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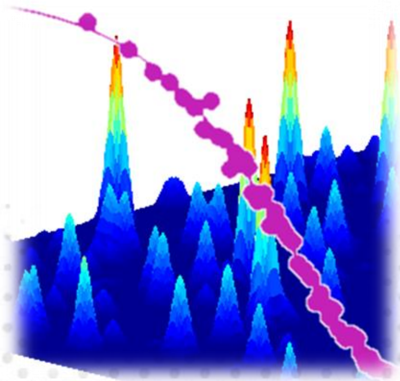
A microscopic picture of the atomic motion during polyamorphism in an ultra-viscous liquid

Beatrice Ruta



ESRF

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European Research Council
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UNIVERSITÄT DES SAARLANDES


I. Gallino

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BARCELONATECH

E. Pineda

Outline

- Dynamical crossover and liquid-liquid transitions
- Coherent X-rays and X-ray Photon Correlation Spectroscopy
- Atomic motion in ultra-viscous alloys
- Conclusions

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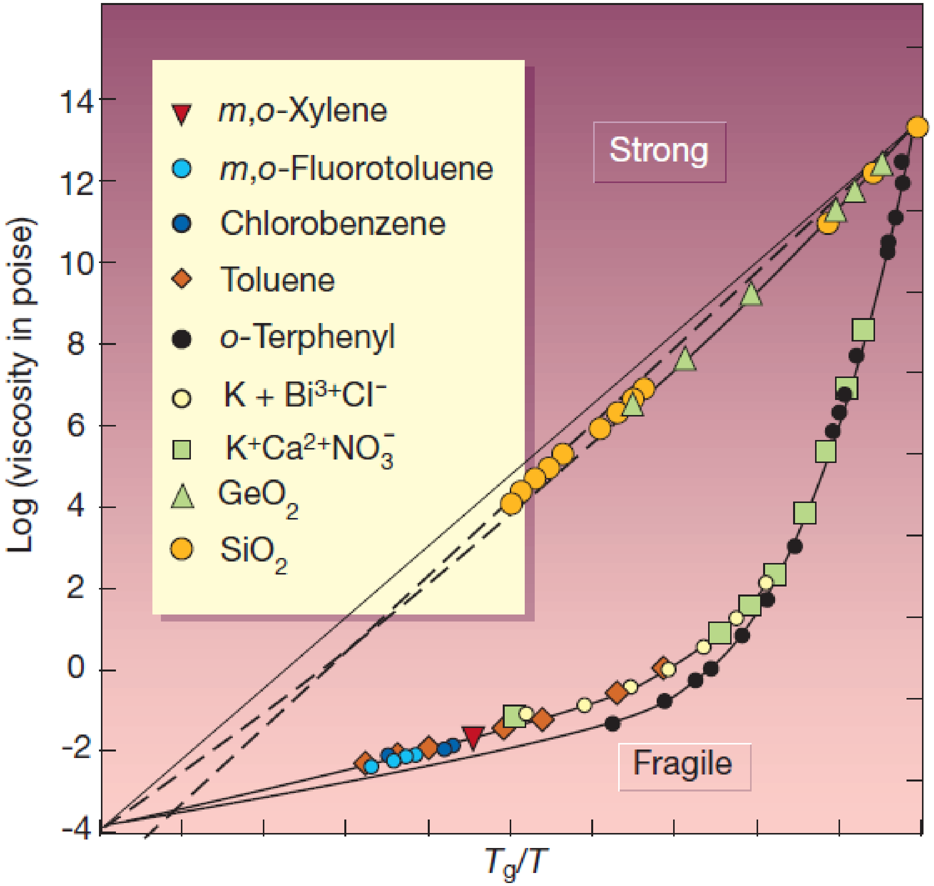
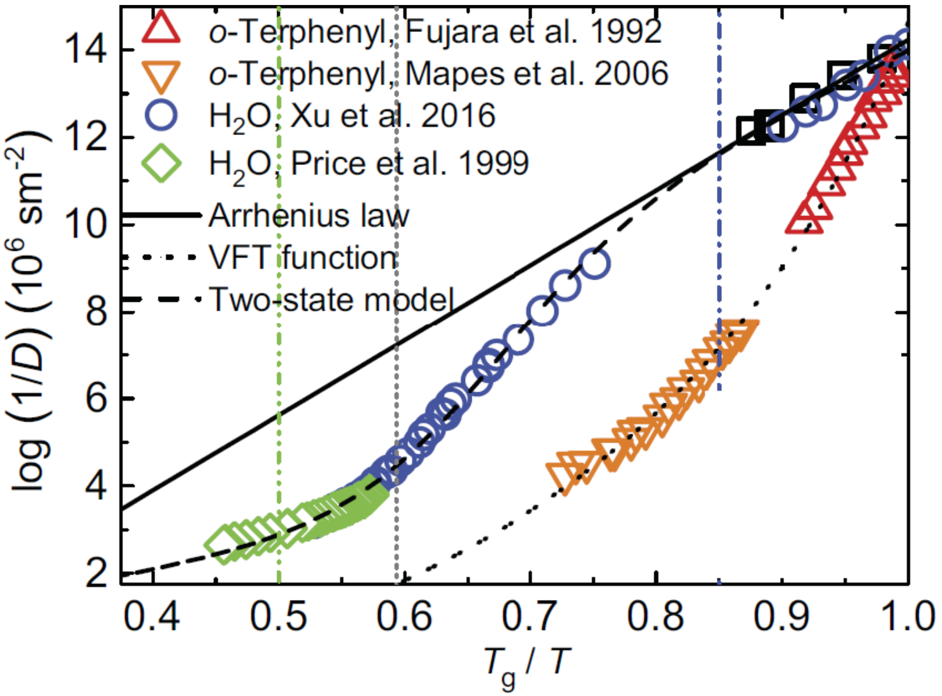
- ❑ Conclusions

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

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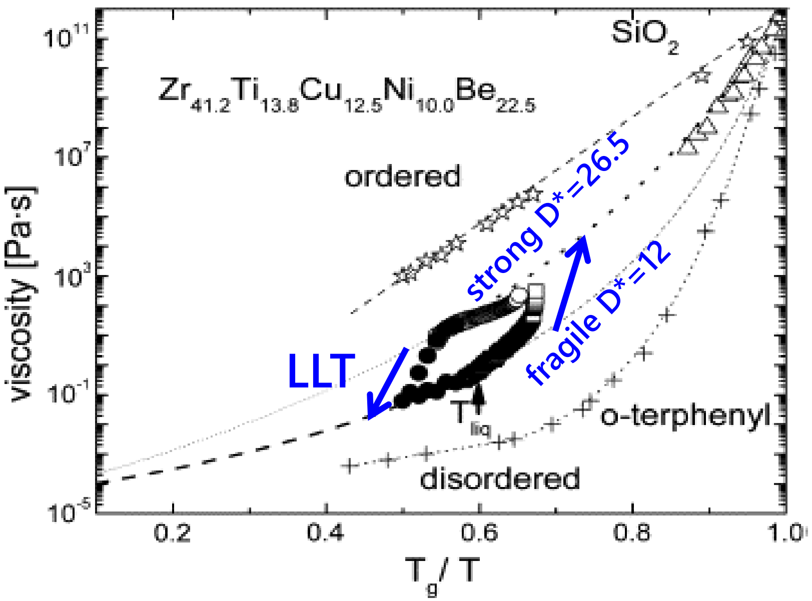
kinetics

2-order of magnitude hysteresis in viscosity

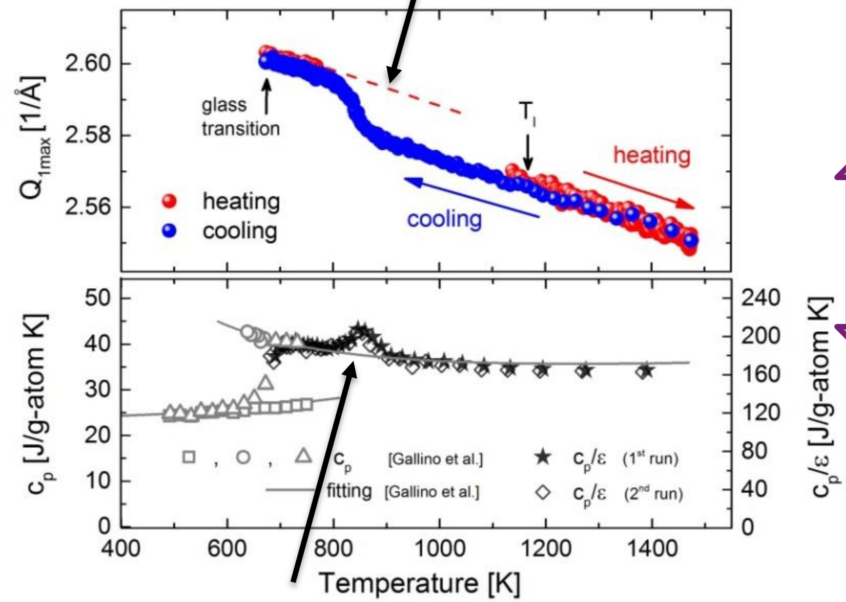
change in fragility: D* = 12 ←→ D* = 26.5



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

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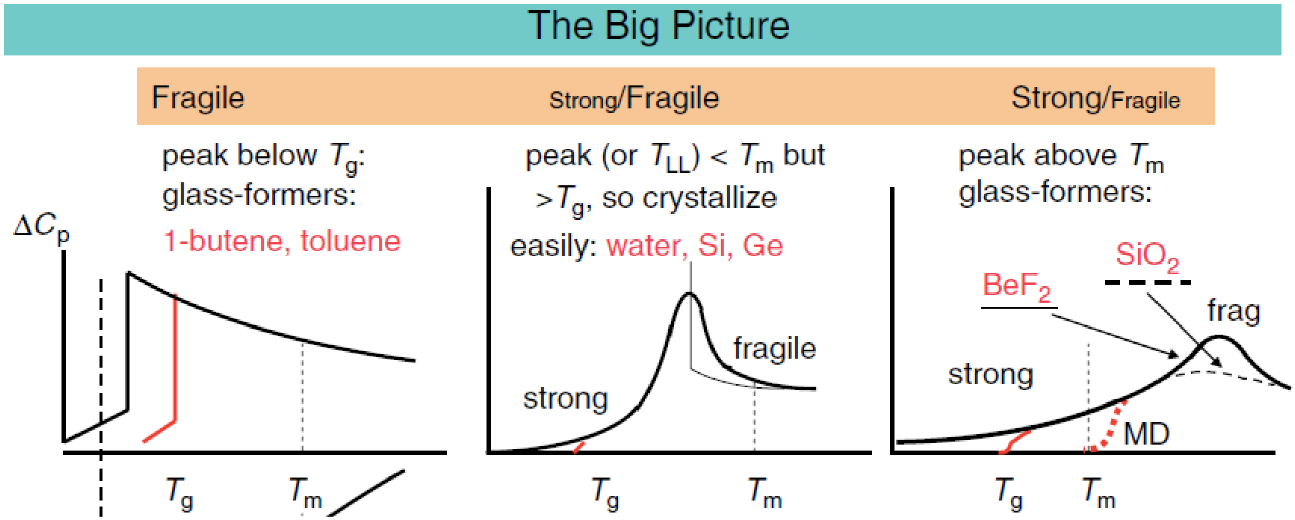
Courtesy of R. Busch

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.

Can we see a signature of the fragile to strong dynamical crossover in fragile systems?

Outline

- ❑ Dynamical crossover and liquid-liquid transitions
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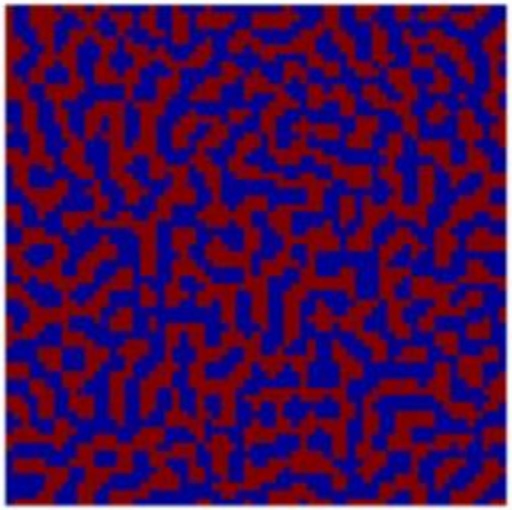
Coherent X-rays

sample with disorder
(e.g. domains)



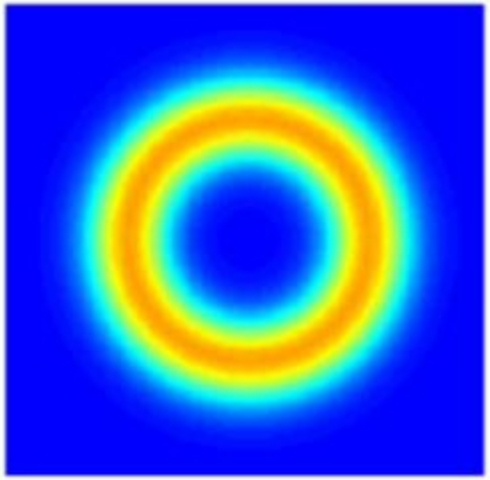
- ***Incoherent Beam:***

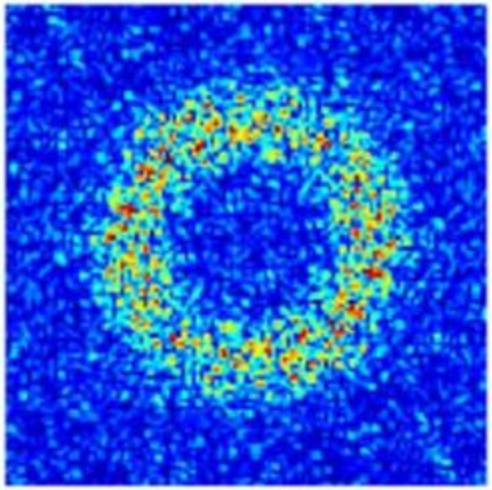
$$I(Q,t) \propto \sum_n \left| f_n(Q) \cdot e^{iQ \cdot r_n(t)} \right|^2$$

- ***Coherent Beam: Speckle***

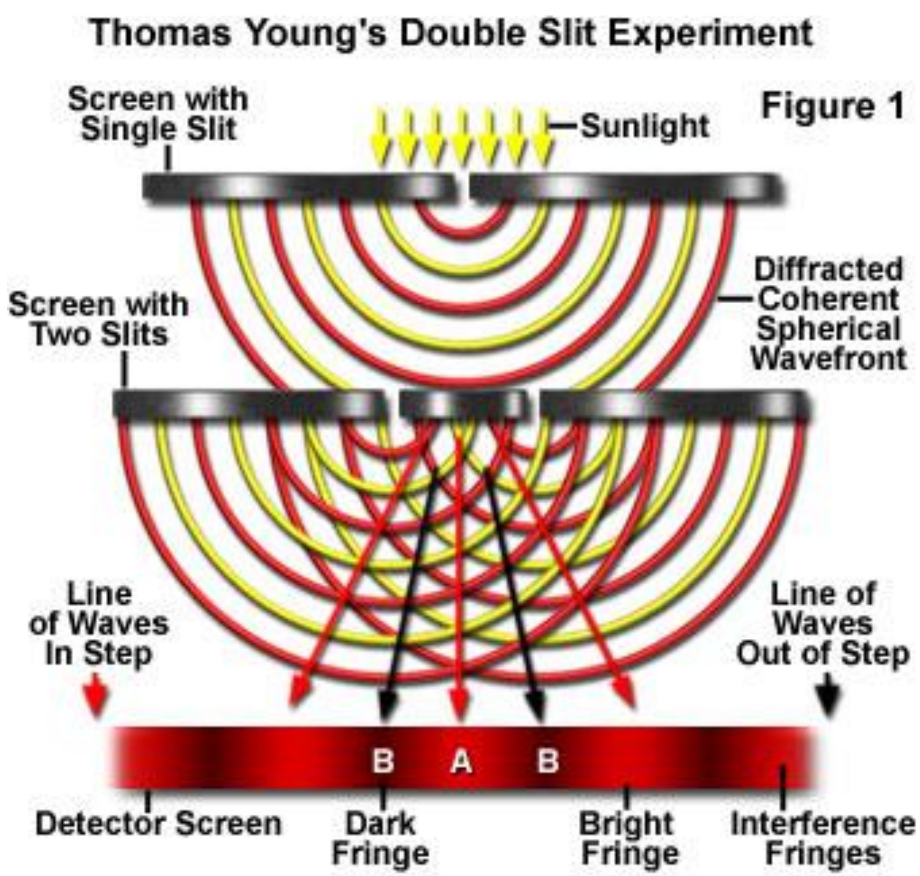
$$I(Q,t) \propto \left| \sum_n f_n(Q) \cdot e^{iQ \cdot r_n(t)} \right|^2$$

scattering





Coherent Radiation

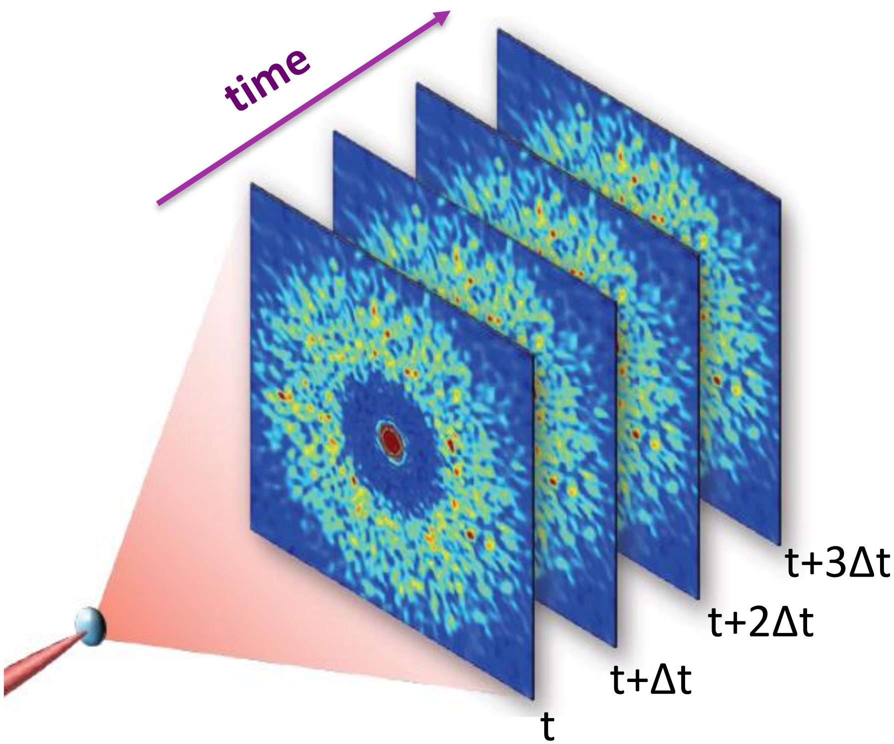


The intensity fluctuations are related to the constructive and destructive interference between the two waves

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

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

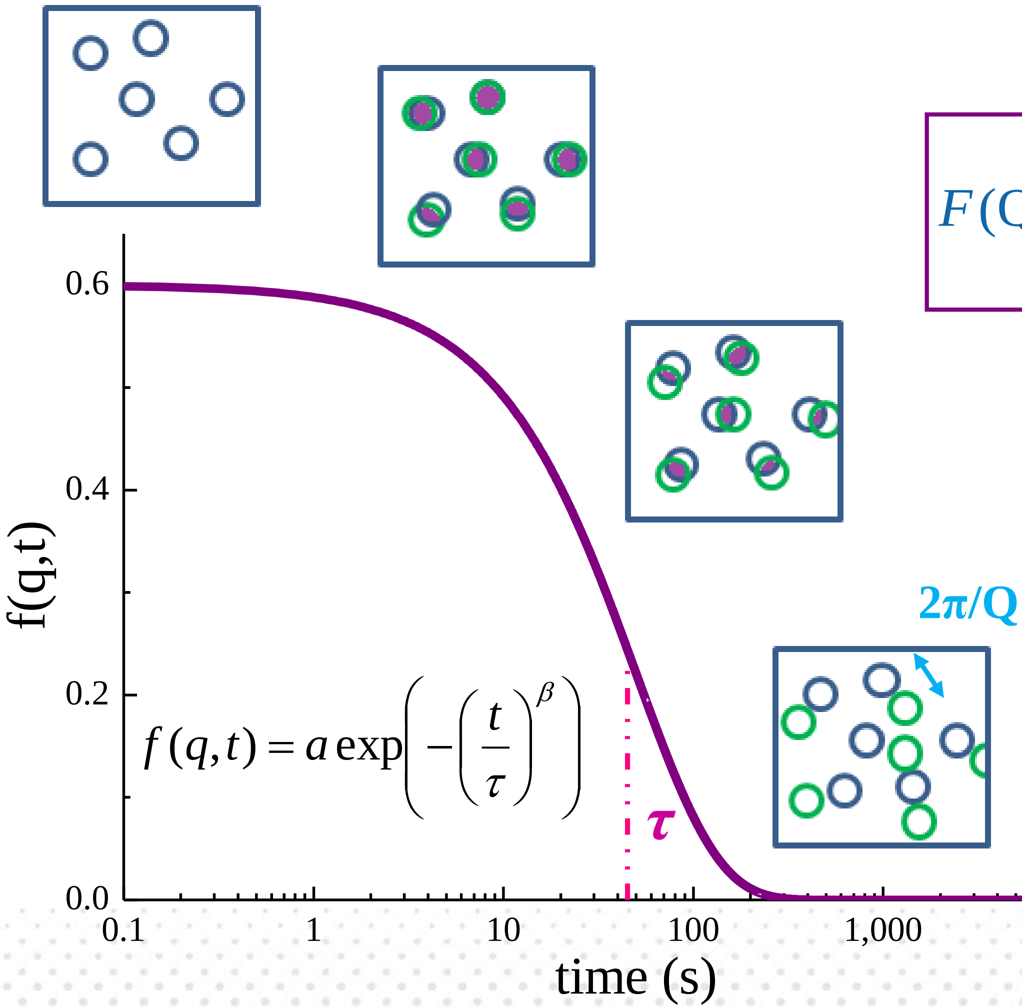
Intermediate scattering function

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

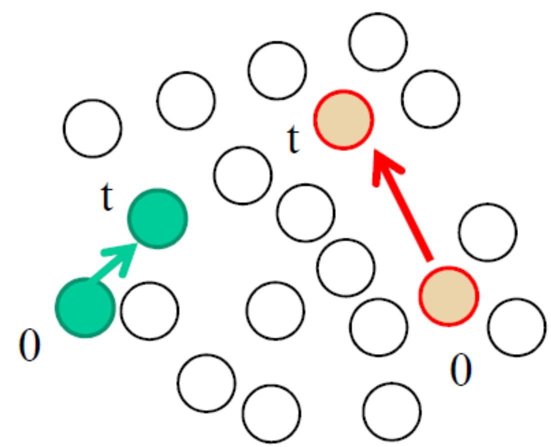
A. Madsen, A. Fluerasu and B. Ruta, XPCS, Springer, 2015

The intermediate scattering function

The intermediate scattering function monitors the decay of the **density fluctuations** on the scale $2\pi/Q$



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



The intermediate scattering function

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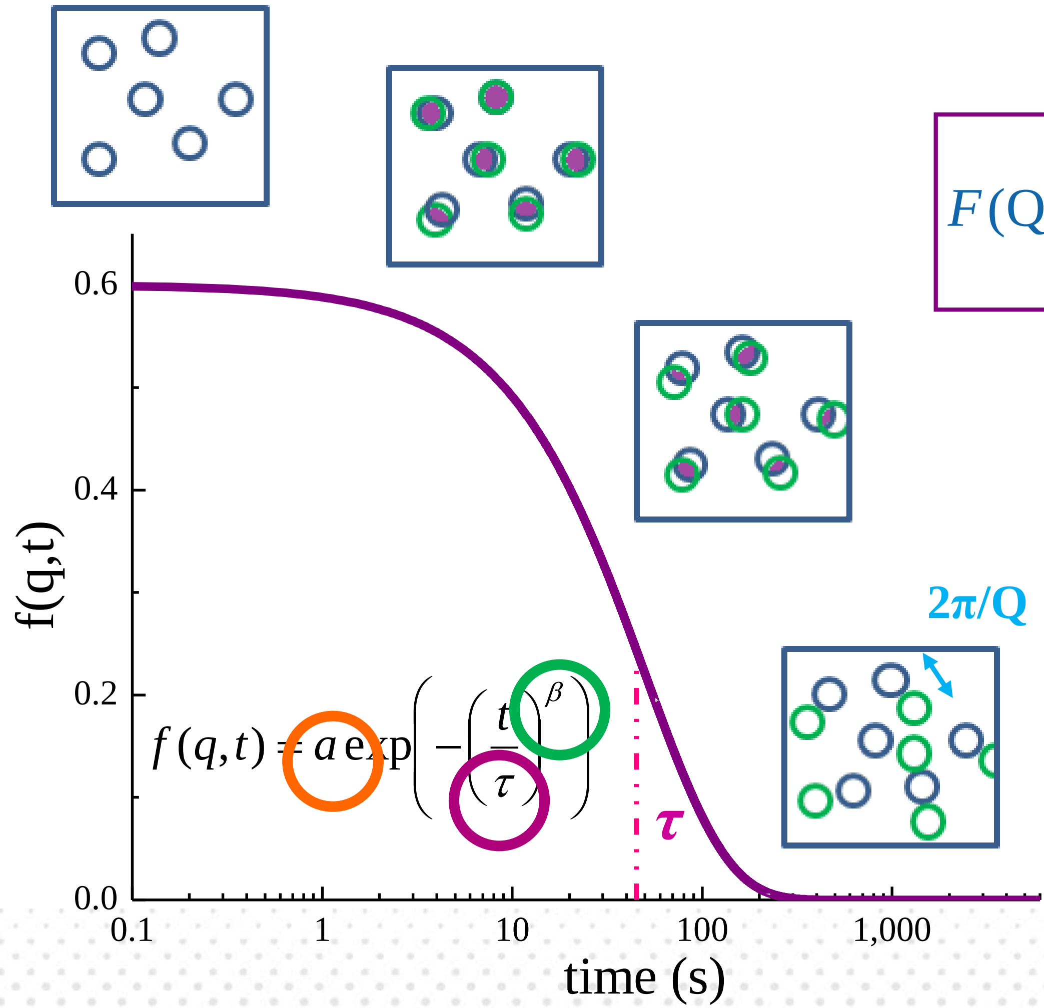

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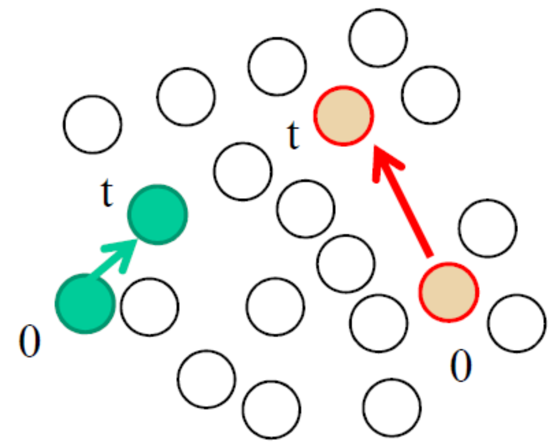

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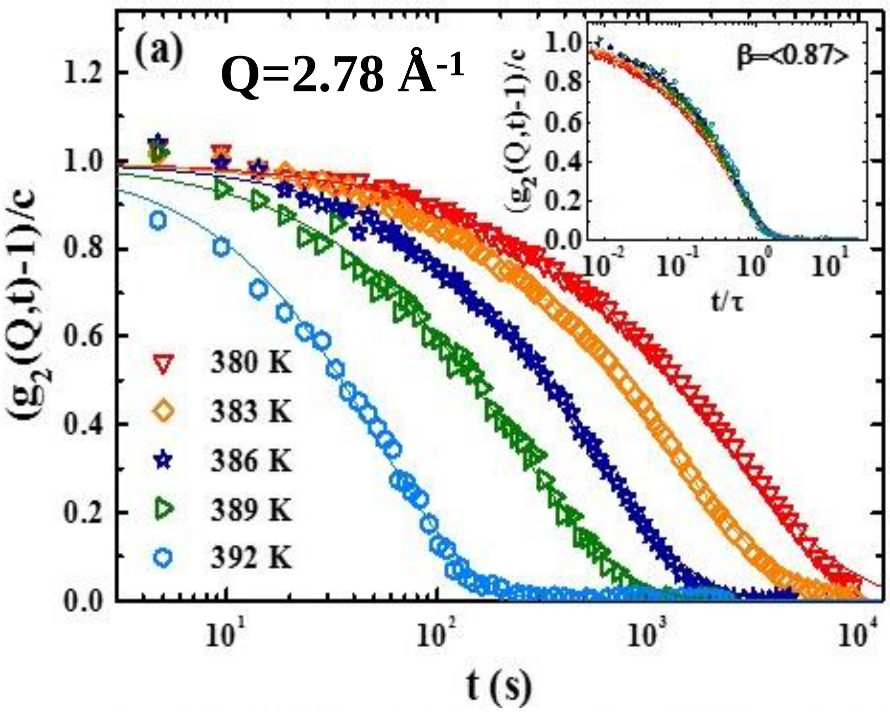
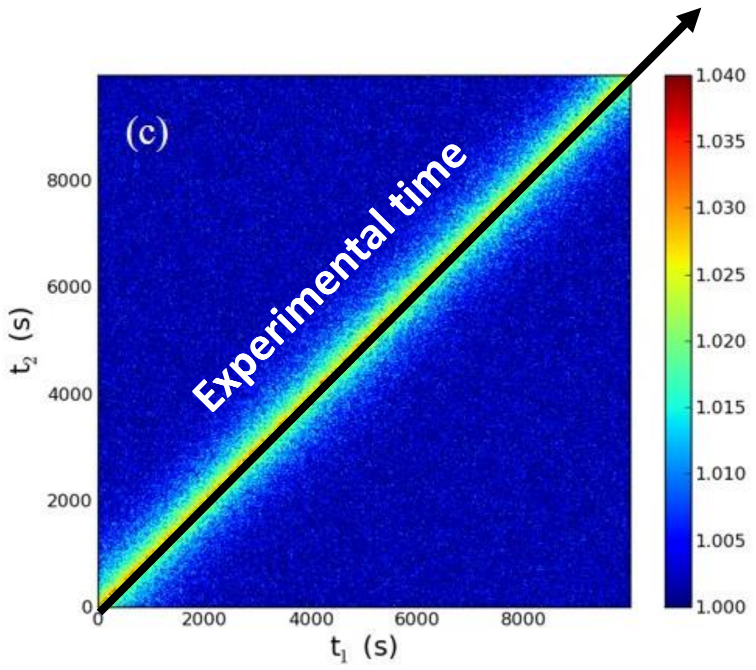
Dynamics in the supercooled liquid phase (XPCS)

Quasi-static cooling: rate of 0.1 K/min and isothermal steps of ΔT=0.5 K

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



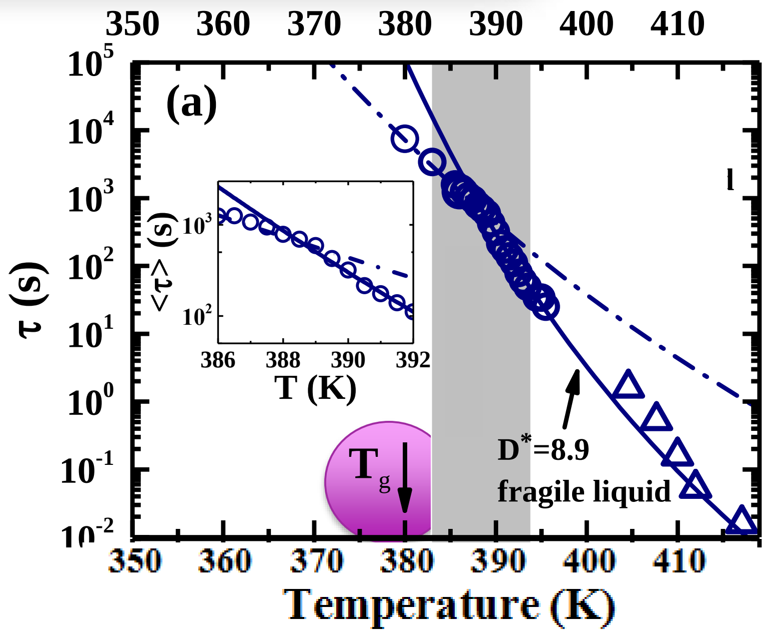


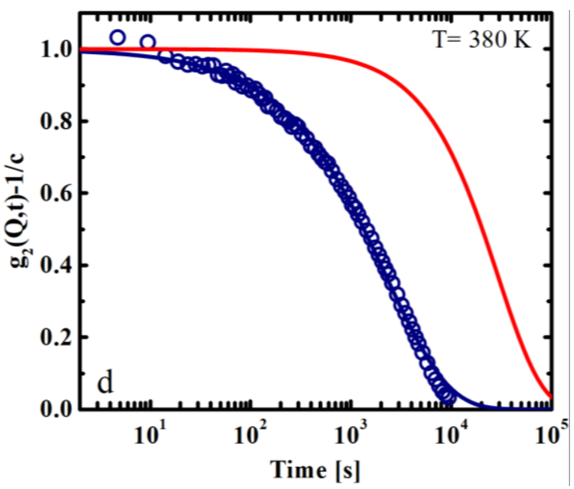
S. Hechler, et al. Phys. Rev. Mat. (2018)

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}





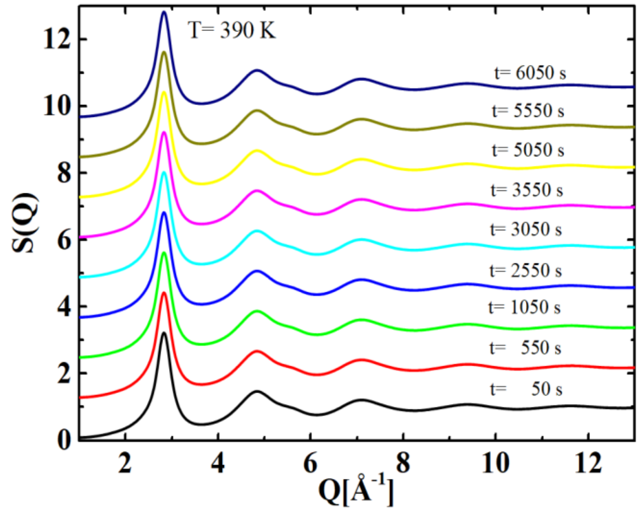
Glass transition?

- 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)

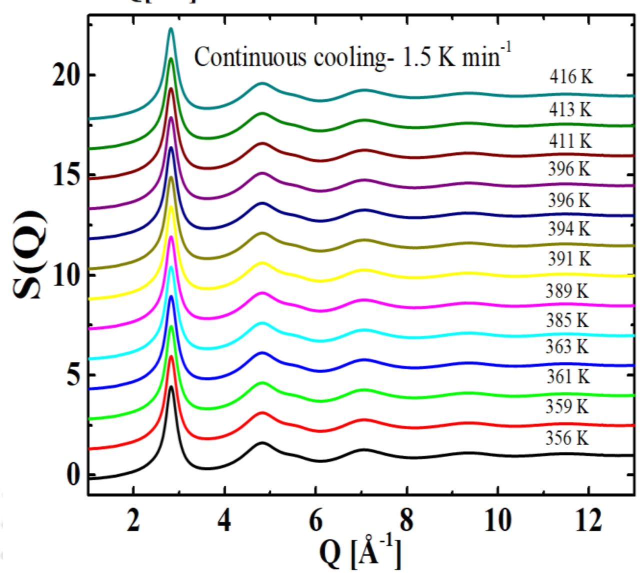
T-step with long isotherms

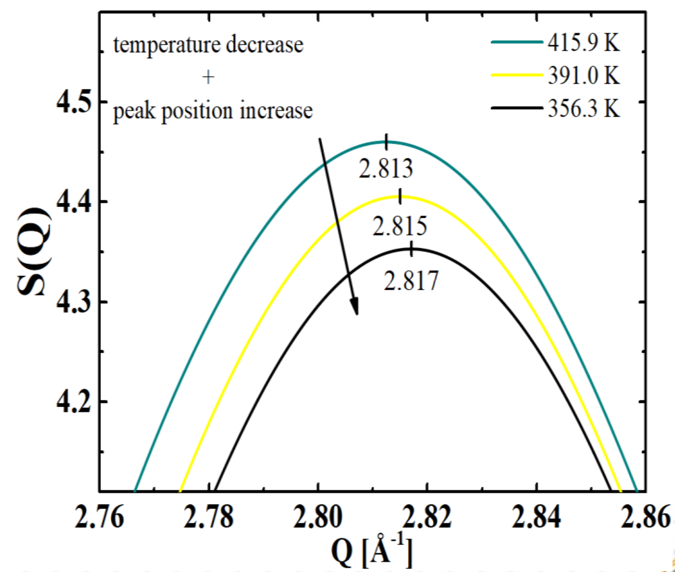


2 XRD experiments

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

Continuous cooling

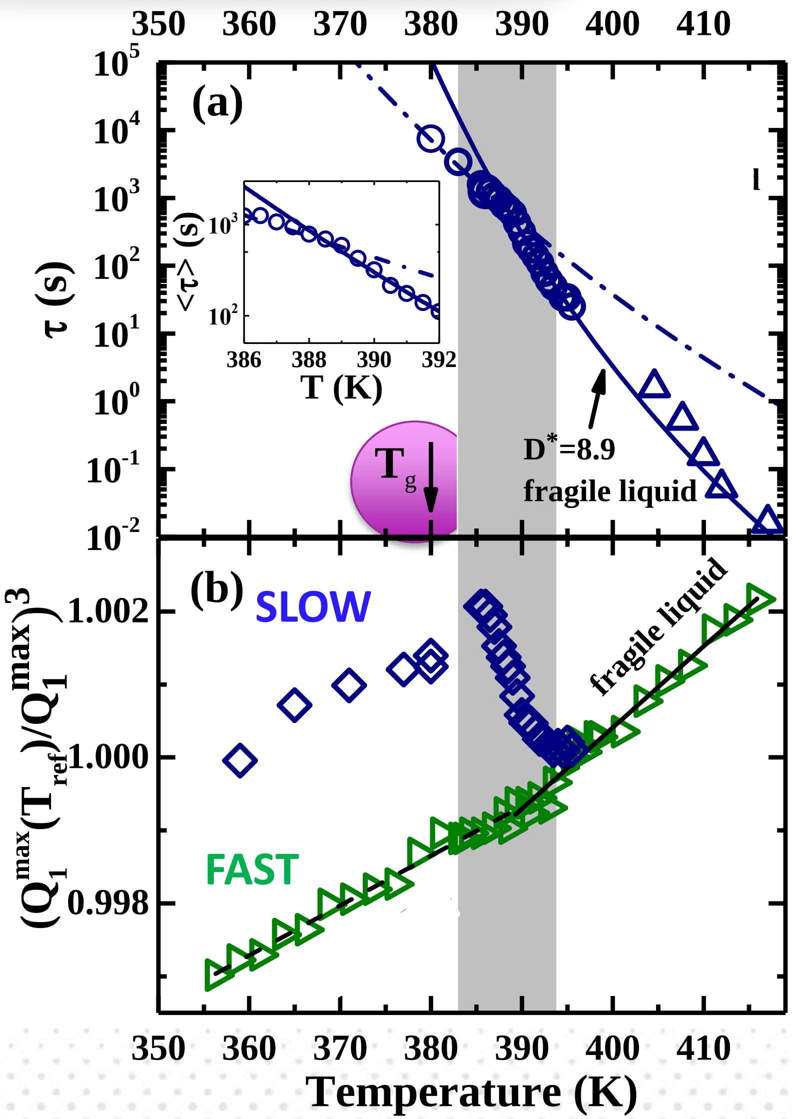




S. Hechler, et al. Phys. Rev. Mat. (2018)

The supercooled liquid phase (XPCS+DMA+XRD)

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

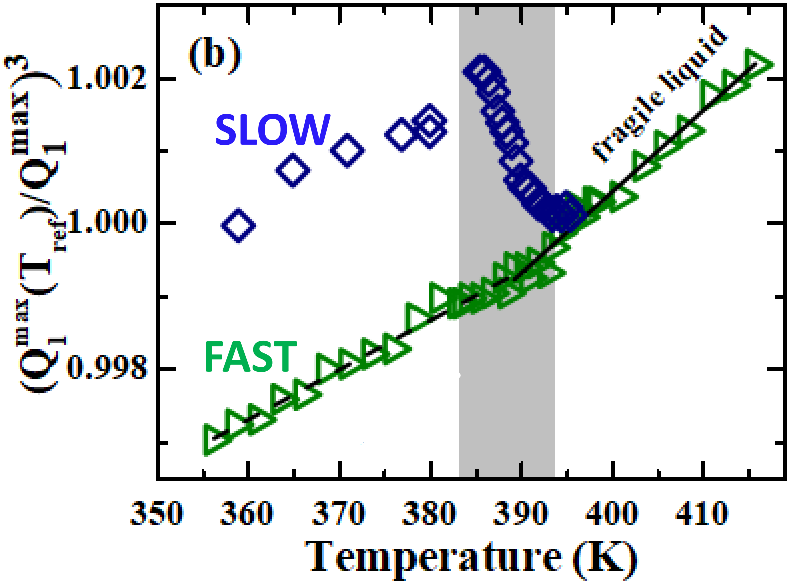


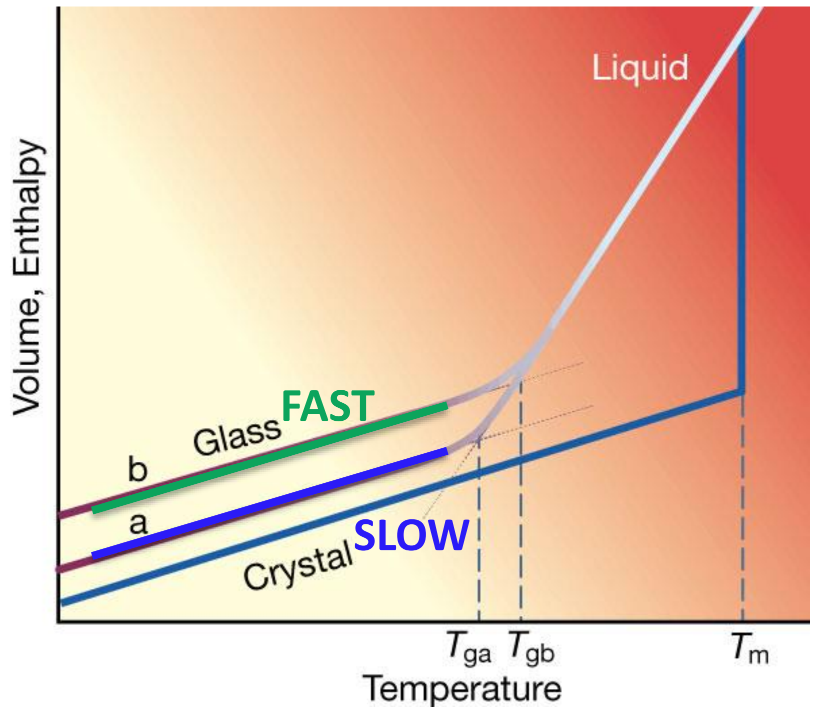
Occurrence of important structural rearrangements which cannot be associated to the glass transition

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

The liquid-liquid transition

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





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)

iLM
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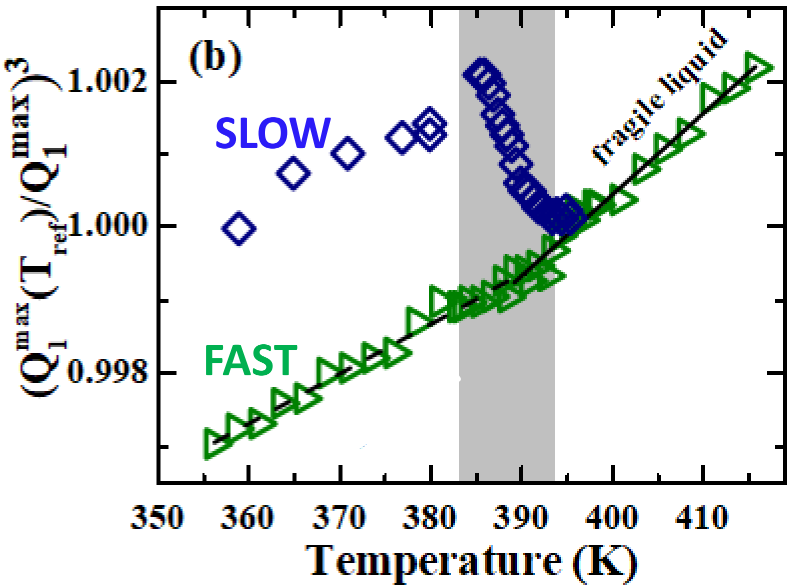
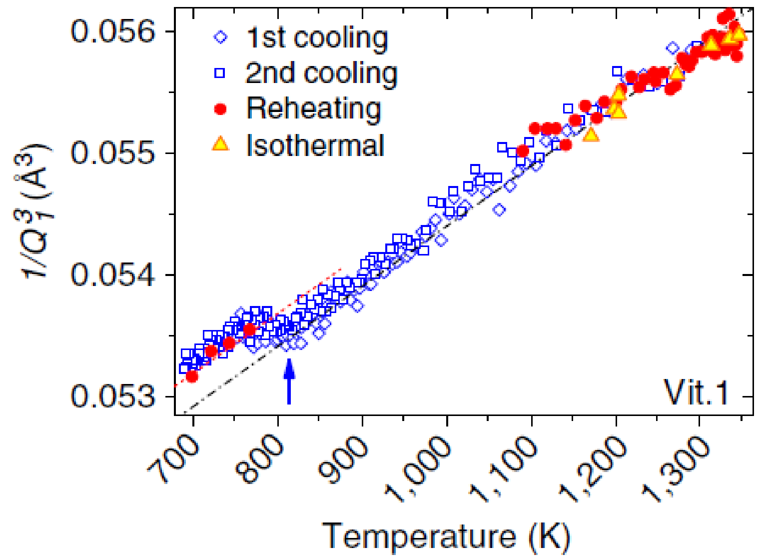
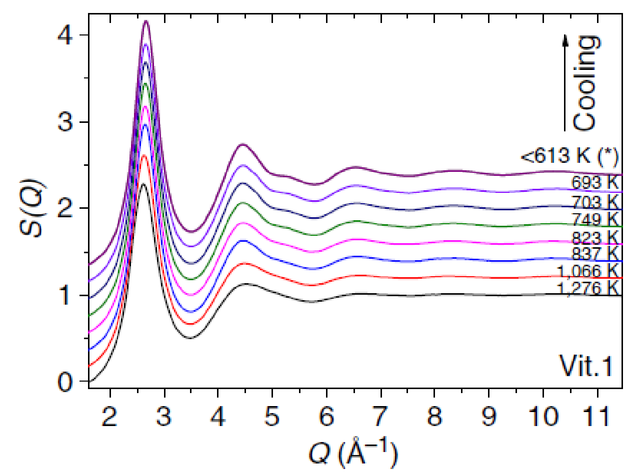
The liquid-liquid transition

S. Wei et al, Nat. Commun. 2013

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







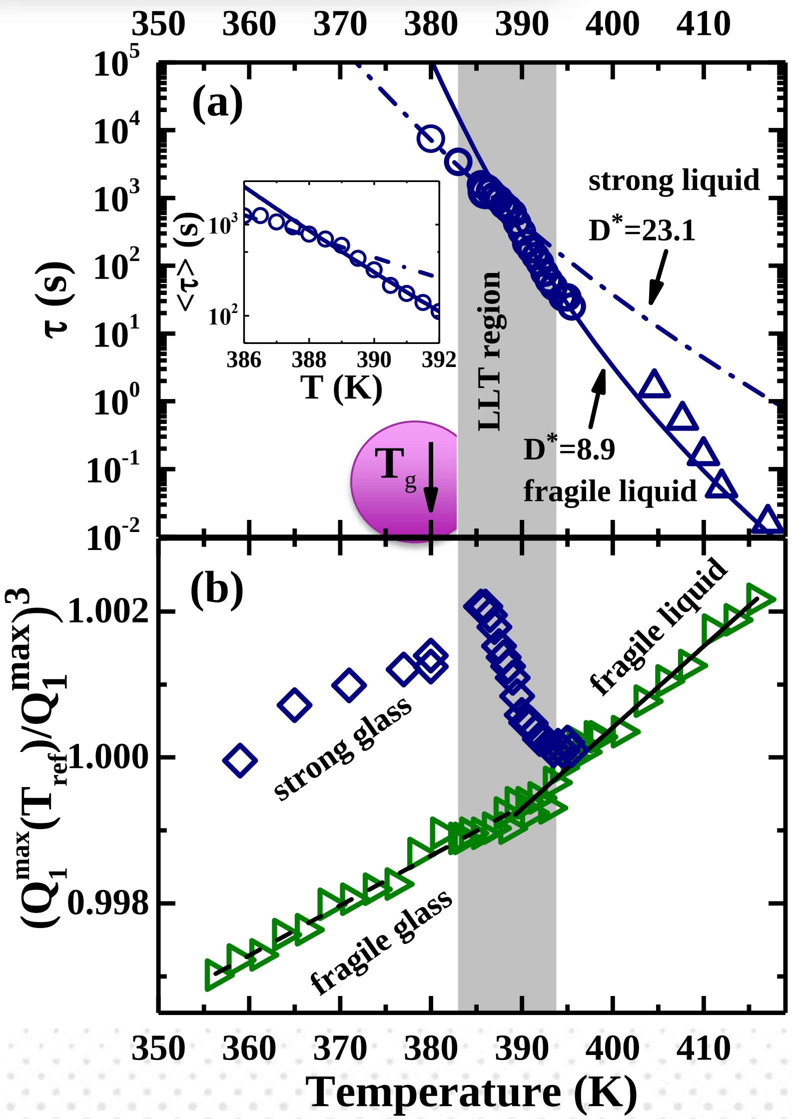
Q= 0.1 K/min: $1/Q^3 \neq V$

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

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

Fragile-to-strong liquid-liquid transition

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

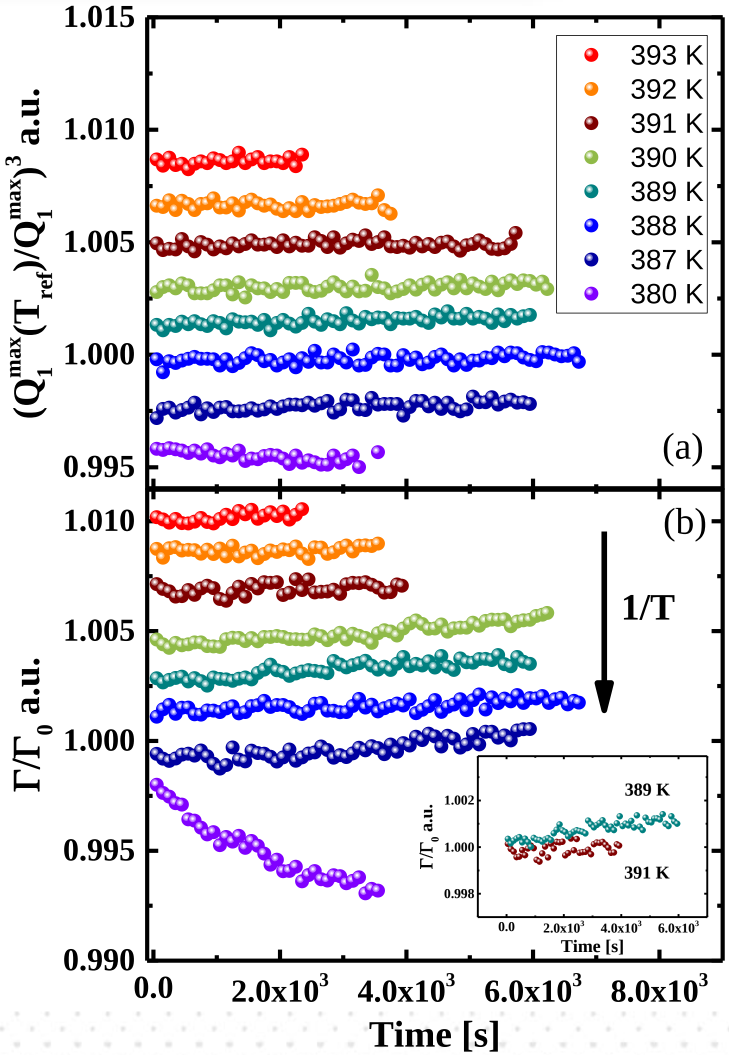


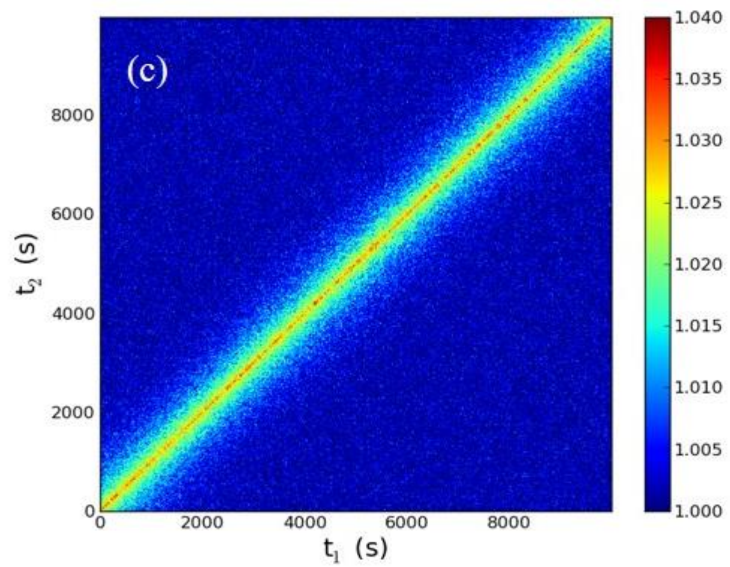
The LLT is accompanied by a **fragile-to-strong dynamical crossover** and a surprising shifting of the main peak of the S(Q) to lower Qs (increasing 1/Q)

The glass transition is the dominant process at faster cooling rates

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

The liquid-liquid transition: a slow process

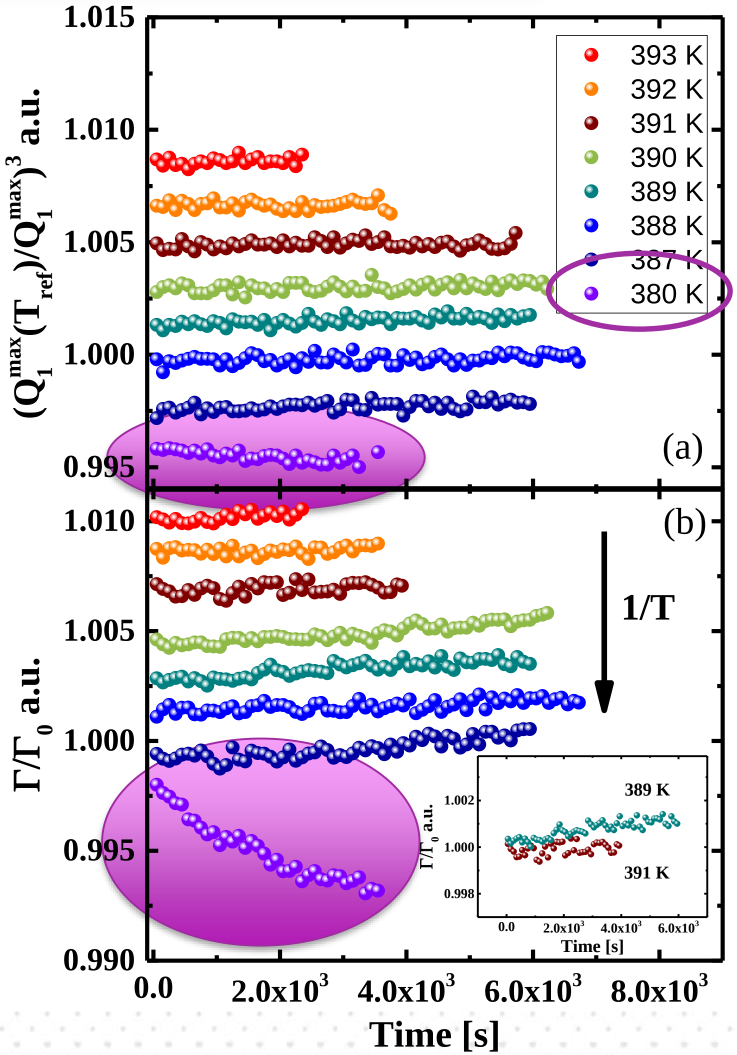




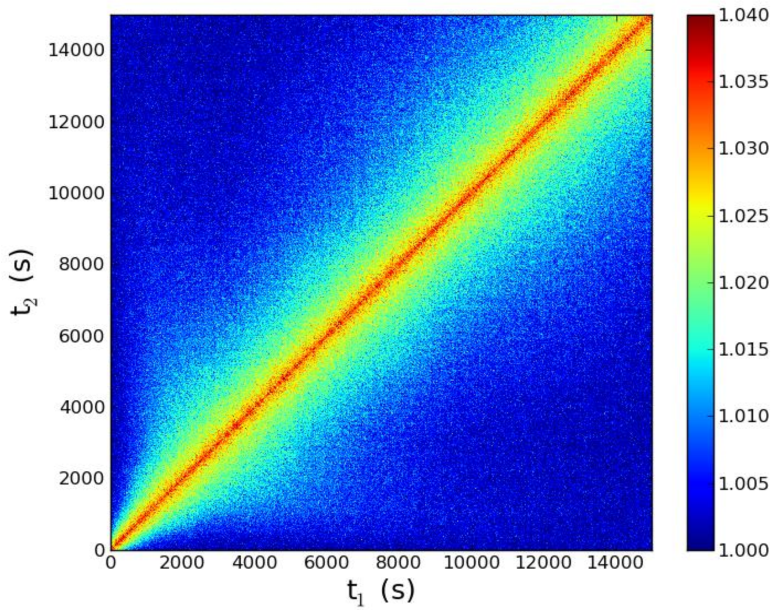
The LLT is accompanied by slow structural rearrangements involving changes in the local order without affecting the average density. In agreement with the XPCS data.

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

The equilibration at the expected T_g

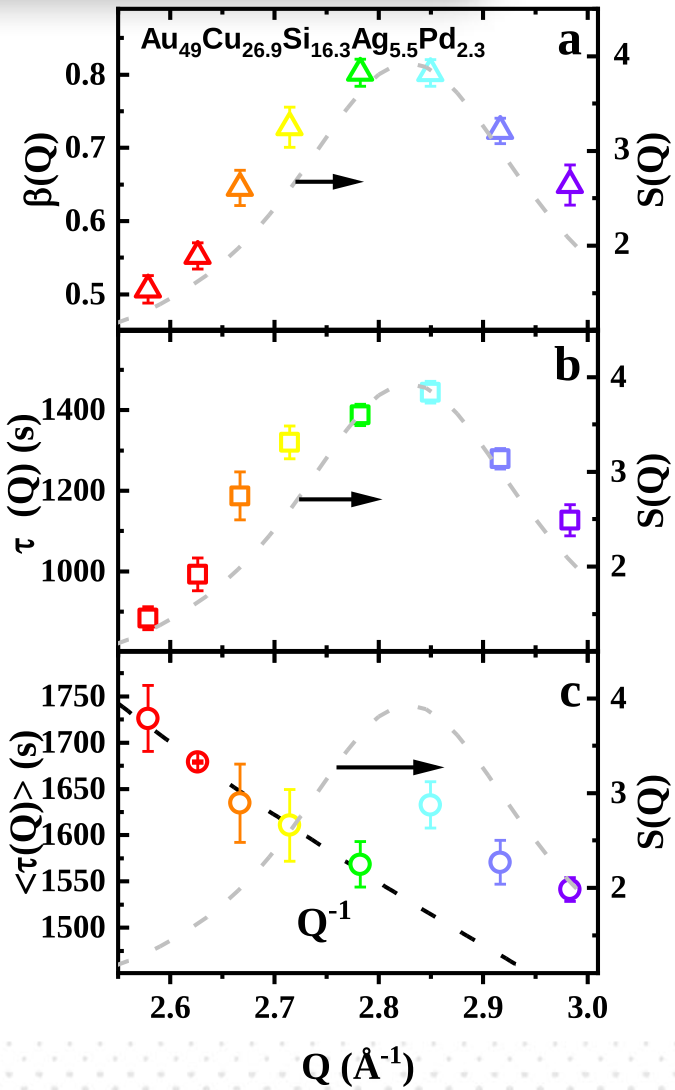


Standard aging and equilibrium restoring after cooling at T_g (10 K below the LLT)
→ confirmed by the dynamics



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

Nature of the dynamics in the strong liquid



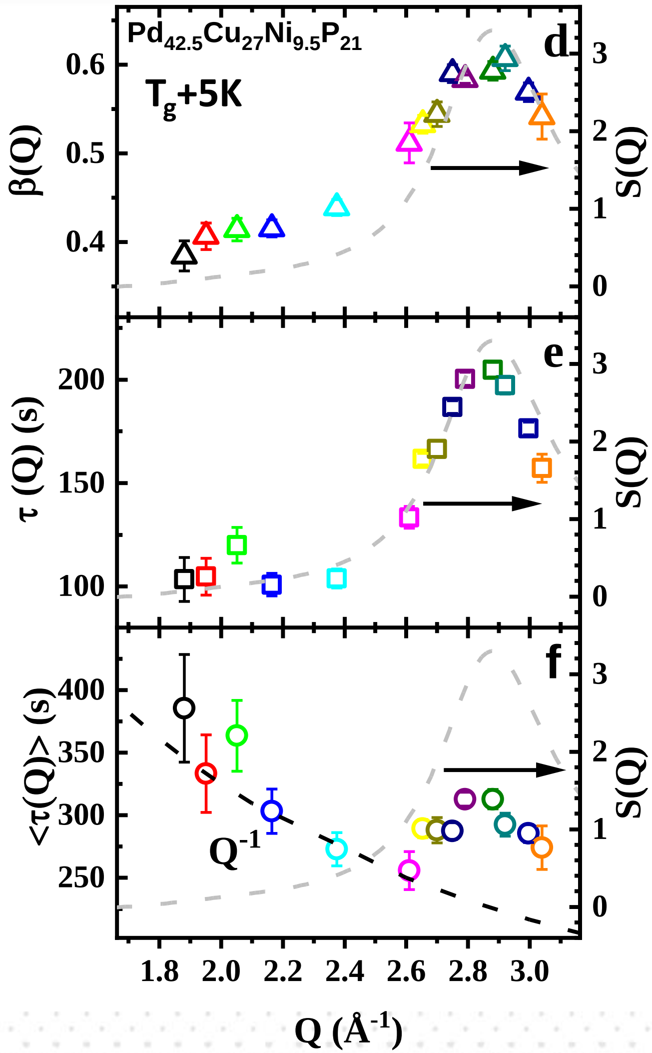
Slow down of the dynamics at the maximum of the S(Q) → reminiscent of the de Gennes narrowing of high temperature liquids.

Sub-diffusive particle motion and large heterogeneities at low Qs.

$$\langle \tau(Q) \rangle = \Gamma\left(\frac{1}{\beta(Q)}\right)\frac{\tau(Q)}{\beta(Q)}$$

B. Ruta, et al. Phys. Rev. Lett. (2020)

General sub-diffusive particle motion ?



B. Ruta, et al. Phys. Rev. Lett. (2020)

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

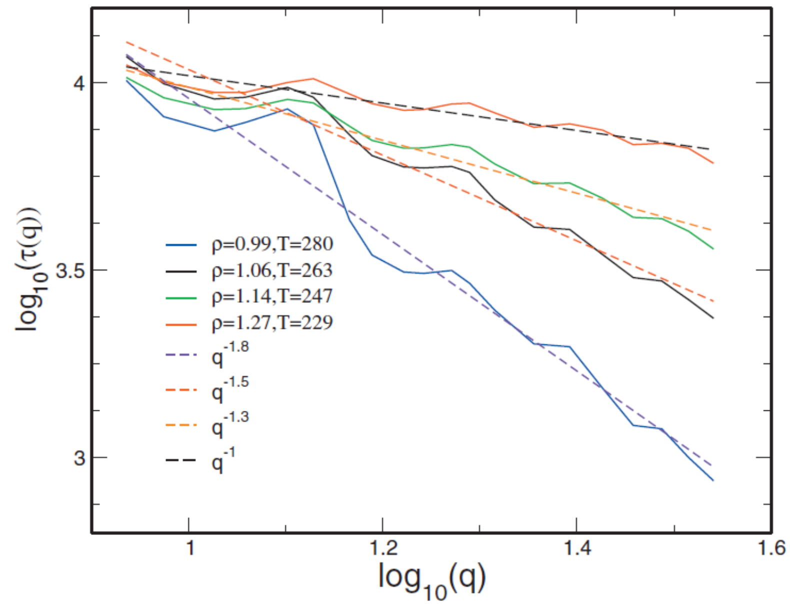
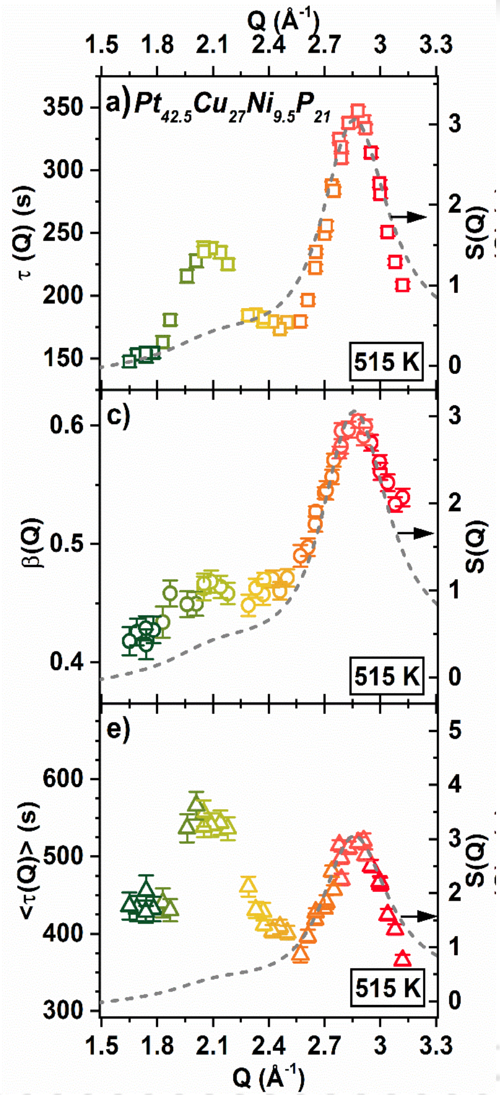


FIG. 1. The α relaxation timescale $\tau(q)$ plotted as a function of q at different densities and temperatures. The $\tau(q)$ values are scaled such that at q =8.6 they have similar values. $\tau(q)$ shows a weaker q dependence as the temperature is lowered.

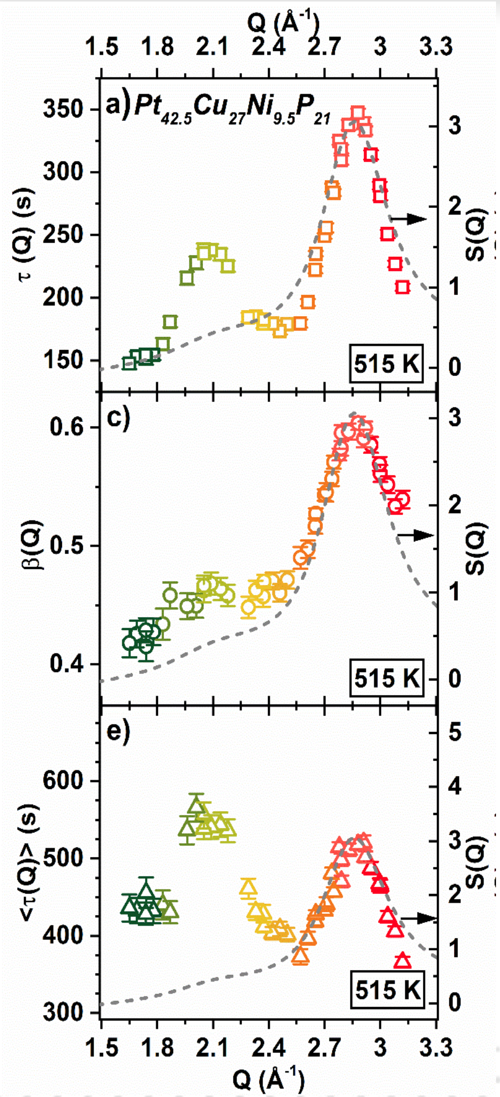
Batthacharryya et al. J. Chem. Phys. 2010

General sub-diffusive particle motion ?



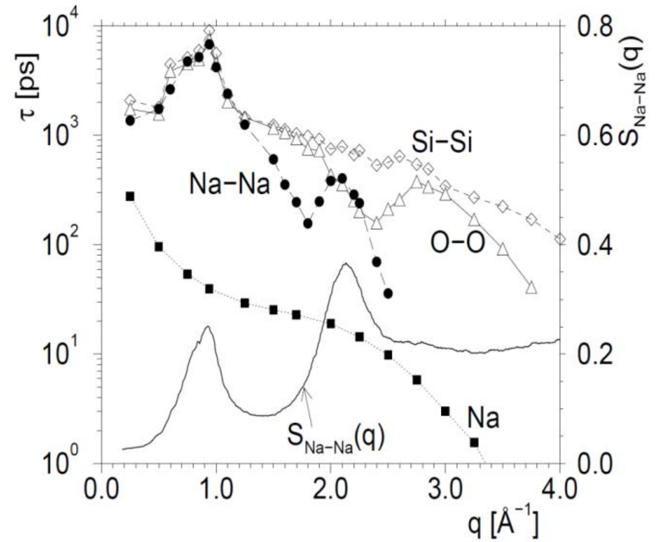
N. Neuber, et al. in preparation

General sub-diffusive particle motion ?

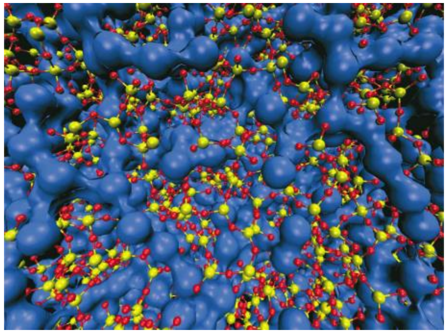


N. Neuber, et al. in preparation

Sodium silicates



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



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

- **Metallic glasses**: influence of chemical short range order
- **Silicates:** fast ion diffusion in a slow relaxing matrix

LLT in ultra-viscous metallic glass-formers

- ❑ Competition between glass transition and LLT
- ❑ LLT is a slow, time consuming process involving changes of the local order not affecting the density
- ❑ Direct link between LLT and fragile-to-strong dynamical crossover
- ❑ Complex particle motion suggesting hopping of caged particles

Thank you for your attention!!!

European Research Council
Established by the European Commission

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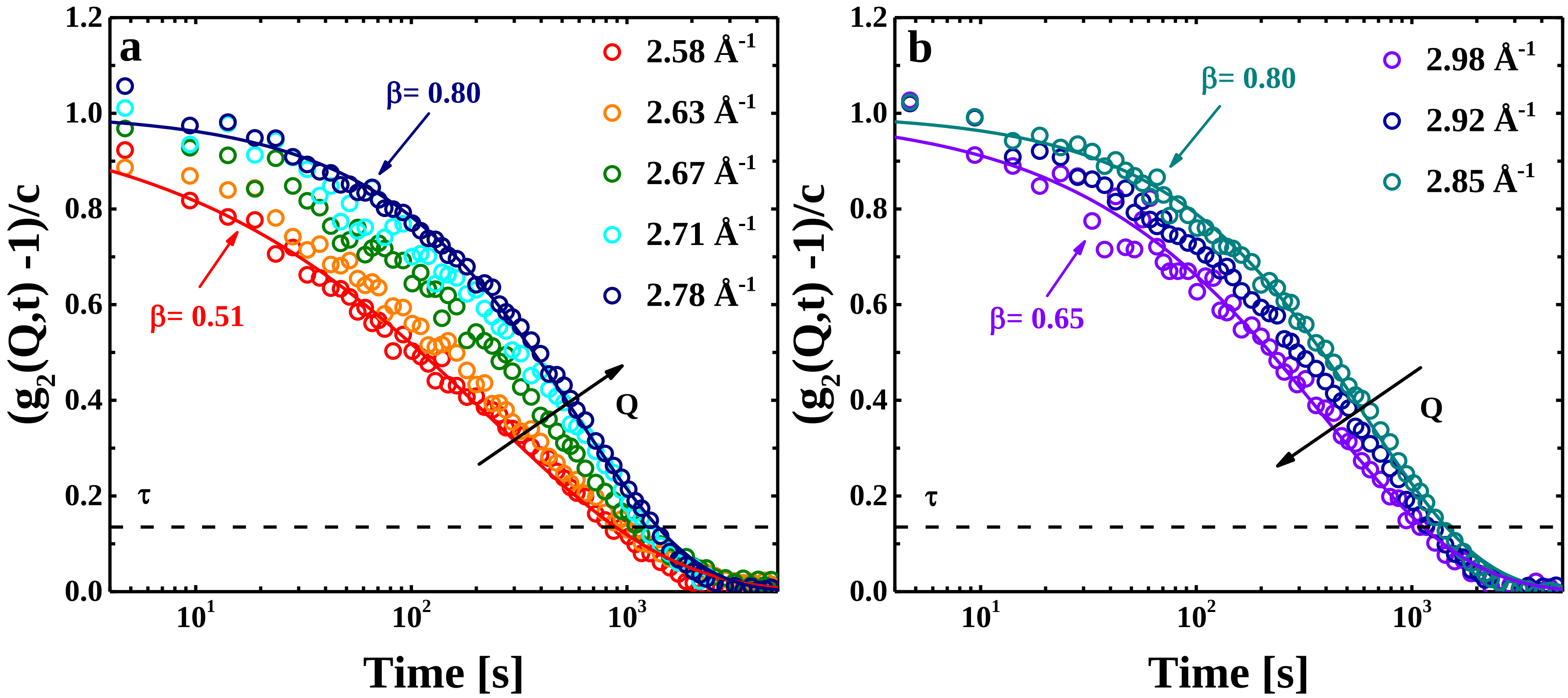
Open post-doc, PhD positions (metallic glasses & chalcogenides)

Nature of the dynamics in the strong liquid



B. Ruta, et al. Phys. Rev. Lett. (2020)

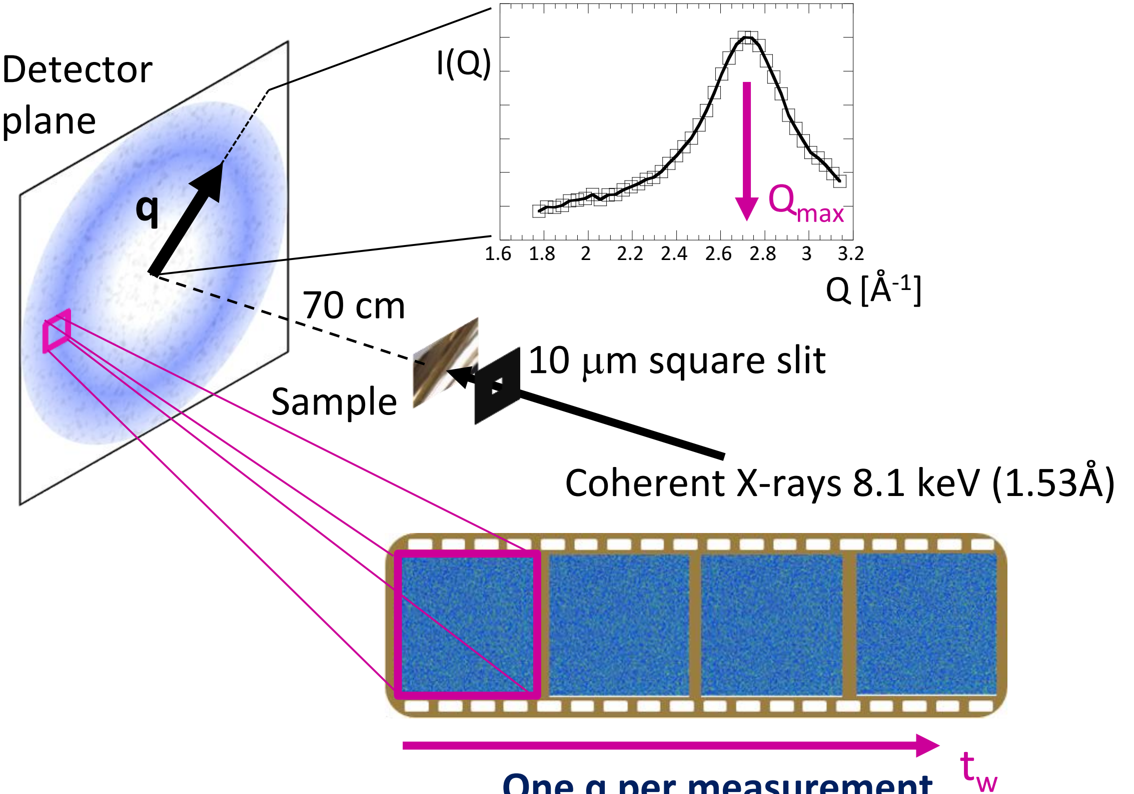
XPCS in glasses

WAXS geometry

8/21 keV: peak at 15°- 45° deg.

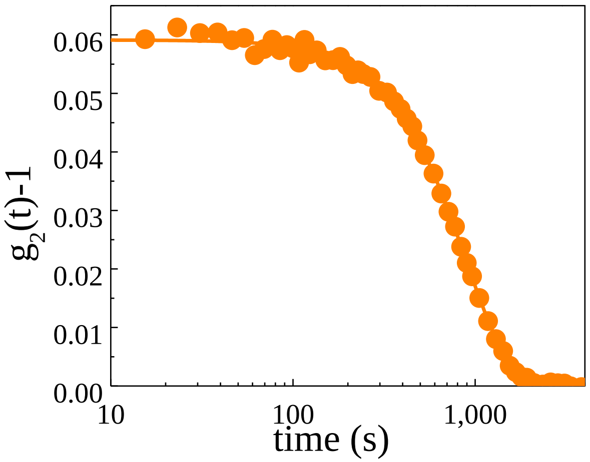
ANDOR CCD

Eiger2x4M



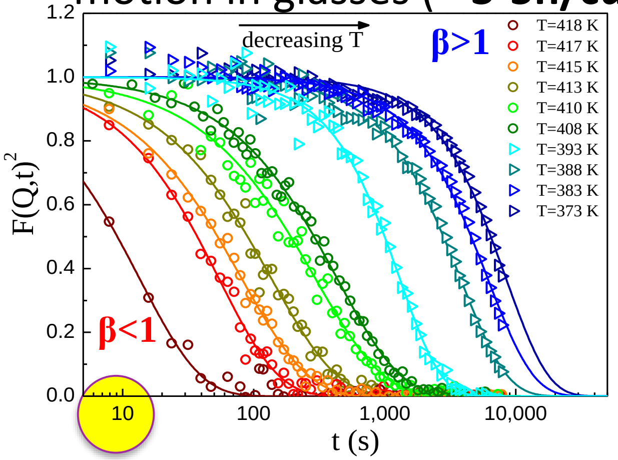
One q per measurement

≈ 0.1ph/px/s/frame



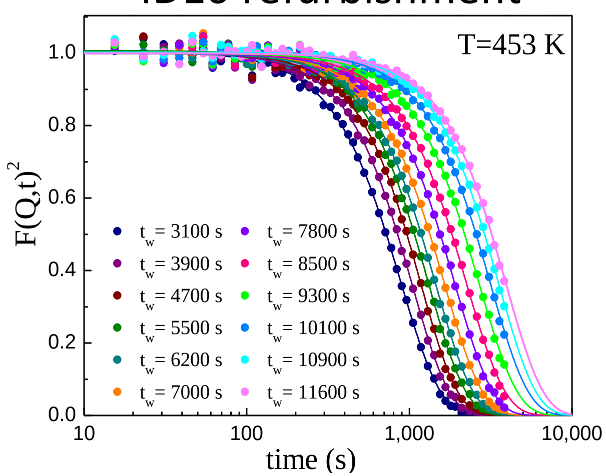
Progresses of last years on WA-XPCS on glasses at ESRF

2011: First measurements of atomic motion in glasses (≈ **3-5h/curve**)



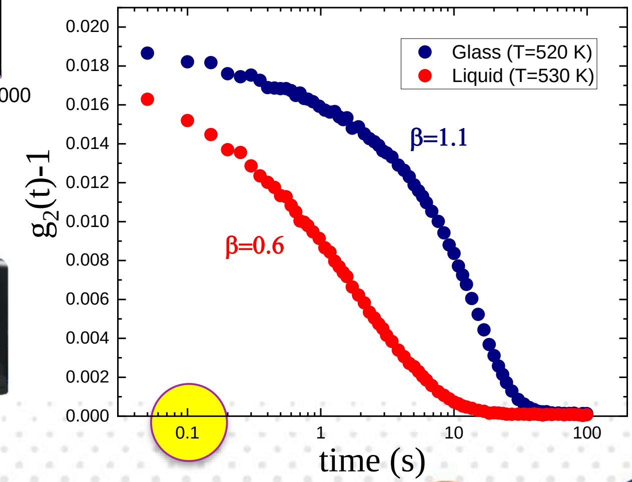
Ruta et al. PRL 2012

2015: better SNR after ID10 refurbishment



Giordano & Ruta Nat. Comm. 2016

2020: EBS larger dynamical range + better SNR (≈ **3 m/curve**)



There's still room for improvement…

4^{th} generation synchrotrons

new ground for XPCS

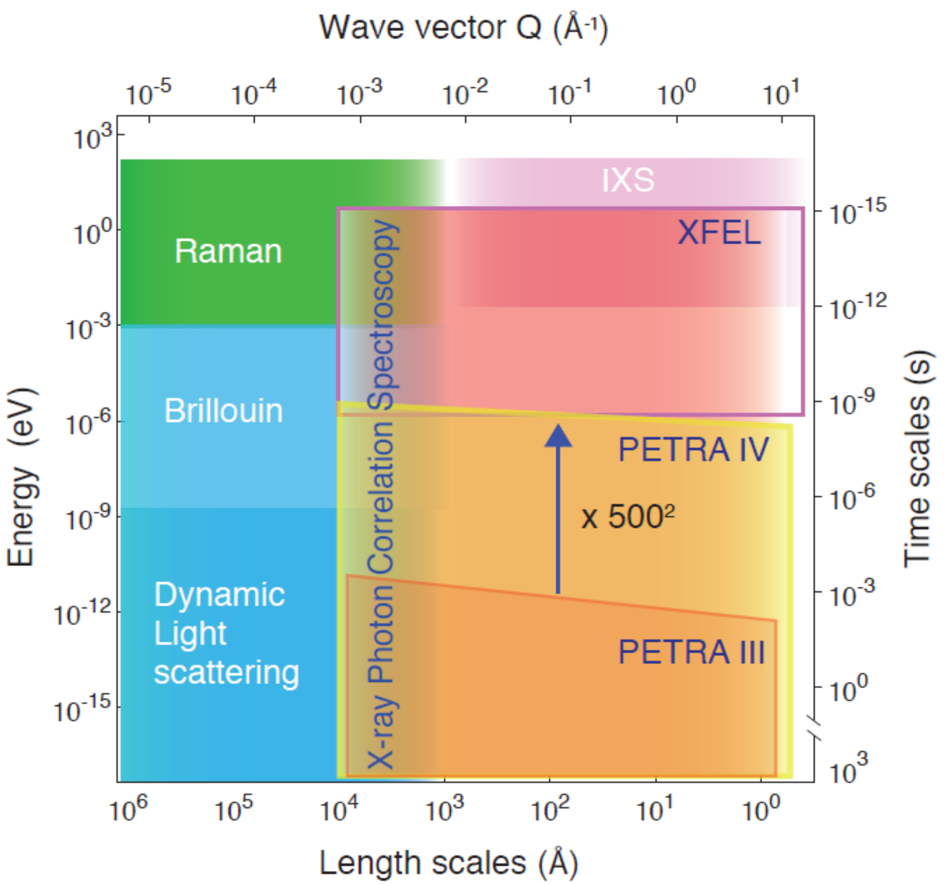
- 4 orders of magnitude faster times
- 100 times larger signal to noise ratio
- Extension into hard x-rays (> 10 keV)

➢ **ESRF – EBS** : already upgraded

➢ **APS-U**: upgrade starting in 2022

➢ **Petra IV**: upgrade foreseen for 2024

➢ & many other national synchrotrons (Max IV, etc..)

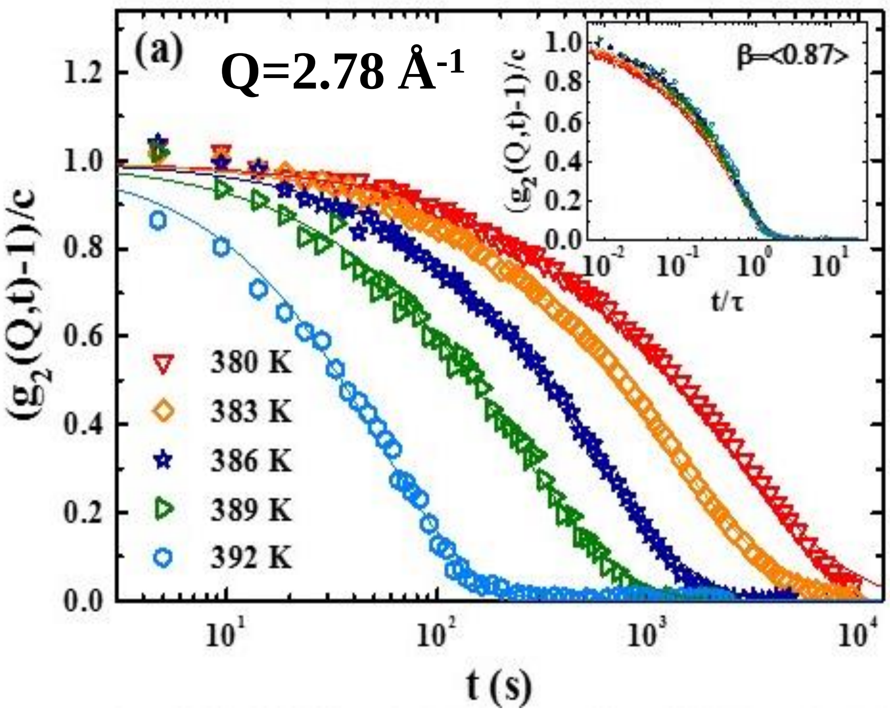


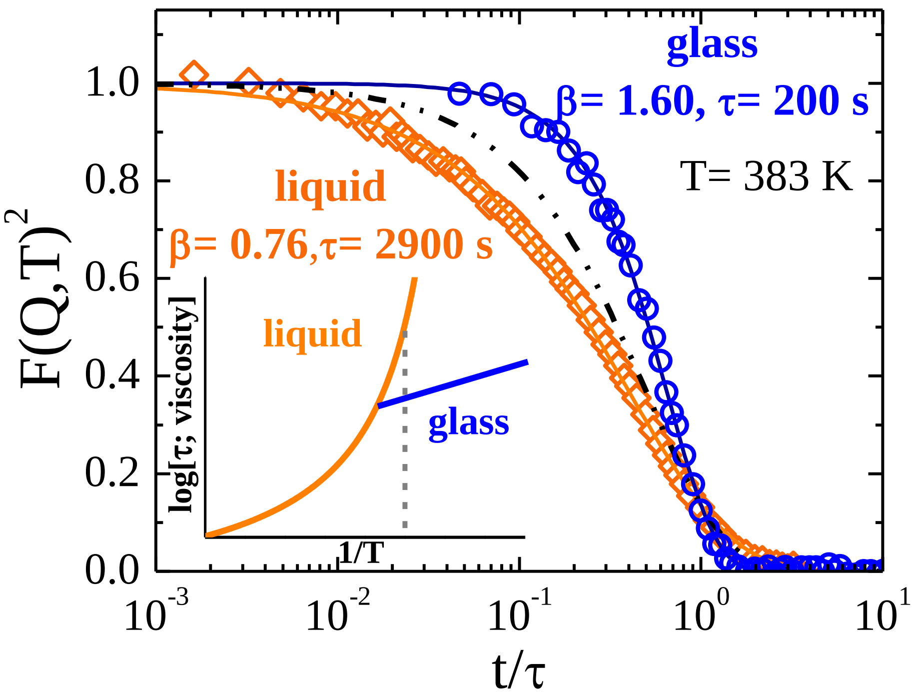
Courtesy of M. Sprung

Dynamics in the supercooled liquid phase (XPCS)

Quasi-static cooling: rate of 0.1 K/min and isothermal steps of ΔT=0.5 K

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

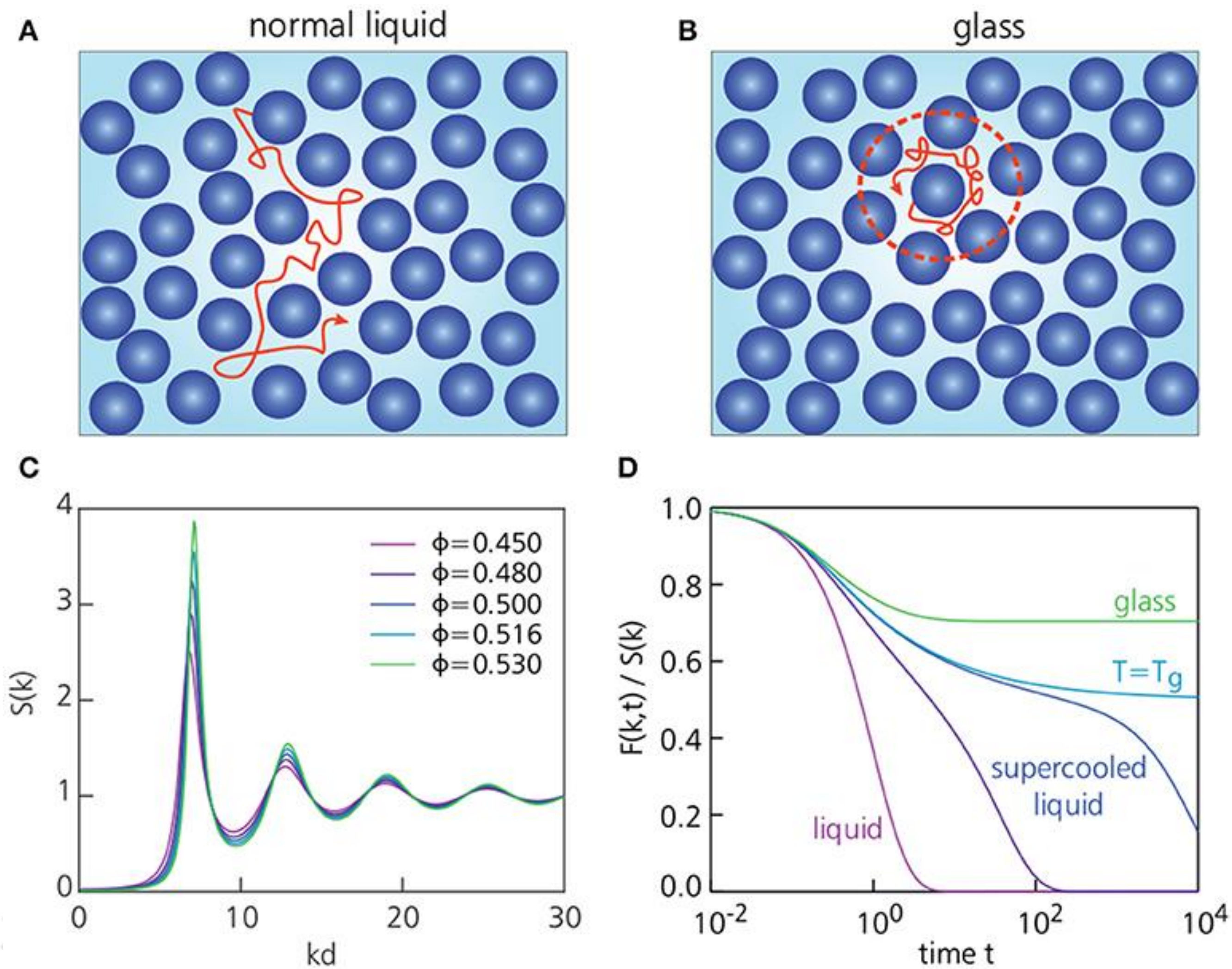




S. Hechler, et al. Phys. Rev. Mat. (2018)

The glass transition: a dynamical process

Liquid:
$\tau_{exp} << \tau$



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

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