Fluctuation-Dissipation Theorem in Liquid and Glassy Glycerol: Frequency-Dependent Dielectric Permittivity and Dielectric Polarization Fluctuation Measurements

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We show frequency-dependent dielectric permittivity and dielectric polarization fluctuation measurements of liquid and glassy glycerol. This allows a direct comparison of both quantities determined independently. After cooling the glycerol sample to 179 K with a cooling rate of 0.85 K/ min we studied the aging time dependence of the dielectric permittivity and the polarization fluctuations using the identical glycerol sample. A cross-correlation technique allows measurements of noise levels below the amplifier noise. In the frequency range between 0.3 and 300 Hz we find the measured data to be in agreement with the fluctuation-dissipation theorem for the liquid and glassy state not depending on the aging time.

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Nonequilibrium properties belong to the most challenging and interesting topics of condensed matter physics. In thermodynamic equilibrium the spontaneous fluctuations of a system are closely related to the response function by the fluctuation-dissipation theorem (FDT) [1]. For nonequilibrium systems like structural glasses the validity of the FDT is not given *a priori*. The question of how to treat nonequilibrium systems in terms of FDT received much attention from experimentalists [2–10] and theoreticians [11–16]. In particular, an effective temperature [11] different from the bath temperature [17] is widely used as a measure of equilibrium FDT violations. We do not use the fictive temperature concept characterizing the structural state of a nonequilibrium system [18,19].

In the following we study the aging dynamics of the prototypical small-molecule organic glass former, glycerol, in the glass transition regime. If FDT violations are present, conventional permittivity measurements alone would not be sufficient to characterize the glass transition dynamics. This makes this investigation highly interesting in terms of understanding the glass transition physics [20–22]. Furthermore previous work determining the aging dynamics with respect to the FDT in the structural glass former glycerol show contradicting results: No FDT violation is reported in [2], and small violations measured at a frequency of 7.7 Hz are seen in [4]. This violation persisted more than 1 d. If such a violation exists, the necessity for a frequency-dependent analysis is apparent. We present experimental results from dielectric permittivity and dielectric polarization fluctuation measurements. The sample was glycerol with a purity of >99.5% spectrophotometric grade by Aldrich Chemical Company and was used without further pretreatment. We used the identical sample and capacitor in the same cryostat for both the dielectric permittivity and polarization fluctuation measurements, minimizing any possible geometric or thermal differences in the two measurements. Furthermore using a special preamplifier stage described later we could improve the sensitivity for measuring the voltage fluctuations by at least a factor of 10 with respect to the voltage fluctuation spectral density given in [3]. The measurements were done in a homemade low vibration liquid nitrogen cooled cryostat which allows cooling rates of about 1 K/ min. An excellent noise and vibration isolation from the surrounding as well as a temperature stability better than 0.05 K are an experimental requirement for studying dielectric polarization fluctuations. Temperature stability of the sample holder is achieved using a Lakeshore Model 330 temperature controller in connection with Pt100 [23] thin film temperature sensors for thermometry and a twisted pair Manganin wire wound heater around the sample holder. The liquid sample is filled at room temperature into a cylindrical capacitor made of stainless steel. The empty capacity was determined to be $C_0 = 21$ pF. To obtain the dielectric permittivity a commercial dielectric spectrometer [24] was used covering a spectral range between several 100 mHz and 3 MHz. To avoid temperature gradients the stainless steel capacitor is clamped in a copper holder. The capacitor holder is suspended from the 77 K plate of the cryostat by a stainless steel rod of about 3 mm diameter and 10 mm length.

The setup for measuring the dielectric polarization fluctuations is shown schematically in Fig. 1. The fluctuating voltage between the capacitor plates is measured using two amplifiers in parallel: Since the intrinsic amplifier noise is uncorrelated to a large extent, this contribution to the signal can be reduced strongly by calculating the cross-correlation function [25,26]. At the preamplifier stage we used instrumentation amplifiers of type INA 116 by Burr Brown. The input impedance of the INA 116 is larger than 10^{14} Ω and its input bias current is as low as about 3 fA already at room temperature. These specifications make the amplifier suitable for measuring voltages of high impedance sources like the glycerol sample. We connected one input line of each preamplifier to the inner electrode of the sample capacitor. The second input line and the outer electrode are grounded. In this circuitry the instrumentation amplifiers act as conventional noninverting amplifiers. The preamplifiers are mounted inside the cryostat to allow a short cable length to the sample. In addition running the amplifiers at low temperature further reduces Nyquist amplifier noise. We kept the temperature of the preamplifier holder at around 200 K. After preamplification by a factor of 10, the voltage is amplified outside the cryostat by a factor 100 using one further precision operational amplifier (OP 27) per channel.

After digitizing the noise signals using an analog-to-digital converter (ADC) [27] with a maximum sampling rate of 500 kHz, the digitized noise signals are stored on a hard disc. Calculating the Fourier transform of the cross-correlation function yields the power spectral density of the voltage fluctuation S_V between the capacitor electrodes. By using the cross-correlation technique we were able to reduce the total noise floor of the setup to about 3 $\mathrm{nV}/\sqrt{\mathrm{Hz}}$. Without the cross-correlation technique the sensitivity of the setup is limited by the white noise level of the INA 116 which we measured to be about 30 $\mathrm{nV}/\sqrt{\mathrm{Hz}}$. One very important point is to be aware of random telegraph noise [28], i.e., of sudden dramatic shifts in the dc offset of the amplifiers. The conditions present in our experiment, low amplifier temperatures and high source impedances, are known to enhance the chances for random telegraph noise events to occur. When one of these parameters changes during an aging experiment, this can result in a decrease of random telegraph noise over time. Thus one has to pay attention that a random telegraph noise event is not interpreted by mistake in terms of aging dynamics. We plotted the recorded signal for each calculated noise spectrum to see if a random telegraph noise event occurred. If this was the case we rejected the data and repeated the measurement. To reduce any disturbance coming from the power line all amplifiers used are battery driven. Thermometry and heater cables are low-pass filtered twisted pair lines. The cables carrying the noise signal are stainless steel minicoax cables [29].

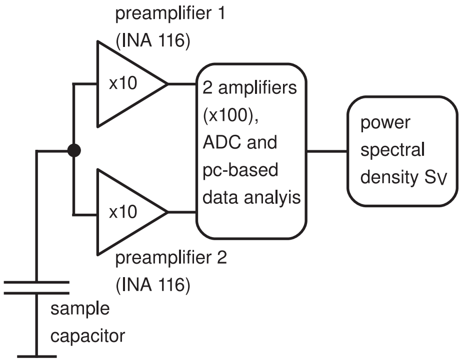

FIG. 1. Essentials of the electrical circuit used: The voltage fluctuations across the sample-filled capacitor are read out by two preamplifiers in parallel [25,26]. A subsequent cross-correlation analysis and Fourier transform give us voltage power spectral density spectra. Hereby the cross-correlation technique suppresses the amplifier noise and allows measurements of noise 1 order of magnitude lower than the intrinsic amplifier noise.

In the classical limit the FDT describing the voltage fluctuations of an electrical network with impedance Z is given by the Nyquist formula [1,30,31]

$$S_V = 4k_B T \,\mathrm{Re}[Z(\omega)], \tag{1}$$

where S_V is the power spectral density of the voltage fluctuations, T the temperature, ω the angular frequency, and $\mathrm{Re}[Z(\omega)]$ the real part of the impedance of the network producing and shaping the noise signal [26,28,32]. Modeling the sample as a parallel circuit of resistance R and capacity C we get

$$S_V = 4k_B T \frac{R(\omega)}{1 + [\omega R(\omega) C(\omega)]^2}. \tag{2}$$

In this work both Z and S_V were measured independently. Z is determined by dielectric spectroscopy measuring R and C; S_V by recording and analyzing the noise of the sample-filled capacitor.

To check the setup we measured the noise of several known impedances. Results of such dummy RC networks are not presented here but results of the glycerol sample in the liquid and therefore thermal equilibrium state are shown in Fig. 2. Here the imaginary part $\epsilon'' = 1/\omega R C_0$ of the dielectric permittivity and the measured power spectral density S_V are plotted. Applying the FDT (2) allows a prediction for S_V from the measured permittivity.

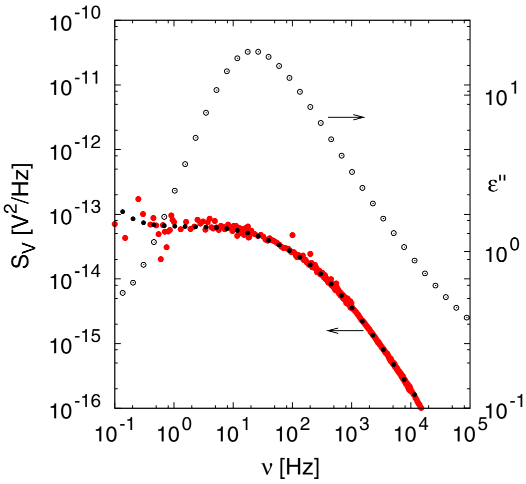

FIG. 2 (color online). Imaginary part ϵ'' (open black circles, right y axis) of the dielectric permittivity measured using a dielectric responses analyzer and voltage power spectral density in comparison: The gray (red) filled circles are directly measured voltage noise, and the black filled circles are based on the dielectric permittivity measurement. The sample temperature was 205.0 ± 0.6 K.

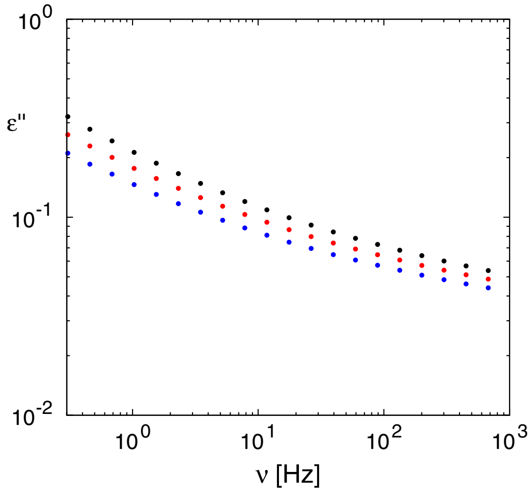

FIG. 3 (color online). The imaginary part ϵ'' of the dielectric function is shown as a function of frequency at 179.0 ± 0.6 K after 10 min (black filled circles), 1 h [light gray (red) filled circles], and 8 h [dark gray (blue) filled circles] waiting time. During aging ϵ'' decreases.

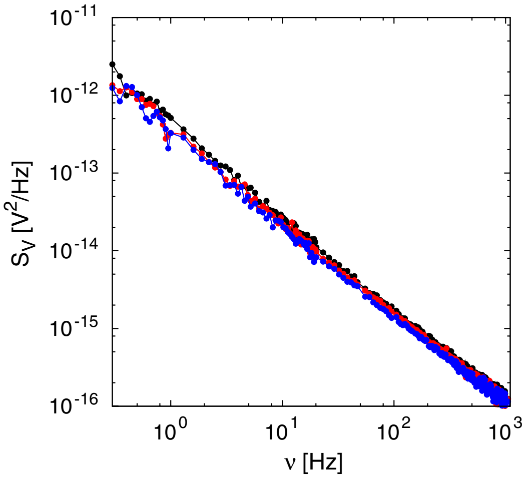

FIG. 4 (color online). The voltage power spectral density S_V at 179.0 ± 0.6 K is shown after 10 min (black filled circles), 1 h [light gray (red) filled circles], and 8 h [dark gray (blue) filled circles] waiting time as a function of frequency. Upon waiting the sample ages. The voltage power spectral density decreases. The relative temperature accuracy was better than 0.1 K.

Both the directly measured data and the calculated noise spectra lie perfectly on top of each other. This is not surprising because the sample is liquid and in thermal equilibrium but it shows the validity of the method and the setup. For sure one can use the setup as a noise thermometer: Knowing Z and S_V and given the validity of the FDT one calculates an effective or noise temperature T_{eff} of the dielectric relaxors in the sample. In thermal equilibrium the bath temperature and the effective temperature should be the same, which they were in our measurements.

We performed two sets of aging measurements. In both experiments we used an identical sample and sample holder. The first experiment was carried out monitoring the dielectric permittivity: Beginning at 205 K, well above the glass transition in the viscous liquid regime, the sample was cooled with a cooling rate of 0.85 K/ min to 179 K. This temperature was kept constant within ±0.05 K during the aging experiments. We chose the final temperature of 179 K because it results in a suitable structural relaxation time for the observation of aging effects during a practical laboratory time scale and provides a starting point far enough away from equilibrium to see distinct aging with a cooling rate of 0.85 K/ min.

After each waiting time we measured a dielectric spectrum. Taking one spectrum lasts a few minutes and the frequency is ramped logarithmically from high to low values. We kept the measuring times in the permittivity experiment comparable to those in the noise experiment. The results for measurements that started after a waiting time of 10 min, 1 h, and 8 h are shown in Fig. 3. The data agree well qualitatively with those measured by Leheny and Nagel [33] in a comparable experiment. The dielectric loss gets smaller with increasing waiting time.

The second experiment was done using the dielectric noise spectrometer. The thermal history, i.e., initial temperature, cooling rate, and waiting time, was kept the same as before. Recording the voltage noise for few minutes and calculating the power spectral density yields the curves shown in Fig. 4. For the sake of clarity we applied a software hum filter suppressing data points at 50 Hz and higher harmonics. Aging time reduces the noise level. Again we show data taken after waiting times of 10 min, 1 h, and 8 h. For better visibility of the aging effects we multiply these data by the frequency and get the filled circles in Fig. 5.

These two independent data sets allow a rigorous check of the validity of the FDT. In a first step of analysis we compare both data sets in a basic way: If we assume that the FDT is still valid during the aging process, we can calculate the voltage noise from the measured permittivity using Eq. (2). Hereby the thermodynamic bath temperature is assumed to be the same as the noise temperature of the dielectric relaxors of the sample. The result is shown in Fig. 5 as the smooth lines.

In the accessible frequency range between 0.3 and 300 Hz one observes a good agreement of the two sets of data. The directly measured noise level scatters around the FDT predicted noise level. The bath temperature and the noise temperature of the dielectric relaxors are the same within the error of our measurement. In a second step of analysis we calculate the effective noise temperature of the relaxors pointwise: In the frequency range of our measurement we have 230 data points, i.e., pairs of noise and permittivity. From each pair we extract the effective temperature according to Eq. (1):

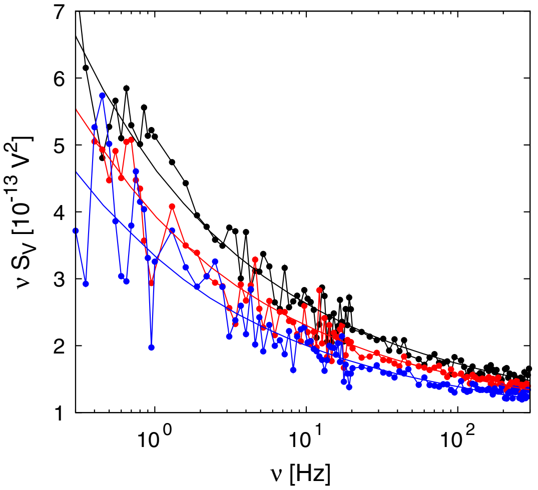

FIG. 5 (color online). The product of voltage power spectral density S_V and frequency ν at 179.0 ± 0.6 K is shown after 10 min (black filled circles), 1 h [light gray (red) filled circles], and 8 h [dark gray (blue) filled circles] waiting time. The multiplication of S_V by frequency makes the aging fingerprint better visible. Upon waiting the sample ages. The relative temperature accuracy was better than 0.05 K. In addition we show the predicted aging behavior of νS_V on the basis of the corresponding dielectric permittivity measurements carried out under identical conditions (smooth lines). In this data set no fitting procedures are involved and no adjustments made.

$$T_{\mathrm{eff}} = \frac{S_V}{4k_B\,\mathrm{Re}[Z(\omega)]}. \tag{3}$$

Under the assumption that each frequency carries the same information we can calculate the arithmetic average over all the 230 effective temperatures, yielding a mean effective temperature $\bar{T}_{\mathrm{eff}} = 179.1 \pm 1.1$ K after 1 h waiting time. Here the uncertainty is the mean error of the mean value. The thermodynamic bath temperature was set to 179.0 K. The absolute accuracy of the temperature sensor is 0.6 K for temperatures around 179 K. The accuracy of the dielectric spectrometer [34] is better than 0.2% for the frequency and impedance range we analyzed. This error contribution can be neglected. In total the FDT is at most violated by 0.7%. Analyzing the data sets after the other waiting times gives very similar results: $\bar{T}_{\mathrm{eff}}$ to 178.8 ± 1.0 K after 10 min waiting time and $\bar{T}_{\mathrm{eff}}$ to 180.1 ± 1.5 K after 8 h waiting time. From our measurements we can conclude that the effective or noise temperature of the relaxors of the sample and the bath temperature measured using a Pt 100 sensor match very well in the accessible frequency window between 0.3 and 300 Hz. This means that the FDT is valid for the shown nonequilibrium situation with an accuracy better than a percent for aging times between a few minutes and several hours. Aging experiments like ours monitoring the dielectric properties can also be interpreted as a linear cross-response experiment: The Brownian motion of the molecules leads to an electric fluctuation which is filtered by the electrical impedance of the sample itself which is know as Onsager's principle [26,35]. Such an interpretation basically would exclude any possibilities of FDT violation observation in the regime where the measured dynamics are relaxation dominated.

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