Mathematical analysis of accelerated dynamics techniques.

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Introduction

The aim of molecular dynamics simulations is to understand the relationships between the macroscopic properties of a molecular system and its atomistic features. In particular, one would like to to evaluate numerically macroscopic quantities from models at the microscopic scale.

Some examples of macroscopic quantities:

(i) Thermodynamics quantities (average of some observable wrt an equilibrium measure): stress, heat capacity, free energy,...

$$\mathbb{E}_\mu(\varphi(\boldsymbol{X})) = \int_{\mathbb{R}^d} \varphi(x)\,\mu(dx).$$

(ii) Dynamical quantities (average over trajectories at equilibrium): diffusion coefficients, viscosity, transition rates,...

$$\mathbb{E}(\mathcal{F}((\boldsymbol{X}_t)_{t\geq 0})) = \int_{\mathcal{C}^0(\mathbb{R}_+,\mathbb{R}^d)} \mathcal{F}((x_t)_{t\geq 0})\,\mathcal{W}(d((x_t)_{t\geq 0})).$$

Introduction

Many applications in various fields: biology, physics, chemistry, materials science. Molecular dynamics computations consume today a lot of CPU time.

A molecular dynamics model amounts essentially in choosing a potential V which associates to a configuration $(\mathbf{x}_1, ..., \mathbf{x}_N) = \mathbf{x} \in \mathbb{R}^{3N}$ an energy $V(\mathbf{x}_1, ..., \mathbf{x}_N)$.

In the canonical (NVT) ensemble, configurations are distributed according to the Boltzmann-Gibbs probability measure:

$$d\mu(\mathbf{x}) = Z^{-1} \exp(-\beta V(\mathbf{x}))\, d\mathbf{x},$$

where $Z = \int \exp(-\beta V(\mathbf{x}))\, d\mathbf{x}$ is the partition function and $\beta = (k_B T)^{-1}$ is proportional to the inverse of the temperature.

Introduction

Typically, V is a sum of potentials modelling interaction between two particles, three particles and four particles:

$$V = \sum_{i<j} V_1(\mathbf{x}_i, \mathbf{x}_j) + \sum_{i<j<k} V_2(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) + \sum_{i<j<k<l} V_3(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k, \mathbf{x}_l).$$

For example, $V_1(\mathbf{x}_i, \mathbf{x}_j) = V_{LJ}(|\mathbf{x}_i - \mathbf{x}_j|)$ where $V_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right)$ is the Lennard-Jones potential.

Difficulties: (i) high-dimensional problem ($N \gg 1$) ; (ii) μ is a multimodal measure.

Introduction

To sample μ, ergodic dynamics wrt to μ are used. A typical example is the *over-damped Langevin* (or gradient) dynamics:

$$d\boldsymbol{X}_t = -\nabla V(\boldsymbol{X}_t)\,dt + \sqrt{2\beta^{-1}}d\boldsymbol{W}_t.$$

It is the limit (when the mass goes to zero or the damping parameter to infinity) of the *Langevin dynamics*:

$$\begin{cases} d\boldsymbol{X}_t = M^{-1}\boldsymbol{P}_t\,dt, \\ d\boldsymbol{P}_t = -\nabla V(\boldsymbol{X}_t)\,dt - \gamma M^{-1}\boldsymbol{P}_t\,dt + \sqrt{2\gamma\beta^{-1}}d\boldsymbol{W}_t, \end{cases}$$

where M is the mass tensor and γ is the friction coefficient.

To compute dynamical quantities, these are also typically the dynamics of interest. Thus,

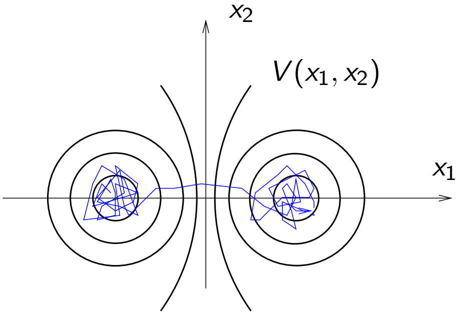
$$\mathbb{E}_\mu(\varphi(\boldsymbol{X})) \simeq \frac{1}{T}\int_0^T \varphi(\boldsymbol{X}_t)\,dt \text{ and } \mathbb{E}(\mathcal{F}((\boldsymbol{X}_t)_{t\geq 0})) \simeq \frac{1}{N}\sum_{m=1}^{N} \mathcal{F}((\boldsymbol{X}_t^m)_{t\geq 0}).$$

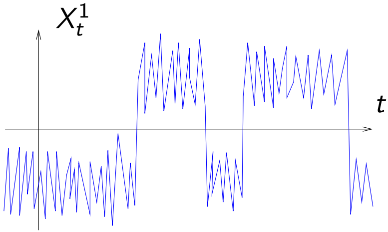
In the following, we mainly consider the over-damped Langevin dynamics.

Introduction: metastability

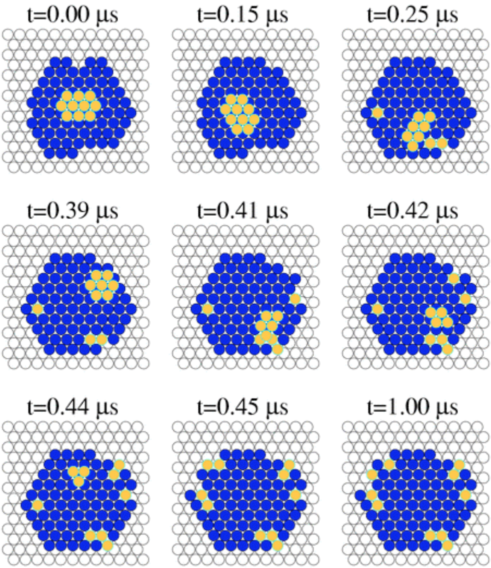
Difficulty: In practice, $\boldsymbol{X}_t$ is a metastable process, so that the convergence to equilibrium is very slow, and sampling metastable trajectories is very difficult.

A 2d schematic picture: X_t^1 is a slow variable (a metastable dof) of the system.





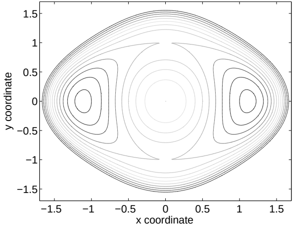
A "real" example: Diffusion of adatoms on a surface. *(A. Voter)*.

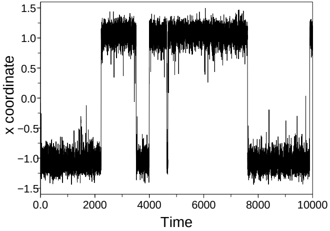


Introduction: metastability

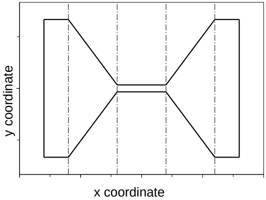
Where does metastability come from ?

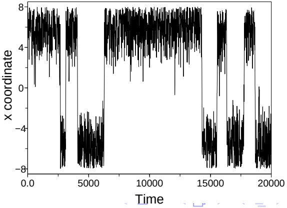
Energetic barrier:





Entropic barrier:





Introduction

For computing thermodynamics quantities, there is a clear classification of available methods, and the difficulties are now well understood (in particular for free energy computations, see for example the review [TL, Rousset, Stoltz, 2010]). On the opposite, computing efficiently dynamical quantities remains a challenge.

In practice, one is only interested in a reduced description of the original full dynamics $(\boldsymbol{X}_t)_{t \geq 0}$. In the following, we will focus on a coarse-graining procedure in a discrete state-space. One is given a continuous state to discrete state map

$$\mathcal{S} : \mathbb{R}^d \to \mathbb{N}$$

and the aim is to capture the dynamics of $(\mathcal{S}(\boldsymbol{X}_t))_{t \geq 0}$.

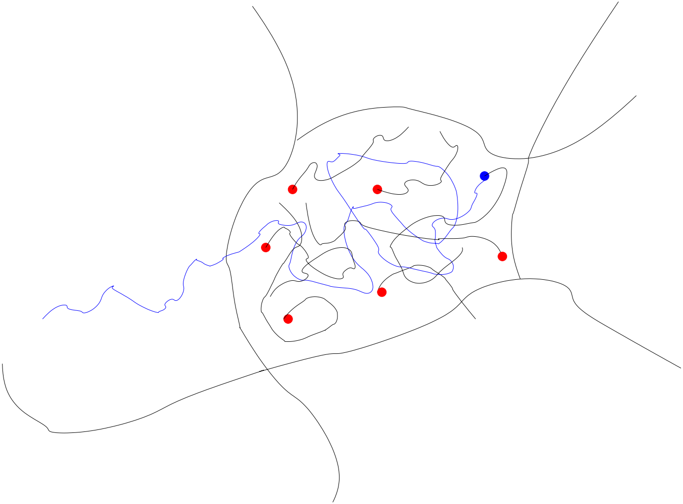
Outline

In the following, I will present the mathematical analysis of two algorithms which have been proposed by A. Voter to approximate $(\mathcal{S}(\boldsymbol{X}_t))_{t\geq 0}$:

1. the Parallel Replica dynamics,
2. and the Hyperdynamics.

There are many other techniques: temperature accelerated dynamics [Voter], the string method [E, Ren, Vanden-Eijnden], transition path sampling methods [Chandler, Bolhuis, Dellago], milestoning techniques [Elber, Schuette, Vanden-Eijnden], adaptive multilevel splitting techniques [Cérou, Guyader, Lelièvre Pommier], etc...

The Parallel Replica Algorithm



The Parallel Replica Algorithm

The Parallel Replica Algorithm, proposed by A.F. Voter in 1998, is a method to get efficiently a "coarse-grained projection" of a dynamics.

Let us consider the overdamped Langevin dyanmics:

$$d\boldsymbol{X}_t = -\nabla V(\boldsymbol{X}_t)\,dt + \sqrt{2\beta^{-1}}d\boldsymbol{W}_t$$

and let assume that we are given a smooth mapping

$$\mathcal{S} : \mathbb{R}^d \to \mathbb{N}$$

which to a configuration in $\mathbb{R}^d$ associates a state number. Think of a numbering of the wells of the potential V.

The aim of the parallel replica dynamics is to generate very efficiently a trajectory $(S_t)_{t\geq 0}$ which has (almost) the same law as $(\mathcal{S}(\boldsymbol{X}_t))_{t\geq 0}$.

The Parallel Replica Algorithm

Initialization: Consider an initial condition $\boldsymbol{X}_0^{ref}$ for a reference walker, the associated initial condition $S_0 = \mathcal{S}(\boldsymbol{X}_0^{ref})$, and a simulation time counter $T_{simu} = 0$.

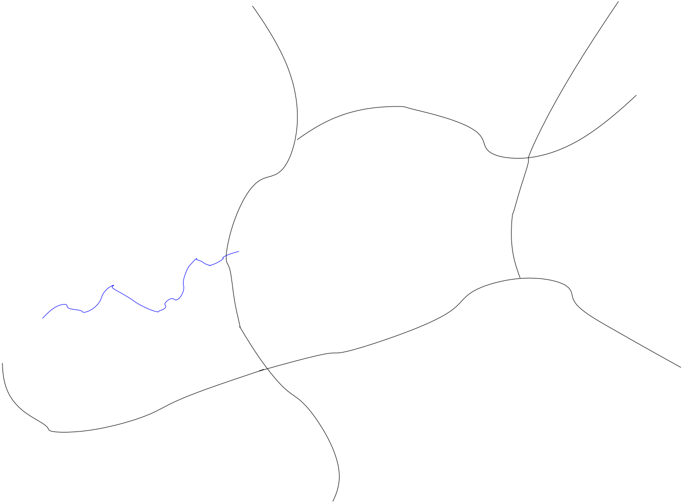
Then, one iteration of the algorithm goes through three steps.

- The decorrelation step: Let the reference walker $(\boldsymbol{X}_{T_{simu}+t}^{ref})_{t\geq 0}$ evolve over a time interval $t \in [0, \tau_{corr}]$. Then,
    - If the process leaves the well during the time interval (*i.e.* $\exists t \leq \tau_{corr}$ such that $\mathcal{S}\left(\boldsymbol{X}_{T_{simu}+t}^{ref}\right) \neq \mathcal{S}\left(\boldsymbol{X}_{T_{simu}}^{ref}\right)$) advance the simulation clock by τ_{corr} and restart the decorrelation step ;
    - otherwise, advance the simulation clock by τ_{corr} and proceed to the dephasing step.

  During all this step, $S_{T_{simu}+t} := \mathcal{S}\left(\boldsymbol{X}_{T_{simu}+t}^{ref}\right)$.

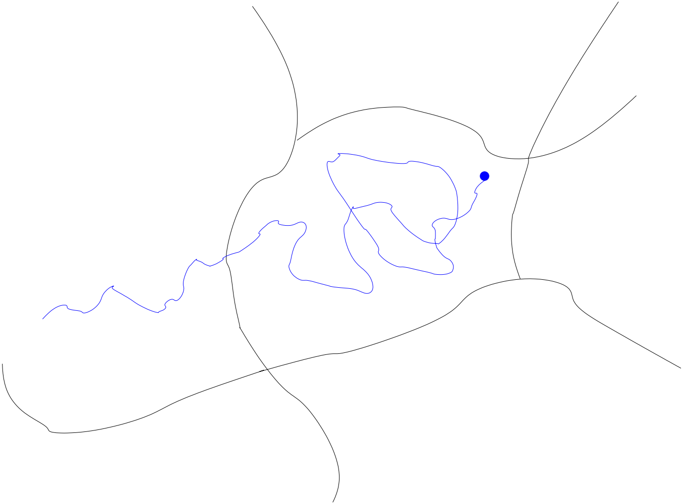
The Parallel Replica Algorithm

The reference walker enters a new state



The Parallel Replica Algorithm

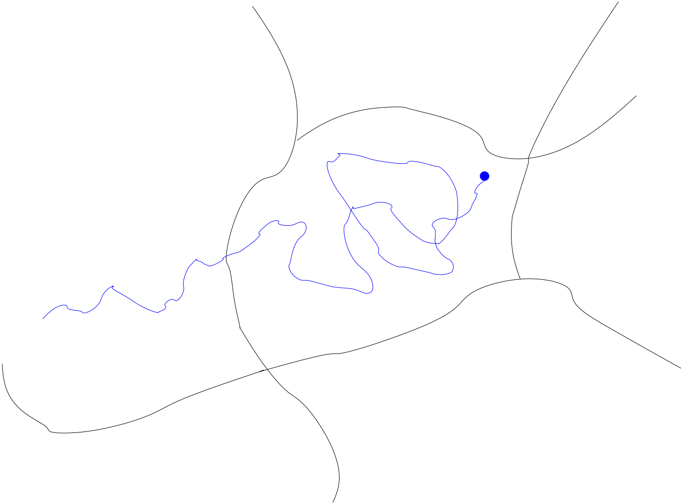
Decorrelation step: wait for a time τ_{corr}.



- The dephasing step: Duplicate the walker $\boldsymbol{X}^{ref}_{T_{simu}}$ into N replicas. Let these replicas evolve independently and in parallel over a time interval of length $\tau_{dephase}$. If a replica leaves the well during this time interval, restart the dephasing step for this replica. Throughout this step, the simulation counter is stopped.

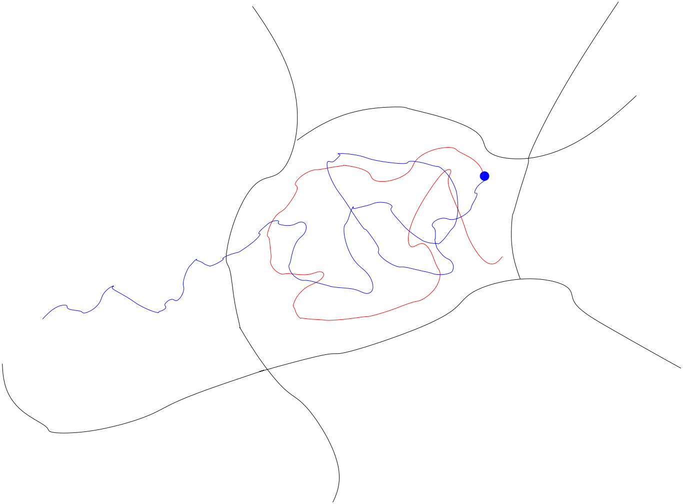
The Parallel Replica Algorithm

Dephasing step.



The Parallel Replica Algorithm

Dephasing step: generate new initial conditions in the state.



The Parallel Replica Algorithm

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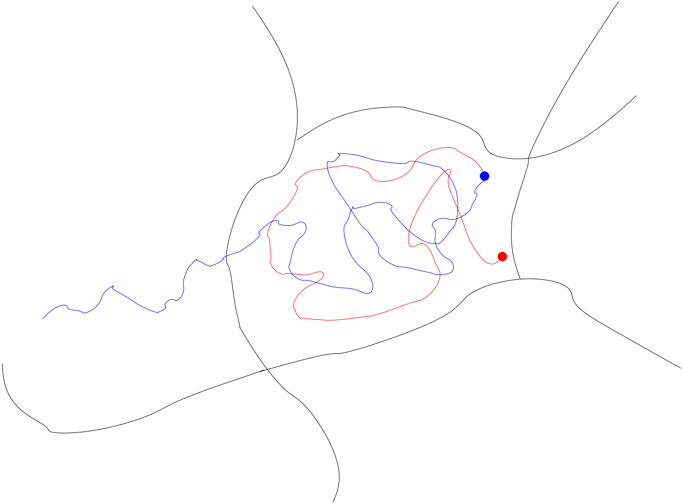

The Parallel Replica Algorithm

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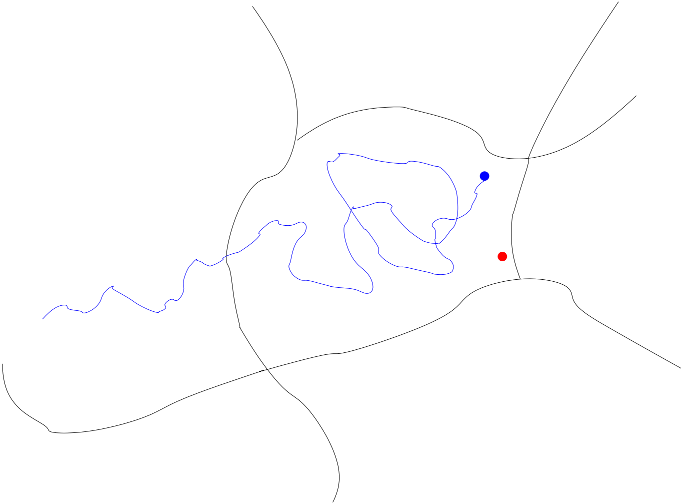
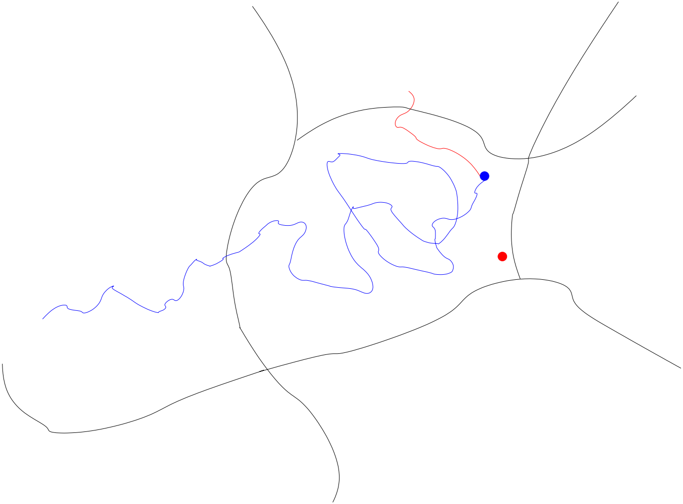


The Parallel Replica Algorithm

Dephasing step: generate new initial conditions in the state.



The Parallel Replica Algorithm

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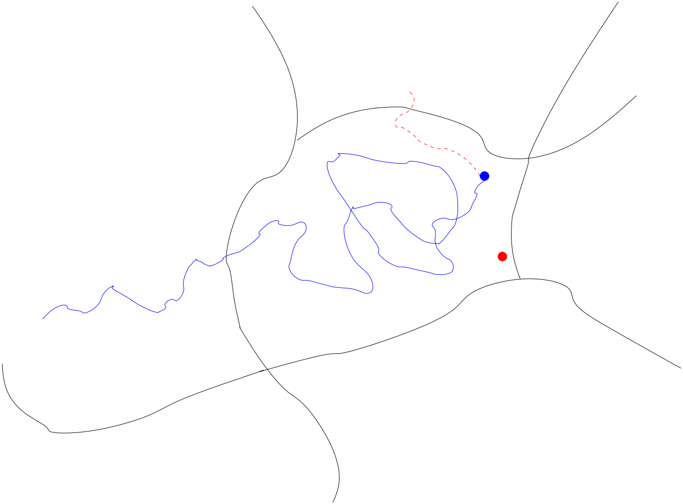
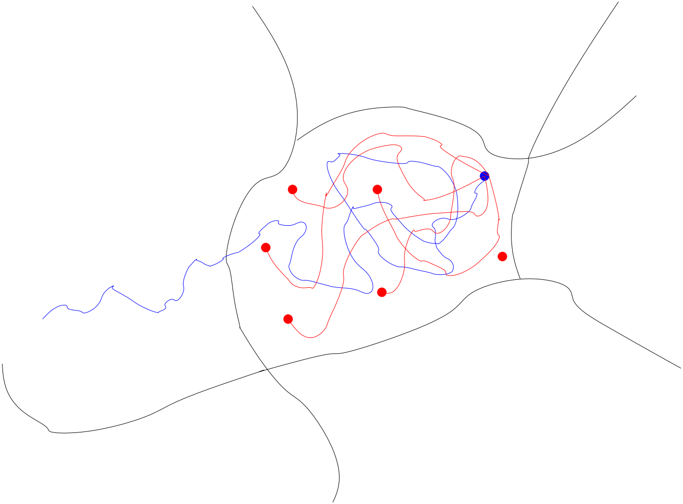


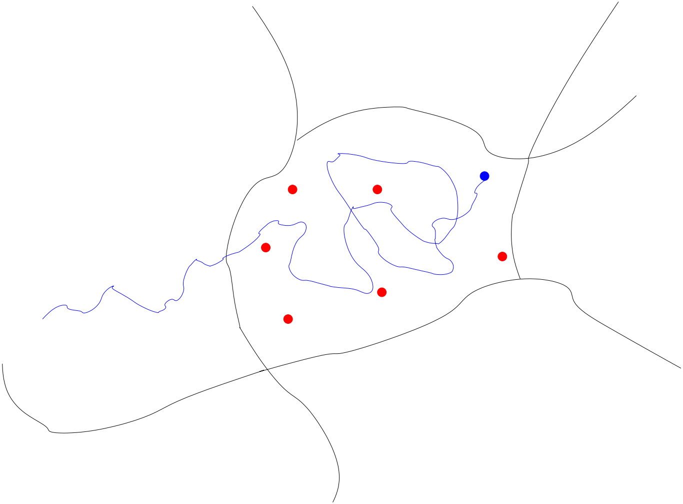
The Parallel Replica Algorithm

Dephasing step: generate new initial conditions in the state.



The Parallel Replica Algorithm

Dephasing step: generate new initial conditions in the state.



- The parallel step: Let all the replicas evolve independently and track the first escape event:

$$T = \inf_k T_W^k = T_W^{K_0}$$

where $K_0 = \arg\inf_k T_W^k$ and

$$T_W^k = \inf\{t \geq 0, \mathcal{S}(\boldsymbol{X}^k_{T_{simu}+t}) \neq \mathcal{S}(\boldsymbol{X}^k_{T_{simu}})\}$$

is the first time the k-th replica leaves the well. Then:

$$T_{simu} = T_{simu} + NT \text{ and } \boldsymbol{X}^{ref}_{T_{simu}+NT} = \boldsymbol{X}^{K_0}_{T_{simu}+T}.$$

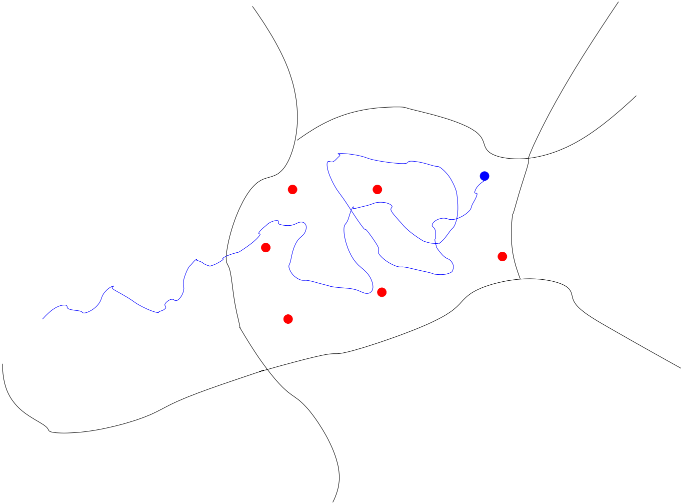
Moreover, over $[T_{simu}, T_{simu} + NT]$, the state dynamics S_t is constant and defined as:

$$S_t = \mathcal{S}(\boldsymbol{X}^1_{T_{simu}}).$$

Then, go back to the decorrelation step...

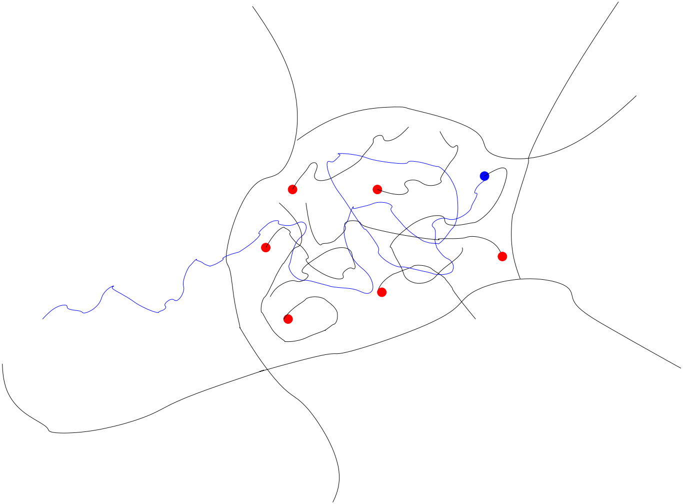
The Parallel Replica Algorithm

Parallel step.



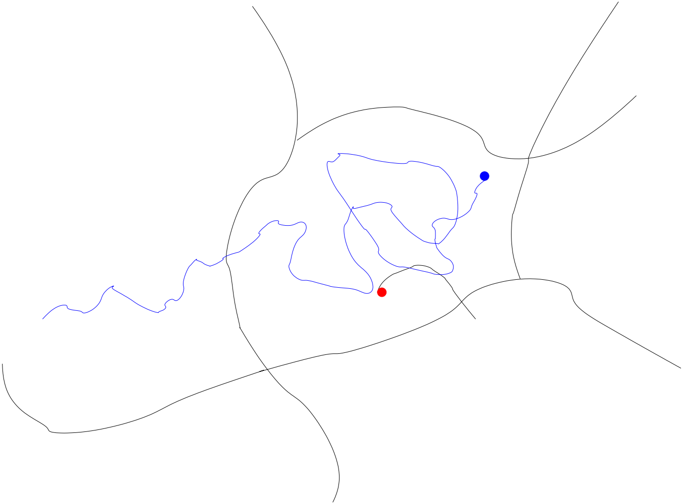
The Parallel Replica Algorithm

Parallel step: run independent trajectories in parallel...



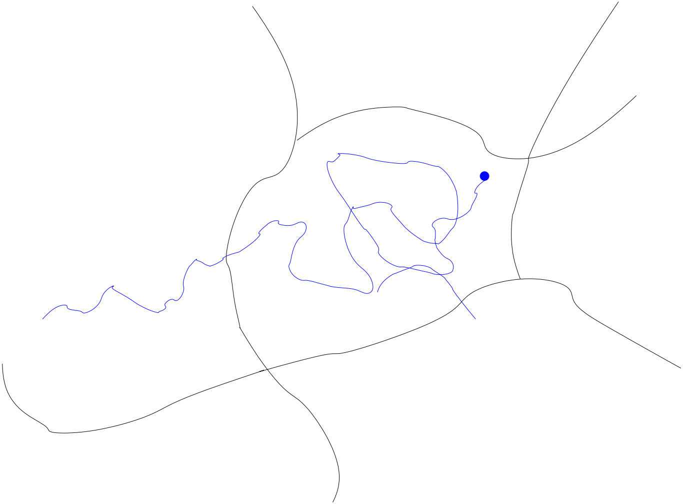
The Parallel Replica Algorithm

Parallel step: ... and detect the first transition event.



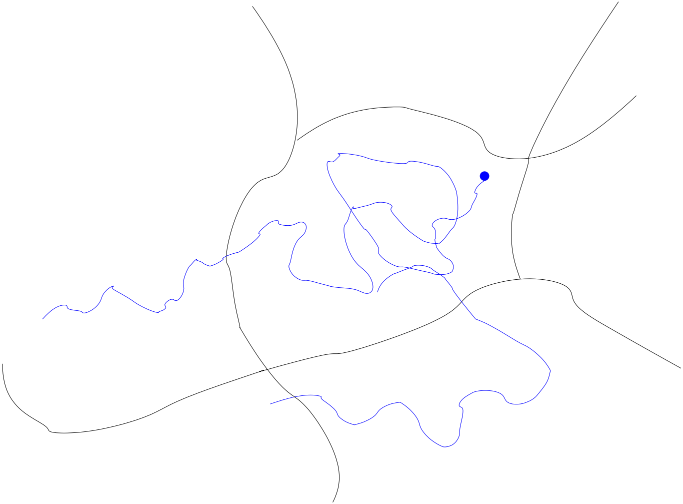
The Parallel Replica Algorithm

Parallel step: update the time clock: $T_{simu} = T_{simu} + NT$.



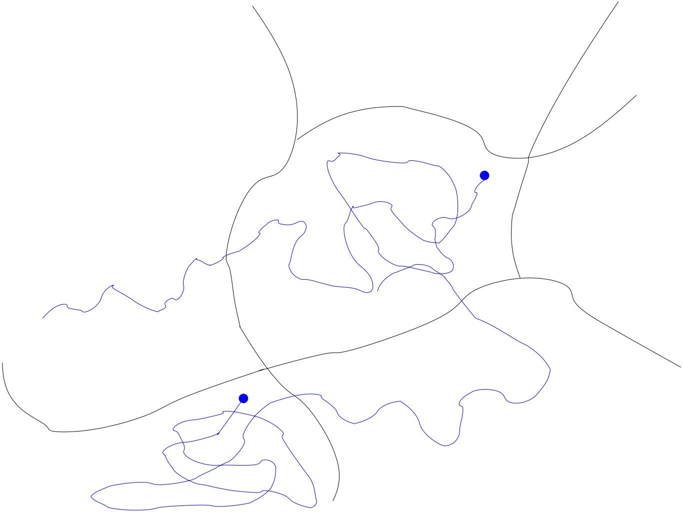
The Parallel Replica Algorithm

A new decorrelation step starts...



The Parallel Replica Algorithm

New decorrelation step



The Parallel Replica Algorithm

Analysis of the algorithm: the parallel step would introduce no error if

- the escape time T_W^1 was exponentially distributed
- and independent of the next visited state.

This essentially amounts to assuming that $\mathcal{S}(\boldsymbol{X}_t)$ is a Markov chain...

How to analyze the error introduced by the algorithm ?

This is related to the general question: how to relate a continuous state space Markov dynamics to a discrete state space Markov dynamics ? Pitfalls: (i) the temperature is not necessarily small (ii) the partition of the state space may be anything (iii) no thermodynamic limit in general (non-homogeneous systems).

The quasi-stationary distribution

The quasi-stationary distribution (QSD) ν for $\boldsymbol{X}_t$ and associated to the actual well W is a probability measure which is (i) supported by W and such that (ii): $\forall t > 0$, $\forall A \subset W$,

$$\nu(A) = \frac{\displaystyle\int_W \mathbb{P}(\boldsymbol{X}_t^{\boldsymbol{x}} \in A,\, t < T_W^{\boldsymbol{x}})\, \nu(d\boldsymbol{x})}{\displaystyle\int_W \mathbb{P}(t < T_W^{\boldsymbol{x}})\, \nu(d\boldsymbol{x})}.$$

If $\boldsymbol{X}_0 \sim \nu$ and if $(\boldsymbol{X}_s)_{0 \le s \le t}$ has not left the well, then $\boldsymbol{X}_t \sim \nu$.

Let $L = -\nabla V \cdot \nabla + \beta^{-1}\Delta$ be the infinitesimal generator of $(\boldsymbol{X}_t)$. Then the density u_1 of ν ($d\nu = u_1(\boldsymbol{x})d\boldsymbol{x}$) is the first eigenfunction of $L^* = \mathrm{div}\,(\nabla V + \beta^{-1}\nabla)$ with absorbing boundary conditions:

$$\begin{cases} L^* u_1 = -\lambda_1 u_1 \text{ on } W, \\ \quad u_1 = 0 \text{ on } \partial W. \end{cases}$$

The quasi-stationary distribution and the dephasing step

Property of the QSD: If $\boldsymbol{X}_0 \sim \nu$ then, the first exit time T_W from W is exponentially distributed with parameter λ_1 and is a random variable independent of the first hitting point $\boldsymbol{X}_{T_W}$ on ∂W.

The dephasing step is very much related to the so-called Fleming-Viot process and may be seen as a way to get N i.i.d. random variables distributed according to the QSD.

Remark: In general, T_W exponentially distribtued is *not* sufficient for $\boldsymbol{X}_0$ to be distributed according to ν.

The parallel step

As announced above, starting from the QSD, the parallel step is exact. This is stated precisely here.

Let us start from N initial conditions $\boldsymbol{X}_0^k$ i.i.d. in the well W and let the processes evolve independently. Let us denote

$$T_W^k = \inf\{t > 0, \boldsymbol{X}_t^k \notin W\}$$

the escape time for the k-th replica, and

$$T = T_W^{K_0} \text{ where } K_0 = \arg \min_{k \in \{1,\ldots,N\}} T_W^k$$

the *first* escape time over all processes.

- Assume that T_W^1 is exponentially distributed [OK starting from QSD.] Then NT has the same law as T_W^1.
- Assume that T_W^1 is independent of $\boldsymbol{X}_{T_W^1}^1$ [OK starting from QSD.] Then $\boldsymbol{X}_{T_W^{K_0}}^{K_0}$ has the same distribution as $\boldsymbol{X}_{T_W^1}^1$ and is independent of $T_W^{K_0}$.

The decorrelation step

We would like to quantify the error introduced by the dephasing and parallel steps, when the decorrelation step is successful.

As shown above, when the decorrelation step is successful, it is assumed that the reference walker is distributed according to the QSD. If it was indeed the case, the algorithm would be exact. The decorrelation step can be seen as a way to probe this assumption. What is the error introduced there ?

The decorrelation step

We have the following error estimate in total variation norm: for $t \geq \frac{C}{\lambda_2 - \lambda_1}$,

$$\sup_{f, \|f\|_{L^\infty} \leq 1} \left| \mathbb{E}(f(T_W - t, \boldsymbol{X}_{T_W}) | T_W \geq t) - \mathbb{E}^{\nu}(f(T_W, \boldsymbol{X}_{T_W})) \right| \leq C \exp(-(\lambda_2 - \lambda_1) t),$$

where $-\lambda_2 < -\lambda_1 < 0$ are the two first eigenvalues of L^* with absorbing boundary conditions on ∂W.

This shows that τ_{corr} should be chosen such that:

$$\tau_{corr} \geq \frac{\overline{C}}{\lambda_2 - \lambda_1}.$$

The Parallel Replica Algorithm: conclusions

Metastable well: For the system to have a chance to enter the parallel step, τ_{corr} should be smaller than the typical time to leave the well, $\mathbb{E}(T_W)$. Since $\mathbb{E}^{\nu}(T_W) = 1/\lambda_1$, this typically implies the spectral gap requirement,

$$\frac{\overline{C}}{\lambda_2 - \lambda_1} \leq \frac{1}{\lambda_1}.$$

Parallel efficiency: Recall that

- The time to dephase (pure overhead) is about $\frac{1}{\lambda_2 - \lambda_1}$;
- the duration of the parallel step is about $\frac{1}{N\lambda_1}$.

If we equal these two times, we get

$$N \simeq \frac{\lambda_2 - \lambda_1}{\lambda_1}.$$

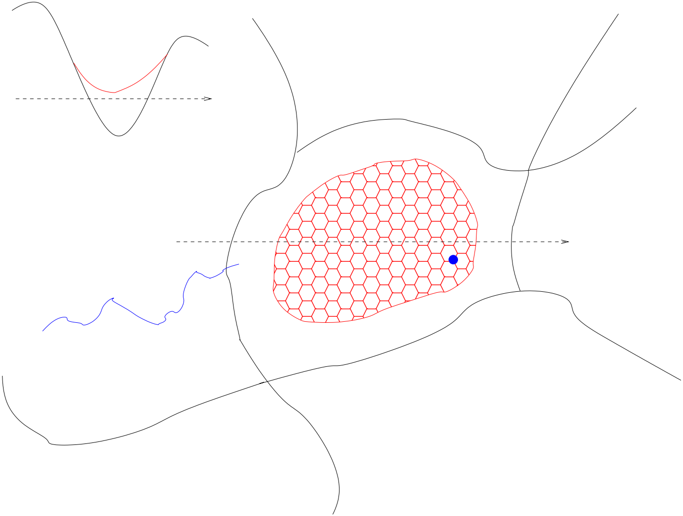
The Parallel Replica Algorithm: conclusions

This algorithm and analysis can be generalized to other dynamics (coarse-graining of kMC for example).

Main results:

- The QSD is a good intermediate between continuous state dynamics and kMC-like approximations.
- The error analysis holds whatever the partition. But the method requires metastability between the states to be computationally efficient.
- The parameter τ_{corr} should be adjusted in terms of the two first eigenvalues of the Fokker-Planck operator with absorbing boundary conditions.

The Hyperdynamics



The Hyperdynamics

The Hyperdynamics, proposed by A.F. Voter in 1997, is again a method to get efficiently a "coarse-grained projection" of a dynamics.
Let us consider again the overdamped Langevin dyanmics:

$$d\boldsymbol{X}_t = -\nabla V(\boldsymbol{X}_t)\,dt + \sqrt{2\beta^{-1}}d\boldsymbol{W}_t.$$

Recall we are given the smooth mapping

$$\mathcal{S} : \mathbb{R}^d \to \mathbb{N}$$

which to a configuration in $\mathbb{R}^d$ associates a state number.

The aim of the hyperdynamics is again to generate very efficiently a trajectory $(S_t)_{t\geq 0}$ which has (almost) the same law as $(\mathcal{S}(\boldsymbol{X}_t))_{t\geq 0}$.

Compared to the parallel replica algorithm, we will need an additional assumption: small temperature regime.

The Hyperdynamics: algorithm

Initialization: Consider an initial condition $\boldsymbol{X}_0$, the associated initial condition $S_0 = \mathcal{S}(\boldsymbol{X}_0)$, and a simulation time counter $T_{simu} = 0$.

Then, one iteration of the algorithm goes again through three steps.

- The decorrelation step: Let the walker $(\boldsymbol{X}_{T_{simu}+t})_{t \geq 0}$ evolve over a time interval $t \in [0, \tau_{corr}]$. Then,
  - If the process leaves the well during the time interval (*i.e.* $\exists t \leq \tau_{corr}$ such that $\mathcal{S}\left(\boldsymbol{X}_{T_{simu}+t}\right) \neq \mathcal{S}\left(\boldsymbol{X}_{T_{simu}}\right)$) advance the simulation clock by τ_{corr} and restart the decorrelation step ;
  - otherwise, advance the simulation clock by τ_{corr} and proceed to the dephasing step.

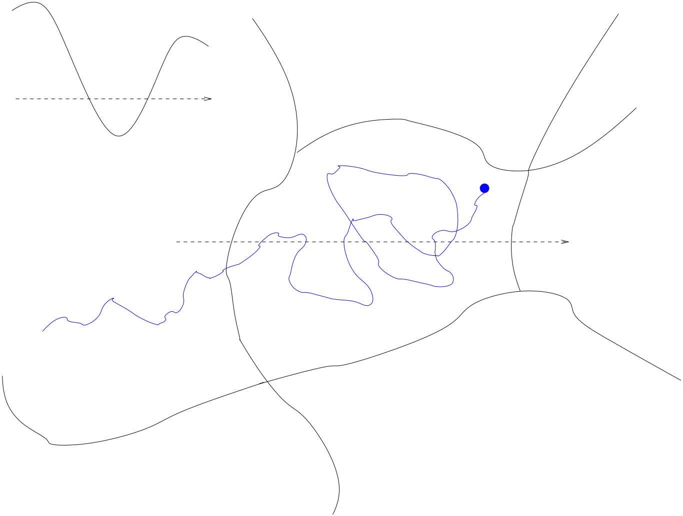
  During all this step, $S_{T_{simu}+t} := \mathcal{S}\left(\boldsymbol{X}_{T_{simu}+t}\right)$.

The Hyperdynamics

The process enters a new state

The Hyperdynamics

Decorrelation step: wait for a time τ_{corr}.



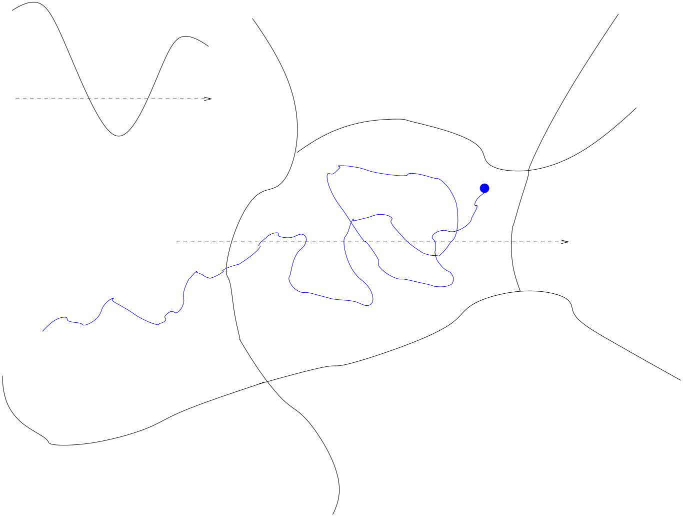
- The preparation step: Introduce a non-negative bias δV in the well, and let the process equilibrate on the biased potential $V+\delta V$, following the dynamics:

$$d\boldsymbol{X}_t = -\nabla(V+\delta V)(\boldsymbol{X}_t)\,dt + \sqrt{2\beta^{-1}}d\boldsymbol{W}_t.$$

If the process leaves the well, restart from one of the points along the trajectory in the well. Throughout this step, the simulation counter is stopped.

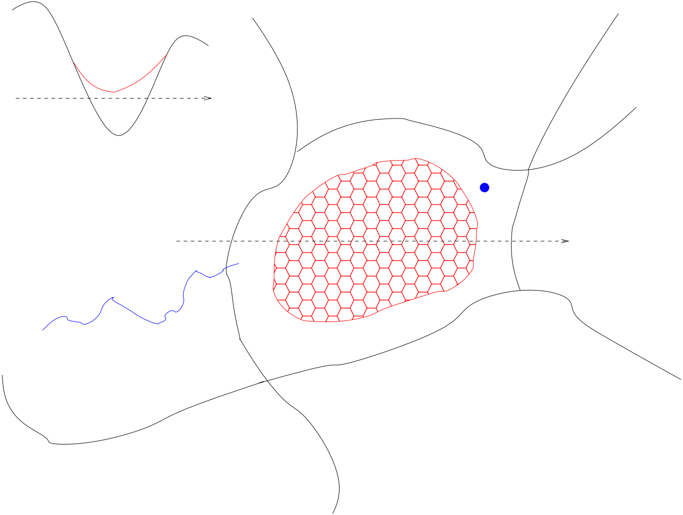
The Hyperdynamics

Preparation step.



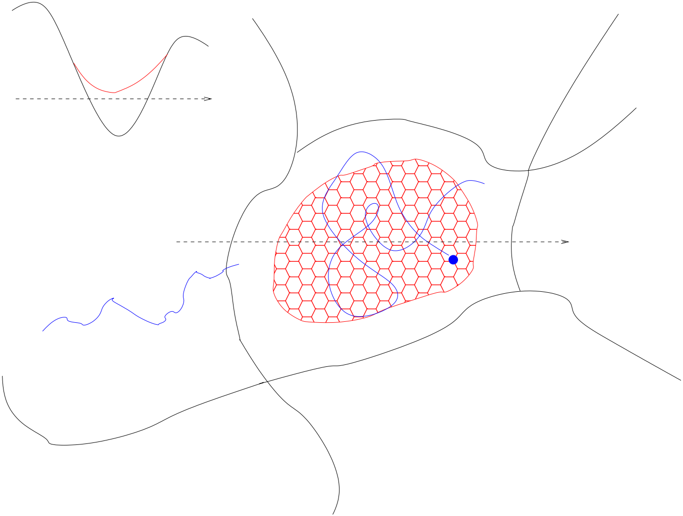
The Hyperdynamics

Preparation step: turn on the biased potential.



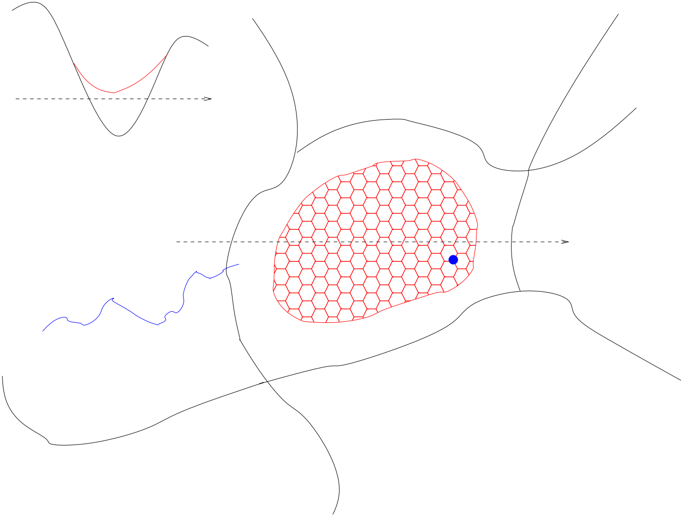
The Hyperdynamics

Preparation step: equilibrate on the biased potential.



The Hyperdynamics

Preparation step: equilibrate on the biased potential.



- Hyperdynamics step: Let the system evolve on the biased potential:

$$d\boldsymbol{X}_t = -\nabla(V + \delta V)(\boldsymbol{X}_t)\, dt + \sqrt{2\beta^{-1}} d\boldsymbol{W}_t.$$

When it leaves, consider the exit point as the new initial condition for the next decorrelation step and advance the simulation clock by the hypertime

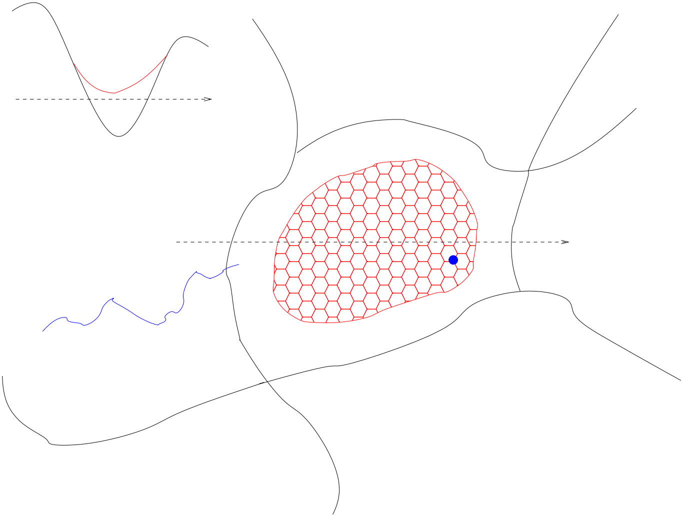
$$\delta T_{simu} = \int_0^{T_W^{\delta V}} \exp(\beta\, \delta V(\boldsymbol{X}_t))\, dt$$

where $T_W^{\delta V}$ is the first exit time on the biased potential. Over $[T_{simu}, T_{simu} + \delta T_{simu}]$, the state dynamics S_t is constant:

$$S_t = \mathcal{S}(\boldsymbol{X}_{T_{simu}}).$$

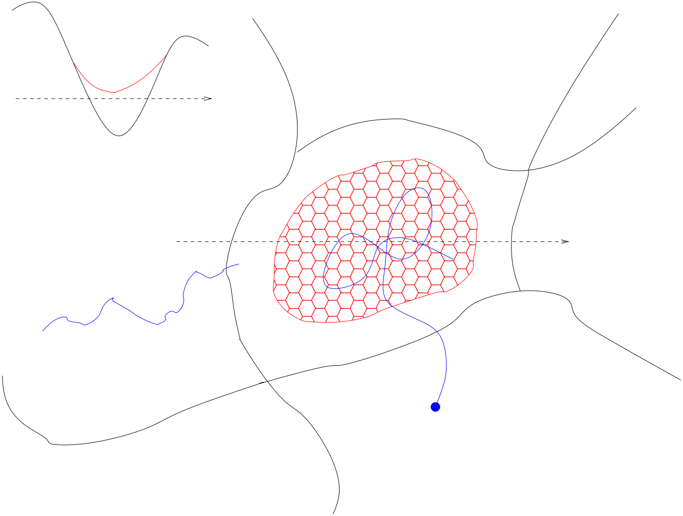
The Hyperdynamics

The Hyperdynamics step.



The Hyperdynamics

The Hyperdynamics step: wait for an escape event on the biased potential.



The Hyperdynamics: algorithm

Remarks:

- In practice, the decorrelation step and the preparation step are not performed: immediate equilibration within the well is assumed (also called *no-recrossing assumption*).
- The original derivation of the algorithm is based on the transition state theory, and requires some assumption on δV. In particular, $\delta V = 0$ on the dividing surfaces.
- The boost factor is $B = \dfrac{\delta T_{simu}}{T_W^{\delta V}}$. It may be in practice of the order of a few thousands.
- Finding a bias potential which yields a large boost without biasing the state to state dynamics remains a challenge [Voter / Miron, Fichthorn / Kim, Falk / ...].

The Hyperdynamics: mathematical analysis

Here is one way to analyze the hyperdynamics.

After the decorrelation step, $\boldsymbol{X}_t$ is approximately distributed according to the QSD ν in the well W, associated to the potential V.

After the preparation step, $\boldsymbol{X}_t$ is approximately distributed according to the QSD $\nu^{\delta V}$ in the well W, associated to the potential $(V + \delta V)$.

The Hyperdynamics: mathematical analysis

We thus have two processes to compare:

$$\begin{cases} \boldsymbol{X}_0 \sim \nu, \\ d\boldsymbol{X}_t = -\nabla V(\boldsymbol{X}_t)\, dt + \sqrt{2\beta^{-1}} d\boldsymbol{W}_t, \end{cases}$$

with exit time $T_W = \inf\{t > 0, \boldsymbol{X}_t \notin W\}$, and

$$\begin{cases} \boldsymbol{X}_0^{\delta V} \sim \nu^{\delta V}, \\ d\boldsymbol{X}_t^{\delta V} = -\nabla (V + \delta V)(\boldsymbol{X}_t^{\delta V})\, dt + \sqrt{2\beta^{-1}} d\boldsymbol{W}_t, \end{cases}$$

with exit time $T_W^{\delta V} = \inf\{t > 0, \boldsymbol{X}_t^{\delta V} \notin W\}$.

The Hyperdynamics: mathematical analysis

Question:
Do we have (approximately) $(T_W, \boldsymbol{X}_{T_W}) \stackrel{\mathcal{L}}{=} (B T_W^{\delta V}, \boldsymbol{X}^{\delta V}_{T_W})$ where

$$B = \frac{\delta T_{simu}}{T_W^{\delta V}} = \frac{1}{T_W^{\delta V}} \int_0^{T_W^{\delta V}} \exp(\beta\, \delta V(\boldsymbol{X}_t))\, dt.$$

is the boost factor ?

The Hyperdynamics: mathematical analysis

Recall that starting from the QSD ν,

- T_W and $\boldsymbol{X}_{T_W}$ are independent,
- $T_W \sim \mathcal{E}(\lambda_1)$,
- and $\boldsymbol{X}_{T_W} \sim -\frac{1}{\beta\lambda_1}\frac{\partial u_1}{\partial n} d\sigma_{\partial W}$

where $d\nu = u_1(\boldsymbol{x})d\boldsymbol{x}$ with

$$\begin{cases} L^* u_1 = -\lambda_1 u_1 \text{ on } W, \\ \quad u_1 = 0 \text{ on } \partial W, \end{cases}$$

$L = -\nabla V \cdot \nabla + \beta^{-1}\Delta$ being the infinitesimal generator of $(\boldsymbol{X}_t)$ (and $L^* = \mathrm{div}\,(\nabla V + \beta^{-1}\nabla)$).

We thus need to understand how λ_1 and $\left.\frac{\partial u_1}{\partial n}\right|_{\partial W}$ are modified when V is changed to $(V + \delta V)$?

The Hyperdynamics: mathematical analysis

Assumptions on V. We assume there exists $W^- \subset\subset W$ such that

- V, $V|_{\partial W^-}$ and $V_{\partial W}$ are Morse functions ;
- $|\nabla V| \neq 0$ in $\overline{W} \setminus W^-$ and $\frac{\partial V}{\partial n} > 0$ on ∂W and ∂W^- ;
- $\{x \in W^-, |\nabla V|(x) = 0\} \subset \{x \in W^-, V(x) < \min_{\partial W} V - c_0\}$ for a positive c_0.
- The critical values of V in W^- are all distinct and the differences $V(y) - V(x)$, where $x \in \mathcal{U}^{(0)}$ ranges over the local minima of $V|_{W^-}$ and $y \in \mathcal{U}^{(1)}$ ranges over the critical points of $V|_{W^-}$ with index 1, are all distinct.
- Let us introduce d_{Ag} the Agmon distance in W^-:

$$d_{Ag}(x, y) = \inf_{\gamma, \gamma(0)=x, \gamma(1)=y} \int_0^1 |\nabla V(\gamma(t)||\dot{\gamma}|(t)\, dt.$$

We assume that:

$$d_{Ag}(\partial W^-, \mathcal{U}^{(0)}) > \max_{y \in \mathcal{U}^{(1)}, x \in \mathcal{U}^{(0)}} (V(y) - V(x)).$$

The Hyperdynamics: mathematical analysis

Assumptions on δV.

- $(V + \delta V)$ also satisfy all the assumptions above, for the same subset $W^- \subset\subset W$.
- $\delta V = 0$ on $W \setminus W^-$

The Hyperdynamics: mathematical analysis

Result: Under the above assumptions on the potentials V and $(V + \delta V)$, there exists $c > 0$ such that:

$$\frac{\lambda_1(V+\delta V)}{\lambda_1(V)} = \frac{\int_W e^{-\beta V}}{\int_W e^{-\beta(V+\delta V)}}(1+\mathcal{O}(e^{-\beta c})),$$

$$\frac{\partial_n [u_1(V+\delta V)]\big|_{\partial W}}{\|\partial_n [u_1(V+\delta V)]\|_{L^1(\partial W)}} = \frac{\partial_n [u_1(V)]\big|_{\partial W}}{\|\partial_n [u_1(V)]\|_{L^1(\partial W)}} + \mathcal{O}(e^{-\beta c}) \quad \text{in} \quad L^1(\partial W).$$

Side result: We also obtain the following estimates:

$$\lambda_1(V) = \frac{\int_{\partial W} 2\partial_n V\, e^{-\beta V}\, d\sigma_{\partial W}}{\int_W e^{-\beta V}}(1+\mathcal{O}(\beta^{-1})),$$

$$\frac{\partial_n [u_1(V)]\big|_{\partial W}}{\|\partial_n [u_1(V)]\|_{L^1(\partial W)}} = -\frac{(\partial_n V)e^{-\beta V}\big|_{\partial W}}{\|(\partial_n V)e^{-\beta V}\|_{L^1(\partial W)}} + \mathcal{O}(\beta^{-1}) \quad \text{in } L^1(\partial W).$$

The Hyperdynamics: mathematical analysis

Computation of the boost factor : Our result says that the boost factor shoud be $\frac{\int_W \exp(-\beta V)}{\int_W \exp(-\beta(V+\delta V))}$.

This is related to the original defintion of the boost factor under an "ergodicity assumption" ($T_W^{\delta V}$ is large):

$$
\begin{aligned}
B &= \frac{\delta T_{simu}}{T_W^{\delta V}} \\
&= \frac{1}{T_W^{\delta V}} \int_0^{T_W^{\delta V}} \exp(\beta\,\delta V(\boldsymbol{X}_t))\,dt. \\
&\simeq \frac{\int_W \exp(\beta\delta V)\exp(-\beta(V+\delta V))}{\int_W \exp(-\beta(V+\delta V))} \\
&= \frac{\int_W \exp(-\beta V)}{\int_W \exp(-\beta(V+\delta V))}.
\end{aligned}
$$

Is there a better way to compute the boost factor (ratio of partition functions) ?

References

- T. Lelièvre, M. Rousset and G. Stoltz, *Free energy computations, a mathematical perspective*, Imperial College Press, 2010.
- C. Le Bris, T. Lelièvre, M. Luskin and D. Perez, *A mathematical formalization of the parallel replica dynamics*, Monte Carlo Methods and Applications, 18(2), 119-146, (2012).
- T. Lelièvre and F. Nier,*Accurate exit law for reversible Brownian motion*, in preparation.