**Theory**

**Spin Diffusion**

In the classic formation of a spin-echo (i.e. $90^\circ$-$\tau$-$180^\circ$-$2\tau$) the intensity of the echo will damp according to $T_2$ relaxation processes. However, in the presence of inhomogeneities in the magnetic field, if a spin drifts to a location in which the magnetic field is different, the Larmor frequency changes and the spin will not refocus with the remaining spins. We can then re-write the Bloch equation to account for diffusion processes

$$\frac{dM}{dt} = \gamma MB - \frac{M_x + M_y}{T_2} - \frac{M_z - M_0}{T_1} + D \nabla^2 M$$

Typically, the changes in the Larmor frequency have a negligible effect. However, application of a Gradient, $G$, will induce a large change in Larmor frequencies experienced at places in the sample.

**Magnetic Field Gradient Echo**

The principle behind the DOSY experiment is the formation of a magnetic field gradient echo. This is a spin-echo in which a magnetic field gradient is applied during the spin evolution. Thus spins that diffuse during this time will not refocus in the spin echo, as the application of the gradient will impart their own magnetic field.

**Pulse Program**

The sequence consists of a conventional Hahn echo (spin echo) sequence in which two gradient pulses are applied at equal timings after the 90 and 180 degree pulses. The gradients are opposite in magnitude. The basic principle relies on the diffusion of spins in the sample. Initially the 90 degree pulse tips the magnetization into the x-y plane, where spins begin to precess with their characteristic Larmor frequencies. The application of a gradient sometime after the 90 degree pulse, encodes a spatial component to the spin. That is the gradient is not uniform over the sample and therefore, the precessional frequencies will change. Next the application of the 180 flips the magnetization to refocus the spins. However, the spins, due to the application of the gradient will not refocus. The application of a gradient at the same time (but with opposite direction) will refocus the spins at a total time of $2 \tau$. If a spin diffuses to a different place in the sample, the refocusing will not occur, leading the dampening of the echo intensity.
Below is the basic pulse sequence for a pulsed field gradient experiment.

Processing

Processing the data is fairly straight forward. Apply a Fourier Transformation along the F2 dimension. The F1 dimension, in which either the time or the gradient was incremented remains in the time domain. The echo intensity of a given peak is then described by:

\[ \ln \mu \left( g_a, t_c \right) - \ln \mu \left( 0, t_c \right) = -C_n \gamma^2 D \delta^2 g_a^2 t_D \]

where \( \mu \left( g_a, t_c \right) \) is the echo amplitude after the gradient application, \( \mu \left( 0, t_c \right) \) is the echo amplitude with no gradient applied, \( C_n \) is a constant that depends on the particular pulse sequence used, \( \gamma \) is the gyromagnetic ratio, \( D \) is the diffusion coefficient, \( \delta \) is the width of the applied gradient, and \( t_D \) is the diffusion time.