Long time averaging for molecular dynamics simulations in the NVT ensemble

Frédéric Legoll

Ecole Nationale des Ponts et Chaussées

`http://cermics.enpc.fr/~legoll/`

Joint work with Eric Cancès, Gabriel Stoltz (CERMICS, ENPC), Mitchell Luskin and Richard Moeckel (U of Minnesota, Minneapolis)

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Description of a classical system

- Microscopic description of a classical system of M particles:

$$(q,p) = (q_1,\dots,q_M,\ p_1,\dots,p_M) \in \mathbb{R}^{6M}$$

- System energy: $$H(q,p) = \sum_{i=1}^{M} \frac{p_i^2}{2m_i} + V(q_1,\dots,q_M)$$

- Thermodynamical properties (pressure, elastic constants, ...):

$$\langle A \rangle = \int_{\Omega \times \mathbb{R}^{3M}} A(q,p)\, d\mu(q,p)$$

To reproduce experimental results at a given temperature, we choose

$$d\mu = Z^{-1}\ \exp(-\beta H(q,p))\, dq\, dp, \quad \beta = 1/(k_B T)$$

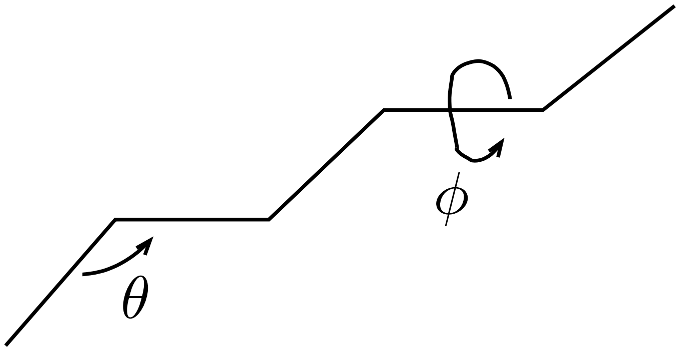
that is, we work in the canonical (NVT, “constant temperature”) ensemble.

Observables

$$\langle A \rangle = \int_{\Omega \times \mathbb{R}^{3M}} A(q,p)\, d\mu(q,p)$$

Examples of observable A:

- Pressure: $A(q,p) = \dfrac{1}{3|\Omega|} \displaystyle\sum_{i=1}^{M} \left(\dfrac{p_i^2}{m_i} - q_i \cdot \nabla_{q_i} V(q) \right)$
- Temperature: $A(q,p) = \dfrac{1}{3M} \displaystyle\sum_{i=1}^{M} \dfrac{p_i^2}{m_i}; \qquad \langle A \rangle_{NVT} = k_B T$.
- End-to-end distance in a linear molecule: $A(q,p) = |q_M - q_1|$.



$A(q,p)$ and $d\mu(q,p)$ are given by physics.

Question: how to compute $\langle A \rangle = \displaystyle\int A(q,p)\, d\mu(q,p)$?

Difficulty: high dimension: $(q,p) \in \Omega \times \mathbb{R}^{3M} \subset \mathbb{R}^{6M}$ with $M \geq 10^5$

- Monte Carlo methods: draw i.i.d. points (q^n, p^n) according to the measure $d\mu$ and make the approximation

$$\langle A \rangle \approx \frac{1}{N} \sum_{n=1}^{N} A(q^n, p^n) \qquad \text{(Law of large numbers)}$$

- (q^n, p^n) is a realization of a Markov chain that leaves $d\mu$ invariant.

- Molecular dynamics methods.

- Find a dynamics for which $d\mu$ is invariant (and that could be ergodic!);
- Compute the flow $(q(t), p(t))$ of the dynamics
- Ergodic assumption: $\langle A \rangle = \lim_{T\to\infty} \frac{1}{T} \int_0^T A(q(t), p(t))\,dt$
- Numerical discretization: $\langle A \rangle \approx \frac{1}{N} \sum_{n=1}^{N} A(q^n, p^n)$

2 types of methods:

– (q^n, p^n) is an approximation of the flow $(q(t), p(t))$ of a deterministic ODE;

– (q^n, p^n) is an approximation of the flow (q_t, p_t) of a stochastic process;

Outline of the talk

$$\langle A \rangle = \frac{1}{Z} \int_{\Omega \times \mathbb{R}^{3M}} A(q,p)\, e^{-\beta H(q,p)}\, dq\, dp \approx \frac{1}{N} \sum_{n=1}^{N} A(q^n, p^n) \quad ?$$

- Description of several methods to sample phase space according to $d\mu$. Theoretical question:

$$\lim_{N \to \infty} \frac{1}{N} \sum_{n=1}^{N} A(q^n, p^n) = \langle A \rangle \quad ?$$

- On the non-ergodicity of some deterministic ODE used in molecular dynamics.

What dynamics to sample $d\mu$?

$$\frac{1}{Z} \int_{\Omega \times \mathbb{R}^{3M}} A(q,p)\, e^{-\beta H(q,p)}\, dq\, dp \approx \frac{1}{N} \sum_{n=1}^{N} A(q^n, p^n)$$

Hamiltonian dynamics (Newton equations):

$\rightarrow$ energy is preserved, so no chance to sample $\dfrac{1}{Z}\exp(-\beta H(q,p))dqdp$.

Need for

- a deterministic system on an extended phase space,
- or stochastic perturbations.

The Nosé-Hoover dynamics (Nosé 1985, Hoover 1985)

Nosé-Hoover: introduce heat bath described by $\xi \in \mathbb{R}$ and postulate

$$\dot{q}_i = \frac{p_i}{m_i}, \qquad \dot{p}_i = -\nabla_{q_i} V(q) - \frac{p_i \xi}{Q}, \qquad i = 1, \dots, M$$

$$\dot{\xi} = \sum_{i=1}^{M} \frac{p_i^2}{m_i} - \frac{3M}{\beta}. \qquad Q \text{ is a free parameter.}$$

This dynamics preserves $d\rho^{\mathrm{NH}} = \exp\left(-\beta\left[H(q,p) + \frac{\xi^2}{2Q}\right]\right) dq\, dp\, d\xi.$

IF the dynamics is ergodic with respect to $d\rho^{\mathrm{NH}}$, then

$$\begin{aligned} \lim_{T\to\infty} \frac{1}{T}\int_0^T A(q(t),p(t))\, dt &= \int A(q,p)\, d\rho^{\mathrm{NH}} \\ &= \frac{1}{Z}\int A(q,p)\; \exp(-\beta H(q,p))\, dq\, dp \end{aligned}$$

and Nosé-Hoover samples the canonical measure!

Ergodicity (i.e. sampling properties) of the Nosé-Hoover dynamics: not guaranteed (see later).

Generalizations:

- Nosé-Hoover Chain method (Martyna, Klein, Tuckerman 1992).
- Thermalization of each dof by its own Nosé-Hoover chain (Tuckerman et al 2004)
- Hamiltonian formulations (Leimkuhler et al, 1999, 2005, . . .)
- . . .

A common feature of all these methods: ergodicity of these ODE is a fundamental assumption that has not been proved.

The Langevin dynamics

$$dq_i = \frac{p_i}{m_i}\,dt, \qquad dp_i = \left(-\nabla_{q_i} V(q) - \xi \frac{p_i}{m_i} \right) dt + \sigma\, dW_i$$

Fluctuation-dissipation relation: if $\sigma = \sqrt{2\xi/\beta}$, then

$$d\mu(q,p) = \frac{1}{Z} \exp\left(-\beta H(q,p)\right) dq dp \quad \text{is an invariant measure}$$

Continuous-in time level: well-understood. Under standard assumptions (V regular enough), convergence along a single path:

For μ-almost all starting points $x = (q^0, p^0)$, and for any $A \in L^1(\mu)$,

$$\lim_{T\to\infty} \frac{1}{T} \int_0^T A(q_t^x, p_t^x)\, dt = \int_{\Omega\times\mathbb{R}^{3M}} A(q,p) d\mu(q,p) \quad \text{almost surely}$$

Configuration space sampling

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

$$d\mu = \underbrace{\frac{1}{Z_q}\,\exp(-\beta V(q))\,dq}_{d\pi(q)=f(q)\,dq}\;\underbrace{\frac{1}{Z_p}\,\exp(-\beta\sum_{i=1}^{M}\frac{p_i^2}{2m_i})\,dp}_{d\kappa(p)=\mathcal{P}(p)\,dp}$$

It is easy to sample according to $d\kappa(p) = \mathcal{P}(p)\,dp$.

Problem: sample points in Ω according to density $f(q)$.

Design a “dynamics” on q such that the numerical flow $(q^n)_{n\geq 1}$ satisfies

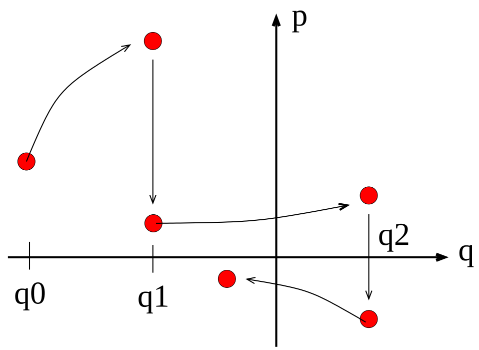
$$\lim_{N\to\infty} \frac{1}{N}\sum_{n=1}^{N} A(q^n) = \int_{\Omega} A(q)d\pi(q)$$

Several methods to sample $Z_q^{-1} \exp(-\beta V(q))\, dq$

- Stochastic DE: biased random-walk:

$$dq_i = -\nabla_{q_i} V(q)\, dt + \sqrt{2/\beta}\, dW_i$$

- Markov chain: Hybrid Monte Carlo (HMC) method, Duane et al. 1987, Schuette et al. 1999.



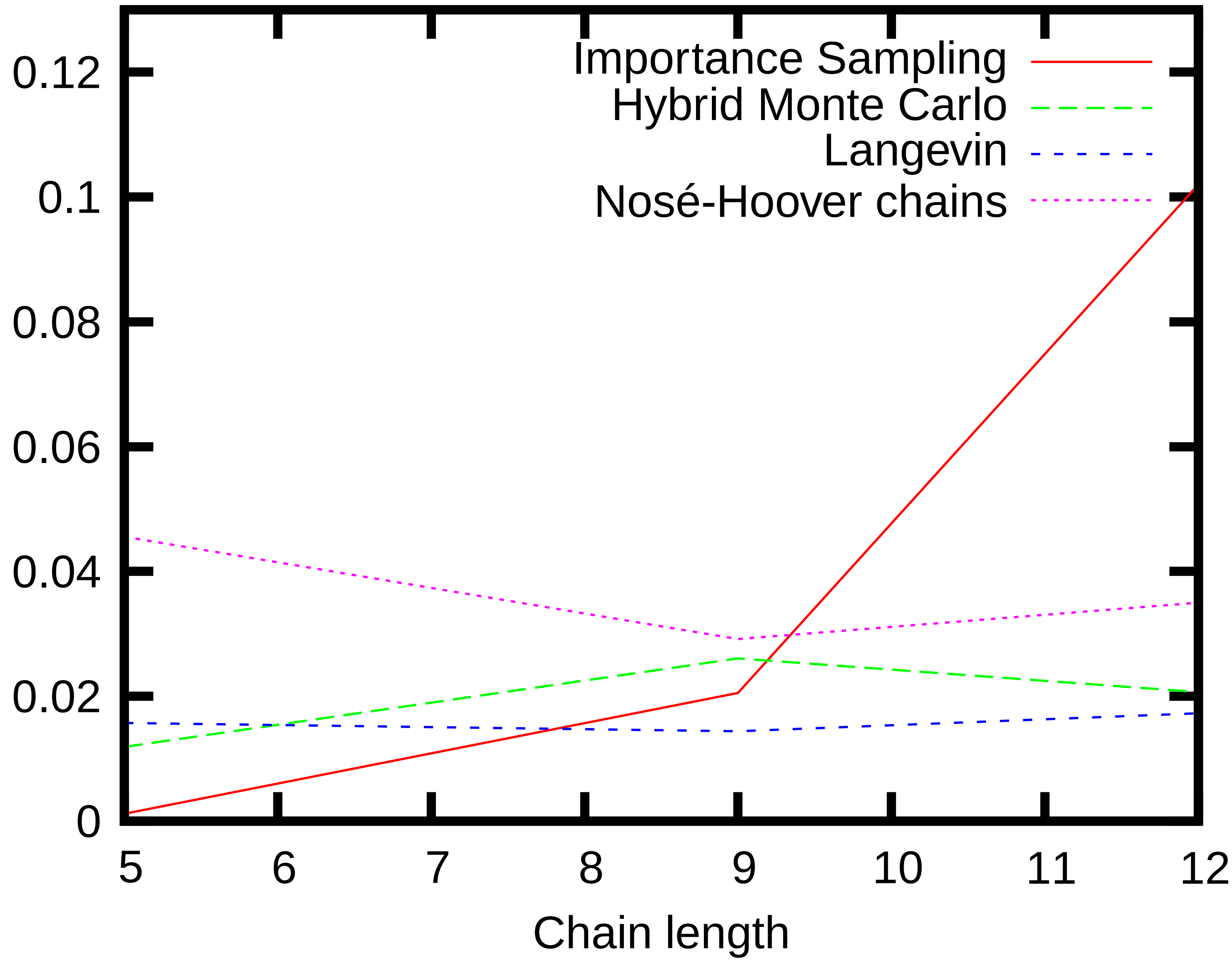
- purely stochastic methods such as importance sampling, . . .

Summary of theoretical properties

	Type	Convergence
Nosé-Hoover	ODE	Open
Langevin	Markov Process	ok
Hybrid Monte Carlo	Markov Chain	ok
Importance Sampling	ind. identically dist.	ok

E. Cancès, F. L., G. Stoltz, *Theoretical and numerical comparison of some sampling methods for molecular dynamics*, preprint IMA April 2005 (# 2040), submitted to M2AN:
Comparison of the numerical efficiency of the different methods (ODE, SDE, Markov chains, purely stochastic methods).

Efficiency of the method as the size of the system increases ($M = 5; 9; 12$)



$$\dot{q}_i = \frac{p_i}{m_i}, \qquad \dot{p}_i = -\nabla_{q_i} V(q) - \frac{p_i \xi}{Q}, \qquad \dot{\xi} = \sum_{i=1}^{M} \frac{p_i^2}{m_i} - \frac{3M}{\beta}.$$

The relation

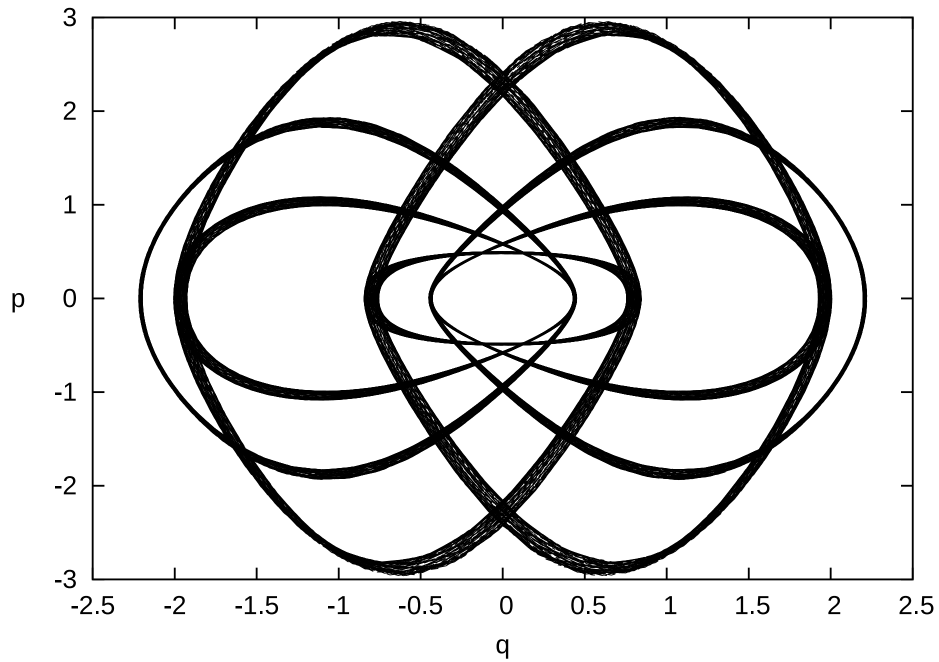
$$\lim_{T\to\infty} \frac{1}{T} \int_0^T A(q(t), p(t))\, dt = \frac{1}{Z} \int A(q,p)\; \exp(-\beta H(q,p))\, dq\, dp$$

is based on the dynamics being ergodic for

$$d\rho^{\mathrm{NH}} = \exp\left(-\beta\left[H(q,p) + \frac{\xi^2}{2Q}\right]\right) dq\, dp\, d\xi.$$

The ergodicity is believed to hold for “complex enough” systems. For simple systems, the situation is different. There is numerical evidence that it does not hold for the harmonic oscillator (Hoover, 1985).

$$\dot{q} = p, \qquad \dot{p} = -q - \frac{p\xi}{Q}, \qquad \dot{\xi} = p^2 - 1.$$



We observe that $0 < c \leq q^2(t) + p^2(t) \leq C$. Hence, for A supported on $B_0(c)$,

$$\lim_{T\to\infty} \frac{1}{T} \int_0^T A(q(t), p(t))\, dt \neq \frac{1}{Z} \int A(q,p)\ \exp(-\frac{1}{2}(q^2 + p^2))\, dq\, dp$$

We will explain this phenomenon in the limit $Q \to +\infty$ (for infinite times, the result is not trivial!).

$$\dot{q} = p, \qquad \dot{p} = -q - \frac{p\xi}{Q}, \qquad \dot{\xi} = p^2 - 1.$$

Introduce action-angle variables $q = \sqrt{2\hat{\tau}}\cos\theta$ and $p = -\sqrt{2\hat{\tau}}\sin\theta$ and rescale according to $\hat{\alpha} = \epsilon\xi$ with $\epsilon = 1/\sqrt{Q}$:

$$\left\{\begin{array}{rcl} \dot{\theta} & = & 1 - \epsilon\hat{\alpha}\sin\theta\cos\theta, \\ \dot{\hat{\tau}} & = & -2\epsilon\hat{\tau}\hat{\alpha}\sin^2\theta, \\ \dot{\hat{\alpha}} & = & \epsilon(2\hat{\tau}\sin^2\theta - 1). \end{array}\right. \Longrightarrow \left\{\begin{array}{rcl} \dot{\theta} & = & 1 - \epsilon\alpha\sin\theta\cos\theta + O(\epsilon^2), \\ \dot{\tau} & = & -\epsilon\tau\alpha + O(\epsilon^2), \\ \dot{\alpha} & = & \epsilon(\tau - 1) + O(\epsilon^2). \end{array}\right.$$

with $\hat{\tau} = \tau + \epsilon\tau\alpha\sin\theta\cos\theta$ and $\hat{\alpha} = \alpha - \epsilon\tau\sin\theta\cos\theta$ (averaging).

These systems preserve the measure $d\Omega = e^{-\hat{\tau} - \hat{\alpha}^2/2}\, d\theta\, d\hat{\tau}\, d\hat{\alpha}$.

Consider

$$(*)\begin{cases}\dot\theta &= 1-\epsilon\alpha\sin\theta\cos\theta+O(\epsilon^2),\\ \dot\tau &= -\epsilon\tau\alpha+O(\epsilon^2),\\ \dot\alpha &= \epsilon(\tau-1)+O(\epsilon^2).\end{cases} \quad \text{and } (**)\begin{cases}\dot\theta &= 1-\epsilon\alpha\sin\theta\cos\theta,\\ \dot\tau &= -\epsilon\tau\alpha,\\ \dot\alpha &= \epsilon(\tau-1).\end{cases}$$

For times $t=O(1/\epsilon)$, the solution of $(*)$ is ϵ-close to the solution of $(**)$.
We observe that $G(\tau,\alpha)=\tau-\ln\tau+\frac{1}{2}\alpha^2-1$ is preserved by $(**)$.

For $t=O(1/\epsilon)$, the trajectory of $(*)$ is such that

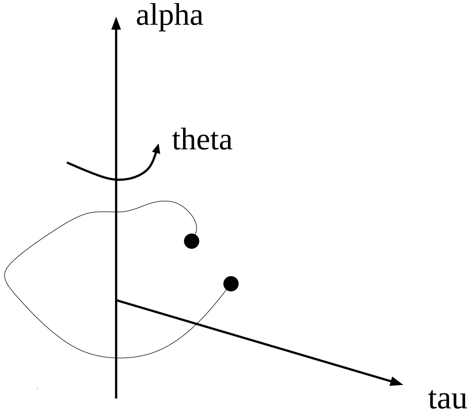
$$g_0-O(\epsilon)\le G(\tau(t),\alpha(t))\le g_0+O(\epsilon)$$

$$\text{so}\quad \tau(t)-\ln\tau(t)\le g_0+1+O(\epsilon)\quad\Longrightarrow\quad 0<c\le\tau(t)\le C.$$

This implies bounds such as $0<c\le q^2(t)+p^2(t)\le C$.

Let $P_\epsilon(\tau, \alpha)$ be the Poincaré return map of the plane $\Sigma = \{(\theta, \tau, \alpha) : \theta = 0[2\pi]\}$ of

$$(*) \begin{cases} \dot{\theta} &= 1 - \epsilon\alpha \sin\theta \cos\theta + O(\epsilon^2), \\ \dot{\tau} &= -\epsilon\tau\alpha + O(\epsilon^2), \\ \dot{\alpha} &= \epsilon(\tau - 1) + O(\epsilon^2). \end{cases}$$

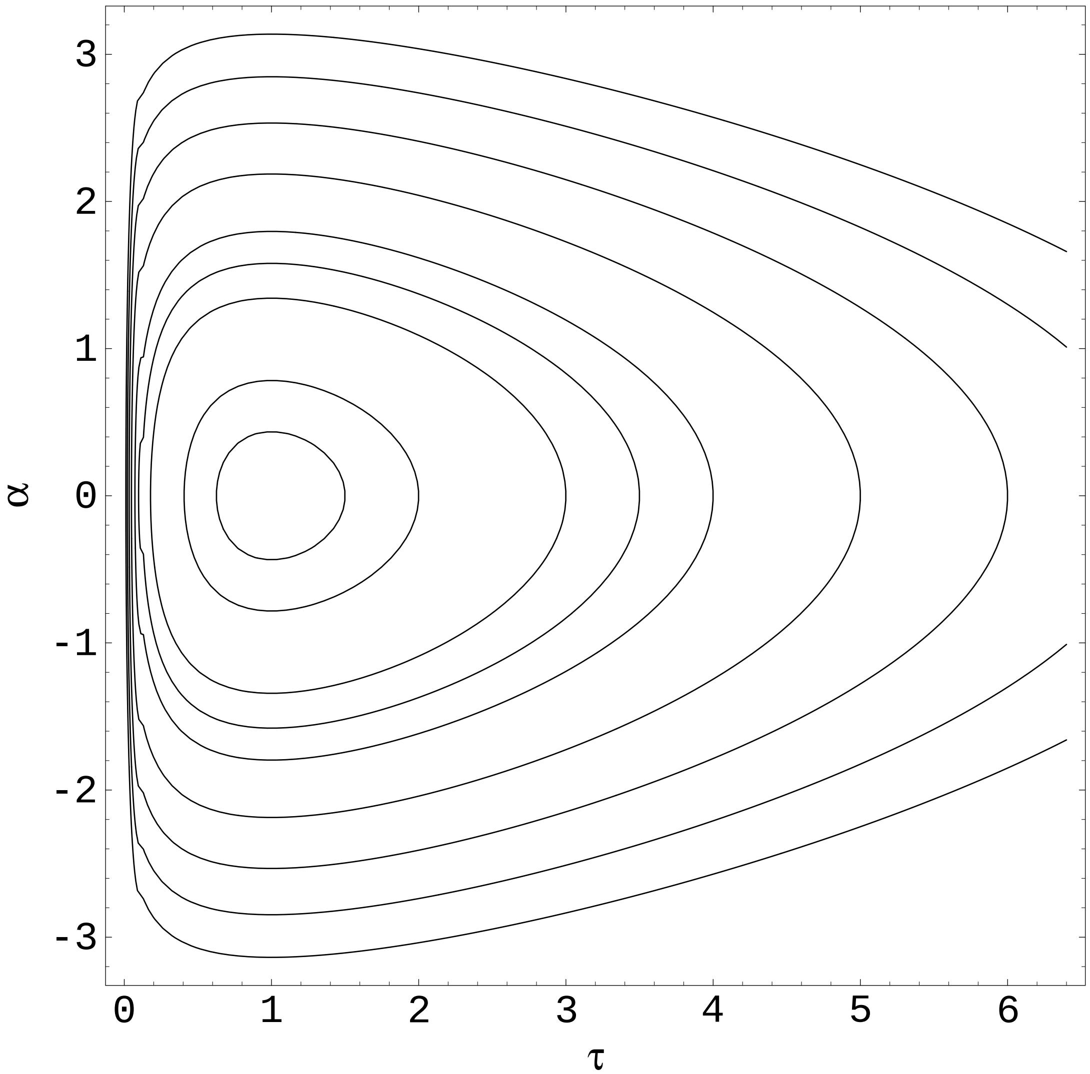


Let $Q_\epsilon(\tau, \alpha)$ be the 2π advance map of

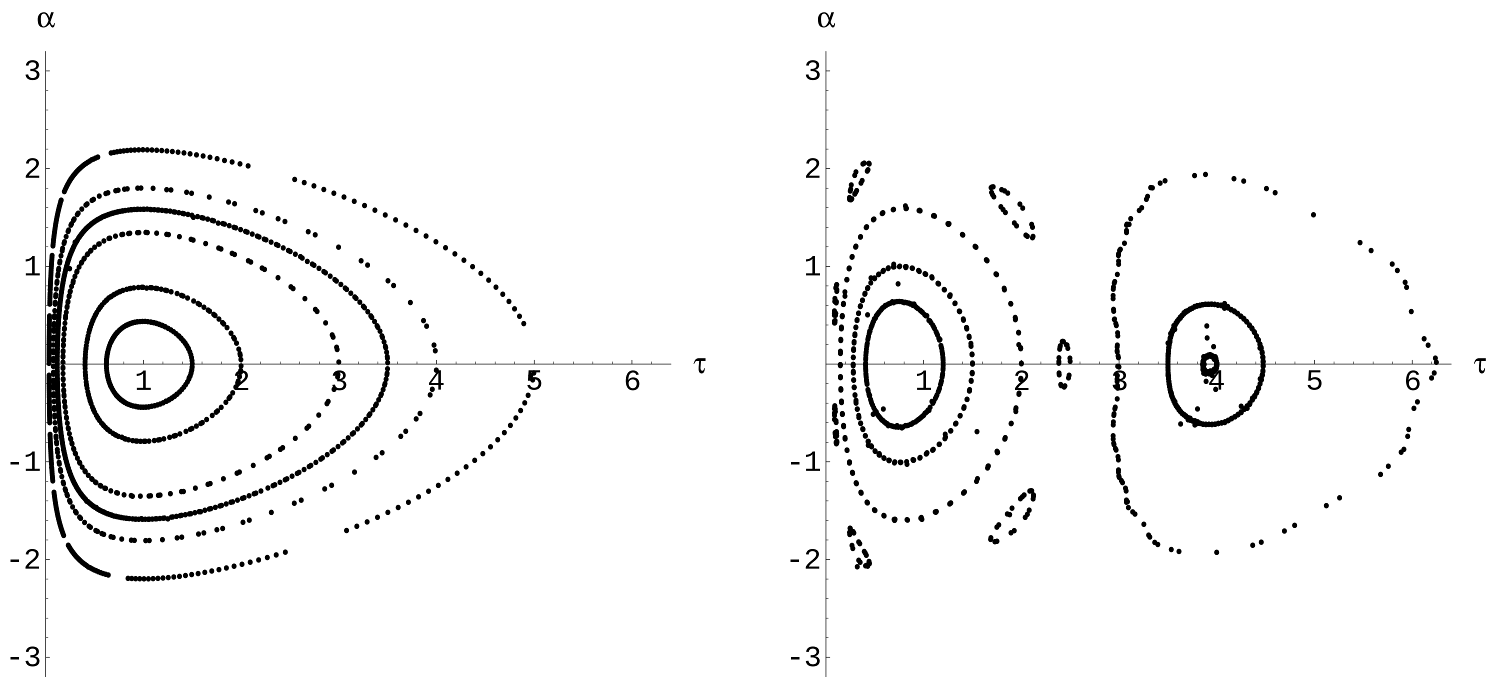
$$(***) \begin{cases} \dot{\tau} &= -\epsilon\tau\alpha, \\ \dot{\alpha} &= \epsilon(\tau - 1). \end{cases}$$

We have $P_\epsilon(\tau, \alpha) = Q_\epsilon(\tau, \alpha) + O(\epsilon^2)$ and $Q_\epsilon(\tau, \alpha)$ has invariant curves defined by $G(\tau, \alpha) = g_0$.

Invariant curves of $Q_\epsilon(\tau, \alpha)$



Computed Poincaré return map $P_\epsilon(\tau, \alpha)$ ($\epsilon = 0.1$ and 1.0)



If $P_\epsilon(\tau, \alpha)$ has invariant curves, then the dynamics in (θ, τ, α) is not ergodic.

We now show that the map $P_\epsilon(\tau, \alpha)$ has invariant curves.
$\rightarrow$ Main tool: $P_\epsilon(\tau, \alpha)$ is a perturbation of $Q_\epsilon(\tau, \alpha)$ and Moser invariant curve theorem.

Change of variables

We have $P_\epsilon(\tau,\alpha) = Q_\epsilon(\tau,\alpha) + O(\epsilon^2)$ and $Q_\epsilon(\tau,\alpha)$ is the 2π advance map of

$$(***) \qquad \dot{\tau} = -\epsilon\tau\alpha, \qquad \dot{\alpha} = \epsilon(\tau - 1).$$

We see that $(1,0)$ is a fixed point of Q_ϵ. Let us introduce coordinates (G,ϕ), where $G(\tau,\alpha)$ is the invariant of Q_ϵ. The variable ϕ is defined such that $(***)$ reads

$$\dot{G} = 0, \qquad \dot{\phi} = 2\pi/T(G).$$

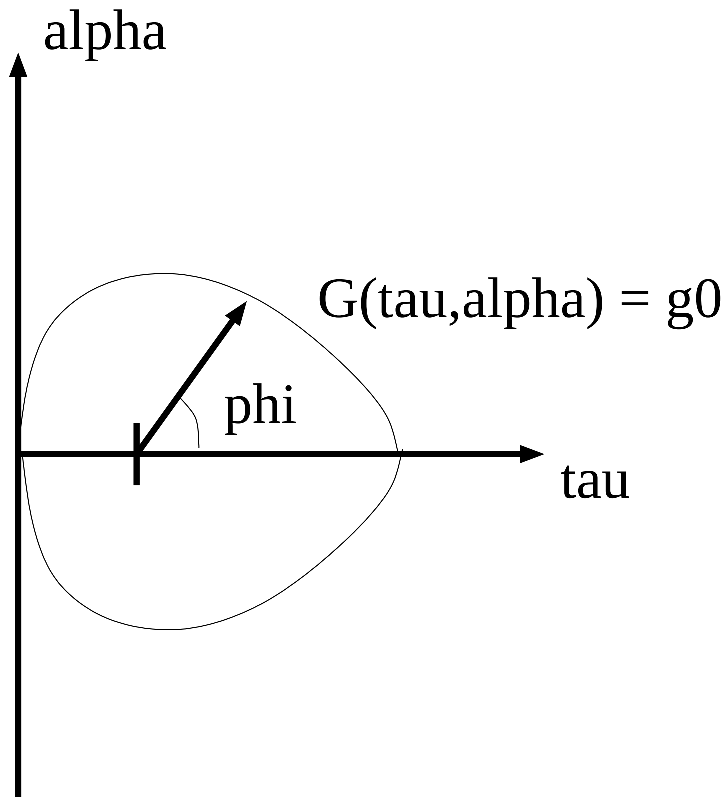
Then $P_\epsilon(G,\phi) = (G_1,\phi_1)$ with

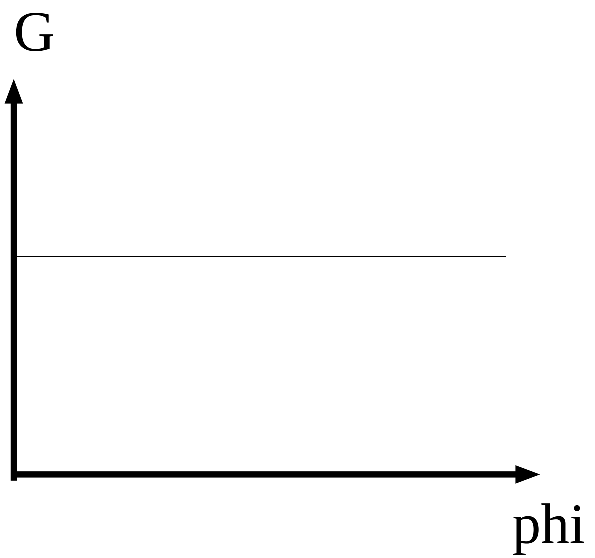
$$(G_1,\phi_1) = Q_\epsilon(G,\phi) + O(\epsilon^2) = (G, \phi + 2\pi\epsilon/T(G)) + O(\epsilon^2)$$

So

$$\begin{cases} G_1 &= G + \epsilon^2 f(\epsilon, G, \phi), \\ \phi_1 &= \phi + 2\pi\epsilon/T(G) + \epsilon^2 g(\epsilon, G, \phi). \end{cases}$$

The map Q_ϵ in variables (τ, α) and (G, ϕ)





Moser invariant curve theorem

The map $P_\epsilon : (G,\phi) \mapsto (G_1,\phi_1)$ is such that:
– it satisfies a twist condition since $T'(G) \neq 0$;
– it satisfies the curve intersection property, that is $P_\epsilon(C) \cap C \neq \emptyset$ for any closed curve in $[0,+\infty) \times [0,2\pi]$. Indeed, P_ϵ is the Poincaré map return of the dynamics $(*)$ which preserves the measure $d\Omega = e^{-\hat\tau-\hat\alpha^2/2}\, d\theta\, d\hat\tau\, d\hat\alpha$. So P_ϵ preserves a measure, which reads here $e^{-\hat\tau-\hat\alpha^2/2}\, d\hat\tau\, d\hat\alpha$.

It is thus of the form

$$\begin{cases} y_1 &= y + g(x,y) \\ x_1 &= x + \gamma\, y + f(x,y), \end{cases}$$

with $\gamma \neq 0$, and f and g small ($y \equiv G$ and $x \equiv \phi$).

We can now apply Moser invariant curve theorem. We obtain that, if ϵ is small enough, P_ϵ has infinitely many invariant curves, close to the level curves $G(\tau,\alpha) = g_0$.

Conclusions

Several methods are available to compute averages with respect to the canonical measure $d\mu = Z^{-1} \exp(-\beta H(q,p)) \, dq \, dp$:

- the purely stochastic methods quickly loose their efficiency as the system size increases;
- methods based on SDEs, such as the Langevin method, perform very well.

Deterministic methods such as Nosé-Hoover or its generalizations are very popular. They seem to provide good results on complex systems. However, some care is required:

- there are many numerical reports of bad behaviour for the harmonic oscillator case;
- we have been able to rigorously explain these bad results.

F. L., M. Luskin, R. Moeckel, *Non-ergodicity of the Nose-Hoover Thermostatted Harmonic Oscillator*, arXiv preprint (November 2005, math.DS/0511178), accepted in Archives for Rational Mechanics and Analysis.