Glasses serve as the prototype for the kind of slow, non–exponential relaxation found in diverse systems from magnets and superconductors to proteins and granular assemblies. Although much has been learned about glassy phenomena, a detailed picture of the underlying dynamical processes remains elusive. Cooperative dynamics on nanometer scales has long been postulated but never been directly observed. A key question, with broad implications, is whether non–exponential dynamics arises primarily from a heterogeneous collection of independent nano–scale exponential processes, or more complex local dynamics. Recently, molecular dynamics simulations revealed the presence near the glass transition of long–lived clusters surrounded by liquid. These mesoscopic scale clusters exhibited a power–law behavior well below the glass transition for a function of frequency. These spectral anomalies would be clearly observable, for example, anomalous variations in ε'' (Debye–like response), but have a distribution of characteristic relaxation times, ξ. Estimates for ξ based on measurements and theory have been in the range 2 – 5 nm for various glass–formers at Tc. Far from the α–peak in ε'' only those nano–regions with τ ∼ 1/ω, will contribute significantly to ε''(ω, T). By using the Kramers–Kronig relations, it is easily shown that ξ relates to the number of nano–regions, N(ω), which contribute near ω within a band, Δω ∼ ω in width (i.e. factor of e) in a sample of volume Ω, via:

$$\xi^3 \approx \frac{\Omega \varepsilon''(0, T)}{N(\omega)\varepsilon'(0, T)}$$ (1)

When N(ω) is of order 10^14, deviations from bulk–like behavior will be clearly observable, for example, anomalous variations in ε'' (or equivalent measured quantity) as a function of frequency. These spectral anomalies would be persistent for very long–lived dynamical heterogeneity. Thus a lower–limit on the sample volume needed is of order: Ω ∼ 10^3ε''(0, T)/ε''(ω, T). For ε'' ∼ 0.1 below Tc, we estimate Ω ∼ 1 × 10^{-16} cm^3 for PVAc, e.g. a cube of about 50 nm on a side. If nano–regions are not independent or undergo intermittent or evolving dynamics, or if the amplitude of the response varies significantly from region to region, mesoscopic effects might be observed in larger samples.

Complex dynamics have been studied in great detail using noise spectroscopy in mesoscopic conductors at low temperature and. A sensitive mesoscopic signature involves anomalous statistical variations in the noise power, beyond the expectations of Gaussian statistics, i.e. the noise is non–Gaussian. It was recently demonstrated that 1/f noise can be measured in dielectric materials...
near the glass transition \[17\]. This noise arises from thermal polarization fluctuations, which relate to \(\varepsilon(\omega)\) via the fluctuation–dissipation theorem (FDT). However, extending noise measurements to the mesoscopic scale in dielectrics, as was done in conductors, is not possible with these techniques \[17\], due to overwhelming technical limitations.

In the present experiments, we employed a non–contact capacitance measurement scheme \[14\] using a thermal drift compensated, ultra–high–vacuum, variable temperature SPM \[18\]. A small piezo–resistive cantilever \[19\] with a sharp conductive tip was driven near its resonance frequency in high vacuum close to the 0.5 \(\mu\)m thick sample films, which were spin–coated onto a metal substrate. Details of the instrument design and PVAc film preparation are discussed elsewhere \[18\]. When a voltage bias is applied between tip and the substrate (see Fig. 1 inset), the resonance frequency, \(f\), of the cantilever will decrease due to the electrostatic forces \[14\]. At fixed height, variations in the tip–substrate capacitance or dielectric constant can be directly related to variations in the resonance frequency. Since the second derivative of the capacitance is responsible for the resonance frequency shifts, stray capacitances play a negligible role for tip heights < 100 nm.

In earlier studies of PVAc we showed that dielectric relaxation could be studied using the SPM resonance frequency shift \[18\]. Nearly bulk–like stretched–exponential relaxation was observed on 50 nm scales, and could be used to clearly identify the glass transition and characterize relaxation times, which increased rapidly on cooling through the glass transition. In the course of these relaxation studies, we observed a distinct background noise on relaxation curves or in equilibrium, which appeared only when the sample films were present and only when the tip was close to the film surface \[23\]. See figure 1. PMMA films had an order of magnitude lower noise power than the PVAc films near room temperature \(T_G \sim 110^\circ\)C for PMMA). A variety of checks were carried out to rule out instrumental or other extrinsic sources of noise.

Using a hemispherical tip model \[14\] at a distance \(z < r\), the tip radius, we have calculated \(C(z)\) and \(\Omega\) (effective probed volume). For example for a typical tip of radius 50 nm, held 20 nm from the surface, with \(\varepsilon = 2\), we find \(C = 8 \times 10^{-18}\) F, and \(\Omega \sim 1.3 \times 10^{-16}\) cm\(^3\). It is important to note that subsurface material is probed to a depth \((\sim 50\) nm) significantly larger than the length scales below which surface effects would be expected to dominate the dynamics, as in the experiments on glassy dynamics in porous media, with pores < 10 nm \[24\].

In order to understand these fluctuations, recall that the SPM senses tip–sample capacitance by measuring local electrostatic forces. The system can be modeled as a dielectric filled capacitor \((C_D)\) in series with a vacuum capacitor \((C_V)\) all in parallel with the much larger stray capacitance, \(C_S\). Thermal fluctuations in the dielectric film \[17\] will produce a fluctuating emf with spectral density, \(S_\varepsilon\), across \(C_D\). Voltage noise appearing across the series combination must sum to near zero, since it is “shorted out” by the large parallel \(C_S\), and would not be detectable by any voltmeter. Thus, voltage noise close to \(S_\varepsilon\) will appear with opposite sign across \(C_V\). The tip will therefore feel fluctuations in electric field and thereby force. This acts approximately as a fluctuating voltage, with spectral density \(\sim S_\varepsilon\), added to the constant voltage bias, and the resonance frequency will fluctuate. The spectral density of the thermal resonance frequency noise will be approximately:

![FIG. 2. Voltage noise spectra extracted from SPM resonance frequency fluctuations via eqn. 2 are shown for \(T = 302.9K\) in PVAc and for bare Mo substrate. An instrumental rolloff occurs above 0.2 Hz. Inset: temperature dependence of voltage noise at \(f = 0.015\) Hz vs. temperature for PVAc is shown.](image)
\[ S_f = \left( \frac{\partial f}{\partial V} \right)^2 G(\varepsilon) S_c = \left( \frac{\partial f}{\partial V} \right)^2 G(\varepsilon) \frac{4k_B T \varepsilon''}{|C|^2 \omega} \]  

(2)

where \( \frac{\partial f}{\partial V} \) is the measured shift in resonance frequency for small changes in bias voltage at the operating point, \( k_B \) is Boltzmann’s constant, \( \omega \) is the fluctuation frequency, and \( G(\varepsilon) \) is a dimensionless geometrical factor which is of order unity and depends weakly on dielectric constant \( \varepsilon \).

Long time series of the resonance frequency were recorded with fixed conditions (\( V = 8V \)), using feedback to periodically reset the resonance frequency (every 500 s). These time series were Fourier analyzed and averaged to produce a power spectrum. Power–law, \( 1/f^a \), spectra were observed. By inverting eqn. 2, \( S_c \) could be calculated from the measured noise. See fig. 2. We used \( G(\varepsilon) = 5 \) at low temperature decreasing monotonically to 2.7 at high temperature, estimated based on a parallel plate model. At temperatures above the glass transition, the noise power decreased and the spectrum flattened as expected based on the known behavior of \( \varepsilon \). A peak in the noise just below the glass transition is predicted, and is observed (see fig. 2 inset). Using our estimates for capacitance, and bulk values for \( \varepsilon \), eqn. 2 predicts a peak voltage noise at 0.015 Hz of \( S_c \approx 4 \times 10^{-3} \) V²/Hz. The measured \( S_c \) peaks at \( 1.5 \times 10^{-3} \) V²/Hz (inset), excellent agreement given the approximations involved.

In addition, explicit expressions for the noise in terms of bias voltage and resonance frequency can be derived, and were found to be consistent with the measurements \( a \). This resonance frequency noise is unrelated to the thermo–mechanical noise \( b \), which can be observed at the resonance frequency.

FIG. 3. Noise spectral exponents, measured between \( f = 0.01 – 0.08 \) Hz, vs. time for successive measurements at 296K are shown.

In order to study variations in the spectral dependence, the local spectral exponent, \( \gamma = -\partial \ln S/\partial \ln f \), was measured in the 0.01 – 0.08 Hz band for spectra averaged over 20 FFTs, and was studied as a function of time at various temperatures. The results of this analysis were quite revealing, as shown in figure 3. At 296K, \( \gamma \) showed anomalous variations between successive measurements, i.e. on a time scale of about \( 10^5 \) s. Similar but smaller anomalous variations were observed at 298K. Figure 4 shows variance of the spectral exponent vs. temperature. Well below and well above this range of temperature, at 292K and 303K respectively, \( \gamma \) exhibited little variation with time beyond the statistical variations found in Gaussian noise or in Monte–Carlo simulations of noise produced by random distributions of two–state exponential processes with fixed characteristic times, (shown as dashed line) \( c \). Also shown (inset) is the autocorrelation function for the spectral exponent at 296K. The characteristic decay time is \( 6 \times 10^4 \) s. By comparison, the measured relaxation time was \( 3 \times 10^4 \) s at 296K \( d \). Variations were also studied on a shorter observation time scale of about \( 2 \times 10^4 \) s, at several temperatures. For this shorter time scale, anomalously large variations occurred only at higher temperatures, 298K and 301K \( e \).

FIG. 4. Variance of spectral exponent (0.01 – 0.08 Hz) measured in a time window centered on \( 1 \times 10^5 \) s is shown vs. temperature. Also shown is a variance for simulation of fixed distribution of exponentials (dotted line). Inset: autocorrelation function for exponent at 296K.

The variations observed in the noise spectrum suggest a superposition of a small number of discrete components with slowly evolving kinetic parameters. Below \( T_G \), memory of the local kinetic parameters is lost on a characteristic time scale about twice the average relaxation time, consistent with NMR results \( f \) measured well above \( T_G \). The matching of the average relaxation time (at 296K) to the experimental observation time explains the peak in variance at 296K. This time–scale rapidly becomes very large on cooling, thus little variance is observed at 292K. Thus dynamical heterogeneity becomes relevant, a few degrees below \( T_G \), for those fluctuations which occur on time scales much shorter than the average. We found that we could produce similar anoma-
lous spectral exponent variations in the simulations of distributions of exponentials by randomizing the characteristic times $\tau$. The size of the variance matched the 296K value when the density of exponential processes is $N(\omega) = 7$. Using eqn. 1, we find $\xi = 10 \pm 4 \text{ nm}$ at this temperature, somewhat larger than conventional estimates.

In summary, we described a new method of probing equilibrium nanoscale glassy dynamics via electric polarization fluctuations. Anomalous temporal variations were observed in the noise spectral dependence below the glass transition in PVAc, a direct indication of cooperative nano–regions with heterogeneous but evolving kinetics. We determined the cooperative length scale, and showed that dynamical heterogeneity persists for times comparable to the average relaxation time, for faster than average processes. This kinetic evolution is qualitatively consistent with models in which the dynamics of neighboring nano–regions are highly coupled. Extending the measurement bandwidth, using FM techniques, will facilitate the use of noise statistics to analyze in greater detail, the local dynamics for comparison with various models and simulations.

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