Applied Clay Science 162 (2018) 83–89

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

# Cylindrical Couette flow of Laponite dispersions

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ARTICLE INFO

*Keywords:*
Laponite
Gelation
Light scattering
Rheology
Taylor-Couette flow

ABSTRACT

Taylor-Couette flow of aqueous dispersions of nanometric Laponite platelets was studied by dynamic light scattering and direct observation. Despite high rotation rates, gel growth was observed starting from the stator, and filling almost the whole gap after some period of time depending on the angular velocity of the rotor. SEM microscopy observations of the flowing liquid showed the presence of spheres in the micrometer range. A mechanism for gel growth is proposed, where lumps of gel are formed in the sheared liquid and form spherical aggregates which eventually adhere to the side of the gel, with a progressing gelling front.

## 1. Introduction

Laponite, a synthetic clay mineral similar to Hectorite (Kloprogge et al., 1999; Nicolai and Cocard, 2000), is widely used as an additive in many industrial applications such as creams or other cosmetic pastes. Laponite is a white powder with aggregates of micrometric size, which separate into individual platelets of 25 nm in diameter and 1 nm in height in water. Due to the anisotropy of the chemical composition, there is a negative electrical charge on the sides and a positive one on the faces of the platelets when dispersed in water, with a net negative charge. The interesting particularity of the system is to form a reversible gel when dispersed in aqueous dispersions (Tanaka et al., 2004; Joshi, 2014), whose nature and structure is under debate (Bonn et al., 1999a; Pek-Ing and Yee-Kwong, 2015) and which also led to extensive fundamental research in the field of gelation mechanisms (Bonn et al., 1999a; Tanaka et al., 2005) and rheology (Bonn et al., 2002a). Being a synthetic material, and thus with a composition more controlled than natural clays, Laponite has been a model system for the study of gel or glassy system in order to elucidate the underlying physical mechanisms. However, the studies proved to be arduous due to the extremely rich behaviour depending on the experimental conditions such as pH, ionic strength, counter-ions and dispersant (Jabbari-Farouji et al., 2008; Mongondry et al., 2005), and their sensitivity to history and preparation (Bonn et al., 1999a). Light scattering experiments on Laponite gels showed a Wigner glass nature, where the solid-like behaviour originates from caging effects (Ruzicka et al., 2004; Bonn et al., 1999b, 2002b). On the other hand, a "house of card" type percolated network is believed to form at high ionic strength (Pek-Ing and Yee-Kwong, 2015; Mourchid and Levitz, 1998).

Laponite gels are often described as displaying shear rejuvenation, where viscosity decreases upon shearing due to the destruction of the structure formed in the gel. However, it has been shown that this destructuration is not complete, and that individual platelets can never be recovered (Bonn et al., 2002b). In the past few years, more energy has been devoted to understand aging and rejuvenation under shear in a precise way (Manneville, 2008), leading to the investigation of local flow profiles. These experiments highlighted the occurence of shear banding or shear localization, where the flow profile diverges from the theoretical one and displays unsheared regions as well (Gibaud et al., 2009; Martin and Hu, 2012; Ianni, 2007).

A typical shearing geometry, very well-studied in the field of fluid mechanics, is the cylindrical Couette cell, consisting in the general case of two concentric cylinders which can rotate independently. A large variety of flowing regimes can be observed, from laminar to complex spirals (Green et al., 1970). In particular, if the outer cylinder is at rest and the inner one is rotating, the flow undergoes several transitions from a laminar regime to Taylor-Couette vortices, which in turn are modulated and eventually attain fully developed turbulent flow. This geometry has been thoroughly investigated and is a model system for fluid mechanics.

In previous works (Gibaud et al., 2009; Martin and Hu, 2012; Ianni, 2007), the effects of shear have often been studied in order to understand rejuvenation, or gel destructuration, under external sollicitations, and gel formation is often investigated at rest. Some authors studied the effect of oscillatory shear on such dispersions (Shukla and Joshi, 2009; Joshi et al., 2012) and found a viscosity increase after performing oscillatory experiments on samples that were left at rest for one day. On the contrary, our aim is to investigate Laponite flow and gelling starting

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https://doi.org/10.1016/j.clay.2018.05.030
Received 22 December 2017; Received in revised form 27 April 2018; Accepted 28 May 2018

from a freshly prepared dispersion, where the applied shear is continuously maintained for a long time. The initial motivations of this study were to examine the effect of a strong non-Newtonian behaviour on the transition towards Taylor-Couette vortices, and thus to extend the study of this system for the flow of ceramic dispersions. In order to measure local quantities of interest, dynamic light scattering (DLS) has been selected for this study. Depending on the experimental configuration, this technique allows measuring velocity, shear rate or diffusion coefficient, in a non invasive way.

## 2. Materials and methods

### 2.1. Material preparation

RD Laponite powder was purchased from Rockwood Chemicals and used as received. The necessary amounts of Laponite and water for dispersions 3% in mass were prepared in a centrifugal mixer (ARE 250, Thinky, Japan) with a cycle of 3 min at 1000 rpm and 5 min at 1500 rpm, and used immediately. After this procedure, the resulting dispersions were clear, indicating that Laponite had dispersed into single platelets. A transmission electron microscopy picture (JEOL 2100F, Japan) of a single platelet is shown in Fig. 1.

The refractive index of Laponite is $n_l = 1.34$. Being almost index-matched with water, and thanks to its nanoscopic size, the dispersion can be considered as dilute from an optical point of view, and thus appropriate for light scattering measurements, even at high solid volumic fractions.

Rheological measurements were performed on a stress-controlled rheometer (ARG2, TA Instruments, USA). In order to characterize the flow behaviour of the freshly prepared dispersion, sweep measurements were performed with a titanium cone geometry (diameter 60 mm and angle 2°). After a pre-shear of several minutes at the maximum shear stress ($\sigma = 2.5$ or 3 Pa), stress *versus* shear rate data was measured on 20 values sampled between the maximum value and the minimum (close to zero). For each sampling point of the sweep, steady-state values were recorded, where the shear rate $\dot{\gamma}$ averaged over 20 s was stable within 5% for 3 consecutive evaluations. A power law behaviour could be fitted to the data, with $\sigma = 5.2 \times 10^{-3}\dot{\gamma}^{0.97}$. The dispersion was almost Newtonian when freshly prepared.

### 2.2. Flow cell

The fluid was sheared in a Couette geometry, consisting of two concentric cylinders: the outer one is fixed (stator), and the inner one (rotor) is rotating by means of a brushless motor (Crouzet, France). A custom made Couette cell was processed in transparent PMMA, following a design close to ref. (Salmon et al., 2003). The outer cell shape is square. The stator and rotor radii are respectively $R_S = 20$ mm and $R_R = 15.9$ mm, leading to a ratio $\alpha = R_S/R_R = 1.26$. The cell is filled up to a height of $H = 51$ mm, corresponding to an aspect ratio $H/e = 12.44$. The dimensionless number describing the system is the Taylor number defined as:

$$Ta = \frac{2\omega^2 R_R^2 e^3}{\nu^2 (R_R + R_S)} \quad (1)$$

where $e$ is the inter-cylinder gap, $R_R$ and $R_S$ the rotor and stator radii respectively, $\omega$ the angular velocity, and $\nu$ the fluid kinematic viscosity. The transition towards non laminar flow starting with Taylor vortices occurs at a critical Taylor number defined as (Chandrasekhar, 1961):

$$Ta_c = 1695\left(1 + \frac{e}{2R_R}\right) \quad (2)$$

leading to a value of $Ta_c = 1914$ with the current geometrical parameters. Except for end effects, the analytical expression for the laminar velocity profile can readily be obtained. Due to symmetry considerations, the velocity is radial $v_\phi(r)$ and depends only on the position $r$. The following equation has to be integrated by considering the relation between torque and shear stress in this geometry, and with the appropriate viscosity function:

$$\dot{\gamma}(r) = r\frac{d}{dr}\left(\frac{v_\phi(r)}{r}\right) \quad (3)$$

For a power law behaviour $\sigma = K\dot{\gamma}^n$ such as the one obtained for the suspension, the velocity profile becomes:

$$v_\phi(r) = \frac{\omega}{\alpha^{2/n} - 1}\left(\frac{R_S^{2/n}}{r^{2/n-1}} - r\right) \quad (4)$$

The shear rate $\dot{\gamma}(r)$ is not uniform:

$$\dot{\gamma}(r) = \frac{2}{n}\frac{\omega}{\alpha^{2/n} - 1}\frac{R_S^{2/n}}{r^{2/n}} \quad (5)$$

In order to estimate $Ta$ for our system, the viscosity has to be known. For the case of non-Newtonian fluids, $\nu$ depends on the shear rate, which is not constant through the gap. Usually, this value is taken at the rotor:

$$\dot{\gamma}_{R_R} = \frac{2}{n}\omega\frac{\alpha^{2/n}}{\alpha^{2/n} - 1} \quad (6)$$

With the rate index of $n = 0.97$, the difference with the Newtonian case is about 2%, and can be neglected.

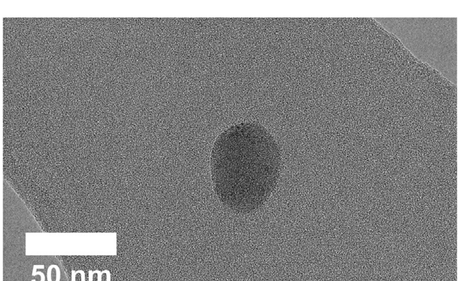


**Fig. 1.** Transmission electron microscopy (TEM) picture of a single platelet of Laponite. Scalebar: 20 nm. Due to its small thickness, the platelet was destroyed by the electron beam during the TEM observation.

### 2.3. Optical bench

The DLS approach consists in analysing the time fluctuations in the light scattered from a sample illuminated by a polarised laser of wavelength $\lambda_0$ (incident vector $k_i$) at a given angle $\theta$ (scattered vector $k_s$). For the case of colloidal suspensions, light scattering occurs because there is a refractive index mismatch between the particle and the surrounding medium, giving rise to a non homogeneous dielectric permittivity of the scattering volume. Time fluctuations in the scattered intensity are due to the motion of the particles in the solvent, resulting in fluctuations in this dielectric permittivity. For diluted (non interacting) dispersions at macroscopic rest, these fluctuations are related to the size of the scatterer since the exponential decays depends on the Brownian diffusion coefficient of the colloids and on the viscosity of the surrounding medium. For colloids with stronger interactions, the exponential decay is more complex to analyse, and encompasses collective effects and contribution of larger size distributions (Barretta et al., 2000). For the case of a flowing fluid however, the fluctuations originate from the macroscopic motion of the scatterers. By combining the scattered light with a small portion of the incident beam, the resulting correlation function $g(t)$ takes the following form for the case of flowing fluid (Pecora, 1985):

$$g(t) = +Bexp^{-\lambda_1 t}\cos(\lambda_2 t) \quad (7)$$