linear therm.: stationary state w/ small I

$$Q = \overline{W} = -TI \leq 0$$

$$\overline{W} = \langle \overline{W}(\mu_0) \rangle \qquad \mu_0 = (n_0, n_1)$$

$$\overline{W}(\mu_0) = -\underset{\substack{\uparrow \\ \text{"force"}}}{f} \; \underset{\substack{\uparrow \\ \text{"dist."}}}{\delta x_{n_1 n_0}}$$

change from state $n_0 \to n_1$

$$\text{If } f = 0 \Rightarrow \overline{W}(\mu_0) = 0 \Rightarrow \overline{W} = 0 \Rightarrow I = 0$$

ESS

assume: $\delta x_{nm} = -\delta x_{mn} \qquad \delta x_{nn} = 0$

when $f \neq 0$: $$\overline{W} = -f \langle \delta x \rangle = -f \sum_{n_1 n_0} \underbrace{P(\mu_0)} \delta x_{n_1 n_0}$$

$$= -f \sum_{n_1 n_0} W_{n_1 n_0} p^s_{n_0} \delta x_{n_1 n_0}$$

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

both W matrix + $\vec{p}^{\,s}$ depend on f

in limit $f \to 0$: $$p^s_n \to p^{eq}_n = \frac{e^{-\beta E_n}}{Z}$$

$$W_{nm} \to W^{eq}_{nm}$$ (equil. trans. matrix)

$$\underbrace{W_{nm} p_m^s}_{g(f)} \approx \underbrace{W_{nm}^{eq} p_m^{eq}}_{g(0)} \Big(1 + \underset{\substack{\uparrow \\ \text{coeff.}}}{c_{nm}}\, f + \underset{\text{higher order in } f}{\cdots} \Big)$$

coeff. related to Taylor exp: $\frac{g'(0)}{g(0)}$

$$g(f) = g(0) + g'(0) f + \frac{1}{2} g''(0) f^2 + \cdots$$

$$= g(0)\left(1 + \frac{g'(0)}{g(0)} f + \cdots\right)$$

plug into expression for avg. $\overline{W}$:

$$\overline{W} = -f \sum_{n_1 n_0} \underbrace{W_{n_1 n_0}^{eq} p_{n_0}^{eq}}_{\text{symm.}} \underbrace{\delta x_{n_1 n_0}}_{\text{anti-symm.}}$$

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

LDB in equil: $W_{n_1 n_0}^{eq} p_{n_0}^{eq} = W_{n_0 n_1}^{eq} p_{n_1}^{eq}$

we also know: $\delta x_{n_1 n_0} = - \delta x_{n_0 n_1}$

first term sums to zero!

$$\Rightarrow \quad \overline{W} = -f \langle \delta x \rangle \qquad \langle \delta x \rangle \approx f \underbrace{\sum_{n_1 n_0} W_{n_1 n_0}^{eq} p_{n_0}^{eq} c_{n_1 n_0} \cdot \delta x_{n_1 n_0}}_{\equiv \ell \text{ some number}}$$

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

$$\overline{W} = -f \langle \delta x \rangle = -f^2 \ell$$

$$\dot{I} = \frac{-\overline{W}}{T} = \frac{f^2 \ell}{T} \geq 0 \quad \Rightarrow \quad \ell \geq 0 \text{ to satisfy second law}$$

$$\sigma = \frac{I}{\delta t} \equiv \text{entropy production rate}$$

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

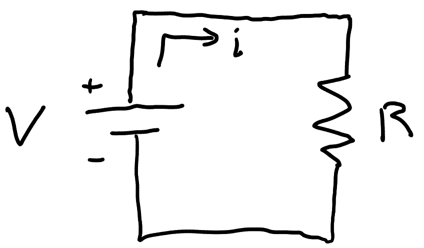
$$\frac{f}{T} \equiv \phi \qquad \text{thermodynamic "force"}$$

rewrite: $\sigma = J\phi = L\phi^2$

$J = L\phi$ where $L \equiv \frac{\ell T}{\delta t}$ (Onsager coeff.) $= \text{constant} \geq 0$

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

example: stationary state of an electrical circuit



$$\underbrace{-\frac{W}{\delta t}}_{\text{power dissipated}} = iV$$

stat. state

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

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

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

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

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

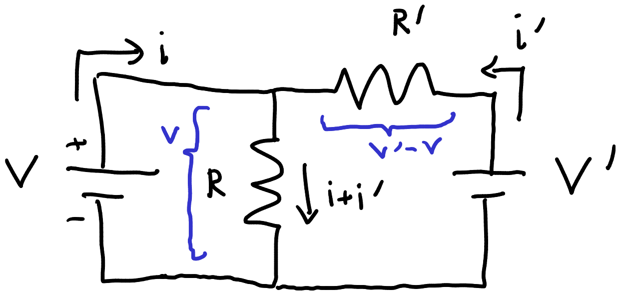
putting everything together:

$J = i$

$\phi = \frac{V}{T}$ $\qquad L = \frac{T}{R}$

$M > 1$ therm. forces :

example w/ $M = 2$



total entropy production $\quad \sigma = -\underbrace{\frac{\overline{W}}{\delta t}}_{\text{power dissipated}} \frac{1}{T} = \frac{1}{T}\left[(i+i')V + i'(V'-V)\right]$

$$= i\frac{V}{T} + i'\frac{V'}{T}$$

$$= J_1\phi_1 + J_2\phi_2$$

in general:

$$\sigma = \sum_{\alpha=1}^{M} J_\alpha \phi_\alpha$$

here $J_1 = i$ current in 1st loop $\qquad \phi_1 = \frac{V}{T}$

$J_2 = i'$ " " 2nd loop $\qquad \phi_2 = \frac{V'}{T}$

$$V = (i+i')R$$

$$V' = i'R' + (i+i')R$$

$$\Rightarrow \quad i = \left(\frac{1}{R} + \frac{1}{R'}\right)V - \frac{1}{R'}V'$$

$$i' = -\frac{1}{R'}V + \frac{1}{R'}V'$$

$$\Rightarrow \begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \underbrace{\begin{pmatrix} \frac{T}{R}+\frac{T}{R'} & -\frac{T}{R'} \\ -\frac{T}{R'} & \frac{T}{R'} \end{pmatrix}}_{\text{matrix } L \text{ of Onsager coeff.}} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

in general: $\vec{J} = L\vec{\phi}$

$L_{\alpha\gamma}$ = transport coeff: how much flux J_α we get from force ϕ_γ

put everything together:

$$\sigma = \sum_\alpha J_\alpha \phi_\alpha = \sum_{\alpha,\gamma} L_{\alpha\gamma} \phi_\alpha \phi_\gamma$$

$$\sigma = \vec{\phi}^T L \vec{\phi} \geq 0$$

always true from 2nd law for any $\vec{\phi}$

Question: do we know anything universal about L?