Time resolved viscoelastic properties during structural arrest and aging of a colloidal glass

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Evolution of the energy landscape during physical aging of glassy materials can be understood from the frequency and strain dependence of the shear modulus but the non-stationary nature of these systems frustrates investigation of their instantaneous underlying properties. Using a series of time dependent measurements we systematically reconstruct the frequency and strain dependence as a function of age for a repulsive colloidal glass undergoing structural arrest. In this manner, we are able to unambiguously observe the structural relaxation time, which increases exponentially with sample age at short times. The yield stress varies logarithmically with time in the arrested state, consistent with recent simulation results, whereas the yield strain is nearly constant in this regime. Strikingly, the frequency dependence at fixed times can be rescaled onto a master curve, implying a simple connection between the aging of the system and the change in the frequency dependent modulus.

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Time evolution of the dynamic and mechanical properties is a hallmark of many disordered materials. Such physical aging is found in polymeric and molecular glass formers below the glass transition temperature, \( T_g \), as well as in dense colloidal systems at rest \([1,2]\). The overarching commonality is the structural arrest that occurs at the glass transition which is manifest in the dramatic slowing of the system’s dynamics. The boundary of the glassy state in colloidal suspensions is defined by volume fraction, \( \phi \), whereas in other structural glasses the boundary is thermal and defined by a nominal \( T_g \). In such systems, structural arrest and aging occur following a rapid temperature quench from the equilibrium liquid state, charting the slow evolution of the glass towards a presumed long-time equilibrium or time-invariant state. In colloidal systems however, with the exception of recent thermoresponsive materials, for fixed \( \phi \), the entry into the glassy state is mechanically controlled by the application and subsequent removal of shear stresses well in excess of the material’s yield stress. This has variously been called shear melting and rejuvenation wherein the effective thermalizing role of stress is utilized to produce a well defined initial state for the colloidal glass \([3,4]\). Rapid cessation of flow produces in effect a mechanical quench from a free-flowing fast relaxing liquid to a metastable fluid which quickly becomes arrested as it enters the glassy or jammed state and undergoes subsequent aging, as shown by Ovarlez and Coussot \([5]\).

Progress has been made in simulations of thermally quenched LJ \([6,7]\) and hard sphere glasses \([8]\), as well as in the phenomenological soft glassy rheology (SGR) model \([9]\) which utilizes an effective temperature concept. Comparatively less is known regarding the evolution of colloidal glasses at short times following a mechanical quench as the system undergoes structural arrest from a metastable fluid. Access to the time evolution of the frequency and strain dependent complex shear modulus, \( G^*(\omega, t) \) and \( G^*(\gamma, t) \), during structural arrest would provide valuable insight into the nature of the colloidal glass transition, particularly as these are properties of interest for theoretical frameworks, including SGR. Recent studies have succeeded in characterizing \( G(t_w, \omega) \) in freshly mixed suspensions at times greater than 30 mins \([10]\). Measurement of these properties at shorter times, however, is a significant challenge in these fast aging materials, and such time resolved properties have not been reported to date. In this Letter we consider the time dependence of \( G^*(\omega) \) and \( G^*(\gamma) \) for a model colloidal system with repulsive interactions. A systematic series of time dependent measurements facilitates reconstruction of the frequency and strain dependence as a function of age after cessation of a strong rejuvenating flow. We are able to observe the structural relaxation time for systems of small age and find that it scales exponentially with elapsed time. The yield stress increases logarithmically with age while viscous dissipation during yielding increases linearly. Remarkably, \( G'(\omega) \) and \( G''(\omega) \) at fixed times can be shifted onto a master curve that describes the frequency dependence of the system over all times considered.

Our system is a repulsive colloidal glass of charged disc-like clay particles, Laponite, in water. At low ionic strength, long-range Coulombic repulsion produces arrested states at low concentrations of a few wt.\% which display aging \([11,12]\). Laponite XLG (Southern Clay Products) was dried overnight and then mixed with wa-
ter at pH 9.5 to produce a 3.5 wt.% suspension. Suspensions were mixed by vortexing for 2 minutes followed by sonication for 20 minutes and then allowed to stand quasi-statically for 4 days. During this time, the clay particles become fully hydrated and form a clear gel-like material. Studies were performed on this resultant material and thus reflect dynamics of the arrested glass and not any changes due to initial hydration [15]. Measurements were conducted on an Anton-Paar MCR301 rheometer in strain-controlled mode in a cone-plate geometry (1°, 50 mm). Samples were subjected to a strong rejuvenating flow at $\dot{\gamma} = 3000\text{s}^{-1}$ for 100 s and then mechanically quenched by a rapid linear cessation of flow over 1 s. This resulted in a reproducible and well defined initial state. A series of time sweeps were conducted either at a fixed strain of $\gamma = 1\%$ for the frequency dependent experiments for 1000 s, or at a fixed frequency of $\omega = 10\text{rad/s}$ for strain dependent studies for 600 s. At the end of each time sweep samples were subjected to the rejuvenating flow step before measurements at the next frequency or strain. A thin film of mineral oil was successfully used at the edge of the cone to suppress evaporation.

The strong shear flow in the rejuvenating step produces a liquid state from an initially solid-like material. At short times after flow cessation, the system exhibits liquid-like behavior, with the loss modulus exceeding the storage modulus, $G'' > G'$. Both moduli increase rapidly with time, but the rate of increase of $G'$ is faster such there is a crossover at a characteristic time, $t_c$, during the experiment, Fig. 1. This time ranged from about 5 to 50 seconds, with the shortest times encountered for the highest frequencies. In all cases, $t_c \gg 1/\omega$, ensuring that data are not affected by sample evolution during a single strain cycle. At long times $G'' \sim \ln(t)$ but the distinction from a weak power-law dependence where $G' \sim t^{0.5}$ and $G'' \sim t^{-0.4}$ is small.

The crossover time is the characteristic timescale for the structural arrest of the system following the perturbation produced by the rejuvenating shear flow [16]. Microscopically, it is related to the timescale for the formation of particle cages responsible for dynamic arrest [2]. This timescale is not the same as the structural relaxation timescale of the system. The structural relaxation time, $\tau$, is given by the inverse of the sampling frequency when the sample is at an age equal to the structural arrest time, $t_c$, inset Fig. 1. This point is made clear in the frequency representation of the data. The frequency dependence at fixed sample age is reconstructed from the time-dependent data across different frequencies. For clarity, 5 times are selected, Fig. 2. At short times, $t \lesssim 10$s, the system displays a frequency dependence that is typical of a liquid-like state, with $G'' > G'$. At intermediate times, $10 < t < 100$s, the frequency dependence lessens and there are crossovers between $G'$ and $G''$ that falls within the accessible frequency space. Finally, at long times, $t > 100$s the frequency dependence has nearly vanished as the relaxation frequency for the system is far outside the observation window, and the system is well arrested. A plot of the inverse of the cross-over frequencies as a function of sample age simply replicates the inset plot of Fig. 1. The relaxation time varies exponentially with sample age, $\tau \sim \exp(t/\tau_a)$, with a characteristic time $\tau_a \approx 10$s. Exponential evolution of relaxation time has been observed in Laponite suspensions during the liquid-solid transition following the initial mixing of clay aggregates with water [17, 18]. In those cases the transition occurred on timescales of several hours and partially reflects the initial hydration of the system. In the present case, the transition occurs on timescales less than $10^2$s in an already well hydrated system. The information contained in the extracted frequency dependent spectra is quite compelling. The spectra represent the instantaneous underlying frequency response of the system as encountered during the rapid aging from a liquid-like to solid-like state.

Remarkably, frequency dependent data at fixed times can be shifted to construct a master curve. Data at short times as expected are shifted to lower frequencies where the response of the system is more liquid-like, and conversely long-time data are shifted to higher frequencies as well aged systems display solid-like behavior. The master curve is constructed using only horizontal shifts, Fig. 3 along with shift factors inset. At short times the shift factor dependence on age mirrors that of the relaxation timescale, with an exponential form. This is followed by a power-law regime at long times. The shift factors are fit as $a_t \sim -a\exp(-t/\tau_a^*) + bt^z + c$. The characteristic time for the exponential component here is $\tau_a^* \approx 9$s and $z \approx 1.8$. The same shift factors have been used to scale both the storage and loss moduli. The correspon-
FIG. 2. Reconstructed frequency dependence of the storage and loss moduli, at 5 times shown in seconds. Lines are visual guides.

dence between the characteristic times, $\tau_s^a \approx \tau_a$, suggests strongly that the evolving structural relaxation underlies the rescaling of the data at short times.

FIG. 3. Master curve of storage and loss moduli (filled and open symbols) as a function of reduced frequency. Lines are shown as visual guides. Inset: Shift factors $a_t$ as a function of system age. The line is a fit to $a_t \sim -a \exp(-t/\tau_s^a) + bt + c$ with $\tau_s^a \approx 9s$ and $x = 1.8$.

We interpret our data as indicative of two distinct processes. The first is structural arrest and the second is aging. Structural arrest as discussed is associated particle localization and the process mediates the transition from the metastable fluid to the arrested glass. Beyond this caging regime, the system settles into power-law aging wherein the evolution of properties occurs via the small scale cage rearrangements that are presumed to characterize the aging of structural glasses. This regime is characterized by the system’s exploration of its energetic landscape and continually slowing evolution towards a stationary state. These results are qualitatively similar to those of Bellour et al. where a transition from exponential to power-law aging of the relaxation time was observed in freshly prepared suspensions after several hours [18]. The strain dependence of the system modulus similarly displays two regimes. The same procedure is applied to time sweep data conducted at different strains to extract the underlying strain dependence of the system at fixed times. Again for clarity, a small subset of such reconstructed data sets is shown, Fig. 4.

FIG. 4. Reconstructed strain dependent storage and loss moduli, at different system ages in seconds as indicated. Lines are shown as visual guides.

At short times, the system is a fluid with $G'' > G'$ whereas at long times it displays the strain sweep typical of a soft glassy solid, with $G' > G''$ and a peak in the loss modulus during yielding. Examination in terms of stress-strain curves permits extraction of the yield point defined for the current purpose as the strain at which the slope (the shear modulus) deviates by more than $\epsilon_{dev} = 5\%$, Fig. 5. The data are robust against variation of $\epsilon_{dev}$ from $2.5\%$ to $10\%$. The yield stress and yield strain, $\sigma_y$ and $\gamma_y$, show opposing tendencies. At short times, $\sigma_y$ is quite independent of system age, but shows a marked upturn around $t = 20 - 30s$ after which it evolves logarithmically with time. By contrast, $\gamma_y$ continually decreases with time, before an asymptotic approach near $t = 100s$ to a relatively constant value, $\gamma_y \approx 4\%$, which is maintained at long times. Logarithmic increase of yield stress with age is known from experiments on polymer glasses [19] and has been recovered in simulations on binary LJ glasses [8, 9] and polymers [20]. As noted in [9], the short time domain where $\sigma_y$ is independent of age is not a common or easily accessed situation experimentally. The data of Fig. 5 however reproduce this behavior quite well and provide experimental verification of the simulation findings. The results are coherent with the framework developed from the frequency dependent data. They corroborate a scenario in which the system evolves first via structural arrest due to cage formation, and then later via aging which continues to increase the modulus and yield stress of the glass. The yielding of
structural glasses is known to occur via a peak in the loss modulus, which is associated with viscous dissipation during the cage breaking process [21]. Prior work has established that the size of this peak, as well as the stress overshoot in start-up flow is correlated to the time at rest or age of the system [11, 22]. Here, we resolve the evolution of this viscous dissipation with time, including at short absolute times, as well as times that are short relative to the timescale for conducting a traditional strain sweep measurement. We define a normalized quantity, \( \Lambda = G''_{\text{peak}}/(G''_{\text{linear}}) - 1 \) based on the ratio of the loss modulus peak to its average value in the linear regime. The data reveal an absence of measurable dissipation at short times, \( t < 100s \), and a linear increase in \( \Lambda \) with time thereafter.

FIG. 5. Left: Stress versus strain at different system ages of 1 (bottom), 10, 30, 60, 100, 200, 300, 400, 500 and 600 (top) seconds. Lines are shown as visual guides. Right: Semi-log plot of \( \sigma_y \) and \( \gamma_y \) as a function of system age on left axis. On right axis: time dependent plot of normalized dissipation \( \Lambda = G''_{\text{peak}}/(G''_{\text{linear}}) - 1 \) during yielding.

These experiments have characterized in detail the frequency and strain dependence of a glassy system during structural arrest and subsequent aging. They rely on the fidelity of the strong rejuvenating flow in consistently returning the system to a well defined fluid-like initial state from which it subsequently evolves. This is in contrast to studies in which relatively weak rejuvenating flows were used, resulting in near-linear or slightly super-linear growth of the relaxation time with age. The use of much higher flow rates to rejuvenate the sample here resulted in access to a much more fluid state than considered in prior reports where strains and shear rates did not exceed \( \gamma \approx 300\% \) and \( \dot{\gamma} \approx 150\text{s}^{-1} \). This may account for the faster rate of aging following structural arrest and underscores the role of flow history as a determinant of the aging response [22].

The present data provide significant insight regarding the dynamics of soft glassy materials in regimes of interest that have been relatively unexplored. They reveal a rapid transition from the arrest regime to an aging regime with a typical timescale that is reflected in the frequency and strain dependent properties. The frequency data permit the unambiguous resolution of the structural relaxation time as a function of age, and display a universal scaling that is consistent with exponential and power-law dependencies in the arrest and aging regimes, respectively. The strain dependent moduli exhibit the same liquid to solid-like transition, with a decreasing yield strain and logarithmically increasing yield stress as a function of age, with marked changes in the yield stress near the timescale associated with structural arrest, \( \tau_a \). Concurrently, enhanced dissipation on yielding is seen to be a feature only of the arrested state, with the magnitude of this dissipation increasing linearly with age. To the best of our knowledge, these are the first experimental data that chart the dynamics and yielding behavior of a colloidal system undergoing structural arrest and subsequent aging at short times where many key features emerge. These results frame a useful picture of the dynamics of an out of equilibrium system in the transition from a metastable liquid to an aging glass.

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