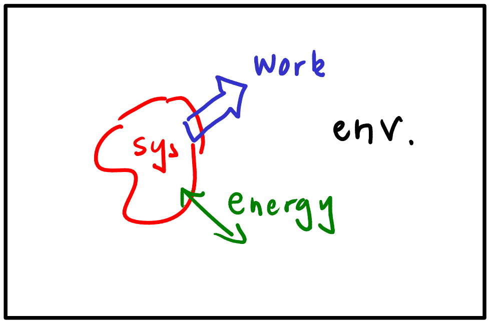

system:

matrix W

$$\vec{p}(t+\delta t) = W \vec{p}(t)$$

work

LDB: $$\frac{W_{ij}}{W_{ji}} = e^{-\beta(E_i - E_j + \omega_{ij})}$$

$$I(\nu) = k_B \ln \frac{p(\nu)}{\tilde{p}(\tilde{\nu})} \qquad \langle I(\nu)\rangle = I \geq 0$$

$$\nu = (n_0, n_1, \dots, n_\tau) \qquad \left\langle e^{-I(\nu)/k_B} \right\rangle = 1 \quad \text{IFT}$$

$$= \sum_{i=1}^{\tau-1} I(\mu_i) \qquad \mu_i = (n_i, n_{i+1})$$

$$I(\nu) = \underbrace{\Delta S(\nu)}_{-k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0))} - \frac{1}{T}\overbrace{\Delta E(\nu)}^{E_{n_\tau} - E_{n_0}} - \frac{1}{T}\underbrace{\overline{W}(\nu)}_{\sum_{i=1}^{\tau-1} \omega_{n_{i+1} n_i}}$$

avg. over ens.

$$\boxed{I = \Delta S - \frac{1}{T}\Delta E - \frac{1}{T}\overline{W} \geq 0}$$

2nd law

$$Q_{n_{i+1} n_i} = E_{n_{i+1}} - E_{n_i} + \omega_{n_{i+1} n_i}$$

$$Q(\nu) = \sum_{i=0}^{\tau-1} Q_{n_{i+1} n_i} = \Delta E(\nu) + \overline{W}(\nu)$$

avg:

$$\boxed{Q = \Delta E + \overline{W}}$$

1st law

notation: A_{nm} : quantity associated w/ transition $m \to n$

A_n : " " state n

$A(\nu)$: " " w/ traj. $\nu = (n_0, n_1, \ldots, n_\tau)$

$\Delta A(\nu)$: " " w/ traj. ν only depends on start + end

line $\Delta E(\nu) = E_{n_\tau} - E_{n_0}$

$$A = \langle A(\nu) \rangle = \sum_\nu \mathcal{P}(\nu) A(\nu)$$

$$\Delta A = \langle \Delta A(\nu) \rangle = \sum_\nu \mathcal{P}(\nu) \Delta A(\nu)$$

Conservative work: $\mathcal{W}(\nu) = A_{n_\tau} - A_{n_0}$
$= \Delta A(\nu)$

non-cons. $\Rightarrow$ cannot find such a $\Delta A(\nu)$

one last technicality:

avg. of conservative quantity

$$\Delta A = \langle \Delta A(\nu) \rangle$$
$$= \sum_\nu \mathcal{P}(\nu) (A_{n_\tau} - A_{n_0})$$
$$= \sum_{n_0} \cdots \sum_{n_\tau} W_{n_\tau n_{\tau-1}} \cdots W_{n_1 n_0} p_{n_0}(t_0) A_{n_\tau}$$
$$- \sum_{n_0} \cdots \sum_{n_\tau} W_{n_\tau n_{\tau-1}} \cdots W_{n_1 n_0} p_{n_0}(t_0) A_{n_0}$$

recall: $W \vec{p}(t_i) = \vec{p}(t_{i+1})$

$$W^{\tau} \vec{p}(t_0) = \vec{p}(t_\tau)$$

1st term: $\sum_{n_\tau} A_{n_\tau} p_{n_\tau}(t_\tau) =$ avg. of A at time t_τ

$= A(t_\tau)$

2nd term: $\sum_{n_0} A_{n_0} p_{n_0}(t_0) = A(t_0)$

b/c cols of W sum to $\underline{1}$

$$\Rightarrow \quad \Delta A = A(t_\tau) - A(t_0)$$

avg. of diff

= diff. of avg.'s

examples: $\Delta E = E(t_\tau) - E(t_0)$

where $E(t) = \sum_n p_n(t) E_n$

$$\Delta S = \langle \Delta S(\nu) \rangle$$

$$\Delta S(\nu) = \underbrace{-k_B \ln p_{n_\tau}(t_\tau)}_{\text{quantity assoc. w/ } n_\tau} - \underbrace{(-k_B \ln p_{n_0}(t_0))}_{\text{" " w/ } n_0}$$

$$\Delta S = S(t_\tau) - S(t_0)$$

$$\boxed{\begin{aligned} S(t) &= -k_B \sum_n p_n(t) \ln p_n(t) \\ &= \text{avg. "surprisal"} \end{aligned}}$$

entropy: $k_B = \left[\frac{J}{K}\right]$ = Gibbs entropy formula

define: $F(t) = E(t) - T\,S(t)$

Helmholtz free energy

$$\Delta F = F(t_\tau) - F(t_0) = \Delta E - T\,\Delta S$$

$$\Rightarrow \quad \boxed{\begin{array}{c} I = -\dfrac{\Delta F}{T} - \dfrac{W}{T} \geq 0 \\ Q = \Delta E + W \end{array}}$$

laws of thermo.

in general: env. temp. T

$Q > 0$ avg. heat into sys

< 0 " out

$W > 0$ work by sys.

< 0 " on sys.

special case: 1) system = total (no env.)

total is ergodic + mixing

$\Rightarrow$ sys. is ergodic + mixing

but is completely isolated

E_{tot} = const: all energy levels $E_n = E$ = const.

+ no work done b/c sys. is isolated $W = 0$

$$E(t) = \sum_n p_n(t)\, E = E$$

$$\Delta E = E(t_\tau) - E(t_0) = 0$$

1st: $Q = 0$ no heat input

2nd: $I = \Delta S - \cancel{\frac{\Delta E}{T}}^{\,0} - \cancel{\frac{W}{T}}^{\,0} \geq 0$

$$\boxed{I = \Delta S \geq 0}$$

2nd law for an isolated (erg. + mixing) system

$$= S(t_\tau) - S(t_0)$$

cannot decrease