Thermodynamics so far:

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

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

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

physical characteristics (averages) at time t

how things change from beg. to end:

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

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

laws:

1st: $Q = \Delta E + W$

2nd: $I = -\frac{\Delta F}{T} + \frac{W}{T} \geq 0$

$$I = \langle I(\nu) \rangle$$

$$I(\nu) = k_B \ln \frac{\mathcal{P}(\nu)}{\tilde{\mathcal{P}}(\tilde{\nu})}$$

or $TI = T\Delta S - \Delta E + W \geq 0$

cases: 1) isolated sys (no env.)

all $E_n = E$ const. $\quad Q = 0, W = 0$

$\Rightarrow \Delta E = 0$ (1st)

$\Rightarrow TI = T\Delta S \geq 0$ (2nd)

$\Rightarrow I = \Delta S \geq 0 \Rightarrow S(t)$ is non-decreasing

Do we know anything else? Answer: YES

Note $S(t)$ is bounded:

$$0 \leq S(t) \leq k_B \ln N$$

$N \rightarrow$ # macrostates (sys. states)

at all times

$$= -k_B \sum_n p_n \ln p_n$$

Zero entropy if prob. all in one state

occurs when $p_n = \begin{cases} 1 & n=k \\ 0 & n\neq k \end{cases}$

$1 \ln 1 = 0$

$0 \ln 0 = \lim_{x\to 0^+} x \ln x = 0$

$\{$ occurs when $p_n = \frac{1}{N}$ for all n

$$-k_B \sum_n \frac{1}{N} \ln \frac{1}{N} = -k_B N \frac{1}{N} \ln \frac{1}{N} = k_B \ln N$$

upper bound proof:

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

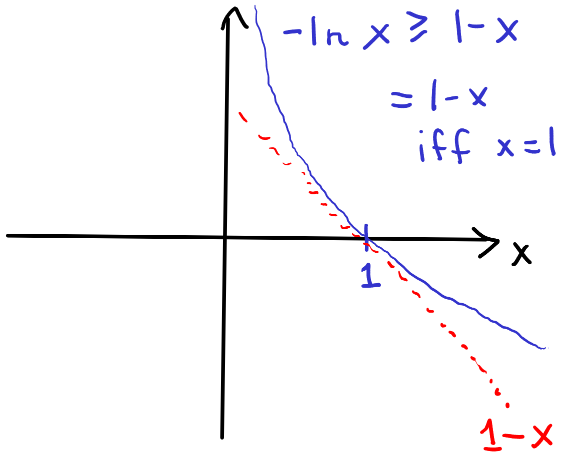
$$= k_B \underbrace{\sum_n p_n}_{1} \ln N + k_B \sum_n p_n \ln p_n$$

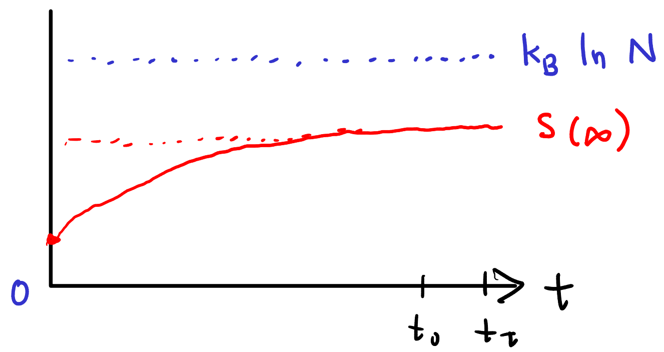
$$= k_B \sum_n p_n \ln (N p_n)$$

$$= k_B \sum_n p_n \left(-\ln \frac{1}{N p_n}\right)$$

$$\geq k_B \sum_n p_n \left(1 - \frac{1}{N p_n}\right)$$

$$= k_B (1 - 1) = 0$$





is this possible? seems consistent w/ 2nd law,

but answer: <u>NO</u>

argument: as $t\to\infty$, $S(t)$ must reach a plateau (b/c $S(t)$ is bounded from above)

as $t\to\infty$, $\Delta S = 0$ (traj. at the plateau)

2nd law: $\Delta S = I = 0$

we will prove if $I = 0 \Rightarrow I(\nu) = 0$ for any traj. ν

proof: $$\overset{\text{IFT}}{1} = \left\langle e^{-I(\nu)/k_B} \right\rangle = \sum_\nu \mathcal{P}(\nu)\, e^{-I(\nu)/k_B}$$

$$\geq \sum_\nu \mathcal{P}(\nu)\left(1 - \frac{I(\nu)}{k_B}\right)$$

$e^{-x} \geq 1 - x$

$= 1 - x$ iff $x = 0$

$$= 1 - \frac{1}{k_B}\langle I(\nu)\rangle$$

$$1 \geq 1 - \frac{1}{k_B} I \Rightarrow I \geq 0$$

if $I = 0$, only way for equality to be satisfied is if x in every term in sum is equal to zero

$$\Rightarrow I(\nu) = 0 \text{ for every } \nu$$

Imagine we have reached long time limit (some stat. state $\vec{p}^{\,s}$) + look at traj. of one step: $\nu = \mu_i$

$$I = 0 \Rightarrow I(\mu_i) = k_B \ln \frac{W_{n_{i+1} n_i}\, \overbrace{p_{n_i}(t_i)}^{p^s_{n_i}}}{W_{n_i n_{i+1}}\, \underbrace{p_{n_{i+1}}(t_{i+1})}_{p^s_{n_{i+1}}}} = 0$$

$$\Rightarrow W_{n_{i+1} n_i}\, p^s_{n_i} = W_{n_i n_{i+1}}\, p^s_{n_{i+1}}$$

from LDB: $$\frac{W_{n_{i+1} n_i}}{W_{n_i n_{i+1}}} = e^{-\beta\left(\underbrace{E_{n_{i+1}} - E_{n_i}}_{0} + \underbrace{\omega_{n_{i+1} n_i}}_{0}\right)}$$

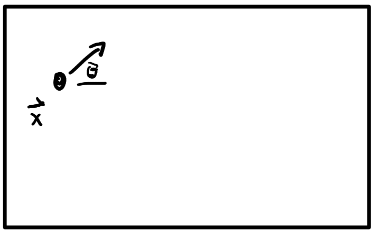
$= 1$

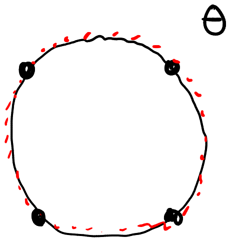
$\Rightarrow \; p^s_{n_i} = p^s_{n_{i+1}} \Rightarrow$ all probs in stat. state are same

$\Rightarrow \; p^s_{n_i} = \frac{1}{N}$ by normalization

$\Rightarrow \; S(t) = k_B \ln N$ as $t \to \infty$

plateau <u>must</u> occur at $k_B \ln N$





2) allow heat from env: $Q \neq 0$

E_n not all const.

but no coupling to work: $W = 0$

1st: $Q = \Delta E$

2nd: $TI = T\Delta S - \Delta E = -\Delta F \geq 0$

$\Rightarrow \Delta F \leq 0$ Helmholtz free energy is non-increasing

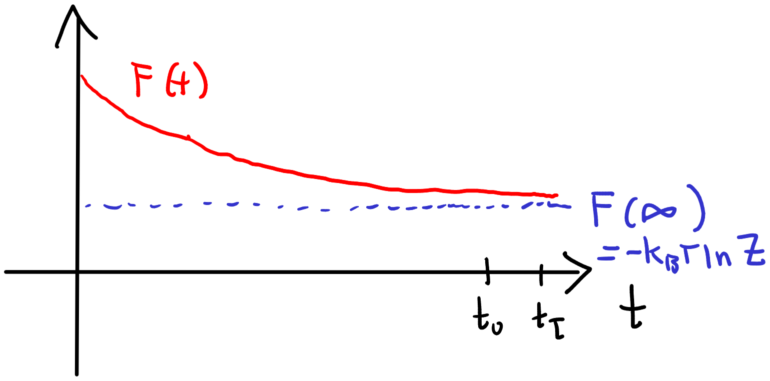
Similar argument: $F(t)$ cannot decrease forever

b/c $F(t) = E(t) - TS(t)$

$S(t): \quad 0 \leq S(t) \leq k_B \ln N$

$E(t): \quad E_{min} \leq E(t) \leq E_{max}$

smallest state energy   largest state energy



look at traj. in long time limit $t \to \infty$

$$\Delta F = -T\mathcal{I} = 0$$

$$\Rightarrow \mathcal{I} = 0$$

$$\mathcal{I} = 0 \Rightarrow \mathcal{I}(\mu_i) = 0$$

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

LDB: $$\frac{W_{n_{i+1} n_i}}{W_{n_i n_{i+1}}} = e^{-\beta(E_{n_{i+1}} - E_{n_i} + \cancel{w_{n_{i+1} n_i}}^{\,0})}$$

$$\Rightarrow e^{\beta E_{n_i}}\, p_{n_i}(t_i) = e^{\beta E_{n_{i+1}}}\, p_{n_{i+1}}(t_{i+1})$$

$\Rightarrow$ satisfied when $p_n(t) = \dfrac{e^{-\beta E_n}}{Z}$

as $t \to \infty$ $\quad p_n(t) \to \dfrac{e^{-\beta E_n}}{Z}$ $\quad$ Boltzmann distrib.

$$F(t \to \infty) = \underset{p_n(t)}{\text{plug in}} = -k_B T \ln Z$$

$$\equiv F^{eq}$$

equil. free energy

free energy minimization principle