One-dimensional diffusion in pulsed gradient spin echo using superoperator sum formalism

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Abstract

We review the pulsed gradient spin echo applied to the study of diffusive behavior. Concentrating on one-dimensional dynamics, we then treat the density operator at the echo center in the superoperator sum formalism, characterizing one set of matrices liable to describe the superoperator associated with the state evolution during the aforementioned experiment as a sum. Using the obtained general results, matrix elements are analytically derived for the regimes of completely free and restricted diffusion. In the limit of infinite diffusion time, free diffusion is shown to be characterized by a fading of the echo signal, whereas in restricted diffusion an asymptotic signal background is present. The limits and crossings of the two regimes descriptions are also investigated.

1 Pulsed gradient spin echo

The pulsed gradient spin echo (PGSE) is a well-studied method to probe diffusive motion of particles with spins. It involves applying on a sample under study a standard spin echo sequence, composed of two radio-frequency pulses, and two additional magnetic field gradients inserted into the dephasing and rephasing intervals.

The sample is prepared in its equilibrium magnetization in the presence of a static magnetic field. A Π/2) radio-frequency pulse starts the experiment, followed by a Π) pulse after an interval τ. An echo is thus expected to form at time 2τ. A magnetic field gradient with magnitude g, duration δ and along a desired direction is applied between the two radio-frequency pulses, beginning at a time t_i, $0 < t_i < \tau$. A second identical gradient pulse follows the Π) pulse, so that an interval Δ has elapsed between them. The interval Δ is chosen such that the second gradient pulse ends before the spin echo formation. Experimentally, $\delta \approx 1ms$ and $\Delta \approx 100ms$, so that in the following discussion we neglect molecular motion during the application of the gradient. Radio-frequency pulses are taken as instantaneous.

Consider the Hamiltonian $\mathcal{H}$ of a spin $\frac{1}{2}$ particle when the static magnetic field and the gradient are both along the $\hat{z}$ direction. In this case, the equilibrium magnetization is along $\hat{z}$ and the radio-frequency pulses have phases of, respectively, $\frac{\pi}{2}$ ("pulse along y") and 0 ("pulse along x"). Following the Π/2) pulse, which aligns the magnetization along $\hat{x}$, inhomogeneities in the local magnetic field cause the individual spins to process with their own Larmor frequencies, leading to a (coherent) dephasing of spins in the transverse magnetization plane. Therefore, in the gradient-free intervals after the first radio-frequency pulse,

$$\mathcal{H} = \frac{\hbar\omega\Sigma_z}{2}, \tag{1}$$

ω being the Larmor frequency of the particle. Henceforth, we denote the i^{th} Pauli matrix as Σ_i.

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During the interval δ of application of the first magnetic gradient, the instantaneous Hamiltonian becomes

$$\mathcal{H}(z,t) = \frac{\hbar(\omega + \gamma g t z)\Sigma_z}{2}, \quad (2)$$

where γ is the gyromagnetic ratio. Clearly, the gradient creates a sinusoidally varying magnetization grating through the spatial extent of the sample along $\hat{z}$, with wavelength $\frac{2\pi}{\gamma g \delta}$, so that to the dephasing of the spins in the transverse plane is added a total modulation of the phase. The phase factor accumulated during the first gradient for a particle at z_0 is $e^{i\gamma g \delta z_0}$. Subsequently, the phases of the particles are inverted by the refocusing Π) pulse. In absence of diffusion, after the second gradient the net accumulated phase for a static particle at z_0 is thus 0. In case of migration of a particle during the diffusion interval Δ, from its initial position z_0 into a final position z falling in a region of different gradient strength, the accumulated phase factor is non-trivial and given by $e^{i\gamma g \delta |z-z_0|}$. The experimental sequence and diffusion mechanism described above are depicted in Figure 1.

Such an accumulated phase factor will remain at the echo center, inducing an attenuation of the echo signal. This signal, here noted $E(\gamma g \delta)$, is a superposition of transverse magnetization, *i.e.*, an ensemble average in which each phase term $e^{i\gamma g \delta |z-z_0|}$ is weighted by the conditional probability that a particle moves from z_0 to z during an interval Δ:

$$E(\gamma g \delta) = \int P(z_0) P(z|z_0, \Delta) e^{i\gamma g \delta |z-z_0|} dz dz_0. \quad (3)$$

The echo signal is simply the Fourier transform of the conditional displacement probability function. At its turn, $P(z|z_0, \Delta)$ is the solution of the inhomogeneous diffusion equation, depending on the desired boundary conditions, and with a point

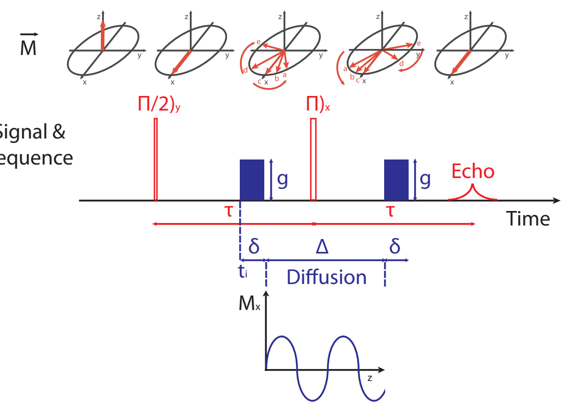

Figure 1: *In red, a standard spin echo sequence, during which the sample magnetization rotates (above, also in red). In blue, two additional magnetic field gradients, inserted into the dephasing and rephasing intervals; they complete the pulsed gradient spin echo sequence, which, in the presence of diffusion, induces a sinusoidally varying transverse magnetization grating through the sample along the gradient direction (below, also in blue).*

source at (z_0, t_0):

$$\left(\frac{\partial}{\partial t} - D\frac{\partial^2}{\partial z^2}\right) P(z|z_0,[t,t_0]) = \delta(z-z_0)\delta(t-t_0), \quad (4)$$

where D, the diffusion coefficient, measures mobility at molecular level. It is thus evident that acquiring the echo along the direction in momentum space given by the gradient allows one to measure D for that direction.

Hereafter, we restrict ourselves to the study in real space of one-dimensional diffusion problems.

2 Superoperator sum formalism for PGSE

It is often desirable to have a closed form for the evolution of the state of the system, given by its density operator $\rho(t)$ at a time of interest t. We can thus define a map from density operators to other density operators; such maps are known as superoperators, denoted hereafter by ϵ. Linear, completely positive trace-preserving superoperators can be expressed in the form [3]:

$$\epsilon(\rho) = \sum_{k=1}^{N^2} E_k \rho E_k^\dagger, \tag{5}$$

with

$$\sum_{k=1}^{N^2} E_k^\dagger E_k = \mathbb{1}, \tag{6}$$

where ρ has dimensions $N \times N$.

In particular, in PGSE, we are interested in obtaining a superoperator sum form for the state of the system at the echo center, $\epsilon(\rho(2\tau)) = \sum_{k=1}^{N^2} E_k \rho(2\tau) E_k^\dagger$. In order to do so, we take the initial ρ_0,

$$\rho_0 \equiv \begin{pmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{pmatrix} [1], \tag{8}$$

to be the density operator describing the system after the $\Pi/2)_y$ pulse, and let it evolve through the action of the evolution operator $\mathcal{U}$,

$$\mathcal{U} =$$

$$\mathrm{U}_F(z, [t_i + 2\delta + \Delta - \tau, 2\tau])\times$$

$$\times U_G(z, [t_i + \delta + \Delta - \tau, t_i + 2\delta + \Delta - \tau])\times$$

$$\times U_{F|G}(z, z_0, [\tau, t_i + \delta + \Delta - \tau])\times$$

$$\times(-i\Sigma_x)\times$$

$$\times U_{F|G}(z, z_0, [t_i + \delta, \tau])\times$$

$$\times U_G(z_0, [t_i, t_i + \delta])\times$$

$$\times U_F(z_0, [0, t_i]). \tag{9}$$

The partial evolution operators U_i are constructed as follows:

$$U_F(z_1, [t_1, t_2]) = e^{-\frac{i\omega(t_2 - t_1)\Sigma_Z}{2}} \sqrt{P(z_1)},$$

$$\mathrm{U}_G(z_1, [t_1, t_2]) = e^{-\frac{i\gamma g(t_2 - t_1) z_1 \Sigma_Z}{2}} e^{-\frac{i\omega(t_2 - t_1)\Sigma_Z}{2}},$$

$$\mathrm{U}_{F|G}(z_2, z_1, [t_1, t_2]) =$$

$$\mathrm{e}^{-\frac{i\omega(t2 - t1)\Sigma_Z}{2}} \sqrt{P(z_2|z_1, t_2 - t_1)}. \tag{10}$$

The desired $\rho(2\tau)$ is then obtained via

$$\rho(2\tau) = \int \mathcal{U} \rho_0 \mathcal{U}^\dagger dz dz_0. \tag{11}$$

PGSE takes the matrix ρ_0 into $\rho(2\tau)$ of the form

$$\rho_0 = \begin{pmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{pmatrix} \mapsto \rho(2\tau) = \begin{pmatrix} \mathbb{A}\rho_{11} & \mathbb{B}\rho_{10} \\ \mathbb{C}\rho_{01} & \mathbb{D}\rho_{00} \end{pmatrix}. \tag{12}$$

The superoperator sum elements E_k are obtained following a straightforward procedure [4]. We first determine a matrix mapping $\rho_0 \mapsto \rho(2\tau)$, and subsequently construct the associated Choi matrix. One set of matrices E_k is then given by, in column form, $E_k = \sqrt{\lambda_k} v_k$, where λ_k and v_k are, respectively, the eigenvalues and corresponding eigenvectors of the Choi matrix. This leads us to the general result for one-dimensional diffusion in PGSE:

$$E_1 = E_2 = \mathbb{O},$$

$$\mathrm{E}_3 = \sqrt{\frac{(\mathbb{A}+\mathbb{D}) - \sqrt{4\mathbb{B}\mathbb{C} + (\mathbb{A}-\mathbb{D})^2}}{2}}\times$$

$$\times \begin{pmatrix} 0 & \frac{(\mathbb{A}-\mathbb{D}) - \sqrt{4\mathbb{B}\mathbb{C} + (\mathbb{A}-\mathbb{D})^2)}}{2\mathbb{C}} \\ 1 & 0 \end{pmatrix},$$

$$\mathrm{E}_4 = \sqrt{\frac{(\mathbb{A}+\mathbb{D}) + \sqrt{4\mathbb{B}\mathbb{C} + (\mathbb{A}-\mathbb{D})^2}}{2}}\times$$

[1] Although the formalism described here is general, for the sake of completeness, the previously defined initial density operator ρ_0 is written explicitly:

$$\rho_0 = \frac{\mathbb{1} + \Sigma_x}{2} = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \tag{8}$$

$$\times \begin{pmatrix} 0 & \frac{(\mathbb{A}-\mathbb{D})+\sqrt{4\mathbb{B}\mathbb{C}+(\mathbb{A}-\mathbb{D})^2)}}{2\mathbb{C}} \\ 1 & 0 \end{pmatrix} . \quad (13)$$

Subsequently, we determine $\mathbb{A}$, $\mathbb{B}$, $\mathbb{C}$ and $\mathbb{D}$ for the completely free and restricted diffusion regimes. Note that, in the absence of diffusion, we expect $\mathbb{A} = \mathbb{B} = \mathbb{C} = \mathbb{D} = 1$.

3 Free diffusion results

The conditional displacement probability density for a free, non-interacting Brownian particle in a one-dimensional homogeneous slab of infinite extent is the free solution of (4):

$$P(z|z_0, \Delta) = \frac{e^{-\frac{(z-z_0)^2}{4D\Delta}}}{\sqrt{4\pi D\Delta}}; \quad (14)$$

it depends only on the relative displacement $|z - z_0|$ of the particle and on the elapsed time Δ. In PGSE experiments where the size of the sample L is much larger than the free diffusion length $\sqrt{2D\Delta}$, diffusion can be correctly approximated as free. Integration over space as in (11), followed by application of the superoperator sum formalism, gives, for free diffusion in a one-dimensional slab of large extent L,

$$\mathbb{A} = \mathbb{D} = \frac{2\sqrt{D\Delta}}{L\sqrt{\pi}}(e^{-\frac{L^2}{4D\Delta}} - 1) + erf\left(\frac{L}{2\sqrt{D\Delta}}\right), \quad (15)$$

tending to 1 as $L \to \infty$, and

$$\mathbb{B} = \mathbb{C} = \frac{2\sqrt{D\Delta}}{L\sqrt{\pi}}\left(e^{-\frac{L^2}{4D\Delta}} \cos\left(\frac{\gamma g \delta L}{2}\right) - 1\right) +$$

$$+ \mathrm{e}^{-\frac{\gamma^2 g^2 \delta^2 D\Delta}{4}} erf\left(\frac{L}{2\sqrt{D\Delta}}\right). \quad (16)$$

These coefficients tend to $e^{-\frac{\gamma^2 g^2 \delta^2 D\Delta}{4}}$ in the same limit. This is just the attenuation of the signal at the echo center; in the absence of diffusion, $\Delta = 0$ and $\mathbb{B} = \mathbb{C} = 1$; for $\Delta \to \infty$, $\mathbb{B} = \mathbb{C} = 0$ and no signal is observed.

4 Restricted diffusion results

In this case, the free diffusion length exceeds the average size of the sample. In other words, it is the regime favored for large Δ. Information about the size of the sample L can thus be extracted.

When the molecular movement is restricted by confinement, the propagator is no longer Gaussian since the diffusion of the molecules in contact with the boundaries is hindered. In analogy to a problem of heat conduction in a one-dimensional slab, the conditional displacement probability distribution can be calculated using (4) [2],

$$P(z|z_0, \Delta) = \frac{1}{L} \times$$

$$\times \left(1 + 2\sum_{n=1}^{\infty} e^{\frac{-n^2\pi^2 D\Delta}{L^2}} \cos\left(\frac{n\pi z}{L}\right) \cos\left(\frac{n\pi z_0}{L}\right)\right), \quad (17)$$

with the boundary condition that $P(z|z_0, \Delta) = 0$ when z_0 or z coincides with one of the edges, located L apart.

Note that when $\Delta \to \infty$, $P(z|z_0, \Delta) \to P(z) = \frac{1}{L}$ reduces to the static molecular density. We can thus speak of fully restricted diffusion, and the conditional displacement probability distribution is independent of the initial position z_0 and of the interval Δ: the system has lost memory.

We find

$$\mathbb{A} = \mathbb{D} = 1 \quad (18)$$

and

$$\mathbb{B} = \mathbb{C} = \frac{16}{L^2}\left(\frac{\sin\left(\frac{\gamma g \delta L}{4}\right)}{\gamma g \delta}\right)^2 +$$

$$+ 32\gamma^2 g^2 \delta^2 L^2 \times$$

$$\times \sum_{n=1}^{\infty} \frac{e^{-\frac{n^2\pi^2 D\Delta}{L^2}} [(\frac{1+(-1)^{n+1}}{2}) + (-1)^n \sin\left(\frac{\gamma g \delta L}{4}\right)^2]}{(\gamma^2 g^2 \delta^2 L^2 - 4\pi^2 n^2)^2}. \quad (19)$$

In the limit $\Delta \to \infty$, $\mathbb{B}$ and $\mathbb{C}$ reach an asymptotic

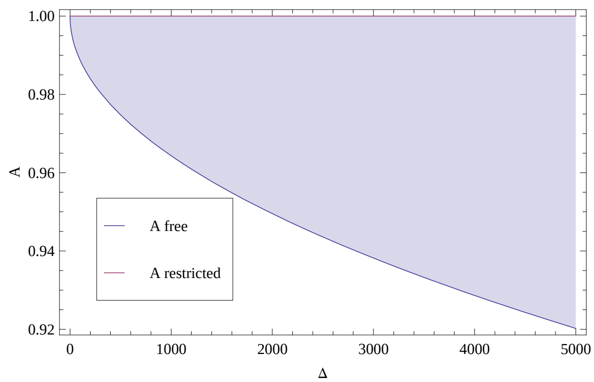

Figure 2: *Coefficient $\mathbb{A}$ in both studied regimes. As expected, $\mathbb{A}$ in the free regime tends to* 1 *for diffusion time* $\Delta = 0$.

value, instead of decreasing indefinitely:

$$\mathbb{B}, \mathbb{C} \rightarrow \frac{16}{L^2} \left(\frac{\sin\left(\frac{\gamma g \delta L}{4}\right)}{\gamma g \delta} \right)^2 ; \qquad (20)$$

this is characteristic of a trapped particle. Moreover, in the limit $\Delta \rightarrow \infty$ and $\gamma g \delta \rightarrow 0$, these coefficients tend to 1, as expected.

5 Analysis

We expect to retrieve free diffusion behavior in the short diffusion time limit of the restricted diffusion regime. This is effectively what is observed in Figures 2 and 3, where we plot the coefficients $\mathbb{A}$ and $\mathbb{B}$ for both regimes, using $L = 1000$, $D = 1$ and $\gamma g \delta = 0.1$. Both $\mathbb{A}$ coefficients coincide for $\Delta = 0$, and restricted $\mathbb{B}$ tends to free $\mathbb{B}$ at the small Δ limit. For long Δ the behaviors of the free and restricted coefficients are diverse. Note the finite value to which $\mathbb{B}$ in the restricted case converges, in comparison to free $\mathbb{B}$ tending to 0.

Conversely, in figure 4, we indicate for free $\mathbb{B}$ the value of Δ at which the free diffusion approximation breaks down, for several values of L. As a threshold, we use L being one order of magnitude larger than $\sqrt{2D\Delta}$.

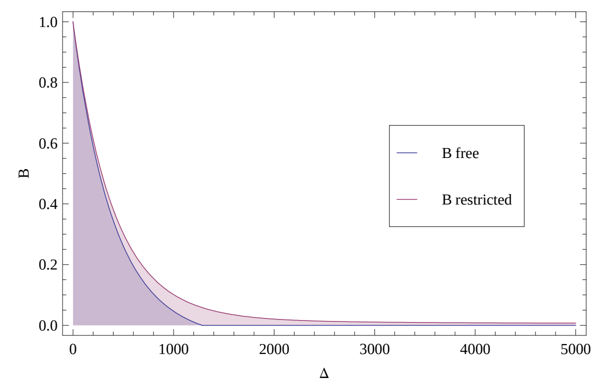

Figure 3: *Coefficient $\mathbb{B}$ in both studied regimes. Both tend to* 1 *for short diffusion times* Δ, *and have different asymptotic forms as* $\Delta \rightarrow \infty$.

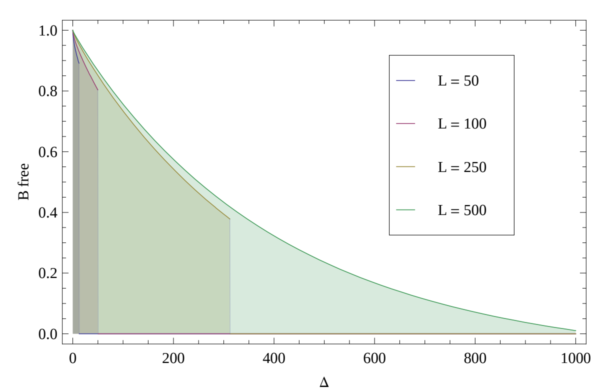

Figure 4: *Diffusion time breakdown of the free diffusion approximation for different medium lengths* L.

6 Conclusion

We have studied the pulsed gradient spin echo in the superoperator sum formalism, and analytically determined the elements of the sum matrices set for two extreme regimes, namely completely free and restricted diffusion. It was then shown that free diffusion results are accordingly recovered by the restricted diffusion evolution in the limit of small diffusion times. The diffusion time threshold that validates the free diffusion approximation were also calculated for different medium lengths.

References

[1] Callaghan, P.T., *Principles of Nuclear Magnetic Resonance Microscopy*. Oxford University Press, Oxford (1991).

[2] Tanner, J.E., Stejskal, E.O., "Restricted self-diffusion of protons in colloidal system by the pulsed-gradient, spin-echo method", *Journal of Chemical Physics* **49**, pp. 1768 (1968).

[3] Kraus, K., *States, Effects, and Operations: Fundamental Notions of Quantum Theory*, Lecture Notes in Physics, Vol. 190. Springer-Verlag, Berlin (1988).

[4] Weinstein, Y.S., *et al.*, "Quantum process tomography of the quantum Fourier transform", *Journal of Chemical Physics* **121**, pp. 6117 (2004).