Aging of a colloidal glass under a periodic shear

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The aging dynamics under a periodic shear of a concentrated suspension of saponite particles is measured. It is observed that the dynamics is fastened by the application of a moderate shear amplitude. Nevertheless, this acceleration does not affect the dynamics of the suspension when the shear is ceased. By applying a succession of shear of various amplitudes, we conclude that the dynamics of the suspension at a time t_w after complete rejuvenation is independent of the shear history between times 0 and t_w, as soon as the amplitude of the applied shear is smaller than the characteristic shear γ_c necessary to completely rejuvenate the suspension.

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I. INTRODUCTION

In a given range of concentration, concentrated colloidal suspensions possess a glass phase. Dynamics of the suspension in this glass phase exhibits a slow evolution of the system towards equilibrium. This phenomenon, called aging, is characteristic of glassy materials, and has been widely studied in polymer glasses [1] and spin glasses [2]. The dynamics of the system may be probed by application of a small probe field (magnetic in the case of spin glasses, respectively, a deformation field for polymer systems). Then the susceptibility (respectively, the free volume) may be deduced, and the dynamics of the system slows down after the quench. More precisely, the characteristic time τ of the dynamic of the system at a waiting time t_w obeys to: $\tau \propto t_w^{\mu}$, where $\mu \sim 1$ [1]. When a larger field amplitude is applied to the system, richer dynamical behaviors are observed. The main observation is an acceleration of the dynamics of the system when the field is applied: this is the rejuvenation phenomenon. Thus, in the case of polymer glasses, if a constant shear rate $\dot{\gamma}$ is applied, the aging law is slowed down, and obeys to: $\tau \propto t_w^{\mu(\gamma)}$, $\mu(\gamma)$ being a decreasing function of γ [3]. Moreover, at longer times $t_w > \dot{\gamma}^{-1}$, aging is stopped by shear. In the case of polymer systems, the dynamics of the glass phase after cessation of shear is decorrelated from the aging dynamics of the system. Indeed, during shear, an increase of the free volume is observed; it then relaxes to the value it would have if no shear had been applied. Thus, changes of the dynamics induced by mechanical deformation relaxes on times much shorter than slowing down of the dynamics due to the quenching [4].

On the other hand, it has been recently proposed that a glassy system may be liquefied either by increasing the temperature above the glass transition temperature, or by applying a mechanical deformation [5], deformation field, and temperature playing a similar role. It is indeed known that colloidal glasses may be liquefied by application of a stress [6]. In that case, temperature plays no role, but liquefaction occurs either for low volume fraction or high applied shear. Continuous shearing of a colloidal suspension increases its dynamics when the shear rate $\dot{\gamma}$ becomes fast enough compared to the age of the system: $\dot{\gamma}^{-1} > t_w$ [7]. Then, as observed for the aging of polymer glasses, aging stops. Thus, application of a periodic shear deformation rejuvenates the system when the amplitude of the shear is larger than a critical shear amplitude, γ_c [6].

In this paper, we probe the evolution of the dynamics of a concentrated suspension submitted to a shear of moderate amplitude, smaller or equal to γ_c, but large enough to partially rejuvenate the suspension. Our goal is to determine the influence of the shear on the dynamics of the suspension both during the shear, and once the deformation has ceased.

The dynamics of the suspension is probed by means of light scattering. We need to follow the dynamics of the suspension under sinusoidal shear, and thus developed a multispeckle diffusing wave scattering (MSDWS) experiment under shear. The experimental setup and procedure are detailed in the first part. Then, we study the dynamics of the system under shear, and thus define the regime when partial rejuvenation occurs. Last, we use various shear histories to determine the memory of the system.

II. SYSTEM

We used a colloidal suspension in water of synthetic smectite particles (Co-op Chemical Co, Japan). The particles are disklike shaped, of 125 nm diameter and 5 nm thickness and are negatively charged at pH values studied. The saponite suspension is prepared by dispersing the powder of saponite in distilled water and stirring at room temperature for three days. The pH of the suspension is then increased to 9 by addition of sodium hydroxyde 0.1 M. Then, at volume fractions larger than $\phi = 1.2\%$, the suspension forms a stable solution with a finite elastic modulus that slowly evolves with time [6]. All the experiments reported here were performed at $\phi = 3\%$. The dynamics of the suspension is probed by adding 1% volume fraction of 1 μm diameter latex particles. The system is thus turbid, and its dynamics may be probed by diffusing wave spectroscopy. We know from previous experiments that application of a large shear completely restarts the dynamics of the suspension [6].

III. MSDWS EXPERIMENT UNDER AN OSCILLATORY SHEAR

The system is placed between two parallel glass plates. The gap between the plates is 1 mm. The upper plate is connected to a piezoelectric device that allows for the periodic shearing of the suspension. The amplitude of the displacement may be controlled between 0.1 and 100 μm, and its frequency may be tuned between 0.1 and 100 Hz. The sample thickness being 1 mm, accessible shear deformations γ are thus comprised between 10^{-4} (or $10^{-2}\%$) and 10^{-1} (or 10%). In order to perform larger shear amplitudes, needed for the complete rejuvenation of the suspension, the piezodevice is itself supported by a linear step motor. Nevertheless, correlation functions under shear are not performed using the step motor, due to the mechanical noise induced by the motion of the motor at each step. The sample is illuminated by an enlarged laser beam and transmitted intensity is collected by means of a charge coupled device (CCD) camera (8 bits), as in standard MSDWS devices [8]. A reference image is chosen at time t_w, and the correlation functions between this image and following images at times t_w+t are computed by averaging over the pixels p of the CCD device:

$$g^{(2)}(t_w,t_w+t)=\frac{\langle I_p(t_w)I_p(t_w+t)\rangle_p}{\langle I_p(t_w)\rangle_p\langle I_p(t_w+t)\rangle_p}, \qquad (1)$$

where $I_p(t)$ is the intensity recorded at time t on pixel p. When the suspension is submitted to a periodic shear, the diffused intensity is modulated by the applied shear, and its temporal correlation function exhibits echoes centered at times multiple of the period of the shear deformation [9,10]. In our case, we do not perform time average of the signal, as we want to study nonstationary dynamics of the system, and the situation is a little bit more complex. Indeed, the sheared plate comes back to a given position twice a period, corresponding to two opposite plate speeds of equal absolute values. Let us thus assume that the period of the shear deformation is T: $\gamma(t)=\gamma_0 \sin 2\pi t/T$. A reference image is taken at time T_{ref}. We define $\psi\in\,]-\pi,\pi]$ the phase shift associated with this image, relative to the shear deformation: $\psi \equiv 2\pi T_{\mathrm{ref}}/T \bmod 2\pi$. Then, during each shear periods, the correlation function will exhibit two echoes, centered at $\psi \bmod 2\pi$ and $\pi-\psi \bmod 2\pi$. The shear rate at these echoes will be $\gamma_0 2\pi/T \cos\psi$. Thus, the speed of the particles will be the smallest for $\psi\equiv\pi/2 \bmod 2\pi$ and the maximum for $\psi \equiv 0 \bmod 2\pi$. For a shear period of 1 s, and a shear amplitude of 1%, this implies that the maximum amplitude of the shear rate may be as high as $2\pi/100\ \mathrm{s}^{-1}$. The shutter time of our CCD device is constant, and its value is 1/60 s. During this time, the shear deformation may thus be as high as $2\pi/60\%\sim 0.1\%$. This maximum value is reached when the phase shift $\psi\equiv 0 \bmod 2\pi$. The motion of the scatterers while the shutter is open thus induces blurring. More precisely, the visibility of successive speckle images is a periodic function of the phase shift ψ, leading to small values of the correlation amplitude $g_2(0)$ when the phase difference is $\psi\equiv 0 \bmod 2\pi$ [11]. In order to obtain the maximum signal to noise ratio, we thus chose to increase the zero value of the correlation function. We synchronized the shear of the system with the speckle image acquisition device, so that each reference image is chosen with a phase shift $\psi\equiv\pi/2 \bmod 2\pi$. Under these conditions, the initial value of the correlation function is maximum, and only one echo exists for each period (Fig. 1).

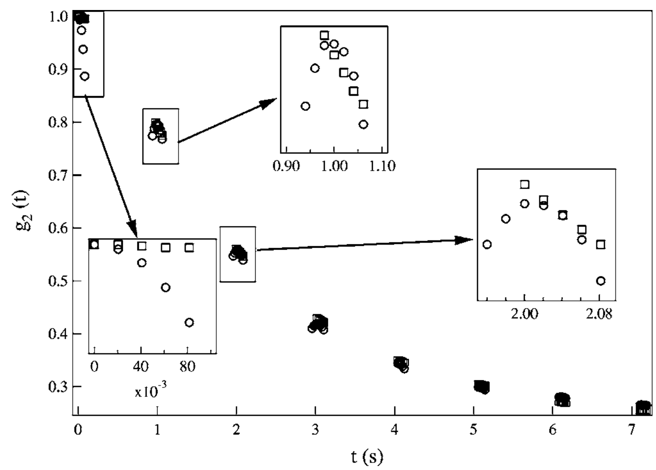

FIG. 1. Correlation function of transmitted light in the absence of shear (□), and under a shear of frequency 1 Hz and amplitude 0.1%, small enough not to induce an increased decorrelation (○). The reference image is chosen so that the shear deformation is maximal at time $t=0$.

IV. AGING AT REST

The suspension is placed between the glass plates, and then sheared for 10 min at $\gamma_0=100\%$, with a frequency equal to 1 Hz. This restarts the dynamics of the system. Then, the system is let age at rest. As previously described [6], just after rejuvenation, the suspension possesses a finite elastic modulus, $G'=300$ Pa, that slowly increases with time. This aging of the suspension is accompanied by a slowing down of the dynamics of the probe particles (Fig. 2). More precisely, all the decorrelation functions may be superimposed by rescaling the time as t/t_w (Fig. 2, inset), and a characteristic decay time τ of the correlation function may be defined, as the time at which the correlation function is equal to e^{-1}. The measured value of the decorrelation time, τ, at a given waiting time, t_w, varies from one sample to the other by as much as 20%. We did not succeed in reducing these variations, neither by changing our sample preparation protocol, nor by improving the cell loading procedure. We were thus led to devise a protocol for measuring the aging behavior $\tau(t_w)$, of our system, with a unique sample. The sample is loaded inside the cell. It is then rejuvenated by application of a periodic shear $\gamma=\gamma_0\sin(2\pi\nu t)$ of amplitude $\gamma_0=100\%$ and frequency 1 Hz during 600 s. The first aging measurement is then performed. On the whole, the measurements are repeated three times, separated by the same rejuvenation protocol. The measured decorrelation times, τ as a function of the waiting time, t_w, are reported in Fig. 3. The three measurements superimpose and τ increases with the elapse time since the end of the preshear, according to $\tau\propto t_w^{\mu}$, with $\mu=0.97\pm0.1$. The average of the noise over the entire set of

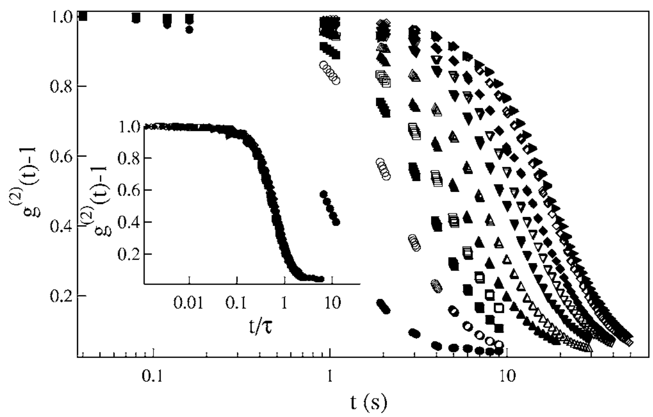

FIG. 2. Correlation functions of the intensity diffused for a sample whose concentration is $\phi=3\%$, with 1% latex particles, at a succession of waiting times after complete rejuvenation of the sample. $t_w=2$ s (●), $t_w=10$ s (○), $t_w=20$ s (■), $t_w=30$ s (□), $t_w=40$ s (▲), $t_w=60$ s (△), $t_w=90$ s (▼), $t_w=120$ s (▽), $t_w=160$ s (◆), $t_w=210$ s (◇), $t_w=260$ s (▶). Inset: correlation curves, as a function of t/τ.

experiments is 3.9%, five times smaller than the observed noise due to sample variation. Thus, in all the following experiments, the same protocol is applied and the mean values of the relaxation times measured for three successive measurements separated by a rejuvenation protocol are reported.

V. AGING UNDER SHEAR

Let us now let the suspension age under the application of a periodic shear. We measure the envelope of the echoes, and

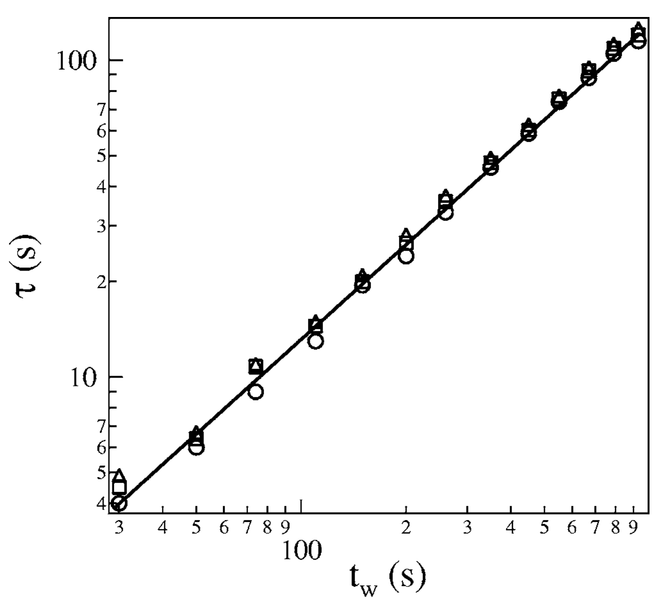

FIG. 3. Evolution of the dynamics of the sample after the end of the complete rejuvenation procedure. The experiment is repeated three times, with the same sample. ○ (respectively, □, △): aging after the first (respectively, the second and the third) rejuvenation processes. Line is a power-law fit of the data, leading to the exponent $\mu=0.97$.

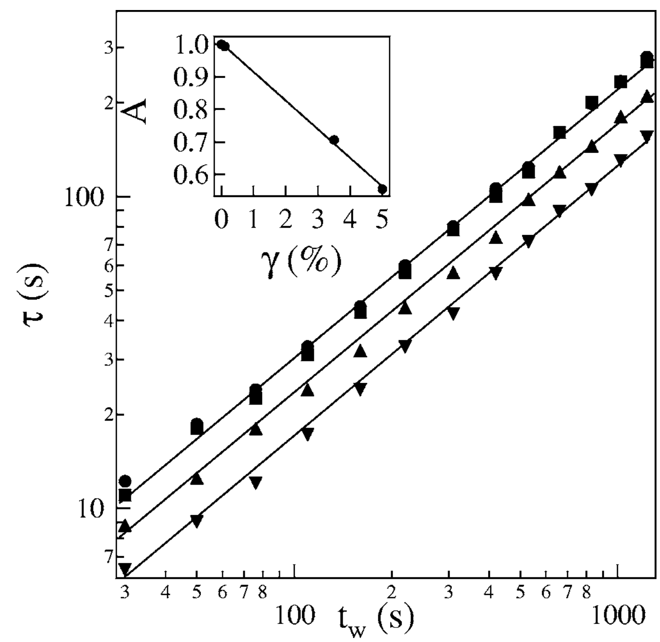

FIG. 4. Characteristic time of the correlation function measured for different shear amplitudes, as a function of the waiting time. ●: no shear, ■: $\gamma=0.1\%$, ▲: $\gamma=3.5\%$, ▼: $\gamma=5\%$. Lines are power-law fits of the data, of common exponent $\mu=0.95$. Inset: prefactor of the aging law: $\tau=A(\gamma)t_w^{\mu}$, as a function of the shear amplitude, γ.

the correlation functions we are interested in are defined for times multiple of the period T of the shear deformation. Whatever the age of the system, the envelopes of these echoes may be superimposed by rescaling the time according to t/t_w. This means that the we do not observe any change in the spectrum of the relaxation times as aging occurs. A characteristic time may be defined as previously. The evolution of the characteristic time τ obeys to the following law (Fig. 4)

$$\tau=A(\gamma)t_w^{\mu}. \tag{2}$$

The exponent μ is an independent function of the shear amplitude, whereas the the factor $A(\gamma)$ is a decreasing function of γ, following $A(\gamma)\sim e^{-\gamma/\gamma_c}$, where $\gamma_c=5\%$. This value of the shear deformation is consistent with the characteristic value of shear needed to completely rejuvenate the system, as obtained by measuring the characteristic time of the decorrelation function after cessation of the shear of amplitude γ [6]. Let us note that the evolution of the aging law as a function of the shear amplitude is qualitatively different from that observed in polymer glasses, for which the exponent μ was a decreasing function of the applied shear [3]. Indeed, in that case, the relaxation of a torsional deformation applied to a melt of polymer also exhibits a faster aging when the amplitude of the deformation increases. During the aging process, the relaxation curves measured at successive waiting times also superimpose when plotted as a function of t/t_w; nevertheless, the exponent μ is a decreasing function of the deformation amplitude.

Since deformations in the range of γ_c are sufficient to observe shear rejuvenation, we now address the question of

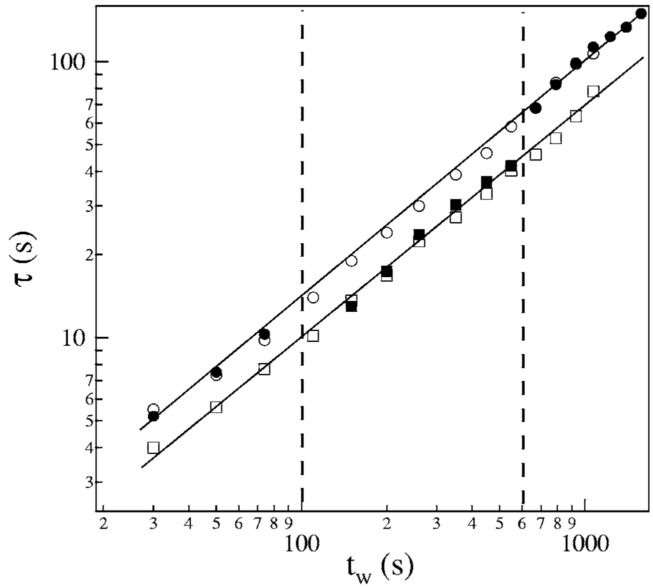

FIG. 5. Characteristic time of the correlation function, τ as a function of the waiting time, t_w, under shear. For $t_w < 100$ s, the sample is not sheared (●), then sheared at 1 Hz, $\gamma = 3.5\%$ (■). For $t_w > 600$ s, the shear is stopped (●). Reference aging in the absence of shear (○) and under shear $(\gamma = 3.5\%)$ (□) is also reported.

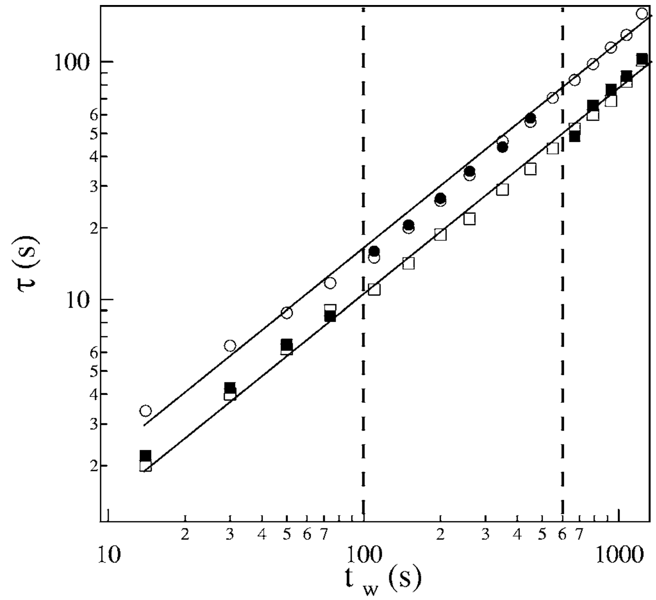

FIG. 6. Characteristic time of the correlation function, τ as a function of the waiting time, t_w, under shear. For $t_w < 100$ s, the sample is sheared at 1 Hz, $\gamma = 3.5\%$ (■), then shear is ceased (●). For $t_w > 600$ s, the sample is sheared again with the same amplitude and frequency (■). Reference aging in the absence of shear (○) and under shear $(\gamma = 3.5\%)$ (□) is also reported.

the consequence of this rejuvenation over the subsequent aging of the suspension, once shear is ceased.

VI. AGING UNDER COMPLEX SHEAR HISTORIES

We now consider the dynamics of the system after partial rejuvenation. The protocol is as follows: the sample is completely rejuvenated by application of sinusoidal strain of $\gamma = 100\%$ at 1 Hz during 600 s. The end of this shearing period defines the origin of waiting times. The sample is then submitted to a shear of amplitude $\gamma_1 = 3.5\%$, for 100 s during which the aging dynamics is measured thanks to the echo technique. Last, the shear is stopped (Fig. 5, $t \in [100, 600\ \text{s}]$). The acceleration of the dynamics induced by the previous low shear amplitude period does not affect the aging behavior in the absence of shear. More precisely, when the shear of amplitude γ_1 is ceased, aging of the sample restarts as if the sample had always aged in the absence of shear. It thus appears that the dynamics of the system at a time t_w after complete rejuvenation is independent of the shear history of the system, as long as amplitude of the applied shear is low enough not to fully rejuvenate the system. This is confirmed by the observation that, when a shear of amplitude $\gamma_1 = 3.5\%$ is applied again after the system was let age in the absence of shear, the observed dynamics is identical as the one observed if the sample has always been sheared with the amplitude γ_1 (Fig. 5, $t_w > 600$ s).

This experiment was repeated by inverting the periods of low and higher shears (Fig. 6), and the above conclusion has been confirmed: the observed dynamics at a given time t_w does not depend on the previous shear history of the system as long as it remains in the glass phase.

In other words, the application of a shear deformation of amplitude smaller than γ_c has two consequences:

• during the application of the shear, rearrangements of the colloids are induced, and an acceleration of the dynamics of the suspension is observed. This acceleration manifests itself by a modified aging law (Fig. 4) and

• nevertheless, after cessation of the shear of moderate amplitude, the induced colloids rearrangements do not affect the subsequent aging of the suspension.

Our MSDWS measurements do not allow to determine whether the dynamics of the colloids is homogeneous throughout the entire sample, or whether different particles rearrange under shear and after cessation of shear.

This experiment is similar to previous experiments on the the aging of spin glasses [12,13] during which the samples were submitted to temperature histories similar to strain histories in our last experiment. A spin glass was let age at a temperature T_1, during time t_1, put at a lower temperature $T_2 < T_1$ during time t_2, and then put again at temperature T_1. The dynamics of the system, measured at temperature T_1 and at time $t_1 + t_2$ is identical to the one measured at time t_1. Thus, everything happens as if the aging period at temperature $T_2 < T_1$ stopped the aging of the system, as measured at temperature T_1.

The response of our colloidal glass to a complex history of applied shear strains thus exhibits a different behavior from the response of a spin glass submitted to a similar temperature history variations. Application of a periodic strain of amplitude lower than the characteristic amplitude needed to fully rejuvenate the suspension does not alter the aging mechanism.

VII. CONCLUSION

The dynamics of a glass phase at a given temperature T below the glass transition temperature T_g, is a function of the time spent below T_g. Moreover, if the sample is submitted to variations of temperatures inside the glass phase, its dynamics at a temperature T becomes also a function of the total time spent at that given temperature since quenching. This behavior has been coined memory effect [3,13]. We looked for the existence of a memory effect in concentrated colloidal suspensions. In that case, the glass phase boundary is a function of the temperature, the volume fraction and the applied stress [5]. We chose to use the applied stress as a means to explore the glass phase dynamics and thus studied the aging of the suspension under the application of a periodic shear of moderate amplitude. Contrary to the case where the exploration of the glass phase is performed by changing the temperature, we observed that the dynamics after quenching is only a function of the total time spent inside the glass phase, and does not depend on the time spent at the applied shear amplitude. We thus rule out the existence of a memory effect in our colloidal suspension.

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