Aging dynamics and spontaneous glass-glass transition in a colloidal clay

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Soft materials have long been the subject of intense research, thanks to their unusual and unexpected behaviours, they offer the possibility to observe new phases and states besides the ones commonly experienced in atomic or molecular systems. Most of these materials are out of thermodynamical equilibrium and present a continuous evolution of the mechanical and dynamical properties (aging). Measuring the time evolution of the dynamic structure factor is the most direct way to access microscopic information on aging. It allows extracting the characteristic times of the system by fitting the decay of the intensity correlation functions through the Kohlrausch-Williams-Watts expression $f(Q,t) \sim exp[-(t/\tau)^{\beta}]$ where τ is an "effective" relaxation time and β 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 $\beta < 1$ which is referred as "stretched behavior". On the contrary, an exponent $\beta > 1$ (compressed behavior) is associated to an anomalous dynamics recognized as a novel salient feature of disordered arrested materials among these, colloidal clays. Here we study the aging dynamics of a colloidal clay and we show that a stretched behavior ($\beta < 1$) is always found for spontaneously aged samples and a compressed exponent ($\beta > 1$) appears only when the system is rejuvenated by the application of a shear field after a critical aging time [1, 2] and in both cases the relaxation times scale as Q^{-1} [2, 3]. These differences are also reflected in the correlation lengths of spontaneously aged and rejuvenated samples [4]. Moreover through a combination of X-ray Photon Correlation Spectroscopy, Small Angle X-ray Scattering (SAXS), dilution experiments, rheological measurements and Monte Carlo (MC) simulations we found the existence of two different behaviours below and above t_c in the dynamical properties of the system indicating a spontaneous glass-glass transition taking place during aging [1]. Two different glassy states are distinguished with evolving waiting time: a first one, occurring at the arrest transition (after a waiting of the order of hours), is dominated by long range screened Coulombic repulsion (Wigner glass) and a second one, previously unreported and stabilized by orientational attractions between clay platelets (Disconnected House of Cards (DHOC) glass) is found at much longer waiting times (of the order of days). The present system offers therefore an overview of various dynamical behaviours previously observed in different systems and the possibility to pass from one to the other choosing ad hoc the time parameter [5]. Finally these findings may have relevance for applications where a fine control of the local order and/or long term stability of amorphous materials are required.

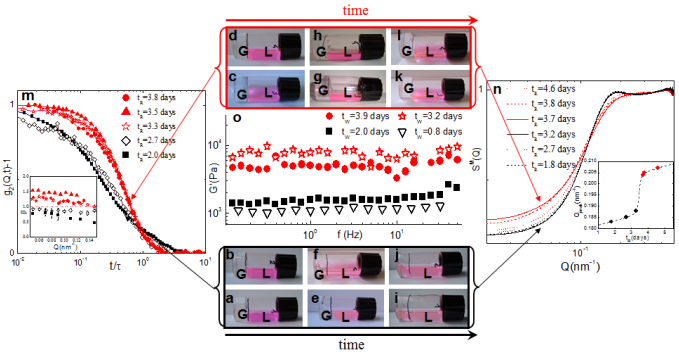

FIG. 1. (a-l) Photographic time sequence of a dilution experiment for Laponite suspensions. (m) XPCS intensity autocorrelation functions for rejuvenated aqueous Laponite suspensions at different rejuvenation times t_R. In the inset, the β exponent is shown as a function of Q. (n) Static structure factor for rejuvenated aqueous Laponite suspensions at different rejuvenation times t_R. In the inset, the peak position as a function of the rejuvenation time t_R shows a transition between two different structures. (o) Frequency dependence of the elastic modulus G' at different waiting times t_w.

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[1] R. Angelini, E. Zaccarelli, F. A. de Melo Marques, M. Sztucki, A. Fluerasu, G. Ruocco and B. Ruzicka. Glass-glass transition during aging of a colloidal clay. *Nature Communications* **5**, 4049 (2014).

[2] R. Angelini, L. Zulian, A. Fluerasu, A. Madsen, G. Ruocco and B. Ruzicka. Dichotomic aging behaviour in a colloidal glass. *Soft Matter* **9**, 10955 (2013).

[3] F. A. de Melo Marques, R. Angelini, E. Zaccarelli, B. Farago, B. Ruta, G. Ruocco and B. Ruzicka. Structural and microscopic relaxations in a colloidal glass. *Soft Matter* **11** 466-471 (2015).

[4] R. Angelini, A. Madsen, A. Fluerasu, G. Rocco and B. Ruzicka. Aging behavior of the localization length in a colloidal glass. *Colloids and Surface A* **460**, 118-122 (2014).

[5] R. Angelini and B. Ruzicka. Non-diffusive dynamics in a colloidal glass: Aging versus rejuvenation. *Colloids and Surface A* **483**, 316-320 (2015).