

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 sample have been submitted to various straining. We show that high shear rejuvenates the system and accelerates its dynamics whereas moderate shear overage the system. We analyze this 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 phenomena is called aging. The out-of-equilibrium nature of these systems compels their physical properties to depend on two times as shown both by 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 to obtain reproducible results. The most common way to control the history as the age of the system 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 erased the memory for these systems and thus 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 phenomenon [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 non trivial shear effects on a dense solution of polybeads. We show that these 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 rejuvenate completely the system, one could imagine that it shuffles the beads arrangements. The resulting configurations could be less stable. The dynamics of rearrangements would be then 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 non-crystalline, configurations. The dynamics would be then 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 $\varphi = 49\%$. 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 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 $\langle \dots \rangle$ 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 in 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 piezoelectric device. Shear strain from 30% to 0.04% could be possibly applied at a fixed frequency of 1Hz. 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 the 10 experiments. The reproducibility was checked 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. Fig 1a 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 $t \ll 5.10^{-2} s$, 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 β mode. This fast mode is not affected by shear as predicted by 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 pseudo plateau region is all the slower as the system is elder. 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 $g_2(t_w + \tau_{1/2}, t_w) - 1 = 0.06$. Fig 1b shows that $\tau_{1/2} \propto t_w^{1.06 \pm 0.08}$ for $t_w > 1s$. 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 aging process and is qualitatively similar to that found for rheology of such systems [2][3][10].

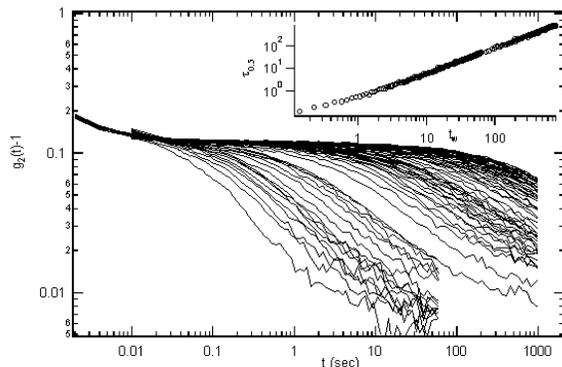


FIG. 1: The intensity autocorrelation function $g_2(t_w + t, t_w) - 1$ for different t_w ranging from 0.5 s to 10^3 s. The first decrease at short times comes from the tail of the β relaxation. The long term decrease is due to the structural relaxation. The insert shows $\tau_{1/2}$ in seconds vs t_w . $\tau_{1/2}$ scales as $t_w^{1.06 \pm 0.08}$

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 2a. The sample is first submitted to an oscillatory strain of amplitude 30% at 1Hz during 40 s in order to rejuvenate it totally. Secondly, we let it age at rest for 10s. Then, a second burst of 1Hz 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.

Fig 2b -resp fig 2c- displays the relaxation time $\tau_{1/2}$ as a function of t_w for different strain amplitudes, with $t_d=1s$ -resp $t_d=100s$. Two limit cases can be considered: that of a complete rejuvenation during the second burst -corresponding to the reference curve of fig1- and that of $\gamma = 0\%$ where the system is unperturbed during the second burst. That last curve is the same than the completely rejuvenated one but shifted in time by $t_s = 10s + t_d$. These two limit curves merge at long time because of the log scale. For a duration of the second burst $t_d=1s$ -fig 2b- we observe that the effect of the second burst 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, one might expect that the amplitude is not the only relevant parameter, but the duration of the shear application has to play a role. Indeed, if the system is left longer under shear, the modification of its dynamic is then dual. When $t_d = 100s$ -fig 2c-, 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 *overaging*. For large strain amplitudes a total rejuvenation is recovered as exemplified by the curve for $\gamma = 11.7\%$ in fig 2c. This experiment demonstrates that a moderate shear can perturb the dynamical properties of the system in a non-trivial way.

This is contradictory with the simple idea that strain or stress simply 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 2c: 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 4a. 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 remark that microscopic aging models including shear in their equations tackles the problem of the modification of the dynamics under

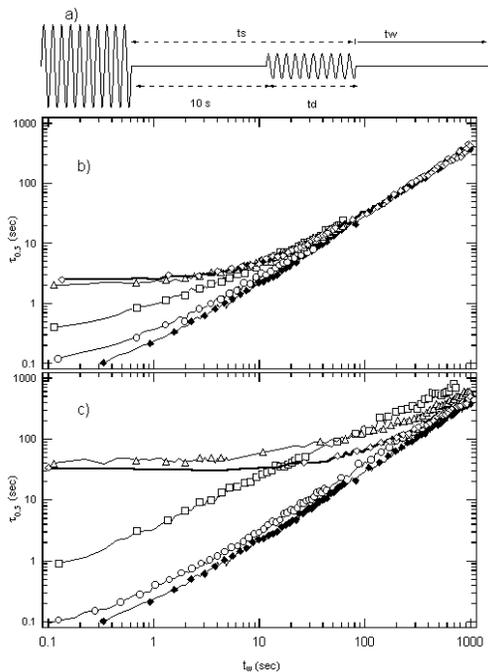


FIG. 2: a) Strain history. b) $\tau_{1/2}$ for $t_s = 11s$ and different strain amplitudes $\gamma = 0\%$ (Diamond), 2.9% (Δ), 7.9% (\square), 11.7% (O) and the reference curve (\blacklozenge). $\tau_{1/2}$ decreases monotonically with the strain amplitude at short times. for $t_w \sim t_s$ all curves merge. c) $\tau_{1/2}$ for $t_s = 110s$ 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.

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 future work [12].

However, we point out here, the similarity of overaging after a transient shear stress and that predicted by the trap model [6] after a temperature step. We thus introduce in this model the oscillatory straining as a change of temperature. This model describes the motion of non interacting particles hopping in an energy landscape with wells of depth E . The distribution of the wells 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 writes:

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

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 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 equation

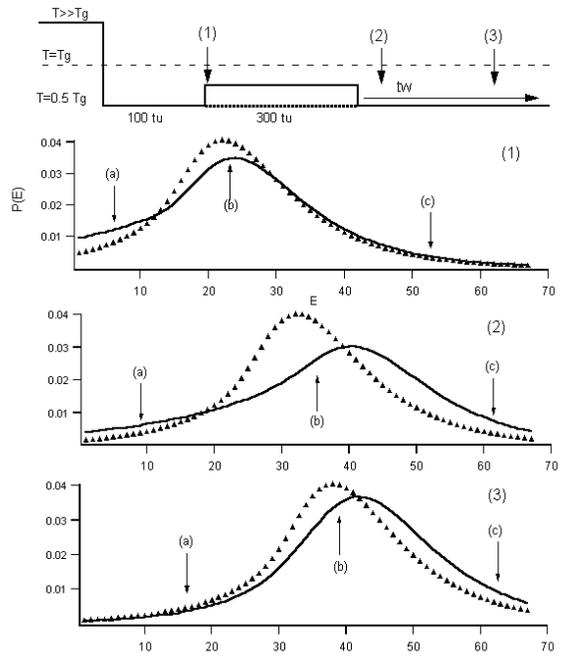


FIG. 3: a) Temperature history b) $P(E,t_w)$ vs E for various t_w . The (\blacktriangle) curve corresponds to the reference case; the full line corresponds to the case with a step ($\Delta T = \frac{1}{3} T_g$). Notice that 1 tu after the sample is reheated (1) the small energies are overpopulated, the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

1 for a quench from $T = \infty$ to $T = \frac{1}{2}T_g$. The energy distribution is presented in dotted line on fig 3b. As expected it shifts progressively with time towards deeper and deeper energy wells. The relaxation time of the system become thus 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 continuous line.

Fig 3b shows that shortly after the system is heated back (1) the small energies -arrow (a) on fig 3- are overpopulated; intermediate energies (b) are depleted and high energies (c) 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 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:

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

Fig4(a) shows the change in the shape of the experi-

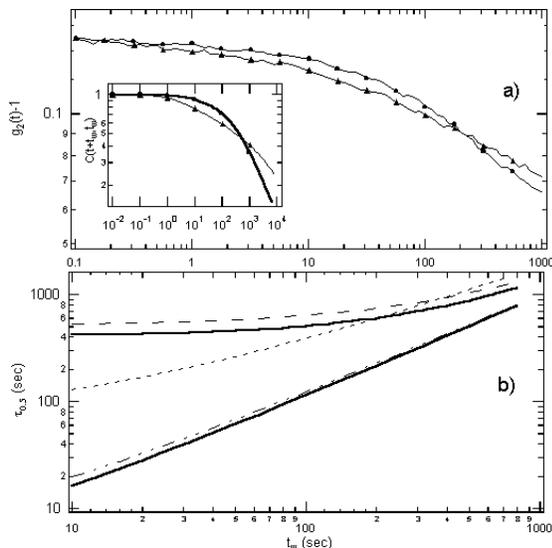


FIG. 4: a) $g_2(t_w + t, t_w) - 1$ for $t_w = 1$ for $\Delta T = 0$ (\blacklozenge) and for $\Delta T = \frac{1}{3}T_g$ (\blacktriangle). The insert shows the similar curves for $C(t_w + t, t_w)$ calculated at $t_w = 0.1$ tu. Notice that for $\Delta T = \frac{1}{3}T_g$ the curves first decrease more 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 overaging in the long time regime. Qualitative agreement with fig 2b is satisfactory.

mental correlation function 1s after the shear cessation. It compares the case $\gamma = 0$ (ref case) with $\gamma = 5.9\%$. Notice when a shear has been applied the decay is faster at short times and becomes more slowly at long times. The reference curve and the perturbed one can then cross each other. The insert shows $C(t_w + t, t_w)$ calculated at 0.1 tu after the temperature step. It compares the case $\Delta T = 0$ (ref case) 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 set of curves. This agreement is reinforced by fig 4(b) that shows the calculated $\tau_{1/2}$ for different ΔT . The calculated $\tau_{1/2}$ are defined so that $C(t_w + \tau_{1/2}, t_w) = 0.5$. Fig 4b is qualitatively similar to fig 2c. We point out that this phenomenon of overaging in the trap model is robust to parameters changes. The values presented here were chosen to obtain good looking curves but are not critical at all. Notice that recent simulations [13] on Edward Anderson's model for spin glasses, show qualitatively the same results for the correlation function with a positive temperature step. Finally, we emphasize the fact that the change in the correlation function shape reflects the change in the relaxation time distribution. We measure how this distribution is transiently modified by shear. We expect that it 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. We also point out that the qualitative agreement with temperature step in the trap model reinforce the idea that shear and temperature may play a similar role in certain glassy systems. We thank J.P.Bouchaud, E.Bertin, C.Caroli, J.Kurchan, L.Berthier for fruitful discussions. The authors thank M.Dorget for providing us with the latex beads.

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