Routes to Gelation in a Clay Suspension

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The gelation of water suspension of a synthetic clay (Laponite) has been studied by dynamic light scattering in a wide range of clay weight concentration ($C_w = 0.003$–0.031). At variance with previous determination, indicating a stable liquid phase for $C_w < C_w^* \approx 0.015$–$0.018$, we find that gelation actually takes place in the whole examined C_w range. We find also that C_w^* marks the transition between two different routes to gelation. We hypothesize that at low concentration Laponite suspension behaves as an attractive colloid and that the slowing down of the dynamics is attained by the formation of larger and larger clusters while at high concentration the basic units of the arrested phase could be the Debye Huckel spheres associated with single Laponite plates.

Colloidal systems are ideal benchmarks for studying, by optical microscopy and light scattering, equilibrium slow dynamical processes and the formation of nonergodic arrested state of matter. Recent works [1] focusing on short-range attractive colloids have attempted a connection between the gel and the glass arrested state of matter. In these systems, a reentrant glass line, two kinds of glasses (attractive and repulsive) and a glass-glass line have been predicted and experimentally observed [1]. Correlations between the dynamical behavior of gels and glasses suggest that a common understanding of these two disordered forms of matter may emerge. In the case further complicated where short-ranged attractive interactions are complemented by weak repulsive electrostatic interactions, the gel formation process can be fully modeled as a glass transition phenomenon [2]. Despite these recent progresses, a deeper comprehension of the still puzzling liquid-gel/glass transition in colloidal system is needed. A recent work [3] has indicated a parallelism between the reentrant phase of Ref. [1] and the phase diagram of a synthetic Hectorite clay: Laponite. Laponite suspensions are composed of nearly monodisperse, rigid, disc-shaped platelets with a thickness of 1 nm, a diameter of about 30 nm, and a negative surface charge of a few hundred e. In spite of intensive research there is no general agreement about the mechanism that originates the arrested phases in Laponite suspensions, attributed by different authors to Wigner glass transition [4], frustrated nematic transition [5–8], micro-segregation [5,9,10], gelation [11–13], etc. Studies of the aggregation in Laponite suspensions will give an important contribution to the understanding of its phase diagram and more generally of the arrested phases process in systems where repulsive long-range and attractive short-range interactions compete.

According to the phase diagram [5] at ionic strength below $I = 10^{-2}$ M Laponite suspensions can be in two different physical states. Low concentration suspensions

$[C_w < C_w^*(I)]$ form a stable, equilibrium fluid phase. Higher concentration suspensions $[C_w \gtrsim C_w^*(I)]$ are initially fluids but experience aging and pass into a gel phase after a time that depends on the clay amount. Several dynamical scattering studies have investigated the aging process of samples belonging to this high C_w phase region [4,14–17], while only two recent papers [12,17] report about the lower concentration region.

In this Letter we present a dynamic light scattering study at increasing concentrations from 0.3 to 3.1 wt % at ionic strength between $I \simeq 10^{-4}$ M and $I \simeq 10^{-3}$ M where $C_w^* \approx 1.5$–1.8% [5]. A new gel region, at $C_w \lesssim C_w^*$, has been identified and the gelation processes in the two arrested phases (at $C_w \lesssim C_w^*$ and at $C_w > C_w^*$) have been accurately studied. Two different routes to gelation for the two regions have been found and a possible explanation for the processes involved in the building of the arrested phases has been proposed.

Particular attention has been given to sample preparation to avoid dissolution of Laponite platelets that occurs if the samples are exposed to air contamination [18,19] and that can seriously affect the measurements. For this reason the whole procedure has been performed in a glove box under N_2 flux and the samples have been always kept in safe atmosphere during and after sample preparation. The powder, manufactured by Laporte Ltd. who kindly supplied us the material, was first dried in an oven at $T = 400$ K for four hours (up to 20% of the powder weight when it is received is due to adsorbed water), then it was dispersed in deionized (pH = 7) water, stirred vigorously until the suspensions were cleared, and filtered through 0.45 μm pore size Millipore filters. The starting aging time ($t_w = 0$) is defined as the time when the suspension is filtered. This sample preparation procedure is similar, but not identical, to that already used in previous works [12,13,16,17]. NMR spectroscopy [20], checking continuously the amount of Na and Mg ions present in the

solutions, indicates that the chemical reaction of Laponite dissolution [18,19] does not affect our samples.

Dynamic light scattering measurements were performed using an ALV-5000 logarithmic correlator in combination with a standard optical setup based on a He-Ne ($\lambda = 632.8$ nm) 10 mW laser and a photomultiplier detector. The intensity correlation function was directly obtained as $g_2(q, t) = <I(q, t)I(q, 0)> / <I(q, 0)>^2$, where q is the modulus of the scattering wave vector defined as $q = (4\pi n/\lambda)\sin(\theta/2)$ ($\theta = 90°$ in the present experiment). For the low concentration samples ($C_w \leq 1.5\%$) the measurements have been repeated once a week for a long period of time (up to four months for the lowest concentration), while for $C_w > 1.5\%$ the sample was left in the scattering system and spectra were continuously acquired until the gelation was reached.

As an example, correlation functions at increasing aging times t_w for two different samples at low [Fig. 1(a): $C_w = 1.1$ wt % $< C_w^*$) and high concentration [Fig. 1(b): $C_w = 2.5$ wt % $> C_w^*$), are reported in Fig. 1. As is evident from the figure, both the samples are aging: the dynamics is in fact becoming slower and slower for increasing waiting time t_w. This behavior was expected
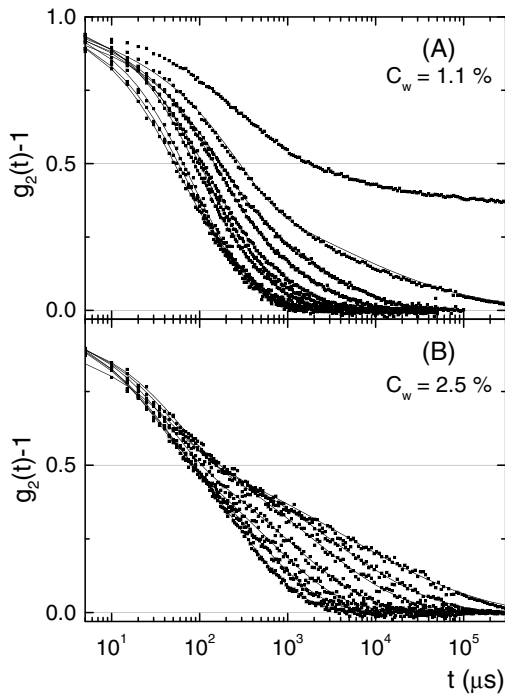

FIG. 1.   Evolution of the measured intensity correlation functions (symbols) and corresponding fits with Eq. (1) (continuous lines) for two different Laponite suspensions at the indicated concentrations at different waiting times t_w. The curves are measured at increasing waiting times that (from left to right) are $t_w = 288, 792, 1128, 1464, 1632, 1800, 1968, 2136, 2328$, and 2640 hours for sample (a) and $t_w = 6, 30, 54, 78, 102, 126$, and 150 hours for sample (b), for which only data in the ergodic phase are reported.

for the higher concentration sample of Fig. 1(b); several measurements [4,14–17], indeed, have shown the existence of aging and a sol-gel transition for long enough waiting times. The aging process was, however, unexpected for the lower concentration sample of Fig. 1(a) where the liquid state is predicted from the phase diagram [5], and confirmed by recent dynamic light scattering measurements [17]. From Fig. 1(a) it is instead evident that the system is aging, and for the longest waiting time reported ($t_w = 2640$ hours), there is a qualitative change in the correlation function: a crossover between a complete and an incomplete decay. This behavior is the indication of a strong ergodicity breaking, signature of a sol-gel transition, as already observed in [4,14] for samples in the higher concentration region and in [12] for a sample at $C_w = 1\%$ with $I = 5 \times 10^{-3} M$. Our dynamic light scattering measurements show that for all the samples studied, down to the lowest concentrated ($C_w = 0.3\%$), there is a typical waiting time t_w^∞, increasing with decreasing clay concentration C_w, at which the system undergoes the gelation. Depending on the initial concentration this gelation time can vary from hours to several months.

Figure 1 shows also that the correlation functions decay following a two step behavior, i. e., there are two different relaxation processes, a fast and a slow one. For this reason the fitting expression should contain two contributions. In this case the squared sum of an exponential and a stretched exponential function is used, as already reported in Ref. [16]:

$$g_2(q, t) - 1 = b\{ae^{(-t/\tau_1)} + (1 - a)e^{[-(t/\tau_2)^\beta]}\}^2, \quad (1)$$

where b represents the coherence factor. The fitting expression describes well the photocorrelation spectra for all the aging times in the liquid (ergodic) phase and for all the investigated concentrations with the relaxation time τ_1 associated with the fast dynamics and the relaxation time τ_2 and the stretching parameter β that describe the slow part of the autocorrelation function. The fits are shown as full lines in Fig. 1 and the resulting chi square is always within its standard deviation.

Another important peculiarity of the correlation functions that can be directly observed in the raw data reported in Fig. 1, is that the aging process evolves differently for the lower and higher concentration samples. While in fact increasing waiting time, the initial decay of the correlation functions (fast dynamics, characterized by the correlation time τ_1) remains constant for the higher concentration sample [Fig. 1(b)], it seems to become slower for the lower concentration sample [Fig. 1(a)]. This different behavior is confirmed from the results of the fits, that also show another major difference between the samples at low and high concentrations.

In the following we will report the t_w and C_w dependence of the fitting parameters; in particular, we focus on the behavior of the parameters of the slow decay: the

relaxation time τ_2, the stretching exponent β, and the "mean" relaxation time τ_m:

$$\tau_m = \tau_2 \frac{1}{\beta} \Gamma(\frac{1}{\beta}), \qquad (2)$$

where Γ is the usual Euler gamma function.

As an example, the values of τ_m obtained for three different concentrations are reported in Fig. 2. It is evident the common behavior of τ_m that seems to diverge at a given $t_w = t_w^\infty$, i.e., when the gelation occurs. This clearly shows that, as already seen from the raw correlation functions, the samples at concentrations lower and/or equal to 1.5 wt % are actually aging and undergo a gelation transition. To have more information about this gelation process we represent the aging time t_w dependence of mean relaxation time τ_m with the law:

$$\tau_m = \tau_0 \exp\left(B \frac{t_w}{t_w^\infty - t_w} \right). \qquad (3)$$

We do not have any rationale behind such a law; it can be considered a generalization of the long waiting time of the exponential growth with t_w observed for τ_2 by Abou *et al.* [16] in the high-concentration samples. Equation (3) (reported in Fig. 2 as full lines) describes the measurements well . The most significative parameters of the fits, t_w^∞ and B, for all the studied concentrations are shown in Fig. 3. Here the vertical dotted region indicates the range of concentrations that, in the phase diagram [5], would mark the transition from the "liquid" to the gel phase in the range of $I \simeq 10^{-3}$–$10^{-4}M$. The results of the fit indicate that t_w^∞, which can be considered as the time at which the gelation actually occurs, is continuously decreasing with increasing clay concentration, without any evident discontinuity in correspondence of the "transi-
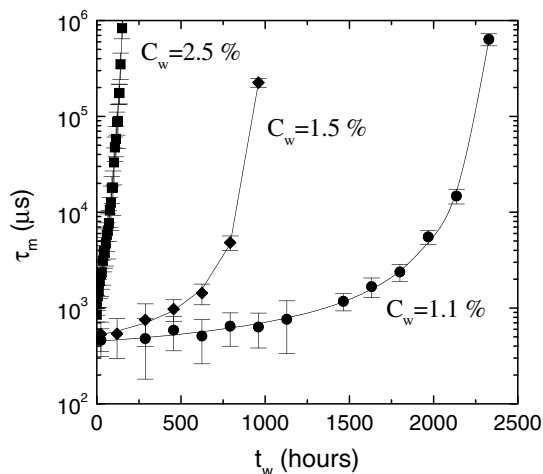
tion" region. The concentration dependence of the parameter B, which measures how fast τ_m approaches the divergence, is shown in Fig. 3(b). This parameter is almost constant for all the samples in the low concentration region, while it shows a large discontinuity on passing in the higher concentration region. It is important to note that this jump takes place in a region that encompass the supposed "liquid-gel transition" region. The fact that the value of the B parameter is almost constant for all the low concentration samples is an indication of the existence of a scaling law. Indeed, if we plot the quantities $\tau_m(t_w)$ and $\beta(t_w)$ as a function of t_w/t_w^∞, all the different C_w data with almost constant B should collapse on a single master curve. The τ_m and the β parameters in function of the normalized waiting time are reported in Fig. 4(a) and 4(b), respectively. As expected, all the data for both the τ_m and the β parameters of lower concentrations collapse, within their statistical uncertainties, on a single curve while the data at higher clay concentrations have a different behavior. We already observed from the direct comparison of Fig. 1(a) with Fig. 1(b) that the aging process is qualitatively different for the low- and high-concentration samples. Figs. 3 and 4 quantify this difference in the physical properties characterizing the aging phenomenon in the two different concentration regions.

In conclusion the present observations indicate that the stable phase of Laponite suspensions in pure water at $C_w \lesssim C_w^*$, expected to be liquid according to previous
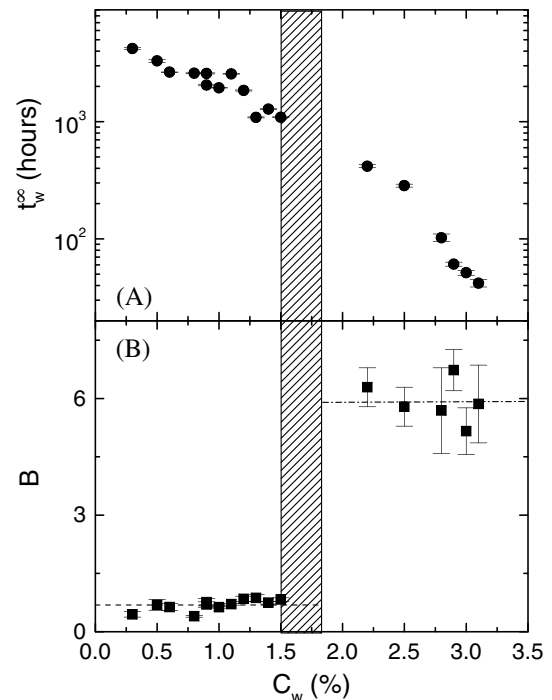
FIG. 2. Waiting time dependence of τ_m [see Eq. (2)], i. e., of the average relaxation time of the slow decay of the correlation functions as those reported in Fig. 1. As an example, the t_w dependence of τ_m is reported for the three indicated concentrations. Continuous lines are fits of the data with Eq. (3).

FIG. 3. Concentration dependence of the divergence time t_w^∞ (a) and of the B parameter (b), entering in Eq. (3). The dashed lines are guides to the eyes. The shadow area indicates the region where the liquid-gel transition was supposed to be according to Ref. .
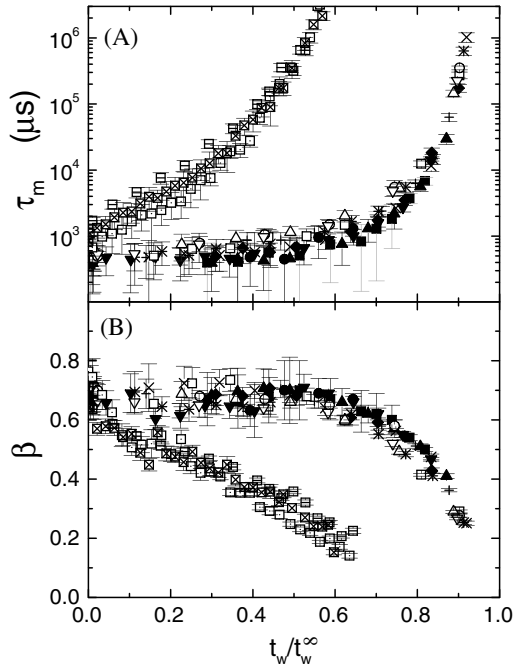
FIG. 4. The waiting time dependence of the τ_m (a) and β (b) are reported as a function of the scaled variable t_w/t_w^∞ for some of the investigated concentrations: $\blacksquare = 0.3\%$, $\bullet = 0.5\%$, $\blacktriangle = 0.6\%$, $\blacktriangledown = 0.8\%$, $\blacklozenge = 0.9\%$, $+ = 0.9\%$, $\times = 1.0\%$, $* = 1.1\%$, $\square = 1.2\%$, $\circ = 1.3\%$, $\triangle = 1.4\%$, $\triangledown = 1.5\%$, $\boxdot = 2.2\%$, $\boxtimes = 2.5\%$, $\boxminus = 2.8\%$. The data for $C_w \leq 1.5\%$ collapse on a single master curve.

the phenomenology of colloidal gels. In Ref. [2] it has been suggested that the gelation taking place in attractive colloidal suspensions at very low concentration involves the growth of larger and larger clusters (driven by the short-range attraction). The glass transition of these clusters, driven by the long-range repulsion, is responsible for the arrest of the dynamics and the formation of a gel phase. The authors prove that the gel is essentially a Wigner glass, composed by clusters of colloidal particles. We can speculate that low concentration Laponite suspensions behave as the attractive colloids in Ref. [2]. This scenario is in agreement with the fact that the long time needed to form the arrested phase in the low concentration range is spent by the system to build up the clusters. Also at high Laponite concentration the arrested state could be a Wigner glass, but in this case the packing fraction of the Debye Huckel sphere associated to each platelet reaches values as high as 0.43 [4] and the single laponite platelet would be the elementary constituent of the Wigner glass.

studies [5], actually is an arrested phase. Recently the phase diagram was revised [11] and Ref. [13] suggested that the equilibrium state in the low concentration region is not liquid but a very fragile gel that takes a long time to appear. Probably this "long time" is the reason why previous measurements indicated this phase as liquid. Our measurements clearly show not only that at all the investigated concentrations the stable phase is an arrested phase but also that the aggregation process is basically different for the samples at $C_w \lesssim C_w^*$ and those at $C_w \gtrsim C_w^*$. This is evident from the behavior of τ_m and β reported in Fig. 4 and from the discontinuity of the B parameter across the $C_w = C_w^*$ region as shown in Fig. 3. In this sense the "liquid-gel" transition line of the phase diagram [5] is not a real liquid-gel transition but rather seems to indicate a sort of "fragile gel-gel" transition.

The origin of the different routes towards an arrested phase observed for low- and high-concentration Laponite suspensions calls for an explanation that goes beyond the aim of the present work. At the level of speculation, it is worthwhile to recall that the microscopic interaction between Laponite plates is due to a screened Coulomb interaction, which can be modeled by a Yukawa-like repulsion at long distances and a quadrupolar electric and/or a van der Waals terms at short distances [21,22]. This competition of short-range attraction and long-range repulsion resembles that recently proposed [2] to describe

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