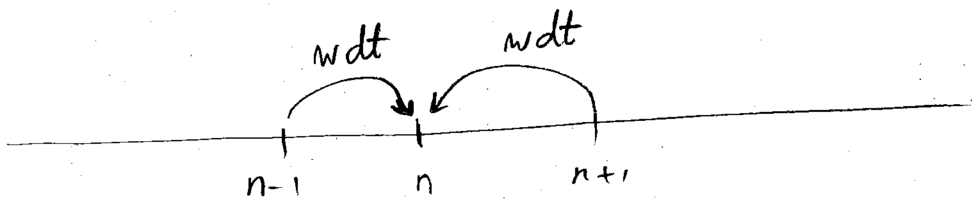
Microstates and Macrostates

(1) Jumping on a discrete one-dimensional space and in continuous time



The transition probability rate $= w$

$$P(n, t+dt) = P(n-1, t)\, w\,dt + P(n+1, t)\, w\,dt + \underbrace{(1 - w\,dt - w\,dt)}_{\text{probability that in the time } dt \text{ the particle remains at the position } n} P(n,t)$$

$$\Rightarrow \frac{P(n, t+dt) - P(n,t)}{dt} = P(n-1, t)\, w + P(n+1, t)\, w - 2w\, P(n,t)$$

so $$\boxed{\frac{\partial P}{\partial t} = P(n-1, t)\, w + P(n+1, t)\, w - 2w\, P(n,t)} \quad (1)$$

Master Equation for $P(n,t)$.

Stationary state

$$P(n,t) = P(n)$$ INDEPENDENT OF TIME t

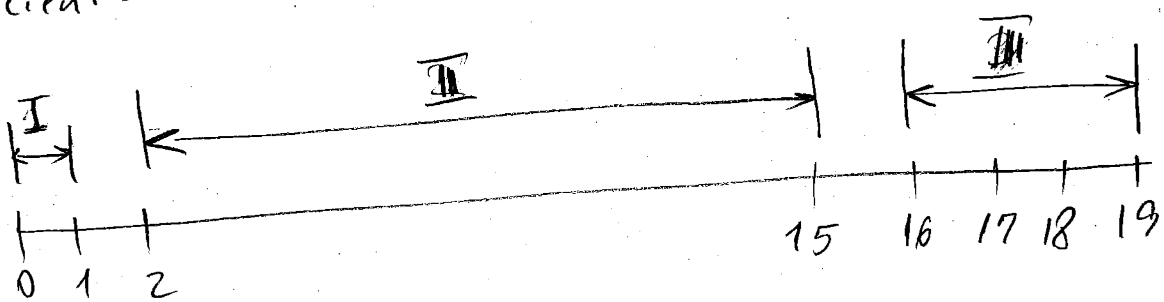
This implies $\boxed{\frac{\partial P}{\partial t} = 0}$ stationarity condition

From (1)

$$P_{stat}(n-1)\,w + P_{stat}(n+1)\,w - 2w\,P_{stat}(n) = 0$$

Solution $P_{stat}(n) =$ CONSTANT for all n.

(2) Take the example from the book of Gillespie "Markov Processes, An introduction for physical scientists"



$0, 1, 2, \ldots 19$] microstates

I, II, III] macrostates

$$P(\text{to find the system in I}) = \frac{2}{20}$$

$$P(\text{macrostate II}) = \frac{14}{20}$$

$$P(\text{macrostate III}) = \frac{4}{20}$$

II is the equilibrium macrostate

Entropy: $S(\text{macrostate}) = k_B \ln [N(\text{macrostate})]$ # of microstates in the macrostate

$N(\text{macrostate I}) = 2$

$N(\text{macrostate II}) = 14$

$N(\text{macrostate III}) = 4$

Paradoxes solved

(1) $\text{Prob}\{15 \to 16 \text{ in } [t, t+dt) \mid X(-\infty) = n_0\} =$

$= \text{Prob}\{X(t+dt) = 16 \mid X(t) = 15\} \cdot \text{Prob}\{X(t) = 15 \mid X(-\infty) = n_0\} = w\,dt \cdot \frac{1}{N+1}$

(2) $\text{Prob}\{\overline{\text{II}} \to \overline{\text{III}} \text{ in } [t, t+dt) \mid X(t) \text{ in } \overline{\text{II}}\} =$

$= \text{Prob}\{X(t+dt) = 16 \mid X(t) = 15\} \cdot$

$\cdot \text{Prob}\{X(t) = 15 \mid X(t) \text{ in } \overline{\text{II}}\} =$

$$= w\, dt \cdot \frac{1}{N(\text{macrostate } \overline{\text{II}})}$$

(3) $\text{Prob}\{16 \to 15 \text{ in } [t, t+dt) \mid X(-\infty) = n_0\} =$

$= \text{Prob}\{X(t+dt) = 15 \mid X(t) = 16\} \cdot \text{Prob}\{X(t) = 16 \mid X(-\infty) = n_0\}$

$$= w\, dt \quad \frac{1}{N+1}$$

(4) $\text{Prob}\{\overline{\text{III}} \to \overline{\text{II}} \text{ in } [t, t+dt) \mid X(t) \text{ in } \overline{\text{III}}\} =$

$= \text{Prob}\{X(t+dt) = 15 \mid X(t) = 16\} \cdot \text{Prob}\{X(t) = 16 \mid X(t) \text{ in } \overline{\text{III}}\}$

$$= w \cdot dt \quad \frac{1}{N(\text{macrostate } \overline{\text{III}})}$$

<u>Compare</u>

$$(*) \quad \frac{\text{Prob}\{15 \to 16 \text{ in } [t, t+dt) \mid X(-\infty) = n_0\}}{\text{Prob}\{16 \to 15 \text{ in } [t, t+dt) \mid X(-\infty) = n_0\}} = 1$$

$$(**) \quad \frac{\text{Prob}\{\overline{\text{II}} \to \overline{\text{III}} \text{ in } [t, t+dt) \mid X(t) \text{ in } \overline{\text{II}}\}}{\text{Prob}\{\overline{\text{III}} \to \overline{\text{II}} \text{ in } [t, t+dt) \mid X(t) \text{ in } \overline{\text{III}}\}} = \frac{N(\overline{\text{III}})}{N(\overline{\text{II}})} \ll 1$$

(*) dynamical democracy when the system is viewed on the microscopic level

(**) dynamical asymmetry when the system is studied on the macroscopic level.

It essentially says that "transitions that decrease the system's entropy are less likely to occur than transitions that increase the system's entropy".