

Handout 32

Electronic Energy Transport and Thermoelectric Effects

In this lecture you will learn:

- Thermal energy transport by electrons
- Thermoelectric effects
 - Seebeck Effect
 - Peltier Effect
- Thermoelectric coolers
- Thermoelectric power converters



Lars Onsager
(1903-1976)

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Note on Notation

In this handout, unless states otherwise, we will assume a conduction band with a dispersion given by:

$$E(\vec{k}) = E_c + \frac{\hbar^2}{2} \vec{k}^T \cdot M^{-1} \cdot \vec{k}$$

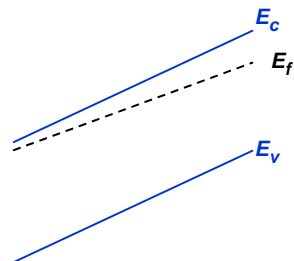
$$\Rightarrow \vec{v}(\vec{k}) = M^{-1} \cdot \hbar \vec{k}$$

In the presence of an electric field:

$$E(\vec{k}, \vec{r}) = E_c(\vec{r}) + \frac{\hbar^2}{2} \vec{k}^T \cdot M^{-1} \cdot \vec{k}$$

where:

$$\nabla E_c(\vec{r}) = e\vec{E}$$



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Thermoelectric Effects

There are two important effects in materials that relate electrical currents, heat flow (or thermal currents), voltage gradients (or electric fields), and temperature gradients:

1) Seebeck Effect

2) Peltier Effect

The Seebeck effect is important technologically since it expresses how temperature differences can be used to generate voltage differences

The Peltier effect expresses how current flow can be used to generate temperature differences.

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Electrical Currents and Thermal Currents of Electrons

$$\nabla_{\vec{r}} T(\vec{r}) \neq 0 \quad \vec{E} \neq 0 \quad \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \neq 0 \text{ (or } \nabla_{\vec{r}} n(\vec{r}) \neq 0 \text{)}$$

In the most general case, when electric field, density gradient, and/or a temperature gradients are all present, the electrical and thermal currents can be written as,

$$\vec{J}(\vec{r}) = \vec{\sigma} \cdot \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) - \vec{\kappa} \cdot \nabla_{\vec{r}} T(\vec{r})$$

$$\vec{J}_{th}(\vec{r}) = T(\vec{r}) \vec{\kappa} \cdot \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) - \vec{\kappa}_{th} \cdot \nabla_{\vec{r}} T(\vec{r})$$

Or in matrix form as:

$$\begin{bmatrix} \vec{J}(\vec{r}) \\ \vec{J}_{th}(\vec{r}) \end{bmatrix} = \begin{bmatrix} \vec{\sigma} & -\vec{\kappa} \\ T(\vec{r}) \vec{\kappa} & -\vec{\kappa}_{th} \end{bmatrix} \cdot \begin{bmatrix} \vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \\ \nabla_{\vec{r}} T(\vec{r}) \end{bmatrix} = \begin{bmatrix} \vec{\sigma} & -\vec{\kappa} \\ T(\vec{r}) \vec{\kappa} & -\vec{\kappa}_{th} \end{bmatrix} \cdot \begin{bmatrix} \frac{1}{e} \nabla_{\vec{r}} E_f(\vec{r}) \\ \nabla_{\vec{r}} T(\vec{r}) \end{bmatrix}$$

- The above equations show that a temperature gradient can generate an electrical current and an electric field (or a carrier density gradient) can generate a thermal current

- The above equations can be used to evaluate the material responses in different situations of practical interest

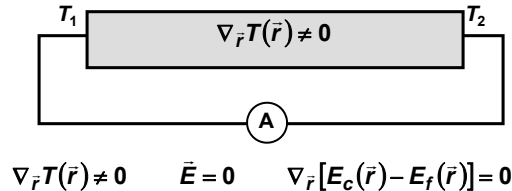
• **NOTE: The contribution of phonons (or the lattice) to the thermal current will be ignored here**

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Electrical Current from Temperature Gradient

A temperature gradient in conductive material can cause an electric current

- Consider electrons in the conduction band of a n-doped semiconductor or a metal
- There is no applied field
- There is a temperature gradient



Assume for the electron density:

$$n(\vec{r}) = 2 \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} f(\vec{k}, \vec{r})$$

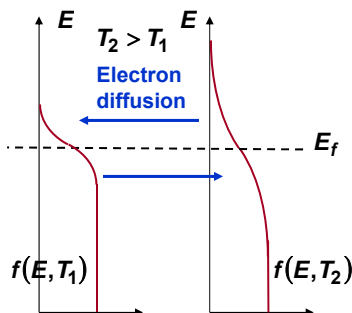
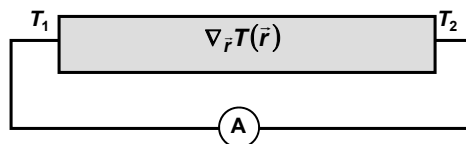
The local equilibrium distribution function is:

$$f_0(\vec{k}, \vec{r}) = \frac{1}{1 + e^{(E(\vec{k}) - E_f)/kT(\vec{r})}}$$

Temperature is position dependent

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A Physical Explanation



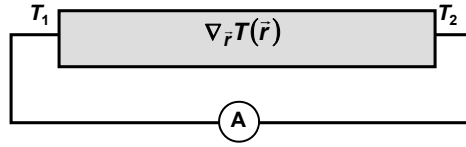
- Electrons with energies higher than the Fermi level diffuse from the region of higher temperature to the region of lower temperature
- Electrons with energies lower than the Fermi level diffuse from the region of lower temperature to region of higher temperature
- The higher energy electrons of course win and the current is in the direction of the temperature gradient

(Q: What will happen in a p-doped semiconductor?)

- Fermi level can also change with temperature but we will assume that it does not

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Electrical Current from Temperature Gradient: Boltzmann Equation



Start from the Boltzmann equation assuming no applied field:

$$\begin{aligned}
 &\Rightarrow -e \nabla_{\vec{r}} f(\vec{k}, \vec{r}) \cdot \frac{\vec{E}}{\hbar} + \nabla_{\vec{r}} f(\vec{k}, \vec{r}) \cdot \vec{v}(\vec{k}) = - \frac{[f(\vec{k}, \vec{r}) - f_0(\vec{k}, \vec{r})]}{\tau} \\
 &\Rightarrow -\tau \nabla_{\vec{r}} f(\vec{k}, \vec{r}) \cdot \vec{v}(\vec{k}) = f(\vec{k}, \vec{r}) - f_0(\vec{k}, \vec{r}) \\
 &\Rightarrow f(\vec{k}, \vec{r}) = f_0(\vec{k}, \vec{r}) - \tau \nabla_{\vec{r}} f(\vec{k}, \vec{r}) \cdot \vec{v}(\vec{k}) \\
 &\Rightarrow f(\vec{k}, \vec{r}) \approx f_0(\vec{k}, \vec{r}) - \tau \nabla_{\vec{r}} f_0(\vec{k}, \vec{r}) \cdot \vec{v}(\vec{k})
 \end{aligned}$$

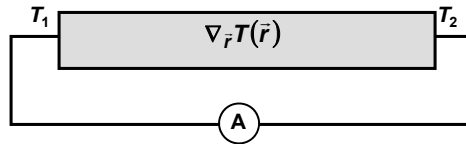
Multiply both sides by $2(-e) \vec{v}(\vec{k})$ and integrate over k-space to get:

LHS:

$$\begin{aligned}
 &2(-e) \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} f(\vec{k}, \vec{r}) \vec{v}(\vec{k}) \\
 &= \vec{J}(\vec{r})
 \end{aligned}$$

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Electrical Current from Temperature Gradient: Boltzmann Equation



RHS:

$$- 2(-e) \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} \tau \nabla_{\vec{r}} f_0(\vec{k}, \vec{r}) \cdot \vec{v}(\vec{k}) \vec{v}(\vec{k})$$

Note that:

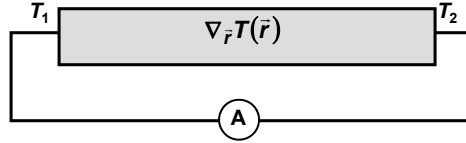
$$f_0(\vec{k}, \vec{r}) = \frac{1}{1 + e^{(E(\vec{k}) - E_f)/KT(\vec{r})}} \Rightarrow \nabla_{\vec{r}} f_0(\vec{k}, \vec{r}) = - \frac{\partial f_0(\vec{k}, \vec{r})}{\partial E} (E(\vec{k}) - E_f) \frac{\nabla_{\vec{r}} T(\vec{r})}{T(\vec{r})}$$

Therefore, RHS becomes:

$$\begin{aligned}
 &= 2e \tau \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} \nabla_{\vec{r}} f_0(\vec{k}, \vec{r}) \cdot \vec{v}(\vec{k}) \vec{v}(\vec{k}) \\
 &= 2e \tau \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} - \frac{\partial f_0(\vec{k}, \vec{r})}{\partial E} \frac{(E(\vec{k}) - E_f)}{T(\vec{r})} [\vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} T(\vec{r})] \vec{v}(\vec{k})
 \end{aligned}$$

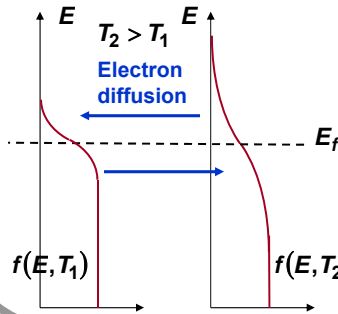
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Electrical Current from Temperature Gradient: Boltzmann Equation



Finally, putting LHS and RHS together we have:

$$\vec{J}(\vec{r}) = 2e \tau \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} - \frac{\partial f_o(\vec{k}, \vec{r})}{\partial E} \frac{(E(\vec{k}) - E_f)}{T(\vec{r})} [\vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} T(\vec{r})] \vec{v}(\vec{k}) = -\vec{\kappa} \cdot \nabla_{\vec{r}} T(\vec{r})$$



- Electrons with energies higher than the Fermi level diffuse from the region of higher temperature to the region of lower temperature

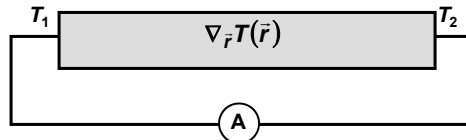
- Electrons with energies lower than the Fermi level diffuse from the region of lower temperature to region of higher temperature

- For n-doped semiconductor: $\kappa < 0$

- For p-doped semiconductor: $\kappa > 0$

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Electrical Current from Temperature Gradient: Semiconductors



$$\vec{J}(\vec{r}) = 2e \tau \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} - \frac{\partial f_o(\vec{k}, \vec{r})}{\partial E} \frac{(E(\vec{k}) - E_f)}{T(\vec{r})} [\vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} T(\vec{r})] \vec{v}(\vec{k}) = -\vec{\kappa} \cdot \nabla_{\vec{r}} T(\vec{r})$$

Example – n-doped semiconductor at high temperatures:

Consider a semiconductor at high temperatures and assume that Maxwell-Boltzmann statistics apply:

$$f_o(\vec{k}, \vec{r}) = \frac{1}{1 + e^{(E(\vec{k}) - E_f)/KT}} \approx e^{-(E(\vec{k}) - E_f)/KT} \quad \left\{ E_c - E_f \gg KT \right.$$

For the conduction band of a semiconductor with the following dispersion:

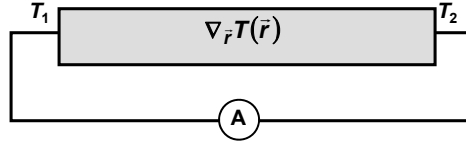
$$E(\vec{k}) = E_c + \frac{\hbar^2}{2} \vec{k}^T \cdot M^{-1} \cdot \vec{k} \quad \vec{v}(\vec{k}) = M^{-1} \cdot \hbar \vec{k}$$

We get (assuming an energy independent scattering rate τ):

$$\vec{\kappa} = -\left(\frac{K}{e}\right) \left(\frac{d}{2} + 1 + \frac{E_c - E_f}{KT}\right) n e^2 \tau M^{-1} = -\left(\frac{K}{e}\right) \left(\frac{d}{2} + 1 + \frac{E_c - E_f}{KT}\right) \vec{\sigma}$$

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Electrical Current from Temperature Gradient: Metals



$$\vec{J}(\vec{r}) = 2e \tau \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} - \frac{\partial f_0(\vec{k}, \vec{r})}{\partial E} \frac{(E(\vec{k}) - E_f)}{T(\vec{r})} [\vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} T(\vec{r})] \vec{v}(\vec{k}) = -\vec{\kappa} \cdot \nabla_{\vec{r}} T(\vec{r})$$

Example – metal or a n-doped semiconductor at low temperatures:

In this case:

$$-\frac{\partial f_0(\vec{k}, \vec{r})}{\partial E} \approx \delta(E(\vec{k}) - E_f)$$

However, using the above approximation will give a zero for $\vec{\kappa}$ so one has to be more careful. For the conduction band with the following isotropic dispersion:

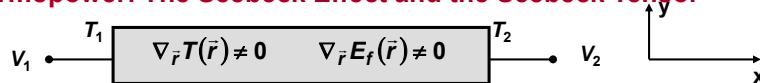
$$E(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_{\text{eff}}}$$

One obtains after a more careful computation of the above integral:

$$\begin{aligned} \vec{\kappa} &= -\frac{\pi^2}{3d} e^2 \tau (\vec{v}_F \otimes \vec{v}_F) \left(\frac{K}{e} \right) \left[g'_{dD}(E_F) + \frac{g_{dD}(E_F)}{E_F} \right] KT \\ &= -\frac{\pi^2}{3} \left(\frac{K}{e} \right) KT \left[\frac{g'_{dD}(E_F)}{g_{dD}(E_F)} + \frac{1}{E_F} \right] \vec{\sigma} = -\frac{\pi^2}{6} d \left(\frac{K}{e} \right) \left(\frac{KT}{E_f} \right) \vec{\sigma} \end{aligned}$$

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Thermopower: The Seebeck Effect and the Seebeck Tensor



- Consider a piece of metal (or semiconductor) with its two ends kept at different temperatures by some external means
- Since no current can flow in the external circuit, an electric field will build up inside the material in response to the temperature gradient resulting in a voltage difference between the two output terminals (this is the “Seebeck Effect”)

The total current density in the material can be written as:

$$\begin{aligned} \vec{J}(\vec{r}) &= \vec{\sigma} \cdot \frac{1}{e} \nabla_{\vec{r}} E_f(\vec{r}) - \vec{\kappa} \cdot \nabla_{\vec{r}} T(\vec{r}) = 0 \\ \Rightarrow \vec{\sigma} \cdot \frac{1}{e} \nabla_{\vec{r}} E_f(\vec{r}) &= \vec{\kappa} \cdot \nabla_{\vec{r}} T(\vec{r}) \\ \Rightarrow \frac{1}{e} \nabla_{\vec{r}} E_f(\vec{r}) &= \vec{\sigma}^{-1} \cdot \vec{\kappa} \cdot \nabla_{\vec{r}} T(\vec{r}) = \vec{S} \cdot \nabla_{\vec{r}} T(\vec{r}) \end{aligned}$$

The **Thermopower tensor** or the **Seebeck tensor** is defined as:

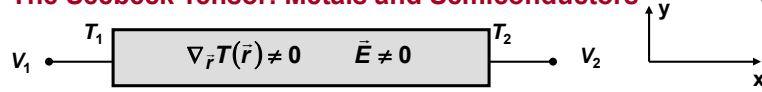
$$\vec{S} = \vec{\sigma}^{-1} \cdot \vec{\kappa}$$

For the diagram above:

$$\nabla_{\vec{r}} E_f(\vec{r}) = \vec{S} \cdot \nabla_{\vec{r}} T(\vec{r}) \Rightarrow \frac{1}{e} \frac{dE_f}{dx} = S_{xx} \frac{dT}{dx} \Rightarrow V_1 - V_2 = S_{xx} (T_2 - T_1)$$

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The Seebeck Tensor: Metals and Semiconductors



CASE I - If the slab was a n-doped semiconductor (and Maxwell Boltzmann statistics applied):

$$n = N_c e^{(E_f - E_c)/KT} \Rightarrow E_f - E_c = KT \log\left(\frac{n}{N_c}\right)$$

$$\bar{S} = \bar{\sigma}^{-1} \cdot \bar{\kappa} \Rightarrow S_{xx} = -\frac{K}{e} \left(\frac{d}{2} + 1 + \log\left(\frac{N_c}{n}\right) \right)$$

$$(V_2 - V_1) = -S_{xx} (T_2 - T_1) = \frac{K}{e} \left(\frac{d}{2} + 1 + \log\left(\frac{N_c}{n}\right) \right) (T_2 - T_1)$$

CASE II - If the slab was a heavily n-doped semiconductor (or a metal):

$$\bar{S} = \bar{\sigma}^{-1} \cdot \bar{\kappa} \Rightarrow S_{xx} = -\frac{\pi^2}{3} \left(\frac{K}{e} \right) KT \left[\frac{g'_{dD}(E_F)}{g_{dD}(E_F)} + \frac{1}{E_F} \right] \bar{\sigma} = -\frac{\pi^2}{6} d \frac{K}{e} \left(\frac{KT}{E_f} \right)$$

Mott's Formula

$$(V_2 - V_1) = -S_{xx} (T_2 - T_1) = \frac{\pi^2}{3} d \frac{K}{e} \left(\frac{KT}{E_f} \right) (T_2 - T_1) \quad \left\{ T = \frac{(T_2 + T_1)}{2} \right.$$

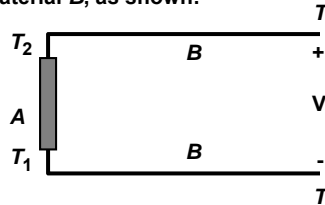
Lesson: compared to metals (in which $E_f \gg KT$), doped semiconductors will produce a larger potential difference for a given temperature difference

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Measurement of the Seebeck Tensor and Thermocouple

Some care is needed in the measurement of the Seebeck Effect

Consider a setup to measure the Seebeck Effect of material A by contacting it with leads made of material B, as shown:



The temperature of the two ends of material A are kept at T_2 and T_1

It is not difficult to show that in the absence of current flow, the potential V measured in the external circuit is:

$$V = (S_A - S_B) (T_2 - T_1)$$

Therefore, the Seebeck tensors of the materials A and B need to be significantly different in order to obtain a large potential difference. If $S_A \approx S_B$, then the voltages generated in each material cancel when going around the loop.

The Seebeck Effect is the principle behind the operation of the temperature sensor called the **thermocouple**

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Thermodynamics and Thermal Currents in Materials

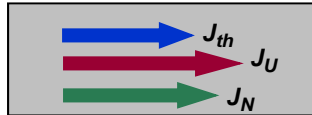
The first law of thermodynamics relates the change dU in the internal energy of a system to the heat energy intake dQ , the mechanical work done by the system PdV , and the particle number change dN :

$$dU = dQ - PdV + \mu dN$$

For electrons in semiconductors or metals, the mechanical work term can be neglected and the chemical potential μ equals the Fermi level E_f :

$$dQ = dU - E_f dN$$

Consider a slab of material in which heat energy, carried by the electrons, is flowing from left to right, as shown:



Suppose each carrier has energy E
 $\Rightarrow J_U = E J_N$

Suppose the heat energy flux (units: Watts/cm²) is J_{th} , the internal energy flux is J_U (units: Watts/cm²), and the carrier number flux is J_N (units: #/cm²), then:

$$J_{th} = J_U - E_f J_N = (E - E_f) J_N$$

The above relation is used to compute the thermal energy flow due to electrons in materials

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Thermal Current from Temperature Gradient

A temperature gradient in a conductive material results in heat flow (thermal current) because of electron flow

- Consider electrons in the conduction band of a n-doped semiconductor or a metal
- There is no applied field but there is a temperature gradient
- As the electrons move from the hot side to the cold side, they also transfer thermal energy

$$T_1 \left[\nabla_{\vec{r}} T(\vec{r}) \neq 0 \right] T_2$$

We have already solved for the distribution function:

$$\begin{aligned} f(\vec{k}, \vec{r}) &\approx f_0(\vec{k}, \vec{r}) - \tau \nabla_{\vec{r}} f_0(\vec{k}, \vec{r}) \cdot \vec{v}(\vec{k}) \\ &\approx f_0(\vec{k}, \vec{r}) + \tau \frac{\partial f_0(\vec{k}, \vec{r})}{\partial E} \left(\frac{E(\vec{k}) - E_f}{T(\vec{r})} \right) \nabla_{\vec{r}} T(\vec{r}) \cdot \vec{v}(\vec{k}) \end{aligned}$$

The contribution to heat flow by the electrons can be obtained by multiplying the distribution function by $(E(\vec{k}) - E_f) \vec{v}(\vec{k})$ and summing over all states:

$$\vec{J}_{th}(\vec{r}) = 2 \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} \tau \frac{\partial f_0(\vec{k}, \vec{r})}{\partial E} \left(\frac{E(\vec{k}) - E_f}{T(\vec{r})} \right)^2 [\vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} T(\vec{r})] \vec{v}(\vec{k}) = -\vec{\kappa}_{th} \cdot \nabla_{\vec{r}} T(\vec{r})$$

Here, $\vec{\kappa}_{th}$ is the **Thermal Conductivity tensor** of the electrons

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Thermal Current from Temperature Gradient: Semiconductors

$$T_1 \left[\nabla_{\vec{r}} T(\vec{r}) \neq 0 \right] T_2$$

$$\vec{J}_{th}(\vec{r}) = 2 \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} \tau \frac{\partial f_o(\vec{k}, \vec{r})}{\partial E} \frac{(E(\vec{k}) - E_f)^2}{T(\vec{r})} [\vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} T(\vec{r})] \vec{v}(\vec{k}) = -\vec{\kappa}_{th} \cdot \nabla_{\vec{r}} T(\vec{r})$$

Example – n-doped semiconductor at high temperatures:

Consider a semiconductor at high temperatures and assume that Maxwell-Boltzmann statistics apply:

$$f_o(\vec{k}, \vec{r}) = \frac{1}{1 + e^{(E(\vec{k}) - E_f)/KT}} \approx e^{-(E(\vec{k}) - E_f)/KT} \quad \left\{ E_c - E_f \gg KT \right.$$

For the conduction band of a semiconductor with the following dispersion:

$$E(\vec{k}) = E_c + \frac{\hbar^2}{2} \vec{k}^T \cdot M^{-1} \cdot \vec{k} \quad \vec{v}(\vec{k}) = M^{-1} \cdot \hbar \vec{k}$$

The thermal conductivity of the electrons comes out to be:

$$\vec{\kappa}_{th} = \left(\frac{K}{e^2} \right) \left(\frac{(E_c - E_f)^2 + (d+2)(E_c - E_f)KT + (d/2+2)(d/2+1)(KT)^2}{KT} \right) \vec{\sigma}$$

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Thermal Current from Temperature Gradient: Metals

$$T_1 \left[\nabla_{\vec{r}} T(\vec{r}) \neq 0 \right] T_2$$

$$\vec{J}_{th}(\vec{r}) = 2 \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} \tau \frac{\partial f_o(\vec{k}, \vec{r})}{\partial E} \frac{(E(\vec{k}) - E_f)^2}{T(\vec{r})} [\vec{v}(\vec{k}) \cdot \nabla_{\vec{r}} T(\vec{r})] \vec{v}(\vec{k}) = -\vec{\kappa}_{th} \cdot \nabla_{\vec{r}} T(\vec{r})$$

Example – metal or a n-doped semiconductor at low temperatures:

In this case:

$$-\frac{\partial f_o(\vec{k}, \vec{r})}{\partial E} \approx \delta(E(\vec{k}) - E_f)$$

However, using the above approximation expression will give a zero for $\vec{\kappa}_{th}$ so one has to be more careful. For the conduction band with the following isotropic dispersion:

$$E(\vec{k}) = E_c + \frac{\hbar^2 k^2}{2m_{eff}}$$

The thermal conductivity of the electrons comes out to be:

$$\vec{\kappa}_{th} = \frac{\pi^2}{3d} \left(\frac{K}{e^2} \right) KT (\vec{v}_F \otimes \vec{v}_F) g_{dD}(E_f) e^2 \tau = \frac{\pi^2}{3} \left(\frac{K^2 T}{e^2} \right) \vec{\sigma}$$

$$\Rightarrow \frac{\kappa_{th}}{T\sigma} = \frac{\pi^2}{3} \left(\frac{K}{e} \right)^2 \longrightarrow \text{Wiedemann-Franz Law for metals}$$

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Thermal Currents from Electric Fields and Density Gradients

$$\nabla_{\vec{r}} T(\vec{r}) = 0 \quad \vec{E} \neq 0 \quad \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \neq 0$$

- Consider electrons in the conduction band of a n-doped semiconductor or a metal
- There is no temperature gradient but there is an applied field and possibly a carrier density gradient as well
- As the electrons move they also transfer thermal energy

We have already solved for the relevant distribution function:

$$f(\vec{k}, \vec{r}) \approx f_0(\vec{k}, \vec{r}) + e\tau \frac{\partial f_0(\vec{k}, \vec{r})}{\partial E} \vec{v}(\vec{k}) \cdot \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right)$$

The contribution to heat flow by electrons can be obtained by multiplying the distribution function by $(E(\vec{k}) - E_f) \vec{v}(\vec{k})$ and summing over all states:

$$\begin{aligned} \vec{J}_{th}(\vec{r}) &= 2e\tau \times \int_{\text{FBZ}} \frac{d^d \vec{k}}{(2\pi)^d} \frac{\partial f_0(\vec{k}, \vec{r})}{\partial E} (E(\vec{k}) - E_f) \left[\vec{v}(\vec{k}) \cdot \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) \right] \vec{v}(\vec{k}) \\ &= T \bar{\kappa} \cdot \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) \end{aligned}$$

Here, $\bar{\kappa}$ is the same tensor found earlier which related electrical current to a temperature gradient

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Electrical Currents and Thermal Currents

$$\nabla_{\vec{r}} T(\vec{r}) \neq 0 \quad \vec{E} \neq 0 \quad \nabla_{\vec{r}} E_f(\vec{r}) \neq 0$$

In the most general case, when electric field, density gradient, and/or a temperature gradients are all present, the electrical and thermal currents can be written as,

$$\vec{J}(\vec{r}) = \bar{\sigma} \cdot \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) - \bar{\kappa} \cdot \nabla_{\vec{r}} T(\vec{r})$$

$$\vec{J}_{th}(\vec{r}) = T(\vec{r}) \bar{\kappa} \cdot \left(\vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \right) - \bar{\kappa}_{th} \cdot \nabla_{\vec{r}} T(\vec{r})$$

Or in matrix form as:

$$\begin{bmatrix} \vec{J}(\vec{r}) \\ \vec{J}_{th}(\vec{r}) \end{bmatrix} = \begin{bmatrix} \bar{\sigma} & -\bar{\kappa} \\ T(\vec{r}) \bar{\kappa} & -\bar{\kappa}_{th} \end{bmatrix} \cdot \begin{bmatrix} \vec{E} - \frac{1}{e} \nabla_{\vec{r}} [E_c(\vec{r}) - E_f(\vec{r})] \\ \nabla_{\vec{r}} T(\vec{r}) \end{bmatrix} = \begin{bmatrix} \bar{\sigma} & -\bar{\kappa} \\ T(\vec{r}) \bar{\kappa} & -\bar{\kappa}_{th} \end{bmatrix} \cdot \begin{bmatrix} \frac{1}{e} \nabla_{\vec{r}} E_f(\vec{r}) \\ \nabla_{\vec{r}} T(\vec{r}) \end{bmatrix}$$

The above equations can be used to evaluate the material responses in different situations of practical interest

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The Peltier Effect and the Peltier Tensor

Consider a material in which thermal (or density) gradients are not present. We have:

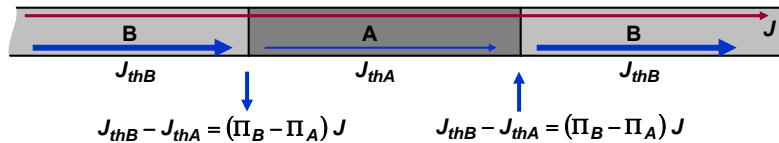
$$\left. \begin{aligned} \vec{J}(\vec{r}) &= \bar{\sigma} \cdot \vec{E}(\vec{r}) \\ \vec{J}_{th}(\vec{r}) &= T(\vec{r}) \bar{\kappa} \cdot \vec{E}(\vec{r}) \end{aligned} \right\} \Rightarrow \vec{J}_{th}(\vec{r}) = T(\vec{r}) \bar{\kappa} \cdot \bar{\sigma}^{-1} \vec{J}(\vec{r}) = \bar{\Pi} \cdot \vec{J}(\vec{r})$$

$\bar{\Pi}$ is called the **Peltier tensor** and is related to the Seebeck tensor. The relation,

$$\vec{J}_{th}(\vec{r}) = \bar{\Pi} \cdot \vec{J}(\vec{r}) \quad \left\{ \begin{array}{l} \text{For an isotropic material: } \Pi = T S \end{array} \right.$$

implies that a **thermal current accompanies an electrical current**

Now consider current flow in a double junction of materials A and B, as shown below, and suppose that $\Pi_A < \Pi_B$. The electrical current J is constant everywhere.

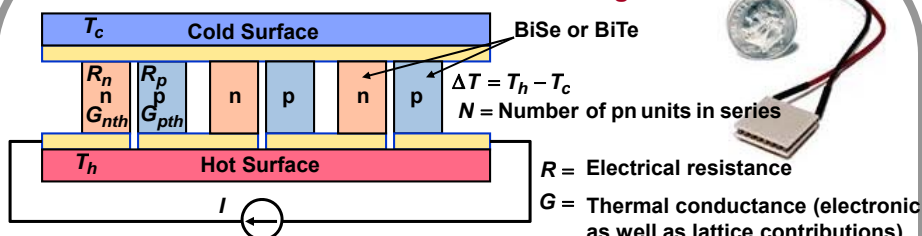


Since material B carries more thermal current than material A for the same electrical current, the extra thermal current needs to be extracted out from the left junction otherwise thermal energy will pile up at that junction and make it hot. Similarly, heat must be provided to the right junction otherwise it will lose heat and become cold

This principle is used in electronic **thermoelectric coolers (or Peltier coolers)**

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Thermoelectric Coolers for Refrigeration



Thermal energy absorbed from the n-semiconductor and top metal junction: $(\Pi_m - \Pi_n) I$

Thermal energy absorbed from the p-semiconductor and top metal junction: $(\Pi_p - \Pi_m) I$

Total thermal energy absorbed from the top metal in single cell: $(\Pi_p - \Pi_n) I = T_c (S_p - S_n) I$

Note that the Seebeck and the Peltier coefficients are negative for n-semiconductors

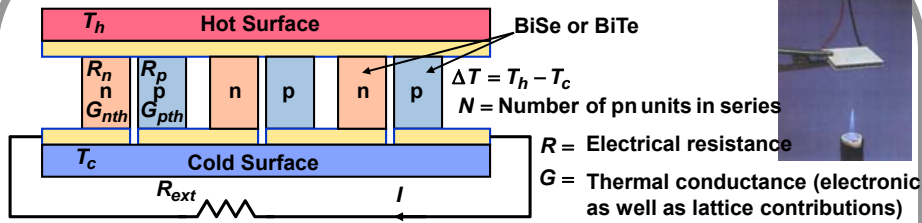
After taking into account Joule losses, and heat conductance, the coefficient of performance (COP) for cooling is:

$$\text{COP} = \frac{\text{Heat removed from cold body}}{\text{Work done by the current source}} = \frac{T_c (S_p - S_n) I - (G_{nth} + G_{pth}) \Delta T - I^2 (R_n + R_p) / 2}{\Delta T (S_p - S_n) I + I^2 (R_n + R_p)}$$

$$\text{COP} \rightarrow \frac{T_c}{T_h - T_c} \quad (\text{Carnot limit for refrigerators}) \quad \text{when} \quad R, G \rightarrow 0$$

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Thermoelectrics for Power Generation



A thermoelectric cooler operated in reverse acts like a heat engine

The power conversion efficiency is given by:

$$\eta = \frac{\text{Power delivered to the external load}}{\text{Heat lost to the cold body}} = \frac{(N(R_n + R_p) + R_{ex}) \Delta T (S_p - S_n) I}{T_h (S_p - S_n) I + (G_{nth} + G_{pth}) \Delta T + I^2 (R_n + R_p) / 2}$$

where: $I = \frac{(S_p - S_n)}{(N(R_n + R_p) + R_{ex})} \Delta T$

$\eta \rightarrow \frac{T_h - T_c}{T_h}$ (Carnot limit for heat engines) when $R, G \rightarrow 0$

A commonly used figure of merit for a pn thermoelectric is: $Z = \frac{(S_p - S_n)^2}{(R_n + R_p)(G_{nth} + G_{pth})}$

Both COP and η approach the Carnot values as $Z \rightarrow \infty$

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Thermoelectric Figure of Merit and 3D Parabolic Band Limit

The FOM is usually expressed as the dimensionless product ZT : $ZT = \frac{S^2 \sigma T}{\kappa_{th}}$

In the ideal scenario where lattice contribution to the thermal conductivity is much smaller compared to the electronic contribution, and the semiconductor is reasonably well doped ($E_c - E_f \sim 0.5KT$), then:

$$ZT = \frac{S^2 \sigma T}{\kappa_{th}} \rightarrow \frac{(0.5 + 5/2)^2}{(0.5 * 0.5 + 5 * 0.5 + 35/4)} = 0.78 \rightarrow \text{Independent of most material parameters!}$$

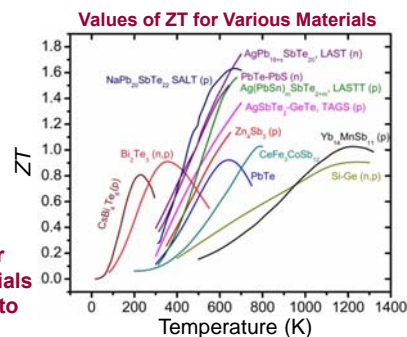
In experiments, electronic κ_{th} is measured under conditions of zero current, which gives:

$$\kappa_{th}^{\text{measured}} = \kappa_{th}(1 - ZT)$$

\Rightarrow The best measured value of ZT to be expected is,

$$(ZT)^{\text{measured}} = \frac{ZT}{1 - ZT} \rightarrow 3.55$$

\Rightarrow a value of $\sim 3-4$ is the maximum upper limit for ZT for 3D parabolic band materials and typically it is 2-4 times smaller due to mostly lattice thermal conductivity



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