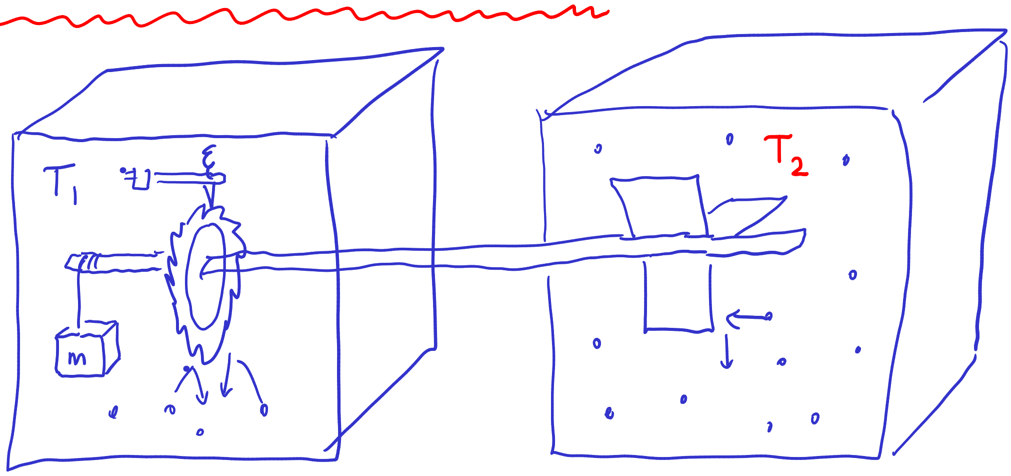
PHYS 414: 3-27-20



states n $\Downarrow$ ratchet wheel states E_n

toy example of "heat engine" $\quad T_2 > T_1$

$\Rightarrow$ converts temp. diff into useful work

superscripts denote heat bath reservoir

$$W_{n+1,n} = W^{(1)}_{n+1,n} + W^{(2)}_{n+1,n}$$

each contrib. is from energy exchange due to collisions w/ particles in that heat bath

we know that heat baths satisfy MR conditions:

$$\frac{W^{(k)}_{n+1,n}}{W^{(k)}_{n,n+1}} = e^{-\beta_k (E_{n+1} - E_n + mg\Delta h)} \qquad \beta_k = \frac{1}{k_B T_k} \quad k=1,2$$

In general, imagine N_r heat baths:

$$W_{nm} = \sum_{k=1}^{N_r} W^{(k)}_{nm} \quad \text{where} \quad \underline{\frac{W^{(k)}_{nm}}{W^{(k)}_{mn}} = e^{-\beta_k (E_n - E_m + V^{(k)}_{nm})}}$$

prob. current
$$J_{nm} = W_{nm} p_m - W_{mn} p_n$$
$$= \sum_k \underbrace{\left[W^{(k)}_{nm} p_m - W^{(k)}_{mn} p_n\right]}_{J^{(k)}_{nm}} = \sum_k J^{(k)}_{nm}$$

master equ: $\quad \dot{p}_n = \sum_m J_{nm} = \sum_{mk} J^{(k)}_{nm}$

Redo Prigogine entropy decomp. deriv from before:

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

take $\frac{d}{dt}$ of this $\Rightarrow$ plug in $\dot{p}_n$ from master equ

(logarithm magic)

$$\dot{S}(t) = \frac{k_B}{2} \sum_{nmk} J_{nm}^{(k)} \ln \frac{W_{nm}^{(k)} p_m}{W_{mn}^{(k)} p_n} \quad \Big\} \text{ term } 1 \equiv \dot{S}^i$$

$$- \frac{k_B}{2} \sum_{nmk} J_{nm}^{(k)} \ln \frac{W_{nm}^{(k)}}{W_{mn}^{(k)}} \quad \Big\} \text{ term } 2 \equiv \dot{S}^e$$

term 1 is a sum of quantities of form $(x-y) \ln \frac{x}{y}$

$\Rightarrow$ $\dot{S}^i \geq 0$ and $=0$ iff all $J_{nm}^{(k)} = 0$

term 2 $\Rightarrow$ plug in $\frac{W_{nm}^{(k)}}{W_{mn}^{(k)}}$ ratio from MR condition

$$\dot{S}^e = \frac{1}{2} \sum_{nmk} \frac{J_{nm}^{(k)}}{T_k} \left(E_n - E_m + V_{nm}^{(k)}\right)$$

$$\equiv \sum_k \frac{\dot{Q}_k}{T_k} \quad \text{where} \quad \dot{Q}_k \equiv \frac{1}{2} \sum_{nm} J_{nm}^{(k)} \left(E_n - E_m + V_{nm}^{(k)}\right)$$

heat flux into sys due to k th reservoir

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

$$\Rightarrow \quad \dot{S}^i = \dot{S} - \dot{S}^e = \boxed{\dot{S} - \sum_k \frac{\dot{Q}_k}{T_k} \geq 0}$$

entropy budget statement

$$\sum_k \dot{Q}_k = \frac{1}{2} \sum_{nmk} J_{nm}^{(k)} (E_n - E_m) + \frac{1}{2} \sum_{nmk} J_{nm}^{(k)} V_{nm}^{(k)}$$

$$= \frac{1}{2} \sum_{nm} J_{nm} (E_n - E_m) + \sum_k \dot{W}^{(k)}$$

work rate from kth reserv.

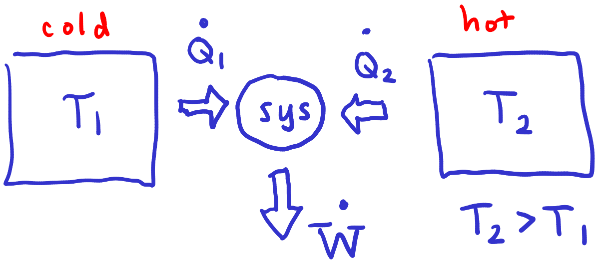
$$= \dot{\bar{E}} + \sum_k \dot{W}_k$$

$$\boxed{\sum_k \dot{Q}_k = \dot{\bar{E}} + \dot{W}}$$

1st law (energy conservation)

where $\dot{W} = \sum_k \dot{W}^{(k)}$ total rate of work

Return to our example: two heat baths



$$\dot{Q}_1 + \dot{Q}_2 = \dot{\bar{E}} + \dot{W}$$

$$\dot{S}^i = \dot{S} - \frac{\dot{Q}_1}{T_1} - \frac{\dot{Q}_2}{T_2} \geq 0$$

i) assume everything goes to stat. state $p_n(t) \rightsquigarrow p_n^s$

$$\left.\begin{array}{l} S = -k_B \sum_n p_n \ln p_n \Rightarrow \dot{S} = 0 \\ \bar{E} = \sum_n p_n E_n \Rightarrow \dot{\bar{E}} = 0 \end{array}\right\} \text{in stat. state}$$

plug in: $\dot{Q}_1 = \dot{W} - \dot{Q}_2$, $\dot{S}^i = -\frac{\dot{Q}_1}{T_1} - \frac{\dot{Q}_2}{T_2} \geq 0$

$$= -\frac{\dot{W}}{T_1} + \frac{\dot{Q}_2}{T_1} - \frac{\dot{Q}_2}{T_2}$$

Case 1: assume $\dot{Q}_2 > 0$ (hot bath donates heat)

$$\underbrace{\frac{\text{rate of work}}{\text{heat input from hot bath}}}_{= \eta \text{ efficiency}} = \frac{\dot{W}}{\dot{Q}_2} = 1 - \frac{T_1}{T_2} - \frac{T_1 \dot{S}^i}{\dot{Q}_2} \leq 1 - \frac{T_1}{T_2}$$

$$\boxed{\eta \leq 1 - \frac{T_1}{T_2}}$$

Carnot efficiency bound