Dynamics of a colloidal glass during stress-mediated structural arrest

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received 9 October 2009; accepted in final form 8 April 2010
published online 19 May 2010

PACS 82.70.Dd – Colloids
PACS 81.05.Kf – Glasses (including metallic glasses)
PACS 83.85.Cg – Rheological measurements—rheometry

Abstract – We employ parallel superposition rheology to study the dynamics of an aging colloidal glass in the presence of a mean-field stress $\sigma_m$. Over a range of intermediate stresses, the loss modulus exceeds the storage modulus at short times but develops a maximum concomitant with a crossover between the two as the system ages. This is attended by a narrowing of the loss peak on increasing stress. We show that this feature is characteristic of the structural arrest in these materials, which is made observable on reasonable timescales by the activating influence of the stress. The arrest time displays an exponential dependence on inverse stress. These results provide experimental validation of the role of stress as an effective temperature in soft glassy systems as has been advanced in recent theoretical frameworks.

The thermalizing effects of shear have been well recognized in colloidal systems [1–4] where an applied shear stress lowers energetic barriers to particle motion, or an imposed shear rate provides higher particle mobility than expected based on the system (bath) temperature. In such scenarios, accelerated dynamics are found in equilibrium systems under shear such as non-Brownian particulate suspensions [5] and polymers in non-linear creep flow where time-stress superposition is observed [6]. However, the effects of imposed stress on the dynamics of out-of-equilibrium glassy materials, that is, in systems which display aging, has not been explored experimentally in great detail. In the presence of an applied stress, such systems, for example gels, pastes, emulsions and slurries, are known to display a viscosity bifurcation [7,8]. Application of a sub-critical stresses $\sigma < \sigma_c$ results in an eventual immobile state as the shear rate developed in response to the stress decreases due to an ever-increasing viscosity as the system ages or structures over time. By contrast, application of a larger than critical stress produces a quasi-steady state response with a well-defined shear rate and finite viscosity. These respective displays are due to the dominance of either aging or rejuvenation in the presence of the applied stresses, where rejuvenation in this sense should be understood simply as a decrease of the characteristic relaxation time of the system, rather than a strict path reversal of aging.

Here, we report on the evolution of stress activated dynamics in an aging repulsive colloidal glass. Considerable attention has been paid to the questions of aging and rejuvenation in these and analogous systems, as often studied by creep [9] or dynamic scattering methods [10] where time-elapsed time rescaling is obtained. By contrast, explicit observations of the loss and storage modes of the system and their evolution during structural arrest after rejuvenation have not been made. Specifically, we focus on the regime of stresses below the viscosity bifurcation where physical aging of the system brings it to a dynamical arrest on timescales that are comparable to the observation time. We find that the time evolution of the complex modulus is strongly dependent on the magnitude of the applied shear stress. At small stresses, the storage modulus increases and the loss modulus decreases, both with weak power laws, with $G'' > G'''$. The system shows an entirely viscous response in the presence of large stresses. At intermediate stresses, $G'' > G'$ at short times but develops a peak concomitant with a crossover between $G'$ and $G''$ as the system ages and undergoes arrest, permitting a novel observation of the structural relaxation “in reverse.” Our results indicate that this is a characteristic feature of structural arrest in these systems. The shape of the loss peak is strongly dependent on the applied stress, with a significant narrowing displayed at higher stresses.

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Our system is an aqueous suspension of Laponite which consists of disc-like clay particles of 25 nm diameter and 1 nm thickness. “Wigner” glasses are formed at low ionic strength in dilute conditions due to long-range electrostatic repulsion between the particles [11]. The system displays glassy dynamics, as shown by previous reports [10,12,13]. Samples are prepared by mixing Laponite XLG (Southern Clay Products) into ultra-pure water, adjusted to pH 9.5 to ensure chemical stability of the particles [14]. The suspensions are mixed for 20 minutes and then allowed to develop quiescently for several days, defining a well-controlled and reproducible initial state. The system is thus in the full aging regime, as opposed to the short time “gelation” regime, the delineation between which has been described in the literature [15]. Measurements are conducted on an MCR 301 rheometer (Anton-Paar) mounted on an air table for mechanical noise isolation. Evaporation of water from the sample is successfully suppressed without perturbing the system via application of a thin film of mineral oil at the sample edge. In all measurements, samples are first subjected to a rejuvenating shear at \( \dot{\gamma} = 100 \text{s}^{-1} \) for 100 s. This eliminates any flow history and provides a reproducible initial state in which the viscosity is well defined within ±5%. The sample is then brought to rest and allowed to sit without external perturbation for 1 second before the start of subsequent measurements.

We monitor the dynamic modulus via application of a small probe stress oscillation \( \sigma_p(t) \) atop a fixed mean-field stress \( \sigma_m \) applied to the sample. The overall stress is \( \sigma(t) = \sigma_m + \sigma_p \sin(\omega t) \) where the applied frequency \( \omega = 10 \text{rad/s} \). Probe stresses were varied from 0.2 to 1 Pa. In each case, the response of the system was verified to be linear in \( \sigma_p \), confirming that the experiment samples the linear properties that exist in the presence of the mean-field stress \( \sigma_m \). Parallel superposition rheology as applied here has been successfully used to study the dynamics of a variety of complex fluids under shear. It is to be noted that the interpretation of results from these flows may be complicated by coupling between the stationary and oscillatory components and a shear rate dependence of the perturbation spectrum [16]. This limits strict quantitative interpretation of data, but not the utility in providing a general description of the stress or shear rate dependence of dynamics [17]. For this reason, we assess our results here only qualitatively, as is common practice [18,19].

For observations of the viscosity bifurcation, following the initialization described, the sample is subjected to a fixed stress and the time dependent shear rate developed in response is observed. The sample is re-initialized and the stress is iteratively increased to cover a suitable range.

We examine the frequency dependent and non-linear dynamics of the system via frequency and strain sweeps. Samples are allowed to sit quiescently for 30 minutes following the rejuvenating shear at \( \dot{\gamma} = 100 \text{s}^{-1} \). This duration is large relative to the sweep time so the system does not age considerably during the actual measurement.

The frequency sweep is typical of this class of materials, with a wide regime where both the storage and loss moduli scale weakly with frequency. In this case, \( G' \sim \omega^{0.01} \) and \( G'' \sim \omega^{-0.2} \), fig. 1a, for \( \varphi = 3.5 \text{wt.\%} \). In the strain sweep, there is a linear viscoelastic regime of constant \( G' \), \( G'' \) extending up to \( \gamma \approx 10\% \). This is followed by a decrease in the storage modulus and a peak in the loss modulus on increasing strain as the system becomes non-linear, fig. 1b. Deep into the non-linear regime, both moduli follow a power law dependence on \( \gamma \) with the ratio between the exponents approaching 2 with increasing strain, indicative of strong fluidization of the system. The system displays physical aging with the complex modulus scaling as \( G^* \sim t^{0.2} \), after cessation of the rejuvenating shear, inset fig. 1a.

Application of a fixed stress \( \sigma_m \) after sample rejuvenation produces an initial shear rate which then evolves in time as the sample ages and its viscosity changes. For stresses larger than some critical stress, \( \sigma_m > \sigma_c \), a steady shear rate was achieved, indicating that physical aging during the measurement window was suppressed. Application of smaller stresses \( \sigma_m < \sigma_c \) resulted in a time-dependent decrease of the shear rate during the course of the measurement. The data show an initial regime of slow

![Figure 1](image-url)
Stress-activated dynamics during structural arrest

Fig. 2: (Colour on-line) Evolution of the shear rate for stresses less than the bifurcation stress $\sigma_c$ for $\varphi = 2.75, 3.0$ and $3.5$ wt.\% (top to bottom).

A power law decay followed by a terminal regime where $\dot{\gamma}(t)$ appears to diverge towards zero as the viscosity increases rapidly, fig. 2.

The dynamical arrest that occurs in the presence of these sub-critical mean-field stresses is due to the aging of the system resulting in eventual vitrification.

One can think of vitrification as a structural relaxation conducted “in reverse”. In an equilibrium system such as a model Maxwellian material, the structural relaxation is traversed by progressively decreasing frequency. In a non-equilibrium system, observation at a fixed frequency as a function of time exposes the underlying frequency dependence as the system ages with the passage of time. The near linear dependence of the characteristic time

Fig. 3: (Colour on-line) Time evolution of storage (solid symbols) and loss moduli (open symbols), under different applied stresses for $\varphi = 2.75, 3.0$ and $3.5$ wt.\% (top to bottom) measured with probe stresses of 0.2, 1 and 1 Pa.
on sample age in many glassy materials which enables time-elapsed time universal scaling and the width of the glassy power law regime where \( G' \sim \omega^x \) with \( 0 < x < 1 \), both underline this point. One can expect then that fluidization of a glassy system by an applied stress \( \sigma < \sigma_c \) will reveal a dynamical signature akin to that of the glassy power law regime where \( G' \sim \omega^x \). The data have been fit to eq. (1), as shown in fig. 5, reflecting the slight curvature observed:

\[
\tau \sim \exp\left[ -\frac{E}{(\sigma_m - \sigma_0)} \right].
\] (1)

In the context of stress as an effective temperature, the timescale for diffusive particle motion should scale as \( \tau_d \sim \exp(E/\sigma_m) \). Correspondingly, the timescale for particle arrest should scale inversely, as \( \tau_d^{-1} \). The parameter \( \sigma_0 \) accounts for the fact that by necessity the arrest timescale diverges above a critical stress beyond which aging of the system will not bring it to arrest. This stress should be identical to the bifurcation stress, \( \sigma_c \), discussed earlier. We observe good correspondence between \( \sigma_d \) from the fits of fig. 5 and estimates of \( \sigma_c \) taken from the time-dependent shear rate experiments. Both \( E \) and \( \sigma_0 \) exhibit an apparent power law dependence on the volume fraction, scaling with an exponent \( \approx 4 \), although the composition range is quite limited, inset fig. 5. More significantly, however, \( E \) scales directly proportional to \( \sigma_0 \), indicating that the critical bifurcation stress can be interpreted in terms of an energetic barrier to particle motion. This is in agreement with observations which note close correspondence between bifurcation stresses and the yield stress in other pasty materials [22].

The loss peak that develops as the sample ages and arrests exhibits a marked dependence on \( \sigma_m \), broadening significantly as the stress is decreased, or conversely, narrowing at higher stresses. A Lorentzian function was used to provide an empirical estimate of the peak width. It was found to decrease markedly from approximately 3 decades for \( \sigma_m = 13 \) Pa to less than 1.4 decades for \( \sigma_m = 28 \) Pa, for \( \varphi = 3.5 \) wt.%. This narrowing can be understood as due to a narrowing of the distribution of lossy modes in the glass, as similarly observed in glassy polymers subjected to external stresses which likewise activate segmental motion the system [23]. This variation in the shape of the loss peak precludes re-scaling into a universal form. As a result, the data do not display time-stress superposition, just as time-temperature superposition is lost in equilibrium systems on approaching \( T_g \) where the width of the loss modes also become temperature dependent, broadening with decreasing \( T \) [24,25].

Coussot et al. have advanced a model which describes a time-dependent viscosity resulting from a competition between aging (structuring) and rejuvenation in the presence of an applied stress [26]. This phenomenological
The approach describes the system in terms of a canonical structural parameter $\lambda$ which grows with a characteristic time, but also is degraded by the action of shear, with system dependent constants of proportionality and a specific viscosity that is a simple power law function of $\lambda$. Our system displays the hallmark behaviors of the model such as an asymptotic characteristic time for the onset of structural arrest at small stresses, an exponential dependence of this time at intermediate stresses and a fast transient leading to a steady state viscosity at high applied stresses. Our results here provide, for the first time, a detailed look at the dynamics of the system in the low stress regime where arrest occurs and shows that the features of this data are broadly consistent with observations made during viscosity bifurcation experiments.

Recent work has shown that the competition between aging and rejuvenation in soft glassy materials is dependent on the magnitude of stress or strain imposed [9], including the observation of an over-aging regime [27]. Here, we see that for our repulsive glass, the flow arrest time increases exponentially, and eventually diverges with increasing stress. We do not observe an overaging regime within which the flow arrest time decreases with increasing stress. The reasons for this remain unclear. One possibility is simply that the stresses used in the current work are too large for the system under study to elicit an over-aging response. For the range of stresses considered here, the elastic modulus of the colloidal glass was independent of the stress applied during structural arrest. As shown in fig. 3, within the experimental uncertainty, the system asymptotes towards a single curve, displaying power law aging of the elastic modulus at long times. This is in contrast to data and a conceptual model derived from bentonite suspensions where both the elastic modulus and the yield strain were seen to increase with the magnitude of the stress applied during the liquid-solid transition [28]. More careful measurements, particularly out to longer times, are required to conclusively test this model in the present system, but it provides a useful starting point for the consideration of the effect of stress on the mechanical properties of the colloidal glass after structural arrest.

The dynamic measurements demonstrate that the aging of the system and resulting arrest give rise to a temporal response that parallels that of the frequency dependence observed in non-aging systems on traversing the structural relaxation time. The peak in the time dependent loss modulus is a dynamical signature of the structural arrest due to aging. Analogous to the manner in which stress activates particle dynamics in equilibrium systems, it is shown here that it slows aging, delaying the onset of structural arrest in this out-of-equilibrium system. The dependence of the arrest time on stress is strikingly similar to that of the relaxation time in thermally activated fragile glass formers on approaching the glass transition, highlighting the activating role of stress in structural glasses and further validating the concept of stress as an effective temperature. To the best of our knowledge, this represents the first systematic characterization of stress mediated structural arrest in a colloidal glass due to physical aging. These results may spur progress on quantitative numerical and experimental investigation of the role of stress in the aging dynamics of soft glassy materials.

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The authors thank P. COUSSOt and G. OVARLEZ for insightful discussions and gratefully acknowledge NSF funding under CBET-0828905. This work was also made possible by support from Chevron Corp.

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