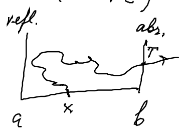
Lecture 9 summary

Mean first passage time

$$T(x) = \langle T \rangle = \int_0^\infty dt\, G(x,t)$$

$$G(x,t) = \int_a^b dx' \, p(x',t / \overset{I.C}{x,0}) = Prob(T \geq t)$$

prob. that the particle is still at time t in (a,b) if it has started at x



$$T(x) = 2 \int_x^b \frac{dy}{\Psi(y)} \int_a^y dz \, \frac{\Psi(z)}{B(z)}$$

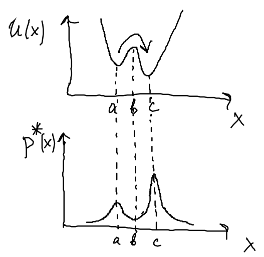
$$\Psi(x) = \exp\left[2 \int_a^x dx' \, \frac{A(x')}{B(x')} \right]$$

Escape over potential barrier: Kramers' problem

Overdamped particle in a bistable potential $U(x)$

$$\dot{x} = -U'(x) = A(x) \quad \text{force}$$

$\mathcal{D} = \frac{B}{2}$ diffusion constant



FPE
$$\boxed{\frac{\partial}{\partial t} p(x,t) = \frac{\partial}{\partial x}\left[U'(x)\, p(x,t)\right] + \mathcal{D} \frac{\partial^2}{\partial x^2} p(x,t)}$$

Stationary solution

$$p^*(x) = \mathcal{N} \exp\left[-\frac{U(x)}{\mathcal{D}}\right]$$

substitutions

$a \longrightarrow -\infty$ (refl.)

$b \rightarrow x_0 \approx b$ (abs.)

$x \rightarrow a$ I.C.

$$\Psi(x) = e^{-\frac{U(x)}{\mathcal{D}}}$$

$T(a \rightarrow x_0)$

The mean first passage time to x_0 is quite small for x_0 in the left well and quite large for x_0 in the right well.

It means that the particle on its way to the right well spends most of the time on overcoming the barrier $\Rightarrow$ the escape time can be seen as the time that the particle requires to reach a point close to c from initial position in a (this time is almost independent of the exact location of initial and final points.

We can now assume that near b we can write:

$$U(x) \simeq U(b) - \frac{1}{2}\left(\frac{x-b}{\delta}\right)^2$$

and near a

$$U(x) \simeq U(a) + \frac{1}{2}\left(\frac{x-a}{\alpha}\right)^2$$

The constant factor in eq. for $T(a \rightarrow x_0)$ is evaluated as:

$$\int_{-\infty}^{b} dz \, \exp\left[-\frac{U(z)}{\mathcal{D}}\right] \sim \int_{-\infty}^{\infty} dz \left[-\frac{U(a)}{\mathcal{D}} - \frac{(z-a)^2}{2\mathcal{D}\alpha^2}\right]$$

$$\sim \alpha \sqrt{2\pi D}\, \exp[-U(a)/D]$$

and the inner factor becomes, on assuming x_0 is well to the right of the central point b,

$$\int_a^{x_0} dy\, \exp\left(\frac{U(y)}{D}\right) \sim \int_{-\infty}^{\infty} \exp\left[\frac{U(b)}{D} - \frac{(y-b)^2}{2D\delta^2}\right] = \delta\sqrt{2\pi D}\, \exp\left[\frac{U(b)}{D}\right]$$

Putting both of these in the eq. for $T(a \to x_0)$:

$$\boxed{T(a \to x_0) \simeq 2\alpha\delta\, \exp\{[U(b) - U(a)]/D\}} \qquad \boxed{r_K = \frac{1}{T}} \text{ Kramers rate}$$

This is the classical Arrhenius formula from chemical reaction theory.

In a chem. reaction we can model the reaction by introducing a coordinate that $x = a$ is species A and $x = c$ is species C.

Diffusion process $\to$ two species separated by the potential barrier at b. For the chem. reaction, statistical mechanics gives the value:

$D = kT$, k - Bolzmann's constant
T - absolute temperature

The most important dependence on temperature

$$\exp\left(\frac{\Delta E}{kT}\right)$$

The exp. factor represents probability that the energy will exceed that of the barrier of the system being in thermal equilibrium. The molecules that reach this energy take part in the chem. reaction with a certain finite probability.

2.3 Langevin equation

$$\boxed{\frac{dx}{dt} = a(x,t) + b(x,t)\,\xi(t)}$$ stochastic diff. equation (SDE)

$\xi(t)$ – random force, fluctuating random term, noise

additive noise: $b(x,t) = \text{const}$
multiplicative noise: $b(x,t)$ depends on x

Two alternative approaches to the analysis of stochastic dynamical systems.

Q: How to include fluctuations into the description of a system?

$\swarrow$ add fluctuating sources into the dynamics and consider statistical ensemble

SDE or Langevin equation

$\searrow$ consider deterministic equations for the dynamics of probability densities

FPE

<u>Example</u> : random movement of a particle (pollen) in a fluid
due to collisions with the molecules of the fluid.

Brownian motion (Robert Brown 1827)

Paul Langevin formulated SDE for time dependent position $x(t)$ 1906

$$m\ddot{x} = \underbrace{-\eta\dot{x}}_{\text{friction}} + \underbrace{\xi(t)}_{\text{noise}}$$

for $\dot{x} = v$: $\boxed{\dot{v} = -\alpha v + \xi(t)}$

Albert Einstein formulated an evolution law for the probability $p(x,t)$ to find a particle in a certain position x at time t 1905

<u>Gaussian white noise</u> (idealization of a realistic fluctuating signal)

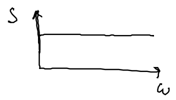
"rapidly varying highly irregular fluctuation"

$\langle \xi(t) \rangle = 0$ zero mean

$\langle \xi(t)\xi(t') \rangle = \delta(t-t')$ for $t \neq t'$ $\xi(t)$ and $\xi(t')$ are statistically independent

$\Rightarrow$ no correlation at dif. times (infinite variance).

higher moment vanish (Gaussian distrib.)



"white" Power spectral density (Wiener – Khinchin theorem):

$$S(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \langle \xi(t)\,\xi(t+s) \rangle e^{-i\omega s}\, ds = \frac{1}{2\pi} = \text{const}$$

Math. difficulty : $\xi(t)$ is discont., not integrable

<u>Calculus for stoch. diff. eq. and stoch. integration</u> (Ito, Stratonovich)

$\boxed{dx = a(x,t)\,dt + b(x,t)\,dW(t)}$ with $\xi(t) = \frac{dW}{dt}$

$W(t)$ stoch. process

$$\Longleftrightarrow \quad x(t) - x(0) = \int_0^t dt'\, a(x,t') + \int_0^t dW(t')\, b(x,t') \quad (\text{Ito})$$

Connection to FPE

$$\boxed{\frac{\partial}{\partial t} p(x,t/x_0,t_0) = \underbrace{-\frac{\partial}{\partial x}\{a(x,t)\,p(x,t/x_0,t_0)\}}_{\text{drift coef. } A = a} + \underbrace{\frac{1}{2}\frac{\partial^2}{\partial x^2}[b(x,t)^2 p(x,t/x_0,t_0)]}_{\text{diffusion coeff. } D = \frac{B}{2} = \frac{b^2}{2}}}$$