# Fixing the Flux: a Dual Approach to Computing Transport Coefficients

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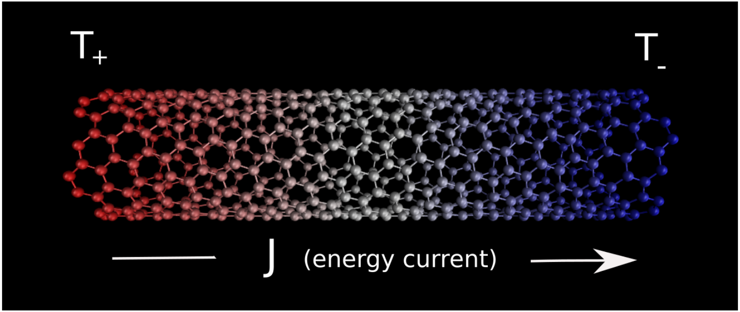
May 31, 2023

[1] N. Blassel & G.Stoltz, (2023), ArXiv 2305.08224

# Transport coefficients

Measure sensitivities of fluxes in response to nonequilibrium perturbations. Characterize dynamic properties of molecular systems (thermal transport, diffusion, shear viscosity...), and parametrize macroscopic evolution equations (e.g. Navier–Stokes).



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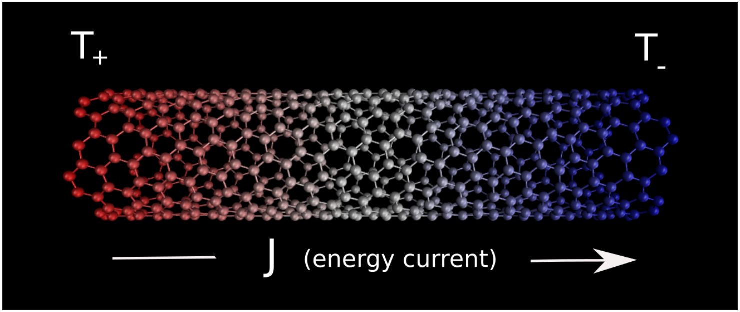


In the small perturbation regime, the magnitude of the flux depends asymptotically linearly on the magnitude of the perturbation. The proportionality constant is the transport coefficient.

# Standard NEMD dynamics: formal framework

Fix a $d$-dimensional configuration space $\mathcal{X}$, a reference drift $b$ and diffusion matrix $\sigma$. External forcing: $F : \mathcal{X} \to \mathbb{R}^d$, modulated in strength by $\eta \in \mathbb{R}$. The response flux is a function $R : \mathcal{X} \to \mathbb{R}$, with zero average at equilibrium.

- Standard NEMD, or "Thévenin":

$$\mathrm{d}X_t^\eta = b(X_t^\eta)\,\mathrm{d}t + \sigma(X_t^\eta)\,\mathrm{d}W_t + \eta F(X_t^\eta)\,\mathrm{d}t.$$

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- We measure averages of the response , with respect to the invariant mesure $\mu^\eta$ (typically using ergodic averages). See[2] for precise $\exists!$ statements for $\mu^\eta$.

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- Challenging to estimate due to low signal-to-noise ratio. Variance reduction techniques are under active investigation[3]

[2] R. Spacek & G. Stoltz (2023)

[3] R. Spacek & G. Stoltz (2023), S. Darshan, A. Eberle & G. Stoltz (In preparation)

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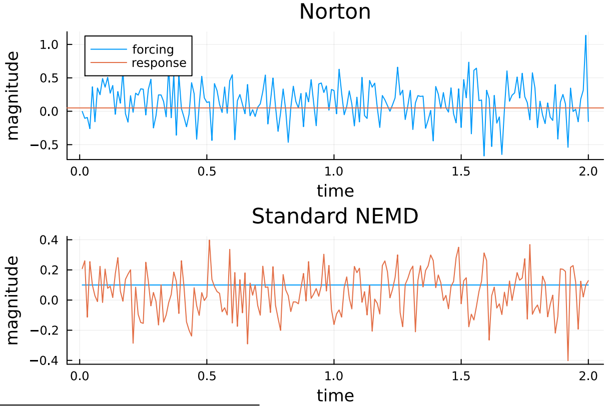


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## Dual approach: formal framewok

- Norton dynamics:

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- And thus for the dynamics:

$$\mathrm{d}Y_t^r = \overline{P}_{F,\nabla R}(Y_t^r)\left[b(Y_t^r)\mathrm{d}t + \sigma(Y_t^r)\mathrm{d}W_t\right] - \frac{\left(\nabla^2 R : \Pi_{F,\nabla R,\sigma}\right) F}{2\nabla R \cdot F}(Y_t^r)\,\mathrm{d}t.$$

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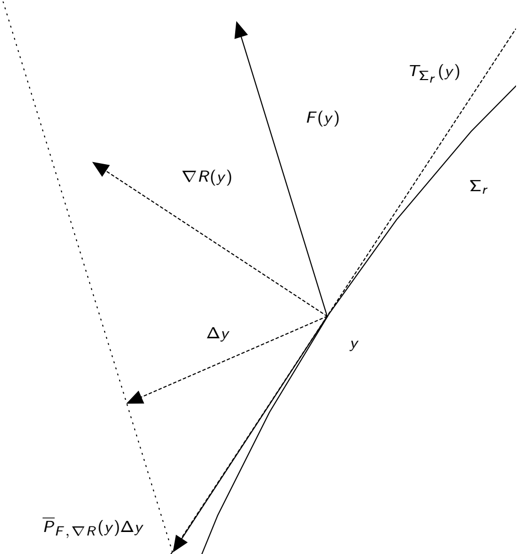
- $\overline{P}_{F,\nabla R}$ is a non-orthogonal projector onto $\nabla R^{\perp}$, the tangent space to the constant-response manifold $\Sigma_r = R^{-1}\{r\}$.

# Geometric picture

The oblique projector $\overline{P}_{F,\nabla R(y)}$



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- In the case $F = \nabla R$, standard constrained dynamics, well-studied in MD (geometrical constraints and thermodynamic integration for free energy computations).
- Loosely, the forcing is given by the magnitude of the recall force in the direction $F(y)$, up to some curvature correction.

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- Generalization 1: the case of constraints on multiple fluxes (Onsager relations).
- Generalization 2: the case of a time-dependent constraint on the flux $R(Y_t^r) = r_t$.

# Example: mobility computations

Constant perturbation $F \in \mathbb{R}^{dN}$. Mass matrix $M$, friction coefficient $\gamma > 0$, inverse temperature $\beta = (k_{\mathrm{B}} T)^{-1}$.

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Nonequilibrium Langevin dynamics:

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Single drift:

$$F_{ix} = \delta(i-1), \quad F_{i,y} = F_{i,z} = 0$$

Color drift:

$$F_{ix} = (-1)^i N^{-1/2}, \quad F_{i,y} = F_{i,z} = 0$$

# Norton mobility dynamics

In this case, the Norton dynamics is very simple: the dynamics on the momenta is just and easily shown to be well-posed:

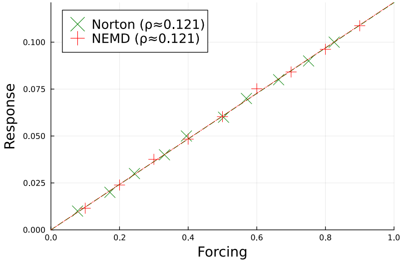
$$\begin{cases} \mathrm{d}q_t = M^{-1} p_t \,\mathrm{d}t, \\ \mathrm{d}p_t = \overline{P}_{F,M^{-1}F} \left( -\nabla V(q_t)\,\mathrm{d}t - \gamma M^{-1} p_t \,\mathrm{d}t + \sqrt{\frac{2\gamma}{\beta}}\,\mathrm{d}W_t \right), \end{cases} \tag{2}$$

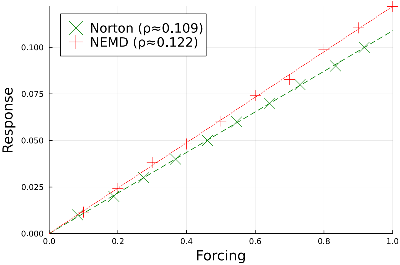
with

$$\overline{P}_{F,M^{-1}F} = \mathrm{Id} - \frac{FF^{\intercal} M^{-1}}{F^{\intercal} M^{-1} F}.$$

# Numerical results: mobility

We apply the method to a Lennard-Jones fluid of 1000 particles. Left: color drift. Right: single drift.



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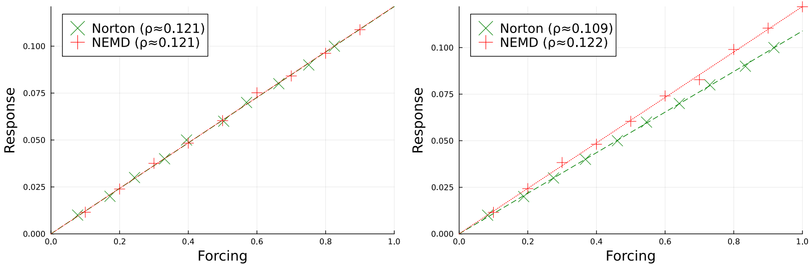


Dual method gives a consistent estimate of the mobility in the case of the bulk forcing (color drift).

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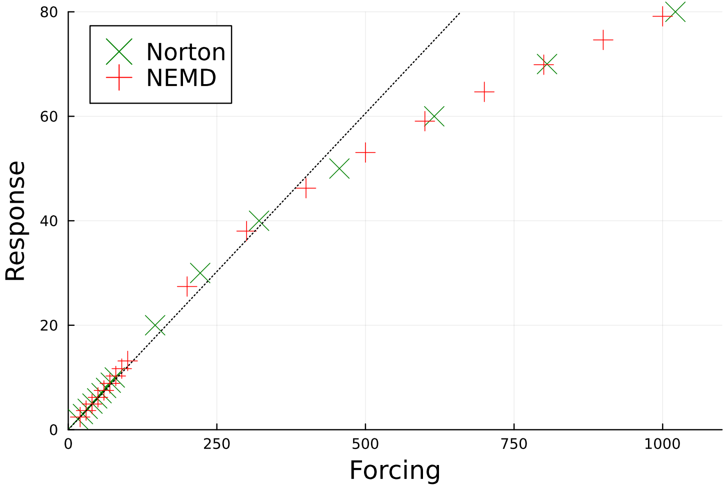

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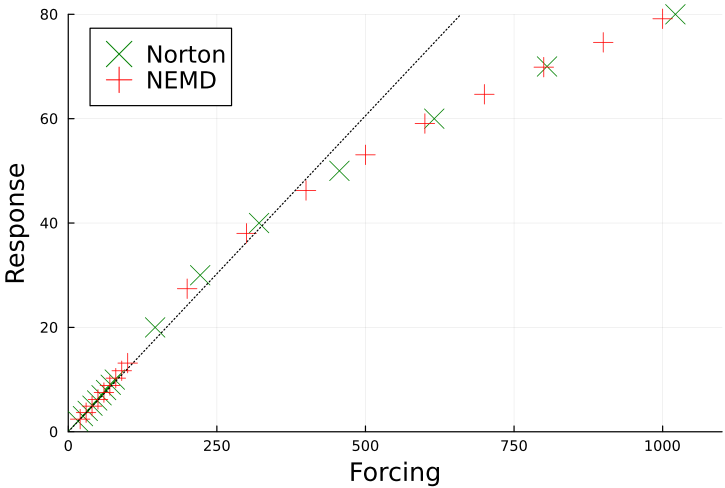
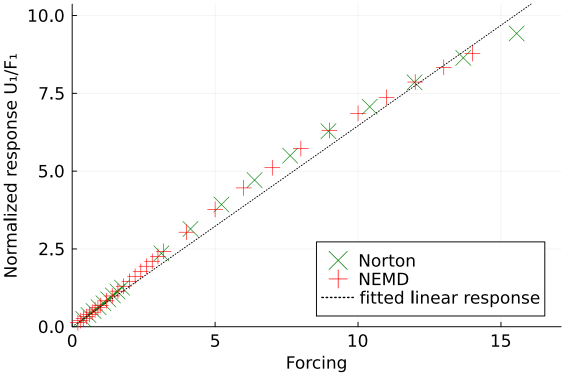



The response curves coincide far in the non-linear regime!

# Numerical results: shear viscosity

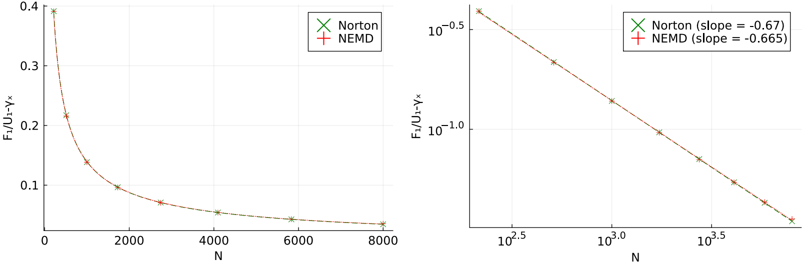
We apply the dual approach to a non-equilibrium system perturbed to estimate the shear viscosity. The forcing direction corresponds to a fixed underlying longitudinal shear flow field, the response to a Fourier coefficient of the longitudinal velocity profile[5]




[5] G. Stoltz & R. Joubaud (2012), Gosling, McDonald & Singer (1973)

# Numerical results: shear viscosity

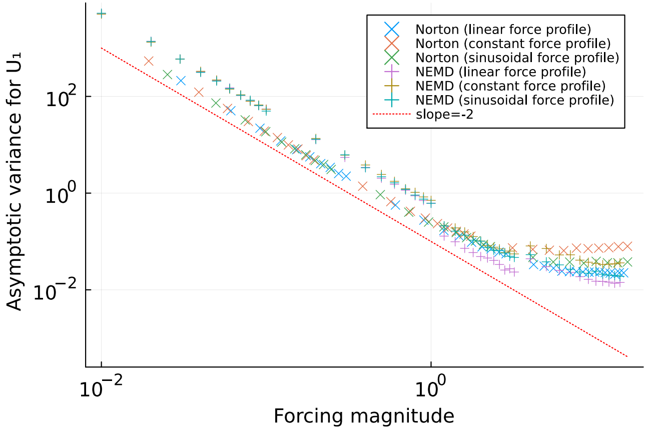
We check that the finite-estimators of the linear response give consistent results in the large $N$ limit.




Here, $F_1$ and $U_1$ are the Fourier coefficients of the forcing profile and the response velocity profile, $\gamma_x$ is the friction coefficient in the direction $x$. Extrapolating to the thermodynamic limit $N \to \infty$ yields close estimates of the shear viscosity for the NEMD and dual approach.

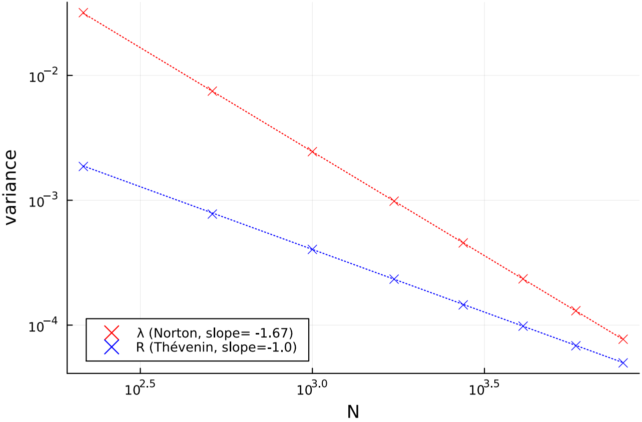
# Numerical results: shear viscosity

In the shear viscosity case, observe an improvement in the asymptotic variance of Norton estimators.



## Numerical results: shear viscosity

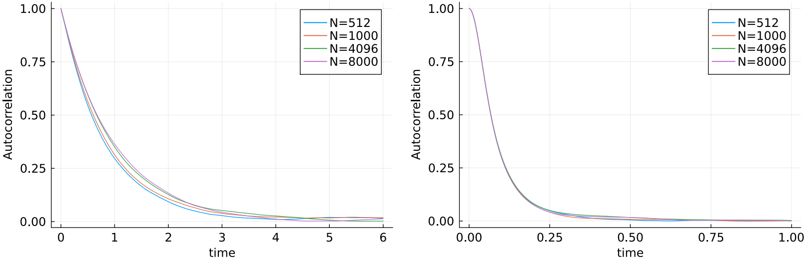
To explain this discrepancy, we compare the variance for $\lambda$ in the Norton ensemble with the variance for $R$ in the standard NEMD equilibrium ensembles.




Surprising and asymptotically better scaling for the Norton method, but higher variance: improvement comes from correlation time.

# Numerical results: shear viscosity

Indeed, this is what we observe.




Pearson autocorrelations functions for $\eta = r = 0$ in the standard NEMD and Norton ensembles. Left: standard NEMD, Right: Norton.

## Many questions for the future:

- Continuous/stochastic analysis: criteria for well-posedness, existence/uniqueness of steady-state, pathwise ergodicity, rates of convergence to Norton equilibrium.
- Theory: equivalence of ensembles at equilibrium, linear response theory for Norton dynamics, consistency results for linear responses, equivalence of non-equilibrium ensembles.
- Numerical analysis: explain concentration rate of $\lambda$/shorter correlation times, error analysis for splitting schemes.