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SLOW DYNAMICS AND AGEING OF COLLOIDAL HARD SPHERE GLASSES

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Abstract

Echo Dynamic Light Scattering experiments were performed on a colloidal hard sphere glass to measure the intensity autocorrelation function in the range 1 to 10^3 s. The first derivative of the intensity autocorrelation function is used to determine the inflection point, and isolate the two processes characterizing the decay of the intensity autocorrelation function – the “fast” process (often designated β decay) and the “slow” process (α decay). The behaviour of both processes are studied as a function of the age of the colloidal glass, defined as the time since the quench. The end of the fast process follows a stretched exponential law at early ageing times, and becomes more and more stretched, tending eventually towards a power law. The slow process follows a power law for all sample ages.

Introduction

Colloidal hard sphere suspensions are a widely used model for the fundamental study of crystallization and the glass transition. Such suspensions exhibit crystallization for volume fractions exceeding the freezing volume fraction \( \phi_0 = 0.494 \), in agreement with molecular dynamics simulations of ideal hard spheres. Once the volume fraction exceeds \( \phi_0 = 0.565 \), however, crystallization is suppressed, yielding long lived metastable colloidal glasses. These systems exhibit slow dynamics and ageing effects, which are of great fundamental interest, as well as being relevant to a range of problems in applied materials science. Colloidal hard sphere have been extensively used for the last two decades as the simplest model for investigating the traditional glass transition in condensed state matter. There are also many soft materials, such as gels, pastes, blood and foams that exhibit similar out-of-equilibrium behaviour. However, this behaviour is still poorly understood due to a range of experimental obstacles. First, colloidal glasses exhibit slow dynamics and ageing behaviour as function of the elapsed time since the quench. Second, colloidal glasses are non-ergodic, which means that statistically meaningful results can only be obtained by making a large number of equivalent measurements on different regions of the sample. The recently developed echo dynamic light scattering technique makes it possible to study the slow dynamics and ageing of colloidal glasses and achieve a better understanding of the glass transition and colloidal glasses. Here, we present the initial results of such experiments.

Materials and Methods

Particles

The preparation and characterization of suspensions used here have been described in previous work (Underwood and van Megen, 1996; Bryant et al., 1999). Here we mention briefly the most important points. The particles consist of a core of methylmethacrylate (MMA) and trifluoroethyl acrylate (TFEA). Particles were coated by an approximately 10nm thick layer of poly(12-hydroxystearic acid) to prevent any coagulation. The hydrodynamic radius \( R_h = 200 \) nm and polydispersity 6% of the particles were determined by Dynamic Light Scattering (DLS) on very dilute samples. The particles are suspended in a solvent of cis-decalin, which has a refractive index very close to that of the particles. Due to this index matching there is no significant multiple scattering at wave vectors in the range 1.5<qR<4 (e.g. Williams and van Megen, 2001). The effective hard-sphere volume fraction was determined by scaling the observed freezing volume fraction to the known freezing volume fraction for hard-sphere particles \( \phi_0 = 0.494 \) (Hoover and Ree, 1969). This gives a glass transition volume fraction \( \phi_g = 0.565 \pm 0.005 \). The sample studied here has an effective volume fraction of 0.58 and thus is in the glassy region.

DLS

Dynamic Light Scattering (DLS) has been extensively used for the last two decades to measure particle dynamics, and details can be found elsewhere (Berne and Pecora, 1990). Here we describe the main points. A laser with a wavelength \( \lambda = 632.8 \) nm is focussed onto a small region within the particle suspension. The incident light is scattered by the particles and creates a time varying speckle (diffraction) pattern. A single photon detector measures the intensity scattered by the suspension in the far field at the scattering vector \( q \):

\[ q = \frac{4 \pi n}{\lambda} \sin \left( \frac{\theta}{2} \right) \]  \hspace{1cm} (1)

Where \( n \) and \( \theta \) are the refractive index and scattering angle respectively. As the particle positions evolve due to Brownian motion, the speckle pattern fluctuates. The intensity fluctuations provide information about the particle dynamics. The quantity of interest is the ensemble average autocorrelation function (ACF) of the
scattered intensity fluctuations $g^{(2)}_E(q, \tau)$. Normal DLS measures the time average intensity ACF $g^{(2)}_T(q, \tau)$ of the scattered intensity fluctuations, which is related to the electric field ACF $f(q, \tau)$, also known as the intermediate scattering function (ISF), by the Siegert relation:

$$
g^{(2)}_E(q, \tau) = \frac{\langle f(q, \tau) J(q, \tau + \tau) \rangle_{T,E}}{\langle f(q, \tau) \rangle^2_{T,E}} \quad \quad g^{(2)}_T(q, \tau) = 1 + c|f(q, \tau)|^2
$$

(2)

Where $\langle \rangle_T$ and $\langle \rangle_E$ denote time and ensemble averages respectively. For a colloidal fluid at low volume fractions, $\phi < \phi_c$, fluctuations in the scattered intensity decay in less than about 1 s. Thus, for a measurement lasting several hundred seconds, the time and ensemble average of the intensity ACF are equivalent, i.e.

$$
g^{(2)}_E(q, \tau) = g^{(2)}_T(q, \tau)
$$

(3)

In others words, the particles are able to evolve through a representative fraction of the spatial configurations on the experimental time scale. Such a system is called ergodic.

Increasing the volume fraction above the glass transition, $\phi > \phi_c$, the particle motions are restricted and only small scale motions are permitted. Only a sub-ensemble, rather than a full ensemble, of spatial configurations is accessed on the experimental time scale. Thus the fluctuation time of the scattered intensity is of the same order as the measurement time once the glass transition is reached. In other words, the time and ensemble averages of the intensity ACF are no longer equivalent.

$$
g^{(2)}_E(q, \tau) \neq g^{(2)}_T(q, \tau)
$$

(4)

Such a system is called non-ergodic, and ensemble averaging needs to be performed to measure the particle dynamics. To achieve this we have implemented a newly developed technique, called echo DLS (Pham et al., 2004). This technique allows the measurement of the ensemble average intensity ACF for non-ergodic systems.

**Echo DLS**

The echo DLS method is an efficient technique for the measurement of the ensemble average intensity ACF. Details of the technique can be found elsewhere (Pham et al., 2004). The method involves a continuous rotation of the sample while measuring the scattered intensity. At a certain time $t$, a speckle $i$ illuminates the detector. At every revolution of the sample $nT$, where $n$ and $T$ are respectively the number and period of the revolution, the same speckle illuminates the detector. The time average intensity ACF of the speckle $i$, $g^{(2)}_{i,T}(q, \tau)$, is calculated at every delay time $\tau = nT$ and results in peaks, or echoes. The maximum height of the peak corresponds to the speckle $i$. Either side of the peaks corresponds to multiple speckles. During one rotation, thousands of speckles illuminates the detector and thus thousands of time average intensity ACFs are calculated over a measurement time scale corresponding to the last delay time of interest, typically $10^4$ s for our colloidal glasses. Pham et al. found that the shape of the peak is independent of the samples and depends only on how many speckles are measured, and the rotation quality. The area under the peak is independent on the quality of the rotation, and is used to correct for imperfect rotation. For colloidal glasses, every speckle corresponds to a sub ensemble $i$ of the full spatial configurations. Averaging the independent intensity ACF of the sub ensembles gives the intensity ACF of the full spatial configuration.

$$
g^{(2)}_E(q, \tau) = \left\{ g^{(2)}_{i,T}(q, \tau) \right\}_i
$$

(5)

The bracket $\langle \rangle_i$ denotes an average over thousands of independent speckles providing the required ensemble average. Due to the limitations of the accuracy of the rotation period, and to minimize the risk of disturbing the particle dynamics, the period of the rotation is limited to $T = 1$ s. This places a lower limit on the measured delay time. The maximum delay time is fixed by the measurement time, typically $10^4$ s for our samples. The Echo DLS method must be combined with conventional DLS to measure the particle dynamics at shorter delay times (van Megen et al., 1998).
Analysis

The aim of this study is to try to characterise the ageing of a colloidal hard sphere glass. The dynamics of colloidal glasses are characterized by an initial decay at short delay times, typically less than about 1s, called $\beta$ decay or the “fast” process, following by a plateau and another decay at longer delay time, typically more than about 5000s, called $\alpha$ decay or the “slow” process. The objective here is to separate and study both processes as functions of the age of the sample, which is quantified by the waiting time $t_m$, also named ageing time, from the end of the quench to the start of the measurement. The sample is tumbled gently to destroy any crystals inside the sample in order to erase the memory of particles in term of particle motions and particle positions. The quench is achieved by stopping the tumbling. The plateau or inflection point between the fast and slow processes was observed to occur at delay times between 50s and 1000s. Thus, in this study we restrict our measurement to Echo DLS experiments and delay times in the range $1-10^4$. The intensity ACF was normalized to the point $\tau=1$ s. Analyses of the autocorrelation function were made in several steps.

(i) First, we determine the position of the inflection point, and the corresponding delay time $\tau_m$, by calculating the minimum of the first derivative of the intensity ACF (van Megen et al., 2005):

$$\frac{d}{d \log \tau} \left[ \log \left( \log \left( g_E^{(2)}(q,\tau) \right) \right) \right]$$

(ii) Second, we calculate the quantity $P(q,\tau)$, which translates the ACF so that $g_E^{(2)}(q,\tau_m)=0$ at the inflection point.

$$P(q,\tau) = \left| \frac{g_E^{(2)}(q,\tau) - g_E^{(2)}(q,\tau_m)}{1 - g_E^{(2)}(q,\tau_m)} \right|$$

We refer to $P(q,\tau < \tau_m)$ as the “fast” component of the fluctuations and $P(q,\tau > \tau_m)$ as the “slow” component.

(iii) Third, we apply appropriate fits to the “fast” and “slow” processes as a function of the sample age.

The purpose of this paper is to determine what information the quantities $P(q,\tau < \tau_m)$ or $P(q,\tau > \tau_m)$ reveal about the ageing process.

Results and Discussion

The experiments were all performed at a scattering angle of 60°, near the main peak of the structure factor, and at a temperature of 23°C. The ACFs are shown in fig. 1a.

Figure 1: (a) Ensemble average of the intensity ACF and its first derivative as functions of the delay time for $\phi=0.58$ at different ageing times. The inset shows the derivative (eq. 6) from which the inflection point is determined. (b) $P(q,\tau)$ as function of the delay time for $\phi=0.58$ at different ageing time. The lines are a stretched exponential fit $P(\tau < \tau_m) = \exp \left[ - (t / t_0)^\beta \right]$ and a power law fit $P(\tau > \tau_m) = (t / t_0)^\gamma$ for the “fast” and “slow” process respectively at an ageing time of 40 min. (c) Delay time of the inflection point, as a function of the ageing time $t_m$. The straight line is power law fit.

Figure 1b clearly shows that the quantity $P(q,\tau)$ (fig 1b) highlights the behaviour around the inflection point, and allows a quantitative comparison of the fast and slow processes as functions of the ageing time. The inflection point is shown to follow a power law as a function of the ageing time, as shown in figure 1c.
We turn now to the parameters extracted from the fits to the fast and slow processes. The decay time $t_0$ (fig 2a) for the stretched exponential fit shows no significant change as a function of ageing time. The stretching parameter $\beta$ (fig 2b) on the other hand shows a small but steady reduction as ageing time increases – in other words, the stretching is becoming more pronounced as a function of ageing. However, it is in the power law fits to the slow process that the ageing process is highlighted. The characteristic time $t_c$ (fig 2c) behaves as a power law with ageing time, while the exponent $\lambda$ (fig 2d) is linear with ageing time. By extrapolating to zero, we can estimate the delay time which would be needed for the plateau in fig 1a to become completely flat – i.e. for the sample to become a perfect glass. For the current sample this occurs at a delay time of $\sim 300$ hours.

![Figure 2: Fit parameters for the “fast” and “slow” processes as functions of the ageing time $t_0$: (a) $t_0$ and (b) $\beta$ for stretched exponential fits to the fast process; (c) $t_c$ and (d) $\lambda$ for the power law fits to the slow process.](image)

Although there are no quantitative experimental studies of ageing of colloidal hard spheres in the glassy state, several ageing studies has been performed on other systems such as gels formed by the aggregation of colloids (Cipelletti et al., 2000) and glassy laponite samples (Abou et al., 2001; Bellour et al., 2003). The three authors use different models to characterize the decay, so comparison is difficult. However, both Cipelletti et al. and Bellour et al. find that the characteristic decay time decays at long times as a power law with an exponent of $\sim 1$. In the case of the hard spheres studied here, this exponent is $0.8 \pm 0.05$. Clearly the hard sphere glass is dynamically slower than these systems.

**Conclusions**

These results demonstrate that this technique and analysis provides a viable method for the analysis of ageing in colloidal glasses. Further experiments are currently underway to study ageing as functions of both volume fraction and scattering vector. This work will shed new light on our understanding of ageing processes in colloidal glasses, and will have wider application to the study of ageing in a range of glasses and gels.

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**References**


