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

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Outline

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

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

[2] 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)

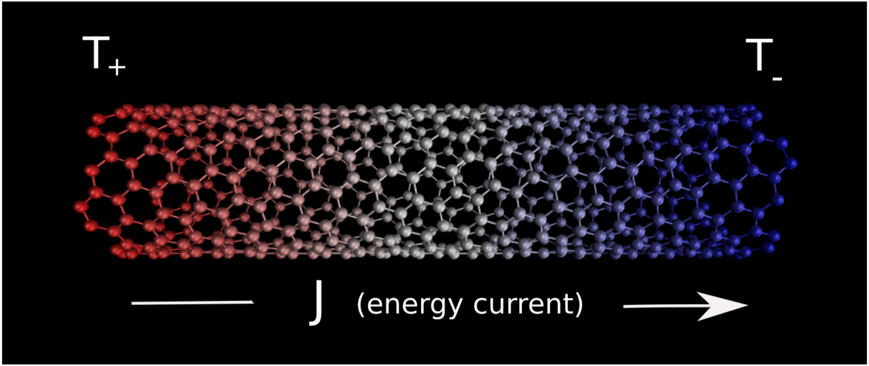
Linear response for steady-state nonequilibrium dynamics

Physical context and motivations

Predicting properties of matter from atomistic simulations

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

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



Long computational times to estimate κ (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 $\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \gamma \mathcal{L}_{\mathrm{FD}}$ with

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

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

Ergodicity results for Langevin dynamics (1)

Almost-sure convergence[3] of ergodic averages $\widehat{\varphi}_t = \frac{1}{t}\int_0^t \varphi(q_s,p_s)\,ds$

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

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

Central limit theorem[4] 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 $L_0^2(\mu) = \Pi_0 L^2(\mu)$

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

[3] Kliemann, *Ann. Probab.* **15**(2), 690-707 (1987)

[4] Bhattacharya, *Z. Wahrsch. Verw. Gebiete* **60**, 185–201 (1982)

Ergodicity results for Langevin dynamics (2)

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

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

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

[5] Wu ('01); Mattingly/Stuart/Higham ('02); Rey-Bellet ('06); Hairer/Mattingly ('11)

[6] Villani (2009) and before Talay (2002), Eckmann/Hairer (2003), Hérau/Nier (2004),...

[7] F. Hérau, *J. Funct. Anal.* (2007)

[8] G. Deligiannidis, D. Paulin and A. Doucet, *Ann. Appl. Probab.* (2020)

[9] Hérau (2006), Dolbeaut/Mouhot/Schmeiser (2009, 2015)

[10] Armstrong/Mourrat (2019), Cao/Lu/Wang (2019)

[11] A. Eberle, A. Guillin and R. Zimmer, *Ann. Probab.* (2019)

[12] 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 $F \in \mathbb{R}^{3N}$

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

Existence and uniqueness of invariant measure (Lyapunov techniques)

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

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

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

Definition of transport coefficients (2)

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

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

In practice:

- Identify the response function
- Construct a physically meaningful perturbation
- Obtain the transport coefficient α (thermal cond., shear viscosity,...)
- Non physical forcings giving same transport coefficient ("synthetic")

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

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

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

Timestep bias for the computation of transport coefficients

Practical computation of average properties (1)

Numerical scheme: Markov chain characterized by evolution operator

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

Discretization of the Langevin dynamics: splitting strategy

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

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

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

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

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

Practical computation of average properties (2)

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

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

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

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

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

Error estimates on average properties

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

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

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

- Central Limit Theorem and asymptotic variance: from analysis for Green–Kubo formulas,[14]

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

- Finite time integration error[15]
- Timestep discretization error[16]

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

[15] J.C. Mattingly, A.M. Stuart and M.V. Tretyakov, *SIAM J. Numer. Anal.* (2010)

[16] Talay/Tubaro, *Stoch. Proc. Appl.* (1990); Talay, *Stoch. Proc. Appl.* (2002); Debussche/Faou, *SIAM J. Numer. Anal.* (2012); Abdulle/Vilmart/Zygalakis (2015)

Timestep discretization error (1)

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

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

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 $P_{\Delta t}^{\gamma C,B,A} = \mathrm{Id} + \Delta t \mathcal{L} + \frac{\Delta t^2}{2} \left(\mathcal{L}^2 + S_1 \right) + \Delta t^3 R_{1,\Delta t}$

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

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

Timestep discretization error (2)

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

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

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

Rely on the "nice" properties of the continuous dynamics, *i.e.* functional estimates[17] on $\mathcal{L}^{-1}$ to use pseudo-inverses

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

[17] D. Talay, Stoch. Proc. Appl. (2002); M. Kopec (2015)

Error estimates on the Green-Kubo formula (1)

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

$$\|P_{\Delta t}^n\|_{\mathcal{B}(B^\infty_{W,\Delta t})} \leqslant C\mathrm{e}^{-\kappa n \Delta t}, \qquad \int_{\mathcal{E}} \phi \, d\mu_{\Delta t} = \int_{\mathcal{E}} \phi \, d\mu + \Delta t^{\alpha} r_{\phi,\Delta t}$$

Uniform-in-time convergence follows from Lyapunov condition (with W) and uniform minorization[18]

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

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

[18] A. Durmus, A. Enfroy, E. Moulines, G. Stoltz (2021)

Error estimates on the Green-Kubo formula (2)

Formulated for generic stochastic dynamics

For R, S with average 0 w.r.t. μ,

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

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

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

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

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

- Statistical error with asymptotic variance $\mathrm{O}(\eta^{-2})$
- 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

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

where the remainder is compatible with linear response

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

Corollary: error estimates on the numerically computed mobility

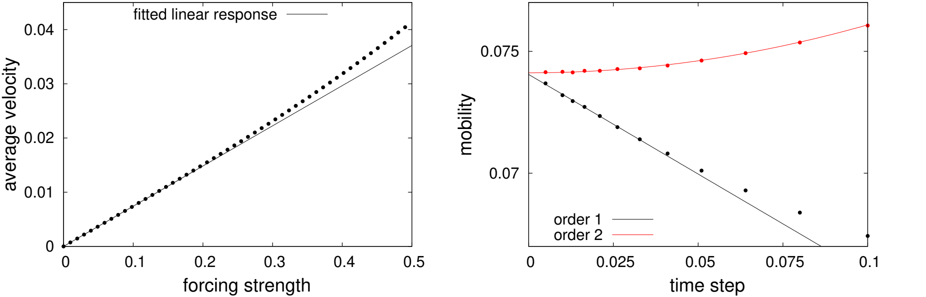
$$\nu_{F,\gamma,\Delta t} = \lim_{\eta \to 0} \frac{1}{\eta} \left(\int_{\mathcal{E}} F^T M^{-1} p \, \mu_{\gamma,\eta,\Delta t}(dq\,dp) - \int_{\mathcal{E}} F^T M^{-1} p \, \mu_{\gamma,0,\Delta t}(dq\,dp) \right)$$

$$= \nu_{F,\gamma} + \Delta t^\alpha \int_{\mathcal{E}} F^T M^{-1} p \, f_{\alpha,1,\gamma} \, d\mu + \Delta t^{\alpha+1} r_{\gamma,\Delta t}$$

Results in the overdamped limit

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 η for the scheme associated with $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$ and $\Delta t = 0.01, \gamma = 1$.

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

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 $\to$ unique invariant measure ν_η

Estimator of the linear response

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

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

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

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

Sensitivity estimator: proof

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

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

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

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

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

Variance uniformly bounded in time: by similar manipulations,

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

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 $P_{\Delta t}^{\lceil T/\Delta t \rceil} \geqslant a\, m(dx)$

Discrete sensitity estimator (slightly idealized)

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

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

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

$$\operatorname{Var}_{\Delta t}\left\{\mathcal{M}^{[1]}_{\Delta t, N_{\text{iter}}}(R)\right\} \leqslant C_1 + C_2\left(\Delta t + \frac{1}{N_{\text{iter}}\Delta t}\right)$$

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

Discretized sensitivity estimator: proofs

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

Manipulations at the discrete level mimicking the ones for SDEs:

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

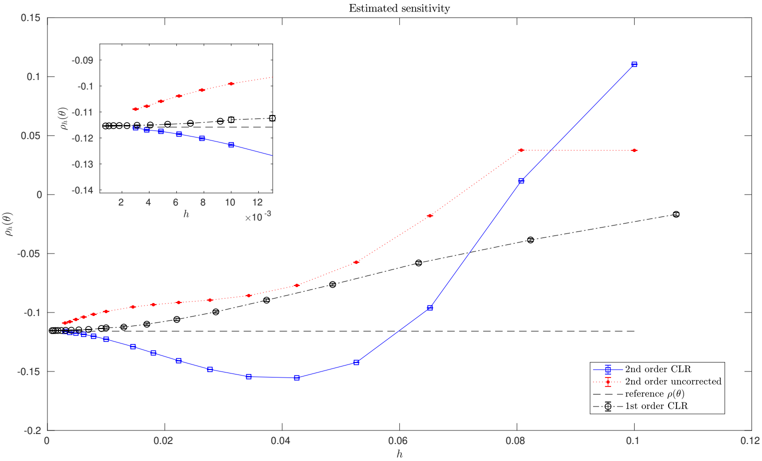
$$= \frac{1}{N_{\mathrm{iter}}\Delta t}\sum_{n=0}^{N_{\mathrm{iter}}-1} \mathbb{E}_{\Delta t}\left\{M^n_{\Delta t}\left(Z^{n+1} - Z^n\right)\right\} + \mathrm{O}\left(\Delta t^{3/2}, \frac{1}{\sqrt{N_{\mathrm{iter}}\Delta t}}\right)$$

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

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

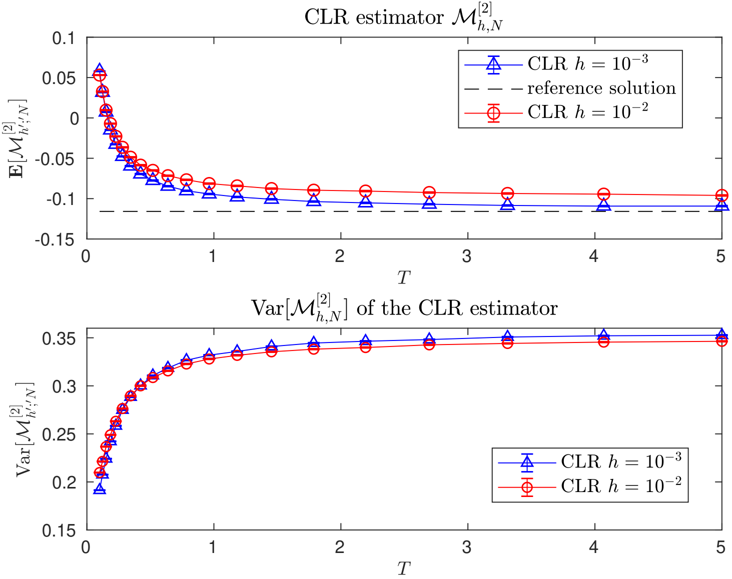
Second order schemes: bias $\mathrm{O}(\Delta t^2)$ with "martingale product" approach

Discretized sensitivity estimator: numerical results (1)



Estimation of α for various values of the timestep Δt. Reference value computed by numerical quadratude (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[19]
  - Resort to efficient coupling methods such as sticky coupling[20]
  - Optimize synthetic forcings[21]

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[19] 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)

[20] Eberle/Zimmer (2019); Durmus/Eberle/Enfroy/Guillin/Monmarché (2021)

[21] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Cambridge University Press, 2008)