Fluctuation-Dissipation Theorem in an Aging Colloidal Glass

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We provide a direct experimental test of the fluctuation-dissipation theorem (FDT) in an aging colloidal glass. The use of combined active and passive microrheology allows us to independently measure both the correlation and response functions in this nonequilibrium situation. Contrary to previous reports, we find no deviations from the FDT over several decades in frequency (1 Hz–10 kHz) and for all aging times. In addition, we find two distinct viscoelastic contributions in the aging glass, including a nearly elastic response at low frequencies that grows during aging.

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Developing a statistical mechanical description of nonequilibrium systems such as glasses still remains an important challenge. One of the most interesting recent developments along these lines is the proposal to generalize the fluctuation-dissipation theorem (FDT) to nonequilibrium situations [1]. The FDT relates the response of a system to a weak external perturbation to the spontaneous fluctuations about equilibrium [2]. The response function is proportional to the power spectral density of thermal fluctuations, with a temperature-dependent prefactor. This suggests a generalization for systems out of equilibrium, in which the (nonequilibrium) fluctuations are related to the response via an effective temperature. While this has been studied extensively theoretically [3], the experimental support for a meaningful effective temperature is unclear [4–6], and possible extensions of the FDT to nonequilibrium situations remain controversial.

Here, we introduce a combination of both active and passive (fluctuation-based) microrheology techniques [7–9] that provide a way to directly test the FDT. We do this in Laponite [10–12], a synthetic clay. For this system conflicting results have been reported [5,6], that may in part be due to the use of a limited experimental window in both frequency and aging time. Here, we perform measurements over a wide range of frequencies and aging times. Contrary to previous reports, we find no violation of the FDT and thus no support for an effective temperature different from the bath temperature.

These measurements provide new insights into the physics of the aging process. By performing microrheology during aging, we can explore the evolution of viscoelasticity of the glass over a wider frequency range than hitherto explored, spanning nearly six decades in frequency. The measurements reveal the existence of two distinct contributions to the viscoelasticity of the system: (i) a high-frequency viscoelastic response in which the shear modulus increases rapidly with frequency; and (ii) a predominantly elastic (weakly frequency dependent) response at lower frequencies, which becomes increasingly important as the system ages.

The Einstein relation connecting the diffusion of a particle to its mobility is a special case of the FDT. Its generalization to a viscoelastic system relates the power spectral density (PSD) of position fluctuations to the imaginary part of the complex response function $\alpha''(\omega)$ [7,8]:

$$\langle |x(\omega)|^2\rangle = \int_0^\infty \langle x(t)x(0)\rangle e^{i\omega t}\,dt = \frac{2k_BT}{\omega}\alpha''(\omega). \qquad (1)$$

In a nonequilibrium system this suggests the introduction of an effective temperature $T_{\mathrm{eff}}(\omega)$, replacing T in Eq. (1). Prior experiments [7] have shown apparent agreement between (active) macroscopic rheology and passive microrheology, which supports the validity of a generalized Stokes-Einstein (SE) formula. However, since the SE formula is neither necessary nor sufficient to prove the validity of FDT, we directly measure and compare the quantities appearing in Eq. (1).

To investigate the aging of our system, we study the motion of probe particles using optical tweezers. An inverted microscope [13], equipped with two overlapping optical tweezers formed by two independent lasers ($\lambda =$ 830 nm and 1064 nm) focused to diffraction-limited spots. The latter drives oscillations of a trapped particle with an Acousto-Optical Deflector, allowing us to measure the response function. The (x, y) position of the particle is determined by a quadrant photo diode [14] with a spatial resolution of $\sim$0.1 nm. The output signal is fed into a lock-in amplifier that measures the amplitude and phase of the particle displacement $x(t)$ caused by an oscillatory motion of the drive laser. From this we determine the force $F(t)$ acting on the particle. The response function is then given by $\alpha(\omega) = x_\omega/F_\omega$, where x_ω and F_ω denote the Fourier transforms of $x(t)$ and $F(t)$. By measuring the PSD of the same beads under the same conditions in water, we are able to calibrate both trap stiffness [8,13] and particle displacement [8].

For the passive measurements the shutter in front of the driving laser was closed and the spontaneous fluctuations of the particle position were recorded for a minimum time of 45 s. From the displacement time series, we calculate the displacement power spectral density by fast Fourier transform [8]. Comparing the response function from the active microrheology with the fluctuation spectra, we can directly check the validity of the FDT, as well as resolve the frequency-dependent viscoelastic properties during the aging of the glass.

The colloidal glass under study is a suspension of Laponite XLG in ultrapure water. After mixing, the system spontaneously evolves from an initially liquid and ergodic state to a nonergodic glassy state that exhibits elastic behavior [11]. For a particle concentration of 2.8 wt%, the rate of aging is slow enough that no changes occur during each individual active and passive microrheology measurements lasting at most 2 min. Nevertheless, the system evolves fast enough to allow us to follow the evolution from "liquid" to "solid" (the glass no longer flows when the sample cell is tilted) within about 8 h. The dispersions are filtered to obtain a reproducible initial state [10]. This defines the zero of aging time $t_a = 0$. Immediately after filtration, a small fraction ($<10^{-4}$ vol%) of silica probe beads (diameter 1.16 μm ± 5%) are mixed with the Laponite dispersion. The solution is then introduced into a sample chamber of about 50 μl volume, consisting of a coverslip and a microscope slide separated by a spacer of thickness 70 μm. This is sealed with vacuum grease to avoid evaporation. We then trap a single silica bead and perform the active and passive experiments on it.

Since the system evolves toward a nonergodic state, the time average may not be equal to ensemble average for the measured PSDs. To investigate this, we confirmed that reproducible PSDs were obtained for the same aging time, independent of bead position, during all stages of aging. We also confirmed that our results do not depend on the time interval used to compute the time average. Thus, we can use the time-averaged PSD without averaging over several beads in our study. Figure 1 shows the (passive) displacement PSD for different aging times. It is evident that the particle motion progressively slows down with increasing aging time, reflecting the increase in viscosity of the system. Qualitatively two regimes of aging are seen: for $t_a < 200$ min the PSD can be described by a single power law. At longer aging times two distinct slopes appear in the log-log plot (Fig. 1).

We measure the (active) response of the same bead used in passive measurements, as a function of aging time and for oscillation frequencies of $f = 1.2$, 10.8, 116, 1035, and 12 000 Hz. To directly compare the (passive) fluctuations with the (active) response, we express our fluctuation PSDs normalized in such a way as to permit a direct comparison with the measured α in the form of Eq. (1). Thus, we plot the measured PSD multiplied by $\omega/(2k_BT)$. We obtain the real part using a Kramers-Kroning (principal-value) integral [2] $\alpha'(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\xi\alpha''(\xi)}{\xi^2-\omega^2} d\xi$. The cutoff error due to a finite range of frequencies sets an upper limit to $\alpha'(\omega)$ about a decade lower than that of $\alpha''(\omega)$. Figure 2 depicts the real and imaginary parts obtained from the active and passive methods at an early ($t_a = 100$ min) and a late stage of aging ($t_a = 300$ min). We see that the results are identical to within the experimental accuracy, showing that there are no deviations from the FDT in this system over the range of frequencies and aging times probed in our experiments. Note that the small deviations between the respective $\alpha'(\omega)$ values at high frequencies are likely due to cutoff errors in the Kramers-Kronig integrals because the drawn lines, obtained by extrapolating the measured power law of α'' to infinity, show significantly better agreement. Since we have directly compared both the real and imaginary parts of the response functions, this represents a stronger test of the FDT than previous measurements [6] and demonstrates that the FDT holds in this nonequilibrium system.

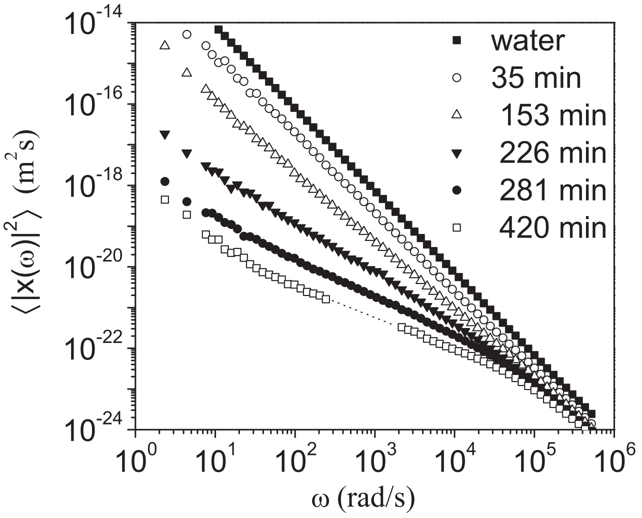

FIG. 1. The displacement power spectral densities (PSD) as a function of frequency for 1.16 μm silica probe particles with increasing age after preparing the sample. Fluctuations were recorded for 45 seconds with the 830 nm laser focus and results averaged in *x, y* directions for 1 bead several times. Aging times are given in the legend. The solid squares show the PSD of a bead in pure water for comparison. An acoustic noise signal around $f \approx 200$ Hz is cut out from the curve at the latest stage of aging where the displacement signal was the lowest. All experiments were performed at 21 °C.

In Fig. 3, we plot the extracted α'' as a function of aging time for several different frequencies. As can be seen the active and passive data agree very well. This figure confirms again that the FDT holds: the measured effective temperature does not differ from the bath temperature. The resulting effective temperature $T_{\mathrm{eff}}/T_{\mathrm{bath}} = \alpha''_{\mathrm{passive}}/\alpha''_{\mathrm{active}}$ is shown in the Table I. We conclude that

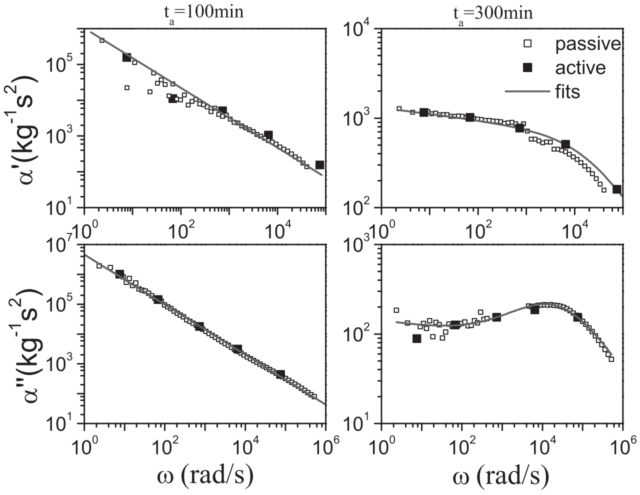

FIG. 2. Comparison of active and passive results: Real $\alpha'(\omega)$ and imaginary $\alpha''(\omega)$ at $t_a = 100$ and 300 min obtained from active (solid symbols) and passive (open symbols) microrheology performed on the same 1.16 μm diameter silica bead in the same sample. For the passive experiments, the imaginary parts of the response functions are obtained directly and real parts are calculated with a Kramers-Kronig integral. The lines show the fits to Eq. (2). At early stages of aging the data can be described with one power law, while at later stages, a superposition of two power laws is needed to describe the whole frequency range. The amplitude of oscillation for the active experiments was 77 nm.

the measurements show the FDT is valid for all frequencies probed here, and can be used for all the stages of aging in this system. The method also allows us to obtain the viscoelastic properties over a very wide frequency range; classical (macroscopic) rheology is limited to frequencies up to about 10 Hz [11]. In Fig. 1 we observe a gradual decrease of the PSD for higher frequencies and a more rapid change at lower frequencies. The response function is directly proportional to the PSD which in turn should be inversely related to the complex shear modulus $G^* = G' + \imath G''$. With increasing aging time, as the sample becomes more viscous and solidlike, one would expect that both the elastic modulus G' and the viscous modulus G'' increase. This is consistent with the decrease of the PSD and consequently of the response function. As was mentioned above, at late stages of aging two distinct slopes appear in the PSD (Fig. 1). This suggests the existence of two distinct contributions to the viscoelasticity during aging. Assuming the generalized Stokes formula for the viscoelastic response function [7,8], we obtain excellent fits to the data assuming a simple addition of two power-law contributions to the complex shear modulus (only a single power-law contribution at the early stages of aging):

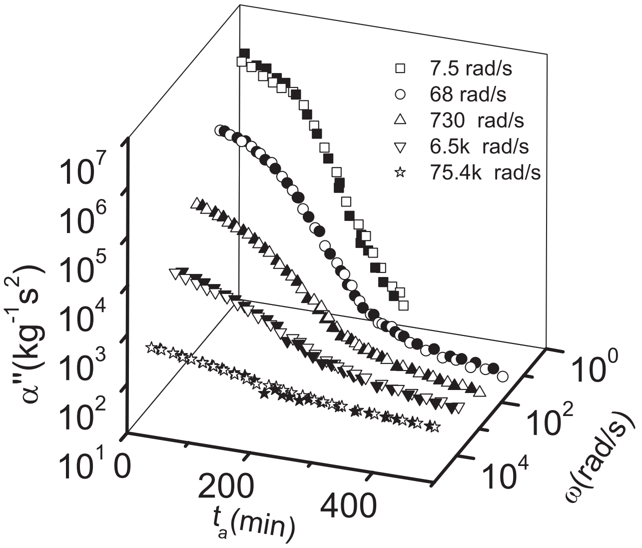

FIG. 3. The comparison of α'' extracted from passive (open symbols) and active (solid symbols) measurements as a function of aging time. For the lowest frequency, we could not measure reliable data longer than 300 min, since the signal to noise to ratio became of the order of 1 with increasing aging time, as the material became stiff.

$$\alpha(\omega) = \frac{1}{6\pi R G^*(\omega)} = \frac{1}{C_1(-\imath\omega)^a + C_2(-\imath\omega)^b}. \qquad (2)$$

The fit of the imaginary part of the response function from the passive measurements with the imaginary part of the above functional form is shown by the drawn lines in Fig. 2. To demonstrate the quality of this model for describing the data, we also plot the real part with the fitting parameters obtained from the imaginary part. The agreement is remarkable, especially with the active data at high frequencies. Figure 4 depicts the evolution of the fitting parameters, i.e., the exponents of power laws and the weight factors for the contribution of the two viscoelastic contributions as a function of aging time. The exponent and amplitude of one of the components do not change with aging time while the amplitude of the other one grows appreciably for aging times longer than about 250 min.

These results demonstrate the existence of two distinct contributions in the viscoelasticity of the system. In addition to a strongly frequency-dependent viscoelastic response at high frequencies, we also observe the slow development of a more elastic (weakly frequency-dependent) response during the aging. In fact, this appears to be the main characteristic of the aging in this system. A similar description in terms of a network in a more fluidlike background has been suggested before for polymeric gels

TABLE I. The effective temperature obtained for different frequencies averaged over 2 h time intervals. Within the uncertainty in the experiments, $T_{\mathrm{eff}}/T_{\mathrm{bath}} = 1$.

	$T_{\mathrm{eff}}/T_{\mathrm{bath}}$				
t_a	7.5 rad/s	68 rad/s	728 rad/s	6.5 rad/s	75 rad/s
0–2 h	0.75 ± 0.3	1 ± 0.1	0.95 ± 0.1	0.85 ± 0.1	1.0 ± 0.1
2–4 h	1.2 ± 0.3	1 ± 0.1	1 ± 0.1	0.9 ± 0.1	1.0 ± 0.1
4–6 h	1.4 ± 0.3	1 ± 0.1	1.1 ± 0.1	1.1 ± 0.1	1.1 ± 0.1
6–8 h		0.85 ± 0.1	1.0 ± 0.1	1.1 ± 0.1	1.0 ± 0.1

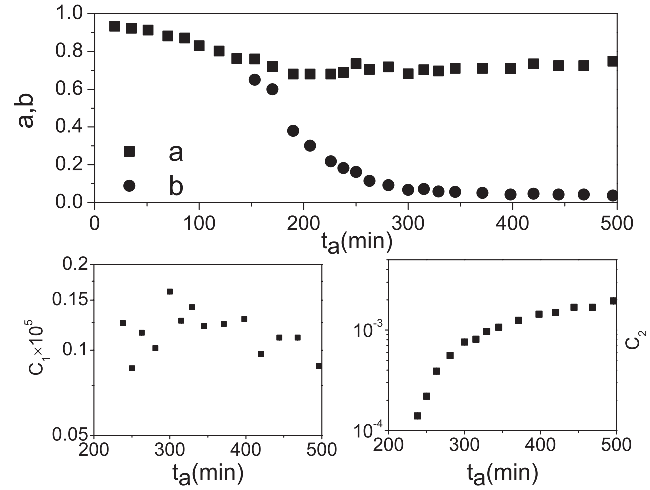

FIG. 4. For $t_a < 150$ min, the complex response function can be described by single power law of the form $1/(-\imath\omega)^a$. After about 150 min, a slowly relaxing contribution emerges leading to a response function of the from in Eq. (2).

[15,16]. In that case, this can be attributed to a tenuous elastic network structure, in the presence of a viscous background.

In summary, we see a good quantitative agreement between the response function and the spontaneous thermal fluctuations, implying that we observe no violation of the FDT in this nonequilibrium system. Equivalently, we find an effective temperature that does not differ from the system temperature. It is important to note that these measurements provide a direct test of the FDT, since we directly measure the response and the corresponding fluctuations over the same wide range of frequencies. This technique has the potential for application to a wide range of nonequilibrium situations such as biological systems [17].

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