky sample-radiation interactions

Thank you for your attention!

The future beamline EBS-L1

The 200 m long High-Energy "Speckles Factory"

Large coherent beams at high energy

Temporal or longitudinal coherence length

$$\xi_l = \frac{\lambda^2}{2\Delta\lambda}$$

$\Delta\lambda/\lambda = 1.4\times10^{-4}$

$\lambda = 1.0\ \mathring{A}$

$\xi_l = 0.5\ \mu\text{m}$

$R = 200$ m

Spatial or transverse coherence length

$$\xi_s = \frac{\lambda R}{2 r_s}$$

$\xi_h = 150\ \mu\text{m}$

$\xi_v = 696\ \mu\text{m}$

$r_v = 14.36\ \mu\text{m}$

$r_h = 66.41\ \mu\text{m}$

Techniques with optimized Optics and Instruments

SAXS/GI-SAXS XPCS, CXDI

WAXS XPCS

EoI from the European User Community

ESRF Upgrade – XPCS at diffraction limited storage rings

C. Gutt[1], B. Ruta[2], Y. Chushkin[2], F. Zontone[2], K. Nygard[3], P. Schurtenberger[4], A. Fernandez-Martinez[5], L. Cristofolini[6], D. Orsi[6], J. Wagner[7], M. Zanatta[8], A. Ricci[9], G. Grübel[9], F. Lehmkühler[9], W. Roseker[9], A. Madsen[10], V.M. Giordano[11], R. Busch[12], I. Gallino[12], M. Stolpe[12], S. Hechler[12], Z. Evenson[13], S. De Panfilis[14], B. Ruzicka[15], R. Angelini[15], F. Pignon[16], G. Baldi[17], G. Monaco[18], A. Matic[19], G. Portale[20], D. Constantin[21], D. LeBolloc'h[21], J. Vincent[21], E. Pineda[22], D. Crespo[22], G. Beutier[23], M. de Boissieu[23], B. Rufflè[24], B. Fischer[25], P. Huber[26]

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14 Italian Institute of Technology, Rome, Italy
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16 CNRS, Laboratoire Rhéologie et Procédés, Université Grenoble, France
17 IMEM-CNR, Parma – Italy
18 Trento University, Italy
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21 Laboratoire de Physique des Solides, Universite Paris Sud, France
22 Universitat Politècnica Catalunya, Castelldefels, Spain
23 University Grenoble Alpes and CNRS, SIMaP, Grenoble, France
24 Université Montpellier 2, Laboratoire Charles Coulomb, Montpellier, France
25 Physikalische Chemie, Universität Hamburg, Germany
26 Technische Universität, Hamburg-Harburg, Germany

40 authors:

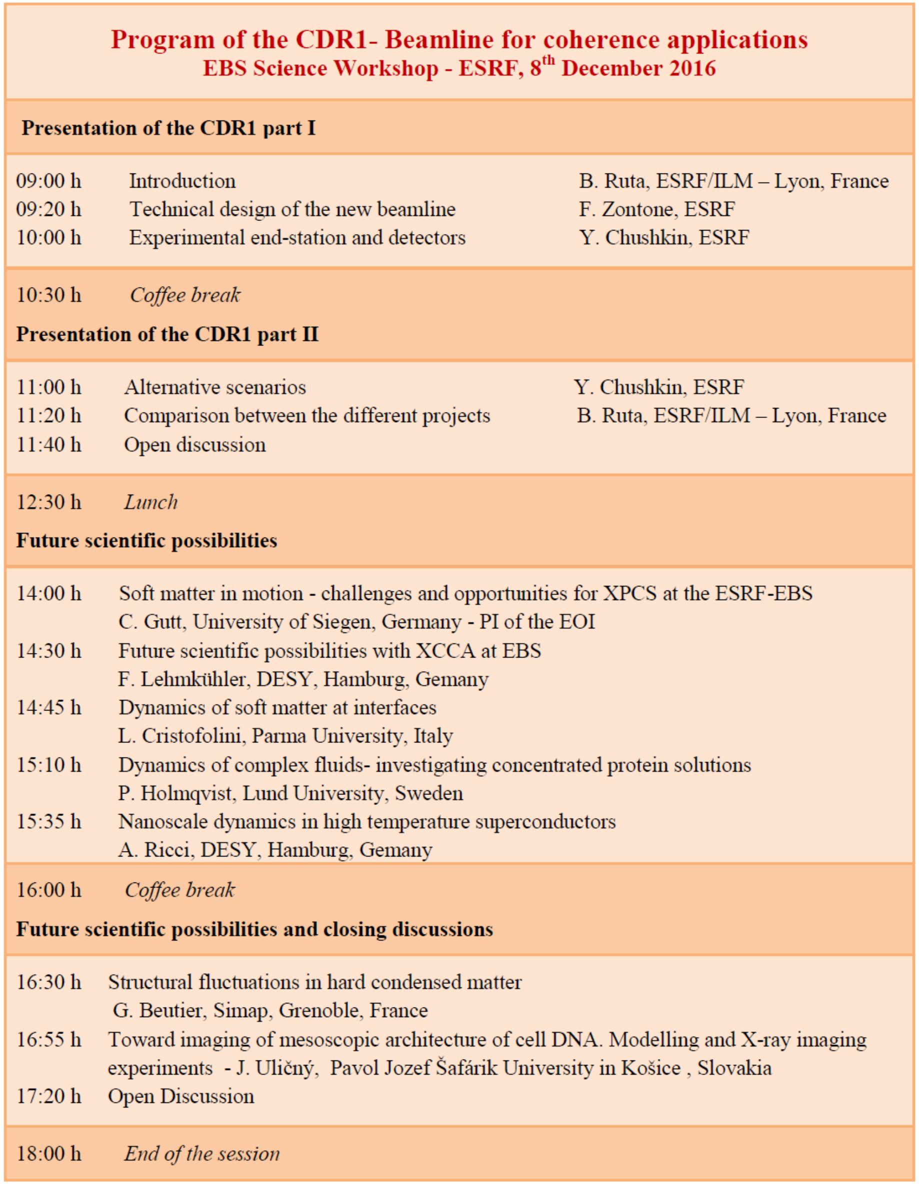
- 26 different institutes
- 6 countries: Germany, France, Italy, Sweden, Netherlands, Spain

+

EoI for CXDI:

High resolution imaging using coherent diffraction in the far field

ESRF-EBS
EBS Science Workshop
8 • 9 December 2016, ESRF, Grenoble



Program of the CDR1- Beamline for coherence applications
EBS Science Workshop - ESRF, 8th December 2016

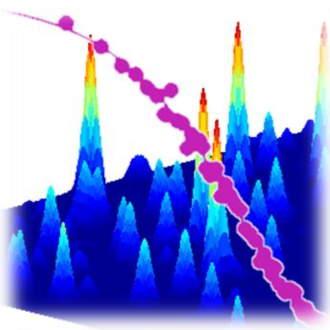
Presentation of the CDR1 part I		
09:00 h	Introduction	B. Ruta, ESRF/ILM – Lyon, France
09:20 h	Technical design of the new beamline	F. Zontone, ESRF
10:00 h	Experimental end-station and detectors	Y. Chushkin, ESRF
10:30 h	*Coffee break*	
Presentation of the CDR1 part II		
11:00 h	Alternative scenarios	Y. Chushkin, ESRF
11:20 h	Comparison between the different projects	B. Ruta, ESRF/ILM – Lyon, France
11:40 h	Open discussion	
12:30 h	*Lunch*	
Future scientific possibilities		
14:00 h	Soft matter in motion - challenges and opportunities for XPCS at the ESRF-EBS	C. Gutt, University of Siegen, Germany - PI of the EOI
14:30 h	Future scientific possibilities with XCCA at EBS	F. Lehmkühler, DESY, Hamburg, Gemany
14:45 h	Dynamics of soft matter at interfaces	L. Cristofolini, Parma University, Italy
15:10 h	Dynamics of complex fluids- investigating concentrated protein solutions	P. Holmqvist, Lund University, Sweden
15:35 h	Nanoscale dynamics in high temperature superconductors	A. Ricci, DESY, Hamburg, Gemany
16:00 h	*Coffee break*	
Future scientific possibilities and closing discussions		
16:30 h	Structural fluctuations in hard condensed matter	G. Beutier, Simap, Grenoble, France
16:55 h	Toward imaging of mesoscopic architecture of cell DNA. Modelling and X-ray imaging experiments	J. Uličný, Pavol Jozef Šafárik University in Košice , Slovakia
17:20 h	Open Discussion	
18:00 h	*End of the session*	

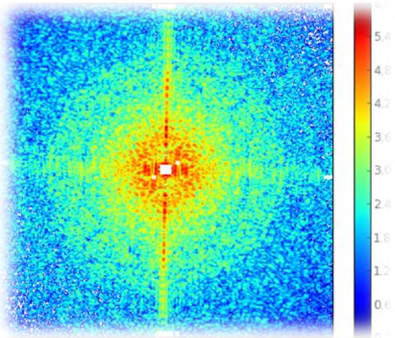
50 participants:

- 30 different institutes
- 9 countries: Germany, France, Italy, England, Sweden, Slovakia, Russia, Japan, United States

EBS-L1: A new beamline for coherence based structural & dynamical studies

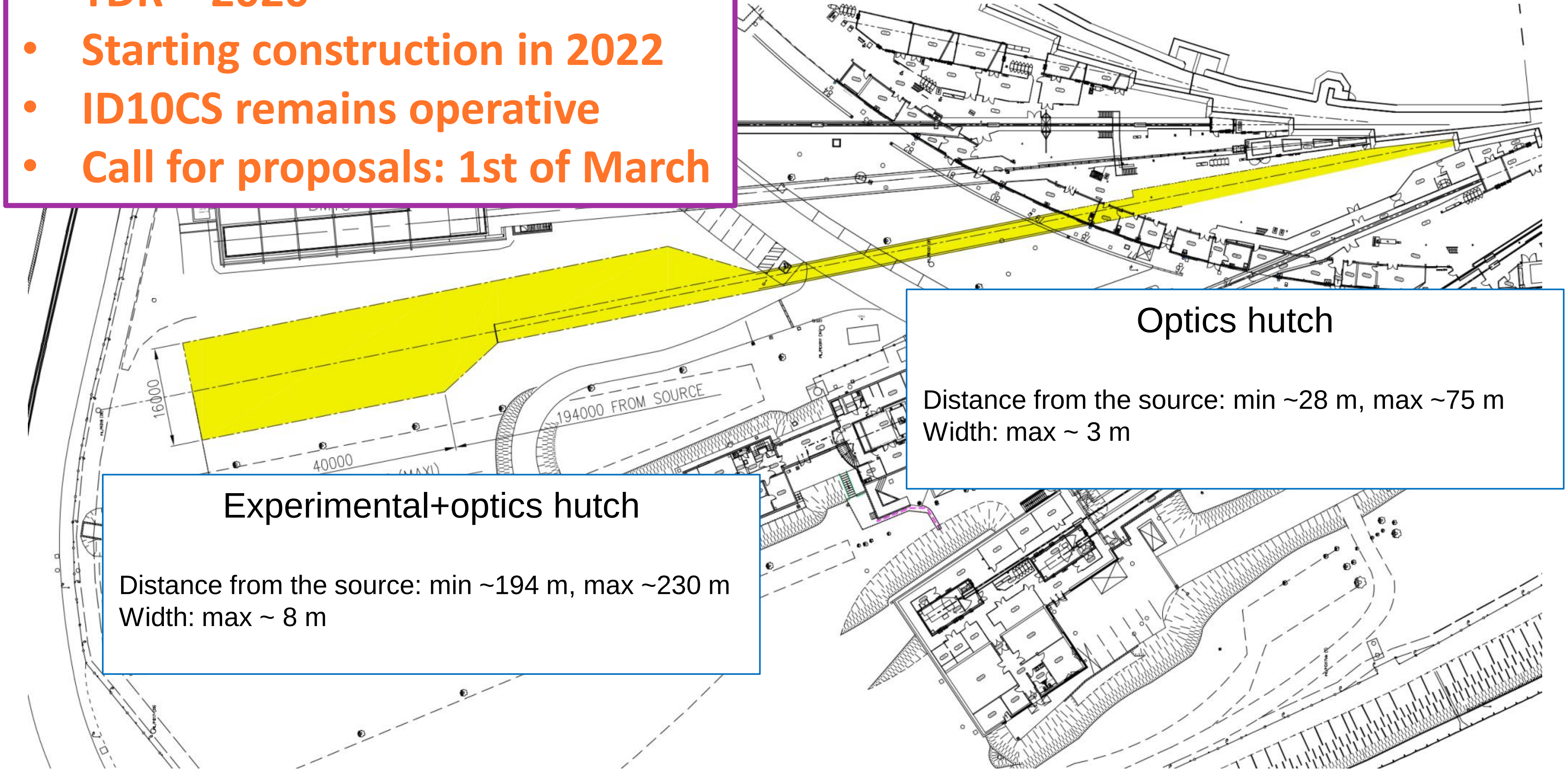
Approved by SAC in June 2017





The future beamline EBS-L1

- **TDR – 2020**
- **Starting construction in 2022**
- **ID10CS remains operative**
- **Call for proposals: 1st of March**



Optics hutch

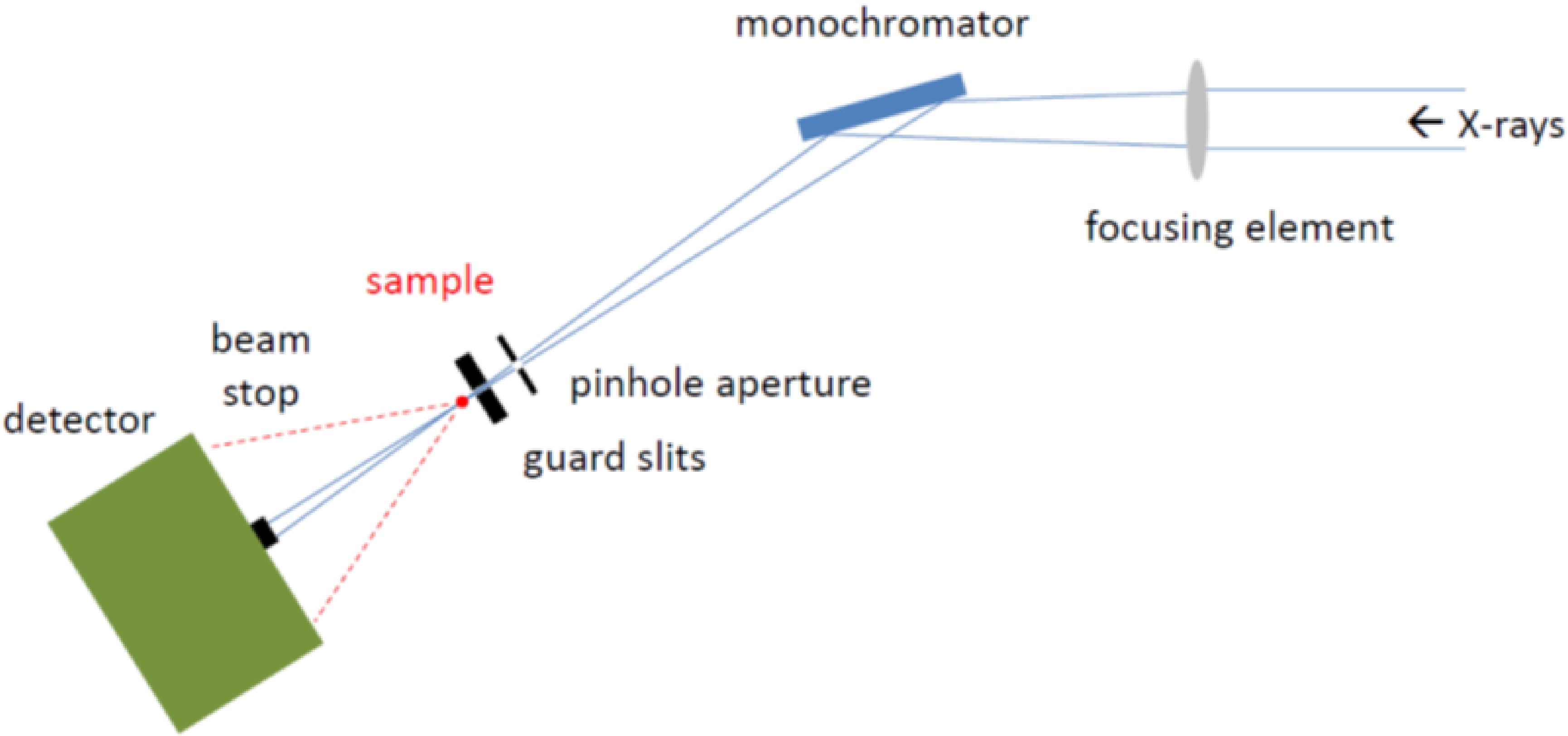
Distance from the source: min ~28 m, max ~75 m
Width: max ~ 3 m

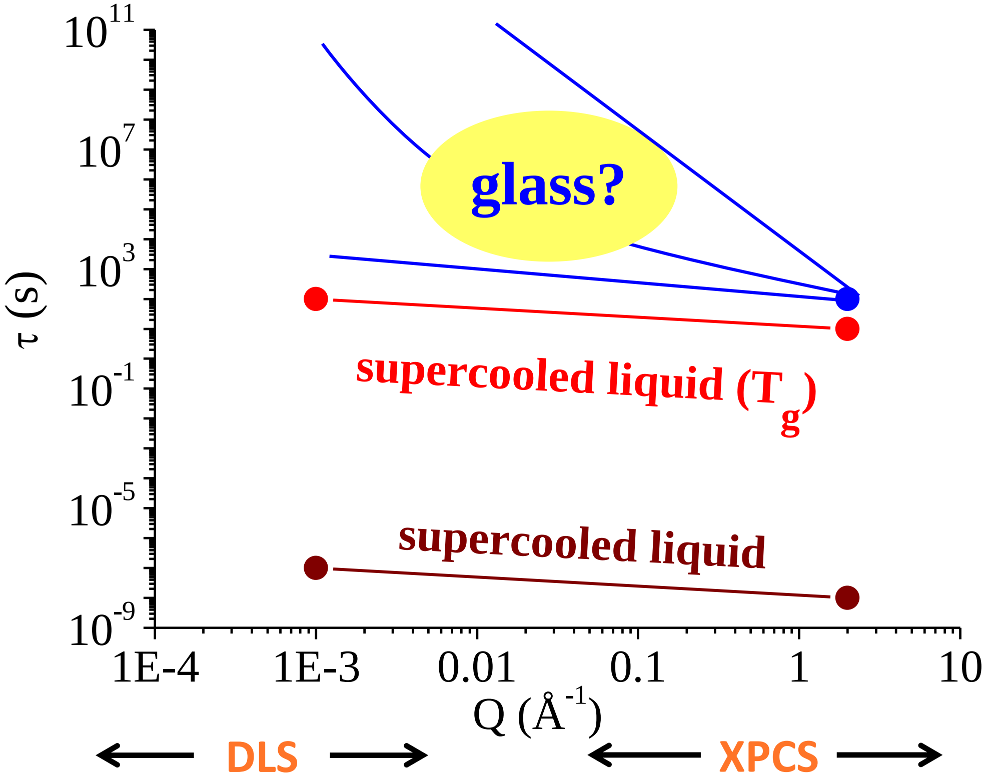
Experimental+optics hutch

Distance from the source: min ~194 m, max ~230 m
Width: max ~ 8 m

Courtesy of T. Marchial, Group Head of "Buildings & Infastructure", ESRF

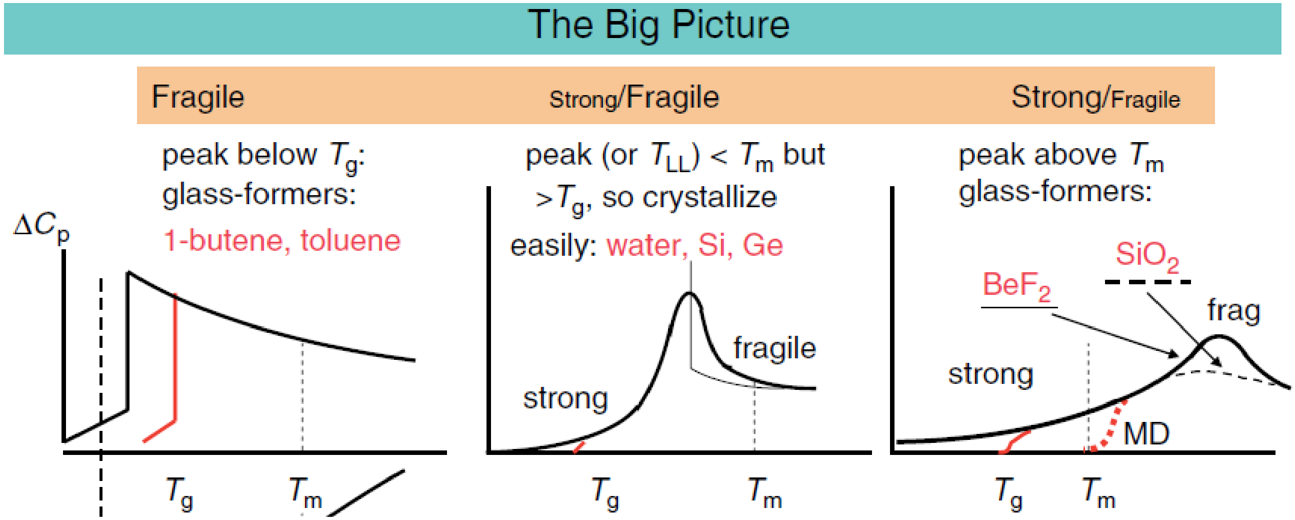
X-Ray Photon Correlation Spectroscopy




glass?
supercooled liquid (T_g)
supercooled liquid
τ (s)
10^{11}
10^{7}
10^{3}
10^{-1}
10^{-5}
10^{-9}
1E-4
1E-3
0.01
0.1
1
10
Q (Å^{-1})
DLS
XPCS

Angell's big picture

In the investigate cases the LLT and the fragile to strong transition have been observed in intermediate or strong glass formers at temperatures well above T_g even T_m



C.A. Angell MRS bulletin 2008

Following the "big picture" proposed by Angell in 2008, the LLT is likely to be located at too low temperatures to be observed in a fragile system being hidden by the glass transition.