Lecture 9

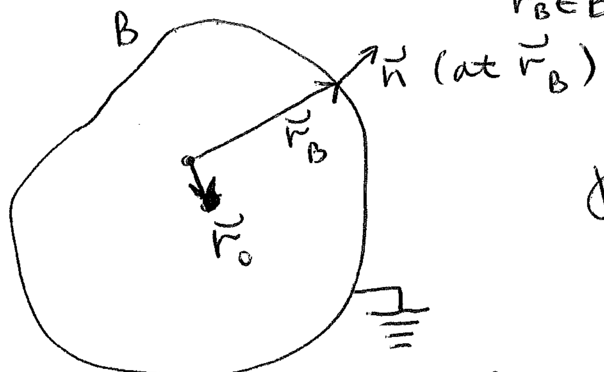
Connections between diffusion and electrostatics

Consider
$$\begin{cases} C_t = D\nabla^2 C \\ C(\vec r, t=0) = \delta(\vec r - \vec r_0) \\ C(\underbrace{\vec r \in B}_{\equiv \vec r_B}) = 0 \quad \text{absorbing boundary} \end{cases}$$

Then $j(\vec r_B, t) = -D\underbrace{\nabla_n}_{\equiv \vec n \cdot \frac{\partial}{\partial \vec r}} C$ is the flux into the boundary at $\vec r_B$,
$\uparrow$ scalar

and $\int_0^\infty dt\, j(\vec r_B, t) \equiv \mathcal{E}(\vec r_B)$ is the eventual exit prob. through $\vec r_B$

$$\int_{\vec r_B \in B} d\vec r\, \mathcal{E}(\vec r_B) = 1$$



To simplify the problem, consider

$$\varphi(\vec r) = \int_0^\infty dt\, C(\vec r, t).$$

Then $\int_0^\infty dt\, C_t = \underbrace{C(\vec r, \infty)}_{0} - \underbrace{C(\vec r, 0)}_{\delta(\vec r - \vec r_0)} =$

$= -\delta(\vec r - \vec r_0)$,

and we have

$$-\delta(\vec r - \vec r_0) = D\nabla^2 \varphi.$$

So φ is like the electrostatic potential,

and

$\mathcal{E}(\vec{r}_B)$ is like electric field for a point charge of magnitude $q = \frac{1}{D\underbrace{\Omega_d}}$

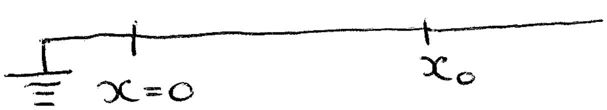
surface area of a unit sphere in d dim's, e.g. 4π in 3D

Indeed, $\mathcal{E}(\vec{r}_B) = \int_0^\infty dt\, j(r_B, t) =$

$$= -D \int_0^\infty dt\, \nabla_{\vec{n}} C = -D \nabla_{\vec{n}} \varphi .$$

The boundary is grounded $(\varphi(\vec{r}_B) = 0)$ due to absorbing BCs.

<u>Semi-infinite</u> <u>1D line</u>



QQ:

1. What is the prob. of hitting $x=0$ at t for the 1st time?
2. What is the average hitting time?

Here, $\begin{cases} C_t = D C_{xx}, \\ C(x, t=0) = \delta(x - x_0), \\ C(x=0, t) = 0 \end{cases}$

Let's use the image method:

Then $$C(x,t) = \frac{1}{\sqrt{4\pi D t}}\left[e^{-(x-x_0)^2/4Dt} - e^{-(x+x_0)^2/4Dt} \right]$$

satisfies the eq'n & the BCs.

Note that $$\left.\frac{\partial c}{\partial x}\right|_{x=0} = \frac{1}{\pi^{1/2}(4Dt)^{3/2}} \times$$

$$\times \left.\left[-2(x-x_0)\, e^{-(x-x_0)^2/4Dt} + 2(x+x_0)\, e^{-(x+x_0)^2/4Dt} \right]\right|_{x=0} =$$

$$= \underline{\underline{\frac{x_0}{(4\pi)^{1/2}(Dt)^{3/2}}\, e^{-x_0^2/4Dt}}}.$$

Then $$j(x=0,t) = -D\left.\frac{\partial c}{\partial x}\right|_{x=0} = -\frac{x_0}{\sqrt{4\pi D t^3}}\, e^{-x_0^2/4Dt}.$$

Eventual exit prob. is given by

$$f(x=0) = \int_0^\infty dt\, |j(x=0,t)| =$$

$$= +\frac{x_0}{\sqrt{4\pi D}} \int_0^\infty \frac{dt}{t^{3/2}}\, e^{-x_0^2/4Dt} = \left\{ \begin{array}{l} u^2 = \frac{1}{t}, \\ dt = -2\frac{du}{u^3} \end{array} \right.$$

$$= \frac{x_0}{\sqrt{4\pi D}} \underbrace{2\int_0^\infty du\, e^{-\frac{x_0^2}{4D}u^2}}_{= \int_{-\infty}^{\infty} du \ldots = \frac{\sqrt{4\pi D}}{x_0}} = 1, \text{ as } \underline{\underline{\text{expected}}}$$

Moreover,

$$\langle t \rangle = \frac{\int_0^\infty dt\, t\, j(x=0,t)}{\underbrace{\int_0^\infty dt\, j(x=0,t)}_{=1}} = \infty$$

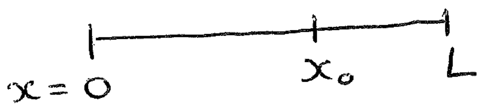
on average, takes infinite time to get absorbed

Indeed, $\int_0^\infty dt\, t\, j(x=0,t) \sim \int_0^\infty \frac{du}{u^2} e^{-\frac{x_0^2}{4D} u^2}$ diverges.

Higher moments diverge as well.

Finite 1D interval

QQ:



1. What is the survival prob. $S(t)$?
2. What is the 1st passage prob. (FPP) to $\emptyset$ or L, at time t?
3. What are the eventual exit probs. to $\emptyset$ or L?
4. What is the average time $t(x_0)$ to reach $\emptyset$ or L?
5. What are the conditional average times to reach L $(t_+(x_0))$ or $\emptyset$ $(t_-(x_0))$?

We have
$$\begin{cases} C_t = D\, C_{xx}, \\ C(x,t=0) = \delta(x-x_0), \\ C(0,t) = C(L,t) = 0 \end{cases}$$

The diff'n eq'n is like a time-dep. SE in a square-well potential:

$$\begin{cases} V(x)=0, & 0<x<L \\ V(x)=\infty & \text{otherwise} \end{cases}$$

with $D \leftrightarrow -\dfrac{\hbar^2}{2m}$

So we can use SE technique to solve this eq'n.

1. Survival prob. $S(t)$.

Try variable separation on $C(x,t)$:

$$C(x,t) = f(t)\, g(x).$$

Then $\dot{f} g = D f g''$, or

$$\frac{\dot{f}}{f} = D \frac{g''}{g} \Rightarrow D^{-1}\frac{\dot{f}}{f} = \frac{g''}{g} \equiv \underbrace{-k}_{\text{const}}$$

This gives $g'' = -kg$, or

$$g \sim \sin\Big(\underbrace{\frac{\pi n}{L}}_{\sqrt{k}}\, x\Big), \quad n \in \mathbb{Z}$$
to satisfy the BCs

Furthermore,

$$\dot{f} = -Dkf \quad \text{gives}$$

$$f \sim e^{-D\underbrace{\left(\frac{\pi n}{L}\right)^2}_{k} t}$$

So, $$C(x,t) = \frac{2}{L}\sum_{n=1}^{\infty} \sin\frac{n\pi x_0}{L}\sin\frac{n\pi x}{L} \times$$
$$\times\, e^{-D\left(\frac{\pi n}{L}\right)^2 t} \qquad (*)$$

Note that $C(0,t) = C(L,t) = 0$ by construction.

Also, the $n=0$ term is $\emptyset$ everywhere and the expression is symm. wrt n.

Indeed, consider

$$C(x,0) = \delta(x-x_0) = \sum_{n=1}^{\infty} A_n \sin\frac{n\pi x}{L}$$

dot with $\int_0^L dx \sin\left(\frac{n'\pi x}{L}\right) *$ on both sides:

$n' = 1, 2, 3, \ldots$

$$\sin\frac{n'\pi x_0}{L} = \sum_{n=1}^{\infty} A_n \int_0^L dx \sin\frac{n'\pi x}{L}\sin\frac{n\pi x}{L} =$$

$$= \sum_{n=1}^{\infty} A_n \frac{1}{2}\int_0^L dx \left[\cos\left(\frac{\pi x}{L}(n-n')\right) - \underbrace{\cos\left(\frac{\pi x}{L}(n+n')\right)}_{\substack{\text{will always give } \emptyset \\ \text{since } n, n' > 0}}\right].$$

$$\int_0^L dx \cos\left(\frac{\pi x}{L}(n-n')\right) = \frac{L}{\pi(n-n')} \sin(\pi(n-n')) =$$

$$= \begin{cases} 0 & n \neq n' \\ L & n = n' \end{cases}$$

But then $\quad \sin \frac{n'\pi x_0}{L} = A_{n'} \frac{L}{2}$, or

$$A_n = \frac{2}{L} \sin \frac{n\pi x_0}{L}$$, which gives (*)

Finally, $S(t) = \int_0^L dx\, c(x,t) \sim \underbrace{e^{-D\pi^2 t/L^2}}_{\text{the slowest-decaying mode } (n=1)} \equiv e^{-t/\tau}$,

where $\tau \sim \frac{L^2}{D}$ is the diffusion time-scale.

(2.) FPP $\Rightarrow$ use Laplace domain

$$c(x,s) = \int_0^\infty dt\, e^{-st} c(x,t)$$

$$\int_0^\infty dt\, e^{-st} \frac{\partial c(x,t)}{\partial t} = e^{-st} c(x,t)\Big|_0^\infty +$$

$$+ s\int_0^\infty dt\, e^{-st} c(x,t) = -c(x,0) + s\,c(x,s).$$

With $c \equiv c(x,s)$, we have:

$$\begin{cases} sc - \delta(x-x_0) = Dc'', \\ c(0,s) = c(L,s) = 0 \end{cases}$$

This is solved by

$$C(x,s) = \frac{1}{\sqrt{Ds}} \frac{\sinh\left(\sqrt{\frac{s}{D}}\, x_<\right) \sinh\left(\sqrt{\frac{s}{D}}(L - x_>)\right)}{\sinh\left(\sqrt{\frac{s}{D}}\, L\right)}$$

$$\begin{cases} x_< = \min(x, x_0) \\ x_> = \max(x, x_0) \end{cases}$$

Indeed, $\quad C(0,s) = C(L,s) = 0$.

$$[C(x,s)] = \frac{T}{L} \text{ in 1D}$$

$$[s] = \frac{1}{T} \quad \Rightarrow \left[\frac{1}{\sqrt{Ds}}\right] = \frac{1}{\sqrt{L^2/T^2}} = \frac{T}{L},$$

as expected

Finally,

$$\lim_{\epsilon\to 0} DC'\Big|_{x_0-\epsilon}^{x_0+\epsilon} = \frac{D}{\sqrt{Ds}}\left[\frac{\sinh\left(\sqrt{\frac{s}{D}}\, x_0\right)}{\sinh\left(\sqrt{\frac{s}{D}}\, L\right)}\left(-\sqrt{\frac{s}{D}}\right)\cosh\left(\sqrt{\frac{s}{D}}(L-x_0)\right)\right.$$

$$\left. - \sqrt{\frac{s}{D}} \cosh\left(\sqrt{\frac{s}{D}}\, x_0\right) \frac{\sinh\left(\sqrt{\frac{s}{D}}(L-x_0)\right)}{\sinh\left(\sqrt{\frac{s}{D}}\, L\right)}\right] =$$

$$= -\frac{1}{\sinh\left(\sqrt{\frac{s}{D}}\, L\right)} \sinh\left(\sqrt{\frac{s}{D}}(\cancel{x_0} + L - \cancel{x_0})\right) = -1,$$

as expected

$$-\int_{x_0-\epsilon}^{x_0+\epsilon} dx\, \delta(x - x_0) = -1.$$

But then

$$\tilde{j}_+(s) = -D \left.\frac{\partial c(x,s)}{\partial x}\right|_{x=L} =$$

$-D$

$$= \frac{1}{\sqrt{Ds}} \frac{\sinh\left(\sqrt{\frac{s}{D}}\, x_0\right)}{\sinh\left(\sqrt{\frac{s}{D}}\, L\right)} \sqrt{\frac{s}{D}}\,(-1) =$$

$$= \frac{\sinh\left(\sqrt{\frac{s}{D}}\, x_0\right)}{\sinh\left(\sqrt{\frac{s}{D}}\, L\right)}.$$

$$\tilde{j}_-(s) = -D \left.\frac{\partial c(x,s)}{\partial x}\right|_{x=0} = - \frac{\sinh\left(\sqrt{\frac{s}{D}}\,(L-x_0)\right)}{\sinh\left(\sqrt{\frac{s}{D}}\, L\right)}$$

Eventual exit prob.:

$$\mathcal{E}_-(x_0) = \left|\int_0^\infty dt\, j_-(0,t)\right| = \left|\left.\int_0^\infty dt\, j_-(0,t)\, e^{-st}\right|_{s=0}\right| =$$

into $x=0$ ↑ ↑ starting point

$$= |\tilde{j}_-(s=0)| = 1 - \frac{x_0}{L}.$$

Likewise,

$$\mathcal{E}_+(x_0) = |\tilde{j}_+(s=0)| = \frac{x_0}{L}.$$

Note that $\mathcal{E}_+(x_0) + \mathcal{E}_-(x_0) = 1$, as expected

Finally, consider

$$t(x) = \frac{\int_0^\infty dt\, t\, [\overbrace{j_-(t) + j_+(t)}^{\equiv j(t)}]}{\underbrace{\int_0^\infty dt\, [j_-(t) + j_+(t)]}_{=1}} \;\text{(=)}$$

$=1$ since you leave the system eventually

$\parallel$ "average time to reach $\emptyset$ or L starting from x"

$$\text{(=)}\; \int_0^\infty dt\, t\, j(t)\, e^{-st}\Big|_{s=0} = \left(-\frac{\partial}{\partial s}\int_0^\infty dt\, j(t)\, e^{-st}\right)\Big|_{s=0} =$$

$$= -\frac{\partial \tilde{j}(s)}{\partial s}\Big|_{s=0}$$

In this way, one can obtain

$$t(x) = \frac{x(L-x)}{2D}\,,$$ as well as

$t_+(x)$ & $t_-(x)$.

However, there is a more straightforward approach, as discussed next.