

Some nonlinear stochastic dynamics for computational statistical physics

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Description of a classical system

- Positions q (configuration), momenta $p = M\dot{q}$ (M diagonal mass matrix)
- **Microscopic** description of a classical system (N particles):

$$(q, p) = (q_1, \dots, q_N, p_1, \dots, p_N) \in \mathcal{E}$$

- For instance, $\mathcal{E} = T^*\mathcal{D} = \mathcal{D} \times \mathbb{R}^{3N}$ with $\mathcal{D} = \mathbb{R}^{3N}$ or \mathbb{T}^{3N}
- More complicated situations can be considered... (constraints defining submanifolds of the phase space)
- **Hamiltonian**

$$H(q, p) = \sum_{i=1}^N \frac{p_i^2}{2m_i} + V(q_1, \dots, q_N)$$

- All the physics is contained in V
- For instance, pair interactions $V(q_1, \dots, q_N) = \sum_{1 \leq i < j \leq N} v(|q_j - q_i|)$

- Given the structure and the laws of interaction of the particles, what are the **macroscopic properties** of the matter composed of these particles?
- Equilibrium thermodynamic properties (pressure, . . .):

$$\langle A \rangle = \int_{T^* \mathcal{D}} A(q, p) \mu(dq dp)$$

- Choice of **thermodynamic ensemble** (probability measure $d\mu$):
constrained maximisation of entropy

$$S(\rho) = -k_B \int \rho \ln \rho,$$

under the constraints $\rho \geq 0$, $\int \rho = 1$, $\int A_i \rho = \mathcal{A}_i$

- The choice of the variables and the observables A_i ($1 \leq i \leq m$) determines the ensemble

Some examples: NVT, NPT ensembles

- **Canonical** ensemble = measure on (q, p) , **average energy** fixed $A_0 = H$

$$\mu_{\text{NVT}}(dq dp) = Z_{\text{NVT}}^{-1} e^{-\beta H(q,p)} dq dp,$$

where β is the Lagrange multiplier associated with the constraint

$$\int_{T^*\mathcal{D}} H(q, p) \rho(q, p) dq dp = E_0$$

- **NPT** ensemble = measure on (q, p, x) , where x indexes volume changes (for a **fixed geometry**). For instance, $\mathcal{D} = \left((1+x)L\mathbb{T} \right)^{3N}$

- Average energy and **average volume** $\int \text{Vol}(x) \rho(dq dp dx)$ fixed

- Denoting by βP (pressure) the Lagrange multiplier of the volume constraint,

$$\mu_{\text{NPT}}(dx dq dp) = Z_{\text{NPT}}^{-1} e^{-\beta P \text{Vol}(x)} e^{-\beta H(q,p)} \mathbf{1}_{\{q \in [L(1+x)\mathbb{T}]^{3N}\}} dx dq dp$$

- SDE on the **configurational** part only (momenta trivial to sample)

$$dq_t = -\nabla V(q_t) dt + \sigma dW_t,$$

where $(W_t)_{t \geq 0}$ is a standard Wiener process of dimension dN

- **Invariance of the canonical measure**

$$\nu(dq) = Z^{-1} e^{-\beta V(q)} dq, \quad Z = \int_{\mathcal{M}} e^{-\beta V(q)} dq$$

if steady state of Fokker-Planck equation $\partial_t \psi_t = \text{div} \left(\nabla V \psi_t + \frac{\sigma^2}{2} \nabla \psi_t \right)$

- Fluctuation/dissipation relation $\sigma = \sqrt{\frac{2}{\beta}}$
- Invariance + **irreducibility** (elliptic process):

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(q_t) dt = \int_{\mathcal{D}} A(q) d\nu \quad \text{a.s.}$$

Satisfying constraints in average

Formulation of the problem

- Set some **external parameter** (temperature, pressure/volume) to obtain the **right value** of a given thermodynamic property
- For instance, vary the **temperature** in the **canonical** ensemble
- Given some observable A , the problem then reads

Find T such that $\langle A \rangle_T = 0$,

- Since the momenta are straightforward to sample, there is no restriction in considering $A \equiv A(q)$
- In this case,

$$f(T) = \langle A \rangle_T = \int_{\mathcal{D}} A(q) \mu_T(dq),$$

$$\mu_T(q) = \frac{1}{Z_T} \exp\left(-\frac{V(q)}{k_B T}\right), \quad Z_T = \int_{\mathcal{D}} \exp\left(-\frac{V(q)}{k_B T}\right) dq,$$

Physical motivation: Computation of the Hugoniot curve

- Hugoniot curve = all **admissible shocks** $\mathcal{E} - \mathcal{E}_0 - \frac{1}{2}(\mathcal{P} + \mathcal{P}_0)(\mathcal{V}_0 - \mathcal{V}) = 0$
- Statistical physics reformulation?
- Reference temperature T_0 , simulation cell $\mathcal{D}_c = \left((1+c)L\mathbb{T} \times (L\mathbb{T})^2 \right)^N$
with $c = 0$ at the pole \rightarrow **vary the compression rate** $c = \frac{|\mathcal{D}|}{|\mathcal{D}_0|}$
- Consider the observable

$$A_c(q, p) = H(q, p) - \langle H \rangle_{|\mathcal{D}_0|, T_0} + \frac{1}{2} (P_{xx}(q, p) + \langle P \rangle_{|\mathcal{D}_0|, T_0}) (1-c) |\mathcal{D}_0|$$

where $P_{xx}(q, p) = \frac{1}{|\mathcal{D}|} \sum_{i=1}^N \frac{p_{i,x}^2}{m_i} - q_{i,x} \partial_{q_{i,x}} V(q)$

- For a **given compression** $c_{\max} \leq c \leq 1$, **find** $T \equiv T(c)$ such that

$$\langle A_c \rangle_{|\mathcal{D}_c|, T} = 0$$

Possible strategies

- **Finding a zero** of the function $f(T) = \langle A \rangle_T \dots$ Several methods!
- Assume that there exists an interval $I_T^A = [T_{\min}^A, T_{\max}^A]$, a temperature $T^* \in (T_{\min}^A, T_{\max}^A)$, and constants $a, \alpha > 0$ such that

$$\forall T \in I_T^A, \quad \langle A \rangle_T - \langle A \rangle_{T^*} \leq \frac{\alpha (T - T^*)}{T - T^*} \leq a$$

- **Newton strategy**: requires the computation of the derivative, either through $f'(T) \propto \langle AH \rangle_T - \langle A \rangle_T \langle H \rangle_T$, or through finite differences.
Difficult to converge in both cases
- **New thermodynamic ensemble** = (**unknown**) ergodic limit of dynamics such as

$$\begin{cases} \dot{q} &= M^{-1}p \\ \dot{p} &= -\nabla V(q) - \xi p \\ \dot{\xi} &= \nu^2 \frac{A(q, p)}{A_{\text{ref}}} \end{cases}$$

- Notice that the (deterministic) dynamics $T'(t) = -\gamma \langle A \rangle_{T(t)}$ is such that $T(t) \rightarrow T^*$
- On the other hand, the dynamics

$$dq_t = -\nabla V(q_t) dt + \sqrt{2k_B T} dW_t$$

is ergodic for the canonical measure $\mu_T(q) dq = Z^{-1} \exp\left(-\frac{V(q)}{k_B T}\right)$

- Approximate the equilibrium canonical expectation by the current one:

$$\begin{cases} dq_t &= -\nabla V(q_t) dt + \sqrt{2k_B T(t)} dW_t, \\ T'(t) &= -\gamma \mathbb{E}(A(q_t)), \end{cases}$$

- Notice that (T^*, μ_{T^*}) is invariant
- Extensions possible: $T'(t) = -\gamma(t) f\left(\mathbb{E}(A(q_t))\right)$ with $\gamma(t) > 0$

- **Nonlinear PDE** on the law ψ_t of the process q_t

$$\begin{cases} \partial_t \psi &= k_B T(t) \nabla \cdot \left[\mu_{T(t)} \nabla \left(\frac{\psi}{\mu_{T(t)}} \right) \right] = k_B T(t) \Delta \psi + \nabla \cdot (\psi \nabla V), \\ T'(t) &= -\gamma \int_{\mathcal{D}} A(q) \psi(t, q) dq \end{cases} \quad (1)$$

Theorem 1 (Short time existence/uniqueness) *Assume that the observable $A \in C^3(\mathcal{D})$ and $V \in C^2(\mathcal{D})$. For a given initial condition (T^0, ψ^0) , with $T^0 > 0$ and $\psi^0 \in H^2(\mathcal{D})$, $\psi^0 \geq 0$, $\int_{\mathcal{D}} \psi^0 = 1$, there exists a time $\tau \geq \frac{T^0}{2\gamma \|A\|_\infty} > 0$ such that (1) has a **unique solution** $(T, \psi) \in C^1([0, \tau], \mathbb{R}) \times C^0([0, \tau], H^2(\mathcal{D}))$.*

- In particular, the **temperature remains positive**
- Proof = Schauder fixed-point theorem using a mapping $T \mapsto \psi_T \mapsto g(T)$

- Convergence results for initial conditions close to the fixed-point
- **Total entropy** $\mathcal{E}(t) = E(t) + \frac{1}{2}(T(t) - T^*)^2$, where the reference measure in the **spatial entropy** is time-dependent:

$$E(t) = \int_{\mathcal{D}} h(f) \mu_{T(t)}, \quad f = \frac{\psi}{\mu_{T(t)}}.$$

- For instance, relative entropy estimates $h(x) = x \ln x - x + 1 \geq 0$
- If $\mathcal{E}(t) \rightarrow 0$ then $T(t) \rightarrow T^*$ and $\psi \rightarrow \mu_{T^*}$
- It holds

$$E'(t) = -k_B T(t) \int_{\mathcal{D}} h''(f) |\nabla f|^2 \mu_{T(t)} + \frac{T'(t)}{k_B T(t)^2} \int_{\mathcal{D}} \dots \mu_{T(t)}$$

- First term bounded by $-\rho E(t)$ using some **functional inequality**, remainder small when γ small enough (since $T'(t) \propto \gamma$)

Assumption 1 *There exists an interval $I_T^{\text{LSI}} = [T_{\min}^{\text{LSI}}, T_{\max}^{\text{LSI}}]$ such that $\{\mu_T\}_{T \in I_T^{\text{LSI}}}$ satisfies a **logarithmic Sobolev inequality** with uniform constant $1/\rho$:*

$$\int_{\mathcal{D}} h(f) \mu_T \leq \frac{1}{\rho} \int_{\mathcal{D}} \frac{|\nabla f|^2}{f} \mu_T.$$

Theorem 2 *Consider an initial data (T^0, ψ^0) with $\psi^0 \in H^2(\mathcal{D})$, $\psi^0 \geq 0$, $\int_{\mathcal{D}} \psi^0 = 1$, and associated entropy $\mathcal{E}(0) \leq \mathcal{E}^*$, where*

$$\mathcal{E}^* = \inf \left\{ \frac{1}{2} (T_{\min}^A - T^*)^2, \frac{1}{2} (T_{\max}^A - T^*)^2, \frac{1}{2} (T_{\min}^{\text{LSI}} - T^*)^2, \frac{1}{2} (T_{\max}^{\text{LSI}} - T^*)^2 \right\}.$$

*Then, there exists $\gamma_0 > 0$ such that, for all $0 < \gamma \leq \gamma_0$, (1) has a unique solution $(T, \psi) \in C^1([0, \tau], \mathbb{R}) \times C^0([0, \tau], H^2(\mathcal{D}))$ for all $\tau \geq 0$, and **the entropy converges exponentially fast to zero**: There exists $\kappa > 0$ (depending on γ) such that $\mathcal{E}(t) \leq \mathcal{E}(0) \exp(-\kappa t)$. In particular, the temperature remains positive at all times, and it converges exponentially fast to T^* .*

- The **convergence rate is larger** when
 - $\mathcal{E}(0)$ is smaller (the dynamics starts closer from the fixed point and/or closer from a spatial local equilibrium)
 - the slope of the function $T \mapsto \langle A \rangle_T$ is steeper around T^*
 - ρ is larger (the relaxation of the spatial distribution of configurations at a fixed temperature happens faster)
- The proof relies on the estimates

$$E'(t) \leq - \left(\rho k_B T(t) - \frac{2|T'(t)| \|V\|_\infty}{k_B T(t)^2} \right) E(t) + \frac{2\sqrt{2}|T'(t)| \|V\|_\infty}{k_B T(t)^2} \sqrt{E(t)}$$

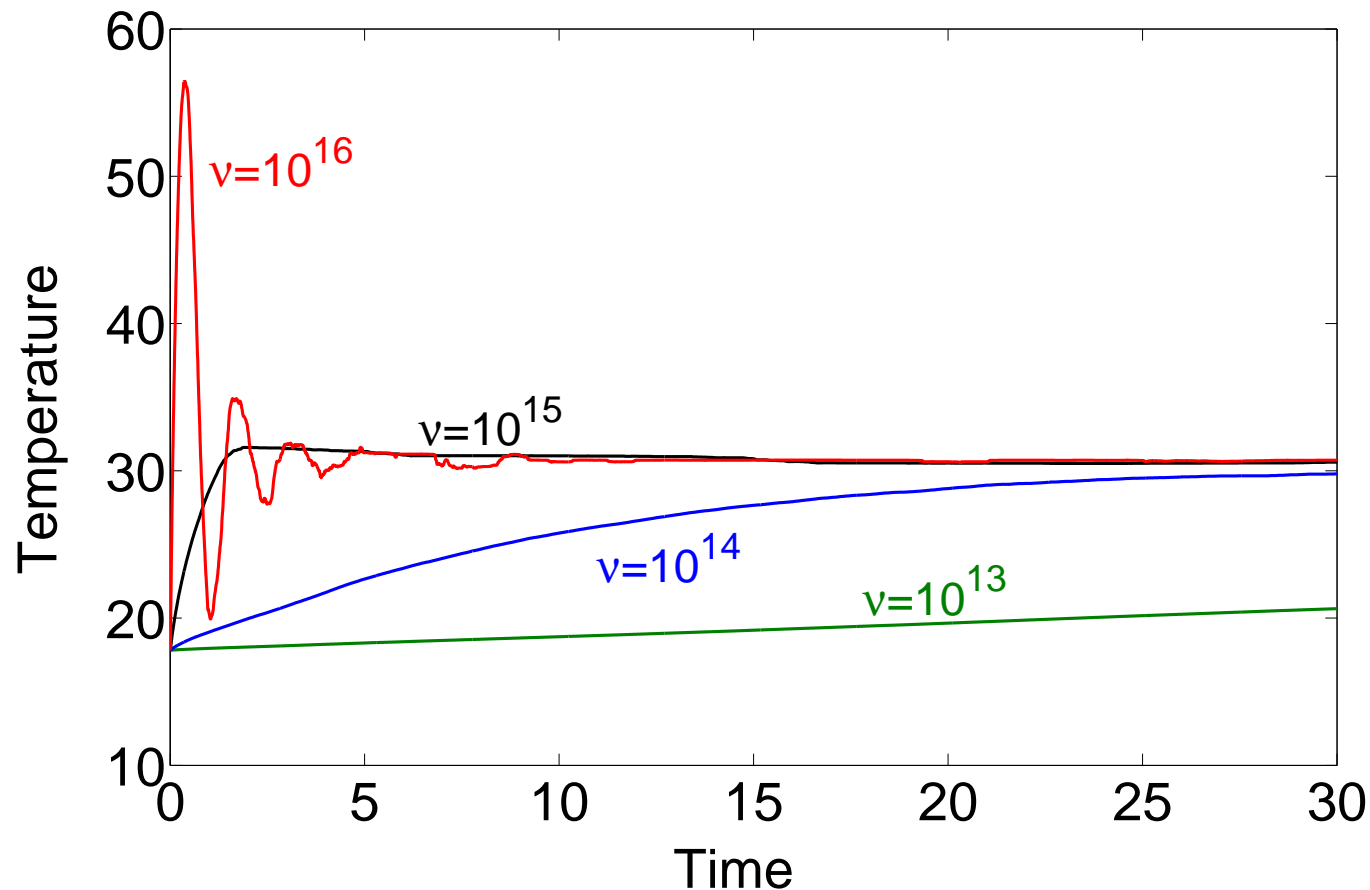
$$|T'(t)| \leq \gamma \left(a |T(t) - T^*| + \|A\|_\infty \sqrt{2E(t)} \right)$$

so that a Gronwall inequality can be shown to hold for \mathcal{E} upon **choosing γ small enough**

- **Multiple replica implementation** (interacting only through the update of their common temperature)
- In many codes, **ergodic limits for a single replica** are easier to implement:

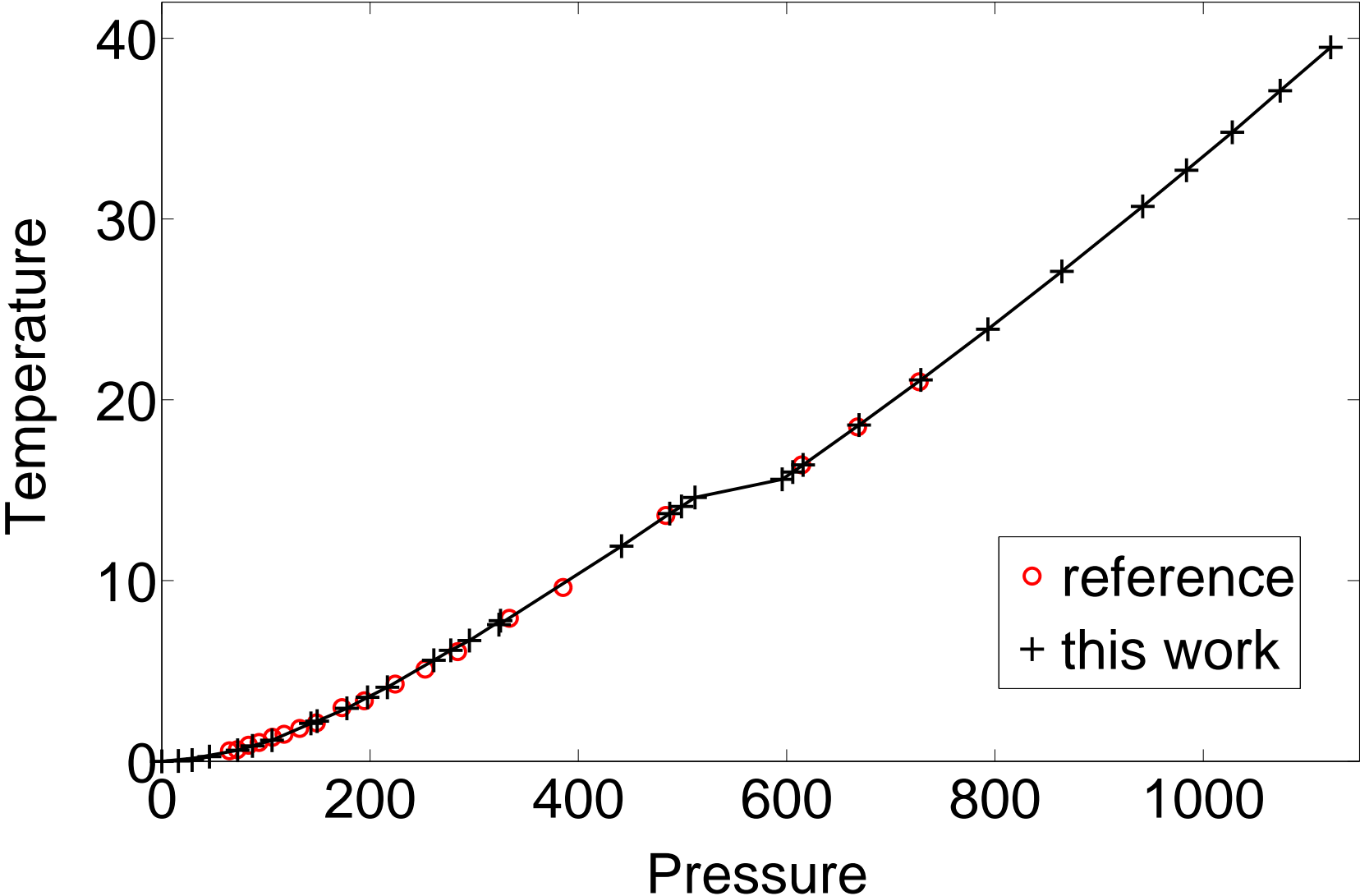
$$\left\{ \begin{array}{l} dq_t = -\nabla V(q_t) dt + \sqrt{2k_B T_t} dW_t, \\ dT_t = -\gamma \left(\frac{\int_0^t A(q_s) \delta_{T_t - T_s} ds}{\int_0^t \delta_{T_t - T_s} ds} \right) dt, \end{array} \right.$$

- (Remark) In both cases, the temperature is now **random**
- Obtain orders of magnitude for γ by some recasting the problem in non-dimensional terms
- In the Hugoniot case, $d \left(\frac{T_t}{T_{\text{ref}}} \right) = -\frac{\mathcal{A}_t(T_t)}{N k_B T_{\text{ref}}} \nu dt$



Temperature as a function of time (in reduced units) for different values of the frequency ν (in s^{-1}), for a system of size $N = 4,000$, and a fixed compression $c = 0.62$. Pole: $T_0 = 10$ K, $\rho_0 = 1.806 \times 10^3$ kg/m³ (so that $P_0 \simeq 0$).

Hugoniot curve (reduced units)

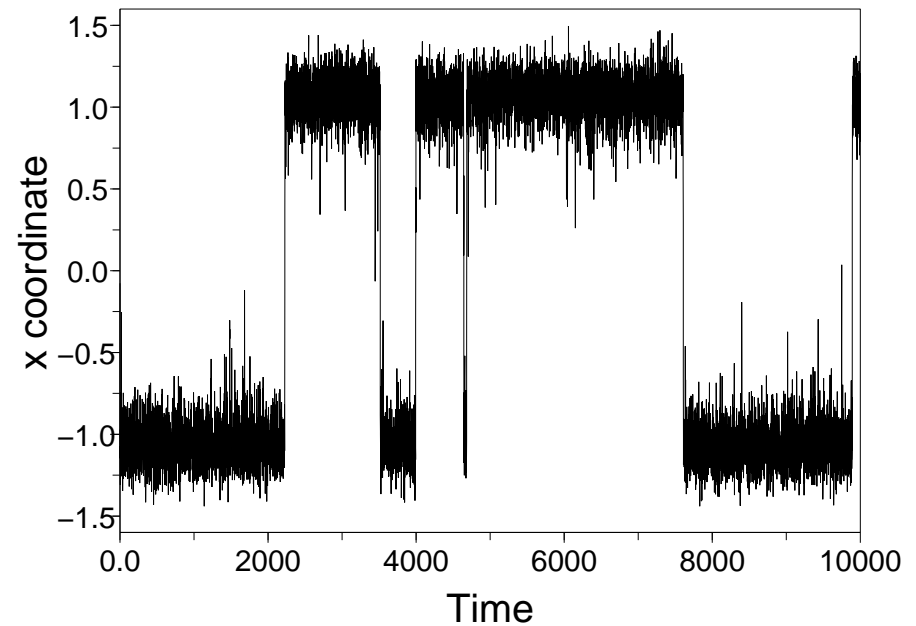
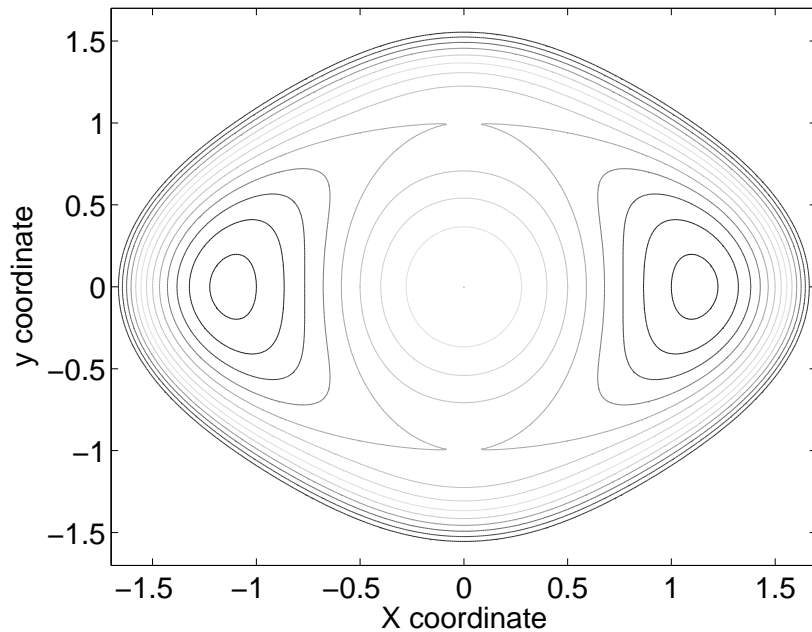


Adaptive computation of free energy differences

Numerical discretization of the overdamped Langevin dynamics:

$$q^{n+1} = q^n - \Delta t \nabla V(q^n) + \sqrt{\frac{2\Delta t}{\beta}} G^n$$

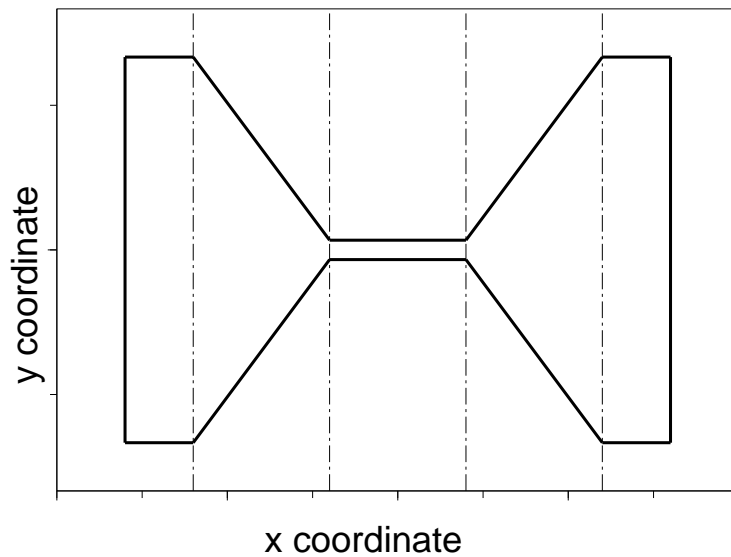
where $G^n \sim \mathcal{N}(0, \text{Id}_{dN})$ i.i.d.



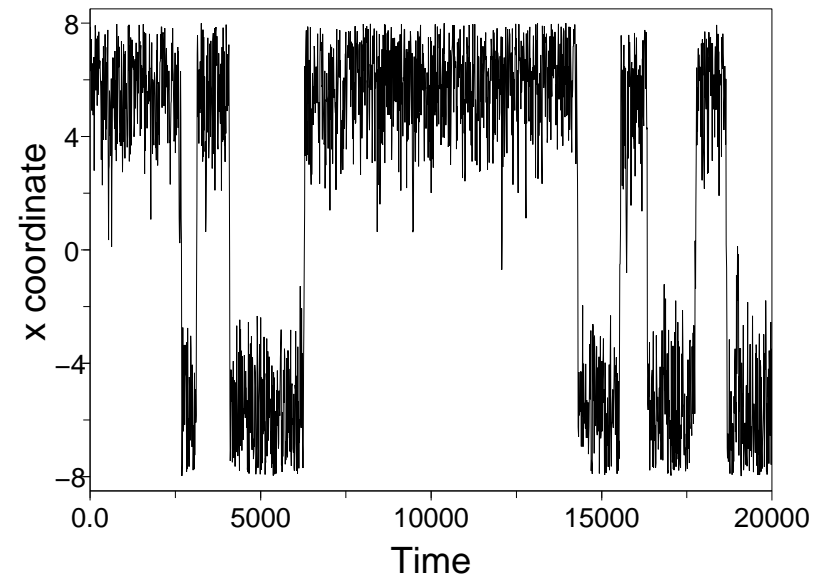
Projected trajectory in the x variable for $\Delta t = 0.01$, $\beta = 8$.

Metastability (2)

- Although the trajectory average converges to the phase-space average, the convergence may be **slow**...
- Slowly evolving macroscopic function of the microscopic degrees of freedom: **reaction coordinate** $\xi(q) \in \mathbb{R}^m$ with $m \ll N$
- Two origins : **energetic** or **entropic** barriers (in fact, **free energy** barriers)



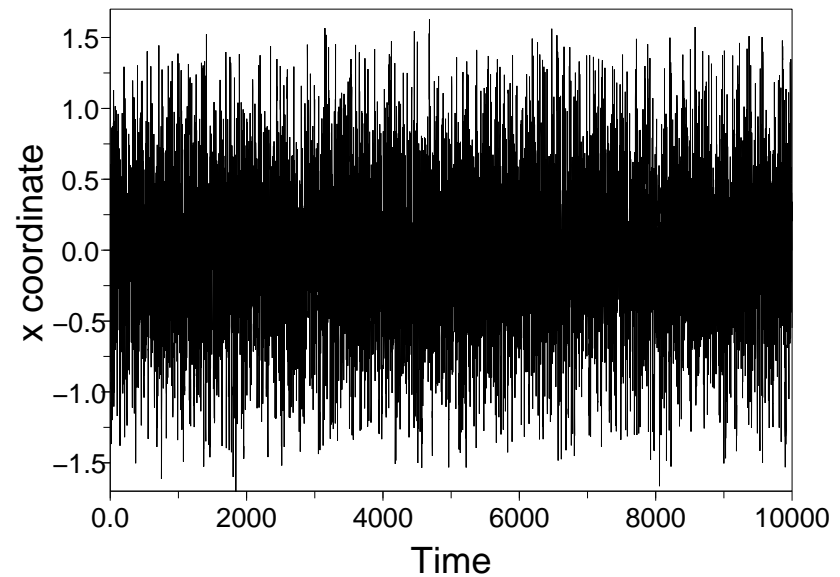
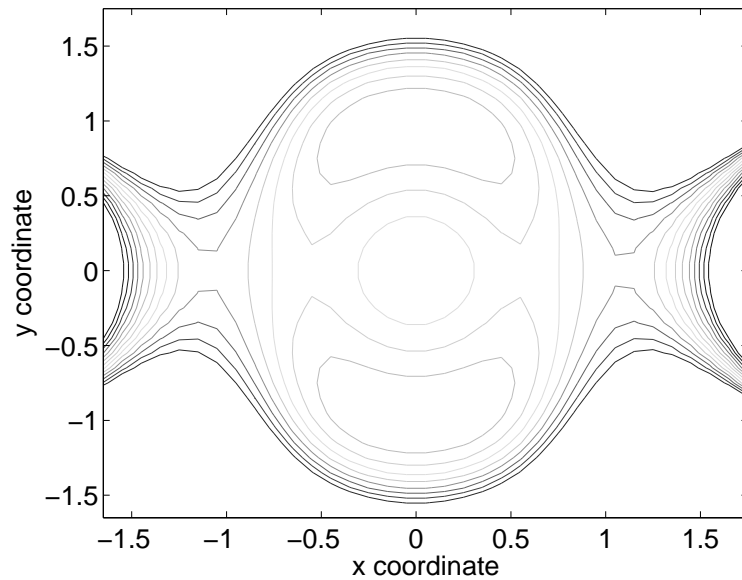
(a) Entropic barrier.



(b) Associated trajectory.

Metastability (3)

- Assume the free energy F associated with the slow direction x has been computed, and **sample the modified potential** $\mathcal{V}(x, y) = V(x, y) - F(x)$.



Projected trajectory in the x variable for $\Delta t = 0.01$, $\beta = 8$.

- Many more transitions! The variable x is **uniformly distributed**.
- Reweighting** with weights $e^{-\beta F(x)}$ to compute canonical averages
- Compute efficiently the free energy?

- Simplified setting: $q = (x, y)$ and $\xi(q) = x \in \mathbb{R}$ so that

$$F(x_2) - F(x_1) = -\beta^{-1} \ln \left(\frac{\bar{\psi}_{\text{eq}}(x_2)}{\bar{\psi}_{\text{eq}}(x_1)} \right), \quad \bar{\psi}_{\text{eq}}(x) = \int e^{-\beta V(x,y)} dy$$

- Notice that the **mean force** $F'(x) = \frac{\int \partial_x V(x, y) e^{-\beta V(x,y)} dy}{\int e^{-\beta V(x,y)} dy}$

- The dynamics $dq_t = -\nabla V(q_t) dt + \sqrt{\frac{2}{\beta}} dW_t$ is **metastable**, contrarily to

$$\begin{cases} dq_t = -\nabla \left(V(q_t) - F(\xi(q_t)) \right) dt + \sqrt{\frac{2}{\beta}} dW_t \\ F'(x) = \mathbb{E}_\mu \left(\partial_x V(q) \mid \xi(q) = x \right) \end{cases}$$

- Replace equilibrium expectations by $F'(t, x) = \mathbb{E} \left(\partial_x V(q_t) \mid \xi(q_t) = x \right)$

- Nonlinear PDE on the law $\psi(t, q)$:

$$\left\{ \begin{array}{l} \partial_t \psi = \operatorname{div} \left[\nabla (V - F_{\text{bias}}(t, x)) \psi + \beta^{-1} \nabla \psi \right], \\ F'_{\text{bias}}(t, x) = \frac{\int_{\mathcal{D}} \partial_x V(x, y) \psi(t, x, y) dy}{\int_{\mathcal{D}} \psi(t, x, y) dy}. \end{array} \right.$$

- Stationary solution $\psi_\infty \propto e^{-\beta(V - F \circ \xi)}$
- **Simple diffusion** for the marginals $\partial_t \bar{\psi} = \partial_{xx} \bar{\psi}$
- Decomposition of the total entropy $H(\psi | \psi_\infty) = \int_{\mathcal{D}} \ln \left(\frac{\psi}{\psi_\infty} \right) \psi$
into a **macroscopic contribution** (marginals in x) and a **microscopic** one (conditioned measures)
- Convergence of the microscopic entropy provided some **uniform logarithmic Sobolev inequality** holds for the conditioned measures

- Sampling constraints in averages:

J.B. MAILLET AND G. STOLTZ, Sampling constraints in average: The example of Hugoniot curves, *Appl. Math. Res. Express* **2008** abn004 (2009)

- Adaptive computation of free energy differences

- T. LELIÈVRE, M. ROUSSET AND G. STOLTZ, Computation of free energy profiles with parallel adaptive dynamics, *J. Chem. Phys.* **126** (2007) 134111

- T. LELIÈVRE, M. ROUSSET AND G. STOLTZ, Long-time convergence of an adaptive biasing force method, *Nonlinearity* **21** (2008) 1155-1181 (special thanks to Felix Otto)

- Some advertisement for a book to appear this year:

T. LELIÈVRE, M. ROUSSET AND G. STOLTZ *Free energy computations: A Mathematical Perspective*, Imperial College Press.