Fluctuation theorems

Markov Chain dynamics

Forward trajectory: $\mathcal{C}_0 \to \mathcal{C}_1 \to \cdots \cdots \mathcal{C}_{M-1} \to \mathcal{C}_M$

Γ

$$P_F(\Gamma) = P_{\lambda_0}(\mathcal{C}_0) \prod_{0}^{M-1} {}_K W_{\lambda_{K+1/2}}(\mathcal{C}_K \to \mathcal{C}_{K+1})$$

$$S(\Gamma) = \ln\left[\frac{P_{\lambda_0}(\mathcal{C}_0)}{\underbrace{P_{\lambda_M}(\mathcal{C}_M)}}\right] + \sum_{0}^{M-1} {}_K \ln\left[\frac{W_{K+1/2}(\mathcal{C}_K \to \mathcal{C}_{K+1})}{W_{K+1/2}(\mathcal{C}_{K+1} \to \mathcal{C}_K)}\right]$$

$\langle \exp(-S) \rangle = 1 \to$ KAWASAKI identity

$\Rightarrow \langle S \rangle \geq 0 \longrightarrow$ stochastic 2nd law

$P_{\lambda_M}(\mathcal{C}_M)$ generic PDF

$$P_{\lambda_M}(\mathcal{C}_M) \neq P(\mathcal{C}_M) = \sum_{\mathcal{C}_0, \mathcal{C}_1, \dots, \mathcal{C}_{M-1}} P(\Gamma)$$

Reverse trajectory Γ^* (with $\lambda_M, \lambda_{M-1/2} \cdots \lambda_{1/2}, \lambda_0$)

$\mathcal{C}_M \to \mathcal{C}_{M-1} \to \cdots \mathcal{C}_1 \to \mathcal{C}_0$

$$P_R(\Gamma^*) = \underbrace{P_{\lambda_M}(\mathcal{C}_M)}_{\text{PDF to sample } \mathcal{C}_M \text{ for reverse trajectory}} \prod_{0}^{M-1} {}_K W_{K+1/2}(\mathcal{C}_{K+1} \to \mathcal{C}_K)$$

$$\underbrace{S(\Gamma) = \ln\left[\frac{\rho_F(\Gamma)}{\rho_R(\Gamma^*)}\right]}$$

$S(\Gamma) > 0$

$\Updownarrow$

$\rho_F(\Gamma) > \rho_R(\Gamma)$

$$S(\Gamma^*) = -S(\Gamma)$$

$$\rho_F(\Gamma) = \rho_R(\Gamma^*) \cdot \exp[S(\Gamma)]$$

$$\begin{aligned}
\rho_F(S) &= \sum_\Gamma \rho_F(\Gamma)\,\delta(S(\Gamma)-S) \\
&= \sum_\Gamma \rho_R(\Gamma^*)\exp(S(\Gamma))\,\delta(S(\Gamma)-S) \\
&= \exp(S)\underbrace{\sum_{\Gamma^*} \rho_R(\Gamma^*)\,\delta(S(\Gamma^*)+S)}_{\rho_R(-S)} \\
&= \exp(S)\,\rho_R(-S)
\end{aligned}$$

$\Rightarrow$ Crook's FT $\boxed{\dfrac{\rho_F(S)}{\rho_R(-S)} = \exp(S)}$

$$\rho_R(-S) = \rho_F(S)\exp(-S)$$

$$\int_{-\infty}^{+\infty} ds\, \rho_R(-s) = \int_{-\infty}^{+\infty} \exp(-s)\, \rho_F(s)\, ds$$

FT $\Rightarrow$

$$\underbrace{1 = \langle \exp(-S) \rangle}$$

Kawasaki identity

SO FAR: no assumption on Detailed Balance

If DB holds for all λ values

$$\longrightarrow \frac{W_{k+1/2}(\varphi_k \to \varphi_{k+1})}{W_{k+1/2}(\varphi_{k+1} \to \varphi_k)} = \frac{\rho^{eq}_{k+1/2}(\varphi_{k+1})}{\rho^{eq}_{k+1/2}(\varphi_k)}$$

$$S(\Gamma) = \underbrace{\ln\left[\frac{\rho^{eq}_{\lambda_0}(\varphi_0)}{\rho^{eq}_{\lambda_n}(\varphi_n)}\right] + \sum_0^{n-1}{}_k \ln\left[\frac{\rho^{eq}_{k+1/2}(\varphi_{k+1})}{\rho^{eq}_{k+1/2}(\varphi_k)}\right]}_{\text{boundary term}}$$

$$\left[\begin{array}{l} \text{if } \lambda_k = \lambda \ \forall k \quad (\Gamma = \text{eq. trajectory}) \\ \Rightarrow S(\Gamma) = 0 \qquad (k_B = 1) \end{array}\right]$$

Canonical ensemble: $\rho^{eq}_\lambda(\varphi) = \dfrac{\exp(-E_\lambda(\varphi)/T)}{Z_\lambda}$

$Z_\lambda = \exp(-\beta F_\lambda)$

$$= \exp\left(-\frac{E_\lambda(\varphi)}{T} + \frac{F_\lambda}{T}\right)$$

$$TS(\Gamma) = \underbrace{\Delta U - \Delta F}_{\text{boundary term}} - \underbrace{\sum_{k=0}^{M-1}\left[E_{k+1/2}(\varphi_{k+1}) - E_{k+1/2}(\varphi_k)\right]}_{\text{heat absorbed by the system } \Delta Q(\Gamma)}$$

$$\Delta U = E_{\lambda_M}(\varphi_M) - E_{\lambda_0}(\varphi_0)$$

$$\Delta F = F_{\lambda_M} - F_{\lambda_0}$$

$$TS(\Gamma) = \Delta U - \Delta F - \Delta Q(\Gamma)$$

$$\Delta U = \underbrace{TS(\Gamma) + \Delta F}_{W(\Gamma)} + \Delta Q(\Gamma)$$

$W(\Gamma)$ work exerted on the system

1st law for stochastic thermodynamics

$$TS(\Gamma) + \Delta F = \Delta U - \Delta Q(\Gamma)$$

$$\overset{!}{=} E_{1/2}(\varphi_0) - E_0(\varphi_0) + \sum_{k=1}^{M-1}\left[E_{k+1/2}(\varphi_k) - E_{k-1/2}(\varphi_k)\right] + E_M(\varphi_M) - E_{M-1/2}(\varphi_M)$$

$$\underbrace{W_{diss}(\Gamma) = W(\Gamma) - \Delta F}_{} = T\underbrace{S(\Gamma)}_{\text{total entropy produced along } \Gamma}$$

$$\frac{\rho_F(W_{diss})}{\rho_R(-W_{diss})} = \boxed{\frac{\rho_F(W)}{\rho_R(-W)} = \exp\left(\frac{W_{diss}}{T}\right)}$$

$$\Delta F^* = -\Delta F$$

Crook's F.T in the canonical ensemble

$$\langle \exp(-S) \rangle = 1 \qquad S(\Gamma) = \frac{W(\Gamma)}{T} - \frac{\Delta F}{T}$$

$$\Rightarrow \boxed{\left\langle \exp\left(-W/T\right)\right\rangle = \exp\left(-\frac{\Delta F}{T}\right)}$$

Jarzinsky identity

$$\boxed{\frac{\rho_F(W)}{\rho_R(-W)} = \exp\left(\frac{W-\Delta F}{T}\right)}$$

Crook's FT in canonical ensemble

In experiments: (measure $\rho_F(W)$, $\rho_R(W)$) $\Rightarrow$ deduce ΔF)

(1) $W^* / \rho_F(W^*) = \rho_R(-W^*)$

$$\Rightarrow \Delta F = W^*$$

(2) $$\ln\left(\frac{P_F(W)}{P_R(-W)}\right) = \frac{W}{T} - \frac{\Delta F}{T}$$

linear function of W — linear fit to get ΔF

Pulling RNA-hairpins → initial state → folded hairpin

final state → unfolded hairpin

x = control parameters (position of the pulled end of RNA-hairpin)

f = force exerted on the pulled end

stochastic quantity

Trajectory $f(x)$ is measured

exp. protocol → $\underbrace{x = vt}$ fixed pulling speed v (forward)

reverse protocol → $\underbrace{x = -vt}$

exp. performed at fixed N, p, T → Gibbs free energy

pressure

$dW = f\,dx$ $\qquad G(N, T, p)$

$$W(\Gamma) = \int_{x_{min}}^{x_{max}} f(x)\,dx$$ work associated to trajectory $f(x)$

APPENDIX: Fluctuation Theorems in Large Deviation Theory

time $\mathcal{T} \to n$ MC dynamics

total entropy per unit time $\underline{W_n(\sigma)} = \dfrac{1}{n} \underline{\ln\left[\dfrac{P(\sigma)}{P(\sigma^R)}\right]}$

for a trajectory $\sigma = \{\sigma_1, \dots, \sigma_n\}$; σ^R = reverse trajectory

$$\lim_{n\to\infty} \langle W_n \rangle = \lim_{n\to\infty} \frac{1}{n} \sum_\sigma P(\sigma) \ln\left[\frac{P(\sigma)}{P(\sigma^R)}\right]$$

$$= \lim_{n\to\infty} \frac{1}{n} D[F|R]$$

DB $\Leftrightarrow$ reversible Markov Chains $\Leftrightarrow$ $P(\sigma) = P(\sigma^R)$ (at least asymptotically $n\to\infty$)

$\Rightarrow D[F|R] = 0$

$$= \lim_{n\to\infty} \frac{1}{n} \left[\overbrace{\sum_\sigma P(\sigma) \ln[P(\sigma)]}^{-h} - \underbrace{\sum_\sigma P(\sigma) \ln[P(\sigma^R)]}_{h^R} \right]$$

$= h^R - h \to$ difference between the entropy rates of reverse and forward trajectories

Large deviation principle for $W_n(\sigma) \Rightarrow P(W_n = w) \underset{n \gg 1}{\simeq} \exp(-n I(w))$

rate function $I(w)$

Gärtner-Ellis theorem $\rightarrow$ compute the scaled cumulant generating function

$$\langle \exp(n k W_n) \rangle = \sum_{\sigma} P(\sigma) \cdot \frac{P(\sigma)^k}{P(\sigma^R)^k} \cdot \frac{P(\sigma^R)}{P(\sigma^R)}$$

$$= \sum_{\sigma^R} P(\sigma^R) \cdot \frac{P(\sigma)^{k+1}}{P(\sigma^R)^{k+1}}$$

$$= \langle \exp(n(-1-k) W_n) \rangle$$

$$\boxed{\lambda(k) = \lambda(-1-k)}$$

$$\boxed{\left(\lambda(k) = \lim_{n \to \infty} \frac{1}{n} \ln \left[\langle \exp(n k W_n) \rangle \right] \right.}$$

Legendre-Fenchel transform

$$I(w) = \sup_k \left[k w - \lambda(k) \right] = \sup_k \left[k w - \lambda(-1-k) \right]$$

$$= \sup_k \underbrace{\left[(-1-k)(-w) - \lambda(-1-k) \right]}_{\lambda} - w$$

$$\overset{!}{=} I(-w) - w$$

$$\boxed{I(w) = I(-w) - w}$$

$$P(S) \underset{n \gg 1}{\simeq} \exp(-n I(w)); \quad P(-S) \underset{n \gg 1}{\simeq} \exp(-n I(-w))$$

$$(S = n W_n)$$

$$\boxed{P(S) / P(-S) \underset{n \gg 1}{\simeq} \exp(n w) = \exp(S)}$$