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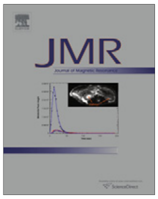

Communication

Structural properties of 2D NMR relaxation spectra of diffusive systems

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ABSTRACT

Much has been learnt and speculated about the form of 2D NMR relaxation spectra of diffusive systems. Herein we show that the eigen-modes formalism can help to establish a number of fundamental structural properties, i.e. symmetries, overall intensities, signs and relative intensities of the diagonal and cross components, of such spectra, on which one can safely rely in analysing experimental data. More specifically, we prove that the correlation T_1–T_2 spectra will always have negative peaks, thus making questionable the nowadays wide spread strategy in developing inverse Laplace transformation algorithms.

1. Introduction

The development of two-dimensional (2D) relaxation techniques is one of the major advances in NMR over the last ten years. Correlating various relaxation mechanisms rather than Larmor frequencies and chemical shifts, these techniques provide new scope for the use of ideas originating in the multi-dimensional Fourier Transformation (FT) spectroscopy [1]. Numerous heterogeneous systems can't be studied by the FT spectroscopy either because their spectra are of no interest or because the acquisition of the latter is hindered by the intrinsic inhomogeneity in magnetic susceptibility. Relaxation rates can turn out extremely valuable to identify different constituents or various compartments in such systems [2]. This is the case of confined fluids in porous media, in which relaxation rates can be related direct to the pore sizes [3]; foods, in which various ingredients have distinct relaxation rates [4]; or complex fluids, such as cements during its setting, in which the measurement of relaxation rates allows to monitor the formation of organised structures [5]. Since the late 1980s, one-dimensional (1D) Inverse Laplace Transformation (ILT) spectroscopy has allowed observation of relaxation rate distributions in various materials [6].

Nowadays the 2D ILT spectroscopy, correlating various processes that drive relaxation, holds out hope of more in-depth understanding of composition and dynamics of those materials. Unlike the FT spectroscopy, its ILT counterpart is also of great interest for those NMR studies where only spectrometers with an externalised magnet, RF transmitter and receiver coils must be used, e.g. NMR-Mouse [7] or GarField [8]. Both types of spectroscopy saw the light three decades ago or so [9,10]. Constant progress has been made in the FT spectroscopy ever since, while the early development of the ILT spectroscopy was relatively slow. The reason for this was, as their mere names suggest, that one type of spectroscopy relies on the FT of raw NMR data collected in experiments as a function of the time, while the other necessitates the ILT of the data. The numerical implementation of the multidimensional FT never posed any fundamental problem. On the contrary, performing the multidimensional ILT numerically had long been a formidable task and one had to wait until 2002 to see the first 2D ILT algorithm that could be run on an ordinary PC [11,12]. This was followed by the development of several rather straightforward NMR experimental schemes, viz. the T_1–T_2 correlation [11,12], where a period of spin–spin relaxation follows a period of spin–lattice relaxation, thus correlating the spin–lattice and spin–spin relaxation rates; the T_2–T_2 correlation [13], where two periods of spin–spin relaxation are separated by a period of fixed duration during which the spin system is subject to spin–lattice relaxation, and which correlates the spin–spin relaxation rates with themselves; as well as the T_1–T_1 correlation [14], where spin–lattice relaxation rates are correlated with themselves, and where a period of fixed duration during which the spin system is subject to spin–spin relaxation is sandwiched between two periods of spin–lattice relaxation.

Study of various systems have already benefited from the 2D ILT spectroscopy, viz. polymers [7], fruits and vegetables [15], cement-based materials [8], as well as water and oil in rocks [16]. The relaxation rates T_1 and T_2 are sometimes completed by other information, such as molecular diffusion [17] or chemical shifts [14]. The ratio T_1/T_2 – a key element in the relaxation analysis-could be determined direct from correlation spectra T_1–T_2 [13].

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Observation of cross-peaks in correlation spectra of cements was the first experimental proof that water migrates between certain types of pore [13]. Systematic studies of those peaks allow to measure chemical exchange rates between particular sites [18].

Nevertheless, assignment of various components and interpretation of 2D spectra encountered in ILT spectroscopy is still difficult [19], as they are subject to defects introduced by the 2D ILT programmes available to date. These defects, described in literature [20], consist in each of the large components of the spectrum bursting into a number of smaller peaks as well as in appearing spurious peaks. Furthermore, the present algorithm was designed on a premise that all the components of a spectrum have positive amplitudes. Recent theoretical studies, though, showed spectra containing peaks of both signs [21,22]. Thus, a mathematically rigorous study of the structure of 2D spectra correlating various relaxation rates could, we believe, considerably benefit the future analysis of experimental data.

Two approaches have been used in the modelling of relaxation spectra. One of them, largely inspired by the first-order two-site exchange model [21], has allowed to analyse quantitatively spectra of numerous systems, but turned out much too specific to permit by its self to thoroughly understand the fundamental structural features of the spectra. Another one [22], based on the eigen-modes formalism, is much more general, but, being rather abstract, has not attracted enough spectroscopists' attention. In this report, we show that within this latter formalism a wealth of useful structural properties of the spectra can be expressed in a mathematically rigorous way.

2. Theory

2.1. Diffusive systems

Being placed in the magnet of an NMR spectrometer, porous media and live tissues can be regarded as diffusive systems, in which local magnetisation $m(\boldsymbol{r})$ stems essentially from an interstitial fluid – often water or oil – free to diffuse in pores. The magnetisation density difference from its equilibrium value satisfies the equation

$$\phi(\boldsymbol{r})\frac{\partial m}{\partial t} = \nabla(\boldsymbol{D}(\boldsymbol{r})\nabla m) - \phi(\boldsymbol{r})\mu_\alpha(\boldsymbol{r})m \quad (1)$$

where $\phi(\boldsymbol{r})$, $\boldsymbol{D}$ and μ_α stand for the local concentration of the fluid, diffusion tensor and relaxation rate, respectively [2]. The subscript $\alpha = 1$ or 2, depending on whether it deals with spin–lattice or spin–spin relaxation. At the surface between the fluid and solid phases of the system, the relaxation rate ρ_α may be much higher than that μ_α inside the fluid. It is governed by the boundary condition

$$\boldsymbol{n}(\boldsymbol{r})\cdot\boldsymbol{D}(\boldsymbol{r})\nabla m = \phi(\boldsymbol{r})\rho_\alpha(\boldsymbol{r})m \quad (2)$$

where $\boldsymbol{n}$ is the normal unit vector directed towards the inside of the fluid phase.

2.2. Eigen-modes formalism

This system has orthonormal bases of spin–lattice $|\Psi_{1,n}(\mathbf{r})\rangle$ and spin–spin $|\Psi_{2,n}(\mathbf{r})\rangle$ relaxation eigen-states with real relaxation eigen-times $\tau_{1,n}$ and $\tau_{2,n}$ associated to them [23]. One can then express [24] the non-equilibrium part of the NMR signal collected in the inversion-recovery, for T_1 measurements, or CPMG, for T_2 measurements, experiments as

$$M_\alpha(t) = m_0\sum_n \langle 1|\Psi_{\alpha,n}\rangle^2 \exp(-t/\tau_{\alpha,n}) \quad (3)$$

and conclude that corresponding 1D spectra, obtained after the ILT, has non-zero values only for the times $\tau_{\alpha,n}$ with positive intensities

$$S_{T_\alpha}(n) = m_0\sum_n \langle 1|\Psi_{\alpha,n}\rangle^2 \quad (4)$$

where m_0 is the magnetisation density at equilibrium and $|1\rangle$ stands for a homogeneous magnetisation state equal to one all over the system. Using the same eigen-states, the intensities of the T_1–T_2 and T_2–T_2 correlation spectra for coordinates $(\tau_{1,n},\tau_{2,m})$ and $(\tau_{2,n},\tau_{2,m})$ were analytically calculated [22] as

$$S_{T_1-T_2}(n,m) = m_0\langle 1|\Psi_{1,n}\rangle\langle\Psi_{1,n}|\Psi_{2,m}\rangle\langle\Psi_{2,m}|1\rangle \quad (5)$$

$$S_{T_2-T_2}(n,m) = m_0\sum_p \langle 1|\Psi_{2,n}\rangle\langle\Psi_{2,n}|\Psi_{1,p}\rangle\langle\Psi_{1,p}|\Psi_{2,m}\rangle\langle\Psi_{2,m}|1\rangle \times \exp(-\tau_{mix}/\tau_{1,p}) \quad (6)$$

where τ_{mix} is the duration of the mixing period. From physical point of view, the peaks observed in the spectra indicate a correlation or exchange between various relaxation modes. We could obtain the amplitudes of the peaks in the T_1–T_1 spectrum by exchanging indices 1 and 2 in Eq. (6).

3. Previous structural results

From Eqs. (5) and (6), the authors of [22] made appear the following important properties, though, largely ignored in numerous recent experimental studies, and which deserves that we give them special emphasis

(**a**) The T_2–T_2 spectra are symmetrical according to $S_{T_2-T_2}(n,m) = S_{T_2-T_2}(m,n)$.

(**b**) When eigen-modes $|\Psi_{1,n}(\mathbf{r})\rangle$ and $|\Psi_{2,n}(\mathbf{r})\rangle$ are identical, the T_1–T_2 and T_2–T_2 spectra have diagonal peaks only.

(**c**) The spectra can contain peaks with negative amplitudes, as was showed theoretically for 1D pores. Quite clearly, the ILT algorithm available to the NMR spectroscopists at the moment does not allow observation of such peaks experimentally. We shall attach particular attention to whether these negative peaks are merely occasional minor faults, which can be ignored, or systematically encountered major features of the relaxation correlation spectra, to take into account in analysis.

4. Results and discussion

Unfortunately, the above-mentioned expressions have not, we believe, been exploited enough and we now show that they can indeed provide much more information on general features of the spectra. For the sake of simplicity, we shall limit ourselves in what follows to the case of non-degenerated relaxation states knowing that the results obtained below can be easily extended to the more general case. Taking into account formal similarity between the T_1–T_1 and T_2–T_2 spectra, we shall hereafter discuss the T_1–T_2 and T_2–T_2 spectra only.

(**d**) The sum of the intensities of all peaks in the spectrum is preserved, i.e. independent of the durations of the relaxation periods. This conservation law is deduced from the closure relation

$$\sum_n |\Psi_{\alpha,n}\rangle\langle\Psi_{\alpha,n}| = Id \quad (7)$$

by writing

$$\sum_{n,m} S_{T_1-T_2}(n,m) = m_0\langle 1|1\rangle = M_1(0) \quad (8)$$

and