Cooperative Jump Motions in Colloidal Glass

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We report Brownian dynamics simulation results on binary colloidal mixtures of particles of two different diameters interacting via a repulsive DLVO potential. As the effective temperature is lowered by reducing charged impurity concentration, a transition from liquid to crystal at a total volume fraction $\phi$ of 0.2 and to glassy state at $\phi = 0.3$ are observed. The mean squared displacements show a marked subdiffusive behavior at intermediate and long times below a certain temperature. The particle motion in supercooled liquid with $\phi = 0.3$ is strongly cooperative as revealed by mean squared displacements, self-part of van-Hove density correlation functions and non-Gaussian parameter. Interestingly, a few particles exhibit cooperative hop and subsequent hop-back motion at temperatures very close to the glass transition.

§1. Introduction

Our understanding of the static and dynamic properties of supercooled liquids and glasses is still far from being complete. The recent use of the non-linear mode coupling theory (MCT)\(^1\) has contributed to some extent in understanding the dynamical behavior of supercooled liquids near the glass transition. The results of laboratory and computer experiments have been compared with the MCT predictions on diverse systems such as molecular systems, polymers, proteins, ionic systems and hard-sphere colloids.\(^2\) The latter together with soft-sphere charge-stabilized colloids of polystyrene particles have proved to be ideal model systems by virtue of easy tunability of interparticle interactions to study a rich variety of cooperative behavior in equilibrium and non-equilibrium conditions.\(^3\) It has been shown that monodisperse polystyrene particles (polyballs) in aqueous suspensions order themselves either into a body-centered cubic phase at low volume fraction $\phi$ or a face-centered cubic phase at high $\phi$. The concentrated suspension at $\phi \sim 0.2$ has, however, revealed a glassy state as inferred from the static structure factor.\(^4\) In hard-sphere colloids consisting of sterically stabilized polymethylmethacrylate particles,\(^5\) the liquid-crystal transition occurs at effective $\phi \sim 0.49$ whereas, a glassy state is formed at higher $\phi$. In binary colloids, the formation of the glassy state has been identified in computer simulations\(^6,7\) as well as from the measurements of the shear modulus,\(^8\) static structure factor\(^9\) and intensity autocorrelation function using light scattering.\(^10\) Our computer simulation\(^6,7,11,12\) studies were aimed to understand structural evolution and dynamics of dense binary mixtures of polyballs with varying volume fractions as the strength of interaction (effective temperature) is gradually increased (decreased) by reducing the concentration of charged impu-

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rity ions $n_i$. Brownian dynamics (BD) simulations have been performed on binary mixtures of polyballs with different particle diameters and charges. For a given total $\phi$, the effective temperature was lowered in many steps by reducing $n_i$ to study the evolution of structure and dynamics. The binary liquid with a total volume fraction $\phi = 0.2$ freezes into a crystal as the effective temperature is lowered whereas at $\phi = 0.3$, it freezes into a glassy state. The structure is characterized by the partial and total pair distribution functions $g(r)$, the static structure factors, time averaged $g(\tau)$ and quadratic rotational invariant. The dynamical quantities studied are the mean squared displacements (MSD), two- and four-point density autocorrelation functions, bond-orientational correlation functions, self- and distinct-parts of the van-Hove correlation function and non-Gaussian parameter. Some of our results follow the predictions of the MCT, namely the factorization property of the van-Hove distinct-correlation function, the stretched-exponential form of the self-correlation function in terms of properly scaled time and the temperature behavior of the non-ergodicity parameter. In this paper, we present some of our results on the mean squared displacements, van-Hove self-correlation functions, non-Gaussian parameter and individual particle trajectories which showed strongly cooperative particle motion in the supercooled liquid with $\phi = 0.3$. A few particles show an interconnected cooperative hop and subsequent reverse hop motion very close to the glass transition.

§2. System of interest

We have performed BD simulations on a system of binary colloidal mixture of $N_1 = 216$ particles with radius $a_1 = 545 \text{ Å}$, valence $Z_1 = 300$ and $N_2 = 216$ particles with $a_2 = 1100 \text{ Å}$ and $Z_2 = 600$. The particles interact at large distances via a purely repulsive size-corrected DLVO potential: 

$$U_{ij}(r) = \frac{Z_i Z_j e^2}{\epsilon} \frac{e^{\kappa(a_i + a_j)}}{(1 + \kappa a_j)(1 + \kappa a_j)} \frac{e^{-\kappa r}}{r},$$

where $\epsilon$ is the dielectric constant of water ($= 78$) at temperature $T (= 298 \text{ K})$, and $\kappa$ is the inverse Debye-Hückel screening length given by $\kappa^2 = 4\pi \epsilon^2 (n_p \bar{Z} + n_i)/(\epsilon k_B T)$. Here $n_p$ is the total number density of particles, $\bar{Z} = xZ_1 + (1-x)Z_2$, $x = N_1/(N_1 + N_2) = 0.5$ and $n_i$ is the concentration of monovalent impurity ions. The simulations have been performed by using the center-of-mass corrected finite difference BD algorithm with the cubic periodic boundary conditions. The system is specified by its total $\phi = 4\pi n_p^2 [x a_1^3 + (1-x) a_2^3]$ and reduced temperature $T^* = k_B T/U_0$, where $U_0$ is the energy scale defined by $U_0 = (Ze^2/\epsilon) \left( \frac{e^{\kappa \bar{a}}}{1 + \kappa \bar{a}} \right)^2 e^{-\kappa a_s/a_s}$. Here $a_s = n_p^{-1/3}$ is the average interparticle distance and $\bar{a} = xa_1 + (1-x)a_2$ is the average radius of the particle.

The starting liquid configuration at each $\phi$ is obtained by melting a body-centered cubic lattice with a high impurity concentration $n_i = 5n_p \bar{Z}$. This is then sequentially cooled by reducing $n_i$ in 11 more steps to obtain a crystal at $\phi = 0.2$ or a glass at $\phi = 0.3$ ($T^*$ varies from $\sim 1$ to $\sim 0.03$). At each $T^*$, the equilibration
is ensured from a steady value (rms deviation $\leq 0.15\%$) of the internal energy per particle $E = (1/Nk_BT) \sum_{j \neq i} U_{ij}(r)$ together with monitoring the pair distribution functions over the equilibration run of $\sim 2 \times 10^6 \delta t$, where $\delta t$ is the basic time step. The next $\sim 3 \times 10^6 \delta t$ are used for evaluating the static and dynamic quantities reported here, as well as the density and the bond-orientational correlation functions.\(^7\) For $\phi = 0.3$, $\delta t = 3 \times 10^{-6}$ sec and the glass transition temperature is $T^*_g \approx 0.0312$. While, for $\phi = 0.2$, $\delta t = 7 \times 10^{-6}$ sec and the crystal transition temperature is $T^*_f \approx 0.0374$.

§3. Results

3.1. Mean squared displacement

The partial MSD for both types of particles ($\alpha = 1$ or 2), defined by

$$\left\langle (\Delta \bar{r}_\alpha(t))^2 \right\rangle = \left\langle \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} (\bar{r}_i(t + t_0) - \bar{r}_i(t_0))^2 \right\rangle_{t_0} \quad (3.1)$$

has been calculated. Here $\bar{r}_i(t)$ is the position of the particle $i$ at time $t$, $\langle \cdots \rangle_{t_0}$ is

![Graph](https://example.com/graph.png)

Fig. 1. $\left\langle (\Delta \bar{r}_i(t))^2 \right\rangle/a^2$ versus time for (a) $\phi = 0.2$ and (b) $\phi = 0.3$. 

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the averaging over a set of 50 initial configurations \( \{t_0\} \), chosen at times separated by \( \tau_d \sim 10^{-3} \) sec, in the same run. In liquid state, \( \tau_d \) is sufficient for a particle to diffuse a distance \( \sim a_s \). Figure 1 shows the temporal evolution of the lighter species (\( \alpha = 1 \)) MSD in a log-log plot for (a) \( \phi = 0.2 \) and (b) \( \phi = 0.3 \) for various temperatures while cooling the system towards \( n_i = 0 \) state.\(^{11} \) It can be seen that at high temperatures (\( T^* > 0.0722 \) for \( \phi = 0.2 \) and \( T^* > 0.0876 \) for \( \phi = 0.3 \)), the motion is diffusive at all times, i.e., \( \langle (\Delta \bar{r}(t))^2 \rangle \propto t^m, m = 1 \); while the particles are localized (\( m \sim 0 \) for all \( t \)) at the lowest \( T^* \). At intermediate temperatures, the MSD shows three stages in time. The initial stage associated with the "cage-diffusion" and long time MSD (in the high and intermediate temperatures) has \( m = 1 \), with diffusivity higher in the initial stage. In intermediate time, the motion is subdiffusive (\( m < 1 \)). The span of the subdiffusive regime increases successively as \( T^* \) is lowered. In the supercooled liquid near the glass transition, the subdiffusive regime covers the entire simulation length. We also note that at intermediate temperatures, the MSD for the system with \( \phi = 0.3 \) shows steps which are absent in the system with \( \phi = 0.2 \). It is rather interesting to see that the steps are present in MSD which is calculated after averaging over all the particles and the initial configurations. It is likely that the initial configurations chosen at \( 10^{-3} \) sec apart in the same run at low temperatures are not completely different from each other. If the averaging is performed over the initial configurations chosen completely independently at a given temperature, these steps may smear out. Such an averaging procedure will be prohibitively computationally expensive. We feel that in laboratory experiments it should be possible to see these steps in MSD of the particles, if it is measured by the digital video imaging of the binary colloids in the supercooled liquid state. The steps in MSD of supercooled liquid indicate that a few particles, in their course of movement, repeatedly get arrested for a period of time in cages formed by their neighbors and subsequently jumps to other cages. The cooperative nature of these activated jumps is confirmed by our detailed study of the van-Hove self-correlation functions and the individual particle displacements.

3.2. **van-Hove self-correlation function**

The self-part of the van-Hove density autocorrelation function is defined by

\[
G_\alpha^s(r, t) = \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \langle \delta(|\bar{r}_i^\alpha(t) - \bar{r}_i^\alpha(0)| - r) \rangle. \tag{3.2}
\]

The angular brackets denote an average over the initial times to improve statistics. The quantity \( S_\alpha(r, t) = 4\pi r^2 G_\alpha^s(r, t) \) gives the probability that a particle of type \( \alpha \) has moved a distance \( r \) in time \( t \), given that it was at origin at \( t = 0 \). Figure 2 shows\(^{11} \) \( S_1(r, t) \) for (a) \( \phi = 0.2, T^* = 0.0378 \) and (b) \( \phi = 0.3, T^* = 0.0313 \). In Fig. 2(a), the supercooled liquid close to the freezing transition to a crystalline state shows typical liquid like features, i.e., the function has a single peak whose maximum moves rapidly to larger \( r \) in time \( t \) and reasonably reproduces the long-time hydrodynamic limit [shown by dashed lines in (a)]. This limit will not be reached if the particles perform discrete jumps. Figure 2(b) shows the case \( \phi = 0.3 \) at temperatures close to \( T_g^* \). The first-peak position becomes nearly independent
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Fig. 2. The function $S_1(r, t)$ at a few different times.

of time, implying that the system is kinetically frozen. The area under the first peak reduces gradually to give rise to a second peak at the interparticle spacing $r = a_s$, whose height increases with time, as shown by the magnified curves. This, in contrast with the situation in (a), is a clear manifestation of the slow relaxation of quenched disordered states via activated jump processes which must be taking place cooperatively to reflect in the statistically averaged quantities like the MSD and $S_0(r, t)$. Interestingly, there is an anomalous increase in the first-peak height at a later time ($t = 1.02$ sec) (at the cost of the second peak), after the expected decrease at somewhat earlier time ($t = 0.306$ sec). This clearly indicates that some particles must be hopping back very much cooperatively to their original positions!

3.3. Non-Gaussian parameter

The importance of the activated processes near the glass transition is also seen in the non-Gaussian parameter $a_\alpha(t)$, defined by

$$a_\alpha(t) = \frac{3 \langle |r^\alpha_1(t) - r^\alpha_1(0)|^4 \rangle}{5 \langle |r^\alpha_1(t) - r^\alpha_1(0)|^2 \rangle^2} - 1,$$

where $r^\alpha_1(t)$ denotes the particle trajectory at time $t$.
Fig. 3. The non-Gaussian parameters for both the species. (a) and (b): $\phi = 0.2$; The temperatures are marked as X0: $T^* = 0.9098$, Xe: $T^* = 0.0446$, Xf: $T^* = 0.0407$, Xh: $T^* = 0.0378$, Xj: $T^* = 0.0372$, Xk: $T^* = 0.0369$. Panel (c) and (d) are for $\phi = 0.3$ with the temperatures marked as Gb: $T^* = 0.0876$, Ge: $T^* = 0.0356$, Gg: $T^* = 0.0313$, Gj: $T^* = 0.0302$, Gk: $T^* = 0.0300$.

where $\langle |r_i^{\alpha}(t) - r_i^{\alpha}(0)|^n \rangle_{t_0} = \int r^n G_\alpha(r, t) dr$.

Miyagawa et al. suggested $a_\alpha(t \to \infty)$, (which is non-zero for $T < T_g$ and is zero for $T > T_g$) as a suitable candidate for the order parameter. Odagaki et al. used the maximum of $a_\alpha(t)$ to define the glass transition point in their recent trapping diffusion theory. Figure 3 shows our BD results on $a_\alpha(t)$ ($\alpha = 1$ and 2) for the crystal transition [Figs. 3(a) and 3(b)] and glass transition [Figs. 3(c) and 3(d)]. It can be noted that the maximum in $a_\alpha(t)$ for $\phi = 0.3$ in panels (c) and (d) as compared to those for $\phi = 0.2$ in panels (a) and (b) are unusually high before the glass transition, implying a significant enhancement of the activated mechanisms (such as correlated jumps) in liquids near the glassy state.

3.4. Tagged-particle motion

The individual particle motion is studied by measuring $\delta r_i(t) \equiv |r_i(t) - r_i(0)|$ and the other two polar coordinates $\delta \theta_i(t)$ and $\delta \phi_i(t)$. Figure 4 shows $\delta r_i(t)$ for $\phi = 0.3$ and $T^* = 0.0313$ with their maximum $\delta r_i^{\text{max}}$ decreasing from top to bottom. Clearly, there are four types of particle motions present: (i) vibrations around the local potential minimum, (ii) hopping of the order of $a_s$ to a neighboring equilibrium position and persisting there till the end of the simulation run, (iii) hopping by $\sim a_s$ to a new position, staying there for a short while and hopping back to its original position, and (iv) motion similar to (iii) but residence time in the hopped position being
Fig. 4. The function \( \delta r_c(t) \) (in units of \( a_s \)) for a few representative particles in run Gg \((T^* = 0.0313)\). The curves are shifted vertically by some multiples of \( a_s \) from each other for the clarity of presentation. The panels marked 2 are for the heavier particles and the rest are for the lighter particles.

Fig. 5. The average coordinates for the seven particles A through G of Fig. 4. The dimensions of \( X \) and \( Y \) denote the simulation boxlength in units of \( a_s \).
high. Interestingly, we note that a few particles (labelled A through G in Fig. 4) have executed jump motion cooperatively at the same time. In particular, these seven particles hop simultaneously at $t \sim 0.3$ sec with $0.9a_s < \delta r_{t}^{\text{max}} < 1.2a_s$ and persist in the new position up to $t \sim 0.5$ sec before they hop-back to their respective initial positions. It is seen that the particle G hops to some position $G'$, leaving a vacancy behind, where E hops in. Other events occurring at the same time are A to D, D to B, and B to C; particle F makes a jump to a neighboring position $F'$. Figure 5 shows the averaged coordinates for the seven particles A through G. In a recent molecular dynamics simulation of soft spheres, Oligschleger and Schober \(^{17}\) also mentioned reversible (jumps where the system eventually reverts to its starting configuration) and irreversible relaxations. Collective hopping motions have also been observed in recent simulations of binary Lennard-Jones and soft-sphere mixtures \(^{18},^{19}\) as well as in amorphous argon after introduction of vacancies. \(^{20}\)

§4. Conclusions

In summary, our BD simulations reveal interesting cooperative jumps at temperatures just above the glass transition temperature. It will be worth looking for these aspects in laboratory experiments on the colloidal glasses.

References