Partial rejuvenation of a colloidal glass

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We study the effect of shear on the aging dynamics of a colloidal suspension of synthetic clay particles. We find that a shear of amplitude γ reduces the relaxation time measured just after the cessation of shear by a factor $\exp(-\gamma/\gamma_c)$, with $\gamma_c \sim 5\%$, and is independent of the duration and the frequency of the shear. This simple law for the rejuvenation effect shows that the energy involved in colloidal rearrangements is proportional to the shear amplitude γ rather than γ^2, leading to an Eyring-like description of the dynamics of our system.

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I. INTRODUCTION

Molecular and spin glasses exhibit very intriguing dynamical properties, which are still poorly understood. One of the most striking features is the aging phenomenon: a slowing down of the microscopic dynamics with the elapsed time. This behavior is generally associated with the existence of many accessible metastable states spanning a broad energy distribution. As time goes on, the material gets trapped in deeper and deeper energy wells for increasing escaping times. As a result, many physical characteristics of these systems (such as rheological [1], or dielectric properties) depend in a nontrivial way on their thermal history.

In recent years, aging dynamics has been evidenced in very different systems, such as colloidal suspensions [2,3], dense emulsions, amorphous polymers, or weak gels. In these so-called soft glassy materials, temperature cannot be varied without drastically modifying the underlying weak interactions between their constituents. It is thus not a convenient parameter to probe such history dependent effects. However, it has been recently suggested that shearing could play an analogous role as temperature by allowing a renewal of the microscopic structure [4–6]. Quenching of colloidal glasses, for instance, can be obtained by applying a temporary strong shearing to the material and then stopping the shear. This temperature/strain analogy has been extensively developed in different models, and allowed to account for some rheological features of soft glassy materials.

The relative success of this approach actually hides important conceptual issues: What is the effect of a macroscopic strain on microscopic scales in such disordered systems? Can this mechanical energy input yield a spatially homogeneous energy term equivalent to a temperature raise? If so, how does this local energy depend on the amplitude, frequency, or duration of the shear?

In the present paper, we address these questions by measuring slow relaxation times in a colloidal glass submitted to shear sequences of various amplitude, frequency, and duration. We focus on the modification of the aging dynamics of the quiescent material after a finite shear period has been applied to identify the relevant mechanical parameters.

II. SYSTEM AND TECHNIQUE

The system used is a suspension of synthetic smectite particles (Sumecton SA, provided by Kunimine Industries Co., Ltd., Tokyo, Japan) dispersed in water. These clay particles consist in negatively charged disks of diameter 125 nm and thickness 5 nm. The solution is prepared by dispersing the powder in water, and stirring at room temperature for 3 days. At pH$=9$ and concentrations higher than $\phi=1.2\%$, they form a stable solution with a finite elastic modulus that slowly evolves with time. In all the experiments, the concentration is set to $\phi=3\%$ for which we measure an elastic modulus $G'=300$ Pa (Fig. 1). In order to probe the internal dynamics, we add latex polystyrene particles of diameter 1 μm at a volume fraction of 1%. These particles render the system turbid thus allowing for subsequent multiple light diffusion studies. The sample is placed in a 1-mm-thick transparent shear cell controlled by a linear stepper motor, and illuminated with an enlarged laser beam. Dynamics of the particles is monitored by multispeckle diffusing wave spectroscopy [7]. Using a charge-coupled device camera, we record the multispeckle pattern at the outside surface of our sample. The correlation functions of transmitted intensity
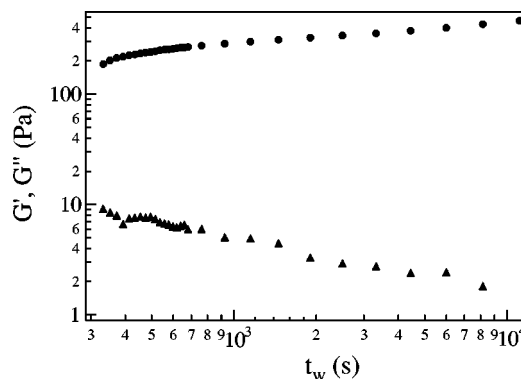

FIG. 1. Elastic (●) and loss (▲) moduli of a suspension of smectite at $\phi=3\%$.

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were then computed by averaging the intensity fluctuations over the entire pattern that consists of over 5000 speckles. Though, rather than computing the correlation function of diffused intensity by averaging over temporal fluctuations, one averages the intensity correlation over spatial fluctuations of the speckle pattern. We thus access

$$g_{2t_w}(t) = \frac{\langle I(t_w)I(t_w+t)\rangle}{\langle I(t_w)\rangle\langle I(t_w+t)\rangle},$$

where $\langle \cdots \rangle$ denotes averaging over the speckle pattern and t_w is the reference time of the first image and t is the time elapsed since t_w. Then the field correlation function at time t_w, $g_{1t_w}(t) = \sqrt{g_{2t_w}(t)-1}$, is computed. This technique allows us to study slow transient phenomena with characteristic times between 1 and 5000 s, each of them being uncorrelated and q independent.

In a first series of experiments, we investigate the aging dynamics of the system at rest. We prepare the system by submitting it to a sinusoidal shear strain of amplitude $\gamma = 300\%$, at frequency 0.3 Hz, during 210 s. We observed that the turbidity of the system did not change when shearing was applied. The shear is stopped at time $t=0$; we then measure the correlation functions of the intensity at various waiting times $t_w > 0$ [Fig. 2(a)]. From the slope of these curves when $t \rightarrow 0$, we extract a correlation time τ that increases with time t_w. This time τ corresponds to the slow relaxation processes of glassy dynamics, called α relaxation. Using a photomultiplier and a fast correlator, we checked that the fast (β) relaxation time, associated with the rapid thermal motion of the particles inside transient traps, did not depend on the age of the system, as already observed in a similar system [8]. We notice that the plateau value of the correlation function, between fast and slow decays, is almost constant, which is consistent with our observation that the elastic modulus of the sample barely evolves with time. We observe that after this strong shearing the relaxation time τ increases as t_w^α with $\alpha = 1.1 \pm 0.16$ [Fig. 2(b)]. This value $\alpha \sim 1$ corresponds to a full aging behavior which has been commonly reported in dense solid suspensions and noncolloidal glassy systems [8]. By performing successive shearing of amplitude $\gamma = 300\%$ at frequency 0.3 Hz, followed by aging measurements, we obtain reproducible aging curves, which indicates that the applied shear allows for a complete rejuvenation of the system. In the rest of this paper, we focus on the evolution of the slow relaxation time τ after shear of moderate amplitudes.

III. SHEAR OF MODERATE AMPLITUDE

We thus now apply the following protocol: after complete rejuvenation of the sample (300% shear at frequency 0.3 Hz for 180 s), we let the system age at rest for 240 s then apply a moderate sinusoidal shear.

Let us first study the dynamics of the system after a moderate shear, of amplitude $\gamma = 5\%$, frequency 1 Hz, and duration 1080 s. Rather than following the standard aging curve for a quiescent material, the dynamics rapidly recover the original one, corresponding to $\gamma = 0$ (Fig. 3). τ is thus not a
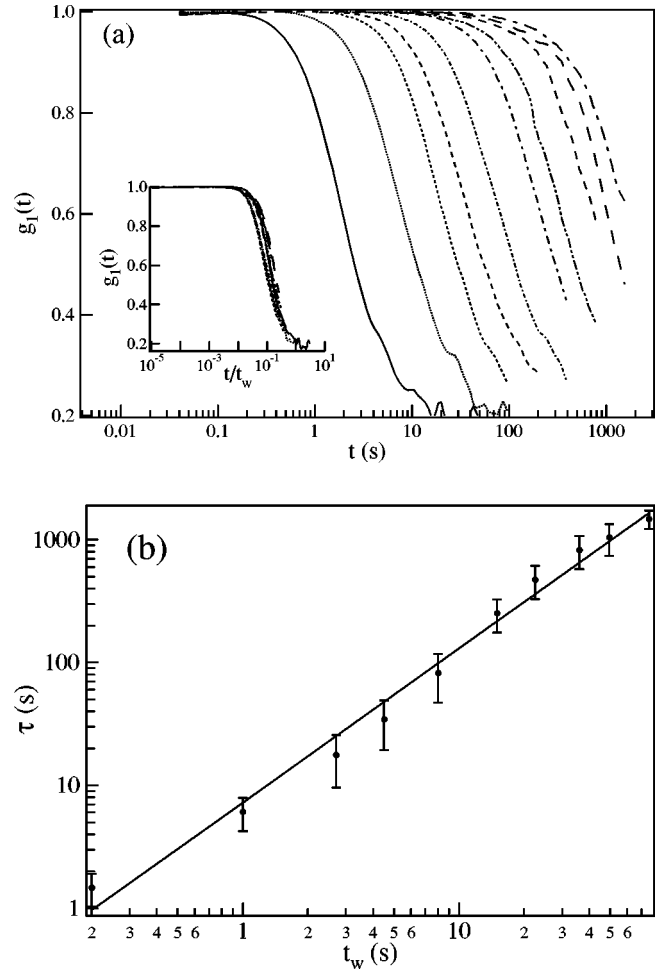

FIG. 2. (a) Intensity correlation functions at increasing waiting times, from left to right: $t_w = 12$ s, 60 s, 162 s, 270 s, 480 s, 900 s, 1350 s, 2160 s, 2970 s, and 4536 s. Inset: correlation functions vs rescaled time t/t_w. (b) Decay time τ of the intensity correlation function as a function of time spent in the glassy phase, t_w. The solid line is a power-law fit: $\tau \propto t_w^{1.1}$.

sufficient parameter to measure the age of the system, since two systems with the same relaxation time can evolve differently depending on the history of their preparation. We thus recover the same property of the dynamical properties of concentrated suspensions of colloidal particles in the glassy phase studied in Ref. [4]. It is claimed by these authors that these different evolutions are related to a modification of the energy trap *distributions* induced by the intermediate shearing. Identical effects can be observed in spin glasses following a quench inside the glassy phase.

Dependence of τ just after cessation of shear, with the duration of the shear, t_s, its frequency ν, and its amplitude γ, is now studied. With our experimental device, we could vary γ between 0 and 500%, and ν between 0.3 and 3 Hz. Shear duration t_s was varied between 1 and 100 s. The relaxation time τ measured 60 s after shear cessation is found to be decreased relatively to the value it would have reached if no shear had been applied (Fig. 4). The reduction factor appears to be a sole function of the amplitude γ. As shown in Fig. 4, τ can be written as
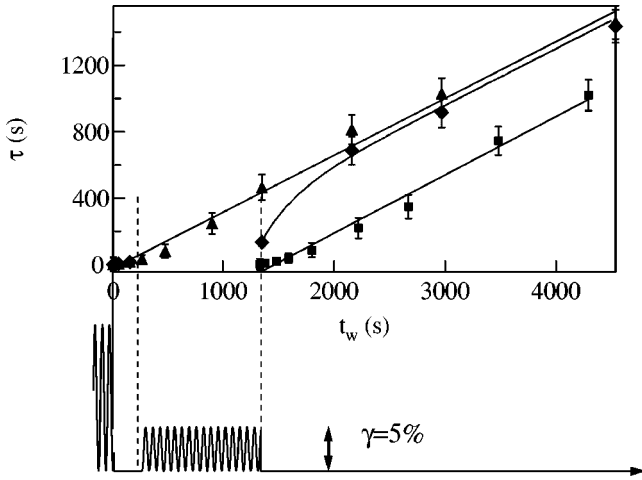
FIG. 3. Relaxation time after several histories, each of them being preceded by a phase of full rejuvenation (300% shear during 210 s). Aging only (no applied shear, ▲). Aging during 4 min, and application of a moderate shear of amplitude 5% during 18 min (◆). Aging during 4 min, and application of a shear of amplitude 300% during 18 min (■). The reference time $t_w=0$ is taken after the phase of full rejuvenation. Lines are guides to the eye.

$$\tau(\gamma)/\tau(\gamma=0)=\exp(-\gamma/\gamma_c) \qquad (1)$$

with $\gamma_c=0.05$ being the typical strain amplitude necessary to rejuvenate the system.

This result provides a direct quantitative evaluation of the effect of a moderate shear period on the relaxation dynamics in soft glassy systems. In particular, we note that τ is independent of the frequency ν of the applied shear (in the range 0.3–3 Hz explored) and of the shear duration t_s (in the range 1–100 s). This rules out any cumulative or frequency dependent effect (at least within our experimental range) in the way shearing may affect the internal dynamics.

In order to understand the peculiar form of Eq. (1), we use a simple physical picture of the aging process [9,10]. In this scheme, the dynamics results from the simultaneous relaxation of frozen structures of different characteristic energies. We do not discuss here the microscopic details of these structural relaxations. They might correspond to different length scales (cooperative relaxation), or just be associated with different local yield energy barriers due to the disordered nature of the suspension. After a time t_w following a quench, we can define a limiting energy $E(t_w)$ which separates structures of energy $E<E(t_w)$ that have been fully relaxed, from out-of-equilibrium structures of energy $E>E(t_w)$. At a given waiting time t_w, the relaxation time $\tau(t_w)$ is controlled by the dynamics of the yet unrelaxed structures of lowest energy barriers, through a simple activation-type equation: $\tau(t_w) \sim \exp[-E(t_w)/kT]$.

The applied intermediate shearing provides an extra energy input $\Delta E(\gamma)$ to the system. When the system is quenched again, structures of energy lower than $\Delta E(\gamma)$—which have been entirely rejuvenated—rapidly relax [for $\Delta E(\gamma)\ll kT$, this dynamics rapidly freezes out, so that this initial period is not accessible to our measurement].
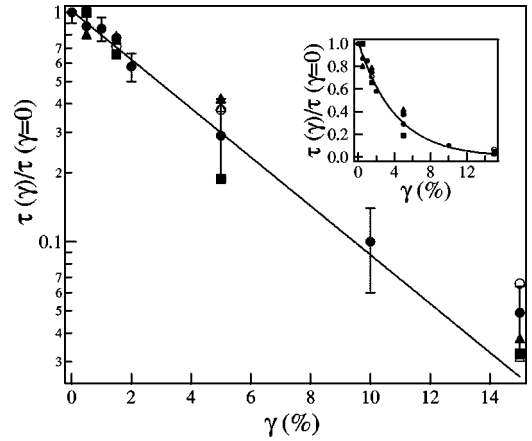

FIG. 4. Decay time of the intensity correlation function, τ, measured 60 s after cessation of sinusoidal shear of amplitude γ, frequency ν, and duration t_s vs the shear amplitude γ. The absolute value of $\tau(\gamma=0,t_s)$ should be read in Fig. 2(b), at time $t_w=300+t_s$. ●, $\nu=1$ Hz, $t_s=10$ s; ■, $\nu=0.3$ Hz, $t_s=10$ s; ▲, $\nu=3$ Hz, $t_s=10$ s; ○, $\nu=1$ Hz, $t_s=1$ s; △, $\nu=1$ Hz, $t_s=100$ s. Inset: linear plot of the data.

Moreover, the heights of the energy barriers greater than $\Delta E(\gamma)$ have been randomly redistributed around their values by a quantity $\Delta E(\gamma)$. As a result, the apparent energy barrier of the first accessible relaxation processes becomes $E=E(t_w)-\Delta E(\gamma)$ and the associated relaxation time has been reduced by a factor $\exp[-\Delta E(\gamma)]$.

Equation (1) demonstrates that the mechanical energy input $\Delta E(\gamma)$ is proportional to the shear amplitude γ. This result is at odds with the γ^2 dependence used in previous models which assumed a local elastic response of the material [11,12]. The correct scheme is rather similar to Eyring's activated process description of fluid flows. According to this description, one defines a fluid element of size a, the characteristic interparticle distance. Then, the fluid flows as soon as this element is deformed by 100%, meaning that the energy input to this element, when submitted to the stress σ, is $E\sim(\sigma a^2)a$, i.e., if G' is the elastic modulus of the element, $E\sim G'\gamma a^3$ [13]. We can now estimate the equivalent temperature increase $\Delta T(\gamma)$ induced by the shear strain of amplitude γ_c that rejuvenates the system. We first estimate the activation volume as a^3 where $a\sim100$ nm is the typical distance between neighboring particles. The mechanical energy input is then written as $\Delta E(\gamma)=k_B\Delta T(\gamma)\sim G'\gamma a^3$ where G' is the elastic shear modulus of the material. Since $\gamma_c=0.05$ is the typical strain necessary to rejuvenate the system, we can in particular estimate that the deviation from the glass transition necessary to rejuvenate the system is of the order of $T_g-T=G'\gamma_c a^3/k_B\approx T/10$.

IV. CONCLUSION

We have shown that an externally applied deformation plays the same role in our colloidal glass as a temperature raise in glassy liquids, by allowing a restarting of the internal

dynamics. We have demonstrated that the maximum amplitude of the deformation is the only parameter which controls the magnitude of the rejuvenation effect: a very simple correspondence between temperature and shear amplitude can therefore be drawn.

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