Error estimates in molecular dynamics

Gabriel STOLTZ

(CERMICS, Ecole des Ponts & MATHERIALS team, INRIA Paris)

Work also supported by ANR Funding ANR-14-CE23-0012 ("COSMOS")

Outline

Some elements of statistical physics

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

Practical computation of average properties

- Ergodic averages using Langevin dynamics
- Bias vs. variance

Timestep bias for the computation of average properties

- Discretization of Langevin dynamics
- A priori estimates on the invariant measure

Extensions[1]

- Error estimates on transport coefficients (nonequilibrium dynamics)
- Nonlinear dynamics (Feynman-Kac)

[1] Time permitting...

Some elements of statistical physics

General perspective (1)

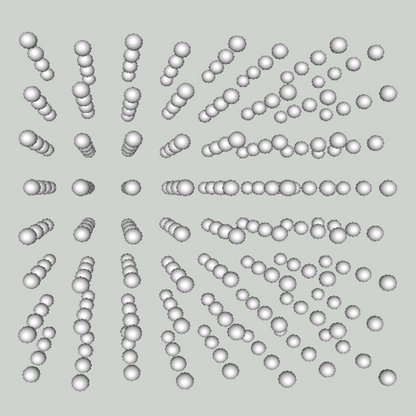
- Aims of computational statistical physics:
  - numerical microscope
  - computation of average properties, static or dynamic

- 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 $\sim \mathcal{N}_A = 6.02 \times 10^{23}$

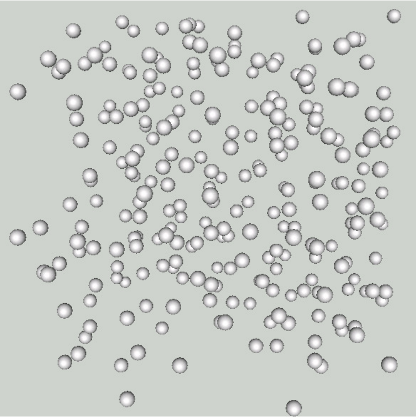
- "Standard" simulations
  - 10^6 particles ["world records": around 10^9 particles]
  - integration time: (fraction of) ns ["world records": (fraction of) μs]

General perspective (2)

What is the melting temperature of argon?



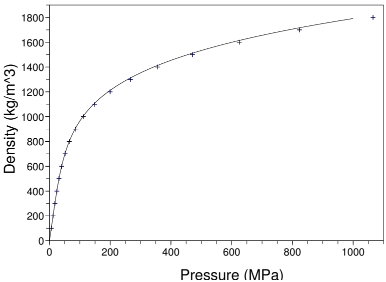
(a) Solid argon (low temperature)

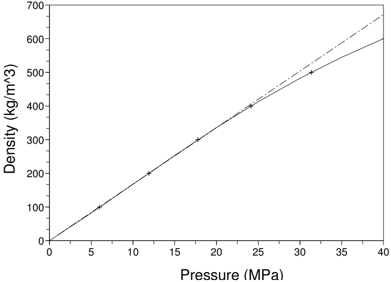


(b) Liquid argon (high temperature)

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?"

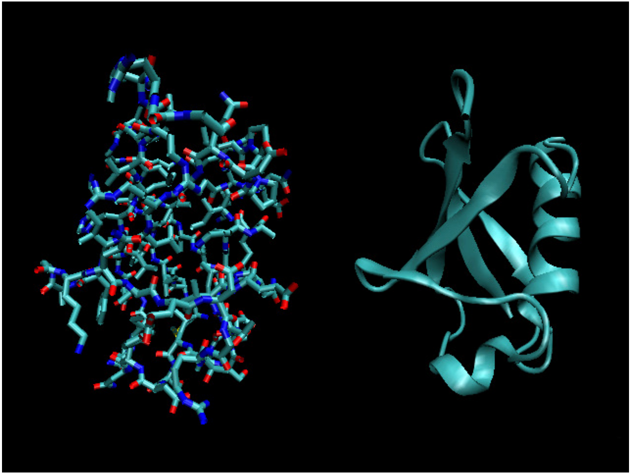




Equation of state (pressure/density diagram) for argon at $T = 300$ K

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

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

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

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

Microscopic description: interaction laws

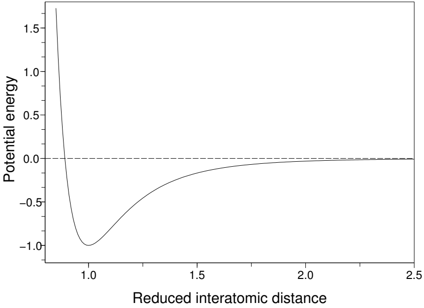
- All the physics is contained in V
  - ideally derived from quantum mechanical computations
  - in practice, empirical potentials for large scale calculations

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

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

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

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



Average properties

- Macrostate of the system described by a probability measure

Equilibrium thermodynamic properties (pressure,...)

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

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

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

Practical computation of average properties

Computing average properties

Main issue

Computation of high-dimensional integrals... Ergodic averages

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

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

$=$ Stochastic perturbation of the Hamiltonian dynamics

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

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

Convergence of the Langevin dynamics

- Irreducibility + smoothness of the transition probabilities (hypoellipticity)
- Invariance of the canonical measure
  - Generator of SDE $dx_t = b(x_t)\,dt + \sigma(x_t)\,dW_t$

$$\mathcal{L} = b \cdot \nabla + \frac{1}{2}\sigma\sigma^T : \nabla^2$$

  - Evolution of the law: $\dfrac{d}{dt}\mathbb{E}\Big(\varphi(q_t,p_t)\Big) = \mathbb{E}\Big(\mathcal{L}\varphi(q_t,p_t)\Big)$, *i.e.*

$$\int_{\mathcal{E}} \varphi \partial_t \psi = \int \mathcal{L}\varphi\,\psi \qquad \text{or} \qquad \partial_t \psi = \mathcal{L}^\dagger \psi$$

  - Here $\mathcal{L} = \mathcal{L}_{\rm ham} + \gamma \mathcal{L}_{\rm thm}$ with

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

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

Statistical error

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

$$\sigma_\varphi^2 = 2\int_0^{+\infty}\int_{\mathcal{E}} (\mathrm{e}^{t\mathcal{L}}\Pi\varphi)\Pi\varphi d\mu\, dt = 2\int_{\mathcal{E}} (-\mathcal{L}^{-1}\Pi\varphi)\Pi\varphi\, d\mu$$

- Well-defined provided $-\mathcal{L}\Phi = \Pi\varphi$ has a solution in $L_0^2(\mu) = \Pi L^2(\mu)$
- Sufficient condition: integrability of the semigroup, *e.g.*

$$\|\mathrm{e}^{t\mathcal{L}}\|_{\mathcal{B}(L_0^2(\mu))} \leqslant C\mathrm{e}^{-\lambda t}$$

Provided here by hypocoercivity results[2]

- A Central Limit Theorem holds in this case[3]: $\widehat{\varphi}_t - \mathbb{E}_\mu(\varphi) \simeq \frac{\sigma_\varphi}{\sqrt{t}}\mathcal{G}$

[2]Villani, Dolbeaut/Mouhot/Schmeiser, Hairer/Pavliotis, Hérau/Nier,...

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

Practical computation of average properties

- Numerical scheme = Markov chain characterized by evolution operator

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

- Discretization of the Langevin dynamics: 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: $P_{\Delta t}^{ZYX} = \mathrm{e}^{\Delta t Z}\mathrm{e}^{\Delta t Y}\mathrm{e}^{\Delta t X} \simeq \mathrm{e}^{\Delta t \mathcal{L}}$
- Example: $P_{\Delta t}^{B,A,\gamma C}$ corresponds to (with $\alpha_{\Delta t} = \exp(-\gamma M^{-1}\Delta t)$)

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

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

Practical computation of average properties (2)

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

- Example: $P_{\Delta t}^{\gamma C,B,A,B,\gamma C}$ (Verlet in the middle)

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

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

Error estimates on the computation of average properties

Error estimates on the computation of average properties

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

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

- Statistical errors *vs.* systematic errors (bias)

Systematic error estimates: α order of the splitting scheme

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

- Correction function $f_{\alpha,\gamma}$ solution of an appropriate Poisson equation

$$\mathcal{L}^* f_{\alpha,\gamma} = g_\gamma$$

where g_γ depends on the numerical scheme (adjoints taken on $L^2(\mu)$)

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

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

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

- 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

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

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

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

This requirement can be rewritten as

$$0 = \int_{\mathcal{E}} \left(\frac{1}{2} S_1 \phi + (\mathcal{L}\phi) f_{1,\gamma} \right) d\mu = \int_{\mathcal{E}} \varphi \left[\frac{1}{2} S_1^* \mathbf{1} + \mathcal{L}^* f_{1,\gamma} \right] d\mu,$$

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

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

- Rely on the "nice" properties of the continuous dynamics, *i.e.* functional estimates[4] on $\mathcal{L}^{-1}$ to use pseudo-inverses

$$Q_{1,\Delta t} = -\mathcal{L}^{-1} + \frac{\Delta t}{2} (\mathrm{Id} + \mathcal{L}^{-1} S_1 \mathcal{L}^{-1})$$

[4] D. Talay, Stoch. Proc. Appl. (2002); M. Kopec (2015)

Practical computation of transport properties

Definition of transport coefficients (1)

- Example: $\mathcal{D} = (L\mathbb{T})^d$, non-gradient force $F \in \mathbb{R}^{3N}$

Nonequilibrium dynamics

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

- Existence and uniqueness of invariant measure (Lyapunov techniques)

- Generator $\mathcal{L} + \eta \widetilde{\mathcal{L}}$, invariant measure $f_\eta \mu$

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

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

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

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

Error estimates on the Green-Kubo formula

For ϕ, φ with average 0 w.r.t. μ,

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

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

- 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

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

where the remainder is compatible with linear response

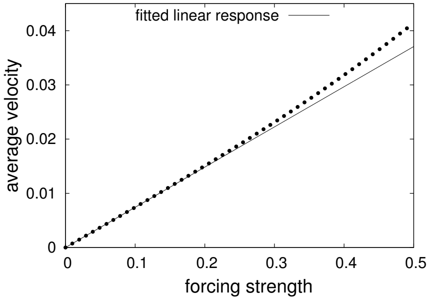
$$|r_{\varphi,\gamma,\eta,\Delta t}| \leqslant K(\eta^2 + \Delta t^{\alpha+1}), \qquad |r_{\varphi,\gamma,\eta,\Delta t} - r_{\varphi,\gamma,0,\Delta t}| \leqslant K\eta(\eta + \Delta t^{\alpha+1})$$

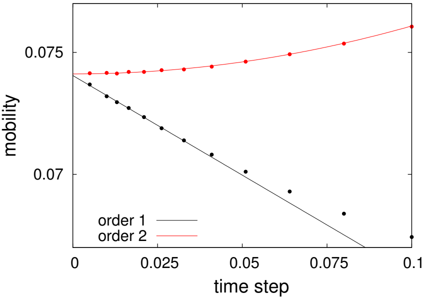
- Corollary: error estimates on the numerically computed mobility

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

- 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 $P_{\Delta t}^{\gamma C, B_\eta, A, B_\eta, \gamma C}$.

Discretization of Feynman-Kac semigroups

Discretization of Feynman-Kac semigroups

- Dynamics $dq_t = b(q_t)\,dt + \sigma\,dW_t$, weighted nonlinear average

$$\Phi_t^g(\mu)(\varphi) = \frac{\mathbb{E}_\mu\left[\varphi(q_t)\,\mathrm{e}^{\int_0^t g(q_s)\,ds}\right]}{\mathbb{E}_\mu\left[\mathrm{e}^{\int_0^t g(q_s)\,ds}\right]} \xrightarrow[t\to\infty]{} \int_{\mathcal{D}} \varphi\,d\nu_g$$

- Discretization of the SDE and of the time integral in the weight

$$\Phi_{\Delta t,n}^g(\mu)(\varphi) = \frac{\mathbb{E}_\mu\left[\varphi(q^n)\,\mathrm{e}^{\Delta t\sum_{i=0}^{n-1} g(q^i)}\right]}{\mathbb{E}_\mu\left[\mathrm{e}^{\Delta t\sum_{i=0}^{n-1} g(q^i)}\right]} \xrightarrow[n\to+\infty]{} \int_{\mathcal{D}} \varphi\,d\nu_{g,\Delta t}$$

- Error estimates $\displaystyle\int_{\mathcal{D}} \varphi\,d\nu_{g,\Delta t} = \int_{\mathcal{D}} \varphi\,d\nu_g + \Delta t^\alpha \int_{\mathcal{D}} \varphi f\,d\nu_g + \mathrm{O}(\Delta t^{\alpha+1})$

- Based on an approximation result for the first eigenvalue/eigenfunction of the non-selfadjoint operator $\mathcal{L} + g$

References

Some references

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