Rejuvenation and Overaging in a Colloidal Glass under Shear

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We report the modifications of the microscopic dynamics of a colloidal glass submitted to shear. We use multispeckle diffusing wave spectroscopy to monitor the evolution of the spontaneous slow relaxation processes after the samples have been submitted to various straining. We show that high shear rejuvenates the system and accelerates its dynamics, whereas moderate shear over-ages the system. We analyze these phenomena within the frame of the Bouchaud's trap model.

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The physical properties of glassy systems such as supercooled liquids, spin glasses, amorphous polymers, and colloidal glasses are well known to evolve slowly with time. This phenomenon is called aging. The out-of-equilibrium nature of these systems compels their physical properties to depend on two times as shown by both theoretical and experimental studies. The first time is the age of the system, i.e., the time spent in the glassy phase. The second time is the time elapsed since the measurement started. Consequently, a well controlled history is a key requirement for obtaining reproducible results. The most common way to control the history is to quench it from an equilibrium state at high temperature into an aging state at low temperature. Since the system is at equilibrium at high temperature, all the history preceding the quench is erased and a complete rejuvenation of the physical properties is achieved. For colloidal glasses, however, temperature may not be a practical parameter. Liu and Nagel recently suggested [1] that shear may act equivalently to temperature for such materials. Indeed, a high shear proves to be able to be erased from the memory for these systems and thus to completely rejuvenate them [2,3]. In that sense the cessation of a shear is similar to a temperature quench. Moreover, different approaches were recently introduced to describe the coupling between mechanical deformations and aging phenomena [4,5]. However, quantitative experiments are still lacking to determine unambiguously how shear acts on a microscopic level and how it should be introduced in a mean field model.

In this Letter we report nontrivial shear effects on a dense solution of polybeads. We show that theses effects can be mimicked by temperature changes in the Bouchaud's trap model [6]. Our underlying physical picture is the following: slow relaxations, of characteristic time τ, are determined by the structural rearrangements of the particles. The dynamics slows down with the age t_w of the system as the beads find more and more stable configurations. τ is thus an increasing function of t_w. Since a shear flow seems to be able to completely rejuvenate the system, one could imagine that it shuffles the beads' arrangements. The resulting configurations could be less stable. The dynamics of rearrangements would then be accelerated and the relaxation time τ would decrease. Oppositely, one could imagine that a moderate oscillatory strain is able to help the system to find more stable, though always noncrystalline, configurations. The dynamics would then be slowed down, and τ would be increased. In order to elucidate these two contradictory pictures, we experimentally tested the effect of an oscillating shear strain on the evolution of the microscopic dynamics of our dense suspension. The sample is a commercial suspension of polystyrene spherical beads of diameter 162 nm copolymerized with acrylic acid (1%) that creates a charged corona stabilizing the microspheres. It is concentrated by dialysis to a volume fraction $\varphi = 49\%$. Because of the hairy corona surrounding our particles, this volume fraction is high enough to lie in the glass region of the phase diagram.We use multispeckle diffusing wave spectroscopy (MSDWS) to probe the slow relaxation dynamics of the system after various strain histories. MSDWS is an extension of regular DWS, a technique that measures the average displacement of the particles through the intensity fluctuations of multiply scattered light. Whereas DWS performs a time average of the fluctuations, MSDWS makes a spatial average of them. It is thus a well suited technique to study slow transient phenomena such as aging processes. A precise description of the technique can be found in [7]. It allows one to measure in real time the two times intensity autocorrelation function $g_2(t_w + t, t_w) = \frac{\langle I(t_w+t)I(t_w)\rangle}{\langle I(t_w)\rangle^2}$, where t_w is the reference time and t the elapsed time since t_w. The average $\langle \cdots \rangle$ is spatially performed over the speckle pattern. This correlation function is a decreasing function of the number of rearrangements that occurred between t_w and $t_w + t$ as demonstrated in [8,9]. Thus the principle of the whole experiment is the following: the suspension is submitted to different shear history detailed below; the modification of its dynamical properties is recorded after shear cessation. The sample is placed in a custom-made shear cell consisting of two parallel glass plates with a variable gap. For all presented experiments, the gap was set to 1.3 mm. Oscillatory straining was realized by moving the bottom plate, thanks to a

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piezoelectric device. The shear cell was synchronized with the light scattering detection via a PC. For optical considerations, backscattering geometry was used. We confirmed that the suspension did not slip on the wall by checking that we obtained identical results for various gap size. Moreover, no macroscopic crystallization was observed. All the experiments were performed at room temperature. In order to increase the signal to noise ratio, each test presented in this paper was performed 10 times and each correlation function was averaged over 10 experiments. The reproducibility was check to be better than 5%.

We first submit the sample to a series of 40 oscillations for different strain amplitudes γ. For $\gamma > 20\%$ the measurement after the shear cessation becomes insensitive to the shear strain amplitude showing that the rejuvenation is then total. The age t_w of the system is defined from the shear cessation as usually done for temperature quench. Figure 1 shows the correlation function versus t for different values of t_w. This set of curves displays two important features: on the one hand, in the region where $t \ll 5 \times 10^{-2}$ s, all the curves overlap. The correlation functions show an initial decrease that is the end of a short time relaxation. It corresponds to restricted thermal fluctuations of the particles and is called the β mode. This fast mode is not affected by shear as predicted by the models [5]. On the other hand, in the long time limit, we observe a slow decay, known as α relaxation, typical of glasses. This decay from the pseudoplateau region is all the slower as the system is older. It thus means that the average rate of the structural rearrangements decreases with t_w. We arbitrarily define the structural relaxation time $\tau_{1/2}$ for this regime so that $g_2(t_w + \tau_{1/2}, t_w) - 1 = 0.06$. The inset of Figure 1 shows that $\tau_{1/2} \propto t_w^{1.06\pm0.08}$ for $t_w > 1$ s. The aging part of the correlation function can be rescaled with the reduced variable $\frac{1}{1-\mu}[(t + t_w)^{1-\mu} - t_w^{1-\mu}]$ with $\mu = 1.06$. In addition, the shape of the correlation function is invariant by such a scaling. This result is a typical feature of the aging process and is qualitatively similar to that found for rheology of such systems [2,3,10].

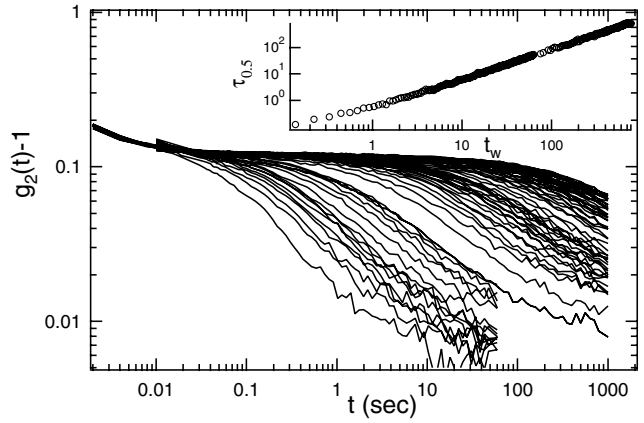

FIG. 1. The intensity autocorrelation function $g_2(t_w + t, t_w) - 1$ for different t_w ranging from 0.5 to 10^3 s. The first decrease at short times comes from the tail of the β relaxation. The long term decrease is due to the structural relaxation. The inset shows $\tau_{1/2}$ in seconds vs t_w. $\tau_{1/2}$ scales as $t_w^{1.06\pm0.08}$.

In order to better understand the influence of shear on the dynamics of the particles, we apply to the system the strain history described in Fig. 2(a). The sample is first submitted to an oscillatory strain of amplitude 30% at 1 Hz during 40 s in order to rejuvenate it totally. Second, we let it age at rest for 10 s. Then, a second burst of 1 Hz oscillations is applied during t_d. After its cessation, we examine how the amplitude γ and the duration t_d of the burst have modified the dynamical properties of the sample. t_w is now referenced from the end of the second burst.

Figures 2(b) and 2(c) display the relaxation time $\tau_{1/2}$ as a function of t_w for different strain amplitudes, with $t_d = 1$ s and $t_d = 100$ s, respectively. Two limit cases can be considered: that of a complete rejuvenation during the second burst, corresponding to the reference curve of Fig. 1, and that of $\gamma = 0\%$ where the system is unperturbed during the second burst. These two limit curves are the same but shifted in time by $t_s = 10$ s + t_d. They merge at long time because of the log scale. For the duration of the

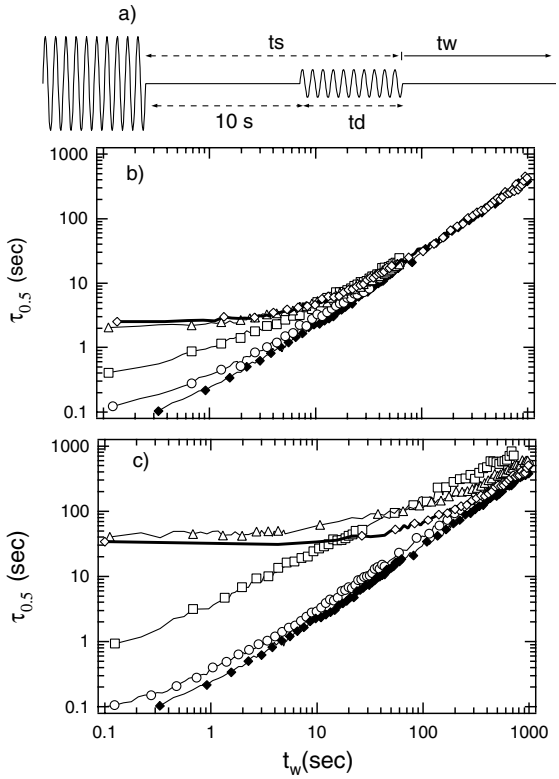

FIG. 2. (a) Strain history. (b) $\tau_{1/2}$ for $t_s = 11$ s and different strain amplitudes $\gamma = 0\%$ (◇), 2.9% (△), 7.9% (□), 11.7% (O), and the reference curve (◆). $\tau_{1/2}$ decreases monotonically with the strain amplitude at short times. For $t_w \sim t_s$ all curves merge. (c) $\tau_{1/2}$ for $t_s = 110$ s for the same strain amplitude. $\tau_{1/2}$ for $\gamma = 2.9\%$ and 7.9% is superior to $\gamma = 0\%$ in the long time regime.

second burst $t_d = 1$ s [Fig. 2(b)], we observe that its effect is to rejuvenate *partially* the system: for any t_w the relaxation time is a monotonically decreasing function of γ. All the curves lie between the two limit case curves. This is coherent with the idea that the shear has to be strong enough to rejuvenate totally the system. However, if the system is left longer under shear, the modification of its dynamic is then dual. When $t_d = 100$ s [Fig. 2(c)], in the limit of short t_w, the relaxation time behaves similarly, as previously described. However, for longer t_w the relaxation time after a moderate strain (see, e.g., $\gamma = 7\%$) is surprisingly longer than the one for the sample without solicitation during the second burst. In other words moderate shear strain results in a system with a slower relaxation time. We call this overshoot in the relaxation time *over-aging*. This definition is loose, and a more precise one will be given after a more complete analysis. Let us also note that for large strain amplitudes a total rejuvenation is recovered as exemplified by the curve for $\gamma = 11.7\%$ in Fig. 2(c).

This experiment is thus contradictory with the simple idea that strain or stress always rejuvenates the system and accelerates the dynamics. It shows that a transient strain changes not only the average value of the relaxation time but also the distribution of relaxation times within the sample. The change of the distribution is clearly demonstrated by the crossing of the curves in Fig. 2(c): two similar systems with the same relaxation time and different histories can evolve differently. The shape of the correlation function is also altered by the change in the distribution of relaxation time as demonstrated in Fig. 4(a). Similar modifications of the shape of the response function have already been noticed on spin glasses after a temperature step; see Fig. 5 of Ref. [11]. We note that microscopic aging models including shear in their equations were solved only with a steady shear. To our knowledge, no calculation of the modification of the microscopic dynamic after a transient shear has been performed for these models. This problem will be addressed in a future work [12]. However, we point out here the similarity of over-aging after a transient shear stress and the predictions of the trap model [6] after a temperature step. This model describes the motion of noninteracting particles hopping in an energy landscape with wells of depth E. The distribution of the wells of depth $\rho(E)$ is fixed *a priori*. $P(E, t)$ is the probability for a particle to be in a trap of depth E at time t. The evolution of $P(E, t)$ is simply governed by thermally activated hopping and is written as

$$\frac{\partial P(E,t)}{\partial t} = -P(E,t)e^{-E/T} + \Gamma(t)\rho(E), \qquad (1)$$

where T is the thermal energy and $\Gamma(t) = \int_0^\infty P(E', t)e^{-E'/T}dE'$ is the average hopping rate. The time unit (tu) is set to 1. Following [6], we take $\rho(E) = \exp(-E/T_g)$. For $T > T_g$, $P(E, t)$ has a stationary limit $P(E, t) \propto \exp[(1/T - 1/T_g)E]$. For $T < T_g$, $P(E, t)$ has no stationary limit and keeps evolving with time with a dynamics scaling as $\frac{t}{t_w}$. We solved numerically Eq. (1) for a quench from $T = \infty$ to $T = \frac{1}{2}T_g$. The energy distribution is presented by the dotted line in Fig. 3(b). As expected, it shifts progressively with time towards deeper and deeper energy wells. The relaxation times of the system thus become longer and longer. In order to mimic the strain sequence of Fig. 2, we now solve the model for the following temperature history: The system is quenched from infinite temperature to $T = \frac{1}{2}T_g$. After a delay of 100 time units (tu) the temperature T is raised to $T = \frac{1}{2}T_g + \Delta T$ with $\Delta T = \frac{1}{3}T_g$, during 300 tu, then quenched back to $\frac{1}{2}T_g$. t_w is referenced after the second quench.The solution is plotted in the continuous line.

Figure 3(b) shows that shortly after the system is heated back [(1)] the small energies [arrow (α) in Fig. 3] are overpopulated, intermediate energies [(β)] are depleted, and high energies [(γ)] remain unperturbed compared to the reference case where no temperature step is applied. The system ages then in a higher temperature state. When the second quench happens [(2)], both low and high energies are overpopulated, whereas intermediate ones are

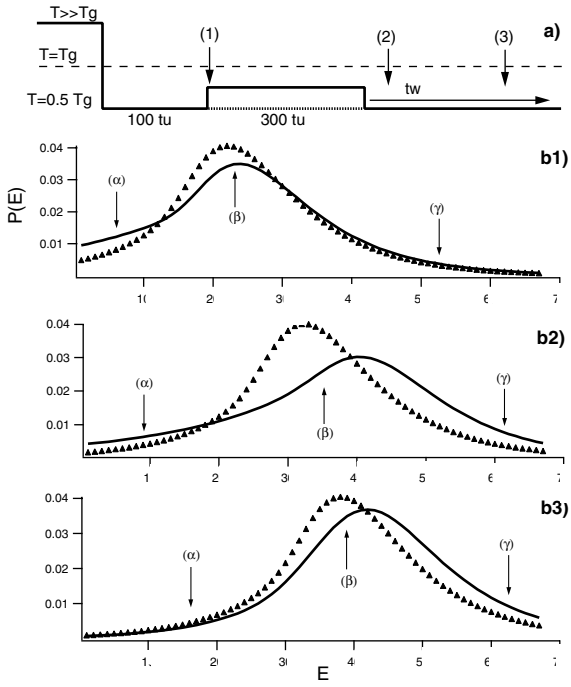

FIG. 3. (a) Temperature history. (b) $P(E, t_w)$ vs E for various t_w. The (▲) curve corresponds to the reference case; the full line corresponds to the case with a step ($\Delta T = \frac{1}{3}T_g$). Notice that 1 tu after the sample is reheated (1) the small energies are overpopulated, the intermediate ones are depleted, and the large ones remain unchanged. At 1 tu after the second quench (2) both small and large energies are overpopulated. At 3000 tu after the second quench, small energies and intermediate energies are depleted, whereas large energies stay overpopulated.

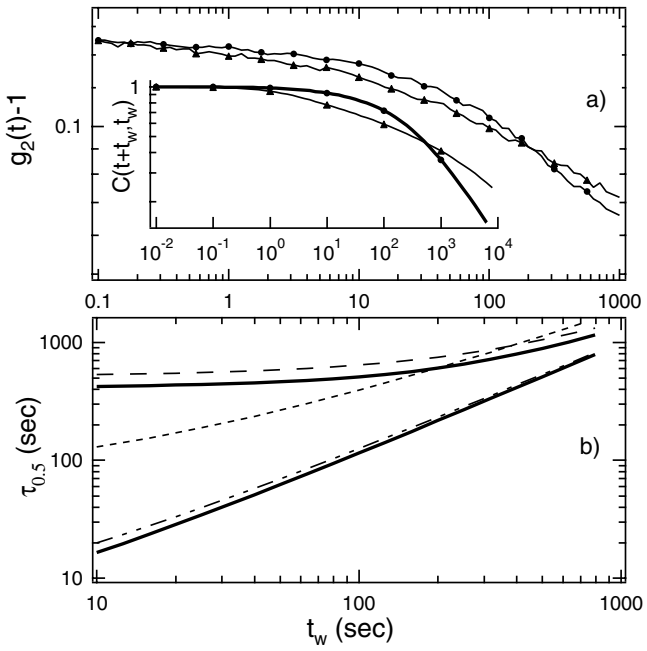

FIG. 4. (a) $g_2(t_w + t, t_w) - 1$ for $t_w = 1$ s for $\gamma = 0\%$ (•) and for $\gamma = 7.9\%$ (▲). The inset shows similar curves for $C(t_w + t, t_w)$ calculated at $t_w = 0.1$ tu and $\Delta T = 0$ (•) and for $\Delta T = \frac{1}{3} T_g$ (▲). Notice that for $\Delta T = \frac{1}{3} T_g$ the curves first decrease more rapidly (small energies overpopulated), then lies over the reference one (large energies overpopulated). The agreement is qualitatively excellent. (b) $\tau_{1/2}$ calculated from $C(t_w + t, t_w)$ vs t_w for various $\Delta T = 0\%$ (bold line), $\frac{1}{10} T_g$ (—), $\frac{1}{3} T_g$ (...), $\frac{3}{2} T_g$ (-..-), and the reference curve (bold line). Notice the presence of over-aging in the long time regime. Qualitative agreement with Fig. 2(b) is satisfactory.

depleted. After a while [(3)] low energies recovered their reference population, whereas high energies stay overpopulated compare to the case without temperature step. The system has consequently a longer average relaxation time. Actually, we do not measure $P(E, t)$ directly, but we probe it experimentally via $g_1(t + t_w, t)$. The correlation function g_1 is a monotonically increasing function of the probability that a particle has not changed trap between t_w and $t + t_w$. Within the frame of this model this probability can be written

$$C(t_w + t, t_w) = \int_0^\infty P(E, t_w) \exp[-te^{-E/T}] dE.$$

Figure 4(a) shows the change in the shape of the experimental correlation function 1 s after the shear cessation. It compares the case $\gamma = 0$ with $\gamma = 5.9\%$. Notice that when a shear has been applied the decay is faster at short times and becomes slower at long times. The reference and the perturbed curves can then cross each other. The inset shows $C(t_w + t, t_w)$ calculated at 0.1 tu after the temperature step. It compares the case $\Delta T = 0$ with $\Delta T = \frac{1}{3} T_g$. The modification in $P(E, t_w)$ due to the step temperature is reflected in the change of the correlation shape: the decrease is quicker at short times (overpopulated low energies) and slower at long times (overpopulated high energies). We observe an excellent qualitative agreement between the two sets of curves. This agreement is reinforced by Fig. 4(b), which shows the calculated $\tau_{1/2}$ for different ΔT. The calculated $\tau_{1/2}$ are defined so that $C(t_w + \tau_{1/2}, t_w) = 0.5$. Figure 4(b) is qualitatively similar to Fig. 2(c).

We can now define properly *over-aging*. It is the fact that the long time tail of the relaxation times distribution is overpopulated when a solicitation is applied during aging, as compared to the case without any solicitation. We point out that this phenomenon of over-aging in the trap model is robust for parameter changes. Notice that recent simulations [13] on Anderson's model for spin glasses show qualitatively the same results for the correlation functions with a positive temperature step. Finally, we emphasize the fact that the change in the correlation function shape that reflects the change in the relaxation time distribution corresponds to over-aging when the long time decay is slower after a solicitation than before. Moreover, we expect that our measurement will provide an accurate selectivity on the models coupling mechanics and thermal aging, but a more precise analysis with the existent models is beyond the scope of this Letter.

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