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Achievements and Mysteries**

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**Unified Theory of Thermal Transport in Bulk, Thin Films and Nanowires (Model  
for the Thermal Transport in 3D, 2D and 1D Materials)**

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# **THERMAL AND ELECTRICAL TRANSPORT AND THERMOELECTRIC FIGURE-OF-MERIT IN LOW- DIMENSIONAL NANOSTRUCTURES**

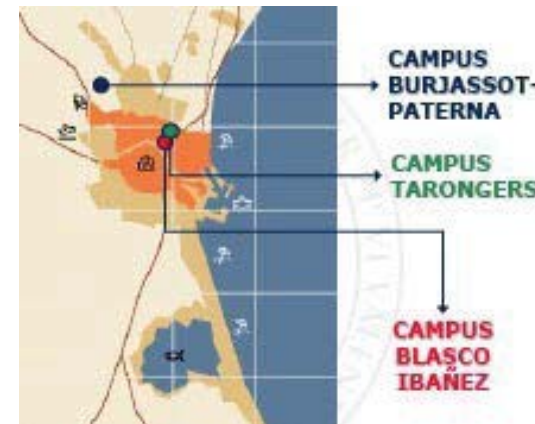
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# Valencia and its University

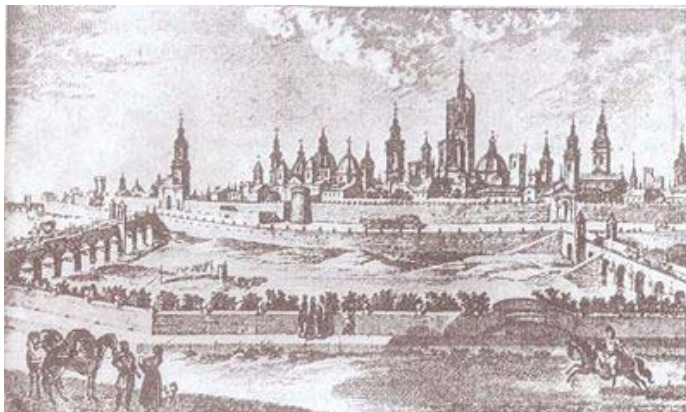


Valencia, 138 bce, 800,000 p; 1,500,000 mr



The University was founded in 1499  
We have around 60,000 students

Image of Valencia in the 19th C



# City of the Arts and Sciences



City of the Arts and Sciences



Palace of Arts



Oceanographic Museum

# La paella



Paella for 110000 persons  
Record Guinness, 2/10/2001



# Content

- Deduction of the Boltzmann transport equation
- The relaxation time approximation
- Electronic current density and electronic energy density
- Electronic current in an isotropic medium
- Electric and heat flow and Onsager coefficients
- Thermoelectric effects
  - Seebeck effect
  - Peltier effect
- The figure of merit
  - Low dimensional effects on the figure of merit

# Boltzmann transport equation

The distribution function for electrons in thermal equilibrium is given by the Fermi-Dirac statistics:

$$f_0(E(\mathbf{k})) = \frac{1}{1 + e^{(E(\mathbf{k}) - E_F)/kT}}$$

Out of equilibrium, the rate of change of the distribution function can be written as:

$$\frac{df(\mathbf{r}, \mathbf{k}, t)}{dt} = \frac{\partial f}{\partial t} + \nabla_{\mathbf{r}} f \cdot \frac{d\mathbf{r}}{dt} + \frac{1}{\hbar} \nabla_{\mathbf{k}} f \cdot \mathbf{F}_a$$

where all applied forces are considered. Since the number of states is constant,

$$-\frac{\partial f}{\partial t} = \mathbf{v} \cdot \nabla_{\mathbf{r}} f + \frac{1}{\hbar} \mathbf{F}_a \cdot \nabla_{\mathbf{k}} f$$

The total applied forces can be split into external and internal (defects, impurities, phonons, etc.):  $\mathbf{F}_a = \mathbf{F} + \mathbf{F}_D$

$$\frac{\partial f}{\partial t} = \left( \frac{\partial f}{\partial t} \right)_{\text{fields}} + \left( \frac{\partial f}{\partial t} \right)_{\text{collisions}} \left\{ \begin{array}{l} \left( \frac{\partial f}{\partial t} \right)_{\text{collisions}} = \frac{1}{\hbar} \mathbf{F}_D \cdot \nabla_{\mathbf{k}} f \\ \left( \frac{\partial f}{\partial t} \right)_{\text{fields}} = \mathbf{v} \cdot \nabla_{\mathbf{r}} f + \frac{1}{\hbar} \mathbf{F} \cdot \nabla_{\mathbf{k}} f \end{array} \right.$$

Let us call  $W(\mathbf{k}, \mathbf{k}')$  the probability per unit time that an electron located in a given position with a given wave number is scattered. The number of occupied states in  $dt$  must change

$$-dt \left\{ W(\mathbf{k}, \mathbf{k}') \frac{1}{4\pi^3} d^3 \mathbf{k} f(\mathbf{r}, \mathbf{k}) [1 - f(\mathbf{r}, \mathbf{k}')] \frac{1}{4\pi^3} d^3 \mathbf{k}' \right\} +$$

$$+dt \left\{ W(\mathbf{k}', \mathbf{k}) \frac{1}{4\pi^3} d^3 \mathbf{k}' f(\mathbf{r}, \mathbf{k}') [1 - f(\mathbf{r}, \mathbf{k})] \frac{1}{4\pi^3} d^3 \mathbf{k} \right\}.$$

Finally, it is easy to show that the Boltzmann equation can be written as

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} f + \frac{1}{\hbar} \mathbf{F} \cdot \nabla_{\mathbf{k}} f = \int W(\mathbf{k}, \mathbf{k}') [f(\mathbf{r}, \mathbf{k}) - f(\mathbf{r}, \mathbf{k}')] \frac{1}{4\pi^3} d^3 \mathbf{k}'$$

Let us assume that in  $t=0$  we suppress the external fields. In that case,

$$\left( \frac{\partial f}{\partial t} \right) = - \left( \frac{\partial f}{\partial t} \right)_{\text{scattering}} = - \frac{f(\mathbf{r}, \mathbf{k}, t) - f_0(\mathbf{r}, \mathbf{k})}{\tau(\mathbf{k})}$$

Where  $\tau$  is the relaxation time. The solution of this equation is

$$f(\mathbf{r}, \mathbf{k}, t) - f_0(\mathbf{r}, \mathbf{k}) = [f(\mathbf{r}, \mathbf{k}, 0) - f_0(\mathbf{r}, \mathbf{k})] e^{-t/\tau(\mathbf{k})}$$

We can define the relaxation time in terms of the probability of scattering:

$$\frac{1}{\tau(\mathbf{k})} = \frac{1}{4\pi^3} \int W(\mathbf{k}, \mathbf{k}') [f(\mathbf{r}, \mathbf{k}') - f(\mathbf{r}, \mathbf{k})] d^3 \mathbf{k}'$$



If there is only an electric field, the Boltzmann equation in the relaxation time approximation is

$$\frac{e}{\hbar} \mathcal{E} \cdot \nabla_{\mathbf{k}} f = -\frac{f(\mathbf{k}) - f_0(\mathbf{k})}{\tau(\mathbf{k})}$$

The distribution function is, in terms of that in equilibrium

$$f(\mathbf{k}) = f_0(\mathbf{k}) - \frac{e}{\hbar} \tau(\mathbf{k}) \mathcal{E} \cdot \nabla_{\mathbf{k}} f$$

If the electric field is not so large, we can assume linearity,

$$f(\mathbf{k}) \approx f_0(\mathbf{k}) - \frac{e}{\hbar} \tau(\mathbf{k}) \mathcal{E} \cdot \nabla_{\mathbf{k}} f_0 \longrightarrow f(\mathbf{k}) \approx f_0 \left( \mathbf{k} - \frac{e}{\hbar} \tau(\mathbf{k}) \mathcal{E} \right)$$

In the general case of an electric and magnetic field the external force is the Lorentz force:

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} f + \frac{e}{\hbar} [\mathcal{E} + \mathbf{v} \times \mathbf{B}] \cdot \nabla_{\mathbf{k}} f = -\frac{f(\mathbf{r}, \mathbf{k}) - f_0(\mathbf{r}, \mathbf{k})}{\tau(\mathbf{k})} = -\frac{f^{(1)}(\mathbf{r}, \mathbf{k})}{\tau(\mathbf{k})}$$

In order to solve the Boltzmann equation we need the derivatives of the distribution function.

The equilibrium distribution function for electrons (Fermi-Dirac) is:

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

The derivative with respect to the vector position is

$$\nabla_{\mathbf{r}} f_0 = -\frac{e^{(E - E_F) / kT}}{[1 + e^{(E - E_F) / kT}]^2} \nabla \left( \frac{E - E_F}{kT} \right)$$

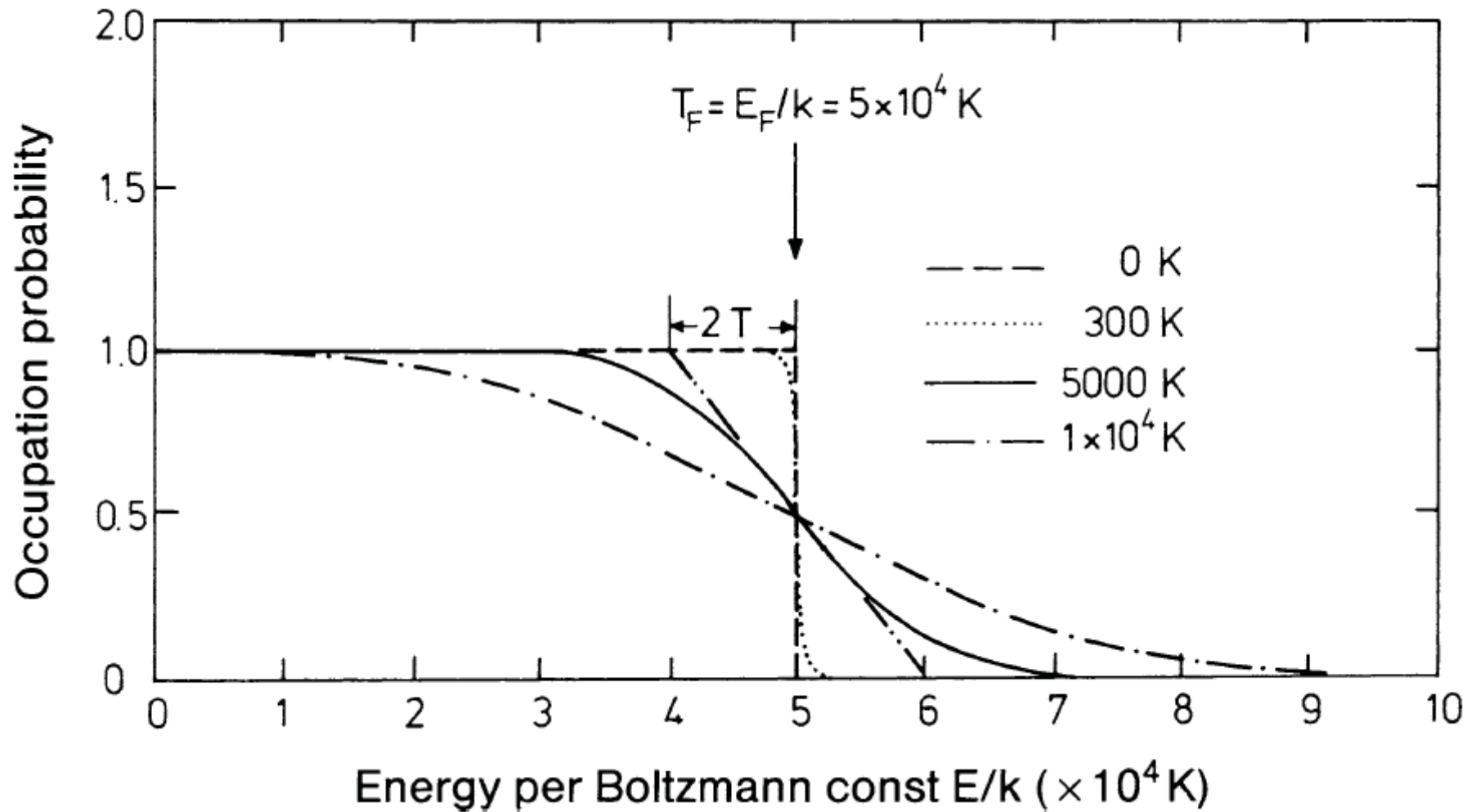
$$\nabla_{\mathbf{r}} f_0 = -\frac{\partial f_0}{\partial E} [\nabla E_F + (E - E_F) \nabla \ln T]$$

which is conveniently written in terms of the derivative of the distribution function with respect to the energy

$$\frac{\partial f_0}{\partial E} = -\frac{e^{(E - E_F) / kT}}{[1 + e^{(E - E_F) / kT}]^2} \frac{1}{kT}$$

The derivative with respect to the wavenumber is written directly in terms of an energy derivative:

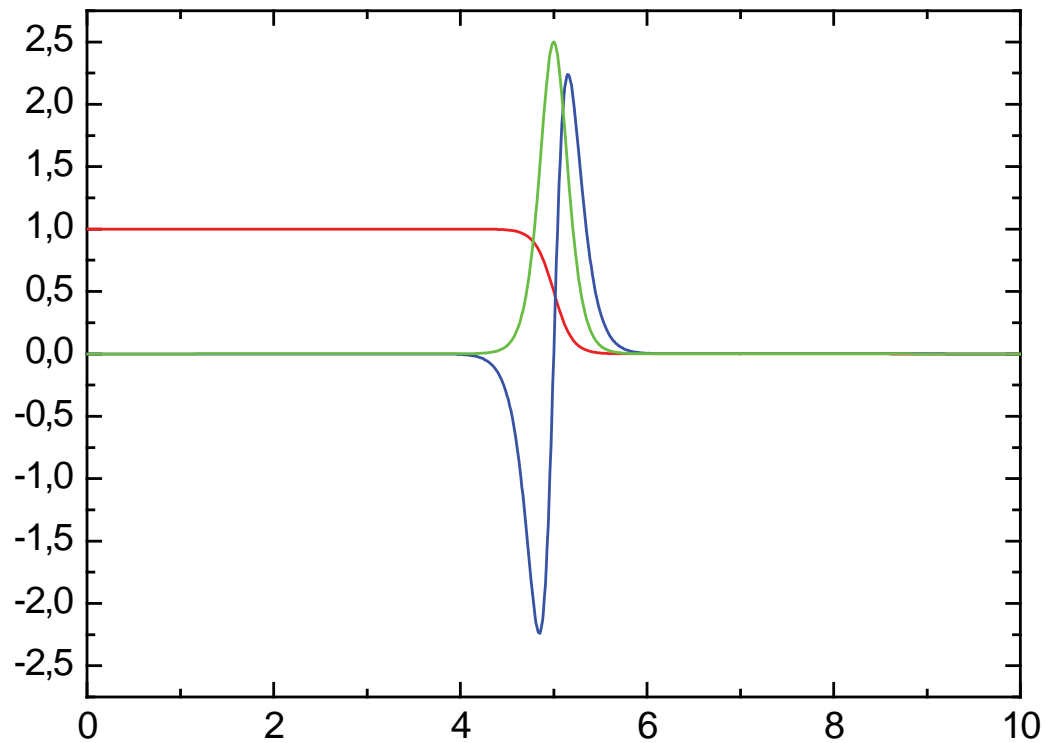
$$\nabla_{\mathbf{k}} f_0 = \frac{\partial f_0}{\partial E} \hbar \mathbf{v}$$



Derivatives of the distribution function with respect to the temperature and the energy

$$\frac{\partial f}{\partial T} = \frac{e^{(E-E_F)/k_B T}}{[1 + e^{(E-E_F)/k_B T}]^2} \frac{E - E_F}{k_B T^2}$$

$$-\frac{\partial f}{\partial E} = \frac{e^{(E-E_F)/k_B T}}{[1 + e^{(E-E_F)/k_B T}]^2} \frac{1}{k_B T}$$



Our initial Boltzmann equation writes

$$-\frac{f^{(1)}(\mathbf{r}, \mathbf{k})}{\tau(\mathbf{k})} = \mathbf{v} \cdot \nabla_{\mathbf{r}} f^{(1)} + \frac{1}{\hbar} \mathbf{F}_L \cdot \nabla_{\mathbf{k}} f^{(1)}$$

Assuming that the distribution function is not very far from that of equilibrium,

$$f^{(1)}(\mathbf{r}, \mathbf{k}) \approx -\frac{\partial f_0}{\partial E} \tau(\mathbf{k}) \mathbf{v} \cdot [e\mathcal{E} - \nabla E_F - (E - E_F) \nabla \ln T]$$

If we define

$$\mathbf{A} = -\tau [\nabla(e\phi + E_F) + (E - E_F) \nabla \ln T]$$

The deviation of the distribution function can be written in the compact form

$$f^{(1)} = -\frac{\partial f_0}{\partial E} \mathbf{v} \cdot \mathbf{A}$$

If there is no magnetic field, this is the right expression. But we have lost actually the magnetic field because it is a second order effect as compare to the electric field. It can be recovered through a recurrent expression. We include the term

$$\frac{e}{\hbar} \mathbf{v} \times \mathbf{B} \cdot \nabla_{\mathbf{k}} f^{(1)}$$

The final result can be also written in a compact way

$$f^{(1)} = -\frac{\partial f_0}{\partial E} \mathbf{v} \cdot \boldsymbol{\chi}$$

but now  $\boldsymbol{\chi}$  is a more bulky expression

$$\boldsymbol{\chi} = \frac{\mathbf{A} + e\tau \frac{\mathbf{A}}{m^*} \times \mathbf{B} + \frac{e^2\tau^2}{|m^*|} \mathbf{A} \cdot \mathbf{B} \frac{\mathbf{B}}{m^*}}{1 + \frac{e^2\tau^2}{|m^*|} \mathbf{B} m^* \mathbf{B}}$$

All the microscopic expressions like the electrical current or the current flow can be written in terms of  $f^{(1)}$ .

# Electric and energy density

The electric current density can be defined as

$$\mathbf{j} = \frac{e}{4\pi^3} \int \mathbf{v} f(\mathbf{r}, \mathbf{k}) d^3 \mathbf{k} = \frac{e}{4\pi^3} \int \mathbf{v} f^{(1)}(\mathbf{r}, \mathbf{k}) d^3 \mathbf{k}$$

In terms of the derived expressions,

$$\mathbf{j} = -\frac{e}{4\pi^3} \int \mathbf{v} \frac{\partial f_0}{\partial E} \mathbf{v} \cdot \boldsymbol{\chi} d^3 \mathbf{k} = -\frac{e}{4\pi^3 \hbar^2} \int \frac{\partial f_0}{\partial E} (\nabla_{\mathbf{k}} E \cdot \boldsymbol{\chi}) \nabla_{\mathbf{k}} E d^3 \mathbf{k}$$

In a similar way, for the heat or energy density flow

$$\mathbf{j}_Q = \frac{1}{4\pi^3} \int E(\mathbf{k}) \mathbf{v} f(\mathbf{r}, \mathbf{k}) d^3 \mathbf{k} = \frac{1}{4\pi^3} \int E(\mathbf{k}) \mathbf{v} f^{(1)}(\mathbf{r}, \mathbf{k}) d^3 \mathbf{k}$$

which can be written as

$$\mathbf{j}_Q = -\frac{1}{4\pi^3 \hbar^2} \int E \frac{\partial f_0}{\partial E} (\nabla_{\mathbf{k}} E \cdot \boldsymbol{\chi}) \nabla_{\mathbf{k}} E d^3 \mathbf{k}$$

# Electrical conductivity

If there is no magnetic field or gradients of temperature or concentration,

$$\mathbf{j} = -\frac{e^2}{4\pi^3} \int \tau \frac{\partial f_0}{\partial E} (\mathbf{v} \cdot \boldsymbol{\mathcal{E}}) \mathbf{v} d^3\mathbf{k} = \sigma \boldsymbol{\mathcal{E}}$$

Actually, in this expression the conductivity is a tensor:

$$\sigma_{ij} = -\frac{e^2}{4\pi^3} \int \tau \frac{\partial f_0}{\partial E} v_i v_j d^3\mathbf{k}$$

In the case of an isotropic material, the conductivity can be reduced to

$$\sigma = -\frac{4e^2}{3m^*} \int_0^\infty E \tau(E) D(E) \frac{\partial f_0}{\partial E} dE$$

For a non-degenerated semiconductor, taking the approximation  $-\frac{\partial f_0}{\partial E} = \frac{f_0}{kT}$

$$\sigma = -\frac{4e^2}{3kTm^*} \int_0^\infty E \tau D(E) f_0 dE$$



Introducing the carrier density as

$$n = 2 \int_0^{\infty} D(E) f_0 dE$$

and the relaxation time average

$$\langle \tau \rangle = \frac{2}{3kT} \frac{\int_0^{\infty} E \tau dn(E)}{\int_0^{\infty} dn(E)}$$

The conductivity can be written with the well known expression

$$\sigma = en \frac{e \langle \tau \rangle}{m^*} \equiv en \mu_d$$

If we have a degenerate semiconductor (or a metal),

$$-\frac{\partial f_0}{\partial E} = \delta(E - E_F) \quad \sigma = en \mu(E_F)$$

If a semiconductor is submitted to a temperature gradient, there is a heat flow in the opposite direction of the temperature gradient:

$$\mathbf{j}_Q = -\kappa \nabla T$$

There are two contributions to the thermal conductivity  $\kappa$ , the contribution to the heat due to the electron current and that due to the lattice (phonons). In a semiconductor  $\kappa_L \gg \kappa_e$  while in a metal  $\kappa_e \gg \kappa_L$ .

The electron contribution in a semiconductor strongly depends on the temperature and composition. We can calculate it very easily. Let us write the transport equations in the way

$$\mathbf{j} = \left( e\mathcal{E} - T\nabla \frac{E_F}{T} \right) e\mathcal{L}_{11} - \frac{\nabla T}{T} e\mathcal{L}_{21}$$

$$\mathbf{j}_Q = \left( e\mathcal{E} - T\nabla \frac{E_F}{T} \right) \mathcal{L}_{21} - \frac{\nabla T}{T} \mathcal{L}_{31}$$

where  $\mathcal{L}_{rs} = \frac{n}{m^*} \frac{2}{3kT} \frac{\int_0^\infty E^r \tau^s dn(E)}{\int_0^\infty dn(E)}$  are the Onsager coefficients.

If there is no electrical current (open circuit conditions)

$$e\mathcal{E} - T\nabla\frac{E_F}{T} = \frac{\mathcal{L}_{21}}{\mathcal{L}_{11}T}\nabla T$$

Substituting in the second equation,

$$j_Q = \frac{\mathcal{L}_{21}^2}{\mathcal{L}_{11}T}\nabla T - \mathcal{L}_{31}\frac{\nabla T}{T} = -\frac{\mathcal{L}_{31}\mathcal{L}_{11} - \mathcal{L}_{21}^2}{\mathcal{L}_{11}T}\nabla T$$

And we can easily derive an expression for electronic contribution to the thermal conductivity

$$\kappa_e = \frac{\mathcal{L}_{31}\mathcal{L}_{11} - \mathcal{L}_{21}^2}{\mathcal{L}_{11}T} = \frac{n}{m^*} \frac{\langle E^3\tau\rangle\langle E\tau\rangle - \langle E^2\tau\rangle^2}{\langle E\tau\rangle T}$$

The ratio  $\frac{\kappa_e}{\sigma T} \equiv L$  is defined as the Lorentz number, which in terms of the Onsager coefficient reads

$$L = \frac{\mathcal{L}_{31}\mathcal{L}_{11} - \mathcal{L}_{21}^2}{e^2\mathcal{L}_{11}^2T^2}$$

The Wiedeman-Franz law establishes that the ratio between the electronic contribution to the thermal conductivity and the electrical conductivity is a constant  $\frac{\kappa_e}{\sigma} = LT$  and the Lorentz number is

$$L = \frac{\pi^2}{3} \frac{k^2}{e^2} = 2.45 \times 10^{-8} \text{W}\Omega\text{K}^{-2}$$

# Thermoelectric effects

Without a magnetic field, there are basically three effects, the last one related to the first two effects through the Kelvin relations. The first one is called the Seebeck effect. It is the appearance of a voltage difference produced by a temperature difference between two ends of a semiconductors or a semiconductor junction.

$$dV_{12} = \alpha_{12}dT$$

$$T_2 > T_1$$

The total voltage will be

$$V_{12} = \int_{T_1}^{T_2} \alpha_{12}(T)dT$$

and  $\alpha$  is called Seebeck coefficient

If an electromotive force is applied to the contact between two materials, a heat flow appears in the sense of the current or opposite to it. The quantity of supplied heat is proportional to the charges crossing the surface of separation between the materials.

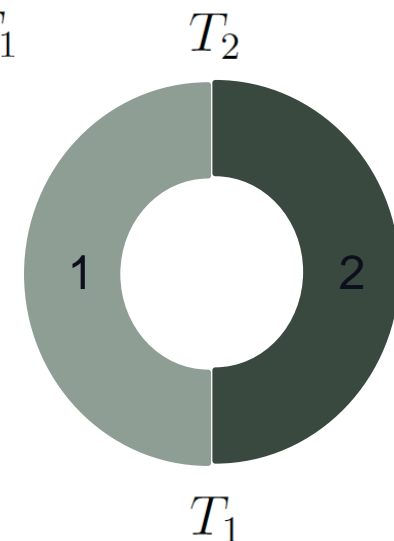
$$j_Q = \Pi_{12}j$$

The thermoelectric coefficients can be derived from the Onsager coefficients:

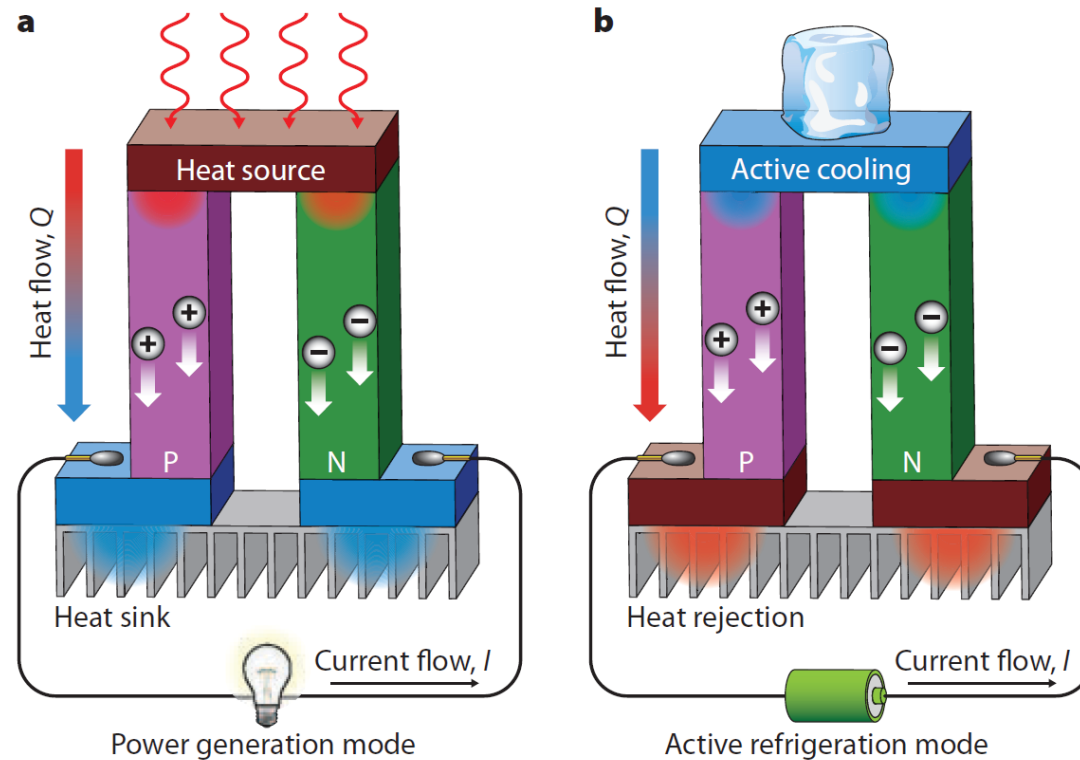
$$\alpha = \frac{1}{eT} \frac{L_{12}}{L_{11}}$$

$$\Pi = \frac{1}{e} \frac{L_{12}}{L_{11}}$$

$$\Pi = \alpha T$$



# Seebeck and Peltier effects



Schematic illustrations of a thermoelectric module for (a) power generation (Seebeck effect) and (b) active refrigeration (Peltier effect). (a) An applied temperature difference causes charge carriers in the material (electrons or holes) to diffuse from the hot side to the cold side, resulting in current flow through the circuit. (b) Heat evolves at the upper junction and is absorbed at the lower junction when a current is made to flow through the circuit.

# Thermoelectric figure of merit

The efficiency of a thermoelectric material can be written as

$$\eta_{TE} = \eta_C \left( \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_C/T_H} \right)$$

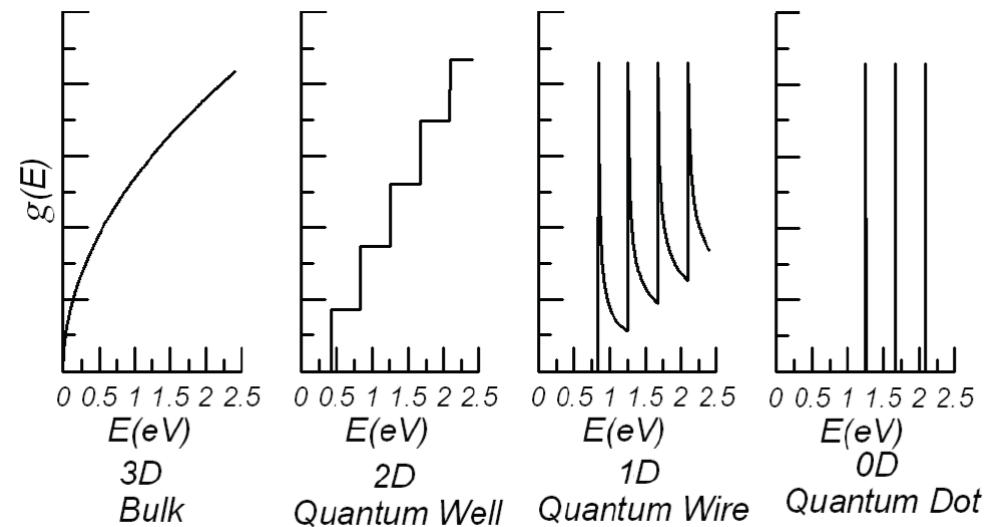
where  $ZT = \frac{\alpha^2 \sigma T}{\kappa}$  is called undimensional figure of merit.

In 3D materials the three properties governing thermoelectrics are related. By increasing the doping we increase the thermal conductivity but decrease the Seebeck coefficient.

The idea of low-dimensional materials is to separate the inter-relation between the material parameters. The following ideas are:

1. Low-dimensional systems can reduce the thermal conductivity without leaving basically unchanged the mobility. The phonon mean free path will be limited by the dimensions of the system.
2. By increasing the Seebeck coefficient without decreasing the electrical conductivity. This can be done by optimizing mainly the shape in the DOS.

## Density of states of bulk, quantum wells, quantum wires or quantum dots



There are several other ideas, like to change the dependence of the relaxation time on the energy, but all of them have the common objective of separating the material properties or act on them in a separated way to optimize them.



Thanks for your attention

Questions?