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Abstract
Bidisperse colloidal suspensions of temperature-sensitive microgel spheres were quenched from liquid to glass states by a rapid temperature drop, and then the glass was permitted to age. Irreversible rearrangements, events that dramatically change a particle's local environment, were observed to be closely related to dynamic heterogeneity. The rate of these irreversible events decreased during aging and the the number of particles required to move as part of these irreversible rearrangements increased. Thus, the slowing dynamics of aging were governed by growing, correlated domains of particles. Additionally, short-range order developed, and a spatial decay length scale associated with orientational order was found to grow during aging.

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Irreversible Rearrangements, Correlated Domains, and Local Structure in Aging Glasses

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Bidisperse colloidal suspensions of temperature-sensitive microgel spheres were quenched from liquid to glass states by a rapid temperature drop, and then the glass was permitted to age. Irreversible rearrangements, events that dramatically change a particle's local environment, were observed to be closely related to dynamic heterogeneity. The rate of these irreversible events decreased during aging and the the number of particles required to move as part of these irreversible rearrangements increased. Thus, the slowing dynamics of aging were governed by growing, correlated domains of particles. Additionally, short-range order developed, and a spatial decay length scale associated with orientational order was found to grow during aging.

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After initial formation, glasses relax via a nonequilibrium process called aging during which their dynamics slow dramatically and become more heterogeneous. Interestingly, diverging relaxation time scales and viscosities characteristic of the glass transition likely derive from an analogous emergence of heterogeneous particle domains that rearrange in a correlated manner [1]. The structural causes of this so-called dynamic heterogeneity, however, remain elusive. Recent work has searched for connections between dynamics and structure [2–8], for example, suggesting short-range crystalline order as a structural cause of dynamic heterogeneity [3,4]. The fruits of this continued search, if attained, will be directly applicable to the concepts of dynamical arrest as they apply to the glass transition and will thereby unify physical phenomena observed across a broad spectrum of jammed systems including colloidal suspensions [5], granular media [3,9], metallic glasses [6,10], and polymer glasses [11].

The slow nature of glass dynamics makes them intrinsically challenging to study, requiring observations on very short and very long time scales. In this Letter we ameliorate the time scale problem by studying the aging of colloidal glasses immediately after a deep quench [12]. Bidisperse suspensions of temperature-sensitive colloidal particles confined in two dimensions (2D) are quenched from liquid to glass states. The rapid and deep quench permits study of glass dynamics from very short time scales to very long time scales, i.e., over observation times sufficient for significant structural changes to occur and evolve. Video microscopy measurements reveal the development of short-range order during aging and establish a direct connection between locally ordered particles and dynamic heterogeneity. We discover that most of the fast-moving particles are not major participants in the aging process. However, a careful analysis of fast particle dynamics during aging identified an increase in the cluster size of a particular class of correlated particles, clusters of fast particles participating in irreversible rearrangements. These irreversible rearrangements are similar to those recently identified in simulation studies [2]. The increase of irreversible rearrangement cluster size, as well as the observed increase in number of stable particle configurations, directly leads to the slowing dynamics characteristic of aging. Additionally, we find that particles with local crystalline order are very unlikely to irreversibly rearrange. Thus a direct link between local crystalline order, particle rearrangement, and slowing dynamics is experimentally demonstrated.

The experiment employs an aqueous suspension of poly(N-isopropyl acry-lamide) microgel colloidal spheres (i.e., NIPA particles), whose diameters increase as temperature is reduced [13,14]. The particles are similar to those used in recent phase transformation experiments and are described therein [15]. A binary mixture of NIPA particles (small and large diameters $D_S = 1.09\ \mu$m and $D_L = 1.55\ \mu$m, respectively, at temperature $T = 28.0\,^\circ$C) is sandwiched between two glass cover slips, thereby creating a quasi-2D system. Approximately 45% (by number) of the particles are large. The softness of the NIPA colloid interparticle potential, by contrast to that of hard spheres, permits access to area fractions far above the glass transition [18].

Rapid quenching from liquid to glass is achieved by optical heating. A small amount of red dye (Chromatech–Chromatint Red 1064), 0.3% by weight, is released into the suspension. This dye absorbs light from a mercury lamp focused through the microscope objective. In the illuminated region, the temperature is increased by $\sim$4 deg in $\sim$0.1 sec via light absorption and relaxation processes. The NIPA particle radii are thus abruptly decreased by $\sim$0.1 μm, and the local area fraction (ϕ_A) is decreased by $\sim$10%. While the lamp is on, the particles are in the liquid state, as evidenced by their diffusive mean-square particle displacements (MSD): MSD $= \langle \Delta x_i^2 \rangle$ (see Fig. 1). When the mercury lamp is turned off, excess heat

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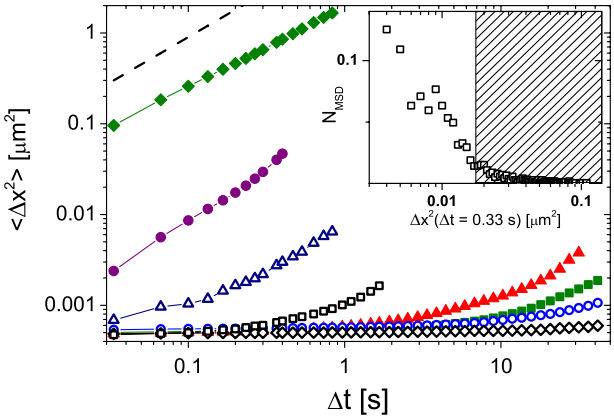

FIG. 1 (color online). Aging dynamics. Mean-square displacement at different times after the quench (t_w): the liquid state before the quench (solid diamonds), $t_w = 0.25$ s (solid circles), 1 (open triangles), 3.33 (open squares), 36 (solid triangles), 86 (solid triangles), 143 (open circles), and 10 000 sec (open diamonds). Inset: N_{MSD}, the fraction of particles with a given mean-square displacement for $0 \leq t_w \leq 3$ sec and $\Delta t = 0.33$ sec. Particles that irreversibly rearrange have mean-square displacements that fall in the shaded region. Solid lines guide the eye, and the dashed line has a slope of 1 on a log-log plot.

rapidly dissipates, and particles swell to their original size in less than 0.1 sec. The rapid change from small-ϕ_A (liquid) to large-ϕ_A creates a glass. Aging begins once the sample returns to thermal equilibrium and particles have completely returned to their original size, which is verified *in situ*. More information about the experimental setup and this glass forming technique is available in the online supplemental information [19] (OSI).

The data contained were collected at five final area fractions ranging from $\phi_A = 0.81$ to $\phi_A = 0.84$; data in Figs. 1–4 are taken solely from samples with $\phi_A = 0.84$, where the effects are strongest (see OSI). This rapid and deep quench is a unique feature of the NIPA particle experiments which permits measurement of aging over a broad range of time scales [12] that were not accessible to previous aging experiments [20]. A similarly deep quench was reported recently by Assoud *et al.* [21]; their experiment used rapid magnetic field changes to quench long-range repulsive magnetic particles from liquid to glass.

During aging, glass dynamics depend on elapsed time from the quench, i.e., waiting time, t_w. The ensemble-averaged particle MSD, shown for different t_w in Fig. 1, exhibit aging dynamics of a typical glass. The initial MSD plateau corresponds to caged particle behavior, and the "upturn" at longer times occurs when these cages rearrange. As t_w increases, the MSD upturn occurs at later times until it finally falls outside the experimental window (see OSI [19] for a full characterization of MSD versus t_w).

Constituent particles in glasses tend to rearrange in a correlated manner involving many neighbors [1,5,22,23], making it difficult to determine which particle configuration was initially unstable by use of mean-square displacements [24,25]. Thus a different dynamic quantity appears to be required, one that isolates the dynamic heterogeneity essential to relaxation. In recent two-dimensional simulations, Widmer-Cooper *et al.* identified a class of particles that undergo irreversible rearrangements (IRs) [2]. They found that if a motional event causes a particle to lose four of its nearest neighbors, then the particle rarely recovers its initial configuration. These so-defined irreversible rearrangements facilitate differentiation between affine motions that maintain local structural configurations, and nonaffine motions that contribute to relaxation. In the present experiments, neighbors are calculated using a cut-off distance defined by the first minimum in the particle pair correlation function [26]. Defining neighbors by Voronoi tessellation gave qualitatively similar results (see OSI [19]). Within our experimental time window, particles never regain their original configurations after losing three nearest neighbors; thus we say that these particles experience an IR. These particles are among the fastest in the system (see Fig. 1 inset); less than 1% are large spheres [27].

To study the variation in correlated rearrangements with t_w, we first determined the number of IR events occurring as a function of t_w [Fig. 2(a)]. The rate of IRs is initially high; ~90 events occur when $t_w < 0.4$ sec. However, the rate slows dramatically thereafter, and only ~15 events occur during the remaining time. Next, we identified particles that move much farther than average. During a time period Δt, the 10% largest particle displacements were found, and these particles were identified as "fast" (this definition of fast particles follows previous experiments [5] and simulations [22,28]). Clusters of fast particles were identified by connecting nearest-neighbor pairings of fast

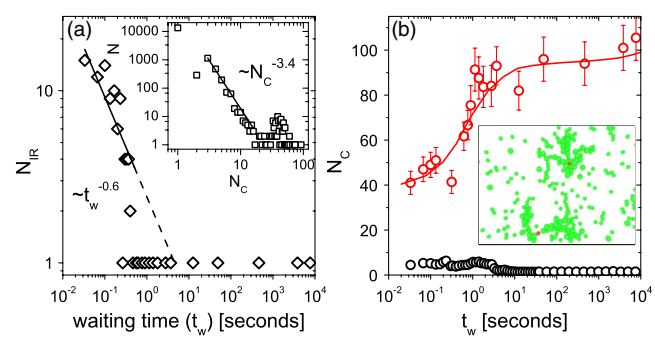

FIG. 2 (color online). Irreversible rearrangements during aging. (a) N_{IR}, the number of irreversible rearrangements, versus t_w. The line is a power law fit to guide the eye. Inset: Histogram of N_C, fast particle cluster sizes, for $0.03 \leq t_w \leq 3$ sec. The line is a power law fit to guide the eye. (b) Average number of fast particles per cluster for all clusters (black circles) and the average number of fast particles per cluster for only clusters containing a particle undergoing an irreversible rearrangement (red circles), versus t_w. The line guides the eye. Inset: Snapshot of the 10% fastest particles at $t_w = 0.62$ sec, featuring two large clusters. Particles that irreversibly rearrange are plotted in red.

particles. Since the time required for a complete rearrangement varied, we chose Δt to maximize the average number of particles per cluster at each t_w (see OSI [19]). The average number of particles per fast cluster versus t_w is plotted in Fig. 2(b); it actually decreases from ~5 particles immediately after the quench, to ~2 particles at $t_w = 10\,000$ sec. This result is surprising, as previous simulations reported a dynamic length scale that grew during aging [29].

However, closer inspection reveals that very large clusters exist, some containing ~100 particles [Fig. 2(a), inset]. Interestingly, we found that most of these large clusters contained a particle undergoing an IR. A snapshot of the 10% fastest particles, featuring two such large clusters, is shown in the inset of Fig. 2(b). We calculated the average size of these clusters of fast particles, all of which contain a particle that underwent an IR. The results are plotted in Fig. 2(b). The average size of these clusters increases from ~40 particles just after the quench, to ~100 particles at $t_w = 10\,000$ sec; the radius of gyration of these clusters correspondingly increases from ~2.5 to ~4.5 μm. In other words, as the glass ages, more particles must move for IRs to occur. The observation that clusters of fast-moving particles are dramatically larger when an IR is involved demonstrates an intimate connection between IRs and dynamic heterogeneity. This effect is reminiscent of the Adam and Gibbs hypothesis, which states that as the glass transition is approached, the number of correlated particles involved in a rearrangement increases [1,30]. In the present case, the number of correlated fast particles involved in an irreversible rearrangement event increases with aging. Rearrangements thus become progressively more difficult to achieve, leading to slow glass dynamics and kinetic arrest (Fig. 1). At the time of the irreversible rearrangement, the cluster of fast-moving particles contains ~20% of the particles that will ultimately join in the correlated domain. The remaining ~80% begin to move after the irreversible rearrangement. This observation provides strong evidence that irreversible rearrangements cause the development of correlated domains of fast-moving particles. (See OSI for further discussion [19].)

Data derived from different final area fractions displayed similar behavior. The average size of a cluster containing at least one particle undergoing an IR after $t_w = 1000$ sec, increases from ~70 particles at $\phi_A = 0.81$, to ~100 particles at $\phi_A = 0.84$.

To better understand this growing correlated domain, we calculated the initial coordination number of particles that irreversibly rearrange, and found that 90% had CN = 5, 5% had CN = 4, and 5% had CN = 6. For comparison, at $t_w = 10\,000$ sec, 60% of all particles have CN = 6, 31% have CN = 5, 8% have CN = 7, and 1% have CN = 4. This distribution of locally ordered stable particle configurations provides a structural source for heterogeneous dynamics in glasses [31].

In fact, the enhanced stability of locally ordered particle configurations is evident during aging. The evolution of the distribution of CN during aging is readily visualized by snapshots of the glass at different t_w and is plotted in Figs. 3(a) and 3(b). Patches of particles with coordination number CN = 6, i.e., particles with local crystalline order, develop during aging, as first observed in [21].

We found that $\frac{N_6}{N_{\rm tot}}$, where N_6 is the number of particles with CN = 6 and $N_{\rm tot}$ is the total number of particles, increases from ~0.48 to ~0.59 during aging. Both large and small particles exhibit the same trend (see OSI [19]).

The spatial distribution of locally ordered configurations was studied, and clusters of particles with CN = 6 were identified by connecting nearest-neighbor pairings. We then identified the largest cluster of particles with CN = 6 at each t_w [Fig. 4(b)]. At $t_w = 0.03$ sec, 20% of the particles with CN = 6 are in the largest cluster, at $t_w = 0.43$ sec, 80% of the particles with CN = 6 are in the largest cluster and it percolates across the entire field of view (80 μm), and at $t_w = 10\,000$ sec, almost 100% of the particles with CN = 6 are in the largest cluster. (Recall, only 15 IRs occur after $t_w = 0.4$ sec.) This large cluster of particles with CN = 6 is evident in Fig. 3(b).

The degree of local order is also characterized by the average bond orientational order parameter, $\psi_6 = \frac{1}{N_{\rm tot}{\rm CN}} \times \sum_{j=1}^{N_{\rm tot}} \sum_{k=1}^{\rm CN} e^{i6\theta_{jk}}$. Here θ_{jk} is the angle between the x axis and the j-k bond between particles j and k; CN is the coordination number of particle j. ψ_6 is plotted in Fig. 4(c), wherein it is apparent that bond orientational order increases with t_w, consistent with previous work [3,4,21].

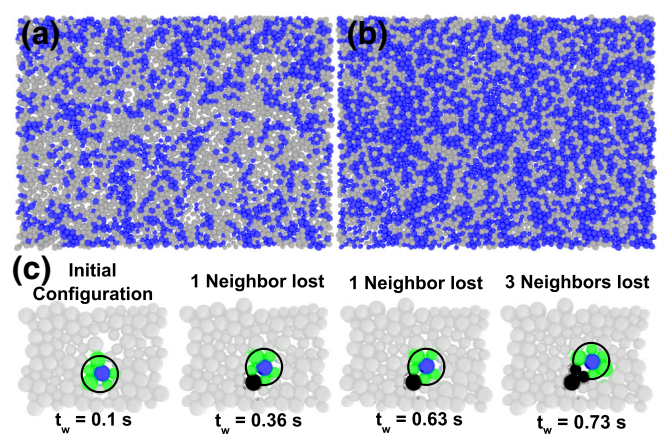

FIG. 3 (color online). Particle configuration snapshots. (a) Snapshot of colloidal glass immediately after the quench, at $t_w = 0.03$ s. Particles with six nearest neighbors are plotted in blue. (b) Snapshot of aged colloidal glass long after the quench, at $t_w = 10,000$ s. Particles with six nearest neighbors are plotted in blue. (c) Example of an irreversible rearrangement that finishes at $t_w = 0.67$ s. The irreversibly rearranging particle is blue, its nearest neighbors are green, and nearest neighbors it loses are black. The circle represents the cutoff distance that defines nearest neighbors.

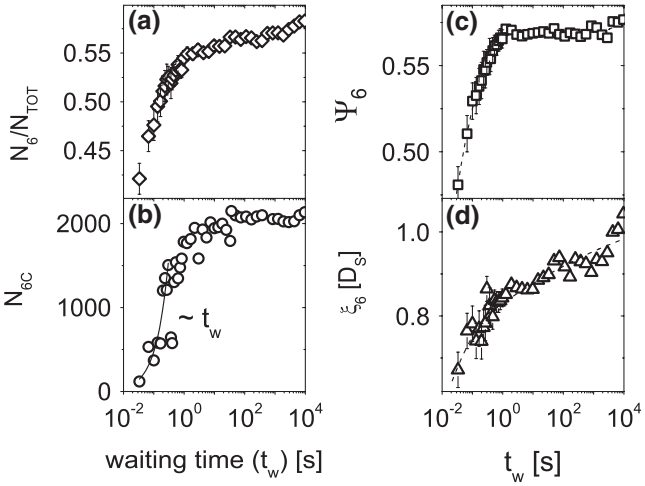

FIG. 4. Growth of local order during aging. (a) $\frac{N_6}{N_{\rm tot}}$, the fraction of particles with a coordination number of 6 versus t_w. (b) N_{6C}, the number of particles in the largest cluster of particles with 6 nearest neighbors versus t_w. (c) Bond orientational order parameter, ψ_6 versus t_w. (d) Orientational order correlation decay length ξ_6, extracted from g_6, versus t_w.

Correlations of ψ_6 in space are constructed, yielding the correlation function $g_6(r = |\mathbf{r}_i - \mathbf{r}_j|) = \langle \psi_{6i}^*(r_i)\psi_{6j}(r_j)\rangle$. We fit the envelope of $g_6(r)$ to an exponential (e^{-r/ξ_6}) in order to extract a correlation decay length ξ_6 for orientational order [Fig. 4(d)] [3,4]. Initially, ξ_6 is $\sim 0.75 D_S$, where D_S is the diameter of the small particles. Thus, immediately after the quench, the bond orientational order of a particle typically has minimal relation to that of its neighbor. However, after 10 000 seconds, ξ_6 increased to $\sim D_S$. Taken together, the increase in N_6, ψ_6, and ξ_6 suggest that short-range order increases during aging. Thus the dramatic structural and dynamic variation that occurs during aging clearly demonstrates that particles with short-range order are more stable than particle configurations with CN $\neq$ 6, in agreement with Tanaka and co-workers [31], as well as with other theories that emphasize the importance of local structure [8,33].

To summarize, heterogeneous glass dynamics are governed by domains of fast particles coupled to irreversible rearrangements. As a glass ages, the motion of more particles is required to accompany these irreversible rearrangement events, thus making relaxation more difficult to achieve and slowing glass dynamics. The fraction of particles with local crystalline order increases during aging. Particles with local crystalline order are especially stable and unlikely to irreversibly rearrange. These experimental results exhibit a clear connection to the slowing dynamics characteristic of aging, and to the heterogeneous dynamics of glasses.

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