Activated bond-breaking processes preempt the observation of a sharp glass-glass transition in dense short-ranged attractive colloids

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We study — using molecular dynamics simulations — the temperature dependence of the dynamics in a dense short-ranged attractive colloidal glass to find evidence of the kinetic glass-glass transition predicted by the ideal Mode Coupling Theory. According to the theory, the two distinct glasses are stabilized one by excluded volume and the other by short-ranged attractive interactions.

By studying the density autocorrelation functions, we discover that the short-ranged attractive glass is unstable. Indeed, activated bond-breaking processes slowly convert the attractive glass into the hard-sphere one, preempting the observation of a sharp glass-glass transition.

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Short-ranged attractive colloidal systems have recently become the focus of many experimental and theoretical studies. The interest in these systems stems from their peculiar dynamics, for showing structural arrest phenomena both of gelation and vitrification type, and for being amenable of analytic treatments. Previous studies have convincingly shown that unusual dynamical phenomena emerge from the competition between two characteristic localization length scales; the hard-core and the short-ranged attraction localization lengths. In hard-sphere colloids, when the packing fraction $\phi$ exceeds roughly 0.58, the colloidal suspension turns into a glass and particles are confined in cages of size of the order of 10% of the hard core diameter (the hard-sphere localization length). In attractive colloids, localization can be realized not only via excluded volume (i.e. tuning $\phi$) but also thermally (i.e. tuning the ratio between temperature $T$ and potential depth). Hence, slowing down of the dynamics can be induced not only by increasing $\phi$ but also by progressively lowering $T$, i.e. increasing the inter-particle bonding. Previous studies have shown that when the range of the attractive interaction is smaller than 10% of the hard-core diameter, an additional localization length, controlled by the potential, sets in and an efficient mechanism of competition between the hard-sphere and the short-ranged bonding localization lengths arises. In the fluid phase-region where the two localization mechanisms compete, a highly non trivial dynamics is observed: particle diffusion shows a maximum on heating, the fluid can be transformed at constant $\phi$ into a glass both on cooling and heating, the time dependence of dynamical quantities like the mean squared displacement and the density-density correlation function, have an uncommon behavior at intermediate times, showing respectively a sub-diffusive and a logarithmic regime. These anomalous properties have been recently observed in a series of beautiful experiments, and extensive simulations of particles interacting via short-ranged square-well and Asakura-Oosawa potential.

Hard sphere colloids have been an important system for accurately testing theoretical predictions. It has been shown that the ideal Mode Coupling Theory (MCT), which neglects hopping phenomena, provides an accurate description of the dynamics close to the hard-sphere glass transition. Ideal MCT provides an accurate description of the fluid phase dynamics also in short-ranged attractive colloids, despite the complex dynamical processes alluded to previously. Several theoretical predictions have been recently quantitatively confirmed by experiments and simulations.

An untested important prediction of the theory regards the presence of a kinetic (as opposed to thermodynamics) glass-glass transition which should take place in the glass phase on crossing a critical temperature. Heating a short-ranged attractive glass should produce a sudden variation of all dynamical features, without significant structural changes. For example, at the transition temperature, the value of the long-time limit of the density-density correlation function, the non-ergodicity factor, should jump from the value characteristic of the short-ranged attractive glass to the significantly smaller value characteristic of the hard-sphere glass.

In this Letter we report an extensive numerical study of the binary short-ranged square well (SW) potential in the glass phase aiming at studying the $T$-evolution of the glass dynamics and detecting the location of the glass-glass transition. We discover that hopping phenomena destabilize the attractive glass and prevent the observation of the a discontinuous glass-glass transition.

We perform molecular dynamics (MD) calculations of a 50% - 50% binary mixture of $N = 700$ particles of unitary mass interacting via a square-well potential of unitary depth $-u_0$. The asymmetry between the two hard-core diameters is fixed to 20%. The attractive well width $\Delta_{ij}$ is given by $\Delta_{ij}/(\Delta_{ij} + \sigma_{ij}) = 0.03$, where $\sigma_{ij}$ is the hard-core diameter for the $ij$-type interaction, with $i, j = A, B$. In this model, a bond between two particles can be unambiguously defined when the pair interaction energy is $-u_0$. The one-component version...
of this model has been extensively studied within MCT\cite{17}. The binary mixture case, which allows to prevent crystallization without substantial changes in the dynamics, has been studied numerically in the fluid phase\cite{10}. The iso-diffusivity curves in the $\phi - T$ region are re-entrant and, close to the re-entrance, correlation functions show a logarithmic decay in agreement with MCT predictions. Comparing the theoretical MCT calculations for this specific model, with the numerical results reported in Ref.\cite{10} — following the procedure first used by Sperl\cite{22} — the glass-glass transition line has been located between $\langle \phi \simeq 0.625, T \simeq 0.37 \rangle$ and the end-point $\langle \phi \simeq 0.64, T \simeq 0.42 \rangle$\cite{23}. At $\phi = 0.635$, the packing fraction studied in this work, the glass-glass temperature is predicted to be $T \simeq 0.4$.

To generate glass configurations, we compress\cite{24}, to $\phi = 0.635$, 136 independent equilibrium configurations generated at $T = 0.6$ and $\phi \simeq 0.612$ in a previous study\cite{10}. We checked that the results presented in this Letter do not depend on the $T$ and $\phi$ of the starting uncompressed configurations. Since the simulated system is out-of-equilibrium, ensemble averages are requested to reduce the noise level. Each compressed configuration was instantly quenched to several temperatures $T$ by proper rescaling of the initial velocities and let to evolve in a NVT simulation\cite{25}. On the time scale of our study the system behaves as a glass at all $T$ values, i.e. no diffusional processes are observed. We analyze nine different $T$ values, from $T = 1.5$ to $T = 0.1$. Each $T$ requested about 15 CPU days on fast AMD Athlon processor.

Since the system is in an out-of-equilibrium state, correlation functions depend not only on $t$ but also on the time elapsed from the compression, the waiting time $t_w$. For $t \ll t_w$, correlation functions for different $t_w$ collapse on the same curve — a phenomenon connected to the equilibration of the degrees of freedom faster than $t_w$\cite{24}. We exploit such feature to generate $t_w$-independent data and focus only on the $T$-dependence. For this reason we consider the dynamics for times up to approximately 400 time units and $t_w > 4000$.

To confirm that in the time window $0 < t < 400$, no $t_w$-dependence is observed for $t_w \gtrsim 4000$, we calculate the density-density correlation function

$$\phi_q(t_w + t, t_w) \equiv \langle \rho_q^*(t_w + t)\rho_q(t_w) \rangle / \langle |\rho_q(t_w)|^2 \rangle \quad (1)$$

where $\rho_q(t) = \frac{1}{\sqrt{N}} \sum_i e^{iqr_i(t)}$ and $r_i(t)$ are the coordinates of particle $i$ at time $t$. Fig. 1 shows $\phi_q(t_w + t, t_w)$ for the case $T = 0.35$, at $q\sigma_{BB} \simeq 25$. For $t_w > 4000$, $\phi_q(t_w + t, t_w)$ becomes independent of $t_w$ for $t \lesssim 400$. We confirmed such $t_w$-independence at all studied $T$-values.

Before presenting the numerical data, we discuss the ideal-MCT predictions for the one-component system, using the Percus-Yevick static structure factor as input, extending the calculation reported in Ref.\cite{17}. Fig. 2 (top panel) shows $\phi_q^{MCT}(t)$ at different $T$ values. The long-time limit $f_q$ of the correlation function separates two groups of temperatures. At high $T$ values, correlation functions tend to $f_q^{HS} \approx 0.6$, while for lower $T$, $f_q > 0.9$, a figure typical of the short-ranged attractive glass. The sharp jump in $f_q$ is the signature of a discontinuous glass-glass transition.

Fig. 2 (bottom panel) shows $\phi_q(t_w + t, t_w)$ in the $t_w$-independent time window, calculated from MD trajectories. At the highest $T$, $T = 1.5$, $\phi_q(t_w + t, t_w)$ quickly approaches a plateau, consistent with the hard-sphere glass value, as expected since the kinetic energy is larger than

![FIG. 1: Waiting-time dependence of $\phi_q(t_w + t, t_w)$ for $T = 0.35$, at $q\sigma_{BB} \simeq 25$. For $t_w > 4000$, no aging is observed in the chosen time window. Time is measured in reduced units.](image)

![FIG. 2: Top panel: Density correlators predicted by MCT, $\phi_q^{MCT}(t)$, for a one-component SW system for different temperatures, crossing the glass-glass transition at $\phi \simeq 0.54$, for $q\sigma = 14.5$. Such $q$-value has been chosen to reproduce comparable differences in the non-ergodicity parameters. The temperatures have been chosen such that $T/T_c$ ($T_c$ is the MCT transition temperature) is close the simulation one for the reported $T$‘s. Bottom Panel: Same curves from the simulation for $q\sigma_{BB} \simeq 25$. Temperatures from top to bottom: 0.1, 0.2, 0.35, 0.4, 0.5, 0.65, 0.9, 1.5. $t_w = 3754$.](image)
the depth of the square well. On cooling, the approach to the plateau takes longer and longer, consistently with the MCT predictions. Around $T = 0.4$, the decay is well represented by a logarithmic law, in agreement with the location of the MCT higher order singularity — the source of the logarithmic dynamics. For $T \lesssim 0.4$, the correlation functions show a very ill-defined plateau, around 0.9, a value consistent with the MCT prediction for the short-ranged attractive glass. While in the theoretical predictions the attractive plateau lasts for ever, in the simulated systems all correlation functions, independently from $T$, appear to decay well below 0.9. The correlation functions for the two extreme temperatures in Fig. 2 (bottom panel) show that a clear difference in the dynamics is indeed observed. However, the sharp glass-glass transition predicted by ideal MCT is not found. These results suggest that the range of stability of the attractive glass is considerably shorter than theoretically expected. Even lowering $T$ down to 0.1, i.e. when $T$ is one tenth of the potential well depth and the system is expected to be deep in its attractive glass phase, the attractive plateau lasts less than two decades in time. We also note that the time window in which the correlation function is close to the attractive plateau value does not extend on increasing $t_w$, as clearly shown in Fig. 1. The absence of a clear short-ranged attractive plateau seems to suggest that the attractive cages are not as stable (in time) as the hard-sphere ones and that particles do manage to break the bond confinement.

A possible explanation of the observed instability of the attractive glass can be formulated in term of the so-called activated (or hopping) processes, decay processes which are not included in the ideal MCT. While in hard-spheres hopping phenomena are not significant due to the absence of an energy scale, in molecular systems it is well known that the "MCT glass" is destabilized by activated processes, which slowly restore ergodicity. Indeed, in these systems the calorimetric glass transition temperature is located well below the MCT critical temperature. In short-ranged attractive colloids, activated processes can be associated with thermal fluctuations of order $u_0$, which are able to break the bonds. These processes generate a finite bond lifetime and destabilize the attractive glass. If $\phi$ is sufficiently large, the underlying hard-core repulsive glass should emerge as limiting disordered arrested structure.

It is tempting to formulate the hypothesis that an ideal MCT short-ranged attractive glass would be stable if bond-breaking processes were negligible. Such ideal attractive glass should be characterized by bond-cages with infinite lifetime, in analogy with the hard-sphere glass which is characterized by neighbor-cages of infinite lifetime. To substantiate this claim, we artificially build a model in which bonds are never broken on the time scale of our numerical observation. To do so we add a finite barrier of infinitesimal width in the potential, just outside the attractive well (see Fig. 3), with the purpose to make the bonds longer lived, and solve the Newton equations exactly. The nice feature of this modified system is that the thermodynamics is identical to the one of the original potential, since the width of the repulsive barrier is infinitesimal. Dynamics are instead different, since bond-breaking now takes place on longer time-scales; for example, by choosing as height of the repulsive barrier $100u_0$, we find that no bond is formed or broken in the timescale of the simulation.

Fig. 3 contrasts the decay of $\phi_{q}(t_{w} + t, t_{w})$ for different $T$ values in the range of $T$ where attractive glass is expected, both for the SW model and for the case of the square well complemented by a barrier (SWB) of height $100u_0$. The same initial configurations (at $t = 0$) are used for both models, so that at time $t = 0$ the bonding pattern is identical. By construction, only decorrelation processes which do not modify the bonding pattern, i.e. the rattling motion within the bond-cages, are possible in the SWB model. We observe that, in the case of the SWB model, the correlation functions decay to a stable plateau, whose value, larger than 0.9, is consistent with the expected value for the attractive glass. In contrast, correlation functions for the unmodified SW model, already at short times, decay below the plateau value. Still, the extrapolated amplitude of the long-time decay (see Fig. 3) provides an estimate of $f_q$ very similar to the one of the SW model plus barrier. These results support the view that ideal-MCT, by neglecting the bond-
breaking processes, predicts a stability window for the short-ranged attractive glass larger than numerically observed.

The present study suggests that the ideal attractive glass line in short-ranged attractive colloids has to be considered, in full analogy with what has been found in the study of glass-forming molecular liquids,[24] as a cross-over line between a region where ideal-MCT predictions are extremely good (in agreement with the previous calculation in the fluid phase) and an activated-dynamics region, where ideal-MCT predictions apply in a limited time window. The anomalous dynamics which stem from the presence of an higher-order singularity in the MCT-equations,[11, 17], still affect the dynamical processes in the fluid and in the glass, even if activated processes pre-empt the possibility of fully observing the glass-glass transition phenomenon, at least in the SW case. Short-ranged inter-particle potentials which stabilize bonding could produce dynamics which are less affected by hopping processes, favoring the observation of the glass-glass phenomenon.[8]

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[24] To quickly compress, we run a simulation of a system of particles interacting with a hard-core followed by a repulsive shoulder. The configuration to be compressed is used as initial conditions in the Newton Equations. The height of the shoulder is set to a value much larger than T, forcing closely particles to quickly separate. As soon as the energy of the system goes back to zero, the simulation is interrupted and the configuration is saved. A proper rescaling of the coordinates produce a configuration consistent with the original square-well potential but with a larger packing fraction (fixed by the width of the repulsive shoulder). In this way, we were able to generate configurations up to about φ = 0.65.
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