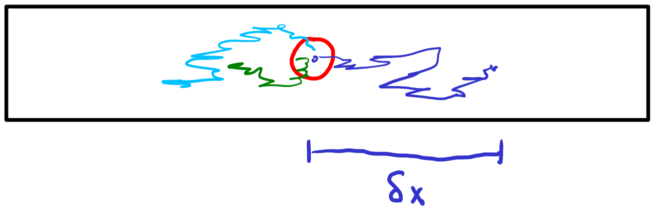
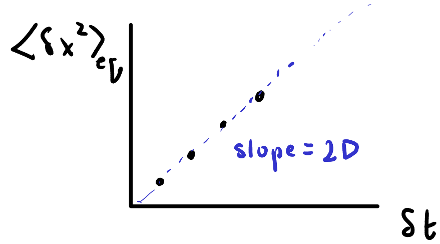


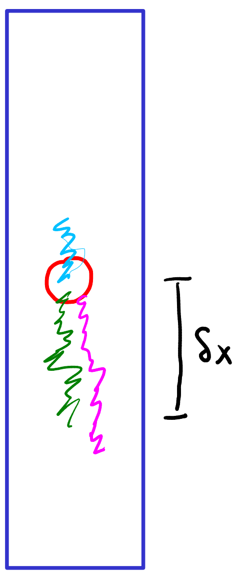
equilibrium



$$\langle \delta x \rangle_{eq} = 0$$

$$\langle \delta x^2 \rangle_{eq} = 2 D \, \delta t \Rightarrow$$ describes fluctuations in equil.

↳ diffusion



under force (gravity) $f = mg$

$$\frac{\langle \delta x \rangle}{\delta t} = \frac{1}{\gamma} f$$

γ = drag friction coefficient

$$\langle \delta x \rangle = \frac{f \, \delta t}{\gamma} \neq 0$$

Perrin exper. checked this ⇓ 1921 Nobel Prize

Einstein relation $D = \dfrac{k_B T}{\gamma}$

19th century fluid mechanics (Stokes) : $\gamma = 6 \pi \eta R$

already known

η = viscosity of fluid

R = radius of bead

Very similar example: resistive electrical circuits

J = current

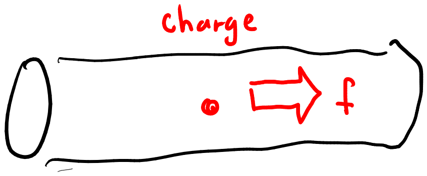
f = voltage

$$L = \frac{J}{R}$$

R is resistance

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

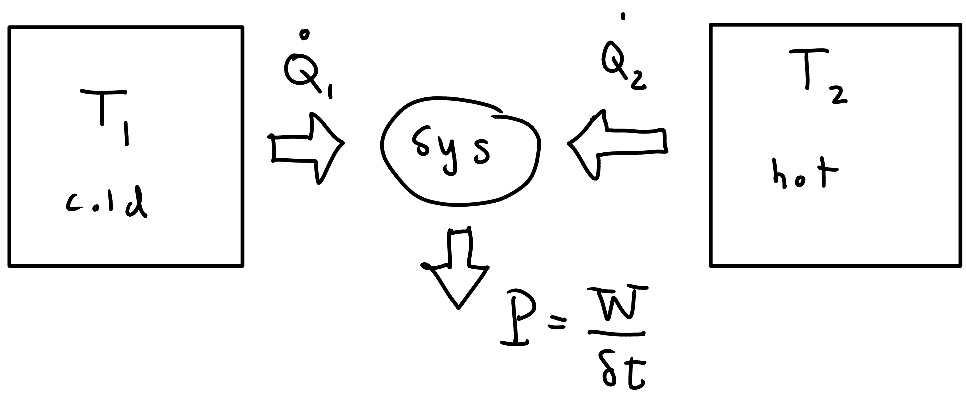
$$\frac{\langle \delta x \rangle}{\delta t} = \underbrace{J = L \phi}_{\text{Ohm's law}} = L \frac{f}{T}$$



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

mean squared charge motion fluctuations at zero voltage — Johnson-Nyquist noise [1926]

Examples w/ multiple driving "forces":



Stationary state (or cycle)

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

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

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

linear thermo: want to write this as

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

assume close to equil: $T_1 = T$ $\quad T_2 = T + \Delta T$

$\Delta T > 0$

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

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

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

$$\sigma = \underbrace{\dot{Q}_2}_{J_H} \underbrace{\frac{\Delta T}{T^2}}_{\phi_H} - \underbrace{\dot{x}}_{J_W} \underbrace{\frac{f}{T}}_{\phi_W} \geq 0 \qquad \sigma = \vec{J} \cdot \vec{\phi}$$

J_H heat current, ϕ_H heat "force", J_W "work" current, ϕ_W work force

$$\vec{J} = \begin{pmatrix} J_H \\ J_W \end{pmatrix} \qquad \vec{\phi} = \begin{pmatrix} \phi_H \\ \phi_W \end{pmatrix}$$

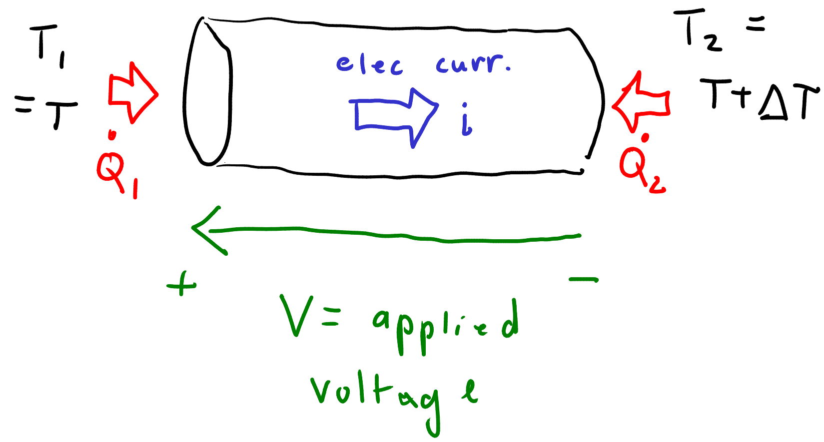
$$\vec{J} = L\vec{\phi} \Rightarrow \begin{pmatrix} \dot{Q}_2 \\ -\dot{x} \end{pmatrix} = \underbrace{\begin{pmatrix} L_{HH} & L_{HW} \\ L_{WH} & L_{WW} \end{pmatrix}}_{\text{Onsager matrix}} \begin{pmatrix} \frac{\Delta T}{T^2} \\ \frac{f}{T} \end{pmatrix}$$

$$L_{HW} = L_{WH}$$

$$\sigma = \vec{J} \cdot \vec{\phi} = \vec{\phi}^T L \vec{\phi} \geq 0 \quad \text{for all } \vec{\phi}$$

$$\Rightarrow \det L \geq 0 \Rightarrow L_{HH}L_{WW} - L_{HW}L_{WH} \geq 0$$

Specialize to a wire:



$$P = -iV$$

$$0 = \underbrace{\dot{Q}_2}_{J_H} \underbrace{\frac{\Delta T}{T^2}}_{\phi_H} + \underbrace{i}_{J_E} \underbrace{\frac{V}{T}}_{\phi_E}$$

Earlier observations:

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

α ← Seebeck coeff.

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:

$$i = \frac{T}{R}\frac{V}{T} - \frac{\alpha T^2}{R}\frac{\Delta T}{T^2}$$

$$J_E = L_{EE}\,\phi_E + L_{EH}\,\phi_H$$

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

other observation: Peltier effect [1834]

heat is carried by moving charges

$$\dot{Q}_2 = K \Delta T - C \frac{V}{T} \qquad C = \text{coeff.}$$

$\uparrow$ thermal conductivity

$$\dot{Q}_2 = K T^2 \frac{\Delta T}{T^2} - C \frac{V}{T} \qquad L_{HE} = -C$$

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

traditional definition: $\Delta T = 0$ $\quad V = iR$

$$\Rightarrow \dot{Q}_2 = -C \frac{V}{T}$$

$$= -\underbrace{\frac{CR}{T}}_{\Pi} i$$

$$\Pi = \frac{CR}{T} \equiv \text{Peltier coeff.}$$

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

explained by Onsager in 1930's

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

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

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

Peltier coeff. $\qquad$ Seebeck coeff.

found empirically by Kelvin in 1854

One more example of linear thermo:

What is efficiency when power is maximum?

$$\eta = \eta_{max} = 1 - \frac{T_1}{T_2} \Rightarrow P = 0$$

$$P = P_{max} \Rightarrow \eta = ?$$

van der Broeck et al. PRL 95 (2005)