Structure and Pertinent Length Scale of a Discotic Clay Gel

Frédéric Pignon, Jean-Michel Piau, and Albert Magnin
Laboratoire de Rhéologie, B.P. 53 38041 Grenoble Cedex 9, France

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A characteristic length scale of the structure of a thixotropic colloidal clay suspension of discotic texture was demonstrated by static light scattering. The length scale, of the order of a micron, corresponds to a fractal dimension that increases from 1 to 1.8 close to a critical volume fraction. Simultaneously, the change in yield stress with the volume fraction was studied by the vane method. A scaling law enabled these fractal dimensions to be correlated with the effect of the volume fraction on the yield stress. [S0031-9007(96)00429-2]

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The material investigated was a suspension of synthetic hectorite-type clay (Laponite). In an aqueous medium, this forms a transparent thixotropic gel above a certain volume fraction, at a low ionic strength ($\leq 5 \times 10^{-3}$ mol/l) and pH of 9.5. The clay consists of discotic particles of uniform size, about 30 nm in diameter and about 2 nm in thickness [1]. Owing to its high purity and very small crystal size, this is perfectly suited to light scattering measurements as, unlike natural clays at the same concentration, it does not produce any multiple scattering.

A matter of crucial importance in the field of colloidal suspensions is to relate the macroscopic bulk properties to the mesoscopic properties of the system, i.e., its structure. Indeed, this type of colloidal suspension exhibits strongly non-Newtonian behavior under shear. The main features of this are the appearance of a yield stress, the reversible time dependence of its viscoelastic properties and the localization of shear in the strain field [2]. These macroscopic properties depend to a great extent on the physical parameters of the system and must be closely linked with particle organization and interactions within the suspension. This is why it is of prime importance to establish relationships between the structural changes produced by variations in these physical parameters and the mechanical properties of the suspension.

Many structural models relating to this clay suspension have already been proposed by different authors in order to try to explain the mechanism of gel formation and its thixotropic behavior. Certain authors have described the formation of a so-called "house of cards" network, where electrostatic attraction appears to occur between the edges of the positively charged platelets and the negatively charged faces [3,4]. Others have concluded that the particles are associated with one another in tactoids, i.e., piles of two to four individual platelets separated by a few layers of water [5,6]. Finally, Ramsay and Lindner concluded from small-angle neutron scattering measurements that the formation of an equilibrium gel structure is due essentially to repulsion between the individual clay microcrystals [7]. They detected short-range correlation and alignment between the particles, in a structure which is isotropic over longer ranges.

The preceding studies revealed, on the one hand, the existence and nature of the interactions occurring between the suspended particles and, on the other hand, the structural schemes. However, as far as the present authors are aware, no pertinent length scale has been proposed for the structure in suspensions of Laponite. The purpose of this Letter is twofold: first, to identify these characteristic length scales and relate them to a macroscopic rheometric property of the suspension and second, to define the influence of the volume fraction on the value of the yield stress and identify a scaling law that will be related to the fractal dimension of the objects. The yield stress corresponds to the total energy that is required in the suspension to break the network of particles.

The clay is mixed in a solution of distilled water and NaCl at a concentration of 10^{-3} mol/l at a temperature of about 20 °C. Interactions between the particles develop during the swelling that occurs following preparation of the suspension. The suspended particles are then subjected to electrostatic repulsion and attraction effects that compete with the van der Waals attraction, interparticle volume effects, and Brownian motion. Changes were observed in the elastic moduli and fractal dimensions of the present system over periods of several weeks, but will not be reported here. This temporal instability is probably due, on the one hand, to osmotic swelling caused by repulsion between the double layers and, on the other hand, to the progressive organization of the particles in fractal aggregates over increasing distances. In the remainder of this discussion, the rest time elapsing between the end of the preparation phase and the performance of the test will be about 200 days, i.e., greater than the equilibrium gelation time. The pH value of all the preparations studied was adjusted to 9.5 in order to avoid any congruent dissolution of the material. Indeed, Thomson and Butterworth [8] showed that there is significant dissolution of magnesium silicate with pH values of less than 7. The study domain corresponds to that in which a thixotropic gel is obtained. With a weak ionic strength ([NaCl] $= 10^{-3}$ mol/l), at a

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pH of 9.5, this domain extends in concentration from 0.9×10^{-2} to 5×10^{-2} g/ml, corresponding to a volume fraction ϕ_v of 0.35 to 2%. The density of the particles is 2.53 g/cm^3 [6].

The structure was examined by static light scattering (SLS) over a wave vector domain ranging from 2×10^{-5} to 4×10^{-4} Å^{-1}. The scattering vector Q is defined as $Q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the suspending medium, λ the wavelength of the radiation, and θ the scattering angle. The laser test facility used for the experiment was developed and built at the Laboratoire de Rhéologie at Grenoble [9]. It consists of a 2 mW laser beam (He-Ne) with a wavelength $\lambda =$ 6328 Å and a Fresnel lens acting as scattering screen. The detector is a video camera with a charge coupled device 752×582 pixel sensor. Image processing is used for the analysis, and the conventional integration operations are carried out by a specific software. The sample is placed between two plates of glass in a parallel-sided shear cell. The thickness of the sample is fixed at 0.30 mm, and transmission measurements give satisfactory results for this thickness ($I_{\mathrm{trans}}/I_{\mathrm{inc}} \approx 0.95$).

Yield stress measurements were carried out using the vane method on a Weissenberg-Carrimed controlled speed rheometer. These enabled the change in yield stress to be defined as a function of volume fraction. The measurement principle is the following: Two fine rectangular blades intersect at 90° to form a cross ($h =$ 40.5 mm) high and ($d =$ 19.9 mm) in diameter. This vane is connected to a torque sensor and is plunged slowly into a recipient containing the suspension at rest. After waiting 10 min, the recipient is then rotated at an angular speed of 1×10^{-3} rad/s and the torque exerted by the suspension on the vane is recorded by means of torsion bars. This method has long been used in studying the mechanics of granular media and has already been employed on bentonite gels [10]. The stress σ_0 as a function of the torque T_0 is given by $\sigma_0 = (\pi d^3/2)(h/d + \frac{1}{3})T_0$. During start-up with a low shear rate, the stress increases linearly with time, corresponding to elastic strain of the material. There is then a deviation from this linear pattern, leading to a maximum stress, which is taken to be the yield stress of the suspension. The experimental error over the yield stress measured is 25%. This method was chosen as it causes little structural disruption when the vane is introduced into the sample. In addition, it avoids the phenomenon of wall slip which is frequently found with other conventional shear measurement geometries.

Light scattering measurements revealed a characteristic dimension of the structure of the order of a micron and enabled a fractal behavior depending on the volume fraction to be defined. Fractal behavior can be observed when there is a sufficient number of particles in the aggregate for it to have the same internal structure repeatedly over a length much larger than the size of the component particles. There is then a relation of the type $I(Q) \approx Q^{-D}$, in which D is the fractal dimension of the aggregate [11]. Figure 1(a) shows the intensity of scattering $I(Q)$ as a function of the wave vector, with a fixed ionic strength ([NaCl] $= 10^{-3}$ mol/l) and fixed pH (pH $= 9.5$). For all volume fractions, the intensity of scattering follows a Q^{-3} power law decay over a wave vector domain ranging from 2×10^{-4} to 1.2×10^{-4} Å^{-1}. This Q^{-3} power law decay has already been detected on Laponite gels [12,13] using SAXS, for a wave vector domain ranging from 5×10^{-4} to 3×10^{-3} Å^{-1}. This Q^{-3} power law decay, according to these authors, is attributed to the existence of microdomains which are connected to form a large scale dense structure. A break of this Q^{-3} power law around 1.2×10^{-4} Å^{-1} then extends $I(Q)$ by another power law of the type Q^{-D} over a wave vector domain ranging from 1.2×10^{-4} to 2×10^{-5} Å^{-1}. The change in the slope $I(Q)$ near a wave vector equal to 1.2×10^{-4} Å^{-1} and the fractal behavior demonstrate the existence of micron-sized aggregates. The fractal dimension D over this domain depends on the volume fraction. Experimental data scatter over fractal dimensions D is

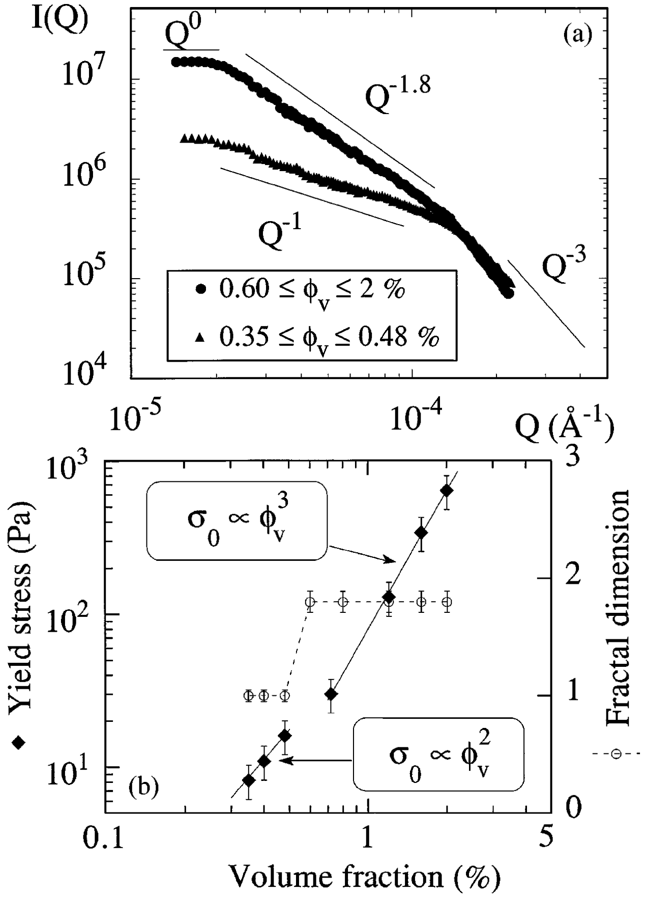

FIG. 1. (a) SLS of suspension of Laponite under static conditions at different volume fractions. (b) Evolution of yield stress at different volume fractions. [NaCl] $= 10^{-3}$ mol/l, pH $= 9.5$.

5%, taking into account several measurements at all volume fractions. For a volume fraction close to the sol-gel transition ($\phi_v \approx 0.35\%$), the fractal dimension D is equal to 1 ± 0.05, suggesting a very loose filament arrangement of the micron-sized aggregates. When the volume fraction increases beyond 0.55%, the critical concentration, there is a sudden variation in the fractal dimension, which rises from unity near the sol-gel transition to 1.8 ± 0.1 for immediately higher volume fractions. The fractal dimension of 1.8 suggests a more compact arrangement of the micron-sized aggregates, possibly obtained through the diffusion-limited aggregation model [14] or the cluster-cluster aggregation model [15]. Finally, at Q values below 2×10^{-5} Å^{-1}, the scattering curve becomes flat, indicating that there are no heterogeneities of sizes larger than $R = 5$ μm, the maximum radius of gyration of the fractal aggregates.

A scaling law [9] developed on a silica-silicon compound in a semidilute [16] fractal object domain enables the fractal dimension measured by light scattering to be linked to the change in yield stress as a function of the volume fraction. The scaling law is defined as follows: $\sigma_0 \approx \beta(kT/a^3)\,(R/a)\,(\Phi_v)^{4/(3-D)}$, in which σ_0 is the yield stress, ϕ_v the particle volume fraction, D the fractal dimension, β take into account the rigidity of the structure, as well as a volume fraction cofactor due to the inner density of subunits and in addition effective interaction much larger than kT. k is the Boltzmann constant, T the temperature, a the radius of a single particle (here a single subunit), and R the radius of gyration of the aggregates.

Yield stress measurements using the vane method show that there are two power law relations governing yield stress as a function of the volume fraction Fig. 1(b). The first (dependence to power 3 ± 0.3) occurs with gels whose volume fraction ranges from 0.6% to 2%. With these gels, the fractal dimension of the micron-sized aggregates is 1.8 ± 0.1, corresponding to a prediction $\sigma_0 \propto \Phi_v^{3.3\pm0.3}$, according to the above scaling law. The second dependence (power 2 ± 0.3) occurs with gels close to the sol-gel transition ($\phi_v = [0.35, 0.48]\%$). With these low volume fractions, the fractal dimension of the micron-sized aggregates is 1 ± 0.05, which gives a yield stress behavior of the type $\sigma_0 \propto \Phi_v^{2\pm0.05}$, using the scaling law.

There is obviously good agreement between the rheometric measurements and the predictions based on the scaling law associated with light scattering measurements. The change in behavior of the yield stress near the critical concentration (around 0.55%) is correctly described by both the light scattering measurements and rheometric measurements. Below the critical concentration a fractal dimension of unity suggests a beam-type alignment of the micron-sized aggregates, leading to the formation of a mechanically weak fibrous structure. Beyond the critical concentration, the transition to a fractal dimension of 1.8 would then correspond to an entanglement of these fibers that would thus form a denser network of the micron-sized aggregates, which is mechanically more resistant (Fig. 2).

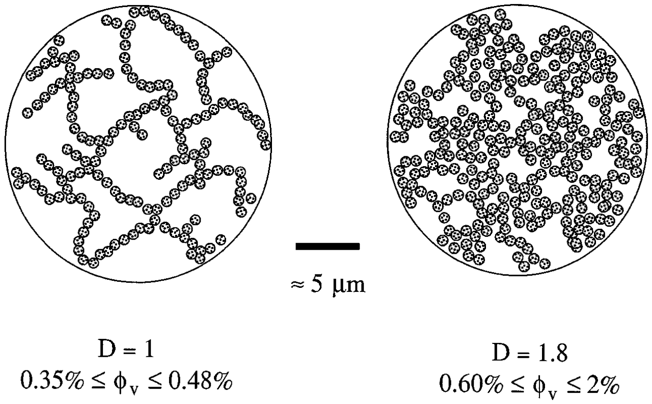

FIG. 2. Structure of Laponite according to volume fractions and fractal dimensions.

In conclusion, this study of a discotic colloidal clay suspension identified a characteristic length scale of the structure of the order of a micron. The network that is created as the suspension swells, leading to the formation of a thixotropic gel, is due to the formation of micron-sized aggregates with a fractal dimension that depends on the volume fraction. This influence of the volume fraction on the fractal dimension was correlated with the change in yield stress according to volume fraction by means of a scaling law.

This work stresses the following point: It is necessary to conduct a careful analysis of the structure of concentrated colloidal suspensions in order to understand their rheological behavior. A correlation was established between the fractal dimensions and the yield stress, a rheometrical property of this clay suspension. It can be noticed that the influence of the fractal dimension on a change in a yield stress as a function of pH in natural clay suspensions of Bentonite [17] has already been pointed out, as well as its influence on the change in elastic moduli with volume fraction in boehmite alumina gels [18]. All these correlations suggest that the gels at hand are suspensions of big objects, made by a more or less open aggregation of dense subunits. This point is crucial as it is these scales of the largest structure (the big objects) that are mainly responsible for the rheological behaviors observed in these types of suspension.

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