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► To cite this version:

Guo-Jian Lyu, Ji-Chao Qiao, Yao Yao, Yun-Jiang Wang, Julien Morthomas, et al.. Microstructural effects on the dynamical relaxation of glasses and glass composites: A molecular dynamics study. *Acta Materialia*, 2021, 220, pp.117293. 10.1016/j.actamat.2021.117293 . hal-03356046

HAL Id: hal-03356046

<https://hal.science/hal-03356046v1>

Submitted on 16 Oct 2023

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1 **Microstructural effects on the dynamical relaxation of glasses and glass**
2 **composites: a molecular dynamics study**

3

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35 **Abstract**

36 One way to increase the ductility of metallic glasses is to induce heterogeneous
37 microstructures, as for example in nanoglasses and crystal-glass composites. The
38 heterogeneities have important consequences not only on the development of shear
39 bands, but also on the structural relaxations in the glass phase. Experiments using
40 dynamical mechanical spectroscopy (DMS) have been conducted, but an atomic-scale
41 picture is still lacking. Here we apply DMS within molecular dynamics simulations to
42 a classical CuZr metallic glass to study how structural relaxations and mechanical
43 energy dissipation are affected by different microstructures, including nanoglasses,
44 crystal-glass nanolaminates and glasses with spherical crystalline inclusions. We find
45 that in a fully glassy system, not only the fraction but also the spatial homogeneity of
46 “hard” icosahedral environments matter. When hard crystalline particles are
47 introduced, the storage modulus simply results from volumetric averages consistent
48 with the classical Voigt and Reuss bounds. On the other hand, loss moduli are much
49 more complex and can be smaller or larger than in a pure glass depending on the
50 microstructure and loading condition. Atomistic processes leading to these evolutions
51 are discussed and remaining open questions are highlighted.

52

53 **Keywords:** Metallic glasses; Composites; Nanoglass; Dynamic Mechanic spectrum;
54 Interfaces

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64 **1 Introduction**

65
66 Metallic glasses are a classical example of ‘strong-yet-brittle’ materials [1]. A
67 general strategy to, at least, delay their brittle failure is to create a microstructure that
68 can impede the development of an unstable shear band. One successful approach has
69 been to design composites, with a crystalline phase embedded in the glass matrix [2–
70 4]. The crystalline phase may be ex-situ or in-situ. In the former case, crystalline
71 fibers [5] or laminates [6] were incorporated into a glassy matrix. In the latter case,
72 crystalline dendrites [2,3,7–10] or more spherical precipitates [11] were obtained by a
73 partial crystallization of the glass. Careful optimization of the process parameters
74 allows to significantly increase the toughness and tensile ductility, while retaining a
75 high tensile strength [12]. Another successful way to induce microstructural
76 heterogeneities is to produce nanoglasses, by consolidating nanometer-sized glassy
77 particles [13–16].

78 In-situ composites particularly studied both in experiments [11,17–21] and
79 simulations [22–25] are CuZr-based metallic glasses with a B2-CuZr crystalline
80 phase. In-situ crystallites are near spherical and show transformation-induced
81 plasticity with a shape memory effect, leading to large plastic deformability and
82 pronounced work hardening [26–28].

83 So far, most of the attention has been on the mechanical properties of metallic
84 glass matrix composites for structural engineering purposes, i.e. on the yield stress
85 and fracture toughness. However, glasses are also characterized by complex structural
86 relaxation processes [29,30] that are bound to be affected by crystalline phases,
87 particularly at the nanoscale. Relaxation processes are best studied using dynamical
88 mechanical spectroscopy (DMS) [31,32]. DMS is a convenient and useful tool to
89 characterize viscoelasticity and relaxation properties of amorphous materials, as it can
90 detect the structural changes at a molecular or atomic scale for wide temperature and
91 frequency ranges. In pure glasses, several peaks have been observed in both
92 experiments [33] and simulations [34]. The α -relaxation is the main relaxation mode,
93 directly related to viscous flow and the glass transition. At lower temperature, a
94 secondary β -relaxation is observed, intimately related to plasticity [35–37] and
95 connected to string-like events through molecular dynamics simulations [38,39].
96 Other peaks, i.e., the γ -relaxation [40] and anomalous α_2 relaxation [41], have also
97 been reported. Much less is known about relaxation processes in metallic glass matrix
98 composites. So far, DMS has been applied experimentally to in-situ and ex-situ glassy
99 composites, leading to a wealth of processes, due either to the release of internal
100 stresses during DMS heating [42] or to solid-state transformations (phase
101 transformation, precipitation) of the crystalline phase leading to new peaks [43–45],
102 to the doubling of existing peaks [42,46] or to weakened, broadened and shifted
103 relaxation peaks induced by doping [47]. The atomic-scale mechanisms controlling
104 microstructural effects on dissipation remain however unknown.

105 In this work, we perform Molecular Dynamics (MD) simulations of dynamical
106 mechanical spectroscopy (MD-DMS) to study the effect of different microstructures
107 on the relaxation and viscoelasticity of glass composites and nanoglasses. We
108 consider a classical CuZr glass with B2-CuZr crystallites, which we deform
109 cyclically, either longitudinally or by shear. The same MD-DMS technique has been
110 applied to study pure glasses [34,41,48,49]. Here, to investigate the effect of a
111 microstructure, we modelled several systems of varying complexity: pure glasses
112 quenched at different rates, glass-glass nanocomposites as well as crystal-glass
113 composites with B2-CuZr crystallites of different geometries representative of either
114 in-situ (spherical precipitates), ex-situ (nanolaminates) and more intricate
115 (interconnected gyroid phases) composites.

118 2 Methodology

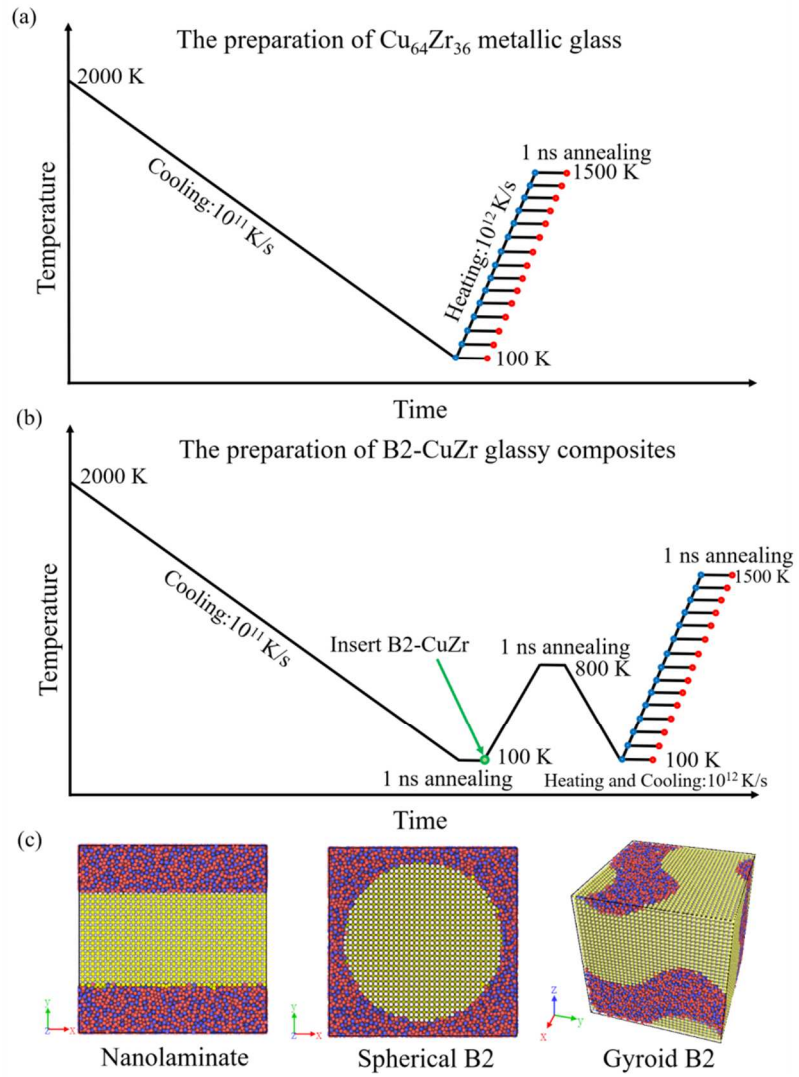
120 All the simulations were conducted using the open source LAMMPS package
121 [50]. A Finnis-Sinclair type Cu-Zr embedded atom method (EAM) potential
122 developed by Mendeleev et al. was used to describe interatomic interactions [51]. This
123 potential has been used many times in the past to study the properties of CuZr
124 metallic glasses, including the formation and interaction of shear bands [52], the
125 brittle-to-ductile transition [53], as well as the aging and rejuvenation under cyclic
126 deformation [54]. This potential was also recently used by the present authors to study
127 the dynamic correspondence principle in pure glasses [48]. Nosé-Hoover thermostat
128 and barostat were applied during the entire preparation protocol for all glasses and
129 glassy composites. Atomic visualizations were performed using Ovito [55].

130 As sketched in Fig. 1, to produce the crystal-glass composites, we start by
131 generating $\text{Cu}_{64}\text{Zr}_{36}$ metallic glasses by quenching a $\text{Cu}_{64}\text{Zr}_{36}$ liquid from 2000 K to
132 100 K at 10^{11} K/s at zero pressure. The dimensions of glasses are about $11.9 \text{ nm} \times$
133 $11.9 \text{ nm} \times 11.9 \text{ nm}$, containing 108,000 atoms. As expected and illustrated in Fig.
134 2(a), a clear deviation during cooling can be observed in the linear curve of averaged
135 atomic volume, corresponding to a glass transition with a glass-transition temperature
136 (T_g) of about 800 K. As illustrated in Fig. 1(a), to produce pure glass structures for
137 DMS deformation while mimicking the experimental DMS process, the glass was
138 heated again to each target temperature at a heating rate of 10^{12} K/s, and 15
139 configurations (blue dots in Fig. 1(a)) with a temperature interval of 100 K were
140 generated for subsequent 1 ns-annealing (red dots in Fig. 1(a)) and DMS deformations.
141 For a better understanding of the kinetic behavior around the glass transition, atomic
142 configurations extracted during heating at temperatures between 600 K to 1100 K
143 were annealed for 40 ns. The result is shown in Fig. 2(b). The potential energy
144 remains constant at 1000 K and 1100 K indicating that the samples are in an
145 equilibrated liquid state. At the lowest temperatures (600 and 700 K), the energy
146 variation is slow, due to kinetically-limited aging of the glassy state. In-between (800

147 and 900 K), the potential energy first increases rapidly to reach the same level as
148 during cooling, then remains almost constant for about 2 ns, before decreasing
149 dramatically as annealing takes place. High temperatures near the glass-transition
150 temperature allow for an accelerated aging resulting in low energy glasses as already
151 demonstrated by Derlet et al. [56].

152 As shown in Fig. 1(b), to obtain the composite structures, atoms in specific
153 regions of the glass were replaced with B2-CuZr crystals after the initial cooling and a
154 1 ns-annealing at 100 K. The crystal directions [100], [010] and [001] of B2-CuZr
155 were set along the X, Y and Z axes of simulation box. In this work, composites with
156 geometries of spheres, laminates and gyroids [57] were investigated, as illustrated in
157 Fig. 1(c). After insertion of B2-CuZr crystals, all composites were heated to 800 K at
158 10^{12} K/s and annealed for 1 ns to relax the glass-crystalline interface, and finally
159 cooled back down to 100 K at 10^{12} K/s. Similar to the pure glass, 15 configurations
160 were then extracted at 100 K intervals during a 10^{12} K/s-heating and annealed for 1 ns
161 before being tested by MD-DMS.

162 To study the effect of an internal microstructure in a glass, we also generated
163 nanoglasses using the Poisson-Voronoi tessellation method [58]. Each nanograin was
164 taken from the original 10^{11} K/s quenched $\text{Cu}_{64}\text{Zr}_{36}$ glass with a random orientation at
165 100 K, corresponding to the green dot in Fig. 1(b). The sample was first energy
166 minimized to avoid atomic overlaps inside the glass-glass interfaces. A hydrostatic
167 pressure of 1.5 GPa was then applied for 1 ns at 100 K to eliminate the voids near the
168 interfaces, then followed by another 1 ns-annealing at 100 K. The reason for not
169 annealing at 800 K is to avoid eliminating the artificial glass-glass interfaces due to
170 fast atomic diffusion. The subsequent procedures before MD-DMS simulations are
171 the same as with the pure glass and crystal-glass composites.



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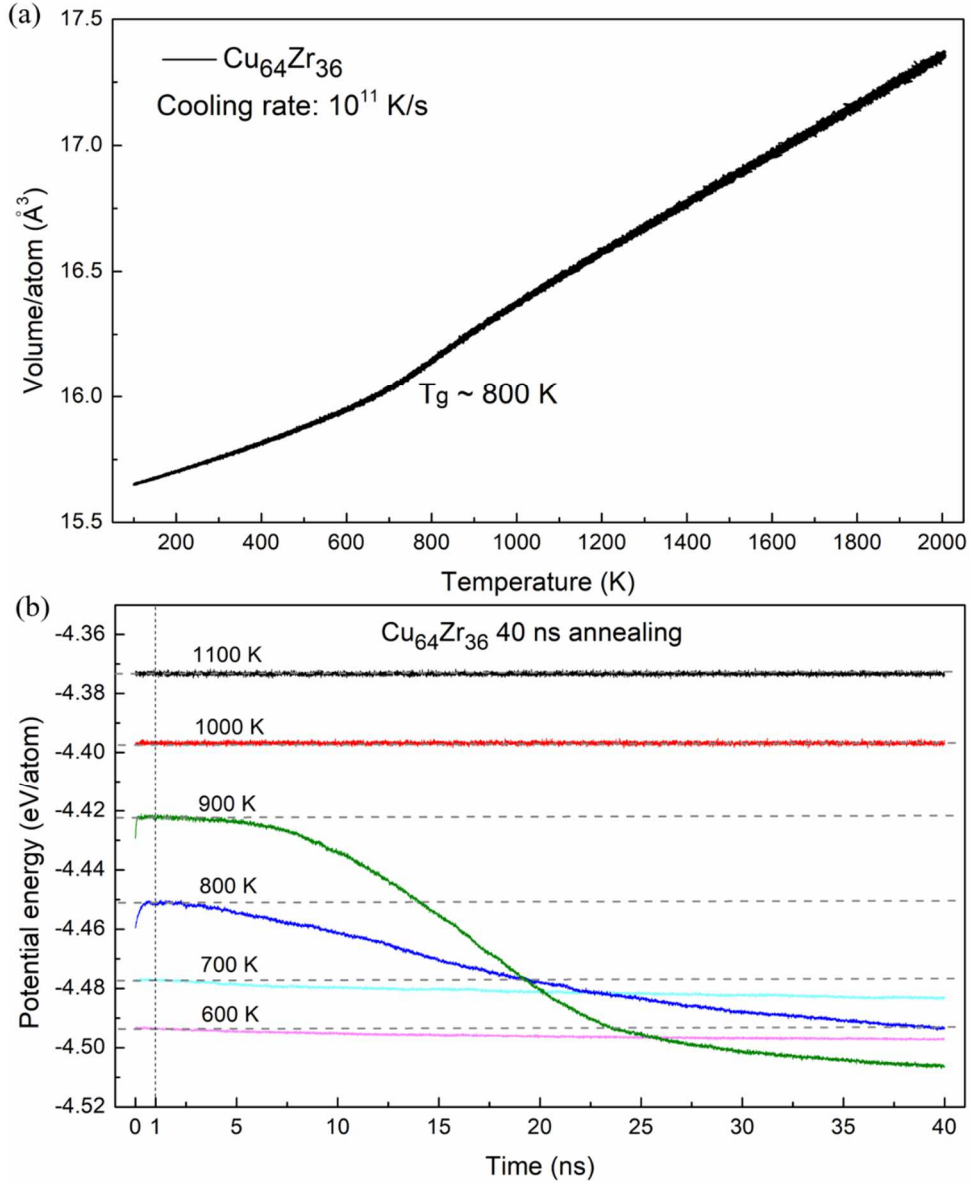
174 **Fig. 1** (a-b) Protocols to produce $\text{Cu}_{64}\text{Zr}_{36}$ metallic glasses and B2-CuZr glassy

175 composites, respectively; (c) Examples of atomic configurations of a nanolaminate, a

176 spherical and a gyroid B2 composite. Red and blue atoms are Cu and Zr atoms in the

177 glass phase; yellow and white atoms are Cu and Zr atoms in the B2-CuZr crystals.

178



179

180 **Fig. 2** (a) Averaged atomic volume while cooling a liquid from 2000 K to 100 K; (b)

181 Atomic potential energy as a function of annealing time at different temperatures.

182

183 The MD-DMS method proposed by Yu et al. [34] was used in this work. In order
 184 to obtain the complex moduli, for instance the complex longitudinal moduli M^* , a
 185 strain $\varepsilon_{xx}(t) = \varepsilon_A \sin(\omega t)$ was applied along the X direction while holding the Y
 186 and Z dimensions fixed, with ε_A the strain amplitude and $f = \omega/2\pi$ the
 187 deformation frequency. During the MD-DMS deformation, a Nosé-Hoover thermostat
 188 was applied to keep the temperature constant. The resulting stress was then fitted as
 189 $\sigma_{xx}(t) = \sigma_0 + \sigma_A \sin(\omega t + \delta)$, with σ_A the stress amplitude and δ the phase shift.
 190 The complex longitudinal modulus is given as $M^* = (\sigma_A/\varepsilon_A) [\cos(\delta) + i\sin(\delta)]$,
 191 with a real part, i.e. the storage modulus, $M' = (\sigma_A/\varepsilon_A) \cos(\delta)$ and an imaginary
 192 part, i.e. the loss modulus, $M'' = (\sigma_A/\varepsilon_A) \sin(\delta)$. Details for DMS deformation
 193 procedures can be found in our previous work [48]. In the current work, only the

194 complex longitudinal modulus M^* and shear modulus G^* are considered, which
195 suffices to know all storage and loss moduli for the pure glass, thanks to the dynamic
196 correspondence principle [48]. We used a reference deformation frequency of 10 GHz,
197 with a strain amplitude of 2.5%, well within the static elastic regime of the glasses in
198 MD simulations. To limit statistical errors, each data was averaged over 5
199 deformation cycles. The cyclic deformation was thus applied for a total of 0.5 ns,
200 short enough to avoid aging of glass, even near the glass transition temperature, as
201 seen in Fig. 2(b).

202

203 **3 Results**

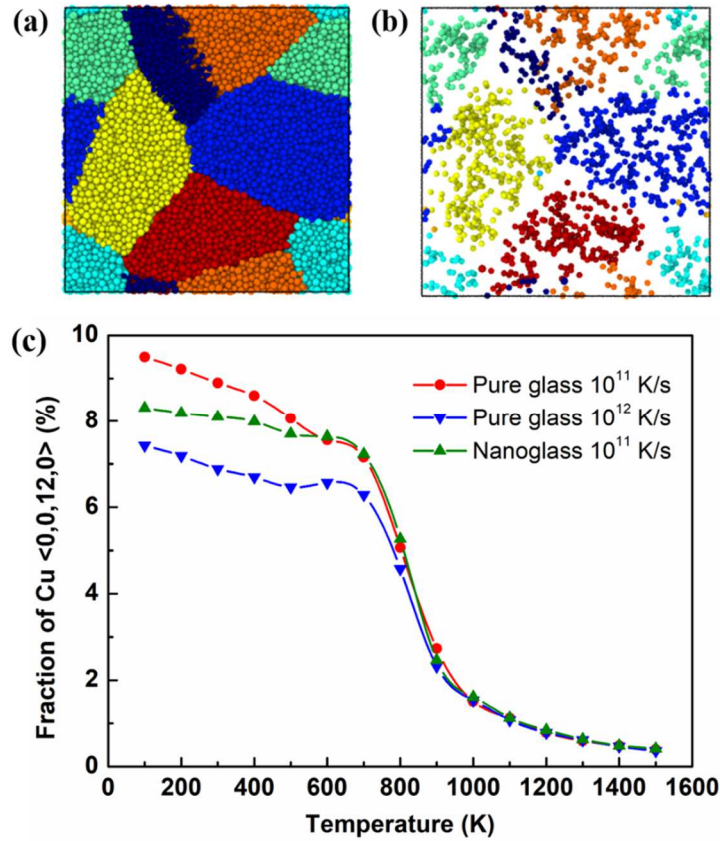
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205 **3.1 Pure glasses and nanoglasses**

206

207 Cu-centered icosahedral clusters are the dominant structural motif in CuZr
208 glasses. As extensively investigated in the literature [59–61], they form stable atomic
209 configurations, with a relatively high local atomic packing density and a high shear
210 resistance. Under deformation, they form a rigid backbone, which deforms mostly
211 elastically. As a result, their density has been shown anticorrelated with energy
212 dissipation [34,48,62], i.e. the more Cu-centered icosahedral clusters in the glass, the
213 less energy dissipation. Other types of clusters, typically considered as “geometrically
214 unfavored motifs” (GUM) [63–65] or “soft regions”, are loosely packed and undergo
215 irreversible rearrangements, which contribute to energy dissipation [48]. To obtain
216 structures with varying fractions of Cu-centered icosahedral environments, a classical
217 method is to change the cooling rate, since a higher cooling rate results in a lower
218 fraction of icosahedral clusters. Another way is to generate a nanoglass, since the
219 highly perturbed glass-glass interfaces will contain very low fractions of icosahedral
220 clusters.

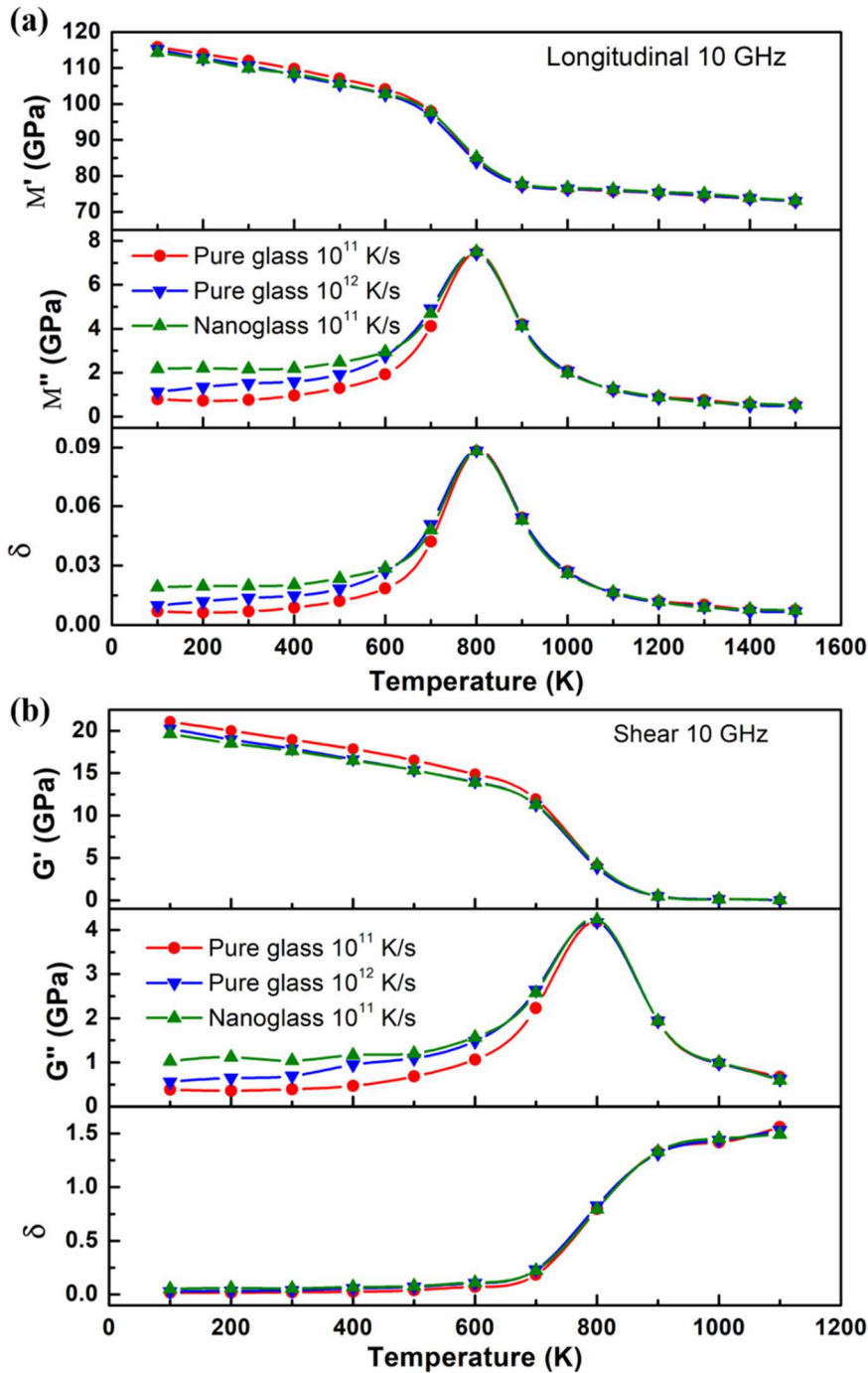
221 In this section, we designed three types of $\text{Cu}_{64}\text{Zr}_{36}$ metallic glasses with different
222 fractions of Cu-centered icosahedral clusters: two pure glasses generated with cooling
223 rates of 10^{11} K/s and 10^{12} K/s, and a nanoglass constructed from the 10^{11} K/s
224 quenched glass. Fig. 3(a) illustrates the atomic structure of the nanoglass composed of
225 14 grains with periodic boundary conditions. Fig. 3(b) shows only the Cu atoms at the
226 center of icosahedral clusters, illustrating that there are no such atoms near the
227 glass-glass interfaces. As explained above, we prepared 15 configurations from both
228 initial glasses and from the nanoglass to perform MD-DMS. Fig. 3(c) shows the initial
229 fraction of Cu-centered icosahedral clusters. We see that at low temperatures, the
230 most slowly quenched glass has the highest fraction of icosahedral clusters, while the
231 most rapidly quenched glass has the lowest fraction. The nanoglass is in-between. At
232 higher temperatures, the difference between the different systems decreases and above
233 the glass-transition temperature ($T_g=800$ K), all systems are equivalent, which is
234 expected since they are all in the liquid state.



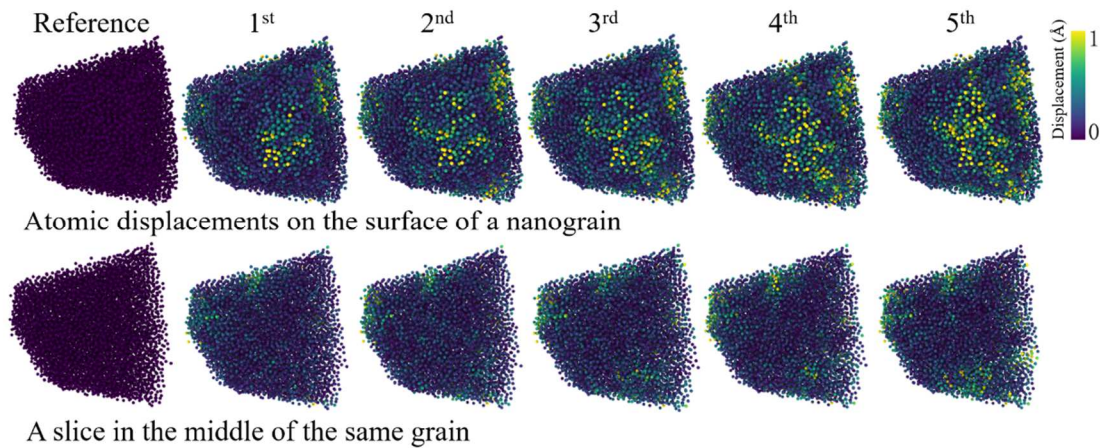
235
 236 **Fig. 3** (a) Atomic structure of a $\text{Cu}_{64}\text{Zr}_{36}$ nanoglass and (b) $\text{Cu}\langle 0,0,12,0 \rangle$ atoms in
 237 the nanoglass; (c) Temperature dependence of the fraction of $\text{Cu}\langle 0,0,12,0 \rangle$ atoms in
 238 a slowly- and a rapidly-quenched glass as well as in a nanoglass.
 239

240 We conducted MD-DMS simulations on the three glasses. **Fig. 4** presents the
 241 measured complex longitudinal moduli M^* and complex shear moduli G^* . Both
 242 M'' and G'' present a marked relaxation peak at the glass transition temperature
 243 ($T_g=800$ K), above which all samples are in the liquid state where they have lost the
 244 memory of their initial state and thus show identical properties. Below 800 K, both
 245 glasses and the nanoglass have similar longitudinal storage moduli M' while in
 246 shear, G' is slightly larger for the slowly quenched glass than for the rapidly
 247 quenched glass and the nanoglass. The microstructure has a stronger effect on the loss
 248 moduli. First, we recover that the rapidly quenched glass has larger M'' and G''
 249 than the slowly quenched glass, which is consistent with the lower density of
 250 icosahedral clusters in the former than in the latter. More surprising is the fact that the
 251 nanoglass, despite having a density of icosahedral clusters in-between both glasses,
 252 has the highest loss modulus. The reason can be found in **Fig. 5**, in which we show the
 253 residual atomic displacements at the end of each loading cycle both on the surface and
 254 in the interior of a representative nanograin. We see that the residual atomic
 255 displacements are mainly concentrated in the glass-glass interfaces and are close to
 256 zero in the interior of the grain. Since the global strain returns back to zero at the end

257 of each loading cycle, the residual atomic displacements visible in the interface are
 258 irreversible atomic rearrangements, which increase the energy dissipation.



259
 260 Fig. 4 (a) Complex longitudinal moduli M^* and (b) shear moduli G^* of different
 261 metallic glasses: CuZr glass with cooling rates of 10^{11} K/s and 10^{12} K/s and a CuZr
 262 nanoglass.
 263



264

265 **Fig. 5** Atomic displacements at the end of each loading cycle on the surface of a
 266 nanograin (upper figures) and in a slice in the middle of the same grain at 100 K
 267 (bottom figures) under longitudinal deformation.

268

269 This first set of glassy systems shows that not only the density of icosahedral
 270 clusters but also the localized deformation within the glass-glass interfaces affects
 271 energy dissipation. The nanoglass has a higher density of clusters than the rapidly
 272 quenched glass (10^{12} K/s) but has also a higher dissipation at low temperatures
 273 because the glass-glass interfaces are localized “soft” regions prone to irreversible
 274 atomic rearrangements. Icosahedral clusters may also be destroyed in the course of
 275 the deformation, which will further increase the dissipation. By way of contrast,
 276 icosahedral clusters are less dense in the rapidly quenched glass but they are
 277 homogeneously distributed and thus still limit atomic rearrangements. Therefore, the
 278 glass-glass interfaces play an important role in the dynamic mechanical response by
 279 creating non-icosahedral environments in nanoglasses.

280

In the case of a nanoglass, we introduced “soft” regions in a pure glass. We now
 281 consider the opposite case, where we introduce “strong” crystalline regions in the
 282 glass.

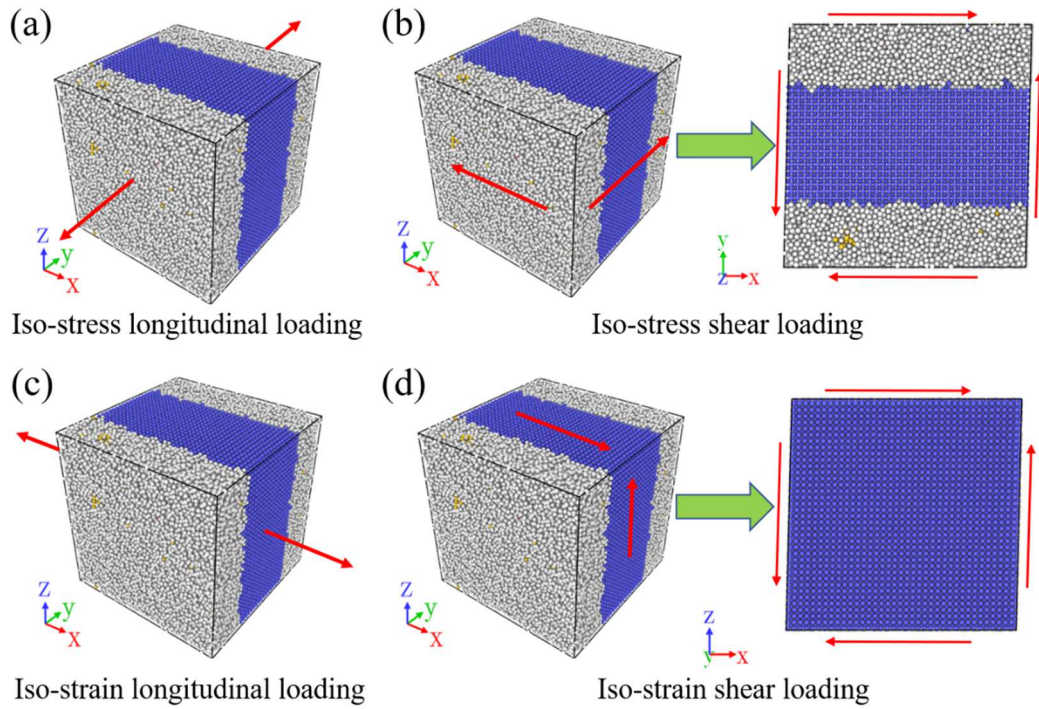
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284 3.2 Nanolaminates

285

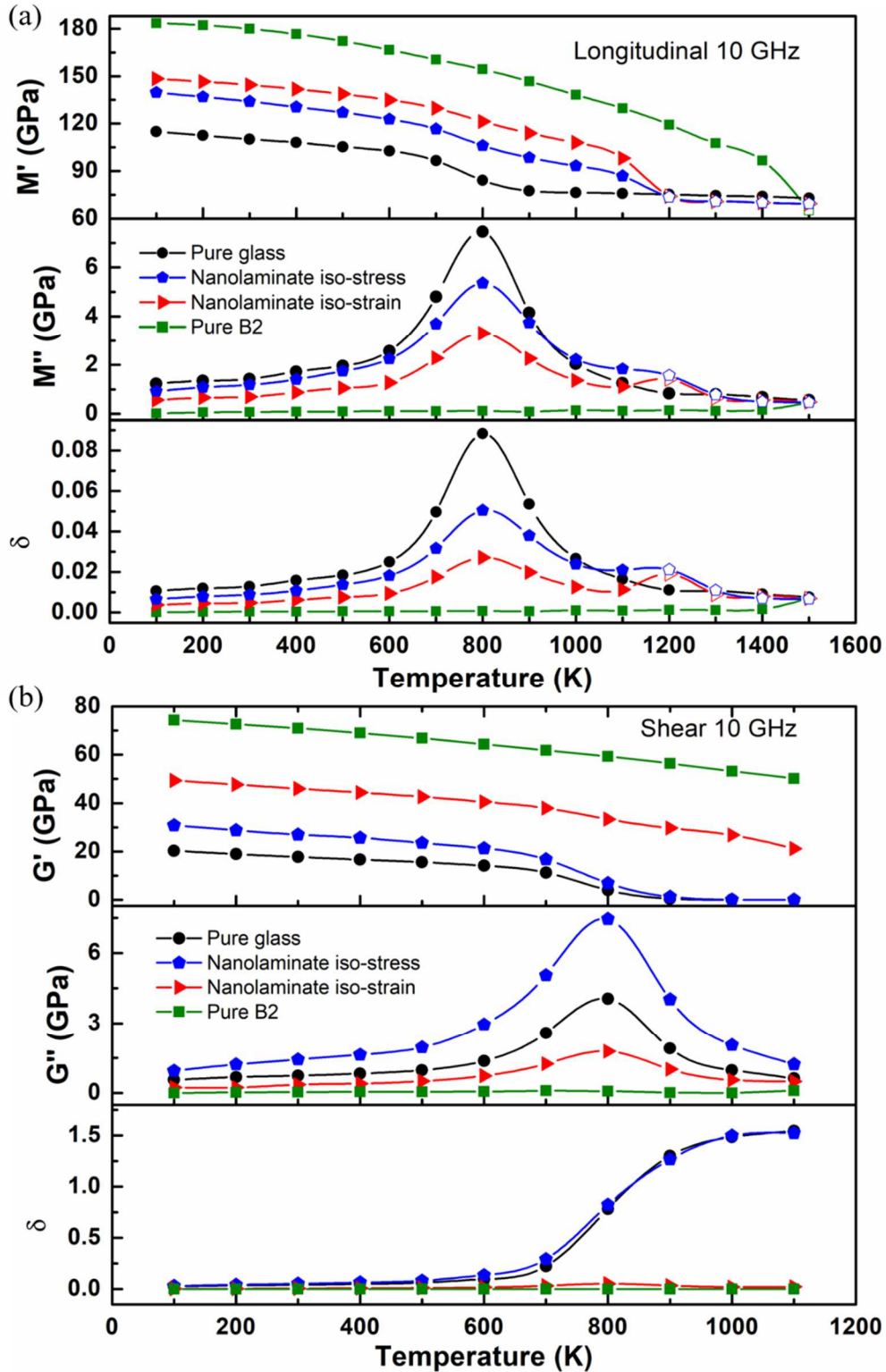
286 The first crystal-glass composite to be considered is a nanolaminate made of 50%
 287 $\text{Cu}_{64}\text{Zr}_{36}$ glass, 50% B2-CuZr crystal. Since this structure is not isotropic, we need to
 288 distinguish different directions of loading illustrated in Fig. 6. For longitudinal
 289 deformations, the cyclic deformation can be applied either perpendicularly (Y) or
 290 parallel (X) to the glass-crystal interface, which are denoted as iso-stress and
 291 iso-strain longitudinal loadings, respectively. Similarly, two cyclic shear deformations
 292 can be applied, in planes either perpendicular (XY) or parallel (XZ) to the interface,
 293 hereinafter denoted as iso-stress and iso-strain shear loadings, respectively. For the
 294 iso-stress longitudinal loading (Fig. 6(a)), both phases are subjected to the same
 295 applied stress in the Y direction, while the lateral dimensions are fixed. By way of

296 contrast, with the iso-strain longitudinal loading (Fig. 6(c)), the glass and crystalline
 297 phases are compressed or stretched equally in the X direction with the Y and Z
 298 dimensions fixed. The cases of iso-stress (Fig. 6(b)) and iso-strain ((Fig. 6(d)) shear
 299 loadings are similar. Due to the different elastic moduli of the glass and B2-CuZr
 300 crystal, when subjected to the same stress, both phases undergo different strains, and
 301 inversely, under the same strain, they develop different stresses.
 302



303
 304 **Fig. 6** Loading modes of a glass-crystal nanolaminate composite: (a) iso-stress
 305 longitudinal loading with a longitudinal strain applied in the Y direction perpendicular
 306 to the laminate interface, (b) iso-stress shear loading with a shear strain applied in the
 307 XY plane perpendicular to the laminate interface, (c) iso-strain longitudinal loading
 308 with a longitudinal strain in the X direction parallel to the interface, (d) iso-strain
 309 shear loading with a shear strain in the XZ plane parallel to the interface.

310



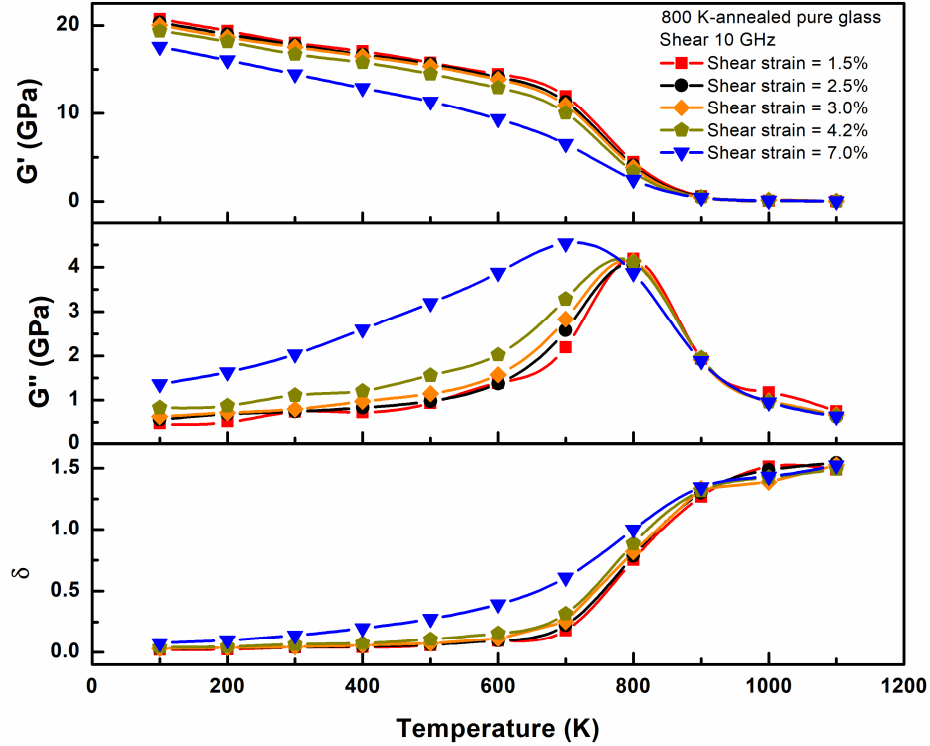
311
 312 **Fig. 7** Complex longitudinal (a) and shear (b) moduli of a 50% crystal- 50% glass
 313 nanolaminate composite under iso-stress and iso-strain loadings. Pure glass and pure
 314 crystal data are added for comparison. Hollow symbols indicate that the crystalline
 315 phase completely disappeared during the cyclic deformation.
 316

317 Due to the additional heating, cooling and annealing during the preparation of
318 composite samples (see Fig. 1(b)), the structure and mechanical properties of the glass
319 phase may change. To identify more clearly the effect induced by the crystal phase,
320 the pure glasses used in this section as reference were treated with the same thermal
321 processes as the composites.

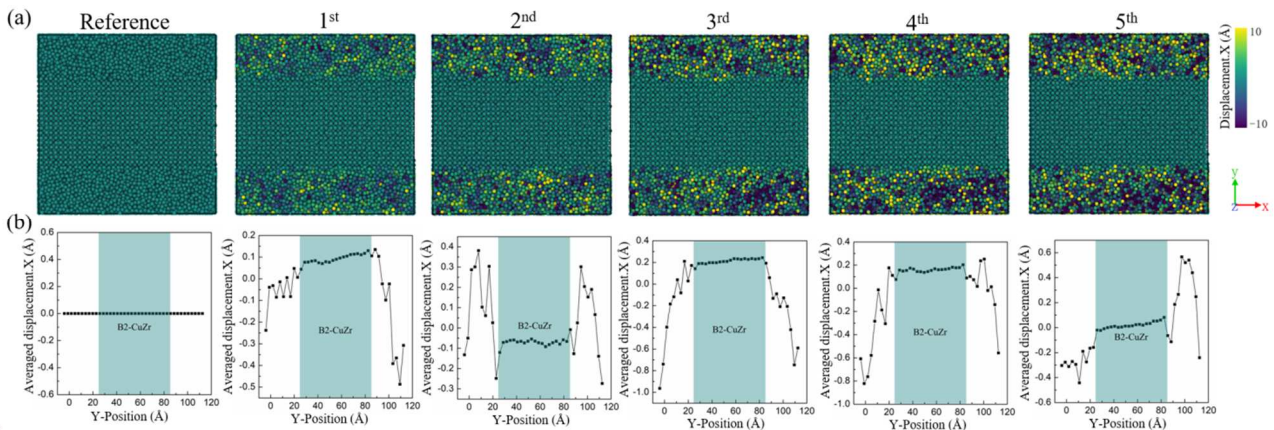
322 Fig. 7 (a) presents the complex longitudinal moduli M^* for the pure glass, the
323 pure B2-CuZr crystal and the nanolaminate composite. The pure crystal has as
324 expected a higher storage modulus and an almost zero loss modulus. We therefore
325 expect that, by a simple volumetric effect, adding a crystalline phase in the glass will
326 increase the storage modulus and decrease loss modulus compared to the pure glass.
327 This is precisely what is seen in Fig. 7 (a) for longitudinal loading. Moreover, the
328 storage modulus M' in iso-strain is higher than in iso-stress as expected from the
329 Voigt and Reuss effective moduli discussed in section 4. Conversely, the loss
330 modulus and lag angle are lower in iso-strain than in iso-stress. The case of iso-strain
331 shear shown in Fig. 7 (b) is similar to longitudinal iso-strain, with a higher G' and a
332 lower G'' compared to the pure glass. With iso-strain loading, whether longitudinal
333 or shear, both crystal and glass phases deform equally and the effective modulus of
334 the composite results from a volumetric average of the crystal and glass moduli.

335 The case of iso-stress shear loading shown in Fig. 7(b) is more complex because
336 G'' is larger than in the pure glass over the entire temperature range. The relaxation
337 peak occurs at the same temperature as in the pure glass (800 K), but has a larger
338 amplitude. With iso-stress loading, the crystal and glass phases are subjected to the
339 same stress but develop different shear strains. Since the glass phase has a much
340 lower G' than the crystal (20 GPa compared to 75 GPa at 100 K), it deforms
341 significantly more. We measured that the strain amplitude at 100 K in the glass phase
342 is close to 4.2% for a 50% crystal-50% glass composite, compared to the overall 2.5%
343 strain amplitude. The strain amplitude in the glass phase also varies with the volume
344 fraction of B2 crystal, i.e., for 20% crystal-80% glass and 80% crystal-20% glass
345 composites at 100 K it is close to 3.0% and 7.0%, respectively. As shown in Fig. 8,
346 the shear loss modulus of a pure glass increases with the strain amplitude. The
347 increase of the strain amplitude in the glass phase due to the presence of the hard
348 crystal phase thus induces an increase of G'' . However, the overall increase of the
349 iso-stress shear loss modulus of the nanolaminate seen in Fig.7(b) is larger than in the
350 pure glass in Fig. 8. Moreover, the excess G'' in the composite extends beyond the
351 relaxation peak (Fig.7(b) for $T > 800$ K) when the glass is in a liquid phase, while the
352 strain amplitude has no effect on the dissipation of the pure glass in the liquid phase
353 (Fig. 8 for $T > 800$ K). At these high temperatures, the liquid reorganizes quickly,
354 leading to large positive and negative atomic displacements illustrated in Fig. 9(a).
355 However, if we average the X displacements parallel to the laminate interfaces in
356 slabs perpendicular to the Y direction in order to remove the effect of the local
357 rearrangements, we find as shown in Fig. 9(b) that the displacements are
358 discontinuous at the interface at the end of each cycle. This is a signature of sliding, or

359 shear motion, between the liquid and the glass, which in turn produces dissipation.
 360 We therefore conclude that the excess dissipation in the nanolaminate composites
 361 with an iso-stress shear loading results from the combined effects of an increased
 362 strain amplitude in the glass and shear motions at the crystal-glass interface.



363
 364 **Fig. 8** Complex shear modulus of a pure glass tested with different strain
 365 amplitudes noted in the figure. We checked that even at the largest amplitude, the
 366 stresses can be accurately fitted by a sinusoid. The values of the shear strains in the
 367 legend correspond to the strain amplitudes in the glass phase of sheared
 368 nanolaminates with different crystal volume fractions, as explained in the text.
 369



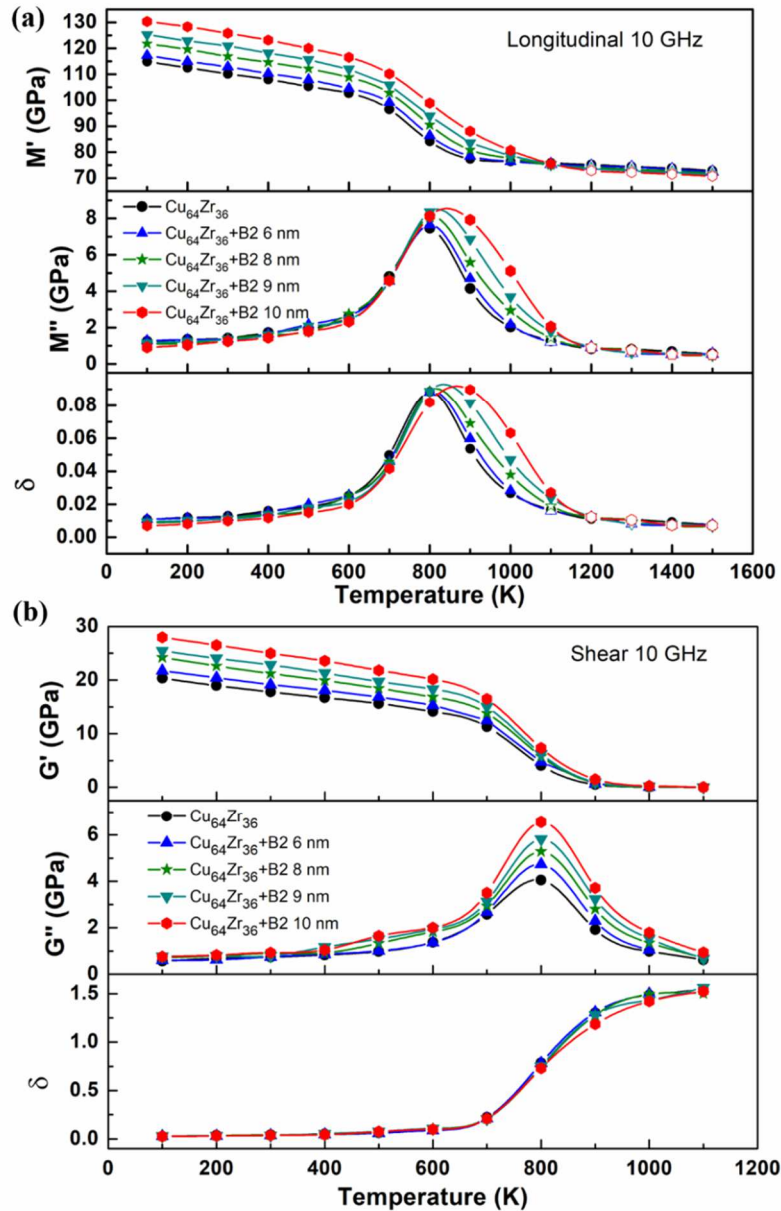
371 **Fig. 9** Non-affine atomic displacements in the X direction at the end of iso-stress
 372 shear loading cycles at 1000 K shown (a) with colors in the central Z plane and (b)
 373 averaged in slabs perpendicular to the Y direction.

374

375 3.3 Spherical B2 composites

376

377 We now consider another geometry for the crystal-glass composite, where
378 spherical B2-CuZr crystals are embedded in the glassy matrix. The diameter of the
379 crystalline spheres was varied from 6 nm to 10 nm. As can be seen in Fig. 10, the
380 storage moduli M' and G' again follow an expected volumetric effect and gradually
381 increase as larger B2 spheres are introduced.
382



383

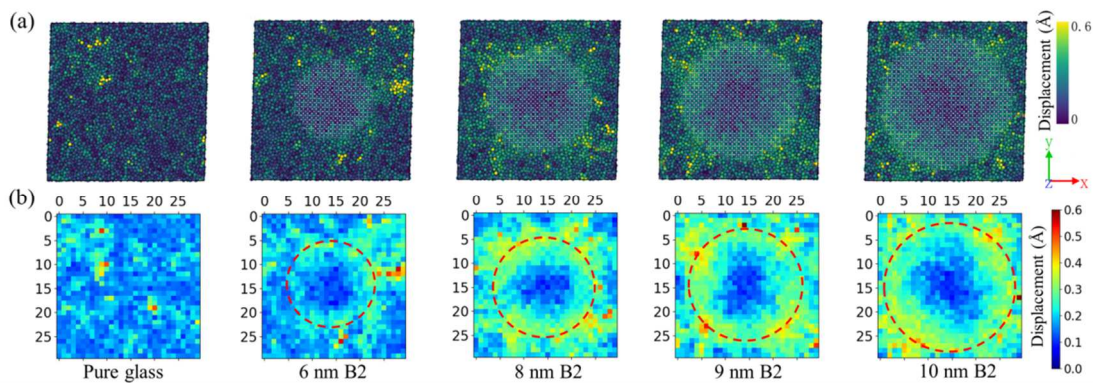
384 Fig. 10 Complex longitudinal (a) and shear (b) moduli of a composite containing
385 spherical B2-CuZr crystallites of different radii in a glassy matrix. Hollow symbols
386 indicate that the sample completely amorphized during the cyclic deformation.
387

388 With spherical inclusions, the stresses and strains are no longer homogeneous in
 389 the glassy matrix and the distinction between iso-stress and iso-strain does not apply.
 390 However, since the crystalline inclusion is fully embedded in the glassy matrix,
 391 crystal and glass phases can deform differently and we should expect a dissipation in
 392 the spherical composite closer to the iso-stress rather than the iso-strain nanolaminate.
 393 We indeed see in Fig. 10(b) that G'' is larger in the composite than in the pure glass
 394 as observed with the iso-stress sheared nanolaminates (Fig. 7(b)). Also, the relaxation
 395 peak increases in amplitude but remains at 800 K.

396 Another observation from Fig. 10(b) is that G'' increases with the sphere radius.
 397 We will see below in Fig. 12 that the same is true for iso-stressed nanolaminates. The
 398 non-affine displacements shown in Fig. 11 provide an atomistic picture of this
 399 behavior. Firstly, we observe a pronounced increase of the atomic displacements near
 400 the glass-crystal interface, particularly visible in the heatmaps of Fig. 11(b) generated
 401 by averaging the non-affine displacements of Fig. 11(a) on a 30×30 grid in a 1 nm
 402 thick slice perpendicular to the Z axis in the middle of the simulation box. The
 403 increased non-affine displacements at the interface confirm that the spherical
 404 composites behave closer to an iso-stress rather than an iso-strain nanolaminate.
 405 Secondly, we see that the atomic displacements at the interface get larger when the
 406 size of the spherical inclusion increases due to the larger strain contrast between the
 407 two phases, which explains that the dissipation increases as a function of the sphere
 408 radius. The case of longitudinal loading shown in Fig. 10(a) is different since we see
 409 that M'' hardly depends on the sphere radius before the relaxation peak. In the glassy
 410 phase, the presence of spherical crystalline inclusions affects only the storage
 411 modulus but not the loss modulus. On the other hand, we see a large effect at high
 412 temperatures where the relaxation peak does not increase in amplitude but is shifted
 413 towards higher temperatures, with a shift amplitude which increases rapidly with the
 414 sphere radius.

415 This behavior is phenomenologically different from the laminate geometry in Fig.
 416 7 and the shear loading in Fig. 10(b) and implies that the presence of the crystalline
 417 spherical inclusions and the interactions between the glass and the crystal stabilize the
 418 glassy phase and increases the glass transition temperature.

419



420

421 **Fig. 11** Non-affine atomic displacements (a) and corresponding heatmaps of
422 non-affine displacements averaged on a 30×30 grid (b) for a pure glass and
423 spherical B2 composites with different B2 sizes shown in a 1 nm thick slice in the
424 middle of the simulation box deformed at 2.5% shear strain.

427 **4 Discussion**

429 **4.1 Microstructural effects on complex moduli**

431 The results shown above demonstrate that while storage moduli are mainly
432 dominated by the volumetric effect of mixing hard and soft phases, loss moduli are
433 much more complex and there is no simple relation between the loss modulus and the
434 microstructure of a glass-glass or a glass-crystal composite. First, we have shown in
435 section 2 that not only the density of “hard” icosahedral environments but also their
436 structural heterogeneities (induced here at the glass-glass interfaces) play important
437 roles in the dynamic mechanical responses. A similar situation may also be expected
438 in glasses containing shear bands where the localized deformation strongly
439 rejuvenates the glass, which locally contains a low fraction of icosahedral clusters.
440 Under DMS, shear bands are expected to be prone to irreversible rearrangements,
441 leading to an increased energy dissipation compared to an undeformed glass with a
442 similar average cluster density.

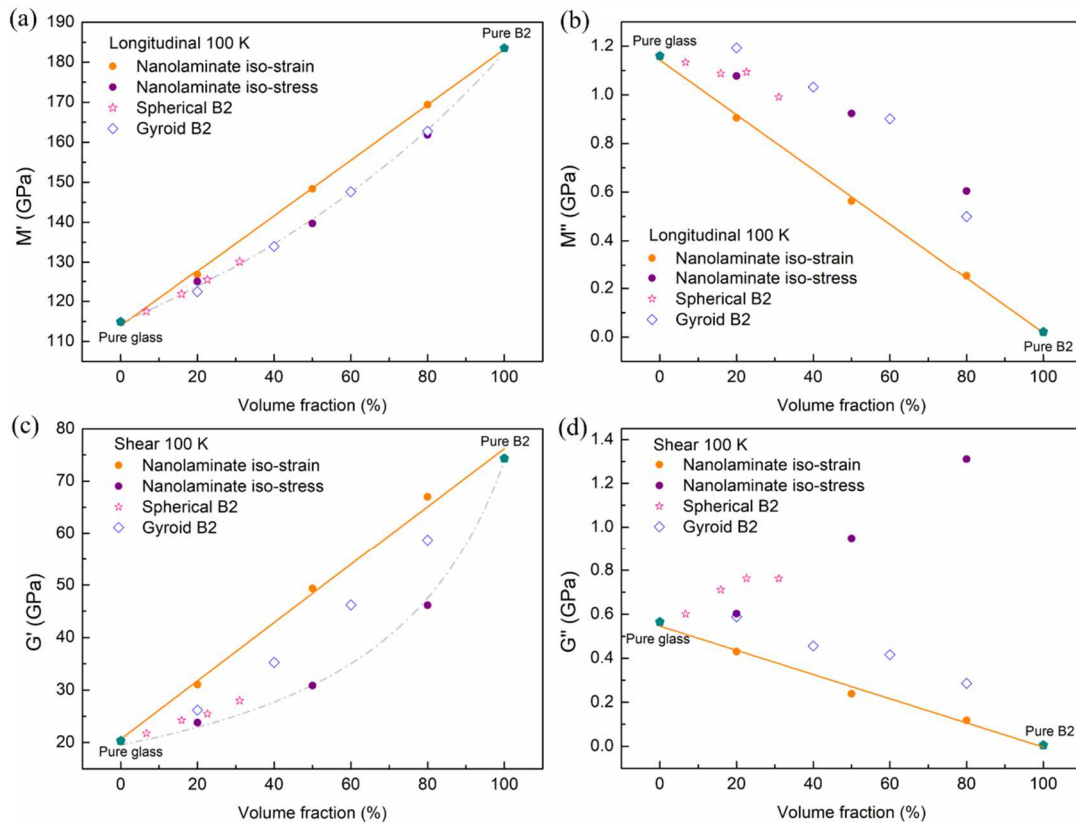
443 Second, we have shown that the dissipation in crystal-glass composites depends
444 on both the microstructure and loading. When the crystal and the glass phases are
445 forced to deform equally, both the loss and storage moduli result from the volumetric
446 average of the loss and storage moduli in both phases. This point is analyzed
447 quantitatively below. By way of contrast, when the crystal and the glass phases can
448 deform differently, as in the iso-stressed nanolaminate (**Fig. 7**) or the spherical
449 inclusions (**Fig. 10**), we have seen that there is a second volumetric effect related to
450 the increased strain amplitude in the glassy matrix, which in turn induces an increased
451 dissipation by triggering an increasing number of plastic events during the
452 deformation cycles. This feature was also reported in the work of Yu et. al [66], who
453 found that mechanical strain has a similar effect as temperature in accelerating the
454 relaxation dynamics. This effect is accompanied by a surface effect related to slipping
455 at the crystal-glass interface, which is analogous to the shear motions seen in the
456 glass-glass interfaces (**Fig. 5**). This effect is probably present at all temperatures but is
457 difficult to measure below the relaxation peak while **Fig. 9** shows a clear evidence of
458 slippage at 1000 K. We therefore believe that such shear motion explains the
459 increased energy dissipation at and above the relaxation peak seen with shear loading,
460 in both the iso-stressed nanolaminate (**Fig. 7(b)**) and the spherical inclusions (**Fig.**
461 **10(b)**).

462 The case of spherical inclusions loaded longitudinally is even more intriguing
463 (**Fig. 10(a)**) since the spherical inclusions hardly affect the low-temperature

464 dissipation but stabilize the glass phase by shifting the relaxation peak to higher
 465 temperatures. It is well-known that a nanoconfinement affects the glass-transition
 466 temperature [67,68], but it remains unclear (1) why in our simulations the
 467 glass-transition temperature increases while it classically decreases with
 468 nanoconfinement and (2) why the relaxation peak temperature varies only with a
 469 longitudinal loading and not for instance in shear. **From the existing results, we know**
 470 **that the atomic structure of the composite samples as well as the loading condition can**
 471 **influence significantly relaxation behaviors. The volume variation under longitudinal**
 472 **loading and the localized atomic motions near the spherical interface might be key**
 473 **clues to the underlying mechanisms. However, no direct evidence has been found**
 474 **from the atomic trajectory to support these speculations.** Despite our best efforts, we
 475 have not been able to identify atomistic mechanisms which could explain these
 476 observations.

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4.2 Dependence on crystalline volume fraction



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Fig. 12 Relation between complex moduli and volume fraction of B2-CuZr phase for different microstructures (nanolaminates, spherical inclusions and gyroid composites) loaded either longitudinally (a-b) or in shear (c-d).

487 To explore more quantitatively the low-temperature dependence of the complex
 488 moduli on the crystalline phase, the storage and loss moduli were computed at 100 K
 489 as function of the volume fraction of B2-CuZr crystal for different microstructures:
 490 the nanolaminates and spherical inclusions discussed above, but also interconnected
 491 gyroid structures generated with the algorithm proposed in [57] and relaxed using the
 492 same protocol as the other composites. The result is shown in Fig. 12. Classical
 493 effective modulus calculations [69] yield longitudinal iso-strain and iso-stress moduli
 494 for a laminate geometry expressed as

$$495 \quad M'_{iso-strain} = (1 - \phi)M'_a + \phi M'_c \quad (1)$$

496 and

$$497 \quad M'_{iso-stress} = \frac{M'_a M'_c}{(1-\phi)M'_c + \phi M'_a} \quad (2)$$

498 with M'_a (resp. M'_c) the storage modulus of the amorphous (resp. crystal) phase and
 499 ϕ , the volume fraction of crystal phase. The same expressions apply for the shear
 500 modulus. Note that these expressions reflect only the volumetric effect of mixing
 501 phases with different elastic moduli.
 502

503 In Fig. 12(a) and (c), we recover the linear relationship between M' and G' and
 504 the volume fraction ϕ for the iso-strained nanolaminates expected from Eq. (1), as
 505 well as the convex relation for the iso-stressed nanolaminates expected from Eq. (2).
 506 The same convex curve is followed by the spherical and gyroid composites for
 507 longitudinal loading, while in shear, the corresponding G' are in-between
 508 $G'_{iso-strain}$ and $G'_{iso-stress}$. This is expected since the iso-strain and iso-stress moduli
 509 correspond respectively to the upper bound (Voigt estimation) and lower bound
 510 (Reuss estimation) of effective moduli of composites [69]. Storage moduli are
 511 therefore simply controlled by the volumetric effect related to the relative fraction of
 512 hard and soft phases in the composite.

513 As discussed above, loss moduli are more intricate. As seen in Fig. 12(b) and (d),
 514 for iso-strained nanolaminates, the longitudinal and shear loss moduli (M'' and G'')
 515 follow the same linear relation as in Eq. (1) and thus also result from the volumetric
 516 effect of mixing glassy dissipative and crystalline non-dissipative phases. The
 517 longitudinal loss modulus M'' of the iso-stress nanolaminate follows a concave
 518 shape, which is also followed by the spherical and gyroid B2-CuZr glassy composites.
 519 Dissipation is therefore lower than in the pure glass but larger than with the simple
 520 volumetric average of Eq. (1). We also see that due to the concave shape of the curve,
 521 M'' is close to constant at low volume fractions, which explains why M'' with
 522 spherical inclusions does not depend on the sphere radius in Fig. 10(a).

523 We see a different effect with G'' , which is larger in the iso-stressed
 524 nanolaminate and spherical composite than in the pure glass. The reason is the
 525 sensitivity of G'' on the strain amplitude in the glassy phase discussed in Section 3
 526 and illustrated in Fig. 8. This effect is stronger than the simple volumetric effect due
 527 to the absence of dissipation in the crystalline phase and leads to an overall increase

528 of G'' . Note that the same confinement effect is not seen with M'' because the
529 storage modulus contrast between the glass and the crystal is smaller for M' than for
530 G' , such that the strain in the glassy phase is closer to the overall applied strain with a
531 longitudinal loading than with shear.

532

533 **5 Conclusions**

534

535 Dynamic mechanical relaxation has been an important topic in the field of
536 metallic glasses. However, the origin of mechanical relaxation is still far from fully
537 understood. In the current work, MD-DMS simulations in the CuZr metallic glasses
538 and composites with various microstructures were performed to reveal the relaxation
539 characteristics from the atomic scale. We have shown that in a fully glassy system,
540 not only the fraction but also the homogeneity of “hard” icosahedral environments are
541 important. When hard crystalline particles are introduced, the storage modulus simply
542 results from volumetric averages consistent with the classical Voigt and Reuss bounds.
543 Loss moduli are much more complex and depend sensitively on the microstructure
544 and loading condition. In particular, we have seen that while a laminate geometry
545 does not affect the temperature of the relaxation peak, i.e. the glass-transition
546 temperature, but only changes its amplitude, spherical particles can stabilize the glass
547 phase by increasing the temperature of the relaxation peak without affecting its height.
548 Such differentiated nanoconfinement effects deserve a deeper analysis and will be the
549 subject of a future work.

550 Although the above results are about composites with embedded B2-CuZr crystals,
551 they provide inspiration for understanding the origin of energy dissipation or
552 mechanical relaxation in monolithic metallic glasses. Due to the feature of structural
553 heterogeneities in pure glass, analog to the composites, there are also regions with
554 different moduli, such as “soft regions” and “hard regions”, even though without clear
555 boundaries between them. Different regions possess different moduli, and between
556 them there are different strains under cyclic deformation, which induce energy
557 dissipation in the pure glass. Therefore, we can expect for an ideal glass containing
558 absolutely no heterogeneous structure and no imperfection, that there will be no
559 relaxation and energy dissipation. Furthermore, it can be inferred that if there is no
560 shear motion between regions with different moduli, there will still be no energy
561 dissipation. For instance, in the nanolaminates when both phases are deformed with
562 the same strain, there is no shear motion at the glass-crystal interface, which has no
563 effect on energy dissipation. Another evidence in pure glass can also be found in our
564 previous work [48] where the loss modulus derived from the isostatic deformation on
565 the pure $\text{Cu}_{64}\text{Zr}_{36}$ glass was almost negligible, as expected since no shear exists as the
566 same deformation is applied on three principal directions simultaneously, while for
567 other deformation modes, such as longitudinal deformation, shear or uniaxial
568 deformations, there is shear motion. The above analysis shows that for the energy
569 dissipation or the mechanical relaxation to occur in a pure glass, two conditions must

570 be met: one is the structural heterogeneity, i.e. the “hard regions” and “soft regions”,
571 with different moduli in different regions, and the other is a local shear deformation,
572 resulting in atomic shear motions between different regions.

573

574

575 **Acknowledgements**

576 Simulations were performed using HPC resources from “Fédération Lyonnaise de
577 Modélisation et Sciences Numériques” (FLMSN), partner of EQUIPEX
578 EQUIP@MESO. GJL thanks China Scholarship Council (CSC) for providing a
579 scholarship. YJW and GJL were financially supported by the NSFC (Nos. 12072344
580 and 11790292), and the Youth Innovation Promotion Association of Chinese
581 Academy of Sciences (No. 2017025).

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