Nonequilibrium systems and computation of transport coefficients

SINEQ Summer school

Urbain Vaes
urbain.vaes@inria.fr

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Some references

- T. Lelièvre and G. Stoltz. Partial differential equations and stochastic methods in molecular dynamics. *Acta Numer.*, 2016
- G. A. Pavliotis. *Stochastic processes and applications*. Texts in Applied Mathematics. Springer, New York, 2014
- M. E. Tuckerman. *Statistical Mechanics: Theory and Molecular Simulation*. Oxford Graduate Texts. Oxford University Press, 2010
- Lecture notes by Gabriel Stoltz on computational statistical physics: `http://cermics.enpc.fr/~stoltz/Cours/intro_phys_stat.pdf`

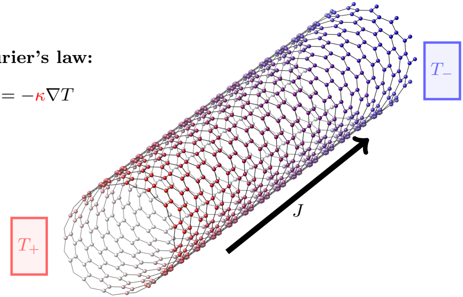
Introduction

Aims of computational statistical physics

- numerical microscope
- computation of average properties, static or dynamic

Fourier's law:

$$J = -\kappa \nabla T$$



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

Transport coefficients

At the macroscopic level, transport coefficients relate an external forcing to an average response expressed through some steady-state flux.

Examples:

- The *mobility* relates an external force to a velocity;
- The *heat conductivity* relates a temperature difference to a heat flux;
- The *shear viscosity* relates a shear velocity to a shear stress.

They can be estimated from molecular simulation at the microscopic level.

- Defined from *nonequilibrium* dynamics;
- Three main classes of methods to calculate them.

Outline of this talk

- Equilibrium vs nonequilibrium dynamics;
- Definition and computation of the mobility;
- Computation of other transport coefficients;
- Error analysis.

Part I: Definition and examples of nonequilibrium systems

- Equilibrium vs nonequilibrium dynamics
- Uniqueness of an invariant measure for nonequilibrium dynamics
- Convergence to the invariant measure
- Perturbation expansion of the invariant measure

Equilibrium and nonequilibrium dynamics

Consider a general diffusion process of the form

$$\mathrm{d}x_t = b(x_t)\,\mathrm{d}t + \sigma(x_t)\,\mathrm{d}W_t,$$

and assume that it admits an invariant distribution μ.

Definition (Time-reversibility)

A stationary ($x_0 \sim \mu$) stochastic process (x_t) is time-reversible if its law is invariant under time reversal: the law of the *forward paths* $(x_s)_{0 \leqslant s \leqslant t}$ coincides with the law of the *backward paths* $(x_{t-s})_{0 \leqslant s \leqslant t}$.

Theorem

A stationary diffusion processes x_t in $\mathbf{R}^d$ with generator $\mathcal{L}$ and invariant measure μ is reversible if and only if $\mathcal{L}$ is self-adjoint in $L^2(\mu)$.

In this lecture, equilibrium = reversible, possibly up to a one-to-one transformation preserving the invariant measure.

Paradigmatic examples of nonequilibrium dynamics

Overdamped Langevin dynamics perturbed by a constant force term

$$dq_t = -\nabla V(q_t)\,dt + \eta F + \sqrt{2}\,dW_t \tag{NO}$$

Langevin dynamics perturbed by a constant force term

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

In the rest of this section, we take $M = \mathrm{Id}$ for simplicity.

where

- $F \in \mathbf{R}^d$ with $|F| = 1$ is a given direction
- $\eta \in \mathbf{R}$ is the strength of the external forcing.

Is there an invariant probability measure?

When $\eta = 0$, these dynamics are reversible

- For overdamped Langevin dynamics

$$\mathcal{L}_{\rm ovd}\Big|_{\eta=0} = -\nabla V \cdot \nabla + \Delta = -\nabla^* \nabla, \qquad \mu(\mathrm{d}q) = \frac{1}{Z}\,\mathrm{e}^{-V(q)}\,\mathrm{d}q.$$

where $\nabla^* := (\nabla V - \nabla)\cdot$. For any $f, g \in C_c^\infty(\mathcal{E})$, we have

$$\int_{\mathcal{E}} (\mathcal{L}_{\rm ovd} f) g \,\mathrm{d}\mu = -\int_{\mathcal{E}} \nabla f \cdot \nabla g \,\mathrm{d}\mu = \int_{\mathcal{E}} (\mathcal{L}_{\rm ovd} g) f \,\mathrm{d}\mu.$$

- For Langevin dynamics, $\mu(\mathrm{d}q\,\mathrm{d}p) = \frac{1}{Z}\exp\left(-V(q) - \frac{|p|^2}{2}\right)\mathrm{d}q\,\mathrm{d}p$.

$$\mathcal{L}\Big|_{\eta=0} = p \cdot \nabla_q - \nabla V \cdot \nabla_p + \gamma\left(-p \cdot \nabla_p + \Delta_p\right) = \nabla_p^* \nabla_q - \nabla_q^* \nabla_p - \gamma \nabla_p^* \nabla_p,$$

where $\nabla_q^* := (\nabla V - \nabla_q)\cdot$ and $\nabla_p^* = (p - \nabla_p)\cdot$ are the formal $L^2(\mu)$ adjoints.

$$\begin{aligned}\int_{\mathcal{E}} (\mathcal{L} f) g \,\mathrm{d}\mu &= \int_{\mathcal{E}} g\left(\nabla_p^* \nabla_q - \nabla_q^* \nabla_p\right) f - \gamma \nabla_p f \cdot \nabla_p g \,\mathrm{d}\mu \\ &= \int_{\mathcal{E}} -f\left(\nabla_p^* \nabla_q - \nabla_q^* \nabla_p\right) g - \gamma \nabla_p f \cdot \nabla_p g \,\mathrm{d}\mu \\ &= \int_{\mathcal{E}} (f \circ S)\big(\mathcal{L}(g \circ S)\big)\,\mathrm{d}\mu \qquad Sf(q,p) := f(q,-p).\end{aligned}$$

Another example useful for thermal transport

Langevin dynamics with modified fluctuation

$$\begin{cases} \mathrm{d}q_t = p_t \,\mathrm{d}t, \\ \mathrm{d}p_t = -\nabla V(q_t)\,\mathrm{d}t - \gamma p_t \,\mathrm{d}t + \sqrt{2\gamma T_\eta(q)}\,\mathrm{d}W_t, \end{cases}$$

with non-negative temperature

$$T_\eta(q) = T_{\mathrm{ref}} + \eta \widetilde{T}(q)$$

Typically, $\widetilde{T}$ constant and positive on $\mathcal{D}_+ \subset \mathcal{C}$, and constant and negative on $\mathcal{D}_- \subset \mathcal{D}$.

- Non-zero energy flux from $\mathcal{D}_+$ to $\mathcal{D}_-$ expected in the steady-state
- Simplified model of thermal transport (in 3D materials or atom chains)

Worked example in dimension one

Consider the perturbed overdamped Langevin dynamics with $q_t \in \mathbf{T} = \mathbf{R}/2\pi\mathbf{Z}$

$$\mathrm{d}q_t = -V'(q_t)\,\mathrm{d}t + \eta\,\mathrm{d}t + \sqrt{2}\,\mathrm{d}W_t,$$

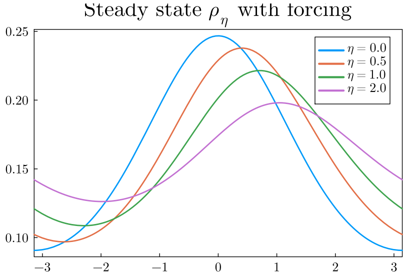
The associated Fokker–Planck equation reads

$$\frac{\mathrm{d}}{\mathrm{d}q}\left(\left(\frac{\mathrm{d}V}{\mathrm{d}q} - \eta\right)\rho_\eta + \frac{\mathrm{d}\rho_\eta}{\mathrm{d}q}\right) = 0.$$

The solution is unique and given by

$$\rho_\eta(q) \propto \mathrm{e}^{-V(q)} \int_{\mathbf{T}} \mathrm{e}^{V(q+y)-\eta y}\,\mathrm{d}y.$$

Example: ρ_η with $V(q) = \frac{1}{2}(1-\cos q)$.



In general, how can we prove existence of an invariant measure for

$$\mathrm{d}q_t = -\nabla V(q_t)\,\mathrm{d}t + \eta F + \sqrt{2}\,\mathrm{d}W_t\,?$$

- If the state space is compact (e.g. $\mathbf{T}^d$), apply Doeblin's theorem.
- If not, use its generization, Harris' theorem.

Fix $t = 1$ and denote by $p\colon \mathcal{E} \times \mathcal{B}(\mathcal{E}) \to [0,1]$ the Markov transition kernel

$$p(x, A) := \mathbf{P}\left[q_t \in A \,|\, q_0 = x\right].$$

For an observable $\phi\colon \mathcal{E} \to \mathbf{R}$ and a probability measure μ, we let

$$(\mathcal{P}\phi)(x) := \int_{\mathcal{E}} \phi(y)\, p(x, \mathrm{d}y), \qquad (\mathcal{P}^\dagger \mu)(A) := \int_{\mathcal{E}} p(x, A)\, \mu(\mathrm{d}x).$$

Note that $\mathcal{P}$ and $\mathcal{P}^\dagger$ are formally L^2 adjoints:

$$\int_{\mathcal{E}} (\mathcal{P}\phi)\,\mathrm{d}\mu = \int_{\mathcal{E}} \phi\,\mathrm{d}(\mathcal{P}^\dagger \mu).$$

Existence of an invariant measure for compact state space (1/2)

Let $d(\bullet, \bullet)$ denote the total variation metric.

Theorem (Doeblin's theorem)

If there exists $\alpha \in (0,1)$ and a probability measure π such that

$$\forall x \in \mathcal{E}, \qquad p(x, \bullet) \geqslant \alpha\pi, \qquad \textit{(Minorization condition)}$$

then $\exists!\, \mu_*$ such that $\mathcal{P}^\dagger \mu_* = \mu_*$, and $d({\mathcal{P}^\dagger}^n \mu, \mu_*) \leqslant (1-\alpha)^n d(\mu, \mu_*)$.

Sketch of proof. Define the Markov transition kernel

$$\widetilde{p}(x, \bullet) := \frac{1}{1-\alpha} p(x, \bullet) - \frac{\alpha}{1-\alpha} \pi(\bullet),$$

Let $\mathcal{F}$ denote the set of measurable functions $\phi \colon \mathcal{E} \to [-1, 1]$. We have

$$\begin{aligned} d(\mathcal{P}^\dagger \mu, \mathcal{P}^\dagger \nu) &= \sup_{\phi \in \mathcal{F}} \int_{\mathcal{E}} \phi(x)(\mathcal{P}^\dagger \mu - \mathcal{P}^\dagger \nu)(\mathrm{d}x) = \sup_{\phi \in \mathcal{F}} \int_{\mathcal{E}} \mathcal{P}\phi(x)\big(\mu - \nu\big)(\mathrm{d}x) \\ &= (1-\alpha) \sup_{\phi \in \mathcal{F}} \int_{\mathcal{E}} \widetilde{\mathcal{P}}\phi(x)(\mu - \nu)(\mathrm{d}x) \leqslant (1-\alpha)\, d(\mu, \nu). \end{aligned}$$

Conclude using Banach's fixed point theorem.

Existence of an invariant measure for compact state space (2/2)

Two simple corollaries:

- Suppose that ϕ is uniformly bounded. Then

$$\left|\mathcal{P}^n\phi(x) - \overline{\phi}\right| = \int_{\mathcal{E}} \mathcal{P}^n(\phi - \overline{\phi})\, \mathrm{d}(\delta_x - \mu_*) = \int_{\mathcal{E}} (\phi - \overline{\phi})\, (\mathcal{P}^{\dagger n}\delta_x - \mathcal{P}^{\dagger n}\mu_*)(\mathrm{d}q)$$
$$\leqslant \left\|\phi - \overline{\phi}\right\|_{L^\infty} (1-\alpha)^n d(\delta_x, \mu_*) \leqslant 2\left\|\phi - \overline{\phi}\right\|_{L^\infty} (1-\alpha)^n.$$

  This shows that

$$\left\|\mathcal{P}^n\phi(x) - \overline{\phi}\right\|_{L^\infty} \leqslant 2(1-\alpha)^n \left\|\phi - \overline{\phi}\right\|_{L^\infty}.$$

- The Neumann series $\mathrm{Id} + \mathcal{P} + \mathcal{P}^2 + \cdots$ is convergent as a bounded operator on

$$L^\infty_* := \left\{\phi \in L^\infty(\mathcal{E}) : \int_{\mathcal{E}} \phi \, \mathrm{d}\mu_* = 0\right\}.$$

  Thus $\mathrm{Id} - \mathcal{P}$ is invertible on L^∞_* and

$$(\mathrm{Id} - \mathcal{P})^{-1} = \mathrm{Id} + \mathcal{P} + \mathcal{P}^2 + \cdots$$

Consider the overdamped Langevin dynamics on $\mathbf{T}^d$:

$$\mathrm{d}q_t = -\nabla V(q_t)\,\mathrm{d}t + \eta F\,\mathrm{d}t + \sqrt{2}\,\mathrm{d}W_t, \qquad q_t \in \mathbf{T}^d.$$

- The **minorization condition** is satisfied. Indeed for $t > 0$

$$p(x,A) = \mathbf{E}\left[q_t \in A \,|\, q_0 = x\right] = \int_A p_t(x,y)\,\mathrm{d}y \qquad p_t = \text{transition pdf}$$

$$\geqslant \left(\inf_{(x,y)\in\mathcal{E}^2} p_t(x,y)\right)\lambda(A) \qquad \lambda := \text{Lebesgue measure.}$$

  The infimum is > 0 by parabolic regularity and Harnack's inequality.

- **Decay of the semigroup**: For $t \in [0,\infty)$ and $\varphi \in L^\infty_*$, it holds that

$$\left\|\mathrm{e}^{t\mathcal{L}_{\mathrm{ovd}}}\varphi\right\|_{L^\infty} = \left\|\mathrm{e}^{(t-\lfloor t\rfloor)\mathcal{L}_{\mathrm{ovd}}}\left(\mathrm{e}^{\lfloor t\rfloor\mathcal{L}_{\mathrm{ovd}}}\varphi\right)\right\|_{L^\infty}$$

$$\leqslant \left\|\mathrm{e}^{\lfloor t\rfloor\mathcal{L}_{\mathrm{ovd}}}\varphi\right\|_{L^\infty} \leqslant 2\,\mathrm{e}^{\alpha}\,\mathrm{e}^{-\alpha t}\|\varphi\|_{L^\infty}.$$

- **Corollary**: $\mathcal{L}_{\mathrm{ovd}}$ is invertible on L^∞_*, and

$$\mathcal{L}_{\mathrm{ovd}}^{-1} = -\int_0^\infty \mathrm{e}^{t\mathcal{L}_{\mathrm{ovd}}}\,\mathrm{d}t.$$

Existence of an invariant measure for perturbed Langevin dynamics

Consider the paradigmatic dynamics

$$
\begin{aligned}
\mathrm{d}q_t &= p_t \,\mathrm{d}t, \\
\mathrm{d}p_t &= -\nabla V(q_t)\,\mathrm{d}t + \eta F\,\mathrm{d}t - \gamma p_t\,\mathrm{d}t + \sqrt{2\gamma}\,\mathrm{d}W_t,
\end{aligned}
$$

where $(q_t, p_t) = \mathbf{T}^d \times \mathbf{R}^d$ and $F \in \mathbf{R}^d$ with $|F| = 1$ is a given direction.

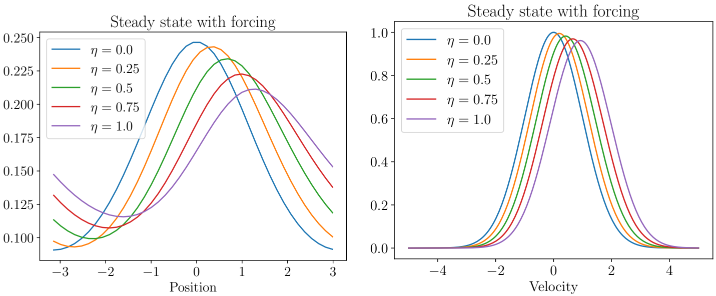


Figure: Marginals of the steady state solution of the Langevin dynamics with forcing

Harris' theorem [1]

Let $p(x, A)$ denote a Markov transition kernel and let

$$(\mathcal{P}\phi)(x) := \int_{\mathcal{E}} \phi(y)\, p(x, \mathrm{d}y), \qquad (\mathcal{P}^\dagger \mu)(A) := \int_{\mathcal{E}} p(x, A)\, \mu(\mathrm{d}x).$$

Theorem (Harris's theorem)

Suppose that the following conditions are satisfied:

- *There exists* $\mathcal{K} \colon \mathcal{E} \to [1, \infty)$ *and constants* $a > 0$ *and* $b \geqslant 0$ *such that*

$$\forall x \in \mathcal{E}, \qquad \mathcal{L}\mathcal{K}(x) \leqslant -a\mathcal{K}(x) + b,$$

- *There exists a constant* $\alpha \in (0, 1)$ *and a probability measure* π *such that*

$$\inf_{x \in \mathcal{C}} p(x, \mathrm{d}y) \geqslant \alpha\, \pi(\mathrm{d}y),$$

  where $\mathcal{C} = \{x \in \mathbf{R} \,|\, \mathcal{K}(x) \leqslant K_{\max}\}$ *for some* $K_{\max} \geqslant 1 + 2\,\frac{b}{a}$.

Then $\exists!\ \mu_*$ *such that* $\mathcal{P}^\dagger \mu_* = \mu_*$. *Furthermore there is* $\gamma \in (0, 1)$ *such that*

$$\left\| \frac{\mathcal{P}^n \phi - \overline{\phi}}{\mathcal{K}} \right\|_{L^\infty} \leqslant C\gamma^n \left\| \frac{\mathcal{P}^n \phi - \overline{\phi}}{\mathcal{K}} \right\|_{L^\infty}, \qquad \overline{\phi} := \int_{\mathcal{E}} \phi \, \mathrm{d}\mu_*.$$

[1] M. Hairer and J. Mattingly, *Progr. Probab.* (2011)

Application to perturbed Langevin dynamics

For $\mathcal{K}\colon \mathcal{E} \to [1,\infty)$, let

$$L^\infty_{\mathcal{K}} := \left\{ \varphi \text{ measureable } : \left\| \frac{\varphi}{\mathcal{K}} \right\|_{L^\infty} < \infty \right\}$$

Theorem

Fix $\eta > 0$ and $n \geqslant 2$, and let $\mathcal{K}_n(q,p) := 1 + |p|^n$. There exists a unique invariant probability measure, with a smooth density $\psi_\eta(q,p)$ with respect to the Lebesgue measure. Furthermore there exists $C = C(n,\eta) > 0$ and $\lambda = \lambda(n,\eta) > 0$ such that

$$\forall \phi \in L^\infty_{\mathcal{K}_n}(\mathcal{E}), \qquad \left\| \mathrm{e}^{t\mathcal{L}_n} \phi - \int_{\mathcal{E}} \phi \, \psi_\eta \right\|_{L^\infty_{\mathcal{K}_n}} \leqslant C \, \mathrm{e}^{-\lambda t} \left\| \phi - \int_{\mathcal{E}} \phi \, \psi_\eta \right\|_{L^\infty_{\mathcal{K}_n}}$$

Idea of the proof. Show that the assumptions of Harris' theorem are satisfied, in particular that

$$\mathcal{L}\mathcal{K}_n \leqslant -a\mathcal{K}_n(q,p) + b,$$

for $a > 0$ and $b \geqslant 0$.

Perturbation expansion for η sufficiently small (1/3)

Consider the perturbed Langevin dynamics and write

$$\mathcal{L}_\eta = \mathcal{L}_0 + \eta\widetilde{\mathcal{L}}, \qquad \widetilde{\mathcal{L}} = F \cdot \nabla_p$$

It is expected that $\psi_\eta = f_\eta \psi_0$ with $\psi_0(q,p) = Z^{-1}\,\mathrm{e}^{-\beta H(q,p)}$ and

$$f_\eta = \mathbf{1} + \eta \mathfrak{f}_1 + \mathcal{O}(\eta^2)$$

The invariance of ψ_η can be written as

$$\int_{\mathcal{E}} (\mathcal{L}_\eta \varphi)\psi_\eta = 0 = \int_{\mathcal{E}} (\mathcal{L}_\eta \varphi) f_\eta \psi_0$$

Fokker-Planck equation on $L^2(\psi_0)$

$$\mathcal{L}_\eta^* f_\eta = 0$$

Observe that $\mathcal{L}_\eta^* = \mathcal{L}_0^* + \widetilde{\mathcal{L}}^*$ with

$$\mathcal{L}_0^* = -\nabla_p^* \nabla_q + \nabla_q^* \nabla_p - \gamma \nabla_p^* \nabla_p, \qquad \widetilde{\mathcal{L}}^* \bullet = \nabla_p^*(F \bullet)$$

Questions: Can the expansion for f_η be made rigorous? What is $\mathfrak{f}_1$?

Perturbation expansion for η sufficiently small (2/3)

Formal asymptotics

Write $f_\eta = \mathfrak{f}_0 + \eta \mathfrak{f}_1 + \eta^2 \mathfrak{f}_2 + \cdots$ and expand

$$\begin{aligned} \mathcal{L}_\eta^* f_\eta = \mathcal{L}_0^* \mathfrak{f}_0 & \\ & + \eta \left(\widetilde{\mathcal{L}}^* \mathfrak{f}_0 + \mathcal{L}_0^* \mathfrak{f}_1 \right) \\ & + \eta^2 \left(\widetilde{\mathcal{L}}^* \mathfrak{f}_1 + \mathcal{L}_0^* \mathfrak{f}_2 \right) \\ & + \eta^3 \left(\widetilde{\mathcal{L}}^* \mathfrak{f}_2 + \mathcal{L}_0^* \mathfrak{f}_3 \right) + \cdots \end{aligned}$$

This suggests that $\mathfrak{f}_{i+1} = -(\mathcal{L}_0^*)^{-1}(\widetilde{\mathcal{L}}^* \mathfrak{f}_i)$ and so

$$f_\eta = \sum_{i=0}^{\infty} (-\eta)^i \left((\mathcal{L}_0^*)^{-1} \widetilde{\mathcal{L}}^* \right)^i \mathbf{1} = \left(\mathrm{Id} + \eta (\mathcal{L}_0^*)^{-1} \widetilde{\mathcal{L}}^* \right)^{-1} \mathbf{1}.$$

Elements of proof

Let Π_0 denote the following projection operator

$$\Pi_0 f := f - \int_{\mathcal{E}} f\,\psi_0$$

- The operator $\mathcal{L}_0^{-1}$ is a well defined bounded operator on $L_0^2(\psi_0)$ (Hypocoercivity + hypoelliptic regularization)
- Since $\gamma\|\nabla_p\varphi\|^2_{L^2(\psi_0)} = -\langle \mathcal{L}_0\varphi, \varphi\rangle_{L^2(\psi_0)}$, it follows that

$$\|\widetilde{\mathcal{L}}\varphi\|^2_{L^2(\psi_0)} \leqslant \|\nabla_p\varphi\|^2_{L^2(\psi_0)} \leqslant \frac{1}{\gamma}\|\mathcal{L}_0\varphi\|_{L^2(\psi_0)}\|\varphi\|_{L^2(\psi_0)}$$

  Thus $\Pi_0\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}$ is bounded on $L_0^2(\psi_0)$.

$$\|\widetilde{\mathcal{L}}\mathcal{L}_0^{-1}\varphi\|^2_{L^2(\psi_0)} \leqslant \frac{\beta}{\gamma}\|\varphi\|_{L^2(\psi_0)}\|\mathcal{L}_0^{-1}\varphi\|_{L^2(\psi_0)}.$$

- It follows that $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*\Pi_0 = (\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*$ is also bounded on $L_0^2(\psi_0)$
- Invariance of f_η by $\mathcal{L}_\eta^* = \mathcal{L}_0^* + \eta\widetilde{\mathcal{L}}^*$

$$\mathcal{L}_\eta^* f_\eta = \mathcal{L}_0^*\left(1 + \eta(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*\right) f_\eta = \mathcal{L}_0^*\mathbf{1} = 0$$

- Prove that $f_\eta \geqslant 0$.

Perturbation expansion for η sufficiently small (3/3)

Power expansion of the invariant measure

Spectral radius r of the bounded operator $(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^* \in \mathcal{B}(L_0^2(\psi_0))$:

$$r = \lim_{n \to +\infty} \left\| \left[\left(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1} \right)^* \right]^n \right\|^{1/n}.$$

Then, for $|\eta| < r^{-1}$, the unique invariant measure can be written as $\psi_\eta = f_\eta \psi_0$, where $f_\eta \in L^2(\psi_0)$ can be expanded as

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

Note that $\displaystyle\int_{\mathcal{E}} \psi_\eta = 1$.

Part II: Definition and calculation of the mobility

- Definition through linear response
- Green–Kubo reformulation
- Link with effective diffusion

Three main classes of methods:

- Non-equilibrium steady state techniques.
    - Calculations from the steady state of a system out of equilibrium.
    - Comprises bulk-driven and boundary-driven approaches.
- Equilibrium techniques based on the Green–Kubo formula

$$\rho = \int_0^{\infty} \mathbf{E}_{\mu}\left[\varphi(x_t)\phi(x_0)\right] \mathrm{d}t.$$

  We will derive this formula from linear response.

- Transient methods.
    - System locally perturbed
    - Relaxation of this perturbation enables to calibrate macroscopic model.

We illustrate the first two for the simplest transport coefficient: the mobility.

Linear response of nonequilibrium dynamics

Consider the nonequilibirium dynamics with V periodic:

$$\begin{aligned} dq_t &= p_t \, dt, \\ dp_t &= -\nabla V(q_t)\, dt + \eta F \, dt - \gamma p_t \, dt + \sqrt{2\gamma}\, dW_t, \end{aligned}$$

- The force ηF induces a non-zero velocity in the direction F
- Encoded by $\mathbf{E}_\eta(R) = \int_{\mathcal{E}} R\, \psi_\eta$ with $R(q,p) = F^\mathsf{T} p$

Definition (Mobility)

The mobility in direction F is defined mathematically as

$$\rho_F = \lim_{\eta \to 0} \frac{\mathbf{E}_\eta[R] - \mathbf{E}_0[R]}{\eta} = \lim_{\eta \to 0} \frac{1}{\eta} \mathbf{E}_\eta[R]$$

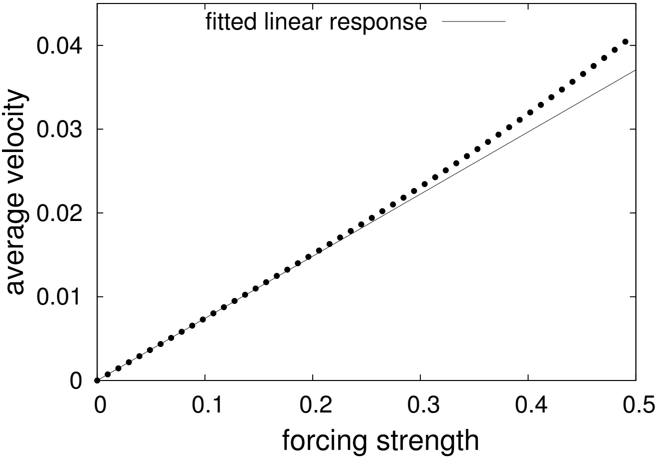
We proved that $\psi_\eta = f_\eta \psi_0$ with $\psi_0(q,p) = Z^{-1}\, e^{-\beta H(q,p)}$ and

$$f_\eta = \mathbf{1} + \eta \mathfrak{f}_1 + \mathcal{O}(\eta^2), \qquad \mathfrak{f}_1 = -(\mathcal{L}_0^*)^{-1} \widetilde{\mathcal{L}}^* \mathbf{1}.$$

Therefore

$$\rho_F = \int_{\mathcal{E}} R \mathfrak{f}_1 \psi_0 = -\int_{\mathcal{E}} \left(\mathcal{L}_0^{-1} R\right) \left(\widetilde{\mathcal{L}}^* \mathbf{1}\right) \psi_0$$

Numerical results (1)



Numerical results (2)

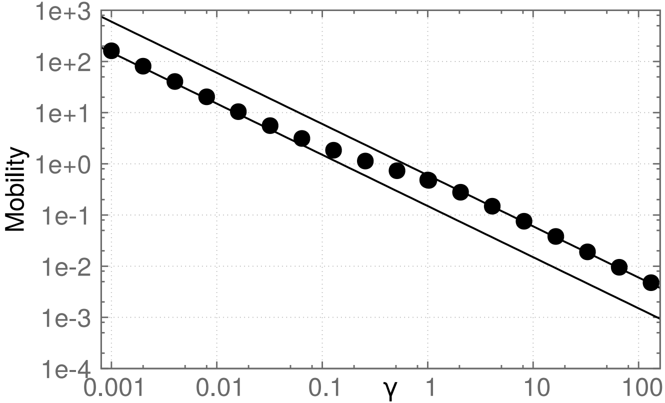


Figure: Mobility as a function of γ [2]

[2] See J. Roussel and G. Stoltz, *ESAIM: M2AN* (2018)

Reformulation as integrated correlation function

Define the conjugate response

$$S = \widetilde{\mathcal{L}}^* \mathbf{1} = \nabla_p^*(F\mathbf{1}) = F^\mathsf{T} p.$$

Green–Kubo formula

For any $R \in L_0^2(\psi_0)$,

$$\lim_{\eta \to 0} \frac{\mathbf{E}_\eta(R)}{\eta} = \int_0^{+\infty} \mathbf{E}_0\Big(R(q_t, p_t) S(q_0, p_0)\Big) dt,$$

where $\mathbf{E}_\eta$ is w.r.t. to $\psi_\eta(q,p)\,\mathrm{d}q\,\mathrm{d}p$, while $\mathbf{E}_0$ is w.r.t. initial conditions $(q_0, p_0) \sim \psi_0$ and over all realizations of the equilibrium dynamics.

For the mobility, it holds $S(q,p) = R(q,p) = F^\mathsf{T} p$ and so

$$\rho_F = \lim_{\eta \to 0} \frac{\mathbf{E}_\eta\left(F^\mathsf{T} p\right)}{\eta} = \int_0^{+\infty} \mathbf{E}_0\Big(\left(F^\mathsf{T} p_t\right)\left(F^\mathsf{T} p_0\right)\Big)\,\mathrm{d}t$$

Elements of proof

- Proof based on the following equality on $\mathcal{B}\big(L_0^2(\psi_0)\big)$

$$-\mathcal{L}_0^{-1} = \int_0^{+\infty} \mathrm{e}^{t\mathcal{L}_0}\,\mathrm{d}t.$$

- Then,

$$\begin{aligned}
\lim_{\eta\to 0} \frac{\mathbf{E}_\eta(R)}{\eta} &= -\int_{\mathcal{E}} R\left[(\widetilde{\mathcal{L}}\mathcal{L}_0^{-1})^*\mathbf{1}\right]\psi_0 = -\int_{\mathcal{E}} [\mathcal{L}_0^{-1}R][\widetilde{\mathcal{L}}^*\mathbf{1}]\,\psi_0 \\
&= \int_0^{+\infty}\left(\int_{\mathcal{E}}\left(\mathrm{e}^{t\mathcal{L}_0}R\right)\,S\,\psi_0\right)\mathrm{d}t \\
&= \int_0^{+\infty}\mathbf{E}\Big(R(q_t,p_t)S(q_0,p_0)\Big)\,\mathrm{d}t
\end{aligned}$$

- Note also that S has average 0 w.r.t. invariant measure since

$$\int_{\mathcal{X}} S\,\mathrm{d}\pi = \int_{\mathcal{X}} \widetilde{\mathcal{L}}^*\mathbf{1}\,\mathrm{d}\pi = \int_{\mathcal{X}} \widetilde{\mathcal{L}}\mathbf{1}\,\mathrm{d}\pi = 0$$

Connection with effective diffusion

It is possible to show a functional central limit theorem for the Langevin dynamics:

$$\varepsilon \widetilde{q}_{s/\varepsilon^2} \xrightarrow[\varepsilon \to 0]{} \sqrt{2\mathbf{D}}\, W_s \qquad \text{weakly on } C([0,\infty)), \qquad \widetilde{q}_t := q_0 + \int_0^t p_s \, ds \in \mathbf{R}^d.$$

In particular, $\widetilde{q}_t/\sqrt{t} \xrightarrow[t \to \infty]{} \mathcal{N}(0, 2\mathbf{D})$ weakly.

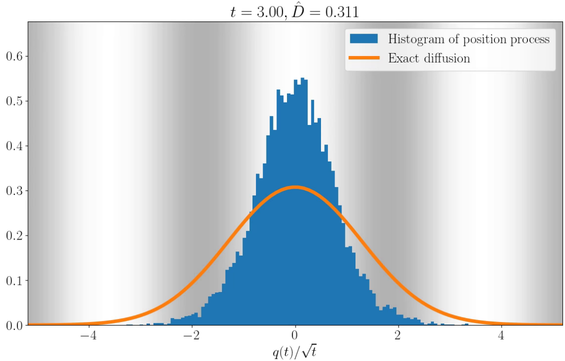


Figure: Histogram of $q_t/\sqrt{t}$. The potential $V(q) = -\cos(q)/2$ is illustrated in the background.

Mathematical expression for the effective diffusion (dimension 1)

Expression of D in terms of the solution to a Poisson equation

Effective diffusion tensor given by $D = \langle \phi, p \rangle_{L^2(\mu)}$ and ϕ is the solution to

$$-\mathcal{L}\phi = p, \qquad \phi \in L_0^2(\mu).$$

Key idea of the proof: Apply Itô's formula to ϕ

$$\mathrm{d}\phi(q_s, p_s) = -p_s \,\mathrm{d}s + \sqrt{2\gamma}\, \frac{\partial \phi}{\partial p}(q_s, p_s)\, \mathrm{d}W_s$$

and then rearrange:

$$\begin{aligned} \varepsilon(\widetilde{q}_{t/\varepsilon^2} - \widetilde{q}_0) &= \varepsilon \int_0^{t/\varepsilon^2} p_s \,\mathrm{d}s \\ &= \underbrace{\varepsilon\big(\phi(q_0, p_0) - \phi(q_{t/\varepsilon^2}, p_{t/\varepsilon^2})\big)}_{\to 0} + \underbrace{\sqrt{2\gamma}\varepsilon \int_0^{t/\varepsilon^2} \frac{\partial \phi}{\partial p}(q_s, p_s)\, \mathrm{d}W_s}_{\to \sqrt{2D} W_t \text{ weakly by MCLT}}. \end{aligned}$$

In the multidimensional setting, $D_F = \left\langle \phi_F, F^\mathsf{T} p \right\rangle$ with $-\mathcal{L}\phi_F = F^\mathsf{T} p$.

Einstein's relation: we just showed $D_F = \beta^{-1} \rho_F$.

Summary: numerical approaches for calculating the mobility

- Linear response approach:

$$\rho_F = \lim_{\eta \to 0} \frac{1}{\eta} \mathbf{E}_\eta \left[F^\mathsf{T} p \right].$$

where μ_η is the invariant distribution of the system with external forcing.

- Einstein's relation:

$$\rho_F = \lim_{t \to \infty} \frac{1}{2t} \mathbf{E}_\mu \left[\left| F^\mathsf{T} (\widetilde{q}_t - q_0) \right|^2 \right].$$

- Deterministic method, e.g. Fourier/Hermite Galerkin, for the Poisson equation

$$-\mathcal{L}_0 \phi_F = F^\mathsf{T} p, \qquad \rho_F = \left\langle \phi_F, F^\mathsf{T} p \right\rangle.$$

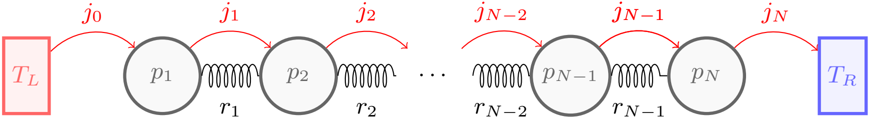
- Green–Kubo formula:

$$\rho_F = \int_0^\infty \mathbf{E}_0 \big((F^\mathsf{T} p_0)(F^\mathsf{T} p_t) \big) \, \mathrm{d}t.$$

Part III: Computation of other transport coefficients

- Thermal conductivity
- Shear viscosity

Consider a chain of N atoms with nearest-neighbor interactions



Mathematical model:

$$\begin{cases} \mathrm{d}r_n = (p_{n+1} - p_n)\,\mathrm{d}t, \\ \mathrm{d}p_1 = v'(r_1)\,\mathrm{d}t - \gamma p_1 \mathrm{d}t + \sqrt{2\gamma(T+\eta)}\,\mathrm{d}W_t^L, \\ \mathrm{d}p_n = \big(v'(r_n) - v'(r_{n-1})\big)\,\mathrm{d}t, \\ \mathrm{d}p_N = -v'(r_{N-1})\,\mathrm{d}t - \gamma p_N \mathrm{d}t + \sqrt{2\gamma(T-\eta)}\,\mathrm{d}W_t^R, \end{cases}$$

The Hamiltonian of the system is the sum of the potential and kinetic energies:

$$H(r,p) = V(r) + \sum_{n=1}^{N} \frac{p_n^2}{2}, \qquad V(r) = \sum_{n=1}^{N-1} v(r_n).$$

Thermal transport in one-dimensional chains (2/3)

- When $\eta = 0$, invariant distribution given by

$$\pi(\mathrm{d}r\,\mathrm{d}p) = Z_\beta^{-1} \exp\left(-\beta\left(\frac{|p|^2}{2} + V(r)\right)\right) \mathrm{d}r\,\mathrm{d}p, \qquad \beta = T^{-1}.$$

- Generator of the dynamics:

$$\mathcal{L}_\eta = \sum_{n=1}^{N-1} (p_{n+1} - p_n)\partial_{r_n} + \sum_{n=1}^{N} \Big(v'(r_n) - v'(r_{n-1})\Big)\partial_{p_n}$$
$$- \gamma p_1 \partial_{p_1} + \gamma T \partial_{p_1}^2 - \gamma p_N \partial_{p_N} + \gamma T \partial_{p_N}^2 + \gamma\eta(\partial_{p_1}^2 - \partial_{p_N}^2).$$

The perturbation $\widetilde{\mathcal{L}} = \gamma(\partial_{p_1}^2 - \partial_{p_N}^2)$ is not bounded relatively to $\mathcal{L}_0$...

$\rightarrow$ Existence/uniqueness of the invariant measure more difficult to prove[3]

[3] P. Carmona, *Stoch. Proc. Appl.* (2007)

Thermal transport in one-dimensional chains (3/3)

- Response function: total energy current

Definition of the heat flux

$$J = \frac{1}{N-1} \sum_{n=1}^{N-1} j_n, \qquad j_n = -v'(r_n) \frac{p_n + p_{n+1}}{2}$$

- Motivation: Local conservation of the energy (in the bulk $2 \leqslant n \leqslant N-1$)

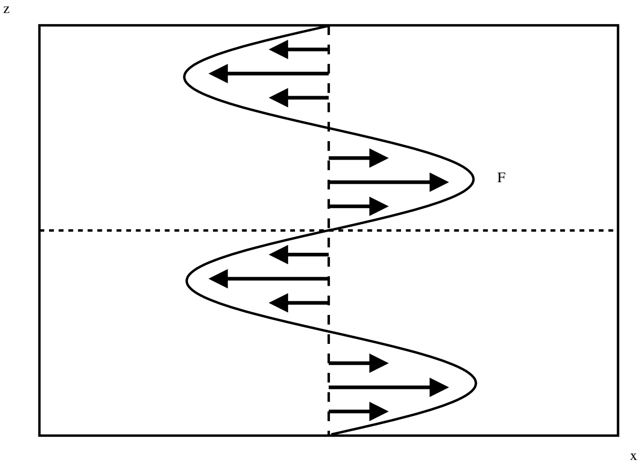
$$\frac{\mathrm{d}\varepsilon_n}{\mathrm{d}t} = \mathcal{L}_\eta \varepsilon_n = j_{n-1} - j_n, \qquad \varepsilon_n = \frac{p_n^2}{2} + \frac{1}{2}\Big(v(r_{n-1}) + v(r_n)\Big)$$

- Definition of the thermal conductivity: linear response

$$\kappa_N = \lim_{\eta \to 0} \frac{(N-1)}{2\eta} \mathbf{E}_\eta[J].$$

Shear viscosity in fluids (1/4)

Consider a fluid in $\mathcal{D} = (L_x\mathbb{T} \times L_y\mathbb{T})^N$ subjected to a sinusoidal forcing



Suppose that the box contains N particles of mass m, each subjected to a force F.

Shear viscosity in fluids (2/4)

Assume pairwise interactions

$$V(q) = \sum_{1 \leqslant \ell < n \leqslant N} \mathcal{V}(|q_\ell - q_n|).$$

- Add a smooth nongradient force in the x direction, depending on y

Langevin dynamics under flow

$$\begin{cases} dq_n = \dfrac{p_n}{m}\, dt, \\ dp_{n,x} = -\partial_{q_{n,x}} V(q_t)\, dt + \eta F(q_{n,y})\, dt - \gamma \dfrac{p_{n,x}}{m}\, dt + \sqrt{\dfrac{2\gamma}{\beta}}\, dW_t^{n,x}, \\ dp_{n,y} = -\partial_{q_{n,y}} V(q_t)\, dt - \gamma \dfrac{p_{n,y}}{m}\, dt + \sqrt{\dfrac{2\gamma}{\beta}}\, dW_t^{n,y}. \end{cases}$$

- Existence/uniqueness of a smooth invariant measure provided $\gamma > 0$
- The perturbation $\widetilde{\mathcal{L}} = \sum_{n=1}^{N} F(q_{n,y}) \partial_{p_{n,x}}$ is $\mathcal{L}_0$-bounded

Shear viscosity in fluids (3/4)

- Linear response:

$$\lim_{\eta\to 0}\frac{\mathbf{E}_\eta[\mathcal{L}_0 h]}{\eta} = -\frac{\beta}{m}\left\langle h, \sum_{n=1}^N p_{n,x} F(q_{n,y})\right\rangle_{L^2(\psi_0)}.$$

- Average longitudinal velocity $u_x(Y) = \lim_{\varepsilon\to 0}\lim_{\eta\to 0}\frac{\mathbf{E}_\eta\left[U_x^\varepsilon(Y,\bullet)\right]}{\eta}$ where

$$U_x^\varepsilon(Y,q,p) = \frac{L_y}{Nm}\sum_{n=1}^N p_{n,x}\,\chi_\varepsilon(q_{n,y}-Y)$$

- Average off-diagonal stress $\sigma_{xy}(Y) = \lim_{\varepsilon\to 0}\lim_{\eta\to 0}\frac{\mathbf{E}_\eta[\dots]}{\eta}$, where

$$\dots = \frac{1}{L_x}\left(\sum_{n=1}^N \frac{p_{n,x}p_{n,y}}{m}\chi_\varepsilon(q_{n,y}-Y) - \sum_{1\leqslant n<\ell\leqslant N}\mathcal{V}'(|q_n-q_\ell|)\frac{q_{n,x}-q_{\ell,x}}{|q_n-q_\ell|}\int_{q_{\ell,y}}^{q_{n,y}}\chi_\varepsilon(s-Y)\,ds\right)$$

- Local conservation of momentum[4]: replace h by U_x^ε

$$\frac{\mathrm{d}\sigma_{xy}(Y)}{\mathrm{d}Y} + \gamma\overline{\rho}u_x(Y) = \overline{\rho}F(Y), \qquad \overline{\rho} = \frac{N}{|\mathcal{D}|}.$$

[4] Irving and Kirkwood, *J. Chem. Phys.* **18** (1950)

Shear viscosity in fluids (4/4)

- Definition $\sigma_{xy}(Y) := -\nu(Y)u_x'(Y)$, closure assumption $\nu(Y) = \nu > 0$.

Velocity profile in Langevin dynamics under flow

$$-\nu u_x''(Y) + \gamma\overline{\rho}u_x(Y) = \overline{\rho}F(Y)$$

Therefore, integrating against the test function $\mathrm{e}^{2i\pi\frac{y}{L_y}}$ and rearranging, we have

$$\nu = \overline{\rho}\left(\frac{F_1}{U_1} - \gamma\right)\left(\frac{L_y}{2\pi}\right)^2,$$

where

$$U_1 = \frac{1}{L_y}\int_0^{L_y} u_x(x)\,\mathrm{e}^{2i\pi\frac{y}{L_y}}\,\mathrm{d}y, \qquad F_1 = \frac{1}{L_y}\int_0^{L_y} F(y)\,\mathrm{e}^{2i\pi\frac{y}{L_y}}\,\mathrm{d}y.$$

The coefficient U_1 can be rewritten as

$$U_1 = \lim_{\eta\to 0}\frac{1}{\eta}\mathbf{E}_\eta\left[\frac{1}{N}\sum_{n=1}^{N}\frac{p_{n,x}}{m}\exp\left(2i\pi\frac{q_{n,y}}{L_y}\right)\right].$$

Numerical illustration

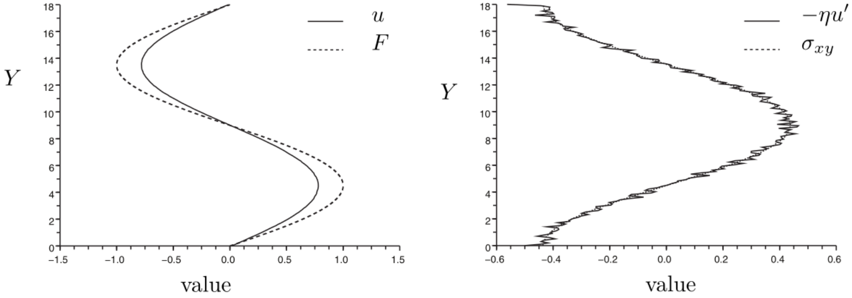
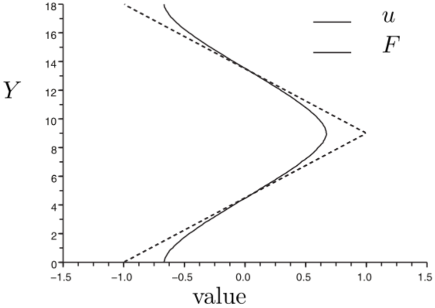
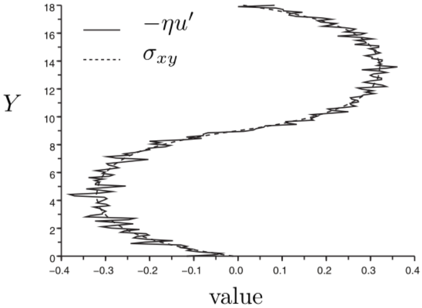


Figure: Numerical results from [5]

[5] See R. Joubaud and G. Stoltz, *Multiscale Model. Simul.* (2012)

Numerical illustration





Part IV: Error estimates on the estimation of transport coefficients

- Reminders: strong order, weak order
- Error analysis for the linear response method
- Error analysis for the Green–Kubo method

Reminder: Error estimates in Monte Carlo simulations

Consider the general SDE

$$dx_t = b(x_t)\,dt + \sigma(x_t)\,dW_t$$

with invariant measure π.

- Discretization $x^n \simeq x_{n\Delta t}$, invariant measure $\pi_{\Delta t}$. For instance,

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

- Ergodicity of the numerical scheme with invariant measure $\pi_{\Delta t}$

$$\frac{1}{N_{\text{iter}}} \sum_{n=1}^{N_{\text{iter}}} A(x^n) \xrightarrow[N_{\text{iter}} \to +\infty]{} \int_{\mathcal{X}} A(x)\,\pi_{\Delta t}(dx)$$

Error estimates for finite trajectory averages

$$\widehat{A}_{N_{\text{iter}}} = \frac{1}{N_{\text{iter}}} \sum_{n=1}^{N_{\text{iter}}} A(x^n) = \mathbf{E}_\pi(A) + \underbrace{\frac{C}{N_{\text{iter}}\Delta t}}_{\text{bias}} + \underbrace{C\Delta t^\alpha}_{\text{bias}} + \underbrace{\frac{\sigma_{A,\Delta t}}{\sqrt{N_{\text{iter}}\Delta t}}\mathscr{G}}_{\text{statistical error}}$$

Weak type expansions

- Numerical scheme = Markov chain characterized by evolution operator

$$P_{\Delta t}\varphi(x) = \mathbf{E}\left(\varphi\left(x^{n+1}\right) \middle| x^n = x\right)$$

where (x^n) is an approximation of $(x_{n\Delta t})$

- Standard notions of error: fixed integration time $T < +\infty$
  - Strong error:

$$\sup_{0 \leqslant n \leqslant T/\Delta t} \mathbf{E}|x^n - x_{n\Delta t}| \leqslant C\Delta t^p$$

  - Weak error: for any φ,

$$\sup_{0 \leqslant n \leqslant T/\Delta t} \left| \mathbf{E}\left[\varphi\left(x^n\right)\right] - \mathbf{E}\left[\varphi\left(x_{n\Delta t}\right)\right] \right| \leqslant C\Delta t^p$$

Δt-expansion of the evolution operator

$$P_{\Delta t}\varphi = \varphi + \Delta t\, \mathcal{A}_1\varphi + \Delta t^2 \mathcal{A}_2\varphi + \cdots + \Delta t^{p+1}\mathcal{A}_{p+1}\varphi + \Delta t^{p+2} r_{\varphi,\Delta t}$$

Weak order p when $\mathcal{A}_k = \mathcal{L}^k/k!$ for $1 \leqslant k \leqslant p$.

Elements of proof

- Rewrite the weak error as a telescopic sum

$$\mathbf{E}\left[\varphi(x^N)\right] - \mathbf{E}\left[\varphi(x_{N\Delta t})\right] = P_{\Delta t}^N \varphi(x_0) - \mathrm{e}^{N\Delta t \mathcal{L}} \varphi(x_0)$$
$$= \sum_{n=0}^{N-1} \left(P_{\Delta t}^{N-n} \, \mathrm{e}^{n\Delta t \mathcal{L}} \varphi(x_0) - P_{\Delta t}^{N-(n+1)} \, \mathrm{e}^{(n+1)\Delta t \mathcal{L}} \varphi(x_0) \right)$$
$$= \sum_{n=0}^{N-1} P_{\Delta t}^{N-(n+1)} \left(P_{\Delta t} - \mathrm{e}^{\Delta t \mathcal{L}} \right) \mathrm{e}^{n\Delta t \mathcal{L}} \varphi(x_0)$$

- Since $u(t,x) := \mathrm{e}^{t\mathcal{L}} \varphi(x)$ solves the backward Kolmogorov equation

$$\partial_t u = \mathcal{L} u, \qquad u(0,x) = \varphi.$$

we can write formally

$$\mathrm{e}^{\Delta t \mathcal{L}} \varphi = \mathrm{Id} + \Delta t \mathcal{L} \varphi + \frac{\Delta t^2}{2} \mathcal{L}^2 \varphi + \cdots$$

Example: Euler-Maruyama, weak order 1

Consider the scheme

$$x^{n+1} = \Phi_{\Delta t}(x^n, G^n) = x^n + \Delta t\, b(x^n) + \sqrt{\Delta t}\, \sigma(x^n)\, G^n$$

- Note that $P_{\Delta t}\varphi(x) = \mathbf{E}_G \left[\varphi\big(\Phi_{\Delta t}(x, G)\big)\right]$
- Technical tool: Taylor expansion

$$\varphi(x+\delta) = \varphi(x) + \delta^\mathsf{T}\nabla\varphi(x) + \frac{1}{2}\delta^\mathsf{T}\nabla^2\varphi(x)\delta + \frac{1}{6}D^3\varphi(x) : \delta^{\otimes 3} + \dots$$

- Replace δ with $\sqrt{\Delta t}\,\sigma(x)\,G + \Delta t\, b(x)$ and gather in powers of Δt

$$\varphi\big(\Phi_{\Delta t}(x, G)\big) = \varphi(x) + \sqrt{\Delta t}\,\sigma(x)\,G \cdot \nabla\varphi(x) + \Delta t \left(\frac{\sigma(x)^2}{2} G^\mathsf{T} \left[\nabla^2\varphi(x)\right] G + b(x)\cdot\nabla\varphi(x) \right) + \dots$$

- Taking expectations w.r.t. G leads to

$$P_{\Delta t}\varphi(x) = \varphi(x) + \Delta t \underbrace{\left(\frac{\sigma(x)^2}{2}\Delta\varphi(x) + b(x)\cdot\nabla\varphi(x) \right)}_{=\mathcal{L}\varphi(x)} + \mathcal{O}(\Delta t^2)$$

Error estimates on $\pi_{\Delta t}$

Suppose that

- For all smooth φ, the following expansion holds

$$P_{\Delta t}\varphi = \varphi + \Delta t\, \mathcal{A}_1\varphi + \Delta t^2 \mathcal{A}_2\varphi + \cdots + \Delta t^{p+1}\mathcal{A}_{p+1}\varphi + \Delta t^{p+2} r_{\varphi,\Delta t}$$

- The probability measure π is invariant by $\mathcal{A}_k$ for $1 \leqslant k \leqslant p$, namely

$$\int_{\mathcal{X}} \mathcal{A}_k \varphi \, d\pi = 0$$

- + Technical assumptions usually satisfied

Then

$$\int_{\mathcal{X}} \varphi \, \mathrm{d}\pi_{\Delta t} = \int_{\mathcal{X}} \varphi \Big(1 + \Delta t^p f_{p+1}\Big) \mathrm{d}\pi + \Delta t^{p+1} R_{\varphi,\Delta t},$$

where $g_{p+1} = \mathcal{A}_{p+1}^* \mathbf{1}$ and $f_{p+1} = -\left(\mathcal{A}_1^*\right)^{-1} g_{p+1}$.

Error on invariant measure can be (much) smaller than the weak error

Motivation of the result

We verify the error estimate for $\varphi \in \mathrm{Ran}(P_{\Delta t} - \mathrm{Id})$.

- Idea: $\pi_{\Delta t} = \pi(1 + \Delta t^p f_{p+1} + \dots)$
- by definition of $\pi_{\Delta t}$

$$\int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t} - \mathrm{Id}}{\Delta t} \right) \varphi \right] \mathrm{d}\pi_{\Delta t} = 0$$

- compare to first order correction to the invariant measure

$$\begin{aligned} \int_{\mathcal{X}} \left[\left(\frac{P_{\Delta t} - \mathrm{Id}}{\Delta t} \right) \varphi \right] (1 + \Delta t^p f_{p+1}) \, \mathrm{d}\pi \\ = \Delta t^p \int_{\mathcal{X}} \Big(\mathcal{A}_{p+1}\varphi + (\mathcal{A}_1 \varphi) f_{p+1} \Big) \, \mathrm{d}\pi + \mathcal{O}\left(\Delta t^{p+1}\right) \\ = \Delta t^p \int_{\mathcal{X}} \Big(g_{p+1} + \mathcal{A}_1^* f_{p+1} \Big) \varphi \, \mathrm{d}\pi + \mathcal{O}\left(\Delta t^{p+1}\right) \end{aligned}$$

Suggests $f_{p+1} = -\left(\mathcal{A}_1^*\right)^{-1} g_{p+1}$

Examples of splitting schemes for Langevin dynamics (1)

- Example: Langevin dynamics, discretized using a splitting strategy

$$A = M^{-1}p \cdot \nabla_q, \quad B_\eta = \Big(-\nabla V(q) + \eta\, F \Big) \cdot \nabla_p, \quad C = -M^{-1}p \cdot \nabla_p + \frac{1}{\beta}\Delta_p$$

- Note that $\mathcal{L}_\eta = A + B_\eta + \gamma C$

- Trotter splitting $\to$ weak order 1

$$P_{\Delta t}^{ZYX} = \mathrm{e}^{\Delta t Z}\, \mathrm{e}^{\Delta t Y}\, \mathrm{e}^{\Delta t X} = \mathrm{e}^{\Delta t \mathcal{L}} + \mathcal{O}(\Delta t^2)$$

- Strang splitting $\to$ weak order 2

$$P_{\Delta t}^{ZYXYZ} = \mathrm{e}^{\Delta t Z/2}\, \mathrm{e}^{\Delta t Y/2}\, \mathrm{e}^{\Delta t X}\, \mathrm{e}^{\Delta t Y/2}\, \mathrm{e}^{\Delta t Z/2} = \mathrm{e}^{\Delta t \mathcal{L}} + \mathcal{O}(\Delta t^3)$$

- Other category: Geometric Langevin[6] algorithms, *e.g.* $P_{\Delta t}^{\gamma C, A, B_\eta, A}$
$\to$ weak order 1 but measure preserved at order 2 in Δt

[6] N. Bou-Rabee and H. Owhadi, *SIAM J. Numer. Anal.* (2010)

Examples of splitting schemes for Langevin dynamics (2)

- $P_{\Delta t}^{B_\eta,A,\gamma C}$ corresponds to $\begin{cases} \widetilde{p}^{n+1} = p^n + \Big(-\nabla V(q^n) + \eta F \Big)\Delta t, \\ q^{n+1} = q^n + \Delta t \, M^{-1}\widetilde{p}^{n+1}, \\ p^{n+1} = \alpha_{\Delta t}\widetilde{p}^{n+1} + \sqrt{\dfrac{1-\alpha_{\Delta t}^2}{\beta} M} \, G^n \end{cases}$

where G^n are i.i.d. Gaussian and $\alpha_{\Delta t} = \exp(-\gamma M^{-1}\Delta t)$

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

Aim: For observable R, approximate

$$\alpha = \lim_{\eta \to 0} \frac{\mathbf{E}_{\eta}[R]}{\eta}$$

Estimator of linear response (up to time discretization):

$$\widehat{A}_{\eta,t} = \frac{1}{\eta t} \int_0^t R(q_s^\eta, p_s^\eta)\, \mathrm{d}s \xrightarrow[t \to +\infty]{\text{a.s.}} \alpha_\eta := \frac{1}{\eta} \int_{\mathcal{E}} R\, f_\eta \, \mathrm{d}\mu = \alpha + \mathcal{O}(\eta)$$

Contributions to the error

- Statistical error with asymptotic variance $\mathcal{O}(\eta^{-2})$
- Bias $\mathcal{O}(\eta)$ due to $\eta \neq 0$
- Bias from finite integration time
- Timestep discretization bias

- **Statistical error** dictated by Central Limit Theorem:

$$\sqrt{t}\left(\widehat{A}_{\eta,t} - \alpha_\eta\right) \xrightarrow[t\to+\infty]{\text{law}} \mathcal{N}\left(0, \frac{\sigma^2_{R,\eta}}{\eta^2}\right), \qquad \sigma^2_{R,\eta} = \sigma^2_{R,0} + \mathcal{O}(\eta)$$

so $\widehat{A}_{\eta,t} = \alpha_\eta + \mathcal{O}_{\mathrm{P}}\left(\frac{1}{\eta\sqrt{t}}\right)$ $\to$ requires long simulation times $t \sim \eta^{-2}$

- **Finite time integration bias**: $\left|\mathbf{E}\left(\widehat{A}_{\eta,t}\right) - \alpha_\eta\right| \leqslant \dfrac{K}{\eta t}$

Bias due to $t < +\infty$ is $\mathcal{O}\left(\frac{1}{\eta t}\right)$ $\to$ typically smaller than statistical error

- Key equality for the proofs: introduce $-\left(\mathcal{L} + \eta\widetilde{\mathcal{L}}\right)\mathscr{R}_\eta = R - \int_{\mathcal{E}} R f_\eta \, \mathrm{d}\mu$

$$\widehat{A}_{\eta,t} - \frac{1}{\eta}\int_{\mathcal{E}} R f_\eta \, \mathrm{d}\mu = \frac{\mathscr{R}_\eta(q_0^\eta, p_0^\eta) - \mathscr{R}_\eta(q_t^\eta, p_t^\eta)}{\eta t} + \frac{\sqrt{2\gamma}}{\eta t\sqrt{\beta}}\int_0^t \nabla_p \mathscr{R}_\eta(q_s^\eta, p_s^\eta)^T \mathrm{d}W_s$$

Error estimates on linear response (3/3)

Finite integration time bias and timestep bias

There exist functions $f_{0,1}$, $f_{\alpha,0}$ and $f_{\alpha,1}$ such that

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

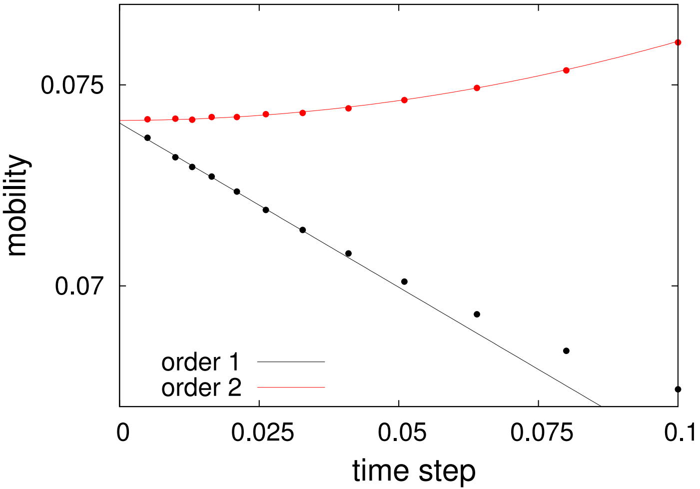
where the remainder is compatible with linear response

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

- Corollary: error estimates on the numerically computed mobility

$$\begin{aligned} \rho_{F,\Delta t} &= \lim_{\eta \to 0} \frac{1}{\eta} \left(\int_{\mathcal{E}} F^{\mathsf{T}} p \, \mu_{\eta,\Delta t}(\mathrm{d}q \, \mathrm{d}p) - \int_{\mathcal{E}} F^{\mathsf{T}} p \, \mu_{0,\Delta t}(\mathrm{d}q \, \mathrm{d}p) \right) \\ &= \rho_F + \Delta t^{\alpha} \int_{\mathcal{E}} F^{\mathsf{T}} p \, f_{\alpha,1} \, \mathrm{d}\mu + \Delta t^{\alpha+1} r_{\Delta t} \end{aligned}$$

Numerical results



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

Error estimates on the Green–Kubo formula (1/3)

Aim: For observable R, approximate

$$\alpha = \int_0^{+\infty} \mathbf{E}_0 \Big(R(q_t, p_t) S(q_0, p_0) \Big) \, \mathrm{d}t$$

"Natural" estimator (up to time discretization)

$$\widehat{A}_{K,T} = \frac{1}{K} \sum_{k=1}^{K} \int_0^T R(q_t^k, p_t^k) S(q_0^k, p_0^k) \, \mathrm{d}t$$

- **Contributions to the error:**
  - Truncature of time (exponential convergence of $\mathrm{e}^{t\mathcal{L}}$)
  - The statistical error increases linearly with T.
  - Timestep bias and quadrature formula

Error estimates on the Green–Kubo formula (2/3)

- **Truncation bias**: small due to generic exponential decay of correlations

$$\left|\mathbf{E}\left(\widehat{A}_{K,T}\right) - \alpha\right| \leqslant C\,\mathrm{e}^{-\kappa T}$$

- **Statistical error**: large, increases with the integration time

$$\forall T \geqslant 1, \qquad \mathrm{Var}\left(\widehat{A}_{K,T}\right) \leqslant C\,\frac{T}{K}$$

- **Time discretization and quadrature bias**: if
  - uniform-in-Δt convergence
  - error on the invariant measure of order Δt^a
  - $P_{\Delta t} = \mathrm{Id} + \Delta t \mathcal{L} + \Delta t^2 L_2 + \cdots + \Delta t^a L_a + \dots$

Then for R, S with average 0 w.r.t. μ,

$$\int_0^{+\infty} \mathbf{E}\Big(R(X_t)S(X_0)\Big)dt = \Delta t \sum_{n=0}^{+\infty} \mathbf{E}_{\Delta t}\left(\widetilde{R}_{\Delta t}\left(X^n\right) S\left(X^0\right)\right) + \mathrm{O}(\Delta t^a)$$

with

$$\widetilde{R}_{\Delta t} = \left(\mathrm{Id} + \Delta t\, L_2 \mathcal{L}^{-1} + \cdots + \Delta t^{a-1} L_a \mathcal{L}^{-1}\right) R - \mu_{\Delta t}(\dots)$$

Error estimates on Green-Kubo formulas (3/3)

- For methods of **weak order** 1, Riemman sum (ϕ, φ average 0 w.r.t. π)

$$\int_0^{+\infty} \mathbf{E}\Big(\phi(x_t)\varphi(x_0)\Big)dt = \Delta t \sum_{n=0}^{+\infty} \mathbf{E}_{\Delta t}\left(\Pi_{\Delta t}\phi\left(x^n\right)\varphi\left(x^0\right)\right) + \mathrm{O}(\Delta t)$$

where $\Pi_{\Delta t}\phi = \phi - \int_{\mathcal{X}} \phi \, d\pi_{\Delta t}$

- For methods of **weak order** 2, trapezoidal rule

$$\int_0^{+\infty} \mathbf{E}\Big(\phi(x_t)\varphi(x_0)\Big)dt = \frac{\Delta t}{2}\mathbf{E}_{\Delta t}\left(\Pi_{\Delta t}\phi\left(x^0\right)\varphi\left(x^0\right)\right) + \Delta t \sum_{n=1}^{+\infty} \mathbf{E}_{\Delta t}\left(\Pi_{\Delta t}\phi\left(x^n\right)\varphi\left(x^0\right)\right) + \mathrm{O}(\Delta t^2)$$

Summary

- **Definition and examples of nonequilibrium systems**
  - Convergence to invariant measure
  - Perturbation expansion of invariant measure
- **Definition and computation of transport coefficients**
  - Mobility, heat conductivity, shear viscosity
  - Linear response theory
  - Relationship with Green-Kubo formulas
- **Elements of numerical analysis**
  - estimation of biases due to timestep discretization
  - (largely) open issue: variance reduction