§4 Dynkin equation for mean first passage times.

- initial condition

$$P(x,0) = \delta(x - x_1)$$

- absorbing b.c. at x_2

$$P(x_2, t) = 0, \quad \dot{P} = -\nabla J.$$

$J(x_2,t) =$ current to absorbing b.c.

Def: Mean first passage time (MFPT)

$$T(x_2|x_1) = \int_0^\infty dt \; t \, J(x_2, t). \qquad [s]$$

Aim: Eqn. for T.

$$x_1 \xrightarrow[\Delta t]{} x' \xrightarrow[T(x_2|x')]{} x_2 \qquad , \; x' < x_2 .$$

$$(*) \quad T(x_2|x_1) = \Delta t + \int_{-\infty}^{x_2} dx' \, T(x_2|x') \cdot P(x', \Delta t | x_1, 0)$$

$$\frac{d}{d\Delta t}: \quad 0 = 1 + \int_{-\infty}^{x_2} dx' \, T(x_2|x') \cdot L_{x'} P$$

$$= 1 + \int_{-\infty}^{x_2} dx' \, L^*_{x'} T(x_2|x') \, P.$$

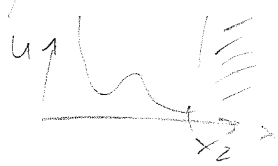
$$\Delta t \to 0: \quad P(x', \Delta t | x_1, 0) \longrightarrow \delta(x' - x_1)$$

$$\boxed{-1 = L^*_{x'} T(x_2|x_1)} \qquad T(x_2|x_2) = 0.$$

= Dynkin equation

Apply to diffusion in a potential

$$\gamma \dot{x} = -\frac{\partial U}{\partial x} + \xi(t)$$



$$\langle \xi(t)\xi(t')\rangle = 2D\,\delta(t-t'), \quad D = \frac{k_B T}{\gamma}$$

- Let $v = \frac{\partial}{\partial x_1} T(x_2|x_1)$ short-hand

- Dynkin: $D v' - \frac{U'}{\gamma} v = -1$
- Multiply $\frac{1}{D}\exp(-\beta U)$, $\beta = \frac{1}{k_B T}$

$$\underbrace{v'\exp(-\beta U) - \beta U' v \exp(-\beta U)}_{\frac{d}{dx_1}[v\exp(-\beta U)]} = -\frac{1}{D}\exp(-\beta U)$$

$$\Rightarrow v = -\frac{1}{D}\exp(+\beta U)\left[\int_{-\infty}^{x_1} dx' \exp(-\beta U) + C\right]$$

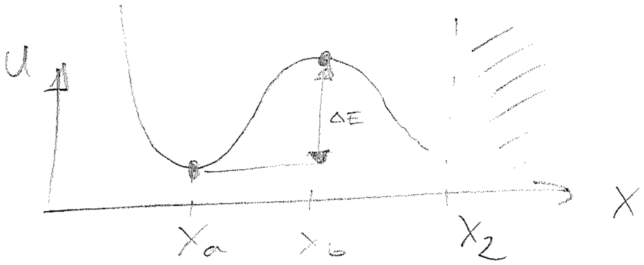
- We assume $\lim_{x\to-\infty} U(x) = +\infty$.

Then $|v| < \infty \Rightarrow C = 0$.

$$T(x_2|x_1) = +\frac{1}{D}\int_{x_1}^{x_2} dx' \exp(\beta U(x')) \cdot \int_{-\infty}^{x'} dx'' \exp(-\beta U(x''))$$

$$\left[-\int_{x_2}^{x_1} dx' \Rightarrow +\int_{x_1}^{x_2} dx', \quad T(x_2|x_2) = 0\right]$$

Special case: Kramer's escape rate theory



$$T(x_2|x_1) = \int dx' \int dx'' \quad \dots$$

Assume: $\beta \Delta u \gg 1$:

- $\int dx''$: sizeable only near x_a.
- $\int dx'$: — " — x_b.

Quadratic expansion

$$U(x'') = U(x_a) + \underbrace{\tfrac{1}{2} U''(x_a)}_{\substack{k_a = \gamma/T_a \\ \text{el. stiffness}}} (x'' - x_a)^2$$

$$U(x') = U(x_b) + \underbrace{\tfrac{1}{2} U''(x_b)}_{-\gamma/T_b} (x' - x_b)^2$$

- $$\int_{-\infty}^{x'} dx'' \exp\left[-\tfrac{1}{2}\beta u''(x_a)(x'' - x_a)^2\right]$$

$$\approx \int_{-\infty}^{\infty} \quad \text{— " —} \quad = \sqrt{2\pi\sigma^2}$$

$$\sigma^2 = T_a/\beta\gamma.$$

- $$\int_{x_1}^{x_2} dx' \exp\left[+\tfrac{1}{2}\beta\, u''(x_b)(x'' - x_b)^2\right]$$

$$\approx \int_{-\infty}^{\infty} \quad \text{— " —} \quad = \sqrt{\frac{2\pi T_b}{\beta\gamma}}$$

$$\bullet \quad \tau(x_2|x_1) = \frac{1}{D} \cdot \frac{2\pi\sqrt{\tau_a \tau_b}}{\beta \gamma} \cdot \exp \beta\left(U(x_b) - U(x_a)\right)$$

$$= 2\pi\sqrt{\tau_a \tau_b} \; \exp + \beta \Delta E$$

$\Rightarrow$ Kramer's escape rate

$$r = \frac{1}{\tau(x_2|x_1)} \sim \underbrace{\exp(-\beta \Delta E)}_{\text{Arrhenius factor.}}$$

Diffusion to capture

Example: diffusing particle released between two absorbing plates.

$x_1 \quad x_0 \qquad x_2$

$$P(x,t\,|\,x_0,0) = -D\,\partial_{x_1}$$

Probability to become absorbed at $x=x_1$

$$\Pi_1(x_0) = \int_0^\infty dt\ \partial(x_1,t\,|\,x_0,0).$$

Solution 1

$$\Pi_1(x_1) = 1, \qquad \Pi_1(x_2) = 0.$$

$$\frac{\partial}{\partial x_0}\Pi_1 = \int_0^\infty dt\ \frac{\partial}{\partial x_0}\underbrace{\partial(x_1,t\,|\,x_0,0)}_{\partial(x_1,0\,|\,x_0,-t)}$$

[illegible]

$$= \int_0^\infty dt\ \mathcal{L}^{*}_{x_0} P \qquad -D\frac{\partial}{\partial x_0}P(x_1,0\,|\,x_0,-t)$$

$$= \int_0^\infty dt\ \frac{d}{dt}\underbrace{P(x_1,0\,|\,x_0,-t)}_{=0} = 0.$$

$\Rightarrow \quad \Pi_1(x_0)$ linear

$$\Rightarrow \quad \Pi_1(x_0) = \frac{x_2-x_0}{x_1-x_0}.$$

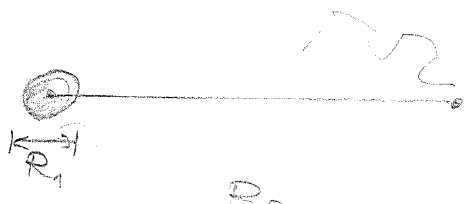
Solution 2: Method of images

$$P(x,t) = N(x_0, 2Dt) - N(2x_1-x_0, 2Dt)$$
$$- N(2x_2-x_0, 2Dt)$$

Polya's theorem

Diffusion in $\mathbb{R}^d$

to a d-dimensional absorbing ball.



$P(R_0)$ = probability to become absorbed

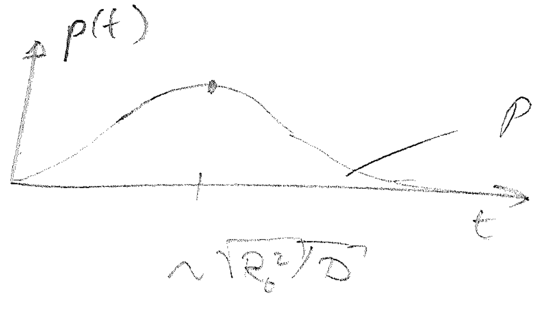
$d=1$: $P(R_0) = 1$.

$d=2$: — " —

$d=3$: $P(R_0) = \frac{R_1}{R_0}$

Conditional mean first passage time diverges. (but most traj. that find the target found it for $t \sim R_0^2/D$)

Arrival times



$\sim t^{-\frac{3}{2}} \exp\left(-\frac{(R_0-R_1)^2}{4Dt}\right)$

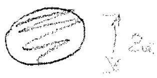
[Infinite reservoir]

$$0 \stackrel{!}{=} \dot{c} = D \nabla^2 c$$

$$c(\underline{x}) = c_0 \quad \text{for } |\underline{x}| \to \infty$$

$$c(\underline{x}) = 0 \quad \text{for } \underline{x} \in S = \text{absorbing surface.}$$

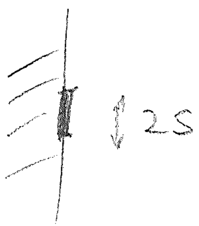
• Diffusion to an absorbing sphere



$$J = 4\pi D a c_0 .$$

[= diffusion equation formally equivalent to Poisson eqn. for electrostatic potential
→ [Jack]].

• Diffusion to a disk-like absorber.



$$J = 4 D s \cdot c_0$$