The Kramers law :
Validity, derivations and generalizations

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Partly based on joint work with
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Institut Henri Poincaré, Paris, 26 January 2011

Stochastic differential equation
a.k.a. (overdamped) Langevin equation

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

- ▷ $V : \mathbb{R}^d \to \mathbb{R}$: potential, growing at infinity
- ▷ W_t: d-dim Brownian motion

Equivalent notation :

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

- ▷ ξ_t: Gaussian white noise, $\langle \xi_t \rangle = 0$, $\langle \xi_t \xi_s \rangle = \delta(t-s)$

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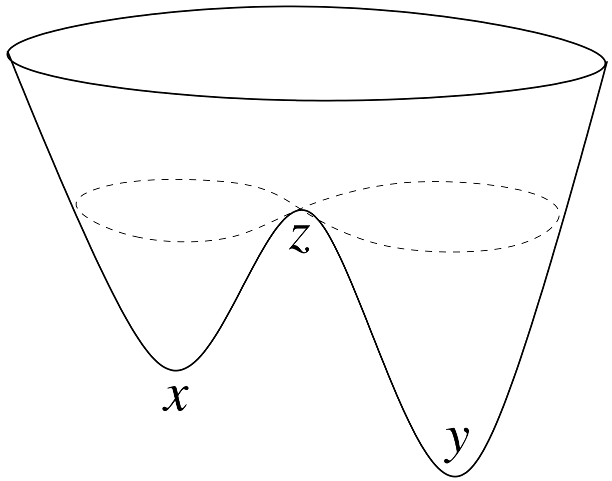
Some properties :

- ▷ Invariant probability measure : $\mu(\mathrm{d}x) = \frac{1}{Z}\,\mathrm{e}^{-V(x)/\varepsilon}\,\mathrm{d}x$
- ▷ System is reversible w.r.t. μ (detailed balance)
  $p(y,t|x,0)\,\mathrm{e}^{-V(x)/\varepsilon} = p(x,t|y,0)\,\mathrm{e}^{-V(y)/\varepsilon}$

Main question



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How long does the system need on average to go from one minimum to another one (for $\varepsilon \ll 1$)?

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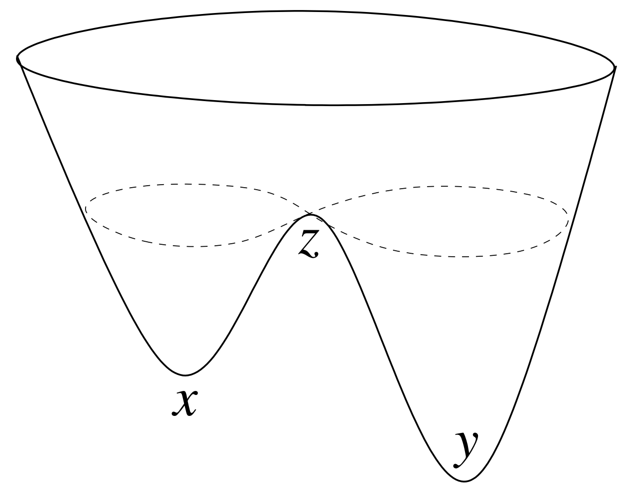

τ_y^x: first-hitting time of small ball $\mathcal{B}_\varepsilon(y)$, starting in x

"Arrhenius law" (van 't Hoff 1885, Arrhenius 1889)

$$\mathbb{E}[\tau_y^x] \simeq \mathit{const}\, \mathrm{e}^{[V(z)-V(x)]/\varepsilon}$$

"(Eyring–)Kramers law" (Eyring 1935, Kramers 1940)

- Dim 1: $\mathbb{E}[\tau_y^x] \simeq \dfrac{2\pi}{\sqrt{V''(x)|V''(z)|}} \mathrm{e}^{[V(z)-V(x)]/\varepsilon}$
- Dim$\geqslant$ 2: $\mathbb{E}[\tau_y^x] \simeq \dfrac{2\pi}{|\lambda_1(z)|}\sqrt{\dfrac{|\det(\nabla^2 V(z))|}{\det(\nabla^2 V(x))}}\, \mathrm{e}^{[V(z)-V(x)]/\varepsilon}$

Plan

Proof(s) of Kramers' law

- ▷ Theory of large deviations [Freidlin, Wentzell]
- ▷ Analytic approaches
  - – WKB theory
  - – Potential theory [Bovier, Eckhoff, Gayrard, Klein]
  - – Witten Laplacian [Helffer, Klein, Nier]

Generalizations and limits

- ▷ Non-quadratic saddles
- ▷ SPDEs
- ▷ Non-gradient systems : cycling

Theory of large deviations (I/III) [Freidlin, Wentzell, '69]

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

Large-deviation principle (LDP) :

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

More precisely, for any set Γ of continuous paths on $[0,T]$

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

Infinite-dimensional Laplace (saddle point) method $\int_\Gamma \mathrm{e}^{-w(x)/2\varepsilon}\,\mathrm{d}x \simeq \mathrm{e}^{-\inf_\Gamma w/2\varepsilon}$

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LDP is known to hold with the rate function

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

- ▷ Case $f=0$: Schilder's theorem (1966)
  Proof uses Cameron-Martin-Girsanov formula
- ▷ General f : Freidlin and Wentzell (1969)
  Proof uses contraction principle and Euler approximation

Theory of large deviations (II/III) - exit problem

First exit time from $\mathcal{D} \subset \mathbb{R}^d$: $\tau = \inf\{t > 0 \colon x_t \notin \mathcal{D}\}$

Assume $\overline{\mathcal{D}} \subset$ basin of attraction of stable equilibrium point $x^\star \in \mathcal{D}$

Quasipotential : $\overline{V} = \inf_{z \in \partial\mathcal{D}} \inf_{T>0} \inf_{\varphi \colon \varphi(0)=x^\star, \varphi(T)=z} I(\varphi)$

Theorem [Freidlin, Wentzell, '69] : $\forall x_0 \in \mathcal{D}, \lim_{\varepsilon \to 0} 2\varepsilon \log \mathbb{E}^{x_0}[\tau] = \overline{V}$

Proof :

- ▷ For any $x_0 \in \mathcal{D}$, x_t is likely to hit small nbh of $x^\star$ in finite time
- ▷ LDP $\Rightarrow$ probability of leaving $\mathcal{D}$ in time T close to $p = \mathrm{e}^{-\overline{V}/2\varepsilon}$
- ▷ By Markov property, attempts of leaving $\mathcal{D}$ almost independent $\Rightarrow \mathbb{E}[\tau] \simeq 1/p$

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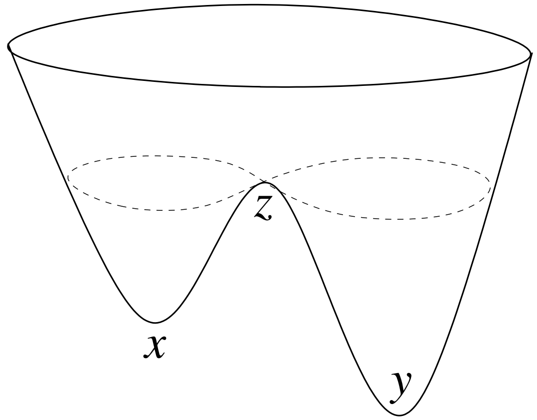
Gradient case : $f = -\nabla V$

$$I(\varphi) = \frac{1}{2} \int_0^T \|\dot\varphi(t) - \nabla V(\varphi(t))\|^2 \, \mathrm{d}t + 2 \underbrace{\int_0^T \langle \dot\varphi(t), \nabla V(\varphi(t)) \rangle \, \mathrm{d}t}_{= V(\varphi(T)) - V(\varphi(0))}$$

First term can be made arbitrarily small $\Rightarrow$ $\overline{V} = 2[\inf_{\partial\mathcal{D}} V - V(x^\star)]$

Theory of large deviations (III/III) - conclusion



Corollary : For double-well potential

$$\lim_{\varepsilon \to 0} \varepsilon \log \mathbb{E}^x \Big[\tau_{\mathcal{B}_\varepsilon(y)} \Big] = V(z) - V(x)$$

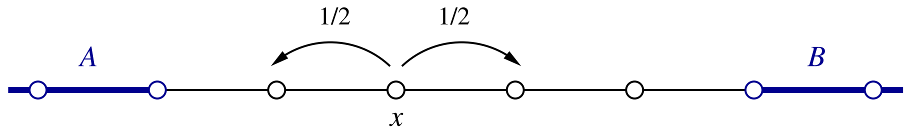
(Arrhenius law)

Remarks

- ▷ LDP also yields information on exit location and optimal path
- ▷ Multiwell case described by hierarchy of "cycles"
- ▷ Nongradient case : described by solving variational problem
- ▷ Prefactor cannot be obtained by this approach

Analytic approaches (I/V)

Symmetric random walk on $\mathbb{Z}$



▷ Prob of hitting A before B starting in x :

$$
\begin{aligned}
h_{A,B}(x) &= \mathbb{P}^x\{\tau_A < \tau_B\} \\
&= \mathbb{P}^x\{\tau_A < \tau_B | X_1 = x-1\}\tfrac{1}{2} + \mathbb{P}^x\{\tau_A < \tau_B | X_1 = x+1\}\tfrac{1}{2} \\
&= \tfrac{1}{2} h_{A,B}(x-1) + \tfrac{1}{2} h_{A,B}(x+1)
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$\Rightarrow \Delta h_{A,B} = 0$, Δ discrete Laplacian (⇒ $h_{A,B}$ is harmonic)

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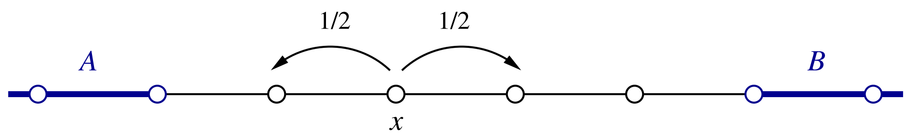

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$\Rightarrow \Delta h_{A,B} = 0$, Δ discrete Laplacian (⇒ $h_{A,B}$ is harmonic)

▷ Expected first-hitting time of A starting in x :

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

$\Rightarrow \Delta w_A = -2$

Analytic approaches (I/V)

Brownian motion in $\mathbb{R}^d$:

▷ $h_{A,B}(x) = \mathbb{P}^x\{\tau_A < \tau_B\}$ satisfies

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

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

Same PDEs hold with $\frac{1}{2}\Delta$ replaced by $L = \varepsilon\Delta - \nabla V(x) \cdot \nabla$
[Dynkin, 1965]
Generator of diffusion L is adjoint of Fokker–Planck operator

Analytic approaches (II/V) : one-dimensional case

$(Lu)(x) = \varepsilon u''(x) - V'(x)u'(x)$

▷ $A = (-\infty, a), B = (b, \infty), a < x < b$

$$\mathbb{P}^x\{\tau_A < \tau_B\} = \frac{\displaystyle\int_x^b \mathrm{e}^{V(y)/\varepsilon}\,\mathrm{d}y}{\displaystyle\int_a^b \mathrm{e}^{V(y)/\varepsilon}\,\mathrm{d}y} \simeq \exp\frac{1}{\varepsilon}\Big[\sup_{[x,b]} V - \sup_{[a,b]} V\Big]$$

– close to 1 if x in basin of attraction of a

– exponentially small otherwise

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▷ $A = (-\infty, a), x > a$

$$\mathbb{E}^x[\tau_A] = \frac{1}{\varepsilon}\int_a^x \int_y^\infty \mathrm{e}^{[V(y)-V(z)]/\varepsilon}\,\mathrm{d}z\,\mathrm{d}y$$

Assume $x > c > b > a$, b local maximum, c minimum of V
$\Rightarrow$ Integrand maximal for $(y, z) = (b, c)$
Laplace method yields Kramers law

Analytic approaches (III/V) : link to semiclassical analysis

▷ $L = \varepsilon\Delta - \nabla V(x) \cdot \nabla$ is self-adjoint in $L^2(\mathbb{R}^d, \mathrm{e}^{-V/\varepsilon}\,\mathrm{d}x)$
Manifestly self-adoint form : $L = \varepsilon\,\mathrm{e}^{V/\varepsilon}\,\nabla \cdot \mathrm{e}^{-V/\varepsilon}\,\nabla$

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- ▷ $\widetilde{L} = \mathrm{e}^{-V/2\varepsilon}\,L\,\mathrm{e}^{V/2\varepsilon}$ is self-adjoint in $L^2(\mathbb{R}^d, \mathrm{d}x)$
  In fact $\widetilde{L} = \varepsilon\Delta + \frac{1}{\varepsilon}U(x)$ is a Schrödinger operator
  with potential $U(x) = \frac{1}{2}\varepsilon\Delta V(x) - \frac{1}{4}\|\nabla V(x)\|^2$

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- ▷ Example :

$$V(x) = \tfrac{1}{4}x^4 - \tfrac{1}{2}x^2 \quad \Rightarrow \quad U(x) = -\tfrac{1}{4}x^2(x^2-1)^2 + \tfrac{1}{2}\varepsilon(x^2-1)^2$$

Tunelling through nonresonant wells requires hard methods (microlocal analysis)

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  Tunelling through nonresonant wells requires hard methods (microlocal analysis)
- $\triangleright$ Results based on matched asymptotic expansions
  e.g. Matkowsky and Schuss (1979), Buslov and Makarov (1988), Kolokoltsov and Makarov (1996), Maier and Stein (1997)
- $\triangleright$ Rigorous bounds on eigenvalues of L
  e.g. Holley, Kusuoka and Stroock (1989), Mathieu (1995), Miclo (1995)

Analytic approaches (IV/V) : Potential theory

[Bovier, Eckhoff, Gayrard, Klein, '04]

Consider again Brownian motion

First-hitting time $\tau_A = \inf\{t > 0 \colon W_t \in A\}$, $A \subset \mathbb{R}^d$

Recall : $w_A(x) = \mathbb{E}^x[\tau_A]$ satisfies

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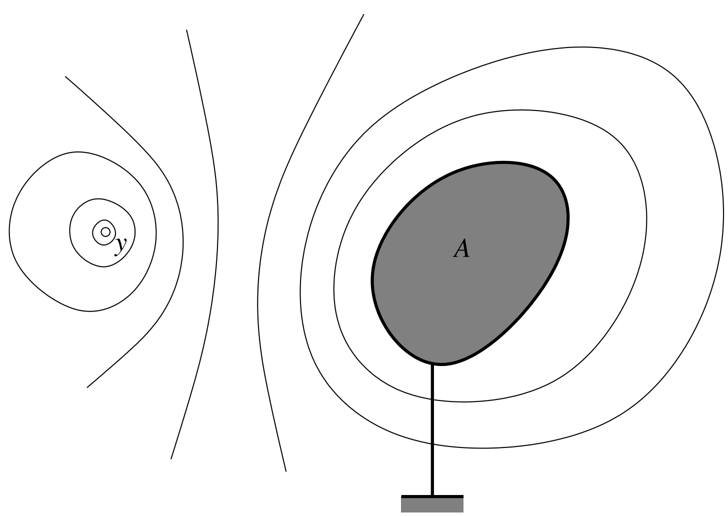
$G_{A^c}(x,y)$ Green's function $\Rightarrow w_A(x) = -\int_{A^c} G_{A^c}(x,y)\,\mathrm{d}y$



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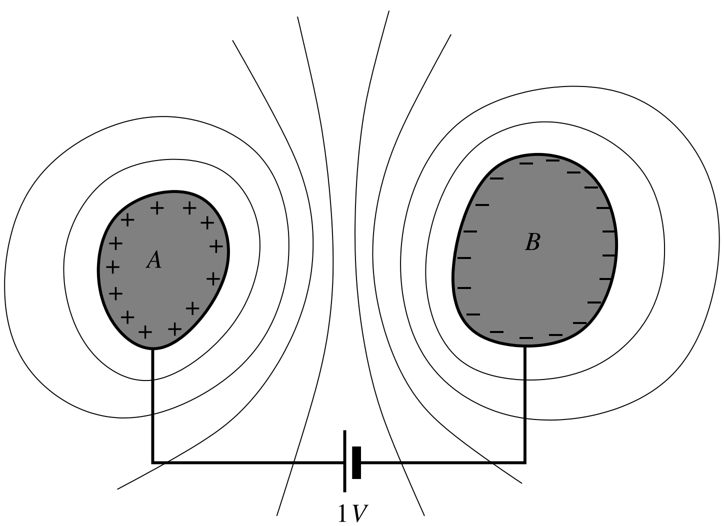
$$\Rightarrow h_{A,B}(x) = \int_{\partial A} G_{B^c}(x,y)\, \rho_{A,B}(\mathrm{d}y)$$

$\rho_{A,B}$: "surface charge density" on ∂A



Analytic approaches (IV/V) : Potential theory

Capacity: $\mathsf{cap}_A(B) = \left| \int_{\partial A} \rho_{A,B}(\mathsf{d}y) \right|$

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Key observation: let $C = \mathcal{B}_\varepsilon(x)$, then (using $G(y,z) = G(z,y)$)

$$\begin{aligned}\int_{A^c} h_{C,A}(y)\,\text{d}y &= \int_{A^c}\int_{\partial C} G_{A^c}(y,z)\rho_{C,A}(\text{d}z)\,\text{d}y \\ &= -\int_{\partial C} w_A(z)\rho_{C,A}(\text{d}z) \simeq w_A(x)\,\text{cap}_C(A)\end{aligned}$$

$$\Rightarrow \qquad \mathbb{E}^x[\tau_A] = w_A(x) \simeq \frac{\int_{A^c} h_{\mathcal{B}_\varepsilon(x),A}(y)\,\text{d}y}{\text{cap}_{\mathcal{B}_\varepsilon(x)}(A)}$$

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Variational representation: Dirichlet form

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

($\mathcal{H}_{A,B}$: set of sufficiently smooth functions satisfying b.c.)

Analytic approaches (IV/V) : Potential theory

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

Generator : $\varepsilon\Delta - \nabla V \cdot \nabla$

Then

$$\mathbb{E}[\tau_A^x] = w_A(x) \simeq \frac{\displaystyle\int_{A^c} h_{\mathcal{B}_\varepsilon(x),A}(y)\,\mathrm{e}^{-V(y)/\varepsilon}\,\mathrm{d}y}{\mathrm{cap}_{\mathcal{B}_\varepsilon(x)}(A)}$$

where

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

Rough a priori bounds on h show that if x potential minimum,

$$\int_{A^c} h_{\mathcal{B}_\varepsilon(x),A}(y)\,\mathrm{e}^{-V(y)/\varepsilon}\,\mathrm{d}y \simeq \frac{(2\pi\varepsilon)^{d/2}\,\mathrm{e}^{-V(x)/\varepsilon}}{\sqrt{\det(\nabla^2 V(x))}}$$

Analytic approaches (IV/V) : Potential theory

Theorem [A. Bovier, M. Eckhoff, V. Gayrard, M. Klein 2004]

In the double-well situation :

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

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Proof :

- ▷ Upper bound on capacity : use one-dimensional solution for h
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Analytic approaches (IV/V) : Potential theory

Theorem [A. Bovier, M. Eckhoff, V. Gayrard, M. Klein 2004]

In the double-well situation :

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

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More results by [BEGK] :

- ▷ Distribution of $\tau_{\mathcal{B}_\varepsilon(y)}$ is close to exponential (see also [Day, 1983])
- ▷ Multiwell case (metastable hierarchy)
- ▷ Sharp estimates for small eigenvalues of generator
- ▷ Eigenfunction of generator well-approximated by certain $h_{A,B}$

Analytic approaches (IV/V) : Potential theory

Multiwell case : $\exists$ order $x_1 \prec x_2 \prec \cdots \prec x_n$ on local minima of V

Metastable hierarchy $\mathcal{M}_k = \{x_1, \ldots x_k\}$

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Example :

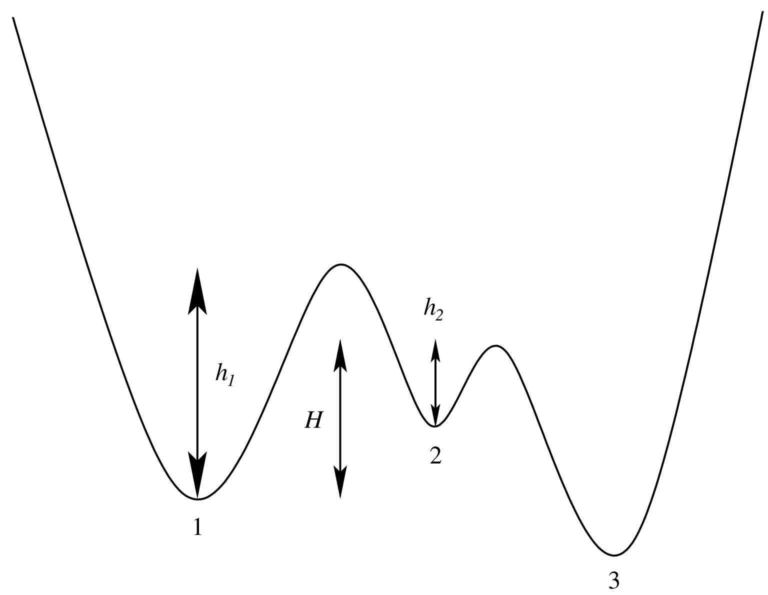
$3 \prec 1 \prec 2$

$\mathbb{E}^1[\tau_3] \simeq C_1\, \mathrm{e}^{h_1/\varepsilon}$

$\mathbb{E}^2[\tau_{\{1,3\}}] \simeq C_2\, \mathrm{e}^{h_2/\varepsilon}$

However $\mathbb{E}^2[\tau_3] \gg C_2\, \mathrm{e}^{h_2/\varepsilon}$

In fact, $\mathbb{E}^2[\tau_3] \simeq C'\, \mathrm{e}^{H/\varepsilon}$



Analytic approaches (V/V) : Witten complex [Helffer, Klein, Nier, '04]

▷ Hodge Laplacian or Laplace-de Rham operator :
$\Delta_H = \mathrm{d}\mathrm{d}^* + \mathrm{d}^*\mathrm{d} = (\mathrm{d} + \mathrm{d}^*)^2$ where d exterior derivative
$\Delta_H^{(p)}$: Δ_H restricted to p-forms. $\Delta_H^{(0)} = -$ usual Laplacian
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▷ Results :

- Full asymptotic expansion of prefactor
  [Helffer, Klein and Nier 2004]
- Case of manifold with boundary
  [Helffer and Nier 2006]

Extension 1 : Non-quadratic saddles

What happens when $\det(\nabla^2 V(z)) = 0$?

Occurs at bifurcations in parameter-dependent systems

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Normal form : $V(y) = -u_1(y_1) + u_2(y_2, \dots, y_k) + \frac{1}{2}\sum_{j=k+1}^{d} \lambda_j y_j^2 + \dots$

Theorem [B, Gentz, MPRF 2010] Under growth conditions on u_1, u_2

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

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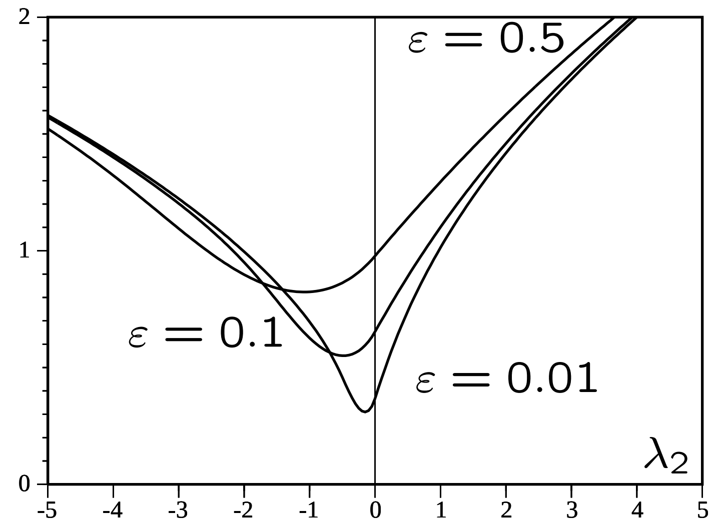
Example : Pitchfork bifucation

$u_1 = \frac{1}{2}|\lambda_1| y_1^2, \; u_2 = \frac{1}{2}\lambda_2 y_2^2 + C_4 y_2^4$

Kramers law holds with prefactor

$$2\pi \sqrt{\frac{(\lambda_2 + \sqrt{2\varepsilon C_4})\lambda_3 \dots \lambda_d}{|\lambda_1| \det(\nabla^2 V(x))}} \Psi_+\left(\frac{\lambda_2}{\sqrt{2\varepsilon C_4}}\right)$$

where $\Psi_+(\alpha) = \sqrt{\frac{\alpha(1+\alpha)}{8\pi}} e^{\alpha^2/16} K_{1/4}\left(\frac{\alpha^2}{16}\right)$



Extension 2 : SPDEs

Allen-Cahn with space-time white noise :

$$\partial_t u(t,x) = \partial_{xx} u(t,x) + u(t,x) - u(t,x)^3 + \sqrt{2\varepsilon}\ddot{W}_{tx}$$

$u \in \mathbb{R}$, $x \in [0, L]$, e.g. Neumann b.c.

Energy functional : $V[u] = \int_0^L \Big[\frac{1}{2}u'(x)^2 - \frac{1}{2}u(x)^2 + \frac{1}{4}u(x)^4\Big]\,\mathrm{d}x$

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Global minima : $u_\pm(x) = \pm 1$

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

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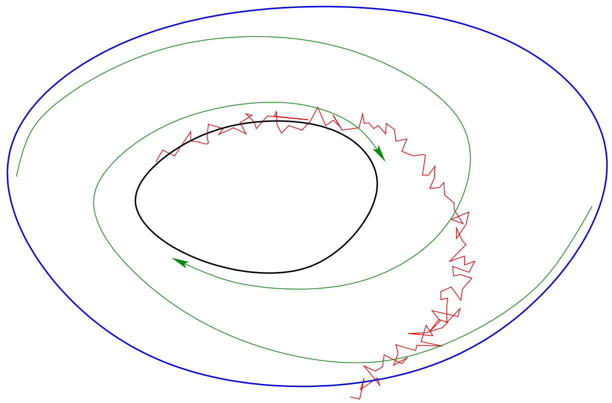
- ▷ Theorem [Barret, B, Gentz, in progress]

  The formal result is correct

  Proof : Spectral Galerkin approximation
  Dimension-independent control of error terms [Barret, Bovier, Méléard 2010]

Limitation : Cycling



Planar vector field

$\mathcal{D} \in \mathbb{R}^2$, $\partial\mathcal{D}$ unstable periodic orbit

- Not reversible
- Quasipotential $\overline{V}$ constant on $\partial\mathcal{D}$

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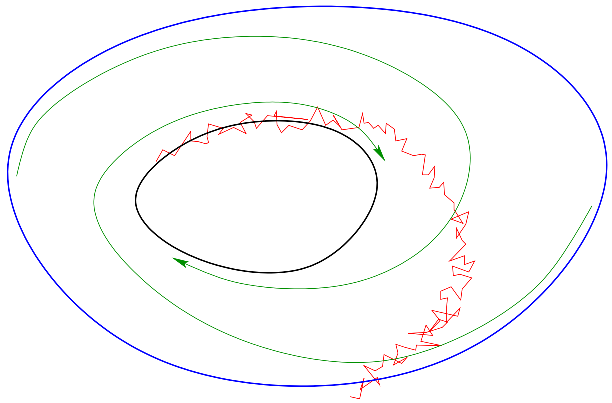

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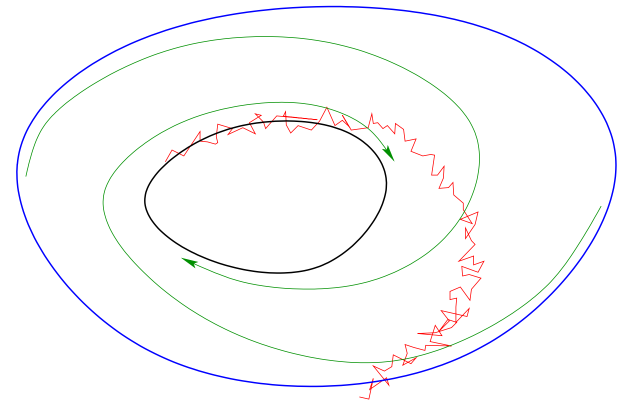

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▷ Theorem [B, Gentz, J. Statist. Phys. 2004]
In explicit parametrization of $\partial\mathcal{D}$ distribution of exit location is

$$p(\theta) = f_{\text{transient}}(\theta) \frac{e^{-(\theta-\theta_0)/\lambda T_K}}{\lambda T_K} P_{\lambda T}(\theta - \log(\varepsilon^{-1}))$$

- T period, λ Lyapunov exponent
- $T_K = C\varepsilon^{-1/2} e^{\overline{V}/\varepsilon}$ Kramers time
- $P_{\lambda T}(x) = \sum_{k\in\mathbb{Z}} A(x - k\lambda T)$, $A(z) = \frac{1}{2} e^{-2z-\frac{1}{2}e^{-2z}}$ (Gumbel)

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