Dynamics of dense hard sphere colloidal systems: A numerical analysis

Paolo Sibani and Carsten Svaneborg

Department of Physics, Chemistry, and Pharmacy, University of Southern Denmark, Campusvej 55, DK5230, Odense M, Denmark

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The applicability to dense hard sphere colloidal suspensions of a general coarse-graining approach called Record Dynamics (RD) is tested by extensive molecular dynamics simulations. We reproduce known results as logarithmic diffusion and the logarithmic decay of the average potential energy per particle. We provide quantitative measures for the cage size and identify the displacements of single particles corresponding to intermittent cage breakings. We then partition the system into spatial domains and show that, within each domain, a subset of such intermittent events called quakes constitutes a log-Poisson process, as predicted by RD. Specifically, quakes are shown to be statistically independent and Poisson distributed with an average depending on the logarithm of time. Finally, we discuss the nature of the dynamical barriers surmounted by quakes and link RD to the phenomenology of aging hard sphere colloids.

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I. INTRODUCTION

Hard sphere colloidal suspensions (HSCs) are a paradigmatic and intensively investigated complex system [1–8], featuring two different dynamical regimes [8]: a time translationally invariant diffusive regime below a critical volume fraction and, above it, an aging regime, where time homogeneity is lost. Here the particle mean-square displacement (MSD) grows at a decelerating rate through all experimentally accessible timescales.

Coarse-graining nonequilibrium processes as the above usually requires the identification of the degrees of freedom and/or key dynamical events which control the system evolution. A natural starting point in glassy dynamics is spatial heterogeneity, the fact that only a small fraction of the system’s particles is dynamically active in any observational time interval [9]. The dichotomy between active and inactive (or “fast” and “slow”) particles is demonstrated in Ref. [9] by direct trajectory inspections and by measuring the self part of the Van Hove distribution, where the fast particles produce an exponential tail. In glass formers [10] the two different types of motion are reversible “in-cage rattlings,” where a particle moves reversibly within the small region bounded by its neighbors, and “cage breakings,” where it performs larger displacements which alter its neighborhood relations. Cage rattlings are overwhelmingly the most frequent events, but since they are not associated to a net translation, diffusive spreading in glass formers [10] and diluted colloidal systems is caused by the much rarer cage breakings. The latter hence carry the configurational evolution of the system and are key elements in coarse-graining their dynamics.

Cage breakings have been modeled [11,12] using a continuous-time random walk (CTRW) [13], a popular coarse-graining device recently criticized in Refs. [14,15]. Other approaches to coarse graining are, e.g., synergetics [16], self-organized criticality [17], and Record Dynamics (RD) [18–20]. The last posits that the decelerating evolution of a variety of complex dynamical systems, aka “aging,” is controlled by increasingly rare nonequilibrium events termed “quakes.” In RD, the physical appearance of a quake is system dependent [21–26], but quaking is in all cases described as a log-Poisson process, i.e., a Poisson process where the number of events expected between times $t_w < t$ and $t$ is proportional to the “log-waiting time” $\ln t - \ln t_w = \ln(t/t_w)$.

Diffusion in HSCs has attracted both experimental [1–5] and computational [6,7] work, but “logarithmic diffusion” in dense HSCs is not yet widely acknowledged. That the particles’ MSD grows with the logarithm of time was observed [24] in a reanalysis of three-dimensional (3D) confocal microscopy data by Courtland et al. [2], a behavior fully confirmed by the present data (see Fig. 1).

Accompanied by theoretical analyses and model calculations [24,27], these observations promote RD as a coarse-grained description of aging dynamics in HSC systems. The validity of the RD description was further supported by the analysis [28] of experimental two-dimensional (2D) data provided by Yunker et al. [29] and by a recent molecular dynamics (MD) study of a 2D colloidal system [30] which confirms two related RD predictions: (1) the rate of quakes is inversely proportional to time and (2) the particles’ MSD grows logarithmically in time. These results are presently extended by explicitly showing the Poisson nature of the quake statistics in a 3D dense colloidal suspension.

To summarize, the phenomenology of glass formers and aging HSCs is experimentally [1,2,4,5,7,29] and numerically [3,6,9,10] well described, but a unified theoretical description [11,12,28] is not yet available. RD has been proposed [15,24,28] as a viable candidate, and its validity is investigated in the present work by extensive MD simulations of 3D HSCs which extend over six orders of magnitude in time. We first provide a macroscopic characterization of the dynamics in terms of particle MSD and potential energy, and compare with homologous results [6]. We then proceed to investigate single-particle jump statistics and find a quantitative measure of the cage size and the length distribution associated with cage-breaking jumps. The information is used to identify
The interaction between colloids is modeled by the steeply repulsive potential between them is
\[ U(r_{ij}) = \epsilon \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{36}, \]
where we take \( k_B = 1 \) such that \( \epsilon \) is our unit of both energy and temperature. The distance between a pair of particles is denoted \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \), while the length scale of the repulsive potential between them is \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \), where \( \sigma_i \) denotes the diameter of the \( i \)th particle. To avoid crystallization, we choose diameters from a uniform distribution \( \sigma_i \in [\sigma - \Delta \sigma, \sigma + \Delta \sigma] \), where \( \sigma \) is our unit of length and \( \Delta \) is the dimensionless width of the distribution. Finally, all colloidal particles have a mass \( m \), which we choose as our unit of mass. From the definition of energy, length, and mass, the formal definition of the simulation unit of time is \( \tau = \sigma \sqrt{\epsilon/m} \). This is the characteristic time it takes an isolated particle to move its own diameter with ballistic motion at thermal speed. We note that while mapping most of our units (and hence results) to experimental data is straightforward, mapping of timescales should not be done using the formal definition, since the latter has no physical relevance for glassy colloids. Time should rather be mapped by matching emergent dynamical properties such as the diffusion coefficients observed in experiments and simulations.

Colloidal simulations were performed in the NVT ensemble at temperature \( T = \epsilon/3 \) as in Refs. [6,31]. Our systems comprised \( N = 50,000 \) colloidal particles in a cubic box with periodic boundary conditions. The system volume was determined based on the desired target volume fractions \( \phi \) resulting in box sizes larger than \( 34\sigma \). Hence we do not expect any finite-size effects in our data. We choose \( \Delta = 0.2 \) corresponding to a 11.5% polydispersity index [6], since we observed crystallization when using \( \Delta = 0.1 \) as in Ref. [31]. Taking the polydispersity average, the volume fraction is given by \( \phi = \pi \rho \sigma^3 [1 + \Delta]/6 \).

We have simulated volume fractions \( \phi = 0.5, 0.575, 0.590, 0.605, 0.620, 0.633, 0.647, \) and 0.662. The glass transition is expected at \( \phi_c \approx 0.620 \), hence we have seen dynamical behavior ranging from simple time homogeneous diffusion to aging dynamics. During the simulations, we continuously monitored the local orientational order parameters [32] to ensure the system did not spontaneously crystallize. For each glassy system we ran two statistically independent replicas up to times in excess of \( 10^6\tau \times (4 \times 10^8 \text{ integration steps}) \). We choose velocity rescaling as a thermostat due to its computational efficiency. Particle velocities were rescaled every 0.25\( \tau \), while the linear and angular momenta of the whole system were reset every 1000\( \tau \) to prevent flying ice-cube effects [33]. The dynamics was numerically integrated using velocity Verlet with time step \( \Delta \tau = 0.0025\tau \) using a customized version of the Large Atomic Molecular Massively Parallel Simulator [34]. Each glassy system required about 60 days of continuous simulation time on a 24 core computer node [35]. The total computational effort of the simulations reported here is approximately 36 core years.

A. System preparation

In the experimental colloidal systems of Yunker et al. [29], soft NIPA microgel particles shrink in size under optical heating. The particles then rapidly swell when the heating is turned off, and if the initial volume fraction is sufficiently high, they reach a volume fraction above the critical value where time homogeneity is lost. In this way, glassy dynamics with a well-defined initial time can be observed experimentally.

To mimic the preparation of experimental glassy colloidal systems, we insert \( N \) mono-disperse (\( \sigma = \bar{\sigma} \)) colloids in the simulation box at random positions and minimize the energy to eliminate particle overlaps. Each particle has an integer tag \( i = 1, \ldots, N \). To quench the system, we assign a unique size given by \( \sigma_i/\sigma = 1 + \Delta(2/N - 1) \) to each particle. This prevents any statistical correlation between the spatial position and the size of the particles and furthermore prevents system-to-system variation due to different realizations of finite-sized samples taken from the size distribution.

The quenched polydisperse configuration will have strong overlaps between particles and cannot be used as initial state, since the numerical integration would be unstable due to excessively large forces. On the other hand, minimizing the energy could, in principle, lead to arbitrary large configurational reorganizations, which would blur the definition of the time elapsed from the initial quench. Hence inspired by the experimental procedure, we run a short simulation with a Langevin thermostat with a very high friction of \( \Gamma = 50m\tau^{-1} \) and a numerical integrator that maximally displaces a bead by 0.05\( \sigma \) during one time step. During a very short simulation lasting 2\( \tau \) or equivalently 800 integration steps, all overlaps are removed and the distribution of the particles’ velocities, but definitely not of their positions, is concomitantly
thermalized to the target temperature. The postquench system state thus obtained defines age zero for the subsequent data production run. The procedure just described is followed for all the volume fractions investigated.

III. SYSTEMIC PROPERTIES

The MSD and the potential energy versus time are both systemic properties obtained by averaging observables over all particles. Specifically, the data shown are obtained as follows: a set of logarithmically equidistant points is placed on the time axis, and, for each particle, the MSD or potential energy values falling in each of the corresponding intervals are time averaged and assigned to the midpoint of the interval. The values thus obtained are then averaged over all particles, and a final average is carried out over the outcomes of two independent simulations. These outcomes are, however, already practically indistinguishable at the resolution level of our figures.

The same repulsive interaction and size polydispersity are used as in Ref. [6], but our systems contain 50 000 rather than 500 and 4000 particles, and we follow them for one more decade of simulation time. Finally, as explained in the previous section, our system is not initially compressed as theirs. Instead, the particle sizes are initially inflated to achieve the desired volume fractions. We note for clarity that our time \( t \) is the system age, which is denoted by \( t_w \) in Ref. [6], a symbol we here reserve for expressions having two time arguments.

For several values of the volume fraction \( \phi \), the evolution of the MSD is plotted versus time in Fig. 1 using a logarithmic abscissa. The lowest volume fraction, \( \phi = 0.575 \), produces standard diffusive behavior, as shown explicitly in the insert. For all other volume fractions, the MSD grows, after a short transient, as the logarithm of time for more than four decades of simulation,

\[
\text{MSD}(t) = D_{\ln}(\phi) \ln(t/\tau),
\]

where \( \tau \) is the smallest time unit in the simulation. For similar results, see Refs. [24,30].

In the following, times will always be measured in units of \( \tau \), and the symbol will be omitted from the notation. The logarithmic rate of diffusion \( D_{\ln}(\phi) \) decreases monotonically with increasing volume fraction \( \phi \), and its values are well fitted with two free parameters by the function \( y(\phi) = 0.835(\phi - 0.603)^{-1} \times 10^{-3} \). With two parameters to four data points, the evidence the above expression provides is only anecdotal. Nonetheless, the divergence it features at \( \phi_0 \approx 0.603 \) correctly detects the presence of an upper limit to the validity of the logarithmic diffusion regime. Finally, even though the MSD data shown in Fig. 1 are rather well fitted by logarithms, the small deviations from the fit, best seen for \( \phi = 0.620 \), have a systematic character which we do not attempt to explain.

Figure 2 shows the time decay of the potential energy per particle, averaged over all particles. After a short initial transient \( t \sim 20\tau \), the decay is seen to be a linear function of the logarithm of time. The initial value of the potential energy increases, as expected, with increasing \( \phi \). Finally, the logarithmic rates of change of the potential energies are, in order of increasing \( \phi \), \([-5.8; 5.9; 6.3; 7.9] \times 10^{-3} \). The clear growing trend can be contrasted with the decreasing trend of the logarithmic “diffusion” coefficient \( D_{\ln}(\phi) \). This implies that the physical effect of a particle rearrangement grows with growing density. Taken together, our observations suggest logarithmic time as a natural variable for describing the dynamical evolution of systemic properties of glassy systems.

Qualitatively, the data in Ref. [6] concur with ours as far as the age decay of the potential energy per particle is concerned. Note however that two different types of fit of comparable quality are offered in Ref. [6] for the asymptotic form of the decay, none of which is identical to our simple logarithmic decay. In their Fig. 4, the particle MSD is plotted versus the time lag \( \tau \) spent after waiting time \( t_w \), which is the traditional choice in studies of aging dynamics.\(^1\) It is nevertheless clear from the same figure that the MSD grows logarithmically as a function of \( \tau \) if \( \tau \gg t_w \), i.e., when time and lag time can be identified. Finally, the figure’s inset shows that the power-law fits of the MSD versus lag time are based on data which only little more than one decade. Since the exponent of the subdiffusive MSD growth is itself a function of the age (see their Fig. 5), the subdiffusive behavior observed in Ref. [6] cannot be simply described as a power law.

IV. DISPLACEMENT STATISTICS

In this section, the “cage size” is extracted from the central part of the Van Hove function, the age dependence of its exponential tails is analyzed, and the length distribution of the associated “long jumps” is shown to be age independent.

The distribution of single-particle displacements, aka the self part of the Van Hove function, was investigated in Ref. [6] for a number of time lags after a fixed waiting time \( t_w \). The results, shown in their Fig. 6, can be summarized as follows:

\(^1\)To avoid notational confusion, we stress that our symbol \( \tau \) stands for the simulation unit of time and not for the lag time, except for one paragraph of the final section.
The distribution has a central Gaussian part of zero mean, whose shape depends only weakly on the lag time. Large displacements of both signs are described by exponential tails, whose weight increases with increasing lag time.

Our analysis is patterned on the method introduced in Ref. [36] to describe heat transfer in a spin-glass model, and its results concur broadly with those of Ref. [6] and precisely with those of a more recent simulational study of 2D HSCs [30] which obtains a data collapse by scaling the lag time with the system age, as we presently do.

The probability density function (PDF) of displacements $\Delta x$ occurring over a short time interval $\Delta t$ (lag time) for given values of the system age $t_w$ is written as

$$G_{\Delta s|t_w,t} (x) = \sum_i \delta [x_i(t_w) - x_i(t_w + \Delta t) - x],$$

which is normalized over all values of the dummy variable $x$. Specifically, $G$ is sampled by collecting all positional changes $x_i(t_w + \Delta t) - x_i(t_w)$ occurring at age $t_w$ over time intervals of duration $\Delta t$, i.e., in the interval $I(t_w) = (t_w, t_w + \Delta t)$.

To improve the statistics, spherical and reflection symmetry is used (1) to merge the independent displacements in the three orthogonal directions $x, y, z$ into a single file, representing a fictitious “$x$” direction, and (2) to invert the sign of all negative displacements. Compatibility with the requirement $\Delta t \ll t_w$ needed to associate $G$ with a definite age $t_w$, a $\Delta t$ much larger than the mean time between collisions is preferable, as it accommodates many in-cage rattlings. We note in passing that in the opposite limit the particles move in near ballistic fashion and that their displacements inherit the Gaussian distribution of the components of their velocities.

Figure 3 depicts PDFs of single-particle displacements in a colloid of volume fraction $\phi = 0.620$. Small displacements have an age-independent Gaussian PDF, corresponding to the staggered line, while larger displacements strongly deviate from Gaussian behavior, as already seen in Fig. 6 of Ref. [6]. The displacements occur over short time intervals of length $\Delta t \ll t_w$ and are sampled in three longer observation intervals of the form $[t \pm 1.1r]$ where time values $t = 2 \times 10^4 r, t = 8 \times 10^4 r$, and $t = 8 \times 10^5 r$ were chosen. (We recall that $r$ is our simulational time unit.) Since the length of these intervals is only a tenth of the time at which observations commence, aging effects occurring during observation can be neglected and $t$ can be identified with the system age, i.e., $t_w \approx t$. In Fig. 3(a) a single value $\Delta t = 100 r$ was used for all data sampling, while in Fig. 3(b) values proportional to the system age, $\Delta t = 100, 400, 4000 r$ were used.

That the central part of $G_{\Delta s|t_w,t}$ is a Gaussian distribution with zero mean indicates that displacements of small length arise from many independent and randomly oriented contributions, which stem from multiple in-cage rattlings. The typical size of the cage can then be identified with the standard deviation of the Gaussian part of the PDF, which is seen to be independent of age. The Gaussian standard deviation of the data is estimated to be $\sigma_G = 0.05\sigma$ and the “cage width” $c_w$ defined as the standard deviation of the 3D Gaussian displacement PDF is $c_w = \sqrt{3\sigma_G} = 0.086\sigma \approx 0.1\sigma$. Recall that $\sigma$ is the average particle diameter. This result concurs...
with the estimate obtained from 2D simulations [30], which suggest “a caging length between about 1% and 10% of a particle diameter.”

The exponential tail is then produced by cage breakings, i.e., displacements well beyond the cage size. The weight of the non-Gaussian tail seen in Fig. 3(a) is seen to decrease with increasing age while the length distribution of displacements of length exceeding 0.5σG is seen in Fig. 4 to be exponential and age independent. Figure 3(b) shows that scaling Δt with the age tw reasonably collapses the data. The same effect is obtained in Ref. [30] for 2D colloidal suspensions and for other values of the ratio Δt/tw.

RD explains the observed scaling behavior by assuming that the non-Gaussian tail of G stems from quakes, which, as shown later, are log-Poisson distributed. Taking that for granted, the average number of quakes occurring in an arbitrary time interval (t1, t2) is proportional to ln(t2/t1) and, in our case, proportional to ln(1 + Δt/tw) ≈ Δt/tw. Replacing the (small) crossover region between Gaussian and intermittent fluctuations by a sharp boundary, we let G(x) be a truncated Gaussian PDF, normalized within the cage, and let E(x) be the PDF of the intermittent events, normalized in the semi-infinite interval outside the cage limit. With this notation, the probability density for an event of size x is given by

\[ G_{Δt/τ_0, Δt}(x) = G(x) + \frac{Δt}{τ_0} E(x) \left(1 + \frac{Δt}{τ_0}\right)^{-1}. \]  

Choosing, as we did, Δt = cτw, c ≪ 1 leads to

\[ G_{Δt/τ_0, Δt}(x) \approx (1-c)G(x) + cE(x) \approx G(x) + cE(x). \]  

Since, as confirmed below, E(x) is independent of τw, the observed data collapse follows from our choice of Δt ∝ τw.

The empirical distribution E(x) of the length of the “long” jumps associated to cage breakings, is sampled in two widely separated time intervals and depicted in Fig. 4 for volume fraction φ = 0.620 together with a one-parameter data fit. The latter shows that E(x) is exponential and effectively age independent, as already assumed in Eq. (4). The empirical standard deviation of the jump length is in this case σq = 0.545σδ, where σ is the average particle diameter. Note that σq is an order of magnitude larger than the standard deviation σG describing in-cage rattling. The other investigated volume fractions, φ = 0.633, 0.647 and φ = 0.662, show the same overall behavior, and the corresponding jump length standard deviations, σq = 0.544, 0.543, and 0.541σ, show a small but systematic decrease with increasing volume fraction.

Summarizing, our analysis of the self part of the Van Hove function indicates that cage breakings occur at a rate which decreases with the inverse of the system age; see Refs. [28,30] for corroborating experimental and simulational evidence. Consequently, the number of these events increases logarithmically with time. Since cage rattlings do not contribute to the particle diffusion, the result explains the observed logarithmic diffusion. The next section provides fuller evidence for RD and for the logarithmic nature of HSC diffusion.

V. QUAKE STATISTICS AND RECORD DYNAMICS

A comparative discussion in Ref. [14] highlights that while CTRW and RD predictions might in some cases be superficially similar, the physical picture behind them is very different: in CTRW the system visits a succession of identical traps, each lacking a finite average trapping time; in RD all trapping times have a finite average, but the traps visited gradually deepen as the system ages.

That the rate of irreversible rearrangements in HSCs decreases with the inverse of the system age was noticed by the authors of Ref. [28] in previously published experimental 2D data [29] and was later confirmed by 2D MD simulations [30]. As discussed in Ref. [15], these observations already clash with CTRW descriptions. Here additional statistical evidence in favor of RD is obtained by extracting irreversible dynamical events called quakes, and showing that they are statistically independent, homogeneously distributed on a logarithmic time axis and described by an exponential distribution of the “logarithmic waiting times” ln τk − ln τk−1, where τk is the time of the kth quake. Together, these properties imply that quaking is a log-Poisson process, i.e., a Poisson process whose average has a logarithmic time dependence. The Poissonian nature of the process (1) guarantees the correct system size scaling of the number of quakes, (2) demonstrates a finite, albeit growing, average trapping time, and (3) is conspicuously absent in CTRW descriptions.

The key step of quake identification in a given setting has some leeway, but, as we argue below, in spatially extended systems spatiotemporal correlations play a major role. The existence of spatial domains, a property which reflects the strong spatial heterogeneity of glassy dynamics [9], is required in a RD description of aging systems.

Spatially extended aging systems of size N [18] contain an extensive number α(N) ∝ N of equivalent spatial domains such that events occurring in different domains are statistically independent. Events occurring in the same domain have long-lived temporal correlations, which are formally removed in RD by the global variable transformation t → ln t. If this device works, the total number of quakes occurring in the system between times τw and t > τw is a Poisson process with average

\[ \mu(t, τw) = α(N)r_q \ln(t/τw), \]  

where r_q is the average logarithmic quake rate in each domain. The number of quakes is extensive and grows at a constant rate in log time and at a rate proportional to 1/t in real time. Within each domain, the rate r_q can be read off the log-waiting time PDF F_{Δln(t)}(x) = r_q e^{-xe^{-c}}, i.e., the probability density that the log-waiting time to the next quake equals x.

To ascertain the applicability of the above RD scheme in a specific system, the log-waiting times between successive quakes within each domain, d ln τ = ln τk − ln τk−1, are formed and their statistical properties are checked: specifically, log-waiting times must be independent and identically distributed stochastic variables uniformly distributed on a logarithmic time axis, as shown in Fig. 5(a). Second, the PDF of the log-waiting time must be exponential, as shown in Fig. 5(b). Figure 6 shows that the logarithmic quake rate decreases linearly with increasing volume fraction, as also expected from the MSD data shown in Fig. 1.

To see why a domain structure is inherently part of the RD description of a system of N degrees of freedom, assume for a moment that domain partitioning can be neglected. The time lags δk between successive quake times then decrease...
FIG. 5. (a) Logarithmic waiting times \( \Delta \ln t_k = \ln t_k / t_{k-1} \), where \( t_k \) is the time of the \( k \)th cage breaking are observed in small domains of the simulation box and plotted, on a log scale, vs the time at which they are observed. Only data with \( \Delta \ln t_k > 0.4 \) are included. The yellow circles are local binned log-time averages of these data, and the line is the average logarithmic waiting time. That local averages are nearly independent of log-time is evidence that the transformation \( t \to \ln(t) \) renders the dynamics log-time homogeneous. (b) The PDF of the log-waiting times is estimated and plotted for two independent sets of simulational raw data, using yellow square and cyan diamond symbols, respectively. The line is an exponential fit to both estimated PDFs. The insert shows the normalized autocorrelation function of the sequence of logarithmic waiting times corresponding to the yellow square PDF. To a good approximation, the log-waiting times are uncorrelated and their PDF decays exponentially, which implies that quaking is a log-Poisson process. The volume fraction of the system is \( \phi = 0.620 \).

with increasing \( N \), and, since \( d \ln t_k \overset{\text{def}}{=} \ln(t_k / t_{k-1}) = \ln(1 + \delta_k / t_{k-1}) \approx \delta_k / t_{k-1} \), the “log-waiting times” can never be log-time homogeneous in the limit \( N \to \infty \). The latter property clearly requires \( \delta_k \propto t_k \), which is incompatible with \( \delta_k \propto N^{-1} \). In contrast, if the dynamics is time translational invariant, \( \ln(t / t_w) \) in Eq. (5) is replaced by \( t - t_w \) and the prefactor to \( r_q \) is \( N \), no matter how the system is partitioned.

Usually, only a minuscule fraction of configuration space is explored during an aging process, and many variables do not participate in any quake. Hence, the domain size can grow in time with no changes in \( \alpha(N) \), which is best understood as the number of active domains where quake activity occurs.

A statistical analysis of domain size and domain growth is an important issue not presently considered. In the present work, the simulation box is simply subdivided into \( 16^3 \) equal and adjacent subvolumes, each containing, on average, slightly more than 10 particles. The size was chosen self-consistently as the largest possible size yielding log-time homogeneous quake statistics. Many subvolumes in the partition had no quaking activity, showing the strong spatial heterogeneity of the HSC dynamics.

VI. SUMMARY AND DISCUSSION

In this study, large 3D polydisperse hard sphere colloidal systems (HSCs) are studied by extensive MD simulation. The initial state is generated by a sudden expansion of the particles’ volume, leading to volume fractions \( \phi \) both below and above the critical value. The systems’ development is subsequently followed for more than six decades in time.

At the systemic level our analysis concerns the growth of the particles’ MSD and the decay of their potential energy as a function of time, both shown to be simple functions of the logarithm of the system age above the critical density. At least for the MSD, this concurs with similar results, both experimental [24] and numerical [30], but apparently differs from the more usual [6] description in terms of power laws.

At the level of single-particle displacement, we study the self part of the Van Hove function and confirm [6,9] that cage rattlings and cage breakings have a Gaussian and exponential length distribution, respectively. We find that both distributions are age independent, and that the weight of the exponential tail is a function of the ratio of the lag time and the system age. This extends a result recently obtained [30] for a 2D HSC system and is akin to the behavior of heat transfer in a spin glass model [36].
We note that one-time averages, e.g., the MSD and the potential energy per particle, are most naturally described in terms of a single time variable $t$, i.e., the time elapsed from the quench into the glassy phase. Experimentally, the time origin can be difficult to determine, and a description in terms of two variables, conventionally age $t_w$ and lag time $\tau \equiv t - t_w$, is generally preferred. (For notational convenience, our symbol $\tau$ is here redefined and used for the lag time.) We have shown that MSD per particle has the form $\text{MSD}(t) = D_0 \ln t = \ln(t_w + t)$, which grows first linearly in $\tau$ and than crosses over to a logarithmic growth. This is seen in Fig. 4 of Ref. [6], but their data are there fitted by several power laws with age-dependent exponents; see Eq. (10) and Fig. 5 of the same reference.

Even though a power law with a small exponent and a logarithm may look similar over restricted timescales, the physical pictures behind them are different [14]. Dense HSC dynamics is usually interpreted in CTRW terms [6,10,11], while logarithmic laws, or equivalently, the fact that macroscopic rates fall off as the inverse of the system age, clearly support the competing RD description [20,24,28,30]. To clearly distinguish between the two pictures motivates our detailed analysis of the statistics of quake events. The system is partitioned into a number of spatial domains wherein the quake statistics is shown to be log-Poissonian, as expected from RD.

Complex system dynamics is often affected by how the quench generates the “initial” state from which an aging process “starts” is carried out. For example, in spin glasses the rate of cooling across the critical temperature determines how well experimental data conform to “pure aging,” i.e., the time that grows strongly with the domain size, which is also the case in HSCs. We expect only small, albeit systematic, effects based on the following qualitative arguments: (1) the particle MSD increases as the logarithm of time irrespective of the initial procedure followed [24,28,29] and (2) within each spatial domains the RD picture we advocate has a hierarchy of free energy barriers controlling the relaxation dynamics of the domain. By analogy with a previous RD spin-glass analysis [38], the initial quench generates a spatial distribution of initial barriers heights and hence of initial effective ages which determine how the dynamic unfolds. For example if the initial barrier of a domain is very high, its effective initial age at time zero is correspondingly high, and the domain remains inert (no quakes) up to that effective age. This spatially heterogeneous dynamics is observed in our simulations, where approximately one third of the domains show no quake activity. Changing the initial quenching procedure can modify the barrier structure present at the beginning of the simulation but cannot change the log-Poissonian nature of the quake dynamics at the core of our analysis.

Two related questions remain: what is the nature of the records which RD refers to, and how domains should be understood. The logarithmic decay of the average potential energy per particle shown in Fig. 2 indicates that the particles—or, equivalently, the voids between them—become more uniformly distributed in space. Accordingly, it becomes increasingly difficult for random cage rattling to create a void large enough for a cage breaking to happen. In other words, the latter requires the crossing of a mainly entropic barrier, whose height increases with time.

Record events in exploring the associated hierarchy of free energy barriers generate quakes, and the increase in the size of the barrier crossed corresponds to an increasing number of adjacent particles which must be rearranged in the process, i.e., to a growing domain. This type of growing spatial domains relate to the dynamical nature of rare local density fluctuations, and they are not easily expressed in terms of single-particle density fluctuations. They are also seen in the aging dynamics of the one-dimensional kinetically constrained model known as the parking lot model [25]. There, the key feature is that random rearrangements of a domain produce a quake in a time that grows strongly with the domain size, which is also the central hypothesis in the “cluster” model of Refs. [24,27]. By identifying domains and studying their growth in HSCs, it should be possible to ascertain whether the same mesoscopic mechanism is at play in HSC systems.

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