Aging under Shear: Structural Relaxation of a Non-Newtonian Fluid

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The influence of an applied shear field on the dynamics of an aging colloidal suspension has been investigated by the dynamic light scattering determination of the density autocorrelation function. Though a stationary state is never observed, the slow dynamics crosses between different non-equilibrium regimes as soon as the structural relaxation time \(\tau_s\) approaches the inverse shear rate \(\dot{\gamma}^{-1}\). In the shear dominated regime (at high \(\dot{\gamma}\) values) the structural relaxation time is found to be strongly sensitive to shear rate \((\tau_s \sim \dot{\gamma}^{-1})\) while aging proceeds at a very slow rate. The effect of shear on the detailed shape of the density autocorrelation function is quantitatively described assuming that the structural relaxation process arises from the heterogeneous superposition of many relaxing units each one independently coupled to shear with a parallel composition rule for timescales: \(1/\tau \to 1/\tau + A \dot{\gamma}\).

One of the most peculiar and intriguing behaviour of soft materials is the strong sensitivity of their flow properties to the application of an even slight external deformation. When a liquid flows in a steady shear state, the inverse shear rate \(\dot{\gamma}^{-1}\) introduces a new relevant timescale in the dynamics. On a microscopic level a non-Newtonian character reflects a competition between the natural timescale of those particle rearrangements controlling the macroscopic flow properties. For moderate shear rates, i.e. those occurring in the macroscopic world, mainly the slow modes are affected by shear and give rise to complex rheological behaviour. Understanding the physical mechanism governing the interaction between slow dynamics and shear has been the subject of great theoretical and numerical efforts in recent years.

On the theoretical side, some of the most powerful tools for the investigation of slow dynamics in complex systems, such as mode coupling theory \(\textsuperscript{2,3}\), mean-field models \(\textsuperscript{4}\), trap models \(\textsuperscript{5}\) and molecular dynamics simulations \(\textsuperscript{6-8}\), have been recently extended to account for the presence of shear. The general picture emerging from these studies indicates that the structural dynamics is very sensitive to even moderate shear rates whenever \(\dot{\gamma}^{-1}\) becomes of the order of the characteristic timescale for structural rearrangements. In particular, even starting from non-equilibrium, aging states, the presence of shear ensures the existence of a stationary state whose correlation functions decay to zero on a timescale governed by \(\dot{\gamma}^{-1}\).

Despite the growing amount of numerical and theoretical work investigating the shear-influenced slow dynamics, an experimental microscopic counterpart is still relatively poor. Evidences for a shear dependent structural relaxation time have been obtained by diffusing wave spectroscopy \(\textsuperscript{6,10}\) and Light Scattering Echo experiments \(\textsuperscript{11}\), though it is not straightforward to deduce the microscopic dynamics from the observables probed in the multiple scattering regime. No attempt has been made up to now to use dynamic light scattering (DLS) in the single scattering regime, a technique that directly probes the density autocorrelation function, which plays a central role in both theoretical and numerical approaches.

In this Letter we investigate the evolution of the density autocorrelation function of an aging colloidal suspension subject to a steady shear flow. The sample is an aqueous suspension of Laponite, a highly thixotropic liquid which undergoes structural arrest on a timescale which strongly depends on concentration and ionic strength \(\textsuperscript{12}\) and that can be as long as few months \(\textsuperscript{13}\). We found that the aging dynamics displays two different regimes whose boundary is marked by the condition \(\tau_s \dot{\gamma} \sim 1\). As long as the characteristic relaxation time \(\tau_s\) is small on the time-scale \(\dot{\gamma}^{-1}\), aging is unaffected by the presence of shear. During aging dynamics slows down, and when \(\tau_s\) becomes of the order of \(\dot{\gamma}\), the system enters a shear dominated regime where aging is strongly reduced and the structural relaxation time is very sensitive to \(\dot{\gamma}\). The intermediate scattering functions, characterising the slow non-equilibrium dynamics of the sheared sample, are well described assuming an heterogeneous scenario where the complex dynamics results from the superposition of relaxing units each one independently coupled to shear rate with a parallel composition rule for timescales: \(1/\tau \to 1/\tau + A \dot{\gamma}\).

The system consists of an aqueous suspension of Laponite RD, a synthetic layered silicate provided by Laporte Ltd. Particles are disk shaped with a diameter of 25 nm and 1 nm thickness. Laponite powder is dispersed in ultrapure water at 3% wt concentration, stirred for \(\sim 30\) min and then filtered through a Millipore Millex-45 \(0.45\) \(\mu\)m filter. The obtained suspension, which is optically transparent and initially liquid, is loaded into a home made cone and plate shear cell having a flat optical window as the static plate. Incident laser beam (He-Ne, 10 mW) and scattered light pass through the same optical window. The scattered light is collected by a mono-mode optical fiber, detected by a photomultiplier and analyzed by a home made software correlator, after being optionally mixed with a coherent local oscillator.
field. The scattering geometry is fixed (scattering vector \( q = 25 \, \mu m^{-1} \)). The possibility of choosing an heterodyne correlation scheme enables direct access to the detailed velocity profile in the shear cell. Wall slip and distortion from linearity in the velocity profile are found to be negligible in the whole shear rate range here investigated. The non-equilibrium dynamics of Laponite suspensions flowing in a “steady” shear state is then constantly monitored through the normalized intensity autocorrelation function \( g^{(2)}(t_w, t) = \langle I(q, t_w)I(q, t_w + t) \rangle / \langle I(q, t_w) \rangle^2 \). Where \( \langle . \rangle \) indicates temporal average over the acquisition time \( T \) which is always much longer than the characteristic slow relaxation time \( \tau (T/\tau \geq 10^2) \) but also much shorter than the time one should wait before changes in \( \tau \) are significant \( (T \partial \log \tau / \partial t_w \lesssim 10^{-2}) \). In the single scattering regime and within the Gaussian approximation \( g^{(2)}(t_w, t) = 1 + F_q(t_w, t)^2 \) where \( F_q(t_w, t) = \langle \rho_{-q}(t_w)p_q(t_w + t) \rangle / \langle \rho_{-q}(t_w)p_q(t_w) \rangle \) is the intermediate scattering function of the colloidal particles. In order to avoid purely geometric decorrelation of scattered light, due to both advection and transit time effects, steady shearing is interrupted every ten minutes and the correlation functions are collected in short (few tens of seconds) time intervals during which the rotor is stopped \( (\dot{\gamma} = 0) \). The robustness of the results with respect to changes in acquisition protocol has been checked. The top frame of Fig. 1 shows the evolution of \( g^{(2)}(t_w, t) \), in the absence of shear, for an evenly spaced set of waiting times \( t_w \) spanning the interval \( 0.1 - 15 \) hours. As already observed in \[17\], aging dynamics displays a two step relaxation scenario: i) a fast exponential relaxation process related to single particle diffusion and whose characteristic time \( \tau_f \) remains of the same order of magnitude found in very dilute suspensions; ii) a slow stretched exponential process related to cooperative rearranging motions and whose characteristic time \( \tau_e \) grows exponentially fast with waiting time \( t_w \) while becoming strongly stretched (stretching parameter \( \beta \) down to 0.2).

In the bottom frame of Fig. 1 we reported the evolution of \( g^{(2)}(t_w, t) \), observed on the same set of \( t_w \) reported in top frame, when a shear rate \( \dot{\gamma} = 223 \, s^{-1} \) is applied. Though a stationary state is never reached in the observation time window, for long enough waiting times, the slow relaxation time grows slower than exponentially (the correlation functions come closer), while the shape of the relaxation function approaches a constant profile (constant stretching exponent). The two step decay for \( F_q(t_w, t) \):

\[
F_q(t_w, t) = f \exp \left[ -t/\tau_s \right] + (1 - f) \exp \left[ -t/\tau_f \right]
\]

where all parameters \( (f, \tau_s, \beta, \tau_f) \) depend on \( t_w \) and on \( q \). provides a very good fit for all the correlators corresponding to the different \( \dot{\gamma}, t_w \) values here investigated. The presence of a shear induced crossover becomes more evident if we plot the fitting parameters \( (\tau_s) \) (average slow relaxation time \( \tau_s/\beta \Gamma(1/\beta) \), where \( \Gamma \) is the Euler gamma function) and \( \beta \) (stretching exponent) as a function of \( t_w \) for different shear rates as in Fig. 2. As long as the system’s dynamics is fast on the timescale \( \dot{\gamma}^{-1} \) (indicated by arrows in the plot), non-equilibrium dynamics takes place as if shear were not present: both the relaxation time \( \tau_s \) and the corresponding stretching exponent \( \beta \) evolve with waiting time following the \( \dot{\gamma} = 0 \) curve (full circles). The presence of shear starts to affect the dynamics as soon as \( \tau_s \) becomes larger than \( \dot{\gamma}^{-1} \): the growth of \( \tau_s \) is dramatically reduced (even if not completely stopped) and the stretching parameter \( \beta \) behaviour flattens. Though aging is never completely absent, the slow relaxation dynamics, for a given waiting time, appears to be very sensitive to \( \dot{\gamma} \) being faster and less stretched as \( \dot{\gamma} \) increases. If we suddenly increase \( \dot{\gamma} \), rejuvenation is observed leading to faster relaxation time and smaller stretching (higher \( \beta \)). Crosses in Fig. 2 are the average relaxation times and stretching exponents of two rejuvenated samples obtained by the two subsequent shear rate jumps: \( 63 \, s^{-1} \rightarrow 223 \, s^{-1} \) and \( 223 \, s^{-1} \rightarrow 446 \, s^{-1} \).

It is also instructive to look at the values of \( (\tau_s(\dot{\gamma}, t_w)) \) for constant \( t_w \) as a function of \( \dot{\gamma} \) as reported in Fig. 3. The grey region represents the half-plane \( (\tau_s) < \dot{\gamma}^{-1} \) where slow dynamics takes place on a timescale shorter than \( \dot{\gamma}^{-1} \). This region is not affected by the presence of shear: the fluid is Newtonian and, similarly to viscosity, \( \langle \tau_s \rangle \) is not dependent on \( \dot{\gamma} \). On the other hand shear plays an important role in the complementary half-plane...
FIG. 2: Average slow relaxation time $\langle \tau_s \rangle$ and stretching exponent $\beta$ as a function of waiting time $t_w$ during aging under different shear rates $\dot{\gamma}$: (△)446, (○)223, (◇)67, (□)22 s$^{-1}$. Solid symbols (●) refer to aging without shear. Arrows in top frame indicate the $\dot{\gamma}^{-1}$ values corresponding to each curve.

FIG. 3: Average slow relaxation time $\langle \tau_s \rangle$ as a function of shear rate $\dot{\gamma}$ for seven evenly spaced waiting times between 0 and 30 hours. Grey area represents the half-plane $\langle \tau_s \rangle < \dot{\gamma}^{-1}$. Dashed line is a fit to a $\dot{\gamma}^{-1}$ power law.

where $\langle \tau_s \rangle$ displays a strong sensitivity to $\dot{\gamma}$. The non-Newtonian behaviour in the upper half-plane of Fig. 3 resembles the same $\dot{\gamma}^{-1}$ power law (dashed line) observed in rheological measurements of Laponite viscosity [9].

The whole scenario depicted above provides a microscopic counterpart of the strong shear-thinning behaviour observed in rheological studies of Laponite [9] and of many other soft materials. In both real [1] and simulated [2, 3] liquids, the viscosity crossover from a Newtonian to a non-Newtonian regime (power law dependence on $\dot{\gamma}$), is usually found to be described by scaling laws such as:

$$\eta(\dot{\gamma}) \simeq \frac{\eta(0)}{1 + \dot{\gamma} \tau_\eta}$$

(1)

Since viscosity is related to structural relaxation, one could think, as suggested in [3], of a dynamical analogue of (1) in the form:

$$\frac{1}{\tau(\dot{\gamma})} \simeq \frac{1}{\tau(0)} + A \dot{\gamma}$$

(2)

Which has also the advantage of an easily readable meaning: shear rate provides a parallel relaxation channel to the system which becomes predominant as soon as $1/\tau(0) \ll A \dot{\gamma}$. This simple relation is indeed found to work remarkably well in computer models for supercooled liquids [4]. Using the same kind of reasoning, one would expect that even in an aging sample, as soon as the unperturbed relaxation time grows large enough, shear rate will fix the relevant timescale and the system will become stationary even in the non-ergodic phases. This is actually what has been observed in a number of recent numerical and theoretical papers, and also by rheological studies.

We are now in the position of testing (2) by directly investigating the complete time behaviour of density dynamics in the presence of a shear flow. At a first glance one would conclude that Fig. 2 is in contradiction with (2) and the expectation that shear stops aging. It is, in fact evident that relaxation time continues to grow, even if no longer exponentially fast, at least for more than one order of magnitude since it first “feels” the shear field. On the other hand, as shown in Fig. 2 when the crossover occurs, the value of the stretching exponent is about 0.5 or less. This means that the unperturbed dynamics occurs on a broad spectrum of timescales (spanning two decades at least) and that $\langle \tau_s \rangle$ only represents an average relaxation time. Many approaches to slow dynamics in complex systems [10] suggest that such a broad spectrum of time scale arises from the heterogeneous character of slow dynamics. Assuming this heterogeneous scenario, shear is only effective in interrupting aging for those timescales growing longer than a fixed, shear dependent, cutoff. In other words we expect that (2) holds separately for every timescale composing structural relaxation. The above scenario qualitatively accounts for
both the observations of a slowly growing (non saturating) structural relaxation time after the crossover and a narrowing in the distribution of timescales with respect to the unperturbed case. We want to push now the above observations on a more quantitative ground. Assuming that Eq. (2) holds separately for each timescale and calling $G(t, \tau)$ the unperturbed distribution of timescales

$$F_q^0(t_w, t) = \int_0^\infty G(t, \tau) \exp[-t/\tau] d\tau \quad (3)$$

we would expect that shear affects $F_q$ as follows

$$F_q^\gamma(t_w, t) = \int_0^\infty G(t, \tau) \exp[-t(1/\tau + A\gamma)] d\tau \quad (4)$$

$$= F_q^0(t_w, t) \exp[-tA\gamma] \quad (5)$$

In other words if we divide the correlation function measured at a given waiting time $t_w$ and shear rate $\gamma$ by the corresponding unperturbed ($\gamma = 0$) correlation measured at the same $t_w$ and plot the result as a function of $\gamma t$, we should obtain the master curve $\exp[-A\gamma t]$. In Fig. 4 we report the result of such a procedure obtained for three different values of $\gamma$ and two waiting times. All curves collapse on the same master curve which is well represented by a simple exponential with $A = 0.22$ (solid line). Similarly, we could predict the shape of relaxation for given $t_w$ and $\gamma$ by simply multiplying the unperturbed correlation function for the same $t_w$ by the function $\exp[-A\gamma t]$. If we do this for the $\gamma$ values here investigated and fit the result with a stretched exponential we obtain a prediction for $\tau_\alpha(t_w, \gamma)$ and $\beta(t_w, \gamma)$. The results of such a procedure, for those $t_w$ values where $F_q^0(t_w, t)$ is available, are shown in Fig. 5 as solid lines. The overall agreement with the directly measured data points (open symbols) is very satisfactory and supports the picture of the slow non-equilibrium dynamics of Laponite as a heterogeneous superposition of relaxing units each independently coupled to shear.

In conclusion, we investigated the effect of shear on the non-equilibrium structural dynamics of an aging colloidal suspension of Laponite. The presence of a shear flow strongly affects dynamics as soon as structural relaxation enters the timescale $\gamma^{-1}$. In this shear dominated region the shear rate dependence of the average slow relaxation time $\langle \tau_\alpha \rangle$ is well approximated by the power law $\gamma^{-\alpha}$ with $\alpha \sim 1$. The effect of shear on the detailed shape of the intermediate scattering function can be well described assuming that the slow relaxation process arises from the heterogeneous superposition of many relaxing units each one independently coupled to shear rate with a parallel composition rule for timescales: $1/\tau \rightarrow 1/\tau + A\gamma$. The authors wish to thank F. Zamponi for helpful discussions.

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