# Computing Linear Response of Stochastic Dynamics Out-of-Equilibrium

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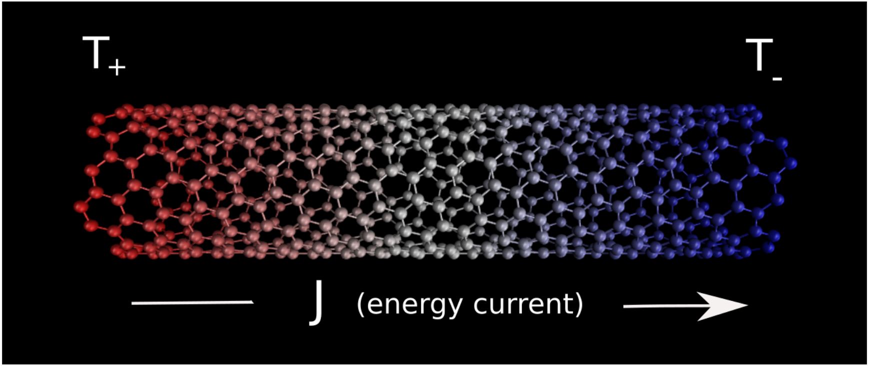
# Outline

- **An introduction to molecular dynamics**
- **Linear response for steady-state nonequilibrium dynamics**
  - Equilibrium dynamics and their perturbations
  - Definition of transport coefficients
  - Variance & bias of NEMD estimator
- **Improving upon the Standard Estimator**
  - Couplings based estimators
  - Synthetic Forcing
  - Norton Dynamics

**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)

We could describe microscopic dynamics of the all the particles relevant to the system under consideration using the laws of classical mechanics:
Positions $q \in \mathcal{D}$ (typically $\mathcal{D} = (L\mathbb{T})^d$ or $\mathbb{R}^d$), momenta $p \in \mathbb{R}^d$
Phase-space $\mathcal{E} = \mathcal{D} \times \mathbb{R}^d$

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

$$\begin{cases} \dot{q}_t = M^{-1} p_t \\ \dot{p}_t = -\nabla V(q_t) \end{cases}$$

For non-trivial systems simulating these dynamics is *intractable*. $d = 3N$ with $N$ the number of particles. Avogadro's number, number of particles in a mole, $\sim 10^{23}$

# Computational statistical physics (3)

- 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

Add stochastic thermostat with friction $\gamma > 0$ to Hamiltonian dynamics that fixes temperature

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

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

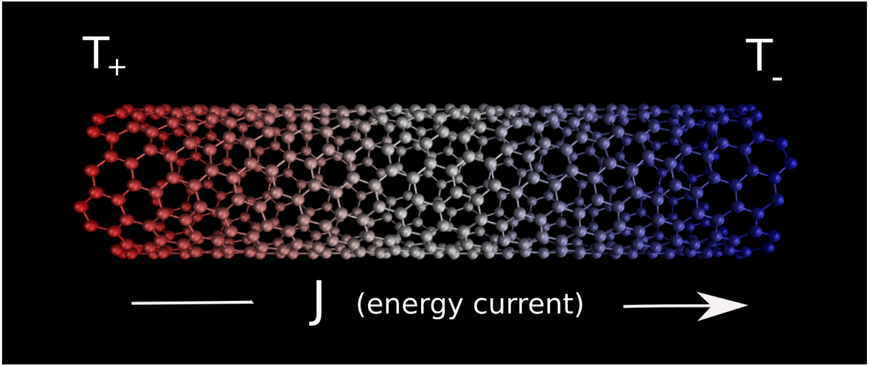
$$\forall\varphi, \quad \int_{\mathcal{E}} \mathcal{L}\varphi\,d\mu = 0 \qquad \Longleftrightarrow \qquad \mathcal{L}^\dagger\mu = 0$$

# 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 $\kappa$ (up to several weeks/months)

# Nonequilibrium stochastic dynamics

We perturb our reference dynamics by a small forcing $\eta F$, where $F$ is a smooth function and $\eta \in \mathbb{R}$

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

Under some technical this dynamics admits a unique invariant probability measure $\mu_\eta$ satisfying $\mu_\eta = f_\eta \mu_0$ with $f_\eta = 1 + \mathrm{O}(\eta)$, i.e non-equilibrium behavior is a *perturbation* of the equilibrium behavior.
For an observable $R$, the transport coefficient is defined as:

$$\alpha_R = \lim_{\eta \to 0} \frac{1}{\eta} \left( \int_{\mathbb{R}^d} R \, d\mu_\eta - \int_{\mathbb{R}^d} R \, d\mu \right)$$

# A reminder of statistics

Recall from statistics that we can quantify the quality of an estimator $\widehat{\Theta}$ of a value $\theta$ via it bias and variance:

$$\mathrm{Bias}\left(\widehat{\Theta}\right) := \mathbb{E}[\widehat{\Theta}] - \theta,$$

$$\mathrm{Var}\left(\widehat{\Theta}\right) := \mathbb{E}[\widehat{\Theta}^2] - \mathbb{E}[\widehat{\Theta}]^2.$$

The mean-squared error is then satisfies $\mathrm{MSE}(\widehat{\Theta}) = \mathrm{Bias}(\widehat{\Theta})^2 + \mathrm{Var}(\widehat{\Theta})$. If we can show that the error is normal (or at least asymptotically normal), i.e.

$$\widehat{\Theta} - \theta \sim \mathcal{N}\left(\mathrm{Bias}\left(\widehat{\Theta}\right), \mathrm{Var}\left(\widehat{\Theta}\right)\right)$$

then we can also use the bias and variance to construct confidence intervals.

# Principle of nonequilibrium molecular dynamics

Estimator of linear response (observable $R$ average 0 with respect to $\nu_0$)

$$\widehat{\Phi}_{\eta,t} = \frac{1}{\eta t}\int_0^t R(X_t^\eta)\,ds \xrightarrow[t\to+\infty]{\text{a.s.}} \alpha_{R,\eta} := \frac{1}{\eta}\int_{\mathbb{R}^d} R\,d\nu_\eta = \alpha_R + \mathrm{O}(\eta)$$

**Issues with linear response methods:**

- Statistical error with asymptotic variance $\mathrm{O}(\eta^{-2})$
- Bias from finite integration time

- Timestep discretization bias
- Bias $\mathrm{O}(\eta)$ due to $\eta \neq 0$

# Analysis of variance / finite integration time bias

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

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

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

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

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

# Improving upon the standard estimator

# Couplings Based Estimator

## Definition

A coupling of two random variables $X$ and $Y$ is a couple $\left(\widetilde{X}, \widetilde{Y}\right)$ of random variables such that $\widetilde{X} \overset{\text{Law}}{=} X$ and $\widetilde{Y} \overset{\text{Law}}{=} Y$

**Idea:** Use the reference dynamics[1] to reduce the variance and bias of the estimator:

$$\widehat{\Psi}_{\eta,t} = \frac{1}{\eta t} \int_0^t \left[ R\left(q_s^\eta, p_s^\eta\right) - R\left(q_s^0, p_s^0\right) \right] ds, \tag{1}$$

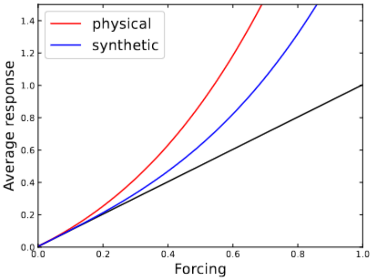
with $\left\{ \left(q_t^\eta, p_t^\eta\right), \left(q_t^0, p_t^0\right) \right\}_{t \geqslant 0}$ are a clever coupling of the perturbed and reference dynamics.

Using *sticky coupling* we can reduce the variance and bias by a factor $\eta$ in the overdamped case.

[1] S. Darshan, A. Eberle, G. Stoltz *Sticky coupling as a control variate for sensitivity analysis*. In preparation

# Synthetic forcing

Taking small $\eta$ is causing problem, however with out taking $\eta$ small we risk being outside the linear response regime.




**Idea:** We modify $F$ by adding a *synthetic forcing*[2] so that linear regime, i.e. the set of $\eta$'s for which $\int_{\mathbb{R}^d} R\, d\mu_\eta - \int_{\mathbb{R}^d} R\, d\mu \approx \alpha_R \eta$, is extended.

[2] R. Spacek and G. Stoltz *Extending the regime of linear response with synthetic forcings* (2023)

# Norton dynamics

Is the NEMD paradigm—fix our forcing in advance and measure our observable—the only possible paradigm?
Instead, we can try to fix the value of our observable and measure the size of forcing necessary to induce this response[3].

$$\begin{cases} dq_t^r = M^{-1} p_t^r \, dt \\ dp_t^r = -\nabla V(q_t^r) \, dt - \gamma M^{-1} p_t^\eta \, dt + \sqrt{\frac{2\gamma}{\beta}} \, dW_t + F(q_t^\eta) d\Lambda_t \\ \qquad \Lambda_t \text{ such that } R(q_0^r, p_0^r) = R(q_t^r, p_t^r) = r \end{cases}$$

Initial numerical results suggest that this setup induces the same response as NEMD and has better scaling properties with large system size[3].

[3] N. Blassel and G. Stoltz *Fixing the flux: A dual approach to computing transport coefficients* (2023)