

Boltzmann transport equation (II)
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Using the Boltzmann equation, we discuss the transport phenomena such as electrical conductivity and thermoelectric effect.

1. Definition of current density

$$I = \frac{\Delta q}{\Delta t}$$

$$\begin{aligned} J &= \frac{1}{\Delta A} I \\ &= \frac{1}{\Delta A} \frac{\Delta q}{\Delta t} \\ &= \frac{1}{\Delta A} \frac{n(-e)(v\Delta t)\Delta A}{\Delta t} \\ &= n(-e)v \end{aligned}$$

Since $n = \frac{N}{V}$,

$$\begin{aligned} \mathbf{J} &= (-e) \frac{1}{V} \sum_k \mathbf{v}_k \delta f_k \\ &= (-e) \frac{2V}{(2\pi)^3} \int d\mathbf{k} (\mathbf{v}_k \delta f_k) \end{aligned}$$

Note that

$$d\mathbf{k} = dS dk_{\perp} = \frac{dS d\varepsilon}{|\nabla_{\mathbf{k}} \varepsilon|}$$

$\mathbf{v}_k = \frac{1}{\hbar} \nabla_{\mathbf{k}} \varepsilon_k$ is the group velocity.

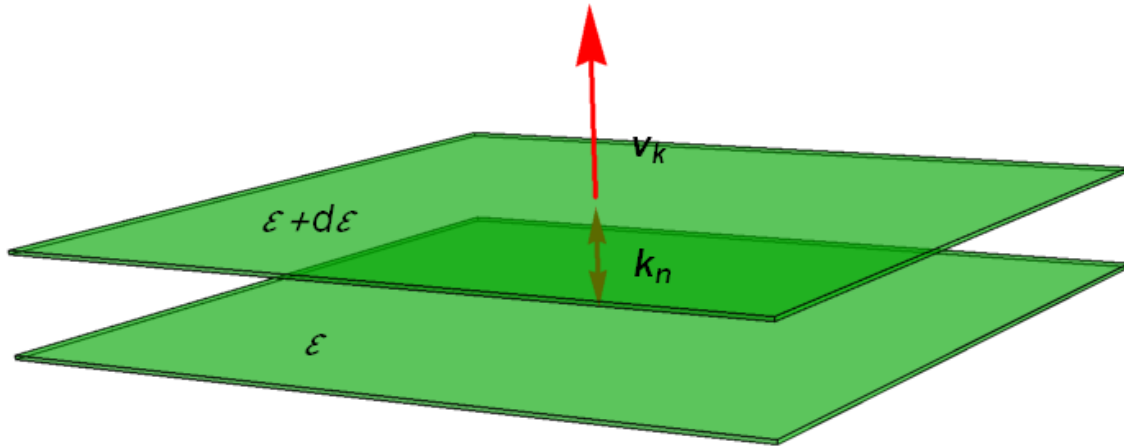


Fig. The separation $\delta k_n = \delta k_\perp$ between the two adjacent energy surfaces ε and $\varepsilon + d\varepsilon$. The group velocity \mathbf{v}_k is normal to the energy surface.

Thus the current density is defined by

$$\begin{aligned}
 \mathbf{J} &= (-e) \frac{1}{V} \sum_k \mathbf{v}_k \delta f_k \\
 &= (-e) \frac{2V}{(2\pi)^3 V} \int d\mathbf{k} (\mathbf{v}_k \delta f_k) \\
 &= (-e) \frac{2}{(2\pi)^3} \int \frac{dS d\varepsilon}{|\nabla_k \varepsilon|} (\mathbf{v}_k \delta f_k)
 \end{aligned}$$

We use the distribution function

$$\delta f_k = e\tau (\mathbf{E} \cdot \mathbf{v}_k) \frac{\partial f_0}{\partial \varepsilon}$$

where τ is the relaxation time, and

$$\frac{\partial f_0}{\partial \varepsilon} \approx -\delta(\varepsilon - \mu).$$

Thus we have

$$\mathbf{J} = \frac{e^2}{4\pi^3\hbar} \int \tau(\varepsilon) \frac{\mathbf{v}_k(\mathbf{v}_k \cdot \mathbf{E})}{v_k} \left(-\frac{\partial f_0}{\partial \varepsilon}\right) dS d\varepsilon,$$

with the conductivity tensor as

$$\boldsymbol{\sigma} = \frac{e^2}{4\pi^3\hbar} \int \tau(\varepsilon) \frac{(\mathbf{v}_k \otimes \mathbf{v}_k)}{v_k} \left(-\frac{\partial f_0}{\partial \varepsilon}\right) dS d\varepsilon$$

with

$$\sigma_{\alpha\beta} = \frac{e^2}{4\pi^3\hbar} \int \tau(\varepsilon) \frac{v_{k,\alpha}v_{k,\beta}}{v_k} \left(-\frac{\partial f_0}{\partial \varepsilon}\right) dS d\varepsilon.$$

((Note)) Definition of dyadic

Dyadic

$$\mathbf{a} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix},$$

$$\mathbf{ab} = \mathbf{a} \otimes \mathbf{b} = \mathbf{ab}^T = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix} \begin{pmatrix} b_1 & b_2 & b_3 \end{pmatrix} = \begin{pmatrix} a_1^2 & a_1a_2 & a_1a_3 \\ a_2a_1 & a_2^2 & a_2a_3 \\ a_3a_1 & a_3a_2 & a_3^2 \end{pmatrix}$$

We calculate one of the conductivity tensor

$$\begin{aligned} \sigma_{xx} &= \frac{e^2\tau}{4\pi^3\hbar} \int \frac{v_{k,x}v_{k,x}}{v_k} \left(-\frac{\partial f_0}{\partial \varepsilon}\right) dS d\varepsilon \\ &= \frac{e^2\tau}{4\pi^3\hbar} \int \frac{v_F^2}{3v_F} \left(-\frac{\partial f_0}{\partial \varepsilon}\right) dS d\varepsilon \\ &= \frac{e^2v_F\tau}{12\pi^3\hbar} \int \left(-\frac{\partial f_0}{\partial \varepsilon}\right) dS d\varepsilon \\ &= \frac{e^2v_F\tau}{12\pi^3\hbar} S_F \\ &= \frac{e^2l_F S_F}{12\pi^3\hbar} \end{aligned}$$

where $v_{k,x}^2 \rightarrow \frac{1}{3}v_k^2$, $l_F = v_F\tau$ is the mean free path, Here we note that the density of states is defined by

$$D(\varepsilon) = \sum_k \delta(\varepsilon - \varepsilon_k)$$

or

$$\begin{aligned} D(\varepsilon) &= \frac{2V}{(2\pi)^3} \int d\mathbf{k} \delta(\varepsilon - \varepsilon_k) \\ &= \frac{V}{4\pi^3} \int \frac{dS d\varepsilon}{|\nabla_{\mathbf{k}} \varepsilon|} \delta(\varepsilon - \varepsilon_k) \\ &= \frac{V}{4\pi^3 \hbar} \int_{\varepsilon} \frac{dS}{v_k} \end{aligned}$$

or

$$D(\varepsilon_F) = \frac{VS_F}{4\pi^3 \hbar v_F}$$

where dS is the surface element in \mathbf{k} - space, and the integral is over the surface of constant energy ε . The density of states per unit volume is

$$\begin{aligned} N(\varepsilon_F) &= \frac{D(\varepsilon_F)}{V} \\ &= \frac{S_F}{4\pi^3 \hbar v_F} \end{aligned}$$

Using this expression of $N(\varepsilon_F)$, the conductivity can be rewritten as

$$\sigma_{xx} = \frac{1}{3} e^2 l_F v_F N(\varepsilon_F) = \frac{1}{3} e^2 \tau v_F^2 N(\varepsilon_F)$$

which is equal to

$$\sigma_{xx} = \frac{ne^2\tau}{m}$$

for free electrons.

((Note)) Discussion on free electrons

All parameters in this conductivity are the values on the Fermi surface. For free electrons,

$$N(\varepsilon_F) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{1/2}$$

$$\varepsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$

$$v_F = \frac{\hbar}{m} (3\pi^2 n)^{1/3}$$

Using these values, we have

$$\begin{aligned} m v_F^2 N(\varepsilon_F) &= m \frac{\hbar^2}{m^2} (3\pi^2 n)^{2/3} \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \left(\frac{\hbar^2}{2m} \right)^{1/2} (3\pi^2 n)^{1/3} \\ &= 3n \end{aligned}$$

leading to

$$n = \frac{1}{3} m v_F^2 N(\varepsilon_F)$$

2. Distribution function

We have

$$f_k = f_k^0 + \delta f_k$$

where

$$\delta f_k = e\tau(\mathbf{E} \cdot \mathbf{v}_k) \frac{\partial f_0}{\partial \varepsilon}, \quad \delta \mathbf{k} = -\frac{e\tau}{\hbar} \mathbf{E}.$$

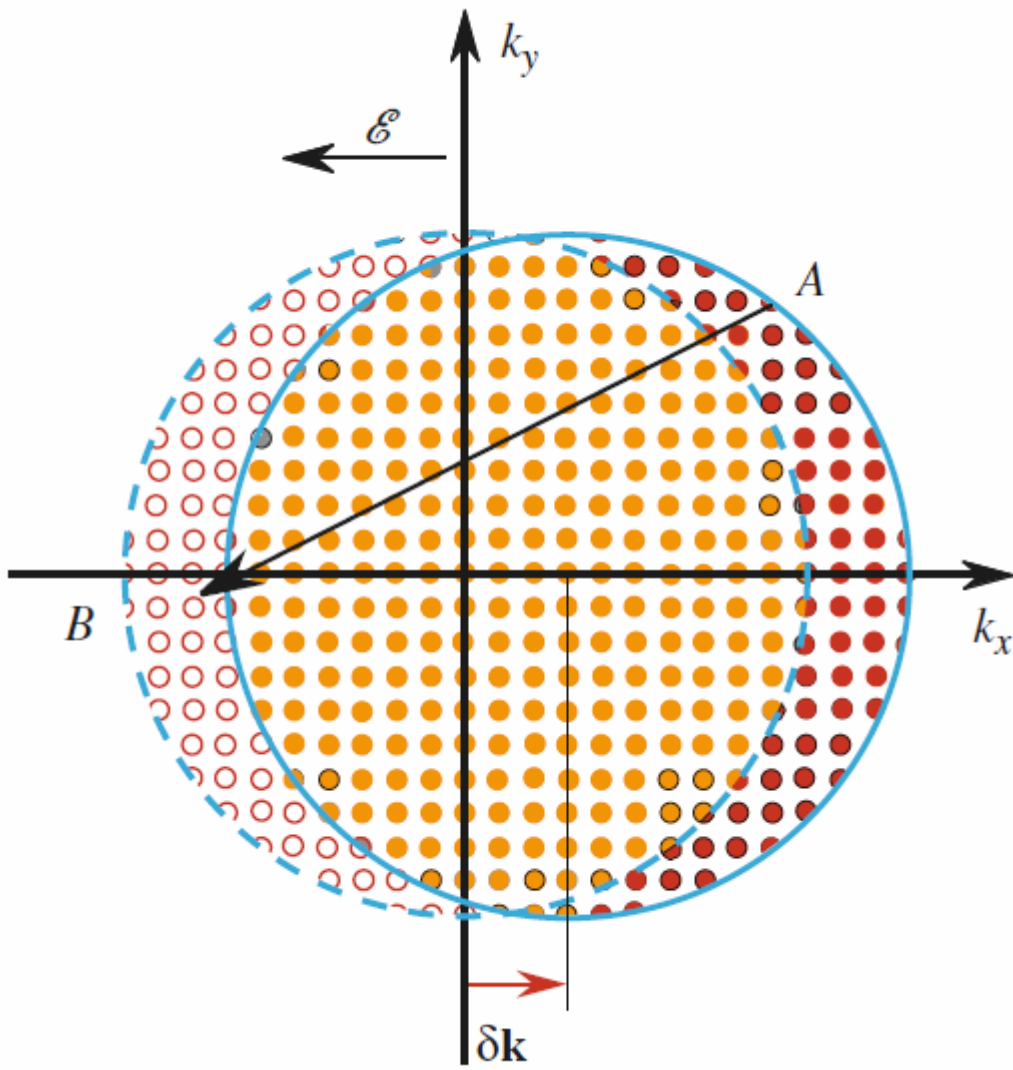
and

$$\begin{aligned}
\frac{\partial f_k^0}{\partial \mathbf{k}} \cdot \delta \mathbf{k} &= \hbar \mathbf{v}_k \frac{\partial f_0}{\partial \varepsilon} \cdot \left(-\frac{e\tau}{\hbar} \mathbf{E}\right) \\
&= -e\tau (\mathbf{v}_k \cdot \mathbf{E}) \frac{\partial f_0}{\partial \varepsilon} \\
&= -\delta f_k
\end{aligned}$$

Thus we get

$$\begin{aligned}
f(\mathbf{k}) &= f^0(\mathbf{k}) + \delta f_k \\
&= f^0(\mathbf{k}) - \frac{\partial f^0(\mathbf{k})}{\partial \mathbf{k}} \cdot \delta \mathbf{k} \\
&= f^0(\mathbf{k} - \delta \mathbf{k}) \\
&= f^0\left(\mathbf{k} + \frac{e\tau}{\hbar} \mathbf{E}\right)
\end{aligned}$$

by Taylor's theorem. It is as if the whole Fermi surface had been shifted by the amount $-\frac{e\tau}{\hbar} \mathbf{E}$ in the \mathbf{k} -space.



3. Boltzmann transport theory

$$\frac{df}{dt} = 0 = \left(\frac{df}{dt} \right)_{fields} + \left(\frac{df}{dt} \right)_{coll.}$$

or

$$-\left(\frac{df}{dt} \right)_{fields} = \left(\frac{df}{dt} \right)_{coll.}$$

$$\left(\frac{df}{dt}\right)_{coll.} = -\frac{f - f_0}{\tau} = -\frac{\delta f}{\tau}$$

$$\begin{aligned} \left(\frac{df}{dt}\right)_{fields} &= -\frac{d\mathbf{r}}{dt} \cdot \nabla_{\mathbf{r}} f - \frac{d\mathbf{k}}{dt} \cdot \nabla_{\mathbf{k}} f \\ &\approx -\mathbf{v}_{\mathbf{k}} \cdot \nabla_{\mathbf{r}} f_0 - \frac{d\mathbf{k}}{dt} \cdot \nabla_{\mathbf{k}} f_0 \end{aligned}$$

where

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}_{\mathbf{k}}, \quad \hbar \frac{d\mathbf{k}}{dt} = (-e)\mathbf{E}$$

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \varepsilon \quad (\text{group velocity})$$

We note that the Fermi-Dirac function is given by

$$f_0(\mathbf{k}, \mathbf{r}) = \frac{1}{e^{\beta(\mathbf{r})(\varepsilon_{\mathbf{k}} - \mu(\mathbf{r}))} + 1}$$

and

$$\frac{\partial f_0(\varepsilon)}{\partial \varepsilon} = -\frac{\beta e^{\beta(\varepsilon - \mu)}}{[e^{\beta(\varepsilon - \mu)} + 1]^2}$$

$$\begin{aligned} \nabla_{\mathbf{r}} f_0 &= \frac{-e^{\beta(\varepsilon - \mu)}}{[e^{\beta(\varepsilon - \mu)} + 1]^2} \\ &= \frac{1}{\beta} \frac{\partial f_0}{\partial \varepsilon} \nabla_{\mathbf{r}} \beta(\varepsilon - \mu) \end{aligned}$$

$$\begin{aligned}
\nabla_{\mathbf{k}} f_0 &= \frac{-e^{\beta(\varepsilon-\mu)}}{[e^{\beta(\varepsilon-\mu)} + 1]^2} \nabla_{\mathbf{k}} \beta(\varepsilon - \mu) \\
&= \frac{1}{\beta} \frac{\partial f_0}{\partial \varepsilon} \beta \nabla_{\mathbf{k}} \varepsilon \\
&= \frac{\partial f_0}{\partial \varepsilon} \nabla_{\mathbf{k}} \varepsilon \\
&= \hbar \mathbf{v}_{\mathbf{k}} \frac{\partial f_0}{\partial \varepsilon}
\end{aligned}$$

Thus we get

$$\begin{aligned}
\left(\frac{df}{dt} \right)_{fields} &= -\mathbf{v}_{\mathbf{k}} \cdot \nabla_r f_0 - \frac{d\mathbf{k}}{dt} \cdot \nabla_{\mathbf{k}} f_0 \\
&= -T \mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f_0}{\partial \varepsilon} \nabla_r \left(\frac{\varepsilon - \mu}{T} \right) - \left(\frac{d\mathbf{k}}{dt} \cdot \nabla_{\mathbf{k}} \varepsilon \right) \frac{\partial f_0}{\partial \varepsilon} \\
&= -T \mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f_0}{\partial \varepsilon} \nabla_r \left(\frac{\varepsilon - \mu}{T} \right) - \left(\hbar \frac{d\mathbf{k}}{dt} \cdot \mathbf{v}_{\mathbf{k}} \right) \frac{\partial f_0}{\partial \varepsilon}
\end{aligned}$$

Newton's second law:

$$\frac{d\mathbf{k}}{dt} = (-e) \frac{1}{\hbar} \mathbf{E},$$

where \mathbf{E} is an electric field. The group velocity:

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \varepsilon,$$

Then we have

$$\begin{aligned}
\left(\frac{df}{dt} \right)_{fields} &= -T \mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f_0}{\partial \varepsilon} \nabla_r \left(\frac{\varepsilon - \mu}{T} \right) + e \mathbf{E} \cdot \mathbf{v}_{\mathbf{k}} \frac{\partial f_0}{\partial \varepsilon} \\
&= [T \mathbf{v}_{\mathbf{k}} \cdot \nabla_r \left(\frac{\varepsilon - \mu}{T} \right) - e \mathbf{E} \cdot \mathbf{v}_{\mathbf{k}}] \left(-\frac{\partial f_0}{\partial \varepsilon} \right) \\
&= [T \nabla_r \left(\frac{\varepsilon - \mu}{T} \right) - e \mathbf{E}] \cdot \mathbf{v}_{\mathbf{k}} \left(-\frac{\partial f_0}{\partial \varepsilon} \right)
\end{aligned}$$

Using the relation

$$\left(\frac{df}{dt}\right)_{fields} = -\left(\frac{df}{dt}\right)_{coll.} = \frac{f - f_0}{\tau}$$

we have

$$f = f_0 + [T\nabla_r\left(\frac{\varepsilon - \mu}{T}\right) - e\mathbf{E}] \cdot \tau \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon}\right)$$

Noting that

$$\begin{aligned} T\nabla_r\left(\frac{\varepsilon - \mu}{T}\right) &= T\nabla_r\left(\frac{\varepsilon}{T}\right) - \nabla_r\left(\frac{\mu}{T}\right) \\ &= -\frac{\varepsilon}{T}\nabla_r T - T\nabla_r\left(\frac{\mu}{T}\right) \end{aligned}$$

we have

$$\begin{aligned} \delta f &= f - f_0 \\ &= \left[-\frac{\varepsilon}{T}\nabla_r T - T\nabla_r\left(\frac{\mu}{T}\right) - e\mathbf{E}\right] \cdot \tau \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \end{aligned}$$

where

$$\begin{aligned} -\frac{\varepsilon}{T}\nabla_r T - T\nabla_r\left(\frac{\mu}{T}\right) - e\mathbf{E} &= -\frac{\varepsilon}{T}\nabla_r T - \nabla_r \mu + \frac{\mu}{T}\nabla_r T - e\mathbf{E} \\ &= -\frac{(\varepsilon - \mu)}{T}\nabla_r T - e\left(\mathbf{E} + \frac{1}{e}\nabla_r \mu\right) \end{aligned}$$

4. Current density

$$\begin{aligned} \mathbf{J}_e &= (-e)\frac{1}{V}\sum_k \mathbf{v}_k \delta f_k \\ &= (-e)\frac{2}{(2\pi)^3}\int d\mathbf{k}(\mathbf{v}_k \delta f_k) \\ &= -\frac{e}{4\pi^3}\int d\mathbf{k}(\mathbf{v}_k \delta f_k) \end{aligned}$$

where

$$\delta f_k = \left[-\frac{(\varepsilon - \mu)}{T} \nabla_r T - e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \right] \cdot \tau \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right)$$

$$\begin{aligned} \mathbf{J}_e &= -\frac{e}{4\pi^3} \int d\mathbf{k} \mathbf{v}_k \left\{ -\frac{(\varepsilon_k - \mu)}{T} \nabla_r T - e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \right\} \cdot \tau \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \\ &= (-e) \left(-\frac{1}{T} \nabla_r T \right) \left[\frac{1}{4\pi^3} \int d\mathbf{k} \tau \mathbf{v}_k (\varepsilon_k - \mu) \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \right] \\ &\quad + e^2 \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \left[\frac{1}{4\pi^3} \int d\mathbf{k} \tau \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \right] \\ &= e^2 \mathbf{K}^{(0)} \cdot \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) - e \mathbf{K}^{(1)} \cdot \left(-\frac{1}{T} \nabla_r T \right) \end{aligned}$$

or

$$\mathbf{J}_e = e^2 \mathbf{K}^{(0)} \cdot \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) - e \mathbf{K}^{(1)} \cdot \left(-\frac{1}{T} \nabla_r T \right)$$

5. The energy flux

The energy density is given by

$$\begin{aligned} U &= \frac{1}{V} \sum_k \mathbf{v}_k \varepsilon_k \delta f_k \\ &= \frac{1}{4\pi^3} \int d\mathbf{k} (\mathbf{v}_k \varepsilon_k \delta f_k) \end{aligned}$$

or

$$\begin{aligned} U &= \frac{1}{4\pi^3} \int d\mathbf{k} \mathbf{v}_k \varepsilon_k \left\{ \varepsilon_k \left(-\frac{1}{T} \nabla_r T \right) + \left[-e \mathbf{E} - T \nabla_r \left(\frac{\mu}{T} \right) \right] \right\} \cdot \tau \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \\ &= \left(-\frac{1}{T} \nabla_r T \right) \frac{1}{4\pi^3} \int d\mathbf{k} \tau \varepsilon_k^2 \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) + \left[-e \mathbf{E} - T \nabla_r \left(\frac{\mu}{T} \right) \right] \frac{1}{4\pi^3} \int d\mathbf{k} \tau \varepsilon_k \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \end{aligned}$$

or

$$\begin{aligned}
U &= \frac{1}{4\pi^3} \int d\mathbf{k} \mathbf{v}_k \varepsilon_k \left\{ -\frac{(\varepsilon_k - \mu)}{T} \nabla_r T - e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \right\} \cdot \tau \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \\
&= -\frac{1}{T} \nabla_r T \frac{1}{4\pi^3} \int d\mathbf{k} \tau \varepsilon_k (\varepsilon_k - \mu) \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \\
&\quad - e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \frac{1}{4\pi^3} \int d\mathbf{k} \tau \varepsilon_k \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right)
\end{aligned}$$

((**Note**)) This expression of U is not used in the discussion below. In the above expression, there are two kinds of integrals; $\int d\mathbf{k} \tau \varepsilon_k (\varepsilon_k - \mu) \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right)$ and $\int d\mathbf{k} \tau \varepsilon_k \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right)$. Instead of using the expression of U , we use the heat current density \mathbf{J}_Q .

6. Heat current density \mathbf{J}_Q

Here we define

$$\begin{aligned}
\mathbf{K}^{(n)} &= \frac{1}{4\pi^3} \int d\mathbf{k} \tau [\mathbf{v}_k \otimes \mathbf{v}_k] (\varepsilon_k - \mu)^n \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \\
&= \frac{1}{4\pi^3 \hbar} \int \frac{dS d\varepsilon}{v_k} \tau [\mathbf{v}_k \otimes \mathbf{v}_k] (\varepsilon - \mu)^n \left(-\frac{\partial f_0}{\partial \varepsilon} \right)
\end{aligned} \tag{dyadic}$$

From these above relations, we see that there is a close connection between \mathbf{J}_e and \mathbf{Q} . The heat current density may be formulated through the thermodynamic relation

$$dQ = Tds = dU - \mu dN$$

Here we introduce the heat current density which is defined by

$$\begin{aligned}
\mathbf{J}_Q &= \frac{1}{V} \sum_k f_k^1 (\varepsilon_k - \mu) \mathbf{v}_k \\
&= \frac{2}{(2\pi)^3} \int d\mathbf{k} f_k^1 (\varepsilon_k - \mu) \mathbf{v}_k
\end{aligned}$$

or

$$\begin{aligned}
\mathbf{J}_Q &= \frac{2}{(2\pi)^3} \int d\mathbf{k} \delta f_k(\varepsilon_k - \mu) \mathbf{v}_k \\
&= \frac{1}{4\pi^3} \int d\mathbf{k} (\varepsilon_k - \mu) \mathbf{v}_k \left[-\frac{(\varepsilon_k - \mu)}{T} \nabla_r T - e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \right] \cdot \tau \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \\
&= -\frac{1}{T} \nabla_r T \frac{1}{4\pi^3} \int d\mathbf{k} \tau (\varepsilon_k - \mu)^2 \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right) \\
&\quad - e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \frac{1}{4\pi^3} \int d\mathbf{k} \tau (\varepsilon_k - \mu) \mathbf{v}_k \cdot \mathbf{v}_k \left(-\frac{\partial f_0}{\partial \varepsilon_k} \right)
\end{aligned}$$

or

$$\mathbf{J}_Q = \mathbf{K}^{(2)} \cdot \left(-\frac{1}{T} \nabla_r T \right) - \mathbf{K}^{(1)} \cdot e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right)$$

We note that

$$\begin{aligned}
\Phi_n(\varepsilon) &= \frac{1}{4\pi^3 \hbar} \int_{\mathbf{v}_k} \frac{dS}{v_k} \tau [\mathbf{v}_k \otimes \mathbf{v}_k] (\varepsilon - \mu)^n \\
&= (\varepsilon - \mu)^n \mathbf{K}^{(0)}(\varepsilon)
\end{aligned}$$

$$\mathbf{K}^{(0)}(\varepsilon) = \frac{1}{4\pi^3 \hbar} \int_{\mathbf{v}_k} \frac{dS}{v_k} \tau [\mathbf{v}_k \otimes \mathbf{v}_k]$$

where $\mathbf{K}^{(0)}(\varepsilon)$ is the integral over a surface of constant energy ε . We use the Sommerfeld's formula:

$$\begin{aligned}
\int_0^\infty \Phi_n(\varepsilon) \left(-\frac{\partial f_0}{\partial \varepsilon} \right) d\varepsilon &= \int_0^\infty \Phi_n'(\varepsilon) f_0(\varepsilon) d\varepsilon \\
&= \int_0^\mu \Phi_n'(\varepsilon) d\varepsilon + \frac{\pi^2}{6} k_B^2 T^2 \Phi_n''(\mu) \\
&= \Phi_n(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \Phi_n''(\mu) \\
&= \frac{\pi^2}{6} k_B^2 T^2 \Phi_n''(\mu)
\end{aligned}$$

where $\Phi_n(\mu) = 0$ for positive integer of n .

(a) Relation: $\mathbf{K}^{(2)} = \frac{\pi^2}{3} k_B^2 T^2 \mathbf{K}^{(0)}$

((Proof))

For this proof, we use the Sommerfeld's formula

$$\begin{aligned} \mathbf{K}^{(2)} &= \int d\varepsilon \Phi_2(\varepsilon) \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \\ &= \Phi_2(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \Phi_2''(\mu) \\ &= \frac{\pi^2}{3} k_B^2 T^2 \mathbf{K}^{(0)} \end{aligned}$$

with

$$\Phi_2(\varepsilon) = (\varepsilon - \mu)^2 \mathbf{K}^{(0)}(\varepsilon)$$

(b) Relation: $\mathbf{K}^{(1)} = \frac{\pi^2}{3} k_B^2 T^2 \left[\frac{d\mathbf{K}^{(0)}(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\mu}$

((Proof))

$$\begin{aligned} \mathbf{K}^{(1)} &= \int d\varepsilon \Phi_1(\varepsilon) \left(-\frac{\partial f_0}{\partial \varepsilon}\right) \\ &= \Phi_1(\mu) + \frac{\pi^2}{6} k_B^2 T^2 \Phi_1''(\mu) \\ &= \frac{\pi^2}{6} k_B^2 T^2 \Phi_1''(\mu) \\ &= \frac{\pi^2}{3} k_B^2 T^2 \left[\frac{d\mathbf{K}^{(0)}(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\mu} \end{aligned}$$

7. Transport properties

Using two equations

$$\mathbf{J}_e = (-e) \mathbf{K}^{(0)} \cdot \left[-e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \right] + (-e) \mathbf{K}^{(1)} \cdot \left(-\frac{1}{T} \nabla_r T \right)$$

$$\mathbf{J}_Q = \mathbf{K}^{(2)} \cdot \left(-\frac{1}{T} \nabla_r T \right) + \mathbf{K}^{(1)} \cdot \left[-e \left(\mathbf{E} + \frac{1}{e} \nabla_r \mu \right) \right]$$

or

$$\mathbf{J}_e = e^2 \mathbf{K}^{(0)} \cdot \mathbf{E}' + \frac{e}{T} \mathbf{K}^{(1)} \cdot \nabla_r T$$

$$\mathbf{J}_Q = -\frac{1}{T} \mathbf{K}^{(2)} \cdot \nabla_r T - e \mathbf{K}^{(1)} \cdot \mathbf{E}'$$

where

$$\mathbf{E}' = \mathbf{E} + \frac{1}{e} \nabla_r \mu$$

for $e > 0$.

(a) Current density

For $\nabla_r T = 0$

$$\mathbf{J}_e = e^2 \mathbf{K}^{(0)} \cdot \mathbf{E}', \quad \mathbf{J}_Q = -e \mathbf{K}^{(1)} \cdot \mathbf{E}'$$

The conductivity tensor is

$$\boldsymbol{\sigma} = e^2 \mathbf{K}^{(0)}$$

We can use this relation to express $\mathbf{K}^{(0)}$ in terms of the known electrical conductivity.

$$\mathbf{K}^{(0)} = \frac{\boldsymbol{\sigma}}{e^2}, \quad \mathbf{K}^{(1)} = \frac{\pi^2 k_B^2 T^2}{3e^2} \left[\frac{d\boldsymbol{\sigma}(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\mu}, \quad \mathbf{K}^{(2)} = \frac{\pi^2 k_B^2 T^2}{3e^2} \boldsymbol{\sigma}$$

(b) Thermal conductivity

For $\mathbf{J}_e = 0$

$$e \mathbf{E}' = -(\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)} \frac{1}{T} \cdot \nabla_r T$$

$$\begin{aligned}
\mathbf{J}_Q &= -\mathbf{K}^{(2)} \frac{1}{T} \cdot \nabla_r T - e\mathbf{K}^{(1)} \cdot \mathbf{E}' \\
&= -\mathbf{K}^{(2)} \frac{1}{T} \cdot \nabla_r T + [\mathbf{K}^{(1)} (\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)}] \frac{1}{T} \cdot \nabla_r T \\
&= -\frac{1}{T} [\mathbf{K}^{(2)} - \mathbf{K}^{(1)} (\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)}] \cdot \nabla_r T
\end{aligned}$$

The thermal conductivity tensor:

$$\boldsymbol{\kappa} = \frac{1}{T} [\mathbf{K}^{(2)} - \mathbf{K}^{(1)} (\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)}]$$

$$\mathbf{J}_Q = \boldsymbol{\kappa} \cdot (-\nabla T)$$

The correction is negligible for a metal. So that

$$\boldsymbol{\kappa} = \frac{1}{T} \mathbf{K}^{(2)}$$

((Wiedermann-Franz law))

$$\boldsymbol{\sigma} = e^2 \mathbf{K}^{(0)}, \quad T\boldsymbol{\kappa} = \mathbf{K}^{(2)}, \quad \mathbf{K}^{(2)} = \frac{\pi^2}{3} k_B^2 T^2 \mathbf{K}^{(0)}$$

Using these relations, we get the Wiedermann-Franz law;

$$\boldsymbol{\kappa} = \frac{\pi^2 k_B^2}{3e^2} T \boldsymbol{\sigma}$$

(c) Thermoelectric power

$$\mathbf{J}_e = 0$$

$$\mathbf{E}' = -\frac{1}{e} (\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)} \cdot \frac{1}{T} \nabla_r T = \mathbf{S} \cdot \nabla_r T$$

\mathbf{S} is the thermoelectric power.

$$\mathbf{S} = -\frac{1}{e}(\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)} \frac{1}{T}$$

Using the relations

$$\mathbf{K}^{(0)} = \frac{\sigma}{e^2}, \quad \mathbf{K}^{(1)} = \frac{\pi^2 k_B^2 T^2}{3e^2} \left[\frac{d\sigma(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\mu},$$

we have

$$\begin{aligned} \mathbf{S} &= -\frac{1}{e}(\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)} \frac{1}{T} \\ &= -\frac{1}{e} \left(\frac{\sigma}{e^2} \right)^{-1} \frac{\pi^2 k_B^2 T^2}{3e^2} \left[\frac{d\sigma(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\mu} \\ &= -\frac{\pi^2 k_B^2 T^2}{3e} (\sigma)^{-1} \left[\frac{d\sigma(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\mu} \\ &= -\frac{\pi^2 k_B^2 T^2}{3e} \left[\frac{d \ln \sigma(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\mu} \end{aligned}$$

where $\sigma(\varepsilon)$ means the conductivity tensor for a hypothetical metal in which the Fermi level is ε .

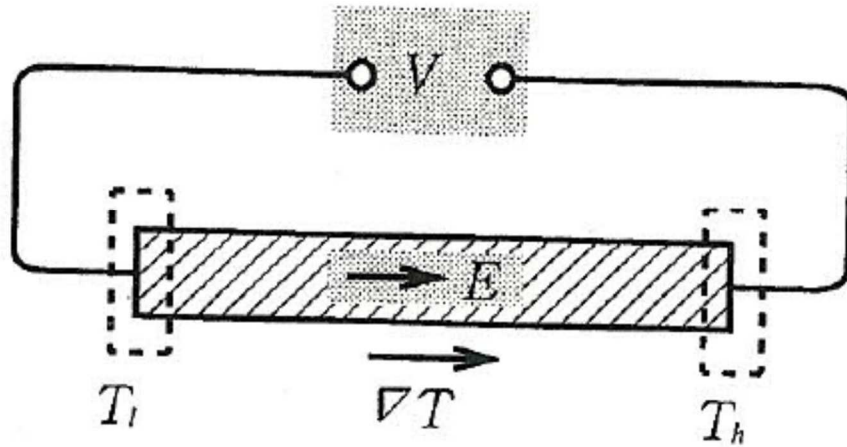


Fig. Seebeck effect

(d) Peltier effect

$$\nabla T = 0, \quad \mathbf{J}_e \neq 0$$

$$\mathbf{J}_e = e^2 \mathbf{K}^{(0)} \cdot \mathbf{E}'$$

$$\mathbf{J}_Q = -e \mathbf{K}^{(1)} \cdot \mathbf{E}' = -e \mathbf{K}^{(1)} \frac{1}{e^2} (\mathbf{K}^{(0)})^{-1} \cdot \mathbf{J}_e = -\frac{1}{e} \mathbf{K}^{(1)} (\mathbf{K}^{(0)})^{-1} \cdot \mathbf{J}_e = \Pi \cdot \mathbf{J}_e$$

or

$$\Pi = -\frac{1}{e} \mathbf{K}^{(1)} (\mathbf{K}^{(0)})^{-1}$$

where Π is called the Peltier co-efficient. Using the relation $\mathbf{S} = -\frac{1}{e} (\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)} \frac{1}{T}$,

$$T\mathbf{S} = -\frac{1}{e} (\mathbf{K}^{(0)})^{-1} \mathbf{K}^{(1)},$$

we get the relation

$$\Pi = T\mathbf{S}$$

We note that

$$\mathbf{K}_0 \mathbf{K}_1 = \mathbf{K}_1 \mathbf{K}_0$$

since

$$\mathbf{K}^{(1)} = \frac{\pi^2}{3} k_B^2 T^2 \left[\frac{d\mathbf{K}^{(0)}(\varepsilon)}{d\varepsilon} \right]_{\varepsilon=\mu}$$

The heat current is proportional to the electric current, but is also dependent on the Peltier coefficient, which is material specific. Since \mathbf{J} is the same in both segments, for different materials A and B, the heat current is different in the two branches. This leads to a warming of one junction and a cooling of the other (solid state refrigeration)

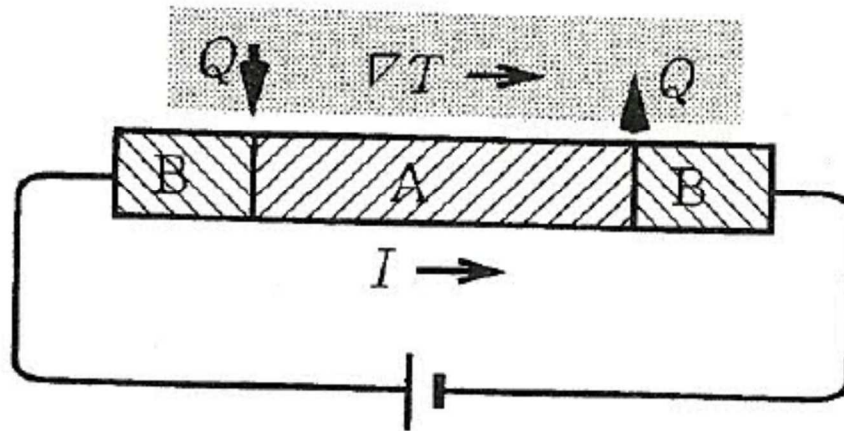


Fig. Peltier effect

(e) Thomson effect

The electric current density for the one dimensional case

$$J_e = e^2 K^{(0)} \left(E + \frac{1}{e} \frac{\partial \mu}{\partial x} \right) + \frac{e}{T} K^{(1)} \frac{\partial T}{\partial x}$$

$$E = \frac{1}{e^2} K^{(0)-1} J_e - \frac{1}{e} \frac{\partial \mu}{\partial x} - \frac{1}{eT} K^{(0)-1} K^{(1)} \frac{\partial T}{\partial x}$$

The heat current density for the one dimensional case

$$J_Q = -\frac{1}{T} K^{(2)} \frac{\partial T}{\partial x} - eK^{(1)} \left(E + \frac{1}{e} \frac{\partial \mu}{\partial x} \right)$$

In a metal the heat ΔQ , produced per second in unit volume is given by

$$\begin{aligned}
\Delta Q &= J_e E - \frac{\partial}{\partial x} J_Q \\
&= J_e \left(\frac{1}{e^2} K^{(0)-1} J_e - \frac{1}{e} \frac{\partial \mu}{\partial x} - \frac{1}{eT} K^{(0)-1} K^{(1)} \frac{\partial T}{\partial x} \right) \\
&\quad + \frac{\partial}{\partial x} \left[\frac{1}{T} K^{(2)} \frac{\partial T}{\partial x} + e K^{(1)} \left(E + \frac{1}{e} \frac{\partial \mu}{\partial x} \right) \right] \\
&= \frac{1}{e^2} K^{(0)-1} J_e^2 + \frac{J_e T}{e} \frac{\partial}{\partial x} \left(\frac{K^{(0)-1} K^{(1)} - \mu}{T} \right) + \frac{\partial}{\partial x} \left[\frac{1}{T} K^{(2)} \frac{\partial T}{\partial x} \right] \\
&\approx \frac{1}{e^2} K^{(0)-1} J_e^2 + J_e T \frac{\partial}{\partial x} \left(\frac{K^{(0)-1} K^{(1)}}{eT} \right) + \frac{\partial}{\partial x} \left[\frac{1}{T} K^{(2)} \frac{\partial T}{\partial x} \right]
\end{aligned}$$

or

$$\begin{aligned}
\Delta Q &\approx \frac{1}{\rho} J_e^2 - J_e T \frac{\partial S}{\partial x} + \frac{\partial}{\partial x} \left(\kappa \frac{\partial T}{\partial x} \right) \\
&= \frac{1}{\rho} J_e^2 - J_e T \frac{\partial S}{\partial T} \frac{\partial T}{\partial x} + \frac{\partial}{\partial x} \left(\kappa \frac{\partial T}{\partial x} \right)
\end{aligned}$$

The Thomson coefficient is defined by

$$\mu_T = T \frac{dS}{dT}.$$

where

$$E' = E + \frac{1}{e} \frac{\partial \mu}{\partial x} = \frac{1}{e^2} K^{(0)-1} J_e - \frac{1}{eT} K^{(0)-1} K^{(1)} \frac{\partial T}{\partial x}$$

$$K^{(0)} = \frac{\sigma}{e^2}$$

$$S = -\frac{1}{eT} (K^{(0)})^{-1} K^{(1)}, \quad \kappa = \frac{1}{T} K^{(2)}$$

The first term is the Joule heat, the second the thermoelectric heat, and the third being due to the heat conduction.

((MacDonald)) Physical explanation

The electric current:

$$I = \frac{\Delta q}{\Delta t}$$

The resistance:

$$R = \frac{1}{\sigma} \frac{\Delta x}{\Delta A}$$

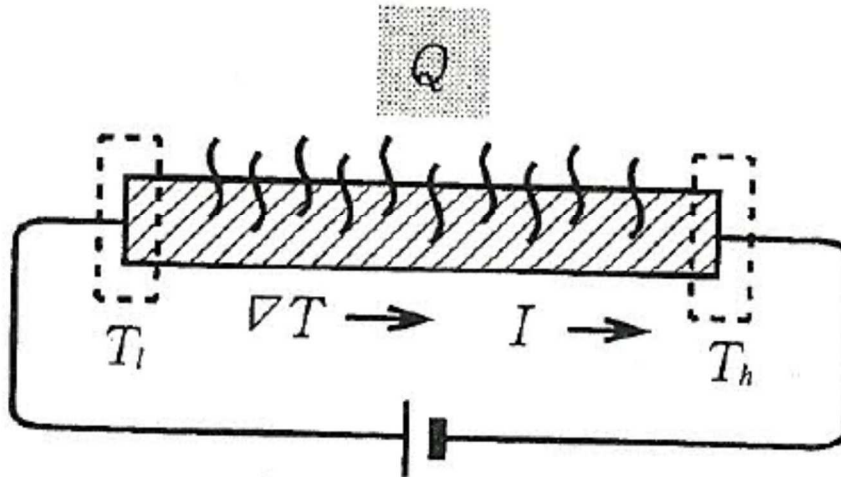


Fig. Thomson effect

The electric current density:

$$J_e = \frac{I}{\Delta A} = \frac{\Delta q}{\Delta A \Delta t} = (-e)nv$$

J_Q is the heat current density transported by the electrons per unit area per unit time

$$\begin{aligned} (J_e E) &= \frac{J_x^2}{\sigma} - \mu_T J_x \frac{\Delta T}{\Delta x} \\ &= \frac{(\Delta q)^2}{(\Delta A)^2 (\Delta t)^2} \frac{R \Delta A}{\Delta x} - \mu_T \frac{\Delta q}{\Delta A \Delta t} \frac{\Delta T}{\Delta x} \\ &= \frac{1}{\Delta A \Delta t \Delta x} \left[\frac{R (\Delta q)^2}{(\Delta t)} - \mu_T \Delta q \Delta T \right] \end{aligned}$$

or

$$(J_E E) \Delta A \Delta t \Delta x = \frac{R(\Delta q)^2}{(\Delta t)} - \mu_T \Delta q \Delta T$$

where This equation points out that if a given electric charge Δq is moved through a conductor, then the amount of heat involved or absorbed depends on the rate at which the electric charge Δq is transported. If the rate is made slow enough (Δt sufficiently long), then the first (Joule) term will become insignificant in comparison with the Thomson heat term, and it is clear that the amount of heat or entropy involved is then directly related to the electric charge transported and is independent of the rate at which this is done (as long as the rate is slow enough). Thus we can (perhaps best) refer to the Thomson heat as the heat absorbed per unit (positive) charge and unit temperature difference, when this charge is transported sufficiently slowly in the direction of increasing temperature.

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