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Dynamics of internal stresses and scaling of strain recovery in an aging colloidal gel

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We monitor the relaxation of internal stresses in a fractal colloidal gel on cessation of flow and find a weak power-law decay, $\sigma_i \sim t^{-\alpha}$ over five decades of time where $\alpha \approx 0.07$. The system exhibits physical aging of the elastic modulus, $G' \sim t^{\beta}$, with $\beta \approx \alpha$. Imposition of zero stress after waiting time t_w results in strain recovery as the system relaxes without constraint. Remarkably, recoveries at different t_w can be shifted to construct a master curve where data are scaled vertically by $1/\sigma_i(t_w)$ and plotted horizontally as $(t-t_w)/t_w^{\mu}$, where $\mu \approx 1.25$, indicative of a superaging response.

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Many out of equilibrium systems display a slow evolution of their dynamics and properties in time, toward an eventual stationary or equilibrium state. This process is referred to as "aging," and it is the hallmark of many disordered materials ranging from molecular, polymer, and spin glasses to colloidal gels and glasses [1–5]. Although the origin of the aging response varies widely in these systems, they share the commonality of a slow recovery of some canonical structural or dynamic quantity after a departure from equilibrium, usually initiated by a rapid change in a corresponding control parameter. For example, after a sudden temperature quench in polymer glasses, evolution of free volume and heat capacity lend themselves to both conceptual and experimental investigations and have proved highly successful as metrics for the recovery behavior of polymers [6]. In spin glasses, below the spin-glass transition temperature T_c, removal of the external magnetic field leads to a slow and nonexponential decay of remanent magnetization on long time scales [7]. In colloidal systems, the picture is somewhat murkier [8]. Attempts to correlate the evolution in dynamics to measurable changes in structure have so far been unsuccessful [9]. The concept of internal strains and the resultant stresses due to out of equilibrium locations of constituent matter is a potential starting point for systems with soft potentials. It has been advanced with some success as a model for the dynamics of metallic glasses [10] wherein the distribution of stresses in the system defines the energy landscape that is traversed in the slow return to equilibrium during aging.

In this Rapid Communication, we consider strain recovery as a possible structural metric for the aging of an attractive colloidal system and examine the relationship between strain recovery and internal stress present in the system. We study a dispersion which exhibits rapid gelation via the formation of a fractal network on cessation of shear flow and follow the evolution of the shear modulus in time after gelation. We separately conduct experiments to monitor the relaxation of internal stresses after flow cessation as well as the strain recovery of the system after various waiting times during the stress relaxation. We find that the strain recovery behavior as a function of system age can be collapsed into a single curve using a vertical shift factor that is inversely proportional to the internal stress at the start of the strain recovery and a horizontal shift that scales inversely with elapsed time.

Our system consists of dilute dispersions (2–6 wt %) of carbon black particles (Cabot Vulcan XC72R) in a 3:1 mixture of mineral oil and tetradecane (Aldrich Chemical Co.). Samples are prepared by dispersing the particles in the solvent under vigorous vortexer mixing for 2 min followed by sonication for at least 30 min. Samples are studied in a stress controlled rheometer (Anton-Paar MCR301) using a 50 mm 1° cone-plate geometry. The instrument is mounted on an air table (Newport) to eliminate ambient mechanical vibrations which could perturb the sample. Two separate sets of measurements were performed. The first was of the time evolution of the system modulus. The second characterized internal stress relaxation and subsequent strain recovery. The protocol for the modulus evolution consists of four steps: (1) a high shear rate rejuvenation step at $\dot{\gamma}=1000\ \mathrm{s}^{-1}$ which completely erases the flow history of the material and ensures a reproducible starting point [11], (2) preshear at the shear rate of interest ($\dot{\gamma}=100\ \mathrm{s}^{-1}$) for 1200 s to achieve a steady-state viscosity, (3) cessation of flow (the shear rate was reduced from $100\ \mathrm{s}^{-1}$ to 0 in 0.1 s), and (4) measurement of the modulus as a function of time at $\omega=1$ rad/s and $\gamma=0.1\%$, within the, linear viscoelastic regime. We set $t=0$ at the end of step 3, where flow stoppage leads to rapid system gelation. The protocol for the second set of experiments consists of five steps. Steps 1–3 are identical to that of the first protocol. In step 4, the sample is maintained under a quiescent or zero strain rate condition (the system is stationary). The finite decaying stress required to maintain the stationary condition is the internal stress [12]. We measured the internal stress after cessation of flow as a function of time for a waiting period t_w. In step 5, at $t=t_w$, the zero strain rate is replaced by a zero stress condition, allowing the system to undergo strain recovery, analogous to that in traditional creep recovery experiments but without a zero strain reference state. The recovered strain is measured as a function of time via the displacement of the rheometer tool. Measurements consisting of steps 1–5 were conducted for a range of t_w from 1 to 10^4 s. The fourth step of our protocol provides a waiting time during which the sample ages quiescently. In typical rheological and dynamic scattering investigations, system properties are not monitored during the waiting step. The

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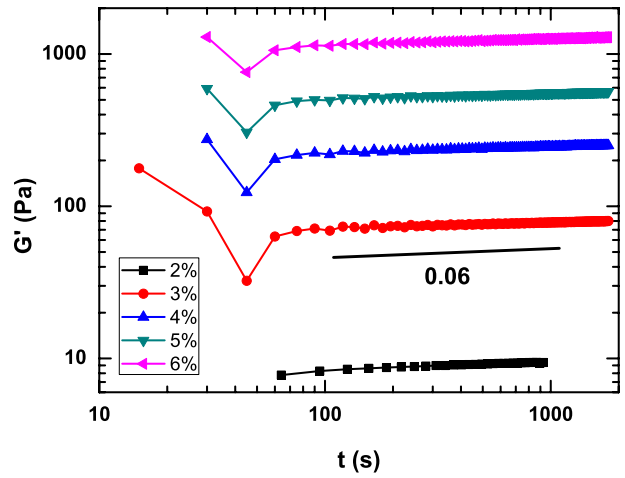

FIG. 1. (Color online) Evolution of elastic modulus as measured via oscillatory shear with $\gamma=0.1\%$ and $\omega=1$ rad/s.

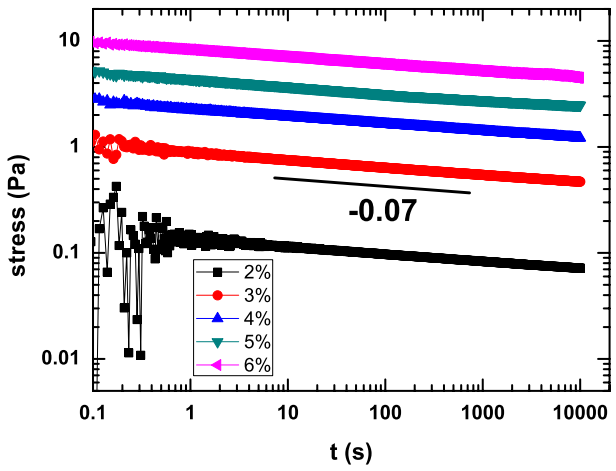

FIG. 2. (Color online) Relaxation of internal stress as a function of time t across different samples studied.

protocol applied here, however, permits correlation of the system properties measured after the waiting time with the internal stress dynamics characterized therein. It should be noted that application of this protocol requires the use of a stress controlled instrument.

Under the conditions of the experiment, the carbon black particles interact via an attractive van der Waals potential [13] that results in the formation of a colloidal gel at rest. Gelation in these systems is extremely fast [12,14] such that a substantial elastic modulus, well in excess of the viscous modulus, is observed at the earliest measurable times after cessation of flow, ~0.1 s. The elastic modulus displays a slow power-law increase with time (Fig. 1) where $G' \sim t^{\beta}$, with $\beta \approx 0.06$. This slow growth is due to thermally driven structural evolution of the fractal gel as observed for analogous systems [15].

Conversely, the internal stresses that are established in the system during the rapid gelation on cessation of flow exhibit a weak decay in time. The data are well fit by a power law, where the stress decays as $\sigma_i \sim t^{-\alpha}$ over five decades of time with $\alpha \approx 0.07$ as shown in Fig. 2. The close correspondence between the scaling exponents of the stress relaxation and the aging of the gel modulus suggests that the relaxation of internal stresses may be a key indicator for the aging of the system. Strain recoveries were recorded after various stress relaxation durations, t_w. The trajectories of the stress decays are well preserved across the numerous iterations of the stress relaxation and strain recovery measurements as shown for a 4 wt % sample in Fig. 3. Similar consistent behavior was observed for the other concentrations underlining the efficacy of the rejuvenating step in effectively eradicating the flow history of the sample.

The imposition of zero stress after waiting times t_w of 1, 10, 100, 10^3, and 10^4 s resulted in strain recoveries ranging from 1–5 %, measured over 2000 s (Fig. 4). At very short times, oscillations are present in the data due to inertially driven ringing of the sample. Such "creep ringing" is commonly observed in elastic gels when subjected to a stress impulse [16]. Here, the impulse originates from the internal stress of the sample itself which drives an initial fast recoil of the tool that is quickly damped out by the viscosity of the sample. Thereafter, the material undergoes a slow strain recovery as structural rearrangements occur during aging. Younger samples, those at smaller t_w, display an initial rapid strain recovery which appears to asymptote toward a long-time plateau value. By contrast older samples exhibit slower initial recovery from a short time plateau, followed by a gradual rise at long time. Samples of intermediate age show an inflection in their recovery. Remarkably, strain recovery data from different sample ages can be shifted to construct a single master curve at each composition (Fig. 5).

The vertical shift factors are simply inversely proportional to the value of the internal stress at the start of the strain recovery, $b(t_w)=1/\sigma_i(t_w)$. The horizontal shift factor $a(t_w)=t_w^{-\mu}$ where the best overlay is obtained for $\mu=5/4$. The vertical shift of the data by the inverse of the internal stress is strikingly simple. It is representative of an elastic strain that is recovered quickly at short times upon the start of the mea-

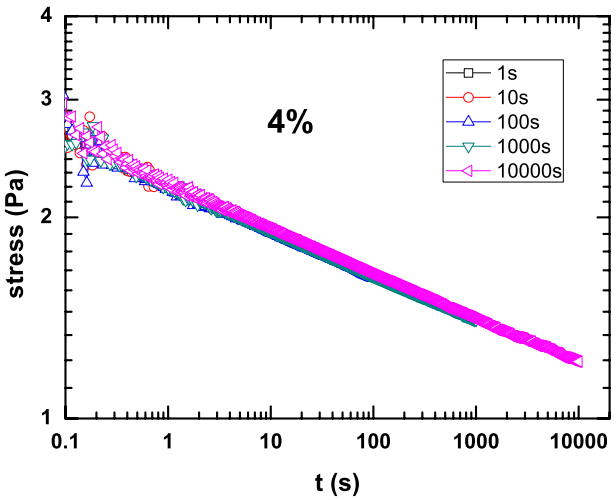

FIG. 3. (Color online) Internal stress decay during different waiting times $t=t_w$ for the 4 wt % sample. The stress is monitored up to the different values of t_w shown in the legend in separate iterations of the experiment.

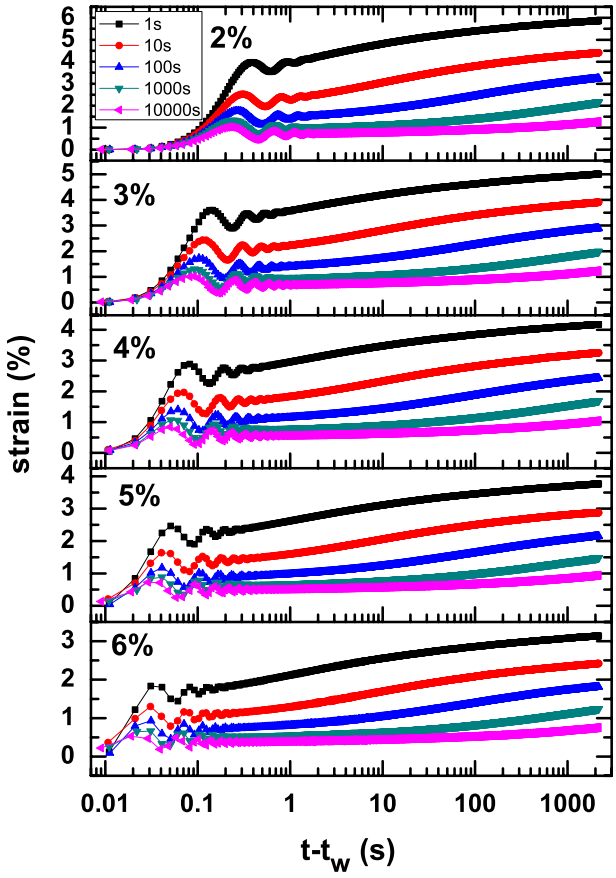

FIG. 4. (Color online) Strain recovery after preshear at 100 s^{-1} for different samples after different waiting times t_w. The concentration is mentioned in the figure. The times mentioned in the legend are different values of t_w.

surement. At long times, there is a far slower and continuous recovery of strain that persists out to the longest times measured, over 1000 s. We have ruled out external influences such as tool drift or room vibration in the system. It should be noted that the complex modulus and thus the dynamic viscosities of the samples are large, >200 Pa for the data of Fig. 4, so any small perturbations from external sources would be quickly dissipated. The shifting of dynamical responses for older samples to short rescaled time is commonly encountered in soft glassy systems [17–20] and has been related phenomenologically to the elapsed time rescaling first successfully advanced for polymer melts [21]. In these systems, however, either simple aging ($\mu=1$) or sub-aging ($\mu<1$) are observed, whereas here we obtain the best overlap for $\mu>1$ indicative of a superaging response. The master curves indicate that the dynamics of strain recovery at long times should be understood from the behavior of young materials, and vice versa, that the dynamics at short times are exhibited within the observation window by older samples. Such a display is counterintuitive if viewed simply in the context of recovered strain as marking the proximity to long-time equilibrium. In that sense, older samples would show more asymptotic tendency than younger samples and not the other way around as observed. This display, however, depends on the duration of the waiting time relative to the time

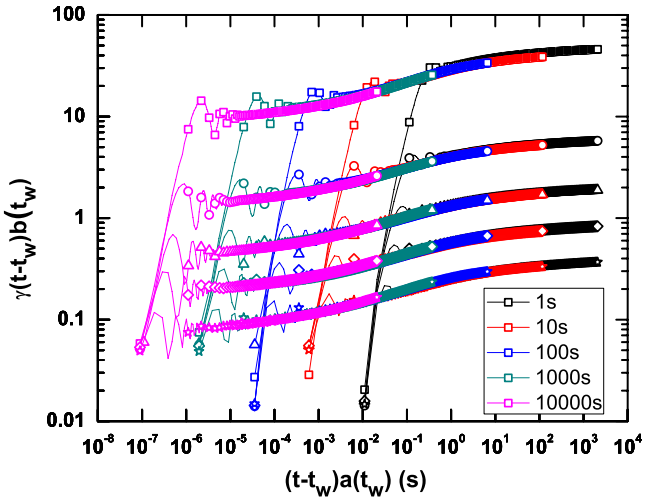

FIG. 5. (Color online) Strain recovery master curves assembled from data taken as a function of t_w. Squares, circles, triangles, diamonds, and stars denote 2, 3, 4, 5, and 6 wt % concentrations, respectively. $a(t_w)=t_w^{-5/4}$ and $b(t_w)=\sigma_i(t_w)^{-1}$. The times mentioned in the legend are different values of t_w.

scale for complete relaxation. For short t_w, we can view the response purely as a reflection of the slow vs fast dynamics of old vs young samples. Thus we expect elapsed time superposition to hold as it indeed does. The near uniform scaling of the internal stress relaxation with time across the different compositions studied (Fig. 2, $\langle\alpha\rangle=0.07\pm0.002$) enables the strain recovery to be simply scaled in terms of waiting time alone where the vertical shift factor is now $b\sim t_w^{\alpha}$. The data of Fig. 5, across 5 compositions, can all be rescaled with the same shift factors with very good fidelity.

Internal stresses are known to persist for long times in a variety of disordered systems [22–25]. Stochastic local stress relaxation events have been invoked as a concept to explain the unusual intermittency and ballistic dynamics observed in various soft materials [22,24,25]. The origin of these stresses is in the nonequilibrium location of system constituents. In colloidal systems with soft potentials, the sudden nature of an ergodicity breaking transition results in the arrest of particles away from preferred locations, that is, those where the gradient of the interparticle potential is minimized. As a result, forces exist among particles locally and are propagated throughout the system along particle contact chains or branches of the fractal network in the case of gels. The departure of the system from equilibrium is encoded by the distribution of local displacements of particles with respect to their equilibrium positions. Aging occurs via structural rearrangements that minimize these internal stresses as particles conduct a thermally driven exploration of their local potential energy landscape. In this framework, it is clear that the evolution of local strain, and in response, local stress chart the aging process. In a gel which is formed by the slow aggregation of freely diffusing species, such local displacements and stresses are directionally random and the resultant macroscopically observable stress is zero or vanishingly small. In the present system, the application of shear implies that the displacement of particles from their preferred equilibria and the deformation of particle clusters will be biased

along the flow direction. The rapid gelation that occurs on cessation of flow then results in residual stresses that are macroscopically nonzero. As expected, the stress acts counter to the direction of the deformation, so the sign of the stress is reversed if the direction of the shear flow is changed [12].

The correspondence between the relaxation of internal stress and the increase in the gel modulus points strongly to the identification of the internal stress state as an indicator for the aging response of the system. From a microscopic perspective, due to the deforming effect of the shear flow before gelation, structural rearrangements involved in aging are anisotropic and thus give rise to macroscopically observable strain recovery. The dynamics of this strain recovery then serve as a well-rationalized metric of the aging behavior of the system as demonstrated here. At long times, the total recovered strain, $[\gamma(t-t_w)]_{t=\infty}$, should be smaller for older samples, which have undergone longer stress relaxation under zero strain. The master curves however imply no significant difference in the long-time asymptotic values of recovered strain for different sample ages. This is an implication of the smallness of the experimental time scales relative to that for the full aging of the system. This point is underscored by the continuous power-law dependence of the internal stress relaxation over five decades of time.

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