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):

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

- 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

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

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

Extracting macroscopic properties: Statistical physics

- 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

$$S(\rho) = -k_{\mathrm{B}} \int \rho \ln \rho,$$

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

- 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 $A_0 = H$

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

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, $\mathcal{D} = \Big((1+x)L\mathbb{T}\Big)^{3N}$
- Average energy and average volume $\int \mathrm{Vol}(x)\,\rho(dq\,dp\,dx)$ fixed
- Denoting by βP (pressure) the Lagrange multiplier of the volume constraint,

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

Sampling the canonical ensemble: Overdamped Langevin dynamics

- 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

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

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

- Fluctuation/dissipation relation $\sigma = \sqrt{\frac{2}{\beta}}$

- Invariance + irreducibility (elliptic process):

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

- Several notions of convergence: here, longtime convergence in law
- Evolution PDE $\partial_t \psi = \mathrm{div}\left(\psi_\infty \nabla\left(\frac{\psi}{\psi_\infty}\right)\right), \quad \psi_\infty = Z^{-1}\exp(-\beta V)$
- Relative entropy $\mathcal{H}(\psi(t,\cdot)\,|\,\psi_\infty) = \int \ln\left(\frac{\psi(t,\cdot)}{\psi_\infty}\right)\psi_\infty$
- It holds $\|\psi(t,\cdot) - \psi_\infty\|_{TV} \leq \sqrt{2\mathcal{H}(\psi(t,\cdot)\,|\,\psi_\infty)}$
- Fisher information $I(\psi(t,\cdot)\,|\,\psi_\infty) = \int \left|\nabla \ln\left(\frac{\psi(t,\cdot)}{\psi_\infty}\right)\right|^2 \psi_\infty$
- A simple computation shows $\frac{d}{dt}H(\psi(t,\cdot)\,|\,\psi_\infty) = -\beta^{-1} I(\psi(t,\cdot)\,|\,\psi_\infty)$
- When a Logarithmic Sobolev Inequality holds for ψ_∞, namely $H(\phi|\,\psi_\infty) \leq \frac{1}{2R} I(\phi\,|\,\psi_\infty)$, then, by Gronwall's lemma, the relative entropy converges exponentially fast to 0, as well as the total variation distance
- Obtaining LSI: Bakry-Emery criterion (convexity), Gross (tensorization), Holley-Stroock's perturbation result

Satisfying constraints in average

- 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

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

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

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

$$\mu_T(q) = \frac{1}{Z_T} \exp\left(-\frac{V(q)}{k_{\rm B}T}\right), \qquad Z_T = \int_{\mathcal{D}} \exp\left(-\frac{V(q)}{k_{\rm B}T}\right) dq,$$

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 $c_{\text{max}} \leq c \leq 1$, find $T \equiv T(c)$ such that

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

- Finding a zero of the function $f(T) = \langle A \rangle_T$... 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

$$\forall T \in I_T^A, \quad \langle A \rangle_T = 0\alpha \leq \frac{\langle A \rangle_T - \langle A \rangle_{T^*}}{T - T^*} \leq a$$

- 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

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

Alternative strategy

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

$$dq_t = -\nabla V(q_t)\, dt + \sqrt{2 k_\mathrm{B} T}\, dW_t$$

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

- Approximate the equilibrium canonical expectation by the current one:

$$\left\{ \begin{array}{rcl} dq_t & = & -\nabla V(q_t)\, dt + \sqrt{2 k_\mathrm{B} T(t)}\, dW_t, \\ T'(t) & = & -\gamma\, \mathbb{E}(A(q_t)), \end{array} \right.$$

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

Partial differential equation reformulation

- Nonlinear PDE on the law ψ_t of the process q_t

$$\left\{ \begin{array}{rcl} \partial_t \psi & = & k_{\rm B} T(t)\, \nabla \cdot \left[\mu_{T(t)} \nabla \left(\dfrac{\psi}{\mu_{T(t)}} \right) \right] = k_{\rm B} T(t)\, \Delta \psi + \nabla \cdot (\psi \nabla V), \\ T'(t) & = & -\gamma \displaystyle\int_{\mathcal{D}} A(q)\, \psi(t,q)\, dq \end{array} \right. \qquad (1)$$

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

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

Longtime convergence

- 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:

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

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

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

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

Precise convergence result

Assumption 1 *There exists an interval* $I_T^{\mathrm{LSI}} = [T_{\min}^{\mathrm{LSI}}, T_{\max}^{\mathrm{LSI}}]$ *such that* $\{\mu_T\}_{T \in I_T^{\mathrm{LSI}}}$ *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* $\psi^0 \in \mathrm{H}^2(\mathcal{D})$*,* $\psi^0 \geq 0$*,* $\displaystyle\int_{\mathcal{D}} \psi^0 = 1$*, and associated entropy* $\mathcal{E}(0) \leq \mathcal{E}^*$*, where*

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

Then, there exists $\gamma_0 > 0$ *such that, for all* $0 < \gamma \leq \gamma_0$*,* (1) *has a unique solution* $(T, \psi) \in \mathrm{C}^1([0,\tau], \mathbb{R}) \times \mathrm{C}^0([0,\tau], \mathrm{H}^2(\mathcal{D}))$ *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^**.*

Some comments

- 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

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

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

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

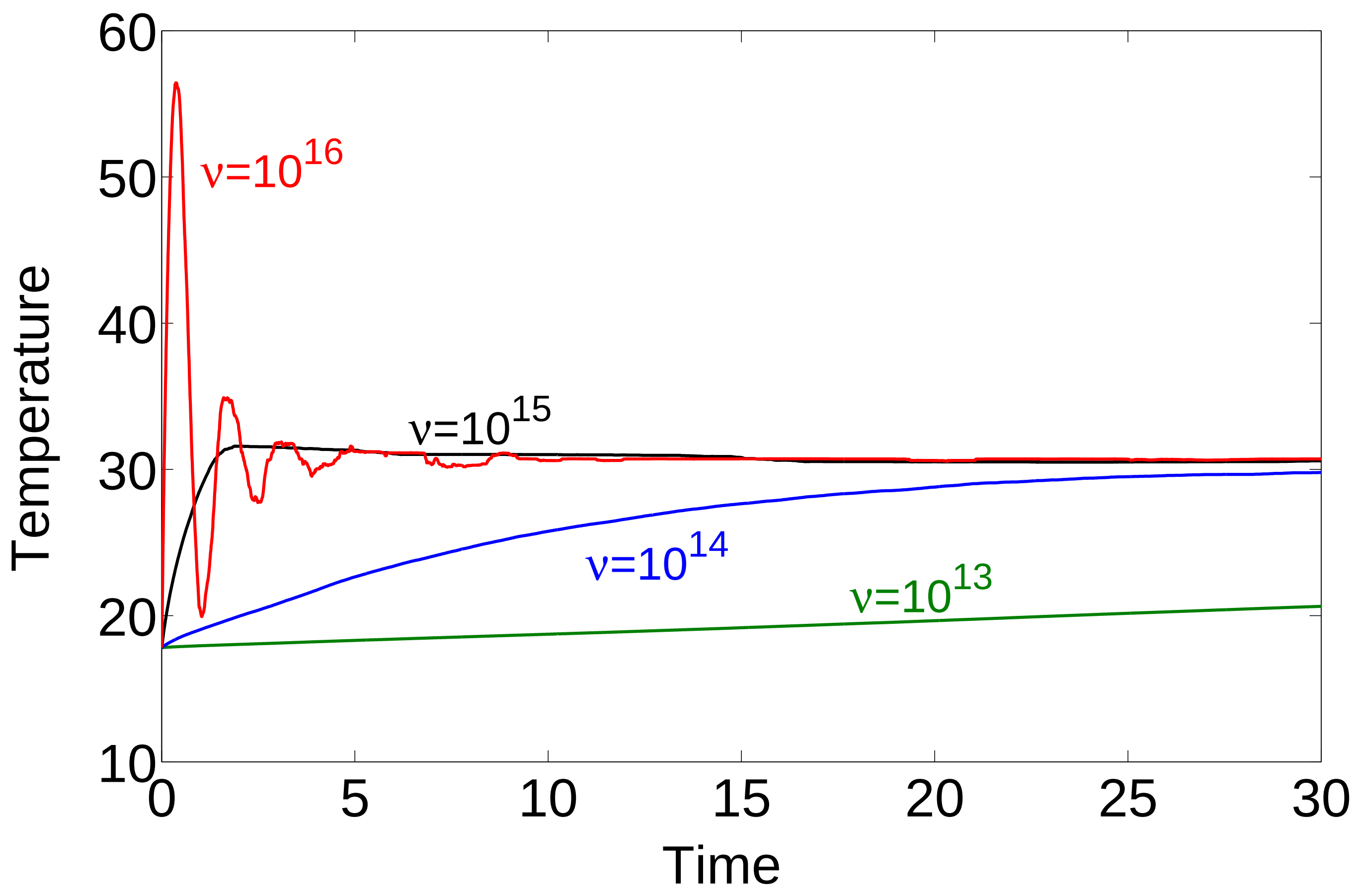
- Other functional setting possible: L^2 estimates and Poincaré inequalities

Numerical results

- 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:

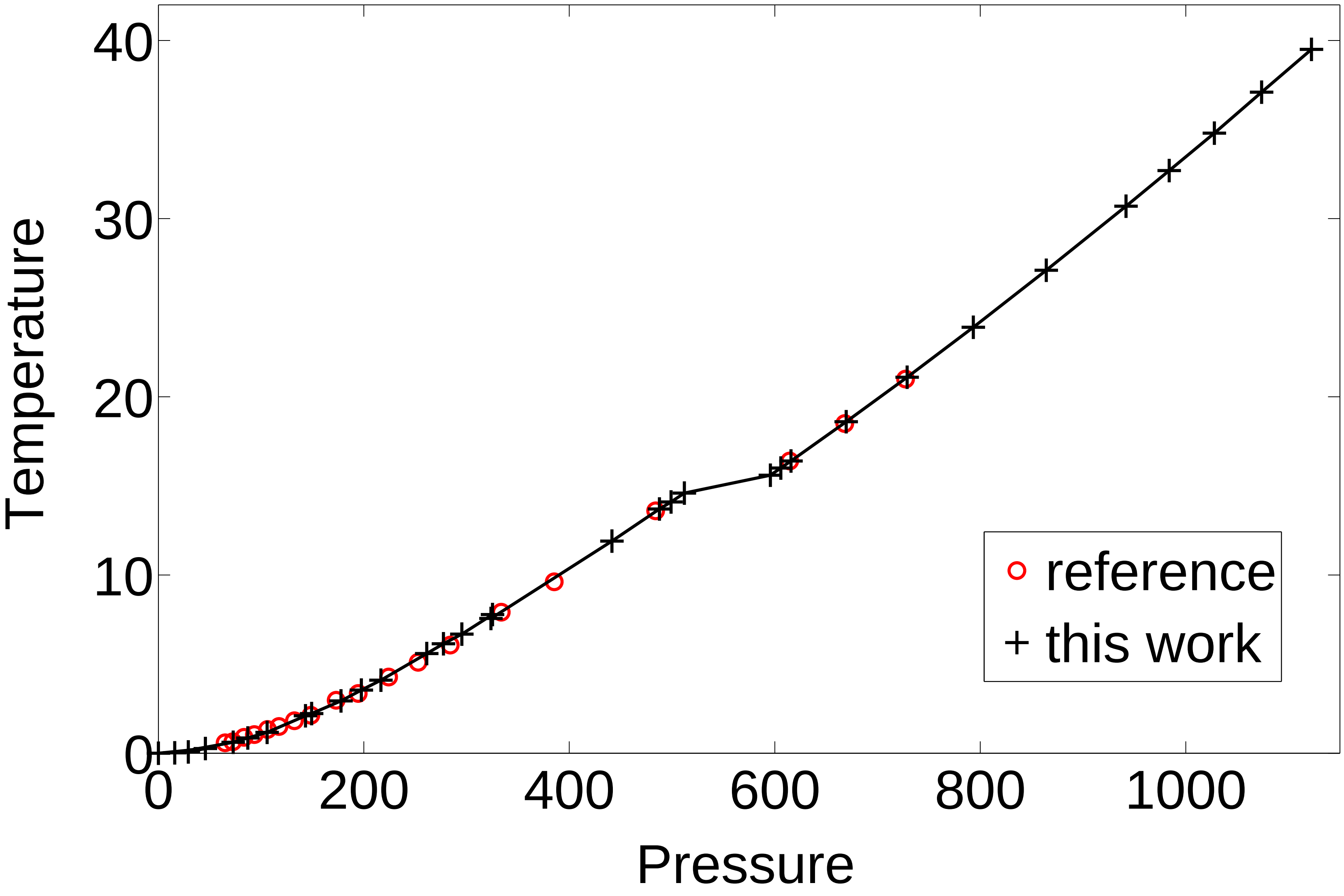
$$\left\{ \begin{aligned} dq_t &= -\nabla V(q_t)\,dt + \sqrt{2k_{\mathrm{B}}T_t}\,dW_t, \\ dT_t &= -\gamma \left(\frac{\displaystyle\int_0^t A(q_s)\,\delta_{T_t - T_s}\,ds}{\displaystyle\int_0^t \delta_{T_t - T_s}\,ds} \right) dt, \end{aligned} \right.$$

- (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, $d\left(\frac{T_t}{T_{\text{ref}}}\right) = -\frac{\mathcal{A}_t(T_t)}{N k_{\mathrm{B}} T_{\mathrm{ref}}}\,\nu\,dt$



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/m^3 (so that $P_0 \simeq 0$).

Hugoniot curve (reduced units)

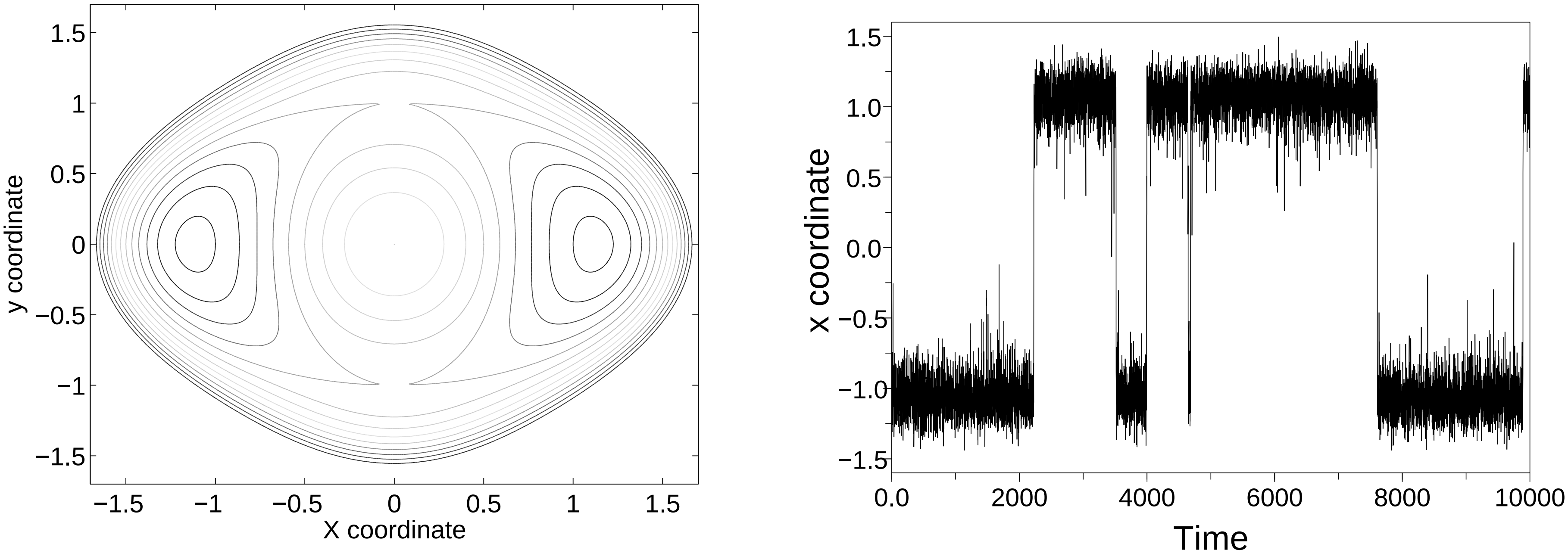


Adaptive computation of free energy differences

Numerical discretization of the overdamped Langevin dynamics:

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

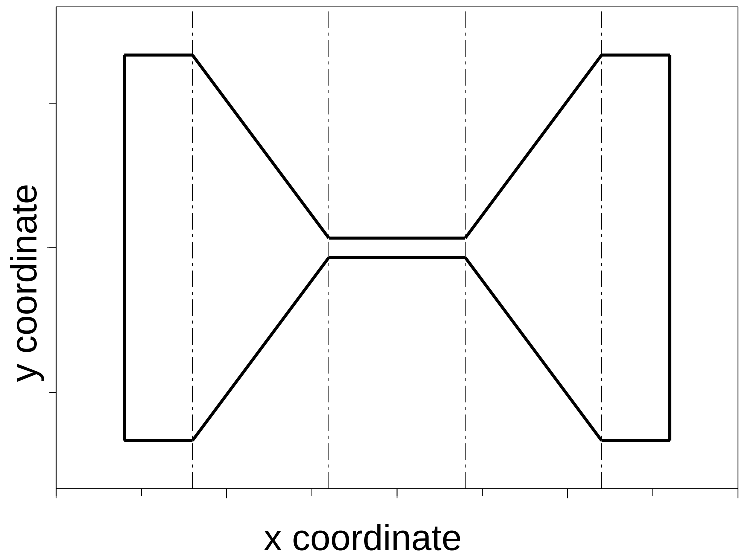
where $G^n \sim \mathcal{N}(0, \mathrm{Id}_{dN})$ i.i.d.



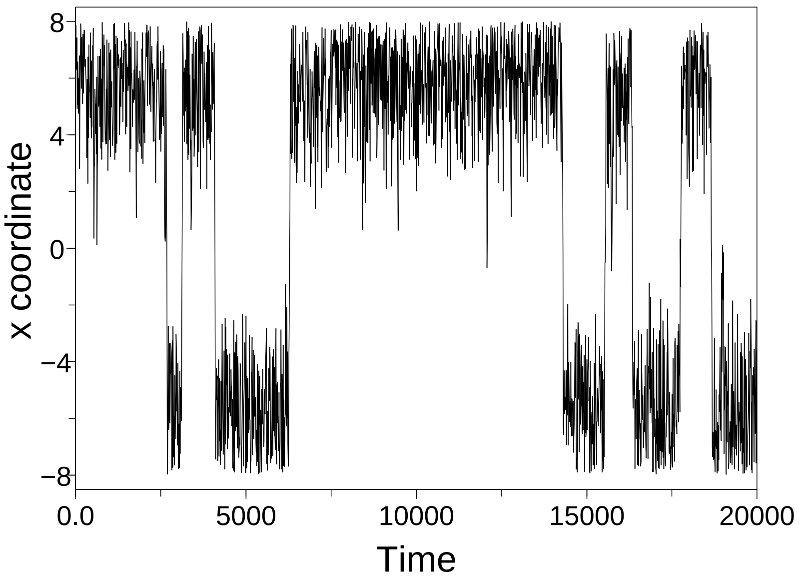
Projected trajectory in the x variable for $\Delta t = 0.01$, $\beta = 8$.

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)



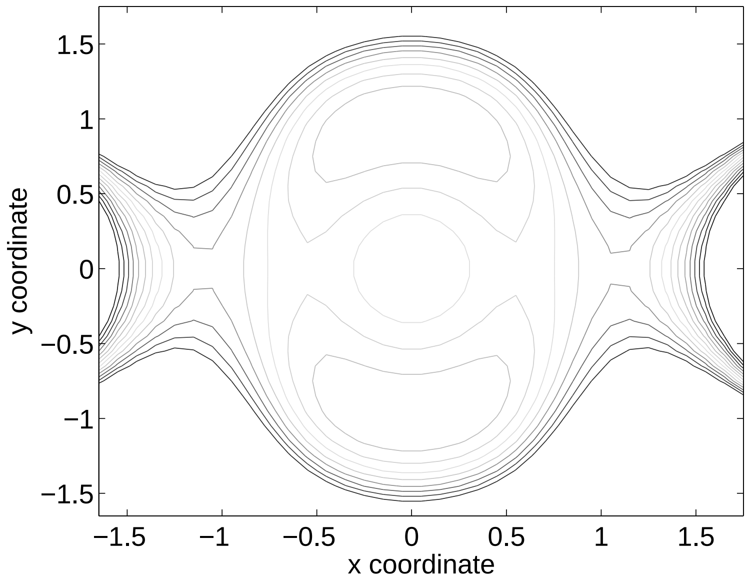
(a) Entropic barrier.

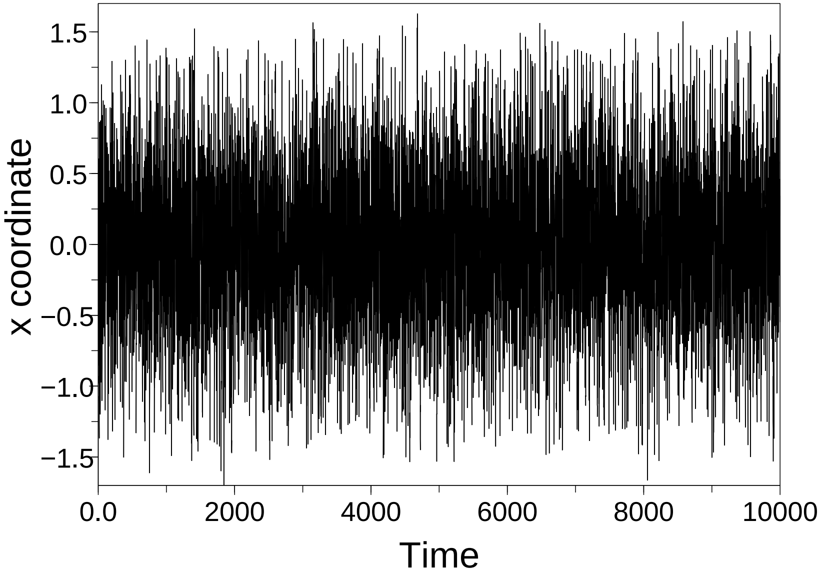


(b) Associated trajectory.

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 $\mathrm{e}^{-\beta F(x)}$ to compute canonical averages
- Compute efficiently the free energy?

Adaptive dynamics (1)

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

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

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

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

$$\left\{ \begin{array}{l} dq_t = -\nabla \Big(V(q_t) - F(\xi(q_t)) \Big) \, dt + \sqrt{\dfrac{2}{\beta}} \, dW_t \\ F'(x) = \mathbb{E}_\mu \Big(\partial_x V(q) \, \Big| \, \xi(q) = x \Big) \end{array} \right.$$

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

Adaptive dynamics: convergence

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

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

- Stationary solution $\psi_\infty \propto \mathrm{e}^{-\beta(V - F\circ\xi)}$
- Simple diffusion for the marginals $\partial_t \overline{\psi} = \partial_{xx}\,\overline{\psi}$
- Decomposition of the total entropy $H(\psi\,|\,\psi_\infty) = \displaystyle\int_{\mathcal{D}} \ln\left(\frac{\psi}{\psi_\infty}\right)\psi$ 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

References

- 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.