1   Solution: Relaxation Theory

Solving the questions requires to implement the equations given in the exercise in MATLAB or another matrix calculation package. An example implementation is included in the solution.

There are some user-defined functions that are used in the exercise:

• define_constants.m

```
% This file defines all important constants used
% for relaxation calculation.
% started12.3.1991MAER
%
%
mu0= 4*pi*1e-7;
mu04pi= 1e-7;
hbar= 1.05457266e-34;
h = 6.6260755e-34;
gh_gc= 3.979;
gh_gn= -9.869;
gammah= 2.67522128e8;
gammac= gammah / gh_gc;
gamman= gammah / gh_gn;
gammae  =-1.7608598e11;
betae   = 9.274e-24;
rch= 1.09e-10;
rnh = 1.1e-10;
rad= pi/180;
kB      = 1.3806488e-23;
```

• J.m

```
function Jiso = J(omega, tau)
Jiso = 2/5 * tau ./(1+(omega .* tau).^2);
```

• T1.m

```
function T1 = T1(delta, sigmazz, omegaI, omegaS, tau)

T1 = ((delta/4)^2*(1*J(omegaI-omegaS,tau)+3*J(omegaS,tau) + ...
                 6*J(omegaI+omegaS,tau))+ ...
     3/4*(sigmazz*omegaS).^2.*J(omegaS,tau)).^-1;
```

• T2.m

```
function T2 = J(delta, sigmazz, omegaI, omegaS, tau)

T2 = (delta^2/32*(4*J(0,tau)+1*J(omegaI-omegaS,tau)+3*J(omegaS,tau) + ...
              6*J(omegaI,tau) +6*J(omegaI+omegaS,tau))+ ...
     1/2*(sigmazz*omegaS).^2.*J(0,tau) + ...
     3/8*(sigmazz*omegaS).^2.*J(omegaS,tau)).^-1;
```

- T1x.m

```
function T1x = T1x(delta, sigmazz, omegaI, omegaS, tau)

T1x = ((delta/4)^2*(-1*J(omegaI-omegaS,tau) + ...
                    6*J(omegaI+omegaS,tau))).^-1;
```

1.1 T_1 Dependence on Magnetic Field and Correlation Time

- Calculate T_{1S} as a function of the correlation time τ_c assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)}$ = 0 ppm. Generate a double-logarithmic plot of T_{1S} vs. $\omega_0^{(S)}\tau_c$. Where do you observe a minimum of the T_{1S} time? Rationalize the position of the minimum by discussing the form of the spectral-density function.
- **Solution**:

Figure 1.1 shows a log-log plot of T_1 as a function of the correlation time. One can clearly see that the T_1 curve has a minimum that is roughly at the position $\omega_0^{(S)}\tau_c$ = 1.

MATLAB code to plot the T_1 dependence on the correlation time:

```
clear;
define_constants;
colormap(jet);

omegaS = 14.1*gamman;
omegaI = 14.1*gammah;
delta = -2*mu04pi*gamman*gammah*hbar/rnh^3;
sigmazz00=0;
sigmazz05=50e-6;
sigmazz15=150e-6;

tauc = 10 .^ (-12:0.01:-5);
T1N00 = T1(delta,sigmazz00,omegaI,omegaS,tauc);
T1N05 = T1(delta,sigmazz05,omegaI,omegaS,tauc);
T1N15 = T1(delta,sigmazz15,omegaI,omegaS,tauc);

loglog(omegaS*tauc,T1N00,'b');
hold on
loglog(omegaS*tauc,T1N05,'r');
loglog(omegaS*tauc,T1N15,'g');
hold off
axis([-1e3 -1e-3 1e-1 1e3])
set(gca,'XDir','Reverse')
set(gca,'FontSize',14);
xlabel('\omega_0^{(S)}\tau_c')
```

```
ylabel('T_1 [s]')
legend('\sigma_{zz}^{(S)} = 0 ppm','\sigma_{zz}^{(S)} = 50
  ppm','\sigma_{zz}^{(S)} = 150 ppm')
```

The location of the minimum can be understood when looking at the spectral-density functions as a function of the correlation time as shown in Figure 1.2. One can clearly see that the spectral density function at frequency $\omega_0^{(S)}$ is largest and will dominate the behavior of T_1. Each of the spectral-density functions will have a maximum at $\omega_0^{(S)}\tau_c = 1$ and, therefore, T_1 will have a minimum there. There are some additional features visible in Figure 1.1 which come from the minima of the spectral-density functions at the frequencies $\omega_0^{(S)} - \omega_0^{(I)}$ and $\omega_0^{(S)} + \omega_0^{(I)}$.

MATLAB code to plot the spectral density functions:

```
loglog(omegaS*tauc,J(omegaS,tauc),'b');
hold on
loglog(omegaS*tauc,J(omegaS-omegaI,tauc),'r');
```
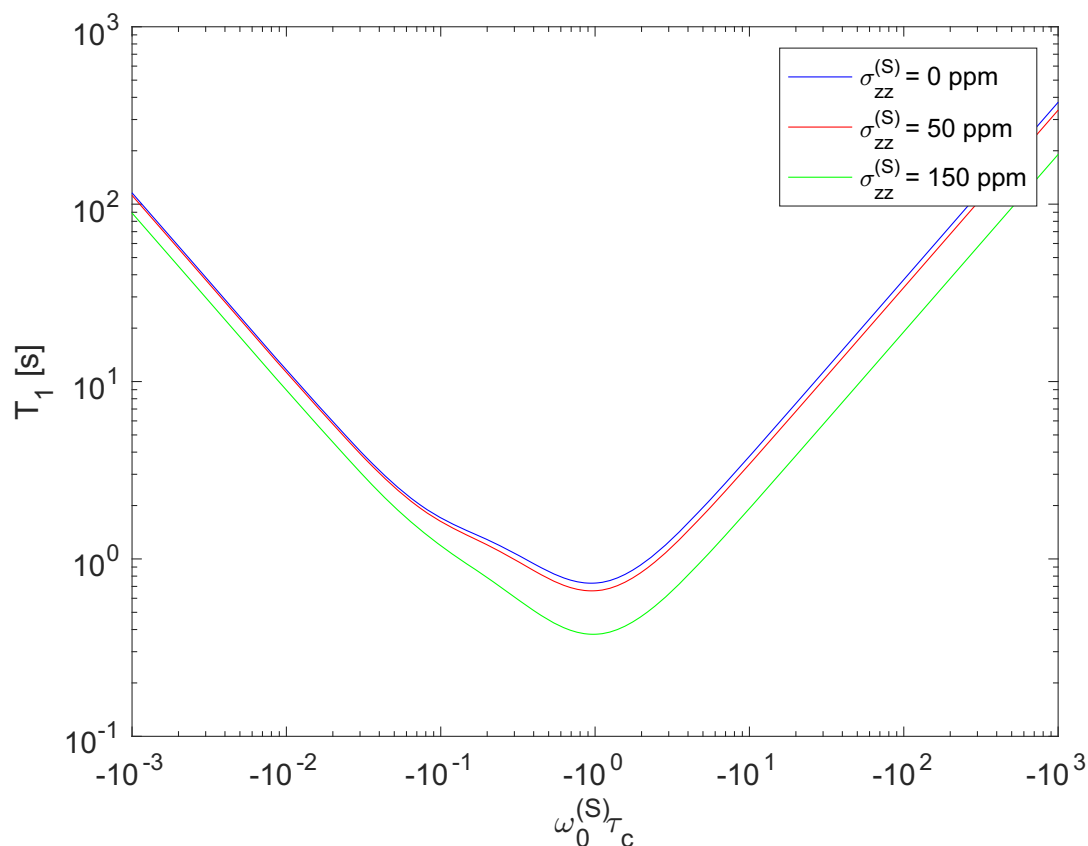

Figure 1.1: Plot of Longitudinal T_1 Relaxation Times
Plot of the longitudinal relaxation times for a N-H two-spin system in a static magnetic field of 14.1 T with a bond length of 1.1 Å. Three different values for the chemical-shielding tensor are shown.

```
loglog(omegaS*tauc,J(omegaS+omegaI,tauc),'g');
loglog(omegaS*tauc,J(0,tauc),'b');
hold off
axis([-1e3 -1e-3 1e-14 1e-6])
set(gca,'XDir','Reverse')
set(gca,'FontSize',14);
xlabel('\omega_0^{(S)}\tau_c')
ylabel('J(\omega)')
legend('\omega_0^{(S)}','\omega_0^{(S)}-
  \omega_0^{(I)}','\omega_0^{(S)}+\omega_0^{(I)}','0')
```

- Calculate and plot T_{1S} for chemical-shielding tensor values of $\sigma_{zz}^{(S)}$ = 50 ppm and 150 ppm. What do you observe?
- **Solution**:

Increasing the chemical-shielding tensor value will lead to additional relaxation that makes the rate constant larger and, therefore, decreases the T_1 time as can be seen in Figure 1.1.

MATLAB code for this is already included in the first part.
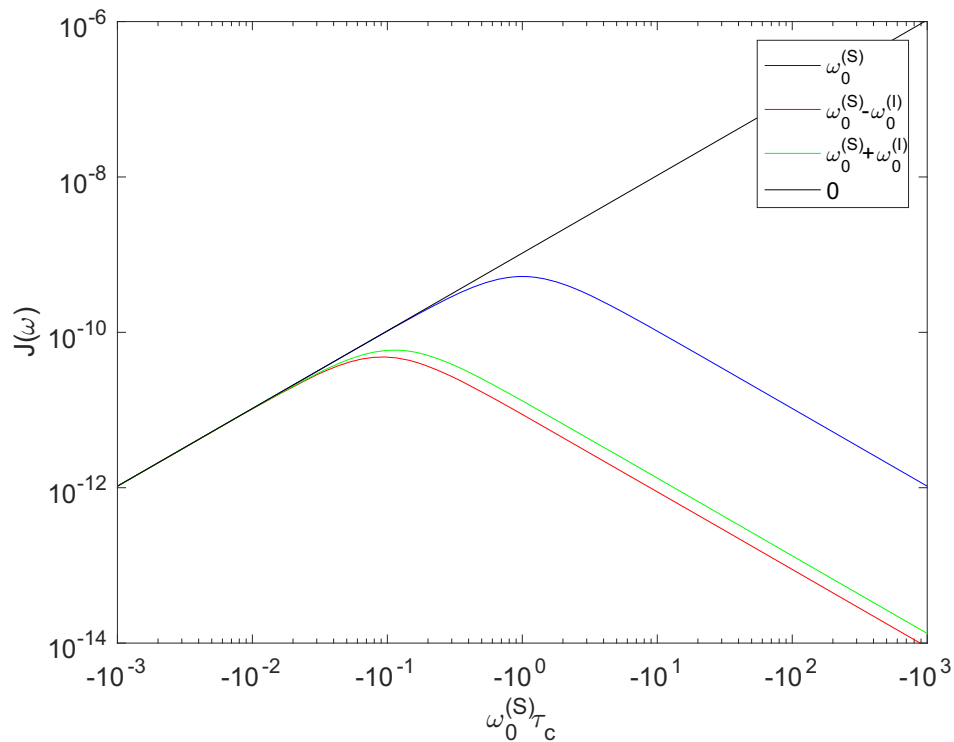
Figure 1.2: Plot of Spectral-Density Functions
Plot of the spectral-density functions as a function of the correlation time for different frequencies ($\omega_0^{(S)}$, $\omega_0^{(S)} - \omega_0^{(I)}$, $\omega_0^{(S)} + \omega_0^{(I)}$, and 0). The spectral-density function at frequency $\omega_0^{(S)}$ has the largest value and will dominate the behavior of T_1.
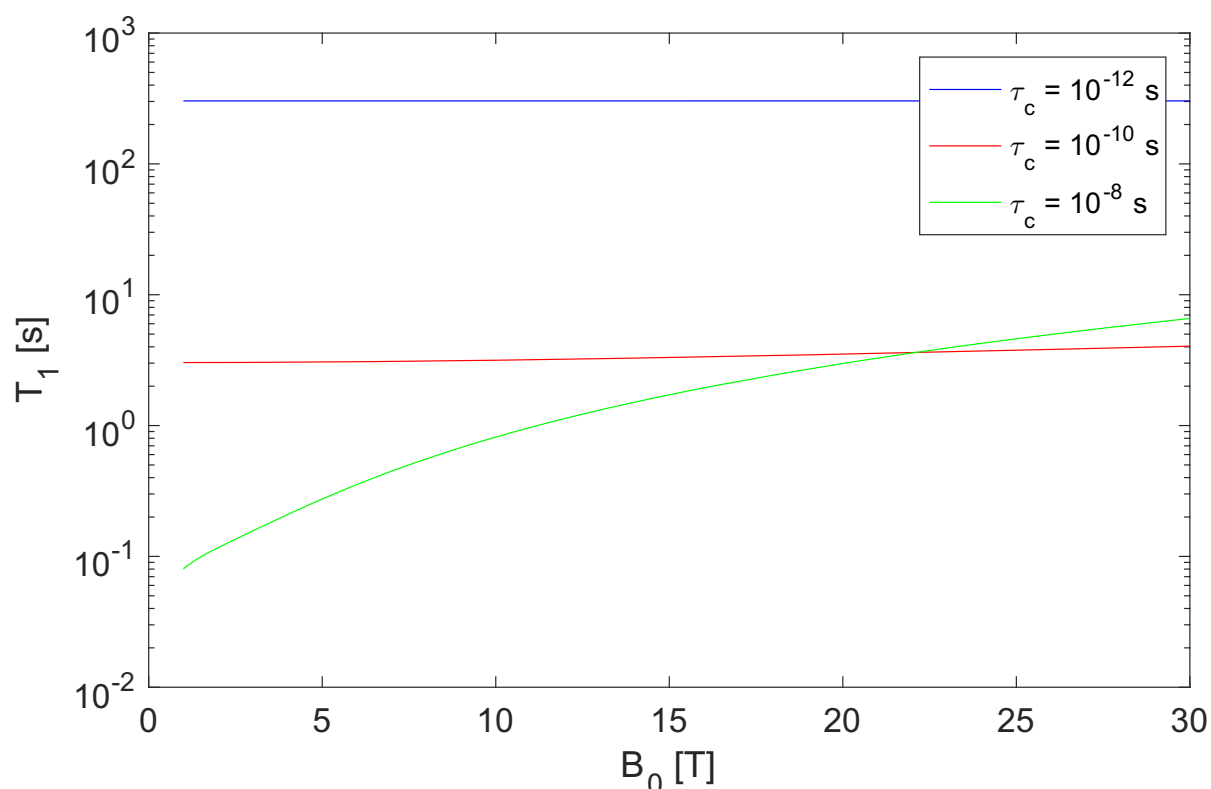
- Calculate T_{1S} as a function of the static magnetic field B_0 between 1 and 30 T for correlation times τ_c of 10^{-12}, 10^{-10}, and 10^{-8} s. We assume that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm.

- **Solution**:

  The dependence of T_1 on the static magnetic field is shown in Figure 1.3 for three different correlation times. For the correlation times of 10^{-12} and 10^{-10} s we are always in the extreme narrowing limit ($\omega_0^{(S)}\tau_c < 1$) and the value of the spectral-density function does not depend on the static magnetic field. Only for the correlation time of 10^{-8} s can we observe a dependence of T_1 on B_0 since $\omega_0^{(S)}\tau_c > 1$.

  MATLAB code to plot the B_0 dependence of T_1:

```
tauc1=1e-12;
tauc2=1e-10;
tauc3=1e-8;
B0=1:0.01:30;
omegaI=gammah*B0;
omegaS=gamman*B0;
```


Figure 1.3: Plot of T_1 as a Function of B_0
Plot of the ^{15}N T_1 relaxation time as a function of the static magnetic field B_0 for three different values of the correlation time.

```
T1N1 = T1(delta,sigmazz00,omegaI,omegaS,tauc1);
T1N2 = T1(delta,sigmazz00,omegaI,omegaS,tauc2);
T1N3 = T1(delta,sigmazz00,omegaI,omegaS,tauc3);

semilogy(B0,T1N1,'b');
hold on
loglog(B0,T1N2,'r');
loglog(B0,T1N3,'g');
hold off
set(gca,'FontSize',14);
xlabel('B_0 [T]')
ylabel('T_1 [s]')
legend('\tau_c = 10^{-12} s','\tau_c = 10^{-10} s','\tau_c = 10^{-8} s')
```

1.2 T_2 Dependence on Magnetic Field and Correlation Time

- Calculate T_{2S} as a function of the correlation time τ_c assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm. Generate a double-logarithmic plot of T_{2S} vs. $\omega_0^{(S)}\tau_c$. Rationalize why the T_2 relaxation time shows no minimum but decreases continuously with increasing correlation time.

- **Solution**:

  Implementing the T_2 calculation in MATLAB is straightforward using the equations given in the exercise. The plot shown in Figure 1.4 shows no minimum like the T_1 plot but decreases monotonically. This is due to the fact that the equation for T_2 relaxation contains the spectral-density function at frequency 0 (see Figure 1.2) which dominates the behavior at longer correlation times.

  MATLAB code to plot T_2 as a function of the correlation time:

```
omegaS = 14.1*gamman;
omegaI = 14.1*gammah;
delta = -2*mu04pi*gamman*gammah*hbar/rnh^3;
sigmazz00=0;
sigmazz05=50e-6;
sigmazz15=150e-6;

tauc = 10 .^ (-12:0.01:-5);
T2N00 = T2(delta,sigmazz00,omegaI,omegaS,tauc);
T2N05 = T2(delta,sigmazz05,omegaI,omegaS,tauc);
T2N15 = T2(delta,sigmazz15,omegaI,omegaS,tauc);

loglog(omegaS*tauc,T2N00,'b');
hold on
loglog(omegaS*tauc,T2N05,'r');
loglog(omegaS*tauc,T2N15,'g');
```

```
hold off
axis([-1e3 -1e-3 1e-4 1e3])
set(gca,'XDir','Reverse')
set(gca,'FontSize',14);
xlabel('\omega_0^{(S)}\tau_c')
ylabel('T_2 [s]')
legend('\sigma_{zz}^{(S)} = 0 ppm','\sigma_{zz}^{(S)} = 50
  ppm','\sigma_{zz}^{(S)} = 150 ppm')
```
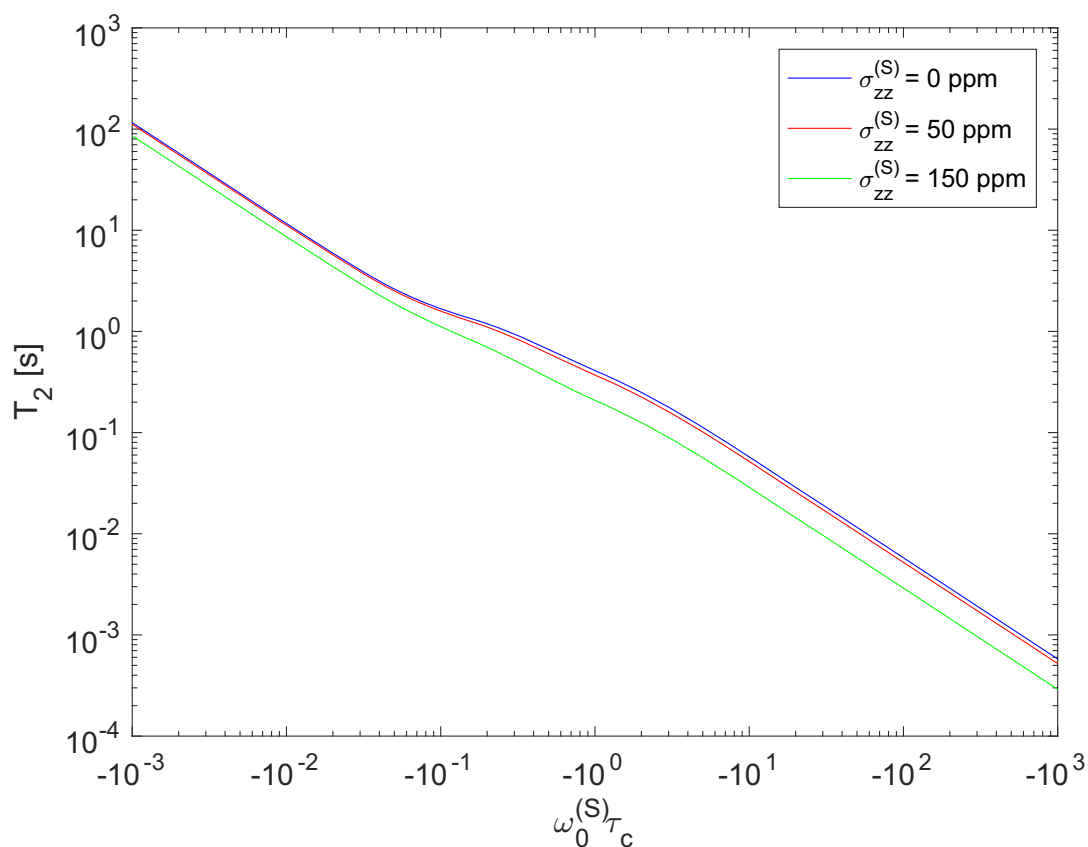
- Calculate and plot T_{2S} for chemical-shielding tensor values of $\sigma_{zz}^{(S)}$ = 50 ppm and 150 ppm. What do you observe?

- **Solution**:

    As in the case of T_1 relaxation, increasing the CSA tensor will increase the relaxation rate constant and, therefore, decrease the T_2 time as can be seen in Figure 1.4

    MATLAB code already included in the previous question.

Figure 1.4: Plot of Transverse T_2 Relaxation Times
Plot of the transverse relaxation times for a N-H two-spin system in a static magnetic field of 14.1 T with a bond length of 1.1 Å. Three different values for the chemical-shielding tensor are shown.
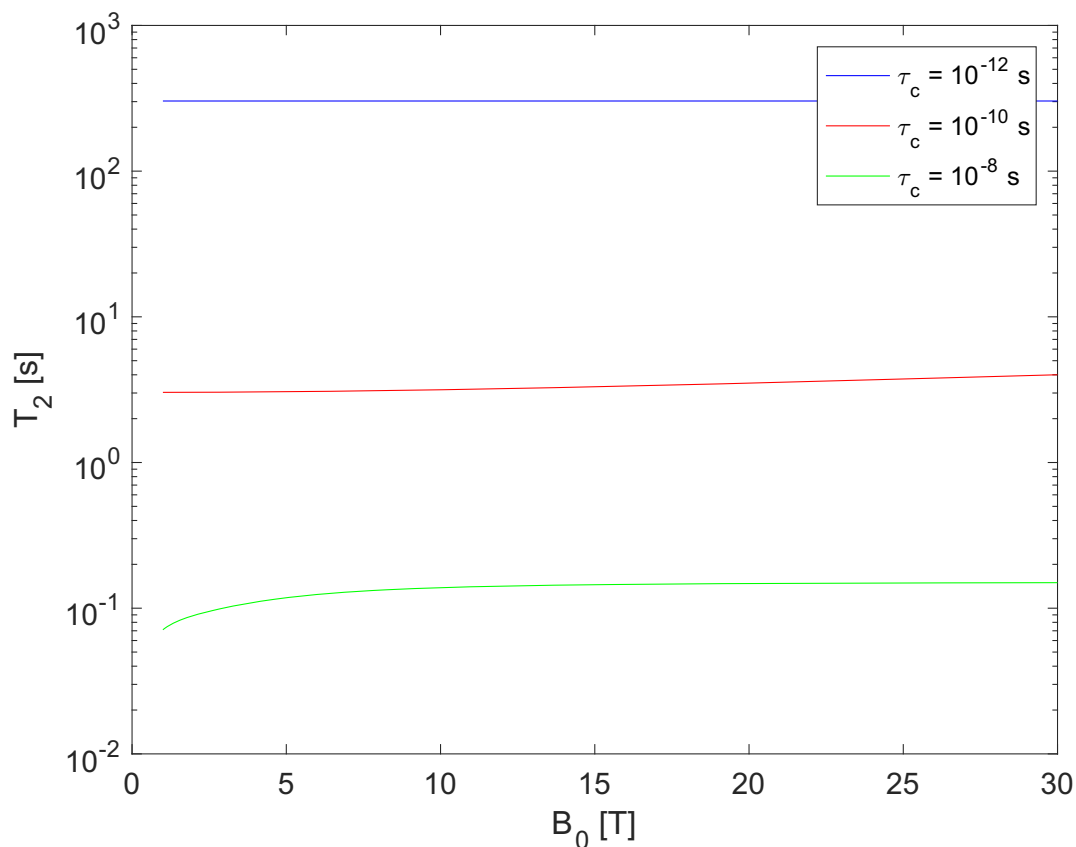
- Calculate T_{2S} as a function of the static magnetic field B_0 between 1 and 30 T for correlation times τ_c of 10^{-12}, 10^{-10}, and 10^{-8} s. We assume that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm.

- **Solution**:

The B_0-field dependence of T_2 relaxation can be seen in Figure 1.5. There is only a weak dependence on the B_0 field since for all three correlation time T_2 is mainly determined by the J(0) spectral-density contribution.

MATLAB code to plot the B_0 dependence of T_2:

```
tauc1=1e-12;
tauc2=1e-10;
tauc3=1e-8;
B0=1:0.01:30;
omegaI=gammah*B0;
omegaS=gamman*B0;
T2N1 = T2(delta,sigmazz00,omegaI,omegaS,tauc1);
T2N2 = T2(delta,sigmazz00,omegaI,omegaS,tauc2);
```


Figure 1.5: Plot of T_2 as a Function of B_0
Plot of the ^{15}N T_2 relaxation time as a function of the static magnetic field B_0 for three different values of the correlation time.

```
T2N3 = T2(delta,sigmazz00,omegaI,omegaS,tauc3);
semilogy(B0,T2N1,'b');
hold on
loglog(B0,T2N2,'r');
loglog(B0,T2N3,'g');
hold off
set(gca,'FontSize',14);
xlabel('B_0 [T]')
ylabel('T_2 [s]')
legend('\tau_c = 10^{-12} s','\tau_c = 10^{-10} s','\tau_c = 10^{-8} s')
```

- Back calculate the correlation time from the T_1 and T_2 values calculated for the chemical-shielding tensor of $\sigma_{zz}^{(S)} = 0$ ppm. Plot the back calculated values against the input correlation times. In which range of correlation times is Equation [3.6] valid? Derive Equation [3.6] from the analytical Equations [3.4] and [3.5] for T_1 and T_2.

- **Solution**:

    The plot of the back calculated correlation time against the theoretical correlation time is shown in Figure 1.6. From this it is clear that Equation [3.6] is valid only for large molecules with a correlation time longer than about 1 ns. To obtain
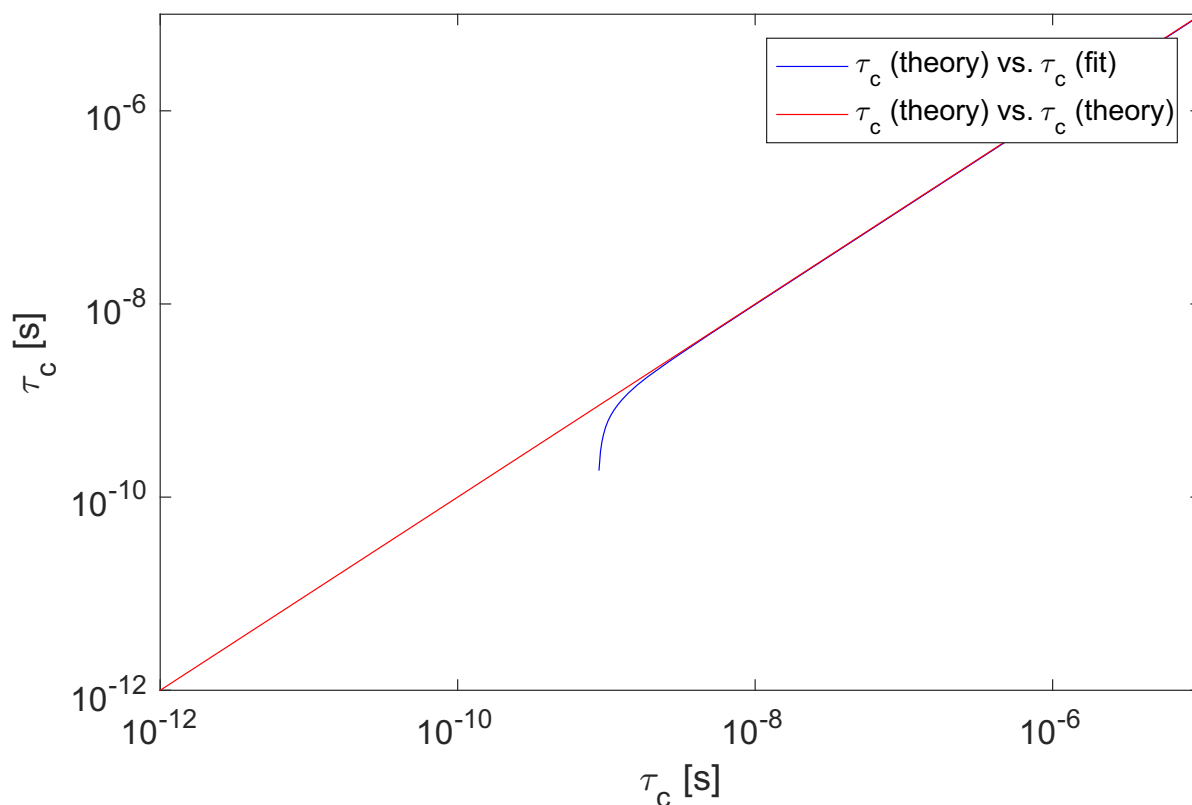
Figure 1.6: Plot Back Calculated Correlation Time
Plot of the back calculated correlation time against the theoretical correlation time.

Equation [3.6], we assume that only the spectral densities at frequency 0 and frequency ω_S are important which is correct for long correlation times or big molecules that tumble slowly. Using this assumption, we find:

$$\frac{T_1}{T_2} = \frac{2J(0) + \frac{3}{2}J(\omega_S)}{3J(\omega_S)} = \frac{2}{3}\frac{J(0)}{J(\omega_S)} + \frac{1}{2} = \frac{2}{3}(1 + (\omega_S\tau_c)^2) + \frac{1}{2} \qquad \text{[S-1.1]}$$

Equation [S-1.1] can be solved for τ_c and leads to Equation [3.6].

MATLAB code to plot the back calculated correlation time:

```
tauc = 10 .^ (-12:0.01:-5);
loglog(tauc,-real(1/(2*omegaS)*sqrt(6*T1N00./T2N00-7)),'b');
hold on
loglog(tauc,tauc,'r')
hold off
xlabel('\tau_c [s]')
ylabel('\tau_c [s]')
axis([1e-12 1e-5 1e-12 1e-5])
set(gca,'FontSize',14);
legend('\tau_c (theory) vs. \tau_c (fit)','\tau_c (theory) vs. \tau_c
  (theory)')
```

1.3 Coupled Relaxation Modes

- Calculate the time evolution of the S_z magnetization after a 180° inversion pulse, i.e., for an initial condition $\sigma_0 = -S_z$ by solving the differential Equation [3.8] assuming isotropic rotational tumbling at correlation times of $\tau_c = 10^{-8}$ and 10^{-10} s assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm. Compare the curve with a mono-exponential buildup towards thermal equilibrium with a time constant of T_{1S}. Discuss the results.

- **Solution**:

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

$$\frac{d}{dt}\begin{bmatrix} \langle I_z \rangle(t) \\ \langle S_z \rangle(t) \end{bmatrix} = -\begin{bmatrix} \Gamma_{I_z, I_z} & \Gamma_{S_z, I_z} \\ \Gamma_{S_z, I_z} & \Gamma_{S_z, S_z} \end{bmatrix}\begin{bmatrix} \langle I_z \rangle(t) - \langle I_z \rangle_{\text{eq}} \\ \langle S_z \rangle(t) - \langle S_z \rangle_{\text{eq}} \end{bmatrix} \qquad \text{[S-1.2]}$$

with the formal solution

$$\begin{bmatrix} \langle I_z \rangle(t) \\ \langle S_z \rangle(t) \end{bmatrix} = \exp\left(- \begin{bmatrix} \Gamma_{I_z, I_z} & \Gamma_{S_z, I_z} \\ \Gamma_{S_z, I_z} & \Gamma_{S_z, S_z} \end{bmatrix} t \right) \begin{bmatrix} \langle I_z \rangle(0) - \langle I_z \rangle_{eq} \\ \langle S_z \rangle(0) - \langle S_z \rangle_{eq} \end{bmatrix} + \begin{bmatrix} \langle I_z \rangle_{eq} \\ \langle S_z \rangle_{eq} \end{bmatrix}. \qquad \text{[S-1.3]}$$

The initial conditions are given by $\langle I_z \rangle(0) = \langle I_z \rangle_{eq} = -10 \langle S_z \rangle_{eq}$ and $\langle S_z \rangle(0) = -\langle S_z \rangle_{eq}$. In principle 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 $\Gamma_{S_z, I_z} = 0.1495$ $^{-1}$. 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 $\Gamma_{S_z, I_z} = 0.0153$ $^{-1}$. 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.

MATLAB code to plot the time evolution of the coupled system:

```
omegaS = 14.1*gamman;
omegaI = 14.1*gammah;
delta = -2*mu04pi*gamman*gammah*hbar/rnh^3;
sigmazz00=0;
tauc=1e-10;
T1S = T1(delta,sigmazz00,omegaI,omegaS,tauc);
T1I = T1(delta,sigmazz00,omegaS,omegaI,tauc);
T1IS = T1x(delta,sigmazz00,omegaS,omegaI,tauc);

R = [1/T1I,1/T1IS;1/T1IS,1/T1S];
t=0:0.01:15;
Sz=zeros(size(t));
Iz=zeros(size(t));

for k=1:length(t)
  z = expm(-R*t(k))*[0;-2]+[10;1];
  Iz(k)=z(1);
  Sz(k)=z(2);
end
plot(t,Sz,t,exp(-t/T1S)*(-2)+1)
```
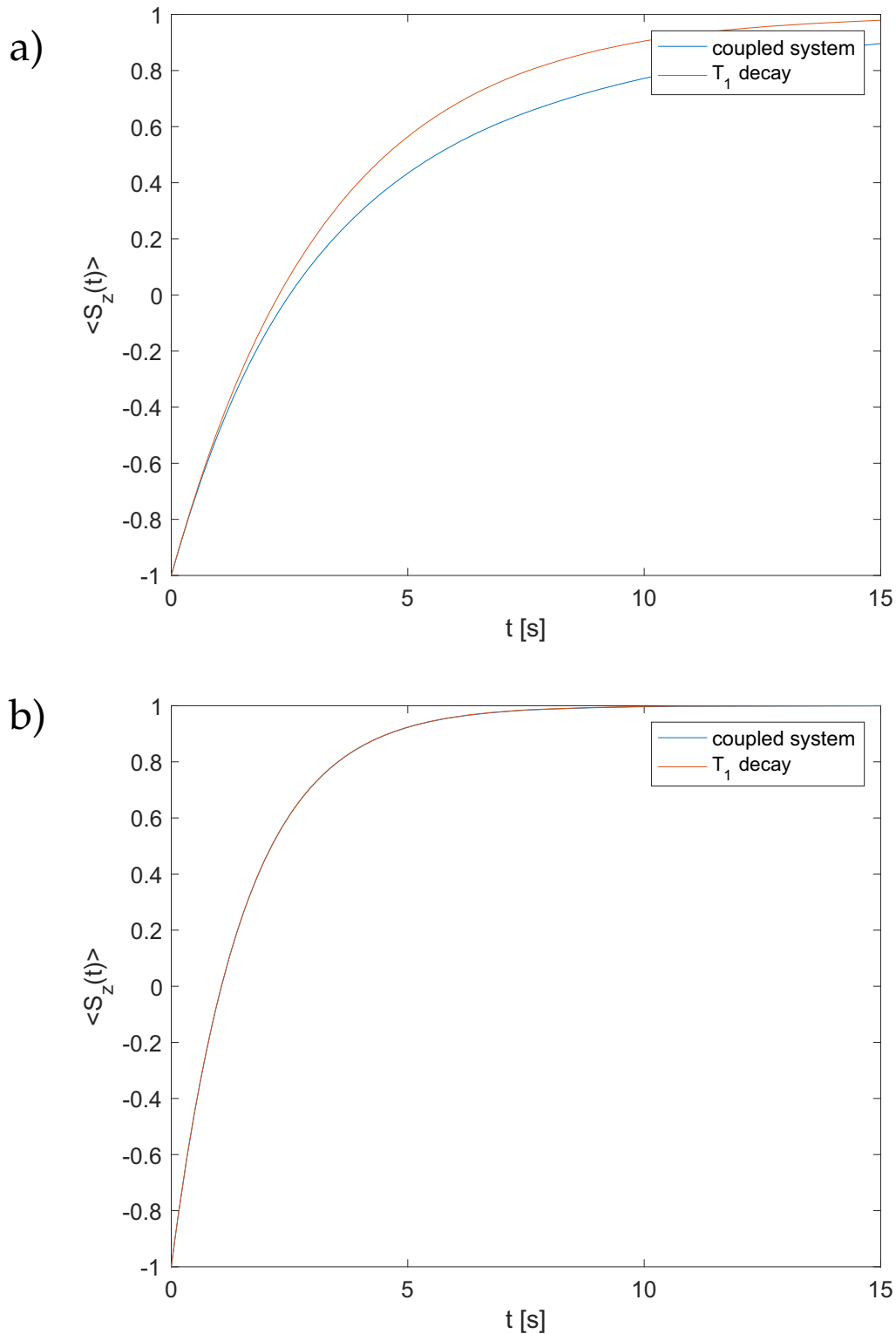
Figure 1.7: Plot of the Time Evolution of $<S_z>$

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 (blue lines) and as a mono-exponential decay with the time constant T_{1S} (red lines). a) for a correlation time 10^{-10} s and b) for a correlation time of 10^{-8} s.

```
ylabel('<S_z(t)>')
xlabel('t [s]')
set(gca,'FontSize',14);
legend('coupled system','T_1 decay')
```

There is also an alternate solution which uses the capability of MATLAB to solve differential equations:

```
clear all
%% Initializing constants

mu_0=4*pi*1e-7;
h_bar=1.05457*1e-34;
gamma_H=2.675e8;
gamma_N=-2.716e7;

B0=14.1;
r12=1.1e-10;
delta_iso=0;
delta_iso_H=0;
tau_c=1e-10; % correlation time

omega_H=-gamma_H*B0;
omega_N=-gamma_N*B0;

delta_HN=-2*mu_0*gamma_H*gamma_N*h_bar/4/pi/(r12^3);
S_z0=-1; % initital condition for S spin after inversion
S_zeq=1; % thermal equilibrium
I_z0=S_zeq*omega_H/omega_N; % I spin in thermal equilibrium = I_z(eq)
I_zeq=I_z0;

J_tau=@(omega) 2/5*tau_c/(1+(omega*tau_c).^2); % isotropic rotational
  tumbling

G_Iz=(delta_HN/4)^2*(J_tau(omega_H-
  omega_N)+3*J_tau(omega_H)+6*J_tau(omega_H+omega_N))+3/
  4*(omega_H*delta_iso_H)^2*J_tau(omega_H); %matrix elements of relaxation
  matrix
G_Sz=(delta_HN/4)^2*(J_tau(omega_H-
  omega_N)+3*J_tau(omega_N)+6*J_tau(omega_H+omega_N))+3/
  4*(omega_N*delta_iso)^2*J_tau(omega_N);
G_IzSz=(delta_HN/4)^2*(-J_tau(omega_H-omega_N)+6*J_tau(omega_H+omega_N));

%% Coupled differential equations

syms Iz(t) Sz(t) % integrated solver for coupled differential equations in
  matlab;
G = -[G_Iz G_IzSz; G_IzSz G_Sz]; % relaxation matrix
Y = [Iz; Sz]; % time dependence of spins
B = [I_zeq; S_zeq]; % equilibrium value
C = Y(0) == [I_z0; S_z0]; % initial condition
eqn = diff(Y) == G*(Y-B);
[IzSol(t), SzSol(t)] = dsolve(eqn, C);

figure(1)
```

```
ezplot(SzSol,[0 15])
hold on;
title('')
xlabel('t / s')
ylabel('<S_Z(t)>')
ylim([-1 1])

%% Monoexponential decay

T1 = 1/G_Sz; % T1 for monoexponential decay of S_z
t=(0:0.02:15); % generate time axis
Sz_mono = 1-2*exp(-t/T1); % evolution of S_z magnetization during inversion
  recovery

figure(1)
plot(t,Sz_mono,'r')
legend('coupled system', 'T_1 decay')
```

- 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.

- **Solution**:

  If we assume hat $\langle I_z \rangle(t) = 0$, Equation [S-1.2] simplifies to

$$\frac{d}{dt}\begin{bmatrix}\langle I_z \rangle(t) \\ \langle S_z \rangle(t)\end{bmatrix} = -\begin{bmatrix}\Gamma_{I_z, I_z} & \Gamma_{S_z, I_z} \\ \Gamma_{S_z, I_z} & \Gamma_{S_z, S_z}\end{bmatrix}\begin{bmatrix}-\langle I_z \rangle_{\text{eq}} \\ \langle S_z \rangle(t) - \langle S_z \rangle_{\text{eq}}\end{bmatrix} \qquad \text{[S-1.4]}$$

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

$$\frac{d}{dt}\langle S_z \rangle(t) = \Gamma_{S_z, I_z}\langle I_z \rangle_{\text{eq}} - \Gamma_{S_z, S_z}(\langle S_z \rangle(t) - \langle S_z \rangle_{\text{eq}}) \qquad \text{[S-1.5]}$$

The solution for Equation [S-1.5] can be calculated and gives

$$\langle S_z \rangle(t) = \langle I_z \rangle_{\text{eq}}\frac{\Gamma_{S_z, I_z}}{\Gamma_{S_z, S_z}} + \langle S_z \rangle_{\text{eq}} - \left(\langle I_z \rangle_{\text{eq}}\frac{\Gamma_{S_z, I_z}}{\Gamma_{S_z, S_z}} + 2\langle S_z \rangle_{\text{eq}}\right)e^{-\Gamma_{S_z, S_z}t} . \qquad \text{[S-1.6]}$$

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).

- The same experiment, i.e., saturation of the *I* spin is the so-called steady-state NOE experiment. Calculate analytically the steady-state value of the NOE. What is the signal enhancement generated by the NOE? Calculate the signal enhancement numerically as a function of the correlation time assuming that the chemical-shielding tensor is $\sigma_{zz}^{(S)} = 0$ ppm.

- **Solution**:

We can again start from Equation [S-1.5] and assume a steady-state condition, i.e. $\frac{d}{dt}\langle S_z \rangle(t) = 0$. This leads to

$$\Gamma_{S_z, I_z}\langle I_z \rangle_{\text{eq}} - \Gamma_{S_z, S_z}(\langle S_z \rangle(t) - \langle S_z \rangle_{\text{eq}}) = 0 \qquad \text{[S-1.7]}$$

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

$$\langle S_z \rangle(t) = \frac{\Gamma_{S_z, I_z}}{\Gamma_{S_z, S_z}}\langle I_z \rangle_{\text{eq}} + \langle S_z \rangle_{\text{eq}} = \langle S_z \rangle_{\text{eq}}\left(1 + \frac{\Gamma_{S_z, I_z}}{\Gamma_{S_z, S_z}}\frac{\langle I_z \rangle_{\text{eq}}}{\langle S_z \rangle_{\text{eq}}}\right) = \langle S_z \rangle_{\text{eq}}(1 + \eta) . \quad \text{[S-1.8]}$$

Therefore, the signal enhancement is given by

$$\eta = \frac{\Gamma_{S_z, I_z}}{\Gamma_{S_z, S_z}}\frac{\langle I_z \rangle_{\text{eq}}}{\langle S_z \rangle_{\text{eq}}} = \frac{\Gamma_{S_z, I_z}}{\Gamma_{S_z, S_z}}\frac{\gamma_I}{\gamma_S} \qquad \text{[S-1.9]}$$

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 η 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.

MATLAB code to generate the NOE plot:

```
tauc = 10 .^ (-12:0.01:-5);
omegaS = 14.1*gamman;
omegaI = 14.1*gammah;
delta = -2*mu04pi*gamman*gammah*hbar/rnh^3;
sigmazz00=0;
T1S = T1(delta,sigmazz00,omegaI,omegaS,tauc);
T1IS = T1x(delta,sigmazz00,omegaS,omegaI,tauc);

eta = T1S./T1IS*gammah/gamman;
```

```
semilogx(omegaS*tauc,eta,'b');

ylabel('\eta')
set(gca,'FontSize',14);
axis([-1e3 -1e-3 -6 1])
set(gca,'XDir','Reverse')
set(gca,'FontSize',14);
xlabel('\omega_0^{(S)}\tau_c')
```

If you find mistakes or want to suggest additions/corrections, please E-mail me at maer@ethz.ch.
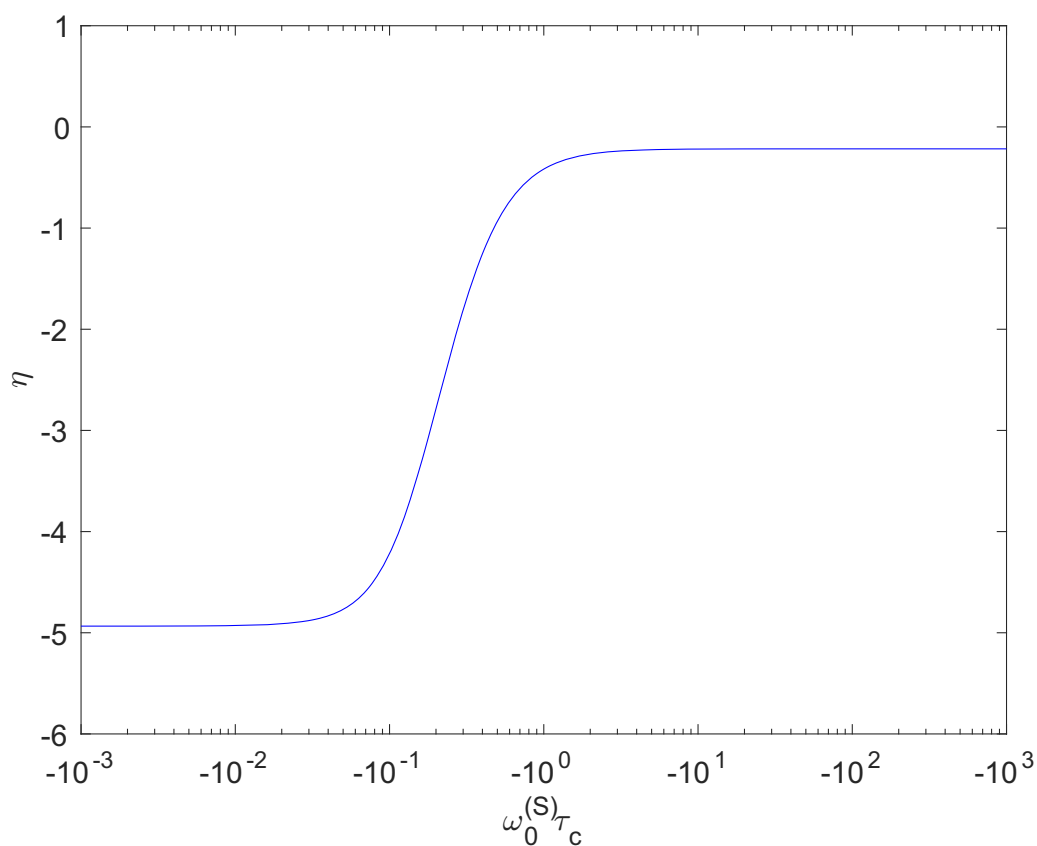
Figure 1.8: Plot of the NOE Enhancement η as a function of the correlation time τ_c
For short correlation times (small molecules) a significant enhancement of the steady-state polarization is obtained compared to the Boltzmann polarization. For larger molecules (long correlation times), only a small enhancement is observed.