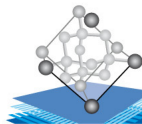




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Nonequilibrium stochastic dynamics: Error estimates and variance reduction

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Sciade 2026

Molecular dynamics

- Microscopic description of physical systems
- Macroscopic description: average properties

Practical computation of static properties

- Ergodic averages using Langevin dynamics
- Error estimates (statistical error, bias)

Estimation of transport coefficients

- Linear response of nonequilibrium dynamics
- Error estimates
- Variance reduction: some examples

N. Blassel, L. Carillo, S. Darshan, R. Gastaldello, A. Iacobucci, E. Marini, R. Santet, X. Shang, G. Stoltz and U. Vaes, Mathematical analysis and numerical methods for the computation of transport coefficients in molecular dynamics, *arXiv preprint* **2605.10507** (2026)

Molecular dynamics

General perspective (1)

- **Aims of computational statistical physics:**

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

- **Orders of magnitude**

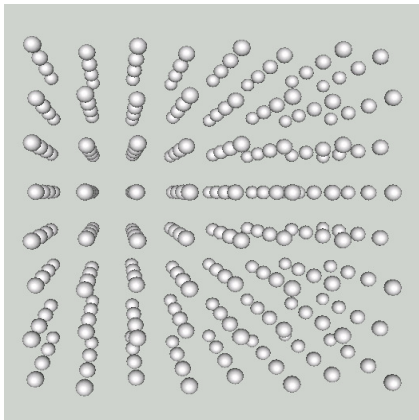
- distances $\sim 1 \text{ \AA} = 10^{-10} \text{ m}$
- energy per particle $\sim k_B T \sim 4 \times 10^{-21} \text{ J}$ at room temperature
- atomic masses $\sim 10^{-26} \text{ kg}$
- time $\sim 10^{-15} \text{ s}$
- number of particles $\sim \mathcal{N}_A = 6.02 \times 10^{23}$

- **“Standard” simulations**

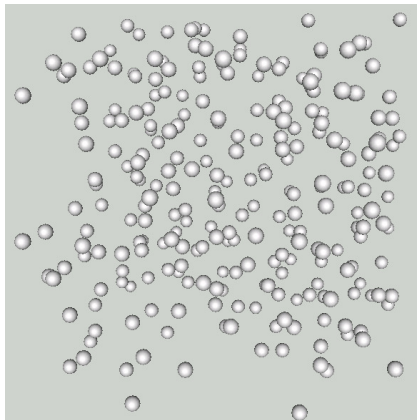
- 10^6 particles [“world records”: around 10^9 particles]
- integration time: (fraction of) ns [“world records”: (fraction of) μs]

General perspective (2)

What is the **melting temperature** of Argon?



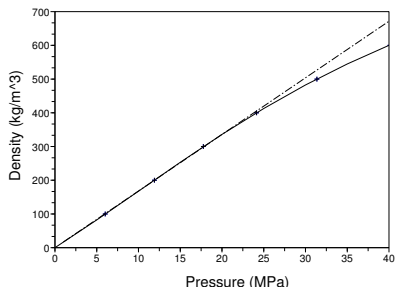
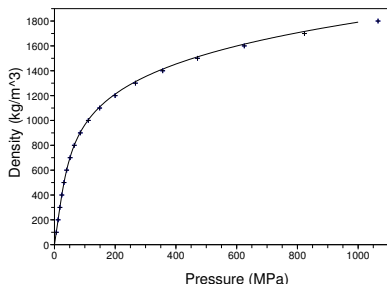
(a) Solid Argon (low temperature)



(b) Liquid Argon (high temperature)

General perspective (3)

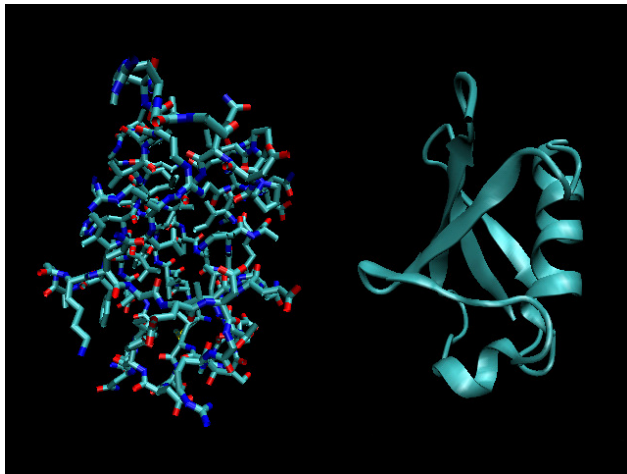
“Given the structure and the laws of interaction of the particles, what are the **macroscopic properties** of the matter composed of these particles?”



Equation of state (pressure/density diagram) for Argon at $T = 300$ K

General perspective (4)

What is the **structure** of the protein? What are its **typical conformations**, and what are the **transition pathways** from one conformation to another?



Microscopic description of physical systems

- **Microstate** of a classical system of N particles:

$$(q, p) = (q_1, \dots, q_N, p_1, \dots, p_N) \in \mathcal{E}$$

Positions q (configuration), **momenta** p (to be thought of as $M\dot{q}$)

- Here, periodic boundary conditions: $\mathcal{E} = \mathcal{D} \times \mathbb{R}^{3N}$ with $\mathcal{D} = (L\mathbb{T})^{3N}$
- More complicated situations can be considered: molecular **constraints** defining submanifolds of the phase space
- **Hamiltonian** $H(q, p) = E_{\text{kin}}(p) + V(q)$, where the kinetic energy is

$$E_{\text{kin}}(p) = \frac{1}{2} p^\top M^{-1} p, \quad M = \begin{pmatrix} m_1 \text{Id}_3 & & 0 \\ & \ddots & \\ 0 & & m_N \text{Id}_3 \end{pmatrix}.$$

Average properties

- **Macrostate** of the system described by a **probability measure**

Equilibrium thermodynamic properties (pressure,...)

$$\mathbb{E}_\mu(\varphi) = \int_{\mathcal{E}} \varphi(q, p) \mu(dq dp)$$

- Examples of **observables**:

- Pressure $\varphi(q, p) = \frac{1}{3|\mathcal{D}|} \sum_{i=1}^N \left(\frac{p_i^2}{m_i} - q_i \cdot \nabla_{q_i} V(q) \right)$

- Kinetic temperature $\varphi(q, p) = \frac{1}{3Nk_B} \sum_{i=1}^N \frac{p_i^2}{m_i}$

- **Canonical** ensemble = measure on (q, p) (average energy fixed)

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

Practical computation of average properties

Computing average properties

Main issue

Computation of **high-dimensional** integrals... **Ergodic** averages

$$\mathbb{E}_\mu(\varphi) = \lim_{t \rightarrow +\infty} \widehat{\varphi}_t, \quad \widehat{\varphi}_t = \frac{1}{t} \int_0^t \varphi(q_s, p_s) ds$$

- One possible choice: **Langevin** dynamics with friction parameter $\gamma > 0$
= **Stochastic** perturbation of the Hamiltonian dynamics

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

Almost-sure convergence of ergodic averages¹

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

Hamiltonian and overdamped limits

- As $\gamma \rightarrow 0$, the **Hamiltonian** dynamics is recovered

$$\frac{d}{dt} \mathbb{E} [H(q_t, p_t)] = -\gamma \left(\mathbb{E} [p_t^\top M^{-2} p_t] - \frac{1}{\beta} \text{Tr}(M^{-1}) \right) dt$$

Time $\sim \gamma^{-1}$ to change energy levels in this limit²

- Overdamped** limit $\gamma \rightarrow +\infty$ with $M = \text{Id}$: rescaling of time γt

$$\begin{aligned} q_{\gamma t} - q_0 &= -\frac{1}{\gamma} \int_0^{\gamma t} \nabla V(q_s) ds + \sqrt{\frac{2}{\gamma\beta}} W_{\gamma t} - \frac{1}{\gamma} (p_{\gamma t} - p_0) \\ &= -\int_0^t \nabla V(q_{\gamma s}) ds + \sqrt{2\beta^{-1}} B_t - \frac{1}{\gamma} (p_{\gamma t} - p_0) \end{aligned}$$

which converges to the solution of $dQ_t = -\nabla V(Q_t) dt + \sqrt{2\beta^{-1}} dB_t$

- In both cases, **slow convergence**, with rate scaling as $\min(\gamma, \gamma^{-1})$

²Hairer and Pavliotis, *J. Stat. Phys.*, **131**(1), 175-202 (2008)

Statistical error (1/2)

- **Evolution semigroup** $(e^{t\mathcal{L}}\varphi)(q, p) = \mathbb{E} \left[\varphi(q_t, p_t) \mid (q_0, p_0) = (q, p) \right]$,
generator $\mathcal{L} = \mathcal{L}_{\text{ham}} + \gamma \mathcal{L}_{\text{FD}}$

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

- **Asymptotic variance** $\sigma_\varphi^2 = \lim_{t \rightarrow +\infty} t \text{Var}_\mu(\widehat{\varphi}_t)$: with $\Pi\varphi = \varphi - \int_{\mathcal{E}} \varphi d\mu$,

$$\begin{aligned} \sigma_\varphi^2 &= \lim_{t \rightarrow +\infty} \int_0^t \left(1 - \frac{s}{t}\right) \mathbb{E}_\mu [\Pi\varphi(q_t, p_t) \Pi\varphi(q_0, p_0)] ds \\ &= 2 \int_0^{+\infty} \int_{\mathcal{E}} (e^{s\mathcal{L}} \Pi\varphi) \Pi\varphi d\mu ds = 2 \int_{\mathcal{E}} (-\mathcal{L}^{-1} \Pi\varphi) \Pi\varphi d\mu \end{aligned}$$

Well-defined provided $-\mathcal{L}\Phi = \Pi\varphi$ has a solution in $L_0^2(\mu) = \Pi L^2(\mu)$

A **Central Limit Theorem** holds in this case³: $\widehat{\varphi}_t - \mathbb{E}_\mu(\varphi) \simeq \frac{\sigma_\varphi}{\sqrt{t}} \mathcal{G}$

³R. N. Bhattacharya, *Z. Wahrsch. Verw. Gebiete* (1982)

Statistical error (2/2)

Prove **exponential convergence** of the semigroup $e^{t\mathcal{L}}$ on $E \subset L_0^2(\mu)$

- Lyapunov techniques⁴ $L_{\mathcal{X}}^\infty(\mathcal{E}) = \left\{ \varphi \text{ measurable, } \sup \left| \frac{\varphi}{\mathcal{X}} \right| < +\infty \right\}$
- “historic” hypocoercive⁵ setup $H^1(\mu)$
- $L^2(\mu)$ after hypoelliptic regularization⁶ from $H^1(\mu)$
- direct transfer from $H^1(\mu)$ to $L^2(\mu)$ by spectral argument⁷
- directly⁸ $L^2(\mu)$ (recently⁹ Poincaré using $\partial_t - \mathcal{L}_{\text{ham}}$)
- coupling arguments¹⁰
- direct estimates on the resolvent using Schur complements¹¹

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

⁴Wu (2001); Mattingly/Stuart/Higham (2002); Rey-Bellet (2006); Hairer/Mattingly (2011)

⁵Villani (2009) and before Talay (2002), Eckmann/Hairer (2003), Hérau/Nier (2004),...

⁶Hérau, *J. Funct. Anal.* (2007)

⁷Deligiannidis/Paulin/Doucet, *Ann. Appl. Probab.* (2020)

⁸Hérau (2006), Dolbeaut/Mouhot/Schmeiser (2009, 2015)

⁹Albritton/Armstrong/Mourrat/Novack (2019), Cao/Lu/Wang (2019), Brigati (2021), Dietert/Hérau/Hutridurga/Mouhot (2022), Brigati/Stoltz (2023), Eberle/Guillin/Hahn/Lörler (2025), ...

¹⁰Eberle/Guillin/Zimmer, *Ann. Probab.* (2019)

¹¹Bernard/Fathi/Levitt/Stoltz, *Annales Henri Lebesgue* (2022)

Practical computation of average properties

- 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** strategy¹²

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

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

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

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

- Second order splittings schemes (Verlet + FD or BAOAB)

¹²Leimkuhler/Matthews (2013, 2016); Leimkuhler/Matthews/Stoltz (2016)

Types of errors

Estimators of $\mathbb{E}_\mu(\varphi)$

$$\hat{\varphi}_t = \frac{1}{t} \int_0^t \varphi(q_s, p_s) ds, \quad \hat{\varphi}^{N, \Delta t} = \frac{1}{N} \sum_{n=1}^N \varphi(q^n, p^n)$$

Statistical error (variance of the estimator)

- $O\left(\frac{\sigma_\varphi}{\sqrt{N\Delta t}}\right)$ from central limit theorem for continuous dynamics
- discrete dynamics: asymptotic variance **coincides** at order Δt^α

Bias (expectation of the estimator)

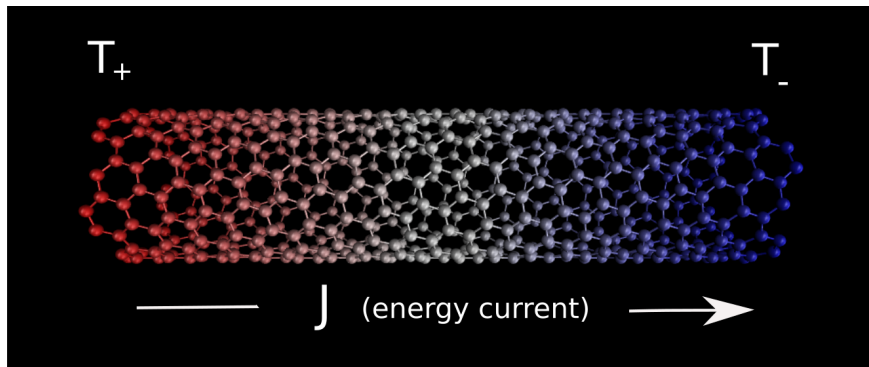
- **finite time** integration time $\rightarrow$ bias $O\left(\frac{1}{N\Delta t}\right)$
- **discretization** of the dynamics $\rightarrow$ bias $O(\Delta t^\alpha)$

Estimation of transport coefficients

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**

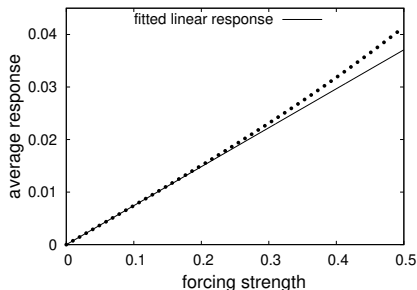
Long computational times to estimate κ (up to several weeks/months)

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



Existence/uniqueness of invariant probability measure (Lyapunov)

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

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

$\alpha =$ **transport coefficient**

Definition of transport coefficients (1)

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

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

$*$ = 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 $\Pi\varphi = \varphi - \mu(\varphi)$)

$$f_\eta = 1 + \eta \mathfrak{f}_1 + \eta^2 \mathfrak{f}_2 + \dots, \quad -\mathcal{L}^* \mathfrak{f}_1 = \tilde{\mathcal{L}}^* \mathbf{1} = \Pi \tilde{\mathcal{L}}^* \mathbf{1} = S$$

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 $R \in L^2_0(\mu) = \Pi L^2(\mu)$, conjugated 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 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)

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

Issues with linear response methods:

- Statistical error with asymptotic variance $O(\eta^{-2}t^{-1})$
- Bias $O(\eta)$ due to $\eta \neq 0$
- Bias from finite integration time
- Timestep discretization bias¹³

¹³Leimkuhler/Matthews/Stoltz (2016), Darshan/Eberle/Stoltz (2024)

Analysis of variance / finite integration time bias

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

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

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

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

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 $-\left(\mathcal{L} + \eta \tilde{\mathcal{L}} \right) \mathcal{R}_{\eta} = R - \int_{\mathcal{E}} R f_{\eta} d\mu$

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

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) $\hat{\alpha}_{K,T} = \frac{1}{K} \sum_{k=1}^K \int_0^T R(q_t, p_t) S(q_0, p_0) dt$

Sources of error : **trade off** in truncation time T

- Time truncation bias $|\mathbb{E}_\pi[\hat{\alpha}_{K,T}] - \alpha| \leq \frac{C}{\kappa} \|R\|_{L^2(\mu)} \|S\|_{L^2(\mu)} e^{-\kappa T}$
- Statistical error¹⁴ $\text{Var}[\hat{\alpha}_{K,T}] \sim \frac{2T}{K} \|S\|_{L^2(\mu)}^2 \langle R, -\mathcal{L}^{-1} R \rangle$
- **Timestep bias and quadrature formula** when numerically integrating¹⁵

For statistical error, proof based on the following equality, with $-\mathcal{L}\mathcal{R} = R \in L^2_0(\mu)$:

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

¹⁴Pavliotis/Spacek/Stoltz/Vaes (2025); Gastaldello/Stoltz/Vaes (2025)

¹⁵Leimkuhler/Matthews/Stoltz (2016), Duncan/Pavliotis/Zygalakis (2017)

Variance reduction attempts: past, present and future

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

- **Alternative fluctuation** formulas
- Importance sampling (Girsanov) for Green-Kubo formulas¹⁶
- Control variate approaches¹⁷ (better solutions to Poisson equation needed...)
- Use coupling methods between X_t^η and X_t^0 , e.g. sticky coupling¹⁸
- Rely on tangent dynamics¹⁹ for $T_t = \lim_{\eta \rightarrow 0} (X_t^\eta - X_t^0)/\eta$
- Optimize **synthetic forcings**
- Large deviation techniques to estimate second order cumulants²⁰
- Norton dynamics²¹ (dual approach where the flux is fixed)
- Transient methods: **subtraction** and TTCF²²

Quantify variance and bias and apply to physical systems

¹⁶ Donati/Hartmann/Keller (2017), Gastaldello/Stoltz/Vaes (2026)

¹⁷ Mangaud/Rotenberg (2020); Roussel/Stoltz (2019), Pavliotis/Stoltz/Vaes (2022), Pavliotis/Spacek/Stoltz/Vaes (2024)

¹⁸ Eberle/Zimmer (2019); Durmus/Eberle/Enfroy/Guillin/Monmarché (2021); Darshan/Eberle/Stoltz (2024)

¹⁹ Assaraf/Jourdain/Lelièvre/Roux (2018)

²⁰ Limmer/Gao/Poggioli (2021)

²¹ Evans/Morriss (2008); Blassel/Stoltz (2023) and now Darshan/Stoltz

²² Evans/Morriss (1987, 1988)

Synthetic forcings (1/2)

Same linear response with **smaller nonlinearities**

Idea: replace the physical perturbation by a family of perturbations

$$\mathcal{L}_{\eta,a} = \mathcal{L} + \eta \left(\tilde{\mathcal{L}}_{\text{phys}} + a \tilde{\mathcal{L}}_{\text{extra}} \right), \quad a \in \mathbb{R}$$

Admissibility condition $\tilde{\mathcal{L}}_{\text{extra}}^* \mathbf{1} = 0$

Conjugate response $S = \tilde{\mathcal{L}}_{\text{phys}}^* \mathbf{1}$ (hence transport coefficient) unchanged

Minimize nonlinear remainder: choose a so that $\rho_2(a)$ is small

$$f_{\eta,a} = 1 + \eta f_1 + \eta^2 f_{2,a} + \dots, \quad \frac{\mathbb{E}_{\eta,a}(R)}{\eta} = \alpha + \eta \rho_2(a) + O(\eta^2)$$

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

R. Spacek and G. Stoltz, Extending the regime of linear response with synthetic forcings, *Multiscale Model. Sim.* **21**(4) 1602-1643 (2023)

Synthetic forcings (2/2)

Examples of admissible extra perturbations

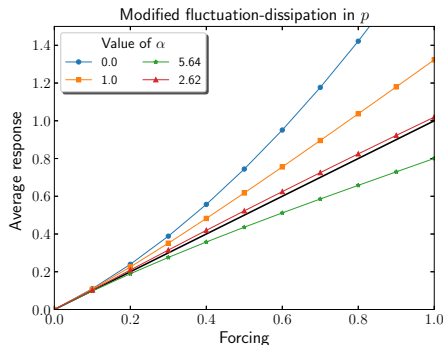
- Divergence-free fields: $\tilde{\mathcal{L}}_{\text{extra}} = G^\top \nabla$ with $\text{div}(G\mu) = 0$
- Modified fluctuation–dissipation: $\tilde{\mathcal{L}}_{\text{extra}} = -\nabla^* D \nabla$

Benefit for NEMD estimators

$$\hat{A}_{a,\eta,t} = \frac{1}{\eta t} \int_0^t R(X_s^{\eta,a}) ds$$

$$\text{Var} \left(\hat{A}_{a,\eta,t} \right) \simeq \frac{\sigma_{R,0}^2}{\eta^2 t}$$

Linearity for larger η : much smaller statistical error for fixed computational cost



Transient subtraction: coupled control variate

Transient formula for linear response: with $\tilde{\mu}_\eta = (1 + \eta S)\mu + O(\eta^2)$,

$$\alpha = \lim_{\eta \rightarrow 0} \frac{1}{\eta} \int_0^{+\infty} \mathbb{E} [R(X_t^\eta) - R(Y_t^0)] dt$$

where Y_t^0 and X_t^η follow **equilibrium** dynamics with $Y_t^0 \sim \mu$ and $X_t^\eta \sim \tilde{\mu}_\eta$

Proof: $\frac{1}{\eta} \int_0^\infty \mathbb{E} [R(x_t^\eta)] dt = \frac{1}{\eta} \int_0^\infty \int_{\mathcal{X}} (e^{t\mathcal{L}_0} R) d\tilde{\mu}_\eta dt = \int_0^\infty \int_{\mathcal{X}} (e^{t\mathcal{L}_0} R) S d\mu dt + O(\eta) = \alpha + O(\eta)$

Couple two trajectories

$$\begin{cases} dY_t^0 = b(Y_t^0)dt + \sigma dW_t, & Y_0^0 \sim \mu, \\ dX_t^\eta = b(X_t^\eta)dt + \sigma dW_t, & X_0^\eta = \Phi_\eta(Y_0^0), \end{cases}$$

with $\Phi_\eta(x) = x + \eta\phi_1(x)$ and $\Phi_\eta\#\mu = (1 + \eta S)\mu + O(\eta^2)$

$\phi_1(q, p) = (0, F(q))$ for underdamped Langevin (solution to **PDE**)

G. Ciccotti and G. Jacucci, *Physical Review Letters* **35**(12), 789 (1975)

P. Monmarché, R. Spacek and G. Stoltz, *J. Stat. Phys.* **192** (2025)

Transient subtraction: estimator and error balance

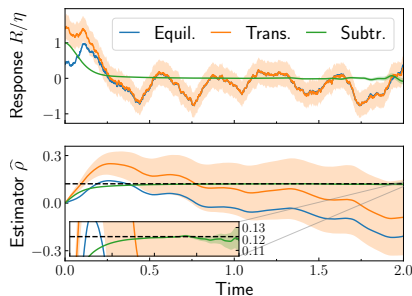
Estimator $\hat{\alpha}_{T,K,\eta}^{\text{sub}} = \frac{1}{\eta K} \sum_{k=1}^K \int_0^T \left[R(X_t^{\eta,k}) - R(Y_t^{0,k}) \right] dt$

Variance: when $(x - y)^\top (b(x) - b(y)) \leq B|x - y|^2$,

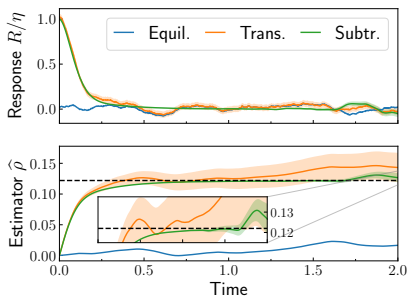
$$\text{Var} \left(\hat{\alpha}_{T,K,\eta}^{\text{sub}} \right) \leq \frac{\|R\|_{\text{Lip}}^2}{K} \frac{\mathbb{E} [|X_0^\eta - Y_0^0|^2]}{\eta^2} \left(\int_0^T e^{tB} dt \right)^2 = O(1)$$

Equilibrate bias (exp. small in T) and variance (exp. growth in T)

$\eta = 0.01$



$\eta = 0.1$



Alternative fluctuation formula (1/3)

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 $\rightarrow$ unique invariant measure ν_η

Estimator of the linear response (fluctuation at **equilibrium**)

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

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

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

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

Alternative fluctuation formula (2/3)

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

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

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

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

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

Variance uniformly bounded in time: by similar manipulations,

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

Alternative fluctuation formula (3/3)

Discrete sensitivity estimator (slightly idealized)

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

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

$$\left| \mathbb{E}_{\Delta t} \left\{ \mathcal{M}_{\Delta t, N_{\text{iter}}}^{[1]}(R) \right\} - \alpha \right| \leq C \left(\Delta t + \frac{1}{\sqrt{N_{\text{iter}} \Delta t}} \right)$$
$$\text{Var}_{\Delta t} \left\{ \mathcal{M}_{\Delta t, N_{\text{iter}}}^{[1]}(R) \right\} \leq C_1 + C_2 \left(\Delta t + \frac{1}{N_{\text{iter}} \Delta t} \right)$$

Finite-time bias $O(\text{time}^{-1/2})$ (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**, S593-S623 (2021)

P. Plechac, G. Stoltz, T. Wang, *IMA J. Numer. Anal.* **43**(6), 3430–3477 (2023)