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Pulsed NMR measurements on glycerin and
characterization of a NdFeB permanent magnet for
compact NMR applications

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Abstract

Nuclear Magnetic Resonance (NMR) is one of the most powerful and widely used techniques for investigating the structural and dynamical properties of matter, with applications ranging from fundamental physics to chemistry, materials science, and biomedical research. In this thesis, a pulsed NMR setup based on an electromagnet was characterized and used to perform measurements on glycerin, a well-established reference sample for relaxation time studies. The experimental activity included the optimization of the radiofrequency excitation and detection chain, the implementation of pulse sequences, and the measurement of NMR signals to determine the characteristic relaxation parameters of the sample. In addition, the thesis investigated the feasibility of replacing the electromagnet with a compact NdFeB permanent-magnet system. This study focused on the design and characterization of the magnetic field generated by permanent magnets, in order to assess whether a magnetic field homogeneity at the level of 10^{-4} over the sample volume can be achieved, as required for pulsed NMR measurements. The results demonstrated the need for shim coils in order to develop a compact, energy-efficient NMR instrument based on permanent magnets.

1. Fundamentals of nuclear magnetic resonance

This section explains how the behavior of nuclei, in particular of their intrinsic property known as *spin*, in magnetic fields is used in NMR spectroscopy.

1.1 Larmor precession

The magnetic moment $\vec{\mu}$ of a nucleus is proportional to its spin angular momentum according to the following expression:

$$\vec{\mu} = \gamma \vec{I} \quad (1.1)$$

where γ is the gyromagnetic ratio, which for protons is $2,675 \times 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$. This constant can be rewritten in terms of the nuclear magneton μ_N times a dimensionless factor g_I

$$\gamma = \frac{\mu_N g_I}{\hbar} = \frac{g e}{2m_P} \quad (1.2)$$

where e and m_P are respectively the elementary charge and the mass of the proton. The hamiltonian that describes the energy of this magnetic moment in a magnetic field B is

$$\hat{H} = - \hat{\mu} \cdot B \quad (1.3)$$

If the magnetic field conventionally defines the z-direction and has a magnitude of B_0 , then the expression 1.3 becomes

$$\hat{H} = - \hat{\mu}_z \cdot B_0 = - \gamma B_0 \hat{I}_z \quad (1.4)$$

Knowing from quantum mechanics that the eigenvalues of the operator $\hat{I}_z$ for the z-component of the spin angular momentum are $m_I \hbar$, we can demonstrate that the only energies levels allowed for the nucleus are

$$E_{m_I} = - \gamma \hbar B_0 m_I \quad (1.5)$$

For nuclei of spin $I = 1/2$ such as protons, the energy difference between the two states is $\gamma\hbar B_0$, so transition can be induced by RF pulses of resonant frequency ν (see Fig 1.1).

$$\nu = \frac{\gamma B_0}{2\pi} \quad (1.6)$$

The same situation can be described from a semiclassical point of view, according to which a nucleus of moment $\vec{\mu}$ behaves like a bar magnet: if placed in a magnetic field $\vec{B}_0$ it will experience a torque

$$\vec{\tau} = \vec{\mu} \times \vec{B}_0 = \frac{d\vec{I}}{dt} = \frac{1}{\gamma} \frac{d\vec{\mu}}{dt} \quad (1.7)$$

that would cause a precession of $\vec{\mu}$ about the direction of $\vec{B}_0$ (see Fig 1.2). The rate of precession is called the Larmor precession frequency ν_L , which is the same as the resonant frequency of equation 1.6

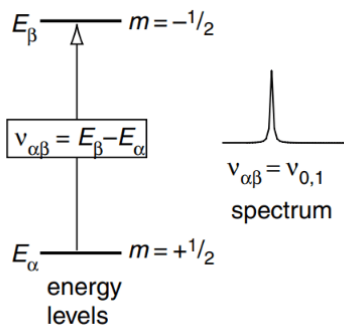


Figure 1.1: The transition between the two energy levels of a spin-half is allowed, and results in a single line at the Larmor frequency of the spin.

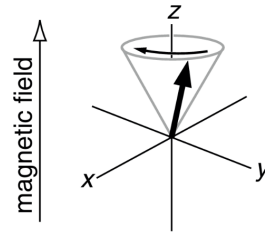


Figure 1.2: Precession of $\vec{\mu}$ about the direction of $\vec{B}_0$.

1.2 NMR techniques

1.2.1 Net magnetization and RF excitation

NMR signals arise from the collective behavior of a large number of nuclei in a macroscopic sample. Therefore, it is necessary to define the net magnetization $\vec{M}$ of the sample as the vector sum of all individual moments $\vec{\mu}_i$. Its projection onto

the z-axis, called *longitudinal magnetization*, is:

$$M_z = \sum \gamma \hbar m_{Ii} = \frac{1}{2} \gamma (N_+ - N_-) \quad (1.8)$$

where N_+ and N_- are the numbers of protons in the $+\frac{1}{2}$ and $-\frac{1}{2}$ state, respectively. In the presence of a magnetic field, a sample of protons at an absolute temperature T will reach thermal equilibrium with more spins in the lower energy (spin-up) state; the ratio of the populations is given by the Boltzmann factor:

$$\frac{N_-}{N_+} = e^{-\Delta E/kT} = e^{-\gamma \hbar B_0/kT} \quad (1.9)$$

From equations 1.8 and 1.9, it is clear that, to have $M_z \neq 0$, a magnetic field B_0 must be applied along the z-axis. To observe Larmor precession we also need to achieve a non-zero *transverse magnetization*. In pulsed NMR, radiofrequency is employed to tilt the net magnetization by a certain angle relative to its equilibrium alignment with the z-axis (see Fig 1.3).

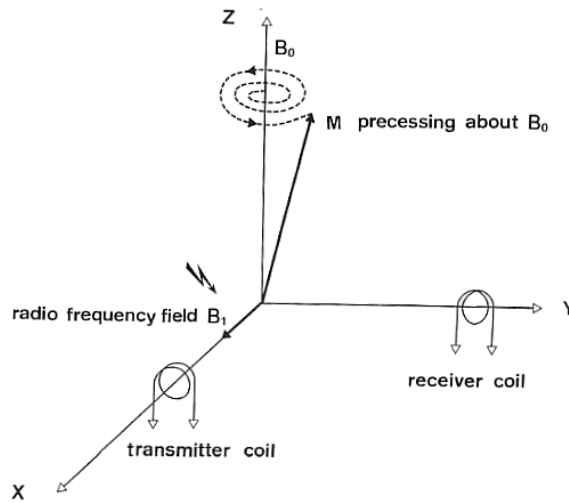


Figure 1.3: Pulsed NMR. The presence of an alternating voltage in the receiver coil arises by Faraday's law $V = -d\Phi/dt$ because of the precession of $\vec{M}$. In our apparatus the transmitter coil that produces B_1 with radiofrequencies is the same that collects the signal. Adapted from [7]

The AC voltage in the transmitter coil must be at a frequency near ν_L , creating a linearly polarized magnetic field $\vec{B}_1$ that can be expressed as the sum of two counter-rotating circularly polarized components:

$$\begin{aligned}\vec{B}_1(t) &= B_1(\cos \omega t \hat{x} - \sin \omega t \hat{y}) \\ &\quad + B_1(\cos \omega t \hat{x} + \sin \omega t \hat{y})\end{aligned}\tag{1.10}$$

By applying the so called *rotating wave approximation* we can neglect the counter-rotating component (which has no significant interaction with the magnetization) and write the $\vec{B}_1$ field as

$$\vec{B}_1 = B_1(\cos \omega t \hat{x} - \sin \omega t \hat{y})\tag{1.11}$$

The equation that describes the motion is:

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times (\vec{B}_0 + \vec{B}_1(t))\tag{1.12}$$

The time dependence caused by the presence of the RF field is easier to manage by adopting a **rotating frame**, that rotates around the z-axis at the Larmor frequency. In the rotating frame $\vec{B}_1$ appears stationary; the net magnetization is tilted in the xy-plane and Larmor-processes flat on it. To adapt equation 1.12 to the new reference frame we use Poisson's equation for a general time-dependent vector $\vec{v}$ in a rotating frame of angular velocity $\vec{\omega}$.

$$\frac{d\vec{v}}{dt} = \left(\frac{d\vec{v}}{dt} \right)' + \vec{\omega} \times \vec{v}\tag{1.13}$$

Therefore, the new dynamic equation becomes:

$$\left(\frac{d\vec{M}}{dt} \right)' = \gamma \vec{M} \times \left(\vec{B}_0 + \vec{B}_1 + \frac{\vec{\omega}}{\gamma} \right)\tag{1.14}$$

where the term multiplied to $\gamma \vec{M}$ is the effective field $\vec{B}'$. The net magnetization processes clockwise about the effective field at the so called *Rabi frequency* $\omega' = \gamma B'$. Note that for exact resonance $\omega = \omega_L = \gamma B_0$, the effective field consists entirely of $\vec{B}_1$ along the rotating x' -axis. Therefore, with the so-called $\pi/2$ pulses, $\vec{M}$ will be tilted by 90° towards the rotating y' -axis. In a π -pulse the duration of the pulse is doubled and alignment of $\vec{M}$ with $-\hat{z}$ is obtained.

1.2.2 Relaxation mechanisms

Relaxation is the process by which the spins return to equilibrium after a pulse. The rate of relaxation is influenced by the physical properties of the molecule and

the sample, so a study of relaxation phenomena can provide information on these properties.

The process that restores the equilibrium nonzero M_z involves the release of energy from the spins to the surroundings to enable the transition $\beta \xrightarrow{\gamma\omega_0} \alpha$. This **longitudinal relaxation** follows an exponential law characterized by the *spin-lattice relaxation time* T_1 .

$$M_z(t) = M_0 - (M_0 - M_i)e^{-t/T_1} \quad (1.15)$$

where M_0 M_i are the values of M_z at equilibrium and at $t = 0$, respectively.

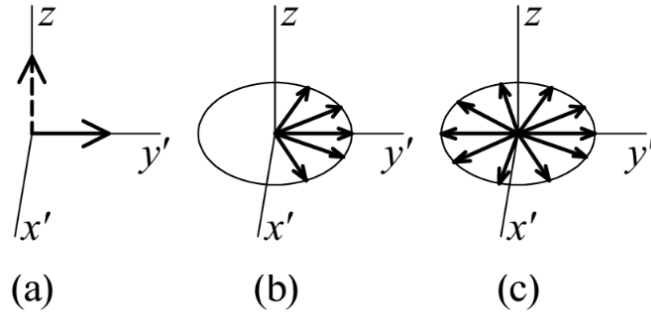


Figure 1.4: (a) With $\pi/2$ -pulse the spins are Rabi-precessed to the rotating y' -axis. (b) Afterward, transverse magnetization decreases because of individual spins precessing at slightly different angular velocities. (c) The transverse magnetization cancels out when the spins spread in the xy -plane. From reference [8].

The **transverse relaxation** described in Fig 1.4 is called *spin-spin relaxation*, and it is induced by phase loss between the individual spins: the experience of a slightly different local magnetic field makes them precess at faster or slower Larmor frequencies. This process occurs exponentially with a time constant T_2 known as *spin-spin relaxation time*.

$$M_{xy} \propto e^{-t/T_2} \quad (1.16)$$

Experimentally, the transverse decay that produces the signal picked up by the receiver coil, called free induction decay (FID), is best described by another expression:

$$M_{xy}^{exp}(t) = M_i e^{-t/T_2^*} \quad (1.17)$$

This trend comes from a combination of spin-lattice and spin-spin relaxation, added to the prevailing effect of the dephasing of the spins due to field inhomogeneity

$\Delta \vec{B}_0$ over the volume of the sample. Therefore, the characteristic time constant T_2^* is defined as

$$\frac{1}{T_2^*} = \frac{1}{T_1} + \frac{1}{T_2} + \gamma \Delta B_0 \quad (1.18)$$

In pulsed NMR it is possible to derive T_2^* from the a signal proportional to Eq. 1.17 that arises immediately after a RF pulse. T_1 is accessible with the inversion recovery technique (which will not be treated in this work). To measure T_2 , which usually is much longer than T_2^* , it is necessary to cancel the effect of field inhomogeneities: this can be achieved with the spin echo sequence.

1.2.3 Pulse sequence in the rotating frame

Illustration 1.5 shows how the pulse sequence $\pi/2 - \pi$ gives rise to the echo.

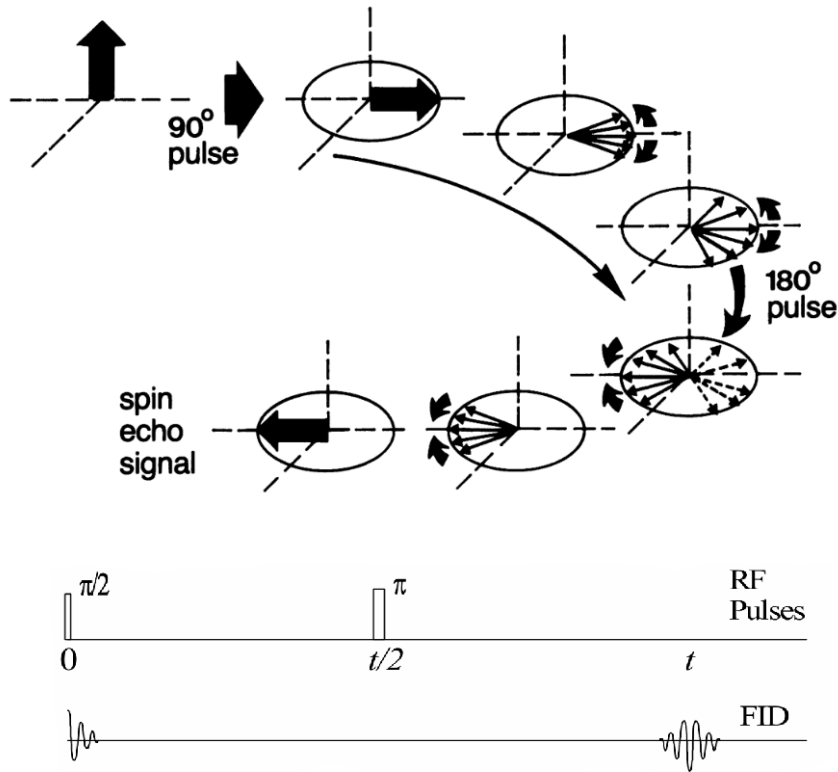


Figure 1.5: Spin echo created by $\pi/2 - \pi$ pulse sequence. Adapted from [6].

Initially, the $\pi/2$ pulse tilts the net magnetization on $y' - axis$; thereafter, dephasing of the spins occurs due to nonuniform $\vec{B}_0$. A π -pulse is applied at the *delay time* $t = \tau$, before the moments eventually spread into a uniform pancake in the xy -plane. The collection of spins is flipped by this "refocusing" pulse: now the moments that process at $\nu > \nu_L$ are behind the moments that process at $\nu < \nu_L$. At time $t = 2\tau$, the fastest spins reach the slowest, and their realignment produces the echo signal. The second FID will have a smaller amplitude than the original because spin-spin relaxation occurs during the time between the two pulses. The reduction in FID magnitude for increasing τ follows T_2 rather than T_2^* , as it arises from time-dependent variations in the local field (spin-spin relaxation), not from static variations of the applied B_0 .

1.2.4 FID signal and its FFT

It is convenient to think of the FID signal as arising from a vector of length S_0 rotating at frequency Ω (see Fig 1.6); its components $S_x(t)$ and $S_y(t)$ are the real and imaginary part of complex signal $S(t)$, which decays exponentially over time:

$$\begin{aligned}
 S(t) &= (S_x(t) + iS_y(t)) \exp\left(\frac{-t}{T_2^*}\right) \\
 &= (S_0 \cos \Omega t + iS_0 \sin \Omega t) \exp\left(\frac{-t}{T_2^*}\right) \\
 &= S_0 \exp(i\Omega t) \exp\left(\frac{-t}{T_2^*}\right)
 \end{aligned} \tag{1.19}$$

Fourier transformation of signals like this gives the frequency domain signal, called spectrum, which has both real and imaginary parts. As illustrated in Fig 1.7, the real part shows an *absorption mode* line, that has a shape of a Lorentzian function; the imaginary part gives a lineshape known as the *dispersion mode*.

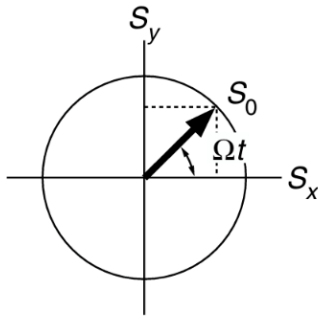


Figure 1.6: Rotating vector representation.

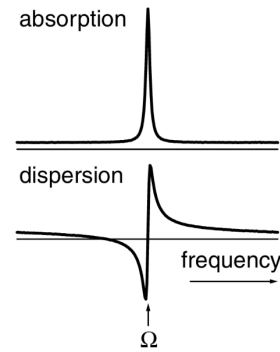


Figure 1.7: Absorption and dispersion signals.

We are interested in the absorption peak to verify the frequency at which it occurs (that should correspond to the one of the demodulated signal) and its full width at half maximum (FWHM), as it is related to T_2^* by

$$FWHM = \frac{1}{\pi T_2^*} \quad (1.20)$$

In most cases, computing the FFT of the raw signal does not provide a decent spectrum to work with. The following corrections are widely used during the data processing stage to improve the quality of the spectrum:

- **FID data selection**

Data corrupted by instrument faults must be filtered out of the FID signal (further details will be discussed in section 3.1).

- **DC offset removal**

During data acquisition, a non-zero voltage bias might be added by the analog receiver hardware. This offset must be removed by subtracting the average of the signal from the signal itself, to avoid an artificial central peak at 0 Hz in the spectrum.

- **Zero-filling**

The signal is converted in digital form in a series of data points. Its Fourier transform also consists of a series of data points. To better define the line in the spectrum, a set of zeros can be added to the signal. This does not improve resolution but makes the data points more closely spaced (see Fig 1.8).

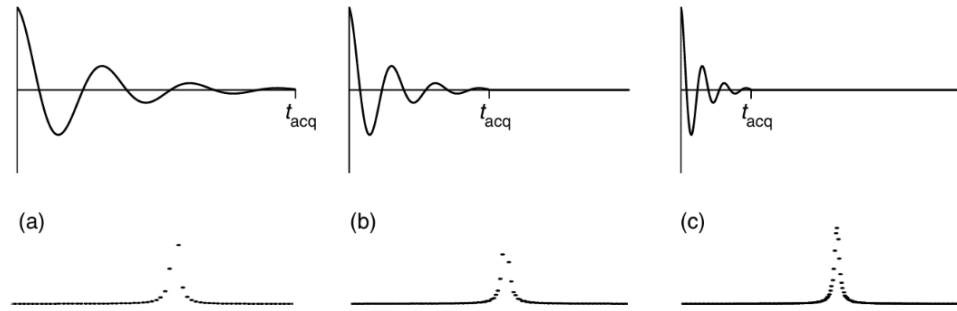


Figure 1.8: (a) Few data points represent the spectrum obtained with just experimental data. In (b) and (c) a set of zeroes is added at the end of the FID, resulting in a better defined line in the spectrum. Illustration taken from [5].

- **Zero order phase correction**

In most cases, the spectrum obtained computing the FFT of the raw signal does not present pure absorption lineshape. This is due to the phase shift ϕ that corresponds to the unknown phase of the signal at time zero.

$$S(t) = S_0 \exp(i\phi) \exp(i\Omega t) \exp\left(-\frac{t}{T_2}\right) \quad (1.21)$$

The zero order phase correction is applied by iteratively searching for the right $\phi_{corr} = -\phi$ that restores pure absorption spectrum for $\exp(i\phi_{corr})S(t)$.

Once corrections are applied to the FID signal, it is possible to compute the Fourier transform and fit it with a Lorentzian function of form

$$y = y_0 + A \left(\frac{FWHM^2}{4(x - f_0)^2 + FWHM^2} \right) \quad (1.22)$$

where A is the maximum height of the peak centered at the frequency f_0 . The vertical offset y_0 is ideally zero for Fourier transform of perfect FID signal. The full width at half maximum (FWHM) has already been mentioned in Eq. 1.20.

2. Experimental apparatus

2.1 NMR setup

The electronic circuit consists of the following components:

- RF generator (mod. Tektronix AFG1062).
- Electronic pulses system based on CPLD(Complex Programmable Logic Device, mod. epm570) and controlled by a LabVIEW program.
- Peripheral Interface Controller (PIC) that converts the digital signal into an analogue one.
- A switch (mod. ZASWA-2-50DRA+) that allows to acquire only the signal induced by the sample by closing the RF gate when the pulse ends.
- Various amplifiers.
- A mixer that demodulates the signal down to $\sim 10kHz$ to reduce reflections in the coaxial cable.

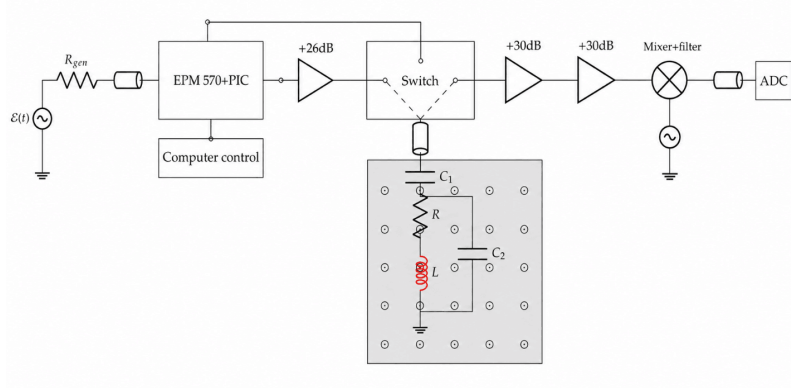


Figure 2.1: Electronic circuit used for the NMR experiment. The sample is inside the coil of the RLC circuit (shown in red).

The impedance of the RLC circuit has been accurately matched to the impedance of the transmission line ($50\ \Omega$). The procedure for obtaining a good signal included the following steps:

1. Determine the resonant frequency ν_0 of the RLC circuit
2. Adjust the Larmor frequency ν_L of the sample to match ν_0

In the first step, a 3-port directional coupler (see Fig 2.2) is employed: the input port is connected to the RF source, which generates the RF waves that pass through the transmission port and enter the RLC circuit. If the circuit is off-resonance, part of the wave is reflected back and travels through the coupled port into the oscilloscope (HDO4000A High Definition Oscilloscope). By a sweep of frequencies it is possible to find the right ν_0 that corresponds to a minimum in reflected power (Fig 2.3). The minimum was found at $\sim 25\text{MHz}$, so the carrier frequency was set to 25,13 MHz.

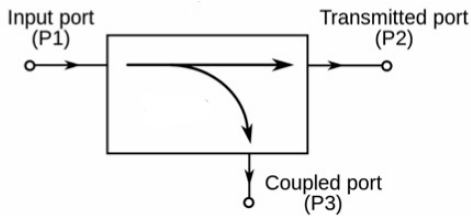


Figure 2.2: Directional coupler scheme

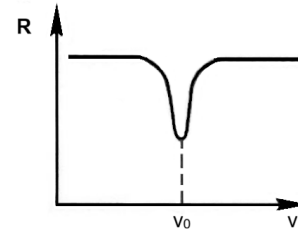


Figure 2.3: Reflected power (R) for different frequencies

For the second step, adjustments were made to the current flowing in the electromagnet (Bruker Magnet B-E 15 in Fig 2.4) to generate a magnetic field B_0 sufficient to bring the sample into resonance with the circuit ($\nu_0 = \nu_L$).

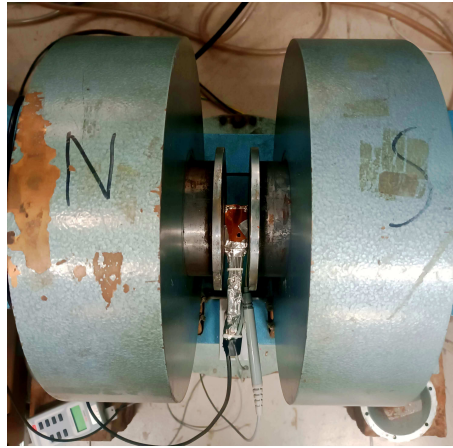


Figure 2.4: Electromagnet used to provide for B_0 . A Hall probe, positioned near the sample, was employed to keep track of the magnetic field.

The dependence of field strength on current and distance between the poles is plotted in Fig 2.5. The effective field was measured with a Hall probe; it was necessary to monitor variations in the magnetic field caused by changes in temperature, occurred despite the water-cooling system.

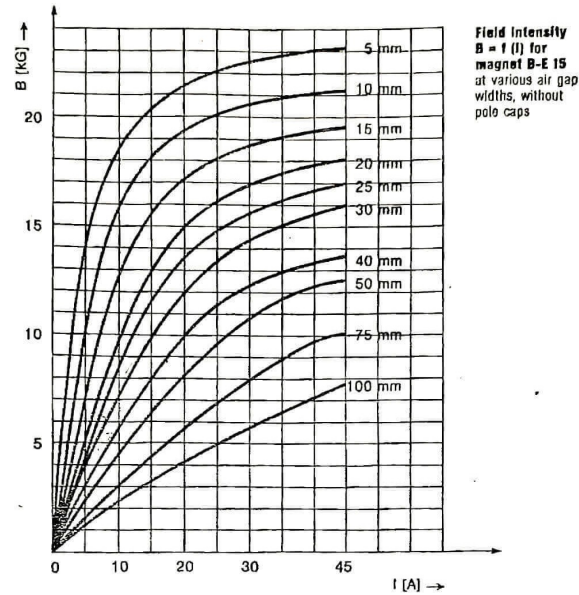


Figure 2.5: Graph of magnetic field produced vs current with different space between poles

Initially, the current was set to obtain a field based on the expression:

$$B_0^{teor} = \frac{\nu_L}{\gamma} \approx \frac{25,13 \text{ MHz}}{42,58 \text{ MHz/T}} \approx 0,590 \text{ T} \quad (2.1)$$

Then fine regulations were made to maximize the signal visible on the oscilloscope screen. The ultimate applied field was $B_0 = 0,592 \text{ T}$.

2.2 Permanent magnet setup

In order to determine the field homogeneity of the NdFeB permanent magnet it is necessary to measure the field strength between its plates. For this purpose, a 3-Channel Gaussmeter (Model 460 Lake Shore Cryotronics) has been used: the probe was fixed on a linear translation stage governed by a micrometric screw, so as to allow controlled movement only along the z-axis, parallel to the plates (see Fig 2.6 and Fig 2.7). The probe was positioned equidistant from the cylindrical plates and halfway up their height. Both the stage and the magnet were firmly clamped to the optical table to prevent movements during the measurement.

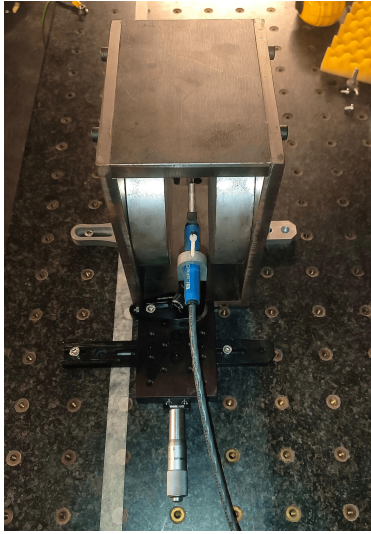


Figure 2.6: Setup with the gaussmeter probe fixed on a translation stage

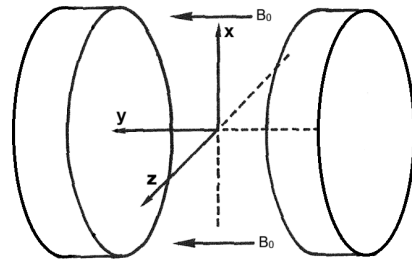


Figure 2.7: Convention adopted for the axes

The gaussmeter returned three space direction values of the magnetic field on the screen. The environmental background was measured using the ‘Zero probe’ function, with the probe positioned away from the magnet on the optical table.

3. Results

3.1 Measurement of T_2^*

The pulse sequence $\pi/2 - \pi$ described in Sec 1.2.3 has been adopted to detect the following signal. The duration of $200\ \mu s$ and the frequency $\nu \sim 25\text{MHz}$ of the pulse have been chosen to maximize the amplitude of the FID.

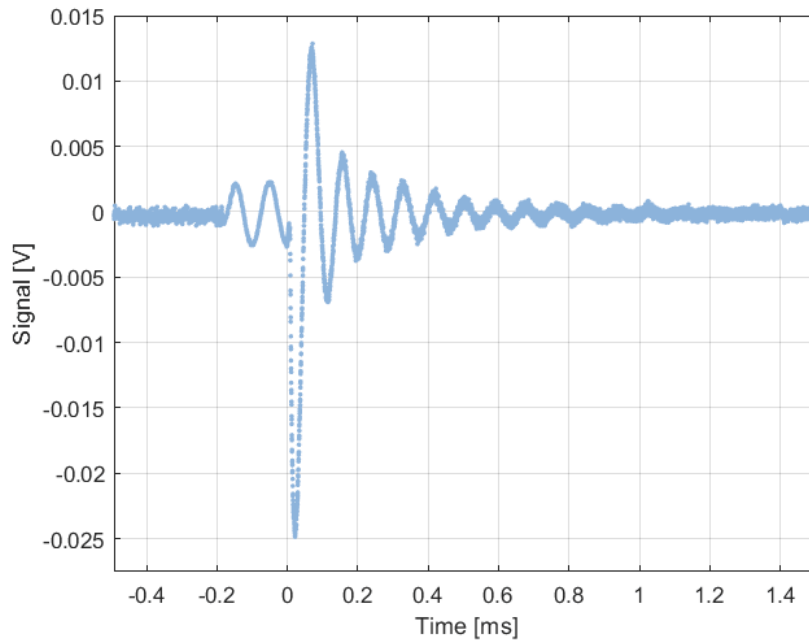


Figure 3.1: FID signal. Time is displayed as negative before the pulse drop.

The first part of the FID presents distorted peaks that can be caused by elements such as:

- Electronic Ring-Down: after the pulse, the electronic components of the receiver require a finite time to recover, leaving a residual oscillation that adds to the useful signal.
- Acoustic ringing: RF currents passing through the coil within B_0 generate Lorentz forces, causing mechanical vibrations in the probe components that induce spurious electrical signals.

Therefore, the initial part (up to time $t \sim 0,1 \text{ ms}$) has not been considered in the following data elaborations.

In Sections 1.2.2 and 1.2.4 we saw that the characteristic relaxation time T_2^* can be extracted from the exponential decay of the FID (Method A) or from the FWHM of its Fourier transform (Method B).

There are a few different options to choose from to fit the signal in Method A. The exponential decay of the oscillation amplitude (determined by identifying the peaks with a smoothing spline) is illustrated in Fig. 3.2.

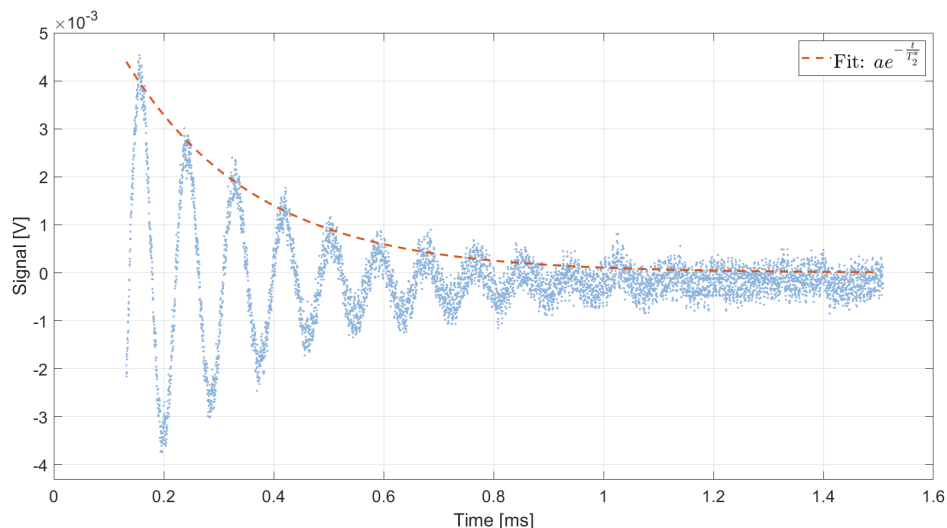


Figure 3.2: Exponential fit of the FID signal, calculated with the first four peaks. Subsequent peaks were not taken into account due to low Signal-to-Noise ratio, but it can be seen that the red line accurately reflects the decay of the signal down to zero.

The signal can also be represented by an exponentially damped cosine function, as represented in Fig 3.3.

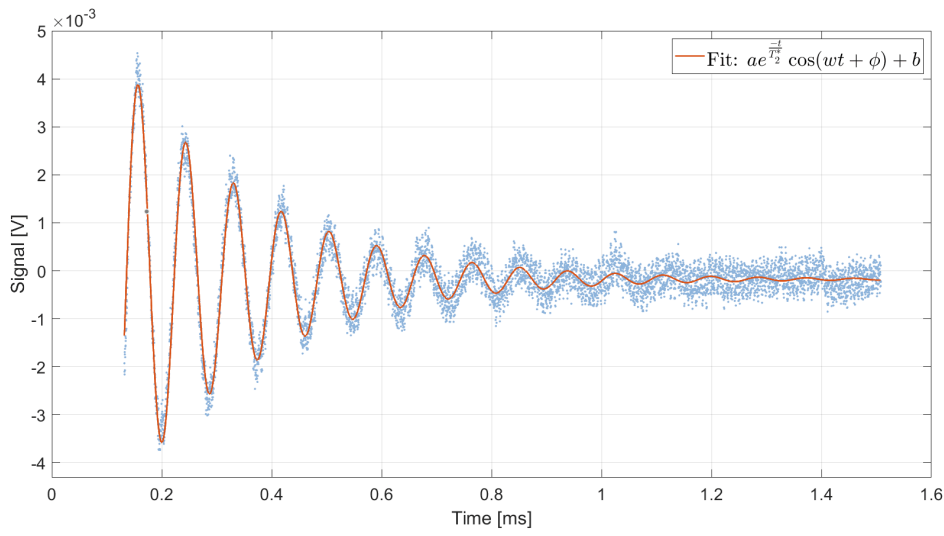


Figure 3.3: Exponentially decaying cosine fit of the FID signal. The angular velocity ω is initialized at a value $\sim 2\pi \times 10 \text{ kHz}$ as we expect from the demodulation of the signal. The fit returned a value ω from which we calculate the frequency $f_0 = \frac{\omega}{2\pi} = (11,518 \pm 0,008) \text{ kHz}$, similar (but yet not compatible within the confidence interval) to the result obtained with the FFT, which will be discussed later.

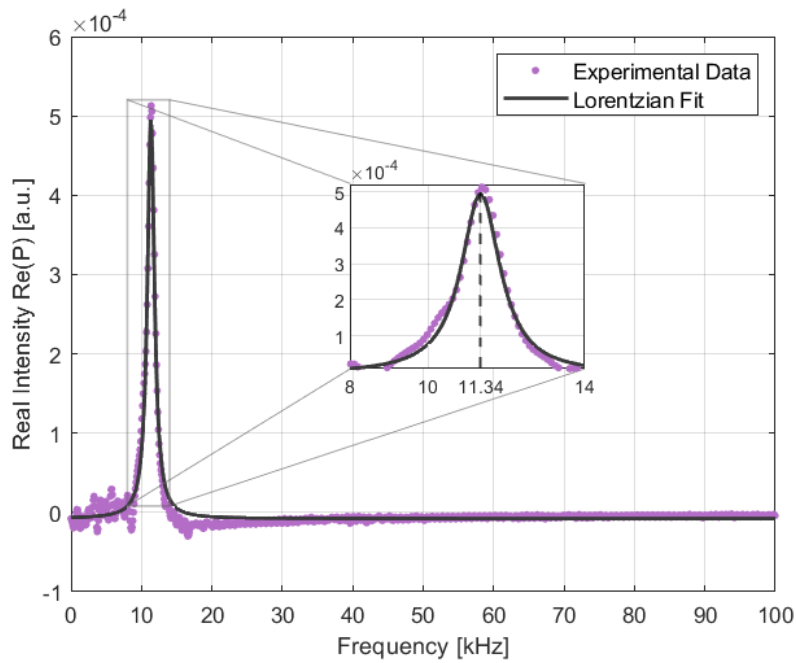


Figure 3.4: Real FFT of the FID signal fitted with a Lorentzian function.

Method B instead requires computing the Fourier transform of the signal, which has to be previously corrected with the techniques discussed in Sec 1.2.4. The peak was found at a frequency $f_0 = (11, 34 \pm 0, 01) \text{ kHz}$ with $FWHM = (1, 209 \pm 0, 02) \text{ kHz}$ (see Fig 3.4).

The frequency is not compatible with the expected value found with the cosine fit. This may be due to the main difficulty of the FID signal correction: the adjustment of the phase to obtain a pure absorption lineshape is rather subjective, and it is hindered by the noise to the left of the peak. If the spectrum still contains part of the dispersion mode, the peak will appear distorted. The same critical issue has compromised the measure of T_2^* , resulting in a value that differs from those obtained using Method A. Measures are compared in Table 3.1.

Fit function	$T_2^* [\mu s]$
Exponential for first 4 peaks	234 ± 50
Exponentially decaying cosine	247 ± 3
FWHM of the FFT	263 ± 4

Table 3.1: Comparison of T_2^* values extracted with different methods. The confidence interval was derived from the propagation of errors returned by the Curve Fitter tool of MATLAB software

Peak fitting with exponential is hampered by the estimation of the peaks themselves and by their limited number, as the smaller peaks have a poorer signal-to-noise ratio. This results in a T_2^* estimate with greater uncertainty.

3.2 Measurement of T_2

The value of the transverse relaxation time T_2 is measured by fitting the echo amplitude obtained with the pulse sequence $\pi/2 - \pi$ for different delay times τ (see Fig 3.5) with the equation:

$$a = e^{-\frac{\tau}{T_2}} \quad (3.1)$$

The amplitude has been measured with the oscilloscope tool that calculates the peak-to-peak distance of the echo (Fig 3.6). The errors displayed by the software are calculated from the standard deviation of 20 measurements. The resulting relaxation time is $T_2 = (35, 6 \pm 1) \text{ ms}$.

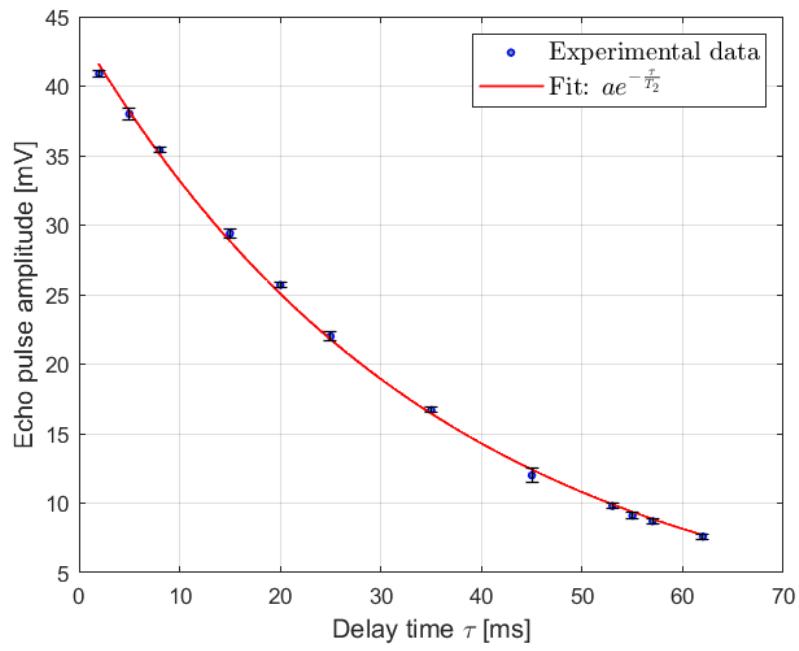


Figure 3.5: Amplitude of the echo signal for different delay times τ between $\pi/2$ - π pulses.

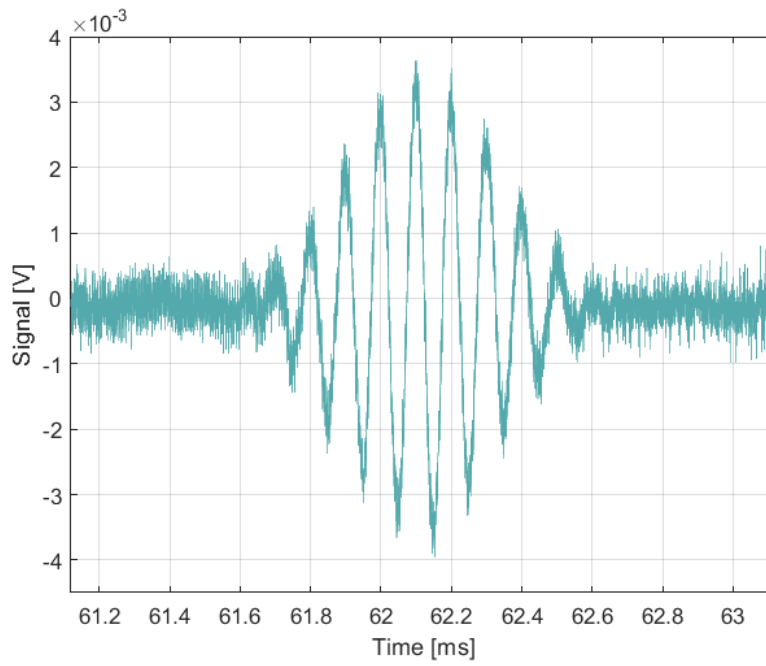


Figure 3.6: Echo signal

3.3 Measurement of field homogeneity of NdFeB permanent magnet

Field homogeneity is calculated with the expression:

$$homogeneity = \frac{\Delta B}{\bar{B}} \quad (3.2)$$

Where ΔB is the difference between the maximum and minimum value of the field in the considered area. To simplify, calculations were carried out only along the z-axis parallel to the plates (the least homogeneous direction) within a cubic region of 1 cm^3 , as the sample used in the NMR experiment has similar dimensions.

Experimental measurements yielded an average value of $\bar{B} = 0,561 \text{ T}$, and a field homogeneity of $1,03 \times 10^{-3}$. In order to facilitate future work on optimizing uniformity through the addition of correction coils, a simulation was created in COMSOL, here reported in Fig 3.7 by courtesy of the researcher Gerardo Iannone.

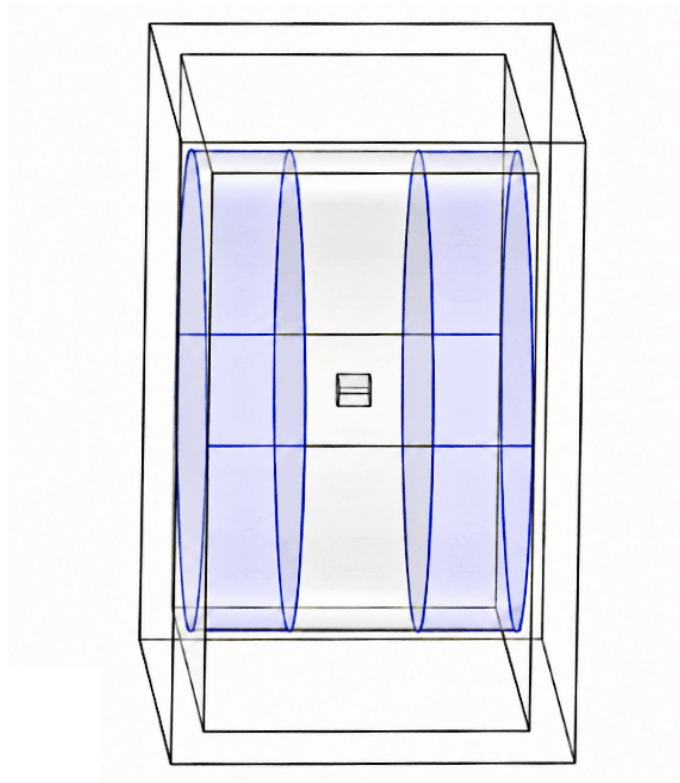


Figure 3.7: Magnet modelling on COMSOL. The magnetic field is simulated in the cubic region of 1 cm^3 between the blue plates.

The model is designed to replicate the experimental trend of the field along the z-axis, especially in the region of interest (see Fig 3.8).

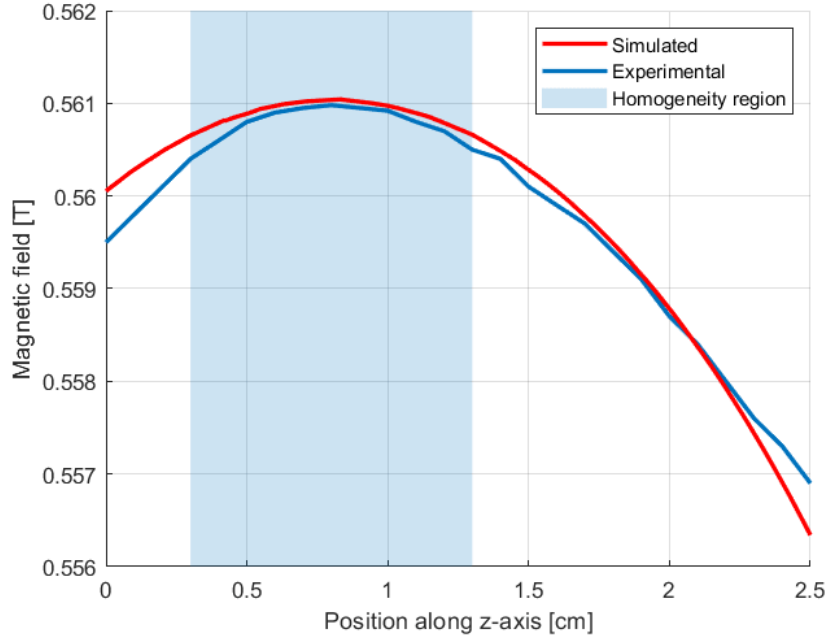


Figure 3.8: Comparison of experimental and simulated data. The simulation well reproduces the measured values in the 1 cm area used to calculate field homogeneity.

This model proves useful for planning future corrections with shim coils to improve uniformity. In fact, a higher value of homogeneity is required to at least replicate the electromagnet performance. To demonstrate the necessity of better homogeneity to enable the measures discussed in this thesis, a simulation is presented below.

3.4 Comparison of electromagnet and permanent magnet

First, we need to quantify the field homogeneity of the electromagnet. From Eq 1.18 we can derive ΔB and divide it by the field measured with the Hall probe $B_0 = 0,592 \text{ T}$. Spin-lattice relaxation has been neglected ($\frac{1}{T_1} \approx 0$): in glycerin the value of T_1 ranges from 20 ms to 2 s, depending on the viscosity [2]; however, the factor with the greatest impact is T_2^* .

$$\frac{\Delta B}{B_0} = \left(\frac{1}{T_2^*} - \frac{1}{T_2} \right) \frac{1}{\gamma B_0} \quad (3.3)$$

whose value is $2,5 \times 10^{-5}$ if we consider T_2^* derived from the exponentially decaying cosine fit. Another value can be extracted from the FFT of the FID because of the relationship between FWHM and the frequency dispersion:

$$FWHM = \frac{\gamma \Delta B}{2\pi} \quad (3.4)$$

Recall that $\nu_0 = \frac{\gamma B_0}{2\pi}$. Therefore, homogeneity can be calculated with

$$\frac{\Delta B}{B_0} = \frac{FWHM}{\nu_0} \quad (3.5)$$

Taking care not to confuse the frequency $\nu_0 = 25,21 \text{ MHz}$ of the carrier RF with the demodulated $f_0 \approx 10 \text{ kHz}$. The homogeneity value found is $4,8 \times 10^{-5}$. It should be noted, however, that this calculation depends on the efficiency of the data pre-processing prior to the FFT, for which the definition of a correctly phased spectrum is rather subjective [5]. For the purpose of the simulation, there is little difference between choosing the first or second value; what matters is the order of magnitude of $\approx 10^{-5}$. The simulation was created using LabVIEW software. It is structured into the following units:

- a For loop that scales the loop index to generate the time variable t with the same sampling rate as the oscilloscope in the laboratory.
- A code that contains the declarations of variables and the equations to compute the theoretical form of the signal.
- A gaussian white-noise generator
- Fourier transform tool.
- Two screens to visualize the signal and the FFT.

Parameters such as the frequency of the demodulated signal or the dead time of the switch are set based on the values of the laboratory activity. The FID signal is simulated by an exponentially decaying cosine whose maximum amplitude a_{max} depends on the duration of the first pulse t_{90° .

$$a_{max} = A \sin(\omega_1 t_{90^\circ}) \quad (3.6)$$

where A is set to obtain a signal similar to the experimental one and ω_1 is the nutation angular velocity (or Rabi angular velocity). It corresponds to the angular velocity at which the magnetization vector is tilted towards the xy -plane. Its value is set based on the pulse duration that experimentally gave the strongest signal (and is therefore thought to have tilted the magnetization to $\pi/2$)

$$\omega_1 = \frac{\pi/2}{t_{90^\circ}} \quad (3.7)$$

The signal frequency is already set to f_0 , rather than being set to the carrier frequency ν_0 and then demodulated. This does not affect the simulation, as demodulation merely shifts the peak of the spectrum without altering its shape. The signal is computed starting from the end of the pulse, but is only displayed after the dead time during which the switch is open ($5\mu s$). The spin echo envelope is modeled with a hyperbolic secant (sech) centered at 2τ from the center of the first pulse. This shape is more accurate than a rising and falling exponential: in reality, B_0 continuously varies within a physical sample, causing a gradual realignment of the spin phases and resulting in a rounded curve rather than a sharp change. The amplitude of the echo is governed by τ , as already mentioned in Sec 1.2.3. The simulation was first run with the homogeneity of the electromagnet (to verify that the result was consistent with the experimental data) and then with homogeneity in the permanent magnet to predict the shape of the signal (see Fig 3.9 and Fig 3.10).

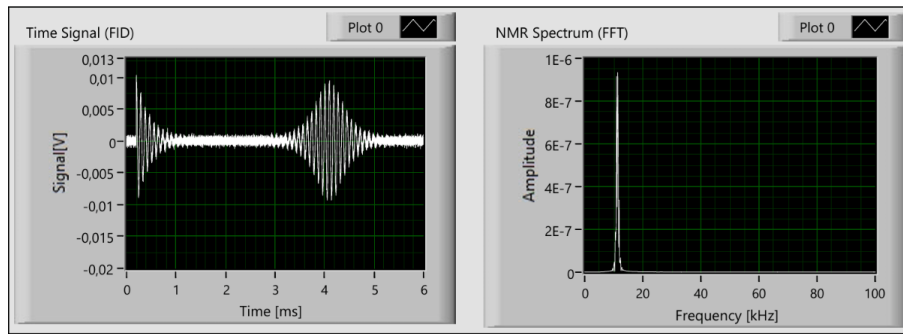


Figure 3.9: Simulation of the signal with electromagnet homogeneity

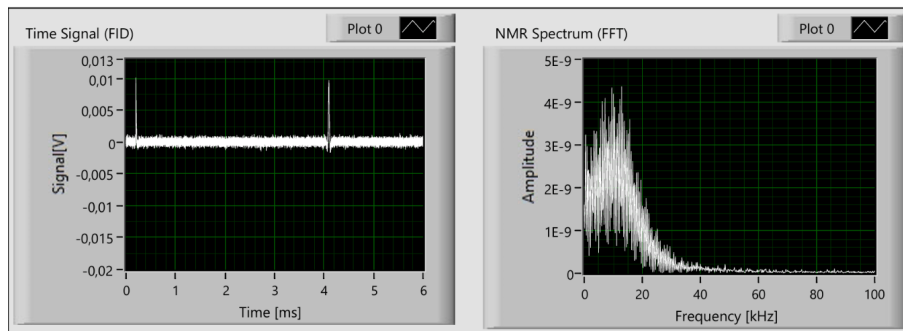


Figure 3.10: Simulation of the signal with permanent magnet homogeneity

From Fig 3.10 it is evident that a field homogeneity of 10^{-3} is not sufficient to guarantee a good signal.

4. Conclusions

The experimental activity involved the measurement of the transverse relaxation time T_2 and the effective transverse relaxation time T_2^* of a glycerin sample using pulsed NMR. The apparatus included an electromagnet providing a static magnetic field $B_0 = 0.592\text{ T}$, which produces a non-zero equilibrium magnetization along the field direction. By applying RF pulses, the magnetization is tilted into the transverse plane, giving rise to a free induction decay (FID) signal. The decay of the transverse magnetization is determined by the intrinsic spin-spin relaxation, characterized by T_2 , together with additional dephasing caused by static magnetic-field inhomogeneities. Their combined effect is described by the effective transverse relaxation time T_2^* .

The FID envelope was analyzed using different fitting approaches. An exponential fit to the first four local maxima yielded $T_2^* = (234 \pm 50)\mu s$, while fitting the entire signal with an exponentially decaying cosine gave $T_2^* = (247 \pm 3)\mu s$. An independent estimate, giving $T_2^* = (263 \pm 4)\mu s$, was obtained from the full width at half maximum (FWHM) of the resonance peak in the Fourier-transformed signal, assuming a Lorentzian lineshape. The three estimates are mutually consistent within their uncertainties.

The transverse relaxation time was measured using a $\pi/2 - \pi$ spin-echo sequence. Following the $\pi/2$ pulse, the spins dephase in the transverse plane. The subsequent π pulse reverses the phase evolution associated with static field inhomogeneities, leading to spin refocusing and the formation of an echo. From the decay of the echo amplitude, a value of $T_2 = (35,6 \pm 1.0)\text{ ms}$ was obtained. The measured relaxation times are compatible with the literature values reported in Ref. 2.

This thesis also investigated the possibility of replacing the electromagnet with a compact NdFeB permanent-magnet system. The magnetic-field inhomogeneity within a 1 cm^3 cubic region was evaluated using a COMSOL model validated against magnetic-field measurements performed with a three-channel Gaussmeter. The resulting relative field inhomogeneity, $\Delta B_0/B_0 = 1.03 \times 10^{-3}$, was then used as an input to a LabVIEW simulation to assess whether the resulting NMR signal would be suitable for reliable measurements. The results indicate that the proposed permanent-magnet system cannot replace the electromagnet in its present configuration and that additional field-correction techniques, such as shimming coils, would be required to achieve sufficient field homogeneity.

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