# Fractional Langevin equation model for characterization of anomalous Brownian motion from NMR signals

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- The work connects two fields: the stochastic dynamics of different particles and Nuclear Magnetic Resonance as a tool of its observation.

- Brownian particles in complex fluids often show interesting behaviors (such as anomalous diffusion at long times).

- NMR has proven to be an effective means for studying molecular self-diffusion and diffusion in various materials and has a wide range of applications.

- The influence of diffusion on the signal of the NMR experiments is described by the diffusion suppression function $S(t)$.

So far $S(t)$ is calculated by using the Bloch-Torrey equation for the spin magnetization

$$\frac{\partial \vec{M}}{\partial t} = \gamma \vec{M} \times \vec{B} - \frac{M_x \vec{i} + M_y \vec{j}}{T_2} - \frac{M_z - M_0}{T_1} \vec{k} + D \Delta \vec{M}$$

or through the resonance frequency offset, which is expressed through the position of the nuclear spin. The attenuation of the signal induced by the magnetization (Free Induction Decay) is given by

$$\ln S(t) \sim -Dt^3$$

- The known results in both the approaches are valid only within the long-time approximation (except the standard memoryless Langevin equation model). Possible memory effects are ignored or not correctly taken into account.

## Aim of the work

**- To overcome this limitation and to calculate $S(t)$ for any times and kind of the stochastic motion of spins, including their dynamics with memory.**

## Main results

- $S(t)$ for an ensemble of spins in a magnetic-field gradient is calculated through the accumulation of the phase shifts due to the particle displacements.

- The results are expressed through the mean square displacement (MSD), the well-defined function for both unbounded and bounded Brownian motion.

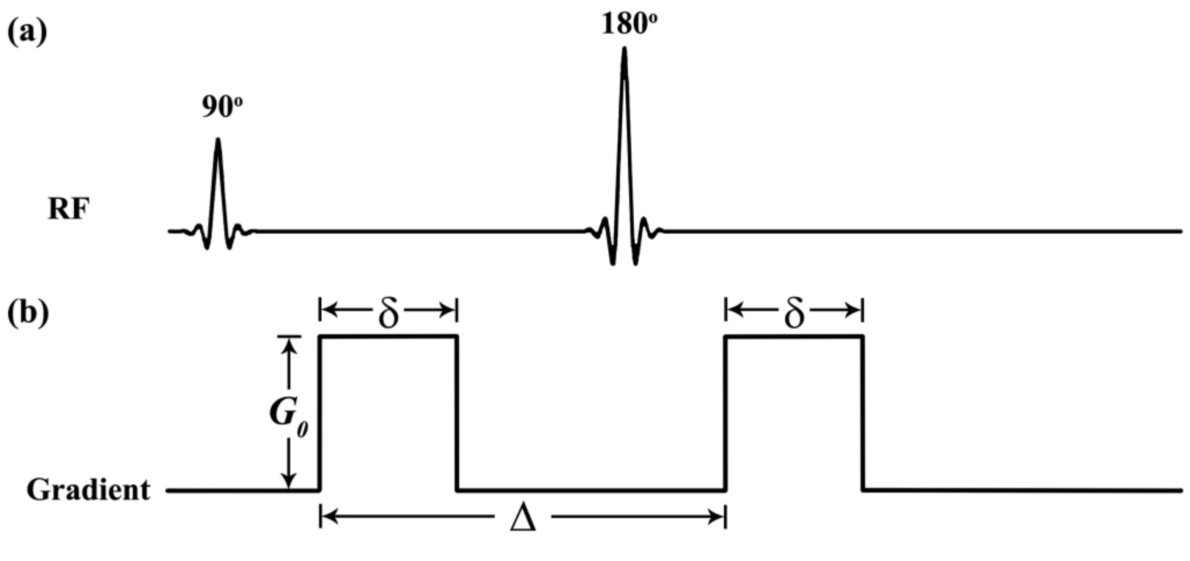
- The obtained formulas for $S(t)$ due to the particle motion generalize the known ones and are model-independent and thus applicable for the Brownian motion with memory.

- FID and spin echo NMR experiments are considered in detail for the model of fractional BM.

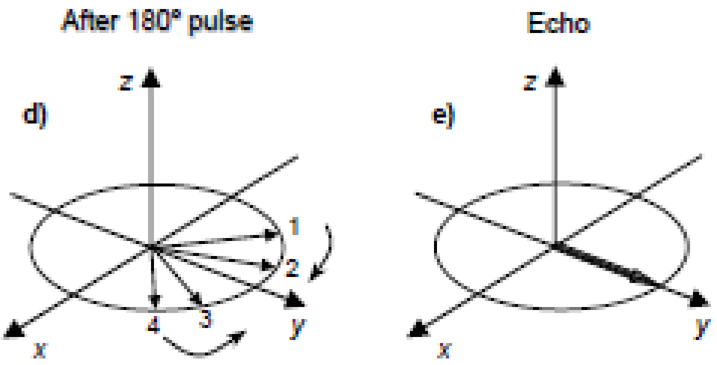
- The expressions valid for normal and anomalous diffusion are only special cases at long-time approximation within our consideration.

## Nuclear induction signal in the presence of a field gradient

We consider the following experiment:




At time $t = \tau$ after the first 90° rf pulse the spins are inverted by a 180° pulse. The echo signal amplitude is measured at time $2\tau$. A static magnetic field creates macroscopic magnetization and a constant magnetic field gradient $g$ is applied.




**More than 60 years after this experiment its description is valid only for long times** (except the simplest standard Langevin theory for the Brownian motion [Stepisnik (1991), Cooke (2009), Fan (2015)]).

## The attenuation function

$$S(t) = \langle \exp[i\phi(t)] \rangle = \left\langle \exp\left[ i\int_0^t \omega(\tau)\,d\tau \right] \right\rangle$$

$\omega(t)$ is the time-dependent resonance frequency offset. For Gaussian distribution of random variables (or for small $\phi$)

$$S(t) = \exp\left[ -\frac{1}{2}\langle \phi^2(t) \rangle \right]$$

The phase accumulation is calculated by using $\omega = -\gamma_n B$ and $B = B_0 + g(t)z(t)$

$$\phi(t) = -\gamma_n \int_0^t \left[ B(z(t')) - B(z(0)) \right] dt' = -\gamma_n \int_0^t g\left[ z(t') - z(0) \right] dt',$$

$g$ is the applied gradient strength, $\gamma_n$ is the nuclear gyromagnetic ratio, $z(t)$ is the spin position.

Assuming stationary random processes, for a constant gradient during $t$,

$$S(t) = \exp\left[ -\frac{1}{2}\gamma_n^2 g^2 \int_0^t t' Z(t')\,dt' \right], \qquad Z(t) = \langle [z(t) - z(0)]^2 \rangle.$$

In the same way the echo attenuation can be found, $S(\delta,\Delta)$, taking into account the inversion of the spins at time Δ.

At long times, in the standard diffusion regime, when $Z(t)=2Dt$, the textbook expressions are recovered,

$$S(t)=\exp\left[-\frac{1}{3}\gamma_n^2 g^2 D t^3\right] \text{ (FID)}$$

$$S(\delta,\Delta)=\exp\left[-\gamma_n^2 g^2 D\delta^2(\Delta-\delta/3)\right] \text{ (Hahn echo)}$$

In the case of anomalous diffusion, $Z(t)=Ct^{\alpha}$ ($\alpha<1$ – subdiffusion, $\alpha>1$ – superdiffusion)

$$S(\delta,\Delta)=\exp\left\{-\frac{C\gamma_n^2 g^2}{2(\alpha+1)(\alpha+2)}\left[(\Delta+\delta)^{\alpha+2}+(\Delta-\delta)^{\alpha+2}-2\Delta^{\alpha+2}-2\delta^{\alpha+2}\right]\right\}$$

If $\alpha = 1$, the result is for normal diffusion. The case $\delta << \Delta$ can be represented directly through the MSD

$$S(\Delta,\delta<<\Delta)\approx\exp\left[-\gamma_n^2 g^2 Z(\Delta)/2\right].$$

## Fractional Langevin equation for the Brownian motion

If a particle is moving in a trap modeled by a Hookean potential with elastic constant *k*, the generalized Langevin equation (GLE) reads

$$M\dot{\upsilon}(t)+\int_0^t \Gamma(t-t')\upsilon(t')dt'+k\int_0^t \upsilon(t')dt'=f(t)$$

For fractional Brownian motion the memory kernel

$$\Gamma(t)=\gamma_\varepsilon \varepsilon t^{\varepsilon-1},\ \ 1>\varepsilon>0,\ \ t>0$$

$\langle f(t)f(0)\rangle=k_B T\Gamma(t)$ (2nd fluctuation-dissipation theorem).

This model emerges naturally, e.g., in viscoelastic media, and interpolates between the standard memoryless LE with the white noise force and a purely viscous Stokes friction force $-\gamma\upsilon(t)$ ($\varepsilon\to 0$, $\Gamma(t)\to 2\gamma\delta(t)$), and a model with constant memory.

The simplest way to solve this equation is as follows:

$$M\ddot{Z}(t)+\int_0^t \Gamma(t-t')\dot{Z}(t')dt'+kZ(t)=2k_BT$$

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

Exact representation in the time domain is through the Mittag-Leffler functions,

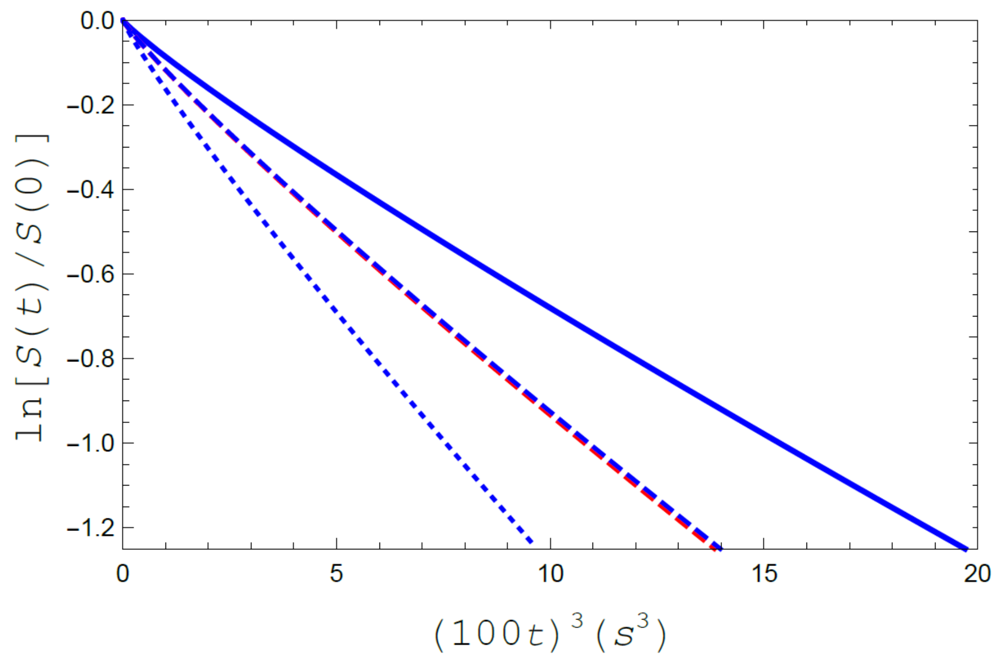
$$Z(t)=\frac{2k_BT}{M}\sum_{k=0}^{\infty}\frac{(-1)^k}{k!}(\omega t)^{2k}\,t^2E^{(k)}_{1+\varepsilon,3+k-\varepsilon k}\left(-\varepsilon\gamma_\varepsilon\Gamma(\varepsilon)t^{1+\varepsilon}/M\right),$$

$$E^{(k)}_{\alpha,\beta}(y)=\left(d^k/dy^k\right)\sum_{j=0}^{\infty}y^j\Gamma^{-1}(\alpha j+\beta),\ \alpha>0,\ \beta>0$$

By using this solution, the attenuation $S(t)$ have been calculated.

**Free particle ($k$ = 0),** steady-gradient echo case when $\Delta=\delta=t$

At long times, $\gamma_\varepsilon\Gamma(\varepsilon+1)t^{\varepsilon+1}/M>>1, -\ln\left[\frac{S(t)}{S(0)}\right]\approx\frac{4\left(2^{1-\varepsilon}-1\right)\gamma_n^2g^2k_BT}{(2-\varepsilon)(3-\varepsilon)\Gamma(2-\varepsilon)\gamma_\varepsilon}t^{3-\varepsilon}$

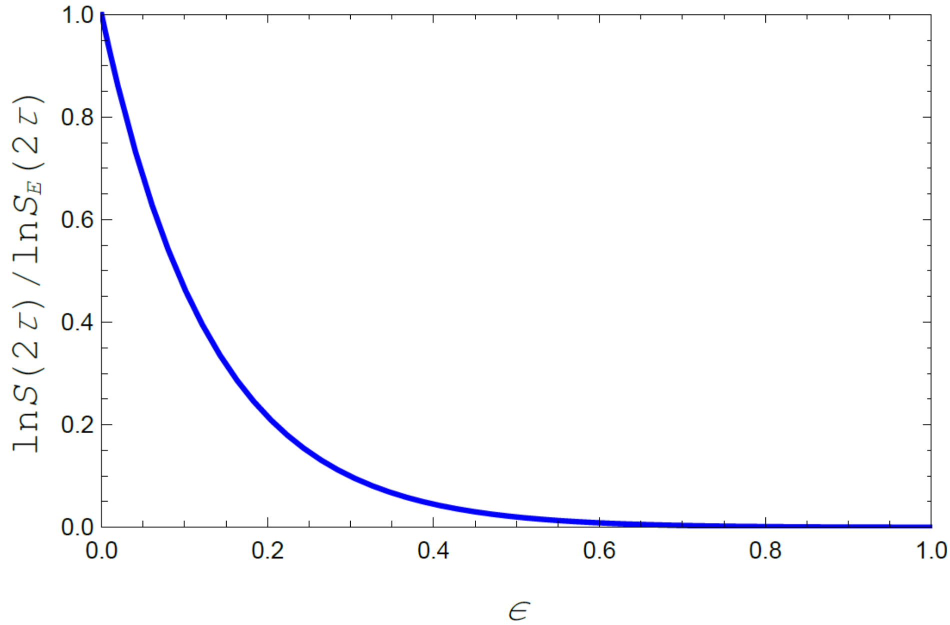



$\varepsilon=0.3$, blue – different $D_\varepsilon$. The theory can be very well fitted to the experiment (red) on human neuronal tissue [Cooke, PRE 2009].

## Trapped particles, long times, steady-gradient echo

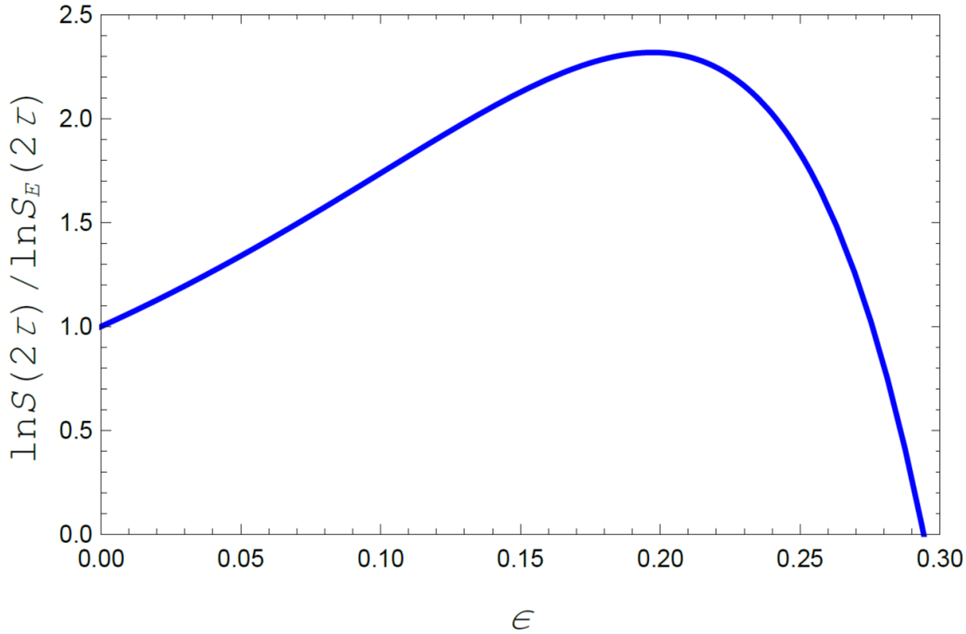
**Strong trap,** $M\omega^2 t^{1-\varepsilon} >> \gamma_\varepsilon \Gamma(1+\varepsilon)$

Illustration for a micron-sized particle (with $S_E(2\tau) = \exp\left(-2k_B T \gamma_n^2 g^2 k^{-2} \gamma\tau\right)$), $\tau$ = 10 ms, viscosity as for water at room $T$, $k \sim 10^2$ μN/m




**Weak trap,** $M\omega^2 t^{1-\varepsilon} << \gamma_\varepsilon \Gamma(1+\varepsilon)$, $k$ = 1 μN/m, viscosity as for blood

$S_E(2\tau) \approx \exp\left(-2k_B T \gamma_n^2 g^2 \tau^3 / 3\gamma\right)$



## Conclusion

Many years after the invention of the NMR the theoretical description of its application in studies of the Brownian motion (BM) with memory is lacking:

either improper formulas for the attenuation function $S(t)$ are used or the BM is not correctly described.

In the present work

– new formulas for $S(t)$ are proposed that generalize the classical expressions to any times of observation of the motion of spin-bearing particles, taking into account memory in the dynamics; $S(t)$ is expressed through the MSD

– an exceedingly simple method is applied to evaluate the MSD of the particles in the fractional Brownian motion

– by using it, $S(t)$ is calculated and analyzed in detail for free and trapped particles.

The results could have an impact on the determination of friction forces and diffusion characteristic of particles moving in complex systems.

Parts of this work have been published by us in:

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J. Molec. Liquids **234** (2017) 182; Acta Phys. Pol. **131** (2017) 1111.