Convergence and approximation of Langevin-like dynamics

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Outline

- **Some elements of statistical physics**

- **Equilibrium Langevin dynamics**
  - Convergence results: a review
  - A focus on the approach by Dolbeault, Mouhot and Schmeiser
  - Various extensions/modifications

- **Numerical approximation of Langevin dynamics**
  - Splitting schemes
  - Numerical analysis: error estimates on invariant measures

Some elements of statistical physics

General perspective (1)

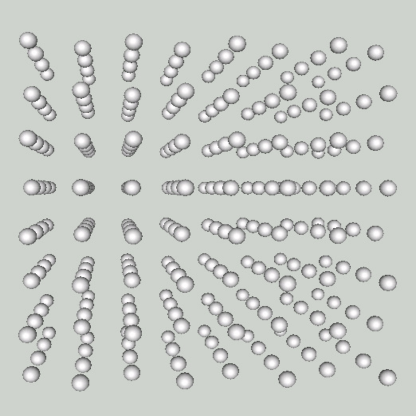
- Aims of computational statistical physics:
  - numerical microscope
  - computation of average properties, static or dynamic

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

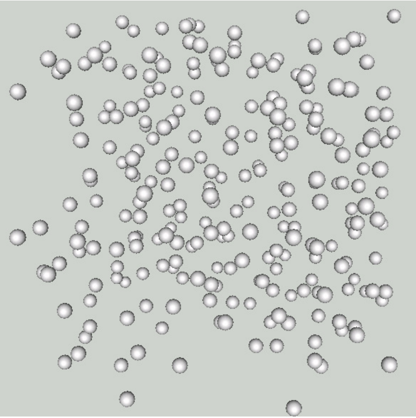
- "Standard" simulations
  - 10^6 particles ["world records": around 10^9 particles]
  - integration time: (fraction of) ns ["world records": (fraction of) μs]

General perspective (2)

What is the melting temperature of argon?



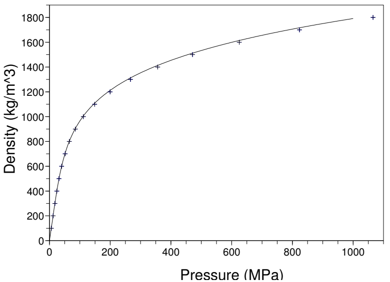
(a) Solid argon (low temperature)

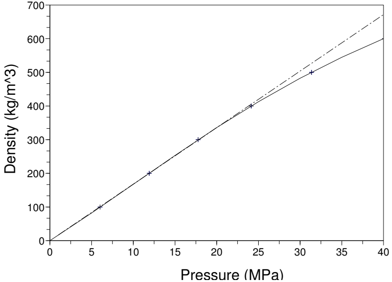


(b) Liquid argon (high temperature)

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?"

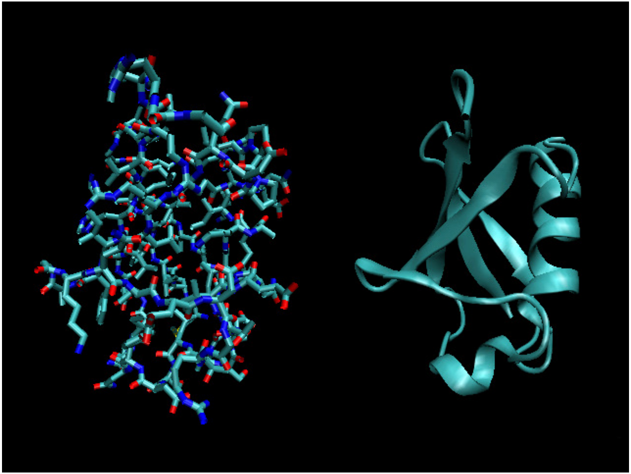




Equation of state (pressure/density diagram) for Argon at $T = 300$ K

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:

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

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 $H(q,p) = E_{\mathrm{kin}}(p) + V(q)$, 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

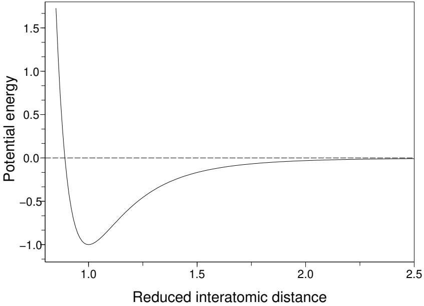
- All the physics is contained in V
  - ideally derived from quantum mechanical computations
  - in practice, empirical potentials for large scale calculations

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

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

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

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



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 $\varphi(q,p) = \dfrac{1}{3Nk_{\rm B}} \sum_{i=1}^{N} \dfrac{p_i^2}{m_i}$
- Canonical ensemble = measure on (q,p) (average energy fixed)

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

Aims of computational statistical physics

- **"Numerical microscope"**
  - gaining some insight into physical mechanisms at the atomic scale
  - From the press release for the Nobel prize in Chemistry 2013 (Karplus/Levitt/Warshel)

    Today the computer is just as important a tool for chemists as the test tube. Simulations are so realistic that they predict the outcome of traditional experiments.

- **Computation of average properties**: high dimensional integrals

$\rightarrow$ ergodic averages

- **Computation of dynamical quantities**
  - reactive paths, transition kinetics
  - transport coefficients (nonequilibrium steady state simulations)

Standard Langevin dynamics

Langevin dynamics (1)

- Positions $q \in \mathcal{D} = (L\mathbb{T})^d$ or $\mathbb{R}^d$ and momenta $p \in \mathbb{R}^d$

$\rightarrow$ phase-space $\mathcal{E} = \mathcal{D} \times \mathbb{R}^d$

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

Stochastic perturbation of the Hamiltonian dynamics friction $\gamma > 0$

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

- Almost-sure convergence[1] of ergodic averages $\widehat{\varphi}_t = \frac{1}{t} \int_0^t \varphi(q_s, p_s) \, ds$

[1] Kliemann, *Ann. Probab.* **15**(2), 690-707 (1987)

Langevin dynamics (2)

- Evolution semigroup $\left(\mathrm{e}^{t\mathcal{L}}\varphi\right)(q,p) = \mathbb{E}\left[\varphi(q_t,p_t)\,\middle|\,(q_0,p_0)=(q,p)\right]$

- Generator of the dynamics $\mathcal{L}$

$$\frac{d}{dt}\left(\mathbb{E}\left[\varphi(q_t,p_t)\,\middle|\,(q_0,p_0)=(q,p)\right]\right) = \mathbb{E}\left[(\mathcal{L}\varphi)(q_t,p_t)\,\middle|\,(q_0,p_0)=(q,p)\right]$$

Generator of the Langevin dynamics $\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \gamma\mathcal{L}_{\mathrm{FD}}$

$$\mathcal{L}_{\mathrm{ham}} = p^T M^{-1}\nabla_q - \nabla V^T \nabla_p, \qquad \mathcal{L}_{\mathrm{FD}} = -p^T M^{-1}\nabla_p + \frac{1}{\beta}\Delta_p$$

- Existence and uniqueness of the invariant measure characterized by

$$\forall \varphi \in C_0^\infty(\mathcal{E}), \qquad \int_{\mathcal{E}} \mathcal{L}\varphi \, d\mu = 0$$

- Here, canonical measure

$$\mu(dq\,dp) = Z^{-1}\mathrm{e}^{-\beta H(q,p)}\,dq\,dp = \nu(dq)\,\kappa(dp)$$

Fokker–Planck equations

- Evolution of the law $\psi(t,q,p)$ of the process at time $t \geqslant 0$

$$\frac{d}{dt}\left(\int_{\mathcal{E}} \varphi\, \psi(t)\right) = \int_{\mathcal{E}} (\mathcal{L}\varphi)\, \psi(t)$$

- Fokker–Planck equation (with $\mathcal{L}^\dagger$ adjoint of $\mathcal{L}$ on $L^2(\mathcal{E})$)

$$\partial_t \psi = \mathcal{L}^\dagger \psi$$

- It is convenient to work in $L^2(\mu)$ with $f(t) = \psi(t)/\mu$
  - denote the adjoint of $\mathcal{L}$ on $L^2(\mu)$ by $\mathcal{L}^*$

$$\mathcal{L}^* = -\mathcal{L}_{\mathrm{ham}} + \gamma \mathcal{L}_{\mathrm{FD}}$$

  - Fokker–Planck equation $\partial_t f = \mathcal{L}^* f$

- Convergence results for $\mathrm{e}^{t\mathcal{L}}$ on $L^2(\mu)$ are very similar to the ones for $\mathrm{e}^{t\mathcal{L}^*}$

Hamiltonian and overdamped limits

- As $\gamma \to 0$, the Hamiltonian dynamics is recovered
- Overdamped limit $\gamma \to +\infty$ (or masses going to 0)

$$
\begin{aligned}
q_{\gamma t} - q_0 &= -\frac{1}{\gamma}\int_0^{\gamma t} \nabla V(q_s)\,ds + \sqrt{\frac{2}{\gamma\beta}} W_{\gamma t} - \frac{1}{\gamma}(p_{\gamma t} - p_0) \\
&= -\int_0^{t} \nabla V(q_{\gamma s})\,ds + \sqrt{2\beta^{-1}} B_t - \frac{1}{\gamma}(p_{\gamma t} - p_0)
\end{aligned}
$$

which converges to the solution of $dQ_t = -\nabla V(Q_t)\,dt + \sqrt{2\beta^{-1}}\,dB_t$

- In both cases, slow convergence to equilibrium
  - it takes time to change energy levels in the Hamiltonian limit[2]
  - for fixed masses, time has to be rescaled by a factor γ

[2] Hairer and Pavliotis, *J. Stat. Phys.*, **131**(1), 175-202 (2008)

Ergodicity results (1)

- Almost-sure convergence[3] of ergodic averages $\widehat{\varphi}_t = \frac{1}{t}\int_0^t \varphi(q_s, p_s)\, ds$

- Asymptotic variance of ergodic averages

$$\sigma_\varphi^2 = \lim_{t\to+\infty} t\mathbb{E}\left[\widehat{\varphi}_t^2\right] = 2\int_{\mathcal{E}} \left(-\mathcal{L}^{-1}\Pi_0\varphi\right)\Pi_0\varphi\, d\mu$$

where $\Pi_0\varphi = \varphi - \mathbb{E}_\mu(\varphi)$

- A central limit theorem holds[4] when the equation has a solution in $L^2(\mu)$

Poisson equation in $L^2(\mu)$

$$-\mathcal{L}\Phi = \Pi_0\varphi$$

- Well-posedness of such equations?

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[3] Kliemann, *Ann. Probab.* **15**(2), 690-707 (1987)

[4] Bhattacharya, *Z. Wahrsch. Verw. Gebiete* **60**, 185–201 (1982)

Ergodicity results (2)

- Invertibility of $\mathcal{L}$ on subsets of $L^2_0(\mu) = \left\{ \varphi \in L^2(\mu) \,\middle|\, \int_{\mathcal{E}} \varphi \, d\mu = 0 \right\}$?

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

- Prove exponential convergence of the semigroup $\mathrm{e}^{t\mathcal{L}}$
  - various Banach spaces $E \cap L^2_0(\mu)$
  - Lyapunov techniques[5] $L^\infty_W(\mathcal{E}) = \left\{ \varphi \,\mathrm{measurable}, \left\| \frac{\varphi}{W} \right\|_{L^\infty} < +\infty \right\}$
  - standard hypocoercive[6] setup $H^1(\mu)$
  - $E = L^2(\mu)$ after hypoelliptic regularization[7] from $H^1(\mu)$
  - coupling arguments[8]

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[5] L. Wu, *Stoch. Proc. Appl.* (2001); Mattingly, Stuart and Higham, *Stoch. Proc. Appl.* (2002); L. Rey-Bellet, *Lect. Notes Math.* (2006); Hairer and Mattingly, *Progr. Probab.* (2011)

[6] Villani (2009) and before Talay (2002), Eckmann/Hairer (2003), Hérau/Nier (2004)

[7] F. Hérau, *J. Funct. Anal.* **244**(1), 95-118 (2007)

[8] A. Eberle, A. Guillin and R. Zimmer, *arXiv preprint* **1703.01617** (2017)

Direct $L^2(\mu)$ approach: lack of coercivity

- The generator, considered on $L^2(\mu)$, is the sum of...
  - a degenerate symmetric part $\mathcal{L}_{\mathrm{FD}} = -p^T M^{-1}\nabla_p + \frac{1}{\beta}\Delta_p$
  - an antisymmetric part $\mathcal{L}_{\mathrm{ham}} = p^T M^{-1}\nabla_q - \nabla V^T \nabla_p$

- Standard strategy for coercive generators: consider φ with average 0 with respect to μ and compute

$$\frac{d}{dt}\left(\left\|\mathrm{e}^{t\mathcal{L}}\varphi\right\|^2_{L^2(\mu)}\right) = \left\langle \mathrm{e}^{t\mathcal{L}}\varphi, \mathcal{L}\mathrm{e}^{t\mathcal{L}}\right\rangle_{L^2(\mu)} = \left\langle \mathrm{e}^{t\mathcal{L}}\varphi, \mathcal{L}_{\mathrm{FD}}\mathrm{e}^{t\mathcal{L}}\right\rangle_{L^2(\mu)}$$
$$= -\frac{1}{\beta}\left\|\nabla_p \mathrm{e}^{t\mathcal{L}}\varphi\right\|^2_{L^2(\mu)} \leqslant 0,$$

but no control of $\|\phi\|_{L^2(\mu)}$ by $\|\nabla_p\phi\|_{L^2(\mu)}$ for a Gronwall estimate...

- Change of scalar product in order to use the antisymmetric part

Almost direct $L^2(\mu)$ approach: convergence result

- Assume that the potential V is smooth and[9,10]
  - the marginal measure ν satisfies a Poincaré inequality

$$\|\Pi_0\varphi\|_{L^2(\nu)}^2 \leqslant \frac{1}{C_\nu}\|\nabla_q\varphi\|_{L^2(\nu)}^2$$

  - there exist $c_1 > 0$, $c_2 \in [0,1)$ and $c_3 > 0$ such that V satisfies

$$\Delta V \leqslant c_1 + \frac{c_2}{2}|\nabla V|^2, \quad |\nabla^2 V| \leqslant c_3\,(1+|\nabla V|)$$

There exist $C > 0$ and $\lambda_\gamma > 0$ such that, for any $\varphi \in L_0^2(\mu)$,

$$\forall t \geqslant 0, \qquad \left\|\mathrm{e}^{t\mathcal{L}}\varphi\right\|_{L^2(\mu)} \leqslant C\mathrm{e}^{-\lambda_\gamma t}\|\varphi\|_{L^2(\mu)}.$$

with convergence rate of order $\min(\gamma,\gamma^{-1})$: there exists $\overline{\lambda} > 0$ such that

$$\lambda_\gamma \geqslant \overline{\lambda}\min(\gamma,\gamma^{-1}).$$

[9] Dolbeault, Mouhot and Schmeiser, *C. R. Math. Acad. Sci. Paris* (2009)

[10] Dolbeault, Mouhot and Schmeiser, *Trans. AMS*, **367**, 3807–3828 (2015)

Sketch of proof

- Modified square norm $\mathcal{H}[\varphi] = \frac{1}{2}\|\varphi\|^2 - \varepsilon \langle A\varphi, \varphi \rangle$ for $\varepsilon \in (-1,1)$ and

$$A = \Big(1 + (\mathcal{L}_{\rm ham}\Pi_p)^*(\mathcal{L}_{\rm ham}\Pi_p)\Big)^{-1}(\mathcal{L}_{\rm ham}\Pi_p)^*, \qquad \Pi_p\varphi = \int_{\mathbb{R}^D} \varphi \, d\kappa$$

- $A = \Pi_p A(1-\Pi_p)$ and $\mathcal{L}_{\rm ham}A$ are bounded so that $\mathcal{H} \sim \|\cdot\|^2_{L^2(\mu)}$

Coercivity in the scalar product $\langle\langle \cdot, \cdot \rangle\rangle$ induced by $\mathcal{H}$

$$\mathscr{D}[\varphi] := \langle\langle -\mathcal{L}\varphi, \varphi \rangle\rangle \geqslant \widetilde{\lambda}_\gamma \|\varphi\|^2$$

- Idea: control of $\|(1-\Pi_p)\varphi\|^2$ by $\langle -\mathcal{L}_{\rm FD}\varphi, \varphi\rangle$ (Poincaré); for $\|\Pi_p\varphi\|^2$,

$$\|\mathcal{L}_{\rm ham}\Pi_p\varphi\|^2 \geqslant \frac{DC_\nu}{\beta m}\|\Pi_p\varphi\|^2, \qquad \text{hence } A\mathcal{L}_{\rm ham}\Pi_p \geqslant \lambda_{\rm ham}\Pi_p$$

- Gronwall inequality $\dfrac{d}{dt}\left(\mathcal{H}\left[\mathrm{e}^{t\mathcal{L}}\varphi\right]\right) = -\mathscr{D}\left[\mathrm{e}^{t\mathcal{L}}\varphi\right] \leqslant -\dfrac{2\widetilde{\lambda}_\gamma}{1+\varepsilon}\mathcal{H}\left[\mathrm{e}^{t\mathcal{L}}\varphi\right]$

Extensions and modifications

- General kinetic energy function $U(p)$ in the Langevin dynamics
  - The generator $\mathcal{L}$ may not be hypoelliptic... (even jump processes)
  - Convergence using Lyapunov[11] or hypocoercive[12] techniques

- Nonequilibrium Langevin dynamics
  - Invariant measure not known...
  - Perturbative results,[13] with some uniformity on the range of perturbations[14]
  - Temperature accelerated molecular dynamics[15]

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[11] S. Redon, G. Stoltz and Z. Trstanova, *J. Stat. Phys.* (2016)
[12] G. Stoltz and Z. Trstanova, *SIAM MMS* (2018)
[13] E. Bouin, F. Hoffmann, and C. Mouhot, *SIAM J. Math. Anal.* (2017)
[14] A. Iacobucci, S. Olla and G. Stoltz, *Ann. Math. Quebec* (2019)
[15] G. Stoltz and E. Vanden-Eijnden, *Nonlinearity* (2018)

Direct L^2 hypocoercivity for modified Langevin (2)

- Spectral discretization of generator of Langevin dynamics
  - Approximate solutions of Poisson equation for control variates[16]
  - Bounds on convergence rates as a function of the basis size[17]

- Adaptive Langevin dynamics[18] for mini-batching in large scale Bayesian inference

- **Current lines of work:**
  - An even more direct approach avoiding the change of scalar product? (with Antoine Levitt, Inria/CERMICS)
  - Quantitative bounds for atom chains (Very long term goal...)
  - Non-perturbative approach for nonequilibrium dynamics

[16] J. Roussel and G. Stoltz, *SIAM MMS* (2019)

[17] J. Roussel and G. Stoltz, *M2AN* (2018)

[18] Upcoming work with B. Leimkuhler and M. Sachs; currently I. Sekkat

Numerical approximation of Langevin dynamics

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)

$$\left\{\begin{aligned} \widetilde{p}^{n+1/2} &= \alpha_{\Delta t/2} p^n + \sqrt{\frac{1-\alpha_{\Delta t}}{\beta} M}\, G^n, \\ p^{n+1/2} &= \widetilde{p}^{n+1/2} - \frac{\Delta t}{2} \nabla V(q^n), \\ q^{n+1} &= q^n + \Delta t\, M^{-1} p^{n+1/2}, \\ \widetilde{p}^{n+1} &= p^{n+1/2} - \frac{\Delta t}{2} \nabla V(q^{n+1}), \\ p^{n+1} &= \alpha_{\Delta t/2} \widetilde{p}^{n+1} + \sqrt{\frac{1-\alpha_{\Delta t}}{\beta} M}\, G^{n+1/2}, \end{aligned}\right.$$

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

Error estimates on the computation of average properties

- The ergodicity of numerical schemes can be proved (bounded position domain):

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

- Statistical errors *vs.* systematic errors (bias)[19]

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 $L^2(\mu)$)

[19] B. Leimkuhler, Ch. Matthews and G. Stoltz, *IMA J. Numer. Anal.* (2016)

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

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

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

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

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

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

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

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

- Rely on the "nice" properties of the continuous dynamics, *i.e.* functional estimates[20] on $\mathcal{L}^{-1}$ to use pseudo-inverses

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

[20] D. Talay, Stoch. Proc. Appl. (2002); M. Kopec, arxiv 1310.2599 (2013)

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  - D. Frenkel and B. Smit, *Understanding Molecular Simulation, From Algorithms to Applications* (Academic Press, 2002)
  - M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford, 2010)
  - M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, 1987)
  - D. C. Rapaport, *The Art of Molecular Dynamics Simulations* (Cambridge University Press, 1995)

- Sampling the canonical measure
  - L. Rey-Bellet, Ergodic properties of Markov processes, *Lecture Notes in Mathematics*, **1881** 1–39 (2006)
  - T. Lelièvre, M. Rousset and G. Stoltz, *Free Energy Computations: A Mathematical Perspective* (Imperial College Press, 2010)
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  - T. Lelièvre and G. Stoltz, Partial differential equations and stochastic methods in molecular dynamics, *Acta Numerica* **25**, 681-880 (2016)