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Structure and Formation of a Gel of Colloidal Disks[1]

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We have performed static scattering experiments on the gel state of a suspension of disk-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 form factor develops nematic-like order. This order decays to random orientation in the gel state. This suggests that local reorientation of the disks leads to the gel state, as opposed to aggregation.

KEY WORDS: colloids; gels; structure of glasses; light scattering; x-ray scattering.

1. 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), the density of particles, and on the interaction between the particles. Onsager [1] has shown that an isotropic–nematic transition occurs even in simple systems, such as hard needles or hard disks. Indeed, a large amount of liquid crystalline phases with complex structures and exotic symmetries is found to exist in nature [2]. Molecular dynamics simulations on hard-disk systems reveal isotropic, nematic, cubatic, and columnar liquid–crystalline phases [3]. The recent availability of synthetic colloidal clays, laponite [4], made of well-characterized disk-like particles, promised the physical realization of these phases on a mesoscopic colloidal scale.

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Considering the aspect ratio of 25 of these colloidal disks one expects, according to the Onsager criterion, an isotropic-nematic (I–N) phase transition at a volume fraction $\phi_v = 0.12$. However, the colloidal particles are charged and interact by way of a screened Coulomb potential [5]. 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 $\phi_v = 0.005$ to 0.03, suspensions of these charged colloidal disks are observed to undergo a transition from a fluid-like *sol* to a solid-like *gel*, instead of entering a liquid–crystalline phase [6–14]. This gelation process occurs as a function of time (denoted 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 [15], temperature [16], or pressure [17].

Recently we have performed extensive dynamic light scattering experiments on this sol-gel transition [12, 13]. Our measurements reveal the slowing-down of the collective dynamics toward 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 [18]. The picture emerging is one of frustration of the particle motion by the algebraically increasing viscosity [14], 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 types of three-dimensional ordering are proposed for the final gel state. The first one is the "house of cards" structure for the gel [19, 20]. 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 [6, 7]. The more isotropic long-range part of the electrostatic interaction favors 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.

2. EXPERIMENTAL

Because of its high purity and very small crystallite size, the synthetic clay laponite [4] 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 colloidal disks 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 h with a magnet stirrer. The volume fraction ϕ_v is defined as the partial volume occupied by the colloidal particles in the total volume of the samples. After 10 h the suspensions are colorless, transparent, and charge-stabilized sols, where the light scattering entity is a single colloidal disk [9, 12]. As time proceeds we observe the suspension thickening by tumbling the original stock tubes. Finally, after 100 h the suspension behaves as a macroscopically immobile structure which we call the gel. The gel does not flow or adapt its shape when turned in the gravitational field.

In our static light scattering (SLS) setup, a He–Ne laser beam is focused on the sample, which 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} 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.

3. 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. The vertical scales are adjusted to merge at the regions of overlap in q. We observe the following. (i) At the largest values of q (SAXS), between 10^{-1} and 10^{0} nm^{-1}, $I_s(q)$ roughly follows a q^{-2} power-law decay, which is consistent with the form factor $T(q)$ of randomly oriented thin disks [21]. Based on these data we previously estimated the particle diameter $2R = 25 \pm 0.5$ nm and the thickness $2H = 1.0 \pm 0.1$ nm [12], in good agreement with the values reported earlier [6, 9, 10]. (ii) There is a plateau at intermediate values of q (SAXS), between 10^{-2} and 10^{-1} nm^{-1}. In this region one would expect the usual liquid-like peak of the structure

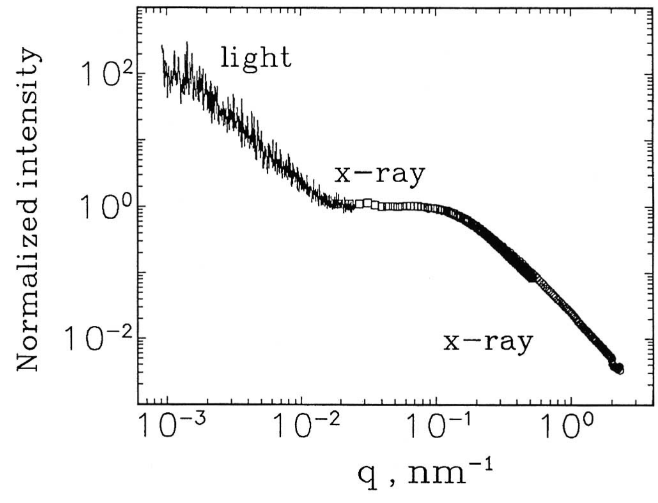

Fig. 1. Overview of the static scattered intensity $I_s(q)$ as obtained from the three scattering experiments. The intensities have been scaled to merge at the regions where the range in q overlaps.

factor. This is not observed in the gel state. (iii) At the smallest q (SLS), between 10^{-3} 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 [22], $S(q) - 1 \sim q^{-2.1}$, which is typical for a structure with self-similar, or fractal, properties [23]. This result is in qualitative agreement with a previous study by Pignon et al. [11] 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 inserted 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 [14], 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 [24]. 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 disks, as expected for a sol. Within a few hours the form factor decreases more rapidly than $(qR)^2$. This can be explained only by the orientational ordering of the disks, with their faces parallel to the windows. According to the Onsager criterion one expects an isotropic-nematic phase transition at only slightly higher volume

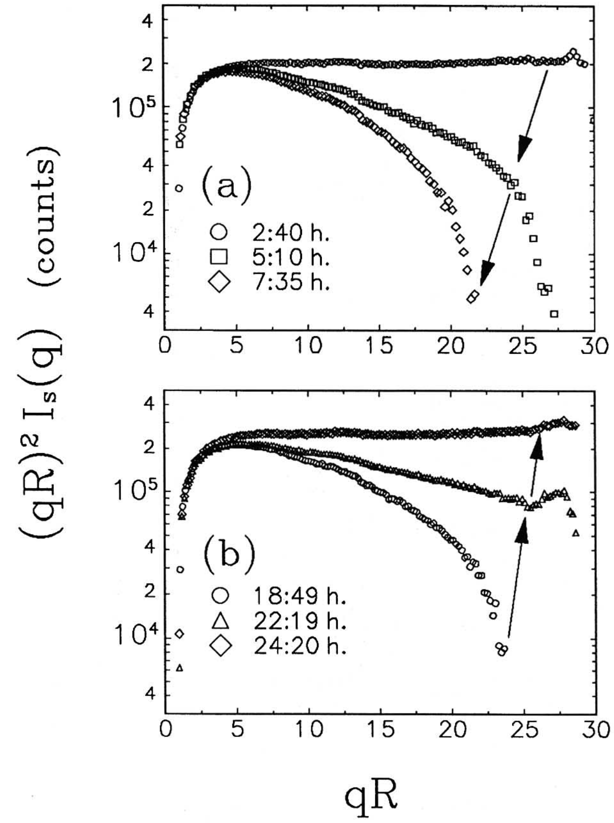

Fig. 2. Typical series of SAXS profiles of the colloidal suspension of disks after loading the sample in the cell under shear. Time after preparation is shown in the legend. The original SAXS profiles have been multiplied by $(qR)^2$. On this scale a horizontal straight line is obtained when dealing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

fractions. After 8 h however, this process is reversed and, after 40 h, the form factor times $(qR)^2$ is constant. Thus, the gel state also has a random orientation of the disks.

We have interpreted our data in terms of the nematic order parameter S_2 [2, 22]. A value $S_2 = 0$ denotes the absence of orientational order, whereas $S_2 > 0$ denotes orientational ordering of the disks with their faces parallel to the windows. Fits of this model to the experimental data yield the behavior shown in Fig. 3. The order parameter increases immediately

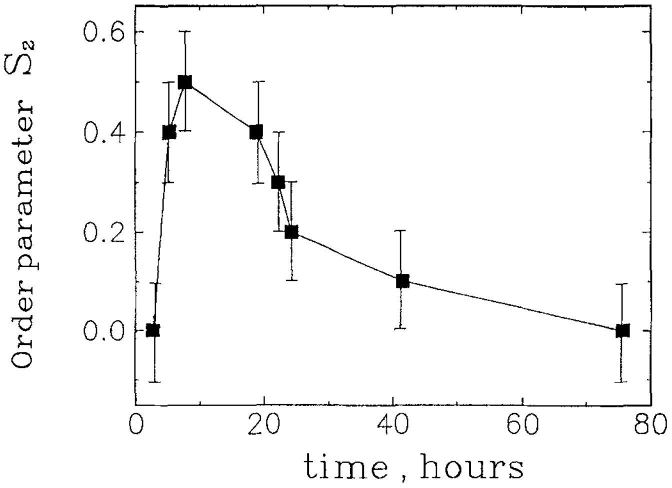

Fig. 3. Time dependence of the nematic order parameter S_2 characterizing the distribution function of the disk orientation, fitted to data in Fig. 2. The positive value of S_2 indicates a preferential ordering of the colloidal disks parallel to the container walls.

after sample preparation, reaches a maximum after 8 h and then decays to zero after 40 h. The error bars on S_2 in Fig. 3 are determined mainly by background corrections, which become increasingly important at the large qR.

At first sight it seems surprising that the colloidal disks tend to nematic-like order before returning to random orientations. This can be explained as follows: when inserting a gel in between two plates, one expects an "inverse plug flow." A thin low-viscosity boundary layer with a 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 by Chignon et al. [25]. The observed growth of nematic order is induced from the boundary layer inward, becoming thicker with time. At the same time, local reorientation driven by thermal motion breaks down the order, overtaking the first process and eventually leading to the observed random gel state.

4. CONCLUSIONS

We have measured the structure factor of the gel state of charged disks over three orders of magnitude 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 reorientation 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 [22]. They also refute aggregation—the growth of spatially defined clusters with characteristic orientation or density—as the road to gelation.

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REFERENCES

1. L. Onsager, *Ann. N.Y. Acad. Sci.* **51**:627 (1949).
2. P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Clarendon, Oxford, 1993).
3. D. Frenkel, in *Liquids, Freezing and Glass Transition*, J. P. Hansen, D. Levesque, and J. Z. Justin, eds. (North Holland, Amsterdam, 1991), p. 689. J. A. C. Veerman and D. Frenkel, *Phys. Rev. A*. **45**:5632 (1992).
4. Laponite (RD) is manufactured by Laporte Absorbents, P.O. Box 2, Cheshire, UK.
5. E. Trizac and J. P. Hansen, *J. Phys. Condens. Matter* **8**:9191 (1996).
6. J. D. F. Ramsey, *J. Colloid Interface Sci.* **109**:441 (1986).
7. R. G. Avery and J. D. F. Ramsey, *J. Colloid Interface Sci.* **109**:448 (1986).
8. L. Rosta and H. R. von Gunten, *J. Colloid Interface Sci.* **134**:397 (1990).
9. D. W. Thompson and J. T. Butterworth, *J. Colloid Interface Sci.* **151**:236 (1992).
10. A. Mourchid, A. Delville, and P. Levitz, *Faraday Discuss.* **101**:275 (1986).
11. F. Pignon, J. M. Piau, and A. Magnin, *Phys. Rev. Lett.* **76**:4857 (1996); F. Pignon, A. Magnin, J. M. Piau, B. Cabane, P. Lindner, and O. Diat, *Phys. Rev. E* **56**:3281 (1996).
12. M. Kroon, G. H. Wegdam, and R. Sprik, *Phys. Rev. E* **54**:6541 (1996).
13. M. Kroon, G. H. Wegdam, and R. Sprik, *Europhys. Lett.* **35**:621 (1996).
14. N. Willenbacher, *J. Colloid Interface Sci.* **182**:501 (1996).
15. E. Bartsch, M. Antonietti, W. Schupp, and H. Sillescu, *J. Chem. Phys.* **97**:3950 (1992); W. van Megen, S. M. Underwood, and P. N. Pusey, *Phys. Rev. Lett.* **67**: 1586 (1991).
16. G. Li, W. M. Du, J. Hernandez, and H. Z. Cummins, *Phys. Rev. E* **48**:1192 (1993).
17. C. A. Herbst, R. K. Cook, and H. E. King, *Nature* **361**:518 (1993); M. J. P. Brugmans and W. L. Vos, *J. Chem. Phys.* **103**:2661 (1995).
18. W. Götze and L. Sjögren, *Phys. Rev. A* **43**:5442 (1991).
19. H. van Olphen, *Clay Colloid Chemistry*, 2nd ed. (John Wiley, New York, 1977).

20. M. Dijkstra, J. P. Hansen, and P. A. Madden, *Phys. Rev. Lett.* **75**:2236 (1995); *Phys. Rev. E* **55**:3044 (1997).
21. A. Guinier and G. Fournet, *Small Angle Scattering of X-Rays* (Wiley, New York, 1955).
22. M. Kroon, W. L. Vos, and G. H. Wegdam, *Phys. Rev. E* **57**:, in press (1998).
23. H. E. Stanley and N. Ostrowsky, *On Growth and Form, Fractal and Non-Fractal Patterns in Physics* (NATO ASI No. 100, Kluwer, Dordrecht, 1986).
24. Furthermore, we found no pronounced differences in the observed tendency after inserting the suspension when using kapton or mica as window materials, although these materials are quite different. Mica can be wetted by water while kapton can not.
25. F. Pignon, A. Magnin, and J. M. Piau, *J. Rheol.* **40**:573 (1996).