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Ageing, shear rejuvenation and avalanches in soft glassy materials

Daniel Bonn[1,2], **Hajime Tanaka**[3], **Philippe Coussot**[4]
and Jacques Meunier[1]

[1] Laboratoire de Physique Statistique, Ecole Normale Supérieure, Paris, France
[2] van der Waals-Zeeman Institute, University of Amsterdam, The Netherlands
[3] Institute for Industrial Science, University of Tokyo, Japan
[4] LMSGC, Champs-sur-Marne, France

E-mail: bonn@lps.ens.fr

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Abstract

We study the nonlinear rheological behaviour and the microscopic particle dynamics for a colloidal glass. The measurements allow us to relate the microscopic diffusion dynamics to the macroscopic viscosity of the system. We demonstrate that the competition between the spontaneous restructuration (ageing) and the destruction of the internal structure by the shear ('shear rejuvenation') leads to a bifurcation in rheological behaviour. For a stress smaller than a (time-dependent) critical value, the viscosity increases in time and the material eventually stops flowing. For slightly larger stresses the viscosity decreases continuously with time and the flow accelerates. Thus the viscosity jumps discontinuously to infinity at the critical stress.

Glasses are a nonequilibrium form of matter and are, maybe for that reason, still ill understood. The usual way of looking at the glass transition is given by the so-called mode-coupling theory. In this theory, the glass transition is a strong ergodic to non-ergodic transition. In real systems, however, the 'transition' always appears rounded. The rounding of the transition is due to the appearance of a 'slow mode' in the system. The ageing is then the nonequilibrium evolution of a system quenched into a glassy state. Understanding the ageing processes in a glassy system is crucial for the description of glassy dynamics [1].

We will focus here on the behaviour of the colloidal glass of Laponite, a synthetic clay consisting of discoid colloidal particles with a diameter of 25 nm and a height of 1 nm. We use this system as it allows determining both the microscopic diffusion dynamics and the rheological behaviour in detail. Solutions of Laponite are strongly viscoelastic, even at very low particle concentrations. The formation of a gel, evidenced by the existence of a fractal

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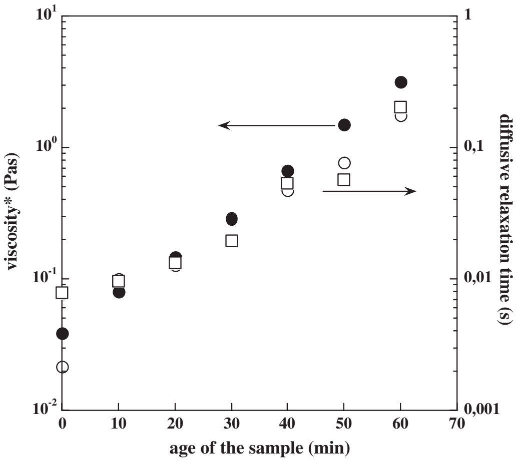

Figure 1. Complex viscosity and diffusive relaxation time (see figure 2) as a function of the age of the sample. Both behave very similarly and show a roughly exponential increase with the age of the sample.

network, has been invoked in explaining the viscoelasticity. We previously studied the structure and viscosity of Laponite using static light scattering [2]. Contrary to previous observations, we find no evidence of a fractal-like organization of the colloidal particles in the absence of salt. Therefore, it has now been firmly established that, for our concentration and salinity, it is in fact a colloidal glass stabilized by electrostatic repulsions [2–4], without any structuration at large length scales, making its microstructure fundamentally different from that of gels. For higher salinities, a gel may form (see [3], and references therein, for a complete discussion of the phase diagram) with a structure quite different from that of a glass.

The experiments are performed by dissolving the particles at a concentration of 3.5 wt% in ultrapure water (corresponding to a volume fraction $\phi = 0.014$) with NaOH to obtain a pH $= 10$. We dissolve the Laponite under vigorous stirring for 15 min and subsequently pass the solution through a Millipore Millex AA (0.8 μm) filter, to obtain a reproducible initial liquid state. In order to allow for the diffusive wave spectroscopy measurements of the dynamics, we add a small quantity of 0.5 μm latex particles to the samples after filtration. We subsequently let the sample age.

A direct measurement of the viscosity during the ageing shows that the viscosity increases with time. These measurements are performed on a Reologica Stress-Tech rheometer in a Couette geometry with a gap of 1 mm. In order not to disturb the system by a continuous shear, the measurements are performed using small oscillations at a frequency of 0.1 Hz at an imposed stress of 0.5 Pa. Such oscillation measurements yield the dynamic moduli G' and G'', the storage and loss modulus, respectively. The complex viscosity η^* can be calculated from these quantities by using $\eta^* = (G'^2 + G''^2)^{1/2}/\omega$. In figure 1 we plot the complex viscosity as a function of ageing time. It can be observed that the viscosity changes by three orders of magnitude over a time that is of the order of an hour.

The key structural parameter that characterizes the ageing is the slowing down of the diffusion of the colloidal particles [4]. The diffusion process can be characterized by looking at the correlation functions of particle positions for different ageing times. This we do by diffusing wave spectroscopy [5]. By our method of preparation, we have in fact performed a quench into the glassy phase. We can subsequently follow the dynamics of glass formation

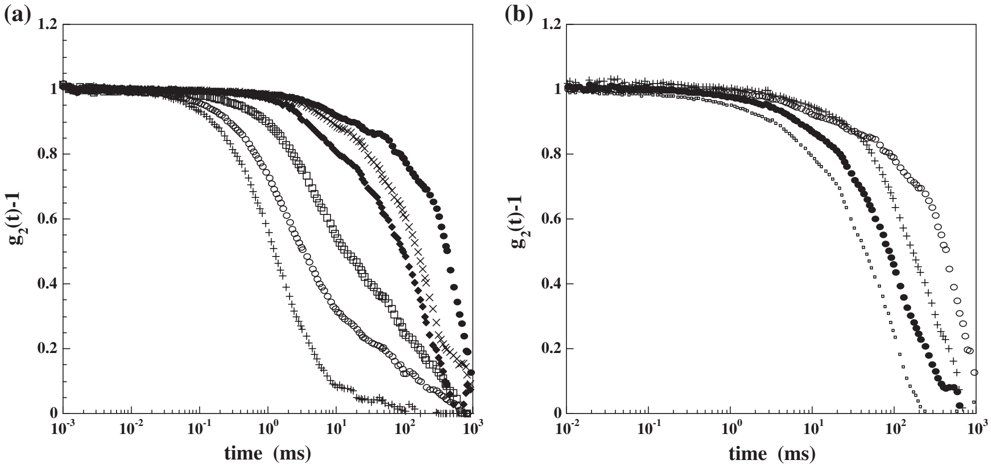

Figure 2. (a) Ageing of the Laponite sample: correlation functions measured using diffusive wave spectroscopy at different ages of the sample. The decay of the correlation function is a measure for the time a particle needs to 'forget' its initial position (at time zero). Therefore, as the sample ages, the diffusive relaxation time increases. The ageing increases in time steps of 10 min going from left to right. (b) Shear rejuvenation of the Laponite sample: correlation functions measured using diffusive wave spectroscopy for different shear rates. The curve to the right is the reference without shear, and after 1 h of ageing. After that, from right to left: shear rates of 0.25, 2.5 and 25 s^{-1} respectively.

in time, using diffusive wave spectroscopy to measure the diffusion of the colloidal particles. This is depicted in figure 2, where the measured correlation functions are shown as a function of the age of the samples. The characteristic diffusion times extracted from these measurements are shown in figure 1. The results can be described in terms of a cage-diffusion process [4]. For short ageing times, the dominant dynamical process is the escape of the particles from dynamic 'cages' formed by neighbouring particles. However, at long times the cages stiffen; the particles cannot escape any more, and the diffusion becomes much slower, concomitant with the increase in viscosity of the sample (figure 1).

The important observation that we make here is that if, after a certain ageing time, the sample is submitted to a continuous shear, both the viscosity and the diffusion time decrease [5]. This is shown in figure 2(b) for the diffusion, and figure 3 for the viscosity. Therefore, the shear reverses the ageing process, and consequently allows the glass to 'rejuvenate'. The incipient flow therefore destructures the material, entailing a viscosity decrease. If the measurements are performed under constant stress conditions, the shear rate will consequently increase, and the destructuration will be stronger. This will in turn accelerate the flow again and so on: an avalanche behaviour results [6].

This behaviour turns out to be qualitatively similar amongst a very large number of structured fluids: colloidal glasses, colloidal and polymer gels, foams and emulsions, and even granular matter [6, 7]. The common denominator between these physically very different systems is that they are all believed to exhibit a yield stress: if they are solicited below a certain critical (yield) stress, they do not flow, but respond elastically to the deformation. An ideal yield stress fluid can be defined as a fluid for which the stress (the shear force per unit area) goes to a finite nonzero value, the yield stress, if the shear rate (the velocity gradient) goes to zero. As a consequence, the steady-state viscosity (the ratio of shear stress to shear rate) diverges in a continuous fashion when the yield stress is approached from above [8].

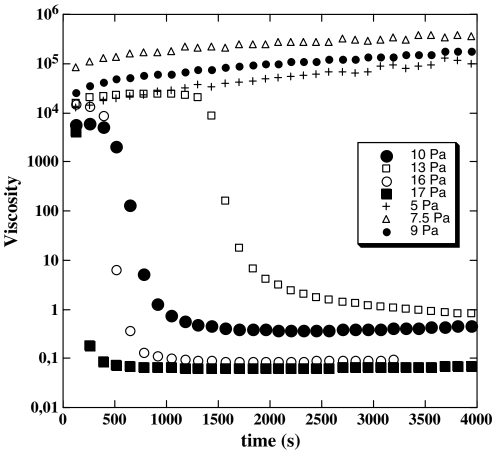

Figure 3. Bifurcation in the rheological behaviour: viscosity as a function of time for the colloidal glass: 3% Laponite RD in water at pH = 10.

In practice it has proven very difficult to experimentally determine a yield stress for a given fluid: very different answers can be obtained depending on the experimental protocol [8]. In view of the above, it is likely that the most important reason for the difficulty of determining a yield stress is the competition between ageing and shear rejuvenation. Because of the ageing, the yield stress becomes time dependent, and because of the shear rejuvenation, it also depends on the shear history. For typical yield stress fluids such as clay suspensions, emulsions and foams, the yield stress is mostly due to the microstructure of the fluid that resists large rearrangements: the system is jammed and stops or starts flowing abruptly. When submitted to flow, this microstructure is partly destroyed, which is generally observed in rheological tests as a viscosity that slowly decreases in time: the system is said to be thixotropic. In addition, for most of these systems at rest the microstructure reforms or evolves spontaneously: the system *ages* also. If the microstructure reestablishes at rest, experimentally, one observes an increase of an apparent yield stress with time. The mechanical behaviour of these systems consequently results from the competition between ageing and progressive 'rejuvenation' (destruction of the microstructure) by the shear flow [6].

Due to the effect of flow on the microstructure, for different 'typical' yield stress fluids, it is therefore impossible to unambiguously define a yield stress. Our experiments show that typical yield stress fluids (gels, clay suspensions) and soft glassy materials (colloidal glasses) do *not* have such a well-defined yield stress. Instead, they exhibit a (time-dependent) critical stress at which the viscosity jumps discontinuously to infinity [6].

As a typical example we consider Laponite again. For the data shown in figure 3, the Laponite solution was presheared and left to rest for a given fixed time to obtain a reproducible initial state. Starting from this state, we observe that, above a critical stress, the viscosity decreases to reach a low steady-state value after a long time. For a stress smaller than this critical value the viscosity increases indefinitely. Therefore, around the critical stress σ_c the flow either stops completely or evolves through the avalanche effect to a rapid flow: the shear destructures the material, whose viscosity consequently decreases. Because the stress is imposed, this leads to a higher shear rate, and therefore to an even larger destructuration and so on (figure 3). For stresses slightly smaller than σ_c, the viscosity increases in time, until the flow is halted altogether: *the steady-state viscosity is infinite*. This implies that at the critical

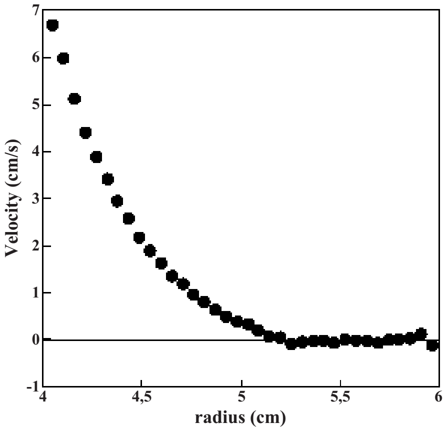

Figure 4. Typical velocity profile under imposed low shear rate for the 3.5 wt% Laponite colloidal glass, in which the shear localization is clearly visible. The velocity profile is made in a Couette cell with a rotation inner cylinder of 4 cm radius, and a stationary outer cylinder of 6 cm radius.

stress, the steady-state viscosity jumps discontinuously from infinity to a finite and low value at σ_c. This is in striking contrast with what an ideal (Herschel–Bulkley) yield stress fluid would do [8].

Another very important consequence of the viscosity bifurcation is that it naturally leads to shear localization. We all know that the shear invariably localizes in a narrow band for typical yield stress fluids (foams, emulsions, granular matter, and so on). This is *not* predicted for ideal (Herschel–Bulkley) yield stress fluids; for those fluids $\sigma = \sigma_y + a\dot{\gamma}^n$; this means that any shear rate can be realized provided the stress is close enough to the yield stress σ_y [8]. The bifurcation, on the other hand, shows that stable flows are impossible below a critical stress σ_c, and that at that stress there is a discontinuous jump in the shear rate from a finite and rather large value to zero. What happens if we impose a shear rate (rather than a stress) that is between the large finite value and zero is shown in figure 4: the shear localizes [6, 9]. These experiments were performed with a velocity controlled ‘MRI-rheometer’, which allows for a direct measurement of the local velocity distribution in a Couette geometry using proton magnetic resonance velocimetry in a home-made rheometer [10]. The shear localization is a natural consequence of the viscosity bifurcation, and can easily be included in a model that features both ageing and shear rejuvenation [6]. This therefore solves, we believe, the yield stress puzzle.

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