Recap: $\frac{dp_n}{dt} = \sum_m J_{nm}$ curr. $m \to n$

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

edge func: B_{nm}

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

state func. A_n

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

$\frac{d}{dt} A(t) = \sum_{nm} J_{nm}(t) A_n$

$= \frac{1}{2} \sum_{nm} J_{nm} (A_n - A_m)$

$\equiv \dot{A}(t)$

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

showed $\mathring{I}(t) = \frac{1}{2} \sum_{nm} J_{nm} I_{nm} \geq 0$ irreversibility

physical intuition: $\mathring{I}(t) = 0$ happens if + only if

$\Omega_{nm} p_m(t) = \Omega_{mn} p_n(t)$ for every connected edge (m,n)

$\Leftrightarrow J_{nm}(t) = 0$ for every conn. edge

$\Leftrightarrow \frac{dp_n}{dt} = \sum_m J_{nm}(t) = 0$

$$\boxed{\mathring{I}(t) = 0 \Leftrightarrow \text{ESS}}$$

we can think of $\mathring{I}(t)$ as a "distance" from equilibrium (ESS)

$\mathring{I}(t) > 0$ $\to$ NESS $\left(\frac{dp_n}{dt} = 0\right)$

$\to$ not in a stationary state $\left(\frac{dp_n}{dt} \neq 0\right)$

Connect to physical quantities (energy + work):

plug in: $\dfrac{\Omega_{nm}}{\Omega_{mn}} = e^{-\beta Q_{nm}} = e^{-\beta(E_n - E_m - W_{nm})}$

$\beta = \dfrac{1}{k_B T}$

Q_{nm}: heat from env. in $m \to n$ trans.

W_{nm}: work on sys. in $m \to n$ trans.

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

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

$$S_n(t) \equiv -k_B \ln p_n(t) = \text{"surprisal"}$$

$0 \le p_n(t) \le 1$

new state function

$$= \begin{cases} \text{large + positive when } p_n(t) \text{ is small} \\ \approx 0 \text{ when } p_n(t) \approx 1 \end{cases}$$

$\Rightarrow$ how surprised you are to observe state n

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

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

$\dot{Q}(t)$: mean rate of heat into system

$\dot{I}(t)$: production rate of irreversibility

$\dot{S}(t)$: rate of change of entropy

here $S(t) = \sum_n p_n(t) S_n(t)$ mean surprisal

$= -k_B \sum_n p_n(t) \ln p_n(t)$ entropy (Gibbs)

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

$$\Rightarrow \quad \dot{S}(t) \geq \frac{\dot{Q}(t)}{T} \quad \text{+ only } = \frac{\dot{Q}(t)}{T} \text{ iff ESS}$$

2nd law of thermodyn. (Clausius form)

conventional notation:

$$dS \geq \frac{đQ}{T}$$

interpretation:

$$\underbrace{\dot{S}(t)}_{\text{rate of change of system entropy}} = \underbrace{\frac{\text{rate of heat from env.}}{\text{temperature}}}_{\text{"entropy flow from environ. due to heat transfer"}} + \underbrace{\text{irreversible entropy production rate } (\dot{I}(t))}$$

units:

$$\text{entropy} \sim k_B \sim \frac{J}{K}$$

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

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

$$Q_{nm} = E_n - E_m - W_{nm} \qquad (2)$$

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

$$\boxed{\dot{Q}(t) = \dot{E}(t) - \dot{W}(t)} \qquad \text{where} \quad \dot{E}(t) = \frac{d}{dt} E(t)$$

1st law of thermodyn. (energy conserv.)

rate of heat into sys = rate of mean sys. energy change − rate at which work is done on sys. (net power on sys.)

$$\left.\begin{array}{ll} \text{1st:} & \dot{E} = \dot{Q} + \dot{W} \\ \text{2nd:} & \dot{S} = \frac{\dot{Q}}{T} + \dot{I} \end{array}\right\} \xRightarrow{\text{combine}} \dot{S} = \frac{\dot{E} - \dot{W}}{T} + \dot{I}$$

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

new state function: $F_n = E_n - T S_n$

mean : $\underbrace{F(t) = E(t) - T S(t)}_{\text{Helmholtz free energy}}$

$$\Rightarrow \boxed{\dot{F}(t) = \dot{W}(t) - T \dot{I}(t)}$$

What happens if we approach a stat. state as $t \to \infty$?

$$\boxed{p_n(t) \to p_n^s}$$

can we prove this is true?

E^s, S^s, F^s indep. of time

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

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

$$F(t) \to F^s \Rightarrow \dot{F}(t) \xrightarrow[t \to \infty]{} 0$$

any state func $\dot{E} \to 0$

$\dot{S} \to 0$

etc.