Probing memory effects in porous media using Nuclear Magnetic Resonance

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Abstract: Nuclear Magnetic Resonance is a powerful method to investigate transport properties, and among other observables it measures the characteristic function of path integrals of fluid particle motions. Such measurements are commonly interpreted on the basis of Brownian motion, and allow us measuring mean velocities and dispersion coefficients, in media where tarnsport is normal. In porous media where memory effects are supposed to occur, the NMR signal can be computed on the basis of a more general model: it allows us discriminating between normal and anomalous dispersion.

Keywords: Sub-diffusion, Nuclear Magnetic Resonance

1. INTRODUCTION

Transport in complex media often shows sub-diffusive behaviors. Inserting in Brownian motion a random time change based upon stable Lévy laws of stability exponent γ yields a more general stochastic model, representing normal diffusion for $\gamma = 1$ and sub-diffusion for $0 < \gamma < 1$. Assuming this model, small scale displacements of fluid particles (between two given instants) have characteristic functions that are measured by Nuclear Magnetic Resonance. Moreover, mathematical expressions are available Néel et al. (2011) and show that they oscillate around a limit value when the conjugate variable (of displacements) becomes large. Such asymptotic behavior is difficult to observe when the diffusivity is small. Nevertheless, numerical studies indicate that the characteristic function of path integrals using two opposite step functions shows the same behavior and is more easily observed. After having detailed the stochastic model, generalizing Brownian motion, we recall the link with NMR echoes. Then, we show that echoes corresponding to large magnetic gradients behave differently according to the values of γ.

2. A STOCHASTIC MODEL FOR NORMAL DIFFUSION AND SUB-DIFFUSION IN POROUS MEDIA

An essential component of porous media is the solid matrix, that gives to fluid and solute particles opportunities of being arrested, then released. Assuming first order kinetics for trapping and release yields the Mobile Immobile Model Van Genuchten et al. (1976): at time instant t, each individual particle has position

$$x(t) = x_0 + vZ(t) + \sqrt{2D}B(Z(t)). \tag{1}$$

Here $B(t)$ represents standard Brownian motion, while v and D are a mean velocity and a diffusivity with, moreover $Z(t) = \frac{t}{1+\Lambda}$. Number Λ represents the probability for a particle to be arrested, or, equivalently, the fraction of immobile fluid in the medium. This model helped interpreting many field and laboratory data, especially in complex porous media.

There still remain porous media where early break-through and late arrival show heavy tails that suggest using the fractal Mobile Immobile Model Benson et al. (2009) Schumer et al. (2003), obtained by defining $Z(t)$ as a random time change. In the above described case, $Z(t)$ computes the inverse of $t = z + \Lambda z$, that links instant t to the time z, each particle has spent moving before time t. Assuming instead that trapping periods are random, and, moreover, distributed as $\Lambda z^{1/\gamma} W_1$, where W_1 is a maximally skewed stable Lévy law of exponent $\gamma \leq 1$, allows a more general link between physical time t and operational time z of each fluid particle: $t = z + \Lambda z^{1/\gamma} W_1$. The corresponding random time change is the inverse of process $z \to z + \Lambda z^{1/\gamma} W_1$, itself defined by

$$Z(t) = inf\{z \in R^+ / z + z^{1/\gamma} \Lambda W_1 > t\}. \tag{2}$$

The above addressed case is achieved by setting $\gamma = 1$ since, then, W_1 is a Dirac atom.

The four parameters D, v, Λ, γ are linked to functionals of that processes, measured by Nuclear Magnetic Resonance.

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3. NUCLEAR MAGNETIC RESONANCE AND CHARACTERISTIC FUNCTION

In NMR experiments, the spins carried by water molecules can be coded at two distinct times t_1 and t_2 (with $0 < t_1 < t_2$) by applying a gradient $g(t) = a[\delta(t-t_2)-\delta(t-t_1)]$ consisting of two narrow pulses. Then, the measured magnetization signal is the ensemble average $< e^{i\Phi} >$ Callaghan (2001) with $\Phi = \int_0^t g(t')x(t')dt'$, where $x(t)$ represents the position of each water molecule, in the gradient's direction. With the two gradient pulses as mentioned above, the phase change resulting from the displacement of spins following their own trajectories during time $t > t_2$ is $\Phi = a[x(t_2) - x(t_1)]$. Hence, the magnetization signal $< e^{i\Phi} >$ is the mathematical expectation $< e^{ia[x(t_2)-x(t_1)]} >$. Upon varying gradient's intensity a, it yields the characteristic function of $x(t_2) - x(t_1)$. Exact expressions were obtained by Néel et al. (2011), upon assuming walkers displacements represented by the fractal Mobile-Immobile Model. Instead of narrow pulses, piecewise constant gradient $g(t) = a[1_{[t_2-d,t_2+d]}(t) - 1_{[t_1-d,t_1+d]}(t)]$ can be applied: the then measured echo is still $< e^{i\Phi} >$, with now $\Phi = \int_0^t g(t')x(t')dt'$.

The mathematical expectation of walkers displacements between t_1 and t_2 is given by the following expression, uing the Mittag-leffler function $E_\alpha(z) = \Sigma_{k=0}^{\infty} \frac{z^k}{\Gamma(\alpha k+1)}$:

$$\begin{gathered} < e^{ia(x(t_2)-x(t_1))} >= \\ [1 + iav[E_{1-\gamma}(-\Lambda(t+t_1)^{1-\gamma})* \\ (Id + \Lambda I_{0,+}^{1-\gamma} - iavI_{0,+}^{1})^{-1}(Id + \Lambda I_{0,+}^{1-\gamma})(1)](t_2 - t_1)] \\ \times[1 - a^2 D[E_{1-\gamma}(-\Lambda(t+t_1)^{1-\gamma})* \\ (Id + \Lambda I_{0,+}^{1-\gamma} + a^2 D I_{0,+}^{1})^{-1}(Id + \Lambda I_{0,+}^{1-\gamma})(1)](t_2 - t_1)]. \quad (3) \end{gathered}$$

Here $*$ represents Laplace convolution, and operator $I_{0,+}^{\alpha}$ is the convolution of kernel $\frac{t^{1-\alpha}}{\Gamma(\alpha)}$.

4. HIGHLIGHTING MEMORY EFFECTS

At large values of Da^2 and t_1, the real part of $< e^{ia[x(t_2)-x(t_1)]} >$ tends to become constant, as on Figure 1, because of the asymptotic behavior of Mittag-Leffler functions. For $\gamma < 1$ the characteristic function oscillates around $1 - (Id + \Lambda I_{0,+}^{1-\gamma})E_{1-\gamma}(-\Lambda(t+t_1)^{1-\gamma})$ when a is large. If, moreover, $t_2 - t_1$ is small, this expression is near $E_{1-\gamma}(-\Lambda(t_1)^{1-\gamma})$. For $\gamma = 0$, differently, the limit is 0, because then, Mittag-Leffler functions in (3) are exponentials that decrease rapidly to 0 when $a \to \infty$. Unfortunately, large values of a are necessary if D is small, as it often occurs in practice. Since such values are achieved by huge magnetic field gradients the picture represenetd by Figure 1 cannot be observed.

Nevertheless, Monte Carlo simulations of $< e^{i\Phi} >$, with $\Phi = \int_0^t g(t')x(t')dt'$ show that the asymptotic behavior is also obtained when two opposite gradient pulses of equal finite duration are applied. We see from Figure 2 that varying pulse durations allows us to see the difference between slight age effects corresponding to $\gamma < 1$ though not very different from 1, and the Markovian case $\gamma = 1$ that corresponds to normal diffusion. Smaller values of γ (i.e. very irregularly distributed arrest periods) yield even larger echoes at large values of a.

Moreover, the asymptotic echo value is a function of age t_1 of the system: this function depends on γ and Λ, hence that parameters can be deduced upon recording echoes an difefrent values of t_1.

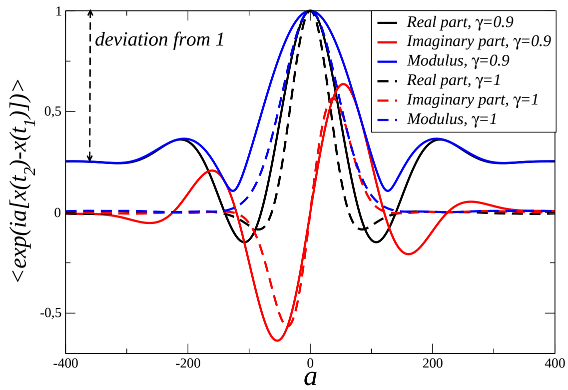

Fig. 1. Mathematical expectation of the exponential of the displacement $e^{ia(x(t_2)-x(t_1))}$, for $D = 0.0001$, $\Lambda = 1$, $v = 0.1$ and $t_2 - t_1 = 0.5$. Function $< e^{ia(x(t_2)-x(t_1))} >$ was computed from Monte Carlo simulation, and checked against (3) for some values. For $\gamma = 0.9$, the real part does not fall of to zero at large values of the gradient, while for $\gamma = 1$ it does.

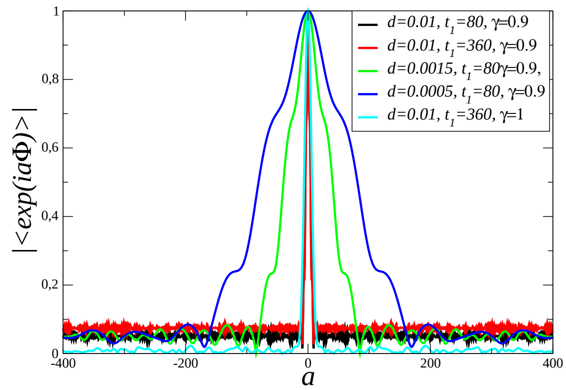

Fig. 2. Mathematical expectation of the exponential of the path integral $e^{ia[1_{[t_2-d,t_2+d]}(t)-1_{[t_1-d,t_1+d]}(t)]}$, for $D = 0.0001$, $\Lambda = 1$, and $v = 0.1$. Pulses of various durations are represented: with longer pulses, smaller gradients achieve the asymptotic behavior. Increasing age t_1 of the system

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