Two-Time Correlations for Probing the Aging Dynamics of Jammed Colloids

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We present results for the aging dynamics of a jammed 2D colloidal system obtained with molecular dynamics simulations. We performed extensive simulations to gather detailed statistics about rare rearrangement events. With a simple criterion for identifying irreversible events based on Voronoi tessellations, we find that the rate of those events decelerates hyperbolically. We track the probability density function for particle displacements, the van-Hove function, with sufficient statistics as to reveal its two-time dependence that is indicative of aging. Those displacements, measured from a waiting time \( t_w \) after the quench up to times \( t = t_w + \Delta t \), exhibit a data collapse as a function of \( \Delta t/t_w \). These findings can be explained comprehensively as manifestations of “record dynamics”, i.e., a relaxation dynamic driven by record-breaking fluctuations. We show that an on-lattice model of a colloidal system that was built on record dynamics indeed reproduces the experimental results in great detail.

A rapid quench of a colloid from a liquid state to densities well beyond the jamming transition initiates a far-from-equilibrium relaxation dynamics known as “physical aging” [1] or glassy relaxation. Understanding physical aging carries implications for many fields, from theories of complex systems [2] to manufacturing of packaging materials [3]. Glassy dynamics appear in granular media [4] and biological systems [5, 6], and have applications to food handling and drug design [7]. In aging, observables retain a memory of the waiting time \( t_w \) since the quench, signifying the breaking of time-translational invariance and the non-equilibrium nature of the state. For example, measures of the activity within the system taken over some time-window \( \Delta t = t - t_w \), such as the van-Hove distribution of particle displacements, are now a function of two time-scales, \( \Delta t \) and \( t_w \), instead of just the lag-time \( \Delta t \), as would be the case in a steady state. As has been observed previously [8–11], those distributions are characterized by broadened, non-Fickian tails that get broader with time \( \Delta t \), but each in a manner that is characteristic of its age. Those tails clearly emphasize the fact that anomalously large fluctuations in the displacement of particles drive the structural relaxation, which proves intimately related [12, 13] to the spatial dynamic heterogeneity as well as the temporal intermittency that have been observed in many experiments [8, 11, 14–22]. The dynamic events of interest are therefore rare and non-self-averaging, requiring many independent simulations of large systems to yield clear results. Further, examination of both short and long time scales requires both a high temporal resolution and long simulation runs. For these reasons, an experimental study of an aging colloidal system on two timescales with sufficient accuracy is a daunting task and has not been attempted yet.

In this Letter, we measure the two-time behavior of the fundamental van-Hove distribution of particle displacements during aging, provide a scaling collapse of the data, and comprehensively explain our observations in terms of the preeminence of intermittent, record-sized events. To this end, we reconstruct the setting of the simplest of such an experiment [20], a planar bi-disperse colloid quenched rapidly into a jammed state, as a molecular dynamics simulation. In our simulations we first reproduce previously published results of the experiment for mean-square displacements of particles in great detail. Using an equivalent criterion to identify irreversible relaxation events as in Ref. [20], we find in particular that the rate of such events declines with age as \( \sim 1/t \), shown also for the experimental data recently in Ref. [23]. Those results demonstrate that the simulation significantly extends the accuracy of the measurements by using a large number of instances. Then, we present results for the particle displacement distribution, i.e., the van-Hove function, that indeed reveal a dependence on both \( \Delta t \) and \( t_w \), indicative of aging. The distribution of displacements spreads out with increasing \( \Delta t \), as one would expect in any relaxing system. However, if \( \Delta t \) is fixed but \( t_w \) is increased, the distribution narrows, demonstrating the decreasing activity due to structural changes during aging. The data readily collapses as a function of \( \Delta t/t_w \) over a wide range of times. By the fundamental nature of the van-Hove function [24], this implies similar scaling in many other observables. We finally show that all of these results can be reproduced with a recently proposed lattice model [13] based on the simple fact that the relaxation dynamics requires ever larger (record-sized) fluctuations in the cluster of activated particles [2, 12, 25].

The simulations of the colloidal system are performed using the Python molecular dynamics package HOOMD-Blue [26, 27]. Each simulation contains 100,000 particles with periodic boundary conditions. The particles form a 50/50 bidisperse mixture with diameter ratio 1.4. Trajectories are computed using Newtonian integration with a harmonic repulsive interaction potential given by \( E(r_1, r_2) = \epsilon \left( |r_1 - r_2| - r_1 - r_2 \right)^2 \), where \( r_1 \) and \( r_2 \) are the positions of particles 1 and 2, and \( r_1 \) and \( r_2 \) are their radii. The simulation temperature and particle interaction strength \( \epsilon \) are chosen to make dynamic time and length scales comparable to previous work. In this manner, one simulation “second” corresponds roughly to one
second in the experiments of Ref. [20]. The simulations are run at 74\% packing fraction for 5 seconds, which is empirically found to equilibrate the system. Then the simulation box is rapidly compressed in 0.1 sec to a packing fraction of 84\%. We then record particle positions every 10^{-2} sec for 20 sec. This protocol is repeated for 10 independent realizations.

All particles in our simulations obviously experience many collisions during a simulation, most of which re-strain a particle to a local “cage” formed by the tight constraints its neighbors impose on its mobility [8]. After some time particles might spontaneously undergo a cooperative rearrangement. Such a rearrangement is noticeable in a single particle’s trajectory as a shift to a new position. It is noteworthy that the distance traveled to a new cage is usually within the normal range of in-cage rattling displacements, making the distinction between the two types of motion a subtle one. In fact, the difference in a particle’s position before and after a rearrangement can be less than 10\% of its diameter and only changes in the neighborhood topology (as detectable by a Voronoi tessellation, for example) may suffice to qualify such a displacement as irreversible (see below). Nevertheless, we argue that these spontaneous rearrangements are the mechanism responsible for aging in glassy systems.

Simulation results for the system-averaged mean squared displacement (MSD) starting from different waiting times are shown in Fig. 1(a). MSD is usually considered as a function of waiting time \( t_w \) and lag-time \( \Delta t = t - t_w \), as shown. The system demonstrates the typical plateau associated with caging, followed by diffusion on longer time scales as cages are escaped. The height of the plateau suggests a caging length scale between about 1\% and 10\% of a particle diameter. Beyond that, the dynamics is driven by activated events and the particles intermittently move > 10\% of a diameter. These ranges are consistent with the trajectories seen in Ref. [20]. We also see the plateaus getting longer with increased \( t_w \). For very early waiting times, the cages are so short-lived that there is no apparent plateau, but the growing caging time scale is still apparent as a shift in the diffusive part of the curve. It should be noted that the word “diffusive” is used loosely here. If the MSD curves were truncated earlier, then one could mistake the upturn in them for straight lines on a log-log scale, see Fig. 1(a). However, on longer time scales, the curves for the earlier waiting times begin to level off. We do not consider this as the approach to another plateau, but rather indicative of the nature of physical aging. If cooperative rearrangements are due to record-breaking fluctuations, and each rearrangement between \( t_w \) and \( t \) ratchets up the MSD, then the MSD increases roughly logarithmically with \( \Delta t \) [13, 23], as explained via Eq. (2) below. This expectation is verified by Fig. 1(b), which shows the exact same MSD data collapsed when plotted as function of log \((t/t_w)\).

Measurement of the rate at which cooperative rearrangements occur requires some sort of discretization of the system dynamics. The distribution of particle displacements itself does not easily allow for discrimination between caged and rearranging particles. As we will discuss below that distribution is characterized by a Gaussian core at shorter distances and an exponential tail further out, with merely a gradual transition between them, see Fig. 3. The exponential tail has been attributed to rearranging particles, but may also be due to heterogeneity in cage sizes [28]. These facts make rearrangement detection based on particle displacements dubious. However, subtle changes in the configuration can be detected by considering changes among neighboring particles. To that end, the radical Voronoi tessellation is computed for each frame of six simulations using the C++ library
Voro++ [29]. A history is constructed of every pair of particles which are neighbors at any point in the simulation. For each neighbor pair, the first frame of the simulation in which that pair are neighbors is also recorded. In this manner, a particle which never rearranges in the entire simulation would have roughly six "new" neighbors in the first frame, then none for the rest of the simulation. When a rearrangement occurs, the Voronoi tessellation changes, and a few particles encounter new neighbors. Reversible in-chage fluctuations might create flickering Voronoi networks, but these changes can be shaken out in a few frames by only counting the first contact with a neighbor. Not all particles in a rearranging region will make new contacts, and some rearrangements send particles back to old neighbors, but as long as a consistent fraction of rearranging particles encounter new neighbors, a count of the new neighbors in a given frame is a reasonable measure of the rearrangement event rate.

For their particle tracking experiments, Yunker et al [20] also defined irreversible neighborhood swaps that were shown to decay with time after the quench. Simply binning their data logarithmically, it was shown in Ref. [23] that the experimental rate of those events decays with age in a manner that is consistent with \( \sim 1/t \). Using the Voronoi method described above, we determine the corresponding event rate in the simulations to find a perfect match with that experimental data, as seen in Fig. 2. Moreover, due to the ability to rerun the simulation many times, the decay in the rate appears to be hyperbolic to a high degree of statistical significance.

Going beyond mere comparisons with existing experimental results, we can now use our simulation to study two-time correlations that are difficult to access with sufficient accuracy in experiments. For example, in Fig. 3 we show results for the single-axis particle displacement distribution over a time-window \( \Delta t \) starting at \( t_w \):

\[
G_s (\Delta x, t_w, \Delta t) = \sum_i \delta (|x_i (t_w + \Delta t) - x_i (t_w)| - \Delta x),
\]

also known as the self-part of the van Hove function [24]. In our simulations, for \( \Delta t < 10^{-3} \) sec (not shown), few collisions have occurred, so the distribution of displacements would be largely due to the distribution of particle velocities. On intermediate time scales, \( \Delta t \approx 10^{-2} \) sec, the distribution is determined by the cage size distribution. On longer time scales, the distribution begins to spread out, as previously observed in similar simulations in Ref. [10, 30], for example. In Fig. 3(a) for \( t_w \approx 1 \) sec, this spreading begins at around \( .1 \) sec, but the spreading begins later with increasing \( t_w \).

Note that \( G_s \) in Fig. 3 exhibits exponential "non-Fickian" tails, beyond the dominant Gaussian fluctuations at short distances, that signify rare intermittent behavior, similar to observations in spin-glass simulations [31–33]. It has been measured previously in various colloidal experiments and simulations [8–11, 28, 34, 35], but averaged over long time intervals that blend together various waiting times \( t_w \). While the shape of \( G_s \) is generally invariant, the weight of this tail increases with \( \Delta t \), but it decreases with age \( t_w \), since activated cage rearrangements become increasingly harder. Amazingly, all data collapses when the time-window \( \Delta t \) is rescaled by the age \( t_w \). Similar to the analysis of the MSD in Fig. 1(b), by scaling the lag time with the waiting time, we should observe the same number of rearrangements for any given \( \Delta t/t_w \), if the rearrangements correspond to record breaking fluctuations. In Fig. 3, two collections of curves are plotted accordingly, one set with \( \Delta t/t_w = 1 \), and another with \( \Delta t/t_w = 5 \). Note that many common dynamical observables, such as MSD or the self-intermediate scattering function (and, thus, the persistence [10, 13, 23]) can be calculated from the van Hove function [24]. In demonstrating the collapse of \( G_s \), we have shown that all measures involving averages over single-particle displacements would collapse similarly. The collapse of these curves suggests that the dynamics of this aging system is driven by record-sized fluctuations: if \( \Delta t \ll t_w \), quasi-equilibrium in-cage rattle dominates while rare, intermittent and irreversible cage-breaks encountered for \( \Delta t \gtrsim t_w \) drive the actual non-equilibrium relaxation process. As these break-ups require record-sized fluctuations that decelerate with \( \sim 1/t \), the statistics is invariant for \( \Delta t/t_w \), as the following considerations explain.

In the experiment and simulations, anomalously large cage break events are found to substantially relax the system and must be viewed as distinct from the Gaussian fluctuations of in-cage rattle. Yet, such a relaxation must entail a structural change, which makes subsequent relaxations even harder. For example, to facilitate a cage-break, Yunker et al [20] observed that a certain number of surrounding particles have to conspire via some rare, random fluctuation. For that event to qualify as irreversible, the resulting structure must have increased stability, however marginal. A following cage-break thus requires even more particles to conspire. With each of those fluctuations exponentially unlikely in the number of participating particles [35], cage-breaks represent records in an independent sequence of random events that "set the clock" for the activated dynamics. In such a statistic, record events are produced at a decelerating rate of \( \lambda(t) \propto 1/t \), consistent with the results in Fig. 2. As those records do not cause each other, we obtain a log-Poisson statistics, for which the average number of intermittent events in an interval \( t_w < t < t_w + \Delta t \) is

\[
\langle n_I (\Delta t, t_w) \rangle \propto \int_{t_w}^{t_w + \Delta t} \lambda(\tau) d\tau \propto \ln (1 + \Delta t/t_w),
\]

which explicitly depends on the age \( t_w \). Then, any two-
To verify that record-breaking fluctuations are sufficient to produce the observed dynamics, we also apply our analysis of the van Hove function to a simple course grained model. We examine the recently proposed cluster model of aging [13], which forgoes the simulation of microscopic dynamics, and places particles on a lattice. Each particle belongs to a cluster, and clusters are contiguous, non-overlapping, and space filling. In every update, a cluster of size $h$ has $P(h) \propto e^{-h}$ chance to break into $h$ single-particle clusters. If $h = 1$ already, then the updating particle swaps position with a random neighbor while also joining its cluster. In this manner, when a cluster breaks up, it’s neighboring clusters spread rapidly over its territory in a series of such smaller displacement and attachment events. The number of clusters thereby decreases by one, and the average cluster size increases marginally [38], slowing the system dynamics.

Within clusters, fast dynamics (“in-cage rattle”), perceived as leading to the re-arrangements preceding a cluster break, are intentionally coarse-grained out, with their collective effect replaced by $P(h)$. As shown in Ref. [13], cluster-breaking events indeed decelerate as $\sim 1/t$, comparable to Fig. 2, and follow the log-Poisson process in Eq. (2). With particles re-mobilizing only when activated by a cluster break, their mean-squared displacement (MSD) grows indeed logarithmically with time, similar to Fig. 1, i.e., proportional to the accumulated number of those events in Eq. (2). Following the definition in Eq. (1), we have measured $G_s$ for displacements of particles in the cluster model. Fig. 4 shows that this data reproduces the $\Delta t/t_w$-collapse for the van Hove distribution of particle displacements found in the molecular dynamics simulations.

In future simulations, we intend to analyze the effect on aging of varying the density attained after a quench. As in the experiments, we expect that those variations (above a certain threshold of about 81%) will merely af-
fect some pre-factors numerically without changing the log-Poisson characteristic of the aging [23]. The corresponding variation in the cluster model is achieved by varying the exponential in $P(h)$, which affects each observable there. Finding a response to such variation that is equivalent for all observables between cluster model and molecular dynamics simulation provides a substantial test for the record dynamics interpretation.

We like to thank Paolo Sibani and Eric Weeks for many enlightening discussions, and Justin Burton for computational resources.

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