# Nanometer Scale Dielectric Fluctuations at the Glass Transition

E. Vidal Russell, N. E. Israeloff, L. E. Walther, and H. Alvarez Gomariz
*Department of Physics and Center for Interdisciplinary Research on Complex Systems, Northeastern University, Boston, Massachusetts 02115*

(Received 16 March 1998)

Using noncontact scanning probe microscopy techniques, dielectric properties were studied on 50 nm length scales in polyvinyl-acetate films in the vicinity of the glass transition. Low frequency $(1/f)$ noise observed in the measurements was shown to arise from thermal fluctuations of the electric polarization. Anomalous variations observed in the noise spectrum provide direct evidence for cooperative nanoregions with heterogeneous kinetics. The cooperative length scale was determined. Heterogeneity was long lived only well below the glass transition for faster than average processes. [S0031-9007(98)06831-8]

PACS numbers: 64.70.Pf, 73.61.Jc, 77.55.+f

Glasses serve as the prototype for the kind of slow, nonexponential relaxation found in diverse systems from magnets and superconductors to proteins and granular assemblies. Although much has been learned about glassy phenomena [1], a detailed picture of the underlying dynamical processes remains elusive. Cooperative dynamics on nanometer scales has long been postulated [2,3], but never been directly observed. A key question, with broad implications, is whether nonexponential dynamics arises primarily from a heterogeneous collection of independent nanoscale exponential processes [2,3] or more complex local dynamics [4]. Recently, molecular dynamics simulations revealed the presence near the glass transition of long-lived clusters surrounded by liquid [5]. These mesoscopic scale clusters exhibited a power-law size distribution. Some macroscopic experiments have inferred that very long-lived nanoscale structural [6] and dynamical [7] heterogeneities develop near the glass transition, while others find very short-lived dynamical heterogeneity [8]. Such heterogeneities and their evolution may play a key role in dynamical scaling behavior [9], and possible dynamical [10] or phase [11] transitions, and have implications for protein dynamics [12].

Since the invention of the atomic force microscope in 1986 [13], a number of related, powerful, scanning probe microscopy (SPM) techniques have been developed. By sensing local electrostatic forces, noncontact SPM techniques can be used to measure variations in local dielectric constants [14]. In this paper, we describe investigations of dynamics on 50 nm length scales in polyvinyl-acetate (PVAc) films near the glass transition, $T_G \sim 306$ K, via measurements of dielectric properties using an ultrahigh vacuum, variable temperature SPM. We observed low-frequency "$1/f$" fluctuations, which are shown to arise from thermal polarization noise, and can be used to study the equilibrium nanoscale dynamics. Anomalous temporal variations in the spectral dependence of the noise were found. The variations were used to determine cooperative length scales and related to the time evolution of dynamical heterogeneity.

If a mesoscopic volume of a structural glass could be probed, deviations from macroscopic response might be observed in, for example, the frequency-dependent dielectric susceptibility, $\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, or similar response or correlation (e.g., noise) functions. In the simplest picture [2], independent nanoregions of cooperativity of typical size $\xi$ [1–3,5–7] relax exponentially (Debye-like response), but have a distribution of characteristic relaxation times $\tau$. Estimates for $\xi$ based on measurements [7] and theory [2] have been in the range 2–5 nm for various glass formers at $T_G$. Far from the $\alpha$ peak in $\varepsilon''$, only those nanoregions with $\tau \sim 1/\omega$ will contribute significantly to $\varepsilon''(\omega, T)$. By using the Kramers-Kronig relations, it is easily shown that $\xi$ can be related to the number of nanoregions, $N(\omega)$, which contributes near $\omega$ within a band $\Delta\omega \sim \omega$ in width (i.e., factor of $e$) in a sample of volume $\Omega$ via

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

When $N(\omega)$ is of order 10 [15], deviations from bulklike behavior will be clearly observable, for example, anomalous variations in $\varepsilon''$ (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 $\Omega \sim 10\xi^3\varepsilon'(0, T)/\varepsilon''(\omega, T)$. For $\varepsilon'' \sim 0.1$ below $T_G$, we estimate $\Omega \sim 1 \times 10^{-16}$ cm$^3$ for PVAc, e.g., a cube of about 50 nm on a side. If nanoregions are not independent [4] or undergo intermittent or evolving dynamics [12,15], 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 [15,16]. 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 [15]. 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. However, extending noise measurements to the mesoscopic scale in dielectrics, as was done in conductors, has not been possible with these techniques [17], due to overwhelming technical limitations.

In the present experiments, we employed a noncontact capacitance measurement scheme [14] using a thermal drift compensated, ultrahigh vacuum, variable temperature SPM [18]. A small piezoresistive 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 the tip and the substrate (see Fig. 1 inset), the resonance frequency $f$ of the antilever 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.

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 $\varepsilon = 4$, 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 (~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 [20].

In earlier studies of PVAc, we showed that dielectric relaxation could be studied using the SPM resonance frequency shift [18]. Nearly bulklike 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 [21] (see Fig. 1). PMMA (polymethylmethacrylate) 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.

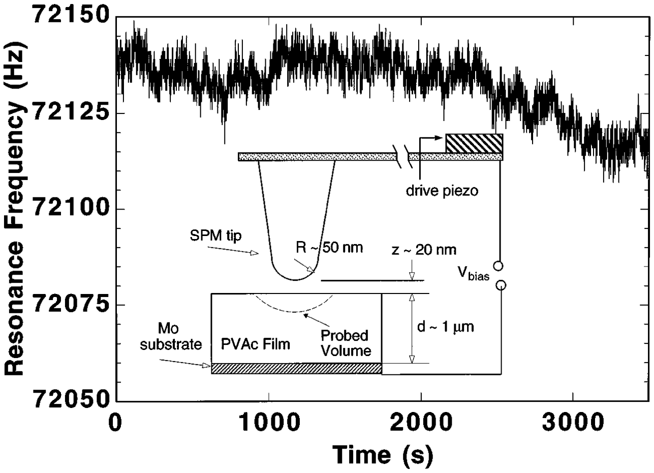

FIG. 1. Resonance frequency vs time after equilibration with 4 V bias, tip height 20 nm, at 305 K is shown. Inset: cantilever and tip measurement configuration.

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 $S_e$ 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 $S_e$ 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 $\sim S_e$ added to the constant voltage bias, and the resonance frequency will fluctuate. The spectral density of the thermal resonance frequency noise will be approximately

$$S_f = \left(\frac{\partial f}{\partial V}\right)^2 G(\varepsilon) S_e = \left(\frac{\partial f}{\partial V}\right)^2 G(\varepsilon)\, \frac{4 k_B T \varepsilon''}{|C|^2 \omega}, \qquad (2)$$

where $\partial f/\partial V$ 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 [21].

Long time series of the resonance frequency were recorded with fixed conditions ($V = 8$ V), using feedback to periodically reset the resonance frequency (every 500 s). These time series were Fourier analyzed to produce a power spectrum. Power-law $1/f^\alpha$ spectra were observed. By inverting Eq. (2), $S_e$ could be calculated from the measured noise (see Fig. 2). We used $G(\varepsilon) = 5.0$ 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 $\varepsilon$ [17]. 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 $\varepsilon$

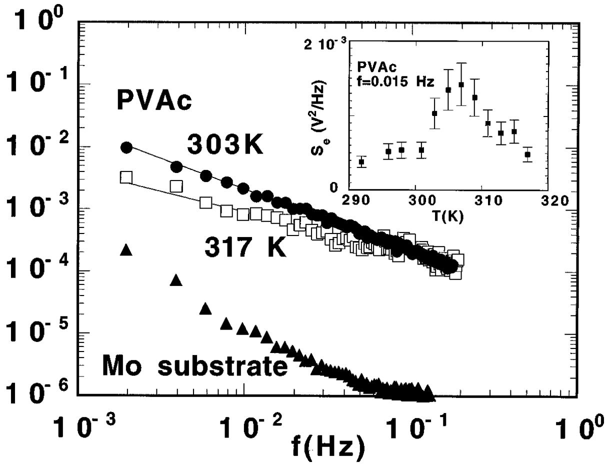

FIG. 2. Voltage noise spectra extracted from SPM resonance frequency fluctuations via Eq. (2) are shown for $T = 303$ and 317 K in PVAc and for bare Mo substrate at 303 K. Inset: Temperature dependence of voltage noise at $f = 0.015$ Hz vs temperature for PVAc is shown.

[22,23], Eq. (2) predicts a peak voltage noise at 0.015 Hz of $S_e \sim 4 \times 10^{-3}$ V$^2$/Hz. The measured $S_e$ peaks at $1.5 \times 10^{-3}$ V$^2$/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 [21]. The resonance frequency noise is unrelated to thermomechanical noise [19], which can be observed at the resonance frequency.

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 averages of 20 spectra and was studied as a function of time at various temperatures. The results of this analysis were quite revealing, as shown in Fig. 3. At 296 K, $\gamma$ 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 298 K. Figure 4 shows variance of the spectral exponent vs temperature. Well below and well above this range of temperature, at 292 and 303 K, 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) [21]. Also shown (inset) is the autocorrelation function for the spectral exponent at 296 K. The characteristic decay time is $6 \times 10^4$ s. By comparison, the measured relaxation time was $3 \times 10^4$ s at 296 K [18]. 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, 298 and 301 K [21].

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 [8] measured well above $T_G$ in this material. The matching of the average relaxation time (at 296 K) to the experimental observation time explains the peak in variance at 296 K. This time scale rapidly becomes very large on cooling; thus little variance is observed at 292 K. 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 anomalous spectral exponent variations in the simulations of distributions of exponentials by randomizing the characteristic times [21]. The size of the variance matched the 296 K value when the density of exponential processes was $N(\omega) = 7$. Using Eq. (1), we find $\xi = 10 \pm 4$ nm at this temperature, somewhat larger than conventional estimates [7].

In summary, we described a new method of probing equilibrium nanoscale glassy dynamics via electric

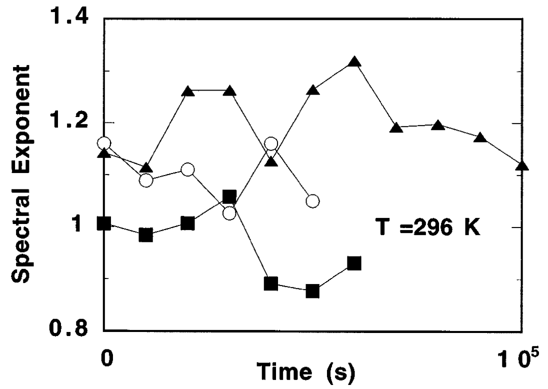

FIG. 3. Noise spectral exponents, measured between $f = 0.01 - 0.08$ Hz vs time for successive measurements at 296 K are shown.

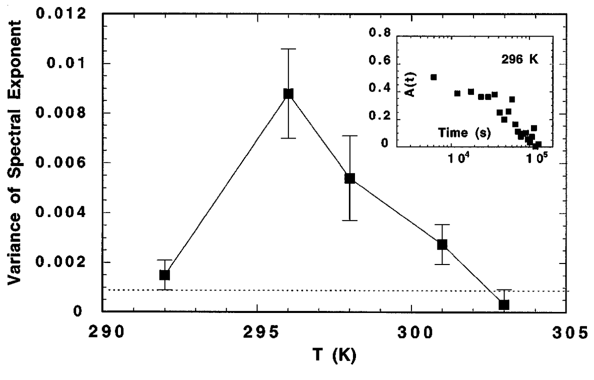

FIG. 4. Variance of spectral exponent (0.1–0.08 Hz) measured in a time window centered on $1 \times 10^5$ s is shown vs temperature. Also shown is variance for simulation of fixed distribution of exponentials (dotted line). Inset: autocorrelation function for exponent at 296 K.

polarization fluctuations. Anomalous temporal variations were observed in the noise spectral dependence below the glass transition in PVAc, a direct indication of cooperative nanoregions 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 nanoregions are highly coupled [4]. Extending the measurement bandwidth, using frequency modulation techniques [24], will facilitate the use of noise statistics to analyze in greater detail the local dynamics for comparison with various models and simulations.

We thank S. R. Nagel, Harvey Gould, W. Klein, B. Chakraborty, and D. Braunstein for helpful discussions, and M. Tortonese and Park Scientific for the piezolevers. This work was supported by NSF Grant No. DMR 9458008.

[1] See the recent reviews: M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13 200 (1996); C. A. Angell, Science **267**, 1924 (1995), and following articles in this issue.

[2] G. Adam and J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965).

[3] E. Donth, J. Non-Cryst. Solids **53**, 325 (1982); J. P. Sethna, J. D. Shore, and Ming Huang, Phys. Rev. B **44**, 4943 (1993); S. A. Kivelson, X. Zhao, D. Kivelson, T. M. Fischer, and C. M. Knobler, J. Chem. Phys. **101**, 2391 (1994).

[4] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984); M. F. Shlesinger and E. W. Montroll, Proc. Natl. Acad. Sci. U.S.A. **81**, 1280 (1984); K. L. Ngai, R. W. Rendell, and D. J. Plazek, J. Chem. Phys. **94**, 3018 (1991).

[5] Andrew I. Mel'cuk, Raphael A. Ramos, Harvey Gould, W. Klein, and Raymond D. Mountain, Phys. Rev. Lett. **75**, 2522 (1995); W. Kob, C. Donati, S. J. Plimpton, P. H. Poole, and S. C. Glotzer, Phys. Rev. Lett. **79**, 2827 (1997).

[6] C. T. Moynihan and J. Schroeder, J. Non-Cryst. Solids **160**, 52 (1993).

[7] K. Schmidt-Rohr and H. Spiess, Phys. Rev. Lett. **66**, 3020 (1991); Marcus T. Cicerone and M. D. Ediger, J. Chem. Phys. **103**, 5684 (1995); **104**, 7210 (1996); Inyong Chang and Hans Sillescu, J. Phys. Chem. **101**, 8794 (1997).

[8] A. Heuer, M. Wilhelm, H. Zimmermann, and H. W. Spiess, Phys. Rev. Lett. **75**, 2851 (1995); B. Schiener, R. Bohmer, A. Loidl, and R. V. Chamberlin, Science **274**, 752 (1996).

[9] P. K. Dixon *et al.,* Phys. Rev. Lett. **65**, 1108 (1990); D. L. Leslie-Pelecky and N. O. Birge, Phys. Rev. Lett. **72**, 1232 (1994).

[10] W. Gotze and L. Sjogren, Rep. Prog. Phys. **55**, 241 (1992); W. van Megen and S. M. Underwood, Phys. Rev. Lett. **70**, 2766 (1993); W. Kob and H. C. Anderson, Phys. Rev. Lett. **73**, 1376 (1994); H. Teichler, Phys. Rev. Lett. **76**, 62 (1996).

[11] Narayanan Menon and Sidney R. Nagel, Phys. Rev. Lett. **74**, 1230 (1995).

[12] Jim Wang and Peter Wolynes, Phys. Rev. Lett. **74**, 4317 (1995); I. E. T. Iben *et al.,* Phys. Rev. Lett. **62**, 1916 (1989).

[13] G. Binnig, C. F. Quate, and Ch. Gerber, Phys. Rev. Lett. **56**, 930 (1986).

[14] Y. Martin, C. C. Williams, and H. K. Wickramasinghe, J. Appl. Phys. **61**, 4723 (1987); Y. Martin, D. W. Abraham, and H. K. Wickramasinghe, Appl. Phys. Lett. **52**, 1103 (1988).

[15] G. A. Garfunkel, G. B. Alers, M. B. Weissman, and N. E. Israeloff, Phys. Rev. B **40** (RC), 8049 (1989); M. B. Weissman, Rev. Mod. Phys. **60**, 537 (1988); N. E. Israeloff, G. B. Alers, and M. B. Weissman, Phys. Rev. B **44**, 12 613 (1991).

[16] D. C. Ralph and R. A. Burman, Phys. Rev. Lett. **72**, 3401 (1994); Kookjin Chun and Norman O. Birge, Phys. Rev. B **48**, 11 600 (1993); Neil M. Zimmermann, Brage Golding, and William H. Haemmerle, Phys. Rev. Lett. **67**, 1322 (1992).

[17] N. E. Israeloff, Phys. Rev. B **53**, R11 913 (1996); N. E. Israeloff and W. Wang, Rev. Sci. Instrum. **68**, 1543 (1997); N. E. Israeloff, in *Glasses and Glass Formers: Current Issues*, edited by K. L. Ngai, MRS Symposia Proceedings (Materials Research Society, Pittsburgh, 1997).

[18] L. E. Walther, N. E. Israeloff, E. Vidal Russell, and H. Alverez Gomariz, Phys. Rev. B **57**, R15 112 (1998).

[19] Park Scientific Piezolevers; see, e.g., F. J. Giessibl and B. M. Trafas, Rev. Sci. Instrum. **65**, 1923 (1994); M. Tortonese, Ph.D. thesis, Stanford University, 1993.

[20] See, e.g., J. Schuller, Yu. B. Mel'nichenko, R. Richert, and E. W. Fischer, Phys. Rev. Lett. **73**, 2224 (1994).

[21] L. E. Walther, N. E. Israeloff, E. Vidal Russell, and H. Alvarez Gomariz, Appl. Phys. Lett. **72**, 3223 (1998); (to be published).

[22] P. Tormala, J. Macromol. Sci. Rev. Macromol. Chem **C17**, 297 (1979).

[23] N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Dover, New York, 1991).

[24] T. R. Albrecht, P. Grütter, D. Horne, and D. Rugar, J. Appl. Phys. **69**, 668 (1991).