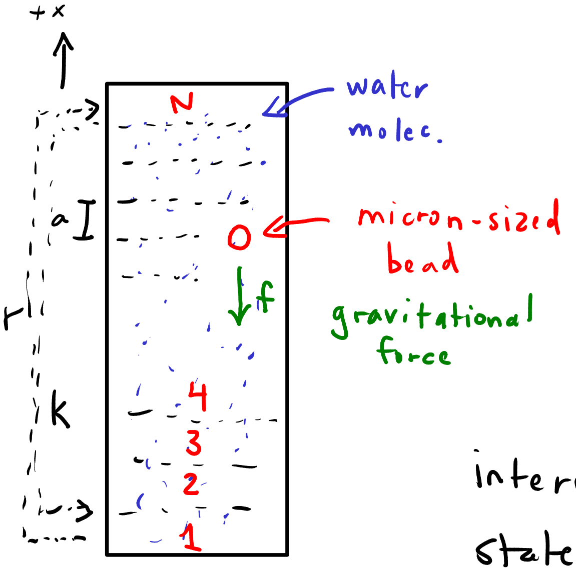
fluctuation-dissipation thm:

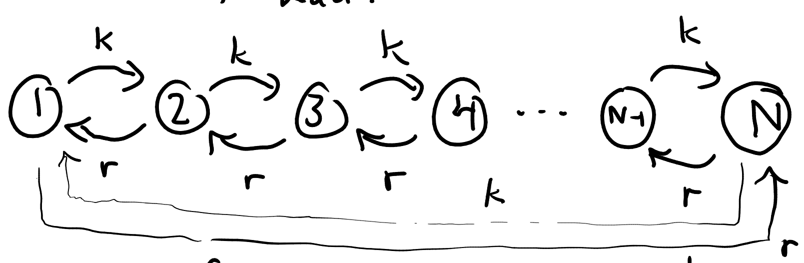
$$L_{\alpha\gamma} = \frac{1}{2 k_B \delta t} \left\langle \delta y^{(\alpha)} \delta y^{(\gamma)} \right\rangle_{eq}$$

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

Taylor coeff's of $\vec{p}^{\,s}(f)$



state of bead:



internal energy of bead same in all states: $E_n =$ const.

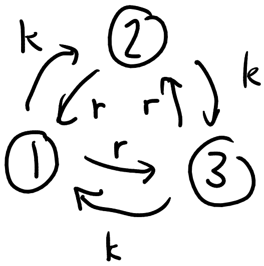
$$\text{LDB: } \quad \frac{k}{r} = e^{-\beta(\overbrace{E_{n+1} - E_n}^{0} + \underbrace{f a}_{\text{work}})}$$

work done against gravity $n \to n+1$

$$= e^{-\beta f a}$$

coupling to one force $(M=1)$

add periodic BC for math. convenience



by symmetry any loop like this must have a stat. state w/ $p_n^s = \frac{1}{N} = p_n^{eq}$ (in this case $\vec{p}^{\,s}(f)$ does not depend on f)

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

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

FDT: 1×1 matrix L (scalar)

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

$$\frac{\langle \delta x \rangle}{\delta t} = \underset{\substack{\text{current} \\ \equiv \\ \text{mean velocity} \\ \text{of bead}}}{J} = L \phi = L \frac{f}{T}$$

f: applied force

from fluid mechanics we know $J = \frac{1}{\gamma} f$

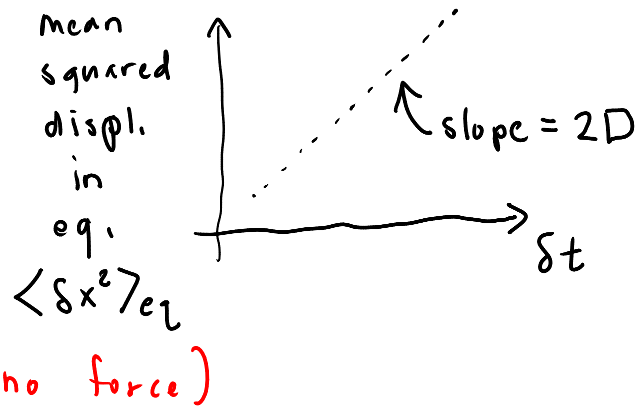
γ = drag friction coefficient

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

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

$$= 2 \underbrace{\frac{k_B T}{\gamma}}_{D} \delta t$$

D diffusion coeff.



$$\Rightarrow \boxed{D = \frac{k_B T}{\gamma}}$$

Einstein 1905

another similar example: resistive electrical circuit

J = current

f = voltage

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

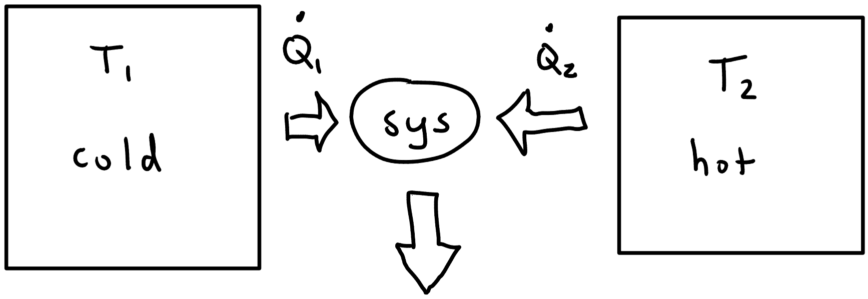
R = resistance

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

mean squared charge fluctuations at zero voltage

(Johnson-Nyquist noise [1926])

What about examples w/ multiple "forces"?



$$\frac{W}{\delta t} = P$$

stationary state (or cycle):

$$P = \dot{Q}_1 + \dot{Q}_2 \Rightarrow \dot{Q}_1 = P - \dot{Q}_2 \quad (1)$$

$$\sigma = \frac{I}{\delta t} = -\frac{\dot{Q}_1}{T_1} - \frac{\dot{Q}_2}{T_2} \geq 0 \quad (2)$$

$$\sigma = \dot{Q}_2\left(\frac{1}{T_1} - \frac{1}{T_2}\right) - \frac{P}{T_1} \geq 0$$

linear thermo approx: $T_1 = T \quad T_2 = T + \Delta T \quad \Delta T > 0 \quad \frac{\Delta T}{T} \ll 1$

$$\frac{1}{T_1} - \frac{1}{T_2} \approx \frac{\Delta T}{T^2}$$ Taylor series in small ΔT

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

$$P = \frac{W}{\delta t} = f\underbrace{\frac{\langle \delta x \rangle}{\delta t}}_{\dot{x}} = f\dot{x}$$

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

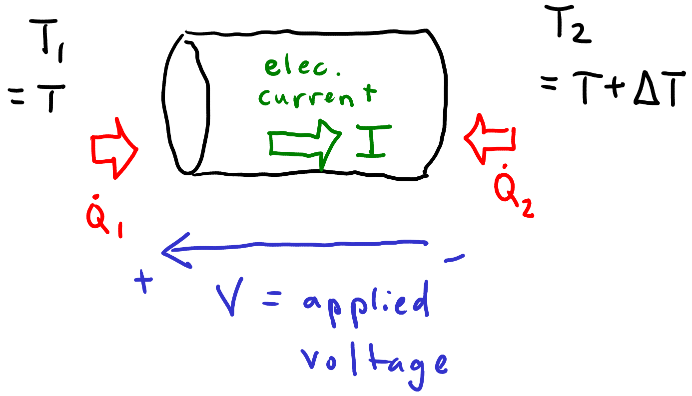
$$\Rightarrow \sigma = \underbrace{\dot{Q}_2}_{\substack{J_H \\ \text{heat current}}} \underbrace{\frac{\Delta T}{T^2}}_{\substack{\phi_H \\ \text{heat "force"}}} - \underbrace{\dot{x}}_{\substack{J_W \\ \text{work current}}} \underbrace{\frac{f}{T}}_{\substack{\phi_W \\ \text{work "force"}}} \geq 0$$

Onsager matrix

$$\begin{pmatrix} J_H \\ J_W \end{pmatrix} = \begin{pmatrix} \dot{Q}_2 \\ -\dot{x} \end{pmatrix} = \underbrace{\begin{pmatrix} L_{HH} & L_{HW} \\ L_{WH} & L_{WW} \end{pmatrix}}_{\text{Onsager matrix}} \begin{pmatrix} \phi_H \\ \phi_W \end{pmatrix}$$

we must have:
$$L_{WH} = L_{HW}$$

specialize to a wire:



$$P = -VI$$

$$\sigma = \underbrace{\dot{Q}_2}_{J_H} \underbrace{\frac{\Delta T}{T^2}}_{\phi_H} + \underbrace{I}_{\substack{J_E \\ \text{elec.} \\ \text{current}}} \underbrace{\frac{V}{T}}_{\substack{\phi_E \\ \text{elec.} \\ \text{"force"}}}$$

from earlier observations:

$$I = \frac{1}{R}\left(V - \alpha \Delta T\right)$$

α ← Seebeck coeff.

related to Seebeck effect:
charges diffusing from hot to cold creating a current (1821)

$\alpha > 0$: free charges are mainly holes (+)
~ i.e. p-type semicond.

$\alpha < 0$: " " " electrons (-)
~ i.e. n-type semicond.

rewrite:
$$I = \frac{T}{R}\frac{V}{T} - \frac{\alpha T^2}{R}\frac{\Delta T}{T^2}$$
$$J_E = L_{EE}\,\phi_E + L_{EH}\,\phi_H$$

also: $\dot{Q}_2 = \kappa \Delta T - C \frac{V}{T}$ → due to heat carried by moving charges

κ: thermal conductivity

$C \frac{V}{T}$: Peltier effect, 1834

$$\dot{Q}_2 = \kappa T^2 \frac{\Delta T}{T^2} - C \frac{V}{T}$$

$$J_H = L_{HH} \phi_H + L_{HE} \phi_E$$

when $\Delta T = 0 \Rightarrow \dot{Q}_2 = -C \frac{\overset{\text{"IR"}}{V}}{T} = -\underbrace{\frac{CR}{T}}_{\Pi} I$ Peltier coeff.

$$\Pi = \frac{CR}{T}$$

Onsager reciprocity: $L_{HE} = L_{EH}$

$$-C = -\frac{\alpha T^2}{R}$$

$$\Rightarrow C = \frac{\alpha T^2}{R}$$

$$\Rightarrow \boxed{\Pi = \frac{CR}{T} = \alpha T}$$

found empirically by Kelvin in 1854