Error estimates in the numerical computation of transport properties

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Outline

Numerical computation of static properties

- Ergodic averages using Langevin dynamics
- Error estimates
- The overdamped limit

Numerical computation of transport properties

- Examples and general formulas for continuous dynamics
- Error estimates for Green-Kubo formulas
- Error estimates for the linear response of nonequilibrium dynamics

B. Leimkuhler, Ch. Matthews and G. Stoltz, The computation of averages from equilibrium and nonequilibrium Langevin molecular dynamics, *arXiv preprint* **1308.5814** (2013)

General perspective (1)

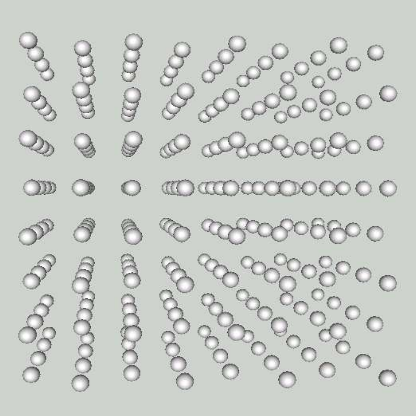
- Aims of computational statistical physics:
  - numerical microscope
  - computation of average properties, static or dynamic

- Orders of magnitude
  - distances $\sim 1\ \mathring{A} = 10^{-10}$ m
  - energy per particle $\sim k_{\rm B}T \sim 4 \times 10^{-21}$ J at room temperature
  - atomic masses $\sim 10^{-26}$ kg
  - time $\sim 10^{-15}$ s
  - number of particles $\sim \mathcal{N}_A = 6.02 \times 10^{23}$

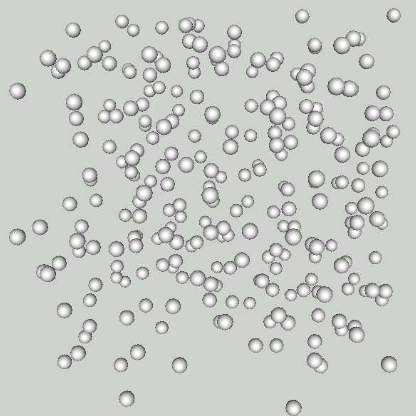
- "Standard" simulations
  - 10^6 particles ["world records": around 10^9 particles]
  - integration time: (fraction of) ns ["world records": (fraction of) μs]

General perspective (2)

What is the equation of state of argon?
What is its thermal conductivity or shear viscosity?



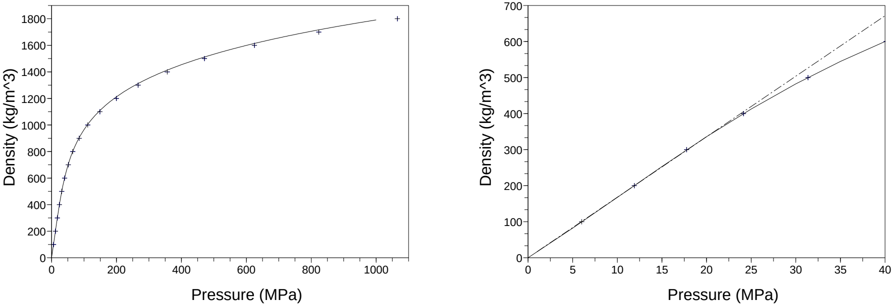
(a) Solid argon (low temperature)



(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

Microscopic description of physical systems: unknowns

- Microstate of a classical system of N particles:

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

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 $\mathcal{M} = (L\mathbb{T})^{3N}$

- More complicated situations can be considered: molecular constraints defining submanifolds of the phase space

- Hamiltonian $H(q,p) = E_{\mathrm{kin}}(p) + V(q)$, where the kinetic energy is

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

Microscopic description: interaction laws

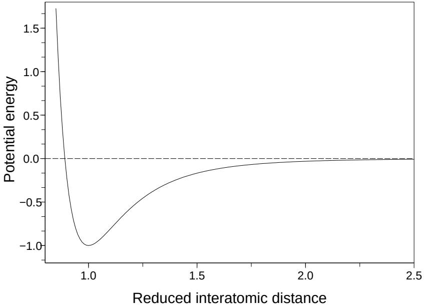
- All the physics is contained in V
  - ideally derived from quantum mechanical computations
  - in practice, empirical potentials for large scale calculations

- An example: Lennard-Jones pair interactions to describe noble gases

$$V(q_1,\dots,q_N) = \sum_{1\leqslant i<j\leqslant N} v(|q_j-q_i|)$$

$$v(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\text{Argon:}\quad \begin{cases} \sigma = 3.405\times 10^{-10}\ \text{m} \\ \varepsilon/k_{\rm B} = 119.8\ \ \text{K} \end{cases}$$



Numerical computation of static properties

Average properties

- Macrostate of the system described by a probability measure

Equilibrium thermodynamic properties (pressure,. . .)

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

- Examples of observables:
  - Pressure $A(q,p) = \dfrac{1}{3|\mathcal{D}|} \displaystyle\sum_{i=1}^{N} \left(\frac{p_i^2}{m_i} - q_i \cdot \nabla_{q_i} V(q) \right)$
  - Kinetic temperature $A(q,p) = \dfrac{1}{3N k_{\mathrm{B}}} \displaystyle\sum_{i=1}^{N} \frac{p_i^2}{m_i}$
- Canonical ensemble = measure on (q,p) (average energy fixed)

$$\mu_{\mathrm{NVT}}(dq\, dp) = Z_{\mathrm{NVT}}^{-1}\, \mathrm{e}^{-\beta H(q,p)}\, dq\, dp, \qquad \beta = \frac{1}{k_{\mathrm{B}} T}$$

Computing average properties

Main issue

Computation of high-dimensional integrals... Ergodic averages

$$\langle A \rangle_\mu = \lim_{t \to +\infty} \frac{1}{t} \int_0^t A(q_s, p_s)\, ds$$

- One possible choice: Langevin dynamics with friction parameter $\gamma > 0$

$=$ Stochastic perturbation of the Hamiltonian dynamics

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

- Denote by $\psi(t, q, p)$ the law of (q_t, p_t)

Convergence and properties of the Langevin dynamics (1)

- Irreducibility (control problem/Stroock-Varadhan support theorem)
- Smoothness of the transition probabilities (hypoellipticity)
- Invariance of the canonical measure
  - Fokker-Planck equation $\partial_t \psi = \mathcal{L}^\dagger \psi$ (adjoints taken on $L^2(dq\,dp)$)
  - Generator $\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \mathcal{L}_{\mathrm{thm}}$ with

$$\mathcal{L}_{\mathrm{ham}} = \frac{p}{m} \cdot \nabla_q - \nabla V(q) \cdot \nabla_p, \qquad \mathcal{L}_{\mathrm{thm}} = \gamma \left(-\frac{p}{m} \cdot \nabla_p + \frac{1}{\beta} \Delta_p \right)$$

  - A simple computation shows that $\mathcal{L}^\dagger \left(\mathrm{e}^{-\beta H} \right) = 0$

- This already implies ergodicity
  - Convergence of averages along one trajectory (LLN)
  - Convergence of $\psi(t)$ to μ in total variation
- Convergence rates? functional estimates $\left\| \mathrm{e}^{t\mathcal{L}} h \right\| \leqslant C \mathrm{e}^{-\lambda t} \|f\|$

Convergence and properties of the Langevin dynamics (2)

- Two "standard" functional settings
  - Hypocoercivity[1] $H^1(\mu)\backslash\mathrm{Ker}(\mathcal{L})$
    (use $\mathcal{L}_{\mathrm{ham}}^* = -\mathcal{L}_{\mathrm{ham}}$, $\mathcal{L}_{\mathrm{thm}} = \sum_i \partial_{p_i}^* \partial_{p_i}$ and commutator properties)
  - Lyapunov condition[2] $\mathcal{L}W \leqslant -aW + b$
    ($W \geqslant 1$ going to infinity at infinity, norm $\|f\|_{L^\infty_W} = \sup \dfrac{|f(q,p)|}{W(q,p)}$)
- Pointwise estimates on derivatives,[3] with $W_n(q,p) = 1 + |p|^{2n}$

For any $k \geqslant 1$, there exists $C > 0$ and integers $n, m, N \geqslant 1$ such that

$$|D^k \mathcal{L}^{-1} f(q,p)| \leqslant C W_n(q,p) \sup_{r \in \mathbb{N}^{2d}, |r| \leqslant N} \|\partial^r f\|_{L^\infty_{W_m}}$$

[1] Eckmann/Hairer (2003), Hérau/Nier (2004), Villani (2009), ...
[2] L. Rey-Bellet, *Lecture Notes in Mathematics* (2006)
[3] D. Talay, *SPA* (2002), M. Kopec *arXiv* (2013)

Practical computation of average properties

- Numerical scheme = Markov chain characterized by evolution operator

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

where (q^n,p^n) is an approximation of $(q_{n\Delta t},p_{n\Delta t})$

- (Infinitely) Many possibilities! Numerical analysis allows to discriminate

- Here: discretization using a splitting strategy

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

- First order splitting schemes: Trotter splitting

$$P_{\Delta t}^{ZYX} = \mathrm{e}^{\Delta t Z}\mathrm{e}^{\Delta t Y}\mathrm{e}^{\Delta t X} \simeq \mathrm{e}^{\Delta t \mathcal{L}}$$

- Second order schemes: Strang splitting

$$P_{\Delta t}^{ZYXYZ} = \mathrm{e}^{\Delta t Z/2}\mathrm{e}^{\Delta t Y/2}\mathrm{e}^{\Delta t X}\mathrm{e}^{\Delta t Y/2}\mathrm{e}^{\Delta t Z/2}$$

- Other category: Geometric Langevin algorithms, *e.g.* $P_{\Delta t}^{\gamma C,A,B,A}$

Examples of splitting schemes

- $P_{\Delta t}^{B,A,\gamma C}$ corresponds to $\begin{cases} \widetilde{p}^{n+1} = p^n - \Delta t\, \nabla V(q^n), \\ q^{n+1} = q^n + \Delta t\, M^{-1} \widetilde{p}^{n+1}, \\ p^{n+1} = \alpha_{\Delta t} \widetilde{p}^{n+1} + \sqrt{\dfrac{1-\alpha_{\Delta t}^2}{\beta} M}\, G^n \end{cases}$

where G^n are i.i.d. Gaussian and $\alpha_{\Delta t} = \exp(-\gamma M^{-1} \Delta t)$

- $P_{\Delta t}^{\gamma C,B,A,B,\gamma C}$ for $\begin{cases} \widetilde{p}^{n+1/2} = \alpha_{\Delta t/2} p^n + \sqrt{\dfrac{1-\alpha_{\Delta t}}{\beta} M}\, G^n, \\ p^{n+1/2} = \widetilde{p}^{n+1/2} - \dfrac{\Delta t}{2} \nabla V(q^n), \\ q^{n+1} = q^n + \Delta t\, M^{-1} p^{n+1/2}, \\ \widetilde{p}^{n+1} = p^{n+1/2} - \dfrac{\Delta t}{2} \nabla V(q^{n+1}), \\ p^{n+1} = \alpha_{\Delta t/2} \widetilde{p}^{n+1} + \sqrt{\dfrac{1-\alpha_{\Delta t}}{\beta} M}\, G^{n+1/2} \end{cases}$

Error estimates on the computation of average properties

- The ergodicity of numerical schemes can be proved ($\mathcal{M}$ bounded):

$$\frac{1}{N_{\rm iter}} \sum_{n=1}^{N_{\rm iter}} A(q^n, p^n) \xrightarrow[N_{\rm iter}\to+\infty]{} \int A(q,p)\, \mu_{\gamma,\Delta t}(dq\,dp)$$

- Uniform-in-Δt rate convergence rate[4]

$$\left\| P_{\Delta t}^n f - \int_{\mathcal{E}} f \, d\mu_{\gamma,\Delta t} \right\|_{L^\infty_{W_m}} \leqslant K\, \mathrm{e}^{-\lambda n \Delta t} \, \|f\|_{L^\infty_{W_m}}$$

- Statistical errors (CLT/variance) *vs.* systematic errors (bias)

Systematic error estimates: α order of the splitting scheme

$$\int_{\mathcal{E}} \psi(q,p)\, \mu_{\gamma,\Delta t}(dq\,dp) = \int_{\mathcal{E}} \psi(q,p)\, \mu(dq\,dp) + \Delta t^\alpha \int_{\mathcal{E}} \psi(q,p) f_{\alpha,\gamma}(q,p)\, \mu(dq\,dp) + \mathrm{O}(\Delta t^{\alpha+1})$$

with $\mathcal{L}^* f_{\alpha,\gamma} = g_\gamma$ (adjoints taken on $L^2(\mu)$, g_γ depends on the scheme)

[4] M. Hairer and J. Mattingly, *Progr. Probab.* (2011)

Proof for the first-order scheme $P_{\Delta t}^{\gamma C,B,A}$ (1)

- By definition of the invariant measure, $\displaystyle\int_{\mathcal{E}} P_{\Delta t}\varphi \, d\mu_{\gamma,\Delta t} = \int_{\mathcal{E}} \varphi \, d\mu_{\gamma,\Delta t}$, so

$$\int_{\mathcal{E}} \left[\left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t} \right) \varphi \right] d\mu_{\gamma,\Delta t} = 0$$

- In view of the BCH formula $\mathrm{e}^{\Delta t A_3}\mathrm{e}^{\Delta t A_2}\mathrm{e}^{\Delta t A_1} = \mathrm{e}^{\Delta t \mathcal{A}}$ with

$$\mathcal{A} = A_1 + A_2 + A_3 + \frac{\Delta t}{2}\Big([A_3, A_1 + A_2] + [A_2, A_1] \Big) + \dots,$$

it holds $P_{\Delta t}^{\gamma C,B,A} = \mathrm{Id} + \Delta t \mathcal{L} + \dfrac{\Delta t^2}{2}\left(\mathcal{L}^2 + S_1\right) + \Delta t^3 R_{1,\Delta t}$ with

$$S_1 = [C, A+B] + [B, A], \qquad R_{1,\Delta t} = \frac{1}{2}\int_0^1 (1-\theta)^2 \mathcal{R}_{\theta \Delta t} \, d\theta,$$

- Not a standard perturbative expansion: the order of the derivatives increases in the higher order terms!

Proof for the first-order scheme $P_{\Delta t}^{\gamma C,B,A}$ (2)

- The correction function $f_{1,\gamma}$ is chosen so that

$$\int_{\mathcal{E}} \left[\left(\frac{\mathrm{Id} - P_{\Delta t}^{\gamma C,B,A}}{\Delta t} \right) \varphi \right] (1 + \Delta t f_{1,\gamma})\, d\mu = \mathrm{O}(\Delta t^2)$$

This requirement can be rewritten as

$$\int_{\mathcal{E}} \left(\frac{1}{2} S_1 \varphi + (\mathcal{L}\varphi) f_{1,\gamma} \right) d\mu = \int_{\mathcal{E}} \varphi \left[\frac{1}{2} S_1^* \mathbf{1} + \mathcal{L}^* f_{1,\gamma} \right] d\mu,$$

which suggests to choose $\mathcal{L}^* f_{1,\gamma} = -\dfrac{1}{2} S_1^* \mathbf{1}$ (well posed equation)

- Replace φ by $\left(\dfrac{\mathrm{Id} - P_{\Delta t}^{\gamma C,B,A}}{\Delta t} \right)^{-1} \psi$? No control on the derivatives...

- Introduce pseudo-inverse $Q_{1,\Delta t} = -\mathcal{L}^{-1} + \dfrac{\Delta t}{2} (\mathrm{Id} + \mathcal{L}^{-1} S_1 \mathcal{L}^{-1})$ with

$$\left(\frac{\mathrm{Id} - P_{\Delta t}^{\gamma C,B,A}}{\Delta t} \right) Q_{1,\Delta t} = \mathrm{Id} + \Delta t^2 Z_{1,\Delta t}$$

and replace φ by $Q_{1,\Delta t} \psi$

Estimating the correction

- Standard procedure: Romberg extrapolation from the a priori estimate

$$\int_{\mathcal{E}} \psi(q,p)\, \mu_{\gamma,\Delta t}(dq\, dp) \simeq \int_{\mathcal{E}} \psi(q,p)\, \mu(dq\, dp) + C\Delta t^{\alpha}$$

- Estimate the leading order correction term $\displaystyle\int_{\mathcal{E}} \psi(q,p) f_{\alpha,\gamma}(q,p)\, \mu(dq\, dp)$?
- Use the operator identity (valid on $H^1(\mu)\backslash \mathrm{Ker}(\mathcal{L})$ for instance)

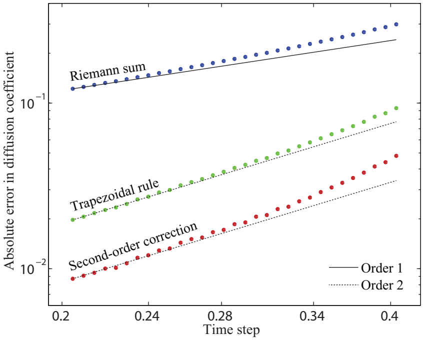
$$\mathcal{L}^{-1} = -\int_0^{+\infty} \mathrm{e}^{t\mathcal{L}}\, dt$$

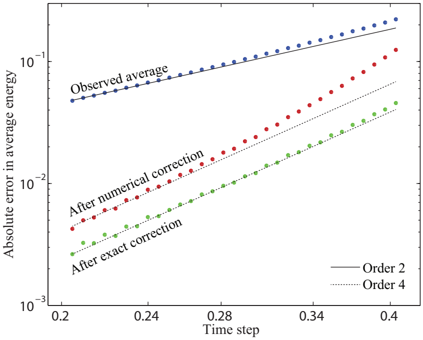
to rewrite the correction as integrated correlation (recall $f_{\alpha,\gamma} = (\mathcal{L}^*)^{-1} g_\gamma$)

$$\int_{\mathcal{E}} \psi(q,p) f_{\alpha,\gamma}(q,p)\, \mu(dq\, dp) = -\int_0^{+\infty} \mathbb{E}\Big(\psi(q_t,p_t) g_\gamma(q_0,p_0)\Big) dt$$

- We will see later how to compute approximations of such quantities!

Numerical results





Potential $V(x,y) = 2\cos(2x) + \cos(y)$, scheme $P_{\Delta t}^{\gamma C,B,A,B,\gamma C}$ with $\beta = \gamma = 1$.

Left: Error on the integrated velocity auto-correlation.
Right: Error on the average energy.

The overdamped limit (1)

- Limit $\gamma \to +\infty$ with $M = \mathrm{Id}$: solution $(q_{\gamma,\gamma s}, p_{\gamma,\gamma s})_{s\geqslant 0}$ pathwise converges (finite times) to solution of overdamped Langevin dynamics

$$dQ_t = -\nabla V(Q_t)\,dt + \sqrt{\frac{2}{\beta}}\,dW_t$$

with generator $\mathcal{L}_{\mathrm{ovd}} = -\nabla V(q)\cdot\nabla_q + \frac{1}{\beta}\Delta_q$

- Introduce $(\pi\varphi)(q) = (\beta/2\pi)^{dN/2}\sqrt{\det(M)}\int_{\mathbb{R}^{dN}} \varphi(q,p)\,\mathrm{e}^{-\beta p^T M^{-1}p/2}dp$

Uniform hypocoercivity estimates

There exists a constant $K > 0$ such that, for any $\gamma \geqslant 1$,

$$\left\|\mathcal{L}_\gamma^{-1} - \gamma\mathcal{L}_{\mathrm{ovd}}^{-1}\pi - p^T\nabla_q\mathcal{L}_{\mathrm{ovd}}^{-1}\pi + \mathcal{L}_{\mathrm{ovd}}^{-1}\pi(A+B)C^{-1}(\mathrm{Id}-\pi)\right\|_{\mathcal{B}(\mathcal{H}^1)} \leqslant \frac{K}{\gamma}$$

where $\mathcal{H}^1 = \left\{ f \in H^1(\mu) \,\middle|\, \int_{\mathcal{E}} f\,d\mu = 0 \right\}$.

The overdamped limit (2)

• Invariant measure $\overline{\mu}(dq) \propto \mathrm{e}^{-\beta V(q)}\, dq$ for the continuous dynamics

• Overdamped limit well defined only for certain second order splitting schemes (A and B not intertwinned with C)

Error estimates in the overdamped limit

$$\int_{\mathcal{M}} \psi(q)\, \overline{\mu}_{\gamma,\Delta t}(dq) = \int_{\mathcal{M}} \psi\, d\overline{\mu} + \Delta t^2 \int_{\mathcal{M}} \psi\, f_{2,\infty}\, d\overline{\mu} + r_{\psi,\gamma,\Delta t},$$

with remainder of order Δt^4 up to terms exponentially small in $\gamma\Delta t$:

$$|r_{\psi,\gamma,\Delta t}| \leqslant a\Delta t^4 + b\,\mathrm{e}^{-\kappa\gamma\Delta t}$$

• Consistency of the limit for the correction terms: $f_{2,\gamma} \xrightarrow[\gamma\to+\infty]{H^1(\mu)} f_{2,\infty}$

$$\lim_{\Delta t\to 0} \lim_{\gamma\to+\infty} \frac{1}{\Delta t^2}\left(\int_{\mathcal{M}} \psi\, d\overline{\mu}_{\gamma,\Delta t} - \int_{\mathcal{M}} \psi\, d\overline{\mu}\right) = \lim_{\gamma\to+\infty} \lim_{\Delta t\to 0} \dots$$

Sketch of proof for $P_{\Delta t}^{\gamma C,A,B,A\gamma C}$

- Reduction to a limiting operator up to exponentially small terms

$$\left\| \mathrm{e}^{\gamma t C} - \pi \right\|_{\mathcal{B}(L^\infty_W)} \leqslant K \mathrm{e}^{-\alpha \gamma t}, \qquad W(q,p) = 1 + |p|^2$$

- Error estimates for the limiting operator $P_{\infty,\Delta t} = \pi P_{\mathrm{ham},\Delta t} \pi$:

$$P_{\infty,\Delta t} = \pi + h \mathcal{L}_{\mathrm{ovd}} + \frac{h^2}{2} \left(\mathcal{L}_{\mathrm{ovd}}^2 + D \right) \pi + h^3 R_{\infty,\Delta t}, \qquad h = \frac{\Delta t^2}{2}$$

corresponding to the limiting numerical scheme

$$\begin{cases} q^{n+1/2} = q^n + \dfrac{\Delta t}{2} \sqrt{\dfrac{1}{\beta}} G^n \\ p^{n+1} = \sqrt{\dfrac{1}{\beta}} G^n - \Delta t \nabla V \left(q^{n+1/2} \right) \\ q^{n+1} = q^{n+1/2} + \dfrac{\Delta t}{2} p^{n+1} \end{cases}$$

Practical computation of transport properties

Definition of transport coefficients (1)

- Nonequilibrium dynamics: generator $\mathcal{L} + \eta\widetilde{\mathcal{L}}$, invariant measure $\rho_\eta \mu$

$$\left(\mathcal{L}^* + \eta\widetilde{\mathcal{L}}^*\right) f_\eta = 0$$

- Formally, $\rho_\eta = \left(\mathrm{Id} + \eta(\mathcal{L}^*)^{-1}\widetilde{\mathcal{L}}^*\right)^{-1}\mathbf{1} = \sum_{n=0}^{+\infty}(-\eta)^n \left[(\mathcal{L}^*)^{-1}\widetilde{\mathcal{L}}^*\right]^n \mathbf{1}$

- To make such computations rigorous (for η small): prove *e.g.* that
  - $\mathrm{Ker}(\mathcal{L}^*) = \mathbf{1}$ and $\mathcal{L}^*$ is invertible on $\mathcal{H} = L^2(\mu) \cap \mathbf{1}^\perp$
  - (weak perturbation) $\|\widetilde{\mathcal{L}}\varphi\| \leqslant a\|\mathcal{L}\varphi\| + b\|\varphi\|$

- Example: non-gradient force $F \in \mathbb{R}^{3N}$, invariant measure $\mu_{\gamma,\eta}(dq\,dp)$

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

Definition of transport coefficients (2)

- Response property $R \in \mathcal{H}$, conjugated response $S = \widetilde{\mathcal{L}}^* \mathbf{1}$:

$$\alpha = \lim_{\eta \to 0} \frac{\langle R \rangle_\eta}{\eta} = -\int_{\mathcal{E}} \left[\mathcal{L}^{-1} R\right] \left[\widetilde{\mathcal{L}}^* \mathbf{1}\right] \mu = \int_0^{+\infty} \mathbb{E}\Big(R(q_t, p_t) S(q_0, p_0)\Big) dt$$

- In practice:
  - Identify the response function
  - Construct a physically meaningful perturbation
  - Obtain the transport coefficient α (thermal cond., shear viscosity,...)
  - It is then possible to construct non physical perturbations allowing to compute the same transport coefficient ("Synthetic NEMD")

- For the previous example, definition of mobility with $R(q,p) = F^T M^{-1} p$

$$\lim_{\eta \to 0} \frac{\left\langle F^T M^{-1} p \right\rangle_\eta}{\eta} = \beta \, F^T D F$$

with effective diffusion $D = \displaystyle\int_0^{+\infty} \mathbb{E}\Big((M^{-1} p_t) \otimes (M^{-1} p_0)\Big) \, dt$

Error estimates on the Green-Kubo formula

Assume $\dfrac{P_{\Delta t} - \mathrm{Id}}{\Delta t} = \mathcal{L} + \Delta t S_1 + \cdots + \Delta t^{\alpha-1} S_{\alpha-1} + \Delta t^{\alpha} \widetilde{R}_{\alpha,\Delta t}$ and

$$\left\| \left(\frac{\mathrm{Id} - P_{\Delta t}}{\Delta t} \right)^{-1} \right\|_{\mathcal{B}(L^\infty_W)} \leqslant C, \qquad \int_{\mathcal{E}} \psi \, d\mu_{\Delta t} = \int_{\mathcal{E}} \psi \, d\mu + \Delta t^{\alpha} r_{\psi,\Delta t}$$

Error estimates on the Green-Kubo formula

For ψ, φ with average 0 w.r.t. μ,

$$\int_0^{+\infty} \mathbb{E}\Big(\psi(q_t,p_t)\varphi(q_0,p_0)\Big) dt = \Delta t \sum_{n=0}^{+\infty} \mathbb{E}_{\Delta t}\Big(\widetilde{\psi}_{\Delta t}\left(q^n,p^n\right)\varphi\left(q^0,p^0\right)\Big) + \mathrm{O}(\Delta t^{\alpha})$$

with $\widetilde{\psi}_{\Delta t} = \Big(\mathrm{Id} + \Delta t\, S_1 \mathcal{A}^{-1} + \cdots + \Delta t^{\alpha-1} S_{\alpha-1} \mathcal{A}^{-1}\Big)\psi - \mu_{\Delta t}(\dots)$

- Reduces to trapezoidal rule for second order schemes

Error estimates on linear response

- Splitting schemes obtained by replacing B with $B_\eta = B + \eta F \cdot \nabla_p$

$\rightarrow$ invariant measures $\mu_{\gamma,\eta,\Delta t}$

- For instance, $P_{\Delta t}^{A,B+\eta\widetilde{\mathcal{L}},\gamma C}$ for

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

- Discard schemes obtained by replacing C with $C + \eta\widetilde{\mathcal{L}}$ since they do not perform well in the overdamped limit

- Recall that the mobility is defined as

$$\nu_{F,\gamma} = \lim_{\eta\to 0} \frac{1}{\eta} \int_{\mathcal{E}} F^T M^{-1} p\, \mu_{\gamma,\eta}(dq\,dp) = \int_{\mathcal{E}} F^T M^{-1} p\, f_{0,1,\gamma}(q,p)\, \mu(dq\,dp)$$

where the correction function satisfies $\mathcal{L}^* f_{0,1,\gamma} = -\beta F^T M^{-1} p$

Error estimates on the mobility

Error estimates for nonequilibrium dynamics

There exists a function $f_{\alpha,1,\gamma} \in H^1(\mu)$ such that

$$\int_{\mathcal{E}} \psi \, d\mu_{\gamma,\eta,\Delta t} = \int_{\mathcal{E}} \psi \Big(1 + \eta f_{0,1,\gamma} + \Delta t^\alpha f_{\alpha,0,\gamma} + \eta \Delta t^\alpha f_{\alpha,1,\gamma} \Big) d\mu + r_{\psi,\gamma,\eta,\Delta t},$$

where the remainder is compatible with linear response

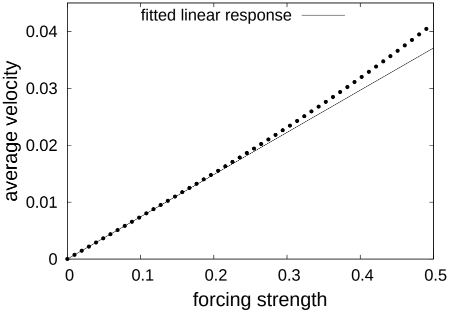
$$|r_{\psi,\gamma,\eta,\Delta t}| \leqslant K(\eta^2 + \Delta t^{\alpha+1}), \qquad |r_{\psi,\gamma,\eta,\Delta t} - r_{\psi,\gamma,0,\Delta t}| \leqslant K\eta(\eta + \Delta t^{\alpha+1})$$

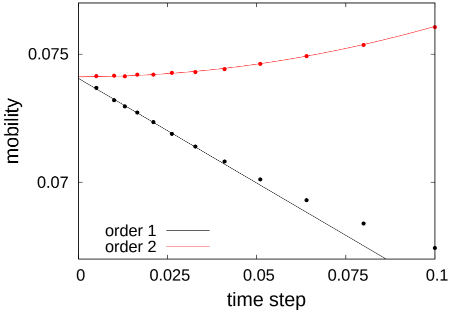
- Corollary: error estimates on the numerically computed mobility

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

- Results in the overdamped limit

Numerical results





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 $\nu_{F,\gamma,\Delta t}$ for the first order scheme $P_{\Delta t}^{A, B_\eta, \gamma C}$ and the second order scheme $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$.

In conclusion...

The full content of this work

• Standard but systematic error estimates à la Talay-Tubaro for splitting schemes of the equilibrium Langevin dynamics, spectral approach

• Alternative way to estimate the correction, on-the-fly, for a single simulation (using some integrated correlation)

• Overdamped limit fully treated (uniform hypocoercivity estimates), Hamiltonian limit only partially

• Error estimates on blue transport coefficients, computed either

- through a Green-Kubo formula (general)
- or with the linear response of an appropriate nonequilibrium dynamics (demonstrated on a specific case)

• Any result for splitting schemes on unbounded position spaces? Need for an appropriate Lyapunov function...

B. Leimkuhler, Ch. Matthews and G. Stoltz, The computation of averages from equilibrium and nonequilibrium Langevin molecular dynamics, *arXiv preprint* **1308.5814** (2013)