stationary state w/ small I:

work $\overline{W} = -f\langle \delta x \rangle$

$$= -f^2 \sum_{n_1 n_0} \underbrace{W_{n_1 n_0}^{eq} \, p_{n_0}^{eq} \, c_{n_1 n_0} \, \delta x_{n_1 n_0}}_{\ell \text{ some number}}$$

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

$$\overline{W} = -f^2 \ell$$

$$I = -\frac{\overline{W}}{T} = \frac{f^2 \ell}{T} \geq 0 \Rightarrow \ell \geq 0 \text{ to satisfy 2nd law of therm.}$$

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

$\dfrac{\langle \delta x \rangle}{\delta t} \equiv J$ thermodynamic "flux"

$\dfrac{f}{T} \equiv \phi$ thermodynamic "force"

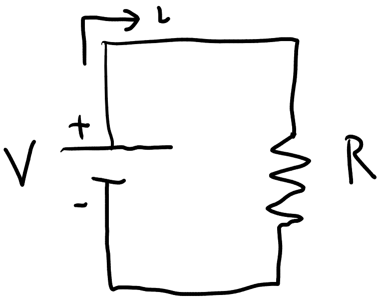
Onsager coeff.

rewrite: $\sigma = J\phi = L\phi^2$ $\quad L \equiv \dfrac{\ell T}{\delta t}$

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

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

example: stationary state of an electrical circuit



power dissipated $\quad -\frac{\bar{W}}{\delta t} = iV$

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

$$Q = \bar{W} = -TI$$

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

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

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

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

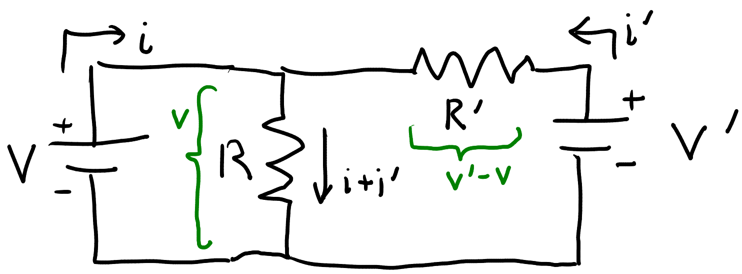
in summary:

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

$$\phi = \frac{V}{T}$$

generalization: $M > 1$ therm. forces

example: $M = 2$ electric circuit



total entropy prod. $\quad \sigma = \frac{I}{T} = -\frac{1}{T}\frac{\bar{W}}{\delta t}$

$$= \frac{1}{T}\left[(i+i')V + i'(V'-V)\right]$$

$$\phi_1 = \frac{V}{T} \qquad\qquad = i\frac{V}{T} + i'\frac{V'}{T}$$

$$\phi_2 = \frac{V'}{T} \qquad\qquad = J_1\phi_1 + J_2\phi_2$$

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

$= \vec{J}\cdot\vec{\phi}$

J_1 = current in 1st loop

J_2 = current in 2nd loop

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

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

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

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

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

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

$L_{\alpha\gamma}$ = transport coeff (Onsager)

= how much flux J_α we get from force ϕ_γ

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

$$\sigma = \vec{\phi}^T L \vec{\phi} \geq 0$$ from 2nd law for any force $\vec{\phi}$ (assuming linear therm. is valid)

What are universal properties of L?

$\Rightarrow$ L is positive semi-definite ($\vec{\phi}^T L \vec{\phi} \geq 0$ for any $\vec{\phi}$)

$\Leftrightarrow$ eigenvals of $L \geq 0$

$\Leftrightarrow$ $\det(L) \geq 0$

Anything else?

Start w/ IFT: $\langle e^{-I(\nu)/k_B} \rangle = 1$

$$\sum_\nu P(\nu) \underbrace{e^{-I(\nu)/k_B}}_{\simeq 1 - \frac{I(\nu)}{k_B} + \frac{I^2(\nu)}{2k_B^2} + \cdots} = 1$$

close to equil.
all $I(\nu)$ small

$$1 - \frac{1}{k_B}\langle I(\nu)\rangle + \frac{1}{2k_B^2}\langle I^2(\nu)\rangle = 1$$

$$\Rightarrow \quad \langle I(\nu)\rangle = \frac{1}{2k_B}\langle I^2(\nu)\rangle \quad \text{[Eq. 1]}$$

$\Rightarrow$ two consequences:
- Symmetry of L (Onsager reciprocity)

- fluctuation-dissipation theorem

focus on one-step traj: $\nu = \mu_0 = (n_0, n_1)$

[Eq. 2] $$I(\nu) = k_B \ln \frac{W_{n_1 n_0} p^s_{n_0}}{W_{n_0 n_1} p^s_{n_1}}$$

LDB: $$\frac{W_{n_1 n_0}}{W_{n_0 n_1}} = e^{-\beta\left(E_{n_1} - E_{n_0} - \underbrace{\sum_{\alpha=1}^{M} f_\alpha \delta x^{(\alpha)}_{n_1 n_0}}_{\text{work } \omega_{n_1 n_0}}\right)}$$

$W_{n_1 n_0}(\vec{f}) \quad p^s_{n_1}(\vec{f})$

multiple forces f_α associated w/ phys. observables $\delta x^{(\alpha)}_{n_1 n_0}$

when all $f_\alpha \to 0 \Rightarrow$ sys $\to$ equil.

$$p^s_{n_1} = p^{eq}_{n_1}\left(1 + \sum_\alpha f_\alpha b^{(\alpha)}_{n_1} + \dots\right)$$

$$p^s_{n_0} = p^{eq}_{n_0}\left(1 + \sum_\alpha f_\alpha b^{(\alpha)}_{n_0} + \dots\right)$$

$$\frac{p^{eq}_{n_1}}{p^{eq}_{n_0}} = e^{-\beta(E_{n_1} - E_{n_0})}$$

$$p^{eq}_{n_0} = \frac{e^{-\beta E_{n_0}}}{Z}$$

$$p^{eq}_{n_1} = \frac{e^{-\beta E_{n_1}}}{Z}$$