Direct Evidence of Void-Induced Structural Relaxations in Colloidal Glass Formers

Cho-Tung Yip,[1] Masaharu Isobe,[2] Chor-Hoi Chan,[1] Simiao Ren,[1,3] Kin-Ping Wong,[3] Qingxiao Huo,[1] Chun-Shing Lee,[3] Yuen-Hong Tsang,[3] Yilong Han,[4] and Chi-Hang Lam[3,*]

[1]*School of Science, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China*
[2]*Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan*
[3]*Department of Applied Physics, Hong Kong Polytechnic University, Hung Hom, Hong Kong, China*
[4]*Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China*

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Particle dynamics in supercooled liquids are often dominated by stringlike motions in which lines of particles perform activated hops cooperatively. The structural features triggering these motions, crucial in understanding glassy dynamics, remain highly controversial. We experimentally study microscopic particle dynamics in colloidal glass formers at high packing fractions. With a small polydispersity leading to glass-crystal coexistence, a void in the form of a vacancy in the crystal can diffuse reversibly into the glass and further induces stringlike motions. In the glass, a void takes the form of a quasivoid consisting of a few neighboring free volumes and is transported by the stringlike motions it induces. In fully glassy systems with a large polydispersity, similar quasivoid actions are observed. The mobile particles cluster into stringlike or compact geometries, but the compact ones can be further broken down into connected sequences of strings, establishing their general importance.

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The microscopic origin of kinetic arrest and relaxation mechanisms in deeply supercooled glass-forming liquids have been debated actively for decades [1,2]. Optical microscopy experiments on colloidal liquids play an important role because detailed motions of individual particles are accessible [3]. Important progress has been the experimental confirmation of stringlike motions [4–7], first discovered in molecular dynamics (MD) simulations [8]. During a stringlike event, particles arranged in a line hop to replace the preceding ones. It can be portraited by a string of participating particles [7–9] or by a smooth line formed by the joint trajectories of these particles [4,10,11]. A synchronous segment of a string is called a microstring [9], which has been suggested as elementary relaxations in glasses [11–13]. Theoretically, free volumes [14] are widely believed to play a pivotal role in glassy dynamics. In particular, voids, i.e., free volumes each roughly the size of a particle, have long been studied [15] and are often applied to explain glassy phenomena [16]. However, voids of sizes comparable to the particles show only small correlations with particle dynamics [10,17,18].

We study colloidal liquid sandwiched between two glass plates. Glass-crystal coexisting and glassy systems are obtained using particle size distributions following unimodal (average diameter 3.77 μm) and bimodal (average diameters 3.77 and 4.62 μm) forms, respectively. They are small enough to exhibit strong Brownian motions, but are larger than those in typical experiments [4–7] in order to guarantee a perfect monolayer arrangement of particles upon sinking to the lower plate, forming a quasi-two-dimensional system. For all results reported here, all particles are practically identified by image analysis software. Their slower movements due to the relatively large particle sizes also enable snapshots to be taken at rates much faster than the dynamics so that time-averaged particle positions are very accurately measured. We study particle dynamics close to the relaxation time even at a packing fraction, to our knowledge, higher than those used in similar hard sphere experiments previously [4,6,7]. This requires imaging in a single experiment for up to 10^6 s, compared with typical durations of an hour or less. See the Supplemental Material for details [19].

Figure 1(a) shows time-colored coarse-grained particle trajectories [11] covering a period T_{traj} in a glassy colloidal system with bimodal particle sizes at the highest packing fraction $\phi = 0.80$. The trajectory of particle i is based on its coarse-grained position $\mathbf{r}_i^c(t)$ at time t obtained by averaging its instantaneous position $\mathbf{r}_i$ over a coarsening time Δt_c, i.e., $\mathbf{r}_i^c(t) = \langle \mathbf{r}_i(t') \rangle_{t' \in [t, t+\Delta t_c]}$. It is plotted by joining consecutive positions $\mathbf{r}_i^c(t)$ and $\mathbf{r}_i^c(t + \Delta t_c)$ within time T_{traj} with line segments colored according to t. From Fig. 1(a), a feature characteristic at high ϕ is a strong mobility contrast with highly mobile particles neighboring nearly stationary ones. This is verified by MD simulations of hard disks. (See Supplemental Material for more detailed experimental and simulations results [19].) We also observe stringlike motions [8] revealed as smoothly connected trajectories of the mobile particles [4,10,11]. All results presented in the following are based on coarse-grained particle positions and trajectories. Figures 1(b) and 1(c)

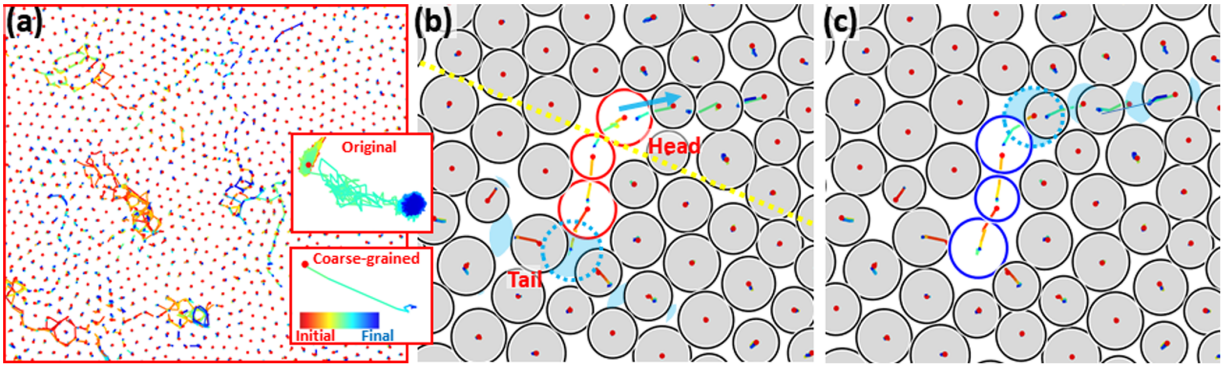

FIG. 1. (a) Coarse-grained particle trajectories at packing fraction $\phi = 0.80$ over a duration $T_{\text{traj}} = 10^6$ s. Line segments in trajectories are colored according to the times of occurrence. Initial positions are denoted by red dots. Trajectories of hopped particles connect smoothly, revealing stringlike motions. Inset: magnified views of the original and the coarse-grained trajectories of a typical particle. (b), (c) Coarse-grained trajectories for duration $T_{\text{traj}} = 20000$ s showing a typical stringlike particle hopping motion. Particle configurations at the beginning (b) and the end (c) of the period are also shown. A quasivoid consisting of fragmented free volumes (blue areas) is transported by the string across a line of otherwise stationary particles (yellow dotted line). Note that the blue dotted circles show the final position of the particle at the string tail in (b) and the initial position of the particle at the string head in (c).

magnify the coarse-grained trajectories showing a typical stringlike motion. The initial and final particle configurations of the period are also shown. The time-coloring approach conveniently illustrates if the motions are synchronous [11]. For example, the string in Figs. 1(b) and 1(c) are asynchronous and consist of three microstrings [9] colored in red, yellow, and green.

The high mobility contrast among particles allows easy interpretation of the flow of mass and hence also of free volume. Noting that a hopping particle nearly completely replaces the preceding one and adjacent nonhopping particles are practically stationary, a free volume comparable to the typical particle size is transported by the string through any cross section of the sample penetrated by the string, e.g., yellow dotted line in Fig. 1(b). For convenience, we designate the direction of a string along the free-volume flow direction and that a string points from its tail to head, so that subsequent extension of the string emerges from the head. Importantly, a continuous free volume of a particle size is not observed, consistent with previous studies [10,17,18]. Instead, the transported free volume is fragmented and distributed among a few neighboring interstitial areas both before and after the motion, as schematically illustrated in Figs. 1(b) and 1(c). Despite being fragmented, the coupled free volumes are transported in whole and behave as a quasiparticle, which we refer to as a quasivoid [11]. Further explanation of a quasivoid is discussed in the Supplemental Material [19].

The physical relevance of a quasivoid is directly evident from its reversible conversion into a vacancy, an established quasiparticle. Figure 2(a) shows particle trajectories in a unimodal colloidal system with coexisting glassy and crystalline regions. A single stringlike motion traverses between the phases. Figures 2(b)–2(f) show the detailed sequence of events. In the crystal, the trajectories of adjacent hopping particles smoothly connect to form a continuous line, which can be self-crossing and backtracking occasionally. We refer to these joint trajectories

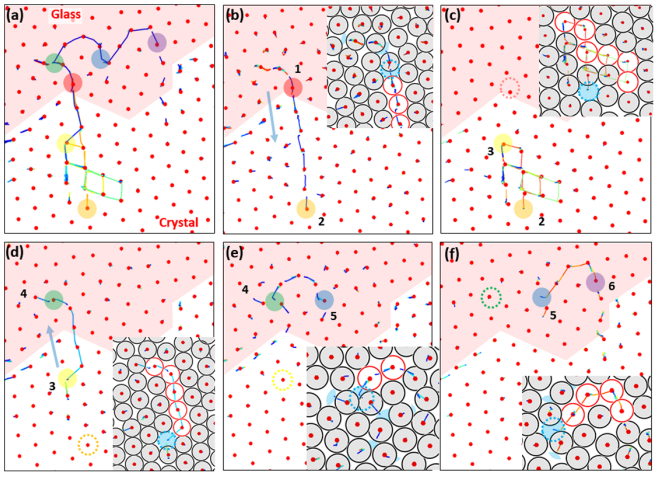

FIG. 2. Coarse-grained particle trajectories covering a time $T_{\text{traj}} = 29\,120$ s from a unimodal colloidal system with a small size dispersion exhibiting coexisting glassy (while) and crystalline (red) regions with $\phi = 0.81$ and 0.83, respectively. (a) A single stringlike motion traverses remarkably smoothly across both regions, depicting the motion of a void. (b)–(f) The same trajectories as in (a) split up over consecutive time subintervals showing detailed motions. Numbered circles mark the initial and final positions of the void at the time subintervals. (b) A void moves from the glass to the crystal (blue arrow) and (c) diffuses along lattice edges. (d) It moves back to the glass (blue arrow) and (e),(f) induce a sequence of two microstring motions. Insets in (b)–(f): trajectories shown together with initial particle configurations of the time subinterval. The void takes the form of a vacancy (blue solid circles) in the crystal (c),(d), and a quasivoid with fragmented free volumes (blue areas) in the glass (b),(e),(f).

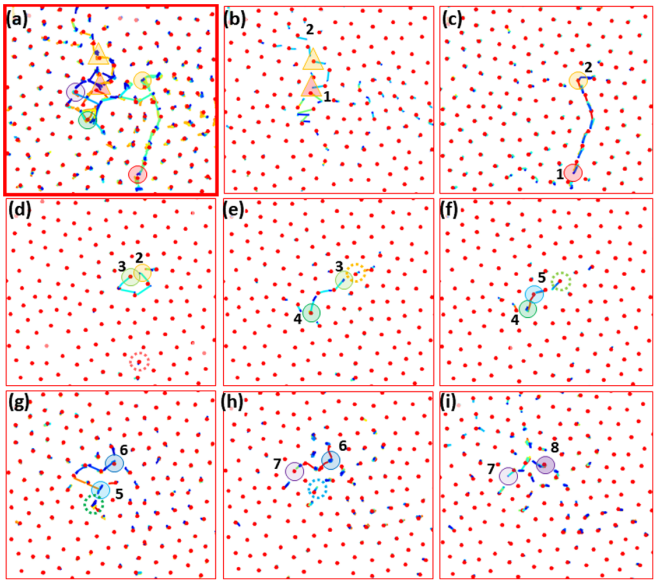

FIG. 3. (a) Coarse-grained trajectories in a region from Fig. 1(a) with a corelike cluster of mobile particles, as revealed by their highly interconnected trajectories. (b)–(i) Trajectories from (a) split up over consecutive time subintervals, showing two independent stringlike motions in (b) and (c)–(i). Numbered triangles and circles mark the initial and final positions of the two quasivoids in each time subinterval.

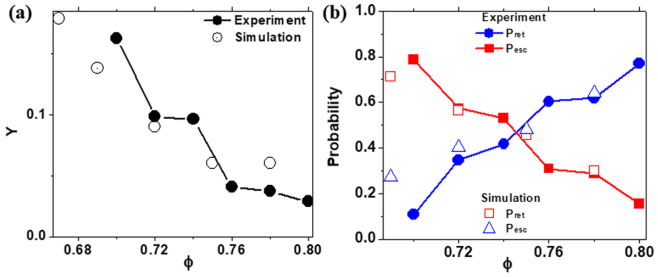

FIG. 4. (a) Displacement correlation Y measuring the mobility of the neighbors of a hopping particle. At large ϕ, values tend toward 0, corresponding to existence of stationary neighbors for all hopping particles. (b) Returning and escaping probabilities, P_{ret} and P_{esc}, of hopped particles against ϕ. They tend toward 1 and 0, respectively, at large ϕ corresponding to the dominance of back-and-forth hopping motions.

in the crystal also as strings, generalizing the usual definition of stringlike motions. The vacancy induces such stringlike motions during which it is transported from tail to head, analogous to the description above for quasivoids. Importantly, the string extends remarkably smoothly across the glass-crystal interface.

Remarkably, the excellent continuity of the string even across the phase boundary in Fig. 2(a) directly shows that the stringlike motion in the glassy region is ultimately caused by the vacancy. The vacancy upon entering the glass turns into a quasivoid, which is thus essentially a dressed vacancy. We refer to both as a void, which manifests itself as a quasivoid or vacancy in a glass or crystal, respectively.

Stringlike motions have been suggested to diminish in importance against compact rearranging groups as supercooling deepens [7,24]. To study it critically, we classify the mobile particles as stringlike and corelike and reproduce the trend of an increasing density of corelike particles as observed previously [7] (see Supplemental Material [19]). Figure 3(a) shows the coarse-grained trajectories in a region with a typical corelike group. In sharp contrast to suggestions in Ref. [7], they can, however, be broken down into two sequences of stringlike motions induced by two quasivoids as shown in Figs. 3(b)–3(k). More examples are shown in the Supplemental Material [19]. This fully supports that strings dominate relaxations even at deep supercooling [11–13]. The apparent corelike geometries, in fact, result from an increased dynamic heterogeneity so that strings are more localized and overlap each other. This is also observed in our lattice model of glass characterized by void dynamics [25].

We now study particle hopping statistics. A particle is considered hopped if its coarse-grained displacement exceeds 0.8σ ($\sigma = 3.77\ \mu$m), which equals the position of the dip in the van Hove self-correlation function (see Supplemental Material [19]). At a large packing fraction ϕ, dynamics is dominated by particle-activated hops organized as strings. Collective flows typical of nonglassy liquids, however, still exist locally in a diminished role. To quantify this, we measure a correlation Y of the displacements Δr_i and Δr_j of a hopping particle and its neighbors during a time δt defined by

$$Y = \langle \min\{\Delta r_j\}_{j\in\Omega_i}/\Delta r_i\rangle_{i\in\Omega_{\mathrm{hop}}}, \tag{1}$$

where the minimization is performed over the set Ω_i of nearest neighbors of particle i, while the average is over the set Ω_{hop} of all hopped particles. Figure 4(a) plots Y against ϕ. As ϕ increases, Y decreases toward 0, corresponding to the limiting case of particle hops in a background of stationary particles and thus an absence of collective flow. The decline of Y to a small value is verified by our MD simulations (see Supplemental Material [19]). Our result again supports the dominant nature of stringlike hopping motions under deep supercooling. It also shows the importance of adopting a large ϕ for suppressing collective flow in order to access true glassy dynamics.

Theoretical descriptions of void-induced dynamics traditionally assume free diffusion of voids [15]. However, we observe strong temporal correlations as revealed by abundant back-and-forth particle hopping motions. They occur not only in our glassy systems but also in the crystalline regions, noting that our unimodal system also admits a small particle size dispersion and hence a nontrivial free energy landscape. Such memory effects are exemplified in the reversed motions in Fig. 2(d) versus those in Fig. 2(b).

To quantify the temporal correlations, after a particle has hopped, we monitor its subsequent motions for a long time in order to calculate the probabilities P_{ret} and $P_{\mathrm{esc}} \simeq 1 - P_{\mathrm{ret}}$ that it may next perform a returning hop to the original position or an escaping hop to a third position, respectively. The results shown in Fig. 4(b) are in agreement with our MD simulations (see Supplemental Material [19]) and provide an experimental confirmation to polymer and lattice simulation results [11,25]. In particular, P_{ret} increases with ϕ and reaches a high value of 0.8 at $\phi = 0.80$. Particle and void dynamics thus differ drastically from free diffusion. A large P_{ret} supports that stringlike hopping motions are mostly β relaxations and only a vanishingly small fraction of them, i.e., the escaping hops, are structural relaxations [11,26]. A theory of glass accounting for these correlations has been suggested recently [27,28].

Strings can extend step by step to long lengths as shown in Figs. 2 and 3. The extensions are always observed to emerge from the string heads rather than the tails, as is easily explained by the transport of the quasivoid from tail to head from which further propagations can occur. Moreover, the long string lengths imply good integrity and long lifetimes of the quasivoids. This is unexpected because the fragmented free volumes constituting a quasivoid are not energetically bounded and apparently can be easily dispersed. We believe that once a quasivoid, which is usually isolated at a high ϕ, is momentarily dispersed, the free-volume fragments become immobile. The likely evolution is then the reassembly of the quasivoid, a possibility guaranteed by the time-reversal symmetry of the underlining particle dynamics under local quasiequilibrium conditions. The robustness of the quasivoids distinguishes our description from a generic free-volume picture. Creation and annihilation of quasivoids appear to occur mostly in highly active regions with multiple quasivoids.

The void-induced particle dynamics reported here is fundamentally a straightforward generalization of vacancy-induced motions in crystals. Vacancies are also believed to be responsible for particle dynamics in high-entropy alloys in crystalline form, which show glasslike sluggish dynamics [29]. Our work also explains the irrelevance of compact voids [17,18], as they have lower entropies and should be statistically unfavorable compared with quasivoids. Dynamics in glasses have been found to be correlated with soft spots and local structures [30–34]. These are consistent with our picture because the presence of a quasivoid clearly impacts the local softness and structures. The quasivoid notion may shed light on the evolution dynamics of these local properties, which is still lacking.

In conclusion, we have studied quasivoids in glass formers consisting of fragmented free volumes, which induce and are transported by stringlike particle hopping motions. Their relevance is evidenced by the reversible conversion of a quasivoid into a vacancy in a crystalline region. The induced stringlike motions are shown to dominate relaxations even in deep supercooling. We have also presented quantitatively a reduced role of collective flow and drastically enhanced temporal correlations in particle motions as supercooling deepens.

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*C.H.Lam@polyu.edu.hk

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