PHYS 414: 3-23-20

Last lecture:

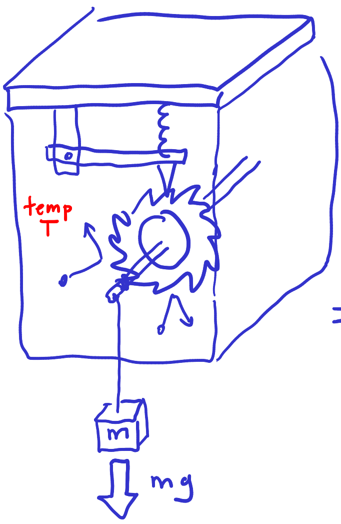
$$\dot{S}(t) = \underbrace{\dot{S}^i(t)}_{\frac{k_B}{2}\sum_{nm} J_{nm} \ln \frac{W_{nm} p_m}{W_{mn} p_n}} + \underbrace{\dot{S}^e(t)}_{-\frac{k_B}{2}\sum J_{nm} \ln \frac{W_{nm}}{W_{mn}}}$$

$\dot{S}(t)$: rate of change of sys entropy

$\dot{S}^i(t) \geq 0$: internal entropy prod.

$\dot{S}^e(t)$: entropy flow, >0 or <0

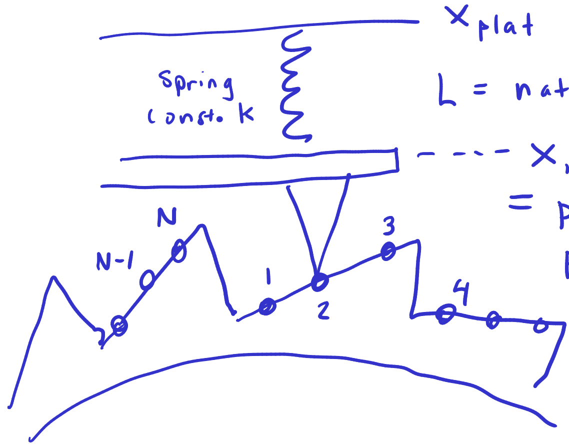
Special case: when $\frac{W_{nm}}{W_{mn}} = e^{-\beta(E_n - E_m)} \Rightarrow \dot{S}^e(t) = \frac{\dot{E}(t)}{T}$



sys = pawl + ratchet

n th state E_n

$= \frac{1}{2} k (x_{plat} - x_n - L)^2$



x_{plat}

L = nat. length of spring

x_n = pawl position

$$\cdots \; N \rightleftarrows 1 \rightleftarrows 2 \rightleftarrows 3 \; \cdots$$

sys (pawl + ratchet) coupled to external deg. of freedom ($\Rightarrow$ "work")

$N+1 \equiv 1$

state $n \to n+1$ (CCW rot.) mass is raised by Δh

$n \to n-1$ (CW rot.) mass is lowered by Δh

$$\begin{array}{l} n \to n+1 \\ n+1 \to n \end{array} \quad \frac{W_{n+1,n}}{W_{n,n+1}} = e^{-\beta(E_{n+1} - E_n + mg\Delta h)}$$

$mg\Delta h$: pot. difference due to ext. coupling

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

$V_{nm}(t)$: energy change in ext. deg. of freedom during $m \to n$ trans.

plug into $\mathring{S}^e(t)$ equ:

$$\mathring{S}^e = -\frac{k_B}{2}\sum_{n,m} J_{nm} \ln \frac{W_{nm}(t)}{W_{mn}(t)}$$

$$= \frac{\mathring{E}}{T} + \frac{1}{T}\underbrace{\sum_{n,m}\frac{1}{2}J_{nm}V_{nm}}_{\mathring{W}}$$

definition of rate of work

$\mathring{W}$ = rate at which sys does "work" on ext. deg. of freedom

$$\mathring{E} = \frac{1}{2}\sum_{n,m} J_{nm}(E_n - E_m)$$

rate of change of mean "internal" (sys) energy

note: often we can write

$V_{nm} = V_n - V_m$ diff in pot. energies associated w/ states n + m

where $V_{nm} = -V_{mn}$

but we don't need this assumption right now (keep things general)

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

"heat" = energy taken from or dumped into env.

define $\mathring{Q} = \mathring{E} + \mathring{W}$

$\mathring{Q}$: energy flux from env. $\equiv$ heat flux

$\mathring{E}$: rate of change of sys. energy

$\mathring{W}$: rate at which sys does work on ext. degrees

energy conservation relation

$\Rightarrow$ "1st law of thermodynamics"

from before: when no coupling to ext. deg.

$$\mathring{Q} = \mathring{E}$$

in general:

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

$\equiv Q_{nm}$ = heat exch. in $m \Rightarrow$ trans.

energy that env. needs to provide to facilitate $m \to n$ trans.

$$\dot{Q} = \frac{1}{2} \sum_{n,m} J_{nm} Q_{nm}$$

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

where $\dot{E} = \frac{1}{2} \sum_{n,m} J_{nm} (E_n - E_m)$

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