RECAP: $\frac{dp_n}{dt} = \sum_m J_{nm}$

$$J_{nm} = \Omega_{nm} p_m - \Omega_{mn} p_n$$

two types of observables: state funcs: A_n

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

$$\frac{d}{dt} A(t) = \underbrace{\frac{1}{2} \sum_{nm} J_{nm}(A_n - A_m)}_{\equiv \dot{A}(t)}$$

examples: energy E_n

surprisal $S_n = -k_B \ln p_n$

$\hookrightarrow$ avg. $E(t)$ avg. energy

$S(t) = \sum_n p_n S_n$

$=$ "entropy"

edge func B_{nm}

$$\dot{B}(t) = \frac{1}{2} \sum_{nm} J_{nm} B_{nm}$$

examples: $I_{nm} = k_B \ln \frac{\Omega_{nm} p_m}{\Omega_{mn} p_n}$

showed $\dot{I}(t) \geq 0$ $\quad \dot{I}(t) = 0$ if and only if ESS

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

$\dot{Q}(t) =$ mean rate of heat into sys.

$$\Rightarrow \quad \dot{I}(t) = -\frac{\dot{Q}(t)}{T} + \dot{S}(t), \qquad \dot{S}(t) = \frac{dS(t)}{dt}$$

$$\boxed{\dot{S}(t) = \frac{\dot{Q}(t)}{T} + \underbrace{\dot{I}(t)}_{\geq 0} \Rightarrow \dot{S}(t) \geq \frac{\dot{Q}(t)}{T}}$$

$= \frac{\dot{Q}(t)}{T}$ iff ESS

Clausius form of 2nd law of thermodynamics

Conventional notation

$$dS \geq \frac{đQ}{T}$$

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

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

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

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

$$\dot{S}(t) = \underbrace{\frac{\dot{Q}(t)}{T}}_{\text{"entropy flow" from envir. due to heat transfer (pos. or negative)}} + \underbrace{\overbrace{\dot{I}(t)}^{\geq 0}}_{\text{"irreversible entropy production rate"}}$$

rate of change of sys. entropy

What about 1st law?

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

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

$$\Rightarrow \boxed{\dot{Q}(t) = \dot{E}(t) - \dot{W}(t)}$$

$$\dot{E}(t) = \frac{d}{dt} E(t)$$

1st law of thermo. (energy conserv.)

rate of heat into sys.

rate of sys. energy change

rate of work on sys.

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

2nd $\mathring{S} = \frac{\mathring{Q}}{T} + \mathring{I}$

$$\Longrightarrow \mathring{S} = \frac{\mathring{E} - \mathring{W}}{T} + \mathring{I}$$

$$\Rightarrow \underbrace{\mathring{E} - T\mathring{S}}_{\text{state funcs}} = \underbrace{\mathring{W} - T\mathring{I}}_{\text{edge funcs}}$$

new state func: $F_n = E_n - TS_n$

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

Helmholtz free energy

$$\mathring{F} = \mathring{W} - T\mathring{I}$$

What happens as $t \to \infty$?

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

have to prove this

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

$$S(t) = -k_B \sum_n p_n \ln p_n \to -k_B \sum_n p_n^s \ln p_n^s \equiv S^s$$

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

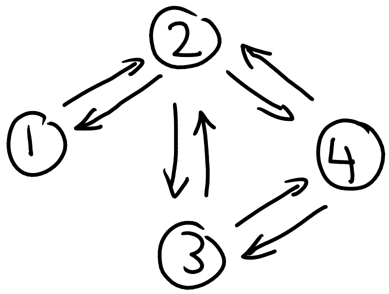
$\mathring{F} \to 0$ along with $\mathring{E} \to 0$

$\mathring{S} \to 0$

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 any j exists)

Build analogy to quantum:

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

claim: $\vec{p}(t) = e^{\Omega t}\vec{p}(0)$ solves master equ.

$$e^{\Omega t} = \mathbb{1} + \Omega t + \frac{\Omega^2 t^2}{2!} + \frac{\Omega^3 t^3}{3!} + \cdots$$

ident. matrix

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

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

$$= \Omega e^{\Omega t} = e^{\Omega t} \Omega$$

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

master eqn. is satisfied!