



## Field-cycling NMR relaxometry of viscous liquids and polymers

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### List of abbreviations and symbols

AAO	anodic aluminium oxide	PPG	polypropylene glycol
BPP	Bloembergen, Purcell, Pound	PVME	polyvinylmethylether
CD	Cole–Davidson	TNB	trinaphthylbenzene
CHB	chlorobenzene	TTS	time–temperature superposition
DD	dipole–dipole	$\beta_{CD}$	stretching parameter of Cole–Davidson function
DE	Doi/Edwards	$C^{(l)}(t)$	collective reorientational correlation function of rank $l$
DM/FPI	double monochromator/Fabry–Perot interferometry	$C^{DD}(t)$	dipolar correlation function
DQ	double quantum	$g^{(l)}(t)$	single-particle reorientational correlation function of rank $l$
DS	dielectric spectroscopy	$D$	translation diffusion coefficient
FC	field cycling	$G(\ln \tau)$	distribution of correlation times
FTS	frequency–temperature superposition	$J(\omega)$	spectral density
LJ	Lennard–Jones	$M_c$	critical molecular mass
LS	light scattering	$M_e$	entanglement molecular mass
MCT	mode coupling theory	$M_R$	mass of Rouse unit
MD	molecular dynamics	$N$	number of monomeric units
NS	neutron scattering	$\eta$	viscosity
OKE	optical Kerr effect	$\langle \mathbf{r}^2(t) \rangle$	mean square displacement
OTP	o-terphenyl	$\tau_\alpha$	correlation time of glassy dynamics
PB	polybutadiene	$\tau_s$	segmental (local) correlation time of polymer dynamics
PC	propylene carbonate	$T_g$	glass transition temperature
PCS	photon correlation spectroscopy	$T_m$	melting temperature
PDMS	polydimethylsiloxane	$\chi''(\omega)$	normalized imaginary part of susceptibility
PEO	polyethylene oxide	$\chi''_{DD}(\omega)$	“dipolar susceptibility” defined in Eq. (22)
PG	propylene glycol		
PI	polyisoprene		

## 1. Introduction

Field-cycling (FC) NMR relaxometry is a very important source of information on dynamical and structural features of molecules. It is especially well established for liquids and polymers. By performing relaxation experiments versus frequency motional processes of different time scales are detected. This can be achieved by electronic or mechanical FC NMR relaxometry; in both cases the external magnetic field is “switched” between a variable relaxation field and a constant detection field. A wider use of the electronic FC method became possible due to commercial availability of FC STELAR spectrometers [1]. Further instrumental developments are under way [2]. By using such spectrometers one can measure nuclear spin relaxation in the range of 10 kHz to 20 MHz (for  $^1\text{H}$ ). In special cases including conventional NMR spectrometers the range can be extended from 1 kHz to 500 MHz. When discussing frequency dependent relaxation studies one should also mention the concept of  $T_{1\rho}$  experiments [3] which can be treated to a certain extent as a counterpart of low frequency FC NMR experiments.

The most common way to employ FC relaxometry is to perform  $^1\text{H}$  spin–lattice relaxation studies. Other frequently investigated nuclei are  $^2\text{H}$  and  $^{19}\text{F}$ . One can also apply the FC technique to  $^{31}\text{P}$ ,  $^7\text{Li}$ , and  $^{111}\text{Cd}$  [1]. This method is also used for spin–spin relaxation studies. In the case of  $^1\text{H}$  and  $^{19}\text{F}$  the relaxation processes are driven by dipole–dipole interactions, while for  $^2\text{H}$  the relaxation mechanism is quadrupolar. The measured relaxation rates (times,  $T_1$  and  $T_2$  for the spin–lattice and spin–spin relaxation processes, respectively) are given as linear combinations of spectral densities, which are Fourier transforms of

corresponding correlation functions encoding information on the molecular dynamics. To fully benefit from the spectral features of the NMR relaxation data and to compare them with the results of other methods one can analyse the NMR relaxation results in the susceptibility representation. We shall adopt this approach in our review.

The review is devoted to recent applications of FC  $^1\text{H}$  NMR relaxometry to study cooperative dynamics of viscous liquids and polymers. The “local” dynamics in these systems is governed by the glass transition phenomenon. The presentation begins with simple liquids progressively discussing dynamics of short chain polymers (the short chain limit corresponds to the case of simple liquids), polymers of different chain lengths and eventually ending with the issue of polymer dynamics in confinement. The NMR results are discussed in a comparative way with those from other NMR techniques, as well as from dielectric spectroscopy (DS) and light scattering (LS). Such a joint analysis provides a more comprehensive picture of the dynamics in complex systems.

Special attention is drawn to the role of the intermolecular dipolar interaction which allows information about translational diffusion in viscous liquids to be obtained, *i.e.*, translational diffusion coefficients can be determined, which makes NMR relaxometry an alternative to field-gradient NMR. Another large part of the review is devoted to accessing the dipolar correlation functions of polymers and their interpretation by means of polymer theories, in particular the tube–reptation model. Here, we will also refer to recent double quantum  $^1\text{H}$  NMR results which allow the dynamic time window of FC  $^1\text{H}$  NMR relaxometry to be considerably extended. Applying frequency–temperature superposition (FTS) as is usually done in rheological studies of polymers, *i.e.*, assuming

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