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Multiscale NMR and relaxation / RMN et relaxation multi-échelles

Multi-dimensional inverse Laplace spectroscopy in the NMR of porous media

Spectroscopie RMN dans les milieux poreux par inversion Laplace multi-dimensionnelle

Petrik Galvosas*, Paul T. Callaghan

MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

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ABSTRACT

Multi-dimensional NMR methods based on Inverse Laplace Transformations (ILT) may be used to examine the behavior of liquid state molecules in a porous matrix. The ILT is particularly useful when the signal is characterized by multi-exponential decay, for example in spin relaxation or in the dephasing of the NMR spin echo signal associated with molecular diffusion under the influence of pulsed magnetic or internal field gradients. Both correlation and exchange experiments are possible, the latter providing insight regarding the migration of molecules between regions characterized by different local dynamics.

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R É S U M É

Les méthodes de RMN multi-dimensionnelles basées sur les transformations de Laplace inverses (TLI) peuvent être utilisées pour examiner le comportement de molécules des liquides dans les matrices poreuses. La TLI est particulièrement utile quand le signal est caractérisé par une décroissance multi-exponentielle, par exemple dans la relaxation de spin ou dans le déphasage d'un signal d'écho de spin RMN associé à la diffusion moléculaire sous l'influence de gradients de champ produits par impulsions ou internes. Des expériences de corrélation ou d'échange sont toutes deux possibles, la seconde fournissant des aperçus sur la migration de molécules entre des régions caractérisées par des dynamiques locales différentes.

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1. Introduction

In high resolution nuclear magnetic resonance (NMR) spectroscopy, the Larmor frequencies of the spins under observation are sensitive to local interactions characteristic of the molecular structure. In particular the chemical shift and spin–spin couplings provide remarkable insight. In a classical 1D NMR experiment the raw signal is a time-dependent electromotive force induced in a detector coil by precessing nuclear spins. This signal is subsequently Fourier transformed to reveal the spectrum. The advent of multi-dimensional NMR in the 1970s resulted from a realization that the signal could be multiplexed in independent time domains by allowing the spins to evolve over well-defined time intervals, each independently varied, prior to the final detection stage. Fourier transformation with respect to each of these independent time domains

* Corresponding author.

E-mail addresses: petrik.galvosas@vuw.ac.nz (P. Galvosas), paul.callaghan@vuw.ac.nz (P.T. Callaghan).

yields the final multi-dimensional spectrum. The same idea lies at the heart of multi-dimensional magnetic resonance imaging, where phase-encoding prior to final readout provides information about spin positions in different Cartesian directions. Multi-dimensional Fourier spectroscopy has been categorized by Ernst, Bodenhausen and Wokaun [1] as either separation, correlation or exchange. Separation spectroscopy is designed to separate different interactions (e.g. shifts and couplings) along orthogonal dimensions with the purpose of resolving 1D spectra by spreading resonances in a second dimension. Correlation spectroscopy is designed to correlate transitions of coupled spins by transferring coherences from one transition to another in the course of suitably designed mixing processes. Exchange spectroscopy is designed to study dynamic processes.

In the application of NMR to the study of porous media, the information is often encoded in a quite different manner than in high resolution NMR spectroscopy. Rather than seeking chemical shifts and spin-couplings characteristic of molecular structure, we are more often concerned with gaining information about molecular rotational and translational dynamics of imbibed liquid molecules, dynamics that are associated with the structure of the surrounding solid matrix. The best-known example concerns the use of nuclear spin relaxation rates to determine pore size distributions, an effect which arises because collisions of spin-bearing molecules with pore walls induces a more rapid relaxation, so that there exists a simple correlation between relaxation rate and pore surface-to-volume ratio. Another example concerns the measurement of the molecular diffusion using Pulsed Gradient Spin Echo (PGSE) methods, where the decay rate of the signal under the increasing strength of magnetic field gradient pulses giving information about the diffusion coefficient, and hence the ability of molecules to migrate within and between pores.

These relaxation and diffusion experiments feature exponential signal decays, or, where a more complex superposition of behaviors is present in the molecular ensemble, multi-exponential decay. Fourier analysis is unable to separate these different decay rates. A more natural transformation for such attenuating data is the inverse Laplace transform, which leads ideally, in the case of superposed exponential decays, to a sum of well-resolved delta functions corresponding to the “relaxation spectrum”. The problem with the inverse Laplace transformation is that it is unstable to small variations in the input data, and is numerically ill-defined. The usual approach to analyzing multi-exponential data is to adopt a Non-Negative Least Squares (NNLS) fitting procedure [2], under suitable regularization constraint, as used, for example in dynamic light scattering, and for instance implemented by the software package CONTIN [3]. Whittall and Mackay [4] have used this method to provide 1D analyses of NMR relaxation data in order to ascertain relaxation time distributions. It was first applied, in conjunction with Fourier transformation, to 2D NMR by Morris and Johnson [5] who analyzed 2D data sets comprising the acquisition (spectral) dimension and the q^2 space (diffusion) dimension to produce spectra ordered by diffusion coefficients. They termed this approach diffusion-ordered spectroscopy (DOSY) [5]. Stilbs et al. [6] extended this approach by performing a global least-square approach (CORE-NMR), a feature still present in current multi-dimensional ILT procedures.

In this review, we shall be concerned with the analysis of exponential decay characteristics in the signals associated with both nuclear spin relaxation and PGSE NMR, in two or more dimensions. We term this “multi-dimensional Laplace inversion”. Such an analysis has the potential to correlate or separate relaxation and diffusion phenomena. Because of the non-linear nature of the ILT, simply applying the 1D transformation independently in each independent dimension is not a viable option. A solution has been provided by Venkataramanan et al. [7] who reduced the size of the 2D matrices associated with the data sets and the inversion kernel using Singular Value Decomposition, and then transformed the 2D matrices associated with the input and output data sets to 1D vectors by consecutive ordering of the matrix rows or columns. By this means they transformed the problem back to a 1D NNLS format, with large but manageable vector space dimensions.

2. Data processing

Consider a two-dimensional experiment correlating relaxation rates $R^{(1)}$ and $R^{(2)}$ in which the signal is given by

$$S(t_i^{(1)}, t_j^{(2)}) = \sum_{k,l} \exp\{-R_k^{(1)} t_i^{(1)}\} \exp\{-R_l^{(2)} t_j^{(2)}\} P(R_k^{(1)}, R_l^{(2)}) + E(t_i^{(1)}, t_j^{(2)}) \quad (1)$$

where $i = 1, \dots, N_1$ and $j = 1, \dots, N_2$. The signal $S(t_i^{(1)}, t_j^{(2)})$ is represent by a sum of exponentials with two discrete sets of relaxation rates $R_k^{(1)}$ and $R_l^{(2)}$, where $k = 1, \dots, M_1$ and $l = 1, \dots, M_2$. $P(R_k^{(1)}, R_l^{(2)})$ is the spectral weighting and $E(t_i^{(1)}, t_j^{(2)})$ is the noise term. The equation can be rewritten in matrix form as:

$$S = K_1 P K_2' + E \quad (2)$$

where K_1 and K_2' are the known $N_1 \times M_1$ and $M_2 \times N_2$ matrices $\exp\{-R_k^{(1)} t_i^{(1)}\}$ and $\exp\{-R_l^{(2)} t_j^{(2)}\}$, respectively. Without going through the details of the SVD [8] and one-dimensionalization process, described in detail in Ref. [7], 2D regularization is performed by minimizing

$$\chi^2 = \|K_1 P_2' - S\|^2 + \alpha^2 \|\Gamma P\|^2 \quad (3)$$

where α^2 is an adjustable regularization parameter and ΓP is a function of the calculated spectrum, typically its curvature, and $\|\cdot\|$ is the Frobenius norm. Using the principle of parsimony, the solution curvature (the amount of detail in the spectrum) is increased until $\|K_1 P_2' - S\|^2$ is just minimized.

Table 1
Categories of multi-dimensional ILT NMR experiments.

| Transformation category | Function measured | Name or Proposed name | mD type | Reference |
|--------------------------|-----------------------|---------------------------|-------------------------------------|-----------|
| q^2-t | $P(D, \omega)$ | DOSY | 1D Laplace + 1D Fourier correlation | [5] |
| $q_1^2-q_2^2$ | $P(D, D)$ | DEXSY | 2D Laplace | [9,10] |
| $\tau-\tau$ | $P(T_2, T_2)$ | REXSY | exchange | [11–13] |
| $\tau-\tau$ | $P(T_1, T_2)$ | RRCOSY | 2D Laplace | [14] |
| $q^2-\tau$ | $P(D, T_2)$ | DRCOSY | correlation | [15,16] |
| $q_1^2-q_2^2$ | $P(D_1, D_2)$ | DDCOSY | | [9,17,18] |
| $q^2-\tau-\tau_\epsilon$ | $P(D, T_2, g_\tau^2)$ | DRICOSY | 3D Laplace correlation | [19] |
| $\tau-\tau-q$ | $P(T_2, T_2, Z)$ | Propagator-resolved REXSY | 2D Laplace + 1D Fourier exchange | [20] |

Note: q^2 refers to the wave-vector-squared domain of PGSE NMR, t to the acquisition time dimensions, τ to the time domain of spin relaxation and τ_ϵ the echo spacing in a CPMG multi-echo experiment.

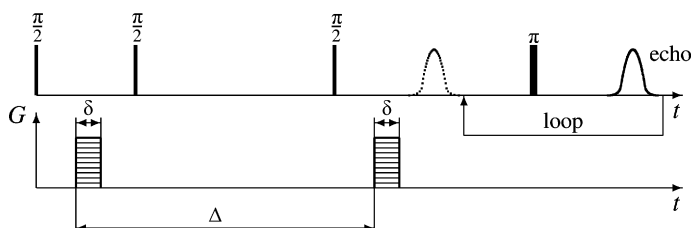


Fig. 1. DRCOSY pulse sequence consisting of a leading PGSTE experiment and a subsequent multi-echo sampling CPMG loop.

3. Categories of experiment

We now outline the different categories on multi-dimensional ILT NMR experiments and their applications to porous media. Broadly speaking, two-dimensional variants separate into correlation and exchange experiments. In the former, the advantage of greater separation of spectral features is an additional benefit, especially so since the ILT is generally unable to separate peaks more than a factor of three apart in relaxation rate.

Table 1 shows the various experiments based on combinations of relaxation and diffusion measurement, involving 2D ILT and 3D ILT. By adding a Fourier dimension associated with the PGSE NMR encoding for the displacement propagator, it is possible to produce a 3D data set in which 2D planes of ILT are separated by molecular displacement.

4. Diffusion–relaxation and relaxation–relaxation correlation

Although multi-dimensional ILT experiments were proposed as early as 1993 by Lee et al. [21] the approach of Venkataraman et al. [7] allowed the implementation of the ILT on personal computers. Since then the method has become widely available and is used in a rapid growing number of applications. Using this new algorithm, the very first 2D ILT correlation experiments were carried out by Song et al. and Hürlimann et al. who applied the method to T_1-T_2 [14] and T_2-D [15] correlation experiments in porous rock samples respectively.

4.1. DRCOSY

A typical pulse sequence for the diffusion–relaxation correlation spectroscopy experiment (DRCOSY) is shown in Fig. 1 while Fig. 2 shows an example of a corresponding T_2-D correlation map carried out on a plant leaf sample [18]. A large number of peaks are resolved which correspond to different water compartments. The very separation into 2 dimensions has made possible the resolution of many more components than would be visible with 1D ILT alone. Further, by being able to ascertain the T_2 value corresponding to each D value, it becomes possible to correct for T_2 signal decays during the leading PGSTE NMR measurement of multi-component diffusion spectroscopy, thus gaining information about the correct amplitude for each component in the distribution.

4.2. DDCOSY

The diffusion–diffusion correlation spectroscopy experiment (DDCOSY) enables the investigation of local diffusion anisotropy in a sample that is macroscopically isotropic, examples of which include polydomain lyotropic liquid crystals

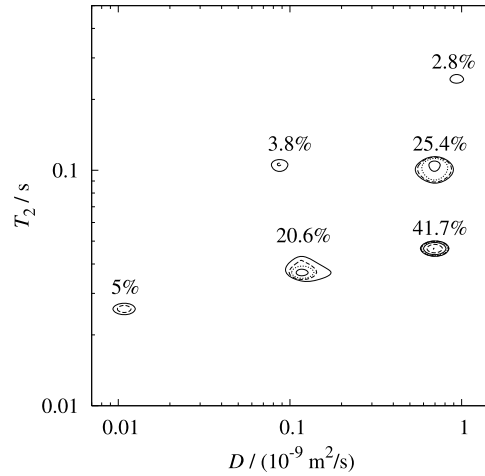


Fig. 2. DRCOSY map for inter- and intracellular water in chive leaves. [Reprinted from [18], Copyright 2005, with permission from Elsevier.]

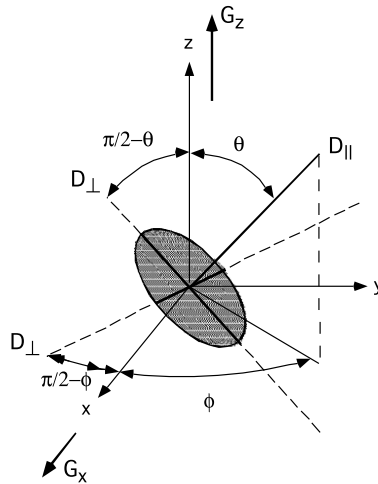


Fig. 3. Schematic showing the polar geometry of a randomly oriented locally anisotropic diffusion domain in which axial symmetry is assumed. Two convenient directions in the D_{\perp} plane are shown. [Reprinted with permission from [9]. Copyright 2004, American Institute of Physics.]

[9,17], porous solids, polymer melts, cell tissue [18] or semi-dilute solutions and strained elastomers. In the first example [9] the water solvent may be trapped in thin (i.e. ~ 10 nm) sheets between lamellar bilayers with the diffusion severely restricted normal to the bilayer and relatively free within the sheet. Such diffusion is locally two-dimensional. Alternatively the porous medium may comprise a network of channels so that absorbed fluid is restricted to diffuse in one dimension along the channel axis. Both examples will exhibit a crossover length scale corresponding to the domain size, beyond which diffusion becomes isotropic. In the case of the lyotropic liquid crystal, this size may be greater than or on the order of many tens of microns. Fig. 3 shows the relevant local geometry in which the polar axis is used to define the direction of the applied gradient. Under locally anisotropic motion the spins have diffusion coefficient D_{\parallel} along a particular director at polar angle θ and azimuth ϕ , and D_{\perp} in the plane normal to this director. For convenience we can choose two representative orthogonal axes in the plane of D_{\perp} with (polar, azimuth) directors, $(\pi/2 - \phi, \theta)$ and $(\pi/2, \pi/2 - \phi)$ as shown.

The DDCOSY double PGSE sequence is shown in Fig. 4. Here the spin magnetization is subjected to two successive gradient encoding pairs, G_1 and G_2 whose \mathbf{q} -vectors are defined respectively by \mathbf{q}_1 and \mathbf{q}_2 , and may be applied in different directions. This enables one to detect molecular displacements along the two \mathbf{q} -vectors and to determine the local anisotropy of the sample if the measured displacements in orthogonal directions differ.

Correlation of the (D_1, D_2) distribution when the successive directions are respectively collinear or orthogonal leads to distinctive patterns dependent on local anisotropy which can be expressed via

$$E(G_{1z}, G_{2z}) = \int_0^1 d \cos \theta \exp \left\{ - (q_{1z}^2 + q_{2z}^2) (D_{\parallel} \cos^2 \theta + D_{\perp} \sin^2 \theta) \right\} \quad (4a)$$

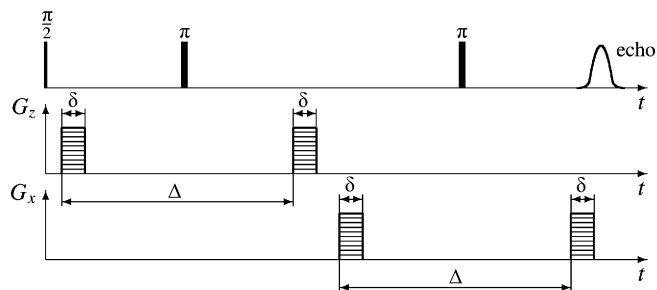


Fig. 4. DDCOSY pulse sequence with two subsequent PGSE experiments with gradient pairs applied in different directions and stepped independently.

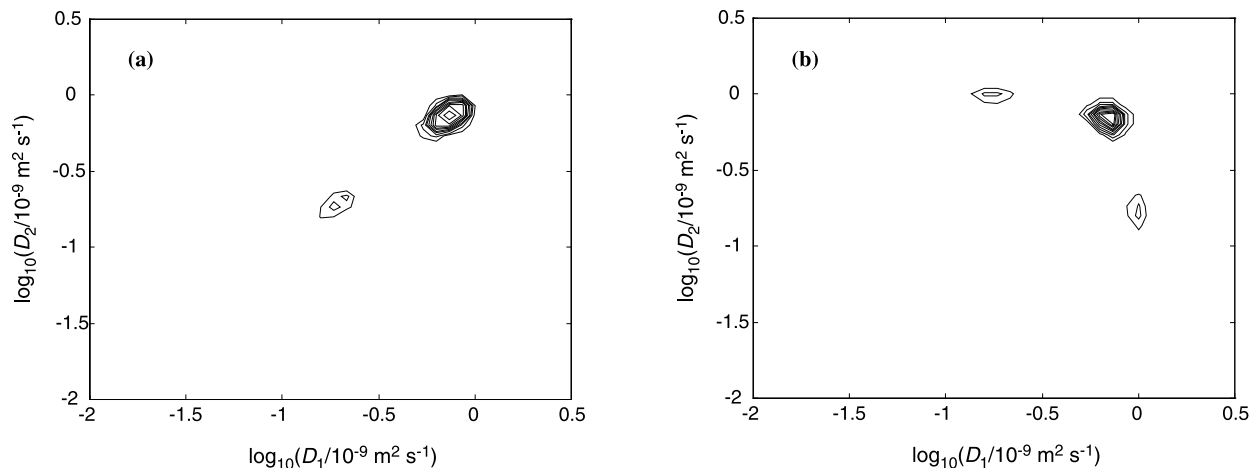


Fig. 5. DDCOSY pattern obtained from locally anisotropic diffusion data simulated with $D_{\parallel} = 0.1D_{\perp}$ and $D_{\perp} = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Gradient pulses are applied collinear (a) and orthogonal (b). [Reprinted with permission from [9]. Copyright 2004, American Institute of Physics.]

and

$$E(G_{1z}, G_{2x}) = \int_0^1 d \cos \theta \exp\{-q_{1z}^2 (D_{\parallel} \cos^2 \theta + D_{\perp} \sin^2 \theta)\} \\ \times \int_0^{2\pi} \frac{d\phi}{2\pi} \exp\{-q_{2z}^2 (D_{\parallel} \sin^2 \theta \cos^2 \phi + D_{\perp} \sin^2 \phi + D_{\perp} \cos^2 \theta \cos^2 \phi)\} \quad (4b)$$

Using simulated data with $D_{\parallel} = 0.1D_{\perp}$ and $D_{\perp} = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ respectively, DDCOSY diffusion–diffusion patterns as obtained by ILT are shown in Fig. 5 for collinear applied gradients (which yields diagonal spectra according to Eq. (4a)) and orthogonal gradients for which an off-diagonal pattern characteristic of locally two-dimensional diffusion is predicted (following Eq. (4b)).

Fig. 6 shows DDCOSY patterns obtained from the lyotropic liquid crystal in a polydomain lamellar phase formed by the non-ionic surfactant $C_{10}E_3$ at 40 wt% in water [9]. Note that the time between the successive encoding pairs must be shorter than the time to diffuse between domains if local anisotropy is to be revealed in this manner.

5. Relaxation–relaxation and diffusion–diffusion exchange

5.1. REXSY

An early T_2 exchange experiment was carried out by Lee et al. in 1993 [21]. This study utilized independent 1D Laplace transforms along the orthogonal time domain directions. Using the 2D ILT algorithm instead, McDonald et al. [11] performed a double T_2 encoding experiment on a white cement paste for fixed separation times. Although no quantization was attempted, this 2D ILT exchange experiment was able to demonstrate the movement of water between differing environments and to prove that the exchange pattern as shown in Fig. 7 depends on the hydration time of the cement paste.

Later, Washburn and Callaghan [12] used the two-dimensional transverse relaxation exchange spectroscopy experiment (REXSY) to track the movement of spin bearing water molecules in a Castlegate sandstone. This was accomplished by

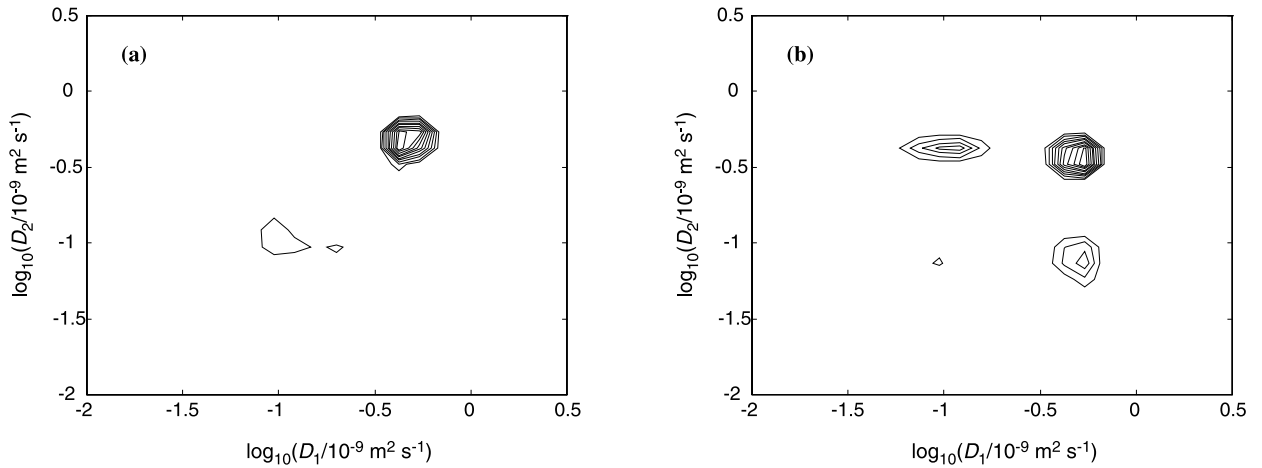


Fig. 6. DDCOSY pattern obtained from a lamellar phase lyotropic liquid crystal. Gradient pulses are applied collinear (a) and orthogonal (b). [Reprinted with permission from [9]. Copyright 2004, American Institute of Physics.]

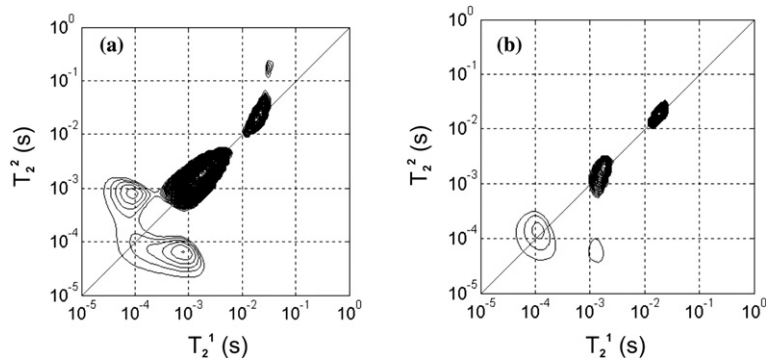


Fig. 7. T_2 - T_2 exchange pattern for water in a white cement paste. Off-diagonal features along with their corresponding diagonal peaks can be observed after one day of hydration in the lower left corner (a). The impact of 4 days of hydration is evident in figure (b). [Reprinted with permission from [11]. Copyright 2005, American Physical Society.]

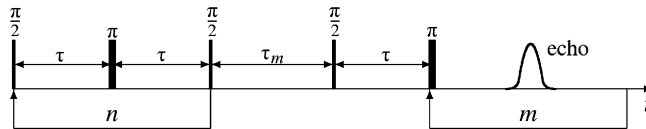


Fig. 8. REXS pulse sequence consisting of a leading CPMG sub sequence with varying loop number n , a mixing time τ_m and a second multi-echo sampling CPMG with m echoes.

performing a first T_2 encode with an increasing number of loops n (1st dimension) followed by a magnetization storage interval τ_m to allow the molecules to diffuse, and finally a second T_2 encode with a multi-echo sampling CPMG (fixed number m of echos, 2nd dimension), as shown in Fig. 8.

T_2 provides a crude measure of local pore size. After a mixing time, spins remaining in their original environment (i.e. same pore size) lie along the diagonal of an inverse Laplace exchange spectrum as shown in Fig. 9 (a). On the other hand, the appearance of cross peaks in the spectrum in Fig. 9 (a) indicates that molecules have changed environments between the first and second encode interval. Integrating the exchange peak intensities at different mixing times, Washburn and Callaghan [12] determined the relative number of spins in the sample that had moved between two particular T_2 environments or, by integration of the diagonal peaks, had remained in the same T_2 environment. Plotting these intensities as a function of the mixing time τ_m they extracted, from the exponential growth and decay curves in Fig. 9 (b) and (c), the exchange time constants related to the migration between different T_2 environments.

A nice validation of T_2 exchange experiments has been carried out by Mitchell et al. [13]. Their model porous medium comprised mixtures of non-porous borosilicate and soda lime glass spheres in water. The spheres had mean diameter 100 μm , providing an approximately constant characteristic pore dimension throughout the structures, while the use of two glass types ensured that water in different pore-space regions had significantly different T_2 relaxation rates. By constructing the bead packs in different ways with controlled glass type domain sizes, these authors were able to validate a model for

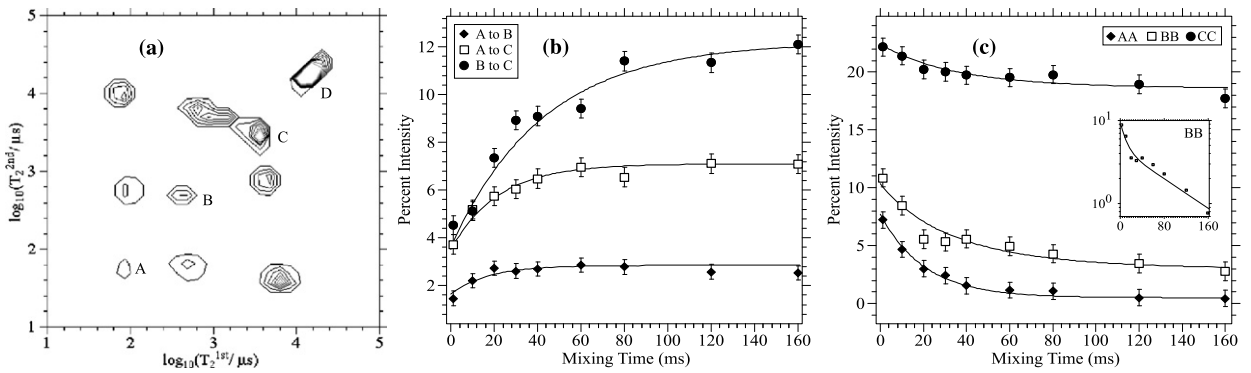


Fig. 9. REXSY map (a) of a Castlegate sandstone exhibiting exchange processes by off-diagonal features between sites A, B and C along with its growth of off-diagonal peaks (b) and the decay of diagonal elements (c). [Reprinted with permission from [12]. Copyright 2006, American Physical Society.]

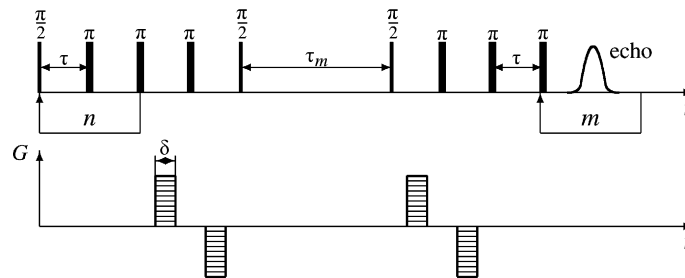


Fig. 10. Propagator resolved REXSY pulse sequence consisting of a leading CPMG subsequence with varying loop number n , pulsed field gradient pairs for diffusion encoding around the mixing time τ_m and a second multi-echo sampling CPMG with m echoes.

region-to-region exchange of water. From the determined exchange times, the corresponding length scales, calculated from the known molecular self-diffusion, agreed well with the known domain sizes.

5.2. Propagator resolved REXSY

One disadvantage of the simple transverse relaxation exchange technique is that one cannot tell whether signal along the diagonal comes from molecules that remained in their original location (or perhaps returned to origin) or instead, comes from molecules that migrate to another location with a similar T_2 value. By adding a propagator dimension to the T_2 exchange experiment, one can not only find where the spins move and how quickly they get there, but how far they travel. Hence, one can determine whether changes in T_2 values over the mixing interval comes from intra- or inter-pore transport. Washburn and Callaghan [20] have demonstrated this effect using the pulse sequence shown in Fig. 10. The sequence begins with a T_2 encode interval using a short fixed echo spacing of $75 \mu\text{s}$ to avoid the effects of internal gradients, T_2 encoding occurs by varying the number of refocusing π pulses. A π pulse is used to refocus the magnetization for propagator encoding, bipolar gradients being used to avoid possible spurious effects from the interaction between the applied and internal gradients [22]. A $\pi/2$ pulse stores the magnetization in z direction, allowing spins to diffuse during the mixing interval τ_m without accruing any further T_2 relaxation. Another $\pi/2$ pulse returns the magnetization to the transverse plane, where the second set of bipolar gradients are applied. Finally, the second T_2 encode is performed simultaneously with data acquisition. Each experiment required about 14 hours to complete!

Applying this pulse sequence to a Castlegate sandstone as done by Washburn and Callaghan [20], the power of the third (Fourier) dimension becomes immediately apparent. Although the T_2 exchange plots in Fig. 11 have been both acquired at a mixing time of $\tau_m = 200 \text{ ms}$, no exchange can be seen from Fig. 11 (a), this map having been taken at zero displacements in the propagator dimension. On the contrary, for the same mixing time, strong off-diagonal features are evident on Fig. 11 (b), where displacements of $45 \mu\text{m}$ are selected from the Fourier dimension. Walking along the Fourier dimension, the obtained exchange pattern can be easily related to the topology of the sample (inter- or intra-pore length scale).

5.3. DEXSY

REXSY exchange experiments rely on different environments in the sample causing different T_2 relaxation times for corresponding subsets of spins. Furthermore, in order that exchange should mostly occur during the mixing time, rather than during T_2 encoding, we require that the T_2 relaxation times for all subsets are short compared to the mixing time τ_m .

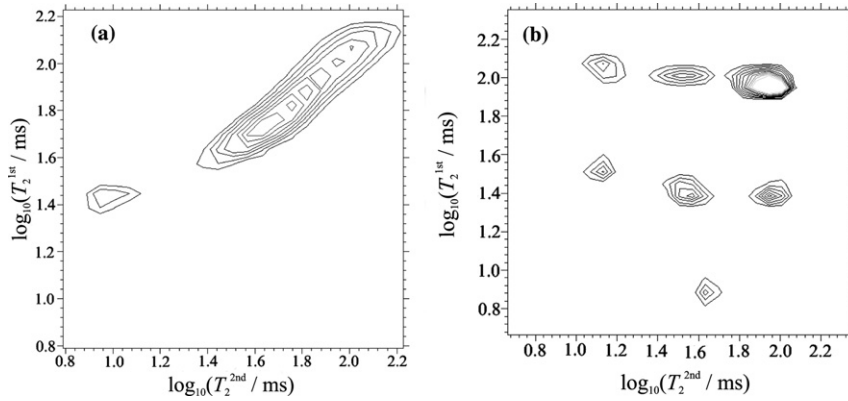


Fig. 11. Exchange pattern as taken by the propagator resolved REXSY for water in a Castlegate sandstone for a mixing time of 200 ms. The displacements as selected along the Fourier dimension are 0 μm (a) and 45 μm (b). [Reprinted from [20], Copyright 2007, with permission from Elsevier.]

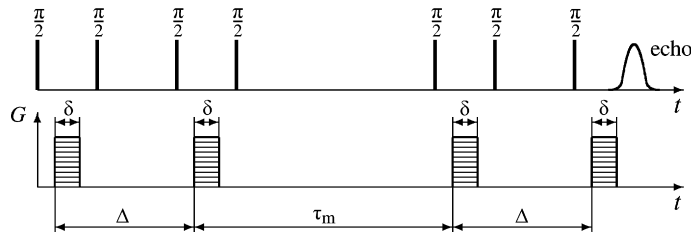


Fig. 12. DEXSY pulse sequence in a variant with two PGSTE subsequences for diffusion encoding, separated by the mixing τ_m .

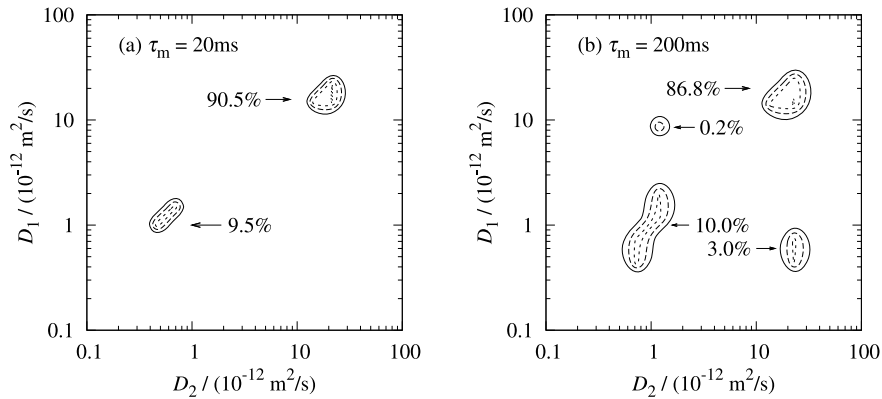


Fig. 13. DEXSY map for dextran diffusing in a suspension of hollow polyelectrolyte multi-layer capsules at a mixing time of 20 ms (a) and 200 ms (b). Off-diagonal peaks represent dextran leaving or entering the capsule during the mixing time. [Reprinted with permission from [10]. Copyright 2005, American Institute of Physics.]

Alternatively, one may use as a label the different diffusion coefficients of molecules migrating in the pore space of a heterogeneous host material. The design of the diffusion exchange spectroscopy (DEXSY) [9,23] is very similar to REXSY, with two PGSTE intervals for diffusion encoding instead of T_2 sensitive CPMG subsequences as shown in Fig. 12.

Qiao et al. [10] exploited the different diffusional properties of dextran diffusing in a suspension of polyelectrolyte multi-layer capsules in D_2O . For sufficiently high molecular weights, the capsule wall, itself a porous membrane, hinders the diffusion of the dextran molecules, leading to different apparent diffusivities inside the capsule and the free fraction outside the capsules. Nonetheless, dextran molecules may permeate through the capsule wall with a certain probability. Given a mixing time of 200 ms, we find off-diagonal features in Fig. 13 (b), indicating the change of the diffusion coefficient and, hence, the exchange of dextran between the interior of the capsule and the free volume outside the capsules. Remarkably, this exchange pattern cannot be observed in Fig. 13 (a) at a mixing time of 20 ms, suggesting a rather slow exchange process with a time constant of the order of 1 s.

Gratz et al. [24] used a similar pulse sequence as shown in Fig. 12, but simplified it to a Hahn echo, while utilizing pulsed field gradients of up to 35 Tm^{-1} . This way, diffusion encoding times of only 2 ms were necessary, while still maintaining sufficient NMR signal attenuation. With these diffusion encoding times, mixing times as short as 5 ms have become possible

for the acquisition of DEXSY exchange maps for *n*-pentane in a bed of overloaded NaX zeolites. Applying the same processing for the diagonal and off-diagonal peak intensities as suggested by Washburn and Callaghan [12] for REXSY, the time constant for the exchange between the interior and the exterior of the zeolite crystals was determined using DEXSY [24].

6. Conclusion

This short review indicates the potential for multi-dimensional inverse Laplace methods to characterize both the structure of porous materials, and the migration of imbibed liquid molecules between different parts of the pore space. Pulse sequences that incorporate signal encoding in different dimensions allow for combinations of relaxation times, diffusion coefficients and translational displacements, both as correlation and exchange measurements. Most importantly, quantitative interpretation of intensities has proven to be possible, one of the first consequences being the measurement of exchange times between compartments or pores. Significant extensions to the methods presented here are possible, in particular where multi-phase studies are desired, since in nearly every case, NMR spectral resolution can be included to allow for molecular identification by chemical shift. The methods presented here are also applicable to low field and portable NMR systems, and hence have the potential to be used in a range of industrial applications.

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