

# *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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- **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.

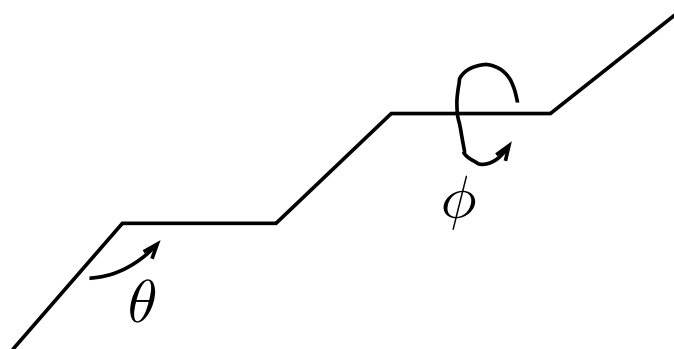
$$\langle A \rangle = \int_{\Omega \times \mathbb{R}^{3M}} A(q, p) d\mu(q, p)$$

Examples of observable  $A$ :

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

- Temperature:  $A(q, p) = \frac{1}{3M} \sum_{i=1}^M \frac{p_i^2}{m_i}; \quad \langle A \rangle_{NVT} = k_B T.$

- 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  $\langle A \rangle = \int A(q, p) d\mu(q, p)$  ?

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

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

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

# Molecular dynamics to compute $\int A(q, p) d\mu(q, p)$

- 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:  $\langle A \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(q(t), p(t)) dt$
- 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;

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

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

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

- 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):

→ **energy is preserved**, so no chance to sample  $\frac{1}{Z} \exp(-\beta H(q, p)) dq dp$ .

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**

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

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

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

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

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

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.

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

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

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

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

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

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

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

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

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

Problem: **sample points in  $\Omega$  according to density  $f(q)$ .**

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

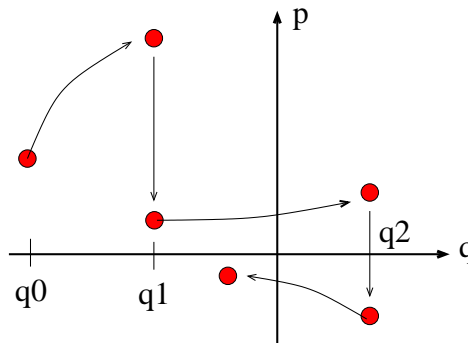
$$\lim_{N \rightarrow \infty} \frac{1}{N} \sum_{n=1}^N A(q^n) = \int_{\Omega} A(q) d\pi(q)$$

# 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, ...

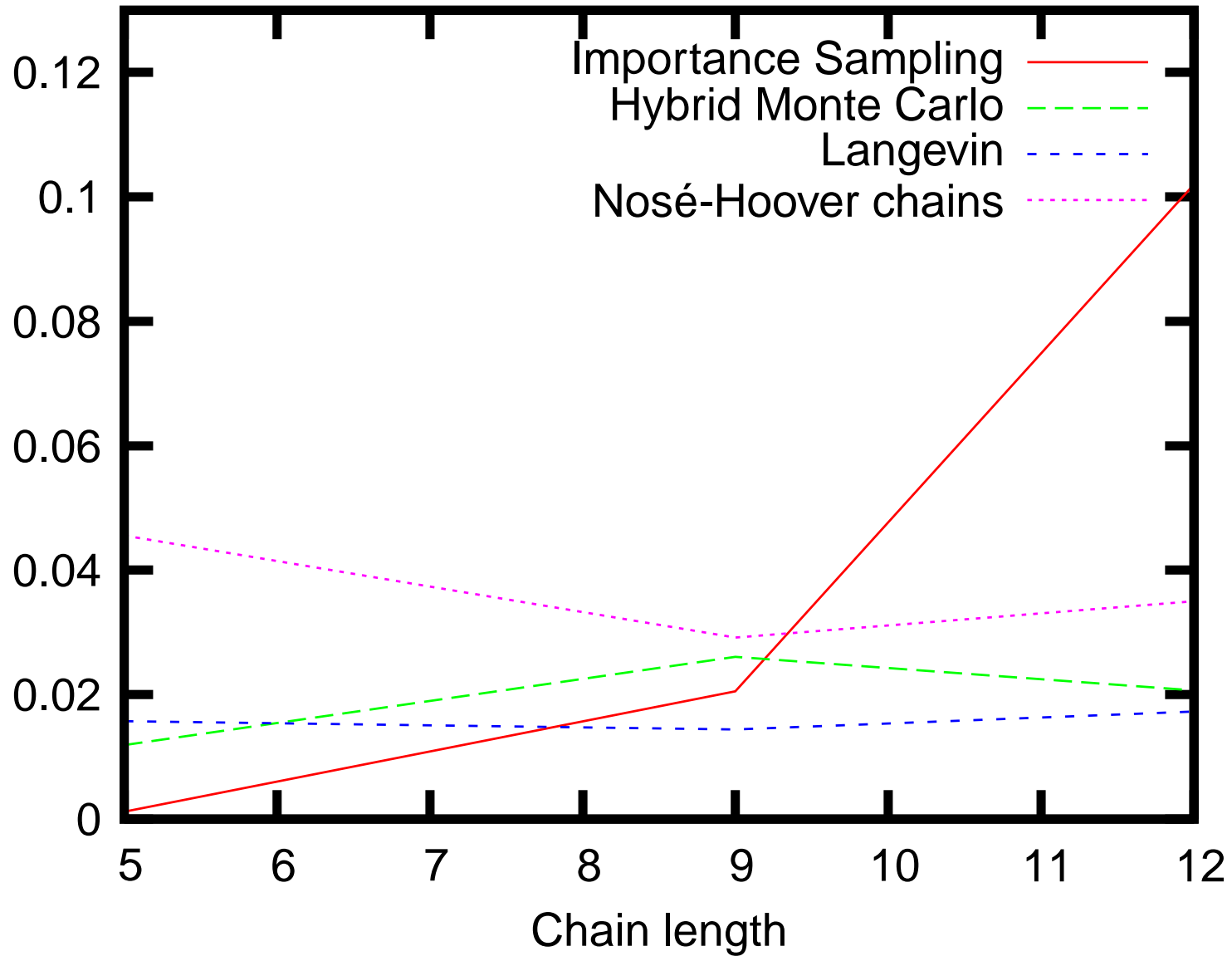
## Summary of theoretical properties

	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 ( $M = 5; 9; 12$ )*



## Back to the ergodicity of Nosé-Hoover

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

The relation

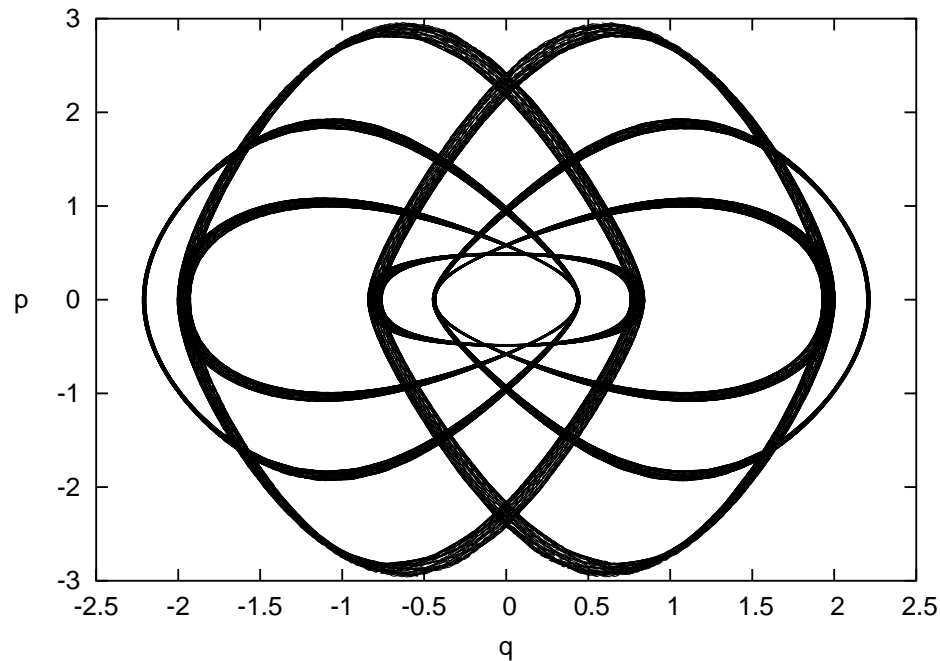
$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(q(t), p(t)) dt = \frac{1}{Z} \int A(q, p) \exp(-\beta H(q, p)) dq dp$$

is based on the dynamics being ergodic for

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

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).

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



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

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



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

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

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  $\epsilon = 1/\sqrt{Q}$ :

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

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  $\epsilon$ -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

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

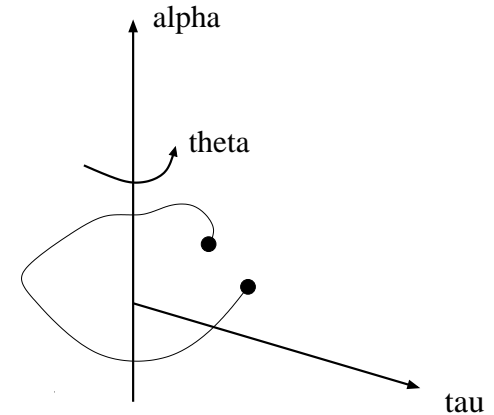
$$\text{so } \tau(t) - \ln \tau(t) \leq g_0 + 1 + O(\epsilon) \implies 0 < c \leq \tau(t) \leq C.$$

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

# Poincaré return map

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

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

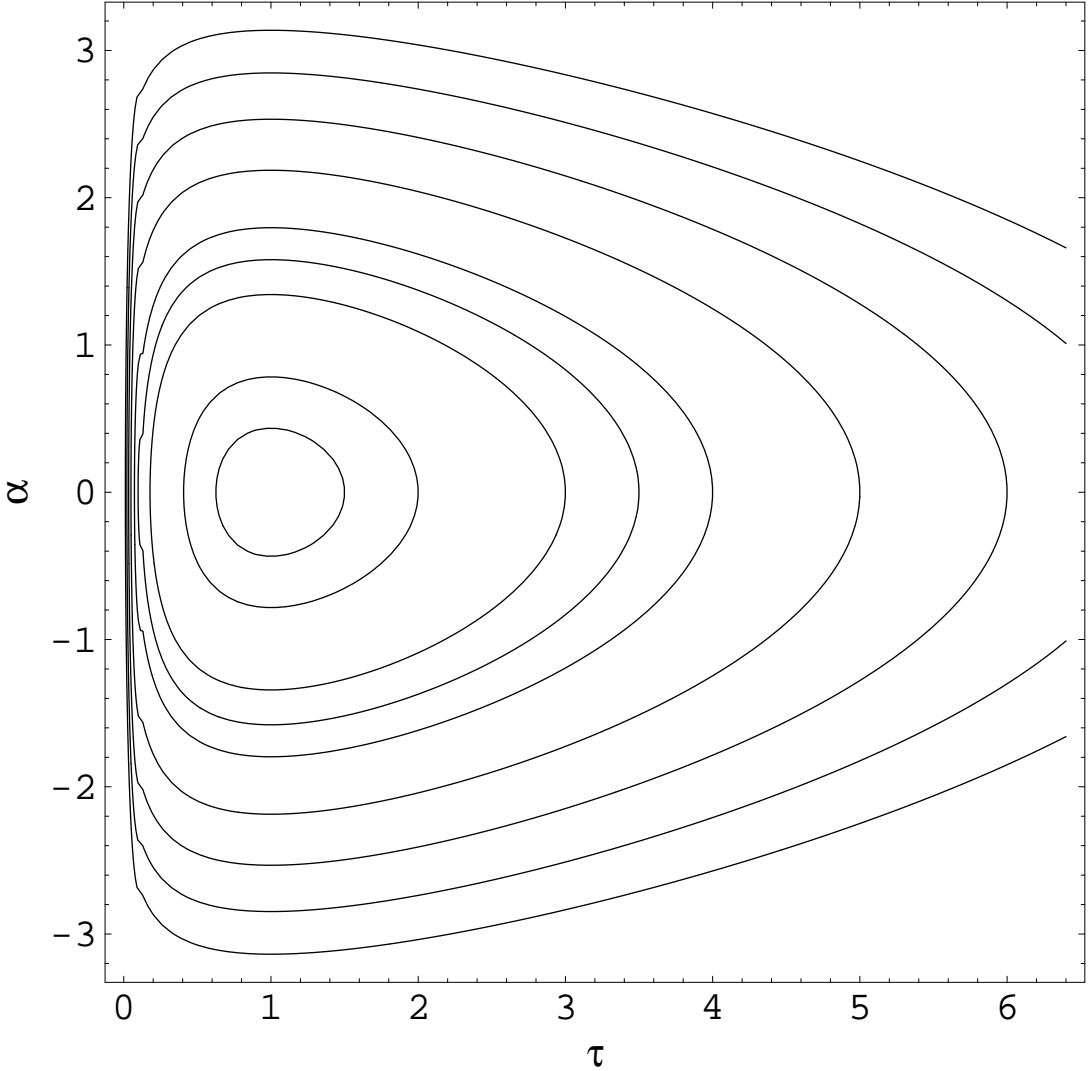


Let  $Q_\epsilon(\tau, \alpha)$  be the  $2\pi$  advance map of

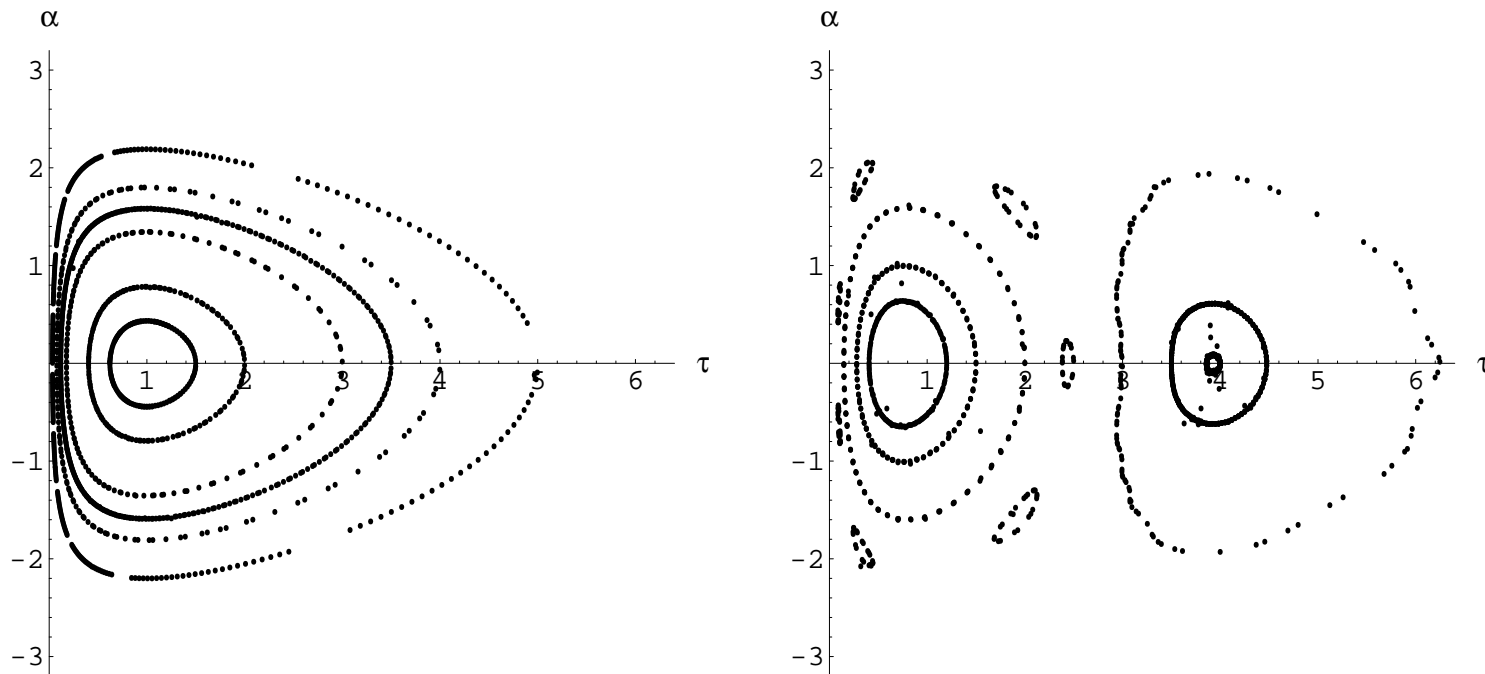
$$(***) \begin{cases} \dot{\tau} &= -\epsilon\tau\alpha, \\ \dot{\alpha} &= \epsilon(\tau - 1). \end{cases}$$

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  $(\theta, \tau, \alpha)$  is not ergodic.

We now show that the map  $P_\epsilon(\tau, \alpha)$  has invariant curves.

→ Main tool:  $P_\epsilon(\tau, \alpha)$  is a perturbation of  $Q_\epsilon(\tau, \alpha)$  and Moser invariant curve theorem.

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

$$(\ast \ast \ast) \quad \dot{\tau} = -\epsilon\tau\alpha, \quad \dot{\alpha} = \epsilon(\tau - 1).$$

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

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

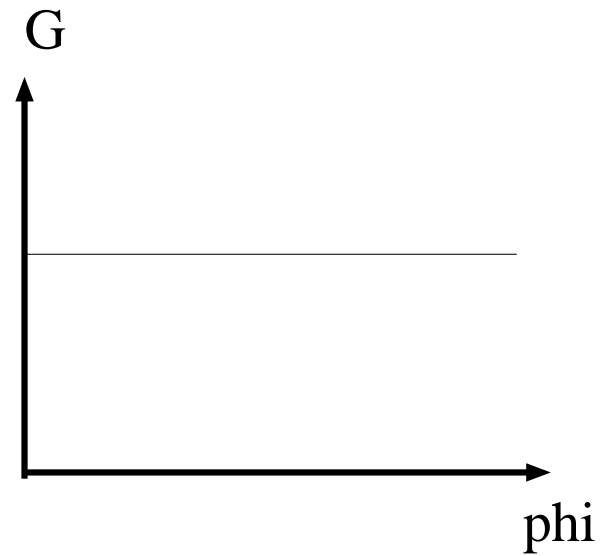
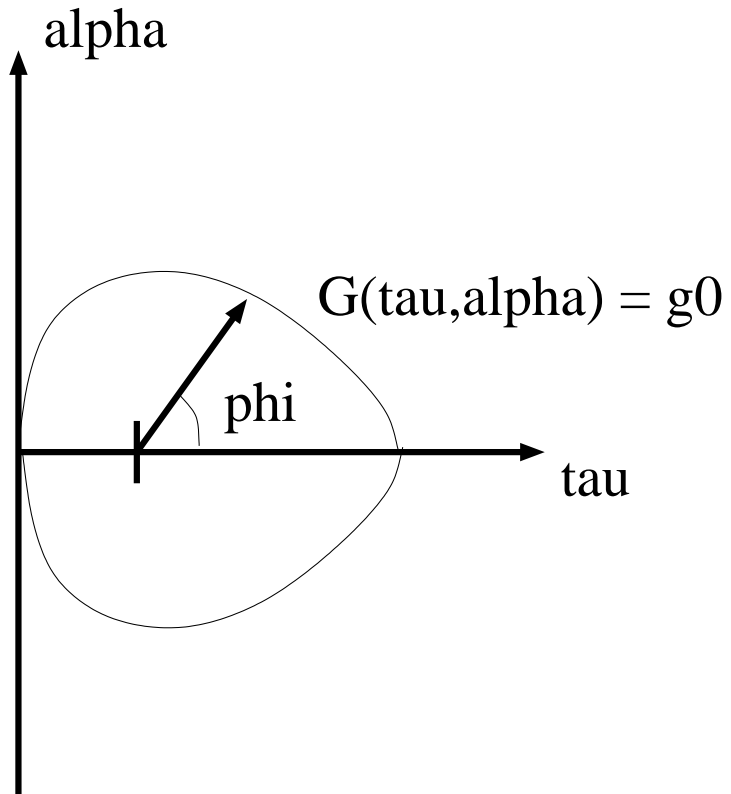
Then  $P_\epsilon(G, \phi) = (G_1, \phi_1)$  with

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

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  $Q_\epsilon$  in variables  $(\tau, \alpha)$  and  $(G, \phi)$



## 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,  $P_\epsilon$  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  $P_\epsilon$  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  $\epsilon$  is **small enough**,  $P_\epsilon$  has infinitely many invariant curves, close to the level curves

$$G(\tau, \alpha) = g_0.$$



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 **lose 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.