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

"fluxes" "forces"

matrix of Onsager coeff.

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

entropy production

true for any $\vec{\phi}$

2nd law

Question: what are universal properties of L?

- L is positive semi-definite ($\vec{\phi}^T L \vec{\phi} \geq 0$ for any $\vec{\phi}$)
  - $\Rightarrow$ eigenvals of $L \geq 0$
  - $\Rightarrow \det(L) \geq 0$
- anything else?
- start w/ IFT: $\langle e^{-I(\nu)/k_B} \rangle = 1$

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

Close to equ.
$I(\nu)$ small

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

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

$\Rightarrow$ two consequences:

- symmetry of L (Onsager reciprocity)
- fluctuation-dissipation theorem

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

Eq. (2) $$I(\nu) = k_B \ln \frac{W_{n_1 n_0} p^s_{n_0}}{W_{n_0 n_1} p^s_{n_1}}$$ start in stat. state out of equil.

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

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

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

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

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

$\hookrightarrow$ some coeff.

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

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

Plug into Eq. (2): $$I(\nu) = -k_B \ln\left[\frac{\left(1 + \sum_\alpha f_\alpha b^{(\alpha)}_{n_1}\right)}{\left(1 + \sum_\alpha f_\alpha b^{(\alpha)}_{n_0}\right)}\right] + \frac{1}{T}\sum_\alpha f_\alpha \delta x^{(\alpha)}_{n_1 n_0}$$

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

simplify notation: $$I(\nu) \equiv \frac{1}{T}\sum_\alpha f_\alpha \delta y^{(\alpha)}_{n_1 n_0}$$

system-specific quantity $\Rightarrow$ $$\delta y^{(\alpha)}_{n_1 n_0} \approx \delta x^{(\alpha)}_{n_1 n_0} - k_B T\left(b^{(\alpha)}_{n_1} - b^{(\alpha)}_{n_0}\right)$$

using approx: $\ln(1+\epsilon) \approx \epsilon$ for small ϵ

$$\phi_\alpha = \frac{f_\alpha}{T} \Rightarrow I(0) = \sum_\alpha \phi_\alpha \, \delta y^{(\alpha)}_{n,n_0} \qquad \text{(Eq. 3)}$$

Plug Eq. 3 into Eq. 1 + divide by δt:

$$\frac{\langle I(0) \rangle}{\delta t} = \frac{1}{2k_B \delta t} \langle I^2(0) \rangle$$

$$\sigma = \frac{1}{2k_B \delta t} \left\langle \sum_{\alpha\gamma} \phi_\alpha \phi_\gamma \, \delta y^{(\alpha)} \delta y^{(\gamma)} \right\rangle$$

$$\sum_{\alpha\gamma} L_{\alpha\gamma} \phi_\alpha \phi_\gamma = \frac{1}{2k_B \delta t} \sum_{\alpha\gamma} \phi_\alpha \phi_\gamma \langle \delta y^{(\alpha)} \delta y^{(\gamma)} \rangle$$

has to be true for any ϕ_α + ϕ_γ :

Eq. 4

$$L_{\alpha\gamma} = \frac{1}{2k_B \delta t} \langle \delta y^{(\alpha)} \delta y^{(\gamma)} \rangle$$

$\Rightarrow$ gives a prescription for calculating $L_{\alpha\gamma}$

$\Rightarrow$ reveals $L_{\alpha\gamma} = L_{\gamma\alpha}$ for any $\alpha \neq \gamma$

[Onsager reciprocity [1931] $\Rightarrow$ Nobel prize]

two loop circuit: $L = \begin{pmatrix} \frac{T}{R} + \frac{T}{R'} & -\frac{T}{R'} \\ -T/R' & T/R' \end{pmatrix}$

Write out Eq. 4 in detail:

$$L_{\alpha\gamma} = \frac{1}{2k_B\,\delta t} \sum_{n, n_0} W_{n,n_0}\, p^s_{n_0}\, \delta y^{(\alpha)}_{n,n_0}\, \delta y^{(\gamma)}_{n,n_0}$$

$$W_{n,n_0}\, p^s_{n_0} = \underbrace{W^{eq}_{n,n_0}\, p^{eq}_{n_0}}_{\substack{\text{value} \\ \text{when } f_\gamma = 0}} \Big(1 + \sum_\alpha f_\alpha\, c^{(\alpha)}_{n,n_0} + \dots\Big)$$

some other coeff.

$$\Rightarrow \quad L_{\alpha\gamma} = \frac{1}{2k_B\,\delta t} \sum_{n,n_0} W^{eq}_{n,n_0}\, p^{eq}_{n_0}\, \delta y^{(\alpha)}_{n,n_0}\, \delta y^{(\gamma)}_{n,n_0} + \dots$$

$$L_{\alpha\gamma} \approx \underbrace{\frac{1}{2k_B\,\delta t} \left\langle \delta y^{(\alpha)}\, \delta y^{(\gamma)} \right\rangle_{eq}}$$

fluctuation-dissipation theorem (Callen, Welton, Kubo 1950's)

can be evaluated using equilib. trajectories (fluctuations in equil.)

control entropy production via $\sigma = \vec{\phi}^T L \vec{\phi}$

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

heat per unit time dissipated into env. when out of equil. for small forces (dissipation)