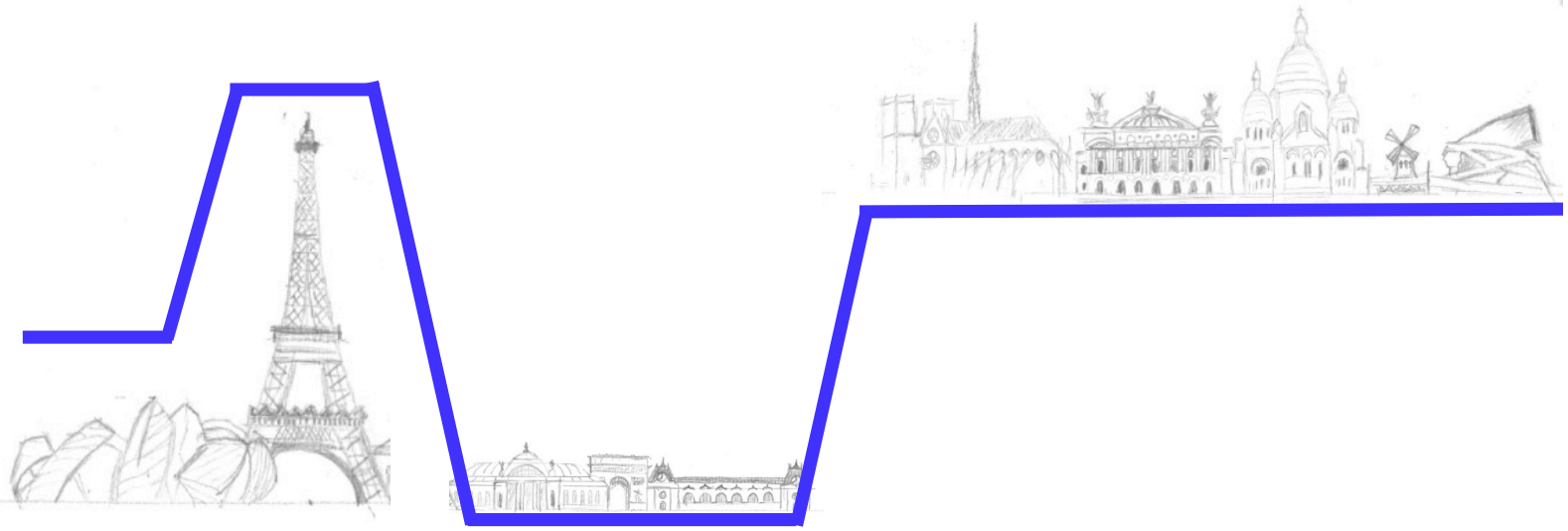
14th Conference on Fast Field Cycling NMR Relaxometry



PARIS 16-19 June 2026

Welcome to the 14th Conference on Fast Field Cycling NMR Relaxometry

The 14th Conference on Fast Field Cycling NMR Relaxometry will open its door on the 16th of June 2026 for 4 days. June 19th will be devoted to demonstrations and tests on various NMR relaxometers and benchtop NMR spectrometers (further description in sponsors page).

This FFC NMR relaxometry conference aims at opening new perspectives beyond relaxation measurements using the fast field cycling technique. It will combine and confront knowledge about:

- Field Cycling NMR
- Fast Field Cycling NMR relaxometry
- Time domain low field NMR relaxometry
- Fast field cycling MRI
- Ultra-low field MRI
- Statistical Physics applied to transport phenomena at the mesoscale

The topics developed during FFC NMR relaxometry conference, also includes applications of techniques in material science (polymer, building staff, colloidal suspensions,…), biology (proteins, contrast agent, biological tissue, medicine,…), food (characterization, fraud control,…), energy (electrolytes, battery, oil, catalysis, fuel cell,…), cultural heritage (paint, 3D porous art works, …), environment (clay deposit, soil,…) and more.

About the Conference

Since the first meeting, which was held in Berlin in 1998, the Fast Field Cycling NMR Relaxometry community has grown in number and interests, and we have come a long way since then. The past conferences have managed to strengthen the interactions among researchers from different scientific areas (chemists, physicists, engineers, biologists, physicians), which have brought advancements in the theory and the experiment and have extended the fields of application of the technique to a variety of disciplines, as materials science, earth sciences, medicine, just to cite a few.

More information on past conferences at https://ffcrelax.org.

Speakers

Esteban Anoardo (CONICET/UNC) will open the conference with a plenary lecture that will embrace many fields discussed during this week!

Tutorials led by renowned experts throughout the conference will enable everyone to get the most out of all the presentations: Kay Saalwächter (TD-NMR), Jean-Pierre Korb (FFC NMR), Claudio Luchinat (FC NMR), Denis Grebenkov (Statistical Physics).
For each domain there will be also an invited talk: Ville-Veikko Telkki (TD-NMR), Simonetta Geninatti Crich (FFC NMR), Maxim Dogulshev (Stat. Phys.), Andrey Pradivtsev (FC NMR).

Scientific committee

- Anne-Laure Rollet (CNRS - Sorbonne Université)
- Lionel Broche (University of Aberdeen)
- Jordan Ward-Williams (University of Cambridge)
- Dermot Brougham (University College Dublin)
- Fabien Ferrage (Sorbonne Université - École Normale Supérieure)
- Giaccomo Parigi (University of Florence)
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- Gianni Ferrante (Stelar Srl)
- Olivier Benichou (CNRS - Sorbonne Université)
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- Anne Strate (Universität Rostock)
- Céline Henoumont (Université de Mons)
- Pedro José Sebastião (Universidade de Lisboa)

Local organizing committee

- Anne-Laure Rollet (PHENIX/CNRS/Sorbonne Université)
- Guillaume Mériguet (PHENIX/Sorbonne Université/CNRS)
- Pierre Levitz (PHENIX/CNRS/Sorbonne Université)
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- Baptiste Rigaud (Fcmat/CNRS/Sorbonne Université)
- Cédric Lorthioir (LCMCP/CNRS/Sorbonne Université)
- Fabien Ferrage (CPCV/CNRS/Sorbonne Université/Ecole normale supérieure)

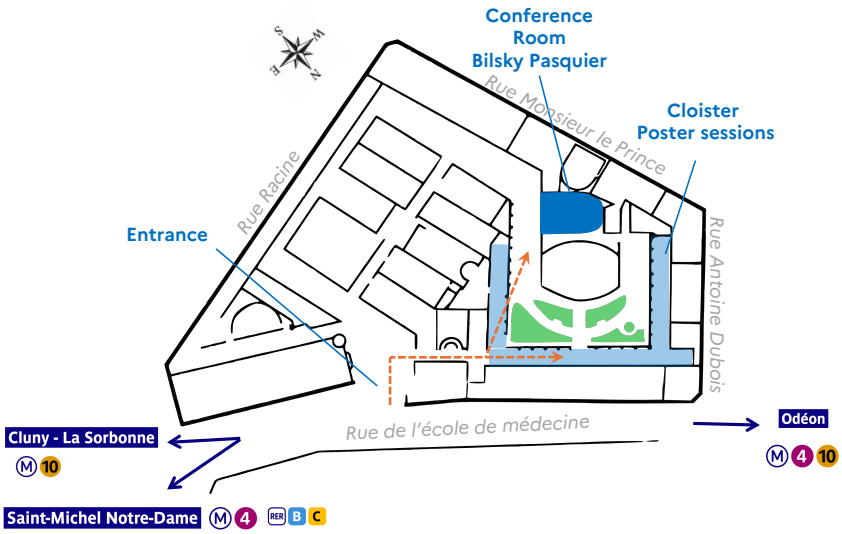
Venue

The Campus des Cordeliers of Sorbonne University, located at 15 rue de l'École de Médecine in Paris's 6th arrondissement, is a historic site with deep roots in French academic and medical history. Originally, the site was part of the Couvent des Cordeliers, a Franciscan convent founded in the 13th century. During the French Revolution, the convent's refectory became a key gathering spot for radical clubs, most notably the Club des Cordeliers, founded in 1790. This club was one of the most influential political groups of the Revolution, advocating for democratic reforms and the overthrow of the monarchy. After the French Revolution, the buildings were repurposed for educational and medical use. Today, the campus is known for its role in hosting academic and professional events, including conferences, symposiums, and public gatherings. It is situated near the Latin Quarter, a traditional hub of intellectual and student life in Paris, and is accessible by metro, RER, and bus:

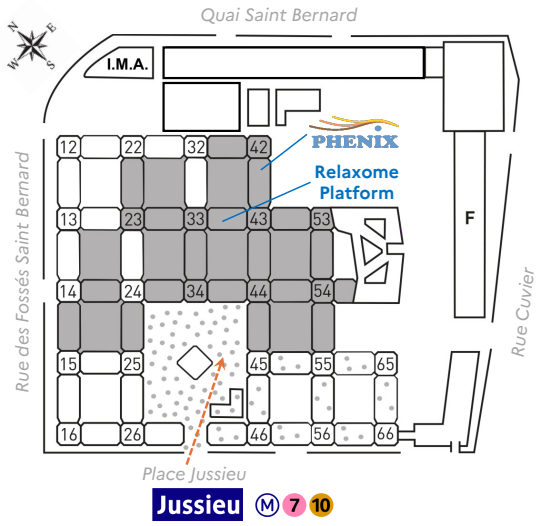
- Metro: Lines 4 or 10 (Odéon)
- RER B: Saint-Michel or Luxembourg stations
- RER C: Saint-Michel station
- Bus: Lines 38, 27, 58 (Rue des Ecoles or Odéon) and lines 63 and 86 (Cluny)
- Paid parking nearby (entrance on Rue de l'École de Médecine

The cloister will host the poster sessions while the conferences will be located in the Bilsky Pasquier amphitheater.

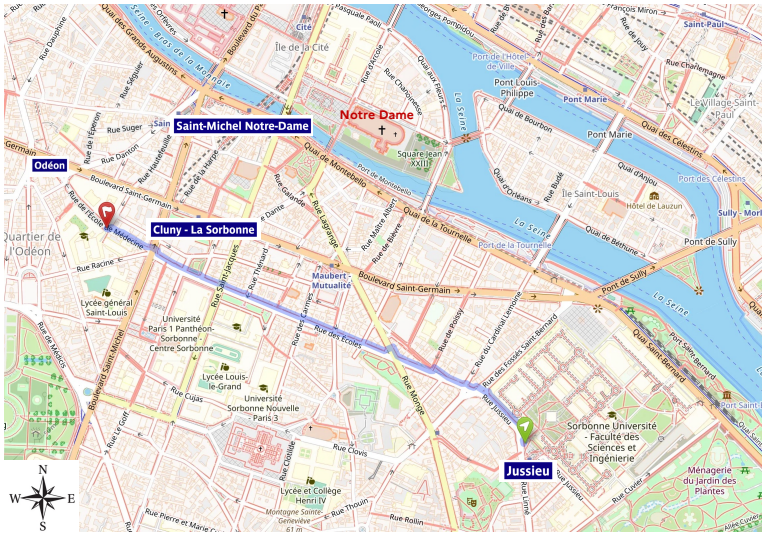
Map of the Campus des Cordeliers



Map of the Campus Pierre and Marie Curie



Path between the campuses



Sponsors

Stelar

Stelar designs and manufactures advanced Fast Field Cycling (FFC) NMR relaxometers, powerful analytical instruments that reveal how molecules move and interact inside materials.

Since 1984, researchers and industries worldwide have relied on Stelar's technology to explore physical and chemical properties in fields ranging from materials science to life sciences.

The Spinmaster (standard and wide bore) will be available on RELAXOME facility (Sorbonne University facility for NMR relaxometry). The Smartracer will be available at PHENIX laboratory.
Contact for planning visit and tests: info@stelar.it

Lab-Tools Ltd

Lab-Tools is a Micro/SME spin-off from the University of Kent Physics department, but has now moved the NMR research and development laboratory to a new purpose designed facility near Ramsgate, in Kent.

It develops Nano- to Micro- Science & Metrology, Scientific Instrumentation and Software and especially cost-sensitive materials-science physical characterisation by compact benchtop NMR.

Contact for planning visit and tests: dr.beauwebber@gmail.com

DIM MaTerRe

MaTerRE is one of nine major research and innovation areas (DIM) designated by the Île-de-France Region for the period 2022–2026. It brings together researchers from a variety of disciplines to work on advanced eco-friendly materials. DIM MaTerRE's main objective is to develop tools and methods for the accelerated discovery of advanced materials for sustainable development and new energies. These discoveries enable us to tackle several key societal challenges: transportation, housing, energy, recycling, and many others.

Bruker

Bruker is the industry leader in the manufacturing of high-performance magnetic resonance instruments, software, and solutions for academic, industrial, and clinical research.

Magritek

Founded in 2004, Magritek is the global leader in manufacturing cryogen-free benchtop Nuclear Magnetic Resonance (NMR) spectrometers for the analytical instrument market. Magritek's Spinsolve family of benchtop NMR models 100MHz, 90MHz, 80MHz, and 60MHz offers the highest sensitivity and resolution available in the market.

Fédération de Chimie et Matériaux de Paris-Centre (FCMat)

The Fédération de Chimie et Matériaux de Paris-Centre (FCMat) is a support and research unit (UAR 2482) operating under the joint supervision of the CNRS (Institute of Chemistry) and Sorbonne University (Faculty of Science and Engineering, Department of Chemistry). FCMat is affiliated with six research laboratories (LAMS, LCMCP, LISE, LRS, PHENIX, SIMM) and manages five technical platforms (NMR spectroscopy, microscopy, XRD-SAXS, XPS and NMR relaxometry) open to academic and industrial researchers for the characterisation of materials

Sorbonne University

Sorbonne University is a world-renowned public research institution in Paris, France, formed in 2018 by merging Paris-Sorbonne University and Pierre and Marie Curie University. It carries the historic legacy of the Sorbonne, founded in 1257, and is celebrated for its leadership in the humanities, sciences, and medicine. Sorbonne University's Faculty of Science brings together disciplines such as mathematics, physics, chemistry, biology, computer science, and engineering. The faculty is renowned for its high-impact research, state-of-the-art laboratories, and close ties with major French research institutions like the CNRS. It attracts top researchers and students from around the globe, fostering innovation and interdisciplinary collaboration in both fundamental and applied sciences. Located primarily in the Latin Quarter, Sorbonne University is globally recognized for its academic excellence, strong international collaborations, and vibrant community of students and scholars from around the world.

Program at a glance

	Tuesday 16	Wednesday 17	Thursday 18	Friday 19
09:00	Opening	Telkki	Pradivtsev	FFC user meeting
09:20	Anoardo			
09:40		Sousa	Martin	
10:00		Stapf	Fraenza	Establishment of a European infrastructure for NMR relaxometry
10:20	Flash	Marzola-Coronel	Broche	
10:40		Licciardi	Lahrech	
11:00	Break	Break	Break	Statistical physics and modelling of the NMRD profiles
11:20	*Tutorial FC NMR Luchinat*	*Tutorial Stat. Phys. Grebenkov*	*Tutorial TD NMR Saalwächter*	
11:40				
12:00	Flash	Faux	Kruk	
12:20	Webber	Sidi-Boulenouar	Cinquegrani	
12:40	lunch and poster	lunch and poster	lunch	
13:00				
13:20				
13:40			Brougham	
14:00			Pierige	
14:20			Robbiani	
14:40	Mattea	*Tutorial FFC NMR Korb*	Parigi	
15:00	Boulogne		poster	
15:20	Geninatti	Strate		
15:40		Nagmutdinova		
16:00	poster	poster	Ricci	
16:20			Fritsche	
16:40			Cutard	
17:00	Lalli	Henoumont	Apih	
17:20	Tan	Dogulshev	Closing	
17:40	Taraban			
			Conference Dinner	

Detailed Program

Tuesday 16

Plenary lecture

80 Years of Field-Cycling in Magnetic Resonance: A Historical Journey through Spin Manipulation

Esteban Anoardo

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The early days of magnetic resonances were defined by seminal physical insights derived from the work of I. I. Rabi (NMR, 1939), Y. K. Zavoiskii (EPR, 1944), and S. Altshuler (AMR, 1952). BloembergenPurcell-Pound (BPP) introduced their relaxation picture already in 1946. After the 70s, Fourier and field-cycling (FC) NMR were well established, and strong schools evolved in Germany and France with impact on FC. The CEA group in Saclay (A. Abragam) introduced relevant contributions to the semiclassical formalism of spin relaxation and the spin-temperature concept. From the very beginning, the theory was experimentally validated by moving the sample between magnets. An evolutionary jump was to leave the sample quiet and change the magnetic field, transitioning from the 'electric' (batteries and relays) approach of C. P. Slichter and C. Hebel (Illinois, 1957) to solid-state switching using thyristors, introduced by H. Sprinz (Leipzig, 1967). The evolution to active current regulation via transistor banks came shortly after with A. Redfield (IBM Watson, 1968) and R. Kimmich & F. Noack (Stuttgart, 1970). These advances coexisted with excellent pneumatic shuttling systems, like R. E. Slusher and E. L. Hahn's 1968 machine, a superb double resonance setup. It was casually in 1968 when the group of Córdoba (Argentina) came into play with NQR (A. Pissanetzky, A. Brunetti). In the 70s and 80s, many groups consolidated as "field-cyclers": the Slovenian group in Ljubljana (indirect NQR detection), Berkeley (zero-field), Aberdeen (MRI), and Lisbon, St. Petersburg and others (relaxometry). Groups in Mons, Florence and Torino got machines derived from Redfield's legacy at IBM (Koenig-Brown). In 1984, Stelar (Mede, Italy) entered the scene, enabling the exploration of relaxometric properties in a plethora of materials, a contribution that continues today and well into tomorrow. In the 90s, new relaxometry hardware developments appeared in Ulm (Seiter-Kimmich) and Darmstadt (Privalov-Fujara), and many new users enter into the game.

The FC project in Córdoba started in the 90s. The machine was built using a 10-layer copper magnet machined in Noack's lab and a homemade fully-electronic power supply management system using the capacitor- storage concept based on the "MOSFET- GTO" approach. The machine was able to switch from zero to 0.41T in 1.3ms. Years later we got a used Stelar machine donated by Bertil Halle (Lund), which we modified incorporating own designed parts and an own magnet [1]. This project ended with our field-cycling MRI relaxometer. Along the 2000s, using a nice sonicator available in Kimmich's lab in Ulm, we could explore the relaxation properties under ultrasonic excitation in liquid crystals [2]. The incorporation of a new Stelar relaxometer in 2013 allowed us to study relaxometric properties in liposomes and lubricant oils. In the field of MRI, we mainly focused in the limits of getting a usable image from critical hardware conditions, double resonance and active contrast [3] and fast imaging [4]. In the field of relaxometry, our main recent concern was related to the extraction of trustable information from relaxation dispersion curves [5]. We are also integrating hardware diagnostics, fault prognosis, and fault-tolerance to better understand how to build highly robust power management architectures. In summary, this will be a journey through time from the early days of FC to today, complemented by our own contributions to the field.

References

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[2] F. Bonetto, E. Anoardo. J. Chem. Phys. 121, 554 (2004).
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[4] G. G. Rodriguez, E. M. Erro, E. Anoardo. J. Phys. D: Appl. Phys. 54, 025003 (2021).
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Measurement of viscosity in the bulk and in pores using T1rho

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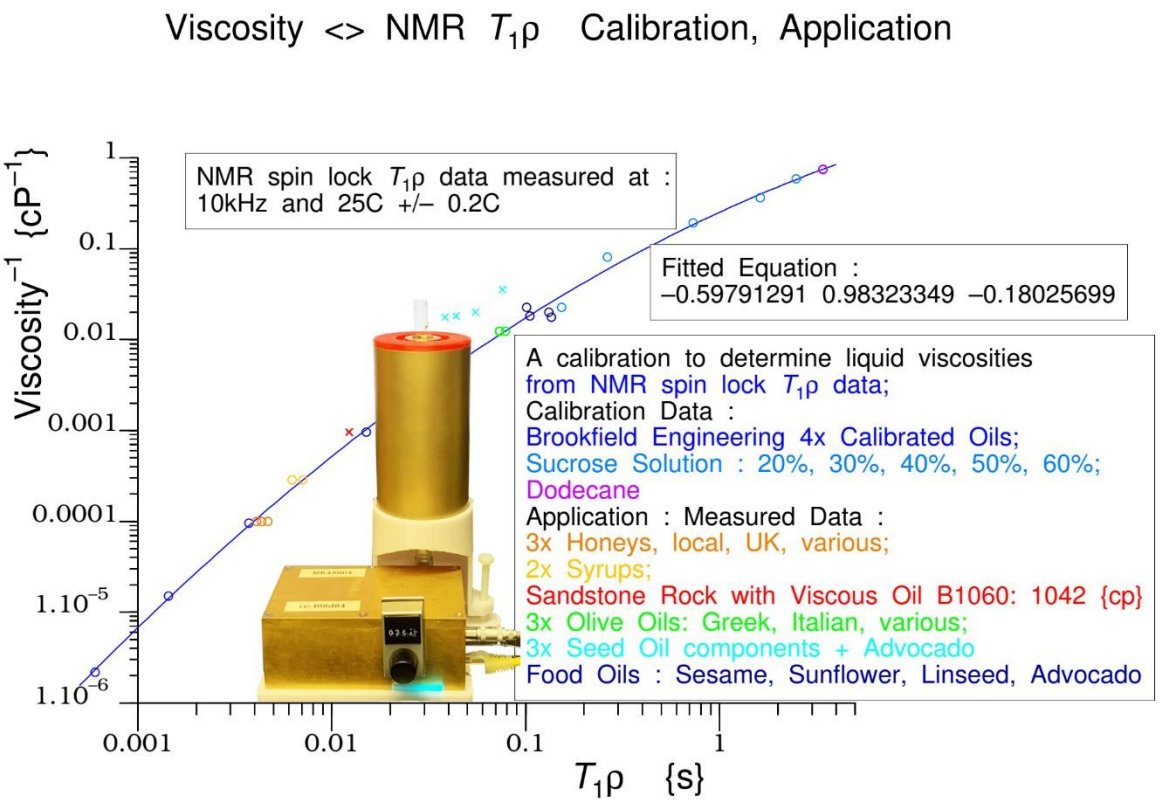
We present a recent method for quantitatively measuring viscosities, using spin-lock $T_{1\rho}$ NMR. Prior work studying a set of oils of calibrated viscosity using fast-field-cycling NMR, to measure the T_1 relaxation times at different rotational frequencies, has demonstrated a clear resolution of the different viscosities at lower frequencies. At frequencies above 2 MHz, and at high viscosities, T_1 is proportional to frequency. i.e. in the slow motion regime. However in the fast motion regime, i.e. at low frequency and viscosity, no frequency dependence is observed for bulk liquids. Here we extend this work to even lower rotational frequencies using the simpler technique of spin-lock $T_{1\rho}$, and demonstrate that calibrated viscosities may be determined both in bulk liquids and in liquids in pores, from the spin-lock relaxation times. Particular cases examined to obtain calibrations in the bulk include high viscosity oils and lower viscosity sugar solutions. This calibration has then been applied to measurements in bulk liquids including food oils, syrups and honeys. It was also possible to study liquids in pores, and this includes the determination of quantified viscosities of oil and water in recovered geological rocks and of the quantified viscosities of oil and water naturally found in seeds.



Blue dots: Viscosity <> T1rho Calibration Data, then applied to measure the viscosity of other samples in the bulk and in pores.

Molecular dynamics in polymer-ionic liquid systems studied by NMRD

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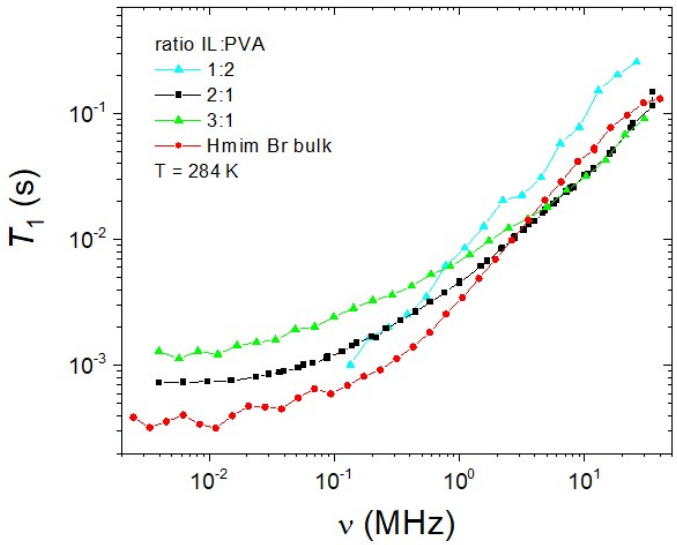
The molecular dynamics, structural features, and ionic conductivity of imidazolium-based ionic liquids (ILs) containing bromide anions, combined with poly(vinyl alcohol) (PVA) to form ionconducting gels, are investigated using NMR relaxation dispersion (NMR Fast Field Cycling). Blending ILs with polymers enables applications in materials science, particularly in energy-storage devices (electrolytes, batteries, supercapacitors) and functional soft materials such as electroresponsive gels for actuators. ILs offer certain advantages over conventional organic solvents or water in polymer electrolyte membranes; however, achieving confinement or immobilization of ILs within polymer matrices while maintaining ion transport and mechanical flexibility remains a key challenge.

On the microscopic scale, restrictions in the mobility of ILs and polymer chains, governed by interactions between monomers and ions, are probed through NMR relaxation times. The IL concentration determines whether the system forms rigid polymer-rich structures, where ILs remain confined but dynamically fast, or homogeneous gels in which both polymer and IL exhibit slower dynamics. We discuss how the variation of PVA-IL ratios correlates with changes in the amorphous fraction of the polymer network, which in turn regulates hydrogen-bond formation between polymer chains and cations.

Films with higher IL content are flexible, whereas PVA-rich films are rigid. Because the only structural difference between the ILs studied, 1-butyl- and 1-hexyl-3-methylimidazolium bromide (BmimBr, HmimBr), is the alkyl chain length, their influence on transport can be assessed through diffusion and conductivity measurements. Differential scanning calorimetry (DSC) provides melting and decomposition temperatures and allows estimation of relative crystallinity, which is compared with values obtained from X-ray diffraction (XRD). Together with 2D NMR T_1-T_2 correlated relaxation times, these results offer a comprehensive picture of molecular interactions and ion dynamics in PVA-IL gels.



Frequency dependence of longitudinal NMR relaxation times of the ionic liquid Hmim-Br combined with the polymer PVA at different concentrations. The polymer and IL system mostly retain their dynamics at the low and high concentration of IL.

Probing gelator self-assembly and water mobility during hydrogel formation by combined High-Resolution and FFC NMR

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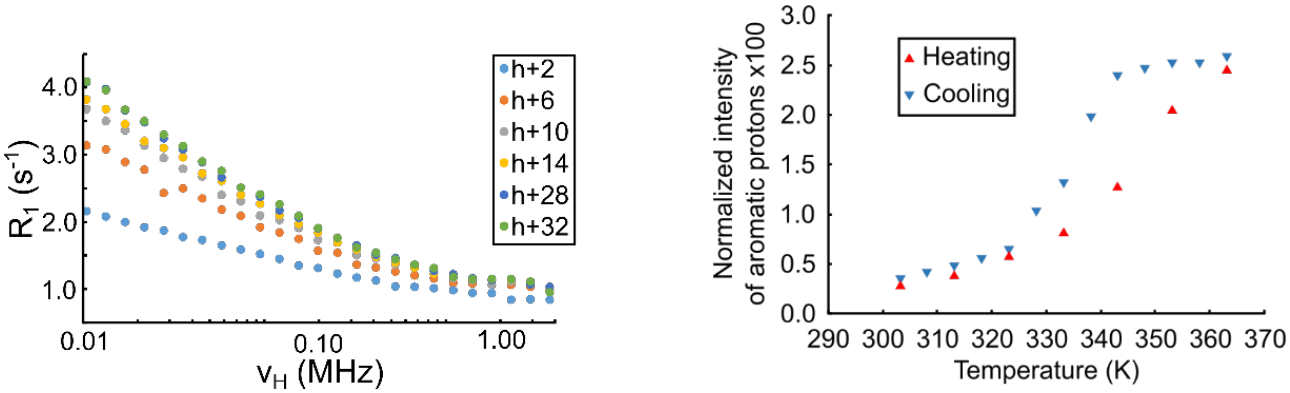
Nucleopeptide-based hydrogels are capable of forming complex supramolecular assemblies that result in mechanically robust materials. Owing to their multicomponent design, these hydrogels can be tailored for a wide range of biotechnological applications. However, achieving precise control over their properties requires a detailed understanding of their structure and dynamics at the atomic scale. In this study, the gelation of such physical hydrogels was investigated using a combination of highresolution NMR spectroscopy and fast field-cycling (FFC) NMR relaxometry. Gelation kinetics were indeed monitored at two different temperatures through high-resolution ^{1}H NMR measurements at 400 MHz, focusing on the gelator signal, alongside with low-field measurements of the water proton longitudinal relaxation rate (R_1) at 0.035 MHz. Additionally, a series of NMR dispersion (NMRD) profiles were recorded throughout the gelation process, providing valuable insights into the distinct water populations and the evolution of their mobility as the gelator network forms. Analysis of each dispersion curve enabled the extraction of correlation times and structural parameters, allowing precise characterization of water equilibration dynamics accompanying gelator self-assembly. Highresolution NMR was also employed to examine hydrogel behavior during heating and cooling cycles by monitoring the gelator signal across a range of temperatures. This approach offers mechanistic insight into the solution-to-gel transition and the molecular processes governing hydrogel formation.



NMRD profiles during gelation process (left) and gelator ^{1}H signal intensity evolution with temperature (right).

Invited lecture

Fast Field-Cycling Relaxometry as a Tool to Investigate Pathological States through Water Dynamics in Tissues

Simona Baroni[1], Sahar Rakhshan[1], Diego Alberti[1], Maria Rosaria Ruggiero[1], Alessandra Pittaro[2], Isabella Castellano[2], Hana Lahrech[3], Lionel Broche[4], Silvio Aime[1], **Simonetta Geninatti Crich**[1]*

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2. Pathology Unit, Department of Medical Sciences, University of Turin, 10126 Torino, Italy

3. Inserm U1205, BrainTech Lab, University Grenoble Alpes, Grenoble, France

4. Aberdeen Biomedical Imaging Centre, University of Aberdeen, Aberdeen, UK

Conventional MRI, at high field strengths, excels in providing detailed morphological images; however, it has limitations in assessing key functional features, including those related to metabolism. In this study, we demonstrate that novel, easy to apply strategies performed at low and ultra-low magnetic fields allow to obtain relevant information that are invisible at standard, clinically used MRI. Our work developed along two main directions: one without and the second with the use of contrast agents.

The first is based on the observation that at low fields (in contrast to what is observed at clinically used magnetic fields), the recovery of ^{1}H magnetisation depends on the rate of water exchange across the cell membrane. The extent of water cycling is related to the activity of membrane transporters, and the relaxometric readout then becomes a biomarker for the metabolic state of the tumour cells, providing important information on tumour aggressiveness and grading,[1] which is fundamental for deciding on therapeutic strategies and for monitoring treatment in real time[2,3], as recently demonstrated on a glioblastoma model. Furthermore, the method is also proposed for tumour margin assessment and lymph node status in breast conserving surgery.

The second propose two different innovative contrast enhancement strategies exploiting different contrast agents: i) a clinical approved iron oxide particle (Ferumoxytol). The method is based on R_1 measurements at low field (0.01–1 MHz) to assess the presence of Tumour associated Macrophages (TAM) in melanoma tumours. R_1 at low magnetic fields appears highly dependent on the intra or extra cellular localization of the nanoparticles thus allowing an unambiguous TAM quantification; ii) alternative contrast agents displaying remarkable relaxation effects in the absence of paramagnetic metal ions. They contain poly-histidine chains (poly- His), whose imidazole groups generate ^{14}N quadrupolar-peaks that cause a relaxation enhancement of water protons at a frequency (1.38 MHz) that is readily detectable from the frequencies associated with endogenous proteins, peaks whose characteristics can provide additional information on the investigated tumour tissues as the pH. Both approaches could significantly improve clinical diagnosis, treatment selection, and therapy monitoring in oncology. Although FFC relaxometry currently lacks spatial resolution, the knowledge gained from these studies open the way for the development of next-generation diagnostic tools and may accelerate the broader adoption of FFC-MRI scanners worldwide.

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[3]Sahar Rakhshan [1$], Simona Baroni [1$], Michèle El-Atifi [2], Ayda Zarechian Soudani[1], Lionel Broche[3], François Berger [2], Simonetta Geninatti Crich [1 *] and Hana Lahrech [2, 3] 2026, under review

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Multinuclear and multi-frequency NMR investigations of halide binding to metal complexes

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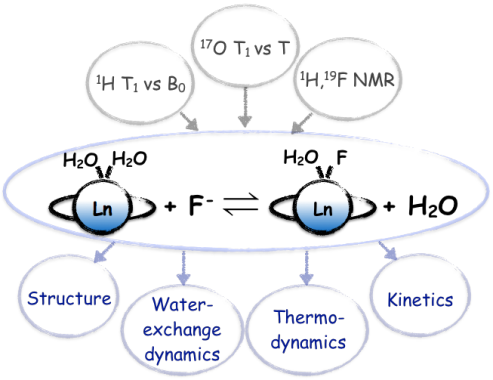
Halide recognition by metal complexes represents a major challenge in coordination chemistry, with implications in environmental, biological, and diagnostic fields[1]. In this context, Ln(III)-complexes have proven to be highly valuable tools for halide sensing, thanks to their excellent ability to establish strong interactions with hard anions, combined with their versatile optical and magnetic properties. [2, 3].

Here we investigate the interactions between fluoride and a series of metal-complexes (M = Gd(III) and Y(III)) characterized by different structure, coordination geometry, charge and hydration numbers ($q = 1$ and $q = 2$), with the aim of determining the influence of the ligand's nature on halide recognition. By integrating low-resolution multi-frequency NMR approaches with high-resolution multinuclear NMR techniques, we access the magnetic and structural properties of the ternary adducts alongside the thermodynamic and kinetic parameters of the anion-binding events. In particular, the observed reduction in ^{1}H longitudinal relaxation rates upon halide substitution of one coordinated water molecule enabled determining the binding affinity. Water ^{1}H longitudinal relaxation rates vs B_0, and ^{17}O transverse relaxation rates vs T enabled characterizing the magnetic properties and the water exchange dynamics of the ternary chelates. Finally, high-resolution NMR analysis of the diamagnetic Y(III) ternary complexes allowed for structural characterization, while variable temperature ^{19}F NMR spectroscopy enabled measuring the rate constants and activation thermodynamic parameters associated with fluoride binding.

The results of this study represent a step forward in understanding the halides interactions with metal-chelates, which is essential for the rational design of high-performance probes for molecular imaging and anion sensing.



Implemented NMR methods and main outcomes

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Polyelectrolyte – clay interactions in a composite hydrogels studied by Fast Field Cycling (FFC) NMR relaxometry

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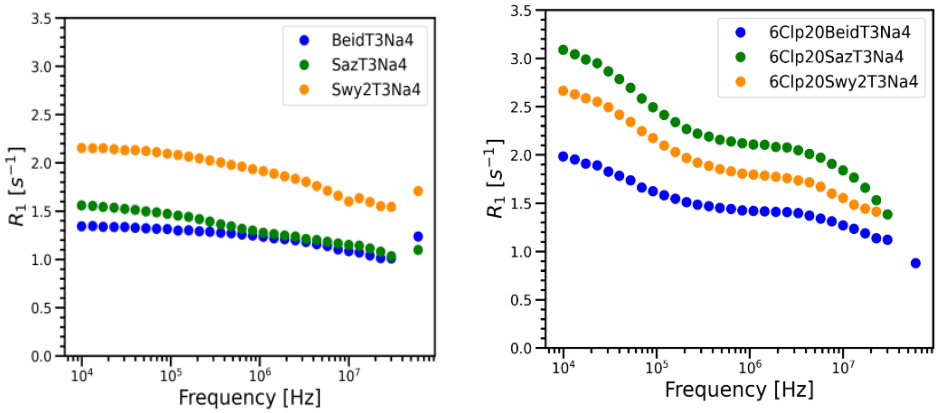
Hydrogels are polymeric materials that form three-dimensional (3D) networks through chemical or physical crosslinking upon hydration. They exhibit high water uptake and responsiveness to external stimuli (pH, temperature, light, magnetic fields, etc.), making them attractive for a wide range of applications, including drug delivery, sensing, wound dressing, and soft robotics [1,2]. Their performances can be further enhanced by incorporating inorganic fillers to form composite systems [3]. Here, we investigate the organization of clay nanoparticles (montmorillonite and beidellite) within a polyelectrolyte hydrogel network based on 6Cl-modified ionene, using Fast Field Cycling (FFC) NMR relaxometry. This technique probes molecular dynamics over a broad timescale ($\sim 10^{-9} - 10^{-6}$ s) and provides indirect insight into water-clay, water-macromolecule, and macromolecule-clay interactions. Proton (^{1}H) NMRD profiles are analysed using a combination of modified Solomon-Bloembergen-Morgan (SBM) and Jean-Pierre Korb (JPK) models, commonly applied to systems containing paramagnetic species such as clays [4]. In this model, the SBM contribution describes water dynamics at clay edges, while the JPK contribution relates to water diffusion along basal surfaces. Relaxation is assumed to be dominated by through-space dipolar interactions between nuclei and unpaired electrons. Our results show that intrinsic differences between clays) namely surface charge magnitude and location strongly influence water dynamics in pure clay suspensions. However, once incorporated into the hydrogel network, these differences are largely suppressed, leading to a homogenization of dynamical behavior irrespective of clay type.



^{1}H NMRD profiles in pure clay aqueous suspensions (left) and in 6Cl-modified ionene / clay composites (right). BeidT3Na refers to beidellite while SazT3Na and SwyT3Na are two montmorillonites. The "6Clp20" on b) refers to the 6Cl-modified ionene.

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Noninvasive pharmaceutical analysis using *w*NMR

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The water proton NMR signal, often regarded as a nuisance, interferes with accurate spectral quantification of critical process parameters and quality attributes in pharmaceutical products. However, as the most abundant component in many drug products, water can be indirect sensor for quantitative characterization of aqueous drug formulations. Water proton nuclear magnetic relaxometry (*w*NMR) measurements can be carried out using benchtop instruments, typically within a minute. The results provide a range of important conventional quantitative attributes such as concentration, aggregate content, etc., but also could be advantageously used to develop new quantitative markers for quality control and fingerprinting of drug products. Most importantly, however, *w*NMR measurements can be carried out in an in situ and contact-free manner. This opens the door for rapid formulation screening, noninvasive product inspection and contact-free in-line processing monitoring. In this presentation, examples of different *w*NMR applications will be presented, including flow *w*NMR as in-line PAT.

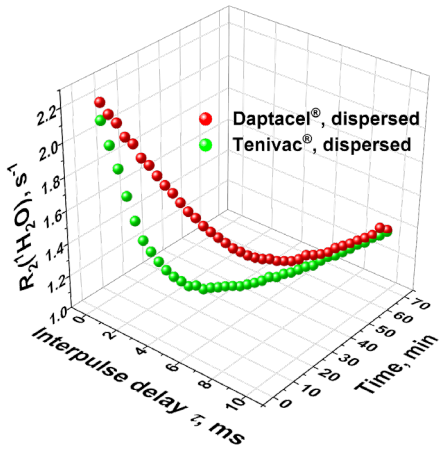

Figure 1. *Fingerprinting of vaccines in 3D space of $R_2(^1H_2O)$ vs. time, vs. interpulse delay.*

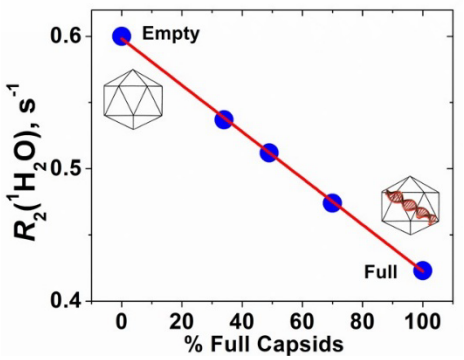

Figure 2. *$R_2(^1H_2O)$ enables rapid and precise quantification of the empty/full ratio of viral capsids.*

In this presentation, we also demonstrate the advantageous application of the *w*NMR technology to obtain quantitative data on a wide variety of different drug products—high concentration mAb formulations, vaccines (e.g., for fingerprinting of different vaccine products, see Figure 1), and precise estimates of the empty/full ratio of the viral capsids containing therapeutic gene material (e.g., using linear dependence shown in Figure 2). Our results enable broader applications of the innovative quantitative *w*NMR technology in real biomanufacturing settings including R&D and QC.

Wednesday 17

Invited lecture

Ultrafast Laplace NMR for probing molecular dynamics, aggregation, and microstructures

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NMR relaxation and diffusion measurements – collectively known as Laplace NMR – offer powerful, label free, and non-invasive access to molecular translational and rotational dynamics. When extended into multiple dimensions, these experiments reveal correlations between distinct motional modes and enable quantitative characterization of exchange, aggregation, and microstructural features in complex systems. Their versatility makes them valuable across chemistry, materials science, geoscience, biology, and industrial research.

This contribution presents recent advances that dramatically accelerate single- and multidimensional Laplace NMR using spatial encoding and related ultrafast methodologies[1-7]. These single scan approaches not only reduce experiment times by orders of magnitude but also integrate seamlessly with modern hyperpolarization techniques, enabling sensitivity enhancements that were previously inaccessible. Because the methods rely on spin echo–based detection, they are inherently compatible with low field and portable NMR platforms [8].

We will highlight new applications spanning arctic mining tailings, aerosol–climate interactions, battery materials, biosensing, cellular metabolism, protein–ligand binding, lignocellulosic biomaterials, sustainable cement formulations, surfactant aggregation, and the characterization of rubber and tire materials, illustrating how ultrafast Laplace NMR opens new windows into molecular dynamics and microstructure in real world, multidisciplinary contexts.

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The FFC-NMR apparatus- pathways to integration with standard consoles

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Due to financial and technical constraints, research laboratories are increasingly seeking equipment with low power consumption, reduced size and weight, and the ability to complement and integrate with existing systems and experimental protocols. When these requirements are considered in the context of NMR equipment – from the magnet to the console – there is a clear need for integration between systems covering different field ranges, each developed to optimize specific factors and based on different technological stages.

In the case of electronic FFC-NMR apparatus, the evolution is evident when comparing solutions available a couple of decades ago with more recent developments [1–2]. While benchtop and portable FFC systems with low thermal and electrical power consumption are now a reality, one of the next challenges is their integration with existing conventional NMR consoles.

The most recent FFC solution developed at the NMR FFC IST laboratory, designed to cover a field range of up to ~ 0.2 T, features a more compact magnet capable of incorporating superconducting components. In addition, it is designed to be adaptable to different experimental protocols, ensuring compatibility with other NMR consoles.

Front view of the FFC power supply and electromagnet.

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Tales of mixing and demixing: liquids in mesopores

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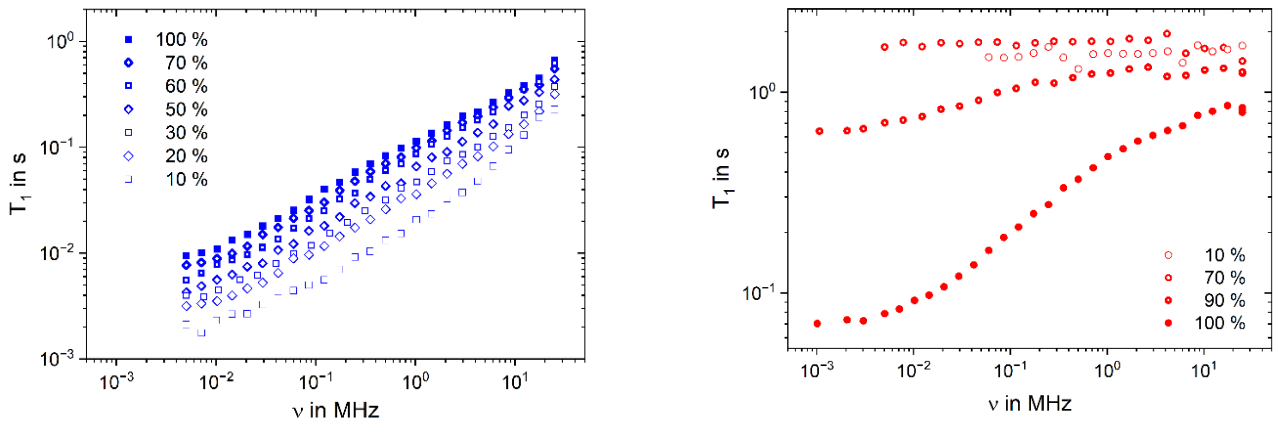
Combinations of polar and non-polar liquids that are fully miscible in bulk were studied while saturating mesoporous media of different pore sizes. For the example of acetone and cyclohexane, a clear apparent phase separation was observed by MD simulations where acetone is preferably located at the polar silica wall and severely slowed down in its short-time translational dynamics; equivalent long-time diffusometry results by NMR agree in the sense that acetone diffusivity is reduced up to 1000 times compared to intraporous cyclohexane in 4 nm porous glass. The difference between adsorbed and non-adsorbed phases is much more striking in frequency-dependent T_1 relaxation where surface-mediated RMTD and bulk-like isotropic reorientation are clearly distinguished for several systems, including water and acetone. The equivalence of ^{1}H and ^{2}H relaxation properties again suggests RMTD, i.e. purely intramolecular relaxation mechanisms. Investigations in controlled-pore glass (CPG) of up to 50 nm pore diameter confirm the apparently complete phase separation for acetone and cyclohexane which is further corroborated by freezing experiments of the same system, whereas mixtures of two non-polar liquids, depending on individual molecule-surface affinity, cover the range from ideal mixtures to noticeable concentration gradients that also affect freezing behavior of the confined mixtures. Strategies are presented to quantify the degree of demixing by means of computed radial density functions and MSD as well as experimentally accessible relaxation and diffusion results.



^{1}H relaxation times for acetone (left) and cyclohexane (right) in 4 nm pore diameter glass for mixtures with the given weight ratios, where the second component is perdeuterated. Note that acetone maintains a strong dispersion typical for polar adsorbates, while the dispersion for cyclohexane disappears when acetone is covering the glass surface.

Optimizing Relaxometry Data Fitting: Noise and Dynamic Range Insights

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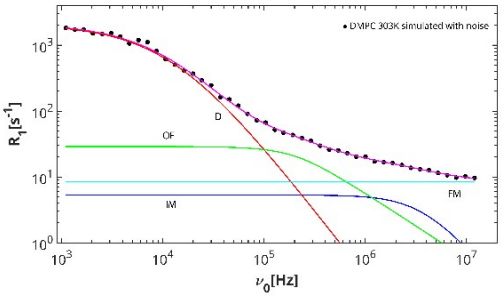
The extraction of physically meaningful parameters from field-cycling (FFC) NMR relaxometry data critically depends not only on the validity of the underlying physical model, but also on the experimental design, the characteristics of the data, and the optimization strategy employed during fitting. In this context, the consistency of the model alone does not guarantee reliable parameter estimation.

In this work, we investigate the role of the fitting procedure in the robust determination of physical quantities using liposomal systems as a representative case study. The physical model employed, previously developed in our laboratory [1-7], describes the proton spin-lattice relaxation dispersion in terms of multiple dynamical contributions, enabling the simultaneous estimation of key parameters such as the membrane bending modulus of the liposome membrane (κ) and the lipid diffusion constant in the liposome membrane (D), within a seven-dimensional parameter space. Given the high dimensionality, the presence of non-trivial parameter couplings, and the computational cost associated with derivatives, a derivative-free, box-constrained optimization approach based on the pattern search (PS) algorithm was adopted. To assess its performance, synthetic datasets were generated from experimentally validated parameters under both noiseless and noisy conditions.

Our earlier results show that, while accurate parameter recovery is achieved in the absence of noise, the inclusion of realistic noise leads to parameter compensation effects, where multiple parameter combinations yield fits of comparable quality but differ in physical meaning. We demonstrate [7] that this limitation is not necessarily intrinsic to the model, but a complex entanglement between the mathematical intricacies of the model function and the explored experimental dynamic range. An experimental frequency window that does not properly allow for the scanning of all involved dynamical contributions may trigger parameter degeneracy. By extending the dynamic range of the experiment, such degeneracies can be eliminated, enabling stable and physically consistent parameter estimation across the full seven-dimensional space. Under these conditions, all parameters can be reliably recovered, with κ and D determined within less than 10 % and 20 % relative error, respectively, in a single experiment.



(•) *DMPC at 303 K synthetic relaxation dispersion extended up to a minimum Larmor frequency of 1 kHz. Solid lines: PS fitting (magenta); contributions from each type of motion are included: translational diffusion (red), order fluctuations (green), intramolecular motions (blue), and fast motions (cyan).*

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Probing multi-timescale dynamics in imidazole glycerol phosphate synthase by combining nuclear magnetic relaxation and computations

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Understanding conformational dynamics across multiple timescales is a key challenge in structural biology. While high-field NMR spectroscopy offers atomic-level resolution of structure and characterization of fast motions, accessing slower or field-dependent processes remains a challenge. On the other hand, fast field-cycling relaxometry (FFC) accesses slow motions at the expense of a full loss of spectral resolution. Ultrafast High-Resolution Relaxometry (UHRR) is a new methodology that overcomes these crucial limitations by combining high-field resolution with low-field relaxation to characterize molecular dynamics. The newly developed Fast Sample Shuttle (FSS) features a high-speed hybrid pneumatic/mechanical shuttle system that transfers samples at velocities up to ~27 m s^{-1} between high (up to 16.4 T) and low magnetic fields, where a field-cycling coil allows measurements at magnetic fields down to 100 μT in less than 2 ms. The device is compatible with standard NMR probes and hardware, without compromising spectral quality or experimental throughput [1]. Here, we discuss the application of UHRR to the study of dynamics in imidazole glycerol phosphate synthase (IGPS), a heterodimeric enzyme composed of two subunits called HisH and HisF. IGPS offers a compelling model for dissecting allosteric mechanisms [2]: despite a 30 Å separation between the catalytic site in HisH and the effector binding site in HisF, ligand binding (PRFAR) leads to a remarkable ~5000-fold enhancement in glutamine hydrolysis [3]. The molecular basis underlying this long-range communication, however, is not yet fully understood.

To shed light on this process, we labeled the methyl groups of isoleucine, leucine, and valine residues in IGPS with $^{13}CHD_2$ isotopomers and, using UHRR, we recorded residue-specific nuclear magnetic relaxation dispersions (NMRD) profiles at over 30 magnetic fields, covering five orders of magnitude (100 μT to 14 T). We analyzed the NMRD profiles using the in-house software MINOTAUR, applying both model-free approaches to extract dynamic parameters from relaxation datasets [4], and the results were compared with order parameters derived from molecular dynamics simulations. To extend the timescale of investigation, we also acquired multiple-quantum Carr-Purcell-Meiboom-Gill (MQ-CPMG) relaxation dispersion experiments to probe slower milliseconds timescale dynamics [5]. Our integrative approach aims at enabling the decomposition of motions probed by methyl groups into contributions from methyl rotation, side-chain rotamer transitions, global tumbling, and slower conformational transitions. Our objective is to fully describe the role of dynamics, over nine orders of magnitude in ,me ranging from picoseconds to milliseconds, in the molecular mechanism of allostery in IGPS.

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Applications of the 3-Tau Model to Medicine, Cheese and Cement

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The 3-Tau model (3TM) [1,2] fits to Fast Field Cycling NMR dispersion curves from both soft and hard material with or without paramagnetic ions. The 3TM assumes two water environments: hydrated surface layers of thickness $\delta = 0.27$ nm and bulk water. The fits supply physically meaningful values for the parameters listed in the table 3TM fitting software is available open source [3].

τ_l	Surface water correlation time	N_σ	Paramagnetic ion spin density
τ_d	Desorption correlation time	N_l	Proton spin density at surface
τ_b	Bulk water correlation time	R_1^{offset}	A constant relaxation rate
x	Spin surface-to-volume ratio	h	A representative pore size found from x

Cement paste: 10 NMRD profiles presented by Badea *et al* [4] for a hydrated grey cement are reanalysed using the 3TM [5].

(i) The rate of curing (see Fig. 1) is assessed by tracking the change in pore size h with time and is an indicator of ultimate product strength.
(ii) τ_l and τ_d provide information about the surface chemistry for both water and cyclohexane imbibed cements.

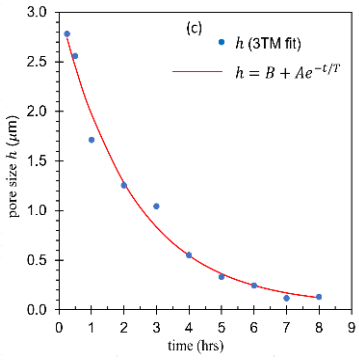

Fig. 1. *Pore size h from 3TM for 10 samples of curing grey cement 0.25-8 hrs after hydration.*

Medical - tumours: Fit parameters x and τ_b each provide a statistically significant correlation with tumour fraction and therefore act as biomarkers [6]. The sensitivity of the biomarker $R_1(f = 0.01\ \text{MHz})$ to tumour fraction arises from changes in x due to water ingress into tumour cells.

Medical - sickle cell disease (SCD): See Fig. 2. The 3TM reveals a clear distinction between healthy and diseased haemoglobin through fit parameters τ_l, τ_d and N_σ [7].

Comté cheese: See Fig. 3. FFC NMR experiments were performed on four Comté cheeses at 9, 13, 25 and 37 months of maturation [8].

(i) High-quality 3TM fits require *both* ^{1}H-^{1}H and ^{1}H-Fe^{3+} interactions.
(ii) Pore size h reduces exponentially with maturation time with a time constant of 23 months.
(iii) The independence of R_1^{offset} with pore size h suggests bulk water is saturated with salt. The increase in $\tau_b$with maturation is consistent with the salt depositing at the surfaces of macromolecules.
(iv) The iron density determined by the 3TM is 0.45-0.51 mg/100g compared to typical values for Comté cheese of 0.49 mg/100g.
(v) The ratio T_1/T_2 is in the range 3.0-3.7 from 3TM and 3.6-3.7 by fixed field relaxometry.
(vi) The Hwang-Freed model is used to determine the self-diffusion coefficient of the bulk water from R_1^{offset}.

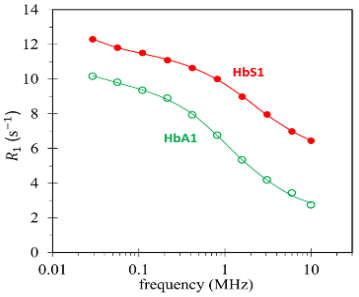

Fig. 2. *3TM fits to healthy haemoglobin (bottom) and SCD haemoglobin (top).*

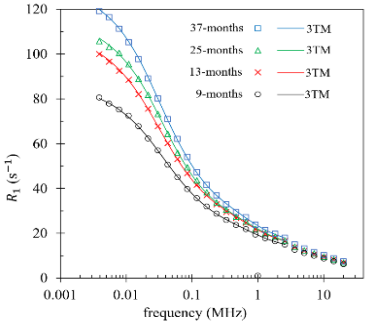

Fig. 3. *3TM fits to four Comté cheese samples at 9, 13, 25 and 37 months.*

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From silicate solutions to colloidal gels: dynamic NMR relaxometry to probe water dynamics and structural evolution in porous media

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In the context of energy- and climate-related challenges involving porous materials, understanding water dynamics across different states of porous matter, from reactive mineral solutions to consolidated colloidal gels, is essential for describing transport, aging, and stability in silicate-based and bio-inspired systems. However, capturing these processes under non-equilibrium conditions and across relevant length and time scales remains experimentally challenging. In this work, we develop and apply a dynamic low-field NMR relaxometry framework to investigate water dynamics and structural evolution in silicate systems, spanning the transition from alkaline silicate solutions to deformable porous gels.

We first investigate aqueous alkali silicate solutions using NMR relaxometry to quantify changes in water mobility and interfacial interactions as a function of hydroxide concentration and alkali nature. Transverse relaxation measurements reveal marked and systematic variations in relaxation behavior, reflecting modifications of solution speciation and mesoscale organization prior to gelation. These results demonstrate that NMR relaxometry provides a sensitive, non-destructive probe of structural evolution in reactive silicate solutions [1].

The approach is then extended to the drying of colloidal and aluminosilicate gels, where water transport is intrinsically coupled to deformation, gradient formation, and particle-network reconfiguration. Using a dynamic relaxometry methodology that follows transverse relaxation times (T_2) as a function of saturation rather than time, and combining global measurements with one-dimensional spatial water profiles, we identify robust power-law relationships linking relaxation efficiency to desaturation. These relationships reveal distinct drying regimes and allow a clear discrimination between ideal homogeneous drying and non-ideal scenarios governed by physical instabilities such as gradients and incomplete network reorganization [2,3].

To rationalize these observations, a minimal numerical framework is introduced, enabling the separation of the respective contributions of hydric gradients, macroscopic contraction, and particle-network reconfiguration. Additional relaxometry measurements performed at different magnetic fields further support the interpretation of relaxation mechanisms and interfacial water dynamics.

Overall, this work establishes dynamic NMR relaxometry as a unifying and quantitative methodology to continuously follow water dynamics from reactive solutions to porous gels, providing physically grounded descriptors relevant for transport, aging, and stability in porous materials, with direct implications for the understanding and control of water-related processes in energy-efficient and climate-resilient porous systems.

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Unraveling Ion Dynamics in Ionic Liquids with Fast Field Cycling NMR Relaxometry

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Fast field cycling (FFC) NMR relaxometry provides unique insights into molecular dynamics across broad frequency and temperature ranges, making it particularly powerful for the investigation of ionic liquids (ILs). This class of materials exhibits a complex interplay of rotational and translational motions that governs their distinctive macroscopic properties. However, capturing these coupled dynamics across multiple timescales remains challenging. In this contribution, we present a framework that combines FFC NMR relaxometry with molecular dynamics (MD) simulations to disentangle rotational and translational motions in ILs.

In our previous work on translational dynamics [1], we demonstrated that intermolecular heteronuclear ^{1}H-^{19}F interactions play a crucial role in the quantitative analysis of NMR dispersion (NMRD) profiles in ILs where both cations and anions carry NMR-active nuclei. In such systems, intermolecular relaxation is not solely governed by homonuclear ^{1}H-^{1}H and ^{19}F-^{19}F interactions, but also includes significant ^{1}H-^{19}F heteronuclear terms. Neglecting these contributions leads to systematic errors in the evaluation of relaxation data, particularly in the low-frequency regime commonly used to extract translational self-diffusion coefficients. In this regime, application of the low-frequency approach (LFA) to total relaxation rates results in a substantial underestimation of self-diffusion coefficients. To overcome this limitation, we employ an isotopic substitution strategy in which either the cation, the anion, or neither component is selectively deuterated, enabling a controlled comparison between "single-spin" and "two-spin" systems. This approach allows for a reliable determination of translational self-diffusion coefficients, either directly from total relaxation rates in the single-spin case or from properly separated intermolecular contributions in two-spin systems.

With respect to rotational dynamics, our recent study [2] introduces advanced motional models that go beyond the commonly assumed isotropic reorientation. Using the model systems [TEA][NTf_2] and [C_5Py][NTf_2], we demonstrate how ion-specific geometry and internal flexibility govern the relaxation behavior. While nearly spherical cations can be described by classical Bloembergen-Purcell-Pound (BPP) models, elongated ions require anisotropic descriptions, and anions containing CF_3 groups necessitate the inclusion of fast internal rotations. The simultaneous analysis of ^{1}H and ^{19}F relaxation data over a wide temperature range enables a consistent decomposition of relaxation rates, including both homo- and heteronuclear intermolecular contributions. The resulting rotational correlation times and self-diffusion coefficients show excellent agreement with MD simulations, providing strong validation of the proposed framework.

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Dairy products authentification by two-components analysis of NMRD profiles

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Many European PDO (Protected designation of origin) cheeses, such as Parmigiano Reggiano, Comté, Roquefort, Idiazabal, or Fiore Sardo, are traditionally made with raw milk, which allows them to develop a particular texture, taste, and aroma. Despite guidelines [1] for cheese production mandating the use of raw milk, some industrial manufacturers have been suspected of using thermized (pasteurized) milk. As for today, official standardized methods used for the quality control of milk products and for differentiating between raw and pasteurized milk cheeses are not uniform, official, reliable, or fast [2, 3]. We present the FFC NMR (Fast Field Cycling Nuclear Magnetic Resonance) Relaxometry technique as a possible method for milk authentication.

In this work, six Fiore Sardo samples were investigated using FFC NMR. Two of the samples were artisanal, and the other four were industrial. By preprocessing the raw FFC NMR data using a quasi-continuous linear inversion, we separated the FFC NMR signal into two components with long and short longitudinal relaxation times (T_1). The T_1 distributions were obtained using UpenWin [4]. We were thus able to create two NMRD profiles, each corresponding to spin populations characterized by different molecular dynamics and apparent at different Larmor frequencies. Then, each NMRD profile was fitted to the Korb-Bryant model, developed for proteins, which assumes a power-law dependence of the relaxation rate on frequency due to fractal protein dynamics [5, 6].

The separation into two NMRD profiles allowed discrimination between industrial and artisanal cheeses in terms of parameters directly related to the material's structural properties, such as protein and water proton populations and hydration level. These parameters allow discrimination between milk treatment in cheeses and could be linked to such cheese qualities as creaminess or graininess.

In this preliminary application, NMRD data preprocessing appears to be a promising tool for discriminating between thermal milk treatments in cheese preparation. Furthermore, it is not merely an indicator of the milk treatment, but helps study the molecular dynamic changes in milk proteins due to the treatment of milk.

Acknowlegements

We acknowledge the NMR-IMPROV project for providing support for this work.

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Development of Mn^{2+} MRI contrast agents based on the Pyclen scaffold

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Magnetic Resonance Imaging (MRI) exams often require the use of a paramagnetic contrast agent, in order to decrease the water protons longitudinal relaxation time and hence, to enlighten the tissues area where the contrast agent is accumulated. Currently, clinically used MRI contrast agents are based on the Gd^{3+} ion. Nevertheless, some toxicity issues have appeared since several years: patients with kidney failure can develop a disease called "nephrogenic systemic fibrosis", caused by a release of free Gd^{3+} ions due to a too slow elimination of the contrast agent; and moreover, an accumulation of gadolinium in the brain of patients after multiple injections has been observed. Additionally, some environmental concerns have also appeared, due notably to the elimination of gadolinium from the patients through urine and the lack of treatment of the wastewater to eliminate gadolinium.

Alternatives to gadolinium-based contrast agents are thus needed, and could come from the use of manganese contrast agents. The Mn^{2+} ion possesses indeed 5 unpaired electrons and is therefore paramagnetic. It is moreover less toxic than the gadolinium ion since it is naturally present in the body. Nevertheless, if injected at high concentrations, it can induce a disease called 'manganism", with symptoms close from the Parkinson disease, so that it is important to develop stable Mn-chelates to be injected *in vivo*.

In this study, we have developed different Mn-chelates based on the pyclen (3,6,9,15tetraazabicyclo [9.3.1]pentadeca-1(15),11,13-triene) scaffold, an interesting 12-membered macrocyclic structure with a pyridine moiety which rigidifies and preorganizes the ligand-coordinating groups. More specifically, the parent compound, Mn-3,9-PC2A (figure 1a), already well described in the literature[1], characterized by a quite low relaxivity, and also a lack of kinetic stability towards transmetallation with endogenous ions like zinc ions (figure 1b), was modified by replacing the carboxylate coordinating groups by other bulkier groups (figure 1a) to evaluate the impact on the relaxivity and on the kinetic stability.

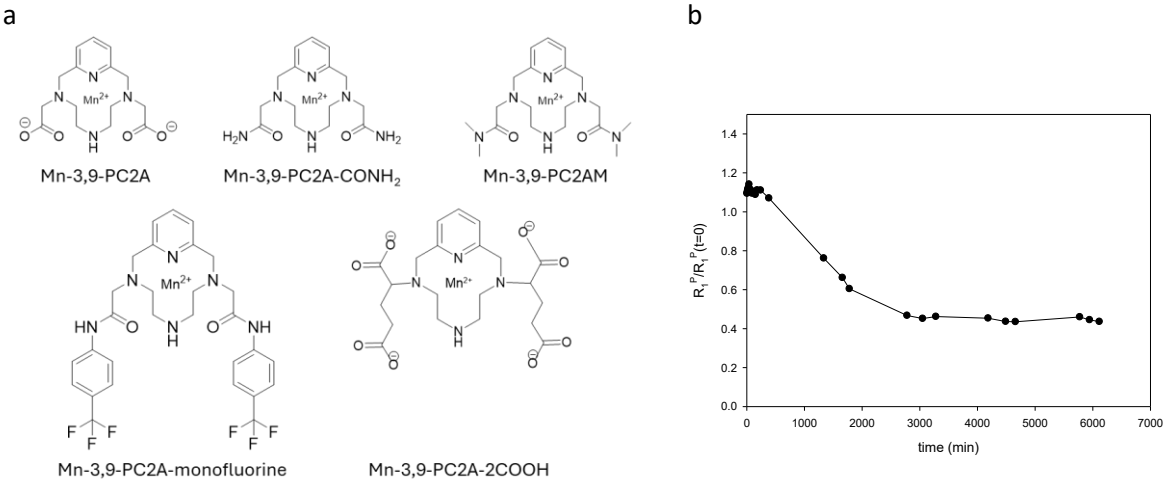

Figure 1: a) Structures of the synthesized Mn-chelates ; b) Transmetallation with Zn^{2+} ions observed for Mn-3,9-PC2A in the presence of a phosphate buffer[1]

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Invited lecture

Local NMR relaxation of dendrimers

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Branched polymers, in contrast to linear chains, possess points of branching; when the concentration of these is high one obtains hyperbranched polymers, whose compact architectures give rise to specific rheological properties and to applications as nanocarriers. The proximity of branching points implies that only a few chemical bonds separate them, so that the local bending energy (i.e. *semiflexibility*) plays a crucial role for the dynamics. Building on a generalized Gaussian framework for semiflexible treelike polymers with arbitrary functionality and stiffness of the branching points, this contribution focuses on how semiflexibility, hydrodynamic interactions, and internal or peripheral functionalization shape the local NMR response of dendrimers.

For perfectly branched dendrimers, the model predicts that the maxima of the reduced proton spin–lattice relaxation rate $[1/T_{1H}](\omega)$ shift toward *lower frequencies* for segments belonging to inner shells, contrary to the prediction of fully flexible bead-spring models (Fig. 1). For sufficiently stiff dendrimers the relaxation of a labeled bond is governed by a single, topologically-determined time τ_g^G, which depends only on the segment's distance to the periphery [1]. This shell-dependent shift agrees qualitatively with NMR experiments [2] and provides a route to extract internal stiffness from frequency-resolved data.

Chemical functionalization introduces qualitatively new features. *Internally* functionalized dendrimers, in which additional non-branching units are inserted within each generation, display in NMR relaxation a clear local signature of the internal architecture through a distinct asymmetric process even when the global mechanical moduli are dominated by the periphery [3] . It appears as a high-frequency maximum in $[\omega/T_1(\omega)]$, whose position is essentially independent of the shell of the labeled segment and which accounts quantitatively for high-frequency anomalies observed in atomistic simulations of carbosilane dendrimer melts [4].

Taken together, these results show that the local dynamics of hyperbranched macromolecules carries detailed structural information once bending rigidity is properly accounted for. NMR relaxation, combined with analytic theory, thus constitutes a sensitive probe of architecture, stiffness, and chemical decoration in complex treelike polymers.

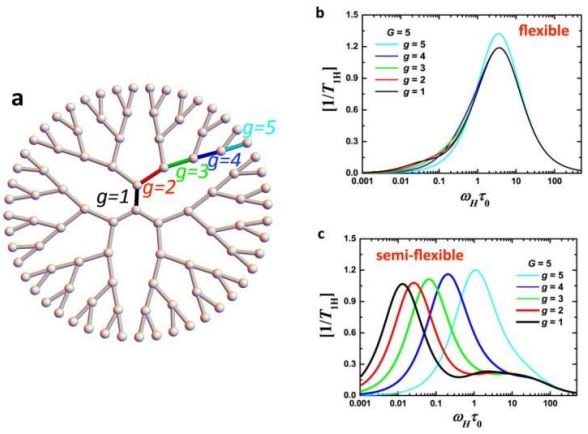

Figure 1: *(a) sketch of a dendrimer of generation $G = 5$, with segments coloured by shell g. (b, c) Reduced ^1H spin–lattice relaxation rates for different shells of flexible (b) and semiflexible (c) dendrimers; for the semiflexible case the maximum of [1/T1H] shifts toward lower frequencies for inner shells (larger $G - g$).*

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Thursday 18

Invited lecture

Magnetic Field Cycling Beyond Relaxometry

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High-resolution Nuclear Magnetic Resonance (NMR) combined with magnetic field cycling (MFC) provides a unique framework for probing molecular systems across a broad range of magnetic fields. Traditionally, such systems have been associated with nuclear magnetic relaxation dispersion (NMRD) and relaxometry, enabling investigations of molecular dynamics, relaxation mechanisms, and correlation times. However, advances in instrumentation and methodology are expanding the role of MFC far beyond classical relaxometry.

I will discuss how field-dependent spin dynamics can be exploited to reveal subtle chemical interactions and to manipulate nuclear spin relaxation and polarization. Recent studies demonstrated that specific chemical environments can substantially prolong nuclear spin lifetimes at low magnetic fields – an effect termed chemically induced deceleration of relaxation (CIDER). Using this approach, relaxation times of ^{15}N-containing molecules such as pyridine and nicotinamide were extended from below one second to tens of seconds, while pyruvate lifetimes approaching several minutes were achieved. These findings suggest that relaxation dispersion measurements can become a sensitive probe of weak intermolecular interactions and chemical exchange processes.

Magnetic field cycling also offers unique opportunities for nuclear spin hyperpolarization methods, including CIDNP, PHIP, SABRE, and dDNP. Access to controlled low-magnetic-field conditions enables optimization of polarization-transfer conditions, characterization of spin–spin and hyperfine interactions, and investigation of relaxation processes relevant to the preparation and transport of hyperpolarized agents.

Finally, I will discuss recent developments in MFC hardware, including faster switching, improved field stability, compact probe designs, and access to ultralow magnetic fields down to the nanotesla regime. Together, these advances are transforming MFC into a versatile platform for studying relaxation, spin dynamics, and hyperpolarization across chemistry, physics, and biomedical imaging.

Acknowledgements

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Monte Carlo study of high-field transverse relaxation induced by iron oxide nanoparticles coated by a slow water diffusion layer

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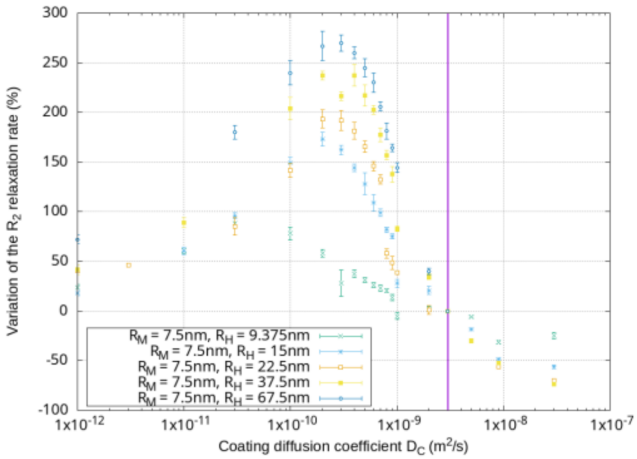
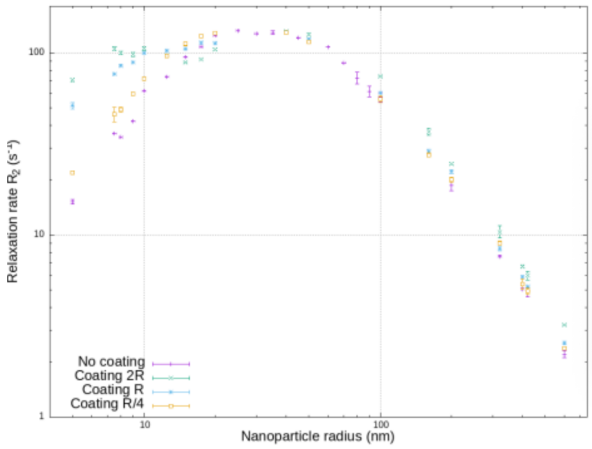
Superparamagnetic iron oxide nanoparticles (SPIONs) are usually nanosize crystals of magnetite or maghemite. Their high saturation magnetisation and null remnant magnetisation make them particularly suitable to be used as contrast agents in nuclear magnetic resonance imaging (MRI). Under the static magnetic fields typically used for MRI, they produce strong magnetic inhomogeneities, which modify the water relaxation rate where they are located. This in turn changes the pixel intensity in the area.

There is a variety of theoretical models that quantitatively predict the proton relaxation rate induced by such nanoparticles [1]. An important parameter is the diffusion coefficient of water molecules that is usually considered as homogeneous in the sample. However, SPIONs are often coated with a layer of material, usually a polymer, which is sometimes permeable to water. The water diffusion coefficient in this coating is usually smaller than that of bulk water: this inevitably affects the contrast induced by such nanoparticles [2]. Because they are complex to model analytically, numerical simulations are useful tools for studying the impact of these diffusion constraints on SPION-induced contrast.

This work hence simulated, through Monte Carlo techniques, the influence of the nanoparticle polymer coating on SPION-induced T_2 NMR relaxation. By varying the coating layer thickness and water diffusion coefficient in the coating, it is shown that, especially with small SPIONs, thick coatings with reasonably slow water diffusion lead to an increase in the water relaxation rate. This in turn leads to an increase in contrast. Our results indicate that efforts to produce thick coatings, permeable to water but with low diffusion coefficients, such as PEG, dextran and gelatin, could improve the performance of SPIONs as contrast agents.





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Evaluation of the effect of free radicals on proton NMR relaxometry of degraded motor oils

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The presence of free radicals in fluids, detectable via electron paramagnetic resonance spectroscopy (EPR), can significantly influence ^{1}H longitudinal nuclear magnetic resonance relaxation processes. The field-cycling nuclear magnetic relaxometry technique (FFC-NMR) provides a unique approach for studying these interactions across a broad Larmor frequency range. The situation is quite common in fluid systems subjected to oxidative stress, such as lubricants in internal combustion engines. Our previous studies in lubricant degradation [1–4] did not specifically address the impact of radicals on ^{1}H longitudinal relaxation. In a recent work [5], we focused on a simplified system in which TEMPOL radicals were introduced in controlled concentrations into ethylene glycol samples. The system's behavior was evaluated at different radical concentrations to elucidate the influence of the paramagnetic species on the relaxation dispersion profile. We proposed the inclusion of an additional relaxation term to account for intermolecular proton–electron interactions. We observed that, for radical concentrations exceeding approximately 2×10^{17} radicals/cm^3, paramagnetic interactions dominated the relaxation dispersion at Larmor frequencies below 1 MHz. Building on these insights, we present a new approach to lubricant oil characterization by examining the impact of free radicals on the proton relaxation of mineral base oil, employing FFC-NMR relaxometry and quantitative EPR measurements.

EME, CCF and LJG have equally contributed to this work.

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Design, construction and commissioning of a next-generation Field-Cycling Imaging scanner operating from 0.2 mT to 200 mT

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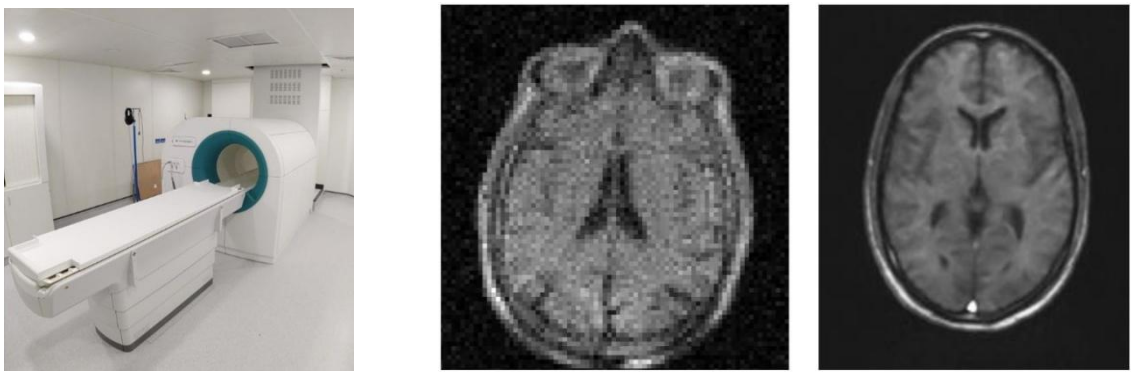
Our group has been developing fast field-cycling technologies over the last three decades and is exploring the possibilities offered by T relaxometry at ultra-low magnetic fields for medicine. In 2017, we completed the commissioning of a whole-body resisitive Field-Cycling Imaging (FCI) scanner that showed high clinical potential in the detection and characterisation of cancer and stroke , amongst other applications. However, that system was limited by its small bore (50 cm), low field homogeneity and long scan times related to a combination of relatively weak gradients, temporal field instabilities and high noise level. Additionally, that system was located inside our physics laboratory and access to patients was possible but restricted to those with good mobility.

Learning from this prototype system, we started designing a next-generation system in 2018 with the vision to place FCI in the local hospital (Figure, left). Here we present the results measured during commissioning and for the first in vivo scans. With this new system, patient access is comparable to that of the commercial 3T MRI scanner located in the corridor next to the FCI scanner. Like-for-like image acquisition time improved from 30 s for the previous prototype to 2 s with the new one. Within an acquisition window of 30 min, we can now obtain 8 slices of 128 × 128 matrix size, 2.5 × 2.5 × 5 mm resolution at 25 kHz acquisition bandwidth, for 9 magnetic fields and 5 evolution times, using a 3D cartesian acquisition. This would have taken us more than 8 hours on the previous system.

Image quality is also significantly improved, with much improved image distortions and typically 20 to 50 % overall SNR gain for similar acquisition times, including images obtained at an evolution field of 0.2 mT (Figure, middle and right).

It is now possible to use FCI to explore T_1 contrast from 0.2 mT to 200 mT for robust in vivo clinical trials on acute patients, with high image quality and multi-slice capabilities, within a scan time comparable to conventional MRI scans. Several clinical studies are already ongoing using this new scanner focusing on stroke, cancer, brain health, cardiovascular diseases and osteoarthritis. FCI technology can now also be replicated at other sites, offering the possibility to conduct multi-centre studies for clinical validation



Left: New-generation FCI system assembled in the Aberdeen Royal Infirmary. Middle and right: typical magnitude images obtained for a 30-min field-cycling acquisition of the head from the previous FCI prototype (left: single-slice, 5 evolution times, 4 evolution fields, 80 × 80 voxels) and the new FCI system (right: 8 slices, 5 evolution times, 9 evolution fields, 128 × 128 voxels).

Imaging of brain tumour invasion using Field-Cycling Imaging

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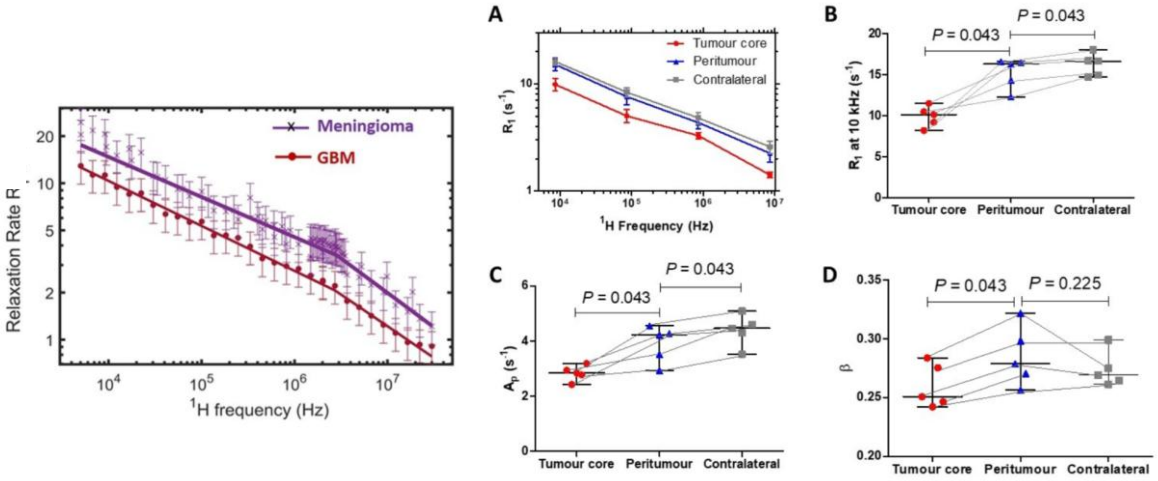
Gliomas and glioblastomas are aggressive brain tumours associated with poor clinical outcomes. Conventional high-field MRI is limited in its ability to characterise the peritumoural region and to differentiate invasive from non-invasive tissue, and accurately visualising these regions could provide critical guidance for surgical planning and targeted therapeutic strategies.

This study aimed at validating the capability of Field Cycling Imaging to distinguish invasive tumour phenotypes and to detect peritumoural regions, which are known to harbour infiltrative glioma cells. This was done with FFC-NMR using *ex vivo* human glioma and meningioma samples, and *in vivo* from patients with known glioma lesions using FCI.

FFC-NMR differentiated invasive GBM from non-invasive meningioma, with mass spectroscopy validation of the presence of aquaporin 4, which is linked to the changes in tissue relaxation rate. R_1 at very low field was also strongly discriminant of tumour core from peritumoural regions. *In vivo* implementation using a clinical FCI prototype successfully differentiated gliomas from meningiomas and peritumoural from core regions – achievements not possible with conventional MRI.

Both ex vivo and in vivo results support FCI as a non-invasive, contrast-free imaging to visualise glioma invasion via R_1 measurements at different low and ultra-low fields. This capability enhances diagnostic and therapeutic precision and provides insights into how invasion is linked to water exchange dynamics, opening new avenues for treatment monitoring.



Left: *Ex vivo R_1-dispersion curves comparing GBM (WHO Grade IV) with a high invasion phenotype to meningioma (WHO Grade I) without invasion.* Right: *A. In vivo R_1-dispersion curves comparing tumour core, peritumoural and unaffected regions in gliomas (WHO grade II and III). C-D. R_1 values at 10 kHz, and Power-Law model parameters (C, A_p) and (D, β), distinguish the tumour core from the peritumoral region.*

Underrated Quadrupole Relaxation Enhancement Effects

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Quadrupole Relaxation Enhancement (QRE) effects originate from dipole-dipole interactions between spin-1/2 nuclei ($I = 1/2$) and nuclei possessing a quadrupole moment ($S \geq 1$). Often QRE effects involves ^{1}H and ^{14}N ($S = 1$) [1,2], although outside the "biomolecular world" there are numerous examples of QRE for higher spin quantum numbers [3,4]. Several intertwined conditions must be met to observe QRE. One of them is the sufficient amplitude of the $I - S$ dipole-dipole coupling. In real systems, the overall ^{1}H (^{19}F) relaxation stems from multiple relaxation pathways and often the $I - S$ relaxation contribution is masked by relaxation terms originating from stronger $I - I$ dipole-dipole interactions. The next condition is related to the time scale of the molecular motion. For QRE effects to be present, one must be outside the extreme narrowing condition ($\omega\tau_c \ll 1$, where τ_c is the correlation time of the fluctuations of the $I - S$ dipole-dipole coupling, while ω is the I-spin resonance frequency matching one of the transition frequencies of S-spin). At the same time, when the dynamics is so slow so the condition $\omega_{DD}\tau_c > 1$ (ω_{DD} denotes the amplitude of the $I - S$ dipole-dipole coupling in angular frequency units) one observes polarization transfer effects [5], instead of QRE. Moreover, the effective correlation time,τ_c, reflets not only the "direct" molecular motion, but also the own relaxation processes of the quadrupole nuclei (independent of the presence of the I spins).

With this complex scenario in mind, I will demonstrate that QRE effects that are often hidden behind other relaxation contributions (manifest themselves as "small deviations" from otherwise smooth frequency dependencies of the I spin relaxation rates), but affect the results. Moreover, when properly revealed, QRE effects provide unique information about subtle changes in the molecular surrounding, that are not available by any other methods.

Acknowledgments

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Evaluation and optimization of magnetic contrast agents by fast field cycling NMR relaxometry

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Traumatic brain injury (TBI) is one of the leading causes of disability and mortality worldwide. In this context, magnetic resonance imaging (MRI) has emerged as a promising technique for detecting brain damage [1–3]. Among MRI tools, contrast agents based on magnetic nanoparticles (MNPs) have demonstrated significant potential [4], attributed to their unique magnetic properties, biodegradability [5,6], and high contrast efficiency [6–8].

This study aims to evaluate the sensitivity of nuclear magnetic relaxometry in detecting neuroinflammatory processes following TBI. Additionally, it seeks to optimize MNP-based contrast agents by elucidating the relationships between their physicochemical properties, biodistribution, toxicity, and contrast efficiency, and by investigating how these factors influence the effective concentration of the active agent reaching the brain.

To this end, agar phantoms (2% w/w) incorporating iron oxide nanoparticles synthesized in our laboratory (0.05–100 mg Fe/L) were developed. ^{1}H relaxation rate dispersion profiles of water molecules in these phantoms were measured by using the fast field cycling nuclear magnetic relaxometry technique, covering the Larmor frequency range from 0.03 to 15 MHz. Efforts are being made to model these profiles and obtain a calibration curve for estimating MNP concentration. These studies also allowed the determination of the MNP detection range of the technique. Modeling of these dispersion profiles is key to understanding and optimizing the performance of contrast agents based on iron oxide MNPs.

This approach aims to advance the understanding of nuclear magnetic relaxation mechanisms in iron oxide nanoparticle-based systems and to the development of diagnostic and therapeutic strategies for inflammatory neurological conditions.

Acknowledgements

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Fast-Field Cycling NMR in developing Functional Nanoprobes for MRI and AC-field hyperthermia

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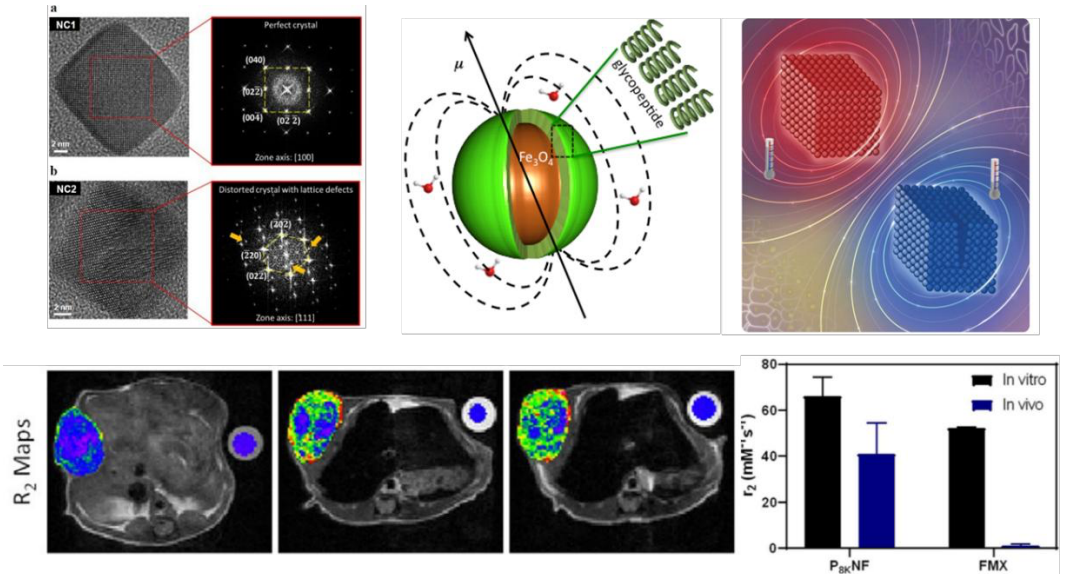
In recent years the development of magnetic iron-oxide nanoparticles (MNPs) for biomedical applications has progressed significantly. A particular focus is on preparing materials with multiple responses, typically any two from MRI image contrast generation, AC-field induced local heating (hyperthermia) and magnetophoretic capture. In this talk some recent work from our laboratory will be presented on the synthesis, surface modification, colloidal stabilization and in vivo use/fate of MNPs, using examples from studies on magnetic nanosphere [1], nanocube[2] and nanoflower[3] suspensions and, time-permitting, on magnetic hydrogels[4,5]. The use of fast-field cycling NMR relaxometry to study magnetic ordering in suspension, in which the ^{1}H nuclei of the H_2O are used as a spy will be described [6]. This information can be used to develop particle dispersion, to understanding particle dissolution, and to control particle assembly into functional clusters determining the hyperthermic and MRI responses in the biological environment.



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Accessing Dynamics of SBR Compounds by Variable Temperature ^{1}H FC NMR and DFMSE Experiments

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Polymers exhibit hierarchical dynamics over a wide range of time scales, from local segmental motions to slow cooperative processes [1]. ^{1}H Field Cycling (FC) NMR relaxometry is a powerful tool to investigate polymer dynamics around the glass transition by probing spin–lattice relaxation over several decades of Larmor frequency [2-3]. Here, ^{1}H FC NMR relaxometry is applied to study the effect of two tackifying resins, one petroleum-based and one of natural origin, on the segmental dynamics of styrene-butadiene rubber (SBR) in compounds of technological relevance for the tire industry. Uncured and vulcanized samples at different resin contents are investigated over a broad temperature range, enabling the construction of master curves over nine frequency decades (Figure 1a). Correlation times for segmental dynamics are determined from the costruction of the mastercurves, which can be consistently described by a Vogel-Fulcher-Tammann (VFT) behavior, allowing a reliable determination of dynamic parameters. FC NMR results are further correlated with low-field ^{1}H time-domain NMR measurements based on an improved Dipolar-Filtered Magic Sandwich Echo (DFMSE) approach [4] (Figure 1b), providing insight into the onset of the glass transition in the elastomer associated with cooperative segmental α-motions. The combined use of FC relaxometry and DFMSE experiments offers a comprehensive view of the dynamic heterogeneity of SBR/resin systems highlighting the different effects of resins of natural and petroleum origin and supporting the design of more sustainable elastomeric formulations.

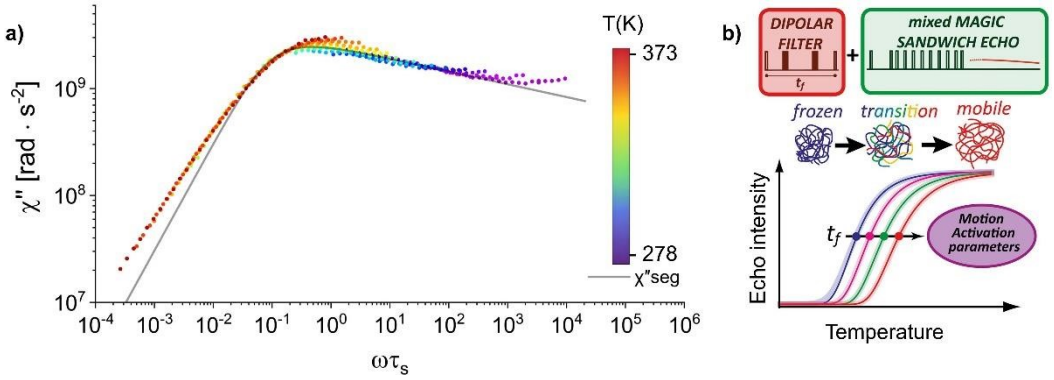

Figure 1. a) SBR ^{1}H FC NMR master curves obtained at extended temperature range. b) Dipolar-filtered MSE pulse sequence.

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Probing the Thermoresponsive Gelation of Polymer Solutions through Solvent Dynamics

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Gels are soft solids formed by a polymer network swollen with solvent. Although the solid phase may constitute as little as 0.1 vol.% of the material, gel properties are traditionally characterized by rheometry, which primarily reflects network architecture. In contrast, the solvent, despite comprising the vast majority of the volume, remains largely overlooked.

Low-field NMR relaxometry has emerged in recent years as a powerful tool for monitoring solvent dynamics and providing molecular-scale insights into the structure of gels. Recent studies of cellulose hydrogels have shown that water mobility, measured from T_2 relaxation times, depends not only on the concentration of solid species but also on the connectivity of the polymer network [1,2]. This raises a key question: to what extent can solvent dynamics be correlated with – or decoupled from – the macroscopic mechanical properties of gels?

To address this question, we investigate the thermoresponsive transitions of three different systems: (i) the lower critical solution temperature (LCST) of Pluronic solutions, (ii) the gelation of ethylcellulose oleogels, and (iii) the conformational transition of succinoglycan solutions. These systems all exhibit sharp, well-defined transitions that depend on the polymer type and concentration. By combining NMR relaxometry and rheometry across the transitions, we unify solvent dynamics and viscoelastic properties, helping to improve the fundamental understanding of the physics of gels.

Our results show that, while the solvent dynamics are systematically affected by the presence of polymer, the response across the transition is not universal. The trends depend on the nature of the transition itself: the LCST of Pluronic solutions leads to a clear change in the activation energy of T_2, whereas oleogelation does not – despite T_2 being sensitive to polymer concentration – likely reflecting differences in polymer–solvent interactions. Succinoglycan solutions show a non-monotonic evolution of T_2: a decrease with temperature before the transition, a sudden increase at the transition, and an Arrhenius-like increase above it. These findings demonstrate that solvent dynamics can carry signatures of network formation, but interpreting them requires an understanding of the specific molecular mechanisms at play.

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Enhancing Water Proton Relaxivity in Gd-Hydrogels and Bio-functionalized MRI Agents

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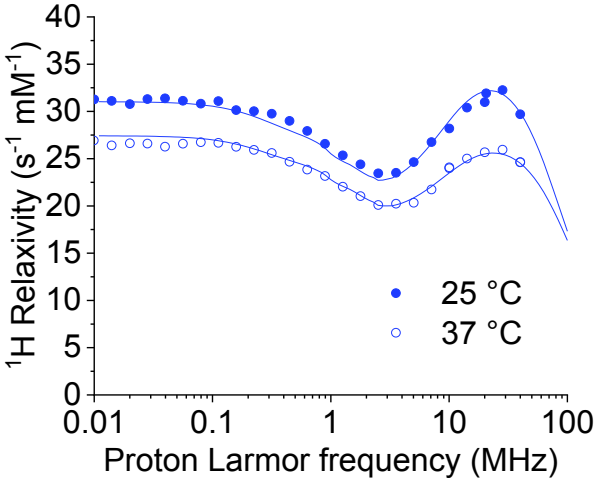
Field-cycling relaxometry represents a key methodology for the rational design of targeted MRI contrast agents. Two primary strategies for the optimization of the image contrast are investigated: the restriction of molecular dynamics by conjugation to macromolecules and the modulation of relaxivity via enzymatic activation (bio-responsiveness). Significant relaxivity enhancements are achieved by incorporating Gd(III) complexes into bulky scaffolds, such as the 55 kDa homotetrameric protein transthyretin, lipoic acid-based hydrogels, or Aggregation-Induced Enhanced tetraphenyl ethylene (TPE) aggregates. In these systems, the transition from a fast-tumbling regime to a restricted rotational state drastically increases the reorientation correlation time. For instance, conjugation into lipoic acid hydrogels or TPE aggregates can shift the correlation time from the picosecond range into the nanosecond range, resulting in up to a sixfold increase in relaxivity. NMRD profiles confirm that these improvements arise from optimized reorientation dynamics and efficient water exchange. Analogously, the functionalization of the human protein transthyretin with the GdC4-IA tag yields a high-relaxivity theranostic platform, where the efficiency gain is driven by optimized water exchange and nanosecond-range rotational dynamics. Beyond structural rigidity, enzymatic activation offers a promising pathway for bio-responsive imaging. Probes such as HexA-Gd and β-galactose-activated agents demonstrate how specific hydrolases can trigger self-immolative linkers and change coordination environments, leading to sizable relaxivity enhancements. Such bioresponsive platforms are ideal for the non-invasive detection of cancer-specific biomarkers and the real-time monitoring of tumor progression or therapeutic response. Collectively, the power of NMR relaxometry in deciphering the complex interplay between molecular motions and paramagnetic efficiency is underscored.



^{1}H relaxivity profiles of Gd-conjugated transthyretin at 25 and 37 °C. Solid lines are the best fit profiles obtained with the Florence NMRD program

Field-Dependent ^{1}H Relaxometry as a General Probe of Hydration Dynamics in Paramagnetic Ln^{3+} Complexes

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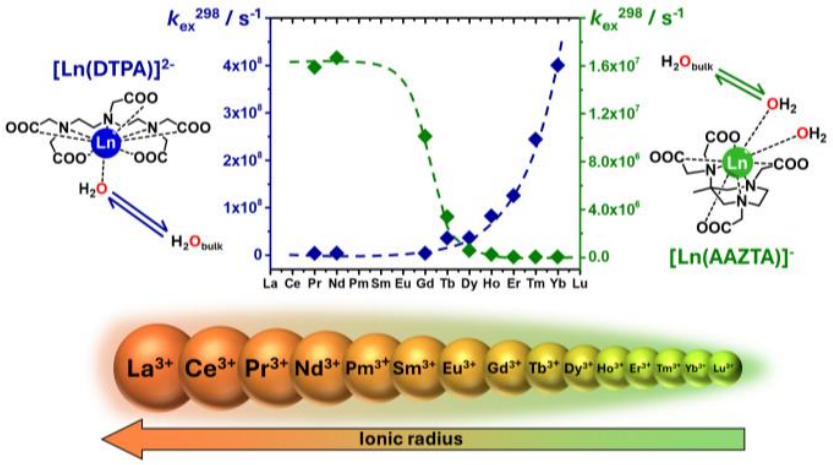
Hydration dynamics at metal ions or complexes govern the reactivity of chemical and biological systems and are central to the function of paramagnetic probes, such as Magnetic Resonance Imaging (MRI) contrast agents [1]. While nuclear magnetic resonance (NMR) offers powerful approaches to interrogate exchange processes, established methodologies like ^{17}O NMR typically require high sample concentrations (for Ln ≠ Gd, > 50 mM). This requirement sometimes limits the investigation when the paramagnetic species is diluted, for example for poorly soluble complexes or supramolecular systems. To overcome these limitations, we present a relaxometric methodology that enables an accurate determination of inner sphere water-exchange dynamics of paramagnetic systems that can be carried out even in dilute solutions. This approach relies on the simultaneous analysis of longitudinal (R_1) and transverse (R_2) ^{1}H relaxation rates over an extended magnetic field range. Since longitudinal relaxivity is strongly dependent on the hydration number (q) and transverse relaxivity on the coordinated water residence time (τ_M), the global fitting of R_1 and R_2 provides quantitative access to both the hydration state and the exchange kinetics[2]. We validated this method using two prototypical series of lanthanide chelates: $[Ln(DTPA)]^{2-}$ and $[Ln(AAZTA)]^{-}$. For the $[Ln(DTPA)]^{2-}$ series ($q = 1$), the fitting of relaxometric profiles confirmed a progressive acceleration of water exchange moving towards heavier lanthanides, with τ_M decreasing drastically from ca. 340 ns for Pr^{3+} to just 2.5 ns for Yb^{3+}. Conversely, the relaxometric investigation of the $[Ln(AAZTA)]^{-}$ series exhibited a pronounced slowing of the exchange kinetics for heavier ions (from ca. 60 ns for Pr^{3+} to > 130 μs for Er^{3+}, Tm^{3+}, and Yb^{3+}), alongside a structural transition in the hydration state from $q = 2$ to $q = 1$ along the series. This relaxometric approach demonstrates the high sensitivity in capturing subtle structural and dynamic variations. By expanding experimental access to metal–water exchange kinetics under conditions previously inaccessible with conventional NMR techniques, relaxometry confirms its role as a powerful tool in coordination chemistry and in the rational design of next-generation MRI probes.



Field-dependent ^{1}H T_1 and T_2 relaxometry is established as a reliable and powerful approach for probing water exchange kinetics and hydration numbers in complexes throughout the lanthanide series

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Shape-Dependent NMR Relaxivity of Magnetic Nanoparticles: From Diffusion Regimes to a Predictive Model

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Superparamagnetic magnetite (Fe_3O_4) nanoparticles are widely used as T_2 contrast agents in magnetic resonance imaging due to their ability to induce local magnetic field inhomogeneities and enhance transverse relaxation. While experimental studies suggest that particle shape anisotropy can improve relaxivity [1, 2], its influence on outer-sphere relaxation remains unclear, as standard models assume a dipolar magnetic field and do not account for anisotropic field distributions.

In this work, we numerically investigate water proton relaxation using Monte Carlo simulations in the presence of non-spherical Fe_3O_4 nanoparticles, following the approach described in [3]. The transverse relaxation rate (R_2) is computed at high static field (B_0) as a function of particle size and magnetization orientation for the particle geometries shown in Fig.1. By comparing anisotropic particles with volume-equivalent spheres, we isolate the contribution of shape to relaxivity. Our results show that for particle sizes above ~30 nm, shape has negligible impact on relaxivity. For smaller particles, geometry-dependent effects emerge but are not systematically beneficial, with some anisotropic shapes even yielding lower relaxivity than spheres. Typically, variations in relaxivity range from -20% to +80%, with the largest enhancements observed for elongated particle geometries.

We further introduce a predictive approach based on a weak-field approximation, demonstrating that relaxivity correlates with the variance of the induced magnetic field. This provides a practical pre-synthesis estimator for contrast efficiency and clarifies the conditions under which shape engineering is advantageous. Overall, this work provides a practical framework to evaluate the impact of nanoparticle shape on MRI contrast.

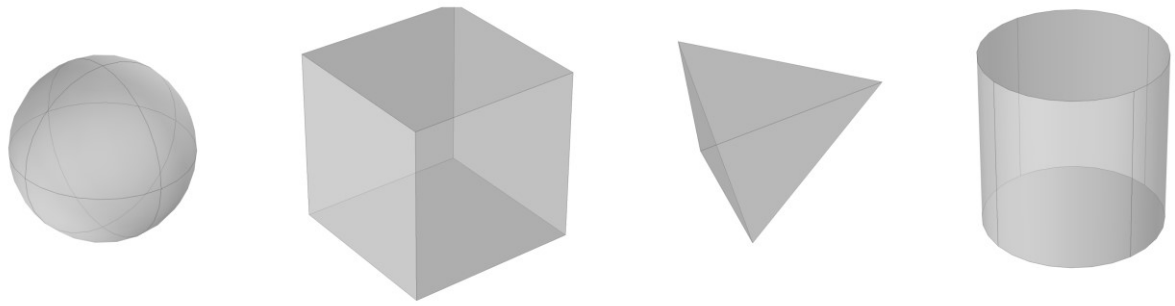

Figure 1: Nanoparticle shapes considered in this study: sphere, cube, tetrahedron, and cylinder. All shapes are defined with equal volume, corresponding to identical iron content.

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Understanding water effects in paint layers using unilateral NMR: penetration, swelling and diffusion

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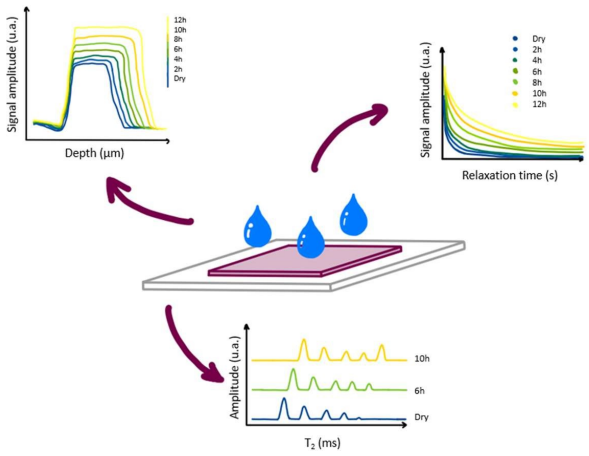
Easel paintings are complex, multilayered systems highly sensitive to moisture, which can induce both mechanical stress and chemical degradation. Water uptake may originate not only from environmental humidity fluctuations but also from water-based cleaning treatments, increasingly favored in the conservation field for their lower toxicity compared to organic solvents. A deeper understanding of interactions between water and paint films is therefore essential for their long-term preservation. In this context, unilateral NMR offers a powerful, non-invasive approach to probe water dynamics in complex materials such as dry paint films.

Here, unilateral NMR is applied to investigate water behavior in model dry paint systems prepared with two binders, linseed oil and egg yolk tempera, and two historically relevant pigments with contrasting moisture responses: hydrocerussite and madder lake. Samples were exposed either to controlled humid atmospheres at varying relative humidity levels or to direct contact with liquid water. ^{1}H depth profiles were used to assess water penetration, retention, and swelling. Transverse relaxation decays were acquired using a CPMG pulse sequence and processed using both inverse Laplace transform (ILT) and multi-exponential fitting, providing complementary access to continuous T_2 distributions and discrete relaxation components associated with distinct proton populations. These results provide insight into the different local environments of water within the paint, allowing the distinction between tightly bound water and more mobile fractions located in larger pores. Stimulated echo (STE) experiments were performed to estimate water self-diffusion coefficients. These diffusion measurements offer complementary structural information by characterizing the connectivity and restriction of microporosity, which govern the macroscopic mobility of the free water fraction.

The results highlight strong formulation-dependent behaviors. Egg tempera systems exhibit fast and extensive water penetration, whereas linseed oil-based samples show slower and more gradual uptake. Madder lakecontaining samples display significant swelling in both binder systems, while water penetration remains very limited in linseed oil/hydrocerussite samples, in agreement with complementary DVS measurements. In systems where water uptake occurs, relaxation data processing reveals the emergence of new proton populations with longer T_2 values, together with an overall shift toward longer relaxation times upon prolonged exposure, indicating increased water mobility. Water retention also differs: release is fast in tempera systems but significantly slower in linseed oil/madder lake samples, suggesting partial confinement of water within the paint film and/or possible interactions with the matrix, which are currently under investigation.



20 Years of Short Signals and Slow Relaxation: Lessons Learned on Solid-State FFC Relaxometry in Solids

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I present practical insights from approximately 20 years of experience with Fast Field Cycling NMR Relaxometry, using a 0.5 T relaxometer and focusing mainly on solid (crystalline) materials. It does not introduce new theory or breakthroughs, but rather summarizes what happens when one insists on applying FFC – an approach largely optimized for liquids – to systems with weak signals, very short transverse relaxation times, and inconveniently long longitudinal relaxation times

The talk will address the practical realities of measuring relaxation dispersion under such conditions, including signals that disappear into dead time and experiments that test the limits of patience, power supplies, and cooling systems. Strategies that proved useful (and some that clearly did not) will be discussed, such as the use of non-polarized measurements at lower fields and various adjustments of pulse sequences and acquisition parameters. Particular emphasis will be placed on seemingly trivial details that turned out not to be trivial at all.

A selection of experimental missteps, questionable interpretations, and slowly learned lessons will also be included, in the hope that others might avoid repeating them.

The presentation is mostly intended for students struggling with FFC measurements, for supervisors trying to understand their students' strange results, as well as for anyone interested in not repeating my mistakes.

Posters

First ^{1}H-NMR spin dynamics measurements and results on $Tb_{0.01}Y_{0.99}$ Tropolonate molecular magnet at low fields

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Single molecule magnets (SMMs) [1] and, more recently, single ion magnets (SIMs) [2], characterized by strong uniaxial anisotropy and progressive slowing down of the magnetization, have been extensively studied both for their peculiar quantum properties [3] and also for their possible technological applications [4]. The aim of the researchers to improve the performance of these molecular nanomagnets (MNMs) have been devoted to increase the anisotropy barrier ΔE and to minimize all the relaxation mechanisms dominating at low temperature [5]. In the past we investigated the spin dynamics and the magnetic properties of the lanthanide - based SIMs system TbTrp $(Tb(Trp)(HBPz_3)_2$, see Figure 1, as a function of temperature and magnetic field applied, through DC and AC susceptibility measurements, ^{1}H NMR measurements (absorption spectra, spin-lattice (T_1) and spin-spin (T_2) nuclear relaxation times) and muon spin resonance μ^+SR measurements [6].

Here we report ^{1}H-NMR measurements on TbTrp diluted by means of Yttrium, with chemical composition $Tb_{0.01}Y_{0.99}$, at medium magnetic field (0.25T< H < 1.00T) and for the first time of any MNMs below 0.25 T using the fast field cycling technology. The study of Ln-based systems diamagnetically diluted at room temperature would determine the dynamical processes that affect the long times electronic spin-spin correlation function [7].

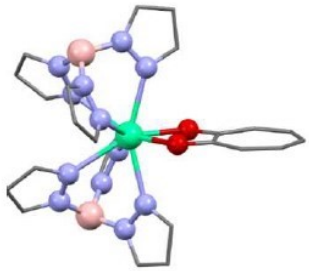

Figure 1 – Schematic view of TbTrp : sticks = Carbon, red = Oxygen, violet = Nitrogen and Cyan = Tb; hydrogen atoms omitted for clarity.

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Poster 2

Development of Water-Soluble Metalloporphyrins as Contrast Agents for MRI

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The search for safer alternatives to gadolinium-based contrast agents (GBCAs) has emerged as a central challenge in MRI contrast agent development. Growing concerns regarding their use, particularly the risk of toxicity in patients with impaired renal function, have fuelled the search for alternative strategies.[1] In this context, increasing attention has been directed toward contrast agents based on biologically relevant paramagnetic ions such as Mn(II), Mn(III), and Fe(III).[2]

Porphyrins stand out as highly promising ligands, since they can strongly chelate these transition metals, which, combined with their intrinsic biocompatibility and structural tunability, makes them well-suited for the development of alternative MRI probes.[3] Nevertheless, the design of effective porphyrin-based contrast agents requires careful control over several structural parameters, including sufficient aqueous solubility, stabilization of the metal ion in its appropriate oxidation and high-spin states, and retention of at least one coordinated water molecule under physiological conditions. Herein, we report the synthesis of water-soluble Mn(III) and Fe(III) porphyrin complexes and investigate their suitability as MRI contrast agents through relaxivity measurements.

Acknowledgments

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FFC-NMR relaxometry detects bumetanide-induced anti-invasive effects in glioblastoma models

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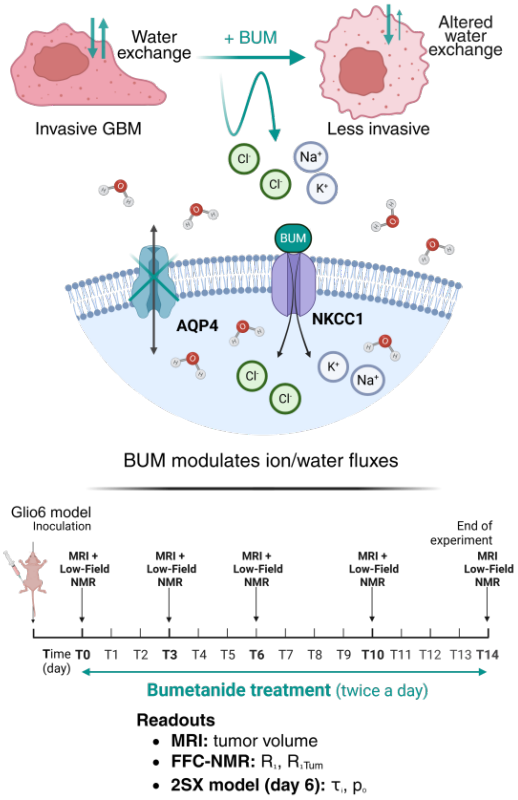
Introduction. Glioblastoma (GBM) is a highly invasive brain tumour for which no effective anti-invasive therapy is currently available [1], while MRI-based follow-up remains limited in distinguishing tumour recurrence from treatment-related changes [2]. This preclinical study applies FFC-NMR relaxometry to non-invasively probe transmembrane water exchange *in vivo* as a functional marker of tumour invasiveness and therapeutic response, without relying on exogenous contrast agents. The diuretic bumetanide (BUM) is a repurposed drug that inhibits NKCC1, which is functionally linked to aquaporin-mediated water transport; among aquaporins, AQP4 is particularly implicated in GBM invasion [3-4] (see scheme). We investigate the effect of BUM on intracellular water lifetime (τ_i) and R_1-dispersion profiles in invasive GBM models.



Methods. *In vitro* experiments were conducted on Glio6 and H_2O_2-stimulated U87 cell lines, the latter used to mimic an invasive phenotype, following treatment with BUM (1 μM) and analysis on a 0.5 T benchtop NMR system (Stelar). *In vivo* studies were performed on a Glio6 mouse model treated with BUM (5 mg/kg, intraperitoneally, twice daily for 14 days). R_1 dispersion profiles (0.5–23 mT) were acquired using an FFC relaxometer (Stelar), following T_{2W} ^{1}H-MRI scans (Avance Neo AV300, Bruker) for tumour size assessment. The τ_i values were quantified *in vitro* and *in vivo* using the two-site exchange (2SX) model, as previously described [5].

Results and Discussion. *In vitro*, BUM treatment caused a consistent elongation of τ_i in both Glio6 and H_2O_2-stimulated U87 cell pellets. Consistently, treated responder (TR) mice showed a 23 % increase in R_1 measured at 0.02 MHz on day 6, rising to 61 % when considering the tumour-specific R_1 contribution. Two treated mice showed a divergent R_1/tumour-growth pattern and were classified as treated divergent (TD), highlighting the sensitivity of FFC-NMR to heterogeneous early treatment responses. Final findings showed increased τ_i in TR mice, consistent with reduced invasiveness. In line with previous studies [5-6], these results confirm that low-field R_1 and τ_i are sensitive biomarkers of glioma invasion/migration and demonstrate their ability to detect the therapeutic effects of drugs targeting ion and water transport pathways. Using BUM, our results highlight its potential to counteract GBM aggressiveness by impeding the invasion process.

Conclusion. This study supports FFC-NMR relaxometry as an enabling technology for functional oncology protocols aimed at distinguishing proliferative tumour growth from infiltrative invasion and detecting early responses to anti-invasive treatment. Further development of emerging Field-Cycling Imaging (FCI, [7]) may extend this approach to spatially resolved assessment of invasive tumour regions, ultimately supporting more personalized and effective therapeutic strategies.

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On the LCST of Pluronic Solutions: A Solvent Perspective from Low-Field NMR Relaxometry

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Pluronic block copolymers in aqueous solution exhibit a lower critical solution temperature (LCST), resulting in a sharp, thermoreversible sol-gel transition. While this transition is commonly characterized by rheometry, which probes the mechanical response of the polymer network, the behavior of the solvent across the transition remains largely unexplored.

Low-field NMR relaxometry has recently proven to be a powerful tool for monitoring solvent dynamics in gels and provides molecular-scale information that is complementary to rheological measurements [1,2]. In particular, the spin-spin relaxation time T_2 and its activation energy have been shown to be sensitive not only to polymer concentration but also to the physical state of the network.

In this work, we use NMR relaxometry to investigate the solvent dynamics across the LCST of Pluronic solutions. To explore the role of the transition temperature and of polymer–solvent interactions, we vary different parameters such as (i) the type and concentration of Pluronic (which sets the baseline LCST), (ii) the addition of silica nanoparticles (Ludox, 26 nm), which shifts the transition temperature, and (iii) the substitution of H_2O by D_2O, which allows us to selectively probe the polymer dynamics. By combining relaxometry and rheometry, we describe how solvent dynamics respond to gelation under varied conditions.

Our results show that NMR relaxometry captures clear signatures of the sol-gel transition, with a measurable decrease in the activation energy of T_2 of water at the LCST from ~24 to ~12-14 kJ/mol. Interestingly, these values seem irrespective of the Pluronic type or concentration. On the other hand, T_2 of the polymer measured in D_2O becomes independent of temperature (i.e. activation energy of zero) upon gelation. This approach allows us to assess the robustness of solvent dynamics as a probe of network formation in thermoresponsive systems.

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Probing Small-Molecule Interactions via Magnetic Relaxometry of Engineered Gd^{3+}-Nanoparticle Platforms

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Molecular sensing of biologically relevant analytes is crucial for revealing cellular function, disease progression, and therapeutic response. Developing sensing strategies that operate non-invasively and with tissue-level depth enables real-time detection of biochemical processes within living systems. Traditional sensing modalities, particularly fluorescence spectroscopy, offer high sensitivity but suffer from intrinsic limitations: shallow tissue penetration, photobleaching, and interference from complex biological matrices. Comparatively, magnetic resonance-based sensing provides labelfree, non-invasive, and quantitative detection of analyte interactions which can be resolved deep within tissues, leveraging the unparalleled penetration and anatomical context of magnetic resonance imaging (MRI)[1,2].

Benchtop magnetic resonance (MR) relaxometry is emerging as a powerful platform for label-free sensing of small molecules, offering quantitative insight into molecular interactions without relying on fluorescent or chromogenic tags. Here, we show how nanoparticle-based MR probes can transduce analyte binding events into measurable relaxation changes, enabling sensitive detection in complex environments. Gadolinium-chelates have been well-established as MRI contrast agents, and macrocycle modifications have been explored for several decades to produce agents which can modulate their signal in response to external environments. Silica nanoparticles functionalised with established Gd^{3+}-chelates can produce enhanced signal compared to their molecular analogues resulting from their bulk and nanoparticle fine structure [3]. Herein, these Gd^{3+}-doped silica nanoparticles were systematically engineered to probe how nanoparticle architecture can modulate relaxivity in response to molecular analytes. Using compact benchtop relaxometers, we reveal mechanistic insight into how nanoscale environments mediate relaxation-based sensing.

By designing MR-active probes that translate molecular binding events into measurable relaxation changes, it becomes possible to bridge the gap between in vitro chemical sensing and in vivo diagnostic imaging, opening routes to track metabolism, detect disease biomarkers, and monitor therapeutic action directly inside the body. The findings advance the rational design of nanoparticle MR sensors for rapid, benchtop detection of small molecules and future diagnostic applications.

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Power-Law-Constrained Multiexponential Fitting of FFC-NMR Relaxation Curves under Finite Field-Switching Conditions

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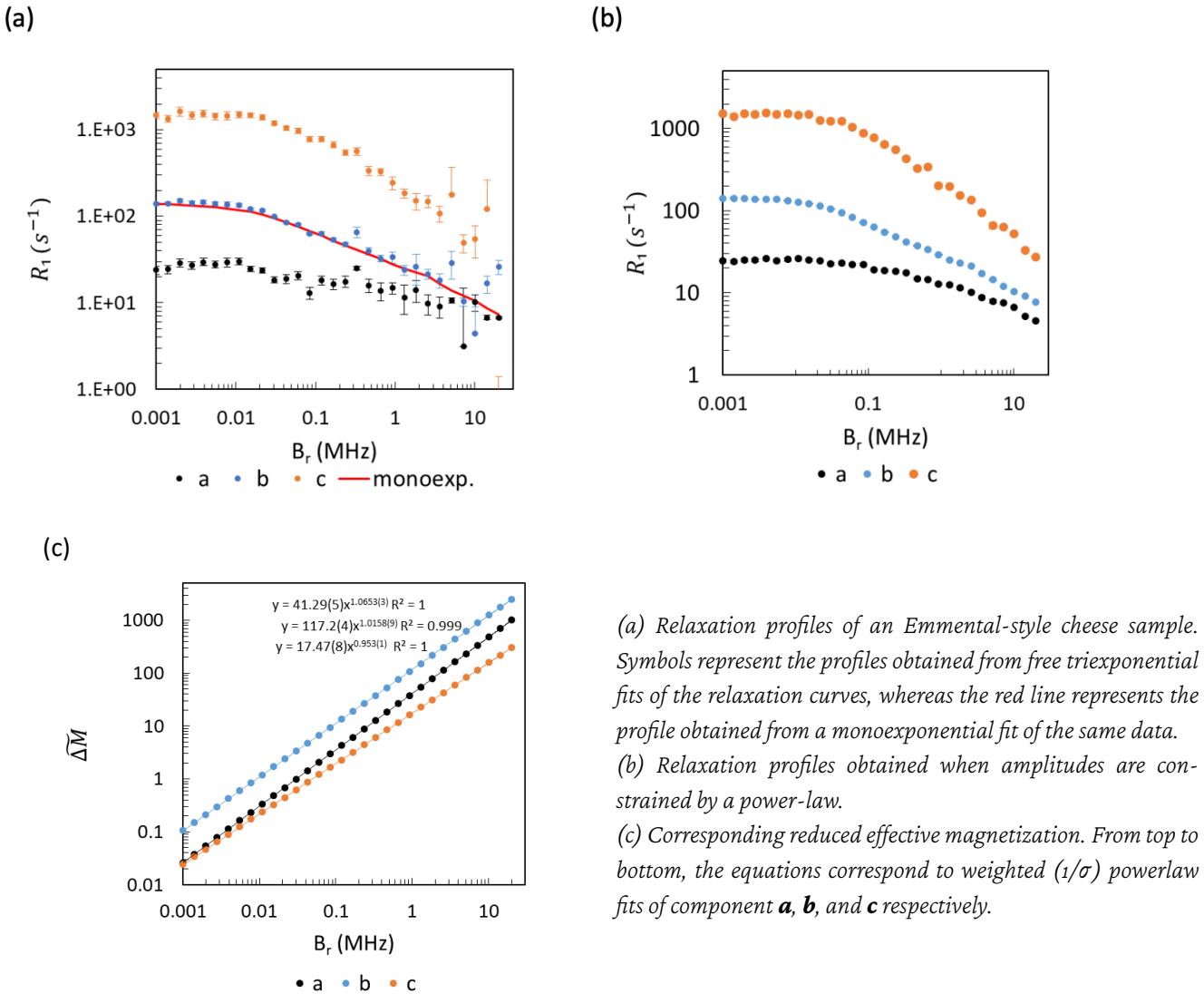
In the frame of Bloch formalism, the evolution of the magnetization amplitude of relaxation curves recorded during a pre-polarized FFC NMR experiment is analyzed in details. Except when field switch are ideal (infinite speed ramp and no settling) evolution of the amplitude is not linear with the relaxation field. However, in realistic cases it can be well approximate with a power-law. When the profile results of multiexponential relaxation curves, the knowledge of this power-law allows to fix the amplitude allowing for a stable multiexponential fit of the relaxation curves that in turns allow to build exploitable individual profiles. Theoretical calculation are developed for general relaxation mechanisms but theoretical illustration are proposed for the BPP model with correlation time varying from 10^{-10} to 10^{-5} s. An application is shown on an Emmental-style cheese samples with a triple exponential fit of the relaxations curves.



(a) Relaxation profiles of an Emmental-style cheese sample. Symbols represent the profiles obtained from free triexponential fits of the relaxation curves, whereas the red line represents the profile obtained from a monoexponential fit of the same data.
(b) Relaxation profiles obtained when amplitudes are constrained by a power-law.
*(c) Corresponding reduced effective magnetization. From top to bottom, the equations correspond to weighted (1/σ) powerlaw fits of component **a**, **b**, and **c** respectively.*

In vivo detection and treatment response assessment of rectal cancer using Field Cycling Imaging

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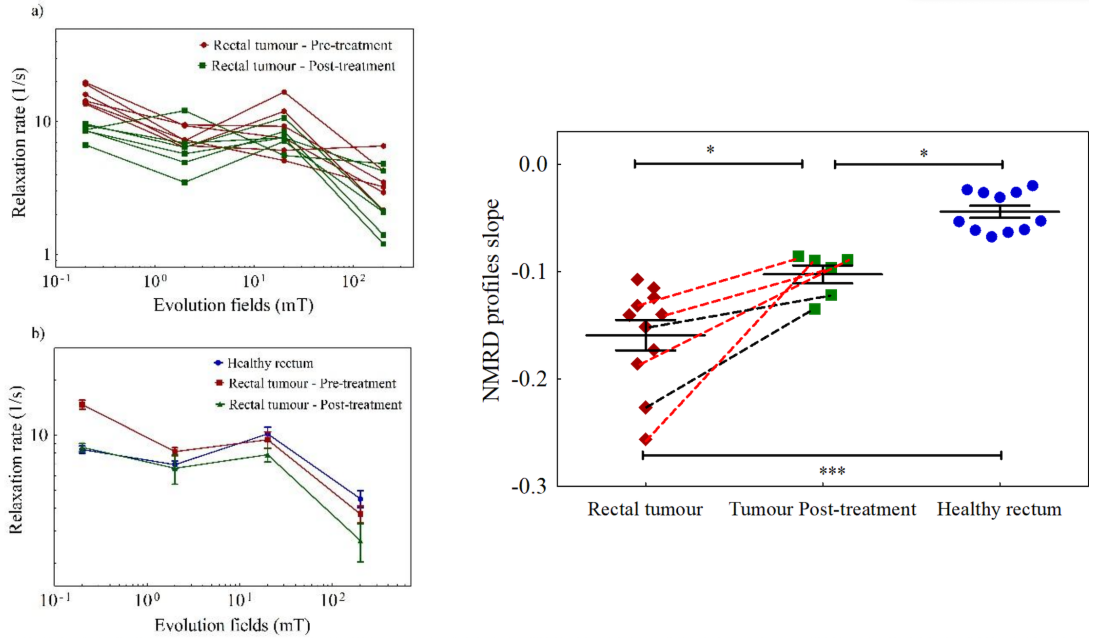
Colorectal cancer (CRC) represents a growing global health challenge, with its burden expected to increase by 60 % reaching 2.2 million new cases annually by 2030. Our preliminary FFC-NMR study on *ex vivo* colorectal tissues showed that ^{1}H NMRD profiles can sensitively capture tumour-associated relaxation changes without the need for contrast agents. This study aimed at confirming if this was also observed *in vivo* using FCI.

Eighteen patients with locally advanced rectal cancer were recruited. In all 11 patients who completed baseline scanning, the rectum was successfully visualised and the tumour average R_1 values were significantly higher than the healthy tissues at the lowest magnetic fields ($p < 0.0001$ and $p = 0.024$, respectively), with steeper dispersion (-0.20 ± 0.05 vs -0.04 ± 0.02; $p < 0.005$). Post-treatment analysis revealed that R_1 dispersion profiles showed significantly decreased relaxation rates in patients who responded well to treatment.

This study provides preliminary *in vivo* findings supporting the use of FCI-derived R_1 dispersion as a non-invasive biomarker for rectal cancer characterisation and treatment monitoring, and demonstrates the potential of FCI as a contrast-free imaging technique for detecting and monitoring rectal cancer.



Left: a) *NMRD profiles of rectal tumour before and after nCRT treatment.* b) *Comparison of the average NMRD profiles of rectal tumour before and after treatment, with non-involved tissues as a reference.* Right: *comparison of R_1 dispersion between rectal tumour pre- and post-treatment in comparison to the healthy tissues. Red dashes: complete response to treatment; black dashes: partial and non-responsive cases. *= p<0.05, ***= p<0.005, ns = not significant*

Secondary-Pulse Mitigation of Residual RF Effects in Early-Time NMR FID Detection

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The problem of the electrical ringing of the probe after a radio-frequency (RF) pulse has been a persistent challenge for researchers since the dawn of Nuclear Magnetic Resonance[1]. The main problem with this kind of ringing is the inability to access earlier parts of Free Induction Decay (FID), which contains information about fast molecular dynamics. Recently, we considered the use of a secondary RF pulse, ideally 180 degree phase-shifted relative to the first[2]. Initially, we wanted to negate the ringing in the RLC tank via destructive interference. However, as we tested and refined the technique, we have discovered a different unexpected benefit of using the secondary pulse, which will be briefly explained here. Due to transient effects, the main RF pulse which tips the magnetization to the transverse plane cannot have exact rectangular envelope. It cannot end abruptly as the energy in the tank cannot be dissipated instantaneously. In rotating frame of reference, the amplitude dissipation follows mono-exponential decay curve, defined by time constant $\tau : s(t) = s_0 e^{-t/\tau}$, where $\tau = 2Q/\omega_0$. It is worth noting, that the sample is not isolated from this ringing tail and in fact is adversely affected by it. Phase dispersion induced by the tail leads to dephasing of spins in the transverse plane and reduces the total signal that is detected. In our testing, we have introduced a carefully calibrated secondary pulse, which follows 100 ns after the end of the first pulse. If the parameters of the secondary pulse are chosen correctly, the total signal from the sample increases. We use crystalline sugar to show this effect. We suppose, that secondary pulse affects the spin system in a way that some transverse magnetization that was lost due to dephasing is restored, so the total signal is higher. We report 10% to 16% (depending on the integration window) increase in signal for crystalline sugar at 21.4 MHz. This figure likely may be improved further with automated pulse calibration techniques.

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FFC-NMR Relaxometry study of novel phosphonate-based coating agents for iron oxide nanoparticles in MRI

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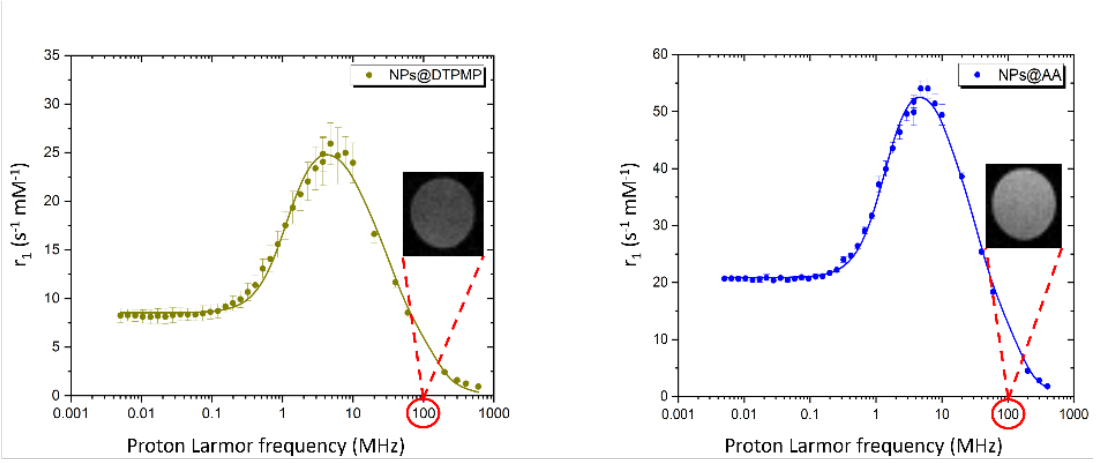
The effective *in vivo* application of iron oxide-based contrast agents relies on the use of strong-affinity coating agents to promote nanoparticle dispersion and reduce surface opsonin adsorption. Phosphonate-based molecules, shown to bind irreversibly to the metal oxide surface, provide both bound and free groups for further functionalization. Novel phosphonate and amine-based agents, methylene phosphonic acid (DTPMP) and alendronic acid (AA), were used via a coprecipitation-assisted microwave synthesis of iron oxide nanoparticles. To study these nanoparticle systems, complete NMR dispersion (NMRD) profiles were measured from 10 kHz to 600 MHz ^{1}H Larmor frequency, covering water ^{1}H dynamics over a broad time scale. The fast-field-cycling NMR technique specially enabled data acquisition over an extensive field range, from 10 kHz to 10 MHz, with a SMARtracer relaxometer from Stelar. Both samples exhibited high longitudinal r_1 and transverse r_2 relaxivities at medically relevant magnetic field strengths, suggesting lower dosing for higher efficiency. The physicochemical properties of the nanoparticles were assessed through the r_1 NMRD curve analysis using the Roch et al. [1] model and backed by other techniques such as TEM, DLS, and VSM, among others [2,3].



Longitudinal r_1 NMRD profiles of superparamagnetic iron oxide nanoparticles coated with DTPMP (left) and AA (right) in the frequency range 0.01- 600 MHz at 37 °C. MRI inset performed at 100 MHz and 50 mg L^{-1}.

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Poster 10

Characterization of raw and transformed bioresources by Time-Domain NMR

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The BIBS (Bioresources: Imaging, Biochemistry & Structure) Facility develops and applies physical and chemical methods for the characterization of raw and processed bioresources, on a scale ranging from molecule to object. Applications range from the characterization of plants, organs, and biopolymers to plant-derived bioresources. BIBS hosts four analytical labs, i.e. chemical phenotyping, mass spectrometry, microscopy, nuclear magnetic resonance and one bioinformatics lab.

BIBS know-how and expertise in time-domain low field NMR spectrometry were used to study:

- **determinants of starch digestion.** The mobility of water and starch protons was consistently related to the macromolecular composition of the glucan chains and to the ultrastructure of the wheat starch granule [1] (French-Australian project).
- **transformation bioprocesses of cereal-based product.** The effect of solid loading on the behaviour of bacterial and fungal xylanases towards white flour, ground whole grain and bran were studied [2]. Four water mobility domains in all the fractions were determined. The porosity (7.5 - 15 nm range) associated with the more mobile water domains could be considered as critical for enzyme diffusion in the cell wall network [3].
- **microstructure of gluten network during dough mixing.** The TD-NMR was used to track water distribution in dough during mixing for different mixing times and hydration levels [4], and proteins and arabinoxylans contents [5] (ANR EVAGRAIN).
- **lignocellulosic biomass recalcitrance.** Impact of hot water pretreatment of maize stem internode [6] or wood [7] on water mobility in relation with pore size, and thus enzyme accessibility.
- **porous water-resistant cellulose-based materials.** The appearance of a new domain of water mobility was linked to the structuring of cellulose-based gel during freeze-casting [8] .

The NMR lab also hosts a 400 MHz vertical wide bore NMR spectrometer equipped with (*i*) microimaging accessory that enables non-destructive, in situ analysis of water distribution and mobility at the tissue level, as well as in plants and plant-based bioresources, and (*ii*) MAS solid-state accessory, to characterize the ultrastucture of polysaccharides and lignocellulosic biomass.

This overview of the key features of some of these studies on the characterisation of bioresources and the tools developed in Nantes demonstrates that BIBS is committed to developing solutions in synergy with other analytical techniques in order to contribute to the advancement of knowledge and a better understanding of phenomena related to bioprocesses.

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Microscopic insights into water-in-salt electrolytes: combining NMR relaxation with molecular dynamics

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Water-in-salt electrolytes are promising candidates for safer, high-voltage lithium-ion batteries, making it essential to understand lithium-ion dynamics at the molecular scale. Nuclear magnetic resonance (NMR) relaxometry offers valuable insights into the dynamics of electrolyte systems by probing nuclear spin relaxation. Many alkaline cations, including $^{7}Li^{+}$, relax predominantly through a quadrupolar mechanism arising from the coupling between the nuclear quadrupolar moment and the fluctuating electric field gradient (EFG).

In this study, we combine classical and ab initio simulations to investigate the dynamics of $^{7}Li^{+}$ relaxation in LiTFSI water-in-salt electrolytes. Electronic polarization effects are incorporated through the Sternheimer approximation, while long-time EFG fluctuations are sampled using classical molecular dynamics simulations. Overall, we demonstrate that the steep increase in the $^{7}Li^{+}$ relaxation rates with concentration is primarily driven by a slowdown in the collective EFG dynamics, whereas the fast inertial contribution associated with short-time local motions remains largely unaffected. We examine how the microscopic processes governing relaxation of $^{7}Li^{+}$ evolve with composition and how they are reflected in changes of the local solvation environment. Our analysis reveals increasingly correlated ion–solvent and ion–ion dynamics at high salt concentration, consistent with the emergence of ionic liquid–like behaviour in water-in-salt electrolytes.

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Beyond capillarity: NMR and MRI insights into textile wetting

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Managing humidity in textiles is a critical issue, as clothing comfort strongly depends on moisture regulation. Optimizing this property requires a thorough understanding of the mechanisms governing wetting and drying processes, such as washing, drying, and perspiration transport.

Imbibition in textiles is commonly described based on concepts developed for porous materials. When a liquid penetrates a fabric, water initially spreads along fibre surfaces (wicking) before filling the inter-fibre pores (wetting) [1-2]. However, in biopolymer-based textiles (e.g., cellulose in cotton or keratin in wool), moisture dynamics cannot be described solely in terms of capillary flow within the pore space. A significant fraction of water is also absorbed within the natural fibres themselves, where it binds to amorphous regions [3]. This bound water can represent up to 30 % of the dry mass, leading to fibre swelling and non-linear moisture transport behaviour.

Nuclear Magnetic Resonance (NMR) is uniquely suited to distinguish between these different water populations in natural textiles. Owing to their distinct molecular mobility, it enables the quantification of water absorbed within fibres and water residing in the pore space. In this work, we use ^{1}H NMR relaxometry to quantify and spatially localize bound and free water during wetting processes [4], and to differentiate the underlying mechanisms in real textile samples (wool and acrylic blankets). Magnetic Resonance Imaging (MRI) is further employed on larger samples to monitor the formation of bound water during vapor diffusion. The resulting profiles show that water is rapidly absorbed within the fibres and propagates into the material during the first hours following contact with liquid water.

Our results demonstrate that the presence of bound water fundamentally alters the overall moisture dynamics. Explicitly accounting for bound water is therefore essential for accurately modelling wetting and drying in textiles, with broader implications for understanding flow and transport in complex porous systems.

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Relaxation induced by iron oxyhydroxide particles

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The relaxation induced by superparamagnetic iron oxide nanoparticles (SPIONs) has been extensively studied and is now theoretically well understood [1]. It arises from the diffusion of water protons through the magnetic field inhomogeneities created by the nanoparticles. A broad variety of systems, often with sophisticated shapes or structures, have been synthesized, characterized and tested in MRI. SPIONs were initially used for their extraordinary ability to enhance transverse relaxation, achieving r_2 values as high as 750 $s^{-1}mM^{-1}$ at clinical magnetic fields (> 1 T). However, they present a significant drawback: their longitudinal relaxivity r_1 tends to decrease significantly at high magnetic fields, approaching zero. This leads to very high r_2/r_1 ratios, making SPIONs negative contrast agents and thereby reducing contrast specificity. To address this limitation, an alternative strategy is to explore iron oxyhydroxides (such as ferrihydrite, akageneite, and goethite [2]) as substitutes for magnetite nanoparticles.

In this work, we evaluate the NMR relaxation efficiency of akageneite, ferrihydrite, and goethite nanoparticles following extensive characterization, including electron microscopy, dynamic light scattering, magnetometry, and X-ray diffraction. Relaxometry measurements comprise longitudinal and transverse ^{1}H NMRD profiles acquired at different temperatures and, when possible, at varying pH values.

The relaxivity values obtained are relatively low, with large r_2/r_1 ratios at high magnetic fields, making these systems poor candidates for positive MRI contrast agents. The relaxation efficiency strongly depends on particle composition, with the best performance observed for commercial ferrihydrite particles (iron–dextran). Goethite and akageneite samples exhibit a pronounced decrease in r_1 with increasing field, with one or two dispersions, consistent with previous reports on commercial akageneite particles [3]. The NMRD profile of ferrihydrite particles displays a maximum r_1 at 25 MHz, with a shape similar to that observed for small SPIONs. However, fitting this profile using the standard diffusion model was unsuccessful and would, in any case, not account for the weak pH dependence observed. For all samples, r_2 increases with magnetic field strength, in agreement with previous studies on iron oxyhydroxide particles. While diffusion-mediated transverse relaxation is expected to scale with the square of the particle magnetization, this behavior is not observed here: instead, $1/T_2$ is proportional to magnetization for all samples. This suggests a significant contribution from proton exchange mechanism in transverse relaxation.

The exact mechanism of the relaxation induced by these iron oxyhydroxide nanoparticles remain to be fully elucidated. Further investigations using ^{17}O and ^{2}H relaxometry will be required. Such studies may provide new insights for the development of new iron-based particles.

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NMR Relaxometry of Trypsin: A Unified Approach to Spin–Lattice and Spin–Spin Relaxation Dynamics

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The molecular dynamics of trypsin were investigated using a combined approach based on ^{1}H spin-lattice and spin-spin relaxation measurements. Fast Field Cycling NMR (FFC-NMR) relaxometry (STELAR s.r.l., Mede, Italy) was employed to measure ^{1}H spin-lattice relaxation over a broad frequency range (10 kHz–10 MHz) and varying temperatures. These measurements were complemented by time-domain NMR (TD-NMR) experiments conducted at 18.5 MHz.

The study focused on mixtures of trypsin with H_2O and D_2O at 50 wt% protein concentration. The analysis revealed that ^{1}H spin-spin relaxation exhibits double-exponential behavior in trypsin H_2O systems and tri-exponential behavior in trypsin-D_2O systems. In contrast, ^{1}H spin-lattice relaxation was bi-exponential for both solvent environments. Notably, the fast component of spinspin relaxation corresponds to the spin-lattice relaxation process. Such multi-exponential relaxation behavior reflects the presence of distinct motional modes and environments within protein systems [1,2]. To interpret the relaxation behavior, several models were considered that relate relaxation characteristics to molecular dynamics across multiple timescales. The ^{1}H spin-lattice relaxation data can be described as a superposition of Lorentzian spectral densities characterized by different correlation times [2]. This approach has been widely used to analyze protein dynamics and internal motions [3].

The combined use of FFC-NMR and TD-NMR provides an intrinsic understanding of trypsin dynamics and structural stability under different solvent conditions. Isotope substitution (H_2O vs. D_2O) enables separation of water- and protein-derived contributions, which is particularly important given the comparable populations of ^{1}H nuclei in both components. Overall, the results highlight the presence of dynamical heterogeneity in the system and demonstrate the strong influence of solvent environment on protein behavior [4].

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Reconstructing the Relaxation Behaviour of the Fully Protonated IL [TEA][OMs] Using Deuterated Analogues

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Fast field cycling (FFC) NMR relaxometry is well known for probing molecular dynamics on a broad timescale in molecular and ionic liquids (ILs), where the latter are considered as 'molten salts' at room temperature consisting solely of ions.[1] Common high viscosities of these ILs enable probing of translational diffusion and rotational motions at NMR frequencies used in FFC, yielding self-diffusion coefficients and rotational correlation times. A majority of FFC studies on ILs focus on systems with proton-bearing cations and/or fluorine-bearing anions, where the dynamics in these liquids can be addressed ion-specifically by employing ^{1}H and ^{19}F NMR.[2] In fully protonated systems, where both ionic species contain protons, it is, however, no longer possible to disentangle the various relaxation pathways and ion-specific dynamics due to the lack of resolution at low frequencies. We demonstrate, using triethylammonium methanesulfonate ([TEA][OMs]) as a model system, that partial deuteration of either the cation or the anion can tackle this problem by reducing the relaxation pathways and thus enabling separate analysis of cation and anion dynamics. We support our approach by comparing the rotational correlation time of the protonated cation with high-field deuteron quadrupole relaxation measurements of the protic deuteron position in selectively deuterated [TEA]-d_1[OMs], which provide the reorientation time of the N–D bond vector.

In a second step, we can also quantify the relaxation contributions arising from cation-anion interactions in the fully protonated IL, by exploiting the ion-specific self-diffusion coefficients determined for the partially deuterated systems and calculated inter-ionic distances. Remarkably, for the first time we show, that this approach even allows reconstruction of the total relaxation rate observed experimentally for the fully protonated IL.[3]

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Poster 16

Dynamics of interfacial water molecules inside a mesoporous material as probed by NMR relaxometry: a multimodal approach

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The interfacial dynamics of water in a porous medium remain a multi-scale process. In the time domain ranging from 1 ns to several μs, NMRD appears as an experimental technique suitable for probing interfacial proton dynamics. However, analysis of R_1 dispersions raises some difficult questions related to the uniqueness of the model used to fit the experimental data. In this work, we propose a multimodal approach to analyze the dynamics of interfacial water molecules inside a mesoporous material, boehmite, a precursor of the catalytic support γ-alumina. Small-angle X-ray scattering, 3D digital image of the pore network, and numerical simulations are used to constrain the analysis of experimental NMRD dispersions.

It is observed that the origin of the surface magnetic fluctuations involved is mainly associated with the intra-dipolar Hamiltonian for H_2O and with the quadrupolar interaction for D_2O. Moreover, R_1 dispersions are associated with a population of water molecules that remain and diffuse in the proximal surface area near the pore walls for a very long time. Numerical simulations of water surface dynamics, carried out using a 3D numerical reconstruction of the Boehmite pore network, confirm the significant contribution of intra-dipolar interaction in the evolution of R_1. The overall dependence of R_1 on frequency depends on the value of water surface diffusion coefficient D_s and follows a simple rescaling withD_s. A good agreement with experimental data is found for $D_s = 10^{-10}$ m^2/s.

Finally, the possibility of having an experimental 3D geometric model of the porous solid allows for a quantitative analysis of the relationships between the spin-lattice relaxation process and the orientational properties of the pore surface. Some preliminary results on this last topic will be discussed.

NMR Relaxometry study of Pyridinium-Based Ionic Liquid Crystals: Effects of Chain Length and Hydration

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Nuclear magnetic relaxation dispersion (NMRD) measurements were performed on four pyridinium-based ionic liquid crystals (ILCs): 1-dodecylpyridinium bromide ([C12-pyr][Br]), 1-hexadecylpyridinium bromide ([C16-pyr][Br]), 1-dodecyl-2-methylpyridinium bromide ([C12-2-Pic][Br]), and 1-hexadecyl-2-methylpyridinium bromide ([C16-2-Pic][Br]). Measurements were carried out by combining Fast Field Cycling (FFC) NMR relaxometry and conventional NMR techniques, covering a frequency range from 10 kHz to 300 MHz [1,2]. All compounds were investigated in their pure form, while the two 2-methylpyridinium systems were additionally studied in aqueous mixtures containing 60 wt% water. This composition provides an optimal balance between hydrophobic tail aggregation and hydrophilic headgroup hydration, allowing a meaningful comparison between thermotropic and lyotropic conditions [3].

The NMRD profiles reveal systematic differences associated with both headgroup substitution and alkyl chain length, demonstrating that relatively small structural variations significantly influence molecular mobility and collective dynamics. Distinct relaxation features were observed in the smectic phases, indicating differences in mesoscale organization and dynamic behavior among the investigated systems [2,4]. The presence of water introduces additional complexity: although the hydrated samples retain liquid crystalline order at lower temperatures, they exhibit enhanced mobility and modified collective dynamics in the smectic phases compared with the those of the non-hydrated thermotropic systems. Ongoing analysis focuses on correlating relaxation behavior with phase structure and temperature-dependent molecular dynamics across multiple time scales [4,5].

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1D and 2D Inverse Laplace Transform Methods for TD-NMR Characterisation of Food and Battery Matrices

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Time-domain NMR (TD-NMR) relaxometry and diffusiometry experiments, combined with unidimensional (1D) and bidimensional (2D) Inverse Laplace Transform (ILT) processing, provide effective tools for probing molecular mobility, particularly in heterogeneous matrices. In addition, 2D ILT enables correlation of multiple experiments – such as T_1 –T_2 relaxation and combined relaxation– diffusion ($T_2 - D$) measurements – allowing overlapping components that cannot be separated by 1D ILT alone to be more resolved [1].

In this work, we demonstrate the application of 1D and 2D ILT processing to characterise food and battery matrices, including plant-based alternatives, dairy products, margarine, and slurry battery materials. Structural and dynamic properties of water and lipids were investigated using 1D ILT T_2 distributions together with 2D ILT T_1 –T_2 correlation and $T_2 - D$ maps. Measurements were performed on the MQC-R (23 MHz for ^{1}H from Oxford Instruments, High Wycombe, UK), with data acquisition and processing using NMR ProLab for MQC-R software (Green Imaging Technologies, Fredericton, Canada).

The results show that T_2 distributions provide insight into water mobility and lipid distribution during storage and cooking, linking directly to food texture and sensory properties. $T_1 - T_2$ maps further enhance component discrimination and structural interpretation, e.g., differences in T_1/T_2 ratios between similar plant-based products reveal variations in water confinement, with higher ratios indicating a tighter microstructure. $T_2 - D$ relaxation-diffusion mapping was also applied to characterise the mobility of water and lipid phases and to gain insight into margarine emulsion microstructure. In slurry battery systems, T_2 distributions reflect particle dispersion and mixing quality, distinguishing samples of identical composition but different mixing times, as shown in Figure 1.

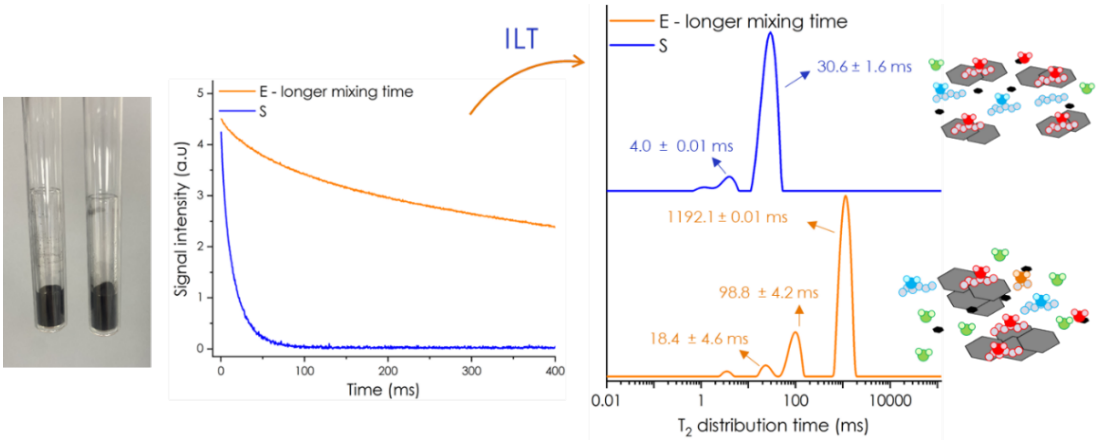

Figure 1 – Slurry battery with a similar composition but a different mixing time.

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Real-Time Noise Bias Compensation in Magnitude-Accumulated TD and FFC-NMR Relaxometry

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Magnitude-mode detection is frequently used in TD and Fast Field Cycling (FFC) NMR relaxometry to reduce sensitivity to phase instabilities and magnetic field fluctuations. By accumulating the absolute value of the complex signal over many scans, stable measurements can be obtained even for unstable fields. However, this approach introduces a systematic effect: Gaussian noise on the I and Q channels becomes nonlinearly transformed, producing a positive offset in the average magnitude signal. At low signal-to-noise ratio (SNR), this noise bias shifts the relaxation curve upward and distorts long-time behavior.

The statistical origin of this effect lies in the fact that Gaussian noise in the quadrature channels leads to a Rician-distributed magnitude signal. In the absence of true magnetization, the distribution reduces to Rayleigh statistics, resulting in a strictly positive mean value proportional to the noise standard deviation [1-3]. Consequently, even when the physical magnetization decays to zero, the accumulated magnitude signal approaches a finite plateau. In relaxation experiments, this causes systematic underestimation of T_1 and T_2 values and may obscure weak components in multi-exponential analysis.

In this work, a modular noise debiasing framework is integrated directly into the acquisition and evaluation workflow a new NMR platform what we have named as `Storm6`. The noise variance is estimated from reference acquisitions performed without RF excitation under identical receiver settings. Based on this estimate, selectable correction models are applied either in real time or during post-processing. These include a Rician-based inversion method, a correction derived from accumulated magnitude statistics in FFC-NMR instrumentation, and a power-based model suitable for low-SNR relaxometry data.

Simulations and experimental datasets were analyzed under varying SNR conditions and unequal noise variance between I and Q channels. When the noise power ratio remains within a moderate range and SNR exceeds approximately two, the corrected signal converges reliably toward zero at long delay times. Application of the correction improves exponential fit convergence and stabilizes relaxation parameter estimation, particularly in the slow-decay regime. The procedure compensates only for the systematic offset and preserves stochastic fluctuations, ensuring reliable uncertainty evaluation.

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Poster 20

FFC-NMR method for acquisition of T_1–T_2 maps at different relaxation fields

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Fast Field Cycling (FFC) NMR relaxometry is a powerful technique for probing molecular dynamics through magnetic-field dependent longitudinal relaxation. While conventional FFC measurements provide nuclear magnetic relaxation dispersion (NMRD) profiles and T_1 distributions, the characterization of transverse relaxation under field-cycling conditions has been wrongly considered technically limited.

In this work, we present the development of a multidimensional FFC-NMR methodology and demonstrate the capability of generating field-dependent T_1–T_2 correlation maps, thus extending relaxometric insights into a frequency-resolved multidimensional framework.

The proposed approach combines Fast Field Cycling relaxometry with CPMG-based measurements through dedicated acquisition protocols, enabling the generation of T_1–T_2 maps at different relaxation fields. The methodology is demonstrated using Parmigiano Reggiano cheese as a representative complex food matrix.

The resulting field-dependent T_1–T_2 maps provide enhanced characterization of molecular dynamics compared with conventional one-dimensional relaxometry approaches.

The results demonstrate the feasibility of multidimensional FFC NMR T_1–T_2 relaxation maps experiments and offers additional methods for investigating complex systems in food science, polymers as well as porous materials soft matter.

Data analysis and graphical representation has been done by means of MUpen2D and "MUpen tool" Software developed by University of Bologna https://shorturl.at/kXCpW

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Connecting Solvent Relaxation and Flow Activation Energies in Carbon Black Gels

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Suspensions of carbon black particles in oil provide a model system for attractive colloidal gels, where a space-spanning network forms through reversible physical interactions. While such systems are most often characterized from the particle-network perspective using rheology, we instead probe the complementary solvent dynamics using time-domain low-field NMR. We investigate carbon black gels over a broad range of particle volume fractions ($0 < \phi < 4$ %) and temperatures (5-70 °C). The transverse relaxation signal measured via Carr-Purcell-Meiboom-Gill (CPMG) sequences is well described by a stretched exponential, from which we extract both a characteristic relaxation time T_2 and a stretching exponent that depends on particle concentration, reflecting increasing dynamical heterogeneity. For all samples, the characteristic relaxation time T_2 follows an Arrhenius-type temperature dependence. The associated activation energy decreases from 27 to 23 kJ mol^{-1} as the particle volume fraction increases beyond the gel point. For weak gels, this activation energy quantitatively matches that obtained independently from rheological measurements through time–temperature superposition of flow curves. At higher particle concentrations, however, the activation energy inferred from rheology becomes smaller, highlighting the growing contribution of interparticle interactions to the mechanical response. Overall, these results demonstrate that low-field NMR provides direct insight into solvent dynamics in colloidal gels and reveal how the solvent contribution to macroscopic flow progressively competes with that of the particle network.

Real-Time Multi-Exponential Component Analysis in TD and FFC NMR Relaxometry

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Fast Field Cycling (FFC) and Time-Domain (TD) NMR relaxometry are widely used to study molecular dynamics in heterogeneous systems such as porous media, polymers, foods, and biological tissues. In many practical cases, longitudinal relaxation cannot be described by a single exponential decay, since different molecular environments contribute distinct relaxation components. Although multi-exponential fitting is well known and routinely applied in analysis, it is often carried out only after the experiment is completed, requiring export of data to external software and repeated manual processing.

During routine FFC-NMR measurements, particularly when acquiring full NMRD profiles, users may recognize only after several hours that additional components are needed or that experimental parameters should have been adjusted. This separation between acquisition and analysis creates a practical bottleneck, increases overall experimental time, and can delay informed scientific decisions.

In this work, multi-exponential fitting is implemented in real time during FFC experiments and high-field, variable-field relaxometry [1] by integrating a flexible fitting engine [2] directly into the acquisition environment of Storm6 platform, Mono-, bi-, and tri-exponential models, as well as user-defined functions, are supported. At each magnetic field value, the relaxation curve is fitted immediately after acquisition, and the extracted relaxation rates and component weights are updated live to construct the evolving NMRD profile. This allows early identification of multi-component behavior and timely adjustment of experimental parameters when required.

The approach was validated on heterogeneous samples where mono-exponential analysis produced systematic deviations. Real-time visualization reduced post-processing time and supported more efficient experimental workflows. Ongoing work focuses on uncertainty estimation and regularization strategies to further improve robustness of real-time multi-component analysis.

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Low-Field Magnetic Resonance Fingerprinting Using Upgraded STORM6 Platform

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Keywords: solution NMR, low field NMR, materials, food,polymers, instrumentation.

Magnetic Resonance Fingerprinting (MRF) is a novel imaging technique that offers a rapid quantitative approach for magnetic resonance imaging (MRI). We show the adaptation of the MRF for time-domain NMR at low field, with the objective of accelerating NMR multiparametric analysis for a wide range of applications, which at present necessitate the acquisition of multiple NMR sequences. The use of a pseudo-random RF sequence results in the generation of a unique signal, or "fingerprint", for differing NMR parameters (i.e. T_1, T_2). The matching of these fingerprints against a precomputed dictionary of synthetic signals enables MRF to identify the NMR parameters. In order to accomplish this task and ensure the robustness of the data analysis, RF pulse sequences can be customized for use with laboratory instrumentation.

The acquisition apparatus consisted of a Stelar NMR console connected to a 0.5 T permanent magnet, using 10 mL of 2 mM $MnCl_2$ as sample. The MRF sequence implemented in this study was based on an IR-bSSFP scheme (>1000 RF pulses, flip angle pattern as described in [1], pulse spacing TR = 1 ms, repetition time = 4 s, 16 scans). This upgraded Stelar configuration enabled the use of over ten times more RF pulses compared to previous implementations [3], and more than 3 times compared previous implementation of Stelar configuration [4] enhancing the richness of the acquired signal.

The MRF signals were simulated with an in-house MATLAB toolbox (MARSS) [2]. A fully connected Neural Network (NN) could be designed and trained by adapting the Deep Learning approach presented in [5]. Experimental data showed that B_0 and B_1 inhomogeneities strongly influenced signal modulation, and a procedure to characterize the B_0-B_1 correlation function was established to circumvent this issue.

The preliminary results obtained thus far suggest that low-field nuclear magnetic resonance (NMR) relaxometry is an evolving field of research. The findings indicate the potential for the development of analysis techniques for materials that are versatile and can be employed for a wide range of purposes.

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The Art of Model Fitting: Multiple Data Sets and User Interface Design

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Model fitting is widely used across scientific disciplines, but existing solutions often lack flexibility, accessibility, or long-term sustainability. This work presents the OneFit-Engine (OFE) [1], a standalone and extensible framework derived from the web-based fitteia® platform [2,3]. OFE provides a model fitting core without a graphical interface, enabling both command-line use and web-service operations, as well as integration into user-defined applications [4-7]. It supports arbitrary models and advanced model fitting strategies, including individual, global, and hybrid fitting of multiple datasets. The engine incorporates robust least-squares minimization routines and extends existing methodologies through improved computational performance and flexible model handling. The framework is demonstrated through several application examples, highlighting its capability to handle complex data analysis problems across different scientific domains. By combining efficiency, modularity, and open accessibility, OFE provides a versatile environment for model fitting, facilitating reproducibility, collaboration, and application across diverse scientific problems.

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Impact of surface coating on ^{1}H-NMRD of aqueous suspensions of superparamagnetic nanoparticle: a Monte Carlo study

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Superparamagnetic nanoparticles are magnetic monodomains in which all electron spins are aligned, resulting in a large magnetization. In aqueous suspension, these nanoparticles induce significant variations in proton spin relaxation rates, making them suitable as contrast agents in MRI. Over the past decades, it has been demonstrated that the dominant relaxation mechanism in such systems arises from the bulk diffusion of water molecules (outer-sphere mechanism) and from the interaction of proton spins with the magnetic dipolar field generated by the huge magnetic moments of these nanoparticles [1].

In current theoretical relaxation models, water molecules are assumed to diffuse freely and homogeneously around nanoparticles, which are modelled as impenetrable spheres. However, this is a simplification of real systems, as nanoparticles are generally coated with a layer that prevents their aggregation and ensures their colloidal stability. Several experimental studies have shown that coating layers – particularly their nature and thickness – affect their relaxation rates and their NMRD profiles [2-4]. Therefore, we investigate in this work the effect of nanoparticle coating on NMRD profiles using Monte Carlo simulations.

We extend a previously proposed T_1-T_2 simulation methodology [5] by incorporating a coating layer surrounding the nanoparticles. The coating is modelled as a spherical shell characterized by a homogeneous reduced water diffusion coefficient, such that proton spins entering this region experience slower movement. Our preliminary results indicate that sufficiently thick coating combined with low diffusion coefficients lead to an increase of longitudinal and transverse relaxation rates. Furthermore, the shape of the NMRD curves are impacted by the presence of the coating layer, suggesting that NMRD may serve as a valuable tool for characterizing nanoparticle coatings.

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FFC-NMR and Rheology Measurements of Chlorotrifluoroethylene Oligomers

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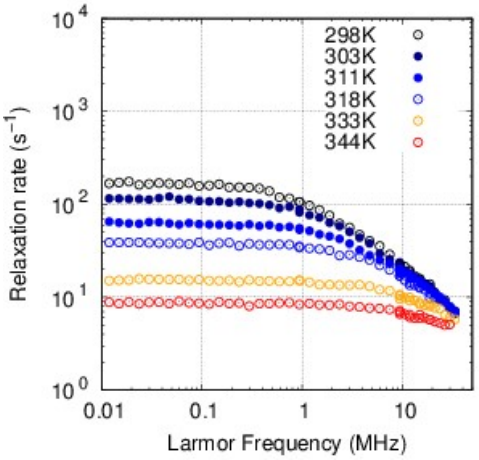
Polychlorotrifluoroethylene (PCTFE) is one of the oldest synthetic fluoropolymers, known for excellent barrier properties [1] . Its short oligomers are available in various forms (oil, wax, grease) and are used as inert lubricants. Those forms arise from the rapid increase in viscosity with oligomer size, which is quite different from the case of n-paraffins [2]. Although these characteristics have been discussed in relation to the internal rotation and free volume of the oligomers, further studies on these issues are scarce. We expected that liquid CTFE oligomers could be a model system to understand the structure and dynamics of fluoropolymers in the solution phase and attempted FFC-NMR and rheological measurements.

Halocarbon Oil 200 (Halocarbon Products Corporation, U.S.A.) was used as received. Spin-lattice relaxation rates of 19F were measured using a Spinmaster 2000 FFC-NMR relaxometer (Stelar, Italy). ^{19}F-NMR spectra were measured using an ECZ-600R NMR spectrometer (JEOL, Japan). Viscoelasticity was measured using a TriPAV high-frequency rheometer (TriJET, U.K.) over $10 - 10^4$ Hz.

Based on the relative intensities of the terminal peaks in the 1D ^{19}F-NMR spectrum, PCTFE was estimated to be a heptamer on average. Complex viscosity was measured between 298 and 323 K, and master curves of storage and loss modulus were obtained by frequency-temperature superposition. While $G''(\nu)$ obeys a power law with the index $\sim 3/4$, $G'(\nu)$ shows a low-frequency plateau that increases with temperature. These features are characteristic of a semiflexible polymer network [3] as observed in F-actin networks [4]. Spin-lattice relaxation rates are plotted in the figure, and a master curve obtained from susceptibility plots $\nu R_1(\nu)$ of spin lattice relaxation rates by FTS changes its index from ~ 1 to $\sim 1/4$ with increasing frequency, implying the absence of chain entanglement and insignificant contribution of intermolecular relaxation process. Apparent activation energy estimated from an Arrhenius plot of the shift factors of $\nu R_1(\nu)$ was 56 kJ mol^{-1}, which is fairly close to 63 kJ mol^{-1} obtained from those of $G''(\nu)$. Further discussion of the relationship between the two relaxation measurements will be presented in the poster.



Spin-lattice relaxation rates of HO200.

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