Memory-effect in glasses at low temperatures

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(Dated: December 30, 2021)

The dielectric constant of amorphous solids at low temperatures is governed by the dynamics of tunneling systems, small groups of atoms which tunnel between quasi equivalent potential minima. Recent experiments showed that at temperatures below 20 mK various glasses exhibit memory for a previously applied electric bias field. A first sweep of an electric bias field may prepare resonant pairs of tunneling systems, which are temporarily formed during the sweep, in metastable states. In subsequent sweeps the same resonant pairs thus significantly contribute to the dielectric constant, leading to a higher dielectric constant. We investigate the dynamics of resonant pairs during a bias field sweep yielding a qualitative explanation of the memory effect.

PACS numbers: 61.43.Fs, 77.22.-d, 75.10.Jm, 05.70.LN

Glasses at low temperatures exhibit properties which differ considerably from those of their crystalline counterparts. They are thought to be caused by tunneling systems (TSs) stemming from the tunneling motion of small atomic entities in double-well potentials. The energy splitting $E$ of these TSs is given by $E^2 = \Delta^2 + \Delta_0^2$, where $\Delta$ is the asymmetry energy due to the difference in the depth of the two wells and $\Delta_0$ is the tunneling splitting originating from the overlap of the wave functions. The randomness of the glassy structure results in broad distributions for these two parameters. The phenomenological tunneling model successfully describes most of the thermal, elastic and dielectric properties of glasses at low temperatures.

However, experiments below 100 mK have revealed that deviations from the predictions of the tunneling model exist. Although a comprehensive theory is still missing, it seems that the interaction between the TSs gives rise to many of these deviations.

In recent experiments D. Rosenberg et al. investigated the AC dielectric constant during the first few sweeps of an electric bias field after the sample was cooled from about 1 K to about 10 mK. The electric bias field was swept in triangular waves for two successive sweeps. The electric bias field amplitude of the second sweep was twice as large as the amplitude $F_1$ of the first but the sweep rate $dF/dt = F_1/t_\circ$ with the period $2t_\circ$ of the first triangular wave, was kept constant. At the beginning of the first sweep the dielectric constant suddenly decreased but then increased slowly with increasing electric field. When the field reached the maximum and started to decrease again the dielectric constant suddenly increased and then decreased slowly with decreasing field to about its original value when the field reached $F = 0$. The solid line in Fig. 1 illustrates the dielectric constant during the bias field sweep. The slow increase/decrease of the dielectric constant while increasing/decreasing the bias field follows the dipole-gap behavior found in earlier experiments. However, the sudden changes of the dielectric constant at $F = 0$ and at $F = F_1$ are remarkable new features. Typically the relative change of the dielectric constant of these sudden changes was $\delta\varepsilon'/\varepsilon' \sim 10^5$. It decreased inversely proportional to the temperature between $T = 5$ mK and $T = 20$ mK, where the effect could not be resolved anymore. $\delta\varepsilon'/\varepsilon'$ also increased with increasing sweep rate. The most remarkable feature yet happened when the second sweep with twice the amplitude was performed. The dielectric constant smoothly increased with increasing field until $F = F_1$. At this point the dielectric constant suddenly decreased to the value it had when this field was applied during the first sweep. Further increasing the field, the dielectric constant increased following the course which we would have extrapolated from the first sweep. The dashed line in Fig. 1 illustrates the dielectric constant during the second sweep. Reaching the maximum field $2F_1$ the dielectric constant suddenly increased and then decreased slowly with decreasing field. This behavior suggests that the sample remembers the field strength which was previously applied to it. Only if the sample was left at zero bias field for several days or warmed above 1 K would the memory as described vanish.

FIG. 1: The change of the dielectric constant is plotted over the electric bias field. The arrows show the behavior in time. In a first sweep the field is swept in a triangle wave between zero and $F_1$. The full line illustrates the change of the dielectric constant during the first sweep. The dashed line represent the behavior during the second sweep where the maximum field is twice as large as in the first sweep but the sweep rate is the same.
An electric field $\vec{F}$ couples to the dipole moment $\vec{p}$ of a TS, thus, changing the asymmetry energy $\Delta(\vec{F}) = \Delta + \vec{p} \cdot \vec{F}$. Since the distribution of asymmetries is flat over an energy range exceeding typical values of $\vec{p} \cdot \vec{F}$ we expect in thermal equilibrium no changes of the dielectric constant with applied field. However, we expect the changing field to drive TSs out of equilibrium. The TSs, which dominantly contribute to the dielectric constant, have relaxation times $\tau$ typically shorter than $\tau = 1 \text{ s}$ at the temperatures of interest. Accordingly, isolated TSs driven out of equilibrium cannot be responsible for the observed long time effects. We propose that weak interactions between TSs cause the memory effect.

Electrically allowed transitions lead to a dielectric response inversely proportional to the energy splitting and proportional to the occupation difference between the two states. Thus, small energy splittings result in large contributions to the dielectric constant. On the other hand, small energy splittings lead to almost identical occupation numbers for the two states so that their response is suppressed. However, a field sweep drives the TSs out of equilibrium. If two TSs have the same energy splitting $E_1 = E_2$ for a specific field $F_{RP}$ a weak interaction $J_{12} \ll E_1, E_2$ between these two TSs lifts their degeneracy resulting in a small splitting $\Delta_{0p} \leq J_{12}$. We illustrate this ‘avoided crossing’ in Fig. 2 where we plot the excited energy levels of two TSs versus bias field. With increasing field the excitation energy of TS 1 (solid line) decreases until it reaches its minimum $\Delta_{01}$ and then increases again. Note that the energy splitting of a TS varies with the electric field since the field shifts its asymmetry. TS 2 (dashed line) behaves the same. The levels cross at $F = F_{RP}$ where these two TSs form a resonant pair (RP). The TSs forming the relevant RPs have energy splittings $E \approx 2k_B T$ and in thermal equilibrium the occupation difference of the split levels is approximately proportional to $\Delta_{0p}/(k_BT)$. Regarding the small number of RP (about one per 200 TSs), the excess dielectric response is negligible. However, we will show later that TSs with long relaxation times form RPs during the field sweep which are far from thermal equilibrium and provide an excess dielectric response of the order of the observed effect.

In order to understand how RPs yield memory for the previously applied bias field consider two TSs forming a RP where TS 1 starts in the ground state and TS 2 in the excited state. An adiabatic field sweep from $F < F_{RP}$ to $F > F_{RP}$ results in a flip-flop leaving TS 1 excited and TS 2 in its ground state (compare Fig. 2). For an ensemble of such TSs the subensemble of TSs 1 interchanges the occupation number of its excited state with that of the ensemble of TSs 2. We further assume that the relaxation time of TS 1 is short, so that it adjusts its occupation number (of its excited state) according to thermal equilibrium to its momentary energy splitting, and the relaxation time of TS 2 is long, so its occupation number stays unaltered during the experiment. The flip-flops exchange the occupation numbers and TS 2 will store the equilibrium occupation number to field $F = F_{RP}$ when the field reaches $F = F_{RP}$ the second time, after it was swept to its maximum value and then decreased, TS 1 has again an equilibrium occupation number to the applied field $F = F_{RP}$. Now both TSs are in thermal equilibrium. All further flip-flops store the equilibrium occupation number into TS 2 and the situation stays unchanged. Only during the very first formation of a RP one TS is in thermal equilibrium. This produces the observed memory effect.

In the following we quantify the above picture and estimate the temperature and sweep rate dependences. We start by calculating the resonant contribution to the dielectric response function of a RP

$$\chi(t-t') = \langle [P(t), P(t')] \rangle \Theta(t-t') .$$

Here $\langle \cdot, \cdot \rangle$ indicates the thermal and ensemble averages and $[,]$ the commutator. $\Theta$ is the Heaviside step function and $P = p_1 \sigma_{z1} + p_2 \sigma_{z2}$ the total dipole moment of the two TSs. The absolute value of $P$ depends on the magnitude and the orientation of the individual dipoles $p_i$ with respect to the external measuring field. The Hamiltonian of a coupled pair of TSs is given by

$$H = \frac{\Delta_{01}}{2} \sigma_{z1} + \frac{\Delta_1}{2} \sigma_{z1} + \frac{\Delta_{02}}{2} \sigma_{z2} + \frac{\Delta_2}{2} \sigma_{z2} + J_{12} \sigma_{z1} \sigma_{z2}$$

with the Pauli matrices $\sigma_{aj}$ describing the two state variables of the two TSs. Considering only lowest order contributions in the interaction we obtain for the excess response $\chi_{RP}$ of a RP

$$\chi_{RP} = \left( p_1 \frac{\Delta_1}{E_1} + p_2 \frac{\Delta_2}{E_2} \right)^2 \left( \frac{\Delta_{0p}}{E_p} \right)^2 (n_+ - n_-)^2 \sin(E_p t)$$

(1)

with the occupation differences $n_+ = \tanh(E_+/(2k_BT))$ between the ground state and the second excited state of the RP and $n_- = \tanh(E_-/(2k_BT))$ between the
ground state and the first excited state. The energies
\[ E_{\pm} = (E_1 + E_2)/2 \pm E_p \]
with \( E_p = \sqrt{\Delta_{op}^2 + (E_1 - E_2)^2/4} \)
are the excitation energies of the RP and \( \Delta_{op} = (\Delta_{01}/E_1)(\Delta_{02}/E_2) \), (see Fig. 2). Note that especially asymmetric TSs, \( \Delta \sim E_i \), forming RPs, have an excess dielectric response whereas isolated TS only contribute substantially to the resonant splitting of the dielectric constant when they are symmetric, \( \Delta \ll \Delta_{op} \).

At first we estimate the response of RPs in thermal equilibrium. The standard tunneling model assumes a distribution function \( P(\Delta, \Delta_{op}) = P_0/\Delta_{op} \) leading to a flat distribution of energy splittings. One further assumes a maximum splitting \( \Delta_{max} \approx 1 \). The number \( \#n \) of relevant RPs, formed by two thermal TSs, \( E_i \approx 2k_B T \), where the coupling fulfills \( 2\Delta_{op} > |E_i - E_j| \), is \#n = \( (P_0 2\Delta_{op})/(P_0 \Delta_{max}) \).

A common estimate for the mean coupling between TSs are \( \overline{J} \approx 10 \) \( k_B \)mK. Due to the \( 1/r^3 \)-dependence of the interaction on the distance \( r \) between the TSs the mean interaction is proportional to the density of TSs and thus, the mean interaction of thermal TSs is \( \overline{J}(T) \approx 100 \) \( k_B \)mK at \( T = 10 \) mK with \( \Delta_{max} \approx 1 \).

Assuming further \( \Delta_i \sim \Delta_{0i} \) for the TSs forming RPs and \( E_p \ll E_1, E_2 \) we roughly estimate the real part of the dielectric constant (given as the complex Fourier transform of the response function) for RPs \( (\Delta_{op} \approx E_p) \) at \( T = 10 \) mK to be
\[ \chi_{RP}' \approx 4 \cdot 10^{-4} \cdot P_0 p^2 \]
with the mean dipole moment \( p \). \( \chi_{RP}' \) is negligible compared to the dielectric response, about \( \approx P_0 p^2 \), of isolated TSs in the tunneling model.

During a field sweep most TSs will not be in thermal equilibrium and we have to investigate the occupation numbers of two TSs which form a RP at a field \( F_{RP} \) during the sweep. For fields \( F \neq F_{RP} \) the coupling between the two TSs is irrelevant. Assuming a typical dipole moment of 1 Debye, typical bias fields \( F_1 = 133 \) kV/m change the asymmetry by an amount corresponding to a temperature \( \Phi/k_B = pF_1/k_B \approx 30 \) mK. With sweep times \( t_R = 10 \) s the temperature during which two TSs fulfill the RP condition \( 2\Delta_{op} > |E_i - E_j| \) during the sweep, is \( 33 \) ms at \( T = 10 \) mK. This time is short compared to relaxation times of thermal TSs. Accordingly we approximate the occupation difference \( n_+ - n_- \) of the split levels by \( n_+ - n_- \approx n_1 - n_2 \). Thereby,
\[ n_i(t) = e^{-\int_0^t ds_n \gamma_i(s)} \{ n_i(0) \}
\]
are the occupation number of isolated TS during an adiabatic field sweep with constant sweep rate and with the initial occupation difference \( n_i(0) \). For an isolated TS typical experimental bias field sweeps are adiabatic if \( \Delta_0 \geq \sqrt{\frac{(pF_1/k_B)(h_{/t_R})}{\Delta_{max}}} \approx 400 \) nK with Planck’s constant \( h \). The flip-flop dynamics of a RP only occurs when the formation of the RP is adiabatic as well and, thus, the two TSs, which form a RP, must fulfill
\[ \Delta_{op} \geq \sqrt{\frac{(pF_1/k_B)(h_{/t_R})}{\Delta_{max}}} \approx 400 \) nK. The relaxation rate \( \gamma_i(s) \) of a TS is given by the one phonon rate
\[ \gamma_i(s) = \tau^{-1}(s) = \gamma_0 \Delta_{0i}^4 E(s) \coth \left( \frac{E(s)}{2k_BT} \right) \]
with \( \gamma_0 = (1/c_i^2 + 2/c_i^2)B^2/(2\pi\rho B^4) \) where \( c_i \) is the longitudinal and transversal speed of sound, \( \rho \) is the mass density of the glass and \( B \) the strain coupling constant. The time dependence is given by the time variation of the asymmetry energy due to the bias field. We neglected additional relaxation processes which might emerge from the interaction between the TSs, since their relevance is still a matter of debate. Including them will change quantitative results but not the qualitative picture evolved.

Statistically a RP \( A \) with tunneling splittings \( \Delta_{01,A} \) and \( \Delta_{02,A} \) has a partner RP \( B \) whose tunneling splittings \( \Delta_{01,B} \) and \( \Delta_{02,B} \) are chosen to match \( \Delta_{01,B} = \Delta_{02,A} \) and \( \Delta_{02,B} = \Delta_{01,A} \). The initial asymmetries have to obey \( \Delta_{1B} = \Delta_{1A} \) and \( \Delta_{2B} = \Delta_{2A} \) in order that both RP are formed at \( F = F_{RP} \). According to Eq. (3) the responses of RPs \( A \) and \( B \) differ only by their occupation numbers and we obtain for the combined response of both RPs
\[ \chi' \approx \chi_0 \{(n_{1A} - n_{2B}) + (n_{1B} - n_{2A})\} \]
where all factors except the occupation numbers are included in \( \chi_0 \) and the occupation numbers are considered at \( F = F_{RP} \) when the RPs are formed. Each of the occupation differences \( n_{1A} - n_{2B} \) and \( n_{1B} - n_{2A} \) only depend on a single tunneling element. Thus, we can discuss these two RPs as if we had two RPs each formed by two TSs with the same energy and the same tunneling splitting.

To obtain a substantial dielectric response the RP must be formed with an occupation difference close to one. If both tunneling elements are the same the only difference between TS 1 and TS 2 (compare Fig. 3) results from the bias field sweep; the energy splitting of TS 1 is only decreasing until the RP is formed whereas the energy splitting of TS 2 goes through a minimum. Accordingly, we expect a maximum value for the occupation difference of TSs whose relaxation time is similar to the time the energy splitting of TS 2 is smaller then \( k_BT \). Note that the relevant RPs are formed by thermal TSs \( E \approx 2k_BT \). In Fig. 4 we plotted \( n_{1A} - n_{2B} \) as a function of \( \Delta_0 \) for various energy splittings \( E \).

Numerically we find a maximum for \( n_{1A} - n_{2B} \) for a tunneling splitting \( \Delta_0^* \) with
\[ \tau(\Delta_0^*(E), E) = \frac{2k_BT}{\overline{J}F_{max}^*} \cdot t_R \]
The full line in Fig. 4 represents \( n_{1A} - n_{2B} \) for an energy splitting \( E = 2k_BT \) and the dotted and dashed line have
Note that the adiabatic assumption for the RP restricts and the number of contributing RPs

\[ \Delta_0^* = \Delta_0^*(E = 2k_B T) = \sqrt{\frac{\mu^2}{2 \gamma_0 T^2}} . \] (3)

with the average dielectric response of a contributing RP

\[ \frac{\delta \varepsilon^{*\prime}}{\varepsilon'} = N_{RP} \overline{\varepsilon}_{RP} \simeq 1.6 \cdot P_0 \frac{\mu B}{E_{\text{max}}} \ln \left( \frac{\Delta_0^*}{\Delta_{0\text{min}}} \right) \] (4)

and the number of contributing RPs

\[ N_{RP} = \int_{k_B T}^{3k_B T} \frac{dE}{\Delta_0} \int_{\Delta_0}^{\Delta_0^*} \frac{d\Delta_0}{\Delta_0} \cdot \frac{P_0 \Delta_0}{(P_0 E_{\text{max}})^2} \] (5)

where we approximated \( P(E, \Delta_0) \approx P_0 / \Delta_0 \) since \( \Delta_0 \ll E \) for the relevant tunneling splittings. We estimated the number of TSs as \( P_0 E_{\text{max}} \). Eq. (5) predicts a linear increase up to a maximum and then a linear decrease of \( \delta \varepsilon^{*\prime}/\varepsilon' \) with increasing temperature. Eq. (5) further predicts a logarithmic dependence on the sweep rate.

Both predictions are in partial agreement with experiments and we refer to Rosenberg et al. [4] for a detailed comparison.

Qualitatively the dynamics of driven RPs explain the experiments except for the initial sudden decrease. The response due to the driven RPs is always positive. Thus, our model predicts a sudden increase in \( \varepsilon' \) at the beginning of the first sweep and another such an increase when the field starts decreasing. The experimental observed initial decrease might be explained by considering the AC measuring field. Typically, the energy shift by the AC field \( \mu F_{AC} \) is of the order of \( 0.24 - 2.4 \) mK \( k_B \) [7] by assuming dipole moments of 1 Debye. At temperatures between 5 - 20 mK one might accordingly expect the AC measuring field to drive the TSs substantially. Thus, the DC field provides only a ‘second’ sweep for the RPs formed near zero field. As soon as the DC field exceeds the AC field all RPs are formed the first time yielding a sudden decrease at the beginning of the DC field sweep as experimental seen. The typical energy splitting of RPs is small compared to the energy shift induced by the experimental AC field. Therefore the AC field influences the flip-flop dynamics of the RPs. A future investigation should take into account the AC field beyond linear response but this is beyond the scope of the present letter.

In conclusion, we have shown that a first sweep of an electric bias field prepares resonant pairs of tunneling systems, which are temporarily formed during the sweep, in metastable states. Resonant pairs in these metastable states significantly contribute to the dielectric constant leading to a higher dielectric constant in subsequent sweeps, and thus yielding a memory for previously applied fields.

I wish to thank D. Rosenberg, S. Ludwig and D.D. Osheroff for helpful discussions. I also wish to thank the DOE grant DE-FG03-90ER45435-M012 and the Alexander-von-Humboldt foundation for support.

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