Power Law dependence of Ageing in a Colloidal Hard Sphere Glass

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Measurements of the Intermediate Scattering Function are performed for a colloidal hard sphere glass as functions of scattering vector and waiting time, t_w. We identify a fast process, which is independent of t_w, and a slow process, which shows significant ageing behaviour. We quantify this behaviour via the stretching index, defined at the crossover between fast and slow processes. This analysis shows that the approach of the sample to an ideal "aged" glass, the state in which particles perform only limited motions about fixed average positions, is algebraic in nature.

1.   Introduction

At high volume fractions, colloidal suspensions can exist in out-of equilibrium states known as colloidal glasses, which exhibit slow dynamics and ageing effects [1]. Recent investigations of the ageing process have concentrated on colloidal gels and glasses (e.g. laponite) as functions of the waiting time, t_w, the time elapsed since the quench. The intermediate scattering functions (ISF) of these soft solids are generally found to decay in two stages as a function of delay time τ: an initial decay onto a plateau, followed by a final, age dependent decay. In some cases the plateau height, or Debye-Waller factor, is observed to be non-stationary [2].

In order to shed more light onto the mechanisms responsible of the ageing process, we perform experiments on a simple model system: a colloidal hard sphere glass. In this paper we present the results of an extensive series of measurements on the ageing behaviour of hard sphere glasses as functions of scattering vector and waiting time, and provide some explanations for the observed behaviour. Some of this data has been presented elsewhere [3].

2.   Methods

The particles used in the experiments reported here consist of cores of methymethacrylate (MMA) and trifluoroethyl acrylate (TFEA). Particles were coated by an approximately 10nm thick layer of poly(12-hydroxystearic acid). The preparation and characterisation of these particles have been extensively described in previous work [4, 5]. Their average hydrodynamic radius (R=200nm) and polydispersity (6%), were determined by DLS on very dilute samples. The particles are suspended in a solvent of cis-decalin providing good optical matching and thus removing multiple scattering effects over the range of wave vectors, $1.5<qR<4.15$, studied here. These suspensions represent a good approximation to a perfect hard-sphere system. Accordingly, after mapping the suspension's equilibrium phase behaviour onto that known for the perfect hard-sphere system, the volume fractions of the freezing and melting points can be identified as $\phi_f=0.493$ and $\phi_m=0.545$. In addition these suspensions exhibit a glass transition at $\phi_g \sim 0.57$ [6, 7].

The sample studied here has an effective volume fraction of 0.58 and thus is in the glassy region. Colloidal glasses are non-ergodic (ie time and ensemble averages are not the same), and specialized experimental methods are needed to measure dynamics in these systems. To make statistically valid measurements, non-ergodic averaging techniques must be employed [1, 8] and separate procedures must be adopted to capture the fast and slow

processes. We measure the fast process, or initial decay of the ISF, via the well-established procedure developed by Pusey & van Megen [8]. The slow process, or long-time decay of the ISF, is measured by the Echo DLS method recently developed by Pham et al. [9]. The results of the two methods are combined to yield dynamical measurements over several decades in time. Details of the methods are described elsewhere [3].

3. Results

Fig. 1 shows the ISF as a function of delay time at $\phi=0.58$ for several waiting times, measured at 4 different scattering vectors. In all cases an inflection point separates a fast decay, with no apparent dependence on t_w, and a slow, non-stationary, process that stretches out as the waiting time increases. The fast process is associated with local motions of the particles around average fixed positions and the slow process with larger scale motions of the particles. Ageing is manifest by the non-stationary behaviour observed at long delay times, which is caused by irreversible particle rearrangements.
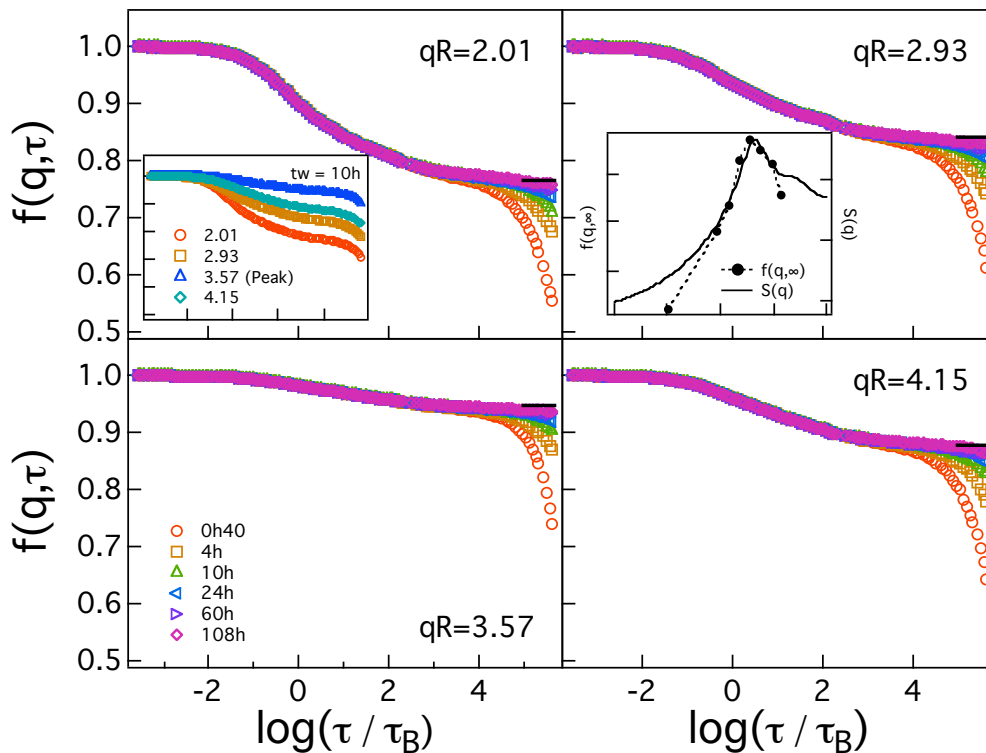

Fig. 1. ISF as function of delay time τ/τ_B for the waiting times indicated. Measurements are made at several scattering vectors, q, around the structure factor peak (qR=3.57). Times are expressed in terms of the Brownian time $\tau_B = R^2/6D_o = 0.0207s$, where R~200nm is the particle radius and D_o the free diffusion coefficient. The upper limit of the delay time window is $\tau_{max}/\tau_B \sim 4 \times 10^5$ and corresponds to $\tau_{max} \sim 8200s$. The inset shows the ISF for an age of 10h at several values of qR. Some of the data has been presented elsewhere [3].

Note that the ISF's do not decay to zero in our time window, which spans approximately nine decades. This contrasts with the results of more complex soft systems, which show a full, or almost full, decay of the measured intensity correlation functions in the experimental time window [10-13]. Despite the limited decay of the ISF, the ageing behaviour can be quantified in a number of ways.

As seen from fig. 1, the t_w-dependency of the ISF increases as delay time is increased – it is most exposed at $\tau=\tau_{max}$ but almost imperceptible at the crossover between the fast and slow process (*ie* the inflection point). One way of quantifying the ageing is by plotting the

actual value of the ISF at the upper time limit of our experimental time window as a function of waiting time [3], but this is somewhat arbitrary as it depends on the time chosen. An alternative method, with no ambiguity, is to calculate the "width" function $w(q,\tau) = -q^2 \ln f(q,\tau)$, defined by analogy with the mean squared displacement for single particle statistics. If the relaxation responsible of the decay of the ISF were diffusive, $w(q,\tau)$ would grow linearly with the delay time τ. Fig. 2 shows $w(q,\tau)$ as function of delay time for the same values of qR and waiting times as fig. 1. It is clear that $w(q,\tau)$ is linear (diffusive) at short times, but non-diffusive, or non-Fickian, processes emerge at intermediate times.
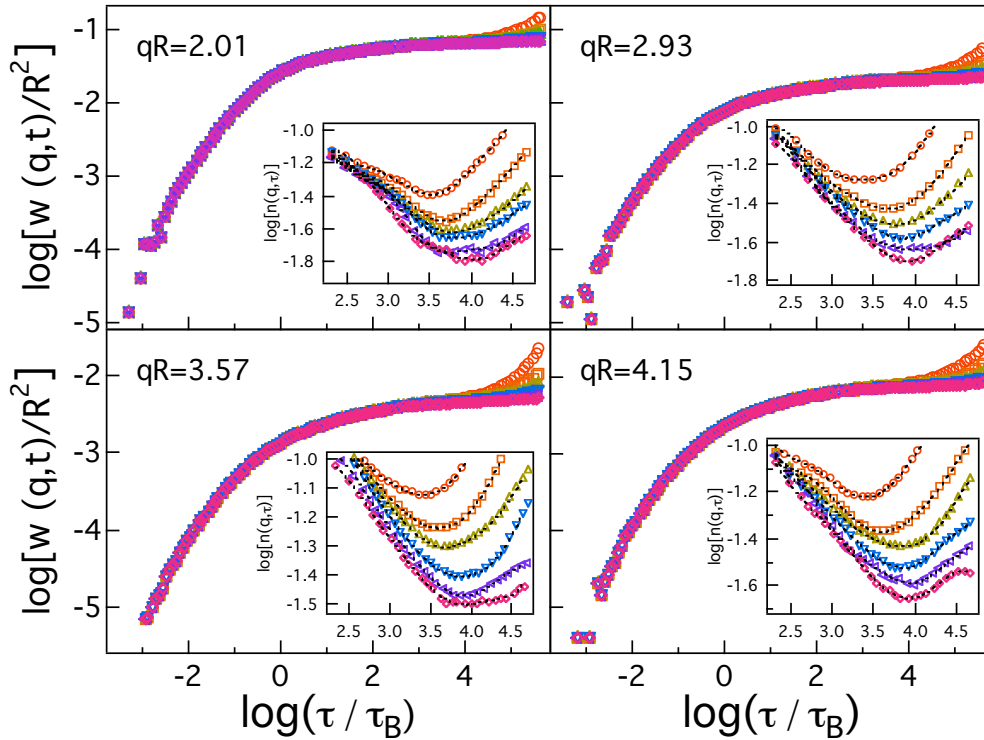

Fig. 2. The width function $w(q,\tau)/R^2$, expressed in terms of R^2, as function of delay time from the data in fig. 1. Insets: $n(q,t)$ in the Echo DLS range, where the inflection is observed. Lines are polynomial fit in the minima region to better identify the minima. Some of the data has been presented elsewhere [3].

The crossover between the fast and slow processes (the inflection point) corresponds to the maximum deviation from diffusive behaviour - *ie* this point most clearly exposes the non-Fickian processes. We identify this crossover by calculating the logarithmic derivative $n(q,t)$:

$$n(q,\tau) = \frac{d\log[w(q,\tau)]}{d\log\tau}$$

which is shown in insets of fig. 2. It is obvious that $n(q,t)$ has a minimum, $v(q) = \min[n(q,\tau)]$, that deepens with age, and the delay time of this minimum is designated τ_m. This corresponds with the crossover between the fast and slow processes, and the stretching index $v(q)$ as a measure of the coupling between them. The stretching index is also a measure of the deviation from Fickian behaviour. For an infinitely dilute suspension, where all particles follows random processes, $v(q) = 1$ and τ_m is undefined (no inflection point). For the perfect glass, where all particles are "caged", $v(q) = 0$ and τ_m is infinite. We represent, in fig. 3, $v(q)$ as function of waiting time for several qR values.
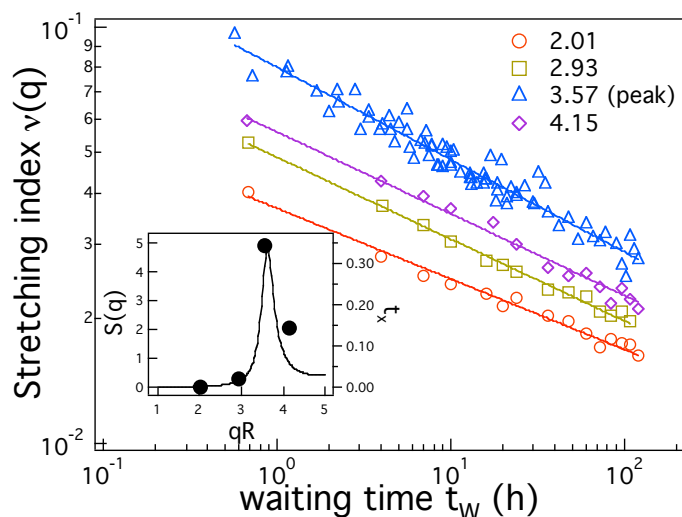
Fig. 3. Stretching index as functions of waiting time, for the indicated values of qR. Lines through the data are power law fits. The inset shows that t_x scales with the structure factor S(q). Some of the data has been presented elsewhere [3].

It is clear that the decay of $v(q)$ follows a power law, for all qR, of the form:

$$v(q,t_w) = \left(\frac{t_w}{t_x}\right)^{\beta}$$

where the amplitude t_x scales approximately with S(q), as shown in inset of fig. 3, and the exponent, b=0.19±0.02, does not show any systematic q dependency.

To conclude, we identify a fast process, with no ageing behaviour, and a slow process with strong ageing behaviour. We quantify the ageing behaviour at the crossover between the fast and slow processes, which corresponds to the maximum deviation from Fickian behaviour. The non-fickian aspects of the density fluctuations, quantified through the stretching index $v(q)$, is found to follow a power law decay with t_w. In other words, following the quench, the colloidal glass approaches its final state algebraically. This final state, the ideal "aged" glass, is defined by $f(q,t \rightarrow \infty) = f(q,\tau_m)$ and $v(q) = 0$, the state in which particles perform only local motions about fixed average positions, with no structural changes.

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