

Error estimates and variance reduction for transport coefficients

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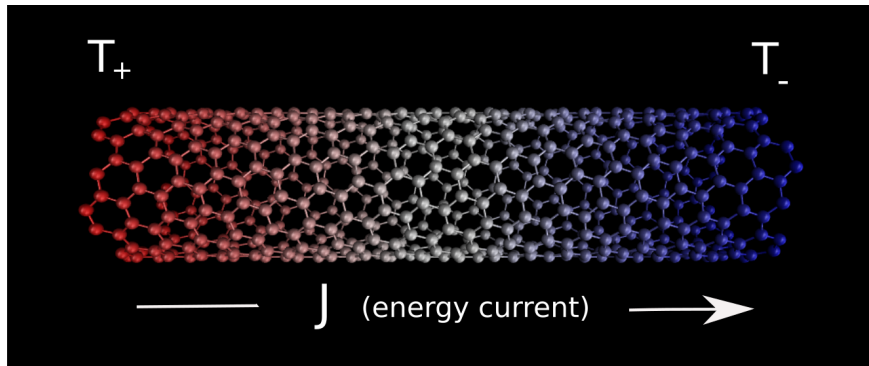
- **A mathematical introduction to molecular dynamics**
- **Linear response for steady-state nonequilibrium dynamics**
 - Equilibrium dynamics and their perturbations
 - Definition of transport coefficients
- **Error estimates (variance, bias)**
 - Nonequilibrium molecular dynamics
 - Green–Kubo formulas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

A mathematical 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

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

with $\beta = \frac{1}{k_B T}$ the Lagrange multiplier of the constraint $\int_{\mathcal{E}} H \rho dq dp = E_0$

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

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

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

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

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

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

Ergodicity results for Langevin dynamics (1)

Almost-sure convergence¹ of **ergodic averages** $\hat{\varphi}_t = \frac{1}{t} \int_0^t \varphi(q_s, p_s) ds$

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

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

Central limit theorem² 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 $L_0^2(\mu) = \Pi_0 L^2(\mu)$

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

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

²Bhattacharya, *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 $E \subset L_0^2(\mu)$

- **Lyapunov** techniques³ $L_{\mathcal{K}}^\infty(\mathcal{E}) = \left\{ \varphi \text{ measurable, } \sup \left| \frac{\varphi}{\mathcal{K}} \right| < +\infty \right\}$
- standard **hypocoercive**⁴ setup $H^1(\mu)$
- $L^2(\mu)$ after hypoelliptic regularization⁵ from $H^1(\mu)$
- direct transfer from $H^1(\mu)$ to $L^2(\mu)$ by spectral argument⁶
- directly⁷ $L^2(\mu)$ (recently⁸ Poincaré using $\partial_t - \mathcal{L}_{\text{ham}}$)
- **coupling** arguments⁹
- direct estimates on the resolvent using Schur complements¹⁰

Rate of convergence $\min(\gamma, \gamma^{-1})$ so **variance** $\sim \max(\gamma, \gamma^{-1})$

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

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

⁵Hérau, *J. Funct. Anal.* (2007)

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

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

⁸Armstrong/Mourrat (2019), Cao/Lu/Wang (2019), Brigatti (2021), Brigati/Stoltz (2025)

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

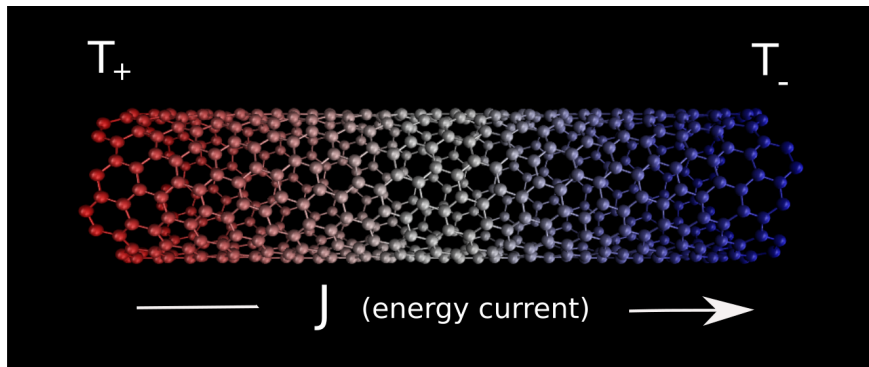
¹⁰Bernard/Fathi/Levitt/Stoltz, *Annales Henri Lebesgue* (2022)

Linear response for steady-state nonequilibrium dynamics

Physical context and motivations

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

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



Slow convergence due to **large noise to signal ratio**

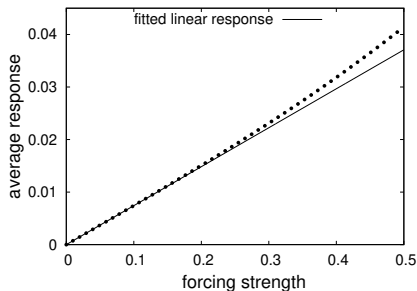
Long computational times to estimate κ (up to several weeks/months)

Linear response of nonequilibrium stochastic dynamics

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

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

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



Existence/uniqueness of invariant probability measure (Lyapunov)

Generator $\mathcal{L} + \eta \tilde{\mathcal{L}}$ with $\tilde{\mathcal{L}} = F^\top \nabla_p$

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

α = **transport coefficient**

Properties of the invariant probability measure

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

$$\forall \varphi, \quad \int_{\mathcal{E}} [(\mathcal{L} + \eta \tilde{\mathcal{L}})\varphi] \psi_\eta = 0$$

- Analytical expression **not known** $\rightarrow$ no Metropolis-type algorithms
- Stratification not possible
- Depends non-locally on the potential $V \rightarrow$ prevents **importance sampling**

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

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

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 $f_\eta = 1 + \mathcal{O}(\eta)$

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

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

Fokker-Planck equation

$$(\mathcal{L} + \eta \tilde{\mathcal{L}})^* f_\eta = 0$$

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

$$f_\eta = 1 + \eta f_1 + \eta^2 f_2 + \dots, \quad -\mathcal{L}^* f_1 = \tilde{\mathcal{L}}^* \mathbf{1} = \Pi_0 \tilde{\mathcal{L}}^* \mathbf{1} = S$$

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

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

Definition of transport coefficients (2)

Response property $R \in L^2_0(\mu) = \Pi_0 L^2(\mu)$, conjugate response $S = \tilde{\mathcal{L}}^* \mathbf{1}$:

$$\begin{aligned}\alpha &= \lim_{\eta \rightarrow 0} \frac{\mathbb{E}_\eta(R)}{\eta} = \int_{\mathcal{E}} R \mathbf{f}_1 \, d\mu = \int_{\mathcal{E}} R \left[(-\mathcal{L}^*)^{-1} S \right] d\mu = \int_{\mathcal{E}} (-\mathcal{L}^{-1} R) S \, d\mu \\ &= \int_0^{+\infty} \left[\int_{\mathcal{E}} (e^{t\mathcal{L}} R) S \, d\mu \right] dt = \int_0^{+\infty} \mathbb{E}_0 \left(R(q_t, p_t) S(q_0, p_0) \right) dt\end{aligned}$$

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 $R(q, p) = F^\top M^{-1} p$

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

Error estimates for NEMD

Principle of nonequilibrium molecular dynamics

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

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

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

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

Issues with linear response methods:

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

$$\sqrt{t} (\hat{\alpha}_{\eta,t} - \alpha_{\eta}) \xrightarrow[t \rightarrow +\infty]{\text{law}} \mathcal{N} \left(0, \frac{\sigma_{R,\eta}^2}{\eta^2} \right), \quad \sigma_{R,\eta}^2 = \sigma_{R,0}^2 + O(\eta)$$

so $\hat{\alpha}_{\eta,t} = \alpha_{\eta} + O_P \left(\frac{1}{\eta\sqrt{t}} \right) \rightarrow$ requires **long simulation times** $t \sim \eta^{-2}$

Finite time integration bias: $|\mathbb{E}(\hat{\alpha}_{\eta,t}) - \alpha_{\eta}| \leq \frac{K}{\eta t}$

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

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

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

Analysis of the timestep discretization bias (1)

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

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

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

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

First and second order splittings, determined by order of operators

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

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

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; $a \geq$ weak order

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

with $f_{0,1,\gamma} = f_1$ and remainder compatible with linear response:

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

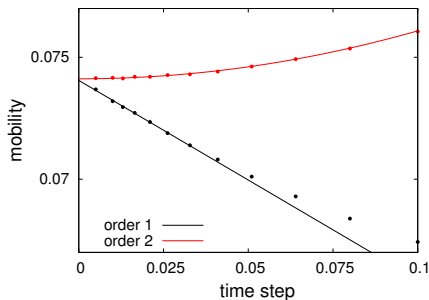
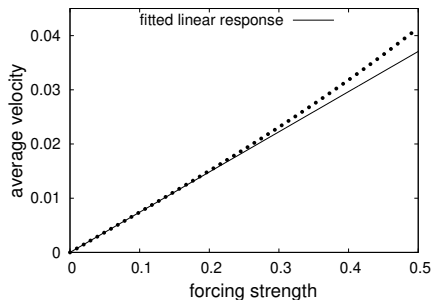
Corollary: error estimates on the **numerically computed mobility**

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

Results in the **overdamped** limit $\gamma \rightarrow +\infty$

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 (2D periodic potential)



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

- Aim: approximate $\alpha = \int_0^{+\infty} \mathbb{E}_0 \left(R(q_t, p_t) S(q_0, p_0) \right) dt$
- **Estimator** (continuous time) $\hat{\alpha}_{K,T} = \frac{1}{K} \sum_{k=1}^K \int_0^T R(q_t^k, p_t^k) S(q_0^k, p_0^k) dt$
- **Sources of error** : trade off in truncation time T
 - Time truncation bias $|\mathbb{E}_\mu[\hat{\alpha}_{K,T}] - \alpha| \leq \frac{C}{\kappa} \|R\|_{L^2(\mu)} \|S\|_{L^2(\mu)} e^{-\kappa T}$
 - **Statistical error** $\text{Var}[\hat{\alpha}_{K,T}] \sim \frac{2T}{K} \|S\|_{L^2(\mu)}^2 \langle R, -\mathcal{L}^{-1} R \rangle$
 - **Timestep bias and quadrature formula** when numerically integrating

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

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

G. A. Pavliotis, R. Spacek, G. Stoltz, and U. Vaes, *SIAM JUQ*, 2025

R. Gastaldello, G. Stoltz, and U. Vaes, *arXiv preprint* **2504.11968**

Timestep bias for Green–Kubo formulas

Generic stochastic dynamics satisfying certain technical conditions:

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

Riemann–like formula

For R, S with average 0 w.r.t. μ ,

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

with $\tilde{R}_{\Delta t} = \left(\text{Id} + \Delta t L_2 \mathcal{L}^{-1} + \dots + \Delta t^{a-1} L_a \mathcal{L}^{-1} \right) R - \mu_{\Delta t}(\dots)$

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

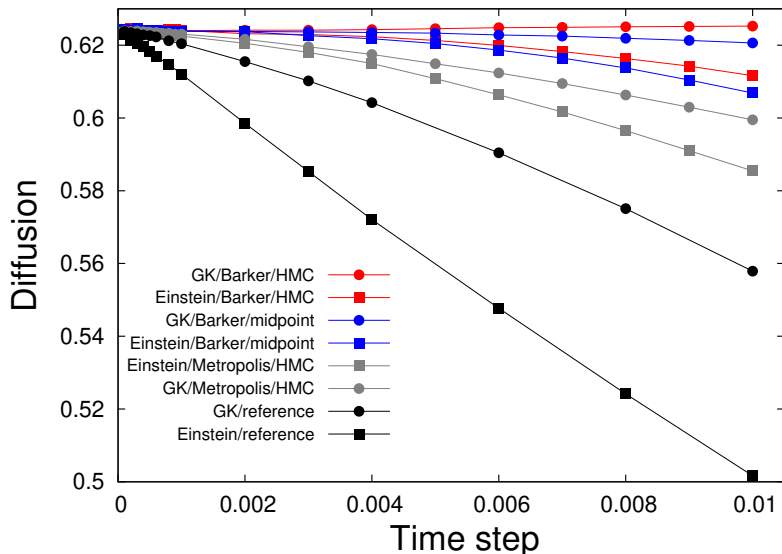
Side result: statistical error for numerical schemes $\approx$ continuous process

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)

A. Durmus, A. Enfroy, E. Moulines, G. Stoltz, *arXiv preprint* **2107.14542** *Ann. Inst. H. Poincaré*

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



Fathi/Stoltz, *Numerische Mathematik* (2017)

Extensions and perspectives

Study of alternative approaches: several year workplan!

Alternatives to direct NEMD/GK, possibly with some **blending**

- Alternative fluctuation formulas¹¹
- Control variate approaches¹² (better solutions to Poisson equation needed...)
- Use coupling methods between X_t^η and X_t^0 , e.g. sticky coupling¹³
- Rely on tangent dynamics¹⁴ for $T_t = \lim_{\eta \rightarrow 0} (X_t^\eta - X_t^0)/\eta$
- Optimize synthetic forcings¹⁵
- Large deviation techniques to estimate second order cumulants¹⁶
- Norton dynamics¹⁷ (dual approach where the flux is fixed)
- Transient methods: subtraction¹⁸ and TTCF¹⁹

Quantify variance and bias and apply to physical systems

¹¹ Plechac/Stoltz/Wang (2021, 2023)

¹² Mangaud/Rotenberg (2020); Roussel/Stoltz (2019), Pavliotis/Stoltz/Vaes (2022), Pavliotis/Spacek/Stoltz/Vaes (2024)

¹³ Eberle/Zimmer (2019); Durmus/Eberle/Enfroy/Guillin/Monmarché (2021); Darshan/Eberle/Stoltz (2024)

¹⁴ Assaraf/Jourdain/Lelièvre/Roux, *Stoch. Partial Differ. Equ. Anal. Comput.* (2018)

¹⁵ Evans/Morriss (2008); Spacek/Stoltz (2023)

¹⁶ Limmer/Gao/Poggioli (2021); currently Guyader/Gastaldello/Stoltz/Vaes

¹⁷ Evans/Morriss (2008); Blassel/Stoltz (2023) and now Darshan/Stoltz

¹⁸ Ciccotti/Jacucci (1975); Monmarché/Spacek/Stoltz (2025)

¹⁹ Evans/Morriss (1987, 1988)