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Low-frequency dielectric fluctuations near the glass transition

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Abstract. – The temperature and frequency dependence of thermal electric polarization noise was investigated in glycerol at and below the glass transition temperature. Polarization fluctuations were observed via voltage noise which was produced within a sample capacitance cell in equilibrium. The high sensitivity and accuracy of the technique provides a useful probe of dynamics in low-loss regimes of various dielectric materials. Noise spectra exhibit a $1/f^{\gamma}$ power law form at lower temperatures just below the glass transition, where the noise also exhibits unusual aging effects. The spectral exponent decreases with temperature, extrapolating to 1.0, *i.e.* $1/f$ noise, at a critical temperature where the noise magnitude extrapolates to a non-zero value. The results support the possibility that a glassy phase transition occurs in the static limit.

Glasses have been intensively investigated not only because they are ubiquitous in nature, but also because they are prototype complex systems [1]. Yet generic *glassy* behaviors such as non-exponential relaxation and glass transitions have yet to be fully explained. The transition from a liquid to an amorphous solid, such as ordinary window glass, occurs at a temperature, $T_{\rm g}$, at which the average relaxation time in the material becomes longer than the measurement time. The measured $T_{\rm g}$ decreases with measuring frequency, however, it extrapolates to a non-zero value, T_0 (Volgel-Fulcher temperature), in the zero-frequency limit for many materials [1]. Scaling behavior is observed over a wide range in temperature and frequency in certain materials [2]. The question of whether a thermodynamic phase transition can occur at T_0 remains a major unsolved mystery.

Recently Menon and Nagel [3] have argued, based on extensive measurements, that the static dielectric susceptibility may have a logarithmic divergence at T_0, indicative of a true phase transition. Similar effects were recently reported for magnetic susceptibility in spin glasses [4]. An important consequence of this picture is that fluctuations with precisely a $1/f$ spectral dependence are expected at T_0. Recently we showed that dielectric polarization noise can be systematically observed and studied near the glass transition [5]. The noise measurements

offer certain advantages over conventional dielectric spectroscopy. Namely, no applied fields which might potentially influence dynamics are needed. The frequency dependence is obtained naturally in a single measurement. And greater accuracy is possible at low values of the imaginary component of susceptibility since there is no need to determine systematic phase shifts in the measurement circuit.

The polarization noise, measured as current or voltage fluctuations produced within a capacitance cell, obeyed predictions of the fluctuation-dissipation theorem (FDT), connecting noise and susceptibility, even when the material was weakly out of equilibrium. Subtle violations of FDT have recently been predicted for glasses which have fallen out of equilibrium [6]. The detailed dependencies of these FDT violations on temperature, frequency, and waiting time may be useful in testing the validity of various models [6], such as low-temperature extensions [7] of mode-coupling theory [MCT] [8]. But FDT violations have yet to be found experimentally [5, 9].

In this paper, we discuss measurements of dielectric polarization noise in glycerol at temperatures well below the glass transition using higher-sensitivity techniques, where noise spectra exhibit a $1/f^{\gamma}$ form. At these temperatures the noise magnitude also exhibits unusual aging effects. The equilibrium spectral exponent decreased linearly with temperature, extrapolating to 1.0, *i.e.* precisely $1/f$ noise, near T_0 where the noise magnitude extrapolates to a non-zero value. The results support the possibility that a glassy phase transition occurs in the static limit and suggest both similarities to and differences from spin glasses.

Because "$1/f$" noise has been observed in a wide variety of conducting materials as well as other diverse problems, a number of exotic theories have been invoked to account for the apparent "universality" of the $1/f$ spectral dependence [10]. In fact the spectral dependence in conducting materials is a non-universal, $1/f^{\gamma}$, with $0.6 < \gamma < 1.5$ [10]. The variations with temperature of γ together with the temperature dependence of the noise magnitude can often be self-consistently explained by thermally activated defect kinetics with a moderately broadened distribution of activation energies [10]. In this picture, a precisely $1/f$ spectrum ($\gamma = 1$) appears *accidentally* and only briefly (if at all) over narrow ranges of temperature (and frequency) in a given material. This is consistent with the observed noise spectra in many materials [10], with one notable exception: metallic spin glasses [11]. In that instance γ increased from 0.6 to 1.0 as the spin glass temperature was approached from above, and was not measurably different from 1.0 over a decade in temperature below the spin glass transition. This implies, in an activated kinetics picture, $1/f$ noise over an extremely broad range of frequency, *e.g.* many more decades than can ever be measured. The question is whether this a generic signature of a thermodynamic glass phase and whether it occurs in structural glasses.

Thermal equilibrium noise in the electric polarization of a lossy dielectric material is expected based on the fluctuation-dissipation theorem. Johnson noise of the conduction electrons in a resistor is a well-known analog. Similar noise was observed in the magnetization of spin glasses using very sensitive SQUID detectors [9]. The FDT voltage noise spectral density within a sample-dielectric filled capacitor is given by

$$S_{\mathrm{V}} = 4k_{\mathrm{B}}T\varepsilon''C_0/|C|^2\omega \sim 4k_{\mathrm{B}}T(\varepsilon''/\varepsilon')/|C|\omega\,, \tag{1}$$

where k_{B} is the Boltzmann constant, T is temperature, ω is angular frequency, C is the capacitance of the sample-filled cell, C_0 is the empty-cell geometrical capacitance, ε', ε'' are the real and imaginary components of the dielectric susceptibility. If the capacitor is electrically isolated, then the voltage fluctuations arise purely from polarization fluctuations. The spectral density of the polarization fluctuations in a parallel plate capacitor with plate separation d

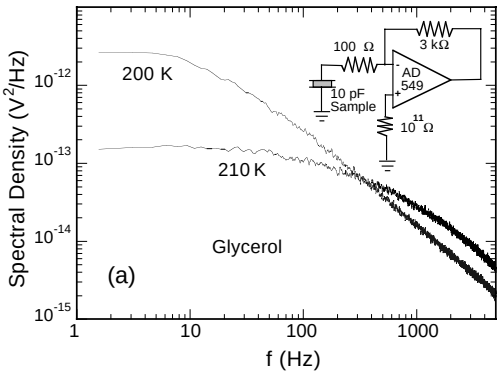

Fig. 1

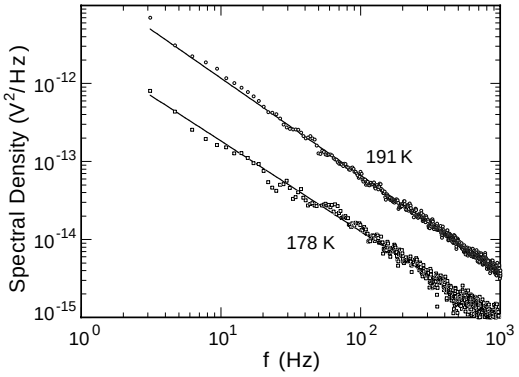

Fig. 2

Fig. 1. – Voltage noise spectra for two temperatures in the vicinity of its glass transition for glycerol. Inset: the measurement circuit located within the cryostat.

Fig. 2. – Noise spectra for glycerol at the indicated temperatures below the glass transition, where power law spectra are observed. The lines are power law fits to the data points.

will be

$$S_{\mathrm{P}} \sim S_{\mathrm{V}} \varepsilon_0^2 / d^2 \,. \tag{2}$$

For the noise spectral studies discussed here, the capacitance sample cell consisted of copper plates separated by Teflon or polypropylene spacer rings (0.1–0.4 mm thickness, 0.5–4.0 cm^2 area). The geometrical capacitances, C_0, ranged from 5 pF to 45 pF ($\pm 10\%$). The sample cell was attached to a copper cold finger in vacuum within a liquid-nitrogen cooled cryostat which sits on a vibration isolation table within an RF shielded room. A custom built preamplifier utilizing an Analog Devices 549L ultra-low current noise JFET op-amp, and a 10^{11} ohm (Victoreen) input resistor, was mounted inside the cryostat close to the sample on the cold finger [12]. See the inset of fig. 1. The stray capacitance in this arrangement was limited to < 1 pF. In order to optimize its performance the op-amp was maintained at a much higher temperature than the sample, by using its self-heating and deliberately poor thermal grounding. With these techniques we can accurately resolve noise spectra and spectral exponents in materials with $\varepsilon''/\varepsilon \sim 10^{-3}$. For the noise aging studies, the capacitance cell was formed by rolling copper foil separated by thin paper onto a copper tube, which gave $C_0 = 20$–40 nF. In this case the sample capacitance formed part of an LC resonant circuit [13], which acted as a narrow-band preamplifier. In both experiments the pre-amplifier output was further amplified with a Stanford Research SR560 amplifier and then digitized using a personal-computer–based data acquisition card and spectrum analyzer.

One must be careful in dealing with the amplifier background. Amplifier current noise produces voltage noise inversely proportional to the sample capacitance at low frequencies with a $1/f^2$ dependence. The relative proportion of background noise at high frequencies due to amplifier voltage noise scales as sample capacitance. Thus an optimal capacitance which gave a large dynamic range was of order 10 pF. The background can be determined by replacing the sample with a vacuum capacitor equal in size to the sample at a specific temperature. Additionally the background was checked by measuring the sample spectrum at lower temperatures.

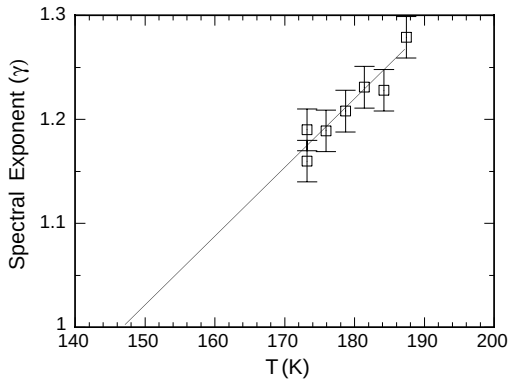

Fig. 3

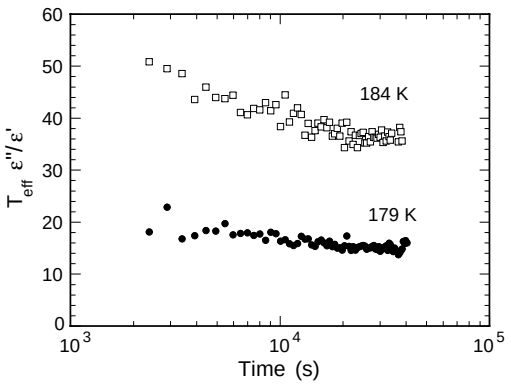

Fig. 4

Fig. 3. – Spectral exponent *vs.* temperature for glycerol. A linear fit (shown) extrapolates to 1.0 near T_0.

Fig. 4. – $T_{\rm eff}\varepsilon''/\varepsilon'$ extracted from voltage noise measured at $f = 7$ Hz, *vs.* time is shown for the indicated temperatures for glycerol. The sample was cooled from 205 K with an equilibration time of 2000 seconds. The zero of time was set by the time at which the sample falls out of equilibrium at $T_{\rm g}$, taken to be 190 K.

Measurements of the dielectric polarization noise were performed on glycerol through the glass transition. Glycerol is one of the most highly studied [1] glass formers and is one which exhibits scaling behavior [2]. Figure 1 shows noise spectra in the vicinity of the glass transition. The spectra exhibit the characteristic knee marking the dominant α relaxation frequency, which moves rapidly to lower frequencies with decreasing temperature. Similar noise spectral behavior was observed in studies of poly-vinyl-chloride (PVC) [12] near its glass transition.

The voltage noise spectrum attains a $1/f^{\gamma}$ power law at lower temperatures in glycerol (see fig. 2). This corresponds to the high-frequency tail of the spectra seen in fig. 1 at higher temperatures. We note that the polarization noise spectrum (eq. (2)) should have the same spectral behavior. We found that the exponent, γ, decreases smoothly with temperature. A simple linear extrapolation of the data crosses $\gamma = 1.00$ near 147 K (fig. 3). The extrapolated static-limit glass transition temperature was previously found to be $T_0 = 137 \pm 10$ K for glycerol [14]. At the same time, the spectral density appears to extrapolate to a non-zero value at this temperature. Together these two results suggest that a $1/f$ spectrum with non-zero spectral density may occur near T_0.

Why expect $1/f$ at T_0? The $1/f$ spectrum is usually associated with a flat distribution of energy barriers [10]. Since the dynamics in supercooled liquids extrapolates to zero frequency at T_0, barriers must grow very large as T_0 is approached. But residual moderate or small barriers may remain, such as those associated with defects in weakly disordered crystalline solids. Thus near T_0 in supercooled liquids energy barriers smoothly extending from extremely large to small values would be expected, producing an extremely broad and hence nearly flat distribution, giving a $1/f$ spectrum like that found in spin glasses. This fails if the density of large barriers grows rapidly on approaching T_0. But this is not in agreement with the dielectric data which indicates that the value of ε'' at low frequencies at the start of the power law regime extraplolates to a fixed value as T approaches T_0 [3]. Would having a $1/f$ spectrum imply a phase transition? Using the Kramers-Kronig relations together with FDT,

the static susceptibility can be shown to be proportional to the polarization noise spectrum integrated over all frequencies it will diverge logarithmically indicating a phase transition [3] for a spectrum which is $1/f$ down to zero frequency and finite at laboratory frequencies. Our results are consistent with this scenario.

The noise spectra also exhibited aging effects after cooling from above T_g to below T_g. By eq. (1) the equilibrium noise is a function of susceptibility and temperature. In non-equilibrium situations, temperature should be replaced by an effective temperature, T_{eff} [6], which may be higher than the temperature and may be time- and frequency-dependent. As shown in fig. 4, the product $T_{\text{eff}}(\varepsilon''/\varepsilon')$ (extracted from the measured voltage noise) slowly relaxes toward a smaller equilibrium value. The equilibration of the noise spectrum required longer than a day at the lowest temperatures studied, making measurement of the equilibrium noise at lower temperatures impractical. The equilibration time was comparable to the average relaxation time of the material at the measurement temperature, even for frequencies far above the inverse waiting time [13]. This is different from the aging in spin glasses, in which the waiting time and frequency scales are intertwined [15]. This behavior is qualitatively similar to that seen in dielectric susceptibility alone [16]. These differences in behavior from that of spin glasses may make supercooled liquids a better candidate for observing predicted FDT violations [6]. This will require separating the effects of T_{eff} and susceptibility in the aging of the noise, for example, by simultaneous measurement of noise and susceptibility.

In conclusion, we have studied electric polarization noise in glycerol near the glass transitions. The polarization noise spectra had power law form below the glass transition and in glycerol extrapolated to a $1/f$ form at a temperature near the presumed critical temperature, T_0. This should be investigated in non-polar materials such as ortho-terphenyl, and more fragile materials such as PVC and toluene [1], for which the measurements can be extended closer to T_0. Interestingly, our results suggest that the $1/f$ spectrum, which was found below the phase transition temperature in spin glasses [9, 11], may be a signature of a glassy phase in structural glasses as well. The noise spectra offer a useful new probe of aging effects in structural glasses. Detailed simultaneous measurements of both noise and susceptibility out of equilibrium would be very interesting in connection with FDT violations [6].

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