Solution Problem Set 6: Coupled Relaxation Modes

Coupled Relaxation Modes

1. If we assume no CSA-dipole and no cross-correlated cross relaxation, the system simplifies to two coupled differential equations

$$\frac{d}{dt}\begin{bmatrix}\langle I_z\rangle(t)\\ \langle S_z\rangle(t)\end{bmatrix} = -\begin{bmatrix}\Gamma_{I_z,I_z} & \Gamma_{S_z,I_z}\\ \Gamma_{S_z,I_z} & \Gamma_{S_z,S_z}\end{bmatrix}\begin{bmatrix}\langle I_z\rangle(t)-\langle I_z\rangle_{\text{eq}}\\ \langle S_z\rangle(t)-\langle S_z\rangle_{\text{eq}}\end{bmatrix} \qquad (1)$$

with the formal solution

$$\frac{d}{dt}\begin{bmatrix}\langle I_z\rangle(t)\\ \langle S_z\rangle(t)\end{bmatrix} = \exp\left(-\begin{bmatrix}\Gamma_{I_z,I_z} & \Gamma_{S_z,I_z}\\ \Gamma_{S_z,I_z} & \Gamma_{S_z,S_z}\end{bmatrix}\right)\begin{bmatrix}\langle I_z\rangle(t)-\langle I_z\rangle_{\text{eq}}\\ \langle S_z\rangle(t)-\langle S_z\rangle_{\text{eq}}\end{bmatrix} + \begin{pmatrix}\langle I_z\rangle_{\text{eq}}\\ \langle S_z\rangle_{\text{eq}}\end{pmatrix} \qquad (2)$$

The initial conditions are given by $\langle I_z\rangle(0) = \langle I_z\rangle_{\text{eq}} = \frac{\gamma_H}{\gamma_N}\langle S_z\rangle_{\text{eq}} \simeq -10\langle S_z\rangle_{\text{eq}}$ and $\langle S_z\rangle(0) = -\langle S_z\rangle_{\text{eq}}$. One can diagonalize the 2x2 matrix analytically but the expressions obtained are quite complicated and it is simpler to calculate a numerical solution in MATLAB. For a correlation time of 10^{-10} s, we obtain values of $\Gamma_{I_z,I_z} = 0.2925\,s^{-1}$, $\Gamma_{S_z,S_z} = 0.3047\,s^{-1}$, and $\Gamma_{S_z,I_z} = 0.1495\,s^{-1}$. For a correlation time of $10^{-8}\,s$, we obtain values of $\Gamma_{I_z,I_z} = 0.0261\,s^{-1}$, $\Gamma_{S_z,S_z} = 0.6537\,s^{-1}$, and $\Gamma_{S_z,I_z} = 0.0153\,s^{-1}$. In the first case, the diagonal and the off-diagonal matrix elements are all in the same order of magnitude and we will get a bi-exponential decay where both time constants contribute about equally. This can be seen by calculating the eigenvalues and the eigenvectors of the relaxation matrix. In the second case, the off-diagonal element is much smaller than the auto-relaxation rate constant of the S spin and we expect a mostly mono-exponential decay with the auto-relaxation rate constant. This can also be seen from the eigenvalues and eigenvectors of the relaxation matrix which show very little coupling between the two modes. This can be seen in Figure 1.7 where the numerical solution of the coupled differential equations is plotted together with the mono-exponential decay for the T_{1S} time constant.

2. If we saturate the protons by applying on-resonance cw irradiation on the I spin during the relaxation delay, the system of differential equations is modified. We can assume that $\langle I_z\rangle(t) = 0$. Calculate the time evolution of the S_z magnetization after a 180° inversion pulse under these conditions analytically. What is now the rate constant with which the system relaxes towards the steady-state equilibrium value. If we assume hat $\langle I_z\rangle(t) = 0$, Equation (1) simplifies to

$$\frac{d}{dt}\begin{bmatrix}\langle I_z\rangle(t)\\ \langle S_z\rangle(t)\end{bmatrix} = -\begin{bmatrix}\Gamma_{I_z,I_z} & \Gamma_{S_z,I_z}\\ \Gamma_{S_z,I_z} & \Gamma_{S_z,S_z}\end{bmatrix}\begin{bmatrix}-\langle I_z\rangle_{\text{eq}}\\ \langle S_z\rangle(t)-\langle S_z\rangle_{\text{eq}}\end{bmatrix} \qquad (3)$$

and we obtain a differential equation for S_z that is no longer coupled to I_z:

$$\frac{d}{dt}\langle S_z\rangle(t) = \Gamma_{S_z,I_z}\langle I_z\rangle_{\text{eq}} - \Gamma_{S_z,S_z}(\langle S_z\rangle(t)-\langle S_z\rangle_{\text{eq}}) \qquad (4)$$

(a) $\tau_c = 10^{-10}$
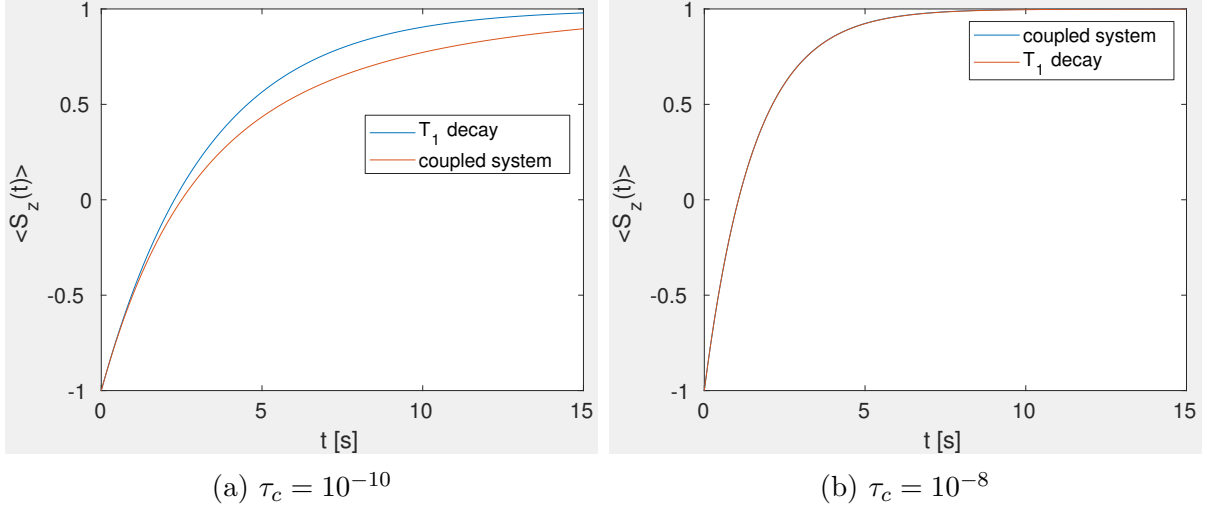
(b) $\tau_c = 10^{-8}$

Figure 1: Plot of the time evolution of the S_z magnetization after inversion of the S spin calculated by solving the system of coupled differential equations (red lines) under the assumption of no CSA and as a mono-exponential decay with the time constant coupled differential equations is plotted together with the mono-exponential decay for the T_{1S} (blue lines).

The solution of Equation (4) is

$$\langle S_z \rangle (t) = \frac{\Gamma_{S_z,I_z}}{\Gamma_{S_z,S_z}} \langle I_z \rangle_{\text{eq}} + \langle S_z \rangle_{\text{eq}} - \left(\frac{\Gamma_{S_z,I_z}}{\Gamma_{S_z,S_z}} \langle I_z \rangle_{\text{eq}} + 2 \langle S_z \rangle_{\text{eq}} \right) e^{-\Gamma_{S_z,S_z} t} \tag{5}$$

This is again a mono-exponential decay with the T_{1S} time constant but the equilibrium value against which the magnetization relaxes has been changed (see next question)

3. We can again start from Equation (5) and assume a steady-state condition $\langle S_z \rangle (t) = 0$. This leads to

$$\Gamma_{S_z,I_z} \langle I_z \rangle_{\text{eq}} - \Gamma_{S_z,S_z} (\langle S_z \rangle (t) - \langle S_z \rangle_{\text{eq}}) = 0 \tag{6}$$

which we can solve for $\langle S_z \rangle (t)$ leading to

$$\langle S_z \rangle (t) = \frac{\Gamma_{S_z,I_z}}{\Gamma_{S_z,S_z}} \langle I_z \rangle_{\text{eq}} + \langle S_z \rangle_{\text{eq}} = \langle S_z \rangle_{\text{eq}} (1 + \eta) \tag{7}$$

Therefore, the signal enhancement is given by

$$\eta = \frac{\Gamma_{S_z,I_z} \langle I_z \rangle_{\text{eq}}}{\Gamma_{S_z,S_z} \langle S_z \rangle_{\text{eq}}} = \frac{\Gamma_{S_z,I_z} \gamma_I}{\Gamma_{S_z,S_z} \gamma_S} \tag{8}$$

which can either be negative of positive depending on the relative sign of the gyromagnetic ratios. Figure 1.8 shows a plot of the enhancement as a function of the correlation time. One can clearly see that for small molecules (short correlation times)a significant enhancement of the steady-state polarization is obtained compared to the Boltzmann polarization. For larger molecules (long correlation times), only a small enhancement is observed.
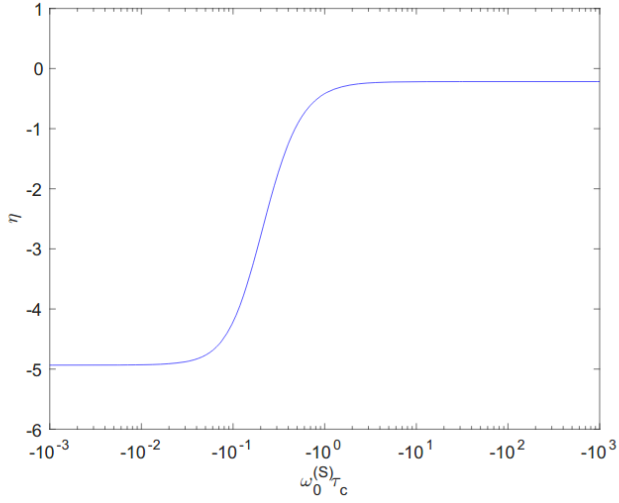
Figure 2: **Plot of the NOE Enhancement as a function of the correlation time** τ_c. For short correlation times (small molecules) a significant enhancement of the steady-state polarization is obtained compared to the Boltzmann polarization. For larger molecules (long correlation times), only a small enhancement is observed.