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Aging behavior of the localization length in a colloidal glass

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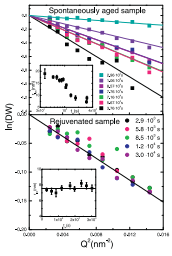
HIGHLIGHTS

- X-ray photon correlation measurements in Laponite glassy samples.
- Debye–Waller analysis of the non-ergodicity parameter.
- Determination of the localization length associated with the fast relaxation.
- Different localization length behavior in spontaneously aged and rejuvenated samples.
- Comparison between calculated and measured shear modulus.

GRAPHICAL ABSTRACT



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ABSTRACT

The localization length r_{loc} associated with a fast secondary relaxation in glassy Laponite is determined by X-ray photon correlation spectroscopy (XPCS) through a Debye–Waller fit of the non-ergodicity parameter. Quantitative differences are observed between the time dependence (aging) of r_{loc} in spontaneously aged and rejuvenated samples. This behavior is also reflected in the calculated shear modulus which matches well with data obtained by rheological measurements.

1. Introduction

Colloidal suspensions are very versatile systems for the study of aging dynamics towards arrested states. By changing parameters like ionic strength and particle concentrations, they offer the possibility of exploring for instance gels [1,2] and glasses [3,4] in a systematic way. These systems are typically characterized by two relaxation processes: a fast microscopic relaxation that is slightly age dependent and a slow structural relaxation which changes with age. The most direct way of accessing microscopic information about the aging process is to study the time evolution of the dynamic structure factor. This allows to extract the characteristic times of the system (relaxation times) as well as their distributions (β_Q exponent – see description of the fitting procedure further below). For this purpose, dynamic light scattering (DLS) and X-ray photon correlation spectroscopy (XPCS) are the most suitable techniques which enable to explore a large range of time and length scales (set by the momentum transfer Q).

Here we report XPCS measurements on a charged colloidal system, Laponite. This colloidal clay is characterized by a complex phase diagram with multiple arrested states depending on clay and salt concentrations. In salt free water, two types of arrested states, an equilibrium gel [5] and a Wigner glass [6] can be distinguished at weight concentration intervals $1.0 \leq C_w < 2.0\%$ and $2.0 \leq C_w \leq 3.0\%$, respectively. Here, we focus on the glassy state at $C_w = 3.0\%$

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where a very recent XPCS study [7] reported a dichotomic long time aging behavior of the correlation functions: stretched ($\beta_Q < 1$) for spontaneously aged samples and compressed ($\beta_Q > 1$) for rejuvenated ones. Supposedly, shear applied by the syringe induces internal stresses that are responsible for the compressed behavior of the rejuvenated sample. In the aforementioned study the fast relaxation time could not be accessed directly because it falls outside the detection window accessible by XPCS. Therefore, in order to address this point we perform in the present work a new specific analysis. We find that the fast dynamics display different aging behaviors for the spontaneously aged and the rejuvenated samples. Specifically, the aging dependence of the Debye–Waller factor and of the localization length r_{loc} is different in the two cases and mimics the difference between the slow dynamics found earlier [7]. The difference is further elucidated by calculating the elastic shear modulus G_g' obtained through r_{loc} and the static structure factor by applying the standard Green–Kubo relation with a factorization approximation [8–10].

2. Materials and methods

2.1. Materials

Laponite is a synthetic clay that, when dispersed in water, forms a charged colloidal suspension of platelets with 25 nm diameter and 0.9 nm thickness and inhomogeneous charge distribution, negative on the faces and positive on the rims. The platelets are usually considered monodisperse in size but a small polydispersity has been reported by different authors [11,12].

Aqueous dispersions of Laponite RD with weight concentrations $C_w = 3.0\%$ were prepared according to the protocol described in [13] ensuring reliable and reproducible samples. The entire preparation process takes place in a glovebox under N_2 flux to prevent CO_2 degradation [14]. Laponite powder, manufactured by Laporte Ltd., is dispersed in pure deionized water, stirred vigorously for 30 min, and filtered soon thereafter through a 0.45 μm pore size Millipore filter. A part of the solution is directly filtered in glass capillaries of 2 mm diameter for the experiments. These are later referred to as "spontaneously aged" samples. The origin of the waiting time ($t_w = 0$) determines the age of the sample and for the spontaneously aged samples it is the time at which the suspension is filtered. Rejuvenated samples are prepared from the stock solution that had rested some time t_R (rejuvenation time) since filtration. The age t_w of a rejuvenated sample is counted from t_R, i.e. the time at which it was taken from the stock and injected into the capillary by a syringe, hence introducing a huge shear field (shear rejuvenation).

2.2. Measurements

The samples were characterized by X-ray photon correlation spectroscopy (XPCS) [15,16] at beamline ID10A of the European Synchrotron Radiation Facility (ESRF) in Grenoble. For the measurements a partially coherent and monochromatic X-ray beam with a photon energy of 8 keV was employed. Long series of scattering images were recorded by a charged coupled device (CCD) placed in the forward scattering direction. The images were post processed following the multi-speckle XPCS approach [15] to get access to the dynamics of the samples. Ensemble averaged intensity autocorrelation functions $g_2(Q,t) = \langle \frac{\langle I(Q,t_0)I(Q,t_0+t)\rangle_p}{\langle I(Q,t_0)\rangle_p \langle I(Q,t_0+t)\rangle_p} \rangle_{t_0}$ were calculated using a standard multi-tau algorithm. Here, $\langle \cdots \rangle_p$ indicates averaging over pixels of the detector mapping onto a single value of the momentum transfer (Q) while $\langle \cdots \rangle_{t_0}$ indicates temporal averaging over t_0.

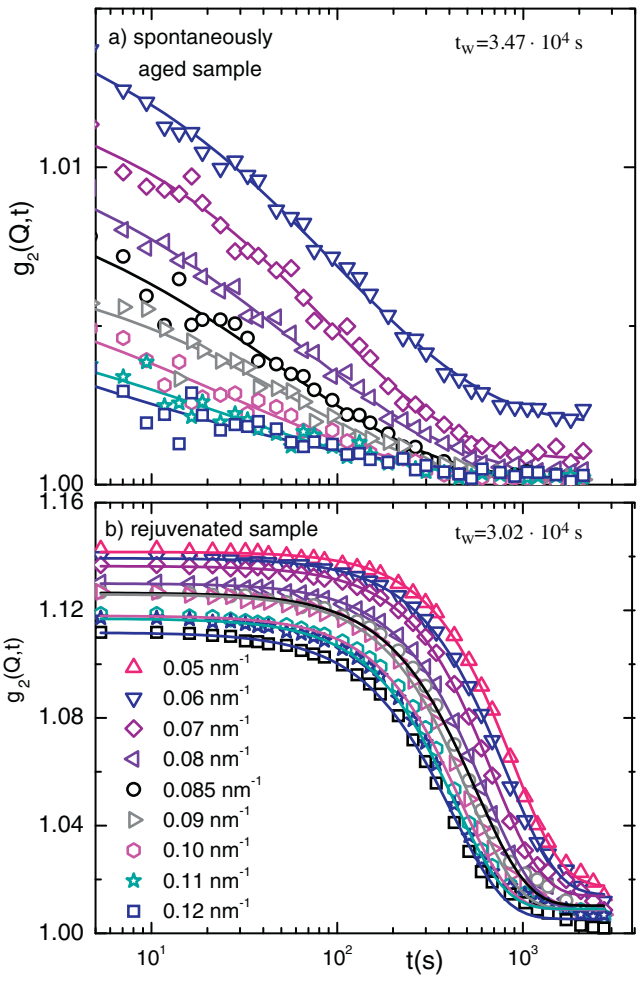

Fig. 1. Intensity autocorrelation functions of aqueous Laponite suspensions (C_w = 3.0%) at different Q values (symbols) for (a) a spontaneously aged sample at $t_w = 3.47 \times 10^4$ s, and for (b) a rejuvenated sample with t_R = 3.5 days and $t_w = 3.02 \times 10^4$ s. The solid lines show the best fits performed by Eq. (1).

3. Results and discussion

Fig. 1 shows, as an example, the intensity autocorrelation functions at different Q values of Laponite suspensions that are either spontaneously aged (Fig. 1a) or rejuvenated (Fig. 1b). For both samples, and at all aging times and Q, the XPCS data are well described by the expression

$$g_2(Q,t) - 1 \propto \left(C \exp\left(-\left(\frac{t}{\tau_Q} \right)^{\beta_Q} \right) \right)^2 = C^2 |f(Q,t)|^2, \qquad (1)$$

where $f(Q, t)$ is known as the intermediate scattering function. C^2 represents the contrast, τ_Q the relaxation time and β_Q the Kohlrausch exponent. The latter two parameters characterize the dynamics of the sample. The fits with Eq. (1) are shown as full lines in Fig. 1.

The exponent β_Q obtained by the fit analysis is plotted vs Q in Fig. 2 for both spontaneously aged and rejuvenated samples. As recently reported in Ref. [7] the value of β_Q is always well below 1 for the spontaneously aged sample in the t_w and Q ranges investigated here. This means that the correlation function in Eq. (1) takes a stretched exponential form which is commonly observed for glass dynamics. For the rejuvenated sample β_Q is always above unity implying that the decay of the correlation function is faster than exponential, i.e. a so-called compressed exponential behavior is observed. This has often been found in gel [17,18] and glassy

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