Model reduction of diffusion process along reaction coordinate and related issues

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joint work with Carsten Hartmann and Christof Schütte

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Outline

- Introduction
- Model reduction : effective dynamics
- Application : eigenvalue estimation

Diffusion process

SDE on $\mathbb{R}^n$

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Invariant measure $d\pi = \rho(x)dx$, where

$$\rho(x) = \frac{1}{Z}e^{-\beta V(x)}, \quad \text{with } Z = \int_{\mathbb{R}^n} e^{-\beta V(x)}dx\,.$$

Diffusion process

Hilbert space $\quad H = L^2(\mathbb{R}^n, \pi)$,

Inner product $\quad \langle f, g \rangle_\pi = \int_{\mathbb{R}^n} f(x)\, g(x) \rho(x)\, dx\,, \quad \forall f, g \in H\,,$

$\implies \quad \langle \mathcal{L} f, g \rangle_\pi = \langle f, \mathcal{L} g \rangle_\pi$.

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Eigenvalues of $-\mathcal{L}$: $\quad \lambda_i \in \mathbb{R}$ with

$$0 = \lambda_0 < \lambda_1 \leq \cdots \leq \lambda_k \leq \cdots\,,$$

and $-\mathcal{L}\varphi_i = \lambda_i\varphi_i\,, \quad \varphi_0 \equiv 1$.

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Question : How to estimate $\lambda_1, \lambda_2, \cdots$ numerically when $n \gg 1$?

Operators

Semigroup operator

$$(T_s f)(x) = \mathbf{E}\big(f(x_s) \mid x_0 = x\big)\,, \quad f \in H\,,\ s \geq 0\,.$$

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$$(\mathcal{T}_\tau u)(y) = \frac{1}{\rho(y)} \int_{\mathbb{R}^n} p(x, y; \tau) u(x) \rho(x) dx\,, \quad y \in \mathbb{R}^n\,,$$

where $p(x, \cdot; \tau)$ is the p.d.f. at time $\tau \geq 0$.

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Connections :

$$\boxed{T_\tau = \mathcal{T}_\tau = e^{-\mathcal{L}\tau}}$$

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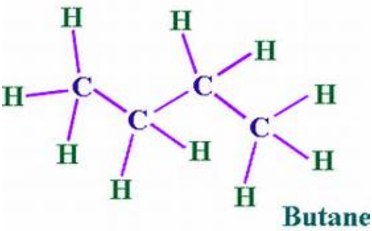
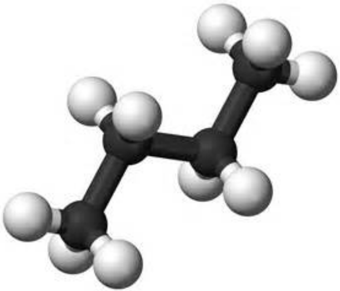
Motivation : Butane





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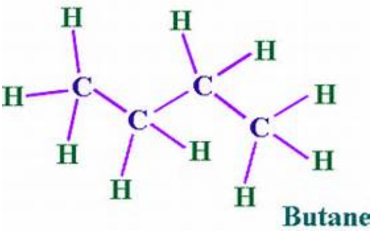

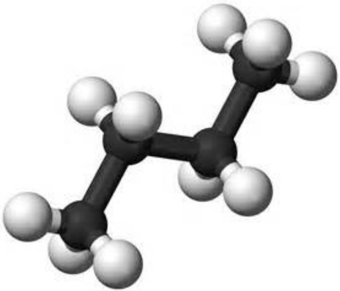

Question : How to study the dynamics of the <u>dihedral angle</u> ?

Effective dynamics

$$dx_s = -\nabla V(x_s)ds + \sqrt{2\beta^{-1}}dw_s$$

Reaction coordinate $\xi : \mathbb{R}^n \to \mathbb{R}^m$

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$$\begin{aligned}\mathbf{P}f(z) &= \int_{\Omega_z} f(x) d\mu_z(x) = \mathbf{E}_\pi(f(x)\,|\,\xi(x) = z)\,,\\ &= \frac{1}{Q(z)} \int_{\mathbb{R}^n} \rho(x) f(x) \delta\big(\xi(x) - z\big)\, dx\,,\\ Q(z) &= \int_{\mathbb{R}^n} \rho(x) \delta\big(\xi(x) - z\big)\, dx\,, \quad \int_{\mathbb{R}^m} Q(z) dz = 1\end{aligned}$$

Effective dynamics

Apply Ito's formula to $\xi(x_s) \Longrightarrow$

$$d\xi_l(x_s) = \mathcal{L}\xi_l(x_s)ds + \sqrt{2\beta^{-1}} \sum_{i=1}^{n} \frac{\partial \xi_l}{\partial x_i}(x_s)\, dw_s^i\,, \quad 1 \leq l \leq m\,.$$

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This motivates the effective dynamics[1]

$$\boxed{dz_s = \widetilde{b}(z_s)\, ds + \sqrt{2\beta^{-1}}\widetilde{\sigma}(z_s)\, dw_s\,, \quad z_s \in \mathbb{R}^m\,,}$$

with

$$\begin{aligned}\widetilde{b}_l(z) &= \mathbf{P}(\mathcal{L}\xi_l)\,,\\ \widetilde{a}_{ll'}(z) &= (\widetilde{\sigma}\widetilde{\sigma}^T)_{ll'}(z) = \mathbf{P}\Big(\sum_{i=1}^{n}\frac{\partial \xi_l}{\partial x_i}\frac{\partial \xi_{l'}}{\partial x_i}\Big)\,.\end{aligned}$$

1. Legoll and Lelièvre, Nonlinearity, 2010 .

Effective dynamics

Alternative expressions :

$$\widetilde{b}_l(z) = \lim_{s\to 0+} \mathbf{E}\Big(\frac{\xi_l(x_s) - z_l}{s} \;\Big|\; x_0 \sim \mu_z\Big)\,,$$

$$\widetilde{a}_{ll'}(z) = \frac{\beta}{2} \lim_{s\to 0+} \mathbf{E}\Big(\frac{(\xi_l(x_s) - z_l)(\xi_{l'}(x_s) - z_{l'})}{s} \;\Big|\; x_0 \sim \mu_z\Big)\,.$$

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Infinitesimal generator of z_s is

$$\widetilde{\mathcal{L}} = \sum_{l=1}^{m} \widetilde{b}_l \frac{\partial}{\partial z_l} + \frac{1}{\beta} \sum_{l,l'=1}^{m} \widetilde{a}_{ll'} \frac{\partial^2}{\partial z_l \partial z_{l'}},$$

We have

$$\boxed{f = \widetilde{f} \circ \xi \quad \Longrightarrow \quad \mathbf{P}\mathcal{L}f = \left(\widetilde{\mathcal{L}}\widetilde{f}\right) \circ \xi \,.}$$

Effective dynamics

Unique invariant measure of z_s is $\quad d\nu = Q(z)\,dz$.

$\widetilde{\mathcal{L}}$ is self-adjoint on space $\quad \widetilde{H} = L^2(\mathbb{R}^m, \nu)$.

Let

$$0 = \widetilde{\lambda}_0 < \widetilde{\lambda}_1 \leq \widetilde{\lambda}_2 \leq \cdots .$$

be the eigenvalues of $-\widetilde{\mathcal{L}}$ and $\widetilde{\varphi}_i \in \widetilde{H}$ be orthonormal eigenfunctions.

Effective dynamics — Time scales

Proposition 1

For $i \geq 0$, we have

$$\lambda_i \leq \widetilde{\lambda}_i \leq \lambda_i + \frac{1}{\beta} \int_{\mathbb{R}^n} |\nabla(\varphi_i - \widetilde{\varphi}_i \circ \xi)(x)|^2 \rho(x) dx.$$

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Especially, let

$$\xi(x) = \big(\varphi_1(x), \varphi_2(x), \cdots, \varphi_m(x)\big) \in \mathbb{R}^m\,,$$

Then $\widetilde{\lambda}_i = \lambda_i\,, \quad 0 \leq i \leq m$.

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$\Longrightarrow$ Optimal reaction coordinate function.

Effective dynamics — Algorithms

Key issue : estimate coefficients in

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1. HMM-like, Blue Moon, constrained dynamics, ...

$$\begin{aligned}\widetilde{b}_l(z) =& \mathbf{P}(\mathcal{L}\xi_l)\,,\\ \widetilde{a}_{ll'}(z) =& (\widetilde{\sigma}\widetilde{\sigma}^T)_{ll'}(z) = \mathbf{P}\Big(\sum_{i=1}^{n} \frac{\partial \xi_l}{\partial x_i}\frac{\partial \xi_{l'}}{\partial x_i}\Big)\,.\end{aligned}$$

2. Equation-free, ...

$$\begin{aligned}\widetilde{b}_l(z) =& \lim_{s\to 0+} \mathbf{E}\Big(\frac{\xi_l(x_s)-z_l}{s}\;\Big|\; x_0\sim\mu_z\Big)\,,\\ \widetilde{a}_{ll'}(z) =& \frac{\beta}{2}\lim_{s\to 0+} \mathbf{E}\Big(\frac{(\xi_l(x_s)-z_l)(\xi_{l'}(x_s)-z_{l'})}{s}\;\Big|\; x_0\sim\mu_z\Big)\,.\end{aligned}$$

3. Extended system, TAMD, ...

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Eigenvalue estimation [1]

Suppose N basis functions $\psi_l = \widetilde{\psi}_l \circ \xi$, $1 \leq l \leq N$, are given.

We want to apply Galerkin method to solve the eigenvalue problem

$$-\mathcal{L}f = \lambda f\,, \tag{1}$$

in the subspace $\mathrm{span}\{\psi_1, \psi_2, \cdots, \psi_N\}$.

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in the subspace span$\{\psi_1, \psi_2, \cdots, \psi_N\}$.

Write $f = \sum_{i=1}^{N} \omega_i \psi_i$,

then (1) $\Longrightarrow$ $CX = \lambda SX$, with

$$C_{ll'} = \langle -\mathcal{L}\psi_l, \psi_{l'} \rangle_\pi, \quad S_{ll'} = \langle \psi_l, \psi_{l'} \rangle_\pi\,, \quad 1 \le l, l' \le N\,,$$

1. Noé and Nüske, Multiscale Model. Simul. 2013.
Pérez-Hernández, Paul, et al. J. Chem. Phys. 2013.

Eigenvalue estimation

Using $\psi_I = \widetilde{\psi}_I \circ \xi$ and $\mathbf{P}\mathcal{L}\psi_I = \left(\widetilde{\mathcal{L}}\,\widetilde{\psi}_I\right) \circ \xi$, we have

$$S_{II'} = \langle \psi_I, \psi_{I'} \rangle_\pi = \langle \widetilde{\psi}_I, \widetilde{\psi}_{I'} \rangle_\nu\,,$$
$$C_{II'} = \langle -\mathcal{L}\psi_I, \psi_{I'} \rangle_\pi = \langle -\widetilde{\mathcal{L}}\widetilde{\psi}_I, \widetilde{\psi}_{I'} \rangle_\nu\,.$$

Eigenvalue estimation

Using $\psi_l = \widetilde{\psi}_l \circ \xi$ and $\mathbf{P}\mathcal{L}\psi_l = \big(\widetilde{\mathcal{L}}\,\widetilde{\psi}_l\big) \circ \xi$, we have

$$\begin{aligned} S_{ll'} =& \langle \psi_l, \psi_{l'} \rangle_\pi = \langle \widetilde{\psi}_l, \widetilde{\psi}_{l'} \rangle_\nu \,, \\ C_{ll'} =& \langle -\mathcal{L}\psi_l, \psi_{l'} \rangle_\pi = \langle -\widetilde{\mathcal{L}}\widetilde{\psi}_l, \widetilde{\psi}_{l'} \rangle_\nu \,. \end{aligned}$$

Since ν is the invariant measure of z_s,

$$\begin{aligned} S_{ll'} =& \lim_{T \to +\infty} \frac{1}{T} \int_0^T \widetilde{\psi}_l(z_s)\widetilde{\psi}_{l'}(z_s)ds \\ \approx& \frac{1}{M - M_0} \sum_{i=M_0+1}^{M} \widetilde{\psi}_l(z_{i\Delta t})\widetilde{\psi}_{l'}(z_{i\Delta t}) \,. \end{aligned}$$

Eigenvalue estimation

Similarly, let τ be a small parameter,

$$C_{ll'} = -\lim_{s\to 0}\lim_{T\to+\infty}\frac{1}{T}\int_0^T \frac{\widetilde{\psi}_{l'}(z_{t+s}) - \widetilde{\psi}_{l'}(z_t)}{s}\widetilde{\psi}_l(z_t)\,dt$$

$$\approx -\frac{1}{2(M-M_0)\tau}\sum_{i=M_0+1}^{M}\Big[\widetilde{\psi}_l(z_{i\Delta t+\tau})\widetilde{\psi}_{l'}(z_{i\Delta t}) + \widetilde{\psi}_l(z_{i\Delta t})\widetilde{\psi}_{l'}(z_{i\Delta t+\tau}) - 2\widetilde{\psi}_l(z_{i\Delta t})\widetilde{\psi}_{l'}(z_{i\Delta t})\Big].$$

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&\approx -\frac{1}{2(M-M_0)\tau}\sum_{i=M_0+1}^{M}\Big[\widetilde{\psi}_l(z_{i\Delta t+\tau})\widetilde{\psi}_{l'}(z_{i\Delta t}) \\
&\qquad + \widetilde{\psi}_l(z_{i\Delta t})\widetilde{\psi}_{l'}(z_{i\Delta t+\tau}) - 2\widetilde{\psi}_l(z_{i\Delta t})\widetilde{\psi}_{l'}(z_{i\Delta t})\Big]\,.
\end{aligned}
$$

$\Longrightarrow$ We can approximate eigenvalues of $CX = \lambda SX$, and therefore $-\mathcal{L}f = \lambda f$, by simulating the effective dynamics.

Eigenvalue estimation — A simple 2D example

Potential $V(x) = V_1(\theta) + \frac{1}{\epsilon} V_2(r,\theta)$,

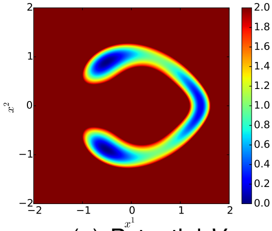
$$V_1(\theta) = \begin{cases} \left[1 - \frac{9}{\pi^2}\left(\theta - \frac{\pi}{3}\right)^2\right]^2 & \theta > \frac{\pi}{3}\,, \\ \frac{3}{5} - \frac{2}{5}\cos 3\theta & -\frac{\pi}{3} < \theta < \frac{\pi}{3} \\ \left[1 - \frac{9}{\pi^2}\left(\theta + \frac{\pi}{3}\right)^2\right]^2 & \theta < -\frac{\pi}{3}\,, \end{cases}$$

$$V_2(r,\theta) = \left(r^2 - 1 - \frac{1}{1 + 4r\theta^2}\right)^2 .$$

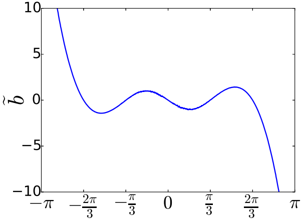
Dynamics $dx_s = -\nabla V(x_s)ds + \sqrt{2\beta^{-1}}dw_s$.

$\beta = 4.0$, $\epsilon = 0.05$, $\xi(x) = \theta(x) \in [-\pi, \pi]$.
9 Gaussian basis functions. $\tau = 20\Delta t$.

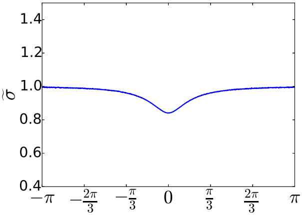
Eigenvalue estimation — A simple 2D example



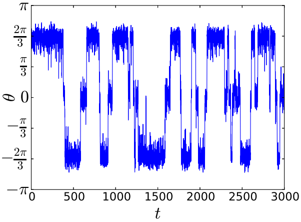
(a) Potential V



(b) $\widetilde{b}$



(c) $\widetilde{\sigma}$



(d) trajectory

Eigenvalue estimation — A simple 2D example

$\mathcal{L}$	0.0000	0.0102	0.0438	1.4579
$\widetilde{\mathcal{L}}$	0.0000	0.0123	0.0430	2.0676
Eff-MC	2.02×10^{-7}	0.0154	0.0444	2.3409

Table: First 4 eigenvalues.

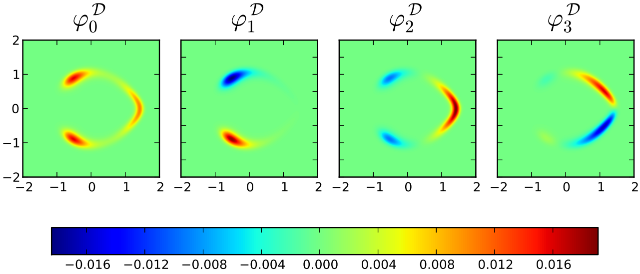


Figure: First 4 eigenfunctions of operator $e^{-\frac{\beta V}{2}}\mathcal{L}e^{\frac{\beta V}{2}}$.

Conclusions

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Related topics & future work :

1. How to choose reaction coordinate, basis functions
2. Langevin dynamics
3. Algorithms for simulating effective dynamics.

Thank you !