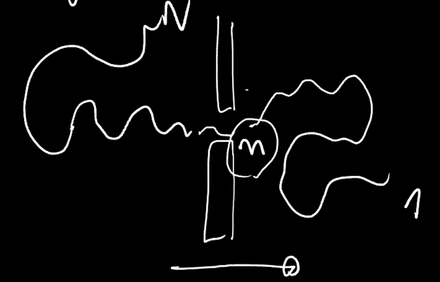
Average exit time:

$x_B \rightarrow$ absorb. boundary $\qquad \beta = 1/k_B T$

$$\langle T(x)\rangle = \frac{1}{D}\int_{x}^{x_B} dy\, \exp\left[\beta U(y)\right] \int_{x_1}^{y} dz\, \exp\left[-\beta U(z)\right]$$

$x_1 \rightarrow$ reflecting boundary

Polymer translocation time



N = # of monomers

n = # of already translocated monomers

n = reaction coord.

$F(n)$ = effective free energy

$D(n)$ = effective diff. coeff.

$$\tau = \int_{1}^{N-1} dn\, \frac{b^2}{D(n)} \exp\left(\beta F(n)\right) \int_{1}^{n} dm\, \exp\left(-\beta F(m)\right)$$

τ: average translocation time

$N-1 \rightarrow$ abs. bound.

1: start. point

b: unit length of a monomer

$1 \rightarrow$ refl. bound.

MARKOV CHAINS (Markov processes)

discrete time, discrete state space

$x(t)$ = stochastic variable

$x \in S = \{S_1, \dots, S_N\}$ $\qquad$ finite state space (but theorems apply to $N \to \infty$)

$t = 1, 2, \dots, n, \dots$

prob. $p(x(t) = S_i) = p_i(t)$

$p_i(t)$ does not depend on previous events $\rightarrow$ NO CORRELATION (NO MEMORY) with MEMORY: $\rightarrow$ conditional probabilities

$$P\left(x(t)=S_i \mid x(t-1)=S_{i_1};\ x(t-2)=S_{i_2}, \ldots, x(t-m)=S_{i_m}\right)$$

process with memory m

$\boxed{m=1}$ $\rightarrow$ MARKOV PROCESS / CHAIN

$$P\left(x(t)=S_j \mid x(t-1)=S_i\right)=W_{ji}$$

transition rates

j arrival state, i initial state

in general $W_{ji}(t)$

HOMOGENEOUS MC W_{ij} does not depend on t

$p_i(t) \rightarrow$ prob. vector (N elements) $\Rightarrow \begin{cases} \sum_{1}^{N} p_i(t)=1 \quad \forall t \\ p_i(t) \geq 0 \quad \forall i, t \end{cases}$

W_{ij} is a STOCHASTIC MATRIX ($N \times N$) $\Rightarrow \begin{cases} W_{ij} \geq 0 \quad \forall i,j \\ \sum_{1}^{N} {}_i W_{ij}=1 \quad \forall j \end{cases}$

Stochastic dynamic rule

$$p_j(t+1)=\sum_i W_{ji}\, p_i(t) \longrightarrow \underbrace{\vec{p}(t+1)=W\vec{p}(t)}$$

After n steps $\vec{p}(t+n)=W^n\vec{p}(t)$

W^n is a stochastic matrix

$$W^n\vec{p}(t)=\underline{W^n W^t}\,\vec{p}(0)=W^{n+t}\vec{p}(0)$$

$\boxed{W^{n+t}=W^nW^t} \rightarrow$ Chapman-Kolmogorov for discrete process

Eigenvalue problem for W: $\det(W - \lambda \mathbb{1}) = 0$

W in general <u>not</u> symmetric → eigenvalues may be complex; right / left eigenvectors

$W \bar{w}^{(\lambda)} = \lambda \bar{w}^{(\lambda)}$ — right eigenvector

One can prove (for W stochastic matrix):

(a) $|\lambda| \leq 1$ | (b) at least one $\lambda = 1$

(c) if $\bar{w}^{(\lambda)}$ for $\lambda \neq 1 \Rightarrow \sum_i w_i^{(\lambda)} = 0$

$\bar{w}^{(1)}$ is a STATIONARY DISTR. for the MARKOV CHAIN

$$W \bar{w}^{(1)} = \bar{w}^{(1)} \Rightarrow \text{if } \bar{p}(0) = \bar{w}^{(1)}$$

$$\bar{p}(t) = \bar{p}(0) \quad \forall t$$

CONDITIONS FOR <u>UNIQUENESS</u> OF AND <u>CONVERGENCE</u> to STATIONARY DISTR.

(1) ACCESSIBILITY → S_j accessible from S_i if $\exists\, t > 0 \,/\, (W^t)_{ji} > 0$

(2) IRREDUCIBILITY
— MC is irreducible if all states are accessible from any other states

(3) PERIOD: state S_i with period

$$T = \gcd\{ t > 0 \,/\, (W^t)_{ii} > 0 \}$$

if $T^i = 1$ — state S_i is aperiodic

MC aperiodic → all states are aperiodic

(MC irreducible → all states share same T^i)

(4) state S_i PERSISTENT (RECURRENT)

(always return to S_i in finite time)

T_i = first return time to S_i (random variable)

$T_i = \inf \{ t \geq 1 \mid x(t) = S_i \}$ (given $x(0) = S_i$)

$q_i^{(n)}$ = prob. that $T_i = n \mid x(0) = S_i$

$$\sum_{n=1}^{\infty} q_i^{(n)} \begin{cases} = 1 \to \text{RECURRENT} \\ < 1 \to \text{TRANSIENT} \end{cases}$$

(5) POSITIVE-RECURRENT STATE S_i

Mean recurrence time : $\langle T_i \rangle = \sum_{n=1}^{\infty} n \, q_i^{(n)}$

(for RECURRENT STATES)

if $\langle T_i \rangle < +\infty \Rightarrow S_i$ POSITIVE-RECURRENT

MC is (POS)-RECURRENT if all states are (POS)-RECURRENT

$\boxed{\text{THEOREM 1}}$

(UNIQUENESS)

IRREDUCIBLE AND POS-RECURRENT MARKOV CHAIN → a UNIQUE STAT. DISTRIB. exists

Stat. $W \bar{w}^{(1)} = \bar{w}^{(1)}$; $w_i^{(1)} = 1/\langle T_i \rangle > 0$

$\boxed{\text{THEOREM 2}}$ ERGODIC MC

(CONVERGENCE) (IRRED., POS. RECURR., APERIODIC)

$\Rightarrow$ $\vec{p}(t)$ converges to the unique stat. distr. $\vec{w}^{(1)}$

for any choice of $\vec{p}(0)$

$\forall \vec{p}(0), \forall j$ $\quad \sum_i (W^n)_{ji}\, p_i(0) = p_j(n)$

$$\boxed{\lim_{n\to\infty} p_j(n) = w_j^{(1)}}$$

ergodicity $\Rightarrow$ ensemble averages = time averages

observable f $\rightarrow$ $\langle f \rangle = \bar{f}$

Corollary of Th. 2 $\rightarrow$

$$\boxed{\sum_i f(x_i)\, w_i^{(1)} = \lim_{t\to\infty} \left[\frac{1}{t} \sum_1^t f(x(t)) \right]}$$

- $\boxed{\langle T_j \rangle = \dfrac{1}{w_j^{(1)}}}$ (for IRRED. and POS.-REC. MC)

(Kac lemma)

$T_j^{(m)}$ = m-th return time to S_j (time needed to return to S_j the m-th time after the $(m-1)$-th visit)

τ_M = total time needed to visit state S_j M times

$$\boxed{\tau_M = \sum_{m=1}^{M} T_j^{(m)}} \; ; \quad \phi_j(\tau_M) = \text{fraction of time spent in } S_j \text{ during time } \tau_M$$

$$\phi_j(\tau_M) = \frac{M}{\tau_M} \xrightarrow{} 1$$

ensemble average (Centr.)

$$\langle T_j \rangle = \lim_{M \to \infty} \frac{\tau_M}{M} = \lim_{M \to \infty} \frac{1}{\phi_j(\tau_M)} = \frac{1}{W_j^{(1)}}$$

time average