Lecture 11 MFPT continued ...

(via the Adjoint F-P operator)

Kolmogorov-Chapman

$$P(x,t|x_0,0) = \int G(x,t|y,t')\, P(y,t'|x_0,0)\, dy$$

MFPT depends ~~on~~ x_0

Fokker-Planck operator: $\frac{\partial P}{\partial t} = -\hat{L}_x P(x,t)$

$\longrightarrow$ then: $\frac{\partial G}{\partial t} = -\hat{L}_x G(x,t)$

We differentiate K.-Ch. w.r.t. t':

$$\frac{\partial P}{\partial t'} \equiv 0 = \int P(y,t'|x_0,0) \frac{\partial}{\partial t'} G(x,t|y,t')\, dy$$

$$+ \int G(x,t|y,t') \underbrace{\frac{\partial}{\partial t'} P(y,t'|x_0,0)}_{\text{F.-P.}}\, dy$$

$$= \int P(y,t'|x_0,0) \frac{\partial}{\partial t'} G(x,t|y,t')\, dy$$

$$- \int G(x,t|y,t') \underbrace{\hat{L}_y P(y,t'|x_0,0)}\, dy$$

Convert this ...

Define "adjoint Fokker-Planck op.".

if $\dot{P} = -\hat{L}_x P$ with general

$$\hat{L}_x = \frac{\partial}{\partial x}\mu(x) - D\frac{\partial^2}{\partial x^2}$$

Then $\int dx \, g(x) \hat{L}_x f(x) \stackrel{\text{def.}}{=} \int dx \, f(x) \hat{L}^+_x g(x)$

$$\langle g \hat{L} f \rangle = \langle f \hat{L}^+ g \rangle$$

integrate by parts,

$$\int g(x) \frac{\partial}{\partial x}\left(\mu(x) f(x)\right) dx = \underbrace{\cancel{[g \cdot \mu \cdot f]}}_{=0} - \int f(x) \, \mu(x) \frac{\partial g}{\partial x} dx$$

gives $\hat{L}^+_x = -\mu(x)\frac{\partial}{\partial x} - D\frac{\partial^2}{\partial x^2}$

So that if $\hat{L}_x = D e^{-\beta V(x)} \frac{\partial}{\partial x}\left(e^{\beta V(x)} \frac{\partial}{\partial x}\right)$

then $\hat{L}^+_x = D e^{\beta V(x)} \frac{\partial}{\partial x}\left(e^{-\beta V(x)} \frac{\partial}{\partial x}\right)$

check by direct differentiation

$$0 = \int P(y,t'|x_0,0) \frac{\partial}{\partial t'} G(x,t|y,t') \, dy$$

$$- \int P(y,t'|x_0,0) \hat{L}^+_y G(x,t|y,t') \, dy$$

$$0 = \int \underline{\left[\frac{\partial}{\partial t} G(x,t|y,t') - \hat{\mathcal{L}}^{+}_{y} G \right]} P(y,t'|x_0,0)\, dy$$

We have: $\frac{\partial}{\partial t'} G = \hat{\mathcal{L}}^{+}_{y} G$

Notice $\ominus$ is gone

$\boxed{\text{acting on the starting position/time in } G(x,t|y,t')}$

Hence $P(x,t|x_0,t_0)$ satisfies the same equation:

$$\boxed{\frac{\partial}{\partial t_0} P(x,t|x_0,t_0) = \hat{\mathcal{L}}^{+}_{x_0} P(x,t|x_0,t_0)}$$

Now we are ready to find MFPT $\tau(x_0)$:

$$\hat{\mathcal{L}}^{+}_{x_0} \left[\tau(x_0) = \int dt \underbrace{\boxed{\int dx\, P(x,t|x_0,t_0)}}_{\Rightarrow S(t)} \right]$$

$$\hat{\mathcal{L}}^{+}_{x_0} \tau(x_0) = \int dt \int dx \frac{\partial}{\partial t_0} \underbrace{P(x,t|x_0,t_0)}_{\text{depends on } t-t_0}$$

Change variable

$$\hat{\mathcal{L}}^{+}_{x_0}\,\tau(x_0) = \int_{0\,(-)}^{\infty (-)} d\tilde t \int dx \,\frac{\partial}{\partial \tilde t} P(x,\tilde t \,|\, x_0, 0)$$

~~flip limits~~

$\tilde t = t - t_0$

$d\tilde t = -dt_0$

$$= +\int d\tilde t \,\frac{\partial}{\partial \tilde t}\underbrace{\int P\,dx}_{-f(\tilde t)}$$

$S(\tilde t)$

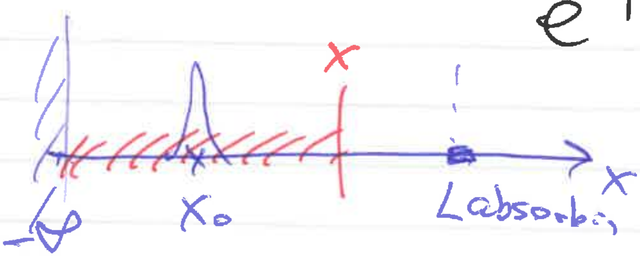
$$= -\int f(\tilde t)\,d\tilde t = -1$$

$$\boxed{\hat{\mathcal{L}}^{+}_{x_0}\,\tau(x_0) = -1}$$ Now unpack it

$$\boxed{D\, e^{\beta V(x)} \frac{\partial}{\partial x}\left(e^{-\beta V(x)} \frac{\partial}{\partial x}\tau(x)\right) = -1}$$

First step:

$$e^{-\beta V(x)} \frac{\partial \tau}{\partial x} = -\frac{1}{D}\int_{\boxed{\cdot}}^{x} e^{-\beta V(y)}\,dy$$



"left boundary"
(could be $-\infty$ if $P(x,t)$ behaves
or reflecting boundary)

Second step

$$\tau(x_0) = -\int_{\boxed{\cdot}}^{x_0} dx \frac{1}{D} e^{\beta V(x)} \int_{\boxed{\cdot}}^{x} e^{-\beta V(y)} dy$$

left boundary

$$\int_{\boxed{\cdot}}^{x_0} \frac{\partial \tau}{\partial x} dx = \tau_{x_0} - 0$$

$\boxed{\text{where } \tau(\cdot) = 0}$ $\rightarrow$ this is the absorbing boundary L

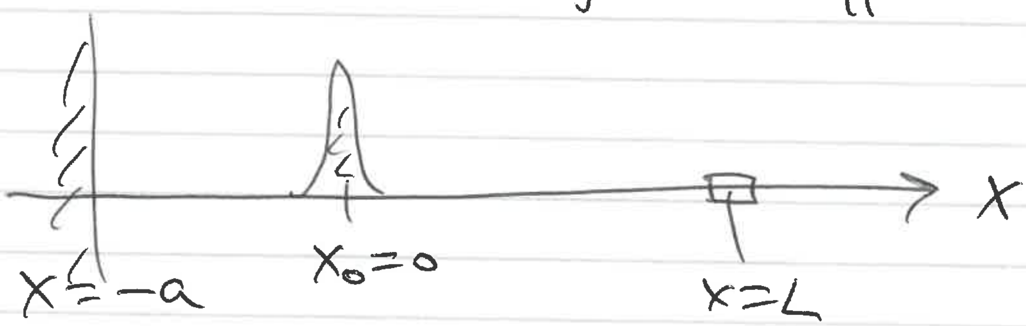
$$\boxed{\tau(x_0) = \frac{1}{D}\int_{x_0}^{\boxed{L}} e^{\beta V(x)} dx \int_{\boxed{\cdot}}^{x} e^{-\beta V(y)} dy}$$

Very promising result, for Wiener SDE.

Examples

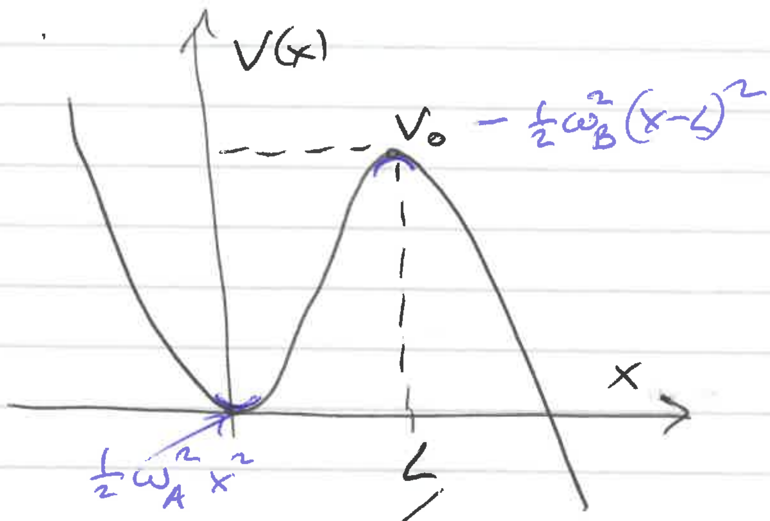
free diffusion

⓪



$$\tau = \frac{1}{D}\int_0^L dx \int_{-a}^{x} dy = \frac{1}{D}\int_0^L dx\,(x+a) = \frac{1}{2D}(L+2a)L$$

⊙ Kramers escape problem



Using MFPT method:

find the time to reach $x = L$, starting from $x=0$

$$\tau = \frac{1}{D}\int_{0}^{L} e^{\beta V(x)}\,dx \int_{0}^{x} e^{-\beta V(y)}\,dy$$

X_0

or $-\infty$, it doesn't matter

dominated by the min V ...

$\sqrt{\frac{2\pi kT}{\omega_A^2}}$

upper limit x irrelevant

dominated by max V

$$\tau = \frac{1}{D} \cdot \underbrace{e^{\beta V_0} \sqrt{\frac{\pi kT}{2\omega_B^2}}}_{\text{Half of Gaussian}} \cdot \sqrt{\frac{2\pi kT}{\omega_A^2}}$$

After reaching the top: ½ chance of escape!

$$\text{rate} = \frac{1}{2} \cdot \frac{D}{\pi kT} \omega_B \omega_A \cdot e^{-\beta V_0}$$

Classical Kramers solution uses flux = constant assumption:

$$J = -D e^{-\beta V(x)} \frac{\partial}{\partial x}\left[e^{\beta V(x)} P(x)\right]$$

integrate!

$$\underbrace{J \cdot \int_0^\infty e^{\beta V(x)}\,dx}_{\text{picks the maximum!}} = -D\, e^{\beta V(x)} P(x) \Big|_0^\infty$$

$V(\infty) \to -\infty$
$V(0) = 0$

$$J \cdot e^{\beta V_0} \sqrt{\frac{2\pi kT}{\omega_B^2}} = D \cdot P(x=0)$$

$$J = D \sqrt{\frac{\omega_B^2}{2\pi kT}}\, e^{-\beta V_0} \cdot P(x=0)$$

already in place!

Need to find $P(x=0)$:

$$\int_{x \approx 0} dN = \int P(x=0)\, e^{-\beta V(x)}\,dx$$

$$N_0 = P(x=0) \cdot \sqrt{\frac{2\pi kT}{\omega_A^2}}$$

rate → $k = \frac{J}{N} = D \frac{\omega_B \omega_A}{2\pi kT} e^{-\beta V_0}$