Influence of Nuclear Dipole-Dipole Interaction on Atomic Tunnelling Systems in Glycerol

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Abstract. A few years ago, surprising magnetic field effects were found in the low-temperature dielectric properties of glasses. They are attributed to the interaction of nuclear electric quadrupole moments with local electric field gradients. In our dielectric polarisation echo measurements on partially deuterated glycerol we found a similar effect on a smaller energy scale which is caused by the interaction of the magnetic dipoles of the hydrogen nuclei. Detailed numerical calculations were performed which allow to create a model for the microscopic nature of tunnelling systems in glycerol. Moreover, an unexpected temperature dependence of the nuclear effects may shed some light on the particularities of relaxation in glasses.

1. Introduction
At temperatures below 100 mK many of the thermal, acoustic and dielectric properties of glasses can be described in the framework of the standard tunnelling model [1, 2]. It proposes that within the potential landscape of a glass, ‘particles’ of mass \( m \) can tunnel between the wells of double well potentials. The two lowest energy levels of such a tunnelling system (TS) have an energy difference \( E = \sqrt{\Delta^2 + \Delta_0^2} \) with the asymmetry energy \( \Delta \) and the tunnel splitting \( \Delta_0 \), which is a measure for the tunnelling probability and is determined by the microscopic properties of the double well potential. Both parameters are assumed broadly distributed. The standard tunnelling model predicts many, but not all low temperature features of glasses and does not provide a microscopic picture of the TSs, i.e. the size and properties of the tunnelling entity or the particularities of the tunnelling motion. The investigation of the microscopic nature of TSs was made especially difficult by the qualitative and quantitative universality of the behaviour of glasses with very different chemical constituents [3].

A new probe to study the microscopic nature of TSs was found recently in the magnetic field dependence of the dielectric polarisation echo amplitude of some non-magnetic glasses [4]. In those experiments, a sample is placed between the bottom and the central post of a \( \lambda/4 \)-resonator. Two short high frequency electric field pulses are applied in a \( \pi/2-\pi \) sequence with a pulse separation time \( \tau_{12} \) of the order of \( \mu \)s. The sample responds with a spontaneous macroscopic polarisation, the echo, at \( t = 2\tau_{12} \). It could be proven that the \( B \)-field effect in the echo amplitude is caused by atoms with nuclear electric quadrupole moments (NQM) on the tunnelling entity interacting with local electric field gradients (EFG) [5]. This causes a fine splitting of the tunnelling levels according to the eigenstates of the NQM. If the tunnelling motion
involves a rotation of the EFG with respect to the nuclear spin by a tunnelling angle $\theta_T$ (note that the spin-lattice relaxation times at millikelvin temperatures are several orders of magnitude longer than the pulse sequence in our experiments), transitions between the quadrupole levels are coupled to the tunnelling motion. In 2-pulse polarisation echo experiments this leads to a quantum beating, i.e. a periodic modulation of the echo amplitude as a function of $\tau_{12}$ with the frequency $E_Q/\hbar$, where $E_Q$ is the corresponding quadrupole splitting. The modulation amplitude $A_{\text{mod}}$ depends on $\theta_T$. As the magnetic field is increased, the Zeeman and quadrupole effects compete. In high fields, where the Zeeman interaction dominates, the echo amplitude returns to its maximum value. If several quadrupoles in equivalent chemical bonds are present on the tunnelling particle, the effect factorises [6]. The quadrupole effect was studied systematically on a series of partially deuterated glycerol samples with polarisation echoes at a frequency of about 1 GHz (i.e. $E/k_B \approx 50$ mK for resonant TSs) and temperatures below 20 mK [6]. For glycerol-d5, $C_3(OH)_3D_5$, we found a frequency $E_Q/\hbar \approx 127$ kHz and the saturation field, where the Zeeman splitting becomes larger than the quadrupole splitting, is around 60 mT. Model calculations were successfully performed; they suggest $\theta_T = 16^\circ$ if a TS is assumed to be formed by one molecule only, or a smaller angle for a larger tunnelling entity.

On closer inspection of the data we found a similar effect with a much smaller saturation field ($\approx 2$ mT) in all samples except for fully deuterated glycerol. We attribute this to a hyperfine splitting of the energy levels caused by the interaction of the magnetic dipole moments of hydrogen nuclei [7]. The dipole moments of the deuterons are here negligible, because their gyromagnetic ratio is about 6 times smaller than the one of hydrogen.

2. Dipole effect

Due to the anisotropic nature of the dipole-dipole interaction, the rotation of the relative position of two spins with respect to their orientation causes transitions between the dipole levels. Analogous to the quadrupole effect, this manifests in a magnetic field dependence of the echo amplitude and a quantum beating at zero magnetic field, though with smaller frequencies (on the order of 30 kHz in glycerol-d5). In contrast to the quadrupole effect, however, all dipoles interact with each other, so that an increase in the number of dipoles not simply leads to an increase in the modulation amplitude but to a larger number of energy levels and thus a distribution of beat frequencies. For the calculation, all relevant dipole pairs have to be considered. The hamiltonian for $N$ interacting dipoles with magnetic moments $\mu_j$ can be written as

$$H_d = \frac{1}{2} \sum_{j=1}^{N} \sum_{k=1}^{N} \frac{\mu_j \cdot \mu_k}{r_{jk}^3} - \frac{3(\mu_j \cdot \mathbf{r}_{jk})(\mu_k \cdot \mathbf{r}_{jk})}{r_{jk}^5},$$

(1)

where $r_{jk}$ is the connecting vector between spins $j$ and $k$. Obviously, the energy eigenvalues of this hamiltonian strongly depend on the distance between the dipoles. Since in glycerol inter- and intramolecular distances are comparable [9], hydrogen nuclei in the vicinity of the tunnelling entity have to be taken into account, although they may not actually participate in the tunnelling motion. Therefore, careful modelling of the dipole effect can give a lot more detailed information on the microscopic nature of the TSs in addition to what can be gained from the quadrupole effect.

The calculation of the echo amplitude in a general multi-level system was discussed in [8]. In the work presented here the echo amplitude in the presence of dipole-dipole-interaction was analytically calculated for the special case of a single dipole pair, when the problem reduces to a 4-level system, using a perturbation theoretical approach. The result is

$$A(t = 2\tau_{12}) \propto \left(\frac{\Delta_0}{E}\right)^4 \left[1 - 4 \left(\frac{\Delta}{E} \sin \theta_T\right)^2 \sin^4 \left(\frac{E_d \tau_{12}}{2\hbar}\right)\right].$$

(2)
Figure 1. a) Assumed dipole configuration for modelling the tunnelling motion in glycerol-d5. The dark and light grey spheres represent the H-atoms on the tunnelling molecule in the two potential wells. The distances between the H-atoms of the OH-groups are 2.6 Å and 5 Å [9]. The white spheres denote stationary H-atoms on neighbouring molecules. Their distances to the tunnelling atoms [9] are shown in Å. b) Magnetic field effect in glycerol-d5 at $T = 12$ mK and pulse separation times $\tau_{12} = 8 \mu s$ and $\tau_{12} = 32 \mu s$. The data sets were shifted vertically for clarity. Grey symbols denote mirrored data. Model calculations are represented as dashed lines when including only the quadrupole effect and solid lines when considering both quadrupole and dipole effects with the dipole configuration as shown in fig. 1a).

The echo amplitude is modulated with the frequencies $\omega_d$ and $2\omega_d$, where $E_d = \hbar \omega_d$ denotes the energy splitting of the dipole levels. The modulation amplitude depends on the tunnelling angle $\theta_T$ and is proportional to $(\Delta/E)^2$. Therefore, it is zero for perfectly symmetric TSs.

For the general case of $N$ dipoles, numerical calculations were performed as follows: The dipole hamiltonian is generated for a specific dipole configuration. The number and position of the spins as well as their rotation angles can be varied. As an example, one configuration to model a TS in glycerol-d5 is shown in fig. 1a). The three hydrogens on one rotating molecule are represented by dark and light grey spheres for the left and right well, respectively. Their distances are 2.6 Å and 5 Å [9]. The tunnelling motion is assumed to be an in-plane rotation by $\theta_T = 16^\circ$. Moreover, three stationary neighbouring hydrogens are assumed in distances of 1.9 Å and 2.3 Å, which are within the range of values for hydrogens connected to the same oxygen [9]. After that, the total hamiltonian including the hamiltonians for the bare tunnelling system and the dipole and Zeeman interactions is calculated and diagonalized. The two rf pulses are introduced as a perturbation to the system to derive the transition matrix. With this the echo amplitude can be calculated [8]. Finally, a powder average over all molecule orientations and the distribution of $\Delta_0$ and $\Delta$ according to the tunnelling model is performed to account for the disorder in the glassy sample.

Both $B$-field and $\tau_{12}$-sweeps were performed for glycerol-d5. To fit the data the results for the dipole and quadrupole effects were achieved separately and multiplied afterwards. In fig. 1 b) they are compared to experimental data for two magnetic field sweeps at different $\tau_{12}$. The dashed curves result when considering only the quadrupole model. Clearly, it models the behaviour at higher $B$-fields quite well, but does not account for the effect around zero field. The solid curve includes the dipole and quadrupole effects. It was obtained with the dipole configuration and parameters from fig. 1 a) and achieves a good fit in the entire magnetic field range.
3. Temperature dependence

As the impact of the nuclear moments on coherent echoes is of purely quantum mechanical nature, one would not in the first place expect it to be affected by temperature. However, as shown in fig. 2, we observe a strong temperature dependence of the quantum beating. The relative echo amplitude of natural glycerol, C\(_3\)(OH)\(_3\)H\(_5\), was measured as a function of \(\tau_{12}\) for a series of temperatures. The echo decay which is caused by phase destroying processes during the experiment and is usually superimposed on the quantum beating was eliminated by dividing the zero-field data by the high-field data. Evidently, the observed modulation amplitude decreases with temperature, while the first minimum of the quantum beating shifts towards shorter pulse separations (note that we do not see a pure sin\(^4\)-behaviour, due to the large number of interacting dipoles and the corresponding complexity of energy levels).

The temperature dependence can be interpreted when considering that relaxation mechanisms affect different TSs differently. If a resonant TS interacts elastically or electrically with a thermal TS which changes its state, its energy eigenvalues can be modified, so that it loses its coherence and no longer contributes to the echo amplitude. Since this coupling is proportional to \((\Delta/E)^2\) [10], asymmetric TSs are expected to have shorter relaxation times than symmetric ones. On the other hand, we showed in eq. 2 that the impact of nuclear moments is largest on asymmetric TSs, while perfectly symmetric ones always contribute maximally to the echo amplitude. This means that with longer pulse separation times, when the asymmetric TSs drop out, the modulation amplitude decays and the echo amplitude returns to its maximum value. Moreover, at higher temperatures the number of thermal TSs is higher and relaxation faster, so that the observed first minimum of the quantum beating is effectively shifted towards shorter \(\tau_{12}\).

In conclusion, the investigation of the influence of nuclear moments on the 2-pulse polarisation echo amplitude offers the possibility of understanding the microscopic nature of tunnelling systems in glasses and allow to study dephasing processes in a new way.

Figure 2. Temperature dependence of the relative echo amplitude with pulse separation time of natural glycerol in zero magnetic field. The observed depth and position of the (first) minimum shift significantly with \(T\).

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