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# Computation of transport coefficients in molecular dynamics: methods and numerical analysis

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- **Linear response for steady-state nonequilibrium dynamics**
  - Equilibrium dynamics and their perturbations
  - Definition of transport coefficients
- **Timestep bias for the computation of transport coefficients<sup>1</sup>**
  - Linear response approach
  - Green–Kubo formulas
- **Mathematical analysis of a linearization approach<sup>2</sup>**
  - Motivation for the estimator of the transport coefficient
  - Numerical analysis (timestep and finite time bias, variance)

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<sup>1</sup>B. Leimkuhler, Ch. Matthews and G. Stoltz, The computation of averages from equilibrium and nonequilibrium Langevin molecular dynamics, *IMA J. Numer. Anal.* (2016)

<sup>2</sup>P. Plechac, G. S. and T. Wang, Convergence of the likelihood ratio method for linear response of non-equilibrium stationary states, *arXiv preprint* **1910.02479** (2019)

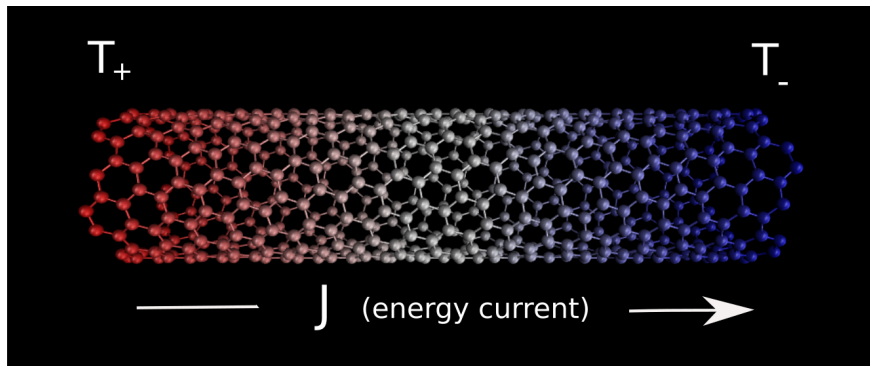
# Linear response for steady-state nonequilibrium dynamics

# Physical context and motivations

Predicting properties of matter from **atomistic simulations**

**Transport coefficients** (e.g. thermal conductivity): **quantitative** estimates

$$J = -\kappa \nabla T \quad (\text{Fourier's law})$$



**Long computational times** to estimate  $\kappa$  (up to several weeks/months)

# Reference equilibrium dynamics (1)

Positions  $q \in \mathcal{D}$  and momenta  $p \in \mathbb{R}^d$ , phase-space  $\mathcal{E} = \mathcal{D} \times \mathbb{R}^d$

**Hamiltonian**  $H(q, p) = V(q) + \frac{1}{2} p^T M^{-1} p$

**Langevin dynamics** (for given  $\gamma > 0$ )

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

Generator  $\mathcal{L} = \mathcal{L}_{\text{ham}} + \gamma \mathcal{L}_{\text{FD}}$  with

$$\mathcal{L}_{\text{ham}} = p^T M^{-1} \nabla_q - \nabla V^T \nabla_p, \quad \mathcal{L}_{\text{FD}} = -p^T M^{-1} \nabla_p + \frac{1}{\beta} \Delta_p$$

Unique invariant measure  $\mu(dq dp) = Z^{-1} e^{-\beta H(q,p)} dq dp = \nu(dq) \kappa(dp)$

# Ergodicity results for Langevin dynamics (1)

Almost-sure convergence<sup>3</sup> of **ergodic averages**  $\widehat{\varphi}_t = \frac{1}{t} \int_0^t \varphi(q_s, p_s) ds$

**Asymptotic variance** of ergodic averages (with  $\Pi_0\varphi = \varphi - \mathbb{E}_\mu(\varphi)$ )

$$\sigma_\varphi^2 = \lim_{t \rightarrow +\infty} t \text{Var} [\widehat{\varphi}_t^2] = 2 \int_{\mathcal{E}} (-\mathcal{L}^{-1} \Pi_0\varphi) \Pi_0\varphi d\mu$$

**Central limit theorem**<sup>4</sup> when Poisson equation can be solved in  $L^2(\mu)$

$$-\mathcal{L}\Phi = \Pi_0\varphi$$

Well-posedness for  $\mathcal{L}$  invertible on subsets of  $L_0^2(\mu) = \Pi_0 L^2(\mu)$

$$-\mathcal{L}^{-1} = \int_0^{+\infty} e^{t\mathcal{L}} dt$$

<sup>3</sup>Kliemann, *Ann. Probab.* **15**(2), 690-707 (1987)

<sup>4</sup>Bhattacharya, *Z. Wahrsch. Verw. Gebiete* **60**, 185-201 (1982)

## Ergodicity results for Langevin dynamics (2)

Prove **exponential convergence** of the semigroup  $e^{t\mathcal{L}}$  on  $E \subset L^2_0(\mu)$

- **Lyapunov** techniques<sup>5</sup>  $L^\infty_W(\mathcal{E}) = \left\{ \varphi \text{ measurable, } \left\| \frac{\varphi}{W} \right\|_{L^\infty} < +\infty \right\}$
- standard **hypocoercive**<sup>6</sup> setup  $H^1(\mu)$
- $E = L^2(\mu)$  after hypoelliptic regularization<sup>7</sup> from  $H^1(\mu)$
- Direct transfer from  $H^1(\mu)$  to  $E = L^2(\mu)$  by spectral argument<sup>8</sup>
- Directly<sup>9</sup>  $E = L^2(\mu)$  (recently<sup>10</sup> Poincaré using  $\partial_t - \mathcal{L}_{\text{ham}}$ )
- **coupling** arguments<sup>11</sup>
- Direct estimates on the resolvent using Schur complements<sup>12</sup>

Rate of convergence  $\min(\gamma, \gamma^{-1})$  in all cases

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<sup>5</sup>Wu ('01); Mattingly/Stuart/Higham ('02); Rey-Bellet ('06); Hairer/Mattingly ('11)

<sup>6</sup>Villani (2009) and before Talay (2002), Eckmann/Hairer (2003), Hérau/Nier (2004),...

<sup>7</sup>F. Hérau, *J. Funct. Anal.* (2007)

<sup>8</sup>G. Deligiannidis, D. Paulin and A. Doucet, *arXiv preprint 1808.04299* (2018)

<sup>9</sup>J. Dolbeaut, C. Mouhot and C. Schmeiser (2009, 2015)

<sup>10</sup>S. Armstrong and J.C. Mourrat, *arXiv preprint 1902.04037* (2019)

<sup>11</sup>A. Eberle, A. Guillin and R. Zimmer, *Ann. Probab.* (2019)

<sup>12</sup>E. Bernard, M. Fathi, A. Levitt, G. Stoltz, *arXiv preprint 2003.00726*

# Definition of transport coefficients (1)

Linear response of **nonequilibrium dynamics**

**Example:**  $\mathcal{D} = (L\mathbb{T})^d$ , **non-gradient** force  $F \in \mathbb{R}^{3N}$

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

Existence and uniqueness of invariant measure (Lyapunov techniques)

Generator  $\mathcal{L} + \eta \tilde{\mathcal{L}}$ , **invariant measure**  $f_\eta \mu$  with  $(\mathcal{L}^* + \eta \tilde{\mathcal{L}}^*) f_\eta = 0$

$$f_\eta = \left( \text{Id} + \eta (\tilde{\mathcal{L}} \Pi_0 \mathcal{L}^{-1} \Pi_0)^* \right)^{-1} \mathbf{1} = \left( 1 + \sum_{n=1}^{+\infty} (-\eta)^n \left[ (\tilde{\mathcal{L}} \Pi_0 \mathcal{L}^{-1} \Pi_0)^* \right]^n \right) \mathbf{1}$$

where adjoints are taken on  $L^2(\mu)$  (so that  $\mathcal{L}^* = -\mathcal{L}_{\text{ham}} + \gamma \mathcal{L}_{\text{FD}}$ )



## Definition of transport coefficients (2)

**Response property**  $R \in L_0^2(\mu)$ , conjugated response  $S = \tilde{\mathcal{L}}^* \mathbf{1}$ :

$$\alpha = \lim_{\eta \rightarrow 0} \frac{\mathbb{E}_\eta(R)}{\eta} = - \int_{\mathcal{E}} [\mathcal{L}^{-1} R] [\tilde{\mathcal{L}}^* \mathbf{1}] d\mu = \int_0^{+\infty} \mathbb{E}_0 \left( R(q_t, p_t) S(q_0, p_0) \right) dt$$

**In practice:**

- Identify the **response** function
- Construct a physically meaningful **perturbation**
- Obtain the transport coefficient  $\alpha$  (thermal cond., shear viscosity,...)
- Non physical forcings giving same transport coefficient (“synthetic”)

For the previous example, definition of **mobility** with  $R(q, p) = F^T M^{-1} p$

$$\lim_{\eta \rightarrow 0} \frac{\mathbb{E}_\eta (F^T M^{-1} p)}{\eta} = \beta F^T D F$$

with **effective diffusion**  $D = \int_0^{+\infty} \mathbb{E}_0 \left( (M^{-1} p_t) \otimes (M^{-1} p_0) \right) dt$

# Timestep bias for the computation of transport coefficients

# Practical computation of average properties (1)

**Numerical scheme:** **Markov chain** characterized by evolution operator

$$P_{\Delta t} \varphi(q, p) = \mathbb{E} \left( \varphi(q^{n+1}, p^{n+1}) \mid (q^n, p^n) = (q, p) \right)$$

Discretization of the Langevin dynamics: **splitting** strategy

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

First order splitting schemes:  $P_{\Delta t}^{ZYX} = e^{\Delta t Z} e^{\Delta t Y} e^{\Delta t X} \simeq e^{\Delta t \mathcal{L}}$

**Example:**  $P_{\Delta t}^{B,A,\gamma C}$  corresponds to (with  $\alpha_{\Delta t} = \exp(-\gamma M^{-1} \Delta t)$ )

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

where  $G^n$  are i.i.d. standard Gaussian random variables

# Practical computation of average properties (2)

Second order splitting  $P_{\Delta t}^{ZYXYZ} = e^{\Delta t Z/2} e^{\Delta t Y/2} e^{\Delta t X} e^{\Delta t Y/2} e^{\Delta t Z/2}$

**Example:**  $P_{\Delta t}^{\gamma C, B, A, B, \gamma C}$  (Verlet in the middle)

$$\left\{ \begin{array}{l} \tilde{p}^{n+1/2} = \alpha_{\Delta t/2} p^n + \sqrt{\frac{1 - \alpha_{\Delta t}}{\beta}} M G^n, \\ p^{n+1/2} = \tilde{p}^{n+1/2} - \frac{\Delta t}{2} \nabla V(q^n), \\ q^{n+1} = q^n + \Delta t M^{-1} p^{n+1/2}, \\ \tilde{p}^{n+1} = p^{n+1/2} - \frac{\Delta t}{2} \nabla V(q^{n+1}), \\ p^{n+1} = \alpha_{\Delta t/2} \tilde{p}^{n+1} + \sqrt{\frac{1 - \alpha_{\Delta t}}{\beta}} M G^{n+1/2}, \end{array} \right.$$

Other category: **Geometric Langevin**<sup>13</sup> algorithms, e.g.  $P_{\Delta t}^{\gamma C, A, B, A}$

<sup>13</sup>N. Bou-Rabee and H. Owhadi, *SIAM J. Numer. Anal.* (2010)

# Error estimates on average properties

**Trajectory ergodicity** of splitting schemes ( $\mathcal{D}$  bounded):

$$\widehat{\Phi}^{N_{\text{iter}}} = \frac{1}{N_{\text{iter}}} \sum_{n=1}^{N_{\text{iter}}} \varphi(q^n, p^n) \xrightarrow{N_{\text{iter}} \rightarrow +\infty} \int \varphi(q, p) d\mu_{\gamma, \Delta t}(q, p) \quad \text{a.s.}$$

**Numerical analysis:** statistical errors vs. systematic errors (**bias**):

- Central Limit Theorem and asymptotic variance: from analysis for Green–Kubo formulas,<sup>14</sup>

$$\text{Var} \left( \widehat{\Phi}^{N_{\text{iter}}} \right) = \frac{2}{\Delta t} \int_{\mathcal{E}} (-\mathcal{L}^{-1} \Pi_0 \varphi) \Pi_0 \varphi d\mu + O(1)$$

- Finite time integration error<sup>15</sup>
- **Timestep discretization** error<sup>16</sup>

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<sup>14</sup>Leimkuhler/Matthews/Stoltz, *IMA J. Numer. Anal.* (2016); Lelièvre/Stoltz, *Acta Numerica* (2016); Duncan/Zygalakis/Pavliotis, *arXiv preprint 1701.04247*

<sup>15</sup>J.C. Mattingly, A.M. Stuart and M.V. Tretyakov, *SIAM J. Numer. Anal.* (2010)

<sup>16</sup>D. Talay and L. Tubaro, *Stoch. Proc. Appl.* (1990); D. Talay, *Stoch. Proc. Appl.* (2002); A. Debussche and E. Faou, *SIAM J. Numer. Anal.* (2021)

# Timestep discretization error (1)

Weak order  $\alpha$  for the splitting scheme ( $P_{\Delta t} = e^{\Delta t \mathcal{L}} + O(\Delta t^{\alpha+1})$ )

$$\int_{\mathcal{E}} \varphi d\mu_{\gamma, \Delta t} = \int_{\mathcal{E}} \varphi d\mu + \Delta t^{\alpha} \int_{\mathcal{E}} \varphi f_{\alpha, \gamma} d\mu + O(\Delta t^{\alpha+1})$$

with correction function solution of  $\mathcal{L}^* f_{\alpha, \gamma} = g_{\gamma}$

**Example:**  $g_{\gamma} = -\frac{1}{2} S_1^* \mathbf{1}$  with  $S_1 = [C, A + B] + [B, A]$  for  $P_{\Delta t}^{\gamma C, B, A}$

Use [BCH formula](#) to write  $P_{\Delta t}^{\gamma C, B, A} = \text{Id} + \Delta t \mathcal{L} + \frac{\Delta t^2}{2} (\mathcal{L}^2 + S_1) + \Delta t^3 R_{1, \Delta t}$

**Proof:** approximation of characterization of invariance of  $\mu_{\gamma, \Delta t}$

$$\int_{\mathcal{E}} \left[ \left( \frac{\text{Id} - P_{\Delta t}}{\Delta t} \right) \phi \right] d\mu_{\gamma, \Delta t} = 0$$

## Timestep discretization error (2)

Correction function  $f_{1,\gamma}$  chosen so that

$$\int_{\mathcal{E}} \left[ \left( \frac{\text{Id} - P_{\Delta t}^{\gamma C, B, A}}{\Delta t} \right) \phi \right] (1 + \Delta t f_{1,\gamma}) d\mu = O(\Delta t^2)$$

This requirement can be rewritten as

$$0 = \int_{\mathcal{E}} \left( \frac{1}{2} S_1 \phi + (\mathcal{L}\phi) f_{1,\gamma} \right) d\mu = \int_{\mathcal{E}} \varphi \left[ \frac{1}{2} S_1^* \mathbf{1} + \mathcal{L}^* f_{1,\gamma} \right] d\mu,$$

Replace  $\phi$  by  $\left( \frac{\text{Id} - P_{\Delta t}^{\gamma C, B, A}}{\Delta t} \right)^{-1} \varphi$ ? No control on the **derivatives**...

Rely on the “nice” properties of the continuous dynamics, *i.e.* functional estimates<sup>17</sup> on  $\mathcal{L}^{-1}$  to use pseudo-inverses

$$Q_{1,\Delta t} = -\mathcal{L}^{-1} + \frac{\Delta t}{2} (\text{Id} + \mathcal{L}^{-1} S_1 \mathcal{L}^{-1})$$

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<sup>17</sup>D. Talay, Stoch. Proc. Appl. (2002); M. Kopec (2015)

# Error estimates on the Green-Kubo formula (1)

Assume  $\frac{P_{\Delta t} - \text{Id}}{\Delta t} = \mathcal{L} + \Delta t S_1 + \dots + \Delta t^{\alpha-1} S_{\alpha-1} + \Delta t^\alpha \tilde{R}_{\alpha, \Delta t}$  and

$$\|P_{\Delta t}^n\|_{\mathcal{B}(B_{W, \Delta t}^\infty)} \leq C e^{-kn\Delta t}, \quad \int_{\mathcal{E}} \phi d\mu_{\Delta t} = \int_{\mathcal{E}} \phi d\mu + \Delta t^\alpha r_{\phi, \Delta t}$$

**Uniform-in-time convergence** follows from Lyapunov condition (with  $W$ ) and **uniform minorization**

$$P_{\Delta t}^{\lceil T/\Delta t \rceil}(X_0, dX) \geq a m(dX)$$

## • Issues with Green-Kubo formula:

- Truncature of time (exponential convergence of  $e^{t\mathcal{L}}$ )
- The **statistical error** for correlations increases a lot with time lag
- **Timestep bias and quadrature formula**



## Error estimates on the Green-Kubo formula (2)

Formulated for generic stochastic dynamics

For  $R, S$  with average 0 w.r.t.  $\mu$ ,

$$\int_0^{+\infty} \mathbb{E} \left( R(X_t) S(X_0) \right) dt = \Delta t \sum_{n=0}^{+\infty} \mathbb{E}_{\Delta t} \left( \tilde{R}_{\Delta t} (X^n) S(X^0) \right) + O(\Delta t^\alpha)$$

with  $\tilde{R}_{\Delta t} = \left( \text{Id} + \Delta t S_1 \mathcal{L}^{-1} + \dots + \Delta t^{\alpha-1} S_{\alpha-1} \mathcal{L}^{-1} \right) R - \mu_{\Delta t}(\dots)$

Reduces to **trapezoidal** rule for **second** order schemes

B. Leimkuhler, Ch. Matthews and G. Stoltz, The computation of averages from equilibrium and nonequilibrium Langevin molecular dynamics, *IMA J. Numer. Anal.* **36**(1), 13-79 (2016)

T. Lelièvre and G. Stoltz, Partial differential equations and stochastic methods in molecular dynamics, *Acta Numerica* **25** (2016)

# Error estimates on linear response (1)

Splitting schemes obtained by replacing  $B$  with  $B_\eta = B + \eta F \cdot \nabla_p$

For instance,  $P_{\Delta t}^{A, B + \eta \tilde{\mathcal{L}}, \gamma C}$  for

$$\begin{cases} q^{n+1} = q^n + \Delta t p^n, \\ \tilde{p}^{n+1} = p^n + \Delta t \left( -\nabla V(q^{n+1}) + \eta F \right), \\ p^{n+1} = \alpha_{\Delta t} \tilde{p}^{n+1} + \sqrt{\frac{1 - \alpha_{\Delta t}^2}{\beta}} G^n \end{cases}$$

**Issues with linear response methods:**  $\alpha \simeq \frac{1}{\eta N_{\text{iter}}} \sum_{n=1}^{N_{\text{iter}}} R(q^n, p^n)$

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

## Error estimates on the mobility (2)

Invariant measure  $\mu_{\gamma,\eta,\Delta t}$  of the numerical scheme

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

where the remainder is compatible with linear response

$$|r_{\varphi,\gamma,\eta,\Delta t}| \leq K(\eta^2 + \Delta t^{\alpha+1}), \quad |r_{\varphi,\gamma,\eta,\Delta t} - r_{\varphi,\gamma,0,\Delta t}| \leq K\eta(\eta + \Delta t^{\alpha+1})$$

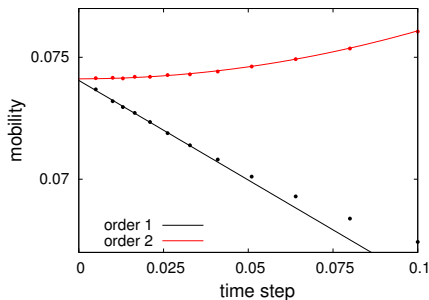
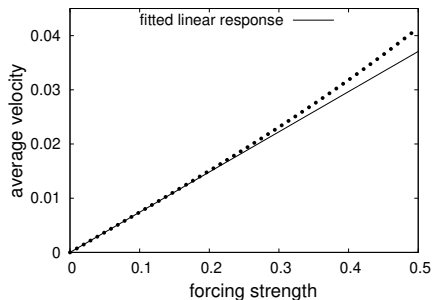
**Corollary:** error estimates on the **numerically computed mobility**

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

Results in the **overdamped** limit

B. Leimkuhler, Ch. Matthews and G. Stoltz, The computation of averages from equilibrium and nonequilibrium Langevin molecular dynamics, *IMA J. Numer. Anal.* **36**(1), 13-79 (2016)

# Numerical results



**Left:** Linear response of the average velocity as a function of  $\eta$  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  $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$ .

# Mathematical analysis of a linearization approach

# Sensitivity estimator: motivation

**General non-degenerate stochastic dynamics** on  $\mathcal{D} = \mathbb{T}^d$

- **Reference dynamics**  $dX_t^0 = b(X_t^0) dt + \sigma(X_t^0) dW_t$
- **Perturbed dynamics**  $dX_t^\eta = (b(X_t^\eta) + \eta F(X_t^\eta)) dt + \sigma(X_t^\eta) dW_t$
- Assume  $\sigma\sigma^T$  positive definite  $\rightarrow$  unique invariant measure  $\nu_\eta$

**Estimator of the linear response**

$$\alpha = \lim_{\eta \rightarrow 0} \frac{\nu_\eta(R) - \nu_0(R)}{\eta} = \lim_{t \rightarrow \infty} \mathbb{E}_0 \left\{ \left( \frac{1}{t} \int_0^t (R(X_s^0) - \nu_0(R)) ds \right) Z_t \right\}$$

with  $Z_t = \int_0^t U(X_s^0)^T dW_s$  and  $\sigma U = F$

Motivation: Girsanov theorem, linearization, and longtime limit (formal)

$$\mathbb{E}_\eta \left[ \frac{1}{t} \int_0^t R(X_s^\eta) ds \right] = \mathbb{E}_0 \left[ \left( \frac{1}{t} \int_0^t R(X_s^0) ds \right) \exp \left( \eta \int_0^t U(X_s^0)^T dW_s - \frac{\eta^2}{2} \int_0^t |U(X_s^0)|^2 ds \right) \right]$$

## Sensitivity estimator: proof

**Proof of consistency:** Generator  $\mathcal{L} + \eta\tilde{\mathcal{L}}$ , Poisson equation  $-\mathcal{L}\hat{R} = \Pi_0 R$   
(well posed)

Rewrite the time integral as a martingale, up to remainder terms

$$\int_0^t \Pi_0 R(X_s^0) ds = M_t + \hat{R}(X_0^0) - \hat{R}(X_t^0), \quad M_t = \int_0^t \nabla \hat{R}(X_s)^T \sigma(X_s^0) dW_s$$

and use Itô isometry to write  $\frac{1}{t} \mathbb{E}(M_t Z_t)$  as

$$\frac{1}{t} \int_0^t \mathbb{E} \left( U(X_s^0)^T \sigma(X_s^0)^T \nabla \hat{R}(X_s^0) \right) ds \xrightarrow[t \rightarrow +\infty]{} \int_{\mathcal{D}} F^T \nabla \hat{R} d\nu_0 = \alpha$$

**Variance uniformly bounded in time:** by similar manipulations,

$$\forall t > 0, \quad \text{Var} \left\{ \left( \frac{1}{t} \int_0^t (R(X_s^0) - \nu_0(R)) ds \right) Z_t \right\} \leq C$$

## Sensitivity estimator: discretization

Euler–Maruyama scheme  $X^{n+1} = X^n + \Delta t b(X^n) + \sqrt{\Delta t} \sigma(X^n) G^n$

Assume again **uniform-in-time minorization** condition  $P_{\Delta t}^{\lceil T/\Delta t \rceil} \geq a m(dx)$

**Discrete sensinty estimator (slightly idealized)**

$$\mathcal{M}_{\Delta t, N_{\text{iter}}}^{[1]}(R) = \frac{1}{N_{\text{iter}}} \sum_{n=0}^{N_{\text{iter}}-1} (R(X^n) - \mathbb{E}_{\Delta t}(R)) Z^{N_{\text{iter}}}$$

with  $Z^{N_{\text{iter}}} = \sum_{n=0}^{N_{\text{iter}}-1} (\sigma(X^n)^{-1} F(X^n))^T G^n$

$$\left| \mathbb{E}_{\Delta t} \left\{ \mathcal{M}_{\Delta t, N_{\text{iter}}}^{[1]}(R) \right\} - \alpha \right| \leq C \left( \Delta t + \frac{1}{\sqrt{N_{\text{iter}} \Delta t}} \right)$$
$$\text{Var}_{\Delta t} \left\{ \mathcal{M}_{\Delta t, N_{\text{iter}}}^{[1]}(R) \right\} \leq C_1 + C_2 \left( \Delta t + \frac{1}{N_{\text{iter}} \Delta t} \right)$$

Finite-time bias  $O(\text{time}^{-1/2})$  ( $\text{time}^{-1}$  for standard time averages)



# Discretized sensitivity estimator: proofs

**Elements of proofs:**  $\frac{\text{Id} - P_{\Delta t}}{\Delta t} \widehat{R}_{\Delta t} = \Pi_{\Delta t} R$  with  $\Pi_{\Delta t} \varphi = \varphi - \mathbb{E}_{\Delta t}(\varphi)$

Manipulations at the discrete level mimicking the ones for SDEs:

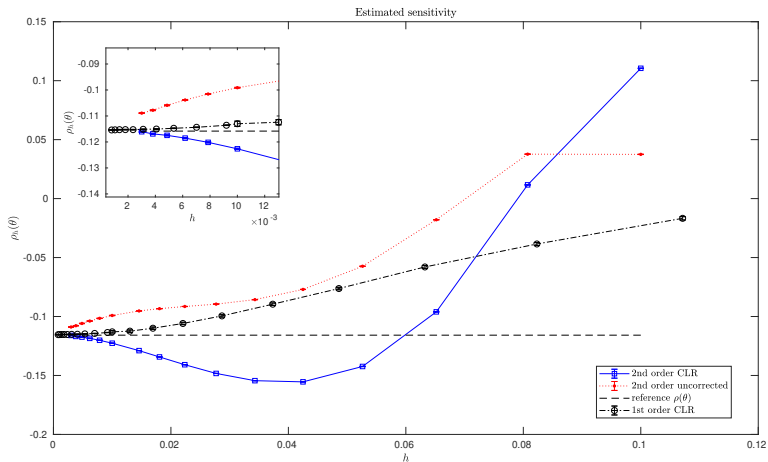
$$\begin{aligned} \mathbb{E}_{\Delta t} \left\{ \mathcal{M}_{\Delta t, N_{\text{iter}}}^{[1]}(R) \right\} &= \frac{1}{N_{\text{iter}} \Delta t} \sum_{n=0}^{N_{\text{iter}}-1} \mathbb{E}_{\Delta t} \left\{ (\text{Id} - P_{\Delta t}) \widehat{R}_{\Delta t}(X^n) Z^{N_{\text{iter}}} \right\}, \\ &= \frac{1}{N_{\text{iter}} \Delta t} \sum_{n=0}^{N_{\text{iter}}-1} \mathbb{E}_{\Delta t} \left\{ M_{\Delta t}^n (Z^{n+1} - Z^n) \right\} + \mathcal{O} \left( \Delta t^{3/2}, \frac{1}{\sqrt{N_{\text{iter}} \Delta t}} \right) \end{aligned}$$

with  $M_{\Delta t}^n = \widehat{R}_{\Delta t}(X^{n+1}) - (P_{\Delta t} \widehat{R}_{\Delta t})(X^n) \simeq \nabla \widehat{R}_{\Delta t}(X^n)^T \sigma(X^n) G^n$  and discrete Itô isometry

**BUT**  $\widehat{R}_{\Delta t}$  is a priori not smooth (use pseudo inverses and control remainders/approximations uniformly everywhere...)

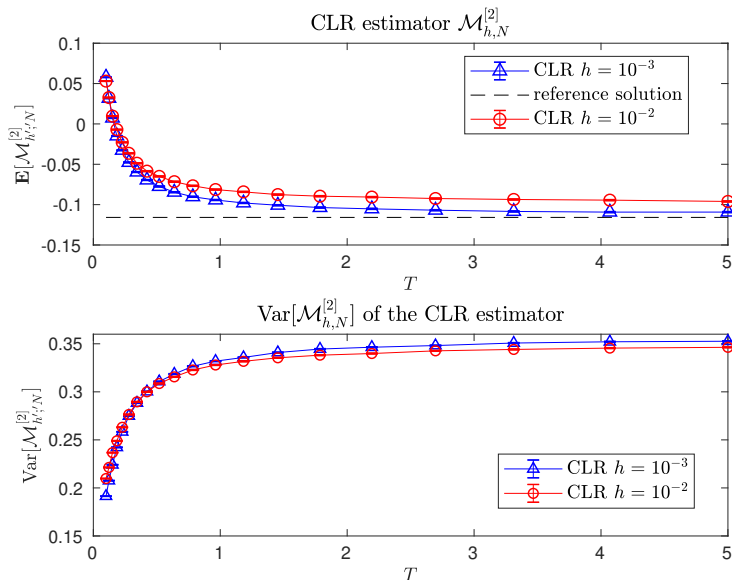
**Second order schemes:** bias  $\mathcal{O}(\Delta t^2)$  with modified martingale (one-dimensional case or constant  $\sigma$ )

# Discretized sensitivity estimator: numerical results (1)



Estimation of  $\alpha$  for various values of the timestep  $\Delta t$ . Reference value computed by numerical quadrature (one-dimensional example)

# Discretized sensitivity estimator: numerical results (2)



# Extensions and future work

# Several year workplan!

- **Sensitivity estimator** (with P. Plechac and T. Wang, “short term”)
  - **Degenerate noise**: Langevin dynamics, thermal transport in chains
  - Compare performance with Green–Kubo type methods
- **Alternative approaches**, possibly with some **blending**
  - Rely on tangent dynamics<sup>18</sup>
  - Resort to efficient coupling methods<sup>19</sup>
  - Optimize synthetic forcings<sup>20</sup>

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<sup>18</sup>R. Assaraf, B. Jourdain, T. Lelièvre, and R. Roux, Computation of sensitivities for the invariant measure of a parameter dependent diffusion, *Stoch. Partial Differ. Equ. Anal. Comput.* (2018)

<sup>19</sup>A. Eberle and R. Zimmer, Sticky couplings of multidimensional diffusions with different drifts, *Ann. Inst. H. Poincaré Probab. Statist.* (2019)

<sup>20</sup>D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Cambridge University Press, 2008)