Switching times and signal τ-dependence in FFC

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I. Introduction

There is a topic which, since the early days of FFC NMR relaxometry, occasionally crops up and causes *doubts about the correctness of the employed procedures*. It regards the interplay between two different FFC parameters:

- the field switching time (fixed) and
- the relaxation period τ (variable).

In particular, one might worry about the fact that during the switching period the sample finds itself in a field which varies over a wide range of values before settling to the desired relaxation field and, in addition, that the duration of its permanence at the relaxation field usually exceeds the τ value.

This Note gives a *mathematical proof* that the τ-dependence of the acquired signals is characterized by the 'correct' T_1, provided that the switching times and waveforms are the same throughout the whole multi-block experiment.

The basic pre-polarized FFC experiment proceeds as follows:

Phase 1. Pre-polarization interval t_p during which the sample magnetization (longitudinal) is allowed to build to a reasonably high value in a stationary polarization field B_p.

Phase 2. The so-called 'switching time' (s) during which the magnetic field changes to the value at which magnetization decay is to be measured. In general, the shape of the curve which the field follows when changing from B_p to B_r (the switching waveform) is considered unknown, even though on modern instruments - such as the Stelar FFC Relaxometer - it is quite accurately controlled. The reason is that there is at present no satisfactory theory permitting the exploitation of such knowledge for the improvement of the measured data.

At the end of Phase 2 the sample magnetization M has some value M_2 which depends in a complex way on the field history during both Phase 1 and Phase 2. We shall see later that we do not really care about this value, as long as

a) the field settles to the B_r value with the precision required by an NMRD profile (~1%),
b) the switching waveform is reproducible and
c) M_2 is large enough to acquire a signal with reasonable S/N ratio.

Phase 3. The so-called 'relaxation period' (τ) during which the field is held constant at B_r and the sample magnetization evolves in a way characteristic of the relaxation field. During a typical T_1 measurement this parameter - and only this parameter - is varied and the final acquired signal is plotted as a function thereof.

Phase 4. Another so-called 'switching time' (s'), required to bring the field to the acquisition value B_a at which the Larmor frequency of the nuclei matches the instrument's observe frequency. The sample magnetization of course changes also during this interval and it does so in a complex, field-dependent way. Again, the shape of the curve which the field follows when changing from B_r to B_a during this interval is considered unknown, even though on modern instruments it may be accurately controlled.

We shall see that we do not really care about this magnetization variation, as long as

d) the field settles to the acquisition value with a precision required by NMR (~10ppm),
e) the field switching curve is reproducible and
f) the magnetization retains enough 'memory' of the value it had at the beginning of this phase; if, in fact, SWT2 were too long, the magnetization would practically reach the equilibrium value corresponding to Bacq and the dependence on τ would be lost.

Phase 5. Application of a detection pulse sequence (e.g., 90^o pulse for a simple FID) and acquisition of the signal while the magnet stays at B_a. The signal intensity S after the pulse is estimated and plotted as a function of τ. The time constant of the resulting exponential transient curve is the desired relaxation rate at B_r while its remaining parameters are ignored.

II. Magnetization evolution during the experiment : mono-exponential relaxation

In order to better grasp the situation, let us see how the longitudinal magnetization M evolves in each Phase. It is, in fact, important to keep in mind that M is always evolving in some way - there is not a single moment when it would keep constant at some magical value.

We shall assume that, at any moment, M follows a first-order differential equation, trying to reach its equilibrium value M_e:

(1) $dM/dt = - r (M-M_e)$.

In a fixed field, this corresponds to a mono-exponential relaxation with relaxation rate r.

The problem is that both r and M_e depend on the current field value B. The equilibrium magnetization is, to a very high degree of precision, proportional to B, i.e.,

(2) $M_e = mB$

where m is a sample-dependent constant specifying the sample magnetization per unit field.

The relaxation rate r is a function of the field, r(B), whose shape is the object FFC relaxometry proposes to measure.

For simplicity, we assume that at the beginning of Phase 1 sample magnetization M is null (a condition which is usually assured by keeping the field at zero for a suitable recycling delay between scan repetitions).

During Phase 1 we have $B=B_p$ (apart from a short switching-on period which can be ignored) to which corresponds the equilibrium magnetization value $M_p=mB_p$. Eq(1) becomes

(3) $dM/dt = - r_p (M-M_p)$

with $r_p = r(B_p)$ and the starting values t=0, M(0)=0. Its solution is

(4) $M = M_p [1-\exp(-r_p t)]$.

At the end of Phase 1 (start of Phase 2), $M \equiv M_1 = M_p [1-\exp(-r_p t_p)]$, where t_p is the polarization time. One usually selects t_p in such a way that $r_p t_p \geq 4$ in which case M_1 is well approximated by M_p.

During Phase 2 the field changes according to some switching waveform B(t) which starts at B_p and terminates at B_r. Since Eq.(1) is invariant under time-shifts, we may temporarily set the time origin to the start of Phase 2, so that $B(0) = B_p$ and $B(s) = B_r$. Eq.(1) becomes

(5) $dM/dt = - r(B(t)) [M-mB(t)]$

with the starting value $M(0) = M_1$ derived above.

Even when B(t) is well known, the solution of this equation requires numeric methods.

Should the switching time s be very long compared to $r(B_r)$, the magnetization value M_2 at the end of Phase 2 would be the equilibrium magnetization at B_r, i.e., $M_2 = M_r = mB_r$. Such a situation is undesirable since it implies loosing the effects of pre-polarization and precludes any measurement (according to Eq.(1), there would be no further variation of M during Phase 3).

One must therefore seek a compromise. The time s must be long enough to cover the field-switching transient but not so long as to make the magnetization reach the vicinity of M_r.

Whatever the choice, the final result is always a value of M_2 which is intermediate between M_1 and M_r and therefore between M_p and M_r:

(6) $M_r < M_2 < M_p$.

The most desirable values of M_2 are those close to M_p. The measurement of $r(B_r)$ carried out in Phase 3 in fact consists of sampling M during its evolution from M_2 to M_r so that the precision of the measurement is proportional to the value[1] of M_2-M_r.

Apart from these considerations, the exact value of M_2 is irrelevant, provided that when the experiment is repeated, its is always the same. From a physical point of view, the end of Phase 2 is the true starting point of the actual measurement.

Since what matters is the final value of M_2 and everything else is just a preparatory treatment, it is clear that, for example, the pre-polarization need not be complete ($r_p t_p = 3$ is usually just as good as 4). Likewise,

[1] In FFC, the elementary S/N ratio is not so important, compared to the ratio of (M_2-M_r) to noise.

polarizing at higher fields leads to higher values of M_1 but should such gains be lost due to longer switching times, it might well be counter-productive.

During Phase 3 the field remains constant at $B=B_r$ and the handling of Eq.(1) becomes again easy. The result is the following expression for the value of M at the end of this phase:

(7) $M_3 = M_r + (M_2 - M_r)\exp(-r\tau) = a + b\exp(-R\tau)$,

where $R=r(B_r)$ is the relaxation rate at the field B_r. Ideally, it is this simple dependence that we try to measure, extracting the value of R and disregarding the values of $a=M_r$ and $b = (M_2-M_r)$.

During Phase 4 we are again in a complicated situation characterized by a changing field value. Setting time origin to the start of Phase 4, we have $B(0) = B_r$ and $B(s') = B_a$ and Eq.(1) becomes

(8) $dM/dt = - r(B(t)) [M - mB(t)]$

with the starting value $M(0) = M_3$. The signal intensity is proportional to the magnetization value at the end of Phase 4, given by the solution of Eq.[8] at the time s', i.e., $S \approx M_4 = M(s')$.

When the switching time s' is much shorter than the relaxation rates, M_4 is practically identical to M_3 and there is no problem. It is much more difficult to show that there is no fundamental distortion due to the field switching even when s' is comparable to the sample relaxation rates involved.

We shall now prove that the final τ-dependence of the signal is always of the correct form.

We shall start by dividing Phase 4 into n sub-intervals of equal duration Δ_k, with the k-*th* interval (k=1,2,...,n) starting at time $t = \xi_k$. Within each sub-interval we shall assume the field B to be constant and equal to $B_k=B(\xi_k)$. At the beginning of the first interval, the magnetization is M_3, given by Eq.[7] and has, with respect to τ,.the generic form $M=a+b.\exp(-R\tau)$. Using induction, we shall show that this functional *form* (including the numeric value of R but not those of a and b) remains invariant when passing from one interval to another.

Assume therefore that at the beginning of the k-th interval $M_k = c+d.\exp(-R\tau)$.

During the interval, M obeys the usual equation

(9) $dM/dt = - r_k (M-M_e)$,

where $r_k = r(B_k)$ and $M_e = mB_k$. Since B_k is assumed constant, so are r_k and M_e and the solution is easily found to be

(10) $M = M_e + (M_0 - M_e)\exp(-r_k t)$,

which, setting $t=\Delta_k$, gives the magnetization at the end of the interval as

(11) $M_{k+1} = c' + d'.\exp(-R\tau)$, with $c' = c.\exp(-r_k\Delta_k) + M_e[1 - \exp(-r_k\Delta_k)]$ and $d' = d.\exp(-r_k\Delta_k)$.

We see that, though the coefficients c,d have changed, the *form* of the τ-dependence of M (including the value of R) did not. Since this statement holds for every interval, it holds also for the magnetization at the end of the last interval, i.e., at the end of Phase 4.

We now remove the discrete step-function character of the switching waveform by letting the number n of sub-intervals go to infinity while keeping s' constant. Since the proof does not depend on n, the result remains valid also for the limit which describes the actual waveform. We have thus proved that

regardless of the field-switching waveform and of the value of the Phase 4 switching time, a longitudinal magnetization which follows a τ-dependence of the form $M=a+b.\exp(-R\tau)$ emerges from the field-switching period as $M=a'+b'.\exp(-R\tau)$, i.e., as one with the same exponential form and relaxation rate. What changes are only the numeric values of the coefficients a and b.

III. Reasons for the recurring doubts

If everything is so clear and error-free, why the occasional doubt keeps reappearing?
The answer involves several factors.

1. The FFC experiment is quite sophisticated. People tend to oversimplify it thinking that matters like those discussed above had not yet been analyzed in detail.
2. There is a semantic confusion between the 'switching times' s,s' which are arbitrarily settable *measurement parameters* and the field-settling times s_m which are *hardware parameters*. There is no direct functional relation between the two except for the requirement $s,s'>s_m$.
3. There is a semantic confusion between the value of τ and the total time t_r the sample is at the relaxation field B_r. Again, there is no direct relationship except for the inequality $\tau \leq t_r$.
4. When s is much larger than s_m, people look at the sequence and say: *'You vary your τ values between 0 and some maximum but the sample is actually at the field B_r for much longer times. This must sure make your results worthless'*. This is incorrect since the net effect of the excessive switching interval is to increase all τ values by a constant amount Δ. Starting with a functional dependence of the type $a+b.\exp(-R\tau)$ and replacing all τ values with $(\tau+\Delta)$, one ends up with $a+b'.\exp(-R\tau)$, where $b'=b.\exp(-R\Delta)$. The new τ-dependence is characterized by *the same relaxation rate* as the original one. The only effect is the reduction of the range parameter ($b'<b$) which, in the presence of noise, may undermine the *precision* of the R estimate but not its mean value.
5.

IV. Magnetization evolution during the experiment : multi-exponential relaxation

Suppose that the sample contains a number of components with different relaxation rates.

Since Eq.(1) is linear in M(t), the superposition principle holds and one can apply the mono-exponential analysis to each component separately and then add up the results. It follows that

a) *The measured relaxation rates of all components are correct*, regardless of the switching times and field-switching waveforms.
b) Unless the fastest relaxation time is still much longer than the field switching times, the *relative weights of the individual components may be unreliable* and possibly even inherently inaccessible (due to the difficulties in solving Eqs.[5] and [8]).

This means that, for example, the relaxation rates of a bi-exponential system come out correct but the relative weights of the two components may be wrong.

The situation is even more serious when attempting to measure samples with a continuous distribution of relaxation rates (e.g., water in some porous materials). Since in this case we essentially consider all relaxation rates to be present and try to estimate their relative weights, current FFC methods may lead to severe distortions of the resulting distributions.

The matter *merits further investigation* since with well-controlled switching waveforms the difficulties with Eqs.[5] and [8] might be overcome and reasonably accurate numeric corrections found.

V. Possible systematic instrumental errors

Until the end of Phase 2, there is nothing much that could lead to a systematic measurement error since any effect occurring before Phase 3 is unrelated to τ.

Discrepancies which might be related to Phase 3 are the obvious ones: calibration of the field, external environmental fields, etc.

Some concern, however, may be related to the field switching in Phase 4. In principle, *the field-driving circuitry may be subject to undesirable memory effects* (thermal drifts, capacitor discharge, charge carriers depletion in transistors, etc.). In such a case it might happen that at low values of τ the Phase 4 field switching waveform might be different than for long τ's. This would be a τ-dependent artifact and therefore a source of systematic error in R. This aspect of the hardware performance is one to which Stelar keeps paying particular attention.