

Surmounting Fluctuating Barriers

PETER HÄNGGI

Abstract. Escape over *fluctuating* barriers in the presence of thermal white noise is addressed. Several general results are established, for stochastic barrier fluctuations being controlled by colored Gaussian noise. Our findings are exact in the limit of white noise sources and (partially) in the limit of extreme large noise color, and are approximate for intermediate noise color. As one main result we find that the escape time can generically exhibit a minimum resonant activation, whenever the colored noise intensity is an increasing function of the noise correlation time. The effects induced by *correlated noise sources* and the influence of quantum tunneling are addressed as well.

1. Introduction

Ever since the seminal achievements by Svante Arrhenius and Hendrik Antonie Kramers, the problem of escape from metastable states continues to attract ever growing interest, e.g. see [1, 2]. In particular, interesting variations of this topic arise when studying transport in complex systems, such as in glasses [3] and in proteins [4]. In this context the problem of escape over stochastic barriers has moved into the limelight within several scientific communities [5–12].¹ The interest in this concept of noise-assisted escape over fluctuating barriers has germinated when describing complex nonequilibrium systems such as the migration of ligands in proteins [4], molecular dissociation in strongly coupled chemical systems [5], or electron transport in a quantum double well structure [13], which is subjected to an external fluctuating voltage-bias, to name only a few examples. The problem area is also closely related to noise-assisted escape in systems with *fluctuating* potential parameters [8–10]. A characteristic feature of all these cases is that these are *open* systems, being in contact with one or more fluctuating environments, i.e. we deal with complex nonequilibrium systems, in which the fluctuations are generally not related to a fluctuation-dissipation theorem of the Einstein–Nyquist type. It must further be emphasized that – although related – the fluctuating barrier concept is different from the phenomenon of *stochastic resonance* [14, 15], with the latter being characterized by time-dependent,

¹ In particular note the *News and Views* contribution in [5].

but *deterministic* barrier modulations; i.e. the continuous time-translation symmetry is broken, thereby rendering these latter systems *nonstationary* nonequilibrium systems.

As correctly emphasized already in [6], noise-assisted escape over fluctuating barriers involves several relevant time-scales. In particular the typical fluctuating barrier time-scale can be either very small, comparable to, or even be much larger than the average molecular time-scale characterizing local relaxation within metastable states. Therefore, the escape dynamics for the reaction coordinate $x(t)$ is generally governed by a *non-Markovian process* driven by both, white environmental noise $\xi(t)$, and colored, generally multiplicative barrier fluctuations $\zeta(t)$. The problem of obtaining the average escape time over fluctuating barriers thus becomes a challenging problem, because generally even the stationary probability is not known. Indeed, in all previous studies [6–12], one has been forced to impose severe limitations. These constitute either the restriction to the white or almost white noise limit (i.e. small colored noise limit) for the barrier-fluctuations [8–12], or the discussion had been restricted to both, the use of a very simple colored noise structure, such as exponentially correlated two-state noise, driving the barrier fluctuations (i.e. dichotomic noise $\zeta(t)$) together with a stylized metastable potential composed of a piecewise linear barrier and piecewise linear wells [6, 7]. Even in this case the analytical analysis is already very complex so that Monte-Carlo simulations had been invoked [6, 7]. Nevertheless, Doering and Gadoua [6] discovered within these latter limitations a most interesting resonance – like phenomenon for the behavior of the average escape time; i.e. the escape time in their study did not grow monotonically with increasing noise color τ , but instead did exhibit a minimum near a ‘resonant’ barrier fluctuation rate τ_r^{-1} . Clearly, the question then arises if this phenomenon is universal, i.e. if it still holds for realistic potential shapes and/or more realistic colored noise sources $\zeta(t)$.

The task to answer these open challenges stimulated the present work. Here, I have succeeded to obtain several results, which describe a variety of general phenomena for noise-assisted escape over fluctuating barriers. Most importantly, one finds that the resonance-phenomenon can occur *generically*, whenever the colored noise intensity, $Q \equiv \int_0^\infty |\langle \zeta(t)\zeta(0) \rangle| dt$ increases with increasing noise-correlation time τ .

2. The approach

The starting point for our considerations is an arbitrary bistable flow for the reaction coordinate x . Explicitly, with the static metastable potential denoted by $U(x)$, we have $\dot{x} = -U'(x) = f(x)$, which possesses *two stable* deterministic fixed points $f(x_\pm)$, with $f'(x_\pm) < 0$, and *one unstable* fixed point $f(x^\#) = 0$, with $f'(x^\#) > 0$, see Figure 1. The barrier fluctuations are governed by a fluctuating potential $W(x, \zeta) = -\zeta(t) \int^x g(y) dy$, with

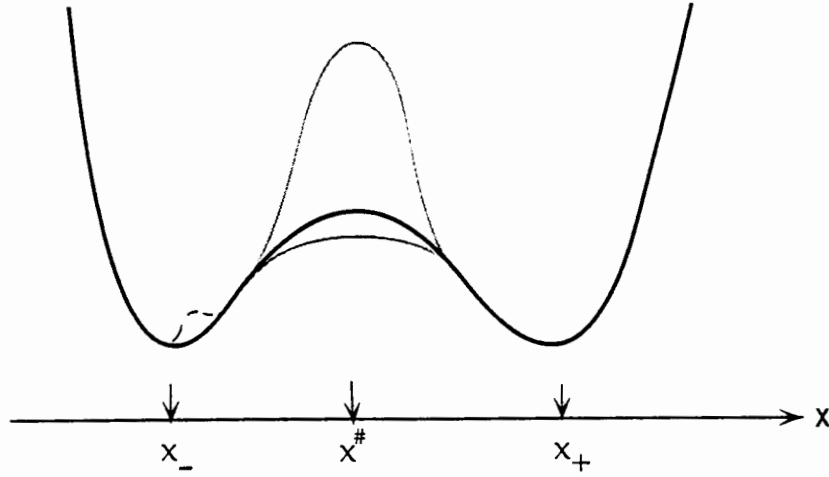


Fig. 1. Escape over a fluctuating barrier. The solid line depicts the static potential with x_{\pm} denoting the stable states and $x^{\#}$ the unstable, activated state. The thin gray lines present two realizations for the fluctuating barrier. The dashed line shows a slight modification of the static potential away from barrier top which in turn changes the corresponding value for the resonant noise color τ_r , see text below Equation (18).

$\zeta(t)$ a colored noise source. The function $g(x) = -W'(x, \zeta = 1)$ denotes the corresponding force-profile, which up to the condition $-g(f/g)' \geq 0$ within the bistable region (x_-, x_+) , can be chosen arbitrarily. Throughout this work, the prime denotes a differentiation with respect to x . The escape over a fluctuating barrier is then governed by the nonlinear non-Markovian Langevin equation

$$\dot{x} = f(x) + g(x)\zeta(t) + \sqrt{2T}\xi(t), \quad (1)$$

where $\xi(t)$ is white Gaussian noise of vanishing mean and correlation $\langle \xi(t)\xi(s) \rangle = \delta(t-s)$, reflecting environmental (thermal) noise, while the colored noise $\zeta(t)$ controls the barrier fluctuations. A common example for $f(x)$ is the archetypal Landau flow $f(x) = ax - bx^3$, $a > 0$, $b > 0$; while $g(x)$ could be Gaussian, i.e. $W(x, \zeta) = -\zeta[2\alpha]^{-1} \exp(-\alpha x^2)$, yielding $g(x) = x \exp(-\alpha x^2)$.² Note, that for $\alpha = 0$ we have $g(x) = x$, which corresponds to a fluctuating barrier curvature [8], i.e. $a \rightarrow a + \zeta(t)$. In order to define the stochastic process in Equation (1) completely it is necessary to specify both the individual and the joint statistical properties of $\zeta(t)$ and $\xi(t)$. Bearing in mind the central limit theorem, we use for $\zeta(t)$ a *Gaussian* statistics. For the sake of simplicity only, we choose an exponentially correlated Gaussian

² In this case $-g(f/g)' = 2bx^2 - 2\alpha x^2(a - bx^2)$, being nonnegative within $[x_- = -\sqrt{a/b}, x_+ = +\sqrt{a/b}]$ for $\alpha < b/a$, see also [22].

noise (Ornstein–Uhlenbeck process) of vanishing mean and the correlation,

$$\langle \zeta(t)\zeta(s) \rangle = \frac{Q}{\tau} \exp\left(-\frac{|t-s|}{\tau}\right). \quad (2)$$

Moreover, to start with we make here the assumption that $\zeta(t)$ and $\xi(t)$ are independent, i.e. $\langle \zeta(t)\xi(s) \rangle = 0$ for all t, s ; see however Section 4.3 below. The non-Markovian, multiplicative Langevin equation in Equation (1) is then equivalently recast as a two-dimensional (Stratonovitch–)Langevin equation, reading

$$\dot{x} = f(x) + g(x)\zeta(t) + \sqrt{2T} \xi(t) \quad (3)$$

$$\dot{\zeta} = -\frac{1}{\tau} \zeta + \frac{\sqrt{2Q}}{\tau} \eta(t), \quad (4)$$

where $\eta(t)$ is again Gaussian white noise, obeying $\langle \eta(t)\eta(s) \rangle = \delta(t-s)$, and $\langle \eta(t)\xi(s) \rangle = 0$. The white noise limit then emerges naturally by observing that $\lim_{\tau \rightarrow 0} \langle \zeta(t)\zeta(0) \rangle = 2Q\delta(t)$.

The idea underlying our approach is as follows: In realistic situations the (dimensionless) noise intensities T and Q are ‘small’. With $T \ll 1$, $Q \ll 1$, but with the ratio $R \equiv Q/T$ finite, we encounter escape times which are exponentially large. Put differently, the (forward: $x_- \rightarrow x_+$) escape time \mathcal{T} exhibits an Arrhenius-like behavior, which is dominated by the ratio of the stationary probability $\bar{p}(x, \tau)$ at the stable state x_- and the unstable state $x^\#$. Setting $\bar{p}(x, \tau) = h(x, \tau) \exp[-\Phi(x, \tau, R)/T]$ one has within exponential accuracy

$$\mathcal{T}(R, \tau) \propto \exp\left(\frac{\Delta\Phi(R, \tau)}{T}\right), \quad (5)$$

where in terms of the effective potential Φ the barrier height equals $\Delta\Phi = \Phi(x^\#) - \Phi(x_-)$. Thus, we are *not* interested in obtaining an accurate approximation of the non-Markovian Langevin dynamics in Equation (1) on all time-scales, but rather are interested in the *long-time* dynamical properties only. Indeed, if one studies the limit of small noise color by expanding Equation (1), via the functional derivative method [16], around the $\tau = 0$ limit one finds – in agreement with the general theory [17] – that there exists to leading order in τ no small $-\tau$ effective Fokker–Planck equation. With $\zeta(t)$ colored, the flow in Equation (1) can thus never be transformed into purely additive noise alone. This fact in turn implies a third order Kramers–Moyal-type contribution for the rate of change $\dot{p}_t(x, \tau)$, being of order τ . Moreover, it is of interest to establish whether novel phenomena such as the resonant-like behavior of Doering and Gadoua [6] persist under realistic conditions; in particular, that they are not the mere result of some ‘prefactor-effect’ appearing only at strong noise intensities Q and/or T within a stylized metastable potential form.

In the presence of a single colored noise source $\zeta(t)$ only, the unified colored noise approximation (UCNA) [18] has proven to accurately model the stationary dynamics of colored noise driven flows [18, 19]. Borrowing the reasoning underlying [18], one can similarly implement this long-time approximation scheme for the flow in Equations (3, 4). In terms of the process $u(t)$, i.e. $ug(x) = f(x) + \zeta g(x)$, Equations (3, 4) can be recast as

$$\dot{x} = ug + \sqrt{2T} \xi \quad (6a)$$

$$\begin{aligned} \dot{u} = & - \left[\frac{1}{\tau} - g(f/g)' \right] u + \tau^{-1}(f/g) \\ & + \tau^{-1}\sqrt{2Q} \eta + (f/g)'\sqrt{2T} \xi. \end{aligned} \quad (6b)$$

By use of the time-scale $\hat{t} = t\tau^{-1/2}$ [18], the deterministic equation corresponding to Equation (6b) reads

$$\frac{du}{d\hat{t}} = -\{\tau^{-1/2} - \tau^{1/2}g(f/g)'\}u + \tau^{-1/2}(f/g). \quad (7)$$

With the nonlinear friction obeying $\gamma(x, \tau) \equiv \tau^{-1/2} - \tau^{1/2}g(f/g)' \geq 0$ for all τ when $-g(f/g)' \geq 0$ we note that $\gamma(x, \tau) \gg 1$ both for $\tau \rightarrow 0$ and $\tau \rightarrow \infty$. An adiabatic elimination of \dot{u} thus renders the generalized UCNA for Equation (1), i.e. the (Stratonovitch-)Markovian-Langevin approximation reads in the original time-scale t

$$\dot{x} = [1 - \tau g(f/g)']^{-1} \{f + g\sqrt{2Q} \eta + \sqrt{2T} \xi\}. \quad (8)$$

which possesses a corresponding Fokker-Planck equation. In passing, we note that the same (Stratonovitch-)Fokker-Planck equation corresponding to Equation (8) results if one performs within the configuration-state path integral representation for the non-Markovian process in Equation (1) a self-consistent Markovian approximation in the non-Markovian-Onsager-Machlup functional, cf. [20]. The stationary probability (up to a normalization constant) thus reads

$$\bar{p}(x, \tau) = \frac{|1 - \tau g(f/g)'|}{[1 + Rg^2(x)]^{1/2}} \exp \int_0^x \frac{f[1 - \tau g(f/g)']}{T(1 + Rg^2)} dy. \quad (9)$$

The result Equation (9) approximates generally (i.e. τ not very large) accurately the stationary non-Markovian probability over the bistable region (x_-, x_+) within its support, i.e. in x -regions obeying $[1 - \tau g(f/g)'] > 0$, see the reported results in [18, 19]. It should not go unnoticed, however, that the generalized UCNA in Equation (8) exhibits some troublesome difficulties for $R = (Q/D) \rightarrow 0$, i.e. for 'small' colored noise in presence of white noise $\xi(t)$. Indeed, setting $Q = 0$ in Equation (8) leaves us – via the term $[1 - \tau g(f/g)']^{-1}$ – with a dependence on noise color τ , which also impacts the stationary behavior in Equation (9). Note, that $\bar{p}(x, \tau)$ in Equation (9)

is still dependent on τ if we let $R \rightarrow 0$, with τ held fixed. Thus, the limit $R \rightarrow 0$, with τ not very small, is problematic for the generalized UCNA in Equation (8). This shortcoming is due to the presence of the additional fast time-scale represented by the (additional) white noise source $\xi(t)$ of strength D [18b] (cf. also the remark stated by Reimann in [7d]); it is being increasingly cured with increasing strength Q of the noise color. The shortcoming can be remedied if we consider the more complicated, auxiliary process $u \rightarrow u = \zeta + (f/g) \cdot \{1 + (T/Qg^2)[1 - \tau g(f/g)']\}^{-1}$. An adiabatic elimination of $u(t)$, i.e. $\dot{u}(t) = 0$, then provides a generalized UCNA with the correct behavior as $\tau \rightarrow 0$, and which with $u(t) \rightarrow 0$ as $\tau \rightarrow \infty$ is correct also for $\tau \rightarrow \infty$ (independent of the strength of the noise intensity Q). As a result the denominator in the exponential in Equation (9) becomes substituted by $[1 + Rg^2] \rightarrow [1 + Rg^2 - \tau g(f/g)']$, see in [22].

3. Average escape time over fluctuating barriers

With the long-time approximation to Equation (1) in hand, it is smooth sailing towards obtaining the average escape time T . This can be estimated by the mean first passage time (MFPT) expression for the one-dimensional Fokker-Planck process in Equation (8), i.e. $T_{\text{MFPT}}(x_- \rightarrow x_+) \equiv T(R, \tau)$ is given by the two quadratures

$$T(R, \tau) = T^{-1} \int_{x_-}^{x_+} \frac{dx}{D_{\text{eff}}(x, \tau) \bar{p}(x, \tau)} \int_{-\infty}^x \bar{p}(y, \tau) dy, \quad (10)$$

where $x = x_+$ has been chosen to be an absorbing boundary, and $D_{\text{eff}}(x, \tau) = (1 + Rg^2)[1 - \tau g(f/g)']^{-2} > 0$. With weak noise, the steepest descent approximation to Equation (10) explicitly reads

$$\begin{aligned} T(R, \tau) &= \frac{2\pi}{|f'(x^*)f'(x_-)|^{1/2}} \\ &\times \{|1 - \tau g(f/g)'|_{x=x^*} |1 - \tau g(f/g)'|_{x=x_-}\}^{1/2} \\ &\times \exp\left(\frac{\Delta\Phi(R, \tau)}{T}\right) \end{aligned} \quad (11)$$

with the effective barrier height given by

$$\begin{aligned} \Delta\Phi(R, \tau) &= - \int_{x_-}^{x^*} \frac{f(y)\{1 - \tau g(y)(f(y)/g(y))'\} dy}{[1 + Rg^2(y)]} \\ &> \Delta\Phi(R, \tau = 0). \end{aligned} \quad (12a)$$

An improved approximation $\Delta\Phi^{\text{improved}}$ for large noise color follows with help of the substitution mentioned below Equation (9); i.e.

$$\Delta\Phi^{\text{improved}}(R, \tau) = - \int_{x_-}^{x^{\#}} \frac{f(y) \{1 - \tau g(y)(f(y)/g(y))'\} dy}{[1 + Rg^2(y) - \tau g(y)(f(y)/g(y))']}$$

$$\xrightarrow{\tau \rightarrow \infty} - \int_{x_-}^{x^{\#}} f(y) dy. \quad (12b)$$

We remark that $\Delta\Phi^{\text{improved}}$ becomes with $g = \text{const}$ and with $f(x)$ piecewise linear an exact result [7c,22].

Here, Equations (11, 12b) present a most accurate approximation to the exact non-Markovian escape time for $\tau \rightarrow \infty$, and $\tau \rightarrow 0$, i.e. $\gamma(x, \tau) \rightarrow \infty$. For other values of noise color, the result in Equation (11) implicitly presents a crossover result, bridging smoothly between the limits of small and large noise color.

We remark that the condition $-g(f/g)' \geq 0$ in (x_-, x_+) can be relaxed without changing the qualitative features of our results (see also in [22]): With $x_-^s(\tau)$, i.e. $(1 - \tau g(f/g)') = 0$ at x_-^s , $x_- \leq x_-^s(\tau) \leq x^{\#}$, the effective diffusion becomes singular at $x_-^s(\tau)$. Escape then predominantly occurs near $x_-^s(\tau)$, i.e. the upper integration limit in Equation (12) is substituted by $x_-^s(\tau)$. The fact that the diffusion is singular at $x_-^s(\tau)$ – just as is also the case for the action-diffusion for the Kramers time at weak friction [1] – nevertheless yields with smooth $\Delta\Phi(R, \tau)$ a well-defined escape time. We also like to point out that the use of $x_-^s(\tau)$, rather than $x_-^c \equiv x_-^s(\tau \rightarrow \infty) < x_-^s(\tau)$, also considerably improves the result for colored noise driven escape at finite τ -values, cf. [18c].

4. Results

From Equations (9–12) we can now establish a variety of general findings. First we shall consider the limit of white noise for both the barrier fluctuations $\zeta(t)$ and the internal thermal noise $\xi(t)$.

4.1. The limit of white noise

For zero noise color $\tau = 0$, the above results in Equations (7–12) become exact. The MFPT in Equation (10) can be evaluated at weak noise up to order $O(T^2)$ to give:

$$\mathcal{T}(R, \tau = 0) \equiv \mathcal{T}(R) = \exp(\Delta\Phi(R)/T) \frac{2\pi}{(|\Phi''(x^{\#})| |\Phi''(x_-)|)^{1/2}}$$

$$\begin{aligned}
& \cdot \left\{ h(x^\#)h(x_-) + T \left[\frac{1}{2} \left(\frac{h''(x^\#)h(x_-)}{|\Phi''(x^\#)|} + \frac{h''(x_-)h(x^\#)}{\Phi''(x_-)} \right) \right. \right. \\
& + \frac{1}{2} \left(\frac{h'(x^\#)h(x_-)\Phi'''(x^\#)}{|\Phi''(x^\#)|^2} - \frac{h(x^\#)h'(x_-)\Phi'''(x_-)}{(\Phi''(x_-))^2} \right) \\
& + \frac{1}{8} \left(\frac{h(x^\#)h(x_-)\Phi''''(x^\#)}{|\Phi''(x^\#)|^2} - \frac{h(x^\#)h(x_-)\Phi''''(x_-)}{(\Phi''(x_-))^2} \right) \\
& \left. \left. + \frac{5}{24} \left(\frac{h(x^\#)h(x_-)(\Phi'''(x^\#))^2}{|\Phi''(x^\#)|^3} + \frac{h(x^\#)h(x_-)(\Phi'''(x_-))^2}{(\Phi''(x_-))^3} \right) \right] \right\}. \quad (13)
\end{aligned}$$

where $\Phi(x)$ is the effective potential

$$\Phi(x) = - \int^x f(1 + Rg^2)^{-1} dy. \quad (14a)$$

and $h(x)$ is a state-dependent form function given by

$$h(x) = (1 + Rg^2(x))^{-1/2}, \quad (14b)$$

which is assumed to be smoothly varying.

The third ($1/8 \dots$) and fourth term ($5/24 \dots$) within the squared brackets in Equation (13) describe the well-known [21] steepest-descent correction to the Smoluchowski escape time, while the additional first and second contribution emerge due to the multiplicative character of the white noise sources, cf. Equation (1).

From Equation (12) we further find

$$\Delta\Phi(R) \leq \Delta\Phi(R = 0). \quad (15)$$

Moreover, from Equations (11) and (15) the escape time $T(R)$ is monotonically *decreasing* with increasing $R = Q/T$, i.e.

$$T(R) \leq T(R = 0). \quad (16)$$

The result in Equation (16) is in agreement with prior studies investigating white noise driven escape over fluctuating barriers [8, 11, 12].

4.2. Case with colored noise

We now turn to the main focus of our work, namely the escape over fluctuating barriers which are modulated by colored noise of *weak-to-moderate-to-strong noise correlation time* τ .

(i) Fixed colored noise intensity. With $T \ll 1$, $Q \ll 1$ let us keep fixed the ratio $R = Q/T$. The colored noise assisted escape time over a fluctuating barrier is then always *enhanced*, i.e.

$$\begin{aligned}
T(R, \tau) & \geq T(R, \tau = 0), \quad \text{with} \\
T(R, \tau) & \rightarrow T(R = 0), \quad \text{as } \tau \rightarrow \infty. \quad (17)
\end{aligned}$$

We note from Equation (12b) that this increase is Arrhenius-like, and it occurs monotonically.

The characteristic behavior in Equations (16, 17) can be made plausible if we observe that in the white noise limit the escape is driven by an *enhanced* state-dependent temperature $T(x, R) = T(1 + Rg^2(x)) > T$, while from Equations (9, 11) colored noise driven escape (at R fixed) is governed by a *lower*, effective temperature $T(x, \tau) = T/(1 - \tau g(f/g)') < T$.

(ii) Resonant activation. If one notes the two inequalities in Equations (16, 17), which are obeyed monotonically, one finds that the overall effective temperature in Equations (9, 11), i.e.

$$\begin{aligned} \hat{T}(x, \tau) &= T(1 + Rg^2(x))\{1 - \tau g(x)(f(x)/g(x))'\}^{-1} \\ &\equiv T^{-1}T(x, R)T(x, \tau) \end{aligned}$$

– which in turn controls the escape process – can be either smaller or larger than T . Therefore, with R not held fixed, but being a function of noise color τ , such that $R(\tau)$ increases with increasing noise color, a *competition* between the monotonic decrease in Equation (16) and the monotonic increase in Equation (17) becomes possible. With $R = R(\tau)$ being increasing with τ , the escape time $\mathcal{T}(R(\tau), \tau)$ can thus attain a minimum at a ‘resonant’ noise correlation time τ_r for which the effective barrier height $\Delta\Phi(R(\tau), \tau)$ assumes a *minimum value*! Setting from Equation (11) $\mathcal{T}(R, \tau) = A(\tau) \exp[\Delta\Phi(R, \tau)/T]$, with $\Delta\Phi(R(\tau), \tau)$ given by Equation (12b), the resonant value (or values) τ_r obeying $d\mathcal{T}(R(\tau), \tau)/d\tau = 0$ can, with $A(\tau) \cong \text{const}$, be estimated from the minimum of $\Delta\Phi(R(\tau), \tau)$, i.e. from (12b)

$$\int_{x_-}^{x^*} f \left\{ \frac{(R(\tau)g^2)g(f/g)' + \left(\frac{dR}{d\tau}\right)g^2(1 - \tau g(f/g)')}{[1 + R(\tau)g^2 - \tau g(f/g)']^2} \right\} dy = 0, \quad (18)$$

which with $f \leq 0, g(f/g)' \leq 0$ within (x_-, x^*) and $(dR/d\tau) > 0$ always possesses, with sufficiently strongly increasing $R(\tau)$, a solution for τ_r . The width of the ‘resonance’ can further be estimated from the inverse of $(d^2\Delta\Phi(R(\tau), \tau)/d\tau^2)$. Most importantly, we note that the value of the ‘resonant’-color time τ_r is not attained at the adiabatic minimum of the fluctuating barrier, but depends *globally* on both the static metastable potential shape (or its force $f(x)$) and the barrier-modulation function $g(x)$. Put differently, modifying slightly the potential *away from the barrier top* dictates already a different ‘resonant’ noise color value τ_r , cf. Figure 1. This resembles very much quantum tunneling where the Gamow-factor for barrier transmission depends globally on the potential shape and not just on the barrier height, as is the case for thermally activated escape [1]. Within the piecewise linear barrier model driven by two-state noise in [6] the authors implicitly used $Q/\tau = \text{const} = C$; i.e. $R(\tau) = Q/T = C\tau/T$ indeed increases with increasing noise color τ .

Thus, upon inspecting Equation (11) with $R(\tau)$ being a function of noise color τ , the effective barrier $\Delta\Phi(R, \tau)$ in Equation (12b) exhibits one amongst

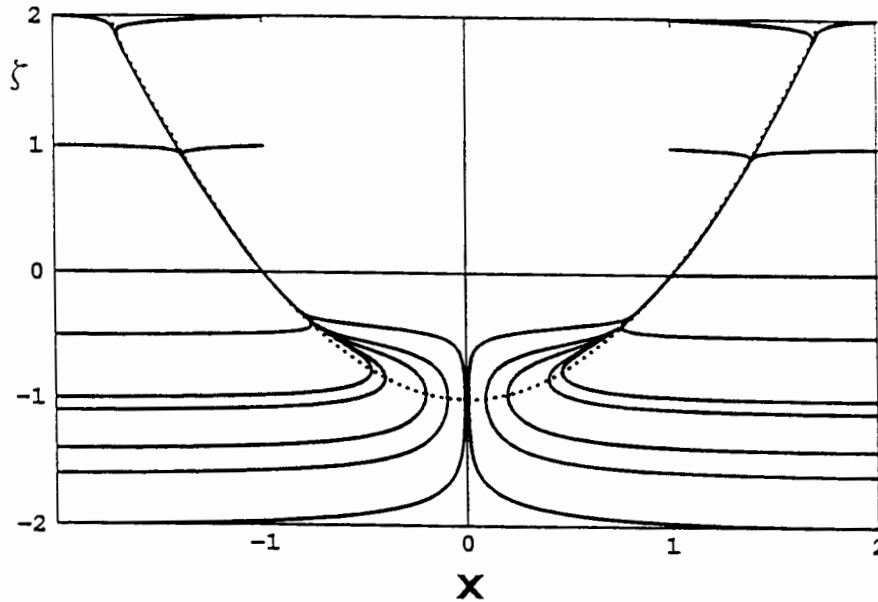


Fig. 2. Deterministic trajectories for the archetypal Landau flow: $\dot{x} = x - x^3 + x\zeta$; $\dot{\zeta} = -\zeta/\tau$, for the noise correlation time $\tau = 15$. The dotted line depicts the line of turning points $\varepsilon(x) = x^2 - 1$. The separatrix is given by the line $x = 0$.

the following three characteristic behaviors: (I) with a solution of Equation (18) at finite τ , the effective barrier depicts a minimum as a function of increasing τ ; (II) with Equation (18) obeyed only for $\tau \rightarrow \infty$ the effective barrier increases towards an asymptotically flat value as $\tau \rightarrow \infty$; (III) with $R(\tau)$ not sufficiently increasing with τ the behavior is as in Equation (17).

(iii) Symmetries. We next consider *symmetric* bistable potentials $U(x)$ such that $-U'(x) = f(x) = -f(-x)$ is an odd function. The flow in Equations (3, 4) then exhibits a different symmetry depending whether the barrier modulation function $g(x)$ is even or odd, respectively; i.e.

$$\text{inversion symmetry: } x \rightarrow -x, \quad \zeta \rightarrow -\zeta, \quad \text{if } g(x) = g(-x) \quad (19)$$

$$\text{reflection symmetry: } x \rightarrow -x, \quad \zeta \rightarrow +\zeta, \quad \text{if } g(x) = -g(-x). \quad (20)$$

These symmetries drastically impact the behavior of the separatrix, which divides the deterministic domain of attraction of the bistable flow in Equations (3, 4). With an odd modulation, the separatrix is described by the line $x = 0$, whereas for even $g(x)$ (e.g. $g(x) = \text{const}$) the separatrix is moving into the $x - \zeta$ -plane, crossing at $(x = \zeta = 0)$ from left to right [18c, 23].

(iv) Behavior at extreme noise ratios R . It turns out that the behavior for $T(R, \tau)$ exhibits a different asymptotic behavior depending on whether $Q/T = R \ll 1$, or $R \gg 1$. In the latter case the escape is dominated by the noise intensity Q , rather than T . Putting a particle initially at $x = x_-$, the escape dynamics within the (x, ζ) -phase space of Equations (3, 4) closely

follows for $R \gg 1$ the line $\varepsilon(x) = -f(x)/g(x)$, where the deterministic flow lines (i.e. $T = Q = 0$ in Equations (3, 4)) exhibit turning points, i.e. $d\zeta/dx = \infty$, see Figure 2. If we denote by ζ_M the maximum of $|f(x)/g(x)|$ within $(x_-, x^\#)$, the asymptotic behavior for $T(R \gg 1, \tau)$ reads

$$T(R \gg 1, \tau) = T(R)(1 + O(\tau)) \exp \left[\tau(\zeta_M^2 + O(R^{-1}))/2Q \right]. \quad (21)$$

Note that for $\tau \rightarrow \infty$, the exponential increase given by the last term dominates over all the remaining contributions.

For the bistable symmetric Landau potential with a fluctuating curvature [22], i.e. $f(x) = ax - bx^3$, $g(x) = x$, one finds $\zeta_M = a$, i.e. Equation (11) yields

$$\begin{aligned} T(R \gg 1, \tau) = & T(R)(1 + 2a\tau)^{1/2} \\ & \times \exp \left\{ \tau \left[\frac{a^2}{2} + \frac{ab}{R} \left(1 - \ln \left(1 + \frac{a}{b} R \right) \right) \right. \right. \\ & \left. \left. + O(R^{-2}, R^{-2} \ln R) \right] / Q \right\}, \end{aligned} \quad (22)$$

while in the opposite limit, $R \ll 1$, which is problematic within the conventional UCNA, cf. below Equation (9), the escape time behaves as

$$T(R \ll 1, \tau) = T(R)(1 + 2a\tau)^{1/2} \exp(a^3\tau/6bT), \quad a\tau < 1. \quad (23)$$

This makes explicit that in the latter case with $Q \rightarrow 0$, $T \rightarrow 0$, $T \gg Q$, the escape is dominated by the additive thermal noise $\xi(t)$.

4.3. Correlated noise sources

Throughout the above analysis we assumed that the colored noise $\zeta(t)$ driving the barrier fluctuations and the internal white noise $\xi(t)$ were *not* correlated. This assumption, however, might not always hold a priori. In particular, when the barrier fluctuations are not imposed externally by the experimenter, but rather are the result of strong couplings to random nonequilibrium environments, additive and multiplicative noise contributions likely become correlated. Within our approach, such a correlation can be described by setting in Equations (3, 4) $\langle \eta(t)\xi(s) \rangle = \rho\delta(t-s)$ with $|\rho| \leq 1$, which guarantees a positive definite diffusion tensor. The corresponding UCNA–Fokker–Planck equation becomes rather complex, reading explicitly

$$\begin{aligned} \dot{p}_t = & -\frac{\partial}{\partial x} \left(\left\{ C^{-1}(x, \tau)f + Q(gC^{-1}(x, \tau))(gC^{-1}(x, \tau))' \right. \right. \\ & \left. \left. + TC^{-1}(x, \tau)(C^{-1}(x, \tau))' + \rho\sqrt{QT} C^{-1}(x, \tau) \right. \right. \\ & \left. \left. \times \left[(gC^{-1}(x, \tau))' + g(C^{-1}(x, \tau))' \right] \right\} p_t \right) \\ & + T \frac{\partial^2}{\partial x^2} \left(\left\{ C^{-2}(x, \tau)[1 + Rg^2 + 2\rho\sqrt{R}g] p_t \right\} \right), \end{aligned} \quad (24)$$

where $C(x, \tau) = 1 - \tau g(f/g)'$ has been used. For the corresponding Arrhenius factor one obtains from Equation (24) the result

$$\Delta\Phi(R, \tau, \rho) = - \int_{x_-}^{x^\#} \frac{f\{1 - \tau g(f/g)'\}}{[1 + Rg^2 + 2\rho\sqrt{Rg}]} dy. \quad (25)$$

Equation (25) again can be improved by setting

$$\Delta\Phi^{\text{improved}}(R, \tau, \rho) = - \int_{x_-}^{x^\#} \frac{f\{1 - \tau g(f/g)'\}}{[1 + Rg^2 + 2\rho\sqrt{Rg} - \tau g(f/g)']} dy. \quad (26)$$

For the important case of a symmetric static barrier, $f(x) = -f(-x)$ and symmetric barrier modulations $W(x) = W(-x)$, i.e. $g(x) = -g(-x)$, the forward and backward escape times $T(R, \tau)$ are no longer equal. From Equations (25, 26) we find with $\rho > 0$: $T_+(R, \tau = 0, \rho) < T_+(R, \tau, \rho)$, and $T_+(R, \tau, \rho) > T_-(R, \tau, \rho) > T_-(R, \tau = 0, \rho)$, where we assumed $g(x - x^\#) < 0$, for $(x - x^\#) < 0$. Here T_\pm denotes the forward ($x_- \rightarrow x_+$) and backward ($x_+ \rightarrow x_-$) escape time, respectively. For zero noise color $\tau = 0$, the *above effective barrier becomes exact*, yielding $T_+(R, \rho) > T_-(R, \rho)$, $\rho > 0$. However, we find that $T_+(R, \rho) \leq T(R = 0)$ generally is *no longer* obeyed. This is so, because the two contributions Rg^2 and $2\rho\sqrt{Rg}$ making up the diffusion coefficient are with $g < 0$ in $(x_-, x^\#)$ of different sign. We thus have the paradoxical finding that in presence of additional white noise $\zeta(t)$ the escape time T_+ – contrary to common belief – can *increase* (correlated slow-down of escape!).

4.4. Influence of quantum tunneling

The escape over fluctuating barrier configurations has thus far been treated solely classical. At low temperatures, the noise sources characterizing environmental fluctuations $\xi(t)$ and/or the fluctuations which control the barrier shape become influenced by quantum effects. The typical temperature scale at which tunneling effects compete with thermal hopping is given by the crossover temperature T_0 [1]

$$T_0 \sim \hbar\omega_b(2\pi k_B)^{-1}, \quad (27)$$

where ω_b denotes a characteristic (average) value for angular frequency at the barrier top. It has been demonstrated elsewhere [27] that within quantum transition state theory the quantum noise near and above T_0 can approximatively be accounted for by merely raising the noise temperature (or noise intensity, respectively) according to

$$T \rightarrow T \left[1 - \hbar^2(\omega_0^2 + \omega_b^2)/(24T\Delta U)^{-1} \right]. \quad (28)$$

Here, ω_0^2 denotes a characteristic value for the curvature at well bottom and ΔU characterizes the average barrier height. At even lower temperatures

$T < T_0$, the analysis of the escape requires a detailed study for a metastable, stationary nonequilibrium *quantum system*.

5. Conclusions and outlook

There are a number of further investigations suggested by our general study of noise – assisted escape over fluctuating barriers. The role of *correlated* noise sources certainly deserves future research efforts. Another area which remained untouched is the study of inertia effects, and more generally, the influence of additional relevant degrees of freedom, i.e. the role of multidimensional (fluctuating) barrier crossing [24]. In presence of colored noise sources this latter task obviously becomes very difficult [1, 18c, 18d].

We could demonstrate that the phenomenon of ‘resonance-like’ escape in [6] is generic if the noise temperature $Q(\tau)$ is sufficiently strongly increasing with increasing noise color τ . This resonance essentially occurs when the color-induced effective barrier in Equation (12b) assumes a minimal value: Its minimum depends globally on both the static potential shape $U(x)$ and the barrier modulation $W(x)$. In the context of surmounting fluctuating barriers in metastable nanostructures, the influence of *non-Gaussian statistics* (e.g. shot-noise) for both the colored noise source $\zeta(t)$ and the white noise $\xi(t)$ is of interest as well. The author hopes to return to this latter area in a future study.³

Acknowledgements

This research was supported by the Volkswagen-Stiftung. Discussions with B. J. Berne, P. Pechukas, and P. Jung are acknowledged.

References

1. P. Hänggi, P. Talkner, and M. Borkovec, *Rev. Mod. Phys.* **62**, 251 (1990).
2. V. I. Melnikov, *Phys. Rep.* **209**, 1 (1991).
3. P. G. De Gennes, *J. Stat. Phys.* **12**, 463 (1975); R. Zwanzig, *Proc. Nat. Acad. Sci. USA* **85**, 2029 (1988); K. Binder and A. P. Young, *Rev. Mod. Phys.* **58**, 801 (1986).
4. H. Frauenfelder and P. G. Wolynes, *Science* **229**, 337 (1985); M. Karplus and J. A. McCammon, *CRC Crit. Rev. Biochem.* **9**, 293 (1981); D. L. Stein and P. W. Anderson, *Proc. Nat. Acad. Sci. USA* **80**, 3386 (1983); N. Agmon and J. J. Hopfield, *J. Chem. Phys.* **79**, 2042 (1983).
5. J. Maddox, *Nature* **359**, 771 (1992).
6. C. R. Doering and J. C. Gadoua, *Phys. Rev. Lett.* **69**, 2318 (1992).

³ For two-state noise, the *exact* result for the escape time $\mathcal{T}(R, \tau, \rho = \pm 1)$ follows from Equation (11) in [25], or Equation (3.5) in [26], which both give the inverse escape time (i.e. the flux-overpopulation escape rate) in terms of two quadratures.

7. U. Zürcher and C. R. Doering, *Phys. Rev. E* **47**, 3862 (1993); C. Van den Broeck, *Phys. Rev. E* **47**, 4579 (1993); P. Hänggi, *Chem. Phys.* **180**, 157 (1994); P. Reimann, *Phys. Rev. E* **49**, 4938 (1994).
8. P. Hänggi, *Phys. Lett.* **78A**, 304 (1980).
9. T. Fonesca, P. Grigolini, and P. Marin, *Phys. Lett.* **88A**, 117 (1981); S. Faetti, P. Grigolini, and F. Marchesoni, *Z. Phys. B* **47**, 353 (1982); H. Fujisaka and S. Großmann, *Z. Phys. B* **43**, 69 (1981).
10. P. Jung, Th. Leiber, and H. Risken, *Z. Phys. B* **66**, 397 (1987); *Z. Phys. B* **68**, 123 (1987); R. F. Fox and R. Roy, *Phys. Rev. A* **35**, 1838 (1987).
11. D. L. Stein, R. G. Palmer, J. L. Van Hemmen, and C. R. Doering, *Phys. Lett. A* **136**, 4668 (1989).
12. D. L. Stein, C. R. Doering, R. G. Palmer, J. L. Van Hemmen, and R. M. McLaughlin, *J. Phys. A* **23**, L203 (1990).
13. C. W. J. Beenakker and H. Van Houten, in *Semiconductor Heterostructures and Nanostructures*, G. Ehrenreich and D. Turnbull (Eds.), Academic, New York (1991); *Adv. Solid State Phys.* **29**, 1 (1989).
14. R. Benzi, A. Sutura, and A. Vulpiani, *J. Phys. A* **14**, L 453 (1981); C. Nicolis, *Tellus* **34**, 1 (1982); B. McNamara, K. Wiesenfeld, and R. Roy, *Phys. Rev. Lett.* **60**, 2626 (1988); P. Jung and P. Hänggi, *Europhys. Lett.* **8**, 505 (1989); L. Gammaitoni, F. Marchesoni, E. Menichella-Saetti, and S. Santucci, *Phys. Rev. Lett.* **62**, 349 (1989); *Phys. Rev. A* **40**, 2114 (1989); P. Jung and P. Hänggi, *Phys. Rev. A* **44**, 8032 (1991); R. F. Fox and Y. N. Lu, *Phys. Rev. E* **48**, 3390 (1993).
15. F. Moss, *Ber. Bunsenges. Phys. Chemie* **95**, 303 (1991); P. Jung, *Phys. Rep.* **234**, 175 (1993).
16. P. Hänggi, *Z. Phys. B* **31**, 407 (1978).
17. H. Dekker, *Phys. Lett.* **90A**, 26 (1982); M. San Miguel and J. M. Sancho, *Phys. Lett.* **76A**, 97 (1980); R. F. Fox, *Phys. Lett. A* **94**, 281 (1983).
18. P. Jung and P. Hänggi, *Phys. Rev. A* **35**, 4464 (1987); *J. Opt. Soc. Am.* **B5**, 979 (1988); P. Hänggi, P. Jung, and F. Marchesoni, *J. Stat. Phys.* **54**, 1367 (1988); P. Hänggi and P. Jung, *Adv. Chem. Phys.* **89**, 239 (1994).
19. R. F. Fox, *Phys. Rev. A* **37**, 911 (1988); M. Aguado and M. San Miguel, *Phys. Rev. A* **37**, 450 (1988); Th. Leiber, F. Marchesoni, and H. Risken, *Phys. Rev. A* **38**, 983 (1988); L. Schimansky-Geier and Ch. Zülicke, *Z. Phys. B* **79**, 451 (1990); Li Cao, D. Wu, and X. Luo, *Phys. Rev. A* **47**, 57 (1993).
20. H. S. Wio, P. Colet, M. San Miguel, L. Pesquera, and M. A. Rodriguez, *Phys. Rev. A* **40**, 7212 (1989).
21. R. S. Larson and M. D. Kostin, *J. Chem. Phys.* **68**, 4821 (1978); O. Edholm and O. Leimar, *Physica A* **98**, 313 (1979); W. Bez and P. Talkner, *Phys. Lett. A* **82**, 313 (1981).
22. A. J. R. Madureira, P. Hänggi, V. Buonomano and W. A. Rodrigues *Escape from a Fluctuating Double Well*, *Phys. Rev. E* (submitted).
23. P. Hänggi, P. Jung, and P. Talkner, *Phys. Rev. Lett.* **60**, 2804 (1988); C. R. Doering, R. J. Bagley, P. S. Hagan, and C. D. Levermore, *Phys. Rev. Lett.* **60**, 2805 (1988).
24. N. Agmon and J. J. Hopfield, *J. Chem. Phys.* **78**, 6947 (1983); N. Agmon and R. Kosloff, *J. Phys. Chem.* **91**, 1988 (1987); M. M. Klosek, B. M. Hoffman, B. J. Matkowsky, A. Nitzan, M. A. Ratner, and Z. Schuss, *J. Chem. Phys.* **95**, 1425 (1991); A. M. Berezhkovskii, E. Pollak, and V. Yu. Zitserman, *J. Chem. Phys.* **97**, 2422 (1992).
25. P. Hänggi and P. Riseborough, *Phys. Rev. A* **27**, 3379 (1983).
26. C. Van den Broeck and P. Hänggi, *Phys. Rev. A* **30**, 2730 (1984).
27. P. Hänggi, H. Grabert, G. Ingold, and U. Weiss, *Phys. Rev. Lett.* **55**, 761 (1985).