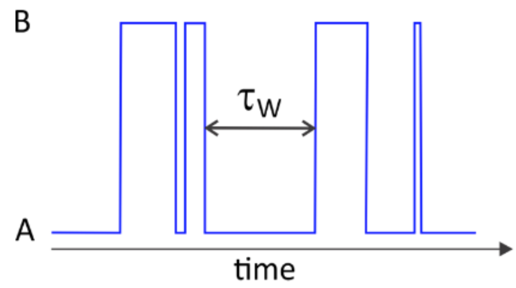
22.4: Analyzing Trajectories

Analyzing Trajectories

Waiting-Time Distributions, P



τ_W: Waiting time between arriving and leaving a state or P(k,t)

P_k: Probability of making k jumps during a time interval, t. → Survival probability

P_w: Probability of waiting a time τ_w between jumps? Waiting time distribution → FPT distribution

Let's relate these...

Assume independent events. No memory of history – where it was in trajectory.

Flux: $\dfrac{dP_R}{dt} = J$

J: Probability of jump during Δt. Δt is small enough that $J \ll 1$, but long enough to lose memory of earlier configurations.

The probability of seeing k jumps during a time interval t, where t is divided into N intervals of width Δt (t = NΔt) is given by the binomial distribution

$$P(k,N) = \frac{N!}{k!(N-k)!} J^k (1-J)^{N-k} \tag{22.4.1}$$

Here $N \gg k$. Define rate λ in terms of the average number of jumps per unit time

$$\lambda = \frac{\langle k \rangle}{t} = \frac{1}{\langle \tau_W \rangle}$$

$$J = \lambda \Delta t \to J = \frac{\lambda t}{N}$$

Substituting this into eq. (22.4.1) Error! Reference source not found.. For $N \gg k$, recognize

$$(1-J)^{N-k} \approx (1-J)^N = \left(1 - \frac{\lambda t}{N}\right)^N \approx e^{-\lambda t}$$

The last step is exact for lim N → ∞.

Poisson distribution for the number of jumps in time t.

$$\langle P(k,t) \rangle = \langle \lambda t \rangle = \frac{\lambda t}{\langle P^2(k,t) \rangle^{1/2}} = (\lambda t)^{1/2}$$

Fluctuations: $\sigma / \langle P(k,t) \rangle = (\lambda t)^{-1/2}$

OK, now what about P_w the waiting time distribution?

Consider the probability of not jumping during time t:

$$P_k(0,t) = e^{-\lambda t}$$

As you wait longer and longer, the probability that you stay in the initial state drops exponentially. Note that $P_k(0, t)$ is related to P_w by integration over distribution of waiting times.

$$\int_t^\infty P_w(t')dt' = P(0,t) = e^{-\lambda t}$$

$$\int_t^\infty P_w dt \to \text{probability of staying for t}$$

$$\int_0^t P_w dt \rightarrow \text{probability of jumping within t}$$

Probability of jumping between t and t+Δt:

Probability of no decay for time <t decay on last

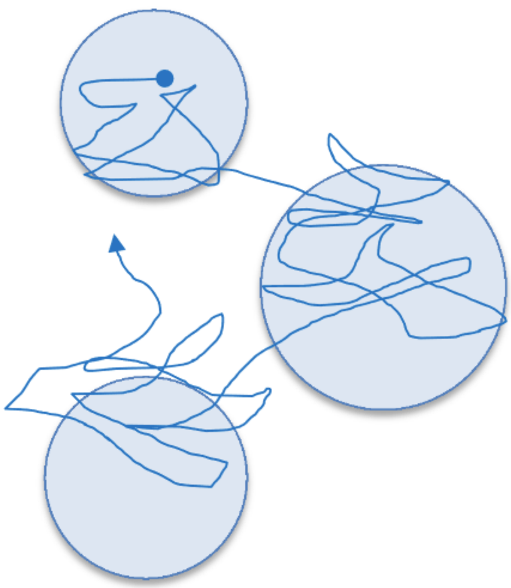
$$\begin{aligned} P_w(t)\Delta t &= \overbrace{(1-\langle k\rangle \Delta t_1)}\,\overbrace{(1-\langle k\rangle \Delta t_2)\ldots(1-\langle k\rangle \Delta t_N)}\,\overbrace{k\Delta t} \\ &= (1-\langle k\rangle \Delta t)^N k\Delta t \approx ke^{-kt}\Delta t \end{aligned}$$

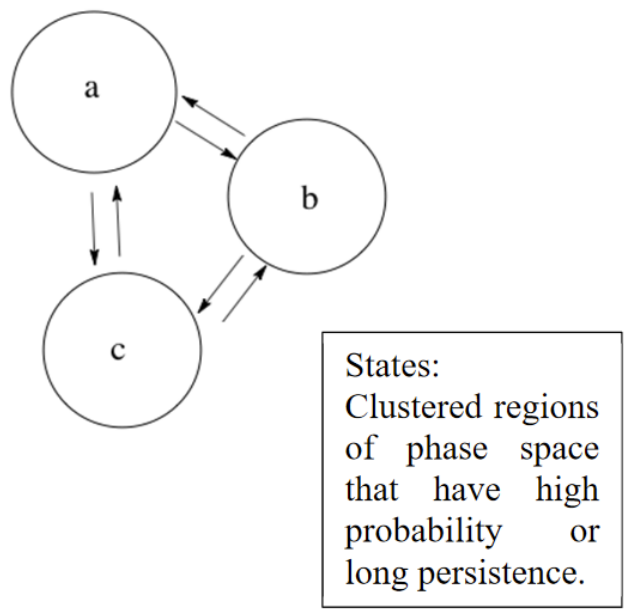
$$\begin{aligned} P_w &= \lambda e^{-\lambda t} \\ \langle\tau\rangle &= \int_0^\infty t p_w(t) t \end{aligned}$$

$$\begin{aligned} \langle\tau_w\rangle &= 1/\lambda \rightarrow \text{the average waiting time is the lifetime} (1/\lambda) \\ \langle\tau_w^2\rangle - \langle\tau_w\rangle^2 &= (1/\lambda)^2 \end{aligned}$$

Reduction of Complex Kinetics from Trajectories

- Integrating over trajectories gives probability densities.
- Need to choose a region of space to integrate over and thereby define states:





- States: Clustered regions of phase space that have high probability or long persistence.
- Markovian states: Spend enough time to forget where you came from.
- Master equation: Coupled first order differential equations for the flow of amplitude between states written in terms of probabilities.

$$\frac{dP_m}{dt} = \sum_n k_{n\rightarrow m} P_n - \sum_n k_{m\rightarrow n} P_m$$

$k_{n\rightarrow m}$ is rate constant for transition from state n to state m. Units: probability/time. Or in matrix form: P=**k**P where **k** is the transition rate matrix. With detailed balance, conservation of population all initial conditions will converge on equilibrium