

Laponite: Aging and Shear Rejuvenation of a Colloidal Glass

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We study the nonlinear rheological behavior and the microscopic particle dynamics for a colloidal glass, to see whether recently developed models for driven glassy systems can be applied to predict the rheology. Qualitatively, all the findings predicted by the models can be retrieved in our system. Notably, the viscosity decreases strongly with the shear rate. Since it is difficult to predict non-Newtonian viscosities of colloidal systems due to long-ranged hydrodynamic interactions, this shows the promise of this approach for predicting flow behavior. In addition, the measurements allow us to relate the microscopic diffusion dynamics to the macroscopic viscosity of the system.

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The flow behavior of “complex fluids” such as, for instance, colloidal suspensions is of both practical and fundamental interest [1]. The large length scales present in these systems, when compared to molecular dimensions, can lead to interactions between the flow field and the organization of the complex fluids. A structural change can affect the viscosity of the fluid and thus, in turn, modify the flow field. This leads to a non-Newtonian viscosity: in general, the resistance to flow decreases with increasing flow velocity [1,2]. Unfortunately, because of the existence of long-range hydrodynamic interactions in these systems, it has turned out to be nearly impossible to predict the non-Newtonian viscosity on the basis of the structure and/or interactions in these systems [2].

It is for this reason that recently a completely different approach has been tried to predict non-Newtonian behavior. Instead of taking all the hydrodynamic interactions into account, one starts [3–6] from a model of a glassy system that has slow degrees of freedom: certain states are said to be jammed. This jamming is a common property of a large number of complex fluids such as foams, gels, and granular systems, which in general hardly flow if a small stress is exerted on them. For a glassy system, the slow modes are affected by an external forcing, which is associated with a flow [3–6]. These models have the advantage that both the linear (viscoelastic) response and the nonlinear behavior under flow, i.e., the non-Newtonian viscosity, can be calculated explicitly. The second advantage is that this opens, for the first time, the possibility to relate the macroscopic rheological behavior to the microscopic dynamics [3–6].

In this Letter we will study both the nonlinear rheological behavior and the microscopic dynamics for a typical “soft glassy material,” to see whether these ideas are applicable to a real system. The detailed predictions that result from the different models and simulations are the following [3–6]: (i) Without an external forcing, the systems evolve spontaneously: they are said to age, meaning that the relaxation time of the slow mode increases in time. (ii) Under an external drive, the system can reach a steady

state: the aging stops, and the relaxation time is constant. (iii) Upon increasing the forcing, the relaxation time in steady state decreases. (iv) Both in the presence of an external drive and during the aging, the viscosity is given by the (distribution of) relaxation time(s) of the “slow mode” of the glassy system. (v) The viscosity decreases strongly with the shear rate (the velocity gradient) applied to the system. It can be accurately described by a power-law dependence: $\eta \propto \dot{\gamma}^{-\alpha}$, with $0.66 < \alpha < 0.9$, depending on the specific system considered.

The aging of glassy systems, prediction (i), has been studied for a number of different systems lately [7–13] and appears to be a general property of such soft glassy materials [5]. Also, it was demonstrated experimentally for a number of very different materials that, under shear, the aging stops and a steady state is reached [14]: prediction (ii) is verified also. We therefore focus here on propositions (iii)–(v), which should provide the “missing link” between the microscopic, nonequilibrium statistical mechanical behavior of the system, and its macroscopic response to flow.

We study the colloidal glass of Laponite [8,10], a synthetic clay consisting of discoid colloidal particles with a diameter of 25 nm and a height of 1 nm; this allows probing the microscopic diffusion dynamics of the particles by light scattering. It was shown previously that the diffusion can be described by a cage-diffusion process: for small displacements “normal” Brownian motion is observed, but for larger excursions, the particles are confined in effective cages formed by their neighbors. The slow mode then corresponds to the escape of the particles from their respective cages, which becomes more and more difficult when the system ages: this shows up in the experiments as an increase of the relaxation time of the slow mode [8,10].

For the light scattering, we add a small amount of latex particles to the solution in order to use diffusive wave spectroscopy (DWS) [10,15]. This is a well-known multiple scattering technique, which allows for measurements in transmission; this facilitates light scattering under shear. We suspend the Laponite at a concentration of 3 wt % in

ultrapure water (with NaOH to obtain a $pH = 10$) under vigorous stirring during 15 min and subsequently pass the solution through a Millipore Millex AA ($0.8 \mu\text{m}$) filter, to obtain a reproducible initial liquid state. In order to be in the multiple scattering limit, we add a small amount (0.2 wt% of $0.5 \mu\text{m}$ latex particles to the samples after filtration. We subsequently let the sample age.

The DWS measurements were performed in a Plexiglas Couette cell with a gap of 1 mm; the outer cylinder is the rotor. The inner cylinder contains a mirror adjusted in such a way that the light from a HeNe laser (mounted parallel to the rotation axis) transverses the gap perpendicular to the surfaces of the two cylinders. The multiply scattered light from the gap is collected in transmission by a monomode optical fiber, detected by a photomultiplier, and analyzed by an ALV-5000 correlator card.

The diffusion process can be characterized by looking at the correlation functions of the particle positions for different aging times. We start by looking at the aging of the system without shear. Figure 1 depicts the measured correlation functions as a function of the age of the samples. We observe a large increase of the relaxation time, defined as the point where the correlation function has decayed by half, showing that the diffusive movement becomes more and more difficult as the system ages.

We simultaneously measure the viscosity increase during the aging of the sample (with latex particles) on a Reologica Stress-Tech rheometer in a Couette geometry, also with a gap of 1 mm. In order not to disturb the

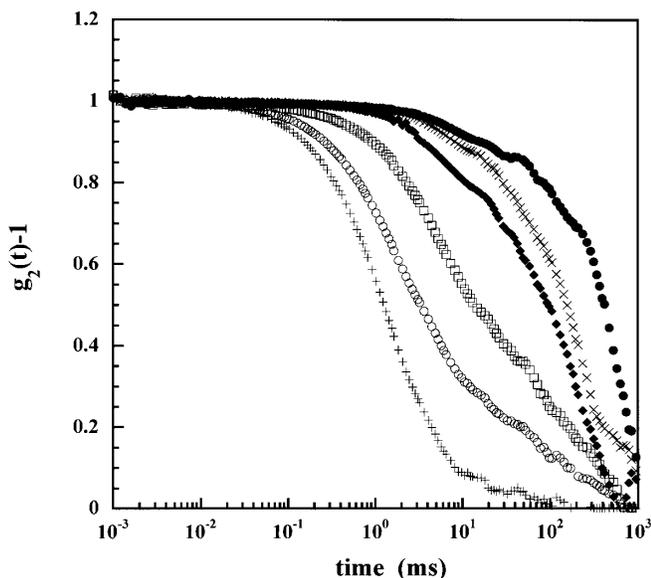


FIG. 1. Aging of the Laponite: correlation functions measured using diffusive wave spectroscopy. The decay of the correlation function is a measure for the time a particle needs to “forget” its initial position (at time zero). Therefore, as the sample ages, the diffusive relaxation time increases. The aging times are from left to right: 10, 20, 30, 40, 50, and 60 min.

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 moduli, respectively. The complex viscosity modulus η^* can be calculated from these quantities by using $\eta^* = (G'^2 + G''^2)^{1/2}/\omega$. In Fig. 2 we plot the complex viscosity, as a function of aging time. It can be observed that the viscosity changes very rapidly, by 2 orders of magnitude over a time that is on the order of an hour.

The aging was studied earlier [8] for Laponite (without latex particles); the results here are very similar; the relaxation time increases exponentially fast with the age of the sample. We compare the relaxation time measured here with those for a Laponite suspension without latex particles in Fig. 3: the dynamics is the same. In addition, as was also found before [8], the distribution of relaxation times for the slow mode becomes larger: if the correlation function is fitted to a stretched exponential, the stretching exponent goes continuously to zero at a finite time [8], and the system becomes nonergodic [8]. Thus, we conclude that the addition of latex particles does not affect the glassy dynamics of the Laponite system significantly.

The slowing down of the diffusion is then concomitant with the increase in viscosity of the sample. This amounts, in fact, to prediction (iv): the viscosity should be given by the relaxation time of the slow mode of the glassy system. In order to see whether this direct connection between viscosity and relaxation time is verified, we show the characteristic diffusion time and viscosity as a function of the age of the sample in Fig. 3. We observe that both increase

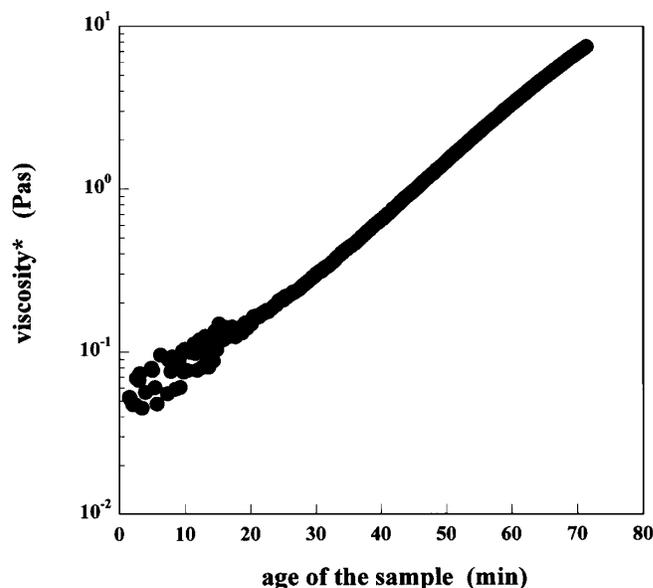


FIG. 2. The complex viscosity modulus as a function of the aging time; $t = 0$ corresponds to the injection of the sample in the Couette cell of the rheometer. We observe that as the sample ages, the viscosity increases exponentially.

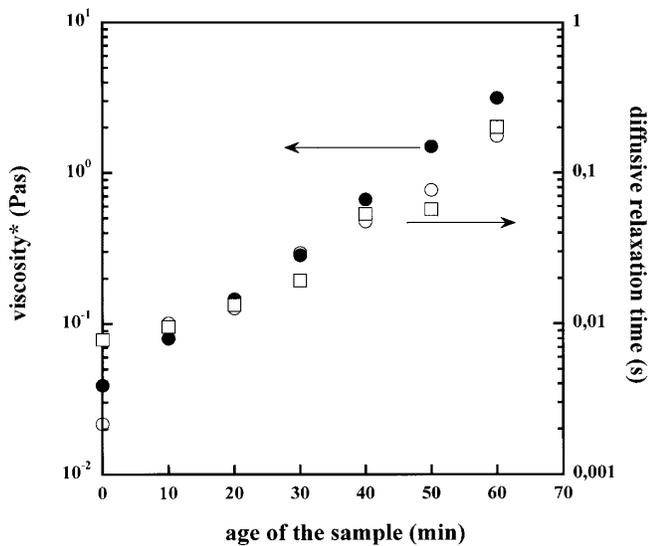


FIG. 3. Complex viscosity (filled circles) and diffusive relaxation time (open symbols) as a function of the age of the sample. Both behave very similarly and show a roughly exponential increase with the age of the sample. The open circles are the DWS measurements, and the open squares are measurements for Laponite without latex particles; see Ref. [8] for experimental details.

exponentially fast with the age of the sample [16], and follow exactly the same dynamics. Therefore, the theoretical prediction (iv) is well borne out by our experiments.

We now focus on the behavior under shear. The experimental procedure is the following: we let the sample age for 1 h, after which the shear is started; we focus here on the behavior for three different shear rates: 25, 2.5, and 0.25 s^{-1} . To do so, we measure the correlation function every 10–15 min while shearing the sample continuously during this period [17]. If three subsequent measurements give indistinguishable correlation functions, we conclude that a steady state has been reached.

The correlation functions for both the system aged for 1 h and the systems under shear are shown in Fig. 4. It follows immediately that the shear has a very large effect on the microscopic dynamics: for the highest shear rate the relaxation time is smaller by more than an order of magnitude: the shear has “rejuvenated” the system. This shear rejuvenation is accompanied by a drastic viscosity decrease [14]. In addition, and in agreement with prediction (iii) given above, we observe that upon increasing the shear rate, the steady-state relaxation time decreases.

To quantify the effect of the shear rejuvenation on the system, we measure the viscosity for different shear rates. If we plot the steady-state viscosities as a function of the applied shear rate, we observe a strongly shear-thinning behavior (Fig. 5). Moreover, in agreement with the theoretical propositions, the viscosity can be accurately described by a power-law dependence: $\eta \propto \dot{\gamma}^{-\alpha}$; we find $\alpha = 0.9 \pm 0.04$, which can be compared with the theoretical and numerical findings, prediction (v).

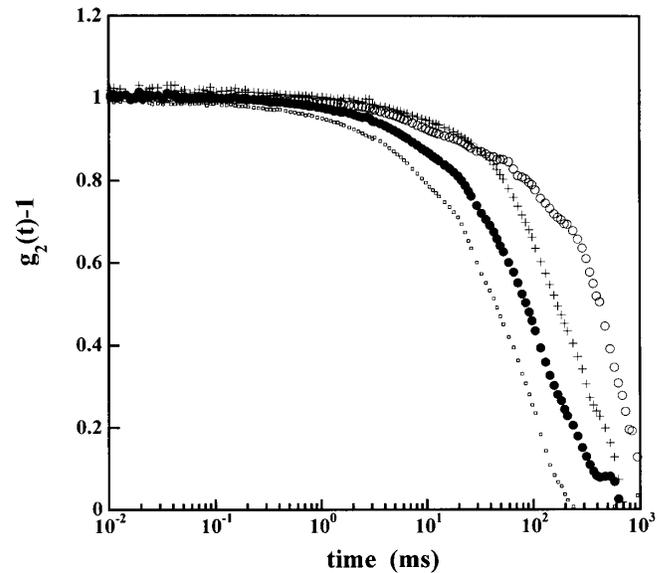


FIG. 4. Shear rejuvenation of the Laponite sample: correlation functions measured using diffusive wave spectroscopy for different shear rates. The curve to the right is the reference without shear, and after 1 h of aging. After that, from right to left: 0.25, 2.5, and 25 s^{-1} .

Among these predictions, Sollich *et al.* extended Bouchaud’s trap model [18] for glassy dynamics to driven systems, leading to the “soft glassy rheology” model [4,14]. In this model, the rheological response of the system depends on the distance from the glass transition temperature. If we assume that we are in the immediate vicinity of the glass transition, it follows from the model that $\alpha = 1$, which appears in reasonable agreement with the experimental value. Berthier *et al.* [6] using mode-coupling theory, study the influence of an external drive on a system undergoing a glass transition. Above the glass transition, for sufficiently high shear rates, they find that the slow relaxation time of the system scales as $\dot{\gamma}^{-2/3}$. As we have seen, it is justified for our systems to take,

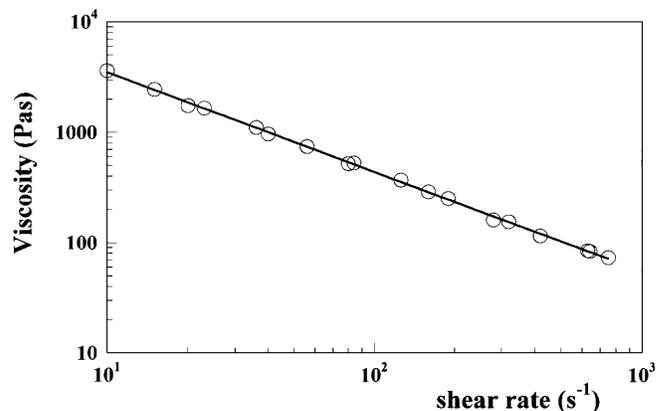


FIG. 5. Steady-state viscosity of the system plotted as a function of the shear rate. A power law with an exponent of -0.9 ± 0.04 is fitted to the data (drawn line).

as they do, the viscosity to be proportional to relaxation time of the slow mode. Therefore, their result reads $\eta \propto \dot{\gamma}^{-2/3}$, again not very different from our observation. Similar results were obtained in the simulations [3,6]: $\eta \propto \dot{\gamma}^{-0.9}$ and $\eta \propto \dot{\gamma}^{-0.8}$. The shear-thinning behavior observed experimentally is therefore in fair agreement with theoretical and numerical predictions.

In conclusion, we have studied the aging and shear rejuvenation of a colloidal system, in order to see whether ideas that originate from the study of the glass transition can be applied to predict the rheology of soft glassy materials. Qualitatively, all the findings predicted by glassy models can be retrieved in our system. More quantitative are the predictions for the shear-thinning viscosity either from model calculations or from simulations. Our result for the shear-thinning viscosity agrees quantitatively with at least one simulation result. Thus, the nontrivial rheological behavior from the models is reproduced by the experiment; this is important since it is difficult to predict non-Newtonian viscosities in any other way. In addition, the system we have studied allows the a microscopic understanding of the very large viscosity of glassy systems in terms of a hindered diffusion of the particles.

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