Coupled transport in continuous systems

- Fourier's law $\vec{j}_u = -\underset{\approx}{K} \vec{\nabla} T = K T^2 \vec{\nabla}\left(1/T\right)$ $\left(= L_{uu} \mathbb{F}_u\right)$

thermal conductivity

- Fick's law $\vec{j}_\rho = -\underset{\approx}{D} \vec{\nabla} \rho = D \vec{\nabla}\left(-\frac{\mu}{T}\right) \left(= L_{\rho\rho} \mathbb{F}_\rho\right)$

diffusion coefficient

in linear regime

$\rho(\vec{r}) = \frac{\mu(\vec{r})}{T}$

$$\rho(\vec{r}) = \rho_0 \exp\left(-\frac{\mu(\vec{r}) - \mu_0}{T}\right)$$

$$= \rho_0 \left(1 - \frac{\mu(\vec{r}) - \mu_0}{T}\right)$$

$|\mu(\vec{r}) - \mu_0| \ll 1$

$$\begin{cases} \vec{j}_u = L_{uu} \vec{\nabla}\left(1/T\right) + L_{u\rho} \vec{\nabla}\left(-\mu/T\right) \\ \vec{j}_\rho = L_{\rho u} \vec{\nabla}\left(1/T\right) + L_{\rho\rho} \vec{\nabla}\left(-\mu/T\right) \end{cases}$$

$L_{\rho u} = L_{u\rho}$

$$\frac{ds}{dt} = \vec{j}_u \cdot \vec{\nabla}\left(1/T\right) + \vec{j}_\rho \cdot \vec{\nabla}\left(-\mu/T\right)$$

TRANSPORT FOR CHARGED PARTICLES

electric field → thermoelectric effect

magnetic field

└ Onsager theorem: $L_{ij}(\vec{B}) = L_{ji}(-\vec{B})$

(time reversal property for $\vec{B}$)

THERMOELECTRIC EFFECTS

(no magnetic field)

1-d metal/semiconductor wires

$$ds = \frac{du}{T} - \frac{\mu}{T}\,dn$$

n = particle density

u = energy density

$$j_s = \frac{j_u}{T} - \frac{\mu}{T}\,j_n$$

electric current: $e j_n$ $(e<0)$

$$dS/dt = j_u\,\partial_x\left(1/T\right) - j_n\,\partial_x\left(\mu/T\right)$$

"change of variables": $j_u \to j_q = T j_s = j_u - \mu j_n$

$$\frac{ds}{dt} = j_q\,\partial_x\left(\frac{1}{T}\right) - \frac{j_n}{T}\,\partial_x\mu$$

Onsager matrix in "heat representation"

$$\begin{cases} -j_n = L_{nn}\,\frac{1}{T}\,\partial_x\mu + L_{nq}\,\partial_x\left(1/T\right) & (a) \\ j_q = L_{qn}\,\frac{1}{T}\,\partial_x\mu + L_{qq}\,\partial_x\left(1/T\right) & (b) \end{cases}$$

Physical interpretation of Onsager coeffic. $L_{nq} = L_{qn}$

$\to$ L_{nn}, L_{qq}, L_{qn}

(1) $\partial_x T = 0$ uniform temperature

electrochemical potential $\mu = \mu_e + \cancel{\mu_c}$ chemical potential

μ_e: electrostatic potential energy (homogeneous material)

$$\partial_x \mu = \partial \mu_e$$

$\mu_e = e \phi$ electrostatic potential

electric conductivity:

$$\sigma = \frac{\text{electric current density}}{\text{electric field}} = \frac{e j_n}{-\partial_x \phi} = -\frac{e^2 j_n}{\partial_x \mu}$$ Ohm's law

$$\partial_x T = 0 \xrightarrow{(a)} L_{nn} = -\frac{T j_n}{\partial_x \mu} = \frac{\sigma T}{e^2}$$

$$\boxed{L_{nn} = \frac{T \sigma}{e^2}} \quad (A)$$

(2) $j_n = 0$ (no electric current)

$$\to K = -\frac{j_q}{\partial_x T} ; \quad j_n = 0 \text{ in } (a)$$

thermal conductivity (Fourier's law)

$$\to \partial_x \mu = -T \frac{L_{nq}}{L_{nn}} \partial_x \left(\frac{1}{T}\right) = \frac{L_{nq}}{T L_{nn}} \partial_x T$$

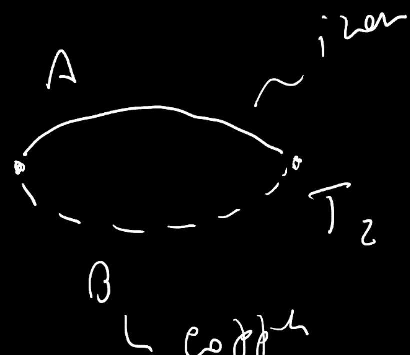
$$(b) \to j_q = \frac{1}{T^2} \frac{L_{nq}^2}{L_{nn}} \partial_x T - \frac{L_{qq}}{T^2} \partial_x T$$

$$j_q = \frac{1}{T^2}\frac{\det L}{L_{nn}}\,\partial_x T \longrightarrow \boxed{\kappa = \frac{\det L}{T^2 L_{nn}}} \quad (B)$$

SEEBECK EFFECT (1821) → thermocouples

PELTIER EFFECT (1834) → heat pumps, refrigerator

SEEBECK

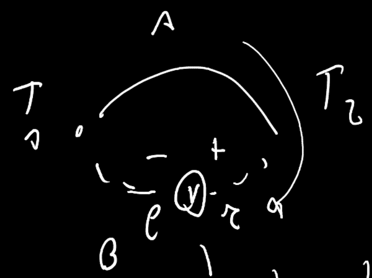


different conductors + temp. gradient

→ $T_1 < T_2$ → Thermoelectric power

→ stationary current flows

Thermocouple setup



ideal voltmeter → $j_n = 0$

(a) → $d\mu = \frac{1}{T}\frac{L_{nq}}{L_{nn}}\,dT$

$$\mu_r - \mu_l = \int_1^2 \left[\frac{L^A_{nq}}{L^A_{nn}} - \frac{L^B_{nq}}{L^B_{nn}}\right]\frac{dT}{T}$$

Measured voltage $V = \frac{\mu_r - \mu_l}{e}$

ε_{AB} = relative thermoelectric power of the thermocouple

$$\varepsilon_{AB} = \varepsilon_B - \varepsilon_A = \lim_{\Delta T \to 0} \frac{\mu_r - \mu_l}{e}\,\frac{1}{\Delta T}$$

absolute thermoelectric power of A, B

voltage change per unit temperature

$$\boxed{\mathcal{E}_x = -\frac{L^x_{mq}}{L^x_{mm}}\,\frac{1}{eT}} \quad (C)$$

rearranging (A), (B), (C)

$$L_{mm} \overset{(A)}{=} \frac{T\sigma}{e^2} \to L_{mq} = L_{qm} \overset{(C)}{=} -\varepsilon e T L_{mm} \overset{(A)}{=} -\frac{T^2\sigma\varepsilon}{e}$$

$$(B) \to L_{qq} = KT^2 + \varepsilon^2\sigma T^3$$

Rewrite coupled transport equation

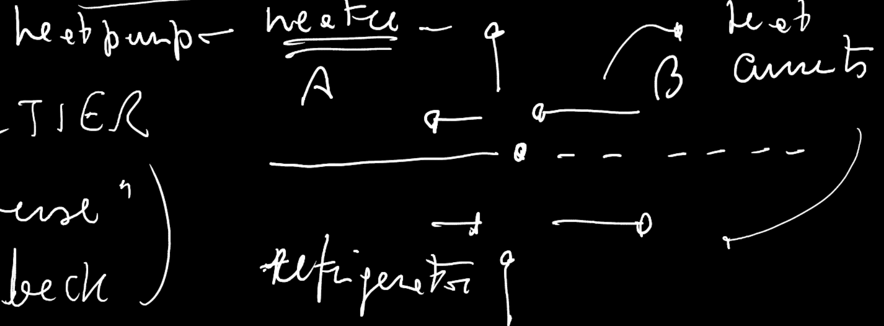
$$\begin{cases} -\dot{j}_m = \dfrac{\sigma}{e^2}\partial_x\mu - \dfrac{T^2\sigma\varepsilon}{e}\partial_x\left(\tfrac{1}{T}\right) & (e) \\[2ex] \dot{j}_q = -\underbrace{\dfrac{T^2\sigma\varepsilon}{e}}\partial_x\mu + \left(\underbrace{\varepsilon^2\sigma T^3} + KT^2\right)\partial_x\left(\tfrac{1}{T}\right) & (b) \end{cases}$$

$$\dot{j}_q = T\varepsilon e\,\dot{j}_m + KT^2\partial_x\left(\tfrac{1}{T}\right)$$

$$\dot{j}_S = \dot{j}_q/T = \varepsilon e\,\dot{j}_m + KT\partial_x\left(\tfrac{1}{T}\right)$$

ε = entropy transported per unit charge

PELTIER ("reverse" Seebeck)



junction between two different conductors at constant T

$\partial_x T = 0$ (a) $\rightarrow$ $j_n = -\frac{\sigma}{e^2}\partial_x \mu$

(b) $j_q = -\frac{T\sigma\mathcal{E}}{e}\partial_x \mu$

$\rightarrow j_q = T\mathcal{E}\underbrace{(e j_n)}_{\text{electric current}}$

discontinuity at the junction in j_q

$\rightarrow \underbrace{j_q^B - j_q^A = T(\mathcal{E}_B - \mathcal{E}_A)(e j_n)}$

Peltier coefficient: $\boxed{\Pi_{AB} = T(\mathcal{E}_B - \mathcal{E}_A)}$

heat supplied to the junction per unit electric current heater

$(\Pi_{AB} > 0)$

$\mathcal{E}_B > \mathcal{E}_A$ $\begin{cases} j_n > 0; & e j_n, j_q < 0 \\ & j_q^B < j_q^A \\ j_n < 0; & e j_n, j_q > 0 \\ \text{cooler} & j_q^B > j_q^A \end{cases}$

Coupled transport (thermoelectricity)

$$\begin{cases} j_n = -\frac{\sigma}{e^2}\partial_x \mu + \frac{T^2\sigma\mathcal{E}}{e}\partial_x\left(\frac{1}{T}\right) & (a) \\ j_q = T\mathcal{E} e j_n + K T^2 \partial_x\left(\frac{1}{T}\right) & (b) \end{cases}$$

$\partial_x\left(\frac{1}{T}\right) = 0 \xrightarrow{(a)} e j_n = -\frac{\sigma}{e}\partial_x \mu$ (Ohm's law)

$$\begin{cases} \partial_x \mu = 0 \xrightarrow{(e)} e j_n = T^2 \sigma \mathcal{E} \, \partial_x \left(1/T\right) & \text{Thermopower} \\ j_n = 0 \xrightarrow{(e)} \partial_x \mu = e T^2 \mathcal{E} \, \partial_x \left(1/T\right) & \end{cases}$$

Seebeck coefficient: $\mathcal{E}$

$\left(\text{Seebeck effect} \quad \partial_x (1/T) \neq 0 \right)$

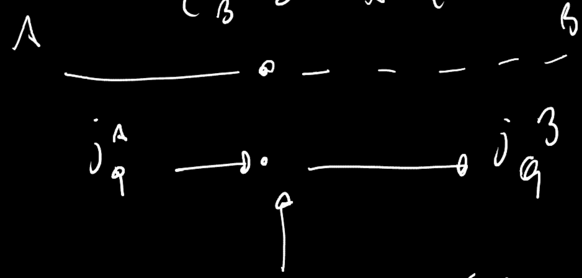
thermocouple

$$\partial_x \left(\frac{1}{T} \right) = 0 \xrightarrow{(b)} \Delta j_q = T \, \Delta \mathcal{E} \, e j_n \qquad \text{Peltier effect}$$

Peltier coefficient: $\Pi_{AB} = T \Delta \mathcal{E} = T(\mathcal{E}_B - \mathcal{E}_A)$

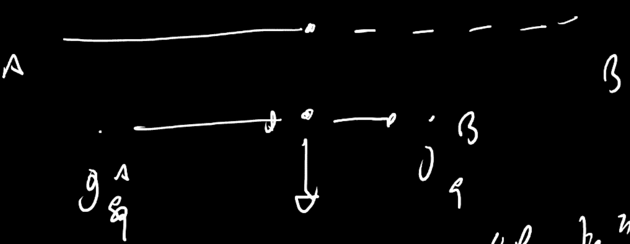
$\Pi_{AB} > 0 \Rightarrow$ heat is supplied to the junction for $e j_n > 0$

$\mathcal{E}_B > \mathcal{E}_A \; (\Pi_{AB} > 0)$ $\qquad$ $\mathcal{E}_B < \mathcal{E}_A \; (\Pi_{AB} < 0)$



"cooler"

$$\Delta j_q = j_q^B - j_q^A > 0$$



"heater"

$$\Delta j_q = j_q^B - j_q^A < 0$$

$\boxed{\text{Thomson-Joule effect}}$ $\qquad \partial_x T \neq 0 \; ; \; \partial_x \mu \neq 0$

$$j_u = j_q + \mu j_n \to \partial_x j_u = \underset{\text{eq. (b)}}{\partial_x j_q} + j_n \underbrace{\partial_x \mu}_{\text{eq. (e)}}$$

j_n is uniform

$$\partial_x j_u = \partial_x \left[T \mathcal{E} e j_n + \kappa T^2 \partial_x (1/T) \right] + j_n \left[-\frac{e^2}{\sigma} j_n + T^2 e \mathcal{E} \partial_x \left(\frac{1}{T} \right) \right]$$

$$\partial_x (1/T) = -\frac{1}{T^2} \partial_x T \; ; \; \mathcal{E}(T) \to \partial_x \mathcal{E} = \frac{d\mathcal{E}}{dT} \cdot \partial_x T$$

$$\partial_x j_u = \mathcal{E} \cancel{e j_m \partial_x T} + T \frac{\partial \mathcal{E}}{\partial T}(\partial_x T) \cdot e j_m + T \mathcal{E} \cancel{\partial_x (e j_m)} -$$

$$- K \partial_{xx} T - \frac{e^2}{\sigma} j_m^2 - \cancel{e j_m \mathcal{E} \partial_x T}$$

(K uniform)

$$\underline{\partial_x j_u} = \underline{T \frac{d\mathcal{E}}{dT}(\partial_x T)(e j_m) - K \partial_{xx} T} - \frac{(e j_m)^2}{\sigma}$$

$$\partial_x T = 0 \rightarrow \partial_x j_u = - \underbrace{\frac{(e j_m)^2}{\sigma}}_{\text{JOULE HEAT}}$$ JOULE EFFECT

$(P = R i^2)$

$$\left[\vec{\nabla} \cdot \vec{j}_u + \underbrace{\frac{\partial e}{\partial t}}_{0 \text{ at stationarity}} = P_{ext} \right]$$

power provided to the system (wire)

$$j_m = 0 \rightarrow \partial_x j_u = - K \partial_{xx} T$$

Fourier's law
uniform energy flux $\partial_x j_u = 0$
$\Rightarrow \partial_{xx} T = 0$

Assume $\underline{\partial_{xx} T = 0}$

$$\partial_x j_u = \underbrace{T \frac{\partial \mathcal{E}}{\partial T}(\partial_x T)(e j_m)}_{\text{THOMSON HEAT}} - \underbrace{\frac{e^2}{\sigma} j_m^2}_{\text{JOULE HEAT}}$$

heat absorbed by the wire

THOMSON COEFFICIENT

$$\boxed{\tau = T \frac{\partial \mathcal{E}}{\partial T}}$$

heat absorbed per unit current and per unit temperature

$$\Pi_{AB} = T(\mathcal{E}_B - \mathcal{E}_A)$$

$$\boxed{\frac{d\Pi_{AB}}{dT} = (\mathcal{E}_B - \mathcal{E}_A) + (\tau_B - \tau_A)}$$

energy needed to establish a T gradient

energy needed to establish a junction