IFT $\Rightarrow$ $$\langle I(\nu)\rangle \approx \frac{1}{2k_B}\langle I^2(\nu)\rangle \qquad (1)$$

$\phi_\alpha = \frac{f_\alpha}{T}$

$$I(\nu) = \frac{1}{T}\sum_\alpha f_\alpha \, \delta y^{(\alpha)}_{n_1 n_0}$$

$$\delta y^{(\alpha)}_{n_1 n_0} = \delta x^{(\alpha)}_{n_1 n_0} - k_B T \left(b^{(\alpha)}_{n_1} - b^{(\alpha)}_{n_0}\right)$$

$$p_n^s \approx p_n^{eq}\left(1 + \sum_\alpha f_\alpha b_n^{(\alpha)}\right)$$

$$I(\nu) = \sum_\alpha \phi_\alpha \, \delta y^{(\alpha)}_{n_1 n_0}$$

Take (1), divide δt:

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

$$\| \qquad\qquad \|$$

$$0 \qquad \frac{1}{2k_B\delta t}\left\langle \sum_{\alpha\gamma} \phi_\alpha \phi_\gamma \, \delta y^{(\alpha)} \, \delta y^{(\gamma)}\right\rangle$$

$$\| \qquad\qquad \|$$

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

for all ϕ_α, ϕ_γ

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

consequence: i) Onsager reciprocity (1931):

$$L_{\alpha\gamma} = L_{\gamma\alpha}$$

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

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

Leading order result:

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

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

fluctuation dissipation theorem

Callen
Welton
Kubo
1950's

controls entropy production

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

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

heat dissipated into env. per unit time

related to fluctuations in equilibrium

Example: 1D large system w/ periodic boundary conditions where all $E_n = 0$ for states $1, \dots, N$

$$\begin{tikzcd} 1 \arrow[r, shift left, "k"] & 2 \arrow[l, shift left, "r"] \arrow[r, shift left, "k"] & 3 \arrow[l, shift left, "r"] \arrow[r, shift left, "k"] & 4 \arrow[l, shift left, "r"] & \cdots & N \arrow[lll, bend right] \end{tikzcd}$$

$$\frac{k}{r} = e^{-\beta \underbrace{f a}_{\text{work done against force } f \text{ when moving one step } (a) \text{ to right}}}$$

$N \to \infty$, single work term $(M=1)$

L is a scalar

Stationary state: $p_n^s = \frac{1}{N}$ for any f

$$= p_n^{eq}(1 + \cancel{b_n}^{\,0} f + \cdots)$$

$$\delta y_{n_1 n_0} = \delta x_{n_1 n_0} = \begin{cases} a & \text{if } n_1 = n_0 + 1 \\ -a & \text{if } n_1 = n_0 - 1 \end{cases}$$

FDT: $$2 k_B \delta t \, L = \langle \delta x^2 \rangle_{eq}$$

$$J = \frac{\langle \delta x \rangle}{\delta t} = L \phi = L \frac{f}{T}$$

interpretations: 1) diffusion: particle moving in 1D w/ a biasing force

(i.e. Brownian colloidal particle in fluid / gas)

J: mean velocity

f: applied force (gravity)

$$J = \frac{L}{T} f \Rightarrow \frac{L}{T} = \frac{1}{\gamma}$$

γ = drag friction coefficient

FDT: $$\langle \delta x^2 \rangle_{eq} = 2 k_B L \delta t$$

$$\langle \delta x^2 \rangle_{eq} = 2 \underbrace{\frac{k_B T}{\gamma}}_{D} \delta t$$

$$= 2 D \delta t$$

D diffusion coefficient

$$\boxed{D = \frac{k_B T}{\gamma}}$$ Einstein (1905)

2) resistive electrical circuit

J: current

f: voltage V

$\frac{L}{T} = \frac{1}{R}$ where R = resistance

$$\langle \delta x^2 \rangle_{eq} = 2 \frac{k_B T}{R} \delta t$$

mean squared charge fluctuations at zero voltage

Johnson-Nyquist noise (1926)

Last note: $L_{\alpha\gamma} = L_{\gamma\alpha}$ L is a real symmetric matrix

$\Rightarrow$ eigenvalues λ_i are real

e-vecs $\vec{u}^{(i)}$ are orthonormal

$$\vec{u}^{(i)} \cdot \vec{u}^{(j)} = \delta_{ij}$$

$$\sigma = \vec{\phi}^T L \vec{\phi} \geq 0 \qquad \text{(2nd law)}$$

for any small $\vec{\phi}$

1) plug in $\vec{\phi} = \varepsilon \vec{u}^{(i)}$ $\Rightarrow$ $\sigma = \varepsilon^2 \vec{u}^{(i)T} L \vec{u}^{(i)}$

$\uparrow$ small

$$= \varepsilon^2 \lambda_i \vec{u}^{(i)T} \vec{u}^{(i)}$$

$$= \varepsilon^2 \lambda_i \geq 0$$

$\Rightarrow$ every eigenvalue $\lambda_i \geq 0$

L is a positive semidefinite matrix

$$\det(L) = \lambda_1 \cdot \cdots \cdot \lambda_M \geq 0$$

2) plug in $\vec{\phi} = \varepsilon \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}$ $\leftarrow$ 1 in in the ith place

$$\Rightarrow \quad \sigma = \vec{\phi} L \vec{\phi} = \varepsilon^2 L_{ii} \geq 0$$

$$\Rightarrow L_{ii} \geq 0 \quad \text{for all } i$$

summary: Onsager matrix always satisfies

- $L_{\alpha\gamma} = L_{\gamma\alpha}$ for all α, γ
- $\det(L) \geq 0$
- $L_{\alpha\alpha} \geq 0$ for all α

Two loop circuit example:

$$L = \begin{pmatrix} \frac{T}{R} + \frac{T}{R'} & -\frac{T}{R'} \\ -\frac{T}{R'} & \frac{T}{R} \end{pmatrix}$$

- symmetric ✓
- $\det(L) = \frac{T^2}{RR'} \geq 0$ ✓
- $L_{11}, L_{22} \geq 0$ ✓