Langevin Methods

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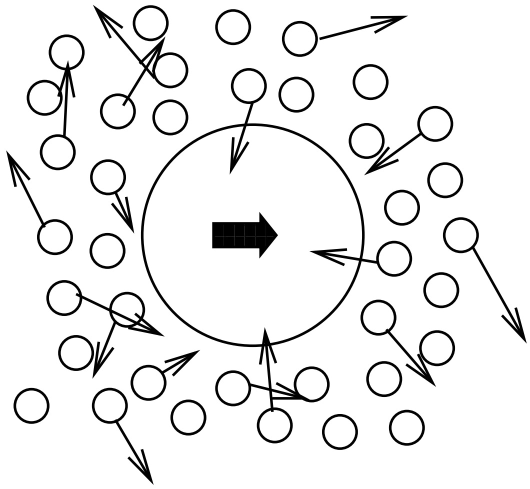
Motivation

Original idea:

- **Fast** and **slow** degrees of freedom
- Example: Brownian motion
- Replace fast degrees by **friction** and **random noise**
- Conceptually and technically simpler



Learn the mathematics of random noise!

Technical interest:

- Original system: Deterministic, **no** additional degrees of freedom
- Add friction and noise to **stabilize** equations of motion
- Permitted if
  - noise does not alter the (relevant) dynamics, or
  - only *static* properties are sought

Markov Processes

- *Continuous* (state) space (x, usually multi–dimensional)
- *Continuous* time (t)

Conditional probability for $x_0(t_0) \rightarrow x(t)$:

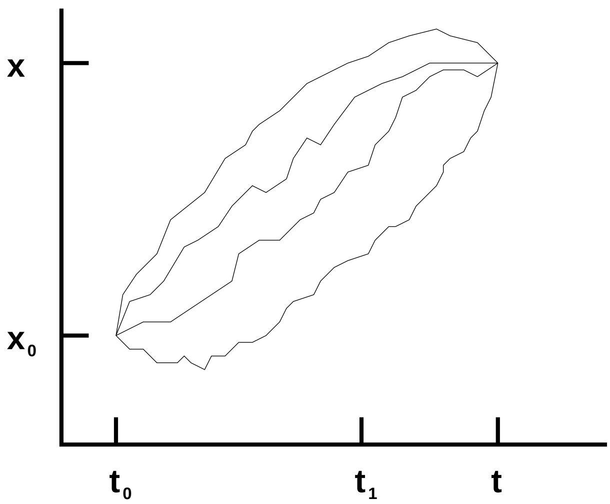
$$P(x, t|x_0, t_0)$$

does not depend on previous history ($t < t_0$)

$$\int dx P(x, t|x_0, t_0) = 1$$

$$P(x, t_0|x_0, t_0) = \delta(x - x_0)$$

Chapman–Kolmogorov:



$$P(x, t|x_0, t_0) = \int dx_1 P(x, t|x_1, t_1) P(x_1, t_1|x_0, t_0)$$

Formal Moment Expansion

Consider:

- $p(x) > 0$
- $\int dx\, p(x) = 1$
- $\mu_n = \int dx\, x^n p(x)$ exists for all x

Then

$$\begin{aligned} \tilde{p}(k) &= \int dx\ \exp(ikx)p(x) \\ &= \sum_{n=0}^{\infty} \frac{(ik)^n}{n!}\mu_n \end{aligned}$$

I. e.

$$p(x) \longleftrightarrow \{\mu_n\}$$

unique

$$p(x) = \sum_{n=0}^{\infty} \left(-\frac{\partial}{\partial x}\right)^n \frac{\mu_n}{n!}\ \delta(x)$$

Proof: Both sides produce the same moments!

Kramers–Moyal Expansion

Define

$$\begin{aligned} \mu_n(t; x_0, t_0) &= \langle (x - x_0)^n \rangle (t, t_0) \\ &= \int dx\ (x - x_0)^n P(x, t|x_0, t_0) \end{aligned}$$

(mean displacement, mean square displacement etc.) $\Rightarrow$

$$\begin{aligned} & P(x, t|x_0, t_0) \\ = & \sum_{n=0}^{\infty} \left(-\frac{\partial}{\partial x} \right)^n \delta(x - x_0) \frac{1}{n!} \mu_n(t; x_0, t_0) \end{aligned}$$

particularly good for short times.

Chapman–Kolmogorov (small τ):

$$\begin{aligned} & P(x, t|x_0, t_0) \\ = & \int dx_1 \sum_{n=0}^{\infty} \left(-\frac{\partial}{\partial x} \right)^n \delta(x - x_1) \frac{1}{n!} \mu_n(t; x_1, t - \tau) \\ & P(x_1, t - \tau|x_0, t_0) \\ = & \sum_{n=0}^{\infty} \left(-\frac{\partial}{\partial x} \right)^n \frac{1}{n!} \mu_n(t; x, t - \tau) \\ & P(x, t - \tau|x_0, t_0) \end{aligned}$$

Subtract $n = 0$ term:

$$\begin{aligned} & \frac{1}{\tau}\left[P(x,t|x_0,t_0) - P(x,t-\tau|x_0,t_0)\right] \\ = \quad & \frac{1}{\tau}\sum_{n=1}^{\infty}\left(-\frac{\partial}{\partial x}\right)^n \frac{1}{n!}\mu_n(t;x,t-\tau)P(x,t-\tau|x_0,t_0) \end{aligned}$$

Short–time behavior of the moments defines the *Kramers–Moyal coefficients* $D^{(n)}$ ($o(\tau)$: Terms of order *higher* than linear!):

$$\left\langle (x-x_0)^n \right\rangle (t_0+\tau, t_0) = n! D^{(n)}(x_0,t_0)\tau + o(\tau)$$

$$\begin{aligned} \mu_n(t;x,t-\tau) &= n! D^{(n)}(x,t-\tau)\tau + o(\tau) \\ &= n! D^{(n)}(x,t)\tau + o(\tau) \end{aligned}$$

Similarly

$$P(x,t-\tau|x_0,t_0) \approx P(x,t|x_0,t_0)$$

Hence

$$\frac{\partial}{\partial t}P(x,t|x_0,t_0) = \sum_{n=1}^{\infty}\left(-\frac{\partial}{\partial x}\right)^n D^{(n)}(x,t)P(x,t|x_0,t_0)$$

generalized Fokker–Planck equation

Shorthand:

$$\frac{\partial}{\partial t}P(x,t|x_0,t_0) = \mathcal{L}P(x,t|x_0,t_0)$$

Pawula Theorem

Only four types of processes:

1. Expansion stops at $n = 0$: No dynamics
2. Expansion stops at $n = 1$: *Deterministic* processes ($\rightarrow$ Liouville equation)
3. Expansion stops at $n = 2$: *Fokker–Planck / diffusion* processes
4. Expansion stops at $n = \infty$

Proof: See Risken, *The Fokker–Planck Equation*.

Truncation at finite order $n > 2$ would produce

$$P < 0!!$$

Proof of Pawula Theorem

Define *scalar product*

$$\langle f|g\rangle = \int dx\, P(x,t|x_0,t_0) f^\star(x) g(x)$$

Moments:

$$\mu_n = \int dx\, P(x,t|x_0,t_0)\,(x-x_0)^n$$

I. e.

$$\mu_{m+n} = \langle (x-x_0)^m | (x-x_0)^n \rangle$$

Schwarz inequality:

$$\mu_{m+n}^2 \le \mu_{2m}\mu_{2n}$$

$\Rightarrow$

$$D^{(m+n)2} \le \frac{(2m)!(2n)!}{[(m+n)!]^2} D^{(2m)} D^{(2n)}$$

for $m \ge 1$, $n \ge 1$

Suppose

$$D^{(2N)} = D^{(2N+1)} = \ldots = 0$$

Set $m = 1$, $n = N, N+1, \ldots$:

$$D^{(N+1)} = D^{(N+2)} = \ldots = 0$$

"Zeroing" always works except for very small N where no new information is obtained.

- $N = 1$:

$$D^{(2)} = \ldots = 0 \qquad \Rightarrow \qquad D^{(2)} = \ldots = 0$$

- $N = 2$:

$$D^{(4)} = \ldots = 0 \qquad \Rightarrow \qquad D^{(3)} = \ldots = 0$$

- $N = 3$:

$$D^{(6)} = \ldots = 0 \qquad \Rightarrow \qquad D^{(4)} = \ldots = 0$$

- $N = 4$:

$$D^{(8)} = \ldots = 0 \qquad \Rightarrow \qquad D^{(5)} = \ldots = 0$$

- etc.

Thus: Truncation at any finite order implies $D^{(3)} = D^{(4)} = \ldots = 0$.

Goal

Langevin simulation $\equiv$

- **Generation of stochastic trajectories**
- **for a process of type 3**
- **with a discretization time step** τ

Physical input:

- Drift coefficient $D^{(1)}$ ($\longrightarrow$ deterministic part)
- Diffusion coefficient $D^{(2)}$ ($\longrightarrow$ stochastic part)

Euler Algorithm

We know for the displacements:

$$\begin{aligned} \langle \Delta x_i \rangle &= D_i^{(1)}(x,t)\tau + o(\tau) \\ \langle \Delta x_i \Delta x_j \rangle &= 2D_{ij}^{(2)}(x,t)\tau + o(\tau) \\ \langle (\Delta x)^n \rangle &= o(\tau) \quad n \geq 3 \end{aligned}$$

Satisfied by

$$x_i(t+\tau) = x_i(t) + D_i^{(1)}\,\tau + \sqrt{2\tau}\, r_i$$

r_i random variables with:

- $\langle r_i \rangle = 0$
- $\langle r_i r_j \rangle = D_{ij}$
- All higher moments exist
- *Some* distribution, e. g. Gaussian or uniform (B. D. & W. Paul, Int. J. Mod. Phys. C 2, 817 (1991))
- Stochastic term dominates for $\tau \rightarrow 0$
- Large number of independent kicks
- Central Limit Theorem $\Rightarrow$ *Gaussian* behavior
- "Gaussian white noise"

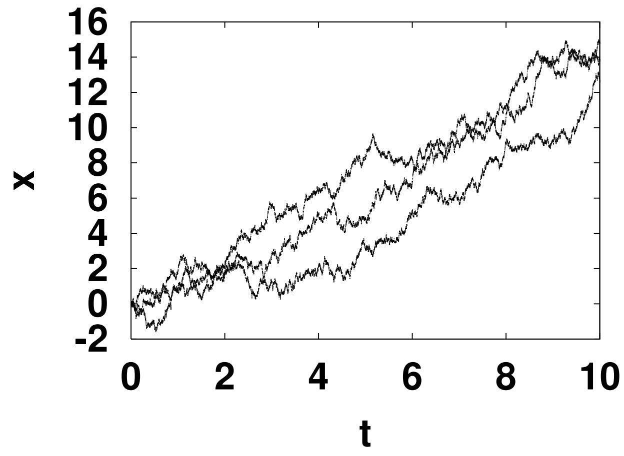
- Often: D_{ij} has a simple structure (diagonal, constant, or both)
- Non–diagonal D_{ij} for systems with *hydrodynamic interactions* (*correlations* in the stochastic displacements): Ermak & MacCammon, J. Chem. Phys. 69, 1352 (1978)

A Simple Example

$d = 1$ diffusion with constant drift.

$D^{(1)} = $ const., $D^{(2)} = $ const.

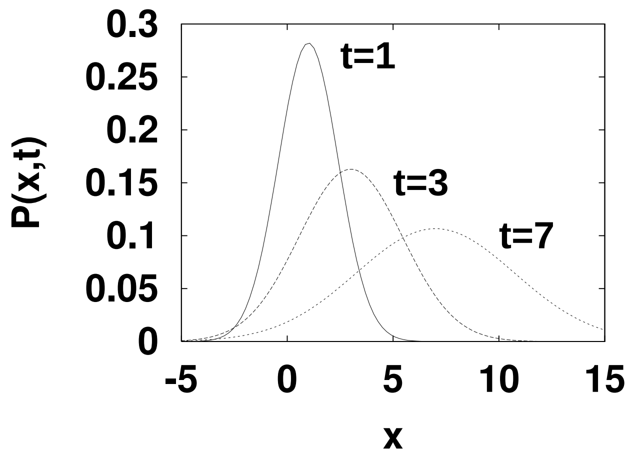
Trajectories:



continuous but not differentiable!

Solution of the Fokker–Planck equation:

$$P(x, t|0, 0) = \frac{1}{\sqrt{4\pi D^{(2)} t}} \exp\left(-\frac{(x - D^{(1)} t)^2}{4D^{(2)} t}\right)$$



Langevin Equation

Formal way of writing the Euler algorithm (stochastic differential equation):

$$\frac{d}{dt} x_i = D_i^{(1)} + f_i(t)$$

$f_i(t)$ "Gaussian white noise" with properties

- $\langle f_i \rangle = 0$
- $\left\langle f_i(t) f_j(t') \right\rangle = 2 D_{ij} \delta(t - t')$
- Thus

$$\langle \Delta x_i \Delta x_j \rangle = \int_0^\tau dt \int_0^\tau dt' \; \left\langle f_i(t) f_j(t') \right\rangle = 2 D_{ij} \tau$$

- Higher–order moments: $\int_0^\tau dt \; f_i(t)$ is *Gaussian*!

Thermal Systems: The Fluctuation–Dissipation Theorem

Langevin dynamics to describe:

- Decay into thermal equilibrium
- Thermal fluctuations *in* equilibrium
- $\Rightarrow D^{(1)}$, $D^{(2)}$ do not explicitly depend on time

Equilibrium state:

- Hamiltonian $\mathcal{H}(x)$
- $\beta = 1/(k_B T)$
- $Z = \int dx\, \exp(-\beta\mathcal{H})$
- $\rho(x) = Z^{-1} \exp(-\beta\mathcal{H})$

Necessary:

$$P(x, t|x_0, 0) \to \rho(x) \qquad \text{for} \qquad t \to \infty$$

$$\mathcal{L} \exp(-\beta\mathcal{H}) = 0$$

Balance between drift and diffusion defines temperature.

Ito vs. Stratonovich

Definition of the process via

- Langevin equation
- **plus** interpretation of the stochastic term!

So far: **Ito** interpretation

Other common interpretation: **Stratonovich**: Assume that the trajectories are differentiable, and take the limit of vanishing correlation time at the end!

Consider

$$\frac{d}{dt}x = F(x) + \sigma(x)f(t)$$

- F deterministic part
- $\sigma(x)$ noise strength (*multiplicative* noise)
- $\langle f \rangle = 0$
- $\big\langle f(t)f(t') \big\rangle = 2\delta(t - t')$

$$\frac{d}{dt}x = F(x) + \sigma(x)f(t)$$

Ito:

$$\Rightarrow \quad \begin{array}{c} \int_0^\tau dt\,\sigma(x(t))f(t) \to \sigma(x(0))\int_0^\tau dt\,f(t) \\ \left\langle \int_0^\tau dt\,\sigma(x(t))f(t) \right\rangle = 0 \end{array}$$

Stratonovich:

$$\begin{aligned}
& \int_0^\tau dt\,\sigma(x(t))f(t) \\
\to \quad & \sigma(x(0))\int_0^\tau dt\,f(t) + \frac{d\sigma}{dx}\int_0^\tau dt\,\Delta x(t) f(t) + \ldots \\
= \quad & \sigma(x(0))\int_0^\tau dt\,f(t) + \sigma\frac{d\sigma}{dx}\int_0^\tau dt\int_0^t dt'\,f(t')f(t) + \ldots \\
\Rightarrow \quad & \\
& \left\langle \int_0^\tau dt\,\sigma(x(t))f(t) \right\rangle \\
= \quad & 0 + \sigma\frac{d\sigma}{dx}\tau + o(\tau)
\end{aligned}$$

“spurious drift”

Brownian Dynamics

- System of particles
- Coordinates $\vec{r}_i$
- Friction coefficients ζ_i
- Diffusion coefficients D_i
- Potential energy U $(\equiv \mathcal{H})$
- Forces

$$\vec{F}_i = -\frac{\partial U}{\partial \vec{r}_i}$$

$$\begin{aligned} \frac{d}{dt}\vec{r}_i &= \frac{1}{\zeta_i}\vec{F}_i + \vec{\delta}_i \\ \left\langle \vec{\delta}_i \right\rangle &= 0 \\ \left\langle \vec{\delta}_i(t) \otimes \vec{\delta}_j(t') \right\rangle &= 2D_i \overset{\leftrightarrow}{1} \delta_{ij}\delta(t-t') \end{aligned}$$

I. e.

$$\mathcal{L} = -\sum_i \frac{\partial}{\partial \vec{r}_i}\frac{1}{\zeta_i}\vec{F}_i + \sum_i D_i \left(\frac{\partial}{\partial \vec{r}_i}\right)^2$$

$$\mathcal{L}\exp(-\beta\mathcal{H}) = 0$$

$\Rightarrow$

$$\sum_i \frac{\partial}{\partial \vec{r}_i}\left[\frac{1}{\zeta_i}\frac{\partial\mathcal{H}}{\partial \vec{r}_i} - \beta D_i \frac{\partial\mathcal{H}}{\partial \vec{r}_i}\right]\exp(-\beta\mathcal{H}) = 0$$

$$D_i = \frac{k_B T}{\zeta_i}$$ **Einstein relation**

Stochastic Dynamics

- Generalized coordinates q_i
- Generalized canonically conjugate momenta p_i
- Hamiltonian $\mathcal{H}$

Hamilton's equations of motion, augmented by friction and noise terms:

$$\begin{aligned} \frac{d}{dt} q_i &= \frac{\partial \mathcal{H}}{\partial p_i} \\ \frac{d}{dt} p_i &= -\frac{\partial \mathcal{H}}{\partial q_i} - \zeta_i \frac{\partial \mathcal{H}}{\partial p_i} + \sigma_i f_i \end{aligned}$$

$$\begin{aligned} \zeta_i &= \zeta_i \left(\{ q_i \} \right) \\ \sigma_i &= \sigma_i \left(\{ q_i \} \right) \\ \langle f_i \rangle &= 0 \\ \left\langle f_i(t) f_j(t') \right\rangle &= 2 \delta_{ij} \delta(t - t') \end{aligned}$$

$$\mathcal{L} = \mathcal{L}_H + \mathcal{L}_{SD}$$

$$\begin{aligned}
\mathcal{L}_H &= -\sum_i \frac{\partial}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} + \sum_i \frac{\partial}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i} \\
&= -\sum_i \frac{\partial \mathcal{H}}{\partial p_i}\frac{\partial}{\partial q_i} + \sum_i \frac{\partial \mathcal{H}}{\partial q_i}\frac{\partial}{\partial p_i}
\end{aligned}$$

$$\mathcal{L}_H \exp(-\beta\mathcal{H}) = 0 \qquad \text{o.k.}$$

$$\mathcal{L}_{SD} = \sum_i \frac{\partial}{\partial p_i}\left[\zeta_i \frac{\partial \mathcal{H}}{\partial p_i} + \sigma_i^2 \frac{\partial}{\partial p_i}\right]$$

$$\mathcal{L}_{SD} \exp(-\beta\mathcal{H}) = 0$$

$$\sum_i \frac{\partial}{\partial p_i}\left[\zeta_i \frac{\partial \mathcal{H}}{\partial p_i} - \beta\sigma_i^2 \frac{\partial \mathcal{H}}{\partial p_i}\right] e^{-\beta\mathcal{H}} = 0$$

$$\sigma_i^2 = k_B T \zeta_i$$

Simple recipe for MD with hard potentials & weak noise:

- Standard velocity Verlet
- Add friction and noise at those instances where forces are calculated
- $\rightarrow$ Symplectic algorithm in the $\zeta = 0$ limit

Dissipative Particle Dynamics (DPD)

Disadvantages of SD:

- $v = 0$ reference frame is special
- Galileo invariance is broken
- Global momentum is not conserved
- No proper description of hydrodynamics

Idea:

- Dampen *relative* velocities of nearby particles
- Stochastic kicks between *pairs* of nearby particles
- satisfying Newton III

Result:

- Galileo invariance
- Momentum conservation
- Locality
- Correct description of hydrodynamics
- No profile biasing in boundary–driven shear simulations

In practice: Define

- $\zeta(r)$ (relative) friction for particles at distance r
- $\sigma(r)$ noise strength for particles at distance r

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j = r_{ij}\hat{r}_{ij}$$

Friction force along interparticle axis:

$$\vec{F}_i^{(fr)} = -\sum_j \zeta(r_{ij}) \left[(\vec{v}_i - \vec{v}_j) \cdot \hat{r}_{ij} \right] \hat{r}_{ij}$$

$\sum_i \vec{F}_i^{(fr)} = 0$ (antisymmetric matrix in ij)

Stochastic force along interparticle axis:

$$\vec{F}_i^{(st)} = \sum_j \sigma(r_{ij}) \, \eta_{ij}(t) \, \hat{r}_{ij}$$

$$\eta_{ij} = \eta_{ji} \qquad \langle \eta_{ij} \rangle = 0$$

$$\left\langle \eta_{ij}(t) \eta_{kl}(t') \right\rangle = 2(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t - t')$$

$\sum_i \vec{F}_i^{(st)} = 0$ (similar)

$$\begin{aligned}\frac{d}{dt}\vec{r}_i &= \frac{1}{m_i}\vec{p}_i \\ \frac{d}{dt}\vec{p}_i &= \vec{F}_i + \vec{F}_i^{(fr)} + \vec{F}_i^{(st)}\end{aligned}$$

$$\mathcal{L} = \mathcal{L}_H + \mathcal{L}_{DPD}$$

$$\begin{aligned}\mathcal{L}_{DPD} &= \sum_{ij} \zeta(r_{ij})\hat{r}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i}\left[\hat{r}_{ij} \cdot \left(\frac{\partial \mathcal{H}}{\partial \vec{p}_i} - \frac{\partial \mathcal{H}}{\partial \vec{p}_j}\right)\right] \\ &- \sum_{i \neq j} \sigma^2(r_{ij}) \left(\hat{r}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i}\right)\left(\hat{r}_{ij} \cdot \frac{\partial}{\partial \vec{p}_j}\right) \\ &+ \sum_i \sum_{j(\neq i)} \sigma^2(r_{ij}) \left(\hat{r}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i}\right)^2 \\ &= \sum_i \hat{r}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i} \sum_{j(\neq i)} \left[\zeta(r_{ij})\hat{r}_{ij} \cdot \left(\frac{\partial \mathcal{H}}{\partial \vec{p}_i} - \frac{\partial \mathcal{H}}{\partial \vec{p}_j}\right)\right. \\ &+ \left.\sigma^2(r_{ij})\hat{r}_{ij} \cdot \left(\frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j}\right)\right]\end{aligned}$$

Fluctuation–dissipation theorem:

$$\sigma^2(r) = k_B T \zeta(r)$$

Force Biased Monte Carlo

Idea: Use a BD step (with large τ) as a *trial move* for Monte Carlo. Accept / reject with Metropolis criterion $\Rightarrow$ correct Boltzmann distribution without discretization errors

Just $d = 1$, set $\gamma = \tau / \zeta$. Algorithm:

- Start position x
- Calculate energy $U = U(x)$
- Calculate force $F = F(x) = -\partial U / \partial x$
- Trial move: Generate

$$x' = x + \gamma F + \sqrt{2 k_B T \gamma}\, \rho$$

  ρ *Gaussian* with

$$\langle \rho \rangle = 0 \qquad\qquad \left\langle \rho^2 \right\rangle = 1$$

- Hence,

$$w_{ap}(x \to x') = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\rho^2}{2} \right) = w_1$$

- Calculate energy $U' = U(x')$
- Calculate $\Delta U = U' - U$
- Calculate force $F' = F(x')$
- Calculate

$$\rho' = (2 k_B T \gamma)^{-1/2} \left(x - x' - \gamma F' \right)$$

  (random number needed to go back)

- Hence,

$$w_{ap}(x' \to x) = \frac{1}{\sqrt{2\pi}} \exp\left(-\frac{\rho'^2}{2}\right) = w_2$$

- Calculate w_{acc}
- Accept with probability w_{acc}

$w_{acc} =?$ Detailed balance:

$$\frac{w_{ap}(x \to x')}{w_{ap}(x' \to x)} \frac{w_{acc}(x \to x')}{w_{acc}(x' \to x)} = \exp(-\beta \Delta U)$$

I. e. standard Metropolis with

$$\exp(-\beta \Delta U) \to \exp(-\beta \Delta U) \frac{w_2}{w_1}$$

Higher–Order Algorithms

Additive noise: Systematic approach via *operator factorization*.

Idea: Fokker–Planck equation:

$$\frac{\partial}{\partial t} P = \mathcal{L} P \qquad \Rightarrow \qquad P = \exp(\mathcal{L} t)\delta(x - x_0)$$

Factorize the exponential, each factor such that the result is known.

Example (2nd order):

$$\mathcal{L} = \mathcal{L}_{det} + \mathcal{L}_{stoch}$$

(deterministic propagation, stochastic diffusion)

$$\begin{aligned} & \exp(\mathcal{L} t) \\ = \quad & \exp(\mathcal{L}_{stoch} t/2) \exp(\mathcal{L}_{det} t) \exp(\mathcal{L}_{stoch} t/2) + O(t^3) \end{aligned}$$

- $\exp(\mathcal{L}_{stoch} t/2)$ acting on $\delta(x - x_0)$: **Exactly known** solution — Gaussian distribution / solution of the diffusion equation
- $\exp(\mathcal{L}_{det} t)$: Just *deterministic* propagation. Can be done up to any desired accuracy with known methods (e. g. Runge–Kutta)

State of the art: Fourth order: H. A. Forbert, S. A. Chin, Phys. Rev. E 63, 016703 (2000).

Multiplicative noise: Schemes of higher–order than Euler are very difficult to construct and apply (Greiner, Strittmatter, Honerkamp, J. Stat. Phys. 51, 95 (1988)). No known general solution for a diffusion equation of type

$$\frac{\partial}{\partial t}P = \frac{\partial^2}{\partial x^2}D(x)P$$