



	Experiment title: Distinguish for a glass or gel phase in a charged colloidal system at low volume fraction.	Experiment number: HD1
Beamline: ID2	Date of experiment: from: 28-04-06 to: 01-05-06	Date of report: 27-02-08
Shifts: 9	Local contact(s): M. Sztucki	<i>Received at ESRF:</i>
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Report:

Light (DLS) and Small Angle X-rays Scattering (SAXS) measurements have been performed on solutions of Laponite, a synthetic clay that dispersed in water originates a charged colloidal suspension.

Laponite suspensions show aging, i.e. sample properties as measured by correlation or response function change continuously with waiting time, as the sample evolves towards equilibrium. The intriguing aging phenomenon of this system has been widely investigated varying salt and clay concentration with standard DLS technique [1,2]. The measurements have shown that the system can be found in an arrested state also at very low packing fractions. The existence of two different routes toward the final arrested state has been found for low and high clay concentrations together with the necessity to redraw Laponite phase diagram [1,2]. The mechanisms that originate the existence of two different non ergodic states are a very interesting point. Moreover, whether or not these two states correspond to really different structures and what is the nature of these arrested states were up to now open and intriguing questions.

During the experiment HD1 we investigated these two different regions to have a clear and direct evidence of their nature (if gel and/or glass) and to study how the $S(Q)$ evolves with waiting time approaching the arrested state both at low and at high volume fractions.

Several samples have been prepared under nitrogen atmosphere in order to avoid contact with air and stored in quartz capillaries of 2 mm of diameter. The aging time evolution from the initial liquid to the final arrested state occurs in a time that strongly depends on salt and clay concentrations and that increases as clay and/or salt concentrations are decreased, reaching the order of some months for low clay concentrations [2]. Because of that high concentration samples were directly prepared at ESRF and the complete evolution with waiting time was followed during the allocated beamtime, while for the low concentration samples this would have not been possible. Therefore several low concentration samples, with same nominal concentrations but physically different, have been prepared in our laboratory at different times starting several months before the

allocated beamtime so to measure different waiting times at the moment of the beamtime. Same sample has been measured at approximately same waiting time with both DLS and SAXS techniques. Light scattering measurements have been performed in DLS laboratory 03.0.03 in front of ID2 beamline on a standard dynamic light scattering setup. The incident beam of SAXS setup was fixed at the energy of 12.6 KeV in a 10m pinhole configuration.

Figure 1 shows as an example the waiting time evolution of both the auto-correlation functions (left panels) and the measured structure factors (right panels) for samples in the low and high concentration regions, at $C_w=1.9\%$ ((A) and (C) panels) and $C_w=2.8\%$ ((B) and (D) panels) respectively. The same sample was measured with the two techniques, DLS and SAXS (same lines in the left and right panels correspond to roughly same waiting time) and therefore a clear and direct comparison between the dynamic and static structure factor behaviors can be obtained.

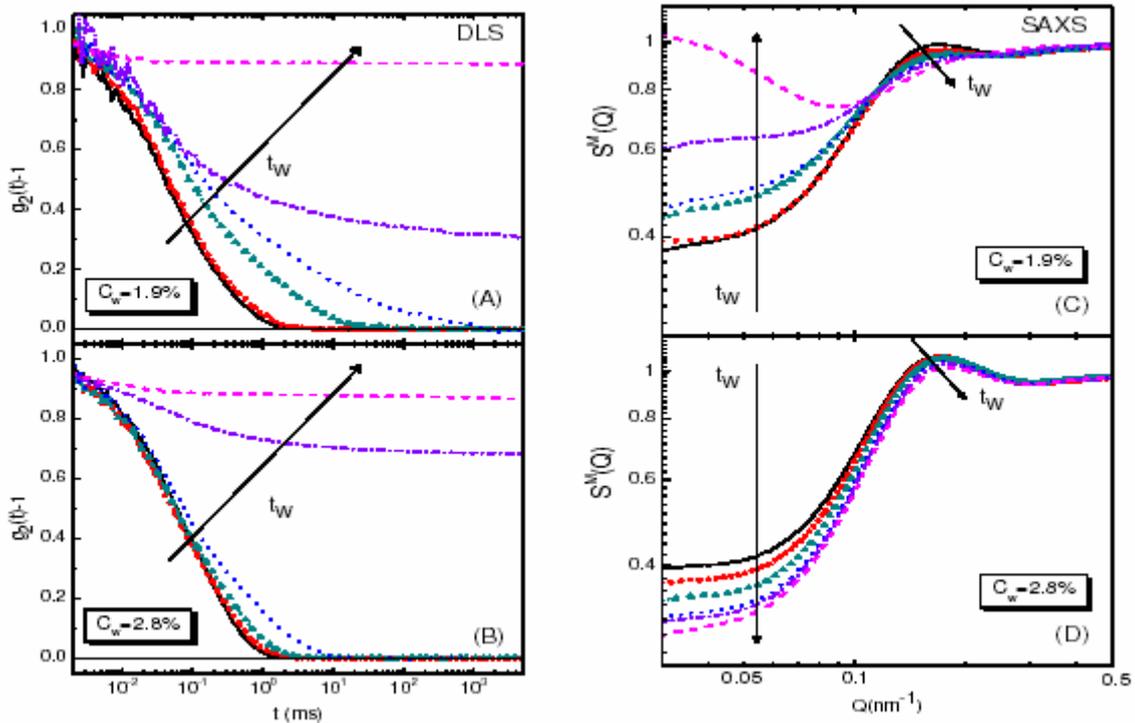


Fig.1: Evolution of the time autocorrelation functions (left panels) and of the measured structure factors (right panels) as a function of the waiting time t_w (same waiting times - same lines) for two different Laponite concentrations: a low one, $C_w = 1.9\%$ ((A) and (C) panels) and a high one, $C_w = 2.8\%$ ((B) and (D) panels).

From Fig. 1 the difference in the behavior of low and high concentration samples is striking. For the high concentration sample ((B) and (D) panels of Fig. 1) there are no significant changes in the structure factor profiles while the sample crosses the ergodic/non ergodic transition (from dot to dashdot and dash curves). As the system is performing aging there is in fact only a progressive and slow decrease in the intensity at very low Q and a very small shift of the main peak to higher Q values. On the contrary, for the low concentration sample ((A) and (C) panels of Fig. 1) there is an evident change of the static structure factor as the sample ages and approaches the non ergodic state (from dot to dashdot and dash curves) specifically a progressive increased excess of scattering is observed at low Q values. Moreover, also a change in the shape of the curve and a shift of the main peak to higher Q values can be recognized.

The results obtained with this proposal (for further details see Ref. [3]), resolve the longstanding controversy about the final arrested state in Laponite suspensions: both an inhomogeneous (gel) and a homogeneous (glass) state exist. They are reached -as the system ages- following two different dynamic routes [1,2].

Moreover this is the first experimental evidence of the evolution with waiting time of the $S(Q)$ both for a gel and a glass state obtained only by increasing volume fraction.

The existence of two different arrested states in this charged colloidal depending only on its concentration, gives a proof of the strong connection existing between the "gel" and "glass" states.

It is also worth to note that the features of the low concentration region fit with those of the newly discovered equilibrium bonding gel region [4], a state found in low density colloids with anisotropic interactions.

A common experimental and theoretical effort for the confirmation of Laponite as the first experimental evidence of an equilibrium bonding gel so as the understanding of the still puzzling liquid-gel/glass transition are needed.

[1] B. Ruzicka, L. Zulian and G. Ruocco Phys. Rev. Lett. **93**, 258301 (2004).

[2] B. Ruzicka, L. Zulian and G. Ruocco Langmuir **22**, 1106 (2006).

[3] B. Ruzicka, L. Zulian, R. Angelini, M. Sztucki, A. Moussaid and G. Ruocco PRE **77**, 20402 (2008).

[4] E. Zaccarelli J. Phys. Cond. Matt. **19**, 323101 (2007).