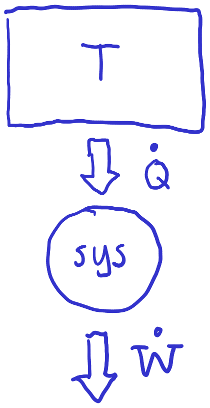
PHYS 414: 3-25-20



heat bath
env. at
temp T

$\dot{Q}>0$ env. donating energy to sys

$\dot{Q}<0$ reverse

$\dot{W}>0$ sys. doing work on ext. deg. of freedom ("raising the mass")

$$\dot{Q} = \dot{E} + \dot{W}$$

$$\dot{E} = \frac{d}{dt}E = \frac{d}{dt}\sum_n p_n E_n$$

$$= \frac{1}{2}\sum_{nm} J_{nm}(E_n - E_m)$$

$$\dot{W} = \frac{1}{2}\sum_{nm} J_{nm} V_{nm}$$

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

$$\frac{W_{n+1,n}}{W_{n,n+1}} = e^{-\beta(E_{n+1} - E_n + mg\Delta h)}$$

entropy flow

$$\dot{S}^e = \frac{\dot{E}}{T} + \frac{\dot{W}}{T} = \frac{\dot{Q}}{T}$$

$$\dot{S} = \dot{S}^i + \dot{S}^e \Rightarrow \dot{S}^i = \dot{S} - \dot{S}^e \geq 0 \text{ by construction}$$

$$= \dot{S} - \frac{\dot{E}}{T} - \frac{\dot{W}}{T}$$

$$\Rightarrow T\dot{S}^i = T\dot{S} - \dot{E} - \dot{W} \qquad F = E - TS$$

Helmholtz free energy

$$= -\dot{F} - \dot{W} \geq 0$$

$$\Rightarrow \boxed{\dot{W} \leq -\dot{F}}$$

rate at which sys can do work is bounded by $-\dot{F}$: for every decrease in F, you can extract up to that amount of work, + no more

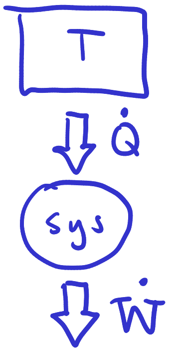
"free" energy: energy that is free to do work perfection in conv. free to work $\quad \mathring{W} = -\dot{F}$ requires $\dot{S}^i = 0 = \frac{1}{2}\sum_{nm} J_{nm} \ln \frac{W_{nm}p_m}{W_{mn}p_n}$

$\Rightarrow$ requires $J_{nm} = 0$ for all (n,m)

$\Rightarrow$ requires equilibrium where $\mathring{W} = 0$, $\dot{F} = 0$

Special cases:

$\bar{E}(t) = \sum_n p_n(t) E_n$



cannot have a "perpetual motion" machine that converts energy from env. into work at a single temp.

1) everything reaches a stat. state as $t \to \infty$

$$p_n(t) = p_n^s$$

$$\bar{E} = \sum_n E_n p_n^s \Rightarrow \mathring{\bar{E}} = 0$$

$$S = -k_B \sum_n p_n^s \ln p_n^s \Rightarrow \dot{S} = 0$$

$$F = \bar{E} - TS \Rightarrow \dot{F} = 0$$

$$\mathring{W} \leq -\dot{F} = 0 \Rightarrow \text{cannot have pos. work}$$

(sys doing work on env.)

$$\mathring{Q} = \underbrace{\cancel{\mathring{\bar{E}}}}_{0} + \mathring{W} \leq 0$$

↳ can't have heat flowing into sys

2) Ext. coupling $V_{nm}(t)$ is periodic in time w/ period τ : $V_{nm}(t+\tau) = V_{nm}(t)$

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

$W_{nm}(t)$ is also periodic in time

Scenario that describes some complicated engine-like cycle

from PS #2 $\Rightarrow$ in this case sys goes to a "periodic" state (non-stationary)

$p_n(t) \rightarrow p_n^{ps}(t)$ where $p_n^{ps}(t+\tau) = p_n^{ps}(t)$

(in our example periodic $V_{nm}(t)$ is the mass varying $m(t)$ periodically in time)

all quantities dependent on $p_n(t)$ become periodic:

$$\bar{E}(t) = \bar{E}(t+\tau)$$
$$S(t) = S(t+\tau)$$
$$F(t) = F(t+\tau)$$

$$\Delta F = \text{free energy change over one cycle} = F(t+\tau) - F(t) = \int_t^{t+\tau} \dot{F}\, dt = 0$$

since $\dot{W} \leq -\dot{F}$

$$\underset{\substack{\parallel \\ \text{work extracted} \\ \text{over one cycle}}}{\Delta W} = \int_t^{t+\tau} \dot{W}\, dt \leq -\Delta F = 0$$

$$\Rightarrow \quad \Delta W \leq 0$$

also know $\dot{Q} = \dot{\bar{E}} + \dot{W}$ $\Rightarrow$ integrate over one cycle

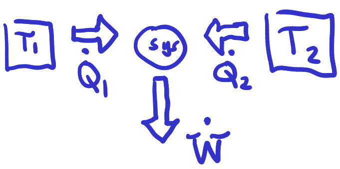
$$\Delta Q = \cancel{\Delta \bar{E}}^{\,0} + \Delta W \leq 0$$

stat. state	periodic state
$\dot{W} \leq 0$	$\Delta W \leq 0$
$\dot{Q} = \dot{W} \leq 0$	$\boxed{\Delta Q = \Delta W \leq 0}$

Kelvin-Planck statement of 2nd law

$\Rightarrow$ cannot get pos net work out of a cycle for sys coupled to a single temp. environment

solution: more than one heat bath!



$$\boxed{\dot{S}^i \geq 0}$$