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Dichotomic aging behaviour in a colloidal glass

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Roberta Angelini,*[ab] Laura Zulian,[b] Andrei Fluerasu,[c] Anders Madsen,[d] Giancarlo Ruocco[be] and Barbara Ruzicka[ab]

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An unexpected dichotomic long time aging behaviour is observed in a glassy colloidal clay suspension investigated by X-ray photon correlation spectroscopy and dynamic light scattering. In the long time aging regime the intensity autocorrelations are non-exponential, following the Kohlrausch–Williams–Watts functional form with an exponent β_Q. We show that for spontaneously aged samples a stretched behaviour ($\beta_Q < 1$) is always found. Surprisingly a compressed exponent ($\beta_Q > 1$) appears only when the system is rejuvenated by application of a shear field. In both cases the relaxation times scale as Q^{-1}. These observations shed light on the origin of compressed exponential behaviour and help in classifying previous results in the literature on anomalous dynamics.

The continuous interest in studying dynamics of colloidal systems has over the last decade led to a broadening of our knowledge on dynamical arrest and glass transition. Many experiments have been performed on colloidal glasses[1] and gels[2,3] as well as theoretical and numerical simulations[4,5] aiming at understanding the nature of the aging phenomena that are typical for systems with time evolving dynamics. Studying the time evolution of the dynamic structure factor is the most direct way to access microscopic information on aging. It allows to obtain the characteristic times of the system (relaxation times) as well as their distribution (β_Q exponent, as described below).

The commonly accepted physical picture in a disordered, glass-like material is that the motion of a particle is constrained by the cage of its neighbors resulting in the emergence of different relaxation times – *e.g.* related to the motion inside the cage, rearrangements of cages, *etc.* In order to fit the decay of the intensity correlation functions over a wide time window, the Kohlrausch–Williams–Watts expression is generally used $f(Q, t) \sim \exp[-(t/\tau_Q)^{\beta_Q}]$ where τ_Q is an "effective" relaxation time and β_Q measures the distribution of relaxation times (associated with simple exponential decays). Most commonly, the different relaxation times present in glassy materials lead to a stretching of the correlation functions and an exponent $\beta_Q < 1$ (which here is referred to as "stretched behaviour").

In contrast, the pioneering work of Cipelletti *et al.*[6] on a gel of colloidal polystyrene has shown the existence of anomalous dynamics. A peculiar aging behavior has been identified with exponential growth of the characteristic relaxation times at early ages t_w and an almost linear trend at larger t_w ($\tau_Q \sim t_w^{\alpha}$ with $\alpha = 0.9 \pm 0.1$). Moreover, $\tau_Q \sim Q^{-1}$ with $\beta_Q > 1$ (compressed behaviour) is found. This unusual dynamics has been attributed to the relaxation of internal stresses.[7]

More recently, this novel anomalous dynamics, fully investigated through X-ray Photon Correlation Spectroscopy (XPCS) in a wide wave vector region, has been recognized as a salient feature of disordered arrested materials ranging from glassy polymers and supercooled molecular liquids to soft matter systems.[8,9] Among these, a colloidal clay (Laponite) has recently emerged as a complex fluid system characterized by peculiar aging dynamics.[10–13]

The Dynamic Light Scattering (DLS) work of Bellour *et al.*[10] on Laponite reports an exponential increase of τ_Q at small t_w and a power law behaviour with $\alpha = 1.0 \pm 0.1$ accompanied by $\beta_Q > 1$ at larger t_w, in agreement with ref. 6. Multi-speckle XPCS measurements performed by Bandyopadhyay *et al.*[11] on Laponite suspensions showed hyper-diffusive dynamics ($\beta_Q > 1$, $\tau \sim Q^{-1}$) and a power law behaviour of the relaxation time $\tau_Q \sim t_w^{\alpha}$ with $\alpha = 1.8 \pm 0.2$ in the large t_w range. Subsequently, Tanaka *et al.*[12] classified these two distinct dynamical aging regimes as cage-forming at small t_w and full aging at larger t_w. Finally, Schosseler *et al.*[13] confirmed the existence of these two dynamical regimes reporting that the crossover between them depends on wave vector and that the full aging is characterized by $\alpha = 1.04 \pm 0.06$ and $\beta_Q > 1$.

[a]*CNR-IPCF, I-00185 Rome, Italy. E-mail: roberta.angelini@roma1.infn.it; Fax: +39 064463158; Tel: +39 0649913433*

[b]*Dipartimento di Fisica, Sapienza Università di Roma, I-00185, Italy*

[c]*Brookhaven National Laboratory, NSLS-II Upton, NY 11973, USA*

[d]*European X-Ray Free-Electron Laser, Albert-Einstein-Ring 19, D-22761 Hamburg, Germany*

[e]*Istituto Italiano di Tecnologie, Center for Life Nano Science, Sapienza, Rome, Italy*

In summary, all the papers discussed above agree on the existence of two regimes: at small t_w an exponential aging regime with $\tau_Q \sim \exp(t_w/(s))$ and at larger t_w a full aging regime with $\tau_Q \sim {t_w}^{\alpha}$ and $1 < \alpha < 2$.

In this Communication we use XPCS and DLS to investigate the aging dynamics of a colloidal system – Laponite suspensions – in the glassy state[14] at weight concentration $C_w = 3.0\%$. The dynamical behaviour of spontaneously aged samples has been compared to that of samples rejuvenated by the application of a shear field after the glass formation. For spontaneously aged samples a stretched behaviour with $\beta_Q < 1$ is found in both aging regimes. Only rejuvenated samples show a compressed behaviour with $\beta_Q > 1$. The rejuvenation process, *i.e.* the application of shear, allows to pass from a slower (stretched) to a faster (compressed) than exponential behaviour. In both cases for long waiting times the relaxation times scale as $\tau_Q \sim Q^{-1}$. These results provide further insights into the topic of anomalous dynamics in soft materials, permitting also to extrapolate analogies with structural glasses.[15]

XPCS measurements were performed at the ID10A beamline at the European Synchrotron Radiation Facility (ESRF) in Grenoble using a partially coherent X-ray beam with a photon energy of 8 keV. A series of scattering images were recorded by using a charged coupled device (CCD) and the ensemble averaged intensity autocorrelation function $g_2(Q,t) = \frac{\langle\langle I(Q,t_0)I(Q,t_0+t)\rangle_p\rangle}{\langle\langle I(Q,t_0)\rangle_p\rangle^2}$, where $\langle\ldots\rangle_p$ is the ensemble average over the detector pixels mapping onto a single Q value and $\langle\ldots\rangle$ is the temporal average over t_0, was calculated by using a standard multiple τ algorithm.[8,9] To explore fast time scales ($t = 10^{-6}$ – 1 s), XPCS data were complemented by DLS measurements performed at the ESRF light scattering laboratory equipped with a Nd–YAG diode pumped laser (532 nm wavelength and 30 mW power), an avalanche photodiode and a logarithmic ALV auto-correlator. The DLS measurements were performed at a scattering angle $\theta = 90°$ which corresponds to a momentum transfer $Q = 0.022$ nm^{-1}. The combination of XPCS and DLS permits to investigate exactly the same sample over a wide range of Q, correlation times t and waiting times t_w.

The samples, Laponite RD dispersions at weight concentration $C_w = 3.0\%$, were prepared using the same protocol described in ref. 16 which produces reliable and reproducible samples. They were prepared and sealed in a glovebox under N_2 flux to prevent CO_2 degradation. The powder, manufactured by Laporte Ltd., was dispersed in pure deionized water, stirred vigorously for 30 min, and filtered soon after through 0.45 μm pore size Millipore filters. When dispersed in water Laponite develops a charged colloidal suspension of disks of 25 nm diameter and 0.9 nm thickness usually considered monodisperse although a grade of polydispersity has been found by different authors.[17,18] The origin of the waiting time ($t_w = 0$) is the time at which the suspension is filtered. Samples were placed and sealed in glass capillaries with a diameter of 2 mm used for both XPCS and DLS measurements.

In Fig. 1 the relaxation time τ_Q is reported as a function of waiting time for a sample of $C_w = 3.0\%$. We distinguish two different aging regimes in two distinct ranges of aging times and for two Q vectors: an exponential growth of the relaxation times at early times t_w measured by DLS at $Q = 0.022$ nm^{-1} and a power law behaviour at larger t_w investigated by XPCS at $Q = 0.10$ nm^{-1}. These results are compatible with the studies discussed in the Introduction where a transition between exponential and power law behaviours has been observed. At low t_w the DLS data (squares) have been obtained through the standard fitting procedure which identifies a fast (almost age independent) and a slow (strongly age dependent) relaxation time.[19] For these early ages, the slow relaxation time τ_Q grows as $\tau_Q \sim \exp(t_w/(s))$, in agreement with other light scattering studies.[6,10,13,19] For larger t_w the fast relaxation time remains out of the XPCS detection window, while the slow relaxation time enters in the XPCS window at $t_w \sim 3 \times 10^4$ s. XPCS measurements (full circles) at $Q = 0.10$ nm^{-1} show a behaviour like $\tau_Q \sim {t_w}^{\alpha}$ with $\alpha = 0.94 \pm 0.07$. They are in good agreement with XPCS measurements performed by Bandyopadhyay *et al.*[11] at $Q = 0.14$ nm^{-1} and at the same concentration (empty circles).

Fig. 2 shows, as an example, the intensity autocorrelation functions of a Laponite sample at weight concentration $C_w = 3.0\%$, after a waiting time $t_w = 1.71 \times 10^5$ s and at different Q values. For all the aging times and Q the XPCS data are well described by the fitting expression:

$$g_2(Q,\ t) = b\left[\left(A e^{-\left(t/\tau_Q\right)^{\beta_Q}}\right)^2 + 1\right] \quad (1)$$

where bA^2 represents the contrast, τ_Q the relaxation time and β_Q the Kohlrausch exponent. The latter two parameters characterize the microscopic dynamics of the sample. The fits are shown as full lines in Fig. 2. The relaxation time τ_Q *vs.* Q, shown in the inset of Fig. 2, displays a $\tau_Q \sim Q^{-1}$ behaviour which is signature of non-free diffusive dynamics. The exponent β_Q is plotted *vs.* Q in the inset of Fig. 2. Its values are always well below 1 for all the

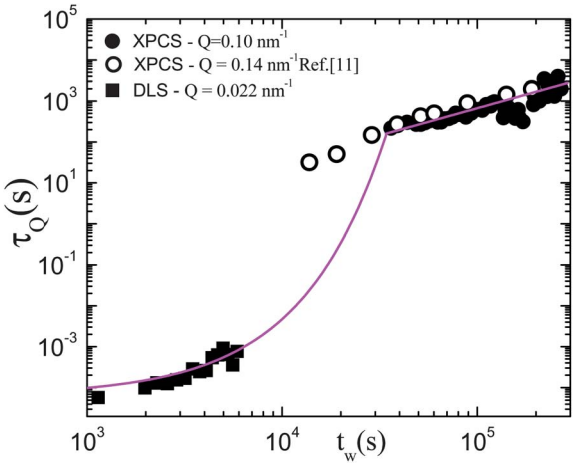

Fig. 1 Relaxation time as a function of the waiting time for an aqueous Laponite suspension at concentration $C_w = 3.0\%$ as measured by DLS at $Q = 0.022$ nm^{-1} (full squares) and XPCS at $Q = 0.10$ nm^{-1} (full circles). The data are compared with XPCS measurements by Bandyopadhyay *et al.*[11] at the same concentration (empty circles). The full lines represent the best fits with an exponential and a power law behaviour at small and large t_w, respectively.

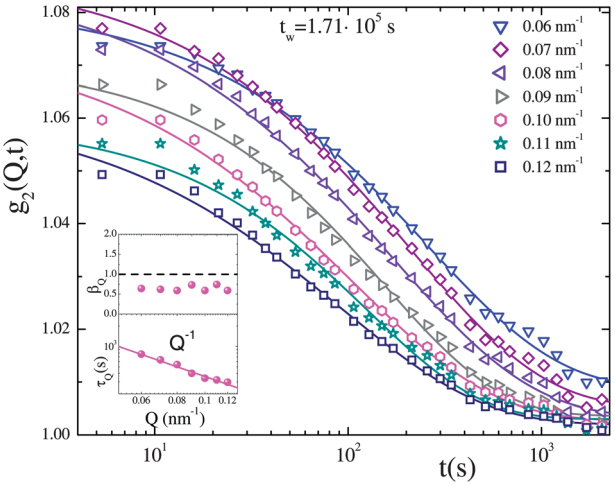

Fig. 2 Intensity autocorrelation functions of an aqueous Laponite suspension at concentration $C_w = 3.0\%$, at waiting time $t_w = 1.71 \times 10^5$ s and at different Q values obtained by XPCS (symbols). The solid lines represent the best fits performed using eqn (1). Insets: β_Q and τ_Q obtained from eqn (1) as a function of Q. The full line in the inset of τ_Q represents a fit with a power law.

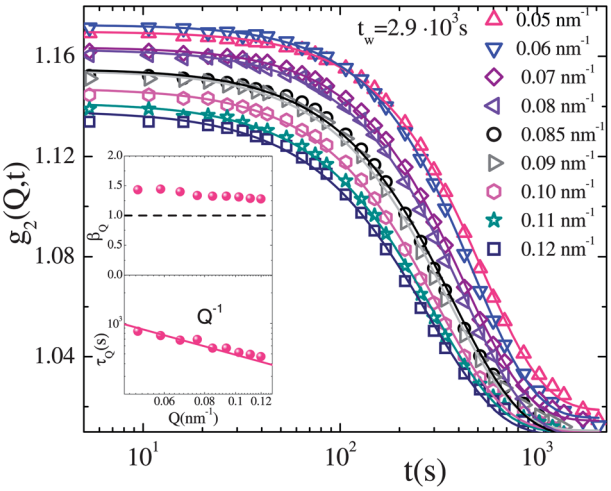

Fig. 4 Intensity autocorrelation functions of a rejuvenated aqueous Laponite suspension ($t_R \sim 3.5$ days) at concentration $C_w = 3.0\%$, at waiting time $t_w = 2.9 \times 10^3$ s and at different Q values obtained through XPCS (symbols). The solid lines represent the best fits performed using eqn (1). Insets: β_Q and τ_Q from eqn (1) as a function of Q. The full line in the inset of τ_Q represents a fit with a power law.

investigated Q and at all the investigated waiting times, as shown in Fig. 3 for $Q = 0.10$ nm^{-1}, indicating a stretched exponential behaviour. This marks an important difference with respect to previous studies of Laponite where compressed relaxations were always observed in the full aging regime.

In summary, our measurements on spontaneously aged samples confirm the well established exponential to power law crossover at increasing waiting time but in addition two new important observations are made: (i) in contrast to previous studies, a stretched behaviour ($\beta_Q < 1$) is also found in the long time regime and (ii) in the full aging regime a ballistic-type behaviour ($\tau_Q \sim Q^{-1}$) is observed together with stretched intensity correlation functions. The $1/Q$ dependence of τ associated with a stretched exponential for the correlation functions is a surprising behavior that calls for theoretical explanations and further experimental studies on different systems. Furthermore these findings are in agreement with theoretical[20] and numerical[21] results on supercooled liquids where the decreasing temperature plays the same role as an increasing waiting time in our system.[22]

In order to reconcile our findings with the previous observations on Laponite, we note that in ref. 10 and 13 the measurements in the full aging regime were performed after the sample, taken from a stock solution, was injected into the sample container by using a syringe, thus applying a shear field to an aged sample. Therefore we decided to study the aging dynamics of a sample rejuvenated by a shear field which corresponds to returning it to earlier aging times. The rejuvenation process never rewinds the sample to the original as prepared one, in particular it has been observed that the dynamical properties of Laponite strongly depend on the time elapsed before rejuvenation.[23] Concerning the structural properties we have verified that the static structure factors of both spontaneously aged and rejuvenated samples are those typical of a glassy Laponite sample.[14] The rejuvenation time t_R is the time elapsed between sample preparation and application of a shear with a syringe on the arrested sample. For these rejuvenated samples the origin of the waiting time $t_w = 0$ is the moment of application of the shear. In Fig. 4 intensity autocorrelation functions of a $C_w = 3.0\%$ sample rejuvenated at

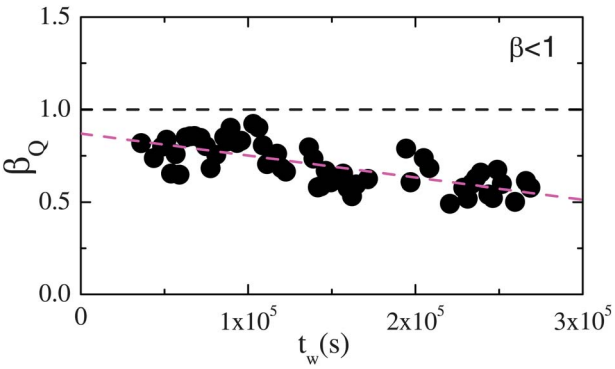

Fig. 3 β_Q from eqn (1) as a function of waiting time for an aqueous Laponite suspension at concentration $C_w = 3.0\%$ and $Q = 0.10$ nm^{-1}.

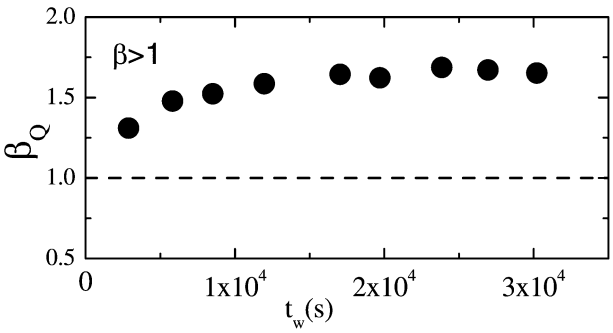

Fig. 5 β_Q from eqn (1) as a function of the waiting time for an aqueous Laponite suspension at concentration $C_w = 3.0\%$ and $Q = 0.10$ nm^{-1} rejuvenated at $t_R \sim 3.5$ days.

$t_R \sim 3.5$ days are shown. The data, in the Q-range between 0.05 nm^{-1} and 0.12 nm^{-1}, are well described by the fitting expression of eqn (1) and the fits are plotted as full lines in Fig. 4. The varying contrast with respect to Fig. 2 suggests that the fast dynamics which is not captured by the XPCS measurements,[24,25] probably, is different for rejuvenated and spontaneously aged samples. The relaxation time τ_Q *vs.* Q, shown in the inset of Fig. 4, still carries the $\tau_Q \sim Q^{-1}$ signature of non-free diffusive dynamics.[8,9] The exponent β_Q *vs.* Q is reported in the inset of Fig. 4 and surprisingly its values are now always above 1 for all the investigated Q values and for all the investigated waiting times, as shown in Fig. 5 for $Q =$ 0.10 nm^{-1}. This is markedly different from the dynamics of the spontaneously aged sample that is always stretched ($\beta_Q < 1$ – Fig. 3).

The compressed exponential behaviour of the intensity autocorrelation functions on the rejuvenated sample is in agreement with the aforementioned experiments on Laponite suspensions.[10,11,13] This similar behaviour indicates that probably the samples of ref. 10, 11 and 13 have been prepared in a way that makes them equivalent to rejuvenated ones.[26]

In the case of rejuvenated samples the shear applied by using the syringe induces internal stresses responsible for the compressed exponential relaxations in agreement with several models explaining this type of phenomenology in aging soft materials: both a heuristic interpretation[6] and a microscopic model[27] underline the importance of internal stresses in these complex systems. In particular ref. 7 proposes that the unusual slow dynamics are due to the relaxation of internal stresses, built into the sample at the transition to the arrested state. An analogous interpretation can be hypothesized for most disordered systems where internal stresses are induced by a quench from the fluid to the glassy state. Recently, this has been experimentally observed for a metallic structural glass[15] where the compressed behaviour was attributed to internal stress relaxations. In this context, our experiment has shed new light on this topic, showing that the same system can feature either stretched or compressed exponential relaxations, depending on whether it is spontaneously aged or rejuvenated. In this case the internal stresses are induced in the rejuvenated sample by shear (applied by the syringe) which plays the same role as temperature quenching does in structural glasses.

In conclusion, through XPCS and DLS measurements, we have found that spontaneously aged colloidal suspensions of Laponite at high concentration $C_w = 3.0\%$ are always characterized by a stretched behaviour ($\beta_Q < 1$) of the time correlation functions both in the cage-forming and in the full aging regimes. A compressed behaviour ($\beta_Q > 1$) is found for the same sample but only after rejuvenation. In both cases the relaxation times scale as Q^{-1} in the full aging regime. These results, addressing the general topic of anomalous dynamics in soft materials, evidence novel dichotomic stretched/compressed dynamics in a colloidal glass. The rejuvenation process, *i.e.* the application of shear, allows to pass from a slower to a faster than exponential decay. The clear correlation between rejuvenation by shear and the occurrence of compressed exponential behaviour will help in classifying past and future experimental observations and connect with simulation studies and theoretical work.

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