Microscopic description of yielding in glass by persistent homology

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The microscopic structural change in glass during yield is studied. Glassy solids exhibit a characteristic stress–strain curve. The shear stress for a small shear strain is almost proportional to the shear strain (linear regime); however, after yielding, the shear stress fluctuates around a finite constant value for a large shear strain (plateau regime). We use a persistence diagram to evaluate the relation between qualitatively different mechanical responses and microscopic atomistic structures. This diagram evaluates the robustness of holes defined by persistent homology. We investigate the relation between robust holes and the stress–strain curve for the configuration obtained through a molecular dynamics simulation. We show that the number of robust holes decreases through yielding and approaches that of the inherent structure of the liquid state with increasing shear. This work reveals the crucial roles of robust holes in yielding and provides an interpretation based on geometry.

I. INTRODUCTION

In principle, mechanical properties are explained through the geometric features embedded in an atomistic configuration based on statistical mechanics. For example, the compressibility of a simple liquid is represented via its radial distribution function (RDF) \[1\] and the elastic properties of a crystalline solid are described by its microscopic periodicity (i.e., long-range order (LRO)) \[2\]. However, glasses lack such an evident geometric feature; hence, introducing appropriate quantities that characterize the glassy structure is difficult, and its relation to mechanical properties is unclear. We discuss herein the relation between structural change and yielding in glass.

In glasses, an intriguing non-linear trend is observed in the stress–strain curve during shear deformation even when the particle density profile is uniform; thus, no macroscopic rupture occurs. Stress is linearly dependent on strain (linear regime) for the small-strain regime, while it shows a plateau with fluctuations (plateau regime) for the large-strain regime. The stress–strain curve in the intermediate regime that connects these two regimes is dependent on the cooling rate for creating glass from the liquid state \[3, 4\]. Glass exhibits yielding when it is created at a sufficiently low cooling rate. Namely, shear stress reaches a maximum, decreases, then converges to a constant value in the plateau regime as strain increases (Fig. 2). The decrease in stress reduces as the cooling rate increases.

To date, several studies have been performed to explain these qualitatively different mechanical responses before and after yield based on embedded atomistic structures \[3, 5–7\]. However, it has been also argued that there is no structural difference before and after yield \[8\]. Thus, the existence of a close relationship between the macroscopic responses and the microscopic structures is still a matter of debate.

Conventionally, the characterization of the atomistic structures of glasses has been developed based on the liquid or crystalline state. In this first case, indicators for multi-atom correlations are introduced as an extension of a liquid’s short-range order, such as the RDF and the structure factor \[9–12\], which are originally used to characterize a uniform and isotropic geometry in the liquid. In the second case, several local crystalline orders known as Steinhardt–Nelson order parameters \[13\] or bond and dihedral angle \[9, 10\] are introduced to describe the distortions from crystalline structures. Another approach has been proposed based on network topology without referring to liquid or crystal structures. This method is particularly useful for characterizing the structures of covalent glass \[14\] or a network liquid \[15\]. These structures are composed of numerous, but a finite number of atoms; thus, they are different from nearest neighbor pairs and the LRO associated with an infinite number of atoms.

In recent years, persistent homology (PH) \[16, 17\] has been found to characterize multi-atom structures, referred to as medium-range order structures, of glass in a unified manner \[16, 17\]. In this method, PH provides a continuous quantity for each local atomistic structure “hole” to describe robustness with respect to the noise in data (see details in Sec. II). As a result, we can distinguish whether holes change from robust to noisy (less robust) or vice versa during deformation. Furthermore, we can calculate robustness according to the types of holes. This enables us to restrict ourselves to the structural changes in robust holes, which can contribute to the qualitative difference observed in a mechanical response.
provide two parameters that represent the size of each hole.

PH is visualized by the persistence diagram (PD), which is a two-dimensional scatter plot of holes. The input of PD is given by a pair of sets $A = (Q, R)$. One of the pair is a set of atomic coordinates, $Q = (r_1, r_2, ..., r_N)$, which corresponds to the point cloud. Here, $r_i \in \mathbb{R}^3$ is the three-dimensional position of the $i$-th atom. In addition to the point cloud, the other is a set of input radii, $R = (R_1, ..., R_N)$, also considered as extra input data.

First, we assign a ball for each atom, $B_i(\alpha)$. The ball is defined by

$$B_i(\alpha) := \{ r \in \mathbb{R}^3 : |r - r_i| \leq r_i(\alpha) \},$$

where the radius $r_i(\alpha)$ is given by

$$r_i(\alpha) = \sqrt{R_i^2 + \alpha}.$$  

Parameter $\alpha$ determines the radius of each ball. We study the topological features of the union of balls $B(\alpha) = \bigcup_{i=1}^{N} B_i(\alpha)$ for each $\alpha$ (see upper Fig. 1). Technically, instead of considering $B(\alpha)$ itself, the homotopy-equivalent simplicial complex is considered because it is computationally easy to handle (see lower Fig. 1). The $k$-th $n$-dimensional hole $c_{n,k}$ will appear at $\alpha = b_{n,k}$ (“birth”) as $\alpha$ increases from $-\min_i(R_i)^2$. The hole persists for a certain interval $\alpha \in [b_{n,k}, d_{n,k}]$, and finally disappears at $\alpha = d_{n,k}$ (“death”) (see Fig. 1(d)). The $n$-dimensional PD denoted by PD$_n$ is a collection of pairs $\text{PD}_n = \{(b_{n,k}, d_{n,k})\}_k$, which provides a two-dimensional scatter plot.

The PD has three properties. First, for each hole, $c_{n,k}$, the inequality $b_{n,k} \leq d_{n,k}$ is satisfied because birth precedes death. Therefore, the point in PD only appears above diagonal. Second, the PD provides a geometric criterion to select the shape of holes in homology. For example, if every input radius is zero (i.e. $R_i = 0$), an obtuse triangle does not appear as a one-dimensional hole (ring) in PD$_1$, while the hole for an acute-angled triangle is detected in PD$_1$, which persists for a finite interval $[b_{1,k}, d_{1,k}]$. A right triangle is situated in between, and the hole is placed on the diagonal, $b_{1,k} = d_{1,k}$. Finally, the degree of persistence for $c_{n,k}$ is parameterized by $\ell_{n,k} \equiv d_{n,k} - b_{n,k} > 0$, which is the so-called “life”. This quantity represents the robustness to satisfy the criterion against a disturbance of the input data. Suppose that the input data are randomly modulated by a numerical noise. Then, $b_{n,k}$ and $d_{n,k}$ continuously change with the modulation of the input data; hence, a hole $c_{n,k}$ with a small $\ell_{n,k}$ tends to reach the diagonal and breaks the criterion and vice versa. In this sense, the quantity $\ell_{n,k}$ represents a robustness of the hole for the criterion in PH.

When the configuration in the MD simulation is dealt, the disturbance on the input data might be realized by thermal fluctuations or external perturbation. Therefore, it is natural to expect that the robustness introduced
earlier describes the robustness against the physical perturbation. We assume the relation between the robustness mathematically introduced by PH and the robustness of atomistic structures in our analysis and verify the assumption compared with the MD simulation results. This is the key assumption in our PH analysis when we apply it to a realistic material system. Furthermore, for a system with a macroscopically uniform and a microscopically disorder structure, statistically similar holes will appear in the given input $A$; hence, instead of scatter plots, we use the distribution of $PD_n$ as a function of birth and death $(b, d)$:

$$PD_n(b, d) = \sum_k \delta(b - b_{n,k})\delta(d - d_{n,k})$$  \hspace{1cm} (3)

and call it simply the $n$-dimensional PD \[10\]. Hereinafter, we will only use two-dimensional PDs and set the input radii to zero (i.e. $R_i = 0$).

III. MODEL AND SIMULATION DETAILS

We perform three-dimensional MD simulations of a glass-forming system referred to as the KA model. This model consists of two types of particles (80% large (A) and 20% small (B) particles). The total number of particles is set as $N = 32000$. Each particle interacts via the Lennard–Jones potential,

$$U_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6,$$  \hspace{1cm} (4)

with $\alpha, \beta \in \{A, B\}$ for $r < r_c$, where $r$ is the distance between the particles of types $\alpha$ and $\beta$. Here, $\epsilon_{\alpha\beta}$ describes the interaction strength between the particles, while $\sigma_{\alpha\beta}$ denotes the length scale. Parameters $\epsilon_{AA}$, $\sigma_{AA}$, and $m_A$ define the reduced units for energy, length, and mass, respectively. Thus, the time unit is $\sigma_{AA}^2/m_A/\epsilon_{AA}$. In this unit, the time step size $\Delta t$ is selected as 0.005. We select $\epsilon_{AB} = 1.5\epsilon_{AA}$, $\epsilon_{BB} = 0.5\epsilon_{AA}$, $\sigma_{AB} = 0.8\sigma_{AA}$, $\sigma_{BB} = 0.88\sigma_{AA}$, and $m_B = m_A$. The interactions are neglected beyond cutoff $r_c = 2.5\sigma_{AA}$. A constant number density of $\rho = 1.2$ and a periodic boundary condition are imposed on the system with a system size of $L_x = L_y = L_z = 29.876$ (cubic box) to eliminate the surface effect and the macroscopic rupture. All simulations are performed using LAMMPS.

This model is based on metallic glass (Ni$_{80}$P$_{20}$) and exhibits glass transition at a temperature of $T_g \simeq 0.435$ \[18\]. Its dynamical \[18\] 20\] 21\] and static \[4\] 22\] properties have been extensively studied.

We prepare the glassy configurations as follows: as equilibration, we perform a 10$^6$-step NVT-MD simulation with temperature $T_1 = 1.0$ (liquid) from an appropriate initial configuration, such as a face-centered cubic lattice, or a random configuration. We use the final configuration in the MD as an equilibrium liquid configuration. We obtain 20 statistically independent liquid configurations by repeatedly performing this process. From each liquid configuration, we then quench the system by changing the thermostat temperature at a cooling rate of $T = 10^{-3}$. After reaching an almost zero temperature, static relaxation is applied using the conjugate gradient method to bring each system to mechanical equilibrium.

After the quench, we apply shear using volume-conserving strain deformation with an athermal quasistatic method \[4\] 22\]. In this method, plastic deformation is imposed on the system by iterating the two following steps: First, we deform the simulation box by small amounts while keeping the fractional coordinates of the particles fixed. The position of each particle, $r = (x, y, z)$, is transformed into $r' = (x - \Delta \gamma y, y, z)$, where $\Delta \gamma = 10^{-5}$. We minimize potential energy with respect to the fractional coordinates using the conjugate gradient method. The intermittent minimization steps essentially couple the system to a heat bath at zero temperature; thus, the aging effect is prevented during deformation. The solid line in Fig. 2 depicts the stress–strain curve for glass. The line exhibits the two qualitatively different regimes before and after yield (i.e., the linear and plateau regimes). Stress $\tau$ is defined by the average of the virial for individual particles, while strain $\gamma$ is the product of the number of deformation steps and $\Delta \gamma$.

For the stress state, the linear deformation provides a trivial contribution to the structural change in addition to the plastic deformation during the sheared process. The linear deformation is the response of the configuration to the finite shear stress, and its effect appears as an anisotropy of the configuration. We calculate a pair

![Figure 2](https://example.com/figure2.png)
distribution function to demonstrate this aspect:

\[
C(X, Y, Z) = \frac{1}{V\Delta^3} \sum_{i=1}^{N} \sum_{j(i \neq j)} \delta(x - x_{ji})\delta(y - y_{ji})\delta(z - z_{ji}),
\]

where \((x_{ji}, y_{ji}, z_{ji})\) is a relative coordinate from the \(i\)th particle to the \(j\)th particle, and \(V\) is the volume of the system (i.e. \(V = L_xL_yL_z\)). We set \(\Delta = 0.1\sigma_{AA}\). In Fig. 3 (a), we plot the pair distribution functions, \(C(X, X, 0)\) and \(C(X, -X, 0)\), as a function of \(X\). The differences of the two functions show that the configuration is anisotropic in the stress state.

We create from the stress states no-stress states, from which we extract the structural change caused by the plastic deformation. We reset the shear stress to zero by decreasing the shear strain in steps while minimizing the energy (see the gray line in Fig. 2). We then obtain the configuration whose shear stress is released to zero. Fig. 3 (b) plots the pair distribution functions, \(C(X, X, 0)\) and \(C(X, -X, 0)\), for the no-stress state. The two functions are almost the same, showing that the configuration is isotropic, and no contribution of the linear deformation is found. Thus, we can study only the structural change caused by the plastic deformation in the no-stress state.

In this paper, we refer to the configuration of the no-stress state as the “configuration of \(\gamma\)”, where \(\gamma\) is the value before decreasing the shear strain. Based on the stress–strain curve shown in Fig. 2 (solid line), we consider the configurations of \(\gamma = 0, 0.02, 0.04, 0.06\) in the linear regime and the configurations of \(\gamma = 0.34, 0.36, 0.38, 0.4\) in the plateau regime.

The inherent structure of the liquid state is analyzed for comparison. We obtain the state quenched from the liquid state at \(T = 1.0\) through energy minimization via the conjugate gradient method. We then perform the same deformation process. We plot the stress–strain curve for the inherent structure in Fig. 2 by the dashed line. The stress–strain curve shows the linear and plateau regimes, but the decrease in stress that occurs during yielding in the intermediate regime is not observed.

A total of 20 independent samples are prepared for the glassy and inherent structures. The shear responses of each configuration are also investigated. We show the average of the PDs (except for Fig. 4) and the RDFs for the configuration of \(\gamma\) over 20 independent samples.

IV. STRUCTURAL CHANGES BEFORE AND AFTER YIELD

This section describes the structural change in holes between the linear and plateau regimes for glass and compares it with the inherent structure.

First, we introduce a method of interpreting the geometric feature of glass observed in the PD for the configuration of \(\gamma = 0\). The following two types of configurations are considered: the configuration with all particles (Fig. 4 (a) inset) and the configuration with only A particles (Fig. 4 (b) inset). The latter configuration is simply obtained by removing all B particles from the former configuration. In the latter configuration, the space occupied by a B particle appears as a hole. Therefore, the PD detects the geometric feature of the cage of the B particle in addition to the holes that the system originally holds.

In Fig. 4 (b), an extra peak is observed in the upper region in addition to the peak in the lower region, which is common in Figs. 4 (a) and (b). Consequently, the extra peak and the common peak represent the cage of each B particle and the vacancy among A particles, respectively. In this manner, we can systematically distinguish the holes. Note that we extract the geometric feature of the cage of a B particle by consid-
erating the configuration for only A particles. This is a typical property of the PD because it is a tool used to characterize the holes. The PD for the latter configuration (only A particles) shows common and extra peaks; hence, considering it for the hole characterization is sufficient. Hereinafter, we only investigate the PDs for the latter configuration and focus on these two peaks. An extra peak at \((b, d) = (0.68, 0.88)\) and a common peak at \((b, d) = (0.67, 0.76)\). The extra peak corresponds to a cluster structure referred to as solute-centered polyhedra \([11, 12]\). The P-centered tricapped trigonal prism is the most frequent structural unit in Ni\(_{80}\)P\(_{20}\) \([24]\) even though various types of structures appear in contrast to crystals \([12, 24]\). This signature is observed in the PD (upper region of Fig. 4 (b)) as a broad distribution, particularly along the horizontal axis.

Based on the above-mentioned interpretation, we move to the argument of the dependence on \(\gamma\) by focusing on these two peaks. We calculate the PDs for the configuration of \(\gamma\) for each \(\gamma\) (see Sec. III). According to the series of PDs, we find no clear difference within the linear and plateau regimes, but remarkable differences between the two regimes.

Let us consider the extra peak corresponding to the cage of a B particle. As seen in Fig. 4 (b), we introduce a box in the upper region, which is specified by a rectangular region, \((b, d) \in [0.63, 0.82] \times [0.85, 0.93]\). The histogram of life (see Fig. 4 (b)) for the points within the box is plotted in Fig. 5 (a) for the linear (blue lines) and plateau (red lines) regimes. We find no difference within the error in each regime, indicating no structural changes within the regimes. However, clear differences are observed between the two regimes, namely, the height of the peak around \(l = 0.2\) decreases, and the number of holes with a smaller \(l\) increases. This result shows that the holes for the cage of a B particle become less robust from the linear regime to the plateau regime. For comparison, we create a histogram of the life for the configuration of \(\gamma = 0\) for the inherent structures, which are considerably close to the structures for glass in the plateau regime. A qualitatively similar behavior is observed for the common peak (Fig. 5 (b)). We introduce a box, \(1.38 \leq b + d \leq 1.48\) and \(0.04 \leq d - b \leq 0.15\), in Fig. 5 (b) and plot the histograms of life for the points within the box.

We compare the dependences of the PDs on \(\gamma\) using partial RDFs. As discussed in [3], the structural change in the cage of a B particle is observed in the partial RDF between B particles, \(g_{BB}(r)\). In Fig. 6 (c), the height of the first peak increases from the linear regime to the plateau regime, while that of the second peak slightly decreases. This observation combined with that of the PD indicates that the direct contact between the B particles is suppressed in the linear regime because of the formation of solute-centered polyhedra \([12]\). Moreover, the
robust local structures are broken through the shearing process. On the contrary, we do not find a clear difference in \( g_{AB}(r) \). In contrast to the cages, the structural change in the vacancies is not described by the partial RDF between the \( A \) particles, \( g_{AA}(r) \). Thus, an indicator for higher-order correlations is necessary for detecting the changes in the structures composed of the \( A \) particles.

Finally, we study how the robust structures are broken through the shearing process. We restrict ourselves to the holes with \( l > 0.17 \) in the upper region of Fig. 4(b) and count the number of holes to provide a quantitative description. This corresponds to the summation of the histogram for \( l > 0.17 \) in Fig. 5(a).

Fig. 7 represents the number of the robust holes, \( N_r \), as a function of shear strain \( \gamma \) for glass (solid line) and the inherent structure (dotted line). For glass, \( N_r \) is almost unchanged until around \( \gamma = 0.1 \), at which shear stress starts decreasing (see Fig. 2). However, \( N_r \) decreases during yielding (in the interval marked by the stripe in Fig. 2 and 7), which clearly shows the close relation between the macroscopic yield phenomenon and the microscopic structural changes from robust holes to noisy holes. In contrast, for the inherent structure, \( N_r \) is almost independent of \( \gamma \) and close to that for glass at a large shear strain. This is referred to as “rejuvenation”, and it was reported in [3] by the observation of potential energy and the partial RDF. We can provide herein an additional perspective from the geometric point of view (i.e., robust local structures are created during cooling and broken by applying a large shear on the system).

V. CONCLUSION

This work investigated the structural changes in glass during yielding using a PD, which characterized the holes embedded in atomistic configurations (Fig. 1). We discussed two types of holes in the PD corresponding to the cages for minor particles (extra peak in Fig. 4(b)) and the vacancies for major particles (common peaks in Figs. 4(a) and 4(b)).

The histograms of the holes for each peak as a function of “life” \( l \) in the PD clearly showed the difference between the configurations in the linear and plateau regimes in
the stress–strain curve (Fig. 2). An apparent decrease was particularly observed in the number of robust holes, which corresponded to the holes with a large \( l \) (Fig. 5). In contrast to these differences, the PDs did not show significant changes within each regime.

Moreover, we discussed the shear–strain dependence of \( N_r \) (i.e., the number of the robust holes around each peak). The decrease in \( N_r \) was closely related to the yield (solid line in Fig. 7), and \( N_r \) approached the value for the inherent structure, which was created without sufficient time to develop the structural order. These results indicated that the geometric object (i.e., robust holes) breaks during yield. This interpretation is consistent with the observation that the inherent structures do not show a shear–strain dependence (dashed line in Fig. 7).

The application of our method to other models of glass is an intriguing problem to be studied in the future. We focused herein only on the KA model. The observations of this study are consistent with those of the other systems, where the degree of a cluster structure decreases under shear [7]. Thus, we conclude that the lack of a structural difference between the linear and plateau regimes in the KA model [7] is caused by the failure of the method to characterize the cluster structure. The unified method of characterizing various types of cluster structures in terms of the robustness of the holes is a highly promising direction to find universal relations between mechanical response and microscopic structures.

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[25] To be precise, another peak exists aside from the diagonal. This peak is extremely close to the diagonal and also observed in the PD of the liquid configuration [16]. Therefore, we regard it as a characteristic of the short-range order observed in liquids and neglect it.
[26] We focus only on the peak in the upper region, but the qualitatively same behavior is observed for the peak in the lower region of Fig 4(b) (not shown).