Field–induced structural aging in glasses at ultra low temperatures

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In non–equilibrium experiments on the glasses Mylar and BK7, we measured the excess dielectric response after the temporary application of a strong electric bias field at mK–temperatures. A model recently developed describes the observed long time decays qualitatively for Mylar [1], but fails for BK7. In contrast, our results on both samples can be described by including an additional mechanism to the mentioned model with temperature independent decay times of the excess dielectric response. The origin of this novel process beyond the "tunneling model" we suggest bias field induced structural rearrangements of "tunneling states" that decay by quantum mechanical tunneling.

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Most low temperature properties of glasses are well described by the phenomenological "tunneling model" [2, 3, 4, 5]. It starts from the assumption that the potential minima of groups of atoms are not "well defined", but can be described as particles moving in "double well" potentials. At low enough temperatures, only the ground states of the two wells are occupied, and the "tunneling states" (TSs) move by quantum mechanical tunneling between them. The energy splitting of these two levels is given by \( E = \sqrt{\Delta_0^2 + \Delta^2} \), where the asymmetry, \( \Delta \), is the energy difference between the two local minima. The tunneling splitting can be estimated using the WKB–approximation as \( \Delta_0 \approx h \Omega \exp(-\lambda) \), with the attempt frequency, \( \Omega \). The tunnel parameter \( \lambda = d\sqrt{2mV/2h} \) contains the effective mass, \( m \), the potential barrier height, \( V \), and the distance between the two wells, \( d \).

Recent experiments revealed deviations from the tunneling model and show that interactions between TSs gain importance with decreasing temperature [1, 3, 5]. Our new results will be discussed within a picture that goes beyond "double well" potentials.

Long time non–equilibrium dynamics of TSs in the polyester glass Mylar after the temporary application of a large electric bias field were previously presented [1]. These data were analyzed using the "dipole gap" theory [6] by extending its predictions to the case of a temporary applied bias field. A central assumption of the "dipole gap" theory is that mutually strongly coupled TSs do not contribute to the dielectric response in thermal equilibrium. However, out of equilibrium these TSs contribute to the dielectric constant as if isolated [6]. The findings in [1] were explained in terms of strongly coupled pairs of TSs that are driven out of equilibrium during a field sweep, not only by relaxation, but also by non–adiabatic driving of one member of two strongly coupled TS–pair by the applied field. Our new results indicate the existence of an additional process leading to non–equilibrium pairs of TSs, while the sum of all processes remains constant. This novel process yields an excess dielectric response with a decay time independent of the bias field history and temperature. For the polyester glass Mylar, the new process becomes significant only at a sufficiently high electric bias field. In our experiments, we measured the dielectric constant of a 15 \( \mu \)m thick Mylar film and a 300 \( \mu \)m thick BK7 wafer, both contained in a \(^3\)He immersion cell. All measurements were performed in the linear response region and at the frequency \( f = 10 \text{ kHz} \).

Figs. 1 and 2 show the excess dielectric response of Mylar after the temporary application of an electric bias field for the waiting time \( t_w = 30 \text{ s} \) and at temperatures \( T = 10 \text{ mK} \). Solid lines are model curves explained in the text. The schematic illustrates the bias field sweep and the definition of \( t = 0 \).

\[ t_w = 30 \text{ s} \]
\[ T = 10 \text{ mK} \]
\[ F = 6.7 \text{ MV/m} \]
\[ T_w = 30 \text{ s} \]

![FIG. 1: Dielectric response of Mylar to a temporary applied bias field with maximal value \( F \) for a waiting time \( t_w = 30 \text{ s} \) and different sweep times at a temperature \( T = 10 \text{ mK} \). Solid lines are model curves explained in the text. The schematic illustrates the bias field sweep and the definition of \( t = 0 \).](image)
bias fields $0.3 \text{ MV/m} \leq F \leq 8.7 \text{ MV/m}$.

A temporary applied bias field causes relaxational processes that bring TSs out of equilibrium. In [1], strong deviations from the expectations due to relaxation were observed in the dependence of the waiting time (Fig. 1). These results were qualitatively explained by considering the evolution of energy splittings $E(t) = \sqrt{\Delta_0^2 + (\Delta + \mathbf{p}F(t))^2}$ while sweeping TSs through zero asymmetry $\Delta + \mathbf{p}F(t) = 0$ (assembling an avoided level crossing situation). If the combination of electric ac– and bias–field changes fast, systems tunneling slowly cannot adjust to their momentary equilibrium while being symmetric, i.e. $\Delta + \mathbf{p}F(t) \lesssim \Delta_0$. Such TSs are driven non–adiabatically and, if part of a strongly coupled pair, suddenly contribute to the dielectric response. Due to the range of relaxation times, the excess response decays in time as $\log(\tau_0/t)$, as long as the ac–field dominates the driving effect, i.e. for small sweep rates $F/t_\text{s}$. At faster sweep rates the bias–field drives TSs non–adiabatically. This situation causes deviations from logarithmic decays [1,10]. In Figs. 1 and 2 the transition between both non–adiabatic limits can be seen [10].

Here, relaxational processes can be omitted, as comparison to the waiting time dependence reported in [1] shows. The slopes of the solid lines in both figures, representing logarithmic decays as expected for non–adiabatic ac–field driving, are calculated from the results in [1]. They depend on temperature and maximal bias field but not on sweep rate and waiting time [1]. The decay times $\tau_0$, defined as the times when the model curves extrapolate to $\delta\varepsilon/\varepsilon = 0$, depend on the many parameters of the model, but we take them here as fit parameters.

Fig. 3 shows double logarithmic plots of decay times as a function of the sweep rate $F/t_\text{s}$. Solid points represent the decay times extracted from measurements with a maximal bias field of $F = 6.7 \text{ MV/m}$ and different sweep times, for $T = 10 \text{ mK}$ (Fig. 1) and $T = 20 \text{ mK}$ in the upper and lower plot, respectively. Non–adiabatic driving causes $\tau_0$ to be a function of the sweep rate $F/t_\text{s}$ [1,10]. If bias field driving is dominant (fast sweeps) the model introduced in [1] proposes a linear dependence $\tau_0 = \xi(T)t_\text{s}/F$. For dominant ac–field driving (slow sweeps) the exact form of the functional dependence is unknown. All data sets presented in Fig. 3 contain the transition between these two limits (fast and slow sweeps). The decay times extracted from our sweep time dependent data (solid points) show the same power law behavior over 4 orders of magnitude in time independent of temperature and bias field history.

The open circles in Fig. 3 present the decay times obtained from the bias field dependent measurements shown in Fig. 2. For bias fields greater than a crossover field $F_c \approx 1.5 \text{ MV/m}$ we observe identical behavior as for the sweep time dependent measurements, that were taken at $F = 6.7 \text{ MV/m}$, much greater than $F_c$. Strikingly, for $F < F_c$ the behavior suddenly changes to the expected linear relation $\tau_0 \propto t_\text{s}/F$ (solid lines in Fig. 3). The temperature dependence mirrors this situation: For $F < F_c$ we find $\tau_0(T = 20\text{mK})/\tau_0(T = 10\text{mK}) \approx 1.8$.
(solid lines), in agreement with the observed temperature dependence of the decay times in the limit of dominant relaxational processes \[1\]. For \( F > F_c \) we observe \( \tau_0(T = 20\text{mK})/\tau_0(T = 10\text{mK}) \simeq 1.8^{0.4} \) (dashed lines), with the identical exponent as for the sweep rate dependence in this limit. Both the non–linear relation \( \tau_0 \propto (t_s/F)^{0.4} \) for \( F > F_c \) as well as the temperature dependence cannot be explained by our model so far.

Our BK7–sample is twenty times thicker than the Mylar film resulting in an accordingly weaker maximal bias field of \( F = 0.4 \) MV/m for our maximum applied voltage. However, the electric coupling between TSs is about 6 times stronger than in Mylar [3] yielding similar excess responses in both samples for otherwise similar parameters. The sweep time dependence for BK7 is displayed in the inset of Fig. 4 for \( t_s \leq 10 \) s and in the main figure for \( t_s \geq 10 \) s. Due to the stronger coupling between TSs in slow tunneling frequencies are driven non–adiabatically. Hence, we expect to observe sweep rate independent decays, if \( E_{\text{min}} \) is larger than a crossover splitting, \( \Delta_\text{c} \), below which non–adiabatic driving of TSs is present. Taking into account all of our measurements [1], we estimate \( E_{\text{min}}/h \gtrsim 1.6 \) mK for BK7 and \( E_{\text{min}}/h \lesssim 40 \) \( \mu \)K for Mylar, in agreement with conclusions drawn from a saturation of the dielectric constant at low temperatures [2]. For relaxational processes bringing pairs out of equilibrium, an upper limit for the decay time can be estimated. By taking only one phonon processes of TSs with \( E \sim k_BT \) at zero field and \( E \sim pF \gg k_BT \) at applied field into account and assuming a typical dipole moment of \( p \sim 1 \) D we find \( \tau_0 \gtrsim \tau_w pF/k_BT \sim 100 \) s. In contrast, we observe decay times scattered around \( \tau_0 = 7100 \pm 500 \) s in our experiments (Fig. 4). The excess dielectric response of BK7 is therefore primarily caused by a novel process, for which the decay time exhibits at most a very weak dependence on temperature [10].

We will now show that the decay time dependence on the sweep rate \( \tau_0(F/t_s) \) in our Mylar sample (Fig. 4) can as well be described by including such an additional process with constant decay time. We assume that TSs contributing to the novel process do not contribute to non–adiabatic driving and therefore \( \delta \varepsilon/\varepsilon \propto [1 - \alpha(F)] \ln[\xi(T)t_s/(Ft)] + \alpha(F) \ln[\tau_0/t] \). Here \( \xi(T)t_s/F \) and \( \tau_0 \) are the decay times due to non–adiabatic driving, containing the temperature dependent pre–factor \( \xi(T) \), and the novel process, respectively, and \( \alpha(F) \) is the amplitude of the novel process. The decay times obtained from the logarithmic theory curves are then given by

\[
\log(\tau_0) = [1 - \alpha(F)] \log[\xi(T)t_s/F] + \alpha(F) \log[\tau_0].
\]

All lines in Fig. 3 are obtained from (1), where we assumed \( \alpha(F > F_c) = \alpha_0 \) and \( \alpha(F < F_c) = 0 \), i.e. that the novel process disappears for \( F < F_c \), in accordance with experiments. The fit parameters are \( \tau_0 \approx 4.7 \cdot 10^3 \) s, \( \alpha_0 \approx 0.6 \) for both temperatures, \( \xi(10\text{mK}) \approx 620 \) MV/m and \( \xi(20\text{mK})/\xi(10\text{mK}) \approx 1.8 \). By including the novel process we can now recalculate the model curves for Figs. 1 and 2 as well as for the data in a previous publication [3]. Hereby, the slopes of all model curves only depend on two common fit parameters, the dipole moment of \( p = 1.2 \pm 0.1 \) D and the interaction constant, \( P_0U_0 \approx 6.3 \cdot 10^{-4} \), where \( P_0 \) is the density of states of TSs and \( U_0 \) the mean interaction energy times volume. Note, that due to the influence of the novel process, our value of \( P_0U_0 \), is slightly higher than previously reported [3].

Using logarithmic decay curves for the novel process we find good agreement with our data by assuming the same dependence of the slopes of the decay curves on temperature and maximal bias field as already proposed in the "dipole gap" theory [3] and observed in our previous experiments for relaxational pair breaking and non–adiabatic driving processes [1]. Thus, the slope of the decay curves (in their logarithmic region) is governed by

![FIG. 4: Sweep time dependence of the relative dielectric constant of BK7 after transient application of a bias field \( F = 0.4 \) MV/m at the temperature \( T = 20 \) mK for long sweep times \( t_s \geq 10 \) s in the main figure and short sweep times \( t_s \leq 10 \) s in the inset.](image-url)
the general dependence on temperature of the dielectric response as well as how far the bias field drives the TSs out of equilibrium. In order to reach good agreement with all our measurements on Mylar [10], we necessarily must make the assumption in (1) that the novel process contributes additional terms to the excess dielectric response due to other processes, i.e. non-adiabatic driving. Undoubtedly, if the dynamics of strongly coupled pairs of TSs governs the other contributions, the novel process influences clusters as well.

The temperature independence of $\tilde{\tau}_0$ points to a process involving quantum mechanical tunneling, wherein thermal transitions are unimportant. The general assumption of a flat distribution of tunneling parameters $\rho(\lambda) = \rho_0$ in a disordered solid yields the distribution of tunneling times $\rho(\tau_\lambda) = \rho_0/\tau_\lambda$, with $\tau_\lambda \propto \exp(\lambda)$. Assuming that strongly coupled pairs stop contributing to the dielectric response once they are in thermal equilibrium, as in the “dipole gap” theory, we find a logarithmic decay $\Delta E / \xi \propto \int_{\tau_\lambda \text{min}}^{\tau_\lambda \text{max}} d\tau \rho(\tau) \Theta(t - \tau) = \rho_0 \ln(\tilde{\tau}_0/t)$, with $\tau_\lambda \text{max} \equiv \tilde{\tau}_0$ and the Heavyside step function $\Theta(t - \tau)$. A strong electric bias field couples to dipole moments, generally present in amorphous solids due to displacements of atoms, and leads to structural rearrangements of the atoms changing the potential energy distribution. This situation yields a different set of low energy states than the TSs provided at zero field. Nevertheless, in thermal equilibrium, experimental observations are identical because of the glassy distribution of parameters. Primarily, we are interested in the effect of a bias field sweep on TSs contributing at zero field to the dielectric constant.

Simulations suggest that the additional low energy internal degrees of freedom observed in glasses include coherent movements of the order of 20–100 atoms [11]. The interaction of that many atoms yields a multiple level scheme, wherein a TS can contribute to the excess dielectric response, if the two lowest levels are close enough in energy, e.g. $\Delta g \lesssim k_B T$ and $E \sim k_B T$. A strong bias field $pF \gg k_B T$ couples to dipole moments and reorganizes the energy eigenstates present in the glass. It thereby brings TSs, including strongly coupled pairs, out of thermal equilibrium. Moreover, energy states that are thermally not accessible at zero bias field will be occupied during the field sweep by quantum mechanical tunneling. It is conceivable that successive tunneling processes while the bias field is swept tend to bring TSs into metastable states that are lower in energy than their neighbor potential wells (in configuration space) during the entire field sweep, i.e. tunneling processes tend to be unidirectional in a non-equilibrium situation. Once back at zero bias field, these TSs are generally still trapped in their metastable states and separated from the lowest energy states (at zero bias field) by a large potential barrier. Intermediate states temporarily occupied during the field sweep are now statistically higher in energy and thermally not accessible ($\delta E \gg k_B T$). While metastable states in single wells are occupied that cannot be counted as TSs, additional metastable two level states exist. Because of the flat distribution of asymmetry energies, the overall number of TSs contributing is the same at any time. However, TSs out of equilibrium that belong to strongly coupled clusters contribute to the excess dielectric constant as being isolated. Our interpretation in terms of structural rearrangements should be considered as a rough outline of a possible scenario. It calls for a detailed examination, including the influence of metastable conditions on the dielectric response dependent on the broadly distributed time constants of the different involved processes.

We observe the novel process in BK7 at relatively small bias fields. However, a minimum bias field is required in the polyester glass Mylar possibly due to a potential barrier necessary to rearrange hydrocarbon chains.

In conclusion, after the temporary application of a sufficiently large electric bias field to a glass sample at ultra low temperatures, we find a long–lasting contribution to the excess dielectric response that decays logarithmically in time with a decay time independent of temperature and bias field history. We assign this novel process to field–induced structural rearrangements in the glass that decay slowly by quantum mechanical tunneling through large potential barriers. Strongly coupled pairs involved cause an excess dielectric response as long as they are not in thermal equilibrium.

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