Progress in Nuclear Magnetic Resonance Spectroscopy 104 (2018) 12–55

Contents lists available at ScienceDirect

Progress in Nuclear Magnetic Resonance Spectroscopy

journal homepage: www.elsevier.com/locate/pnmrs

Multiscale nuclear magnetic relaxation dispersion of complex liquids in bulk and confinement

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Edited by J.W. Emsley and D. Neuhaus

ARTICLE INFO

Article history:
Received 4 July 2017
Accepted 1 November 2017
Available online 10 November 2017

Keywords:
Nuclear magnetic relaxation dispersion
Porous media
Cements
Complex liquids
Shale oils
Proteins

ABSTRACT

The nuclear magnetic relaxation dispersion (NMRD) technique consists of measurement of the magnetic-field dependence of the longitudinal nuclear-spin-lattice relaxation rate $1/T_1$. Usually, the acquisition of the NMRD profiles is made using a fast field cycling (FFC) NMR technique that varies the magnetic field and explores a very large range of Larmor frequencies (10 kHz < $\omega_0/(2\pi)$ < 40 MHz). This allows extensive explorations of the fluctuations to which nuclear spin relaxation is sensitive. The FFC technique thus offers opportunities on multiple scales of both time and distance for characterizing the molecular dynamics and transport properties of complex liquids in bulk or embedded in confined environments. This review presents the principles, theories and applications of NMRD for characterizing fundamental properties such as surface correlation times, diffusion coefficients and dynamical surface affinity (NMR wettability) for various confined liquids. The basic longitudinal and transverse relaxation equations are outlined for bulk liquids. The nuclear relaxation of a liquid confined in pores is considered in detail in order to find the biphasic fast exchange relations for a liquid at proximity of a solid surface. The physical-chemistry of liquids at solid surfaces induces striking differences between NMRD profiles of aprotic and protic (water) liquids embedded in calibrated porous disordered materials. A particular emphasis of this review concerns the extension of FFC NMR relaxation to industrial applications. For instance, it is shown that the FFC technique is sufficiently rapid for following the progressive setting of cement-based materials (plasters, cement pastes, concretes). The technique also allows studies of the dynamics of hydrocarbons in proximity of asphaltene nano-aggregates and macro-aggregates in heavy crude oils as a function of the concentration of asphaltenes. It also gives new information on the wettability of petroleum fluids (brine and oil) embedded in shale oil rocks. It is useful for understanding the relations and correlations between NMR relaxation times T_1 and T_2, diffusion coefficients D, and viscosity η of heavy crude oils. This is of particular importance for interpreting T_1, T_2, $2D$ T_1-T_2 and D-T_2 correlation spectra that could be obtained down-hole, thus giving a valuable tool for investigating *in situ* the molecular dynamics of petroleum fluids. Another domain of interest concerns biological applications. This is of particular importance for studying the complex dynamical spectrum of a folded polymeric structure that may span many decades in frequency or time. A direct NMRD characterization of water diffusional dynamics is presented at the protein interface. NMR experiments using a shuttle technique give results well above the frequency range accessible via the FFC technique; examples of this show protein dynamics over a range from fast and localized motions to slow and delocalized collective motions involving the whole protein. This review ends by an interpretation of the origin of the proton magnetic field dependence of T_1 for different biological tissues of animals; this includes a proposal for interpreting *in vivo* MRI data from human brain at variable magnetic fields, where the FFC relaxation analysis suggests that brain white-matter is distinct from grey-matter, in agreement with diffusion-weighted MRI imaging.

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https://doi.org/10.1016/j.pnmrs.2017.11.001
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1. Introduction

This article reviews the principles and applications of multiscale nuclear magnetic relaxation dispersion (NMRD) techniques [1–4] for characterizing molecular dynamics and transport properties of complex liquids in bulk and in confinement [5,6]. Fig. 1 shows a schematic representation of the commonly used multiscale (time/distance) NMR techniques. Compared to the limited range explored by the standard relaxation technique employing a single, fixed magnetic field $\boldsymbol{B}_0$, the NMRD method can report on molecular dynamics from molecular to sub-micron sizes. The NMRD experiment works by measuring the values of the longitudinal relaxation time T_1 over a wide range of magnetic field strengths B_0. For protonated liquids, nuclear spin relaxation is a stimulated (not spontaneous) process induced by the coupling between the nuclear spins $I = 1/2$ and the incoherent magnetic noise created by the molecular dynamics of the spin-bearing molecules and their surroundings. The main interest of the NMRD technique lies in decreasing the Larmor frequency $\omega_0/2\pi$ to explore correspondingly longer correlation times τ_c of the dipolar fluctuations that are induced by molecular dynamics and cause the spin-lattice relaxation. This relaxation is at its most efficient around $\omega_0\tau_c = 1$: the available power of the random *rf* field is spread over a range of frequencies that extends up to about $2\pi/\tau_c$, so when $\omega_0\tau_c \ll 1$ that power is spread too thinly for efficient relaxation, while for $\omega_0\tau_c \gg 1$ the motion is too slow to generate much *rf* power at the frequency ω_0. As a result, decreasing the magnetic field $B_0 = \omega_0/\gamma$ causes the length of diffusion $\ell_D(\omega_0) = \sqrt{6D\tau_c} \approx \sqrt{6D/\omega_0} \rightarrow d_{pore}$ to become sufficiently extended that translational diffusion of an embedded liquid in porous media can reach the average pore size d_{pore}. The NMRD technique thus becomes a very useful tool for studying the molecular dynamics at pore surfaces even for a fully saturated pore system.

The NMRD data described in the papers reviewed here were recorded using the typical fast-field-cycling FFC NMR sequences (see Section 3 of Ref. [5]) used on a commercially available spectrometer from *Stelar s.r.l.*, *Mede*, *Italy*. This instrument was really a breakthrough in the field because the experimenters have to make their own instruments before. Though this commercial instrument does not have a sufficient homogeneous magnetic field for getting high resolution NMR spectra, it is designed to obtain a longitudinal nuclear magnetic relaxation profile. Fig. 2 displays

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