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Fractional Langevin Equation Model for Characterization of Anomalous Brownian Motion from NMR Signals

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Abstract. Nuclear magnetic resonance is often used to study random motion of spins in different systems. In the long-time limit the current mathematical description of the experiments allows proper interpretation of measurements of normal and anomalous diffusion. The shorter-time dynamics is however correctly considered only in a few works that do not go beyond the standard Langevin theory of the Brownian motion (BM). In the present work, the attenuation function $S(t)$ for an ensemble of spins in a magnetic-field gradient, expressed in a form applicable for any kind of stationary stochastic dynamics of spins with or without a memory, is calculated in the frame of the model of fractional BM. The solution of the model for particles trapped in a harmonic potential is obtained in a simple way and used for the calculation of $S(t)$. In the limit of free particles coupled to a fractal heat bath, the results compare favorably with experiments acquired in human neuronal tissues.

1 Introduction

The present work connects two fields: the Brownian motion (BM) of particles in soft condensed materials and Nuclear Magnetic Resonance (NMR) as a tool of its observation. NMR has proven to be a very effective non-invasive method of studying molecular self-diffusion and diffusion in various materials [1]. Brownian particles in some media often show interesting behaviors, such as a dynamics that significantly differs from that predicted by the standard Langevin theory [2]. It seems natural to apply NMR methods to follow such unusual BM. However, as discussed in [3–5], the mathematical description of suitable NMR experiments in the literature is valid only for long times when the particles are in diffusion regime (normal or anomalous). The only exception is the memoryless Langevin model for which correct interpretations of the NMR experiments have been proposed [6]. Possible memory effects in the shorter-time particle dynamics are ignored or incorrectly taken into account. The aim of our recent papers [3–5, 7] was to overcome this limitation and to calculate the all-time attenuation functions of the NMR signals from spin-bearing particles resulting from the BM with memory. We have considered the Brownian particles in Maxwell fluids [3, 7] and the BM with hydrodynamic memory [4]. Here we focus on a popular model of fractional BM [8–11]. This model emerges naturally,

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e.g., in viscoelastic media, and interpolates between the standard Langevin equation (LE) and a model with constant memory [11]. We obtain the solution of the generalized Langevin equation (GLE) for this model in an exceedingly simple way. The Brownian particles can be free or trapped in a harmonic potential. The results for the mean square displacement (MSD) of the particles are then applied to calculate the attenuation function $S(t)$ for an ensemble of spins in a magnetic-field gradient. $S(t)$ is used in the form obtained by the method of accumulation of phases in the frame rotating with the resonance frequency [3] and applicable for any time and kind of the stochastic motion od spins. Although our work was mainly aimed to contribute to adequate interpretations of the NMR experiments on the BM in complex fluids, in the limit of free particles coupled to a fractal heat bath our results correct the description and give favorable comparison with experiments acquired in human neuronal tissues [12].

2 Harmonically bounded particle described by the fractional LE

If a particle is moving in a trap modeled by a Hookean potential with elastic constant k, the GLE reads

$$M\dot{\upsilon}(t) + \int_0^t G(t-t')\,\upsilon(t')\,dt' + k\int_0^t \upsilon(t')\,dt' = f(t), \tag{1}$$

where M is the mass of the particle, $x(t)$ is its position and $\upsilon(t) = \dot{x}(t)$ its velocity. We will consider the memory kernel $G(t) = \gamma_\varepsilon \varepsilon t^{\varepsilon-1}$, $t > 0$, $1 > \varepsilon > 0$. Within the linear response theory the second fluctuation-dissipation theorem [13] relates $G(t)$ to the random force $f(t)$, $\langle f(t)f(0)\rangle = k_B T G(t)$, where k_B is the Boltzmann constant and T is the temperature. When $\varepsilon \to 0$, $G(t) \to 2\gamma\delta(t)$ and Eq. (1) becomes the standard memoryless LE with the white noise force and a purely viscous Stokes friction force $-\gamma\upsilon(t)$. To our opinion, the simplest method of solving linear GLE equations, which goes back to the old work [14], is as follows [15–19]. If we are interested in finding the MSD of the particle, $X(t) = \langle [x(t) - x(0)]^2\rangle$, we have merely to replace $x(t)$ in (1) by $X(t)$ and to substitute the stochastic force driving the particle with $2k_BT$. With the initial conditions $X(0) = \dot{X}(0) = 0$ the new equation is immediately solved by using the Laplace transformation,

$$\tilde{X}(s) = \int_0^\infty X(t)e^{-st}dt = \frac{2k_BT}{Ms}\left[s^2 + \frac{\gamma_\varepsilon}{M}\Gamma(\varepsilon+1)\,s^{1-\varepsilon} + \frac{k}{M}\right]^{-1}, \tag{2}$$

where $\Gamma(z)$ is the gamma function. Thus, in this way the exact solution of (1), first obtained in [10], can be easily got in a few steps. The limiting cases of short and long times correspond to large and small s, respectively, so that if $\varepsilon < 1$ then at $s \to 0$ one finds $\tilde{X}(s) \simeq 2k_BT/ks$ and $X(t) \simeq 2k_BT/k$, if $t \to \infty$. At $s \to \infty$, $X(s) \simeq 2k_BT/Ms^3$ and $X(t) \simeq k_BTt^2/M$. Corrections to these expressions can be obtained from the exact representation of (2) in the time domain through the Mittag-Leffler functions $E^{(k)}_{\alpha,\beta}(y)$ [10],

$$X(t) = \frac{2k_BT}{M}\sum\nolimits_{k=0}^{\infty}\frac{(-1)^k}{k!}(\omega t)^{2k}t^2E^{(k)}_{1+\varepsilon,3+k-\varepsilon k}\left(-\varepsilon\gamma_\varepsilon\Gamma(\varepsilon)t^{1+\varepsilon}/M\right), \tag{3}$$

where $E^{(k)}_{\alpha,\beta}(y) = \left(d^k/dy^k\right)\sum_{j=0}^{\infty} y^j\Gamma^{-1}(\alpha j+\beta)$, $\alpha > 0, \beta > 0$. It should be noted that the short-time expansion of this solution for $X(t)$, as given in [10], Eq. (41), does not correspond to the solution of the standard LE (Eq. (1) in the limit $\varepsilon \to 0$ [20]). If $\omega^2 = k/M$ and $\omega_M = \gamma/M$, in [10], Eq. (41), the t^4 term should be $(1/12)(\omega_M^2 - \omega^2)t^4$, *i.e*, the term containing ω_M is missing. Another way to show that the expansions in [10] should be completed is to consider the limit of a free Brownian particle (when $\omega = 0$). The velocity autocorrelation function in this case must be $\langle\upsilon(0)\upsilon(t) = (k_BT/M)\exp(-\omega_M t)$, which does not agree with Eq. (42) [10]. The limit of (3) for a free particle was used in [12] to calculate the NMR signals from human neuronal tissues, however, with an incorrect spin-echo attenuation $S(t)$ (see [3]). The basic formulas used to calculate $S(t)$ are presented in the following section.

3 Attenuation of the NMR signals due to Brownian motion

Below we will consider experiments with the NMR signals from a liquid or gaseous system with spin-bearing Brownian particles placed in a strong magnetic field B_0 along the axis x. The magnetization of spins is modulated by a field gradient $g(t)$. General formulas for the attenuation function $S(t)$ of the observed NMR signal that are applicable to any kind of stochastic motion of spins, including their dynamics with memory, have been obtained in [3, 7]. In the evaluation of $S(t)$ it was only assumed that the studied random processes are stationary in the sense that the autocorrelation function of a fluctuating dynamical variable x at times t and t' depends only on the time difference, $t - t'$: $\langle x(t)x(t')\rangle = \langle x(t-t')x(0)\rangle$ [1]. One more assumption is that the distribution of the random variables is Gaussian, or that the accumulated phase ϕ in the frame rotating with the resonance frequency $\gamma_n B_0$, where γ_n is the nuclear gyromagnetic ratio, is small. In these cases the nuclear induction signal observed in the presence of a steady magnetic-field gradient after the $\pi/2$ rf pulse applied at time $t = 0$, $S(t) = \langle \exp[i\phi(t)]\rangle = \exp[-\langle \phi^2(t)/2\rangle]$ [1], is $S(t) = \exp[-(1/2)\gamma_n^2 g^2 \int_0^t t' X(t')dt']$. To our knowledge, this simple formula for a constant gradient g was for the first time proposed in [7]. In the pulsed-gradient spin echo experiment [1] between two gradient pulses, the duration of each being δ, a π rf pulse is applied. Let the first gradient pulse begins at time t_0 after the $\pi/2$ rf pulse and the second one at time $t = \Delta$. The result for $t < \tau$ (up to the second rf pulse) is the same as for a steady gradient (with $t = \delta$). Due to stationarity, after the second rf and gradient pulses the result of the calculation of the echo signal observed at $t = 2\tau$ does not depend on t_0 and can be evaluated from [3]

$$S(\delta, \Delta) = \exp\left\{-(1/2)\gamma_n^2 g^2 \left[\int_0^\delta dt' \int_0^\delta dt'' X(t'' - t' + \Delta) - 2\int_0^\delta dt' (\delta - t') X(t')\right]\right\}. \quad (4)$$

One can check that this equation gives the known results for particles in diffusion regime, when $X(t) = Ct^\alpha$ (C is a temperature-dependent parameter, $\alpha = 1$ corresponds to normal diffusion with $C = 2D$ and the diffusion coefficient $D = k_B T/\gamma$, $\alpha < 1$ to sub-diffusion, and $\alpha > 1$ to super-diffusion [15]. In our study the solution (3) was used to obtain the NMR signal decay from Eq. (4). The function $S(t)$ has been analyzed in detail for different situations (free and trapped particles, weak and strong traps, short and long times). As an important example that generalizes the known results for standard Langevin and diffusion models (normal and anomalous) we show that in the long-time approximation ($\gamma_\varepsilon \Gamma(\varepsilon + 1) t^{\varepsilon+1}/M \gg 1$) and weak traps ($M\omega^2 t^{1-\varepsilon} \ll \gamma_\varepsilon \Gamma(1+\varepsilon)$) the decay of the NMR signal at any time after the second gradient pulse is given by the mean of the square of the accumulated phase

$$\left\langle \phi^2(\delta, \Delta)\right\rangle = \frac{2k_B T \gamma_n^2 g^2}{\gamma_\varepsilon \Gamma(1+\varepsilon)\Gamma(2-\varepsilon)} \left[\psi_{1-\varepsilon} - \frac{M\omega^2 \Gamma(2-\varepsilon)}{\gamma_\varepsilon \Gamma(1+\varepsilon)\Gamma(3-2\varepsilon)} \psi_{2-2\varepsilon} + \cdots\right]. \quad (5)$$

Here, $\psi_\alpha = [(\Delta+\delta)^{\alpha+2} + (\Delta-\delta)^{\alpha+2} - 2\Delta^{\alpha+2} - 2\delta^{\alpha+2}][(\alpha+1)(\alpha+2)]^{-1}$. When $\varepsilon = 0$, $\langle \phi^2(\delta, \Delta)\rangle = 2k_B T \gamma_n^2 g^2 \gamma^{-1}[\psi_1 - M\omega^2 \psi_2/2\gamma + \cdots]$ with $\psi_1 = \delta^2(\Delta - \delta/3)$ and $\psi_2 = (\delta\Delta)^2$. The function $S(t)$ calculated from the first term in (5) at this limit can be compared with the results [12] of the attenuation of steady-gradient ($\Delta = \delta = t$) spin-echo signal from water molecules anomalously diffusing in a human brain tissue. We have obtained a very good agreement with these measurements but, since in [12] an erroneous formula for $S(t)$ was used (see [3]), the parameters ε and the generalized diffusion coefficient $D_\varepsilon = k_B T/\gamma_\varepsilon$ extracted from the experiments are very different. For example, instead of $\varepsilon = 0.31$ determined in [12] (Table 1), the best correspondence with the measurements is obtained for ε about 0.42. Even if ε was correctly extracted from the experiments, D_ε found in [12] would have to be divided by $2(2^{1-\varepsilon} - 1)/(2 - \varepsilon)$, which, for $\varepsilon \in [0, 1]$ changes from 0 to 1 (e.g., if $\varepsilon = 0.5$, see Table II [12], D_ε should be about 1.8 times larger).

4 Conclusion

The phenomenological model of fractional Brownian motion is one of the most popular and best justified models in the soft condensed matter physics. It generalizes other models of the stochastic dynamics described by the generalized Langevin equation. On the other hand, various NMR methods serve as probes for accurate characterization of the random motion of particles in different systems, including the biological ones due to the non-invasive character of these measurements. In spite of the long time since the invention of such methods as the NMR spin echo, its description in the literature is limited to long times when the spin-bearing particles are in the diffusion regime, or to the stochastic motion without memory. Nowadays it is well known that in the description of the behavior of many systems this simplification fails. In our work we have proposed an interpretation of the NMR experiments that could provide a characterization of the Brownian motion in systems described by the fractional generalized Langevin model. The new formulas for the attenuation function of the NMR signals can be directly used to describe the behavior of spins exhibiting any kind of the stochastic dynamics not only in the diffusion limit, but for all times. Although the presented approach assumes Brownian particles much larger than the surrounding molecules, surprisingly it leads to a very good agreement with experiments on diffusion of water molecules in neuronal tissues.

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