Nonlinear rheology of Laponite suspensions under an external drive

Bérengère Abou, a) Daniel Bonn, and J. Meunier

Laboratoire de Physique Statistique, UMR CNRS 8550, Ecole Normale Supérieure, 24, Rue Lhomond, 75005 Paris, France

(Received 5 November 2002; final revision received 13 March 2003)

Synopsis

We investigate the nonlinear rheological behavior of colloidal suspensions of Laponite, a synthetic clay, driven by steady homogeneous shear strain. We show that the external drive leads to drastic slowing down of the aging dynamics or even, in some cases, in rejuvenation of the system. Under shear, after a surprisingly long time, the spontaneous aging process observed at rest is suppressed. The system then reaches a nonequilibrium stationary state that is characterized by complex viscosity depending on the shear rate applied. In addition, the glass exhibits non-Newtonian shear-thinning behavior. This rheological behavior confirms recent numerical and theoretical predictions. © 2003 The Society of Rheology. [DOI: 10.1122/1.1574022]

I. INTRODUCTION

Complex fluids, such as foams, emulsions, pastes and slurries, are known to exhibit a rich phenomenology of nonlinear rheological behavior [Larson (1999)]. In particular, similar low frequency shear rheology is observed for a wide range of these soft materials [see Fielding et al. (2000) for a review]. For many of these materials, the stress response $\sigma$ to shear strain of constant rate $\dot{\gamma}$ is described by $\sigma = A + B\dot{\gamma}^{n}$ that leads to non-Newtonian viscosity [Barnes et al. (1989)]. This common rheological behavior was recently attributed to two properties of these materials, structural disorder and metastability, resulting in a “glassy” dynamics, where thermal motion alone is not sufficient to achieve complete structural relaxation [Sollich et al. (1997); Sollich (1998)].

Due to long-range interactions, it turns out to be a complex task to predict the nonlinear rheological behavior, including non-Newtonian viscosity, on the basis of the structure and interactions in these systems. Numerical simulations have allowed to predict the relationship between the material’s microstructure and its macroscopic properties [Melrose and Ball (1995); Melrose et al. (1999a,b); Brady and Foss (2000)]. Recently, a different approach to the rheology of these “soft” glassy materials has been developed, starting from a model of a glassy system instead of taking all the interactions—including colloidal and hydrodynamic interactions—into account. Because of both their practical and fundamental interest, the nonlinear rheology of such soft glassy systems subjected to external drive has recently attracted particular attention. This was done either by extending approaches for the description of glassy dynamics [Sollich et al. (1997); Cugliandolo

a)Author to whom correspondence should be addressed. Present address: Laboratoire de Bio-rheologie et Hydrodynamique Physico-chimique, UMR CNRS 7057, Université Paris VII, 4 Place Jussieu, 75005 Paris, France. Electronic mail: abou@ccr.jussieu.fr

© 2003 by The Society of Rheology, Inc.
et al. (1997); Sollich (1998); Berthier et al. (2000); Barrat and Berthier (2000); Fielding et al. (2000)] or based on phenomenological approaches [Hébraud and Lequeux (1998); Dérec et al. (2001); Coussot et al. (2002a,b)]. The most interesting situation occurs when the relaxation time scale of the system becomes of the same order of magnitude as the time scale introduced by the shearing process. This usually happens in glassy systems because the typical relaxation time grows together with the waiting time $t_w$, that is, the time that has elapsed after quenching from the ”liquid” into the ”glassy” state.

At rest, the properties of glassy systems thus depend on the waiting time: the system is said to age. Recent theoretical and numerical work, initially developed for supercooled liquids, has allowed an initial detailed description of the aging process [Bouchaud et al. (1996); Kob and Barrat (1997)]. Glassy systems exhibit two modes of relaxation: a fast mode that corresponds to the fast motion of particles in “cages” constituted by their neighbors and a slow mode of relaxation that results from structural rearrangement of these cages. The strongest experimental evidence of the applicability of such predictions (including the classical mode-coupling approach) comes from colloidal glasses [Pusey and Van Megen (1987); Nelson and Allen (1995); Bonn et al. (1999a,b); Abou et al. (2001)]. Because of the experimental advantages they present compared to structural glasses, in which there are two coupled control parameters, temperature and density, these colloidal glasses have been studied extensively.

In this paper, we investigate experimentally the response of a colloidal glass of Laponite to steady shear strain of constant rate. The experimental materials and methods are described in Sec. II. Section III presents the rheological experiments. We discuss our experimental results and conclude in Sec. IV.

II. MATERIALS AND METHODS

The experiments were performed on Laponite RD, a synthetic clay manufactured by Laporte Industry. The chemical composition of the clay is as follows: SiO$_2$, 65.82%; MgO, 30.15%; Na$_2$O, 3.20%; LiO$_2$, 0.83% and corresponds to the chemical formula $\text{Si}_8\text{O}_{24}\text{Mg}_{5.45}\text{Li}_{0.40}\text{H}_{24}\text{Na}_{0.75}$. The particles of Laponite are colloidal disks of 25 nm diameter and 1 nm thickness, with negative surface charge on both faces [Kroon et al., (1998)]. The clay powder was mixed in ultrapure water and NaCl at different clay concentrations of between 2% and 5 wt %. The ionic strength of the suspension, denoted $I$, was subsequently adjusted by dissolution of NaCl in water, in the range $10^{-4} < I < 8 \times 10^{-3}$ M. The $pH$ value of the suspensions was fixed at $pH = 10$ by the addition of NaOH, thereby providing chemically stable particles [Thompson and Butterworth (1992); Mourchid and Levitz (1998)]. The suspension was stirred vigorously for 15 min and then filtered through a Millipore Millex-AA 0.8 μm filter. This preparation procedure allows us to obtain a reproducible initial liquid state. The aging time $t_w = 0$ of the suspension is defined as the moment it passes through the filter. For time varying from a few minutes to a few hours for the different concentrations and ionic strengths considered here, a three order of magnitude increase in suspension viscosity was observed. Being in liquid state right after preparation, the suspension becomes more and more viscous and does not flow anymore. Since the physical properties of the suspension depend on the time that has elapsed since preparation $t_w$, the sample is said to age. The aging dynamics can be characterized by oscillatory shear experiments in order not to disturb the system. These measurements are performed using small oscillations at frequency of 1 Hz with imposed stress of 0.1 Pa. They yield $G'$ and $G''$, the elastic and loss moduli, respectively. The complex viscosity modulus $\eta^*$ can be calculated from these quantities by $\eta^*$...
$\eta(t) = (G' + G''/\omega)^{1/2}$. It can be observed that the viscosity changes very rapidly, by two orders of magnitude over about 1 h, as shown in Fig. 1.

Thus, suspensions of Laponite become strongly viscoelastic over time, even at low volume fraction $\Phi$ in particles (of the order of $\Phi = 0.01$). The formation of a gel, evidenced by the existence of a fractal network, has been invoked to explain the viscoelasticity [Pignon et al. (1997); Mourchid and Levitz (1998)]. Recently, the structure and viscosity of Laponite suspensions at ionic strength $I = 10^{-4}$ M were studied using static light scattering [Bonn et al. (1999a,b)]. Contrary to previous observations, no evidence of a fractal-like organization of particles could be found, provided the suspensions were filtered. Therefore, it has been proposed that Laponite suspensions form so-called repulsive colloidal glasses, and are stabilized by electrostatic repulsion. In such systems, the ergodicity is lost due to blocking of particle movement by the dense surrounding cages formed by their nearest neighbors. This colloidal glass is obtained for very low volume fraction $\Phi = 0.01$ compared to that for usual spherical colloids, for which glasses above $\Phi = 0.5$ are obtained [Pusey and Van Megen (1987)]. To account for this difference, one has to consider the effective volume fraction of a particle, which is done by adding to the particle radius the Debye length. To give an order of magnitude, it is estimated to 30 nm for ionic strength $I = 10^{-4}$ M. Recent experiments have shown that the location of the glass transition line in the (volume fraction/electrolyte concentration) phase diagram is consistent with this assumption [Levitz et al. (2000)].

The addition of salt to a suspension of Laponite disks reduces electrostatic repulsion and can even lead to attraction. Recently, such short-ranged attractive colloidal systems have received renewed attention in terms of their dynamic properties [NICOLAI and Cocard (2001)]. When the strength of short-ranged attraction becomes significantly greater than the thermal energy, the system can form a colloidal gel, in which particle motion will be completely jammed even at very low bulk volume fractions. The system behaves in a nonergodic fashion prior to complete blocking of the particle dynamics. Therefore, by varying the strength and range of attractive interactions, a reentrant transition of the liquid glass line and a glass–glass transition can be realized [Dawson et al. (2001)].

In this paper, we present mainly experimental results obtained with suspensions of Laponite at 1.5 wt%, $I = 7 \times 10^{-3}$ M. Very similar results were obtained with suspen-
sions of Laponite at $I = 10^{-4}$ M. For the ionic strength considered here, static and dynamic light scattering experiments show that the suspensions form colloidal glasses [Bonn et al. (1999a,b)].

III. NONLINEAR RHEOLOGY

Shear experiments were performed on a controlled stress rheometer that can also operate in controlled strain mode (Rheologica StressTech), using Couette geometry or vane geometry with a 1 mm gap in the range of $50 < \dot{\gamma} < 500 \text{ s}^{-1}$, and Couette geometry with a 1/8 mm gap in the range of $500 < \dot{\gamma} < 2000 \text{ s}^{-1}$. The tests were carried out at 20.0±0.5 °C. The evaporation of water or CO$_2$ contamination of the sample was completely avoided by covering the sample with Vaseline oil and a plate made of Plexiglas.

At $t_w = 0$, the sample was exposed to continuous shear strain at a constant rate $\dot{\gamma}$ of $50 < \dot{\gamma} < 2000 \text{ s}^{-1}$. The viscosity of the suspension increased slowly over time and reached a stationary value after a period of, as shown in Fig. 2. Variation of the viscosity of less than 1% per hour was chosen as a criterion for the stationary state to be reached, since this is of the order of magnitude of our measurements precision. This stationary state was obtained after very long time. To give an order of magnitude, for a 4 wt % suspension at ionic strength $I = 10^{-4}$ M, it was reached in about 50 h. By increasing the particle concentration from 1.5% to 5%, we observed a slight decrease in the time to reach the stationary state. Upon an increase in the ionic strength, we were able to reach the stationary state of the system faster, as shown in Fig. 2 for a suspension at 1.5 wt %, with two different ionic strengths.

In order to compare the driven aging dynamics to the spontaneous one, we measured the complex viscosity modulus of the suspension under shear. The experimental procedure was as follows: every 30 min, we stopped shearing for a very short time (typically 30 s) and performed oscillatory shear experiments at frequency of 1 Hz and imposed stress of 0.15 Pa, leading to the elastic and loss moduli. This procedure allowed us to not perturb the shear process. The complex viscosity moduli both for the system that evolves spontaneously and for the system under shear are shown in Fig. 3. Since the complex viscosity modulus can be taken as a measure of the age of the system, it immediately
follows that the aging dynamics under flow is very slow compared to "spontaneous" aging dynamics: the complex viscosity modulus increase is slower when the system is submitted to an external drive.

If the drive was suppressed once the stationary state was attained, the spontaneous aging process again took place as was observed by performing oscillatory shear experiments: the complex viscosity modulus \( \eta^* \) changed very rapidly, by two orders of magnitude over about 1 h, in a way similar to that observed for the spontaneous aging process.

Starting from different aging times \( t_w \), continuous shear strain with the same constant rate was applied to the system: the same nonequilibrium stationary state is attained, characterized by very similar viscosities. Figure 4 shows the rejuvenation and driven aging process under shear rate \( \dot{\gamma} = 500 \text{ s}^{-1} \), starting from different aging times. The steady-state viscosity thus appears to only depend on the shear rate applied. Since the complex viscosity can be taken as the measure of the age of the system, the corresponding age of the stationary state appears to be power dependent. In applying the external drive to a suspension aged for a long enough time \( t_w \), the viscosity decreased over time until the system reached its steady state. During this shear experiment, we measured the complex viscosity modulus using the same procedure as that explained above. The complex viscosity modulus and the dynamic viscosity are shown to evolve in the same direction, they both decrease: so-called rejuvenation of the suspension was observed. It is worth noting that, even by strongly shearing the suspension for hours, in the range of \( 50 < \dot{\gamma} < 2000 \text{ s}^{-1} \), the initial liquid state, obtained at \( t_w = 0 \) described in Sec. II, was never reached again, with the final state only being determined by the rate of the shear strain applied.

The stationary viscosities obtained for different values of applied shear rate from \( t_w = 0 \) are shown in Fig. 5. The larger the shear rate applied, the smaller the value of the stationary viscosity and the faster we reach it. If we consider the typical time necessary to obtain steady state as the time when the viscosity varies less than 1%, we find that for constant respective shear rates of 50, 100 and 500 s\(^{-1}\), the times are, respectively, 10, 5 and 1 h. As a result, it roughly scales with \( 1/\dot{\gamma} \). By reporting the values of the stationary
viscosity as a function of the shear rate applied, shear-thinning behavior was observed as shown in Fig. 6. It can be accurately characterized by a power law, $\eta \propto \dot{\gamma}^{-\alpha}$, with $\alpha = 0.60 \pm 0.10$ for the different suspensions of Laponite considered here.

IV. DISCUSSION

From a theoretical point of view, a number of models have been introduced recently to account for the interplay between the drive and the relaxation of the system. Sollich and co-workers (1997) extended Bouchaud's trap model [Bouchaud (1992); Monthus and Bouchaud (1996)] to driven systems, which led to the "soft glassy rheology" (SGR) model [Sollich (1998); Fielding et al. (2000)]. Other models that capture many of the observed rheological properties have been introduced [Hébraud and Lequeux (1998);
Dérec et al. (2001); Coussot et al. (2002a,b). Cugliandolo et al. (1997), suggested an approach for nonequilibrium systems, in which the nonequilibrium state was generated by “stirring” the system. Further theoretical studies on driven mean-field disordered systems and numerical studies of Lennard-Jones glasses have provided a detailed description of the nonequilibrium behavior, including the rheological properties [Berthier et al. (2000); Barrat and Berthier (2000)]. All these models were shown to account well for a number of rheological behaviors in soft glassy materials. In particular, as a result of these theoretical predictions, it is expected that if we inject power into aging systems, there is a possibility of stabilizing the age of the system on a power dependent level: the younger the larger the power input [Bouchaud et al. (1996); Horner (1996); Sollich (1998); Berthier et al. (2000); Dérec et al. (2001); Kurchan (2001)]. Power injection into the system is derived from the shear rate applied. For a vanishingly small drive, however, the slow mode relaxation time, assumed to be proportional to the viscosity, again diverges [Berthier et al. (2000)].

These theoretical predictions are confirmed by the experimental results described above. The driving force that acts on the system results in the suppression of the aging process. The larger the shear rate, the smaller the stationary viscosity, that means the younger the glassy system, since complex viscosity is known to increase over time $t_w$ and can be therefore taken as a measure of its age. Once drive is suppressed, the spontaneous aging process again takes place. From our experimental results, it appears that the external drive leads to drastic slowing down of the spontaneous aging dynamics or, in some cases, in rejuvenation of the system. The occurrence of rejuvenation or “driven” aging depends on both the external drive power and the age of the system when applying the external drive. This is completely consistent with phenomenological models in which the final stationary state results from the competition between the spontaneous aging dynamics—that strengthens the interactions between particles and leads to less and less accessible configurations in phase space as time evolves—and the mechanically induced rejuvenation of the configurations—the process that works against spontaneous aging and leads to its slowing down. Coussot and co-workers (2002a,b) have shown that, under imposed stress, bifurcation in rheological behavior occurs: for small stress, the viscosity
increases over time: the material eventually stops flowing. For slightly larger stress, the
viscosity decreases continuously over time: the flow accelerates. Thus, the viscosity
jumps discontinuously to ward infinity at critical stress, implying there is a range of shear
rates for which the flow is unstable. Here, we work at sufficiently high imposed shear
rates so that the flows are stable; no shear banding is observed.

In the experiments, the typical time to reach the stationary state is surprisingly long.
Our experiments show that this typical time scales with $1/\dot{\gamma}$, a result which confirms
theoretical expectations and numerical simulations [Berthier et al. (2000)]. However, the
prefactor of $1/\dot{\gamma}$ is of the order of $10^6$ in a typical experiment and suggests that the shear
applied disrupts very large scale structures. We observed that this typical time is of the
same order of magnitude as the time necessary for the spontaneous aging dynamics to
slow down dramatically. This fact strengthens the idea of competition between sponta-
neous aging and the external drive. Furthermore, these steady-shear experiments disprove
a common assumption of Laponite suspensions: when taking an “old” suspension, it is
not sufficient to stir the system for a few minutes in order to obtain the initial state at
t_w = 0 for the shear strain rates considered here.

Shear rejuvenation was studied using diffusive wave spectroscopy (DWS) in a sus-
pension of Laponite [Bonn et al. (2002)]. Shear rejuvenation was shown to have a very
large effect on the microscopic dynamics. Upon an increase in the shear rate, the steady-
state relaxation time decreases. In the experiments reported in this paper, the complex
viscosity modulus associated with the stationary state was also shown to decrease accord-
ing to the shear rate applied. This is consistent with the DWS experiments, where the
measurements allowed us to relate the microscopic diffusion dynamics to the macro-
scopic viscosity of the system.

In the SGR model, the rheological response of the system depends on the distance
from the glass transition temperature $x$. If we assume that we are in the immediate
vicinity of the glass transition, $x = 1$, the shear-thinning exponent found experimentally
is in reasonable agreement with theory. Berthier et al. (2000) studied, within the frame-
work of the mean-field (or mode-coupling) approximation, the influence of an external
drive on a system undergoing a glass transition. Above the glass transition, for high
enough shear rates, the slow mode relaxation time $t_a$ of the system scales as $t_a \propto \dot{\gamma}^{-2/3}$. Since the dynamic viscosity $\eta$ is assumed to be proportional to the slow mode
relaxation time, the system has therefore shear-thinning behavior characterized by power
law $\eta \propto \dot{\gamma}^{-2/3}$. Very similar results are obtained from molecular dynamics simulations,
where the viscosity is directly extracted from the shear rate applied [Yamamoto and
Onuki (1998); Barrat and Berthier (2000)] with $\eta \propto \dot{\gamma}^{-0.9}$ and $\eta \propto \dot{\gamma}^{-0.8}$, respectively.
The shear-thinning behavior observed experimentally (an exponent between $-0.5$ and
$-0.7$) is in fair agreement with the above theoretical and numerical predictions.

In conclusion, we have studied experimentally the nonlinear rheological behavior of a
glassy system under an external drive. Qualitatively, our experimental results confirm all
the findings predicted by the glassy models. They show the competition between the
external drive, which leads to mechanically induced rejuvenation of the configurations,
and the aging dynamics, which lead to a slowing down. Depending on this competition,
driven aging or rejuvenation may be observed. In addition, the shear-thinning viscosity
observed in our experiments agrees quantitatively with at least one simulation result.
Since the value of the exponent depends on the exact model that is chosen, differences
with the model calculations may not be very important. The key result is that nonequi-
librium models for glassy systems are able to predict non-Newtonian behavior without
taking into account specific interactions between particles.
References


