# Pulsed NMR: Spin-Echoes

Emanuele Coradin — 2124732 — emanuele.coradin@studenti.unipd.it and
Alberto Salvador — 2112317 - alberto.salvador.1@studenti.unipd.it
*Department of Physics, University of Padua*
(Dated: May 10, 2024)

This experience looks at nuclear magnetic resonance (NMR) as both a basic scientific concept about atomic nuclei and a useful lab technique for studying nuclei, molecular structures, and substance properties. Using radio waves tuned to specific frequencies, pulsed NMR shakes up a group of spinning particles in a glycerine sample. This allows us to measure the magnetic properties of hydrogen nuclei, using different radio wave patterns to measure the typical relaxation times.

## INTRODUCTION

The experimental setup includes an electromagnet designed to uniformly orient the spins in a direction termed *longitudinal*. This magnet produces a magnetic field $\overrightarrow{B}$, generated by a current $I$ flowing through its coil. The glycerine, contained inside a test tube, is immersed in this static magnetic field surrounded by a separate coil which is regulated by an RF generator. This generator induces an additional oscillating magnetic field whose effect is to rotate the spins transversely, and so also the magnetization vector $\overrightarrow{M}$. The same solenoid is utilized to detect the magnetization signal, which enables us to study the relaxation phenomena.

## PREPARATORY ACTIVITIES

### Estimate of the net magnetic moment of the sample

The sample is made of glycerine($C_3H_8O_3$) in a test tube. Using the ruler to measure its diameter $d$ and height $h$ we find $d = (0.70 \pm 0.03)$ cm, $h = (2.20 \pm 0.03)$ cm [2], so that the volume of the sample can be estimated by $V = \pi r^2 h = (0.85 \pm 0.07)$ cm$^3$. Recall that the magnetization vector field is defined as $\vec{M} = N < \vec{\mu} >$, where N is the number of magnetic dipoles, and $< \vec{\mu} >$ is the ensemble average of the magnetic dipole moment. Considering that the molar mass is $m_M = 92.09362 \, \frac{\text{g}}{\text{mol}}$, the density is $\rho_V = 1.26 \, \frac{\text{g}}{\text{cm}^3}$, the gyromagnetic ratio of the proton is $\gamma_p = 42.5756 \, \frac{\text{MHz}}{\text{T}}$ and the fact that glycerine has 8 hydrogen atoms, we can estimate the maximum magnitude of the magnetization field as $M_{max} = N| < \vec{\mu} > | = 8N_A \frac{\rho_V V}{m_M} \frac{\gamma_p \hbar}{2} = (125 \pm 10) \, \frac{\mu\text{J}}{\text{T}}$.

### Magnetic Field and Local Oscillator settings

Recall that the Larmor frequency of a proton spin in a static external magnetic field is

$$\omega_L = \gamma_p B \tag{1}$$

Since we also want to use the resonant drive circuit to perform the the magnetization vector measurements, it is essential to tune the static magnetic field to set a Larmor frequency close to its resonance. Therefore, a sweep frequency response analysis of the NMR drive resonant circuit is performed with a scope, and from the resulting Lorentzian curve we estimate that the resonant frequency is about $\tilde{\nu_d} = 24.31$ MHz, with a FWHM of $\Delta\nu_d \approx 700$ kHz. Therefore, the reference value of the magnetic field is $B = \frac{\tilde{\nu_d}}{\gamma_p} = 571$ mT, which from the technical sheets of the apparatus corresponds to an input current of about $I = 8.919$ A, while the reference value for the RF drive signal corresponds to the Larmor frequency $\nu_L \approx \tilde{\nu_d}$.

Slightly changing these parameters (together with the length of $\frac{\pi}{2}$-pulse, $t_{90}$) to maximize the amplitudes of the response from the sample, we arrive at the configuration reported in Table I.

| **Parameter** | **Value** |
|---|---|
| $B$ | $(564.0 \pm 0.3)$ mT |
| $I$ | $(8929.0 \pm 0.3)$ mA |
| $\nu_{RF}$ | $(24.29670 \pm 0.00003)$ MHz |
| $\nu_L$ | $(24.01 \pm 0.01)$ MHz |
| $t_{90}$ | 200 $\mu$s |

TABLE I: Parameter values for the experiment.

The magnetic field is measured with a digital Gauss meter, the current and the drive frequency are directly read from the generators, and the Larmor frequency is estimated from the measurement of the magnetic field.

## SIGNAL PROCESSING

### Estimate of $T_2^*$

*Analytical considerations*

Analyzing the Free Induction Decay (FID) it is possible to measure the decay constant $T_2^*$, which is related to the spin-lattice relaxation time $T_1$, the spin-spin relaxation time $T_2$, and the inhomogeneity of the static magnetic field $\Delta B$ by equation 2:

$$T_2^* = \left( \frac{1}{T_1} + \frac{1}{T_2} + \gamma_p \Delta B \right)^{-1} \approx \left( \frac{1}{T_2} + \gamma_p \Delta B \right)^{-1} \tag{2}$$

The FID signal can be modeled by:

$$V_{\mathrm{FID}}(t) = V_0 \exp\left(-\frac{t}{T_2^*}\right) \cdot \sin\left(\omega_L t + \phi\right)\theta(t - t_0) \quad (3)$$

where $V_0$ is the initial amplitude, $\phi$ the initial phase, $\theta(t)$ the Heaviside step function.

It is also useful to inspect it in the frequency domain[3], considering $\phi = 0$ and $t_0 = 0$ to simplify the discussion:

$$\hat{V}_{\mathrm{FID}}(\xi) = \frac{\hat{f}\left(\xi - \frac{\omega_L}{2\pi}\right) - \hat{f}\left(\xi + \frac{\omega_L}{2\pi}\right)}{2i} \quad (4)$$

$$\hat{f}(\xi) = V_0 \cdot \mathscr{F}\left[\exp\left(-\frac{t}{T_2^*}\right) \cdot \theta(t)\right](\xi) = \frac{-iV_0 T_2^*}{-2\pi T_2^* \xi + i} \quad (5)$$

Specializing the expression for the magnitude of the Fourier transformed function in a neighborhood of $\xi = \nu_L$, we can obtain the function 6 that can fit the data:

$$F(\xi) = \frac{\text{Constant}}{\sqrt{4\pi^2 \cdot A^2(\xi - B)^2 + 1}} \quad (6)$$

where "Constant" is a collection of multiplicative factors, $A = T_2^*$ and $B = \nu_L$ (see the plot in Fig. 3).

To extract the maximum amount of information, we proceed by performing both a linearized fit of the exponential envelope of the function 3 and a fit of the function 6 over the FFT of the data in Fig. 1.

### *Practical methods and results*

The FID signal in Fig. 1 is recorded by the scope with a voltage scale of 200 $\frac{\mathrm{mV}}{\mathrm{div}}$ and a timescale of 100 $\mu$s. In principle, two main sources contribute to the measurement errors: the scale factor and the digit error. The former depends on the specific model of scope and on the adopted scale, while the latter depends only on the least significant digit. In our case, the scale factor does not affect the estimation of the important physical fitting parameters that we are interested in, so we will not consider it. We also neglect the timing error because it is orders of magnitude lower than the voltage one. In particular, to treat it we consider a uniform distribution over the maximum error given by the least significant digit: $\sigma_V = \frac{\mathrm{div}}{10\sqrt{6}} = 8$ mV.

From Fig. 1, it can be seen that in the first part of the signal there are some effects due to the switching time, therefore we extract the measurements for the fit after this transient. To linearize the data, we apply the transformation $y_{\mathrm{fit}} = \log V_{\mathrm{FID}(t)}$. So, $\sigma_{\mathrm{fit}} = \frac{\sigma_{V_{\mathrm{FID}}}}{V_{\mathrm{FID}}}$.

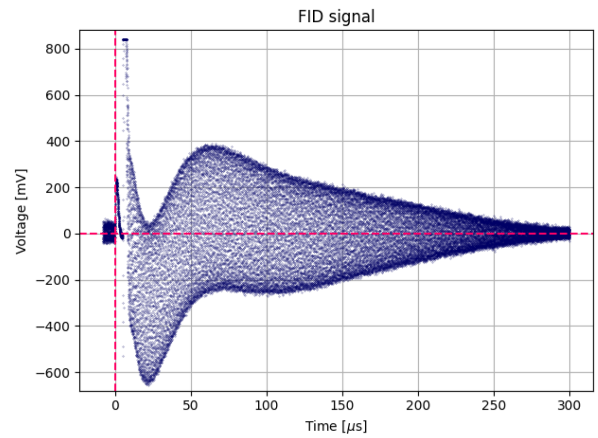
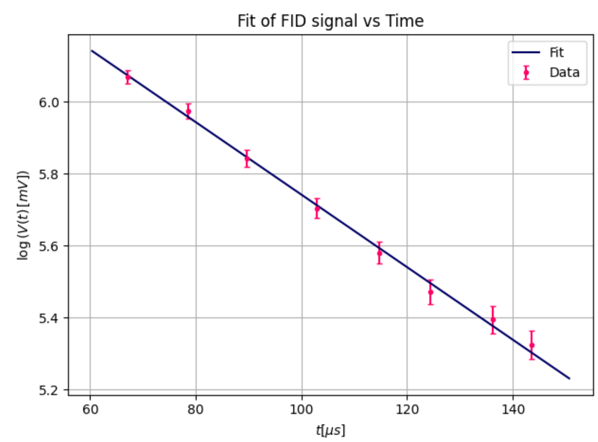
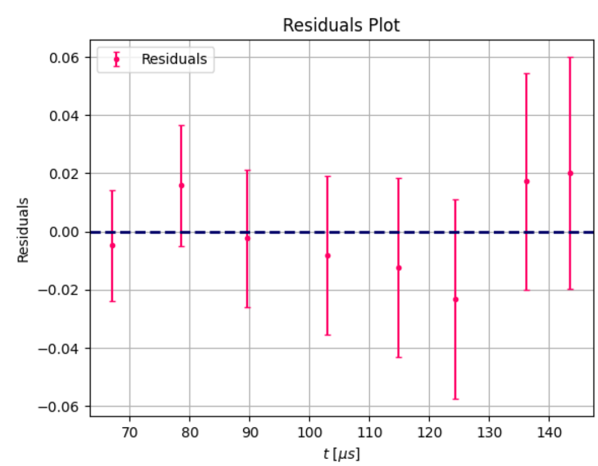



FIG. 1: FID signal after a $\frac{\pi}{2}$-pulse.




(a)




(b)

FIG. 2: Linearized fit of the FID.

The parameters obtained by the fit in Fig. 2 are slope $= (-10.1 \pm 0.4)\ (\mathrm{ms})^{-1}$ and intercept $= 6.75 \pm 0.04$. The residuals plot shows that all the data points have a

1 standard deviation compatibility with the regression line. Finally, from the slope value we can extrapolate an estimate of $\mathbf{T_2^*} = \frac{-1}{\text{slope}} = (\mathbf{99 \pm 3})\ \mu$s.

Calculating instead the FFT of the data set and fitting it, we obtain the plot in Fig. 3. In this case, adapting the discussion available in [1] to the conventions of the adopted library "numpy", the error on the FFT coefficients is $\sigma_{\text{coeff}} \propto \sqrt{N} \cdot \sigma_{V_{\text{FID}}} \approx 2\ V$ (with N being the number of points used by the algorithm), which is negligible in the region we are considering.

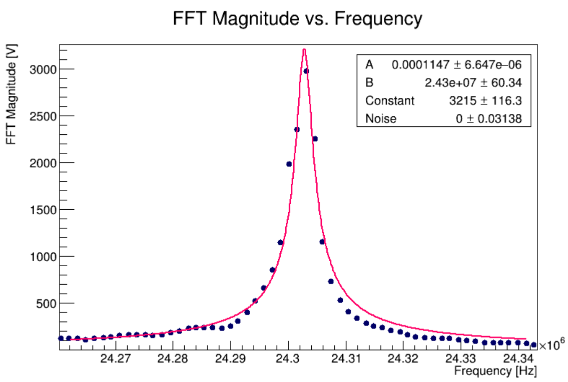



FIG. 3: Fit in the frequency domain.

From this fit, we can extract another estimate for $T_2^* = A = (114.7 \pm 0.7)\ \mu$s and the Larmor frequency $\nu_L = B = (24.30280 \pm 0.00006)$ MHz. The resulting Larmor frequency is consistent with our observation that a good value for the drive frequency is given by $\nu_{\text{RF}} = 24.2967$ MHz (see Tab. I). Hence, we can estimate the average magnetic field value within the glycerine sample $B_{\text{sample}} = (570.820 \pm 0.001)$ mT, which is sensibly different from the measurement made through the Gauss meter. Probably the instrument was not properly calibrated, or the measurements were not taken keeping the probe perpendicular to the field lines. Furthermore, the error is surely underestimated, since the inhomogeneity of the field is higher by two orders of magnitude (see the relative section).

### Estimate of $T_2$

To study the spin-spin relaxation time, we have to focus on the echo signal. It is obtained by placing a $\pi$-pulse after a time $\Delta T$ from the end of the $\frac{\pi}{2}$-pulse (see Fig. 4). This $\pi$-pulse reverses the direction of the angular velocities of the spins (so the magnetization vector's one also), inverting their time evolution, rewinding the dephasing process, and finally restoring coherence, which causes the so-called "spin echo". Then, after reaching the peak, the spins dephase again with the same exponential decay $T_2^*$. Before going on, let us point out a subtlety: let us model the Hamiltonian of the system with $H = H_B + H_{\Delta B}(X) + H_{RF}(t) + H_{\text{spin-spin}}(t)$ where $H_B$ contains the interaction term with the ideal static and uniform magnetic field, $H_{RF}(t)$ is the interaction term with the drive, $H_{\text{spin-spin}}(t)$ is the time-dependent perturbation handling spin-spin interaction, and $H_{\Delta B}(X)$ models the effect of the local inhomogeneity of the field. With a $\pi$-pulse we can just reverse the time-independent sector $H(X) = H_B + H_{\Delta B}(X)$, while the perturbation $H_{\text{spin-spin}}(t)$, being non-trivially time dependent, leads to irreversible effects on the dynamics. Therefore, the amplitude of the spin echo is lower than the initial amplitude of the FID, and it is monotonically decreasing in $\Delta T$.

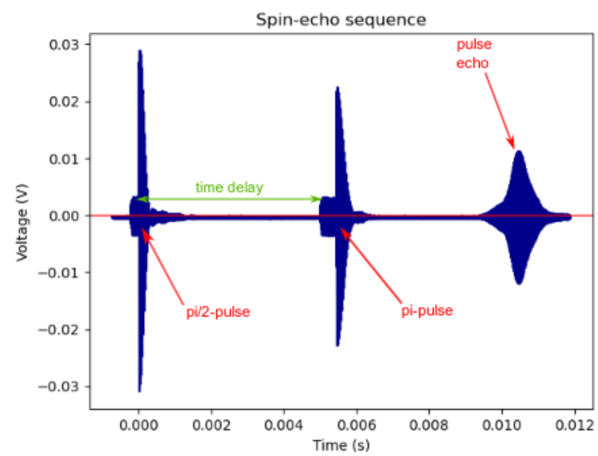



FIG. 4: Signal's evolution after consecutive $\pi/2$ and $\pi$ pulses: the spin echo.

So, to estimate the value of $T_2$ we collect the amplitudes of the spin echoes by varying the time intervals $\Delta T$, both presented in Table II and in Fig. 5. The adopted voltage scale is always 10 $\frac{\text{mV}}{\text{div}}$, and the $\Delta T$ are taken directly from the generator.

By discarding the first six data points, we can perform a linearized fit in the exponential decay regime of the amplitudes (see Fig. 6). The parameters obtained are slope $= (-31.6 \pm 0.4)\ (\mu\text{s})^{-1}$ and intercept $= 4.282 \pm 0.009$. The plot of the residuals is quite good, since all the data points, but the third, are one or two standard deviations compatible with the regression line. Finally, from the slope it is possible to extrapolate an estimate for $\mathbf{T_2} = \frac{-1}{\text{slope}} = (\mathbf{31.7 \pm 0.4})$ ms

| $\Delta T$ (ms) | **Spin echo (mV)** |
|---|---|
| 3.0 | $61.7 \pm 0.6$ |
| 3.7 | $61.3 \pm 0.6$ |
| 4.5 | $60.8 \pm 0.6$ |
| 5.0 | $60.0 \pm 0.6$ |
| 5.7 | $59.7 \pm 0.6$ |
| 8.7 | $56.0 \pm 0.6$ |
| 10.8 | $52.3 \pm 0.6$ |
| 13.4 | $48.5 \pm 0.6$ |
| 16.6 | $40.7 \pm 0.6$ |
| 20.6 | $37.0 \pm 0.6$ |
| 25.5 | $32.8 \pm 0.6$ |
| 31.5 | $26.5 \pm 0.6$ |
| 39.1 | $21.2 \pm 0.6$ |
| 48.4 | $15.8 \pm 0.6$ |
| 60.0 | $11.7 \pm 0.6$ |

TABLE II: Experimental data obtained measuring the maximum amplitude of the spin echo signal as a function of the delay between $\pi/2$ and $\pi$-pulses.

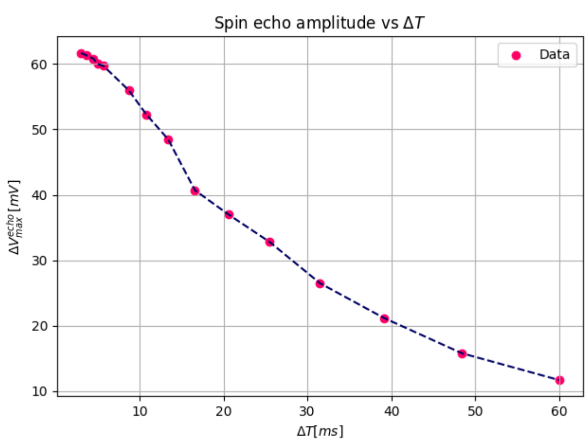
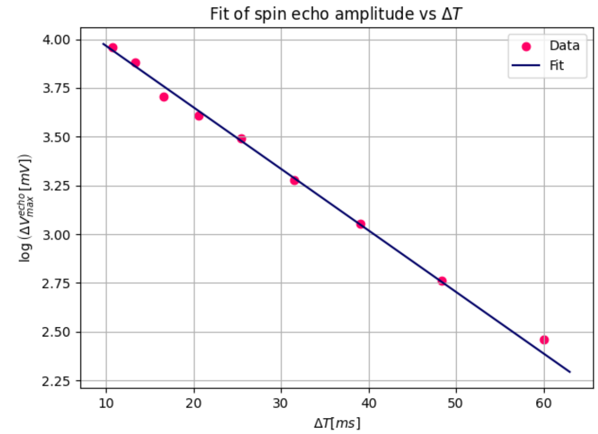
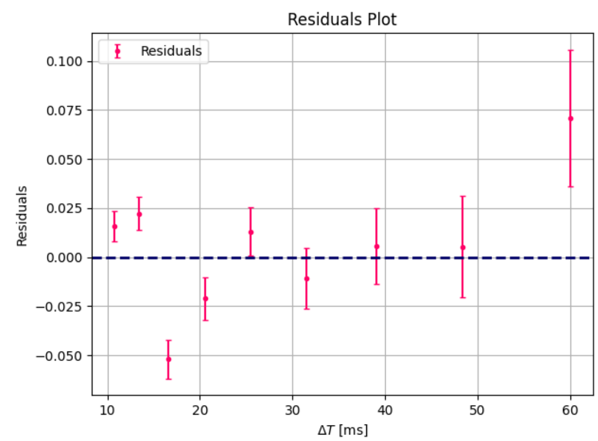



FIG. 5: Plot of the experimental data obtained measuring the maximum amplitude of the spin echo signal as a function of the delay between $\pi/2$ and $\pi$-pulses.
(The error bars are too little to be seen in this scale).




(a) (The error bars are too little to be seen in this scale).




(b)

FIG. 6: Linearized fit of the exponential decay of spin echo amplitudes

From the previous results, it is also possible to give an estimate of the inhomogeneity of the field:
$\Delta B = \frac{T_2^{*-1} - T_2^{-1}}{\gamma_p} = (236 \pm 7)\ \mu\mathrm{T}$

## CONCLUSIONS

In conclusion, we present the following summary of the experimental values:

- Maximum magnitude of the magnetization vector $M = (125 \pm 10)\ \frac{\mu\mathrm{J}}{\mathrm{T}}$
- FID decay constant ${T_2}^* = (99 \pm 3)\ \mu\mathrm{s}$
- Spin-spin relaxation time $T_2 = (31.7 \pm 0.4)$ ms
- Field inhomogeneity: $\Delta B = (236 \pm 7)\ \mu\mathrm{T}$

[1] Betta, Liguori, Pietrosanto. Propagation of uncertainty in a discrete Fourier transform algorithm. https://doi.org/10.1016/S0263-2241(99)00068-8
[2] The casual error is estimated considering a uniform distribution over a maximum error of 1 mm.
[3] Here we use the Fourier transform definition for frequencies: $\mathscr{F}[f(t)](\xi) = \int e^{2\pi\xi \cdot t} f(t) dt$