Thermoelectric Phenomena

$$dQ = T\,dS = dU - \mu\, dN$$

$$\boxed{j_q = T j_s = j_\varepsilon - \mu j_n}$$

$$j_\varepsilon = \int \frac{d^3k}{4\pi^3}\, \varepsilon(k) v(k) f(k,r,t)$$

$$j_n = \int \frac{d^3k}{4\pi^3}\, v(k) f(k,r,t)$$

$$j_q = \int \frac{d^3k}{4\pi^3}\, (\varepsilon(k) - \mu) v(k) f(k,r,t)$$

... eventually sum over bands

Consider a steady state system (no time dependence, $\partial f/\partial t = 0$), but allow for a gradient in μ and T. Again in linear response:

$$\frac{\vec{F}}{\hbar}\cdot \vec{\nabla}_k f \rightarrow \frac{-e\vec{E}}{\hbar}\cdot \vec{\nabla}_k \varepsilon_k \frac{\partial f_{eq}}{\partial \varepsilon} = -e\vec{E}\cdot\vec{v}\,\frac{\partial f_{eq}}{\partial \varepsilon}$$

$$\vec{v}\cdot\vec{\nabla}_r f \rightarrow \vec{v}\cdot\vec{\nabla}_r \frac{1}{1+e^{(\varepsilon-\mu)/k_BT}} = -\vec{v}\cdot\vec{\nabla}\mu\, \frac{\partial f_{eq}}{\partial \varepsilon} + \vec{v}\cdot \frac{-e^{(\varepsilon-\mu)/k_BT}}{\left(1+e^{(\varepsilon-\mu)/k_BT}\right)^2}\cdot \frac{-(\varepsilon-\mu)}{k_B T^2}\vec{\nabla}T$$

Since $\dfrac{\partial f_{eq}}{\partial \varepsilon} = \dfrac{-e^{(\varepsilon-\mu)/k_BT}}{\left(1+e^{(\varepsilon-\mu)/k_BT}\right)^2}\dfrac{1}{k_BT}$

$$v\cdot\vec{\nabla}_r f = -\vec{v}\cdot\vec{\nabla}\mu\,\frac{\partial f_{eq}}{\partial \varepsilon} - \vec{v}\cdot(\varepsilon-\mu)\frac{\vec{\nabla}T}{T}\left(\frac{\partial f_{eq}}{\partial \varepsilon}\right)$$

$$\boxed{\begin{aligned}\frac{\vec{F}}{\hbar}\cdot\vec{\nabla}_k f + \vec{v}\cdot\vec{\nabla}_r f &= \left[-e\left(\vec{E} + \frac{\vec{\nabla}\mu}{e}\right) + (\varepsilon-\mu)\left(-\frac{\vec{\nabla}T}{T}\right)\right]\cdot\vec{v}\left(\frac{\partial f_{eq}}{\partial \varepsilon}\right)\\ &= -\frac{(f-f_{eq})}{\tau(\varepsilon)}\end{aligned}}$$

$$\boxed{f = f_{eq} + \tau(\varepsilon)\left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right)\vec{v}\cdot\left[-e\left(\vec{E}+\frac{\vec{\nabla}\mu}{e}\right)+(\varepsilon-\mu)\left(\frac{-\vec{\nabla}T}{T}\right)\right]}$$

Gradient in electrochemical potential:

$$\vec{\mathcal{E}} = \vec{E} + \frac{\vec{\nabla}\mu}{e}$$

$$\boxed{\begin{aligned}\vec{j} &= L_{11}\vec{\mathcal{E}} + L_{12}(-\vec{\nabla}T)\\ \vec{j}^{q} &= L_{21}\vec{\mathcal{E}} + L_{22}(-\vec{\nabla}T)\end{aligned}}$$

... electrical current

L's are tensors.

$$L_{11} = (-e)\int\frac{d^3k}{4\pi^3}\left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right)\tau(\varepsilon)\vec{v}\,\vec{v}\,(-e) \qquad = \mathcal{L}^{(0)}$$

$$L_{12} = -(e)\int\frac{d^3k}{4\pi^3}\left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right)\tau(\varepsilon)\vec{v}\,\vec{v}\,\frac{(\varepsilon-\mu)}{T} \qquad = -\frac{1}{e}\frac{1}{T}\mathcal{L}^{(1)}$$

$$L_{21} = \int\frac{d^3k}{4\pi^3}\left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right)\tau(\varepsilon)\vec{v}\,\vec{v}\,(-e)(\varepsilon-\mu) \qquad = -\frac{1}{e}\mathcal{L}^{(1)}$$

$$L_{22} = \int\frac{d^3k}{4\pi^3}\left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right)\tau(\varepsilon)\vec{v}\,\vec{v}\,\frac{(\varepsilon-\mu)^2}{T} \qquad = \frac{1}{e^2}\frac{1}{T}\mathcal{L}^{(2)}$$

$$\mathcal{L}^{(\alpha)} \equiv e^2\int\frac{d^3k}{4\pi^3}\left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right)\tau(\varepsilon)\vec{v}\,\vec{v}\,(\varepsilon-\mu)^{\alpha}$$

Let $\sigma(\varepsilon) = e^2\tau(\varepsilon)\int\frac{d^3k}{4\pi^3}\,\delta(\varepsilon-\varepsilon(k))\,\vec{v}\,\vec{v}$,

Then $\mathcal{L}^{(\alpha)} = \int d\varepsilon\left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right)(\varepsilon-\mu)^{\alpha}\sigma(\varepsilon)$.

Sommerfeld expansion:

$$\mathcal{L}^{(0)} = \int d\varepsilon \left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right) \sigma(\varepsilon) \approx \sigma(\varepsilon_F) = \sigma$$

$$\mathcal{L}^{(2)} = \int d\varepsilon \, \frac{\beta e^{\beta(\varepsilon-\mu)}}{(1+e^{\beta(\varepsilon-\mu)})^2} (\varepsilon-\mu)^2 \sigma(\varepsilon)$$

$$\approx \frac{\sigma(\varepsilon_F)}{\beta^2} \underbrace{\int_{-\infty}^{+\infty} dx \, \frac{e^x x^2}{(1+e^x)^2}} \qquad = \frac{\pi^2}{3}(k_B T)^2 \sigma(\varepsilon_F)$$

$$= \int_{-\infty}^{+\infty} dx \, \frac{x^2}{(e^{x/2}+e^{-x/2})^2} = \frac{\pi^2}{3}$$

$$\mathcal{L}^{(1)} = \int d\varepsilon \left(-\frac{\partial f_{eq}}{\partial \varepsilon}\right) (\varepsilon-\mu) \underbrace{\sigma(\varepsilon)}_{\sigma + \sigma_x'(\varepsilon-\mu)+\cdots} = \frac{\pi^2}{3}(k_B T)^2 \sigma'(\varepsilon_F)$$

$$\Rightarrow \boxed{\begin{aligned} L_{11} &= \sigma \\ L_{12} &= -\frac{1}{e}\frac{1}{T}\frac{\pi^2}{3}(k_B T)^2 \sigma' \\ L_{21} &= \frac{-1}{e} \frac{\pi^2}{3}(k_B T)^2 \sigma' \\ L_{22} &= \frac{1}{e^2}\frac{1}{T}\frac{\pi^2}{3}(k_B T)^2 \sigma \end{aligned}}$$

Thermal conductivity:

$j = 0 \ , \ j_q \neq 0$

$$0 = L_{11}\mathcal{E} + L_{12}(-\nabla T)$$
$$j^q = L_{21}\mathcal{E} + L_{22}(-\nabla T)$$

$$\mathcal{E} = -(L_{11})^{-1} L_{12}(-\nabla T)$$

$$j^q = (\underbrace{L_{22} - L_{21}(L_{11})^{-1}L_{12}}_{=K \,=\, \text{thermal conductivity}})(-\nabla T)$$

Estimate: $\sigma' = \sigma/\varepsilon_F$.

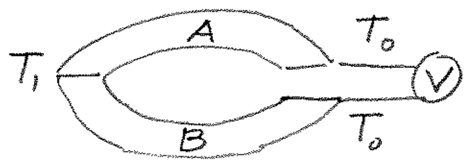
$$-L_{21}(L_{11})^{-1}L_{12} \sim -\frac{\frac{1}{e^2}\frac{1}{T}\left(\frac{\pi^2}{3}(k_B T)^2 \frac{\sigma}{\varepsilon_F}\right)^2}{\sigma}$$

$$L_{22} = \frac{1}{e^2}\frac{1}{T}\left(\frac{\pi^2}{3}(k_B T)^2 \sigma\right)$$

$$\frac{L_{21}(L_{11})^{-1}L_{12}}{L_{22}} \sim \frac{\pi^2}{3}\left(\frac{k_B T}{\varepsilon_F}\right)^2 \ll 1$$

$$\rightarrow \quad K \approx \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T\sigma \qquad \text{Wiedemann-Franz law}$$

Thermoelectric power:



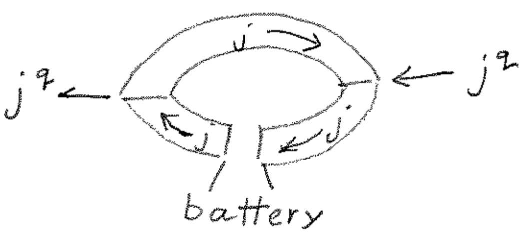
thermopower

$$-\int \mathcal{E} \cdot d\ell = Q \,\Delta T$$
$$\vec{\mathcal{E}} = Q \vec{\nabla} T$$

Again $\vec{j} = 0 = L_{11} \vec{\mathcal{E}} + L_{12} (-\vec{\nabla} T)$

$$\rightarrow Q = \frac{L_{12}}{L_{11}} = -\frac{\pi^2}{3} \frac{k_B^2 T}{e} \frac{\sigma'}{\sigma}$$

Peltier effect:



$j^q = \Pi j$ with $\vec{\nabla} T = 0$

$$\Pi = \frac{L_{21}}{L_{11}} = T Q$$