Microscopic structure of tunneling systems in glasses

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The out-of-equilibrium dielectric response of a glass sample after the application of a strong dc field at low temperatures cannot solely be understood by interacting two-level tunneling systems [S. Ludwig and D. D. Osheroff, Phys. Rev. Lett. **91**, 105501 (2003)]. The usual picture of a particle tunneling between two close potential wells has to be extended to include at least a third well. We investigate such a three-well system. Particles trapped in the third well after the dc field application result in an additional contribution to the out-of-equilibrium response. Analyzing the experiments with regard to our theoretical model we find that the energy of the third well has a minimal value E_c larger than k_BT for the experimental investigated temperatures. Additionally, the tunneling frequencies in between the double well and between the third well and the double well are correlated. Such a correlation is well known for tunneling defects in crystals and we speculate that crystals doped with tunneling defects show glassy low-temperature behavior if heavily strained. Therefore, we want to encourage experiments toward that direction.

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I. INTRODUCTION

Most low-temperature properties of glasses are well described by the phenomenological tunneling model.[1–4] 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 particles 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, Δ, is the energy difference between the two local minima. The tunneling splitting can be estimated using the WKB approximation as $\Delta_0 \simeq \hbar\Omega \exp(-\lambda)$, with the attempt frequency, Ω. The tunnel parameter $\lambda = d\sqrt{2mV}/2\hbar$ contains the effective mass, m, the potential barrier height, V, and the distance between the two wells, d. The tunneling model assumes homogenous distributions for the asymmetry Δ and the tunneling parameter λ.

Recent experiments revealed deviations from the tunneling model and show that interactions between tunneling systems (TSs) gain importance with decreasing temperature.[5,6] These experiments investigate the out-of-equilibrium response during or after the application of a strong dc electric or strain field. The excess response found by the Osheroff group[5] results from strongly coupled pairs of tunneling systems, since isolated tunneling systems relax too fast to contribute to the out-of-equilibrium response.[7,8] Recent similar experiments[9] cannot be explained solely by double-well tunneling systems even when including interactions between them. Ludwig and Osheroff suggested that the application of the strong dc electric field leads to "structural rearrangements." Subsequently, the decay toward equilibrium by quantum mechanical tunneling is observed as a temperature-independent decay mechanism. Ludwig and Osheroff thus evolved a picture where the energy landscape beyond the double-well approximation has to be considered in order to describe their experimental data. The strong dc field lifts the particle out of the double well and the observed decay results from tunneling particles relaxing back into a double well.

In the following sections, the experiments are described by just adding to the local double-well potential of a tunneling system the simplest extension: a third well.

II. THREE WELL SYSTEM

In Fig. 1 we illustrate the potential energy landscape of a three-well system with the third well higher in energy.

With the tunneling frequencies $\Delta_0/\hbar$ and $\Delta_0'/\hbar$ the Hamiltonian in space representation for the three wells is

$$H=\begin{pmatrix} \Delta & \Delta_0 & \Delta_0' \\ \Delta_0 & -\Delta & \Delta_0' \\ \Delta_0' & \Delta_0' & E' \end{pmatrix}, \tag{1}$$

with the asymmetry Δ of the double well and the energy difference E' between the double well and the third well.

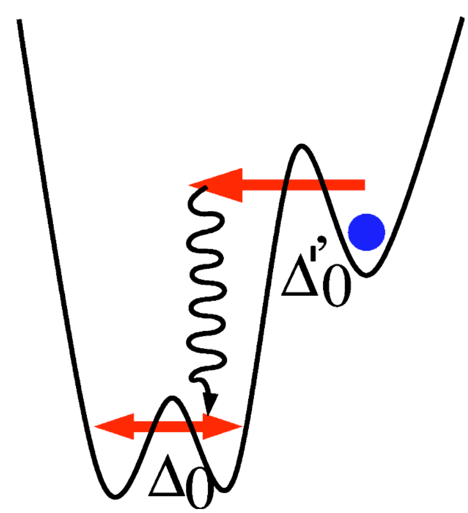

FIG. 1. The potential energy landscape of a three-well system. The arrows illustrate the tunneling path with the associated tunneling frequencies.

In a three-well system electric and strain fields couple to a linear combination of the operators

$$\hat{p}_1 = \begin{pmatrix} p_1 & 0 & 0 \\ 0 & -p_1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \hat{p}_2 = \begin{pmatrix} -p_2 & 0 & 0 \\ 0 & -p_2 & 0 \\ 0 & 0 & 2p_2 \end{pmatrix},$$

and the $\mathbb{1}$ operator. The exact form depends on the spacial structure of the three-well system. Since the general behavior does not depend on the exact form, we assume for simplicity for the coupling to phonons

$$\hat{\gamma} = \begin{pmatrix} \gamma_0 & 0 & 0 \\ 0 & -\gamma_0 & 0 \\ 0 & 0 & \gamma' \end{pmatrix}, \tag{2}$$

with γ_0 the coupling constant between the tunneling particle in the double well and phonons and γ' the coupling constant between the tunneling particle in the third well and phonons. This form tends to the usual dipole operator of a two-level system if we neglect the third well. We expect that γ_0 and γ' are of the same order of magnitude.

Finally we are interested in relaxation times for particles trapped in the third well. Neglecting terms[10] of second and higher order in Δ_0'/E' and of order $\Delta_0\Delta_0'/E'^2$, the eigenstates of a three-well system are

$$|+\rangle = \begin{pmatrix} s_+ \\ -s_- \\ -\dfrac{\Delta_0'}{E'}(s_+ - s_-) \end{pmatrix},$$

$$|-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} s_- \\ s_+ \\ -\dfrac{\Delta_0'}{E'}(s_+ + s_-) \end{pmatrix} \quad \text{and} \quad |\widetilde{3}\rangle = \begin{pmatrix} \dfrac{\Delta_0'}{E'} \\ \dfrac{\Delta_0'}{E'} \\ 1 \end{pmatrix}, \tag{3}$$

with $s_\pm = \pm\sqrt{(E\pm\Delta)/E/2}$.

We investigate systems where, directly after the field sweep, the tunneling particle is in the third well

$$|3\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = |\widetilde{3}\rangle - \frac{\Delta_0'}{E'}(s_+ - s_-)|+\rangle - \frac{\Delta_0'}{E'}(s_+ + s_-)|-\rangle .$$

Typical dephasing (τ_2) times for tunneling systems are shorter than milliseconds at temperatures around $T \simeq 10$ mK, as known from polarization echo experiments.[11] Assuming similar behavior for a three-well system, it is in state $|\widetilde{3}\rangle$ with probability $1-O(\Delta_0'^2/E'^2)$ or in state $|\pm\rangle$ with probability $O(\Delta_0'^2/E'^2)$ after milliseconds. Since the shortest observed time in the experiments by Ludwig and Osheroff is 10 seconds, all three-well systems will be in either one of the eigenstates. Observed in the experiments then are the ones that are not relaxed back into the states $|\pm\rangle$.

The one-phonon relaxation time[12] for a particle from eigenstate $|\widetilde{3}\rangle$ into the eigenstate $|\pm\rangle$ estimated by Fermi's golden rule is

$$\tau_\pm^{-1} = \Gamma_\pm \Delta_0'^2 E' \coth\left(\frac{E'}{2k_B T}\right), \tag{4}$$

with

$$\Gamma_\pm = 2\left(\frac{1}{c_l^5} + \frac{2}{c_t^5}\right)\frac{|\gamma_0(s_+ \pm s_-) \mp \gamma'(s_+ \mp s_-)|^2}{2\pi\rho\hbar^4},$$

where $c_{l,t}$ is the longitudinal (transversal) speed of sound, ρ is the mass density of the glass, and γ and γ_0 the above-introduced strain coupling constants. Note that $0 \leqslant \Gamma_+ \leqslant \Gamma_0$ and $\Gamma_0 \leqslant \Gamma_+ \leqslant 2\Gamma_0$ for arbitrary Δ and Δ_0. Thus the time for a particle to relax out of the third well, i.e., min (τ_+, τ_-), changes only by a factor of two for arbitrary Δ and Δ_0.

III. COMPARISON WITH EXPERIMENTS

The relative change of the dielectric constant measured by Ludwig and Osheroff is dominated by tunneling systems with energies $E \geqslant k_B T$[7], thus $E' \geqslant k_B T$. We should remind the reader that the decay time, which is the time when the measured dielectric response reaches its equilibrium value after the application of a dc electric field, is given by the longest relaxation time of tunneling systems out of equilibrium. In Refs. 5,7,8, the decay times for two-well systems considering various mechanisms to bring them out of equilibrium are discussed. In Ref. 9, however, it was concluded that these mechanism are not able to fully describe the data and that the energy landscape beyond the usual two-well approximation has to be considered. We therefore focus on the effects of the three-well systems. For systems, which are trapped in the third well after the application of a dc electric field, the decay time is given as the longest relaxation time for a particle out of the third well.

If E' is broadly distributed with a minimum smaller or equal $k_B T$, the decay time would be $\tau^{-1} = \Gamma_\pm \Delta_0'^2{}_{\min} k_B T \coth(1/2)$ and thus temperature dependent in contrast to experiments. Keep in mind that only systems with $E \geqslant k_B T$ and thus $E' \geqslant k_B T$ contribute in the discussed experiments. Therefore $E' \geqslant E_c$ with the minimal energy $E_c > k_B T$ for the experimental investigated temperatures of $T=10$ and $T=20$ mK, resulting in a temperature-independent decay time.

An applied electric bias field $\mathbf{F}$ changes energies by $\mathbf{pF}$ with the dipole moment $\mathbf{p}$ of a tunneling system. Only for $\mathbf{pF} \geqslant E' > E_c$ particles can be trapped in the third well after the field application since otherwise the field sweep could not lift the particle into the third well. This explains the critical field,[9] below which the additional temperature-independent decay is not found. The experimental-found critical field,[9] $F_c \simeq 1{,}5$ MV/m, results with a dipole moment,[9] $p \simeq 1{,}2$ D, of the tunneling systems in Mylar in an critical energy $E_c \simeq 2\ k_B$ K. The observed critical field, however, should result in peculiar experimental effects at temperatures around $E_c/k_B \simeq 2$ K, which should be measured and compared with theoretical predictions from a three-well system as an additional test of our proposed model.

According to the WKB formula a tunneling frequency between two wells $\Delta_0/\hbar \simeq \Omega \exp(-\lambda)$ with $\lambda = d\sqrt{2mV}/2\hbar$ is determined by the barrier. We expect that the distances between the three wells are of the same order of magnitude. Compared to typical barrier heights of $V \sim k_B 1000$ K, the difference of the potential minima of the three wells are negligible leading us to the assumption that the barrier heights between the three wells are as well of the same order of magnitude. Thus, we expect a similar distribution of parameters for both tunneling frequencies, Δ_0 and Δ_0' leading to a logarithmic decay of the dielectric response for the systems trapped in the third well in accordance with experiments.[9]

Keep in mind that the discussed out-of-equilibrium dielectric response is a signal by 4 orders of magnitude weaker than the total dielectric response measured. The main contribution to the dielectric response at temperature T comes from isolated tunneling systems with energy splittings of the order of temperature, $E \simeq k_B T$. At the experimental temperatures of $T = 20$ mK and below, the resonant part of the dielectric response dominates, which itself results mainly from symmetric tunneling systems with $\Delta \simeq 0$. Typical relaxation times of these tunneling systems are shorter than 1 s. Therefore, isolated tunneling systems do not contribute to the experimental observed out-of-equilibrium dielectric response after a field sweep but constitute the main contribution to the total dielectric response. The observed out-of-equilibrium behavior is solely due to strongly coupled pairs.[8] The slowly decaying excess dielectric response due to strongly coupled pairs is explained by the dipole gap theory of Burin.[7] Some symmetric tunneling systems are strongly coupled to strongly asymmetric tunneling systems with very long relaxation times. Whereas in thermal equilibrium both systems do not contribute to the dielectric constant due to the strong interaction, the symmetric tunneling system can contribute when the asymmetric one is out of equilibrium.[7] The dipole gap theory predicts after a temporary application of an electric bias field for the time-dependent excess dielectric constant

$$\frac{\delta\varepsilon}{\varepsilon} = f(\mathbf{F},T)\ln\left(\frac{\tau_0}{t}\right),$$

with the decay time τ_0 and a prefactor $f(\mathbf{F},T)$.[8] The additional decay mechanism discussed by Ludwig and Osheroff shows a decay time τ_0 independent of temperature. The excess dielectric constant is as well due to strongly coupled pairs[9] since they found the same functional dependence of the prefactor $f(\mathbf{F},T)$ as predicted by the dipole gap theory. This results in two conclusions: no isolated tunneling system contributing to the dielectric constant is out of equilibrium at the times observed in the experiments. Thus, if all systems are three-well systems, the relaxation time out of the third well, Eq. (4), for a symmetric three-well system with $E \simeq k_B T$ and $\Delta \simeq 0 \Leftrightarrow E \simeq \Delta_0$ must be shorter than 10 s, the shortest observed time in the experiments leading to

$$\Delta_0'^2 \geqslant (10\ \mathrm{s})^{-1}\frac{\tanh(E'/2k_BT)}{\Gamma_\pm E'}. \tag{5}$$

Otherwise the relaxation of isolated three-well systems out of the third well would be observed in experiments.

On the other hand, the experimental long-time behavior results from asymmetric tunneling systems, $E \simeq k_B T$ and $\Delta_0 \ll \Delta$, which are strongly coupled to a second tunneling system.[8] The relaxation time of these systems out of the third well must be very long, $\tau \gg 1$ s, in order to explain the experimental observed decay times of the order of hours. Thus, in this case

$$\Delta_0'^2 \ll (1\ \mathrm{s})^{-1}\frac{\tanh(E'/2k_BT)}{\Gamma_\pm E'}. \tag{6}$$

Since the energies of the experimental relevant systems are fixed as discussed above, $E \sim k_B T$ and $E' \geqslant E_c > k_B T$, the latter arguments can be summarized by

(i) a tunneling splitting $\Delta_0 \ll E$ needs a small Δ_0',

(ii) and a tunneling splitting $\Delta_0 \lesssim E$ needs a large Δ_0',

to be consistent with experiments. Accordingly, the tunneling frequencies, Δ_0 and Δ_0' are correlated.

So far, we have only discussed a third well and ignored the possibility of even more potential wells in the proximity of the double well. In general we expect the same conclusions to hold, since the tunneling back to the double well can always be described by an effective tunneling frequency that results from the potential structure in between.

IV. DISCUSSION

In order to explain the data by Ludwig and Osheroff, we introduced a third well besides the double well forming the tunneling system. We showed that such a model needs a correlation between the tunneling frequency within the double well, and between a third well and the double well in order to be compatible with experimental results.

Such correlated tunneling frequencies between various potenial wells are known for tunneling defects in crystals. These have typically more than two equivalent potential minima. For example, a substitutional lithium defect in potassium chloride has eight potential wells accesible that form the corners of a cube. The tunneling frequencies along any edge of this cube are identical, whereas the tunneling frequencies along the face or space diagonals are smaller due to the longer tunneling path.[13,14]

One might speculate that the tunneling particles in glasses have, due to symmetries, more than two equal potential wells with equal tunneling frequencies between them. For example, in SiO_2 glasses, the tunneling particle might be a SiO_4 tetraeder with three equivalent rotational states. For a polymer like Mylar it is known that side groups of the polymer chains typically have various conformational states that are energetically equivalent. The disorder of glasses leads to large strain fields that break the symmetries. What remains are only few systems where, accidentally, two wells are close in energy so that they act as tunneling systems. The other wells are shifted higher in energy. These strong strain fields might as well break the exact equality of the tunneling frequencies between the various wells, but a correlation would certainly survive. Accordingly, a correlation between the tunneling frequency Δ_0 between the lowest two potential wells and the tunneling frequency Δ_0' between the third well and the other two wells is expected in such a scenario.

If this picture is true, one should be able to turn a crystal doped with tunneling defects into a glass by introducing strain. It is shown that increasing the concentrations of tunneling defects in a crystal, which increases the interactions between the defects, does not lead to glasslike low-temperature behavior,[15] at least as long as the introduction of additional strain fields is avoided. However, in highly strained mixed crystals, which are doped with tunneling defects, a glasslike internal friction was found.[16] In KBr:KCN at CN concentrations of 25, 50, and 70%, a glassy thermal conductivity and specific heat was found.[17] Again the large amount of defects lets one expect large strain fields. Further investigations with control of the introduced strain could verify or falsify the above-introduced picture. From the theoretical side, the question of how the tunneling model distribution emerges needs further investigation as well. Burin and Kagan showed that an ensemble of tunneling systems with an arbitrary distribution of tunneling frequencies, but broad and flat distribution of asymmetries, renormalizes to tunneling systems obeying the standard tunneling model distributions if the systems strongly interact via a dipole-dipole interaction.[18] It would be desirable to understand how these results depend on the distribution of asymmetries to directly compare them with the above-suggested experiments.

V. CONCLUSION

We evolved a picture for the local potential energy landscape of a tunneling system including an additional third well in the standard double-well picture. Such a scenario is able to explain the experiments by Ludwig and Osheroff if one introduces a strong correlation between the tunneling frequency within the double well and the tunneling frequency from the third well into the double well. Such a correlation between tunneling frequencies between different potential wells is known from tunneling defects in crystals and they result from symmetries of the underlying defects.

This suggests that in glasses there are basic tunneling defects with a higher-than-twofold symmetry that are distorted by strain fields due to strong disorder. A strong dipole-dipole-type interaction between the basic tunneling defects might then lead to standard tunneling model distributions for the tunneling frequencies as proposed by Burin and Kagan.[18]

Accordingly, a crystal doped with tunneling defects should show glassy low-temperature behavior if we distort the sample substantially. Some experimental results to test this hypothesis in mixed crystal systems[16,17] are promising but more experimental work toward this direction is desirable.

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