

Weierstraß-Institut für Angewandte Analysis und Stochastik

im Forschungsverbund Berlin e.V.

Preprint

ISSN 0946 – 8633

Metastability: a potential theoretic approach*

Anton Bovier¹

submitted: 13. Dezember 2005

¹ Weierstrass Institute
for Applied Analysis and Stochastics
Mohrenstrasse 39
10117 Berlin
and
Mathematics Institute
Technical University Berlin
Strasse des 17. Juni 136
10623 Berlin
Germany
E-Mail: bovier@wias-berlin.de

No. 1081
Berlin 2005



2000 *Mathematics Subject Classification.* 60J45,82C26.

Key words and phrases. Metastability, Markov processes, potential theory, capacity, spectral theory.

Supported by the German Research Council (DFG) and by the European Science Foundation in the programme RDSES is gratefully acknowledged

* Invited talk at the International Congress of Mathematicians 2006, Madrid.

Edited by
Weierstraß-Institut für Angewandte Analysis und Stochastik (WIAS)
Mohrenstraße 39
10117 Berlin
Germany

Fax: + 49 30 2044975
E-Mail: preprint@wias-berlin.de
World Wide Web: <http://www.wias-berlin.de/>

Abstract

Metastability is an ubiquitous phenomenon of the dynamical behaviour of complex systems. In this talk, I describe recent attempts towards a model-independent approach to metastability in the context of reversible Markov processes. I will present an outline of a general theory, based on careful use of potential theoretic ideas and indicate a number of concrete examples where this theory was used very successfully. I will also indicate some challenges for future work.

1 Introduction

Metastability is a physical phenomenon that is observed in a large variety of situations in nature. The classical school-book example is the time delay in the evaporation of overheated water, resp. the delayed freezing of under-cooled water. Generally speaking, metastability is related to the existence of multiple, well separated time-scales: at a short time-scale, the systems *appears* to be in an equilibrium state, but really explores only a confined section of its available phase space, while, at much larger time scales, it undergoes transitions *between* such *metastable* states. The main mathematical task we want to discuss is the analysis of such system at these very long time-scales.

The mathematical description of metastable systems began in the 1930ies and 1940ies and is linked to the names of Eyring [15] and Kramer [26], who were interested in metastability in the context of chemical reactions. Kramer, in particular, introduced a one-dimensional diffusion process in a double-well potential as a model of a metastable system which is still used today in many applications. This work set the way to study metastability as a phenomenon that takes place in *stochastic processes*, and, in particular, in *Markov processes*, which is the setting that we will consider in this talk.

The mathematically rigorous analysis of metastability phenomena in the context of stochastic dynamics goes back essentially to the work of Freidlin and Wentzell in the early 1970ies (see their seminal book [16]). They considered mainly the setting of finite dimensional dynamical systems perturbed by weak additive noise. In the simplest case, this would be driven by Brownian motion, but alternative settings, such as Levy-processes were also considered. Metastability arises in this context if the unperturbed system possesses several stable attractors. In this case, on short time-scales, the trajectories of the system will track those of the unperturbed system, and hence will converge towards one of the attractors. On much longer time-scales,

however, the random perturbation allow the system to perform transitions between these stable attractors. The method to analyse the occurrence of such transitions introduced by Freidlin and Wentzell in this context was *large deviation theory* on path-space. This allows to control the probability of a “atypical” trajectory, $\gamma(t)$, over some time interval, $[T_1, T_2]$, in terms of an *action functional*, $S(\gamma, T_1, T_2)$, that can be written as

$$S(\gamma, T_1, T_2) = \int_{T_1}^{T_2} \mathcal{L}(\gamma(t), \gamma'(t), t) dt \quad (1.1)$$

in the sense that

$$\lim_{\epsilon \downarrow 0} \epsilon \ln \mathbb{P}(X_\epsilon(t) \sim \gamma(t), t \in [T_1, T_2]) = S(\gamma, T_1, T_2) \quad (1.2)$$

where ϵ is a parameter controlling the strength of the random perturbation, and \mathcal{L} is a *Lagrangian* in the sense of classical mechanics. Clearly, such results allow to compute probabilities, and hence expected times, of the occurrence of transitions between attractors. We will refer to estimates of the type (1.2) as *logarithmic equivalence*. While these are in some sense rather crude estimates, the large deviation method has proven very useful due to its rather universal applicability. It has, in fact, dominated the field on the mathematical side, and large deviations and metastability are often seen as almost synonymous (see e.g. the recent monograph [35]).

Besides the large deviation estimates, Freidlin and Wentzell introduced a very interesting and useful way of looking at metastable systems by associating to it what they called a *Markov chain with exponentially small transition probabilities*. Here they associate to the original system a finite state Markov chain whose states label the different attractors of the underlying dynamical system. The transition probabilities of this new chain are then computed by finding the probability of the most likely trajectory linking two such attractors; by the foregoing discussion, this probability will be exponentially small. The long-time behaviour of the system, viewed on the coarse-grained level, will then be well-described by that of the associated finite Markov chain. It was later noted that such Markov chains arise also in other contexts, notably in stochastic dynamics of interacting particle systems at very low temperatures, and they have become a subject of intensive investigation in their own right [33, 34, 10, 9], initially again mainly through large deviation techniques.

In the physics literature, very early on more precise results than those provided by large deviation theory were sought. The modelling context here was mostly that of stochastic differential equations with small noise, i.e. the multi-dimensional extension of Kramer’s approach. However, while in the one-dimensional case essentially exact solutions are available, the multi-dimensional setting leads to partial differential equations that are not explicitly solvable, and those asymptotic analysis encountered considerable analytic difficulties. Several authors strove to overcome those and to derive asymptotic expansions in the parameter ϵ using methods similar to those used in the study of quantum mechanical tunneling (WKB-method); these results remained, however, on the formal level, as no error estimates could

be proven. We will not enter the details of this development here, but refer to the excellent account given in [27]. Very recently, there has been renewed progress on this issue in the case of the reversible diffusions that we will comment on below [18, 19, 20].

Independent of the issue of rigour, the analytic approach has the disadvantage that it is applicable to a very limited class of models. Thus, more robust techniques that would still give precise results are sought for. Spectral theory for the generator of the Markov process appears as a natural tool, since long-term dynamical properties should find their encoding in the nature of the spectrum. In fact, the analysis of the *spectral gap* between the zero eigenvalue and the next-smallest eigenvalue of the generator has been a prominent topic in the theory of Markov processes, mainly as a tool to control convergence to equilibrium. Let us cite, from the vast body of literature, the papers [24, 31, 30]. The characterisation of metastability in terms of spectral properties was initiated in early work of Davies [11, 12, 13], and more recently continued by Gaveau and Schulman [17]. In view of numerical applications in dynamics of large bio-molecules, this issue was also addressed recently by Huisinga et al. [25].

Our own interest in the issue of metastability form the study of Gibbs distributions of disordered systems, and in particular the Hopfield model of neural networks. Here one is interested in the dynamical behaviour of Markov process on some high-dimensional state space, mostly chosen to be reversible with respect to a *Gibbs measure*. Considerable effort is invested in the analysis of the properties of these Gibbs measures in the limit of infinite dimensions. The question that then arises is what can be learned from these Gibbs measures, or, what do we need to know about the Gibbs measures in order to understand the long-term properties of the dynamics? This question can be seen as the leitmotiv behind our work. Other than that, we were aiming for an approach that would be to a large extent model independent, and that at the same time would provide finer estimates than those obtainable with large deviation methods. Our approach thus makes deliberate use of knowledge of the invariant measure, and, moreover, will always assume that the dynamics is reversible. This certainly leaves many interesting situations out of the the reach of our methods, but still covers a range of important applications.

Acknowledgements. The work reported here is based on a joint effort with Véronique Gayrard, Michael Eckhoff, and Markus Klein to understand metastability. Applications of these ideas in concrete models have been worked out with Gerard Ben Arous, Alessandra Faggionato, Frank den Hollander, Francesco Manzo, and Francesca Nardi. I am deeply indebted to all these collaborators for their immense contributions.

2 Characterisations of metastability

The most general setting we will consider can be described as follows. We consider a Markov process, X_t , on a measure space, $\Gamma \supset X_t$, with discrete or continuous time, t . We will usually assume that the process is uniquely ergodic with invariant measure \mathbb{Q} . We will denote the law of this process by \mathbb{P} . Moreover, we will denote by \mathbb{P}_x the law of the process conditioned on $X_0 = x$. We will denote by τ_D , $D \subset \Gamma$, the first entrance time of X_t in D , i.e.

$$\tau_D \equiv \inf\{t > 0, X(t) \in D\} \quad (2.1)$$

An intuitively appealing definition of metastability could be the following:

A family of Markov processes is called metastable, if there exists a collection of disjoint sets $B_i \subset \Gamma$, such that

$$\frac{\sup_{x \notin \cup_i B_i} \mathbb{E}_x \tau_{\cup_i B_i}}{\inf_{x \in \cup_i B_i} \mathbb{E}_x \tau_{\cup_{k \neq i} B_k}} = o(1) \quad (2.2)$$

Here $o(1)$ should be thought of as an intrinsic small parameter that characterises the “degree” of metastability. Often we will have to do with a family of processes indexed by a parameter, that allows to make (2.2) as small as we like.

Intuitively, this definition says that our process lingers around one of the subsets B_i for a long time (resp. returns to B_i many times) before it visits another of these sets, and so on. This can be re-expressed in a number of ways, e.g. in terms of the behaviour of empirical distributions, but we will not go into this.

This definition characterizes metastability in terms of physical properties, namely hitting times, of the system. The problem is that it is not immediately verifiable, since it involves mean hitting times, that are nor easy to compute. It would thus be desirable to have an equivalent definition involving more manageable quantities.

A further goal will be to derive further general properties of metastable systems. Since the definition implies frequent returns to the small starting set B_i before transit to another set B_j , this suggests an exponential law for the transit times. This also suggests that we may expect to describe the process of successive visits to distinct B_i asymptotically as a Markov process. The most fundamental result we want to achieve in this context is a characterization of the spectrum of the generator, resp. the transition matrix of a metastable process.

3 Markov processes and potential theory

Our approach to metastability relies heavily on some elementary potential theory for Markov processes. Let us briefly recall some basic facts and definitions. We will consider the case of discrete space and discrete time, but the same holds with obvious changes in the continuous setting.

Thus let Γ be a discrete set, \mathbb{Q} be a positive measure on Γ , and P a stochastic matrix on Γ . We will denote by $-L$ the generator of the process in the case of continuous time, and set $L = \mathbb{I} - P$ in the case of discrete time¹. We assume that L is symmetric on the space $L^2(\Gamma, \mathbb{Q})$.

Green's function. Let $\Omega \subset \Gamma$. Consider for $\lambda \in \mathbb{C}$ and g a real valued function on Ω the Dirichlet problem

$$\begin{aligned} (L - \lambda)f(x) &= g(x), & x \in \Omega \\ f(x) &= 0, & x \in \Omega^c \end{aligned} \quad (3.1)$$

Whenever λ is such that the problem has a unique solution, then it can be expressed in terms of the Dirichlet Green's function, $G_\Omega^\lambda(x, y)$, as $(L - \lambda)^\Omega$, i.e. for any $g \in C_0(\Omega)$,

$$f(x) = \sum_{y \in \Omega} G_\Omega^\lambda(x, y)g(y) \quad (3.2)$$

Recall that the spectrum of L (more precisely the Dirichlet spectrum of the restriction of L to Ω , which we will sometimes denote by L^Ω), is the complement of the set of values λ for which G_Ω^λ defines a bounded operator.

Equilibrium potential and equilibrium measure. Let $A, D \subset \Gamma$. Then the λ -equilibrium potential, $h_{A,D}^\lambda$, (of the capacitor (A, D)) is defined as the solution of the Dirichlet problem

$$(L - \lambda)h_{A,D}^\lambda(x) = 0, \quad x \in (A \cup D)^c \quad (3.3)$$

$$h_{A,D}^\lambda(x) = 1, \quad x \in A \quad (3.4)$$

$$h_{A,D}^\lambda(x) = 0, \quad x \in D \quad (3.5)$$

$$(3.6)$$

Note that (3.6) has a unique solution provided λ is not in the spectrum of $L^{(A \cup B)^c}$.

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

$$h_{A,D}^\lambda(x) = \sum_{y \in A} G_{D^c}^\lambda(x, y)e_{A,D}^\lambda(y) \quad (3.7)$$

(3.7) may also be written as

$$e_{A,D}^\lambda(y) = (L - \lambda)h_{A,D}^\lambda(y) \quad (3.8)$$

Capacity. We now restrict our attention to the case $\lambda = 0$. We write $h \equiv h^0$ and $e \equiv e^0$. The *capacity* of the capacitor (A, D) is defined as

$$\text{cap}(A, D) \equiv \sum_{y \in A} \mathbb{Q}(y)e_{A,D}(y) \quad (3.9)$$

¹We choice of the sign is made so that L is a positive definite operator.

Using (3.8) one derives after some algebra that,

$$\text{cap}(A, D) = \frac{1}{2} \sum_{x,y} \mathbb{Q}(y)p(x, y) \|h_{A,D}(x) - h_{A,D}(y)\|^2 \equiv \Phi(h_{A,D}) \quad (3.10)$$

where $p(x, y)$ are the transition probabilities (in discrete time) respectively transition rates (in discrete time). Φ is called the Dirichlet form (or energy) for the operator L .

A fundamental consequence of (3.10) is the variational representation of the capacity, namely

$$\text{cap}(A, D) = \inf_{h \in \mathcal{H}_{A,D}} \Phi(h) \quad (3.11)$$

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

$$\mathcal{H}_{A,D} \equiv \{h : \Gamma \rightarrow [0, 1] : h(x) = 0, x \in D, h(x) = 1, x \in A\} \quad (3.12)$$

Probabilistic interpretation. If $\lambda = 0$, the equilibrium potential has a natural probabilistic interpretation in terms of hitting probabilities of this process, namely,

$$h_{A,D}(x) = \mathbb{P}_x[\tau_A < \tau_D] \quad (3.13)$$

The equilibrium measure has a nice interpretation in the discrete time case if $A = \{y\}$ is a single point:

$$e_{y,D}(y) = \mathbb{P}_y[\tau_D < \tau_y] \quad (3.14)$$

If $\lambda \neq 0$, the equilibrium potential still has a probabilistic interpretation in terms of the Laplace transform of the hitting time τ_A of the process starting in x and killed in D . Namely, we have for general λ , that

$$h_{A,D}^\lambda(x) = \mathbb{E}_x e^{\lambda \tau_A} \mathbb{I}_{\tau_A < \tau_D} \quad (3.15)$$

for $x \in (A \cup D)^c$, whenever the right-hand side is finite.

Note that (3.15) implies that

$$\frac{d}{d\lambda} h_{A,D}^{\lambda=0}(x) = \mathbb{E}_x \tau_A \mathbb{I}_{\tau_A < \tau_D} \quad (3.16)$$

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

$$w_{A,D}(x) = \begin{cases} \mathbb{E}_x \tau_A \mathbb{I}_{\tau_A < \tau_D}, & x \in (A \cup D)^c \\ 0, & x \in A \cup D \end{cases} \quad (3.17)$$

solves the inhomogeneous Dirichlet problem

$$Lw_{A,D}(x) = h_{A,D}(x), \quad x \in (A \cup D)^c \quad (3.18)$$

$$w_{A,D}(x) = 0, \quad x \in A \cup D \quad (3.19)$$

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

$$\mathbb{E}_x \tau_A \mathbb{1}_{\tau_A < \tau_D} = \sum_{y \in (A \cup D)^c} G_{(A \cup D)^c}(x, y) h_{A, D}(y) \quad (3.20)$$

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

$$Lw_A(x) = 1, \quad x \in A^c \quad (3.21)$$

$$w_A(x) = 0, \quad x \in A \quad (3.22)$$

and the representation

$$\mathbb{E}_x \tau_A = \sum_{y \in A^c} G_{A^c}(x, y) \quad (3.23)$$

The full beauty of all this comes out when combining (3.7) with (3.20), resp. (3.23). Namely,

$$\mathbb{Q}(z) \mathbb{E}_z \tau_A e_{z, A}(z) = \sum_{y \in A^c} \mathbb{Q}(y) G_{A^c}(y, z) e_{z, A}(z) \quad (3.24)$$

$$= \sum_{y \in A^c} \mathbb{Q}(y) h_{z, A}(y) \quad (3.25)$$

or

$$\mathbb{E}_z \tau_A = \frac{1}{\text{cap}(z, A)} \sum_{y \in A^c} \mathbb{Q}(y) h_{z, A}(y) \quad (3.26)$$

Remark 3.1. Equation (3.26) relies explicitly on the discrete structure on the state space, or more precisely that for any $x \in \Gamma$, $\mathbb{Q}(x) > 0$. In the case of continuous state space, such formulas do not hold in the strict sense, or are not useful, but suitable “integral versions”, involving integrals over suitably chosen small neighborhoods of e.g. the points z in (3.26) are still valid, and can be used to more or less the same effect as the exact relations in the discrete case. This entails, however, some extra technical difficulties. In these notes we will therefore restrict our attention to the discrete case, where the principle ideas can be explained without being obscured by technicalities.

4 Capacitary characterization of metastability

The relation (3.26) between mean hitting times and capacities suggests an alternative characterisation of metastability through capacities. We will see that this entails many advantages.

Definition 4.1. Assume that Γ is a discrete set. Then a Markov processes X^t is ρ -metastable with respect to the set of points $\mathcal{M} \subset \Gamma$, if

$$\frac{\sup_{x \in \mathcal{M}} \text{cap}(x, \mathcal{M} \setminus x) / \mathbb{Q}(x)}{\inf_{y \notin \mathcal{M}} \text{cap}(y, \mathcal{M}) / \mathbb{Q}(y)} \leq \rho \ll 1 \quad (4.1)$$

Remark 4.2. Definition 4.1 is useful since it involves quantities that are either “known”, or expected to be easily controllable. It becomes intuitively more appealing if we notice that it can be written alternatively as

$$\frac{\sup_{x \in \mathcal{M}} \mathbb{P}_x [\tau_{\mathcal{M} \setminus x} < \tau_x]}{\inf_{y \notin \mathcal{M}} \mathbb{P}_y [\tau_{\mathcal{M}} < \tau_y]} \leq \rho \ll 1 \quad (4.2)$$

Renewal estimates. The estimation of the equilibrium through capacities is based on a renewal argument, that in the case of discrete state space is very simple.

Lemma 4.3. *Let $A, D \subset \Gamma$ be disjoint sets, and let $x \notin A \cup D$. Then*

$$h_{A,D}(x) \leq \min \left(\frac{\text{cap}(x, A)}{\text{cap}(x, D)}, 1 \right) \quad (4.3)$$

Remark 4.4. Note that the power of Lemma 4.3 is more than doubled by judicious use of the elementary fact that $h_{A,D}(x) = 1 - h_{D,A}(x)$.

Ultrametricity. An important fact that allows to obtain general results under our Definition of metastability is the fact that it implies approximate ultrametricity of capacities. This has been noted in [5].

Lemma 4.5. *Assume that $x, y \in \Gamma$, $D \subset \Gamma$. Then, if for $0 < \delta < \frac{1}{2}$, $\text{cap}(y, D) \leq \delta \text{cap}(y, x)$, then*

$$\frac{1 - 2\delta}{1 - \delta} \leq \frac{\text{cap}(x, D)}{\text{cap}(y, D)} \leq \frac{1}{1 - \delta} \quad (4.4)$$

Proof. The proof of this lemma given in [5] is probabilistic and uses splitting and renewal ideas. It should be possible to prove this result with purely analytic arguments. \square

Lemma 4.5 has the following immediate corollary, which is the version of the ultrametric triangle inequality we are looking for:

Corollary 4.6. *Let $x, y, z \in \mathcal{M}$. Then*

$$\text{cap}(x, y) \geq \frac{1}{3} \min(\text{cap}(x, z), \text{cap}(y, z)) \quad (4.5)$$

In the sequel it will be useful to have the notion of a “valley” or “attractor” of a point in \mathcal{M} . We set for $x \in \mathcal{M}$,

$$A(x) \equiv \left\{ z \in \Gamma \mid \mathbb{P}_z[\tau_x = \tau_{\mathcal{M}}] = \sup_{y \in \mathcal{M}} \mathbb{P}_z[\tau_x = \tau_{\mathcal{M}}] \right\} \quad (4.6)$$

Note that valleys may overlap, but from Lemma 4.5 it follows easily that the intersection has a vanishing invariant mass. The notion of a valley in the case of a diffusion process coincides with the intuitive notion.

Mean times. A very pleasant feature of the definition of metastability in terms of capacities is that it allows to relate some key capacities to mean hitting times in a very simple way.

Theorem 4.7. *Let $x \in \mathcal{M}$ and $J \subset \mathcal{M} \setminus x$ be such a that for all $m \notin J \cup x$ either $\mathbb{Q}(m) \ll \mathbb{Q}(x)$ or $\text{cap}(m, J) \gg \text{cap}(m, x)$, then*

$$\mathbb{E}_x \tau_J = \frac{\mathbb{Q}(A(x))}{\text{cap}(x, J)} (1 + o(1)) \quad (4.7)$$

Finally we want to compute the mean time to reach \mathcal{M} starting from a general point.

Lemma 4.8. *Let $z \notin \mathcal{M}$. Let $a \equiv \sup_{y \notin \mathcal{M}} \frac{\mathbb{Q}(y)}{\text{cap}(y, \mathcal{M})}$. Then*

$$\mathbb{E}_z \tau_{\mathcal{M}} \leq a^{-2} |\Gamma| \quad (4.8)$$

Remark 4.9. If Γ is finite, the above estimate combined with Theorem 4.7 shows that the two definitions of metastability we have given in terms of mean times resp. capacities are equivalent. On the other hand, in the case of infinite state space Γ , we cannot expect the supremum over $\mathbb{E}_z \tau_{\mathcal{M}}$ to be finite, which shows that our first definition was somewhat naive. Note however that this case the estimate (4.8) can be improved by placing $|\Gamma|$ with $\sum_{y: \mathbb{Q}(y) \leq \mathbb{Q}(z)} \mathbb{Q}(y) / \mathbb{Q}(z) + \sum_{y: \mathbb{Q}(y) > \mathbb{Q}(z)} 1$.

5 Spectral characterisation of metastability

We now turn to the characterisation of metastability through spectral data. We will show that Definition 4.1 implies that the spectrum of the generator decomposes into a cluster of $|\mathcal{M}|$ very small real eigenvalues that are separated by a gap from the rest of the spectrum.

A priori estimates. The first step of our analysis consists in showing that the matrix $L^{\mathcal{M}^c}$ (i.e. with Dirichlet conditions in all the points of \mathcal{M}) has a minimal eigenvalue that is not smaller than $O(a)$. This result needs sometimes some improvement, but it shows the basic twist. This is a simple application of a Donsker-Varadhan argument.

Lemma 5.1. *Let λ^0 denote the infimum of the spectrum of $L^{\mathcal{M}^c}$. Then*

$$\lambda^0 \geq \frac{1}{\sup_{x \in \Gamma} \mathbb{E}_x \tau_{\mathcal{M}}} \quad (5.1)$$

Remark 5.2. Lemma 5.1 links the fast time scale to the smallest eigenvalue of the Dirichlet operator, as should be expected. Note that the relation is not very precise. We will soon derive a much more precise relation between times and eigenvalues for the cluster of small eigenvalues. As stated, it is useless in the case of infinite state space. It can, however, be improved to give useful bounds under tightness conditions on \mathbb{Q} [5].

Characterization of small eigenvalues. We will now obtain a representation formula for all eigenvalues that are smaller than λ^0 . It is clear that there will be

precisely $|\mathcal{M}|$ such eigenvalues. This representation was first exploited in [5], but already in 1973 Wentzell put forward very similar ideas.

The basic idea is to use the fact that the solution of the Dirichlet problem

$$\begin{aligned} (L - \lambda)f(x) &= 0, & x \notin \mathcal{M} \\ f(x) &= \phi_x, & x \in \mathcal{M} \end{aligned} \quad (5.2)$$

already solves the eigenvalue equation $L\phi(x) = \lambda\phi(x)$ everywhere except possibly on \mathcal{M} . The question is whether an appropriate choice of boundary conditions and the right choice of the value of λ will actually lead to a solution. This is indeed the case.

Lemma 5.3. *Assume that $\lambda < \lambda^0$ is an eigenvalue of L and $\phi(x)$ is the corresponding eigenfunction. Then the unique solution of (5.2) with $\phi_x = \phi(x)$, $x \in \mathcal{M}$, satisfies $f(y) = \phi(y)$, for all $y \in \Gamma$.*

Let us denote by $\mathcal{E}_{\mathcal{M}}(\lambda)$ the $|\mathcal{M}| \times |\mathcal{M}|$ -matrix with elements

$$(\mathcal{E}_{\mathcal{M}}(\lambda))_{xy} \equiv e_{z, \mathcal{M} \setminus z}^\lambda(x) \quad (5.3)$$

Lemma 5.4. *A number $\lambda < \lambda^0$ is an eigenvalue of the matrix L if and only if*

$$\det \mathcal{E}_{\mathcal{M}}(\lambda) = 0 \quad (5.4)$$

Anticipating that we are interested in small λ , we want to re-write the matrix $\mathcal{E}_{\mathcal{M}}$ in a more convenient form. To do so let us set

$$h_x^\lambda(y) \equiv h_x(y) + \psi_x^\lambda(y) \quad (5.5)$$

Then $\mathcal{E}(\lambda)$ can be written in the form

$$\begin{aligned} (\mathcal{E}_{\mathcal{M}}(\lambda))_{xz} &= \mathbb{Q}(x)^{-1} \left(\frac{1}{2} \sum_{\substack{y' \\ y \neq y'}} \mathbb{Q}(y') p(y', y) [h_z(y') - h_z(y)] [h_x(y') - h_x(y)] \right. \\ &\quad \left. - \lambda \sum_y \mathbb{Q}(y) (h_z(y) h_x(y) + h_x(y) \psi_z^\lambda(y)) \right) \end{aligned} \quad (5.6)$$

where the term involving ψ^λ can be viewed as a more or less irrelevant

We are now in a position to relate the small eigenvalues of L to the eigenvalues of the classical capacity matrix. Let us denote by $\|f\|_2$ the ℓ^2 -norm with respect to the measure \mathbb{Q} , i.e. $\|f\|_2^2 = \sum_y \mathbb{Q}(y) f(y)^2$.

Theorem 5.5. *If $\lambda < \lambda^0$ is an eigenvalue of L , then there exists an eigenvalue μ of the $|\mathcal{M}| \times |\mathcal{M}|$ -matrix \mathcal{K} whose matrix elements are given by*

$$\mathcal{K}_{zx} = \frac{\frac{1}{2} \sum_{y \neq y'} \mathbb{Q}(y') p(y', y) [h_z(y') - h_z(y)] [h_x(y') - h_x(y)]}{\|h_z\|_2 \|h_x\|_2} \quad (5.7)$$

such that $\lambda = \mu(1 + O(\rho(\epsilon)))$.

The computation of the eigenvalues of the capacity matrix is now in principle a finite, though in general not trivial problem. The main difficulty is of course the computation of the capacities and induction coefficients.

In fact we will prove the following theorem.

Theorem 5.6. *Assume that there exists $x \in \mathcal{M}$ such that for some $\delta \ll 1$*

$$\frac{\text{cap}_x(\mathcal{M} \setminus x)}{\|h_x\|_2^2} \geq \delta \max_{z \in \mathcal{M} \setminus x} \frac{\text{cap}_z(\mathcal{M} \setminus z)}{\|h_z\|_2^2} \quad (5.8)$$

Then the largest eigenvalue of L is given by

$$\lambda_x = \frac{\text{cap}_x(\mathcal{M} \setminus x)}{\|h_x\|_2^2} (1 + O(\delta)) \quad (5.9)$$

and all other eigenvalues of L satisfy

$$\lambda \leq C\delta\lambda_x \quad (5.10)$$

Moreover, the eigenvector, ϕ , corresponding to the largest eigenvalues normalized s.t. $\phi_x = 1$ satisfies $\phi_z \leq C\delta$, for $z \neq x$.

Theorem 5.6 has the following simple corollary, that allows in many situations a complete characterization of the small eigenvalues of L .

Corollary 5.7. *Assume that we can construct a sequence of metastable sets $\mathcal{M}_k \supset \mathcal{M}_{k-1} \supset \dots \supset \mathcal{M}_2 \supset \mathcal{M}_1 = x_0$, such that, for any i , $\mathcal{M}_i \setminus \mathcal{M}_{i-1} = x_i$ is a single point, and that each \mathcal{M}_i satisfies the assumptions of Theorem 5.6. Then L has k eigenvalues*

$$\lambda_i = \frac{\text{cap}_{x_i}(\mathcal{M}_{i-1})}{\mathbb{Q}(A(x_i))} (1 + O(\delta)) \quad (5.11)$$

The corresponding normalized eigenfunction is given by

$$\psi_i(y) = \frac{h_{x_i}(y)}{\|h_{x_i}\|_2} + O(\delta) \quad (5.12)$$

6 Variational principles and bounds for capacities

While the characterisation of metastability in terms of properties of mean first entrance times did not seem immediately verifiable in a given model, (3.26) already suggests a close relation between these times to capacities. In fact, the key idea in our approach will be to express all quantities of interest ultimately to capacities, and to exploit the fact that these can be estimated remarkably well by exploiting the variational principle (3.11). This observation is not new; in fact, it is the basis of the “electric network” approach to Markov chains (see e.g. the excellent account in Doyle and Snell [14]). The fact that this approach is very useful for metastable systems appears to have been overlooked.

Let us briefly comment on the use of these variational principles and explain why they are efficient. While the specifics of their exploitation are model-dependent, some basic principles are quite general follow directly from the fact that one is considering a metastable system.

Upper bound. Upper bounds on capacities can be gotten readily by judicious choices of a test-function h . Inspecting the Dirichlet form will often suggest rather good choices. There are two major advantages in this variational principle: there are no constraints on the test function except boundary conditions, and the minimizers has a very clear probabilistic interpretation. This is quite different from the situation of the Rayleigh-Ritz variational principle for the spectral gap, which is therefore more difficult to handle. The fact that a system is metastable suggests that there will be rather large regions, surrounding the meatstable points, where the equilibrium potential is constant, and only its behaviour on the (often small) connecting sets has to be guessed with greater care.

Lower bound. A lower bound appears at first sight less obvious; however, the fact that $\Phi(h)$ is monotone in the variables $p(x, y)$ suggests an immediate lower bound in terms of the capacities of a chain there some (or even many) $p(x, y)$ are set to zero (known as Raighley's cut method [14]), hoping of course that the resulting chain will be so simple that explicit computations of the capacities are possible. This idea can, however, be extended considerably. To this end, consider a countable set I , and a let $\mathcal{G} \equiv \{g_{xy}, x, y \in \Gamma\}$, be a collection of sub-probability measures on I , i.e. for each (x, y) , $g_{xy}(\alpha) \geq 0$, and $\sum_{\alpha \in I} g_{xy}(\alpha) \leq 1$. Then

$$\begin{aligned} \text{cap}(A, B) &= \inf_{h \in \mathcal{H}_{A,D}} \sum_{\alpha \in I} \frac{1}{2} \sum_{x,y} \mathbb{Q}(y) g_{xy}(\alpha) p(x, y) \|h_{A,D}(x) - h_{A,D}(y)\|^2 \\ &\geq \sum_{\alpha \in I} \inf_{h \in \mathcal{H}_{A,D}} \sum_{\alpha \in I} \frac{1}{2} \sum_{x,y} \mathbb{Q}(y) g_{xy}(\alpha) p(x, y) \|h_{A,D}(x) - h_{A,D}(y)\|^2 \\ &\equiv \sum_{\alpha \in I} \inf_{h \in \mathcal{H}_{A,D}} \Phi^{\mathcal{G}(\alpha)}(h) \equiv \sum_{\alpha \in I} \text{cap}^{\mathcal{G}(\alpha)}(A, D) \end{aligned} \quad (6.1)$$

As this it true for all \mathcal{G} , we get the variational principle

$$\text{cap}(A, D) = \sup_{\mathcal{G}} \sum_{\alpha \in I} \text{cap}^{\mathcal{G}(\alpha)}(A, D) \quad (6.2)$$

Note that this may look trivial, as of course the supremum is realised for the trivial case $I = \{1\}$, $g_{xy}(1) = 1$, for all (x, y) . The interest in the principle arises from the fact that there may be other choices that still realise the supremum (or at least come very close to it). If we denote by $h_{A,D}^{\mathcal{G}(\alpha)}$ the minimizer of $\Phi^{\mathcal{G}(\alpha)}(h)$, then \mathcal{G} realises the supremum, whenever

$$h_{A,D}^{\mathcal{G}(\alpha)}(x) = h_{A,D}(x), \quad \forall x : g(xy)(\alpha) \neq 0 \quad (6.3)$$

Of course we do not know $h_{A,D}(x)$, but this observation suggest a very good strategy to prove lower bounds, anyhow: guess a plausible test function h for the upper bound, then try to construct \mathcal{G} such that the minimizers, $h^{\mathcal{G}(\alpha)}$, are computable, and are similar to h ! If this succeeds, the resulting upper and lower bounds will be at least very close. Remarkably, this strategy actually does work in many cases.

7 Applications 1. Low-temperature dynamics of spin systems

The somehow simplest example where the general approach outlined above works very well and with remarkable ease is stochastic dynamics of discrete spin systems in the low temperature limit.

Here we have a finite spin-space \mathcal{S} , a finite subset, Λ , of Z^d , and a Hamiltonian function $H_\Lambda : \mathcal{S}^\Lambda \rightarrow \mathbb{R}$. The Markov processes one is interested in are reversible (discrete or continuous time) Markov chains on \mathcal{S}^Λ that are reversible with respect to the *Gibbs measure*,

$$\mu_\beta(\sigma) = \frac{e^{-\beta H_\sigma(\sigma)}}{Z_{\beta,\Lambda}} \quad (7.1)$$

where β will play the rôle of a large parameter, and $Z_{\beta,\Lambda}$ is a normalisation constant, called partition function. To complete the description of the dynamics, one defines a graph, $\Gamma = (\mathcal{S}^\Lambda, \mathcal{E}^\Lambda)$, on \mathcal{S}^Λ , those edges determine the allowed transitions. One may then choose transition probabilities

$$p(\sigma, \sigma') = \frac{1}{C_\sigma} e^{-\beta[H_\Lambda(\sigma') - H_\Lambda(\sigma)]_+}, \quad \text{if } (\sigma, \sigma') \in \mathcal{E}^\Lambda \quad (7.2)$$

where C_σ denotes the coordination number of the vertex σ in Γ , and $[f]_+$ is the positive part of f ; all other transitions have zero probability, except of course the probability to stay at σ , which is determined by the requirement that p be a stochastic matrix. Such a dynamics is usually called a Metropolis algorithm.

Metastability occurs in such dynamics whenever the Hamiltonian has more than one local minimum, if β is large. Our methods allow a full analysis of such dynamics, provided we understand the function H_Λ well enough to know its minima and saddle points. This latter problem is rather non-trivial in general and involves complicated discrete optimisation problems. In the Ising model, these have been studied in great detail by Alonso and Cerf [1]

The two most prominent examples in this class of models are the Glauber dynamics in the Ising spin model and Kawasaki dynamics in the Ising lattice gas.

Ising model under Glauber dynamics. Here the state space is $\mathcal{S} = \{-1, 1\}$, and the Hamiltonian is

$$H_\Lambda(\sigma) = - \sum_{x,y \in \Lambda, \|x-y\|=1} \sigma_x \sigma_y - h \sum_{x \in \Lambda} \sigma_x \quad (7.3)$$

The edges of the graph, Γ , of allowed transitions consists of all pairs, (σ, σ') , such that σ and σ' differ in exactly one coordinate, i.e. the Hamming distance between σ and σ' equals to 1. A detailed analysis of the structure of this Hamiltonian was given in [1, 9]. Here, if $h > 0$, the configurations $+\mathbf{1} \equiv \{\sigma_x \equiv +1, \forall x \in \Lambda\}$, and $-\mathbf{1} \equiv \{\sigma_x \equiv -1, \forall x \in \Lambda\}$, correspond to the deepest, resp. second-deepest minima. One can verify that the set $\mathcal{M} \equiv \{-\mathbf{1}, +\mathbf{1}\}$ is a set of metastable points in the sense of our definition. This dynamics was investigated in particular in [32] ($d = 2$) and [9] ($d = 2, 3$) using large deviation methods, and logarithmic asymptotics (on the regime Λ fixed, $\beta \uparrow \infty$, were obtained, together with a description of the most probable exit path. In [4] we showed that the methods outlined above are readily applicable here and give a radical improvement on the precision of the results. We cite the main theorem of [4] to give a flavour of the type of results one can get.

Theorem 7.1. *Consider the Ising model with Metropolis dynamics in dimension $d = 2$ or $d = 3$ in a torus $\Lambda^d(l)$ with diameter l . Let $0 < h < 1$ such that $2/h$ and (in $d = 3$) $(h/2 \lceil 4/h \rceil (4/h + 1 - \lceil 4/h \rceil))$ is not an integer. Then there exists $\delta > 0$, independent of β , s.t.*

- In dimension 2, let h be such that $2/h$ is not an integer. Let $\ell_2 := \lceil \frac{2}{h} \rceil$ and $\Gamma_2 := 4\ell_2 - h(\ell_2^2 - \ell_2 + 1)$ be the diameter and the activation energy of the “critical droplet”, respectively. Then,

$$\mathbb{E}\tau(-\mathbf{1}) = \frac{3}{8} \frac{1}{\ell_2 - 1} e^{\beta\Gamma_2} (1 + O(e^{-\beta\delta})) = \frac{3}{16} h e^{\beta\Gamma_2} (1 + O(h) + O(e^{-\beta\delta})) \quad (7.4)$$

- In dimension 3, let h be such that $2/h$ and $(h/2 \lceil 4/h \rceil (4/h + 1 - \lceil 4/h \rceil))$ are not integer. Let $\ell_3 := \lceil \frac{4}{h} \rceil$ and $a := \lceil h/2 \lceil 4/h \rceil (4/h + 1 - \lceil 4/h \rceil) \rceil$ (notice that a can take the value 1 or 2). The activation energy of the “critical droplet” is

$$\begin{aligned} \Gamma_3 := & (6\ell_3^2 - (12 - 4a)\ell_3 + 4\ell_2 + 4 - 2a) \\ & - h(\ell_3^3 - (3 - a)\ell_3^2 + (2 - a)\ell_2 + \ell_2^2 - \ell_2 + 1) \end{aligned} \quad (7.5)$$

Then,

$$\begin{aligned} \mathbb{E}\tau(-\mathbf{1}) &= \frac{a}{16(\ell_3 - \ell_2 + 1)(\ell_3 - \ell_2 + a - 1)(\ell_2 - 1)} e^{\beta\Gamma_3} (1 + O(e^{-\beta\delta})) \\ &= \frac{a}{128} h^3 e^{\beta\Gamma_3} (1 + O(h) + O(e^{-\beta\delta})) \end{aligned} \quad (7.6)$$

Moreover, the distribution of $\tau(-\mathbf{1})/\mathbb{E}\tau(-\mathbf{1})$ converges to the exponential distribution, as $\beta \uparrow \infty$.

Local Kawasaki dynamics with open boundary conditions. Kawasaki dynamics is most conveniently thought of as taking place on the configuration space $\{0, 1\}^\Lambda$, where dynamics variable $\eta_x(t)$ is thought of as the number of particles at site x at time t . In contrast to Glauber dynamics, Kawasaki dynamics is *conservative*, i.e. the total number of particles is fixed. In several papers, den Hollander et al. [21, 22] introduced a local version of this dynamics in a finite box where particle number of conserved by transitions within the box, but where particles may appear or disappear at the boundary. This dynamics was introduced as a local approximation of a true Kawasaki dynamics in infinite volume.

The Hamiltonian is written in these variables as

$$H_\Lambda(\eta) = -U \sum_{x,y \in \Lambda; \|x-y\|=1} \eta_x \eta_y - \Delta \sum_{x \in \Lambda} \eta_x \quad (7.7)$$

Again the dynamics is chosen reversible with respect to the corresponding Gibbs measure and this time transition are possible between configurations η, η' such that (i) either two nearest neighbor sites, x, y , exchange their particle numbers, or (ii) the particle number of one site in the boundary of Λ is increased from 0 to 1, or decreased from 1 to 0. This dynamics differs from Glauber dynamics essentially only in the structure of the graph of admissible transitions, but this has rather noticeable consequences.

From the point of view of metastability, the main new feature is that now the saddle points from Gauber dynamics have to be relaced by ‘plateaus’: there is a set of critical configurations where a “critical droplet” has been formed and a free particle has entered the box at the boundary. The droplet will become supercritical if this new particle attaches itself to the droplet. Therefore, in the computation of the capacities, the probability that a simple random walker starting at the boundary of a box Λ will reach some set in the interior before exiting will play a crucial rôle and will in fact modify the prefactor of the nucleation time in a Λ and dimension dependent way.

8 Applications 2. Diffusion processes

In the preceding sections we have explained our approach in the context of discrete Markov chains. A natural challenge was the extension of the methods to the classical examples of the theory of Freidlin and Wentzell, at least in the reversible case, and to consider stochastic differential equations of the type

$$dX_\epsilon(t) = -\nabla F(X_\epsilon(t))dt + \sqrt{2\epsilon}dW(t) \quad (8.1)$$

on a domain in \mathbb{R}^d , where W is a d -dimensional Brownian motion, and F a potential function (that shall satisfy suitable smoothness and boundary conditions). Note that this process is reversible with respect to the measure $\mathbb{Q}(dx) \equiv \exp(-F(x)/\epsilon)dx$.

The difficulties to overcome in this case is that, in dimension greater than 1, the process will not hit given points in finite time, and thus Definition 4.1 cannot be used. A viable alternative turns out to be:

Definition 8.1. Consider a diffusion process on a set $\Omega \subset \mathbb{R}^d$. The processes X^t is ρ -metastable with respect to the set of points $\mathcal{M} \subset \Omega$, if

$$\frac{\sup_{x \in \mathcal{M}} \text{cap}(B_\epsilon(x), \mathcal{M} \setminus x) / \mathbb{Q}(B_\epsilon(x))}{\inf_{z \in \Omega} \text{cap}(B_\epsilon(z), \cup_{x \in \mathcal{M}} (B_\epsilon(x))) / \mathbb{Q}(B_\epsilon(z))} \leq \rho \ll 1 \quad (8.2)$$

where $B_\epsilon(x)$ denotes the Euclidean ball of radius ϵ around x .

Note that, if F has finitely many local minima, one may chose the \mathcal{M} as the set of local minima and $\rho = \exp(-c/\epsilon)$ for some F -dependent constant a .

This definition works, and in fact most of the approach of the discrete setting can be carried over to the diffusion case due to a-priori estimates on regularity properties of harmonic functions with respect to the generator of this process, which is the elliptic operator

$$-L_\epsilon \equiv -\epsilon \Delta - \nabla F(x) \cdot \nabla \quad (8.3)$$

Elliptic regularity theory for local solutions of equation $L_\epsilon h = f$ implies that these tend to be Hölder continuous with constants those dependence on the small parameter can be controlled; typically they imply that the oscillation of such functions over balls of size ϵ is bounded by some positive power of ϵ .

The estimates of capacities in the diffusion setup are again rather easily performed, and one obtains rigorous estimates of the prefactor of exit times from metastable sets as well as sharp asymptotics of the set of exponentially small eigenvalues associated with the local minima of F , under some non-degeneracy conditions (degenerate cases can in principle also be treated, but require special case by case analysis). The following result was proven in [6]:

Theorem 8.2. *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 δ independent of ϵ . Then*

$$\mathbb{E}_{x_i} \tau_D = \frac{2\pi e^{[F(z^*) - F(x_i)]/\epsilon}}{\sqrt{\det(\nabla^2 F(x_i))} \frac{|\lambda_1^*(z^*)|}{\sqrt{|\det(\nabla^2 F(z^*))|}}} (1 + O(\sqrt{\epsilon} |\ln \epsilon|)) \quad (8.4)$$

Here z^* denotes the “minimal saddle point” between x_i and the set D (assumed unique), and $\lambda_i(z^*)$ denote the eigenvalues of the Hessian matrix of $\nabla^2 F(z^*)$ (assumed non-degenerate), $\lambda_1(z^*)$ being the unique negative one.

The following result on the small eigenvalues of L_ϵ is taken from [7]:

Theorem 8.3. *Assume that F has n local minima, x_1, \dots, x_n and that for some $\theta > 0$ the minima x_i of F can be labeled in such a way that, with $\mathcal{M}_k \equiv \{x_1, \dots, x_k\}$ and $\mathcal{M}_0 \equiv \Omega^c$,*

$$F(z^*(x_k, \mathcal{M}_{k-1})) - F(x_k) \leq \min_{i < k} (F(z^*(x_i, \mathcal{M}_k \setminus x_i)) - F(x_i)) - \theta \quad (8.5)$$

holds for all $k = 1, \dots, n$. We will set $B_i \equiv B_\epsilon(x_i)$ and $\mathcal{S}_k \equiv \cup_{i=1}^k B_i$, and $h_k(y) \equiv h_{B_k, \mathcal{S}_{k-1}}(y)$. Assume moreover that all saddle points $z^(x_k, \mathcal{M}_{k-1})$ are unique, and that the Hessian of F is non-degenerate at all these saddle points and at all local minima. Then there exists $\delta > 0$ such that the n exponentially small eigenvalues $\lambda_1 < \lambda_2 < \dots < \lambda_n$ of L_ϵ satisfy:*

$$\lambda_1 = 0 \quad (8.6)$$

and for $k = 2, \dots, n$,

$$\begin{aligned} \lambda_k &= \frac{\text{cap}_{B_k}(\mathcal{S}_{k-1})}{\|h_k\|_2^2} (1 + O(e^{-\delta/\epsilon})) \\ &= \frac{1}{\mathbb{E}_{x_k} \tau_{\mathcal{S}_{k-1}}} (1 + O(e^{-\delta/\epsilon})) \\ &= \frac{|\lambda_1^*(z^*(x_k, \mathcal{M}_{k-1}))|}{2\pi} \sqrt{\frac{\det(\nabla^2 F(x_k))}{|\det(\nabla^2 F(z^*(x_k, \mathcal{M}_{k-1})))|}} e^{-[F(z^*(x_k, \mathcal{M}_{k-1})) - F(x_k)]/\epsilon} \\ &\quad \times (1 + O(\epsilon^{1/2} |\ln \epsilon|)) \end{aligned} \quad (8.7)$$

where $\lambda_1^(z^*)$ denotes the unique negative eigenvalue of the Hessian of F at the saddle point z^* .*

Remark 8.4. After the results of [7] appeared, Helffer and Nier [19] reconsidered earlier work of Helffer and Sjöstrand concerning spectral asymptotics of Schrödinger operators with multi-well potentials. In two papers [18, 20] they showed that using the so-called Witten complex, it is possible to derive similar spectral results and even extend them to complete asymptotic expansions, provided F is assumed smooth. This is an interesting alternative approach, that for the time being has the disadvantage to be limited to the diffusion setting.

9 Challenges

The main challenges to the approach to metastability outlined in this talk are models in very high, respectively infinite, dimensions. The most interesting examples here are stochastic dynamics of spin systems beyond the low-temperature regime and in large or infinite volume. There are two major difficulties that present themselves. The first one is the estimation of capacities, and more precisely the lower bounds. The second problem is that of proving some a priori regularity properties, similar to the case of diffusion processes. Both issues seem at the moment quite open and will probably require the analysis of model problems. If these problems can

be understood, we would feel that metastability is rather well understood in the context of reversible Markov processes. An altogether different and wide open issue is metastability in non-reversible systems. Here, the theory of Freidlin and Wentzell remains the only generally applicable tool, and finding ways to get estimates of higher precision than those obtainable from large deviation theory remains, at least in general, unsolved.

References

- [1] Alonso, L. and Cerf, R., The three-dimensional polyominoes of minimal area. *Electron. J. Combin.* **3** (1996), Research Paper 27.
- [2] Bovier, A. Metastability and ageing in stochastic dynamics. In: *Dynamics and randomness*. (A. Maas, S. Martínez, J. San Martín, Eds.). Nonlinear Phenomena and Complex Systems 10, pp. 17-80, Kluwer Acad. Publishers (2004).
- [3] Bovier, A., Eckhoff, M., Gaynard, V., and Klein, M., Metastability in stochastic dynamics of disordered mean-field models. *Probab. Theory Related Fields* **119** (2001), 99–161.
- [4] Bovier, A., Manzo, F., Metastability in Glauber dynamics in the low-temperature limit: beyond exponential asymptotics. *J. Statist. Phys.* **107** (2002), 757–779.
- [5] Bovier, A., Eckhoff, M., Gaynard, V., and Klein, M., Metastability and low lying spectra in reversible Markov chains. *Commun. Math. Phys.* **228** (2002), 219–255.
- [6] Bovier, A., Eckhoff, M., Gaynard, V., and Klein, M., Metastability in reversible diffusion processes. I. Sharp asymptotics for capacities and exit times. *J. Eur. Math. Soc. (JEMS)* **6** (2004), 399–424.
- [7] Bovier, A., Gaynard, V., and Klein, M., Metastability in reversible diffusion processes. II. Precise asymptotics for small eigenvalues. *J. Eur. Math. Soc. (JEMS)* **7** (2005), 69–99.
- [8] Bovier A., den Hollander F., and Nardi, F.R., Sharp asymptotics for Kawasaki dynamics on a finite box with open boundary conditions. *Probab. Theor. Rel. Fields.*, published online September 2005, DOI: 10.1007/s00440-005-0460-5 .
- [9] Ben Arous, G. and Cerf, R., Metastability of the three-dimensional Ising model on a torus at very low temperatures. *Electron. J. Probab.* **1** (1996), 55 pp. (electronic).
- [10] Catoni, O. and Cerf, R., The exit path of a Markov chain with rare transitions. *ESAIM Probab. Statist.* **1** (1995/97), 95–144 (electronic).
- [11] Davies, E.B., Metastable states of symmetric Markov semigroups. I. *Proc. Lond. Math. Soc. III* **45** (1982), 133–150 .

- [12] Davies, E.B., Metastable states of symmetric Markov semigroups. II. *J. Lond. Math. Soc. II* **26** (1982), 541–556.
- [13] Davies, E.B., Spectral properties of metastable Markov semigroups. *J. Funct. Anal.* **52** (1983), 315–329.
- [14] Doyle, P.G. and Snell, J.L., *Random walks and electrical networks*. Carus Mathematical Monographs 22, Mathematical Association of America, Washington, DC, 1984.
- [15] Eyring, H., The activated complex in chemical reactions. *J. Chem. Phys.* **3** (1935), 107–115.
- [16] Freidlin, M. I. and Wentzell, A. D., *Random perturbations of dynamical systems*. Second edition. Grundlehren der Mathematischen Wissenschaften [Fundamental Principles of Mathematical Sciences] 260, Springer-Verlag, New York, 1998.
- [17] Gaveau, B. and Schulman, L.S., Theory of nonequilibrium first-order phase transitions for stochastic dynamics. *J. Math. Phys.* **39** (1998), 1517–1533.
- [18] Helffer, B., Klein, M., and Nier, F., Quantitative analysis of metastability in reversible diffusion processes via a Witten complex approach. *Mat. Contemp.* **26** (2004), 41–85.
- [19] Helffer, B. and Nier, F., *Hypoelliptic estimates and spectral theory for Fokker-Planck operators and Witten Laplacians*, Lecture Notes in Mathematics 1862, Springer-Verlag, Berlin, 2005.
- [20] Helffer, B. and Nier, F., Quantitative analysis of metastability in reversible diffusion processes via a Witten complex approach. The case with boundary. preprint 04-40 IRMAR Université de Rennes I, 2004.
- [21] den Hollander, F., Olivieri, E., and Scoppola, E., Metastability and nucleation for conservative dynamics. Probabilistic techniques in equilibrium and non-equilibrium statistical physics. *J. Math. Phys.* **41** (2000), 1424–1498.
- [22] den Hollander, F., Nardi, F. R., Olivieri, E., and Scoppola, E., Droplet growth for three-dimensional Kawasaki dynamics. *Probab. Theory Related Fields* **125** (2003), 153–194.
- [23] den Hollander, F., Metastability under stochastic dynamics. *Stochastic Process. Appl.* **114** (2004), 1–26.
- [24] Holley, R.A., Kusuoka, S., and Stroock, W.S., Asymptotics of the spectral gap with applications to the theory of simulated annealing. *J. Funct. Anal.* **83** (1989), 333–347.
- [25] Huisinga, W., Meyn, S., and Schütte, Ch., Phase transitions and metastability for Markovian and molecular systems. *Ann. Appl. Probab.* **14** (2004), 419–458.

- [26] Kramers, H.A., Brownian motion in a field of force and the diffusion model of chemical reactions. *Physica* **7** (1949), 284–304.
- [27] Maier, R.S. and Stein, D.L., Limiting exit location distributions in the stochastic exit problem. *SIAM J. Appl. Math.* **57** (1997), 752–79.
- [28] Martinelli, F., On the kinetic Ising model below the critical temperature. *XIIIth International Congress on Mathematical Physics* (London, 2000), 297–301, Int. Press, Boston, MA, 2001.
- [29] Martinelli, F., Relaxation times of Markov chains in statistical mechanics and combinatorial structures. *Probability on discrete structures*, 175–262, Encyclopaedia Math. Sci. 110, Springer, Berlin, 2004.
- [30] Mathieu, P., Spectra, exit times, and long times asymptotics in the zero white noise limit. *Stoch. Stoch. Rep.* **55** (1995), 1–20.
- [31] Miclo, L., Comportement de spectres d’opérateurs de Schrödinger à basse température. *Bull. Sci. Math.* **119** (1995), 529–553.
- [32] Neves, E.J. and Schonmann, R.H., Critical droplets and metastability for a Glauber dynamics at very low temperature. *Commun. Math. Phys.* **137** (1991), 209–230.
- [33] Olivieri, E. and Scoppola, E., Markov chains with exponentially small transition probabilities: first exit problem from a general domain. I. The reversible case. *J. Statist. Phys.* **79** (1995), 613–647.
- [34] Olivieri, E. and Scoppola, E., Markov chains with exponentially small transition probabilities: first exit problem from a general domain. II. The general case. *J. Statist. Phys.* **84** (1996), 987–1041.
- [35] Olivieri, E. and Vares, M. E., *Large deviations and metastability*. Encyclopedia of Mathematics and its Applications 100, Cambridge University Press, Cambridge, 2005.