

Rheology of soft glassy materials

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Abstract. – We compare the linear and non-linear rheological properties of a typical soft glassy material, the colloidal glass of Laponite, with the predictions of recently developed rheological models based on glassy dynamics, in which particles are trapped in a free-energy landscape with many minima. We find qualitative agreement between theory and experiment for the linear visco-elastic properties. However, for the non-linear response, notably the viscosity under continuous shear flow, important qualitative differences are found. This shows that a developed flow affects the dynamics of relaxation of the material in a more complicated way than what is assumed in the models: not only does the flow alter the energy landscape, but it also modifies the effective temperature controlling the escape rate for a given energy barrier.

Soft materials such as gels, foams, pastes, and concentrated suspensions and emulsions have a remarkable number of rheological properties in common. They mostly exhibit a yield stress, *i.e.*, they will not flow until a certain critical stress is exceeded. On the other hand, when exceeding this stress, all these systems show a strong shear thinning: the viscosity decreases strongly with shear rate. In addition, the linear visco-elastic properties are similar: almost systematically, the storage and loss modulus is found to be independent of the frequency with which the material is excited. Unfortunately, both the linear and non-linear rheological behaviours of these complex fluid systems remain ill understood, in spite of the large number of practical applications associated with these systems [1, 2].

In view of the remarkable similarities, one might wonder if a general framework for the description of such chemically very different systems may be found. In order to do so, much effort has been put recently in the development of models that originate from the study of the glass transition for predicting the rheology of complex fluids [3–6]. The analogy between the complex fluids cited above and glassy materials is that “jammed” configurations of the constituting elements of complex fluids, observed in the mechanical behavior as a yield stress [1, 2], correspond to states below the glass transition temperature for glassy systems. Consequently, one classifies all the above systems as “soft glassy materials”.

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In this letter, we compare the detailed predictions from a glassy rheology model to the rheology of a typical soft glassy material, a colloidal glass. We find that the model predicts the linear visco-elastic properties correctly. However, important deviations from the model predictions are found for the non-linear response. Among these, we observe a coexistence between sheared and unsheared material in a steady-state flow: part of the system is jammed and another part is not, in direct contradiction with the theoretical predictions.

Of the existing models and simulation studies [3–6], the most well-developed is that of Sollich and colleagues [5], who extended Bouchaud’s trap model [7] for glassy dynamics to driven systems, leading to the “Soft Glassy Rheology” (SGR) model. As the predictions of this model are similar (but more extensive) to those of the others, we will focus here on the SGR model.

In brief, the trap model postulates a free-energy landscape with many minima, in which particles are trapped. They can overcome energy barriers and reach adjacent minima by thermal activation. Analogously, in the SGR model, the dynamics of the system is due to the large distribution of metastable configurations of the constituent entities (bubbles, particles, ...). Moreover, two new ingredients are introduced in the model, namely:

- i) Since $k_B T$ is very small compared to the typical trap depth in these soft glassy materials, the thermal temperature is replaced by an “effective temperature” x , acting with an attempt frequency Γ_0 . This effective temperature originates from the interactions between the different entities and allows the particles to hop from one metastable configuration into the other.
- ii) Under a continuous shear flow, there is a modification of the energy landscape induced by the flow itself. Namely, the effective trap energy decreases with time as $E(t) = E - 1/2k\dot{\gamma}^2 t^2$, with $\dot{\gamma}$ the imposed shear rate and t the time elapsed since the shear rate has been imposed; the deformation is $\gamma = \dot{\gamma}t$ and k is the elastic constant that relates the stress to the deformation.

Within the simplest form of the SGR model, both x and Γ_0 are constant material parameters, *i.e.* they are independent of the flow. It is this simplest version we will consider here; if x depends on the flow (a possibility already mentioned in [5]) in an unknown way, there is no way to obtain explicit expressions, for instance, for the steady-state viscosity from the model. From this simplest version, it follows naturally that the response to a mechanical perturbation depends crucially on the value of the effective temperature x relative to the mean value x_g of the energy traps. The limit $x \rightarrow 1$ corresponds to a glass transition temperature in this model; the glass transition is a consequence here of the exponential tail of the trap distribution. For the calculations x_g is set to 1 by an appropriate choice of energy units: $x > 1$ is above the glass transition temperature, and $x < 1$ below. This approach then allows for the formulation of a rheological constitutive equation, which in turn allows for predictions of the rheological properties that can be verified experimentally.

The most common rheological tests are the measurement of the linear visco-elastic moduli, and the measurement of the viscosity in a simple shear flow [2]. The first is a linear-response measurement, for which the measured elastic (G') and viscous (G'') moduli do not depend on either the stress or the deformation applied to the system. The second is highly non-linear, as the viscosity of a system is defined in a steady-state flow, which is usually only achieved at deformations much larger than 1. As a consequence, the flow may affect the organisation of the material, and usually does so for complex fluids.

For these two kinds of perturbations, the SGR model provides us predictions for the elastic and viscous moduli as a function of frequency ω for the linear response. For the non-linear

response, one obtains the viscous stress σ (the product of the viscosity η and the shear rate) as a function of $\dot{\gamma}$. All these quantities now depend on the effective temperature x as

$$\begin{aligned} G' &\propto \omega^2 & (x > 3), \\ G' &\propto \omega^{x-1} & (1 < x < 3), \\ G'' &\propto \omega & (x > 2), \\ G'' &\propto \omega^{x-1} & (1 < x < 2) \end{aligned}$$

and

$$\begin{aligned} \sigma &\propto \dot{\gamma}^{x-1} & (1 < x < 2), \\ \sigma &= \sigma_y & (x \leq 1). \end{aligned}$$

For the linear visco-elastic moduli, the behaviour typical of a Maxwell fluid is retrieved far from the glass transition point ($x > 3$). At the glass transition, the moduli become frequency independent. Under continuous flow the material develops a strong shear thinning behaviour for effective temperatures above $x = 1$. At and below the glass transition, the system is completely jammed: it exhibits a yield stress σ_y .

The only supplementary complication is that, due to the broad distribution of energy barriers, the systems may not reach any equilibrium state but keep evolving endlessly: they are said to age. This aging process, which manifests itself, for instance, as a temporal evolution of the mechanical (rheological) properties, is a generic feature of glasses, and has also been observed experimentally for a number of “soft glassy materials” [8–13].

It follows from the model that the consequences of the aging for the rheological properties are a slow evolution of the frequency dependence of the visco-elastic moduli. The model predicts Maxwellian behaviour for short aging times, whereas the moduli become progressively independent of frequency as time goes on [5]. For the non-linear response, the flow interrupts the aging process: for any value of the effective temperature x a steady-state viscosity is found for a given shear rate [3–6], resulting in the prediction for the viscosity quoted above.

Here, we compare these detailed predictions from the model to the rheology of a typical soft glassy material, a colloidal glass. We study Laponite, a synthetic clay consisting of discoid colloidal particles with a diameter of 25 nm and a height of 1 nm. Under our experimental conditions, this system is a colloidal glass stabilised by electrostatic repulsions without any structure at large length scales [8]. The Laponite is suspended under vigorous stirring at a concentration of 3.5 wt% in ultrapure water (with NaOH to obtain a pH = 10). Subsequently, the solution is passed through a Millipore Millex AA (0.8 μm) filter, to obtain a reproducible initial liquid state.

The rheological measurements show that the aging of the system can be observed as a viscosity increase in time. The measurements are performed on a Reologica Stress-Tech rheometer in a Couette geometry with a gap of 1 mm using small oscillations: we measure the linear response. Such oscillation measurements yield G' and G'' . The complex viscosity η^* can be calculated from $\eta^* = (G'^2 + G''^2)^{1/2}/\omega$. In fig. 1 we plot η^* as a function of aging time at a fixed frequency of 0.1 Hz. It can be observed that the complex viscosity changes by four orders of magnitude over a time that is on the order of an hour. Changing the frequency does not significantly change these results; after roughly 100 minutes the visco-elastic spectra become very flat (*i.e.*, frequency independent). For shorter times, there is some frequency dependence of $\eta^*(t)$, but it is not very pronounced. The interpretation of this aging [8] is that the volume fraction of particles is such that the system is in the glassy region of the phase diagram; the aging is the evolution towards the complete arrest characteristic of glasses.

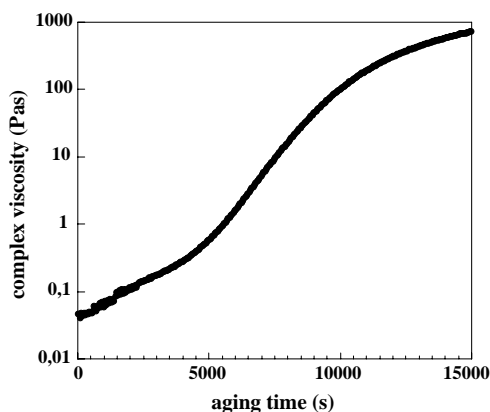


Fig. 1

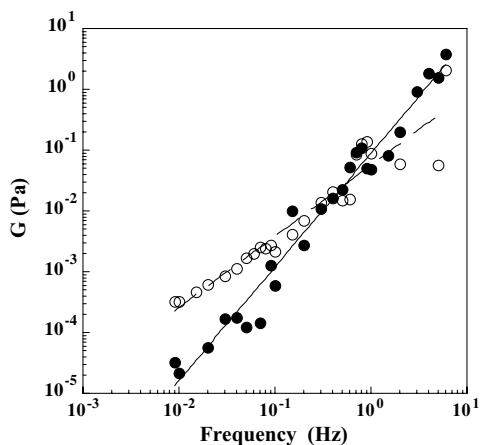


Fig. 2

Fig. 1 – Aging: evolution of the complex viscosity modulus at a frequency of 0.1 Hz at an imposed stress of 0.5 Pa 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 rapidly.

Fig. 2 – Frequency dependence of the visco-elastic moduli for a short aging time (20 minutes): Maxwellian behaviour is found, evident as a linear and quadratic dependence of G'' (open circles) and G' (filled circles) on frequency.

The measurement of the frequency dependence of the linear visco-elastic moduli shows that the SGR model qualitatively describes the dynamics. As foreseen, for short aging times, Maxwellian behaviour is found: the elastic modulus varies as the frequency squared, and the viscous modulus depends linearly on frequency (fig. 2) over the range of frequencies we can probe here. Due to our limited experimental window we do not observe the saturation expected for G' at higher frequencies; for $f > 10$ Hz the inertia of the rheometer becomes important. On the other hand, the duration of the frequency sweep is determined by the lowest frequency we probe; a point at 10^{-2} Hz takes 100 seconds to be measured. The evolution of the power law dependence of the moduli on frequency with the age of the sample shows a crossover between Maxwellian behaviour and a regime for which the moduli become frequency independent (fig. 3). From fig. 3 it can be concluded that the Maxwellian behavior is observed for the first 50 minutes of the aging; after that we see deviations from the values 2 and 1 for G' and G'' , respectively, that are larger than the experimental uncertainty.

In order to find the steady-state viscosity, creep tests (measurement of η *vs.* time) were carried out, imposing different shear stresses. For each test the material was passed through the filter, and left at rest (without any stress applied to the system) for a given fixed time (3h) to obtain a controlled and reproducible initial state. We study an aged sample to be able to compare the results between the steady shear and oscillation measurements in the regime where the latter become frequency independent. Starting from this state, we observe that below a certain critical stress value the viscosity increases indefinitely: the aging that leads to a viscosity increase dominates the response. However, for a stress larger than this critical value the viscosity decreases to reach a low steady-state value after a long time. For a high stress the flow destructures the material; this shear melting competes with the aging process, and allows to “rejuvenate” the glass, entailing a viscosity decrease. From the competition between these two effects, it follows that a bifurcation in the rheological behaviour occurs (fig. 4): for a given load, the fluid either stops flowing altogether, or fluidises, leading to a

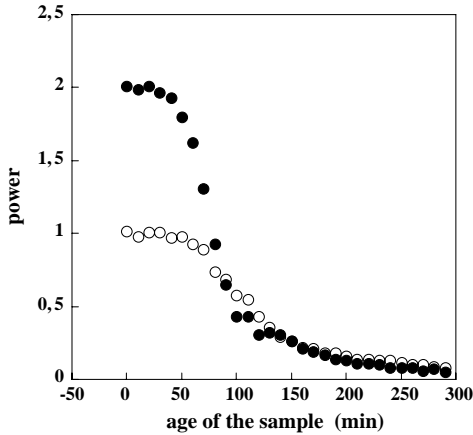


Fig. 3

Fig. 3 – Evolution of the power law dependence of the moduli on frequency with the age of the sample: for G'' (open circles) and G' (filled circles) a crossover between Maxwellian behaviour and a regime for which the moduli become frequency independent is observed.

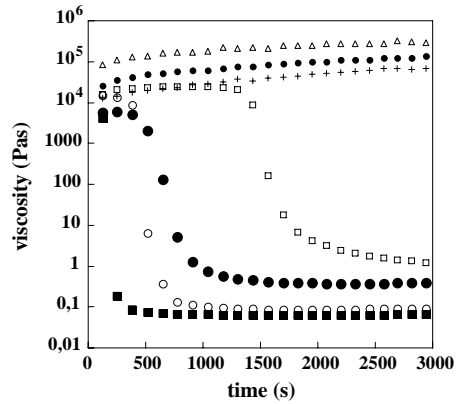


Fig. 4

Fig. 4 – Bifurcation in the rheological behaviour: viscosity as a function of time for different imposed stresses. From top to bottom: stresses are 5, 7.5, 9, 10, 13, 16 and 17 Pa.

steady state. For high stresses, this steady state is only reached after a long time (typically a few hours); as can be observed in fig. 4, the viscosity still increases slightly in time even after 3000 s. For low stresses, the apparent viscosity, for longer times than the ones shown here, shows large fluctuations as the displacements become so small that they can no longer be measured with our rheometer.

For high stresses, a stable flow is obtained and the steady-state viscosity (obtained after a few hours) can again be compared to the predictions of the SGR model (fig. 5); we find that the non-linear rheology is rather different from the predictions from the model. For the dependence of the viscosity on the shear rate, we find a power law behavior $\sigma \propto \dot{\gamma}^n$, with $n = 0.33 \pm 0.04$. The result $n = 0.33$ leads, in terms of the SGR model, to an effective temperature $x = 1.33$. According to the linear visco-elasticity measurements (fig. 3) $x \approx 1.1$ should be expected for a sample with an age of 3 h, as was used for the steady-state measurements. However, from the non-linear-viscosity measurements we find $x = 1.33$. Thus, there appears to be a discrepancy here.

The more important observation is that for stresses slightly smaller than a critical stress σ_c , the viscosity increases in time, until the flow is halted altogether: the steady-state viscosity is infinite and the system is completely jammed. This implies that, depending on the applied stress, the effective value of x changes: *it is not a property of the system, but depends on the way it is forced*. The observation of an infinite viscosity directly implies $x \leq 1$, which is incompatible with the value of $x = 1.33$ found for the same system in the same experiment, but for a slightly different stress. In fact, our measurements, when interpreted with the model, show that an infinitesimal increase in the stress causes a discontinuous jump in the effective temperature x for the same system.

The viscosity bifurcation also implies that, if the stress is imposed, a whole range of shear rates is inaccessible to the system: it either flows rapidly, or stops flowing altogether. This leads to shear banding when the shear rate is imposed. This follows directly from the determination of the velocity profile (fig. 6). These results are obtained in steady state with a

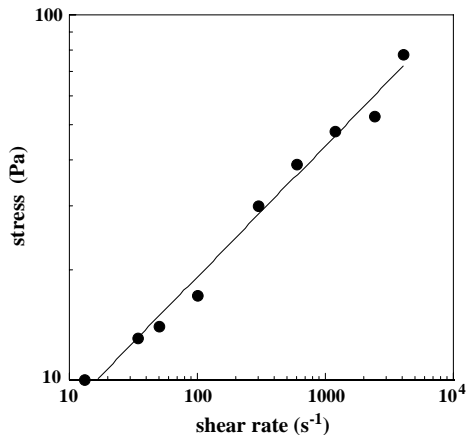


Fig. 5

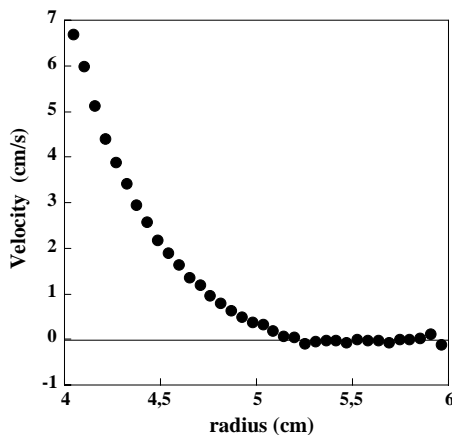


Fig. 6

Fig. 5 – Steady-state shear stress of the system plotted as a function of the shear rate. A power law with a power of -0.33 ± 0.04 is fitted to the data (drawn line).

Fig. 6 – Typical velocity profile for the 3.5 wt% Laponite suspension left at rest 3 h after preparation before beginning the shear. The imposed rotation velocity is 18 rpm. We used a Bruker MRI set-up equipped with a vertical 0.5 T magnet fitted with shielded gradients leaving a free bore of 25.5 cm and delivering a gradient of 50 mT/m.

Couette rheometer inserted in a magnetic resonance imager (MRI) [14]. The velocity profile is composed of two regions, the limit of which is situated at a critical radius r_c : in the first there is no apparent shear while in the second region the fluid is sheared. In terms of the model, this means that *two different values for the effective temperature x can exist in the same system and at the same time*. The shear stress σ at a given radius r as a function of the applied torque C and the fluid height h follows from momentum balance: $\sigma = C/2\pi hr^2$. The magnitude of the shear rate can be deduced from the velocity profile $v(r)$ as $\dot{\gamma} = |r \frac{d}{dr}(\frac{v(r)}{r})|$. Thus r can be eliminated from these two equations to deduce the constitutive equation of the fluid in simple shear, *i.e.* the relation between σ and $\dot{\gamma}$. We find that the viscosity in the sheared region is very well represented by a simple power law relation: $\sigma \propto \dot{\gamma}^n$ with $n = 0.20 \pm 0.04$, which, in the context of the SGR, means: $x = 1.20$. In contrast, in the unsheared region, we again have $x \leq 1$ since the viscosity is infinite. The former result differs only slightly from the steady-flow result of fig. 5 ($n = 0.33$) which is for larger stresses in the regime where the whole material flows.

The observed coexistence of a sheared and an unsheared part of the material is likely to be a general property of these soft glassy materials, and, in addition, of granular matter. Indeed, measurements of the velocity profile in slowly sheared foams and granular systems typically show a strong localization of the strain in a small band close to the moving wall, the rest of the material being essentially undisturbed [15]. The interpretation is the same as that for our model fluid: part of the system is “fluid” and moves, whereas the other part is “solid” and does not move. It is evidently clear that this cannot be described by a glassy model with a single temperature; in fact the “fluid” part corresponds to a subsystem that is, in the language of the glass transition, above T_g , whereas the “solid” part is below T_g . Thus, if one observes a coexistence of these two, a description in terms of a single effective temperature is insufficient.

In terms of the glassy models, this means in fact that it is insufficient to consider that the effect of the flow is to reduce energy barriers between adjacent minima. The existence of

two values of the effective temperature show that this quantity is not intrinsic to the material but depends on the type of excitation to which it is submitted. There are also other model calculations and simulations [3,6] that predict or observe a strong shear thinning for glassy systems under flow. However, these mainly pertain to “fluid” systems (above T_g) and thus miss an essential point in the description of the “soft glassy” materials: the yield stress. The only simulation going below the glass transition [6] predicts a power law behavior for the viscosity also below T_g . However, one should keep in mind that in experiments the shear is imposed at the boundary, whereas in the simulations the forcing is done in the bulk of the material; this may be one of the reasons for the discrepancies observed here.

In conclusion we have studied the rheology 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. We find qualitative agreement between theory and experiment for the linear visco-elastic properties. However, for the non-linear response, notably the viscosity under continuous shear flow, important qualitative differences are found, showing that the effect of flow is more complicated than it is assumed in the models.

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