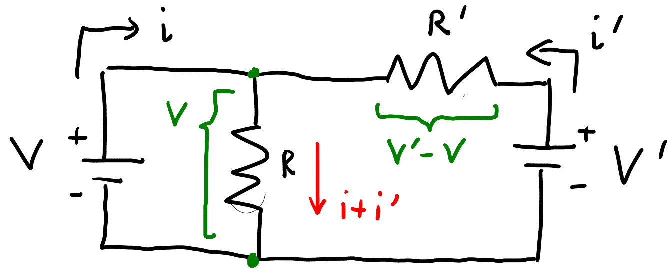
generalization: $M > 1$ thermal forces



$M = 2$ electrical circuit

$$\underset{\text{heat in}}{Q} = \underbrace{W}_{P_{out} - P_{in}} = -T\,\dot{I} \qquad \dot{I} \geq 0$$

total entropy prod.

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

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

$$\phi_1 = \frac{V}{T} \qquad \phi_2 = \frac{V'}{T} \qquad = i\,\frac{V}{T} + i'\frac{V'}{T}$$

$$J_1 = i \qquad J_2 = i' \qquad = J_1\phi_1 + J_2\phi_2$$

in general:

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

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

[generalizing $P = iV$]

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

Ohm's law

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

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

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

$$\Rightarrow \begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = \begin{pmatrix} \frac{T}{R} + \frac{T}{R'} & -\frac{T}{R'} \\ \frac{-T}{R'} & \frac{T}{R'} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

$$\underbrace{\qquad\qquad}_{\text{matrix } L \text{ of Onsager coeff.}}$$

"conductivity"

in general: $\underline{\vec{J} = L\vec{\phi}}$ $\qquad L_{\alpha\gamma}$ = transport coeff.

= Onsager coefficient

how much flux J_α we get from force ϕ_γ

$I \geq 0$

$$\frac{I}{\delta t} = \dot{\sigma} = \sum_\alpha J_\alpha \phi_\alpha = \sum_{\alpha\gamma} L_{\alpha\gamma}\phi_\alpha \phi_\gamma$$

$$= \vec{\phi}^T L \vec{\phi} \geq 0$$ from 2nd law

true for any driving forces $\vec{\phi}$

What are universal properties of L?

$\Rightarrow$ $\underbrace{\vec{\phi}^T L \vec{\phi}}_{\geq 0}$ for any $\vec{\phi}$: L is positive semi-definite

$\Leftrightarrow$ eigenvalues of $L \geq 0$

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

One more property (from physics): symmetry of L

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

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

close to equil: all $I(\nu)$ are small

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

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

use this to prove symmetry of L + fluctuation-dissipation

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

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

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

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

$$\delta x^{(\alpha)}_{n_1 n_0} = \delta x^{(\alpha)}_{n_0 n_1}$$

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

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

$$p^s_{n_1} = p^{eq}_{n_1}\left(1 + \sum_\alpha f_\alpha b^{(\alpha)}_{n_1} + \cdots\right) \qquad p^{eq}_{n_1} = \frac{e^{-\beta E_{n_1}}}{Z}$$

$\uparrow$ related to Taylor coeff.

$$p^s_{n_0} = p^{eq}_{n_0}\left(1 + \sum_\alpha f_\alpha b^{(\alpha)}_{n_0} + \cdots\right) \qquad p^{eq}_{n_0} = \frac{e^{-\beta E_{n_0}}}{Z}$$

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

plug into Eq. 2 for $I(\nu)$:

$$I(\nu) = -k_B \ln\left[\frac{1 + \sum_\alpha f_\alpha b^{(\alpha)}_{n_1}}{1 + \sum_\alpha f_\alpha b^{(\alpha)}_{n_0}}\right] + \frac{1}{T}\sum_\alpha f_\alpha \delta x^{(\alpha)}_{n_1 n_0}$$

when $f_\alpha = 0$ for all $\alpha \Rightarrow I(\nu) = 0$ (ESS)