

# Temporal heterogeneity of the slow dynamics of a colloidal paste

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**Abstract.** We investigate the slow dynamics of a soft glass, a concentrated suspension of polydisperse colloidal particles, by using multispeckle Diffusing Wave Spectroscopy (DWS). Two distinct regimes are observed: for small sample age,  $t_w$ , the dynamics smoothly slows down, as revealed by a nearly linear increase of the characteristic relaxation time,  $\tau_s$ , measured by DWS. At longer ages, the dynamics is quasi stationary, but  $\tau_s$  exhibit anomalously large fluctuations in time. The time scale of the dynamical fluctuations is found to be slightly shorter than the average relaxation time. The variance of the intensity correlation function is maximum for time delays comparable to the average relaxation time, in striking analogy with recent simulations of glass-forming liquids.

## INTRODUCTION

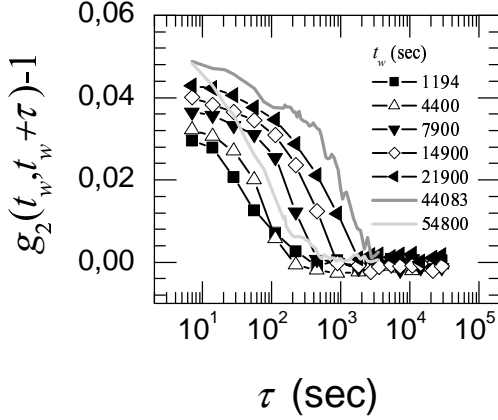
In the past years, experimental and theoretical work has increasingly pointed to the fundamental role of dynamical heterogeneity in the slow dynamics of glassy systems [1, 2]. While investigations on hard condensed matter systems, such as structural or spin glasses, are relatively abundant, until recently much less attention has been devoted to soft matter systems, an exception being the confocal microscopy study of dynamical heterogeneity in hard sphere colloidal glasses [3, 4]. Soft glasses are of great interest, both in view of the numerous industrial applications (e.g. in the food, personal care, and paint industries) and because they can serve as model systems, since the relevant time and length scale are relatively easily accessible and because the interactions between particles can be controlled to a great extent. Therefore, glassy –or *jammed* [5]– soft materials provide a unique opportunity to better understand dynamical heterogeneity and to address issues such as the life time and the spatial extent of dynamical fluctuations.

## MATERIALS AND METHODS

In this paper we present an experimental investigation of temporal heterogeneity in the slow dynamics of a concentrated colloidal suspension. The colloids are xenospheres [6], of typical size  $20 \mu\text{m}$  and large polydispersity, due to the presence of fragmented spheres, as revealed by scanning electron microscopy. They are formed by permanently aggregated primary particles,

latexes of poly-vinylchlorure covered by a surfactant, whose size is of the order of  $0.2 \mu\text{m}$ . The xenospheres are suspended in an organic solvent, dioctylphthalate, at a mass fraction of 40%, corresponding to a volume fraction  $\phi \approx 66.4\%$  (note that, due to the large polydispersity, the maximum packing fraction is estimated to be as high as 75.2%). Similar colloidal pastes are used as a precursor in the industrial production of PVC foams. After loading the sample in a cell, we vigorously shake it (using a vortex mixer) to erase any memory of the shear imposed during the cell filling and to re-initialize the dynamics [7]. We define the age  $t_w$  of the sample as the time elapsed since mixing.

The dynamics of the suspension is probed by Diffusing Wave Spectroscopy (DWS) [8], a non-invasive light scattering technique for highly turbid samples. We use a combination of the multispeckle technique [9] and the Time Resolved Correlation method [10] to measure the slow relaxation mode of the paste and to characterize its temporal heterogeneity. In our experiment, a laser beam of width 1 mm impinges onto a 2 mm thick cell containing the sample. The cell is thermostated at  $23 \pm 0.05 \text{ }^\circ\text{C}$ . Due to the high turbidity of the sample, the incoming photons are scattered a large number of times before exiting the cell. The speckle pattern due to the interference of the scattered photons is recorded by a CCD camera. Any motion in the sample determines a change in the speckle pattern. Accordingly, the dynamics of the sample is measured by quantifying the temporal fluctuations of the speckle pattern. Following the TRC scheme, we measure the degree of correlation  $c_I(t_w, \tau)$  between speckle patterns at time  $t_w$  and  $t_w + \tau$ :

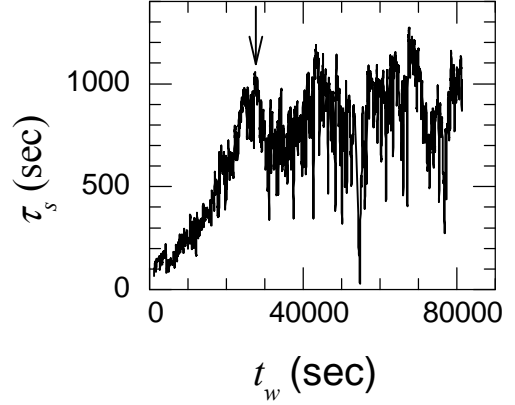


**FIGURE 1.** Final decay of the intensity autocorrelation function measured by multispeckle DWS for a concentrated colloidal paste. The curves are labelled by sample age. For  $t_w < 28000$  sec the dynamics steadily slows down (symbols). At larger  $t_w$ , large fluctuations of the characteristic time are observed and  $g_2 - 1$  is much more noisy (lines).

$c_I(t_w, \tau) = \frac{\langle I_p(t_w)I_p(t_w+\tau) \rangle_p}{\langle I_p(t_w) \rangle_p \langle I_p(t_w+\tau) \rangle_p} - 1$ , where  $I_p(t)$  is the time-dependent intensity at pixel  $p$  and  $\langle \dots \rangle_p$  denotes the average over the CCD pixels. Note that, contrary to previous experiments,  $c_I$  is averaged only over pixels, and not over time or over several runs. This allows us to probe the dynamics with a time resolution equal to the CCD frame rate (in this experiment, a frame is grabbed every 7 sec) and to fully characterize its temporal heterogeneity. In the following, we will first describe the behavior of the two-time intensity autocorrelation function  $g_2(t_w, t_w + \tau)$ , which we obtain by averaging  $c_I(t_w, \tau)$  over a short time window of 70 sec, centered around  $t_w$ . We will then focus on the temporal heterogeneities of the dynamics by analyzing the fluctuations of  $c_I(t_w, \tau)$  at a fixed lag  $\tau$ .

## RESULTS AND DISCUSSION

Figure 1 shows  $g_2(t_w, t_w + \tau)$  as a function of  $\tau$  for several times  $t_w$  after initializing the sample. Because of the limited speed of the CCD camera, only the final decay of  $g_2(t_w, t_w + \tau)$  is accessible. However, a fast relaxation mode must also be present, which is responsible for the reduced value of the correlation function at the smallest lag accessible to the CCD (in our setup, the upper limit of  $g_2 - 1 > 0.3$ ). Initially, the amplitude of the final relaxation mode increases, thus suggesting that the fast motion of the particles is increasingly constrained, and its characteristic time appears to grow steadily with sample age (symbols in Fig. 1). This aging behavior is typical of glassy materials and has been observed in sev-

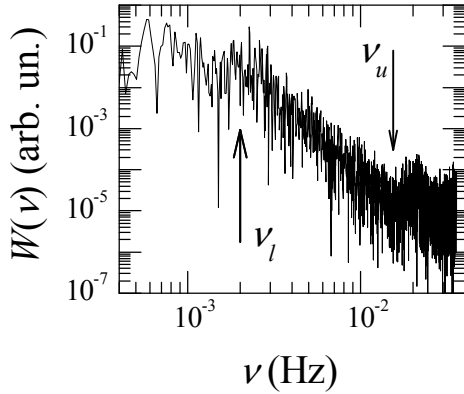


**FIGURE 2.** Age dependence of the characteristic time  $\tau_s$  of the slow dynamics of a concentrated colloidal paste. The arrow indicates the cross-over between the initial regime, where  $\tau_s \propto t_w^{1.1 \pm 0.1}$ , and the quasi-stationary regime, where large fluctuations of  $\tau_s$  are observed

eral colloidal systems [11]. For  $t_w > 28000$  sec, a totally different behavior is observed (lines in Fig. 1). Strikingly, the characteristic time of the final decay of  $g_2(t_w, t_w + \tau)$  exhibits large fluctuations: the dynamics appears to slow down or accelerate in a random fashion. Moreover, the shape of the correlation functions becomes quite erratic: sudden drops and oscillations are often observed. (see for example the curve for  $t_w = 54800$  sec).

To better investigate this surprising behavior, we fit  $g_2(t_w, t_w + \tau) - 1$  by a stretched exponential function  $a \exp[-(\tau/\tau_s)^p]$ . This functional form is found to fit well most of the data and to provide a reasonable estimate of the relaxation time even when  $g_2(t_w, t_w + \tau)$  strongly deviates from a smooth behavior. We plot the age evolution of the characteristic time  $\tau_s$  obtained from the fits in Fig. 2. The smooth growth of  $\tau_s$  for  $t_w < 28000$  sec confirms the existence of an initial aging regime, as suggested by the evolution of the correlation functions shown in Fig. 1. In this regime, the growth of  $\tau_s$  is nearly linear: a fit to a power law in the range  $3000 \text{ sec} < t_w < 28000 \text{ sec}$  (not shown) yields an exponent of  $1.1 \pm 0.1$ . A similar linear growth of the characteristic relaxation time has been observed in many glassy systems, both in hard and soft condensed matter and is often referred to as simple aging.

As can be seen in Fig. 2, after the initial simple aging regime the slow dynamics becomes almost stationary, yet extremely heterogeneous in time. A linear fit to the data shows that in the quasi-stationary regime  $\tau_s$  increases –on average– by less than 20% over 14 hours, to be compared to a 32-fold increase over 8 hours in the initial aging regime. Surprisingly, the TRC method reveals that the relaxation time exhibits extremely large fluctuations, much greater than those in the initial regime. In-

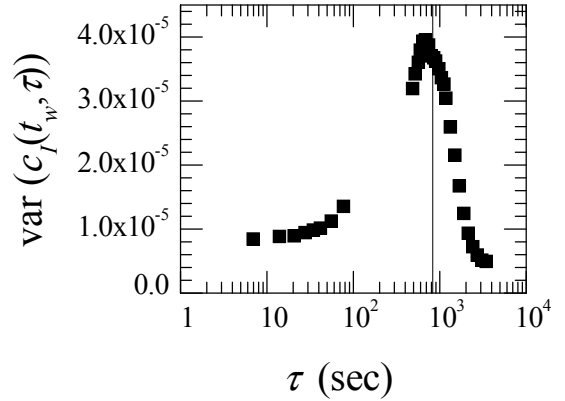


**FIGURE 3.** Power spectrum of the fluctuations of the characteristic time of the slow dynamics in the quasi-stationary regime. The two arrows indicate the lower and upper cutoff frequency, corresponding to 500 and 70 sec, respectively.

deed, the peak-to-peak amplitude of the variation of  $\tau_s$  is comparable to its mean value ( $\langle \tau_s \rangle_{t_w} = 830$  sec) and occasionally  $\tau_s$  drops by more than a factor of 10.

Dynamical heterogeneities have been observed in the past in a variety of glassy systems, and are generally associated to spatial variations of the dynamics, with regions of “fast-moving” molecules or particles coexisting with regions of slower particles. For hard condensed matter systems, the size of these regions is estimated to be of the order of a few nm [1], that is of the order of 10 molecules. Confocal microscopy experiments on supercooled colloidal fluids have shown that the most mobile particles form clusters whose maximum size is also of the order of 10 particles [4]. It is therefore surprising that dynamical heterogeneities are observed in our experiment, where the dynamics is averaged over the whole scattering volume, which contains more than  $3 \cdot 10^5$  particles. Indeed, if the size of the regions over which the dynamics is correlated was the same as in previous experiments, more than 300 such regions would be contained in the scattering volume at any time, thus reducing drastically the temporal fluctuations of the dynamics measured by DWS. Therefore, our experiments suggest that the size of dynamically correlated regions in highly concentrated colloidal pastes may be larger.

In order to quantify the time scale of the fluctuations of the dynamics in the quasi-stationary regime, we calculate the power spectrum of  $\tau_s(t_w)$ ,  $W(v)$ . The results are shown in Fig. 3: at high frequency ( $v > v_u \approx 0.014$  Hz, corresponding to a time scale of 70 sec)  $W(v)$  is flat. This upper cutoff frequency is most likely related to the slight smoothing of the  $c_I$  data (average over a time window of 70 sec), which we perform when calculating  $g_2 - 1$ , as explained above. Between  $v_l \approx 0.002$  Hz and  $v_u$ , the power spectrum rapidly increases with decreasing fre-



**FIGURE 4.** Variance of the degree of correlation  $c_I$  as a function of the time delay between CCD images, in the quasi-stationary regime. The vertical line indicates the average relaxation time of  $g_2 - 1$  over the same time interval.

quency, while below  $v_l$   $W(v)$  is again flat, as one would expect for random, uncorrelated fluctuations. Therefore, the frequency dependence of the power spectrum indicates that the fluctuations of the dynamics occur mainly on time scales up to  $v_l^{-1} = 500$  sec. Similar results are obtained when calculating the time autocorrelation function of  $\tau_s$  (not shown): a decay is observed, whose characteristic time is of the order of 280 sec. Thus, the time scale of the fluctuations of the dynamics is of the order of a few hundreds seconds, close to but slightly smaller than the time-averaged relaxation time,  $\langle \tau_s \rangle_{t_w} = 830$  sec.

The behavior of the characteristic time  $\tau_s$  as a function of  $t_w$  provides a convenient means to describe dynamical heterogeneity. Further information, however, can be obtained by analyzing the fluctuations of the degree of correlation  $c_I(t_w, \tau)$  for all time delays  $\tau$ . Figure 4 shows the variance of  $c_I(t_w, \tau)$ ,  $\sigma^2$ , as a function of  $\tau$ , calculated from the data in the quasi-stationary regime. We recall that in an usual light scattering experiment  $g_2(\tau) - 1$  is obtained by averaging  $c_I(t_w, \tau)$  over time. Therefore,  $\sigma^2$  represents the “spread” around the mean value of the intensity correlation function at any given time delay  $\tau$ . For  $77 \text{ sec} < \tau < 490 \text{ sec}$  the variance is artifactually enhanced due to quasi-periodic fluctuations of the cell temperature: these data are not shown in Fig. 4. These fluctuations, whose amplitude is of the order of  $0.05^\circ\text{C}$ , slightly change the solvent refractive index and thus the phase of the scattered photons, resulting in a periodic loss of correlation. However, they do not affect the particle dynamics, as we checked in control experiments where the sample temperature was varied in a controlled, periodic way. The variance of  $c_I$  is maximum for a delay of 700 sec, very close to the time-averaged relaxation time, indicated by the vertical line in Fig. 4. This behav-

ior is very different from that observed for the dynamics of a diluted suspension of colloids undergoing Brownian motion, for which no dynamical heterogeneities are expected. Indeed, we find that for Brownian particles  $\sigma^2(\tau)$  is constant for all delays.

The fact that the maximum of the variance is very close to  $\langle \tau_s \rangle_{t_w}$ , together with the observation that the typical life time of the fluctuations of the dynamics is again of the order of  $\langle \tau_s \rangle_{t_w}$ , strongly suggest that the only relevant time scale is that of the relaxation of  $g_2 - 1$ , and that large fluctuations of  $\tau$  are an intrinsic feature of the slow relaxation mode. Indeed, a preliminary analysis of the data, where we assume  $g_2(t_w, t_w + \tau) - 1 = a * \exp[-(\tau/\tau_s(t_w))^{p(t_w)}]$  at all  $t_w$ , shows that, up to second order in the fluctuations  $\delta\tau_s$  and  $\delta p$  of  $\tau_s(t_w)$  and  $p(t_w)$ , the variance of  $c_I$  is peaked for  $\tau \approx \langle \tau_s \rangle_{t_w}$ . This analysis will be presented in a forthcoming paper.

Remarkable analogies exist between the experiments presented here and recent simulations of glass-forming liquids [12]. Lačević *et al.* introduce a time-dependent ‘order parameter’  $Q(t)$  that compares the system configuration at two times separated by  $t$  and then calculate the (normalized) variance of  $Q(t)$ ,  $\chi_4(t)$ .  $\chi_4(t)$  is found to be peaked around the characteristic time of the final relaxation of  $Q(t)$ , much as, in our experiments,  $\sigma^2$  is peaked around  $\langle \tau_s \rangle_{t_w}$ . Indeed, the precise form of  $Q(t)$  is irrelevant for the main results of their theory: we can thus identify our  $c_I(t_w, \tau)$  with  $Q(t = \tau)$ , since  $c_I(t_w, \tau)$  compares two speckle patterns, and thus two system configurations, separated by  $\tau$ . Similarly,  $\sigma^2(\tau)$  can be identified with the generalized susceptibility  $\chi_4(t = \tau)$ . Therefore, TRC provides a novel means to access experimentally  $\chi_4(t)$ . The similarities between vastly different systems hint at the generality of the behavior of dynamical fluctuations in glassy systems. Further insight will be gained by a systematic exploration of the behavior of the fluctuations when approaching the fluid-solid transition. For our system, contrary to molecular glasses, this transition is not achieved by decreasing the temperature, but rather by increasing the particle volume fraction. Preliminary results hint at a non-monotonic variation of  $\sigma^2$  with  $\phi$ .

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## REFERENCES

1. Ediger, M. D., *Annu. Rev. Phys. Chem.*, **51**, 99–128 (2000).
2. Glotzer, S. C., *Journal of Non-Crystalline Solids*, **274**, 342–355 (2000).
3. Kegel, W. K., and van Blaaderen, A., *Science*, **287**, 290–293 (2000).
4. Weeks, E., Crocker, J., Levitt, A., Schofield, A., and Weitz, D., *Science*, **287**, 627–630 (2000).
5. Liu, A., and Nagel, S., *Nature*, **396**, 21 (1998).
6. Herk, H. H., Bikoles, N. M., Overgerger, C. G., and Menzes, G., “Vinyl chloride polymerization,” in *Encyclopedia of polymer science and engineering*, edited by H. E. Mark, Wiley-Interscience, New York, 2003, vol. 17, 3rd edn.
7. Viasnoff, V., and Lequeux, F., *Phys. Rev. Lett.*, **89**, 065701 (2002).
8. Weitz, D. A., and Pine, D. J., “Diffusing-wave spectroscopy,” in *Dynamic Light scattering*, edited by W. Brown, Clarendon Press, Oxford, 1993, pp. 652–720.
9. Viasnoff, V., Lequeux, F., and Pine, D. J., *Rev. Sci. Instrum.*, **73**, 2336–2344 (2002).
10. Cipelletti, L., Bissig, H., Trappe, V., Ballesta, P., and Mazoyer, S., *J. Phys.: Condens. Matter*, **15**, S257–S262 (2003).
11. Cipelletti, L., and Ramos, L., *Curr. Opin. Colloid Interface Sci.*, **7**, 228–234 (2002).
12. Lačević, N., Starr, F. W., Schroder, T. B., Norikov, V. N., and Glotzer, S. C., *Phys. Rev. E*, **66**, 030101 (2002).