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Control of reaction rate by asymmetric two-state noise

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We revisit the far from equilibrium escape problem across a fluctuating potential barrier that is driven by asymmetric, unbiased dichotomous noise. Our closed analytical solution for arbitrary noise strengths reveals new aspects of the so-called ''resonant-activation'' effect and leads to interesting implications regarding far from equilibrium or externally controlled chemical reaction processes. Specifically, a genuine asymmetry-induced variant of resonant activation within the constant intensity scaling scheme is discovered, and a new possibility to manipulate reaction rates and yields, as well as the balance between reactants and products, is put forward. © *1999 American Institute of Physics.* [S0021-9606(99)51332-9]

I. INTRODUCTION

Most objects around us look reasonably steady, yet they will clearly not keep their present appearance for eternity; that is, they are in a metastable state. The cause for the ultimate decay of such a metastable state is always some perturbation by the ''environment,'' either in the form of random thermal fluctuations or any other kind of external ''noise,'' which is then termed ''nonequilibrium.''[1] To determine the typical decay time of a metastable state is a problem encountered in many different fields of natural sciences.[2–4] Examples range from the emergence, evolution, and extinction of whole species[5] down to short-living ''resonances'' in nuclear and high-energy physics. A detailed quantitative understanding of how metastable states decay is obviously of foremost practical importance in the context of chemical reactions and complex molecular-biological processes.

The basic theoretical tools to properly describe and successfully tackle such problems have been put forward by H. A. Kramers in his groundbreaking paper.[6] Besides a derivation of the relevant Fokker–Planck equation practically from scratch and a wealth of ingenious technical inventions, another cornerstone in his paper is the flux-over-population formulation of the decay rate, based on a previous line of reasoning by Farkas.[7] The underlying physical picture is that of a Brownian particle[8] in a metastable or bistable potential that is subjected to fluctuations due to its environment and dissipates energy back into this environment, typically via a viscous friction mechanism. Even in the often-considered case that the random noise is weak, a large fluctuation may occasionally arise that is able to push the particle across some ''barrier'' out of the metastable potential well.

While Kramers' original derivation[6] involves an approximation that becomes asymptotically exact for weak thermal noise, we will consider in this paper a model that is technically much easier to handle and one of the few examples which can be solved exactly for arbitrary noise strengths. In this model, an overdamped Brownian particle moves in a one-dimensional metastable or bistable potential under the influence of asymmetric but unbiased dichotomous noise;[9–16] in addition, it is assumed that inertia effects as well as thermal equilibrium fluctuations can be neglected. However simple this model may be from the technical viewpoint, conceptionally it goes beyond Kramers' framework: our situation refers to a steady-state nonequilibrium situation. Moreover, the potential experienced by the Brownian particle cannot realistically be regarded as static, but as subjected to random fluctuations with a characteristic time scale that is comparable with one of the time scales governing the escape problem itself. An example is the escape of an O_2 or CO ligand molecule out of a myoglobin ''pocket'' after photodissociation.[17] Further, a model for the ion channel kinetics in the lipid cell membrane based on fluctuations in the activation energy barriers has been proposed in Ref. 18. In a new paradigm for the intracellular motion of a molecular motor along a microtubule put forward in Ref. 19, the binding of ATP (adenosine triphosphate) and the release of ADP (adenosine diphosphate) serve to randomly modulate the potential experienced by the motor protein as it travels along the biopolymer backbone. Also, in other strongly coupled chemical systems,[20–23] the dynamics of dye lasers,[24] and even for some aspects of protein folding and relaxation in glasses, fluctuating potentials are likely to be of relevance.[17,25,26] In all those examples, one has in mind the picture that the potential fluctuations experienced by the Brownian particle are controlled by some collective motion of the environment with a much larger real or effective mass, such that back-coupling effects can be neglected. On top of that, this collective environmental fluctuations must be *far from thermal equilibrium* since they would be negligibly small otherwise due to their corresponding large (effective) mass. In the above-mentioned example of a ligand escaping from the (''heavy'') myoglobin, the far from equilibrium situation is created by the sudden photodissociation, while in the ion channel kinetics and the molecular motors it is maintained by permanent chemical reactions which are themselves far from thermal equilibrium. Specifically, nonthermal noise of the asymmetric dichotomous type arises, e.g., in point contact devices with a defect tunneling incoherently between two states, see Ref. 27 and further references

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therein. In particular, the noise-strength and correlation-time properties can be controlled externally at will.[27,28] Finally, besides those examples of complex nonequilibrium systems, potential fluctuations without back-coupling, as we will study here, may be realized also by means of external noise imposed on a suitably designed experiment.[15,29–32] For example, a random-telegraph fluctuating electric field stimulates the Rb^+-pumping mode of the Na,K-ATPase. It was observed that electric or electromagnetic fields have an effect on a cell,[33] mostly apparent on plasma membrane, where an external field is greatly amplified. Yet another example provides the nonthermal driven chemical reaction of the iodate–arsenous acid system $IO_3^- + 3H_3AsO_3 \rightleftharpoons I^- + 3H_3AsO_4$. An additive dichotomous noise process could be applied to this system by randomly switching the composition of the iodide and iodate input feeds to the reactor $[I^-]$ and $[IO_3^-]$ between two values. The exchange must be synchronized in such a way that the total input concentration $[I^-]+[IO_3^-]$ stays constant.[15]

The quantity of foremost interest in this context is the mean escape time from the metastable state across the fluctuating barrier as a function of the characteristic time scale of these fluctuations. The possibility that this dependence may be nonmonotonous has been exemplified first in Ref. 34 and has been termed ''resonant activation'' therein. This phenomenon has been further investigated in Refs. 35–55, and is by now qualitatively well understood, see 47 for a recent review. As already emphasized in Refs. 38, 39, 44, 45, and 55, the occurrence (or not) of resonant activation may crucially depend on how the distribution of the potential fluctuations changes upon variation of their characteristic time scale. This point will be reconsidered here with particular emphasis on the two most natural options that (i) the distribution of the potential fluctuations is kept constant (''constant variance scaling''), or (ii) the intensity of those fluctuations (i.e., their integrated time correlation) is kept fixed (''constant intensity scaling'').

II. MODEL

A. Asymmetric dichotomous noise

Our starting point is a dichotomous stochastic process (also called telegraphic noise) $\xi(t)$ that can take on the two values

$$a' > 0, \quad a < 0. \tag{1}$$

The probability to switch during an infinitesimal time interval $[t, t+dt]$ into the opposite state is $dt\,\mu'$ when the present state is $\xi(t)=a'$ and $dt\,\mu$ when $\xi(t)=a$, independent of what happened in the past (Markov property). In the *steady state*, the probabilities that $\xi(t)$ is in the state a' and a are given, respectively, by

$$P(a') = \mu/(\mu'+\mu), \quad P(a) = \mu'/(\mu'+\mu). \tag{2}$$

While we will *not* require symmetry $a=-a'$ and/or $\mu'=\mu$, we will always assume that the noise is unbiased,

$$\langle \xi(t) \rangle = \frac{a'\mu + a\mu'}{\mu'+\mu} = 0, \tag{3}$$

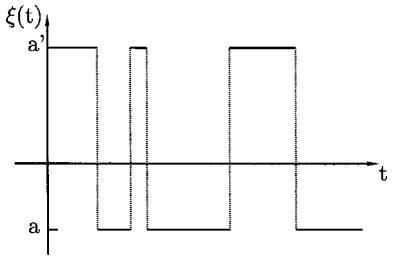

FIG. 1. Cartoon of one realization $\xi(t)$ of the asymmetric dichotomous process as defined in Sec. II A.

see Fig. 1 for an example. The intensity D and the correlation time τ of an arbitrary noise in the stationary state are defined as[16]

$$D = \frac{1}{2}\int_{-\infty}^{\infty} |\langle \xi(t)\xi(0) \rangle|\, dt, \tag{4}$$

$$\tau = D/\langle \xi^2(0) \rangle, \tag{5}$$

when, the correlation of the asymmetric dichotomous noise in the steady state follows as

$$\langle \xi(t)\xi(t') \rangle = \frac{D}{\tau} e^{-|t-t'|/\tau}, \tag{6}$$

with

$$\tau = [\mu' + \mu]^{-1}, \quad D = \tau\, a'|a|. \tag{7}$$

For any $\tau > 0$, we are thus dealing with so-called colored noise. Special cases are:[11,12,56] (i) symmetric dichotomous noise when $a=-a'$ and $\mu'=\mu$, (ii) white (non-Gaussian) shot noise when $\tau \to 0$ and a, $D=a^2/\mu$ fixed, and (iii) white Gaussian noise when μ', $\mu \to \infty$, $\tau \to 0$, a', $|a| \to \infty$, and D fixed.

A suitable measure for the asymmetry of the noise is the following *asymmetry parameter:*

$$A = \frac{a' - |a|}{a' + |a|}. \tag{8}$$

With (3) and (7), one then finds that

$$a' = \sqrt{\frac{1+A}{1-A}}\,\frac{D}{\tau}, \tag{9}$$

$$a = -\sqrt{\frac{1-A}{1+A}}\,\frac{D}{\tau}, \tag{10}$$

$$\mu' = \frac{1+A}{2\,\tau}, \tag{11}$$

$$\mu = \frac{1-A}{2\,\tau}. \tag{12}$$

Thus, in the steady state, the dichotomous noise $\xi(t)$ is completely specified by its intensity D, correlation time τ, and asymmetry A.

B. Fluctuating potential

We consider a one-dimensional Brownian particle in a potential that consists of a static part $U(x)$ and a fluctuating part $V(x)\,\xi(t)$, with $\xi(t)$ an unbiased stationary dichoto-

mous noise as specified in the preceding subsection (see also Fig. 1). The particle is furthermore subjected to viscous friction and we assume that inertia effects as well as thermal fluctuations are negligible. The equation of motion for the particle $x(t)$ thus reads

$$\eta \frac{d}{dt}x(t) = -\frac{d}{dx}\{U(x(t)) + V(x(t))\,\xi(t)\}. \tag{13}$$

It is convenient to absorb the friction coefficient η into the definition of the time unit and to make both the time and the coordinate dimensionless by further appropriate scaling transformations. For simplicity, we will continue to use the same symbols for the rescaled quantities. Finally, we introduce the force fields $f(x) = -U'(x)$ and $g(x) = V'(x)$ to obtain

$$\frac{d}{dt}x(t) = f(x(t)) + g(x(t))\,\xi(t). \tag{14}$$

Equivalent to this stochastic differential equation is the following master equation for the joint probability density $P(x,\alpha,t)$ that at time t the particle resides at the position x and the dichotomous process $\xi(t)$ is in the state $\alpha \in \{a',a\}$:

$$\frac{\partial}{\partial t}P(x,a,t) = -\frac{\partial}{\partial x}\{[f(x) + a\,g(x)]P(x,a,t)\} - \mu\,P(x,a,t) + \mu'\,P(x,a',t) + S(x,a,t). \tag{15}$$

The first term on the right-hand side accounts for the Liouville-type evolution of the probability density $P(x,a,t)$ under the action of the force field $f(x) + a\,g(x)$ that prevails while the noise is in the state $\xi(t) = a$. The second term is a loss term due to transitions from a into a' and similarly the third term accounts for the gain of probability due to transitions from a' to a. The last term represents the sources and sinks of particles. A completely analogous equation is obtained for $P(x,a',t)$ by interchanging primed and unprimed quantities in (15).

C. Kramers rate and mean escape time

We imagine an ensemble of particles [independent realizations of the stochastic dynamics (14)] with a constant source q at an arbitrary point x_{in}, that is, in any time interval $[t,t+dt]$ a number $dt\,q$ of new particles are joining the ensemble with seed x_{in}. Similarly, we imagine a sink at x_{out} such that particles are removed instantaneously (immediate absorption) as soon as they reach this point x_{out} for the first time. If, in the long-time limit a steady state is reached, the average number of particles absorbed per time unit by the sink is thus equal to those injected by the source q. The rate k according to Kramers and Farkas[2,6,7] is then *defined* as this resulting constant net flux of particle through the system normalized by the population of particles

$$k = q/\int P(x)\,dx, \tag{16}$$

where $P(x)$ denotes the steady state (long time limit) of the particle distribution. Since doubling the source-strength q will also double the population $\int P(x)\,dx$, this definition is clearly independent of the actual q-value. The usual choice for x_{in} is at or near the (metastable) potential well, while in the context of the Kramers rate, x_{out} is typically assumed to be sufficiently far away from the basin boundary of this well such that it is very unlikely that a particle $x(t)$, had it not been taken out of the game by the sink, would return into this basin of x_{in} in the near future.

Besides the flux-over-population rate *à la* Kramers and Farkas, various other quantities are available on the market in order to characterize the lifetime of a metastable state:[2] Most notably these are (i) the *mean escape time*,[57–59] defined as the average time $T_{x_{\mathrm{out}}}(x_{\mathrm{in}})$ that a particle (14) with seed x_{in} needs to reach x_{out} for the first time, and (ii) the smallest nonvanishing eigenvalue of the relevant time-evolution operator in (15). While they all are known to become equivalent for asymptotically weak noise, they may notably differ when the timescales of the escape itself is no longer well-separated from all other characteristic relaxation times of the problem. As we will demonstrate in detail in a companion paper,[60] two of them, namely the Kramers rate k as defined in (16) and the associated mean escape time $T_{x_{\mathrm{out}}}(x_{\mathrm{in}})$ satisfy the exact relation

$$k = 1/T_{x_{\mathrm{out}}}(x_{\mathrm{in}}) \tag{17}$$

for arbitrary strengths D, correlations τ, and asymmetries A of the dichotomous noise. Since our choice of the sink x_{out} is not *at* the potential barrier but rather beyond it (see above), we avoid here the more common term *mean first passage time*[57–59] for the quantity $T_{x_{\mathrm{out}}}(x_{\mathrm{in}})$.

Our goal is to calculate the Kramers flux-over-population rate in the case of constant (i.e., time-independent) point-sources and -sinks of particles at some prescribed positions x_{in} and x_{out}, respectively

$$S(x,\alpha,t) = q_\alpha\,\delta(x - x_{\mathrm{in}}) - s_\alpha\,\delta(x - x_{\mathrm{out}}), \tag{18}$$

$\alpha \in \{a',a\}$. So, q_a and $q_{a'}$ can be viewed as streams of particles that are injected at x_{in} in the states a and a' of the noise, respectively, and similarly for the outflowing stream at x_{out}. Since the master Eq. (15) is linear, the case of more complicated source- and sink-distributions than in (18) immediately follows by way of superposition.

According to the definition of the Kramers rate (16), it is the solution in the *steady state*, or equivalently, the long-time limit $t \to \infty$, which matters and on which we will focus further. For the sake of convenience, we will indicate the steady state simply by omitting time arguments, i.e., $P(x,\alpha) = P(x,\alpha,t\to\infty)$, and similarly for $S(x,\alpha,t)$. Furthermore, in order to avoid a flurry of cases that have to be treated separately but do not lead to much new physical insight, we will now make some additional assumptions to single out the most interesting setup. First, we assume that the static force-field $f(x)$ derives from a bistable potential $U(x)$. The source of particles at x_{in} is assumed to be located in the ''left'' potential well of $U(x)$ and the sink in the ''right'' one. We will be interested in transition rates from x_{in} to x_{out}, but also

in the transition rates just in the opposite direction, from $x_{\rm out}$ to $x_{\rm in}$. This allows us to examine the effects of the *asymmetric noise* $\xi(t)$ on those rates, especially in *symmetric potentials*. To guarantee that the dynamics (14) admits such transitions between $x_{\rm in}$ and $x_{\rm out}$ in both directions, we have to require that the quantity

$$D_{\rm eff}(x) = -\tau[f(x)+a\,g(x)]\,[f(x)+a'\,g(x)] \tag{19}$$

is strictly positive in an entire open interval (x_-,x_+) that comprises $[x_{\rm in},x_{\rm out}]$, i.e.,

$$D_{\rm eff}(x)>0 \quad \text{for } x\in(x_-,x_+), \tag{20}$$

$$x_-<x_{\rm in}<x_{\rm out}<x_+ . \tag{21}$$

For simplicity, we further assume that both factors $f(x)+a'g(x)$ and $f(x)+ag(x)$ in (19) are negative for all $x<x_-$ and positive for $x>x_+$, which, in particular, guarantees that particles (14) cannot leave the interval $[x_-,x_+]$. Therefore, we can infer that $P(x,\alpha)=0$ for $x\notin[x_-,x_+]$, and since particles are completely absorbed at $x_{\rm out}<x_+$, we have *a forteriori* that

$$P(x,\alpha)=0 \quad \text{for } x\notin[x_-,x_{\rm out}]. \tag{22}$$

It also follows from (19) and (20) that $g(x)$ must not have zeros on the interval (x_-,x_+), and we can assume without loss of generality that

$$g(x)>0 \quad \text{for } x\in(x_-,x_+). \tag{23}$$

A typical example that incorporates the above-mentioned symmetry and that we will study in detail below is

$$f(x)=x-x^3,\;\; g(x)=1\,, \tag{24}$$

with $x_{\rm in}$ and $x_{\rm out}$ located at the two wells of the static potential $U(x)$

$$x_{\rm in}=-1, \quad x_{\rm out}=1. \tag{25}$$

D. Analytic solution

In the steady state, it follows by adding (15) and the corresponding equation for $P(x,a')=P(t\to\infty,x,a')$ that

$$0=-\frac{d}{dx}\left\{f(x)P(x)-\frac{a}{\mu}g(x)Q(x)-J(x)\right\}, \tag{26}$$

where we have introduced

$$P(x)=P(x,a')+P(x,a), \tag{27}$$

$$Q(x)=\mu'\,P(x,a')-\mu\,P(x,a), \tag{28}$$

$$J(x)=\int_{-\infty}^{x}[S(y,a')+S(y,a)]\,dy. \tag{29}$$

By tracing out the noise states in (27), we are left with the reduced steady-state density $P(x)$ for the particle coordinate x alone. While this density is clearly of central importance, the auxiliary function (28) has no such immediate physical meaning. Finally, $J(x)$ from (29) can be readily identified with the net particle current through x in the steady state. In Eq. (26) the curly brackets must be equal to a constant, and by choosing $x\to-\infty$ it follows with (22) and (29) that this constant is zero, i.e.,

$$\frac{a}{\mu}g(x)\,Q(x)=f(x)\,P(x)-J(x). \tag{30}$$

If $g(x)=0$, this equation fixes the quantity of main interest $P(x)$. If $g(x)\neq0$, a second equation similar to (26) is obtained from the weighted difference like in (28) of (15) and its counterpart for $P(x,a')$. Elimination of $Q(x)$ with the help of (30) then yields

$$\frac{d}{dx}\left\{-\frac{D_{\rm eff}(x)}{g(x)}P(x)\right\}+\frac{f(x)}{g(x)}P(x) = \tau\frac{d}{dx}\frac{f(x)J(x)}{g(x)}+\frac{J(x)}{g(x)}+\tau[aS(x,a')+a'S(x,a)]. \tag{31}$$

In view of (23), this equation is valid wherever $P(x)$ is not yet given by (22). The solution of the first-order equation (31) is straightforward. In particular, the arising free integration constant is fixed through the condition $P(x)=0$ for $x\in(x_{\rm out},x_+)$ following from (22). We remark that while the point sources $q_{a'}$ and q_a [cf. Eq. (18)] can be chosen freely, the sinks are fixed by the conditions (i) that in the steady state the total source strength $q=q_{a'}+q_a$ must equal the total of the sinks $s_{a'}+s_a$, and (ii) that due to (20), particles obeying (14) cannot reach the sink $x_{\rm out}$ when the noise is in the negative a-state. In other words, we have that

$$s_{a'}=q_{a'}+q_a, \quad s_a=0. \tag{32}$$

The natural choice for $q_{a'}$ and q_a is the one according to the steady-state probabilities (2) of the dichotomous process

$$q_{a'}=\mu/(\mu'+\mu), \quad q_a=\mu'/(\mu'+\mu). \tag{33}$$

Here, a free proportionality constant $j=q$, which can be identified with the constant net flux of particles between $x_{\rm in}$ and $x_{\rm out}$ [see also Eq. (29)] has been tacitly chosen so as to achieve a unit flux $j=q=1$. In this case, the solution of (22) and (31) takes the final form

$$P(x)=\left\{\int_{\max\{x,x_{\rm in}\}}^{x_{\rm out}}\frac{1+\tau g(y)\,\dfrac{d}{dy}\dfrac{f(y)}{g(y)}}{D_{\rm eff}(y)\,P_0(y)}\,dy + \tau\frac{f(x_{\rm in})+(a'+a)g(x_{\rm in})}{D_{\rm eff}(x_{\rm in})\,P_0(x_{\rm in})}\Theta(x_{\rm in}-x) - \tau\frac{f(x_{\rm out})+ag(x_{\rm out})}{D_{\rm eff}(x_{\rm out})\,P_0(x_{\rm out})}\right\}\Theta(x_{\rm out}-x)\,P_0(x), \tag{34}$$

where

$$P_0(x)=\frac{g(x)}{D_{\rm eff}(x)}\exp\left\{\int_{x_{\rm in}}^{x}\frac{f(y)}{D_{\rm eff}(y)}dy\right\}\Theta(D_{\rm eff}(x)) \tag{35}$$

can be identified as the (not normalized) steady-state density in the absence of any sources and sinks.

Note that $P(x)$ in general has discontinuities at $x_{\rm in}$ and $x_{\rm out}$ due to the δ-shaped source and sink in (18). On condition that

$$f(x_-)/D'_{\rm eff}(x_-)\leqslant 1\,, \tag{36}$$

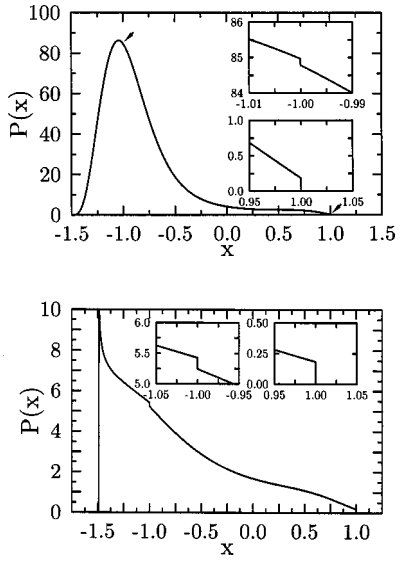

FIG. 2. Steady-state distribution $P(x)$ from (34) (not normalized) for the example (24) and (25). Noise parameters are $D=0.1$, $\tau=0.01$, $A=0.5$ (top), for which (36) is not verified, and $D=0.5$, $\tau=0.05$, $A=0.5$ (bottom), for which (36) is verified. Insets: details of the discontinuities at $x=x_{\mathrm{in}}=-1$ and $x=x_{\mathrm{out}}=1$.

the distribution $P(x)$ furthermore exhibits a singularity at x_- which is inherited from $P_0(x)$ in (35). It reflects a ''jam'' of particles at the left border x_- of the accessible x-region that may arise in the negative state $\xi(t)=a$ of the noise when the correlation time becomes large. For two representative examples, see Fig. 2.

Finally, the Kramers rate of escape (16) out of the domain $(-\infty,x_{\mathrm{out}})$ follows from (34) as

$$k=1/\int_{x_-}^{x_{\mathrm{out}}}P(x)\,dx. \tag{37}$$

By use of the method of steepest descent, we can evaluate the rate for small correlation times τ[12,14] with the result

$$k=\frac{\sqrt{-f'(x_{\mathrm{in}})f'(x_u)}}{2\pi(1+\tau f'(x_u))}\exp\left\{-\frac{1}{\tau}\Delta\Phi\right\}, \tag{38}$$

where the characteristic ''activation energy'' to the top x_{top} of the static potential $U(x)$ is given by

$$\Delta\Phi=\int_{x_{\mathrm{in}}}^{x_{\mathrm{top}}}\frac{f(x)}{(f(x)+ag(x))(f(x)+a'g(x))}dx. \tag{39}$$

In the above calculations, we have assumed strictly delta-shaped sinks and sources of particles. For more general source- and sink-distributions, the solution follows by an appropriately weighted superposition of solutions (34) and may no longer exhibit discontinuities at those places, whereas the discontinuity at x_- remains under the condition (36).

We finally remark that the derivation of the so-called adjoint equation that governs the mean escape time $T_{x_{\mathrm{out}}}(x_{\mathrm{in}})$, especially its correct boundary conditions, as well as the solution of this equation is quite involved.[12–14] Thanks to our identity (17), all these difficulties can be circumvented and the mean escape time immediately follows as

$$T_{x_{\mathrm{out}}}(x_{\mathrm{in}})=\int_{x_-}^{x_{\mathrm{out}}}P(x)\,dx. \tag{40}$$

III. APPLICATIONS

In this section, a detailed discussion is presented for the special case of the symmetric setup (24) with δ-sources and sinks positioned at the two minima (25) of the corresponding bistable static potential $U(x)$. We will consider both ''forward'' transitions from x_{in} to x_{out} as well as ''backward'' transitions from x_{out} to x_{in}, and we are especially interested in the effect of the asymmetry of the unbiased dichotomous noise $\xi(t)$ on these transitions. For the Kramers rates of the forward and backward transitions we use the shorthand notation k_+ and k_-, respectively. While the forward rate k_+ follows immediately from (34) and (37), we remark that due to the symmetry of our present example (24) and (25), the backward problem in (14) can be mapped onto a forward problem if we replace the noise $\xi(t)$ by $-\xi(t)$; that is, if we interchange primed and unprimed quantities. In terms of the asymmetry parameter (8), this implies that

$$k_-(A)=k_+(-A). \tag{41}$$

We also recall that the three noise-determining parameters D, τ, and A [cf. Eqs. (9)–(12)] have to respect the condition (20) and (21); otherwise, transitions in at least one direction are prohibited.

A. Constant variance scaling

Of particular interest, e.g., with respect to the so-called resonant activation phenomenon,[34–42,44–51,54,55] is the dependence of the escape time upon the correlation time τ of the asymmetric dichotomous noise $\xi(t)$ under the assumption that the variance $\sigma^2\langle\xi^2(0)\rangle$ and the asymmetry A are kept constant (constant variance scaling). With (5) and (6), this means a τ-dependent intensity D of the form

$$D=\sigma^2\tau,\quad \sigma^2,A \text{ fixed}. \tag{42}$$

This choice is particularly natural in the context of dichotomous noise since it leaves the two states a' and a as well as the flip rates μ' and μ of the noise unchanged upon variation of τ, cf. Eqs. (9)–(12). Especially, the validity of the condition (20) is not affected by changing τ.

Since the mean escape time is exactly equal to the inverse Kramers rate, we can focus on the discussion of the latter. A representative example of forward rates k_+ for a fixed variance σ^2 and various asymmetries A is depicted in Fig. 3. It clearly reproduces the typical features of resonant activation,[34–42,44–51,54,55] most notably, an ''optimal'' time scale of the potential fluctuations at which the circumstances for a transition are most favorable. The intuitive physical explanation of this effect goes along the by now well-known line of reasoning as reviewed in Ref. 47 and is not reproduced here. We emphasize again that the Kramers rate is well defined and exactly given by (34) and (37) not only for arbitrary noise strengths but also for arbitrary correlation times τ. In contrast, a rate definition based on the smallest

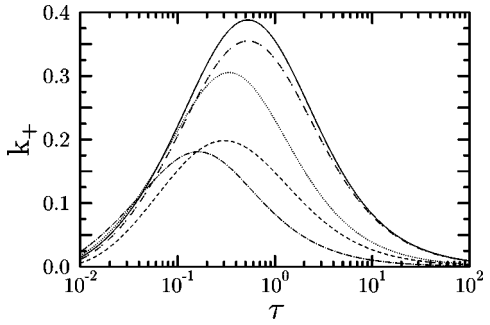

FIG. 3. Forward escape rates k_+ according to (34) and (37) versus correlation time τ for the model (24) and (25) with constant variance scaling (42). The asymmetry parameters are $A=0.8$ (dash–dotted), $A=0.4$ (dotted), $A=0$ (solid), $A=-0.4$ (short–long-dashed), and $A=-0.8$ (dashed), and the variance has the fixed value $\sigma^2=10$. The corresponding backward escape rates k_- follow with (41). For other choices of the variance σ^2 [compatible with (20) and (21)] qualitatively similar results are obtained.

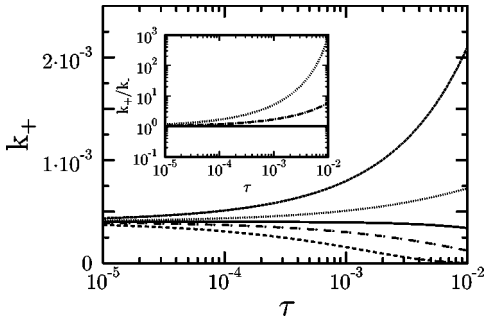

FIG. 5. Same as in Fig. 3 but for constant intensity scaling with $D=0.04$. The ratio k_+/k_- is depicted in the inset. (Other choices of D lead to qualitatively similar results.)

nonvanishing eigenvalue of the time-evolution operator and the closely related exponential decay of the metastable state may lose their physical relevance. In fact, in many cases a breakdown of such a description has been identified[41] as a precondition for the occurrence of the resonant activation peak in the mean escape time.

B. Control of chemical reaction rates

Figure 4 illustrates the effect of the noise asymmetry on the ratio k_+/k_- between forward and backward Kramers rates. One remarkable feature is that the k_+/k_--curves cross the value 1 at some intermediate correlation time τ, indicating a change in the relative predominance of forward versus backward reactions. In order to decide whether this effect is possibly just an artifact of our specific choice (33) of the particle sources, we repeated the same calculation of k_+/k_- with equally distributed sources $q_{a'}=q_a=1/2$ with the result (not shown) that this effect can still be observed. An even more striking feature of Fig. 4 is the divergence of k_+/k_- for $\tau\to0$. One can readily infer from (38) that for small τ both rates $k_\pm$ themselves become arbitrarily small and practically independent of the specific choice of the particle-source distribution in (18). That opens a quite unexpected new possibility to manipulate yields in chemical reactions by

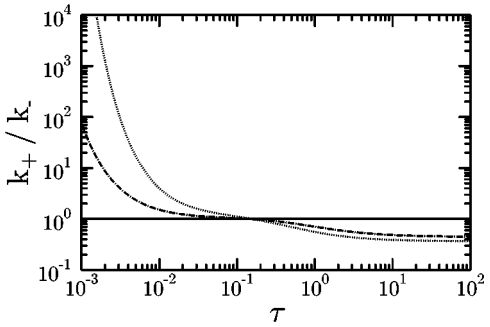

FIG. 4. Ratio k_+/k_- of forward and backward Kramers rates obtained from the results shown in Fig. 3 by means of (41). Since negative asymmetry parameters A follow readily from their positive counterparts according to (41), only the non-negative A-values 0.8 (dotted), 0.4 (dash–dotted), and 0 (solid) are depicted.

means of *unbiased, asymmetric, almost white* ($\tau\to0$) *noise*, be it via an externally applied signal or system-intrinsic far from equilibrium fluctuations of the relevant reaction potential. In fact, this effect is already contained in the results from Ref. 12, without pointing out however its possible spectacular practical implications. For a particular example of this effect, see also Refs. 31,61.

C. Constant intensity scaling

Constant intensity scaling is defined by the prescription that the intensity D and the asymmetry A are kept fixed upon variation of the correlation time τ of the noise. Such a scaling is of particular interest in that it leads to a sensible white noise limit when $\tau\to0$. Especially, this scaling enables one to study what happens if one goes slightly away from the Gaussian white noise case into the realm of weakly colored noise. Since a and a' also change with τ according to (9) and (10), the condition (20) is always fulfilled for very small τ but ultimately will be violated if one increases τ. Examples of how the rates behave for constant intensity scaling are depicted in Fig. 5. In the white noise limit $\tau\to0$, the well-known escape rate for an overdamped Fokker–Planck-process[2] is recovered from (38), irrespective of the asymmetry A. For sufficiently large τ, transitions from $x_{\rm in}$ to $x_{\rm out}$ in (14) are no longer possible ($\tau\geqslant10^{-2}$ in Fig. 5). For moderate τ-values, the escape rates either decrease monotonously or show a resonant activation type behavior, depending on the asymmetry A. A detailed small-τ analysis of the analytical result (34) and (38) confirms the numerical evidence from Fig. 5, namely that a resonant activation peak will occur if and only if $A>0$ (i.e., $a'>|a|$). It has been demonstrated in Refs. 44, 48–51, and 55 that for *symmetric* noise with constant intensity scaling, resonant activation is ruled out except for very specially tailored models. The occurrence of the effect for the very simple example (24) is therefore clearly due to the asymmetry of the noise.

We finally remark that in contrast to Fig. 4 (see also Sec. III B), in the present case of constant intensity scaling, the ratio k_+/k_- of forward and backward rates approaches 1 for $\tau\to0$ and may diverge for sufficiently large τ (see Fig. 5). The latter effect is simply due to the fact that for some asymmetry parameters A, the backward rate k_- vanishes earlier than the forward rate k_+ with increasing τ.

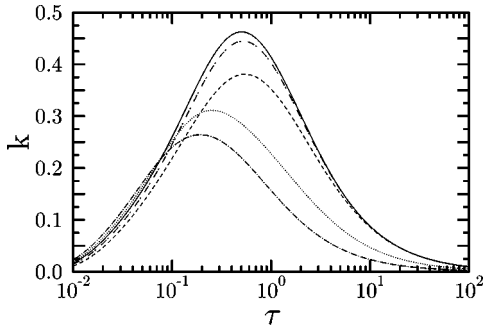

FIG. 6. Same as in Fig. 3 (constant variance scaling) but for the example (43) and (44) and with asymmetry parameters $A=0.6$ (dash–dotted), $A=0.3$ (dotted), $A=0$ (solid), $A=-0.3$ (short–long-dashed), and $A=-0.6$ (dashed).

D. Cubic potential

So far we have restricted ourselves to bistable potentials like in (24) and (25) since one of our main points was the comparison of forward and backward rates in the presence of asymmetric noise. Besides, we have also observed several interesting characteristic features of the forward rates alone, so it seems worthwhile to ask about their robustness. We therefore extended our analysis to potentials with a single metastable well, specifically the paradigmatic cubic potential. The corresponding force fields are [cf. Eq. (24)]

$$f(x)=\tfrac{3}{2}x(x+1), \quad g(x)=1. \tag{43}$$

Here, the factor 3/2 is chosen so as to obtain the same height of the underlying potential $U(x)$ as in the model (24). The source and sink of particles are again assumed to be given by δ-peaks at the potential well and at a point sufficiently well beyond the barrier, respectively

$$x_{\mathrm{in}}=-1, \quad x_{\mathrm{out}}=x_{+}. \tag{44}$$

The Kramers rate (37) following from the steady-state solutions (34) depicted for both constant variance scaling and constant intensity scaling in Figs. 6 and 7, respectively. Comparison with Figs. 3 and 5 shows that the main characteristic features of those rates are indeed quite robust.

IV. CONCLUSIONS

We have studied the far from equilibrium escape problem across a fluctuating potential barrier that is driven by asymmetric, unbiased dichotomous noise. Our closed analytical solution for the steady-state, flux-carrying density (34) and hence following Kramers rate (37) and mean escape time (40) are valid for arbitrary noise strengths and correlation times fulfilling the positivity condition of the effective diffusion in (19) and (20). On this basis, we have identified several new aspects of the so-called resonant activation effect and we have indicated interesting implications regarding far from equilibrium or externally controlled chemical reaction processes. Along this line, we have unraveled a new, purely asymmetry-induced resonant activation effect within the so-called constant intensity scaling scheme. Another important aspect of asymmetric noise is a new possibility to control and manipulate reaction rates and yields as well as the balance between reactants and products in chemical reaction processes.

The existing literature on resonant activation[34–55] seems to suggest that the simultaneous presence of thermal noise and potential fluctuations is an indispensable precondition for the appearance of this effect. In contrast, with our study (see Sec. III) we exemplify[42] that resonant activation may in fact be viewed as a feature of the escape problem with colored noise driven potential fluctuations alone that survives, and actually is reduced,[38] in the presence of additional thermal white noise.

Conceptionally, our approach differs from the original one by Kramers and Farkas.[2,6,7] While in our case the steady-state solution for a given distribution of sources and sinks is determined, their original strategy was to start with an ansatz for the solution and then to determine the corresponding sinks and sources *a posteriori* by inserting that solution back into (15).[2] While, in principle, any such ansatz will solve (15) [or, equivalently Eq. (26)] with a properly adapted distribution of sinks and sources, only those with negligible sinks and sources in the barrier region are admissible as a meaningful rate in the weak noise limit. For the present case of dichotomous noise, this is the point of view adopted in the rate calculations from Refs. 11 and 12.

The second aspect in which our investigation goes beyond the usual Kramers scheme and also that of previous works on resonant activation[34–55] is that we admit here *asymmetric* noise which is, however, still unbiased on average. As detailed in Sec. II, such an asymmetry can be identified as a new sufficient ingredient to generate resonant activation. On top of that, asymmetry provides us with a powerful new tool to manipulate and control yields of chemical reaction processes.

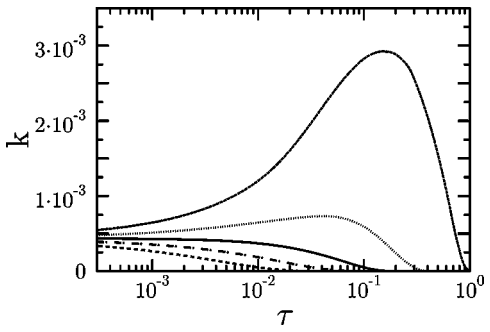

FIG. 7. Same as in Fig. 6 but for constant intensity scaling with $D=0.04$.

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