Eyring-Kramers law and exit rates for the overdamped Langevin process

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Plan

I. The kinetic Monte Carlo method and the Eyring-Kramers law

II. Justification of the use of the kinetic Monte Carlo method to sample the exit from a metastable domain :

- The quasi-stationary distribution approach
- Eyring-Kramers law for the exit rates

Part I

The kinetic Monte Carlo method and the Eyring-Kramers law

Overdamped Langevin process

Molecular dynamics : simulate the evolution of atomistic systems (e.g. macromolecules or clusters of atoms)

$\rightarrow$ compute macroscopic quantities or understand macroscopic mechanisms

Evolution of the positions of the atoms : overdamped Langevin process

$$dX_t = -\nabla f(X_t)dt + \sqrt{h}\, dB_t,$$

where

- $X_t \in \mathbb{R}^d$ $(d = 3N)$
- $f : \mathbb{R}^d \to \mathbb{R}$ is the potential energy of the system (interactions between the atoms)
- $h = 2k_B T_e$

Metastability of the Overdamped Langevin process

When

$$h \ll \Delta f \ (\text{"}h \to 0\text{"})$$

the drift part $-\nabla f(X_t)dt$ is dominant in

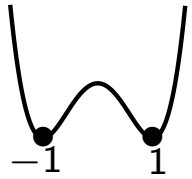
$$dX_t = -\nabla f(X_t)dt + \sqrt{h}\, dB_t$$

$\to (X_t)_{t\geq 0}$ is trapped over a long period of time in a neighborhood Ω of a local minimum x_0 of f (metastable region) before going into another metastable region.

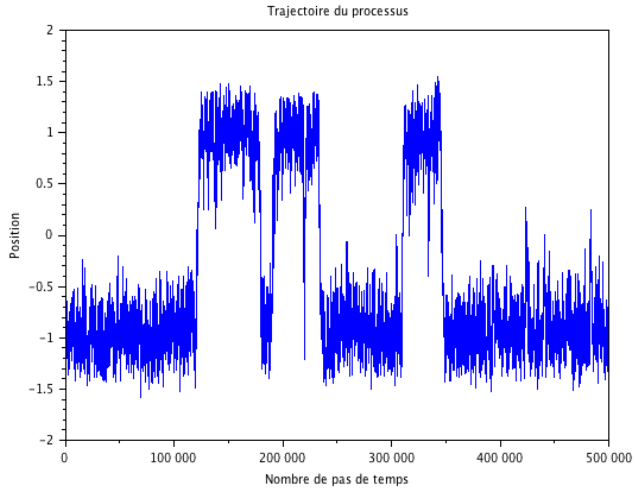
$\to$ Metastability

Illustration of the metastability in a very simple example

$$f(x) = (x-1)^2(x+1)^2$$



- 2 metastable regions $\mathbb{R}_-^*$ et $\mathbb{R}_+^*$ (basin of attractions)
- time evolution of $(X_t)_{t\geq 0}$:



- Transitions between the two metastable regions = **rare events**

How to efficiently sample the exit event from a metastable region ?

Macroscopic evolution

- Macroscopic state = metastable region $\Omega \subset \mathbb{R}^d$

  Macroscopic evolution

  How long does $(X_t)_{t\geq 0}$ stay in Ω and where does it exit Ω (next visited state) ?

  $\rightarrow$ Applications in biology, medecine, material science, nuclear physics

- Macroscopic transition = the move from one metastable region to another

  Not accessible by integrating the trajectories of $(X_t)_{t\geq 0}$

  $\rightarrow$ Major issue in computational statistical physics

How to efficiently sample the exit event $(\tau_\Omega, X_{\tau_\Omega})$ from a metastable state Ω ?
Where

$$\tau_\Omega := \inf\{t \geq 0,\ X_t \notin \Omega\}$$

and $X_{\tau_\Omega} \in \partial\Omega$ = the exit point location from Ω

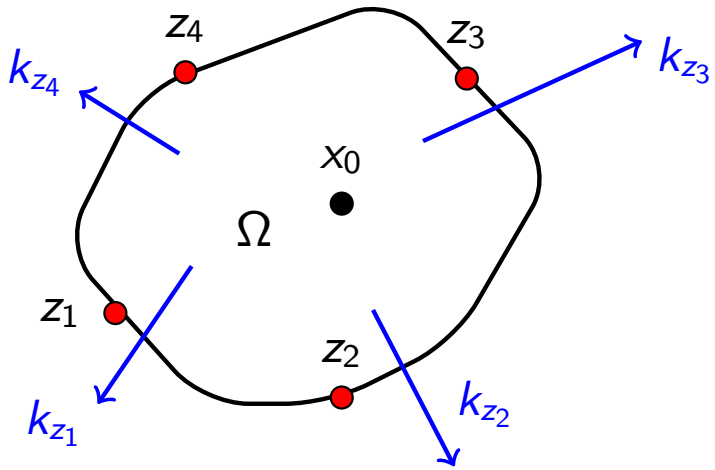
Sample the macroscopic evolution

Kinetic Monte Carlo method (kMC) : generates a jump Markov process

Ingredients to sample the exit from the region Ω with kMC : for all saddle points $z_j \in \partial\Omega$ ($j \in \{1, \ldots, n\}$), the **exit rate**

$$k_{z_j}$$

associated with an exit from Ω around z_j.



Domain Ω ($n = 4$)

How sample the exit event from Ω with kMC ?

First denote by :

- $T \geq 0$ the residence time in Ω
- $Y \in \{z_1, \ldots, z_n\}$ the random variable such that $Y = z_j$ if the exit from Ω occurs around z_j

With a kMC method, the exit event (T, Y) from Ω, is sampled as follows :

1. $T \sim \mathcal{E}\left(\sum_{\ell=1}^{n} k_{z_\ell} \right)$
2. Y is independent of T
3. Y has the following law :

$$\mathbb{P}\Big[Y = z_j\Big] = \frac{k_{z_j}}{\sum_{\ell=1}^{n} k_{z_\ell}}$$

Remark :
(T, Y) = exit event generated by the kMC method
$(\tau_\Omega, X_{\tau_\Omega})$ = exit event for $(X_t)_{t \geq 0}$

It remains to compute k_{z_j} ...

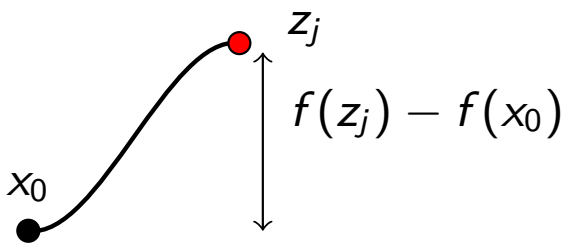
In practice, k_{z_j} is computed with the Eyring-Kramers law :

$$\boxed{k_{z_j} = A_j \, e^{-\frac{2}{h}(f(z_j)-f(x_0))}} \quad \text{where :}$$

- A_j : prefactor (depends on the process $(X_t)_{t\geq 0}$ and the nature of the saddle point z_j) :

$$A_j = \frac{|\lambda(z_j)|}{\pi} \frac{\sqrt{\det \mathrm{Hess}\, f(x_0)}}{\sqrt{|\det \mathrm{Hess}\, f(z_j)|}} \text{ if } \nabla f(z_j) = 0$$

- $f(z_j) - f(x_0)$: activation energy.



Question : $\boxed{(T, Y) \;\; (+\, k_{z_j} \text{ computed with Eyring-Kramers}) \;\simeq\; (\tau_\Omega, X_{\tau_\Omega}) \,?}$

kMC et *accelerated dynamics algorithms*

The kMC model is also used to build accelerated dynamics algorithms such as :

- *Hyperdynamics* [A.F. Voter, Phys. Rev. Lett. (1997)].
- *Temperature Accelerated Dynamics* (TAD) [M.R. Sorensen et A.F. Voter, J. Chem. Phys. (2000)].

More precisely, these 2 algorithms are based on :

$$(T, Y)\ (+\, k_{z_j} \text{ computed with Eyring-Kramers}) \ \simeq\ (\tau_\Omega, X_{\tau_\Omega})$$

Recall, the question was : **is this approximation valid** ?

One advantage of TAD : does not require to know all the saddle points z_j.

[D. Perez, B. P. Uberuaga, Y. Shim, J. G. Amar, and A.F. Voter, *Accelerated Molecular Dynamics Methods : Introduction and Recent Developments*. Annual Reports in computational chemistry (2009)].

Mathematical contributions

The raised question is linked with the following two areas in the mathematical literature :

1. Exit problem.

Large deviations : Freidlin-Wentzell and also Berglund, Day, Galves *and al.*, Gentz

Combined with PDE techniques : Devinatz, Friedman, Kamin, Perthame

2. Investigate the (low-lying) spectrum as $h \to 0$ of the infinitesimal generator $\frac{h}{2}\Delta - \nabla f \cdot \nabla$ of $(X_t)_{t\geq 0}$ in $L^2(\mathbb{R}^d, e^{-\frac{2}{h}f})$

- **Potential theory** :

  Bovier *and al.*, Landim, Seo *and al.*

- **Spectral methods** (semi-classical analysis) :

  Helffer, Hérau, Holley, Michel, Miclo, Nier, Sjöstrand

Part II

Justification of the use of the kinetic Monte Carlo method to sample the exit from a metastable domain

Quasi-stationary distribution (QSD)

Let Ω be a $\mathcal{C}^\infty$ bounded domain of $\mathbb{R}^d$ and $f : \overline{\Omega} \to \mathbb{R}$ be $\mathcal{C}^\infty$.

Definition (QSD). ν_h is a QSD if

$$X_0 \sim \nu_h \Rightarrow \forall t \geq 0,\ \mathcal{L}(X_t | t < \tau_\Omega) = \nu_h$$

Proposition. There exists a unique QSD ν_h and

$$\forall X_0 \in \Omega, \quad \lim_{t \to +\infty} \mathcal{L}(X_t | t < \tau_\Omega) = \nu_h$$

In other words

$$\nu_h = \textbf{local equilibrium} \text{ of the process } (X_t)_{t \geq 0} \text{ in } \Omega$$

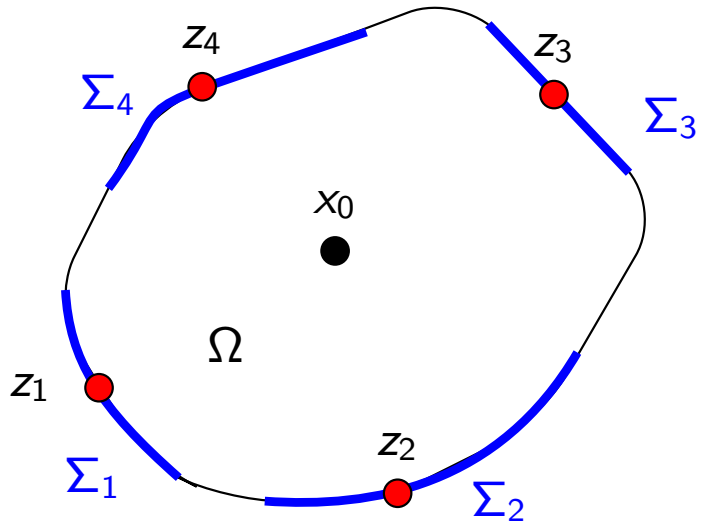
If Ω metastable (reaching $\nu_h \ll$ exiting Ω), it is relevant to study the exit event when

$$X_0 \sim \nu_h$$

Definition of the exit rates in a metastable region Ω

Exit rate associated with an exit through a neighborhood $\Sigma_j \subset \partial\Omega$ of z_j :

$$k_{z_j}^L = \frac{\mathbb{P}_{\nu_h}[X_{\tau_\Omega} \in \Sigma_j]}{\mathbb{E}_{\nu_h}[\tau_\Omega]}$$



Proposition. When $X_0 \sim \nu_h$,

$$\tau_\Omega \sim \mathcal{E}(\sum_{\ell=1}^{n} k_{z_\ell}^L), \quad \tau_\Omega \perp\!\!\!\perp X_{\tau_\Omega}, \text{ and } \mathbb{P}_{\nu_h}[X_{\tau_\Omega} \in \Sigma_j] = k_{z_j}^L / \sum_{\ell=1}^{n} k_{z_\ell}^L$$

$\rightarrow$ We can simulate $(\tau_\Omega, X_{\tau_\Omega})$ with a jump Markov process (kMC)

Eyring-Kramers law for the exit rates $k_{z_j}^L$?

Eyring-Kramers law : case when $\partial_{\mathbf{n}} f > 0$

Assumptions :

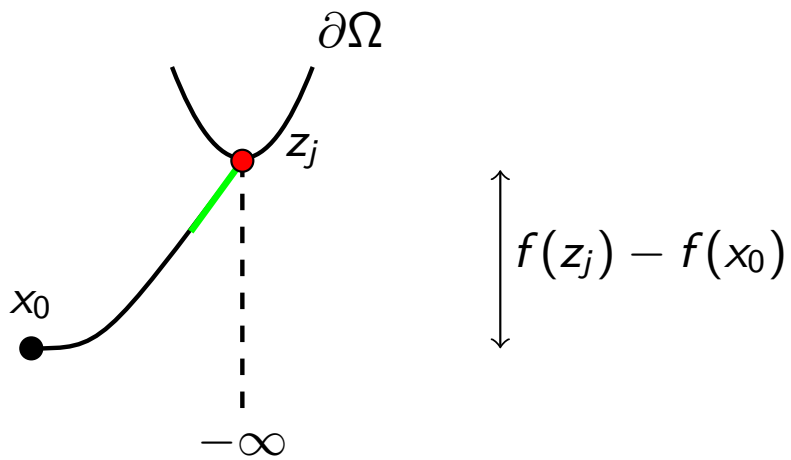
- $\partial_{\mathbf{n}} f > 0$ on $\partial\Omega$
- f has unique critical point x_0 in Ω, and

$$f(x_0) = \min_{\overline{\Omega}} f < \min_{\partial\Omega} f$$

- $f : \overline{\Omega} \to \mathbb{R}$ and $f|_{\partial\Omega}$ are Morse functions

Denote by $z_1, \ldots, z_n$ the **local minima** of $f|_{\partial\Omega}$

Remark : $\nabla f(z_j) \neq 0$ and $z_1, \ldots, z_n$ are the geometric saddle points of f on $\partial\Omega$, if we extend f by $-\infty$ outside $\overline{\Omega}$ (absorbing boundary).



Remark : such edge shaped barriers were considered by Kramers (1940), Matkowsky and Schuss (1982)

Eyring-Kramers law when $\partial_{\mathbf{n}} f > 0$

Theorem 1. *If each z_j is sufficiently far from the other z_k's (for an Agmon distance), then, for all $j \in \{1, \dots, n\}$, when $h \to 0$:*

$$k_{z_j}^L = \frac{\partial_{\mathbf{n}} f(z_j)}{\sqrt{h\,\pi}} \frac{\sqrt{\det \mathrm{Hess}\, f(x_0)}}{\sqrt{\det \mathrm{Hess}\, f|_{\partial\Omega}(z_j)}}\; e^{-\frac{2}{h}(f(z_j)-f(x_0))}(1+O(h))$$

$\to$ This is the expected Eyring-Kramers law for such a z_j ($\nabla f(z_j) \neq 0$)

[*Sharp asymptotics of the first exit point density*. Annals of PDE (2019). G. Di Gesù, T. Lelièvre, D. Le Peutrec, and B.N.]

[*Jump Markov models and transition state theory : the quasi-stationary distribution approach*. Faraday Discussions (2016). G. Di Gesù, T. Lelièvre, D. Le Peutrec, and B.N.]

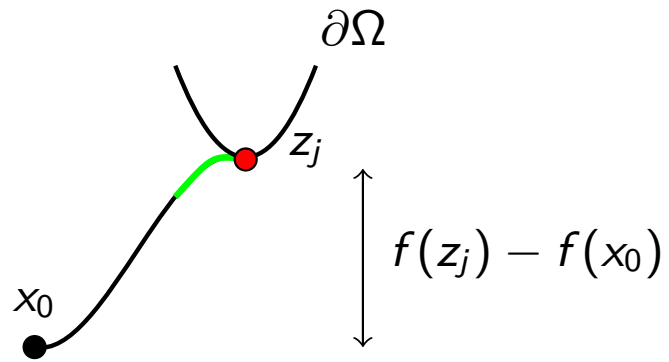
And if f has saddle points $z_j \in \partial\Omega$ with $\nabla f(z_j) = 0$?

Generalization : f has saddle points $z_j \in \partial\Omega$ with $\nabla f(z_j) = 0$

In many applications of the kMC methods and the accelerated dynamics algorithms : $\Omega =$ the basin of attraction of a local minimum x_0 of f in $\mathbb{R}^d$ for the dynamics

$$\dot{x}(t) = -\nabla f(x(t)),\ t \geq 0$$

$\rightarrow$ f has critical points on $\partial\Omega$:



$\rightarrow$ Practical interest in considering such a geometrical setting

Eyring-Kramers law : case when f has saddle points $z_j \in \partial\Omega$ with $\nabla f(z_j) = 0$

Assume that :

- Ω is the basin of attraction of a local minimum x_0 of f in $\mathbb{R}^d$ for the dynamics
$$\dot{x}(t) = -\nabla f(x(t)),\ t \geq 0$$
Denote by
$$z_1, \ldots, z_n$$
the saddle points of f on $\partial\Omega$ ($\nabla f(z_j) = 0$).
- $f : \overline{\Omega} \to \mathbb{R}$ and $f|_{\partial\Omega}$ are Morse functions

Remark : we smooth $\partial\Omega$ (note that $\partial\Omega$ is already smooth around the z_j's)

Eyring-Kramers law when f has saddle points $z_j \in \partial\Omega$ with $\nabla f(z_j) = 0$

Theorem 2. *If each z_j is sufficiently far from the other z_k's (for another Agmon distance), then, for all $j \in \{1, \dots, n\}$, when $h \to 0$:*

$$k_{z_j}^L = \frac{|\lambda(z_j)|}{\pi} \frac{\sqrt{\det \text{ Hess } f(x_0)}}{\sqrt{|\det \text{ Hess } f(z_j)|}} \; e^{-\frac{2}{h}(f(z_j)-f(x_0))}(1 + O(h))$$

$\to$ This is the expected Eyring-Kramers law for such a saddle point z_j ($\nabla f(z_j) = 0$)

[*Eyring-Kramers exit rates for the overdamped Langevin dynamics : the case with saddle points on the boundary*. Submitted. 2022. T. Lelièvre, D. Le Peutrec, and B.N.]

Conclusion

When :

a. $\partial_{\mathbf{n}} f > 0$

or,

b. f has saddle points $z_j \in \partial\Omega$ with $\nabla f(z_j) = 0$

we have justified that

$$(\tau_\Omega,\, X_{\tau_\Omega})$$

can be sampled with the kMC method parametrized by exit rates computed with the Eyring-Kramers law.

Extension

The kinetic Langevin process :

$$\begin{cases} dx_t = v_t dt, \\ dv_t = -\nabla f(x_t)dt - \gamma(x_t, v_t)v_t dt + \Sigma(x_t, v_t)dB_t, \end{cases} \tag{1}$$

where

$$\Omega = \mathrm{O} \times \mathbb{R}^d \text{ and } \mathrm{O} \subset \mathbb{R}^d$$

Existence and uniqueness of the QSD for such hypoelliptic processes :

- [A. Guillin, B.N., and L. Wu, 2020, submitted]
- [T. Lelièvre, J. Reygner, and M. Ramil, 2021, Stoch. Process. their Appl.]
- [A. Guillin, B.N., and L. Wu, 2022, Probab. Theory Relat. Fields]

Thank you