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Two-point approximation to the Kramers problem with coloured noise

Daniel Campos[a] and Vicenç Méndez
Grup de Física Estadística, Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra (Barcelona), Spain

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We present a method, founded on previous renewal approaches as the classical Wilemski-Fixman approximation, to describe the escape dynamics from a potential well of a particle subject to non-Markovian fluctuations. In particular, we show how to provide an approximated expression for the distribution of escape times if the system is governed by a generalized Langevin equation (GLE). While we show that the method could apply to any friction kernel in the GLE, we focus here on the case of power-law kernels, for which extensive literature has appeared in the last years. The method presented (termed as two-point approximation) is able to fit the distribution of escape times adequately for low potential barriers, even if conditions are far from Markovian. In addition, it confirms that non-exponential decays arise when a power-law friction kernel is considered (in agreement with related works published recently), which questions the existence of a characteristic reaction rate in such situations. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3685418]

I. INTRODUCTION

The Kramers escape problem from a well potential represents one of the cornerstones of the reaction-rate theory.[1] According to it, the kinetics of chemical transformations can be interpreted in the light of a Brownian particle moving through a *reaction coordinate space* x subject to an energy potential $V(x)$ which determines the energy landscape of the system. This Brownian dynamics can be represented through the Langevin equation

$$\ddot{x} = -\gamma\dot{x} - \frac{\mathrm{d}V(x)}{\mathrm{d}x} + \xi^{(w)}(t), \tag{1}$$

where we have assumed a unit mass ($m = 1$). In this expression a standard velocity-dependent friction term is used (with a characteristic friction parameter γ), and $\xi^{(w)}(t)$ represents Gaussian white noise. One of the celebrated results by Kramers was on the analysis of the distribution of escape times from one potential well to another.[2] He was able to determine that the decay of this distribution in the steady state is asymptotically exponential, giving rise then to a characteristic reaction (escape) rate k.

During several decades, many researchers have explored the generalized Kramers problem in which this noise-induced escape process is governed by correlated fluctuations (this is, colored noise). In that situation, an asymptotic reaction rate can still be well defined (provided that the integral of the autocorrelation function of the noise does not diverge). The Eq. (1) then turns into the generalized Langevin equation (GLE)

$$\ddot{x} = -\int_0^t \mathrm{d}t'\eta(t-t')\dot{x}(t') - \frac{\mathrm{d}V(x)}{\mathrm{d}x} + \xi(t), \tag{2}$$

where the friction kernel $\eta(t)$ and the noise $\xi(t)$ are connected through

$$\langle\xi(t)\xi(s)\rangle = k_B T\eta(|t-s|). \tag{3}$$

These equations can be rigorously derived using a formalism from statistical mechanics for the case of a particle immersed in a thermal bath of harmonic oscillators.[3] Then the fluctuation dissipation theorem expressed by Eq. (3) holds since fluctuations and friction have a common origin. Likewise, the GLE has also been studied in the presence of additional or external noises.

In the last years special focus has been put on those cases where the noise correlations expand over several timescales (giving rise to autocorrelation functions whose integral diverges) as Mittag-Leffler noise, fractional Gaussian noise (fGn), etc. This interest is motivated by recent experimental findings. Single-molecule experiments with different proteins have shown that the conformational fluctuations observed in these systems are long-lasting correlated,[4,5] and for some specific cases the system (2) and (3) has been specifically proposed as an appropriate model to explain these results.[5,6] Also, ultraslow relaxation in the viscoelastic properties of dense suspensions[7] as well as DNA escape dynamics from nanopores[8,9] are found to admit similar descriptions.

Notably, recent theoretical works carried out in this line have proved that the escape times distributions for these cases do not decay exponentially but as a stretched exponential.[10,11] This is again in agreement with observations done in bistable enzymatic reactions performed at the single-molecule level.[12–16] For a GLE approach governed by fGn, this type of decay is expected to occur in general if potential barriers separating the wells are below a certain threshold value,[11] and (even above that threshold) if the average value of the autocorrelation function diverges (albeit this last case requires careful consideration since an exponential cutoff is always expected to appear in the correlation function at long times).[11,17,18] The escape times then lack a characteristic timescale and a reaction rate (in a classical sense) cannot be well established; this is a topic of major theoretical interest which has been under debate recently.

[a] Author to whom correspondence should be addressed. Electronic mail: daniel.campos@uab.es.

Due to the non-Markovian and the nonlinear nature of the problem, it becomes really difficult to obtain exact or analytical results from Eqs. (2) and (3). The problem simplifies considerably if the reactant well is approximated to a harmonic potential. Then a Fokker-Planck description is available, as was first derived by Adelman[19] and later used to study transmission through a parabolic barrier by Hänggi and Mojtabai[20] (see also Ref. 21). The corresponding dynamical phase diagram for the case of fGn has also been explored recently.[23] In the absence of inertial effects in Eq. (2) an exact asymptotic limit to the escape times distribution has also been obtained for power-law noise, and it has been shown to follow a power-law asymptotic decay.[17] The case of overdamped motion with fGn has also been explored very recently,[24] but in that situation it is observed that the distribution of escape times decays exponentially and so a rate theory can be established without problem. Finally, a quasistatic disorder approximation has also been used to justify the stretched exponential decays found in the general (this is, not overdamped) case.[11]

In the present work we propose a semi-analytical approximation to the escape problem from a harmonic potential governed by the GLE and the fluctuation-dissipation theorem with a Gaussian power-law noise (this is, for example, the same problem addressed recently in Ref. 25). Note, however, that the method we shall present can be extended straightforward to any colored Gaussian noise. The model is inspired on a first-passage approach proposed by Sokolov,[26] and it is not only able to explain the stretched exponential decays observed in Refs. 10 and 11 for large escape times, but it fits reasonably well the whole shape of the escape times distribution (at least in some regimes) without using any adjustable parameters. This will be confirmed by direct comparison with Langevin dynamics simulations performed at different values of the k_BT factor.

II. THE WILEMSKI-FIXMAN APPROXIMATION

In order to present our model it is first convenient to review the well-known approach proposed almost forty years ago by Wilemski and Fixman (WF). Renewal approximations in general represent a quite usual way to address first-passage problems[27] and, in particular, the WF approximation had its origin in the analysis of polymer cyclization,[26,28,29] though has later been extended to many other situations. Consider a stochastic particle moving on the x coordinate subject to a known dynamics, which includes the effect of a harmonic potential (Figure 1). We want to determine the probability to reach *for the first time* the position $x_f > 0$ at time t. Following the van Kampen's derivation,[27] we can split the total number of possible trajectories leading the particle to the position x at time t into those for which the first-passage has already occurred at a previous time $t' < t$, and those for which the first-passage has not occurred yet. Then the probability $G(x, t|x_0)$ to be at x at time t (given the initial condition x_0) reads

$$G(x,t\mid x_0) = Q(x,t\mid x_0) + \int_0^t \mathrm{d}t' G(x,t\mid f(x_f,t'\mid x_0);x_0) \times f(x_f,t'\mid x_0). \tag{4}$$

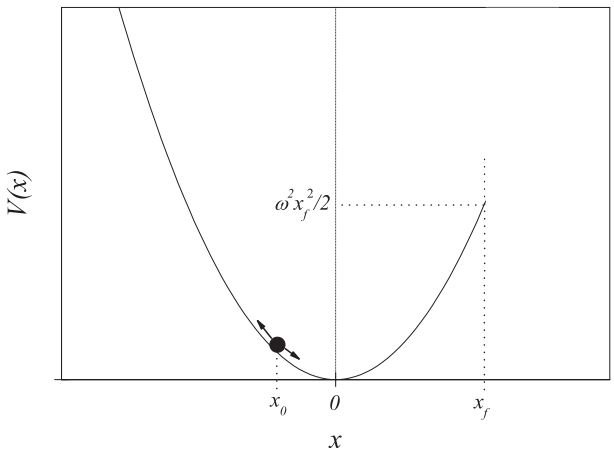

FIG. 1. Schematic representation of the escape problem addressed here.

Here, the probability $Q(x, t|x_0)$ stands for those paths that have not passed yet through x_f during the interval $(0, t)$, and the function $f(x_f, t|x_0)$ is the first-passage probability distribution for particles at time t (in the following, we will omit the explicit dependence of f on initial conditions to simplify notation). In consequence, $G(x, t|f(x_f, t'); x_0)$ represents the probability to be at (x, t) conditional to the first-passage event at time t. In order to deal analytically with the previous expression some sort of simplification is needed; in the WF approximation it is assumed that

$$G(x,t\mid f(x_f,t');x_0) \approx G(x,t-t'\mid x_f). \tag{5}$$

According to this, it is assumed that a new process, independent of the previous history of the particle, starts once the first-passage occurs (this is, a renewal assumption). Note that this approximation completely ignores initial conditions and any other previous memory of the system when x_f is crossed for the first time, so this is not appropriate to describe highly non-Markovian systems in which correlations are long-lasting, as those driven by fGn or similar.

The final step in the WF approximation simply consists of evaluating (4)–(5) at $x = x_f$ so that $Q(x_f, t|x_0) = 0$ (which holds from the definition of Q). Then one obtains

$$G(x_f,t\mid x_0) = \int_0^t \mathrm{d}t' G(x_f,t-t'\mid x_f) f(x_f,t'), \tag{6}$$

from which the first-passage distribution can be obtained (by inversion) in case the G's are known. Also, note that Eq. (6) can be easily transformed into an algebraic equation by taking advantage of the time convolution theorem; this represents one of the main advantages of this approach.

III. TWO-POINT APPROXIMATION

A. The distribution of escape times

In the following we show how to extend the idea above in such a way that correlations are not completely excluded. Our model follows the prescriptions in Ref. 26 but we consider here explicitly the velocity of the particle as a variable. According to this, we can define the probability $G(x, t, v|x_0, v_0)$ to be at x at time t with velocity v if the initial conditions

are x_0, v_0 (with $x_0 < x_f$). In analogy with Eq. (4) we can write

$$G(x, v, t \mid x_0, v_0) = Q(x, v, t \mid x_0, v_0) + \int_0^t \mathrm{d}t' G(x, v, t \mid f(x_f, t'); x_0, v_0) f(x_f, t' \mid x_0, v_0). \quad (7)$$

Now, $Q(x, t, v|x_0, v_0)$ is the probability that the particle, moving with velocity v at time t, has not yet crossed through x_f during the interval $(0, t)$. The first-passage distribution f is now explicitly dependent on the initial speed v_0. Finally, $G(x, v, t|f(x_f, t'); x_0, v_0)$ is the conditional distribution of being at (x, v, t) provided that the first passage occurred at time t'.

Again, we need an approximation in order to make the expression (7) analytically treatable. We propose here

$$G(x, v, t \mid f(x_f, t'); x_0, v_0) \approx G(x, v, t \mid x_f, +, t'), \quad (8)$$

which means that we approximate $G(x, v, t|f(x_f, t'); x_0, v_0)$ as the probability to be at (x, t, v) provided that the particle was at x_f at time t' with positive velocity (denoted by the symbol $+$). This is because the first-passage process necessarily involves a positive velocity of the particle, since $x_f > x_0$. Also, the effect of the initial conditions x_0, v_0 has been obviated since it is expected to be almost negligible.

Note that f does not depend explicitly on the velocity v at time t, so we can integrate Eqs. (7) and (8) over this variable. In principle, we could choose the corresponding integration limits freely. However, our approximation consists of partially neglecting the effect from correlations, so intuitively it is expected to work better as the average time between the first event (first-passage) and the second one (later passage) is longer, so the correlation effects have vanished meanwhile. If we force the second event to occur at positive velocity v then the probability that the first and the second event are very close in time decreases very much, so it is likely that the effect of correlations is smaller (if compared with the case $-\infty < v < \infty$). In agreement with this discussion, we have found numerically that the validity of our approximation is better if the integration is performed only over positive values of v instead of using the whole range $(-\infty, \infty)$. In consequence, we will use at practice

$$\int_0^\infty \mathrm{d}v G(x, v, t \mid f(x_f, t'); x_0, v_0) \approx \int_0^\infty \mathrm{d}v G(x, v, t \mid x_f, +, t'). \quad (9)$$

Let us add that we have not explored yet other choices for the integration limits of v, but that could possibly improve the results we report in the present manuscript.

Now, using the approximation (9) and the Bayes theorem we can integrate Eq. (7) over v and write it in the form

$$\int_0^\infty \mathrm{d}v \frac{P(x, v, t; x_0, v_0)}{P(x_0, v_0)} = \int_0^\infty \mathrm{d}v Q(x, v, t \mid x_0, v_0) + \int_0^t \mathrm{d}t' \int_0^\infty \mathrm{d}v \frac{P(x, v, t; x_f, +, t')}{P(x_f, +, t')} f(x_f, t'), \quad (10)$$

where the P's are the one and two-time joint probability densities. If we write explicitly $P(x_f, +, t) = \int_0^\infty \mathrm{d}v P(x_f, v, t)$ and evaluate the resulting equation at $x = x_f$, Eq. (10) leads to

$$\int_0^\infty \mathrm{d}v \frac{P(x_f, v, t; x_0, v_0)}{P(x_0, v_0)} = \int_0^t \mathrm{d}t' \int_0^\infty \mathrm{d}v \frac{\int_0^\infty \mathrm{d}v' P(x_f, v, t; x_f, v', t')}{\int_0^\infty \mathrm{d}v' P(x_f, v', t')} \times f(x_f, t' \mid x_0, v_0). \quad (11)$$

The distribution of the first-passage or, equivalently, the escape times f can be finally found from this expression. Note that a similar equation (but without explicitly considering the role of the velocity) was derived in Ref. 24. In that case, the authors later assumed a stationary approximation in order to obtain an analytical result for f, while in the present paper we will rather obtain the exact expression for $P(x_f, v, t; x_f, v', t')$ and then we will solve Eq. (11) by quadrature rules.

As in the WF approximation, the expression (11) will only be exact if the particle dynamics is Markovian. However, here we do not consider that the dynamics starts anew after the first passage event. Instead, the approximation (8) consists of assuming that the future dynamics after the crossing will be independent of the fact that the passage of the particle through x_f at time t' is the first one, or it is the second, third ... In order to differentiate this from the WF case (which is strictly a renewal approach) we will term our approach as a *two-point* approximation, since it involves the two-point joint probability density $P(x_f, v, t; x_f, v', t')$.

B. Multi-point probability distributions

The main drawback in applying Eq. (11) is how to evaluate the multi-point distributions. This is analytically feasible for the case of the GLE with a harmonic potential $V(x) = \omega^2 x^2/2$ and a Gaussian noise (regardless its correlation function). The way to proceed is equivalent to that in Ref. 26. Since the resulting GLE is linear and the noise term is Gaussian then x and $\dot{x}$ will be Gaussian variables too, and then the multi-point distribution $P(x_n, v_n, t_n; x_{n-1}, v_{n-1}, t_{n-1}; \ldots; x_1, v_1, t_1)$ for arbitrary n becomes a multi-variate Gaussian distribution, so it must follow[30,31]

$$P(q_{2n}, q_{2n-1}, \ldots, q_1) = \frac{\exp\left(-\frac{1}{2}\mathbf{q}\,(\mathbf{C}_{2n})^{-1}\,\mathbf{q}^{\mathbf{T}}\right)}{(2\pi)^{n/2}\sqrt{\det \mathbf{C}_{2n}}}. \quad (12)$$

Here we define the vector $\mathbf{q}$ (and its corresponding transpose $\mathbf{q}^{\mathbf{T}}$) through $\mathbf{q} = (q_{2n}, q_{2n-1}, \ldots, q_1) \equiv (x_n, v_n, x_{n-1}, v_{n-1}, \ldots, x_1, v_1)$, while $\mathbf{C}_{2n}$ represents the covariance matrix whose coefficients are $c_{ij} = \langle q_i q_j \rangle$. Now, all the functions necessary to find $f(x_f, t)$ from Eq. (11) can be explicitly found using Eq. (12) and its corresponding integrals, provided that the correlation coefficients c_{ij} (and so the corresponding elements of the inverse matrix $(\mathbf{C}_{2n})^{-1}$) are known. In Sec. III C we show how to derive them analytically for any colored Gaussian noise.

C. Covariance matrices

The coefficients of the covariance matrix $\mathbf{C}_{2n}$ can be obtained from the formal solution of the GLE. By carrying out the Laplace transformation of Eq. (2) with $V(x) = \omega^2 x^2/2$ and rearranging terms we obtain

$$\widehat{x}(s) = \frac{\widehat{\xi}(s) + \dot{x}_0 + (s + \widehat{\eta}(s))\, x_0}{s^2 + s\widehat{\eta}(s) + \omega^2}, \tag{13}$$

where s is the Laplace argument and the hat denotes the Laplace transform. Now this expression should be inverted; this cannot be done in general for any arbitrary friction kernel $\widehat{\eta}(s)$, but we can exploit the fact that Eqs. (2) and (3) admit a Markovian embedding in the form,

$$\begin{aligned} \dot{x} &= v, \\ \dot{v} &= -\frac{\partial V(x)}{\partial x} + \sum_{i=1}^{N} u_i(t), \\ \dot{u}_i &= -\eta_i v - \gamma_i u_i + \sqrt{2\gamma_i \eta_i k_B T}\,\xi_i^{(w)}(t), \end{aligned} \tag{14}$$

provided that the initial values $u_i(0)$ are taken randomly from a Gaussian distribution with zero average and a variance equal to $\eta_i k_B T$. This at practice means that we approximate the colored noise $\xi(t)$ as a finite sum of independent exponentially correlated noises $u_i(t)$ (since $\xi_i^{(w)}(t)$ are independent Gaussian white noise terms), an idea which has been further discussed in Ref. 11 and the references therein. Then, the equivalence between Eq. (14) and Eqs. (2) and (3) holds as long as the autocorrelation function of the noise $\xi(t)$ can be expressed as a combination of exponential terms, so by the fluctuation-dissipation theorem the friction kernel reads then

$$\eta(t) = \frac{\langle \xi(\tau)\xi(\tau + t)\rangle}{k_B T} = \sum_{i=1}^{N} \eta_i e^{-\gamma_i t}. \tag{15}$$

Here we focus on the subdiffusive case with $\eta(t) > 0$, for which this Markovian embedding is known to be valid (the case $\eta(t) < 0$ has been explored recently in Refs. 32 and 33). The coefficients η_i , γ_i are to be determined by fitting this sum to the specific friction kernel desired. In Ref. 11 a power-law friction kernel (corresponding to $1/f^{1-\alpha}$ noise) was studied, and a sum of $N = 16$ terms was shown to be enough to obtain an excellent fitting over 15 time decades (for more details see Sec. IV below).

By introducing the Laplace transform of Eq. (15) into Eq. (13) we can formally express the latter as

$$\widehat{x}(s) = \frac{R_0(s)}{R_2(s)}\widehat{\xi}(s) + \frac{R_0(s)}{R_2(s)}\dot{x}_0 + \frac{R_1(s)}{R_2(s)}x_0, \tag{16}$$

where $R_0(s)$, $R_1(s)$, and $R_2(s)$ are polynomials in s of order N, $N + 1$, and $N + 2$, respectively. The coefficients of these polynomials will depend in general on the parameters ω^2, η_i, and γ_i.

Next, we can use the following relation, which is valid for any polynomial of order $N + 2$ with different roots a_1, a_2, $\ldots$ a_{N+2}:[22,23]

$$\frac{s^m}{R_2(s)} = \sum_{k=1}^{N+2} \frac{a_k^m A_k}{s - a_k}, \quad 0 \leqslant m \leqslant N + 1, \tag{17}$$

with the coefficients A_k defined through

$$A_k \equiv \left(\left. \frac{dR_2(s)}{ds} \right|_{s=a_k} \right)^{-1}. \tag{18}$$

The property (17) allows us to write

$$\frac{R_0(s)}{R_2(s)} = \sum_{m=0}^{N} \sum_{k=1}^{N+2} \frac{a_k^m A_k R_0^{(m)}}{s - a_k}, \tag{19}$$

where $R_0^{(m)}$ represents the mth coefficient of the polynomial $R_0(s)$. An equivalent expression to Eq. (19) could be written for $R_1(s)/R_2(s)$, too, just by replacing $R_0^{(m)}$ by $R_1^{(m)}$ and extending the sum up to $m = N + 1$. Then, the corresponding inverse Laplace transform of R_0/R_2 and R_1/R_2 is just a sum of exponentials. To simplify notation we can define now

$$\mathcal{L}^{-1}\left[\frac{R_0(s)}{R_2(s)}\right] = \sum_{m=0}^{N} \sum_{k=1}^{N+2} a_k^m A_k R_0^{(m)} e^{a_k t} \equiv H_0(t), \tag{20}$$

$$\mathcal{L}^{-1}\left[\frac{sR_0(s)}{R_2(s)}\right] = \sum_{m=0}^{N} \sum_{k=1}^{N+2} a_k^{m+1} A_k R_0^{(m)} e^{a_k t} \equiv H_1(t), \tag{21}$$

$$\mathcal{L}^{-1}\left[\frac{R_1(s)}{R_2(s)}\right] = \sum_{m=0}^{N+1} \sum_{k=1}^{N+2} a_k^m A_k R_1^{(m)} e^{a_k t} \equiv H_2(t). \tag{22}$$

This allows us to write the inversion of Eq. (16) in the form

$$x(t) = \int_0^t \mathrm{d}t' H_0(t)\xi(t - t') + \dot{x}_0 H_0(t) + x_0 H_2(t), \tag{23}$$

and, by differentiation, it can be found

$$\dot{x}(t) = \int_0^t \mathrm{d}t' H_1(t)\xi(t - t') + \dot{x}_0 H_1(t) - x_0\omega^2 H_0(t). \tag{24}$$

Now we are in position to evaluate the correlation coefficients; for example, for correlations in the position x we have

$$\begin{aligned} \langle x(\tau)x(\tau + t)\rangle = &\int_0^{\tau} \mathrm{d}t' \int_0^{t+\tau} \mathrm{d}t'' H_0(t')H_0(t'') \\ &\times \langle \xi(\tau - t')\xi(t + \tau - t'')\rangle \\ &+ H_0(\tau)H_0(t + \tau)\langle \dot{x}_0^2\rangle + H_2(\tau)H_2(t + \tau)\langle x_0^2\rangle. \end{aligned} \tag{25}$$

To obtain this expression we have used first Eq. (23) and next the conditions $\langle x_0\rangle = \langle v_0\rangle = \langle x_0 v_0\rangle = 0$, which hold since x_0 and v_0 must be independent Gaussian variables centered at zero (otherwise we could not use the concept of a multivariate Gaussian distribution in Sec. III B). Moreover, using explicitly the relation (15) we finally reach

$$\langle x(\tau)x(\tau+t)\rangle = k_BT\sum_{i=1}^{N}\eta_i\int_0^{\tau}dt'\int_0^{t+\tau}dt''H_0(t')H_0(t'')e^{-\gamma_i(t+t'-t'')} + H_0(\tau)H_0(t+\tau)\langle\dot{x}_0^2\rangle + H_2(\tau)H_2(t+\tau)\langle x_0^2\rangle. \quad (26)$$

From an analogous argument, we can also find the expressions

$$\langle x(\tau)v(\tau+t)\rangle = k_BT\sum_{i=1}^{N}\eta_i\int_0^{\tau}dt'\int_0^{t+\tau}dt''H_0(t')H_1(t'')e^{-\gamma_i(t+t'-t'')} + H_0(\tau)H_1(t+\tau)\langle\dot{x}_0^2\rangle - H_2(\tau)H_0(t+\tau)\langle x_0^2\rangle\omega^2, \quad (27)$$

$$\langle v(\tau)x(\tau+t)\rangle = k_BT\sum_{i=1}^{N}\eta_i\int_0^{\tau}dt'\int_0^{t+\tau}dt''H_1(t')H_0(t'')e^{-\gamma_i(t+t'-t'')} + H_1(\tau)H_0(t+\tau)\langle\dot{x}_0^2\rangle - H_0(\tau)H_2(t+\tau)\langle x_0^2\rangle\omega^2, \quad (28)$$

$$\langle v(\tau)v(\tau+t)\rangle = k_BT\sum_{i=1}^{N}\eta_i\int_0^{\tau}dt'\int_0^{t+\tau}dt''H_1(t')H_1(t'')e^{-\gamma_i(t+t'-t'')} + H_1(\tau)H_1(t+\tau)\langle\dot{x}_0^2\rangle + H_0(\tau)H_0(t+\tau)\langle x_0^2\rangle\omega^4. \quad (29)$$

From Eqs. (26)–(29) we can finally compute all the coefficients c_{ij} , and by inverting the corresponding matrix $\mathbf{C}_{2n}$ we will find the coefficients μ_{ij} appearing in Eq. (12). Note that all the integrals in Eqs. (26)–(29) can be carried out analytically since the integrand is nothing but a sum of exponential terms. Hence, the method described throughout this section is completely analytical except for the resolution of the main equation of Eq. (11), which must be performed by quadrature rules.

IV. RESULTS

Following the prescriptions in Ref. 11 we can approximate a power law noise with great accuracy by taking $\eta_i \sim b^{-i\alpha}$ and $\gamma_i = \gamma^*/b^i$ where the parameters b, γ^* and the proportionality constant must be chosen to fit the specific form of the power-law kernel used. In particular, for the case of $\eta(t) \sim t^{-0.5}$ the choice of parameters $b = 10$, $\gamma^* = 10^3$ with $N = 16$ terms was proved to provide quite satisfactory results while still keeping the number of terms involved quite low (see Ref. 11 for further details). We will focus here in this power-law case, since its interest is experimentally justified[5] and corresponds to an anomalous escape process where the classical reaction rate theory is expected to break down.

Using the results derived in Secs. III B and III C above we computed the multi-point probability distributions appearing in Eq. (11). Numerical inspection of the results show that the two-point distribution $P(x_f, v, t; x_f, v', t')$ diverges algebraically in the limit $t' \to t$. This is an important aspect to take into account in the numerical inversion of Eq. (11), since choosing a wrong integration algorithm would lead us to unstable behavior. To overcome these problems, we inverted Eq. (11) by using a trapezoidal quadrature rule based on an Euler-MacLaurin expansion for functions with weak singularities.[34,35] To verify the performance of our approximation with this quadrature method we compared the results with those obtained from Langevin simulations, in which the escape process from the well potential was explicitly simulated for a particle governed by Eq. (14). For this purpose, we used a Heun algorithm[36] with a time step of 5×10^{-4}. Averages over 2×10^5 particles were typically performed to obtain a good statistics even for large escape times, for which corresponding probabilities are rather small.

Our semi-analytical approach is able to fit the numerical results adequately in the cases reported in Figure 2 and is also computationally faster than performing the Langevin dynamics simulations, especially when mean escape times are large and so the Langevin dynamics becomes rather long. In the insets in Figure 2 we observe that the first passage time distribution obtained from Langevin dynamics realizations (circles) shows a main peak followed by a subsequent decay modulated by an oscillating behavior. These oscillations are noise-driven since their amplitude clearly increase with k_BT. Our approach (solid lines) fits these general tendencies with a reasonable accuracy, specially for lower potential barriers (this is, large k_BT). Also, we show the corresponding scaling of the survival probability

$$S(x_f, t) = \int_t^{\infty} dt' f(x_f, t'),$$

to verify that the corresponding decay is not exponential, but fits very well a stretched exponential function $S(t) \sim e^{-t^{\alpha}}$. The corresponding exponent α varies from values very close to 1 (which corresponds to exponential behavior) for large potential barriers to values close to 0.8 for lower barriers (see Figure 3). This is in qualitative agreement with the findings in Ref. 11 for the case of a quartic potential. However, note that the transition from exponential to non-exponential behavior was found there to occur for larger potential heights (approximately 10 or 12 times the value of the thermal energy), while in the parabolic case studied here we observe that this transition occurs for $\omega^2/2k_BT$ close to 2.5. This means that the parabolic case is able to reproduce qualitatively (despite important differences at a quantitative level) the features found for the more realistic double-well case. On the other side, the fact that the transition from *non-exponential to exponential* occurs at such low values of the barrier height suggests that inertial effects may have an important role within this dynamics. To check this, we have carried out some extra simulations (not shown) giving different values to the mass (in-

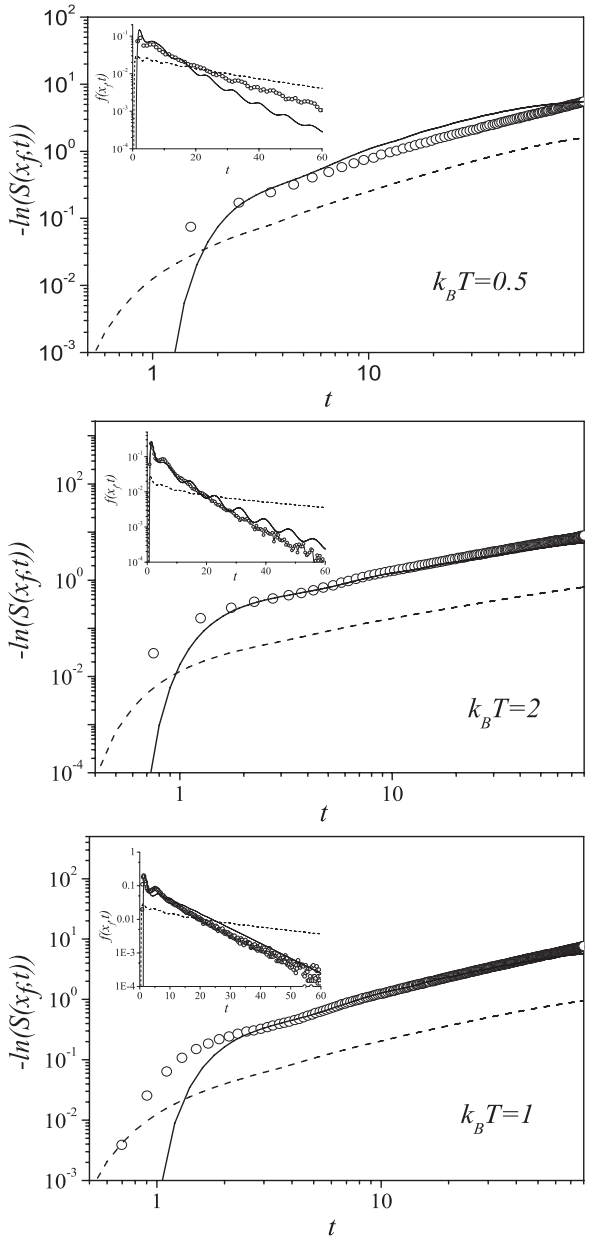

FIG. 2. Distribution of escape times and survival probability for a harmonic potential with a power-law friction kernel for different values of k_BT (see legends). A comparison is performed between Langevin dynamics (circles), the Wilemski-Fixman approximation (dashed lines), and the two-point approximation derived here (solid lines). The logarithm of $S(x_f, t)$ is plotted in order to show the asymptotic scaling $S \sim \exp(-t^\alpha)$. The insets show the corresponding derivative $f(x_f, t)$. The values of the parameters used are $x_0 = v_0 = 0$, $x_f = 1$, $\omega^2 = 0.5$, while the values of the parameters for the friction kernel are given in the text.

stead of assuming $m = 1$ as we have done in all our discussion above and the figures presented in the present paper). So we have verified that reducing the effect of inertia (by taking $m < 1$) the transition occurs at lower values of the barrier height; to give an example, when we chose $m = 0.25$ we observed that the transition occurred at $\omega^2/2k_BT \approx 3.5$. Likewise, we have also numerically verified that, except for this shift in the value of the transition point, the qualitative behavior of the system does not change and so the conclusions of our work remain valid.

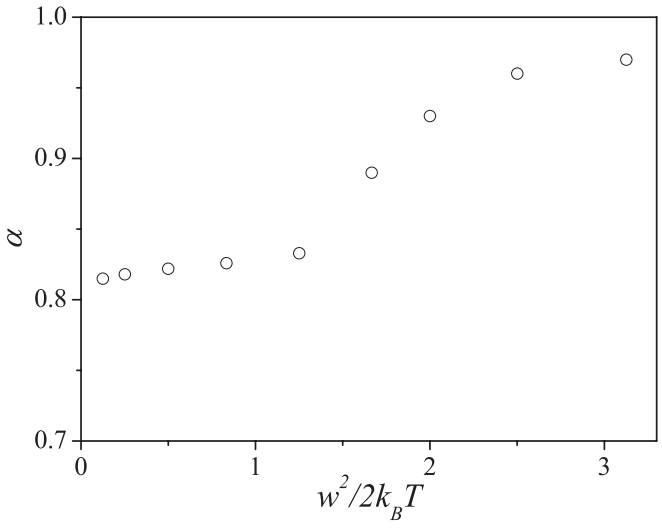

FIG. 3. Values of the exponent α defined through the asymptotic scaling $S \sim \exp(-t^\alpha)$, obtained from Langevin dynamics simulations. All the parameter values are the same as in Figure 2.

For the sake of completeness we also show in Figure 2 the results for $S(x_f, t)$ corresponding to the Wilemski-Fixman approximation (dashed lines). It can be checked that the fitting is much poorer for this classical approximation. As a whole, Figure 2 shows the usefulness of our two-point approximation as a predictive tool for non-Markovian escape problems in the regime of low potential barriers, for which the reaction-rate theory seems to fail. Likewise, it must be pointed out that as long as the distribution $f(x_f, t)$ becomes exponential (this is, for large potential barriers) the two-point approximation derived here performs badly and cannot predict the decay rate obtained from the Langevin dynamics. This is shown in Figure 4, which is the same as Figure 2 but for a larger barrier height $\omega^2/2k_BT = 4$, which according to Figure 3 corresponds to a height above the transition level. The reason why our approximation fails in those cases is probably that for k_BT small

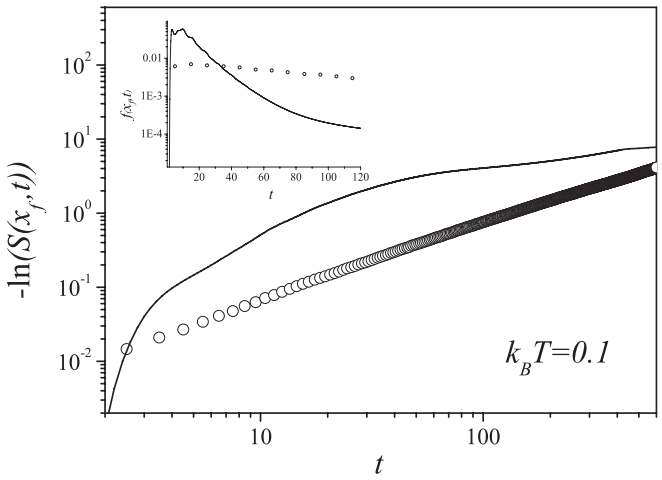

FIG. 4. Distribution of escape times and survival probability for a harmonic potential with a power-law friction kernel for a value of k_BT corresponding to exponential behavior (see legends). A comparison is performed between Langevin dynamics (circles) and the two-point approximation derived here (solid lines). The insets show the corresponding derivative $f(x_f, t)$. The values of the parameters used are the same as in Figure 2.

(low noise) the successive passages of the particle through x_f are more clustered in time. When this happens the importance of the correlations in the particle dynamics increases, so then our approximation (8) is expected to break down. This idea has been further discussed in Ref. 31 and the references therein, where the authors used the concept of *system of nonapproaching points* to identify those subsequent passages which are well separated in time, so correlation effects between them are negligible. Let us finally add that in those cases (high potential barriers) alternative methods based on the explicit assumption that a reaction rate exists (so $f(x_f, t)$ decays exponentially) or based on the non-Markovian reaction-rate theory (as in Ref. 11) are expected to fit the results with a greater accuracy, while our interest here was mainly focused on the non-exponential regime.

V. CONCLUSIONS

We have confirmed that the non-exponential decays obtained in the escape times distributions from the wells of a quartic potential driven by fractional Gaussian noise[11] are also found when a harmonic approximation is used. As a result, ultraslow relaxation in the well makes the determination of a reaction rate impossible in this case, at least in a classical sense. This result contrasts with previous theoretical approaches used to explore the same or similar problems to that addressed here. For example, the expression

$$S_{LB}(x_f, t) \equiv \exp\left[-\int_0^t \mathrm{d}t' \langle L(x_f, t')\rangle\right], \tag{30}$$

has been proposed as a lower bound to the actual survival distribution,[25] where $\langle L(x_f, t)\rangle$ represents the average flux of particles crossing out of the region $x < x_f$ at time t (the brackets refer to an average over different realizations of the particle). This contrasts with the exact expression for the survival probability, which can be proved to be[25]

$$S(x_f, t) = \left\langle \exp\left[-\int_0^t \mathrm{d}t' L(x_f, t')\right]\right\rangle. \tag{31}$$

While the lower bound of Eq. (30) is mathematically correct, that expression does not necessarily imply that $S(x_f, t)$ should decay exponentially, but only slower than an exponential, and then it does not justify *per se* the existence of a constant reaction rate. In those cases where the escape dynamics reaches a stationary situation, the average flux $\langle L(x_f, t)\rangle$ will tend to a constant and then the exponential decay for $S_{LB}(x_f, t)$ will hold. However, our numerical results show that $\langle L(x_f, t)\rangle$ always approaches asymptotically a constant value for power-law friction kernels, even for those values of k_BT for which we have found non-exponential decays in $S(x_f, t)$. This means that the bound provided by Eq. (30), while mathematically valid, is of scarce utility in these situations. To prove this we compare in Figure 5 the expressions for $S_{LB}(x_f, t)$ and $S(x_f, t)$ computed directly from Eqs. (30) and (31) using our Langevin dynamics simulations and for $k_BT = 1$. This plot confirms that the survival probability $S(t)$ decays as a stretched exponential (note that the characteristic exponent $\alpha \simeq 0.83$ coincides with that reported in Figure 3, as can be seen from the auxiliary line $\sim t^{\alpha}$) while $S_{LB}(x_f, t)$ is clearly an exponential lower bound.

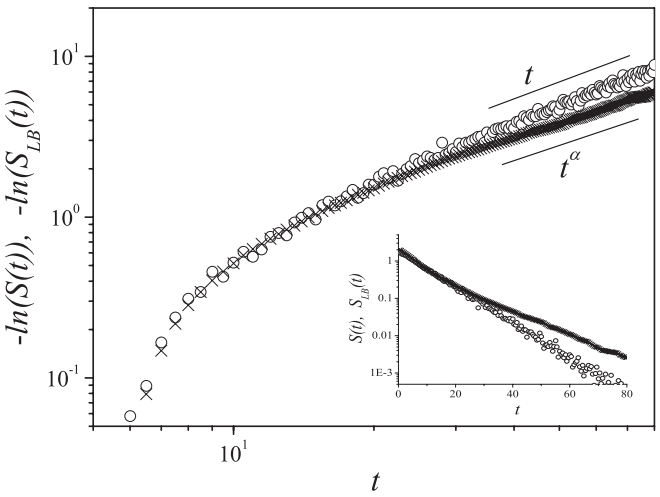

FIG. 5. Comparison between the actual survival probability $S(x_f, t)$ (crosses) and the lower bound $S_{LB}(x_f, t)$ (circles) for the case $k_BT = 1$ (the other parameters values are the same as in Figure 2). Auxiliary lines are used to show the scaling for each case. The inset shows the same results but in a different plot scaling to emphasize the differences observed in the asymptotic behavior.

In general, strong correlations in the reaction kinetics can be mainly attributed to the existence of multiple traps in the configurational landscape. This also admits a description in terms of a multiple kinetic scheme representing a discrete map of configurational states, each intermediate transition between states governed by a characteristic rate. This approach, which has been exhaustively explored in the literature, ensures that an exponential decay (governed by the slowest characteristic timescales) is asymptotically attained for the distribution of escape times. However, it might be that this asymptotic regime is only reached at long times compared to observational timescales. As an alternative, the effective description in terms of a GLE proves very useful at practice, and so analytical and numerical methods focused on this problem (as the one provided here) are welcome. Regarding the two-point approximation derived here, we think that the versatility of the approach represents one of its most interesting properties, since it can be applied straightforward to any friction kernel that can be fitted to a combination of exponential functions (Eq. (15)). In particular, we have here proved its performance for highly non-Markovian conditions (corresponding to a power-law friction kernel) and low potential barriers, where it fits reasonably well the whole shape of the escape times distribution without any adjustable parameters. We also observe, however, that our approximation shows poorer performances for high barrier potentials. This may suggest that a combination of this approach together with other methods, more suited to the exponential regime, could represent a promising strategy to reach a complete description of non-Markovian escape problems. Such hybrid methods will be explored in forthcoming works.

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