

Linear thermodynamics:

focus on one time step δt :

$$\mu_0 = (n_0, n_1)$$

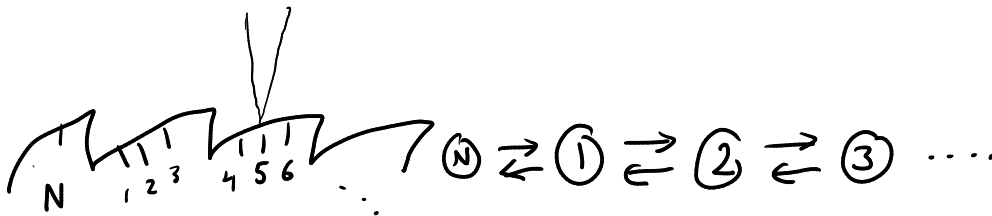
state n_0 : $P_{n_0}^s$
 " n_1 : $P_{n_1}^s$

we are in a stationary state (not necessarily equil, I small but nonzero)

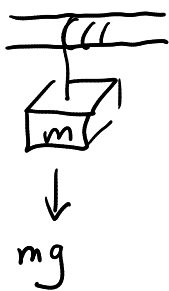
NESS:
$$I = -\frac{1}{T} \bar{W}$$

$$\langle I(\mu_0) \rangle = -\frac{1}{T} \langle W(\mu_0) \rangle$$

assume form for work: $W(\mu_0) = W_{n_1, n_0}$



$= -f \Delta x_{n_1, n_0}$
 \uparrow "force" \uparrow "distance"
 some physical quantity we control change in phys. observ.



$$f = mg$$

$$\Delta x_{n_1, n_0} = \begin{cases} +h & \text{if } n_1 = n_0 + 1 \\ -h & \text{if } n_1 = n_0 - 1 \end{cases}$$

assume

$$\Delta x_{nm} = -\Delta x_{mn}$$

$$\Delta x_{nn} = 0$$

if $f = 0 \Rightarrow \bar{W}(\mu_0) = 0$

$$\Rightarrow \bar{W} = 0 \Rightarrow I = 0 \quad \text{ESS}$$

$$\begin{aligned}
 \text{When } f \neq 0: \quad W &= -f \langle \delta x \rangle \\
 &= -f \sum_{n, n_0} \mathcal{P}(\mu_0) \delta x_{n, n_0} \\
 &= -f \sum_{n, n_0} \underbrace{W_{n, n_0} p_{n_0}^s}_{\text{red wavy line}} \delta x_{n, n_0}
 \end{aligned}$$

$$\text{LDB: } \frac{W_{n, n_0}}{W_{n_0, n_1}} = e^{-\beta(E_{n_1} - E_{n_0} - f \delta x_{n, n_0})}$$

\Rightarrow elements of W depend on f

\Rightarrow stationary state \vec{p}^s (right e-vec of W w/ e-val 1, $W \vec{p}^s = \vec{p}^s$) also depends on f

$$\text{in limit } f \rightarrow 0 \text{ ESS: } p_n^s \xrightarrow{f \rightarrow 0} p_n^{\text{eq}} = \frac{e^{-\beta E_n}}{Z}$$

$$\text{expand for each } n, m: \quad W_{nm} \xrightarrow{f \rightarrow 0} W_{nm}^{\text{eq}}$$

$$\underbrace{W_{nm} p_m^s}_{g(f)} = W_{nm}^{\text{eq}} p_m^{\text{eq}} \left[1 + \underset{\substack{\uparrow \\ \text{some number} \\ \text{related to Taylor exp.}}}{C_{nm}} f + \dots \right]$$

$$\begin{aligned}
 g(f) &= g(0) + g'(0) f + \frac{1}{2} g''(0) f^2 + \dots \\
 &= g(0) \left[1 + \frac{g'(0)}{g(0)} f + \frac{1}{2} \frac{g''(0)}{g(0)} f^2 + \dots \right]
 \end{aligned}$$

plug into expression for avg. work \bar{W} :

$$\bar{W} = -f \sum_{n_1, n_0} \underbrace{W_{n_1, n_0}^{eq} p_{n_0}^{eq}}_{\text{Symm. under } n_0 \leftrightarrow n_1} \delta x_{n_1, n_0} \quad \text{anti-symm. under } n_0 \leftrightarrow n_1$$

1st term = 0

$$-f \sum_{n_1, n_0} W_{n_1, n_0}^{eq} p_{n_0}^{eq} c_{n_1, n_0} f \delta x_{n_1, n_0} + \dots$$

LDB in equil: $\frac{W_{n_1, n_0}^{eq}}{W_{n_0, n_1}^{eq}} = e^{-\beta(E_{n_1} - E_{n_0})} = \frac{p_{n_1}^{eq}}{p_{n_0}^{eq}}$

true for every $n_1, n_0 \Rightarrow W_{n_1, n_0}^{eq} p_{n_0}^{eq} = W_{n_0, n_1}^{eq} p_{n_1}^{eq}$

Work $\bar{W} = -f \langle \delta x \rangle$
 $= -f^2 \underbrace{\sum_{n_1, n_0} W_{n_1, n_0}^{eq} p_{n_0}^{eq} c_{n_1, n_0} \delta x_{n_1, n_0}}_{l \text{ some number}}$

$$\langle \delta x \rangle = f l$$

$$\bar{W} = -f^2 l$$

$$\bar{I} = -\frac{\bar{W}}{T} = \frac{f^2 l}{T} \geq 0 \Rightarrow l \geq 0 \text{ to satisfy 2nd law of thermod.}$$

$$\sigma = \frac{\bar{I}}{\delta t} = \text{entropy prod. rate}$$

$$\frac{\langle \delta x \rangle}{\delta t} \equiv J \quad \text{thermodynamic "flux"}$$

$$\frac{f}{T} \equiv \phi \quad \text{thermodynamic "force"}$$

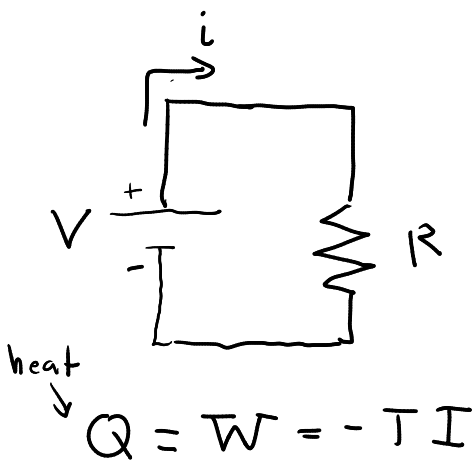
rewrite:
$$0 = J \phi = L \phi^2 \quad L \equiv \frac{dJ}{d\phi}$$

$$J = L \phi \quad = \text{constant} \geq 0$$

Onsager coefficient

L describes response of a sys. (flux) to applied thermo. force ϕ

example: stationary state of an electrical circuit



$$i = \frac{1}{R} V$$

$$J = \frac{L}{R} \phi = \frac{I}{T} \frac{V}{T}$$

power dissipated $-\frac{W}{\delta t} = i V$

$$\frac{Q}{\delta t} = \frac{W}{\delta t} = -\frac{TI}{\delta t}$$

$$-\frac{1}{T} \frac{W}{\delta t} = \frac{I}{\delta t} = 0$$

Summary:

$$J = i \quad L = \frac{T}{R} \geq 0$$

$$\phi = \frac{V}{T} \Rightarrow R \geq 0 \quad \text{2nd law}$$

$$\underbrace{i}_{J} \underbrace{\frac{V}{T}}_{\phi} = 0$$