diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

# Multi-Pulsed Free-Induction NMR Signal from Spins Diffusing in a Spatially Restricted Flow

*Vladimir Lisy, Jana Tothova*

Department of Physics, Technical University of Kosice, Slovakia

Corresponding author: Vladimir Lisy, Department of Physics, Faculty of Electrical Engineering and Informatics, Park Komenskeho 2, 042 00 Kosice, Slovakia, E-Mail: vladimir.lisy@tuke.sk

(received 29 August 2009, accepted 07 September 2009)

## Abstract

A multi-pulsed free-induction NMR experiment is described theoretically for spins diffusing within a cylindrical capillary. The characteristic time for the particles to move on a distance of the capillary diameter is smaller or comparable to the time interval between the applied 90° rf pulses and the relaxation times entering the Bloch equations. In this case the spin diffusion is restricted and the classical solutions of these equations for unbounded media are not applicable. We have calculated the mean magnetization in the cross-section of the capillary after any of the rf pulses and found the induced NMR signal within the Bloch-Torrey-Stejskal theory for spins reflected at boundaries. The problem is extended by considering a possible macroscopic (plug and Poiseuille) flow of the fluid inside a capillary. It is found that with the increase of the rf pulse number, the maxima of the observed signals do not decay to zero but converge to a nonzero value. The proposed theory thus seems to be suitable for the description of experiments on systems rapidly relaxing due to diffusion and flow.

## Keywords

restricted diffusion, fluid flow, NMR, free induction, series of pulses

## 1. Introduction

In a number of physical, chemical, biological, and industrial processes particles diffuse in a confining medium [1-5]. When such particles encounter an interface, they may interact in different ways depending on their physical and chemical properties; in particular, the particle can be reflected. Its observed random motion is then additionally complicated by multiple reflections on the interface. From experimental probes for such observations, NMR is of special interest as being a non-invasive method to "label" Brownian trajectories of spin-bearing particles by using magnetic fields. From numerous NMR techniques, pulse methods, mostly different modifications of spin-echo, have found wide applications in the studies of diffusion [3-5]. In the present contribution, another NMR method will be considered. We shall describe the free-induction NMR experiment for spins diffusing in a thin cylindrical capillary. The method consists in the application of a series of identical rf pulses, each of which causes the 90° rotation of the magnetization of the sample. After the pulses the signal induced by the relaxing magnetic moment, the so called free-induction decay (FID), is registered. The use of this method has a long history [6]. We, however, believe, that in this work a new potential of this multi-pulsed technique will be shown, particularly in connection with investigations of systems rapidly relaxing due to (restricted) diffusion and convection.

Both these phenomena have been extensively studied for more than half a century. The origin of diffusive NMR phenomena can be attributed to Hahn's discovery of spin echoes in 1950 [7], and the first experiment on flowing water was described by Suryan in 1951 [8]. Later, these results have been developed by numerous authors that cannot be mentioned here (for a review on diffusion see e.g. [3], and for the flow characteristics measurements see [9, 10] and more recent works [1, 11] dealing also with NMR imaging in medicine and environmental science). However, in spite of this effort the description of flow in bounded media remains an open problem. This work is aimed to contribute to a particular problem of the diffusion of particles in a bounded area on the background of a flow. It will be shown that the multi-pulsed FID experiment could serve as an efficient tool to study such processes. The reason for this is in the fact that after a finite number of applied rf pulses the maxima of the observed signals are predicted to be constant (they do not decay to zero), which could be important for experiments on fast evolving systems [4].

The paper is organized as follows. First, the problem of finding the magnetization created by particles diffusing in a sample flowing through a cylindrical capillary is formulated within the Bloch-Torrey-Stejskal theory. Next, an auxiliary task for plug flow is solved exactly, neglecting the diffusion. The scheme of this solution is then used to solve a problem which includes both the diffusion and Poiseuille flow. We calculate the time dependent NMR signal induced after any of the applied 90° rf pulses and demonstrate that with the increasing pulse number the envelope of the signals approaches a constant value.

## 2. Restricted diffusion and flow in NMR

Soon after the first spin-echo studies of diffusion by NMR methods it was found [12] that the measured diffusion coefficient $D$ can depend on the parameters of experiment. This can happen if in studied systems particles cannot move on a large distance: the mean time for the nucleus to cross the sample in the direction $x$, where the sample size is given by $a$, is $t_x = a^2/2D$. If $t_x$ is much smaller than the relaxation time and smaller or comparable to the experimental time $\tau$, the effects of restriction on the diffusion should be essential. During the time $\tau$ the magnetization does not relax to its equilibrium value and spins "feel" the existence of the boundaries since they can travel across the whole sample and be reflected or absorbed by the sample walls. Then the apparent $D$ extracted from the data using formulas for unbounded media depends on $\tau$ which means that the theory should be improved. This can be done by using the Bloch-Torrey equations [13] with boundary conditions for magnetization. The effect of flow was included in these equations by Stejskal [14]. The modified equation for the magnetization in the case of incompressible fluid reads

$$\frac{\partial \vec{M}}{\partial t} + \left(\vec{\upsilon}\vec{\nabla}\right)\vec{M} = \gamma \vec{M} \times \vec{H} - \frac{M_x \vec{i} + M_y \vec{j}}{T_2} - \frac{M_z - M_0}{T_1}\vec{k} + D\Delta \vec{M} \ . \qquad (1)$$

Here, $\vec{\upsilon}$ is the flow velocity, $\gamma$ is the gyromagnetic constant, $T_1$ and $T_2$ are the longitudinal and transversal relaxation times of the spins, and $\vec{i}, \vec{j}, \vec{k}$ stay for unit vectors in the laboratory frame. Adding to the left side of (1) the term $\vec{M}\,\mathrm{div}\vec{\upsilon}$, the theory can be used also for compressible fluids. The external magnetic field consists of a strong static field $H_z$ and a much weaker high-frequency field $\vec{H}_1$, that is perpendicular to the axis $z$. This field changes with the frequency close to the resonance one. We assume that it oscillates with the Larmor frequency $\omega = \gamma H_z$, i.e., $H_{1x} + H_{1y} = H_1 \exp(-\mathrm{i}\omega t)$. The field $H_z$ is homogeneous, $H_z = H_0$, and it is assumed that the magnetization is given by the particles with equal Larmor frequencies. The coil of the length $L$ creates the high-frequency magnetic field along $x$ with the resonance frequency. The origin of the coordinate system coincides with the beginning of the coil. The coil at the same time serves as the detector of the free induction signal. To have a possibility to observe these signals, the duration of the 90° pulses must be much shorter than the spin relaxation times. Then the change of the magnetization during the action of the short pulses can be neglected. The time interval between the pulses will be denoted as $\tau$.

### 2.1. Plug flow, no diffusion

Now, let us turn to the problem of finding the signal of FID, first in a methodical case of constant velocity and in the absence of diffusion. Then Eq. (1) significantly simplifies. The flow is assumed in the $x$ direction. In the system rotating with the Larmor frequency and using the quantity $M_x + \mathrm{i}M_y = (\rho + \mathrm{i}m)\exp(-\mathrm{i}\omega t)$, it is possible to divide (1) into the separate equations for $\rho$, $m$ (projections of the magnetic moment onto the $x$ and $y$ axes of the rotating frame) and $M_z$. So, when the rf field is turned off, we have

$$\frac{\partial m}{\partial t} + \upsilon \frac{\partial m}{\partial x} = -T_2^{-1} m\,, \quad \frac{\partial M_z}{\partial t} + \upsilon \frac{\partial M_z}{\partial x} = -T_1^{-1}\left(M_z - M_0\right). \tag{2}$$

The fluid enters the coil with the magnetization $M_0$ along the axis $z$. Thus the boundary conditions are

$$m(x=0,t) = 0\,, \quad M_z(x=0,t) = M_0\,. \tag{3}$$

We have also to find the initial conditions after every of the pulses. The rf pulse rotates the magnetization vector in the plane perpendicular to the $x$ axis of the rotating frame. Neglecting all other processes during the pulse, we have after the first 90° pulse $m(x, 0) = M_0$, $M_z(x, 0) = 0$. After the $n$th pulse

$$m(x, n\tau - \tau + \Delta) = M_z\left(x, n\tau - \tau - \Delta\right), \quad M_z(x, n\tau - \tau + \Delta) = -m\left(x, n\tau - \tau - \Delta\right), \tag{4}$$

where $\Delta << \tau$ is the time of duration of the pulse. The $x$ projection of the magnetization also satisfies (2) for $m$, and $\rho(0, t) = 0$. After the first pulse $\rho(x, 0) = 0$ and since the rotation of $\vec{M}$ does not change this projection, we shall have $\rho(x, t) = 0$ for all times. To find $m(x, t)$ after the $n$th pulse, one must $n$ times step by step solve Eqs. (2) with the conditions (3) and (4). A simple way to do this is to rewrite the task using the Laplace transform in the $k$ space, e.g., for $m(x, t)$

$$m_k(t) = \int_0^\infty m(x,t)\exp(-kx)dx\,. \tag{5}$$

By this way first-order differential equations are obtained and easily solved together with the boundary and initial conditions. For example, after the first pulse one finds

$$M_z = M_0\left[1-\Theta\left(x-\upsilon t\right)\exp\left(-t/T_1\right)\right], \quad (6)$$

where $\Theta(x)$ is the Heaviside function. Since all spins within the volume of the coil of detection contribute to the observed signal $F(t)$, the signal is proportional to the integral over the coil length, so that we have $F(t) \propto L-(L-\upsilon t)\exp(-t/T_1)$ if $L > \upsilon t$, and $F(t) \propto L$ if $L < \upsilon t$. In the general case we solve the equations for all the time intervals of magnetization relaxation in the $k$ space:

$$m_{yk}^{(n)} = \frac{M_0}{k}\exp\left\{-\left(\gamma_2+\upsilon k\right)\left[t-\left(n-1\right)\tau\right]\right\} N_n, \quad (7)$$

where $N_1 = 1$ and for $l = 0, 1, 2,...$

$$N_{2l+2} = A\sum_{m=0}^{l}\left(-B\right)^m, \; N_{2l+3} = N_{2l+2} + \left(-B\right)^{l+1},$$

with $A = 1 - \exp(-\gamma_1\tau + \upsilon k)$, $B = \exp[-(\gamma_1+\gamma_2)\tau + 2\upsilon k]$, and $\gamma_{1,2} = 1/T_{1,2}$. Analogously the formula for $M_z$ is obtained. After the second and next pulses (for the first one see (6)) we have

$$M_{zk}^{(n+1)}\left(t\right) = \frac{M_0}{k} - \left[\frac{M_0}{k} + m_{yk}^{(n+1)}\left(n\tau\right)\right]\exp\left[-\left(t-n\tau\right)\left(\gamma_1+\upsilon k\right)\right]. \quad (8)$$

The inverse transformation of (7) yields $m(x, t)$, and after the integration over the volume of the coil we obtain the detected signal $F(t)$, normalized to $M_0$, in the time intervals $\left(n\tau-\tau, n\tau\right)$:

$$F_n(t) = V_0\exp\left(-t/T_2\right)\Theta\left(V_0\right), \quad n = 1,$$

$$F_n(t) = \exp\left\{-T_2^{-1}\left[t-(n-1)\tau\right]\right\}\sum_{m=0}^{l}(-1)^m\exp\left[-\left(T_1^{-1}+T_2^{-1}\right)m\tau\right]$$

$$\times\left[V_m\Theta\left(V_m\right)-\exp\left(-T_1^{-1}\tau\right)V_{m+1/2}\Theta\left(V_{m+1/2}\right)\right], \quad n = 2l+2,$$

$$F_n(t) = F_{2l+2} + \left(-1\right)^{l+1}\exp\left[\left(l+1\right)\left(T_2^{-1}-T_1^{-1}\right)\tau\right]F_1\left(t\right), \quad n = 2l+3, \quad (9)$$

where $LV_p = L-\upsilon\left[t-\left(n-1\right)\tau+2\tau p\right]$. Note that this description exactly corresponds to an older experiment performed on the mixture of $^3$He in He II [15].

After the $n$th pulse we have for the maxima of the detected signal, i.e. for $F_n$ immediately after the pulse (at $t = (n - 1)\tau$):

$$F_1(0) = 1, \quad (10)$$

$$F_{2l+2}\left[(2l+1)\tau\right] = \sum_{m=0}^{l}(-1)^m\exp\left[-\left(T_1^{-1}+T_2^{-1}\right)m\tau\right]\left[V_m\Theta\left(V_m\right)-\exp\left(-T_1^{-1}\tau\right)V_{m+1/2}\Theta\left(V_{m+1/2}\right)\right],$$

and $F_{2l+3}[(2l+2)\tau]$ is determined by $F_{2l+2}$ and an additional term $(-1)^{l+1}\exp[-(T_1^{-1}+T_2^{-1})(l+1)\tau]$, which decays with increasing $l$. Here, $V_p = 1-2\tau\upsilon p/L$. It is seen that with the increase of $n$ the sums in $F_n$ converge to a constant value. If $\upsilon_{\rm crit} = L/\tau > \upsilon > \upsilon_{\rm crit}/2$, we have $F_n = 1-(1-\upsilon\tau/)\exp(-\tau/T_1)$ for even $n$ > 1, and when $\upsilon > \upsilon_{\rm crit}$, $F_n = 1$. If $\upsilon < \upsilon_{\rm crit}/2$, the sum in $F_{2l+2}$ splits in two sums: the first sum (with $V_m$) is from $m$ = 0 to [$L/2\upsilon\tau$] and the second one runs from $m$ = 0 to [$L/2\upsilon\tau$ - 1/2] ([$x$] is the closest integer number which is lower than $x$). In these cases Θ functions equal to 1. The higher $m$ terms do not contribute to $F_{2l+2}$. Equation (10) can be easily evaluated numerically. Here we only give one more simple analytical result for the special case $\upsilon \to 0$ at $l >> 1$:

$$F_{2l+2}\left[(2l+1)\tau\right] \approx \frac{1-\exp\left(-\tau/T_1\right)}{1+\exp\left[\left(T_1^{-1}+T_2^{-1}\right)\tau\right]}. \tag{11}$$

**2.2. Poiseuille flow with restricted diffusion**

Often for the experimental conditions the Bloch model is not able to ensure the observed decay of the magnetization. Here we assume that another mechanism - diffusion - should be taken into account, not included in the previous consideration. Let the conditions of restricted diffusion are satisfied (as it is in the already mentioned experiment [15]) and the fluid flows through a circular tube with the radius $a$ along the axis $x$. In the system of coordinates rotating with the resonance frequency after the switching off of the rf magnetic field the projections of Eq. (1) on the axes $y$ and $z$ have the form

$$\frac{\partial m}{\partial t} + 2V\upsilon\left(r\right)\frac{\partial m}{\partial x} = -\frac{m}{T_2} + D_s\Delta m, \tag{12}$$

$$\frac{\partial M_z}{\partial t} + 2V\upsilon\left(r\right)\frac{\partial M_z}{\partial x} = -\frac{M_z - M_0}{T_1} + D_s\Delta M_z. \tag{13}$$

Now, the spin self-diffusion coefficient is denoted as $D_s$, and $V$ is the mean velocity in the cross section of the tube. Later we shall explicitly use the Poiseuille profile for the velocity, $\upsilon(r) = 1 - (r/a)^2$. The boundary conditions at $x$ = 0 for all possible $r$, $t$ are the same as above (3). In addition, we assume that the surface of the tube does not create magnetic fields and the diffusion flows on the surface absent. The flow of the magnetization on the tube axis, due to symmetry, is also zero, so that

$$\partial m/\partial r = \partial M_z/\partial r = 0,\ r = 0,\ a. \tag{14}$$

The initial conditions after the rf pulses are already given by Eqs. (4). To determine the time dependence of the free-induction signal one has to solve Eqs. (12) and (13) with the boundary conditions (3) and (14) and initial conditions (4). The solution of this boundary problem is complicated due to the presence of the coefficients depending on the coordinates. One can proceed as follows. Let us introduce the mean magnetization

$$\bar{m}\left(x,t\right) = \frac{1}{S}\int dSm\left(x,r,t\right), \tag{15}$$

where $S$ is the area of the tube cross-section. For this function, a one-dimensional diffusion equation can be obtained by solving the original equation (12), if for $m$ its mean (15) is used as the first approximation. The solution is searched for as an expansion in the Bessel functions $J_0(\lambda_n r/a)$, which are finite at $r$ = 0 and orthogonal in the interval (0, 1), with $\lambda_n$ being the roots of the equation $J_1(\lambda) = 0$ that follows from the boundary condition at $r = a$. The resulting equation for $\bar{m}$ then reads

$$\left(\frac{\partial}{\partial t} + 2V\frac{\partial}{\partial x} + \frac{1}{T_2}\right)\bar{m} = D\frac{\partial^2}{\partial x^2}\bar{m}\,, \tag{16}$$

with an effective diffusion constant (the Taylor-Aris expression [16]) valid for $\lambda_n a^{-2} D_s t \gg 1$,

$$D \approx D_s\left[1 + 64\left(Va/D_s\right)^2 \sum_{n=1}^{\infty}\lambda_n^{-6}\right]. \tag{17}$$

The numerical result for the sum is $64\sum_{n=1}^{\infty}\lambda_n^{-6} = 0.021$. The same equation as (16) (with $T_1$ instead of $T_2$) can be obtained for the mean of $M_z$ - $M_0$. Note that a more exact (time-dependent) diffusion coefficient, which possesses correct limits for both large and small $t$ can be found in [17], where a problem of the diffusion of a solute during laminar flow in tubes is considered,

$$\frac{D(t)}{D_s} = 1 + 64\left(\frac{Va}{D_s}\right)^2 \sum_{n=1}^{\infty}\frac{1}{\lambda_n^6}\left[1 - \frac{1-\exp\left(-\lambda_n^2 t\right)}{\lambda_n^2 t}\right]. \tag{17a}$$

When $t \to 0$, we have purely molecular diffusion, $D = D_s$.

It is easy to see that at arbitrary value of $\sigma$ particular solutions of Eq. (16) can be written in the form

$$\exp\left[\pm i\sigma x + vx - \left(\frac{1}{T} + \sigma^2 D + v^2 D\right)t\right],\ v = V/(2D). \tag{18}$$

The solutions that satisfy the boundary conditions and the initial conditions after the first 90° pulse are

$$\bar{m}^{(1)}\left(x,t\right) = M_0\hat{L}_\sigma \exp\left[-\left(\sigma^2 + v^2\right)Dt - t/T_2\right]\ ,$$

$$\bar{M}_z^{(1)}\left(x,t\right) = M_0\hat{L}_\sigma\left\{1 - \exp\left[-\left(\sigma^2 + v^2\right)Dt - t/T_1\right]\right\}\ , \tag{19}$$

where the integral operator replacing the Laplace operator (5) from the preceding part has been introduced,

$$\hat{L}_\sigma f\left(\sigma\right) = 2\exp\left(xv\right)\int_0^{\infty}\frac{d\sigma}{\pi}\frac{\sigma\sin\left(x\sigma\right)}{\sigma^2 + v^2}f\left(\sigma\right), \tag{20}$$

with the property $\hat{L}_\sigma 1 = 1$. The structure of the solution is the same as above. The magnetization that determines the free-induction signal after the $n$th pulse is

$$\bar{m}^{(n)} = M_0\hat{L}_\sigma \exp\left(-\gamma_2 t_n\right)N_n\,, \tag{21}$$

where $t_n = t - (n - 1)\tau$, $N_1 = 1$, $l = 0, 1, 2,...$,

$$N_{2l+2} = A\sum_{m=0}^{l}\left(-B\right)^m,\ N_{2l+3} = N_{2l+2} + \left(-B\right)^{l+1}, \tag{22}$$

$A = 1 - \exp(-\gamma_1\tau)$, $B = \exp[-(\gamma_1+\gamma_2)\tau]$, $\gamma_{1,2} = (\sigma^2 + v^2)D + 1/T_{1,2}$.

The mean magnetization (15) can be expressed through the error function as follows. After the first pulse we have

$$\overline{m}^{(1)}\left(x,t\right) = M_0\exp\left(-t/T_2\right)u\left(x,t\right),\ \ t \le \tau, \tag{23}$$

where

$$u\left(x,t\right) = \frac{1}{2}\left\{1+\exp\left(\frac{xV}{D}\right)\left[\operatorname{erf}\left(\frac{x+Vt}{2\sqrt{Dt}}\right)-1\right]+\operatorname{erf}\left(\frac{x-Vt}{2\sqrt{Dt}}\right)\right\}. \tag{24}$$

After the second and subsequent pulses it follows from (21) and (22)

$$\overline{m}^{(2l+2)}\left(x,t\right) = M_0\exp\left(-t_n/T_2\right)\sum_{k=0}^{l}\left(-1\right)^k\exp\left[-\left(\frac{1}{T_1}+\frac{1}{T_2}\right)k\tau\right]$$
$$\times\left[u\left(x,t_n+2\tau k\right)-\exp\left(-\tau/T_1\right)u\left(x,t_n+\tau+2\tau k\right)\right], \tag{25}$$

$$\overline{m}^{(2l+3)}\left(x,t\right) = \overline{m}^{(2l+2)}\left(x,t\right) - M_0\left(-1\right)^l\exp\left[-\frac{t_n}{T_2}-\left(\frac{1}{T_1}+\frac{1}{T_2}\right)\left(l+1\right)\tau\right]u\left(x,t\right). \tag{26}$$

If $D = 0$ the function $u$ turns to the Heaviside function $\Theta(x - Vt)$ and Eq. (25) simplifies to the above obtained solution for the plug flow. For other limits we have $\lim_{t\to\infty} u = 0$, $\lim_{t\to 0} u = 1$, and $u \approx 1$ for $x >> \sqrt{Dt}$ and $x >> Vt$.

The signals $F_n$ induced in the coil of the spectrometer are again found by integrating of (23) - (25) over the length $L$. The result is readily obtained analytically but is rather bulky and we do not show it here. Instead, we illustrate the results by numerical calculations presented on Figs. 1 and 2. While Fig. 1 illustrates the monotonically decaying signal after one applied rf pulse, it is seen from Fig. 2 that already after the fourth pulse (for the given parameters) the maximum of the registered signal increased in comparison with the signal maximum after the third pulse.

The envelope of the induced signals (i.e. the series of the signal maxima) is obtained from Eqs. (23) - (25) after the integration over $x$. Here we show only the simplest result valid at very low velocities and at $L/2\sqrt{D\tau} \ll 1$, when the effect of diffusion on the measured signal is significant:

$$F\left[(2l+1)\tau\right] \approx 1 - \frac{L}{2\sqrt{\pi D\tau}}\left\{\exp\left(-\frac{\tau}{T_1}\right) - \sum_{m=1}^{l}(-1)^m\exp\left[-\left(\frac{1}{T_1}+\frac{1}{T_2}\right)\tau m\right]\left[\frac{1}{\sqrt{2m}} - \frac{\exp\left(-\tau/T_1\right)}{\sqrt{2m+1}}\right]\right\}. \tag{27}$$