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# Aging dynamics in a colloidal glass

Bérengère Abou, Daniel Bonn, and Jacques Meunier
*Laboratoire de Physique Statistique, Ecole Normale Supérieure 24, rue Lhomond, 75231 Paris, France*

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The aging dynamics of colloidal suspensions of Laponite, a synthetic clay, is investigated using dynamic light scattering (DLS) and viscometry after a quench into the glassy phase. DLS allows to follow the diffusion of Laponite particles and reveals that there are two modes of relaxation. The fast mode corresponds to a rapid diffusion of particles within "cages" formed by the neighboring particles. The slow mode corresponds to escape from the cages: its average relaxation time increases exponentially fast with the age of the glass. In addition, the slow mode has a broad distribution of relaxation times, its distribution becoming larger as the system ages. Measuring the concomitant increase of viscosity as the system ages, we can relate the slowing down of the particle dynamics to the viscosity.

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## I. INTRODUCTION

Glassy systems are characterized by an equilibration time that is much longer than any laboratory time scale: glasses are out of equilibrium systems. One of the interesting consequences is that, in any case for short times after a quench into the glassy phase, the properties of a glass may still evolve on an observable time scale: we say that the system *ages*. The typical relaxation time of the glass does not become infinite immediately, but grows with the waiting time $t_w$, i.e., the time elapsed after the quench into the glassy phase was done. Understanding the aging processes is of great interest as the glass transition is still ill understood.

Recent progress in out-of-equilibrium developments, including new mode-coupling theory (MCT), has allowed for a first detailed description of the aging process [1]. The aging dynamics of the system is described in term of the evolution of the correlation and response functions with the waiting time. In most systems such as structural glasses, unfortunately correlation and response functions are not easy to obtain experimentally. Testing the applicability of these recent out-of-equilibrium developments has therefore been limited to specific theoretical models and simulations (Lennard-Jones glass) studies [1,2].

Colloidal glasses can be looked upon as model glasses compared to structural glasses where there are two coupled control parameters, density and temperature. In colloidal glasses, the volume fraction of the particles is one of the control parameters that can be varied independently from the others. Because of the experimental difficulties in studying structural glasses, colloidal glasses have been studied extensively. In fact, it is probably fair to say that the strongest evidence for the applicability of classical-mode coupling theory (that applies only above the glass transition temperature and therefore cannot describe aging) comes from colloidal systems [3,4].

In order to see whether colloidal glasses can also be used to investigate the aging process, we study colloidal suspensions of Laponite, a synthetic clay. These colloidal suspensions form very viscous phases at low particle concentrations [5,6]. The first evidence of aging in colloidal glasses of Laponite was reported in [7]. In this paper, we present quantitative results of aging dynamics in a glassy suspension of Laponite using dynamic light scattering measurements and viscometry.

## II. PREPARATION AND VISCOMETRY

The experiments are performed with aqueous suspensions of Laponite RD, a hectorite synthetic clay provided by Laporte Ltd. The particles are colloidal disks of 25 nm diameter and 1 nm thickness [8], with a negative surface charge on both faces. Laponite powder was mixed with ultrapure water at pH $=10$ obtained by addition of NaOH, providing chemically stable particles [9,10]. The suspension was stirred vigorously for 15 min and then filtered through a Millipore Millex-AA 0.8 $\mu$m filter unit. This preparation procedure allows us to obtain a reproducible initial liquid state. Evaporation of water or $CO_2$ contamination of the sample was completely avoided by covering the sample with a layer of vaseline oil. The aging time $t_w=0$ is defined as the moment the suspension passes through the filter.

Suspensions prepared in this way are optically transparent and are initially liquid. Within a time varying from a few minutes to a few hours for the different concentrations considered here (2% wt to 5% wt), a three order of magnitude increase in viscosity is observed: the suspension does not flow anymore when tumbling the recipient. Since the physical properties of the dispersion depend on the time after preparation $t_w$, the conclusion is that the samples age. This large viscosity increase has been so far attributed to the formation of a gel, evidenced by the existence of a fractal network [11,10]. Recently, Bonn *et al.* studied the structure of Laponite suspensions using static light scattering [12]. Contrary to previous observations, they found no evidence for a fractallike organization of the particles, provided the suspensions were filtered. They consequently showed that the observed "fractal network" is an artifact, which is due to an incomplete dissolution of the clustered particles that are responsible for the strong scattering at small scattering vectors [13]. The filtration breaks up these aggregates of particles. Bonn *et al.* proposed that the aging behavior of Laponite suspensions should be interpreted as a glassy dynamics.

The colloidal glass of Laponite is then obtained for very

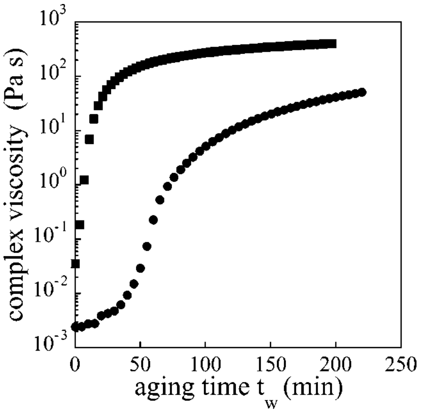

FIG. 1. Complex viscosity as a function of the aging time $t_w$ for Laponite suspensions at 2.5% wt (circles) and 3.5% wt (squares). The visco-elastic moduli are measured on a Reologica Stress-Tech rheometer at a pulsation $\omega = 1\ \mathrm{s}^{-1}$ and with an imposed strain $\gamma_0 = 0.01$.

low volume fractions $\Phi \simeq 0.01$ compared to those for usual spherical colloids, for which glasses are obtained above $\Phi \simeq 0.5$ [4]. To account for this difference, it was proposed [7] that the Laponite suspensions form so-called Wigner glasses, very low-density glasses whose formation is due to the existence of long-range Coulombic repulsions [14–16]. These repulsions originate from the strong surface charges at the faces of the colloidal disks, making that the effective volume fraction, including the Debye length, is very high. For the ionic strength considered here ($10^{-4}$ mol/l), the Debye length is estimated to 30 nm. Recent experiments have shown that the location of the "glass transition" line in the (volume fraction / electrolyte concentration) phase diagram is consistent with this assumption [17].

The Laponite suspensions age on time scales that depend on the particle concentration. Oscillatory shear experiments were performed on a controlled stress (Reologica Stress Tech) rheometer using a Couette geometry with a 1 mm gap. The sample was exposed to a sinusoidal strain $\gamma = \gamma_0 \sin \omega t$, with $\gamma_0 = 0.01$ and $\omega = 1\ \mathrm{s}^{-1}$, and allowing for measurement of the visco-elastic response. The storage modulus $G'$ and the loss modulus $G''$ were determined in the linear visco-elastic regime. At $t_w = 0$, the loss and storage moduli are roughly of the same order of magnitude with $G'' > G'$. As the system ages, the storage modulus increases more rapidly than the loss modulus, becoming easily more than two orders of magnitude larger within a typical experimental time scale. Figure 1 shows the evolution of the complex viscosity $\eta^*$, as a function of the aging time $t_w$, for suspensions with different concentrations. The complex viscosity $\eta^*$ was calculated from the visco-elastic moduli, as $\eta^* = \sqrt{G'^2 + G''^2}/\omega$. The complex viscosity of the suspension with 2.5% wt increases by three orders of magnitude on a time scale of 100 mins while the same increase of viscosity arises on about 10 mins for a suspension with 3.5% wt. The aging dynamics of the suspensions can therefore be varied by changing the particle concentration.

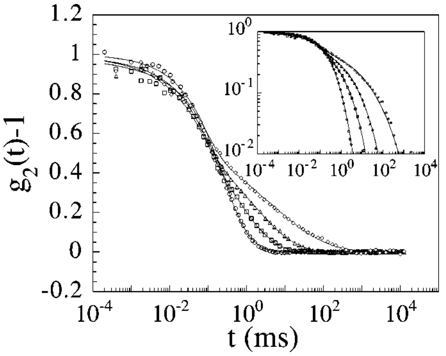

FIG. 2. Autocorrelation functions of the scattered intensity by a 2.5% wt suspension and corresponding fits for aging times $t_w = 0$, 200, 400, 600 min (from left to right) at a scattering angle $\theta = 90°$. The autocorrelation functions and their corresponding fits are also represented on a log-log plot in inset.

## III. DYNAMIC LIGHT SCATTERING

The dynamics of formation of the colloidal glass was investigated using dynamic light scattering (DLS). The light scattering setup is as follows: a He-Ne laser beam ($\lambda = 632.8$ nm) is focused on a cylindrical sample in an index-matching bath of Toluene ($n = 1.50$). The scattered intensity transmitted through the cell is detected by an optical fiber coupled to an avalanche photodiode under a scattering angle $\theta$, defined as the angle between the transmitted and the scattered beam. The signal is then analyzed by a ALV-5000 logarithmic correlator, which directly calculates the normalized intensity autocorrelation function over nine decades in time $g_2(\mathbf{q},t) \equiv \langle I(\mathbf{q},0) I(\mathbf{q},t) \rangle / \langle I(\mathbf{q},0) \rangle^2$, where $t$ is the delay time. The modulus of the scattering wave vector, defined as $q = (4\pi n/\lambda)\sin(\theta/2)$, with $n$ the refractive index of the suspension ($n = 1.33$) was between $9 \times 10^6\ \mathrm{m}^{-1} < q < 3 \times 10^7\ \mathrm{m}^{-1}$, as the scattering angle was varied between 40° and 150°. Its inverse, $1/q$, determines the length scale probed in a DLS experiment.

In our experiments, the intensity correlation function was recorded while the system is aging. In such an experiment, the acquisition time should allow for a good average of the autocorrelation function data without a significant aging of the system occurring during the experiment. Because of that, experiments were performed with suspensions of sufficiently low concentration so that the aging is slow compared to the time necessary to obtain the correlation functions. In the following, we present results obtained with a 2.5% wt suspension. The acquisition time was chosen to be 60 s, allowing for a good average of the whole curve. We experimentally checked that aging was negligible during this acquisition time for the 2.5% wt suspension by recording the autocorrelation functions just before and just after the measurement.

Autocorrelation functions taken for various aging times $t_w$, under a scattering angle $\theta = 90°$, are shown in Figure 2. Mainly two relaxations can be observed. The first one, observed for short delay times $t$, is relatively fast and appears to be independent on the aging time. The second relaxation, observed for long delay times $t$, depends strongly on the waiting time.

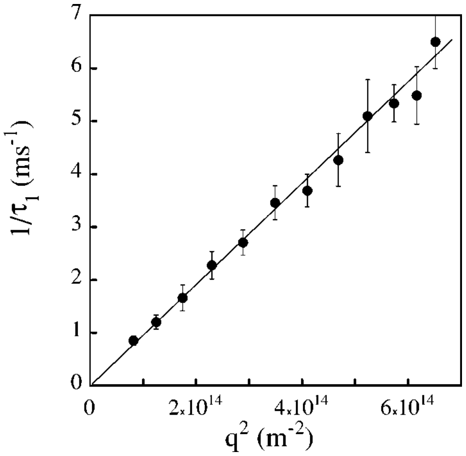

FIG. 3. Inverse of the characteristic time $\tau_1$ of the fast relaxation as a function of the modulus of the wave vector $q$, for a 2.5% wt Laponite suspension.

In order to describe the two processes quantitatively, $g_2(\mathbf{q},t)-1$, was fitted by a sum of an exponential and a stretched exponential function as:

$$g_2(\mathbf{q},t)-1=A\,\exp-(t/\tau_1)+(1-A)\exp-(t/\tau_2)^{\alpha}$$

The stretched exponential is used since it has been found empirically that it provides a good description of the slow relaxation processes encountered in glassy systems. The fits corresponding to different aging times $t_w$ are shown in Fig. 2 and describe the correlation functions very well, for all aging times.

The first term of the fit function corresponds to a fast relaxation. The parameter $\tau_1$ was in fact determined independently by a linear fit of $\ln[g_2(\mathbf{q},t)-1]$ for short delay times $t$, in order to constrain the fitting procedure. This relaxation time was found to be independent on the aging time $t_w$. Furthermore, studying the angular dependence of the scattering, it is found that the inverse of $\tau_1$ varies as $q^2$ as shown in Fig. 3. This shows that, for short times, the Laponite particles undergo "normal" Brownian motion: this $q$ dependence is the same as that found for very dilute colloidal dispersions [18]; for our system, we find a collective diffusion coefficient $D=9.5\times10^{-12}$ m$^2$ s$^{-1}$, of the same order of magnitude as the one measured in a very dilute solution [7]. On the other hand, the relaxation time $\tau_2$, that characterizes the aging, was found to increase exponentially fast as a function of $t_w$ as $\tau_2=\tau_0\exp(t_w/t_0)$, where $\tau_0\sim0.1$ ms and $t_0\sim10^{-5}$ s (Fig. 4; see also the discussion below). As the total decay time of the correlation function is a measure for the time a particle needs to "forget" its initial position, this shows that very rapidly, the aging freezes in certain degrees of freedom of the system.

As was the case for $\tau_1$, the relaxation time $\tau_2$ was found also to scale with $1/q^2$, a feature again reminiscent of classical (Fickian) diffusion, although the stretched exponential shows that there are strong hydrodynamic interactions between the particles. Finally, the stretch exponent $\alpha$ was found to depend only on the aging time and not on the scattering wave vector $q$. The exponent $\alpha$ decreases roughly and linearly between 1 and 0, as shown in Fig. 5. The aging time $t_w$ for which $\alpha\simeq0$ corresponds to the ergodic-nonergodic transition on the time scale of observation [7].

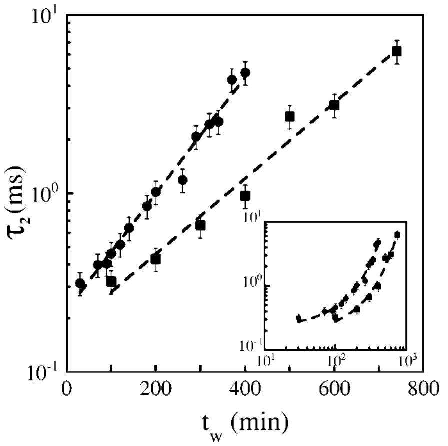

FIG. 4. Characteristic time $\tau_2$ of the slow relaxation as a function of the aging time for 2.5% wt (squares) and 2.8% wt (circles) Laponite suspensions from autocorrelation functions taken under a scattering angle $\theta=90°$. $\tau_2(t_w)$ is also represented on a log-log plot in the inset.

The observation of the scaling of $\tau_1$ and $\tau_2$ with $1/q^2$ allows us to rescale the autocorrelation functions for different scattering angles. Rescaling the time $t$ as $q^2a^2t$, where $a$ is the radius of the Laponite particles, leads to a collapse of the different correlation functions (Fig. 6).

In order to interpret these results, we determine the distribution of relaxation times $\tau$ in the system. This we do using a constrained regularization method (ALV-NonLin data analysis [19]). The method consists in decomposing the intensity autocorrelation function in exponential modes by directly inverting : $g_2(\mathbf{q},t)-1=[\int_{\Gamma_{min}}^{\Gamma_{max}}\exp(-\Gamma t)G(\Gamma)d\Gamma]^2$, yielding the distribution function of decay times $G(\tau)$, where $G(\tau)=G(1/\Gamma)$. Figure 7 shows the decay time distribution functions $G(\tau)$ corresponding to different aging times $t_w=0$ and $t_w=400$ min. One observes two distinct modes,

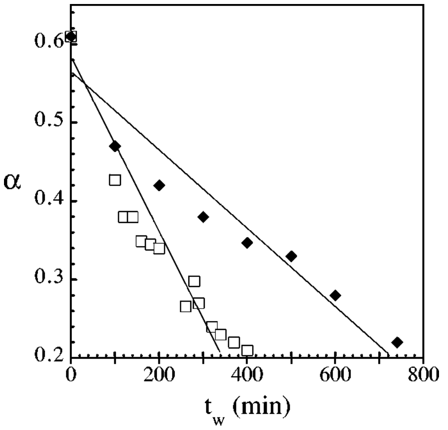

FIG. 5. Stretch exponent $\alpha$ as a function of the aging time for 2.5% wt (diamond) and 2.8% wt (open squares) Laponite suspensions. These fit parameters correspond to autocorrelation functions taken under a scattering angle $\theta=90°$.

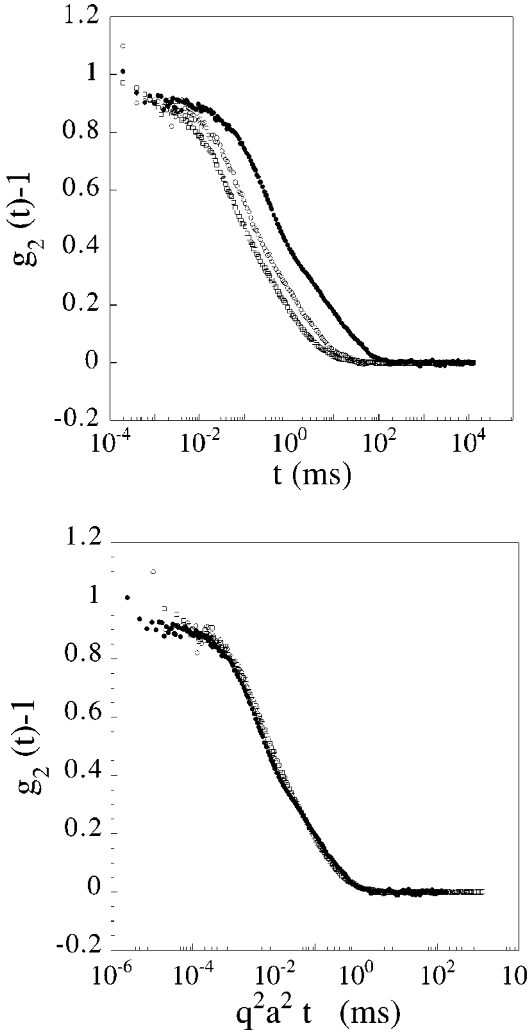

FIG. 6. Scaling of the autocorrelation functions taken under different scattering angles $\theta = 40°$ (open squares), $\theta = 90°$ (open circles), and $\theta = 150°$ (filled circles), for an aging time $t_w = 300$ min (2.5% wt). $a$ is the radius of the particles [8]

the fast one corresponding to the first relaxation time $\tau_1$, and the slow one to $\tau_2$. The intensity of the fast mode has been arbitrarily normalized to unity for the sake of comparison. This fast mode remains almost unchanged as the system ages. The slow relaxation exhibits two different features. First, the maximum of the distribution shifts to larger times, which corresponds to the increase in $\tau_2$ already observed from the direct fit of the correlation function. Second, the distribution of relaxation times $G(\tau)$ becomes wider as the system ages. This corresponds in fact to the decrease in the stretch exponent $\alpha$: the distribution of relaxation times $\tau_2$ becomes wider and wider. These two combined effects make that, very rapidly, the longest relaxation time in the system exceeds the laboratory time scale of observation. The direct consequence of this is that, for short aging times $t_w$, the correlation function decays to zero as shown in Fig. 2. For longer aging times ($t_w > 10$ h for a 2.5 wt % suspension), the autocorrelation function does not decay to zero within the observation time scale: the system is no longer ergodic [7].

Experimentally, the dependence of $\tau_2$ and $\eta^*$ on $t_w$ leads to the consequence that the viscosity of the suspension is not simply proportional to $\tau_2$ (Fig. 8).

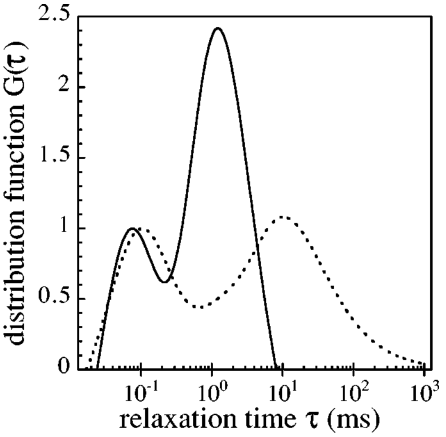

FIG. 7. Relaxation time distribution functions corresponding to aging times $t_w = 0$ (full line) and $t_w = 400$ mins (dashed line) for a 2.5% wt suspension. The corresponding autocorrelation functions are taken under a scattering angle $\theta = 90°$. In order to be able to compare the functions, the peak intensities for the small-scale Brownian motion were normalized to unity.

## IV. DISCUSSION AND CONCLUSION

We propose the following interpretation of our measurements. The diffusion of particles can be described as a cage-diffusion process. The first relaxation $\tau_1$ characterizes the short-time Brownian diffusion of a particle in the suspending liquid. For short times *t*, the particle diffuses freely within a "cage" formed by the surrounding particles. This diffusive motion consequently does not depend on the aging time. The second relaxation process, occurring for long times *t*, can be interpreted as the escape from the cages. The corresponding characteristic time $\tau_2$ increases rapidly with $t_w$, indicating that it becomes more and more difficult for a particle to "escape." This characteristic relaxation time was found also to scale as $1/q^2$, reminescent of diffusive motion. However, this diffusive motion of particles for long times is complex as

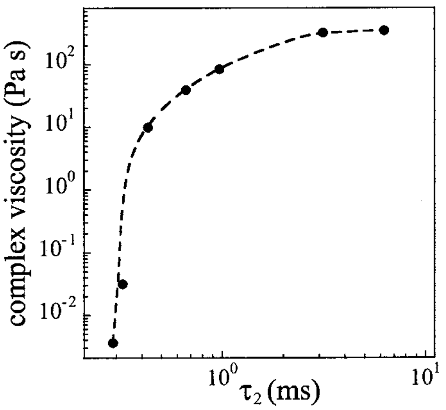

FIG. 8. Complex viscosity as a function of $\tau_2$ for a 2.5% wt Laponite suspension for a pulsation $\omega = 1\ \mathrm{s}^{-1}$.

it is characterized by a broad distribution of relaxation times, leading to the stretched exponential behavior of the correlation function. From this it follows immediately that for short aging times, the system is ergodic: the particles reside in the ‘‘cages’’ formed by surrounding particles and escape from them after a characteristic time that depends on the aging time $t_w$. As the system ages, the escape from the ‘‘cages’’ becomes slower. The particles are subsequently constrained by the ‘‘cages,’’ resulting in the ergodicity breaking within the observation time scale.

The comparison of our experimental results with predictions from MCT [1] shows a qualitative agreement with respect to the slow relaxation (so-called $\alpha$ relaxation) and faster relaxation (so-called $\beta$ relaxation) features of the particle dynamics. The nonaging $\beta$ relaxation part would correspond to the relaxation time $\tau_1$ that is independent of the aging time $t_w$. Nevertheless, we found that the $\beta$ relaxation goes as an exponential rather than a power law as predicted in the mode-coupling prediction. Only the slow $\alpha$-relaxation part of the autocorrelation function is predicted to depend on $t_w$, which is consistent with the dependence of $\tau_2$ on $t_w$. As in the MCT scenario, we found that the typical relaxation time $\tau_2$ increases with increasing $t_w$, which leads to a nonergodic system when the largest $\tau_2$ is comparable to the observation time scale.

In other experiments on aging [20–23], the systems were found to relax on typical time scales that increase as $t_w^{\mu}$, in agreement with calculations from mean field models of aging [24,25]. When $\mu<1$, the process of aging is called subaging; this situation is encountered in spin glasses [20], concentrated colloidal suspension [21], polymer glasses [22] or colloidal gels [23]. Recently, diffusing wave spectroscopy measurements of the motion of the tracer particles in glassy Laponite suspensions have also been performed [26]. The measurements show that the slow collective relaxation time scales linearly with the waiting time $t_w$ (so that $\mu=1$) is called full aging. Interestingly, in our experiments, the typical relaxation time $\tau_2$ is found to grow exponentially fast with $t_w$. The log-log inset plot of Fig. 4 shows indeed that our data are inconsistent with a power law $\tau_2 \propto t_w^{\mu}$. In the experiments cited above, the aging processes were observed in a different regime than our, where the aging times $t_w$ and the decay times $\tau_2$ of the slow relaxation are of the same order of magnitude ($\tau_2 \sim t_w$). In our experiments, the typical decay time $\tau_2$ of the slow relaxation is of the order of 1 to 10 ms and is consequently seven orders of magnitude smaller than the aging time $t_w$ ($\tau_2 \ll t_w$). It may then be expected that for longer aging times $t_w$ than the ones considered in our experiments, the typical decay time of the slow relaxation becomes of the same order of magnitude than $t_w$ and behaves as $t_w^{\mu}$. These two regimes ($\tau_2 \sim \exp t_w$ and $\tau_2 \sim t_w^{\mu}$, $\mu<1$, for respectively $\tau_2 \ll t_w$ and $\tau_2 \sim t_w$) have been observed in colloidal gels [23].

In conclusion, the collective diffusion process of particles can be interpreted as a cage-diffusion process. For short aging times, the system is ergodic. The particles reside in ‘‘cages’’ formed by surrounding particles and escape from them after a characteristic time that is aging time dependent. As the system ages, the escape from the cages become slower, resulting in a strong ergodicity breaking. In our experiments, the characteristic time of the slow relaxation process is found to grow exponentially fast with the aging time. In addition, we find that this dependence on $t_w$ results in a nontrivial relation between the complex viscosity and the relaxation time.

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