Exercise.

recall: $\langle \delta(x-x_t)\, e^{-\beta w_t} \rangle = \frac{1}{Z_A} e^{-\beta \mathcal{H}(x,\lambda_t)}$

① Use Bayes' rule to rewrite the left side of the eqn as

$$f(x,t) \cdot \langle e^{-\beta w_t} \rangle_{x,t}$$

$\langle \cdots \rangle_{x,t}$ = average over all trajectories that pass thru x @ time t

② Then use this result to show that

$$\mathcal{D}(f_t \mid \pi_{\lambda(t)}) \leq \beta\left(\langle w_t \rangle - \Delta F_t\right)$$

$F_{\lambda(t)} - F_A$

This result was derived earlier using a different approach.

Fluctuation Theorems for Entropy Production

= collection of results (mostly obtained mid-late 1990's) that differ <u>mathematically</u>, but make similar <u>physical</u> assertions

basic form: $\dfrac{P(\Delta S)}{P(-\Delta S)} \sim e^{\Delta S}$ ($k_B = 1$)

entropy produced

sometimes an equality, other times only true in the long-time limit

I'll present & derive the FT obtained by Lebowitz & Spohn (1999).

N-state system, usual setup:

$$\frac{d\vec{p}}{dt} = R\vec{p}$$

$$s_{ij} \equiv \Delta S_{j\to i} = \ln \frac{R_{ij}}{R_{ji}}$$

entropy produced in system's surroundings, when transition $j \to i$ occurs.

Assume detailed balance is violated:

$A_c \neq 0$ for some cycle(s)

$\therefore$ system evolves to non-equilibrium steady state, w/ non-zero currents.

NESS

Imagine observing the system in a NESS, from $t \to -\infty$ to $t = +\infty$.

Divide this infinite interval into infinitely many segments of finite duration, τ.

one segment: $X = i_0 \xrightarrow{t_1} i_1 \xrightarrow{t_2} \cdots \xrightarrow{t_K} i_K$

$$n\tau < t_1 < \cdots < t_K < (n+1)\tau$$

$\sigma[X]$ = time-averaged entropy production rate

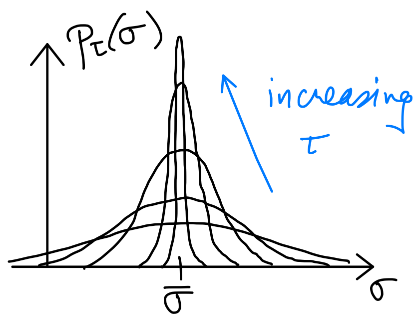
$$= \frac{1}{\tau} \sum_k s_{i_{k+1} i_k} = \frac{1}{\tau} \sum_k \ln \frac{R_{i_{k+1} i_k}}{R_{i_k i_{k+1}}}$$

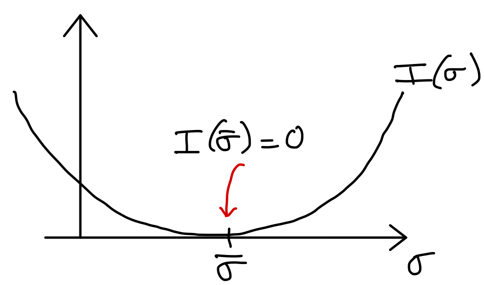
sum over transitions in one segment

$p_\tau(\sigma)$ = probability distribution of values of σ

$$\sigma[X] = \frac{1}{\tau}\sum_k s_{i_{k+1} i_k} = \frac{1}{\tau}\sum_k \ln \frac{R_{i_{k+1} i_k}}{R_{i_k i_{k+1}}} \quad , \; p_\tau(\sigma)$$

Expect $p_\tau(\sigma)$ to become increasingly sharply peaked as $\tau \to \infty$ (law of large numbers)





large dev'n theory: $p_\tau(\sigma) \sim e^{-\tau I(\sigma)}$ for large τ

$$I(\sigma) = \lim_{\tau\to\infty} \frac{-1}{\tau} \ln p_\tau(\sigma)$$

Fluctuation Theorem: $\boxed{I(\sigma) - I(-\sigma) = -\sigma}$

i.e. for large τ,
$$\frac{p_\tau(\sigma)}{p_\tau(-\sigma)} \sim e^{-\tau[I(\sigma) - I(-\sigma)]} = e^{+\underbrace{\tau\sigma}_{=\Delta S}}$$

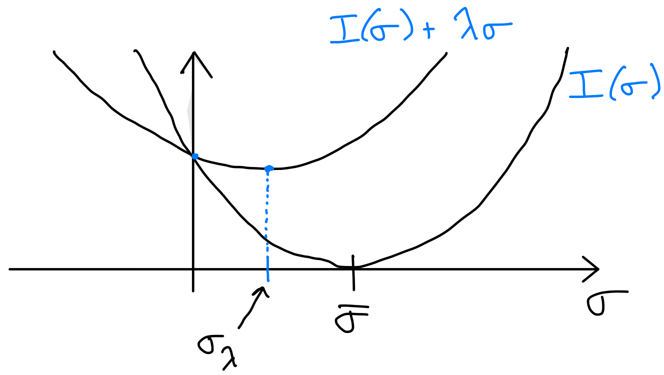
Following Lebowitz & Spohn, I'll derive this F.T. by using a generating function, along with the Perron–Frobenius Theorem.

$$g(\lambda) \equiv \lim_{\tau\to\infty} -\frac{1}{\tau} \ln \langle e^{-\lambda\tau\sigma} \rangle$$

average over all X of duration τ

$$\langle e^{-\lambda\tau\sigma} \rangle = \int d\sigma \; p_\tau(\sigma)\, e^{-\lambda\tau\sigma}$$

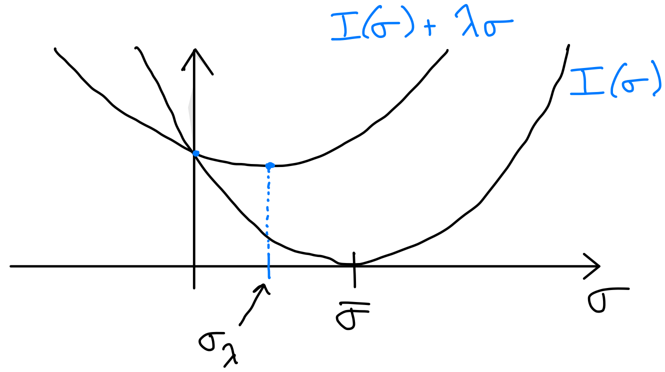
$$\sim \int d\sigma \; e^{-\tau[I(\sigma)+\lambda\sigma]} \quad \leftarrow \text{A}$$



minimum of $I(\sigma)+\lambda\sigma$

The integral in A is dominated (for large τ) by the region around σ_λ ... expand:

$$I(\sigma)+\lambda\sigma \simeq \left[I(\sigma_\lambda)+\lambda\sigma_\lambda\right] + \frac{1}{2} I''(\sigma_\lambda)(\sigma-\sigma_\lambda)^2$$



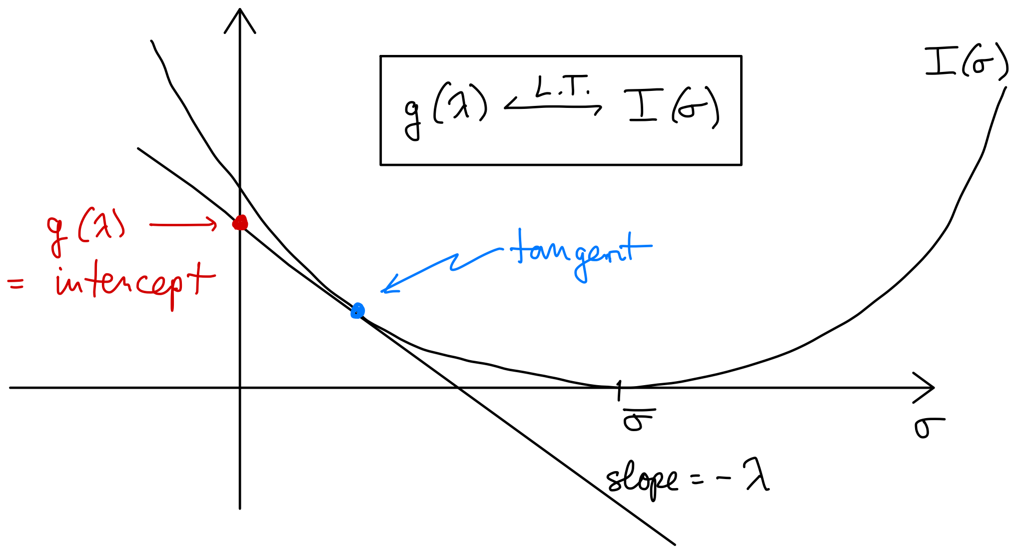
$$I(\sigma)+\lambda\sigma \simeq \left[I(\sigma_\lambda)+\lambda\sigma_\lambda\right] + \frac{1}{2} I''(\sigma_\lambda)(\sigma-\sigma_\lambda)^2$$

$$\langle e^{-\lambda\tau\sigma}\rangle \sim \int d\sigma \; e^{-\tau[I(\sigma)+\lambda\sigma]}$$

$$\sim e^{-\tau[I(\sigma_\lambda)+\lambda\sigma_\lambda]} \cdot \underbrace{\int d\sigma \; e^{-\tau I''(\sigma-\sigma_\lambda)^2/2}}_{\sqrt{2\pi/I''\tau}}$$

$$g(\lambda) = \lim_{\tau\to\infty} -\frac{1}{\tau}\ln\langle e^{-\lambda\tau\sigma}\rangle = I(\sigma_\lambda)+\lambda\sigma_\lambda$$

$$= \min_\sigma \{I(\sigma)+\lambda\sigma\}$$ = Legendre transform (L.T.) of $I(\sigma)$



It follows that $g''(\lambda) < 0$ [since $I''(\sigma) > 0$] .

Also: $g(0) = 0$.

Next, I'll show that:

1. $g(\lambda) = g(1-\lambda)$ using Perron-Frob. Thm.
2. This implies $I(\sigma) - I(-\sigma) = -\sigma$ by L.T.

$$p_i(t) = \langle \delta_{i,i(t)} \rangle \quad , \quad q_i(t) = \langle \delta_{i,i(t)} \cdot e^{-\lambda t \sigma(t)} \rangle$$

$$t\sigma(t) = \sum_{\substack{k \\ [0,t]}} s_{i_{k+1} i_k}$$

$$\begin{cases} \vec{p}(t) = \text{ordinary prob. dist'n} \\ \vec{q}(t) = \text{"weighted" prob. dist'n.} \end{cases}$$

$$g(\lambda) = \lim_{t\to\infty} -\frac{1}{t} \ln \sum_i q_i(t) = \lim_{t\to\infty} -\frac{1}{t} \ln \vec{1} \cdot \vec{q}(t)$$

$$\frac{dp_i}{dt} = \sum_{j\neq i} R_{ij}\, p_j + R_{ii}\, p_i$$

$$\frac{dq_i}{dt} = \sum_{j\neq i} R_{ij}\, q_j \underbrace{e^{-\lambda s_{ij}}}_{} + R_{ii}\, q_i \equiv \sum_j Q_{ij}\, q_j$$

accounts for the fact that the weight $e^{-\lambda t\sigma(t)}$ picks up a factor $e^{-\lambda s_{ij}}$ when the transition $j \to i$ occurs.

$$Q_{ij}(\lambda) = R_{ij}\, e^{-\lambda s_{ij}} \qquad (s_{ii} \equiv 0)$$

$$Q_{ij}(1-\lambda) = R_{ij}\, e^{(\lambda-1)s_{ij}} = R_{ji}\, e^{-\lambda s_{ji}} = Q_{ji}(\lambda)$$

using $s_{ij} = \ln\left(R_{ij}/R_{ji}\right)$

$$\therefore \quad \boxed{Q(1-\lambda) = Q^T(\lambda)}$$

$$Q_{ij}(\lambda) = R_{ij}\, e^{-\lambda s_{ij}}\,, \quad g(\lambda) = \lim_{t\to\infty} -\frac{1}{t} \ln \vec{1}\cdot\vec{q}(t)$$

Perron-Frobenius Thm:

Q has a dominant eigenvalue

$$\underset{\in \mathbb{R}}{\alpha_1} > |\alpha_2| \geq |\alpha_3| \geq \cdots$$

$$\frac{d\vec{q}}{dt} = Q\vec{q} \implies \vec{q}(t) = e^{Qt}\vec{q}(0) \longrightarrow c_1 e^{\alpha_1 t}\vec{u}_1 \quad \text{as } t\to\infty$$

$$Q\vec{u}_1 = \alpha_1 \vec{u}_1$$

(c_1 is determined by $\vec{q}(0)$)

$$g(\lambda) = \lim_{t\to\infty} -\frac{1}{t}\ln \vec{1}\cdot\vec{q}(t)$$

$$= \lim_{t\to\infty} -\frac{1}{t}\left[\ln c_1 + \alpha_1 t + \ln \vec{1}\cdot\vec{u}_1\right] = -\alpha_1(\lambda)$$

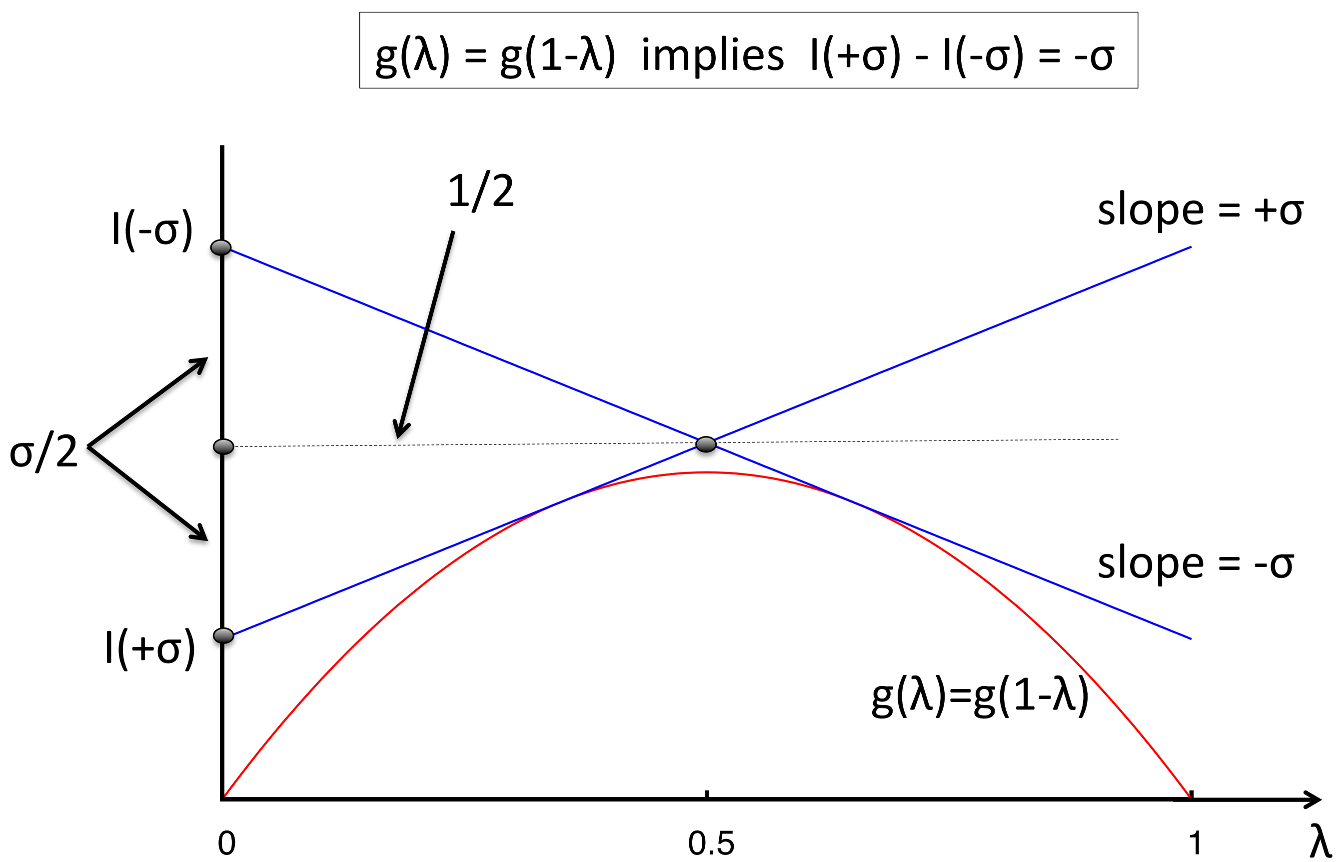
$$g(1-\lambda) = (-1)\times\left[\text{dominant eigenvalue of } Q(1-\lambda)\right]$$

But $Q(1-\lambda) = Q(\lambda)^T$ implies that $Q(1-\lambda)$ & $Q(\lambda)$ share the same spectrum of eigenvalues.

$$\therefore \boxed{g(\lambda) = g(1-\lambda)}$$ as promised.

Now use L.T. to show that $I(\sigma) - I(-\sigma) = -\sigma$

$\longrightarrow$


g(λ) = g(1-λ) implies I(+σ) - I(-σ) = -σ
1/2
slope = +σ
I(-σ)
σ/2
slope = -σ
I(+σ)
g(λ)=g(1-λ)
0
0.5
1
λ