## 4.4 The Pulsed Gradient Spin Echo (PGSE) Experiment

Pulsed gradient spin echo (PGSE) is an versatile experiment and can be used to measure molecular self-diffusion coefficients and fluid flow.

The pulse sequence is shown below (Figure 4.14) and is based around the spin-echo 90° - 180° sequence used for measuring $T_2$ relaxation. However the difference here is that we also apply two narrow magnetic field gradient pulses shortly after each $B_1$ pulse.

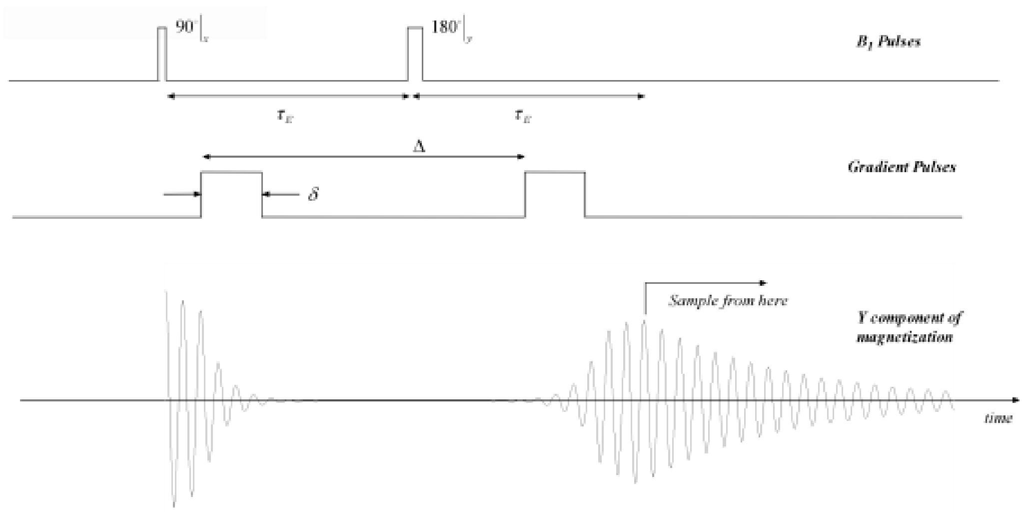
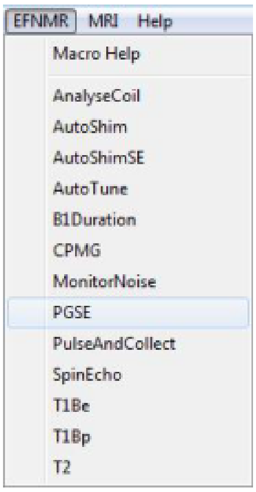



*Figure 4.14. Pulse sequence for measuring diffusion (polarizing pulse not shown)*




During the first gradient pulse, the magnetization vectors in different parts of the sample will precess at very different rates due to the (almost) linearly varying field and so phase coherence is rapidly lost. If no molecular motion occurs before the second gradient pulse is applied, then these vectors will reverse their motion, due to the action of the 180° pulse, and so form an echo as in the simpler $T_2$ sequence. However if motion has occurred in the direction of the applied gradient, either due to self-diffusion or flow - then the re-phasing will be incomplete since the spins will experience a different local field during the second gradient pulse. The result will be a modified echo amplitude. If self-diffusion has occurred, the amplitude will be reduced (since re-phasing will be incomplete), while for pure flow there will be a phase shift. In this experiment we will measure the self-diffusion coefficient of water. To reduce the effects of convection (a problem in large samples) you can use a porous material soaked in water (such as a sponge or small glass beads) as a sample. As long as the pore sizes are not so small as to restrict the motion of the water during the experiment we will see a diffusion coefficient equal to that of free water.

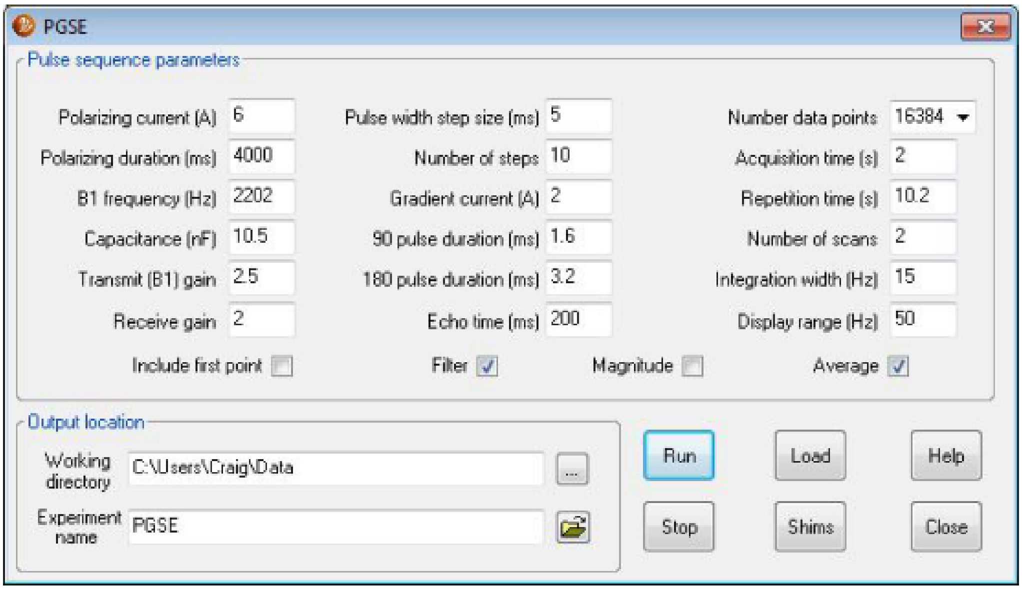



*Figure 4.15. The PGSE dialog*

Set up the experiment as for $T_2$ relaxation. The $B_1$ pulse parameters are chosen as before. The delay between the pulses will depend on the $T_2$ of the sample, but should be long enough to accommodate the gradient pulses and the ring-down they produce (20 ms before and typically 100 ms after the gradient pulse switches off). If you are performing this experiment in an area of high magnetic field homogeneity you may find it necessary to spoil the homogeneity of the field by deshimming the probe. This ensures that excitation transients caused by the switching gradients do not interfere as much with the experiment. (However this is less of an issue with this experiment than $T_2$ because of the dephasing action of the PGSE gradients.)

The gradient parameters determine the number of pulse durations used in the experiment. In the above example there are 10 steps. The first has a gradient pulse 5 ms long , the second 10 ms and so on up to a maximum of 50 ms. All pulse will have an amplitude of 2 A. The zero length step is included if the "Include first point" checkbox is selected. The "Gradient current" text box in the dialog sets the gradient current in the device and informs the macro of the chosen value so that the correct calculation can be performed. Finally, as with the relaxation experiments, you can choose to average data for each separate set of parameters to improve the signal-to-noise ratio.

The output of this experiment, like the $T_1$ and $T_2$ experiments, is a changing echo amplitude, decreasing in this case. The change in amplitude can be understood and analysed by employing a simple model for diffusion and assuming that the molecules only move between and not during the gradient pulses.

Using this narrow gradient pulse approximation it can be shown that a spin at position **r** during the application of the first gradient pulse acquires a phase shift $\gamma g\delta \cdot \mathbf{r}$. If it then moves to position **r′** it will acquire a second phase shift of $-\gamma g\delta \cdot \mathbf{r}'$ during the second gradient pulse. The net phase shift will therefore be $\gamma g\delta \cdot (\mathbf{r}' - \mathbf{r})$. The total signal acquired in the PGSE experiment will be the ensemble average of all the phase shifts $\exp[\,i\,\gamma g\delta \cdot (\mathbf{r}' - \mathbf{r})\,]$ weighted by the probability for a spin to start at position **r** and finish at position **r′**.

The probability can be represented by an averaged propagator $P_s(\mathbf{R},\Delta)$ where $\mathbf{R} = \mathbf{r}' - \mathbf{r}$ . For self-diffusion with coefficient $D$ this propagator will be a Gaussian function

$$\overline{P_s}(Z,\Delta) = (4\pi D\Delta)^{-1/2}\exp\left(-Z^2 \big/ 4D\Delta\right) \qquad [4\text{-}3]$$

and the echo attenuation function, assuming gradients along the $z$-axis direction, will be given by

$$E_0(g) = \int_{-\infty}^{\infty} (4\pi D\Delta)^{-1/2}\exp(-Z^2/4D\Delta)\exp(i\gamma\delta g Z)\,dZ \qquad [4\text{-}4]$$

which simplifies to

$$E_0(g) = \exp(-\gamma^2\delta^2 g^2 D\Delta) \qquad [4\text{-}5]$$

Taking into account the finite duration of the gradient pulses leads to the exact expression determined by Stejskal and Tanner[1] for the echo amplitude, $E$, as a function of gradient field strength, g, namely

$$\frac{E(g)}{E(0)} = \exp\left[-\gamma^2 g^2\delta^2 D(\Delta - \delta/3)\right], \qquad [4\text{-}6]$$

where $\gamma$ is the gyromagnetic ratio of the observed nucleus, $g$ is the gradient field strength of the gradient pulse, $\delta$ is the length of the gradient pulse, $D$ is the diffusion coefficient and $\Delta$ is the delay between the two gradient pulses. This equation can be linearized and used to calculate the diffusion coefficient.

In Figure 4.16 the echo amplitudes are plotted and fitted to the Stejska-Tanner[1] equation to obtain a value for the self-diffusion coefficient of tap water.

The example in Figure 4.16 does not include the first data point. A common error in this experiment is that this first data point is not on the line. This is often due to convection effects in large liquid samples.

It is sometimes difficult to produce a straight line in this graph. Make sure that the range of pulse lengths is not too large relative to the echo time and compensate by using a large current to ensure that there is sufficient attenuation (2 A is the maximum). We recommend an echo time of at least 200 ms and a minimum delay between gradient pulse and 180 pulse of 100 ms.

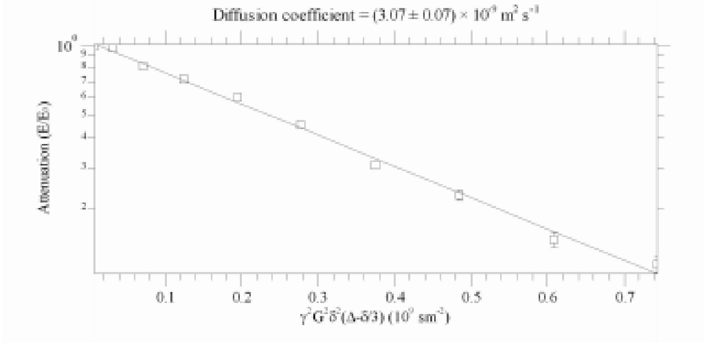



*Figure 4.16. PGSE Analysis*

Attenuations greater than a factor of 10 are difficult to achieve with good signal-to-noise so this should also be considering when choosing parameters. In magnitude mode it is typical to see the data curving

[1] Stejskal, E.O. and Tanner, J.E. (1965). J. Chem. Phys. 42, 288

up at the end of the plot if the attenuation is too great. A line which curves down for larger attenuations is usually caused by insufficient delay between gradient pulse and 180 pulse. In this case increase the echo time or decrease the pulse step size.