Structure and formation of a gel of colloidal discs[1]

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We have performed static scattering experiments on the gel state of a suspension of disc-shaped charged colloidal particles. The combination of static light scattering and small angle X-ray scattering experiments probes more than three orders of magnitude in the scattering vector q. We observe that after application of shear the formfactor develops nematic-like order. This decays to random orientation in the gel-state. This suggests that local re-orientation of the discs leads to the gel state, as opposed to aggregation.

Keywords: colloids, structure of glasses, X-rays scattering.

61.43.Fs, 71.55.Jv, 64.70.Pf, 78.80.Ck, 82.70.Dd

I. INTRODUCTION

Systems of anisotropic particles reveal many different phases, with symmetries and structures that depend strongly on the ratio of particle dimensions (the aspect ratio), and on the interaction between the particles. Onsager [3] has shown that an isotropic-nematic transition occurs even in simple systems, such as hard needles or hard discs. Indeed, a large amount of liquid crystalline phases with complex structures and exotic symmetries are found to exist in nature [4]. Molecular dynamics simulations on hard-disc systems reveal isotropic, nematic, cubatic, and columnar liquid crystalline phases [5]. The recent availability of synthetic colloidal clays, Laponite [6], made of well-characterised disc-like particles, promised the physical realisation of these phases on a mesoscopic colloidal scale.

Considering the aspect ratio (of 25) of these colloidal discs one expects, according to the Onsager criterion, an isotropic-nematic (I-N) phase transition at a volume fraction of 0.12. However, the colloidal particles are charged and interact by way of screened Coulomb potential. Rescaling the actual volume fraction with the Debye screening length one might expect the I-N transition to take place at volume fractions in the range of 0.03. Surprisingly, in the range of $0.005 - 0.03$, suspensions of these charged colloidal discs are observed to undergo a transition from a fluid-like *sol* to a solid-like *gel*, instead of entering a liquid crystalline phase [7–15]. This gelation process occurs as a function of time (denoted by T) at constant temperature and particle density. An observation which is in contrast to systems where the glass transition occurs as a function of the volume fraction [16], temperature [17], or pressure [18].

Recently we have performed extensive dynamic light scattering experiments on this *sol-gel* transition [13,14]. Our measurements reveal the slowing down of the collective dynamics towards the *gel-point* T_g, where the sample becomes a macroscopically immobile structure. No phase separation is observed. The formation of the gel as a function of time has all the characteristics of a glass transition [19]. The picture emerging is one of frustration of the particle motion by the algebraically increasing viscosity [15], barring the system from entering a liquid crystalline phase, just as in the glass transition.

As yet it is unknown how the structure evolves as the gelation proceeds. Generally, two different types of three dimensional ordering are proposed for the final gel state. The first one is the "house of cards" structure for the gel [20,21]. This conjecture is based on the physical intuition that the short-range part of the electrostatic interaction has a strong quadrupolar character. It implies the presence of (on average) T-shaped units. However, the observation of the existence of strong gels at extremely low particle densities has led to the second model, a random structure for the gel [7,8]. The more isotropic long-range part of the electrostatic interaction favours this structure. Little is known about orientational order or the presence of liquid crystalline order. Here, we present a combination of static light scattering (SLS) and small angle X-ray scattering (SAXS) techniques to investigate the colloidal structure and the presence or absence of orientational order.

II. EXPERIMENTAL

Because of its high purity and very small crystallite size, the synthetic clay Laponite [6] forms colorless and transparent suspensions which are particularly suited for scattering studies. For our study we have used Laponite RD, which is the easiest grade to disperse to single colloi-

dal discs and which forms strong gels at relatively low concentrations. Laponite powder and dust free demineralized water are slowly mixed in a volume fraction $\Phi_v = 0.0116$, and stirred vigorously for 2 hours with a magnet stirrer. After 10 hours the suspensions are colorless, transparent, and charge-stabilized *sols*, where the light scattering entity is a single colloidal disc [10,13]. As time proceeds we observe the suspension thickening by tumbling the original stock tubes. Finally, after 100 hours the suspension behaves as a macroscopically immobile structure which we call the *gel*. The gel does not flow nor adapts its shape when turned in the gravitational field.

In our static light scattering (SLS) setup, a He-Ne laser beam is focused in the sample. The sample is contained in a cylindrical quartz cuvette immersed in an index-matching toluene bath. Scattered light is detected with a photo multiplier mounted on a goniometer arm.

Small angle X-ray scattering (SAXS) experiments were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble on beam line ID2/BL4, and at the Daresbury Synchrotron Radiation Source (SRS) on station 8.2. The sample containers used here are made of a brass frame acting as a spacer of 0.5 mm thickness. Windows of Kapton or Mica are glued on both sides. The suspensions are inserted through sealable holes. The combination of static light scattering and small angle X-ray scattering probes more than three orders of magnitude in the scattering vector q, from 10^{-3} nm^{-1} to 10^{0} nm^{-1}. This allows us to investigate the state of the colloidal suspensions from sub-particle length scales to the colloidal arrangement at large length scales.

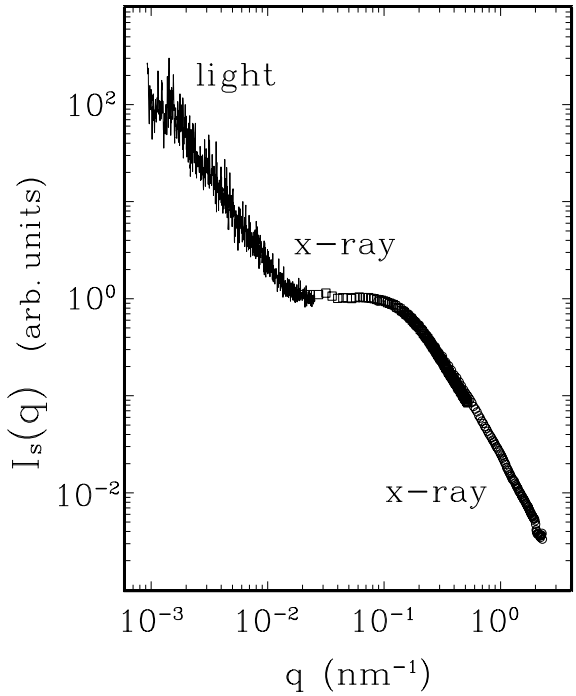

FIG. 1. Overview of the static scattered intensity $I_s(q)$ as obtained from the three scattering experiments. The intensities have been scaled to merge at the regions where the range in q overlaps.

III. RESULTS

In Fig. 1 we show an overall view of the static scattered intensity $I_s(q)$ as obtained with the different scattering set-ups. The intensities as shown there have been measured on a stable gel where no significant changes in time were observed any more. The vertical scales are adjusted to merge at the regions of overlap in q. We observe the following: (i) At the largest q values (SAXS), between 10^{-1} nm^{-1} and 10^{0} nm^{-1}, $I_s(q)$ roughly follows a q^{-2} power-law decay, which is consistent with the form factor $F(q)$ of randomly oriented thin discs [22]. Based on this data we previously estimated the particle diameter $2R = 25 \pm 0.5$ nm and the thickness $2H = 1.0 \pm 0.1$ nm [13], in good agreement with the values reported earlier [7,10,11]. (ii) There is a plateau at intermediate q values (SAXS), between 10^{-2} nm^{-1} and 10^{-1} nm^{-1}. In this region one would expect the usual liquid-like peak of the structure factor. This is not observed in the gel state. (iii) At the smallest q (SLS), between 10^{-3} nm^{-1} and 10^{-2} nm^{-1} a steep decrease in $I_s(q)$ is observed, which is attributed to the static structure factor $S(q)$ of the gel. We find [23], $S(q) - 1 \sim q^{-2.1}$, which is typical for a structure with self-similar, or fractal, properties [24]. Our result is in qualitative agreement with a previous study by Pignon *et.al.* [12] on a comparable colloidal clay.

We have measured the form factor during gelation to investigate the presence or absence of orientational order. The samples were squeezed in between the two parallel windows of the scattering cell (aspect ratio > 100). It is known that these gels are thixotropic, i.e., application of shear above a certain low threshold induces the system into a low-viscosity state. From this low-viscosity state the system evolves again to the gel state. From viscosity experiments by Willenbacher [15], we know that the low-viscosity state can be reached reproducibly. Moreover, after the application of shear the system has lost all memory of its previous history [25]. Thus, we follow the evolution from a low-viscosity or sol-like state to the gel. In Fig. 2 we observe that initially the form factor times $(qR)^2$ is a constant. This indicates a random orientation of the discs, as expected for a sol. Within a few hours the form factor decreases faster than $(qR)^2$. This can be explained only by the orientational ordering of the discs, with their faces parallel to the windows. According to the Onsager criterion one expects an isotropic-nematic phase transition at only slightly higher volume fractions. After 8 hours, however, this process is reversed and after

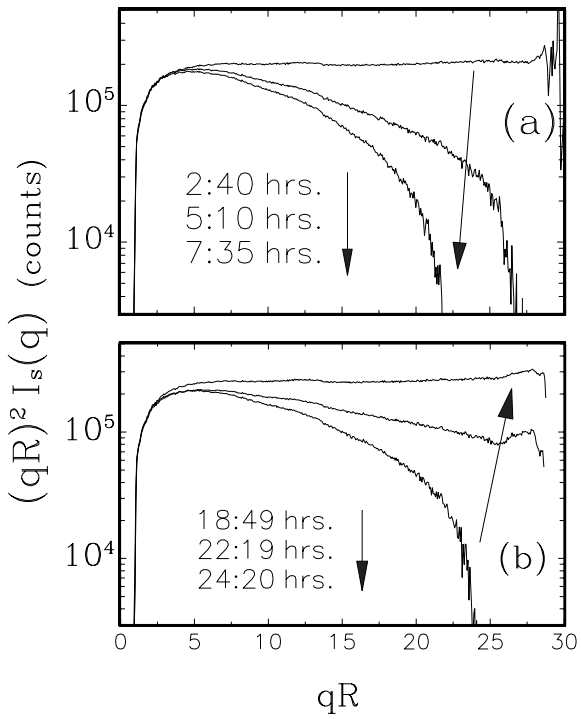

FIG. 2. Typical series of SAXS profiles of the colloidal suspension of discs after loading the sample in the cell under shear. Time after preparation is shown in the legend. The original SAXS profiles have been multiplied with $(qR)^2$. On this scale a horizontal straight line is obtained when dealing with isotropically oriented discs. The tendency observed here is independent of the initial state before shear (sol or gel).

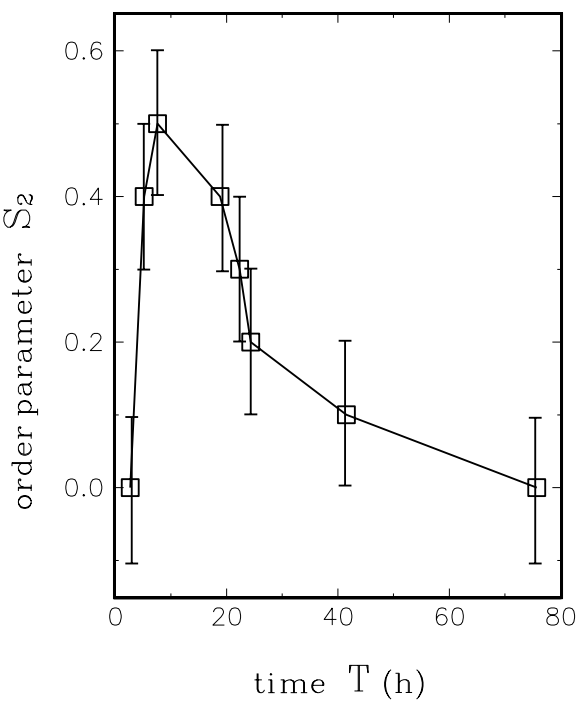

FIG. 3. Time dependence of the nematic order parameter S_2 characterizing the distribution function of the disc orientation, fitted to data of Fig. 2. The positive value of S_2 indicates a preferential ordering of the colloidal discs parallel to the container walls.

40 hours the form factor times $(qR)^2$ is constant. Thus, the gel state also has a random orientation of the discs.

We have interpreted our data in terms of the nematic order parameter S_2 [4]. Fits of this model to the experimental data yields the behavior shown in Fig. 3. The order parameter increases right after sample preparation, reaches a maximum after 8 hours, and then decays to zero after 40 hours. We caution against the values of the order parameter: in this high q range of the experiment, the background is increasingly important. Moreover, preliminary analysis of other X-ray and light scattering data clearly indicate that the bulk of the sample never enters the nematic phase [23].

At first sight it seems surprising that the colloidal discs tend to nematic-like order before returning to random orientations. This can be explained as follows: when squeezing a gel in between two plates, one expects an 'inverse plug flow'. A thin low-viscosity boundary layer with high nematic order exists close to the walls of the sample cell, surrounding an elastic gel in the middle, as borne out by shear experiments of Pignon *et.al* [26]. The observed growth of nematic order is induced from the boundary layer inwards, becoming thicker as time progresses. At the same time, local re-orientation driven by thermal motion breaks down the order, overtaking the first process and eventually leading to the observed random gel state.

IV. CONCLUSIONS

We have measured the structure factor of the gel state of charged discs over three orders in the wavevector. We do not observe any indication for local orientational order in the gel state. Hence, the measurements refute the house of cards picture of the structure in the gel state. The measurements performed after the application of shear indicate that local re-orientation induces the collective rearrangements by which the high-viscosity, and eventually elastic, gel state is reached. Analysis of recently obtained scattering data in the low-q regime during the gelation from low-viscosity states with different orientational order corroborate this conclusion [23]. They also refute aggregation- the growth of spatially defined clusters with characteristic orientation or density- as the road to gelation.

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