

Cooperative jumps and hop-back motion in supercooled liquids near the glass transition in binary colloids

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Abstract. – Brownian Dynamics simulations on binary charged colloids have been performed to get a liquid to crystal (at volume fraction $\phi = 0.2$) or glass ($\phi = 0.3$) as the temperature is lowered. The subdiffusive and staircase behaviours of the mean-squared displacements as well as the behaviour of van-Hove self-correlation functions for the supercooled liquid with $\phi = 0.3$ indicate strongly cooperative particle motion. The van-Hove distinct correlations follow a factorization property predicted by the mode-coupling theory. Most interestingly, a few particles show an interconnected cooperative hop and subsequent hop-back motion very close to the glass transition.

Easy tunability of interparticle interactions simply by controlling the impurity-ion concentration n_i and the particle volume fraction ϕ makes aqueous suspensions of charged polystyrene spheres ideal model systems for studies concerning relaxation dynamics near freezing [1]. Computer simulations provide us with particle level insight into the structural and dynamical aspects of the transitions (CT and GT) from liquid to crystal [2] and glass [3]. Detailed comparisons of experimental and simulation results [4] in diverse systems with the mode-coupling theory (MCT)[5] predictions have improved our understanding of the GT.

In this letter, we report Brownian Dynamics (BD) simulation results on the slow microscopic dynamics of a colloidal liquid as it is “cooled” and the relevance of hopping at low temperatures. Our results show, for the first time, that a few of the particles perform interconnected cooperative jumps to new positions and remarkably hop-back (cooperatively) to their starting positions in the supercooled-liquid state close to its GT.

We consider a binary colloidal mixture [6] of $N_1 = 216$ particles with radius $a_1 = 545 \text{ \AA}$, valence $Z_1 = 300$ and $N_2 = 216$ particles with $a_2 = 1100 \text{ \AA}$ and $Z_2 = 600$. The particles interact at large distances via a purely repulsive, size-corrected DLVO potential [1], $U_{ij}(r) = (Z_i Z_j e^2 / \epsilon) (e^{\kappa a_i} / (1 + \kappa a_i)) (e^{\kappa a_j} / (1 + \kappa a_j)) (e^{-\kappa r} / r)$, where ϵ is the dielectric constant of water ($= 78$) at temperature T ($= 298 \text{ K}$). For a binary suspension, the inverse Debye-Hückel screening length κ is given by $\kappa^2 = (4\pi e^2 / \epsilon k_B T) (n_p \bar{Z} + \sum_i n_i z_i^2)$, where n_p and n_i are the number densities of the particles and the monovalent impurity ions ($z_i = 1$), respectively, $\bar{Z} = x Z_1 + (1 - x) Z_2$ and $x = N_1 / (N_1 + N_2) = 0.5$. As detailed elsewhere[6], we use

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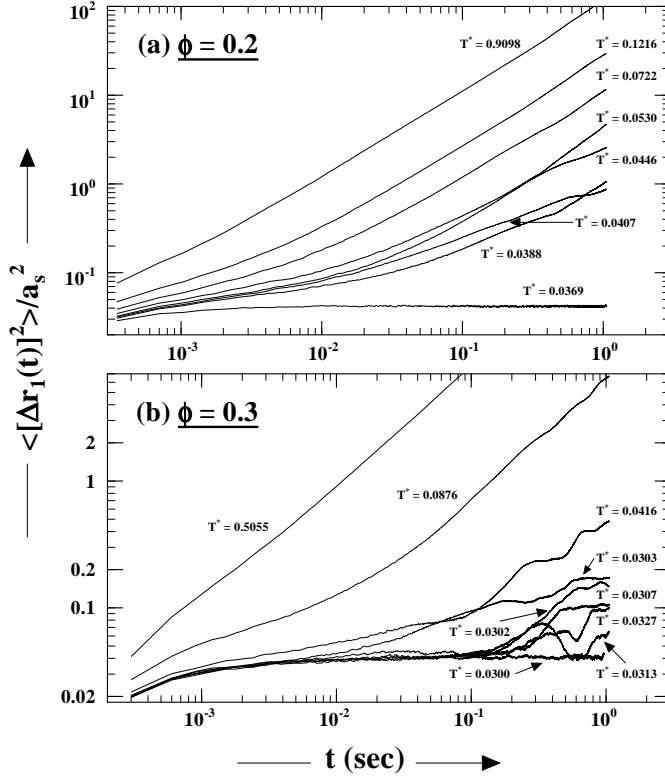


Fig. 1. - $\langle [\Delta \mathbf{r}_1(t)]^2 \rangle / a_s^2$ vs. time for a) $\phi = 0.2$ and b) $\phi = 0.3$.

the centre-of-mass-corrected finite-difference BD algorithm [7] with the usual cubic periodic boundary conditions. The potential is cut off at r_c such that $U_{ij}(r_c) \sim 0.001 k_B T$. The system is characterized by its total $\phi = \frac{4}{3} \pi n_p [x a_1^3 + (1-x) a_2^3]$ and reduced temperature $T^* = k_B T / U_0$ where $U_0 = ((\bar{Z}e)^2 / \epsilon) (e^{\kappa \bar{a}} / (1 + \kappa \bar{a}))^2 (e^{-\kappa a_s} / a_s)$ is the energy scale. Here \bar{a} is the mean radius and $a_s = n_p^{-1/3}$ the average interparticle separation.

The starting liquid configuration at each ϕ is obtained by melting a body-centred 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 a crystal at $\phi = 0.2$ or a glass at $\phi = 0.3$ (T^* varies from ~ 1 to ~ 0.03). At each T^* , the equilibration is ensured from a steady value (rms deviation $\leq 0.15\%$) of the internal energy per particle $E = (1/N k_B T) \sum_{j \neq i} U_{ij}(r)$ together with monitoring the pair distribution functions over the equilibration run of $\sim 2 \times 10^6 \delta t$, where δt 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 [8]. For $\phi = 0.3$, $\delta t = 3 \times 10^{-6}$ s and the GT temperature is $T_g^* \simeq 0.0312$ while, for $\phi = 0.2$, $\delta t = 7 \times 10^{-6}$ s and the CT temperature is $T_f^* \simeq 0.0374$ [6].

Figure 1 shows the temporal evolution of the lighter sublattice ($\alpha = 1$) mean-squared displacement (MSD) $\langle [\Delta \mathbf{r}_\alpha(t)]^2 \rangle$ 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. $\langle \dots \rangle$ indicates an averaging over 50 initial conditions to improve the statistics. At high temperatures ($T^* > 0.0722$ for $\phi = 0.2$ and $T^* > 0.0876$ for $\phi = 0.3$), the motion is clearly diffusive ($\langle [\Delta \mathbf{r}(t)]^2 \rangle \propto t^m$; $m = 1$ for all t), while the particles are localized or trapped ($m = 0$ for all t) at the lowest T^* . We note that the reduction in the long-time value of MSD for the CT is sharp (refer to the curves with $T^* = 0.0388$ and 0.0369 in fig. 1 a)) as compared to the slow kinetic nature

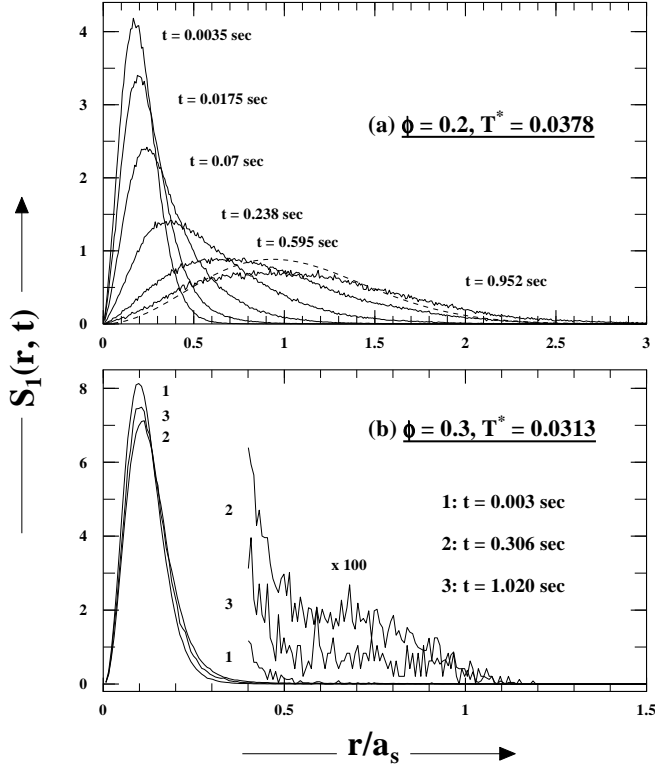


Fig. 2. – The function $S_1(r, t)$ at a few different times.

of the GT (fig. 1b)). At intermediate temperatures, MSD follow three distinct stages. The initial stage can be associated with the “cage-diffusion”, having diffusivity higher than the long-time value. This regime spans up to $t \sim 10^{-3}$ s for $\phi = 0.3$, while the choice of δt does not allow us to see this regime for $\phi = 0.2$. Following this, there is an intermediate subdiffusive regime [9] and a long-time diffusive behaviour for both ϕ . The span of the subdiffusive regime increases successively as T^* is lowered and, as expected, it is more for the denser system ($\phi = 0.3$). Near the GT, this regime covers the entire simulation length and the asymptotic values for the diffusion constants are not reached. We note that these short-time features of the MSD are very similar to the recent experimental [10] and simulation [11] findings. More importantly, we note that the MSD at these intermediate T^* show a “staircase” profile in *b*) which is completely absent in *a*). This supports the cage-concept in supercooled liquids near the GT, indicating that a particle repeatedly gets arrested in a cage-structure formed by its neighbours and intermittently hops from one cage to another. Since the MSD are small for these low- T^* states, cooperative hops $\sim a_s$ by a few particles will always show up in these plots. Interestingly, there is an anomalous increase in the long-time diffusion at some intermediate- T^* range (between 0.0407 and 0.0378 for $\phi = 0.2$ and 0.0313 and 0.0302 for $\phi = 0.3$) with respect to the value at its immediate higher T^* . This could be the result of a constrained dynamics of more mobile lighter particles in the background of heavier particles and/or a structural readjustment at the onset of a CT or a GT.

Figure 2 shows the function $S_\alpha(r, t) = 4\pi r^2 G_\alpha^s(r, t)$ for the lighter particles ($\alpha = 1$), where the van-Hove self-correlation functions are defined as usual [12], $G_\alpha^s(r, t) = (1/N_\alpha) \sum_{i=1}^{N_\alpha} \langle \delta(|\mathbf{r}_i^\alpha(t) - \mathbf{r}_i^\alpha(0)| - r) \rangle$. The supercooled liquid just before the CT in *a*) shows typical liquid-like features, namely the function has a single peak, whose maximum moves rapidly to larger r in time t

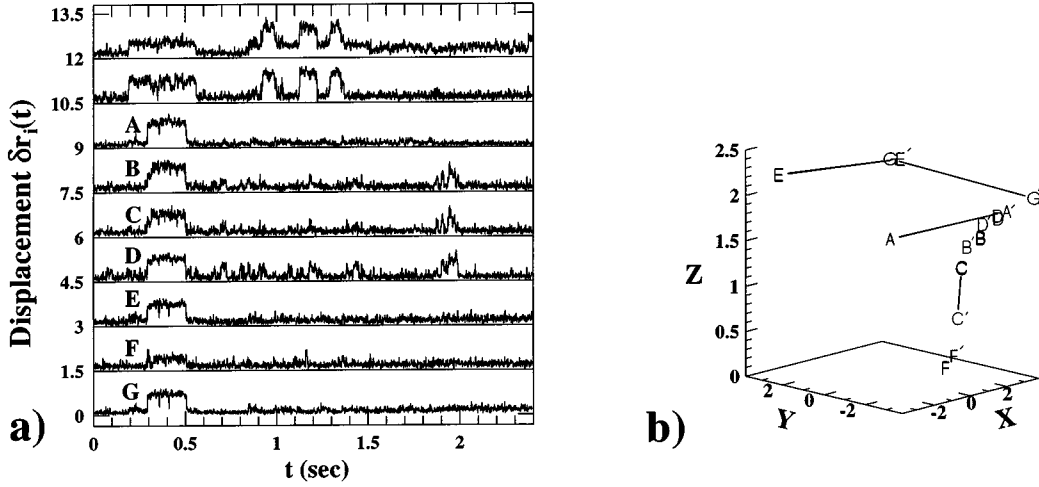


Fig. 3. – $\delta r_i(t)$ of 9 representative particles are shown in *a)* for $\phi = 0.3$ and $T^* = 0.0313$. Averaged coordinates for 7 particles (*A* through *G*) executing to and fro hop motions are shown in *b)*, where the dimensions of *X* and *Y* denote the simulation boxlength in units of a_s .

and reasonably reproduces the long-time hydrodynamic limit (dashed lines in *a)*). This limit is not reached if the particles execute discrete hops. Figure 2 *b)* demonstrates the situation for $T^* \leq T_g^*$. The first-peak position becomes nearly independent 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 $S_\alpha(r, t)$. Interestingly, there is an anomalous increase in the first-peak height at a later time ($t = 1.02$ s) (at the cost of the second peak), after the expected decrease at somewhat earlier time ($t = 0.306$ s). This clearly indicates that some particles must be hopping back very much cooperatively to their original positions!

This unusual observation and a similar inference from our study of non-Gaussian parameters [13] as well as the presence of a staircase behaviour in MSD is borne out by a close look at the tagged-particle dynamics. The analysis of the particle displacements $\delta r_i(t) \equiv |\mathbf{r}_i(t) - \mathbf{r}_i(0)|$ over the entire simulation runs indicates that the motion in a supercooled liquid near the CT is primarily diffusive [13]. By contrast, near the GT, there are four types of particle motions present, namely, *A*) vibrations ($\sim 0.1a_s$) around the local potential minimum, *B*) hopping ($\sim a_s$) to a neighbouring equilibrium position and persisting there till at least the end of the simulation run, *C*) transient vibrations, *i.e.* hopping by $\sim a_s$ to a new position, staying there for a short while (≤ 10 times the time scales of *A*)) and then hopping back to its original position and *D*) motion similar to *C*) but the time of residence in the hopped position being much higher (≥ 100 times the time scales of *A*)).

Figure 3 *a)* shows $\delta r_i(t)$ of 9 particles for $\phi = 0.3$ and $T^* = 0.0313$ in order of decreasing $\delta r_i^{\max} = \max[\delta r_i(t)]$ from top to bottom, shifted by $1.5a_s$ from each other for clarity. We have followed the movements of 7 particles in *b)*, which simultaneously hopped with $0.90a_s < \delta r_i^{\max} < 1.15a_s$ at $t \approx 0.3$ s and after persisting in the new position for up to $t \approx 0.48$ s, have hopped back to their respective initial positions. This is done to check if they permute their positions to show a rotation or a caterpillar motion, seen in earlier simulations [14] as distinct from hole-induced jumps. We have named these particles as *A* through *G*, in descending

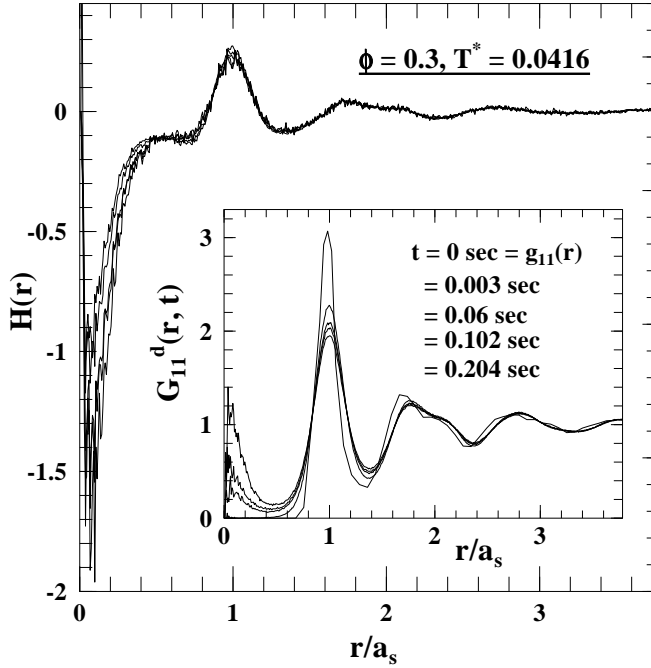


Fig. 4. – The inset shows $G_{\alpha\beta}^d(r, t)$ at times t specified from top to bottom according to the decreasing first-peak height. $H(r)$ for $t = 0.003, 0.03, 0.06, 0.102$ and 0.204 s overlap one another.

magnitude of δr_i^{\max} . All of these, except for A and G , are lighter species. The averaging of the coordinates are performed over all the BD steps i) before the hop, between $t = 0$ and $t = 0.24$ s, ii) at the hopped position, between $t = 0.3$ s and $t = 0.48$ s and iii) after the return, between $t = 0.54$ s and $t = 0.66$ s. Averaged coordinates thus available for these 7 particles at times i) and iii) overlap almost identically and hence, when plotted in fig. 3 b), we can often see only two points corresponding to the initial (marked A through E) and the hopped positions (marked A' through E'). By calculating the interparticle distances in their initial and hopped positions, it is possible to categorize these into three groups: 1) $E \rightleftharpoons G$, 2) $A \rightleftharpoons D \rightleftharpoons B \rightleftharpoons C$ and 3) F . Figure 3 shows that in group 1), at $t \approx 0.3$ s, the particle G hops to some position G' , leaving a vacancy behind where E hops in. During the same time, in a chain-like motion of the particles in group 2), the sequence of events followed are the hops A to D , D to B , and B to C . During this time, the group 3) particle F makes a hop to a neighbouring position F' . After staying at their hopped positions till $t \approx 0.48$ s, surprisingly enough, they almost simultaneously hop back to their respective original positions and persist there! The flight time of these hop or hop-back motion is ~ 0.003 s and the residence time ~ 0.2 s. Any fluctuation in position of one particle at this T^* is very strongly correlated with a few other particles and hence show up in the statistically averaged quantities too. The configurations before and after the cooperative and interconnected hop can perhaps be viewed as two states of the “two-level” system conjectured to occur in the glassy regime. The cooperative hop-back motion was found to be present for three different phase points close to T_g^* (namely the runs with $T^* = 0.0313$ and 0.0302 for one system and $T^* = 0.0360$ for a differently prepared system with $N_1 = N_2 = 128$ [13]) and also in a recent work [15] supporting the universality of such an occurrence.

The collective dynamics of the system is investigated via the van-Hove distinct-correlation function [12], $G_{\alpha\beta}^d(r, t) = (1/\sqrt{N_\alpha N_\beta}) \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} \left\langle \delta(\mathbf{r} - \mathbf{r}_i^\alpha(0) + \mathbf{r}_j^\beta(t)) \right\rangle$, where the prime

indicates $j \neq i$. The inset of fig. 4 shows the relaxation of $G_{11}^d(r, t)$ from its $t = 0$ static counterpart, the pair distribution function $g_{11}(r)$, for a supercooled liquid ($T^* = 0.0416$) approaching the GT. After an initial rapid decay corresponding to the vibration in a cage and the β relaxation steps in its corresponding density correlation function $F_\alpha^s(q, t)$ [13], it stabilizes during the time $0.05 \text{ s} \leq t \leq 0.3 \text{ s}$ corresponding to the plateau in $F_\alpha^s(q, t)$. The difference of the plateau value of $G_{11}^d(r, t)$ from its initial $g_{11}(r)$ is discernible primarily in the first neighbour shell ($r/a_s < 1.2$) in the inset of fig. 4 and in other $G_{\alpha\beta}^d(r, t)$. This clearly supports the picture that β relaxation is a localized process involving only a few nearest neighbours [16]. We have studied this difference by monitoring $[G_{\alpha\beta}^d(r, t) - G_{\alpha\beta}^d(r, t = 0.3 \text{ s})]$ as a function of t . This quantity indeed follows a factorization of the type predicted by MCT in the β relaxation regime, namely, $[G^d(r, t) - G^d(r, t = 0.3 \text{ s})] = H(r) [f(t) - f(0.3 \text{ s})]$, where we have dropped the pair indices $\alpha\beta$. The function $H(r)$ is shown in fig. 4 for different times.

In conclusion, the nature of relaxation when a colloidal liquid approaches the glass transition ($\phi = 0.3$) is completely different from that near the equilibrium transition to a crystal ($\phi = 0.2$). This is perhaps the first observation of the staircase behaviour for a system of Brownian particles. In the β relaxation regime, the difference of $G_{\alpha\beta}^d(r, t)$ from its plateau value obeys a factorization property as per the prediction of MCT. The existing simulations and experiments [4], [14], [17] have already pointed out the importance of cooperative hops in systems near the GT. A significant result of this paper is the unusual observation of strongly cooperative interconnected hop-back motion of about 2% of the particles. A maximum of 10% of the particles show marked cooperative hindrance in their motion during this time, making the effect show up in the statistically averaged MSD and $G_\alpha^s(r, t)$. This calls for a careful analysis of the GT data using the extended MCT incorporating activated hopping processes.

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