Molecular switching with nonexponential relaxation patterns: A random walk approach

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The transition from an initial, locally stable configuration to a globally stable state in molecular switches is investigated in terms of a random walk model, effectively taking the reaction pathway through a potentially rugged energy landscape into account. Exponential and nonexponential scenarios are discussed and the implications on measurable quantities are explored.

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Rotaxanes are but one example of designed molecules which exhibit the particular property that they possess two configurations which are considerably more stable than all other configurations. One of these two configurations is globally stable. In rotaxanes, a ring molecule moves along the backbone strand of the ''mother molecule,'' as sketched in Fig. 1. From the globally stable state G, the system can be excited on the nanosecond scale via a photopulse, shifting the ring into the locally stable state L. The relaxation time from L back to G is remarkably long, ranging to up to 1 week [1]. Molecular switches might be of interest for signal generation, processing, transfer, conversion, and detection, e.g., for quantum computing, and they are part and parcel of the growing field of semiochemistry.

We visualize the motion of the switching unit from the lesser stable state L to the globally stable state G as a random motion on an energy surface which is characteristic of the interaction between the strand molecules and the switching unit. I.e., close to the position of a strand molecule, the ring has to overcome an energy barrier. On its way from state L to state G, the ring encounters a number of energy barriers of different height so that the connected energy landscape is rugged. The interaction between strand and ring is mutual, the moving ring constantly changing the position of the strand molecules. We propose that the subsequent barrier crossing can be taken into account by assuming that a step along the mother molecule strand is governed by a waiting time which is a random variable controlled by the waiting time probability density function (PDF) $w(t)$. This model conforms, in a certain sense, to a recently proposed generalization of the Kramers' escape problem [2].

With this assumption, the transition from L to G can consequently be described as a continuous time random walk [3] within a box of length a which is the chemical distance (distance along the strand) between L and G. The respective box walls in L $(x=0)$ and G $(x=a)$ are reflecting and absorbing; i.e., the switching unit cannot move beyond L, and on arrival in G the process is assumed to terminate. We investigate three possible scenarios for this stochastic process corresponding to Brownian motion, fractional dynamics with a self-similar waiting time PDF, and a logarithmic form of $w(t)$ corresponding to extremely rare events. In this simplistic force-free diffusion process between the boundaries $x=0$ and $x=a$, the effective motion of a particle described by the boundary value solution is biased through the existence of the trap at one end which causes an *overall* drift towards the sink. Our approach is thus similar to that developed for describing charge carrier transport in amorphous semiconductors [4].

From the propagator $W(x,t)$, the PDF of being at position x at time t describing a random walk process with the initial condition $W_0(x)\equiv\lim_{t\to 0+}W(x,t)=\delta(x)$ for natural boundary conditions $\lim_{|x|\to\infty}W(x,t)=0$, the solution to the boundary value problem of a box with absorbing walls at $x=\pm a$ can be constructed through the sum [5]

$$Q(x,t)=\sum_{m=-\infty}^{\infty}[W(x+4ma,t)-W(4ma-x+2a,t)]. \tag{1}$$

Note that we distinguish between the natural boundary conditions propagator $W(x,t)$ and the boundary value solution $Q(x,t)$ from Eq. (1) which fulfills the Dirichlet condition $Q(\pm a,t)=0$. Equation (1) can be rewritten in the form [6]

$$Q(x,t)=\frac{1}{2a}\sum_{m=-\infty}^{\infty}\exp\left(-\frac{(2m+1)\pi ix}{2a}\right)W(k,t),$$

$$\text{at}\quad k=\frac{(2m+1)\pi}{2a}, \tag{2}$$

where $W(k,t)\equiv\int_{-\infty}^{\infty}W(x,t)e^{ikx}dx$ is the Fourier transform of $W(x,t)$.

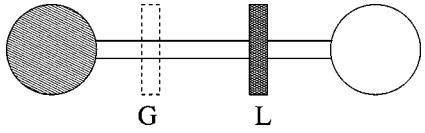

FIG. 1. Schematic picture of a rotaxane switch [1]. G and L denote the two major stable states of the switching unit (globally and locally stable), a ringlike structure. The two balls at the opposite ends of the main dumbbell-like molecule strand are stoppers.

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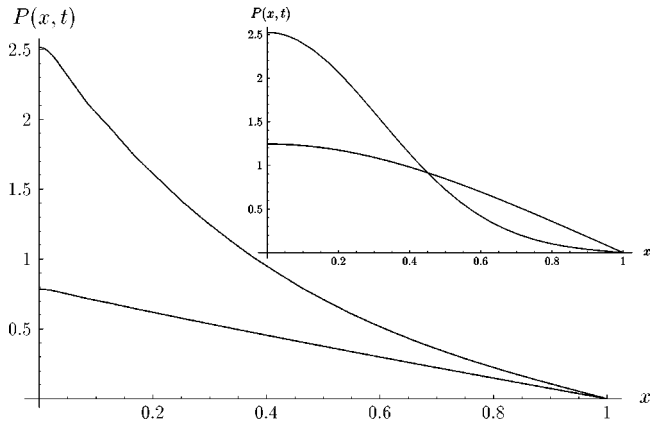

FIG. 2. PDF $P(x,t)$ for the fractional case ($\alpha=1/2$), for dimensionless times 0.01 and 0.4, and the Markovian case, for $t=0.05$ and 0.2 (inset). The box length is $a=1$, and the reflecting boundary is to the left. In the fractional case, the cusp close to the origin at the earlier time and the almost linear behavior for the later time are distinct.

The sought solution $P(x,t)$ for the mixed boundary value problem of having a reflecting wall at $x=0$ and an absorbing wall at $x=a$ can be expressed through $P(x,t)=Q(x,t)+Q(-x,t)$ such that

$$P(x,t)=\frac{1}{a}\sum_{m=-\infty}^{\infty}c_m(t)\cos\left(\frac{(2m+1)\pi x}{2a}\right), \tag{3}$$

with $c_m(t)\equiv W(k,t)$ at $k=(2m+1)\pi/2a$. It is straightforward to show that $P(a,t)=0$ (Dirichlet) and $\partial P/\partial x|_{x=0}=0$ (von Neumann).

Averaging over the coordinate x, one obtains the integrated survival probability

$$p(t)=\frac{2}{\pi}\sum_{m=-\infty}^{\infty}(-1)^m\frac{c_m(t)}{2m+1}, \tag{4}$$

from which the initial normalization $\lim_{t\to 0+}p(t)=1$ is deduced as by the initial condition $W_0(x)=\delta(x)$, one has $\lim_{t\to 0+}c_m(t)=1$, recovering $(2/\pi)\Sigma_{m=-\infty}^{\infty}(-1)^m/(2m+1)=1$. Moreover, we recognize that the summands in Eq. (4) decrease with increasing summation index $|m|$ such that the sum necessarily converges (by a majorant criterion).

Markovian case. Let us start out with the consideration of the Markovian limit. The propagator of the one-dimensional diffusion equation $\partial W/\partial t=K(\partial^2/\partial x^2)W(x,t)$ is given through the Gaussian $(4\pi Kt)^{-1/2}e^{-x^2/(4Kt)}$ so that we find the expression $c_m(t)\equiv\exp(-Kk^2t)$ for the coefficients in Eq. (3). Accordingly, the modes $c_m(t)$ relax exponentially in time, mirroring the Markovian nature of the process. A plot of the PDF $P(x,t)$ is shown in the inset of Fig. 2. The associated integrated survival probability $p(t)$ is dominated by the individual exponential contributions, higher orders of which decay relatively fast. In Fig. 3, the survival is plotted on a $\log_{10}$-$\log_{10}$ scale.

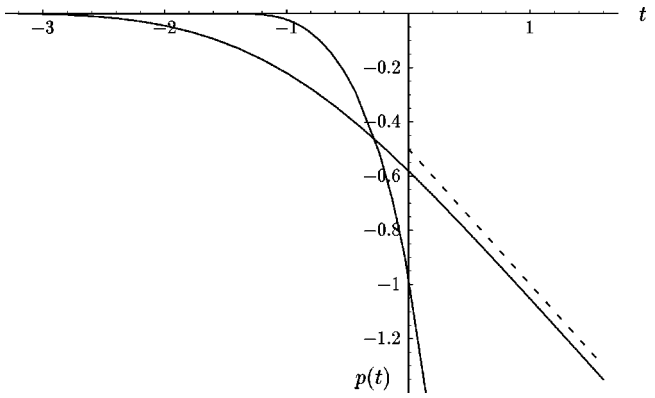

FIG. 3. Survival probability $p(t)$ for the Brownian case and the fractional model with $\alpha=1/2$, in a $\log_{10}$-$\log_{10}$ plot. The Brownian curve shows the fast exponential decay contrasted by the slow power-law pattern in the fractional case. The dashed line indicates the $t^{-1/2}$ proportionality.

Fractional dynamics case. In the non-Markovian case with a self-similar waiting time PDF of the asymptotic power-law form $w(t)\sim A_\alpha\tau^\alpha t^{-1-\alpha}$, $0<\alpha<1$ and A_α a constant, it is assumed that the system explores the reaction space anomalously, featuring a slowly decaying, scale-free memory. For such fractional dynamics systems [7,8] it has been shown that exponential relaxation patterns are replaced by the Mittag-Leffler function; i.e., the mode coefficients become $c_m(t)=E_\alpha(-K_\alpha k^2t^\alpha)$ where K_α is the generalized diffusion constant [8,9]. The Mittag-Leffler function is defined through $E_\alpha(z^\alpha)\equiv\Sigma_{n=0}^{\infty}(-z^\alpha)^n/\Gamma(1+\alpha n)$, and has the asymptotic behaviors $E_\alpha(z^\alpha)\sim\exp[-z^\alpha/\Gamma(1+\alpha)]$, $z\ll 1$, and $E_\alpha(z^\alpha)\sim 1/[z^\alpha\Gamma(1-\alpha)]$, $z\gg 1$ [10].

There exists a map of the Brownian solution P_1 onto the fractional solution P_α in terms of the generalized Laplace transformation [11]

$$P_\alpha(x,t)=\int_0^\infty E(s,t)P_1(x,s)ds, \tag{5}$$

where the kernel E is defined in terms of the one-sided Lévy stable law $\mathbf{L}_\alpha^+$ through

$$E(s,t)=\frac{t}{\alpha s}\mathbf{L}_\alpha^+\left(\frac{t}{(s^*)^{1/\alpha}}\right),\quad s^*\equiv\eta_\alpha s/\eta, \tag{6}$$

which is equivalent to the Fox function representation [8]

$$E(s,t)=\frac{1}{\alpha s}H_{1,1}^{1,0}\left[\frac{(s^*)^{1/\alpha}}{t}\middle|\begin{matrix}(1,1)\\(1,1/\alpha)\end{matrix}\right]$$
$$=\frac{1}{s}\sum_{n=0}^{\infty}\frac{(-1)^n}{\Gamma(1-\alpha-\alpha n)\Gamma(1+n)}\left(\frac{s^*}{t^\alpha}\right)^{1+n}, \tag{7}$$

through which it is possible to find special representations for a given α, e.g.,

$$E(s,t)=\frac{1}{\sqrt{\pi t}}\exp\left(-\frac{(s^*)^2}{4t}\right),$$

for $\alpha=1/2$. The transformation (5) was used to plot the PDF $P(x,t)$ on the basis of the Markovian solution. η and η_α appearing in Eqs. (6) and (7) denote the Brownian and fractional friction constants defined in Ref. [9], η_α being related to the standard friction constant η through a dimensional prefactor.

The fractional dynamics PDF $P(x,t)$ is shown in Fig. 2, and it exhibits a triangular shape with a slight cusp close to the origin. For longer times, an almost linear decay towards the absorbing boundary is observed. The cusp close to $x=0$ is due to the persistence of the initial condition in the fractional case [8]. Both variants, Markovian and fractional, are compared in Fig. 3 where we plotted the integrated survival probability $p(t)$ for the two models, in a double-logarithmic scale. Here, the fast decay of the exponential function contrasts the much slower relaxation of the Mittag-Leffler sum. The dashed line indicates the expected slope of the long-time power-law behavior. The latter is reached rather slowly, owing to the fact that the Mittag-Leffler coefficients $c_m(t)$ of increasing order m do not decay as fast as the exponential terms in the Markovian case.

In fractional dynamics, the anomalous diffusion index α, renders some information about the ''transparency'' of the support on which the random motion takes place, a notion which is analogous to the random walk dimension d_w on fractals where it is connected to the anomalous diffusion exponent α through $\alpha=2/d_w$ [14].

Non-Markovian case with extremely rare events. In molecular switches, the relaxation from the initial state L to the globally stable state G might alternatively be dominated by very rare events. This is possible if (i) the activation of the switching unit on its pathway along the mother molecule strand is not close to thermal equilibrium and hardly ever motion events are activated or (ii) if cooperative effects between switch and molecular backbone come into play. Such rare events have recently been investigated in a dynamical map and studied in terms of a continuous time random walk model with the logarithmic waiting time PDF $w(t) \sim [t \log^{1+\beta}(t/\tau)]^{-1}$, $\beta>0$ [12]. Accordingly, $w(t)$ is normalizable but does not possess even fractional moments. The propagator for such a system is given through the exponential $W(x,t)=[1/2\sigma(t)]\exp[-|x|/\sigma(t)]$ where $\sigma(t) \equiv \log^{\beta/2}(t/\tau)$. The mode coefficients in Eq. (3) follow the logarithmic pattern $c_m(t)=[1+k^2\log^\beta(t/\tau)]^{-1}$, $t>1$ [12]. Due to their asymptotic behavior $c_m(t)\sim[(2m+1)^2\pi^2\log^\beta(t/\tau)/(4a^2)]^{-1}$, they decay extremely slowly. In Fig. 4, we display the approximate PDF $P(x,t)$ for successive times spanning a large range to underline the extremely slow evolution of such a system. The associated integrated survival time, Eq. (4), is shown in the inset.

So far, dynamical patterns of molecular switches have not been measured to detail. An analytical model for the relaxation dynamics of semiochemical switches is therefore timely and might be a basis for the interpretation of future measurements. Moreover, the problem is interesting also from a physical point of view. We have presented a stochastic pathway model for molecular switching or similar relaxation processes in spatially extended systems. This simplistic dynamical model considers the effects of successive barrier crossing in a diffusion approximation. According to an increasing degree of disorder, three different models have been investigated, these being defined by a Markovian process, by a power-law form of the waiting time PDF and by a logarithmic pattern. In the two latter cases, the exponential mode relaxation is replaced by either a Mittag-Leffler behavior or by a logarithmic decay. The resulting behaviors differ considerably, and experimentally a distinction is possible. It should be stressed that in finite systems the fractional or logarithmic behavior does not pertain infinitely, but it is eventually replaced by a cutoff. Depending on the resolution of the experimental window, transitions from the nonexponential to an exponential decay of the survival function might be observed.

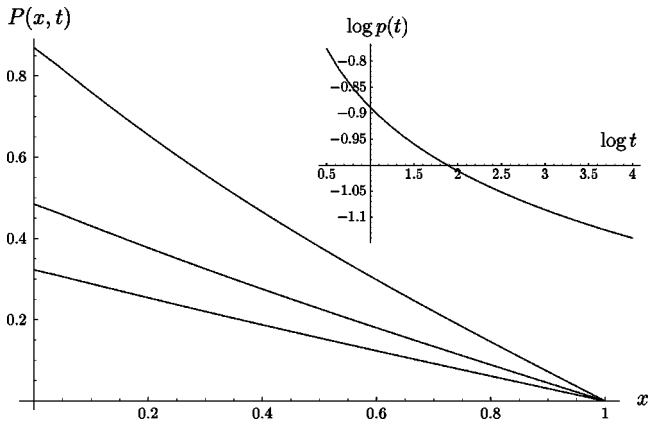

FIG. 4. PDF $P(x,t)$ in the rare event case with logarithmic waiting time distribution, drawn for the dimensionless times $t=2$, 20, 2000, and $\beta=1/2$. The extremely slow decay of the PDF is distinct, even in comparison to the power-law waiting time PDF underlying Fig. 2. The inset shows the survival probability in a $\log_{10}$-$\log_{10}$ plot over more than four decades in time; note the slow drop in $p(t)$ over this interval.

First passage time experiments. A typical study of molecular switching systems would focus on the measurement of the first passage time, i.e., the elapsed time that the ring locks on state G. If the outflow is defined through $j(t)\equiv 1-p(t)$, the first passage time distribution consequently becomes $f(t)\equiv(-d/dt)p(t)$; see also [13].

(i) In the Markovian case, $f(t)$ is composed of exponential summands corresponding to Eq. (4), featuring the mean survival time

$$T_s \equiv \int_0^\infty t\left(\frac{d}{dt}j(t)\right)dt = \frac{a^2}{2K}.$$

In a series of experiments, variations in measured first passage times are expected to be relatively narrow.

(ii) This is no longer true for the fractional case. Here, the derivative of single coefficients involves the generalized Mittag-Leffler function $(-d/dt)c_m(t) = K_\alpha k^2 t^{\alpha-1} E_{\alpha,\alpha}(-K_\alpha k^2 t^\alpha)$ [10], and thus due to the long-time asymptotic behavior $\sim t^{-1-\alpha}$, the mean survival time T_s in the fractional case diverges. Accordingly, in a series of individual measurements, the switching time is expected to vary in a long range, reflecting the scale-free nature of the

process. A first passage time experiment consequently might mislead one to the conclusion that the system is highly inhomogeneous. It might, however, be that the power-law waiting time behavior at some point turns over to a fast decay. Then, the system possesses a finite characteristic survival time T_s encountered for long times measured in a first passage time experiment. Qualitatively the same is true for the extremely rare event case.

It should be noted that in the presence of an external bias, e.g., an electric field pushing the ring towards the *G* position, the mean survival time in the fractional case becomes finite [13]. This might open the scene for an elegant testing of the underlying process, also connected to the question of whether such systems are consistent with linear response theory, i.e., in which way the switching unit responds to a low external, constant force like an electric field.

Temperature variations might give further indication about a specific process whereby an Arrhenius activation is expected in the Markovian and fractional cases [2,8]. The present model may thus be the basis for more quantitative experimental studies of the exact switching patterns encountered in molecular switches. Although single molecule studies might be desirable, even the investigation of ensemble behavior will contribute to the elimination of certain patterns.

The presented random walk model assumes that the relaxation of the system is fully characterized by the waiting time PDF. Alternative interpretations may, however, be possible. Moreover, the presented stochastic analysis leaves the question open what microscopic mechanisms give rise to the particular waiting time PDF. Such points should be addressed when experimental data become available.

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