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Error estimates and variance reduction for nonequilibrium stochastic dynamics

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"Nonequilibrium molecular dynamics" workshop

Outline

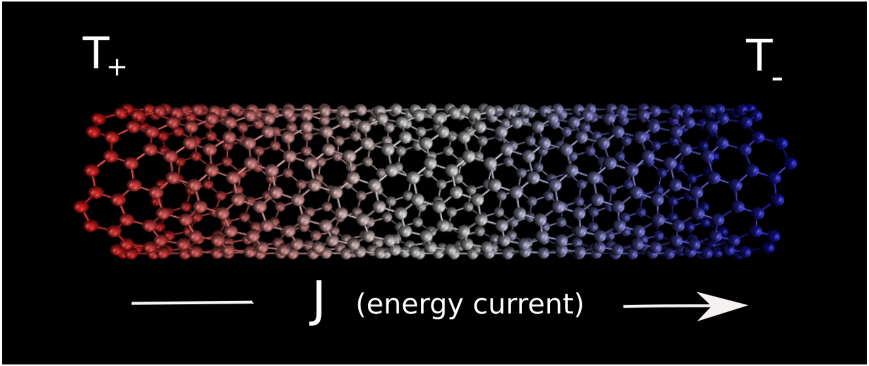
- **An introduction to molecular dynamics**
- **Linear response for steady-state nonequilibrium dynamics**
  - Equilibrium dynamics and their perturbations
  - Definition of transport coefficients
- **Error estimates (variance, bias)**
  - Nonequilibrium molecular dynamics
  - Green–Kubo formulas
- **Extensions and perspectives**

An introduction to molecular dynamics

Computational statistical physics (1)

Aims of computational statistical physics

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



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

Computational statistical physics (2)

- Microstate of the system: positions $q \in \mathcal{D}$, momenta $p \in \mathbb{R}^d$
- Macrostate of the system described by a **probability measure**

Equilibrium thermodynamic properties (pressure,. . .)

$$\mathbb{E}_\mu(\varphi) = \int_{\mathcal{D}\times\mathbb{R}^d} \varphi(q,p)\,\mu(dq\,dp)$$

- Choice of thermodynamic ensemble: least biased probability measure compatible with the observed macroscopic data (volume, energy, number of particles, ... fixed exactly or in average)

- **Boltzmann–Gibbs measure:** average energy fixed H

$$\mu_{\mathrm{NVT}}(dq\,dp) = Z_{\mathrm{NVT}}^{-1}\,\mathrm{e}^{-\beta H(q,p)}\,dq\,dp$$

with $\beta = \dfrac{1}{k_{\mathrm{B}}T}$ the Lagrange multiplier of the constraint $\displaystyle\int_{\mathcal{E}} H\,\rho\,dq\,dp = E_0$

Reference dynamics: (kinetic/underdamped) Langevin

Positions $q \in \mathcal{D}$ (typically $\mathcal{D} = (L\mathbb{T})^d$), momenta $p \in \mathbb{R}^d$
Phase-space $\mathcal{E} = \mathcal{D} \times \mathbb{R}^d$

Hamiltonian $H(q,p) = V(q) + \frac{1}{2}p^T M^{-1} p$, friction $\gamma > 0$

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

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 proba. meas. $\mu(dq\,dp) = \dfrac{\mathrm{e}^{-\beta H(q,p)}}{Z} dq\,dp = \nu(dq)\kappa(dp)$

$$\forall \varphi, \quad \int_{\mathcal{E}} \mathcal{L}\varphi \, d\mu = 0 \qquad \Longleftrightarrow \qquad \mathcal{L}^\dagger \mu = 0$$

Ergodicity results for Langevin dynamics (1)

Almost-sure convergence[1] 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[2] 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 $L_0^2(\mu) = \Pi_0 L^2(\mu)$

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

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

[2] 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[3] $L^\infty_{\mathscr{K}}(\mathcal{E}) = \left\{ \varphi \, \text{measurable}, \, \sup \left| \frac{\varphi}{\mathscr{K}} \right| < +\infty \right\}$
- standard hypocoercive[4] setup $H^1(\mu)$
- $L^2(\mu)$ after hypoelliptic regularization[5] from $H^1(\mu)$
- direct transfer from $H^1(\mu)$ to $L^2(\mu)$ by spectral argument[6]
- directly[7] $L^2(\mu)$ (recently[8] Poincaré using $\partial_t - \mathcal{L}_{\mathrm{ham}}$)
- coupling arguments[9]
- direct estimates on the resolvent using Schur complements[10]

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

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

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

[5] Hérau, *J. Funct. Anal.* (2007)

[6] Deligiannidis/Paulin/Doucet, *Ann. Appl. Probab.* (2020)

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

[8] Armstrong/Mourrat (2019), Cao/Lu/Wang (2019), Brigatti (2021), Brigati/Stoltz (2023)

[9] Eberle/Guillin/Zimmer, *Ann. Probab.* (2019)

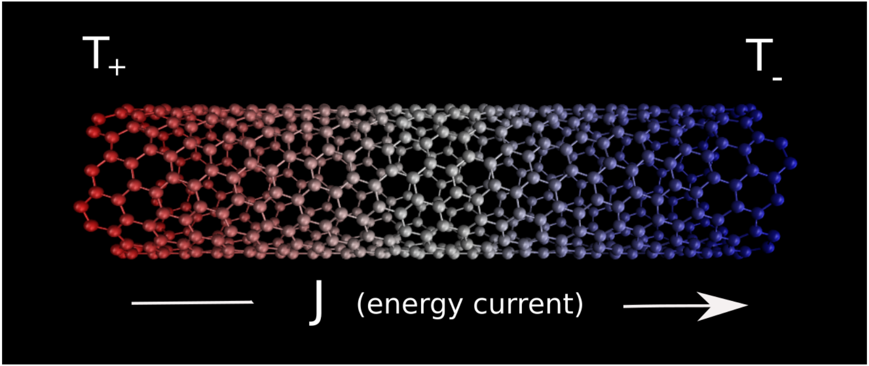
[10] Bernard/Fathi/Levitt/Stoltz, *Annales Henri Lebesgue* (2022)

Linear response for steady-state nonequilibrium dynamics

Physical context and motivations

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

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



Slow convergence due to large noise to signal ratio

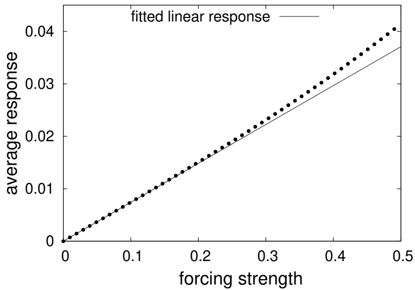
Long computational times to estimate κ (up to several weeks/months)

Linear response of nonequilibrium stochastic dynamics

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

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

Response function $R(q,p) = F^T M^{-1} p =$ velocity in direction F



Existence/uniqueness of invariant probability measure (Lyapunov)

Generator $\mathcal{L} + \eta\widetilde{\mathcal{L}}$ with $\widetilde{\mathcal{L}} = F^T\nabla_p$

$$\mathbb{E}_\eta(R) = \int_{\mathcal{E}} R\,\psi_\eta \approx \alpha\eta$$

$\alpha =$ transport coefficient

Properties of the invariant probability measure

- Solution to the Fokker–Planck equation $\left(\mathcal{L}+\eta\widetilde{\mathcal{L}}\right)^\dagger \psi_\eta = 0$

$$\forall \varphi, \qquad \int_{\mathcal{E}} \left[(\mathcal{L}+\eta\widetilde{\mathcal{L}})\varphi\right] \psi_\eta = 0$$

- Analytical expression not known $\to$ no Metropolis-type algorithms

- Stratification not possible

- Depends non-locally on the potential V $\to$ prevents importance sampling

Example: 1D dynamics $dq_t = (-V'(q_t) + F)\,dt + \sqrt{2}\,dW_t$, invariant measure with density

$$\psi_F(q) = Z_F^{-1} \int_{\mathbb{T}} \mathrm{e}^{V(q+y)-V(q)-Fy}\,dy$$

Because of $F \neq 0$, a modification to V at a given point is felt everywhere in a non trivial way!

Definition of transport coefficients (1)

Perturbative regime: invariant measure $\psi_\eta = f_\eta \mu$ with $f_\eta = 1 + \mathrm{O}(\eta)$

$$\forall \varphi, \qquad 0 = \int_{\mathcal{E}} \left[\left(\mathcal{L} + \eta \widetilde{\mathcal{L}} \right) \varphi \right] f_\eta \, d\mu = \int_{\mathcal{E}} \varphi \left[\left(\mathcal{L} + \eta \widetilde{\mathcal{L}} \right)^* f_\eta \right] d\mu$$

* = adjoints on $L^2(\mu)$ ($\partial_{q_i}^* = -\partial_{q_i} + \beta \partial_{q_i} V$ and $\partial_{p_i}^* = -\partial_{p_i} + \beta (M^{-1} p)_i$)

Fokker–Planck equation

$$\left(\mathcal{L} + \eta \widetilde{\mathcal{L}} \right)^* f_\eta = 0$$

By identifying powers of η (recalling $\Pi_0 \varphi = \varphi - \mu(\varphi)$)

$$f_\eta = 1 + \eta \mathfrak{f}_1 + \eta^2 \mathfrak{f}_2 + \dots, \qquad -\mathcal{L}^* \mathfrak{f}_1 = \widetilde{\mathcal{L}}^* \mathbf{1} = \Pi_0 \widetilde{\mathcal{L}}^* \mathbf{1} = S$$

Running example: $\mathcal{L}^* = -\mathcal{L}_{\mathrm{ham}} + \gamma \mathcal{L}_{\mathrm{FD}}$ and $\widetilde{\mathcal{L}}^* = -\widetilde{\mathcal{L}} + \beta F^T M^{-1} p$

$$S(q,p) = \beta F^T M^{-1} p$$

Definition of transport coefficients (2)

Response property $R \in L_0^2(\mu) = \Pi_0 L^2(\mu)$, conjugated response $S = \widetilde{\mathcal{L}}^* \mathbf{1}$:

$$\alpha = \lim_{\eta \to 0} \frac{\mathbb{E}_\eta(R)}{\eta} = \int_{\mathcal{E}} R \mathfrak{f}_1 \, d\mu = \int_{\mathcal{E}} R \left[(-\mathcal{L}^*)^{-1} S \right] d\mu = \int_{\mathcal{E}} \left(-\mathcal{L}^{-1} R\right) S \, d\mu$$

$$= \int_0^{+\infty} \left[\int_{\mathcal{E}} \left(\mathrm{e}^{t\mathcal{L}} R\right) S \, d\mu \right] dt = \int_0^{+\infty} \mathbb{E}_0\Big(R(q_t, p_t) S(q_0, p_0) \Big) dt$$

In practice:

- Identify the response function and the reference dynamics
- Construct a physically meaningful perturbation (bulk or boundary driven)
- Obtain the transport coefficient α (thermal cond., shear viscosity,...)

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

$$\lim_{\eta \to 0} \frac{\mathbb{E}_\eta\left(F^T M^{-1} p\right)}{\eta} = \beta \, F^T D F, \quad D = \int_0^{+\infty} \mathbb{E}_0\Big((M^{-1} p_t) \otimes (M^{-1} p_0) \Big) \, dt$$

Error estimates for NEMD

Principle of nonequilibrium molecular dynamics

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

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

Estimator of linear response (observable R with equilibrium average 0)

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

Issues with linear response methods:

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

Analysis of variance / finite integration time bias

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

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

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

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

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

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

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

Analysis of the timestep discretization bias (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

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

First and second order splittings, determined by order of operators

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

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

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

Analysis of the timestep discretization bias (2)

Invariant measure $\mu_{\gamma,\eta,\Delta t}$ of the numerical scheme; $a \geqslant$ weak order

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

with $f_{0,1,\gamma} = \mathfrak{f}_1$ and remainder compatible with linear response:

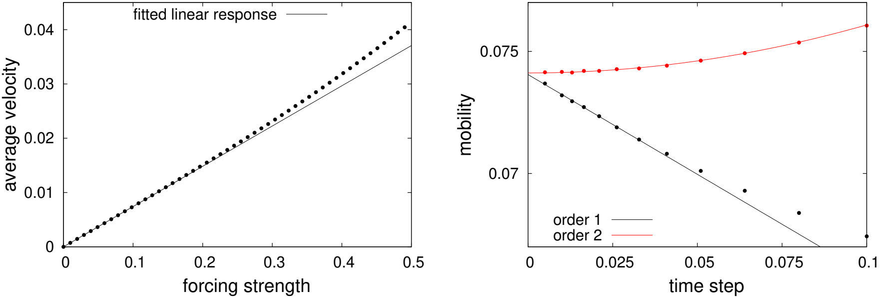
$$|r_{\varphi,\gamma,\eta,\Delta t}| \leqslant K(\eta^2 + \Delta t^{a+1}), \qquad |r_{\varphi,\gamma,\eta,\Delta t} - r_{\varphi,\gamma,0,\Delta t}| \leqslant K\eta(\eta + \Delta t^{a+1})$$

Corollary: error estimates on the numerically computed mobility

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

Results in the overdamped limit $\gamma \to +\infty$

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)



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 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 for Green–Kubo formulas

Error estimates on the Green-Kubo formula (1)

- Aim: approximate $\alpha = \int_0^{+\infty} \mathbb{E}_0\Big(R(q_t,p_t)S(q_0,p_0)\Big)dt$

- **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[11]
  - Timestep bias and quadrature formula

Possible benefits from...

- Fourier approaches and time series analysis[12]
- importance sampling on trajectory space[13]

[11] de Sousa Oliveira/Greaney, *Phys. Rev. E* **95** (2017)
[12] Ercole/Marcolongo/Baroni, *Sci. Rep.* **7** (2017)
[13] Donati/Hartmann/Keller, *J. Chem. Phys.* **146** (2017)

Truncation of time and statistical error

"Natural" estimator $\widehat{A}_{K,T} = \frac{1}{K}\sum_{k=1}^{K}\int_0^T R(q_t^k, p_t^k) S(q_0^k, p_0^k)\, dt$

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

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

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

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

Proof based on the following equality, with $-\mathcal{L}\mathscr{R} = R \in L_0^2(\mu)$:

$$\int_0^T R(q_t, p_t)\, dt = \mathscr{R}(q_0, p_0) - \mathscr{R}(q_t, p_t) + \sqrt{\frac{2\gamma}{\beta}}\int_0^T \nabla_p \mathscr{R}(q_t, p_t)^T dW_t$$

P. Plechac, G. Stoltz, T. Wang, *arXiv preprint* **2112.00126**

Timestep bias for Green–Kubo formulas

Generic stochastic dynamics satisfying certain technical conditions:

- uniform-in-Δt convergence (relies on $P_{\Delta t}^{\lceil T/\Delta t\rceil}(X_0, dX) \geqslant \rho\, m(dX)$)
- error on the invariant measure of order Δt^a
- $P_{\Delta t} = \mathrm{Id} + \Delta t \mathcal{L} + \Delta t^2 L_2 + \cdots + \Delta t^a L_a + \ldots$

Riemann–like formula

For R, S with average 0 w.r.t. μ,

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

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

Reduces to trapezoidal rule for second order schemes

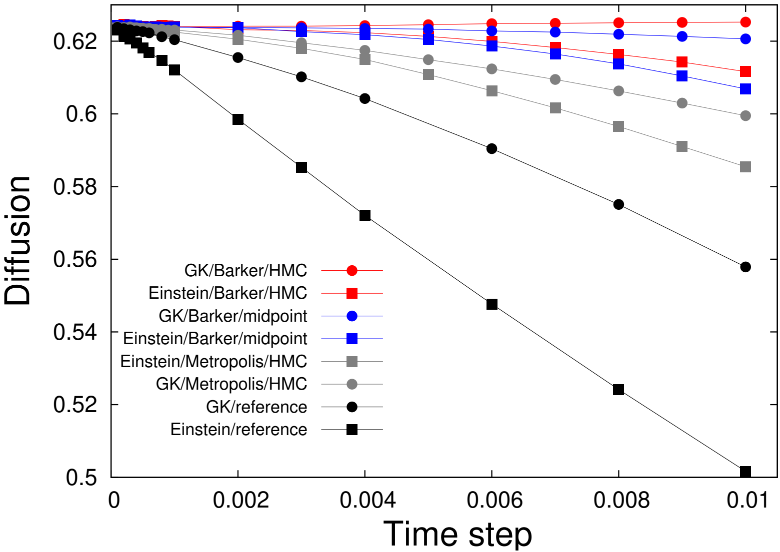
Side result: statistical error for numerical schemes $\approx$ continuous process

B. Leimkuhler, Ch. Matthews and G. Stoltz, *IMA J. Numer. Anal.* **36**(1), 13-79 (2016)

T. Lelièvre and G. Stoltz, *Acta Numerica* **25** (2016)

A. Durmus, A. Enfroy, E. Moulines, G. Stoltz, *arXiv preprint* **2107.14542**

1D overdamped Langevin, $R = S = V'$, cosine potential



Fathi/Stoltz, *Numerische Mathematik* (2017)

Extensions and perspectives

An example of alternative fluctuation formula (1)

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

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

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

An example of alternative fluctuation formula (2)

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

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

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

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

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

Variance uniformly bounded in time: by similar manipulations,

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

An example of alternative fluctuation formula (3)

Discrete sensitivity estimator (slightly idealized)

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

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

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

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

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

Extension to 2nd order schemes and Langevin dynamics (not yet used in MD simulations)

P. Plechac, G. Stoltz and T. Wang, *M2AN* **55** (2021)

P. Plechac, G. Stoltz, T. Wang, *arXiv preprint* **2112.00126**

Study of alternative approaches: several year workplan!

- **Alternatives to direct NEMD/GK**, possibly with some blending
  - Control variate approaches[14] (better solutions to Poisson equation needed...)
  - Use coupling methods between X_t^η and X_t^0, *e.g.* sticky coupling[15]
  - Rely on tangent dynamics[16] for $T_t = \lim_{\eta \to 0}(X_t^\eta - X_t^0)/\eta$
  - Optimize synthetic forcings[17]
  - Large deviation techniques to estimate second order cumulants[18]
  - Norton dynamics[19] (dual approach where the flux is fixed)

For all methods: **quantify variance and bias** (related to Δt, η, ...) and apply to systems (atom chains, LJ fluid)

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[14] Ciccotti/Jacucci (1975); Mangaud/Rotenberg (2020); Roussel/Stoltz (2019), Pavliotis/Stoltz/Vaes (2022)

[15] Eberle/Zimmer (2019); Durmus/Eberle/Enfroy/Guillin/Monmarché (2021); currently Darshan/Eberle/Stoltz

[16] Assaraf/Jourdain/Lelièvre/Roux, *Stoch. Partial Differ. Equ. Anal. Comput.* (2018)

[17] Evans/Morriss (2008); Spacek/Stoltz (2023)

[18] Limmer/Gao/Poggioli (2021); currently Guyader/Stoltz

[19] Evans/Morriss (2008); Blassel/Stoltz (2023) and now Darshan/Iacobucci/Olla/Stoltz