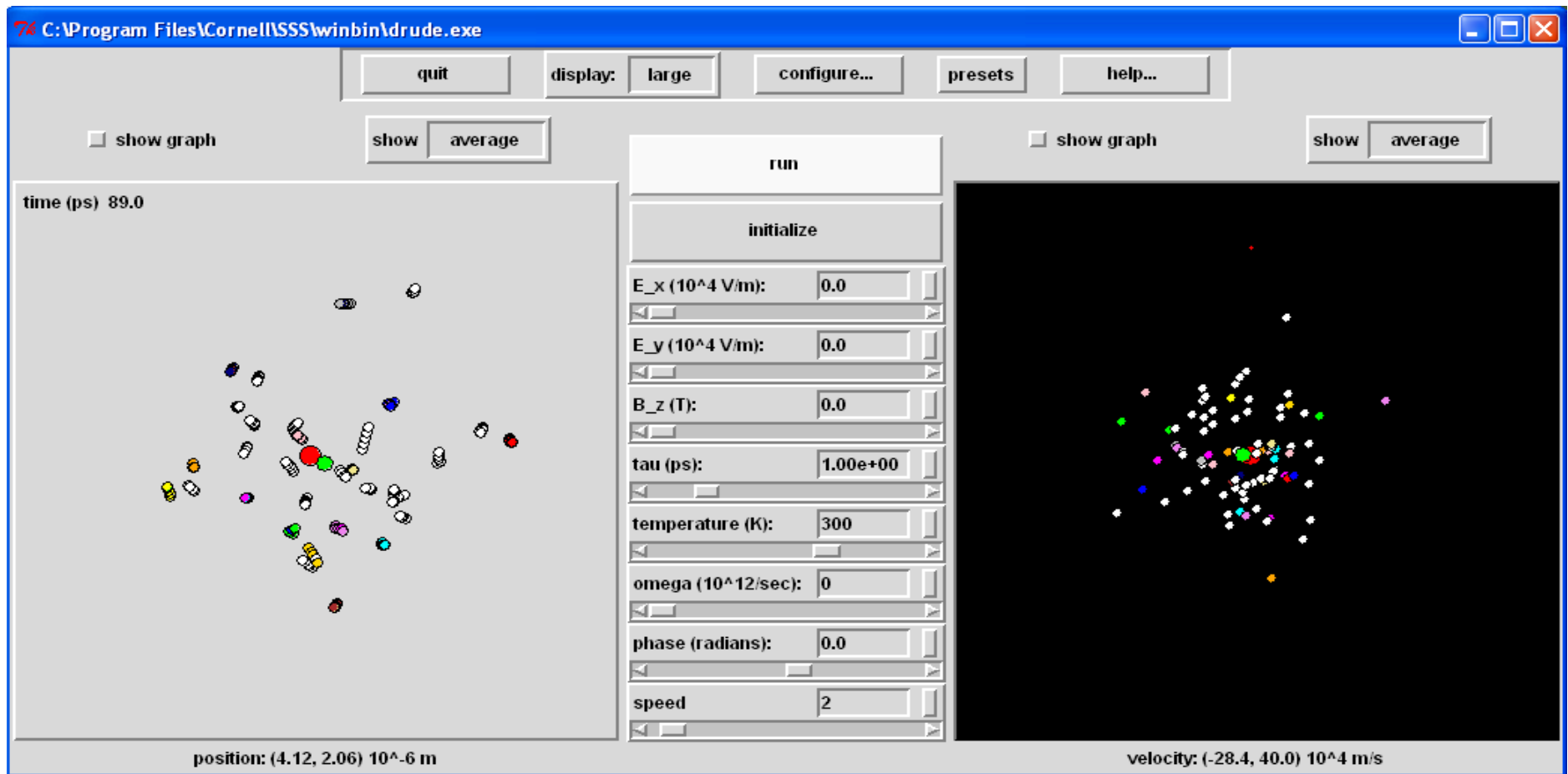# 23.  Transport

Jan. 13, 2020

# Wave/particle nature of electrons

Usually when we think about a current flowing, we imagine the electrons as particles moving along. Really we should be thinking about how the occupation of the wave like eigenstates are changing.

When wave packets are built from the eigenstates, they move like particles with an effective mass.

If no forces are applied, the electrons diffuse.
The average velocity moves against an electric field.
In just a magnetic field, the average velocity is zero.
In an electric and magnetic field, the electrons move in a straight line at the Hall angle.
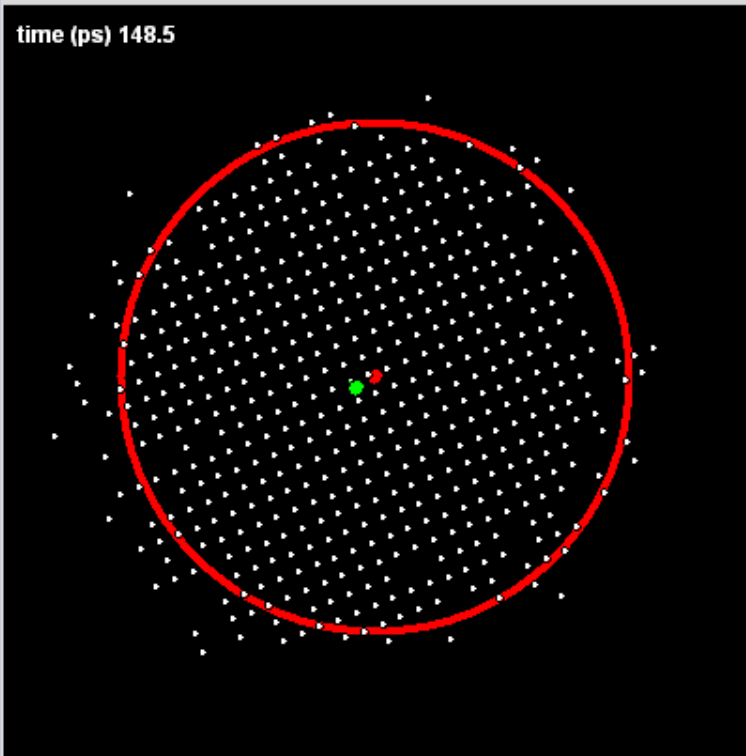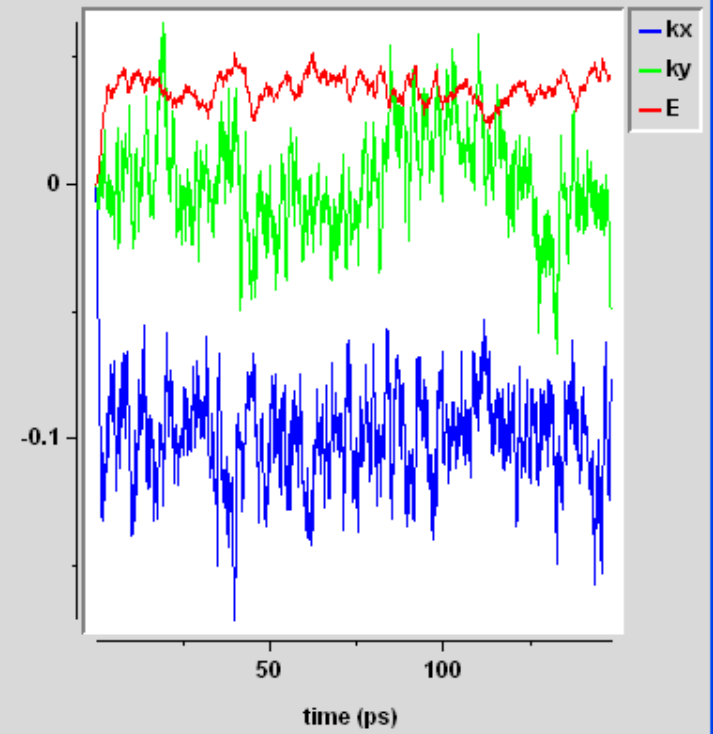
# Master equation
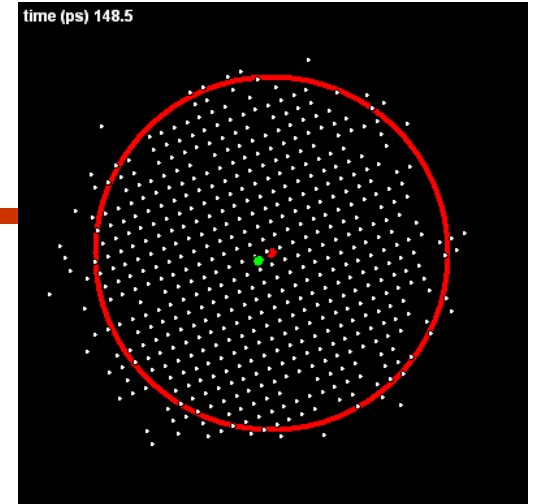
$$\vec{j}_{elec} = -e \int \vec{v}(\vec{k}) D(\vec{k}) f(\vec{k}) d\vec{k}$$

$$\frac{d}{dt}\begin{bmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \end{bmatrix} = \begin{bmatrix} -\sum_{j \neq 1} \Gamma_{1 \to j} & \Gamma_{2 \to 1} & \Gamma_{3 \to 1} & \Gamma_{4 \to 1} \\ \Gamma_{1 \to 2} & -\sum_{j \neq 2} \Gamma_{2 \to j} & \Gamma_{3 \to 2} & \Gamma_{4 \to 2} \\ \Gamma_{1 \to 3} & \Gamma_{2 \to 3} & -\sum_{j \neq 3} \Gamma_{3 \to j} & \Gamma_{4 \to 3} \\ \Gamma_{1 \to 4} & \Gamma_{2 \to 4} & \Gamma_{3 \to 4} & -\sum_{j \neq 4} \Gamma_{4 \to j} \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \\ f_3 \\ f_4 \end{bmatrix}$$

Fermi's golden rule: $\quad \Gamma_{k \to k'} = \dfrac{2\pi}{\hbar} \left| \langle k' | H | k \rangle \right|^2 \delta \left( E_k - E_{k'} \right)$

# Current densities

Electrical
$$\vec{j}_{\text{elec}} = -e \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3 k$$

Particle
$$\vec{j}_n = \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3 k$$

Energy
$$\vec{j}_U = \int \vec{v}_{\vec{k}} E(\vec{k}) D(\vec{k}) f(\vec{k}) d^3 k.$$

1st law:
$$dU = dQ - dW + \mu dN.$$

Heat
$$\vec{j}_Q = \int \vec{v}_{\vec{k}} \left( E(\vec{k}) - \mu \right) D(\vec{k}) f(\vec{k}) d^3 k.$$

# Current densities

Electrical

$$\vec{j}_{\text{elec}} = -e \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3 k$$

$$D(\vec{k}) = \frac{2}{(2\pi)^3} \quad \longleftarrow \quad \text{spin}$$

$$\vec{v}_{\vec{k}} = \frac{\nabla_{\vec{k}} E(\vec{k})}{\hbar}$$

$f(\vec{k})$  Probability that state $k$ is occupied.

# Liouville's theorem

$f(\vec{r}, \vec{k}, t)$  Probability that state $k$ is occupied at position $r$ and time $t$.

Number of electrons:  $N = \displaystyle\int d^3r \int d^3k f(\vec{r}, \vec{k}, t)$

$$\frac{d}{dt} f(\vec{r}, \vec{k}, t) = 0$$

If the probability of finding an electron at a particular position with a particular momentum decreases, the probability must increase somewhere else.

# Boltzmann Equation

$$\frac{d}{dt} f(\vec{r}, \vec{k}, t) = 0$$

$$\frac{d}{dt} f(\vec{r}, \vec{k}, t) = \frac{\partial f}{\partial x}\frac{dx}{dt} + \frac{\partial f}{\partial y}\frac{dy}{dt} + \frac{\partial f}{\partial z}\frac{dz}{dt} + \frac{\partial f}{\partial k_x}\frac{dk_x}{dt} + \frac{\partial f}{\partial k_y}\frac{dk_y}{dt} + \frac{\partial f}{\partial k_z}\frac{dk_z}{dt} + \frac{\partial f}{\partial t} = 0$$

$$\frac{d}{dt} f(\vec{r}, \vec{k}, t) = \frac{d\vec{r}}{dt} \cdot \nabla_{\vec{r}} f + \frac{d\vec{k}}{dt} \cdot \nabla_{\vec{k}} f + \frac{\partial f}{\partial t} = 0$$

Crystal momentum $\qquad \vec{F}_{\text{ext}} = \hbar \frac{d\vec{k}}{dt}$

$$\boxed{\frac{\partial f}{\partial t} = -\frac{1}{\hbar}\vec{F}_{\text{ext}} \cdot \nabla_{\vec{k}} f - \vec{v} \cdot \nabla_{\vec{r}} f + \left.\frac{\partial f}{\partial t}\right|_{collisions}}$$

Collision term describes the transitions between $k$ states.

# Relaxation time approximation

$$\frac{\partial f}{\partial t} = -\frac{\vec{F}_{ext} \cdot \nabla_k f}{\hbar} - \vec{v} \cdot \nabla f + \left.\frac{\partial f}{\partial t}\right|_{collisions}$$

In the relaxation time approximation,

$$\left.\frac{\partial f}{\partial t}\right|_{collisions} = \frac{f_0(\vec{k}) - f(\vec{k})}{\tau(\vec{k})}$$

If the driving field is turned off, the collision term will drive the system back to equilibrium in time $\tau$.

When $\nabla_k f = \nabla_r f = 0$ and the initial condition is $f = f_1$, the solution to the Boltzmann equation is,

$$f(t) = f_0 + f_1 e^{-t/\tau}$$

# Boltzmann equation: relaxation time approx.

The relaxation time approximation:

$$\frac{\partial f}{\partial t} = -\frac{\vec{F}_{ext} \cdot \nabla_k f}{\hbar} - \vec{v} \cdot \nabla f + \frac{f_0(\vec{k}) - f(\vec{k})}{\tau(\vec{k})}$$

in a stationary state

$$\frac{\partial f}{\partial t} = 0$$

If the system is not far from equilibrium, $f \approx f_0$, and we can substitute $f_0$ for $f$ on the right

$$f(\vec{k}) = f_0(\vec{k}) - \frac{\tau(\vec{k})\vec{F}_{ext} \cdot \nabla_k f_0}{\hbar} - \tau(\vec{k})\vec{v} \cdot \nabla f_0$$

$$f_0(\vec{k}) = \frac{1}{\exp\left(\dfrac{E(\vec{k}) - \mu}{k_B T}\right) + 1}$$

# Boltzmann equation: relaxation time approx.

$$f(\vec{k}) \approx f_0(\vec{k}) - \frac{\tau(\vec{k})\vec{F}_{ext} \cdot \nabla_k f_0}{\hbar} - \tau(\vec{k})\vec{v} \cdot \nabla f_0$$

$$\nabla f_0 = \frac{\partial f_0}{\partial T} \nabla T + \frac{\partial f_0}{\partial \mu} \nabla \mu$$

$$f_0(\vec{k}) = \frac{1}{\exp\left(\dfrac{E(\vec{k}) - \mu}{k_B T}\right) + 1}$$

Temperature and chemical potential can depend on position

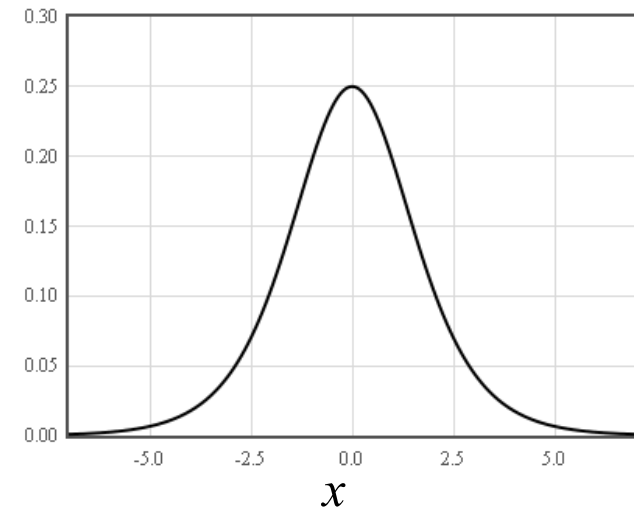$$\vec{F}_{ext} = -e\left(\vec{E} + \vec{v} \times \vec{B}\right)$$

$$f(\vec{k}) \approx f_0(\vec{k}) - \frac{\tau(\vec{k})(-e)\left(\vec{v} \times \vec{B} + \vec{E}\right) \cdot \nabla_k f_0}{\hbar} - \tau(\vec{k})\vec{v} \cdot \left(\frac{\partial f_0}{\partial T} \nabla T + \frac{\partial f_0}{\partial \mu} \nabla \mu\right)$$

Temperature gradient

Concentration gradient

# Boltzmann equation: relaxation time approx.

$$\frac{\partial f_0}{\partial \mu} = \frac{\dfrac{1}{k_B T}\exp\left(\dfrac{E(\vec{k})-\mu}{k_B T}\right)}{\left(\exp\left(\dfrac{E(\vec{k})-\mu}{k_B T}\right)+1\right)^2} = -\frac{\partial f_0}{\partial E}$$

$$\frac{\exp(x)}{\left(\exp(x)+1\right)^2}$$



$$\nabla_k f_0 = \frac{\dfrac{-1}{k_B T}\exp\left(\dfrac{E(\vec{k})-\mu}{k_B T}\right)}{\left(\exp\left(\dfrac{E(\vec{k})-\mu}{k_B T}\right)+1\right)^2}\nabla_k E(\vec{k})$$

$$= \frac{\partial f_0}{\partial E}\nabla_k E(\vec{k})$$

$$\frac{\partial f_0}{\partial T} = \frac{\dfrac{E(\vec{k})-\mu}{k_B T^2}\exp\left(\dfrac{E(\vec{k})-\mu}{k_B T}\right)}{\left(\exp\left(\dfrac{E(\vec{k})-\mu}{k_B T}\right)+1\right)^2}$$

$$= -\frac{\partial f_0}{\partial E}\frac{E(\vec{k})-\mu}{T}$$

Only the states near the Fermi surface contribute.

# Boltzmann equation: relaxation time approx.

$$f(\vec{k},\vec{r}) \approx f_0(\vec{k},\vec{r}) - \frac{\tau(\vec{k})}{\hbar} \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \cdot \left( e\vec{E} + \nabla_{\vec{r}}\mu + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T + \frac{e}{\hbar} \nabla_{\vec{k}} E(\vec{k}) \times \vec{B} \right)$$

$$\vec{j}_{elec} = -e \int \vec{v}(\vec{k}) D(\vec{k}) f(\vec{k}) d\vec{k}$$

spin

density of states $\qquad D(\vec{k}) = \dfrac{2}{(2\pi)^3}$

$$\vec{j}_{elec} = -\frac{e}{4\pi^3 \hbar} \int \nabla_{\vec{k}} E(\vec{k}) \left( f_0(\vec{k},\vec{r}) - \frac{\tau(\vec{k})}{\hbar} \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \cdot \left( e\vec{E} + \nabla_{\vec{r}}\mu + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T + \frac{e}{\hbar} \nabla_{\vec{k}} E(\vec{k}) \times \vec{B} \right) \right) d^3 k.$$

The contribution of $f_0(k)$ is zero $\qquad\qquad \nabla_{\vec{k}} E(\vec{k}) \cdot \left( \nabla_{\vec{k}} E(\vec{k}) \times \vec{B} \right) = 0$

# Current densities

$$\vec{j}_{\text{elec}} = -e \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3k$$

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3 \hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( e\vec{E} + \nabla_{\vec{r}} \mu + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3k.$$

$$\vec{j}_n = \int \vec{v}_{\vec{k}} D(\vec{k}) f(\vec{k}) d^3k,$$

$$\vec{j}_n = -\frac{1}{4\pi^3 \hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( e\vec{E} + \nabla_{\vec{r}} \mu + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3k.$$

$$\vec{j}_U = \int \vec{v}_{\vec{k}} E(\vec{k}) D(\vec{k}) f(\vec{k}) d^3k.$$

$$\vec{j}_U = -\frac{1}{4\pi^3 \hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} E(\vec{k}) \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( e\vec{E} + \nabla_{\vec{r}} \mu + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3k.$$

$$\vec{j}_Q = \int \vec{v}_{\vec{k}} \left( E(\vec{k}) - \mu \right) D(\vec{k}) f(\vec{k}) d^3k$$

$$\vec{j}_Q = -\frac{1}{4\pi^3 \hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left( E(\vec{k}) - \mu \right) \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( e\vec{E} + \nabla_{\vec{r}} \mu + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3k.$$

http://lampx.tugraz.at/~hadley/ss2/transport/currents.php

# Electrochemical potential

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( e\vec{E} + \nabla_{\vec{r}}\mu + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3k.$$

The electrochemical potential $\tilde{\mu} = -e\phi + \mu$
is what a voltmeter measures

$\phi$ is the electrostatic potential
$\mu$ is the chemical potential

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( \nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3k.$$

# Electrical conductivity

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( \nabla_{\vec{r}} \tilde{\mu} + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3 k.$$

no temperature gradient

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \nabla_{\vec{r}} \tilde{\mu} \right) d^3 k.$$

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = e \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} \frac{\partial \tilde{\mu}}{\partial x} \\ \frac{\partial \tilde{\mu}}{\partial y} \\ \frac{\partial \tilde{\mu}}{\partial z} \end{bmatrix}$$

http://lampx.tugraz.at/~hadley/ss2/transport/ecp.php

# Electrical conductivity

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial\mu}\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\nabla_{\vec{r}}\tilde{\mu}\right)d^3k.$$

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = e \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \begin{bmatrix} \frac{\partial\tilde{\mu}}{\partial x} \\ \frac{\partial\tilde{\mu}}{\partial y} \\ \frac{\partial\tilde{\mu}}{\partial z} \end{bmatrix}$$

$$\sigma_{ij} = \frac{e^2}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial\mu}\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_i\left(\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_j\right)d^3k$$

for cubic crystals:

$$\sigma = \frac{e^2}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial\mu}\left(\nabla_{\vec{k}}E(\vec{k})\cdot\hat{z}\right)^2 d^3k$$

http://lampx.tugraz.at/~hadley/ss2/transport/electrical.php

# Free-electron model: electrical conductivity

$$E(\vec{k}) = \frac{\hbar^2 k^2}{2m^*}.$$

$$\nabla_{\vec{k}} E(\vec{k}) = \frac{\hbar^2}{m^*}(k_x \hat{x} + k_y \hat{y} + k_z \hat{z})$$

$$\sigma = \frac{e^2}{4\pi^3 \hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \hat{z} \right)^2 d^3k$$

assuming a single lifetime τ

$$\sigma = \frac{\hbar^2 e^2 \tau}{4\pi^3 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k_z^2 d^3k$$

http://lampx.tugraz.at/~hadley/ss2/transport/fecond.php

# Free-electron model: electrical conductivity

$$\sigma = \frac{\hbar^2 e^2 \tau}{4\pi^3 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k_z^2 d^3 k.$$

The differential volume is,

$$d^3 k = k^2 \sin\theta \, dk d\theta d\varphi \qquad k_z = k\cos\theta,$$

$$\sigma = \frac{\hbar^2 e^2 \tau}{4\pi^3 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k^4 \cos^2\theta \sin\theta \, dk d\theta d\varphi.$$

The integral over $\varphi$ contributes a factor of $2\pi$.

$$\sigma = \frac{\hbar^2 e^2 \tau}{2\pi^2 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k^4 \cos^2\theta \sin\theta \, dk d\theta.$$

The integral over $\theta$ contributes a factor of $2/3$.

$$\sigma = \frac{\hbar^2 e^2 \tau}{3\pi^2 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k^4 dk.$$

# Free-electron model: electrical conductivity

$$\sigma = \frac{\hbar^2 e^2 \tau}{3\pi^2 m^{*2}} \int \frac{\partial f_0}{\partial \mu} k^4 dk.$$

The derivative of the Fermi function is,

$$\frac{\partial f_0}{\partial \mu} = \frac{\exp(x)}{k_B T (\exp(x) + 1)^2}$$

where

$$x = \frac{E - \mu}{k_B T} = \frac{\frac{\hbar^2}{2m^*}(k^2 - k_F^2)}{k_B T},$$

and $\mu = \hbar^2 k_F^2 / 2m^*$. Differentiating to find $dk$

$$dk = \frac{m^* k_B T}{\hbar^2 k} dx$$

The conductivity can be written as,

$$\sigma = \frac{e^2 \tau}{3\pi^2 m^*} \int \frac{\exp(x)}{(\exp(x) + 1)^2} k^3 dx.$$

# Free-electron model: electrical conductivity

$$\sigma = \frac{e^2 \tau}{3\pi^2 m^*} \int \frac{\exp(x)}{(\exp(x)+1)^2} k^3 \, dx.$$

$k$ is approximately $k_F$ and it can be pulled out of the integral.
The remaining integral over $x$ evaluates to 1

$$\sigma = \frac{e^2 \tau k_F^3}{3\pi^2 m^*}.$$

For free electrons,

$$n = \frac{k_F^3}{3\pi^2}.$$

In terms of the electron density, the electrical conductivity is,

$$\sigma = \frac{n e^2 \tau}{m^*}.$$

# Thermal conductivity

The electrons carry heat as well as charge.

$$\vec{j}_Q = -\frac{1}{4\pi^3\hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left(E(\vec{k}) - \mu\right) \nabla_{\vec{k}} E(\vec{k}) \left(\nabla_{\vec{k}} E(\vec{k}) \cdot \left(\frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T\right)\right) d^3k.$$

Generally, the relationship between the thermal current density and the temperature gradient is described by the thermal conductivity matrix,

$$
\begin{bmatrix} j_{Qx} \\ j_{Qy} \\ j_{Qz} \end{bmatrix}
= -
\begin{bmatrix} K_{xx} & K_{xy} & K_{xz} \\ K_{yx} & K_{yy} & K_{yz} \\ K_{zx} & K_{zy} & K_{zz} \end{bmatrix}
\begin{bmatrix} \frac{\partial T}{\partial x} \\ \frac{\partial T}{\partial y} \\ \frac{\partial T}{\partial z} \end{bmatrix}.
$$

The thermal conductivity matrix can be calculated from the dispersion relation as,

$$K_{ij} = \frac{1}{4\pi^3\hbar^2 T} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left(E(\vec{k}) - \mu\right) \nabla_{\vec{k}} E(\vec{k}) \cdot \hat{e}_i \left(E(\vec{k}) - \mu\right) \nabla_{\vec{k}} E(\vec{k}) \cdot \hat{e}_j d^3k.$$

Here $\hat{e}_i$ are the unit vectors $i = [x, y, z]$. For cubic crystals the thermal conductivity is a constant,

$$K = \frac{1}{4\pi^3\hbar^2 T} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left(\left(E(\vec{k}) - \mu\right) \nabla_{\vec{k}} E(\vec{k}) \cdot \hat{z}\right)^2 d^3k.$$

# Thermal conductivity

$$K = \frac{1}{4\pi^3 \hbar^2 T} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left( \left( E(\vec{k}) - \mu \right) \nabla_{\vec{k}} E(\vec{k}) \cdot \hat{z} \right)^2 d^3 k.$$

(Similar calculation as before, See notes)

The electrical contribution to the thermal conductivity in the free electron model is,

$$K = \frac{\pi^2 \tau n k_B^2 T}{3 m^*}.$$

# Free-electron model: Wiedemann–Franz law

$$\frac{K}{\sigma} = LT.$$

Here $K$ is the electrical component of the thermal conductivity, $\sigma$ is the thermal conductivity, $T$ is the absolute temperature, and $L$ is the Lorentz number. For the free-electron model, the electrical and thermal conductivities are,

$$\sigma = \frac{ne^2\tau}{m^*} \qquad K = \frac{\pi^2\tau nk_B^2 T}{3m^*}.$$

The Lorentz number for free electrons is,

$$L = \frac{\pi^2 k_B^2}{3e^2} = 2.44 \times 10^{-8} \, \mathrm{W\,\Omega\,K^{-2}}.$$

Generally, both $K$ and $\sigma$ are matrices so when the crystal does not have a high symmetry, the general relationship between them would be described by a fourth-rank tensor.

# Thermoelectric current

A temperature gradient can cause a current to flow along a wire. The electrons move from the hot side to the cold side. Both charge and energy are transported in this case. The general expression for the electric current density is,

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3 \hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( \nabla_{\vec{r}} \tilde{\mu} + \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3 k.$$

One end of the wire is grounded an the other is attached to an ammeter which is then also grounded. There is no voltage drop across a perfect ammeter so the gradient of the electrochemical potential is zero. The thermoelectric current produced by this temperature gradient is,

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3 \hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3 k.$$

# Thermoelectric current

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \left( \frac{E(\vec{k}) - \mu}{T} \nabla_{\vec{r}} T \right) \right) d^3k.$$

The relationship between the electrical current density and the temperature gradient can be written as a matrix,

$$\begin{bmatrix} j_x \\ j_y \\ j_z \end{bmatrix} = \begin{bmatrix} \kappa_{xx} & \kappa_{xy} & \kappa_{xz} \\ \kappa_{yx} & \kappa_{yy} & \kappa_{yz} \\ \kappa_{zx} & \kappa_{zy} & \kappa_{zz} \end{bmatrix} \begin{bmatrix} \frac{\partial T}{\partial x} \\ \frac{\partial T}{\partial y} \\ \frac{\partial T}{\partial z} \end{bmatrix}.$$
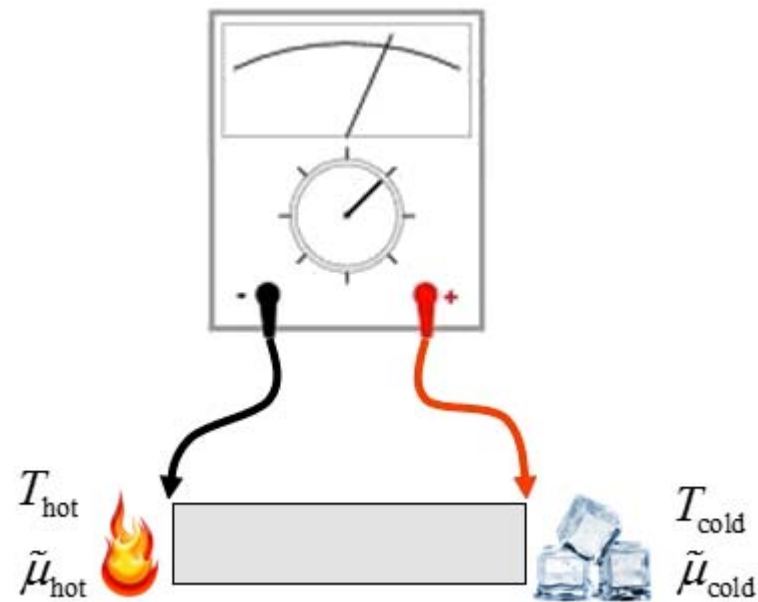
The thermoelectric coefficients

$$\kappa_{ij} = \frac{e}{4\pi^3\hbar^2 T} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \nabla_{\vec{k}} E(\vec{k}) \cdot \hat{e}_i \left( E(\vec{k}) - \mu \right) \nabla_{\vec{k}} E(\vec{k}) \cdot \hat{e}_j d^3k.$$

Here $\hat{e}_i$ are the unit vectors $i = [x, y, z]$. For cubic crystals the thermal coefficient is a constant,

$$\kappa = \frac{e}{4\pi^3\hbar^2 T} \int \tau(\vec{k}) \frac{\partial f_0}{\partial \mu} \left( E(\vec{k}) - \mu \right) \left( \nabla_{\vec{k}} E(\vec{k}) \cdot \hat{z} \right)^2 d^3k.$$

# Seebeck effect

$$\nabla_{\vec{r}}\tilde{\mu} = -S\nabla_{\vec{r}}T.$$



$$T_{\text{hot}}$$
$$\tilde{\mu}_{\text{hot}}$$

$$T_{\text{cold}}$$
$$\tilde{\mu}_{\text{cold}}$$

$$\vec{j}_{\text{elec}} = \frac{e}{4\pi^3\hbar^2}\int\tau(\vec{k})\frac{\partial f_0}{\partial\mu}\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k}) - \mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

$$\vec{j}_{\text{elec}} = 0$$

# Seebeck effect

$$\nabla_{\vec{r}}\tilde{\mu} = -S\nabla_{\vec{r}}T.$$

$$0 = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k})-\mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

$$\begin{bmatrix} \frac{\partial\tilde{\mu}}{\partial x} \\[6pt] \frac{\partial\tilde{\mu}}{\partial y} \\[6pt] \frac{\partial\tilde{\mu}}{\partial z} \end{bmatrix} = -\begin{bmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{yx} & S_{yy} & S_{yz} \\ S_{zx} & S_{zy} & S_{zz} \end{bmatrix}\begin{bmatrix} \frac{\partial T}{\partial x} \\[6pt] \frac{\partial T}{\partial y} \\[6pt] \frac{\partial T}{\partial z} \end{bmatrix}$$

$$0 = \frac{e}{4\pi^3\hbar^2}\int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_i\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\begin{pmatrix}-S_{xj}\\-S_{yj}\\-S_{zj}\end{pmatrix} + \frac{E(\vec{k})-\mu}{T}\hat{e}_j\right)\right)d^3k$$

Solve by guessing $S$ and integrating then iterating.

# Thermal conductivity again

$T_1$ ☐ $T_2$

Open boundary conditions

A heat current will also flow in this case. The expression for the heat current is,

$$\vec{j}_Q = -\frac{1}{4\pi^3\hbar^2} \int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k}) - \mu\right)\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(\nabla_{\vec{r}}\tilde{\mu} + \frac{E(\vec{k}) - \mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

In this experiment, the electrochemical potential and the temperature gradient are related by $\nabla_{\vec{r}}\tilde{\mu} = -S\nabla_{\vec{r}}T$ so this is inserted into the expression for the heat current.

$$\vec{j}_Q = -\frac{1}{4\pi^3\hbar^2} \int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k}) - \mu\right)\nabla_{\vec{k}}E(\vec{k})\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(-S\nabla_{\vec{r}}T + \frac{E(\vec{k}) - \mu}{T}\nabla_{\vec{r}}T\right)\right)d^3k.$$

The thermal conductivity in this case is,

$$K_{ij} = -\frac{1}{4\pi^3\hbar^2} \int \tau(\vec{k})\frac{\partial f_0}{\partial \mu}\left(E(\vec{k}) - \mu\right)\nabla_{\vec{k}}E(\vec{k})\cdot\hat{e}_i\left(\nabla_{\vec{k}}E(\vec{k})\cdot\left(-S\hat{e}_j + \frac{E(\vec{k}) - \mu}{T}\hat{e}_j\right)\right)d^3k.$$

new term

# Thermoelectric effects

**Seebeck effect:**

A thermal gradient causes a thermal current to flow. This results in a voltage which sends the low entropy charge carriers back to the hot end.

$$\nabla \tilde{\mu} = -S \nabla T$$

$S$ is the absolute thermal power (often also called $Q$). The sign of the voltage (electrochemical potential, electromotive force) is the same as the sign of the charge carriers.

The Seebeck effect can be used to make a thermometer. The gradient of the temperature is the same along both wires but the gradient in electrochemical potential differs.
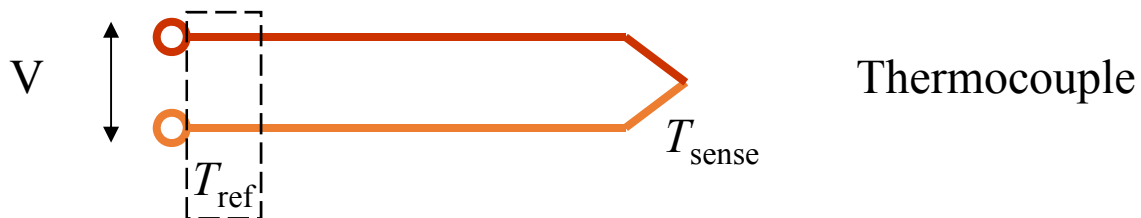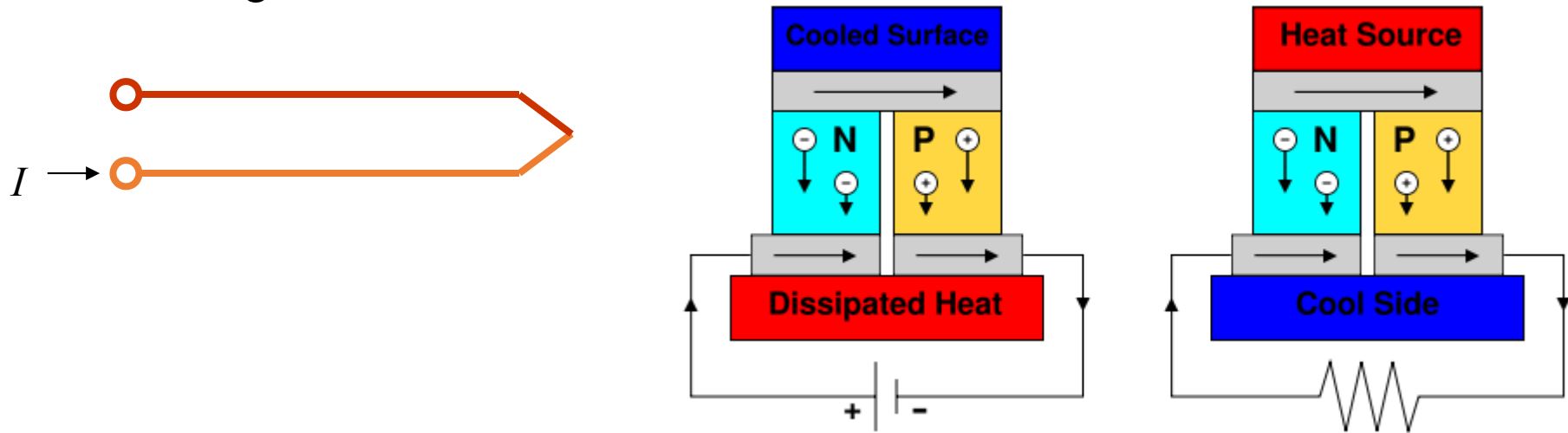
# Thermoelectric effects
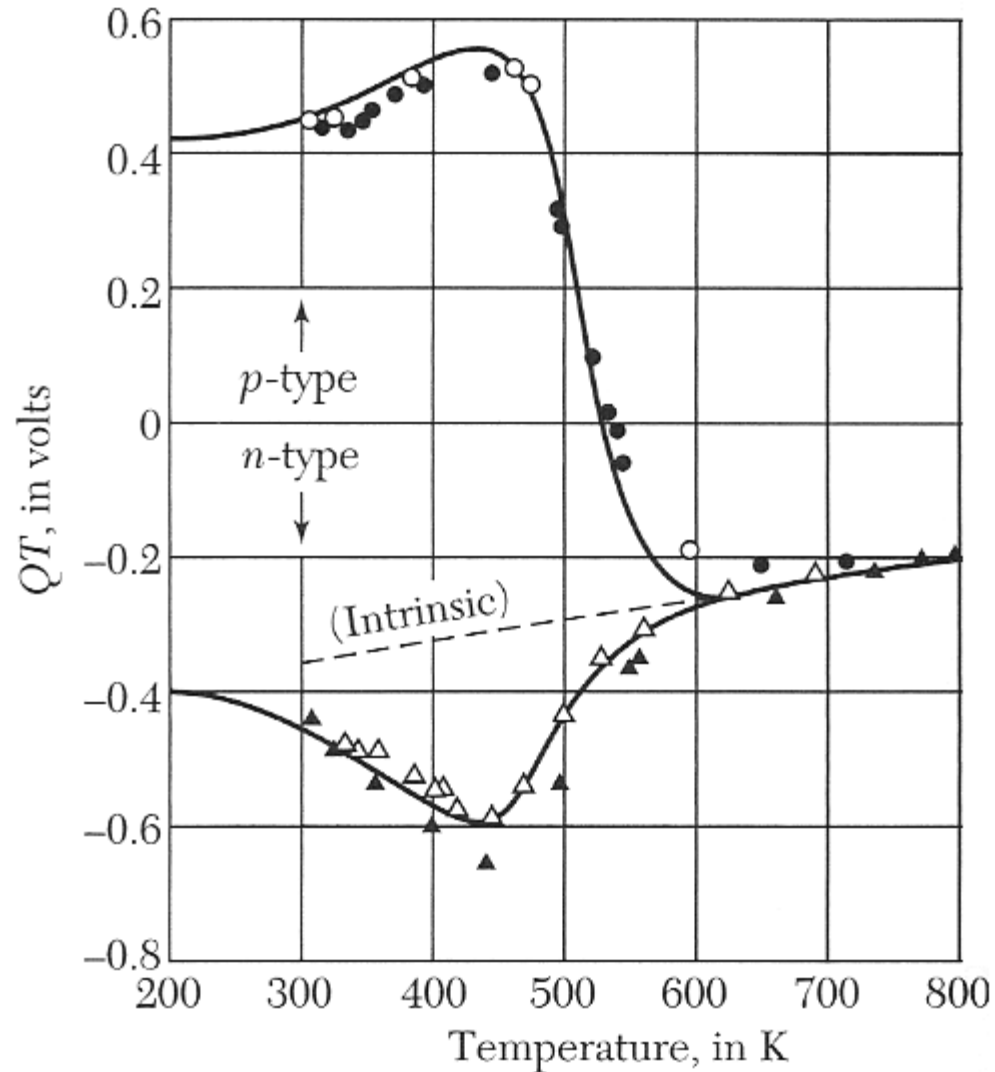


Intrinsic $Q$ is negative because electrons have a higher mobility.

# Thermoelectric effects

**Peltier effect**: driving a through a bimetallic junction causes heating or cooling.



Cooling takes place when the electrons make a transition from low entropy to high entropy at the junction.

Bismuth chalcogenides $Bi_2Te_3$ and $Bi_2Se_3$