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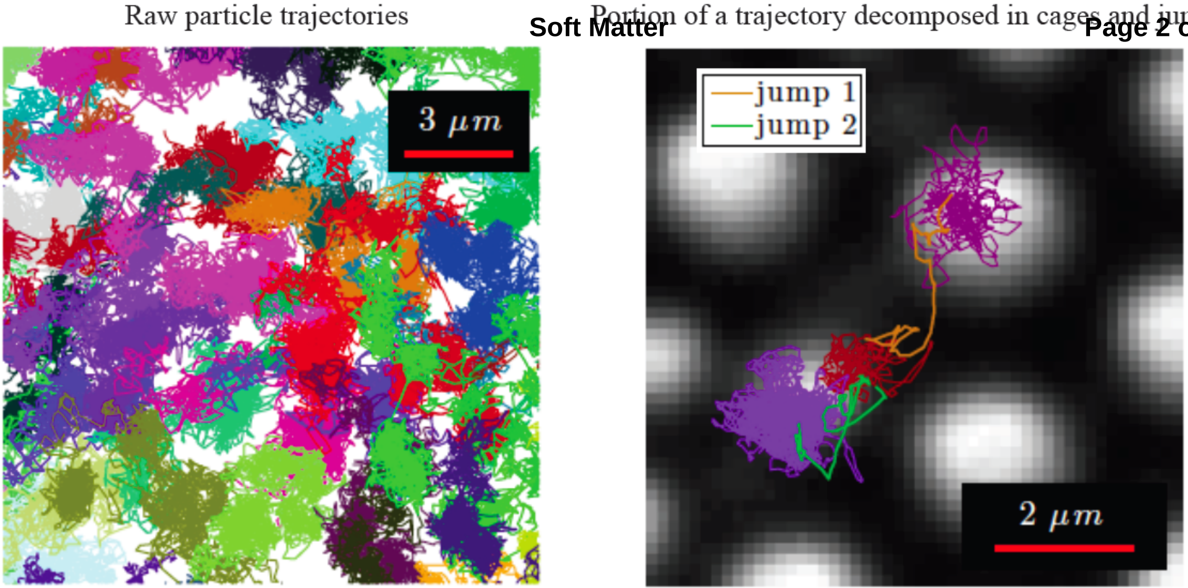
We connect the intermittent single particle motion and the macroscopic dynamics in experiments on colloidal glasses.


Raw particle trajectories
3 μm
Portion of a trajectory decomposed in cages and jumps
jump 1
jump 2
2 μm

Connecting short and long time dynamics in hard–sphere–like colloidal glasses

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Glass–forming materials are characterized by an intermittent motion at the microscopic scale. Particles spend most of their time rattling within the cages formed by their neighbors, and seldom jump to a different cage. In molecular glass formers the temperature dependence of the jump features, such as the average caging time and jump length, characterize the relaxation processes and allow for a short–time prediction of the diffusivity. Here we experimentally investigate the cage–jump motion of a two–dimensional hard—sphere–like colloidal suspension, where the volume fraction is the relevant parameter controlling the slow down of the dynamics. We characterize the volume fraction dependence of the cage–jump features and show that, as in molecular systems, they allow for a short time prediction of the diffusivity.

1 Introduction

The glass transition occurring in many materials can be induced by changing different control parameters. In molecular liquids, for example, the temperature is the relevant control parameter[1,2], while in hard sphere systems the transition is controlled by the density[3–5]. In other systems, such as attractive or soft colloids, both temperature and density play an important role[6–8]. Despite this variety, glass–forming materials exhibit common features. Indeed, on approaching the glass transition one observes a dramatic increase of the relaxation time, a vanishing diffusivity, the breakdown of the Stokes–Einstein relation[9] and the emergence of dynamical heterogeneities[10]. At the microscopic level, one observes the emergence of an increasingly intermittent single particle motion, both in equilibrium supercooled liquids[11,12] and aging glasses[13]. Indeed, in glassy systems particles spend most of their time confined within the cages formed by their neighbors, and seldom make a jump to a different cage. This universality suggests that jumps might be the elementary irreversible events allowing for the relaxation of the structural glasses[12]. If this is so, then particles move performing a random random walk with step size of average length $\langle \Delta r_J \rangle$, and average duration, $\langle \Delta t_J \rangle$. Since the jump duration is small with respect to relaxation time, an important consequence of this scenario is the possibility of determining the diffusivity D on the time–scale of the jump duration, i.e. well before the system enters the diffusive regime. Indeed, one expects

$$D = \rho_J \frac{\langle \Delta r_J^2 \rangle}{\langle \Delta t_J \rangle} \qquad (1)$$

where ρ_J is the density of jumps, i.e. the fraction of particles that are making a jump at every instance of time. We have recently investigated this scenario via numerical simulations based on a molecular liquid model[12], through an algorithm able to segment the trajectory of each particle in cages and jumps. This allowed to verify that jumps are irreversible events, and that the relation between the features of the cage–jump motion and the diffusivity holds as the dynamics slow down by lowering the temperature.

In this paper we experimentally investigate whether a similar scenario holds in hard sphere like systems, where the density is the relevant control parameter and the temperature plays a minor role, as it simply fix the dynamical time-scale. This is not obvious, as the physical mechanisms responsible for the slow down of molecular and of hard sphere systems might be different. Indeed, in the first case the slow down occurs on cooling as the system spends an increasing amount of time close to minima of its potential energy landscape[14–19]. Conversely, in hard sphere systems the slowing down has a purely entropic origin, and the elementary relaxation events might not be single particle jumps, but rather structural rearrangements involving a finite number of particles[20,21]. Via the experimental investigation of a two–dimensional hard–sphere–

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like colloidal system, here we show that particle jumps are irreversible and that they are short lived with respect to the relaxation time. This allows for a short time prediction of the diffusivity of hard–sphere sphere systems via Eq. 1.

2 Methods

2.1 Experiments

We have experimentally investigated the motion of a two–dimensional layer of colloidal particles immersed in water. The sample was a 50:50 binary mixture of silica beads, with bead diameters 3.16 ± 0.08 and 2.31 ± 0.03 μm respectively, in a ≈ 1.4 ratio known to prevent crystallization. The sample cell was prepared with a microscope slide and a No.1 thickness coverslip separated by two Parafilm stripes. Heating the whole cell up to $90\,^{\circ}C$ allowed the Parafilm stripes to melt and then to glue the two glasses. The resulting sample cell thickness was about 90-100 μm. The silica particles, being heavier than water, settle on the bottom coverslip creating a two dimensional system of free diffusing particles. We image the system using a standard microscope equipped with a 40x objective (Olympus UPLAPO 40XS). The images were recorded using a fast digital camera (Prosilica GE680). At the highest volume fraction, we image roughly a thousand of particles in the field of view of our microscope (see Fig. 1a). Particle tracking was performed using custom programs.

To avoid bacterial contamination both the bead mixture and the sample cell were carefully washed several times with ethanol and then with distilled highly purified MilliQ water. To avoid particle sticking through Van der Waals forces, the beads were dispersed in a water surfactant solution (Triton X-100, 0.2 % v/v). With this concentration the particles did not stick to the coverslip for days. The sample temperature was continuously monitored during experiments, remaining stable within $1\,^{\circ}C$ around the room temperature ($T = 22\,^{\circ}C$).

We have investigated different volume fractions ϕ, in the range 0.64–0.79. At higher volume fractions the time required for the particles to settle down in a single monolayer was too long to avoid particle sticking.

2.2 Cage-jump detection algorithm

We segment each of the experimentally recorded particle trajectory in a sequence of cages and jumps, as illustrated in Fig. 1c and d. We use an algorithm[12] that associates to each particle, at each time t, the fluctuations $S^2(t)$ of its position computed over the interval $[t - 10t_b : t + 10t_b]$, with $t_b \simeq 1s$ being the ballistic time. At time t, a particle is considered in a cage if $S^2(t) < \langle u^2 \rangle$, as jumping otherwise. Here $\langle u^2 \rangle$ is the Debye–Waller factor, that we determine from the mean square displacement as in Ref. 22 and whose volume fraction dependence is shown in Fig. 2b. At each instant the algorithm gives access to the density of jumps, ρ_J, defined as the fraction of particles which are jumping, and to the density of cages, $\rho_C = 1 - \rho_J$. By monitoring when S^2 equals $\langle u^2 \rangle$, we are able to identify the time at which each jump (or cage) starts and ends. That is, this approach explicitly considers that jumps are processes with a finite duration.

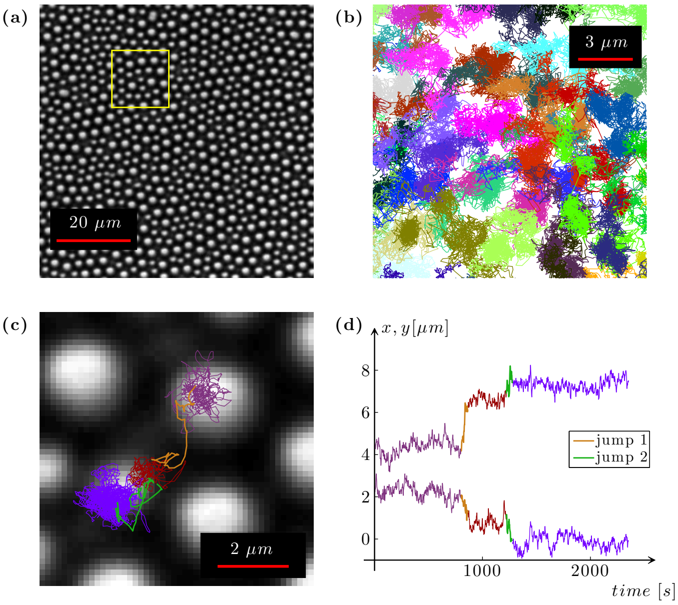

Fig. 1 (a) Snapshot of the investigated system at volume fraction $\phi = 0.76$. (b) Trajectories of all particles in the region highlighted in (a). A portion of one such trajectory segmented in cages and jumps is illustrated in real space (c) and in the (x,t) and (y,t) space (d).

3 Results

3.1 Glassy dynamics

We have investigated the slow dynamics of the system considering the volume fraction dependence of the mean square displacement, $r^2(t)$, and of the persistence correlation functions, $p(t)$, respectively illustrated in Fig. 2a and Fig. 3. The persistence correlation function is defined, in analogy to lattice models, as the fraction of particles that has not jumped up to time t[23–25].

As the volume fraction increases, the mean square displacement develops a long plateau before entering the diffusive regime, as usual in glass–forming systems. The value of this plateau is the Debye–Waller factor $\langle u^2 \rangle$, and estimates the amplitude of the vibrational motion before the system relax. We have measured $\langle u^2 \rangle$ as the value of the mean square displacement at the time at which its logarithmic time derivative

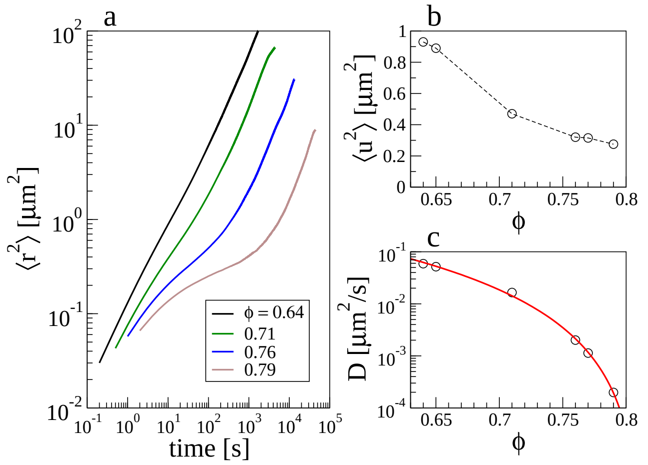

Fig. 2 (a) Mean square displacement for different volume fraction, as indicated. (b) volume fraction dependence of the Debye–Waller factor. The dashed line is a guide to the eye. (c) volume fraction dependence of the diffusivity. The full line corresponds to a power law fit, $D(\phi) \propto (\phi_c - \phi)^b$, with $\phi_c \simeq 0.81 \pm 0.01$ and $b = 2.8 \pm 0.02$.

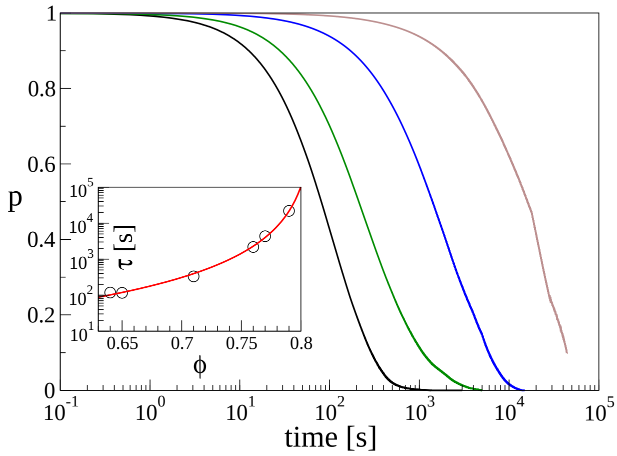

Fig. 3 Persistence correlation functions for increasing values of ϕ, from left to right. The values of ϕ are as in Fig. 2a. The inset illustrates the volume fraction dependence of the persistence relaxation time. The full line is a power law fit, $\tau(\phi) \propto (\phi_c - \phi)^{-c}$, with $\phi_c \simeq 0.81 \pm 0.01$ and $c = 2.6 \pm 0.02$.

acquires its minimum value[22]. Fig. 2b illustrates that $\langle u^2 \rangle$, which is the only parameter required by the algorithm used to segment particle trajectories, gradually decreases as the volume fraction increases. Fig. 2c illustrates the volume fraction dependence of the diffusivity D, that we estimate from the long time behavior $\langle r^2(t) \rangle = Dt$. We observe the diffusivity to decrease by three order of magnitudes following a Mode Coupling power law behavior $D \propto (\phi_c - \phi)^b$, with $\phi_c \simeq 0.81 \pm 0.01$ and $b = 2.8 \pm 0.02$.

Fig. 3 shows the decay of the persistence at different volume fraction. From this decay we have extracted the typical relaxation time, $p(\tau) = 1/e$, whose volume fraction dependence is illustrated in the inset. The relaxation time is well described by a power law functional form, $\tau(\phi) \propto (\phi_c - \phi)^{-c}$, with $\phi_c \simeq 0.81 \pm 0.01$ and $c = 2.6 \pm 0.02$. The critical volume fraction and the critical exponents describing the behavior of τ and that of D are compatible. This indicates that, despite the presence of a marked glassy dynamics, as apparent from the plateau observed in the mean square displacement at the highest investigated volume fraction, the system is still in the so-called mode–coupling regime.

3.2 Cage–jump dynamics

We now consider the temporal and spatial features of the cage–jump motion, and their volume fraction dependence. We start by considering the temporal features, summarized in Fig. 4. Panel a illustrates, for different values of the volume fraction, the distribution $F(t_p)$ of the time particles persist in their own cages before making the first jump after $t = 0$. This is of interest as directly related to the persistence correlation function, $p(t) = 1 - \int_{t_p=0}^{t} F(t_p)dt_p$[26–28]. Panel b illustrates the distribution $P(t_w)$ of the time particles wait in a cage between two subsequent jumps, i.e. the cage duration. In the continuous time random walk approximation[29], these two distributions are related by $F(t_p) \propto \int_{t_p}^{\infty} P(t_w)dt_w$. The two distributions are characterized by different average values, $\langle t_p(\phi) \rangle$ and $\langle t_w(\phi) \rangle$, whose volume fraction dependence is illustrated Fig. 4c, together with the volume fraction dependence of the relaxation time $\tau(\phi)$. We observe $\langle t_p(\phi) \rangle$ and $\langle t_w(\phi) \rangle$ to show a similar behaviour, and the persistence time to scale exactly as the relaxation time, consistently with the relation between $p(t)$ and $F(t_p)$ mentioned above. In the continuous time random walk description of the relaxation of structural glasses, the agreement between $\langle t_p(\phi) \rangle$ and $\langle t_w(\phi) \rangle$ implies the validity of the Stokes–Einstein relation, in agreement with our system being in the mode–coupling regime. As a further characterization of the temporal features of the cage–jump motion, we illustrate in Fig. 4d and e the probability distribution of the jump duration, $Q(\Delta t_J)$, which decays exponentially, and the volume fraction dependence of the average value $\langle \Delta t_J \rangle$, which decreases on compression. An exponential $Q(\Delta t_J)$ distribution has been also observed in model molecular glasses, but in that case the average value was found to be temperature independent[12]. Fig.s 4d,e offer us the opportunity to clarify that the elementary process identified with a jump has a finite duration, which in the present can be of the order of minutes. The use of the term ‘jump’, which suggests the presence of short–lived events, is only justified as the jump duration should be compared with the relaxation time of the system. For instance, in this work the ratio $\tau/\langle \Delta t_J\rangle$ increases from 2, at the smallest volume fraction with glassy features, to ≈ 250, at the highest volume fraction we have considered.

We finally consider that, at every instant of time, a particle is either caged or jumping. Accordingly, by observing the system for a time of the order of the ballistic time, which is the timescale considered by the protocol used to segment the trajectory in cages and jump, we can measure the density of jumps ρ_J. This equals the probability that a particle is jumping at a generic time t, and is therefore related to the fraction of the total time particles spend jumping,

$$\rho_J = \frac{\langle \Delta t_J\rangle}{\langle t_w\rangle + \langle \Delta t_J\rangle}. \qquad (2)$$

Fig. 4f shows that this equation is verified by our data. As mentioned above, as the dynamics slows down the jump duration becomes much smaller than the relaxation time, so that $\Delta t_J(\phi) \ll \langle t_w(\phi)\rangle$, and $\rho_J \simeq \langle t_w\rangle^{-1}$. We also note that in order to compute the r.h.s of the above equation one has to estimate $\langle t_w\rangle$: this requires to reliably sample the waiting time distribution $P(t_w)$, an operation accomplished on a time scale of the order of the relation time τ. Conversely the l.h.s. can be estimated on a small and density independent timescale of the order of $\langle \Delta t_J\rangle$, as the only requirement is to observe a finite number of jumps. As the density decreases, the ratio $\langle \Delta t_J\rangle/\tau$ decreases, which implies that we predict a long time feature from a short time analysis.

As a final characterization of the cage–jump motion, we have considered the jump length Δr_J, defined as the distance between the centers of mass of two adjacent cages, and the cage gyration radius $R_C = \sqrt{\langle r_i^2\rangle - \langle r_i\rangle^2}$, where the averages run over the trajectory points r_i belonging to a given cage. The probability distribution of the jump length, $W(\Delta r_J)$, and the volume fraction dependence of $\langle \Delta r_J^2\rangle$ are illustrated in Fig.s 5a and b. As in molecular systems[12] $W(\Delta r_J)$ decays exponentially, and its average value decreases as the dynamics slow down. We also observe the probability distribution of the gyration radius, $V(R_C)$, to decay exponentially, with an average value decreasing on compression, as illustrated in Fig.s 5c and d. Fig.s 5b and d show the presence of a separation of lengthscales in the dynamics, with the average jump length exceeding the average gyration radius of the cage by at least a factor 5 (at the highest investigated volume fraction). This complements the separation of timescales observed by comparing the cage and the jump duration.

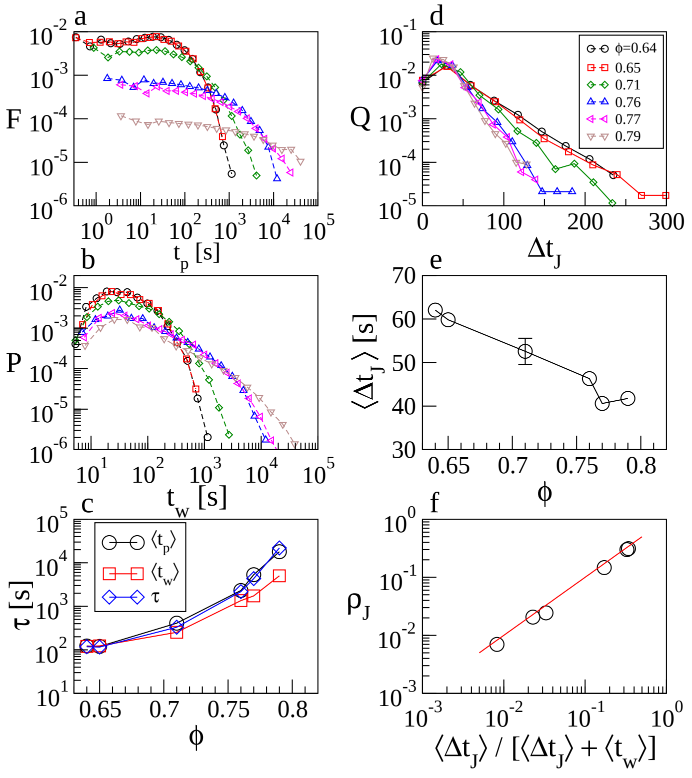

Fig. 4 Probability distribution of the persistence (a) and of the waiting time (b), and volume fraction dependence of their average values (c). Probability distribution of the average jump duration (d), and volume fraction dependence of its average value (e). Panel (f) show that the density of jumps is fixed by the average waiting time and by the average jump duration. In panel (f) the straight line is $y = x$; in all other panels lines are guides to the eye.

3.3 Relating glassy and cage–jump dynamics

The characterization of the features of the cage–jump motion allows to verify the main point of our work, namely the possibility of determining the macroscopic diffusivity from a short time analysis, through Eq. 1. We stress that this relation is only valid if jumps are irreversible events, as in this case particles behave as random walkers[12], and

$$D = \lim_{t\to\infty}\frac{1}{Nt}\sum_{p=1}^{N}[r_p(t)-r_p(0)]^2 = \frac{1}{Nt}\sum_{p=1}^{N}\theta_J^{(p)}(t)\langle\Delta r_J^2\rangle. \qquad (3)$$

The last equality is obtained considering that, at time t, the contribution of particle p to the overall square displacement is due to $\theta_J^{(p)}(t)$ jumps of average square size $\langle \Delta r_J^2\rangle$. The average number of jumps per particle, $\langle\theta_J(t)\rangle = \frac{1}{N}\sum_{p=1}^{N}\theta_J^{(p)}(t)$, appearing in the last equality can be also written as $\langle\theta_J(t)\rangle = t/(\langle\Delta t_J\rangle + \langle t_w\rangle)$. Using Eq. 2, $\langle\theta_J(t)\rangle$ and ρ_J can be related, $\langle\theta_J(t)\rangle = (\rho_J/\langle\Delta t_J\rangle)t$, which substituted in Eq. 3 finally leads to Eq. 1.

In Fig. 6 we compare the measured value of the diffusivity, with that predicted by Eq. 1. We find $D = m\rho_J\frac{\langle\Delta r_J^2\rangle}{\langle\Delta t_J\rangle}$, with m of the order of unity, in good agreement with the theoretical prediction. This suggests that, at least in the investigate volume

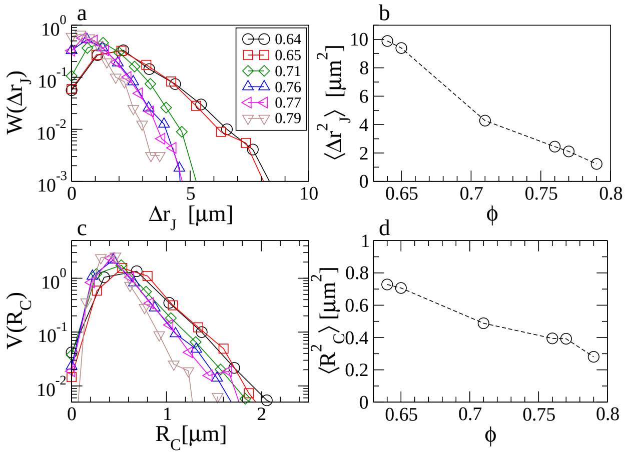

Fig. 5 Probability distribution of the jump length (a), and volume fraction dependence of its square average value (b). The same quantity are reported for the cage gyration radius in panel c and d respectively.

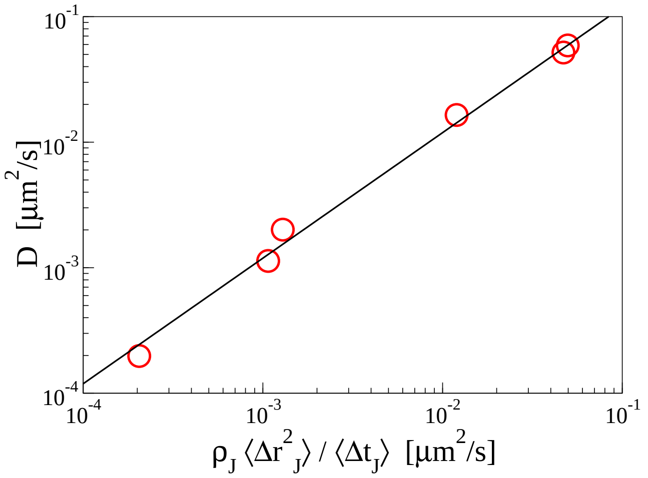

Fig. 6 Linear dependence of the diffusion constant on features of the cage–jump motion. The solid line is the prediction of Eq. 1, with a scaling factor $\simeq 1.2$. We stress that D is estimated at long times, while $\rho_J\langle\Delta r_J^2\rangle/\langle\Delta t_J\rangle$ is estimated at short times, well before the system enters the diffusive regime.

fraction range, jumps are irreversible events.

4 Discussion

Our experimental investigation proves that, in the considered volume fraction range, single particle jumps are the irreversible events that allow for the relaxation of hard sphere colloidal glasses. This allows for a short time prediction of the diffusivity. This result complements our earlier numerical study of a model molecular glass[12], where we also proved single particle jumps to be irreversible events. Indeed, we have found the same physical scenario to capture both the slow down of the dynamics of molecular glass formers, for which temperature is the relevant control parameter, and of colloidal glasses, for which density is the control parameter. This unifying approach is relevant considering that alternative approaches to describe the relaxation of molecular glasses, that identify irreversible events as transition in the energy landscape[14–16], are not relevant in hard–sphere colloidal systems.

Open questions ahead include the investigation of the validity of this approach at higher volume fractions, where the irreversible events might involve the rearrangement of many particles, as previously speculated[20,21]. In addition, it would be interesting to consider three dimensional systems, even tough we expect the dimensionality to play a minor role, both because structural glasses exhibit an intermittent single particle motion in both two and three dimensions, as well as because frustration effects, that might favor collective relaxation processes, are less relevant in high dimensions.

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