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Theory of the spin echo signal in NMR microscopy: analytic solutions of a generalized Torrey–Bloch equation

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Abstract

Exact solutions of a generalization of the Torrey–Bloch equation are obtained for use in nuclear magnetic resonance microscopy. The generalization addresses the motion of the nuclear spins towards an attractive centre with, furthermore, an arbitrary time dependence in the attractive (harmonic) potential. The solutions provide an analytic way to interpret observations made with gradient magnetic fields of arbitrary (finite) pulse duration. Limiting results for infinitesimal pulses are shown to reduce to earlier expressions and new effects are described for finite pulses.

1. Introduction and background

Chemical kinetics, as a subject and a methodology, appears in physics in a variety of guises. Nuclear magnetic resonance (NMR), the topic of the present paper, uses its procedures such as Fokker–Planck formalisms in its theoretical development. In the following we describe some of this use both from a general viewpoint and from the viewpoint of specific experiments on the spin echo signal. A number of new results are presented.

Much interest has centred around NMR experiments that use the pulsed and constant magnetic field gradient in order to study molecular translational motion of diffusing particles. Examples of successful applications of this procedure are studies of porous media in which information about the morphology of the media has been extracted [1, 2], of liquid crystals where confinement in porous silica aerogel matrices has been studied [3], of rocks where, for purposes of oil extraction, characterization of pore sizes has been carried out [4], and of biological tissues where the methodology has been used in various medical contexts [5].

The system under consideration consists, typically, of a large number of particles, each possessing nuclear spin, that diffuse in the presence of two static parallel external magnetic fields, taken to point along the z axis, one strong and homogeneous $\mathbf{B}_0$, and the other weak

and systematically inhomogeneous. The inhomogeneity is designed with a linear gradient $\mathbf{G} = Gxf(t)\hat{\mathbf{x}}$, where $\hat{\mathbf{x}}$ is the unit vector in the x direction, G the strength of the gradient and $f(t)$ its temporal shape function. The experiments take advantage of the inhomogeneous external magnetic field to characterize the attenuation of what is called the NMR signal $M(t)$ or more properly the spin echo amplitude. For instance, freely diffusing spins under the constant field gradient manifest an attenuation of the NMR signal which is cubic in time [6], specifically, $\ln[M(t)/M(0)] = -Dg^2t^3/3$, where g is defined as the product of the strength of the gradient field G and the gyromagnetic ratio of the particles γ, and D is the particle diffusion constant. The attenuation of the NMR signal is due to the combined effects of the inhomogeneous magnetic field and the (diffusive) motion of the particles. This should be clear from the appearance of the product Dg^2 in the attenuation expression above.

While pioneering studies of diffusing spins by NMR were performed in unrestricted geometries under time independent field gradients in the Hahn echo experiment [6–8], more recent growth of interest in the procedure stemmed from Stejskal and Tanner's pulsed gradient spin echo (PGSE) method [9–11]. One reason for the interest is the possibility of a simple interpretation of the PGSE experiment in the limit as the pulse duration $\delta \to 0$ and $g \to \infty$ while δg remains finite, in analogy to the nuclear scattering process. That interpretation serves as the basis of **q**-space magnetic resonance imaging [12]. In that narrow pulse approximation, analytical expressions for the attenuation factor can be obtained by just knowing the conditional probability, $P(\mathbf{r}, \Delta|\mathbf{r}_0)$, of finding a spin particle at position $\mathbf{r}$ at time Δ if initially the particle is at $\mathbf{r}_0$. Thus, provided $\delta \to 0$ (and $g \to \infty$ in the manner described above), the normalized spin echo amplitude is given by

$$M(\Delta) = \int \mathrm{d}\mathbf{r}_0\, P(\mathbf{r}_0) \int \mathrm{d}\mathbf{r} P(\mathbf{r}, \Delta|\mathbf{r}_0) \exp\{\mathrm{i}g\delta\hat{\mathbf{x}} \cdot (\mathbf{r} - \mathbf{r}_0)\}. \tag{1}$$

However, in practice, δ is by no means infinitesimally small, its typical value in actual experiments being of the order of milliseconds. Certainly, important diffusion effects may occur *during* the gradient pulses. A number of analytic attempts have therefore been made to obtain usable expressions for the echo signal that are valid beyond the assumption of vanishing δ. Perhaps the most well known of them is based on the use of the method of cumulants [13, 14]. The probability distribution of the quantity $\varphi(t) \equiv \int_0^t \mathrm{d}t' g f(t') x(t')$ is approximated as a Gaussian. Here $x(t)$, the position of the spin as function of time, is analysed as a random variable. When a truncation approximation is used on the cumulant expansion, the spin echo amplitude is found to be

$$M(t) = \exp\{-\tfrac{1}{2}\langle\varphi^2(t)\rangle\}, \tag{2}$$

where the symbol $\langle\ \rangle$ denotes an average over all possible trajectories $x(t)$.

The truncated cumulant approximation has obviously a limited range of validity. A number of attempts to go beyond that range have been made in the literature [15, 16]. Another way of obtaining usable formulae for the spin echo signal that are valid for non-vanishing pulse extent is to return to the so-called Torrey–Bloch equation (TBE) [6] and to attempt to solve it under the simultaneous action of the field gradient and diffusion. Exact analytical expressions have been obtained [17] in this manner for arbitrary time dependence of the field gradient and for arbitrary initial spin distribution in space. The TBE is the equation of motion that governs the evolution of the transverse magnetization density $M(\mathbf{r}, t)$, which, in its one-dimensional version, has the form

$$\frac{\partial M(x,t)}{\partial t} = -\mathrm{i}gf(t)xM(x,t) + D\frac{\partial^2 M(x,t)}{\partial x^2}. \tag{3}$$

The first term in the right-hand side of (3) refers to the arbitrary time dependent linear gradient field, where $g = G\gamma$ and $f(t)$ is the temporal shape of the gradient field taken to be in the x direction. The second term in the right-hand side of (3) arises from the diffusing spins with diffusion constant D. The quantity of interest is the NMR signal, which, in its simplest spatially unresolved form, is defined as

$$M(t) = \int \mathrm{d}x\, M(x, t). \tag{4}$$

In the present paper we provide analytic solutions of the TBE when it is augmented by terms representing the influence on the spins of a *harmonic potential* in the presence of gradient pulses of arbitrary duration. There are two motivations for carrying out this analysis. The first is the contribution that our formulation can make to the understanding of the NMR signal in *confined* spatial regions [15–19] through a representation of the walls of the confined space by a potential. We will postpone to a future publication our considerations in that context. The second motivation is experimental, is relevant to the observations made by Callaghan and Pinder [20] on polymeric gels for verifying the model of de Gennes [21], and is explained in the next section.

Our paper is outlined as follows. In section 2 we first explain the experimental motivation for our analysis ending with the approximate formula given by Stejskal [9] for spin diffusion in the presence of a potential and applied by the authors of [20] to gels. We then state without derivation the *exact* formula we have obtained and show that, in the limit of infinitesimal pulse duration, it reduces to the approximate expression given by Stejskal and used by Callaghan and Pinder. We express our result as the product of the latter (approximate) result and a correction factor, examine the correction factor for finite pulses, and describe the new predictions expected in Callaghan and Pinder's experiments on the basis of our exact formula. In section 3, we show the analytical detail of the derivation of our exact formula from the generalized Torrey–Bloch equation. The generalization consists of replacing the diffusive term in (3) by its Fokker–Planck extension that describes the attractive potential. We have been able to provide exact solutions not only for a fixed harmonic potential but for a time dependent potential as well. The potential must be harmonic in shape but may have *any* given time dependence. In section 4, we also show several predictions for the NMR signal on the basis of our analysis. Section 5 consists of concluding remarks.

2. Experimental motivation: Callaghan's verification of the de Gennes model of gels

An interesting series of NMR microscopy experiments were performed by Callaghan and Pinder [20] to test a model developed by de Gennes [21] for diffusion in sufficiently concentrated solutions of polystyrene random-coil macromolecules, generally called 'gels'. According to the model of de Gennes, gel segments exhibit 'cooperative diffusion' for experimental observation times shorter than the relaxation gel time. A scaling law emerges [21] for the cooperative diffusion constant $D_\mathrm{c} \sim c^{3/4}$, where c is the polymer concentration. This diffusive process is a consequence of longitudinal gel fluctuations of wavevector $\mathbf{k}$ caused by thermal energy.

To determine D_c and to verify its scaling law, Callaghan and Pinder used the standard PGSE experiment, which consists of the application of two gradient pulses each of duration δ and strength g, following a $\pi/2$ radio-frequency (rf) pulse, the second gradient pulse being applied a time Δ after the first pulse. In order to form the echo, a π rf pulse is applied between the two gradient pulses (figure 1). The authors of [20] modelled each gel segment as a particle undergoing diffusion in a harmonic potential under friction damping. They argued that the ratio

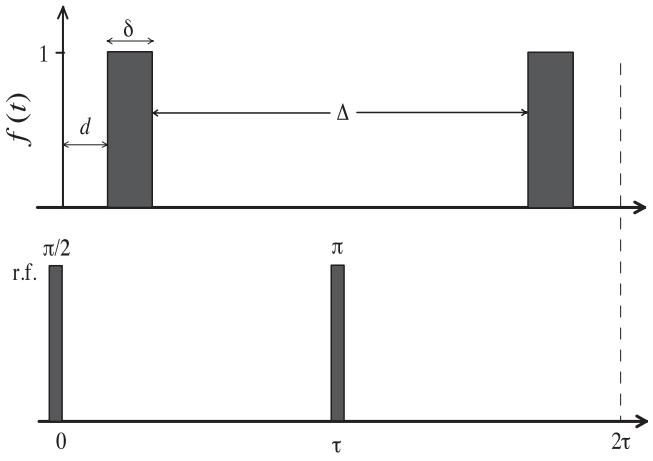

Figure 1. The standard pulse gradient spin echo consists in the application of two gradient pulses each of duration δ. The first pulse is applied a time d after the $\pi/2$ rf pulse, while the second gradient pulse being applied a time Δ after the first pulse. In order to form the echo, a π rf pulse is applied between the two gradient pulses, after a time τ from the $\pi/2$ rf pulse. The acquisition of the signal is made at a time 2τ, but, as explained in standard texts such as [12], is dependent on Δ and not on τ provided that $2\tau > \Delta$.

of the harmonic spring constant and the damping factor, which we call in the present paper A, is simply related to the longitudinal fluctuations of the gel, being proportional to D_c through $A \equiv D_c k^2$, and that the NMR signal is formed from the contribution of all gel segments with given A.

For the purposes of theoretical interpretation of their experimental observations, Callaghan and Pinder used [20] an expression derived by Stejskal [10] for the spin echo amplitude of particles diffusing in a harmonic potential,

$$M_S(\Delta) = \exp\left(-Dg^2\delta^2\left(\frac{1-\mathrm{e}^{-A\Delta}}{A}\right)\right), \tag{5}$$

especially its extreme limits for $A\Delta \ll 1$, and $A\Delta \gg 1$, and drew the important conclusion that the theory of de Gennes could be verified by their NMR observations[1]. Here, we are not interested in the details of that interpretation. Rather, the work reported in [20] provides one of the motivations for our present analysis. The Stejskal expression (5) used in [20] follows from (1) and is valid *only for infinitesimally small* δ and large g. By contrast, we have been able to obtain, through exact analysis for arbitrary pulse duration δ, its counterpart which goes beyond that limitation. What could be added to Stejskal's formula or to its use by the authors of [20] starting from our exact theory that is the content of the present paper? While the details of our derivation will be given below (in the next section), to answer this question briefly but directly, we anticipate our result for the PGSE,

$$M(\Delta) = \exp\left(-Dg^2\delta^2\left(\frac{1-\mathrm{e}^{-A\Delta}}{A}\right)\right)C(\delta,\Delta) \tag{6}$$

and see that our exact expression can be written as the infinitesimal-pulse version of Stejskal

[1] Equation (6) gives the echo attenuation for a gel segment with wavevector k. Generally, the total signal will be given by the superposition of all k dependent local signals of the whole sample. Therefore, if $p(k, T)$ is the distribution of the wavevectors $\mathbf{k}$ at temperature T, the total signal is given by $M_T(\Delta) = 4\pi \int_0^\infty \mathrm{d}k\, k^2\, p(k, T) M(\Delta, k)$.

times a correction factor. The correction factor $C(\delta, \Delta)$ is given by

$$C(\delta, \Delta) = \exp\left\{-\frac{Dg^2}{A^3}[(1 - e^{-A\Delta})[(1 - e^{-A\delta})^2 - A^2\delta^2] + 2A\delta \right.$$
$$+ \tfrac{1}{2}e^{-2A\Delta}(1 - e^{-A\delta})^2(e^{2A\delta} - 1) + -3 + e^{-A\delta}(4 - e^{-A\delta})$$
$$\left. + 2e^{-A\Delta}(1 - e^{-A\delta})[\cosh A\delta - 1]]\right\}. \tag{7}$$

Stejksal's result (5) is recovered from ours in the narrow pulse limit since $C(0, \Delta) = 1$, as can be checked by simple inspection. It is important to realize that, given that $A = D_c k^2$, the crucial quantity $A\Delta$ appearing in the expressions above is the square of the ratio of the experimental diffusion distance $D_c\Delta$ to the wavelength of the disturbance.

The correction to (5) in the same two extreme limits discussed by Callaghan and Pinder takes the following form. In the limit $A\Delta \ll 1$, the correction factor is given by

$$C_{A\Delta\ll 1} = \exp\left\{-\frac{Dg^2}{A^3}[A\Delta[(1 - e^{-A\delta})^2 - A^2\delta^2] + 2A\delta \right.$$
$$+ \tfrac{1}{2}(1 - e^{-A\delta})^2(e^{2A\delta} - 1) + -3 + e^{-A\delta}(4 - e^{-A\delta})$$
$$\left. + 2(1 - e^{-A\delta})[\cosh A\delta - 1]]\right\}. \tag{8}$$

In the limit $A\Delta \gg 1$, the correction is

$$C_{A\Delta\gg 1} = \exp\left\{-\frac{Dg^2}{A^3}[(1 - e^{-A\delta})^2 - A^2\delta^2 - 3 + e^{-A\delta}(4 - e^{-A\delta}) + 2A\delta]\right\}. \tag{9}$$

We show in figure 2 the difference between the δ dependence of our prediction for the signal (solid line) and that of the Stejskal expression (dashed line). For the parameter values chosen (arbitrary, for demonstration purposes only), we notice the expected result that the two coincide for small values of the pulse duration but differ for larger values. Typical values of the ratio δ/Δ appropriate to the Callaghan–Pinder experiments [20] are just under 0.2 and over 0.8. We notice that our expression does not add much in the first case but does make a substantial difference in the second. Surely, our choice $A\Delta = 0.05$ in figure 2 is not based on experimental information but is only illustrative. In the inset, we show, therefore, the signal differences for three widely varying values of $A\Delta$: 0.1, 1, 10.

3. Analytical derivation of the spin echo signal from a Fokker–Planck generalization of the Torrey–Bloch equation

We now present the manner in which the Torrey–Bloch equation can be solved exactly in the presence of the Fokker–Planck generalization for gradient pulses of arbitrary time dependence and duration. We generalize equation (3) by adding to the diffusion process the effects of an attractive external potential, and assume that the spin motion is sufficiently damped to make inertial terms unimportant:

$$\frac{\partial M(x,t)}{\partial t} = -igf(t)xM(x,t) + \frac{\partial}{\partial x}\left[D\frac{\partial M(x,t)}{\partial x} + \left(\frac{\partial}{\partial x}\mathcal{U}(x,t)\right)M(x,t)\right]. \tag{10}$$

We will provide exact analysis for the particular time dependence of the external potential given by $\mathcal{U}(x,t) = A(t)x^2/2$, in which case our point of departure becomes

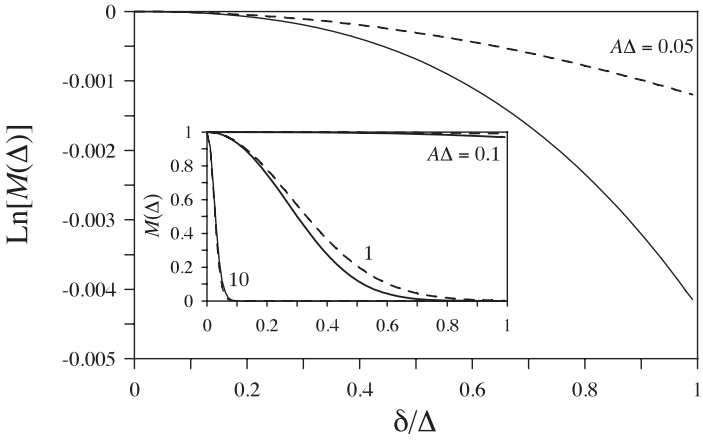

Figure 2. Difference between the dependence on the pulse duration δ, in units of Δ, of our prediction for the signal (solid line) and that of the Stejskal expression (dashed line) for $A\Delta = 0.05$ and $Dg^2\Delta^2/A = 10$. These parameter values are chosen arbitrarily for demonstration purposes only. The inset shows signal differences for three widely varying values of $A\Delta$: 0.1, 1, 10. Typical values of the ratio δ/Δ appropriate to the Callaghan–Pinder experiments [20] are just under 0.2 and over 0.8. The exact signal, as given by our analysis, differs substantially from Stejskal's approximation in the latter, but not in the former, case.

$$\frac{\partial M(x,t)}{\partial t} = -\mathrm{i}gf(t)xM(x,t) + \frac{\partial}{\partial x}\left[D\frac{\partial M(x,t)}{\partial x} + A(t)xM(x,t)\right]. \tag{11}$$

To find the general solution of equation (11), we write $M(x,t)$ as

$$M(x,t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}k\, \mathrm{e}^{\mathrm{i}kx}\hat{M}(k,t) \tag{12}$$

and obtain, for the evolution of the Fourier transform $\hat{M}(k,t)$,

$$\frac{\partial \hat{M}(k,t)}{\partial t} = [gf(t) - A(t)k]\frac{\partial \hat{M}(k,t)}{\partial k} - Dk^2\hat{M}(k,t). \tag{13}$$

In order to make further progress with equation (13), we identify it with an inhomogeneous continuity equation in k-space, and solve it by the method of characteristics [22]. The result, for any initial magnetization density and any time dependent field gradient, is

$$\hat{M}(k,t) = \hat{M}\left(k\,\mathrm{e}^{-\int_0^t \mathrm{d}s\, A(s)} + g\int_0^t \mathrm{d}t' f(t')\mathrm{e}^{-\int_0^{t'} \mathrm{d}s\, A(s)}, 0\right)$$
$$\times \exp\left\{-D\int_0^t \mathrm{d}t'\left[k\mathrm{e}^{-\int_{t'}^t \mathrm{d}s\, A(s)} + g\int_{t'}^t \mathrm{d}s\, f(s)\mathrm{e}^{-\int_{t'}^s \mathrm{d}\rho\, A(\rho)}\right]^2\right\}. \tag{14}$$

The inversion of the transform gives us an explicit solution of the time dependence of the spatially resolved magnetization density $M(x,t)$. The observed NMR signal (4) is obtained by integrating the magnetization density over all space, equivalently from (14) by taking the limit $k \to 0$, since

$$M(t) = \lim_{k\to 0}\int_{-\infty}^{\infty} \mathrm{d}x\, \mathrm{e}^{-\mathrm{i}kx}M(x,t) = \lim_{k\to 0}\hat{M}(k,t). \tag{15}$$

Thus, the time dependent NMR signal is obtained explicitly:

$$M(t) = \hat{M}\left(g \int_0^t \mathrm{d}t' \, f(t') \mathrm{e}^{-\int_0^{t'} \mathrm{d}s \, A(s)}, 0 \right) \exp\left\{ -D \int_0^t \mathrm{d}t' \left[g \int_{t'}^t \mathrm{d}s \, f(s) \mathrm{e}^{-\int_{t'}^s \mathrm{d}\rho \, A(\rho)} \right]^2 \right\}. \tag{16}$$

Equation (14) for the magnetization density, and equation (16) for the observed NMR signal, are the primary analytical results of this paper.

Reduction of our results to previously known expressions in special cases is straightforward. The expression derived in equation (8) of [17] is obtained merely by putting $A(t) = 0$ in our equation (14) above to signify the absence of the attractive potential. In addition, for $g = 0$, equation (14) reduces to

$$\hat{M}(k,t) = \hat{M}\left(k \mathrm{e}^{-\int_0^t \mathrm{d}s \, A(s)}, 0 \right) \exp\left\{ -D \int_0^t \mathrm{d}t' \left[k \mathrm{e}^{-\int_{t'}^t \mathrm{d}s \, A(s)} \right]^2 \right\}, \tag{17}$$

which is the solution, in the Fourier domain, of the Fokker–Planck equation for the time dependent Ornstein–Uhlenbeck process [23].

4. Consequences in specific cases

In this section, we investigate applications of our general formula (16) to several cases, specifically, (i) pulsed field gradient, (ii) constant field gradient, (iii) exponential turn-on, and (iv) sinusoidal turn-on. Case (i) is of widespread and direct observational interest while case (ii) is not only experimentally realizable but theoretically simple and therefore indicative of the essential effects. In any experiment the gradient field turn-on cannot be realized in infinitesimal time. As explained by Price [24] the rapid rise and fall of gradient pulses can generate eddy currents in the surrounding conducting surfaces around the gradient coils even when shielded gradient coils are used. Those eddy currents can cause phase changes in the observed spectrum, anomalous changes in the attenuation, gradient-induced broadening of the observed spectrum, and time dependent but spatially invariant shift effects in the static magnetic field. Therefore, the analysis of the NMR signal in the 'slow turn-on' gradient is important because such slow turn-ons are necessary to avoid these technical problems. The simplest form of a finite time turn-on is the exponential represented by case (iii). Finally, sinusoidal gradients may be employed to extract high frequency information in contrast to the pulsed gradient which is dominated by a zero-frequency lobe of width Δ^{-1} [12, 25].

Notice from equations (14) and (16) that, as in the expression given by Kenkre *et al* [17] for diffusive motion (with $A(t) = 0$), the signal in our present analysis appears as the product of a factor controlled by the initial condition, and a factor controlled by the diffusion constant. The contribution of the attractive potential appears in both factors through $A(t)$. The first factor is the Fourier transform of the *initial* magnetization density evaluated at a value of the Fourier variable k determined by its translation induced by the time integral of $gf(t)$ and its relaxation controlled by the time integral of $A(t)$ in the exponential. If the potential is absent ($A = 0$), the Fourier variable k drifts at a speed determined by the gradient field and, if $f(t)$ is a constant, eventually goes to infinity. If the potential is present, the drifting Fourier variable saturates to the value g/A which in the opposite limit of infinite A actually vanishes. The second (diffusion-controlled) factor introduces differences in the time dependences of the signal which will be described in the case of constant $f(t)$ below.

The effects due to initial conditions are introduced by choosing two distinctive initial distributions: one is a localized distribution, $\hat{M}(x,0) = M_0 \delta(x - x_0)$, where it is assumed that, initially, all the spins are localized at x_0. Of course, all the spins located at one point

is the picture one has in mind in this mesoscopic treatment. The second initial distribution corresponds to the stationary distribution of the transport process involved, i.e. to that of particles diffusing in this harmonic potential called Ornstein–Uhlenbeck process and given by the Gaussian $\mathrm{e}^{-Ax^2/2D}/\sqrt{2\pi\frac{D}{A}}$.

Although further discussion of the general case $A(t)$ is of considerable interest, we postpone it to future publications and concentrate in this paper on constant A. Then, equation (16) takes the simpler form

$$M(t) = \hat{M}\left(g\int_0^t \mathrm{d}t' f(t')\mathrm{e}^{-At'}, 0\right)\exp\left\{-D\int_0^t \mathrm{d}t'\left[g\int_{t'}^t \mathrm{d}s\, f(s)\mathrm{e}^{-A(t'-s)}\right]^2\right\}. \tag{18}$$

We now calculate from (18) the two-pulse formula (6) for the signal acquired at time Δ used in our discussion of the Callaghan–Pinder experiments.

4.1. Pulsed field gradient case

The pulsed field gradient experiment (depicted in figure 1) may be mimicked by the following[2] $f(t)$

$$f(t) = [-\theta(t-d) + \theta(t-d-\delta) + \theta(t-d-\Delta) - \theta(t-d-\Delta-\delta)], \tag{19}$$

where the θ's are Heaviside step functions of their argument. By substituting (19) in (18), the NMR signal acquired at $t = \Delta$ is then given by

$$M(\Delta) = \hat{M}\left[\frac{g}{A}\mathrm{e}^{-Ad}(1-\mathrm{e}^{-A\delta})(1-\mathrm{e}^{-A\Delta}), 0\right]m_{\mathrm{D}}(\Delta), \tag{20}$$

where the diffusion-controlled factor $m_{\mathrm{D}}(\Delta)$ is

$$\begin{aligned} m_{\mathrm{D}}(\Delta) = \exp\Bigg\{-\frac{Dg^2}{2A^3}(1-\mathrm{e}^{-A\delta})^2[(1-\mathrm{e}^{-2A\Delta}) + \mathrm{e}^{-2A\Delta}(\mathrm{e}^{2A\delta}-1) \\ + (1-\mathrm{e}^{-2Ad})(1-\mathrm{e}^{-A\Delta})^2]\Bigg\} \times \exp\Bigg\{-\frac{Dg^2}{A^3}[\mathrm{e}^{-A\delta}(4-\mathrm{e}^{-A\delta}) \\ - 3 + 2A\delta + 2\mathrm{e}^{-A\Delta}(1-\mathrm{e}^{-A\delta})[\cosh A\delta - 1]]\Bigg\}, \end{aligned} \tag{21}$$

while the first factor gives the contribution due to the initial magnetization density.

In the case when the initial magnetization density is localized at position x_0, (20) reduces to

$$M(\Delta) = \cos\left[\frac{gx_0}{A}\mathrm{e}^{-Ad}(1-\mathrm{e}^{-A\delta})(1-\mathrm{e}^{-A\Delta})\right]m_{\mathrm{D}}(\Delta), \tag{22}$$

where an explicit dependence on d, the time when the first pulse is applied, is seen. However, when the initial magnetization density $M(x,0)$ is proportional to the Gaussian $\mathrm{e}^{-Ax^2/2D}$, we get

$$M(\Delta) = \exp\left[-\frac{Dg^2}{2A^3}\mathrm{e}^{-2Ad}(1-\mathrm{e}^{-A\delta})^2(1-\mathrm{e}^{-A\Delta})^2\right]m_{\mathrm{D}}(\Delta). \tag{23}$$

This expression is independent of d because the initial distribution is stationary. Expressions (22), (23) show that the initial distribution plays an important role in the attenuation

[2] The $f(t)$ given by equation (19) represents the two pulses depicted in figure 1, with the exception that the amplitude of the first one is the negative of the second. This change of sign mimics the effect of the second radio-frequency pulse that occurs at τ [12].

of the signal. Of course, one may consider a Gaussian of width L, not related to D/A, as the initial distribution. In that case, the first factor will not depend on the diffusion constant D but indeed will contribute to the attenuation of the signal.

The correction factor $C(\delta, \Delta)$, discussed earlier, is obtained from (23) by simply computing $M(\Delta)\exp\{Dg^2\delta^2(1-\mathrm{e}^{-A\Delta})/A\}$. In the narrow pulse limit (small δ), we get

$$M(\Delta) = \mathrm{e}^{-Dg^2\delta^2(1-\mathrm{e}^{-A\Delta})/A}, \tag{24}$$

which agrees exactly with the result given by Stejskal's formula (1).

4.2. *Constant gradient case:* $f(t) = 1$

The NMR signal for the steady field gradient is given by

$$M(t) = \hat{M}\left[\frac{g}{A}(1-\mathrm{e}^{-At}), 0\right] M_{\mathrm{D}}(t) \tag{25}$$

where we have denoted the factor $m_{\mathrm{D}}(t)$ by $M_{\mathrm{D}}(t)$ for this constant gradient case:

$$M_{\mathrm{D}}(t) = \exp\left(-\frac{Dg^2}{A^2}t\right)\exp\left\{\frac{Dg^2}{A^3}\left[\frac{3}{2}+\frac{1}{2}\mathrm{e}^{-2At}-2\mathrm{e}^{-At}\right]\right\}. \tag{26}$$

For an initial Gaussian magnetization density proportional to $\exp\{-Ax^2/2D\}$, we get from (25)

$$M(t) = \exp\left(-\frac{Dg^2}{A^2}[t-\left(\frac{1-\mathrm{e}^{-At}}{A}\right)]\right), \tag{27}$$

whereas, for an initially localized magnetization density, i.e., when it is proportional to $\delta(x-x_0)$, the signal becomes

$$M(t) = \cos\left[\frac{gx_0}{A}(1-\mathrm{e}^{-At})\right] M_{\mathrm{D}}(t). \tag{28}$$

We notice a variety of possible time dependences of the signal according to the values of the dimensionless ratio $\alpha = A/(Dg^2)^{1/3}$, as well as of At. The physical significance of α can be understood from the well-known cubic dependence of the logarithm of the NMR signal on time if spins diffuse freely. The characteristic time in that free diffusion case is $(Dg^2)^{-1/3}$. The quantity α is simply the ratio of that free diffusion signal time to $1/A$, the characteristic time for the spin to be pulled into its attractive centre. The diffusion-controlled factor, defined in equation (26), has the characteristic free diffusion form, with an exponent cubic in time, for small At: for $At \to 0$, one obtains $M_D(t) \to \mathrm{e}^{-\frac{1}{3}Dg^2t^3}$. In the opposite limit of large At, one has a simple exponential decay: $M_D(t) \to \mathrm{e}^{-\frac{Dg^2}{A^2}t}$. This simple exponential decay also occurs in the limit $\alpha \to \infty$. By contrast, for $At \ll 1$ in the initial Gaussian case, one obtains a quite different time dependence:

$$M(t) = \exp\left(-\frac{Dg^2}{2A}t^2\right). \tag{29}$$

It is interesting as well as instructive to calculate the NMR signal of spins moving ballistically towards an attractive centre in the absence of diffusion. To that end, we set $D = 0$ in the above results and treat, in turn, a localized and a Gaussian initial spin distribution.

In the case of a localized initial distribution, the NMR signal at time t is simply given by equation (28) with $M_{\mathrm{D}}(t) = 1$. Generally, in the long time limit ($At \gg 1$), the signal goes to the constant $\cos(gx_0/A)$. However, it reaches the constant value in two different ways depending on the value of the dimensionless ratio gx_0/A. The signal shows a transition between oscillatory and non-oscillatory behaviour. If gx_0/A is less than $3\pi/2$ the NMR signal

attenuates, reaching the value $\cos(gx_0/A)$ exponentially. On the other hand, if $gx_0/A \geqslant 3\pi/2$, the signal oscillates before reaching the constant $\cos(gx_0/A)$. See figure 3(a). This result is straightforwardly generalized to the case when the initial density of spins is distributed in various well-localized positions, i.e. $M(x,0) = \sum_i M_i \delta(x - x_i)$, leading to

$$M(t) = \sum_i M_i \cos\left[\frac{gx_i}{A}(1 - \mathrm{e}^{-At})\right]. \tag{30}$$

If the x_i's are Gaussian distributed with width w, in the continuum limit we get

$$M(t) = \frac{1}{\sqrt{w^2\pi}} \int_{-\infty}^{\infty} \mathrm{d}x\, M_0(x) \mathrm{e}^{-x^2/w^2} \cos\left[\frac{gx}{A}(1 - \mathrm{e}^{-At})\right]. \tag{31}$$

If we assume $M_0(x) = M_0$, equation (31) reduces to the following attenuated signal:

$$M(t) = \exp\left\{-\frac{1}{2}\left(\frac{gw}{A}\right)^2 [1 - \mathrm{e}^{-At}]^2\right\}. \tag{32}$$

If initially the spins are distributed via a Gaussian of width w centred around x_0, specifically if $M(x,0) = \exp[-(x - x_0)^2/w^2]/\sqrt{w^2\pi}$, we get the following expression for the NMR signal:

$$M(t) = \cos\left[\frac{gx_0}{A}(1 - \mathrm{e}^{-At})\right] \exp\left\{-\frac{1}{2}\left(\frac{gw}{A}\right)^2 [1 - \mathrm{e}^{-At}]^2\right\}. \tag{33}$$

As is evident from the last result, the effect on the NMR signal, of a finite width w of the initial distribution, is an attenuation. How important this attenuation is will depend on the ratio w/x_0. See figures 3(b) and (c).

4.3. Exponential turn-on case

For this case we consider $f(t) = 1 - \exp(-t/\tau)$, τ being the turn-on time of the gradient field. We get

$$M(t) = \exp\left(-\frac{Dg^2}{A^3}[At + h(t)]\right), \tag{34}$$

where

$$\begin{aligned} h(t) = \left[1 - \frac{A\tau}{A\tau + 1}\mathrm{e}^{-t/\tau}\right]\left[\frac{2(A\tau)^2}{(A\tau)^2 - 1}(\mathrm{e}^{-t/\tau} - \mathrm{e}^{-At}) - 2(1 - \mathrm{e}^{-At})\right. \\ \left. - \frac{1}{2}(1 - \mathrm{e}^{-2At})\right] - \frac{A\tau}{(1 + A\tau)^2}\mathrm{e}^{-t/\tau}\left[A\tau(1 + A\tau)(\mathrm{e}^{t/\tau} - 1)\right. \\ \left. \times \tfrac{1}{2}(1 - \mathrm{e}^{-2At}) + -2(A\tau)^2 \sinh(t/\tau)\right]. \end{aligned} \tag{35}$$

The dependence of $M(t)$ upon A is shown in figure 4 for various values of the ratio $\alpha = A/(Dg^2)^{1/3}$.

4.4. Sinusoidal $f(t)$

If the turn-on is not monotonic, indeed, if the gradient is sinusoidal in time, we get $f(t) = \sin\omega t$ and obtain

$$\begin{aligned} M(t) = \exp\left(\frac{-Dg^2\cos\phi}{2(A^2 + \omega^2)^{3/2}}\right) \exp\left\{-\frac{Dg^2}{2(A^2 + \omega^2)}\left[t - \frac{\sin 2(\omega t + \phi)}{2\omega}\right.\right. \\ \left.\left. + \frac{\sin^2(\omega t + \phi)(1 - \mathrm{e}^{-2At})}{A} - \frac{4\sin(\omega t + \phi)(\sin\omega t)}{(A^2 + \omega^2)^{1/2}}\right]\right\} \end{aligned} \tag{36}$$

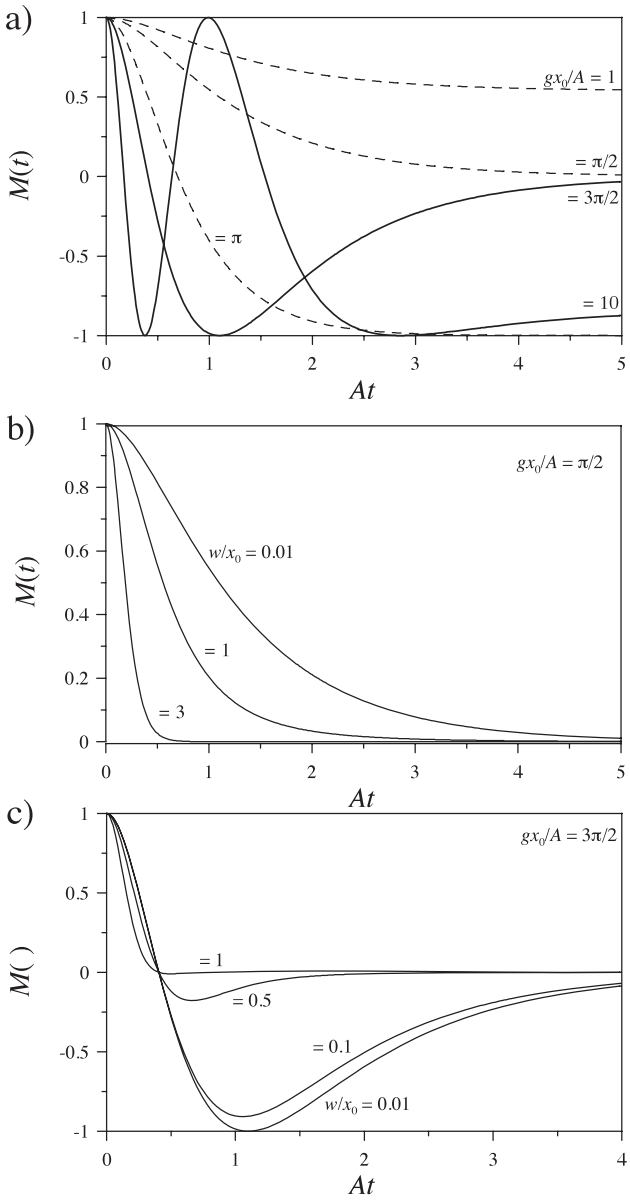

Figure 3. The normalized NMR signal $M(t)$ as function of the dimensionless time At, when there is no diffusion and the initial distribution of spin particles is localized at $x = x_0$. As the spin particles move ballistically from x_0 towards the attractive centre at $x = 0$, the frequency of the signal varies proportional to $(1 - e^{-At})$. If $gx_0/A \leqslant \pi/2$, the signal decays exponentially to the positive value $\cos(gx_0/A)$. If $\pi/2 \geqslant gx_0/A \leqslant \pi$, it decays to a negative value. If $3\pi/2 \geqslant gx_0/A$, it displays oscillations. In (a), the cases in which the NMR signal decays exponentially ($gx_0/A = 1, \pi/2$ and π) are shown by dashed lines. The oscillatory behaviour is shown by solid lines for the values $gx_0/A = 3\pi/2$ and 10. The dependence of the signal on the width of the distribution is shown in (b) for $gx_0/A = \pi/2$ and in (c) for $gx_0/A = 3\pi/2$, for various values of the ratio w/x_0.

where $\phi \equiv \arctan(\omega/A)$. The time dependence is shown in figure 4. Strong oscillations are seen for free diffusion ($\alpha = 0$). The oscillation amplitude reduces significantly as α increases.

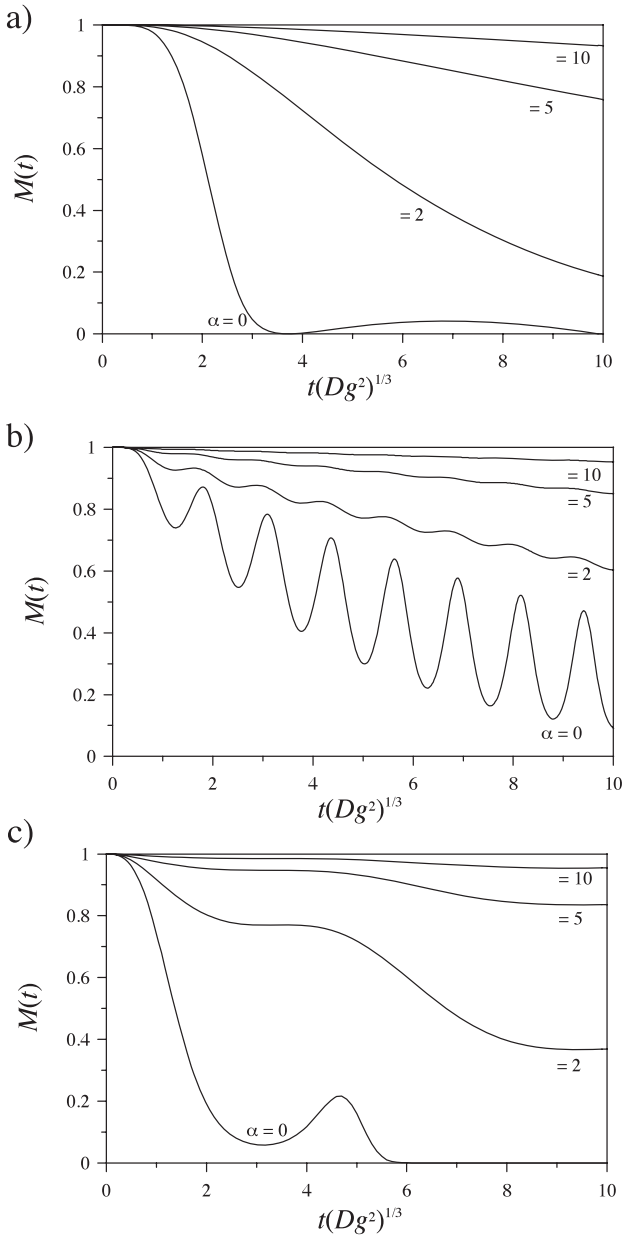

Figure 4. The normalized NMR signal $M(t)$ as function of the dimensionless time $t(Dg^2)^{1/3}$ for three time dependences of the gradient field: (a) slow turn-on, $f(t) = 1 - (\exp -t/\tau)$ with $\tau(Dg^2)^{1/3} = 2$, (b) sinusoidal from initial zero value, $f(t) = \sin \omega t$ with $\omega/(Dg^2)^{1/3} = 2.5$, and (c) sinusoidal from initial non-zero value, $f(t) = \cos \omega t$ with $\omega/(Dg^2)^{1/3} = 0.5$. Different curves correspond to different values of $\alpha = A/(Dg^2)^{1/3}$: 0, 2, 5 and 10 respectively. The curves labelled with $\alpha = 0$ correspond to the case of free diffusion. A conspicuous reduction of the attenuation signal is shown as α increases.

A sinusoidal turn-on from zero initial value of the gradient field has been considered above. For the case when the field is initially non-zero, we may consider $f(t) = \cos(\omega t)$ which

gives

$$M(t) = \exp\left(\frac{Dg^2\cos\phi}{2(A^2+\omega^2)^{3/2}}\right)\exp\left\{-\frac{Dg^2}{2(A^2+\omega^2)}\left[t + \frac{\sin 2(\omega t+\phi)}{2\omega} + \frac{\cos^2(\omega t+\phi)(1-\mathrm{e}^{-2At})}{A} - \frac{4\cos(\omega t+\phi)(\mathrm{e}^{-At}-\cos\omega t)}{(A^2+\omega^2)^{1/2}}\right]\right\}. \tag{37}$$

It is clear on the basis of figure 4 that in the three cases considered before, the effect of the harmonic potential is to reduce the attenuation of the NMR signal $M(t)$ with respect to the free diffusion case [17].

5. Conclusions

Starting from the Torrey–Bloch equation (3) generalized to include a harmonic potential of arbitrary time dependence driving the spin particles towards an attractive centre, specifically (11), we have given analytic usable expressions for the space-resolved magnetization density, as well as for the integrated NMR signal. Our results are equations (14) and (16) respectively. We have shown that a number of results known earlier, including those derived in [9, 17], emerge as particular cases of our expressions. In addition, our analysis provides new practically usable results. These are in equations (20), (25), (34), (36) and (37). We have depicted our results graphically in figures 3, 4.

Our analysis makes it possible to treat a variety of experimental situations, including ballistic motion of the spins toward a fixed target and different shapes of the field gradient. In the PGSE experiment, we give an exact treatment of pulses of arbitrary duration with the added advantage that the initial spin distribution may also be arbitrary. We find that the initial spin distribution plays an important role in the attenuation of the NMR signal. In particular, we have described oscillations in the signal when the initial distribution is localized at specific positions. The oscillations disappear for wide distributions but add up to further attenuation of the signal. One of the obvious applications of our theory is to the Callaghan–Pinder experiment [20] carried out for the verification of the gel model of de Gennes. We will report elsewhere on our further studies of that experiment. Also to be presented elsewhere are the exploration of time dependent $A(t)$, particularly the effects of the interplay of that time dependence with the time dependence of $f(t)$, i.e., of the gradient field. A conceptually independent application of the theory presented in this paper is to the representation of confining walls by potentials $U(x)$. It is under way and will also be discussed elsewhere.

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