Describe NMR relaxation by effective diffusion equation

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Abstract

This paper proposes an effective diffusion equation method to analyze nuclear magnetic resonance (NMR) relaxation. The NMR relaxation is a spin system recovery process, where the evolution of the spin system or the magnetization is affected by random field due to various Hamilton interactions, such as dipolar or quadrupolar couplings. The proposed method treats this evolution of magnetization as a random walk in phase space, which can thus be modeled by normal or fractional diffusion equations. By solving these diffusion equations, the NMR relaxation rates and relaxation equations are obtained. The obtained results include both the normal and anomalous NMR relaxations. These obtained results agree with reported results in the literature. The paper provides additional insights into NMR relaxation.

Keywords: NMR relaxation, angular momentum, KWW function, Mittag-Leffler function, diffusion

1. Introduction

Nuclear magnetic resonance (NMR) relaxation is a powerful technique for detecting molecular dynamics [1,2] in many systems such as biological or polymer systems [3,4,5]. NMR relaxation is a recovery process that a spin system returns to equilibrium after being perturbed. The speed of such a recovery process depends on the molecular motion, which changes relative molecular orientations and thus modulates many fundamental Hamiltonian interactions of NMR spin systems including dipolar coupling, quadrupolar coupling, chemical shift anisotropy, etc. [1,6] These modulated Hamiltonian interactions can be viewed as random fluctuating fields perturbing the spin system. The perturbation affects the spin evolution and changes the spin relaxation process, which can be treated by density operator theory based on quantum mechanics. The traditional theories, such as Bloch-Wangsness-Redfield theory and the second-order perturbation theory, have very successfully explained many normal NMR relaxation processes [1,6]. However, few theoretical treatments explain the anomalous relaxation process.

Anomalous NMR relaxation could arise from various aspects. First, the rotational or translational diffusion modulating the random field could be nonlinear. Fractional rotational or translational diffusion has been applied to describe the anomalous correlational motion for NMR relaxation and other relaxation processes [7, 8,9,10,11,12]. The results from these reports reveal that the time correlation function of the random fluctuating field is either a Mittag-Leffler function \( E_{\alpha,1} \left( - \frac{t}{\tau} \right) \), or a stretched exponential function \( \exp \left( - \left( \frac{t}{\tau} \right)^{\alpha} \right) \), where \( \alpha \) is the order of fractional derivative, and \( \tau \) is the characteristic time. The stretched exponential function is the same as Kohlrausch-Williams-Watts (KWW) function [13,14], which is a commonly used time correlation function for macromolecular systems. The Mittag-Leffler function can be reduced to stretched exponential function when \( \left( \frac{t}{\tau} \right)^{\alpha} \) is small. Second, the relaxation itself, the evolution of the investigated spin system, is anomalous as described by fractional Bloch-equation proposed by Ref. [15]. The anomalous evolution of a spin system is difficult to describe by the perturbation theory. To better understand the normal and anomalous relaxations, a phase diffusion process is proposed to describe anomalous relaxation, mainly on the evolution of the spin system.
The evolution of magnetization affected by a random field can be described by a diffusion process. The NMR relaxation process is the evolution of spin systems affected by random Hamiltonian interactions. It can be described either by the evolution of wavefunctions (Schrödinger representation) or the evolution of observable operators (Heisenberg representation) [1,6]. The evolution of density operator (Schrödinger representation) can be converted to the evolution of observable operators (Heisenberg representation), which can well describe various NMR relaxation processes such as like-spin or unlike spin relaxation due to dipolar coupling, relaxation due to quadrupolar coupling, etc. [1]. Because the evolution of observable under the influence of a random field can be seen as a random walk process, it can thus be described by a diffusion equation. This theoretical treatment is very similar to the effective phase diffusion equation recently developed to describe the phase evolution of spin coherence affected by a pulsed-field gradient (PFG) [16]. From solving the diffusion equation, the distribution of the magnetization vector can be obtained, and the relaxation of magnetization can be determined.

The diffusion describing the evolution of the magnetization can either be normal diffusion or anomalous diffusion. In this paper, both the normal diffusion and anomalous diffusion equation will be applied to analyze NMR relaxation. Based on continuous-time random walk (CTRW) simulation, the fraction diffusion arises from its diffusion waiting time behaving asymptotically to a power-law or its diffusion jump length following a power-law [17,18]. The fractional diffusion can be modeled by fractional calculus [18, 19, 20, 21,22]. Fractional diffusion equation has been applied to describe various anomalous dynamics processes such as anomalous NMR relaxation, and PFG anomalous diffusion [8,12,16,23,24,25,26,27,28]. Unlike normal dynamics processes, the time-dependent behaviors of anomalous dynamics processes, such as PFG signal attenuation, the time correlation function, the NMR relaxation, are often described by Mittag-Leffler function or stretched exponential function, rather than monoexponential function. Normal diffusion can be viewed as a specific case of anomalous diffusion.

In this paper, the relaxation effects of the simple random field and dipolar coupling are illustrated by normal phase diffusion in Section 2.1. Then, the anomalous NMR relaxation arising from fractional phase diffusion and the nonlinear correlation time resulting from anomalous diffusion are described in Section 2.2 and 2.3, respectively. The obtained NMR relaxation results agree with the established results in the literature [1,6]. The results obtained here could provide additional insights into the anomalous NMR relaxation, which may be difficult to be explained by other methods.

2. Theory

2.1 Phase diffusion under random field

2.1.1 Random field

The random molecular motion alerts the relative molecular orientations, which modulates many fundamental Hamiltonian interactions of spin systems. These interactions can be viewed as a random field exerting on the observed spin moments. To see how a random field affects the spin relaxation, a simple random field $H_i(t)$ is used as an example, which is given by [6]

$$H_i(t) = \sum_{q=x,y,z} H_q(t) I_q,$$  \hspace{1cm} (1)

where $I_q$ is the component of the angular momentum, and $H_q(t)$ is the amplitude of the random field described by

$$H_q(t) = \gamma \hbar q G_q(t),$$  \hspace{1cm} (2)

where $\gamma$ is the gyromagnetic ratio, $\hbar$ is the reduced Planck constant, $h_q$ is the field intensity, and $G_q(t)$ is time correlation function resulting from the relative rotational or translational motion of the lattice particles.
First, let us see the effect the component $H_x(t)l_z$, which causes the angular momentum $l_z$ to rotate [1,2,6]

$$I_z e^{i\mathcal{H}t} e^{-i\mathcal{H}t} I_z \cos \phi + I_y \sin \phi,$$

where

$$\phi = \int_0^t \frac{H_x(t)}{\hbar} dt' = \int_0^t \gamma h_x G_x(t) dt'. \quad \text{(4)}$$

Eq. (3) indicates that $I_z$ undergoes a rotation in $zy$ plane, which can be rewritten as

$$I_z e^{i\mathcal{H}t} e^{-i\mathcal{H}t} I_z e^{i\phi}, \quad \text{(5)}$$

Eq. (4) can be rewritten in a discrete mode as

$$\Delta \phi_i = \gamma h_x G_x(t_i) \Delta t_i, \quad \text{(6a)}$$

$$\phi = \sum_{i=1}^n \gamma h_x G_x(t_i) \Delta t_i, \quad \text{(6b)}$$

where $\Delta \phi_i$ is the phase jump length, $\Delta t_i$ is the jump time, and $t_i = \sum_{j=1}^i \Delta t_j$. The time correlation function, $G_x(t)$, arises from the random relative motion of the lattice molecules or atoms. It relates the Hamiltonian interactions at different instants, here time zero and time $t$. A typical correlation time is the monoexponential function [4,5,13,14]

$$G_x(t) = \exp \left(-\frac{t}{\tau}\right), \quad \text{(7)}$$

where $\tau$ is the molecular reorientation time constant. In polymer or macromolecular system, such a monoexponential correlation time corresponds to a mean rotational motion time:

$$\int_0^\infty \exp \left(-\frac{|t|}{\tau}\right) dt = \tau. \quad \text{(8)}$$

Because the correlations exist before and after time zero are equivalent, $2\tau$ could be viewed as an average jump time of the random phase walk, namely

$$\langle \tau_{\text{jump}} \rangle = 2\tau, \quad \text{(9)}$$

The average phase jump length is

$$\langle \Delta \phi_i \rangle = \omega_x \langle \tau_{\text{jump}} \rangle = \omega_x 2\tau, \quad \text{(10)}$$

where

$$\omega_x = \frac{H_x(t)}{\hbar} = \gamma h_x. \quad \text{(11)}$$

Eq. (11) does not consider that the spin system is rotating around the external field $H_0$ at Larmor frequency $\omega_0$. For a quantum coherence of order $n$, the rotating frequency is

$$n \omega_0 = n \gamma H_0. \quad \text{(12)}$$

The average jump time of the phase walks will be

$$\langle \tau_{\text{jump}} \rangle = \int_{-\infty}^\infty \exp \left(-\frac{t}{\tau}\right) \exp \left(-in \omega_0 t\right) dt = \frac{2\tau}{1+(n\omega_0 \tau)^2}. \quad \text{(13)}$$

Note that the domain of $t$ is $(-\infty, \infty)$ because the correlation to $t = 0$ exists both before and after time zero. The $\langle \tau_{\text{jump}} \rangle$ may be apprehended from the following: As the spin moments are consistently rotating at Larmor frequency, only the Hamiltonian interactions within a certain period, $\langle \tau_{\text{jump}} \rangle$, are correlated;
beyond the \( \langle \tau_{\text{jump}} \rangle \), the Hamiltonian belongs to another random jump. Therefore, the random phase walk of the observable vector can be viewed as a phase diffusion process. The phase diffusion constant can be obtained by [16]

\[
D_{\phi x} = \frac{\langle (\Delta \phi)^2 \rangle}{\langle \tau_{\text{jump}} \rangle} = \frac{\omega_{\text{jump}}^2}{2}, \tag{14}
\]

and the normal phase diffusion equation can be described as [16]

\[
\frac{dp_x(\phi,t)}{dt} = D_{\phi x} \Delta P_x(\phi,t). \tag{15}
\]

Applying Fourier transform, \( p_x(k,t) = \int_{-\infty}^{\infty} P_x(\phi,t) \exp(-ik\phi) \, d\phi \), to Eq. (15), we get

\[
\frac{dp_x(k,t)}{dt} = -k^2 D_{\phi x} p_x(k,t). \tag{16}
\]

The solution of Eq. (16) is

\[
p_x(k,t) = A \exp(-D_{\phi x} k^2 t), \tag{17}
\]

where \( A \) is the magnetization at time zero. When \( k=1 \),

\[
p_x(1,t) = A \exp(-D_{\phi x} t). \tag{18}
\]

The signal amplitude is the average magnetization across all possible phases, which is

\[
\int_{-\infty}^{\infty} P_x(\phi,t) \exp(-i\phi) \, d\phi = p_x(1,t) = A \exp(-D_{\phi x} t) \tag{19}
\]

From Eq. (19), the relaxation rate \( W_x \) due to the perturbation of the random field is

\[
W_x = D_{\phi x} = \omega_{\text{jump}}^2 \frac{\tau}{1+(n\omega_0)^2} = (\gamma h_x)^2 \frac{\tau}{1+(n\omega_0)^2}. \tag{19}
\]

Because of the coupling between the spin system and the lattice, a thermal relaxation process always happens, which leads to the equilibrium population distribution [1,6]. To include the thermal relaxation, for \( k=1 \), Eq. (16) can be modified as

\[
\frac{dp_x(1,t)}{dt} = -D_{\phi x} (p_x(1,t) - p_{x0}(1,0)), \tag{21}
\]

where \( p_{x0}(1,0) \) is the probability distribution function of equilibrium magnetization. Eq. (21) can be rewritten as

\[
\frac{d(M_x)}{dt} = -\frac{1}{\tau_1} \langle (M_x) - M_{x0} \rangle, \tag{22}
\]

where

\[
\frac{1}{\tau_1} = D_{\phi x}. \tag{23}
\]

Eq. (22) is the familiar spin-lattice relaxation equation [1,2,6].

In Eq. (1), there are still two other components of the random field, \( H_y(t) \) and \( H_z(t) \), needed to be considered. \( H_z(t) \) commutes with \( I_z \), so it does not affect the evolution of \( I_z \). While the effect of the component \( H_y(t) \) on the angular momentum \( I_x \) is similar to that of \( H_x(t) \), and the phase diffusion constant can thus be obtained similarly as

\[
D_{\phi y} = \omega_{\text{jump}}^2 \frac{\tau}{1+(n\omega_0)^2} = (\gamma h_y)^2 \frac{\tau}{1+(n\omega_0)^2}. \tag{24}
\]

Because \( H_x(t) \) and \( H_y(t) \) are two uncoupled random processes, their effects on the NMR relaxation can be added together as

\[
\frac{1}{\tau_1} = D_{\phi x} + D_{\phi y} = \gamma^2 (h_x^2 + h_y^2) \frac{\tau}{1+(n\omega_0)^2}. \tag{24}
\]
When \( n = 1 \), the single quantum coherence case, Eq. (24) exactly replicates the result obtained by Redfield theory illustrated in Ref. [6].

For the transverse magnetization \( M_z \) and \( M_y \) affected by the random field \( H_z(t) \) described by Eq. (1), the observable angular momentum \( I_x \) corresponding to \( M_z \) is affected by \( H_y(t) \) and \( H_y(t) \), while \( I_y \) is affected by \( H_y(t) \) and \( H_x(t) \) [6]. Only the angular momentum \( I_x \) will be considered. For simplicity, the rotating frame reference is used. Similar to the derivation of Eqs. (1) and (21) for angular momentum \( I_x \) affected by the random field \( H_x(t) \), it is straightforward to obtain

\[
\frac{dP_x(t, l)}{dt} = -DF_x P_x(t, l). \tag{25a}
\]

\[
\frac{dP_y(t, l)}{dt} = -DF_y P_y(t, l). \tag{25b}
\]

The relaxation of transverse magnetization is not affected by the lattice relaxation, and \( M_{xy} \) always relaxes toward zero. Therefore, no correction like Eq. (21) is needed. The combined effect of both \( z \) and \( y \) random fields on spin-spin relaxation of \( M_z \) will be

\[
\frac{1}{\tau_{2x}} = D_{\phi x} + D_{\phi y} = \gamma^2 (h_x^2 + h_y^2) \frac{1}{1 + (\omega_0 t)^2}, \tag{26a}
\]

and

\[
\frac{d(M_{xy})}{dt} = -\frac{1}{\tau_{2x}} (M_{xy}), \tag{26b}
\]

which agrees with the results in Ref. [6].

### 2.1.2 Dipolar coupling

For simplicity, only the dipolar coupling in the systems of two like spins is considered here. The random field arising from the dipolar coupling of a two-spin system can be written as [1]

\[
H_d(\Omega, t) = P(\Omega, t) \sum_q A^q F^q(\Omega), \tag{27a}
\]

where \( P(\Omega, t) \) is the correlation function depending on the molecule random motion, \( F^{(0)}(\Omega) \), \( F^{(1)}(\Omega) \), and \( F^{(2)}(\Omega) \) can be expressed based on normalized spherical harmonics as [1]

\[
F^{(0)}(\Omega) = \frac{1}{r^2} \sqrt{\frac{16\pi}{5}} Y_2^{(0)}(\Omega), \quad F^{(1)}(\Omega) = \frac{1}{r^3} \sqrt{\frac{8\pi}{15}} Y_2^{(1)}(\Omega), \quad F^{(2)}(\Omega) = \frac{1}{r^3} \sqrt{\frac{32\pi}{15}} Y_2^{(2)}(\Omega), \tag{27b}
\]

and

\[
A^{(0)} = -\frac{3}{2} \gamma_1 \gamma_2 h_2^2 \left\{ -\frac{1}{3} I_3 S_x + \frac{1}{6} (I_3 S_+ + I_3 S_-) \right\},
\]

\[
A^{(1)} = \frac{3}{2} \gamma_1 \gamma_2 h_2^2 \left\{ I_3 S_x + I_3 S_+ \right\},
\]

\[
A^{(2)} = \frac{3}{4} \gamma_1 \gamma_2 h_2^2 I_3 S_+. \tag{27c}
\]

We consider the dipolar coupling effects on the evolution of the angular momentum \( I_x \). Because \( A^{(0)} \) has no net effect on the change of the populations of like spins in different energy levels [1,6], we only need to consider the effect of \( A^{(2)} \) and \( A^{(1)} \). Let us consider the \( H^{(2)}(\Omega, t) \) term first. From Eqs. (27a-c), we have

\[
H^{(2)}(\Omega, t) = A^{(2)} F^{(2)}(\Omega) P(\Omega, t) = \frac{3}{r^3} \sqrt{\frac{2\pi}{15}} Y_2^{(2)}(\Omega) P(\Omega, t). \tag{28}
\]

For a normal rotational motion, the correlation function can be obtained from Debye rotational diffusion, which is [1]

\[
P(\Omega, t) = \sum_{lm} Y_l^m(\Omega_0) Y_l^m(\Omega) \exp \left( -\frac{t}{\tau} \right). \tag{29}
\]

where \( \tau_t \) is the rotational time constant.

By performing the spatial average on \( H^{(2)}(\Omega, t) \), we have
\[ \langle H_d^{(2)}(\Omega, t) \rangle = \int H_d^{(2)}(t) d\Omega = \frac{3}{r^3} \frac{2\pi}{15} f_1 y \hbar^2 l_s^4 s_{+} y_2^{(2*)}(\Omega) \exp \left( -\frac{t}{\tau_2} \right). \]  

(30)

For two like spins, the average jump time is \( \langle \tau_{\text{jump}} \rangle = \int_{-\infty}^{\infty} \exp \left( -\frac{t}{\tau_2} \right) \exp \left( -i\omega_0 t \right) dt = \frac{2\tau_2}{1 + (i\omega_0 \tau_2)^2} \), and the diffusion constant affected by \( A^{(\pm 2)} \) is

\[ D_{\phi 2\omega_0} = \frac{\langle (\Delta \phi)^2 \rangle}{2 \langle \tau_{\text{jump}} \rangle} = \frac{8}{5\pi} y^4 \hbar^2 \Big( l + 1 \Big) \frac{\tau_2}{1 + (2\omega_0 \tau_2)^2}. \]  

(31)

where \( l \) is the spin number. Similarly, for \( A^{(\pm 1)} \), we can get

\[ D_{\phi \omega_0} = \frac{\langle (\Delta \phi)^2 \rangle}{2 \langle \tau_{\text{jump}} \rangle} = \frac{2}{5\pi} y^4 \hbar^2 \Big( l + 1 \Big) \frac{\tau_2}{1 + (\omega_0 \tau_2)^2}. \]  

(32)

Based on Eqs. (23), (31), and (32), we get

\[ \frac{1}{\tau_1} = \frac{2}{5\pi} y^4 \hbar^2 \Big( l + 1 \Big) \left[ \frac{\tau_2}{1 + (\omega_0 \tau_2)^2} \right]^{-1} + \frac{4\tau_2}{1 + (2\omega_0 \tau_2)^2}. \]  

(33)

which agrees with Ref. [1].

2.2 Anomalous phase diffusion

In the above, the \( \langle \tau_{\text{jump}} \rangle \) is assumed to be a constant. In a heterogeneous system, it could belong to a distribution behaving asymptotically to a power law. Additionally, the amplitude of the random field \( H_q(t) = \gamma h q G_q(t) \) could belong to a distribution, which leads the phase jump length \( \Delta \phi \) to follow a power-law distribution. Therefore, the phase diffusion could be anomalous [17,18], whose diffusion constant \( D_{\phi \alpha} \) can be obtained by [16,21,22]

\[ D_{\phi \alpha} \propto \frac{\langle (\Delta \phi)^\beta \rangle}{2 \langle \tau_{\text{jump}} \rangle_f} = \frac{\omega_q^\beta \langle \tau_{\text{jump}} \rangle_f}{2}, \]  

(34)

where \( \omega_q^\beta \) is proportional to \( \langle \frac{H_q(t)}{\hbar} \rangle \), and \( \langle \tau_{\text{jump}} \rangle_f \) is the fractional mean jump time constant. The fractional diffusion equation can be described by [21,22]

\[ \frac{\partial}{\partial t} D_{\alpha}^\alpha P = D_{\phi \alpha} \Delta^{\alpha/2} P, \]  

(35)

where \( 0 < \alpha, \beta \leq 2, D_f \) is the fractional diffusion coefficient with units of \( \text{rad}^{\alpha}/\text{s}^{\alpha} \); \( \frac{\partial}{\partial t} D_{\alpha}^\alpha \) is the Caputo fractional derivative defined by [21,22]

\[ \frac{\partial}{\partial t} D_{\alpha}^\alpha f(t) = \begin{cases} \frac{\Gamma(m-\alpha)}{\Gamma(m)} \int_0^t \frac{f^{(m)}(s)}{(t-s)^{\alpha+1-m}} ds, & m - 1 < \alpha < m, \\ \frac{d^m}{dt^m} f(t), & \alpha = m, \end{cases} \]  

(36)

and \( \Delta^{\alpha/2} \) is the symmetric Riesz space-fractional derivative operator [29,30]. Performing Fourier transform on Eq. (35) gives

\[ \frac{\partial}{\partial t} D_{\alpha}^\alpha k(t) = -D_{\phi \alpha} k^\beta p(k, t), \]  

(37)

and the signal amplitude \( p(1, t) \) obeys

\[ \frac{\partial}{\partial t} D_{\alpha}^\alpha p(1, t) = -D_{\phi \alpha} p(1, t). \]  

(38)

The evolution of the angular momentum \( l_s \) and \( l_z \), based on Eqs. (37), and (38), can be described as:

\[ \frac{\partial}{\partial t} D_{\alpha}^\alpha p_{l_s}(1, t) = -D_{\phi \alpha} p_{l_s}(1, t), \]  

(39)

\[ \frac{\partial}{\partial t} D_{\alpha}^\alpha p_{l_z}(1, t) = -D_{\phi \alpha} (p_{l_z}(1, t) - p_{Mz_0}(1, t)). \]  

(40)

In Eq. (40), the thermal relaxation \( p_{Mz_0}(1, t) \) is included as mentioned in obtaining Eq. (21). Replacing \( p_{l_s}(1, t) \) and \( p_{l_z}(1, t) \) with the magnetization \( M_s(t) \) and \( M_z(t) \) in Eqs. (39) and (40) respectively, we have:
\[ tD^\alpha_t M_x(t) = -\frac{1}{T_x} M_x(t), \]  
\[ tD^\beta_t M_x(t) = -\frac{1}{T_1} (M_x(t) - M_{x0}). \]  

Eqs. (41) and (42) are anomalous relaxation equations, which agrees with the results in Ref. [15]. The solutions of Eqs. (41) and (42) are:

\[ M_x(t) = M_x(0) E_{a,1} \left( -\frac{t^a}{T_x} \right), \]  
\[ M_x(t) = M_{x0} + (M_x(0) - M_{x0}) E_{a,1} \left( -\frac{t^a}{T_1} \right). \]

2.3 The anomalous time correlation function

In section 2.1, the time correlation function is a monoexponential function. However, the monoexponential function is often not enough to explain relaxation experiments in macromolecular systems. The commonly used time correlation function is KWW function, \( \exp \left( -\left( \frac{t}{\tau} \right)^\alpha \right) \), which is a stretched exponential function. The time correlation function results from the random motion of lattice particles, which can be modeled by rotational or translational diffusion. The time correlation function is a monoexponential function from normal diffusion, while it is a stretched exponential function or Mittag-Leffler function for anomalous diffusion, which could be described by the fractional rotational or translational diffusion proposed in Refs. [8,12]. The anomalous rotational diffusion can be modeled by [12]

\[ \tau D^\alpha_t P = D_{fr} \frac{\alpha^\beta}{a^\beta} \Delta^\beta/2 P, \]  
where \( 0 < \alpha, \beta \leq 2, D_{fr} \) is the rotational diffusion coefficient, \( a \) is the radius, \( \tau D^\alpha_t \) is the Caputo fractional derivative defined by Eq. (36), and \( \Delta^\beta/2 \) is the symmetric Riesz space-fractional derivative operator [22,23]. The correlation time solved from Eq. (45) is [12]

\[ G(t)=E_{a,1} \left( -\frac{t^a}{\tau_r} \right), \]  
where

\[ \tau_r = \left( \frac{1}{\omega \times D_{fr} \frac{\alpha^\beta}{a^\beta}} \right)^{1/\alpha} \]

is the characteristic rotational time. The effective diffusion jump time is

\[ \langle \tau_{\text{jump}} \rangle_f = \int_0^\infty E_{a,1}(-|t|^a/\tau_r) e^{-i\omega t} dt = \frac{2\omega^{\alpha-1} \tau_r^\alpha \sin(\pi \alpha/2)}{1+2(i\omega \tau_r)^\alpha \cos(\pi \alpha/2)+(i\omega \tau_r)^{2\alpha}}. \]  

When \( \alpha = 1, \beta=2 \), Eq. (47) reduces to Eq. (13), the normal rotational diffusion result.

In some system, the correlation time depends on the translation diffusion. Anomalous diffusion can be modeled by [12]

\[ \tau D^\alpha_t P = 2D_{fr} \Delta^\beta/2, \]  
where \( 2D_{fr} \) is the relative fractional translational diffusion coefficient of the two interactive spins, which have the same translational diffusion coefficient \( D_{fr} \). The correlation time is [12]

\[ G^{(1)}(t) = e^{(1)}(\frac{N}{\alpha}) \int_0^\infty \left[ \int_\frac{x}{2} u^2 \right] E_{a,1} \left( -\frac{2D_{fr} u^{\beta-a}}{d^\beta} \right) du \]  

\[ \left( \frac{\alpha}{\beta} \right)^{1/\alpha} \]
where
\[ e^{(0)} = \frac{48\pi}{15}, \quad e^{(1)} = \frac{8\pi}{15}, \quad e^{(2)} = \frac{32\pi}{15}. \]
d is the distance, \( u = kd \), \( N \) is the density of spins, and \( J_2 \) is Bessel function \([1]\). The average phase jump length based on translational diffusion is
\[ \langle \tau_{\text{jump}} \rangle_f = 2 \int_0^\infty G(t) e^{i\omega t} dt = -\frac{e^{(i)} N_{\ell f} 1-a}{D_f 2^{3-\gamma} (\omega T_2) 1-a} \int_0^\infty u^{2\beta+2\gamma} (\omega T_2)^\alpha \sin \left( \frac{\pi \alpha}{2} u^\beta \right) \left[ J_1(u) \right]^2 du. \tag{50} \]

These two \( \langle \tau_{\text{jump}} \rangle_f \) in Eqs. (47) and (50) can be used to obtain the effective diffusion constants in Eqs. (14) and (34), and the NMR relaxation time can then be obtained, which will not be investigated further in this paper.

3. Results and discussion

A phase diffusion equation method is proposed to explain the NMR spin-lattice and spin-spin relaxation processes. This method treats the evolution of the magnetization affected by the random field as a random walk, which can be described by the normal or fractional diffusion equation. From solving the diffusion equation, it is found that the relaxation rate is \( W = \frac{1}{T_1} = D \phi \propto \left( \frac{H(t)}{h} \right)^2 \), which agrees with the result of the time-dependent perturbation theory \([1,6]\). The obtained relaxation time resulting from the simple random perturbing field \( H(t) = \sum_{q=x,y,z} H_q(t) l_q \) is the same as that obtained based on the Redfield theory presented in Ref. \([6]\). Additionally, the results obtained from dipolar coupling replicate the results obtained by the density operator method \([1,6]\).

In the time-space fractional diffusion equations, (35), (45), and (48), the Caputo fractional derivative \( \frac{d}{dt}^\alpha \) is used, yielding Mittag-Leffler-function-based results. Another type of time-fractional derivative, the time fractal derivative \( \frac{\partial}{\partial t^\alpha} \) has been applied to model various anomalous diffusion \([31,32,33]\). If \( \frac{d}{dt}^\alpha \) is replaced with \( \frac{\partial}{\partial t^\alpha} \), the corresponding results will be changed: In Eqs. (43) and (44), \( E_{a,1} \left( -\frac{t^\alpha}{T_2} \right) \) and \( E_{a,1} \left( -\frac{t^\alpha}{T_1} \right) \) will be replaced with \( \exp \left( -\frac{t^\alpha}{T_2} \right) \) and \( \exp \left( -\frac{t^\alpha}{T_1} \right) \) respectively; in Eq. (46), \( E_{a,1} \left( -\frac{t^\alpha}{T_1} \right) \) will be replaced with \( \exp \left( -\frac{t^\alpha}{T_2} \right) \); in Eq. (49), \( E_{a,1} \left( -\frac{2D f u^\beta t^\alpha}{d^\alpha} \right) \) will be replaced with \( \exp \left( -\frac{2D f u^\beta t^\alpha}{d^\alpha} \right) \).

Two diffusion processes affect NMR relaxation: the phase diffusion of magnetization, and the rotational or translational diffusion due to the relative motion of lattice particles in real space. The kind of phase diffusion determines whether the relaxation equation is normal or anomalous. The normal relaxation function is monoexponential, while the anomalous relaxation function is either a Mittag-Leffler based function or stretched exponential based function. The fitting of practical experimental relaxation data obtained from the same temperature could determine which type of NMR relaxation is present, while the anomalous rotational or translational diffusion determines the correlation time, and thus the \( \langle \tau_{\text{jump}} \rangle \). To determine which type of rotational or translational diffusion is present, experimental data from various temperatures and multiple magnetic fields are often necessary. For example, Ref. \([12]\) applied MLF and SEF function to fit \(^2\)H spin-lattice relaxation of deuterium-labeled head-to-head poly(propylene) (hhPP) in a 70 % polyisobutylene (PIB) and 30 % hhPP blend \([5]\), where the data points come from ten different temperatures and two field frequencies, 30.7 MHz and 61.4 MHz respectively \([5]\).

Eq. (13) gives a simple monoexponential correlation function, \( \langle \tau_{\text{jump}} \rangle = \frac{2\pi}{1+\omega_0 T_2} \), which implies \( \langle \tau_{\text{jump}} \rangle = 1/\omega_0 \) when the perturbation is on resonance. Therefore, the on resonance relaxation rate is \( W = \)
\[ D_\phi = \frac{\omega^2 q(t_{\text{jump}})}{2} = \frac{\omega^2 q}{2\omega_0} = \frac{\hbar^2}{2h} \cdot \frac{\omega q}{\omega_0}. \] 

When the relaxation of the whole system including the spin and the lattice is considered, \( \frac{\omega q}{\omega_0} \) could be a constant or even 1; if the system has two different energy levels, we could have \( \frac{W_1}{W_2} = \frac{H_{1x}(t)}{H_{2x}(t)} = \frac{H_{2x}(t) - (H_{2x}(t) - H_{1x}(t))}{H_{2x}(t)} \), which reduces to \( \frac{W_1}{W_1} = \exp\left(-\frac{H_{2x}(t) - H_{1x}(t)}{H_{2x}(t)}\right) \), when \( (H_{2x}(t) - H_{1x}(t)) \) is small compared to \( H_{2x}(t) \). Because the relaxation is from the whole system, the \( H_{2x}(t) \) could be replaced with \( KT \), and we could have \( \frac{W_1}{W_1} = \exp\left(-\frac{2E_2(t) - E_1(t)}{kT}\right) \), which is a Boltzmann distribution result [1,6].

Most of the theory is based on the classical method. The traditional density operator method is more convenient to calculate the complex Hamiltonian interaction than the diffusion method. However, the diffusion method proposed here may be more convenient to understand the anomalous relaxation process. Meanwhile, the anomalous relaxation time can be analyzed from this method based on \( \frac{1}{T_1} = D_\phi \propto \frac{\omega^2 q(t_{\text{jump}})}{2} \) from this method. The effect of the distribution of \( \langle t_{\text{jump}} \rangle \) on \( \langle t_{\text{jump}} \rangle \), and other complicated interactions such as quadrupolar interaction, anisotropic chemical shift are not considered in the paper. Further effort is needed to improve the current method.

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