Contribution of Slow Clusters to the Bulk Elasticity Near the Colloidal Glass Transition

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We use confocal microscopy to visualize individual particles near the colloidal glass transition. We identify the most slowly-relaxing particles and show that they form spatially correlated clusters that percolate across the sample. In supercooled fluids, the largest cluster spans the system on short time scales but breaks up on longer time scales. In contrast, in glasses, a percolating cluster exists on all accessible time scales. Using molecular dynamics simulation, we show that these clusters make the dominant contribution to the bulk elasticity of the sample.

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Colloidal suspensions of hard-sphere-like particles are an excellent model system for the study of the glass transition. Crowding of colloidal particles drives the glass transition [1,2]. The control parameter for hard spheres is the volume fraction, ϕ, rather than the temperature; colloids undergo a glass transition as ϕ is increased toward $\phi_g \approx 0.58$ [3]. New insight into the colloidal glass transition has been obtained by imaging individual particles with confocal microscopy. The existence of spatial and temporal heterogeneities near the glass transition were confirmed by identifying the spatial correlations between structurally relaxing particles [1,2]. This allowed the direct observation of such heterogeneities [4,5], which had been inferred in other glasses [6–8]. It is the existence of such structural relaxations which distinguish a fluid from a glass. Ultimately, the glass is characterized by its solidlike behavior; even though it is disordered, it has a nonzero shear modulus at low frequencies [8]. The correlated clusters of mobile, relaxing particles, which have been the focus of most prior studies, cannot bear a shear stress, and therefore cannot contribute to the development of the elastic modulus that typifies a glass. Instead, elasticity must result from transiently immobilized regions, which percolate across the sample and can support a shear stress; while earlier studies have posited a relationship between the glass transition and rigidity percolation [9–12], they do not consider the effects of dynamics. Regions of transiently immobilized particles would be directly analogous to the force chains that typify the jamming transition [13]. Such regions have not been identified in experiment, although their structure has been studied in simulation [14,15]. Moreover, the implications of immobile regions on the macroscopic mechanical properties have never been examined.

In this Letter, we use confocal microscopy to image individual particles in colloidal suspensions near the glass transition. We identify the most slowly-rearranging particles and show that they form spatially correlated clusters. On short time scales, the largest of these slow clusters spans the system, reflecting glasslike arrest, whereas on long time scales, the breakup of the spanning cluster reflects bulk, collective relaxation. The mechanical properties of the slow clusters alone cannot be accessed experimentally; instead, we calculate rheological properties of these clusters using molecular dynamics simulation. We show that the slow dynamical clusters are responsible for the dominant contribution to the bulk elasticity of the sample; moreover, their break-up time is nontrivially correlated with the time scale of the liquid-solid crossover identified from the frequency-dependent shear modulus. This provides the first direct evidence of the relationship between the solidlike behavior in a glass and the correlated regions of particles which are transiently immobile.

We study a concentrated suspension of poly-(methylmethacrylate) colloids, sterically stabilized by poly-12-hydroxystearic acid [16], fluorescently dyed with rhodamine, and suspended in a mixture of cycloheptyl bromide and decahydronapthalene. The particles are nearly density- ($\rho \approx 1.225$ g/ml) and index-of-refraction- ($n \approx 1.50$) matched, minimizing both sedimentation and scattering. The average radius is 1.18 μm, with polydispersity ~5%. The particles are nearly hard-spheres but are slightly charged, crystallizing at a volume fraction $\phi = 0.38$ and melting at $\phi = 0.42$ [17], but the glass transition remains at $\phi_g \approx 0.58$ [2]. Prior to each experiment, we initialize the samples by stirring them [2,17]; no crystallization occurs in the samples during the experiment [17]. We image the particles in three dimensions using confocal microscopy, locating their centers to within 0.03 μm in the horizontal plane and 0.05 μm in the vertical plane [2,18]. We follow the time evolution of a 69 $\mu\text{m} \times 64\ \mu\text{m} \times 14\ \mu$m section of the suspension, tracking the positions of ~4000 particles during the experiment [19].

We identify slow particles by measuring $\Delta\text{NN}(\tau)$, the number of changes in each particle's nearest neighbors over a time difference τ [15,20,21]. Nearest neighbors are identified as having separations less than that of the first minimum of the radial distribution function. We identify a slow particle as one for which $\Delta\mathrm{NN}(\tau) = 0$, and confirm that the most rapidly relaxing particles, identified as those with the largest $\Delta\mathrm{NN}(\tau)$, coincide with those identified from the largest motions [2,5].

The slow particles are spatially correlated and form extended clusters that reflect the evolution of the glasslike properties of the sample. For a supercooled fluid sample at $\phi = 0.52$, an extended cluster of slow particles spans the experimental window on time scales shorter than τ^*, which is characterized by the beginning of the long-time rise in the mean-square displacement (MSD) or by the time at which the non-Gaussian parameter, $\alpha_2(\tau)$ [22], attains a maximum [2,4,5] [Fig. 1(a)]. The bulk mechanical response of supercooled fluids is solidlike on short time scales [23]; we hypothesize that these system-spanning clusters of slow particles are directly and quantitatively connected to the solidlike behavior. On a time scale larger than τ^*, the largest cluster breaks up, leaving no remaining space-spanning clusters; we hypothesize that this reflects the loss of the solidlike elasticity [Fig. 1(b)]. Similar behavior is observed for a supercooled fluid sample at higher $\phi = 0.56$: a system-spanning cluster is present at τ^*, when the system is arrested [Fig. 1(c)], but breaks up on longer time scales as the sample fluidizes [Fig. 1(d)]. As ϕ is increased, the spanning cluster contains more particles, and the break-up time increases. By contrast, in a glass sample, the percolating cluster of slow particles present on short time scales [Fig. 1(e)] persists even on the longest experimental time scales [Fig. 1(f)], although the number of particles in the cluster decreases; this reflects its solidlike behavior on all experimentally accessible time scales.

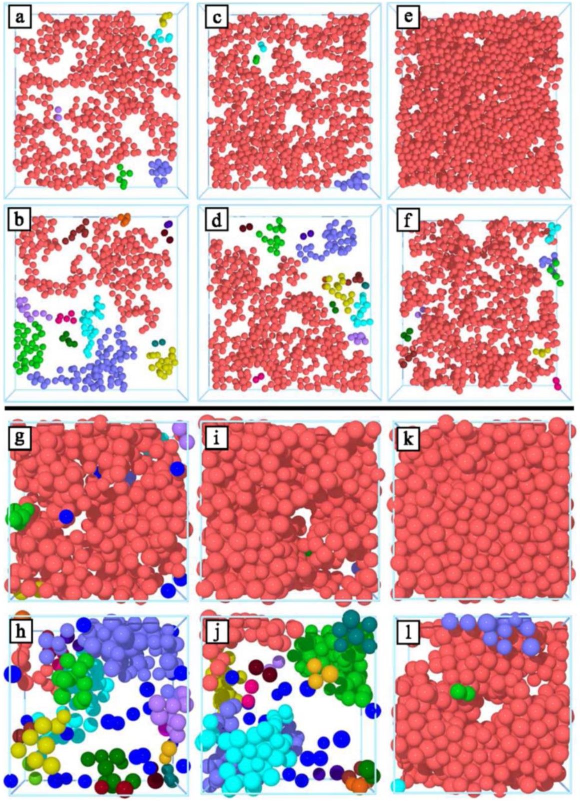

FIG. 1 (color online). Comparison of slow clusters between experiment [(a)–(f)] and simulation [(g)–(l)]. Only slow particles are shown and are shaded by cluster. Simulation times are in rescaled units. $\phi = 0.52$, τ: (a) 600 s, (b) 1500 s. $\phi = 0.56$, τ: (c) 1000 s, (d) 4000 s. $\phi = 0.60$, τ: (e) 3000 s, (f) 40000 s. $\phi = 0.55$, τ (g) 12.5, (h) 25. $\phi = 0.585$, τ: (i) 150, (j) 600. $\phi = 0.60$, τ: (k) 2000, (l) 73000.

To quantify the time evolution of slow clusters, we plot the fraction of particles in the percolating cluster, f, as a function of τ [Fig. 2(a)]. Below ϕ_g, f slowly decreases with increasing τ, and then drops sharply when the spanning cluster dissociates, suggesting that this "melting" process is first-order [24]. By contrast, above ϕ_g, $f > 0$ even at the longest τ. We characterize the structure of all nonspanning slow clusters by measuring their fractal dimensions, d_f, at the cluster break-up time scale (Fig. 3); d_f increases with ϕ, with $d_f = 2.2 \pm 0.1$ as ϕ_g is approached, close to the value for random percolation in three dimensions [25].

Interestingly, the cluster lifetime is significantly longer than τ^*. Only 5–8% of the particles rearrange over τ^* [26], which is insufficient to disconnect the spanning cluster. Correspondingly, the α-relaxation time scale, defined by the $1/e$ time scale of the self-density fluctuations at the nearest-neighbor distance, is also always shorter than the time scale for break-up of a spanning cluster, reflecting the cooperative nature of the melting process [27].

The properties of these slow particles differ markedly from the sample averages. Mobile, large-displacement par-

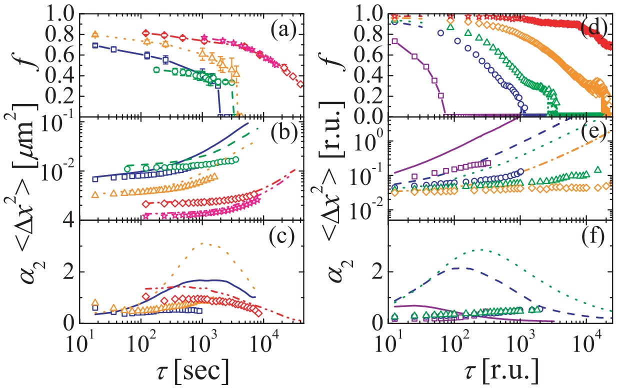

FIG. 2 (color online). Time-dependent properties of slow clusters for experiment [(a)–(c)] and simulation [(d)–(f)]. (a), (d): Fraction of particles in percolating slow cluster, f, versus time scale τ. (b), (e): Sample-averaged MSD (lines) and MSD of slow particles (symbols) versus τ. (c), (f): Sample-averaged $\alpha_2(\tau)$ (lines) and $\alpha_2(\tau)$ of slow particles (symbols) versus τ. Experiment: solid lines + squares: $\phi = 0.52$; dash + circles: $\phi = 0.53$; dot + triangles: $\phi = 0.56$; dash-dot + diamonds: $\phi = 0.60$; dash-dot-dot + stars: $\phi = 0.61$. Simulation: solid + squares: $\phi = 0.57$; dash + circles: $\phi = 0.585$; dot + triangles: $\phi = 0.59$; dash-dot + diamonds: $\phi = 0.595$; dash-dot-dot + stars: $\phi = 0.60$.

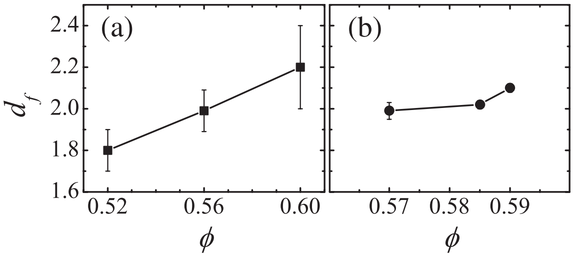

FIG. 3. Fractal dimension, d_f, of slow clusters at the cluster break-up time scale ($\phi < \phi_g$) or at the longest accessible time scale ($\phi > \phi_g$) as a function of ϕ for (a) experiment and (b) simulation. Error bars indicate standard error of the slope from linear regression.

ticles typically have larger local cages than immobile, small-displacement particles [14,26,29]. The slow particles in our experiments also have significantly smaller Voronoi volumes, corresponding to an increase in local ϕ of ~0.005; while small in absolute terms, this increase is significant near ϕ_g. In addition, as ϕ increases, the MSD decreases [Fig. 2(b)], reflecting increased local crowding [2]. For supercooled liquid samples, the MSD of slow particles is smaller than the sample-averaged MSD; moreover, it is both flatter at short τ and less diffusive at long τ. By contrast, in a glassy sample ($\phi = 0.60$), the MSD of slow particles closely follows the sample-averaged MSD, indicating that above ϕ_g, most particles are slow. Similarly, the relatively small Voronoi volume and flat MSD of slow particles at all ϕ suggest that their local environment is glasslike.

To further probe temporal heterogeneity, we compare the sample-averaged $\alpha_2(\tau)$ to that of the slow particles. Below ϕ_g, the sample-averaged $\alpha_2(\tau)$ peaks at τ^* by definition, and the peak height increases with increasing ϕ [Fig. 2(c)]. Above ϕ_g, the peak disappears, indicating that the distribution of displacements in the glass is nearly Gaussian. Notably, the $\alpha_2(\tau)$ of the slow particles does not have a strong maximum for any ϕ, thus indicating that the peak in $\alpha_2(\tau)$ is dominated by the subset of rapidly fluidized particles [2]. By contrast, nonlinear susceptibilities such as $\chi_4(t)$ [28], which probe the growing dynamical length scales close to ϕ_g, are dominated by the slow particles. The $\alpha_2(\tau)$ results for the slow particles make explicit the fact that these nonlinear susceptibilities focus on a different subset of particles than those that contribute to the non-Gaussian fluctuations.

To test our hypothesis that the clusters of slow particles are directly and quantatively connected to the solidlike behavior of the bulk sample requires measurement of the rheological properties. However, in experiment, the low-frequency response of the colloidal particles is difficult to measure, and the rheological response of the slow particles alone is inaccessible. Instead, we use molecular dynamics simulation to investigate the rheology. Our model system consists of 1372 particles interacting via a steep, short-ranged potential, $V(r) \sim (1/r)^{36}$, truncated at twice the average particle diameter [30]. Our simulations are performed with deterministic dynamics in the microcanonical ensemble; the temperature fluctuates around 0.25 with a time step of 0.0025, both measured in rescaled units. While our simulations neglect hydrodynamic interactions, the model qualitatively captures the relevant physics of a hard-sphere colloidal suspension [30,31].

To avoid crystallization during the simulation, we use a polydispersity of 8%, which is larger than the experimental sample, and determine $\phi_g \approx 0.60$ numerically [32]. Because ϕ_g of the model differs from that of the experiment, we compare slightly different ϕ between the two systems; the ϕ for the simulation are chosen to mimic the range of relaxation times spanned in experiment. We use a slightly different criterion to identify slow particles ($\Delta\mathrm{NN}(\tau) = 5$). This allows us to mimic the ϕ-dependence of the cluster lifetimes seen in experiment, making the comparison more direct. Since $\Delta\mathrm{NN}(\tau)$ is fixed for all ϕ, any coincidence between the cluster break-up time scale and the distinguishing features of the complex moduli would be nontrivial. As in the experiment, system-spanning clusters percolate on short time scales below ϕ_g and breakup on long time scales [Fig. 1(g)–1(j)], whereas system-spanning clusters do not breakup above ϕ_g [Fig. 1(k) and 1(l)]. Moreover, analysis of the MSD and $\alpha_2(\tau)$ reveals qualitative agreement with experiment [Fig. 2(d)–2(f)]. Close to ϕ_g, d_f for slow clusters is 2.10 ± 0.04 at the cluster break-up time scale, close to the experimental value [Fig. 3(b)].

We calculate the elastic modulus, $G'(\omega)$, and the viscous modulus, $G''(\omega)$, from the stress autocorrelation function, $\eta(t)$ [33]. Although glasses and supercooled liquids are structurally indistinguishable, their shear moduli differ [23]. At low ϕ, $G''(\omega)$ dominates over $G'(\omega)$ for a wide range of ω [Fig. 4(a) and 4(b)]; the system is thus liquidlike on these time scales. As ϕ is increased, $G'(\omega)$ dominates at intermediate ω, while $G''(\omega)$ dominates at low ω, reflecting the evolution from solidlike to liquidlike behavior with decreasing ω. A close correspondence exists between the features of $G'(\omega)$, $G''(\omega)$, and the lifetime of system-spanning clusters of slow particles [Fig. 4(a) and 4(b)]; the correspondence is quantitative at the highest ϕ. Remarkably, the crossover from liquidlike to solidlike behavior occurs in the narrow range of ω defined by the melting of system-spanning clusters, while the α-relaxation time scale of self-density fluctuations occurs at a systematically higher ω. The function $\eta(t)$, which we transform to obtain the moduli, depends on the coherent density fluctuations $F(k, t)$ in a complicated way [33,34]; therefore, we do not expect a correspondence between the features of G' and G'' and the α-relaxation time of $F(k, t)$ at the nearest-neighbor length scale. The near-quantitative coincidence of the breakup of system-spanning clusters and the crossover between solidlike and liquidlike regimes strongly support our hypothesis that stress is carried by the slow transient clusters.

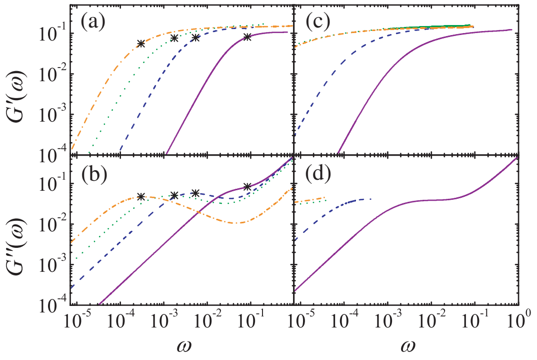

FIG. 4 (color online). Comparison of $G'(\omega)$ and $G''(\omega)$ of (a)–(b) bulk samples and (c)–(d) slow clusters, calculated from η_{mct}^{slow} and η_{mct}^{bulk}. Stars indicate break-up time scale of percolating cluster of slow particles. Note that this breakup coincides with the ω where $G'(\omega) > G''(\omega)$. Solid line: $\phi = 0.57$; dashed line: $\phi = 0.585$; dotted line: $\phi = 0.59$; dashed-dotted line: $\phi = 0.595$.

We also calculate the shear moduli of the slow regions themselves, approximating $\eta(t)$ with the mode-coupling expression and the Vineyard approximation [34]:

$$\frac{\eta_{mct}(t)}{\eta_{mct}(0)} = \int_0^\infty q^4 \left(\frac{S'(q)}{S(q)}\right)^2 F_s(q,t)^2 dq, \qquad (1)$$

where $S(q)$ is the static structure factor and $F_s(q,t) = \langle e^{i\vec{q}\cdot[\vec{r}_1(t)-\vec{r}_1(0)]}\rangle$ is the self-intermediate scattering function. We replace the bulk $F_s(q,t)$ with $F_s^{\text{slow}}(q,t)$ for the slow particles alone, and assume that $S^{\text{slow}}(q)$ may be approximated by that of the bulk [35]. While this approach is approximate, it should give a good estimate of the shift of the frequency spectrum as embodied in the complex moduli. At low ω, the viscoelastic moduli for slow particles are much greater than those of the bulk [Fig. 4(c) and 4(d)], suggesting that clusters of slow particles are more solidlike. These results highlight the role of the slow regions in the emergent elasticity of a glass [6,8,36].

In this Letter, we monitor the temporal evolution of slow, space-spanning clusters in supercooled fluids, connecting them to the stress-bearing properties of the system. Such clusters should also be present in other disordered systems which become arrested or solidlike. They are most directly analogous to the force chains observed in granular materials [37,38]; this analogy is one of the direct implications of the concept of jamming [13].

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