NMR summer school, Windischleuba, 2023: Workshop set 3

The aim of this exercise is to work out the behaviour of thermal equilibrium magnetisation under the repetition of many spin-echo elements.

The setup is as follows:

- Our sample consists of an ensemble of molecules containing an isolated spin-1/2. For example acetone-2-^{13}C. For simplicity we ignore the proton spins of the methyl groups.
- We know from experimental observations that the carbon spin will experience spin relaxation once its been perturbed from its thermal equilibrium.
- We assume that relaxation is caused by dipolar couplings to our solvent molecules.
- We further assume that these effects induce an external random magnetic field (erf), in example: $H_{\text{erf}}(t) = -\gamma \vec{I} \cdot \vec{B}_{\text{rand}}(t) = -\gamma(B_x^{\text{erf}}(t) I_x + B_y^{\text{erf}}(t) I_y + B_z^{\text{erf}}(t) I_z)$.

We now want to construct a relaxation superoperator $\hat{\Gamma}_{\text{erf}}$ which captures the relaxation effects due to $H_{\text{erf}}(t)$. Remember that when using spherical tensor operators the expression for the relaxation superoperator is given by:

$$\hat{\Gamma}_{\text{erf}} = -\frac{1}{2} \sum_{m=-1}^{+1} J_{\text{erf}}(m\omega_0) \hat{T}_{1m}^{\dagger} \hat{T}_{1m}, \tag{1}$$

where $J_{\text{erf}}(\omega)$ is the spectral density describing the external random field flucutations.

In a second step we then have to thermalise the relaxation superoperator. To this end we construct the thermalisation superoperator $\hat{\Theta}$

$$\hat{\Theta} = \hat{\mathbb{1}} - |\rho_{\text{eq}})(\mathbb{1}|. \tag{2}$$

The thermalised superoperator is then given by

$$\hat{\Gamma}_{\text{erf}}^{\theta} = \hat{\Gamma}_{\text{erf}} \hat{\Theta}. \tag{3}$$

Q1. The external random field Hamiltonian is given in terms of Cartesian operators. How does the same Hamiltonian look in terms of spherical tensor operators?

Answer: The first thing to consider is the definition of the spherical tensor operators and their relation to Cartesian operators.

$$\begin{bmatrix} T_{1+1} \\ T_{10} \\ T_{1-1} \end{bmatrix} = \begin{bmatrix} -I^+/\sqrt{2} \\ I_z \\ I^-/\sqrt{2} \end{bmatrix} \tag{4}$$

Note: During the exercise I skipped the factor of $1/\sqrt{2}$ because I didn't think it was important, but in hindsight I should have included it and will do so now. This should have little effect on your overall results.

The shift operators are related to the Cartesian operators through:

$$I^+ = I_x + iI_y, \quad I^- = I_x - iI_y, \tag{5}$$

from which it follows that

$$\begin{bmatrix} I_x \\ I_y \\ I_z \end{bmatrix} = \begin{bmatrix} 1/\sqrt{2}(T_{1-1} - T_{1+1}) \\ i/\sqrt{2}(T_{1-1} + T_{1+1}) \\ T_{10} \end{bmatrix}. \tag{6}$$

Inserting these relations into $H_{\mathrm{erf}}(t)$ and gathering the coefficients infront of the spherical tensor operators leads to

$$H_{\mathrm{erf}}(t) = \frac{\gamma}{\sqrt{2}}\{B_x^{\mathrm{erf}}(t) - iB_y^{\mathrm{erf}}(t)\}T_{1+1} - \gamma B_z^{\mathrm{erf}}(t)T_{10} - \frac{\gamma}{\sqrt{2}}\{B_x^{\mathrm{erf}}(t) + iB_y^{\mathrm{erf}}(t)\}T_{1-1}. \tag{7}$$

Again, your result will probably differ by a factor of $\sqrt{2}$ for the $T_{1\pm1}$ term.
Notice the similarity between the coefficients of the spherical tensor operators (in terms of Cartesian magnetic field components) and the definition spherical tensor operators themselves. In fact we may define

$$\begin{bmatrix} A_{1+1}(t) \\ A_{10}(t) \\ A_{1-1}(t) \end{bmatrix} = -\gamma \begin{bmatrix} \frac{1}{\sqrt{2}}(-B_x^{\mathrm{erf}}(t) + iB_y^{\mathrm{erf}}(t)) \\ B_z(t) \\ \frac{1}{\sqrt{2}}(B_x^{\mathrm{erf}}(t) - iB_y^{\mathrm{erf}}(t)) \end{bmatrix}, \tag{8}$$

which shows that we've essentially just computed the spatial parts A_{1m} of a spherical tensor operator of rank $k = 1$. The random field Hamiltonian then takes the form:

$$H_{\mathrm{erf}}(t) = \sum_{m=-1}^{+1} A_{1m}^*(t)T_{1m} = \sum_{m=-1}^{+1} (-1)^m A_{1-m}(t)T_{1m}. \tag{9}$$

Q2. The external random field are assumed to be isotropic. This means:

- $\overline{B_x^{\mathrm{erf}}(0)B_x^{\mathrm{erf}}(\tau)} = B_{\mathrm{rms}}^2 e^{-|\tau|/\tau_c}$, $\overline{B_y^{\mathrm{erf}}(0)B_y^{\mathrm{erf}}(\tau)} = B_{\mathrm{rms}}^2 e^{-|\tau|/\tau_c}$, $\overline{B_z^{\mathrm{erf}}(0)B_z^{\mathrm{erf}}(\tau)} = B_{\mathrm{rms}}^2 e^{-|\tau|/\tau_c}$
- $\overline{B_x^{\mathrm{erf}}(0)B_y^{\mathrm{erf}}(\tau)} = 0$, $\overline{B_x^{\mathrm{erf}}(0)B_z^{\mathrm{erf}}(\tau)} = 0$, $\overline{B_y^{\mathrm{erf}}(0)B_z^{\mathrm{erf}}(\tau)} = 0$

What does the spectral density $J_{\mathrm{erf}}(\omega)$ look like?
Answer: The spectral density function is defined as the Fourier transform of the correlation function. For an exponentially decaying correlation functon we get:

$$J_{\mathrm{erf}}(\omega) = (-\gamma)^2 B_{\mathrm{rms}}^2 \int_{-\infty}^{+\infty} e^{-|\tau|/\tau_c} e^{-i\omega\tau} d\tau = (-\gamma)^2 B_{\mathrm{rms}}^2 \frac{2\tau_c}{1 + (\omega\tau_c)^2}, \tag{10}$$

which may be recognised as the absorption part of a complex Lorentzian (the real part of an NMR peak).

Q3. From now on we assume the so-called "fast-motiton-limit". This means the correlation time is very short and the spectral density for all values of ω is given by $J(\omega) = J(0)$. What does the spectral density in the fast-motion-limit look like?
Answer: In the fast-motion-limit we assume that the correlation function is much shorter than the inverse of the Lamor frequency

$$\tau_c\omega_0 \ll 1. \tag{11}$$

Since relaxation rates typically only require us to evaluate the spectral density at multiples of the Larmor-frequency, we may essentially replace all products $|\tau_c\omega|$ by zero

$$J_{\mathrm{erf}}(\omega) = (-\gamma)^2 B_{\mathrm{rms}}^2 \frac{2\tau_c}{1 + (\omega\tau_c)^2} \overset{\mathrm{FML}}{\simeq} (-\gamma)^2 B_{\mathrm{rms}}^2 \frac{2\tau_c}{1 + 0} = 2(-\gamma)^2 B_{\mathrm{rms}}^2 \tau_c = J_{\mathrm{erf}}(0). \tag{12}$$

As a result, to us the spectral density appears to be flat and independent of frequency.

Q4. What does $\hat{\Gamma}_{\mathrm{erf}}$ (in the fast-motion-limit) look like when you put all of this together? In example insert the correct spectral density and spherical tensor operators into equation (1).
Answer: Following equation (1) the relaxation superoperator is given by:

$$\hat{\Gamma}_{\mathrm{erf}} = -\frac{1}{2} \sum_{m=-1}^{+1} J_{\mathrm{erf}}(m\omega_0)\hat{T}_{1m}^{\dagger}\hat{T}_{1m}. \tag{13}$$

If we apply the fast-motion-limit $\hat{\Gamma}_{\text{erf}}$ reduces to

$$\hat{\Gamma}^{\text{FML}}_{\text{erf}} \simeq -\frac{1}{2}\sum_{m=-1}^{+1} J_{\text{erf}}(0)\hat{T}^{\dagger}_{1m}\hat{T}_{1m} = -\frac{1}{2}J_{\text{erf}}(0)\sum_{m=-1}^{+1}\hat{T}^{\dagger}_{1m}\hat{T}_{1m}. \tag{14}$$

Now we simply replace $J(0)$ by the expression derived in Q3

$$\hat{\Gamma}^{\text{FML}}_{\text{erf}} = -\frac{1}{2}\times 2(-\gamma)^2 B^2_{\text{rms}}\tau_{\text{c}}\sum_{m=-1}^{+1}\hat{T}^{\dagger}_{1m}\hat{T}_{1m} = -(\gamma B_{\text{rms}})^2\tau_{\text{c}}\sum_{m=-1}^{+1}\hat{T}^{\dagger}_{1m}\hat{T}_{1m}. \tag{15}$$

Q5. Consider now the Liouville space basis given by the operators $\mathcal{B}_{\mathcal{L}} = \{\frac{1}{\sqrt{2}}\mathbb{1}, \sqrt{2}I_z, I^-, I^+\}$.

Calculate the superoperator matrix representation $[\hat{\Gamma}_{\text{erf}}]_{\mathcal{B}_{\mathcal{L}}}$. **Hint**: $[I_z, I^{\pm}] = \pm I^{\pm}$ and $[I^+, I^-] = 2I_z$

Answer: In order to evaluate the matrix representation for the relaxation superoperator $\hat{\Gamma}_{\text{erf}}$ we need to evaluate all matrix elements of the type:

$$(Q_j|\hat{\Gamma}_{\text{erf}}|Q_i) \quad |Q_i), |Q_j) \in \mathcal{B}_{\mathcal{L}} \tag{16}$$

Let us look at the following example:

$$(I^+|\hat{\Gamma}_{\text{erf}}|\sqrt{2}I_z) = -(\gamma B_{\text{rms}})^2\tau_{\text{c}}\sum_{m=-1}^{+1}(I^+|\hat{T}^{\dagger}_{1m}\hat{T}_{1m}|\sqrt{2}I_z). \tag{17}$$

It is now useful to push one commutation superoperator to the right and push the other one to the left. Pushing a superoperator to left requires complex conjugation however

$$\begin{aligned}(I^+|\hat{\Gamma}_{\text{erf}}|\sqrt{2}I_z) &= -(\gamma B_{\text{rms}})^2\tau_{\text{c}}\sum_{m=-1}^{+1}(\hat{T}_{1m}I^+|\sqrt{2}\hat{T}_{1m}I_z) \\ &= -\sqrt{2}(\gamma B_{\text{rms}})^2\tau_{\text{c}}\sum_{m=-1}^{+1}([T_{1m}, I^+]|[T_{1m}, I_z]).\end{aligned} \tag{18}$$

We may now apply the commutation rules given as a hint. In principle these may be used to deduce

$$[T_{1m}, I_z] = -mT_{1m} \quad [T_{1m}, I^+] = -\sqrt{2}T_{1m+1} \qquad [T_{1m}, I^-] = -\sqrt{2}T_{1m-1}. \tag{19}$$

Although this is not really necessary and admittedly a bit tricky. With the relations above the matrix element may be expressed as follows

$$(I^+|\hat{\Gamma}_{\text{erf}}|\sqrt{2}I_z) = -\sqrt{2}(\gamma B_{\text{rms}})^2\tau_{\text{c}}\sum_{m=-1}^{+1}(-\sqrt{2})\times(-m)(T_{1m+1}|T_{1m}) = 0. \tag{20}$$

The last equality follows from the fact that spherical tensor operators, just like shift-operators, are orthogonal to one another for $m \neq m'$.

I hope that with the example and the commutator relations given above you agree that the superoperator matrix representation is given by

$$[\hat{\Gamma}_{\text{erf}}]_{\mathcal{B}_{\mathcal{L}}} = -2(\gamma B_{\text{rms}})^2\tau_{\text{c}}\begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \tag{21}$$

Q6. Following equation (2) we will need the thermal equilibrium density operator ρ_{eq} to thermalise the relaxation superoperator. What is $|\rho_{\text{eq}})$ in the high-temperature limit for $H_0 = \omega_0 I_z$? **Tip:** It might

be useful to abbreviate $\beta = \hbar/(k_B T)$ to simplify the notation.
Answer: The general definition of the thermal equilibrium density operator is given by

$$\rho_{\text{eq}} = \exp\{-\beta H_0\}/\text{Tr}\{\exp\{-\beta H_0\}\}, \tag{22}$$

where β represents the available "thermal" energy, which is in general small $\beta \ll 1$. The high-temperature approximation means that we only keeping the lowest order terms of the exponential

$$e^x = 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \cdots \simeq 1 + x. \tag{23}$$

For the exponential of the Hamiltonian we then have

$$\exp\{-\beta H_0\} \simeq \mathbb{1} - \beta H_0, \tag{24}$$

and the trace is approximately given by

$$\text{Tr}\{\exp\{-\beta H_0\}\} \simeq \text{Tr}\{\mathbb{1} - \beta H_0\} = \text{Tr}\{\mathbb{1}\} - \text{Tr}\{\beta H_0\} = 2 - 0. \tag{25}$$

Putting things together we have

$$\rho_{\text{eq}} \simeq \frac{1}{2}(\mathbb{1} - \beta H_0) = \frac{1}{2}(\mathbb{1} - \beta\omega_0 I_z), \tag{26}$$

Q7. What is the superoperator matrix representation $[\hat{\Theta}]_{\mathcal{B}_\mathcal{L}}$ with respect to $\mathcal{B}_\mathcal{L} = \{\frac{1}{\sqrt{2}}\mathbb{1}, \sqrt{2}I_z, I^-, I^+\}$?

Answer: Let's first recall the definition of the thermal correction superoperator:

$$\hat{\Theta} = \hat{\mathbb{1}} - |\rho_{\text{eq}})(\mathbb{1}|, \tag{27}$$

and split the problem into the two parts indicated above. The identity superoperator $\hat{\mathbb{1}}$ is diagonal in *every* operator basis

$$[\hat{\mathbb{1}}]_{\mathcal{B}_\mathcal{L}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \tag{28}$$

To evaluate the matrix for the thermal projection superoperator $|\rho_{\text{eq}})(\mathbb{1}|$ remember that

$$|\rho_{\text{eq}})(\mathbb{1}|Q) = |\rho_{\text{eq}})\text{Tr}\{Q\}. \tag{29}$$

The only non-traceless operator of $\mathcal{B}_\mathcal{L}$ is $\frac{1}{\sqrt{2}}\mathbb{1}$. This already tells us that only the first column will be non-zero

$$[|\rho_{\text{eq}})(\mathbb{1}|]_{\mathcal{B}_\mathcal{L}} = \begin{bmatrix} \bullet & 0 & 0 & 0 \\ \bullet & 0 & 0 & 0 \\ \bullet & 0 & 0 & 0 \\ \bullet & 0 & 0 & 0 \end{bmatrix}. \tag{30}$$

We also know that ρ_{eq} contains no components along I^- and I^+, so that the last two elements of the first column also must be zero

$$[|\rho_{\text{eq}})(\mathbb{1}|]_{\mathcal{B}_\mathcal{L}} = \begin{bmatrix} \bullet & 0 & 0 & 0 \\ \bullet & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}. \tag{31}$$

We are thus left with only two non-zero matrix elements. These are

$$\begin{aligned} &(\frac{1}{\sqrt{2}}\mathbb{1}|\rho_{\text{eq}})(\mathbb{1}|\frac{1}{\sqrt{2}}\mathbb{1}) = (\frac{1}{\sqrt{2}}\text{Tr}\{\rho_{\text{eq}}\}) \times (\frac{1}{\sqrt{2}}\text{Tr}\{\mathbb{1}\}) = (\frac{1}{\sqrt{2}}) \times (\frac{1}{\sqrt{2}}2) = 1, \\ &(\sqrt{2}I_z|\rho_{\text{eq}})(\mathbb{1}|\frac{1}{\sqrt{2}}\mathbb{1}) = (-\sqrt{2}\frac{1}{2}\beta\omega_0(I_z|I_z)) \times (\frac{1}{\sqrt{2}}\text{Tr}\{\mathbb{1}\}) = (-\sqrt{2}\frac{1}{2}\beta\omega_0(I_z|I_z)) \times (\frac{1}{\sqrt{2}}2) = -\frac{1}{2}\beta\omega_0. \end{aligned} \tag{32}$$

The last line follows from $(\sqrt{2}I_z|\sqrt{2}I_z) = 1$.
Putting all of this together one arrives at

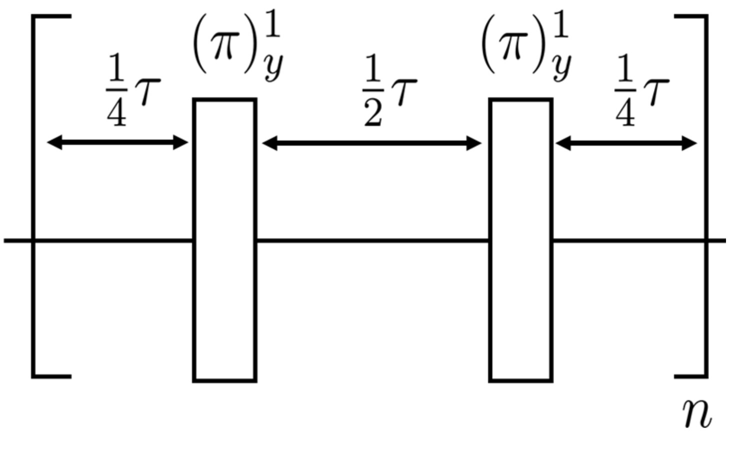
$$[\hat{\Theta}]_{\mathcal{B}_\mathcal{L}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} - \begin{bmatrix} 1 & 0 & 0 & 0 \\ -\frac{1}{2}\beta\omega_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ \frac{1}{2}\beta\omega_0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \tag{33}$$

Q8. Calculate the superoperator matrix representation for $\hat{\Gamma}^\theta_{\mathrm{erf}}$ with respect to $\mathcal{B}_\mathcal{L}$, in example $[\hat{\Gamma}_{\mathrm{erf}}]_{\mathcal{B}_\mathcal{L}} \cdot [\hat{\Theta}]_{\mathcal{B}_\mathcal{L}}$.
Answer: Multiplying out the matrices from Q5 and Q7 leads to

$$\begin{aligned} [\hat{\Gamma}_{\mathrm{erf}}]_{\mathcal{B}_\mathcal{L}} \cdot [\hat{\Theta}]_{\mathcal{B}_\mathcal{L}} &= -2(\gamma B_{\mathrm{rms}})^2\tau_{\mathrm{c}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 0 & 0 & 0 & 0 \\ \frac{1}{2}\beta\omega_0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \\ &= -2(\gamma B_{\mathrm{rms}})^2\tau_{\mathrm{c}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ \frac{1}{2}\beta\omega_0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}. \end{aligned} \tag{34}$$

Consider now the application of the following pulse sequence:

Figure 1: Repeated spin-echo application



Q9. What is the effect of a $(\pi)_y$ rotation onto each of the basis elements $\mathcal{B}_\mathcal{L} = \{\frac{1}{\sqrt{2}}\mathbb{1}, \sqrt{2}I_z, I^-, I^+\}$?

From this knowledge derive the superoperator matrix representation $[(\pi)_y]_{\mathcal{B}_\mathcal{L}}$
Answer: A $(\pi)_y$ pulse changes the sign of x- and z- magnetisation, but not of y-magnetisation. This observation may be combined with the relation of the shift operators to Cartesian operators to arrive at the following matrix representation

$$[(\hat{\pi})_y]_{\mathcal{B}_\mathcal{L}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{bmatrix}. \tag{35}$$

Q10. Consider now the "average" relaxation superoperator: $\frac{1}{2}\{\hat{\Gamma}^\theta_{\mathrm{erf}} + (\hat{\pi}_y)\hat{\Gamma}^\theta_{\mathrm{erf}}(\hat{\pi}_y)\}$. Calculate the superoperator matrix representation $[(\pi)_y]_{\mathcal{B}_\mathcal{L}} \cdot [\hat{\Gamma}^{\theta}_{\text{erf}}]_{\mathcal{B}_\mathcal{L}} \cdot [(\pi)_y]_{\mathcal{B}_\mathcal{L}}$. Combine this with the result of Q7 to derive the average relaxation superoperator.

Answer: As indicated by in the question the matrix representation for the average relaxation superoperator may be calculated as follows

$$\begin{aligned}
[\hat{\Gamma}^{\theta,\text{avg}}_{\text{erf}}]_{\mathcal{B}_\mathcal{L}} &= \frac{1}{2}([\hat{\Gamma}_{\text{erf}}]_{\mathcal{B}_\mathcal{L}} \cdot [\hat{\Theta}]_{\mathcal{B}_\mathcal{L}} + [(\hat{\pi})_y]_{\mathcal{B}_\mathcal{L}} [\hat{\Gamma}_{\text{erf}}]_{\mathcal{B}_\mathcal{L}} \cdot [\hat{\Theta}]_{\mathcal{B}_\mathcal{L}} [(\hat{\pi})_y]_{\mathcal{B}_\mathcal{L}}) \\
&= \frac{1}{2}\left(-2(\gamma B_{\text{rms}})^2 \tau_{\text{c}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ \frac{1}{2}\beta\omega_0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} - 2(\gamma B_{\text{rms}})^2 \tau_{\text{c}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ -\frac{1}{2}\beta\omega_0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \right) \\
&= -2(\gamma B_{\text{rms}})^2 \tau_{\text{c}} \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.
\end{aligned} \tag{36}$$

Q11. What does this matrix physically mean? Which NMR experiment did we just derive?

Answer: The superoperator matrix for the average relaxation superoperator $[\hat{\Gamma}^{\theta,\text{avg}}_{\text{erf}}]_{\mathcal{B}_\mathcal{L}}$ does not contain any thermal corrections anymore. Instead all spin density operator components relax mono-exponentially with a rate proportional to $2(\gamma B_{\text{rms}})^2\tau_{\text{c}}$ until they eventually decay to zero. This experiment should remind you of the first part of a saturation recovery or water suppression experiment for example. In both cases a rapid train of variable flip angle pulses is applied to destroy the equilibrium magnetisation.