Observation of Fluctuation-Dissipation-Theorem Violations in a Structural Glass

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The fluctuation-dissipation theorem (FDT), connecting dielectric susceptibility and polarization noise, was studied in glycerol below its glass transition temperature T_g. Weak FDT violations were observed after a quench from just above to just below T_g, for frequencies above the α peak. Violations persisted up to 10^5 times the thermal equilibration time of the configurational degrees of freedom under study, but comparable to the average relaxation time of the material. These results suggest that excess energy flows from slower to faster relaxing modes.

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When a system is in thermodynamic equilibrium, its linear response functions (e.g., susceptibility) and its equilibrium fluctuations are related by the well-known fluctuation-dissipation theorem (FDT) [1]. Special cases of the FDT include Nyquist's formula [2] relating electrical resistance to voltage noise, and Einstein's relation [3] which links the diffusion and friction coefficients in Brownian motion.

There is no reason to expect the FDT to hold for systems out of equilibrium, and it is indeed known to fail in far-from-equilibrium cases such as Barkhausen noise [4]. Glasses, however, are systems that are out of equilibrium but evolve very slowly. Much has been learned by studying how response functions *age*, that is, depend on the *waiting time* (t_w) elapsed since a temperature quench [5].

Recent theoretical work has shown that the FDT is violated by several mean-field spin glass models below some critical temperature [6], and also that this violation can be used to define an effective temperature [7]. Computer simulations have also found FDT violations in finite-range spin glasses [8], domain growth processes [9], some models of structural glasses [10], elastic strings in random media [11], kinetically constrained lattice gases [12], and Ising models with dipolar interaction [13]. In all cases, violations are found when the characteristic observation time t is of the same order or greater than the age of the system, i.e., when $t \gtrsim t_w$ or $\omega t_w \sim 1$, where $\omega \sim 1/t$ is a measurement frequency.

There is considerable interest in studying FDT violations experimentally, in part because predicted violations are model dependent [14]. Measurements of FDT violations would thus furnish a new way to test models of the glass transition and glassy dynamics. Moreover, recent theoretical results [15] surprisingly indicate that nonequilibrium FDT violations can, at least in spin glasses, give information about an *equilibrium* order parameter, which would be otherwise inaccessible.

Aging in susceptibility [16] and noise [17] has been measured in structural glasses. However, measurements of the *relation* between noise and response thus far reported in structural [18] as well as spin [19] glasses are compatible with the FDT within experimental errors. This gap between theory and experiment may be due to the fact that the regime $t_w\omega \sim 1$ is very difficult to access and/or that actual violations are rather weak.

In this Letter we present results that show a weak violation of the FDT in a supercooled liquid, glycerol, following a quench below its glass transition temperature. The effective temperature (T_{eff}) measured via dielectric noise slowly relaxes towards the thermal bath temperature T. Most surprisingly, violations are observed even with $t_w\omega \gg 1$. The relaxation is so slow compared to the thermal equilibration time of the configurational degrees of freedom (CDF) probed by the experiment, that these results can be understood only in terms of strong coupling between CDF.

The experiment is similar to the "oscillator as thermometer" gedanken experiment proposed by Cugliandolo *et al.* [7]. The idea is to connect a capacitor, whose dielectric is the glass under study, in parallel with a lossless inductor (see Fig. 1). In thermodynamic equilibrium, the average energy of the oscillator $C\langle V^2\rangle$ will be k_BT by equipartition, where $\langle V^2\rangle$ is the integrated voltage noise, k_B is Boltzmann's constant, and T is the temperature. The noise power spectral density S_V will be given by Nyquist's formula [2],

$$\begin{aligned} S_V(\omega) &= \frac{2}{\pi} k_B T \,\mathrm{Re} Z \\ &= \frac{2}{\pi} k_B T \frac{-\omega^3 L^2 C''}{(1 - \omega^2 L C')^2 + \omega^4 L^2 C''^2} . \end{aligned} \quad (1)$$

Here Z is the circuit impedance, L the inductance, and $C = C' + iC'' = C_0\epsilon$ the capacitance (with ϵ the complex dielectric susceptibility).

The strongly peaked noise spectrum produced by the resonant circuit (see Fig. 2) provides *three* independent quantities: peak position, width, and height, which relate directly to C', C'', and T, respectively. If the FDT ceases to be valid, then this would be apparent as a failure of the noise spectrum to satisfy Nyquist's equation with T as the thermodynamic bath temperature.

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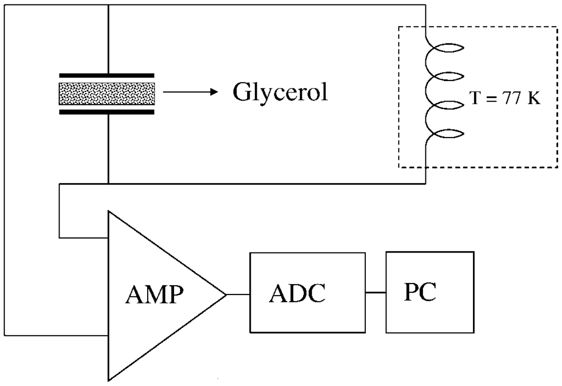

FIG. 1. Experimental setup. The sample forms the dielectric of a capacitor in a resonant circuit, which is driven by the polarization noise of the sample.

Thus, the need for separate measurement of noise and response is eliminated with this method. We note that measurement of broadband noise alone [17] provides only two quantities (spectral density and exponent), and therefore is insufficient to test FDT violations.

For a nonequilibrium (aging) glass, the FDT is believed to fail [6], and an effective temperature, $T_{\mathrm{eff}}(\omega, t_w)$, can be defined [7]. It should replace T in Eq. (1), control the direction of heat flow, and determine the average energy of an oscillator coupled to the sample (as in the equipartition theorem). $T_{\mathrm{eff}}(\omega, t_w)$ should approach the bath temperature for $t_w \longrightarrow \infty$ at any fixed frequency, but its behavior is otherwise system dependent. Whether this scenario is completely valid or not, we can use T_{eff} to quantify any observed FDT violations.

The sample capacitor was fabricated by rolling two copper foils separated by a sheet of high porosity paper on a copper tube, to which a heater and temperature sensor were attached. Liquid glycerol was then absorbed into the paper. The capacitor was connected in parallel with an inductor and both placed inside a liquid nitrogen cryostat at low pressure ($\approx$100 mTorr). To minimize the noise due to the lossy part of the inductance, the inductor was placed at the bottom of the cryostat in good thermal contact with the liquid nitrogen. The voltage noise was amplified with a Stanford SR560 preamplifier, filtered with a Stanford SR640 low-pass filter, digitally sampled with a personal computer, and Fourier analyzed to obtain the voltage power spectrum as a function of aging time.

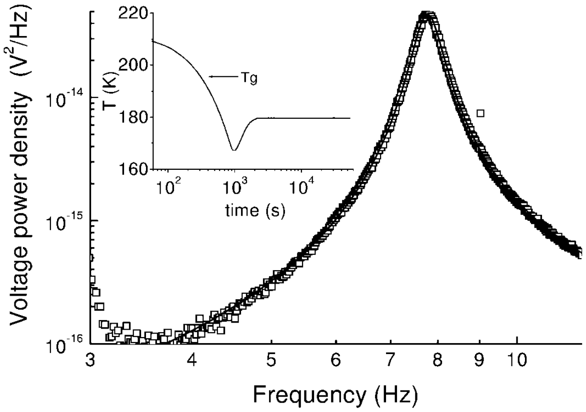

FIG. 2. Typical voltage power spectrum for 179.8 K (squares), and fit to Eq. (2) (solid line). Measurements are made after bath temperature T has stabilized. Inset: Typical thermal history.

Since capacitor and inductor are at different temperatures, Eq. (1) has to be replaced by a generalized formula [20], which for our circuit gives

$$S_V(\omega) = \frac{2k_B}{\pi} \frac{-\omega^3 T_{\mathrm{eff}}(\omega_0, t_w)\,|L|^2 C'' - \omega T_0 L''}{1 - 2\omega^2(L'C' - L''C'') + \omega^4 |L|^2 |C|^2}, \qquad (2)$$

where $T_0 = 77$ K is the inductor temperature, which now has a lossy part ($L = L' + iL''$), which is measured separately with a known capacitor. We disregard any possible ω dependence of T_{eff} because S_V is strongly peaked, and its value at the resonance frequency, ω_0, will dominate. All other quantities being known, a least-squares fit of the power spectra to Eq. (2) yields C', C'', and T_{eff}.

The sample was always heated to a bath temperature of 210 K (above the glycerol glass temperature) and then cooled to T near 180 K. A typical thermal history is shown in Fig. 2 (there is an unavoidable temperature undershoot). All reported results are from data taken after the bath temperature stabilized at its final value. $t_w = 0$ was taken as the time when the sample falls out of equilibrium. This depends on cooling rate and thermal history. We have determined T_g to be $\approx$196 K. Adjustment of T_g by a few degrees will shift the time axis by at most a few hundred seconds, without affecting our results.

Figure 2 shows a typical power spectrum, together with the fit using Eq. (2). The spectrum is an average obtained from voltage noise sampled in a time window around a particular t_w. The time window increased with t_w, so as to reduce errors for large t_w. For shorter t_w ($<10^5$ s), it was necessary to average data from several ($\sim$15) runs. The resonance frequency is $f_0 \approx 7.7$ Hz. The errors in the fitting parameters were estimated by fitting simulated power spectra with Gaussian noise.

Figure 3 plots C' and C'' vs waiting time at $T = 179.8$ K, which clearly shows the aging of the dielectric susceptibility, as previously seen by Leheny and Nagel [16]. The curves can be fitted by a stretched exponential, $C'(t_w) = C'_\infty + \Delta C' \exp\{-(t_w/\tau)^\beta\}$, with τ and β taken from Ref. [16].

The effective temperature is plotted in Fig. 4 against t_w for $T = 179.8$ K. Two features of this graph are noteworthy. First, a fit of the equilibrium data (long t_w) with Eq. (2) yields the bath temperature with high accuracy. Second, a fit of Eq. (2) to the nonequilibrium data at early times *fails* to yield the bath temperature. This failure to fit Nyquist's formula can *only* be explained

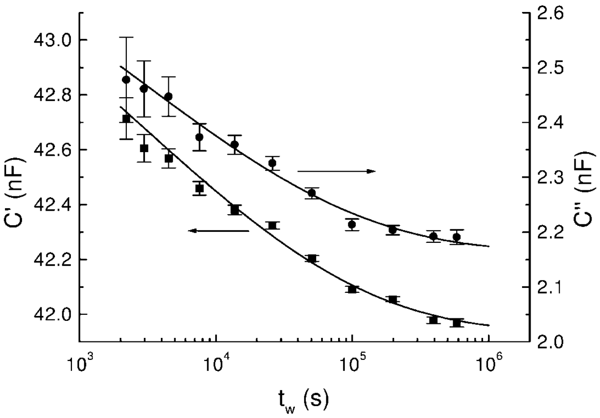

FIG. 3. Real (squares) and imaginary (circles) capacitance vs waiting time, showing aging in the dielectric susceptibility at $T = 179.8$ K. Solid lines: fits to stretched exponentials.

by an FDT violation. Although the violations are small, the statistical certainty of a violation is very high: we performed the fitting procedure on simulated spectra with the same susceptibility as the experimental spectra but obeying the FDT. With $T = 179.8$ K, the T_{eff} obtained by fitting 500 000 simulated spectra was in *no case* greater than 183.67 K, while five experimental points at the earliest t_w are above this value. T_{eff} relaxes slowly towards T on a time scale similar to that of the aging in susceptibility. The decay can be fitted equally well by an exponential or a stretched exponential. Most striking, this FDT violation persists much longer than expected, to $\omega t_w > 10^5$. This effect was clearly observed only in a narrow range of temperatures around 180 K (Fig. 5), while susceptibility aging was seen over the range 177–184 K, in agreement with [16].

It is interesting to compare and contrast the new results for T_{eff} with other thermodynamic measurements. For example, dynamic heat capacity measurements in glycerol [21] show that changes in temperature are accompanied by heat flow on long time scales similar to those found in other dynamical measurements. There are two ways this could be relevant to the present experiments.

First, heat flow will lead to a temperature gradient across the sample, and thereby an apparent rise in T_{eff}. However, if this were important, the susceptibility at early times should correspond to that of higher temperatures in equilibrium, but we find that C' (179.8 K) is at all t_w lower than the final value of C' (181.7 K). Furthermore, a generous estimate of the maximum temperature rise gives 50 mK at 180 K, negligible compared with the measured rise in T_{eff}.

Second, the dynamic heat capacity measurements can be understood [22] in terms of an excess enthalpy, ΔH, trapped in the sample for times comparable to the relaxation time. A fictive temperature T_f [23] can be defined as the temperature at which the glass and liquid lines intersect in a diagram of enthalpy vs temperature. Then $T_f = T + \Delta H/\Delta C$, where $\Delta C = C_g - C_l$ is the heat capacity difference between the liquid and the glass [22]. As the glass relaxes, its enthalpy tends to that of the equilibrium liquid, and so $T_f \rightarrow T$. It is tempting to attribute the excess T_{eff} observed simply to the excess enthalpy per CDF. We can use $T_f - T$ as a rough estimate of the excess enthalpy per CDF stored in the glass as a function of t_w. We computed T_f as described in [22] using the particular thermal history of our sample. As Fig. 5 shows, the deviation of T_{eff} and T_f from T is similar in magnitude at 180 K, but the temperature dependences of the two are distinctly different.

That T_{eff} and T_f behave differently is not unexpected, since the oscillator couples only to those CDF with relaxation time $\tau \sim 1/\omega \sim 0.1$ s. In a parallel relaxation picture, excess enthalpy trapped in these relatively fast CDF would relax in ~0.1 s and independently of slower CDF, too fast for this experiment to detect. It is possible that steplike relaxation of slow CDF near the α peak could contribute enough to be observed at the much higher measurement frequencies, as in Barkhausen noise [4]. Barkhausen noise decreases with frequency as $1/\omega^2$,

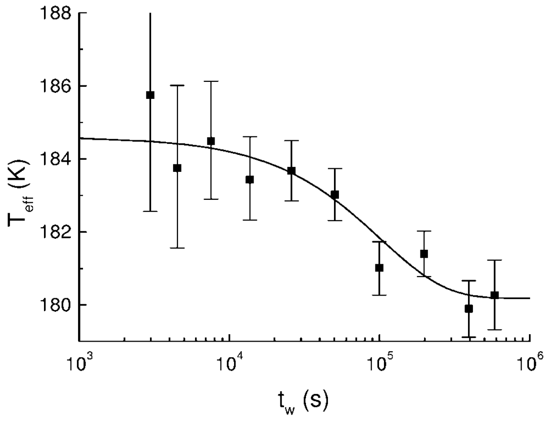

FIG. 4. Effective temperature T_{eff} vs waiting time for $T = 179.8$ K. Points: experimental data; solid line: fit to exponential decay.

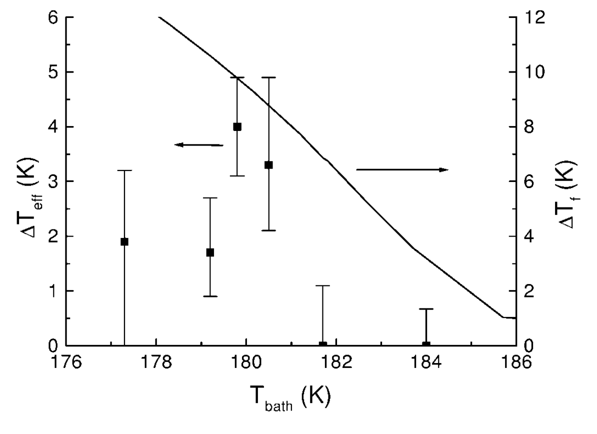

FIG. 5. $\Delta T_{\mathrm{eff}} = T_{\mathrm{eff}}$ $(t_w = 10\,000\ \mathrm{s}) - T_{\mathrm{eff}}(t_w = \infty)$ vs bath temperature (points). Solid line is $T_f - T$.

whereas the equilibrium noise decreases more slowly. This would require a highly improbable $T_{\rm eff}$ of 10^5 K at the α peak frequency to increase $T_{\rm eff}$ by 4 K at the measurement frequency. Moreover, Monte Carlo simulations [24] of a parallel kinetics model with the same relaxation times as our sample show no significant increase in the noise power at the measurement frequency during a quench. Thus our results are inconsistent with parallel kinetics.

Previous results, such as the aging of dielectric response [16] and dielectric hole burning [25] could be qualitatively understood in terms of a slow relaxation of relaxation rates via coupling between barriers and local density. But the present results further require that the CDF under observation be continually "heated" above the phonon temperature. Hence some mechanism must transfer excess energy stored in slower CDF to faster CDF active in the experimental window. This could happen through reshuffling of relaxation times of individual CDF, or by directed energy exchange between different CDF. The peak in Fig. 5 then arises naturally, because at high T the relaxation is too fast to be seen, while at low T the energy release from relaxing CDF is too slow. Some form of series kinetics [26] (as seen in recent simulations [27]), in which relaxation occurs in a series of constrained steps, may explain these results.

In conclusion, we have reported experimental observation of weak FDT violations in glycerol, which we have analyzed in terms of an effective temperature. Like other quantities, the effective temperature ages, but provides different information than fictive temperature, susceptibility, or dynamic heat capacity. Specifically, the present results indicate that successful models of the glass transition must explicitly account for nontrivial energy exchange between slower and faster configurational degrees of freedom. Extending these results to a broader range of temperature, frequency, and other materials would be useful.

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[1] R. Kubo, Rep. Progr. Phys. **29**, 255 (1966); R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II* (Springer-Verlag, Berlin, 1991), 2nd ed.

[2] H. Nyquist, Phys. Rev. **32**, 110 (1928).

[3] A. Einstein, Ann. Phys. (Leipzig) **17**, 549 (1905).

[4] H. Barkhausen, Z. Phys. **20**, 401 (1919).

[5] L. C. E. Struik, *Physical Ageing in Amorphous Polymers and Other Materials* (Elsevier, Amsterdam, 1978).

[6] L. F. Cugliandolo and J. Kurchan, Phys. Rev. Lett. **71**, 173 (1993); J. Phys. A **27**, 5749 (1994); Philos. Mag. B **71**, 501 (1995).

[7] L. F. Cugliandolo, J. Kurchan, and L. Peliti, Phys. Rev. E **55**, 3898 (1997).

[8] S. Franz and H. Rieger, J. Stat. Phys. **79**, 749 (1995); E. Marinari, G. Parisi, F. Ricci-Tersenghi, and J. J. Ruiz-Lorenzo, J. Phys. A **31**, 2611 (1998).

[9] A. Barrat, Phys. Rev. E **57**, 3629 (1998).

[10] G. Parisi, Phys. Rev. Lett. **79**, 3660 (1997); Philos. Mag. B **77**, 257 (1998); J.-L. Barrat and W. Kob, Europhys. Lett. **46**, 637 (1999); J. Phys. Condens. Matter **11**, A247 (1999).

[11] H. Yoshino, Phys. Rev. Lett. **81**, 1493 (1998).

[12] M. Sellitto, cond-mat/9804168.

[13] D. A. Stariolo and S. A. Cannas, Phys. Rev. B **60**, 3013 (1999).

[14] For a review, see J.-P. Bouchaud, L. F. Cugliandolo, J. Kurchan, and M. Mézard, in *Spin Glasses and Random Fields,* edited by A. P. Young (World Scientific, Singapore, 1998).

[15] S. Franz, M. Mézard, G. Parisi, and L. Peliti, Phys. Rev. Lett. **81**, 1758 (1998).

[16] R. L. Leheny and S. R. Nagel, Phys. Rev. B **57**, 5154 (1998).

[17] N. E. Israeloff and T. S. Grigera, Europhys. Lett. **43**, 308 (1998).

[18] N. E. Israeloff, Phys. Rev. B **53**, R11 913 (1996).

[19] M. Ocio, H. Bouchiat, and P. Monod, J. Phys. (Paris) Lett. **46**, L647 (1985); W. Reim, R. H. Koch, A. P. Malozemoff, M. B. Ketchen, and H. Maletta, Phys. Rev. Lett. **57**, 905 (1986); H. Bouchiat and M. Ocio, Comments Condens. Matter Phys. **14**, 163 (1988).

[20] W. R. Bennet, *Electrical Noise* (McGraw-Hill, New York, 1960).

[21] N. O. Birge and S. R. Nagel, Phys. Rev. Lett. **54**, 2674 (1985); N. O. Birge, Phys. Rev. **B34**, 1631 (1986).

[22] S. L. Simon and G. B. McKenna, J. Chem. Phys. **107**, 8678 (1997).

[23] A. Q. Tool, J. Am. Ceram. Soc. **29**, 240 (1946); O. S. Narayanaswamy, J. Am. Ceram. Soc. **54**, 491 (1971); C. T. Moyniham *et al.,* J. Am. Ceram. Soc. **59**, 12 (1976); **59**, 16 (1976).

[24] T. S. Grigera and N. E. Israeloff (to be published).

[25] B. Schiener, R. Böhmer, A. Loidl, and R. V. Chamberlin, Science **274**, 752 (1996); B. Schiener, R. V. Chamberlin, G. Diezemann, and R. Böhmer, J. Chem. Phys. **107**, 7746 (1997).

[26] G. H. Fredrickson and H. C. Andersen, Phys. Rev. Lett. **53**, 1244 (1984); R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).

[27] C. Donati, J. F. Douglas, W. Kob, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **80**, 2338 (1998).