Proceedings of the 17th World Congress
The International Federation of Automatic Control
Seoul, Korea, July 6-11, 2008

# Fractional Calculus in NMR

**Richard Magin** * **Xu Feng** ** **Dumitru Baleanu** ***

* *Department of Bioengineering, University of Illinois at Chicago, 851 South Morgan Street, Chicago, IL 60607, USA(e-mail rmagin@uic.edu)*
** *Department of Bioengineering, University of Illinois at Chicago, 851 South Morgan Street, Chicago, IL 60607, USA(e-mail xfeng6@uic.edu)*
*** *Department of Mathematics and Computer Sciences, Faculty of Arts and Sciences,Çankaya University, 06530 Ankara, Turkey*
*and*
*Institute of Space Sciences, P.O.BOX, MG-23, R 76900, Magurele-Bucharest, Romania*
*(e-mails: dumitru@cankaya.edu.tr,baleanu@venus.nipne.ro)*

**Abstract:** Nuclear magnetic resonance (NMR) is a physical phenomenon widely used to study complex materials. NMR is governed by the Bloch equation, a first order non-linear differential equation. Fractional order generalization of the Bloch equation provides an opportunity to extend its use to describe a wider range of experimental situations. Here we present a fractional generalization of the Bloch equation for a simple spin 1/2 system in a static magnetic field using the Caputo fractional derivative.

## 1. INTRODUCTION

Fractional calculus is an extension of classical calculus. In fractional calculus, definitions are established for integrals and derivatives of non-integral order, such as $d^{1/2}f(t)/dt^{1/2}$. The literature of fractional calculus begins with Leibniz, is quite extensive, and today is growing rapidly (Carpinteri and Mainardi, 1997; Hilfer, 2000; Oldham and Spanier, 1974; Podlubny, 1999; Magin, 2006; Mainardi, 1994; Mainardi et al., 2007; Metzel and Klaffer, 2000; Samko et al., 1993; Zaslavsky, 2005; West et al., 2003). Fractional calculus is particulary useful in describing the dynamics of complex systems (e.g., viscoelastic materials, diffusion in porous composites, and bioelectrode impedance), and it is now being applied to model relaxation and diffusion in nuclear magnetic resonance (NMR) (Magin et al., 2008).

Fractional derivatives have many properties in common with the classical ones, but not all the properties are the same. These differences can be used to describe complex phenomena that arise due to non-local interactions and system memory.

However, an important challenge in fractional calculus is to give a physical meaning for the fractional derivative. One way to develop physical meaning is by studying the behavior of complex systems under known perturbations. A particular and very interesting class of complex phenomena arises in NMR imaging and spectroscopy. The starting point for NMR is to solve the Bloch equation for various combinations of applied static, radio frequency and gradient magnetic fields (Abragam, 2002; Haacke et al., 1999). In this paper we consider the simple case of a spin 1/2 particle in a static magnetic field.

## 2. BASIC DEFINITIONS

There are many similar definitions for the fractional derivative. In this work we employ the left Caputo fractional derivative which is given by (Kilbas et al., 2006) as

$$ {}_a^C D_t^\alpha f(t) = \frac{1}{\Gamma(n-\alpha)} \int_a^t (t-\tau)^{n-\alpha-1} \left(\frac{d}{d\tau}\right)^n f(\tau) d\tau. \quad (1)$$

Since we will restrict the order alpha of our derivative to the range between zero and one this definition can be simplified as

$$ {}_a^C D_t^\alpha f(t) = \frac{1}{\Gamma(1-\alpha)} \int_a^t (t-\tau)^{-\alpha} \frac{df(\tau)}{d\tau} d\tau, \quad (2)$$

where the Gamma function has the form

$$\Gamma(z) = \int_0^\infty e^{-u} u^{z-1} du. \quad (3)$$

One property of the Caputo derivative that is different from its classical analog is the Leibniz rule for the $\alpha$-th order derivative, which is given below for a = 0

$$ {}_0^C D_t^\alpha (\phi(t) f(t)) = \sum_0^\infty \begin{pmatrix} \alpha \\ k \end{pmatrix} \left({}_0^C D_t^{\alpha-k} f\right) \phi^{(k)}(t), \quad (4)$$

where

$$\begin{pmatrix} \alpha \\ k \end{pmatrix} = \frac{\Gamma(\alpha+1)}{k!\Gamma(\alpha-k+1)}. \quad (5)$$

This expression is valid provided both f(t) and $\phi(t)$ and all their derivatives are continuous on the interval [0, t], (Podlubny, 1999).

In addition, for the Caputo derivative we have the following properties

$$ {}_0^C D_t^\alpha t^k = \frac{\Gamma(k+1)t^{k-\alpha}}{\Gamma(k+1-\alpha)}, k > 1, \alpha > 0, \tag{6}$$

$$ {}_0^C D_t^\alpha (1) = 0. \tag{7}$$

In various applications of fractional calculus the Mittag-Leffler function appears. This function is a generalization of the classical exponential function (Carpinteri and Mainardi, 1997; Podlubny, 1999; Kilbas et al., 2006; Samko et al., 1993). The single parameter Mittag-Leffler function is defined by

$$E_\alpha(t) = \sum_{k=0}^{\infty} \frac{t^k}{\Gamma(\alpha k + 1)}, \alpha > 0. \tag{8}$$

By inspection we conclude that

$$E_1(t) = e^t, E_2(t) = cosh(t). \tag{9}$$

The two-parameter Mittag-Leffler function has the form

$$E_{\alpha,\beta}(t) = \sum_{k=0}^{\infty} \frac{t^k}{\Gamma(\alpha k + \beta)}, \alpha, \beta > 0. \tag{10}$$

This function possesses the following properties

$$E_{1,2}(t) = \frac{e^t - 1}{t}, E_{2,2}(t) = \frac{sinh(t)}{\sqrt{t}}, \tag{11}$$

$$E_{2,1}(t) = cosh(t). \tag{12}$$

The Laplace transformations for several Mittag-Leffler functions are summarized below:

$$L(E_\alpha(-\lambda t^\alpha)) = \frac{s^{\alpha-1}}{s^\alpha + \lambda}, \tag{13}$$

$$L(t^{\alpha-1}E_{\alpha,\alpha}(-\lambda t^\alpha)) = \frac{1}{s^\alpha + \lambda}, \tag{14}$$

$$L(t^{\beta-1}E_{\alpha,\beta}(-\lambda t^\alpha)) = \frac{s^{\alpha-\beta}}{s^\alpha + \lambda}, \tag{15}$$

$$L(t^{\beta-1}E^\rho_{\alpha,\beta}(-\lambda t^\alpha)) = \frac{s^{\alpha\rho-\beta}}{(s^\alpha + \lambda)^\rho}, \tag{16}$$

provided that $s >\mid \lambda \mid^{\frac{1}{\alpha}}$ .

## 3. FRACTIONAL BLOCH EQUATIONS

The generalization of the Bloch equation by extension of the time derivative to fractional order suggests a number of interesting possibilities concerning spin dynamics and magnetization relaxation. In this paper we investigate the classical Bloch equations (Haacke et al., 1999).

$$\frac{dM_z}{dt} = \frac{M_0 - M_z}{T_1}, \tag{17}$$

$$\frac{dM_x}{dt} = \omega_0 M_y - \frac{M_x}{T_2}, \tag{18}$$

$$\frac{dM_y}{dt} = -\omega_0 M_x - \frac{M_y}{T_2}. \tag{19}$$

Here $M_x$, $M_y$, and $M_z$ represent the system magnetization (x,y and z components), $M_0$ is the equilibrium magnetization, $T_1$ is the spin-lattice relaxation time, $T_2$ is the spin-spin relaxation time, and $\omega_0$ is the resonant frequency given by the Larmor relationship $\omega_0 = \gamma B_0$, where $B_0$ is the static magnetic field (z-component) and is the gyromagnetic ratio for spin $\frac{1}{2}$ particles (water protons).

For the above equations there are several approaches to follow in fractional generalization; we ultimately should employ the form best suited for fitting experimental data. Nevertheless, the assumption of a time domain fractional derivative suggests a modulation - or weighting - of system memory, an assumption that alters the spin dynamics described by the Bloch equations.

In addition, it is well known that fractional order systems of differential equations (Kilbas et al., 2006) are strongly dependent on the initial conditions; therefore, we should choose the fractional derivative most appropriate for handling the initial conditions of our physical problem. In NMR the initial state of the system is specified by the components of the magnetization, hence these need to be clearly identified. Another more general, and still open issue, is the physical meaning of the fractional Bloch equation. This question ultimately goes back to the basic formulation the Schrödinger equation as a fractional order partial differential equation in quantum mechanics - a topic beyond the scope of the present paper (Herman, 2007; Naber, 2004; Baleanu and Muslih, 2005; Baleanu et al., 2006; Rabei et al., 2007).

In order to preserve the meaning of the initial conditions for the magnetization for our problem, namely, $M_x(0)$, $M_y(0)$, and $M_z(0)$, we will use the fractional order Caputo derivative. Therefore, we obtain the following system: a set of fractional order Bloch equations

$$ {}_0^C D_t^\alpha M_z = \frac{M_0 - M_z}{T_1'}, \tag{20}$$

$$ {}_0^C D_t^\alpha M_x = \bar{\omega_0} M_y - \frac{M_x}{T_2'}, \tag{21}$$

$$ {}_0^C D_t^\alpha M_y = -\bar{\omega_0} M_x - \frac{M_y}{T_2'}. \tag{22}$$

Here $\bar{\omega_0}$, $\frac{1}{T_1'}$ , and $\frac{1}{T_2'}$ each have the units of $(sec)^{-\alpha}$. Using either fractional calculus or the Laplace transformation, the solution for $M_z(t)$ is given by

$$M_z = M_z(0)E_\alpha(\frac{-t^\alpha}{T_1'}) + \frac{M_0}{T_1'}t^\alpha E_{\alpha,\alpha+1}(\frac{-t^\alpha}{T_1'}). \tag{23}$$

For $\alpha = 1$, this equation reduces to

$$M_z = M_z(0)e^{\frac{-t}{T_1}} + \frac{M_0}{T_1}tE_{1,2}(\frac{-t}{T_1}). \tag{24}$$

This can be simplified to the classical result

$$M_z = M_z(0)e^{\frac{-t}{T_1}} + M_0(1 - e^{-\frac{t}{T_1}}), \tag{25}$$

since $zE_{1,2}(z) = E_{1,1}(z) - 1$.

The solutions for $M_x(t)$ and $M_y(t)$ can be found by solving the corresponding fractional order differential equations. If we suppose that

$$M_+(t) = M_x(t) + iM_y(t), \tag{26}$$

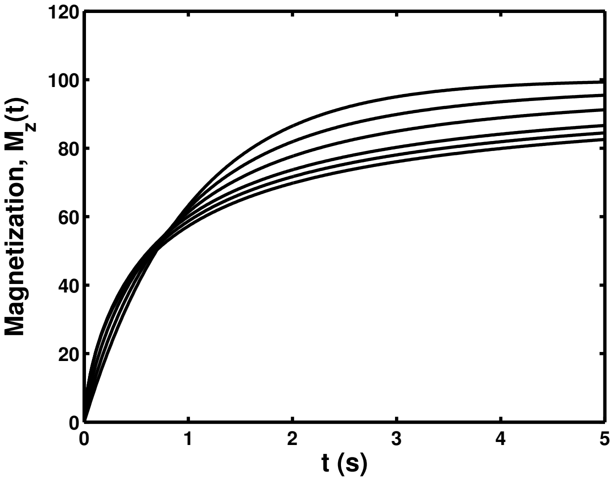


Fig. 1. Plots of $M_z(t)$ for different values of $\alpha$ in the range of $\alpha = 0.5$ (bottom curve) to $\alpha = 1.0$ (top curve) in steps of 0.1. For these plots, equation (23) was used with $M_z(0) = 0$, $T_1$=1 sec and $M_0 = 100$. The Mittag-Leffler function was evaluated using the Matlab function m-file mlf.m found at http://www.mathworks.com/matlabcentral.

with

$$M_+(0) = M_x(0) + iM_y(0), \tag{27}$$

then we can combine the two equations for the x and the y components of magnetization given above to yield

$${}_0^C D_t^\alpha M_+(t) = -i\bar{\omega_0} M_+(t) - \frac{1}{T_2^{'}} M_+(t), \tag{28}$$

Now, assuming

$$M_+(t) = M_+(0) E_\alpha(-\lambda t^\alpha), \tag{29}$$

and using the Caputo derivative of the single parameter Mittag-Leffler function

$${}_0^C D_t^\alpha E_\alpha(-\lambda t^\alpha) = -\lambda E_\alpha(-\lambda t^\alpha), \tag{30}$$

we find that must be

$$\lambda = i\bar{\omega_0} + \frac{1}{T_2^{'}}. \tag{31}$$

In addition, using the definition of the single parameter Mittag-Leffler function, we find

$$M_+(t=0) = M_+(0), M_+(t=\infty) = 0. \tag{32}$$

Finally, for $\alpha = 1$ we obtain the classical result

$$M_x(t) = e^{-\frac{t}{T_2}} (M_x(0) cos(\omega_0 t) + M_y(0) sin(\omega_0 t)), \tag{33}$$

$$M_y(t) = e^{-\frac{t}{T_2}} (M_y(0) cos(\omega_0 t) - M_x(0) sin(\omega_0 t)). \tag{34}$$

The behavior of the transverse magnetization $M_+(t)$ at long times can be estimated by using an asymptotic expansion for the the Mittag-Leffler function. The following formula (Kilbas et al., 2006) is accurate to order $\frac{1}{z^{N+1}}$, when $|arg(z)| \leq \frac{\pi}{2}$

$$E_\alpha(z) = \frac{1}{\alpha} e^{z^{\frac{1}{\alpha}}} - \sum_{k=1}^{N} \left(\frac{1}{\Gamma(1-\alpha k)}\right) \frac{1}{z^k}, \tag{35}$$

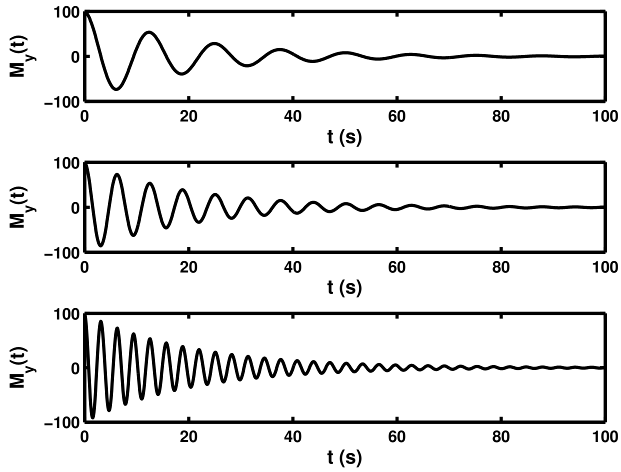


Fig. 2. Plots of $M_y(t)$ for $T_2 = 20$ ms and $f_0 = (2\pi/\omega_0) =$ 80, 160, and 320 Hz, top to bottom, respectively. For these plots, equation (34) was used with $M_x(0) = 0$ and $M_y(0) = 100$.

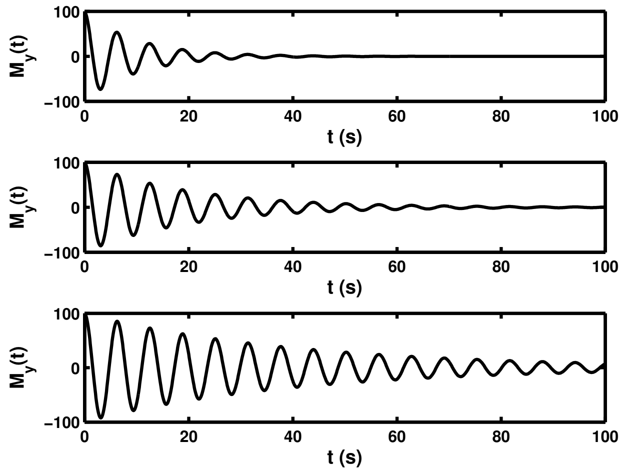


Fig. 3. Plots of $M_y(t)$ for $f_0 = 160$ Hz and $T_2 = 10$, 20, and 40 ms, top to bottom, respectively. For these plots, equation (34) was used with $M_x(0) = 0$ and $M_y(0) = 100$.

where we substitute the following

$$z = -\lambda t^\alpha, \lambda = \rho e^{i\theta}, \theta = arg(\lambda), \rho = |\lambda|. \tag{36}$$

Thus, $\lambda$ can be written in terms of $\bar{\omega_0}$ and $T_2^{'}$ as

$$\rho = \sqrt{\left(\frac{1}{T_2^{'}}\right)^2 + (\bar{\omega_0})^2}, \quad \theta = \tan^{-1}(\bar{\omega_0} T_2^{'}). \tag{37}$$

In NMR $\bar{\omega_0} T_2^{'} > 1$, so that $|arg(z)|$ approaches $\frac{\pi}{2}$. For increasing time we need only consider the first term of equation (35), thus

$$E_\alpha(-\lambda t^\alpha) = \frac{1}{\alpha} exp(e^{i\frac{\pi}{\alpha}} \lambda^{\frac{1}{\alpha}} t), \tag{38}$$

where

$$\lambda^{\frac{1}{\alpha}} = \rho^{\frac{1}{\alpha}} [cos(\frac{\theta}{\alpha}) + isin(\frac{\theta}{\alpha})]. \tag{39}$$

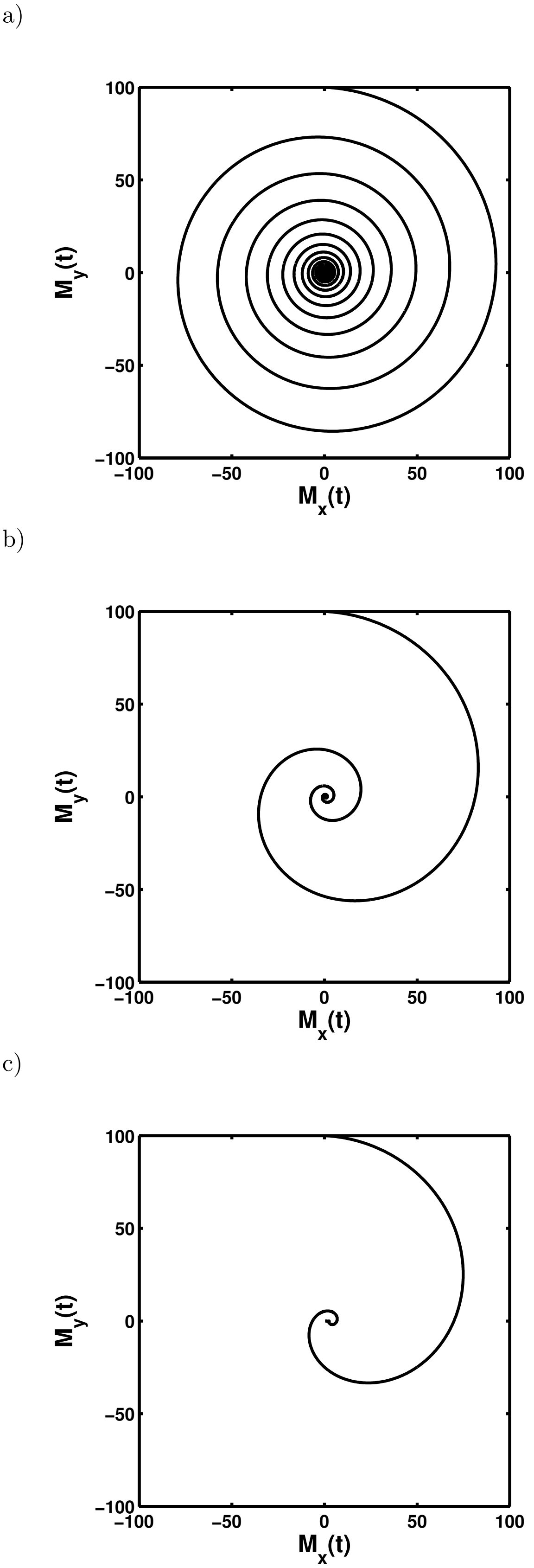


Fig. 4. Plots of $M_+(t)$ in the complex plane with $\alpha = 1$ (a, classical model), $\alpha = 0.9$ (b) and $\alpha = 0.8$ (c). For these plots, equations (26) and (29) were used with $M_x(0) = 0$, $M_y(0) = 100$, $T_2 = 20$ ms and $f_0 = 160$ Hz.

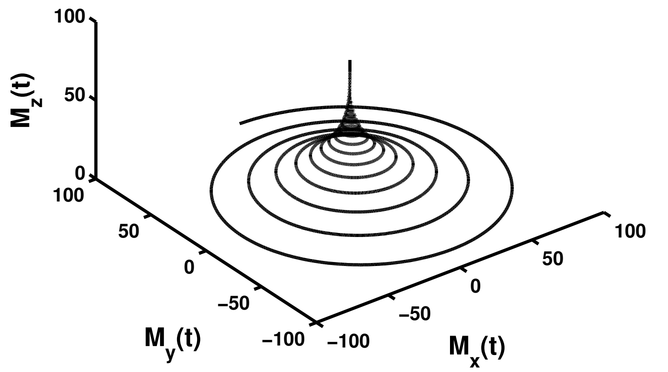


Fig. 5. A plot of fractional order solution to the Bloch equations with $\alpha = 1$ (classical model). For this plot, equations (23), (26) and (29) were used with $M_x(0) = 0$, $M_y(0) = 100$, $M_z(0) = 0$, $T_1 = 1$ s, $T_2 = 20$ ms and $f_0 = 160$ Hz.

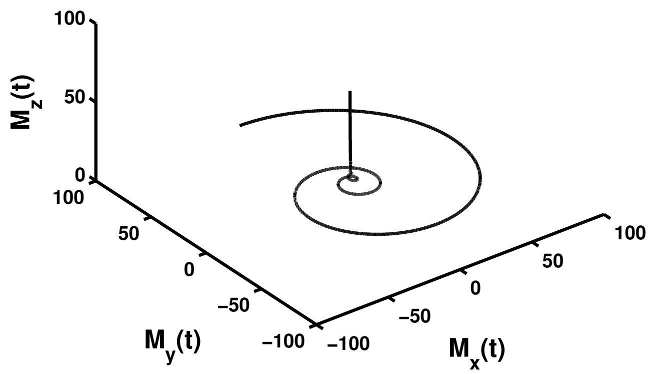


Fig. 6. A plot of fractional order solution to the Bloch equations with $\alpha = 0.9$. For this plot, equations (23), (26) and (29) were used with $M_x(0) = 0$, $M_y(0) = 100$, $M_z(0) = 0$, $T_1 = 1$ s, $T_2 = 20$ ms and $f_0 = 160$ Hz.

Collecting terms we find

$$E_\alpha(-\lambda t^\alpha) = \frac{1}{\alpha} exp(\rho^{\frac{1}{\alpha}} t[cos(\frac{\theta+\pi}{\alpha}) + isin(\frac{\theta+\pi}{\alpha})]). \quad (40)$$

Substitution into the expression for the transverse magnetization we find for the long time limit

$$M_+(t) = \frac{M_+(0)}{\alpha} exp(\rho^{\frac{1}{\alpha}} t[cos(\frac{\theta+\pi}{\alpha}) + isin(\frac{\theta+\pi}{\alpha})]), \quad (41)$$

which for $\alpha = 1$ gives the classical result

$$M_+(t) = \frac{M_+(0)}{\alpha} exp(-\frac{t}{T_2} - i\omega_0 t). \quad (42)$$

We can also examine the cases of very long $T_2'$ and for $\bar{\omega}_0 = 0$. In the first case, $\theta = \frac{\pi}{2}$ and in the second $\theta = 0$. Therefore, for a very long $T_2'$, we find

$$M_+(t) = \frac{M_+(0)}{\alpha} exp(\bar{\omega_0}^{\frac{1}{\alpha}} t e^{i\frac{3\pi}{2\alpha}}), \quad (43)$$

while in the case of $\bar{\omega_0} = 0$, we obtain

$$M_+(t) = \frac{M_+(0)}{\alpha} exp((\frac{1}{T_2'})^{\frac{1}{\alpha}} t e^{i\frac{\pi}{\alpha}}), \quad (44)$$

Both results suggest fractional order processes; fractional order precession (with attenuation) in the case of long $T_2'$ and fractional order relaxation (with a phase shift) in the case of $\bar{\omega}_0 = 0$ . The necessity of ensuring that the magnetization terms decay (not grow) in time when $\bar{\omega}_0 = 0$ is provided by restricting the fractional order parameter to the range, $\frac{2}{3} < \alpha < 2$. This range is consistent with our assumption that a fractionalized Bloch equation should exhibit a fractional damping form of behavior.

## 4. DISCUSSION

The generalization of the Bloch equation presented in this paper is one of several possible approaches. However, given the well defined initial conditions that arise in NMR experiments, the choice of the so-called Caputo form of the fractional derivative appears reasonable. For the case of a simple static magnetic field, the NMR problem was easily solved in terms of Mittag-Leffler functions, using known properties of the fractional derivative - as might be expected, given the nature of the governing linear, fractional order differential equations.

The correspondence of the fractional order solutions with the classical results when the fractional order $\alpha$ is set to one is reassuring and the expected asymptotic behavior of the solutions is consistent with the physics of the NMR problem. For arbitrary values of $\alpha$ an analytical expression of the transverse and the longitudinal components of the magnetization is derived. This solution involves a fractional order generalization of the angular frequency and the relaxation time constants. This is anticipated as similar results arise in the fractional order generalization of viscoelastic and bioelectrode problems (Magin, 2006). And, just as fractional calculus provides expanded models for describing biomaterials and bioelectricity in complex and composite systems, the fractional order generalization of NMR could be expected to find applications in the study of heterogeneous, porous and complex materials exhibiting memory.

The next step in applying fractional calculus to NMR is to extend the analysis to include the effects of RF pulses, gradient pulses, and an entire imaging sequence (MRI). Recent work applying fractional calculus to NMR measurements of diffusion by space and time fractionalization of the Bloch-Torrey equation (Magin et al., 2008) and the theoretical analysis of spin-lattice relaxation by anomalous translational diffusion in heterogeneous systems using the fractional diffusion equation (Sitnitsky et al., 2005) suggests that fractional calculus can play an important role in advancing our understanding of NMR in complex systems. Here we use fractional calculus to solve the much simpler, but fundamental, model for NMR. Examination of this result and other more general cases can be useful in at least two ways. First, fractional calculus models represent a relatively simple way to describe NMR in complex, porous, or composite systems. There is a multi-scale generalization inherent in the definition of the fractional derivative, which accurately represents interactions occurring over a wide dynamic range of space or time. Hence, there is no need to segment or compartmentalize systems into all subsystems or subunits - a system reduction that often creates more complexity than can be experimentally evaluated. Second, NMR experiments and measurements conducted on complex materials can shed light on the meaning of fractional order operations, when the results match the intermediate order system dynamics predicted by fractional calculus. Thus, we can begin to unravel the contributions to the physics that follow from the fundamental model dynamics, the geometry, and the interaction between system components and physical barriers.

In dielectric spectroscopy, fractional order models work well, often extending over large ranges of time and frequency. NMR, like dielectric spectroscopy, may provide another tool for probing the connections between physics and mathematics. In heat transfer and electrochemistry, for example, the half order fractional integral is the natural integral operator connecting the applied gradients (thermal or material) with the diffusion of ions or heat (Magin, 2006).

In what way can NMR experiments add to our understanding of the meaning of the fractional derivative? Can the fractional order Bloch equation be derived from a fractional order Schrödinger equation? What does a fractional order Bloembergen, Purcell and Pound theory predict about $T_1$ and $T_2$ relaxation? What does fractional order Magnetic Resonance Imaging entail?

The answers to these questions are not known, but the questions have been raised and the analysis begun.

## 5. CONCLUSION

Fractional order generalization of the Bloch equations for spins in a simple, static magnetic field $B_0$ is possible using the Caputo definition of the fractional order derivative. The results are analytical expressions for the longitudinal and transverse components of the induced magnetization that can be expressed in terms of Mittag- Leffler functions. The spin dynamics are found to be in general, fractional order, but reduce to the classical case when the order of differentiation is set to one.

## REFERENCES

Abragam, A (2002). *Principles of Nuclear Magnetism.* Oxford University Press, New York.

Baleanu, D. and S. Muslih (2005). Lagrangian formulation of classical fields within Riemann-Liouville fractional derivatives. *Physica Scripta*, **72(2-3)**: 119–121.

Baleanu, D., S.I. Muslih and K. Tas (2006). Fractional Hamiltonian analysis of higher order derivatives systems. *J.Math.Phys.*, **47**: art.no.103503.

Carpinteri, A. and F. Mainardi (1997). *Fractals and Fractional Calculus in Continuum Mechanics* , CISM Courses and Lectures No. 378, Springer-Wien, New York.

Haacke, E.M., R.W. Brown, M.R. Thompson and R. Venkatesan (1999). *Magnetic Resonance Imaging: Physical Principles and Sequence Design*, John Wiley and Sons, New York.
Herrmann, R. (2007). The fractional symmetric rigid rotor. *J.Phys.G-Nuc.Part. Pys.*, **34**: 607-625.
Hilfer, R., (ed). (2000). *Applications of Fractional Calculus in Physics*. World Scientific Publishing Company, Singapore.
Kilbas, A.A., H.H. Srivastava and J.J. Trujillo (2006). *Theory and Applications of Fractional Differential Equations*. Elsevier, The Nederlands.
Magin, R.L. (2006). *Fractional Calculus in Bioengineering*. Begell House Publisher, Inc. Connecticut.
Magin, R.L., O. Abdullah, D. Baleanu and X.J. Zhou (2008). Anomalous diffusion expressed through fractional order differential operators in the Bloch-Torrey equation. *J.Magn.Reson.*, **190**: 255-270.
Mainardi, F. (1994). On the initial problem for the fractional diffusion equation. In : Rionero, S., Ruggeri, T. (ed). *Waves and Stability in Continuous Media*. World Scientific, Singapore.
Mainardi, F., A. Mura, G. Pagnini, and R. Gorenflo (2007). Sub-diffusion equations of fractional order and their fundamental solutions. In: K. Tas, J. A. Tenreiro Machado, (eds) *Mathematical Methods in Engineering*, Springer, New York.
Metzel, R. and J. Klafter (2000). The random walks guide to anomalous diffusion:a fractional dynamics approach. *Phys. Rep.*, **339**: 1-7.
Naber, N. (2004). Time fractional Schrödinger equation. *J. Math. Phys.*, **45**: 3339-3352.
Oldham, K.B. and J. Spanier (1974). *The Fractional Calculus*. Academic Press, New York.
Podlubny, I (1999). *Fractional Differential Equations*. Academic Press, New York.
Rabei, E.M., K.I. Nawafleh, R.S. Hijjawi, S.I. Muslih and D. Baleanu (2007). The Hamilton formalism with fractional derivatives. *J. Math. Anal. Appl.*, **327**: 891–897.
Samko, S.G., A.A. Kilbas and O.I. Marichev (1993) *Fractional Integrals and Derivatives - Theory and Applications*. Gordon and Breach, Linghorne.
Sitnitsky, A.E., G.G. Pimenov and A.V. Anisimov (2005). Spin-Lattice NMR relaxation by anomalous translational diffusion. *J. Magn. Reson.*, **172**: 48-55.
West, B.J., M. Bologna and P. Grigolini (2003). *Physics of Fractal Operators*. Springer-Verlag, New York.
Zaslavsky G. (2005). *Hamiltonian Chaos and Fractional Dynamics*. Oxford University Press, Oxford.