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 non-equilibrium 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 non-equilibrium systems such as glasses still remains an important challenge in physics. One of the most interesting recent developments along these lines is the proposal to generalize the fluctuation dissipation theorem (FDT) to non-equilibrium situations 1. The FDT relates the response of a system to a weak external perturbation to the relaxation of the spontaneous fluctuations in equilibrium 2. The response function is proportional to the power spectral density of thermal fluctuations, with a prefactor given by the temperature. This suggests a generalization for systems out of equilibrium, in which the (non-equilibrium) fluctuations are related to the response via a time-scale-dependent effective temperature. While this has been studied extensively theoretically 3, the experimental support for a meaningful effective temperature is unclear. There have been few experiments 4, 5, 6 and the usefulness of the extension of the FDT to non-equilibrium situations is still a matter of controversy.

Here, we introduce a combination of both active and passive (fluctuation-based) microrheology techniques 7, 8, 9, 10 that provide a way to directly test the applicability of the FDT. We examine the validity of FDT in a colloidal glass, the synthetic clay of Laponite 11, 12, 13. For this system conflicting results have been reported previously 7, 14, 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.

In addition, these measurements provide a new insight into the physics of the aging process. The microrheology done during the aging process allows us to explore the evolution of viscoelastic properties of the glass over a wider frequency range than hitherto explored, spanning nearly 6 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 relates the diffusion of the particle (i.e., position fluctuations) to its mobility. This is a special case of the FDT, and its generalization to a viscoelastic system in Fourier space relates the power spectral density (PSD) of position fluctuations to the imaginary part of the complex response function \( \alpha''(\omega) \) 7, 8:

\[
\langle |x(\omega)|^2 \rangle = \frac{2k_B T}{\omega} \alpha''(\omega) \tag{1}
\]

Here, \( \langle |x(\omega)|^2 \rangle \) denotes the Fourier transform of the ensemble average \( \langle x(t)x(0) \rangle \). In a non-equilibrium system this suggests the introduction of an effective temperature in which \( T \) is replaced by \( T_{\text{eff}}(\omega) \) in Eq. (1).

To investigate the aging of colloidal glass, we study the motion of probe particles using optical tweezers. A custom-built inverted microscope 2, equipped with two overlapping optical tweezers formed by two independent lasers (wavelengths \( \lambda = 830 \text{ nm and } 1064 \text{ nm} \) ) focused to diffraction-limited spots. The latter drives the oscillations of the trapped particle with an Acousto-Optical Deflector, allowing us to measure the (active) response to a driving force. The \((x, y)\) position of the particle is determined by a quadrant photo diode 14 with a spatial resolution of \( \sim 0.1 \text{ nm} \). The output signal from the photodiode 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 focus. From the motion of the drive laser we determine the force \( F(t) \) acting on the particle. The response function is then...
The colloidal glass under study is a suspension of Laponite XLG in ultra pure water. After mixing the colloidal particles with the water, the system spontaneously evolves from an initially liquid and ergodic state to a non-ergodic glassy state that exhibits elastic behavior [12]. The colloidal glass no longer flows when the sample is tilted (the glass no longer flows when the sample is tilted) within about 8 hours. The dispersions are filtered (Millipore Millex AA 0.8 μm filter) to obtain a reproducible initial state [11]. 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 of sample. We then trap a single silica bead and perform the active and passive experiments on it.

Since the system evolves toward a non-ergodic 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 also 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 12000 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 $\alpha$ in the form of Eq. (1). Thus, we plot the measured PSD multiplied by $\omega/(2k_BT)$.

FIG. 1: The displacement power spectral densities (PSD) as a function for frequency of 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 filled squares show the PSD of a bead in pure water for comparison. An acoustic noise signal around $\omega = 200$Hz is cut out from the curve at the latest stage of aging where the displacement signal was the lowest. All experiments were done at 21°C.

given by $\alpha(\omega) = x_\omega/F_\omega$, where $x_\omega$ and $F_\omega$ 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 [8,9] and particle displacement for active and passive data [8].

For the passive measurements the shutter in front of the driving laser is closed and the spontaneous fluctuations of the particle position are 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 during the aging of the system, 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 ultra pure water. After mixing the colloidal particles with the water, the system spontaneously evolves from an initially liquid and ergodic state to a non-ergodic glassy state that exhibits elastic behavior [12]. For a particle concentration of 2.8 wt%$, the rate of aging is slow enough, on the one hand, that no significant structural and dynamic changes occur during each individual active and passive microrheology measurement 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
the whole frequency range. The amplitude of oscillation for the superposition of two power laws is needed to describe 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.

| $\omega$  | $\alpha''$ (kg m$^{-2}$ s$^{-1}$) | $\omega$  | $\alpha''$ (kg m$^{-2}$ s$^{-1}$) |
|---------|-----------------|---------|-----------------|
| 10$^3$  | 10$^{-4}$        | 10$^6$  | 10$^{-4}$        |
| 10$^4$  | 10$^{-4}$        | 10$^7$  | 10$^{-4}$        |
| 10$^5$  | 10$^{-4}$        | 10$^8$  | 10$^{-4}$        |

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

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 (filled symbols) and passive (open symbols) micro-rheology performed on the same 1.16 $\mu$m 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 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, 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):

$$\alpha(\omega) = \frac{1}{6\pi R G(\omega)} = \frac{1}{C_1(-i\omega)^a + C_2(-i\omega)^b}$$

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. Fig. 3 depicts the evolution of the FDT than previous measurements and demonstrates that the FDT holds in this non-equilibrium system.

In Fig. 3 we plot the extracted $\alpha''$ 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 to within the experimental uncertainty the FDT holds: the measured effective temperature does not differ from the bath temperature. The resulting effective temperature $T_{\text{eff}}/T_{\text{bath}} = \alpha''_{\text{passive}}/\alpha''_{\text{active}}$ is shown in the Table I. We conclude that the measurements show the FDT in the form of the Einstein relation 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 100 rad/s. In Fig. 1 we observe a gradual decrease of the PSD 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 $G'' = G' + iG''$. With increasing aging time, the sample becomes more viscous and solid-like, 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, 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):
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 fluid-like background has been suggested before for polymer gels \[15, 16\]. In our case, this can be attributed to the growth of a tenuous network-like structure, in addition to the more viscous response that is always present. We note, however, that although our system also becomes non-ergodic there is no evidence for spatial inhomogeneity, neither in our system, nor in glassy systems in general. Recently, it has been suggested that glassy systems may be dynamically heterogeneous \[17\], and that one should look into the correlation of spatial and temporal dynamics in order to detect the heterogeneity. Therefore the homogeneity of the combined spatial and temporal dynamics merit further detailed study.

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 non-equilibrium 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 much more direct test of the FDT than prior experiments, since we directly measure the response and the corresponding fluctuations over the same and very large range of frequencies.

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[1] L.F. Cugliandolo, J. Kurchan, and L. Peliti Phys. Rev. E 55, 3898 (1997).
[2] E.M. Lifshitz and L.D. Landau, Statistical Physics (Course of Theoretical Physics, Volume 5), 1984
[3] W. Kob, J.L. Barrat, Phys. Rev. Lett. 78, 4581 (1997); G. Parisi, Phys. Rev. Lett. 79, 3660 (1997).
[4] T. Grigera, N. Israeloff, Phys. Rev. Lett. 83, 5038 (1999); D. Hérisson and M. Ocio, Phys. Rev. Lett. 88, 257202 (2002); D. Bonn, W.K. Kegel, J. Chem. Phys. 118, 2005 (2003); C.M. Song, P. Wang, H. A. Makse, Proc. Nat. Acad. Sci. 102, 2299 (2005).
[5] L. Bellon, S. Ciliberto, C. Laroche, Europhys. Lett. 53, 511 (2001); L. Bellon, S. Ciliberto, Physica D 168-169, 325 (2002); L. Buissen, L. Bellon, and S. Ciliberto, J. Phys. Cond. Matt. 15, S1163 (2003).
[6] B. Abou and F. Gallet, Phys. Rev. Lett. 93, 160603 (2004); D. R. Strachan, G. C. Kalur, and S. R. RagHAVAN, Phys. Rev. E73, 041509 (2006); B. Abou, F. Gallet, P. Pottier ccsd-00023745; N. Greinert, T. Wood, and P. Bartlett, cond-mat/0605541; J.L. HARDen, private communication.
[7] T.G. Mason, and D.A. Weitz, Phys. Rev. Lett. 74, 1250 (1995). T.G. Mason, H. Gang and D.A. Weitz J. Opt. Soc. Amer. A 14 (1997) 139; T.G. Mason Rheol. Acta 39 (2000) 371.
[8] F. Gittes, B. Schnurr, B. and Olmsted, P.D. F.C. MacKintosh, and C.F. Schmidt, Phys. Rev. Lett. 79, 3286 (1997); B. Schnurr, F. Gittes, F.C. MacKintosh, C.F. Schmidt, Macromolecules 30, 7781 (1997);
[9] M. Atakhorrami, J. Kwiecinka, K.M. Addas, G.H. Koenderink, A. Levine, F. MacKintosh, and C.F. Schmidt, Phys. Rev. E73, 061501 (2006)
[10] L.A. Hough and H.D. Ou-Yang, Phys. Rev. E65, 021906 (2002);
[11] D. Bonn, H. Kellay, H. Tanaka, G.H. Wegdam and J. Meunier, Langmuir 15, 7534-7536 (1999), D. Bonn, H. Tanaka, H. Kellay, G.H. Wegdam and J. Meunier, Europhys. Lett. 45, 52 (1998).
[12] D. Bonn, P. Coussot, H.T. Huynh, F. Bertrand and G. Debreges, Europhys. Lett. 59, 786 (2002).
[13] A. Knaebel, M. Bellour, J.P. Munch, V. Viasnoff, F. Lequeux and J.L. Harden, Europhys. Lett. 52, 73(2000), S. Kaloun, R. Skouri, M. Skouri, J. P. Munch and F. Schosseler Phys. Rev. E72, 011403 (2005)
[14] F. Gittes and C. F. Schmidt, Phys. Lett. 23, 7 (1998).
[15] F. Brochard and P.G. de Gennes, Macromolecules 10
1157 (1977); S.T. Milner, Phys. Rev. E48 3674 (1993).
[16] V. Trappe and D.A. Weitz, Phys. Rev. Lett. 85 449 (2000); M.L. Gardel, J.H. Shin, F.C. MacKintosh, L. Mahadevan, P.A. Matsudaira and D.A. Weitz, Phys. Rev. Lett. 93 188102 (2004).
[17] M. Merolle, J. P. Garrahan and D. Chandler, Proc. Nat. Acad. Sci. 102 (31), 10837 (2005); P. Mayer, H. Bissig, L. Berthier, L. Cipelletti, J.P. Garrahan, P. Sollich, and V. Trappe, Phy. Rev. Lett. 93, 115701 (2004)