Nanoscale non-equilibrium dynamics and the fluctuation–dissipation relation in an ageing polymer glass

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Response functions¹ and fluctuations² measured locally in complex materials should equally well characterize mesoscopic-scale dynamics. The fluctuation–dissipation relation (FDR) relates the two in equilibrium, a fact used regularly, for example, to infer mechanical properties of soft matter from the fluctuations in light scattering³. In slowly evolving non-equilibrium systems, such as ageing spin^{4,5} and structural glasses^{6,7}, sheared soft matter⁸ and active matter⁹, a form of FDR has been proposed in which an effective temperature¹⁰, T_{eff} , replaces the usual temperature, and universal behaviour is found in mean-field models^{10,11} and simulations^{6–8,12}. Thus far, only experiments on spin-glasses¹³ and liquid crystals¹⁴ have succeeded in accessing the strong-ageing regime, where $T_{\text{eff}} > T$ and possible scaling behaviour are expected. Here we test these ideas through measurements of local dielectric response and polarization noise in an ageing structural glass, polyvinyl acetate. The relaxation-time spectrum, as measured by noise, is compressed, and by response, is stretched, relative to equilibrium, requiring an effective temperature with a scaling behaviour similar to that of certain mean-field spin-glass models.

The FDR expresses the equilibrium thermal fluctuations of an observable, O , in terms of available thermal energy, $k_B T$ (where k_B is the Boltzmann constant), and the linear response of that observable to an applied field, F (ref. 10). It also relates the time (t) dependence of the fluctuations, found in the autocorrelation function, $C(t) = \langle \delta O(t' + t) \delta O(t') \rangle_{t'}$, and the time-dependent susceptibility, $\chi(t) = O(t)/F$, where F is applied at $t = 0$. In equilibrium, $C(t)$ should contain the same information about the dynamics that is found in $\chi(t)$, such as the spectrum of relaxation times. This is seen clearly in plotting $\chi(t)$ versus $C(t)$ and obtaining a straight line, with a negative slope inversely proportional to temperature¹⁰. Deviations from the FDR have been intensively studied theoretically in ageing or driven glassy systems, both on the macroscale^{8,10} and nanoscale¹². Ageing occurs in glassy materials that have been quenched from high to low temperature. During ageing, the response functions depend both on time, t , and on the age of the system since the quench, t_w . However, $\chi(t, t_w)$ and $C(t, t_w)$ need not have the same dependence. This can be understood conceptually by viewing ageing dynamics as hopping on a tilted energy landscape¹¹: energy-lowering transitions cause more rapid decorrelation than is possible by thermal energy alone. Prominent glass-transition models¹⁵ place fragile structural glasses^{6,16} in the same universality class as mean-field p -spin models with single-step replica symmetry breaking¹⁷. In such models¹⁰ and simulations of structural glasses⁷, the $\chi(t, t_w)$ versus $C(t, t_w)$ asymptotically collapse (with increasing t_w) to a single scaling

function $\chi(C)$. $\chi(C)$ has two distinct linear regions, one agreeing with the FDR for short times, $t - t_w < t_w$, then abruptly bending to a second shallower line in the strong-ageing regime, when $t - t_w > t_w$. This second linear regime has a slope reduced by a violation factor, X , relative to equilibrium, and is described as having an effective temperature, $T_{\text{eff}} = T/X$.

Thus far, experiments studying the breakdown of the FDR in structural and soft colloidal glasses have focused on the quasi-equilibrium regime with $t_w > t - t_w$, and have given a range of results that have found strong^{18–20}, weak²¹ or non-existent²² FDR violations. The strong-ageing regime has been difficult to access in these systems, owing largely to instrumental and statistical challenges of measuring thermal noise at the very low frequencies required. Here, using electric force microscopy (EFM) techniques^{23,24}, we probe long-lived nanoscale polarization fluctuations and dielectric responses in polyvinyl acetate (PVAc) films, just below the glass-transition temperature, T_g (304 K), through a.c. detection of local electrostatic forces. This approach allows the probing of much smaller volumes than conventional dielectric spectroscopy. Such volumes produce large polarization fluctuations that can be detected above instrumental background down to very low frequencies. By scanning, we can study, in effect, many samples in parallel, which improves measurement statistics. The time-dependent polarization signal, $V_p(t)$, is measured (see the Methods section) to observe spontaneous noise, δV_p , or after application of a tip bias, $V_{\text{d.c.}}$, to produce an experimental susceptibility signal $\Delta\chi_{\text{ex}}(t) = \Delta V_p(t)/V_{\text{d.c.}}$.

In probing nanometre-scale regions, thermal fluctuations can be seen readily in the polarization as measured locally by $V_p(t)$ (refs 23, 24). The noise can also be used to produce spatiotemporal images of the dynamics^{23,24}. In this approach, V_p is repeatedly measured along a one-dimensional spatial line (see Fig. 1). These space-time images of the surface polarization are striking, in that they clearly show the spatio-temporal aspects of glassy dynamics; for example, the correlations seen along the time axis are distinctly longer at the lower temperatures. The autocorrelation function $C(t) = \langle V_p(t) V_p(t + t') \rangle$ should relate to the glassy part of the susceptibility, $\Delta\chi_{\text{ex}}(t)$, and should obey^{23,24} an FDR of the form:

$$\Delta\chi_{\text{ex}}(t) = \frac{c_{\text{eff}}}{k_B T} [C(0) - C(t)] \quad (1)$$

where c_{eff} is an effective tip capacitance. c_{eff} was calculated from a sphere-plane image charge model of tip capacitance for the experiment to be $6.3 \pm 1.8 \times 10^{-18}$ F. By plotting $\Delta\chi_{\text{ex}}(t)$ versus $C(t)$, equation (1) was verified for several temperatures near T_g in equilibrium. The slopes of the lines were nearly identical, and

Figure 1 | Spatio-temporal images of thermal fluctuations measured on a single spatial dimension in equilibrium. The grey scale indicates the sample polarization. **a,b**, Image recorded at 301.5 K (**a**), showing long-lasting correlations relative to the image at 305.5 K (**b**). Inset: Measurement set-up showing an EFM cantilever with a conducting tip, biased with a sinusoidal voltage, above a dielectric polymer sample coated on a conducting electrode.

required $c_{\text{eff}} = 8.45 \pm 1 \times 10^{-18}$ F to produce correct temperatures, a reasonable agreement given the simplification of the tip geometry.

Four micrometre spatiotemporal images such as those in Fig. 1 were used to determine spatially averaged $C(t)$ and $\Delta\chi_{\text{ex}}(t)$. The instrumental resolution set by the tip radius, tip height, scan speed and filter settings used produced noise that was spatially correlated over 120 nm. Thus, in these scans, 32 independent regions were measured in parallel, and several images were averaged. For $C(t)$, scans with $V_{\text{d.c.}} = \text{constant}$ (near 0) were used. Right and left 2 s/line scans were averaged to give a 0.25 Hz sampling rate. In Fig. 2a, normalized $C(t)$ and $\Delta\chi_{\text{ex}}(t)$ are shown for equilibrium at 303.5 K ($\sim T_g$). The shapes of the two curves are nearly identical and they are fitted by stretched-exponential or Kohlrausch–Williams–Watts (KWW) functions $C(t) = C(0) \exp[-(t/\tau)^\beta]$ and $\Delta\chi_{\text{ex}}(t) = \Delta\chi_{\text{ex}}(\infty) \{1 - \exp[-(t/\tau)^\beta]\}$, where τ is the alpha-relaxation time and β is a stretching exponent. For equilibrium, identical KWW parameters can be used, in this case $\beta = 0.53$ and $\tau = 75$ s, which confirms the FDR is satisfied. The technique produces a slightly reduced β relative to bulk values²⁵.

For ageing experiments, the samples were heated to well above T_g to 324 K, held for 1 min, cooled and stabilized at a final temperature, T_F , with a cooling rate of 5 K min⁻¹ through T_g (see the temperature profile in Fig. 2b). For $T_F = 302$ K, where the equilibrium $\tau \sim 150$ s, there were no observable FDR violations. The data and analysis shown here are for $T_F = 298$ K, where $\tau \sim 2,500$ s. The start of ageing, $t_w = 0$, was defined as the dynamic T_g (~ 304 K) crossing.

Figure 2 | Response and correlation functions. a,b, Normalized local dielectric response (χ) and correlation (C) functions measured in equilibrium (**a**) and during ageing (**b**), all with stretched-exponential (KWW) fits. Equilibrium χ and C curves are fitted with identical KWW parameters: $\tau = 75$ s and $\beta = 0.53$. The ageing curves in **b** require different stretching exponents. For χ , $\beta = 0.40 \pm 0.04$, and for C , $\beta = 0.65 \pm 0.04$, and both require $\tau = 385$ s. Inset: Temperature quench profile with T_g indicated as the start of ageing.

Topographic images showed that thermal drift of the tip position was significant up to $t_w \sim 3$ min. Thereafter, spatiotemporal images were collected, and the small drift contribution to C at early t_w could be determined and subtracted. Ten or more quenches were used for each correlation measurement (> 320 samples) and six or more (> 192 samples) for relaxation. For relaxation, $V_{\text{d.c.}} = 0.2$ V was applied at t_w to give $\Delta\chi_{\text{ex}}(t, t_w)$. Data points at t_w and t were pair-wise correlated to calculate $C(t, t_w)$, but to improve statistics, $C(t, t_w)$ was averaged over 1-min-wide windows of time centred on t_w and t .

In Fig. 2b, normalized correlation and relaxation curves are shown for ageing with $t_w = 3$ min. The shapes of the two curves are now very different, with $\Delta\chi_{\text{ex}}(t, t_w)$ more stretched compared with $C(t, t_w)$. A single KWW is no longer an ideal fit, but can be used to fit reasonably well the intermediate to long times, with $\beta = 0.64 \pm 0.04$ for C and $\beta = 0.39 \pm 0.04$ for $\Delta\chi_{\text{ex}}$ with $\tau = 385$ s. Ageing of response in structural glasses for shallow quenches can be understood as a slow evolution from higher (fictive) temperature dynamics to the lower temperature equilibrium dynamics, modelled as an evolving relaxation rate ($1/\tau$) (ref. 26) that stretches out the dynamics and gives a reduced β . More surprising is that the correlation function has an increased β , indicating a compressed spectrum of relaxation rates.

Given the different stretching parameter, β , for χ and C during ageing, the FDR clearly can no longer hold. In Fig. 3a, a plot of $\Delta\chi_{\text{ex}}(t, t_w)$ versus $C(t, t_w)$ for various t_w and equilibrium is

Figure 3 | Susceptibility versus correlation for ageing and equilibrium.

a, Normalized $\chi(t, t_w)$ plotted versus normalized $C(t, t_w)$ for various waiting times after the quench. Equilibrium data for 303 K are also plotted along with their linear fit. **b**, FDR violation factor, X , of all ageing data in **a** joined and treated as a single universal curve, plotted on a log-log plot versus C , and fit to a power-law.

shown. Whereas the equilibrium curve is linear, as predicted by equation (1), the ageing curves all show a distinct curvature, trending towards horizontal. This is indicative of a failure of the FDR at the smallest values of C , in the strong-ageing regime. Qualitatively, this behaviour is predicted by various mean-field models and simulations^{7,10,12}. Most striking is that there appears to be a near-collapse of all curves onto a global curve, $\chi(C)$. Such a collapse is achieved only in the asymptotic t_w limit in mean-field spin-glass models¹⁰ and with scaled axes in spin-glass experiments¹³. However in Lennard-Jones structural glass simulations, a similar collapse was found⁷. The local slope of the global $\chi(C)$ curve gives the violation factor: $X(C) = -d\chi(C)/dC$ (ref. 10). In simulations, p -spin models and spin-glass experiments, $X(C)$ is a discontinuous step-function with two distinct values: $X = 1$ for $t - t_w < t_w$ and $X < 1$ for $t - t_w > t_w$ (refs 6, 16). The class of models including the Sherrington–Kirkpatrick spin-glass model that show continuous replica symmetry breaking have a continuous $X(C)$ (refs 5, 17). In the present case, if we join all of the data of Fig. 3a, and treat them as a single function, $\chi(C)$, we can determine $X(C)$ from the local slope of this curve. In Fig. 3b, the calculated $X(C)$ is shown. This function appears to be continuous: a linear or power-law fit work equally well, with $R^2 = 0.80$. The power-law fit is shown, giving $X(C) \sim C^{0.57}$. A step function fits the data rather poorly, with $R^2 = 0.35$.

We have found that during ageing in a fragile structural glass, the spontaneous dynamics are very different from relaxation dynamics. The spectrum of relaxation times appears stretched in a relaxation experiment, and compressed in a fluctuation measurement, compared with the equilibrium spectrum, requiring a modified form of the FDR. The way in which the equilibrium FDR

is modified may tell us something about the way the glassy states are organized^{6,27} in equilibrium. A single effective temperature during ageing was not found, but the collapse of the data to $\chi(C)$, with an apparent continuous FDR violation factor, $X(C)$, are distinctive signatures, similar to a Sherrington–Kirkpatrick class of mean-field spin-glass models, and therefore provide guidance in finding a successful model of fragile structural glasses. With larger data sets, a fixed- t analysis could more accurately determine effective temperatures²⁸ and $X(C)$. Open questions include the temperature dependence of X for deep quenches, and how T_{eff} can be larger than the initial temperature of the system. The role of fragility should be explored, because in a fragile glass, dynamics slow markedly in a small range of temperature, requiring energy landscape changes much larger than $k_B T$.

Methods

A variation of scanning probe microscopy, EFM, is used, which involves oscillating a small silicon cantilever with a sharp metal-coated tip at its resonance frequency, f_0 , in ultrahigh vacuum. The EFM tip is held a distance $z = 18 \pm 5$ nm above a dielectric sample, and biased with voltage, V , relative to a conducting substrate on which the sample is coated (see Fig. 1, inset). The bias provides an electrostatic force between the tip and the sample surface, which shifts the cantilever resonance frequency by $\delta f(V)$, which is then measured. The tip electrostatic force can be calculated from the charging energy on the tip capacitance, $U = 1/2 C_{\text{tip}} V^2$ and $F = -dU/dz$. The bias-induced shift in the cantilever resonance frequency, $\delta f(V)$, can be obtained from the force gradient dF/dz , which supplies a fractional change in the cantilever spring constant, k . Sample polarization produces a surface potential and an image charge on the tip, both acting to produce an effective d.c. offset, V_p , to the applied bias. The electrostatic component of δf is therefore:

$$\delta f = \frac{1}{2} \frac{f_0}{k} \frac{\partial F}{\partial z} = -\frac{1}{4} \frac{f_0}{k} \frac{\partial^2 C_{\text{tip}}}{\partial z^2} (V - V_p)^2$$

As the signal is proportional to the force derivative on the sharp tip, it is most sensitive to sample polarization near the surface. For a conical tip with a typical 30 nm tip radius, a region of about 60 nm in diameter and 20 nm in depth below the surface is probed²⁵.

By applying a 200 Hz oscillating bias, $V_{\text{a.c.}} = V_0 \sin(\omega t)$, with $V_0 = 1$ V and using a lock-in amplifier to detect the oscillation in $\delta f \sim 2V_0 V_p \sin \omega t$, the polarization contribution to the tip–sample interaction can be isolated, and V_p can be determined. To study dielectric relaxation, a d.c. bias, $V_{\text{d.c.}} = 0.2$ V, is added as a step function to the a.c. bias, the resulting time-dependent response of $V_p(t)$ is measured and an experimental susceptibility is defined as $\Delta \chi_{\text{ex}}(t) = \Delta V_p(t)/V_{\text{d.c.}}$, where $\Delta V_p(t)$ is the slow portion of the response. Thus, $\Delta \chi_{\text{ex}}(t)$ is proportional to the glassy part of the dielectric susceptibility, $\Delta \chi(t)$. The samples studied here are PVAc, $M_w = 167,000$ (Sigma), which has a bulk glass transition of $T_g = 308$ K. Thin films (1 μm) of PVAc were prepared by dissolving the polymer in toluene and spinning the solution onto Au-coated glass substrates, drying in air and annealing for 24 h in high vacuum at T_g . Samples were mounted in an ultrahigh-vacuum SPM system (RHK SPM 350) for measurements on a chilled-water-cooled stage. Samples are radiatively heated from below and the temperature was measured with a small thermocouple clamped to the sample surface. Previously we showed that the near-surface T_g of PVAc is mildly suppressed by ~ 4 K (ref. 25), as we see in the present experiment.

For the FDR analysis, we use the standard method of plotting fixed- t_w curves. Although this has been shown²⁸ to underestimate T_{eff} , an attempt to use the more accurate fixed- t analysis²⁹ produces very poor-quality curves. Both methods produce the two-slope behaviour in Lennard-Jones glasses²⁸.

Received 3 August 2009; accepted 13 November 2009;
published online 20 December 2009

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Acknowledgements

We acknowledge the support of NSF grant DMR 00606090. We thank L. Cugliandolo for helpful discussions.

Author contributions

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Additional information

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