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## Aging of a colloidal “Wigner” glass

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**Abstract.** – We study the aging of a colloidal glass, which is obtained for extremely low volume fractions due to strong electrostatic repulsions, leading to the formation of a “Wigner glass”. During the aging, a new crossover between a complete and incomplete decay of the correlation function is observed, accompanied by an increase in the non-ergodicity parameter. The dynamics can be described as a cage-diffusion process. For short times, the escape of the particles from “cages” formed by neighbouring particles dominates; for long times the particles cannot escape anymore and the system becomes strongly non-ergodic.

Glasses are a non-equilibrium form of matter and are, maybe for that reason, still ill-understood [1-4]. The usual way of looking at the glass transition is given by the so-called schematic mode-coupling theory [1,2]. In this theory, the glass transition is a strong ergodic to non-ergodic transition. In real systems, however, the “transition” always appears rounded. The rounding of the transition is due to the appearance of a “slow mode” in the system [1-4]. The non-equilibrium evolution of a system quenched into a glassy state is often referred to as aging, and is common to both structural and spin-glasses. Understanding the aging processes in a glassy system is crucial for the description of glassy dynamics; unfortunately, due to its very nature, the classical mode-coupling theory does not provide us with any information on the aging process [2].

A recent careful inspection of the mode-coupling equations [4] reveals that this serious limitation may in fact be overcome. This work presents the first detailed description of the aging process. The evolution of the system is described in terms of the correlation and response functions of the system. Unfortunately, for most of the systems (structural glasses) studied to date, these quantities are not easy to obtain experimentally. For this reason, progress has been limited to a number of recent theoretical (spin-glass) and simulation (Lennard-Jones glass) studies [3,4]. The key result of both theory and simulations is that the diffusion may be looked upon as a cage-diffusion process. The particles reside in dynamic cages formed by

their neighbours, and escape from these cages after a characteristic time that depends on the aging time  $t_w$ .

Colloidal glasses are ideal model glasses and have for this reason been studied extensively. Because of the experimental difficulties in studying structural glasses [5], the strongest evidence for the applicability of the classical mode-coupling theory comes from studies on colloidal glasses [5,6]. The difference of the present work with respect to previous studies on colloidal systems (in which experiments were performed as a function of the volume fraction of particles) [5] is that we can shear-melt our system, and follow the aging in time after a quench into the glassy phase. The main difference with respect to structural glasses is that for the colloidal system the density is the only control parameter, whereas for structural glasses, temperature and density are the two (coupled) parameters. This makes a theoretical description even more difficult than for colloidal glasses.

The second rationale behind the present experiments is the recent prediction of the existence of “Wigner glasses”, very low-density glasses whose formation is due to the existence of long-range Coulombic interactions [7]. Wigner [8] predicted the existence of an electron crystal due to electrostatic interactions. The long range of these interactions causes the interparticle distance in these crystals to be much larger than the particle diameter, leading to very small densities compared to ordinary solids. A recent investigation of the so-called restricted primitive model [7] (RPM, a symmetrical binary mixture of charged spheres with opposite charges) revealed the possible existence of extremely low-density glassy phases stabilized by Coulombic interactions. In addition, for charged colloidal systems, recent theory also predicts the existence of rather low-density glasses due to Coulombic interactions [9].

In this letter we consider a highly charged colloidal system and show that, indeed, a glass can be found for an extremely small volume fraction of particles. We show that the cage-diffusion scenario predicted by the new mode-coupling theory indeed holds, but only for short times after a quench into the glassy state. At late times, the cages become more rigid: the particles hardly escape and the system becomes strongly non-ergodic. At intermediate times there is a crossover between a regime in which the system is still ergodic, and a later one in which non-ergodicity dominates.

The experiments are performed on Laponite, a synthetic clay consisting of discoid colloidal particles with a diameter of 25 nm and a height of 1 nm [10]. The particles are dissolved at a concentration of 3.5 wt% in ultrapure water (corresponding to a volume fraction  $\phi = 0.014$ ) with NaOH to obtain a  $pH = 10$ , which fixes the ionic strength at  $10^{-4}$  M. As was demonstrated recently [10], a reproducible initial state in which the colloidal suspension is fluid can be obtained by subjecting the solution to a strong shear, thereby shear melting any existing structures in the sample. We dissolve the Laponite under vigorous stirring during 15 min and subsequently pass the solution through a Millipore Millex AA ( $0.8 \mu\text{m}$ ) filter, to obtain a reproducible initial liquid state. The evolution of the visco-elastic constants following this preparation is shown in fig. 1. As can be observed, at  $t = 0$  the loss modulus  $G''$  is much larger than  $G'$  (the storage modulus): the sample flows easily. For long times  $G' \gg G''$ ; the sample has vitrified and does not flow anymore. Furthermore, the system appears to evolve continuously, even for very long times.

The key predictions of the new theory concern the particle diffusion. The diffusion process can be characterised by looking at the correlation functions of particle positions for different aging times. Taking  $A = \exp[iqr_i(t)]$ , with  $q$  the wave vector and  $r_i(t)$  the position of a particle  $i$  at time  $t$ , the diffusion is characterised by the usual incoherent scattering function  $f(q, t) = \langle A^*(t_w)A(t_w + t) \rangle$ . For colloids, this quantity can be obtained directly by light scattering. The light-scattering set-up is standard; a 100 mW solid state ( $\lambda = 532$  nm) laser beam is focused onto the cylindrical sample cell immersed in an index-matching bath. The scattered

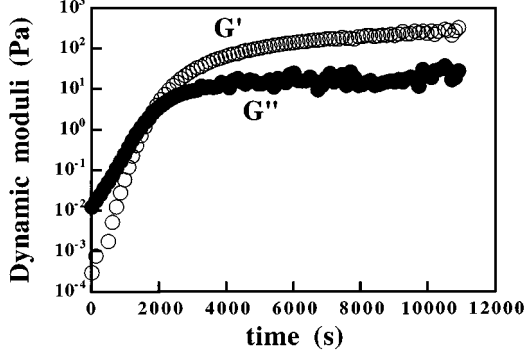


Fig. 1

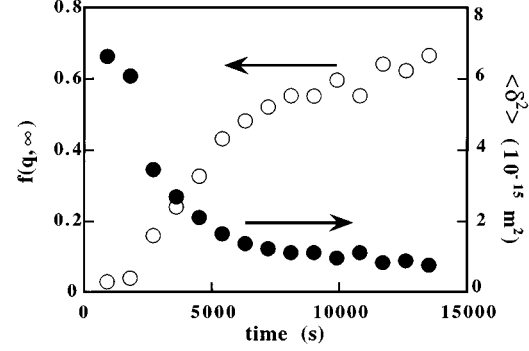


Fig. 2

Fig. 1. – Storage ( $G'$ ) and loss ( $G''$ ) modulus as a function of time;  $t = 0$  corresponds to the injection of the sample through the filter. The curves are measured on a Reologica Stress-Tech rheometer at  $f = 0.1$  Hz and  $\sigma = 0.5$  Pa.

Fig. 2. – Fraction of frozen-in density fluctuations (open circles) and mean-square displacement (filled circles) calculated using the HBBP model as a function of time.

intensity  $I$  is detected by a photomultiplier in  $VV$  polarization under a scattering angle  $\theta$  of  $90^\circ$  (unless otherwise specified). The signal is analysed by an ALV5000 correlator, which directly calculates the normalised intensity correlation function  $g_2(t) = \langle I(0)I(t) \rangle / \langle I(0) \rangle^2$  over nine decades in time. The intensity fluctuations are due to fluctuations in the dielectric constant within the scattering volume, related to the particle diffusion through  $[f(q, t)]^2 = g_2(t) - 1$ . For free Brownian motion,  $g_2(t) - 1 = \exp[-Dq^2t]$ ,  $D$  being the diffusion constant of the particles and  $q$  ( $= 4\pi n / \lambda \sin(\theta/2)$ ) the wave vector [11].

For non-ergodic systems, however, time- and ensemble-averaged measurements do not necessarily yield the same result, since part of the fluctuations are “frozen in” [11]. To construct the time-averaged correlation function  $g_2^T(t)$  we time average the fluctuating signal for a given sample position. To obtain the ensemble-averaged  $g_2^E(t)$ , the sample is slowly ( $0.8 \mu\text{m/s}$ ) translated vertically through the laser beam; a correlation function is taken every 15 min during the aging process. Because of the difference between  $g_2^T(t)$  and  $g_2^E(t)$ , the obtained correlation function cannot be interpreted directly anymore. There are two ways to proceed. First, the incoherent scattering function can be calculated directly from the ensemble-averaged measurements, which will be done below. Second, one can separate the fluctuating and frozen-in part of the fluctuations and consider only the former:  $h(t) = \langle I_f(0)I_f(t) \rangle / \langle I_f(0) \rangle^2$ , where  $f$  stands for fluctuating;  $h(t)$  is directly related to the movement of the particles.  $h(t)$  can be calculated from either the time- or the ensemble-averaged measured  $g_2(t)$ , knowing the ensemble-averaged fraction of frozen-in density fluctuations  $f(q, \infty)$  [11]. Using  $g_2^E(t \rightarrow \infty) - 1 = [f(q, \infty)]^2$ , we obtain the fraction of frozen-in density fluctuations from the long-time asymptote of  $g_2^E(t)$ . In fig. 2, we plot  $f(q, \infty)$  as a function of the aging time. As can be observed, we see a strong ergodicity breaking: a large part of the fluctuations are frozen in. Moreover, the changes happen on exactly the same time scale as those observed in the rheological data.

Considering only the fluctuating part of the field, by definition  $h(t = 0) = 1$  and  $h(t \rightarrow \infty) = 0$  [11]. In fig. 3 we show some representative examples of  $h(t)$ . For short aging times ( $t_w < 1$  hr), two relaxations can be observed. The first one is fast and very similar for different aging times. The second one, which causes the final decay of  $h(t)$  to zero, sets in at a moment that depends strongly on the waiting time. Very similar correlation functions were obtained for

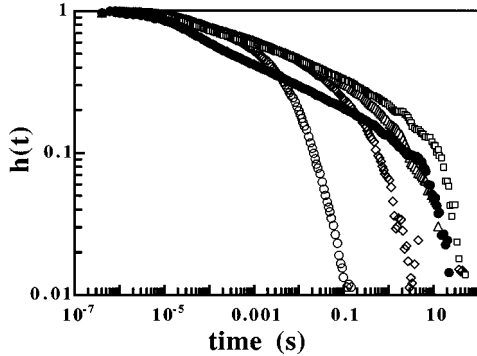


Fig. 3

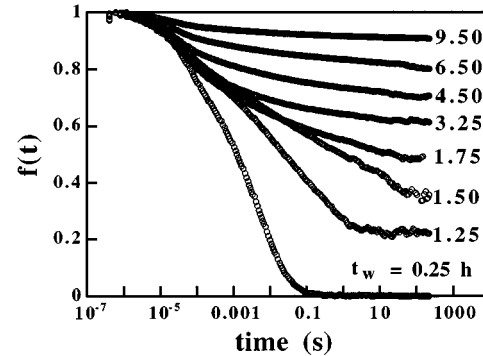


Fig. 4

Fig. 3. – Correlation function  $h(t)$  of the fluctuating part of the intensity. For short  $t_w$ , the decay is governed by free diffusion for short times, and escape from the cages at long times. For larger  $t_w$ , the decay is qualitatively different: the particles are no longer able to escape from the cages. Open circles:  $t_w = 0.25$  hr, diamonds:  $t_w = 0.75$  hr, triangles:  $t_w = 1$  hr, rectangles:  $t_w = 1.25$  hr, filled circles:  $t_w = 2.5$  hr.

Fig. 4. – Intermediate scattering function  $f(q, t)$  for fixed  $q$  and for different aging times  $t_w$ . For short  $t_w$ , the system is at most weakly non-ergodic, whereas for longer times a strong ergodicity breaking can be observed. The aging time  $t_w$  (in hours) is indicated after each measurement.

spin-glass models and in molecular-dynamics simulations [3, 4]. The first decay corresponds to the fast diffusion within the cage formed by surrounding particles (“fast  $\beta$ -relaxation”), whereas the second corresponds to the escape from the cage (“ $\alpha$ -relaxation”). The measured  $h(t)$  then show that the escape from the cages becomes more and more difficult with increasing  $t_w$ , in line with the results from theory [4] and simulations [3]. The surprise comes for the longer times ( $t_w > 1$  hr), for which a strong ergodicity breaking is observed. The correlation functions decay in a manner that is qualitatively different, and even cross  $h(t)$  obtained for short  $t_w$  (fig. 3). The two distinctly different forms of the correlation function for short ( $< 1$  hr) and long ( $> 1$  hr) waiting times correspond to different regimes: for short times the system is ergodic, whereas for late times a strong ergodicity breaking is observed.

This is also borne out in the full intermediate scattering function  $f(q, t)$ , as shown in fig. 4. For short  $t_w$ , the system is ergodic: the particles move in their respective “cages”, but escape from them within the longest time probed by the intermediate scattering function;  $f(q, t)$  consequently decays to zero. However, at longer times the escape from the cages gets slower, resulting in a strong ergodicity breaking and consequently in a large fraction of frozen-in fluctuations. Thus, also in  $f(q, t)$ , we observe a crossover between two different regimes.

To assess the difference between the two regimes, we performed (ensemble-averaged) measurements on the same system aged for 48 hrs; after this time the correlation functions hardly change with aging time. This allows for measurements using different scattering angles and probing different length scales by changing  $q$ . Figure 5 depicts the wave vector dependence of both the short-time slope of  $\ln(g_2(t) - 1)$  and the fraction of frozen-in fluctuations. As stated above, for free diffusion, the former should scale with  $q^2$  if the particle is performing Brownian motion. The data thus show that, indeed, for short times the particle moves freely. Moreover, the collective diffusion coefficient that we get from the slope after correcting for non-ergodic effects [11],  $D = 8.4 \cdot 10^{-11} \text{ m}^2/\text{s}$ , is of the same order of magnitude as the one measured in a very dilute solution,  $D = 1.4 \cdot 10^{-12} \text{ m}^2/\text{s}$  [12].

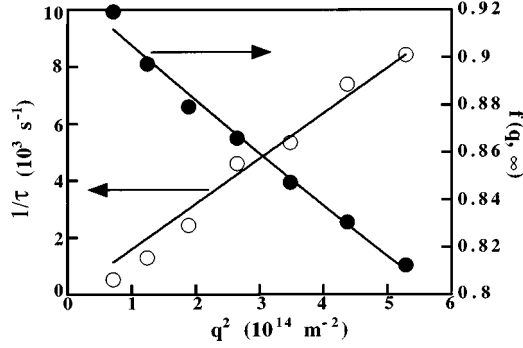


Fig. 5. – Measurements of the wave vector dependence of a sample a long time after preparation. The decay time of the correlation function at short times (open circles) scales with  $q^2$ , indicating that a diffusion process takes place. The fraction of frozen-in density fluctuations (filled circles) scales with  $\exp[-q^2]$ , indicating i) a glassy rather than a gel mode, and ii) that the results can be interpreted in terms of the HBBP model.

For longer times, the particle is constrained by the cages, which results in a decay of  $f(q, t)$  to a non-zero value. This is reflected in the observed wave vector dependence of  $f(q, \infty)$ . The simplest model that accounts for this  $q$ -dependence is that of Brownian particles trapped in a harmonic potential (HBBP) [11, 13]. Within this model,  $f(q, \infty)$  is directly related to the particle displacement  $\delta$  relative to the wave vector:  $f(q, \infty) = \exp[-q^2 \langle \delta^2 \rangle]$ . The fit to the data indeed shows the expected wave vector dependence. Quantitatively, the fit shown in fig. 5 yields  $\langle \delta^2 \rangle \approx 3 \cdot 10^{-16} \text{ m}^2$  after aging for 48 hrs. For comparison, we can fit  $\langle \delta^2 \rangle$  calculated from the HBBP model as a function of aging time (fig. 2) with a curve of the form  $c_1 + c_2/t_w$ ; this yields  $c_1 \approx 6 \pm 3 \cdot 10^{-16} \text{ m}^2$  as the long-time asymptotic value for  $\langle \delta^2 \rangle$ . Although there is no theoretical justification for the specific kind of fit we use, the results from the two different experiments appear to be in good agreement. Moreover, the rms displacement that we find is of the order of the particle radius, which seems reasonable. The conclusion from comparing with HBBP is then that the rms displacement of the particles gets smaller and smaller. Within the model, this corresponds to a larger amplitude of the confining potential. The physical interpretation is that, as  $t_w$  progresses, the cages become more and more rigid. Although the applicability of such a simple model may be (and has been [11]) questioned, it provides a useful and simple physical framework for interpreting the data.

The Laponite system thus has all the features of a colloidal glass, although the volume fraction is extremely low ( $\phi = 0.014$ ), compared to “normal” (spherical) colloids, for which glasses are obtained for  $\phi \approx 0.50$  [6]. This could be due to either the electrostatic interactions, as the particles are charged, or their discoid shape; the effective volume fraction of the colloids may be much larger than one would expect from their size alone. For our electrolyte concentration of  $10^{-4} \text{ M}$ , the Debye screening length is about 30 nm. As the faces of the discoid particles are charged, this length has to be added to the thickness of the disks to calculate an effective volume fraction. This yields  $\phi \approx 0.43$ , very close to volume fractions for which glasses are obtained for hard-sphere colloidal systems. The picture based on the electrostatic repulsion between the charged particles provides us with a picture of colloidal glass of relatively densely packed particles with an effective size determined by the Debye screening length. The observed low-density glass thus has all the features of the “Wigner glass” described in ref. [7].

There is some experimental evidence suggestive of a gel-like fractal network structure for Laponite [10]. Also in a gelation process, an increase of  $f(q, \infty)$  with  $t_w$  may be anticipated since the number of connections in the network increases with time. The observed

$q$ -dependence of the incoherent scattering function, however, cannot be explained by a gel model [11, 13] and is consistent with a glass picture based on particles trapped in harmonic potentials. Moreover, the structure factor for our system, measured over length scales accessible with visible light, is completely flat, ruling out the possible existence of a fractal network.

In conclusion, we studied aging in a colloidal “Wigner” glass. The glass can be shear-melted, which provides us with an ideal situation for the study of the aging process. The data can be well described using the HBBP model. The bounding potential producing cage effects increases in amplitude with  $t_w$ , leading to a strong ergodicity breaking. This feature is not predicted by current spin-glass theories of the aging process, which predict that the fraction of frozen-in fluctuations  $q_{EA}$ , the so-called Edwards-Anderson order parameter, does not vary with  $t_w$  [5]. However, a very recent simulation study [3] also reveals a crossover between a complete and incomplete decay of the correlation function as  $t_w$  increases, very similar to what is reported here. Thus, there appears to be a serious discrepancy between the theory, on the one hand, and our experiments and the Lennard-Jones glass simulations [3], on the other hand. This raises the interesting question whether the increase of a non-ergodicity parameter with  $t_w$  is a generic feature of the aging process or not.

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