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Decoupling between thermodynamics and dynamics during rejuvenation in colloidal glasses*

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Abstract. We rejuvenate well-aged quasi-2D binary colloidal glasses by thermal cycling, and systematically measure both the statistical responses and particle-level structural evolutions during rejuvenation. While the elastic moduli and boson peak are continuously rejuvenated with the increasing number of cycles, the mean square displacement (MSD) fluctuates significantly between the different groups of thermal cycles. The decoupling between the thermodynamical and dynamical evolutions suggests different microscopic origins for the different bulk properties of glasses. We find that a small fraction of structural rearrangements triggered by thermal cycling can alter the *whole* elastic continuum and lead to the significant thermodynamic rejuvenation, while *localized* defects can be activated and deactivated at the positions close to the rearrangements with significantly high mobility change and hence result in the fluctuated dynamics even with only about 10% of the particles as fast regions.



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Our results offer a comprehensive picture for the microscopic mechanisms underlying bulk glass rejuvenation, which can be readily used to refine glass properties or to formulate further statistical theories in glassy systems.

Keywords: colloidal glasses, glasses (colloidal, polymer, etc), defects, dynamical heterogeneities

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1. Introduction

As a typical non-equilibrium system, glasses relax or age. During the physical aging of glassy systems, a continuous evolution of thermodynamic states towards equilibrium is coupled with the gradual slowdown of dynamics [1-5]. Intriguingly, external stimulations such as thermal cycling and mechanical stimuli are found to partially recover or 'rejuvenate' the aged glass properties in bulk glasses such as metallic glasses and polymer glasses [6-12], in colloidal glasses [13-17], in spin glasses [18], and in computer simulations [19-22]. The studies of glass rejuvenation open a door for practically tuning the bulk properties of glasses and for understanding the physics underlying different glass properties. However, the microscopic mechanisms underlying rejuvenation remain unclear and a number of anomalies are hard to explain. For example, while mechanical deformations can lead to a drastic increase of the relaxation dynamics of polymer glasses, some parameters concerning thermodynamic states such as equilibration time and volume recovery show no detectable change [7]; a continued thermal cycling leads to an out-sync evolution among the reversible heat of relaxation, saturated microhardness reduction, and the monotonically strengthened plasticity in metallic glasses [6].

Rejuvenation is related to a general question of how glasses respond to external stimulations. Unlike the uniform atomic environment in a single crystal, each atom in glasses has a unique local structure and responds differently even to uniform perturbations. Thus, it requires the particle-level information as well as macroscopic measurements of statistical properties to understand the mechanisms underlying rejuvenation. Conventionally, bulk glass experiments measure macroscopic properties without particle-level details, whereas local measurements of colloidal particle motions do not directly access the macroscopic properties of thermodynamic states. However, the recently-developed covariance matrix method enables researchers to investigate bulk thermodynamic properties such as boson peak and elastic moduli in colloidal systems [23–28]. With thermal cycling and the covariance matrix method, we measure evolutions of both the local particle motions and statistical properties (elastic moduli boson peak, and MSD plateau) in quasi-2D binary colloidal glasses during thermal cycling. Our results demonstrate a decoupling of the evolution of thermodynamics and that of dynamics during rejuvenation. While both evolutions are induced by local rearrangements, the decoupling suggests that different structural signatures dominate different macroscopic perspectives of glasses. We find that the stiffness undermined by structural rearrangements mainly contributes to the increased plasticity and the intensified boson peak; on the other hand, the activation of localized fast regions originating from emerging high local structural entropy dominates the fluctuated MSD. Our results unveil the particle-level mechanisms underlying the evolutions of the thermodynamic and dynamic properties during rejuvenation in glassy systems.

2. Experimental procedure

2.1. Sample preparation

Two types of thermo-sensitive poly-N-isopropylacrylamide (PNIPAM) particles with different diameters were mixed to prepare colloidal glass samples [29, 30]. The particle diameters were measured to be 1.1 and 1.4 μ m at 22 °C by dynamical light scattering. A 1:1 binary mixture of the two types of particles was sufficient to avoid crystallization. A dense monolayer of the mixture between two coverslips was hermetically sealed using optical glue (Norland 65) to form quasi-2D colloidal glasses. The samples were well aged on the microscope stage for 3h before further stimulations. There were ~3100 particles within the image frame. We used standard bright-field microscopy at 60 fps for the duration of the experiment. The trajectory of each particle was extracted using particle tracking techniques [31, 32].

2.2. Thermal cycling

A small amount of non-fluorescent dye (Chromatch-Chromatint black 2232 liquid, 0.2% by volume) was mixed with the colloidal suspension to absorb incident mercury light and to increase the temperature of the samples by about 0.2K after the mercury lamp was turned on [3, 32–34]. The dye is mixed with water at a molecular level and thus the heating provided by the mercury light is uniform in a region much larger than

the field of view [32]. Before the optical heating, the packing fraction at the ambient temperature (22 $^{\circ}$ C) was about 0.88 and an increase of 0.2K slightly changes the particle diameters by 0.01 microns, as measured by dynamical light scattering and the packing fraction to 0.87, which is still above the jamming packing fraction (~ 0.85). The sample reached new thermal equilibrium in less than 1s after the mercury lamp was turned on, and quickly recovered to the original temperature with original packing fraction when the mercury lamp was turned off. Thermal cycling was achieved by turning the mercury lamp on and off cyclically, similar to the non-destructive thermal cycling in bulk experiments [6]. After several trials, we found that a sequence of short thermal cycles was more efficient than a single cycle to rejuvenate the aged samples. Thus we used a group of ten successive short thermal cycles to stimulate the colloidal glasses and measure the evolution of properties before and after the group of cycles as in figure 1. Each cycle lasted for 40s with 20s light on and 20s light off. To ensure a stable configuration without rearrangements, the data were obtained 400s after a group of cycles. Another nine groups of such thermal cycles were performed for the same sample and the data in the stable configuration after each group were recorded. The realization of glass rejuvenation requires proper stimulation amplitudes and well-aged initial states [15, 19], and can be technically complicated. Here we focus on the microscopic mechanisms of the rejuvenation, rather than best conditions for rejuvenation.

2.3. Covariance matrix

We analyze the thermodynamic properties of solid glass by extracting the vibrational information of the colloidal systems with the covariance matrix methods [24–27]. Due to the damping by the solvent in colloidal solutions, the phonon modes of colloidal glasses cannot be directly obtained by decomposing the motions of particles to different frequencies. We then introduce a shadow system of particles equilibrated in the same configuration with the same interactions as the colloids. Under the assumption of harmonic approximation and equipartition, this shadow system should in principle have the same eigen spectrum as the real damped colloidal systems [23]. The shadow system allows direct comparison between the thermodynamic properties of damped colloidal solid and those of disordered atomic or molecular glasses [24].

A 2N-component displacements vector $u_i(t)$ is defined to characterize all N particles' x and y displacements from their average positions. The displacement covariance matrix $C_{ij} = \langle u_i(t)u_j(t) \rangle_t$, where i, j run over all the 2N degrees of freedom and $\langle \cdot \rangle_t$ is the time average. At high packing, the dynamics around the metastable states in glasses is approximately harmonic. Under the harmonic approximation and in thermal equilibrium, C_{ij} is directly related to the dynamical matrix of the shadow system $D_{ij} = k_{\rm B}T C_{ij}^{-1} / \sqrt{m_i m_j}$, where m_i is the mass of particle *i*. The eigenvectors $\overrightarrow{e_{n,j}}$ of D_{ij} are thus identical to those of C_{ij} , and D_{ij} 's eigenvalues are simply inversely proportional to the eigenvalues λ_n of C_{ij} . The polarization vector of mode *n* is defined as $\overrightarrow{P_n} = \overrightarrow{e_{n,j=1}}, \overrightarrow{e_{n,j=2}}, \ldots, \overrightarrow{e_{n,j=2N}}$. The eigenfrequencies ω_n is extracted by $\omega_n^2 = \frac{k_{\rm B}T}{\sqrt{m_i m_j \lambda_n}}$, and the density of states $D(\omega)$ is defined as $D(\omega) = \langle \sum_i \delta(\omega - \omega_i) \rangle / N$.

There is no perfect plane wave, meaning that wave vector q is no longer a good state parameter for modes, in glasses. Therefore, spectral functions are needed to measure the dispersion relation in glasses. The Fourier decomposition of the eigenmodes yields



Figure 1. Ten groups of thermal cycles were performed. Within each group, there were ten successive short thermal cycles. For each cycle, we turned on the mercury lamp for 20s to increase the temperature by about 0.2K and turned off the mercury lamp for 20s to recover the temperature to its original value. Between two groups of thermal cycles, the samples were relaxed for 400s to ensure a stable configuration without rearrangements followed by the data measurements in 200s.

two spectral functions $f_{\rm T}$ and $f_{\rm L}$. $f_{\rm T}$ corresponds to the transverse components for each mode of frequency ω as a function of wave-vector magnitude q and $f_{\rm L}$ corresponds to the longitudinal counterpart.

$$\begin{aligned} f_{\mathrm{T}} & (q,\omega) = \left\langle \left| \sum_{n} \vec{q} \times \overrightarrow{P_{n}} \left(\omega \right) \exp(\mathrm{i}\vec{q} \cdot \vec{r_{n}}) \right| \right\rangle, \\ f_{\mathrm{T}} & (q,\omega) = \left\langle \left| \sum_{n} \vec{q} \cdot \overrightarrow{P_{n}} \left(\omega \right) \exp(\mathrm{i}\vec{q} \cdot \vec{r_{n}}) \right| \right\rangle, \end{aligned}$$

where \vec{r}_n stands for the averaged position of every particle, and the brackets indicate a direction average over many (>100) directions of \vec{q} . The maxima of the spectral functions are the phonon wave vector constituting the dispersion relation. Following previous practice [27], we fit $f_{\rm T,L}$ (q,ω) to a Gaussian to obtain the maximum $q_{\rm max}$ more cleanly for each mode. In the long-wavelength limit, the dispersion curve is linear. The longitudinal and transverse sound velocities are then defined as: $C_{\rm T,L} = \lim_{q \to 0} \partial \omega / \partial q$. The longitudinal modulus, $M = \rho_{2D}c_l^2$, the shear modulus $G = \rho_{2D}c_t^2$, and the bulk modulus B = M - G, where $\rho_{2D} = \rho h$, ρ is very close to the density of water (1g cm⁻³) since 95% of particles are water and $h \approx 1.4 \times 10^{-6}$ m is the height of the sample cell.

3. Experimental results

3.1. Thermodynamic and mechanical rejuvenation

Figure 2(a) shows the distribution of eigenfrequencies $D(\omega)$ (rescaled by ω^{d-1} , which corresponds to the Debye behavior in crystals) for samples from different groups of thermal cycles, where dimension d = 2 in our system. For each curve, the excess vibrational density of states compared to Debye model is observed as a boson peak [24]. We extract the maximum of the $D(\omega)/\omega$ as the boson peak intensity I^* . As in figure 2(b), I^* tends to increase with the number of thermal groups with few exceptions. This tendency is contrary to the decaying boson peak intensity during aging [35] and is suggestive of the occurrence of thermodynamic rejuvenation from thermal cycles. After significant rejuvenation, the samples are at high energy states and have the possibility to age again, which causes the small drop of I^* after six groups of thermal cycles.

Figure 2(c) plots how bulk modulus and shear modulus evolve with ten groups of thermal cycling. Elastic moduli, especially the bulk modulus, show a roughly monotonic decrease. This decrease suggests that thermal cycling tends to continuously soften the sample with gradually refined plasticity. After ten groups of thermal cycles, the shear (bulk) modulus decreases by more than 40% (30%). This tendency is the reversal of hardening during aging [17, 20, 36–38] and is a signature of mechanical rejuvenation. The elastic moduli also reflect the energy states of the sample and negatively correlate with system energy [22]. The decline in the elastic moduli thus indicates elevated energy states in our systems which is a direct evidence of thermodynamic rejuvenation in the framework of energy landscapes [19].

The coincidence of boson peak intensity increase and elastic moduli decline during thermal cycling indicates a possible correlation between boson peak and elastic moduli. Following previous simulations [39], we fit the I^* and inverse B(G) with an affine function $I^* = a \times (1/G + 1/B) + b$ as the red line in figure 2(d). The high coefficient of determination R2 for the linear fitting demonstrates a linear relation between boson peak intensity and inverse elastic moduli, which indicates that evolutions of the boson peak can be characterized by the variations of the elastic continuum. We note that $b = 2.5 \times 10^{-6} \text{ s}^2/\text{rad}^2$ is not negligible compared to the averaged $I^* = 5 \times 10^{-6} \text{ s}^2/\text{rad}^2$, which can be the result of frictions in experimental systems making the measured elastic moduli slightly larger [27], and is slightly different from the proportional relationship in the simulation of Shintani and Tanaka [39]. Our result is the first experimental evidence of the linearity between the boson peak intensity and inverse bulk and shear modulus.

3.2. Dynamic rejuvenation

Before the displacement covariance matrix method is proposed, accelerated dynamics was considered as a main signature of rejuvenation in colloidal glass [13–17]. Figure 3(a) plots the MSD for the samples after 0 to 10 groups of thermal cycles. Each MSD curve reaches its plateau after around 90 s. In figure 3(b), we summarize the MSD plateau as a function of the number of groups of thermal cycles. Differing from the monotonic evolution of boson peak intensity and elastic moduli in figure 2, the MSD plateau fluctuate significantly in different group of thermal cycles. It increases abruptly after the first group of thermal cycling is applied, and almost recovers to its original state with a small value after the second thermal group; the plateau maintains its small value until the seventh groups of thermal cycles.

3.3. Microscopic origin of thermodynamic rejuvenation

In figures 2 and 3, the thermodynamics and dynamics show distinct dependence on the thermal groups. This distinction is suggestive of fundamentally different microscopic mechanisms underlying the thermodynamic and dynamic rejuvenations. Local



Figure 2. (a) Boson peaks of colloidal samples in different groups of thermal cycles. (b) Boson peak intensity (I^*) as a function of the number of groups of thermal cycling. (c) Evolution of bulk (B) modulus and shear (G) modulus during thermal cycling. (d) Simple linear relation correlating the boson peak intensity to inverse elastic moduli.

particle rearrangements, the elementary process of glass deformation and glass relaxation, are believed to be the microscopic culprit of macroscopic rejuvenation [6, 40]. We thus extract the rearrangements induced by thermal cycling and investigate how these rearrangements alter the local properties and hence the macroscopic properties. Local rearrangements are defined as particles that lose their nearest neighbors which are identified by radical Voronoi tessellation [34]. Clusters with less than five neighboring particles are ignored [25]. We find that only $\sim 5\%$ of the particles are detected to have rearranged during a group of thermal cycles. It is an intriguing question as to how a small fraction of rearrangements leads to significant macroscopic rejuvenation such as $\sim 40\%$ decline of bulk modulus.

We use local stiffness, i.e. the local potential curvature, to characterize a particle's resistance to mechanical deformation. Local stiffness is defined as $K_{ii} = \sqrt{(K_{ii,x}^2 + K_{ii,y}^2)}$, where $K_{ii,x}$ and $K_{ii,y}$ are the diagonal elements in stiffness matrix $K_{ij} = D_{ij}\sqrt{m_i m_j}$ for particle *i* [41]. The K_{ii} averaged over all particles as a function of number of thermal groups is shown in figure 4(a) and the thermal cycle dependence of K_{ii} is very similar to those of elastic moduli (especially the bulk modulus) in figure 2(c), which suggests that K_{ii} is a rough measurement of particle-level modulus. Figure 4(b) plots the local stiffness change (colored contour) from the first group of thermal cycles as an example





Figure 3. (a) Mean square displacements (MSDs) from different groups of thermal cycles. The dash dot line indicates the time (96s) when we extract the MSD plateau value. (b) MSD plateau values as a function of the number of groups of thermal cycles. Dashed lines indicate two dynamic rejuvenation events where the MSD plateau value increases significantly from last group of thermal cycles.

of how local rearrangements (white dots) induced by thermal cycling alter the stiffness. Regions surrounding rearrangements tend to suffer from significant stiffness drop and the stiffness decrease can extend to a distance of several particles away from the rearrangement. We quantify the correlation between the rearrangements and the stiffness change by summarizing the average stiffness change from all ten groups of cycles as a function of the distance to the rearranging particles as shown in the inset of figure 4(a). Statistically, rearranging particles suffer from the most significant stiffness decrease with a functioning range over five particle diameters, suggesting that local rearrangements induced by thermal cycling are responsible for the softening of the elastic moduli and hence the mechanical rejuvenation.

In order to confirm the correlation between boson peak intensity and elastic moduli in figure 2(d) at a particle level, we calculate the boson peak intensity for a single particle $D_i(\omega_{\rm bp})$ and quantify its correlation with K_{ii} . $D_i(\omega_{\rm bp})$ is defined as $D_i(\omega_{\rm bp}) = \frac{1}{2\Delta\omega} \int_{\omega_{\rm bp}+\Delta\omega}^{\omega_{\rm bp}+\Delta\omega} D_i(\omega') d\omega'$ [39], where $\omega_{\rm bp}$ is the boson peak frequency, $D_i(\omega_j) = D(\omega_j) \frac{|e_{i,j}|^2/m_i}{\sum_i (|e_{i,j}|^2/m_i)}$ is the contribution to the vibrational density of states by particle *i*, and $2\Delta\omega$ corresponds to thirty vibrational modes around $\omega_{\rm bp}$. The rank of $D_i(\omega_j)$ is not sensitive to the number of modes chosen. Figure 5(a) plots the one-to-one scatter plot between $D_i(\omega_{\rm bp})$ and K_{ii} . Qualitatively, $D_i(\omega_{\rm bp})$ tends to drop with K_{ii} increasing. We use the Spearman rank correlation to assesses how well the K_{ii} monotonically depends on $D_i(\omega_{\rm bp})$. Spearman rank correlation is calculated by the linear correlation $\frac{\sum_{i=1}^{N} (A_i - \langle A \rangle)(B_i - \langle B \rangle)}{\sqrt{\sum_{i=1}^{N} (A_i - \langle A \rangle)^2} \sqrt{\sum_{i=1}^{N} (B_i - \langle B \rangle)^2}}$ between the rank values of two variables A and B, where A and B correspond to the ranks of $D_i(\omega_{\rm bp})$ and those of K_{ii} and $\langle \cdot \rangle$ denotes average over all particles in each cycle. The Spearman coefficient is about -0.7 regardless of the number of thermal groups as in figure 5(b). This strong negative correlation



Figure 4. (a) Averaged local stiffness as a function of number of thermal groups. Inset: stiffness change ΔK_{ii} as a function of the distance to a rearranging particle (red circles) and to a random particle (black squares). (b) Distributions of ΔK_{ii} (contour) and rearranging particles (white dots) induced by the first group of thermal cycles. The unit of ΔK_{ii} is $10^{14} k_{\rm B} T$ (/m) or 4.14×10^{-7} (N m⁻¹) which is the factor to transfer the units in pixels to physical units.

suggests that the high intensity of boson peak originates from softening of the elastic continuum with low local stiffness and justifies the linear relationship between boson peak intensity and inverse elastic moduli in figure 2(d) at a single-particle level.

3.4. Microscopic origin of dynamic rejuvenation

To investigate into the microscopic mechanisms of dynamic rejuvenation, we calculate the single-particle contribution to MSD, i.e. the local Debye-Waller factor α_i . α_i of particle *i* is defined as $\alpha_i = \langle [r_i(t) - r_i(0)]^2 \rangle_t$, where $r_i(t)$ is the position of particle *i* at time t and $\langle \cdot \rangle_t$ denotes the average within the duration where the MSD curve reaches its plateau. Figures 6(a)–(c) plots the spatial distribution of α_i before thermal cycling, after the first group of thermal cycles and after the second group of thermal cycles. Before thermal cycling, the α_i of more than 99% particles remains at values lower than $0.005 \,\mu \text{m}^2$ (figure 6(a)). The first group of thermal cycles triggers some particles rearranging in the field of view (white dots in figure 6(b)), followed by localized regions with α_i increasing to values readily above $0.005 \,\mu \text{m}^2$. The emerging high α_i regions are located right at the position where the largest rearrangements occur. Most particles' Debye-Waller factors follow a Gaussian-like distribution and those with Debye-Waller factors deviating from the distribution are defined as fast particles ($\sim 10\%$ fast particles in figure 6(b). Unlike the microscopic mechanisms of the thermodynamic rejuvenation where a small fraction ($\sim 5\%$) of rearrangements lead to a stiffness decline that spreads widely to the whole glass sample, the rearrangements create localized fast regions composed of a rather small fraction (10%) of particles by the rearranging regions. The α_i values of the emerging fast regions are much higher than the average and lead to the sharp MSD plateau increase in figure 3(b) even with only 10% of particles facilitated. After the second group of thermal cycles during which new rearrangements occur, the local fast regions disappear with the system MSD plateau recovering to a low value as in figure 6(c). We confirm that the dramatic MSD plateau jump after the seventh





Figure 5. Scatter plot (a) and cycle dependence of Spearman' rank correlation coefficient (b) between individual boson peak intensity and local stiffness.

groups of thermal cycles also result from an emergence of localized fast domains (figure 6(d)).

Next, the structural origin of the emergence of fast regions is explored. Previous simulations and colloidal experiments have demonstrated that the local structural entropy S_2 is highly correlated with particle-level dynamic during the structural relaxation of binary glasses [34, 47–49]. Here we show that this structure-dynamics correlation is still valid at particle level during the rejuvenation of glasses. $S_{2}^{i} = -\frac{1}{2}\sum_{\nu} \rho_{\nu} \int d\boldsymbol{r} \{ g_{i}^{\mu\nu}(\boldsymbol{r}) \ln g_{i}^{\mu\nu}(\boldsymbol{r}) - [g_{i}^{\mu\nu}(\boldsymbol{r}) - 1] \}, \text{ where } \nu, \mu \text{ denotes small or big particles, } \rho_{\nu} \text{ is the number density of } \nu \text{ particle, } g_{i}^{\mu\nu}(\boldsymbol{r}) \text{ is the pair correlation function }$ between particle *i* of type μ and the other particles of type ν . $g_i^{\mu\nu}(\boldsymbol{r})$ is time-averaged over the duration where the MSD curve reaches its plateau to remove short-time fluctuations. In our experiments, the integration is truncated at the third-neighbor shell to avoid the loss of a large fraction of particles due to the boundary effect [34]. S_2 is the entropy reduction induced by pair correlation (relative to ideal gas) and high S_2 values correspond to less correlated or fragile regions prone to relaxation and deformation in glasses. We measure the structural entropy in figures 6(e)-(h) after corresponding thermal groups as in figures 6(a)-(d). In figure 6(e), before thermal cycling almost all particles have S_2 values lower than -17 suggesting that all particles in the well-aged samples are highly correlated with few defects. However, after the first group of thermal cycles as in figure 6(f), a high- S_2 region underlying rearrangements emerges at the same spot as the high α_i domain (figure 6(b)). Another group of thermal cycles eliminates the high- S_2 region and the high- α_i domain. The emergence of fast regions after the seventh groups of thermal cycles is the result of the appearance of high S_2 -defects as well (figure 6(h)). The correspondence between the high- α_i domain in figures 6(a)-(d) and the high- S_2 region in figures 6(e)–(h) qualitatively suggests that the emergence of fast regions can be a result of the activation of high- S_2 regions from rearrangements.

The scatter plot between S_2 and α_i is plotted in figure 7(a). Below a threshold (close to $3 \times 10^{-3} \ \mu m$ [2]) the correlation between S_2 and α_i is weak and the one-to-one Spearman's rank correlation is only about 0.3 if all the ranges are considered (figure 7(b)). However, when α_i is above the threshold or particles with top 10% highest α_i values are considered, a particle with larger α_i value tends to have a smaller absolute



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Figure 6. Top: spatial distribution of local Debye–Waller factor α_i before thermal cycling (a), after the first group of thermal cycles (b), after the second group of thermal cycles (c), and after the seventh group of thermal cycles (d). Spatial distribution of structural entropy S_2 before thermal cycling (e), after the first group of thermal cycles (f), after the second group of thermal cycles (g), and after the seventh group of thermal cycles (g), and after the seventh group of thermal cycles (h). White dots are particles that rearrange after current group of thermal cycles.



Figure 7. Scatter plot (a) and cycle dependence of Spearman' rank correlation coefficient (b) between structural entropy S_2 and local Debye-Waller factor α .

 S_2 value or a larger S_2 value suggesting that only fast particles and high S_2 domains are correlated as in figure 6. Following previous studies on dynamic heterogeneity [42–46], we cluster particles with 10% highest α_i values as cooperative rearranging regions (CRRs) and emphasize the role of the local fast particles in the system dynamics. CRR clusters with fewer than five particles are ignored since separated mobile particles are highly constrained by neighboring particles that are less mobile and are not likely to dominate the overall dynamics. The total number of clustered particles in CRRs (black squares) is shown in figure 8 and evolves synchronously with the system MSD plateau (figure 3(b)). This synchronization suggests that the overall dynamics in our system is dominated by localized fast clusters whose emergence would lead to the macroscopic dynamical rejuvenation. We cluster the particles with 10% highest S_2 values



Figure 8. Number of clustered particles in CRRs and in high S_2 defects as a function of number of groups of thermal cycles. Vertical dashed lines indicate the two dynamical rejuvenation processes in figure 3(b).



Figure 9. (a) Local structure change induced by rearrangements (green contour) during the first group of thermal cycles. Blue particles are those suffering from significant stiffness decrease (by 150, the unit is 4.14×10^{-7} N m⁻¹); red particles are those with significant S_2 increase (by 5); magenta particles are those with significant stiffness decrease and S_2 increase. (b) Stiffness (blue) and S_2 (red) changes subtracted by their average values as a function of distance to a rearranging particle.

as structural defects by ignoring clusters with fewer than five particles. The number of particles contributing to the structural defects after different groups of thermal cycles is also summarized in figure 8. The size of high- S_2 defects and that of CRRs shows a similar dependence on the groups of thermal cycles. Besides the number synchronization, we confirm the correlation between CRRs and S_2 defects by calculating their cluster correlation [25, 50]. First, we define a binarized CRR vector **C** whose number of elements equals the total number of particles N. The component element equals unity if the corresponding particle belong to CRRs, otherwise, it equal zero. High- S_2 defects are characterized by the other binarized vector **S** with the same length as vector **C**. The elements of **S** are assigned with unity when the corresponding particles belong to the particular S_2 defects that have nonzero overlap with **C**. The cluster correlation between CRRs and S_2 defects is then quantified by $C_{\text{CRR, defect}} = \left[\frac{C \cdot S}{m} + \frac{(1-C) \cdot (1-S)}{N-m}\right]$, where m is the average number of non-zero elements in the two vectors. The cluster correlation averaged from samples after different number of thermal groups is calculated to be about 0.6. This high correlation suggests that local high- S_2 defects can be the structural origin of CRRs and be responsible for the macroscopic dynamical rejuvenation. Since significant S_2 -dynamic correlation is found in both thermal equilibrium systems and far-from-equilibrium systems [51], we speculate that a similar connection with S_2 may also exist in mechanically rejuvenated glasses.

4. Conclusion and discussion

Thermal cycling is realized in our colloidal glass systems by optical heating. During thermal cycling, we demonstrate a decoupling between the roughly monotonic thermodynamic rejuvenation and the fluctuated dynamic rejuvenation. Both the thermodynamic and dynamic responses to thermal cycling are induced by a small fraction of local structural rearrangements. However, the comparison between section 3.3 and section 3.4 demonstrates that the dynamic properties and thermodynamic properties of glasses are dominated by two fundamentally different microscopic mechanisms. In section 3.4, we demonstrate that the localized fast regions result from the localized high S_2 -defects induced by structural rearrangements. The localization of high S_2 -defects suggests that low S_2 regions are strongly correlated by forming a large percolating network [34]. The resistance of low S_2 network to rearrangements are so strong that rearrangements can only break the structural correlation nearby and rejuvenate the dynamics in a very localized way. The high- S_2 defects can be annihilated or re-created by further rearrangements as in the figures 6(g) and (h), which results in the fluctuated dynamics. In section 3.3, we show that the thermodynamic properties of glasses mainly rely on the elastic continuum. The elastic continuum depends on the particle-particle contacts, which can be easily disrupted by local rearrangements. The disruption in elastic continuum can propagate to rather a long distance and expand within the whole system as Eshelby's theory suggests [52]. More importantly, the disruption of the elastic continuum is irreversible from thermal cycling as the monotonic decrease of average stiffness in figure 4(a) and hence the softening of the elastic continuum is sustained.

In our experiments, rearrangements change local dynamics in a very localized way while they influence the local thermodynamic properties to a much longer distance. Figure 9(a) plots how the rearrangements (green region in the contour) alter the local S_2 defects and local stiffness in a different way after the first group of thermal cycles. Blue particles are particles suffering from a significant stiffness decrease (by 150 × 4.14×10^{-7} N m⁻¹) that dominate the bulk modulus decrease; red particles are particles that have significant S_2 increase (by 5) and lead to the dynamical rejuvenation; magenta particles are particles that contribute to both the dynamical and thermodynamic rejuvenation. Figure 9(b) quantifies the range influenced by rearrangements for both stiffness changes (blue lines) and S_2 -defect changes (red lines). The rearrangements

only reduce the S_2 values within 3–4 microns, while the stiffness change can extend to 8–10 microns and spread over the whole sample. As shown in figures 6(c) and (g), rearrangements' short-range influence on S_2 defects and local dynamics are reversible, which leads to the fluctuated dynamics. The local stiffness weakened by rearrangements is rather long-ranged and does not tend to be reversible. As a result, the bulk stiffness tends to decrease monotonically.

In conclusion, different glass properties originate from fundamentally different mechanisms. The mechanical and thermodynamic properties are dominated by the elastic continuum, while the dynamics of glasses mainly originate from localized fast regions. Rearrangements monotonically disrupt elastic continuum in a long-ranged way and lead to the continuously rejuvenated (or softened) thermodynamic properties. On the other hand, local structures (high S_2 regions) for fast dynamics only fluctuate locally or propagate very slowly during thermal cycling, due to the resistance from the correlated domains.

The decoupling between the particles involved in the dynamics and in the stiffness change might recall the long-lasting question whether the glass transition is a purely dynamic phenomena or is there any thermodynamic or structural origin responsible for glassy dynamics? Great efforts have been made to link glassy dynamics to a thermodynamic or mechanical basis [47–55]. However, our colloidal experiments demonstrate that the dynamic and thermodynamic properties of glasses during rejuvenation may be controlled by different microscopic mechanisms on different length scales. This result points to the possibility that the divergent glass properties may not be understood within a single unified theoretical frame work in which the dynamics are largely determined by the thermodynamics of the system. On the other hand, the decoupling between the dynamics and elastic properties of the colloidal glasses suggests that different glass properties can be tuned separately, which is desirable for practical applications.

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References

- [1] Struik L C E 1978 Physical Aging in Polymers and Other Amorphous Materials (Amsterdam: Elsevier)
- [2] Angelini R, Zulian L, Fluerasu A, Madsen A, Ruocco G and Ruzicka B 2013 Dichotomic aging behaviour in a colloidal glass Soft Matter 9 10955
- [3] Yunker P, Zhang Z, Aptowicz K and Yodh A 2009 Irreversible rearrangements, correlated domains, and local structure in aging glasses Phys. Rev. Lett. 103 115701
- [4] Kawasaki T and Tanaka H 2014 Structural evolution in the aging process of supercooled colloidal liquids *Phys. Rev. E* 89 0623156
- [5] Kaloun S, Skouri M, Knaebel A, Münch J-P and Hébraud P 2005 Aging of a colloidal glass under a periodic shear Phys. Rev. E 72 011401
- [6] Ketov S V et al 2015 Rejuvenation of metallic glasses by non-affine thermal strain Nature 524 200-3
- [7] McKenna G B 2003 Mechanical rejuvenation in polymer glasses: fact or fallacy? J. Phys.: Condens. Matter 15 S737-63
- [8] Lyulin A V, Hudzinskyy D, Janiaud E and Chateauminois A 2011 Competition of time and spatial scales in polymer glassy dynamics: rejuvenation and confinement effects J. Non-Cryst. Solids 357 567–74

- [9] Dmowski W et al 2010 Structural rejuvenation in a bulk metallic glass induced by severe plastic deformation Acta Mater. 58 429–38
- [10] Tong Y, Iwashita T, Dmowski W, Bei H, Yokoyama Y and Egami T 2015 Structural rejuvenation in bulk metallic glasses Acta Mater. 86 240–6
- [11] Struik L C E 1997 On the rejuvenation of physically aged polymers by mechanical deformation Polymer 38 4053–7
- [12] Concustell A, Méar F O, Suriñach S, Baró M D and Greer A L 2009 Structural relaxation and rejuvenation in a metallic glass induced by shot-peening *Phil. Mag. Lett.* 89 831–40
- [13] Bonn D, Tanaka H, Coussot P and Meunier J 2004 Ageing, shear rejuvenation and avalanches in soft glassy materials J. Phys.: Condens. Matter 16 S4987–92
- [14] Ozon F, Narita T, Knaebel A, Debrégeas G, Hébraud P and Munch J-P 2003 Partial rejuvenation of a colloidal glass Phys. Rev. E 68 032401
- [15] Viasnoff V and Lequeux F 2002 Rejuvenation and overaging in a colloidal glass under shear Phys. Rev. Lett. 89 065701
- [16] Cloitre M, Borrega R and Leibler L 2000 Rheological aging and rejuvenation in microgel pastes Phys. Rev. Lett. 85 4819–22
- [17] Bonn D, Tanase S, Abou B, Tanaka H and Meunier J 2002 Laponite: aging and shear rejuvenation of a colloidal glass Phys. Rev. Lett. 89 015701
- [18] Dupuis V, Vincent E, Bouchaud J P, Hammann J, Ito A and Katori H A 2001 Aging, rejuvenation, and memory effects in Ising and Heisenberg spin glasses Phys. Rev. B 64 174204
- [19] Lacks D J and Osborne M J 2004 Energy landscape picture of overaging and rejuvenation in a sheared glass Phys. Rev. Lett. 93 255501
- [20] Utz M, Debenedetti P G and Stillinger F H 2000 Atomistic simulation of aging and rejuvenation in glasses Phys. Rev. Lett. 84 1471
- [21] Warren M and Rottler J 2008 Mechanical rejuvenation and overaging in the soft glassy rheology model Phys. Rev. E 78 041502
- [22] Isner B A and Lacks D J 2006 Generic rugged landscapes under strain and the possibility of rejuvenation in glasses Phys. Rev. Lett. 96 025506
- [23] Henkes S, Brito C and Dauchot O 2012 Extracting vibrational modes from fluctuations: a pedagogical discussion Soft Matter 8 6092
- [24] Chen K et al 2010 Low-frequency vibrations of soft colloidal glasses Phys. Rev. Lett. 105 025501
- [25] Chen K et al 2011 Measurement of correlations between low-frequency vibrational modes and particle rearrangements in quasi-two-dimensional colloidal glasses Phys. Rev. Lett. 107 108301
- [26] Ghosh A, Chikkadi V, Schall P and Bonn D 2011 Connecting structural relaxation with the low frequency modes in a hard-sphere colloidal glass Phys. Rev. Lett. 107 188303
- [27] Still T, Goodrich C P, Chen K, Yunker P J, Schoenholz S, Liu A J and Yodh A G 2014 Phonon dispersion and elastic moduli of two-dimensional disordered colloidal packings of soft particles with frictional interactions Phys. Rev. E 89 012301
- [28] Klix C L, Ebert F, Weysser F, Fuchs M, Maret G and Keim P 2012 Glass elasticity from particle trajectories Phys. Rev. Lett. 109 178301
- [29] Yunker P J et al 2014 Physics in ordered and disordered colloidal matter composed of poly(N -isopropylacrylamide) microgel particles Rep. Prog. Phys. 77 056601
- [30] Still T et al 2013 Synthesis of micrometer-size poly(N-isopropylacrylamide) microgel particles with homogeneous crosslinker density and diameter control J. Colloid Interface Sci. 405 96–102
- [31] Crocker J C and Grier D G 1996 Methods of digital video microscopy for colloidal studies J. Colloid Interface Sci. 179 298–310
- [32] van der Wel C and Kraft D J 2017 Automated tracking of colloidal clusters with sub-pixel accuracy and precision J. Phys.: Condens. Matter 29 044001
- [33] Wang Z, Wang F, Peng Y, Zheng Z and Han Y 2012 Imaging the homogeneous nucleation during the melting of superheated colloidal crystals Science 338 87–90
- [34] Yang X, Liu R, Yang M, Wang W-H and Chen K 2016 Structures of local rearrangements in soft colloidal glasses Phys. Rev. Lett. 116 238003
- [35] Angell C A, Yue Y, Wang L-M, Copley J R D, Borick S and Mossa S 2003 Potential energy, relaxation, vibrational dynamics and the boson peak, of hyperquenched glasses J. Phys.: Condens. Matter 15 S1051–68
- [36] Derec C, Ducouret G, Ajdari A and Lequeux F 2003 Aging and nonlinear rheology in suspensions of polyethylene oxide–protected silica particles Phys. Rev. E 67 061403
- [37] van Melick H G H, Govaert L E and Meijer H E H 2003 Localisation phenomena in glassy polymers: influence of thermal and mechanical history *Polymer* 44 3579–91

- [38] Varnik F, Bocquet L and Barrat J-L 2004 A study of the static yield stress in a binary Lennard–Jones glass J. Chem. Phys. 120 2788–801
- [39] Shintani H and Tanaka H 2008 Universal link between the boson peak and transverse phonons in glass Nat. Mater. 7 870–7
- [40] Hufnagel T C 2015 Cryogenic rejuvenation: metallic glasses Nat. Mater. 14 867-8
- [41] Yunker P J, Zhang Z, Gratale M, Chen K and Yodh A G 2013 Relationship between neighbor number and vibrational spectra in disordered colloidal clusters with attractive interactions J. Chem. Phys. 138 12A525
- [42] Zhang Z, Yunker P J, Habdas P and Yodh A G 2011 Cooperative rearrangement regions and dynamical heterogeneities in colloidal glasses with attractive versus repulsive interactions Phys. Rev. Lett. 107 208303
- [43] Berthier L, Biroli G, Bouchaud J-P, Cipelletti L, El Masri D, L'Hôte D, Ladieu F and Pierno M 2005 Direct experimental evidence of a growing length scale accompanying the glass transition Science 310 1797–800
- [44] Dauchot O, Marty G and Biroli G 2005 Dynamical heterogeneity close to the jamming transition in a sheared granular material Phys. Rev. Lett. 95 265701
- [45] Lačević N, Starr F W, Schrøder T B and Glotzer S C 2003 Spatially heterogeneous dynamics investigated via a time-dependent four-point density correlation function J. Chem. Phys. 119 7372
- [46] Keys A S, Abate A R, Glotzer S C and Durian D J 2007 Measurement of growing dynamical length scales and prediction of the jamming transition in a granular material Nat. Phys. 3 260–4
- [47] Tanaka H, Kawasaki T, Shintani H and Watanabe K 2010 Critical-like behaviour of glass-forming liquids Nat. Mater. 9 324–31
- [48] Zheng Z, Ni R, Wang F, Dijkstra M, Wang Y and Han Y 2014 Structural signatures of dynamic heterogeneities in monolayers of colloidal ellipsoids Nat. Commun. 5 3829
- [49] Tong H and Xu N 2014 Order parameter for structural heterogeneity in disordered solids Phys. Rev. E 90 010401
- [50] Manning M L and Liu A J 2011 Vibrational modes identify soft spots in a sheared disordered packing Phys. Rev. Lett. 107 108302
- [51] Ingebrigtsen T S and Tanaka H 2018 Structural predictor for nonlinear sheared dynamics in simple glassforming liquids Proc. Natl Acad. Sci. USA 115 87–92
- [52] Eshelby J D 1956 The continuum theory of lattice defects Solid State Phys. 3 79-144
- [53] Tong H and Tanaka H 2018 Revealing hidden structural order controlling both fast and slow glassy dynamics in supercooled liquids Phys. Rev. X 8 011041
- [54] Tong H, Hu H, Tan P, Xu N and Tanaka H 2019 Revealing inherent structural characteristics of jammed particulate packings Phys. Rev. Lett. 122 215502
- [55] Tanaka H, Tong H, Shi R and Russo J 2019 Revealing key structural features hidden in liquids and glasses Nat. Rev. Phys. 1 333–48