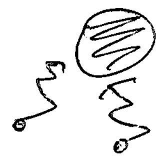
Stochastic Processes.

Example: Diffusion.



- microscopic level
  ($L = 1\,\text{Å} = 10^{-10}\,m$)
  $\Rightarrow$ deterministic & chaotic

$$\dot{p} = -\frac{\partial H}{\partial q}$$

$$\dot{q} = \frac{\partial H}{p}.$$

- mesoscopic level
  ($L = 1\,\mu m = 10^{-6}\,m$)
  $\Rightarrow$ stochastic

$$\gamma \dot{x} = \gamma \xi$$

$\gamma \xi(t) \equiv$ random force.

- symmetry: zero mean
  $\langle \xi(t) \rangle = 0$
- noise strength:
  $\langle \int_{-\infty}^{\infty} \xi(t)\, \xi(t+\tau)\, d\tau \rangle = \langle |\tilde{\xi}(0)|^2 \rangle = 2D$.
- short-time correlations
  $\langle \xi(t)\, \xi(t+\tau) \rangle \approx 0$ for $|\tau| \gg \sigma$.

'back-of-the-envelope'.

$$\sigma = \frac{L}{v} = 1\,ns.$$

$$v^2 = \frac{k_B T}{m}$$

Mean

$$\langle x(t) \rangle = 0 .$$

Mean-square displacement:

$$\langle x(t)^2 \rangle =$$

$$\left\langle \left(\int_0^t dt_1 \, \dot{x}(t_1) \right) \left(\int_0^t dt_2 \, \dot{x}(t_2) \right) \right\rangle =$$

$$= \int_0^t dt_1 \int_0^t dt_2 \, \langle \dot{x}(t_1) \, \dot{x}(t_2) \rangle =$$

$$= \int_0^t dt_1 \int_{-t_1}^{t-t_1} \langle \xi(t_1) \, \xi(t_1+T) \rangle$$

$$\approx \int_0^t dt_1 \int_{-\infty}^{\infty} dT \, \langle \xi(t_1) \, \xi(t_1+T) \rangle .$$

$$= 2 D t .$$

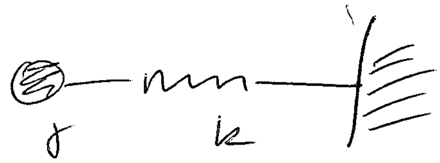
$D \equiv$ diffusion coefficient

What is D?

Great idea (Einstein 1905).

Use equipartition theorem.

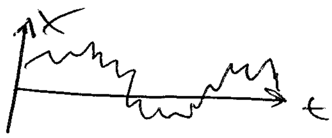
Trick to exploit idea:
add elastic spring.



Stokes $\gamma = 6\pi\eta a$

Overdamped motion.

$$(*) \quad \dot{x} = -\frac{k}{\gamma} x + \xi(t) \equiv \text{Ornstein-Uhlenbeck process}$$



$\langle x(t) \rangle = 0$

Equipart.-theorem:

$$\frac{k}{2} \langle x^2 \rangle = \frac{k_B T}{2}.$$

Formal solution of $(*)$.

$$x(t) = \int_{-\infty}^{t} d\tau \, \xi(\tau) \exp - \frac{k(t-\tau)}{\gamma}.$$

Now

$$\langle x(t)^2 \rangle =$$

$$= \left\langle \left(\int_{-\infty}^{t} dt_1\, \xi(t_1) \exp - \frac{k(t-t_1)}{\gamma} \right) \left(\int_{-\infty}^{t} dt_2\, \xi(t_2) \exp - \frac{k(t-t_2)}{\gamma} \right) \right\rangle$$

$$= \int_{-\infty}^{t} dt_1 \; \exp - \frac{2k(t-t_1)}{\gamma} \underbrace{\int_{-\infty}^{t-t_1} d\tau \,. \langle \xi(t_1) \xi(t_1+\tau) \rangle \exp + \frac{k}{\gamma}\tau}_{\approx 2D}$$

(We need $\sigma \ll \gamma/k$).

$$\approx 2D \cdot \left[\frac{\gamma}{2k} \exp - \frac{2k(t-t_1)}{\gamma} \right]_{-\infty}^{t}$$

$$= 2D \cdot \frac{\gamma}{2k} .$$

$$\frac{k}{2} \cdot \langle x^2 \rangle = \frac{k}{2} \cdot 2D \cdot \frac{\gamma}{2k} \overset{!}{=} \frac{k_B T}{2} .$$

$\Rightarrow$ Einstein relation

$$\boxed{D = \frac{k_B T}{\gamma}}$$

Special instance of FDT.

Fluct. Spectrum = Dissipation Spectrum

What is the structure of the noise term $\xi(t)$?

Mathematicians view

$$W(t) = \int_0^t dT \quad \xi(T).$$

$$\langle W(t) \rangle = 0.$$

$$\langle W(t)^2 \rangle = \int_0^t dt_1 \int_0^t dt_2 \, \langle W(t_1) W(t_2) \rangle$$

$$= \int_0^t dt_1 \int_{-t_1}^{t-t_1} dT \, \langle W(t_1) W(t_1+T) \rangle$$

$$\approx \int_0^t dt_1 \int_{-\infty}^{\infty} dT \, \langle W(t_1) W(t_1+T) \rangle$$

$$= 2Dt.$$

What about $\langle W(t)^4 \rangle = ?$

$\Rightarrow$ Idealization:

$$dW = W(t+dt) - W(t)$$

$\stackrel{!}{=}$ Gaussian random variable with mean zero and variance $2D\,dt$.

$\equiv$ Wiener process.

Physicist's view

$\xi(t) \equiv$ Gaussian white noise

$\sigma \longrightarrow 0. \Rightarrow$

δ-correlated noise.

$$\langle \xi(t) \rangle = 0.$$

$$\langle \xi(t_1)\, \xi(t_2) \rangle = 2D \quad \delta(t_1 - t_2).$$

$$\langle \xi(t_1) \cdot \xi(t_2) \cdot \ldots \cdot \xi(t_m) \rangle$$

$$= \begin{cases} 0 & m = 2n+1 \\ \sum_{\pi} (2D)^n \, \delta(t_{i_1} - t_{i_2}) \ldots \delta(t_{i_{m-1}} - t_{i_m}) & m = 2n \end{cases}$$

Numerics

Example: $\dot{x} = \xi(t)$.

$x_n = x(t_n)$, $t_n = n\,dt$.

Euler scheme:

$$x_{n+1} = x_n + \sqrt{2D\,dt}\; W_n .$$

with W_n normal distributed random variable with mean zero and variance 1.

N.B. $x_{n+1} - x_n = \sqrt{2D}\, dW$.

$\langle dW^2 \rangle = 2D\,dt$.

General case:

$$\dot{x} = f(x) + \xi(t).$$

$$x_{n+1} = x_n + f(x_n)\,dt + \sqrt{2D\,dt}\; W_n .$$

Caution: Take care if $D = D(x)$.

$P(x,t) \equiv$ probability density.

Example: $\dot{x} = \xi(t)$, $x(0) = 0$.

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

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

Check:

$$\dot{P} \quad -\frac{1}{t}P + \frac{x^2}{4D}\frac{1}{t^2}P, = \frac{\partial}{\partial x}P = \frac{-2x}{4Dt}P.$$

$$\frac{\partial^2}{\partial x^2}P = \frac{-2}{4Dt}P + \left(\frac{-2x}{4Dt}\right)^2 P.$$

General Case:

$$\dot{x} = f(x) + \xi(t).$$

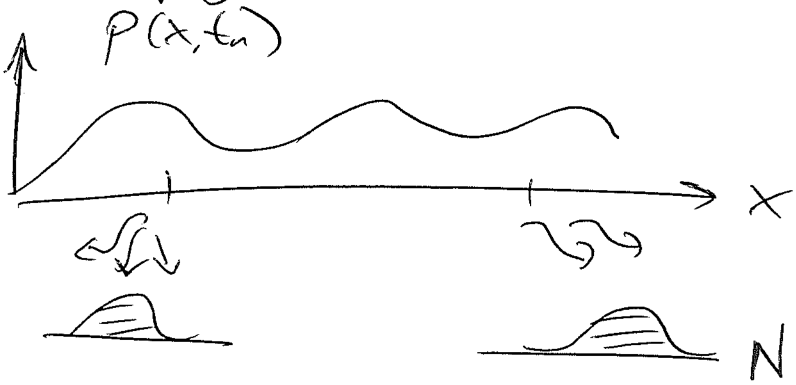
$$\frac{\partial}{\partial t}P(x,t) = L \cdot P(x,t).$$

$$L = -\frac{\partial}{\partial x}f + \frac{\partial}{\partial x}D\frac{\partial}{\partial x}.$$

Caution: if $D = D(x)$!

Q: How to find L?

A: Propagate $P(x, t_n)$ to $P(x, t_{n+1})$.



$$\mathcal{N}\left(\frac{x - x_n - f(x_n)\,dt}{\sqrt{2D\,dt}}\right)$$

$\equiv$ normal distribution

$$x_{n+1} = x_n + f(x_n)\,dt + \sqrt{2Dt}\,\mathcal{N}.$$

Markov property $\Rightarrow$

Chapman-Kolmogorov equation

$$P(x, t_{n+1}) = \int dx_n \, P(x_n, t_n) \cdot \mathcal{N}\left(\frac{x - x_n - f(x_n)\,dt}{\sqrt{2D\,dt}}\right).$$

probability to have been at x_n at $t = t_n$

probability to have moved from x_n to x_{n+1}.

We restrict ourselves to case

$D(x) = D_0$.

let $y = x - x_n$.

$$p(y) = P(x-y, t_n)$$
$$n(y) = N\left(\frac{z - f(x-y)dt}{\sqrt{2D dt}}\right)$$

$$\text{integrand} = p(y)\cdot n(y)$$
$$= p \cdot n\,|_{y=0}$$
$$\mp \frac{\partial}{\partial x}(p\,n)|_{y=0} \cdot y$$
$$+ \frac{\partial^2}{\partial x^2}(pn)|_{y=0} \cdot \frac{y^2}{2} + \dots$$

$$P(x, t_{n+1}) = \int dx_n \ \text{integrand}$$ if we let $z = y$.
$$= \int dy \ \text{integrand}$$
$$= p \cdot \int dy \cdot n$$
$$\mp \frac{\partial}{\partial x}\left[p \int dy\ n \cdot y\right]$$
$$+ \frac{\partial^2}{\partial x^2}\left[p \int dy\ n \cdot \frac{y^2}{2}\right] + \dots$$

[$\int dy \cdot n = 1$, $\int dy\ n \cdot y = f(x)\,dt$, $\int dy\ n y^2 = 2D\,dt + [f(x)\,dt]^2 = 2D\,dt + O(dt^2)$

$$\dots = P + \frac{\partial}{\partial x}[P \cdot f(x)]\,dt + \frac{\partial^2}{\partial x^2} P D\,dt.$$

$$\frac{P(x, t_{n+1}) - P(x_n, t_n)}{dt} = -\frac{\partial}{\partial x}\left(P(x,t) f(x)\right) + D\frac{\partial^2}{\partial x^2} P(x,t).$$

Application

Diffusion in potential $U(x)$.

$$\dot{x} = -\frac{1}{\gamma}\frac{\partial U}{\partial x} + \xi .$$

Steady state: $\frac{\partial}{\partial t} P \stackrel{!}{=} 0$.

$$0 \stackrel{!}{=} +\nabla\left[\left(\frac{1}{\gamma}\nabla U\right) P\right] + D\nabla^2 P.$$

$$= \nabla\left[\left(\frac{1}{\gamma}\nabla U\right)P + D\nabla P\right].$$

$T(x) \equiv T_0 \Rightarrow D = \frac{k_B T_0}{\gamma}$.

$\Rightarrow$ Boltzmann distribution.

$$\boxed{P \sim \exp - \frac{U(x)}{k_B T}}.$$

Check:

$$\nabla P \sim -\frac{1}{k_B T} P \cdot (\nabla U).$$

$$\Rightarrow \left(\frac{1}{\gamma}\nabla U\right)P + D\nabla P = 0.$$

Fokker-Planck equation = Conservation equation

$$\dot{P} = -\nabla J.$$

Different b.c. — different phys. meaning.

- Reflecting b.c.

$$J(x=0) = J(x=L) = 0.$$

$$\Rightarrow \frac{d}{dt}\int_0^L dt\, P = 0.$$

$$\dot{P} = LP, \quad \lambda p = Lp \Rightarrow \lambda_1 \geq \lambda_2 \geq \dots$$

$$\Rightarrow \lambda_1 = 0, \; p_1 = p^*; \quad \lambda_i < 0 \text{ for } i > 1.$$

- Absorbing b.c.

$$P(x=L) = 0.$$

$$\frac{d}{dt}\int_0^L dt\, P(x,t) = -J_L(t)$$

$$\equiv \text{flux to absorber.}$$

$$\lambda_1 < 0 \equiv \text{slowest time-scale.}$$

$$t \gg \frac{1}{\lambda_1}: \quad P(x,t) = a(t)\, p_1(t).$$

$$\dot{a}(t) \sim \exp(-\lambda_1 t).$$