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Structure of the two-dimensional relaxation spectra seen within the eigenmode perturbation theory and the two-site exchange model

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ABSTRACT

The form of the two-dimensional (2D) NMR-relaxation spectra – which allow to study interstitial fluid dynamics in diffusive systems by correlating spin-lattice (T_1) and spin-spin (T_2) relaxation times – has given rise to numerous conjectures. Herein we find analytically a number of fundamental structural properties of the spectra: within the eigen-modes formalism, we establish relationships between the signs and intensities of the diagonal and cross-peaks in spectra obtained by various 1 and 2D NMR-relaxation techniques, reveal symmetries of the spectra and uncover interdependence between them. We investigate more specifically a practically important case of porous system that has sets of T_1- and T_2-eigenmodes and eigentimes similar to each other by applying the perturbation theory. Furthermore we provide a comparative analysis of the application of the, mathematically more rigorous, eigen-modes formalism and the, rather more phenomenological, first-order two-site exchange model to diffusive systems. Finally we put the results that we could formulate analytically to the test by comparing them with computer-simulations for 2D porous model systems. The structural properties, in general, are to provide useful clues for assignment and analysis of relaxation spectra. The most striking of them – the presence of negative peaks – underlines an urgent need for improvement of the current 2D Inverse Laplace Transform (ILT) algorithm used for calculation of relaxation spectra from NMR raw data.

1. Introduction

Over the past 20 years or so, multi-dimensional (MD) NMR Fourier transformation (FT) spectroscopy has grown into a versatile tool for analysis of matter [1]. All experimental techniques of the spectroscopy rely on the measurement of precession frequencies, called Larmor frequencies, of nuclear spins in an intense homogeneous and stable magnetic field to identify molecular structure and/or electronic environment of the individual atoms of chemical substances.

Over the 1D spectroscopy, which measures chemical shifts of only one of the isotopes of the substance, the MD spectroscopy has an additional advantage of establishing correlations either between Larmor frequencies and chemical shifts of different isotopes or between various chemical shifts of the same isotope in chemical compounds. This provides more detailed information on molecular structure and intra-molecular dynamics in a wide range of substances, thus making the MD FT-spectroscopy into one of the most powerful analytical methods in both chemistry [2] and structural biology [3].

Nevertheless, there are numerous systems that cannot benefit from the FT-spectroscopy either because their spectra are of no interest or because their observation is hindered by intrinsic inhomogeneity of their magnetic susceptibility. This is the case of numerous blends of, chiefly, oils and water widely used in food and cosmetics or porous media such as concretes and reservoir rocks. Furthermore there is a wealth of systems which can only be studied at what is becoming to be known as 'mobile' NMR-spectrometers, whose highly inhomogeneous magnetic field prohibits any access to FT spectroscopic data. These include NMR-equipment used in prospecting oil [4] or studying bulky samples [5,6]. In such situations, measurement of relaxation rates – phenomenological quantities describing repolarisation kinetics of macroscopic magnetisation of a system of nuclear spins along the constant field of the NMR spectrometer's magnet after an excitation by radio frequency (RF) irradiation – becomes essential. Being driven by magnetic interactions, fluctuating with time, between nuclear spins and their nearby environment [7], relaxation reveals various chemical and physical aspects of such systems.

Even in the most simple systems, several distinct relaxation times may be useful to measure: the spin-lattice relaxation time T_1, which describes how quickly the longitudinal magnetisation – the component of the magnetisation parallel to the magnetic field – returns to its equilibrium non-zero value, the spin-spin relaxation time T_2, which characterises the decrease of the transverse

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magnetisation – the component of the magnetisation perpendicular to the magnetic field – towards its equilibrium zero value, and the so-called time $T_{1\rho}$, which describes the relaxation of the transverse magnetisation while the system is irradiated at its resonance frequency.

These rates allowed to discriminate between various compartments, containing interstitial water, of live tissues [8] or distinguish between water and oil in emulsions [9]. They permitted to dose solid suspensions in a very large concentration range [10]. They were also used to monitor the formation of organised structures in complex systems such as cements during their setting [11,12] or ageing thixotrope fluids [13]. They proved very sensitive to phase changes and so allowed to monitor freezing and melting cycles in porous media [14]. In the field-cycling NMR, measurements of relaxation rates as a function of the field strength to which the system is exposed allowed to study, at the nanometric scale, the movements of molecules interacting with surfaces and quantify the time scales at which these movements take place [15,16]. Finally relaxation rates are used extensively to create various types of contrasts in biomedical and material science magnetic resonance imaging (MRI) [17].

Heterogeneous systems are usually characterised by distributions of relaxation times rather than one particular relaxation time. This situation could be observed when several fluids of different nature, e.g. water and oils – each having its own relaxation time – were parts of the system, or when a fluid of the same nature was confined in several rather isolated zones, or compartments, of the system with distinctly different physical properties, such as pores of different size in a porous medium or different cells in a live tissue. Nevertheless, viewed within the eigen-modes formalism (see below), the relaxation rate of even a continuous fluid in one and only cavity or in compartments connected to one another can take more than one value. This makes us think that the widely made assumption that each peak in a relaxation spectrum necessarily corresponds to a particular compartment in the system is not always justifiable.

The raw NMR-signal $M(t_i)$ of a system with a limited number N of distinct spin-spin $T_{2,n}$'s can, for instance, be expressed as a series

$$M(t_i) = \sum_{n=1}^{N} w_n \exp\left(\frac{-t_i}{T_{2,n}}\right), \quad t_i > 0 \tag{1}$$

where w_n's are the weights of the various $T_{2,n}$'s and t_i's the moments of time at which the signal was sampled by the analogue-to-digital converter (ADC). The values of $T_{2,n}$ can then be determined by fitting, in the least-square sense, the experimental data with the series of Eq. (1) [13] or by 'curve peeling' technique [18], and formed into a spectrum similar to those of chemical shift distributions in the FT-spectroscopy. The raw NMR-signal of a system with a large number of distinct $T_{2,n}$'s or with a continuous distribution $s(T)$ of $T_{2,n}$ can be formulated as a Laplace integral

$$M(t_i) = \int_T s(T) \exp\left(\frac{-t_i}{T}\right) d\ln T \tag{2}$$

Thus the calculation of the spectrum $s(T)$ consists here in differentiating the first-kind Fredholm integral in Eq. (2).

The numerical solution of this problem is notoriously unstable when applied to noise-impaired signals. To stabilise it, various inverse Laplace transformation (ILT) algorithms have been developed, viz. [19–22]. In all these algorithms, irregular solutions for $s(T)$ are dismissed as highly unlikely spectral structures and $s(T)$ is assumed to be non-negative, the latter premise being corroborated by a theoretical study [23]. In one way or another, the algorithms are aimed at finding the non-negative least-square minimum:

$$Min_{s\geqslant 0}\left\{\sum_i \left(M(t_i) - \int_T s(T)\exp\left(-\frac{t_i}{T}\right)d\ln T\right)^2 + \lambda \int_T \left(\frac{\partial^2 s}{\partial(\ln T)^2}\right)^2 d\ln T\right\} \tag{3}$$

where the Thikonov regularisation term is weighed by the parsimony coefficient λ. In general, the regularisation is applied to the square of the norm of the second derivative of the spectrum, but it could also be applied to the square of the norm of the first derivative or even to that of the spectrum itself without any notable incidence on the form of thus obtained spectrum. The coefficient λ is chosen as large as possible, making, though, sure that the covariance between the experimental data and the signal resulted from the minimisation does not exceed the experimental noise level.

These algorithms encouraged development of the 1D nuclear spin relaxation spectroscopy, or 1D ILT-spectroscopy, which has been extensively used for analysis of fruit and vegetables [24,8] as well as for studying fluids confined in porous materials. The NMR-signal of such systems stems chiefly from the interstitial fluid whose molecules can diffuse in domains delimited by solid boundaries, e.g. cell boundaries or pores surfaces, and with which they can interact in various ways, e. g. adsorption, chemical exchange, magnetic dipole-dipole coupling.

In diffusive systems (see Fig. 1) generally, the local non-equilibrium magnetisation density $m(\mathbf{r})$ of the confined fluid, to which the observable NMR-signal is proportional, can be expressed [25] by the relaxation-diffusion equation:

$$\phi(\mathbf{r})\frac{\partial m}{\partial \mathbf{t}} = \nabla \cdot \boldsymbol{D}(\mathbf{r})\nabla m - \phi(\mathbf{r})R_\alpha(\mathbf{r})m, \tag{4}$$

where ϕ, $\boldsymbol{D}$ and $R_\alpha = 1/T_\alpha$ are the local fluid concentration, diffusion tensor and relaxation rate respectively, and the subscript $\alpha = 1$, 2 or 1ρ depending on which type of relaxation it is dealt with. NMR-relaxation of the fluid driven by its interaction with the boundary between two domains A and B, and magnetisation transfer between these domains are first-order processes taken in account in the boundary condition:

$$\begin{aligned}&\boldsymbol{n}_A(\mathbf{r})\cdot\boldsymbol{D}_A(\mathbf{r})\nabla m_A - \phi_A(\mathbf{r})\rho_{A,\alpha}(\mathbf{r})m_A \\ &\quad = -\boldsymbol{n}_B(\mathbf{r})\cdot\boldsymbol{D}_B(\mathbf{r})\nabla m_B + \phi_B(\mathbf{r})\rho_{B,\alpha}(\mathbf{r})m_B = k(\mathbf{r})\cdot(m_A - m_B)\end{aligned} \tag{5}$$

where subscripts A and B denote quantities pertaining to either side of the boundary: $\boldsymbol{n}_A$ and $\boldsymbol{n}_B$ are the normal unit-vector directed towards the inside of domains A and B respectively, $\rho_{A,\alpha}$ and $\rho_{B,\alpha}$ the surface relaxation rates in either domain, also called 'relaxivities'. The latter can be significantly higher than that inside the fluid R_α. Finally $k(\mathbf{r})$ is the surface permeability. Naturally, the permeability k has to be set to zero when it deals with the boundaries between fluid and solid phases. Eqs. (4) and (5), due to the term ϕ and the

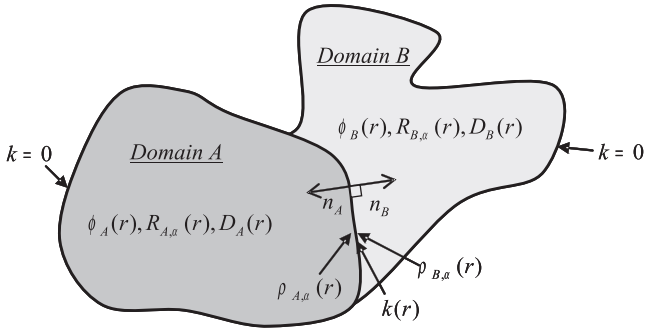

Fig. 1. Scheme of a diffusive system having two domains A and B, here delimited by solid lines, with their own individual porosity $\phi(\mathbf{r})$, relaxation rates $R_\alpha(\mathbf{r})$'s and diffusion tensor $\boldsymbol{D}(\mathbf{r})$ fields. The boundaries of the domains are characterised by surface relaxation rate $\rho_\alpha(\mathbf{r})$ and permeability $k(\mathbf{r})$.