

Local Polarization Fluctuations in an Aging Glass

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Polarization fluctuations were measured in nanoscale volumes of a polymer glass during aging following a temperature quench through the glass transition. Statistical properties of the noise were studied in equilibrium and during aging. The noise spectral density had a larger temporal variance during aging; i.e., the noise was more non-Gaussian, suggesting stronger correlations during aging.

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Recent work has deepened our understanding of glass transitions and glassy dynamics [1,2]. Yet a comprehensive theory remains elusive. Meanwhile, remarkable new glassy phenomena are being discovered. One of the most intriguing behaviors in glasses has been aging, which is characterized by slow relaxation of measured properties such as mechanical, magnetic, or dielectric response, following a temperature quench [3]. Scaling of the response curve versus time or frequency with the age of the system relative to the quench continues to be of interest [4]. Recently striking memory and rejuvenation effects have been found [3,5]. And the slow return to equilibrium during aging has made glass models ideal for studying nonequilibrium statistical mechanics, especially the development of a non-equilibrium fluctuation-dissipation relation (FDR) [6].

An equally important recent development has been the discovery that dynamics in structural glasses are spatially heterogeneous [2,7,8], with transient heterogeneities 1 to 3 nm in size [9]. In molecular dynamics simulations [10] and experiments on colloidal glasses [11], fast and slow regions were directly observed. More recently, local probes [8,12] have been useful for following the dynamics of individual heterogeneities or single probe molecules.

In a confluence of these recent developments, a recent Letter explored *local* aging dynamics, FDR violations, and heterogeneity in a Monte Carlo simulation of an Edwards-Anderson Ising spin glass model [13]. Local fluctuations, responses, and their ratio, which determines an effective temperature T_{eff} , were found to be spatially heterogeneous during aging. For the young regime, i.e., when the observation time $t - t_w$ was comparable to or longer than the waiting time following the quench, t_w , the $T_{\text{eff}} > T$, consistent with previous work. Most striking was that when sampled spatially the local correlation functions (fluctuations) were highly heterogeneous, with non-Gaussian distributions as compared to the narrowly distributed responses, or the near equilibrium fluctuations [14]. A recent macroscopic experiment suggests that aging in polymers is heterogeneous [15]. And in a recent theory of aging in structural glasses [16], Lubchenko and Wolynes predict spatially fluctuating fictive [17] temperatures in the middle stages of aging which can have non-Gaussian distributions. In this Letter we have used a local probe of

dielectric response to measure nonequilibrium fluctuations in a mesoscopic polymer glass during aging just below the glass transition. We find that the local fluctuations during aging are non-Gaussian. The noise measured as a function of time exhibits large modulations, which, however, decrease dramatically with waiting time. This indicates more strongly correlated dynamics during aging.

The samples studied were 0.5–1.0 μm thick poly-vinyl-acetate (PVAc) films with glass transition: $T_g = 308$ K. The films were prepared by spin coating from solution onto a substrate and dried [18] at 340 K for 20 minutes. The macroscopic aging behavior was studied by sandwiching the PVAc films between sputtered thin AuPd crossed electrodes to form a capacitor. Using a Novocontrol based dielectrometer the dielectric susceptibility was measured as a function of frequency, f , and waiting time, t_f following a rapid temperature quench. See Fig. 1. Aging continues to much larger values of $f t_w$ as compared with spin glasses. For example, at 302 K, measuring the complex susceptibility at 1 Hz, the aging continues well beyond 20 hours.

By sensing local electrostatic forces, noncontact atomic force microscopy (AFM) techniques can be used to measure local dielectric properties [18]. In the present experiment, we employed a noise measurement scheme [8] (see

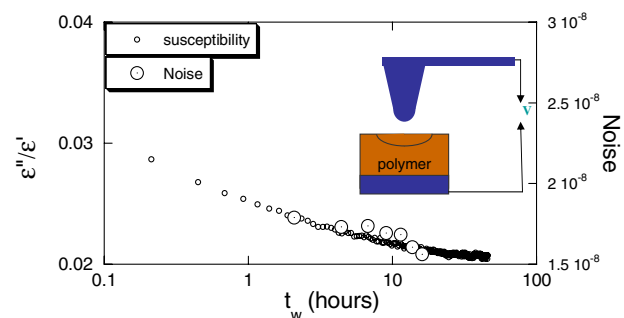


FIG. 1 (color online). The dielectric susceptibility (ratio of imaginary to real components) measured at 1 Hz in a macroscopic sample is plotted vs waiting time following a temperature quench from 315 K to 302 K. The polarization noise measured during aging in a nanoscopic sample in a band centered on 1.4 Hz at 302 K is also shown. Inset: noise measurement setup showing SPM tip, sample, and probed volume.

Fig. 1 inset), which utilized a small cantilever with a sharp (40 nm radius) conductive tip, mounted in a temperature controlled can within a vacuum chamber. The cantilever is driven at its resonance frequency (~ 200 kHz) via a piezoelectric slab and a self-driven oscillator circuit. When a voltage bias is applied between tip and substrate, fluctuations in the sample polarization beneath the tip produce proportional variations in the cantilever resonance frequency, which are detected using frequency modulation techniques. For small tip heights, z , above the sample surface, the resonance frequency is most sensitive to a small region directly beneath the tip. For $z = 30$ nm and bias = 4 V, the effective probed volume: $\Omega \sim 2 \times 10^{-17}$ cm³, and depth: 40 nm. This volume contains of order 10^3 heterogeneities, 3 nm in diameter.

With tip height fixed using feedback to reset the resonance frequency between each set of data points (65 s), time series of PVAc polarization fluctuations were recorded at various temperatures just below T_g , and as a function of waiting time, t_w , following a temperature quench from 315 K. From each time series begun at waiting time t_w the power spectra $S(f, t_w)$, for $f = 0.015$ Hz to 15 Hz, were obtained. The decrease of the noise power with aging is comparable to that of the susceptibility as shown in Fig. 1. To study fluctuations in the power spectra, the local spectral exponent, $\alpha = -d \ln(S)/d \ln(f)$, was measured over typically a decade in frequency in averages of 4 spectra. Then the variations in α were measured as a

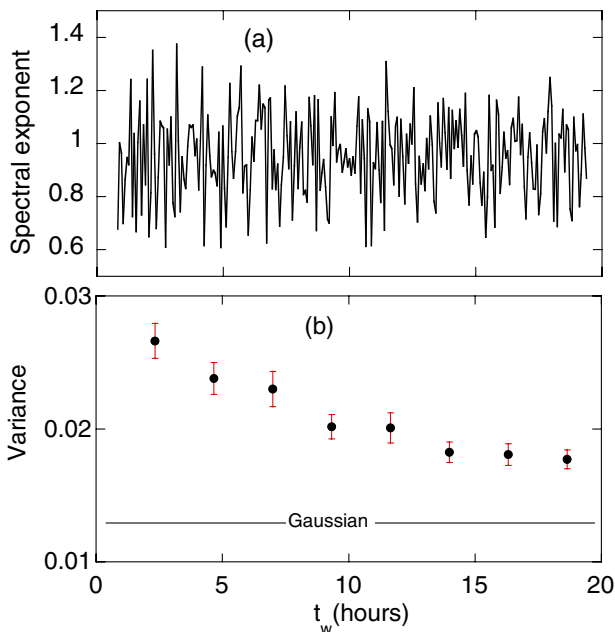


FIG. 2 (color online). The spectral exponent, measured by a power-law fit between 0.1 Hz and 1 Hz, is plotted (a) vs waiting time following a quench to 302 K. In (b) the variance of spectral exponent measured over 2.3 h windows and averaged over 12 quenches is plotted vs waiting time for 302 K. The prediction for Gaussian noise is shown.

function of waiting time t_w , and analyzed similarly to previous experiments, which investigated equilibrium dynamics [8]. This technique measures changes in the shape of the noise spectrum with time and is less sensitive to extrinsic sources of variation in the noise magnitude such as drifts in tip height or feedback effects. Simulated Gaussian noise spectra, and spectra from a Monte Carlo simulation (discussed below) were analyzed in the same way for comparison.

In Fig. 2(a) we show α versus t_w at 302 K. Each α was measured over 0.1 Hz to 1 Hz in a spectrum averaged for 4.3 minutes. Large variations in α occur, particularly at the earlier t_w . The variance was typically double the Gaussian expectation. The temporal variance of α , $\sigma^2(\alpha)$, was measured for 0.1 Hz to 1 Hz over intervals of $\Delta t_w = 2.3$ h, and was averaged over 12 quenches [Fig. 2(b)]. Note that the small systematic change of α with aging makes a negligible contribution to the variance. The non-Gaussian portion of the variance, σ_N^2 , obtained by subtracting the Gaussian variance, is plotted (Fig. 4) versus t_w for several temperatures. The variance clearly decreases t_w with waiting time for all temperatures. The decay of variance occurs on t_w scales similar to the decay of susceptibility. The non-Gaussian variance appears to reach a steady value, still in excess of Gaussian, in equilibrium, which decreases with increasing temperature.

How do these non-Gaussian variations in the noise arise? First, we consider a simple heterogeneous model in which the noise in equilibrium is produced by a superposition of Lorentzians, corresponding to Debye peaks in the dielectric susceptibility, whose characteristic frequencies are randomized on a time scale corresponding to the heterogeneity lifetime, τ_{het} . A Monte Carlo simulation of this model gives fluctuations in α , whose variance is inversely proportional to the mean density of Lorentzians per unit logarithm of bandwidth, n_e . For $1/f$ noise this number is

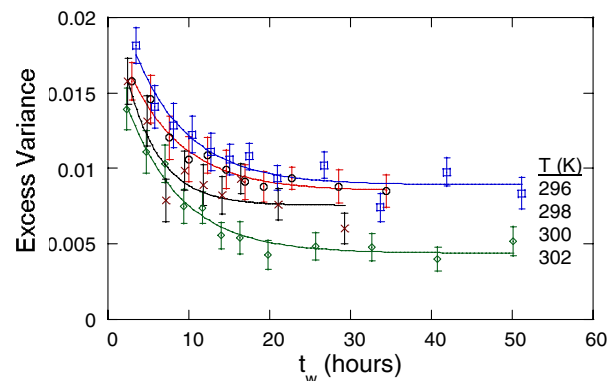


FIG. 3 (color online). The excess (above Gaussian) variance in spectral exponent (0.1 Hz–1 Hz) is plotted vs waiting time for several temperatures (indicated). For waiting times < 20 h the data are averaged over 2.3 h windows and 10 to 20 quenches. After 20 h the variances from several adjacent 2.3 h windows are averaged for 3 to 5 quenches.

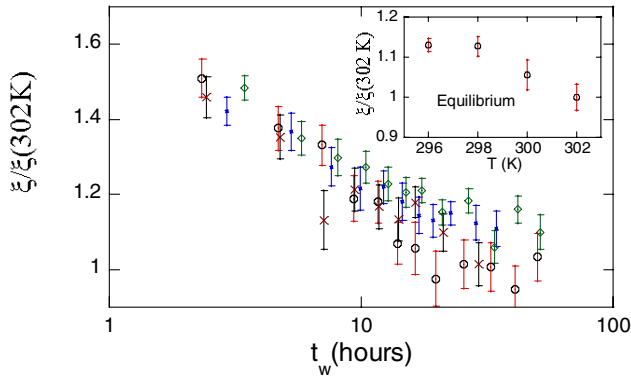


FIG. 4 (color online). Nonequilibrium dynamical correlation length vs waiting time, derived from Eq. (1), and normalized to the equilibrium value at 302 K. Symbols: circles: 302 K, crosses: 300 K, dots: 298 K, diamonds: 296 K. Inset: the equilibrium correlation length grows weakly with decreasing temperature.

independent of frequency. In Fig. 3, the equilibrium σ_N^2 clearly decreases with increasing temperature. When compared with the simulation, this corresponds to an n_e which grows with temperature. This is consistent with the fact that the α peak in the distribution of rates moves to higher frequencies with increasing temperature, increasing the number of heterogeneities active in the measurement band.

We can try to extend this simple heterogeneous model, together with the notion of fictive temperature [17] to the aging regime. Initially after a temperature quench, the distribution of rates, as measured in $\varepsilon''(\omega)$, is similar to that of a higher temperature, i.e., a fictive temperature. Thus we might expect the $\sigma_N^2(t_w)$ to be initially smaller, then *rise* toward the equilibrium value. Instead the opposite occurs. The variations during aging are then not consistent with a smoothly decreasing Lorentzian density. It would seem that the noise during aging is determined by fewer independent noise sources. How can this occur? As found in the aging structural glass model [16], the effective temperatures during early aging were very heterogeneous. The regions with higher effective temperatures would be noisier, perhaps dominating the spectrum and reducing the effective number of noise sources. However, in a simple activated two-level-system model with a broad distribution of energies, heterogeneous effective (or fictive) temperatures always *increase* the effective number of noise sources. Very non-Gaussian distributions of fictive temperatures could help, though this was predicted for deep quenches [16]. The spin glass simulations [13], exhibited broadened, non-Gaussian correlations during extremely early aging, which could conceivably give larger noise temporal variance, but would need to extend to the quasi-stationary aging regime observed here in structural glasses. Alternatively, the usual picture of aging involves traversal of large barriers in the energy landscape. These rare traversals could produce correlated bursts of noise, or freeze the activity in several nearby cooperative regions. In other

words the noise during aging may be more correlated, with correlations decreasing with waiting time.

Within the context of an independent fluctuator model, dynamics are correlated over a length scale corresponding to a cooperatively-rearranging-region (CRR) of characteristic size ξ . The Lorentzian density may be expected to scale [8] as $n_e = \varepsilon''\Omega/\varepsilon'(0)\xi^3$, while the excess variance, σ_N^2 , scales as n_e^{-1} . Since $\varepsilon'(0)$ changes very weakly with temperature and waiting time, we can deduce how an effective dynamical correlation length scales with temperature and waiting time:

$$\xi \approx [\sigma_N^2 \varepsilon'']^{1/3}. \quad (1)$$

In equilibrium (Fig. 4 inset), the correlation length decreases weakly with increasing temperature, consistent with some models [19]. During aging, as shown in Fig. 4, the correlation length decreases similarly with waiting time for all temperatures, and is 50% larger than the equilibrium value at early t_w . This strongly suggests that aging in structural glasses proceeds by events which occur over larger length scales than in equilibrium. In an aging colloidal glass experiment, the CRR length scale was found to remain roughly constant during aging, though it was expected to increase along with relaxation time [20].

In summary, we find a new mesoscopic scale signature of aging in a structural glass. Specifically, fluctuations exhibit a larger temporal variance in a mesoscopic sample during aging than in equilibrium. This can be understood, most simply, as stronger correlation between fluctuations in neighboring regions, i.e., a longer dynamical correlation length. Whether this can be explained in terms of a broadened or non-Gaussian distribution of correlation functions or fictive temperatures is an open question.

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