An Introduction to Molecular Dynamics

Gabriel STOLTZ

stoltz@cermics.enpc.fr

(CERMICS, Ecole des Ponts & MATHERIALS team, INRIA Rocquencourt)

MOMAS meeting, CIRM, 2014

Outline

- **Some elements of statistical physics**
- **Sampling the canonical ensemble**
  - Stochastic differential equations
  - Overdamped Langevin dynamics
  - Langevin dynamics
- **Computation of transport coefficients**

General references (1)

- Statistical physics: theoretical presentations
  - R. Balian, *From Microphysics to Macrophysics. Methods and Applications of Statistical Physics*, volume I - II (Springer, 2007).
  - many other books: Chandler, Ma, Phillies, Zwanzig, ...

- Computational Statistical Physics
  - D. Frenkel and B. Smit, *Understanding Molecular Simulation, From Algorithms to Applications* (Academic Press, 2002)
  - M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford, 2010)
  - M. P. Allen and D. J. Tildesley, *Computer simulation of liquids* (Oxford University Press, 1987)
  - D. C. Rapaport, *The Art of Molecular Dynamics Simulations* (Cambridge University Press, 1995)
  - T. Schlick, *Molecular Modeling and Simulation* (Springer, 2002)

- J.N. Roux, S. Rodts and G. Stoltz, *Introduction à la physique statistique et à la physique quantique*, cours Ecole des Ponts (2009)
`http://cermics.enpc.fr/~stoltz/poly_phys_stat_quantique.pdf`

General references (2)

- Longtime integration of the Hamiltonian dynamics
  - E. Hairer, C. Lubich and G. Wanner, *Geometric Numerical Integration: Structure-Preserving Algorithms for ODEs* (Springer, 2006)
  - B. J. Leimkuhler and S. Reich, *Simulating Hamiltonian dynamics*, (Cambridge University Press, 2005)
  - E. Hairer, C. Lubich and G. Wanner, Geometric numerical integration illustrated by the Störmer-Verlet method, *Acta Numerica* **12** (2003) 399–450

- Sampling the canonical measure
  - L. Rey-Bellet, Ergodic properties of Markov processes, *Lecture Notes in Mathematics*, **1881** 1–39 (2006)
  - E. Cancès, F. Legoll and G. Stoltz, Theoretical and numerical comparison of some sampling methods, *Math. Model. Numer. Anal.* **41**(2) (2007) 351-390
  - T. Lelièvre, M. Rousset and G. Stoltz, *Free Energy Computations: A Mathematical Perspective* (Imperial College Press, 2010)
  - B. Leimkuhler and C. Matthews, *Molecular Dynamics: with deterministic and stochastic numerical methods* (Springer, 2015)

Some elements of statistical physics

General perspective (1)

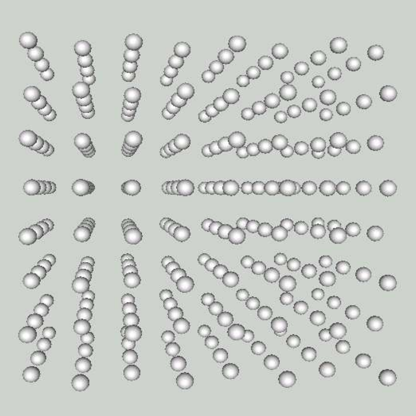
- Aims of computational statistical physics:
  - numerical microscope
  - computation of average properties, static or dynamic

- Orders of magnitude
  - distances $\sim 1\ \mathring{A} = 10^{-10}$ m
  - energy per particle $\sim k_{\mathrm{B}}T \sim 4 \times 10^{-21}$ J at room temperature
  - atomic masses $\sim 10^{-26}$ kg
  - time $\sim 10^{-15}$ s
  - number of particles $\sim \mathcal{N}_A = 6.02 \times 10^{23}$

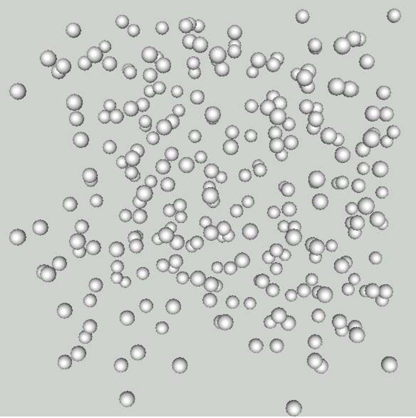
- "Standard" simulations
  - 10^6 particles ["world records": around 10^9 particles]
  - integration time: (fraction of) ns ["world records": (fraction of) μs]

General perspective (2)

What is the melting temperature of argon?

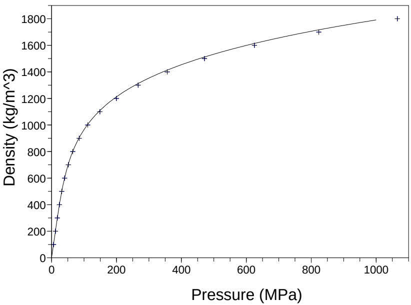


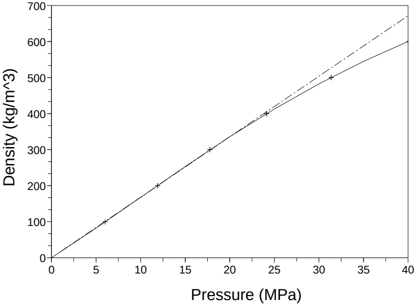
(a) Solid argon (low temperature)



(b) Liquid argon (high temperature)

"Given the structure and the laws of interaction of the particles, what are the macroscopic properties of the matter composed of these particles?"

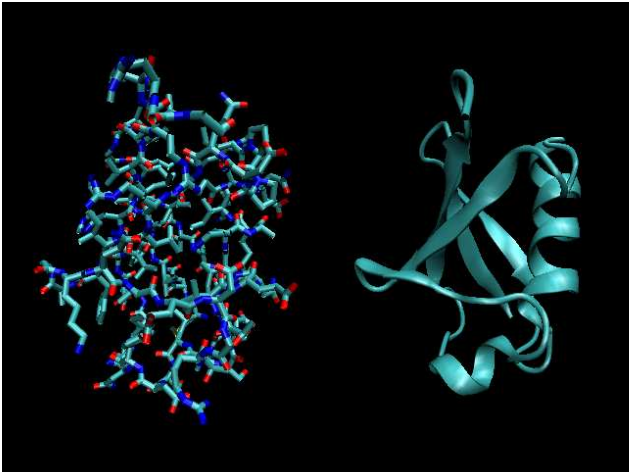




Equation of state (pressure/density diagram) for argon at $T = 300$ K

General perspective (4)

What is the structure of the protein? What are its typical conformations, and what are the transition pathways from one conformation to another?



Microscopic description of physical systems: unknowns

• Microstate of a classical system of N particles:

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

Positions q (configuration), momenta p (to be thought of as $M\dot{q}$)

• In the simplest cases, $\mathcal{E} = \mathcal{D} \times \mathbb{R}^{3N}$ with $\mathcal{D} = \mathbb{R}^{3N}$ or $\mathbb{T}^{3N}$

• More complicated situations can be considered: molecular constraints defining submanifolds of the phase space

• Hamiltonian $H(q,p) = E_{\rm kin}(p) + V(q)$, where the kinetic energy is

$$E_{\rm kin}(p) = \frac{1}{2}\, p^T M^{-1} p, \qquad M = \begin{pmatrix} m_1\,\mathrm{Id}_3 & & 0 \\ & \ddots & \\ 0 & & m_N\,\mathrm{Id}_3 \end{pmatrix}.$$

Microscopic description: interaction laws

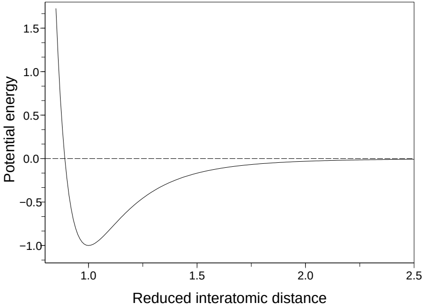
- All the physics is contained in V
  - ideally derived from quantum mechanical computations
  - in practice, empirical potentials for large scale calculations

- An example: Lennard-Jones pair interactions to describe noble gases

$$V(q_1,\dots,q_N) = \sum_{1 \leqslant i<j \leqslant N} v(|q_j - q_i|)$$

$$v(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

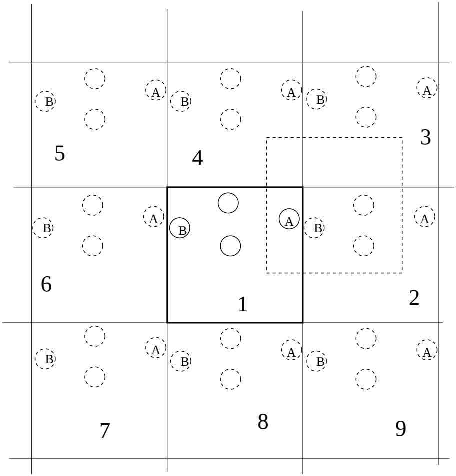
$$\text{Argon:} \quad \begin{cases} \sigma = 3.405 \times 10^{-10} \ \text{m} \\ \varepsilon / k_{\mathrm{B}} = 119.8 \ \ \text{K} \end{cases}$$



Microscopic description: boundary conditions

Various types of boundary conditions:

- Periodic boundary conditions: easiest way to mimick bulk conditions
- Systems *in vacuo* ($\mathcal{D} = \mathbb{R}^3$)
- Confined systems (specular reflection): large surface effects
- Stochastic boundary conditions (inflow/outflow of particles, energy, ...)



Thermodynamic ensembles

- Macrostate of the system described by a probability measure

Equilibrium thermodynamic properties (pressure,...)

$$\langle A \rangle_\mu = \mathbb{E}_\mu(A) = \int_{\mathcal{E}} A(q,p)\, \mu(dq\, dp)$$

- Choice of thermodynamic ensemble
  - least biased measure compatible with the observed macroscopic data
  - Volume, energy, number of particles, ... fixed exactly or in average
  - Equivalence of ensembles (as $N \to +\infty$)

An example: the canonical measure (NVT)

- Constraints satisfied in average: constrained maximisation of entropy

$$S(\rho) = -\int \rho \ln \rho \, d\lambda,$$

(λ reference measure), conditions $\rho \geqslant 0, \quad \int \rho \, d\lambda = 1, \quad \int A_i \, \rho \, d\lambda = \mathcal{A}_i$

- Euler-Lagrange equation using $S'(\rho) = 1 + \ln \rho$

$$1 + \ln \rho + \alpha + \sum_i \beta_i A_i = 0$$

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

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

with $\beta = \dfrac{1}{k_{\mathrm{B}} T}$ the Lagrange multiplier of the constraint $\displaystyle\int_{\mathcal{E}} H \, \rho \, dq\,dp = E_0$

Observables

- May depend on the chosen ensemble! Given by physicists, by some analogy with macrosocpic, continuum thermodynamics
  - Pressure (derivative of the free energy with respect to volume)

$$A(q,p) = \frac{1}{3|\mathcal{D}|} \sum_{i=1}^{N} \left(\frac{p_i^2}{m_i} - q_i \cdot \nabla_{q_i} V(q) \right)$$

  - Kinetic temperature $A(q,p) = \frac{1}{3Nk_{\mathrm{B}}} \sum_{i=1}^{N} \frac{p_i^2}{m_i}$
  - Specific heat at constant volume: canonical average

$$C_V = \frac{\mathcal{N}_{\mathrm{a}}}{Nk_{\mathrm{B}}T^2} \left(\langle H^2 \rangle_{\mathrm{NVT}} - \langle H \rangle_{\mathrm{NVT}}^2 \right)$$

Main issue

Computation of high-dimensional integrals... Ergodic averages

- Also techniques to compute interesting trajectories (not presented here)

Sampling the canonical ensemble

Classification of the methods

- Computation of $\langle A \rangle = \int_{\mathcal{E}} A(q,p)\,\mu(dq\,dp)$ with

$$\mu(dq\,dp) = Z_\mu^{-1} \mathrm{e}^{-\beta H(q,p)}\,dq\,dp, \qquad \beta = \frac{1}{k_\mathrm{B} T}$$

- Actual issue: sampling canonical measure on configurational space

$$\nu(dq) = Z_\nu^{-1} \mathrm{e}^{-\beta V(q)}\,dq$$

- Several strategies (theoretical and numerical comparison[1])
  - Purely stochastic methods (i.i.d sample) $\rightarrow$ impossible...
  - Stochastic differential equations
  - Markov chain methods
  - Deterministic methods *à la* Nosé-Hoover

In practice, no clear-cut distinction due to blending...

[1] E. Cancès, F. Legoll and G. Stoltz, *M2AN*, 2007

Langevin dynamics

- Stochastic perturbation of the Hamiltonian dynamics : friction $\gamma > 0$

$$\begin{cases} dq_t = M^{-1} p_t \, dt \\ dp_t = -\nabla V(q_t) \, dt - \gamma M^{-1} p_t \, dt + \sqrt{\frac{2\gamma}{\beta}} \, dW_t \end{cases}$$

- Motivations
  - Ergodicity can be proved and is indeed observed in practice
  - Many useful extensions (dissipative particle dynamics, rigorous NPT and μVT samplings, etc)
- Aims
  - Understand the meaning of this equation
  - Understand why it samples the canonical ensemble
  - Implement appropriate discretization schemes
  - Estimate the errors (systematic biases vs. statistical uncertainty)

Outline

- **Some elements of statistical physics**
- **Sampling the canonical ensemble**
  - Stochastic differential equations
  - Overdamped Langevin dynamics
  - Langevin dynamics
- **Computation of transport coefficients**

An intuitive view of the Brownian motion (1)

- Independant Gaussian increments whose variance is proportional to time

$$\forall\, 0 < t_0 \leqslant t_1 \leqslant \cdots \leqslant t_n, \qquad W_{t_{i+1}} - W_{t_i} \sim \mathcal{N}(0, t_{i+1} - t_i)$$

where the increments $W_{t_{i+1}} - W_{t_i}$ are independent

- $G \sim \mathcal{N}(m, \sigma^2)$ distributed according to the probability density

$$g(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-m)^2}{2\sigma^2}\right)$$

- The solution of $dq_t = \sigma dW_t$ can be thought of as the limit $\Delta t \to 0$

$$q^{n+1} = q^n + \sigma\sqrt{\Delta t}\, G^n, \qquad G^n \sim \mathcal{N}(0,1) \text{ i.i.d.}$$

where q^n is an approximation of $q_{n\Delta t}$

- Note that $q^n \sim \mathcal{N}(q^0, \sigma n \Delta t)$

- Multidimensional case: $W_t = (W_{1,t}, \dots, W_{d,t})$ where W_i are independent

An intuitive view of the Brownian motion (2)

- Analytical study of the process: law $\psi(t,q)$ of the process at time t

$\rightarrow$ distribution of all possible realizations of q_t for

  - a given initial distribution $\psi(0,q)$, *e.g.* δ_{q^0}
  - and all realizations of the Brownian motion

Averages at time t

$$\mathbb{E}\Big(A(q_t)\Big) = \int_{\mathcal{D}} A(q)\,\psi(t,q)\,dq$$

- Partial differential equation governing the evolution of the law

Fokker-Planck equation

$$\partial_t \psi = \frac{\sigma^2}{2}\Delta\psi$$

Here, simple heat equation $\rightarrow$ "diffusive behavior"

An intuitive view of the Brownian motion (3)

- Proof: Taylor expansion, beware random terms of order $\sqrt{\Delta t}$

$$
\begin{aligned}
A\left(q^{n+1}\right) &= A\left(q^n + \sigma\sqrt{\Delta t}\, G^n\right) \\
&= A\left(q^n\right) + \sigma\sqrt{\Delta t} G^n \cdot \nabla A\left(q^n\right) + \frac{\sigma^2 \Delta t}{2} \left(G^n\right)^T \left(\nabla^2 A\left(q^n\right)\right) G^n + \mathrm{O}\left(\Delta t^{3/2}\right)
\end{aligned}
$$

Taking expectations (Gaussian increments G^n independent from the current position q^n)

$$\mathbb{E}\left[A\left(q^{n+1}\right)\right] = \mathbb{E}\left[A\left(q^n\right) + \frac{\sigma^2 \Delta t}{2} \Delta A\left(q^n\right)\right] + \mathrm{O}\left(\Delta t^{3/2}\right)$$

Therefore, $\mathbb{E}\left[\frac{A\left(q^{n+1}\right) - A\left(q^n\right)}{\Delta t} - \frac{\sigma^2}{2} \Delta A\left(q^n\right)\right] \to 0$. On the other hand,

$$\mathbb{E}\left[\frac{A\left(q^{n+1}\right) - A\left(q^n\right)}{\Delta t}\right] \to \partial_t \Big(\mathbb{E}\left[A(q_t)\right]\Big) = \int_{\mathcal{D}} A(q) \partial_t \psi(t,q)\, dq.$$

This leads to

$$0 = \int_{\mathcal{D}} A(q) \partial_t \psi(t,q)\, dq - \frac{\sigma^2}{2} \int_{\mathcal{D}} \Delta A(q)\, \psi(t,q)\, dq = \int_{\mathcal{D}} A(q) \left(\partial_t \psi(t,q) - \frac{\sigma^2}{2} \Delta \psi(t,q)\right) dq$$

This equality holds for all observables A.

General SDEs (1)

• State of the system $X \in \mathbb{R}^d$, m-dimensional Brownian motion, diffusion matrix $\sigma \in \mathbb{R}^{d\times m}$

$$dX_t = b(X_t)\,dt + \sigma(X_t)\,dW_t$$

to be thought of as the limit as $\Delta t \to 0$ of (X^n approximation of $X_{n\Delta t}$)

$$X^{n+1} = X^n + \Delta t\, b\left(X^n\right) + \sqrt{\Delta t}\,\sigma(X^n)G^n, \qquad G^n \sim \mathcal{N}\left(0, \mathrm{Id}_m\right)$$

• Generator

$$\mathcal{L} = b(x)\cdot\nabla + \frac{1}{2}\sigma\sigma^T(x) : \nabla^2 = \sum_{i=1}^d b_i(x)\partial_{x_i} + \frac{1}{2}\sum_{i,j=1}^d \left[\sigma\sigma^T(x)\right]_{i,j}\partial_{x_i}\partial_{x_j}$$

• Proceeding as before, it can be shown that

$$\partial_t\Big(\mathbb{E}\left[A(q_t)\right]\Big) = \int_{\mathcal{X}} A\,\partial_t\psi = \mathbb{E}\Big[\left(\mathcal{L}A\right)\left(X_t\right)\Big] = \int_{\mathcal{X}} \left(\mathcal{L}A\right)\psi$$

General SDEs (2)

Fokker-Planck equation

$$\partial_t \psi = \mathcal{L}^* \psi$$

where $\mathcal{L}^*$ is the adjoint of $\mathcal{L}$

$$\int_{\mathcal{X}} (\mathcal{L}A)(x)\, B(x)\, dx = \int_{\mathcal{X}} A(x)\, (\mathcal{L}^* B)(x)\, dx$$

• Invariant measures are stationary solutions of the Fokker-Planck equation

Invariant probability measure $\psi_\infty(x)\, dx$

$$\mathcal{L}^* \psi_\infty = 0, \qquad \int_{\mathcal{X}} \psi_\infty(x)\, dx = 1, \qquad \psi_\infty \geqslant 0$$

• When $\mathcal{L}$ is elliptic (*i.e.* $\sigma\sigma^T$ has full rank: the noise is sufficiently rich), the process can be shown to be irreducible = accessibility property

$$P_t(x, \mathcal{S}) = \mathbb{P}(X_t \in \mathcal{S} \,|\, X_0 = x) > 0$$

General SDEs (3)

- Sufficient conditions for ergodicity
  - irreducibility
  - existence of an invariant probability measure $\psi_\infty(x)\,dx$

Then the invariant measure is unique and

$$\lim_{T\to\infty} \frac{1}{T}\int_0^T \varphi(X_t)\,dt = \int_{\mathcal{X}} \varphi(x)\,\psi_\infty(x)\,dx \qquad \text{a.s.}$$

- Rate of convergence given by Central Limit Theorem: $\widetilde{\varphi} = \varphi - \int \varphi\,\psi_\infty$

$$\sqrt{T}\left(\frac{1}{T}\int_0^T \varphi(X_t)\,dt - \int \varphi\,\psi_\infty\right) \xrightarrow[T\to+\infty]{\text{law}} \mathcal{N}(0,\sigma_\varphi^2)$$

with

$$\sigma_\varphi^2 = 2\,\mathbb{E}\left[\int_0^{+\infty} \widetilde{\varphi}(X_t)\widetilde{\varphi}(X_0)dt\right] = \lim_{T\to+\infty} 2\mathbb{E}\left[\int_0^T \widetilde{\varphi}(X_t)\widetilde{\varphi}(X_0)\left(1-\frac{t}{T}\right)dt\right]$$

Generalities on SDEs (4)

- The variance can formally be rewritten as

$$\sigma_\varphi^2 = 2\int_{\mathcal{X}}\int_0^{+\infty} \left(\mathrm{e}^{t\mathcal{L}}\widetilde{\varphi}\right)\widetilde{\varphi}\,\psi_\infty\,dx\,dt = 2\int_{\mathcal{X}} \left(\mathcal{L}^{-1}\widetilde{\varphi}\right)\widetilde{\varphi}\,\psi_\infty$$

- Sufficient condition: exponential decay of the semigroup

$$\left\|\mathrm{e}^{t\mathcal{L}}\right\|_{\mathcal{B}(E)} \leqslant C\,\mathrm{e}^{-\lambda t}$$

- Appropriate functional space E? Explicit rate of convergence?
  - Lyapunov conditions[2] for $\varphi \in L^\infty(W)$ with $\displaystyle\int_{\mathcal{X}} W^2\,\psi_\infty < +\infty$

$$\mathcal{L}W \leqslant -aW + b, \quad W(x) \xrightarrow[|x|\to+\infty]{} +\infty, \quad \|\varphi\|_{L^\infty(W)} = \sup_{x\in\mathcal{X}} \frac{|\varphi(x)|}{W(x)}$$

  - Logarithmic Sobolev/Poincaré inequalities [gradient structure]
  - Hypocoercivity [commutator structure]

---

[2] M. Hairer and J. Mattingly, *Progr. Probab.* (2011); L. Rey-Bellet, *Lecture Notes in Mathematics* (2006)

SDEs: numerics (1)

- Numerical discretization: various schemes (Markov chains in all cases)

- Example: Euler-Maruyama

$$X^{n+1} = X^n + \Delta t \, b(X^n) + \sqrt{\Delta t}\, \sigma(X^n)\, G^n, \qquad G^n \sim \mathcal{N}(0, \mathrm{Id}_d)$$

- Standard notions of error: fixed integration time $T < +\infty$
  - Strong error $\sup_{0 \leqslant n \leqslant T/\Delta t} \mathbb{E}|X^n - X_{n\Delta t}| \leqslant C\Delta t^p$
  - Weak error: $\sup_{0 \leqslant n \leqslant T/\Delta t} \left| \mathbb{E}\left[\varphi\left(X^n\right)\right] - \mathbb{E}\left[\varphi\left(X_{n\Delta t}\right)\right] \right| \leqslant C\Delta t^p$
  - "mean error" *vs.* "error of the mean"

- Example: for Euler-Maruyama, weak order 1, strong order $1/2$ (1 when σ constant)

SDEs: numerics (2)

- Trajectorial averages: estimator $\Phi_{N_{\rm iter}} = \dfrac{1}{N_{\rm iter}} \displaystyle\sum_{n=1}^{N_{\rm iter}} \varphi(X^n)$
- Numerical scheme ergodic for the probability measure $\psi_{\infty,\Delta t}$
- Two types of errors to compute averages w.r.t. invariant measure
  - Statistical error, quantified using a Central Limit Theorem

$$\Phi_{N_{\rm iter}} = \int \varphi\, \psi_{\infty,\Delta t} + \frac{\sigma_{\Delta t,\varphi}}{\sqrt{N_{\rm iter}}} \mathscr{G}_{N_{\rm iter}}, \qquad \mathscr{G}_{N_{\rm iter}} \sim \mathcal{N}(0,1)$$

  - Systematic errors
    - perfect sampling bias, related to the finiteness of Δt

$$\left| \int_{\mathcal{X}} \varphi\, \psi_{\infty,\Delta t} - \int_{\mathcal{X}} \varphi\, \psi_{\infty} \right| \leqslant C_\varphi\, \Delta t^p$$

    - finite sampling bias, related to the finiteness of $N_{\rm iter}$

SDEs: numerics (3)

Expression of the asymptotic variance: correlations matter!

$$\sigma^2_{\Delta t,\varphi} = \mathrm{Var}(\varphi) + 2\sum_{n=1}^{+\infty} \mathbb{E}\Big(\widetilde{\varphi}(X^n)\widetilde{\varphi}(X^0)\Big), \qquad \widetilde{\varphi} = \varphi - \int \varphi\, \psi_{\infty,\Delta t}$$

where $\mathrm{Var}(\varphi) = \displaystyle\int_{\mathcal{X}} \widetilde{\varphi}^2 \psi_{\infty,\Delta t} = \int_{\mathcal{X}} \varphi^2 \psi_{\infty,\Delta t} - \left(\int_{\mathcal{X}} \varphi \psi_{\infty,\Delta t}\right)^2$

Proof: compute $N_{\mathrm{iter}}\mathbb{E}\left(\widetilde{\Phi}^2_{N_{\mathrm{iter}}}\right) = \dfrac{1}{N_{\mathrm{iter}}} \displaystyle\sum_{n,m=0}^{N_{\mathrm{iter}}} \mathbb{E}\Big(\widetilde{\varphi}(X^n)\widetilde{\varphi}(X^m)\Big)$

Stationarity $\mathbb{E}\Big(\widetilde{\varphi}(X^n)\widetilde{\varphi}(X^m)\Big) = \mathbb{E}\Big(\widetilde{\varphi}(X^{n-m})\widetilde{\varphi}(X^0)\Big)$ implies

$$N_{\mathrm{iter}}\mathbb{E}\left(\widetilde{\Phi}^2_{N_{\mathrm{iter}}}\right) = \mathbb{E}\Big(\widetilde{\varphi}\left(X^0\right)^2\Big) + 2\sum_{n=1}^{+\infty}\left(1 - \frac{n}{N_{\mathrm{iter}}}\right)\mathbb{E}\Big(\widetilde{\varphi}(X^n)\widetilde{\varphi}(X^0)\Big)$$

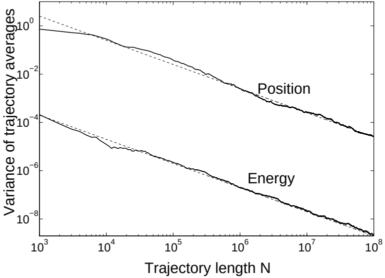
- Useful rewriting: number of correlated steps $\sigma^2_{\Delta t,\varphi} = N_{\mathrm{corr}}\mathrm{Var}(\varphi)$
- Note also that $\sigma^2_{\Delta t,\varphi} \sim \dfrac{2}{\Delta t}\mathbb{E}\left[\displaystyle\int_0^{+\infty} \widetilde{\varphi}(X_t)\widetilde{\varphi}(X_0)\, dt\right]$

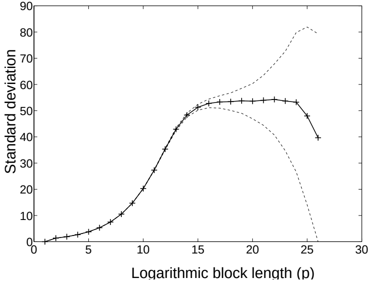
SDEs: numerics (4)

- Estimation of $\sigma_{\Delta t,\varphi}$ by block averaging (batch means)

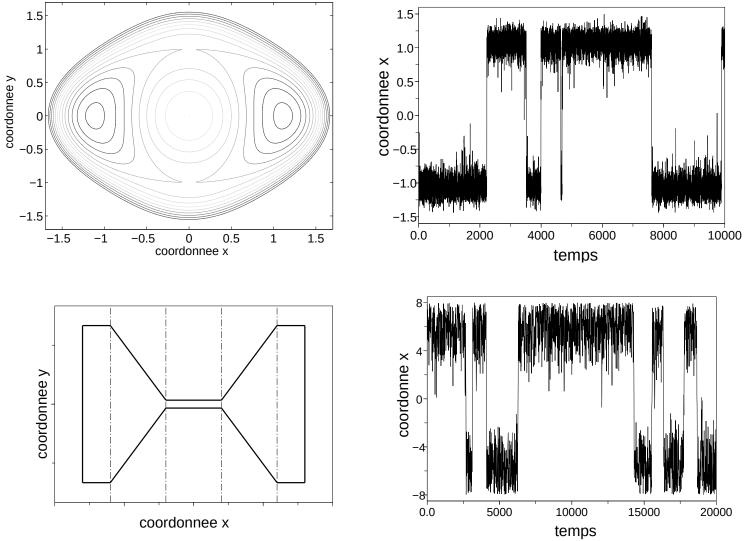
$$\sigma^2_{\Delta t,\varphi} = \lim_{N,M\to+\infty} \frac{N}{M}\sum_{k=1}^{M}\left(\Phi_N^k - \Phi_{NM}^1\right)^2, \quad \Phi_N^k = \frac{1}{N}\sum_{i=(k-1)N+1}^{kN} \varphi(q^i,p^i)$$

Expected $\Phi_N^k \sim \displaystyle\int_{\mathcal{X}} \varphi\,\psi_{\infty,\Delta t} + \frac{\sigma_{\Delta t,\varphi}}{\sqrt{N}}\mathscr{G}^k$, with $\mathscr{G}^k$ i.i.d.





Metastability: large variances...



Need for variance reduction techniques!

Outline

- **Some elements of statistical physics**
- **Sampling the canonical ensemble**
  - Stochastic differential equations
  - Overdamped Langevin dynamics
  - Langevin dynamics
- **Computation of transport coefficients**

Overdamped Langevin dynamics

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

$$dq_t = -\nabla V(q_t)\,dt + \sqrt{\frac{2}{\beta}}dW_t$$

- Invariance of the canonical measure $\nu(dq) = \psi_0(q)\,dq$

$$\psi_0(q) = Z^{-1}\,\mathrm{e}^{-\beta V(q)}, \qquad Z = \int_{\mathcal{D}} \mathrm{e}^{-\beta V(q)}\,dq$$

- Generator $\mathcal{L} = -\nabla V(q)\cdot\nabla_q + \frac{1}{\beta}\Delta_q$
  - invariance of ψ_0: adjoint $\mathcal{L}^*\varphi = \mathrm{div}_q\left((\nabla V)\varphi + \frac{1}{\beta}\nabla_q\varphi\right)$
  - elliptic generator hence irreducibility and ergodicity
- Discretization $q^{n+1} = q^n - \Delta t\,\nabla V(q^n) + \sqrt{\frac{2\Delta t}{\beta}}\,G^n$

Metropolization of the overdamped Langevin dynamics (1)

- Add a Metropolis rule[3,4] to
  - stabilize the discretization when forces are singular
  - remove the bias in the invariant measure

- Given q^n, propose $\tilde{q}^{n+1}$ according to transition probability $T(q^n, \tilde{q})$
- Accept the proposition with probability $\min\left(1, r(q^n, \widetilde{q}^{n+1}\right)$ where

$$r(q,q') = \frac{T(q',q)\,\nu(q')}{T(q,q')\,\nu(q)}, \qquad \nu(dq) \propto \mathrm{e}^{-\beta V(q)}.$$

If acception, set $q^{n+1} = \tilde{q}^{n+1}$; otherwise, set $q^{n+1} = q^n$.

- MALA[5] or SmartMC[6]: $T(q,q') \propto \exp\left(-\frac{\beta}{4\Delta t}\left[q' - q + \Delta t\,\nabla V(q)\right]^2\right)$

[3] Metropolis, Rosenbluth ($\times 2$), Teller ($\times 2$), *J. Chem. Phys.* (1953)
[4] W. K. Hastings, *Biometrika* (1970)
[5] G. Roberts and R.L. Tweedie, *Bernoulli* (1996)
[6] P.J. Rossky, J.D. Doll and H.L. Friedman, *J. Chem. Phys.* (1978)

Metropolization of the overdamped Langevin dynamics (2)

- The normalization constant in the canonical measure needs not be known

- Transition kernel: accepted moves + rejection

$$P(q,dq') = \min\Big(1, r(q,q')\Big) T(q,q')\,dq' + \Big(1-\alpha(q)\Big)\delta_q(dq'),$$

where $\alpha(q) \in [0,1]$ is the probability to accept a move starting from q:

$$\alpha(q) = \int_{\mathcal{D}} \min\Big(1, r(q,q')\Big) T(q,q')\,dq'.$$

- The canonical measure is reversible with respect to ν

$$P(q,dq')\nu(dq) = P(q',dq)\nu(dq')$$

This implies invariance: $\displaystyle\int_{\mathcal{D}} \psi(q')P(q,dq')\,\nu(dq) = \int_{\mathcal{D}} \psi(q)\,\nu(dq)$

Metropolization of the overdamped Langevin dynamics (3)

- Proof: Detailed balance on the absolutely continuous parts

$$\min\left(1, r(q,q')\right) T(q,dq')\nu(dq) = \min\left(1, r(q',q)\right) r(q,q') T(q,dq')\nu(dq)$$
$$= \min\left(1, r(q',q)\right) T(q',dq)\nu(dq')$$

using successively $\min(1,r) = r \min\left(1, \frac{1}{r}\right)$ and $r(q,q') = \dfrac{1}{r(q',q)}$

- Equality on the singular parts $(1-\alpha(q))\,\delta_q(dq')\nu(dq) = (1-\alpha(q'))\delta_{q'}(dq)\nu(dq')$

$$\int_{\mathcal{D}}\int_{\mathcal{D}} \phi(q,q')\,(1-\alpha(q))\,\delta_q(dq')\nu(dq) = \int_{\mathcal{D}} \phi(q,q)(1-\alpha(q))\nu(dq)$$
$$= \int_{\mathcal{D}}\int_{\mathcal{D}} \phi(q,q')(1-\alpha(q'))\delta_{q'}(dq)\nu(dq')$$

- Note: other acceptance ratios $R(r)$ possible as long as $R(r) = rR(1/r)$, but the Metropolis ratio $R(r) = \min(1,r)$ is optimal in terms of asymptotic variance[7]

---

[7] P. Peskun, *Biometrika* (1973)

Outline

- **Some elements of statistical physics**
- **Sampling the canonical ensemble**
  - Stochastic differential equations
  - Overdamped Langevin dynamics
  - Langevin dynamics
- **Computation of transport coefficients**

Langevin dynamics (1)

- Stochastic perturbation of the Hamiltonian dynamics

$$\begin{cases} dq_t = M^{-1} p_t \, dt \\ dp_t = -\nabla V(q_t)\, dt - \gamma M^{-1} p_t \, dt + \sigma \, dW_t \end{cases}$$

- γ,σ may be matrices, and may depend on q

- Generator $\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \mathcal{L}_{\mathrm{thm}}$

$$\mathcal{L}_{\mathrm{ham}} = p^T M^{-1} \nabla_q - \nabla V(q)^T \nabla_p = \sum_{i=1}^{dN} \frac{p_i}{m_i} \partial_{q_i} - \partial_{q_i} V(q) \partial_{p_i}$$

$$\mathcal{L}_{\mathrm{thm}} = -p^T M^{-1} \gamma^T \nabla_p + \frac{1}{2} \left(\sigma \sigma^T\right) : \nabla_p^2 \qquad \left(= \frac{\sigma^2}{2} \Delta_p \text{ for scalar } \sigma \right)$$

- Irreducibility can be proved (control argument)

Langevin dynamics (2)

- Invariance of the canonical measure to conclude to ergodicity?

Fluctuation/dissipation relation

$$\sigma\sigma^T = \frac{2}{\beta}\gamma \qquad \text{implies} \qquad \mathcal{L}^*\left(\mathrm{e}^{-\beta H}\right) = 0$$

- Proof for scalar γ, σ: a simple computation shows that

$$\mathcal{L}_{\mathrm{ham}}^* = -\mathcal{L}_{\mathrm{ham}}, \qquad \mathcal{L}_{\mathrm{ham}} H = 0$$

- Overdamped Langevin analogy $\mathcal{L}_{\mathrm{thm}} = \gamma\left(-p^T M^{-1}\nabla_p + \frac{1}{\beta}\Delta_p\right)$

$\rightarrow$ Replace q by p and $\nabla V(q)$ by $M^{-1}p$

$$\mathcal{L}_{\mathrm{thm}}^*\left[\exp\left(-\beta\frac{p^T M^{-1} p}{2}\right)\right] = 0$$

- Conclusion: $\mathcal{L}_{\mathrm{ham}}^*$ and $\mathcal{L}_{\mathrm{thm}}^*$ both preserve $\mathrm{e}^{-\beta H(q,p)}\, dq\, dp$

Langevin dynamics (3)

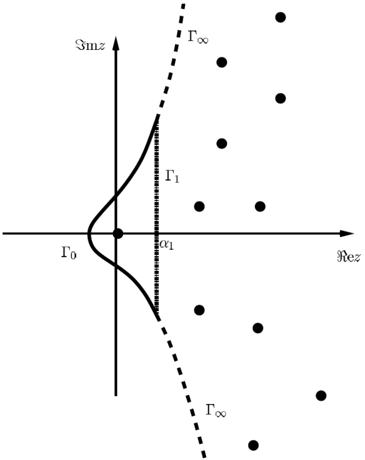
- Rate of convergence?
  Subelliptic estimates[a,b,c,d,e] on

$$\mathcal{H} = \left\{ f \in L^2(\psi_0) \,\middle|\, \int_{\mathcal{E}} f\psi_0 = 0 \right\}$$
$$= L^2(\psi_0) \cap \mathrm{Ker}\,(\mathcal{L})^{\perp}$$

- Operator $\mathcal{L} = X_0 - \sum_{i=1}^{d} X_i^* X_i$

with $X_0 = \mathcal{L}_{\mathrm{ham}}$, $X_i = \sqrt{\frac{\gamma}{\beta}}\,\partial_{p_i}$

- $\mathcal{L}^{-1}$ compact on $\mathcal{H}$



[a] D. Talay, *Markov Proc. Rel. Fields*, **8** (2002)
[b] J.-P. Eckmann and M. Hairer, *Commun. Math. Phys.*, **235** (2003)
[c] F. Hérau and F. Nier, *Arch. Ration. Mech. Anal.*, **171** (2004)
[d] C. Villani, *Trans. AMS* **950** (2009)
[e] G. Pavliotis and M. Hairer, *J. Stat. Phys.* **131** (2008)

Langevin dynamics (4)

- Basic hypocoercivity result: $C_i = [X_i, X_0]$ $(1 \leqslant i \leqslant d)$, assume
  - $X_0^* = -X_0$
  - (for $i, j \geqslant 1$) X_i and X_i^* commute with C_j, X_i commutes with X_j
  - appropriate commutator bounds
  - $\displaystyle\sum_{i=1}^{d} X_i^* X_i + \sum_{i=1}^{d} C_i^* C_i$ is coercive

Then time-decay of the semigroup $\left\| \mathrm{e}^{t\mathcal{L}} \right\|_{\mathcal{B}(H^1(\psi_0)\cap\mathcal{H})} \leqslant C\mathrm{e}^{-\lambda t}$

- The proof uses a scalar product involving mixed derivatives $(a \gg b \gg 1)$

$$\langle\langle u, v \rangle\rangle = a \langle u, v\rangle + \sum_{i=1}^{M} b \langle X_i u, X_i v\rangle + \langle X_i u, C_i v\rangle + \langle C_i u, X_i v\rangle + b\langle C_i u, C_i v\rangle$$

- Langevin: $C_i = \dfrac{1}{m}\partial_{q_i}$, coercivity by Poincaré inequality

Overdamped limit of the Langevin dynamics

- Either $M = \varepsilon \to 0$ (for $\gamma = 1$) or $\gamma = \dfrac{1}{\varepsilon} \to +\infty$ (for $m = 1$ and an appropriate time-rescaling $t \to t/\varepsilon$)

$$\begin{cases} dq_t^\varepsilon = v_t^\varepsilon \, dt \\ \varepsilon \, dv_t^\varepsilon = -\nabla V(q_t^\varepsilon)\, dt - v_t^\varepsilon \, dt + \sqrt{\dfrac{2}{\beta}}\, dW_t \end{cases}$$

- Limiting dynamics $dq_t^0 = -\nabla V(q_t^0)\, dt + \sqrt{\dfrac{2}{\beta}}\, dW_t$

- Convergence result: $\lim_{\varepsilon \to 0} \left(\sup_{0 \leqslant s \leqslant t} \| q_s^\varepsilon - q_s^0 \| \right) = 0$ (a.s.)

The proof relies on the equality

$$q_t^\varepsilon - q_t^0 = v_0 \, \varepsilon \left(1 - \mathrm{e}^{-t/\varepsilon}\right) - \int_0^t \left(1 - \mathrm{e}^{-(t-r)/\varepsilon}\right) \left(\nabla V(q_r^\varepsilon) - \nabla V(q_r^0)\right) \, dr$$
$$+ \int_0^t \mathrm{e}^{-(t-r)/\varepsilon} \, \nabla V(q_r^0)\, dr - \sqrt{2} \int_0^t \mathrm{e}^{-(t-r)/\varepsilon} \, dW_r$$

Numerical integration of the Langevin dynamics (1)

- Splitting strategy: Hamiltonian part + fluctuation/dissipation

$$\left\{ \begin{aligned} dq_t &= \ M^{-1}\, p_t\, dt \\ dp_t &= -\nabla V(q_t)\, dt \end{aligned} \right. \qquad \oplus \qquad \left\{ \begin{aligned} dq_t &= 0 \\ dp_t &= -\gamma M^{-1} p_t\, dt + \sqrt{\frac{2\gamma}{\beta}}\, dW_t \end{aligned} \right.$$

- Hamiltonian part integrated using a Verlet scheme

- Analytical integration of the fluctuation/dissipation part

$$d\left(\mathrm{e}^{\gamma M^{-1} t} p_t\right) = \mathrm{e}^{\gamma M^{-1} t}\left(dp_t + \gamma M^{-1} p_t\, dt\right) = \sqrt{\frac{2\gamma}{\beta}} \mathrm{e}^{\gamma M^{-1} t}\, dW_t$$

so that

$$p_t = \mathrm{e}^{-\gamma M^{-1} t}\, p_0 + \sqrt{\frac{2\gamma}{\beta}} \int_0^t \mathrm{e}^{-\gamma M^{-1}(t-s)}\, dW_s$$

It can be shown that $\displaystyle \int_0^t f(s)\, dW_s \sim \mathcal{N}\left(0, \int_0^t f(s)^2 ds\right)$

Numerical integration of the Langevin dynamics (2)

- Splitting scheme (define $\alpha_{\Delta t} = \mathrm{e}^{-\gamma M^{-1}\Delta t}$, choose $\gamma M^{-1}\Delta t \sim 0.01 - 1$)

$$\begin{cases} p^{n+1/2} = p^n - \dfrac{\Delta t}{2}\,\nabla V(q^n), \\ q^{n+1} = q^n + \Delta t\, M^{-1} p^{n+1/2}, \\ \widetilde{p}^{n+1} = p^{n+1/2} - \dfrac{\Delta t}{2}\,\nabla V(q^{n+1}), \\ p^{n+1} = \alpha_{\Delta t}\widetilde{p}^{n+1} + \sqrt{\dfrac{1-\alpha_{2\Delta t}}{\beta} M}\, G^n, \end{cases}$$

Evolution operator

$$P_{\Delta t}\psi(q) = \mathbb{E}\Big(\psi\left(q^{n+1}\right) \,\Big|\, q^n = q\Big)$$

- Existence of a unique invariant measure $\mu_{\Delta t}$ for compact position spaces

$$\int_{\mathcal{E}} P_{\Delta t}\psi \, d\mu_{\Delta t} = \int_{\mathcal{E}} \psi \, d\mu_{\Delta t}$$

Numerical integration of the Langevin dynamics (3)

- Evolution operator $P_{\Delta t} = \mathrm{e}^{\Delta t\, B/2}\mathrm{e}^{\Delta t\, A}\mathrm{e}^{\Delta t\, B/2}\mathrm{e}^{\Delta t\, C}$ with

$$A = M^{-1}p \cdot \nabla_q, \quad B = -\nabla V(q) \cdot \nabla_p, \quad C = \gamma \left(-M^{-1}p \cdot \nabla_p + \frac{1}{\beta}\Delta_p \right)$$

- Exact remainders for the expansion of the evolution operator

$$P_{\Delta t} = I + \Delta t \mathcal{L} + \frac{\Delta t^2}{2}\Big(\mathcal{L}^2 + [A+B, C] \Big) + \Delta t^3 S_2 + \Delta t^4 R_{\Delta t,2}$$

Error estimates on the bias

For a smooth observable ψ,

$$\int_{\mathcal{E}} \psi \, d\mu_{\Delta t} = \int_{\mathcal{E}} \psi \, d\mu + \Delta t^2 \int_{\mathcal{E}} \psi \, f \, d\mu + \mathrm{O}_\psi(\Delta t^3)$$

with $f = -\left(\mathcal{L}^{-1}\right)^* S_2^* \mathbf{1}$

Numerical integration of the Langevin dynamics (2)

- Structure of the proof[8]
  - by the invariance of $\mu_{\Delta t}$ by $P_{\Delta t}$, it holds $\displaystyle\int_{\mathcal{E}} (I - P_{\Delta t})\varphi \, d\mu_{\Delta t} = 0$,
  - using $\displaystyle\int_{\mathcal{E}} (A + B)\varphi \, d\mu = \int_{\mathcal{E}} C\varphi \, d\mu$, a simple computation shows that

$$\int_{\mathcal{E}} (I - P_{\Delta t})\varphi \cdot \left(1 + \Delta t^2 f\right) d\mu = -\Delta t^3 \int_{\mathcal{E}} \left[\mathcal{L}\varphi \cdot f + S_2\varphi\right] d\mu + \mathrm{O}(\Delta t^4)$$

This suggests that $\mathcal{L}^* f = -S_2^* \mathbf{1}$. Conclude with $\varphi = Q_{\Delta t,2}\psi$ where (pseudo-inverse, defined up to appropriate projections)

$$\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t} Q_{\Delta t,2} = \mathrm{Id} + \Delta t^3 Z_{\Delta t,2}$$

[8] B. Leimkuhler, Ch. Matthews and G. Stoltz, *IMA J. Numer. Anal.* (2014)

Computation of transport coefficients

Computation of transport properties

- There are three main types of techniques
  - Equilibrium techniques: Green-Kubo formula (autocorrelation)
  - Transient methods
  - Steady-state nonequilibrium techniques
    - boundary driven
    - bulk driven

- Definitions use analogy with macroscopic evolution equations

- Example of mathematical questions:
  - (equilibrium) integrability of correlation functions
  - (steady-state nonequilibrium): existence and uniqueness of an invariant probability measure

Steady-state nonequilibrium dynamics: some examples

- Perturbations of equilibrium dynamics by

Non-gradient forces (periodic potential V, $q \in \mathbb{T}$)

$$(1) \qquad \begin{cases} dq_t = M^{-1} p_t \, dt \\ dp_t = \Big(-\nabla V(q_t) + \eta F \Big) dt - \gamma M^{-1} p_t \, dt + \sqrt{\frac{2\gamma}{\beta}} \, dW_t \end{cases}$$

Fluctuation terms with different temperatures

$$\begin{cases} dq_i = p_i \, dt \\ dp_i = \Big(v'(q_{i+1} - q_i) - v'(q_i - q_{i-1}) \Big) dt, \qquad i \neq 1, N \\ dp_1 = \Big(v'(q_2 - q_1) - v'(q_1) \Big) dt - \gamma p_1 \, dt + \sqrt{2\gamma(T + \Delta T)} \, dW_t^1 \\ dp_N = -v'(q_N - q_{N-1}) \, dt - \gamma p_N \, dt + \sqrt{2\gamma(T - \Delta T)} \, dW_t^N \end{cases}$$

- Definition of nonequilibrium systems in physics: existence of currents (energy, particles, ...)

Invariant measure for nonequilibrium steady-states

- Mathematical definition of nonequilibrium systems?

  The generator of the dynamics is not self-adjoint with respect to $L^2(\mu)$, where μ is the invariant measure.

Often, μ replaced by invariant measure of related reference dynamics

- Quantification of the reversibility defaults by entropy production

$$\mathcal{R}\mathcal{L}^*\mathcal{R} = \mathcal{L} - \sigma, \qquad \sigma(q,p) = \eta\beta p^T M^{-1} F \text{ for } (1)$$

- Prove existence/uniqueness of μ: find a Lyapunov function
- May be difficult, *e.g.* 1D atom chains[9,10,11]
- Hypocoercivity? (works on $L^2(\psi_0)$...)

[9] L Rey-Bellet and L. Thomas, *Commun. Math. Phys.* (2002)
[10] P. Carmona, *Stoch. Proc. Appl.* (2007)
[11] J.-P. Eckmann and M. Hairer, *Commun. Math. Phys.* (2000)

Invariant measure for nonequilibrium steady-states

• For equilibrium systems, local perturbations in the dynamics induce local perturbations in the invariant measure

$$dx_t = \Big(-\nabla V(x_t) + \nabla \widetilde{V}(x_t) \Big) dt + \sqrt{\frac{2}{\beta}}\, dW_t$$

so that $\mu(dx) = Z^{-1} \mathrm{e}^{-\beta(V(x) - \widetilde{V}(x))}\, dx$

• For nonequilibrium systems, the invariant measure depends non-trivially on the details of the dynamics and perturbations are non-local!

• For the dynamics $dx_t = \Big(-V'(x_t) + F \Big) dt + \sqrt{2}\, dW_t$ on $\mathbb{T}$,

$$\mu(dx) = Z^{-1} \mathrm{e}^{-V(x)+Fx} \left(\int_x^{x+1} \mathrm{e}^{V(y)-Fy}\, dy \right) dx$$

Linear response (1)

- Generator of the perturbed dynamics $\mathcal{L}_0 + \eta\mathcal{L}_1$, on $L^2(\psi_0)$ (where ψ_0 is the unique invariant measure of the dynamics generated by $\mathcal{L}_0$)
- Fokker-Planck equation: $(\mathcal{L}_0^* + \eta\mathcal{L}_1^*)\, f_\eta = 0$ with $\displaystyle\int f_\eta \psi_0 = 1$

Series expansion of the invariant measure $\psi_\eta = f_\eta \psi_0$

$$f_\eta = (\mathcal{L}_0^* + \eta\mathcal{L}_1^*)^{-1}\mathcal{L}_0^*\mathbf{1} = \left(1 + \sum_{n=1}^{+\infty} \eta^n \left[-\left(\mathcal{L}_0^*\right)^{-1}\mathcal{L}_1^*\right]^n\right)\mathbf{1}$$

- These computations can be made rigorous for η sufficiently small when...
  - (equilibrium) $\mathrm{Ker}(\mathcal{L}_0^*) = \mathbf{1}$ and $\mathcal{L}_0^*$ invertible on

$$\mathcal{H} = \left\{ f \in L^2(\psi_0) \,\middle|\, \int f\psi_0 = 0 \right\} = L^2(\psi_0) \cap \{\mathbf{1}\}^\perp$$

  - (perturbation) $\mathrm{Ran}(\mathcal{L}_1^*) \subset \mathcal{H}$ and $\left(\mathcal{L}_0^*\right)^{-1}\mathcal{L}_1^*$ bounded on $\mathcal{H}$, *e.g.* when $\|\mathcal{L}_1\varphi\|_{L^2(\psi_0)} \leqslant a\|\mathcal{L}_0\varphi\|_{L^2(\psi_0)} + b\|\varphi\|_{L^2(\psi_0)}$

Linear response (2)

- Response property $R \in \mathcal{H}$, conjugated response $S = \mathcal{L}_1^* \mathbf{1}$

Linear response from Green-Kubo type formulas

$$\alpha = \lim_{\eta \to 0} \frac{\langle R \rangle_\eta}{\eta} = -\int_{\mathcal{E}} \left[\mathcal{L}_0^{-1} R\right] \left[\mathcal{L}_1^* \mathbf{1}\right] \psi_0 = \int_0^{+\infty} \mathbb{E}\Big(R(x_t) S(x_0)\Big) dt$$

using the formal equality $-\mathcal{L}_0^{-1} = \displaystyle\int_0^{+\infty} \mathrm{e}^{t\mathcal{L}_0} \, dt$ (as operators on $\mathcal{H}$)

- Autocorrelation of R recovered for perturbations such that $\mathcal{L}_1^* \mathbf{1} \propto R$
- For general property: consider $\displaystyle\lim_{\eta \to 0} \frac{\langle R \rangle_\eta - \langle R \rangle_0}{\eta}$
- In practice:
  - Identify the response function
  - Construct a physically meaningful perturbation
  - Equivalent non physical perturbations ("Synthetic NEMD")

References

- **Some introductory references...**
  - L. Rey-Bellet, Open classical systems, *Lecture Notes in Mathematics*, **1881** (2006) 41–78
  - D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Cambridge University Press, 2008)
  - M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford, 2010)
  - G. Stoltz, *Molecular Simulation: Nonequilibrium and Dynamical Problems*, Habilitation Thesis (2012) [Chapter 3]

- And many reviews on **specific topics**! For instance, thermal transport in one dimensional systems

Example: Autodiffusion (1)

- Periodic potential V, constant external force F

$$\begin{cases} dq_t = M^{-1}p_t\,dt \\ dp_t = \Big(-\nabla V(q_t) + \eta F\Big)dt - \gamma M^{-1}p_t\,dt + \sqrt{\frac{2\gamma}{\beta}}\,dW_t \end{cases}$$

- In this case, $\mathcal{L}_1 = F \cdot \partial_p$ and so $\mathcal{L}_1^* \mathbf{1} = -\beta F \cdot M^{-1} p$
- Response: $R(q,p) = F \cdot M^{-1}p =$ average velocity in the direction F
- Linear response result:

Definition of the mobility

$$\nu_{F,\gamma} = \lim_{\eta \to 0} \frac{\left\langle F \cdot M^{-1}p \right\rangle_\eta}{\eta} = \beta \int_0^{+\infty} \mathbb{E}_{\mathrm{eq}}\Big((F \cdot M^{-1}p_t)(F \cdot M^{-1}p_0)\Big)\,dt$$

(Expectation over canonical initial conditions and realizations of the dynamics)

Example: Autodiffusion (2)

- Einstein formulation: diffusive time-scale for the equilibrium dynamics

Definition of the diffusion

$$F^T D F = \lim_{T \to +\infty} \frac{\mathbb{E}_{\mathrm{eq}}\left[\left(F \cdot (q_T - q_0)\right)^2\right]}{2T}$$

- Relation between mobility and diffusion

$$\nu_{F,\gamma} = \beta\, F^T D F$$

since $\displaystyle \frac{\mathbb{E}\left[\left(F \cdot (q_T - q_0)\right)^2\right]}{2T} = \int_0^T \mathbb{E}\Big((F \cdot M^{-1} p_t)(F \cdot M^{-1} p_0)\Big)\left(1 - \frac{t}{T}\right) dt$

- Various extensions:
  - Random forcings
  - Space-time dependent[12] forcings $F(t,q)$

[12] R. Joubaud, G. Pavliotis and G. Stoltz, *J. Stat. Phys* (2014)

Example: Autodiffusion (3)

- Diffusive rescaling on the dynamics not reprojected into the periodic cell
  - introduce $Q_t = q_0 + \int_0^t M^{-1} p_s \, ds \in \mathbb{R}^d$
  - equilibrium initial conditions $(q_0, p_0) \sim \psi_0(q,p)\, dq\, dp$
  - rescale as $Q_t^\varepsilon = \varepsilon Q_{t/\varepsilon^2}$ for $\varepsilon > 0$

Weak convergence to an effective Brownian motion

As $\varepsilon \to 0$, the process Q_t^ε weakly converges over finite time intervals to the Brownian motion

$$d\overline{Q}_t = \sqrt{2}\, D^{1/2}\, dB_t$$

with initial conditions $\overline{Q}_0 \sim Z^{-1} \mathrm{e}^{-\beta V(q)}\, dq$.

Proof: consider $\mathcal{L}_0^{-1} \Phi_F = F^T M^{-1} p$. The function Φ_F and its derivatives are growing at most polynomially by subelliptic estimates à la Talay. By Itô calculus, $d\Phi_F(q_s) = \mathcal{L}\Phi_F(q_s) + \sqrt{\frac{2\gamma}{\beta}}\, \nabla\Phi_F(q_s) \cdot dW_s$, which shows that $F^T Q_t = \Phi_F(q_t) - \Phi_F(q_0) + \mathcal{M}_{F,t}$, with the martingale $\mathcal{M}_{F,t} = \sqrt{\frac{2\gamma}{\beta}} \int_0^t \nabla\Phi_F(q_s) dW_s$. By the martingale central limit theorem, $\varepsilon \mathcal{M}_{F,t/\varepsilon^2}$ converges to $\frac{2\gamma}{\beta} \int_{\mathcal{E}} |\nabla \Phi_F|^2 \, \psi_0$, which can be shown to be equal to $2F^T D F$.

Error estimates on the Green-Kubo formula

Assume $\dfrac{P_{\Delta t} - \mathrm{Id}}{\Delta t} = \mathcal{L} + \Delta t S_1 + \cdots + \Delta t^{\alpha-1} S_{\alpha-1} + \Delta t^{\alpha} \widetilde{R}_{\alpha,\Delta t}$ and

$$\left\| \left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t} \right)^{-1} \right\|_{\mathcal{B}(L^\infty_W)} \leqslant C, \qquad \int_{\mathcal{E}} \psi \, d\mu_{\Delta t} = \int_{\mathcal{E}} \psi \, d\mu + \Delta t^{\alpha} r_{\psi,\Delta t}$$

Error estimates on the Green-Kubo formula

For ψ, φ with average 0 w.r.t. μ,

$$\int_0^{+\infty} \mathbb{E}\Big(\psi(q_t,p_t)\varphi(q_0,p_0)\Big) dt = \Delta t \sum_{n=0}^{+\infty} \mathbb{E}_{\Delta t}\Big(\widetilde{\psi}_{\Delta t}\left(q^n,p^n\right) \varphi\left(q^0,p^0\right)\Big) + \mathrm{O}(\Delta t^{\alpha})$$

with $\widetilde{\psi}_{\Delta t} = \Big(\mathrm{Id} + \Delta t \, S_1 \mathcal{L}^{-1} + \cdots + \Delta t^{\alpha-1} S_{\alpha-1} \mathcal{L}^{-1}\Big)\psi - \mu_{\Delta t}(\dots)$

- Reduces to trapezoidal rule for second order schemes

Error estimates on linear response

• Splitting schemes obtained by replacing B with $B_\eta = B + \eta F \cdot \nabla_p$
$\rightarrow$ invariant measures $\mu_{\gamma,\eta,\Delta t}$

• For instance, $P_{\Delta t}^{A,B+\eta\widetilde{\mathcal{L}},\gamma C}$ for $\begin{cases} q^{n+1} = q^n + \Delta t\, p^n, \\ \widetilde{p}^{n+1} = p^n + \Delta t\Big(-\nabla V(q^{n+1}) + \eta F \Big), \\ p^{n+1} = \alpha_{\Delta t} \widetilde{p}^{n+1} + \sqrt{\dfrac{1-\alpha_{\Delta t}^2}{\beta}}\, G^n \end{cases}$

• Discard schemes obtained by replacing C with $C + \eta F \cdot \nabla_p$ since they do not perform well in the overdamped limit

• Recall that the mobility is defined as

$$\nu_{F,\gamma} = \lim_{\eta \to 0} \frac{1}{\eta} \int_{\mathcal{E}} F^T M^{-1} p \, \mu_{\gamma,\eta}(dq\,dp) = \int_{\mathcal{E}} F^T M^{-1} p \, f_{0,1,\gamma}(q,p)\, \mu(dq\,dp)$$

where the correction function satisfies $\mathcal{L}^* f_{0,1,\gamma} = -\beta F^T M^{-1} p$

Error estimates on the mobility

Error estimates for nonequilibrium dynamics

There exists a function $f_{\alpha,1,\gamma} \in H^1(\mu)$ such that

$$\int_{\mathcal{E}} \psi \, d\mu_{\gamma,\eta,\Delta t} = \int_{\mathcal{E}} \psi \Big(1 + \eta f_{0,1,\gamma} + \Delta t^\alpha f_{\alpha,0,\gamma} + \eta \Delta t^\alpha f_{\alpha,1,\gamma} \Big) d\mu + r_{\psi,\gamma,\eta,\Delta t},$$

where the remainder is compatible with linear response

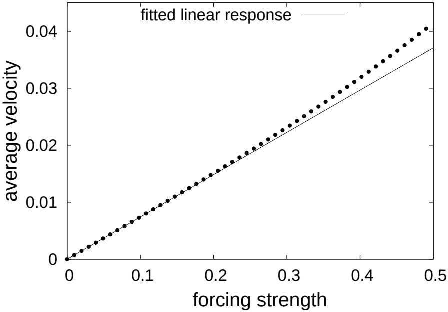
$$|r_{\psi,\gamma,\eta,\Delta t}| \leqslant K(\eta^2 + \Delta t^{\alpha+1}), \qquad |r_{\psi,\gamma,\eta,\Delta t} - r_{\psi,\gamma,0,\Delta t}| \leqslant K\eta(\eta + \Delta t^{\alpha+1})$$

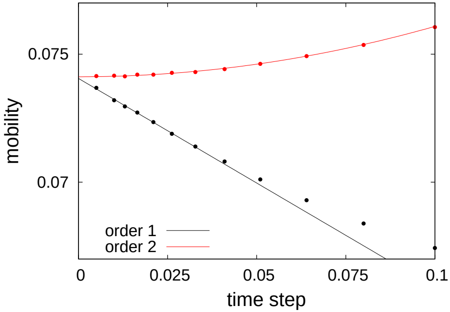
- Corollary: error estimates on the numerically computed mobility

$$\nu_{F,\gamma,\Delta t} = \lim_{\eta \to 0} \frac{1}{\eta} \left(\int_{\mathcal{E}} F^T M^{-1} p \, \mu_{\gamma,\eta,\Delta t}(dq\,dp) - \int_{\mathcal{E}} F^T M^{-1} p \, \mu_{\gamma,0,\Delta t}(dq\,dp) \right)$$
$$= \nu_{F,\gamma} + \Delta t^\alpha \int_{\mathcal{E}} F^T M^{-1} p \, f_{\alpha,1,\gamma} \, d\mu + \Delta t^{\alpha+1} r_{\gamma,\Delta t}$$

- Results in the overdamped limit, possibly with superimposed Metropolis procedure (SmartMC)

Numerical results





Left: Linear response of the average velocity as a function of η for the scheme associated with $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$ and $\Delta t = 0.01, \gamma = 1$.

Right: Scaling of the mobility $\nu_{F,\gamma,\Delta t}$ for the first order scheme $P_{\Delta t}^{A, B_\eta, \gamma C}$ and the second order scheme $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$.

A list of topics I haven't mentioned...

- Sampling other thermodynamic ensembles
  - NVE by discretization of Hamiltonian dynamics
  - NPT, μVT, etc
- Variance reduction techniques
- Computation of free energy differences
- Sampling of reactive trajectories (metastability)
- Coupling MD with
  - finer scales (QM/MM)
  - coarser scales (DPD, SPH, etc)
- Developping better potential energy functions (electrostatics, polarizability, etc)