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Diffusion in fluctuating media: first passage time problem

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Abstract

We study the actual and important problem of *Mean First Passage Time* (MFPT) for diffusion in fluctuating media. We exploit van Kampen's technique of *composite stochastic processes*, obtaining analytical expressions for the MFPT for a general system, and focus on the two state case where the transitions between the states are modelled introducing both Markovian and non-Markovian processes. The comparison between the analytical and simulations results show an excellent agreement.

Diffusion in the presence of global and local fluctuating media has been extensively studied for many years. Examples of such processes are random walks in dynamically disordered systems [1–3] such as ionic conduction in polymeric solid electrolytes [4]; transport of "Brownions" [5,6], i.e., particles that can be in two or more states, executing a diffusion process in each of them but with different diffusion constants; resonant activation over fluctuating barriers [7] and escape from a fluctuating system [8,9]; diffusion of ligand with stochastic gating [10–12]; dynamical trapping problems [13–16], etc.

The above indicated problems share the property that the switching between the different configurations or states of the medium is independent of the transport or diffusion processes of the walker. Usually, it is assumed that the states are independent of each other and that the particles are subject to a Markovian process inducing its motion in each state, described by Master or Fokker–Planck equations with different transition rates or diffusion coefficients.

In this Letter we present an appropriate framework based on a technique developed by van Kampen: *composite stochastic processes* [17] that allows us to tackle transport problems in global *and* local fluctuating media in an unified way. The advantage of such an approach is the possibility of handling the important case of non-Markovian transitions between the different states of the media. We anticipate that, by exploiting this scheme, we have been able to study the influence of Markovian and non-Markovian switchings in a fluctuating medium over the *first passage time density* and the *mean first passage time*, and have found general (analytical) expressions for these magnitudes as functions of the switching statistics and the "propagators"

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in each state of the medium. It is worth here remarking that some of the previously indicated works (see also [18]) clearly show the actual interest in the study of first passage problems in chemical and biological contexts.

The *First Passage Time Density* (FPTD) and the *Mean First Passage Time* (MFPT) are magnitudes of fundamental interest for studying solid state transport [19]; dielectric relaxation [20], biological problems [21], etc. Recently, various generalizations of the original *Polya* problem have been solved [22,23] including MFPT in global fluctuating systems [7,8]. In particular, Klafter and coworkers [8,9], have shown that a *resonant activation* phenomenon appears when the changes between the states of the medium are assumed Markovian and symmetric. Here we extend such a MFPT problem in a fluctuating media to non-Markovian and non-symmetric transitions.

We start with the problem of a particle performing a random walk on a continuous or discrete fluctuating medium characterized by N states which are labelled by the index j $(j = 1, 2, \dots, N)$. Following van Kampen [17] we define the probability $u_j(t)$ that the medium has stayed in the j state after a time t since its arrival at $t = 0$ as

$$u_j(t) = \exp\left(-\int_0^t \sum_i \gamma_{ij}(t')\,dt'\right), \tag{1}$$

where $\gamma_{ij}(t)$ is the probability per unit time for the medium to jump from level j to level i and t is the time it has sojourned in j.

We now define the *switching statistics* of the medium $v_{ij}(t)$ as the probability that the medium ends its sojourn in the state j, after a time between t and $t + dt$ since it arrived at state j at $t = 0$, by jumping to a given state i

$$v_{ij}(t)\,dt = u_j(t)\gamma_{ij}(t)\,dt. \tag{2}$$

We want to remark that Eq. (2) is completely general and no assumption has been made in writing it [17]. As is well-known, if the $v_{ij}(t)$ are exponential functions of time, that is the $\gamma_{ij}(t)$ are t-independent functions (see for instance [22]), we have a Markovian switching process between the states of the medium.

For each fixed state j of the medium the transport process is Markovian and we denote its corresponding "propagator" [17] by A_j. These propagators are differential operators (matrices) in the case of a continuous (discrete) medium and its structure depends strongly on the character of fluctuation. As an example consider diffusion in a *discrete global fluctuating medium*, in this case all the elements of the matrice A_j are different of that of A_i when $i \neq j$. If local fluctuations are present and if there is a single "dynamic impurity" the matrices differ only in one element.

We define the conditional joint probability density $P_j(\vec{r}, t|\vec{r}_0, t_0)\,d\vec{r}$, as the probability that the walker is in $\vec{r}$ and the system is in state j at time t given that the walker was in $\vec{r}_0$ at $t = t_0$. When $\gamma_{ij}(t)$ are t-independent functions the conditional joint probability satisfies the following set of coupled Master equations

$$\dot{P}_j(\vec{r}, t) = A_j P_j(\vec{r}, t) + \sum_i \big(\gamma_{ji} P_i(\vec{r}, t) - \gamma_{ij} P_j(\vec{r}, t)\big), \tag{3}$$

with $j = 1, 2, 3, \dots, N$.

We also define two $N \times N$ arrays as

$$V_{ij}(t) = v_{ij}(t)e^{tA_j}, \tag{4}$$

$$U_{ij}(t) = \delta_{ij} u_j(t)e^{tA_j}. \tag{5}$$

Here we remark that the expressions in Eqs. (4) and (5) represent "matrix operators" for the continuous case [7] or "block matrices" for the discrete case [8].

The Laplace transform of the joint conditional probability can be expressed in terms of the Laplace transforms of the matrices V and U [17] as

$$\widehat{P}_j(\vec{r}, s|\vec{r}_0, 0) = \sum_{i=1}^{N} \big[\widehat{U}(s)\big[I - \widehat{V}(s)\big]^{-1}\big]_{ji} P_i(\vec{r}_0, t = 0), \tag{6}$$

where $\widehat{P}_j(\vec{r}, s|\vec{r}_0, 0)$ is the Laplace transform of the conditional probability. Eq. (6) will be used hereafter in order to obtain the FPTD for the walker in a globally dynamic fluctuating medium.

Finally we define the *marginal* or *total* probability distribution $P(\vec{r}, t|\vec{r}_0, t_0)$, corresponding to the particle being in the lattice site $\vec{r}$ at t independently of the state of the medium as

$$P(\vec{r}, t|\vec{r}_0, t = 0) = \sum_j P_j(\vec{r}, t|\vec{r}_0, t = 0), \tag{7}$$

where the sum is performed over all the N states of the medium. The process whose probability distribution corresponds to Eq. (7) in general is non-Markovian as can be seen, for example in [25] where a generalized Master equation is presented for the marginal probability distribution.

The Laplace transform of the FPTD to reach the origin for the first time starting at the site $\vec{r}_0$ assuming the "synchronized condition" could be obtained by an extension of the "renewal equation" [24] for general non-Markovian processes under the indicated assumption as [23]

$$\hat{f}(\vec{r}_0, s) = \frac{\widehat{P}(\vec{0}, s|\vec{r}_0, t=0)}{\widehat{P}(\vec{r}_0, s|\vec{r}_0, t=0)}, \tag{8}$$

where $\widehat{P}(\vec{0}, s|\vec{r}_0, t=0)$ is the Laplace transform of the marginal or total probability distribution given in Eq. (7). As it was stated above, the process defined in Eq. (7) is in general non-Markovian and a waiting time density for the *first jump* must be defined; the "synchronized condition" assumes that the instant $t=0$ coincides with the transition of the walker to $\vec{r}_0$ [23].

Eqs. (8) and (6) are the most important results of this Letter: the FPTD for a particle in a fluctuating medium with arbitrary switching statistics $\upsilon_{ij}(t)$. The Markovian and symmetric case [7,8] may be obtained as the particular exponential assumption for the switching transition probabilities.

The MFPT for reaching the origin for a particle in an arbitrary fluctuating medium is

$$\Gamma(\vec{r}_0) = \int_0^\infty t f(r_0, t)\, dt = -\frac{\partial \hat{f}(\vec{r}_0, s)}{\partial s}\bigg|_{s=0}. \tag{9}$$

A general expression for $\Gamma(\vec{r}_0)$ can be found for a *short memory time* of the medium fluctuations compared to the time scale determined by the propagator A_j [17]. In the case of FTPD problems this approximation may be stated as follow: the average life time for each level j (see below) must be much smaller than the MFPT for all j.

In order to obtain $\hat{f}(\vec{r}_0, s)$ in this limit we exploit the important result for the behavior of the $P_j(\vec{r}, t|\vec{r}_t, 0)$ when the $\upsilon_{ij}(t)$ have a *finite first moment* [17]. With this assumption we have

$$P_j(\vec{r}, t|\vec{r}_0, t=0) = \zeta_j P(\vec{r}, t|\vec{r}_0, t=0), \tag{10}$$

with $P(\vec{r}, t|\vec{r}_0, t=0) = \sum_j P_j(\vec{r}, t|\vec{r}_0, t=0)$. $P(\vec{r}, t)$ satisfies the following equation

$$\frac{\partial P(\vec{r}, t)}{\partial t} = \widehat{A} P(\vec{r}, t). \tag{11}$$

The ζ_j are the components of the right eigenvector of the array $\hat{\upsilon}_{ij}(s=0)$ with eigenvalue 1, and satisfying $\sum_{j=1}^{N} \zeta_j = 1$.

The operator $\widehat{A}$ is determined by the A_j according to the following expression

$$\widehat{A} = \sum_{j=1}^{N} \alpha_j A_j, \tag{12}$$

where

$$\alpha_j = \frac{T_j \zeta_j}{\sum_{j=1}^{N} T_j \zeta_j}, \tag{13}$$

and the average life time for state j is

$$T_j = \int_0^\infty t \sum_{i=1}^{N} \upsilon_{ij}(t)\, dt = -\frac{\partial \left(\sum_{i=1}^{N} (\hat{\upsilon})_{ij}(s)\right)}{\partial s}\bigg|_{s=0}. \tag{14}$$

Hence, we deduce that for short memory time, the marginal probability $P = \sum_j P_j$ represents an *effective Markovian random walk*.

We assume that the propagators A_j are arrays W describing a discrete one-dimensional random walk in each state of the lattice. We also assume that the W are tridiagonal arrays, that is they only include jumps to first neighbors. The jumps within each state are characterized by two parameters: λ_j, the temporal rate of jump and the "bias" η_j to make a jump in a given direction. By using Eqs. (11)–(14) we identify the *effective* jump rate by

$$\lambda_{\text{eff}} = \sum_{j=1}^{N} \lambda_j \alpha_j, \tag{15}$$

and the *effective* bias by

$$\eta_{\text{eff}} = \frac{\sum_{j=1}^{N} \eta_j \lambda_j \alpha_j}{\sum_{j=1}^{N} \lambda_j \alpha_j}. \tag{16}$$

In order to calculate $\hat{f}(s, r_0)$ and $\Gamma(\vec{r}_0)$ we use Eqs. (8) and (9).

We now restrict the problem to a system with only two states. In this case the array $\hat{\upsilon}_{ij}(s=0)$ has the

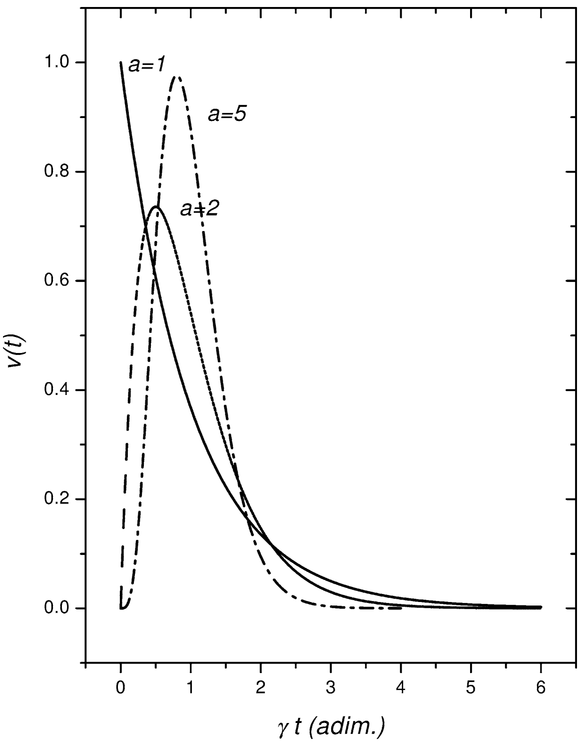

Fig. 1. Probability density function (pdf) used for the rate of transitions on the lattice. Solid line $a=1$, dash line $a=2$, dash-dot $a=5$.

following form

$$\hat{v}_{ij}(s=0)=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}.$$

Its right eingenvectors are $\zeta_1=\zeta_2=0.5$ and

$$\alpha_1=\frac{T_1}{T_1+T_2},\qquad \alpha_2=\frac{T_2}{T_1+T_2}. \tag{17}$$

The *effective* parameters λ_{eff} and η_{eff} are

$$\lambda_{\mathrm{eff}}=\frac{\lambda_1 T_1+\lambda_2 T_2}{T_1+T_2}, \tag{18}$$

$$\eta_{\mathrm{eff}}=\frac{\lambda_1\eta_1 T_1+\lambda_2\eta_2 T_2}{\lambda_1 T_1+\lambda_2 T_2}. \tag{19}$$

Finally, the expression of MFPT for a walker initialy in the position n_0 is

$$\Gamma(n_0)=\begin{cases}\frac{n_0}{\lambda_{\mathrm{eff}}(2\eta_{\mathrm{eff}}-1)} & \text{if } \eta_{\mathrm{eff}}>1/2,\\ \infty & \text{if } \eta_{\mathrm{eff}}<1/2.\end{cases}$$

These theoretical results were verified with Monte Carlo simulations and are shown in the following fig-

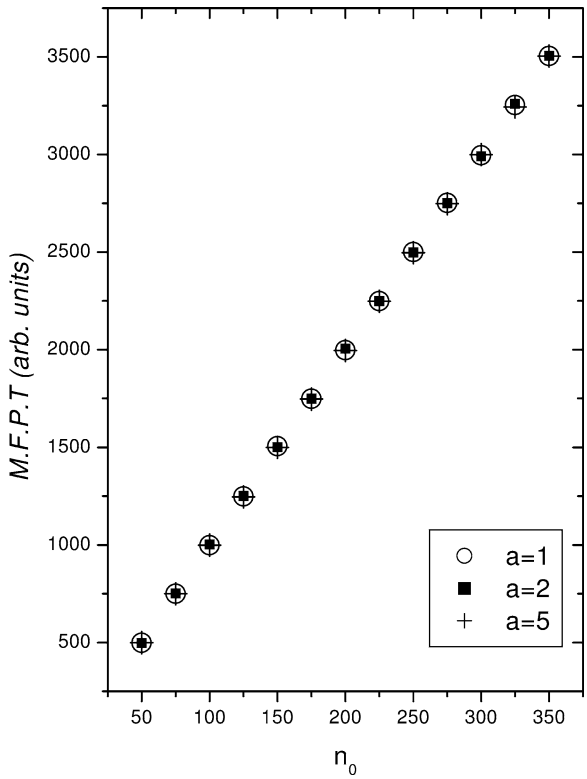

Fig. 2. MFPT as a function of the initial site of the motion (n_0) for three different parameters a. Open circles correspond to $a=1$ (Markovian case), squares to $a=2$, and crosses to $a=5$. The other simulation parameters were: $\lambda_1=0.5$, $\lambda_2=1.0$, $\eta_1=0.9$, $\eta_2=0.4$, $\gamma_{12}=1.0$, $\gamma_{21}=1.0$.

ures. For simplicity we assume that $v_{12}(t)=v_{21}(t)=v(t)$ given $T_1=T_2$.

Fig. 1 shows the switching probability distributions $v(t)$ used in the simulations versus γt. These distributions have the following form

$$v(t)=\gamma a\frac{(\gamma a t)^{(a-1)}}{\Gamma(a)}e^{-\gamma a t}, \tag{20}$$

where γ is the state transition rate and is related to the average life time by $T=\gamma^{-1}$ *for all a* and $\Gamma(a)$ is the gamma or factorial function. The parameter a corresponds when $a=1$ to the Markovian case, and when $a\neq 1$ to the non-Markovian case.

Fig. 2 depicts the dependence of MFPT on n_0, the starting point of the motion, for a fixed characteristic lattice parameter. The simulations confirm that the MFPT as function of n_0 is independent of the parameter a. The theoretical result shows excellent agreement

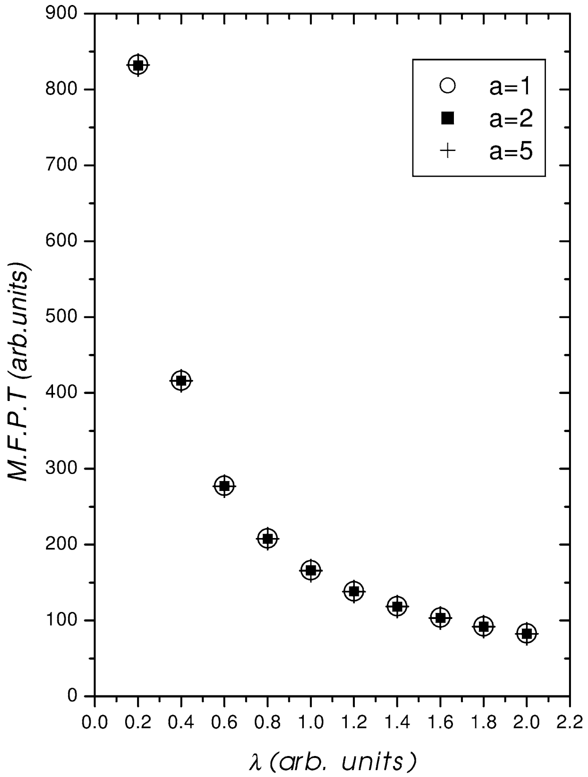

Fig. 3. MFPT as a function of the transition rate in a given state λ for three different parameters a. Open circles correspond to $a = 1$ (Markovian case), square to $a = 2$, and crosses to $a = 5$. The other simulation parameters were: $\eta_1 = 0.9$, $\eta_2 = 0.4$, $\gamma_{12} = 1.0$, $\gamma_{21} = 1.0$.

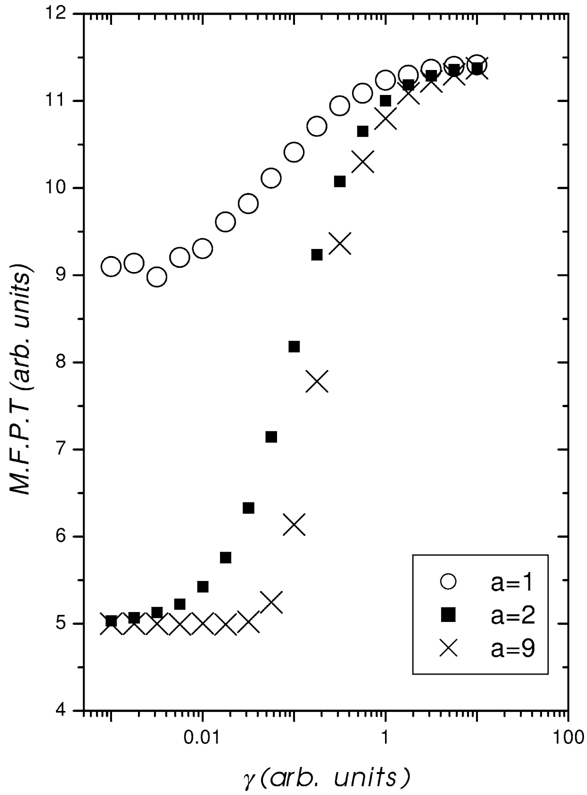

Fig. 4. MFPT as a function of the state transition rate γ for three different parameters a. Open circles correspond to $a = 1$ (Markovian case), square to $a = 2$, and crosses to $a = 9$. The other simulation parameters were: $\lambda_1 = 1.0$, $\lambda_2 = 0.5$, $\eta_1 = 0.9$, $\eta_2 = 0.4$.

with the Monte Carlo simulations. In Fig. 3 we depict the MFPT as a function of λ, the temporal rate of jump in a given state.

In Fig. 4 we observe the relation between the MFPT and the state transition rate γ for a wide range of this parameter and for three different values of parameter a. Here we can witnessed the important effect on the non-Markovian behavior for small transition rates. For values of γ greater than one the short time approximation is valid as can be observed in the figure.

The scheme presented in this Letter offers the possibility of studying the influence of non-Markovian switching in a fluctuating medium over the FPTD and the MFPT. We want here to stress that we have found general expressions for these magnitudes as functions of the switching statistics and the "propagators" in each state of the (continuous or discrete) medium. We have shown that in the short memory time limit an "effective" Markovian processes can be defined, even for non-Markovian (finite first moment) switching statistics; for the particular case of Markovian random walks in each state of the lattice with jumps only to first neighbours an "effective" bias and "effective" jump were found. The application of this technique to resonant activation and local dynamic disorder is in progress. Also, the interesting problem of gated or dynamical traps will be developed in a future paper.

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