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Ageing and ultra-slow equilibration in concentrated colloidal hard spheres

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Abstract

We study the dynamic behaviour of concentrated colloidal hard spheres using time resolved correlation, a light scattering technique that can detect the slow evolution of the dynamics in out-of-equilibrium systems. Surprisingly, equilibrium is reached a very long time after sample initialization, the non-stationary regime lasting up to three orders of magnitude more than the relaxation time of the system. Before reaching equilibrium, the system displays unusual ageing behaviour. The intermediate scattering function decays faster than exponentially and its relaxation time evolves non-monotonically with sample age.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the last two decades, colloidal hard spheres have been widely studied as a model system that exhibits a transition to an arrested glassy state as particle volume fraction, φ, increases [1]. Above $\varphi \approx 0.49$, the dynamics dramatically slows down and exhibits a two-step relaxation, where the initial relaxation corresponds to the motion of the particles within the cage formed by their neighbours, while the final, α-relaxation is due to cage-escape processes [2, 3]. Probably, the most popular experimental technique for investigating these dynamics has been dynamic light scattering, which has allowed the microscopic dynamics of samples at thermal equilibrium to be probed for volume fractions up to $\varphi \approx 0.55$ [3]. Light scattering experiments measure the time autocorrelation function of the fluctuations of the scattered intensity, $g_2(\tau) - 1$, which is proportional to the squared intermediate scattering function [4]. Confocal microscopy was used in more recent works that focused on dynamic heterogeneity, identifying localized clusters of particles whose dynamics differ from the average [5, 6].

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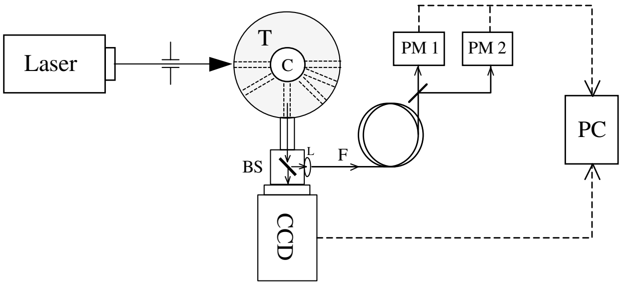

Figure 1. Sketch of the experimental set-up described in section 2.1.

By contrast, experiments probing the non-equilibrium or ageing behaviour of concentrated samples are scarce [3, 7–9]. This is because conventional light scattering techniques require a considerable time averaging to get sufficient statistics. Clearly, extensive time averaging prevents ageing dynamics from being precisely characterized in systems where the dynamics are not stationary. Microscopy experiments can in principle provide time-resolved information, but they often have very limited statistics, since they are forced to deal with rather large particles, for which the dynamics is too slow to be followed in the ageing regime over several decades.

In this work, we take advantage of recently introduced dynamic light scattering techniques, multispeckle [10, 11] and time resolved correlation (TRC) [12], to follow the slow evolution of the dynamics of concentrated suspensions of colloidal hard spheres, from an initial ageing regime up to times where thermal equilibrium is reached. We find that hard spheres display an ageing behaviour that is quite different from the one observed in molecular supercooled liquids. Strikingly, thermal equilibrium is reached only for times that considerably exceed the relaxation time of the system and an unusual 'compressed' exponential relaxation of $g_2 - 1$ is observed in the ageing regime. Additionally, we find that in the stationary regime the dynamics appears to be extremely sensitive to a small shear, an issue possibly relevant when devising experimental methods dealing with very concentrated samples.

2. Experimental methods

2.1. Experimental set-up

The experimental set-up is shown in figure 1. The light source is a frequency-doubled Nd:YAG laser whose vertically polarized beam impinges on a cylindric scattering cell, C. The cell temperature is set to $T = 20 \pm 0.05\,^{\circ}\mathrm{C}$ via water circulating in a copper cell holder, T. Light scattered within a volume of about 1 mm^3 at a scattering angle $\theta = 90^{\circ}$ (which corresponds to wavevectors close to the first peak of the structure factor of our hard sphere system) is split by the beam splitter BS so as to illuminate a charge-coupled device (CCD) detector and to be collected by a single-mode, polarization-maintaining fibre optics. Two photomultipliers connected to a hardware correlator hosted in a personal computer (PC) allow the fibre optics signal to be analysed to obtain $g_2(\tau) - 1$ down to a lag time $\tau = 50$ ns, for samples whose relaxation time does not exceed 100 s and whose dynamics are stationary (here, $g_2 - 1$ is obtained by extensive time averaging).

The CCD images of the speckle pattern generated by the sample are transferred to the PC via a frame grabber and stored on the hard drive for later processing via a software correlator. The quantity measured in our TRC experiments is the degree of correlation, $c_I(t, \tau)$, of the scattered intensity of two images separated by a lag τ [12]:

$$c_I(t,\tau) = \frac{\langle I_p(t) I_p(t+\tau)\rangle_p}{\langle I_p(t)\rangle_p \langle I_p(t+\tau)\rangle_p} - 1, \tag{1}$$

where $I_p(t)$ is the instantaneous value of the scattered intensity measured by the pth pixel at time t, and the average $\langle\cdots\rangle_p$ is taken over all CCD pixels. Note that no time average is performed; thus, the degree of correlation depends on both the time lag τ between the two images analysed and the time t at which the first image of the pair is taken. In systems with stationary dynamics a further average over t can be performed. The normalized auto-correlation function is then obtained

$$g_2(\tau) - 1 = \langle c_I(t,\tau)\rangle_t, \tag{2}$$

similarly to conventional dynamic light scattering techniques. The minimum time lag for which c_I can be calculated, $\tau \simeq 20$ ms, is limited by the speed of the CCD camera and the exposure time. By coupling DLS data obtained from the hardware correlator to TRC, we are able to measure simultaneously and on the same sample the intensity correlation function from $\tau = 50$ ns up to very large lag times, $\tau \simeq 10^4$ s.

2.2. Sample preparation

The particles used in this work are poly-methylmethacrylate (PMMA) spheres of radius $R = 140$ nm, with a degree of polydispersity of about 10% that prevents crystallization in the experimental timescale. The particles are sterically stabilized by a thin layer of poly-12-hydroxystearic acid of approximately 10 nm thickness. They are suspended in a mixture of organic solvents (*cis,trans*-decalin and tetralin) that closely matches their refractive index and reduces van der Waals interactions.

Samples are prepared by centrifugation of a stock suspension for about 24 h at 1000 g to obtain a dense amorphous sediment, assumed to be near random close packing, $\varphi_0 \approx 0.67$, for a 10% polydispersity [13]. The clear supernatant is removed and a controlled mass of solvent is added to obtain the desired volume fraction, φ. Samples are then dispersed by vortexing and tumbling for about 24 h. Before starting measurements the sample is thermalized at 20 °C for 15 min. In ageing experiments, the waiting time, t_w, is taken from the end of the dispersion, which corresponds to $t_\mathrm{w} = 0$. Since our sample is very polydisperse we cannot use the freezing volume fraction to precisely control volume fractions [1–3], leading to rather large uncertainties on the calculated φ. Indeed, a comparison of our dynamic data with the literature [1–3] suggests that we systematically underestimate volume fractions by 2–4%. This should be kept in mind when comparing the present results to the literature.

3. Results

The left panel of figure 2 shows the waiting time evolution of the degree of correlation $c_I(t_\mathrm{w},\tau)$ measured for a sample at $\varphi = 0.545$, for various time lags τ ranging from 2 to 2000 s and corresponding to the α-relaxation of the system. At fixed lag, c_I continuously increases with t_w, demonstrating that changes of the sample configuration during a fixed time interval become smaller when t_w increases. In other words, the dynamics slows down when the system gets older, a clear manifestation of ageing [14]. The right panel shows a set of representative intensity correlation functions $g_2(t_\mathrm{w},\tau) - 1$ obtained by averaging c_I over a short time window (a few hundreds of seconds), starting at various t_w. To extract the characteristic time, $\tau_\alpha(t_\mathrm{w})$, of the α-relaxation, we fit the curves by a stretched exponential: $g_2(t_\mathrm{w},\tau) - 1 = a \exp[-(\tau/\tau_\alpha)^p]$. The inset shows τ_α versus t_w, indicating that the relaxation time increases linearly with sample

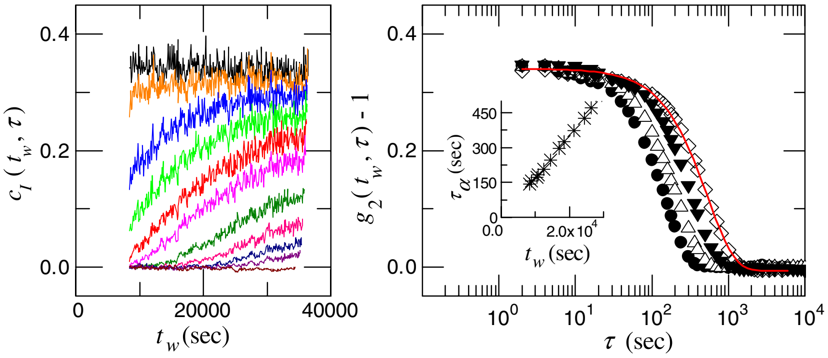

Figure 2. Left: age dependence of the degree of correlation, $c_I(t_w, \tau)$, measured for a sample with $\varphi = 0.545$. From bottom to top, $\tau = 2000$, 1200, 1000, 800, 600, 400, 300, 200, 120, 40, 2 s. The steady growth of $c_I(t_w, \tau)$ with t_w indicates ageing. Right panel: time decay of $g_2(t_w, \tau) - 1$, obtained by averaging $c_I(t_w, \tau)$ over a time window of a few hundred seconds, for $t_w = 8400$, 12 400, 18 400, and 29 400 s (from left to right). The shape of the relaxation is well described by a 'compressed' exponential form, as shown by the full line, which has a stretching exponent $p = 1.22$. Inset: linear dependence of the α-relaxation time on t_w typical of a 'simple ageing' behaviour.

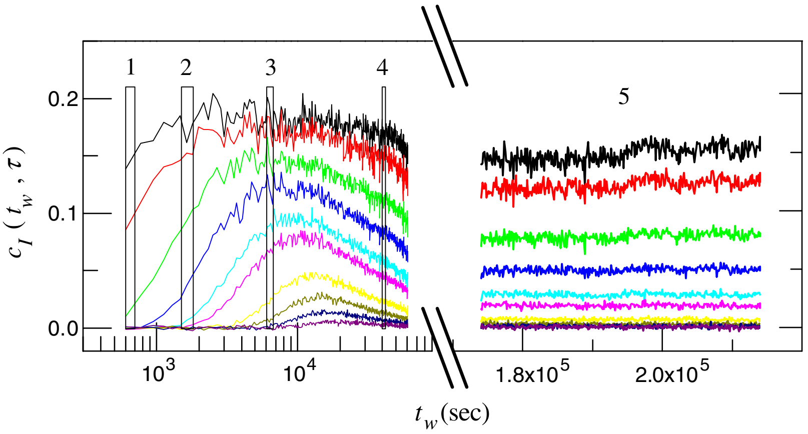

Figure 3. Degree of correlation as a function of t_w for a sample with $\varphi = 0.505$. From bottom to top, $\tau = 200$, 140, 100, 70, 40, 30, 18, 10, 4, 2 s. Before the x axis break, the scale is logarithmic, in order to better appreciate the initial evolution of the dynamics. The rectangles indicate the time windows over which c_I is averaged to obtain $g_2 - 1$ shown in figure 4.

age, a behaviour observed in many glassy systems [14] and referred to as 'simple ageing'. Note however that $\tau_\alpha / t_w \ll 1$, thus ruling out the simple explanation stating that the relaxation time is set by the age, $\tau_\alpha \approx t_w$. Surprisingly, we find that for all curves $p \approx 1.3$. This behaviour is in contrast with that of concentrated colloidal hard spheres at equilibrium, where $p < 1$ [2]. Intriguingly, it is similar to the 'compressed' exponential relaxation found in a variety of soft glassy materials out of equilibrium [15].

The sample shown in figure 2 does not reach equilibrium on the experimental timescale. In order to investigate how a stationary state is eventually reached, we turn to a more diluted sample, $\varphi = 0.505$. Figure 3 shows the t_w dependence of c_I. A striking behaviour is observed. Initially, c_I grows, as also observed in figure 2. However, after reaching a maximum, the degree of correlation then decreases with t_w, before eventually reaching a stationary regime.

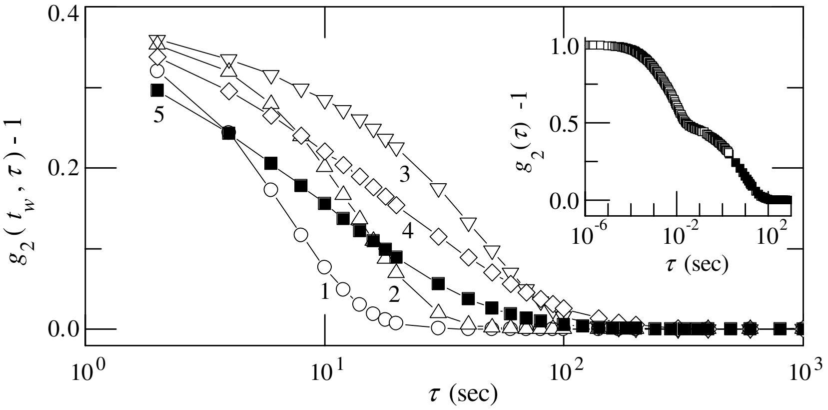

Figure 4. Intensity correlation functions calculated from the c_I of figure 3. Each curve is labelled by the time window shown in figure 3. The initial ageing regime (1 → 2 → 3) is followed by an acceleration of the dynamics (3 → 4 → 5) and finally by a stationary regime (5). Inset, CCD data (solid squares) and hardware correlator data (open squares) collected simultaneously in the stationary regime.

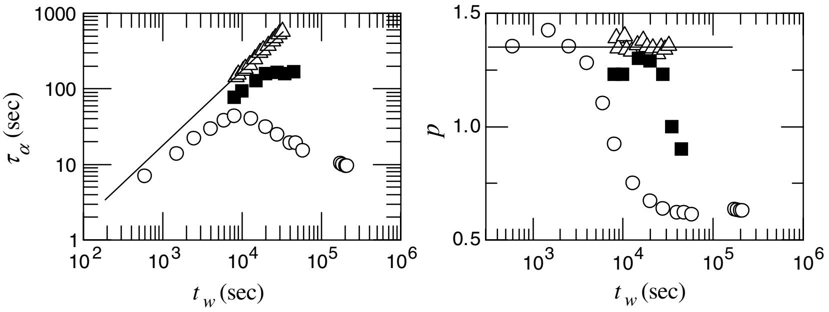

Figure 5. Age evolution of the relaxation time τ_α (left panel) and the stretching exponent p (right panel) for samples at $\varphi = 0.545$ (open triangles), $\varphi = 0.54$ (solid squares), and $\varphi = 0.505$ (open circles). The lines $\tau_\alpha \propto t_w$ and $p = 1.3$ are guides to the eye.

This implies that after the initial simple ageing regime, the dynamics accelerates and finally becomes stationary. Moreover, for different τ the maximum of c_I occurs at different ages, implying that the shape of $g_2 - 1$ also changes with time.

The evolution of $g_2 - 1$ is shown in figure 4. Initially the relaxation time increases and the correlation functions are compressed ($p \approx 1.3$). Then, τ_α goes back to smaller values. Concomitantly, the shape changes and becomes more stretched. For $t_w \geqslant 1.8 \times 10^5$ s the dynamics becomes stationary. Thus, equilibrium is reached after more than 1000 relaxation times, a behaviour at odds with that of molecular glassy systems [14]. This suggests that motion on length scales much larger than the particle size might be involved in this process. At equilibrium, we measure the fast dynamics with the hardware correlator by averaging $g_2 - 1$ over 12 h. The inset of figure 4 shows the full $g_2 - 1$ obtained by pasting together hardware correlator and CCD data. A typical two-step decay with a final stretched relaxation ($p \approx 0.6$) is observed.

Values of the t_w dependence of τ_α and p are shown in figure 5 for the two samples discussed above and for an additional intermediate volume fraction. For the lower φ (open circles), three

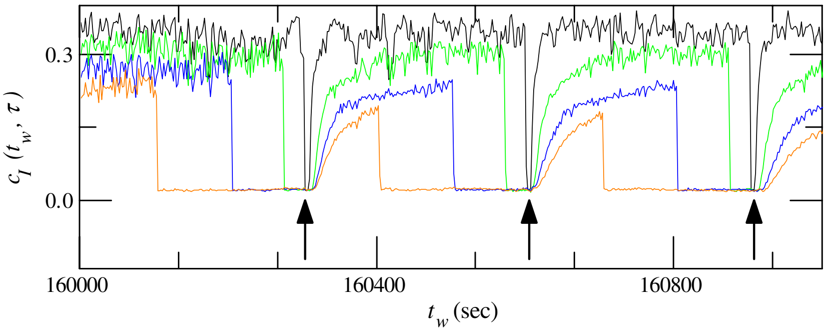

Figure 6. Time evolution of the degree of correlation for a sample with $\varphi = 0.496$, after reaching equilibrium (from bottom to top, $\tau = 200, 100, 30, 2$ s). The sample is slightly rotated at three different times indicated by the arrows. Recovery after each rotation is very slow.

regimes are observed: ageing ($\tau_\alpha \propto t_\mathrm{w}$ and $p \approx 1.3$), acceleration of the dynamics (τ_α and p decrease with t_w), and stationary dynamics (τ_α and p constant). As the volume fraction increases, the end of the ageing regime shifts towards larger t_w, eventually becoming too large to be detected.

Our findings indicate that it takes a surprisingly long time for concentrated hard spheres to recover from a mechanical perturbation, such as the initial homogenization. This equilibration time may become prohibitively long when τ_α exceeds 1000 s. Moreover, ultra-slow equilibration is potentially relevant to several measuring schemes used to deal with glassy dynamics, where the sample cell is rotated to accumulate statistics, either in between short DLS runs when measuring short time dynamics (‘brute force’ method [16]), or continuously to access the slow dynamics (‘interleaved’ [17] or ‘echo’ [18] methods). Indeed, we show the effect of a tiny rotation of the cell in figure 6. Initially, the degree of correlation is almost constant, since the sample is at equilibrium. When the sample is turned manually by the smallest possible amount (arrows in the figure), c_I drops to zero, because the speckle pattern changes completely. Strikingly, it takes a very long time for c_I to grow back to its initial value. Moreover, the larger τ the longer the recovery time. We note that at the smallest delay shown in figure 6, c_I stabilizes in a few seconds, suggesting that the short time dynamics should not be significantly affected by the sample rotation. By contrast, on the longer timescales probed by the interleaved or echo methods, sample rotation may spuriously accelerate the dynamics. It would be interesting to also test these effects in set-ups where sample rotation is done by a stepper motor.

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References

[1] Pusey P N and van Megen W 1986 *Nature* **320** 340
[2] van Megen W and Underwood S M 1993 *Phys. Rev.* E **47** 248

[3] van Megen W, Mortensen T C, Williams S R and Müller J 1998 *Phys. Rev.* E **58** 6073

[4] Berne B J and Pecora R 1976 *Dynamic Light Scattering* (New York: Wiley)

[5] Weeks E R, Crocker J C, Levitt A C, Schofield A and Weitz D A 2000 *Science* **287** 627

[6] Kegel W K and van Blaaderen A 2000 *Science* **287** 290

[7] Pham K N, Egelhaaf S U, Pusey P N and Poon W C K 2004 *Phys. Rev.* E **69** 011503

[8] Courtland R E and Weeks E R 2003 *J. Phys.: Condens. Matter* **15** S359

[9] Simeonova N B and Kegel W K 2004 *Phys. Rev. Lett.* **93** 035701

[10] Bartsch E, Frenz V, Baschnagel J, Schartl W and Sillescu H 1997 *J. Chem. Phys.* **106** 3743

[11] Cipelletti L and Weitz D A 1999 *Rev. Sci. Instrum.* **70** 3214

[12] Cipelletti L, Bissig H, Trappe V, Ballesta P and Mazoyer S 2003 *J. Phys.: Condens. Matter* **15** S257

[13] Schaertl W and Sillescu H 1994 *J. Stat. Phys.* **77** 1007

[14] Bouchaud J P, Cugliandolo L F, Kurchan J and Mézard M 1998 *Spin Glasses and Random Fields* ed A P Young (Singapore: World Scientific)

[15] Cipelletti L and Ramos L 2005 *J. Phys.: Condens. Matter* **17** R253

[16] Pusey P N and van Megen W 1989 *Physica* A **157** 705

[17] Muller J and Palberg T 1996 *Prog. Colloid Polym. Sci.* **100** 121

[18] Pham K N, Egelhaaf S U, Moussaid A and Pusey P N 2004 *Rev. Sci. Instrum.* **75** 2419