Two Distinct Time-Scale Regimes of the Effective Temperature for an Aging Colloidal Glass

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Colloidal dispersions of Laponite platelets are known to age slowly from viscous sols to colloidal glasses. We follow this aging process by monitoring the diffusion of probe particles embedded in the sample via dynamic light scattering. Our results show that the time-dependent diffusion of the probe particles scales with their size. This implies that the fluctuation-dissipation theorem can be generalized for this out-of-equilibrium system by replacing the bath temperature with an effective temperature. Simultaneous dynamic rheological measurements reveal that this effective temperature increases as a function of aging time and frequency. This suggests the existence of two regimes: at probed time scales longer than the characteristic relaxation time of the Laponite dispersion, the system thermalizes with the bath, whereas at shorter time scales, the system is out-of-equilibrium with an effective temperature greater than the bath temperature.

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For a system in thermodynamic equilibrium with a heat bath at temperature $T_{bath}$, the well-known fluctuation-dissipation theorem (FDT) relates the response under an external disturbance to the random fluctuations that exist in the absence of the disturbance \[1\]. Recently, there has been extensive interest in extending this formulism to out-of-equilibrium systems by incorporating an effective temperature $T_{eff}$ that differs from $T_{bath}$ \[2, 3\]. The allure of extending the FDT is that it could help to generalize the behavior of some widely encountered out-of-equilibrium materials, such as glasses, gels, and granular media, which evolve or relax over very long time scales. Attempts to extend the FDT to glassy systems \[4, 5, 6\], granular materials \[7, 8\], and to a variety of soft materials \[9, 10, 11, 12\] have been reported. In particular, for an aging colloidal glass, $T_{eff}$ has recently been found to increase with age for short aging times \[12\]. To test the validity of this result, the dependence of $T_{eff}$ on the observation time scale (inverse of the probed frequency $\omega$) needs to be examined \[12, 13\]. It is also imperative to demonstrate that the generalized FDT has the same form as the classic version, but with $T_{eff}$ replacing $T_{bath}$.

In this Letter we demonstrate a generalized FDT for an aging colloidal glass formed by nanoscale platelets of Laponite RD in water. As the sample ages, we measure the diffusion of immersed probe particles of different sizes via dynamic light scattering (DLS). Significantly, we find the time-dependent diffusion of the probe particles to scale with their size. This, in turn, implies that the FDT can be generalized for this aging system by replacing the bath temperature with a $T_{eff}$. We then determine the dependence of $T_{eff}$ on aging time and frequency by combining DLS measurements with simultaneously taken dynamic rheological measurements. The results show that $T_{eff}$ increases as a function of aging time and probe frequency. This suggests that there are two distinct regimes of the effective temperature relevant for this colloidal glass, corresponding to probed time scales greater than and less than the characteristic relaxation time of the system.

The system studied here consists of a colloidal dispersion of Laponite RD platelets (roughly 3 nm thick and 25 nm in diameter) immersed in an aqueous solution at pH 10. To start the experiment, 3 wt % of Laponite RD is added to about 65 mL of water and stirred for 20 min. The dispersion is then pushed through a 0.45 mm filter to break up any remaining particle aggregates. At this stage, we mark time equal to zero for the Laponite aging experiment \[14, 15, 16\]. The sample is then distributed among several light scattering cuvettes and the couette of a Rheometrics strain-controlled (RDAIII) rheometer for simultaneous studies via DLS and rheology. The dynamic rheological response at different aging times is measured at small strains well within the linear viscoelastic range so as to ensure that the measurements do not disturb the aging. Figure \[1\] shows the evolution of the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, with aging time $t_w$ for the Laponite dispersion. The sample is seen to evolve from a viscous sol at short $t_w$ (\sim 82 min) to an elastic medium at large $t_w$ (\sim 178 min). To simultaneously probe the

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fluctuations of the system as it ages, small amounts of polystyrene spheres (of diameter 50, 100, or 200 nm) are added to the light scattering cuvettes. The intensity autocorrelation function is measured on these samples with a Photocor-FC light scattering instrument employing a 5 mW laser light source at 633 nm and a multi-tau logarithmic correlator. Because simultaneous measurements are performed on portions divided out from a single prepared dispersion, we are able to ensure that the rheology and DLS measurements correspond to the same aging time and frequencies.

Our intent with the DLS experiments is to measure the mean-squared displacement of probe particles embedded in the Laponite dispersion while the sample is aging. For this, we exploit the fact that the scattering from the probes dominates over the scattering from the Laponite particles themselves. This is shown by Fig. 2, where we plot the intensity autocorrelation function $g_2$ taken at $90^\circ$ for different concentrations of 50 nm probes. The correlation function is found to be independent of probe concentration for concentrations of 0.02% or higher. In this regime, we can assume the scattering to be predominantly due to the probes, and thereby determine the average mean-squared displacement of the probes through

$$g_2(q, t) - 1 = \frac{\langle i(q, 0) i(q, t) \rangle}{\langle i(q, 0) \rangle^2} - 1 = f(A) |F_s(q, t)|^2$$

(1)

Here, the magnitude of the scattering wave vector $q$ is $q = \frac{4\pi n}{\lambda} \sin(\theta/2)$, $F_s(q, t) = \exp(-q^2 \langle \Delta r^2(t) \rangle/6)$ is the self-intermediate scattering function, $i(q, t)$ is the intensity at the detector, and $f(A)$ is the spatial coherence factor.

At higher concentrations than shown in Fig. 2, the addition of probe particles alters the aging of the Laponite dispersion. This indicates that only a range of probe particle concentrations will be large enough to dominate scattering while not affecting the Laponite aging (e.g., for 50 nm spheres, this corresponds to concentrations of roughly 0.02 to 0.06 wt %). We now use the determined $\langle \Delta r^2(t) \rangle$ of the embedded probe particles to determine whether a generalization of the FDT is compatible with the data for this out-of-equilibrium system. By assuming that the bulk stress relaxation is the same as the local stress relaxation affecting the probe particle, it has been shown that probe particles immersed in a viscoelastic medium can obey the generalized Stokes-Einstein relation

$$a\langle \Delta r^2(s) \rangle = T \left( \frac{k_B}{sG(s)\pi} \right).$$

(2)

In the above, $s$ is the Laplace frequency, $\langle \Delta r^2(s) \rangle$ is the Laplace transform of the mean squared displacement of probe particle of radius $a$, and $G(s)$ is the viscoelastic modulus. Equation (2) can be generalized to out-of-equilibrium systems by replacing the temperature $T$ with an effective temperature $\Theta(s)$, yielding

$$a\langle \Delta r^2(s) \rangle = \Theta(s) \left( \frac{k_B}{sG(s)\pi} \right).$$

(3)

This can be cast into a frequency-dependent form by substituting $s = i\omega$, with the effective temperature given by

$$T_{eff}(\omega) \Im \left[ \frac{1}{G^*(\omega)} \right] = \Im \left[ \frac{\Theta(\omega)}{G^*(\omega)} \right].$$

(4)
The effective temperature \( \Theta(s) \) of Eq. (3) accounts for deviations from the equilibrium relation of Eq. (2). If \( \Theta(s) \) is to act like a temperature it must be an intensive variable and independent of the size \( a \) of the probe particle. Assuming \( \tilde{G}(s) \) is also intensive, this would require that the term \( a \langle \Delta s^2(s) \rangle \) be independent of \( a \). To demonstrate the \( a \) independence, we multiply Eq. (3) by \( s/6 \), which can be arranged to yield

\[
a \tilde{D}(s) = \Theta(s) \left( \frac{k_B}{G(s)6\pi} \right). \quad (5)
\]

In the above we have used \( \tilde{D}(s) = \frac{s \langle \Delta s^2(s) \rangle}{6} \), which is the Laplace transform of the time-dependent diffusivity, \( D(t) = \frac{1}{6} \cdot \frac{\partial \langle \Delta s^2(t) \rangle}{\partial t} \). The inverse Laplace transform of Eq. (5) yields

\[
aD(t) = f_w(t), \quad (6)
\]

where \( f_w(t) \) is an unspecified function of time that should be independent of \( a \) if the effective temperature acts as an intensive variable.

To test Eq. (6) we first determine \( D(t) \) by numerically differentiating the logarithm of the autocorrelation function, which eliminates the coherence factor \( f(A) \) in the analysis. As a check that this yields a reasonable result, we analyzed the probe particles (at the same concentrations) in pH 10 water without Laponite, which gave the three marked lines in Fig. 3 and are in reasonable agreement with the diffusion of spheres in water at 298 K, represented as a horizontal gray line. When attempted on the 3 wt \% Laponite solution from Fig. 1, \( aD(t) \) again shows good agreement between the various probe sizes at early \( t_w \), but with a reduced diffusion. This suggests that a general temperature is appropriate in this aging regime. As the system ages, the diffusion decreases further until \( t_w \approx 100 \text{ min} \), when the diffusion of the 50 nm spheres no longer decreases at the same rate as the 100 nm and 200 nm spheres. At still later times, when \( t_w \approx 146 \text{ min} \), the diffusion of the 100 nm spheres no longer decreases at the same rate as the 200 nm spheres. This suggests that the Laponite platelet structure begins to show inhomogeneities with age. The smaller probes (which diffuse faster) are the first to sense these inhomogeneities.

Having demonstrated agreement with an intensive general temperature up to certain aging times, we now determine the \( T_{eff} \). To do this we numerically calculate the Laplace transform of \( D(t) \) and fit the term \( k_B/6\pi aD(s) \) to a fourth order expansion of \( \ln(s) \). Substituting \( i\omega \) for \( s \) yields \( k_B/6\pi aD(\omega) \). This, along with the measured \( G^*(\omega) \) from Fig. 4, can be directly related to \( \Theta(\omega) \) through \( 6\pi aD(\omega)G^*(\omega)/k_B = \Theta(\omega) \), which in turn can be used to determine \( T_{eff} \) from Eq. (4). We limited the analysis to \( t_w \leq 135 \text{ min} \) where \( D(t) \) for the 100 nm and 200 nm spheres showed reasonable agreement, and to frequencies where \( D(\omega) \) could be determined for both sizes.

FIG. 3: Time dependent diffusion, \( D(t) \), normalized with the radius, \( a \), of the probe particles. The measurements were performed in portions taken from the the same 3 wt \% Laponite dispersion as used in the rheological measurements of Fig. 1. The aging times are noted next to the curves. A comparison to probe particles immersed in pH 10 water is shown at the top of the plot. The gray line is the value expected for spheres immersed in water at 298 K.

Figure 4 shows the frequency dependence of \( T_{eff} \). To determine this, we obtained \( T_{eff} \) for the 100 and 200 nm spheres with \( \tilde{D}(s) \) determined with a Laplace transform only over the experimental time scales. A third \( T_{eff} \) was determined from the 200 nm spheres by taking the transform up to \( t = \infty \), assuming \( D(t) \) is constant for \( t \) beyond the experimental range. All three curves for \( T_{eff} \) show the same general trends, with the average of the three plotted in Fig. 4 and their standard deviation represented by error bars. For the aging times and frequencies accessible to our experiment, there is a systematic rise of \( T_{eff} \) in Fig. 4 with aging time and with frequency, starting near room temperature of 298 K. (For a \( t_w \) of 82 min, \( T_{eff} \) shows only a weak frequency dependence and its value is 335 ± 63 K.) This behavior is distinctly different to some other determinations of effective temperatures in soft matter, which have the opposite trend in aging time and frequency. Yet, our increase of \( T_{eff} \) with temperature seems to corroborate the short aging-time behavior of Abou et al. In that work, Abou et al. found \( T_{eff} \) to increase from room temperature as a function of \( t_w \) and then to decrease at longer \( t_w \). To account for this, they proposed that there were three regimes: when the system is probed at a time scale (1) less than, (2) equal to, and (3) greater than the characteristic relaxation time of the Laponite system which increases with \( t_w \). For cases (1) and (3) Abou et al. argue that the system can thermalize to the bath and so \( T_{eff} \) is approximately room temperature, whereas for case (2) the Laponite dispersion behaves as an out-of-equilibrium
A system with an increased $T_{\text{eff}}$ when driven at its characteristic relaxation frequency. Contrary to this view, our results suggest that there are instead only two regimes – for probed time scales (1) less than and (2) greater than the characteristic relaxation time of the Laponite. This stems from the fact that we find only a rise in $T_{\text{eff}}$ without a subsequent decrease [24]. In our picture, the Laponite system is in thermal equilibrium with the bath when probed at time scales greater than its characteristic relaxation time. At probed time scales less than this relaxation time, the system cannot thermalize and behaves as an out-of-equilibrium system with a $T_{\text{eff}}$ greater than the bath temperature.

In conclusion, we have measured the diffusion of probe particles in an aging Laponite suspension which suggests that a general temperature describes the system for short aging times. This is indicated by the scaling of the diffusion with probe size, which suggests that the system has a homogeneous viscoelastic behavior on the length and time scales measured. Using our diffusion and rheological measurements we determine a $T_{\text{eff}}(\omega)$ which increases with frequency and aging time. This behavior suggests two time-scale regimes; (1) for probing times greater than the characteristic relaxation time of the glass where the system can thermalize with the bath, and (2) for probing times less than the characteristic relaxation time where the system is out of equilibrium with the bath and has a $T_{\text{eff}} > T_{\text{bath}}$.

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