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Off equilibrium fluctuations in a polymer glass

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Abstract

The fluctuation–dissipation relation (FDR) is measured on the dielectric properties of a polymer glass (polycarbonate). It is observed that the fluctuation–dissipation theorem is strongly violated after a quench from above to below the glass transition temperature. The amplitude and the persistence time of this violation are decreasing functions of frequency. Around 1 Hz, it may persist for several hours. The origin of this violation is a highly intermittent dynamics characterized by large fluctuations and strongly non-Gaussian statistics. The intermittent dynamics depends on the quenching rate and it disappears after slow quenches. The relevance of these results for recent models of aging are discussed.

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1. Introduction

Glasses are materials that play an important role in many industrial and natural processes. One of the most puzzling properties of these materials is the very slow relaxation towards equilibrium, named aging, that presents an interesting and unusual phenomenology. More specifically, when a glassy system is quenched from above to below the glass transition temperature T_g, any response function of the material depends on the time t_w elapsed from the quench [1]. For obvious reasons related to industrial applications, aging has been mainly characterized by the study of the slow time evolution of response functions, such as the dielectric and elastic properties of these materials. It has been observed that these systems may present very complex effects, such as memory and rejuvenation [1–4]; in other words, their physical properties depend on the thermal history of the sample. Many models and theories have been constructed in order to explain the observed phenomenology, which is not yet completely understood. These models either predict or assume very different dynamical behaviors of the systems during aging. These dynamical behaviors can be directly related to the thermal noise features of these aging systems and the study of response functions alone is unable to give definitive answers on the models that are the most adapted to explain the aging of a

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specific material. Thus, it is important to associate the measure of thermal noise to that of response functions. The measurement of fluctuations is also related to another important aspect of aging dynamics, that is the definition of an effective temperature in these systems which are weakly, but durably, out of equilibrium. Indeed, recent theories [5] based on the description of spin glasses by a mean field approach proposed to extend the concept of temperature using a fluctuation–dissipation relation (FDR), which generalizes the fluctuation–dissipation theorem (FDT) for a weakly out-of-equilibrium system (for a review, see [6–8]).

For all of these reasons, in recent years, the study of the thermal noise of aging materials has received a growing interest. However, in spite of the large amount of theoretical studies [24–31], there are only a few experiments dedicated to this problem [9–18]. The available experimental results are in some way in contradiction and they are unable to give definitive answers. Therefore, new experiments are necessary to increase our knowledge on the thermal noise properties of the aging materials.

We present in this paper measurements of the dielectric susceptibility and polarization noise, in the range 20 mHz–100 Hz, of a polymer glass (polycarbonate). These results demonstrate the appearance of a strong intermittency of the noise when this material is quickly quenched from the molten state to below its glass transition temperature. This intermittency produces a strong violation of the FDT at very low frequency. The violation is a decreasing function of the time and frequency and it is observed at $\omega t_{\mathrm{w}} \gg 1$ and it may last for more than 3 h for $f > 1$ Hz. We have also observed that the intermittency is a function of the cooling rate of the sample and it almost disappears after a slow quench. In this case, the violation of FDT remains but it is very small.

The paper is organized in the following way. In Section 2, we describe the experimental set-up and the measurement procedure. In Section 3, we report the results of the noise and response measurements. The statistical analysis of the noise is performed in Section 4. In Section 5, the dependence on the quench speed of the FDT violation is discussed. The temporal behavior of the effective temperature after a slow quench is described in Section 6. In Section 7, we first compare the experimental results with the theoretical ones before concluding.

2. Experimental set-up

The polymer used in this investigation is Makrofol DE 1-1 C, a bisphenol A polycarbonate, with $T_{\mathrm{g}} \simeq 419$ K, produced by Bayer in form of foils. We have chosen this material because it has a wide temperature range of strong aging [1] (see Appendix A). This polymer is totally amorphous: there is no evidence of crystallinity [19]. Nevertheless, the internal structure of polycarbonate changes and relaxes as a result of a change in the chain conformation by molecular motions [1,20,21]. Many studies of the dielectric susceptibility of this material exist, but none had an interest on the problem of noise measurements.

In our experiment, polycarbonate is used as the dielectric of a capacitor. The capacitor is composed by 14 cylindrical capacitors in parallel in order to reduce the resistance of the sample and to increase its capacity (see Appendix A). Each capacitor is made of two aluminum electrodes, 12 μm thick, and by a disk of polycarbonate of diameter 12 cm and thickness 125 μm. The experimental set-up is shown in Fig. 1(a). The 14 capacitors are sandwiched together and put inside two thick aluminum plates which contain an air circulation used to regulate the sample temperature. This mechanical design of the capacitor is very stable and gives very reproducible results even after many temperature quenches. The capacitor is inside four Faraday screens to insulate it from external noise. The temperature of the sample is controlled within a few percent. Fast quench of about 1 K/s are obtained by injecting nitrogen vapor in the air circulation of the aluminum plates. The electrical impedance of the capacitor is $Z(\omega, t_{\mathrm{w}}) = R/(1 + i\omega RC)$, where C is the capacitance and R is a parallel resistance which accounts for the complex dielectric susceptibility. This is measured by a lock-in amplifier associated with an impedance adapter (see Appendix A). The noise spectrum $S_Z(\omega, t_{\mathrm{w}})$ of the impedance $Z(\omega, t_{\mathrm{w}})$ is:

$$S_Z(f, t_{\mathrm{w}}) = 4k_{\mathrm{B}} T_{\mathrm{eff}}(f, t_{\mathrm{w}})\,\mathrm{Re}[Z(\omega, t_{\mathrm{w}})] = \frac{4k_{\mathrm{B}} T_{\mathrm{eff}}(f, t_{\mathrm{w}}) R}{1 + (\omega RC)^2}, \qquad (1)$$

where k_{B} is the Boltzmann constant and T_{eff} is the effective temperature of the sample. This effective temperature takes into account the fact that FDT (Nyquist relation for electric noise) can be violated because the