Localized Excitations and the Morphology of Cooperatively Rearranging Regions in a Colloidal Glass-Forming Liquid

Shreyas Gokhale,[1,*] Rajesh Ganapathy,[2,†] K. Hima Nagamanasa,[3,‡] and A. K. Sood[1,2]
[1]Department of Physics, Indian Institute of Science, Bangalore 560012, India
[2]International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India
[3]Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India
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We develop a scheme based on a real space microscopic analysis of particle dynamics to ascertain the relevance of dynamical facilitation as a mechanism of structural relaxation in glass-forming liquids. By analyzing the spatial organization of localized excitations within clusters of mobile particles in a colloidal glass former and examining their partitioning into shell-like and corelike regions, we establish the existence of a crossover from a facilitation-dominated regime at low area fractions to a collective activated hopping-dominated one close to the glass transition. This crossover occurs in the vicinity of the area fraction at which the peak of the mobility transfer function exhibits a maximum and the morphology of cooperatively rearranging regions changes from stringlike to a compact form. Collectively, our findings suggest that dynamical facilitation is dominated by collective hopping close to the glass transition, thereby constituting a crucial step towards identifying the correct theoretical scenario for glass formation.

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Dynamical heterogeneity, which refers to distinct spatial regions exhibiting vastly different mobilities, is a hallmark feature of liquids that are en route to forming a glass [1,2]. In particular, structural relaxation in glass-forming liquids comprises sporadic collective rearrangements of particles interspersed with long periods with negligible particle motion. According to the prominent theoretical framework of dynamical facilitation (DF) [3,4], these rearrangements, also known as cooperatively rearranging regions (CRRs), emerge in a hierarchical manner, from the correlated motion of localized mobility carrying defects, called excitations. While the DF theory was initially confined to kinetically constrained spin models [5], a recent computational study has extended it to particulate systems [6]. Further, colloid experiments have validated several qualitative predictions of the DF theory over area fractions ϕ spanning from the onset of glassy dynamics to the mode coupling crossover ϕ_{MCT} [7,8]. Moreover, these studies have even extended the DF scenario to random pinning glass transitions [7] as well as reentrant glass transitions in systems with anisotropic particles [8].

The facilitation approach also faces daunting challenges. First, it offers no explanation for the change in morphology of the CRRs from stringlike to compact form, which is anticipated within the random first-order transition theory (RFOT) [9] and has recently been observed in colloid experiments [10]. Second, the same colloid experiments have also shown that the peak of the mobility transfer function (MTF) [11], which quantifies the degree of facilitation, exhibits a maximum in the vicinity of ϕ_{MCT}. The presence of such a peak usually signifies a diminishing role for facilitation close to the glass transition [12]. Crucially, the experiments in Ref. [10] found that the maximum in the peak of the MTF coincides with the change in morphology of the CRRs, suggesting that facilitation is not the dominant relaxation mechanism beyond ϕ_{MCT}, and therefore fails to account for the transition from stringlike to compact CRRs. However, the MTF examines mobility correlations over time scales longer than those associated with excitations and is therefore a rather indirect probe of the connection between excitation dynamics and structural relaxation. Moreover, the maximum in the peak of the MTF may also arise from finite size effects rather than diminishing facilitation [12]. It is therefore imperative to devise a method that directly investigates the relationship between the localized excitations of the DF theory and the shapes of the CRRs, in order to ascertain the relevance of facilitation as a mechanism of structural relaxation in glass-forming liquids.

In this Letter, by analyzing data from experiments on a 2D colloidal glass former [10], we develop a protocol based on the overlap between most mobile particles and excitations and unravel the influence of excitation dynamics on the shapes of the CRRs. In particular, by investigating the partitioning of excitations between the shell-like and corelike regions of the CRRs as well as their spatial organization within the corelike regions, we demonstrate that facilitation can successfully account for the shapes of the CRRs from low to moderate area fractions ϕ, but cannot explain the observed compaction of the CRRs at large ϕ.

Strikingly, the crossover between these two regimes occurs in the vicinity of the maximum in the peak of the MTF. Our results can be understood as a competition between the facilitated dynamics of excitations on the one hand and cooperative activated hopping events on the other. Most importantly, our study demonstrates that facilitation governs structural relaxation from low to moderate supercooling but is ultimately overshadowed by another relaxation process, a fact that has profound implications for identifying the correct theoretical scenario for glass formation.

The experimental system and techniques have been described in detail in Refs. [10,13]. Particle trajectories were generated using standard Matlab algorithms [14]. To identify the CRRs, we chose the top 10% most mobile particles over a given time interval $\Delta\tau$ and clustered them based on a nearest-neighbor distance cutoff [15]. The cutoff distance was chosen to be 1.4σ, σ being the mean diameter of large and small particles of our binary glass former. Defining the CRRs as clusters of mobile particles not only enabled us to quantify changes in morphology [10], but also allowed us to establish a direct connection with excitations, which are, by definition, carriers of mobility [3]. For further analysis, we only considered CRRs defined over $\Delta\tau = t^*$, where t^* corresponds to the time interval over which the mean CRR size is maximal [10]. To quantify the morphology of the CRRs, particles within the CRRs were identified as shell-like or corelike based on their local neighborhood [10]. First, particles having more than two nearest neighbors were identified as corelike and the remaining particles were labeled shell-like. In this step, some particles that form the periphery of compact corelike regions can get incorrectly identified with the shell. This was corrected in a second step, in which we considered all particles labeled shell-like in the first step and counted the number of corelike nearest neighbors to these particles. Particles were relabeled corelike if at least two of their nearest neighbors were corelike. CRRs containing fewer than ten particles do not possess well-defined corelike and shell-like regions and those larger than 35 particles occur with a low probability and are undersampled in our experiments, especially at low ϕ. We therefore restricted our analysis to CRRs that contain 10–35 particles. To study the effect of CRR size on the spatial organization of excitations within the CRRs, we considered three groups of CRRs, which contained 25–35 particles, 16–24 particles, and 10–15 particles.

Having identified the corelike and shell-like constituent particles of the CRRs [Figs. 1(a)–1(c)], we examined whether the particles in the CRRs were associated with excitations. To identify the excitations, we followed the procedure described in Refs. [6,7]. We first coarse grained trajectories of the most mobile particles over a suitable interval $\delta \sim 2$ s [8]. Operationally, a particle is said to be associated with an excitation of size a and instanton time

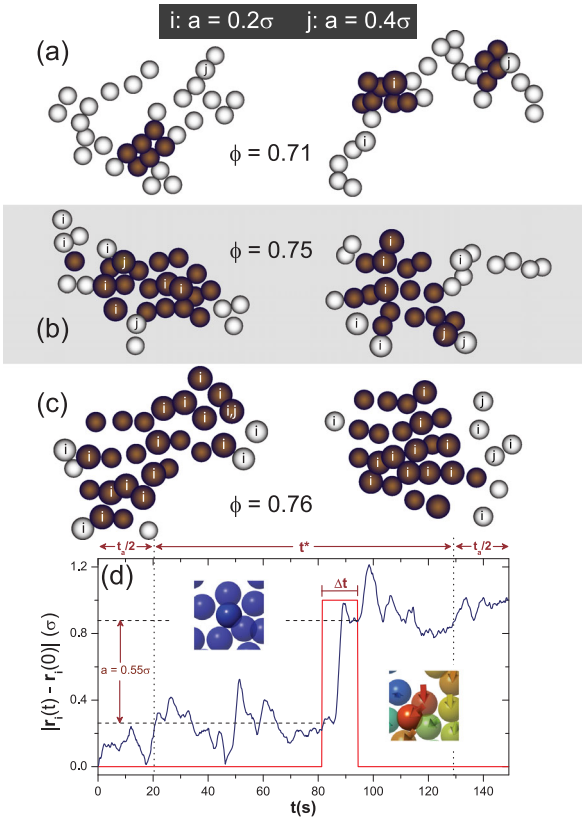

FIG. 1. Representative CRRs containing $N = 30$ particles for $\phi = 0.71$ (a), $\phi = 0.75$ (b), and $\phi = 0.76$ (c). In panels (a)–(c), particles belonging to the core are shown in brown and those belonging to the shell are shown in white. Excitations of size $a = 0.2\sigma$ that overlap with the CRRs are denoted by "i" and those of size $a = 0.4\sigma$ are denoted by "j." (d) Procedure for identifying excitations. A representative coarse-grained subtrajectory (blue curve) of a tagged particle and its associated functional $h_i(t, t_a; a)$ (red) over the interval $[-t_a/2, t^* + t_a/2]$. The panel on the left side denotes the positions of the tagged particle and its nearest neighbors at the initiation time of the excitation, i.e., the time at which $h_i(t, t_a; a)$ switches from 0 to 1. The panel on the right side denotes the final positions of the particles at the termination of the excitation, i.e., the time at which $h_i(t, t_a; a)$ switches from 1 to 0. The color scheme encodes the magnitude of the displacement, with brown indicating high mobility and blue indicating low mobility. The arrows begin at the initial positions and terminate at the final positions and the lengths are proportional to the magnitude of the displacement.

duration Δt if it undergoes a displacement of magnitude a over time Δt and persists in its initial as well as final state for at least Δt [6]. Formally, excitations are identified by computing for every trajectory the functional

$$h_i(t, t_a; a) = \prod_{t'=t_a/2-\Delta t}^{t_a/2} \theta(|\vec{\mathbf{r}}_i(t+t') - \vec{\mathbf{r}}_i(t-t')| - a), \quad (1)$$

where $\theta(x)$ is the Heaviside step function [6,7] and $h_i(t, t_a; a)$ returns 1 if the particle is associated with an excitation at time t, and 0 otherwise. Here, t_a, known as the

commitment time, is the smallest time interval required to identify excitations of size a and is typically about 3 times the mean instanton time. Our mobile particles are defined over the time interval $[t, t+t^*]$. An excitation of duration Δt may contribute to the mobility of these particles even if it lies only partially within the interval $[t, t+t^*]$. In order to take such excitations into account, we computed $h_i(t, t_a; a)$ for particle subtrajectories over the extended interval $[t - t_a/2, t + t^* + t_a/2]$ [Fig. 1(d)]. If $h_i(t, t_a; a)$ was nonzero anywhere within this interval, we concluded that the mobile particle over $[t, t+t^*]$ is associated with an excitation of size a [see Figs. 1(a)–1(c) for representative CRRs and their associated excitations].

Next, we analyzed the partitioning of excitations into the corelike and shell-like regions of the CRRs as a function of ϕ and a. Within the DF theory, the CRRs emerge from the hierarchical facilitated dynamics of excitations [6] and one would therefore expect excitations to be partitioned randomly between the shell-like and corelike regions of the CRRs. To test this conjecture, we calculated the fraction of excitations associated with the shell-like (F_s^a) as well as the corelike (F_c^a) regions of the CRRs [Fig. 2(a)]. We have also shown the evolution of the fraction of shell-like and corelike mobile particles, F_s^{mob} and F_c^{mob}, respectively, as a function of ϕ [Fig. 1(a)], which serve as baselines for the data. First, we note that F_s^{mob} decreases whereas F_c^{mob} increases monotonically with ϕ, consistent with the compaction of the CRRs on approaching the glass transition [10] [Figs. 1(a)–1(c)]. If the excitations are indeed partitioned randomly between the shell-like and corelike regions of the CRRs, F_s^a and F_c^a must follow the ϕ dependence of the corresponding baselines F_s^{mob} and F_c^{mob}. We observe that for $\phi < 0.76$, for CRRs containing 25–35 particles, the curves for excitations of two different sizes indeed follow the baselines [Fig. 2(a)]. Strikingly, however, for $\phi \geq 0.76$, both F_s^a and F_c^a deviate systematically from their respective

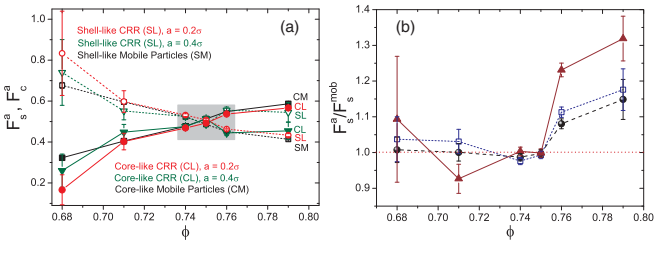

FIG. 2. (a) The fraction of excitations associated with the shell-like (F_s^a; hollow circles and triangles) and corelike (F_c^a; solid circles and triangles) regions of CRRs of size 25–35 particles for $a = 0.2\sigma$ (circles) and $a = 0.4\sigma$ (triangles). The fractions of shell-like mobile particles (F_s^{mob}; hollow black squares) and corelike mobile particles (F_c^{mob}; filled black squares) are also shown. (b) The ratio F_s^a/F_s^{mob} for $a = 0.4\sigma$ for CRRs of size 25–35 particles (triangles), 16–24 particles (squares), and 10–15 particles (circles). The horizontal dotted line corresponds to the equipartition of excitations between the shell-like and corelike regions.

baselines for $a = 0.4\sigma$. This result is robust and does not depend on the nearest neighbor cutoff used to construct CRRs from mobile particles (Fig. S1 [13]). Indeed, in this regime, for $a = 0.4\sigma$, F_c^a appears to follow F_s^{mob} rather than F_c^{mob} [Fig. 2(a), green curves]. This indicates that the excitations are preferentially partitioned into the stringy shell-like regions of the CRRs for $\phi \geq 0.76$. Remarkably, however, for a smaller excitation size $a = 0.2\sigma$, F_s^a and F_c^a follow F_s^{mob} and F_c^{mob}, respectively. Given the hierarchical nature of facilitated dynamics, deviations from the DF theory should be stronger for larger excitations as smaller excitations correspond to rapid reversible particle motions and do not contribute significantly to structural relaxation [6]. Larger excitations on the other hand, contribute more to irreversible displacements and hence to structural relaxation. Thus, these results provide the first indication that facilitation dominates structural relaxation for $\phi < 0.76$ but is superseded by some other dynamical process at larger ϕ.

The dependence of F_s^a, or F_c^a, on a possesses several intriguing features. At low ϕ, we observe that F_s^a decreases slightly with a, whereas for $\phi \geq 0.76$ it increases strongly with a [Fig. 2(a) and Fig. S2 [13]]. This once again suggests the existence of two qualitatively distinct dynamical regimes at low and high ϕ. According to the DF theory, rare large excitations often give rise to smaller excitations in their vicinity [6]. This suggests that large excitations have a higher probability of being associated with the corelike region of the CRRs. As a consequence, the expectation from the facilitation picture is that F_s^a should decrease with a. While this is indeed true for low ϕ, F_s^a actually increases with a at large ϕ. This strongly suggests that facilitation is not the dominant mechanism of relaxation close to the glass transition. Moreover, one can conjecture that facilitation is successful in a regime dominated by stringlike CRRs, but does not adequately capture the compaction of the CRRs with increasing ϕ. Since small CRRs are predominantly stringlike in shape, one should expect deviations from the DF prediction for these CRRs to be smaller than those observed for large CRRs. We tested this possibility by comparing the ratio F_s^a/F_s^{mob} for different CRR sizes [Fig. 2(b)]. From the facilitation picture, we expect that F_s^a/F_s^{mob} should remain close to 1 for all ϕ. We observe that for a sufficiently large excitation size ($a = 0.4\sigma$), and for all CRR sizes considered, $F_s^a/F_s^{\mathrm{mob}} \sim 1$ for $\phi < 0.76$, whereas $F_s^a/F_s^{\mathrm{mob}} > 1$ for $\phi \geq 0.76$. Furthermore, the deviation from the facilitation prediction is indeed much stronger for large CRRs (25–35 particles) compared to small ones (10–15 particles). These findings strongly suggest that facilitation can account for the stringlike morphology of the CRRs but cannot capture their transition to compact form.

While F_s^a quantifies the proportion of excitations associated with the shell-like regions of the CRRs, it does not provide information on the spatial organization of these excitations within the CRR. A measure of this spatial

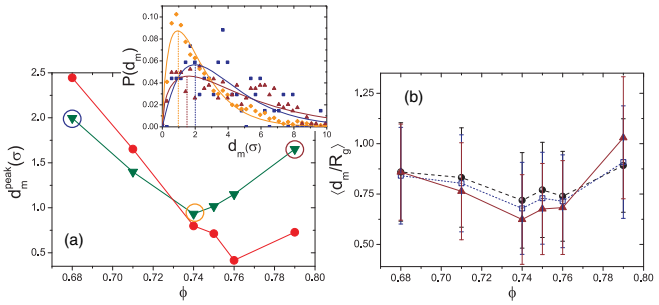

FIG. 3. (a) The peak d_m^{peak} of the distributions $P(d_m)$ as a function of ϕ for $a = 0.2\sigma$ (filled circle) and $a = 0.4\sigma$ (down-pointing triangle) for CRRs containing 25–35 particles. The inset shows the distributions $P(d_m)$ and corresponding fits of the form $Ax^b \exp(-cx)$ for the three data points circled in the main plot of panel (a). The d_m^{peak} values in (a) have been extracted using these fits. (b) $\langle d_m/R_g \rangle$ vs ϕ for $a = 0.4\sigma$ for CRRs of size 25–35 particles (triangles), 16–24 particles (squares), and 10–15 particles (spheres). Here, R_g denotes the radius of gyration of the CRR and $\langle \cdots \rangle$ denotes averaging over the CRRs.

organization is the minimum distance d_m of an excitation of given size from the center of mass of the corelike region of the CRR. We generated distributions $P(d_m)$ of these distances by sampling different CRRs and studied the variation of the peak d_m^{peak} of these distributions with a as well as ϕ [Fig. 3(a) and inset]. We observe that d_m^{peak} decreases with a at low ϕ, consistent with the expectation from the DF theory that larger excitations must occur closer to the core. Further, for $\phi < 0.75$, d_m^{peak} decreases with ϕ for different a, which is once again in concord with the hierarchical nature of excitation dynamics. Most remarkably, d_m^{peak} increases dramatically for $\phi > 0.75$, in stark contrast to the facilitation picture [Fig. 3(a)]. Lastly, we observe that at large ϕ, d_m^{peak} shows a strong increase with a, which is once again inconsistent with the DF scenario (Fig. S3 [13]). The average value of d_m, $\langle d_m \rangle$, also exhibits a similar trend as a function of ϕ and a (Fig. S4 [13]). An extremely crucial point to note is that the drastic increase in d_m^{peak} at large ϕ cannot be inferred directly from the corresponding increase in F_s^a/F_s^{mob} [Fig. 2(b)]. In particular, an increase in F_s^a/F_s^{mob} implies a reduction in the number of excitations in the core relative to the shell, but is insensitive to their distribution within the core. A smaller number of excitations can still be distributed evenly within the core in a manner that leaves d_m^{peak} unchanged. On the other hand, an increase in d_m^{peak} in conjunction with the increase in F_s^a directly implies the existence of a second dynamically distinct process that actively expels excitations out to the periphery of the CRR. This claim is further bolstered by the observed dependence of $\langle d_m \rangle$ on CRR size. On average, the radius of gyration R_g of the CRRs increases with increasing CRR size. Thus, to compare $\langle d_m \rangle$ across different windows of CRR size, we normalized each value of d_m with the corresponding R_g and plotted $\langle d_m/R_g \rangle$ as a function of ϕ for $a = 0.4\sigma$ for various CRR sizes [Fig. 3(b)]. We see that within experimental error the increase in $\langle d_m/R_g \rangle$ at large ϕ is stronger for large CRRs (25–35 particles) compared to small ones (10–15 particles) [Fig. 3(b)]. This implies that smaller CRRs are less influenced by a growing core size and therefore experience weaker expulsion of excitations to the periphery. Collectively, these observations clearly point towards a crossover in the dominant relaxation mechanism on approaching the glass transition.

We hypothesize that structural relaxation for $\phi > 0.75$ is dominated by collective activated hopping events that are compact in shape and grow in size on approaching the glass transition. Such collective hops constitute the primary relaxation events within the RFOT [16,17]. The observed trends in F_s^a (Fig. 2) and d_m^{peak} (Fig. 3) can then be understood as a competition between two distinct relaxation processes. We claim that the particles constituting the CRRs acquire mobility either through excitation dynamics or through nonfacilitated thermal activation. In the low ϕ regime, the size of the thermally activated hops is too small to influence the spatial distribution of excitations within a CRR, as a result of which F_s^a mimics the ϕ dependence of F_s^{mob}. Beyond $\phi = 0.75$, the compact nonfacilitated hopping events contribute significantly to the corelike region of the CRRs, expelling excitations to the periphery of the CRR in the process. This conjecture is strongly supported by the dramatic increase in d_m^{peak} of large excitations for $\phi > 0.75$ (Fig. 3 and Fig. S4(a) [13]). The depletion of these excitations from the CRR core is directly reflected as a decrease in F_c^a, which is in turn manifested as an increase in F_s^a [Fig. 2(a)].

The competition between facilitation and hopping is strongly reminiscent of the dynamics of kinetically constrained spin models [5] in which the kinetic constraint is systematically violated by the presence of a nonfacilitated activated relaxation process [12]. Elmatad and Keys have shown [12] that these models can exhibit a crossover from facilitation to activated hopping that is signalled by the presence of a maximum in the peak of the mobility transfer function [11]. Most strikingly, our system indeed exhibits such a peak in the vicinity of $\phi = 0.75$ [10], suggesting a similarity between colloidal glass formers and the aforementioned class of spin models. It is important to note that facilitation can also be incorporated within the RFOT as a secondary relaxation process that emerges from the nonlinear interaction between mode coupling and activated hopping [18,19]. However, our present data as well as previous experiments seem to suggest that facilitation is the dominant relaxation mechanism from low to moderate ϕ, rather than a secondary process. Hence, further studies are necessary to determine whether our observations are consistent with the role of facilitation described in the RFOT.

In general, distinct thermodynamic theories such as geometric frustration-based models [20], Tanaka's two order parameter model [21], and the RFOT envision some form

of collective activated hopping as the dominant relaxation mechanism close to the glass transition. DF on the other hand describes a completely different type of dynamical process. In the present study, we have shown that this important distinction between thermodynamic approaches and facilitation has observable consequences in local relaxation dynamics. Given the dominance of collective hopping at large ϕ observed in our experiments, a natural step forward would be to attempt to make finer distinctions between the relaxation mechanisms envisioned in different thermodynamic frameworks. It is clear that it is not possible to distinguish between different kinds of activated hopping events based on dynamics alone. Indeed, a comparative analysis of the dominant relaxation mechanisms at large ϕ will involve various measures of local and global structural order and their link to relaxation dynamics.

In summary, through an in-depth real space analysis of the particle dynamics, we have examined the relationship between localized excitations and the shapes of the CRRs in a colloidal glass-forming liquid (Fig. 1). We have identified a crossover from a facilitation dominated regime at low ϕ to one dominated by collective hopping at high ϕ. Our analysis of the partitioning of excitations into the shell-like and corelike regions of the CRRs (Figs. 2 and 3) provides a microscopic explanation for the recently observed peak in the maximum of the mobility transfer function [10]. Importantly, our work shows that the DF approach in its present form does not account for the change in morphology of the CRRs and that facilitation does not dominate structural relaxation close to the glass transition. One cannot rule out that a reformulation of the DF theory may yet be able to explain our results. However, given the present state of the art, our findings lean towards a thermodynamic origin of the glass transition.

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*Corresponding author.
gokhales@mit.edu
Present address: Physics of Living Systems group, MIT, 400 Technology Square, NE46-629, Cambridge, Massachusetts 02139, USA.

†Corresponding author.
rajeshg@jncasr.ac.in

‡Present address: Center for Soft and Living Matter, Institute for Basic Sciences, 50 UNIST-gil, Ulju-gun, Ulsan 44919, Republic of Korea.

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