Dynamics of local magnetization in the eigenbasis of the Bloch-Torrey operator

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We consider diffusion within pores with general shapes in the presence of spatially linear magnetic field profiles. The evolution of local magnetization of the spin bearing particles can be described by the Bloch-Torrey equation. We study the diffusive process in the eigenbasis of the non-Hermitian Bloch-Torrey operator. It is possible to find expressions for some special temporal gradient waveforms employed to sensitize the nuclear magnetic resonance (NMR) signal to diffusion. For more general gradient waveforms, we derive an efficient numerical solution by introducing a novel matrix formalism. Compared to previous methods, this new approach requires a fewer number of eigenfunctions to achieve the same accuracy. This shows that these basis functions are better suited to the problem studied. The new framework could provide new important insights into the fundamentals of diffusion sensitization, which could further the development of the field of NMR. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4978621>]

I. INTRODUCTION

Characterizing the morphological features of porous structures is paramount to many areas of science. When a fluid-saturated porous medium is to be examined, incessant thermal movements of the fluid molecules can be exploited to infer the microstructural parameters of the specimen. By introducing external magnetic fields and electromagnetic radiation in the radio frequency (RF) range, nuclear magnetic resonance (NMR) experiments take advantage of the Larmor precession of the particles' magnetic moments to manipulate the magnetization within the medium. To study such phenomena and link the MR signal to the microstructural descriptors, a mesoscopic quantity referred to as "local magnetization" can be employed. Studying the temporal evolution of the local magnetization is thus crucial to understand the NMR signal response for general pore shapes and under various experimental schemes.

The dynamics of local magnetization is governed by the Bloch-Torrey equation¹ in the following form:

$$\frac{\partial M(\mathbf{r}, t)}{\partial t} = D \Delta M(\mathbf{r}, t) - i \gamma \mathbf{g}(t) \cdot \mathbf{r} M(\mathbf{r}, t). \quad (1)$$

Here, $M(\mathbf{r}, t)$ denotes the local magnetization at position $\mathbf{r}$ and time t . D and γ denote the diffusion coefficient and the gyromagnetic ratio, respectively. Finally, $\mathbf{g}(t)$ is the magnetic field gradient, which is also referred to as the "gradient waveform." The dimension, region, and boundary conditions are determined by the particular problem.

When general gradient waveforms are to be studied, a time slicing is typically performed. In the "multiple propagator (MP)" method, a general gradient waveform is represented by a sequence of impulses.² Diffusion during the infinitesimally short pulses can then be neglected, and the NMR signal intensity is represented as the product of matrices whose components are obtained from the diffusion propagators connecting the instances at which the subsequent gradient impulses are envisioned to be applied.^{3–6} This approach is essentially a brute-force evaluation of the path integral associated with the diffusion process.⁷

In another technique called the "multiple correlation function (MCF)" method, the gradient waveform is represented as a piecewise constant function.^{8–10} The solution of the Bloch-Torrey equation for a constant gradient then becomes relevant for each time interval, and the signal arising from the general waveform can once again be written as a matrix product.^{11–14} The matrices are merely representations of the time evolution operator in the eigenbasis of the Laplacian operator, which is just a special case of the full operator for $\mathbf{g} = \mathbf{0}$ (see Eq. (1) above).

The MP and MCF approaches can be regarded as different representations of the same problem, former being based on the position representation while the latter addresses the problem in the eigenfunctions of the Laplacian operator. As discussed in Ref. 15, MCF should be preferred over MP in pulsed field gradient measurements wherein the gradient waveform is already piecewise constant. However, considering that the full time-evolution operator includes both the Laplacian and the position operator, perhaps a more natural approach would be to represent the problem in the eigensystem of the full Bloch-Torrey

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(BT) operator, $\Delta - iD^{-1}\gamma\mathbf{g} \cdot \mathbf{r}$. In this work, we revisit several problems of interest with this perspective.

The work in this paper relates to the results reported in the papers by Stoller *et al.*¹⁶ and de Swiet and Sen,¹⁷ although there is a slightly different focus. In the seminal work by Stoller *et al.*, the one-dimensional Bloch-Torrey equation is discussed in detail, covering many aspects of both bounded and unbounded diffusion under the influence of a magnetic field. In de Swiet and Sen, higher dimensions are also considered and this paper gives several important asymptotic behaviours depending on the relation between the intrinsic length scale of the field gradient and the characteristic length scale of the region considered. In this work, our focus lies rather in providing a framework for actually computing the signal from a general geometry and a general magnetic field gradient profile, although important special cases where the calculations are particularly simple are also considered.

Our manuscript is organized as follows: In Section II, we consider a constant gradient field and give the expansion of the magnetization in terms of the eigenfunctions to the BT operator. In Section III we treat some special waveforms where the approach from Section II can be utilized in the sense that only one set of basis functions needs to be calculated. In Section IV, we consider a time varying gradient field and demonstrate how temporal slicing gives a convenient matrix product approach for the temporal evolution of the magnetization. In Section V we provide some results that establish the soundness of the formulations, and in Sec. VI, we discuss crucial points related to our approach including how it compares to the MCF method in terms of its computational efficiency.

II. MAGNETIZATION UNDER A CONSTANT FIELD GRADIENT

A. One dimension

When a time-independent gradient of magnitude g is applied in the $\hat{\mathbf{x}}$ -direction, i.e., $\mathbf{g} = g\hat{\mathbf{x}}$, the one-dimensional Bloch-Torrey equation can be written as

$$\frac{\partial M(x, t)}{\partial t} = D \frac{\partial^2 M(x, t)}{\partial x^2} - iD\alpha x M(x, t), \quad (2)$$

where $\alpha = \gamma g/D$. We shall consider diffusion taking place between two reflective parallel plates situated at $x = \pm L$ so that the Neumann¹⁸ boundary conditions,

$$\left. \frac{\partial M(x, t)}{\partial x} \right|_{x=\pm L} = 0,$$

are satisfied.

By separation of variables, we make the ansatz $M(x, t) = \sum_{n=0}^{\infty} T_n(t) u_n(x)$ so that for each n ,

$$\frac{T'_n(t)}{T_n(t)} = -iD\alpha x + D \frac{u''_n(x)}{u_n(x)} = \lambda_n,$$

where the eigenvalues λ_n are determined by the condition $u'_n(-L) = u'_n(L) = 0$. Hence, the time-dependence is provided by the solution $T_n(t) \propto e^{\lambda_n t}$ while the function $u_n(x)$ satisfies, for the appropriate eigenvalues λ_n , the equations

$$u''_n(x) - i\alpha x u_n(x) = D^{-1}\lambda_n u_n(x), \quad u'_n(\pm L) = 0. \quad (3)$$

Disregarding the boundary conditions, we can write down the general solution to (3). Namely, with $\text{Ai}(x)$ and $\text{Bi}(x)$ being the Airy functions,^{19,20} which satisfy the Airy equation $y''(x) - xy(x) = 0$, and by putting $v_n = D^{-1}\lambda_n$, one can easily check that^{16,17}

$$u_n(x) = C_1 \text{Ai}\left(\frac{v_n + i\alpha x}{(i\alpha)^{2/3}}\right) + C_2 \text{Bi}\left(\frac{v_n + i\alpha x}{(i\alpha)^{2/3}}\right) \quad (4)$$

gives a solution to (3). The boundary conditions imply that we are looking for the existence of non-trivial C_1, C_2 such that

$$C_1 \text{Ai}'\left(\frac{v_n + i\alpha L}{(i\alpha)^{2/3}}\right) + C_2 \text{Bi}'\left(\frac{v_n + i\alpha L}{(i\alpha)^{2/3}}\right) = 0,$$

$$C_1 \text{Ai}'\left(\frac{v_n - i\alpha L}{(i\alpha)^{2/3}}\right) + C_2 \text{Bi}'\left(\frac{v_n - i\alpha L}{(i\alpha)^{2/3}}\right) = 0,$$

i.e., we are looking for v_n which implies that

$$\begin{aligned} & \text{Ai}'\left(\frac{v_n + i\alpha L}{(i\alpha)^{2/3}}\right) \text{Bi}'\left(\frac{v_n - i\alpha L}{(i\alpha)^{2/3}}\right) \\ & - \text{Ai}'\left(\frac{v_n - i\alpha L}{(i\alpha)^{2/3}}\right) \text{Bi}'\left(\frac{v_n + i\alpha L}{(i\alpha)^{2/3}}\right) = 0. \end{aligned} \quad (5)$$

Via the relations

$$\text{Ai}'((-1)^{2/3}z) = \frac{1}{4}(1 - i\sqrt{3})(\text{Ai}'(z) - i\text{Bi}'(z)),$$

$$\text{Bi}'((-1)^{2/3}z) = \frac{1}{4}(-i - \sqrt{3})(3\text{Ai}'(z) + i\text{Bi}'(z)),$$

(5) can be cast in a simpler form. Namely, with $z_n = -v_n/\alpha^{2/3}$, $\mu = \alpha^{1/3}L = \left(\frac{\gamma g}{D}\right)^{1/3}L$, (5) becomes

$$\text{Ai}'(z_n - i\mu) \text{Bi}'(z_n + i\mu) - \text{Ai}'(z_n + i\mu) \text{Bi}'(z_n - i\mu) = 0, \quad (6)$$

and we also denote the LHS of (6) with $P(z_n, \mu)$. From the conjugate symmetries $\text{Ai}'(\bar{z}) = \overline{\text{Ai}'(z)}$ and $\text{Bi}'(\bar{z}) = \overline{\text{Bi}'(z)}$, it then follows that if z_n is a root of (6) then so is $\bar{z}_n$. This is expected from the physics, as with u_n defined on the symmetric interval $[-L, L]$, we can make the coordinate change $x \rightarrow -x$ so that $u_n(-x)$ have the same domain as u_n . However, a subsequent conjugation of (3) shows that $\bar{u}_n(-x)$ is indeed an eigenfunction to (3) with eigenvalue $D^{-1}\bar{\lambda}_n$. See also Lemma 2 in Appendix A.

Equation (6) has to be addressed numerically to find the spectral values v_n . This is facilitated by the fact that if z_n , i.e., v_n , is real, then $P(z_n, \mu)$ is purely imaginary. Thus these roots can be found by localizing the roots of a real valued function, namely, $\text{Im}(P(x, \mu))$.

The solutions to (4) which satisfy $u'_n(L) = u'_n(-L) = 0$ are now

$$u_n(x) = C_n \left[\text{Ai}\left(\frac{v_n + i\alpha x}{(i\alpha)^{2/3}}\right) - \frac{\text{Ai}'\left(\frac{v_n + i\alpha L}{(i\alpha)^{2/3}}\right)}{\text{Bi}'\left(\frac{v_n + i\alpha L}{(i\alpha)^{2/3}}\right)} \text{Bi}\left(\frac{v_n + i\alpha x}{(i\alpha)^{2/3}}\right) \right],$$

where each C_n is an arbitrary nonzero constant. Note that $u'_n(L) = 0$ is trivially satisfied, while $u'_n(-L) = 0$ depends on the choice of v_n . Since the Bloch-Torrey operator is non-Hermitian,²¹ its eigenfunctions are not orthogonal. Rather, if $\lambda_n \neq \lambda_m$ (or equivalently $v_n \neq v_m$), it holds that u_n is orthogonal to $\bar{u}_m$ in the sense that $\int_{-L}^L u_n(x) \bar{u}_m(x) dx = 0$ so that the functions $\{u_n\}$ are self-dual,¹⁶ see also Lemma 1 in Appendix A.

We now write the solution to Equation (2) as, using $\lambda_n = D\nu_n$,

$$M(x, t) = \sum_{n=0}^{\infty} a_n u_n(x) e^{\lambda_n t},$$

where a_n are chosen so that $\sum_{n=0}^{\infty} a_n u_n(x) = M(x, 0)$. Starting with a uniform magnetization, i.e., $M(x, 0) = 1$, the self-duality of the functions u_n gives $a_n \int_{-L}^L u_n^2(x) dx = \int_{-L}^L u_n(x) dx$, i.e.,

$$a_n = \int_{-L}^L u_n(x) dx \left/ \int_{-L}^L u_n^2(x) dx \right.,$$

so that $M(x, t)$ is completely known.

B. Two and three dimensions

Consider now a region Ω in $\mathbf{R}^2$ or $\mathbf{R}^3$ with boundary $\partial\Omega$. Suppose that we consider the Bloch-Torrey equation with constant magnetic field gradient $\mathbf{g}$, i.e.,

$$\frac{\partial M(\mathbf{r}, t)}{\partial t} = D\Delta M(\mathbf{r}, t) - i\gamma(\mathbf{g} \cdot \mathbf{r})M(\mathbf{r}, t), \quad \mathbf{r} \in \Omega,$$

with homogeneous Robin boundary conditions

$$\rho_s M(\mathbf{r}, t) + D\hat{\mathbf{n}} \cdot \nabla M(\mathbf{r}, t) = 0, \quad \mathbf{r} \in \partial\Omega, \quad (7)$$

where $\hat{\mathbf{n}}$ is the (outward) normal vector of the region Ω , and ρ_s denotes the surface relaxivity. Define, for a given vector $\mathbf{g} \in \mathbf{R}^n$, $n = 2, 3$, the Torrey operator $\Delta_{\mathbf{g}}$ by

$$D\Delta_{\mathbf{g}} M(\mathbf{r}, t) = [D\Delta - i\gamma(\mathbf{g} \cdot \mathbf{r})]M(\mathbf{r}, t), \quad \mathbf{r} \in \Omega.$$

For each $\mathbf{g}$, we expand M in eigenfunctions to $\Delta_{\mathbf{g}}$, i.e., we write

$$M(\mathbf{r}, t) = \sum_n a_n(t) u_n(\mathbf{r}) = \sum_n a_n^{(\mathbf{g})}(t) u_n^{(\mathbf{g})}(\mathbf{r}), \quad (8)$$

where we have used the superscript $(\mathbf{g})$ to indicate that the expansion is with respect to the basis belonging to $\Delta_{\mathbf{g}}$, and where each function $u_n^{(\mathbf{g})}$ is an eigenfunction to $\Delta_{\mathbf{g}}$, i.e.,

$$D\Delta_{\mathbf{g}} u_n^{(\mathbf{g})}(\mathbf{r}) = \lambda_n^{(\mathbf{g})} u_n^{(\mathbf{g})}(\mathbf{r}), \quad \mathbf{r} \in \Omega \quad (9)$$

together with the boundary condition (7)

$$\rho_s u_n^{(\mathbf{g})}(\mathbf{r}) + D\hat{\mathbf{n}} \cdot \nabla u_n^{(\mathbf{g})}(\mathbf{r}) = 0, \quad \mathbf{r} \in \partial\Omega.$$

Since the functions $u_n^{(\mathbf{g})}$ are eigenfunctions, the time evolution becomes trivial, i.e., the functions $a_n^{(\mathbf{g})}(t) = c_n^{(\mathbf{g})} e^{\lambda_n^{(\mathbf{g})} t}$, so that (8) becomes

$$M(\mathbf{r}, t) = \sum_n c_n^{(\mathbf{g})} e^{\lambda_n^{(\mathbf{g})} t} u_n^{(\mathbf{g})}(\mathbf{r}). \quad (10)$$

Again, the coefficients $c_n^{(\mathbf{g})}$ are determined by the initial magnetization. If $M(\mathbf{r}, 0) = 1$, Lemma 1 in Appendix A then gives

$$c_n^{(\mathbf{g})} = \int_{\Omega} u_n^{(\mathbf{g})}(\mathbf{r}) dS \left/ \int_{\Omega} (u_n^{(\mathbf{g})}(\mathbf{r}))^2 dS \right. \quad (11)$$

Equation (10) above represents the local magnetization in terms of the eigenvalues and eigenfunctions of the Bloch-Torrey operator. As such, the eigen problem will have to be solved for the particular geometry in order for this expression to be employed as a formal solution. However, an important inference can be made when one considers the magnetization at long times. In this regime, the terms corresponding to

the eigenvalues whose real parts have the smallest modulus dominate the series, and the spatial dependence of the magnetization is determined by the corresponding eigenfunctions. This observation will be exploited below.

III. GRADIENT WAVEFORMS WITH SPECIAL PROPERTIES

Though insightful, the time-independent gradient profile considered in Sec. II B is of limited relevance to many NMR acquisitions. In practice, one is rather interested in situations where the gradient waveform integrates to 0 so that the resulting signal is independent of the absolute positions of the pores in which the particles are diffusing, and variations in the signal intensity can be attributed solely to motion.²² In some cases of interest, however, the solution for the case of constant gradient can be employed to compute the signal for waveforms that integrate to 0. Mathematical properties of the governing Bloch-Torrey equation enable such a development.

In this section, we shall consider three gradient profiles that exploit three relevant mathematical properties of the problem. What is common to these three waveforms is that only one set of eigenfunctions $\{u_n^{(\mathbf{g})}(\mathbf{r})\}$ has to be calculated, i.e., we have to look at only one value $\mathbf{g}$ of the magnetic field gradient. However, we note that, the tools developed in this section are applicable to more general gradient waveforms as long as certain parts of those waveforms exhibit features such as gradient reversal, infinitesimal and/or long pulses, and rotating gradients. We consider an arbitrary region Ω in Subsections III A and III B while in Subsection III C, we assume that Ω has axial symmetry. The boundary conditions are the general Robin conditions, which will not be stated explicitly.

A. Gradient reversal: Spin echo in the presence of a constant field gradient

First we shall consider a scenario wherein the gradient is continuously applied; however, its direction is reversed during the second half of the waveform. This situation naturally arises as the “effective” gradient profile when a spin echo experiment is performed in the presence of a constant field gradient.²³ The same situation can be realized as a special case of the Stejskal-Tanner pulse sequence²⁴ featuring a pair of pulsed field gradients applied one after the other, i.e., when the duration of the pulses (δ) is equal to the delay between their start times (Δ). In either case, the effective gradient waveform can be expressed by the function

$$\mathbf{g}(t) = \begin{cases} +\mathbf{g}_0, & 0 \leq t \leq \delta \\ -\mathbf{g}_0, & \delta < t \leq 2\delta. \end{cases}$$

Let λ_n^+ denote the n th eigenvalue of the operator $D\Delta_{\mathbf{g}_0}$ and $u_n^+(\mathbf{r})$ be the corresponding eigenvector. Here, the superscript “+” is to indicate that the eigenvalue and eigenvector correspond to the case when the gradient is $+\mathbf{g}_0$. When the gradient is applied in the opposite direction, the n th eigenvalue and eigenvector will be denoted by λ_n^- and $u_n^-(\mathbf{r})$, respectively. We expand $M(\mathbf{r}, t)$ in this eigenbasis so that $M(\mathbf{r}, t) = \sum_n c_n^+ e^{\lambda_n^+ t} u_n^+(\mathbf{r})$ for $0 \leq t \leq \delta$. In particular $M(\mathbf{r}, \delta) = \sum_n c_n^+ e^{\lambda_n^+ \delta} u_n^+(\mathbf{r})$. We assume that the eigenfunctions

are “normalized” in the sense that $\int_{\Omega} (u_n^+(\mathbf{r}))^2 dS = 1$, which implies that $c_n^+ = \int_{\Omega} u_n^+(\mathbf{r}) dS$.

To express $M(\mathbf{r}, t)$ for $\delta < t < 2\delta$, we need the eigen-system to the operator $D\Delta_{\mathbf{g}_0}$, which would enable the expansion $M(\mathbf{r}, t) = \sum_n c_n^- e^{\lambda_n^-(t-\delta)} u_n^-(\mathbf{r})$ in analogy with the above paragraph. Here, the use of the exponentials $e^{\lambda_n^-(t-\delta)}$ instead of $e^{\lambda_n^+ t}$ is just for convenience. However, it is easy to see that if $D\Delta_{\mathbf{g}_0} u = \lambda u$ then $D\Delta_{-\mathbf{g}_0} \bar{u} = \bar{\lambda} \bar{u}$. Hence no new set of basis functions needs to be calculated, and we find that $M(\mathbf{r}, t) = \sum_n c_n^- e^{\lambda_n^-(t-\delta)} \bar{u}_n^+(\mathbf{r})$ for $\delta < t < 2\delta$. The values of the coefficients c_n^- are given by the condition that at $t = \delta$, $\sum_n c_n^+ e^{\lambda_n^+ \delta} u_n^+(\mathbf{r}) = \sum_n c_n^- \bar{u}_n^+(\mathbf{r})$. Multiplication by $\bar{u}_m^+(\mathbf{r})$ followed by an integration over Ω then implies that

$$c_m^- = \sum_n c_n^+ e^{\lambda_n^+ \delta} \Gamma_m^n, \text{ where } \Gamma_m^n = \int_{\Omega} u_n^+(\mathbf{r}) \bar{u}_m^+(\mathbf{r}) dS$$

so that, suppressing $\mathbf{r}$,

$$M(2\delta) = \sum_m c_m^- e^{\lambda_m^+ \delta} \bar{u}_m^+ = \sum_m \sum_n c_n^+ e^{\lambda_n^+ \delta} \Gamma_m^n e^{\lambda_m^+ \delta} \bar{u}_m^+.$$

In Section IV the same idea will be exploited in greater generality through a matrix formalism.

B. Long and narrow pulses: Application to diffusion pore imaging (DPI)

Consider the following sequence, introduced by Laun *et al.*:²⁵

$$\mathbf{g}(t) = \begin{cases} \mathbf{g}_0, & 0 \leq t \leq T \\ -\frac{T}{\delta} \mathbf{g}_0, & T < t \leq T + \delta, \end{cases}$$

where the duration of the first pulse, T , is “long” and that of the second pulse, δ , is “short.” Expanding M in the form (10), we also order the eigenvalues according to their real parts so that $\text{Re}(\lambda_1) \geq \text{Re}(\lambda_2) \geq \text{Re}(\lambda_3) \dots$. At time $t = T$, the local magnetization is given by

$$M(\mathbf{r}, T) = \sum_n c_n^{(\mathbf{g}_0)} e^{\lambda_n^{(\mathbf{g}_0)} T} u_n^{(\mathbf{g}_0)}(\mathbf{r}).$$

For the influence of the gradient during the second interval $T < t \leq T + \delta$, diffusion can be neglected if δ is small enough. This implies that the effect of the subsequent narrow pulse can be incorporated conveniently by a pointwise multiplication with the phase factor $e^{i\gamma T \mathbf{g}_0 \cdot \mathbf{r}}$. Thus, at the end of the sequence, the local magnetization is just

$$M^{(\mathbf{g}_0)}(\mathbf{r}, T + \delta) = \sum_n c_n^{(\mathbf{g}_0)} e^{\lambda_n^{(\mathbf{g}_0)} T} u_n^{(\mathbf{g}_0)}(\mathbf{r}) e^{i\gamma T \mathbf{g}_0 \cdot \mathbf{r}}.$$

With the definition $\mathbf{q} = (2\pi)^{-1} \gamma \mathbf{g}_0 T$, the DPI signal at the reciprocal space vector $\mathbf{q}$ is obtained by integrating the local magnetization over the pore space, i.e.,

$$E(\mathbf{q}) = \sum_n c_n^{(\mathbf{g}_0)} e^{\lambda_n^{(\mathbf{g}_0)} T} \int_{\Omega} u_n^{(\mathbf{g}_0)}(\mathbf{r}) e^{i2\pi \mathbf{q} \cdot \mathbf{r}} dS. \quad (12)$$

As indicated in Refs. 25 and 26, the Fourier transform of the $E(\mathbf{q})$ function approximates the indicator function defining the pore space, thus the shape of the boundaries restricting the diffusion process.

C. Rotating field gradients: Probing isotropic environments

In this section, we shall consider a pulse sequence featuring a rotating field gradient (RFG), which can be realized by applying sine- and cosine-modulated field gradients along perpendicular directions. Such sequences could be used, e.g., for direct measurement of the orientation distribution function (ODF) in fibrous specimens^{27,28} or as an alternative to oscillating gradient sequences to accentuate diffusion sensitivity.²⁹

If the domain Ω has rotational symmetry about the axis of gradient rotation, the signal for such sequences can be calculated (without time slicing, see Section IV) by a variation of the approach presented so far. In the two-dimensional case, we consider the gradient field $\mathbf{g}(t) = g_0(\cos(\beta t)\hat{\mathbf{x}} + \sin(\beta t)\hat{\mathbf{y}})$ so that Eq. (1) becomes, in polar coordinates,

$$\frac{\partial M(r, \phi, t)}{\partial t} = D\Delta M(r, \phi, t) - i\gamma g_0 r \cos(\phi - \beta t) M(r, \phi, t).$$

Due to the rotational symmetry of Ω , we can define $\tilde{M}$ by $\tilde{M}(r, \phi, t) = M(r, \phi + \beta t, t)$, which implies that

$$\frac{\partial \tilde{M}}{\partial t} = \beta \frac{\partial \tilde{M}}{\partial \phi} + D\Delta \tilde{M} - i\gamma g_0 r \cos(\phi) \tilde{M}.$$

In analogy to the procedure in Section II B, we now let u_n be the eigenfunctions of the operator $D\Delta - i\gamma g_0 r \cos(\phi) + \beta \frac{\partial}{\partial \phi}$ so that

$$\left[D\Delta - i\gamma g_0 r \cos(\phi) + \beta \frac{\partial}{\partial \phi} \right] u_n = \lambda u_n$$

with appropriate (also rotation invariant) boundary conditions and write the full solution (for the given values of g_0, β)

$$M(r, \phi, t) = \sum_n c_n e^{\lambda_n t} u_n(r, \phi - \beta t). \quad (13)$$

Again the coefficients c_n must be determined, but this time we cannot use a relation like (11) since Lemma 1 is not applicable. Instead we employ Lemma 4 which readily gives the coefficients c_n .

IV. GENERAL TIME-DEPENDENT GRADIENT WAVEFORMS

For a general time-varying gradient $\mathbf{g}(t)$, the techniques from Section III have to be modified. In a sense, we will extend the procedure from Section III A in the following way. Suppose that the magnetic field gradient waveform $\mathbf{g}(t)$ over the interval $[0, T]$ is given or approximated by a piecewise constant function so that $0 = t_0 < t_1 < t_2 < \dots < t_{N-1} < t_N = T$ and

$$\mathbf{g}(t) = \mathbf{g}_j, \quad t_{j-1} \leq t < t_j,$$

and let us also define $\Delta_j = t_j - t_{j-1}$. For each j , we calculate eigenfunctions $\{u_n^{(\mathbf{g}_j)}(\mathbf{r})\}$ and eigenvalues $\{\lambda_n^{(\mathbf{g}_j)}\}$, and we also use the notation $u_n^{(j)}(\mathbf{r}) = u_n^{(\mathbf{g}_j)}(\mathbf{r})$, $\lambda_n^{(j)} = \lambda_n^{(\mathbf{g}_j)}$. To proceed, we place the basisfunctions $\{u_n^{(j)}\}$ into a vector $\mathbf{u}^{(j)}$ and define the diagonal matrix $\Lambda^{(\mathbf{g}_j)} = \Lambda^{(j)}$ by

$$\Lambda_{nm}^{(j)} = \delta_{nm} \lambda_n^{(j)}.$$

By also putting the coefficients $\{c_n^{\mathbf{g}}\}$ from (10) into a vector $\mathbf{c}_n^{\mathbf{g}}$, (10) now reads

$$M(t) = \mathbf{u}^{(1)T} e^{\Lambda^{(1)}t} \mathbf{c}^{(1)}, \quad 0 \leq t \leq t_1,$$

where T stands for transpose. We also insist on the “normalization” $\langle u_n^{(j)}, \bar{u}_n^{(j)} \rangle = \int_{\Omega} u_n^{(j)}(\mathbf{r}) \bar{u}_n^{(j)}(\mathbf{r}) dS = 1$, for all j, n , which in particular implies $c_n^{(1)} = \langle M_{t=0}, \bar{u}_n \rangle = \int_{\Omega} M(\mathbf{r}, 0) u_n^{(1)}(\mathbf{r}) dS$.

Moreover, with the vector $\mathbf{d}^{(j)} = \{d_n^{(j)}\}$, defined by $d_n^{(j)} = \langle 1, \bar{u}_n^{(j)} \rangle = \int_{\Omega} u_n^{(j)}(\mathbf{r}) dS$, the signal $E(t)$ is given by

$$E(t) = \int_{\Omega} M(\mathbf{r}, t) dS = \mathbf{d}^{(1)T} e^{\Lambda^{(1)}t} \mathbf{d}^{(1)}, \quad 0 \leq t \leq t_1.$$

In particular, at time t_1 , we have

$$M(t_1) = \mathbf{u}^{(1)T} e^{\Lambda^{(1)}\Delta_1} \mathbf{d}^{(1)}, \quad E(t_1) = \mathbf{d}^{(1)T} e^{\Lambda^{(1)}\Delta_1} \mathbf{d}^{(1)}.$$

Now, let $\mathbf{\Gamma}_i^j$ be the transition matrix of the coordinates $\mathbf{c}^{(i)}$ of the magnetization in the basis $\mathbf{u}^{(i)}$ to the coordinates $\mathbf{c}^{(j)}$ in the basis $\mathbf{u}^{(j)}$, so that $M(t_1) = \mathbf{u}^{(1)T} e^{\Lambda^{(1)}\Delta_1} \mathbf{d}^{(1)} = \mathbf{u}^{(2)T} \mathbf{\Gamma}_1^2 e^{\Lambda^{(1)}\Delta_1} \mathbf{d}^{(1)}$, which implies

$$\begin{aligned} M(t_2) &= \mathbf{u}^{(2)T} e^{\Lambda^{(2)}\Delta_2} \mathbf{\Gamma}_1^2 e^{\Lambda^{(1)}\Delta_1} \mathbf{d}^{(1)}, \\ E(t_2) &= \mathbf{d}^{(2)T} e^{\Lambda^{(2)}\Delta_2} \mathbf{\Gamma}_1^2 e^{\Lambda^{(1)}\Delta_1} \mathbf{d}^{(1)}. \end{aligned}$$

In a similar manner, we end up with the final magnetization and echo at $t_N = T$, expressed in the N th basis

$$\begin{aligned} M(t_N) &= \mathbf{u}^{(N)T} e^{\Lambda^{(N)}\Delta_N} \prod_{j=1}^{N-1} \left(\mathbf{\Gamma}_j^{j+1} e^{\Lambda^{(j)}\Delta_j} \right) \mathbf{d}^{(1)}, \\ E(t_N) &= \left(\mathbf{d}^{(N)} \right)^T e^{\Lambda^{(N)}\Delta_N} \prod_{j=1}^{N-1} \left(\mathbf{\Gamma}_j^{j+1} e^{\Lambda^{(j)}\Delta_j} \right) \mathbf{d}^{(1)}. \end{aligned}$$

A major advantage of the above expression is that all matrices $\Lambda^{(j)}$ are diagonal, and hence that the time evolution through the exponentiation is trivial. Since the cost for computing $e^{\Lambda^{(j)}\Delta_j}$ for different j and Δ_j is negligible, all computational cost lies in the determination of the basis functions $\{u_n^{(j)}\}$ and the transition matrices $\mathbf{\Gamma}_i^j$. This will be compared with the traditional MCF approach in Sec. IV A. We will also discuss the connected question of the size of the truncated matrices $\Lambda^{(j)}$, i.e., the number N_j of basis functions $\{u_n^{(j)}\}_{n=1}^{N_j}$ used for each magnetization. As in MCF, the number of basis functions is infinite, and for calculations, some finite approximation has to be employed. As we will see, this truncation which affects both accuracy and computation time has different features in the approach presented here, as compared to traditional MCF.

A. Comments on implementation

For certain regions like interval, circles, and rectangles, Equation (9) can be addressed through known functions such as the Airy or Bessel functions; see Section II A and Appendix B 1. For a general region, however, Equation (9) has to be addressed numerically. For a given region (and chosen value of $\mathbf{g}$), the eigenfunctions $\{u_n^{(\mathbf{g})}\}$ and eigenvalues $\{\lambda_n^{(\mathbf{g})}\}$ can be determined numerically by producing a matrix eigenvalue problem. In principle, the equation can be solved for all eigenvalues captured by the discretization of the region.³⁰ If a large number of eigenvalues are to be used, iterative methods could be employed.

Thus, for each $\mathbf{g}$, there is a (determined/chosen) number $N_{\mathbf{g}}$ and corresponding eigenvalues $\{\lambda_n^{(\mathbf{g})}\}_{n=1}^{N_{\mathbf{g}}}$ and eigenfunctions $\{u_n^{(\mathbf{g})}\}_{n=1}^{N_{\mathbf{g}}}$. In practice, each function $u_n^{(\mathbf{g})}$ is given by a finite set of K values. These can be the values at a discrete set of points in Ω or the coefficients in an expansion in a set of basis functions. Regardless, we can consider a function $u_n^{(\mathbf{g})}$ as a $K \times 1$ vector, i.e., a column vector with K elements. To the given region Ω and chosen discretization, there is also a positive definite symmetric matrix G such that $\int_{\Omega} u v dS = \mathbf{u}^T G \mathbf{v}$. When each function is represented by the function values at a finite set, G is typically sparse. For the basis functions $\{u_n^{(\mathbf{g})}\}_{n=1}^{N_{\mathbf{g}}}$, we put the functions as columns in the $K \times N_{\mathbf{g}}$ matrix $U^{(\mathbf{g})}$. Under the condition $\int_{\Omega} u_n^{(\mathbf{g})}(\mathbf{r}) u_n^{(\mathbf{g})}(\mathbf{r}) dS = 1$, the self-duality property implies that $U^{(\mathbf{g})T} G U^{(\mathbf{g})}$ is the $N_{\mathbf{g}} \times N_{\mathbf{g}}$ identity matrix.³¹

To the values $\mathbf{g}_j$ and corresponding sets of eigenfunctions, we now similarly create the $K \times N_j = K \times N_{\mathbf{g}_j}$ matrices, $U^{(j)} = U^{(\mathbf{g}_j)}$. The matrices $\mathbf{\Gamma}_i^j$ then become $\mathbf{\Gamma}_i^j = U^{(j)T} G U^{(i)}$ so that

$$M(t_N) = U^{(N)} e^{\Lambda^{(N)}\Delta_N} \prod_{j=1}^{N-1} \left(U^{(j+1)T} G U^{(j)} e^{\Lambda^{(j)}\Delta_j} \right) \mathbf{d}^{(1)}, \quad (14a)$$

$$E(t_N) = \left(\mathbf{d}^{(N)} \right)^T e^{\Lambda^{(N)}\Delta_N} \prod_{j=1}^{N-1} \left(U^{(j+1)T} G U^{(j)} e^{\Lambda^{(j)}\Delta_j} \right) \mathbf{d}^{(1)}. \quad (14b)$$

The overall computational cost is highly dependent on the type of calculation to be performed. For instance, the computation time is affected not only by the dimension, the geometry, and the mesh size but also on the gradient profile. To compare the computational cost for the approach presented in this paper and, e.g., the MCF approach, one can roughly divide the computations into two steps. In the first step, one has to compute the set of basis functions to be employed. In the second step, these sets of basis functions, together with the prescription of one or more gradient profiles, are used to produce the signal.

To compute the basis functions, one can use direct or iterative methods, but for larger problems, i.e., when the number K is large, it is expected that iterative methods are preferred and these scale (for fixed K) with the number of basis functions required. For the MCF approach, let us assume that one calculates N eigenfunctions $\{u_n\}$ to Laplace's equation. For the Torrey based approach, we assume that we calculate M sets of basis functions (i.e., we consider M values of $\mathbf{g}$), each set having $N_{\mathbf{g}}$ elements. Hence, for fixed K , a very rough estimate is that this initial step requires $\propto N$ operations for the MCF approach and $\propto M N_{\mathbf{g}}$ operations for the Torrey based approach. Here $M N_{\mathbf{g}}$ is typically larger than N although one could consider other situations. (To prepare for the second step, one has for the Torrey based approach also to compute the matrices $\mathbf{\Gamma}_i^j = U^{(j)T} G U^{(i)}$, but since G is (normally) sparse and U^j has only $N_{\mathbf{g}}$ columns, this is of limited effort. For the MCF approach, on the other hand, one has to calculate the integrals $\int_{\Omega} u_m(\mathbf{r}) u_n(\mathbf{r}) \mathbf{r} d\mathbf{r}$.)

In the second step, the signal must be calculated from the preparatory calculations. For each gradient waveform $\mathbf{g}$, where $\mathbf{g}$ is approximated with a piecewise constant function, the MCF approach requires calculation of an expression of

the type $\prod_j e^{A_j}$ while the Torrey based approach requires $\prod_j \Gamma_j^{j+1} e^{\Lambda^{(j)} \Delta_j}$. Here, the crucial difference is that the matrices A_j , which depend on the magnetization and the time interval $\Delta_j = t_j - t_{j-1}$ are full, while $\Lambda^{(j)} \Delta_j$ is a diagonal matrix. This means that the exponentiation $e^{\Lambda^{(j)} \Delta_j}$ is immediate and hence that the calculation of $\prod_j \Gamma_j^{j+1} e^{\Lambda^{(j)} \Delta_j}$ reduces to a number of (small) matrix multiplications, while $\prod_j e^{A_j}$ requires a number of matrix exponentiations. (It could also be the case that the *sizes* of the matrices in the Torrey based approach is smaller.) This means that the Torrey based approach in this second step is faster, and this could be significant if, e.g., the task is to design a waveform where $\mathbf{g}$ is varied, and $\prod_j \Gamma_j^{j+1} e^{\Lambda^{(j)} \Delta_j}$ has to be computed repeatedly.

Clearly, there are competing effects that favor either of these methods. With the above reservations, we still provide a rough illustration but warn that conclusions should be made with care. For typical problems addressed in this work, the numerical determination of a family of eigenfunctions to the Torrey or Laplace operator typically takes some or a few tenths of a second on a laptop (using Matlab or Mathematica). In the Torrey case, the eigenfunctions for, e.g., 100 different values of $\mathbf{g}$, have been calculated well below half a minute. To calculate the signal for one gradient profile after this first step is then fast; typical numbers we find are that the signal calculated using the Torrey based approach takes a couple of hundredths of seconds, while the MCF requires a couple of tenths of seconds. Thus, the initial computational cost using the Torrey-based approach is quickly saved if one wants to compute the signal for many gradient profiles. We foresee that the Torrey-based method will be significantly more efficient for pulse sequences featuring repeated application of the same pulse (e.g., oscillating gradient measurements^{32,33}). Another application that would favor the Torrey-based formulation involves the design of optimal gradient waveforms, e.g., to assess their microstructure sensitivity.^{34,35} In such applications, the matrices for a library of gradient pulses can be determined, and numerous combinations of these gradient pulses could be simulated very efficiently using the Torrey-based method.

V. RESULTS

In this section, we provide various interesting features or results to demonstrate the correctness and utility of the above developments. The formalism presented here is applicable (with the exception of Section III C) on general geometries. However, some of our results are based on calculations for a disc, which enables us to verify and compare our results with semi-analytic solutions where the magnetization is expressed in terms of Bessel functions; see Appendix B. In Figures 2, 5, and 6, the results are compared with a series solution (Figures 2 and 5) and also the “multiple correlation function” or MCF technique,^{8–10,12} which is based on solutions to Laplace’s equation.

We start by considering a general region Ω as shown at the center of Figure 1 (left subfigure). For this region, we have computed the spectra, i.e., eigenvalues, for several magnetic field gradients $\mathbf{g}$. For each such value $\mathbf{g}$, the locations of the eigenvalues are displayed in the complex plane. In Figure 1, the small subfigure k , $k = 0, 1, \dots, 7$, displays the spectra for gradients in the direction $\cos(\frac{k\pi}{4})\hat{\mathbf{x}} + \sin(\frac{k\pi}{4})\hat{\mathbf{y}}$. For this direction, the modulus $|\mathbf{g}|$ varies over mg_0 , $m = 0, 1, \dots, 20$. Hence each eigenvalue follows a path in the complex plane as m goes from 0 to 20. The first value, $m = 0$, yields the Laplace spectrum and is displayed with large black dots. The maximum value $m = 20$ are shown with blue dots while the intermediate values $m = 10$ are displayed in red. As a general feature, the spectra in subfigures k and $k + 4$ (i.e., when the gradient direction is reversed), are the complex conjugates of each other. Due to the symmetry of Ω , Lemma 2 tells us that the subfigure 0 is symmetric about the real axis, as is subfigure 4. From Lemma 3, the form of Ω also tells us that subfigures 1 and 3 are equal as are subfigures 0 and 4 and also 5 and 7. It should be remembered that these spectra are dependent on the choice of the reference frame. More specifically, a translation of the coordinate axes, or equivalently the pore location, affects the imaginary components of the eigenvalues. To the right in Figure 1, with the same interpretation of the location of the subgraphs, we have displayed contour plots of the magnitude of the

FIG. 1. Left: For the region displayed at the center, the locations of the eigenvalues to the Torrey operator $\Delta_{\mathbf{g}}$ are calculated for several values of the gradient $\mathbf{g}$. For each subfigure k , $k = 0, 1, \dots, 7$, the eigenvalues displayed belong to $\mathbf{g}$ of the form $mg_0 [\cos(\frac{k\pi}{4})\hat{\mathbf{x}} + \sin(\frac{k\pi}{4})\hat{\mathbf{y}}]$, $m = 0, 1, \dots, 20$. $m = 0$ is the Laplacian spectrum (black dots), $m = 10$ is displayed in red, and $m = 20$ is displayed in blue. As described in the text, there are various symmetry relations between the subgraphs. The scaling of the axes is implicitly given by the Laplacian spectrum, which is directly related to the geometry of the region Ω , and the magnitude of g_0 is related to Ω by $D^{-1}\gamma g_0 a^3 = 8$, where a is the diameter of Ω . Right: Again, the location of the subgraphs indicates the direction of $\mathbf{g}$. The contour plots in each subgraph display the modulus of the magnetization for very long times (where larger values are indicated in yellow). Although small in absolute terms, this shows the effect of the edge enhancement, an effect which is captured by the dominant eigenfunctions.

magnetizations for long times (smaller values in blue, larger values in yellow). For long times and sufficiently large magnetic field gradients, the magnetization is small in absolute terms, but the relative strength (as shown by the contour plots) is reflected by the dominant eigenfunctions. The “edge enhancement” effect, observed in NMR micro-imaging,^{36–38} is one manifestation of the localization of the magnetization, which is evident in this figure.

We illustrate the utility of the developments above on several simulations. First, we consider diffusion within a disc of radius R under a Stejskal-Tanner sequence featuring a pair of diffusion gradients of duration δ and separation Δ where the timing parameters are chosen such that $D\delta/R^2 = 0.96$ and $D\Delta/R^2 = 2.4$. The echo is calculated using (i) the explicit series solution from Appendix B, (ii) the matrix method using eigenfunctions to the Bloch-Torrey operator, which is described in Section IV, and (iii) the traditional MCF technique, which is based on the Laplace operator. The results should be independent of the choice of method, which is indeed the conclusion from Figure 2.

In Figure 3 we compare the total magnetization for a disc with radius R under a rotating field gradient of magnitude $g_0 = 10$ mT/m rotating with frequency β on the plane of the disc. The signal is calculated for $0 \leq t \leq 0.1$ s, for the parameter values $R = 41 \mu\text{m}$, $\beta = 10$ rad/s and $R = 81 \mu\text{m}$, $\beta = 30$ rad/s. The signal is calculated at different time points (i) using the method from Section III C (which is described in more detail in Appendix B 2) with a result of the form (13) and (ii) using the matrix product method described in Section IV. The agreement of the results obtained through these two methods suggests that the representation of this continuous waveform with a piecewise constant function provides a good approximation, and the general formulation, featuring different eigensystems at different times, correctly reproduces the expected result.

Next, we demonstrate how the eigenspectra of a set of Bloch-Torrey operators (e.g., see Figure 1) can be used

FIG. 2. The signal for a disc of radius R through a Stejskal-Tanner sequence with pulse duration $\delta = 0.96R^2/D$ and pulse separation $\Delta = 2.4R^2/D$. The echo intensity is calculated using three methods: the explicit series solution from Appendix B (red crosses), the Torrey-eigenfunction based approach from Section IV (solid black), and the Laplace based MCF method (blue circles).

FIG. 3. The predicted dynamics of the total (integral) magnetization for an acquisition from a disc with radius R when a field gradient, rotating on the plane of the disc with frequency β , is applied. The diffusivity of water was taken to be $2.3 \times 10^{-9} \text{ m}^2/\text{s}$, and the magnitude of the rotating field gradient (RFG) was taken to be $g_0 = 10$ mT/m. The computations were performed with two different sets of parameter values: $R = 81 \mu\text{m}$, $\beta = 30$ rad/s gives the curve with four distinct peaks, while the curve which almost vanishes at $t = 0.1$ s has $R = 41 \mu\text{m}$, $\beta = 10$ rad/s. The magnetization is calculated at several instants during the application of the RFG using the approach from Section III C and Appendix B 2 (solid blue lines) and compared with the matrix formalism from Section IV (red circles).

synergistically to simulate a DPI acquisition. To this end, we consider a triangular region Ω and apply a family of magnetic field gradients, each gradient being described by the sequence involving a weak and long gradient, followed by a narrow pulse in the reverse direction as described in Section III B. The duration of the first pulse was taken so that $DT/a^2 \approx 0.56$, where a is the length of the triangle’s longest edge. We define $\mathbf{q}_{ij} = (2\pi)^{-1}\gamma\mathbf{g}_{ij}T$, where $\mathbf{g}_{ij}$ denotes the gradient vector applied during the time interval $0 \leq t \leq T$ of the experiment specified by the indices i and j . A regular 128×128 grid on the $\mathbf{q}$ -plane was sampled. It is then known^{25,26} that the two-dimensional Fourier transform of the array of signal values $E(\mathbf{q}_{ij})$ at time $T + \delta$ should result in the indicator function for the region considered.

Note that in this sequence, since the duration of the first pulse (T) is long, $c_n^{(\mathbf{g})} e^{\lambda_n^{(\mathbf{g})}T}$, $n \geq 2$ will in general be negligible compared to $c_1^{(\mathbf{g})} e^{\lambda_1^{(\mathbf{g})}T}$ and we can approximate the magnetization $M(\mathbf{r}, T)$ with only *one*³⁹ term. Therefore, the DPI signal at the reciprocal lattice point $\mathbf{q}_{ij}$ is

$$E(\mathbf{q}_{ij}) \approx c_1^{(\mathbf{g}_{ij})} e^{\lambda_1^{(\mathbf{g}_{ij})}T} \int_{\Omega} u_1^{(\mathbf{g}_{ij})}(\mathbf{r}) e^{i2\pi\mathbf{q}_{ij} \cdot \mathbf{r}} dS,$$

where the function $u_1^{(\mathbf{g}_{ij})}(\mathbf{r})$ is the eigenfunction corresponding to the eigenvalue $\lambda_1^{(\mathbf{g}_{ij})}$ whose real part has the smallest modulus. $c_1^{(\mathbf{g}_{ij})}$ is determined as earlier, assuming uniform initial magnetization. The result, which should be the indicator function of the geometry, is then shown in Figure 4.

Next, we would like to discuss the *size* of the matrices used. This is connected to terms used in the expansions of the type (10). Namely, if the expansion (10) is known with only a few terms, that expansion is still very useful if the terms

FIG. 4. Diffusion inside a triangular geometry is considered. A family of signal values, indexed by ij , due to long and narrow pulses as described in Section III B, was applied. The duration T of the pulse sequences is taken so that $DT/a^2 \approx 0.56$, where a denotes the length of the triangle's longest side. With $\mathbf{g}_{ij}$ being the vector representing the long magnetic field gradient applied during the acquisition ij , we define $\mathbf{q}_{ij} = (2\pi)^{-1}\gamma\mathbf{g}_{ij}T$. For each such experiment, 28 basis functions for the Torrey operator were calculated. A rectangular 128×128 grid was sampled in the $\mathbf{q}$ -plane. Diffusion pore images are provided in subfigures A (left) and B (middle). In subfigure A, all 28 basis functions were used, while in subfigure B only one basis function, belonging to the lowest eigenvalue, was used. Their difference is shown in subfigure C (right).

correspond to the eigenvalues closest to the imaginary axis. The missing terms then all have a decay which is faster than the known terms, meaning that the (relative) error vanishes faster than the sum, i.e., the approximation gets better and better as t increases. In contrast, an expansion based on Laplace eigenfunctions does not have this property. In that case, the number of functions needed to express the long term behavior stays constant. This difference is illustrated in Figures 5 and 6. We take the diffusivity of water to be $2.3 \times 10^{-9} \text{ m}^2/\text{s}$ and consider a disc of radius $31 \text{ }\mu\text{m}$ along with a magnetic field gradient waveform, which is indicated in the figure via green shading. The process starts with a uniform magnetization at $t = 0$ and is monitored for 70 ms. The total magnetization is calculated using the series solution from Appendix B 1 as a reference and then also using the Torrey eigenfunctions and the Laplace based MCF technique. Although the condition $\int \mathbf{g}(t)dt = \mathbf{0}$ is fulfilled only at the end of the sequence, it is instructive to examine the integral of the magnetization for all

FIG. 5. Total magnetization plotted as a function of time, comparing a Torrey based solution with the Laplace based MCF technique. A series solution based on Appendix B 1 is also given as the ground truth. Diffusion inside a disc of radius $31 \text{ }\mu\text{m}$ was considered. The green-filled curve indicates the gradient intensity, which takes the maximum and minimum values of $+300 \text{ mT/m}$ and -300 mT/m , respectively. The diffusion coefficient of water was $2.3 \times 10^{-9} \text{ m}^2/\text{s}$. The gradient echo condition is met at $t = 70 \text{ ms}$, and the intensity at this time is the measurable quantity, but the full time evolution is also provided. The initial behavior for small t stems from the fact that the initial uniform magnetization is an eigenfunction to the Laplace operator, but not to the Torrey operator.

FIG. 6. The geometry and gradient sequence are given in the text and in Figure 5. The signal at the end time was plotted against the number of basis functions used, comparing the solution based on the Torrey operator with solutions using MCF which is based on the Laplace operator.

t . For both the Torrey based solution and the Laplace based ditto, we have chosen to use series expansions with ten terms.

It is noteworthy that the magnetization for small t is much better captured by a Laplace based solution than for the Torrey based version. This is because the initial uniform magnetization corresponds to an eigenfunction of the Laplace operator but not of the Torrey operator (with the initial value of $\mathbf{g}$). In the long run, on the other hand, the Torrey eigenfunctions are well-adapted to describe the process, and at $t = 70 \text{ ms}$, the final signal is close to the desired value (in contrast to the Laplace based approach.) This behavior is of course dependent on the number of functions used, see Figure 6, where the spin echo at $t = 70 \text{ ms}$ is displayed as a function of the number of basis functions used. With only few basis functions, the Torrey based method outperforms the MCF technique, while with a higher number of basis functions, both methods produce satisfactory results.

VI. DISCUSSION AND CONCLUSION

We have introduced a new scheme for evaluating the effect of restricted diffusion on the dynamics of mesoscopic

magnetization. Unlike in traditional approaches that employ the eigenbasis for the Laplace operator, we have tackled the full spatial operator of the Bloch-Torrey equation and addressed the problem in the resulting basis, which is more natural for the problem. A similar approach is employed for the Schrödinger equation in quantum mechanics wherein the eigenfunctions are referred to as the “stationary states” as they lead to time-independent observables. Because the eigenvalues typically have both real and imaginary parts, local magnetization in an eigenstate of the Bloch-Torrey operator “spirals” towards the origin on the plane orthogonal to the main magnetic field. The frequency of rotation is determined by the imaginary part of the eigenvalue while its real part determines the radial decay rate during such motion. It should be mentioned that we have not addressed the appropriate function space for the non-Hermitian operator $\Delta_{\mathbf{g}}$ but rather demonstrated a proof of concept through various examples.

Matrix formalisms appear in various contexts in the field of NMR.⁴⁰ Here, we introduced a new matrix formalism to quantify the effect of restricted diffusion on the NMR signal obtained via general gradient waveforms. The main advantage of employing the spectrum of the Bloch-Torrey operator is that in Equations (14a) and (14b), the exponentiated matrices are diagonal. Conversely, in traditional methods like the MCF technique, the eigenspectrum of the Laplacian is employed, which leads to expressions of the type $e^{A\tau}$ with non-diagonal matrices A . Despite this important advantage of the present method, there is a trade-off. When the Bloch-Torrey operator is employed for the case of general gradient waveforms, one has to calculate a family of basis functions $\{u_n^{(\mathbf{g})}\}$ for each $\mathbf{g}$ of interest. However, with these families determined and with the relatively small matrices $\mathbf{I}_i^j$ (for transforming the coefficients to the basis associated with the subsequent gradient) precalculated, it is almost immediate to compute the signal for many different gradient sequences $\mathbf{g}(t)$.

As was also indicated by the results shown in Figures 5 and 6, even if the number of matrix operations may be comparable between, e.g., the proposed method and the MCF approach, there can be a difference in the *sizes* of the matrices required. This will not only affect the computational time when evaluating, e.g., different gradient profiles $\mathbf{g}(t)$, but also when determining the basis functions. Namely, for larger and more complicated geometries, the problem of determining the eigenfunctions to either the Laplace or the Bloch-Torrey operator can give a very large eigenvalue problem. Hence direct solvers may be too expensive, and one may have to resort to iterative solvers. This gives a method which requires, fewer basis functions, a clear advantage. This was also demonstrated in Figure 4 where the calculations for each signal value used only one basis function.

Though our focus has been on quantifying the effect of restricted diffusion due to possibly relaxing walls, we note that the formalism could be extended to the case of free diffusion. However, since the *exact* solution for arbitrary gradient waveforms is known,⁴¹ the case of free diffusion was not treated here. We refer the reader to a recent article⁴² in which the exact expression has been obtained by evaluating a path integral, and a numerical method based on a stepwise-constant representation of the gradient waveform has been demonstrated as well.

Since it can be based on the same temporal representation of the gradient waveform, the said numerical approach⁴² can be envisioned to be complementary to the technique introduced in this work.

In conclusion, we have studied the dynamics of the local magnetization in the presence of constant and time-dependent gradients using the eigenbasis of the Bloch-Torrey operator that includes the impressed gradient. Our findings suggest the feasibility of this approach to reliably and efficiently predict the effect of restricted diffusion on the local magnetization—hence the NMR signal attenuation—for general gradient waveforms and pore shapes.

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APPENDIX A: SELF-DUALITY AND SYMMETRY PROPERTIES

In this Appendix, we prove several results that were employed in the developments above. For brevity, we take the diffusion coefficient to be unity.

Lemma 1. Suppose that u and v are eigenfunctions to the Torrey operator $\Delta_{\mathbf{g}}$ with eigenvalues λ and μ , respectively, which also satisfy the Robin boundary condition (7). Then, if $\lambda \neq \mu$, $\int_{\Omega} uvdS = 0$.

Proof. $\lambda \int_{\Omega} uvdS = \int_{\Omega} (\Delta_{\mathbf{g}}u)vdS = \int_{\Omega} (\Delta u)v dS - i\gamma \int_{\Omega} (\mathbf{g} \cdot \mathbf{r})uv dS = \int_{\Omega} u\Delta v dS + \int_{\partial\Omega} (v\nabla u - u\nabla v) \cdot \hat{n} ds - i\gamma \int_{\Omega} (\mathbf{g} \cdot \mathbf{r})uv dS = \int_{\Omega} u\Delta_{\mathbf{g}}v dS = \mu \int_{\Omega} uvdS$, since $\int_{\partial\Omega} (v\nabla u - u\nabla v) \cdot \hat{n} ds$ vanishes by virtue of the Robin condition (7). Hence $\lambda \int_{\Omega} uvdS = \mu \int_{\Omega} uvdS$ and the statement follows. $\square$

Here we have used Green’s identity $\int_{\Omega} [(\Delta u)v - u\Delta v]dS = \int_{\partial\Omega} (v\nabla u - u\nabla v) \cdot \hat{n} ds$ (which follows by applying the divergence theorem to the RHS).

The eigenvalues to the Torrey operator under the boundary conditions (7) are in general complex and with no particular symmetry. However, if Ω has a certain symmetry, the following holds:

Lemma 2. Suppose that $\mathbf{g}$ is fixed, and suppose that the coordinate axes are chosen such that $\mathbf{g} = g_0\hat{\mathbf{x}}$, i.e., $\mathbf{g}$ points along the x -axis. Suppose further that λ is an eigenvalue of $\Delta_{\mathbf{g}}$, i.e., there is a function u with $\Delta_{\mathbf{g}}u = \lambda u$. If $\Omega \subset \mathbf{R}^2$ is such that $(x, y) \in \Omega \Rightarrow (-x, y) \in \Omega$, then $\bar{\lambda}$ is also an eigenvalue of $\Delta_{\mathbf{g}}$. Moreover, with $v(x, y) = \bar{u}(-x, y)$, $\Delta_{\mathbf{g}}v = \bar{\lambda}v$.

Proof. Define $\hat{\cdot}$ by $\hat{v}(x, y) = v(-x, y)$. Then all of $\hat{\cdot}$, $\bar{\cdot}$ and Δ commute, and $\Delta_{\mathbf{g}}v = \Delta v - i\gamma g_0 x v = \Delta \hat{u} - i\gamma g_0 x \hat{u} = \overline{\Delta \hat{u} + i\gamma g_0 x \hat{u}} = \overline{\Delta \hat{u} - i\gamma g_0 (-x) \hat{u}} = \overline{\Delta u - i\gamma g_0 x u} = \overline{\Delta_{\mathbf{g}}u} = \bar{\lambda}u = \bar{\lambda}v$. $\square$

Lemma 3. Suppose that $\Omega \subset \mathbf{R}^2$ is such that $(x, y) \in \Omega \Rightarrow (-x, y) \in \Omega$, and suppose that $\Delta_{(g_x, g_y)} u = \lambda u$. With $v(x, y) = u(-x, y)$, it then holds that $\Delta_{(-g_x, g_y)} v = \lambda v$, i.e., the operators $\Delta_{(g_x, g_y)}$ and $\Delta_{(-g_x, g_y)}$ have the same eigenvalues.

Proof. With the notation from Lemma 2, $\Delta_{(-g_x, g_y)} v = (\Delta - i\gamma(-g_x x + g_y y))\hat{u} = ((\Delta - i\gamma(g_x x + g_y y))\hat{u}) = (\Delta_{(g_x, g_y)} \hat{u}) = \lambda \hat{u} = \lambda v$. (Here, we have also written $(\cdot)$ for $\hat{\cdot}$.) $\square$

By the same argument, these results of Lemmas 2 and 3 hold also in $\mathbf{R}^3$ if $(x, y, z) \in \Omega \Rightarrow (-x, y, z) \in \Omega$.

Lemma 4. Suppose that, $\{u_n\}$ and $\{v_n\}$ are the solutions to

$$\Delta u_n - i\gamma g_0 x u_n - \beta \frac{\partial u_n}{\partial \phi} = \lambda_n u_n, \quad r \leq R, \quad (\mathbf{r} \cdot \nabla u_n)|_{r=R} = 0, \quad (\text{A1})$$

$$\Delta v_n - i\gamma g_0 x v_n + \beta \frac{\partial v_n}{\partial \phi} = \mu_n v_n, \quad r \leq R, \quad (\mathbf{r} \cdot \nabla v_n)|_{r=R} = 0, \quad (\text{A2})$$

i.e., the eigenfunctions with the corresponding eigenvalues $\{\lambda_n\}$ and $\{\mu_n\}$. Then the sets $\{\lambda_n\}$ and $\{\mu_n\}$ are identical, and if $\lambda_n \neq \mu_m$, $\int_{B_R} u_n v_m dS = 0$.

Proof. Let $B_R = \{(x, y) : x^2 + y^2 \leq R^2\}$ represent the set of points within a two-dimensional disc. If (in polar coordinates), $u(\rho, \phi)$ is an eigenfunction to (A1) with eigenvalue λ , then $v(\rho, \phi) = u(\rho, -\phi)$ is an eigenfunction to (A2) with the same eigenvalue. Moreover

$$\begin{aligned} \lambda_n \int_{B_R} u_n v_m dS &= \int_{B_R} \left(\Delta u_n - i\gamma g_0 x u_n - \beta \frac{\partial u_n}{\partial \phi} \right) v_m dS \\ &= \int_{B_R} (\Delta u_n - i\gamma g_0 x u_n) v_m dS - \beta \int_{B_R} \frac{\partial u_n}{\partial \phi} v_m dS \\ &= \int_{B_R} u_n (\Delta v_m - i\gamma g_0 x v_m) dS + \beta \int_{B_R} u_n \frac{\partial v_m}{\partial \phi} dS \\ &= \mu_m \int_{B_R} u_n v_m dS, \end{aligned}$$

where we have used that $\int_{B_R} \frac{\partial u_n}{\partial \phi} v_m dS = - \int_{B_R} u_n \frac{\partial v_m}{\partial \phi} dS$, which also follows from integration by parts. $\square$

APPENDIX B: EXPLICIT SERIES SOLUTIONS

Although the formalism described in this work is intended for general geometries, it is interesting to calculate the solutions for those geometries where the signal can be found by other means. In this section, we will therefore derive series solutions for the disc in two dimensions when the magnetic field gradient is either constant or is given by a rotating field gradient.

1. The two dimensional disc, constant g

Consider the disc, $B_R = \{(x, y) : x^2 + y^2 \leq R^2\}$. By introducing dimensionless parameters $\boldsymbol{\rho} = \mathbf{r}/R$, $\tau = Dt/R^2$, and $\mathbf{G} = \gamma \mathbf{g} R^3/D$, Equation (1) becomes

$$\frac{\partial M}{\partial \tau} = \Delta M - i(\mathbf{G} \cdot \boldsymbol{\rho})M, \quad \rho \leq 1, \quad (\boldsymbol{\rho} \cdot \nabla M)|_{\rho=1} = 0, \quad (\text{B1})$$

where $\Delta = \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2}$ with $\xi = x/R = \rho \cos \phi$ and $\eta = y/R = \rho \sin \phi$ are the components of $\boldsymbol{\rho}$.

We seek a solution of the principal form $M(\xi, \eta, \tau) = \sum a_n e^{\lambda_n \tau} u_n(\xi, \eta)$. With such an expansion, no evolution equation needs to be addressed, as the time dependence is explicit. Thus, we seek eigenvalues λ_n and solutions u_n to the equation

$$\Delta u_n(\xi, \eta) - i(G_x \xi + G_y \eta) u_n(\xi, \eta) = \lambda_n u_n(\xi, \eta), \quad (\boldsymbol{\rho} \cdot \nabla u_n)|_{\rho=1} = 0. \quad (\text{B2})$$

Determining the eigenfunctions u_n and eigenvalues λ_n is slightly more complicated in two dimensions than in one, as there is no obvious two dimensional counterpart to the Airy functions. In this particular case, we proceed as follows. We expand $u_n(\xi, \eta)$ in terms of Bessel functions so that (in polar coordinates)

$$u_n(\xi, \eta) = \sum_{m=-\infty}^{\infty} \sum_{k=1}^{\infty} a_{m,k}^{(n)} J_m(\lambda_{m,k} \rho) e^{im\phi}, \quad (\text{B3})$$

where the Neumann condition is ensured by choosing, for each m , $\lambda_{m,k}$ to be the roots to the equation $J'_m(\lambda) = 0$. These are easily found numerically (up to some arbitrary value). We note that $\Delta(J_m(\lambda_{m,k} \rho) e^{im\phi}) = -\lambda_{m,k}^2 J_m(\lambda_{m,k} \rho) e^{im\phi}$. We also note that $G_x \xi + G_y \eta = \rho(G_x \cos \phi + G_y \sin \phi) = \rho(h_+ e^{i\phi} + h_- e^{-i\phi})$ where $h_+ = \frac{G_x - iG_y}{2}$, $h_- = \frac{G_x + iG_y}{2}$. By considering only eigenvalues $\lambda_{m,k}$ with $\lambda_{m,k} \leq \Lambda$ for some Λ , the ansatz for u_n takes the form

$$u_n(\xi, \eta) = \sum_{m=-M}^M \sum_{k=1}^{K(m)} a_{m,k}^{(n)} J_m(\lambda_{m,k} \rho) e^{im\phi}. \quad (\text{B4})$$

Plugging this into (B2), we get

$$\begin{aligned} &\sum -\lambda_{m,k}^2 a_{m,k}^{(n)} J_m(\lambda_{m,k} \rho) e^{im\phi} \\ &- ih_+ \sum a_{m,k}^{(n)} \rho J_m(\lambda_{m,k} \rho) e^{i(m+1)\phi} \\ &- ih_- \sum a_{m,k}^{(n)} \rho J_m(\lambda_{m,k} \rho) e^{i(m-1)\phi} \\ &= \lambda_n \sum a_{m,k}^{(n)} J_m(\lambda_{m,k} \rho) e^{im\phi}. \end{aligned}$$

This is an eigenvalue problem for the coefficients $\{a_{m,k}^{(n)}\}$ which are linearly ordered and put into a vector $\vec{a}$. Namely, for each m (covering the coefficients $a_{m,k}$, $1 \leq k \leq K(m)$), we have

$$\begin{aligned} &\sum_{\kappa=1}^{K(m)} -\lambda_{m,\kappa}^2 a_{m,\kappa}^{(n)} J_m(\lambda_{m,\kappa} \rho) - ih_+ \sum_{\kappa=1}^{K(m-1)} a_{m-1,\kappa}^{(n)} \rho J_{m-1}(\lambda_{m-1,\kappa} \rho) \\ &- ih_- \sum_{\kappa=1}^{K(m+1)} a_{m+1,\kappa}^{(n)} \rho J_{m+1}(\lambda_{m+1,\kappa} \rho) \\ &= \lambda_n \sum_{\kappa=1}^{K(m)} a_{m,\kappa}^{(n)} J_m(\lambda_{m,\kappa} \rho). \end{aligned} \quad (\text{B5})$$

We now use that (under the condition $J'_m(\lambda_{m,\kappa}) = J'_m(\lambda_{m,k}) = 0$)

$$\int_0^1 J_m(\lambda_{m,\kappa} \rho) J_m(\lambda_{m,k} \rho) \rho d\rho = \begin{cases} 0, & k \neq \kappa \\ (1 - \frac{m^2}{\lambda_{m,k}^2}) \frac{1}{2} J_m^2(\lambda_{m,k}), & k = \kappa \end{cases}$$

and that⁴³ (where $m \rightarrow m-1$ is also used)

$$\begin{aligned} \int_0^1 J_m(\lambda_{m,\kappa} \rho) J_{m+1}(\lambda_{m,k} \rho) \rho^2 d\rho &= \frac{\lambda_{m,\kappa}^2 + \lambda_{m,k}^2 - 2m(m+1)}{(\lambda_{m,\kappa}^2 - \lambda_{m,k}^2)^2} \\ &\quad \times J_m(\lambda_{m,\kappa}) J_{m+1}(\lambda_{m,k}). \end{aligned}$$

Thus, multiplying (B5) with $\rho J_m(\lambda_{m,k}\rho)$ and integrating from 0 to 1, a division of $(1 - \frac{m^2}{\lambda_{m,k}^2})\frac{1}{2}J_m^2(\lambda_{m,k})$ leaves us with a linear equation $M\bar{a} = \lambda_n\bar{a}$ which is easily solved numerically. This gives us a set of eigenvalues, with corresponding eigenvectors $\bar{a}^{(n)} = \{a_{m,k}^{(n)}\}$ and eigenfunctions u_n of the form (B4).

The (truncated) function M is then

$$M(\xi, \eta, \tau) \approx \sum_{n=0}^N a_n e^{\lambda_n \tau} u_n(\xi, \eta), \quad (\text{B6})$$

or, reverting to original variables

$$M(x, y, t) \approx \sum_{n=0}^N a_n e^{\lambda_n D t / R^2} u_n(x/R, y/R). \quad (\text{B7})$$

The coefficients a_n are determined by $M(\xi, \eta, 0) \approx \sum_{n=0}^N a_n u_n(\xi, \eta)$, where $N = \sum_{m=-M}^M K(m)$.

It is possible to determine the coefficients a_n even if only a few terms is used in the sum (B6). Due to Lemma 1, in the expansion $M_{t=0} = \sum a_n u_n$, we find that

$$a_n = \frac{\int_{\Omega} M u_n dS}{\int_{\Omega} u_n^2 dS}$$

and hence the expansion (B7) is determined.

2. The two dimensional disc, rotating field gradient

There is (at least) one particular situation where it is possible to derive a rather explicit solution even when there is an explicit time dependence in the applied gradient $\mathbf{g}(t)$. Namely, we again consider the disc B_R with the applied gradient field $\mathbf{g}(t) = g_0(\cos(\tilde{\beta}t)\hat{\mathbf{x}} + \sin(\tilde{\beta}t)\hat{\mathbf{y}})$. With the same dimensionless variables as in Appendix B 1, and with $\beta = \tilde{\beta} \frac{R^2}{D}$, Equation (B1) becomes

$$\frac{\partial M}{\partial \tau} = \Delta M - iG_0 \rho \cos(\phi - \beta\tau)M, \quad \rho \leq 1, \quad (\boldsymbol{\rho} \cdot \nabla M)|_{\rho=1} = 0. \quad (\text{B8})$$

The idea is now to express M in a series of the type (B6), but where the functions u_n in a sense are “time dependent spatial eigenfunctions.” Namely, with the ansatz (in polar coordinates)

$$M(\rho, \phi, \tau) = \sum a_n e^{\lambda_n \tau} u_n(\rho, \phi - \beta\tau),$$

Equation (B8) separates and gives, for each function u_n ,

$$\begin{aligned} \lambda_n u_n(\rho, \phi - \beta\tau) - \beta \frac{\partial u_n}{\partial \phi}(\rho, \phi - \beta\tau) &= \Delta u_n(\rho, \phi - \beta\tau) \\ &- iG_0 \rho \cos(\phi - \beta\tau) u_n(\rho, \phi - \beta\tau), \end{aligned} \quad (\text{B9})$$

$$\rho \leq 1, \quad (\boldsymbol{\rho} \cdot \nabla u_n)|_{\rho=1} = 0.$$

Here we have used that the Laplacian commutes with translations with respect to ϕ , i.e., $\Delta[u_n(\rho, \phi - \beta\tau)] = [\Delta u_n](\rho, \phi - \beta\tau)$. In (B9) we can set $\tau = 0$ and get the eigenvalue problem

$$\Delta u_n - iG_0 \xi u_n + \beta \frac{\partial u_n}{\partial \phi} = \lambda_n u_n, \quad \rho \leq 1, \quad (\boldsymbol{\rho} \cdot \nabla u_n)|_{\rho=1} = 0.$$

Using again the ansatz (B3), we get an equation as in (B5) but with an additional term

$$\begin{aligned} \beta \frac{\partial u_n}{\partial \phi} &= \beta \frac{\partial}{\partial \phi} \sum_{m,k} a_{m,k}^{(n)} J_m(\lambda_{m,k}\rho) e^{im\phi} \\ &= \beta \sum_{m,k} i m a_{m,k}^{(n)} J_m(\lambda_{m,k}\rho) e^{im\phi}. \end{aligned}$$

This again gives a linear equation $M\bar{a} = \lambda_n\bar{a}$, where the term $\beta \frac{\partial u_n}{\partial \phi}$ only affects the diagonal elements of M . To the new set of eigenvalues and eigenfunctions, the corresponding solution M becomes

$$M(r, \phi, t) \approx \sum_{n=0}^N a_n e^{\lambda_n D t / R^2} u_n(r/R, \phi - \beta t).$$

Again the coefficients a_n should be determined from the condition that

$$M(r, \phi, 0) \approx \sum_{n=0}^N a_n u_n(r/R, \phi), \quad (\text{B10})$$

where the coefficients a_n now are given by Lemma 4, i.e.,

$$a_n = \frac{\int_{\Omega} M u_n dS}{\int_{\Omega} u_n v_n dS},$$

where $v_n(\rho, \phi) = u_n(\rho, -\phi)$.

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