Successive exponential and full aging regimes evidenced by tracer diffusion in a colloidal glass

S. Kaloun,[1,3] R. Skouri,[4] M. Skouri,[3] J. P. Munch,[1] and F. Schosseler[2,*]

[1]*I.P.C.M.S., UMR 7504, 23 rue du Loess, BP 43, 67034 Strasbourg Cedex, France*
[2]*I.C.S., UPR 22, 6 rue Boussingault, 67083 Strasbourg Cedex, France*
[3]*L.E.I., Faculté des Sciences Semlalia, Université Cadi ayyad, Marrakech, Morocco*
[4]*Faculté des Sciences et Techniques, BP 509 Boutalamine, Errachidia, Morocco*

We study the aging of a colloidal laponite glass by measuring the dynamic structure factor of dilute embedded tracer particles on micrometric length scales. We show that an initial aging regime, where the decay time grows exponentially with aging time t_w, $\tau \sim \exp(\gamma t_w)$, is followed by a full aging regime, $\tau \sim t_w^v$ with $v \approx 1$. The dynamics of the tracers is diffusive in the exponential regime and hyperdiffusive in the full aging regime, up to micrometric length scales.

PACS number(s): 82.70.Dd, 64.70.Pf, 61.20.Lc, 83.85.Ei

I. INTRODUCTION

Glasses are out of equilibrium systems and their physical properties never stop evolving after they have been quenched out of equilibrium. This evolution is called physical aging and is usually dependent on the whole history of the sample and in particular on the aging time, i.e., the time elapsed since the system has been quenched. This process has been observed and studied for numerous examples, in particular in colloidal suspensions [1–4].

Recent theories [5–8] and experiments [9] have focused on isolating the universal, i.e., system and history independent, features of physical aging. Physical aging can be studied through the measurement of macroscopic quantities (relaxation time, viscosity, etc.) as a function of the aging time t_w. A nonperturbative approach is possible by following the evolution with aging time of the dynamic structure factor $f(q,t,t_w)$ of the glassy system, defined as the normalized spatial Fourier transform of the time dependent autocorrelation function of concentration fluctuations. Here q is the wave vector associated with the fluctuations of concentration.

Alternately, it is possible to follow the evolution of the macroscopic viscosity by measuring the dynamic structure factor of dilute tracer particles embedded in the aging matrix since the relaxation time of the dynamic structure factor of Brownian tracers is proportional to the viscosity they experience. Significant advances in this second approach have been made possible by the elaboration of a rigorous link between the characteristics of the motion of embedded tracer particles and the viscoelastic properties of the surrounding matrix [10], thus introducing the new microrheology technique. Moreover, the design of dynamic light scattering experiments with multispeckle detection on CCD chips has allowed the measurement of relaxation times on a time scale with the same order of magnitude [11,12]. This is a critical improvement for systems that are evolving in time.

We study aqueous colloidal suspensions of laponite clay by following the diffusion of Brownian tracer particles em-

bedded in the aging matrix. Laponite platelets are 1 nm thick disks with a diameter about 30 nm and are negatively charged at pH = 10. The phase diagram as a function of ionic strength and volume fraction exhibits a nematic phase at high concentration. At lower concentrations, corresponding roughly to the close packing of the spherical volume excluded by the rotating disks, the system is amorphous. The following interactions are at work in Laponite suspensions at pH 10: hard core excluded volume, Coulombic repulsion between negatively charged surfaces of the disks, Coulombic attraction between oppositely charged rims and surfaces of the disks, attractive dispersive forces between parallel disks. Depending on their balance, the amorphous system can be trapped in the glassy state (net repulsive forces) or in the gel state (net attractive forces). Throughout this paper, we work at low ionic strength and close to the overlap concentration of the rotating disks. In these conditions, the orthogonal orientation (rim on surface) that would minimize the energy of an isolated pair of disks does not necessarily minimize the interactions with the surrounding pairs: the equilibration of the system implies a high level of cooperativity generating a lot of frustrations that become increasingly difficult to relax as the system evolves, and a glassy state is obtained. The preparation of this glass is possible after a careful filtration of the concentrated laponite suspension [1,3].

Our group has shown [3] that the physical aging of this system proceeds then with the following characteristics: (i) the scattering intensity remains independent of q; (ii) the average level of total scattering intensity decreases; (iii) the relaxation time increases linearly with the aging time. These are the features expected in the full aging regime of a glassy system. This would not be expected for a gelling system: in particular attractive forces between platelets with diameter circa 30 nm would result in an increase of the scattering intensity in the investigated q range. Abou *et al.* [4] studied the dynamics of laponite glasses at short aging times and reported a different behavior, i.e., the relaxation time increases exponentially with the aging time. They suggested that the exponential aging at short t_w could be followed by the full-aging regime observed in [3] for larger t_w.

Indeed experiments made in the absence of tracer particles and measuring the dynamics of the matrix gave some

hints for the existence of two successive aging regimes [13]. However the short t_w limit below 10^3 s could not be probed with the multispeckle technique based on CCD detection and the fixed angle detection did not allow to fully characterize the dependence of the relaxation time on the scattering wave vector q.

In fact it is very difficult to follow the dynamics of the glassy matrix in a large window of aging time with the same experimental techniques: the fast dynamics at short t_w can only be studied with a photomultiplier and a hardware correlator but the necessary ensemble averages can only be performed at long t_w through appropriate CCD detection, which cannot easily resolve dynamics faster than 100 ms. Characterizing the aging of the matrix through the displacement of tracer particles might be a better approach if the appropriate conditions are met to ensure that the same experimental setup can measure the relaxation time all the way from the quenching, where it corresponds to the Brownian diffusion of the tracers in the solvent, up to when it equals the aging time. These conditions can be met for large enough Brownian particles in the small angle limit ($\theta \lesssim 10°$) of dynamic light scattering with a CCD detection.

In this paper, we study the aging of a laponite colloidal glass by following the dynamics of tracer particles on length scales that are comparable to their size, i.e., much larger than the size of the glass constituents and the range of the perturbations induced by their local rearrangement. The dynamic structure factor is measured by small angle light scattering techniques that allow a real-time ensemble average on a CCD multidetector and the determination of the wave vector dependence of the dynamic structure factor of the tracer particles.

II. EXPERIMENT

A. Sample preparation

The laponite particles were obtained from Southern Clay Products (Gonzales, TX). Aqueous suspension of laponite for light scattering measurements were prepared at the desired volume fraction by mixing oven-dried clay in stirred 18 MV deionized water for 2 h, and filtering the clarified solutions through 0.45 μm cellulose acetate filters (Millipore), in order to break up particle aggregates that would otherwise lead to spurious small angle scattering. The tracer particles were polystyrene latices (Polysciences, nominal diameter 0.5 μm) and were added after the filtration under stirring. The age t_w of the samples is measured from the time where the stirring is stopped and the scattering cell (1 mm optical path) filled through a syringe. We never observe sedimentation in these samples. In particular, at the end of the experiments, the cell can be turned upside down, showing that the sample is sustaining its own weight, and there is no solvent flow. Throughout this paper the concentration of tracer particles is kept low enough ($\approx 10^{-4}$ in volume fraction) to allow the measurement of the dynamic structure factor of isolated particles (no interactions between tracer particles) in the single scattering regime. However this concentration remains large enough to ensure that the scattering contribution of the tracer particles is much larger than that of the host matrix (intensity

ratio ≈ 3230). Thus the latter contribution remains below the electronic noise in these conditions.

B. Dynamic light scattering

We have used two different setups. In the first one, a fraction of the volume illuminated by the expanded collimated incident beam (wavelength 4880 Å), is imaged by an afocal optical system with a magnification about unity onto the CCD detector of a camera that is positioned at a given angle off the axis of the incident beam ($\theta \approx 5°$ measured from the Brownian diffusion of the tracer particles in water). The correlation function is built in real time as described in Ref. [3] from image frames exposed for 40 ms. In this setup, each pixel on the CCD (752×582, 8.6 μm $\times$ 8.3 μm) sees a different scattering volume under the same transfer wave vector **q** ($|\mathbf{q}| \approx 1.5 \times 10^{-4}$ Å^{-1}), which allows one to measure with very good statistics the ensemble-averaged dynamic structure factor as a function of the aging time since, by an appropriate choice of the optics, one pixel area corresponds roughly to one coherence area.

In the second setup, which has been detailed elsewhere [14], the same scattering volume is seen by each pixel under a unique transfer wave vector **q** differing in module and/or orientation. It is essentially the same geometry as in small angle neutron or x-ray scattering with the detector centered on the incident beam and protected by a beamstop. The detection area used on the CCD is a disk with a diameter about 550 pixels (6.7 μm $\times$ 6.7 μm). For each aging time, a stack of 100 image frames (1 ms exposure time) has been accumulated, with a constant delay time between each frame. After the subtraction of a constant electronic noise, the intensity correlation function for each pixel in the detection area has been calculated as a function of delay time. These functions were then averaged on 21 pixels wide annular regions centered on the origin defined by the position of the incident beam, to obtain ensemble-averaged intensity time correlation functions. The average q values have been calculated at the middle of each annulus and the angular resolution $\Delta q/q$ resulting from this spatial average ranges between 0.32 (q $=0.93$ μm^{-1}) and 0.079 ($q=3.28$ μm^{-1}). The average size of the speckles has been estimated from the calculation of the spatial intensity–intensity correlation function on the detector area. We found that the characteristic area of the speckles is about 25 pixels. Therefore the averages for the ensemble-averaged time correlation functions are obtained on a number of coherence areas comprised between about 220 and 1400.

Both setups were checked by measuring the dynamic structure factor of the tracer particles in water (short time calibration) and in viscous wormlike micellar solutions (long time calibration). The results obtained with these ergodic stationary systems were found in satisfactory agreement with those obtained through standard dynamic light scattering experiments using a goniometer, a photomultiplier, and a hardware correlator.

C. Data analysis

Throughout the present paper, the correlation time τ has been simply defined as the time at which the dynamic struc-
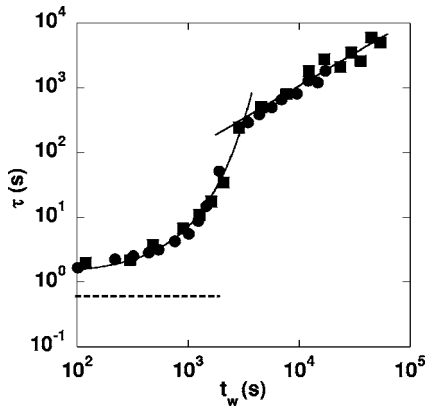
FIG. 1. Plot of the relaxation time τ vs t_w for two experiments ($\blacksquare$), ($\bullet$): $(\phi)_{\text{laponite}}(w/w)=2.75\times 10^{-2}$, $\phi_{\text{latex}}(w/w)=10^{-4}$. The continuous lines are fits for the exponential—and full aging regimes, respectively, $\tau=1.29\exp(t_w/582)$ and $\tau=9.87\times 10^{-2}t_w^{1.008}$. The horizontal dotted line shows the relaxation time measured for the same latices in pure water, at the same scattering angle, $\theta=5°$.

ture factor has decayed by a factor $1/e$. In previous papers [13] a much more elaborated analysis was used by fitting the dynamic structure factor as $At^{-x}\exp[-(t/\tau_{\text{se}})^{\beta}]$, where τ_{se} is the fitted stretched exponential relaxation time. However in all measurements reported here $x\ll 1$, this initial decay can be neglected and $\tau_{\text{se}}=\tau$. Then the use of the present operative definition allows one to decouple the mean decay time τ from the value of the exponent β.

III. RESULTS AND DISCUSSION

Figure 1 shows a typical evolution with waiting time t_w of the relaxation time τ measured at fixed scattering angle with the first experimental setup. The laponite weight fraction is 2.75×10^{-2}. Two different regimes are clearly distinguished with first an exponential growth $[\tau\sim\exp(\gamma t_w)]$ followed by a linear growth $(\tau\sim t_w)$. The intersection of the corresponding fits in Fig. 1 can be used to define a crossover time that will be discussed in a forthcoming paper.

Figure 2 shows the corresponding squared dynamic structure factors plotted as a function of the reduced time t/τ. Here again two distinct shapes can be distinguished. In the exponential regime, the dynamic structure factors show a single exponential decay while in the linear regime, their decay is best described by a stretched exponential function with an exponent $\beta=1.5\pm 0.1$. It can be noticed that the dynamic structure factors decay to zero in both regimes because they are measured for delay times large enough compared with the largest relaxation time of the matrix.

The q dependence of the relaxation times has been measured with the second experimental setup and shows also distinct behaviors according to the aging time (Fig. 3). In the exponential regime, it shows a diffusive behavior, i.e., $\tau\sim q^{-2}$, as expected for continuity at $t_w=0$, where the tracer particles are diffusing in a medium that is a liquid essentially consisting of water. In the linear regime, a different scaling of the relaxation time with scattering wave vector is obtained, $\tau\sim q^{-1.25\pm 0.10}$. Here the exponent value is the average
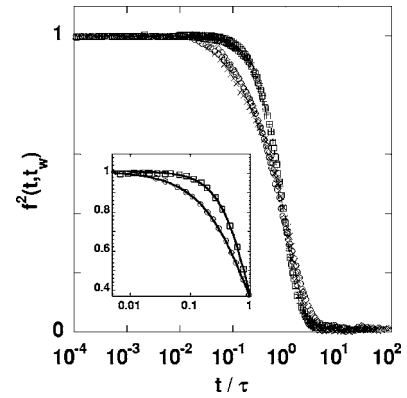

FIG. 2. Squared dynamic structure factor $f^2(t,t_w)$ plotted vs reduced time t/τ at different aging times: $t_w=360$ s, $\tau=2.7$ s ($\times$); $t_w=1140$ s, $\tau=7.4$ s ($\diamond$); $t_w=1700$ s, $\tau=29.8$ s ($\bigcirc$); $t_w=9300$ s, $\tau=850$ s ($\square$); $t_w=13\,800$ s, $\tau=1860$ s ($+$); $t_w=32\,220$, $\tau=4880$ s ($\triangle$). The inset magnifies the time window $5\times 10^{-3}\leqslant t/\tau\leqslant 1$ for two measurements and shows the corresponding fits [$t_w=1700$ s ($\bigcirc$), single exponential; $t_w=9300$ s ($\square$) stretched exponential, $\beta=1.5$]. In the inset, only one data point out of five is shown for the sake of clarity. Same experimental conditions as in Fig. 1.

obtained for different aging times in the full aging regime. In the vicinity of the crossover aging time, these power law dependences are not obeyed across the whole q range. The progressive transition between the two regimes will be detailed in a further paper.

Thus the diffusion of tracer particles in the aging suspension shows clearly the existence of two successive diffusion regimes. The first one displays the characteristics of usual Brownian diffusion and is observable for a rather short aging of the system (typically 1 h at this concentration). In this regime, an effective diffusion coefficient of the tracer particles can be calculated and it decreases exponentially with aging time t_w. At $t_w=0$, this effective diffusion coefficient is consistent with the value obtained by extrapolating the values measured in dilute laponite suspensions to the concentration used in this study. Interestingly, the numerical time fac-
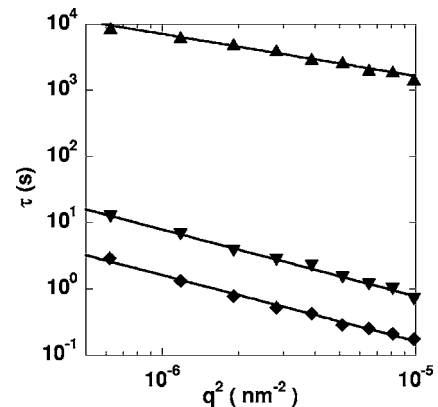

FIG. 3. Variation of the decay time τ vs the square of the scattering wave vector q^2 for two aging times, with the corresponding power law fits: ($\blacktriangledown$) $t_w=600$ s, $\tau=6.8\times 10^{-6}q^{-2.02}$; ($\blacktriangle$) $t_w=18\,180$ s, $\tau=1.067q^{-1.27}$. For comparison, experimental points measured for tracer particles in pure water ($\blacklozenge$) are included.

tor ensuring a dimensionless argument in the exponential function is found to be about $\gamma^{-1} \approx 580$ s (see Fig. 1). Thus this factor cannot be related easily to a microscopic time scale of the system. On the other hand, it could give an order of magnitude for the time evolution of an energy landscape of the system.

The second regime is observed during most of the aging process, when the duration of a measurement becomes comparable with the aging time. It corresponds to a hyperdiffusive limit for the mean square displacement of the tracer particles ($\beta \approx 1.5$) and to a linear growth of the relaxation time with t_w, similarly to the so-called full-aging regime in glassy systems. Such a behavior was already reported in laponite systems, for the dynamic structure factor of the whole system [3] or for short time displacements of tracer particles [$t \approx 0.1$ s, $\langle r^2(t)\rangle \approx 10$ nm^2] [3], as well as in restructuring fractal colloidal gels [2].

The possibility for hyperdiffusive motion of the constituents in aging glassy systems has already been considered [1,9]. Heuristic arguments showed it could happen through local microcollapses at the scale of the constituting grains of the glass [6]. The perturbation range of such collapses should be larger than a few grain sizes and could induce strains on much larger scale. It has been argued that such strains could trigger ballistic episodes in the motion of individual grains [9].

This argument could still hold in the case of tracer particles, much larger than the constituents but moving on distances still smaller than the size of these constituents, as in DWS experiments. However, in the present case, it lacks plausibility since the ballistic motion of our spherical probes on distances comparable to their size would imply the collective rearrangement of a too large number of clay particles.

A different approach is possible by defining a frequency-dependent effective temperature of the aging medium $T_{\mathrm{eff}}(t_w, \omega)$ through a generalization of the fluctuation-dissipation theorems [7,8]. In the particular case of tracer particles diffusing in the aging medium, this can be done through the well-known Einstein relation, $k_B T_{\mathrm{eff}}(t_w, \omega) = D(t_w, \omega)/\mathrm{Re}\,\mu(t_w, \omega)$, where k_B is Boltzmann's constant, $D(t_w, \omega)$ the effective diffusion constant, $\mathrm{Re}\,\mu(t_w, \omega)$ the real part of the effective mobilty and ω the frequency. In an aging laponite suspension, $T_{\mathrm{eff}}(t_w, \omega)$ has been measured and can be modeled as [15]:

$$T_{\mathrm{eff}}(t_w, \omega) \approx T[\omega/\omega_0(t_w)]^{-\alpha}, \quad \omega \ll \omega_0(t_w) = T,$$

$$\omega \gg \omega_0(t_w),$$

where $\omega_0(t_w)$ is a decreasing function of t_w and α is about 4 [15]. Physically, the above behavior reflects that the fastest modes, with frequencies larger than ω_0, equilibrate rapidly with the thermal bath while the slowest modes keep for a longer time a memory of the temperature before quenching, i.e., their effective temperature is larger than that of the thermal bath. Within this context, the mean square displacement of tracer particles can be calculated. In particular, if a power

law behavior is assumed for the real part of the mobility, i.e., $\mathrm{Re}\,\mu(t_w, \omega) \sim \omega^{1-\delta}(0 < \delta < 2)$, then $\langle r^2(t)\rangle \sim t^\nu$ with $\nu = \delta + \alpha$.

The concept of effective temperature and generalized fluctuation–dissipation theorems is interesting since it provides some ground to analyze the decay of the dynamic structure factor in the linear regime through a mean square displacement of the tracer particles, i.e., $f(q, t, t_w) \approx \exp[-q^2\langle r^2(t)\rangle/6] \approx \exp[-(t/\tau)^\beta]$. This implies $\beta = \nu$ and $\tau \sim q^{-2/\beta}$, in agreement with the measured values within error bars. Clearly, within this scheme, our β value is not consistent with $\alpha \approx 4$, whatever the value for δ.

However, very different behaviors for the effective temperature have been deduced by different groups working on the same system [15,16]. Apart from possible concentration effects, it has been argued [16] that this could be due to the different observables measured in each case, as predicted earlier [17]. Our experiments cannot distinguish δ and α and this point is left for future work.

To conclude, we have measured the time evolution of the dynamic structure factor of tracer particles embedded in an aging laponite suspension and we have shown that two different regimes are successively observed. In the first one, the dynamic structure factor has a single exponential shape, its decay time τ increases exponentially with aging time t_w, and the mean square displacement of the tracer particles corresponds to the usual Fickian diffusion. In the second regime, the dynamic structure factor is a stretched exponential function ($\beta = 1.5 \pm 0.1$) and $\tau \sim t_w q^{-2/\beta}$, consistent with a hyperdiffusive motion of the tracer particles $\langle r^2(t)\rangle \sim t^\beta$. The first major conclusion of this work is that the second regime, which was previously observed for nanometric displacements of the probes has been confirmed for micrometric displacements of the same probes. Moreover it corresponds to a behavior, $\tau \sim t_w$, that has been previously reported for the dynamic structure factor of the whole glass. This confirms that the tracer particles probe the aging of the glassy medium. What is exactly probed remains an open question even if there is experimental evidence that the tracer particles probe the macroscopic viscosity in the beginning of the exponential aging regime [18]. The concept of effective temperature appears as an appealing way to explain phenomenologically the hyperdiffusive motion of the tracers. However new experiments are needed to measure simultaneously and consistently the observables used to define this effective temperature [15,16].

The second major conclusion is that the two successive aging regimes are in fact distinguished if the experimental technique used allows one to cover the appropriate extension of time window. It has been shown that the exponential regime starts from the very beginning after the cessation of stirring. Interestingly, similar successive regimes have been observed during the restructuration of aggregated colloids [2], suggesting that these two successive regimes might be a rather general feature. It remains however an open question, whether the exponential regime is a true aging regime or a transient regime corresponding to the effective duration of the quench. Theoretical work to clarify this point is clearly needed.

[1] D. Bonn, H. Tanaka, G. Wegdam, H. Kellay, and J. Meunier, Europhys. Lett. **45**, 52 (1998).

[2] L. Cipelletti, S. Manley, R. C. Ball, and D. A. Weitz, Phys. Rev. Lett. **84**, 2275 (2000).

[3] A. Knaebel, M. Bellour, J.-P. Munch, V. Viasnoff, F. Lequeux, and J. L. Harden, Europhys. Lett. **52**, 73 (2000).

[4] B. Abou, D. Bonn, and J. Meunier, Phys. Rev. E **64**, 021510 (2001).

[5] J. P. Bouchaud, L. Cugliandolo, J. Kurchan, and M. Mézard, in *Spin Glasses and Random Fields*, edited by A. P. Young (World Scientific, Singapore, 1998).

[6] J.-P. Bouchaud and E. Pitard, Eur. Phys. J. E **9**, 287 (2002).

[7] N. Pottier and A. Mauger, Physica A **332**, 15 (2004).

[8] N. Pottier, Physica A **345**, 472 (2004).

[9] L. Cipelletti, L. Ramos, S. Manley, E. Pitard, D. A. Weitz, E. E. Pashkovski, and M. Johansson, Faraday Discuss. **123**, 237 (2003).

[10] T. G. Mason and D. A. Weitz, Phys. Rev. Lett. **74**, 1250, (1995).

[11] S. Kirsch, V. Frenz, W. Schärtl, E. Bartsch, and H. Sillescu, J. Chem. Phys. **104**, 1758 (1996).

[12] L. Cipelletti and D. A. Weitz, Rev. Sci. Instrum. **70**, 3214 (1999).

[13] M. Bellour, A. Knaebel, J. L. Harden, F. Lequeux, and J.-P. Munch, Phys. Rev. E **67**, 031405 (2003).

[14] V. Weber and F. Schosseler, Rev. Sci. Instrum. **73**, 2537 (2002).

[15] L. Bellon, S. Ciliberto, and C. Laroche, Europhys. Lett. **53**, 511 (2001).

[16] B. Abou and F. Gallet, Phys. Rev. Lett. **93**, 160603 (2004).

[17] S. Fielding and P. Sollich, Phys. Rev. Lett. **88**, 050603 (2002).

[18] D. Bonn, S. Tanase, B. Abou, H. Tanaka, and J. Meunier, Phys. Rev. Lett. **89**, 015701 (2002).