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Nils Berglund

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Kramers' law: Validity, derivations and generalisations

Nils Berglund

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Abstract

Kramers' law describes the mean transition time of an overdamped Brownian particle between local minima in a potential landscape. We review different approaches that have been followed to obtain a mathematically rigorous proof of this formula. We also discuss some generalisations, and a case in which Kramers' law is not valid. This review is written for both mathematicians and theoretical physicists, and endeavours to link concepts and terminology from both fields.

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1 Introduction

The overdamped motion of a Brownian particle in a potential V is governed by a first-order Langevin (or Smoluchowski) equation, usually written in the physics literature as

$$\dot{x} = -\nabla V(x) + \sqrt{2\varepsilon}\,\xi_t \;, \tag{1.1}$$

where ξ_t denotes zero-mean, delta-correlated Gaussian white noise. We will rather adopt the mathematician's notation, and write (1.1) as the Itô stochastic differential equation

$$\mathrm{d}x_t = -\nabla V(x_t)\,\mathrm{d}t + \sqrt{2\varepsilon}\,\mathrm{d}W_t \;, \tag{1.2}$$

where W_t denotes d-dimensional Brownian motion. The potential is a function $V : \mathbb{R}^d \to \mathbb{R}$, which we will always assume to be smooth and growing sufficiently fast at infinity.

The fact that the drift term in (1.2) has gradient form entails two important properties, which greatly simplify the analysis:

1. There is an invariant probability measure, with the explicit expression

$$\mu(\mathrm{d}x) = \frac{1}{Z}\,\mathrm{e}^{-V(x)/\varepsilon}\,\mathrm{d}x \;, \tag{1.3}$$

   where Z is the normalisation constant.
2. The system is *reversible* with respect to the invariant measure μ, that is, the transition probability density satisfies the *detailed balance condition*

$$p(y,t|x,0)\,\mathrm{e}^{-V(x)/\varepsilon} = p(x,t|y,0)\,\mathrm{e}^{-V(y)/\varepsilon} \;. \tag{1.4}$$

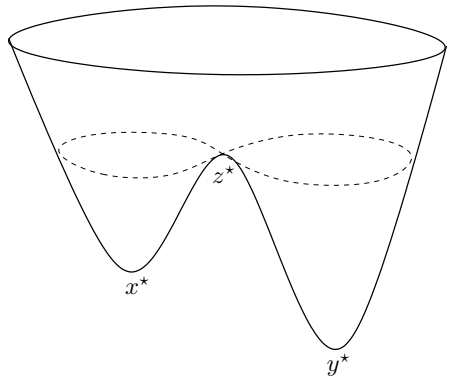

FIGURE 1. Graph of a potential V in dimension $d = 2$, with two local minima $x^\star$ and $y^\star$ and saddle $z^\star$.

The main question we are interested in is the following. Assume that the potential V has several (meaning at least two) local minima. How long does the Brownian particle take to go from one local minimum to another one?

To be more precise, let $x^\star$ and $y^\star$ be two local minima of V, and let $\mathcal{B}_\delta(y^\star)$ be the ball of radius δ centred in $y^\star$, where δ is a small positive constant (which may possibly depend on ε). We are interested in characterising the first-hitting time of this ball, defined as the random variable

$$\tau_{y^\star}^{x^\star} = \inf\{t > 0 \colon x_t \in \mathcal{B}_\delta(y^\star)\} \qquad \text{where } x_0 = x^\star \,. \tag{1.5}$$

The two points $x^\star$ and $y^\star$ being local minima, the potential along any continuous path γ from $x^\star$ to $y^\star$ must increase and decrease again, at least once but possibly several times. We can determine the maximal value of V along such a path, and then minimise this value over all continuous paths from $x^\star$ to $y^\star$. This defines a *communication height*

$$H(x^\star, y^\star) = \inf_{\gamma : x^\star \to y^\star} \Big(\sup_{z \in \gamma} V(z) \Big) \,. \tag{1.6}$$

Although there are many paths realising the infimum in (1.6), the communication height is generically reached at a unique point $z^\star$, which we will call the *relevant saddle* between $x^\star$ and $y^\star$. In that case, $H(x^\star, y^\star) = V(z^\star)$ (see Figure 1). One can show that generically, $z^\star$ is a critical point of index 1 of the potential, that is, when seen from $z^\star$ the potential decreases in one direction and increases in the other $d - 1$ directions. This translates mathematically into $\nabla V(z^\star) = 0$ and the Hessian $\nabla^2 V(z^\star)$ having exactly one strictly negative and $d - 1$ strictly positive eigenvalues.

In order to simplify the presentation, we will state the main results in the case of a double-well potential, meaning that V has exactly two local minima $x^\star$ and $y^\star$, separated by a unique saddle $z^\star$ (Figure 1), henceforth referred to as "the double-well situation". The Kramers law has been extended to potentials with more than two local minima, and we will comment on its form in these cases in Section 3.3 below.

In the context of chemical reaction rates, a relation for the mean transition time $\tau_{y^\star}^{x^\star}$ was first proposed by van t'Hoff, and later physically justified by Arrhenius [Arr89]. It reads

$$\mathbb{E}\{\tau_{y^\star}^{x^\star}\} \simeq C \, \mathrm{e}^{[V(z^\star) - V(x^\star)]/\varepsilon} \,. \tag{1.7}$$

The Eyring–Kramers law [Eyr35, Kra40] is a refinement of Arrhenius' law, as it gives an approximate value of the prefactor C in (1.7). Namely, in the one-dimensional case $d = 1$, it reads

$$\mathbb{E}\{\tau_{y^\star}^{x^\star}\} \simeq \frac{2\pi}{\sqrt{V''(x^\star)|V''(z^\star)|}}\, \mathrm{e}^{[V(z^\star)-V(x^\star)]/\varepsilon}\,, \tag{1.8}$$

that is, the prefactor depends on the curvatures of the potential at the starting minimum $x^\star$ and at the saddle $z^\star$. Smaller curvatures lead to longer transition times.

In the multidimensional case $d \geqslant 2$, the Eyring–Kramers law reads

$$\mathbb{E}\{\tau_{y^\star}^{x^\star}\} \simeq \frac{2\pi}{|\lambda_1(z^\star)|}\sqrt{\frac{|\det(\nabla^2 V(z^\star))|}{\det(\nabla^2 V(x^\star))}}\, \mathrm{e}^{[V(z^\star)-V(x^\star)]/\varepsilon}\,, \tag{1.9}$$

where $\lambda_1(z^\star)$ is the single negative eigenvalue of the Hessian $\nabla^2 V(z^\star)$. If we denote the eigenvalues of $\nabla^2 V(z^\star)$ by $\lambda_1(z^\star) < 0 < \lambda_2(z^\star) \leqslant \cdots \leqslant \lambda_d(z^\star)$, and those of $\nabla^2 V(x^\star)$ by $0 < \lambda_1(x^\star) \leqslant \cdots \leqslant \lambda_d(x^\star)$, the relation (1.10) can be rewritten as

$$\mathbb{E}\{\tau_{y^\star}^{x^\star}\} \simeq 2\pi\sqrt{\frac{\lambda_2(z^\star)\dots\lambda_d(z^\star)}{|\lambda_1(z^\star)|\lambda_1(x^\star)\dots\lambda_d(x^\star)}}\, \mathrm{e}^{[V(z^\star)-V(x^\star)]/\varepsilon}\,, \tag{1.10}$$

which indeed reduces to (1.8) in the case $d = 1$. Notice that for $d \geqslant 2$, smaller curvatures at the saddle in the stable directions (a "broader mountain pass") decrease the mean transition time, while a smaller curvature in the unstable direction increases it.

The question we will address is whether, under which assumptions and for which meaning of the symbol $\simeq$ the Eyring–Kramers law (1.9) is true. Answering this question has taken a surprisingly long time, a full proof of (1.9) having been obtained only in 2004 [BEGK04].

In the sequel, we will present several approaches towards a rigorous proof of the Arrhenius and Eyring–Kramers laws. In Section 2, we present the approach based on the theory of large deviations, which allows to prove Arrhenius' law for more general than gradient systems, but fails to control the prefactor. In Section 3, we review different analytical approaches, two of which yield a full proof of (1.9). Finally, in Section 4, we discuss some situations in which the classical Eyring–Kramers law does not apply, but either admits a generalisation, or has to be replaced by a different expression.

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2 Large deviations and Arrhenius' law

The theory of large deviations has applications in many fields of probability [DZ98, DS89]. It allows in particular to give a mathematically rigorous framework to what is known in physics as the path-integral approach, for a general class of stochastic differential equations of the form

$$\mathrm{d}x_t = f(x_t)\,\mathrm{d}t + \sqrt{2\varepsilon}\,\mathrm{d}W_t\ , \tag{2.1}$$

where f need not be equal to the gradient of a potential V (it is even possible to consider an x-dependent diffusion coefficient $\sqrt{2\varepsilon}\,g(x_t)\,\mathrm{d}W_t$). In this context, a *large-deviation principle* is a relation stating that for small ε, the probability of sample paths being close to a function $\varphi(t)$ behaves like

$$\mathbb{P}\big\{x_t \simeq \varphi(t), 0 \leqslant t \leqslant T\big\} \simeq \mathrm{e}^{-I(\varphi)/2\varepsilon} \tag{2.2}$$

(see (2.4) below for a mathematically precise formulation). The quantity $I(\varphi) = I_{[0,T]}(\varphi)$ is called *rate function* or *action functional*. Its expression was determined by Schilder [Sch66] in the case $f = 0$ of Brownian motion, using the Cameron–Martin–Girsanov formula. Schilder's result has been extended to general equations of the form (2.1) by Wentzell and Freidlin [VF70], who showed that

$$I(\varphi) = \frac{1}{2}\int_0^T \|\dot\varphi(t) - f(\varphi(t))\|^2\,\mathrm{d}t\ . \tag{2.3}$$

Observe that $I(\varphi)$ is nonnegative, and vanishes if and only if $\varphi(t)$ is a solution of the deterministic equation $\dot\varphi = f(\varphi)$. One may think of the rate function as representing the cost of tracking the function φ rather than following the deterministic dynamics.

A precise formulation of (2.2) is that for any set Γ of paths $\varphi : [0,T] \to \mathbb{R}^d$, one has

$$-\inf_{\Gamma^\circ} I \leqslant \liminf_{\varepsilon\to 0} 2\varepsilon \log \mathbb{P}\big\{(x_t) \in \Gamma\big\} \leqslant \limsup_{\varepsilon\to 0} 2\varepsilon \log \mathbb{P}\big\{(x_t) \in \Gamma\big\} \leqslant -\inf_{\overline{\Gamma}} I\ . \tag{2.4}$$

For sufficiently well-behaved sets of paths Γ, the infimum of the rate function over the interior Γ° and the closure $\overline{\Gamma}$ coincide, and thus

$$\lim_{\varepsilon\to 0} 2\varepsilon \log \mathbb{P}\big\{(x_t) \in \Gamma\big\} = -\inf_{\Gamma} I\ . \tag{2.5}$$

Thus roughly speaking, we can write $\mathbb{P}\{(x_t) \in \Gamma\} \simeq \mathrm{e}^{-\inf_\Gamma I/2\varepsilon}$, but we should keep in mind that this is only true in the sense of logarithmic equivalence (2.5).

Remark 2.1. The large-deviation principle (2.4) can be considered as an infinite-dimensional version of Laplace's method. In the finite-dimensional case of functions $w : \mathbb{R}^d \to \mathbb{R}$, Laplace's method yields

$$\lim_{\varepsilon\to 0} 2\varepsilon \log \int_\Gamma \mathrm{e}^{-w(x)/2\varepsilon}\,\mathrm{d}x = -\inf_\Gamma w\ , \tag{2.6}$$

and also provides an asymptotic expansion for the prefactor $C(\varepsilon)$ such that

$$\int_\Gamma \mathrm{e}^{-w(x)/2\varepsilon}\,\mathrm{d}x = C(\varepsilon)\,\mathrm{e}^{-\inf_\Gamma w/2\varepsilon}\ . \tag{2.7}$$

This approach can be extended formally to the infinite-dimensional case, where it yields to a Hamilton–Jacobi equation, which is often used to derive subexponential corrections to large-deviation results via a (see e.g. [MS93]). We are not aware, however, of this procedure having been justified mathematically.

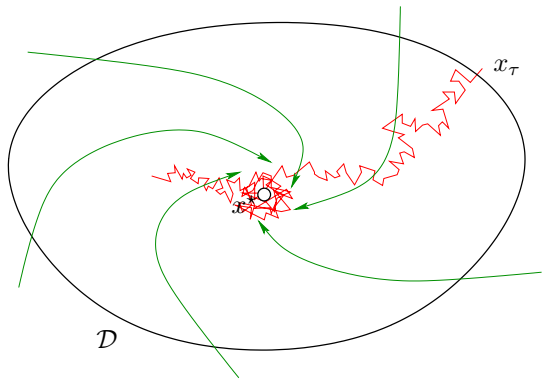

FIGURE 2. The setting of Theorems 2.2 and 2.3. The domain $\mathcal{D}$ contains a unique stable equilibrium point $x^\star$, and all orbits of the deterministic system $\dot{x} = f(x)$ starting in $\overline{\mathcal{D}}$ converge to $x^\star$.

Let us now explain how the large-deviation principle (2.4) can be used to prove Arrhenius' law. Let $x^\star$ be a stable equilibrium point of the deterministic system $\dot{x} = f(x)$. In the gradient case $f = -\nabla V$, this means that $x^\star$ is a local minimum of V. Consider a domain $\mathcal{D} \subset \mathbb{R}^d$ whose closure is included in the domain of attraction of $x^\star$ (all orbits of $\dot{x} = f(x)$ starting in $\overline{\mathcal{D}}$ converge to $x^\star$, see Figure 2). The *quasipotential* is the function defined for $z \in \overline{\mathcal{D}}$ by

$$\overline{V}(z) = \inf_{T>0} \inf_{\varphi:\varphi(0)=x^\star,\varphi(T)=z} I(\varphi) \; . \tag{2.8}$$

It measures the cost of reaching z in arbitrary time.

Theorem 2.2 ([VF69, VF70])**.** *Let $\tau = \inf\{t > 0 \colon x_t \notin \mathcal{D}\}$ denote the first-exit time of x_t from $\mathcal{D}$. Then for any initial condition $x_0 \in \mathcal{D}$, we have*

$$\lim_{\varepsilon\to 0} 2\varepsilon \log \mathbb{E}^{x_0}\{\tau\} = \inf_{z\in\partial\mathcal{D}} \overline{V}(z) =: \overline{V} \; . \tag{2.9}$$

SKETCH OF PROOF. First one shows that for any $x_0 \in \mathcal{D}$, it is likely to hit a small neighbourhood of $x^\star$ in finite time. The large-deviation principle shows the existence of a time $T > 0$, independent of ε, such that the probability of leaving $\mathcal{D}$ in time T is close to $p = \mathrm{e}^{-\overline{V}/2\varepsilon}$. Using the Markov property to restart the process at multiples of T, one shows that the number of time intervals of length T needed to leave $\mathcal{D}$ follows an approximately geometric distribution, with expectation $1/p = \mathrm{e}^{\overline{V}/2\varepsilon}$ (these time intervals can be viewed as repeated "attempts" of the process to leave $\mathcal{D}$). The errors made in the different approximations vanish when taking the limit (2.9). □

Wentzell and Freidlin also show that if the quasipotential reaches its minimum on $\partial\mathcal{D}$ at a unique, isolated point, then the first-exit location x_τ concentrates in that point as $\varepsilon \to 0$. As for the distribution of τ, Day has shown that it is asymptotically exponential:

Theorem 2.3 ([Day83])**.** *In the situation described above,*

$$\lim_{\varepsilon\to 0} \mathbb{P}\big\{\tau > s\,\mathbb{E}\{\tau\}\big\} = \mathrm{e}^{-s} \tag{2.10}$$

for all $s > 0$.

In general, the quasipotential $\overline{V}$ has to be determined by minimising the rate function (2.3), using either the Euler–Lagrange equations or the associated Hamilton equations. In the gradient case $f = -\nabla V$, however, a remarkable simplification occurs. Indeed, we can write

$$\begin{aligned} I(\varphi) &= \frac{1}{2}\int_0^T \|\dot\varphi(t) + \nabla V(\varphi(t))\|^2 \,\mathrm{d}t \\ &= \frac{1}{2}\int_0^T \|\dot\varphi(t) - \nabla V(\varphi(t))\|^2 \,\mathrm{d}t + 2\int_0^T \langle \dot\varphi(t), \nabla V(\varphi(t))\rangle \,\mathrm{d}t \\ &= \frac{1}{2}\int_0^T \|\dot\varphi(t) - \nabla V(\varphi(t))\|^2 \,\mathrm{d}t + 2\big[V(\varphi(T)) - V(\varphi(0))\big] \,. \end{aligned} \tag{2.11}$$

The first term on the right-hand vanishes if $\varphi(t)$ is a solution of the time-reversed deterministic system $\dot\varphi = +\nabla V(\varphi)$. Connecting a local minimum $x^\star$ to a point in the basin of attraction of $x^\star$ by such a solution is possible, if one allows for arbitrarily long time. Thus it follows that the quasipotential is given by

$$\overline{V} = 2\Big[\inf_{\partial\mathcal{D}} V - V(x^\star)\Big] \,. \tag{2.12}$$

Corollary 2.4. *In the double-well situation,*

$$\lim_{\varepsilon\to 0} \varepsilon \log \mathbb{E}\big\{\tau_{\mathcal{B}_\delta(y^\star)}\big\} = V(z^\star) - V(x^\star) \,. \tag{2.13}$$

Sketch of proof. Let $\mathcal{D}$ be a set containing $x^\star$, and contained in the basin of attraction of $x^\star$. One can choose $\mathcal{D}$ in such a way that its boundary is close to $z^\star$, and that the minimum of V on $\partial\mathcal{D}$ is attained close to $z^\star$. Theorem 2.2 and (2.12) show that a relation similar to (2.13) holds for the first-exit time from $\mathcal{D}$. Then one shows that once x_t has left $\mathcal{D}$, the average time needed to hit a small neighbourhood of $y^\star$ is negligible compared to the expected first-exit time from $\mathcal{D}$. □

Remark 2.5.

1. The case of more than two stable equilibrium points (or more general attractors) can be treated by organising these points in a hierarchy of "cycles", which determines the exponent in Arrhenius' law and other quantities of interest. See [FW98, Fre00].
2. As we have seen, the large-deviations approach is not limited to the gradient case, but also allows to compute the exponent for irreversible systems, by solving a variational problem. However, to our knowledge a rigorous computation of the prefactor by this approach has not been achieved, as it would require proving that the large-deviation functional I also yields the correct subexponential asymptotics.
3. Sugiura [Sug95, Sug96, Sug01] has built on these large-deviation results to derive approximations for the small eigenvalues of the diffusion's generator (defined in the next section).

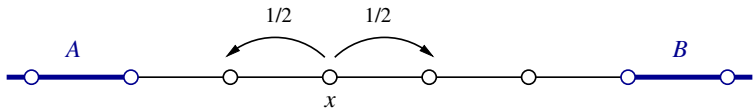

FIGURE 3. Symmetric random walk on $\mathbb{Z}$ with two absorbing sets A, B.

3 Analytic approaches and Kramers' law

The different analytic approaches to a proof of Kramers' law are based on the fact that expected first-hitting times, when considered as a function of the starting point, satisfy certain partial differential equations related to Feynman–Kac formulas.

To illustrate this fact, we consider the case of the symmetric simple random walk on $\mathbb{Z}$. Fix two disjoint sets $A, B \subset \mathbb{Z}$, for instance of the form $A = (-\infty, a]$ and $B = [b, \infty)$ with $a < b$ (Figure 3). A first quantity of interest is the probability of hitting A before B, when starting in a point x between A and B:

$$h_{A,B}(x) = \mathbb{P}^x\{\tau_A < \tau_B\} \; . \tag{3.1}$$

For reasons that will become clear in Section 3.3, $h_{A,B}$ is called the *equilibrium potential* between A and B (some authors call $h_{A,B}$ the *committor function*). Using the Markov property to restart the process after the first step, we can write

$$\begin{aligned} h_{A,B}(x) &= \mathbb{P}^x\{\tau_A < \tau_B, X_1 = x+1\} + \mathbb{P}^x\{\tau_A < \tau_B, X_1 = x-1\} \\ &= \mathbb{P}^x\{\tau_A < \tau_B | X_1 = x+1\}\mathbb{P}^x\{X_1 = x+1\} \\ &\quad + \mathbb{P}^x\{\tau_A < \tau_B | X_1 = x-1\}\mathbb{P}^x\{X_1 = x-1\} \\ &= h_{A,B}(x+1) \cdot \tfrac{1}{2} + h_{A,B}(x-1) \cdot \tfrac{1}{2} \; . \end{aligned} \tag{3.2}$$

Taking into account the boundary conditions, we see that $h_{A,B}(x)$ satisfies the linear Dirichlet boundary value problem

$$\begin{aligned} \Delta h_{A,B}(x) &= 0 \; , & x &\in (A \cup B)^c \; , \\ h_{A,B}(x) &= 1 \; , & x &\in A \; , \\ h_{A,B}(x) &= 0 \; , & x &\in B \; , \end{aligned} \tag{3.3}$$

where Δ denotes the discrete Laplacian

$$(\Delta h)(x) = h(x-1) - 2h(x) + h(x+1) \; . \tag{3.4}$$

A function h satisfying $\Delta h = 0$ is called a (discrete) *harmonic* function. In this one-dimensional situation, it is easy to solve (3.3): $h_{A,B}$ is simply a linear function of x between A and B.

A similar boundary value problem is satisfied by the mean first-hitting time of A, $w_A(x) = \mathbb{E}^x\{\tau_A\}$, assuming that A is such that the expectation exist (that is, the random walk on A^c must be positive recurrent). Here is an elementary computation (a shorter

derivation can be given using conditional expectations):

$$\begin{aligned} w_A(x) &= \sum_k k\mathbb{P}^x\{\tau_A = k\} \\ &= \sum_k k\Big[\tfrac{1}{2}\mathbb{P}^{x-1}\{\tau_A = k-1\} + \tfrac{1}{2}\mathbb{P}^{x+1}\{\tau_A = k-1\}\Big] \\ &= \sum_\ell (\ell+1)\Big[\tfrac{1}{2}\mathbb{P}^{x-1}\{\tau_A = \ell\} + \tfrac{1}{2}\mathbb{P}^{x+1}\{\tau_A = \ell\}\Big] \\ &= \tfrac{1}{2}w_A(x-1) + \tfrac{1}{2}w_A(x+1) + 1 \,. \end{aligned} \tag{3.5}$$

In the last line we have used the fact that τ_A is almost surely finite, as a consequence of positive recurrence. It follows that $w_A(x)$ satisfies the Poisson problem

$$\begin{aligned} \tfrac{1}{2}\Delta w_A(x) &= -1 \,, & x &\in A^c \,, \\ w_A(x) &= 0 \,, & x &\in A \,. \end{aligned} \tag{3.6}$$

Similar relations can be written for more general quantities of the form $\mathbb{E}^x\left\{\mathrm{e}^{\lambda\tau_A}\,1_{\{\tau_A<\tau_B\}}\right\}$.

In the case of Brownian motion on $\mathbb{R}^d$, the probability $h_{A,B}(x)$ of hitting a set A before another set B satisfies the Dirichlet problem

$$\begin{aligned} \tfrac{1}{2}\Delta h_{A,B}(x) &= 0 \,, & x &\in (A\cup B)^c \,, \\ h_{A,B}(x) &= 1 \,, & x &\in A \,, \\ h_{A,B}(x) &= 0 \,, & x &\in B \,, \end{aligned} \tag{3.7}$$

where Δ now denotes the usual Laplacian in $\mathbb{R}^d$, and the expected first-hitting time of A satisfies the Poisson problem

$$\begin{aligned} \tfrac{1}{2}\Delta w_A(x) &= -1 \,, & x &\in A^c \,, \\ w_A(x) &= 0 \,, & x &\in A \,. \end{aligned} \tag{3.8}$$

For more general diffusions of the form

$$\mathrm{d}x_t = -\nabla V(x_t)\,\mathrm{d}t + \sqrt{2\varepsilon}\,\mathrm{d}W_t \,, \tag{3.9}$$

Dynkin's formula [Dyn65, Øks85] shows that similar relations as (3.7), (3.8) hold, with $\frac{1}{2}\Delta$ replaced by the infinitesimal generator of the diffusion,

$$L = \varepsilon\Delta - \nabla V(x)\cdot\nabla \,. \tag{3.10}$$

Note that L is the adjoint of the operator appearing in the Fokker–Planck equation, which is more familiar to physicists. Thus by solving a boundary value problem involving a second-order differential operator, one can in principle compute the expected first-hitting time, and thus validate Kramers' law. This turns out to be possible in the one-dimensional case, but no general solution exists in higher dimension, where one has to resort to perturbative techniques instead.

Remark 3.1. Depending on the set A, Systems (3.6) and (3.7) need not admit a bounded solution, owing to the fact that the symmetric random walk and Brownian motion are null recurrent in dimensions $d = 1, 2$ and transient in dimensions $d \geqslant 3$. A solution exists, however, for sets A with bounded complement. The situation is less restrictive for diffusions in a confining potential V, which are usually positive recurrent.

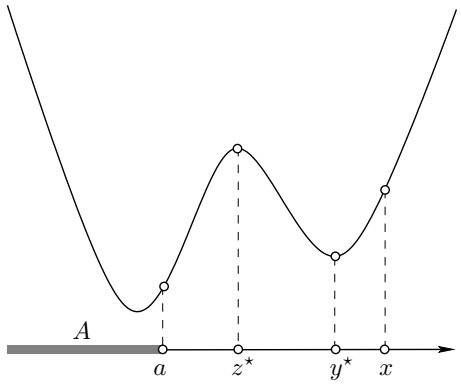

FIGURE 4. Example of a one-dimensional potential for which Kramers' law (3.15) holds.

3.1 The one-dimensional case

In the case $d = 1$, the generator of the diffusion has the form

$$(Lu)(x) = \varepsilon u''(x) - V'(x)u'(x) \ , \tag{3.11}$$

and the equations for $h_{A,B}(x) = \mathbb{P}^x\{\tau_A < \tau_B\}$ and $w_A(x) = \mathbb{E}^x\{\tau_A\}$ can be solved explicitly.

Consider the case where $A = (-\infty, a)$ and $B = (b, \infty)$ for some $a < b$, and $x \in (a, b)$. Then it is easy to see that the equilibrium potential is given by

$$h_{A,B}(x) = \frac{\displaystyle\int_x^b \mathrm{e}^{V(y)/\varepsilon}\,\mathrm{d}y}{\displaystyle\int_a^b \mathrm{e}^{V(y)/\varepsilon}\,\mathrm{d}y} \ . \tag{3.12}$$

Laplace's method to lowest order shows that for small ε,

$$h_{A,B}(x) \simeq \exp\biggl\{-\frac{1}{\varepsilon}\biggl[\sup_{[a,b]} V - \sup_{[x,b]} V\biggr]\biggr\} \ . \tag{3.13}$$

As one expects, the probability of hitting A before B is close to 1 when the starting point x lies in the basin of attraction of a, and exponentially small otherwise.

The expected first-hitting time of A is given by the double integral

$$w_A(x) = \frac{1}{\varepsilon}\int_a^x \int_z^\infty \mathrm{e}^{[V(z)-V(y)]/\varepsilon}\,\mathrm{d}y\,\mathrm{d}z \ . \tag{3.14}$$

If we assume that $x > y^\star > z^\star > a$, where V has a local maximum in $z^\star$ and a local minimum in $y^\star$ (Figure 4), then the integrand is maximal for $(y, z) = (y^\star, z^\star)$ and Laplace's method yields exactly Kramers' law in the form

$$\mathbb{E}^x\{\tau_A\} = w_A(x) = \frac{2\pi}{\sqrt{|V''(z^\star)|V''(y^\star)}}\,\mathrm{e}^{[V(z^\star)-V(y^\star)]/\varepsilon}\bigl[1 + \mathcal{O}(\sqrt{\varepsilon})\bigr] \ . \tag{3.15}$$

3.2 WKB theory

The perturbative analysis of the infinitesimal generator (3.10) of the diffusion in the limit $\varepsilon \to 0$ is strongly connected to semiclassical analysis. Note that L is not self-adjoint for the canonical scalar product, but as a consequence of reversibility, it is in fact self-adjoint in $L^2(\mathbb{R}^d, \mathrm{e}^{-V/\varepsilon}\,\mathrm{d}x)$. This becomes immediately apparent when writing L in the equivalent form

$$L = \varepsilon\,\mathrm{e}^{V/\varepsilon}\,\nabla \cdot \mathrm{e}^{-V/\varepsilon}\,\nabla \tag{3.16}$$

(just write out the weighted scalar product). It follows that the conjugated operator

$$\widetilde{L} = \mathrm{e}^{-V/2\varepsilon}\,L\,\mathrm{e}^{V/2\varepsilon} \tag{3.17}$$

is self-adjoint in $L^2(\mathbb{R}^d, \mathrm{d}x)$. In fact, a simple computation shows that $\widetilde{L}$ is a Schrödinger operator of the form

$$\widetilde{L} = \varepsilon\Delta + \frac{1}{\varepsilon}U(x)\ , \tag{3.18}$$

where the potential U is given by

$$U(x) = \frac{1}{2}\varepsilon\Delta V(x) - \frac{1}{4}\|\nabla V(x)\|^2\ . \tag{3.19}$$

Example 3.2. For a double-well potential of the form

$$V(x) = \frac{1}{4}x^4 - \frac{1}{2}x^2\ , \tag{3.20}$$

the potential U in the Schrödinger operator takes the form

$$U(x) = -\frac{1}{4}x^2(x^2-1)^2 + \frac{1}{2}\varepsilon(x^2-1)^2\ . \tag{3.21}$$

Note that this potential has 3 local minima at almost the same height, namely two of them at ± 1 where $U(\pm 1) = 0$ and one at 0 where $U(0) = \varepsilon/2$.

One may try to solve the Poisson problem $Lw_A = -1$ by WKB-techniques in order to validate Kramers' formula. A closely related problem is to determine the spectrum of L. Indeed, it is known that if the potential V has n local minima, then L admits n exponentially small eigenvalues, which are related to the inverse of expected transition times between certain potential minima. The associated eigenfunctions are concentrated in potential wells and represent metastable states.

The WKB-approach has been investigated, e.g., in [SM79, BM88, KM96, MS97]. See [Kol00] for a recent review. A mathematical justification of this formal procedure is often possible, using hard analytical methods such as microlocal analysis [HS84, HS85b, HS85a, HS85c], which have been developed for quantum tunnelling problems. The difficulty in the case of Kramers' law is that due to the form (3.19) of the Schrödinger potential U, a phenomenon called "tunnelling through nonresonant wells" prevents the existence of a single WKB ansatz, valid in all $\mathbb{R}^d$. One thus has to use different ansatzes in different regions of space, whose asymptotic expansions have to be matched at the boundaries, a procedure that is difficult to justify mathematically.

Rigorous results on the eigenvalues of L have nevertheless been obtained with different methods in [HKS89, Mic95, Mat95], but without a sufficiently precise control of their subexponential behaviour as would be required to rigorously prove Kramers' law.

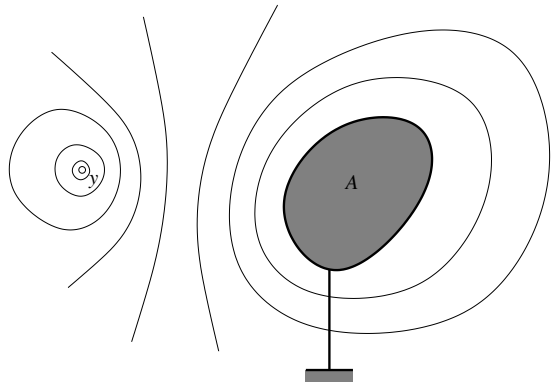

FIGURE 5. Green's function $G_{A^c}(x,y)$ for Brownian motion is equal to the electrostatic potential in x created by a unit charge in y and a grounded conductor in A.

3.3 Potential theory

Techniques from potential theory have been widely used in probability theory [Kak45, Doo84, DS84, Szn98]. Although Wentzell may have had in mind its application to Kramers' law [Ven73], this program has been systematically carried out only quite recently by Bovier, Eckhoff, Gayrard and Klein [BEGK04, BGK05].

We will explain the basic idea of this approach in the simple setting of Brownian motion in $\mathbb{R}^d$, which is equivalent to an electrostatics problem. Recall that the first-hitting time τ_A of a set $A \subset \mathbb{R}^d$ satisfies the Poisson problem (3.6). It can thus be expressed as

$$w_A(x) = -\int_{A^c} G_{A^c}(x,y)\,\mathrm{d}y\ , \tag{3.22}$$

where $G_{A^c}(x,y)$ denotes Green's function, which is the formal solution of

$$\begin{aligned} \tfrac{1}{2}\Delta u(x) &= \delta(x-y)\ , && x \in A^c\ , \\ u(x) &= 0\ , && x \in A\ . \end{aligned} \tag{3.23}$$

Note that in electrostatics, $G_{A^c}(x,y)$ represents the value at x of the electric potential created by a unit point charge at y, when the set A is occupied by a grounded conductor (Figure 5).

Similarly, the solution $h_{A,B}(x) = \mathbb{P}^x\{\tau_A < \tau_B\}$ of the Dirichlet problem (3.7) represents the electric potential at x, created by a capacitor formed by two conductors at A and B, at respective electric potential 1 and 0 (Figure 6). Hence the name *equilibrium potential*. If $\rho_{A,B}$ denotes the surface charge density on the two conductors, the potential can thus be expressed in the form

$$h_{A,B}(x) = \int_{\partial A} G_{B^c}(x,y)\rho_{A,B}(\mathrm{d}y)\ . \tag{3.24}$$

Note finally that the capacitor's capacity is simply equal to the total charge on either of the two conductors, given by

$$\mathrm{cap}_A(B) = \left|\int_{\partial A} \rho_{A,B}(\mathrm{d}y)\right|\ . \tag{3.25}$$

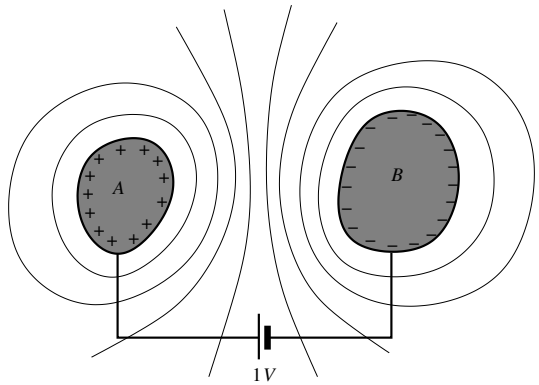

FIGURE 6. The function $h_{A,B}(x) = \mathbb{P}^x\{\tau_A < \tau_B\}$ is equal to the electric potential in x of a capacitor with conductors in A and B, at respective potential 1 and 0.

The key observation is that even though we know neither Green's function, nor the surface charge density, the expressions (3.22), (3.24) and (3.25) can be combined to yield a useful relation between expected first-hitting time and capacity. Indeed, let C be a small ball centred in x. Then we have

$$\begin{aligned}\int_{A^c} h_{C,A}(y)\,\mathrm{d}y &= \int_{A^c}\int_{\partial C} G_{A^c}(y,z)\rho_{C,A}(\mathrm{d}z)\,\mathrm{d}y \\ &= -\int_{\partial C} w_A(z)\rho_{C,A}(\mathrm{d}z)\ . \end{aligned} \tag{3.26}$$

We have used the symmetry $G_{A^c}(y,z) = G_{A^c}(z,y)$, which is a consequence of reversibility. Now since C is a small ball, if w_A does not vary too much in C, the last term in (3.26) will be close to $w_A(x)\,\mathrm{cap}_C(A)$. This can be justified by using a Harnack inequality, which provides bounds on the oscillatory part of harmonic functions. As a result, we obtain the estimate

$$\mathbb{E}^x\big\{\tau_A\big\} = w_A(x) \simeq \frac{\displaystyle\int_{A^c} h_{C,A}(y)\,\mathrm{d}y}{\mathrm{cap}_C(A)}\ . \tag{3.27}$$

This relation is useful because capacities can be estimated by a variational principle. Indeed, using again the electrostatics analogy, for unit potential difference, the capacity is equal to the capacitor's electrostatic energy, which is equal to the total energy of the electric field ∇h:

$$\mathrm{cap}_A(B) = \int_{(A\cup B)^c} \|\nabla h_{A,B}(x)\|^2\,\mathrm{d}x\ . \tag{3.28}$$

In potential theory, this integral is known as a *Dirichlet form*. A remarkable fact is that the capacitor at equilibrium minimises the electrostatic energy, namely,

$$\mathrm{cap}_A(B) = \inf_{h\in\mathcal{H}_{A,B}} \int_{(A\cup B)^c} \|\nabla h(x)\|^2\,\mathrm{d}x\ , \tag{3.29}$$

where $\mathcal{H}_{A,B}$ denotes the set of all sufficiently regular functions h satisfying the boundary conditions in (3.7). Similar considerations can be made in the case of general reversible diffusions of the form

$$\mathrm{d}x_t = -\nabla V(x_t)\,\mathrm{d}t + \sqrt{2\varepsilon}\,\mathrm{d}W_t\ , \tag{3.30}$$

a crucial point being that reversibility implies the symmetry

$$\mathrm{e}^{-V(x)/\varepsilon}\, G_{A^c}(x,y) = \mathrm{e}^{-V(y)/\varepsilon}\, G_{A^c}(y,x)\ . \tag{3.31}$$

This allows to obtain the estimate

$$\mathbb{E}^x\big\{\tau_A\big\} = w_A(x) \simeq \frac{\displaystyle\int_{A^c} h_{C,A}(y)\,\mathrm{e}^{-V(y)/\varepsilon}\,\mathrm{d}y}{\mathrm{cap}_C(A)}\ , \tag{3.32}$$

where the capacity is now defined as

$$\mathrm{cap}_A(B) = \inf_{h\in\mathcal{H}_{A,B}} \int_{(A\cup B)^c} \|\nabla h(x)\|^2\,\mathrm{e}^{-V(x)/\varepsilon}\,\mathrm{d}x\ . \tag{3.33}$$

The numerator in (3.32) can be controlled quite easily. In fact, rather rough a priori bounds suffice to show that if $x^\star$ is a potential minimum, then $h_{C,A}$ is exponentially close to 1 in the basin of attraction of $x^\star$. Thus by straightforward Laplace asymptotics, we obtain

$$\int_{A^c} h_{C,A}(y)\,\mathrm{e}^{-V(y)/\varepsilon}\,\mathrm{d}y = \frac{(2\pi\varepsilon)^{d/2}\,\mathrm{e}^{-V(x^\star)/\varepsilon}}{\sqrt{\det(\nabla^2 V(x^\star))}}\big[1+\mathcal{O}(\sqrt{\varepsilon}|\log\varepsilon|)\big]\ . \tag{3.34}$$

Note that this already provides one "half" of Kramers' law (1.9). The other half thus has to come from the capacity $\mathrm{cap}_C(A)$, which can be estimated with the help of the variational principle (3.33).

Theorem 3.3 ([BEGK04])**.** *In the double-well situation, Kramers' law holds in the sense that*

$$\mathbb{E}^x\big\{\tau_{\mathcal{B}_\varepsilon(y^\star)}\big\} = \frac{2\pi}{|\lambda_1(z^\star)|}\sqrt{\frac{|\det(\nabla^2 V(z^\star))|}{\det(\nabla^2 V(x^\star))}}\,\mathrm{e}^{[V(z^\star)-V(x^\star)]/\varepsilon}\big[1+\mathcal{O}(\varepsilon^{1/2}|\log\varepsilon|^{3/2})\big]\ , \tag{3.35}$$

where $\mathcal{B}_\varepsilon(y^\star)$ is the ball of radius ε (the same ε as in the diffusion coefficient) centred in $y^\star$.

Sketch of proof. In view of (3.32) and (3.34), it is sufficient to obtain sharp upper and lower bounds on the capacity, of the form

$$\mathrm{cap}_C(A) = \frac{1}{2\pi}\sqrt{\frac{(2\pi\varepsilon)^d|\lambda_1(z)|}{\lambda_2(z)\dots\lambda_d(z)}}\,\mathrm{e}^{-V(z)/\varepsilon}\big[1+\mathcal{O}(\varepsilon^{1/2}|\log\varepsilon|^{3/2})\big]\ . \tag{3.36}$$

The variational principle (3.33) shows that the Dirichlet form of any function $h\in\mathcal{H}_{A,B}$ provides an upper bound on the capacity. It is thus sufficient to construct an appropriate h. It turns out that taking $h(x)=h_1(x_1)$, depending only on the projection x_1 of x on the unstable manifold of the saddle, with h_1 given by the solution (3.12) of the one-dimensional case, does the job.

The lower bound is a bit more tricky to obtain. Observe first that restricting the domain of integration in the Dirichlet form (3.33) to a small rectangular box centred in the saddle decreases the value of the integral. Furthermore, the integrand $\|\nabla h(x)\|^2$ is bounded below by the derivative in the unstable direction squared. For given values of the equilibrium potential $h_{A,B}$ on the sides of the box intersecting the unstable manifold of the saddle, the Dirichlet form can thus be bounded below by solving a one-dimensional variational problem. Then rough a priori bounds on the boundary values of $h_{A,B}$ yield the result. □

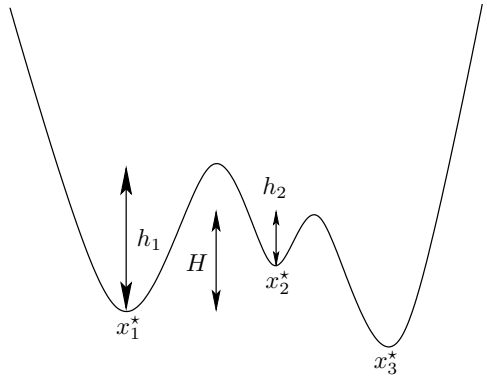

FIGURE 7. Example of a three-well potential, with associated metastable hierarchy. The relevant communication heights are given by $H(x_2^\star, \{x_1^\star, x_3^\star\}) = h_2$ and $H(x_1^\star, x_3^\star) = h_1$.

Remark 3.4. For simplicity, we have only presented the result on the expected transition time for the double-well situation. Results in [BEGK04, BGK05] also include the following points:

1. The distribution of $\tau_{\mathcal{B}_\varepsilon(y)}$ is asymptotically exponential, in the sense of (2.10).
2. In the case of more than 2 local minima, Kramers' law holds for transitions between local minima provided they are appropriately ordered. See Example 3.5 below.
3. The small eigenvalues of the generator L can be sharply estimated, the leading terms being equal to inverses of mean transition times.
4. The associated eigenfunctions of L are well-approximated by equilibrium potentials $h_{A,B}$ for certain sets A, B.

If the potential V has n local minima, there exists an ordering

$$x_1^\star \prec x_2^\star \prec \cdots \prec x_n^\star \tag{3.37}$$

such that Kramers' law holds for the transition time from each $x_{k+1}^\star$ to the set $\mathcal{M}_k = \{x_1^\star, \dots, x_k^\star\}$. The ordering is defined in terms of communication heights by the condition

$$H(x_k^\star, \mathcal{M}_{k-1}) \leqslant \min_{i<k} H(x_i^\star, \mathcal{M}_k \setminus x_i^\star) - \theta \tag{3.38}$$

for some $\theta > 0$. This means that the minima are ordered from deepest to shallowest.

Example 3.5. Consider the three-well potential shown in Figure 7. The metastable ordering is given by

$$x_3^\star \prec x_1^\star \prec x_2^\star \,, \tag{3.39}$$

and Kramers' law holds in the form

$$\mathbb{E}^{x_1^\star}\big\{\tau_3\big\} \simeq C_1\, \mathrm{e}^{h_1/\varepsilon} \,, \qquad \mathbb{E}^{x_2^\star}\big\{\tau_{\{1,3\}}\big\} \simeq C_2\, \mathrm{e}^{h_2/\varepsilon} \,, \tag{3.40}$$

where the constants C_1, C_2 depend on second derivatives of V. However, it is *not* true that $\mathbb{E}^{x_2^\star}\{\tau_3\} \simeq C_2\, \mathrm{e}^{h_2/\varepsilon}$. In fact, $\mathbb{E}^{x_2^\star}\{\tau_3\}$ is rather of the order $\mathrm{e}^{H/\varepsilon}$. This is due to the fact that even though when starting in $x_2^\star$, the process is very unlikely to hit $x_1^\star$ before $x_3^\star$ (this happens with a probability of order $\mathrm{e}^{-(h_1-H)/\varepsilon}$), this is overcompensated by the very long waiting time in the well $x_1^\star$ (of order $\mathrm{e}^{h_1/\varepsilon}$) in case this happens.

3.4 Witten Laplacian

In this section, we give a brief account of another successful approach to proving Kramers' law, based on WKB theory for the Witten Laplacian. It provides a good example of the fact that problems may be made more accessible to analysis by generalising them.

Given a compact, d-dimensional, orientable manifold M, equipped with a smooth metric g, let $\Omega^p(M)$ be the set of differential forms of order p on M. The exterior derivative d maps a p-form to a $(p+1)$-form. We write $\mathrm{d}^{(p)}$ for the restriction of d to $\Omega^p(M)$. The sequence

$$0 \to \Omega^0(M) \xrightarrow{\mathrm{d}^{(0)}} \Omega^1(M) \xrightarrow{\mathrm{d}^{(1)}} \dots \xrightarrow{\mathrm{d}^{(d-1)}} \Omega^d(M) \xrightarrow{\mathrm{d}^{(d)}} 0 \tag{3.41}$$

is called the *de Rham complex* associated with M.

Differential forms in the image $\operatorname{im} \mathrm{d}^{(p-1)}$ are called *exact*, while differential forms in the kernel $\ker \mathrm{d}^{(p)}$ are called *closed*. Exact forms are closed, that is, $\mathrm{d}^{(p)} \circ \mathrm{d}^{(p-1)} = 0$ or in short $\mathrm{d}^2 = 0$. However, closed forms are not necessarily exact. Hence the idea of considering equivalence classes of differential forms differing by an exact form. The vector spaces

$$H^p(M) = \frac{\ker \mathrm{d}^{(p)}}{\operatorname{im} \mathrm{d}^{(p-1)}} \tag{3.42}$$

are thus not necessarily trivial, and contain information on the global topology of M. They form the so-called *de Rham cohomology*.

The metric g induces a natural scalar product $\langle \cdot, \cdot \rangle_p$ on $\Omega^p(M)$ (based on the Hodge isomorphism $*$). The *codifferential* on M is the formal adjoint d^* of d, which maps $(p+1)$-forms to p-forms and satisfies

$$\langle \mathrm{d}\,\omega, \eta \rangle_{p+1} = \langle \omega, \mathrm{d}^*\,\eta \rangle_p \tag{3.43}$$

for all $\omega \in \Omega^p(M)$ and $\eta \in \Omega^{p+1}(M)$. The *Hodge Laplacian* is defined as the symmetric non-negative operator

$$\Delta_H = \mathrm{d}\,\mathrm{d}^* + \mathrm{d}^*\,\mathrm{d} = (\mathrm{d} + \mathrm{d}^*)^2 \ , \tag{3.44}$$

and we write $\Delta_H^{(p)}$ for its restriction to Ω^p. In the Euclidean case $M = \mathbb{R}^d$, using integration by parts in (3.43) shows that

$$\Delta_H^{(0)} = -\Delta \ , \tag{3.45}$$

where Δ is the usual Laplacian. Differential forms γ in the kernel $\mathcal{H}^p_\Delta(M) = \ker \Delta_H^{(p)}$ are called *p-harmonic forms*. They are both closed ($\mathrm{d}\,\gamma = 0$) and co-closed ($\mathrm{d}^*\,\gamma = 0$). Hodge has shown (see, e.g. [GH94]) that any differential form $\omega \in \Omega^p(M)$ admits a unique decomposition

$$\omega = \mathrm{d}\,\alpha + \mathrm{d}^*\,\beta + \gamma \ , \tag{3.46}$$

where γ is p-harmonic. As a consequence, $\mathcal{H}^p_\Delta(M)$ is isomorphic to the pth de Rham cohomology group $H^p(M)$.

Given a potential $V : M \to \mathbb{R}$, the *Witten Laplacian* is defined in a similar way as the Hodge Laplacian by

$$\Delta_{V,\varepsilon} = \mathrm{d}_{V,\varepsilon}\,\mathrm{d}^*_{V,\varepsilon} + \mathrm{d}^*_{V,\varepsilon}\,\mathrm{d}_{V,\varepsilon} \ , \tag{3.47}$$

where $\mathrm{d}_{V,\varepsilon}$ denotes the deformed exterior derivative

$$\mathrm{d}_{V,\varepsilon} = \varepsilon\,\mathrm{e}^{-V/2\varepsilon}\,\mathrm{d}\,\mathrm{e}^{V/2\varepsilon} \ . \tag{3.48}$$

As before, we write $\Delta_{V,\varepsilon}^{(p)}$ for the restriction of $\Delta_{V,\varepsilon}$ to $\Omega^p(M)$. A direct computation shows that in the Euclidean case $M = \mathbb{R}^d$,

$$\Delta_{V,\varepsilon}^{(0)} = -\varepsilon^2 \Delta + \frac{1}{4}\|\nabla V\|^2 - \frac{1}{2}\varepsilon \Delta V \ , \tag{3.49}$$

which is equivalent, up to a scaling, to the Schrödinger operator (3.18).

The interest of this approach lies in the fact that while eigenfunctions of $\Delta_{V,\varepsilon}^{(0)}$ are concentrated near local minima of the potential V, those of $\Delta_{V,\varepsilon}^{(p)}$ for $p \geqslant 1$ are concentrated near saddles of index p of V. This makes them easier to approximate by WKB theory. The intertwining relations

$$\Delta_{V,\varepsilon}^{(p+1)} \, \mathrm{d}_{V,\varepsilon}^{(p)} = \mathrm{d}_{V,\varepsilon}^{(p)} \, \Delta_{V,\varepsilon}^{(p)} \ , \tag{3.50}$$

which follow from $\mathrm{d}^2 = 0$, then allow to infer more precise information on the spectrum of $\Delta_{V,\varepsilon}^{(0)}$, and hence of the generator L of the diffusion [HN05].

This approach has been used by Helffer, Klein and Nier [HKN04] to prove Kramers' law (1.9) with a full asymptotic expansion of the prefactor $C = C(\varepsilon)$, in [HN06] to describe the case of general manifolds with boundary, and by Le Peutrec [LP10] for the case with Neumann boundary conditions. General expressions for the small eigenvalues of all p-Laplacians have been recently derived in [LP11, LPNV12].

4 Generalisations and limits

In this section, we discuss two generalisations of Kramers' formula, and one irreversible case, where Arrhenius' law still holds true, but the prefactor is no longer given by Kramers' law.

4.1 Non-quadratic saddles

Up to now, we have assumed that all critical points are quadratic saddles, that is, with a nonsingular Hessian. Although this is true generically, as soon as one considers potentials depending on one or several parameters, degenerate saddles are bound to occur. See for instance [BFG07a, BFG07b] for a natural system displaying many bifurcations involving nonquadratic saddles. Obviously, Kramers' law (1.9) cannot be true in the presence of singular Hessians, since it would predict either a vanishing or an infinite prefactor. In fact, in such cases the prefactor will depend on higher-order terms of the Taylor expansion of the potential at the relevant critical points [Ste05]. The main problem is thus to determine the prefactor's leading term.

There are two (non-exclusive) cases to be considered: the starting potential minimum $x^\star$ or the relevant saddle $z^\star$ is non-quadratic. The potential-theoretic approach presented in Section 3.3 provides a simple way to deal with both cases. In the first case, it is in fact sufficient to carry out Laplace's method for (3.34) when the potential V has a nonquadratic minimum in $x^\star$, which is straightforward.

We discuss the more interesting case of the saddle $z^\star$ being non-quadratic. A general classification of non-quadratic saddles, based on normal-form theory, is given in [BG10].

Consider the case where in appropriate coordinates, the potential near the saddle admits an expansion of the form

$$V(y) = -u_1(y_1) + u_2(y_2, \dots, y_k) + \frac{1}{2} \sum_{j=k+1}^{d} \lambda_j y_j^2 + \mathcal{O}(\|y\|^{r+1}) \ , \tag{4.1}$$

for some $r \geqslant 2$ and $2 \leqslant k \leqslant d$. The functions u_1 and u_2 may take negative values in a small neighbourhood of the origin, of the order of some power of ε, but should become positive and grow outside this neighbourhood. In that case, we have the following estimate of the capacity:

Theorem 4.1 ([BG10])**.** *There exists an explicit $\beta > 0$, depending on the growth of u_1 and u_2, such that in the double-well situation the capacity is given by*

$$\varepsilon \frac{\displaystyle\int_{\mathbb{R}^{k-1}} \mathrm{e}^{-u_2(y_2,\dots,y_k)/\varepsilon}\,\mathrm{d}y_2\dots\mathrm{d}y_k}{\displaystyle\int_{-\infty}^{\infty} \mathrm{e}^{-u_1(y_1)/\varepsilon}\,\mathrm{d}y_1} \prod_{j=k+1}^{d} \sqrt{\frac{2\pi\varepsilon}{\lambda_j}} \Big[1 + \mathcal{O}(\varepsilon^{\beta}|\log\varepsilon|^{1+\beta})\Big] \,. \tag{4.2}$$

We discuss one particular example, involving a pitchfork bifurcation. See [BG10] for more examples.

Example 4.2. Consider the case $k = 2$ with

$$\begin{aligned} u_1(y_1) &= -\frac{1}{2}|\lambda_1| y_1^2 \,, \\ u_2(y_2) &= \frac{1}{2}\lambda_2 y_2^2 + C_4 y_2^4 \,, \end{aligned} \tag{4.3}$$

where $\lambda_1 < 0$ and $C_4 > 0$ are bounded away from 0. We assume that the potential is even in y_2. For $\lambda_2 > 0$, the origin is an isolated quadratic saddle. At $\lambda_2 = 0$, the origin undergoes a pitchfork bifurcation, and for $\lambda_2 < 0$, there are two saddles at $y_2 = \pm\sqrt{|\lambda_2|/4C_4} + \mathcal{O}(\lambda_2)$. Let $\mu_1, \dots, \mu_d$ denote the eigenvalues of the Hessian of V at these saddles.

The integrals in (4.2) can be computed explicitly, and yield the following prefactors in Kramers' law:

- For $\lambda_2 \geqslant 0$, the prefactor is given by

$$C(\varepsilon) = 2\pi \sqrt{\frac{(\lambda_2 + \sqrt{2\varepsilon C_4}\,)\lambda_3 \dots \lambda_d}{|\lambda_1| \det(\nabla^2 V(x^\star))}} \frac{1}{\Psi_+(\lambda_2/\sqrt{2\varepsilon C_4})} \,, \tag{4.4}$$

  where the function Ψ_+ is bounded above and below by positive constants, and is given in terms of the modified Bessel function of the second kind $K_{1/4}$ by

$$\Psi_+(\alpha) = \sqrt{\frac{\alpha(1+\alpha)}{8\pi}}\, \mathrm{e}^{\alpha^2/16}\, K_{1/4}\Big(\frac{\alpha^2}{16}\Big) \,. \tag{4.5}$$

- For $\lambda_2 < 0$, the prefactor is given by

$$C(\varepsilon) = 2\pi \sqrt{\frac{(\mu_2 + \sqrt{2\varepsilon C_4}\,)\mu_3 \dots \mu_d}{|\mu_1| \det(\nabla^2 V(x^\star))}} \frac{1}{\Psi_-(\mu_2/\sqrt{2\varepsilon C_4})} \,, \tag{4.6}$$

  where the function Ψ_- is again bounded above and below by positive constants, and given in terms of the modified Bessel functions of the first kind $I_{\pm 1/4}$ by

$$\Psi_-(\alpha) = \sqrt{\frac{\pi\alpha(1+\alpha)}{32}}\, \mathrm{e}^{-\alpha^2/64} \Big[I_{-1/4}\Big(\frac{\alpha^2}{64}\Big) + I_{1/4}\Big(\frac{\alpha^2}{64}\Big) \Big] \,. \tag{4.7}$$

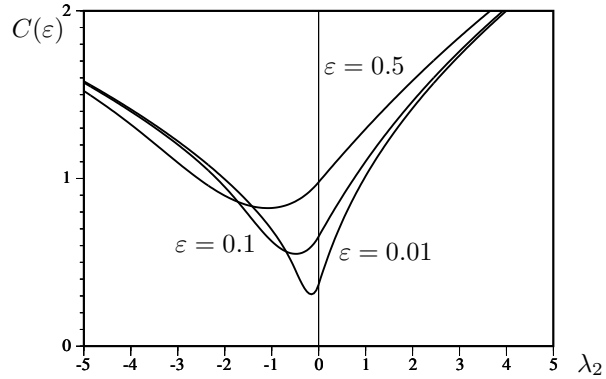

FIGURE 8. The prefactor $C(\varepsilon)$ in Kramers' law when the potential undergoes a pitchfork bifurcation as the parameter λ_2 changes sign. The minimal value of $C(\varepsilon)$ has order $\varepsilon^{1/4}$.

As long as λ_2 is bounded away from 0, we recover the usual Kramers prefactor. When $|\lambda_2|$ is smaller than $\sqrt{\varepsilon}$, however, the term $\sqrt{2\varepsilon C_4}$ dominates, and yields a prefactor of order $\varepsilon^{1/4}$ (see Figure 8). The exponent 1/4 is characteristic of this particular type of bifurcation.

The functions $\Psi_\pm$ determine a multiplicative constant, which is close to 1 when $\lambda_2 \gg \sqrt{\varepsilon}$, to 2 when $\lambda_2 \ll -\sqrt{\varepsilon}$, and to $\Gamma(1/4)/(2^{5/4}\sqrt{\pi})$ for $|\lambda_2| \ll \sqrt{\varepsilon}$. The factor 2 for large negative λ_2 is due to the presence of two saddles.

4.2 SPDEs

Metastability can also be displayed by parabolic stochastic partial differential equations of the form

$$\partial_t u(t,x) = \partial_{xx} u(t,x) + f(u(t,x)) + \sqrt{2\varepsilon}\ddot{W}_{tx} \ , \tag{4.8}$$

where $\ddot{W}_{tx}$ denotes space-time white noise (see, e.g. [Wal86]). We consider here the simplest case where $u(t,x)$ takes values in $\mathbb{R}$, and x belongs to an interval $[0,L]$, with either periodic or Neumann boundary conditions (b.c.). Equation (4.8) can be considered as an infinite-dimensional gradient system, with potential

$$V[u] = \int_0^L \left[\frac{1}{2}u'(x)^2 + U(u(x))\right] \mathrm{d}x \ , \tag{4.9}$$

where $U'(x) = -f(x)$. Indeed, using integration by parts one obtains that the Fréchet derivative of V in the direction v is given by

$$\frac{\mathrm{d}}{\mathrm{d}\eta} V[u+\eta v]\Big|_{\eta=0} = -\int_0^L \big[u''(x) + f(u(x))\big] v(x)\,\mathrm{d}x \ , \tag{4.10}$$

which vanishes on stationary solutions of the deterministic system $\partial_t u = \partial_{xx} u + f(u)$.

In the case of the double-well potential $U(u) = \frac{1}{4}u^4 - \frac{1}{2}u^2$, the equivalent of Arrhenius' law has been proved by Faris and Jona-Lasinio [FJL82], based on a large-deviation principle. For both periodic and Neumann b.c., V admits two global minima $u_\pm(x) \equiv \pm 1$. The relevant saddle between these solutions depends on the value of L. For Neumann b.c., it is given by

$$u_0(x) = \begin{cases} 0 & \text{if } L \leqslant \pi \ , \\ \pm\sqrt{\frac{2m}{m+1}}\,\mathrm{sn}\Big(\frac{x}{\sqrt{m+1}} + \mathrm{K}(m), m\Big) & \text{if } L > \pi \ , \end{cases} \tag{4.11}$$

where $2\sqrt{m+1}\,\mathrm{K}(m) = L$, K denotes the elliptic integral of the first kind, and sn denotes Jacobi's elliptic sine. There is a pitchfork bifurcation at $L = \pi$. The exponent in Arrhenius' law is given by the difference $V[u_0] - V[u_-]$, which can be computed explicitly in terms of elliptic integrals.

The prefactor in Kramers' law has been computed by Maier and Stein, for various b.c., and L bounded away from the bifurcation value ($L = \pi$ for Neumann and Dirichlet b.c., $L = 2\pi$ for periodic b.c.) [MS01, MS03, Ste04]. The basic observation is that the second-order Fréchet derivative of V at a stationary solution u is the quadratic form

$$(v_1, v_2) \mapsto \langle v_1, Q[u]v_2 \rangle \ , \tag{4.12}$$

where

$$Q[u]v(x) = -v''(x) - f'(u(x))v(x) \ . \tag{4.13}$$

Thus the rôle of the eigenvalues of the Hessian is played by the eigenvalues of the second-order differential operator $Q[u]$, compatible with the given b.c. For instance, for Neumann b.c. and $L < \pi$, the eigenvalues at the saddle u_0 are of the form $-1 + (\pi k/L)^2$, $k = 0, 1, 2, \dots$, while the eigenvalues at the local minimum u_- are given by $2 + (\pi k/L)^2$, $k = 0, 1, 2, \dots$. Thus formally, the prefactor in Kramers' law is given by the ratio of infinite products

$$\begin{aligned} C &= 2\pi \sqrt{\frac{\prod_{k=0}^{\infty} |-1 + (\pi k/L)^2|}{\prod_{k=0}^{\infty} [2 + (\pi k/L)^2]}} \\ &= 2\pi \sqrt{\frac{1}{2} \prod_{k=1}^{\infty} \frac{1 - (L/\pi k)^2}{1 + 2(L/\pi k)^2}} = 2^{3/4} \pi \sqrt{\frac{\sin L}{\sinh(\sqrt{2} L)}} \ . \end{aligned} \tag{4.14}$$

The determination of C for $L > \pi$ requires the computation of ratios of spectral determinants, which can be done using path-integral techniques (Gelfand's method, see also [For87, MT95, CdV99] for different approaches to the computation of spectral determinants). The case of periodic b.c. and $L > 2\pi$ is even more difficult, because there is a continuous set of relevant saddles owing to translation invariance, but can be treated as well [Ste04]. The formal computations of the prefactor have been extended to the case of bifurcations $L \sim \pi$, respectively $L \sim 2\pi$ for periodic b.c. in [BG09]. For instance, for Neumann b.c. and $L \leqslant \pi$, the expression (4.14) of the prefactor has to be replaced by

$$C = \frac{2^{3/4}\pi}{\Psi_+(\lambda_1/\sqrt{3\varepsilon/4L})} \sqrt{\frac{\lambda_1 + \sqrt{3\varepsilon/4L}}{\lambda_1}} \sqrt{\frac{\sin L}{\sinh(\sqrt{2} L)}} \ , \tag{4.15}$$

where $\lambda_1 = -1 + (\pi/L)^2$. Unlike (4.14), which vanishes in $L = \pi$, the above expression converges to a finite value of order $\varepsilon^{1/4}$ as $L \to \pi_-$.

These results have recently been proved rigorously, by considering sequences of finite-dimensional systems converging to the SPDE as dimension goes to infinity, and controlling the dimension-dependence of the error terms. The first step in this direction was made in [BBM10] for the chain of interacting particles introduced in [BFG07a], where a Kramers law with uniform error bounds was obtained for particular initial distributions. Full proofs of the Kramers law for classes of parabolic SPDEs have then been obtained in [BG12b], using spectral Galerkin approximations for the converging sequence, and in [Bar12] using finite-difference approximations.

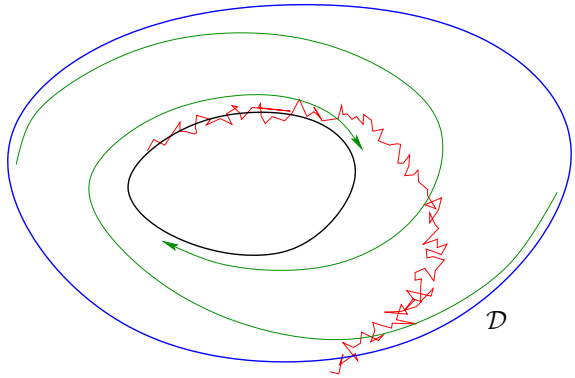

FIGURE 9. Two-dimensional vector field with an unstable periodic orbit. The location of the first exit from the domain $\mathcal{D}$ delimited by the unstable orbit displays the phenomenon of cycling.

4.3 The irreversible case

Does Kramers' law remain valid for general diffusions of the form

$$\mathrm{d}x_t = f(x_t)\,\mathrm{d}t + \sqrt{2\varepsilon}\,\mathrm{d}W_t\ , \tag{4.16}$$

in which f is not equal to the gradient of a potential V? In general, the answer is negative. As we remarked before, large-deviation results imply that Arrhenius' law still holds for such systems. The prefactor, however, can behave very differently than in Kramers' law. It need not even converge to a limiting value as $\varepsilon \to 0$.

We discuss here a particular example of such a non-Kramers behaviour, called *cycling*. Consider a two-dimensional vector field admitting an unstable periodic orbit, and let $\mathcal{D}$ be the interior of the unstable orbit (Figure 9). Since paths tracking the periodic orbit do not contribute to the rate function, the quasipotential is constant on $\partial\mathcal{D}$, meaning that on the level of large deviations, all points on the periodic orbit are equally likely to occur as first-exit points.

Day has discovered the remarkable fact that the distribution of first-exit locations rotates around $\partial\mathcal{D}$, by an angle proportional to $\log\varepsilon$ [Day90, Day94, Day96]. Hence this distribution does not converge to any limit as $\varepsilon \to 0$.

Maier and Stein provided an intuitive explanation for this phenomenon in terms of most probable exit paths and WKB-approximations [MS96]. Even though the quasipotential is constant on $\partial\mathcal{D}$, there exists a well-defined path minimising the rate function (except in case of symmetry-related degeneracies). This path spirals towards $\partial\mathcal{D}$, the distance to the boundary decreasing geometrically at each revolution. One expects that exit becomes likely as soon as the minimising path reaches a distance of order $\sqrt{\varepsilon}$ from the boundary, which happens after a number of revolutions of order $\log\varepsilon$.

It turns out that the distribution of first-exit locations itself has universal characteristics:

Theorem 4.3 ([BG04, BG12a])**.** *There exists an explicit parametrisation of $\partial\mathcal{D}$ by an angle θ (taking into account the number of revolutions), such that the distribution of first-exit locations has a density close to*

$$p(\theta) = f_{\text{transient}}(\theta)\frac{\mathrm{e}^{-(\theta-\theta_0)/\lambda T_{\mathrm{K}}}}{\lambda T_{\mathrm{K}}} P_{\lambda T}(\theta - \log(\varepsilon^{-1}))\ , \tag{4.17}$$

where

- $f_{\text{transient}}(\theta)$ *is a transient term, exponentially close to* 1 *as soon as* $\theta \gg |\log \varepsilon|$*;*
- T *is the period of the unstable orbit, and* λ *is its Lyapunov exponent;*
- $T_{\mathrm{K}} = C\varepsilon^{-1/2}\,\mathrm{e}^{\overline{V}/\varepsilon}$ *plays the rôle of Kramers' time;*
- *the universal periodic function* $P_{\lambda T}(\theta)$ *is a sum of shifted Gumbel distributions, given by*

$$P_{\lambda T}(\theta) = \sum_{k\in\mathbb{Z}} A(\theta - k\lambda T)\ , \qquad A(x) = \frac{1}{2}\,\mathrm{e}^{-2x-\frac{1}{2}\,\mathrm{e}^{-2x}}\ . \tag{4.18}$$

Although this result concerns the first-exit location, the first-exit time is strongly correlated with the first-exit location, and should thus display a similar behaviour.

Another interesting consequence of this result is that it allows to determine the residence-time distribution of a particle in the wells of a periodically perturbed double-well potential, and therefore gives a way to quantify the phenomenon of stochastic resonance [BG05].

4.4 Some recent developments

Since the first version of this review appeared as a preprint, there have been quite a number of new results related to the Kramers formula, which shows that this field of research is still very active. Here is a non-exhaustive list.

A number of new approaches analyse the generator of the diffusion using variational methods from the theory of PDEs. In [MS12], Menz and Schlichting prove Kramers' law for the first nonzero eigenvalue of the generator using Poincaré and logarithmic Sobolev inequalities. In [PSV12], Peletier, Savaré and Veneroni use Γ-convergence to obtain a Kramers law from a more realistic Kramers–Smoluchowski equation, in which particles are described by their position and their chemical state. See also [AMP+12] for an approach based on the Wasserstein distance, and [HN11, HNV12] for related work.

A situation where saddles are even more degenerate than in the cases considered in Section 4.1, due to the existence of a first integral, has been considered by Bouchet and Touchette in [BT12].

In [CGLM12], Cérou, Guyader, Lelièvre and Malrieu show that the Gumbel distribution, which we have seen governs the first-exit distribution through an unstable periodic orbit, also describes the length of the reactive path, that is, the first successful excursion out of a potential well.

Concerning irreversible diffusions, semiclassical analysis has been extended to the Kramers–Fokker–Planck equation, which describes the motion of a particle in a potential when inertia is taken into account, that is, without the assumption that the motion is overdamped. See for instance [HHS08, HHS11].

One limitation of the results on SPDEs in Section 4.2 is that the interval length L is fixed. This implies that the transition states are stationary solutions that change sign only once or twice per period (depending on the b.c.). Stationary solutions with more sign changes have a higher energy, and do not contribute to the transition rate. This is no longer true if $L = L(\varepsilon)$ grows sufficiently fast as $\varepsilon \to 0$. Recent results by Otto, Weber and Westdickenberg [OWW13], who study the Allen–Cahn equation in that regime, may help to prove a Kramers formula in that case. In such systems, metastability may be due to the fact that long time spans are spent on the stable manifold of transition states, see also the discussion in [BW11].

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Nils Berglund
Université d'Orléans, Laboratoire Mapmo
CNRS, UMR 7349
Fédération Denis Poisson, FR 2964
Bâtiment de Mathématiques, B.P. 6759
45067 Orléans Cedex 2, France
E-mail address: `nils.berglund@univ-orleans.fr`