Microscopic evidence of the connection between liquid-liquid transition and dynamical crossover in an ultra-viscous metallic glass former

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Liquid-liquid transitions are interesting to many researchers since they occur in systems as diverse as monoatomic liquids, multicomponent oxides and metallic glass-formers. In some cases, the crossover is accompanied by changes in the dynamical properties, although a direct microscopic evidence of this connection has not been reported so far. By combining state-of-the-art synchrotron techniques, we followed the structure and atomic motion during quasi-static cooling the $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ metallic glass-former from the low-temperature supercooled liquid. With this thermal protocol, we were able to lower the glass transition temperature far enough to reveal a liquid-liquid crossover between two amorphous structures corresponding to two ultra-viscous liquids with different kinetic behavior. This transition is in competition with vitrification, which occurs at conventional cooling rates, and is accompanied by structural changes not affecting the average density. Our results provide a direct connection between polyamorphism and dynamical crossover, and an alternative case to add in the highly-debated topic on the low-temperature divergence of the dynamics in supercooled liquids.

Many systems, ranging from monoatomic liquids [1–3] to amorphous alloys [4–7], exhibit transitions between liquid phases of different local structure. In glass-formers, liquid-liquid transitions (LLTs) have been reported either in high temperature melts [3,8–13] or in supercooled liquids [4–6,14,15], suggesting the existence of intrinsic connections between the kinetic properties of the system and the transition temperature [16]. LLTs are sometime associated to a dynamical crossover with changes in the kinetic fragility [6,10,17]. When observed upon cooling, the liquid evolves from a high temperature fragile phase with a steep temperature dependence of viscosity and structural relaxation time, to a strong phase less affected by temperature changes. For fragile liquids, like molecular and some metallic glass-formers, the LLT is expected at such a low temperature that the system may arrest beforehand in the glass [16]. Still, no direct microscopic evidence of this and more in general of a direct connection between LLT and dynamical crossover have been reported so far. This is also due to the extreme difficulty of obtaining experimental measurements of the atomic collective motion in glass-formers.

By taking advantage of state-of-the-art synchrotron techniques like x-ray photon correlation spectroscopy (XPCS) and high energy x-ray diffraction (XRD), we present the first experimental measurements of the microscopic dynamics of an ultra-viscous glass former with relaxation times which were not accessible until now, neither experimentally nor with numerical simulations. Our data show the occurrence of a LLT upon quasi-static cooling the $Au_{49}Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3}$ metallic glass-former, which can be *directly connected* with a fragile-to-strong dynamical crossover. Our thermal approach consists of isothermal steps of 0.5 K at a cooling rate of 0.1 K min^{-1} in the supercooled region between 396 K and 380 K (see SM). With this protocol the glass transition temperature, T_g, is lowered more than 30 degrees in comparison to a standard cooling rate of 20 K min^{-1}, allowing us to unveil the polyamorphic crossover in the ultra-viscous regime as predicted also by Ref. [16]. Interestingly, while the kinetic transition seems to occur at a determined temperature and leads to stationary microscopic dynamics, the structure exhibits much slower transformation rates over a broader transition region. This scenario provides a unique picture of polyamorphism at the atomic level and supports the idea of the formation of a new liquid phase that is locally more ordered and which does not affect the average density, as suggested for other types of complex systems [18–22].

XPCS experiments were performed at beamline ID10 at ESRF, France. Details on the sample and the technique are reported in the SM. Fig. 1 shows a selection of XPCS data measured at a wave vector Q_p=2.78 $Å^{-1}$ corresponding to the maximum of the structure factor, S(Q), for

different isothermal steps between 392 K and 380 K during cooling from the supercooled liquid. These temperatures lie slightly above the T_g for the applied cooling rate, which is determined to be 380 K, thus 33 K below the standard calorimetric T_g^{end} = 413 K (see ref. [23] and SM). The time average intensity auto-correlation functions are reported in Fig. 1a together with the fits with a Kohlrausch-Williams-Watts (KWW) model function: $g_2(Q,t) = 1 + c\left|\exp(-2(t/\tau)^{\beta}\right|$. Here, τ is the structural relaxation time, β the shape parameter, and c the product between the experimental contrast and the nonergodicity level of the glass, which is basically unity at Q_p [24]. All data are normalized by c, which is found constant at 4%. As discussed in ref. [25], $g_2(Q,t)$ is connected to the decay of density fluctuations and provides information on the collective dynamics at the probed length scale and time interval.

The quintessential behavior of supercooled liquid dynamics is seen in Fig. 1a. (1) Longer time decays are observed upon cooling, with a dramatic shift of two orders of magnitude from ~10^2 to ~10^4 s in a span of just 12 K. (2) The shape of the curve is described by a stretched parameter (i.e. $\beta < 1$) with average value of 0.87 ± 0.10, which is the signature of the heterogeneous dynamics usually found in metallic glass-formers [26–28]. (3) All data collapse onto a single curve when rescaled in reduced time units t/τ confirming the validity of time-temperature superposition (inset Fig. 1a) [29–31].

The stretched shape of the correlation functions in the supercooled liquid contrasts dramatically with the behavior observed in glasses. At the atomic level, metallic glasses exhibit stress-dominated dynamics characterized by an anomalous compressed decay of the correlation functions (i.e. with $\beta > 1$) [27,32–35], reminiscent of that reported in some soft glasses [25,26] and likely related to microscopic elastic frustrations [36–38]. This is also the case for the system studied in this work. As an example, Fig. 1b shows two normalized $g_2(Q_p,t)$ rescaled in reduced time units, measured both at 383 K but in two different amorphous states reached by following different thermal paths. Open diamonds correspond to a supercooled liquid obtained by applying the quasi-static cooling reported in this work, while the open circles are measured directly at 383 K in a glass produced by melt spinning (i.e. cooled with ~10^6 K/s). In the glass, the data decay fast and can be modeled with a compressed shape parameter β *two times larger* than the value found in the viscous liquid. Similar stretched behavior of the liquid and compressed behavior of the glass in terms of the $g_2(Q_p,t)$ have been reported also in a Mg-based metallic glass during cooling from the liquid into the glass and vice-versa [33,39]. It is important to note, that even if the data in Fig. 1b are measured at the same temperature, they correspond to dynamics that differ by a factor 15 in time, as schematically shown in the inset, with τ of ~200 s in the glass and of ~3000 s in the corresponding ultra-viscous liquid.

In the supercooled liquid, the system displays equilibrium dynamics. Representative data are shown in Fig. 1c at 386 K through the evolution of the two-times correlation function (TTCF), which describes the instantaneous correlation between intensity fluctuations in subsequent speckle patterns [25] (see SM). Here, the width of the intensity along the main diagonal is proportional to τ. The atomic dynamics appears stationary with no sign of aging over the entire observation time of 9000 s, thus for a temporal interval ≈8 times larger than the corresponding structural relaxation time. This applies to all temperatures but 380 K, the corresponding TTCF is reported in Fig. 2. In this case, we cooled the material from 385.5 K with a rate of 7 K min^{-1} to 380 K without any step. The system is not able to equilibrate during cooling and temporarily freezes into the glass from which it equilibrates in about 2800 s, as indicated by the continuous broadening of the intensity at the beginning of the measurement. After reaching equilibrium, the dynamics is stationary again and the system is in the liquid state, evidenced by a β of 0.71±0.05. The corresponding $g_2(Q_p,t)$ at 380 K is shown in Fig. 1a. It should be noted that equilibration of the ultra-viscous liquid is highly promoted by down-jumps in temperature. This is the reason why the system does not vitrify and remains a supercooled liquid during the whole quasi-static cooling. Differently, the equilibration from the as-quenched glass toward the liquid phase requires much longer times than those probed here. As a consequence, the $g_2(Q_p,t)$ measured by heating the glass and shown in Fig.1b remain compressed with fast relaxation times and no signs of equilibration (i.e. a transition from compressed to stretched and an increase in τ). Asymmetric equilibration mechanisms are typical of glass-formers [40]. They have been also reported in previous XPCS studies [27] and suggest the existence of a strong microscopic barrier to overcome for the equilibration from the glass toward the liquid phase.

The temperature dependence of the mean relaxation time $\langle\tau\rangle = \Gamma\left(\frac{1}{\beta}\right)\frac{\tau}{\beta}$ obtained from the XPCS data is shown in Fig. 3a. A clear change in the trend is observed at 389 K where $\langle\tau\rangle$ evolves from a steep to a weaker temperature dependence as highlighted in the inset. At a first sight, one would intuitively associate this behavior with the glass transition. This interpretation is, however, *in contradiction* with several observations. (1) The change occurs at a temperature ≈10 K above the expected T_g. (2) The shape of the corresponding $g_2(Q_p,t)$ remains stretched without any signature of the stress-dominated dynamics universal for metallic glasses and reported in Fig. 1b for the studied alloy. (3) Evidence of an aging glass is observed only at the lowest investigated temperature of 380 K (Fig. 2), while at higher temperatures the TTCFs exhibit exclusively stationary dynamics of the liquid (Fig. 1c). (4) The relaxation time still

displays a pronounced temperature dependence even at low temperatures, which is weaker than that at higher temperatures.

To better understand the dynamical results, we employed XRD to investigate the associated structural changes occurring in the material while applying the *identical* thermal protocol. We find a transition from one liquid structure to a different one before the system freezes into a *glass*, which is different from that obtained by faster cooling. This reveals the existence of a complex dynamical pattern that cannot be associated to a simple glass transition.

The XRD results are shown in Fig. 3b where we report the temperature dependence of the position of the first sharp diffraction peak (FSDP) of the static structure factor as $(Q_p(T_{ref})/Q_p(T))^3$, with T_{ref}=395.5 K (see SM). During a standard vitrification, this quantity continuously decreases upon cooling and then bends over to a weaker temperature dependence at T_g, due to the kinetic arrest and the transition into one isoconfiguration of the glass. This is indeed the case for a second dataset, which has been taken by *continuously cooling* the liquid with a *faster rate* of 1.5 K min^{-1} (green open triangles, T_g=390 K). XRD data of the quasi-static cooling were collected at the beamline ID11 at ESRF, while the fast-cooled glass was measured at the beamline P02.1 at DESY, Hamburg, Germany (see SM).

By applying the quasi-static cooling, T_g is lowered to 380 K. Normally, one would simply expect to observe the same departure from the liquid at this lower temperature (dashed grey line in the figure). In stark contrast to this, $(Q_p(T_{ref})/Q_p(T))^3$ (blue diamonds) displays a steady anomalous increase between 395.5 and 385.5 K, thus above the expected T_g (see also SM). This increase indicates the occurrence of *pronounced structural changes* in the material which *cannot* be associated to the vitrification. The bend of the XRD data below 380 K also confirms that the glass transition temperature of the strong liquid corresponds to T_g=380 K. Additional data taken below this temperature decrease upon cooling with a slope similar to that of the fast-cooled glass (green open triangles). The observed structural changes imply the existence of *different liquid phases* and strongly resemble what has been reported during a LLT in a Zr-based metallic liquid far above T_g [6].

In the light of these observations, the dynamical crossover measured by XPCS and shown in Fig. 3a must be associated with the structural changes during the LLT. The data above and below 389 K can be fitted separately with a Vogel-Tamman-Fulcher (VFT) equation $\langle\tau\rangle = \tau_0 \cdot exp\left(\frac{D^* \cdot T_0}{T - T_0}\right)$, where τ_0 is the high temperature relaxation time (10^{-14} s), D^* is the kinetic fragility and T_0 is the temperature, at which τ would diverge within this empirical description. The high-temperature liquid exhibits a fragile behavior with D^* = 8.9 ± 0.4 and T_0 = 315.9 ± 2.3 K. This fit is in good agreement with the fragility obtained at higher temperatures from α-relaxation

times (open triangles in Fig. 3a) measured using a dynamic mechanical analyzer (DMA, see SM). Differently, the low-temperature liquid is best fitted with $D^* = 23.1 \pm 0.8$ and $T_0 = 243.3 \pm 3$ K, showing a clearly stronger kinetic nature of that liquid and, hence, a fragile-to-strong LLT in the ultra-viscous state. Similar results can be obtained also by using an Arrhenius model for the data (see SM). The value of D^* obtained for the strong liquid is comparable to that of other strong metallic glass-formers [41,42] in the vicinity of T_g, whereas that obtained for the fragile liquid is among the smallest reported in literature [42,43]. In Zr-based metallic glass-forming systems, for example, such a fragile behavior is typically detected in the stable liquid well above the LLT [4,6,7].

Interestingly, the structure of the fragile high-temperature liquid evolves steadily towards the strong low-temperature liquid within a narrow temperature interval of 10 K, whereas the dynamical crossover occurs at a more defined temperature within our resolution. Similar results have been observed in glasses where sudden dynamical changes are accompanied by smeared-out structural modifications [33]. In our case, calorimetric studies show that the associated entropy change during the LLT is very small, i.e. 0.2 J g-atom^{-1} K^{-1}, which is in the order of only 2.4% of the entropy of fusion of this system [44]. This suggests the occurrence of extremely slow ordering kinetics during the LLT, as in other systems [22], which cannot be directly associated to a two state crossover scenario [45].

As discussed before, the polyamorphic transition is not observed when the system is cooled with a faster rate. In this case, T_g is close to the temperature of the dynamical transition (triangles in Fig. 3b), and the fragile liquid freezes into the glass before the LLT can occur. Between the two competing processes, vitrification is the dominant one. This is obvious if we consider that the glass transition is manifested by marked changes to dynamical quantities, while the structure of a glass is virtually indistinguishable from that of the corresponding supercooled liquid (isoconfigurational) at the moment of freezing. Without major structural modifications, it is therefore clear that vitrification occurs on a much faster time scale than the order-driven LLT, which instead consists of time-consuming structural rearrangements in the highly viscous supercooled liquid state probed here.

It is important to stress that the XRD data do not allow to speculate on the evolution of the density during the LLT, as the correlation between the macroscopic density and $1/Q^3$ is not straightforward for multicomponent liquids [13]. This information would require additional macroscopic measurements. In Zr-based metallic glass-formers for instance, the evolution between two liquid phases is accompanied by tiny structural changes (as those reported here) but without any anomaly in the density [6,7]. In that case, thus, the LLT is driven more by

changes in the entropy and in the local (chemical) order than by density changes. This could be the case also in our system.

We can get some indication on the density from the XPCS data as a change in density would reflect in a change in the decay of the density fluctuations and thus in the temporal evolution of the $g_2(t)$. The stationary dynamics in the XPCS data at each isotherm implies that the density changes only with temperature, although without further information. Differently, it remains constant during the isotherms. This is in agreement with the constant value of $(Q_p(T_{ref})/Q_p(T))^3$ during the isotherms (Fig. 4a and SM) and with the dynamic-to-structure connection recently proposed by some of us [46]. In contrast, the relative change of the FWHM, $\Gamma/\Gamma_0(T_{ref})$, of the FSDP exhibits a small, but still significant increase with time in the transition region below 391 K, whereas there is no evidence of changes above (Fig. 4b, inset and SM). This behavior, together with the stationary dynamics observed with XPCS, suggests the existence of local rearrangements which do not affect the average density. At 380 K, instead, both parameters in Fig. 4 decrease with time as a consequence of the aging towards the equilibrium [46]. As shown in Fig. 2, at this low temperature, the system freezes into the glass upon cooling and subsequently equilibrates within ~2800 s. The same applies for the structural metrics in Fig. 4 (see also SM) and can be attributed to a densification and medium range ordering during aging [35,46].

In conclusion, our study reports microscopic evidence of the direct connection between polyamorphism and fragile-to-strong dynamical crossover in an ultra-viscous metallic glass-former. In the specific system studied in this work, this phenomenology is usually hidden by the vitrification at higher cooling rates and appears associated with the slow formation of a distinct local order without affecting the average density [18,21]. This scenario shares similarities with the liquid-liquid transitions reported at high temperatures in the Zr- based alloys Vit1 and Vit106a [6,7], and with the case of supercooled Triphenyl Phosphite Ref. [47]. In these cases, the transitions are also accompanied by structural changes not affecting the density, without however a direct connection to a fragile-to-strong dynamical crossover. Further studies will clarify whether similar LLTs could occur also in other fragile glass-formers as it was suggested [16] or even in more systems.

Finally, it is worth to briefly discuss our results at the light of the current discussions about a possible divergence [48] or not [49–51] of the relaxation time below the conventional glass transition. Our present findings show a specific case where a sudden change in the temperature dependence of the relaxation time in the ultra-viscous regime comes from subtle structural

changes in the liquid and not from a dynamical divergence, which could however still occur at lower temperatures.

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References

[1] P. F. McMillan, M. Wilson, D. Daisenberger, and D. Machon, Nat. Mater. **4**, 680 (2005).

[2] S. Sastry and C. Austen Angell, Nat. Mater. **2**, 739 (2003).

[3] M. H. Bhat, V. Molinero, E. Soignard, V. C. Solomon, S. Sastry, J. L. Yarger, and C. A. Angell, Nature **448**, 787 (2007).

[4] C. Way, P. Wadhwa, and R. Busch, Acta Mater. **55**, 2977 (2007).

[5] Z. Evenson, T. Schmitt, M. Nicola, I. Gallino, and R. Busch, Acta Mater. **60**, 4712 (2012).

[6] S. Wei, F. Yang, J. Bednarcik, I. Kaban, O. Shuleshova, A. Meyer, and R. Busch, Nat. Commun. **4**, 2083 (2013).

[7] M. Stolpe, I. Jonas, S. Wei, Z. Evenson, W. Hembree, F. Yang, A. Meyer, and R. Busch, Phys. Rev. B **93**, 14201 (2016).

[8] S. Aasland and P. F. McMillan, Lett. to Nat. **369**, 633 (1994).

[9] Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata, and K.

Funakoshi, Nature **403**, 170 (2000).

[10] I. Saika-Voivod, P. H. Poole, and F. Sciortino, Nature **412**, 514 (2001).

[11] V. Molinero, S. Sastry, and C. A. Angell, Phys. Rev. Lett. **97**, 75701 (2006).

[12] A. Jaiswal, A. Podlesynak, G. Ehlers, R. Mills, S. O'Keeffe, J. Stevick, J. Kempton, G. Jelbert, W. Dmowski, K. Lokshin, T. Egami, and Y. Zhang, Phys. Rev. B - Condens. Matter Mater. Phys. **92**, 24202 (2015).

[13] W. Xu, M. T. Sandor, Y. Yu, H.-B. Ke, H.-P. Zhang, M.-Z. Li, W. H. Wang, L. Liu, and Y. Wu, Nat. Commun. **6**, 7696 (2015).

[14] P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley, H. Tanaka, C. Vega, L. Xu, and L. G. M. Pettersson, Chem. Rev. **116**, 7463 (2016).

[15] S. Wei, M. Stolpe, O. Gross, W. Hembree, S. Hechler, J. Bednarcik, R. Busch, and P. Lucas, Acta Mater. **129**, 259 (2017).

[16] C. A. Angell, MRS Bull. **33**, 544 (2011).

[17] A. Faraone, L. Liu, C.-Y. Mou, C.-W. Yen, and S. H. Chen, J. Chem. Phys. **121**, 10843 (2004).

[18] H. Tanaka, Phys. Rev. E **62**, 6968 (2000).

[19] H. Tanaka, R. Kurita, and H. Mataki, Phys. Rev. Lett. **92**, 25701 (2004).

[20] K. Murata and H. Tanaka, Nat. Mater. **11**, 436 (2012).

[21] H. Tanaka, Eur. Phys. J. E **35**, 113 (2012).

[22] M. Kobayashi and H. Tanaka, Nat. Commun. **7**, 13438 (2016).

[23] Z. Evenson, S. E. Naleway, S. Wei, O. Gross, J. J. Kruzic, I. Gallino, W. Possart, M. Stommel, and R. Busch, Phys. Rev. B **89**, 174204 (2014).

[24] B. Ruta, G. Monaco, V. M. Giordano, F. Scarponi, D. Fioretto, G. Ruocco, K. S.

Andrikopoulos, and S. N. Yannopoulos, J. Phys. Chem. B **115**, 14052 (2011).

[25] A. Madsen, A. Fluerasu, and B. Ruta, in *Synchrotron Light Sources Free. Lasers* (Springer International Publishing, Cham, 2015), pp. 1–21.

[26] L. Cipelletti, L. Ramos, S. Manley, E. Pitard, D. A. Weitz, E. E. Pashkovski, and M. Johansson, Faraday Discuss. **123**, 237 (2003).

[27] B. Ruta, Y. Chushkin, L. Cipelletti, E. Pineda, P. Bruna, and V. M. Giordano, Phys. Rev. Lett. **109**, 165701 (2012).

[28] L. Berthier, Physics (College. Park. Md). **4**, 7 (2011).

[29] D. Richter, B. Frick, and B. Farago, Phys. Rev. Lett. **61**, 2465 (1988).

[30] P. Lunkenheimer, R. Wehn, U. Schneider, and A. Loidl, Phys. Rev. Lett. **95**, 55702 (2005).

[31] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. Lett. **86**, 1271 (2001).

[32] Z. Evenson, B. Ruta, S. Hechler, M. Stolpe, E. Pineda, I. Gallino, and R. Busch, Phys. Rev. Lett. **115**, 175701 (2015).

[33] B. Ruta, V. M. Giordano, L. Erra, C. Liu, and E. Pineda, J. Alloys Compd. **615**, 45 (2014).

[34] B. Ruta, G. Baldi, G. Monaco, and Y. Chushkin, J. Chem. Phys. **138**, 54508 (2013).

[35] B. Ruta, E. Pineda, and Z. Evenson, J. Phys. Condens. Matter **29**, (2017).

[36] P. Chaudhuri and L. Berthier, arXiv **1605**, 097770v1 (2016).

[37] E. E. Ferrero, K. Martens, and J. L. Barrat, Phys. Rev. Lett. **113**, 248301 (2014).

[38] M. Bouzid, J. Colombo, L. V. Barbosa, and E. Del Gado, Nat. Commun. **8**, 15846 (2016).

[39] B. Ruta, Y. Chushkin, and G. Monaco, AIP Conf. Proc. **1518**, 181 (2013).

[40] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).

316 [41] R. Busch, W. Liu, and W. L. Johnson, J. Appl. Phys. **83**, 4134 (1998).

317 [42] I. Gallino, J. Schroers, and R. Busch, J. Appl. Phys. **108**, 1 (2010).

318 [43] O. Gross, B. Bochtler, M. Stolpe, S. Hechler, W. Hembree, R. Busch, and I. Gallino,
319 Acta Mater. **132**, 118 (2017).

320 [44] I. Gallino, D. Cangialosi, Z. Evenson, L. Schmitt, S. Hechler, and B. Ruta, arXiv **1706**,
321 3830 (2017).

322 [45] H. Tanaka, J. Phys. Condens. Matter **15**, L703 (2003).

323 [46] V. M. Giordano and B. Ruta, Nat. Commun. **7**, 10344 (2015).

324 [47] M. Kobayashi and H. Tanaka, Nat. Commun. **7**, 13438 (2016).

325 [48] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

326 [49] J. Zhao, S. L. Simon, and G. B. Mckenna, Nat. Commun. **4**, 1783 (2013).

327 [50] E. Arianna, A. Pogna, C. Rodríguez-Tinoco, G. Cerullo, C. Ferrante, and J. Rodríguez-
328 viejo, PNAS **112**, 2331 (2015).

329 [51] T. Hecksher, A. I. Nielsen, N. B. Olsen, and J. C. Dyre, Nat. Phys. **4**, 737 (2008).

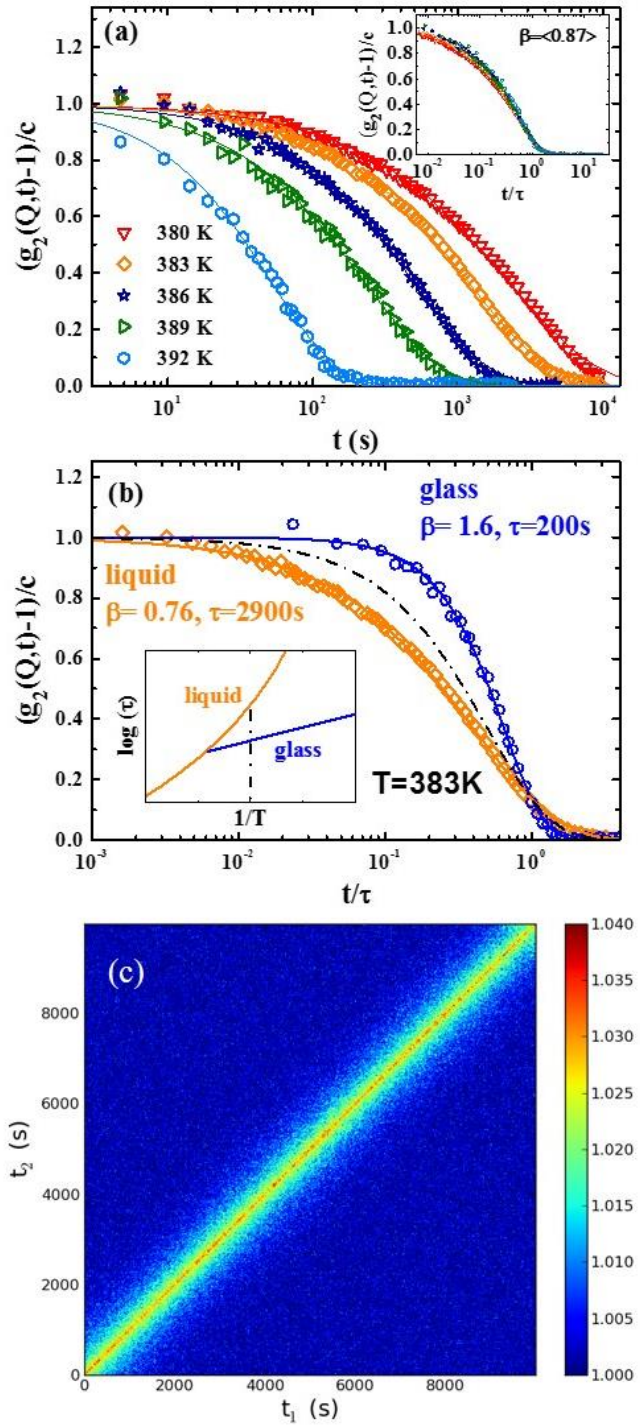
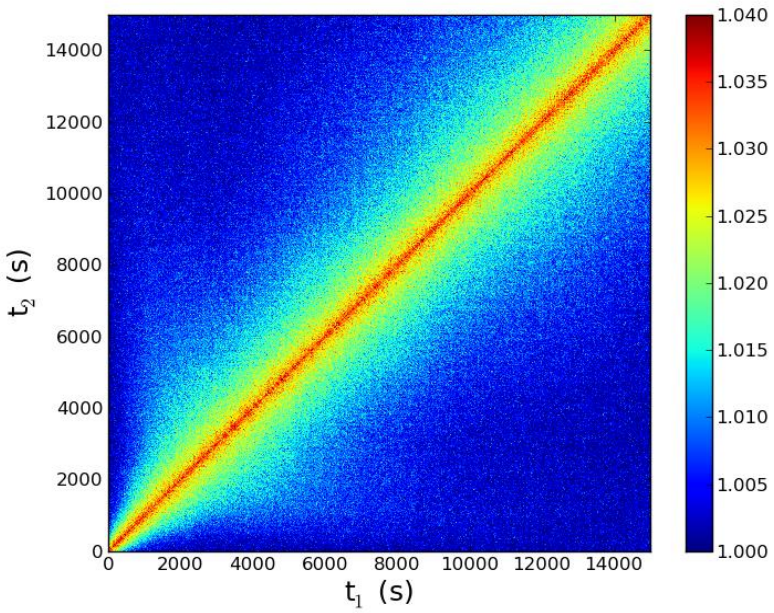


Figure 1: (a) Temperature dependence of normalized intensity autocorrelation functions measured with XPCS at Q_p=2.78 Å^{-1}. Lines are fits using the KWW function. **Inset**: Same data reported as t/τ. **(b)** $g_2(Q_p,t)$-1/c as a function of t/τ measured at 383 K in an hyperquenched glass heated from low temperature (blue circles), and in the supercooled liquid shown in panel (a) (orange diamonds). The dashed line is a single exponential decay. The two curves correspond to two distinct dynamics as sketched in the inset by the intersection of the vertical line with the glass or the liquid. **(c)** TTCF at 386 K showing stationary dynamics.



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340 **Figure 2**: TTCF measured with XPCS at 380 K after quenching from 385.5 K with 7 K min^{-1}.
341 The broadening at short times due to equilibration stops after ~2800 s.

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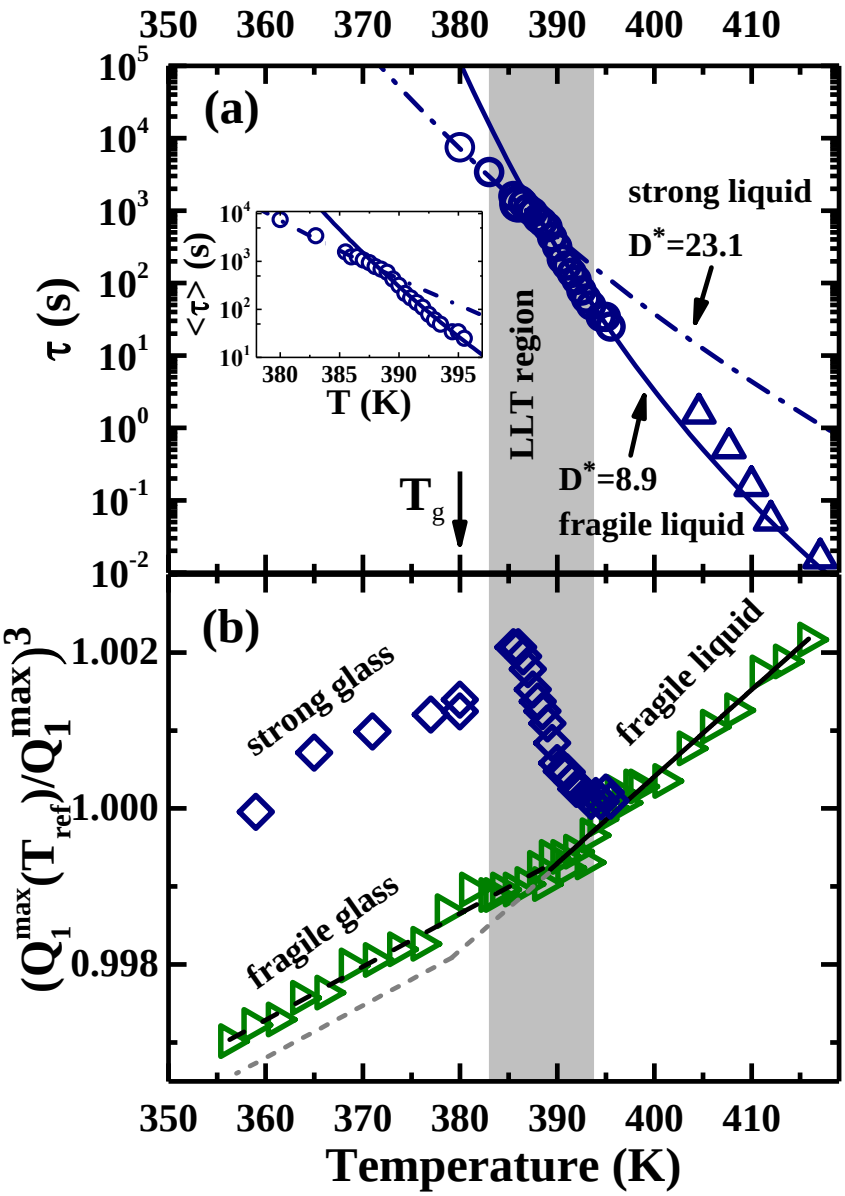

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345 **Figure 3: (a)** Temperature dependence of τ measured by XPCS (circles) and DMA (triangles).
346 The LLT occurs at 389 K leading to two regimes with distinct fragilities (magnified in the inset).
347 **(b)** Temperature dependence of the relative shift $(Q_1^{max}(T_{ref})/Q_1^{max})^3$ of the FSDP measured
348 with XRD by continuous cooling with 1.5 K min^{-1} (green triangles), and by applying the quasi-
349 static protocol used for the XPCS data (blue diamonds). The grey dashed line shows the
350 standard behavior that one would have expected to see in absence of the LLT.

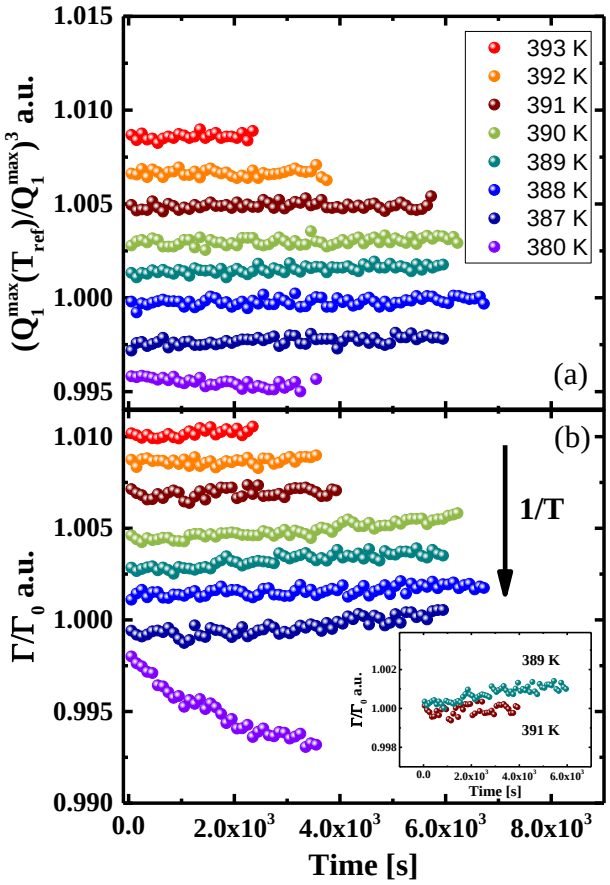

Figure 4: Temporal evolution of $(Q_1^{max}(T_{ref})/Q_1^{max})^3$ (a) and FWHM (b) during isotherms at selected temperatures between 395.5 and 380 K. All data are vertically shifted for clarity. We can distinguish three different behaviors: 1) at high temperature between 395.5 k and 391 K, both $(Q_1^{max}(T_{ref})/Q_1^{max})^3$ and the FWHM are constant with time; 2) between 390 and 385.5 K $(Q_1^{max}(T_{ref})/Q_1^{max})^3$ remains constant while the FWHM slightly increases with time. This behavior can be attributed to changes in the local order not affecting the average density; 3) At the glass transition temperature of the quasi-static cooling, i.e. 380 K, both parameters decrease due to aging and thus to the equilibration at short times from the glass toward the liquid phase. The same equilibration is also observed in the dynamics in Fig. 2.