INTRODUCTION TO THE NMR FIELD-CYCLING TECHNIQUE AND BASIC INSTRUMENTATION

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**Relaxometry:** Larmor frequency dependence of a given NMR relaxation parameter

*Example:* \( T_1 = f(\nu_0) \) spin-lattice relaxation time

\[ \nu_0 = \gamma B / 2\pi \]
What is field-cycling?

Defines $\nu_0$
Why magnetic field cycling in NMR experiments?
Signal to noise ratio in NMR experiments

\[ S/N \propto B_0 \xi \sqrt{\frac{\eta Q V_s}{k_B T} \left( \frac{\nu_0}{\Delta \nu} \right)} \]

\[ S/N \propto B_p \xi \sqrt{\frac{\eta Q V_s}{k_B T} \left( \frac{\nu_d}{\Delta \nu} \right)} \]
Example 1: field-cycling NMR relaxometry

Bulk 8CB
- ISOTROPIC 323K
- NEMATIC 309K

$T_1 [\text{ms}]$ vs $\nu [\text{kHz}]$

$\nu^{1/2}$

$T_1 [\text{ms}]$ vs $\nu [\text{kHz}]$

- 8CB+Aerosil
- 8CB Bulk

323K
Example 2: nuclear quadrupole double resonance (NQDOR)
Example 3: zero field NMR

**Fig. 1.** Proton NMR spectra of barium chlorate hydrate $[\text{Ba(CIO}_3\text{)}_2\cdot 2\text{H}_2\text{O}]$. All $\text{H}_2\text{O}$ proton-proton vectors are coparallel in the unit cell. (a) High-field powder spectrum showing normal broadened $\text{H}_2\text{O}$ doublet. (b) High-field single-crystal spectrum. The sample is oriented in an arbitrary direction. The observed splitting depends on both intermolecular distance and orientation. (c) Zero-field powder spectrum. The major features are those predicted by the simple treatment given in the text for a pair of coupled spins of $\frac{1}{2}$. The observed splitting is a direct, orientation-independent measure of the intermolecular distance. The central peak arises from spins in crystallite orientations which did not evolve in zero field.
Example 4: electron-nuclear double resonance (ENDOR)

Detection of Anisotropic Hyperfine Transitions in Zero Magnetic Field Using Field-Cycling Techniques

G. Sturm, D. Kilian, A. Lotz, and J. Voitlander
Institut für Physikalische Chemie, Universität München, Butenandtstraße 5–13, D-81377 München, Germany


FIG. 2. Pulsed field-cycled ENDOR spectrum of a coal sample at 4.2 K obtained with our old field-cycling solenoid (see text). Echo intensity versus RF irradiation frequency in MHz. Two low-power microwave pulses of 300 ns length were used for the detection. (Bottom) Recovered EPR amplitude after irradiation in zero field. No accumulation. (Top) Equal experimental conditions, yet without RF irradiation. Experimental parameters: \( t_{\text{field}} = 2 \) s, \( t_{\text{cold}} = 0.5 \) ms, \( t_{\text{delay}} = 0.5 \) ms, \( t_{\text{excit}} = 0.8 \) ms, \( t_{\text{shift}} = 0.2 \) ms, \( t_{\text{det}} = 2 \) ms.
Quadrupole dips

NQR frequencies
I=1

\[ \nu_+ \]

\[ \nu_- \]

\[ \nu_0 \]

Larmor frequency
I=1/2

External magnetic field

DIP 1
DIP 2
DIP 3

Lattice

\( \mathcal{H}_Z \)
\( \mathcal{H}_Q \)

\( T_{CR} \)
\( T_z \)
\( T_Q \)
Example 5: field-cycling MRI

T₁ dispersion plot of volunteer’s thighs

FC inversion recovery images

Data acknowledged to David Lurie (Aberdeen)
Field-cycling: the roots

1949-1951:
Turner and Sachs, Ramsey and Pound (Cambridge).
Hebel, Slichter and Lurie (Illinois).
Hahn @IBM Watson Lab (New York).

1950s:
At IBM: Redfield, Anderson, Kung and Genak: relaxometry.
Hahn: NQR.

1960s:
Fite, Bleich and Redfield and later Koenig, Brown and Kiselewsy at IBM.
Noack - Kimmich: relaxation spectroscopy (Stuttgart).
Hahn (Berkeley).
1997: first prototype
“Spinmaster FFC”

2000: FFC-2000

2003: 1T magnet

2006: Compact version

2006: SMARtracer
Basic Experiment: measurement of the Larmor frequency dependence of $T_1$
$T_1$

**Sample**

- $B_0$ at $t=0$
- $B_0$ at $t=\tau$

**Exponential growth curve**

- Signal vs. Time in number of $T_1$ periods

- $\tau$ represents the time period of interest.
MAGNETIZATION DECAY

Signal intensity

Magnetic Field cycle

Time

Defines de Larmor frequency!

$T_1$

Time

Frequency

$T_1$
What do we measure?

Data: Data1_B
Model: ExpDec1
\( y_0 + A_1 e^{(-x/t_1)} \)

\( \text{Chi}^2 = 0.00011 \)
\( R^2 = 0.99905 \)

\( T_1 \) or \( 1/T_1 = R_1? \)

\( Y_0 + A_1 e^{(-r_1 x)} \)

\( \Delta t_1 = 2.6\% \)

Magnetization decay

```
y0  0.19773 ± 0.00563
A1  0.99187 ± 0.01106
t1  0.99018 ± 0.026
```

Effective relaxation delay
About the magnetic field sequence

Data: Data1_C
Model: ExpDec1
$y_0 + A_1 e^{-x/t_1}$

$\chi^2 = 7.7417 \times 10^{-6}$
$R^2 = 0.99327$

$y_0 = 0.99729 \pm 0.00151$
$A_1 = 0.09907 \pm 0.00294$
$t_1 = 1.00385 \pm 0.07037$

$\Delta t_1 = 7\%$
Magnetization evolutions with same $T_1$

Relaxation field level

Zero field level
NP sequence
How is obtained the relaxation curve

Basic prepolarised sequence

Basic nonpolarised sequence

Source: Stelar
Switching times

\[ M_z(\tau) = M_0(B_r) + [M_0(B_p) - M_0(B_r)] \exp\{-\tau/T_1(B_r)\} \]

\[ M_z[\tau + (\Delta t)_d + (\Delta t)_u] = [(M_z[(\Delta t)_d] - M_0^r)e^{-\pi T_1(B_r)} + M_0^r]e^{-c^r} + c^u. \]

\[ M_z^{\text{detected}}(\tau) = M_z^\infty + \Delta M_z^{\text{eff}}e^{-\pi T_1}. \]
T₁ relaxation dispersion [s]
T₁ profile
Relaxation rate (1/T₁ or R₁) dispersion [s⁻¹]
NMRD: nuclear magnetic relaxation dispersion
NMRD profile

Relaxivity: relaxation rate for a given concentration in a solution [mM⁻¹ s⁻¹]
Hardware
Different approaches

- High detection field
- Superconducting magnet
- Keep spectroscopic resolution
- Typical switching times 50ms – 500ms
- Movable sample
- Pneumatic or mechanic system

- Moderate detection field
- Air-cored electromagnet
- Low resolution, relaxation applications
- Typical switching times 0.2ms – 2ms.
- Sample at fixed position
- Power electronics

Fast-Field-Cycling (FFC)
I- Power network
Basic circuit

$R_{\text{high}} \ll R_{\text{low}}$ and $R \ll R_{\text{low}}$

$$\frac{dI}{dt} = \frac{1}{L} \left[ V_0 - I(t)(R_{\text{high}} + R) \right]$$

Low-to-high
Capacitor assistance

Vc \gg Vo
Subdamped
Examples
Mosfet – GTO. Energy-storage.
Mosfet-driven network without energy storage capacitor
Typical Mosfet-bank
II- Magnet
Premises of design

- Low inductance and resistance.
- Good magnetic field to power ratio (G-factor).
- NMR homogeneity.
- Efficient cooling.
- Simple mechanical assembly.
Field-cycling magnets

\[ dB = \left( \frac{\mu_0}{4\pi} \right) \xi_l f(r, z) \left[ \frac{r^2}{(r^2 + z^2)^{3/2}} \right] dr \, dz. \]

\[ dW = \left( \frac{\rho}{\lambda} \right) \xi_l f^2(r, z) r \, dr \, dz, \]

\[ B = G \sqrt{\frac{W \lambda}{\rho r_0}}, \]

\[ G = \left( \frac{\mu_0}{4\pi} \right) \frac{\int_{-\beta}^{+\beta} d\gamma \int_{-\alpha}^{+\alpha} f(\delta, \gamma) \frac{\delta^2 d\delta}{(\delta^2 + \gamma^2)^{3/2}}}{\left[ \int_{-\beta}^{+\beta} d\gamma \int_{-\alpha}^{+\alpha} d\delta f^2(\delta, \gamma) \delta \right]^{1/2}} \]

with \( \gamma = z / r_0, \delta = r / r_0, \alpha = r_1 / r_0 \) and \( \beta = l / r_0. \)
The Dvinskikh-Molchanov approach (1985)

\[ y = b \sqrt{1 - \frac{x^2}{a^2} + c_1 x^3 + c_2 x^4}. \]
Schweikert-Noack Magnet (1989)
• Inversion of the Biot-Savart law

• Lagrange minimization procedure: field to power ratio, homogeneity and volume
10 layer magnet (Stuttgart-Córdoba, 1992)
Notch-coil
Rommel - Seitter -
Kimmich
(1993-1995)
Stelar 2L-0.5T system (1997-2000)
Stelar 4L-1T system (2003)
Magnet cooling

![Graph showing thermal jump in polarization time for different frequencies.](image-url)
ULF regime

- External magnetic field components: magnetic field compensation.
- Internal magnetic field components: local fields.
Switching the Zeeman Field

\[ B(t) = B_0(t) + B_P \]

\[ B_N \]

\[ \alpha(t) \]

\[ \frac{1}{B_0^2} \left| \vec{B} \times \frac{d\vec{B}}{dt} \right| \ll \gamma B, \]
Time-dependence of the field

**A**

- $B_{pol} = 10$ MHz
- $B_{def} = 9.3$ MHz

**B**

- $B_{rel} = 10$ kHz

$B_0$ [MHz]

$t$ [ms]

$B_0$ [kHz]

$t$ [ms]
1.6ms

100kHz = 10mV

Shunt Voltage [mV]

Slew Rate 14MHz/ms

50kHz

100kHz

Slew Rate 12MHz/ms

Sequence Timing [s]
Adiabatic & non-adiabatic switching

Signal Amplitude [au]

\( \tau [s] \)

- \( B_r = 4 \text{kHz} \)
- \( B_r = 7 \text{kHz} \)
Magnetic field compensation

![Graphs showing magnetic field compensation](image)

- **A**: GdCl₃ 2mM 294K, $B_{\text{offset}} = +4.4\text{kHz}$
- **B**: $B_{\text{offset}} = 0\text{kHz}$
- **C**: $B_{\text{offset}} = -7.8\text{kHz}$

Signal Signed Magnitude [au]

NAFID Signal Intensity [au]
Figure 3

PDMS 294K
- Compensated
- Non compensated

$\nu_0$ [MHz]

$T_s [s^-1]$

$\nu_0 [kHz]$

$x = (0.249 \pm 0.004)$
Automatic compensation
Plateaus and false dispersions

A

5CB - 303K

B

5CB - 298K
Sources for low-frequency plateau

- Cut-off of the effective relaxation mechanism
- Hardware
  - Current Offset in the Magnet
  - Magnetic Field Offset
  - Magnetic Field time dependence
- Local Fields
  - Dipolar
  - Quadrupolar
\[ T_1(\nu_0) = A. ((\nu_0 + (\nu_L^2 - \nu_N^2)^{1/2})^2 + \nu_N^2)^{1/2} \]
Local fields

• Plateau
• Data scattering

Liposomes
DMPC – D₂O 100nm
Yesterday and today....
R. E. Slusher (1966): “The author is shown in typical operating position with an instrument used to soothe the electric apparatus (and the author)”

Source: Slusher’s Thesis (E. Hahn lab)
Stuttgart Instrument by 1970

Pictures from R. Kimmich
“Relaxometry”

The IBM first Prototype, as later upgraded at the University of Florence

Alfred Redfield
Relaxation theory 1957

Source: internet
Córdoba, 1993
Stelar (Mede – Italy): first prototype FFC-2000
Compact version
SMARtracer

Stellar Magnetic Relaxation tracer
Basic literature

- F. Noack, Progr. NMR Spectrosc. 18, 171 (1986).