$$I(\nu) = \Delta S(\nu) - \frac{1}{T}\Delta E(\nu) - \frac{1}{T} W(\nu)$$

avg. over ensemble

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

2nd law of therm.

modified LDB: $\frac{W_{nm}}{W_{mn}} = e^{-\beta(\underbrace{E_n - E_m + \omega_{nm}}_{Q_{nm}})}$

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

notation:

A_{nm} : quantity assoc. w/ trans. $m \to n$

A_n : " " w/ state n

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

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

i.e. $\Delta E(\nu) = E_{n_\tau} - E_{n_0}$

$$A = \langle A(\nu) \rangle = \sum_\nu \mathcal{P}(\nu) A(\nu) \quad \text{avg. over all traj.}$$

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

focus on work:

$$W(\nu) = \sum_{i=0}^{\tau} \omega_{n_{i+1} n_i} \overset{\text{if we can write as}}{=} A_{n_\tau} - A_{n_0} = \Delta A(\nu)$$

for some ΔA

$\Rightarrow$ then we call this <u>conservative</u> work

compare the def'n in classical mech:

$\omega = \nabla U$ there exists a potential U

$$\Rightarrow \int_{path} \omega = U(\text{end}) - U(\text{beginning})$$

if no such $A(\nu)$ exists $\Rightarrow$ $\mathcal{W}(\nu)$ is <u>not</u> conservative

---

define heat from thermal env. during $n_i \to n_{i+1}$ trans:

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

define total heat taken up during traj. ν

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

if $\mathcal{W}(\nu) = \Delta A(\nu)$ is conservative, $Q(\nu)$ is also consorvative: $Q(\nu) = \Delta B(\nu)$

where $\Delta B(\nu) = \Delta E(\nu) + \Delta A(\nu)$

avg. over traj.

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

1st law of thermodynamics

One last technicality:

avg. of conservative quantity

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

$$= \sum_{\nu} \mathcal{P}(\nu)\left(A_{n_\tau} - A_{n_0}\right)$$

$$= \sum_{n_0} \cdots \sum_{n_\tau} W_{n_\tau n_{\tau-1}} \cdots W_{n_1 n_0}\, p_{n_0}(t_0)\, A_{n_\tau}$$

$$- \sum_{n_0} \cdots \sum_{n_\tau} W_{n_\tau n_{\tau-1}} \cdots W_{n_1 n_0}\, p_{n_0}(t_0)\, A_{n_0}$$

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

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

$= A(t_\tau)$

2nd term: $\quad \sum_{n_0} A_{n_0} p_{n_0}(t_0) =$ avg. of A at time t_0

columns of W's sum to 1

$= A(t_0)$

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

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

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

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

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

surprisal of state n_τ

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

"avg." surprisal

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

= average "surprisal"

= Gibbs formula for entropy

define: $$F(t) = E(t) - T S(t)$$ Helmholtz free energy

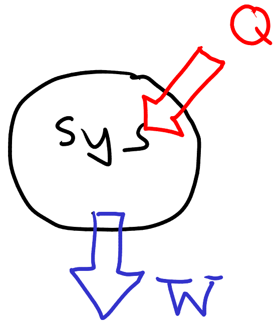
$$\Delta F = F(t_\tau) - F(t_0)$$
$$= \Delta E - T \Delta S$$

$$\Rightarrow \boxed{\begin{aligned} I &= -\frac{\Delta F}{T} - \frac{W}{T} \geq 0 \\ Q &= \Delta E + W \end{aligned}}$$

two laws of thermodyn.

(for sys. coupled to env. w/ temp. T)

env. at temp T



Q avg. heat from therm. env.
> 0 into sys
< 0 out sys

W avg. work done
> 0 by sys
< 0 on the sys

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

total is ergodic + mixing
$\Rightarrow$ sys. is ergodic + mixing, completely isolated

all energy levels of sys. are same
$E_n = E$ const.

+ no work done because sys. is isolated : $W = 0$

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

$$\Delta E = 0$$

1st law: $Q = 0$ no heat input

2nd law: $I = \Delta S - \dfrac{\cancelto{0}{\Delta E}}{T} - \dfrac{\cancelto{0}{W}}{T} \geq 0$

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

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

for an isolated, ergodic + mixing system entropy cannot decrease