Physica A 661 (2025) 130413

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Barrier-crossing driven by fractional Gaussian noise in the context of reactive flux formalism: An exact result

Evangelos Bakalis [*], Francesco Zerbetto

Dipartimento di Chimica "G. Ciamician", Università di Bologna, V. P. Gobetti 85, 40129, Bologna, Italy

ARTICLE INFO

Keywords:
Kramers' reaction rate
Fractional Gaussian noise
Reactive flux method
Multinomial Mittag–Leffler

ABSTRACT

The problem of barrier-crossing is considered in the case when the surroundings of the barrier maintain some memory, while, at the same time, the heat bath is at equilibrium. The system is modelled by the generalised fractional Langevin equation with the noise term described by fractional Gaussian noise (fGn). The analytical solutions, in the time domain, are given in terms of the multinomial Mittag-Leffler function and the transmission coefficient is expressed in closed form as a function of the friction coefficient, of the barrier height, and of the Hurst exponent. Kramers' theory rate constant is a special case of the present treatment.

1. Introduction

Many processes in diverse scientific fields can be comprehended under the magnifying lens of reaction rate theory that offers pertinent information on the long-term behaviour of systems with various metastable states. Arrhenius was the first who quantified the rate k of a chemical reaction, $k = \nu exp(-\Delta U/k_BT)$, in terms of a free energy-like quantity, ΔU, and of a prefactor ν whose units contain $1/s$ [1]. k_BT is the Boltzmann's constant times the temperature of the bath, and the exponential factor $exp(-\Delta U/k_BT)$ is attributed to van't Hoff [2], see also discussion in Ref [3]. Application of Arrhenius law in complex kinetics is questionable because the estimation of ΔU and ν is challenging. Theories trying to unravel these two parameters usually consider the reaction as a conformational transition along a one-dimensional path (reaction coordinate) containing a peak, which is called the transition state (TS), also known as the point of no return since if the reactant passes the TS, it automatically becomes product.

Kramers, in his seminal work [4], presented an appealing explanation of chemical kinetics in solution. He considered the dynamics along the reaction coordinate as Brownian motion within a force field. In this theoretical framework, the TS is no longer the no-return point but rather a point where environmental fluctuations decide if the reactant moves towards the product state or returns back to its initial one. Kramers used the Langevin equation — constant friction coefficient and thus a memoryless noise term (white noise). He derived in phase space a Fokker–Planck equation also known as Kramers equation. He demonstrated that in the high friction regime, the mean first passage time (τ) is proportional to the magnitude of the friction coefficient. This finding is the opposite of the low friction limit, where τ is proportional to the inverse of the friction coefficient [4]. Kramers used the flux over population formulation for the rate constant [5], and in his approach assumed three time scales: (a) the collision timescale, which is shorter than, (b) the equilibration time within the well, which is shorter than (c) the escape time from the well. The three timescales imply that barrier-crossing is a thermally activated process. Over time, Kramers theory has undergone numerous tests and extensions [3,6–9].

Grote and Hynes calculated the transmission coefficient for Gaussian-distributed and oscillatory friction coefficients [10], relaxing the coupling between heat bath and reaction coordinate around the barrier by considering only local memory effects in the barrier

* Corresponding author.
E-mail addresses: evangelos.bakalis2@unibo.it (E. Bakalis), francesco.zerbetto@unibo.it (F. Zerbetto).

https://doi.org/10.1016/j.physa.2025.130413
Received 30 October 2024; Received in revised form 14 January 2025
Available online 31 January 2025

region while at the same time assuming the dynamics of the population in the potential well to be Markovian. Mel'nikov and Meshkov, by using an integral equation in energy variable, bridged the gap between low and high friction regimes, and their approach is valid for the entire spectrum of friction values [11]. Hanggi and Mojtabai by using the flux over population method generalised Kramers' modelling for thermally activated processes with long time memory, and turned out to the Grote–Hynes transmission coefficient [12]. Some years later, Pollak made use of the equivalency of the generalised Langevin equation GLE to a harmonic bath, and by using normal mode analysis for the system plus the Hamiltonian of the bath, ended up with the Grote–Hynes formula [13].

Tannor and Kohen by using the reactive flux method obtained Kramers formula. In their derivation, they exploited the equivalence of the Fokker–Planck equation and the Langevin equation [14]. The reactive flux method (RFM) assumes that reactants and products are at equilibrium and the total flux through any surface that divides reactants and products is zero, trajectories start at the top of the barrier, and one enquires, in the long time limit, whether they end up as products or reactants. RFM due to its computational ease, has become the major tool for determining rate constants through molecular dynamics simulations. Details of the method can be found in Ref. [14] and the references therein.

By using the reactive flux formalism [14], the Grote–Hynes transmission coefficient for the rate of barrier crossing in the presence of memory friction has been extracted, and the behaviour of the rate constant at all times has been provided [15]. The transmission coefficient in the presence of coloured noises, using the same approach, has been expressed with the help of the two-parameter Mittag-Leffler function, which provides closed results for some specific values of the Hurst exponent [16]. It is important to note that the RFM applies when the different time scales that depict equilibration within the well and escape times are well separable, as, for instance, happens in the presence of high barriers, opposed to the low ones where different time scales coexist [17]. Moreover, according to recent reports, the first passage time of a Brownian particle at a target point is not minimised by free diffusion or, equivalently, by the absence of a barrier; rather, the process is sped up by the barrier itself [18]. As of right now, there is still no straightforward expression for the transmission coefficient that takes into account the barrier height, the Hurst exponent, and the friction coefficient. Since the Hurst exponent is a measure of memory of the dynamics of the molecules involved in the reaction and ultimately influences how the barrier is overcome, it is desirable to establish a direct relationship between the transmission coefficient, this exponent, and the rest of the parameters.

Herein, in the context of the RFM we solve the generalised Langevin equation, which describes the motion of a reactant (probe particle) in the presence of an inverted parabola playing the role of the barrier, in the presence of a fractional Gaussian noise (fGn) that incorporates memory effects around the barrier. The heat bath is considered to be at equilibrium, and we consider the strong damping limit. The analytical solutions are given in terms of the multinomial Mittag-Leffler function, and the transmission coefficient at equilibrium takes a simple form that depends only on the parameters of the system, i.e., the friction coefficient, the barrier height, and the type of noise represented by the corresponding Hurst exponent. We show that anti-correlated noises favour barrier-crossing as opposed to correlated ones. The result states that anti-correlated noises extend the time a probe molecule stays over the barrier before being renewed.

2. Crossing over a barrier

Assuming that conditions RFM must satisfy are fulfilled, and by following the work of Tannor and Kohen [14,15], the reaction rate reads

$$k_r(t) = \frac{m}{hQ} e^{-\frac{E^\dagger}{k_B T}} \int_{-\infty}^{\infty} du_0 e^{-\frac{mu_0^2}{2k_B T}} u_0 \int_0^\infty dx \int_{-\infty}^{\infty} du \times P(x,u,t;x_0=0,u_0,0) \tag{1}$$

where the term $k_{TST} = \frac{k_B T}{Qh} e^{-\frac{E^\dagger}{k_B T}}$ is the reaction rate according to TST, with $E^\dagger$ being the energy difference between the top of the barrier and reactants. The propagator $P(x,u,t;x_0=0,u_0,0)$ is defined by Eq. (2).

$$P(x,u,t;x_0=0,u_0,0) = \frac{1}{2\pi\sqrt{\sigma(t)}} e^{-\frac{1}{2}[r^\dagger \sigma(t)^{-1} r(t)]} \tag{2}$$

where $x(t)$ describes the reaction coordinate, $u(t)$ is the velocity along the reaction coordinate, $r(t) = [x(t) - \langle x(t)\rangle, u(t) - \langle u(t)\rangle]$ is a vector, and $\sigma(t)$ is the covariance matrix containing the second moments: $\sigma_{11}(t) = \sigma_{xx}(t) = \langle (x(t) - \langle x(t)\rangle)^2\rangle$, $\sigma_{12}(t) = \sigma_{21}(t) = \sigma_{xu}(t) = \sigma_{ux}(t) = \langle (x(t) - \langle x(t)\rangle)(u(t) - \langle u(t)\rangle)\rangle$, and $\sigma_{22}(t) = \sigma_{uu}(t) = \langle (u - \langle u\rangle)^2\rangle$, x_0 the position along the reaction coordinate at the initial time $t = 0$.

We start with an inverted parabola as potential energy, $V(x) = V(x_b) - \frac{1}{2}m\omega^2(x-x_b)^2$, ω is the angular frequency in the transition state that plays a major role in Kramers' theory, and x_b is the location of the barrier that separates reactants from products. The motion of a probe particle in this potential field under the influence of fGn noise [19] is described by the generalised Langevin Eq. (3). [20–22]

$$m\ddot{x}(t) + \int_0^t \gamma(t-t')\dot{x}(t')dt' - m\omega^2(x(t) - x_b) = \xi_{fGn}(t) \tag{3}$$

where, $\gamma(t) \sim \frac{\gamma_a}{\Gamma(1-a)} t^{-a}$ expresses the generalised friction as a power law, and the thermal $\xi_{fGn}(t)$ noise is the time derivative of fractional Brownian motion (fBm), which was defined by Mandelbrot and van Ness [19] as $B_H(t) := \frac{1}{\Gamma(H+\frac{1}{2})}\Big(\int_0^t (t-t')^{H-\frac{1}{2}} dB(t') + \int_{-\infty}^0 ((t-t')^{H-\frac{1}{2}} - (-t')^{H-\frac{1}{2}}) dB(t')\Big)$. B being the ordinary Brownian motion and H the Hurst exponent with $H \in (0,1)$. fBm is the only

Gaussian self-similar process, $B_H(\lambda t) \sim |\lambda|^t B_H(t)$, with stationary increments [19,23]. fBm is widely used to describe phenomena across diverse fields of science, and is especially helpful when modelling diffusion in noisy and crowded environments [24–28]. Eq. (3) can be formally recast as a fractional Langevin equation in the overdamped limit ($m \to 0$) [29], and its ergodic properties have been noted (the time average mean square displacement equals the ensemble-averaged mean squared displacement) [30]. However, the ergodicity of fBm has recently been questioned due to either inertial effects [31] or the impact of nonlinear time and space properties superimposed onto the fBm-type dynamics [32]. The covariance function of a fBm process has the form $\langle B_H(t)B_H(t')\rangle \sim t^{2H} + t'^{2H} - |t-t'|^{2H}$ for $t, t' > 0$, and accordingly the covariance of a fGn noise ($\xi_{fGn}(t) = \frac{dB_H(t)}{dt}$) reads as follows $\langle \xi_{fGn}(t)\xi_{fGn}(t')\rangle \sim \sigma^2 H(2H-1)|t-t'|^{2H-2} + 4H|t-t'|^{2H-1}\delta(t-t')$ [33]. Asymptotically, for an internal noise, the second dissipation fluctuation relation holds true $\langle \xi_{fGn}(t)\xi_{fGn}(t')\rangle = k_B T\gamma(|t-t'|)$ [34]. The friction term thus has the form $\gamma(t) \sim \frac{\gamma_a}{\Gamma(2H-1)} t^{2H-2}$, where we identify $a = 2-2H$. For $H \in (0, \frac{1}{2})$ / $H \in (\frac{1}{2}, 1)$, the values of a represent antipersistent/persistent noises, respectively.

The integral, $\int_0^t \gamma(t-t')\dot{x}(t')dt'$ is well defined for $H \in (\frac{1}{2}, 1)$, but it diverges for $H \in (0, \frac{1}{2})$. This divergency is at odds with the physical model of a power law friction force that affects the motion for large times compared to the collision time between the bath molecules, and of course the latter time scale is larger than 0; too much of importance at zero. There are two options: either raise the exponent's power and continue with integration by parts, or truncate the integral from below. We will proceed with the former [20]. We write the term $\int_0^t (t-t')^{-a}\dot{x}(t')dt'$ as $\int_0^t \left(\frac{1}{a-1}\frac{d}{dt'}(t-t')^{-a+1}\right)\dot{x}(t')dt'$ and integrating by parts we end up with $\frac{t^{1-a}}{a-1} + \frac{1}{a-1}\int_0^t (t-t')^{1-a}\ddot{x}(t')dt'$, which is a well-defined integral for $1 < a < 2$. By using the Laplace pair, $L\{f(t)\}(s) = \int_0^\infty e^{-st} f(t)dt$, and the initial conditions $x(t=0) = x_0$, $u(t=0) = u_0$, we find that the Laplace transform of the kernel $\gamma_a \int_0^t (t-t')^{-a}\dot{x}(t')dt'$ for both $1 < a < 2$ and $0 < a < 1$ are identical the same and reads $\gamma_a s^a - \gamma_a x_0 s^{-1+a}$.

We use the Laplace pair to solve Eq. (3), after some algebra we find

$$x(s) = \frac{x_0}{s} + (u_0 + \frac{\xi_{fGn}(s)}{m})G(s) + \omega^2(x_0 - x_b)I(s) \tag{4}$$

and

$$u(s) = (u_0 + \frac{\xi_{fGn}(s)}{m})g(s) + \omega^2(x_0 - x_b)G(s) \tag{5}$$

where, $G^{-1}(s) = s^2 + \frac{1}{m}s\gamma(s) - \omega^2$, $I(s) = G(s)/s$, and $g(s) = sG(s)$ are response functions. We define the generalised response function [35],

$$R_\delta(s) = \frac{s^\delta}{s^2 + \frac{s}{m}\gamma(s) - \omega^2} \tag{6}$$

whose inversion in the time domain provides the analytical forms of $g(s), G(s), I(s)$ since for $\delta = -1, 0, 1$, it holds true that $R_{-1}(s) = I(s)$, $R_0(s) = G(s)$, and $R_1(s) = g(s)$. The Laplace pair of the generalised friction function reads $L\{\gamma(t)\} = \gamma_a s^{-1+a}$, and the denominator of Eq. (6) has the form $s^2 + \frac{\gamma_a}{m}s^a - \omega^2$. Note that the parameter γ_a has units M/T^{2-a}, and all arguments present in Eqs. (7), (8), and (9) are dimensionless. It is worth mentioning that if the noise were white, then the denominator would take the simpler form of $s^2 + \frac{\gamma_a}{m}s - \omega^2$ whose inversion in the time domain is made through factoring the denominator.

The inversion of Eq. (6) in the time domain is made through the multinomial Mittag-Leffler function, see the Ref. [35] and references therein, and has the form

$$R_\delta(t) = t^{1-\delta}E_{(2,2-a),2-\delta}(\omega^2 t^2, -\frac{\gamma_a}{m}t^{2-a}) \tag{7}$$

For $\frac{\gamma_a}{m}t^{2-a} > 1$, Eq. (7) is reduced to a two-parameter Mittag-Leffler function and reads

$$R_\delta(t) = \frac{m}{\gamma_a}t^{a-\delta-1}E_{a,a-\delta}(\frac{m\omega^2}{\gamma_a}t^a) \tag{8}$$

Eq. (8) expresses the generalised response function in the overdamped limit, which can also be taken from Eq. (6) by considering the limit $s \to 0$, $s^\delta/(\frac{\gamma_a}{m}s^a - \omega^2)$, and then inverting it in the time domain. Eq. (7) provides the response functions $g(t)$, $G(t)$, and $I(t)$ in the entire time domain. For $t \to 0$, we find $g(t=0) = 1$, $G(t=0) = 0$, and $I(t=0) = 0$. On the other hand, asymptotic expansion of Eq. (8), $E_{n,m}(z) = \frac{1}{n}z^{\frac{(1-m)}{n}}e^{z^{1/a}} - \sum_{k=1}^N \frac{1}{\Gamma(m-nk)}z^{-k}$ when $0 < n < 2$ and $\mu \in R$: $\frac{\pi n}{2} < \mu < min[\pi, n\pi]$ [36], leads to

$$R_\delta(t) = \frac{m}{\gamma_a}\frac{1}{a}(\frac{m\omega^2}{\gamma_a})^{\frac{(1-a+\delta)}{a}}e^{(\frac{m\omega^2}{\gamma_a})^{1/a}t} \tag{9}$$

Assuming that $x_0 = 0$ as well as $x_b = 0$, we find from Eq. (4) that $\langle x\rangle(t) = u_0 G(t)$. Substitution of the latter into Eq. (1) and integrating yields

$$k_r(t) = \frac{G(t)}{\sqrt{G^2(t) + \frac{m}{k_B T}\sigma_{x,x}(t)}}k_{TST} \tag{10}$$

where $\sigma_{x,x}(t) = \frac{k_B T}{m}(2I(t) - G^2(t) + \omega^2 I^2(t))$, see Appendix A.

Substituting into Eq. (10) the response functions, $G(t)$ and $I(t)$, as predicted by Eq. (9), and taking the limit $t \to \infty$ obtains

$$k_r(H) = \frac{1}{\omega}\left(\frac{m\omega^2}{\gamma_a}\right)^{1/(2-2H)}k_{TST} \tag{11}$$

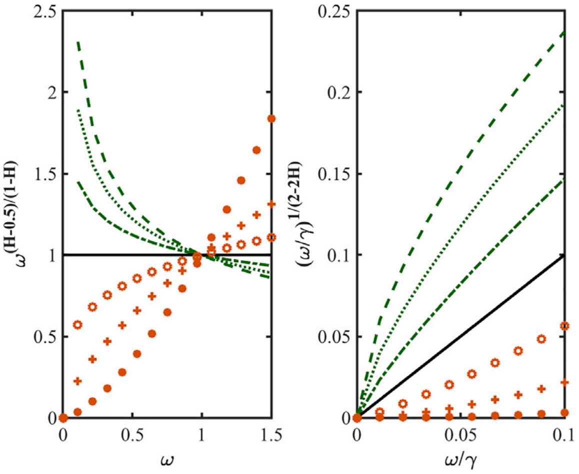

Fig. 1. Left Panel: The energy barrier frequency raised to a power that is a function of the Hurst exponent of the applied noise, $\omega^{\frac{H-0.5}{1-H}}$ versus the barrier frequency, ω, is depicted. Right panel: $\left(\frac{\omega}{\gamma}\right)^{\frac{1}{2-2H}}$ versus the parameter $\frac{\omega}{\gamma_a}$ for various values of H is illustrated. The values of H cover both anti-persistent and persistent noises. Dashed line for $H = 0.2$, dot line for $H = 0.3$, and dashed-dot line for $H = 0.4$; dark green for antipersistent noises. For $H = 0.5$, a solid black line represents white noise. For persistent noises, dark orange is used: filled circles for $H = 0.8$, crosses for $H = 0.7$, and open circles for $H = 0.6$.

Assuming that $\gamma_a/m \to \gamma$, we write Eq. (11) that allows direct comparison to the reaction rate predicted by TST.

$$\frac{k_r(H)}{k_{TST}} = \omega^{\frac{H-1/2}{1-H}} \left(\frac{\omega}{\gamma}\right)^{1/(2-2H)} \tag{12}$$

Eq. (11) is the primary outcome of this work. It provides the reaction rate, as far as the reaction flux formalism is in use, as a function of the energy barrier, the friction coefficient, and the Hurst exponent for both persistent and antipersistent noises. For the same barrier and friction coefficient, Eq. (11) states that the reaction rate is higher for antipersistent noises than for white noise (Kramers' formula), which, in turn, is higher in relation to the impact of a persistent noise on the reaction rate; see also discussion. Our findings are in line with reports where an overdamped Langevin equation has been integrating and the dependence of the mean escape time on the noise intensity and the Hurst exponent for both persistent and antipersistent noises, as well as the probability density for the escape times, have been evaluated [37]. Eq. (12) provides the same information as Eq. (11). However, when the ambient noise is not white, it also provides a straightforward final result in the strong damping limit, which includes the Kramers' result as a special case of the value of H and its correction. The ratio $\frac{k_r(H)}{k_{TST}}$ has been examined before in a variety of ways; for instance, for persistent fractional Gaussian noises in Ref. [16], the authors express it as the ratio of two Mittag-Leffler functions; see Appendix B.

3. Discussion

Kramers, in his seminal work [4], found that the reaction rate as predicted by TST is reduced by a transmission coefficient of the form $k(\gamma) = \frac{-\frac{\gamma}{2}+\sqrt{\frac{\gamma^2}{4}+\omega^2}}{\omega}$. By setting $\epsilon = \frac{\gamma}{2\omega}$, the reaction rate becomes $k_r(H = \frac{1}{2}) = (-\epsilon + \epsilon\sqrt{1+\frac{1}{\epsilon^2}})k_{TST}$. In the strong damping limit, $\gamma \gg \omega$, by setting $y = \epsilon^{-1}$ and taking the expansion, we find $k_r(H = \frac{1}{2}) = \frac{\omega}{\gamma} k_{TST}$. By substituting in Eq. (12) $H = 1/2$, one can readily verify that the ratio of the two rates satisfies Kramers' theory.

Eq. (11) is a direct generalisation of Kramer's result, since the latter is a subcase of the former. It is an exact result under the assumption that the reactive flux formalism is valid and describes the impact of antipersistent and persistent noises on a molecule for crossing a barrier. The value of the transmission coefficient, Eq. (12), is the result of the competition of two power law terms, namely, $\omega^{\frac{H-1/2}{1-H}}$ and $\left(\frac{\omega}{\gamma}\right)^{\frac{1}{2-2H}}$

Both terms are functions of the Hurst exponent, which takes values in the range $H \in (0, 1)$. The first term, $\omega^{\frac{H-1/2}{1-H}}$, is always equal to one if $\omega = 1$ (in arbitrary units) or if $H = 0.5$. If $\omega < 1$, then $\omega^{\frac{H-1/2}{1-H}} > 1$ for antipersistent noises ($0 < H < 0.5$) and its value grows by lowering the value of H. On the other hand, for $\omega > 1$ the value of this term is larger the higher the value of the persistent noise is; see details in the left panel of Fig. 1. The second term describes Kramers' result in the strong damping limit raised to a power that is equal to the reciprocal of the exponent $2 - 2H$.

On the other hand, the right panel of Fig. 1 shows the dependence of the parameter describing the strong damping limit, $\frac{\omega}{\gamma_a} \ll 1$, when it is expressed as a power law of $\frac{1}{2-2H}$. For the illustration we use a cut-off value of 0.1 as the maximum value the damping parameter can take. The value of the second term becomes larger the lower the value of H, which means that for strong antipersistent

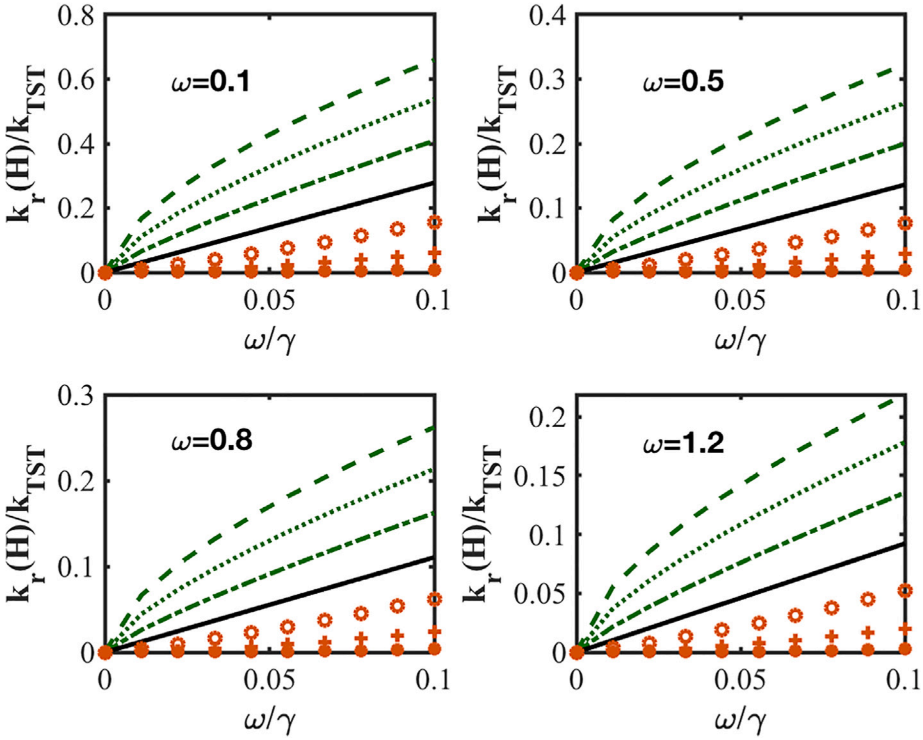

Fig. 2. The reaction rate as it is predicted by (12) is shown. The type of lines and the colour code remain the same as in Fig. 1.

noises, the contribution of this term is maximised. The combination of these two terms, which are displayed in Fig. 1 defines the reaction rate, as it is expressed by (12), and it is shown in Fig. 2. The latter displays the dependency of the reaction rate on the damping parameter, $\frac{\omega}{\gamma}$, for four different values of the energy barrier, $\omega = 0.1, 0.5, 0.8, 1.2$. In every instance, the rate decreases to zero when $\frac{\omega}{\gamma} \to 0$, indicating that a very strong damping environment is not conducive to any reaction.

As the hypothesis of very strong damping weakens, the value of the reaction rate increases as the value of the Hurst exponent decreases. Moreover, the lower the value of the energy barrier, the higher the value of the reaction rate for a given value of the Hurst exponent; see Fig. 2, where for some values of the frequency term the reaction rate is displayed as a function of the damping parameter. This observation is in line with the first passage behaviour of fBm, whose analytical form is known [38,39] and has been confirmed by numerical simulations [40]. And yet, it is worth mentioning the linear increase of the rate when it is subject to white noise (the solid line), whose magnitude depends on the height of the energy barrier.

4. Conclusions

In the present work we examined the barrier crossing problem, assuming that the reactive flux formalism is valid. The problem is formulated with a fractional Langevin equation whose noise term is given by a fractional Gaussian noise and describes the fluctuations around the barrier. The solutions are expressed in terms of the multinomial Mittag-Leffler functions. In the long-time limit, we get a closed analytical form for the reaction rate. In fact, we proved in a straightforward and precise manner the dependency of the reaction rate on the energy barrier, the Hurst exponent that classifies the type of fGn noise, and the friction coefficient. Moreover, the result states that anticorrelated noises extend the time a probe molecule stays over the barrier before being renewed. The compact form and simplicity of the reaction rate make it an excellent candidate for understanding experimental systems and the role that environmental noise plays in crossing barriers.

CRediT authorship contribution statement

Evangelos Bakalis: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Conceptualization. **Francesco Zerbetto:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding sources

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Appendix A

The mean square displacement, $\langle (x(t)-x(t'))^2\rangle = \langle x(t)^2\rangle - 2\langle x(t)x(t')\rangle + \langle x(t')^2\rangle$, and $C_{u,u}(t,t') = \langle u(t)u(t')\rangle$ the velocity autocorrelation function, are quantities directly evaluated in an experiment. Towards assessing the dynamics of a tracer particle the following response functions are also of interest; position covariance $\sigma_{x,x}(t,t') = \langle x(t)-\langle x\rangle\rangle\langle x(t')-\langle x\rangle\rangle$, velocity covariance $\sigma_{u,u}(t,t') = \langle u(t)-\langle u\rangle\rangle\langle u(t')-\langle u\rangle\rangle$, and $\sigma_{x,u}(t,t') = \langle x(t)-\langle x\rangle\rangle\langle u(t')-\langle u\rangle\rangle$ the position velocity covariance. Common in all mentioned measures is either the term $\langle x(t)x(t')\rangle$ or the term $\langle u(t)u(t')\rangle$, which can be easily constructed in Laplace space by using Eqs. (4) and (5) of the main text.

$$\langle x(s)x(s')\rangle = A(s)A(s') + \frac{1}{m^2}\langle \xi_{fGn}(s)\xi_{fGn}(s')\rangle G(s)G(s') \tag{A.1}$$

and

$$\langle u(s)u(s')\rangle = B(s)B(s') + \frac{1}{m^2}\langle \xi_{fGn}(s)\xi_{fGn}(s')\rangle g(s)g(s') \tag{A.2}$$

where, $A(s) = \frac{x(0)}{s} + u(0)G(s) + \omega^2(x_0 - x_b)I(s)$, and $B(s) = u(0)g(s) + \omega^2(x_0 - x_b)G(s)$. In Laplace space the covariance functions read

$$\sigma_{x,x}(s,s') = \frac{\langle \xi_{fGn}(s)\xi_{fGn}(s')\rangle G(s)G(s')}{m^2} \tag{A.3}$$

$$\sigma_{u,u}(s,s') = \frac{\langle \xi_{fGn}(s)\xi_{fGn}(s')\rangle g(s)g(s')}{m^2} \tag{A.4}$$

$$\sigma_{x,u}(s,s') = \frac{\langle \xi_{fGn}(s)\xi_{fGn}(s')\rangle G(s)g(s')}{m^2} \tag{A.5}$$

By using the fluctuation dissipation relation, which in Laplace space reads, $\langle \xi_{fGn}(s)\xi_{fGn}(s')\rangle = k_B T\frac{\gamma(s)+\gamma(s')}{s+s'}$, and after some algebra [41], Eqs. (A.3) and (A.4) take the form

$$\frac{\langle \xi(s)\xi(s')\rangle G(s)G(s')}{m^2} = \frac{k_B T}{m}\{\frac{I(s')}{s} + \frac{I(s)}{s'} - \frac{I(s)+I(s')}{s+s'} - G(s)G(s') + \omega^2 I(s)I(s')\} \tag{A.6}$$

and

$$\frac{\langle \xi(s)\xi(s')\rangle g(s)g(s')}{m^2} = \frac{k_B T}{m}\{\frac{g(s)+g(s')}{s+s'} - g(s)g(s') + \omega^2 G(s)G(s')\} \tag{A.7}$$

In the time-domain, position and velocity covariance read

$$\sigma_{x,x}(t,t') = \frac{k_B T}{m}(I(t) + I(t') - I(|t-t'|) - G(t)G(t') + \omega^2 I(t)I(t')) \tag{A.8}$$

and

$$\sigma_{u,u}(t,t') = \frac{k_B T}{m}(g(|t-t'|) - g(t)g(t') + \omega^2 G(t)G(t')) \tag{A.9}$$

Eqs. (A.8) and (A.9) can be used to define variances, when we set $t = t'$ [35,41–43],

$$\sigma_{x,x}(t) = \frac{k_B T}{m}(2I(t) - I(0) - G^2(t) + \omega^2 I^2(t)) \tag{A.10}$$

$$\sigma_{u,u}(t) = \frac{k_B T}{m}(g(0) - g^2(t) + \omega^2 G^2(t)) \tag{A.11}$$

and

$$\sigma_{x,u}(t) = \frac{1}{2}\frac{d\sigma_{x,x}(t)}{dt} = \frac{2k_B T}{m}G(t)(1 - g(t) + \omega^2 I(t)) \tag{A.12}$$

Appendix B

In Ref. [16], the authors have defined the transmission coefficient $\kappa(t) = -\frac{\eta(t)}{\omega}$ with $\kappa(t) = \frac{k(t)}{k_{TST}}$. The function $\eta(t)$ is given through a modified response function as follows

$$\eta(t) = -\frac{\dot{\chi}(t)}{\chi(t)} \tag{B.1}$$

where $\chi(s) = \frac{\gamma\phi(s)}{s\gamma\phi(s)-\omega^2}$ in Laplace space. For $\phi(t) \sim t^{2H-2}$, the inverse Laplace pair gives, $\chi(t) = E_{2-2H}((t/\tau)^{1/(2-2H)})$, with $\tau = (\frac{\gamma}{\omega^2})^{1/(2-2H)}$.

Since, $\dot{\chi}(t) = (1/\tau)^{1/(2-2H)} t^{1-2H} E_{2-2H,2-2H}((t/\tau)^{1/(2-2H)})$, and by using the asymptotic expansion $E_{n,m}(z) = \frac{1}{n} z^{\frac{(1-m)}{n}} e^{z^{1/a}} - \sum_{k=1}^{N} \frac{1}{\Gamma(m-nk)} z^{-k}$ when $0 < n < 2$ and $\mu \in R : \frac{\pi n}{2} < \mu < min[\pi, n\pi]$ [36], leads to

$$k(\tau \to \infty) = \frac{1}{\omega} (\frac{\omega^2}{\gamma})^{1/(2-2H)} \tag{B.2}$$

Eq. (B.2) is exactly the transmission coefficient presented in the main text, Eq. (11) for $\frac{\gamma_a}{m} \to \gamma$.

Data availability

No data was used for the research described in the article.

References

[1] S. Arrhenius, Über die Reaktionsgeschwindigkeit bei der Inversion von Rohrzucker durch Säuren, Z. Phys. Chem. 4 (1889) 226.
[2] J.H. Van't Hoff, in: M. Amsterdam (Ed.), Etudes de dynamique chimique, 1884.
[3] E. Pollak, P. Talkner, Reaction rate theory: What it was, where is it today, and where is it going? Chaos 15 (2005) 026116.
[4] H.A. Kramers, Brownian motion in a field of force and the diffusion model of chemical reactions, Phys. A. 7 (1940) 284–304.
[5] L. Farkas, Keimbildungsgeschwindigkeit in übersättigten Dämpfen, Z. Phys. Chem. (1927).
[6] B.J. Berne, M. Borkovec, J.E. Straub, Classical and modern methods in reaction rate theory, J. Phys. Chem. 92 (1988) 3711–3725.
[7] P. Hänggi, P. Talkner, M. Borkovec, Reaction-rate theory: fifty years after Kramers, Rev. Modern Phys. 62 (1990) 251.
[8] D.E. Makarov, Barrier crossing dynamics from single-molecule measurements, J. Phys. Chem. B 125 (2021) 2467–2476.
[9] E. Pollak, S. Miret-Artes, Recent developments in Kramers' theory of reaction rates, ChemPhysChem 24 (2023) e202300272.
[10] R.F. Grote, J.T. Hynes, The stable states picture of chemical reactions. II. Rate constants for condensed and gas phase reaction models, J. Chem. Phys. 73 (1980) 2715–2732.
[11] V.I. Mel'nikov, S.V. Meshkov, Theory of activated rate processes: Exact solution of the Kramers problem, J. Chem. Phys. 85 (1986) 1018–1027.
[12] P. Hänggi, F. Mojtabai, Thermally activated escape rate in presence of long-time memory, Phys. Rev. A 26 (1982) 1168(R).
[13] E. Pollak, Theory of activated rate processes: A new derivation of Kramers' expression, J. Chem. Phys. 85 (1986) 865–867.
[14] D.J. Tannor, D. Kohen, Derivation of Kramers' formula for condensed phase reaction rates using the method of reactive flux, J. Chem. Phys. 100 (1994) 4932–4940.
[15] D. Kohen, D.J. Tannor, Phase space distribution function formulation of the method of reactive flux: Memory friction, J. Chem. Phys. 103 (1995) 6013–6020.
[16] S. Chaudhury, B.J. Cherayil, Complex chemical kinetics in single enzyme molecules: Kramers's model with fractional Gaussian noise, J. Chem. Psys. 24 (2006) 024904.
[17] A. Bose, N. Makri, Non-equilibrium reactive flux: A unified framework for slow and fast reaction kinetics, J. Chem. Phys. 147 (2017) 152723.
[18] M. Chupeau, J. Gladrow, A. Chepelianski, U. Keyser, E. Trizac, Optimizing Brownian escape rates by potential shaping, Proc. Natl. Acad. Sci. 117 (2020) 1383.
[19] B.B. Mandelbrot, J.W. Van Ness, Fractional Brownian motions, fractional noises and applications, SIAM Rev. 10 (1968) 422.
[20] E. Lutz, Fractional Langevin equation, Phys. Rev. E. 64 (2004) 051106.
[21] S.C. Kou, Stochastic modeling in nanoscale biophysics: Subdiffusion within proteins, Ann. Appl. Stat. 2 (2008) 501–535.
[22] I. Goychuk, Viscoelastic subdiffusion: Generalized Langevin equation approach, Adv. Chem. Phys. 150 (2012) 187–253.
[23] B.B. Mandelbrot, Some noises with 1/f spectrum, a bridge between direct current and white noise, IEEE Trans. Inform. Theory 13 (1967) 289–298.
[24] V. Tejedor, O. Bénichou, R. Voituriez, R. Jungmann, F. Simmel, C. Selhuber-Unkel, L.B. Oddershede, R. Metzler, Quantitative analysis of single particle trajectories: mean maximal excursion method, Biophys. J. 98 (2010) 1364–1372.
[25] J.-H. Jeon, H.M.-S. Monne, M. Javanainen, R. Metzler, Anomalous diffusion of phospholipids and cholesterols in a lipid bilayer and its origins, Phys. Rev. Lett. 109 (2012) 188103.
[26] E. Bakalis, S. Höfinger, A. Venturini, F. Zerbetto, Crossover of two power laws in the anomalous diffusion of a two lipid membrane, J. Chem. Phys. 142 (2015) 215102.
[27] I.M. Sokolov, Models of anomalous diffusion in crowded environments, Soft Matter 8 (2012) 9043–9052.
[28] R. Metzler, J.-H. Jeon, A.G. Cherstvy, E. Barkai, Anomalous diffusion models and their properties: non-stationarity, non-ergodicity, and ageing at the centenary of single particle tracking, Phys. Chem. Chem. Phys. 16 (2014) 24128.
[29] I. Goychuk, P. Hänggi, Anomalous escape governed by thermal 1/f noise, Phys. Rev. Lett. 99 (2007) 200601.
[30] W. Deng, E. Barkai, Ergodic properties of fractional Brownian-Langevin motion, Phys. Rev. E. 79 (2009) 011112.
[31] A.G. Cherstvy, W. Wang, R. Metzler, I.M. Sokolov, Inertia triggers nonergodicity of fractional Brownian motion, Phys. Rev. E. 104 (2021) 024115.
[32] Y. Liang, W. Wang, R. Metzler, A.G. Cherstvy, Anomalous diffusion, nonergodicity, non-Gaussianity, and aging of fractional Brownian motion with nonlinear clocks, Phys. Rev. E. 108 (2023) 034113.
[33] G. Samorodnitsky, M. Taqqu, Stable Non-Gaussian Random Processes: Stochastic Models with Infinite Variance, Chapman and Hall, New York, 1994.
[34] R. Kubo, The fluctuation-dissipation theorem, Rep. Progr. Phys. 29 (1966) 255–284.
[35] E. Bakalis, F. Zerbetto, Hydrodynamic fluctuations in the presence of one parameter Mittag-Leffler friction, Phys. A 620 (2023) 128780.
[36] H.J. Haubold, A.M. Mathai, R.K. Saxena, Mittag-Leffler functions and their applications, J. Appl. Math. 2011 (2011) 298628.
[37] O.Y. Sliusarenko, V.Y. Gonchar, A.V. Chechkin, Barrier crossing induced by fractional Gaussian noise, Ukr. J. Phys. 55 (2010) 579–585.
[38] M. Ding, W. Yang, Distribution of the first return time in fractional Brownian motion and its application to the study of on-off intermittency, Phys. Rev. E 52 (1995) 207.
[39] J. Krug, H. Kallabis, S.N. Majumdar, S.J. Cornell, A.J. Bray, C. Sire, Persistence exponents for fluctuating interfaces, Phys. Rev. E 56 (1997) 2702.
[40] O.Y. Sliusarenko, V.Y. Gonchar, A.V. Chechkin, I.M. Sokolov, R. Metzler, Kramers-like escape driven by fractional Gaussian noise, Phys. Rev. E 81 (2010) 041119.
[41] M.A. Despósito, A.D. Viñales, Memory effects in the asymptotic diffusive behavior of a classical oscillator described by a generalized Langevin equation, Phys. Rev. E 77 (2008) 031123.
[42] K.G. Wang, Long-time-correlation effects and biased anomalous diffusion, Phys. Rev. A 45 (1992) 833–837.
[43] A.D. Viñales, K.G. Wang, M.A. Despósito, Anomalous diffusive behavior of a harmonic oscillator driven by a Mittag-Leffler noise, Phys. Rev. E 80 (2009) 011101.