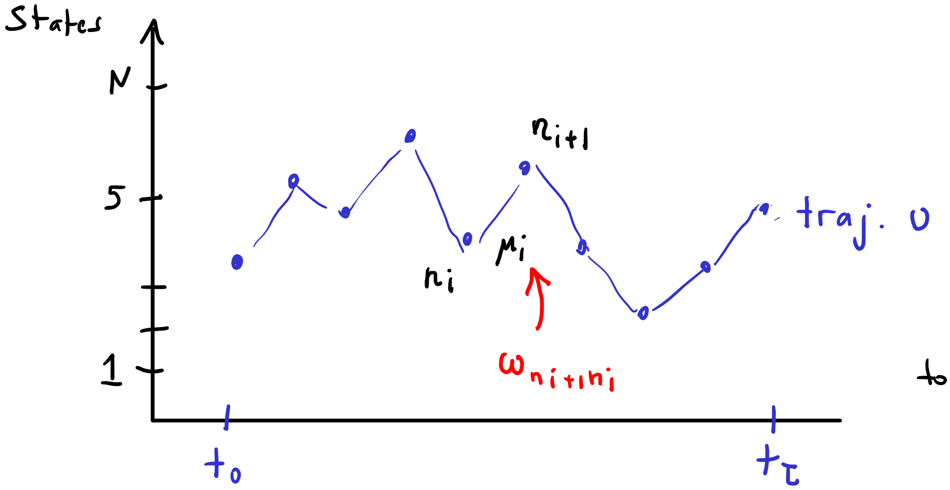


$$I(\mu_i) = k_B \ln \frac{W_{n_{i+1}n_i}\, p_{n_i}(t_i)}{W_{n_i n_{i+1}}\, p_{n_{i+1}}(t_{i+1})}$$

$$I(\upsilon) = \sum_{i=0}^{\tau-1} I(\mu_i)$$

total energy change

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

total work done by sys.

$$W(\upsilon) = \sum_{i=0}^{\tau-1} \omega_{n_{i+1}n_i}$$

total "entropy" change:

$$\Delta S(\upsilon) = -k_B \ln p_{n_\tau}(t_\tau) - (-k_B \ln p_{n_0}(t_0))$$

"surprisal" $= -k_B \ln p_n(t_i)$

large $p_n(t_i)$ $\Rightarrow$ not surprised to observe n
$\Rightarrow$ low surprisal value
($\to 0$ as $p_n(t_i) \to 1$)

small $p_n(t_i)$ $\Rightarrow$ very surprised to observe n
$\Rightarrow$ high surprisal

$\Delta S(\upsilon)$ = difference in surprisal b/t end + the beginning

last time: $I(\upsilon) = \Delta S(\upsilon) - \frac{1}{T}\Delta E(\upsilon) - \frac{1}{T} W(\upsilon)$

$\big\downarrow$ avg. over ensemble

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

2nd law

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

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

example: ω_{nm} = work during $m \to n$

A_n : " " state n

example: energy E_n

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

$\Delta A(\nu)$: " " traj. ν, but using only beg. + end of traj.

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

$$A = \langle A(\nu) \rangle = \sum_\nu P(\nu) A(\nu)$$ avg. over all traj.

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

$= \Delta A(\nu)$ for some $A(\nu)$

$\Rightarrow$ known as conservative work

compare $\omega = \nabla U$

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

if no such $A(\nu)$ exists $\Rightarrow$ $W(\nu)$ is not conservative heat (energy from thermal env.) during $n_i \to n_{i+1}$ trans:

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

define total heat taken up from env:

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

take avg: $\boxed{Q = \Delta E + W}$ 1st law of thermodynamics

one last technicality:

avg. of a conservative quantity $\Delta A(\nu)$

$$\Delta A(\nu) = A_{n_\tau} - A_{n_0}$$

$$\Delta A = \langle \Delta A(\nu) \rangle = \sum_\nu P(\nu)\,(A_{n_\tau} - A_{n_0})$$

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

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

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

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

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

(columns of W sum to 1)

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

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

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

$\Delta S = \langle \Delta S(\upsilon) \rangle = S(t_\tau) - S(t_0)$

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

= average "surprisal"

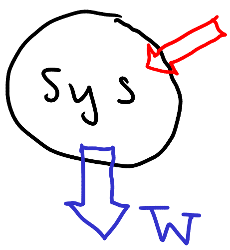
= Gibbs formula for entropy

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

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

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

two laws of thermodyn.



Q avg. heat from env.

> 0 into sys

< 0 out of sys

W avg. work done:

> 0 by the sys

< 0 on the sys

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

total ergodic + mixing

$\Rightarrow$ sys. is ergodic & mixing,
completely isolated

$\Rightarrow$ all energy levels of sys. are same $\underset{\text{const.}}{E_n = E}$

& no work done b/c sys. is isolated

$$E(t) = \sum_n p_n(t) E_n = E \quad \text{const. in time}$$

1st law: $\Delta E = 0, W = 0 \Rightarrow Q = 0$ no heat input

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

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

for an isolated, ergodic & mixing system
entropy cannot decrease!