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To cite this article: Xiunan Yang et al. J. Stat. Mech. (2020) 024007

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Decoupling between thermodynamics and dynamics during rejuvenation in colloidal glasses*

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Received 17 November 2019
Accepted for publication 12 December 2019
Published 21 February 2020

Online at stacks.iop.org/JSTAT/2020/024007
https://doi.org/10.1088/1742-5468/ab6b17

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].

https://doi.org/10.1088/1742-5468/ab6b17
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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 µm 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 3 h 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 0.2 K 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
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Before the optical heating, the packing fraction at the ambient temperature (22 °C) was about 0.88 and an increase of 0.2 K 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 1 s 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 40 s with 20 s light on and 20 s light off. To ensure a stable configuration without rearrangements, the data were obtained 400 s 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 \( D_{ij} = k_B T C^{-1}_{ij} / \sqrt{m_i m_j} \), where \( m_i \) is the mass of particle \( i \). The eigenvectors \( e_{n,j} \) of \( D_{ij} \) are thus identical to those of \( C_{ij} \), and \( D_{ij} \)’s eigenvalues are simply inversely proportional to the eigenvalues \( \lambda_n \) of \( C_{ij} \). The polarization vector of mode \( n \) is defined as \( P_n = e_{n,j=1}, e_{n,j=2}, \ldots e_{n,j=2N} \). The eigenfrequencies \( \omega_n \) is extracted by \( \omega_n^2 = k_B T \sqrt{m_i m_j} \lambda_n \), and the density of states \( D(\omega) \) is defined as \( D(\omega) = \langle \sum_j \delta(\omega - \omega_j) \rangle / N \).

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
two spectral functions $f_T$ and $f_L$. $f_T$ corresponds to the transverse components for each mode of frequency $\omega$ as a function of wave-vector magnitude $q$ and $f_L$ corresponds to the longitudinal counterpart.

$$f_T(q, \omega) = \left\langle \sum_n \vec{q} \times \vec{P}_n(\omega) \exp(i\vec{q} \cdot \vec{r}_n) \right\rangle,$$

$$f_L(q, \omega) = \left\langle \sum_n \vec{q} \cdot \vec{P}_n(\omega) \exp(i\vec{q} \cdot \vec{r}_n) \right\rangle,$$

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 $f_{T,L}(q, \omega)$ to a Gaussian to obtain the maximum $q_{\text{max}}$ 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: $C_{T,L} = \lim_{q \to 0} \partial \omega / \partial q$. The longitudinal modulus, $M = \rho_2 c_1^2$, the shear modulus $G = \rho_2 c_0^2$, and the bulk modulus $B = M - G$, where $\rho_2 = \rho h$, $\rho$ is very close to the density of water (1 g 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 $\omega^{d-1}$, 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 cycle, 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 $R^2$ 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 $b = 2.5 \times 10^{-6}$ s$^2$/rad$^2$ is not negligible compared to the averaged $I^* = 5 \times 10^{-6}$ s$^2$/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.
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 ~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 ~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.
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 \(D_i(\omega_{bp})\) and quantify its correlation with \(K_{ii}\). \(D_i(\omega_{bp})\) is defined as

\[
D_i(\omega_{bp}) = \frac{1}{2\Delta \omega} \int_{\omega_{bp} - \Delta \omega}^{\omega_{bp} + \Delta \omega} D_i(\omega')d\omega' \quad [39],
\]

where \(\omega_{bp}\) is the boson peak frequency, \(D_i(\omega_j) = D(\omega_j) \sum_{i} (|e_{ij}|^2 / m_i)\) is the contribution to the vibrational density of states by particle \(i\), and \(2\Delta \omega\) corresponds to thirty vibrational modes around \(\omega_{bp}\). 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 \(D_i(\omega_{bp})\) and \(K_{ii}\). Qualitatively, \(D_i(\omega_{bp})\) tends to drop with \(K_{ii}\) increasing. We use the Spearman rank correlation to assesses how well the \(K_{ii}\) monotonically depends on \(D_i(\omega_{bp})\). Spearman rank correlation is calculated by the linear correlation

\[
\frac{\sum_{i=1}^{N}(A_i - \langle A \rangle)(B_i - \langle B \rangle)}{\sqrt{\sum_{i=1}^{N}(A_i - \langle A \rangle)^2 \sum_{i=1}^{N}(B_i - \langle B \rangle)^2}}
\]

between the rank values of two variables A and B, where A and B correspond to the ranks of \(D_i(\omega_{bp})\) 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

https://doi.org/10.1088/1742-5468/ab6b17
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 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 \( \alpha_i \). \( \alpha_i \) 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 \( \alpha_i \) before thermal cycling,
after the first group of thermal cycles and after the second group of thermal cycles.
Before thermal cycling, the \( \alpha_i \) of more than 99% particles remains at values lower than
0.005 \( \mu m^2 \) (figure 6(a)). The first group of thermal cycles triggers some particles rear-
ranging in the field of view (white dots in figure 6(b)), followed by localized regions
with \( \alpha_i \) increasing to values readily above 0.005 \( \mu m^2 \). The emerging high \( \alpha_i \) 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 (~10% fast particles
in figure 6(b)). Unlike the microscopic mechanisms of the thermodynamic rejuvenation
where a small fraction (~5%) of rearrangements lead to a stiffness decline that spreads
widely to the whole glass sample, the rearrangements create localized fast regions com-
posed of a rather small fraction (10%) of particles by the rearranging regions. The \( \alpha_i \)
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
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.

$$S_i^2 = -\frac{1}{2} \sum_{\nu} \rho_{\nu} \int d\mathbf{r} \left\{ g^{\mu\nu}_i(\mathbf{r}) \ln g^{\mu\nu}_i(\mathbf{r}) - [g^{\mu\nu}_i(\mathbf{r}) - 1] \right\},$$

where $\nu, \mu$ denotes small or big particles, $\rho_{\nu}$ is the number density of $\nu$ particle, $g^{\mu\nu}_i(\mathbf{r})$ is the pair correlation function between particle $i$ of type $\mu$ and the other particles of type $\nu$. $g^{\mu\nu}_i(\mathbf{r})$ 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 $\alpha_i$ domain (figure 6(b)). Another group of thermal cycles eliminates the high-$S_2$ region and the high-$\alpha_i$ 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-$\alpha_i$ 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 $\alpha_i$ is plotted in figure 7(a). Below a threshold (close to $3 \times 10^{-3}$ $\mu$m [2]) the correlation between $S_2$ and $\alpha_i$ 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 $\alpha_i$ is above the threshold or particles with top 10% highest $\alpha_i$ values are considered, a particle with larger $\alpha_i$ value tends to have a smaller absolute
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 $\alpha_i$ 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
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 $C$. 

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 $4.14 \times 10^{-7}$ 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.
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 $C_{\text{CRR, defect}} = \frac{C \cdot S + (1-C) \cdot (1-S)}{N-m}$, 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 $150 \times 4.14 \times 10^{-7}$ 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.

**Acknowledgment**

We thank Chenhong Wang, Rui Liu, Mingcheng Yang, and Arjun G Yodh for instructive discussions.

**References**


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