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New pathways to control the evolution of the atomic motion in metallic glasses

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Abstract

Metallic glass formers are a relatively new entry in glass physics, which has attracted large interest in both physics and materials science communities due to the unique mechanical and structural properties of these materials. Physical aging is however one of the main obstacle to their widespread use as it affects their properties at all length scales. The knowledge of the microscopic mechanisms inducing aging and relaxation is therefore extremely important for both fundamental and applied sciences. In this article we present a review of the recent advances made with the x-ray photon correlation spectroscopy technique on the study of the collective particle motion and physical aging in metallic glasses at the atomic level. We show that a careful tuning of the sample preparation or the application of specific thermal protocols have the potential to drive the glass into more aged or rejuvenated microscopic configurations with different stabilities.

Introduction

Glasses are essential materials in our daily life and they have accompanied progresses in civilization for millennia. Although they are used in a wide range of applications, spanning from engineering to medicine or environmental science, a full comprehension of the mechanisms responsible for their unique properties is still missing [1]. Within the broad family of glassy materials, metallic glasses (MGs) are considered a relatively young entry. Discovered in the nineteen sixties, in few decades they have obtained a dominant role in material science and are currently considered among the most actively studied metallic materials [2]. MGs present an outstanding combination of properties such as high strength, large elastic elongation and high corrosion resistance. In addition, in the temperature region between the glass transition temperature and the crystallization temperature, MGs can be easily deformed in very precise

32 complex shapes, which makes them promising candidates for many small-scale devices for
33 advanced technological applications, like fuel cell electrodes, storage devices and micro
34 electro-mechanical systems [3]. Metallic glasses are extremely interesting materials also for
35 fundamental science. Thanks to the nature of the metallic bonds, their microscopic dynamics is
36 subject only to translational motion, which make them model candidates for the study of the
37 glass transition nature. MGs share also many similarities with colloidal materials [4], and can
38 be used to find common properties between hard and soft glass formers materials.

39 As all glasses, MGs are unstable with time and exhibit physical aging. This means that all their
40 properties evolve spontaneously with time and are strongly influenced by the material
41 production and processing. Physical aging can be particularly severe in MGs, more than in other
42 glasses like network or molecular systems, and can lead to ductile to brittle transitions, fractures
43 and crystallization. Aging can therefore produce annoying technological drawbacks, since it
44 makes the amorphous arrested state difficult to control during technological applications [5],
45 [6]. In this respect, the knowledge of the microscopic mechanisms responsible for relaxation
46 and aging in MGs is critical as it allows to predict and control the behaviour of glasses over
47 time and during applications.

48 In the last decade, coherent x-rays and in particular the x-ray photon correlation spectroscopy
49 (XPCS) technique have emerged as a powerful tool to probe the collective atomic motion of
50 MG during aging [7], [8]. This technique monitors the fluctuations in the scattered intensity
51 generated by the impinging of coherent x-rays on disordered systems, and provides information
52 on the intermediate scattering function (ISF), $f(q,t)$, and thus on the electron density fluctuations
53 at a length scale $2\pi/q$ defined by the probed wave-vector q [9].

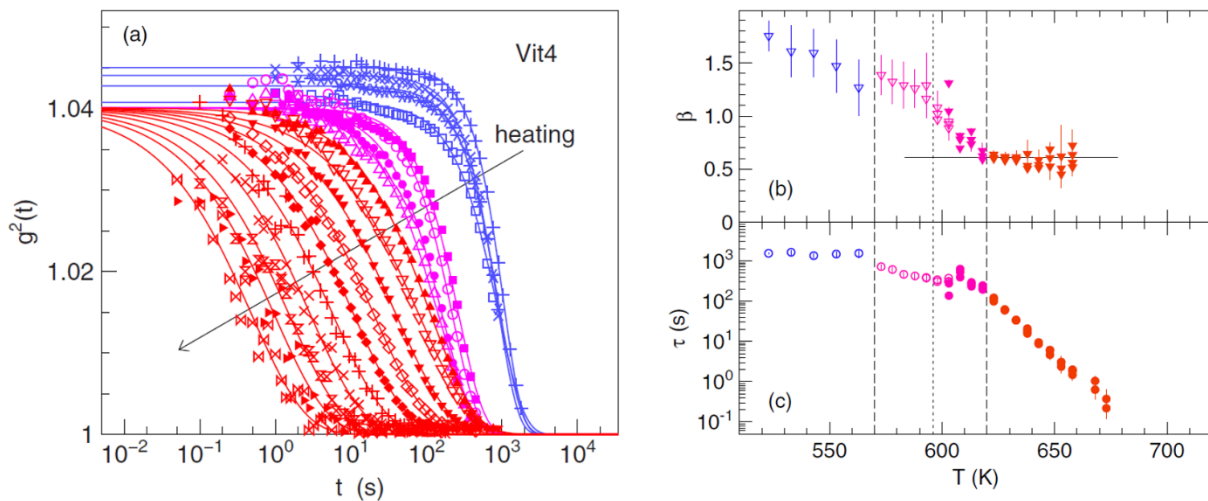
54 Aging studies on MGs have revealed a complex behavior [7]. At the microscopic level, aging
55 is intermittent and dominated by the interplay between density-driven rearrangements
56 associated to the release of residual stresses, and ordering processes at length scales
57 corresponding to the medium range order, which do not affect the local density [10]–[12].
58 Numerical simulations and elastic measurements suggest avalanche-like mechanisms triggering
59 the relaxation in glasses [13]. Aging is found hierarchical even at the macroscopic scale, and
60 multiple relaxations have been reported during long time enthalpy recovery and stress
61 relaxation measurements in polymers and metallic systems [14]–[16].

62 After briefly recalling these results, we present here some recent attempts which have been
63 made to control the evolution of the collective particle motion and therefore the aging in MGs

64 by applying external parameters such as stresses, thermal cycling or specific sample
 65 preparations.

66 Atomic motion across the glass transition

67 Metallic glasses are usually produced by rapidly cooling the corresponding melt with rates of
 68 the order of 10^4 - 10^6 K/s. Such a fast quenching is fundamental to avoid crystallization and
 69 freeze the system in an amorphous solid state. On approaching the glass transition temperature,
 70 T_g , from the liquid phase, the collective particle motion evolves from diffusive at high
 71 temperatures to a regime of activated dynamics in the supercooled liquid phase [17], [18]. In
 72 this region the intermediate scattering function splits in two main processes: i) a fast
 73 microscopic decay associated to the rattling of the particles in the cage formed by the
 74 neighbouring particles, and ii) the main structural relaxation process corresponding to the
 75 escape of the particles from their cages [19]. The latter process corresponds to the long-time
 76 decay of the ISF and can be modelled by the empirical Kohlrausch-Williams-Watts (KWW)
 77 function $f(q,t)=f_q \exp(-t/\tau)^\beta$. In this expression, τ is the structural relaxation time and describes
 78 the time necessary for the system to reorganize the structure in a more stable configuration at
 79 the probed length scale. In the liquid phase, $\tau(q)$ is equal to the equilibration time and is
 80 proportional to the viscous flow. The parameter $\beta(q)$ provides instead information on the degree
 81 of heterogeneity of the dynamics and on the nature of particle motion, and $f_q(q)$ is the non-
 82 ergodicity parameter representing the long-time plateau preceding the structural relaxation.



83

Figure 1. a) Temperature dependence of the correlation functions measured with XPCS in a Vit4 MG during isothermal steps of 5 K between 520K and 675K, obtained by heating the glass with a rate of 1 K/min. The as-cast sample was annealed at 600K prior to the measurements to remove eventual stresses related to the sample preparation. The data are collected at $q=2.6\text{\AA}^{-1}$ corresponding to the first maximum of the atomic structure

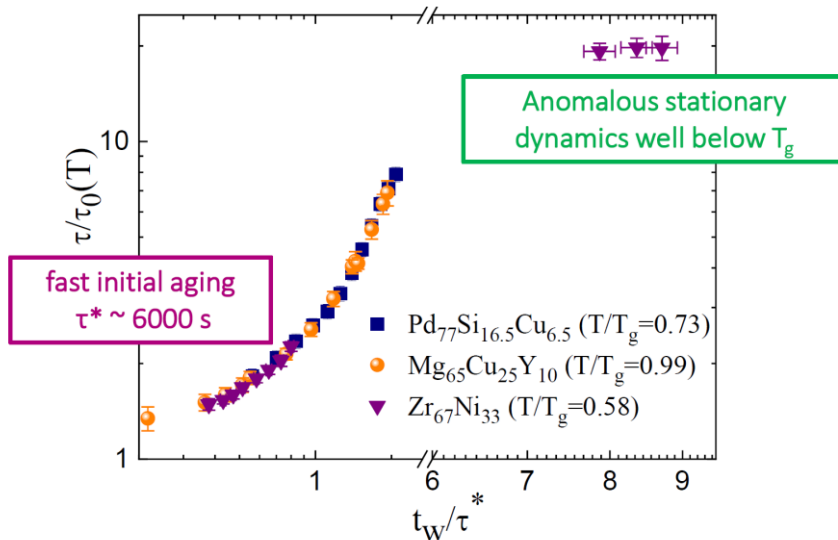
factor. b) and c) Corresponding shape parameter (b) and structural relaxation time (c) obtained by modelling the data in a) with a KWW function. Taken from [20].

84

85

86 Upon further decreasing the temperature, the structural relaxation time increases by several
87 orders of magnitude until the material solidifies in a metastable glassy state. Studies on MGs
88 have shown that the glass transition is accompanied by a dynamical crossover at the atomic
89 level where the decay of the ISF evolves from the well-known stretched exponential shape (i.e.
90 described by $\beta < 1$) of supercooled liquids, to an unusual compressed form in the glass which
91 can be modelled with an exponent $\beta > 1$ [4]. The same transition is reported also by heating from
92 the glassy state. An example of the dynamical crossover occurring in MGs at the glass transition
93 temperature is reported in Fig. 1a. This figure shows the temperature evolution of the intensity-
94 intensity correlation functions, $g_2(q,t)$ measured with XPCS at the atomic scale upon heating a
95 glass of Vit4 from ambient temperature up to the liquid phase with a heating rate of 1 K/min
96 [20]. In this case, the as-cast glass was relaxed at 600K prior to the measurements to remove
97 the presence of stresses related to the fast-quenching used during the sample preparation. XPCS
98 measurements were performed at the maximum of the static structure factor during isotherms
99 every 5K from 520K up to 675 K. We recall that the $g_2(q,t)$ functions are proportional to the
100 intermediate scattering functions being $g_2(q,t) = 1 + f(q,t)^2$ [9]. The corresponding KWW
101 parameters τ and β are shown in Fig. 1b and 1c. Three different dynamical regions have been
102 reported for MGs and are visible in the figure. At low temperatures (blue data), the correlation
103 functions vary little with temperature, with an almost constant structural relaxation time and a
104 constant shape parameter $\beta > 1$, which has been attributed to the occurrence of a stress-induced
105 dynamics [20]. In the glass transition region (pink data), τ increases in an Arrhenius way with
106 a small activation energy, and is accompanied by a continuous decrease of β toward a stretched
107 value $\beta < 1$ which is then reached for temperatures, T , larger than the glass transition temperature
108 $T_g = 600$ K. At these temperatures, the system is in the liquid phase and the relaxation time
109 decreases with the typical super Arrhenius behaviour of supercooled metallic liquids (red
110 values) and is accompanied by a constant stretched parameter describing the decay of the
111 correlation functions, close to the value reported with mechanical measurements [20]. Several
112 attempts have been made to explain the compressed decorrelation in the glassy state, from both
113 theoretical and numerical sides [21], [22]. A comparison with macroscopic mechanical
114 measurements associates the dynamical crossover to the separation between the anelastic and
115 viscoelastic response to mechanical stresses at T_g , the former being active also well below T_g

116 [23]. Numerical simulations in metallic liquids glass-formers report on the existence of
 117 compressed intermediate scattering functions in the high temperature liquid phase which appear
 118 related to an increasing number of icosahedral clusters on approaching the vitrification and
 119 generate additional frustration in the material [24]. Whether a similar argument could be applied
 120 to the glassy state is not verified yet. Experiments in soft glasses report instead on a very similar
 121 dynamical crossover in a variety of systems including colloids, foams, biopolymers and
 122 microgels measured with both x-ray and light scattering photon correlation spectroscopy [25],
 123 [26]. In these cases, the crossover is often accompanied by a transition from diffusive dynamics,
 124 i.e. described by a sub-quadratic dependence of the relaxation time, $\tau(q)=1/q^2$, to an anomalous
 125 super-diffusive, ballistic-like particle motion with $\tau(q)\approx 1/q$. Stress relaxation in the disordered
 126 structure can qualitatively describe this phenomenology, although a detailed understanding is
 127 still missing [21], [22], [27]. At present, the idea is that the dynamics of soft glasses are triggered
 128 by random collapses of the structure due to highly stressed regions in the material. In MGs these
 129 regions could be associated to the presence of elastic inhomogeneities at the nanometric scale
 130 [28], which could be related to the presence of flow units [2]. Information on the wave-vector
 131 dependence of the dynamics in MGs could help clarifying the nature of the dynamical
 132 crossover. Due to the out-of-equilibrium nature of glasses, such information is very difficult to
 133 obtain below T_g both experimentally and with numerical simulations and only few information
 134 about the dynamics in the supercooled liquid phase have been reported so far [18].



135

136 **Figure 2.** Temporal evolution of the structural relaxation time measured with XPCS in binary and ternary rapidly
 137 quenched MG obtained upon heating the as-cast glasses up to specific temperatures in the glassy state with slow
 138 heating rates (3K/min for $\text{Pd}_{77}\text{Si}_{16.5}\text{Cu}_{6.5}$ and $\text{Zr}_{67}\text{Ni}_{33}$, 1K/min for $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$). The data are rescaled for the
 139 initial value of the relaxation time at each temperature, $\tau_0(T)$ and reported as a function of the time elapsed since

140 the beginning of the isotherm (waiting time, t_w) rescaled by a parameter τ^* that describes the short time exponential
141 growth rate during aging through the expression $\tau(T, t_w) = \tau_0(T) \exp\left(\frac{t_w}{\tau^*}\right)$. Pd₇₇Si_{16.5}Cu_{6.5} data are taken from
142 Ref. [11], Mg₆₅Cu₂₅Y₁₀ data from Ref. [4] and the Zr₆₇Ni₃₃ data from Ref. [29].

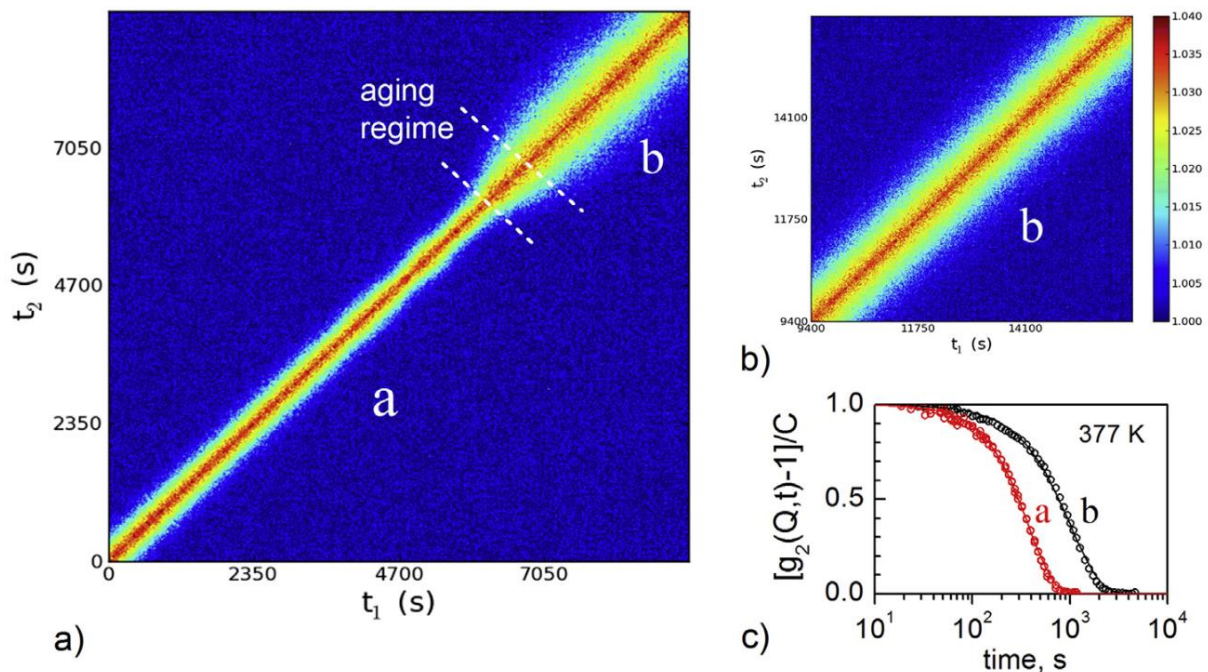
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144 The main difficulty arises from the impossibility to compare data acquired at different times
145 due to the strong evolution of the microscopic dynamics due to physical aging. The first studies
146 on the dependence of the collective atomic motion on aging have been performed on rapidly
147 quenched MGs, i.e. on ribbons of amorphous metals which were produced with a fast cooling
148 rates of 10⁶ K/s from the melt and then subsequently heated up in the glassy state. Studies on
149 binary and ternary fast quenched MGs, showed the occurrence of two dynamical regimes which
150 are summarized in Fig. 2: a first exponential increase of the relaxation time during isotherms in
151 the glass, followed by an anomalous stationary regime at longer annealing times (see Fig. 2).
152 X-ray diffraction studies suggest that the first fast dynamical regime arises from density release
153 mechanisms likely involving the annihilation of defects or excess free volume stored in the
154 system, while the stationary regime would be more related to ordering processes occurring at a
155 length scale corresponding to the medium range order [11]. During this stationary regime, the
156 system is trapped in a metastable state from which aging seems then to pursue through irregular,
157 intermittent evolutions of the collective particle motion which would bring the system in
158 another metastable state. An example of this intermittent dynamics is shown in Fig. 3 for a
159 multicomponent ribbon of Au₄₉Cu_{26.9}Si_{16.3}Ag_{5.5}Pd_{2.3} measured during an isothermal annealing
160 of 5 h at 377 K, well below the glass transition temperature $T_g=396$ K of this composition. The
161 figure reports the temporal evolution of the two-times correlation functions (TTCF), another
162 important quantity which can be extracted from an XPCS experiment. The TTCF is a time
163 resolved version of the standard intensity-intensity correlation functions and provides
164 information on the temporal evolution of the correlation between configurations measured at
165 different times t_1 and t_2 . Each pixel on the TTCF expresses the correlation between the intensity
166 of two frames acquired at times t_1 and t_2 in a colour coded fashion. The main diagonal from
167 bottom left corner to the top high corner indicates increasing elapsed times from the beginning
168 of the measurement and corresponds to the condition $t_1=t_2$, hence showing maximum
169 correlation in red. Horizontal or vertical lines (in the lower and upper quadrants respectively)
170 from a single point along the main diagonal corresponds to correlation measured at increasingly
171 longer delay time $\Delta t=t_2-t_1$ from this fixed reference frame. The loss of correlation (blue values)
172 occurs when the system has relaxed in a new configuration. The width of the yellow profile

173 along the main diagonal is therefore proportional to the structural relaxation time, the larger
 174 this width is, the slower is the dynamics.

175 In the specific case of Fig. 3a, the TTCF shows two stationary regimes, termed (a) and (b), with
 176 constant intensity profiles along the main diagonal but different relaxation times, being the
 177 dynamics in the regime ‘b’ slower than in ‘a’. A short temporal period of aging leads to a
 178 ‘smooth’ transition between these two distinct metastable configurations after about 7000s from
 179 the beginning of the isotherm. Standard intensity-intensity correlation functions can be obtained
 180 by temporal averaging the frames corresponding to each stationary regime ((a) and (b)) and can
 181 be used to quantify the increase in the relaxation time induced by the aging, as shown in Fig.3c.

182 Similar intermittent aging dynamic has been reported in few other compositions and often
 183 dominates the dynamics when the glass is subjected to mechanical deformations [30]. Although
 184 there is a common idea of an avalanche like particle motions triggering the aging, a clear
 185 explanation for the observed behaviour is still missing. Multiple aging regimes have been
 186 observed in few macroscopic studies in metallic, polymeric and chalcogenide glass formers
 187 [14]–[16]. In these works, the authors report on the existence of multiple decays during enthalpy
 188 relaxation interconnected by stationary regimes suggesting a strong connection with the atomic
 189 scale dynamics.



190
 191 **Figure 3.** a) TTCF measured with XPCS in an Au-based alloy during isothermal annealing at 377 K for 5 h below
 192 T_g . Data show a crossover between two stationary regimes, termed *a* and *b*, connected by a short period of aging
 193 occurring after about 7000s from temperature equilibration. b) Continuation of the TTCF at longer annealing times

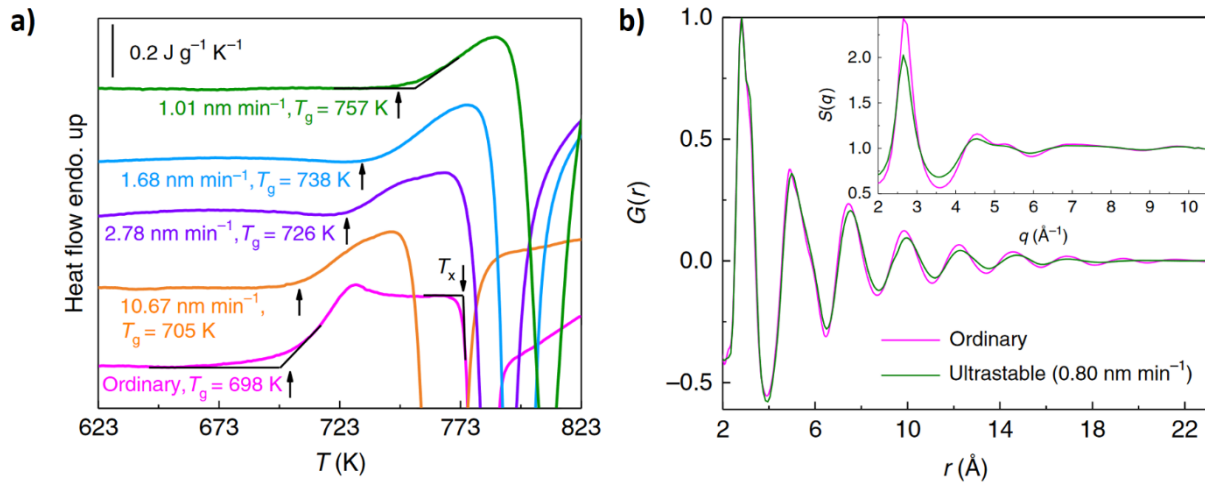
194 showing that the dynamics keep stationary in the regime b for longer times. c) Intensity correlation functions
195 calculated by temporal averaging the data collected in the two stationary regimes reported in panel (a). Taken from
196 [15].

197

198 **Controlling the aging through external parameters**

199 Last decades have witnessed an impressive amount of excellent scientific works aimed toward
200 the control of the relaxation behavior and physical aging in MGs by using physical vapor
201 deposition techniques [31], or by altering the relaxation state by applying external parameters,
202 such as stress [32] or extreme thermal cycling [33].

203 Since the excellent works of Ediger and his group on organic glassy compounds [31], the
204 possibility to dramatically improve the stability of a glass by creating the amorphous solid state
205 by means of physical vapour deposition techniques has fascinated the glass community. The
206 basic idea is that during the deposition the particle mobility at the free surface is orders of
207 magnitude larger than in the bulk and allows for a more efficient particle packing, lowering the
208 energy of the system and bringing therefore the glass in a deeper minimum of the potential
209 energy landscape. Ultrastable glasses formed by physical vapour deposition are considered as
210 an analogue of glassy materials aged for geological times. Among their different physical
211 chemical properties, their improved thermal stability, signalled by a higher calorimetric glass
212 transition temperature on heating, makes them excellent promising candidates for many
213 technological applications. The first vapour deposited MG was produced by the group of K.
214 Samwer and exhibited an increased stability of about 10K with respect to the standard fast-
215 cooled glass [34]. This work paved the way to a large number of studies, although the possibility
216 to obtain metallic ultrastable glasses has been largely debated [35]–[37]. Structural studies of
217 vapour deposited MG have shown that by lowering the deposition rate is possible to improve
218 the stability up to 60K with respect to standard cooled glasses (Fig. 4 a). Curiously, this
219 improved stability comes with a less ordered structure (Fig. 4 b) with respect to an ordinary
220 rapidly cooled MG [38].

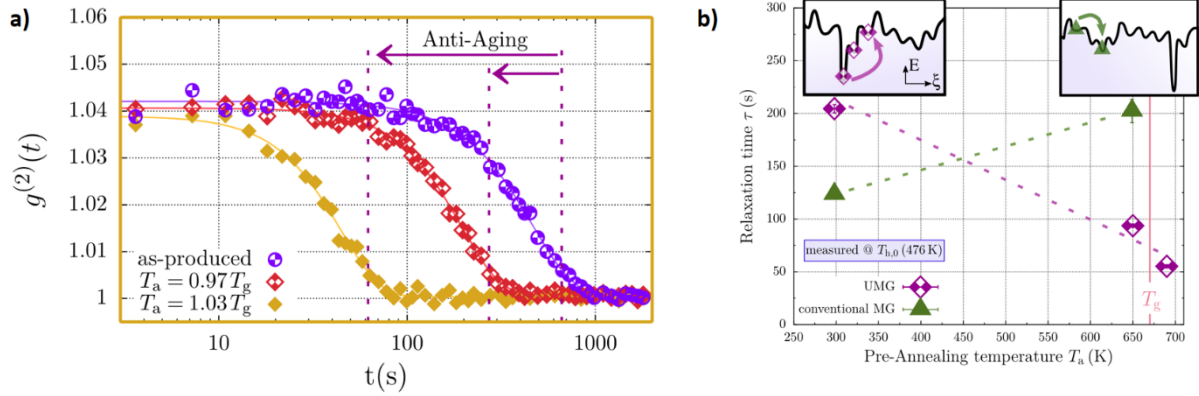


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222 **Figure 4.** a) Differential scanning calorimetric profiles of an ordinary (i.e. fast quenched) MG and MGs produced
 223 by physical vapour deposition highlighting the increasingly stability and thus larger T_g on lowering the deposition
 224 rate. An increase of T_g up to 60 K can be obtained with the slowest deposition rate. b) Reciprocal space (inset) and
 225 real space static profile of an ordinary and a vapour deposited MG showing larger stability in the calorimetric
 226 profile. The improved stability comes with a less ordered structure than in a standard MG. Taken from Ref. [38].

227

228 The influence of the ultrastability on the collective particle motion and aging has been
 229 investigated in an MG of Cu₅₀Zr₅₀ produced by physical vapour deposition following the
 230 procedure reported in Ref. 34 [35]. Signatures of an improved stability have been reported at
 231 the atomic scale in vapour-deposited MG. This is shown in Fig. 5a which reports correlation
 232 functions measured with XPCS in different vapour-deposited MGs: as-prepared, and pre-
 233 annealed at different annealing temperatures T_a, above and below the calorimetric T_g and then
 234 cooled back to ambient temperature prior to the measurements. Data collected during an
 235 isotherm in the glassy state show that the relaxation dynamics is slower in the as-cast vapour
 236 deposited MG with respect to that measured on the same material, pre-annealed at higher
 237 temperatures (Fig. 5). This means that the highest stability, and thus the slower relaxation time,
 238 is obtained with the vapour deposition protocol, while it decreases with further thermal
 239 annealing. This process, called in the work *anti-aging*, is opposite to the standard slowing down
 240 of the relaxation dynamics due to physical aging induced by thermal treatments. Indeed, in
 241 conventional MG, the dynamics slows down significantly by pre-annealing the desired glass
 242 just below its T_g [7]. This process does not apply to vapour deposited MG as their structure
 243 already corresponds to the most stable state and thus to a deeper minimum configuration in the
 244 potential energy landscape.



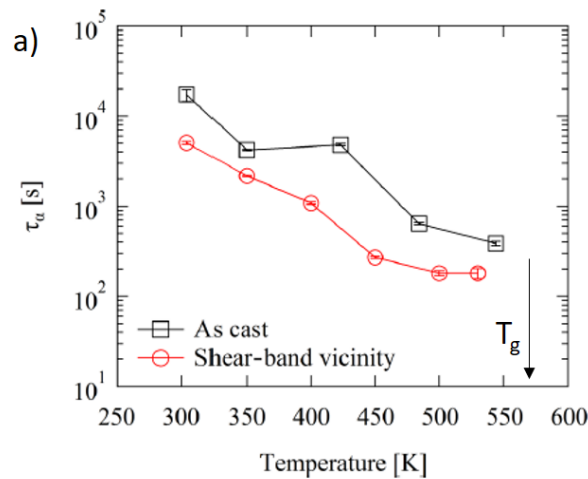
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246 **Figure 5.** a) Intensity scattering functions measured with XPCS in a $\text{Cu}_{50}\text{Zr}_{50}$ ultrastable glass as-cast and pre-
 247 annealed at different temperatures T_a (1 min annealing, heating rate: 7K/min). Data have been acquired after
 248 heating the samples in the glassy state at 476 K. The increased stability of the vapour deposited glass is signalled
 249 by the longer decay times (violet data) with respect to the same glass annealed at higher temperatures prior to the
 250 measurements. b) Relaxation times corresponding to the data in the left panel (violet diamonds) together with
 251 relaxation times measured in a standard fast-quenched MG which was pre-annealing at different temperatures T_a
 252 prior to the experiment (1 min annealing, heating rate: 7K/min) and then measured with XPCS at 476K. While the
 253 pre-annealing at high temperature slows down the dynamics of the standard MG due to aging, the ultrastable glass
 254 loses its improved stability with thermal heating. Taken from [35].

255

256 Similar anti-aging has been observed in metallic glasses recovered from anelastic and plastic
 257 deformation. The applied shear promotes the glass to a higher energy state evidenced through
 258 exothermic events upon further annealing [39], with reported values including a sevenfold
 259 increase of the relaxation enthalpy in a $\text{Zr}_{50}\text{Cu}_{40}\text{Al}_{10}$ MG between the annealed and deformed
 260 states [40]. Deformation also moves the glass structure toward an apparent lower density and
 261 higher disorder state [41], [42], in an opposite way with respect to the aging described above.

262 Shear stress can also alter the microscopic dynamics as it triggers plasticity localized in narrow
 263 shear bands, which accommodate the stress and eventually lead to catastrophic failure.
 264 Structurally, these bands are characterized by high disorder, density changes [43], [44], nano-
 265 cavities [45], and potential nano-crystals [46], [47]. Typical dimensions of x-ray beams are
 266 much larger than the thickness of the shear bands, 5-10 μm against 10-200 nm respectively
 267 [45], [48], which prevents the monitoring of the dynamics within the shear bands with XPCS.
 268 However, results from site-specific XPCS in the vicinity of a single shear band in a $\text{Zr}_{65}\text{Cu}_{25}\text{Al}_{10}$
 269 MG revealed an acceleration of the atomic scale dynamics 10 μm away from the shear band
 270 (Fig. 6a), a length scale greater than the shear band classical thickness by three orders of
 271 magnitude [49].



272

273 **Figure 6.** Temperature dependence of characteristic time τ obtained from site-specific isothermal XPCS
 274 measurements at 10 μm from an individual shear band and in the bulk in a $\text{Zr}_{65}\text{Cu}_{25}\text{Al}_{10}$ MG (as-cast from suction
 275 casting, stepwise heating from the ambient temperature). The significant decrease of τ in the shear band vicinity
 276 demonstrate an effect in an area much larger than the shear band itself. Figure taken from [49].

277

278 Interestingly, the acceleration of the dynamics remains constant during heating from room
 279 temperature to $0.95 \times T_g$ (Fig. 6a). This indicates that the structural and dynamical changes due
 280 to the shear band do not relax back to the as-cast (or annealed) state during the experimental
 281 time even close to T_g , and that the faster dynamics could persist over a very long time at ambient
 282 temperature, enabling true control of the glassy dynamics.

283 The fast dynamics near a single shear band described above occur also in the case of a severely
 284 deformed bulk MG. Results from XPCS performed on $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$ glasses annealed and later
 285 deformed through high pressure torsion (Fig. 6b) show a trend nearly identical to the single
 286 shear band case before structural relaxation close to T_g (“Crossover” zone in the Fig. 6b) [50].

287 Different deformation protocols not triggering the formation of shear bands can also induce
 288 rejuvenation or affect the dynamics. Hydrostatic compression was shown to allow large
 289 volumetric changes without the development of shear bands, and leads to a significant
 290 rejuvenation visible from calorimetry measurement [51]. How this translates to the atomic scale
 291 dynamics compared to sheared samples remains an open question. On the other hand, while the
 292 deformation of a metallic glass below the yield stress of the material do not produce permanent
 293 modifications by definition, XPCS performed in-situ during the elastic bending of
 294 $\text{Zr}_{44}\text{Ti}_{11}\text{Cu}_{10}\text{Ni}_{10}\text{Be}_{25}$ glassy ribbons shows a deformation influence on the dynamics that
 295 depends on the thermal history of the sample [30]. On the as-cast samples quenched from the

296 melt by rapid cooling, the deformation increases the intermittent nature of the aging. On the
297 other hand, when the sample has been brought to a lower energy state by pre-annealing just
298 below T_g , the deformation leads to faster but steady dynamics.

299 All these works show how the relaxation dynamics of MGs can be tuned by different
300 experimental protocols, which can involve either the glass formation or their treatment. While
301 physical vapor deposition can effectively bring the glass in lower energy microscopic
302 configuration associated to larger barriers and longer times for structural rearrangements,
303 applied stresses and deformations rejuvenate the system, bringing the glass in a microscopic
304 state characterized by fast structural relaxation times but at the same time more homogeneous
305 dynamics with respect to physical aging. Further studies will be necessary to better clarify the
306 controlling physical mechanisms controlling the collective particle motion.

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