Diffusion processes

Consider the motion of a Brownian walker, e.g., a colloidal particle suspended in a fluid. The particle is being bombarded by lots of collisions with the solvent molecules:

$$m\left[v(t+\Delta t) - v(t)\right] = \int_{t'=t}^{t+\Delta t} F_{ext}(r(t'))\,dt'$$

$$+ \sum_{\text{collisions}} \Delta p_i$$

Δp_i ← collisional momentum exchange

We could do MCMC to simulate this, but there will be lots of transitions (collisions) to process. Can we approximate?

Assume that the dynamics of a system follows a continuous time continuous space Markov chain, without jumps.

This means that we can define moments of the local dynamics over a short interval Δt:

$$M_1 = \langle x(t+\Delta t) - x(t) \rangle = \langle \Delta x \rangle$$

$$M_2 = \langle [x(t+\Delta t) - x(t)]^2 \rangle = \langle \Delta x^2 \rangle$$

i.e. mean displacement and mean square displacement.

More generally,

$$M_n(t; x_0, t_0) = \langle (x - x_0)^n \rangle$$

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

transition probability

The moments fully define $P(x, t \mid x_0, t_0)$, specifically

$$P(x, t \mid x_0, t_0) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} M_n \frac{\partial^n}{\partial x^n} \delta(x - x_0)$$

formal moment expansion (moments match on two sides)

For small time intervals

$$\mu_n(\Delta t) = \mu_n(t_0 + \Delta t ; x_0, t_0) = (n!) \cdot D^{(n)} \cdot \Delta t$$

+ terms of order higher than linear

Then

$$\frac{\partial P(x,t)}{\partial t} = \sum_{n=0}^{\infty} (-1)^n \cdot \frac{\partial^n}{\partial x^n} \left[D^{n}(x,t)\, P(x,t) \right]$$

Proof:

$$P(x, t+\Delta t) = \int P(x, t+\Delta t \,|\, x', t)\, P(x', t)\, dx' \quad \leftarrow \text{Chapman Kolmogorov}$$

and then integrate by parts.

<u>Pawula theorem</u>: Either all terms have to be included or only the first two!

$$\begin{cases} \dfrac{\partial P(x,t)}{\partial t} = -\dfrac{\partial}{\partial x}\left[A(x)\,P(x,t)\right] + \dfrac{\partial^2}{\partial x^2}\left[B(x)\,P(x,t)\right] \end{cases}$$

<u>Fokker Planck</u> equation

<u>Drift</u>, deterministic dynamics

<u>Diffusion</u>, Brownian dynamics

Recall
$$\begin{cases} A(x)\cdot\Delta t = \langle \Delta x \rangle & \text{(velocity)} \\ 2B(x)\cdot\Delta t = \langle \Delta x^2 \rangle & \text{(diffusion)} \end{cases}$$

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The Fokker-Planck equation is the extension of the Master equation to diffusion processes, which are the limit where transitions are very small (local) jumps.

Multivariable generalization:

Drift vector

$$\frac{\partial P}{\partial t}(\vec{x},t) = -\sum_{x_i} \frac{\partial}{\partial x_i}\left[A_i(x)\,P(x,t)\right]$$

diffusion matrix $\longrightarrow$

$$+\sum_{i,j} \frac{\partial^2}{\partial x_i\,\partial x_j}\left[B_{ij}(x)\,P(x,t)\right]$$

$$\boxed{\langle \Delta x_i\,\Delta x_j\rangle = 2\,B_{ij}\cdot \Delta t}$$

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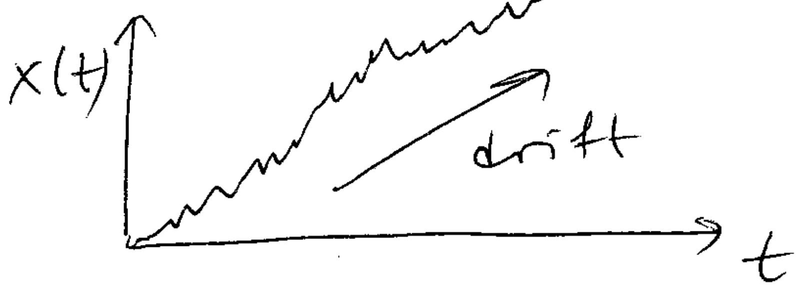
If one looks at a small interval Δt over which A and B are held fixed at their initial values, then

$P(x, t+\Delta t)$ is a **Gaussian**
centered around $x_0 + A \cdot \Delta t$
with covariance matrix $2B\Delta t$

In one dimension, this gives for $A=0$ **Brownian motion**, or the **Wiener process**



This suggests the following numerical scheme or approximation:

$$X(t+\Delta t) = X(t) + A\left[x(t), t\right]\Delta t +$$

$$+ \left(2B\Delta t\right)^{1/2} \cdot \mathcal{N}(0,1)$$

normally-distributed i.i.d random variables

Denote $\boxed{\widetilde{W}(t) \equiv \mathcal{N}(0,1)}$

Going back to the Brownian walker:

$$\begin{cases} m\left[v(t+\Delta t) - v(t)\right] \approx F\left[r(t)\right]\Delta t + \sqrt{2D\left[r(t)\right]\Delta t} \cdot \widetilde{W}(t) \\ r(t+\Delta t) = r(t) + v(t) \cdot \Delta t \end{cases}$$

average over MANY EVENTS in KMC

In the limit $\Delta t \to 0$, this gives rise to a stochastic differential equation

$$\dot{x}(t) = a[x(t)] + \overset{\equiv \sqrt{2D}}{b}[x(t)]\, W(t)$$

where $W(t)$ formally denotes the time derivative of Brownian motion (does not exist classically), and is termed white noise. It is a Gaussian process with mean and covariance

$$\begin{cases} \langle W_i(t) \rangle = 0 \\ \langle W_i(t) W_j(t') \rangle = \delta(t-t') \end{cases}$$

Dirac "function" (distribution)

Stochastic differential equations are often written in differential form to avoid derivatives of the nowhere differentiable white noise

$$dx(t) = a[x(t)]\,dt + b[x(t)]\,d(Br(t))$$

Brownian motion

But physicists will usually write it as a differential equation.

In math $W(t)$ often denotes a Wiener process and $\dot{W}(t)$ denotes white noise, so watch out for notation.

What we have so far is an <u>Ito</u> differential equation, which means that

$$\dot{x} = a(x,t) + b(x,t)\, W(t)$$

is the limit as $\Delta t \to 0$ of the <u>Euler - Maryama</u> numerical method

$$x(t+\Delta t) = x(t) + a[x(t),t]\,\Delta t$$

$$+ b[x(t),t] \underbrace{\sqrt{\Delta t} \cdot \mathcal{N}(0,1)}_{\text{denote as}}$$

"discrete" white noise $\longrightarrow \left(\dfrac{\widetilde{W}}{\sqrt{\Delta t}}\right) \cdot \Delta t$

Recall that the Fokker-Planck equation associated with this Ito equation is

$$\frac{\partial P}{\partial t}(x,t) = -\frac{\partial}{\partial x}\cdot\left[a(x,t)\,P(x,t)\right] + \frac{\partial^2}{\partial x^2} : \left[\frac{1}{2}(b b^*)\,P(x,t)\right]$$

Ito here refers to the convention that the noise covariance is evaluated at the beginning of a timestep, keeping the Markov character (non-anticipatory)

Ito calculus does ~~not~~, however, follow the ordinary rules of calculus, notably, the chain rule.

For example, what SODE does $f[x(t)]$ follow? Ordinary calculus would say $\dot{f} = f' \cdot \dot{x} = f' [a + bW]$, but in fact because of the $\sqrt{\Delta t}$ one must keep <u>second</u> order terms in the Taylor expansion for the noise terms

) Drift for $f[x(t)]$

$$\langle f[x(t+\Delta t)] - f[x(t)] \rangle =$$

$$= \langle f'[x(t)]\,\Delta x + \frac{1}{2} f''[x(t)]\,\Delta x^2 + O(\Delta x^3) \rangle$$

lower case o

$$= f' \langle a\,\Delta t + b\,\tilde{W}\sqrt{\Delta t} \rangle + o(\Delta t)$$

$$+ \frac{1}{2} f'' \langle b^2 \Delta t\ \tilde{W}^2 \rangle$$

order higher than Δt

$$= \left(f' \cdot a + \frac{1}{2} f'' b^2 \right) dt$$

extra or "spurious" drift

(2) Diffusion for $f[x(t)]$:

$$\langle [f(t+\Delta t) - f(t)]^2 \rangle = (f')^2 \langle b^2 \Delta t \, \tilde{W}^2 \rangle$$

$$= \underbrace{(f' b)^2}_{\text{new diffusion coefficient}} \Delta t$$

In summary, the SODE for $f[x(t)]$ is:

$$\boxed{\dot{f}[x(t)] = \left(a f' + \frac{b^2}{2} f''\right) + b f' W(t)}$$

This is one version of "Ito's" formula

Now, what if we had interpreted the SODE

open circle

$$\dot{x} = a(x,t) + b(x,t) \circ W(t)$$

in the <u>Stratonovich</u> sense, meaning, we used a <u>midpoint rule</u> to integrate the stochastic term:

$$x(t+\Delta t) = x(t) + a[x(t),t]\,\Delta t + b\left[\frac{x(t+\Delta t)+x(t)}{2},\, t+\frac{\Delta t}{2}\right] \tilde{W}\sqrt{\Delta t}$$

<u>Ignore</u> time dependence

$$\approx b[x(t)] + \frac{1}{2} b' \cdot \Delta x$$

Look now at the drift of the new Stratonovich interpretation:

$$\langle x(t+\Delta t) - x(t) \rangle = a[x(t)]\,\Delta t + \langle \tfrac{1}{2} b' \,\Delta x\, \tilde{W} \sqrt{\Delta t} \rangle$$

But note that

$$\text{extra drift} = \langle \tfrac{1}{2} b' (a\,\Delta t + b\,\tilde{W}\sqrt{\Delta t})\,\tilde{W}\sqrt{\Delta t} \rangle + o(\Delta t)$$

$$= \tfrac{1}{2} b' b \,\Delta t$$

The extra terms only appear in the drift.

Yet another, less common in math, but very important for Langevin equations, is a <u>non-Ito</u> interpretation, which means we use a <u>backward Euler</u> implicit method:

$$x(t+\Delta t) = x(t) + a[x(t)]\Delta t + b[x(t+\Delta t)]\widetilde{W}\sqrt{\Delta t}$$

giving extra drift $b'b\,\Delta t$

explicit integrator "<u>Fixman</u>" method

$$\begin{cases} \widetilde{X} = x(t) + a[x(t)]\Delta t + b[x(t)]\widetilde{W}\sqrt{\Delta t} \\ x(t+\Delta t) = x(t) + a[x(t)]\Delta t + b[\widetilde{X}]\widetilde{W}\sqrt{\Delta t} \end{cases}$$

same $\widetilde{W}$!

Therefore, the Stratonovich equation

$$\dot{x} = a(x) + b(x) \circ W(t)$$

is equivalent to the Ito equation:

$$\dot{x} = \left[a(x) + \frac{1}{2} b b' \right] + b(x) \cdot W(t)$$

Similarly, if we had adopted a non-Ito interpretation, we would have obtained

$$\dot{x} = \left[a(x) + b b' \right] + b(x) \cdot W(t)$$

Observe: If $b(x) \equiv b_0 = \text{const}$ then all interpretations are equivalent

Stratonovich interpretation follows the rules of ordinary calculus and can be seen as the limit of smooth noise with a very short correlation time (so more physical).

So, the Stratonovich SODE for $f[x(t)]$ is:

$$\dot{f} = af' + (bf') \circ \mathcal{W}(t)$$

To see this, rewrite as Ito via

$$\frac{d(bf')}{df} = b' + b\frac{f''}{f'} \Rightarrow \frac{1}{2}(bf')\frac{d}{df}(bf') =$$

$$\left(\frac{1}{2}bb'\right)f' + \left(\frac{1}{2}b^2\right)f''$$

therefore the Ito equation for $f[x(t)]$ is

$$\dot{f} = \left[a f' + \frac{1}{2} b b' f' + \frac{b^2}{2} f'' \right] + (b f') \cdot W(t)$$

which is <u>indeed</u> the transformed version of the Ito equation

$$\dot{x} = \left[a + \frac{1}{2} b b' \right] + b \cdot W(t)$$

as we derived earlier.

The non-Ito or anti-Ito interpretation will become important when looking at overdamped Langevin equations (Brownian dynamics)