

## Size-dependent diffusion in 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 at early times and for the larger particles. This implies that within this regime the measurements can be used to investigate the generalized fluctuation-dissipation theorem for this out-of-equilibrium system, where the bath temperature is replaced with an effective temperature. Simultaneous dynamic rheological measurements reveal that this effective temperature increases as a function of aging time and frequency which suggests the existence of two measured time-scale regimes. In accord with recent work by Abou *et al.* [Phys. Rev. Lett. **93**, 160603 (2004)], our results suggest that 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 formalism 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 [4–6], granular materials [7,8], and to a variety of soft materials [9–12] have been reported. In particular, the aging colloidal glass of Laponite RD in water has shown several conflicting results for the behavior of the effective temperature [9,10,12]. In contradiction with other measurements,  $T_{eff}$  has recently been found in this system to increase with age for short aging times [12]. To investigate this possibility, the dependence of  $T_{eff}$  on the observation time scale (inverse of the probed frequency  $\omega$ ) needs to be examined [12,13].

Here 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 implies that these measurements can be used to investigate

the generalized FDT for this system where the bath temperature is replaced with  $T_{eff}$ . We then determine the dependence of  $T_{eff}$  on aging time and frequency by combining these 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 we are measuring two time-scale regimes of the effective temperature relevant for this colloidal glass: At probed time scales longer than the characteristic relaxation time 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.

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  $\mu\text{m}$  filter to break up any remaining particle aggregates. At this stage, we mark time equal to zero for the Laponite aging experiment [14–16]. 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 fluctuations of the system as it ages, small amounts of polystyrene spheres (of diameter 50, 100, or 200 nm) [17] are added to the light scattering cuvettes prior to the addition of the Laponite dispersion. To disperse the polystyrene spheres in the

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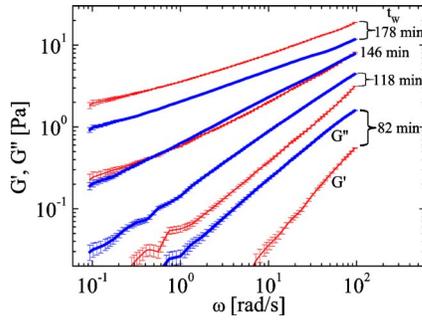


FIG. 1. (Color online) Aging behavior of  $G'$  (thin lines) and  $G''$  (thick lines) of a 3.0 wt. % Laponite suspension. Data are determined at set aging times by making measurements of the viscoelastic modulus at 25 frequencies between 0.1 rad/s and 100 rad/s every 10 min. These data are then interpolated to specific aging times and frequencies.

Laponite dispersion the cuvettes are sealed and flipped upside-down once. We assume that this induced shear is negligible in comparison to the initial shear (when passing the Laponite dispersion through the filter) and thus does not significantly alter the aging. 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 multitaue logarithmic correlator. Because simultaneous measurements are performed on portions divided out from a single prepared dispersion, the rheology and DLS measurements correspond to the same aging time  $t_w$ .

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

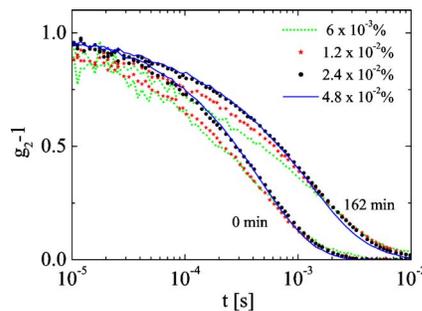


FIG. 2. (Color online) The two sets of correlation functions,  $g_2(\mathbf{q}, t) - 1$ , are measured at two different aging times for four different concentrations of 50 nm polystyrene spheres in a 3 wt. % dispersion of Laponite.

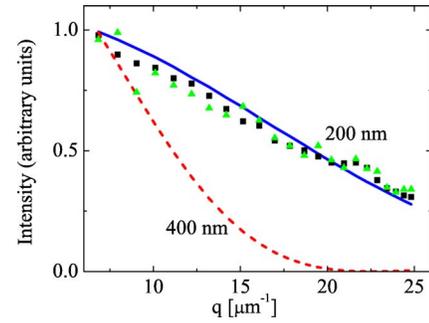


FIG. 3. (Color online) Intensity as a function of scattering vector for  $7.4 \times 10^{-3}$  wt. % of 200 nm polystyrene spheres in water (squares) and in a 3 wt. % dispersion of Laponite after aging for 193 min (triangles). The solid curve is the scattering intensity expected for 200 nm spheres and the dashed curve is for 400 nm spheres [18]. The curves are normalized to 1 at the lowest value of  $q$ .

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

Here, the magnitude of the scattering wave vector  $\mathbf{q}$  is  $q = \frac{4\pi m}{\lambda} \sin(\theta/2)$ ,  $F_s(\mathbf{q}, t) = e^{[-q^2 \langle \Delta r^2(t) \rangle / 6]}$  is the self-intermediate scattering function,  $i(\mathbf{q}, t)$  is the intensity at the detector, and  $f(A)$  is the spatial coherence factor [18].

Static light scattering (SLS) can be used to give further evidence that the light scattering intensity [ $\langle i(\mathbf{q}) \rangle$ ] is dominated by the embedded polystyrene spheres in the Laponite dispersion. Figure 3 shows the intensity as a function of scattering vector for  $7.4 \times 10^{-3}$  wt. % of 200 nm polystyrene spheres in water (represented by the squares) and the same concentration of these spheres in a 3 wt. % dispersion of Laponite after aging for 193 min (represented by the triangles). Both curves show good agreement with the expected SLS intensity function for 200 nm spheres which is represented as the solid line [18]. For comparison, we have also plotted the expected SLS intensity function for 400 nm spheres which illustrates that the reduced diffusion of the probe particles with age is not a result of particle aggregation.

To determine the correlation function of the polystyrene spheres embedded in the aging Laponite dispersion the correlator averages over approximately one minute, which is a time span that is short compared to the aging of the system. Figure 4 demonstrates that the determined correlation function is not significantly altered by the aging over the time scale of its accumulation. The curve at left is the initial correlation function measured just after filtering for a 3 wt. % dispersion of Laponite with  $7.4 \times 10^{-3}$  wt. % of 100 nm polystyrene spheres. The 9 curves on the right are all started after the system has aged for 171 min and are accumulated for times ranging from 13 to 300 s. As the accumulation time is increased the scatter of the correlation function is reduced but its shape is not significantly altered. This indicates that the aging plays an insignificant roll during the accumulation of the correlation function.

At higher concentrations than shown in Fig. 2, the addi-

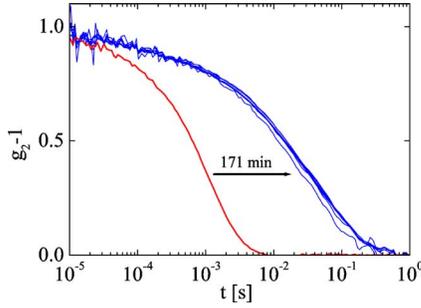


FIG. 4. (Color online) Correlation functions taken for a 3 wt. % dispersion of Laponite with  $7.4 \times 10^{-3}$  wt. % of 100 nm polystyrene spheres. The curve at left is the initial correlation function measured just after filtering while the 9 curves on the right are all started after the system has aged for 171 min. These latter 9 correlation functions are determined by averaging over accumulation times ranging from 13 to 300 s.

tion 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 significantly altering the Laponite aging over the regime investigated. This corresponds (in wt. %) to concentrations of roughly  $2 \times 10^{-2}\%$  to  $6 \times 10^{-2}\%$  for 50 nm spheres,  $5 \times 10^{-3}\%$  to  $2 \times 10^{-2}\%$  for 100 nm spheres, and  $3 \times 10^{-3}\%$  to  $2 \times 10^{-2}\%$  for 200 nm spheres [19]. The slight amount of aqueous solution that accompanies the polystyrene spheres slightly reduces the total Laponite concentration from its initial 3 wt. % value. For the concentrations used later in this report, this corresponds to a roughly 2.989 wt. % Laponite dispersion for the sample with  $3.7 \times 10^{-2}$  wt. % of 50 nm spheres and to a roughly 2.978 wt. % Laponite dispersion for the samples with  $7.4 \times 10^{-3}$  wt. % of 100 and 200 nm spheres.

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 [20] that probe particles immersed in a viscoelastic medium can obey the generalized Stokes-Einstein relation

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

In the above,  $s$  is the Laplace frequency,  $\langle \Delta \tilde{r}^2(s) \rangle$  is the Laplace transform of the mean squared displacement of a probe particle of radius  $a$ , and  $\tilde{G}(s)$  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

$$a \langle \Delta \tilde{r}^2(s) \rangle = \Theta(s) \left( \frac{k_B}{s \tilde{G}(s) \pi} \right). \quad (3)$$

This can be cast into a frequency-dependent form by substituting  $s = i\omega$ , with the effective temperature given by [21–23]

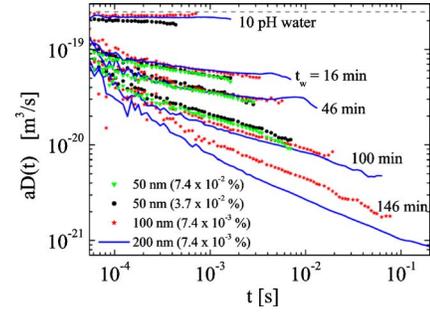


FIG. 5. (Color online) Time dependent diffusion,  $D(t)$ , normalized with the radius,  $a$ , of the probe particles. The measurements were performed in portions taken from the the same 3 wt. % Laponite dispersion as used in the rheological measurements of Fig. 1. The aging times are noted next to the curves with the wt. % noted in the key. A comparison to probe particles immersed at the same concentrations in pH 10 water is shown at the top of the plot. These correspond to  $3.7 \times 10^{-2}$  and  $7.4 \times 10^{-2}$  wt. % for the 50 nm spheres and  $7.4 \times 10^{-3}$  wt. % for the 100 and 200 nm spheres. The gray line is the value expected for spheres immersed in water at 298 K. The curves for the 50 nm particles at  $t_w = 146$  min are omitted for clarity of the plot.

$$T_{eff}(\omega) \text{Im} \left[ \frac{1}{G^*(\omega)} \right] = \text{Im} \left[ \frac{\Theta(\omega)}{G^*(\omega)} \right]. \quad (4)$$

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  $a \langle \Delta \tilde{r}^2(s) \rangle$  be independent of  $a$ . To demonstrate the  $a$  independence, we multiply Eq. (3) by  $s/6$ , which can be arranged to yield

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

In the above we have used  $\tilde{D}(s) = \frac{s \langle \Delta \tilde{r}^2(s) \rangle}{6}$ , which is the Laplace transform of the time-dependent diffusivity,  $D(t) = \frac{1}{6} \frac{\partial \langle \Delta r^2(t) \rangle}{\partial t}$  [24]. 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. 5 and are in reasonable agreement with the diffusion of spheres in water at 298 K, represented as a horizontal gray line. These measurements in water indicate that multiple scattering by the polystyrene spheres has an insignificant af-

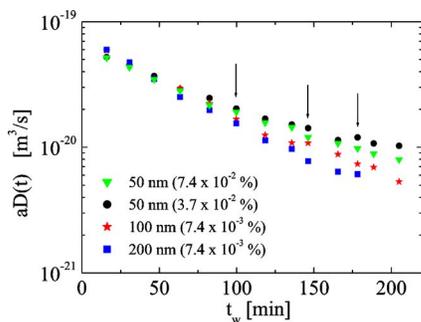


FIG. 6. (Color online)  $aD(t)$  at  $t=1$  ms for the Laponite dispersion in Fig. 5.

fect on the  $D(t)$  determined from the spheres at similar concentration in the Laponite dispersion. When the analysis is 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 the general temperature of the system can be probed by the diffusion of the spheres in this aging regime. As the system ages, the diffusion decreases further until  $t_w \approx 100$  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  $t_w \approx 146$  min, the diffusion of the 100 nm spheres no longer decreases at the same rate as the 200 nm spheres.

The assumption that the local environment of the probe particle reflects the bulk is not obviously satisfied in the system studied here since the typical distance between Laponite particles ( $\sim 40$  nm) is only slightly smaller than the polystyrene spheres [25,26]. The scaling in Fig. 5 for short aging ( $< 100$  min) suggests that the rapidly diffusing platelets appear as a continuous medium at the size scale of all three probe particles within this aging regime. This is also demonstrated by plotting  $aD(t)|_{t=1ms}$  as a function of  $t_w$  in Fig. 6, where all three probe particles show good agreement up to the aging time designated by the first arrow on the left ( $t_w = 100$  min). After that time,  $aD(t)$  is found to decrease at a slower rate for the 50 nm spheres than for the larger spheres. This suggests that as the Laponite platelets diffuse more slowly, voids appear on size and time scales great enough for the smaller 50 nm spheres to diffuse through. In this picture the 100 and 200 nm spheres are too large to pass through the voids so that their diffusion still reflects the bulk properties of the system in this intermediate aging regime. Consistent with this view,  $aD(t)$  is found to decrease more slowly for the 100 nm spheres at an even later aging time ( $t_w = 146$  min) which is designated by the middle arrow in Fig. 6. At still later times (designated by the third arrow), a slight variation in  $aD(t)$  is evident between the samples with 50 nm spheres at a factor of 2 difference in concentrations. This probe-concentration effect occurs at an aging time outside the regime used to investigate  $T_{eff}$  in this study; which indicates that the comparison between the light scattering portions with probe particles and the dynamic rheological portions without probe particles is not significantly affected by the probe particles within this aging regime. At higher probe particle concentrations than used here, the regime showing a

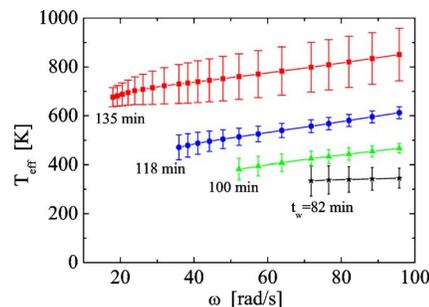


FIG. 7. (Color online)  $T_{eff}$  determined from the rheological measurements in Fig. 1 and the time-dependent diffusion of 200 nm diameter probe particles shown in Fig. 5.

concentration-effect encroaches upon the earlier aging times investigated in our study. Agreement of the two portions of Laponite dispersion with the 50 nm particles in the relevant aging regime also indicates that determining the correlation from a single sample is sufficient and, thus, averaging several realizations of the experiment is not necessary.

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  $k_B/6\pi a\tilde{D}(s)$  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. 1, 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  $t_w \leq 135$  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. Figure 7 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. 7 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. 7 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  $335 \pm 63$  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 [9,11]. Yet, our increase of  $T_{eff}$  with temperature seems to corroborate the short aging-time behavior of Abou *et al.* [12] 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 tem-

perature, whereas for case (2) the Laponite dispersion behaves as an out-of-equilibrium system with an increased  $T_{eff}$  when driven at its characteristic relaxation frequency. Though our short aging behavior agrees with that found by Abou *et al.*, we do not see the subsequent decrease in  $T_{eff}$  with  $t_w$  or  $\omega$ . This could simply stem from the fact that our measurements do not probe long enough aging times or high enough  $\omega$ . Another possibility is that the  $T_{eff}$  we measure reflects the vastly different size scales probed by our experiment. It remains a possibility that the small probe particles used here are passing through structural voids in the Laponite dispersion that are only sensed by the macroscopic rheological measurements. Such a scenario would also likely lead to an increasing  $T_{eff}$ , which would be a size effect not related to the original theory of out-of-equilibrium systems.

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  $T_{eff}(\omega)$  which increases with frequency and aging time. This suggests there are two measured 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 shorter probing times where the system is out of equilibrium with the bath and has a  $T_{eff} > T_{bath}$ .

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