$$I_{nm}(t) = k_B \ln \frac{\Omega_{nm}\, p_m(t)}{\Omega_{mn}\, p_n(t)}$$

$$\dot{I}(t) = \frac{1}{2}\sum_{n,m} J_{nm} I_{nm} \geq 0 \Rightarrow \begin{cases} = 0 & \text{iff ESS} \\ \neq 0 & \text{otherwise} \end{cases}$$

$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta Q_{nm}} = e^{-\beta(E_n - E_m - W_{nm})}$$

heat from env. during $m \to n$ trans

plug in $\Rightarrow$ $$I_{nm} = -\frac{1}{T} Q_{nm} + k_B \ln \frac{p_m(t)}{p_n(t)}$$

$$= -\frac{1}{T} Q_{nm} + \left(-k_B \ln p_n(t) - \left(-k_B \ln p_m(t)\right)\right)$$

define new state function:

$$S_n(t) = -k_B \ln p_n(t)$$

"surprisal": measures how shocked you would be to observe state n

$S_n(t)$ is large + positive when $p_n(t)$ is small

$S_n(t) \to 0$ when $p_n(t) \to 1$

$$I_{nm} = -\frac{1}{T} Q_{nm} + \left(S_n(t) - S_m(t)\right) \qquad (1)$$

recall: state func A_n edge func.

$$A(t) = \sum_n p_n(t) A_n$$

$$\dot{A}(t) = \frac{1}{2}\sum_{nm} J_{nm}(A_n - A_m) \qquad \dot{B}(t) = \frac{1}{2}\sum_{nm} J_{nm} B_{nm}$$

$$= \frac{dA}{dt}$$

take eq. (1), multiply by $\frac{1}{2} J_{nm}$ + $\sum_{nm}$:

$$\dot{I}(t) = -\frac{\dot{Q}(t)}{T} + \dot{S}(t) \qquad \text{where}$$

prod. rate of "irreversibility"

mean rate of heat into sys.

$$\dot{S}(t) = \frac{dS}{dt}$$

+

avg. surprisal

$$S(t) = \sum_n p_n(t) S_n(t)$$

$$\Rightarrow \boxed{S(t) = -k_B \sum_n p_n(t) \ln p_n(t)}$$

Gibbs formula for entropy

$$\dot{S}(t) = \frac{\dot{Q}(t)}{T} + \underbrace{\frac{\dot{I}(t)}{}}_{\geq 0} \Rightarrow \boxed{\begin{aligned}\dot{S}(t) &\geq \frac{\dot{Q}(t)}{T} \\ &= \frac{\dot{Q}(t)}{T} \quad \text{iff ESS}\end{aligned}}$$

2nd law

conventional notation: $dS \geq \frac{đQ}{T}$

$$dS = d(S(t)) \qquad đQ \neq d(Q(t))$$

$$\frac{dS}{dt} \geq \frac{đQ}{dt}\frac{1}{T}$$

$$\mathring{S}(t) \geq \mathring{Q}(t)\frac{1}{T}$$

units: entropy $\sim k_B \sim \frac{J}{K}$

$$\dot{I}(t) \sim \frac{\text{entropy}}{\text{time}} \sim \frac{J}{K \cdot s}$$

$$\dot{Q} \sim \frac{\text{energy}}{\text{time}} \sim \frac{J}{s}$$

What about 1st law?

$$Q_{nm} = E_n - E_m - W_{nm}$$

multiply by $\frac{1}{2} J_{nm}$ & $\sum_{nm}$:

1st law

$$\boxed{\mathring{Q}(t) = \mathring{E}(t) - \mathring{W}(t)} \qquad \dot{E}(t) = \frac{dE}{dt}$$

heat rate into sys.

rate of sys. mean energy change

rate of work on sys (>0) by sys (<0)

1st law: $\dot{E} = \dot{Q} + \dot{W}$

2nd law: $\dot{S} = \frac{\dot{Q}}{T} + \dot{I}$

$\Rightarrow \dot{S} = \frac{\dot{E} - \dot{W}}{T} + \dot{I}$

$\dot{E} - T\dot{S} = \dot{W} - T\dot{I}$

$\frac{d}{dt}$ (state funcs)

prod. rates of edge funcs

new state func: $F_n = E_n - TS_n$

avg. $F(t) = E(t) - TS(t)$

Helmholtz free energy

$$\frac{d}{dt}F = \dot{F} = \dot{W} - T\dot{I}$$

another form of 2nd law

What happens as $t \to \infty$?

if $p_n(t) \to p_n^s$ stationary state

will prove

$$E(t) = \sum_n p_n(t) E_n \to \sum_n p_n^s E_n \equiv E^s$$

$$S(t) = -k_B \sum_n p_n(t) \ln p_n(t)$$

$$\to -k_B \sum_n p_n^s \ln p_n^s \equiv S^s$$

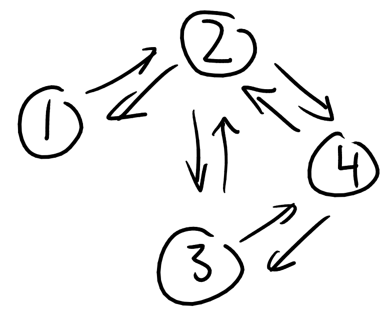
$$F(t) \to F^s = E^s - TS^s$$

$\dot{F} \to 0$ along w/ $\dot{E} \to 0$ + $\dot{S} \to 0$

Want to prove: $p_n(t) \to p_n^s$

assumptions: • time-ind. matrix Ω

• graph for Ω is connected (path from any i to j exists)



$$\frac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta Q_{nm}}$$

Build analogy to quantum:

	quantum	master eqn.
description of state	$\vert\psi(t)\rangle$ vector in Hilbert space	$\vec{p}(t)$ vector in prob. space
dynamical eqn.	$i\hbar \frac{\partial}{\partial t}\vert\psi(t)\rangle = \hat{H}\vert\psi(t)\rangle$	$\frac{\partial}{\partial t}\vec{p}(t) = \Omega\vec{p}(t)$
solution	$\vert\psi(t)\rangle = e^{i\hat{H}t/\hbar}\vert\psi(0)\rangle$	$\vec{p}(t) = e^{\Omega t}\vec{p}(0)$

$$\frac{\partial}{\partial t} f = af \Rightarrow f(t) = f(0)e^{at}$$

claim: $$e^{\Omega t} \equiv \underbrace{\hat{\mathbb{1}}}_{\text{ident. matrix}} + \Omega t + \frac{\Omega^2 t^2}{2!} + \frac{\Omega^3 t^3}{3!} + \cdots$$

$$\frac{d}{dt}e^{\Omega t} = 0 + \Omega + \Omega^2 t + \frac{\Omega^3 t^2}{2!} + \cdots$$

$$= \Omega \left(\hat{\mathbb{I}} + \Omega t + \frac{\Omega^2 t^2}{2!} + \cdots \right)$$

$$= \Omega e^{\Omega t} = e^{\Omega t} \Omega$$ b/c Ω commutes w/ itself

$$\frac{d}{dt} \Big(\underbrace{e^{\Omega t} \vec{p}(0)}_{\vec{p}(t)} \Big) = \Omega e^{\Omega t} \vec{p}(0)$$

$$= \Omega \vec{p}(t)$$

$\Rightarrow$ $\vec{p}(t)$ solves master equ.