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Passage over a random energy barrier with dynamical disorder

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Abstract

The hopping of a moving particle over an activation barrier with a Markovian fluctuating height is investigated by assuming that the process is characterized by two characteristic time scales: the minimum hopping time τ_h corresponding to zero activation energy and the regression time scale τ_{fl} of the fluctuations of the activation energy. The moments $\langle l^m(t)\rangle$, $m > 0$ of the fluctuating survival function $l(t)$ at time t as well as the average probability of the passage time $\psi(t)$, are evaluated by taking into account all contributions of the different fluctuation paths of the activation energy $E(t')$, $t \geqslant t' \geqslant 0$. The survival statistics obeys a fractal scaling law only if the regression of the fluctuations is slower than the hopping process. In this case a statistical fractal behavior emerges for the time interval $\tau_{fl} > t > \tau_h$ for which $\langle l^m(t)\rangle \sim t^{-H}$, $\psi(t) \sim t^{-(1+H)}$, where $1 \geqslant H > 0$ is a positive fractal exponent. For larger times $t > \tau_{fl}$ the survival statistics is exponential: $\psi(t)$, $\langle l^m(t)\rangle \sim \exp(-t/\tau_{fl})$, $t > \tau_{fl}$. The condition $\tau_{fl} > \tau_h$ defines a non-ideal statistical fractal for which self-similarity exists only in the time window $\tau_{fl} > t > \tau_h$; for larger times $t > \tau_{fl}$ the tail of the probability density $\psi(t)$ is exponential and thus the moments of the passage time are finite. In the limit $\tau_{fl} \to \infty$ the ideal statistical fractal behavior of the static random activation energy model is recovered: the fluctuations of the activation energy barrier are frozen, the tails of the functions $\langle l^m(t)\rangle$ and $\psi(t)$ are self-similar up to infinity and the moments of the passage time are infinite. It is shown that the fluctuations of the energy barrier increase the efficiency of the hopping process. The results are extended to non-Markovian fluctuation dynamics for which $\omega = 1/\tau_{fl}$ is a random rate selected from a generalized Porter–Thomas distribution. In this case the passage over the barrier is even more efficient. The hopping occurs with certainty in a finite time interval of a given length t_p. At the end of the interval the moments $\langle l^m(t)\rangle$ of the survival function $l(t)$ collapse to zero.

A simple mechanism generating fractal time is the hopping of a particle over a distribution of activation barriers. This approach, known as the random activation energy model (RAEM), has been applied to many problems in condensed matter physics [1–3] and molecular biology [4,5]. Considering an exponential distribution of activation energies

$$\eta(E) = (k_B T_0)^{-1} \exp(-E/k_B T_0), \tag{1}$$

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which corresponds to a canonical distribution "frozen" at temperature T_0, the probability distribution of the passage time is a weighted distribution of Poisson processes,

$$\psi(t) = \int \eta(E) W \exp(-Wt)\, \mathrm{d}E, \tag{2}$$

where the hopping frequency W is given by the usual expression

$$W = \nu \exp(-E/k_B T), \tag{3}$$

ν is the maximum jump frequency and $T \leqslant T_0$ is the system temperature. From Eqs. (1)–(3) it follows that the probability density of the passage time $\psi(t)$ has a long tail,

$$\psi(t) = H\nu(\nu t)^{-(1+H)} \gamma(1+H, \nu t) \sim H\Gamma(1+H)\nu(\nu t)^{-(1+H)}, \qquad t \gg 1/\nu, \tag{4}$$

where the fractal exponent H is equal to

$$H = T/T_0 \leqslant 1, \tag{5}$$

$\gamma(x, a) = \int_0^a y^{x-1} \exp(-y)\, \mathrm{d}y$ is the incomplete gamma function and $\Gamma(x) = \gamma(x, \infty)$ is the complete gamma function.

The main assumption of the RAEM approach is that a fluctuation of the height of the energy barrier lasts forever, which justifies the validity of the static ensemble average in Eq. (2). Although reasonable for some problems of condensed matter physics, the validity of this assumption is questionable in molecular biology. In the case of protein-ligand interactions [4] and in ion channel kinetics [5] the distribution of energy barriers is due to conformational fluctuations which have a dynamic nature and thus the fluctuations of the activation energy are continuously generated and destroyed by thermal agitation. The purpose of this Letter is to generalize the RAEM approach by assuming that the fluctuations of the activation energy have a dynamic nature.

We start by noticing that for static disorder the probability density $\eta(E)$ (Eq. (1)) is the normalized solution of a Bloch-type equation,

$$\eta(E) + k_B T_0 \partial_E \eta(E) = 0. \tag{6}$$

The simplest type of dynamical disorder conceivable is the one for which the fluctuations of the activation energy E are stationary and Markovian. Denoting by ω the regression rate of the fluctuations the stationary Bloch equation (6) is replaced by a stochastic Liouville equation,

$$\partial_t \eta(E, t) = \mathbb{L}\eta(E, t), \tag{7}$$

where

$$\mathbb{L} \ldots = -\omega[\ldots + k_B T_0 \partial_E \ldots] \tag{8}$$

is a linear evolution operator. In the static limit $\omega \to 0$ the characteristic time scale of the fluctuations $\tau_{fl} = 1/\omega$ tends to infinity $\tau_{fl} \to \infty$ and the stochastic Liouville equation (7) reduces to the static Bloch equation (6). The solution of the stochastic Liouville equation (7) should fulfill the normalization condition $\int \eta\, \mathrm{d}E = 1$. By integrating Eq. (7) term by term with respect to E we can show that the solution $\eta(E, t)$ is normalized to unity provided that it satisfies the boundary condition

$$\eta(E = 0, t) = 1/k_B T_0. \tag{9}$$

For stationary Markovian fluctuations the one-time probability density of the activation energy is equal to the stationary solution of Eq. (6),

$$\eta_1(E, t) = (k_B T_0)^{-1} \exp(-E/k_B T_0), \qquad \text{independent of } t, \tag{10}$$

and the multi-time joint probability densities $\eta_m(E_1, t_1; \ldots; E_m, t_m)$ are completely determined by $\eta_1(E, t)$ and by the Green function $\eta_1(E_1, t_1 \mid E_2, t_2) = \eta_1(E_1, t_1 - t_2 \mid E_2, 0)$ of the Liouville equation (7) which depends only on the time difference $t_1 - t_2$ and not on the individual times t_1 and t_2. In particular for $m = 2$ we have

$$\eta_2(E_1, t_1; E_2, t_2) = h(t_1 - t_2)\eta_1(E_2)\eta_1(E_1, t_1 - t_2 \mid E_2, 0) + h(t_2 - t_1)\eta_1(E_1)\eta_1(E_2, t_2 - t_1 \mid E_1, 0), \tag{11}$$

where $h(x)$ is the usual Heaviside step function. The Green function $\eta_1(E, t \mid E', 0)$ can be found by solving Eq. (7) with the boundary condition (9) and the initial condition

$$\eta_1(E, t=0 \mid E', 0) = \delta(E - E'). \tag{12}$$

By intergrating Eq. (7) along the characteristics we obtain

$$\eta_1(E, t \mid E', 0) = (k_B T_0)^{-1} \exp(-E/k_B T_0) h(\omega t k_B T_0 - E) + \delta(E - E' - \omega t k_B T_0) \exp(-\omega t). \tag{13}$$

Now the correlation function of the activation energy $\langle \Delta E(t) \Delta E(t') \rangle$ can be easily computed by using Eqs. (10), (11) and (13). We obtain

$$\langle \Delta E(t) \Delta E(t') \rangle = \int\int (E_1 - \langle E \rangle)(E_2 - \langle E \rangle) \eta_2(E_1, t; E_2, t') \, dE_1 \, dE_2$$
$$= (k_B T_0)^{-2} \exp(-\omega |t - t'|). \tag{14}$$

As expected for a one-dimensional Markov process the fluctuation of the activation energy decays exponentially with time.

For dynamic fluctuations of the activation energy the probability density of the passage time is given by a dynamic average,

$$\psi(t) = \left\langle \nu \exp[-E(t)/k_B T] \exp\left(-\nu \int_0^t \exp[-E(t')/k_B T] \, dt' \right) \right\rangle. \tag{15}$$

In Eq. (15) we should take into account all contributions of the different fluctuating paths $E(t')$, $t \geq t' \geq 0$ and thus for evaluating the probability density $\psi(t)$ we should evaluate a path integral over the random function $E(t')$.

Since the fluctuation dynamics is Markovian we can avoid the use of path integrals by applying a technique suggested by van Kampen [6]. We introduce the instantaneous value $l(t)$ of the survival function at time t, that is, the instantaneous value of the probability that in a time interval of length t the particle has not passed over the barrier. For a given realization of the activation energy path $E(t')$, $t \geq t' \geq 0$, the survival function $l(t)$ is the solution of the differential equation

$$\partial_t l(t) = -\nu \exp[-E(t)/k_B T] l(t), \qquad l(0) = 1. \tag{16}$$

Since the energy fluctuations are Markovian and for a given fluctuation path the survival function is deterministic it follows that the pair $(l(t), E(t))$ is also Markovian and the corresponding one-time probability density $P(E, l; t)$ obeys a compound stochastic Liouville equation,

$$\partial_t P(E, l; t) = \partial_l \{ P(E, l; t) l \nu \exp[-E(t)/k_B T] \} + \mathbb{L} P(E, l; t), \tag{17}$$

with the initial condition

$$P(E, l; t=0) = (k_B T_0)^{-1} \exp(-E/k_B T_0) \delta(l - 1). \tag{18}$$

The requirement that the solution of Eq. (17) is normalized to unity $\int\int P \, dE \, dl = 1$ leads to a boundary condition for $P(E, l; t)$ similar to Eq. (9),

$$\int_0^1 P(E=0, l; t) \, dl = 1/k_B T_0. \tag{19}$$

The positive moments of the survival function $l(t)$ are equal to

$$\langle l^m(t) \rangle = \int_0^\infty \int_0^1 l^m P(E, l; t) \, dE \, dl = \int_0^\infty \Lambda_m(E, t) \, dE, \tag{20}$$

where the functions $\Lambda_m(E, t)$ are marginal averages,

$$\Lambda_m(E, t) = \int_0^1 l^m P(E, l; t) \, dl. \tag{21}$$

By integrating Eqs. (17)–(19) over l we get a chain of partial differential equations for $\Lambda_m(E, t)$,

$$\partial_t \Lambda_m(E, t) = -m \Lambda_m(E, t) \nu \exp(-E/k_B T) + \mathbb{L} \Lambda_m(E, t), \tag{22}$$

with the initial and boundary conditions

$$\Lambda_m(E, t=0) = (k_B T_0)^{-1} \exp(-E/k_B T_0), \tag{23}$$

$$\Lambda_m(E=0, t) = (k_B T_0)^{-1}. \tag{24}$$

Eqs. (22)–(24) can be solved by using the method of characteristics. By inserting the resulting expressions for $\Lambda_m(E, t)$ into Eq. (20) and integrating over E, after lengthy manipulations we obtain the following expressions for the moments of the survival function $l(t)$,

$$\langle l^m(t) \rangle = H\left(\frac{\nu H m}{\omega}[\exp(\omega t/H) - 1]\right)^{-H} \gamma\left(H, \frac{\nu H m}{\omega}[\exp(\omega t/H) - 1]\right). \tag{25}$$

By applying Eq. (25) for $m = 1$ and expressing the average survival function $\langle l(t) \rangle$ as a path average we obtain

$$\langle l(t) \rangle = \left\langle \exp\left(-\nu \int_0^t \exp[-E(t')/k_B T] \, dt'\right)\right\rangle$$
$$= H\left(\frac{H\nu}{\omega}[\exp(\omega t/H) - 1]\right)^{-H} \gamma\left(H, \frac{H\nu}{\omega}[\exp(\omega t/H) - 1]\right). \tag{26}$$

By comparing Eqs. (15) and (26) we note that

$$\psi(t) = -\partial_t \langle l(t) \rangle = H\left(\frac{H\nu}{\omega}[\exp(\omega t/H) - 1]\right)^{-(H+1)} \gamma\left(H+1, \frac{H\nu}{\omega}[\exp(\omega t/H) - 1]\right)$$
$$\times \nu \exp(\omega t/H). \tag{27}$$

Expressions (25) and (27) for $\langle l^m(t) \rangle$ and $\psi(t)$ may have a scaling behavior of statistical fractal type only if the passage over the barrier for zero activation energy is faster than the decay of the fluctuations of the activation energy,

$$\nu > \omega, \qquad \text{i.e. } \tau_{fl} > \tau_h, \tag{28}$$

where $\tau_{\mathrm{fl}} = 1/\omega$ is the characteristic time scale for the regression of the fluctuations and $\tau_{\mathrm{h}} = 1/\nu$ is the minimum hopping time scale for zero activation energy. If condition (28) is fulfilled then the asymptotic behavior of $\langle l^m(t)\rangle$ and $\psi(t)$ for large time is given by

$$\langle l^m(t)\rangle \sim \Gamma(H+1)(\nu m t)^{-H}, \qquad \tau_{\mathrm{fl}} > t > \tau_{\mathrm{h}}, \quad t \gg 0, \tag{29a}$$

$$\sim \Gamma(H+1)[\omega/(\nu H m)]^{H} \exp(-\omega t), \qquad t > \tau_{\mathrm{fl}}, \quad t \gg 0, \tag{29b}$$

$$\psi(t) \sim H\Gamma(H+1)\nu(\nu t)^{-(H+1)}, \qquad \tau_{\mathrm{fl}} > t > \tau_{\mathrm{h}}, \quad t \gg 0, \tag{30a}$$

$$\sim H\Gamma(H+1)\nu[\omega/(\nu H)]^{H+1} \exp(-\omega t), \qquad t > \tau_{\mathrm{fl}}, \quad t \gg 0. \tag{30b}$$

The physical interpretation of Eqs. (29), (30) is straightforward. In the time window $\tau_{\mathrm{fl}} > t > \tau_{\mathrm{h}}$ the decay of the activation energy fluctuations is practically nonexistent and the dynamic path averages in Eqs. (15) and (25) are practically equivalent to a static average of type (2) over a time-invariant distribution of activation energies. In this case the inverse power law scaling behavior is generated by the equilibration between the contribution of very large activation energies which are exponentially rare and the characteristic hopping time $t_{\mathrm{h}} = 1/W = \nu^{-1}\exp(E/k_{\mathrm{B}}T)$ which diverges exponentially to infinity as $E \to \infty$. This is a typic feature for the static random activation energy model [1–5]. For larger times $t > \tau_{\mathrm{fl}}$ the fluctuations of the activation energy decay exponentially to zero (see Eq. (14)): in this time scale the process is dominated by the regression of the fluctuations of the energy barrier, resulting in the exponential decay laws (29b)–(30b). The conditions $\tau_{\mathrm{fl}} > \tau_{\mathrm{h}}$, τ_{fl} = finite (Eq. (28)) define a non-ideal statistical fractal for which the self-similar behavior occurs only at the beginning of the tails of the functions $\langle l^m(t)\rangle$ and $\psi(t)$. In the limit $\tau_{\mathrm{fl}} \to \infty$ this non-ideal fractal becomes an ideal fractal and we recover the static random activation energy model: the fluctuations of the barrier height become completely frozen for any time and the fractal scaling of the tails of $\langle l^m(t)\rangle$ and $\psi(t)$ holds up to infinity,

$$\langle l^m(t)\rangle \sim \Gamma(H+1)(\nu m t)^{-H}, \qquad t \gg 0, \quad \tau_{\mathrm{fl}} \to \infty, \tag{31}$$

$$\psi(t) \sim H\Gamma(H+1)\nu(\nu t)^{-(H+1)}, \qquad t \gg 0, \quad \tau_{\mathrm{fl}} \to \infty. \tag{32}$$

The moments of the passage time are given by

$$\langle t^m\rangle = \int_0^\infty t^m \psi(t)\,\mathrm{d}t. \qquad m \geqslant 1. \tag{33}$$

For an ideal fractal all these moments are infinite. For a non-ideal fractal, however, the moments of the passage time, although possibly large, should be finite because of the exponential decay of the end of the tail of the function $\psi(t)$. These moments can be explicitly evaluated for large but finite values of the fluctuation time scale $\tau_{\mathrm{fl}} \gg 0$. By inserting Eq. (27) into Eq. (33) and keeping only the dominant contributions in $\tau_{\mathrm{fl}} = 1/\omega$ as $\omega \to 0$ we obtain

$$\langle t^m\rangle \sim H\Gamma(1+H)\nu^{-H}(H/\omega)^{m-H} f_m(H), \qquad \tau_{\mathrm{fl}} = 1/\omega \gg 0, \quad m > H, \tag{34}$$

where

$$f_m(H) = \int_0^\infty y^m \exp(-Hy)[1-\exp(-y)]^{-(H+1)}\,\mathrm{d}y = \Gamma(m+1)\sum_{q=0}^{\infty} \frac{\Gamma(H+q+1)}{\Gamma(H+1)q!}(H+q)^{-(m+1)}. \tag{35}$$

It is easy to check that for $m > H$ both the integral and the series in Eq. (35) are convergent.

Since the passage time t is a non-negative variable the characteristic function of the probability density $\psi(t)$ can be defined by means of a Laplace transformation,

$$\bar{\psi}(s) = \int_0^\infty \exp(-st)\psi(t)\, dt, \tag{36}$$

where s is the Laplace variable conjugate to the passage time. The characteristic function $\bar{\psi}(s)$ can be evaluated in the limit of large values of the fluctuation time scale $\tau_{fl} = 1/\omega$. We insert expression (27) into Eq. (36), use the integral representation of the incomplete gamma function, expand the integrand of the resulting equation in a double series, keep the dominant terms in the limit $\tau_{fl} \gg 0$ and sum the resulting series. The result of these operations is

$$\bar{\psi}(s) \sim \exp\left[-H\Gamma(1+H)\left(\frac{\omega}{H\nu}\right)^H \int_0^\infty dy\, \frac{\exp(-Hy)[1-\exp(-sHy/\omega)]}{[1-\exp(-y)]^{H+1}}\right], \qquad \tau_{fl} \gg 0. \tag{37}$$

By expanding the exponent in Eq. (37) in a Taylor series in s we can evaluate the cumulants of the passage time in the limit $\tau_{fl} \gg 0$,

$$\langle\langle t^m \rangle\rangle \sim H\Gamma(1+H)\nu^{-H}(H/\omega)^{m-H} f_m(H), \qquad \tau_{fl}/\omega \gg 0, \qquad m > H. \tag{38}$$

We arrive at the surprising conclusion that for $\tau_{fl} \gg 0$ the cumulants of the passage time are approximately equal to the corresponding moments. The explanation of this result is simple: both Eqs. (34) and (38) give only the dominant contribution in $\tau_{fl} = 1/\omega$ as $\omega \to 0$ which both for the cumulants and the moments scale as $\omega^{-(m-H)} \sim (\tau_{fl})^{m-H}$. Although the cumulants and the moments are generally different, the other contributions depend on lower powers of τ_{fl} and thus in the limit $\tau_{fl} \to \infty$ the differences between the moments and the cumulants are negligible.

An important consequence of the asymptotic expressions (38) for the cumulants is that for $\tau_{fl} \gg 0$ the fluctuations of the passage time are intermittent. For proving the existence of intermittency we compute the relative fluctuation of order m ($m \geqslant 2$)

$$\rho_m(\omega) = \frac{\langle\langle t^m \rangle\rangle^{1/m}}{\langle\langle t \rangle\rangle} \sim [H\Gamma(1+H)]^{-(1-1/m)} \frac{[f_m(H)]^{1/m}}{f_1(H)} \left(\frac{\nu H}{\omega}\right)^{H(1-1/m)},$$

$$\tau_{fl} = 1/\omega \gg 0, \qquad m \geqslant 2. \tag{39}$$

The relative fluctuation of order m increases with the increase of τ_{fl} as $(\tau_{fl})^{H(1-1/m)}$. As expected in the static limit $\tau_{fl} \to \infty$ all relative fluctuations $\rho_m(\omega)$, $m \geqslant 2$ diverge to infinity.

Our analysis shows that the dynamic fluctuations of the barrier height increase the efficiency of the passage process. Due to the decay of activation energy fluctuations for a dynamical system the contribution of very large activation energies which cause very small passage rates is smaller in comparison with the static case $\tau_{fl} \to \infty$. The increase of efficiency can be analyzed by evaluating the large time behavior of the effective passage rate,

$$W_{eff}(t) = \psi(t)/\langle l(t) \rangle.$$

For a system with dynamic disorder in the limit $t \to \infty$ the effective rate W_{eff} tends towards the regression rate ω,

$$W_{eff} \sim \omega \qquad \text{as } t > \tau_{fl}, \qquad \tau_{fl} \gg 0, \qquad \tau_{fl} \text{ finite}, \tag{40}$$

whereas for a system with static disorder it decreases hyperbolically to zero,

$$W_{eff} \sim H/t, \qquad t \gg 0, \qquad \tau_{fl} \to \infty. \tag{41}$$

One usually expects that if the regression rate ω is also random the passage over the barrier is even more efficient. The simplest possible generalization of our model is to assume that the regression rate is a random variable selected from a given probability law,

$$g(\omega)\,\mathrm{d}\omega, \qquad \int g(\omega)\,\mathrm{d}\omega = 1. \tag{42}$$

In this case, although the pair of random variables (l, E) has a non-Markovian behavior a Markovian description is still possible by considering the rate ω as an additional random variable. The detailed analysis of this model will be presented elsewhere. Here we give only the final expression for the moments of the survival function,

$$\langle l^m(t)\rangle \sim H\nu^{-H}\int_0^\nu W^{H-1}\exp\left\{-mHW\int_0^\infty \mathrm{d}\omega\, g(\omega)\frac{\exp(\omega t/H)-1}{\omega}\right\}\mathrm{d}W. \tag{43}$$

For instance if the probability density $g(\omega)$ is given by a generalized Porter Thomas law [7] with a fractal exponent α and an average value $\langle\omega\rangle$,

$$g(\omega)\,\mathrm{d}\omega = [\Gamma(\alpha)]^{-1}(\alpha/\langle\omega\rangle)^{\alpha}\omega^{\alpha-1}\exp(-\alpha\omega/\langle\omega\rangle)\,\mathrm{d}\omega, \qquad 1>\alpha>0, \tag{44}$$

we arrive at

$$\langle l^m(t)\rangle = H\left\{\frac{mH\nu\alpha}{\langle\omega\rangle(1-\alpha)}\left[1-\left(1-\frac{\langle\omega\rangle t}{\alpha H}\right)^{1-\alpha}\right]\right\}^{-H}\gamma\left(H, \frac{mH\nu\alpha}{\langle\omega\rangle(1-\alpha)}\left[1-\left(1-\frac{\langle\omega\rangle t}{\alpha H}\right)^{1-\alpha}\right]\right),$$

$$t<t_{\mathrm{p}}, \tag{45a}$$

$$=0 \quad t\geqslant t_{\mathrm{p}}, \tag{45b}$$

where

$$t_{\mathrm{p}} = \alpha H/\langle\omega\rangle. \tag{46}$$

Due to the random behavior of the decay rate ω the passage occurs with certainty after a time interval of length t_{p} and for $t = t_{\mathrm{p}}$ all moments of the survival function collapse to zero.

We conclude this Letter by comparing our approach with other recent treatments of the passage over a fluctuating energy barrier presented in the literature [8–11]. Until now the study of fluctuating energy barriers has focused mainly on certain types of resonance phenomena such as stochastic resonance or resonant activation. The starting point of these approaches is a one- or two-dimensional Fokker–Planck equation which describes the passage over the barrier. The Fokker–Planck equation is integrated by assuming that the barrier height has known stochastic properties. These approaches are of course more appropriate from the statistical mechanical point of view; they are generalizations of the classical Kramers theory of activated processes [12]. In contrast in our approach we take the Arrhenius equation (3) for granted and assume that the corresponding activation energy is a random function of time with known stochastic properties described by Eqs. (7) and (10), (11). Although from the theoretical point of view the validity of such an assumption is questionable, it has been shown in the literature of RAEM [1–5] that for static disorder it is consistent with experimental data for a large class of natural phenomena.

Our main purpose has been to investigate the possible occurrence of fractal time statistics for a fluctuating energy barrier with dynamic disorder. The fractal time statistics is due to the occurrence of a broad spectrum of very large barrier heights which are exponentially rare; in the models of fluctuating energy barriers considered in the literature [8–11] one assumes the existence of a limited number of possible values of the activation energy, the passage from one value to another being described for instance by a random telegraph Markov process [11]. It is therefore not surprising that the results reported here concerning the non-ideal fractal time statistics are absent from the literature.

Concerning the validity range of our approach we would expect it to be reasonably valid for systems in which the fluctuations of the energy barrier are due to the interaction of a large number of degrees of freedom, such as the protein-ligand interactions or ion channel kinetics [4,5] for which the main source of randomness is the conformational fluctuations.

Of course the question of establishing the validity range of the Arrhenius equation (3) for fluctuating barriers with dynamic disorder is still open. A more satisfactory theoretical approach should start from a multidimensional Fokker–Planck equation with a fluctuating energy barrier described by the stochastic Liouville equation (7) and then eliminate the irrelevant degrees of freedom by deriving a reduced evolution equation depending on a limited number of collective coordinates. This is a very difficult undertaking and the possibilities of carrying it out are uncertain.

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