Thermally activated escape over potential barriers is of relevance in a large variety of physical, chemical, and biological contexts. In the most common case, a potential barrier $\Delta U$ much larger than the thermal energy $kT$ yields an escape rate exponentially small in $\Delta U/kT$. A first major generalization, of importance for conceptual reasons as well as due to numerous applications, is periodically modulated potentials, resulting in a renormalization of $\Delta U$ which depends in a very complicated manner on the details of the model. In all these cases the rate is thus a very rapidly increasing function of the temperature $T$. In our present work, the main focus is on the complementary case of a static potential and a time dependent temperature. In particular, we will demonstrate that in a suitably chosen, but still fairly simple and generic potential landscape, the escape rate of the unperturbed system at constant temperature may decrease upon temporally increasing the temperature. In view of the above mentioned results for constant temperature, this is a quite unexpected and counter-intuitive result. Indeed, given that thermal noise is indispensable to escape, one would expect that an “extra dose” of noise should always enhance escape. Somewhat reminiscent previous findings always concern quite different types of systems: Dissipative quantum tunneling in the deep cold non-dynamical systems [12]. As our main tool, we put forward a new path integral approach, which unifies and extends several related approximations [2, 3, 4, 5, 6, 13, 14]. Briefly, in different parameter regimes of the temporal modulations, the most relevant escape paths are of quite different character. Therefore, each regime was so far treated separately and the crossover omitted. Here, all potentially relevant paths are represented in terms of a suitable, one-dimensional parametrization and are kept till the final rate formula via an integral over all of them.

We consider the overdamped 1D Langevin equation

$$\eta(t) \dot{x}(t) = -U'(x(t),t) + \sqrt{2\eta(t)kT(t)} \xi(t)$$

with time-dependent friction $\eta(t) > 0$, temperature $T(t) > 0$, and potential $U(x,t)$. Dot and prime indicate temporal and spatial derivatives, $k$ is Boltzmann’s constant, and thermal fluctuations are modeled as usual by $\delta$-correlated Gaussian noise $\xi(t)$. For $T \to 0$, the deterministic dynamics is required to exhibit exactly one stable orbit (attractor) $x_s(t)$ and one unstable orbit (repeller) $x_u(t) > x_s(t)$. Our main interest concerns the noise induced transitions of $x(t)$ across $x_u(t)$ for small but finite temperatures $T(t)$, quantified by the rate $\Gamma(t) := -\dot{n}(t)$ at which the probability $n(t)$ that $x(t) \leq x_u(t)$ changes in time.

To avoid unnecessary complications, we focus on initial conditions $x(0) = x_s(0)$, and we require the existence of $D := \lim_{t \to -\infty} \int_0^t dr b(r)$ with $b(t) := kT(t)/\eta(t)$. Next, we divide $D$ by $\eta(t)$ and employ transformed times $\tilde{t}(t) := \int_0^t dr /D$, positions $\tilde{x}(\tilde{t}) := x(t(\tilde{t}))$, and forces $\tilde{F}(x,\tilde{t}) := -D U'(x(t(s)), t(s))/kT(t(s))$, yielding, after dropping again the tildes,

$$\dot{x}(t) = F(x(t), t) + \sqrt{2D} \xi(t).$$

In the general formalism, we will work with [2], with specific examples will refer to [11]. The corresponding (back-)transformation of the rates $\tilde{\Gamma}(t) = b(t) \tilde{\Gamma}(\tilde{t}(t))/D$ readily follows from the obvious transformation of the probabilities $\tilde{n}(t) = n(t(\tilde{t}))$.

We first recall some basics, previously derived and discussed in detail in Refs. [5]: For any given initial condition $x(0) = x_0$, the probability density to find the stochastic process [2] at any “final” time $t_f > t_0$ at the position $x_f$ can be represented as path-integral

$$\rho(x_f, t_f \mid x_0, t_0) = \int_{x(\tau_0) = x_0}^x \mathcal{D}x(t) e^{-S[x(t)]/D},$$

with action $S[x(t)] := \int_{x_0}^{x_f} dt [\dot{x}(t) - F(x(t), t)]^2/4$. Once this formal integral is evaluated, the rate follows as

$$\Gamma(t) = -D \partial_x \rho(x_u(t), t \mid x_s(t_0), t_0) / \partial x_u(t).$$

For small $D$, the integral [3] is dominated by the path $q(t)$ which minimizes the action $S[q(t)]$ and thus satisfies the Euler-Lagrange equation

$$\tilde{p}(t) = -\partial_q S[q(t)], \quad p(t) := \dot{q}(t) - F(q(t), t) \quad \text{with boundary conditions} \quad q(t_0) = x_0 \quad \text{and} \quad q(t_f) = x_f.$$  

Accounting for all paths $x(t)$ “close” to $q(t)$ by means of a functional saddle point approximation in [3] yields

$$\rho(x_f, t_f \mid x_0, t_0) = [4\pi DQ(t_f)]^{-\frac{1}{2}} e^{-S[q(t)]/D},$$

where $Q(t_f) := \int_{x(0) = x}^x \mathcal{D}x(t) e^{-S[x(t)]/D}$.

The problem of thermally activated escape over a potential barrier is solved by means of path integrals for one-dimensional reaction dynamics with very general time-dependences. For a suitably chosen, but still quite simple static potential landscape, the net escape rate may be substantially reduced by temporally increasing the temperature above its unperturbed, constant level.

PACS numbers: 05.40.-a, 82.20.Pm, 02.50.Ey
where $Q(t)$ satisfies $Q(t_0) = 0$, $\dot{Q}(t_0) = 1$, and
\[
\dot{Q}(t) = \frac{d}{dt}[2Q(t) F'(q(t), t)] - Q(t) p(t) F''(q(t), t). \tag{7}
\]

Eqs. (4), (5) yield an approximation to the rate $\Gamma(t)$, which in principle becomes asymptotically exact as $D \to 0$ for any given $t > t_0$ with a unique absolute minimum of $S(x(t))$, which generically is the case. But under many circumstances of foremost interest (e.g., relatively large $t - t_0$) even fairly small $D$ are still far from this asymptotic regime, i.e., the saddle point approximation (6) does not properly account for all relevant paths in (3): Basically, a typical escape path $x(t)$ spends almost all its time near $x_s(t)$, then crosses over into the vicinity of $x_u(t)$, and remains there for the rest of its time. Any other behavior would yield a much larger action $S[x(t)]$ and thus is negligible in (6). However, rather different cross over “time windows” may still lead to almost equal $S[x(t)]$, and a simple saddle point approximation is unable to properly account for such quite remote regions in path space. In some cases, there may exist local minima of $S[x(t)]$ and additional saddle point approximations around each of them may save the case (3).

The remaining problem is to keep track of all relevant minima and not to double count their neighborhoods if they get too close in path space. In other cases, e.g., for $t$-independent $y$, $T$, and $U$ in (11), there is a continuous “soft direction” in path space, invalidating plain saddle point methods altogether (3).

To overcome these problems we impose on top of the boundary conditions $x(t_0) = x_s(t_0)$ and $x(t_f) = x_u(t_f)$ the extra condition that $x(t_f)$ arrives at some intermediate point $x_i$ at a given time $t_i$, and in the end integrate over all $t_i \in [t_0, t_f]$ (12). The pertinent formal relation, satisfied by the conditional probability density (3), is
\[
\rho(x_f, t_f| x_0, t_0) = \int_{t_0}^{t_f} dt_i \rho(x_f, t_f| x_i, t_i) \Psi_x(t_i| x_0, t_0) \tag{8}
\]
where $\Psi_x(t| x_0, t_0)$ denotes the first passage time density across $x$, given $x(t_0) = x_0$. For simplicity only, we assume from now on that $x_i$ is located well in between $x_s(t)$ and $x_u(t)$ and is $t$-independent. Then, all non-negligible paths in (3) starting from $x(t_i) = x_i$ must immediately cross over to $x_u(x_i)$ and thus admit for $\rho(x_f, t_f| x_i, t_i)$ in (8) a saddle point approximation (6) free of all the above mentioned problems. Focusing on $x_0 = x_s(t_0)$ according to (4), an analogous approximation (6) holds for $\rho(x_i, t_i| x_0, t_0)$, since all relevant paths in (3) now may leave the vicinity of $x_s(t)$ only in the very end. By definition, $\rho(x_i, t_i| x_0, t_0)dx_i$ is the probability that $x(t)$ from (2) is encountered within $[x_i, x_i + dx_i]$, at time $t_i$, given $x(t_0) = x_0 = x_i(t_0)$. Most such $x(t)$ closely resemble the most probable path $q(t)$ connecting $q(t_0) = 0$ with $q(t_i) = x_i$. On the other hand $\Psi_x(t_i| x_0, t_0)dt_i$ is the probability that $x(t)$ crosses $x_i$ for the first time during $t \in [t_i, t_i + dt_i]$. It seems reasonable to guess that most such $x(t)$ once again closely resemble $q(t)$. Hence, $\rho(x_i, t_i| x_0, t_0)dx_i$ will essentially account for the same “events” as $\Psi_x(t_i| x_0, t_0)dt_i$, provided we relate the considered intervals $dx_i$ and $dt_i$ via $dx_i = \dot{q}(t_i)dt_i$. Up to finite-$D$ corrections we thus obtain
\[
\Psi_x(t_i| x_0, t_0) = \dot{q}(t_i) \rho(x_i, t_i| x_0, t_0), \tag{9}
\]
where $q(t)$ satisfies $q(t_0) = x_0 = x_s(t_0)$, $q(t_i) = x_i$, and (2). More rigorously, our key relation (9) follows by adapting Ref. (16) to evaluate the derivative by (8) in the limit $\dot{x}_f \to x_i$. Details will be given elsewhere.

The evaluation of the escape rate (11) by means of (8), (9), and (6) is the first main result of our present work. Similarly as in (3), (4), (5, 6), closed analytical solutions of the concomitant differential equations (5) are only possible for special $F(x, t)$. To this end, we focus on piecewise parabolic potentials $U(x, t)$ in (11), corresponding to piecewise linear force fields in (2) of the form
\[
F(x \leq 0, t) = \lambda_s(t)(x - y_s(t)) + f(t)
\]
\[
F(x > 0, t) = \lambda_u(t)(x - y_u(t)) + f(t) \tag{10}
\]
with $\lambda_s(t)y_s(t) = \lambda_u(t)y_u(t)$ (continuity at $x = 0$). Further, the existence of stable and unstable orbits with $x_s(t) < x_i$ and $x_u(t) > x_i$ is required, in particular $y_s(t), \lambda_s(t) < 0, y_u(t), \lambda_u(t) > 0$. For the natural choice $x_i = 0$, a straightforward but somewhat tedious calculation (6) then yields for the rate (11) the result
\[
\Gamma(t) = \int_{t_0}^{t} d\tau \frac{Z(t, \tau, t_0)}{D} e^{-\Phi(t, \tau, t_0)/D} \tag{11}
\]
\[
\Phi(t, \tau, t_0) := \frac{x_s^2(\tau)}{4I_s(\tau, t)} + \frac{x_u^2(\tau)}{4I_u(\tau, t_0)} \tag{12}
\]
\[
Z(t, \tau, t_0) := \frac{[Y(\tau, t_0) - y_s(\tau)]y_s(\tau)}{8\pi[I_s(\tau, t) I_u(\tau, t_0)]^{3/2}} \tag{13}
\]
\[
Y(\tau, t_0) := I_s(\tau, t_0)[f(\tau) - y_s(\tau) \lambda_s(\tau)] \tag{14}
\]
\[
\Lambda_{s,u}(t_0, \tilde{t}) := 2 \int_{t_0}^{t} d\tau \lambda_{s,u}(\tau) \tag{15}
\]
\[
I_{s,u}(t_0, \tilde{t}) := \int_{t_0}^{t} d\tau e^{\Lambda_{s,u}(t, \tau)} \tag{16}
\]

We have verified that previous findings for time-periodic (3, 4, 6) and time-independent systems (11, 12) are recovered as special cases. Those from (4) are formally similar but contain quantities (called $\mathcal{E}$ and $s(\phi)$) which are not explicitly available in general.

As a first example we consider the dynamics (11) with constant friction $\eta(t) \equiv 1$, a temperature pulse $T(t)$ according to Fig. 1a, and a static, piecewise parabolic potential $U(x)$, see Fig. 1b. Already for the moderately small temperatures from Fig. 1c, the accuracy of the analytical approximation (11) is quite good. We found that it quickly improves even further upon decreasing temperatures. After initial transients (omitted in Fig. 1c), Kramers rate is recovered until the temperature pulse

\[
\frac{\partial \rho}{\partial t} = \frac{\delta}{\delta x} F(q, t) \rho(q, t) \tag{7}
\]
sets in at $t = 0$. Then, the rate rapidly increases and approaches the Kramers rate corresponding to $T_0 + \Delta T$, provided the pulse lasts sufficiently long. Finally, an analogous relaxation back to the original Kramers rate follows. Discontinuities of $T(t)$ entail jumps of $\Gamma(t)$. While the initial transients are well understood [14], to the best of our knowledge no previously existing analytical approximation would be able to faithfully describe the “perturbed and interfering transients” for largely arbitrary pulses and pulse-sequences.

Next, we consider [1] with a periodically pulsating temperature $T(t)$ and a piecewise parabolic potential $U(x)$ exhibiting two barriers and two wells, see Fig. 2. Transitions from $x_1^0$ to $x_2^0$ are described by the rate $\Gamma_{1-2}(t)$, those from $x_2^0$ to $x_1^0$ by $\Gamma_{2-1}(t)$, and those from $x_2^0$ towards $x = \infty$ by $\Gamma_{2-\infty}(t)$. After suitable time- and space-transformations (cf. [2]), each rate can be approximated according to [11]. Since they are small (transitions are rare), it is sufficient – as far as the populations $n_1(t)$ and $n_2(t)$ of the two wells are concerned – to consider their averages over one period $T$, denoted by $\bar{\Gamma}_{1-2}$, $\bar{\Gamma}_{2-1}$, and $\bar{\Gamma}_{2-\infty}$. Then, the populations $\bar{n}(t) := (n_1(t), n_2(t))$ are governed by the master equation [1] $\dot{\bar{n}}(t) = -M \bar{n}(t)$ with matrix elements $M_{11} = -M_{21} = \bar{\Gamma}_{1-2}$, $M_{12} = -\bar{\Gamma}_{2-1}$, and $M_{22} = \bar{\Gamma}_{2-1} + \bar{\Gamma}_{2-\infty}$. The smallest eigenvalue of $M$ is denoted by $\bar{\Gamma}$ and represents the ultimate rate of escape towards $\infty$ after initial relaxation processes, governed by the other eigenvalue of $M$, have died out. Since the two eigenvalues differ by a huge, Boltzmann-Arrhenius-type factor, the total probability $n_1(t) + n_2(t)$ that $x(t) < x_0^0$ is expected and numerically observed to actually exhibit a practically perfect exponential decay $e^{-\bar{\Gamma} t}$ for all $t > 0$. The analytical results for $\bar{\Gamma}$ are depicted in Fig. 2c. Their agreement with our numerical findings for the decay rate (not shown) is comparable to Fig. 1c.

The most striking feature of Fig. 2c is a substantial reduction of the net escape rate $\bar{\Gamma}$ upon superimposing temperature pulses of suitable duration $\tau$ and amplitude $\Delta T$ to the “unperturbed” temperature $T_0$. Roughly speaking, $\bar{\Gamma}(t)$ in Fig. 1b approaches the instantaneous Kramers rate the quicker, the larger the curvatures in
Fig. 1b are [14]. Since the curvatures relevant for $\bar{\Gamma}_{2-1}$ are larger than those for $\bar{\Gamma}_{1-2}$ and $\bar{\Gamma}_{2-\infty}$ (see Fig. 2b), sufficiently small $\tau$ mainly affect $\bar{\Gamma}_{2-1}$ and thus lead to a reduction of the net decay rate $\bar{\Gamma}$. We verified that already a single temperature pulse (Fig. 1a) indeed yields an analogous reduction of escapes events. Fig. 2c further shows that the effect is overruled by competing secondary effects when $\tau$ and/or $\Delta T$ become too small. Finally, we have obtained very similar results also for $U(x^*_1) < U(x^*_2)$, but from the viewpoint of equilibrium rates [1], the case $U(x^*_1) > U(x^*_2)$ shown in Fig. 2 seems even more surprising to us.

Experimentally, potentials like in Fig. 2b are ubiquitous in the context of chemical reactions. E.g. in the modified case $U(x^*_1) < U(x^*_2)$ these are reactions proceeding in two-steps via an intermediate (metastable state $x^*_2$). Temperature pulses could be generated, among others [7], by means of a flashing black body radiator. More realistic are short laser pulses [17], whose basic effects (on the reacting molecules and their environment) may still be roughly modeled by a temperature pulse. On the other hand, we expect that our above mentioned main finding will be qualitatively robust against various modifications of the pulsed perturbation, including more realistic models for tailored laser pulses. A further experimental playground are colloidal particles in a suitably designed potential landscape by exploiting light [18], di-electrophoretic [19], or magnetic [20] forces. Temperature pulses in the form of acousto-mechanical white noise may be generated by means of piezo elements [21].

Since temperature pulses in [1] are basically equivalent to potential modulations in [2], we arrive at yet another quite astonishing conclusion: The escape rate for a $t$-independent temperature and a potential landscape as in Fig. 2b may decrease if the amplitude (multiplicative factor) of the potential is temporarily reduced without any other change of its “shape”. This effect should be readily observable with colloidal systems [18, 19, 20] and possibly also with cold atoms in laser induced optical lattices [22] or in complex reaction networks [23].

We thank B. Gentz for stimulating discussions. This work was supported by DFG under SFB 613.

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