

Reaction rates when barriers fluctuate: A singular perturbation approach¹

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Abstract

We study the thermally activated surmounting of a potential barrier with a randomly fluctuating shape. For weak thermal and potential fluctuations analytical approximations based on path integral techniques are compared with accurate numerical results. Particular emphasis is put on the dependence of the potential fluctuation statistics upon their characteristic time scale (constant intensity versus constant variance). While many qualitative features are satisfactorily captured by the exponentially leading Arrhenius-type contribution to the rate, prefactor effects must be included for reliable quantitative predictions. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The thermally activated escape of a Brownian particle over a potential barrier plays an important role in a wide variety of physical, chemical, and biological contexts [1,2]. Correspondingly, with the word ‘Brownian particle’ one may refer either to a true physical particle but also to a chemical reaction coordinate, or some other relevant state variable or collective coordinate of the problem under investigation. In many cases, the potential experienced by the Brownian particle cannot 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 a O₂ or CO ligand molecule out of a myoglobin ‘pocket’ after photodissociation [3].

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 [4,5]. In a new paradigm for the intracellular motion of a molecular motor along a microtubule put forward in Ref. [6], the binding of ATP and the release of ADP 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 [7–10], the dynamics of dye lasers [11–13], and even for some aspects of protein folding and relaxation in glasses, fluctuating potentials are likely to be of relevance [3,14,15]. 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*

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¹ Dedicated to the memory of V.I. Mel’nikov.

since otherwise they would be negligibly small due to their 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. Finally, besides those examples of complex non-equilibrium systems, potential fluctuations without back-coupling, as we will study them here, can obviously be realized also by means of external noise imposed on a suitably designed experiment [16,17].

If the 'intrawell relaxation' of the Brownian particle is much faster than the potential fluctuations, the escape problem can be recast into the form of a 'kinetic model' [18,19] by means of an adiabatic elimination procedure [20–22]. Such models have already been extensively studied in the literature (see [8–10,14,23–28], and further references therein) with the most prominent qualitative results being temporally non-exponential decay laws. Here, we will not consider such 'slow' potential fluctuations, but focus instead on the regime where an exponential decay law is valid. This is guaranteed if the typical escape time is the slowest time scale of the problem, in particular, much slower than the potential barrier fluctuations. Additionally, both the thermal noise and the typical barrier fluctuations must be reasonably small in comparison with the (average) potential barrier. Being abundant in natural systems as well as in technical applications, we will assume Gaussian distributed potential fluctuations. In the simplest case, they are furthermore stationary and Markovian, thus they correspond to an Ornstein–Uhlenbeck process (e.g. see in Ref. [29]). Generalizations for non-stationary cases, pertaining, e.g. the above-mentioned myoglobin photodissociation, are straightforward. Also generalizations including inertial effects of the Brownian particle, which are neglected in our present study, are possible and will be discussed in detail elsewhere.

The quantity of foremost interest in this context is the mean escape time across the fluctuating barrier as a function of the characteristic time scale of these fluctuations. The possibility that this dependence may be non-monotonous has been exemplified first

in Ref. [30] and has been termed 'resonant activation' therein. This 'surprising phenomenon' [7] has been further investigated in Refs. [19–22,31–36], and is by now at least qualitatively well understood [20–22]; see also Ref. [37] for a recent review. As already emphasized in [32–35], 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 problem is addressed in more detail here with particular emphasis on the two most natural options that the (in our case Gaussian) distribution of the potential fluctuations is kept constant ('constant variance scaling') [19–22,30,31] or the intensity of those fluctuations (i.e. their integrated time-correlation) is kept fixed ('constant intensity scaling') [15,16,38–41]. While for constant variance scaling 'resonant activation' is typical [20,21,32], we find that for constant intensity scaling it is rather untypical, though not completely impossible. Similar findings have been obtained in the previous 'constant intensity' studies [38–41] of particular systems, where no 'resonant activation' has been found, and in the recent work [34], where resonant activation has been predicted for carefully tailored potentials even with constant intensity scaling. For related studies of somewhat different working models we also refer to [42–44].

Note that a somewhat related phenomenon occurring for deterministic, time-*periodic* potential oscillations is presently much discussed under the label of 'stochastic resonance' [45]. While such periodic oscillations might in first priority be of interest in technical applications, random fluctuations as studied here might be more typical in natural or laboratory systems. Potential fluctuations mediating between the purely random and periodic cases (aperiodic stochastic resonance) have been studied in Refs. [46–48]. It is not surprising that in all these models many qualitatively similar features are observed.

From a technical point of view we are concerned in this paper with a singular perturbation theory for a two-dimensional dynamical flow perturbed by asymptotically weak Gaussian white noise in the absence of detailed balance (since we are far from thermal equilibrium).

In spite of the extensive literature on the closely related topics of 'colored noise' [49], the principal

mathematical difficulties inherent in such a singular perturbation theory have become clear only very recently [50]. In view of these problems, we will restrict ourselves mainly to the exponentially dominating contribution (Arrhenius factor) to the escape rate. In fact, a *consistent* analytical treatment of the non-exponential prefactor is at present still an unsolved problem in our opinion. All the more, accurate numerical methods are of paramount importance in this context [41]. A prominent such method is based on matrix continued fraction techniques [49,51] which will be extensively invoked to test our analytical approximations. We finally mention that some of our results have been derived already previously in the literature [22,39,41]. Here, we will put forward a streamlined path-integral type formalism which greatly simplifies the actual calculations needed for the derivation of these known as well as various novel results.

2. The fluctuating double well

As motivated in Section 1, the model we are going to study is given by the following overdamped Brownian motion in one dimension:

$$\dot{x}(t) = -\partial_x V(x(t), y(t)) + \sqrt{2D} \xi(t) \quad (1)$$

$$V(x, y) := U(x) + yW(x), \quad (2)$$

where the time derivative is indicated by the dot and the partial derivative with respect to x by ∂_x . The friction coefficient of the particle $x(t)$ has been absorbed into the time scale, the thermal fluctuations $\xi(t)$ are modeled as usual by Gaussian noise of zero mean and correlation $\langle \xi(t)\xi(s) \rangle = \delta(t-s)$, and D controls the strength of those thermal fluctuations. The potential $V(x, y)$ consists of a static double well $U(x)$ and a fluctuating part $W(x)$ that is driven by the stationary Ornstein–Uhlenbeck process

$$\dot{y}(t) = -\frac{y(t)}{\tau} + \frac{\sqrt{2Q}}{\tau} \eta(t) \quad (3)$$

of correlation time τ and strength Q . With $\eta(t)$ being a second δ -correlated Gaussian noise independent of $\xi(t)$, the stationary distribution and the

time-correlation of the Ornstein–Uhlenbeck process (3) follow as

$$\rho_0(y) = \sqrt{\frac{\tau}{2\pi Q}} \exp\left\{-\frac{y^2\tau}{2Q}\right\} \quad (4)$$

$$\langle y(t)y(s) \rangle = \frac{Q}{\tau} \exp\left\{-\frac{|t-s|}{\tau}\right\}. \quad (5)$$

A possible relaxation of the non-equilibrium fluctuations $y(t)$ towards thermal equilibrium (cf. Section 1) could be incorporated by allowing in (3) for initial distributions different from (4) and a time-dependence of Q but is omitted here for the sake of simplicity.

We denote the left minimum of the double well potential $U(x)$ by a (for ‘attractor’), the local maximum by b (for ‘barrier’), and the right minimum by c . A common example is the quartic double well (we use an appropriate scaling to yield dimensionless quantities)

$$U(x) = \frac{x^4}{4} - \frac{x^2}{2}, \quad (6)$$

corresponding to $a = -1$, $b = 0$, and $c = 1$. Typical examples for the fluctuating part of the potential $W(x)$ complementing the static part from (6) are:

$$W(x) = U(x) \quad (7)$$

$$W(x) = x \quad (8)$$

$$W(x) = x - x^3 \quad (9)$$

$$W(x) = \frac{x^2}{2}. \quad (10)$$

In the first example (7) the qualitative shape of the potential $V(x, y) = U(x)(1+y)$ experienced by the Brownian particle (1) is always the same and only the overall factor $(1+y)$ is fluctuating in time. The second example (8) corresponds to a spatially constant but temporally fluctuating force. In the third example (9), the extrema $a = -1$, $b = 0$, $c = 1$ of the bare potential (6) are left unaffected by the noise $y(t)$, while producing a fluctuating shape of the potential $V(x, y)$ in between these extrema. The fourth example (10) has been introduced in Refs. [35,40,41] and is included here for comparison. Note that in Eqs. (7)–(10) we omitted a free coupling constant on the right hand side since such an extra parameter can always be absorbed into the noise strength Q from (3). Indeed, in our numerical exam-

ples below we will have to choose quite different Q -values in (7)–(10) to produce roughly comparable effects in the rates. We further note that a change of sign in $W(x)$ does not affect the escape rates. Taking those invariances into account, (7)–(10) is a fairly representative selection of polynomials up to fourth order.

Like in our specific examples (6)–(10) we will in our more general theoretical calculations always assume that the potentials $U(x)$ and $W(x)$ are sufficiently smooth, whereas their symmetry about the barrier $x = b$ will in general *not* be required. Finally, for the sake of simplicity we will sometimes make the additional weak assumption that $U(x)$ is strictly monotonically increasing between the well $x = a$ and the barrier $x = b$.

The main objective of our study will be the calculation of the typical transition time of a particle (1) from the left well $x = a$ into the right well $x = c$ of the static potential $U(x)$ in the regime where such transitions are rare events and therefore can be described by a meaningful escape rate k [2]. This means that both the thermal and the potential fluctuations must be sufficiently much smaller than the average barrier $\Delta U := U(b) - U(a)$. In order that none of these two noises is practically negligible in comparison with the other, we express the intensity Q of the potential fluctuations in units of the thermal noise strength D ,

$$Q = RD, \quad (11)$$

keeping R fixed whenever D becomes asymptotically small. Of central interest is the dependence of the escape rate k on the features of the fluctuating potential $W(x)$ and on the characteristic time scale τ of these fluctuations. Regarding the latter dependence, there are basically two different options [32–35]: either one considers a model for which the ‘intensity’ $\int_{-\infty}^{\infty} \langle y(t)y(s) \rangle dt$ of the potential fluctuations is kept fixed upon variation of τ , i.e.

$$R = R_{\text{CI}} \quad (\text{constant intensity scaling}) \quad (12)$$

or one keeps their distribution (4) (and thus their variance) independent of τ , i.e.

$$R = \tau R_{\text{CV}} \quad (\text{constant variance scaling}). \quad (13)$$

Here, R_{CI} and R_{CV} are meant to be τ -independent, while R and thus Q from (11) will henceforth be

considered as in general dependent on τ . The constant intensity scaling [15,16,38–41] is motivated by the fact that it guarantees a sensible white noise limit of the Ornstein–Uhlenbeck process $y(t)$ when $\tau \rightarrow 0$ and is commonly used in investigations of the escape problem with a single colored noise [49]. In the constant variance scaling [20–22,32–35] the probability that the particle (1) experiences at any given time instance t a certain potential $V(x, y)$ is τ independent. This scaling is particularly natural when $y(t)$ is a dichotomous noise [19–21,30,31,36], since then the potential $V(x, y)$ simply performs flips between its two (τ -independent) realizations. In general, the proper choice of $R = R(\tau)$ will depend on the physical situation under consideration [32,33]. Though still other $R(\tau)$ than in (12) and (13) may arise, we will mainly focus on these two possibilities from now on. Scalings $R(\tau) = R_0 \tau^\alpha$, $0 \leq \alpha \leq 1$, mediating between (12) and (13) have been studied in detail in Ref. [34]. A generalization to such cases of our results follows usually immediately, but will not be discussed in detail.

3. Basic theoretical concepts

In order to get rid of the non-Markovian nature of the one-dimensional Brownian motion (1) it is convenient to work with the extended two-dimensional Markov process (1), (3). The corresponding probability density $\rho(x, y, t)$ is governed by the Fokker–Planck equation [29,51]

$$\dot{\rho}(x, y, t) = \Gamma \rho(x, y, t) \quad (14)$$

$$\Gamma := \partial_x [\{\partial_x V(x, y)\} + D \partial_x] + \partial_y \left[\frac{y}{\tau} + \frac{R}{\tau^2} D \partial_y \right]. \quad (15)$$

In the quasi-stationary state $\rho(x, y, t)$ will decay like $\rho(x, y)e^{-kt}$ provided particles are discarded from the system once they have reached the well of $U(x)$ at $x = c$. Here, k is the escape rate, in which we are interested, and $\rho(x, y)$ is the quasi-stationary density, satisfying

$$\Gamma \rho(x, y) = -k \rho(x, y) \quad (16)$$

for $x \simeq c$ and $\rho(x, y) = 0$ for $x \geq c$. This standard concept for calculating the escape rate goes back to Farkas and Kramers and is reviewed in detail, e.g. in Mel'nikov's report [1].

For small values of D , on which we will focus from now on, the problem (16) is still not even qualitatively well understood in all its aspects [50]. We only sketch here those parts of the presently known general theory which will be needed later. Expecting the usual Boltzmann-type structure of the quasi-invariant density we make the ansatz

$$\rho(x, y) = Z(x, y)e^{-\phi(x, y)/D}, \quad (17)$$

where the so-called 'quasipotential' $\phi(x, y)$ is required to be D -independent and the 'pre-factor' $Z(x, y)$ may depend on D at most algebraically. Introducing this WKB type ansatz (17) into (16) and collecting leading order D terms yields the following Hamilton–Jacobi equation for the quasipotential [52–56]

$$H(\partial_x \phi(x, y), \partial_y \phi(x, y), x, y) = 0 \quad (18)$$

$$H(p, q, x, y) := p^2 + q^2 R / \tau^2 - p \partial_x V(x, y) - yq / \tau, \quad (19)$$

where p and q denote the canonical momenta conjugate to x and y , respectively. Similarly, the remaining terms in Eq. (16) give rise to a partial differential equation for the prefactor $Z(x, y)$ which, however, has no elementary classical-mechanical interpretation.

In order to determine the rate k it turns out that one only needs to solve these partial differential equations for $\phi(x, y)$ and $Z(x, y)$ (or directly (16)) close to the stable fixed point ($x = a, y = 0$) and the saddle point ($x = b, y = 0$) of the deterministic dynamics (1), (3). Outside these two small regions the problem can be reduced to the solution of ordinary differential equations due to the smallness of D . However, the local solution about the saddle point ($b, 0$) is unfortunately not unique and the proper choice, corresponding to the (unique) global solution is not known in general. Yet, one can show that the rate must be of the Arrhenius type from [52–54]

$$k = \zeta e^{-\Delta \phi / D}. \quad (20)$$

The exponentially leading part $\Delta \phi = \phi(b, 0) - \phi(a, 0)$ can be obtained as

$$\Delta \phi = \min_{x(t), y(t)} \int_{-\infty}^{\infty} L[x(t), y(t)] dt, \quad (21)$$

where the Lagrangian

$$L[x, y] = \frac{[\dot{x} + \partial_x V(x, y)]^2}{4} + \frac{[\tau \dot{y} + y]^2}{4R} \quad (22)$$

follows from the Hamiltonian (19) by Legendre transformation and arguments t have been dropped in (22). The minimization in (21) is over all paths $x(t), y(t)$ starting at time $t = -\infty$ at the stable fixed point ($a, 0$) and ending at time $t = \infty$ at the saddle point ($b, 0$). The minimizing $x(t), y(t)$ in (21) can be interpreted as the most probable escape path (MPEP) for asymptotically small D [55,56]. While referring to [52] for a detailed derivation of (20)–(22) we only note here that the appearance of Hamilton's principle of the least action (21) is plausible in view of the Hamilton–Jacobi Eq. (18) governing the quasipotential $\phi(x, y)$. We further mention that the Hamiltonian dynamics corresponding to (19) is typically non-integrable [53,54]. Even though we actually only need the 'separatrix' of the deterministic dynamics (see (18)) it is not surprising that quantitative analytical results can be usually obtained only close to 'integrable' situations, see Sections 5 and 6 below.

Turning to the prefactor ζ in (20), a way of avoiding in the small D limit the solution of the full problem (16) (which is analytically hopeless) is known if and only if the quasipotential $\phi(x, y)$ is at least twice continuously differentiable at the saddle point ($b, 0$) [2,57]. In this case one first has to determine the second derivatives of the quasipotential along the MPEP. This can be accomplished by solving three coupled ordinary differential equations (equivalent to a matrix Riccati equation [55] with initial conditions at time $t = -\infty$ that can be readily extracted from the straightforward local solution of (16) about the stable fixed point ($a, 0$). The prefactor $Z(x(t), y(t))$ for asymptotically small D along the MPEP then follows immediately [53]. For the prefactor ζ of the rate (20) this finally yields [2,57]:

$$\zeta = \frac{|U''(b)|}{2\pi} \left| \frac{\phi''(a)}{\phi''(b)} \right|^{1/2} \frac{Z(b, 0)}{Z(a, 0)}, \quad (23)$$

where $\phi''(a)$ denotes the determinant of the second derivative (Hessian) of $\phi(x, y)$ at the stable fixed point $(a, 0)$ and similarly $\phi''(b)$ at the saddle point $(b, 0)$. Unfortunately the assumption that the quasipotential $\phi(x, y)$ is at least twice continuously differentiable at the saddle point $(b, 0)$ is typically not fulfilled². (In our case this is so whenever the potential fluctuations $y(t)$ in (1) are not an effective white noise at least near $x = b$, that is, for a generic $W(x)$ whenever $\tau \neq 0$, and for special $W(x)$ at least beyond a certain critical $\tau > 0$.) As demonstrated in Ref. [50], in some cases the quasipotential $\phi(x, y)$ is still piecewise smooth, but with a discontinuity of $\phi'(x, y)$ along a line that passes through the saddle $(b, 0)$. Though the Hessian of $\phi(x, y)$ does not exist at $(b, 0)$, it is well-behaved along the entire MPEP, even upon approaching $(b, 0)$. In other cases, the Hessian at $(b, 0)$ may still exist, but exhibits a vanishing determinant, and related problems will then occur already along the MPEP. As a consequence of those intriguing features of the quasipotential, Eq. (23) is no longer valid and an analytically practicable, consistent way of how to calculate ζ in this case is apparently not known. However, at least the qualitative property of (23) that ζ converges to a finite limit when $D \rightarrow 0$ is expected to remain valid in the (generic) general case [2,50]. Assuming in addition a sufficiently smooth dependence of this limiting $\zeta = \zeta(\tau)$ upon τ it follows that qualitative features of $\Delta\phi(\tau)$ like monotonicity or the occurrence of extrema will usually also apply to the full rate (20), if D becomes sufficiently small. (However, counterexamples exist, see in Section 8.) In view of the above-mentioned subtle problems encountered near the saddle point $(b, 0)$ it might not be superfluous to mention that at least the MPEP minimizing the right hand side of (21) is always guaranteed to be sufficiently smooth, in spite of the possible non-analyticities of the quasipotential $\phi(x, y)$ off the MPEP.

² This fact has been unraveled only very recently by Maier and Stein in their work [50]. Although they study the mean first passage time problem from the stable fixed point $(a, 0)$ across the separatrix of the deterministic dynamics (1), (3) their main conclusions remain valid also for the ‘well-to-well’ escape problem considered here.

4. Streamlined framework

Due to the generic intractability of the prefactor ζ in the rate (20) we will be mainly concerned with the exponentially leading part $\Delta\phi$ defined through (21). The analysis of this quantity is greatly simplified by taking advantage of some simple observations as given in the following.

First, it is convenient to solve the variational problem (19) not by means of the corresponding Euler–Lagrange equations but rather by means of the equivalent Hamilton equations

$$\dot{x} = \partial_p H = 2p - \partial_x V(x, y) \quad (24)$$

$$\dot{p} = -\partial_x H = p\partial_{xx}V(x, y) \quad (25)$$

$$\dot{y} = \partial_q H = 2qR/\tau^2 - y/\tau \quad (26)$$

$$\dot{q} = -\partial_y H = pW'(x) + q/\tau, \quad (27)$$

where arguments t have been omitted, the Hamiltonian H is given in (19), and

$$p := [\dot{x} + \partial_x V(x, y)]/2 \quad (28)$$

$$q := \tau[\tau\dot{y} + y]/2R \quad (29)$$

are the canonical momenta conjugate to x and y . Introducing

$$r(t) := q(t) - \tau y(t)/R \quad (30)$$

it follows from (26), (27) that

$$\dot{r} = pW'(x) - r/\tau. \quad (31)$$

The boundary conditions supplementing these equations are $x(-\infty) = a$, $x(+\infty) = b$, while $y(t)$, $p(t)$, $q(t)$, and $r(t)$ must vanish for $t = \pm\infty$. The (formal) solutions of (27) and (31) are readily found to be

$$q(t) = -\int_t^\infty e^{(t-s)/\tau} W'(x(s)) p(s) ds \quad (32)$$

$$r(t) = \int_{-\infty}^t e^{(s-t)/\tau} W'(x(s)) p(s) ds \quad (33)$$

and we are left with only the two Eqs. (24) and (25) to be solved. A further integration can be saved by using the conservation of energy (cf. (18))

$$H(p(t), q(t), x(t), y(t)) = 0 \quad \text{for all } t \quad (34)$$

in place of either (24) or (25).

Next, let us denote by λ an arbitrary parameter of the escape problem (1), for instance the correlation

time τ of the barrier fluctuations, their relative strength R , or some other parameter characterizing the fluctuating potential $W(x)$. Then, on the right hand side of (21) in general both the Lagrangian *and* the minimizing MPEP will change upon variation of this parameter λ . However, since the MPEP by definition minimizes the integral in (21) those changes are negligible when λ is modified infinitesimally, yielding

$$\frac{d}{d\lambda} \Delta\phi = \int_{-\infty}^{\infty} dt \frac{\partial}{\partial\lambda} L[x(t), y(t)], \quad (35)$$

where $x(t), y(t)$ denote the MPEP corresponding to the λ -value under consideration. As a caveat we remark that (24)–(34) clearly should not be introduced into the Lagrangian (22) before the differentiation with respect to λ in (35) but only afterwards.

It is plausible that any *local* minimum $x(t), y(t)$ on the right hand side of (21) that might be a possible candidate for the MPEP, i.e. the absolute minimum, changes smoothly upon variation of the parameter λ . If several such local minima exist then at certain λ -values a former absolute minimum may become a relative minimum, while a former relative minimum takes over the role of the absolute minimum, leading to a discontinuous change of the MPEP. Typically, those special λ -values are isolated points and they can be ruled out sufficiently close to a ‘white noise situation’ such as $\lambda = \tau = 0$ or $\lambda = R = 0$ in (1), (3). Even more, close to $\lambda = \tau = 0$ or $\lambda = R = 0$ one expects that apart from the MPEP there exists no further local minima nor maxima of the integral in (21), i.e. the solution of Hamilton’s Eqs. (24)–(27) plus boundary conditions is unique. This property will be tacitly taken for granted in Sections 5 and 6 below. It further follows that if some feature, for instance a monotonous dependence of $\int_{-\infty}^{\infty} L[x(t), y(t)]dt$ upon λ , can be demonstrated for any solution $x(t), y(t)$ of (24)–(27) then the same follows for the ‘true’ MPEP $x(t), y(t)$ and thus for $\Delta\phi$ from (21). This observation will be exploited in Sections 7 and 8 below.

5. Small τ approximation for constant intensity scaling

As demonstrated in [20–22], a small- τ approximation for constant variance scaling (13) is very

easy. Much more delicate is the case of constant intensity scaling (12) as addressed in the following, see e.g. the discussion in Ref. [40].

Assuming constant intensity scaling (12) of the potential fluctuations, it follows from (22) that $\partial L/\partial\tau = [\tau\dot{y} + y]\dot{y}/2R_{CI}$. With (35) and taking into account that $\int_{-\infty}^{\infty} y(t)\dot{y}(t)dt = 0$ we obtain

$$\frac{d}{d\tau} \Delta\phi(\tau) = \frac{\tau}{2R_{CI}} \int_{-\infty}^{\infty} \dot{y}(t)^2 dt. \quad (36)$$

(Here and in the following terms like $\dot{y}(t)^2$ stands for $[\dot{y}(t)]^2$.) For later use we note that this is an exact result for arbitrary τ . Turning now to small τ , one readily verifies by inspection that in leading order τ the solution of Hamilton’s Eqs. (24)–(27) (see also (30)–(34)) can be written as

$$\dot{x}(t) = U'(x(t)) \quad (37)$$

$$p(t) = \psi(x(t)) \quad (38)$$

$$r(t) = -q(t) = \tau\psi(x(t))W'(x(t)), \quad (39)$$

where

$$\psi(x) := \frac{U'(x)}{1 + R_{CI}W'(x)^2}. \quad (40)$$

Introducing these results into $\Delta\phi$ from (20), (21), going over from the integration variable t to x by exploiting (37), and letting $\tau \rightarrow 0$ one obtains

$$\Delta\phi(\tau=0) = \int_a^b \psi(x) dx. \quad (41)$$

Similarly, one finds from (36) that in leading order τ

$$\begin{aligned} \frac{d}{d\tau} \Delta\phi(\tau) &= 2\tau R_{CI} \int_a^b U'(x) \\ &\times \left[\frac{d}{dx} \psi(x) W'(x) \right]^2 dx. \end{aligned} \quad (42)$$

We therefore can infer that

$$\begin{aligned} \Delta\phi(\tau) &= \int_a^b \psi(x) dx + \tau^2 R_{CI} \int_a^b U'(x) \\ &\times \left[\frac{d}{dx} \psi(x) W'(x) \right]^2 dx + O(\tau^4), \end{aligned} \quad (43)$$

where we omitted the straightforward proof that no contribution of order τ^3 occurs. The very same result (43) has been derived previously in Ref. [39] but within our streamlined formalism from Section 4 the actually needed calculations become now almost trivial.

A somewhat more involved calculations is needed to determine the prefactor $\zeta(\tau)$ in the rate (20) according to the recipe and Eq. (23) given in Section 3. Up to first order in τ one finds that

$$\zeta(\tau) = \frac{|U''(a)U''(b)|^{1/2}}{2\pi} \left(1 - \frac{1}{2}\tau R_{\text{Cl}} B \right) \quad (44)$$

$$B = \frac{U''(a)W'(a)^2}{1 + R_{\text{Cl}}W'(a)^2} + \frac{|U''(b)|W'(b)^2}{1 + R_{\text{Cl}}W'(b)^2} - 4 \int_a^b dx \psi(x) W'(x) \frac{d}{dx} \frac{W''(x)}{1 + R_{\text{Cl}}W'(x)^2}. \quad (45)$$

Although in the course of the evaluation of this prefactor all expressions and manipulations are well

defined, the problems with Eq. (23) mentioned in Section 3 can be rigorously ruled out only under the extra condition that $W'(b) = 0$. (Only then, the Hessian of the quasipotential $\phi(x, y)$ is guaranteed to exist in leading order τ at the saddle point $(b, 0)$ and can be obtained from its evolution along the MPEP, see the discussion at the end of Section 3 and also section 6 in Ref. [50] for more details). For $W'(b) \neq 0$ we thus can truly justify (44) only by invoking the good agreement with the numerical results in Fig. 1b,c, and the obviously correct behavior in the white noise limit $\tau = 0$. Similar troubles are well known from previous small τ studies with constant intensity scaling, see, e.g. the discussions in Refs. [32,40]. For the special case that $W'(a) = W'(b) = 0$ the same result (45) has been obtained already by Iwaniszewski

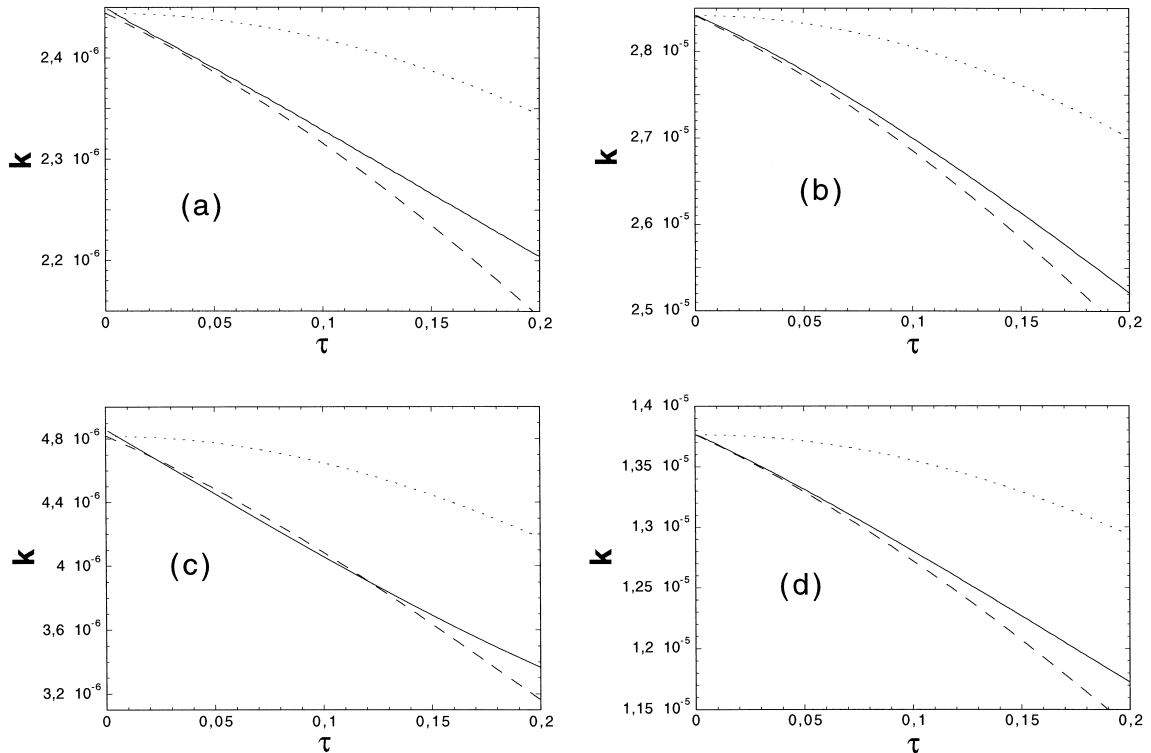


Fig. 1. Escape rate k versus correlation time τ of the potential fluctuations for constant intensity scaling (11), (12) with $D = 0.02$, $R_{\text{Cl}} = 1$ in (a) and (d), and $R_{\text{Cl}} = 0.4$ in (b) and (c). (Those different R -values are chosen to obtain roughly comparable values for the rates in all 4 examples.) The static part of the potential is given by the quartic double well (6) and the fluctuating part by (7) in (a), (8) in (b), (9) in (c), and (10) in (d). The solid lines are accurate numerical results from matrix continued fraction calculations, the dashed lines are the small- τ predictions from (43)–(47), and the dotted lines represent the same theoretical prediction but without the prefactor corrections for finite τ , i.e. with $B = 0$ in (46).

[34] in a rather different way, namely by extending the approach of the early work [39]. Within the same restrictions on $W(x)$, also the case of arbitrary noise-strengths D and a more general τ -dependence of R can be found in this work [34].

Through the prefactor (44) the rate acquires a linear dependence on τ although the exponentially leading part (43) starts only like τ^2 . Taking into account this feature, previous approximations [38–40], which maybe seemed contradictory at first sight, become perfectly compatible with each other and with our findings (within their respective accuracy and regime of validity).

In order to reduce finite- D effects in the comparison of the small- τ approximations (43) and (44) with the numerics in Fig. 1 we plot

$$k(\tau) = k(\tau = 0) \left(1 - \frac{1}{2} \tau R_{\text{Cl}} B\right) \times \exp\left\{\frac{\Delta\phi(0) - \Delta\phi(\tau)}{D}\right\} \quad (46)$$

rather than (20), where $k(\tau = 0)$ is chose as half the inverse of the exactly know mean first passage time (MFPT) from a to b (see, e.g. in Ref. [2])

$$k(\tau = 0) = \frac{1}{2} \left[\int_a^b dx \int_{-\infty}^x dy \right. \\ \left. \times \frac{\exp\left\{\int_y^x \psi(z) dz\right\}}{D \sqrt{[1 + R_{\text{Cl}} W'(x)]^2 [1 + R_{\text{Cl}} W'(y)]^2}} \right]^{-1}. \quad (47)$$

In Fig. 1 we compare those analytical small- τ approximations with accurate numerical results from matrix continued fraction calculations [49,51]. In these calculations, the smallest non-vanishing eigenvalue of the Fokker–Planck operator (15) has been determined which is known to approach twice the escape rate k in (16) in the weak noise limit (see Ref. [58] for more details). Results for the four fluctuating potentials (7)–(10) are depicted in Fig. 1. Note that in order to obtain roughly comparable values of the rate in the considered τ -range, different choices of the R_{Cl} values are necessary. We see that in all cases the agreement between theory and numerics is very good. The deviations at $\tau = 0$ are due to deviations (for finite D) of the exact inverse

MFPT from (47) and the smallest non-vanishing eigenvalue of the Fokker–Planck operator (15) as determined in our numerical calculations. In part, they may also be due to the finite numerical accuracy. (The estimated numerical uncertainty is definitely below 1% in (a), (b), (d) and at most a few percent in (c).) The remaining discrepancies in the slopes at asymptotically small τ are very small. They can be attributed to finite- D corrections [34] of B from (45). The dotted curves shown in Fig. 1 make it very clear that the exponentially leading small- τ contributions [39] alone are not sufficient even for rather small noise strengths D .

6. Small R expansion of $\Delta\phi$

For large R (with $D \rightarrow 0$ and $Q = RD$ constant) the process (1), (3) approaches a single colored noise driven problem, and therefore is practically intractable for general values of τ [49]. In the opposite limit of small R , a comparatively straightforward analytical solution at least of the exponentially leading part $\Delta\phi$ of the rate (20) is possible [22]. Introducing

$$\gamma := \sqrt{R}, \quad \tilde{y}(t) := y(t)/\gamma \quad (48)$$

Eqs. (1)–(3) take the form

$$\dot{x} = -U'(x) + \tilde{y}\gamma W'(x) + \sqrt{2D} \xi \quad (49)$$

$$\dot{\tilde{y}} = -\frac{\tilde{y}}{\tau} + \frac{\sqrt{2D}}{\tau} \eta, \quad (50)$$

where we exploited (11) and arguments t have been dropped. If we now omit the tilde, one readily sees that in the formalism from Sections 3 and 4 this simply amounts to replacing R by 1 and $W(x)$ by $\gamma W(x)$ everywhere. From (22) and (24) it then follows that $\partial L/\partial\gamma = p\gamma W'(x)$. Introducing the solution (30), (32), (33) for y and taking into account (35) we can infer that

$$\frac{d}{d\gamma} \Delta\phi = -\frac{2\gamma}{\tau} \int_{-\infty}^{\infty} dt \int_t^{\infty} ds e^{(t-s)/\tau} W'(x(t)) p(t) \\ \times W'(x(s)) p(s). \quad (51)$$

Similarly to (36), this is an exact relation for arbitrary $\gamma = \sqrt{R}$. Turning to small γ , one readily veri-

fies by inspection that the solution of Hamilton's Eqs. (24)–(27) in leading order γ is of the form

$$\dot{x}(t) = p(t) = U'(x(t)), q(t) = y(t) = 0. \quad (52)$$

For the sake of simplicity we now restrict ourselves to potentials $U(x)$ that are strictly monotonically increasing between the well at $x = a$ and the barrier at $x = b$. With (52) this implies that $x(t)$ has a well defined inverse $t(x)$ for $x \in [a, b]$. Introducing (52) into (51) and using x instead of t as integration variable one finds in leading order γ that [22]

$$\frac{d}{d\gamma} \Delta\phi = -\frac{2\gamma}{\tau} \int_a^b dx \int_x^b dy W'(x) W'(y) e^{\frac{1}{\tau} \int_y^x U'(z) dz}. \quad (53)$$

The next order corrections can be obtained likewise. Using the obvious identity $\Delta\phi = \Delta U := U(b) - U(a)$ for $\gamma = 0$ and replacing γ again by \sqrt{R} we finally arrive at our central result

$$\Delta\phi = \Delta U + RA_1 + R^2A_2 + O(R^3), \quad (54)$$

where the τ -dependent coefficients A_1 and A_2 are given by:

$$A_1 := -\frac{1}{\tau} \int_a^b dx \int_x^b dy W'(x) W'(y) e^{\frac{1}{\tau} \int_y^x U'(z) dz}, \quad (55)$$

$$A_2 := -\frac{1}{2\tau^3} \int_a^b dx \int_x^b dy K(x, y) W'(x) \times W'(y) e^{\frac{1}{\tau} \int_y^x U'(z) dz} \quad (56)$$

$$K(x, y) := \frac{r_+(x)r_-(x)}{U'(x)^2} + \frac{r_+(y)r_-(y)}{U'(y)^2} + \int_x^y dz \frac{r'_+(z)r_-(z) - r_+(z)r'_-(z)}{U'(z)^2} \quad (57)$$

$$r_+(x) := \int_a^x dy W'(y) e^{\frac{1}{\tau} \int_y^x U'(z) dz} \quad (58)$$

$$r_-(x) := -\int_x^b dy W'(y) e^{\frac{1}{\tau} \int_y^x U'(z) dz}. \quad (59)$$

To get a feeling of how the corrections of order $O(R^3)$ in (54) behave as a function of τ , we have to specify the τ -dependence of R . We start with a closer look at constant intensity scaling (12) when τ

becomes small. A straightforward calculation then shows that $\Delta\phi$ from (54) indeed converges to a finite limit for $\tau \rightarrow 0$:

$$\Delta\phi(\tau=0) = \int_a^b dx U'(x) \left[1 - R_{\text{CI}} W'(x)^2 + R_{\text{CI}}^2 W'(x)^4 + O(R_{\text{CI}}^3) \right] \quad (60)$$

which is in perfect agreement with our previous result (39) expanded in powers of R_{CI} . This observation suggests that the term $O(R^3)$ in (54) will vanish for small R uniformly in τ for moderate-to-small τ in constant intensity scaling. The same can be concluded for constant variance scaling (13) since in this case the small τ regime is obviously less 'dangerous' than for constant intensity scaling (12). Even more, we can infer that for constant variance scaling the result (54) is not restricted to small R_{CV} for $\tau \rightarrow 0$, i.e. the term $O(R^3)$ becomes small for arbitrary R_{CV} when τ approaches zero. Next we turn to large τ in constant variance scaling (13), which is the 'dangerous' choice in this limit. Again, $\Delta\phi$ from (54) is found to converge to a finite limit and to agree with a previously derived large τ expansion [22]. Since higher order terms are not very illuminating, we only give here the dominant contributions to this large τ asymptotics of (54):

$$\Delta\phi = \Delta U - R_{\text{CV}} \frac{\Delta W^2}{2} + \frac{R_{\text{CV}}}{\tau} Z \times \int_a^b \frac{[W(b) - W(x)][W(x) - W(a)]}{U'(x)} dx + O\left(R_{\text{CV}}^2, \frac{R_{\text{CV}}}{\tau^2}\right), \quad (61)$$

where $\Delta W := W(b) - W(a)$. As before, this suggests that the $O(R^3)$ term in (54) is uniformly bounded for moderate-to-large τ in constant variance scaling, while for constant intensity we even expect that (54) will be valid for arbitrary R_{CI} when τ becomes large. These theoretical expectations about the extended validity of the small- R approximation (54) will be fully confirmed by the numerical results presented in the following sections.

Without going into much details, we mention that all the intriguing features of the quasipotential $\phi(x, y)$ unraveled in [50] can be recovered already

within our small R approximation, as far as these features manifest themselves along the MPEP. For instance, when τ exceeds the critical value $1/|U''(b)|$, the quasipotential near the saddle point $(b, 0)$ is no longer (piecewise) quadratic but more ‘flat’ and the MPEP $x(t), y(t)$ becomes tangential to the separatrix of the two attraction basins of the deterministic dynamics (1), (3).

Turning to the prefactor ζ in the rate (20), we first note that its limiting value for $R=0$ is known exactly in the same sense as the rate in (47), namely via the exact MFPT:

$$\zeta(R=0) = \frac{1}{2} e^{\Delta U/D} \left[\int_a^b dx \int_{-\infty}^x dy \times \frac{\exp\{[U(x) - U(y)]/D\}}{D} \right]^{-1}. \tag{62}$$

In the weak noise limit $D \rightarrow 0$ this yields by means of a saddle point approximation

$$\zeta(R=0, D \rightarrow 0) = \frac{|U''(a)U''(b)|^{1/2}}{2\pi}. \tag{63}$$

Due to the intriguing problems discussed at the end of Section 3, even leading order R corrections to (62) cannot be obtained. It is only for small τ that we can conclude indirectly from (44), (45) that the leading order corrections are quadratic in R , i.e. (62) remains valid up to first order R for small τ . Similarly, from a different large τ approach (eq. (4.16) in [22]) it is possible to infer indirectly the coefficient of the leading order corrections of (62) for small R and large τ . In view of these problems, in the comparison with the numerical results in the following sections we will be bound to use for the prefactor the zeroth order approximation (62).

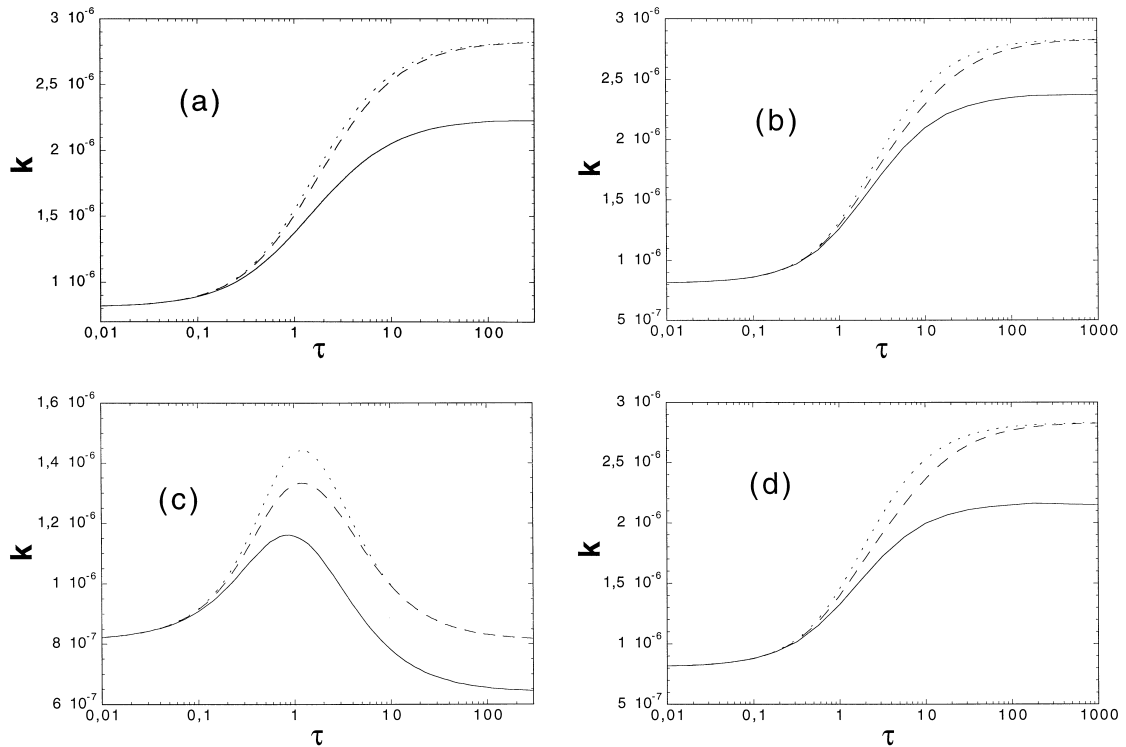


Fig. 2. Same as in Fig. 1 but for constant variance scaling (13) with $R_{CV} = 0.8$ in (a), $R_{CV} = 0.05$ in (b), and $R_{CV} = 0.2$ in (c) and (d). Accurate numerical results (solid) are compared with the small- R approximation (20), (54), (62), neglecting the terms of order R^3 (dashed) and R^2 (dotted) in (54).

7. Constant variance scaling

Introducing the definition of constant variance scaling (13) into the Lagrangian (22) one obtains $\partial L/\partial \tau = [\dot{y}^2 - (y/\tau)^2]/4R_{CV}$. Exploiting (27)–(31) it follows that $d\Delta\phi(\tau)/d\tau$ from (35) takes the form

$$\frac{d}{d\tau}\Delta\phi(\tau) = \frac{R_{CV}}{\tau^2} \int_{-\infty}^{\infty} q(t)r(t)dt. \quad (64)$$

Following [22], we call a fluctuating potential $W(x)$ of ‘type I’ if $W'(x)$ does not change sign for $a \leq x \leq b$, like for instance in (7), (8), (10). It is suggestive and can be proven rigorously [22] that in this case the $x(t)$ component of the MPEP does not leave the domain between the well $x=a$ and the barrier $x=b$ of the static potential $U(x)$ and $p(t)$ never changes sign (cf. (25)). With (32), (33) this implies that for a potential $W(x)$ of type I the derivative $d\Delta\phi(\tau)/d\tau$ from (64) is negative and thus $\Delta\phi(\tau)$ is strictly monotonically decreasing with τ . Correspondingly, a monotonous increase is ex-

pected for the rate (20) at sufficiently small noise strengths D . However, it should not be overlooked that for any small but finite D , the escape is reasonably described by a single rate only within the separation of time scales $\tau \ll 1/k$ [2]. For even larger τ values the typical mean escape time is no longer given by $1/k$ [20,21] and can be shown to be a monotonically increasing function of τ . Consequently, the typical mean escape time must exhibit a minimum as a function of τ (‘resonant activation’ [30]). For type I potentials $W(x)$ it further follows that the ‘resonant activation’ minimum occurs at a τ value where the rate concept starts to break down and thus tends to ∞ as D approaches 0. Since our numerical results are essentially also rates (cf. Section 4), we only plotted τ values substantially smaller than $1/k$ in Figs. 2 and 3. Therefore no ‘resonant activation’ minimum is visible in the type I examples (a), (b), and (d) depicted in Figs. 2 and 3.

Next we turn to type II potentials $W(x)$ defined by the property [21,22] that $\Delta W = W(b) - W(a)$ equals zero, see for instance (9). In this case, the

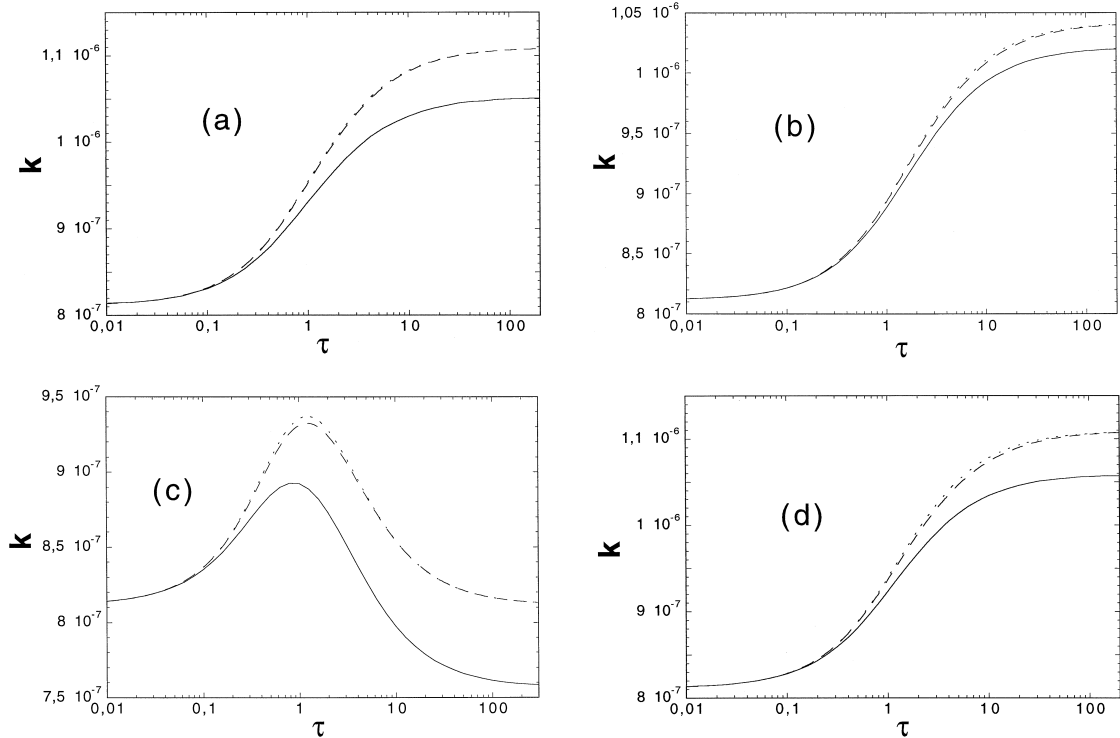


Fig. 3. Same as in Fig. 2 but with $R_{CV} = 0.2$ in (a), $R_{CV} = 0.01$ in (b), and $R_{CV} = 0.05$ in (c) and (d).

location of the well $x = a$ and the barrier $x = b$ as well as the barrier height ΔU are unaffected by the potential fluctuations in (1). It is only the shape in between a and b of the potential $V(x, y)$ that is modulated by the Ornstein–Uhlenbeck noise $y(t)$. Replacing R_{CI} by τR_{CV} (see (12) and (13)) it already follows from the zeroth order result (39) that $\Delta\phi(\tau)$ equals ΔU for $\tau = 0$ and then decreases with τ . On the other hand, we see from (61) that $\Delta\phi(\tau)$ approaches again ΔU for $\tau \rightarrow \infty$, but now from below. It turns out [22] that this feature of (61) remains valid even if R_{CV} is not assumed to be small. It follows that $\Delta\phi(\tau)$ and thus the typical escape time $1/k$ must exhibit a ‘resonant activation’ minimum at a τ value that remains finite when $D \rightarrow 0$ (cf. Figs. 2b and 3b). For the occurrence of this type II ‘resonant activation’ the breakdown of the rate concept is thus not crucial, in contrast to the type I case. Without going into further details we mention that for potentials $W(x)$ which are neither

type I nor II (so-called mixed type) one finds at least one ‘resonant activation’ minimum of the typical escape time which is either qualitatively similar to the type I or the type II case [22]. For some mixed type $W(x)$ also both kinds of minima may occur simultaneously. In other words, for constant variance scaling and sufficiently small D ‘resonant activation’ occurs always [20,21]. For the generalization of this result beyond small D values see [20,21].

In Figs. 2 and 3 we compare the theoretical approximations from (54) and (62) for small R_{CV} with accurate numerical results. Our first observation is that our qualitative predictions for both type I and type II potentials $W(x)$ are nicely confirmed. Second, the agreement for small τ is always excellent. We did not include in Figs. 2 and 3 the small- τ approximation from Section 5 (with R_{CI} replaced by τR_{CV}) since, as long as the latter approximation itself can be trusted, it is almost indistinguishable from the shown small- R curves. Thus, for constant

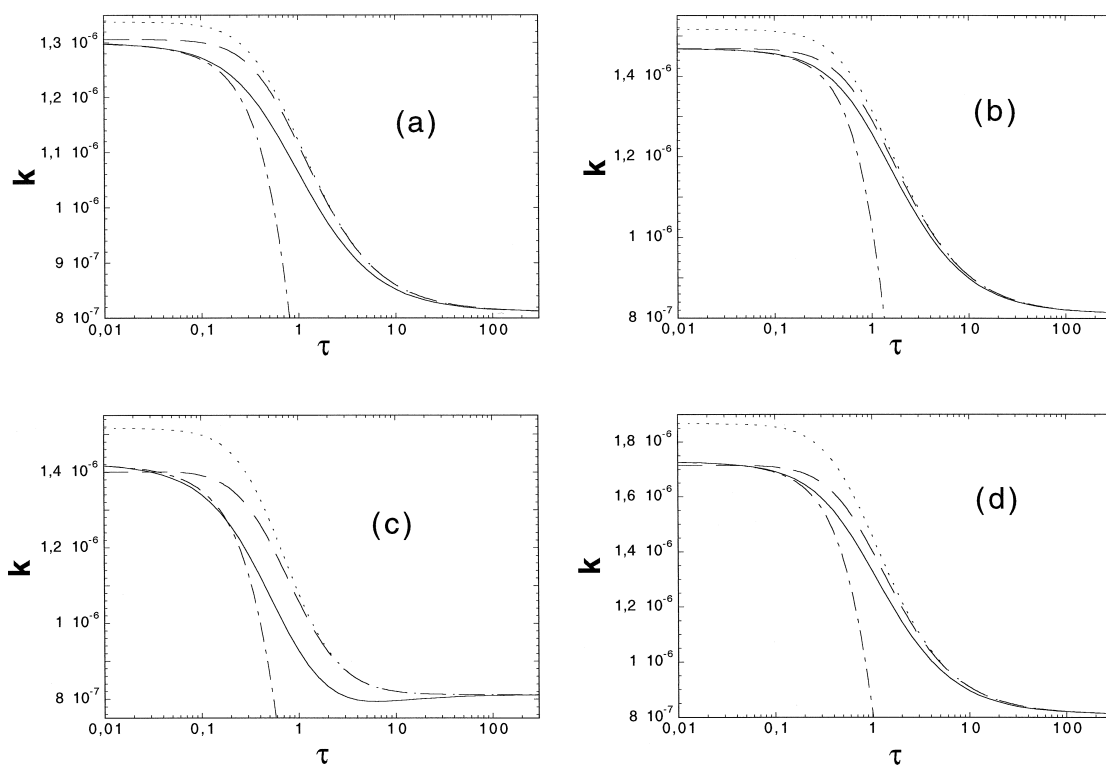


Fig. 4. Same as in Fig. 2 but for constant intensity scaling (12) with $R_{CI} = 0.4$ in (a), $R_{CI} = 0.05$ in (b), $R_{CI} = 0.1$ in (c), and $R_{CI} = 0.2$ in (d). Additionally, the small- τ approximations from (43)–(47) are shown as dashed-dotted lines.

variance scaling our ‘small- R ’ approximation indeed seems to be a very good small- τ approximation even if R_{CV} is actually not so small, as predicted below Eq. (60). Third, the comparison of Fig. 2 and Fig. 3 shows that the second order correction in (54) becomes less relevant with decreasing R and is in fact practically negligible in Fig. 3, implying the same conclusions for the neglected higher order terms in (54). In other words, the remaining difference between numerics and theory is almost entirely due to the neglected finite- R prefactor corrections in (62). While these prefactor corrections indeed decrease with decreasing R_{CV} (roughly speaking linearly), they are apparently still appreciable even for rather small R_{CV} values. We also checked that their relative importance indeed decreases with decreasing noise strength D . Yet, the domain of D - and R -values where those corrections are faithfully negligible even from a quantitative viewpoint is virtually of academical interest only.

8. Constant intensity scaling

Recalling that (36) is an exact result for arbitrary τ for constant intensity scaling (12), it immediately follows that $\Delta\phi(\tau)$ is *always* strictly monotonically increasing with τ . One therefore might expect that also the rate k is always monotonically decreasing with τ , at least for sufficiently small D . Yet this is true in most cases, it should not be overlooked that the small τ expansion of $\Delta\phi$ in (43) has no linear term and thus for sufficiently small τ the prefactor (44) dictates whether the rate (20) increases or decreases as a function of τ . Though B from (45) will be positive in most cases, it is not difficult to tailor $U(x)$ and $W(x)$ such that B is negative, leading to a decreasing prefactor and thus a decreasing rate in the small- τ regime. The same prediction of a prefactor-induced resonant activation scenario for constant intensity scaling and specially tailored potentials $U(x)$ and $W(x)$ has been made also in the work [34] and an explicit example has been figured out therein.

In Fig. 4 we compare our small- R predictions

from (54), (62) with numerical results for the usual potentials $W(x)$ from (7)–(10). For large τ the agreement is excellent, in accordance with the theoretical expectation below (61). For small-to-moderate τ the agreement is somewhat worse. From the small deviations between the dashed and dotted lines in Fig. 4 we conclude, like in the previous section, that the discrepancy between theory and numerics in Fig. 4 is mainly due to the neglected R -dependence of the prefactor in (62). As already seen in Fig. 1, these prefactor contributions are especially important in the small- τ regime (see also the dashed-dotted lines in Fig. 4). A particularly interesting feature is the non-monotonicity of the numerical results in Fig. 4c. An analytical explanation of this effect follows immediately from formula (4.16) in Ref. [22]. The latter theoretical result also confirms that the effect is entirely due to prefactor contributions. A similar effect in a rather different model has already been described in Ref. [33]. A more closely related effect has been predicted theoretically in [34] under the label of ‘resonant inhibition of activation’, and has been confirmed numerically as well as explained in simple terms in [35]. We, however, emphasize that the latter effect is only possible in the regime of very large τ , while in our case the effect appears for moderate τ . In further accordance with this distinction is: (i) that in [35] the effect under discussion has been observed for the fluctuating potential (10), while it is absent in our corresponding Fig. 4d within the here considered τ -regime, and (ii) that also the analytical explanations are completely different.

9. Conclusions

We have studied the thermally activated rate of escape in a double well potential that is itself subjected to fluctuations driven by additive or multiplicative Ornstein–Uhlenbeck noise. The dependence of the rate upon the correlation time τ of the potential fluctuations has been addressed for both most often considered cases, namely constant intensity scaling and constant variance scaling (11)–(13).

Under the assumption of small noise strengths we have tackled this problem by means of analytical path integral methods as well as accurate numerical matrix continued fraction calculations. Particular emphasis has been put on a clear statement of the principal analytical difficulties and on an efficient formulation of the path integral approach.

Our main results for the rate (20) are the small- τ approximation (43)–(47) and the small- R approximation (54), (62). The qualitative agreement of those predictions with the numerical findings in Figs. 1–4 is very good and in some limits also an excellent quantitative comparison is achieved. Especially, all numerically observed qualitative features are well understood analytically.

On the quantitative side, substantial further progress seems possible only if prefactor effects will be successfully included. As repeatedly emphasized, to do this in a systematic and controlled manner is a very difficult task. One possible way out are non-systematic approximations like for instance the unified colored noise approximation put forward in [32,40,41]. Another possibility are ad-hoc interpolations between the by now well understood small- and large- τ limits [20–22,34]. A paradigm for such an approach has been worked out in [36] for dichotomous potential fluctuations, where the respective regimes of validity of ‘small’- and ‘large’- τ approximations have been systematically extended so far that they overlap.

We finally mention the possibility of generalizing our analytical approximations to include mass effects of the Brownian particle. That will be the subject of a forthcoming work [59].

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