The dipole echo in glasses in a magnetic field.
Comparison of theory with experiment.

D Parshin and A Shumilin
St.Petersburg State Polytechnical University, Polytekhnicheskaya 29, 195251 St.Petersburg, Russia
E-mail: dparshin@online.ru, hegny@list.ru

Abstract. Using a perturbation approach we built a theory of magnetic field dependence for two-pulse polarization echo in glasses. The theory is based on interaction of soft potentials (two level systems) and nuclear quadrupole moments with microscopic electric field in glasses. We also take into account random positions and orientations of soft potentials in a glass. We showed that taking this interaction in the first order of the perturbation theory we can explain all the main features of magnetic field dependence for the echo amplitude, observed on experiment. For our purposes we developed a simple diagram technique which is able to describe the echo amplitude in a multilevel system and showed the difference between integer and half-integer nuclear spins. Using the diagram technique we obtained a simple analytical formula that allowed us to compare our theory with experimental data. We have found a very good agreement of experimental and theoretical results. Finely we show that experimental results can be used for evaluating the properties of the microscopic electric field. We describe how to use these data to evaluate the electric field gradient and some of its symmetry properties.

It is well known that many low-temperature properties of glasses (below 1 K) are determined by two-level systems (TLS’s) [1]. A TLS consists from atom or group of atoms which move in a double-well potential between two minima. While the low-temperature properties of glasses are universal (they are similar for all glasses) the microscopic structure of TLS’s in different glasses is different. For example in vitreous silica the tunnelling motion includes rotation of several coupled tetrahedra. But unfortunately the microscopic structure of tunnelling units is not known for other glasses. Which atoms participate in tunnelling and which atoms not, what is the distance between the two minima we know well only for simplest case of tunnelling defects in crystals. For most of usual glasses it remains to be unclear.

However, recently it was discovered a very interesting phenomenon which can help to understand more about microscopic structure of tunnelling units in glasses. It was experimentally observed that the electric-dipole echo amplitude in non-magnetic glasses oscillates as a function of applied magnetic field [2, 3]. Similar behavior was found in insulating crystals with tunnelling impurities [4]. In a recent paper [5] such behavior was attributed to quadrupole nuclear moments of tunnelling particles (with spin \( J \geq 1 \)) interacting with magnetic field and with gradient of internal microscopic electric field. Therefore it becomes possible to identify different nuclei participating in tunnelling since they have different nuclear magnetic and quadrupole moments and microscopic electric field gradients. Such attempt was made recently for glycerol \( \text{C}_3\text{H}_8\text{O}_3 \) [6] where one can replace hydrogen atoms H which do not have quadrupole moment \( (J = 1/2) \) with deuterium atoms D possessing the nuclear quadrupole moment \( (J = 1) \).
On Fig. 1 the experimental data are shown for glycerol-d$_3$: C$_3$H$_5$D$_3$O$_3$ [7]. Depending on the time interval between the two pulses $\tau_{12}$, one has either minimum or maximum for echo amplitude at zero magnetic field. The purpose of the present paper is to explain this phenomenon and compare the results of recent analytical theory [8] with experiment.

In the paper [8] (Eq. 44) using the perturbation theory a general formula was derived for the two-pulse echo amplitude as a function of applied magnetic field $B$

$$ P_{\text{echo}} \propto 1 - A \sum_{n,m>n} \frac{|(\tilde{V}_Q)_{mn}|^2}{\varepsilon_{mn}^2} \sin^4 \frac{\varepsilon_{mn}\tau_{12}}{2\hbar}. $$  \hfill (1)

Here $A$ is a coefficient independent of magnetic field, $\varepsilon_{mn} = \varepsilon_m - \varepsilon_n$ is a distance between a pair of nuclear quadrupole energy levels in magnetic field, $(\tilde{V}_Q)_{mn}$ is a matrix element of nuclear quadrupole - TLS interaction in magnetic field. The second term in this equation should be averaged over the orientations of external magnetic field $B$ relative to the microscopic electric field gradient tensor of TLS.

In Eq. (1) we have three characteristic energy scales: the quadrupole energy $E_Q$ in zero magnetic field, Zeeman energy $E_B$ and energy $E_\tau = \hbar/\tau_{12}$. When magnetic field $B$ is sufficiently big, Zeeman energy $E_B$ is much larger than the other two characteristic energies. Then $\varepsilon_{mn} \simeq E_B$ and echo amplitude is independent of $B$ (the second term in (1) is small in comparison with unity). The dependence of echo amplitude on magnetic field appears when $E_B$ is comparable with at least one of two energies, $E_Q$ or $E_\tau$. Let us first consider the simplest case when quadrupole energy $E_Q \ll E_\tau$. In this case we can easily find energy intervals $\varepsilon_{mn}$ (as functions of magnetic field) and averaged module squared matrix elements $|(|\tilde{V}_Q)_{nm}|^2$ (they will not depend on magnetic field in this case). Then echo amplitude can be described by general formula valid for any nuclear spin $J$

$$ P_{\text{echo}} \propto 1 - C \frac{1}{B^2} \left[ \sin^4(\gamma B\tau_{12}) + 4 \sin^4(\gamma B\tau_{12}/2) \right] $$ \hfill (2)

where $\gamma$ is nuclear gyromagnetic ratio. The magnetic field dependence described by this formula is shown on Fig. 2. It serves as a good approximation for large magnetic fields even in the case when we can not neglect of the quadrupole energy $E_Q$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Experimental data for echo amplitude in glycerol-d$_3$: C$_3$H$_5$D$_3$O$_3$ [7].}
\end{figure}
Figure 2. Echo amplitude, Eq. 2, in the case of small quadrupole energy $E_Q \ll E_B, E_\tau$.

Let us consider now a general case when all three characteristic energies $E_B$, $E_Q$ and $E_\tau$ are of the same order of magnitude. The main point which we want to understand is when one has a minimum or a maximum in the echo amplitude at zero magnetic field (see experimental data on Fig. 1). The answer to this important question depends on the ratio of two energies $E_Q/E_\tau$.

Indeed it follows from Eq. (1) that a pair of levels contribute to the echo amplitude according to function $\sin^4 x/x^2$ where $x = \varepsilon/2E_\tau$. At small magnetic fields $\varepsilon \approx E_Q$. Therefore dependence of echo on magnetic field at small field is determined by position of $x_0 = x(B = 0) = E_Q/2E_\tau$ relative to minima or maxima of the oscillating function $\sin^4 x/x^2$. If $x_0$ coincides with a maximum of this function then echo amplitude has a minimum at $B = 0$. In the opposite case when $x_0$ coincides with a minimum of this function we have a maximum of the echo amplitude at zero magnetic field.

Figure 3. Left: Plot of the function $\sin^4 x/x^2$ and position of $x_0 \approx 1.2$ (dashed line). Right: Result of numerical calculations of echo amplitude as a function of magnetic field for $J = 1$.

Let us illustrate this point for interesting case of nuclear spin $J = 1$ (D in glycerol). In this case we have three pairs of levels. As one can show the main contribution to the echo amplitude comes from the smallest energy splitting $\varepsilon_{mn}$. Fig. 3 shows the plot of the function $\sin^4 x/x^2$, position of $x_0$ (left) and calculated numerically echo amplitude as a function of magnetic field.

We can see that echo in this case has a minimum at zero magnetic field. The opposite case is shown on Fig. 4. In this case $x_0 = \pi$ what corresponds to the minimum of the function $\sin^4 x/x^2$. 


Therefore, echo has a maximum at zero field.

![Graph](image1)

**Figure 4.** The same as in Fig. 3 but with different value of $x_0 = \pi$.

As one can see from Fig. 4, there is a flat plateau at $B = 0$. It exists when $x_0$ is exactly equal to $n\pi$ where $n$ is a positive integer. In this case function $\sin^4\frac{x}{x^2}$ approaches zero as $(x - x_0)^4$ and the Taylor expansion of the echo amplitude at low magnetic fields starts from term $H^8$.

For nuclear spins different from $J = 1$ ($J = 3/2, 2, 5/2, ...$) we have similar situation if one of the quadrupole splittings is much smaller then others. This smallest energy interval should be set as $E_Q$. However in the case of half integer spin we should not take into account energy splittings which go to zero when $B = 0$ due to Kramers theorem. In these cases matrix elements $(\tilde{V}_Q)_{nm}$ go to zero when $B = 0$ as well and participate in echo amplitude much less then other levels. For example in the case of $J = 3/2$ the only essential splitting in zero field between two pairs of degenerate levels should be set as $E_Q$.

Comparing experimental data with theory, one can get important information about microscopic electric field gradient for given nuclear position in the glass. As follows from Fig. 1 in glycerol-d$_3$ we have a minimum for echo amplitude at zero magnetic field for $\tau_{12} = 3.5\mu s$ and maximum for $\tau_{12} = 7\mu s$. It corresponds to the first maximum and second minimum of the function $\sin^4\frac{x}{x^2}$ correspondingly. From these data we can estimate smallest quadrupole energy splitting $E_Q \approx 6.28\hbar/7\mu s \approx 0.6 \cdot 10^{-9}eV \approx 160kHz$ what coincides well with the result obtained in [6] from the time dependence of the echo signal. Using this value of $E_Q$ and quadrupole moment of deuterium, one can estimate a microscopic electric field gradient for deuterium atoms in glycerol.

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