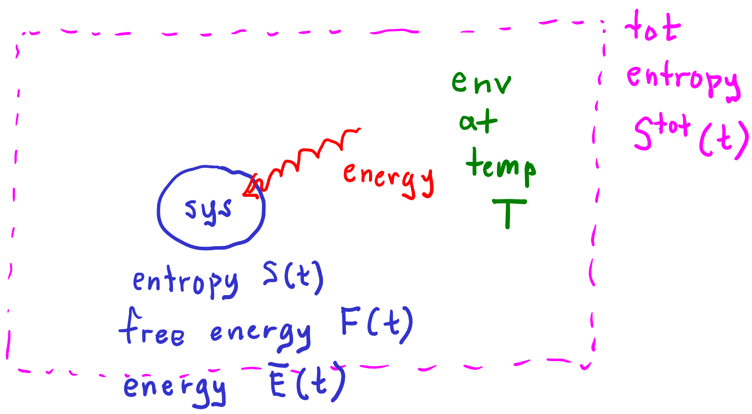
PHYS 414 : 3-20-20



could be <0 or >0

$$\dot{S}(t) = \underbrace{\dot{S}^e(t)}_{\substack{\text{entropy flow} \\ = \frac{\dot{E}}{T}}} + \underbrace{\dot{S}^i(t)}_{\substack{\text{entropy production} \\ = -\frac{\dot{F}}{T} \geq 0}}$$

specific: $$\frac{W_{nm}}{W_{mn}} = e^{-\beta(E_n - E_m)} \qquad \beta = \frac{1}{k_B T}$$

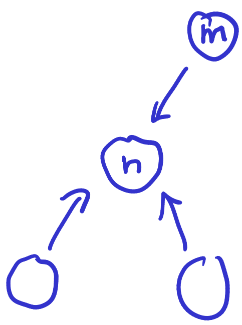
$$\dot{S}^{tot}(t) = \dot{S}^i(t) \geq 0$$

Generality of: $\dot{S} = \dot{S}^e + \dot{S}^i$ where $\dot{S}^i \geq 0$

(Ilya Prigogine, Nobel in Chem. 1977)

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

$$\dot{p}_n = \sum_m \underbrace{\left[W_{nm} p_m - W_{mn} p_n \right]}_{J_{nm}} = \sum_m J_{nm}$$



J_{nm} = prob. current from m to n

$$= \frac{(\#\text{ trans. } m \to n) - (\#\text{ trans. } n \to m)}{\text{unit time}}$$

$$\dot{S} = -k_B \sum_n \dot{p}_n \ln p_n - k_B \underbrace{\sum_n \dot{p}_n}_{\frac{d}{dt}\sum_n p_n = \frac{d}{dt} 1 = 0}$$

$$= -k_B \sum_{nm} J_{nm} \ln p_n$$

$$= \frac{1}{2}\left[-k_B \sum_{nm} J_{nm} \ln p_n - k_B \sum_{mn} \underbrace{J_{mn}}_{= -J_{nm}} \ln p_m \right]$$

$$= +\frac{k_B}{2} \sum_{nm} J_{nm} \ln \frac{p_m}{p_n}$$

$$\dot{S}(t) = \underbrace{\frac{k_B}{2}\sum_{nm} J_{nm} \ln \frac{W_{nm}\,p_m}{W_{mn}\,p_n}}_{\text{i) general expression for } \dot{S}^i(t) \text{ will show } \geq 0} - \underbrace{\frac{k_B}{2}\sum_{nm} J_{nm} \ln \frac{W_{nm}}{W_{mn}}}_{\text{ii) general expression for } \dot{S}^e(t) \text{ entropy flow}}$$

if $\dfrac{W_{nm}}{W_{mn}} = e^{-\beta(E_n - E_m)}$

$\Rightarrow \dot{S}^e = \dot{E}/T$

i) $J_{nm} = W_{nm}\,p_m - W_{mn}\,p_n$

$\dot{S}^i(t) \geq 0$ b/c each term has form $(x-y)\ln\dfrac{x}{y} \geq 0$ always + $=0$ iff $x=y$

$\underline{\underline{\dot{S}^i(t) = 0}}$ iff $W_{nm}\,p_m = W_{mn}\,p_n$ ✓

general definition of equilibrium

$$\frac{W_{nm}}{W_{mn}} = \frac{p_n}{p_m}$$

satisfied at Boltzmann equil.

$$p_n = p_n^s = \frac{e^{-\beta E_n}}{Z}$$

$\dot{S}^i(t) > 0$: <u>not in equilibrium</u>

ii) check $\dot{S}^e = \dfrac{\dot{E}}{T}$ for sys coupled to env at temp T (special case)

$$\frac{W_{nm}}{W_{mn}} = e^{-\beta(E_n - E_m)} \Rightarrow$$

$E_n - E_m \overset{\text{def'n of}}{\equiv} Q_{nm}$

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

$$\dot{S}^e = \frac{1}{2T}\sum_{nm} J_{nm}(E_n - E_m)$$

$$\dot{S}^e = \frac{1}{2T}\sum_{nm} J_{nm} Q_{nm}$$

$$= \frac{1}{2T}\left[\sum_{nm} J_{nm} E_n - \sum_{nm} J_{nm} E_m\right]$$

$$\equiv \frac{\dot{Q}}{T}$$

def'n of heat flow rate $\dot{Q}$

$$= \frac{1}{2T}\left[\sum_{nm} J_{nm} E_n + \sum_{nm} J_{mn} E_m\right]$$

$$= \frac{1}{2T}\left[\sum_{nm} J_{nm} E_n + \sum_{nm} J_{nm} E_n\right]$$

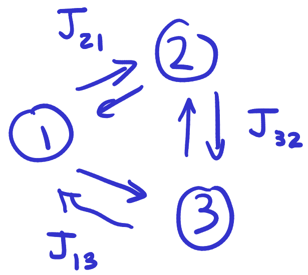
$$dS \equiv \frac{dQ}{T} = \frac{1}{T}\sum_{nm} J_{nm} E_n \qquad \sum_m J_{nm} = \dot{p}_n$$

$$= \frac{1}{T}\sum_n \dot{p}_n E_n = \frac{1}{T}\dot{\bar{E}} \qquad \bar{E} = \sum_n p_n E_n$$

$$T\dot{S}^e = \frac{1}{2}\sum_{nm} J_{nm} Q_{nm}$$

analogy

power ~ current × voltage



$$T\dot{S}^e = J_{21}(E_2 - E_1) + J_{32}(E_3 - E_2) + J_{13}(E_1 - E_3)$$

Equilibrium is boring:

W_{nm} is const. in time

$$p_n(t) \longrightarrow p_n^s = \frac{e^{-\beta E_n}}{Z}$$

satisfies: $\dfrac{W_{nm}}{W_{mn}} = \dfrac{p_n^s}{p_m^s} \Rightarrow J_{nm}^s = W_{nm} p_m^s - W_{mn} p_n^s = 0$

for every conn. (n,m)

$$\dot{S}^i = \frac{k_B}{2}\sum_{nm} J_{nm} \ln\frac{W_{nm} p_m}{W_{mn} p_n} = 0$$

$$\dot{S}^e = \frac{-k_B}{2}\sum_{nm} J_{nm} \ln\frac{W_{nm}}{W_{mn}} = 0$$

$$\dot{S} = \dot{S}^i + \dot{S}^e = 0$$