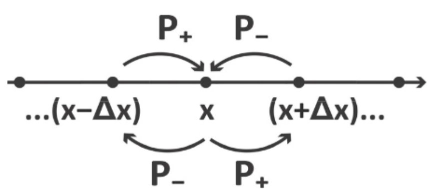
11.2: Markov Chain and Stochastic Processes

Working again with the same problem in one dimension, let's try and write an equation of motion for the **random walk probability distribution**: $P(x,t)$.

- This is an example of a stochastic process, in which the evolution of a system in time and space has a random variable that needs to be treated statistically.
- As above, the movement of a walker only depends on the position where it is at, and not on any preceding steps. When the system has no memory of where it was earlier, we call it a **Markovian system**.
- Generally speaking, there are many flavors of a stochastic problem in which you describe the probability of being at a position x at time t, and these can be categorized by whether x and t are treated as continuous or discrete variables. The class of problem we are discussing with discrete x and t points is known as a **Markov Chain**. The case where space is treated discretely and time continuously results in a **Master Equation**, whereas a Langevin equation or Fokker–Planck equation describes the case of continuous x and t.
- To describe the walkers time-dependence, we relate the probability distribution at one point in time, $P(x,t+\Delta t)$, to the probability distribution for the preceding time step, $P(x,t)$ in terms of the probabilities of a walker making a step to the right (P_+) or to the left (P_-) during the interval Δt. Note, when $P_+ \neq P_-$, there is a **stepping bias** in the system. If $P_+ + P_- < 1$, there is a resistance to stepping either as a result of an energy barrier or excluded volume on the chain.
- In addition to the loss of probability by stepping away from x to the left or right, we need to account for the steps from adjacent sites that end at x.



Then the probability of observing the particle at position x during the interval Δt is:

$$\begin{aligned} P(x,t+\Delta t) &= P(x,t) - P_+ \cdot P(x,t) - P_- \cdot P(x,t) + P_+ \cdot P(x-\Delta x,t) + P_- \cdot P(x+\Delta x,t) \\ &= (1-P_+-P_-)\cdot P(x,t) + P_+ \cdot P(x-\Delta x,t) + P_- \cdot P(x+\Delta x,t) \\ &= P(x,t) + P_+[P(x-\Delta x,t) - P(x,t)] + P_-[P(x+\Delta x,t) - P(x,t)] \end{aligned}$$

and the net change probability is

$$P(x,t+\Delta t) - P(x,t) = P_+[P(x-\Delta x,t) - P(x,t)] + P_-[P(x+\Delta x,t) - P(x,t)]$$

We can cast this as a time-derivative if we divide the change of probability by the time-step Δt:

$$\begin{aligned} \frac{\partial P}{\partial t} &= \frac{P(x,t+\Delta t) - P(x,t)}{\Delta t} \\ &= P_+[P(x-\Delta x,t) - P(x,t)] + P_-[P(x+\Delta x,t) - P(x,t)] \\ &= P_+\Delta P_-(x,t) + P_-\Delta P_+(x,t) \end{aligned} \tag{11.2.1}$$

Where $P_\pm = P_\pm/\Delta t$ is the right and left stepping rate, and $\Delta P_\pm(x,t) = P(x\pm\Delta x,t) - P(x,t)$

We would like to show that this random walk model results in a diffusion equation for the probability density ρ(x,t) we deduced in Equation (11.1.5). To simplify, we assume that the left and right stepping probabilities $P_+ = P_- = \frac{1}{2}$, and substitute

$$P(x,t) = \rho(x,t)dx$$

into Equation (11.2.1):

$$\frac{\partial \rho}{\partial t} = P[\rho(x-\Delta x,t) - 2\rho(x,t) + \rho(x+\Delta x,t)]$$

where $P = 1/2\,\Delta t$. We then expand these probability density terms in x as

$$\rho(x,t) = \rho(0,t) + \frac{\partial \rho}{\partial x} x + \frac{1}{2}\frac{\partial^2 \rho}{\partial x^2} x^2$$

and find that the probability density follows a diffusion equation

$$\frac{\partial \rho}{\partial t} = D\frac{\partial^2 \rho}{\partial x^2}$$

where $D = \Delta x^2 / 2\Delta t$.

Reading Materials

- A. Nitzan, Chemical Dynamics in Condensed Phases: Relaxation, Transfer and Reactions in Condensed Molecular Systems. (Oxford University Press, New York, 2006).