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Nuclear Magnetization Evolution During the Switching Time in Field Cycling NMR

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Introduction

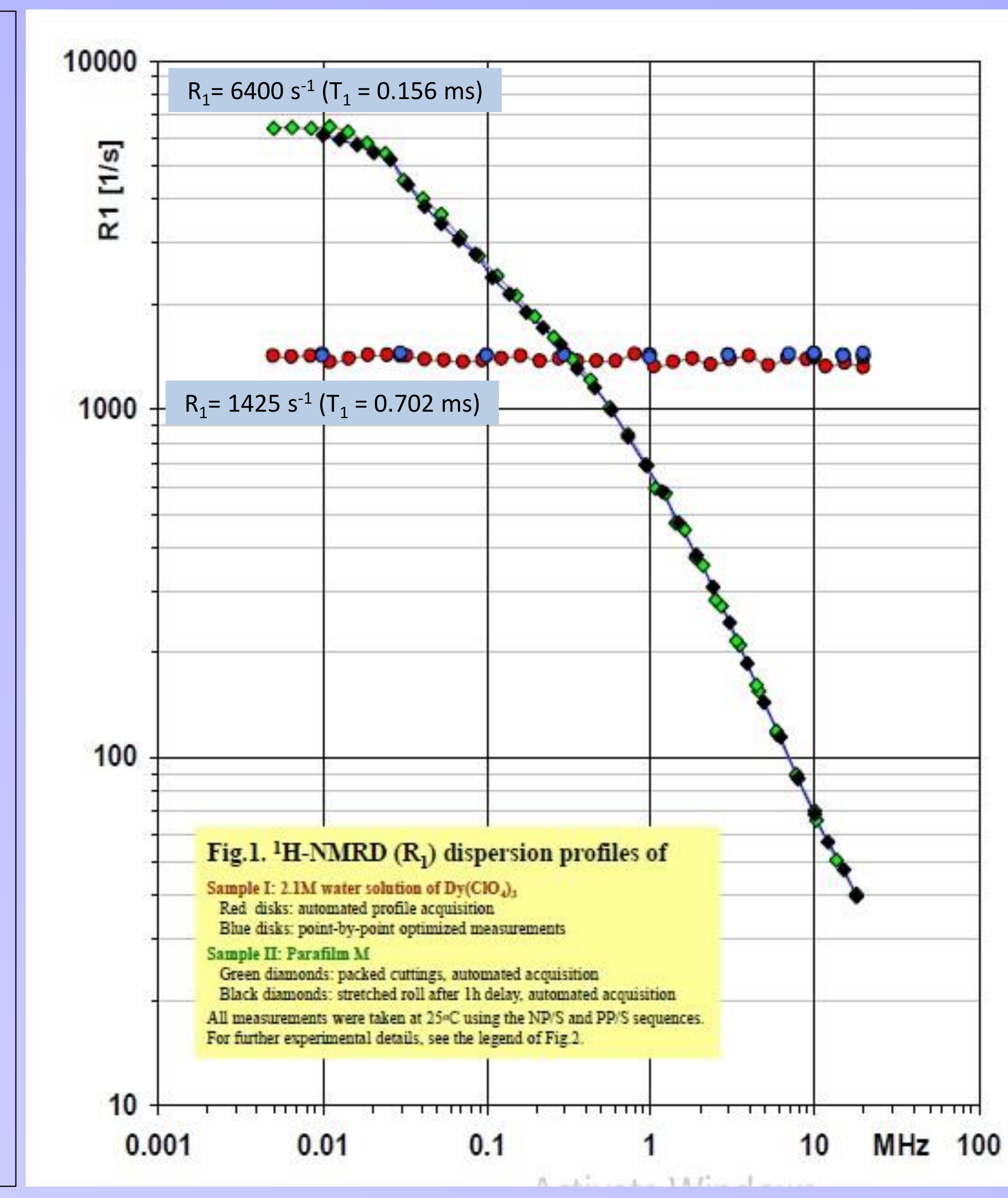
Magnetic Resonance techniques permit to measure the evolution of the longitudinal component of nuclear magnetization. In a suitable magnetic field B_{acq} the magnitude of this component ($M_{||}$) can be assessed at any desired moment by applying a 90-degrees RF pulse and acquiring the subsequent free-induction decay (FID). In static magnetic fields, various pulse sequence are used to measure either the longitudinal or the transverse "relaxation curves" and, in the most common mono-exponential cases, to estimate the relaxation rates R_1 and R_2, respectively. This is part of general NMR know-how and will not be discussed here.

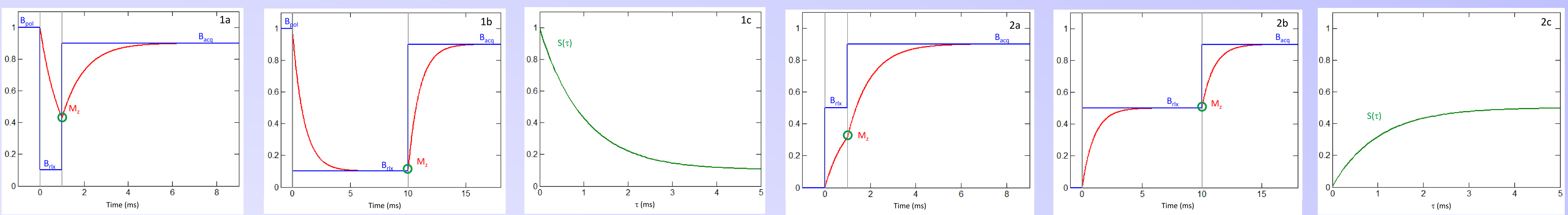
Relaxation theories show, however, that an isolated value of R_1 (or R_2) is not particularly useful, while a lot more information – in general regarding molecular dynamics – can be obtained from the dependencies of these values on temperature and/or on the strength of the magnetic field (B_{rlx}) in which the relaxation occurs. Of particular interest are the dependencies $R_1(B_{rlx})$ measured over several orders of magnitude of Brlx values, called **NMR dispersion curves**, or **NMRD profiles**. In general, such profiles are measured on instruments in which the magnetic field perceived by the sample can be commuted between four possible field values: zero (or a vary low one), a polarization field B_{pol}, , an acquisition field B_{acq} at which signals can be acquired, and a freely settable relaxation field B_{rlx} at which the relaxation rate of the sample is to be estimated. The *field switching* can be achieved by *mechanical shuffling* of the sample between areas with the different field strengths (the field-cycling, or FC-NMR methods), a procedure that is relatively slow (switching times of the order of 20-40 ms). Alternatively, the sample can be fixed and the magnetic field (generated by a current energizing a special solenoid) is commuted electronically by switching the current. The latter method, called fast-field-cycling or FFC-NMR) is much faster (switching times of the order of 1-2 ms) but incompatible with high-resolution NMR spectroscopy.

Whichever field switching method is used, it is evident that ideally the $T_1 = 1/R_1$ relaxation time of the measured sample should be much longer than the *switching times* compatible with the fastest achievable *field-slewing rates*. The fact is that the *switching waveshape* the field is following during the switching time may play a role in the phenomenon, and that it can be neglected only when the whole switching process occurs in a time negligible in comparison to the relaxation time T_1. This would mean that samples with T_1 smaller than several ms (R_1 in the range 100 – 1000) might not be reliably measured on present-day FFC instruments. Yet practical experience shows (see the Figure on the right) that this is not true – experience shows that one can measure samples with R_1 greater than 1000, in some cases even up to 10000 !!! Much depends upon the exact *field-switching waveshape*, with a large advantage deriving from keeping the latter linear (i.e., switching at a controlled *constant field-slewing rate*).

This poster indicates the way to analyze this kind of phenomena. The results lead to several interesting insights and the resulting capability to simulate them computationally opens new avenues to the optimization of the FFC technology. Unfortunately, the thematic is too broad to present in a single poster. A comprehensive article will follow which will include also the aspects we can not mention here for lack of space.

In the schematic graphic appearing in this poster, blue curves represent the magnetic field strength, red curves the nuclear magnetization, green curves the detected signal amplitude measured at the points indicated by a green circle. In all cases, the vertical size is normalized so that the highest achievable magnetic field, the magnetization in that field, and the corresponding signal all appear as having the value of 1.0 (it is the shape of the curves that matters here, not the absolute values).





The row of figures above exemplifies an idealized case of an FFC relaxation time measurement if switching times could be of zero duration. Figures 1a – 1c show the so called pre-polarized (PP) field-switching sequence, while Figures 2a – 2c refer to non-polarized (NP) sequence. We assume a field-independent relaxation rate of R = 1000. In the PP sequence, the polarization field B_{pol} corresponds to 1.0 (normalized), while the relaxation field B_{rlx} is 0.1. In the NP sequence (used for high relaxation fields B_{rlx} is 0.5, In all cases, the acquisition field B_{acq} is 0.9. The green circles marks the time where the signal is sampled (i.e., as soon as the acquisition field is reached). The relaxation intervals are τ = 1 ms in 1a and 2a, and τ = 10 ms in 1b and 2b. The figures 1c and 2c show the expected dependence of the measured signal on the tau value (1c for the PP case and 2c for the NP case). Note that in this idealized case, all the encountered curves are of simple exponential type and their computation is very simple.

Theory

In the mono-exponential cases in a fixed magnetic field, the magnetization evolution curves are well described by a simple exponential function (Eq.1). The longitudinal magnetization M(t) starts at some value M(0) and then **pursuits** the magnetic field, tending to decrease exponentially the initial difference $M(0) – M(\infty)$, where $M(\infty)$ is proportional to the field B (Eqs 2-3). Note that for display properties, it is possible to normalize the proportionality constant c to 1.0. Eqs 1 – 3 are compatible with the simple differential Eq.4 and the specified 'border' values at t = 0 and $t \rightarrow \infty$. Equation 4 stresses the point that the magnetization always tries to reach the equilibrium, field-dependent value c*B, and that it does so at a rate proportional to the current difference between c*B and M. The proportionality constant R is the relaxation rate.

Now, when the field B is variable, Eq. 4 gets modified as shown in Eq. 5 (proving that this passage is legitimate is not quite trivial, but it is true). Moreover, in those (very common) cases in which the relaxation rate is field-dependent, R=R(B), Eq. 5 generalizes further to Eq. 6 which is the final **master equation for the evolution of longitudinal nuclear magnetization in magnetic fields undergoing isotropic variations**. It is an instance of a **pursuit differential equation** which, in a general case, requires **numerical integration** to compute the resulting **pursuit curve**. Fortunately, the numeric approach is quite easy and we have the code to solve it for any given B(t) and R(B) input functions.

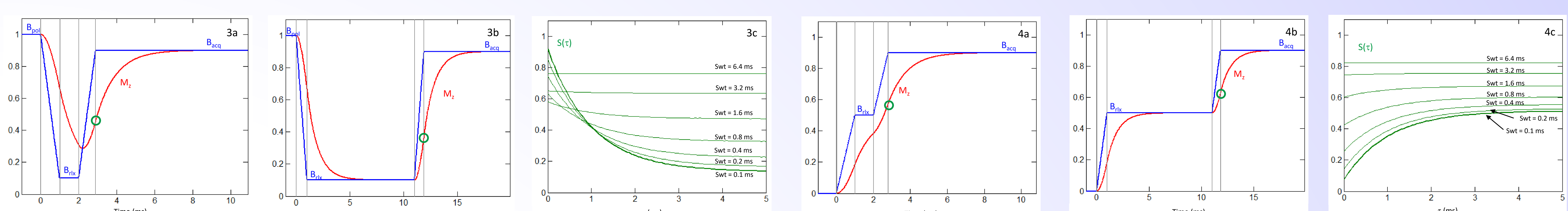
1. **M(t) = exp(-R*t)*[M(0) - M(∞)] + M(∞)**
2. **M(∞) = c*B**
3. **M(t) = exp(-R*t)*[M(0) - c*B] + c*B**
4. **dM/dt = - R*[M - c*B]**
5. **dM/dt = - R*[M - c*B(t)]**
6. **dM/dt = - R(B(t))*[M - c*B(t)]**

Simulations with constant $R(B) \equiv R_1 = 1000\ [s^{-1}]$, T_1 = 1 ms, which is of the same type (and of similar order of magnitude) as observed with the 1M dysprosium aquaions.

The Figures below exemplify the field pursuit curves which the magnetization follows when the field-switching waveform is linear. The graphs 3a – 4c are closely related to the graphs 1a – 1c above. The only difference is that the switching times are no longer zero. In Figures 3a, 3b, 4a and 4b the first switching, the one between the initial field (be it B_{pol} or 0) and B_{rlx}, is set to 1 ms, while the second one, from B_{rlx} to B_{acq} is computed so that the field slewing rate remains the same as in the first interval. In Figures 3c and 4c, the green signal-versus-tau curves are computed assuming a wide range of different switching time settings (some unrealistically fast, considering that today's technology which, even in FFC, can not switch between extreme field values in less than about 1 ms). Compared to the ideal case of infinitely fast switching, the differences one observes are:

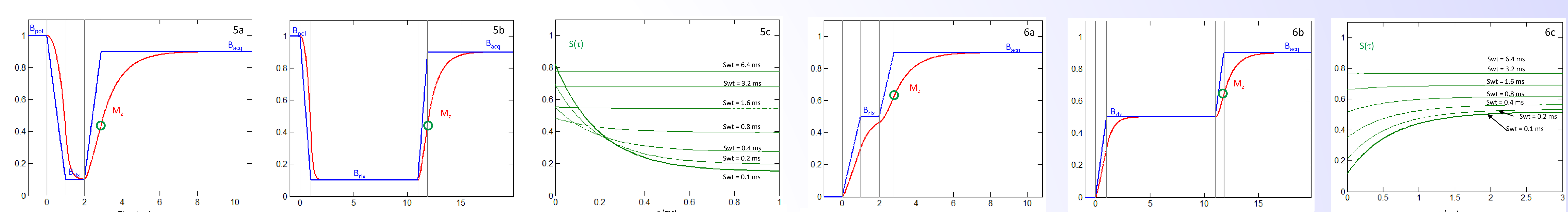
- During the switching intervals, M(t) evolves in a way which is neither linear nor exponential (in this simple case one can still derive an explicit solution of the master equation, but the brute force approach is simpler).
- With the switching time set to 1 ms, the measured signal values are substantially different and, though computable, not quite intuitive.
- The signal-versus-tau curves (which are those actually used to estimate the relaxation rate) are now quite strongly dependent on the switching time value. What does change are the initial and final values, not the relaxation rate coefficient (this may somewhat strain belief, but there exists a theoretical proof of that, and it is born out empirically). When field switching times are shorter than about 0.1/R, we have (almost) the ideal situation with maximum range of the measured signal-versus-tau curve. When the switching is slower, the signal curves get progressively flatter, making it progressively more and more difficult to estimate from them the relaxation rate coefficient. When the switching times get to about 1.0/R, the useful range is down by almost an order of magnitude. Which may be still sufficient to get reasonable results, but it implies much longer data acquisition times.

One more thing needs to be underlined, even though we have no graphic illustration for it: from our simulations it turns out that if the switching waveform is anything but linear, the deleterious magnetization loss (when switching down) or gain (when switching up) during the switching intervals becomes more serious and the estimate of R from the acquired data becomes more difficult.



Simulations with variable R(B), compatible with the experimental data for the parafilm shown at the top of this poster.

The series of simulated data show below corresponds in all respects to the preceding one, except that the relaxation rate R(B) is assumed to be even higher at B = 0 (R = 6400 [s^{-1}]) but than drops down following a rather steep dispersion curve which is characteristic of many important compounds and materials (many polymers, waxes, tissues, etc). Considering the fact that at very low fields the considered sample relaxes much faster than the preceeding one, one might expect considerable problems. However, the simulations as well as the experiments show that this is not so. The final differences in the green signal-versus-tau curves are surprisingly modest. This is no doubt due to the fact that, during the field switching, the interval during which the sample is exposed to a field in which it relaxes very fast is just a small fraction of the total switching time. It is thefore actually easier to measure an NMRD profile of a sample like parafilm than to mearure a sample like dysprosium aquaion, even if part of its dispersion profile reaches substantially higher relaxation rates.



B_{rlx}

Conclusions

We have developed a differential master pursuit equation which describes the evolution of longitudinal nuclear magnetization in varying magnetic fields, such as those present in FC-NMR.

We have also coded an Utility to numerically integrate this equation for even the most general cases.

With this tool we have confirmed earlier insights regarding NMRD measurements of samples with very high relaxation rates (T1 comparable to or smaller than the switching time).

We have also gained a number of additional insights.

There is more work in progress…

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