Error estimates for transport coefficients in molecular dynamics

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Outline

- **Transport coefficients:** "steady-state" dynamical information
  - mobility
  - shear viscosity
  - thermal conductivity

- **Bias** due to timestep for
  - Green-Kubo formulas
  - linear response approaches

- **Variance** reduction for linear response approaches

Linear response and Green–Kubo formula

$$\lim_{\eta \to 0} \frac{\mathbb{E}_\eta(R)}{\eta} = \int_0^{+\infty} \mathbb{E}_0(R(x_t)S(x_0))dt$$

T. Lelièvre and G. Stoltz, PDEs and stochastic methods in molecular dynamics, *Acta Numerica* **25**, 681-880 (2016)

A paradigmatic example

Langevin dynamics perturbed by a constant force term

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

where

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

- Non-zero velocity in the direction F is expected in the steady-state

- F **does not derive from the gradient of a periodic function**
  - of course, $F = -\nabla W_F(q)$ with $W_F(q) = -F^T q$
  - ...but W_F is not periodic!

Mobility and self-diffusion

- **Linear response approaches:** averages in a nonequilibrium steady-state

Mobility

$$\nu_F = \lim_{\eta \to 0} \frac{\mathbb{E}_\eta \left(F^T M^{-1} p \right)}{\eta} = \beta \int_{\mathcal{E}} F^T M^{-1} p \, f_{0,1}(q,p) \, \mu(dq\,dp) = \beta \, F^T D F$$

- **Green-Kubo formulas:** integrated correlation functions

Effective diffusion at equilibrium ($\eta = 0$)

Unperiodized displacement $Q_t - Q_0 = \displaystyle\int_0^t M^{-1} p_s \, ds$

$$F^T D F = \int_0^{+\infty} \mathbb{E}_0 \left[\left(F^T M^{-1} p_t \right) \left(F^T M^{-1} p_0 \right) \right] dt$$

Timestep bias for linear response

Examples of splitting schemes for Langevin dynamics (1)

- Example: Langevin dynamics, discretized using a splitting strategy

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

- First order splitting schemes: Trotter splitting

$$P_{\Delta t}^{ZYX} = \mathrm{e}^{\Delta t Z}\mathrm{e}^{\Delta t Y}\mathrm{e}^{\Delta t X} \simeq \mathrm{e}^{\Delta t \mathcal{A}}$$

- Second order schemes: Strang splitting

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

- Other category: Geometric Langevin algorithms, *e.g.* $P_{\Delta t}^{\gamma C, A, B_\eta, A}$
- Invariant measure $\mu_{\gamma,\eta,\Delta t}$ (different from μ)

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)

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

Error estimates on linear response

Error estimates for nonequilibrium dynamics

There exists a function $f_{\alpha,1,\gamma} \in H^1(\mu)$ such that

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

where the remainder is compatible with linear response

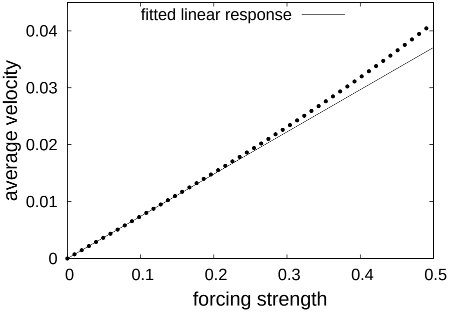
$$|r_{\psi,\gamma,\eta,\Delta t}| \leqslant K(\eta^2 + \Delta t^{\alpha+1}), \qquad |r_{\psi,\gamma,\eta,\Delta t} - r_{\psi,\gamma,0,\Delta t}| \leqslant K\eta(\eta + \Delta t^{\alpha+1})$$

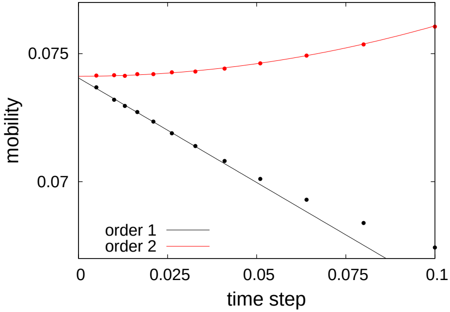
- Corollary: error estimates on the numerically computed mobility

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

- Results in the overdamped limit

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 $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$.

Timestep bias for Green–Kubo formulas

Error estimates on Green-Kubo formulas (1)

- Results valid for Langevin or overdamped Langevin dynamics

$$dq_t = -\nabla V(q_t)\, dt + \sqrt{\frac{2}{\beta}}\, dW_t$$

- Error of order α on invariant measure: $\displaystyle\int_{\mathcal{X}} \psi \, d\pi_{\Delta t} = \int_{\mathcal{X}} \psi \, d\pi + \mathrm{O}(\Delta t^{\alpha})$

- Expansion of the evolution operator $P_{\Delta t}\varphi(x) = \mathbb{E}\Big(\varphi\left(x^{n+1}\right) \,\Big|\, x^n = x\Big)$

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

- Suitable ergodicity conditions on $P_{\Delta t}$

M. Fathi and G. Stoltz, Improving dynamical properties of stabilized discretizations of overdamped Langevin dynamics, accepted for publication in *Numer. Math.* (2016)

Error estimates on Green-Kubo formulas (2)

Error estimates on integrated correlation functions

Observables φ, ψ with average 0 w.r.t. invariant measure π

$$\int_0^{+\infty} \mathbb{E}\Big(\psi(x_t)\varphi(x_0)\Big)\,dt = \Delta t \sum_{n=0}^{+\infty} \mathbb{E}_{\Delta t}\left(\widetilde{\psi}_{\Delta t,\alpha}\left(x^n\right)\varphi\left(x^0\right)\right) + \Delta t^{\alpha} r_{\Delta t}^{\psi,\varphi},$$

where $\mathbb{E}_{\Delta t}$ denotes expectations w.r.t. initial conditions $x_0 \sim \pi_{\Delta t}$ and over all realizations of the Markov chain (x^n), and

$$\widetilde{\psi}_{\Delta t,\alpha} = \psi_{\Delta t,\alpha} - \int_{\mathcal{X}} \psi_{\Delta t,\alpha}\, d\pi_{\Delta t}$$

with $\psi_{\Delta t,\alpha} = \Big(\mathrm{Id} + \Delta t\, \mathcal{A}_2\mathcal{L}^{-1} + \cdots + \Delta t^{\alpha-1}\mathcal{A}_\alpha\mathcal{L}^{-1}\Big)\psi$

- Useful when $\mathcal{A}_k\mathcal{L}^{-1}$ can be computed, *e.g.* $\mathcal{A}_k = a_k\mathcal{L}^k$
- Reduces to trapezoidal rule for second order schemes

Metropolized overdamped Langevin dynamics

- Superimpose Metropolis-Hastings correction to discretization of SDE

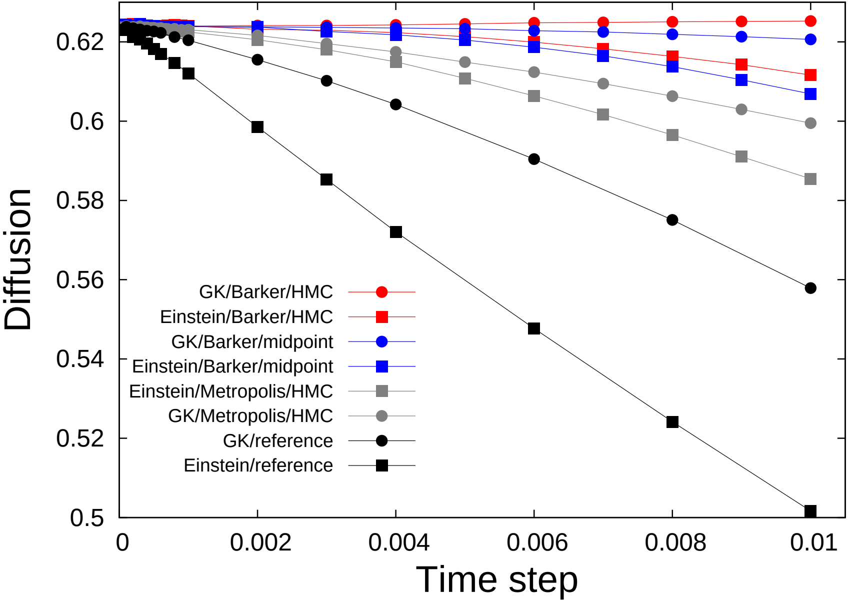
$$\widetilde{q}^{n+1} = q^n + \Delta t \, \nabla V(q^n) + \sqrt{\frac{2\Delta t}{\beta}} \, G^n$$

$\longrightarrow$ no bias on invariant measure / stabilization for singular potentials
$\longrightarrow$ error estimates on the diffusion of order Δt

- HMC-like scheme $\widetilde{q}^{n+1} = q^n + \Delta t \, \nabla V \left(q^n + \sqrt{\frac{\Delta t}{2\beta}} \, G^n \right) + \sqrt{\frac{2\Delta t}{\beta}} \, G^n$
  - Error of order $\Delta t^{3/2}$ when the Metropolis-Hastings rule is used
  - Reduced to Δt^2 when a Barker rule is used (replace $\min(1, r)$ by $r/(r+1)$)
  - Requires some time renormalization since rejection rate $\simeq 1/2$
  - Trade-off between increased variance (factor 2) and reduced bias

- Extension to diffusions with multiplicative noise

Results in 1D for $\varphi = \psi = V'$ and cosine potential



Variance reduction approaches for linear response

The need for variance reduction

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

- Standard approach: compute the steady-state average as

$$\frac{1}{t}\int_0^t R(q_s,p_s)\,ds \xrightarrow[t\to+\infty]{} \int_{\mathcal{E}} R\,\psi_\eta = \mathrm{O}(\eta)$$

when R vanishes at equilibrium

- Variance of order 1 $\to$ relative error of order $1/\eta$!

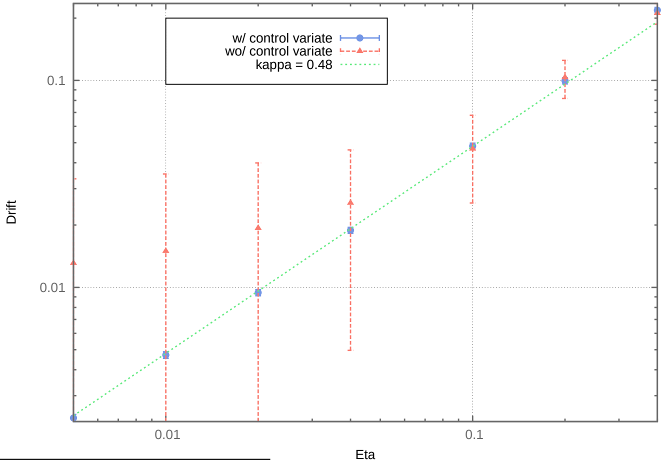
- Need for variance reduction... but
  - no straightforward importance sampling
  - no easy stratification

Control variate approach

$$\frac{\mathbb{E}_\eta(R)}{\eta} = \frac{\mathbb{E}_\eta(R-\mathcal{L}_\eta\Phi)}{\eta} \quad \text{with} \quad \mathrm{Var}_\eta(R-\mathcal{L}_\eta\Phi) \ll \mathrm{Var}_\eta(R)$$

Control variates for linear response

- Idea:[1] consider Φ such that $-\mathcal{L}_0\Phi = R$ (Galerkin discretization)
- Variance of order η^2 when Φ is exactly computed $\to$ relative error $\mathrm{O}(1)$



[1] J. Roussel and G. Stoltz, in preparation