

# METASTABILITY IN REVERSIBLE DIFFUSION PROCESSES I. SHARP ASYMPTOTICS FOR CAPACITIES AND EXIT TIMES

Anton Bovier<sup>1,2</sup>, Michael Eckhoff<sup>3</sup>,  
Véronique Gayraud<sup>4,5</sup>, Markus Klein<sup>6,7</sup>

**Abstract:** We develop a potential theoretic approach to the problem of metastability for reversible diffusion processes with generators of the form  $-\epsilon\Delta + \nabla F(\cdot)\nabla$  on  $\mathbb{R}^d$  or subsets of  $\mathbb{R}^d$ , where  $F$  is a smooth function with finitely many local minima. In analogy to previous work on discrete Markov chains, we show that *metastable exit times* from the attractive domains of the minima of  $F$  can be related, up to multiplicative errors that tend to one as  $\epsilon \downarrow 0$ , to the capacities of suitably constructed sets. We show that these capacities can be computed, again up to multiplicative errors that tend to one, in terms of local characteristics of  $F$  at the starting minimum and the relevant *saddle points*. As a result, we are able to give the first rigorous proof of the classical *Eyring-Kramers formula* in dimension larger than 1. The estimates on capacities make use of their variational representation and monotonicity properties of Dirichlet forms. The methods developed here are extensions of our earlier work on discrete Markov chains to continuous diffusion processes.

*Keywords:* Metastability, diffusion processes, potential theory, capacity, exit times

*AMS Subject Classification:* 82C44, 60K35

---

<sup>1</sup>Weierstrass-Institut für Angewandte Analysis und Stochastik, Mohrenstrasse 39, 10117 Berlin, and Institut für Mathematik, Technische Universität Berlin, Strasse des 17. Juni 136, 10623 Berlin, Germany. e-mail: bovier@wias-berlin.de

<sup>2</sup>Work partially supported by the DFG Research Center FZT 86.

<sup>3</sup>Institut für Angewandte Mathematik, Universität Zürich, Winterthurer Strasse 190, CH-8057 Zürich, Switzerland. e-mail: meckhoff@amath.unizh.ch

<sup>4</sup>EPFL, FSB, SMA, IMB, 1015 Lausanne, Switzerland  
present address: Département de Mathématiques et Statistiques, Université de Montréal, CP 6128, succ. centre ville, Montréal QC H3C 3J7, Canada. email: gayraud@dms.umontreal.ca  
on leave from: Centre de Physique Théorique, CNRS, Luminy, Case 907, F-13288 Marseille, Cedex 9, France.

<sup>5</sup>Work partially supported by the FNS under contract No. FN-21-65267.01

<sup>6</sup>Institut für Mathematik, Universität Potsdam, Am Neuen Palais 10, D-14469 Potsdam, Germany. e-mail: mklein@math.uni-potsdam.de

<sup>7</sup>Work partially supported by Sfb 288.



## 1. Introduction.

In this paper and a follow-up paper [BGK] we investigate reversible diffusion processes  $X_\epsilon(t)$ , given as solutions of an Itô stochastic differential equation

$$dX_\epsilon(t) = -\nabla F(X_\epsilon(t))dt + \sqrt{2\epsilon}dW(t) \quad (1.1)$$

on a regular domain  $\Omega \subseteq \mathbb{R}^d$ , where the drift  $\nabla F$  is generated by a potential function that is sufficiently regular. We are interested in the case when the function  $F(x)$  has several local minima. We always assume that  $X_\epsilon$  is killed on  $\Omega^c$  if it exists.

This problem is a special case of the more general class of *small random perturbations of dynamical systems* studied since the early 1970s by Freidlin and Wentzell (see their standard text [FW]) using large deviation methods. However, investigations into this problem can be traced back much further in the physical and chemical literature [Ey,Kra]. One of the earliest textbook sources is the book by Eyring et al. [GLE]. Typical questions related to this problem are

- What are the typical times to reach the neighborhoods of minimum  $a$  starting from a minimum  $b$  of the function  $F$ ? (average, distribution).
- What are typical paths for such a process?
- What is the nature of the low-lying spectrum of the generator of this process? What are the eigenfunctions associated to small eigenvalues?

It should come as no surprise that these questions are on a qualitative level well understood. However, there is at present still a considerable gap between *mathematically rigorous* and *heuristic* results. Rigorous results are mostly based on the theory of Large Deviations developed in this context by Freidlin and Wentzell. They are very flexible and apply in a variety of situations well beyond the setting of (1.1). However, they yield generally only rough asymptotic estimates in the parameter  $\epsilon$  ('logarithmic equivalence') for exponentially small (or large) quantities such as escape times or small eigenvalues. A second, very natural approach that was initiated very early in the physical and chemical literature is based on what is called *semi-classical analysis* or *WKB-theory* (for a very recent review on these methods, see e.g. [Kolo]). This methods provide *formal* asymptotic series expansions in  $\epsilon$  and can be seen as an infinite dimensional version of the saddle point method. In many cases, such expansions can today be justified by what has become to be called *microlocal analysis*, which was mainly developed in view of solving quantum mechanical tunneling prob-

lems [HS1,HS2,HS3,HS4]. Unfortunately, the stochastic tunneling problem between potential wells corresponds to a particularly intricate quantum mechanical problem, called “tunneling through non-resonant wells”. In this situation, classical WKB theory breaks down, since it is not possible to find a global solution based on a single power-series ansatz. On a formal level, these problems can be solved using matched series expansions where different ansätze in different domains are matched in overlapping regions to determine coefficients (see in particular [MatSch1,BuMa1,BuMa2,MS1]). Justifying these expansions is, however, far from trivial and constitutes, as Kolotsolkov [Kolo] points out “one of the main and still open questions of the theory”, except in the case  $d = 1$  where considerable simplifications occur [KoMak,BuMa1,BuMa2,KN]. Indeed, while it appears clear that the methods introduced in the third paper on quantum mechanical tunneling by Helffer and Sjöstrand [HS3] should in principle allow to solve this problem, this program has not been carried out in this context yet.

Here we take a new look at this old problem using neither large deviations, nor semi-classical expansions, but some rather classical ideas from *potential theory*. The deep connection between Markov processes and potential theory has been well-known since at least the work of Kakutani [Kaku] and is the subject of numerous textbooks (see in particular the fundamental monograph by Doob [Doo]). This connection has found numerous and widespread applications (see e.g. [DS,Szni] and references therein).

The particular approach we present here is distinguished by the fact that it largely avoids the attempt to solve the boundary value problems that arise in this connection by straightforward PDE methods, but that it tries to reduce most problems to that of the computation of *Newtonian capacities* which then are estimated using *variational principles* and *monotonicity properties*. In this it is in spirit close to the “electric network” approach used extensively in the study of recurrence and transience properties of Markov chains [NS,DS]. This approach to the metastability problem was initiated in fact in two preceding papers [BEGK1,BEGK2] in the context of *discrete* Markov chains, including, in particular, (in [BEGK1]) discrete versions of (1.1). In fact, the discrete setting offers (as we shall point out in due place) several advantages for this approach and makes it appear probabilistically much more transparent than in the diffusion setting. We suspect that this may have been the reason why the ideas to study the spectral problem of generators of Markov chains presented in the 1973 paper of Wentzell [Wen] and that are somewhat similar to our approach were apparently not developed in the direction we are going. While the diffusion case makes probabilistic interpretations more complicated, the present paper may clarify our approach as it forces us to develop in

much more detail the fundamental potential theoretic background from a purely analytic point of view. Let us mention that in our view the approach presented here offers two main advantages over the micro-local approach. First, it is technically considerably simpler, as we hope these papers will demonstrate, and second, it is more flexible and can be applied in a broad range of discrete and continuous Markov processes. Its drawback, on the other hand, is that it may not readily be extended to yield systematic asymptotic expansions to all orders in  $\epsilon$ . Also, we make strongly use of the fact that we investigate a stochastic (or sub-stochastic) operator, and our method cannot be extended to arbitrary elliptic operators.

We will now formulate our assumptions on  $F$  in a precise way.

**Assumptions (H.1)**

- (i)  $F \in C^3(\Omega)$ ,  $\Omega \subseteq \mathbb{R}^d$  open and connected.
- (ii) If  $\Omega$  is unbounded,
  - (ii.1)  $\liminf_{x \rightarrow \infty} |\nabla F(x)| = \infty$ , and
  - (ii.2)  $\liminf_{x \rightarrow \infty} (|\nabla F(x)| - 2\Delta F(x)) = +\infty$

Define for any two sets,  $A, B \subset \Omega$ , the *height of the saddle between A and B* by

$$\widehat{F}(A, B) \equiv \inf_{\omega: \omega(0) \in A, \omega(1) \in B} \sup_{t \in [0, 1]} F(\omega(t)) \quad (1.2)$$

where the infimum is over all continuous paths  $\omega$  in  $\Omega$ .

**Remark:** Condition (H.1) ensures that the resolvent of the generator  $L_\epsilon$  is compact is compact for  $\epsilon$  sufficiently small. Moreover, it implies that  $F$  has exponentially tight level sets in the sense that for all  $a \in \mathbb{R}$ ,

$$\int_{y: F(y) \geq a} e^{-F(y)/\epsilon} dy \leq C e^{-a/\epsilon} \quad (1.3)$$

where  $C = C(a) < \infty$  is uniform in  $\epsilon \leq 1$ .

In the sequel the notion of saddle points of  $F$  will be crucial. The set of saddle points is intuitively the subset of the set  $\mathcal{G}(A, B) = \{z : F(z) = \widehat{F}(A, B)\}$  that cannot be avoided by any paths  $\omega$  that try to stay as low as possible. In general we have to define this set as follows:

**Definition 1.1:** Let  $\mathcal{P}(A, B)$  denote the set of minimal paths from  $A$  to  $B$ ,

$$\mathcal{P}(A, B) \equiv \{\omega \in C([0, 1], \Omega) : \omega(0) \in A, \omega(1) \in B, \sup_{t \in [0, 1]} F(\omega(t)) = \widehat{F}(A, B)\} \quad (1.4)$$

Call a gate  $G(A, B)$  a minimal subset of  $\mathcal{G}(A, B)$  with the property that all minimal paths intersect  $G(A, B)$ . Note that  $G(A, B)$  is in general not unique. Then the set of saddle points  $S(A, B)$  is the union over all gates  $G(A, B)$ .

To avoid complications that are not our main concern here, we will make the general assumption that all saddle points we will deal with are non-degenerate in the sense that

**Assumption (ND):**

- (o) The set,  $\mathcal{M}$ , of local minima of  $F$  is finite, and for any two local minima  $x, y$  of  $F$ , the set  $G(x, y)$  is uniquely defined and consists of a finite set of isolated points  $z_i^*(x, y)$ .
- (i) The Hessian matrix of  $F$  at all local minima  $x_i \in \mathcal{M}$  and all saddle points  $z_i^*$  is non-degenerate (i.e. has only non zero-eigenvalues).

When dealing with domains  $\Omega$  with non-empty boundary we will encounter situations where saddle points in  $\partial\Omega$  are relevant. While this does not lead to serious problems per se, there appears rather naturally a great variety of cases that makes the formulation of general results rather cumbersome. We prefer to avoid having to discuss these issues by dealing exclusively with situations in which the boundary is never reached by the process, i.e. we make the further

**Assumption (IB):** For any sequence of points  $x_i \in \Omega$  such that  $\lim_{i \uparrow \infty} x_i \in \partial\Omega$ ,  $\lim_{i \uparrow \infty} F(x_i) = +\infty$ .

Assumptions (H1), (ND), and (IB) will be assumed to hold throughout this paper.

**Remark:** For many of the results of this paper, these conditions can be relaxed greatly. In particular, one may consider functions  $F = F_\epsilon$  depending on  $\epsilon$ , and one may also consider cases with infinitely many minima. This may, however, lead to different questions and different results, and we prefer to explain our methods in a simple and well-confined setting.

Our main interests are the distribution of stopping times

$$\tau_A \equiv \inf \{t > 0 | X(t) \in A\} \tag{1.5}$$

for the process starting in one minimum, say  $x \in \mathcal{M}$ , of  $F$ , when  $A = B_\rho(y)$  is a small ball of radius  $\rho$  around another minimum,  $y \in \mathcal{M}$ . It will actually become apparent that the precise choice of the hitting set is often not important, and that the problem is virtually equivalent to considering the escape from a suitably chosen neighborhood of  $x$ , provided this neighborhood contains the relevant *saddle points* connecting  $x$  and  $y$ .

In this paper we will study the mean values of such stopping times. Our approach will consist of two distinct steps:

- (i) Using variational principles, we will give very sharp estimates on some relevant *capacities*.
- (ii) We will then show that expected times of interest can be expressed in terms of these capacities and *equilibrium potentials*.

In the follow-up paper [BGK] we will consider the associated spectral problems. A corollary will then show that metastable exit have an asymptotically exponential distribution.

To be able to state our results, we need to recall a number of key concepts from potential theory which will allow us to establish some notation.

**Acknowledgements:** We thank anonymous referees for judicious comments that helped to improve the presentation of the paper. A. Bovier thanks the EPFL and V. Gaynard the WIAS for hospitality and financial support that made this collaboration possible.

## 2. Some basic background on potential theory.

In this section we collect notations and formulas from potential theory that will be used throughout the paper. All of these results are standard and can be found in the classical textbooks on potential theory, e.g. [BluGet,Doo,Szni].

The generator of our diffusion processes are linear elliptic operators  $L_\epsilon$  of the form

$$L_\epsilon = -\epsilon e^{F(\cdot)/\epsilon} \nabla e^{-F(\cdot)/\epsilon} \nabla = -\epsilon \Delta + (\nabla F(\cdot), \nabla) \quad (2.1)$$

defined (a priori) on  $C^2(\Omega)$ , where  $\Omega \subseteq \mathbb{R}^d$ , and  $F \in C^2(\Omega)$ .  $\Omega$ , and in fact all subsets of  $\mathbb{R}^d$  that we will consider in this paper will be regular (A set  $A \subset \mathbb{R}^d$  is called *regular* if and only if its complement is a region with continuously differentiable boundary). By construction,  $L_\epsilon$  is symmetric on  $L^2(\Omega, e^{-F(x)/\epsilon} dx)$  with Dirichlet boundary conditions on  $\Omega^c$ .

**Green's function.** Consider for  $\lambda \in \mathbb{C}$  the Dirichlet problem

$$\begin{aligned} (L_\epsilon - \lambda)f(x) &= g(x), & x \in \Omega \\ f(x) &= 0, & x \in \Omega^c \end{aligned} \quad (2.2)$$

The associated Dirichlet Green's function  $G_\Omega^\lambda(x, y)$  is the kernel of the inverse of the operator  $(L_\epsilon - \lambda)$ , i.e. for any  $g \in C_0(\Omega)$ ,

$$f(x) = \int_\Omega G_\Omega^\lambda(x, y) g(y) dy \quad (2.3)$$

Note that the Green's function is symmetric with respect to the measure  $e^{-F(x)/\epsilon} dx$ , i.e.

$$G_\Omega^\lambda(x, y) = e^{-F(y)/\epsilon} G_\Omega^\lambda(y, x) e^{F(x)/\epsilon} \quad (2.4)$$

Recall that the spectrum of  $L_\epsilon$  (more precisely the Dirichlet spectrum of the restriction of  $L_\epsilon$  to  $\Omega$ , which we will sometimes denote by  $L_\epsilon^\Omega$ ), is the complement of the set of values  $\lambda$  for which  $G_\Omega^\lambda$  defines a bounded operator.

**Poisson kernel.** Consider for  $\lambda \in \mathbb{C}$  the boundary value problem

$$\begin{aligned} (L_\epsilon - \lambda)f(x) &= 0, \quad x \in \Omega \\ f(x) &= \phi(x), \quad x \in \Omega^c \end{aligned} \quad (2.5)$$

We denote by  $H_\Omega^\lambda$  the associated solution operator which can be represented in the form

$$f(x) = (H_\Omega^\lambda \phi)(x) = -\epsilon \int_{\partial\Omega} e^{-[F(y)-F(x)]/\epsilon} \phi(y) \partial_{n(y)} G_\Omega^\lambda(y, x) d\sigma_\Omega(y) \quad (2.6)$$

where  $d\sigma_\Omega$  denotes the Euclidean surface measure on  $\partial\Omega$ , and  $\partial_{n(y)}$  denotes the derivative in the direction of the *exterior* normal vector on  $\partial\Omega$  at  $y$ , acting on the first argument of the function  $G_\Omega^\lambda(y, x)$ .

The relation between the operator  $H_\Omega^\lambda$  and the Green function (2.6) is a consequence of the two Green's identities that here take the form

$$\int_\Omega dx e^{-F(x)/\epsilon} (\epsilon \nabla \phi(x) \cdot \nabla \psi(x) - \psi(x) (L_\epsilon \phi)(x)) = \epsilon \int_{\partial\Omega} e^{-F(x)/\epsilon} \psi(x) \partial_{n(x)} \phi(x) d\sigma_\Omega(x) \quad (2.7)$$

(first Green's identity) and

$$\begin{aligned} \int_\Omega e^{-F(x)/\epsilon} dx (\phi(x) (L_\epsilon - \lambda) \psi(x) - \psi(x) (L_\epsilon - \lambda) \phi(x)) \\ = \epsilon \int_{\partial\Omega} e^{-F(x)/\epsilon} (\psi(x) \partial_{n(x)} \phi(x) - \phi(x) \partial_{n(x)} \psi(x)) d\sigma_\Omega(x) \end{aligned} \quad (2.8)$$

(second Green's identity), where  $\phi, \psi \in C^2(\Omega)$ .

**Equilibrium potential and equilibrium measure.** Let  $A, D \subset \mathbb{R}^d$  be regular and such that  $(A \cup D)^c \subset \text{dom}(F)$ . Then the equilibrium potential (of the capacitor  $(A, D)$ ),  $h_{A,D}^\lambda$ , is defined as the solution of the Dirichlet problem

$$\begin{aligned} (L_\epsilon - \lambda)h_{A,D}^\lambda(x) &= 0, \quad x \in (A \cup D)^c \\ h_{A,D}^\lambda(x) &= 1, \quad x \in A \\ h_{A,D}^\lambda(x) &= 0, \quad x \in D \end{aligned} \quad (2.9)$$



Note that (2.9) has a unique solution provided  $\lambda$  is not in the spectrum of  $L_\epsilon^{(A \cup B)^c}$ .

The equilibrium measure,  $e_{A,D}^\lambda$ , is defined as the unique measure on  $\partial A$ , such that

$$h_{A,D}^\lambda(x) = \int_{\partial A} G_{D^c}^\lambda(x, y) e_{A,D}^\lambda(dy) \quad (2.10)$$

If we consider  $L_\epsilon$  as a map from  $H^n(\Omega)$  to  $H^{n-2}(\Omega)$ , (2.10) may also be written as

$$e_{A,D}^\lambda(dy) = (L_\epsilon - \lambda)h_{A,D}^\lambda(y) \quad (2.11)$$

where of course both sides are to be interpreted as measures equipped with the weak topology. A simple computation using the second Green's identity and the Poisson kernel representation (2.6) allows to compute the right hand side of (2.11) as

$$(L_\epsilon - \lambda)h_{A,D}^\lambda(x) = \epsilon \partial_{n(x)} h_{A,D}^\lambda(x) d\sigma_{A \cup D}(x) - \lambda \mathbb{1}_A dx \quad (2.12)$$

**Capacity.** Given a capacitor,  $(A, D)$ , and  $\lambda \in \mathbb{R}$ , the  $\lambda$ -capacity of the capacitor is defined as

$$\text{cap}_A^\lambda(D) \equiv \int_{\partial A} e^{-F(y)/\epsilon} e_{A,D}^\lambda(dy) \quad (2.13)$$

Using (2.12) and the Green's second identity, one obtains from (2.13) that

$$\text{cap}_A^\lambda(D) = \epsilon \int_{(A \cup D)^c} dx e^{-F(x)/\epsilon} \left[ \|\nabla h_{A,D}^\lambda(x)\|_2^2 - \frac{\lambda}{\epsilon} (h_{A,D}^\lambda(x))^2 \right] \equiv \Phi_{(A \cup D)^c}^\lambda(h_{A,D}^\lambda) \quad (2.14)$$

$\Phi_\Omega^\lambda$  is called the Dirichlet form (or energy) for the operator  $L_\epsilon - \lambda$  on  $\Omega$ .

A fundamental consequence of (2.14) is the variational representation of the capacity if  $\mathbb{R} \ni \lambda \leq 0$ , namely

$$\text{cap}_A^\lambda(D) = \inf_{h \in \mathcal{H}_{A,D}} \Phi_{(A \cup D)^c}^\lambda(h) \quad (2.15)$$

where  $\mathcal{H}_{A,D}$  denotes the set of function

$$\mathcal{H}_{A,D} \equiv \{h \in W^{1,2}(\Omega) : h(x) = 0, x \in D, h(x) = 1, x \in A\} \quad (2.16)$$

where  $W^{k,n}(\Omega)$  denotes the space of  $k$ -times weakly differentiable functions whose derivatives of order  $\leq k$  are in  $L^n(\Omega)$ .

**Probabilistic interpretation: equilibrium potential.** Note that  $L_\epsilon$  generates a Markov diffusion process  $X_\epsilon(t)$  on  $\Omega$  (killed on  $\partial\Omega$ ). If  $\lambda = 0$ , the equilibrium potential has a natural probabilistic interpretation in terms of hitting probabilities of this process, namely,

$$h_{A,D}(x) \equiv h_{A,D}^0(x) = \mathbb{P}_x[\tau_A < \tau_D] \quad (2.17)$$

The equilibrium measure also has an interpretation, namely

$$e_{A,D}(dy) = \lim_{t \downarrow 0} t^{-1} \mathbb{E}_y \mathbb{P}_{X_\epsilon(t)}[\tau_D < \tau_A] dy \quad (2.18)$$

(see e.g. [Szni], Section 2.3). While this gives in principle a probabilistic interpretation of the capacity as well, this is much less useful than in the discrete space, discrete time setting (see [BEGK2]).

If  $\lambda < 0$ , the equilibrium potential still has a probabilistic interpretation in term of the sub-stochastic process  $X_\epsilon^\lambda(t)$  obtained by killing the process  $X_\epsilon(t)$  with rate  $-\lambda$  (and on  $\partial\Omega$ ). If  $\tau$  denotes the time when  $X_\epsilon^\lambda$  is killed, we have that

$$h_{A,D}^\lambda(x) = \mathbb{P}_x^\lambda[\tau_A < \tau_D \wedge \tau] \quad (2.19)$$

More importantly, we have for general  $\lambda$ , that

$$h_{A,D}^\lambda(x) = \mathbb{E}_x e^{\lambda\tau_A} \mathbb{1}_{\tau_A < \tau_D} \quad (2.20)$$

for  $x \in (A \cup D)^c$ , whenever the right-hand side exists. so that  $h^\lambda$  can be seen as the Laplace transform of the hitting time  $\tau_A$  of the process starting in  $x$  and killed in  $D$ .

Note that (2.20) implies that

$$\frac{d}{d\lambda} h_{A,D}^{\lambda=0}(x) = \mathbb{E}_x \tau_A \mathbb{1}_{\tau_A < \tau_D} \quad (2.21)$$

Differentiating the defining equation of  $h_{A,D}^\lambda$  then implies that the function

$$w_{A,D}(x) = \begin{cases} \mathbb{E}_x \tau_A \mathbb{1}_{\tau_A < \tau_D}, & x \in (A \cup D)^c \\ 0, & x \in A \cup D \end{cases} \quad (2.22)$$

solves the inhomogeneous Dirichlet problem (to simplify notation, we set from now on  $h_{A,D} \equiv h_{A,D}^0$ , etc.)

$$\begin{aligned} L_\epsilon w_{A,D}(x) &= h_{A,D}(x), & x \in (A \cup D)^c \\ w_{A,D}(x) &= 0, & x \in A \cup D \end{aligned} \quad (2.23)$$

Therefore, the mean hitting time in  $A$  of the process killed in  $D$  can be represented in terms of the Green's function as

$$\mathbb{E}_x \tau_A \mathbb{1}_{\tau_A < \tau_D} = \int_{(A \cup D)^c} dy G_{(A \cup D)^c}(x, y) h_{A,D}(y) \quad (2.24)$$

Note that in the particular case when  $D = \emptyset$ , we get the familiar Dirichlet problem

$$\begin{aligned} L_\epsilon w_A(x) &= 1, & x \in A^c \\ w_A(x) &= 0, & x \in A \end{aligned} \quad (2.25)$$

and the representation

$$\mathbb{E}_x \tau_A = \int_{A^c} dy G_{A^c}(x, y) \quad (2.26)$$

The full beauty of all this comes out when combining (2.10) with (2.24), resp. (2.26). Namely, let  $B_\rho(x)$  be the ball of radius  $\rho$  centered at  $x$ . Then, using Fubini's theorem,

$$\begin{aligned} \int_{\partial B_\rho(x)} e^{-F(z)/\epsilon} \mathbb{E}_z \tau_A e_{B_\rho(x), A}(dz) &= \int_{A^c} dy e^{-F(y)/\epsilon} \int_{\partial B_\rho(x)} G_{A^c}(y, z) e_{B_\rho(x), A}(dz) \\ &= \int_{A^c} dy e^{-F(y)/\epsilon} h_{B_\rho(x), A}(y) \end{aligned} \quad (2.27)$$

and

$$\int_{\partial B_\rho(x)} e^{-F(z)/\epsilon} \mathbb{E}_z \tau_A \mathbb{1}_{\tau_A < \tau_D} e_{B_\rho(x), A \cup D}(dz) = \int_{(A \cup D)^c} dy e^{-F(y)/\epsilon} h_{B_\rho(x), A \cup D}(y) h_{A, D}(y) \quad (2.28)$$

Notice that in the case of discrete Markov processes, we can replace the ball  $B_\rho(x)$  by the single point  $x$ . In that case (2.27) and (2.28) yield directly formulae for mean hitting times in terms of capacities and equilibrium potentials. In this context they provided the basis for connecting in a precise way capacities and mean exit times, and, ultimately, eigenvalues of  $L_\epsilon$  [BEGK2]. In the diffusion case, the usefulness of these equations will become apparent only when we have some a priori regularity estimates for the mean times as functions of the starting point.

### 3. Results.

We are now ready to state the main results of this paper. The basis for the success of our approach is the fact that capacities can be estimated very sharply.

**Theorem 3.1:** *Assume that  $A, B \subset \mathbb{R}^d$  are closed and*

- (i)  $\text{dist}(\mathcal{S}(A, B), A \cup B) \geq \delta > 0$  for some  $\delta$  independent of  $\epsilon$
- (ii) both  $A$  and  $B$  contain a closed ball of radius at least  $\epsilon$ .

Then, if  $\mathcal{S}(A, B) = \{z_1^*, \dots, z_n^*\}$ ,

$$\text{cap}_A(B) = e^{-F(z^*(x, y))/\epsilon} \frac{(2\pi\epsilon)^{d/2}}{2\pi} \sum_{i=1}^k \frac{|\lambda_1^*(z_i^*)|}{\sqrt{|\det(\nabla^2 F(z_i^*))|}} (1 + O(\sqrt{\epsilon} |\ln \epsilon|)) \quad (3.1)$$

where  $\lambda_1^*(z_i^*)$  denotes the negative eigenvalue of the Hessian at  $z_i^*$ .

**Remark:** In cases when some saddle points are degenerate, one can also obtain precise, but somewhat less explicit expressions, as will be clear from the proof.

Our next result concerns the mean metastable exit times from a minimum  $x_i$ .

**Theorem 3.2:** *Let  $x_i$  be a minimum of  $F$  and let  $D$  be any closed subset of  $\mathbb{R}^d$  such that:*

- (i) *If  $\mathcal{M}_i \equiv \{y_1, \dots, y_k\} \subset \mathcal{M}$  enumerates all those minima of  $F$  such that  $F(y_j) \leq F(x_i)$ , then  $\cup_{j=1}^k B_\epsilon(y_j) \subset D$ , and*
- (ii)  *$\text{dist}(\mathcal{S}(x_i, \mathcal{M}_i), D) \geq \delta > 0$  for some  $\delta$  independent of  $\epsilon$ . Then*

$$\mathbb{E}_{x_i} \tau_D = \frac{2\pi e^{[F(z^*) - F(x_i)]/\epsilon}}{\sqrt{\det(\nabla^2 F(x_i))} \sum_{j=1}^k \frac{|\lambda_1^*(z_j^*)|}{\sqrt{|\det(\nabla^2 F(z_j^*))|}}} (1 + O(\sqrt{\epsilon} |\ln \epsilon|)) \quad (3.2)$$

**Remark:** In the case when there is a single saddle point  $z^*$ , this reduces to the classical Eyring formula [GLE,MS1]

$$\mathbb{E}_{x_i} \tau_D = \frac{2\pi}{|\lambda_1(z_i^*)|} \frac{\sqrt{|\det(\nabla^2 F(z^*))|}}{\sqrt{\det(\nabla^2 F(x_i))}} e^{[F(z^*) - F(x_i)]/\epsilon} (1 + O(\epsilon^{1/2} |\ln \epsilon|)) \quad (3.3)$$

Note that the coefficient  $2\pi$  differs from the  $\pi$  that is found in [MS1] by a factor 2 since we consider the transition through, and not just the arrival at the saddle point.

#### 4. Some useful tools and a-priori estimates

This section collects a number of tools and a-priori estimates that extend the simple probabilistic instruments used in the discrete context of [BEGK2] to the diffusion setting.

**Regularity estimates.** To be able to pass from the discrete setting of [BEGK1, BEGK2] to the setting of diffusion processes, we will need some a priori control on the regularity properties of solutions of the Dirichlet problems introduced before. Fortunately, this theory is well developed in the general setting of second order linear elliptic differential equations, and we can draw on standard results.

The following two key lemmata are taken from [GT], more precisely Corollaries 9.24 and 9.25. They concern second order elliptic operators  $L = a_{ij}(x)D_{ij} + b_i(x)D_i + c(x)$ . where  $a_{ij} \in C^0(\Omega)$ ,  $b_i, c \in L^\infty(\Omega)$ . Assume that

$$\Lambda(\xi, \xi) \geq (\xi, a(x)\xi) \geq \lambda(\xi, \xi) > 0 \quad \forall \xi \in \mathbb{R}^d \quad (4.1)$$

let moreover  $\gamma = \frac{\Lambda}{\lambda}$ , and choose  $\nu$  such that  $\left(\frac{\|b\|}{\lambda}\right)^2 \leq \nu$ , and  $\frac{|c|}{\lambda} \leq \nu$ . Let  $W^{2,n}(\Omega)$  denote the Banach space of two-times (weakly) differentiable functions whose derivatives of order  $\leq 2$  are in  $L^n(\Omega)$ .

**Lemma 4.1:** (Corollary 9.25 in [GT]) *If  $u \in W^{2,n}(\Omega)$  is positive and satisfies  $Lu = 0$  in  $\Omega$ , then for any ball  $B_{2R}(y) \subset \Omega$ ,*

$$\sup_{z \in B_R(y)} u(z) \leq C \inf_{z \in B_R(y)} u(z) \quad (4.2)$$

where the constant  $C = C(n, \gamma, \nu R^2) < \infty$  depends only on  $\gamma$  and  $\nu R^2$

**Lemma 4.2:** (Corollary 9.24 in [GT]) *If  $u \in W^{2,n}(\Omega)$  is positive and satisfies  $Lu = f$  in a ball  $B_{R_0}(x)$ , then for any ball  $B_R(x)$ ,  $R \leq R_0$ ,*

$$\text{osc}_{B_R(x)} u \leq C \left(\frac{R}{R_0}\right)^\alpha \left(\text{osc}_{B_{R_0}(x)} u + R_0 \|f - cu\|_{n, B_{R_0}(x)}\right) \quad (4.3)$$

where  $\text{osc}_A u \equiv \sup_A u - \inf_A u$  and the constants  $\alpha = \alpha(n, \gamma, \nu R_0^2) > 0$  and  $C = C(n, \gamma, \nu R_0^2) < \infty$  depend only on  $\gamma$  and  $\nu R_0^2$ .

The way we will use these lemmata is to consider domains depending on  $\epsilon$  chosen in such a way that the numerical constants  $C$  and  $\alpha$  are independent of  $\epsilon$ . Since for the operator  $L_\epsilon$   $\Lambda = \lambda = \epsilon$ ,  $\gamma = 1$ , and we can choose  $\nu = \epsilon^{-2} \sup_{y \in \Omega} \|\nabla F(y)\|_\infty^2$ .

**An analytic renewal estimate.** In this section we consider only the case  $\lambda \equiv 0$  and we omit the superscript 0. One of the most useful formulas used in our analysis of discrete Markov chains was the *renewal equation*

$$\mathbb{P}_x[\tau_A < \tau_D] = \frac{\mathbb{P}_x[\tau_A < \tau_{D \cup x}]}{\mathbb{P}_x[\tau_{A \cup D} < \tau_x]} \quad (4.4)$$

obtained from decomposing the event  $\{\tau_A < \tau_D\}$  according to whether the process visits  $x$  before going to  $A$  or not and using the Markov property. While this formula is still true in the diffusion case (if  $d > 1$ ), it is useless, since the denominator equals one and the numerator equals the left-hand side. A natural idea in this situation would be to decompose not according to whether the starting point  $x$  is revisited, but whether a suitably chosen small neighborhood of  $x$  is revisited *after* a suitably chosen short time, or not (in analogy to the probabilistic representation of capacity). However, any such procedure runs quickly into problems, as it is impossible to obtain an exact renewal argument.

Fortunately, it is rather easy to obtain a useful analogue of (4.4) by purely analytic considerations. In fact we will prove the following proposition:

**Proposition 4.3:** *Let  $A, D$  be disjoint closed sets whose complement is regular, and let  $x \in (A \cup D)^c$ , such that  $\text{dist}(x, A \cup D) > c\epsilon$ . Let  $B_\rho(x)$  denote the ball of radius  $\rho$  centered at  $x$ . Then for any  $\rho \leq c\epsilon$ ,  $c < \infty$ , there exists a finite positive constant (depending only on  $c$  and on the value of  $\|\nabla F(x)\|_\infty$ ), such that*

$$h_{A,D}(x) \leq C \frac{\text{cap}_{B_\rho(x)}(A)}{\text{cap}_{B_\rho(x)}(D)} \quad (4.5)$$

**Proof:** We begin by proving the following lemma.

**Lemma 4.4:** *With the notation of the proposition,*

$$\begin{aligned} h_{A,D}(x) &\leq \sup_{z \in \partial B_\rho(x)} G_{(A \cup D)^c}(z, x) e^{F(x)/\epsilon} \int_{\partial B_\rho(x)} e^{-F(y)/\epsilon} e_{D \cup B_\rho(x), A}(dy) \\ h_{A,D}(x) &\geq \inf_{z \in \partial B_\rho(x)} G_{(A \cup D)^c}(z, x) e^{F(x)/\epsilon} \int_{\partial B_\rho(x)} e^{-F(y)/\epsilon} e_{D \cup B_\rho(x), A}(dy) \end{aligned} \quad (4.6)$$

where  $e_{A \cup D, B_\rho(x)}$  is the equilibrium measure defined in (2.10).

**Proof:** Let  $\Omega$  be a regular domain, and let  $f$  be a function defined on  $\partial\Omega$ . Recall that the operator  $H_\Omega \equiv H_\Omega^{\lambda=0}$  defined in (2.6) can be seen as mapping a function  $f$  defined on  $\partial\Omega$  to a harmonic function (with respect to the operator  $L_\epsilon$ ) on  $\Omega$ . We call  $H_\Omega f$  the *harmonic extension* of  $f$ .

Choosing  $\Omega \equiv (A \cup D)^c$ , we see that the equilibrium potential  $h_{A,D}$  satisfies the mean-value property

$$h_{A,D}(x) = H_{(A \cup D)^c} h_{A,D}(x), \quad (4.7)$$

Now let  $C \subset (A \cup D)^c$  be a regular neighborhood of  $x$ . Now since  $h_{A,D \cup C}$  and  $h_{A,D}$  coincide on  $\partial(A \cup D)$ , it is obvious that

$$h_{A,D} = H_{(A \cup D)^c} h_{A,D \cup C} \quad (4.8)$$

holds on  $(A \cup D \cup C)^c$ . Using the first Green's identity (2.7) for  $\Omega = \Gamma \equiv (A \cup D \cup C)^c$ ,

$\phi \equiv G_{(A \cup D)^c}(x, \cdot)$  and  $\psi \equiv h_{A, D \cup C}$ , we get

$$\begin{aligned}
H_{(A \cup D)^c} h_{A, D \cup C}(x) &= -\epsilon \int_{\partial(A \cup D)} e^{(F(x)-F(y))/\epsilon} h_{A, D \cup C}(y) \partial_{n(y)} G_{(A \cup D)^c}(y, x) d\sigma_{A \cup D}(y) \\
&= -\epsilon \int_{\partial C} e^{(F(x)-F(y))/\epsilon} G_{(A \cup D)^c}(y, x) \partial_{n(y)} h_{A, D \cup C}(y) d\sigma_C(y) \\
&\quad - \int_{\partial C} e^{(F(x)-F(y))/\epsilon} G_{(A \cup D)^c}(y, x) e_{A, D \cup C}(dy)
\end{aligned} \tag{4.9}$$

where  $n(y)$  is the inner unit normal at  $y \in \partial(A \cup D \cup C)$ . Here we have used that  $h_{A, D \cup C}$  vanishes on  $\partial C$  and that the Green's function vanishes when  $x \in \partial(A \cup D)$ . The last equality follows from (2.12) together with (2.11).

We now choose  $C \equiv B_\rho(x)$ . If we could replace  $G_{(A \cup D)^c}(y, x)$  by a constant value on  $\partial B_\rho(x)$ , we could extract this value from the integral; the remaining integral then would be some partial capacity. In fact, in the discrete case we could choose instead of the ball  $B_\rho(x)$  just the point  $x$ , and then this problem was absent, and we would readily get (4.4). In the present situation we still get two bounds, namely

$$\begin{aligned}
h_{A, D}(x) &\geq - \sup_{z \in \partial B_\rho(x)} G_{(A \cup D)^c}(z, x) e^{F(x)/\epsilon} \int_{\partial B_\rho(x)} e^{-F(y)/\epsilon} e_{A, D \cup B_\rho(x)}(dy) \\
h_{A, D}(x) &\leq - \inf_{z \in \partial B_\rho(x)} G_{(A \cup D)^c}(z, x) e^{F(x)/\epsilon} \int_{\partial B_\rho(x)} e^{-F(y)/\epsilon} e_{A, D \cup B_\rho(x)}(dy)
\end{aligned} \tag{4.10}$$

But, trivially,  $h_{A \cup B, C} = 1 - h_{C, A \cup B}$ , and hence, by (2.11) with  $\lambda = 0$ ,  $-e_{A \cup B, C} = e_{C, A \cup B}$ , which implies (4.6).  $\diamond$

At this point it is clear that we will need to be able to control the Green's function near the diagonal. Before turning to these estimates, we bring (4.10) in a slightly more suitable form. Namely we will show that

**Lemma 4.5:** *Within the situation of the previous lemma*

$$h_{A, D}(x) \leq \sup_{z \in \partial B_\rho(x)} G_{(A \cup D)^c}(z, x) e^{F(x)/\epsilon} \text{cap}_{B_\rho(x)}(A) \tag{4.11}$$

**Proof:** By (2.18), it is obvious that  $e_{D \cup B_\rho(x), A}(dy) \leq e_{B_\rho(x), A}(dy)$ . But then

$$\int_{\partial B_\rho(x)} e^{-F(y)/\epsilon} e_{D \cup B_\rho(x), A}(dy) \leq \int_{\partial B_\rho(x)} e^{-F(x)/\epsilon} e_{B_\rho(x), A}(dy) = \text{cap}_{B_\rho(x)}(A) \tag{4.12}$$

Thus the upper bound in (4.6) implies (4.11).  $\diamond$

At this point we want to express the Green's function in the bounds of Lemma 4.4 in terms of capacities, too. We proceed as in (2.27), to get this time

$$\begin{aligned} e^{F(x)/\epsilon} \int_{\partial B_\rho(x)} e^{-F(z)/\epsilon} G_{(A \cup D)^c}(x, z) e_{B_\rho(x), A \cup D}(dz) &= \int_{\partial B_\rho(x)} G_{(A \cup D)^c}(z, x) e_{B_\rho(x), A \cup D}(dz) \\ &= h_{B_\rho(x), A \cup D}(x) = 1 \end{aligned} \quad (4.13)$$

This implies that

$$\begin{aligned} 1 &\geq e^{F(x)/\epsilon} \inf_{z \in B_\rho(x)} G_{(A \cup D)^c}(x, z) \int_{B_\rho(x)} dz e^{-F(z)/\epsilon} e_{B_\rho(x), A \cup D}(dz) \\ &= e^{F(x)/\epsilon} \inf_{z \in B_\rho(x)} G_{(A \cup D)^c}(x, z) \text{cap}_{B_\rho(x)}(A \cup D) \end{aligned} \quad (4.14)$$

i.e.

$$e^{F(x)/\epsilon} \inf_{z \in B_\rho(x)} G_{(A \cup D)^c}(x, z) \leq \frac{1}{\text{cap}_{B_\rho(x)}(A \cup D)} \quad (4.15)$$

It is clear at this point that we cannot continue unless we can compare the infimum and the supremum of  $G_{(A \cup D)^c}(z, x)$  with  $z \in B_\rho(x)$ . But such a result is provided by the Harnack inequalities.

**Lemma 4.6:** *If  $\rho = c\epsilon$ , for some  $c < \infty$ , then there exists a constant  $C$  depending only on  $c$ , such that*

$$\sup_{z \in B_\rho(x)} G_{(A \cup D)^c}(z, x) \leq C \inf_{z \in B_\rho(x)} G_{(A \cup D)^c}(z, x) \quad (4.16)$$

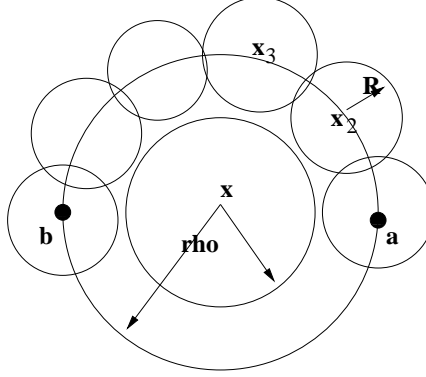
**Proof:** We will apply Lemma 4.1. If we choose  $R \leq \epsilon$ , we can use (4.2) with a constant that does not depend on  $\epsilon^8$ .

Note that  $u(z) \equiv G_{(A \cup D)^c}(z, x)$  is harmonic in  $(A \cup D)^c \setminus x$ . Thus if  $\rho > 2R$ ,  $u$  is harmonic in  $B_{2R}(z)$ , for any  $z \in \partial B_\rho(x)$ . Now let  $a, b \in \partial B_\rho(x)$ . Assume that  $a$  is such that  $\sup_{z \in \partial B_\rho(x)} u(z) = u(a)$ , and  $\inf_{z \in \partial B_\rho(x)} u(z) = u(b)$ . Then we can find  $k \leq \pi\rho/R$  points  $x_1, \dots, x_k \in \partial B_\rho(x)$  such that  $x_1 = a$ ,  $b \in B_R(x_k)$ , and  $B_R(x_i) \cap B_R(x_{i+1}) \neq \emptyset$ .

---

<sup>8</sup>If  $x$  is a (quadratic) critical point of  $F$ , then we can even choose  $R = \epsilon^{1/2}$ .





Clearly then

$$\begin{aligned}
 u(a) &\leq C \inf_{z \in B_R(a)} \leq C \inf_{z \in B_R(a) \cap B_R(x_2)} u(z) \leq C \sup_{z \in B_R(x_2)} u(z) \leq C^2 \inf_{z \in B_R(x_2)} u(z) \leq \dots \\
 &\dots \leq C^{k-1} \sup_{z \in B_R(x_k)} u(z) \leq C^k \inf_{z \in B_R(x_k)} u(z) = u(b)
 \end{aligned} \tag{4.17}$$

Thus  $u(a) \leq C^{\rho/R} u(b)$ . Therefore, if  $\rho = c\epsilon$ , for some finite constant  $c$ , and  $R = \epsilon$ , sup and inf are related by at most a finite  $\epsilon$ -independent constant. This proves the lemma.  $\diamond$

Combining now Lemma 4.6 with Lemma 4.5 and equation (4.14), we arrive at the assertion of the proposition.  $\diamond$

**A-priori bounds on capacities.** To make use of the renewal estimate (4.4) we need of course some bounds on the capacities. The next proposition provides a first set of rough bounds, that provide the necessary estimates in the equilibrium potential that will later be used to get sharp bounds on capacities.

**Proposition 4.7:** *Let  $D$  be a closed set, and  $x \in D^c$ . Denote by  $z^* = z^*(x, D)$  a point such that*

$$F(z^*) = \inf_{\gamma: \gamma(0)=x, \gamma(1) \in D} \left( \sup_{t \in [0,1]} [F_N(\gamma(t))] \right) \tag{4.18}$$

where the infimum is over all continuous paths leading from  $x$  to  $D$ . Let  $\rho \leq c\epsilon / \|\nabla F(z^*)\|_\infty$ . Then there is a constant  $C > 0$  such that

(i)

$$\text{cap}_{B_\rho(x)}(D) \geq C(\|\nabla F(z^*)\|_\infty + \sqrt{\epsilon})\rho^{d-1} e^{-F(z^*)/\epsilon} \tag{4.19}$$

(ii)

$$\text{cap}_{B_\rho(x)}(D) \leq \epsilon C \rho^{d-2} e^{-F(z^*)/\epsilon} \tag{4.20}$$

**Proof:** To prove the lower bound we use the variational representation of capacities (2.15) and some obvious monotonicity properties. We begin by choosing a smooth path  $\omega$  going from  $x$  to  $D$  in such a way that it remains in the level set  $F(z) \leq F(z^*)$ , with equality holding only when passing  $z^*$ . In fact, the canonical path can be constructed using pieces of the deterministic trajectory of the unperturbed equation  $dX_\epsilon(t) = -\nabla F(X_\epsilon(t))dt$  in rather obvious manner, but this is not important at the moment. Given this path, we parametrize it by arc-length, so that  $\|\dot{\omega}(t)\|_2 = 1$  for all time.

Given  $\omega(t)$ , we construct the tube of width  $\rho$  around  $\omega(t)$ ,

$$\omega^\rho \equiv \{z \in \mathbb{R}^d | \exists t \in [0, |\omega|] \|\omega(t) - z\|_2 \leq \rho\} \quad (4.21)$$

Let us denote the  $d - 1$ -dimensional disk of radius  $\rho$  centered at the origin by  $D_\rho$ . The important point to notice is that

$$\|\nabla h(\omega(t) + z_\perp)\|_2^2 \geq \left[ \frac{d}{dt} h(\omega(t) + z_\perp) \right]^2 \quad (4.22)$$

Therefore we may bound the Dirichlet form

$$\Phi_\Omega(h) \geq \epsilon \int_{D_\rho} dz_\perp \int_0^{|\omega|} dt e^{F(\omega(t)+z_\perp)/\epsilon} \left[ \frac{d}{dt} h(\omega(t) + z_\perp) \right]^2 \quad (4.23)$$

The minimization problem is now trivial, i.e. it decomposes for each fixed  $z_\perp$  into a one-dimensional problem whose solution is well known. In fact, the minimizer  $h_{z_\perp}(t)$  is the solution of the 1-dimensional Dirichlet problem

$$\begin{aligned} \left[ -\epsilon \frac{d}{dt} + \frac{d}{dt} F(\omega(t) + z_\perp) \right] \frac{d}{dt} h_{z_\perp}(t) &= 0 \\ h_{z_\perp}(0) &= 1 \\ h_{z_\perp}(|\omega|) &= 0 \end{aligned} \quad (4.24)$$

whose solution is readily found to be

$$h_{z_\perp}(t) = \frac{\int_t^{|\omega|} ds e^{F(\omega(s)+z_\perp)/\epsilon}}{\int_0^{|\omega|} ds e^{F(\omega(s)+z_\perp)/\epsilon}} \quad (4.25)$$

Inserting this solution into the lower bound (4.23) yields

$$\text{cap}_{B_\rho(x)}(D) \geq \epsilon \int_{D_\rho} dz_\perp \left[ \int_0^{|\omega|} dt e^{F(\omega(t)+z_\perp)/\epsilon} \right]^{-1} \quad (4.26)$$

From here the stated lower bounds results follow from simple saddle point evaluations of the integral in the denominator.

To prove the upper bound, just note that in the case when  $z^* = x$ , we can always choose a function  $h$  that is equal to one on  $B_\rho(x)$  and that decays to zero over a distance  $\rho$ . Then  $\|\nabla h\|_2 \leq 1/\rho$  on a set of volume  $C\rho^d$ , and zero elsewhere. The upper bound (4.20) follows immediately. If  $z^* \neq x$ , we choose a trial function that changes from 0 to 1 in a  $\rho$ -neighborhood of the saddle  $z^*$ ; away from  $z^*$  the change takes place in a set where  $F(y) > F(z^*)$ , so that the resulting additional contribution to the Dirichlet form is exponentially suppressed. This also yields (4.20).  $\diamond$

**Remark:** This estimate is in general quite poor, in particular when  $z^* \neq x$ . We will prove sharp results in that case in Section 6. The crude bounds serve two purposes: 1) to yield an a priori bound on the equilibrium potential (in conjunction with Proposition 4.3) that will then be used to prove a sharp estimate on capacities, and 2) to get an a priori estimate on the spectrum of certain Dirichlet operators.

**Bounds on the equilibrium potential.** Combining the renewal bound on the equilibrium obtained in Proposition 4.5 with the bound on capacities from proposition 4.7 yields very sharp estimates on the equilibrium potential in the level set of the saddle between the sets  $A$  and  $D$ .

**Corollary 4.8:** *Let  $A$  and  $D$  be closed sets and assume that  $z^*(A, D) \notin A \cup D$ . Then there is a finite positive constant  $C$  such that, for  $x \notin A \cup D$ , and  $z^*(x, D) \neq x$ ,*

$$h_{A,D}(x) \leq C\epsilon^{-1/2} e^{-|F(z^*(x,A)) - F(z^*(x,D))|/\epsilon} \quad (4.27)$$

**Remark:** This bound is useful only when  $F(z^*(x, D)) > F(x)$ . If this is not the case one may use that  $h_{A,D}(y) = 1 - h_{D,A}(y)$  and apply (4.27) on  $h_{D,A}(y)$ . This yields good control whenever  $x$  is below the level set of the saddle  $z^*(A, D)$ .

**Proof:** The proof is straightforward. We just insert the bounds on capacities of Proposition 4.7 into the renewal bound on the equilibrium potential of Proposition 4.5, choosing  $\rho = C\epsilon$ .  $\diamond$

## 5. Sharp estimates on capacities.

In this section we show how to get coinciding upper and lower bound on the relative

Newtonian capacity of two balls of radius  $\rho$  centered at the local minima  $x, y$  of the function  $F$ . We assume that  $\rho$  is so small that  $z^*(x, y)$  is not contained in these balls, and that the radii are at least  $\epsilon^9$ . Let us denote these sets by  $B_x$  and  $B_y$ , respectively.

We denote by  $\mathcal{S}_{x,y}$  the set of points that realize the minimax in the definition  $\widehat{F}(x, y)$  (c.f. (1.2)). We will assume that  $\mathcal{S}_{x,y}$  is a (finite) union of points.

**Theorem 5.1:** *Let  $s_1^*, \dots, s_k^*$  denote the saddle points connecting  $x$  to  $y$ , and suppose that Assumption (ND) holds for  $S(xy)$ . Let  $\lambda_1^*(s_i^*)$  denote the unique negative eigenvalue of the Hessian of  $F$  at  $s_i^*$ . Then, under the above hypothesis on the function  $F$ ,*

$$\text{cap}_{B_x}(B_y) = e^{-\widehat{F}(x,y)/\epsilon} \frac{(2\pi\epsilon)^{d/2}}{2\pi} \sum_{i=1}^k \frac{|\lambda_1^*(s_i^*)|}{\sqrt{|\det(\nabla^2 F(s_i^*))|}} (1 + O(\sqrt{\epsilon} |\ln \epsilon|)) \quad (5.1)$$

**Proof:** The capacity  $\text{cap}_{B_x}(B_y)$  verifies the Dirichlet principle (2.15)

$$\text{cap}_{B_x}(B_y) = \inf_{h \in \mathcal{H}_y^x} \Phi(h) \quad (5.2)$$

(where we abbreviate for simplicity  $\Phi \equiv \Phi_{(B_x \cup B_y)^c}$ ) where the space  $\mathcal{H}_y^x$  is the function space

$$\mathcal{H}_y^x \equiv \{h \in W^{1,2}(\mathbb{R}^d, \mathbb{Q}(dx)) : h(z) \in [0, 1], h|_{B_x} \equiv 1, h|_{B_y} = 0\} \quad (5.3)$$

For simplicity we consider the case of a single saddle point,  $s^*$ , first. Without restriction of generality we can choose co-ordinates such that  $s^* = 0$  and that

$$F(z) = F(0) - \frac{|\lambda_1^*|}{2} z_1^2 + \sum_{i=2}^d \frac{\lambda_i^*}{2} z_i^2 + O(\|z\|_2^3) \quad (5.4)$$

for small  $\|z\|_2$ . Define a neighborhood of zero

$$C_\delta \equiv \left[ -\delta/\sqrt{|\lambda_1^*|}, \delta/\sqrt{|\lambda_1^*|} \right] \bigotimes_{i=2}^d \left[ -2\delta/\sqrt{\lambda_i^*}, 2\delta/\sqrt{\lambda_i^*} \right] \quad (5.5)$$

Since we have assumed that there is a single saddle point at the communication height between  $x$  and  $y$ , it is possible to choose  $\delta > 0$  so small that there exists a strip  $\mathcal{S}_\delta$  of width  $2\delta/\sqrt{|\lambda_1^*|}$  containing 0 and separating  $x$  and  $y$  in the sense that any path connecting these

---

<sup>9</sup>It will become clear from the proof that the precise form of these sets is irrelevant for the result.

points must cross  $\mathcal{S}_\delta$ , and that for all  $z \in \mathcal{S}_\delta \setminus C_\delta$ ,  $F(z) \geq \delta^2$ . Let  $D_x$  and  $D_y$  be the connected components of  $\mathbb{R}^d \setminus \mathcal{S}_\delta$  containing  $x$  and  $y$ , respectively.

**The upper bound.** To prove an upper bound on the capacity we just choose a function  $h^+$  to our convenience. We will make the choice

$$\begin{aligned} h^+(z) &= 1, z \in D_x, \quad h^+(z) = 0, z \in D_y \\ h^+ &\text{ on } \mathcal{S}_\delta \setminus C_\delta \text{ arbitrary, except } \|\nabla h^+\|_2 \leq c\sqrt{|\lambda_1^*|}/\delta \\ &\text{for } z \in C_\delta, h^+(z) = f(z_1) \end{aligned} \quad (5.6)$$

where  $f$  is the solution of the one-dimensional Dirichlet problem

$$\begin{aligned} \left(-\epsilon \frac{d}{dz_1} + \frac{d}{dz_1} F(z_1; 0, \dots, 0)\right) \frac{d}{dz_1} f(z_1) &= 0 \\ f(-\delta/\sqrt{|\lambda_1^*|}) &= 1 \\ f(+\delta/\sqrt{|\lambda_1^*|}) &= 0 \end{aligned} \quad (5.7)$$

The solution of this problem is obviously

$$f(z_1) = \frac{\int_{z_1}^{\delta/\sqrt{|\lambda_1^*|}} e^{F(t,0)/\epsilon} dt}{\int_{-\delta/\sqrt{|\lambda_1^*|}}^{\delta/\sqrt{|\lambda_1^*|}} e^{F(t,0)/\epsilon} dt} \quad (5.8)$$

Inserting this function into (5.2), we see that

$$\begin{aligned} \text{cap}_{B_x}(B_y) &\leq \epsilon \int_{-2\delta/\sqrt{\lambda_2^*}}^{2\delta/\sqrt{\lambda_2^*}} dz_2 \cdots \int_{-2\delta/\sqrt{\lambda_d^*}}^{2\delta/\sqrt{\lambda_d^*}} dz_d \left( \int_{-\delta/\sqrt{|\lambda_1^*|}}^{\delta/\sqrt{|\lambda_1^*|}} dz_1 e^{-F(z)/\epsilon} \|f'(z_1)\|^2 \right) \\ &\quad + \epsilon c \delta^{-2} \int_{\mathcal{S}_\delta \setminus C_\delta} dz e^{-F(z)/\epsilon} \end{aligned} \quad (5.9)$$

The second term is bounded by  $\epsilon c \delta^{-2} e^{-\delta^2/\epsilon} \text{const.}$  by assumption on  $F$ .

The first term is given by

$$\Phi_{C_\delta}(h^+) = \epsilon \frac{\int_{C_\delta} dz e^{-F(z)/\epsilon} e^{2F(z_1,0)/\epsilon}}{\left( \int_{-\delta/\sqrt{|\lambda_1^*|}}^{\delta/\sqrt{|\lambda_1^*|}} e^{F(t,0)/\epsilon} dt \right)^2} \quad (5.10)$$

Now on  $C_\delta$  we have that

$$F(z) = F(0) + \frac{-|\lambda_1^*|z_1^2 + \lambda_2^*z_2^2 \cdots + \lambda_d^*z_d^2}{2} + O(\|z\|_2^3) \quad (5.11)$$

and thus

$$F(z) - 2F(z_1, 0) = -F(0) + \frac{|\lambda_1^*|z_1^2 + \lambda_2^*z_2^2 \cdots + \lambda_d^*z_d^2}{2} + O(\|z\|_2^3) \quad (5.12)$$

But on  $C_\delta$ ,  $\|z\|_2 \leq C'\delta$  and if we choose  $\delta = K\sqrt{\epsilon|\ln \epsilon|}$  for some constant  $K$ , the numerator in (5.10) satisfies the bound

$$\begin{aligned} \int_C dz e^{-F(z)/\epsilon} e^{2F(z_1, 0)/\epsilon} &\leq e^{-F(0)/\epsilon} e^{C\epsilon^{1/2}|\ln \epsilon|^{3/2}} \int_{\mathbb{R}^d} \exp\left(-\frac{|\lambda_1^*|z_1^2 + \cdots + \lambda_d^*z_d^2}{2\epsilon}\right) dz \\ &= e^{-F(0)/\epsilon} \frac{(2\pi\epsilon)^{d/2}}{\prod_{i=1}^d \sqrt{|\lambda_i^*|}} \left(1 + O\left(\epsilon^{1/2}|\ln \epsilon|^{3/2}\right)\right) \end{aligned} \quad (5.13)$$

Similarly, the integral in the denominator is bounded from below by

$$\begin{aligned} \int_{-\delta/\sqrt{|\lambda_1^*|}}^{\delta/\sqrt{|\lambda_1^*|}} e^{F(t, 0)/\epsilon} dt &\geq e^{-C\epsilon^{1/2}|\ln \epsilon|^{3/2}} e^{+F(0)/\epsilon} \left(\frac{(2\pi\epsilon)^{1/2}}{\sqrt{|\lambda_1^*|}} - 2 \int_{\delta/\sqrt{|\lambda_1^*|}}^{\infty} dt e^{-|\lambda_1^*|t^2/\epsilon}\right) \\ &\geq e^{-C\epsilon^{1/2}|\ln \epsilon|^{3/2}} e^{+F(0)/\epsilon} \left(\frac{(2\pi\epsilon)^{1/2}}{\sqrt{|\lambda_1^*|}} - \frac{e^{-\delta^2/\epsilon}}{\delta\epsilon^{-1/2}}\right) \\ &= e^{+F(0)/\epsilon} \frac{\sqrt{2\pi\epsilon}}{\sqrt{|\lambda_1^*|}} \left(1 + O\left(\epsilon^{1/2}|\ln \epsilon|^{3/2}\right)\right) \end{aligned} \quad (5.14)$$

Combining the estimates (5.13), (5.14), and (5.9), we arrive at the upper bound

$$\Phi_{C_\delta}(h^+) \leq e^{-F(0)/\epsilon} (2\pi\epsilon)^{d/2} \frac{|\lambda_1^*|}{2\pi\sqrt{|\det(\nabla^2 F(0))|}} \left(1 + O\left(\epsilon^{1/2}|\ln \epsilon|^{3/2}\right)\right) \quad (5.15)$$

Since this results coincides with the heuristic results, we may expect to get a corresponding lower bound.

**The lower bound.** For the lower bound we will consider a different domain

$$\begin{aligned} \widehat{C}_\delta &\equiv \left[-2\delta/\sqrt{|\lambda_1^*|}, 2\delta/\sqrt{|\lambda_1^*|}\right] \bigotimes_{i=2}^d \left[-\delta/\sqrt{(d-1)\lambda_i^*}, \delta/\sqrt{(d-1)\lambda_i^*}\right] \\ &\equiv \left[-2\delta/\sqrt{|\lambda_1^*|}, 2\delta/\sqrt{|\lambda_1^*|}\right] \otimes \widehat{C}_\delta^\perp \end{aligned} \quad (5.16)$$

Let  $h^*$  denote the minimizer of the variational problem (5.2), i.e. the equilibrium potential of the capacitor  $(B_x, B_y)$ . Then

$$\inf_{h \in \mathcal{H}_y^c} \Phi(h) = \Phi(h^*) \geq \Phi_{\widehat{C}_\delta}(h^*) \quad (5.17)$$

Obviously,

$$\begin{aligned}
\Phi_{\widehat{C}_\delta}(h) &\geq \bar{\Phi}_{\widehat{C}_\delta}(h) \equiv \epsilon \int_{\widehat{C}_\delta} dz e^{-F(z)/\epsilon} \left( \frac{\partial h(z)}{\partial z_1} \right)^2 \\
&= \epsilon \int_{\widehat{C}_\delta^\perp} dz_\perp \left( \int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} dz_1 e^{-F(z)/\epsilon} \left\| \frac{\partial h(z_1, z_\perp)}{\partial z_1} \right\|^2 \right) \\
&\geq \epsilon \int_{\widehat{C}_\delta^\perp} dz_\perp \left( \inf_{f: f(\pm\delta/\sqrt{|\lambda_1^*|})=h^*(\pm\delta/\sqrt{|\lambda_1^*|})} \int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} dz_1 e^{-F(z)/\epsilon} \|f'(z_1)\|^2 \right)
\end{aligned} \tag{5.18}$$

The minimization problem for fixed values of  $z_\perp$  is of course the solution of the Dirichlet problem

$$\begin{aligned}
\left( -\epsilon \frac{d}{dz_1} + \frac{d}{dz_1} F(z_1; z_\perp) \right) \frac{d}{dz_1} f(z_1) &= 0 \\
f\left(-2\delta/\sqrt{|\lambda_1^*|}\right) &= h^*\left(-2\delta/\sqrt{|\lambda_1^*|}, z_\perp\right) \\
f\left(+2\delta/\sqrt{|\lambda_1^*|}\right) &= h^*\left(2\delta/\sqrt{|\lambda_1^*|}, z_\perp\right)
\end{aligned} \tag{5.19}$$

The solution of this Dirichlet problem is readily obtained: let us set  $a = h^*(-2\delta/\sqrt{|\lambda_1^*|}, z_\perp)$  and  $b = h^*(2\delta/\sqrt{|\lambda_1^*|}, z_\perp)$ , and  $g(z_1) = F(z_1; z_\perp)$ . The general solution of the differential equation in (5.19) is

$$f(z_1) = c \int_{z_1}^s e^{g(t)/\epsilon} dt \tag{5.20}$$

where the constants  $c$  and  $s$  are determined by the boundary conditions, i.e.

$$\begin{aligned}
c \int_{-2\delta/\sqrt{|\lambda_1^*|}}^s e^{g(t)/\epsilon} dt &= a \\
c \int_{2\delta/\sqrt{|\lambda_1^*|}}^s e^{g(t)/\epsilon} dt &= b
\end{aligned} \tag{5.21}$$

from which we get that

$$c = \frac{a}{\int_{-2\delta/\sqrt{|\lambda_1^*|}}^s e^{g(t)/\epsilon} dt} \tag{5.22}$$

while  $s$  is determined through the equation

$$\frac{\int_{2\delta/\sqrt{|\lambda_1^*|}}^s e^{g(t)/\epsilon} dt}{\int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} e^{g(t)/\epsilon} dt + \int_{2\delta/\sqrt{|\lambda_1^*|}}^s e^{g(t)/\epsilon} dt} = \frac{b}{a} \tag{5.23}$$

or

$$\int_{2\delta/\sqrt{|\lambda_1^*|}}^s e^{g(t)/\epsilon} dt = \frac{b}{a-b} \int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} e^{g(t)/\epsilon} dt \tag{5.24}$$

and thus

$$\int_{-2\delta/\sqrt{|\lambda_1^*|}}^s e^{g(t)/\epsilon} dt = \frac{a}{a-b} \int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} e^{g(t)/\epsilon} dt \quad (5.25)$$

Inserting this solution into (5.18) yields

$$\begin{aligned} \Phi_{\widehat{C}_\delta}(h^*) &\geq \epsilon \int_{\widehat{C}_\delta^\perp} dz_\perp \int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} dz_1 \frac{e^{-F(z_1, z_\perp)/\epsilon} \left( h^*(-2\delta/\sqrt{|\lambda_1^*|}, z_\perp) \right)^2 e^{2F(z_1, z_\perp)/\epsilon}}{\left( \int_{-2\delta/\sqrt{|\lambda_1^*|}}^{s(z_\perp)} e^{F(t, z_\perp)/\epsilon} dt \right)^2} \\ &= \epsilon \frac{\int_{\widehat{C}_\delta^\perp} dz_\perp \left( h^*(-2\delta/\sqrt{|\lambda_1^*|}, z_\perp) - h^*(2\delta/\sqrt{|\lambda_1^*|}, z_\perp) \right)^2}{\int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} e^{F(t, z_\perp)/\epsilon} dt} \end{aligned} \quad (5.26)$$

But using again (5.4), we see that

$$\begin{aligned} \int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} e^{F(t, z_\perp)/\epsilon} dt &= \left( e^{+\sum_{i=2}^d \frac{\lambda_i^* z_i^2}{2\epsilon}} + O(\delta^3/\epsilon) \right) \int_{-2\delta/\sqrt{|\lambda_1^*|}}^{2\delta/\sqrt{|\lambda_1^*|}} dt e^{-\frac{|\lambda_1^*| t^2}{2\epsilon}} \\ &\leq \frac{\sqrt{2\pi\epsilon}}{\sqrt{|\lambda_1^*|}} e^{+\sum_{i=2}^d \frac{\lambda_i^* z_i^2}{2\epsilon}} + O(\delta^3/\epsilon) \end{aligned} \quad (5.27)$$

and so

$$\begin{aligned} \Phi_{\widehat{C}_\delta}(h^*) &\geq \frac{\sqrt{\epsilon|\lambda_1^*|}}{\sqrt{2\pi}} \exp\left(-\sum_{i=2}^d \frac{\lambda_i^* z_i^2}{2\epsilon} + O(\delta^3/\epsilon)\right) \\ &\quad \times \int_{\widehat{C}_\delta^\perp} dz_\perp \left( h^*(-2\delta/\sqrt{|\lambda_1^*|}, z_\perp) - h^*(2\delta/\sqrt{|\lambda_1^*|}, z_\perp) \right)^2 \end{aligned} \quad (5.28)$$

Now we use the fact that  $h^*(z) = \mathbb{P}_z[\tau_{B_x} < \tau_{B_y}] = h_{B_x, B_y}(z)$ . Then Corollary 4.8 implies

**Lemma 5.2:** *Uniformly in  $z_\perp \in \widehat{C}_\delta^\perp$ ,*

$$\begin{aligned} 1 - h^*\left(-2\delta/\sqrt{|\lambda_1^*|}, z_\perp\right) &\leq C\epsilon^{-1/2} e^{-\delta^2/(4\epsilon)} \\ h^*\left(2\delta/\sqrt{|\lambda_1^*|}, z_\perp\right) &\leq C\epsilon^{-1/2} e^{-\delta^2/(4\epsilon)} \end{aligned} \quad (5.29)$$

As an immediate consequence, we see that

$$\Phi_{\widehat{C}_\delta}(h^*) \geq \left(1 - C\epsilon^{-1/2} e^{-\delta^2/(4\epsilon)}\right)^2 e^{-O(\delta^3/\epsilon)} \frac{(2\pi\epsilon)^{d/2}}{2\pi} \frac{\sqrt{|\lambda_1^*|}}{\prod_{i=2}^{d-1} \sqrt{\lambda_i^*}} \left(1 - \frac{\sqrt{\epsilon(d-1)}}{\delta} e^{-\frac{\delta^2}{2(d-1)\epsilon}}\right)^{d-1} \quad (5.30)$$



Choosing as before  $\delta^2 = C\epsilon |\ln \epsilon|$ , we see that to leading order (5.30) coincides with the upper bound (5.15), which proves the theorem in the case  $k = 1$ .

The generalization of this estimate to the case when several saddle points exist on the communication height is completely straightforward and will be left to the reader. The result is the formula stated in the theorem.  $\diamond$

## 6. Metastable exit times and capacities.

In this section we compute the mean value of certain *metastable exit times* in terms of capacities. This will be largely analogous to the results on mean transition times obtained in [BEGK1,BEGK2]. The only new ingredient needed is the following sharpening of (2.27), resp. (2.28) when a process starts in a local minimum of  $F$ .

**Proposition 6.1:** *Let  $x$  be a (non-degenerate quadratic) critical point of  $F$  and let  $A, D$  be closed sets. Then there exists  $\alpha > 0$  such that*

$$\mathbb{E}_x \tau_D = \frac{\int_{D^c} dy e^{-F(y)/\epsilon} h_{B_\epsilon(x), D}(y)}{\text{cap}_{B_\epsilon(x)}(D)} \left(1 + O(\epsilon^{\alpha/2})\right) \quad (6.1)$$

and

$$\mathbb{E}_x \tau_D \mathbb{1}_{\tau_D < \tau_A} = \frac{\int_{(A \cup D)^c} dy e^{-F(y)/\epsilon} h_{B_\epsilon(x), D \cup A}(y) h_{D, A}(y)}{\text{cap}_{B_\epsilon(x)}(A \cup D)} \left(1 + O(\epsilon^{\alpha/2})\right) \quad (6.2)$$

**Proof:** The proofs of (6.1) and (6.2) are completely analogous, and we will only consider the former. Let us write  $w_D(y) \equiv \mathbb{E}_y \tau_D$ ,  $y \in D^c$ . Recall that  $w_D(y)$  solves the inhomogeneous Dirichlet problem (2.25) (with  $A = \emptyset$ ). We will consider this function on a ball  $B_{R_0}(x)$ , where  $x$  is a critical point of  $F$ . This implies that for some constant  $K$ ,  $\sup_{y \in B_{R_0}(x)} \|\nabla F(y)\|_\infty \leq KR_0$  (if  $R_0$  is small). Thus the Hölder and Harnack inequalities Lemmata (4.23) and (4.22) have uniform constants if  $R_0 \leq \sqrt{\epsilon}$ .

Now note first that due to (2.26),  $w_D(y)$  inherits from Lemma 4.6 the uniform Harnack bound

$$\sup_{y \in B_{\sqrt{\epsilon}}(x)} w_D(y) \leq C \inf_{y \in B_{\sqrt{\epsilon}}(x)} w_D(y) \quad (6.3)$$

Now use Lemma (4.22) with  $R = \epsilon$ , since  $w_D$  solves  $L_\epsilon w_D = 1$ . This yields that

$$\text{osc}_{B_\epsilon(x)} w_D \leq C\epsilon^{\alpha/2} \left( \sup_{y \in B_{R_0}(x)} w_D(y) + R_0 \right) \quad (6.4)$$

This implies immediately that

$$\begin{aligned} \sup_{y \in B_\epsilon(x)} w_D(y) &\leq w_D(x) + C^2 e^{\alpha/2} w_D(x) + C\epsilon^{1/2+\alpha/2} \\ \inf_{y \in B_\epsilon(x)} w_D(y) &\geq w_D(x) - C^2 e^{\alpha/2} w_D(x) - C\epsilon^{1/2+\alpha/2} \end{aligned} \quad (6.5)$$

Using these estimates in (2.27) with  $\rho = \epsilon$  resp. (2.28) proves the proposition.  $\diamond$

By the preceding proposition, all we need to know in order to compute the mean arrival times are the capacities and the equilibrium potential. The latter is quite well controlled by Proposition 4.3 and the rough estimates on capacities Proposition 4.7, and this will allow us to get already quite remarkable formulae.

**Theorem 6.2:** *Let  $x_j$ ,  $j = 1, \dots, n$  be the local minima of  $F$ . Let  $\mathcal{S}_k = \cup_{i=1}^k B_\rho(x_i)$  be a collection of balls  $B_\rho(x_i)$  where  $\rho \geq \epsilon$  and no ball contains any other minimum or saddle point of  $F$ . Assume moreover that for a given  $j$ , all  $i > k$ ,  $i \neq j$ , either*

$$F(z^*(x_i, x_j)) - F(x_j) > F(z^*(x_i, \mathcal{S}_k)) - F(x_i) \quad (6.6)$$

or

$$F(z^*(x_i, x_j)) < F(z^*(x_i, \mathcal{S}_k)) \quad (6.7)$$

Then, for  $j > k$ ,

$$\begin{aligned} \mathbb{E}_{x_j} \tau_{\mathcal{S}_k} &= \\ &= \frac{1}{\text{cap}_{B_\epsilon(x_j)}(\mathcal{S}_k)} \sum_{i: F(z^*(x_i, \mathcal{S}_k)) > F(z^*(x_i, x_j))} \frac{(2\pi\epsilon)^{d/2}}{\sqrt{\det(\nabla^2 F(x_i))}} e^{-F(x_i)/\epsilon} (1 + O(\epsilon^{1/2} |\ln \epsilon|, \epsilon^{\alpha/2})) \end{aligned} \quad (6.8)$$

Note that the sum always includes the term  $i = j$ . In particular, if for all  $i > k$ ,  $F(x_i) > F(x_j)$ , then

$$\mathbb{E}_{x_j} \tau_{\mathcal{S}_k} = \frac{1}{\text{cap}_{B_\epsilon(x_j)}(\mathcal{S}_k)} \frac{(2\pi\epsilon)^{d/2}}{\sqrt{\det(\nabla^2 F(x_j))}} e^{-F(x_j)/\epsilon} (1 + O(\epsilon^{1/2} |\ln \epsilon|, \epsilon^{\alpha/2})) \quad (6.9)$$

**Remark:** A transition to a set  $D$  for which (6.9) holds will be called a *metastable exit* and the formula (6.9) is the mean metastable exit time from the minimum  $j$ .

**Proof:** Let us consider the set  $\Gamma_j \equiv \{y : F(y) > F(z^*(x_j, \mathcal{M})) + \delta\}$  for some sufficiently small  $\delta > 0$ . Let  $\Gamma_j(i)$  denote the connected component of  $\Gamma_j$  that contains  $x_i$ . Note that

some of these sets may be empty, and some may coincide. Let  $\{\Gamma_j(\tilde{i})\}_{\tilde{i}}$  be an enumeration of the distinct non-empty members of this collection. Let us write

$$\begin{aligned} \int_{\mathcal{S}_k^c} dy e^{-F(y)/\epsilon} h_{B_\epsilon(x_j), \mathcal{S}_k}(y) &= \int_{\Gamma_j^c} dy e^{-F(y)/\epsilon} h_{B_\epsilon(x_j), \mathcal{S}_k}(y) \\ &= \sum_{\tilde{i}} \int_{\Gamma_j(\tilde{i}) \setminus \mathcal{S}_k} dy e^{-F(y)/\epsilon} h_{B_\epsilon(x_j), \mathcal{S}_k}(y) \end{aligned} \quad (6.10)$$

The first integral is bounded by  $C \exp(-[F(z^*(x_j, \mathcal{M})) + \delta]/\epsilon)$  and will be negligible. The remaining contributions will be split into those for which  $F(z^*(x_{\tilde{i}}, \mathcal{S}_k)) > F(z^*(x_{\tilde{i}}, x_j))$  and those for which the contrary is true. The point is that for the former  $h_{B_\epsilon(x_j), \mathcal{S}_k}(y)$  is close to one, while for the latter, it is typically very small. Here we make use of the fact that if  $y \in \Gamma_j(\tilde{i})$ , and  $F(z^*(x_{\tilde{i}}, \mathcal{S}_k)) > F(z^*(x_{\tilde{i}}, x_j))$ , then  $z^*(y, \mathcal{S}_k) = z^*(x_{\tilde{i}}, \mathcal{S}_k)$  and  $z^*(y, x_j) = z^*(x_{\tilde{i}}, x_j)$ . Then

$$\begin{aligned} &\sum_{i: F(z^*(x_{\tilde{i}}, \mathcal{S}_k)) > F(z^*(x_{\tilde{i}}, x_j))} \int_{\Gamma_j(\tilde{i}) \setminus \mathcal{S}_k} dy e^{-F(y)/\epsilon} h_{B_\epsilon(x_j), \mathcal{S}_k}(y) \\ &= \sum_{i: F(z^*(x_{\tilde{i}}, \mathcal{S}_k)) > F(z^*(x_{\tilde{i}}, x_j))} \int_{\Gamma_j(\tilde{i}) \setminus \mathcal{S}_k} dy e^{-F(y)/\epsilon} (1 - h_{\mathcal{S}_k, B_\epsilon(x_j)}(y)) \end{aligned} \quad (6.11)$$

Now by Corollary 4.8,

$$0 \leq h_{\mathcal{S}_k, B_\epsilon(x_j)}(y) \leq C \epsilon^{-1/2} e^{-[F(z^*(x_{\tilde{i}}, \mathcal{S}_k)) - F(z^*(x_{\tilde{i}}, x_j))]/\epsilon} \quad (6.12)$$

which by assumption is exponentially small. On the other hand, if  $x_{\tilde{i}}$  is the absolute minimum of  $F$  within  $\Gamma_j(\tilde{i})$ , and if the Hessian,  $\nabla^2 F(x_{\tilde{i}})$ , at this minimum is non-degenerate,

$$\int_{\Gamma_j(\tilde{i}) \setminus \mathcal{S}_k} dy e^{-F(y)/\epsilon} = \frac{(2\pi\epsilon)^{d/2}}{\sqrt{\det(\nabla^2 F(x_{\tilde{i}}))}} e^{-F(x_{\tilde{i}})/\epsilon} (1 + O(\epsilon^{1/2} |\ln \epsilon|)) \quad (6.13)$$

by standard Laplace asymptotics. Thus

$$\begin{aligned} &\sum_{i: F(z^*(x_{\tilde{i}}, \mathcal{S}_k)) > F(z^*(x_{\tilde{i}}, x_j))} \int_{\Gamma_j(\tilde{i}) \setminus \mathcal{S}_k} dy e^{-F(y)/\epsilon} h_{B_\epsilon(x_j), \mathcal{S}_k}(y) \\ &= \sum_{i: F(z^*(x_{\tilde{i}}, \mathcal{S}_k)) > F(z^*(x_{\tilde{i}}, x_j))} \frac{(2\pi\epsilon)^{d/2}}{\sqrt{\det(\nabla^2 F(x_{\tilde{i}}))}} e^{-F(x_{\tilde{i}})/\epsilon} (1 + O(\epsilon^{1/2} |\ln \epsilon|)) \end{aligned} \quad (6.14)$$

The remaining terms cannot be computed as precisely; however, often the upper bound will show that they are totally negligible (but this is not always the case). Using again Corollary

4.8, when  $F(z^*(x_i, \mathcal{S}_k)) \leq F(z^*(x_i, x_j))$ ,

$$\begin{aligned}
& \int_{\Gamma_j(\tilde{\ell}) \setminus \mathcal{S}_k} dy e^{-F(y)/\epsilon} h_{B_\epsilon(x_j), \mathcal{S}_k}(y) \leq C\epsilon^{-1/2} \int_{\Gamma_j(\tilde{\ell}) \setminus \mathcal{S}_k} dy e^{-F(y)/\epsilon} e^{-[F(z^*(y, x_j)) - F(z^*(y, \mathcal{S}_k))]/\epsilon} \\
& = C\epsilon^{-1/2} \int_{\Gamma_j(\tilde{\ell}) \setminus \mathcal{S}_k : z^*(y, \mathcal{S}_k) = y} dy e^{-F(z^*(x_i, x_j))/\epsilon} \\
& + C\epsilon^{-1/2} e^{-F(x_j)/\epsilon} \int_{\Gamma_j(\tilde{\ell}) \setminus \mathcal{S}_k : z^*(y, \mathcal{S}_k) \neq y} dy e^{-[F(y) - F(x_i)]/\epsilon} e^{-[F(z^*(x_i, x_j)) - F(x_j) - F(z^*(x_i, \mathcal{S}_k)) + F(x_i)]/\epsilon} \\
& = C\epsilon^{-1/2} e^{-F(z^*(x_i, x_j))/\epsilon} |\{\Gamma_j(\tilde{\ell}) \setminus \mathcal{S}_k : z^*(y, \mathcal{S}_k) = y\}| \\
& + C\epsilon^{-1/2} e^{-F(x_j)/\epsilon} e^{-[F(z^*(x_i, x_j)) - F(x_j) - F(z^*(x_i, \mathcal{S}_k)) + F(x_i)]/\epsilon} \frac{(2\pi\epsilon)^{d/2}}{\sqrt{\det(\nabla^2 F(x_i))}} (1 + O(\epsilon^{1/2} |\ln \epsilon|))
\end{aligned} \tag{6.15}$$

The first summand is always exponentially negligible compared to the principle terms, since of course  $F(z^*(x_i, x_j)) > F(x_j)$ . The second summand is negligible only when (6.6) holds, which will be the case in the main applications. This implies (6.8). (6.9) is an immediate consequence.  $\diamond$

**Proof of Theorem 3.2:** The proof of Theorem 3.2 is immediate by inserting the formula for the Capacity of Theorem 3.1 into (6.8), except for the error terms of order  $\epsilon^{\alpha/2}$  which we will now show can be removed easily. Namely, note that nothing changes in the proof of Theorem 6.2 if we replace the starting point  $x_j$  by some point  $x \in B_{\sqrt{\epsilon}}(y)$ . Also, inspecting the proof of Theorem 5.1 one sees that the difference between  $\text{cap}_{B_\epsilon x_j}(\mathcal{S}_k)$  and  $\text{cap}_{B_\epsilon x}(\mathcal{S}_k)$  for  $x \in B_{\sqrt{\epsilon}}(y)$  is in fact much smaller than the error terms. Thus we get that in fact

$$\text{osc}_{x \in B_{\sqrt{\epsilon}}(x_j)} \mathbb{E}_x \tau_{\mathcal{S}_k} \leq C(\epsilon^{\alpha/2} + \epsilon^{1/2} |\ln \epsilon|) \mathbb{E}_{x_j} \tau_{\mathcal{S}_k} \tag{6.16}$$

which improves the input in the Hölder estimate by a factor  $\epsilon^{\alpha/2}$ , which in turn allows to improve the error estimates in Theorem 6.2 from  $\epsilon^{\alpha/2}$  to  $\epsilon^\alpha$ . Iterating this procedure, we can reduce this errors until they are of the same order as the  $\epsilon^{1/2} |\ln \epsilon|$  terms. This proves Theorem 3.2.  $\diamond$

## References

- [BEGK1] A. Bovier, M. Eckhoff, V. Gaynard, and M. Klein, Metastability in stochastic dynamics of disordered mean-field models, *Probab. Theor. Rel. Fields* **119**, 99–161(2001).
- [BEGK2] A. Bovier, M. Eckhoff, V. Gaynard, and M. Klein, Metastability and low-lying spectra in reversible Markov chains, *Commun. Math. Phys.* **228**, 219-255 (2002).

- [BGK] A. Bovier, V. Gayrard, and M. Klein, Metastability in reversible diffusion processes II. Precise asymptotics for small eigenvalues, preprint (2002).
- [BluGet] R.M. Blumenthal and R.K. Gettoor, Markov processes and potential theory, Academic Press, New York, London, 1968.
- [BuMa1] V.A. Buslov and K.A. Makarov, A time-scale hierarchy with small diffusion, *Teoret. Mat. Fiz.* **76**, 219–230 (1988); translation in *Theoret. Math. Phys.* **76**, 818–826 (1989).
- [BuMa2] V.A. Buslov and K.A. Makarov, Life spans and least eigenvalues of an operator of small diffusion (Russian), *Mat. Zametki* **51**, 20–31 (1992); translation in *Math. Notes* **51**, 14–21 (1992).
- [DS] P.G. Doyle and J.L. Snell, Random walks and electrical networks, Carus Mathematical Monographs, 22, Mathematical Association of America, Washington, DC, 1984.
- [Doo] J.L. Doob, Classical potential theory and its probabilistic counterpart, *Grundlehren der mathematischen Wissenschaften* 262, Springer Verlag, Berlin, 1984.
- [Ey] H. Eyring, The activated complex in chemical reactions, *J. Chem. Phys.* **3**, 107–115 (1935).
- [FW] M.I. Freidlin and A.D. Wentzell, Random perturbations of dynamical systems, Springer, Berlin-Heidelberg-New York, 1984.
- [GLE] S. Glasstone, K.J. Laidler, and H. Eyring, The theory of rate processes, McGraw-Hill, New York, (1941).
- [GT] D. Gilbarg and N.S. Trudinger, Elliptic partial differential equations of second order, Second edition. *Grundlehren der Mathematischen Wissenschaften*, 224. Springer-Verlag, Berlin, 1983.
- [HS1] B. Helffer, and J. Sjöstrand, J. Multiple wells in the semiclassical limit. I, *Comm. Partial Differential Equations* **9**, 337–408 (1984).
- [HS2] B. Helffer, and J. Sjöstrand, Puits multiples en limite semi-classique. II. Interaction moléculaire. Symétries. Perturbation, *Ann. Inst. H. Poincaré (Phys. Théor.)* **42**, 127–212 (1985).
- [HS3] B. Helffer, and J. Sjöstrand, Multiple wells in the semiclassical limit. III. Interaction through nonresonant wells, *Math. Nachr.* **124**, 263–313 (1985).

- [HS4] B. Helffer, and J. Sjöstrand, Puits multiples en mécanique semi-classique. IV. Étude du complexe de Witten, *Comm. Partial Differential Equations* **10**, 245–340 (1985).
- [Kaku] S. Kakutani, Markov processes and the Dirichlet problem, *Proc. Jap. Acad.* **21**, 227–233 (1941).
- [Kra] H.A. Kramers, Brownian motion in a field of force and the diffusion model of chemical reactions, *Physica* **7**, 284–304 (1940).
- [Kolo] V.N. Kolokoltsov, *Semiclassical analysis for diffusions and stochastic processes*, Springer, Berlin, 2000.
- [KoMak] V.N. Kolokoltsov and K.A. Makarov, Asymptotic spectral analysis of a small diffusion operator and the life times of the corresponding diffusion process, *Russian J. Math. Phys.* **4**, 341–360 (1996).
- [KN] C. Kipnis and C.M. Newman, The metastable behavior of infrequently observed, weakly random, one-dimensional diffusion processes, *SIAM J. Appl. Math.* **45**, 972–982 (1985).
- [MatSch1] B.J. Matkowsky and Z. Schuss, The exit problem: a new approach to diffusion across potential barriers, *SIAM J. Appl. Math.* **36**, 604–623 (1979).
- [MS1] R.S. Maier and D.L. Stein, Limiting exit location distributions in the stochastic exit problem, *SIAM J. Appl. Math.*, **57**, 752–790 (1997).
- [NS] C.St.J.A. Nash-Williams, Random walk and electric currents in networks, *Proc. Camb. Phil. Soc.* **55**, 181-194 (1959).
- [S] Ch. Schütte, *Conformational dynamics: modelling, theory, algorithm, and application to biomolecules*, preprint SC 99-18, ZIB-Berlin (1999).
- [SFHD] Ch. Schütte, A. Fischer, W. Huisinga, and P. Deuffhard, A direct approach to conformational dynamics based on hybrid Monte Carlo, *J. Comput. Phys.* **151**, 146–168 (1999).
- [Szni] A.-S. Sznitman, *Brownian motion, obstacles and random media*, Springer Monographs in Mathematics. Springer, Berlin, 1998.
- [Wen] A.D. Wentzell, Formulas for eigenfunctions and eigenmeasures that are connected with a Markov process, *Teor. Veroyatnost. i Primenen.* **18**, 329 (1973).