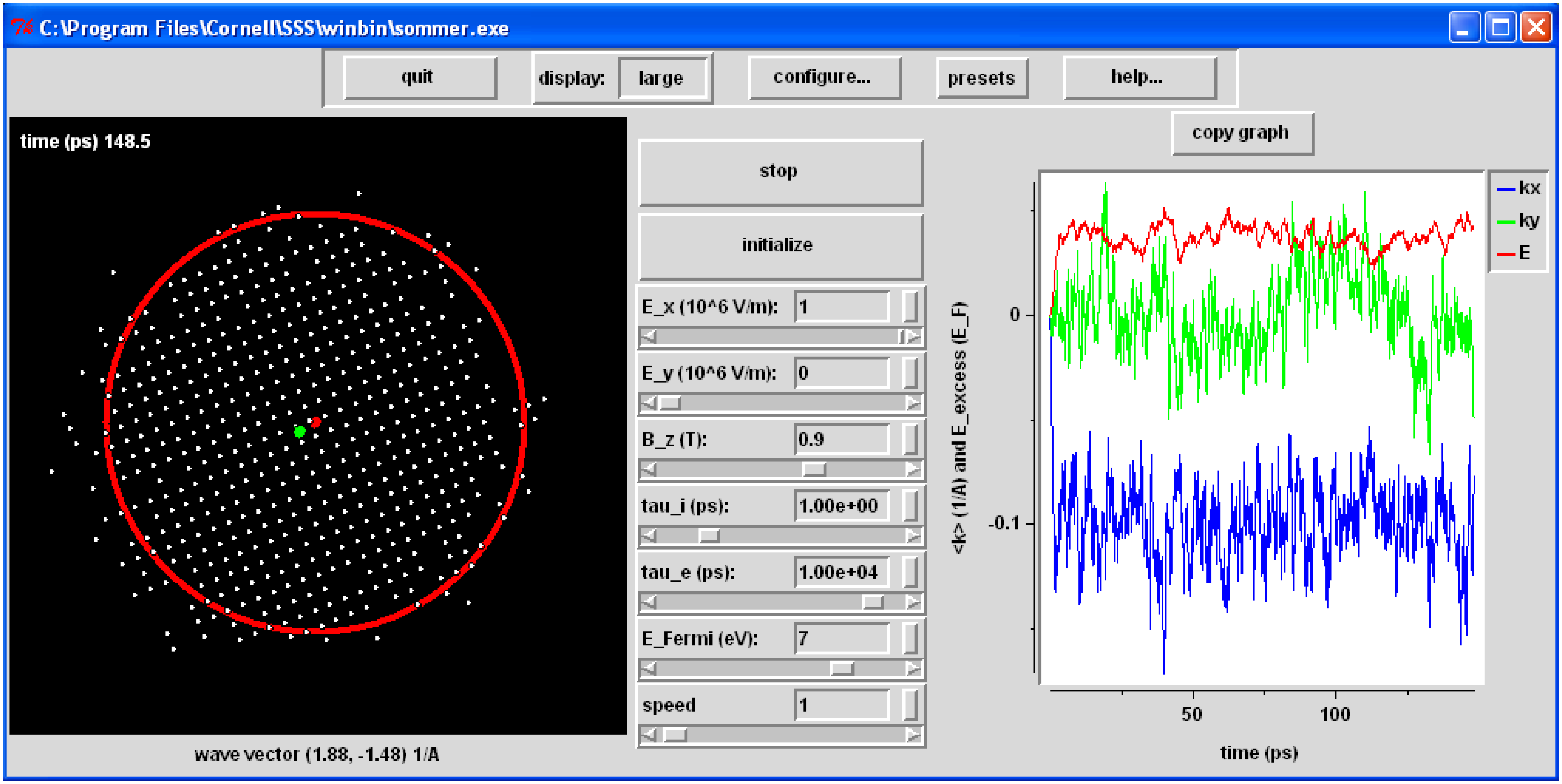
# Boltzmann equation


C:\Program Files\Cornell\SSS\winbin\sommer.exe
quit
display:
large
configure...
presets
help...
time (ps) 148.5
stop
initialize
copy graph
E_x (10^6 V/m):
1
E_y (10^6 V/m):
0
B_z (T):
0.9
tau_i (ps):
1.00e+00
tau_e (ps):
1.00e+04
E_Fermi (eV):
7
speed
1
wave vector (1.88, -1.48) 1/A
kx
ky
E
<k> (1/A) and E_excess (E_F)
0
-0.1
50
100
time (ps)

# Current densities

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

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

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

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

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

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

# Liouville's theorem

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

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

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

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

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

# 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 $\vec{F}_{\text{ext}} = \hbar \frac{d\vec{k}}{dt}$

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

Collision term describes the transitions between *k* states.

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

# 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 $\vec{F}_{ext} = \nabla_r f = 0$ 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

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

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

# Boltzmann equation: relaxation time approx.

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

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

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

Temperature and chemical potential can depend on position

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

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

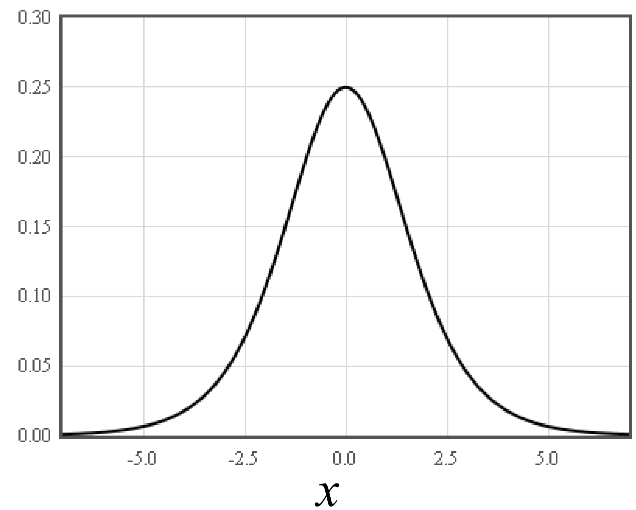
Temperature gradient

Concentration gradient

# Boltzmann equation: relaxation time approx.

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

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




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

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

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

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

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 $\qquad D(\vec{k}) = \frac{2}{(2\pi)^3}$

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

The contribution of $f_0(k)$ is zero

$$\nabla_{\vec{k}}E(\vec{k}) \cdot \left( \nabla_{\vec{k}}E(\vec{k}) \times \vec{B} \right) = 0$$

# 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

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

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

# Electrical conductivity

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

no temperature gradient

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

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

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 $\tau$

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

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,

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