

## Arrested state of clay-water suspensions: Gel or glass?

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The aging of a charged colloidal system has been studied by small-angle x-ray scattering, in the exchanged momentum range  $Q=0.03\text{--}5\text{ nm}^{-1}$ , and by dynamic light scattering, at different clay concentrations ( $C_w=0.6\text{--}2.8\%$ ). The static structure factor  $S(Q)$  has been determined as a function of both aging time and concentration. This is the direct experimental evidence of the existence and evolution with aging time of two different arrested states in a single system simply obtained only by changing its volume fraction: an inhomogeneous state is reached at low concentrations, while a homogeneous one is found at high concentrations.

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In recent years, dynamical arrest in colloidal, and more generally in soft matter systems, has gained increasing attention [1]. Specifically, much effort has been devoted to clarifying the dynamical behavior at large packing fraction, where the dynamical arrest is commonly identified as a kind of glass transition. In colloids where both short-range repulsion and attraction are present, a rich phenomenology is found: a reentrant liquid-glass line, two kinds of glasses (named “attractive” and “repulsive”), and a glass-glass transition line have been predicted and experimentally observed [2]. Very recently, increasing attention has also been devoted to the arrest at much smaller densities, in what is usually called the gel region of the phase diagram [1]. Experimental and simulation [3] studies have proved that, for hard-core plus spherically symmetric pairwise attractive potentials, arrest at low density occurs only through an interrupted phase separation. More complex attraction is necessary to produce gelation in equilibrium, which occurs when the gel state is reached continuously from an ergodic phase. This happens when a long-range repulsion, induced, for example, by residual charges on the colloidal particles, is added to the short-range depletion attraction [4]. Very recently a suppression of the phase separation has also been achieved by using an anisotropic interaction potential [5]. In this scenario lowering the coordination number, i.e., the number of nearest neighbors allowed by the interaction potential, pushes the spinodal line to lower and lower packing fraction, opening up the possibility to reach very low temperatures (and hence states with extremely long bond lifetimes) without encountering phase separation. This permits the formation of an equilibrium bonding gel, i.e., a spanning network of long-living “physical” bonds at very low colloid concentrations [1].

The study of different arrested states in colloidal systems is therefore of crucial importance. In fact gels and glasses have often been viewed in a unifying framework due to unambiguous similarities in the phenomenology accompanying the transition to the kinetically arrested state. However, the limits of this unifying scenario are emerging as the matter is further investigated: a deeper comprehension of the differences and the common features of gels and glasses in colloids is necessary and there is a lively debate in the recent literature.

In Laponite suspensions—the system under investigation in the present work—nanometric-size disks form a charged

colloidal dispersion with a rich phase diagram. The competition between attractive and repulsive interactions and/or the anisotropy of the potential originates the complexity of the phase diagram and the existence of several aggregation processes. Therefore, in recent years, Laponite suspensions have been widely studied, not only for the important industrial applications [6], but especially for their peculiar experimental and theoretical properties [7–19]. The first dynamic light scattering (DLS) study [8] on this system has shown a slowing down of its dynamics (aging) as it evolves toward equilibrium. Therefore evolution with respect to waiting time from a liquid to a gel or glass state has been usually investigated for samples at clay concentration of  $C_w=3\%$  and at salt concentration of  $C_s=1\times 10^{-4}M$ . A recent complete DLS study in a wide range of clay and salt concentrations has permitted a surprising final arrested state to be defined, not only for high but also for very low clay concentrations [13], at variance with previous [7] and recent [11] proposed phase diagrams. 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 [13], reaching the order of some months for  $C_s=1\times 10^{-4}M$  and  $C_w=0.3\%$ . The differences in the aging time evolution of both the raw spectra and the parameters obtained by their analysis have also permitted two different routes to be distinguished that can lead to two final nonergodic states at low and high clay concentrations [13] (see Fig. 6 of [20]). The mechanisms that originate the existence of two different nonergodic 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 are intriguing and up to now open questions.

In this Rapid Communication, we give direct experimental evidence of the existence of two different arrested states in Laponite suspensions and of their nature. The study of the aging time evolution of both the dynamic and the static structure factors has been performed through the combination of DLS and small-angle x-ray scattering (SAXS) techniques. These measurements permit us to observe directly the evolution with aging time of the system and to distinguish between final inhomogeneous and homogeneous states, resolving the long-standing controversy about the gel or glass nature of the Laponite arrested state [10,11]. More generally, while the signature for the time evolution of a gel was

quite well known [21] this experiment gives the direct evidence of the  $S(Q)$  time evolution for two different arrested states obtained only by changing the sample's volume fraction.

Laponite suspensions were prepared in a glovebox under  $N_2$  flux and were always kept in a safe atmosphere to avoid sample degradation [22]. The powder, manufactured by Laporte Ltd., was first dried in an oven at  $T=400$  °C for 4 h and it was then dispersed in pure deionized water ( $C_s \approx 10^{-4}M$ ), stirred vigorously for 30 min, and filtered soon after through  $0.45 \mu\text{m}$  pore size Millipore filters. The identical protocol has been strictly followed for the preparation of each sample, a fundamental condition to obtain reliable and reproducible results, as also recently reported by [23]. The starting aging time ( $t_w=0$ ) is defined as the time when the suspension is filtered. Samples were placed and sealed in thin glass capillaries with a diameter of 2 mm to be used for both DLS and SAXS measurements. As already discussed, the waiting time evolution of the aging dynamics requires a few hours for high clay concentrations and months for low ones. Therefore only the aging of samples at high concentrations can be directly followed during the allocated SAXS beamtime. To investigate samples at low concentrations, nominally identical concentration samples have been prepared at different dates starting three months before the planned experiment, so as to have different waiting times at the moment of the measurements.

DLS experiments were carried out using a goniometer fitted with a toluene bath. The laser was a 30 mW diode-pumped, frequency-doubled neodymium-doped yttrium aluminum garnet (Nd:YAG) ( $\lambda=532$  nm). The scattered intensity was recorded with an avalanche photodiode. The intensity correlation function was directly obtained as  $g_2(Q,t) = \langle I(Q,t)I(Q,0) \rangle / \langle I(Q,0) \rangle^2$ , where  $Q$  is the modulus of the scattering wave vector defined as  $Q = (4\pi n/\lambda)\sin(\theta/2)$ . In the present experiment  $\theta=90^\circ$  and the acquisition time of each  $g_2(Q,t)$  was 120 s.

SAXS measurements were performed at the high-brilliance beam line (ID2) at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France using a 10 m pinhole SAXS instrument. The incident x-ray energy was fixed at 12.6 keV. The form factor  $F(Q)$  was measured using a flowthrough capillary cell. In the SAXS data analysis the corrections for empty cell and water have been taken into account. The measured structure factor has been obtained as  $S^M(Q) = I(Q)/F(Q)$ . Figure 1 shows as an example the waiting time evolution of both the clay density autocorrelation functions (top panels) and the measured structure factors (low panels) for samples in the low and high concentration regions, at  $C_w=1.9\%$  [Figs. 1(A) and 1(C)] and  $C_w=2.8\%$  [Figs. 1(B) and 1(D)], respectively. The same sample was measured with the two techniques, DLS and SAXS (the same lines styles in the top and bottom panels correspond to roughly the same waiting time), and therefore a clear and direct comparison between the dynamic and static structure factor behaviors can be obtained. While, in fact, static light scattering measurements on Laponite samples have been previously carried out [8,10,15], the full evolutions of the structure factor with waiting time for both low- and high-

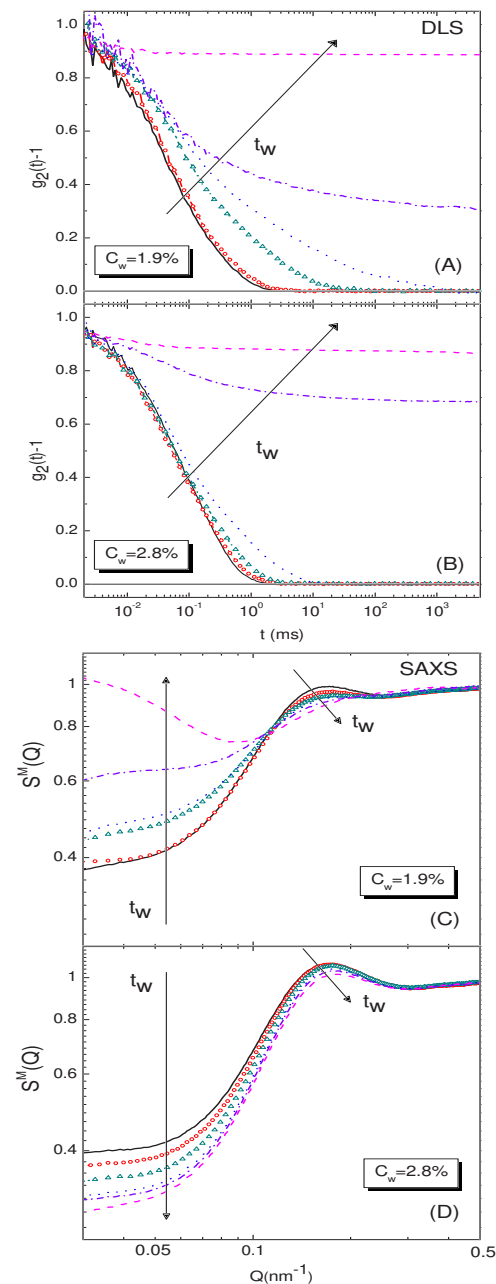


FIG. 1. (Color online) Evolution of the time autocorrelation functions (top panels) and the measured structure factors (bottom panels) as a function of the waiting time  $t_w$  (same waiting times, same lines styles) for two different Laponite concentrations: a low one,  $C_w=1.9\%$  (A),(C), and a high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

concentration samples have not been reported to our knowledge.

From Fig. 1 the difference in the behavior of low- and high-concentration samples is striking. For the high-concentration sample [Figs. 1(B) and 1(D)] there are no significant changes in the structure factor profiles while the sample crosses the ergodic-nonergodic transition (from dotted to dash-dotted and dashed 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. In contrast, for the

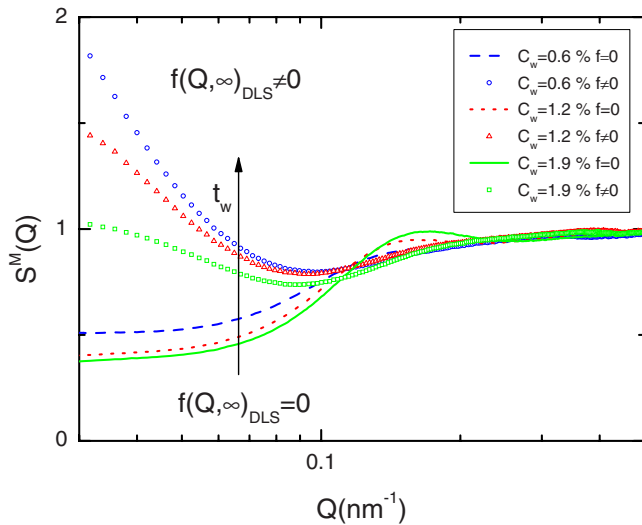


FIG. 2. (Color online) Waiting time evolution of the static structure factors from full [ $f(Q, \infty) = 0$ ] to incomplete decay [ $f(Q, \infty) \neq 0$ ] in the corresponding DLS spectra for three different low Laponite concentrations at  $t_w \approx 1.2t_w^\infty$ .

low-concentration sample [Figs. 1(A) and 1(C)] there is an evident change of the static structure factor as the sample ages and approaches the nonergodic state (from dotted to dash-dotted and dashed curves); specifically, a progressively increased excess of scattering is observed at low  $Q$  values. Moreover, a change in the shape of the curve and a shift of the main peak to higher  $Q$  values can also be recognized. These differences are clear evidence that the two samples are reaching the final nonergodic states following different routes [13] and, furthermore, that the two final arrested states are actually different.

The same behavior shown in Figs. 1(A) and 1(C) has been found for all the investigated low-concentration samples. In Fig. 2 we show the static structure factors measured for three different low ( $C_w < 2.0\%$ ) Laponite concentrations corresponding to full (small waiting time, lines) and incomplete decay (long waiting time, symbols) of the DLS spectra. Due to different aging “velocities,” we show here the  $S^M(Q)$  at the same  $t_w/t_w^\infty$ ,  $t_w^\infty$  being the  $C_w$ -dependent arrest time, as defined in Ref. [13]. It is clear that in the low- $Q$  region the same increase of intensity is found as the sample arrests. Moreover, this excess of scattering at low  $Q$  increases as the Laponite concentration is decreased. This indicates the existence of strong inhomogeneity in the suspension, which we attribute to the formation of a network, which—as the aging time goes by—grows and eventually forms a gelled network. Also observable is the disappearance of the main peak and/or its shift to higher  $Q$  values. On the contrary, none of these features is observed for the high-concentration ( $C_w > 2.0\%$ ) samples where all the measurements have shown the same trend as the one drawn in Fig. 1(D). This indicates the homogeneity of the high- $C_w$  arrested state. The observed concentration dependence of the low- $Q$  scattering intensity seems to suggest that the transition between the two different final states is not discontinuous but the arrested state becomes more and more homogeneous with increasing clay

concentration. Summarizing, the data reported here give a clear proof of the existence of two structurally different arrested states in Laponite suspensions, completing the information—already reported in the literature [13]—that low and high clay concentrations reach the arrested state following two different routes. Static structure factor measurements, indeed, show an excess of scattering in the low- $Q$  region for the low-concentration samples, thus indicating the formation of an inhomogeneous state, while for the high-concentration samples the  $S^M(Q)$  data are in agreement with the formation of a homogeneous arrested state.

The present experimental findings, together with the phenomenology associated with gel and glass formation in colloids, allow us to speculate on the nature of the observed arrested states. Despite the apparently simple definition that “colloidal gels are arrested states of matter at low density where the particles are tightly bonded to each other so that the thermoreversible bond time is comparable to or longer than the experimental observation time,” the essence of the (colloidal) gel state is still under debate [24]. In this context, it is important to stress that sometimes the discussion on what is a gel and what a glass becomes a nominalistic dispute. In fact, the formation of a bonding gel, which in a part of the colloidal community provides indication of gel formation, for another part of the scientific community would be rather classified as glass formation [24]. In this sense we can follow the proposition that in a “gel” the attraction between colloidal particles is the leading mechanism for gelation, while a “glassy state” can be driven either by repulsion (hard-sphere or Wigner glass) or by attraction (attractive glass). Moreover, while the gel state is characterized by structural inhomogeneities (signaled by a nontrivial low- $Q$  signal in the scattering intensity) the glass is structurally homogeneous [1].

On the grounds of the previous discussion, the low-clay-concentration inhomogeneous arrested state can be considered as a gel and the high-concentration homogeneous state as a glass. Moreover, in Laponite, with increasing salt concentrations the arrested states are still observed and occur even more rapidly [10,13]. This observation is in clear contradiction with the formation of a colloidal glass induced by strong repulsive interactions that are decreased (due to the effect of screening) as the ionic strength is increased. Therefore, the attractive interaction must be responsible for the final arrested state. For these reasons we can call the homogeneous state at high clay concentrations an attractive glass, i.e., a homogeneous state governed by attractive interactions (which can also be called a homogeneous gel). In contrast, in the low-concentration region, the inhomogeneous state is compatible with the formation of a gel state where the aging dynamics is supposed to be characterized by the growth of a region of strongly correlated platelets which increases in size and, eventually, spans the whole system at the gel transition.

It is worth noting that the features of this concentration region fit with those of the newly discovered equilibrium bonding gel region [1], a state found in low-density colloids with anisotropic interactions. In fact, the interaction potential between Laponite platelets is certainly nonspherical, with a privileged relative orientation, an aspect that probably has not been properly accounted for in previous studies. More-

over, the waiting time evolution of  $S(Q)$  in Fig. 1(C) strongly resembles the temperature evolution of  $S(Q)$  of Fig. 5(a) of Ref. [5] obtained in simulation of a valence-limited colloidal system. The increased intensity at small wave vectors of  $S(Q)$  as the waiting time (temperature) is increased (decreased) indicates that the system becomes more and more compressible, with large inhomogeneities that can be seen as an echo of the nearby phase separation or, equivalently, as a consequence of building up a fully connected network. In fact, one can suppose that as the time goes by the system experiences the attraction more and more, approaching, through successive equilibrium states, the final arrested state as do ideal systems [5] with decreasing temperature. Also, the evolution of  $S(Q)$  with concentration seems to be in qualitative agreement with Fig. 5(b) of Ref. [5]: on moving away from the spinodal line (increasing  $C_w$ ) the  $Q \rightarrow 0$  peak decreases and the nearest neighbor peak grows, signaling the increasing importance of the packing. It is important to underline that, besides the qualitative agreement between the behavior of the model and Laponite suspensions no quantitative comparison can be done between the systems due to the peculiarity of Laponite. Therefore, at present, we are also

not able to locate the spinodal line in Laponite suspensions. It could be in fact possible that some of the samples at very low concentrations are “inside” the spinodal line and that for those systems a separation phase at very long waiting times could occur.

In conclusion, the results reported here resolve the long-standing controversy about the final arrested state in Laponite suspensions [10,11]: both an inhomogeneous and a homogeneous state exist. They are reached—as the system ages—following two different dynamic routes [13]. The existence of two different arrested states in this charged colloidal system with a nonspherical potential (further complicated by the presence of charges), depending only on its concentration, gives a proof of the strong connection existing between the gel and glass states. A common experimental and theoretical effort toward the understanding of the still puzzling liquid-gel (-glass) transition and a theoretical investigation of the features of the different arrested states in the presence of charged nonspherical potentials, is needed.

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