Invited lectures

Recent Fourier and Laplace perspectives for multidimensional NMR in porous media

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Abstract

Multidimensional NMR techniques used in the measurement of molecular displacements, whether by diffusion or advection, and in the measurement of nuclear spin relaxation times are categorised. Fourier–Fourier, Fourier–Laplace and Laplace–Laplace methods are identified, and recent developments discussed in terms of the separation, correlation and exchange perspective of multidimensional NMR spectroscopy.

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1. Introduction

Since the original suggestion by Jeener in 1971 \cite{1}, much of the power of NMR has derived from its multidimensional character. In the mainstream of NMR spectroscopy, the plethora of multidimensional techniques operates via a Fourier domain associated with spin phase evolution under the various spin Hamiltonian interactions of nuclear spins with their molecular environment \cite{2}. In MRI, multidimensionality arises via a Fourier domain associated with the \textit{k}-space and the spatial dependence of spin interactions with applied magnetic field gradients. Again, a wide range of methods and associated pulse sequences arise.

In recent years, a new perspective on NMR multidimensionality has arisen because of a realisation that many other NMR parameters of interest are worthy of correlation and comparison via a multiplexed encoding scheme. In particular, this article will summarise the domain of multidimensional NMR in the measurement of molecular displacements, whether by diffusion or advection, and in the measurement of nuclear spin relaxation times. These types of measurements are of especial interest in the physics of porous media. Some recent developments are briefly reviewed.

2. Summary of multidimensional displacement and relaxation methods

By virtue of the stochastic nature of diffusion and relaxation, the response of the spin Hamiltonian to these phenomena involves decoherence effects in the spin phase, leading to signals which decay with time, or, in the case of diffusion in the presence of the pulsed gradient spin echo (PGSE) NMR experiment \cite{3}, decay with applied magnetic field gradient. By contrast with most of NMR spectroscopy, where coherent phase shift experiments lead to a signal that is oscillatory, and therefore amenable to Fourier analysis, such exponentially decaying signals suggest the use of inverse Laplace analysis \cite{4–6}. Nonetheless, for flow of molecules, in the presence of the PGSE experiment, such coherent phase shifts do arise \cite{7,8}, and Fourier analysis provides a suitable means of obtaining the probability distribution of spin displacements. The choice of when to use Fourier or Laplace inversion therefore depends on the parameter to be measured.

For example, consider the simple case of isotropic molecular self-diffusion and the PGSE experiment with gradient pulses of duration \( \delta \) and amplitude \( g \) \cite{3}. The echo attenuation has the well-known exponential dependence on gradient pulse area \( q = \gamma \delta g \) of \( \exp(-q^2D_t) \), where \( D_t \) is the reduced diffusion time. Inverse Fourier transformation with respect to \( q \) yields the Gaussian probability distribution. By...
contrast, an idealized inverse Laplace transformation (ILT) yields a Dirac Delta function in the diffusion space. Clearly, where information about diffusion coefficients is desired, the ILT is the preferred analysis tool whereas when information about displacements is desired, Fourier transformation is more useful. It is the mix of such analysis schemes that is leading to the unfolding of a new plethora of experiments of particular relevance to NMR studies or porous media.

More importantly, while multidimensional Fourier transformation has been well established for many decades, the idea of using two-dimensional ILT in NMR came later [9]. Furthermore, development of robust multidimensional inverse Laplace algorithms is very recent [10–14]. It is this latter development that has given such a significant impetus to the invention and application of a wide variety of multidimensional relaxation, diffusion and molecular displacement experiments in the field of porous media research. To understand the relationships between these, it is helpful to begin with a reminder of the categories of multidimensional NMR Fourier spectroscopy as outlined by Ernst et al. [2]. These categories are equally applicable when considering multi Laplace dimensions, or mixed Fourier–Laplace dimensions (Table 1).

Table 1 lists the categorization of multidimensional NMR in terms of separation, correlation and exchange, in accordance with Ref. [2].

Table 2 gives a list of two- and three-dimensional separation, correlation and exchange experiments in which relaxation, diffusion and flow have been mapped in porous media, along with references to early reports. As a result of developments over the past 2 years, the list has become quite extensive. It includes, among the parameters measured, $T_1$ and $T_2$ relaxation, diffusion, molecular displacement distributions and the effect of diffusion in internal gradients. Most importantly, the measurements traverse the three categories of Ernst et al. [2], and in particular, the emergence of exchange experiments, in which the time dependencies of the listed parameters are able to give insight regarding the exchange rates. Two examples are the recent diffusion–diffusion exchange experiment (DEXSY [18]) of Qiao et al. [20,21], in which the exchange rate of dextran molecules between the interior and exterior of a polyelectrolyte capsule was measured, and the $T_2$–$T_2$ exchange (REXSY) measurement by Washburn and Callaghan [22] of pore-to-pore water molecule migration in a Castlegate sandstone. In this latter work, analysis of exponential decays of off-diagonal peaks led to evaluation of pore-to-pore exchange times. The REXSY rf pulse sequence used is shown in Fig. 1.

Another intriguing dimension [19,24] introduced to the inverse Laplace domain has been through analysis of the

![Fig. 1. REXSY, relaxation exchange pulse sequence consisting of double CPMG segments separated by a storage period corresponding to mixing time, $\tau_m$. (Adapted from Washburn and Callaghan [22].)](image1)

![Fig. 2. Pulse sequence for DRICOSY three-dimensional correlation map of diffusion, internal gradient and $T_2$ relaxation, consisting of a PGSE and two CPMG segments. (Adapted from Arns et al. [20].)](image2)
dephasing due to molecular diffusion in the distribution of internal gradients [23]. g, present in a porous medium due to diamagnetic susceptibility differences between the pore matrix and the saturating fluid. The “relaxation encoding” is based on a CPMG segment in which the delay time $\tau'$ between the 180°/RF pulses is varied but the total relaxation time $n\tau'$ remains fixed. The measurement is sensitive to an averaged product $gD$.

In the case of the inverse Laplace transform, the ability to move to three or higher dimensions is very recent [25]. Arns et al. [20] have used the 3D experiment to obtain a correlation map between the effective diffusion coefficient $D$, $T_2$ and the exponential rate of dephasing due to diffusion in an internal gradient. The pulse sequence for this latter experiment (DRICOSY) is shown in Fig. 2 and consists of a standard PGSE encoding segment and two CPMG segments, one of which uses a fixed echo time with variable echo number, $m$, and the other a variable echo time $2\tau'$ and fixed total relaxation period $2n\tau'$. One of the more unusual exchange experiments in the diffusion-flow parameter space is the measurement of the nonlocal dispersion tensor, $D_{NL}(Z, \tau_m)$ [26]. Here the velocity autocorrelation function for molecules undergoing flow in a porous medium is obtained in “spatially relative” mode by use of an additionally encoded propagator for spin displacements. The method involves a superposition of echo experiments of the echo amplitude set, $E(q, q_u, q_d), E(q, \overline{-q_u}, \overline{-q_d}), E(q, \overline{-q_u}, q_d), E(q, q_u, \overline{-q_d})$, where $q$ and $q_u$ are independent PGSE $q$-encodes for the displacement propagator and the velocity separately. The measurement is of the Fourier–Laplace type, although in the Laplace domain the data are simply fitted to a $q^2u$ dependence of signal amplitude. The pulse sequence is shown in Fig. 3.

3. Conclusion

The list of multidimensional relaxation–diffusion-flow experiments is now quite extensive, involving a variety of inverse Laplace and Fourier combinations. Sufficient experience is emerging in the use of multidimensional inverse Laplace analysis that quantitative interpretations can be made with some confidence. In porous media studies, the “exchange” varieties have particular interest because they have the capacity to provide valuable insight regarding pore-to-pore transport.

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