

Application note

Inversion of Multi-component FFC-NMR relaxation decays

Abstract This note describes the possibility of inverting NMR decay signals (longitudinal or transverse relaxation decay) using the UPEN (Uniform-Penalty) algorithm [1].

The use of the inverse Laplace transform (ILT) to investigate NMR relaxation curves is a well-known problem in many fields of materials research.

The inversion makes it possible to obtain the distribution function of the relaxation times, which is directly connected to the physical proprieties of materials, such as porosity. This is a valuable investigation tool especially for heterogeneous systems where the relaxation efficiency is distributed over a wide range of values.

In the nuclear magnetic resonance dispersion distributions (NMRD-D), the distribution of relaxation times is measured at different Larmor frequencies (i.e., different applied magnetic fields) and the variation in those distributions can be examined as a function of the frequency. It can be used to monitor aggregation in fluids or in porous media and is particularly sensitive for probing molecular structure and dynamics.

This note describes the application of the inverse Laplace transform by UPEN on both simulated numerical data and on real experimental data.

Overview

The analysis of the nuclear magnetization decay is the base of low-resolution NMR.

The relaxation constants T_1 and T_2 can be determined by NMR experiments where the magnetization decays as a function of time. Generally the NMR relaxation decay is the sum of exponentially decaying components. It can be described by the following equation:

$$s(t) = \sum_{j=1}^M p_j \cdot e^{-\frac{t}{T_j}}$$

where M is the number of micro-domains with a p_j spin density and having the same relaxation time T_j . T_j can indicate the longitudinal relaxation time T_{1j} or the transverse relaxation time T_{2j} , according to the NMR experiment.

Depending on the system considered, M can range from 1 to a large number in highly heterogeneous systems.

For small values of M , the parameters p_j and T_j can be calculated by performing a non-linear least-squares regression on the experimental data.

In complex multiphase systems, when the decay constants have values close enough to each other, a continuous distribution may be a better representation of the proton spin population and the Laplace transform is the most widely accepted algorithm used to describe the NMR decay:

$$s(t) = \int_0^{\infty} P(\alpha) e^{-\alpha t} d\alpha \quad (1)$$

Given the NMR data $s(t)$, the aim is to determine the function $P(\alpha)$. Several algorithms and software packages can be found in literature for the numerical inversion of the Laplace equation (1). One of the most successful regularization processes applied to NMR relaxation data is UPEN.

Herein, this note describes a systematic analysis of UPEN using both simulated data and experimentally generated data.

Simulation Data

The theoretical distribution of relaxation times from which the simulated data are derived is shown in the following equation and Figure 1:

$$G(T) = 3 \cdot \exp\left\{-\frac{1}{2} \left[\frac{T-0.03}{0.007}\right]^2\right\} + \exp\left\{-\frac{1}{2} \left[\frac{T-0.2}{0.05}\right]^2\right\}$$

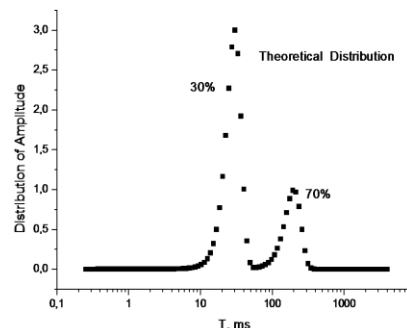


Figure 1. Theoretical distribution $G(T)$.

From $G(T)$ the theoretical signal $S(\tau)$ can be derived (equation 2 and Figure 2):

$$S(\tau) = \int G(T) e^{-\tau/T} dT \quad (2)$$

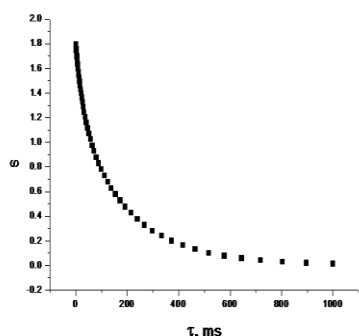


Figure 2. Theoretical signal $S(\tau)$.

$S(\tau)$ simulates a relaxation data signal and it can be elaborated according to the UPEN procedure (results shown in Figure 3).

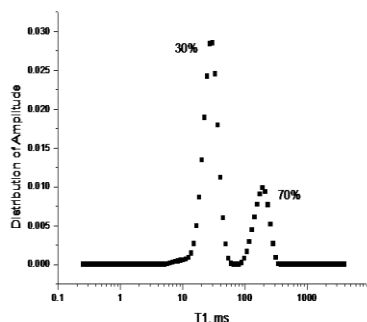


Figure 3. Distribution of relaxation decay $S(\tau)$ obtained by UPEN.

The distributions in Figures 1 and 3 are shown in a hybrid plot: the distributions with respect to time are plotted against the log-time, thus equal areas do not represent equal amplitudes. The real percentage amplitudes are indicated in the graphics.

Experimental Data

In real heterogeneous systems, nuclei belonging to different phases and with different line-shapes can contribute to the NMR signal. In this case the NMR decay takes into account the correct relaxation mechanism in a particular phase; the calculated distribution will appear as the convolution of different signals. It is possible to obtain information about the distributions of relaxation times of the longitudinal (T_1) and transverse (T_2) components of the nuclear magnetization, even if major assumptions are usually required for the interpretation of experimental relaxation data.

Rocks

^1H -NMR relaxation times of water-saturated rock samples are widely employed to characterize the architecture of pore space and to estimate petro-physical properties, such as permeability and irreducible water saturation. These parameters are used both in laboratory studies and in well logging (NML). The following figures show the T_1 distributions for two rock samples (Feldspathic quartz and Quartzarenite sandstone). Cylindrical rock samples ($\varnothing 1''$) were saturated with water under vacuum. Figures 4 and 5 report the corresponding MPI distributions.

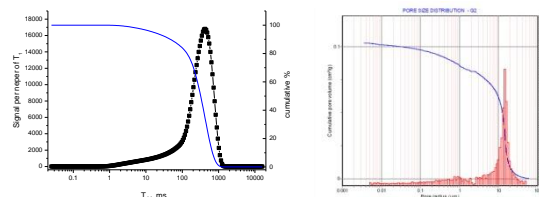


Figure 4. Feldspathic quartz sandstone: UPEN distribution of T_1 relaxation decay (left); MPI distribution (right).

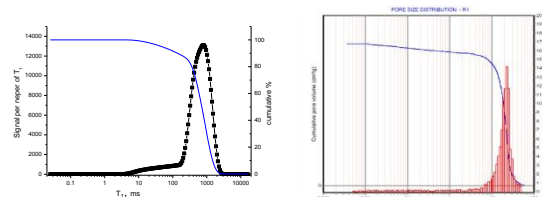


Figure 5. Quartzarenite sandstone: UPEN distribution of T_1 relaxation decay (left); MPI distribution (right).

The T_1 distributions were calculated from NMR relaxation decay curves by means of UpenWin. The MPI "pore-size distributions" show a behavior consistent with the T_1 distributions.

Foodstuff

Low-resolution nuclear magnetic resonance can also be useful to provide information on water localization and displacements within foodstuff.

The relaxation times give information about the modulation of magnetic interactions of water protons with the surrounding environment and are therefore dependent on the molecular re-orientation time of the water molecules. Moreover the relationship between the relaxation time and the dynamics of the magnetic interactions is dependent on the frequency of observation. The field dependence of T_1 provides information on the structure and dynamics of molecules.

Fast Field Cycling Relaxation can provide information on different types of water present in a cheese matrix, that is, free and bound water. It plays an essential role in determining the structure of proteins, polysaccharides and lipid aggregates, thus influencing the texture and stability of the final product.

Significant differences were detected in two different samples, taken from two different parts of **Parmesan Cheese** using a combination of FFC and UPEN.

The results are shown in figure 6.

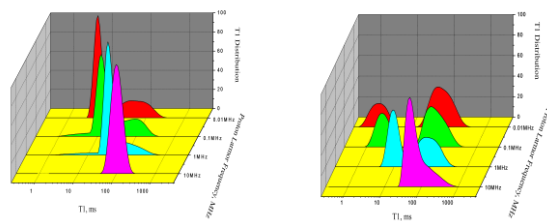


Figure 6. Upen T_1 distribution of samples of **Parmesan Cheese** taken from internal soft part (left) and from crust (right).

Polymers

NMR relaxation measurements provide a powerful method for investigating molecular motions in anisotropic systems. In particular, when several different motions are present, NMR measurements made as function of frequency can in principle give information about the amplitude and characteristic times for each of the motions. Furthermore different components may be encountered if protons belong to different molecules or if they are involved in different physical states.

Fast Field Cycling (FFC) NMR is a well-established method for studying molecular dynamics in condensed matter, based on determination of the frequency dispersion of the spin-lattice relaxation time $T_1(\omega)$ or relaxation rate $R_1(=1/T_1)$, called NMRD. Generally it reflects the spectrum of re-orientational and diffusional dynamics of molecules.

In NMRD-D, the distribution of relaxation times is measured at different Larmor frequencies (*i.e.*, different applied magnetic fields) and the variation in those distributions can be examined as function of the frequency to monitor aggregation and the collective effect (Figure 7).

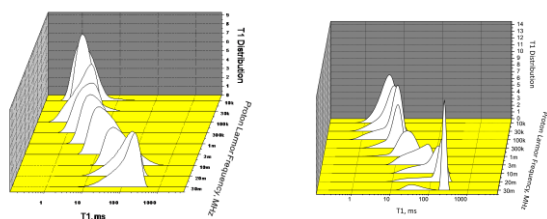


Figure 7. Comparison of two NMRD-D of two polymer samples (sample3 on the left and sample1 on the right) with different chemical structures.

From distributions we can get the mean T_1 , obtaining a NMRD profile weighted on the distribution. The results are shown in the figure 8.

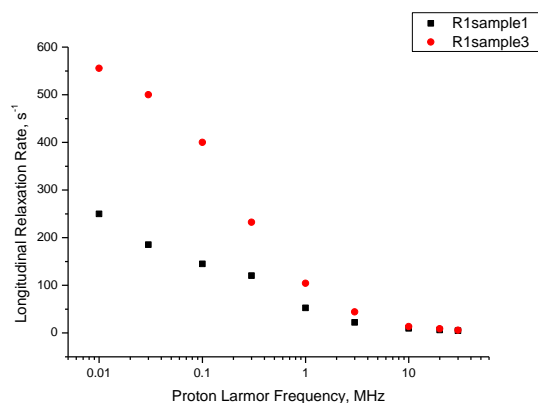


Figure 8. NMRD profiles weighted on the relative distributions of Figure 7.

Hetero-nuclei

It is possible also to carry out FFC NMR relaxation experiments directly on hetero-nuclei with low receptivity and detectability, and to evaluate the relative relaxation time distribution.

Figure 9 shows the Deuteron T_1 decays of a fuel cell membrane measured directly on a solid sample at three different magnetic fields (0.0023 T, 0.023 T and 0.5 T).

The decays show an evident multi-exponential behavior particularly at low field. The relaxation data were evaluated with discrete and continuous methods.

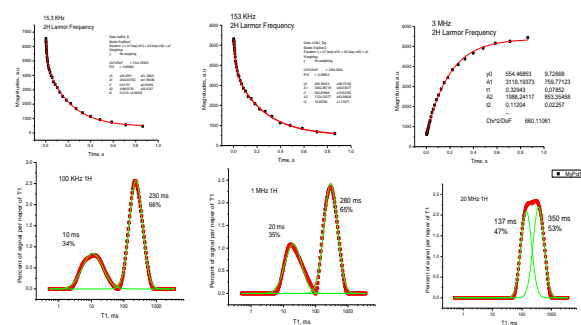


Figure 9. ^2H T_1 relaxation decay: discrete (top) and continuous (bottom) evaluation fit.

Figure 9 (below) shows the distribution curves obtained by UPEN, the green lines indicate the Gaussian de-convolution curves. The de-convolution process allows calculation of the relative percentage of the components and the evaluation of peaks corresponding to the relative T_1 .

Conclusion

Herein, a novel method has been presented using nuclear magnetic resonance dispersion distributions (NMRD-D) to measure the T_1 relaxation distribution profile as a function of the magnetic field, or the Larmor frequency of the nucleus. The technique is particularly sensitive to correlation times between tens of microseconds and tens of nanoseconds and it is useful to study molecular structure and dynamics.

UPEN software is a fast and efficient Laplace inversion algorithm. It also provides diagnostic information to help identify problems in the data such as effects of noise and resolution or apparent resolution of features of a computed distribution of relaxation times.

Ref

[1] Borgia G.C., Brown R.J.S., Fantazzini P. J. Magn. Reson. 147, 273 (2000)