Quantifying errors in the computation of transport coefficients

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Outline

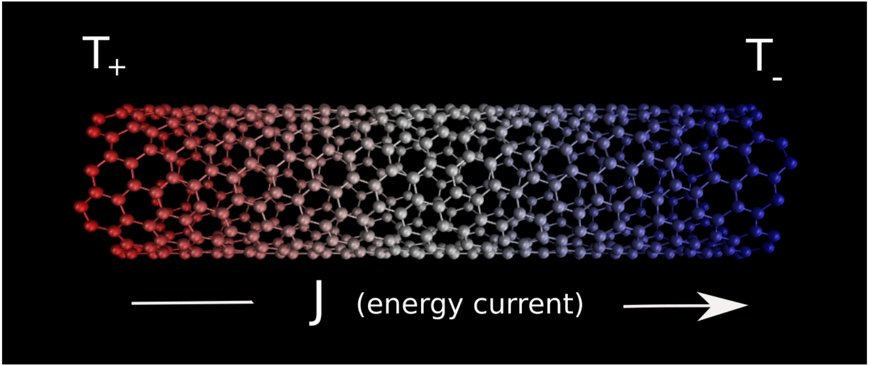
- **Linear response for steady-state nonequilibrium dynamics**
  - Equilibrium dynamics and their perturbations
  - Definition of transport coefficients
- **Error estimates (variance, bias)**
  - Nonequilibrium molecular dynamics (NEMD)
  - Green–Kubo formulas
- **Perspectives**
  - Variance reduction strategies
  - Alternative numerical approaches

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)

Reference equilibrium dynamics

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

Definition of transport coefficients (1)

Linear response of **nonequilibrium dynamics**

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

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

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 $L^2(\mu)$ and $\Pi_0 \varphi = \varphi - \int_{\mathcal{E}} \varphi \, d\mu$

Definition of transport coefficients (2)

Response property $R \in L_0^2(\mu) = \Pi_0 L_0^2(\mu)$, 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 (bulk or boundary driven)
- Obtain the transport coefficient α (thermal cond., shear viscosity,...)

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

Error estimates for NEMD

Principle of nonequilibrium molecular dynamics

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

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

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:

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

so $\widehat{A}_{\eta,t} = \alpha + \mathrm{O}\left(\frac{1}{\eta\sqrt{t}}\right)$ → 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

- Bias $\mathrm{O}(\eta)$ and statistical error equilibrated for $t \sim \eta^{-3}$

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 $\alpha_{\Delta t} = \exp(-\gamma M^{-1}\Delta t)$)

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

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

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

where the remainder is compatible with linear response

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

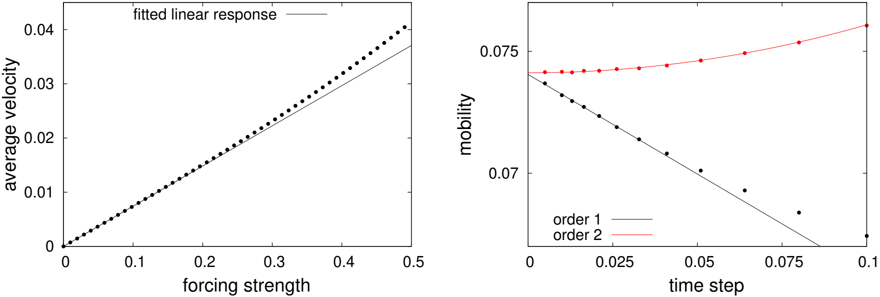
Corollary: error estimates on the numerically computed mobility

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

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)

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

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[1]
  - Timestep bias and quadrature formula

Possible benefits from...

- Fourier approaches and time series analysis[2]
- importance sampling on trajectory space[3]

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[1] de Sousa Oliveira/Greaney, *Phys. Rev. E* **95** (2017)
[2] Ercole/Marcolongo/Baroni, *Sci. Rep.* **7** (2017)
[3] 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 $-\mathcal{L}\mathscr{R} = R$:

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

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
- error on the invariant measure of order Δt^a
- $P_{\Delta t} = \mathrm{Id} + \Delta t \mathcal{L} + \Delta t^2 S_1 + \dots + \Delta t^a S_{a-1} + \dots$

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 $\widetilde{R}_{\Delta t} = \Big(\mathrm{Id} + \Delta t\, S_1 \mathcal{L}^{-1} + \dots + \Delta t^{a-1} S_{a-1} \mathcal{L}^{-1}\Big) R - \mu_{\Delta t}(\dots)$

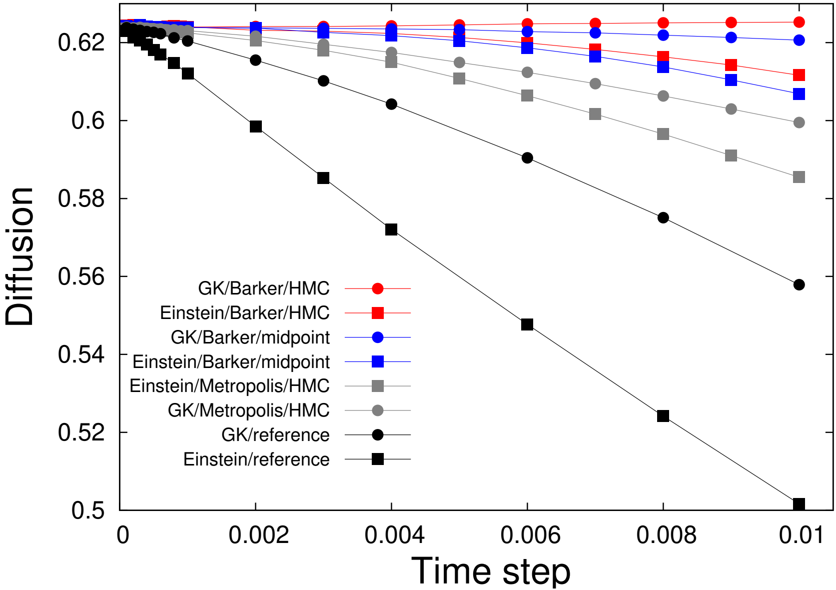
Reduces to trapezoidal rule for second order schemes

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)

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



Variance reduction techniques and alternative dynamics

Variance reduction for NEMD and Einstein methods

- **Control variate approach**: reduce variance by subtracting a quantity with known average, correlated (in a good way) with the target quantity

- Some instances of control variate techniques for transport coefficients[4]

- In the NEMD context, consider

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

Zero variance control variate $\Phi_\eta = \mathcal{L}_\eta^{-1}\left(R - \int_{\mathcal{E}} R f_\eta \, d\mu\right)$

More practical choice[5] $-\mathcal{L}_0 \Phi = R$ for some approximate operator $\mathcal{L}_0$

- Variance of order η^2 when $\mathcal{L}_0 = \mathcal{L} \to$ relative error $\mathrm{O}(1)$

[4] Ciccotti/Jacucci (1975); Mangaud/Rotenberg (2020); ...

[5] Roussel/Stoltz, *SIAM MMS* (2019)

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

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

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

Sensitivity estimator: discretization

Discrete sensitivity estimator (slightly idealized)

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

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

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

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

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

Extension to Langevin dynamics; not yet used in actual 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!

- **Alternative approaches**, possibly with some blending
  - Rely on tangent dynamics[6]
  - Resort to efficient coupling methods such as sticky coupling[7]
  - Optimize synthetic forcings[8]
  - Large deviation techniques to estimate second order cumulants[9]
  - Consider using transient dynamics
  - ... other options too prospective to be mentioned...

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

[6] Assaraf/Jourdain/Lelièvre/Roux, *Stoch. Partial Differ. Equ. Anal. Comput.* (2018)
[7] Eberle/Zimmer (2019); Durmus/Eberle/Enfroy/Guillin/Monmarché (2021)
[8] Evans/Morriss (2008); see presentation by Renato Spacek
[9] Limmer/Gao/Poggioli, *Eur. Phys. J. B* (2021)