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Mesoscopic model of aging in colloids
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Abstract
A model of dense hard sphere colloids building on simple notions of particle mobility and spatial coherence is presented and shown to reproduce results of experiments and simulations for key quantities such as the intermediate scattering function, the particle mean-square displacement and the $\chi_4$ mobility correlation function. All results are explained by two emerging and interrelated dynamical properties: \textit{i)} a rate of intermittent events, quakes, which decreases as the inverse of the system age $t$, leading to $\mu_q(t_{\text{w}}, t) \propto \log(t/t_{\text{w}})$ as the average number of quakes occurring between the ‘waiting time’ $t_{\text{w}}$ and the current time $t$; \textit{ii)} a length scale characterizing correlated domains, which increases linearly in $\log t$.

1. Introduction
Aging is a spontaneous off-equilibrium relaxation process, which entails a slow change of thermodynamic averages. In amorphous materials with quenched disorder \cite{Struik1978, Nordblad1986, Rieger1993, Kob2000, Crisanti2004, Sibani2005}, measurable quantities such as the thermo-remanent magnetization \cite{Kenning2006} and the thermal energy \cite{Crisanti2004, Sibani2007, Christiansen2008, Christiansen2008b} decrease, on average, at a decelerating rate during the aging process. In dense colloidal suspensions, light scattering \cite{Cipelletti2000, Masri2005} and particle tracking techniques \cite{Weeks2000, Courtland2003, Lynch2008, Candelier2009} have uncovered intermittent dynamics and a gradual slowing down of the rate at which particles move. Intermittency suggest a hierarchical dynamics, instead of coarsening, as the origin of this process. However, changes in spatially averaged quantities such as energy and particle density are difficult to measure and the question of which physical properties are actually evolving in an aging colloid \cite{Hentschel2007, Cianci2006} lacks a definite answer.

A recent paper by Boettcher and Sibani \cite{Boettcher2011} has proposed that kinetic constraints bind colloidal particles together in ‘clusters’. As long as a cluster persists, its center of mass position remains fixed, on average, but once it breaks down the particles which belong to it can move independently in space, and are able to join other clusters. The dynamics is controlled by the probability per unit of time, $P(h)$, that a cluster of size $h$ collapses through a quake. Specifically, if the cluster-collapse probability is exponential, as in Eq. (1) below, quakes follow a Poisson process whose average is proportional to the logarithm of time. Log-Poisson processes describe the aging phenomenology of a wide class.
of glassy systems [see Crisanti and Ritort (2004); P. Sibani (2007); Sibani and Christiansen (2008); Christiansen and Sibani (2008); G.G. Kenning, G.F. Rodriguez and R. Orbach (2006)] and, specifically in our case, imply that particle motion is (nearly) diffusive on a logarithmic time scale, as found in our analysis by Boettcher and Sibani (2011) of tracking experiments by Courtland and Weeks (2003).

2. Cluster Model for Colloidal Dynamics

We describe a recently introduced model of cluster dynamics based on these principles that explicitly accounts for the spatial form of the clusters on a lattice in any dimension. This enables us to compare with simulational data by Masri et al. (2010) and experimental by data by Berthier et al. (2005); Berthier (2011). Our particles reside on a lattice with periodic boundary conditions, each lattice site occupied by exactly one particle. Particles are either mobile singletons (cluster-size $h = 1$) or form immobile contiguous clusters of size $h > 1$. When picked for an update, mobile particles exchange position with a randomly selected neighbor and join that neighbor’s cluster. If the particle is not mobile, either its entire cluster “shatters” into $h$ newly mobile particles with probability

$$P(h) = e^{-h}, \quad (1)$$

or no action is taken. When starting with an initial state consisting of singletons, i.e., without any structure, the model develops spatially heterogeneous clusters with a length scale growing logarithmically in time. The rate of events decelerates as $1/t$, which makes random-sequential updates inefficient. In our simulations, we therefore use the Waiting Time Method [see Bortz et al. (1975); Dall and Sibani (2001)], where a random “lifetime” is assigned to each cluster based on the geometric distribution associated with $P(h)$; the cluster with the shortest remaining lifetime is shattered and lifetimes for other pre-existing or newly formed clusters are adjusted or newly assigned, following the Poisson statistics. With this event-driven algorithm, we have been able to follow our model evolution over 15 decades in time, far exceeding current experimental time windows.

Important aspects of aging dynamics are described by observable quantities with two time arguments. Here, we denote by $t$ the current time and by $t_w$ the waiting time before measurements are taken for a system initialized at $t = 0$. To conform to common usage, the lag time $\tau = t - t_w$ is used as abscissa.

3. Comparison with Lennard-Jones Simulations

Using the details of the Lennard-Jones potential in their molecular dynamics simulation, Masri et al. (2010) were able to determine the evolution of the internal energy of a colloidal system in terms of its pressure. We simply monitor the interface between clusters as a proxy of the internal energy, assuming that a shrinking interface indicates a decline in free volume which allows particles within clusters to relieve their mutual repulsion. The average number of clusters $\langle n \rangle$ can be written in terms of average cluster size $\langle h \rangle$ as $\langle n \rangle = L^2/\langle h \rangle$. Since the average cluster size increases with $\langle h \rangle \sim \log(t)$, and since for compact clusters in two dimensions the interface-length scales as $S(h) \propto \sqrt{\langle h \rangle}$, the average energy per particle $\langle e_{\text{int}} \rangle$ is estimated as

$$\langle e_{\text{int}} \rangle = S(h) \frac{\langle n \rangle}{L^2} \sim \frac{1}{\sqrt{\langle h \rangle}} \sim \frac{1}{\sqrt{\log t}}. \quad (2)$$

The slow decay matches that of the Lennard-Jones simulations in Fig. 1 of Masri et al. (2010), and it is reminiscent of granular compactification studied by Nowak et al. (1998), where noisy tapping slowly anneals away excess free volume. The same process drives our cluster growth, although density changes are not explicitly expressed in the model.

Readily available through light scattering experiments, the self-intermediate scattering function (SISF) $f_s$ assesses two-time correlations used to resolve dynamical characteristics of non-equilibrium systems. Formally, it is defined as the spatial Fourier transform,

$$f_s(\vec{q}, t_w, t) = \int d\vec{r} \hat{G}_s(\vec{r}, t_w, t) \exp[-i\vec{q} \cdot \vec{r}], \quad (3)$$
of the self-part of the van Hove distribution function,

\[ G_s(\vec{r}, t_w, t) = \frac{1}{N} \sum_j \delta\left[\vec{r} - \Delta\vec{r}_j\right], \tag{4} \]

with \( \Delta\vec{r}_j(t_w, t) = \vec{r}_j(t) - \vec{r}_j(t_w) \) as displacement of particles \( j \) in the time interval between \( t_w \) and \( t \). In general, SISF can be interpreted as a measure of the “reciprocal of movement”, meaning the average tendency of particles to stay confined in cages whose size scales with inverse magnitude of the wave vector \( \vec{q} \). Using symmetry and the integer values of the positions, the discrete version of SISF reduces to

\[ f_s(q, t_w, t) = \left\{ \frac{1}{N} \sum_{j=1}^{N} \cos\left(\vec{q} \cdot \Delta\vec{r}_j\right) \right\}. \tag{5} \]

Due to spatial isotropy, the SISF is only a function of the magnitude \( q \), with \( q_{\text{min}} = 2\pi/L \leq q \leq \pi\sqrt{2} = q_{\text{max}} \).

Figure 1 shows the results of simulating an \( L = 64 \) system using 2000 instances and waiting times varying from \( 2^{10} \) to \( 2^{18} \) in powers of two. Note that the decay is comparable to the same exponent found in expensive Lennard-Jones simulations, see Fig. 2 of Masri et al. (2010).

The positional variance or mean square displacement (MSD) between times \( t_w \) and \( t \) is computed by averaging the square displacement, first over all particles and then over the ensemble. Using \( \langle \cdot \rangle \) for the ensemble average and \( |\cdot| \) for the Euclidean norm, it is written as

\[ \Delta r^2(t_w, t) = \left\{ \frac{1}{N} \sum_{j=1}^{N} |\vec{r}_j(t) - \vec{r}_j(t_w)|^2 \right\}. \tag{6} \]

Figure 2 shows the MSD for a system of size \( L = 64 \) with waiting times \( t_w = 2^k \) for \( k = 10, 11 \ldots 18 \). Note that a system aged up to time \( t_w \) has a “plateau” of inactivity for lag times up to \( \tau \sim t_w \). These plateaus, associated with
the “caging” of particles by Weeks et al. (2000), are easily removed with $t/t_w$ as independent variable, see Fig. 2(b), leading to the approximate scaling behavior $\Delta r^2 \sim \log(t/t_w)$.

4. Summary and Acknowledgements

In summary, our lattice model of colloidal dynamics coarse-grains away the “in-cage rattling” of particles while incorporating time intermittency and spatial heterogeneity. Its behavior, which qualitatively accounts for relevant experimental findings, can be described analytically using the log-Poisson statistics of cluster collapses following Boettcher and Sibani (2011).

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References

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