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 \((x, \text{usually multi-dimensional})\)
- 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

\[
\tilde{p}(k) = \int dx \, \exp(ikx)p(x)
\]

\[
= \sum_{n=0}^{\infty} \frac{(ik)^n}{n!} \mu_n
\]

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

\[ \mu_n(t; x_0, t_0) = \langle (x - x_0)^n \rangle (t, t_0) \]

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

(mean displacement, mean square displacement etc.) ⇒

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

particularly good for short times.

Chapman–Kolmogorov (small \( \tau \)):

\[ P(x, t|x_0, t_0) \]

\[ = \int dx_1 \sum_{n=0}^{\infty} \left( -\frac{\partial}{\partial x} \right)^n \delta(x - x_1) \frac{1}{n!} \mu_n(t; x_1, t - \tau) \]

\[ P(x_1, t - \tau|x_0, t_0) \]

\[ = \sum_{n=0}^{\infty} \left( -\frac{\partial}{\partial x} \right)^n \frac{1}{n!} \mu_n(t; x, t - \tau) \]

\[ P(x, t - \tau|x_0, t_0) \]
Subtract $n = 0$ term:

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

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

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

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

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 $n = \infty$


Truncation at finite order $n > 2$ would produce

$$P < 0!!$$
Proof of Pawula Theorem

Define scalar product

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

Moments:

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

I. e.

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

Schwarz inequality:

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

$$\Rightarrow$$

$$D^{(m+n)^2} \leq \frac{(2m)! (2n)!}{(m + n)!^2} D^{(2m)} D^{(2n)}$$

for $m \geq 1$, $n \geq 1$

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.
• $N = 1$:
  \[ D^{(2)} = \ldots = 0 \implies D^{(2)} = \ldots = 0 \]

• $N = 2$:
  \[ D^{(4)} = \ldots = 0 \implies D^{(3)} = \ldots = 0 \]

• $N = 3$:
  \[ D^{(6)} = \ldots = 0 \implies D^{(4)} = \ldots = 0 \]

• $N = 4$:
  \[ D^{(8)} = \ldots = 0 \implies D^{(5)} = \ldots = 0 \]

• 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 $\tau$

Physical input:

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

We know for the displacements:

\[
\langle \Delta x_i \rangle = D_i^{(1)}(x, t) \tau + o(\tau)
\]

\[
\langle \Delta x_i \Delta x_j \rangle = 2D_{ij}^{(2)}(x, t) \tau + o(\tau)
\]

\[
\langle (\Delta x)^n \rangle = o(\tau) \quad n \geq 3
\]

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 \(\tau \to 0\)
- 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)
A Simple Example

\( d = 1 \) diffusion with constant drift.

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

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

- \( \langle f_i \rangle = 0 \)
- \( \langle f_i(t) f_j(t') \rangle = 2D_{ij} \delta(t - t') \)
- Thus
  \[
  \langle \Delta x_i \Delta x_j \rangle = \int_0^\tau dt \int_0^\tau dt' \langle f_i(t) f_j(t') \rangle = 2D_{ij} \tau
  \]

- 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:

\[
P(x, t|x_0, 0) \to \rho(x) \quad \text{for} \quad t \to \infty
\]

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

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

\[
\frac{dx}{dt} = F(x) + \sigma(x)f(t)
\]

- \(F\) deterministic part
- \(\sigma(x)\) noise strength (multiplicative noise)
- \(\langle f \rangle = 0\)
- \(\langle f(t)f(t') \rangle = 2\delta(t - t')\)
\[
\frac{d}{dt} x = F(x) + \sigma(x) f(t)
\]

**Ito:**

\[
\int_0^\tau dt \sigma(x(t)) f(t) \rightarrow \sigma(x(0)) \int_0^\tau dt f(t)
\]

\[
\Rightarrow \quad \left\langle \int_0^\tau dt \sigma(x(t)) f(t) \right\rangle = 0
\]

**Stratonovich:**

\[
\int_0^\tau dt \sigma(x(t)) f(t)
\]

\[
\rightarrow \sigma(x(0)) \int_0^\tau dt f(t) + \frac{d\sigma}{dx} \int_0^\tau dt \Delta x(t) f(t) + \ldots
\]

\[
= \sigma(x(0)) \int_0^\tau dt f(t) + \sigma \frac{d\sigma}{dx} \int_0^\tau dt \int_0^t dt' f(t') f(t) + \ldots
\]

\[
\Rightarrow \quad \left\langle \int_0^\tau dt \sigma(x(t)) f(t) \right\rangle
\]

\[
= 0 + \sigma \frac{d\sigma}{dx} \tau + o(\tau)
\]

“spurious drift”
Brownian Dynamics

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

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

$$\frac{d}{dt} \vec{r}_i = \frac{1}{\zeta_i} \vec{F}_i + \vec{\delta}_i$$

$$\left\langle \vec{\delta}_i \right\rangle = 0$$

$$\left\langle \vec{\delta}_i(t) \otimes \vec{\delta}_j(t') \right\rangle = 2D_i \delta_{ij} \delta(t - t')$$

I. e.

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

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

$$\Rightarrow$$

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

$$D_i = \frac{k_B T}{\zeta_i} \quad \text{Einstein relation}$$
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:

$$\frac{d}{dt}q_i = \frac{\partial \mathcal{H}}{\partial p_i}$$

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

$$\zeta_i = \zeta_i (\{q_i\})$$

$$\sigma_i = \sigma_i (\{q_i\})$$

$$\langle f_i \rangle = 0$$

$$\langle f_i(t) f_j(t') \rangle = 2\delta_{ij}\delta(t - t')$$

$$\mathcal{L} = \mathcal{L}_H + \mathcal{L}_{SD}$$
\begin{equation}
\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}
\end{equation}

\begin{equation}
\mathcal{L}_H \exp(-\beta \mathcal{H}) = 0 \quad \text{o.k.}
\end{equation}

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

\begin{equation}
\mathcal{L}_{SD} \exp(-\beta \mathcal{H}) = 0
\end{equation}

\begin{equation}
\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
\end{equation}

\begin{equation}
\sigma_i^2 = k_B T \zeta_i
\end{equation}

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:

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

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

Stochastic force along interparticle axis:

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

\[ \eta_{ij} = \eta_{ji} \quad \langle \eta_{ij} \rangle = 0 \]

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

\[ \sum_i \vec{F}^{(st)}_i = 0 \text{ (similar)} \]
\[
\begin{align*}
\frac{d}{dt} \vec{r}_i &= \frac{1}{m_i} \vec{p}_i \\
\frac{d}{dt} \vec{p}_i &= \vec{F}_i + \vec{F}_i^{(fr)} + \vec{F}_i^{(st)}
\end{align*}
\]

\[\mathcal{L} = \mathcal{L}_H + \mathcal{L}_{DPD}\]

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

\[= \sum_{i} \hat{r}_{ij} \cdot \frac{\partial}{\partial \vec{p}_i} \sum_{j(\neq i)} \left[ \zeta(r_{ij}) \hat{r}_{ij} \cdot \left( \frac{\partial \mathcal{H}}{\partial \vec{p}_i} - \frac{\partial \mathcal{H}}{\partial \vec{p}_j} \right) \right] + \sigma^2(r_{ij}) \hat{r}_{ij} \cdot \left( \frac{\partial}{\partial \vec{p}_i} - \frac{\partial}{\partial \vec{p}_j} \right) \]

Fluctuation–dissipation theorem:

\[\sigma^2(r) = k_B T \zeta(r)\]
**Force Biased Monte Carlo**

**Idea:** Use a BD step (with large $\tau$) 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 $F = F(x) = -\frac{\partial U}{\partial x}$
- Trial move: Generate
  $$x' = x + \gamma F + \sqrt{2k_BT\gamma} \rho$$
  $\rho$ Gaussian with
  $$\langle \rho \rangle = 0 \quad \quad \langle \rho^2 \rangle = 1$$
- Hence,
  $$w_{ap}(x \rightarrow x') = \frac{1}{\sqrt{2\pi}} \exp \left( -\frac{\rho^2}{2} \right) = w_1$$
- Calculate energy $U' = U(x')$
- Calculate $\Delta U = U' - U$
- Calculate force $F' = F(x')$
- Calculate
  $$\rho' = (2k_BT\gamma)^{-1/2} \left(x - x' - \gamma F'\right)$$
  (random number needed to go back)
• Hence,

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

• Calculate \( w_{acc} \)
• Accept with probability \( w_{acc} \)

\[ w_{acc} = ? \] Detailed balance:

\[ \frac{w_{ap}(x \rightarrow x') w_{acc}(x \rightarrow x')}{w_{ap}(x' \rightarrow x) w_{acc}(x' \rightarrow x)} = \exp(-\beta \Delta U) \]

i. e. standard Metropolis with

\[ \exp(-\beta \Delta U) \rightarrow \exp(-\beta \Delta U) \frac{w_2}{w_1} \]
Higher–Order Algorithms

Additive noise: Systematic approach via operator factorization.

Idea: Fokker–Planck equation:

\[ \frac{\partial}{\partial t} P = \mathcal{L} P \quad \Rightarrow \quad P = \exp(\mathcal{L} t) \delta(x - x_0) \]

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

Example (2nd order):

\[ \mathcal{L} = \mathcal{L}_{\text{det}} + \mathcal{L}_{\text{stoch}} \]

(deterministic propagation, stochastic diffusion)

\[ \exp(\mathcal{L} t) = \exp(\mathcal{L}_{\text{stoch}} t/2) \exp(\mathcal{L}_{\text{det}} t) \exp(\mathcal{L}_{\text{stoch}} t/2) + O(t^3) \]

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

**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

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