Fixing the Flux: a Dual Approach to Computing Transport Coefficients

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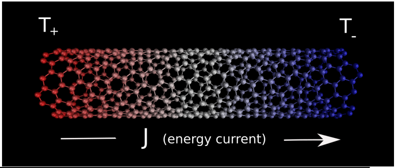
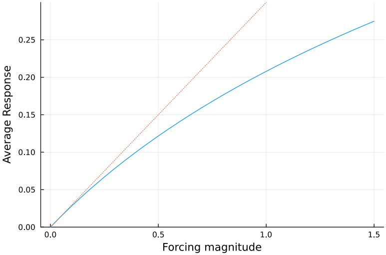
[1] N. Blassel & G.Stoltz, (2023), ArXiv 2305.08224

Transport coefficients

- Measure sensitivity of flux induced by nonequilibrium perturbation
- Parametrize macroscopic evolution equations (e.g. Navier–Stokes)
- Dynamical quantities: thermal conductivity, mobility, shear viscosity...
- Magnitude of flux depends linearly on the flux in the small perturbation regime.
- Equilibrium methods (Green–Kubo, tangent dynamics[2], martingale product estimators[3]).
- Nonequilibrium dynamics.





[2] R. Assaraf, B. Jourdain, T. Lelièvre & R. Roux (2015)
[3] P. Plecháč, G. Stoltz & T. Wang (2021)

Standard NEMD dynamics: formal framework

Fix a d-dimensional configuration space $\mathcal{X}$, a reference drift b and diffusion matrix σ. 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:

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

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- We measure averages of the response , with respect to the invariant mesure μ^η (typically using ergodic averages). See[4] for precise $\exists!$ statements for μ^η.

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

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- Challenging to estimate due to scaling of the variance in $\mathrm{O}(\eta^{-2})$ for the standard estimator. Variance reduction techniques: active area of research[5]

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

Dual approach: formal framewok

- Idea: fix value of the flux r exactly, measure average magnitude of the forcing needed to induce it. Stochastic version of the Norton method.[6]

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

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- $\overline{P}_{F,\nabla R}$ is a non-orthogonal projector onto $\nabla R^{\perp} = T\Sigma_r$ in the direction F.

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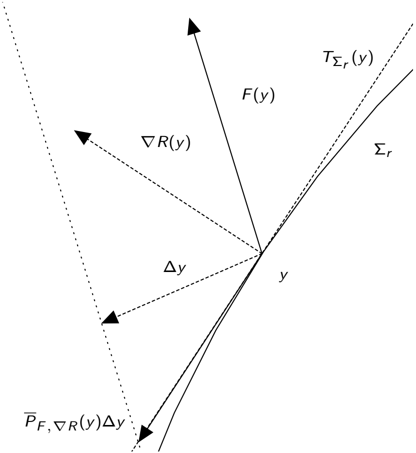
Geometric picture

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



$$\overline{P}_{F,\nabla R}(y) = \mathrm{Id} - \frac{F(y) \otimes \nabla R(y)}{F(y) \cdot \nabla R(y)}, \qquad \Pi_{F,\nabla R,\sigma} = \overline{P}_{F,\nabla R}\sigma\sigma^{\intercal}\overline{P}^{\intercal}_{\nabla F,R}.$$

Dual transport coefficients

Assume ∃! Norton steady-state $\mu^{r,*}$ for all r small enough.

- Average forcing magnitude determined by the bounded variation component of the forcing process

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- The procedure can be generalized to vector-valued responses and time-dependent constraints.
- Nonequilibrium analog of microcanonical/canonical duality (equivalence of ensembles).

Norton Langevin dynamics

Apply the general framework to kinetic Langevin equations, with responses of the form

$$R(q,p) = p^\intercal G(q).$$

Typical examples: mobility, shear viscosity.

- NEMD:

$$\begin{cases} \mathrm{d}q_t^\eta = M^{-1} p_t^\eta \, \mathrm{d}t, \\ \mathrm{d}p_t^\eta = \left[-\nabla V(q_t^\eta) + \eta F(q_t^\eta) \right] \mathrm{d}t - \gamma M^{-1} p_t^\eta \, \mathrm{d}t + \sqrt{\dfrac{2\gamma}{\beta}} \, \mathrm{d}W_t. \end{cases} \tag{1}$$

  M=mass matrix, $0 < \gamma$=damping coefficient, $\beta = (k_\mathrm{B} T)^{-1}$=inverse temperature.

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Example: mobility computations

Forcing: constant perturbation $F \in \mathbb{R}^{dN}$.

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Single drift – singular forcing:

$$F_{i,x} = \delta_{i,1}, \quad F_{i,y} = F_{i,z} = 0$$

Color drift – bulk forcing:

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

Norton mobility dynamics

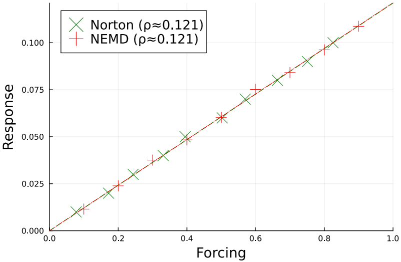
Projection of equilibrium momentum dynamics

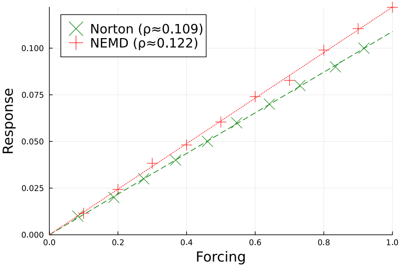
$$\begin{cases} \mathrm{d}q_t = M^{-1} p_t \,\mathrm{d}t, \\ \mathrm{d}p_t = \overline{P}_{F,M^{-1}F} \left(-\nabla V(q_t)\,\mathrm{d}t - \gamma M^{-1} p_t \,\mathrm{d}t + \sqrt{\frac{2\gamma}{\beta}}\,\mathrm{d}W_t \right), \end{cases} \tag{3}$$

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

Numerical results: mobility

Lennard-Jones fluid of 1000 particles (liquid argon). Left: color drift (bulk forcing/response). Right: single drift (singular forcing/response).





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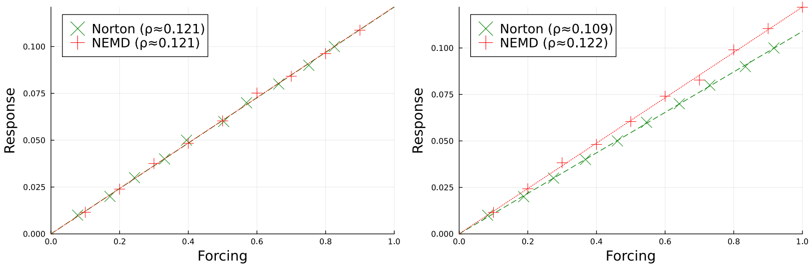
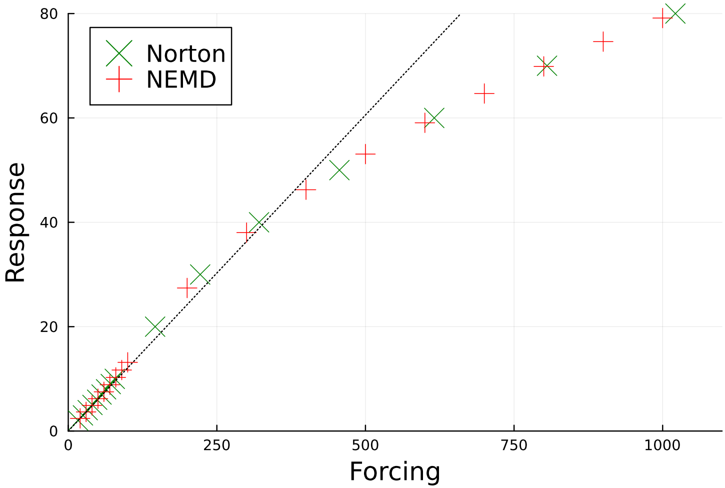


Linear responses coincide in the case of bulk forcings.

Numerical results: mobility with a bulk forcing

Non-linear responses coincide as well:



Shear viscosity[7]

Forcing F acts only on x-components, according to a y-profile f.

$$\forall\, 1 \leq i \leq N,\ \forall\, 2 \leq \alpha \leq d, \quad F(q)_{i,x} = f(q_{i,y}), \quad F(q)_{i\alpha} = 0,$$

In non-equilibrium steady-state, measurable y-profile in the x-components of velocity. Localized linear response: $u_x(y)$. Shear viscosity ν:

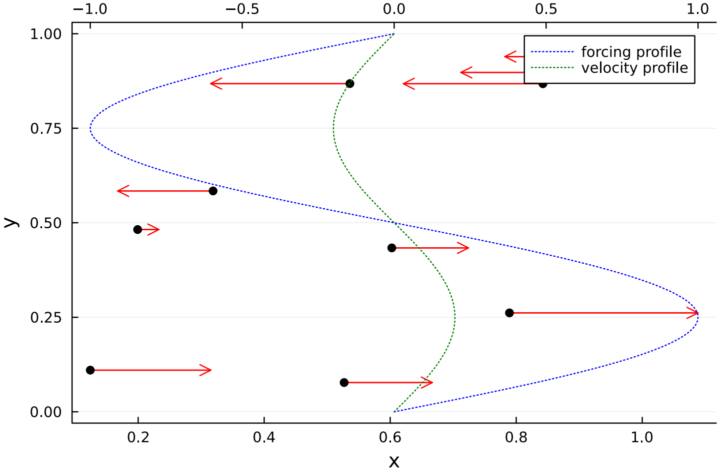
$$-\nu u_x''(y) + \gamma_x \rho u_x(y) = \rho f(y) \implies \nu = \rho \left(\frac{F_1}{U_1} - \gamma_x \right) \left(\frac{L_y}{2\pi} \right)^2,$$

Fourier coefficients F_1, U_1 of f and u_x. Response observable

$$R(q,p) = \frac{1}{N} \sum_{j=1}^{N} \left(M^{-1} p \right)_{j,x} \exp\left(\frac{2i\pi q_{j,y}}{L_y} \right). \tag{4}$$

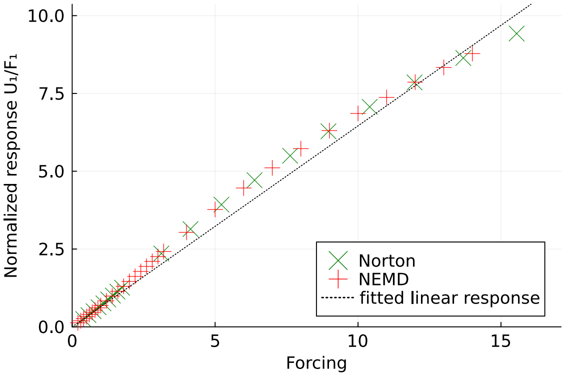
[7] G. Stoltz & R. Joubaud (2012), Gosling, McDonald & Singer (1973)

Shear viscosity



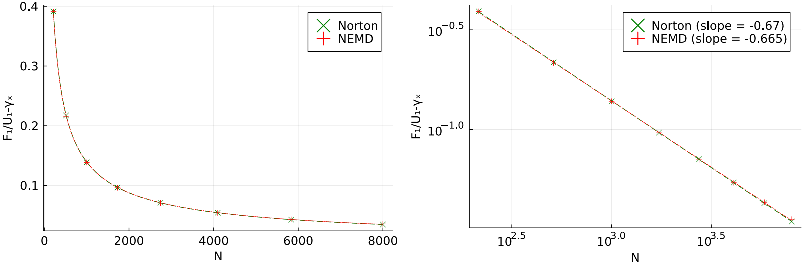
Shear viscosity: equivalence of nonlinear responses

Lennard–Jones fluid: consistent (non)linear response profiles:



Shear viscosity: consistency in the thermodynamic limit

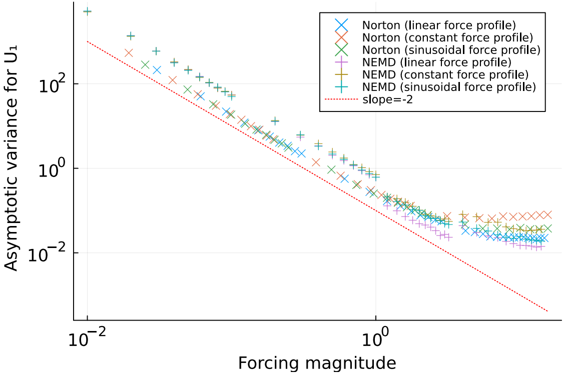
Ergodic estimators of the linear response are consistent results in the limit $N \to \infty$:



Extrapolating the estimated shear viscosity to the limit $N \to \infty$ give close estimates for NEMD and dual approach.

Shear viscosity: gain in asymptotic variance

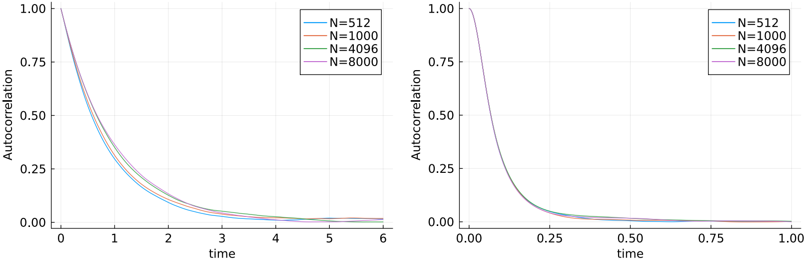
Asymptotic variance of estimators for F_1/U_1 from ergodic averages:



Standard NEMD $\approx$ doubles the asymptotic variance with respect to dual approach.

Shear viscosity: decay of autocorrelations

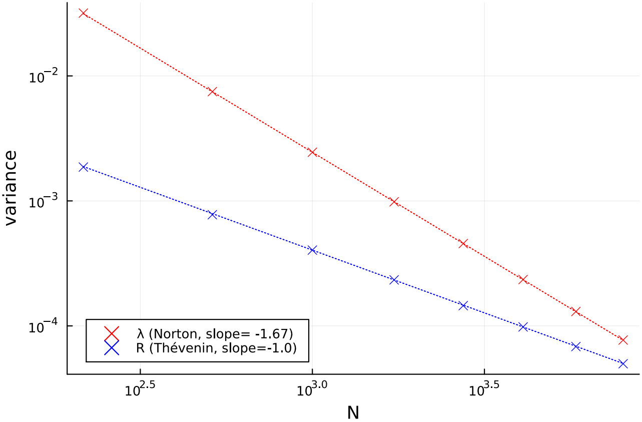
To explain this discrepancy, we compare the variance for λ in the Norton ensemble with the variance for R in the standard NEMD equilibrium ensembles.



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

Shear viscosity: scaling of variance

Scaling of the variance with system size:



NEMD: $\mathrm{Var}_{\mu^0}(R) = \mathrm{O}(N^{-1}) \to$ consistent with spatial CLT.

Dual method: $\mathrm{Var}_{\mu^{0,*}}(\lambda) = \mathrm{O}(N^{-5/3}) \to$ gain in asymptotic variance increases with system size.

Conclusion

This work:

- General framework to derive dual nonequilibrium dynamics.
- Consistency/promising scaling properties of the approach on simple but realistic systems.
- Class of numerical methods (splitting schemes for dual Langevin dynamics).

Many theoretical questions are opened:

- Well-posedness, existence/uniqueness of steady-state, ergodicity/convergence to equilibrium for the dual dynamics.
- Equivalence of (non)equilibrium ensembles, equivalence of linear responses, Green–Kubo type formulas.
- Numerical analysis: scaling law for $\mathrm{Var}(\lambda)$ / correlation times, error analysis for numerical schemes.

Simulations using Molly: `https://github.com/JuliaMolSim/Molly.jl`
Code available at: `https://github.com/noeblassel/ArticleNorton/`

Preprint: `https://arxiv.org/abs/2305.08224`

Thank you!