Recap of thermodynamics:

system coupled to env. at temp T
W

physical characteristics at time

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

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

$$F(t) = E(t) - T S(t)$$

How things change between time points:

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

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

laws:

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

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

$$I = \langle \underbrace{I(v)}_{k_B \ln \frac{\mathcal{P}(v)}{\tilde{\mathcal{P}}(\tilde{v})}} \rangle$$

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

cases: 1) isolated sys (no env.)

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

$\Rightarrow \Delta E = 0, \quad I = \Delta S \geq 0$

$\Rightarrow S(t)$ is non-decreasing

Do we know anything else? ANSWER: yes

note: $S(t)$ is bounded:

$$0 \leq \underbrace{S(t)}_{= -k_B \sum_n p_n(t) \ln p_n(t)} \leq k_B \ln N$$

N: # macro states

occurs when:

$$p_n = \begin{cases} 1 & \text{for } n=k \\ 0 & \text{for } n \neq k \end{cases}$$

$$1 \ln 1 = 0$$

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

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

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

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

$$= k_B \ln N$$

proof of upper bound:

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

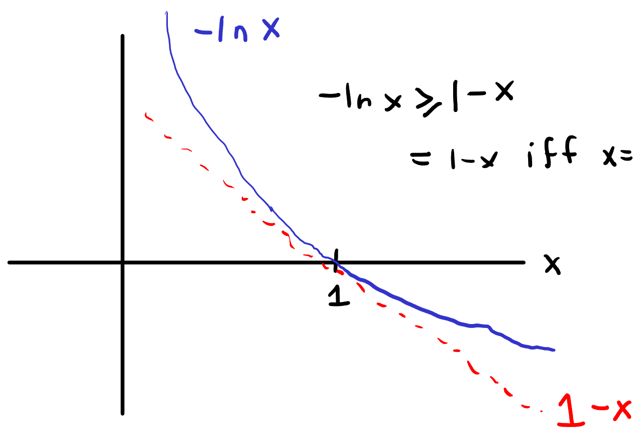
$$= k_B \sum_n p_n \ln N + k_B \sum_n p_n \ln p_n$$

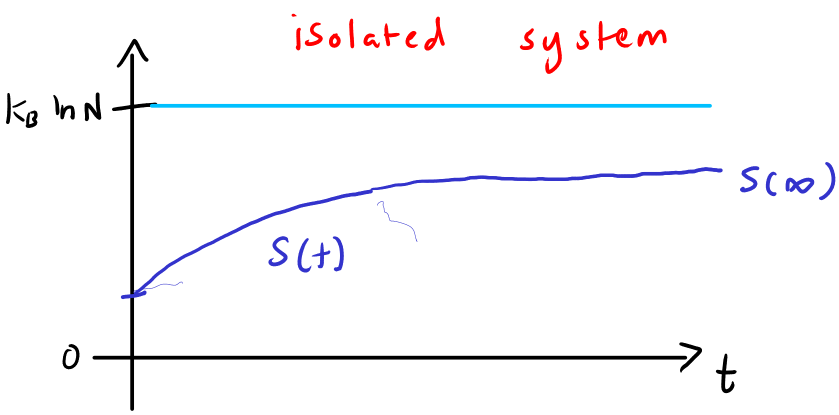
$$= k_B \sum_n p_n \ln (N p_n)$$

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

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

$$= k_B (1-1) = 0 \quad \checkmark$$





is this possible? seems consistent w/ therm. laws, but answer: no

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

$\Rightarrow$ as $t \to \infty$ $\quad \Delta S = 0$ traj. is at the plateau

$$\underset{\displaystyle S(t_\tau) - S(t_0)}{\Delta S} = 0$$

initial pt. of traj. at plateau

$$\text{2nd law: } \quad \Delta S = \overset{\displaystyle 0}{\overset{\shortparallel}{I}}$$

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

proof: IFT $\quad 1 = \left\langle e^{-I(\nu)/k_B} \right\rangle$

$$= \sum_\nu \mathcal{P}(\nu)\, e^{-I(\nu)/k_B}$$

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

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

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

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

$$\Rightarrow \quad 1 \geq 1 - I/k_B \Rightarrow I \geq 0$$

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

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

Recall we are in $t \to \infty$ limit, hence $\vec{p}(t) = p^s$

stat. state

let's look at any traj. of length 1

$$\nu = \mu_i = (n_i, n_{i+1})$$

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

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

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

isolated sys.

$$= 1$$

$$\Rightarrow \quad p^s_{n_i} = p^s_{n_{i+1}} \quad \text{for any } n_i \,\&\, n_{i+1} \text{ connected by trans.}$$

$$= \text{const.}$$

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

$$\Rightarrow \quad \boxed{S(t) = k_B \ln N \quad \text{as } t \to \infty}$$

plateau has to occur at $k_B \ln N$ for isolated system case: 2) allow heat from env. $Q \neq 0$

E_n = not const.

but no coupling to work: $W = 0$

1st: $Q = \Delta E$

2nd: $T\mathcal{I} = T\Delta S - \Delta E = -\Delta F$

≥ 0

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

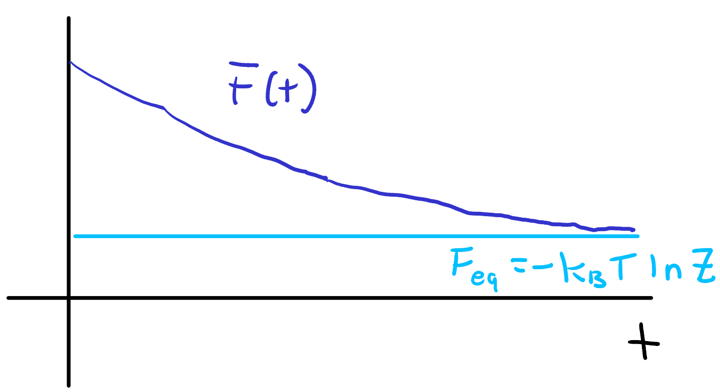
similar argument: $F(t)$ cannot decrease forever

b/c $F(t) = E(t) - T S(t)$

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

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

$\overset{\shortparallel}{\sum_n p_n(t) E_n}$ smallest sys. state energy, largest " "



look at traj. at long times $t_0, t_I \to \infty$

plateau $\Rightarrow \Delta F = 0 \Rightarrow \mathcal{I} = 0$

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

$$\frac{W_{n_{i+1} n_i}}{W_{n_i n_{i+1}}} = e^{-\beta\left(E_{n_{i+1}} - E_{n_i} + \cancelto{0}{\omega_{n_{i+1} n_i}}\right)}$$

denom.

numerator

$$\Rightarrow \quad e^{\beta E_{n_i}} \underbrace{p_{n_i}(t_i)}_{p^s_{n_i}} = e^{\beta E_{n_{i+1}}} \underbrace{p_{n_{i+1}}(t_{i+1})}_{p^s_{n_{i+1}}}$$

$\Rightarrow$ satisfied when $p^s_n = \dfrac{e^{-\beta E_n}}{Z}$

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

$F(t\to\infty) =$ plug in p^s_n $= -k_B T \ln Z$

$\equiv F^{eq}$ equil. free energy