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# Inducing mechanical self-healing in polymer glasses

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Polymer glasses such as the plastics used in pipes, structural materials, and medical devices are ubiquitous in daily life. The nature of their low molecular mobility is still poorly understood and it leads to brittle mechanical behavior, damage, and fracture over time. It also prevents the design of self-healing mechanisms that expand the material's lifespan, as more commonly done in recent years for higher mobility amorphous polymers such as gels and rubbers. We demonstrate through numerical simulations that controlled oscillatory deformations enhance the local molecular mobility of glassy polymers without compromising their structural or mechanical stability. We apply this principle to increase the molecular mobility around the surface of a cylindrical crack, counterintuitively inducing fracture repair and recovering the mechanical properties of the pristine material. Our findings are a first step to establish a general physical mechanism of self-healing in glasses that may inspire the design and processing of new glassy materials.

Self-healing refers to the ability of a material to restore functionality after undergoing physical damage. This characteristic is prominent in living materials such as plants<sup>1</sup>, mammalian cells<sup>2</sup>, and human skin<sup>3</sup>. In contrast, synthetic materials lack self-healing mechanisms, and the accumulated damage over time leads to macroscopic fractures and mechanical failure. In recent decades, the search for self-healing mechanisms in synthetic materials has become increasingly important for a sustainable environment<sup>4,5</sup>, promising to lower waste production and energy costs by diminishing the need for manufacturing replacements. Chemical modifications introducing dynamic covalent<sup>6,7</sup> and physical bonds<sup>8,9</sup> that break and reform reversibly can add self-healing abilities to synthetic materials. However, these mechanisms strongly rely on a sufficiently high molecular mobility within the material which facilitates mass transport, favoring the reconnection of crack surfaces and subsequent healing<sup>10,11</sup>.

Molecular mobility typically shows a dramatic decrease once a material is cooled below its glass-transition temperature  $T_g$ . Below  $T_g$ , materials exhibit rigidity because molecules are kinetically arrested. Above  $T_g$ , materials become flexible and viscous. Although soft materials such as elastomers and hydrogels maintain a solid shape due to covalent bonds, molecular segments have high local mobility at room temperature  $T_r$ , i.e.  $T_g < T_r$ , which enables the use of intrinsic mechanisms to induce self-healing in soft materials<sup>12-16</sup>. In contrast,

polymer glasses evidence an extremely low local mobility, since  $T_{g} >> T_{r}$ . The kinetically arrested nature of glassy systems gives rise to mechanical stability and a high elastic modulus, but disables potential intrinsic mechanisms that induce self-healing in soft materials. To overcome this low mobility, alternative approaches rely on the polymers with synthesis of complex architectures or functionalization<sup>8,17,18</sup> that are not suited for large-scale production since the synthesis becomes complex, expensive and may give rise to mechanical properties different from those required<sup>19-22</sup>. Therefore, these strategies apply only to very specific materials and create a critical bottleneck for the development of general self-healing polymer glasses such as everyday plastics.

Here, we demonstrate by numerical simulations a general alternative approach that involves applying controlled oscillatory deformations on damaged polymer glasses to heal micro-cracks. Traditionally, deformations are associated with damage and fracture propagation. Large deformations in glassy materials trigger mechanical rejuvenation, restoring the system to an unaged state, similar to the thermodynamic effect of temperature increase<sup>23</sup>. However, experimental studies on glassy polymers undergoing uniaxial deformation have shown enhanced molecular mobility before altering the underlying physical aging<sup>24,25</sup>. Recent experiments on metallic glasses have phenomenologically demonstrated cold welding induced by

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ultrasound vibrations<sup>26–28</sup>, which was attributed to localized processes enabling the formation of metallic bonds. Additionally, metallic polycrystalline alloys, also characterized by low molecular mobility and amorphous structure at the crystalline domain level, can undergo healing under well-controlled tensile high-cycle fatigue<sup>29</sup> by merging the crack propagation front at the surface of grain boundaries. Numerical simulations also revealed that stress-driven grain boundary migration occurs as a result of tensile and oscillatory shear deformations in nanocrystalline metals<sup>30</sup>.

From the theoretical perspective of glasses, recent works by Sastry and coworkers<sup>31-33</sup> have shown in the athermal regime that mechanical oscillations can promote glass annealing at the molecular scale, and we recently proved a quantitative equivalence between temperature and shear rate in the molecular relaxation of glasses at  $T \gtrsim T_{g}$  subjected to steady-state shear flow<sup>23</sup>. Building on these results, here we subject glassy systems to volume-preserving oscillatory deformations at varying amplitude and frequency. We identify specific deformation conditions under which molecular mobility can be accelerated without affecting the overall out-of-equilibrium nature of the polymer glasses, and we apply this principle to glasses in which an artificially-generated cylindrical crack can be healed. We find that oscillatory deformations can selectively accelerate the dynamics on the crack surface, promoting crack closure without leading to full melting of the glass in the bulk region. The theoretical understanding of different out-of-equilibrium dynamical regimes is a paradigm shift for the use of mechanical deformations to promote self-healing in polymer glasses.

#### Results

Our framework involves polymer glasses with short chains to avoid entanglement effects. Beads belonging to the same chain interact via harmonic covalent bonds. Non-consecutive beads and beads from different chains interact attractively, corresponding to non-covalent interactions<sup>23</sup>. The bead size is *d*, setting our length units (see the *Methods* section for a detailed model description). We explore a range of temperatures *T* from a fluid  $(T>T_g)$  to a glassy  $(T<T_g)$  state. We quantify the molecular mobility from the  $\alpha$ -relaxation time  $\tau_{\alpha}$  obtained from the decay of the intermediate self-scattering function  $F_s(q^*, t)$ , with  $q^*$  and *t* corresponding to the length scale of the glassy cage and the simulation time, respectively, see Fig. S1. The structural relaxation time  $\tau_{\alpha}$ , in equilibrium and under deformation, is extracted by imposing that  $F_s(q^*, \tau_{\alpha}) = 1/e$ .

#### Steady shear deformations

Before showing that oscillatory deformations can heal artificiallygenerated cylindrical cracks in glassy systems, we characterize the bulk  $\alpha$ -relaxation dynamics under shear. The oscillatory deformation depends on the strain amplitude  $\gamma_A$  and frequency  $\omega$ , as  $y(t) = y_A sin(\omega t)$ , which represents the strain applied to the material as a function of time. The combination of possible values within the set  $\{\gamma_A, \omega\}$  is vast, even when restraining our simulations to a regime where the system temperature remains stable in the canonical NVT ensemble. To restrict and rationalize our design space, we first study the rheological behavior of polymer glasses under steady shear deformations. The stress-strain evolution picture is well established in amorphous solid materials<sup>34</sup>: there is an initial linear response corresponding to solid elastic behavior at small deformations dominated by sterical cages, while plastic deformations at large strains eventually trigger a viscous-fluid behavior due to cage breaking. This transition is marked by a stress overshoot, placed at the yielding point  $y_{v,2}$ . This picture is true for particle suspensions interacting sterically. However, in the present system, we consider linear chains interacting through attractive non-covalent bonds. As illustrated in Fig. 1a, where the stress component  $\sigma_{xy}$  is normalized by  $k_B T/d^3$  (with  $k_B$  being the Boltzmann constant), a first yielding point  $y_{v,1}$  emerges at small strain values as transient bonds break, allowing monomers to escape from interparticle attraction and partially dissipate energy<sup>35–37</sup>. In addition, Fig. S2 shows that  $\gamma_{y,1}$  is shear rate dependent. The existence of two yielding points allows us to identify three different regimes of  $\gamma_A$ , with  $\omega$ remaining a free parameter. Focusing on systems at  $T/T_g \ge 1.0$ , for which the polymer melt reaches equilibrium, we observe from Fig. 1b that  $\gamma_A$  defined in each regime induces different molecular mobility. Both axes are rescaled by the relaxation time at equilibrium  $\tau_{\alpha}^0$ , so that relaxation times are reported in comparison to their equilibrium value, and deformation rates are reported as dimensionless Deborah numbers. This number defines the ratio of the material's characteristic relaxation time, in our case  $\tau_{\alpha}^0$ , to the characteristic flow time, which for oscillatory deformation is defined as  $\gamma_A \omega$ . The molecular mobility is extracted from  $F_s(q^*, t)$  under oscillatory deformation, see Fig. S3.

#### Linear regime ( $\gamma_A < \gamma_{\nu,1}$ )

Oscillatory deformations have no effect on the  $\alpha$ -relaxation, as indicated by the flat behavior of  $\tau_{\alpha}/\tau_{\alpha}^{0} \simeq 1$ . However, the potential energy per particle *E/N* as a function of the accumulated strain  $\gamma_{acc} = 4N_{cyc}\gamma_A$ , shown in Fig. 1c and where  $N_{cyc}$  represents the deformation cycles, is slightly smaller than the corresponding energy for the system immediately before applying oscillatory deformations. Previous numerical simulations of oscillatory athermal quasistatic shear (AQS) deformations of dense amorphous samples<sup>31,38,39</sup> established the limit at small strain deformations, i.e.,  $\gamma_A \ll \gamma_{y,2}$ , as a way to obtain better-annealed glasses. In particular, AQS assumes that the relaxation after deformation occurs on shorter timescales than  $\omega^{-1}$ . Thus, deformations in the AQS approach depend on the deformation length scale encoded in the amplitude deformation. In our case, the deformation frequency  $\omega$ introduces a timescale dependence that plays a key role in annealing glasses by accessing deeper energy states at small amplitude deformations<sup>33,40</sup>. Although the study of this regime is beyond the scope of this investigation, we could anticipate that in the limit of poorly annealed glasses<sup>33,40</sup>, and with decreasing  $\omega$  (indicating that the deformation timescale is so large that it allows the system to relax the accumulated stress) our findings would align with the observations discussed in AQS simulations<sup>41</sup>.

### Nonlinear regime ( $\gamma_A > \gamma_{y,2}$ )

Oscillatory deformations promote melting similarly to steady shear flow<sup>23</sup>. In this regime, each oscillatory cycle induces a strain larger than the characteristic deformation that triggers the viscous-fluid transition. As a result,  $\tau_{\alpha}$  decreases below  $\tau_{\alpha}^{0}$  as  $\gamma_{A}\omega$  increases through  $\omega$ . Actually, we find that the slope of  $\tau_{\alpha}/\tau_{\alpha}^{0}$  tends to an asymptotic behavior as  $x^{-0.8}$  by decreasing *T* and increasing the deformation. The exponent is related to the shear thinning behavior, which is characterized by an apparent viscosity that decreases with increasing shear rate<sup>23,42</sup>. Additionally, *E/N* monotonically increases with  $\gamma_{A}\omega$ , shown in Fig. 1c, whereas the characteristic plateau observed in  $F_{s}(q^{*}, t)$  shortened, see Fig. S3.

#### Intermediate regime ( $\gamma_{y,1} < \gamma_A < \gamma_{y,2}$ )

Intermediate strain amplitudes can speed up the molecular mobility without changing the underlying structure of the system. When the characteristic deformation time exceeds the structural relaxation time of the system, identified by Deborah numbers larger than 1, the dynamics accelerates until it reaches a plateau. Maintaining a constant strain amplitude, we detect that the plateau length increases as we approach  $T_g$ . On the other hand,  $\tau_{\alpha}$  falls to a plateau of lower height as  $\gamma_A$  approaches  $\gamma_{y,2}$ , see Fig. S4. As  $\gamma_A \omega$  increases by increasing  $\omega$ , the system approaches a critical value after which  $\tau_{\alpha}$  resembles that of a polymer fluid. This striking behavior is in agreement with the enhanced molecular mobility observed for polymer glasses under tensile deformations prior to flow<sup>24,25</sup>. Similarly, regions of high local mobility have been detected for amorphous materials under oscillatory shear



**Fig. 1** | **Quantifying bulk mobility. a** Shear stress tensor  $\sigma_{xy}$  as a function of the strain  $\gamma$  for a shear rate  $\dot{\gamma} = 0.01$  applied in the xy-plane. The first yielding point corresponding to physical bond breaking is referred to as  $\gamma_{y,1}$ , whereas  $\gamma_{y,2} \simeq 2.6$  indicates the yielding point corresponding to the transition from elastic solid to viscous-fluid behavior. The existence of these two yielding points delineates three regimes where all beads are frozen (linear regime, blue beads), partially relaxing (intermediate regime), or fully relaxing (nonlinear regime, red beads).

**b** Normalized relaxation time  $\tau_{\alpha}/\tau_{\alpha}^{a}$  as a function of the Deborah number  $\gamma_{A}\omega\tau_{\alpha}^{a}$ , for systems at different *T* subjected to oscillatory deformations. In all plots, the error bars indicate the standard deviation over configurations. **c** Energy per particle *E/N* 

deformations<sup>32,40,41,43</sup>. These regions of high local mobility forming shear bands were identified at  $\gamma_A > \gamma_{y,2}$ , and we investigate if a similar mechanism is observed in our systems.

One way to detect shear bands is by monitoring the particle energy *E*/*N* as a function of  $\gamma_{acc}$ . As discussed in ref. 41, *E*/*N* would exhibit a sharp upward shift because of the spontaneous onset of shear banding. In the intermediate and nonlinear regime, depicted in Fig. 1c and Fig. S5, we see that *E*/*N* evolves smoothly without showing abrupt changes. However, we note that oscillatory deformations with a strain amplitude just above the first yielding point induce strong energy fluctuations, see Fig. S5. Likewise, the evolution of *E*/*N* as a function of *γ* follows nearly identical trajectories in each cycle, reflecting the predominant elastic response of the material (see Fig. S5). Once  $\gamma_A > \gamma_{y,1}$ , the elastic behavior gradually weakens due to the breaking of noncovalent bonds, resulting in greater energy dissipation and system reorganization. Consequently, energy fluctuations decrease. Aiming to look for any signs of shear banding, we examine the mean-squared

as a function of accumulated strain  $\gamma_{acc}$  and  $\gamma_A \omega$  for a system at  $T/T_g = 1.00$ . **d** General representation of the local mobility under oscillatory shear deformation,  $\tau_{\alpha}(\gamma_A, \omega, T)$ . Black arrows emphasize how the structural relaxation time changes with increasing  $\gamma_A$  and T of the system. **e** Snapshots at different accumulated strain  $\gamma_{acc}$  for a polymer melt system at  $T/T_g = 1.00$ , subjected to an oscillatory deformation in the intermediate regime with  $\gamma_A = 0.4$  and  $\gamma_A \omega = 0.01$ . We also represent the displacement of the center of mass for the polymer chains. In this case, chains whose center of mass displaces equal to or more than the radius of gyration  $R_g$  are not found.

displacement  $\langle r^2 \rangle$  for single beads and for the center of mass of each chain as a function of  $\gamma_{acc}$  (see *Methods* for more details). In Fig. 1e, we identify beads that undergo a displacement  $\langle r^2 \rangle \ge d^2$ , and chains whose center of mass undergo a displacement equal to or larger than the radius of gyration  $R_{g}$ , for a glassy system subjected to  $\gamma_A = 0.4$  and  $\gamma_A \omega = 10^{-1}$ . Contrary to what has been observed in refs. 40,41,44, particles with high displacement do not develop a shear band. Furthermore, Fig. S6 shows that higher  $\gamma_A$  promotes the formation of a branched percolating cluster of particles with a high displacement, resembling the scenario observed under steady shear<sup>45</sup>. Therefore, the enhanced molecular mobility we observe does not involve shear banding. This difference can be attributed to the fact that the deformation-induced dynamics are too fast to allow sufficient time for the formation of shear bands. Indeed, in ref. 41, the maximum shear rate explored is two orders of magnitude lower. Instead, the existence of these plateaus suggests that in the intermediate amplitudes regime, the oscillatory deformation breaks the microscopic cages responsible



**Fig. 2** | **Healing crack in oscillating glasses. a** A cylindrical crack of diameter D/d = 1.0 in a polymer glass is repaired after several cycles of oscillatory deformations at  $\gamma_A = 1.0$  and  $\gamma_A \omega = 0.1$ . Beads are colored according to their depth within the material. Dotted circles highlight the initial position of the cylindrical crack. **b** *T*–*D* phase diagram indicating the percentage of closed samples by increasing the overall system temperature. The dashed box highlights the range of cylindrical

crack diameters we explore under the action of an oscillatory deformation. **c** Structural relaxation time  $\tau_{\alpha}$  as a function of amplitude  $\gamma_A$  and frequency  $\omega$ deformation. The error bars indicate the standard deviation over configurations. **d**  $\gamma_A - \gamma_A \omega$  phase diagram for healed glasses at different *D* values of cylindrical cracks and varying strain amplitude and shear rate.

for the material vitrification. This mechanism, inducing local yielding, allows the system to remain globally arrested but to relax locally. Fig. 1d schematizes molecular dynamics (MDs) behavior under oscillatory deformation, expressed as  $\tau_{\alpha}(\gamma_A, \omega, T)$ .

#### Promoting self-healing with oscillatory shear deformations

The accelerated dynamics observed in Fig. 1 can be leveraged to heal an artificially-generated cylindrical crack in a glassy system via oscillatory deformations, as shown in Fig 2. As explained in the Methods section, polymer glass systems at  $T/T_g = 0.5$  are prepared with a cylindrical crack of diameter D along the y axis, with walls preventing particles from entering the crack region. Once the glassy state is reached, we remove the cylinder and allow the system to evolve freely. We recognize that these configurations differ in shape and stress distribution from more realistic cracks naturally arising from material aging or damage. Nevertheless, inducing ad-hoc cracks enables precise and rigorous quantification of the mechanisms that trigger healing under mechanical oscillatory deformations, and is a first step to solve the broader problem of fracture healing in glassy materials. The first snapshot in Fig. 2a shows a polymer glass with a cylindrical crack of diameter D/d = 1.0. The evolution of the crack surface area is monitored over time, shown in Fig. S8 and Supplementary Video 1 and 2, respectively. For cylindrical cracks of diameter half the particle size, i.e., D/d = 0.5, the attractive interaction between different chains promotes inward flow. However, for  $D/d \ge 1.0$ , the cracks are stable over time, as shown in Fig. S8a, because of the extremely long relaxation time, which is indicative of the very low molecular mobility that hinders any relaxation time in our observable timescale. Higher temperatures are therefore required, as shown in Figs. 2b and S8a, to close the crack.

Keeping  $T/T_g = 0.5$  (glass regime), we focus on the highlighted range shown in Fig. 2b and apply oscillatory deformations. Firstly, we repeat the previous study discussed in Fig. 1b by computing the evolution of  $\tau_{\alpha}$  as a function of oscillatory deformations (see Fig. 2c). While we cannot estimate  $\tau^0_{\alpha}$  because the system is out-of-equilibrium (see Fig. S1), we observe qualitatively the same behavior as we approach  $T_{g}$ . Oscillations with  $y_A > y_{v,2}$  lead to the melting of the glass material, whereas for  $\gamma_{\nu,1} < \gamma_A < \gamma_{\nu,2}$ , the dynamics can be locally accelerated by breaking microscopic cages. Additionally, we also observed that even in the glassy state, no shear band formation occurs (see Fig. S6), which may be attributed to the polymer chain connectivity of our model and the high oscillation frequencies. However, we also note that  $\tau_{\alpha}$  develops a stark maximum by increasing  $\omega$ . This trend is already observed for  $T \ge T_{g}$  (see intermediate regime in Fig. S4). The presence of this maximum following a sharp decrease in  $\tau_{\alpha}$  could indicate non-trivial annealing behavior of the glasses, similar to that observed near the yielding point in Kob-Anderson binary mixtures<sup>41</sup>. However, in Fig. S7, we have attempted to establish a connection between  $\tau_{\alpha}$  and the degree of molecular mobility by computing the distribution of perparticle Debye-Waller factor, but we do not see signs of any annealing. Instead, we observe that this peak marks the transition from a welldefined unimodal distribution to a distribution with a long tail. Returning to the mechanical self-healing, Fig. 2a displays the closure of a crack of D/d = 1.0 after  $N_{cvc} = 72$  deformation cycles. Fig. 2d displays a set of  $\gamma_A - \gamma_A \omega$  phase diagrams as a function of the initial D. These diagrams illustrate the percentage of samples in which oscillatory deformations in the intermediate regime successfully closed the crack. While for D/d = 1.0 we consistently achieve crack closure, as D increases, the efficiency of oscillatory deformation decreases. However, we note that this decline begins at high values of  $\omega$  for D/d = 1.5, and



**Fig. 3** | **Local mobility and restoration of mechanical properties.** Local mobility  $\langle u^2 \rangle$  for particles on the crack surface and bulk as a function of time *t* for polymer glasses subjected to oscillatory deformations of  $\gamma_A = 1.0$  and  $\gamma_A \omega = 0.1$ , with a cylindrical crack of diameter (a) D/d = 1.0 and b D/d = 2.0. Horizontal lines represent the bulk local mobility as a function of *T* at mechanical rest. Circles highlight the times at which the snapshots were taken, represented on the right. The crack

region is represented in light gray, whereas dark gray beads correspond to beads on the crack surface. **c** The healed system at  $\omega = 0.1$  and different  $\gamma_A$  values is subjected to steady shear flow at shear rate  $\dot{\gamma} = 0.01$ . The resulting stress tensor is compared with the stress curve of the glass at rest, showing that mechanical properties are recovered.

becomes more pronounced for D/d = 2.0. This trend is rationalized by the fact that the oscillation rate of the deformation imposed by  $\omega$ overcomes the characteristic particle diffusion rate. This, along with the fact that the crack diameter is large enough to suppress particle interactions across the crack, favors particles following the same trajectory in each deformation cycle. Thus, an increase in  $y_4$  is required to bring particles in contact across the crack. Fig. S8b shows the evolution of the crack surface area over time for an initial cylindrical crack of diameter D/d = 1.5 under oscillatory deformations. In addition, we also explore the case in which the system has been previously subjected to an affine oscillatory deformation, taking the system configuration at the maximum deformation and then letting it evolve (see Supplementary information for additional details). Notably, affine deformations and the shape variation of the crack under large deformations are not sufficient to initiate particle flow, and dynamic oscillatory deformations are needed, as we further prove in Fig. S8. At least qualitatively, this healing mechanism seems to also apply to less artificial crack configurations, as we show in Fig. S9 where the glassy material is punctured by indenting it with a sharp object before applying deformations. Still, a systematic extension of our findings to realistic fracture configurations is beyond the scope of this work and should be an important focus of future studies.

One may wonder if we genuinely induce self-healing by accelerating the local dynamics exclusively around the crack. This is a legitimate doubt because deformations are often associated with the breakdown of the material's structure, inducing mechanical rejuvenation in amorphous materials<sup>23,46,47</sup>. In addition to showing that this amplitude regime precedes the material's yielding point  $\gamma_{y,2}$ , Fig. 3 shows that indeed cracks can heal purely by accelerated local dynamics, while the bulk remains globally glassy and the final mechanical properties of the healed glass are comparable to those of the pristine equilibrium glass. We identify particles on the surface of the crack and in the bulk, i.e., far away from the crack, and compute their mobility during deformation through the Debye-Waller factor  $\langle u^2 \rangle$ , which corresponds to the value of the mean square displacement at local minima of its logarithmic derivative<sup>48,49</sup>, as shown in Fig. S1e. Fig. 3a displays results corresponding to a polymer glass with a crack of

diameter D/d = 1.0, subjected to  $\{\gamma_A, \omega\} = \{1.0, 0.1\}$ , equivalent to  $y_A \omega = 0.1$ . The crack surface and particles on the surface are represented in the snapshots in light gray and dark gray colors, respectively, while particles in the bulk are omitted to enhance the clarity of the snapshots. Furthermore, we depict the evolution of  $\langle u^2 \rangle$  as a function of the time t alongside the corresponding mobility at different T in the absence of deformation, indicated by a horizontal line. While  $\langle u^2 \rangle$ slightly increases for particles in the bulk, we note that the dynamics for surface particles aligns with that observed for a bulk equilibrium system at  $T/T_g = 1.0$ . As the crack closes, the surface dynamics converges to the bulk dynamics, at a value slightly higher than the equilibrium dynamics at  $T/T_g = 0.50$  because of the oscillatory deformations. It is important to note how the particles initially located on the surface remain localized around the region where the crack was. This indicates that local melting induces an inward flow of material, filling the damaged space. In the case where the crack does not close, as depicted in Fig. 3b, the surface and bulk dynamics do not match.

Finally, we assess the mechanical properties of the material immediately after closing the crack. In Fig. 3c, we compare the mechanical response under steady shear of the healing glass material with that obtained from a polymer glass in which no crack is present. At low-strain deformations, the first yielding point  $\gamma_{y,1}$ , associated with physical bond breaking, is less apparent in the stress curves of the healed material. This issue is attributed to the slightly accelerated bulk dynamics, see Figs. 3a and S10. However, the position of  $\gamma_{y,2}$  and the stress overshoot  $\sigma_{xy}(\gamma_{y,2})$ , indicating the opposing resistance of the material to break and flow, perfectly match. Thus, our findings suggest that the application of small oscillatory deformations has the potential to induce complete self-healing in glassy polymer materials.

#### Discussion

In recent decades, oscillatory deformations have emerged as an avenue for exploring new frontiers in the fundamental physics of amorphous materials. This includes enhancing annealing<sup>39,40</sup> and inducing memory<sup>50,51</sup> in amorphous glasses. Here, we used oscillatory deformations to induce self-healing in glassy polymer materials by overcoming their intrinsically low local mobility. The enhanced mobility would enable the use of intrinsic healing mechanisms such as dynamic covalent bonds or supramolecular bonds that strongly depend on the local dynamics<sup>9</sup>.

First, we have studied the local mobility in bulk model glasses without damage. We have identified a range of oscillatory deformations, placed above the strain deformation  $\gamma_{y,1}$  corresponding to breaking transient bonds, and below the critical strain  $y_{v,2}$  value, which leads to melting, and where the molecular mobility can be meticulously accelerated without globally modifying the underlying structure or mechanical properties of the system. In this range of deformations, which we define as the intermediate regime, particle dynamics are locally accelerated as microscopic cages responsible for the glassy state are broken, while overall dynamics remain arrested. We have shown that the structural relaxation time exhibited a plateau likely due to the acceleration of local dynamics which does not lead to a fully liquid behavior, since the strain amplitude does not exceed  $y_{y,2}$ . Furthermore, carefully observing the particle displacement, we have found that the presence of a plateau in relaxation time is not accompanied by the formation of shear bands in our simulations, and  $\tau_{\alpha}$ dramatically decreases at critical  $\omega$  values that are strain amplitudedependent. We have then demonstrated that this range can be exploited to induce mechanical self-healing under highly controlled conditions. In particular, we have studied damaged polymer glasses at  $T < T_{g}$  where the low molecular mobility hinders any relaxation and makes artificially-generated cylindrical cracks stable at equilibrium at any observable timescale. By monitoring the local mobility of the particles,  $\langle u^2 \rangle$  we were able to observe that the dynamics under oscillatory deformations is more prominently accelerated for the particle located at the crack surface. In oscillatory deformations within the intermediate regime, this leads to a mass flow into the crack within the simulation timescale, while the bulk dynamics is largely unchanged. Furthermore, stress-strain curves for healed samples closely match the pristine material.

Since glassy polymers are out-of-equilibrium materials, their rheological response depends on the aging history and preparation protocol. In the past, it has been studied that more stable glasses are more brittle, making the yielding point a spinodal instability characterized by a sharp discontinuous stress jump<sup>44</sup>. It would be relevant in the future to understand if local mobility controlled by oscillatory deformations depends on the glass stability. Likewise, cracks induced by realistic mechanical deformation are an important next step to investigate since the perfect cylindrical cracks investigated in our study might not represent the structure and distribution of stresses of cracks naturally emerging from material aging or damage. In this scenario, local dynamics and stability would be affected by the highly heterogeneous stress concentrations and irregularity of the surface created by the mechanical deformation<sup>25,52</sup>. Furthermore, mechanical deformations could promote the presence of multiple small cracks, giving rise to a yet unexplored scenario that is worth investigating. Nevertheless, our results on polymer glasses, along with previous observations of healing in metal alloys<sup>29</sup>, nanocrystalline metals<sup>30</sup> and metallic glasses<sup>26,28</sup> under mechanical deformations, point to the fact that oscillatory deformations represent a general strategy to induce mechanical self-healing in materials with extremely low local mobility. Previous computational results showing equivalent equilibrium glassy dynamics at the surface of thin films and the curved interface of spherical nanoparticles<sup>49,53,54</sup> suggest that this mechanism might be general regardless of the interface nanostructure, though further studies are needed, given the experimentally known complexity of glassy dynamics at realistic, rough interfaces<sup>55,56</sup>. In this respect, ultrasonic vibrations of frequency  $f = [0.02 - 7] \times 10^4$  Hz and strain amplitude of  $\gamma_A = 10^{-2}$ % applied to metallic glasses appear to be particularly promising to study mechanical self-healing<sup>26</sup>. With the assumption of an experimental structural relaxation time of 100 s at  $T_g^{57}$ , these deformations correspond to Deborah numbers  $De_{exp} \in [10^2 - 10^4]$ , similar to the value  $De_{sim} = 10^3$  of our simulations if we use a fairly common estimate for a computational  $T_g$  when  $\tau_{\alpha} = 10^4 t_{LJ}$ . Therefore, we hope that the broader theoretical discussion and the explicit demonstration of molecular self-healing without volume-changing deformations presented here in controlled conditions can stimulate further theoretical studies in more realistic conditions and targeted experimental activities toward the study of selfhealing in polymer glassy materials.

# Methods

#### Modeling

We perform MDs simulations of fully flexible linear chains of beads linked by harmonic springs. Nonbonded monomers belonging to the same or different chains interact with a truncated LJ potential defined as

$$U_{lJ}(r) = \begin{cases} 4\varepsilon \left[ \left(\frac{d}{r}\right)^{12} - \left(\frac{d}{r}\right)^6 \right] + U_{cut} & \text{if } r \le 2.5d \\ 0 & \text{if } r > 2.5d \end{cases},$$
(1)

where *d* is the particle diameter, which sets the unit of length,  $\epsilon$  controls the energy scale, and  $U_{cut}$  ensures that  $U_{LJ}(r=2.5d)=0$ . Defining *m* as the mass of the particles, the time units are defined as  $t = \sqrt{md^2/\epsilon}$ . On the other hand, chemical bonds between connected monomers are modeled by

$$U_b(r) = k_b (r - r_0)^2$$
, (2)

where  $k_b = 555.5\epsilon/d^2$  is the spring constant and  $r_0 = 0.97d$  is the equilibrium bond length. Henceforth, all quantities are expressed in terms of reduced LJ units, i.e.,  $\epsilon = 1$  and d = 1, with unit monomer mass *m* and Boltzmann constant. The reduced units can be mapped onto physical units relevant to generic nonequilibrium fluids, by taking MD time, length, and energy units as corresponding roughly to 2 ps, 0.5 nm, and 3.7 kJ/mol, respectively.

We consider systems of  $N_c$  = 500 chains of M = 20 monomers, thus avoiding the entanglement, and doing a total of N = 10<sup>4</sup> monomers. All simulations were performed using LAMMPS simulation package<sup>58</sup>, considering a simulation time step  $\delta t$  = 0.002. Results are averaged over 5 independent simulations.

#### Sample preparation

Initially, an equilibration process was performed by considering polymer chains enclosed in an orthogonal cubic box of size *L* with periodic boundary conditions. First,  $10^7$  simulation steps were performed in the NPT ensemble by employing a Nosé-Hoover thermostat and barostat with T = 1.0 and  $\langle P \rangle = 0$  allowing full correlation loss of the end-to-end vector of the polymer chains. Next, a quenching was made in the range of temperatures from  $T/T_g = 0.50$  to  $T/T_g = 1.38$ , maintaining  $\langle P \rangle = 0$  during  $10^7$  simulation steps. In both equilibration procedures, the simulation box was allowed to fluctuate in an isotropic fashion in all three directions of space.

#### Static and dynamic characterization

Once the system was equilibrated to the required temperature, the volume was fixed by performing simulations in the *NVT* ensemble by using a Nosé-Hoover thermostat at the required temperature, and static and dynamic properties were computed to characterize the polymer system as a function of *T*. In particular, the static structure factor was computed as  $S(q) = \langle \frac{1}{N} \sum_{ij} e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \rangle$ , where **q** is the wave vector,  $\mathbf{r}_i$  indicates the position of the *i*th particle, and  $\langle \cdots \rangle$  denotes an ensemble average. Likewise, the dynamic of the system was quantified through the mean-squared displacement  $\langle \Delta r^2(t) \rangle = \langle \frac{1}{N} \sum_{i=1}^{N} [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle$  and the self-intermediate scattering function  $F_s(q^*, t) = \langle \frac{1}{N} \sum_{i}^{N} e^{i\mathbf{q}^*} \cdot [\mathbf{r}_i(t+t) - \mathbf{r}_i(t)] \rangle$ ,

computed on the wave vector  $q^* = 2\pi/l$  corresponding to the main peak of the static structure factor. The relaxation time  $\tau_{\alpha}$  was extracted by imposing  $F_s(q^*, \tau_{\alpha}) = 1/e$ .

#### Shear deformation

After equilibration, we perform two kinds of simulations: (i) steady shear deformations at a fixed shear rate  $\dot{y}$ ; (ii) oscillatory shear deformations by applying a sinusoidal deformation in the xy plane defined as  $y(t) = y_A sin(\omega t)$ , where  $y_A$  is the strain amplitude and  $\omega$  is the frequency. In both cases, deformations are performed at constant volume and temperature, and hence, the SLLOD equations of motion were used along with the thermostat, in combination with Lees-Edwards boundary conditions. During the steady shear deformation, we monitor the stress tensor component  $\sigma_{\alpha\beta} = \frac{1}{A} \langle \sum_{i>j} f_{ij}^{\alpha} r_{ij}^{\beta} \rangle$ , where  $f_{ij}^{\alpha}$  is the  $\alpha$ component of the force with respect to interaction defined in eq. (1) and eq. (2),  $r_{ii}^{\beta}$  corresponds the  $\beta$ -component of the distance vector between particles *i* and *j*. In this case, the steady shear deformation was applied in all three directions of space and subsequently averaged. On the other hand, during the oscillatory deformation, we first apply an accumulated strain  $\gamma = 4N_{cyc}\gamma_A = 100\%$ , where  $N_{cyc}$  corresponds to the number of deformation cycles. Then, we compute the selfintermediate scattering function on the wave vector  $q^*$  corresponding to the main peak of the static structure factor before applying any deformation. Since oscillatory deformations were applied on the xy plane,  $F_s(q^*, t)$  was computed excluding  $q_x$  components, see Fig. S3. Furthermore, we computed the mean-squared displacement per particle, defined as  $\Delta r^2(t)_i = [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2$ , excluding the *x*-component.

#### Inducing self-healing

To study self-healing, we create a crack on polymer glasses with  $T/T_g = 0.50$  and *N* monomers. The equilibration previously described above is performed in the presence of a cylinder placed at the center of the simulation box of length  $L_y$  and diameter *D*. Monomers interact with the cylinder wall through the Weeks-Chandler-Andersen potential:

$$U_{WCA}(r) = \begin{cases} 4\epsilon \left[ \left( \frac{d}{r} \right)^{12} - \left( \frac{d}{r} \right)^{6} \right] + \epsilon & \text{if } r \le 2^{1/6} d \\ 0 & \text{if } r > 2^{1/6} d \end{cases}$$
(3)

Then, the cylinder is removed, and NVT simulations and oscillatory deformation simulations are independently performed during  $10^7$  up to  $3 \times 10^7$  simulation steps. In both cases, the volume of the crack is monitored by employing the surface area algorithm<sup>59</sup>. During both simulations, we compute the mobility  $\langle u^2 \rangle$  of the monomers as a function of the distance from the center of the simulation box, as well as a function of time. Since the mobility is statistically very noisy, we apply a Savitzky-Golay filter on windows of 21 points and equations of 2 order.

#### Mechanical properties after the self-healing

Glassy polymer systems, on which the crack was closed, are subjected to steady shear flow at  $\dot{\gamma} = 0.01$ , and the evolution of  $\sigma_{xy}$  as a function of  $\gamma = \dot{\gamma}t$  is compared with the corresponding  $\sigma_{xy}$  for the glass at rest.

#### Data availability

The figures source data generated in this study have been deposited in the Zenodo database under accession code https://doi.org/10.5281/ zenodo.15170122. Source data are provided with this paper.

#### Code availability

The LAMMPS code used to perform our simulations is available at the Zenodo repository https://doi.org/10.5281/zenodo.15170122.

#### References

- París, R., Lamattina, L. & Casalongué, C. A. Nitric oxide promotes the wound-healing response of potato leaflets. *Plant Physiol. Biochem.* 45, 80–86 (2007).
- 2. Han, R. & Campbell, K. P. Dysferlin and muscle membrane repair. *Curr. Opin. Cell Biol.* **19**, 409–416 (2007).
- Chortos, A., Liu, J. & Bao, Z. Pursuing prosthetic electronic skin. Nat. Mater. 15, 937–950 (2016).
- Bekas, D., Tsirka, K., Baltzis, D. & Paipetis, A. S. Self-healing materials: a review of advances in materials, evaluation, characterization and monitoring techniques. *Compos. Part B: Eng.* 87, 92–119 (2016).
- 5. Liu, X. et al. Healable and recyclable polymeric materials with high mechanical robustness. *ACS Mater. Lett.* **4**, 554–571 (2022).
- Terryn, S., Brancart, J., Lefeber, D., Van Assche, G. & Vanderborght, B. Self-healing soft pneumatic robots. *Sci. Robot.* 2, eaan4268 (2017).
- 7. Canadell, J., Goossens, H. & Klumperman, B. Self-healing materials based on disulfide links. *Macromolecules* **44**, 2536–2541 (2011).
- Chen, Y., Kushner, A. M., Williams, G. A. & Guan, Z. Multiphase design of autonomic self-healing thermoplastic elastomers. *Nat. Chem.* 4, 467–472 (2012).
- Urban, M. W. et al. Key-and-lock commodity self-healing copolymers. Science 362, 220–225 (2018).
- Wang, S. & Urban, M. W. Self-healing polymers. Nat. Rev. Mater. 5, 562–583 (2020).
- Hager, M. D., Greil, P., Leyens, C., Van Der Zwaag, S. & Schubert, U. S. Self-healing materials. *Adv. Mater.* 22, 5424–5430 (2010).
- Li, C.-H. et al. A highly stretchable autonomous self-healing elastomer. Nat. Chem. 8, 618–624 (2016).
- Wu, J., Cai, L.-H. & Weitz, D. A. Tough self-healing elastomers by molecular enforced integration of covalent and reversible networks. *Adv. Mater.* 29, 1702616 (2017).
- Jeon, I., Cui, J., Illeperuma, W. R., Aizenberg, J. & Vlassak, J. J. Extremely stretchable and fast self-healing hydrogels. *Adv. Mater.* 28, 4678–4683 (2016).
- 15. Bilodeau, R. A. & Kramer, R. K. Self-healing and damage resilience for soft robotics: a review. *Front. Robot. Al* **4**, 48 (2017).
- Fan, L. et al. Advances in synthesis and applications of self-healing hydrogels. Front. Bioeng. Biotechnol. 8, 654 (2020).
- Yanagisawa, Y., Nan, Y., Okuro, K. & Aida, T. Mechanically robust, readily repairable polymers via tailored noncovalent cross-linking. *Science* 359, 72–76 (2018).
- Wang, H. et al. Room-temperature autonomous self-healing glassy polymers with hyperbranched structure. *Proc. Natl. Acad. Sci.* 117, 11299–11305 (2020).
- Boils, D. et al. Molecular tectonics. disruption of self-association in melts derived from hydrogen-bonded solids. *Macromolecules* 37, 7351–7357 (2004).
- Lebel, O., Maris, T., Perron, M.-È., Demers, E. & Wuest, J. D. The dark side of crystal engineering: creating glasses from small symmetric molecules that form multiple hydrogen bonds. J. Am. Chem. Soc. 128, 10372–10373 (2006).
- Sheiko, S. S. & Dobrynin, A. V. Architectural code for rubber elasticity: from supersoft to superfirm materials. *Macromolecules* 52, 7531–7546 (2019).
- 22. Asadi, V., Ruiz-Franco, J., van der Gucht, J. & Kodger, T. E. Tuning moduli of hybrid bottlebrush elastomers by molecular architecture. *Mater. Des.* **234**, 112326 (2023).
- 23. Giuntoli, A., Puosi, F., Leporini, D., Starr, F. W. & Douglas, J. F. Predictive relation for the  $\alpha$ -relaxation time of a coarse-grained polymer melt under steady shear. *Sci. Adv.* **6**, eaaz0777 (2020).
- 24. Lee, H.-N. & Ediger, M. Mechanical rejuvenation in poly (methyl methacrylate) glasses? molecular mobility after deformation. *Macromolecules* **43**, 5863–5873 (2010).

- Bennin, T., Ricci, J. & Ediger, M. Enhanced segmental dynamics of poly (lactic acid) glasses during constant strain rate deformation. *Macromolecules* 52, 6428–6437 (2019).
- 26. Ma, J. et al. Fast surface dynamics enabled cold joining of metallic glasses. *Sci. Adv.* **5**, eaax7256 (2019).
- Li, X., Liang, X., Zhang, Z., Ma, J. & Shen, J. Cold joining to fabricate large size metallic glasses by the ultrasonic vibrations. *Scr. Mater.* 185, 100–104 (2020).
- 28. Li, L. et al. Joining of metallic glasses in liquid via ultrasonic vibrations. *Nat. Commun.* **14**, 6305 (2023).
- 29. Barr, C. M. et al. Autonomous healing of fatigue cracks via cold welding. *Nature* **620**, 552–556 (2023).
- Xu, G. & Demkowicz, M. Healing of nanocracks by disclinations. Phys. Rev. Lett. 111, 145501 (2013).
- Leishangthem, P., Parmar, A. D. & Sastry, S. The yielding transition in amorphous solids under oscillatory shear deformation. *Nat. Commun.* 8, 14653 (2017).
- Bhaumik, H., Foffi, G. & Sastry, S. The role of annealing in determining the yielding behavior of glasses under cyclic shear deformation. *Proc. Natl. Acad. Sci.* **118**, e2100227118 (2021).
- Bhaumik, H., Foffi, G. & Sastry, S. Yielding transition of a two dimensional glass former under athermal cyclic shear deformation. J. Chem. Phys. 156, 064502 (2022).
- Ghosh, A. & Schweizer, K. S. Microscopic activated dynamics theory of the shear rheology and stress overshoot in ultradense glass-forming fluids and colloidal suspensions. J. Rheol. 67, 559–578 (2023).
- Pham, K. et al. Yielding behavior of repulsion-and attraction-dominated colloidal glasses. J. Rheol. 52, 649–676 (2008).
- Koumakis, N. & Petekidis, G. Two step yielding in attractive colloids: transition from gels to attractive glasses. Soft Matter 7, 2456–2470 (2011).
- 37. Moghimi, E. & Petekidis, G. Mechanisms of two-step yielding in attractive colloidal glasses. *J. Rheol.* **64**, 1209–1225 (2020).
- Regev, I., Lookman, T. & Reichhardt, C. Onset of irreversibility and chaos in amorphous solids under periodic shear. *Phys. Rev. E* 88, 062401 (2013).
- Schinasi-Lemberg, E. & Regev, I. Annealing and rejuvenation in a two-dimensional model amorphous solid under oscillatory shear. *Phys. Rev. E* 101, 012603 (2020).
- Yeh, W.-T., Ozawa, M., Miyazaki, K., Kawasaki, T. & Berthier, L. Glass stability changes the nature of yielding under oscillatory shear. *Phys. Rev. Lett.* **124**, 225502 (2020).
- Parmar, A. D., Kumar, S. & Sastry, S. Strain localization above the yielding point in cyclically deformed glasses. *Phys. Rev. X* 9, 021018 (2019).
- Chen, K. & Schweizer, K. S. Theory of yielding, strain softening, and steady plastic flow in polymer glasses under constant strain rate deformation. *Macromolecules* 44, 3988–4000 (2011).
- Bhaumik, H., Foffi, G. & Sastry, S. Avalanches, clusters, and structural change in cyclically sheared silica glass. *Phys. Rev. Lett.* **128**, 098001 (2022).
- Ozawa, M., Berthier, L., Biroli, G., Rosso, A. & Tarjus, G. Random critical point separates brittle and ductile yielding transitions in amorphous materials. *Proc. Natl Acad. Sci.* **115**, 6656–6661 (2018).
- Shrivastav, G. P., Chaudhuri, P. & Horbach, J. Yielding of glass under shear: a directed percolation transition precedes shear-band formation. *Phys. Rev. E* 94, 042605 (2016).
- Viasnoff, V. & Lequeux, F. Rejuvenation and overaging in a colloidal glass under shear. *Phys. Rev. Lett.* 89, 065701 (2002).
- Ruiz-Franco, J., Gnan, N. & Zaccarelli, E. Rheological investigation of gels formed by competing interactions: a numerical study. *J. Chem. Phys.* **150**, 024905 (2019).
- Larini, L., Ottochian, A., De Michele, C. & Leporini, D. Universal scaling between structural relaxation and vibrational dynamics in glass-forming liquids and polymers. *Nat. Phys.* 4, 42–45 (2008).

- 49. Zhu, Y. et al. The effect of nanoparticle softness on the interfacial dynamics of a model polymer nanocomposite. *J. Chem. Phys.* **157**, 094901 (2022).
- 50. Fiocco, D., Foffi, G. & Sastry, S. Encoding of memory in sheared amorphous solids. *Phys. Rev. Lett.* **112**, 025702 (2014).
- Adhikari, M. & Sastry, S. Memory formation in cyclically deformed amorphous solids and sphere assemblies. *Eur. Phys. J. E* 41, 1–17 (2018).
- 52. Bera, P. K., Medvedev, G. A., Caruthers, J. M. & Ediger, M. D. Structural relaxation time of a polymer glass during deformation. *Phys. Rev. Lett.* **132**, 208101 (2024).
- Hanakata, P. Z., Douglas, J. F. & Starr, F. W. Interfacial mobility scale determines the scale of collective motion and relaxation rate in polymer films. *Nat. Commun.* 5, 4163 (2014).
- Zhang, W. et al. The interfacial zone in thin polymer films and around nanoparticles in polymer nanocomposites. J. Chem. Phys. 151, 124705 (2019).
- Panagopoulou, A., Rodríguez-Tinoco, C., White, R. P., Lipson, J. E. & Napolitano, S. Substrate roughness speeds up segmental dynamics of thin polymer films. *Phys. Rev. Lett.* **124**, 027802 (2020).
- Beena Unni, A., Winkler, R., Duarte, D. M., Chat, K. & Adrjanowicz, K. Influence of surface roughness on the dynamics and crystallization of vapor-deposited thin films. *J. Phys. Chem. B* 126, 8072–8079 (2022).
- 57. Chen, Z. & Richert, R. Dynamics of glass-forming liquids. xv. dynamical features of molecular liquids that form ultra-stable glasses by vapor deposition. *J. Chem. Phys.* **135**, 124515 (2011).
- Thompson, A. P. et al. LAMMPS a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comp. Phys. Comm.* 271, 108171 (2022).
- Stukowski, A. Visualization and analysis of atomistic simulation data with ovito-the open visualization tool. *Model. Simul. Mater. Sci. Eng.* 18, 015012 (2009).

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# Author contributions

J.R.-F. and A.G.: methodology (equal); investigation (equal); data curation (equal); formal analysis (equal); validation (equal); writing–original draft (equal); visualization (equal). A.G.: conceptualization; funding acquisition; project administration; resources; supervision.

# **Competing interests**

The authors declare no competing interests.

# **Additional information**

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