ECE-656: Fall 2011

Lecture 11: Coupled Current Equations: and thermoelectric devices

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basic equations of thermoelectricity

$$\mathcal{E}_x = \rho_n J_x + S_n \frac{dT_L}{dx}$$

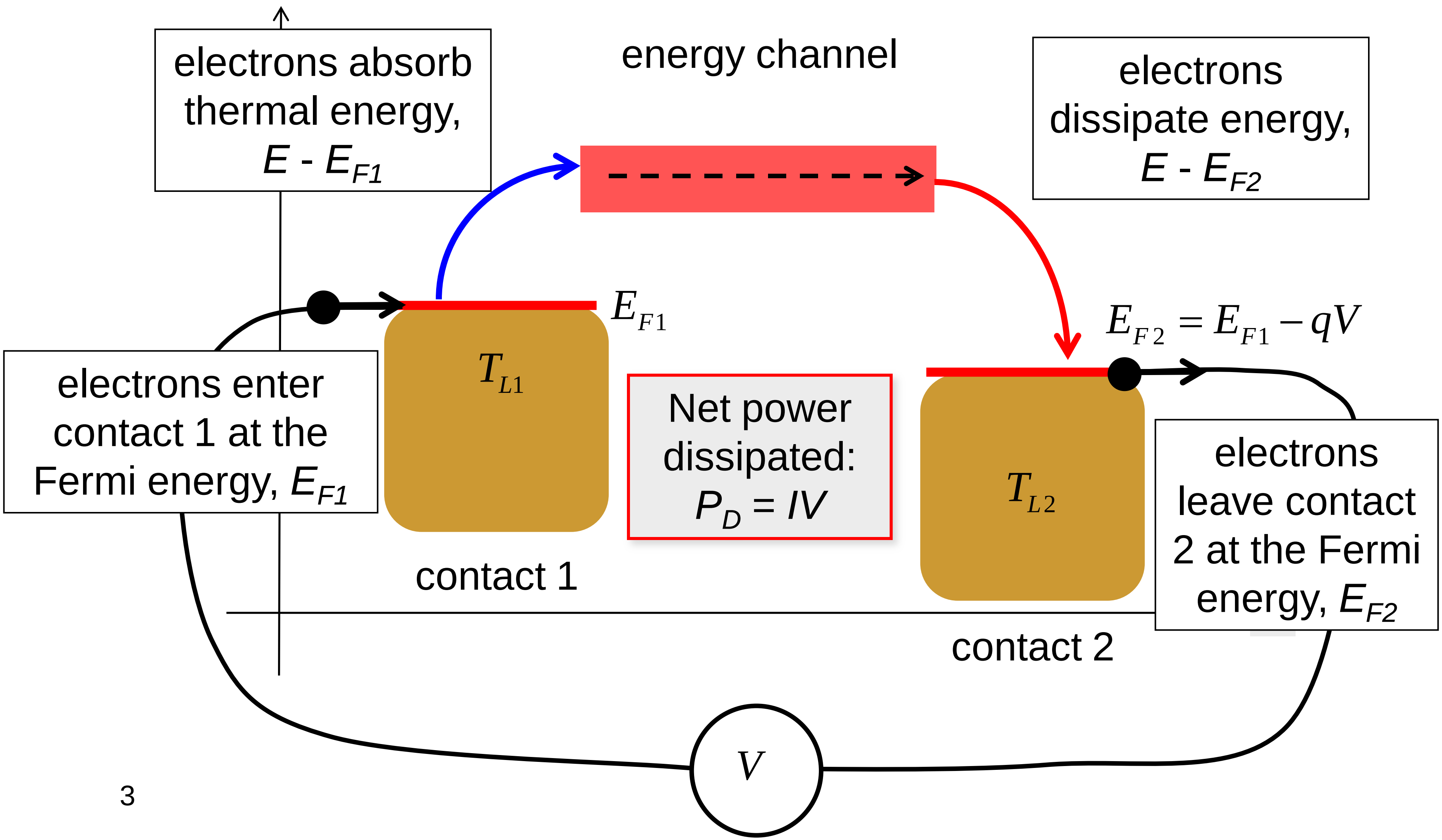
$$J_x^q = \pi_n J_x - \kappa_n \frac{dT_L}{dx}$$

Four transport coefficients:

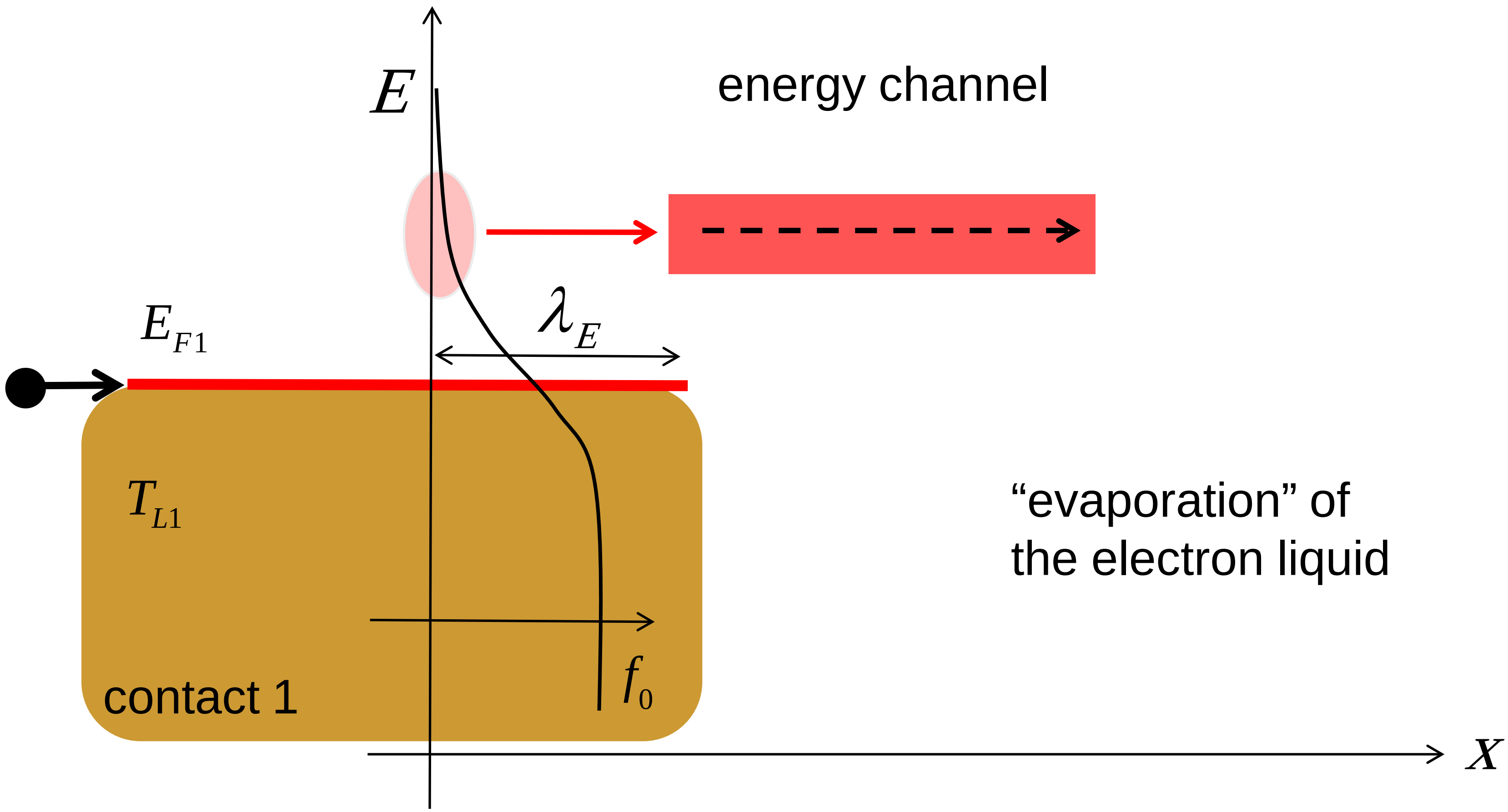
1) resistivity (Ω-cm) = 1/conductivity (S/cm)
2) Seebeck coefficient (V/K)
3) Peltier coefficient (W/A)
4) Electronic heat conductivity (W/m-K)

Note: These equations describe electric and heat currents due to electrons – in the diffusive limit and in 3D.

physics of Peltier cooling



a closer look at contact 1



"evaporation" of the electron liquid

Monte Carlo simulation

"It is interesting that the thermoelectric cooling and heating regions are contained in the highly doped contact layers."

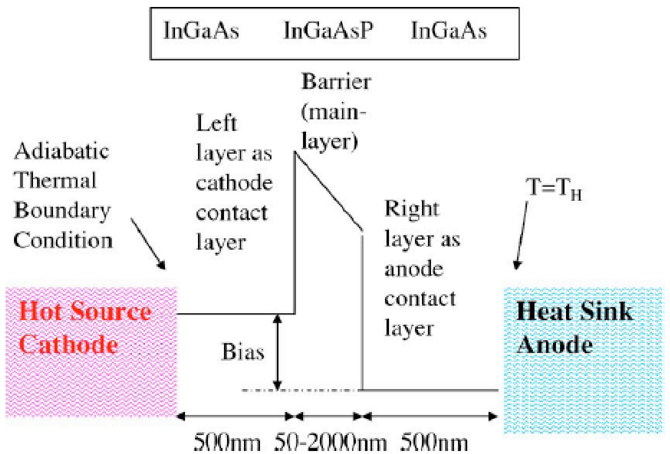


FIG. 1. (Color online) Schematic of the heterostructure.

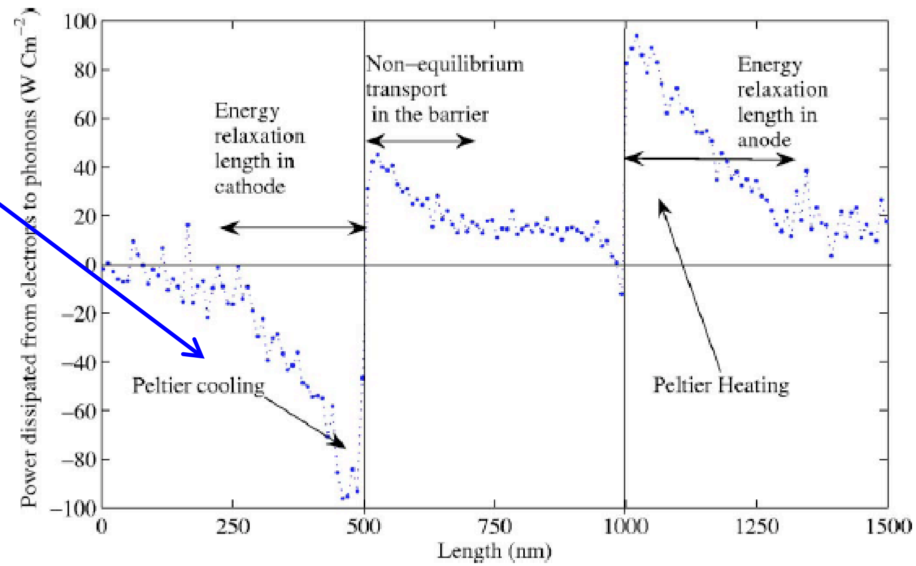


FIG. 3. (Color online) Source term (electron-phonon energy exchange) along the heterostructure obtained from MC simulation. The applied bias is 40 mV. Nonequilibrium regions at the ends of the contacts are disregarded as explained before. Peltier cooling at the cathode-barrier junction and Peltier heating at the anode-barrier junction can be observed.

Mona Zebarjadi, Ali Shakouri, and Keivan Esfarjani, "Thermoelectric transport perpendicular to thin-film heterostructures calculated using the Monte Carlo technique," *Phys. Rev. B*, **74**, 195331 (2006).

outline

1) Introduction
2) **Coupled flow equations**
3) Thermoelectric devices
4) Discussion
5) Summary

for bulk 3D semiconductors

$$J_x = \sigma \mathcal{E}_x - \sigma S \, dT_L / dx$$

$$J_x^q = T_L \sigma S \mathcal{E}_x - \kappa_0 \, dT_L / dx$$

$$\mathcal{E}_x = \rho J_x + S \frac{dT_L}{dx}$$

$$J_x^q = \pi J_x - \kappa_e \frac{dT}{dx}$$

(diffusive transport)

$$\sigma = \int \sigma'(E) dE$$

$$\sigma'(E) = \frac{2q^2}{h} \lambda(E) \frac{M(E)}{A} \left(-\frac{\partial f_0}{\partial E} \right)$$

$$S = -\frac{k_B}{q} \int \left(\frac{E - E_F}{k_B T_L} \right) \sigma'(E) dE \Big/ \int \sigma'(E) dE$$

$$\pi = T_L S$$

$$\kappa_0 = T_L \left(\frac{k_B}{q} \right)^2 \int \left(\frac{E - E_F}{k_B T_L} \right)^2 \sigma'(E) dE$$

$$\kappa_e = \kappa_0 - \pi S \sigma$$

transport parameters (3D, diffusive)

1) Assume parabolic energy bands

2) Assume power law scattering

$$\lambda(E) = \lambda_0 \left[\left(E - E_C \right) / k_B T_L \right]^r$$

Ionized impurity scattering: $r = 2$
Acoustic phonon scattering: $r = 0$

$$\sigma = \int \sigma'(E) dE$$

$$\sigma'(E) = \frac{2q^2}{h} \lambda(E) \frac{M(E)}{A} \left(-\frac{\partial f_0}{\partial E} \right)$$

$$S = -\frac{k_B}{q} \int \left(\frac{E - E_F}{k_B T_L} \right) \sigma'(E) dE \Big/ \int \sigma'(E) dE$$

$$\pi = T_L S$$

$$\kappa_0 = T_L \left(\frac{k_B}{q} \right)^2 \int \left(\frac{E - E_F}{k_B T_L} \right)^2 \sigma'(E) dE$$

$$\kappa_e = \kappa_0 - \pi S \sigma$$

transport parameters

$$\sigma = \frac{2q^2}{h}\left[g_V \frac{m^* k_B T_L}{2\pi\hbar^2} \mathcal{F}_0(\eta_F) \right] \left\{ \lambda_0 \frac{\Gamma(r+2)}{\Gamma(2)} \frac{\mathcal{F}_r(\eta_F)}{\mathcal{F}_0(\eta_F)} \right\}$$

$$S = -\left(\frac{k_B}{q}\right) \left\{ \frac{(r+2)\mathcal{F}_{r+1}(\eta_F)}{\mathcal{F}_r(\eta_F)} - \eta_F \right\}$$

$$\pi = T_L S$$

$$\kappa_0 = T_L \left(\frac{k_B}{q}\right)^2 \frac{2q^2}{h} g_V \frac{m^* k_B T_L}{2\pi\hbar^2} \lambda_0 \times$$
$$\left[\Gamma(r+4)\mathcal{F}_{r+2}(\eta_F) - 2\eta_F \Gamma(r+3)\mathcal{F}_{r+1}(\eta_F) + \eta_F^2 \Gamma(r+2)\mathcal{F}_r(\eta_F) \right]$$

$$\kappa_e = \kappa_0 - \pi S \sigma$$

transport parameters in a different form

$$\sigma = \frac{2q^2}{h}\langle M\rangle\langle\langle\lambda\rangle\rangle$$

$$\sigma = \frac{2q^2}{h}\langle M\rangle\langle\langle\lambda\rangle\rangle$$

$$S = -\left(\frac{k_B}{q}\right)\frac{\int\left(\frac{E-E_F}{k_B T_L}\right)\sigma'(E)\,dE}{\int\sigma'(E)\,dE}$$

$$S = -\left(\frac{k_B}{q}\right)\left(\frac{E-E_F}{k_B T_L}\right)_{\text{ave}}$$

$$\pi = T_L S$$

$$\kappa_0 = T_L\left(\frac{k_B}{q}\right)^2\int\left(\frac{E-E_F}{k_B T_L}\right)^2\sigma'(E)\,dE$$

$$\kappa_0 = \sigma T_L\left(\frac{k_B}{q}\right)^2\left\{\left(\frac{E-E_F}{k_B T_L}\right)^2\right\}_{\text{ave}}$$

$$\kappa_e = \kappa_0 - \pi S\sigma$$

Wiedemann-Franz "Law"

$$\frac{\kappa_0}{\sigma} = T_L \left(\frac{k_B}{q}\right)^2 \left\{ \left(\frac{E - E_F}{k_B T_L}\right)^2 \right\}_{\text{ave}} = T_L L'$$ *"Wiedeman Franz Law"*

$$\frac{\kappa_e}{\sigma} = \left(\frac{k_B}{q}\right)^2 \left\{ \left\langle \left(\frac{E - E_F}{k_B T_L}\right)^2 \right\rangle - \left\langle \left(\frac{E - E_F}{k_B T_L}\right) \right\rangle^2 \right\} T_L = L T_L$$ *Wiedeman Franz "Law"*

electronic heat conductivity

$$\kappa_n = \sigma_n T_L L$$

L is the "Lorenz number"

The Lorenz number depends on details of bandstructure, scattering, dimensionality, and degree of degeneracy, but for a constant mfp and parabolic energy bands, it is useful to remember:

$$L \approx 2\left(\frac{k_B}{q}\right)^2$$

non-degenerate,
3D semiconductors

$$L \approx \frac{\pi^2}{3}\left(\frac{k_B}{q}\right)^2$$

fully degenerate
e.g. 3D metals

a "rule of thumb" not a "law of nature"

(G.D. Mahan and M. Bartkowiak, *Appl. Phys. Lett.*, **74**, 953, 1999)

Peltier and Seebeck coefficient

$$\pi_n = T_L S_n\left(T_L\right)$$ “Kelvin relation”

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx}$$

$$J_{Qx} = \pi_n J_{nx} - \kappa_n \frac{dT_L}{dx}$$

“Onsager relations” for coupled flows

Onsaeger relations

$$J_x = L_{11}\frac{dF_n}{dx} + L_{12}\frac{d}{dx}\left(\frac{1}{T_L}\right)$$

$$J_q^x = L_{21}\frac{dF_n}{dx} + L_{22}\frac{d}{dx}\left(\frac{1}{T_L}\right)$$

$$J_1 = L_{11}\left(\vec{B}\right)F_1 + L_{12}\left(\vec{B}\right)F_2$$

$$J_2 = L_{21}\left(\vec{B}\right)F_1 + L_{22}\left(\vec{B}\right)F_2$$

J_1, J_2 "generalized fluxes"

F_1, F_2 "generalized forces"

$L_{12} = L_{21}$ Onsager relation

Onsaeger relations: example

1) temperature differences produce heat currents

2) pressure differences produce matter currents

→

3) heat flow per pressure difference = matter flow per temperature difference

Lars Onsaeger, Nobel Prize in Chemistry, 1968.

http.en.wikipedia.org/wiki/Onsaeger_reciprocal_relations

outline

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2) Coupled flow equations
3) **Thermoelectric devices**
4) Discussion
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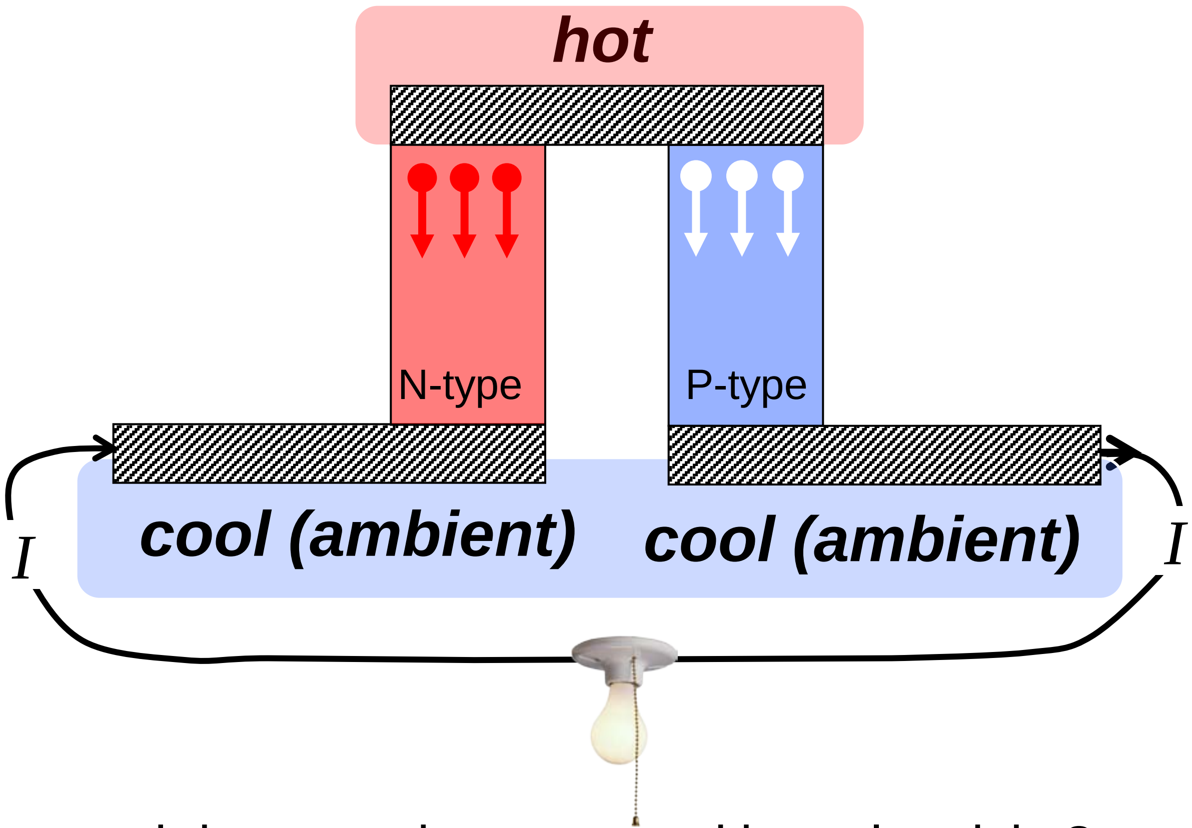
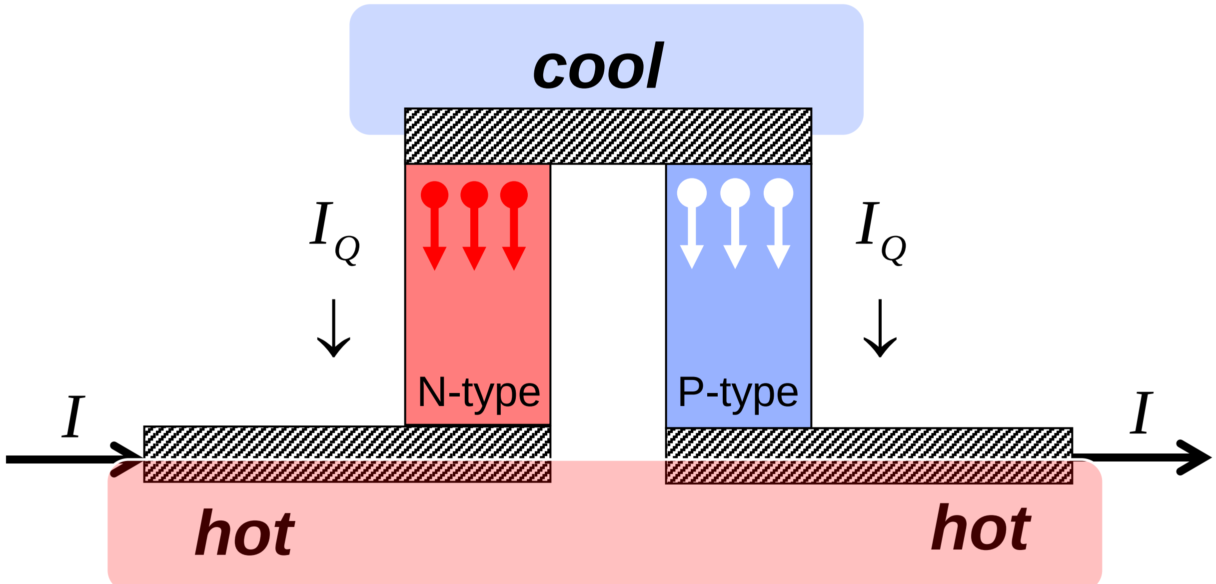
thermoelectric power generation



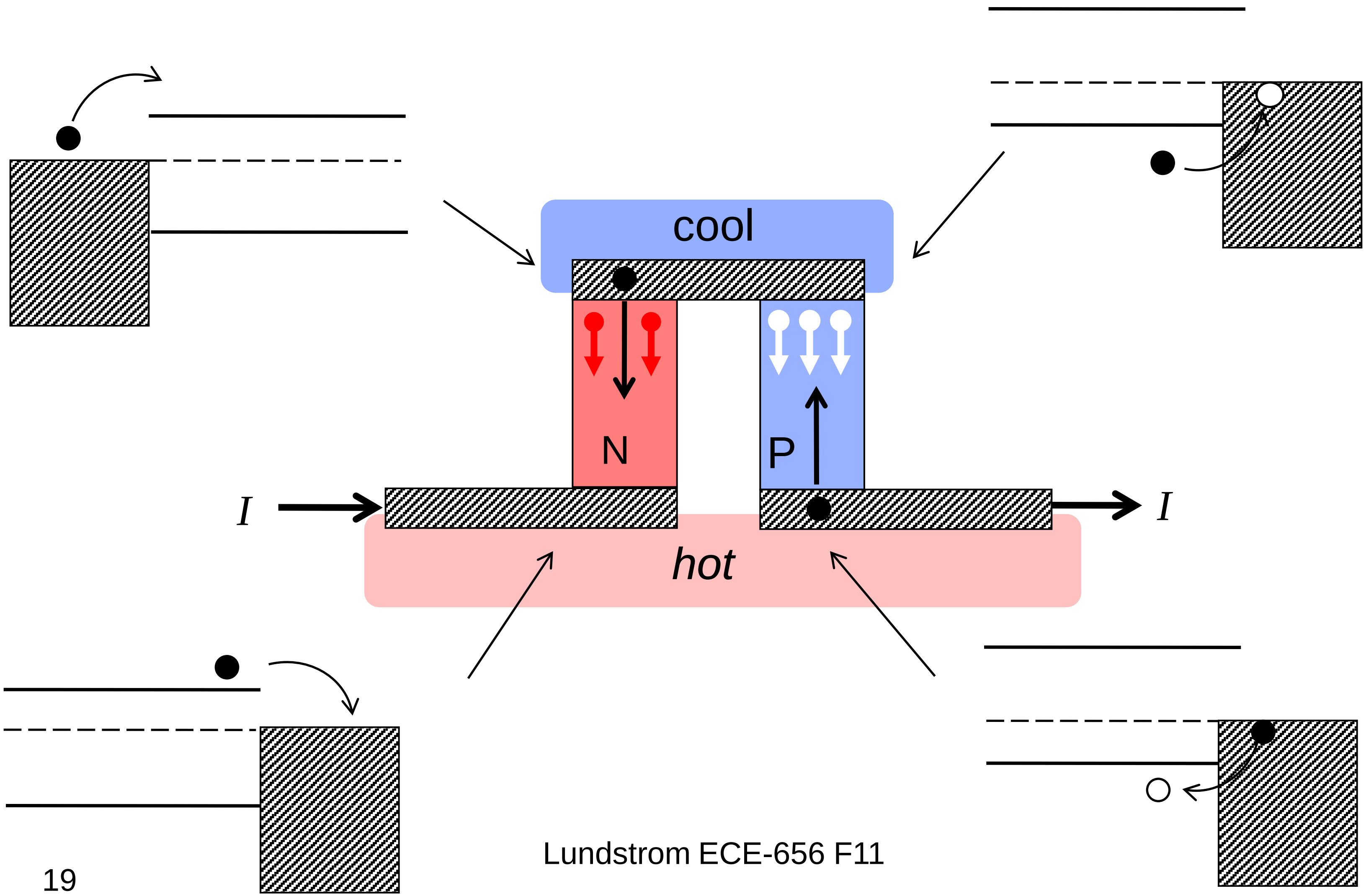
1) How much heat can be converted into electricity?
(what determines the efficiency?)

thermoelectric cooling

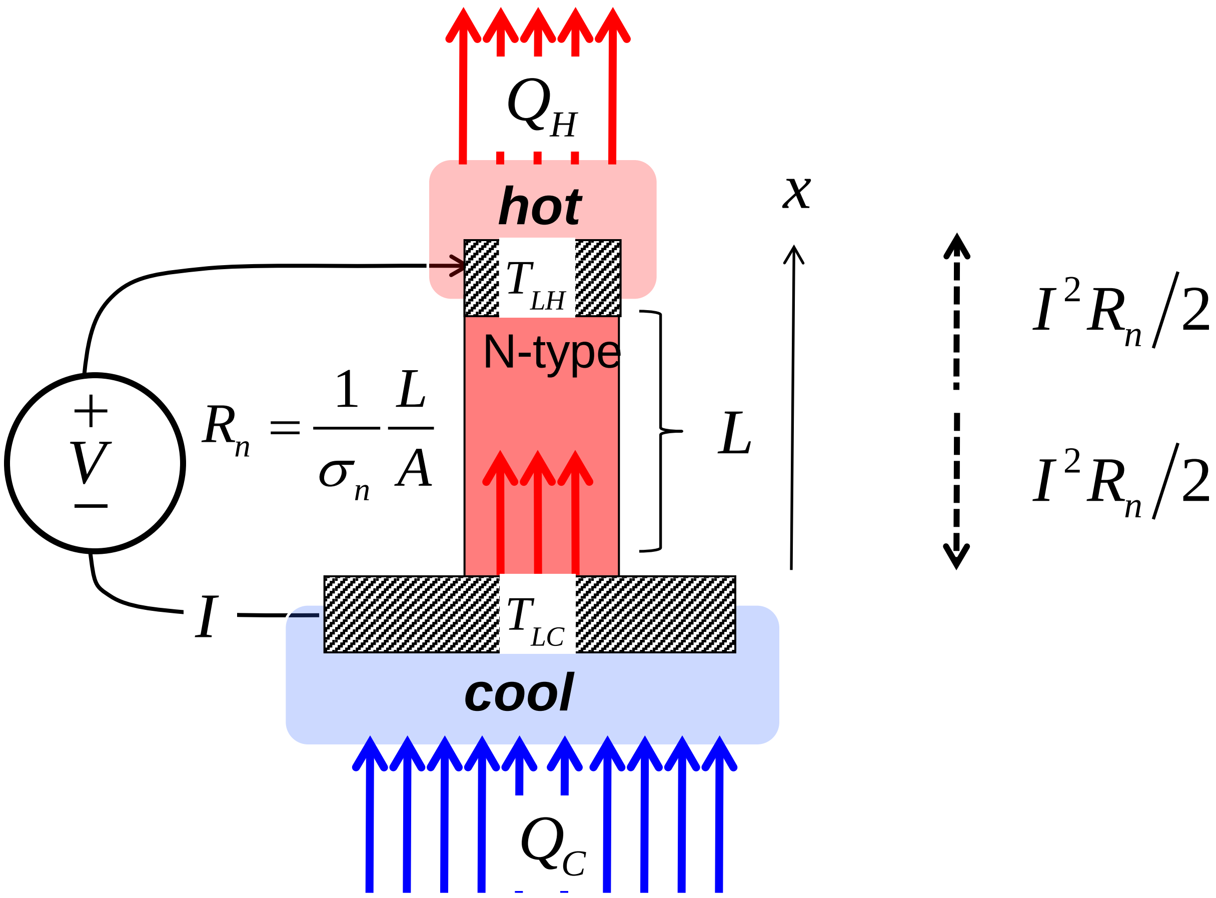


1) What determines the maximum temperature difference?
2) How much heat can be pumped?
3) What is the coefficient of performance?

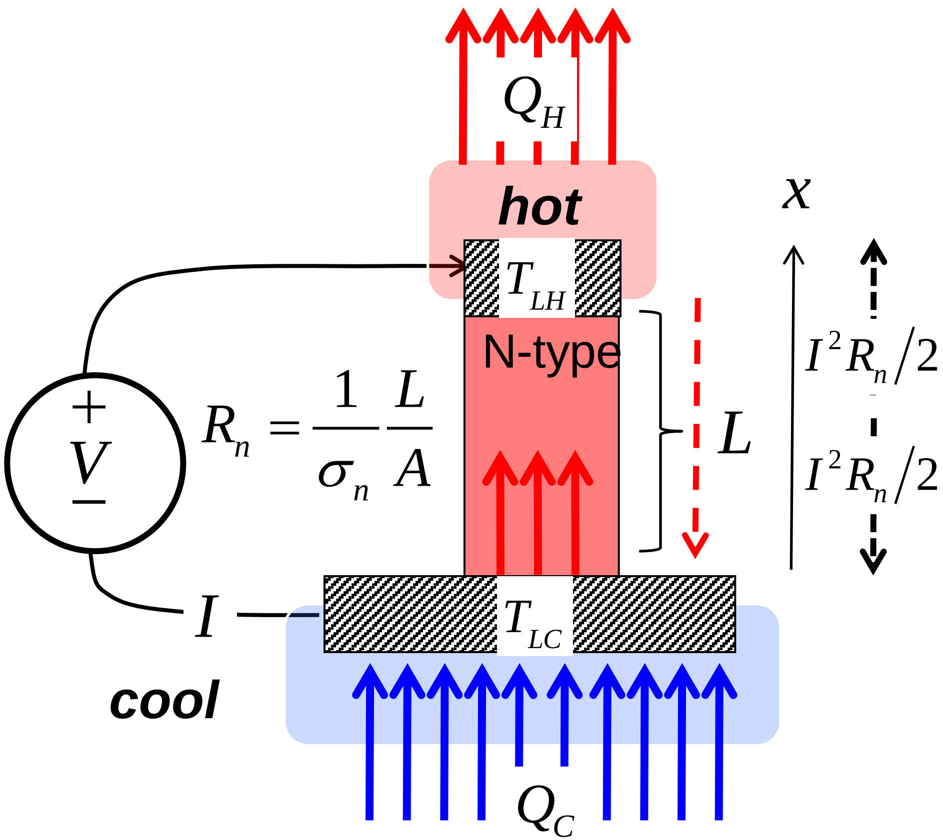
inside view of heat absorbtion/emission



simplified TE device (one leg)



simplified TE cooling device (one leg)



1) heat extracted from the cold side

=

2) heat pumped by Peltier effect

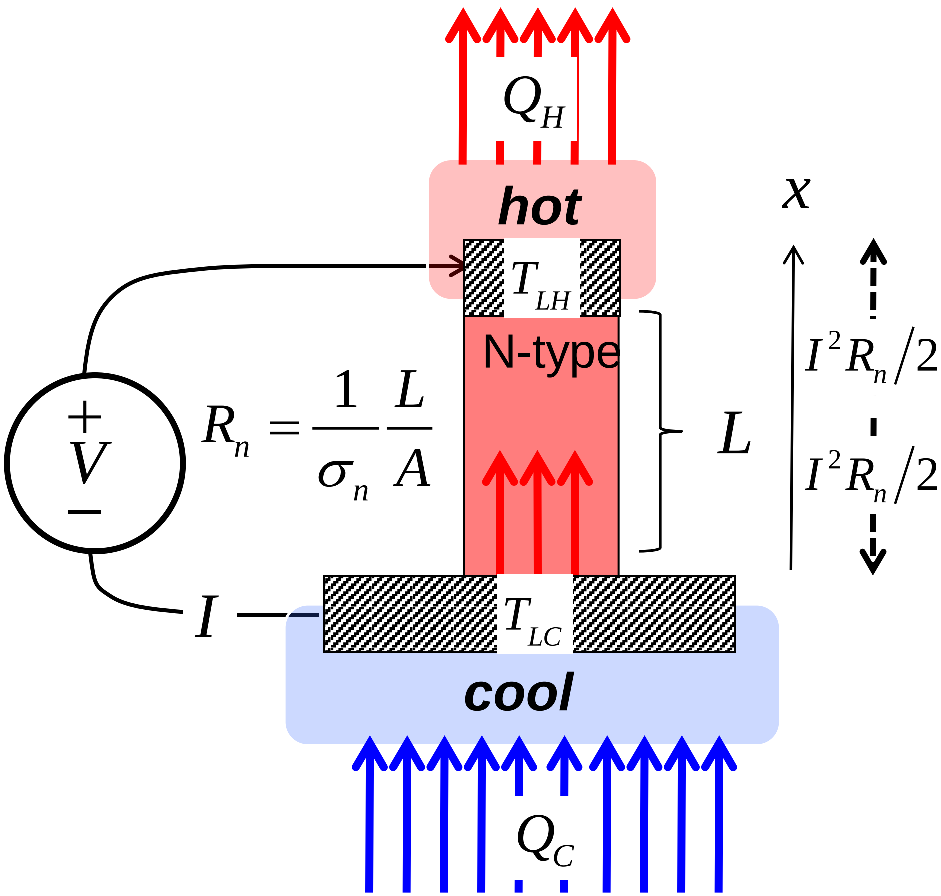
-

3) heat diffusing down the thermal gradient

-

4) heat generated by Joule heating

simplified TE cooling device (one leg)



$$Q_C = \pi_n \frac{I}{A} - \kappa \frac{dT_L}{dx} - \frac{I^2 R_n}{2A} \quad \left(\frac{\mathrm{W}}{\mathrm{m}^2}\right)$$

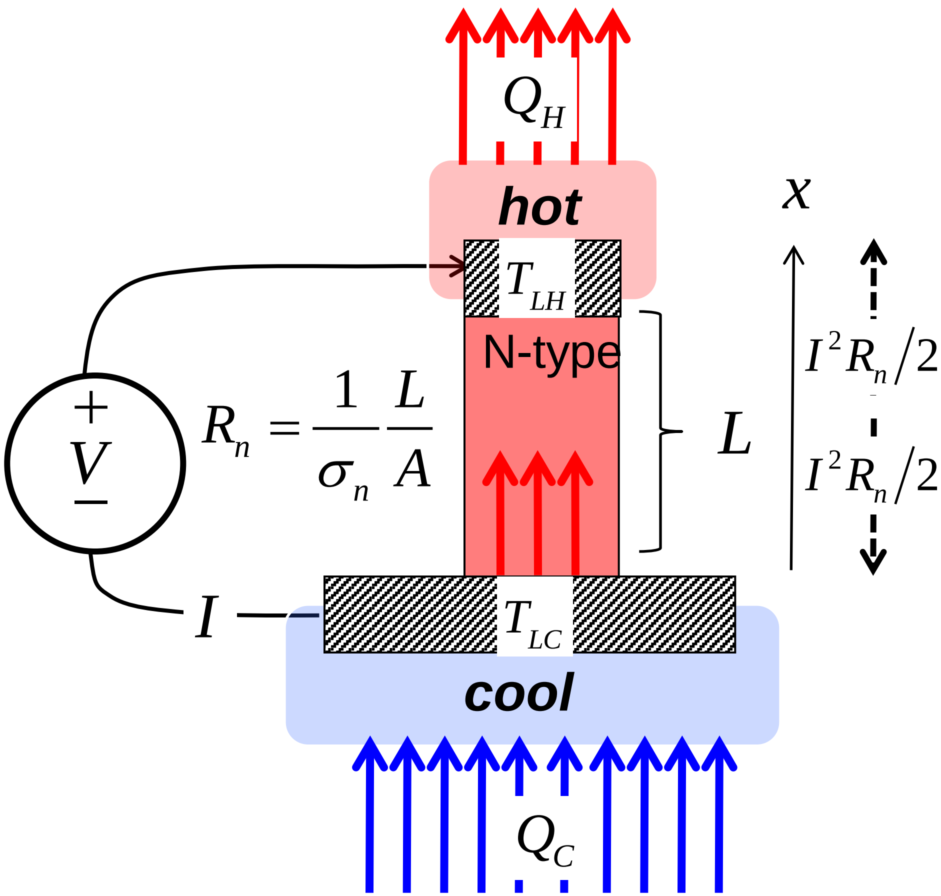
$$\frac{dQ_C}{dI} = 0 \rightarrow I_{\max,}\ Q_{C\max}$$

$$Q_{C\max} = 0 \rightarrow \Delta T_{\max}$$

$$\Delta T_{\max} = \frac{1}{2} Z T_{LC}^2 \qquad Z = \frac{S_n^2 \sigma_n}{\kappa}$$

TE figure of merit (FOM)

cooling efficiency (COP)



$$Q_C = \pi_n \frac{I}{A} - \kappa \frac{dT_L}{dx} - \frac{I^2 R_n}{2A} \quad \left(\frac{\mathrm{W}}{\mathrm{m}^2}\right)$$

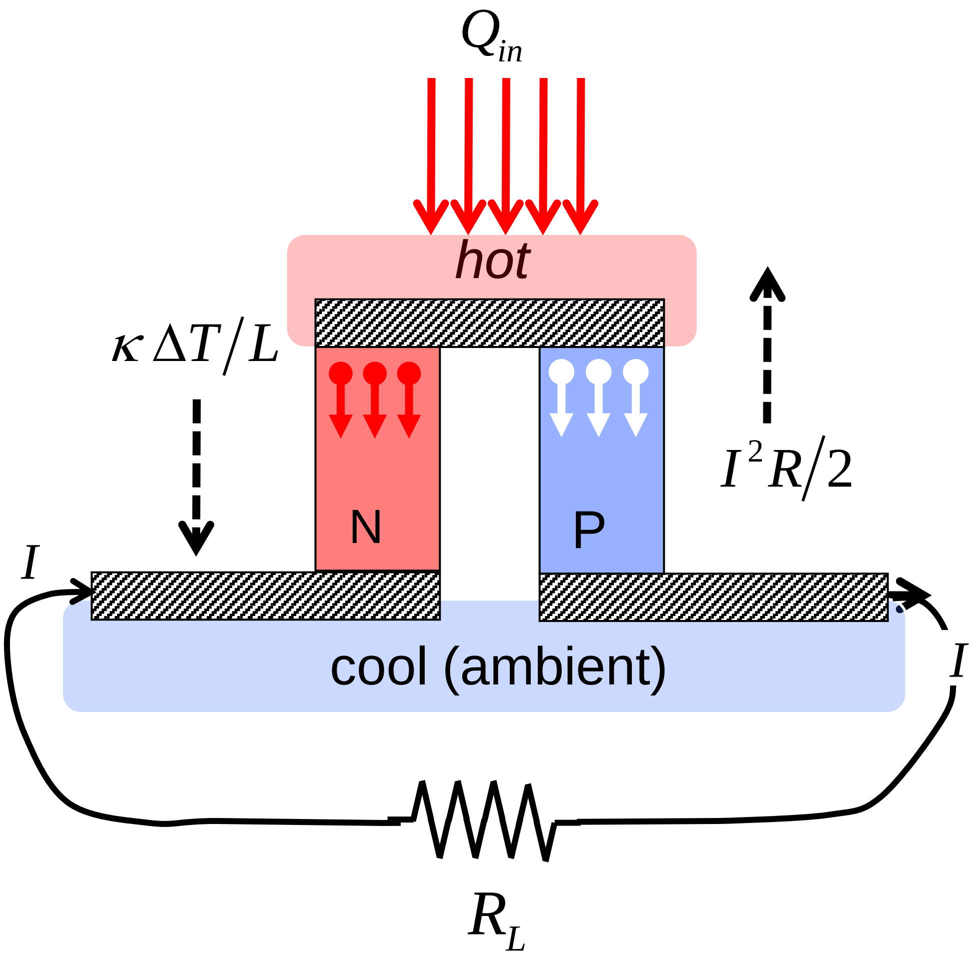
$$\frac{dQ_C}{dI} = 0 \rightarrow I_{\max}, \; Q_{C\max}$$

$$\eta = \frac{Q_{C_{\max}}}{P_{in}}$$

COP at maximum cooling power:

$$\eta = \frac{Q_{C\max}}{P_{in}} = f\left(T_{LC}, T_{LH}, Z\right)$$

TE power generation



Similarly, an analysis of the power conversion efficiency,

$$\eta = \frac{P_{out}}{P_{in}} = \frac{I^2 R_L}{A Q_{in}}$$

shows that it is also determined by the TE figure of merit, *Z*.

FOM

$$Z = \frac{S_n^2 \sigma_n}{\kappa} \text{ K}^{-1}$$

$$ZT = \frac{S_n^2 \sigma_n T_L}{\kappa}$$

dimensionless figure of merit

The higher the ZT figure of merit, the more efficient a TE device.

1) What material properties are needed for a high ZT?
2) Given a material, how can we optimize ZT?

FOM

$$ZT = \frac{S_n^2 \sigma_n T_L}{\kappa}$$

Numerator:

$$S_n(T_L) = \left(\frac{k_B}{-q}\right)\left\{\frac{(E_C - F_n)}{k_B T_L} + \delta_n\right\}$$

Mostly determined by position of band edge and E_F. Similar for most materials.

$$\sigma_n = \left(\frac{2q^2}{h}\right)\langle M \rangle \langle\langle \lambda \rangle\rangle$$

Need a large no. of channels (large *M*, E_F). Need large m.f.p. (mobility)

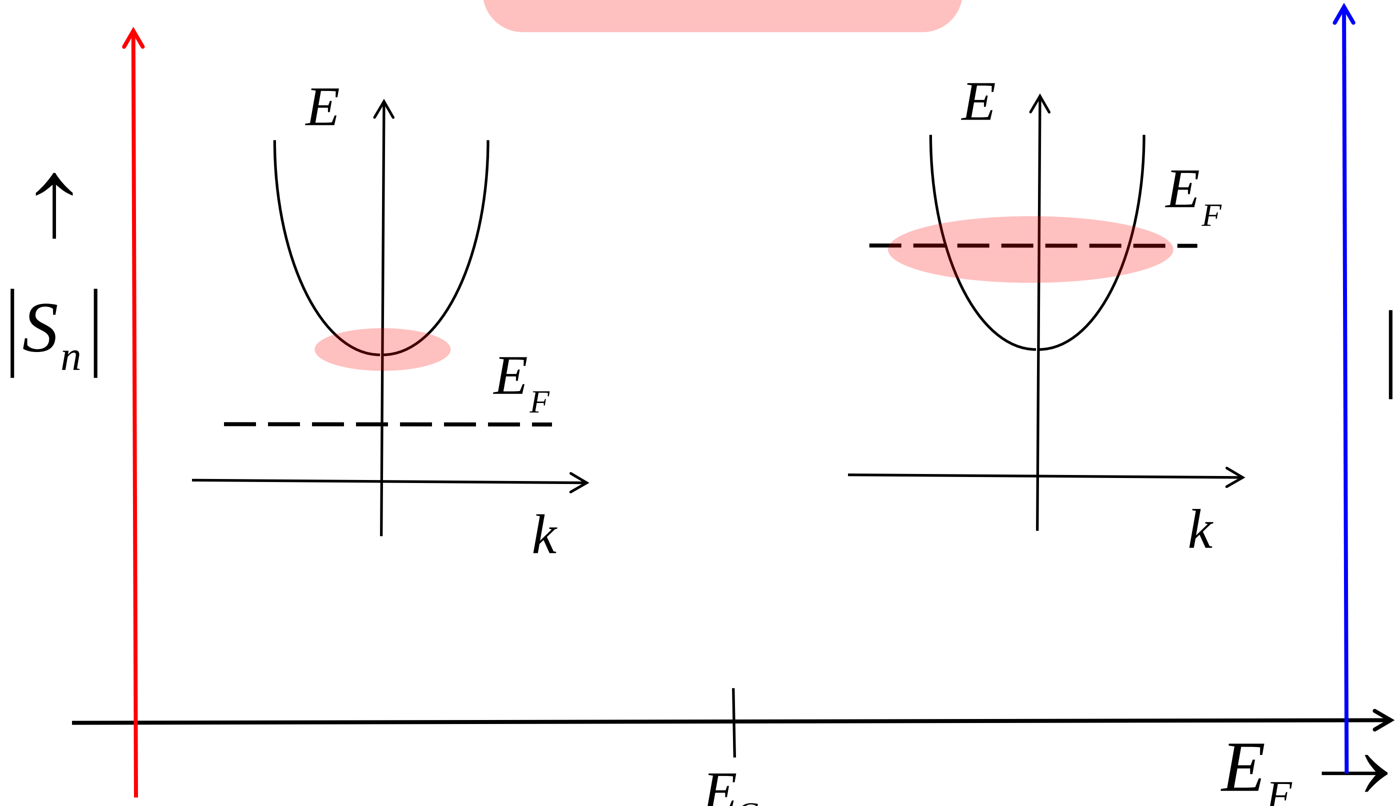
Denominator:

$$\kappa_L >> \kappa_n$$

Mostly determined by lattice thermal conductivity. (Lecture 9 in notes)

FOM: PF vs. Fermi level

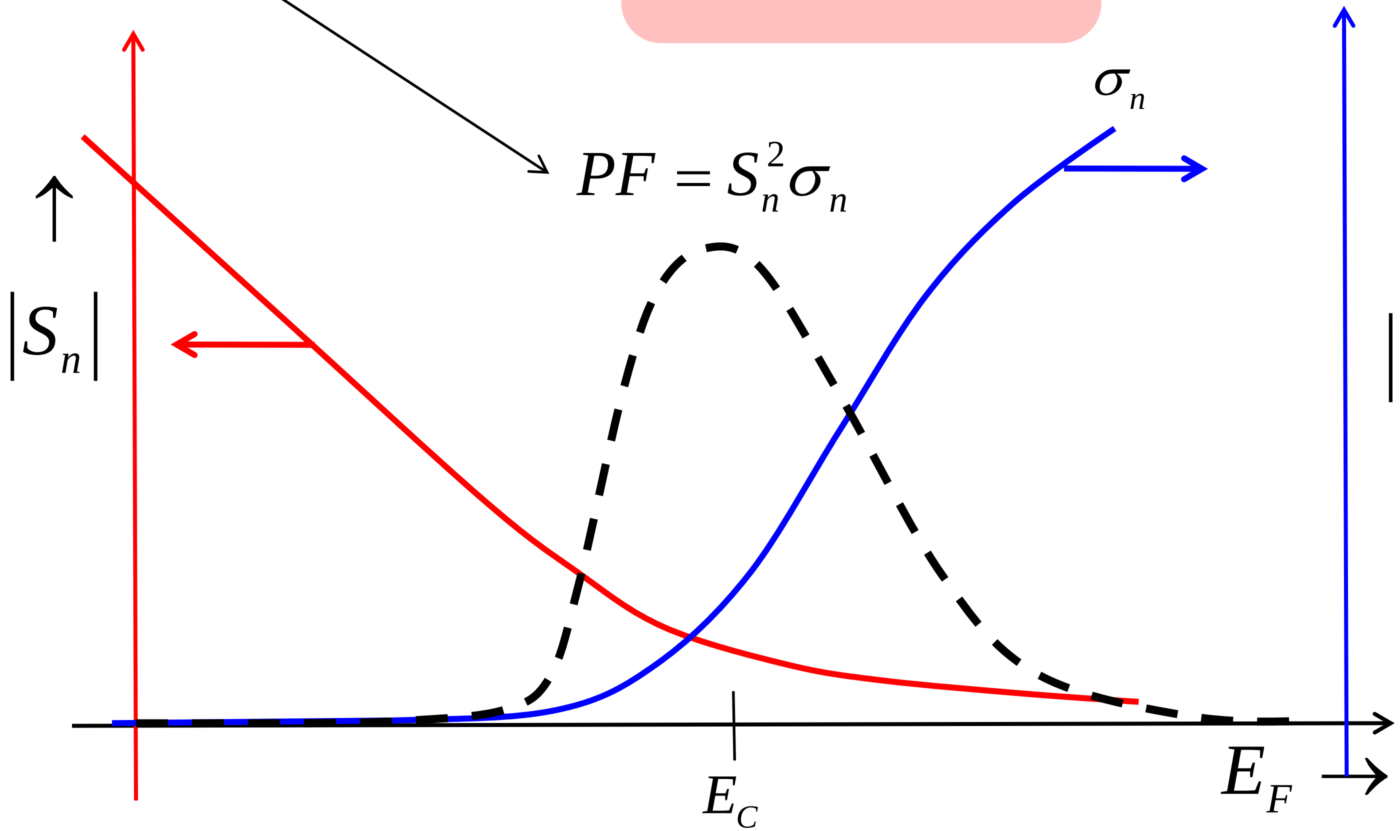
$$ZT = \frac{S_n^2 \sigma_n T_L}{\kappa}$$



FOM: PF vs. Fermi level

The peak PF occurs when E_F is near the band edge.

$$ZT = \frac{S_n^2 \sigma_n T_L}{\kappa}$$



outline

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basic equations of thermoelectricity

$$\mathcal{E}_x = \rho_n J_x + S_n \frac{dT_L}{dx}$$

$$J_x^q = \pi_n J_{nx} - \kappa_n \frac{dT_L}{dx}$$

We can write these equations in **vector notation** as:

$$\vec{\mathcal{E}} = \rho_n \vec{J} + S_n \vec{\nabla} T_L$$

$$\vec{J}_q = \pi_n \vec{J} - \kappa_n \vec{\nabla} T_L$$

or in **indicial notation** as:

$$\mathcal{E}_i = \rho_n J_i + S_n \partial_i T_L$$

$$J_i^q = \pi_n J_i - \kappa_n \partial_i T_L$$

$$i = x, y, z$$

transport tensors

$$\vec{\mathcal{E}} = \rho \vec{J} + S \vec{\nabla} T_L$$

$$\vec{J}_q = \pi \vec{J} - \kappa_n \vec{\nabla} T_L$$

$$\vec{\mathcal{E}} = [\rho] \vec{J} + [S] \vec{\nabla} T$$

$$\vec{J}_q = [\pi] \vec{J} - [\kappa_n] \vec{\nabla} T$$

$$\begin{bmatrix} \mathcal{E}_x \\ \mathcal{E}_y \\ \mathcal{E}_z \end{bmatrix} = \begin{bmatrix} \rho_{11} & \rho_{12} & \rho_{13} \\ \rho_{21} & \rho_{22} & \rho_{23} \\ \rho_{31} & \rho_{32} & \rho_{33} \end{bmatrix} \begin{bmatrix} J_x \\ J_y \\ J_z \end{bmatrix}$$

$$\mathcal{E}_i = \sum_{j=1}^{3} \rho_{ij} J_j$$

$\mathcal{E}_i \equiv \rho_{ij} J_j$ "summation convention"

coupled current equations again

$$\vec{\mathcal{E}} = [\rho]\vec{J} + [S]\vec{\nabla}T$$

$$\vec{J}_q = [\pi]\vec{J} - [\kappa_n]\vec{\nabla}T$$

$$\mathcal{E}_i = \rho_{ij} J_j + S_{ij}\partial_j T$$

$$J_i^Q = \pi_{ij} J_j - \kappa_{ij}^n \partial_j T$$

For isotropic materials, the tensors are diagonal.

$$\mathcal{E}_i = \rho_0 J_j + S_0 \partial_j T$$

$$J_i^q = \pi_0 J_j - K_0^e \partial_j T$$

$$[\rho] = \rho_0 \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

"Kronecker delta"

$$\rho_{ij} = \rho_0 \delta_{ij}$$

$$\delta_{ij} = 1 \quad (i = j)$$

$$= 0 \quad (i \neq j)$$

form of the transport tensors

$$\mathcal{E}_i = \rho_{ij} J_j + S_{ij} \partial_j T$$

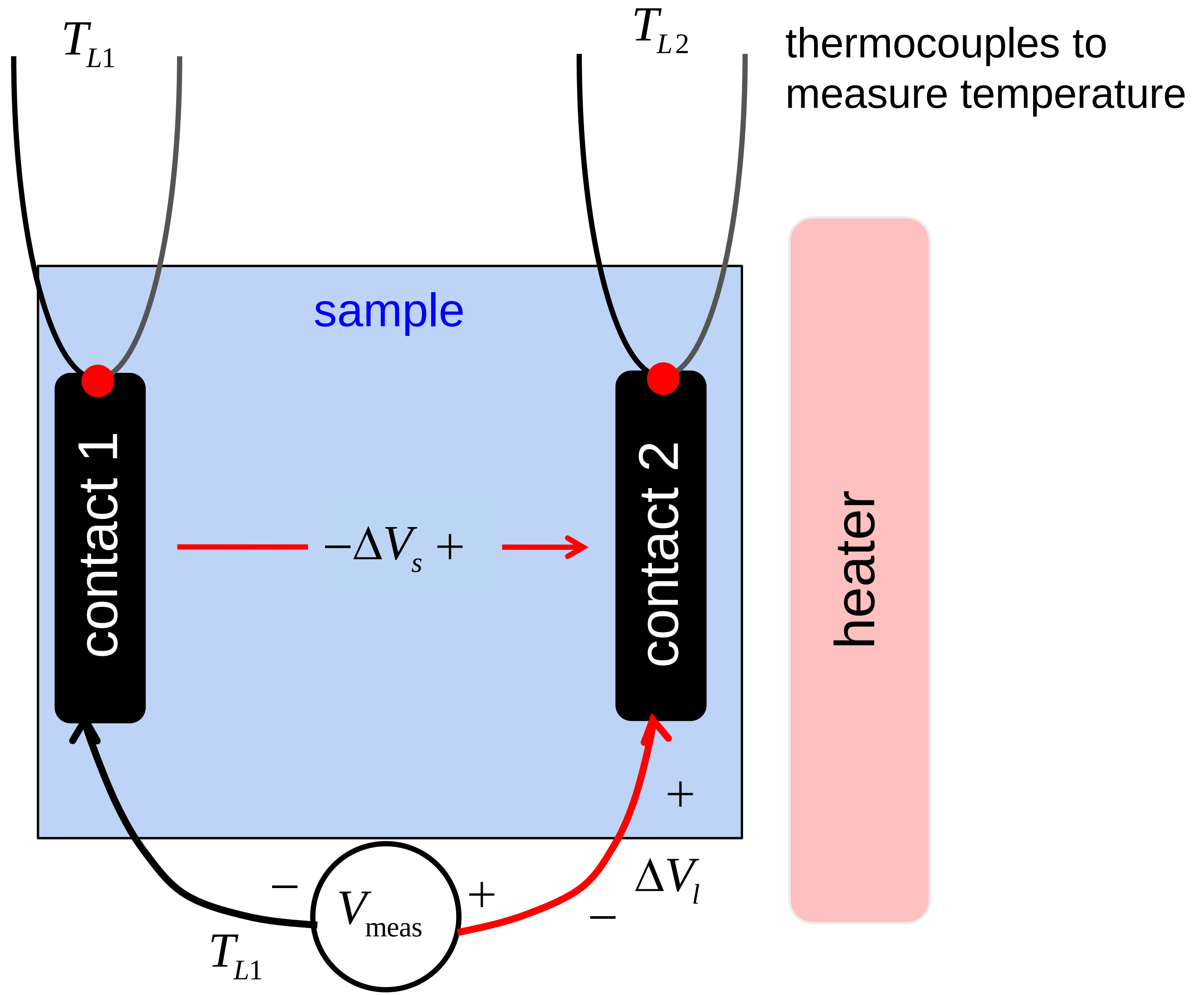
$$J_i^q = \pi_{ij} J_j - \kappa_{ij}^e \partial_j T$$

For isotropic materials, such as common, cubic semiconductors, the tensors are diagonal (under low-fields).

For a given crystal structure, the form of the tensors (i.e. which elements are zero and which are non-zero) can be deduced from symmetry arguments. (See Smith, Janak, and Adler, Chapter 4.)

The transport tensors can be readily computed by solving the Boltzmann Transport Equation (BTE).

measuring *S*



$$V_{meas} = \Delta V_s - \Delta V_l$$

$$\Delta V_s = -S_s \Delta T$$

$$\Delta V_l = -S_l \Delta T$$

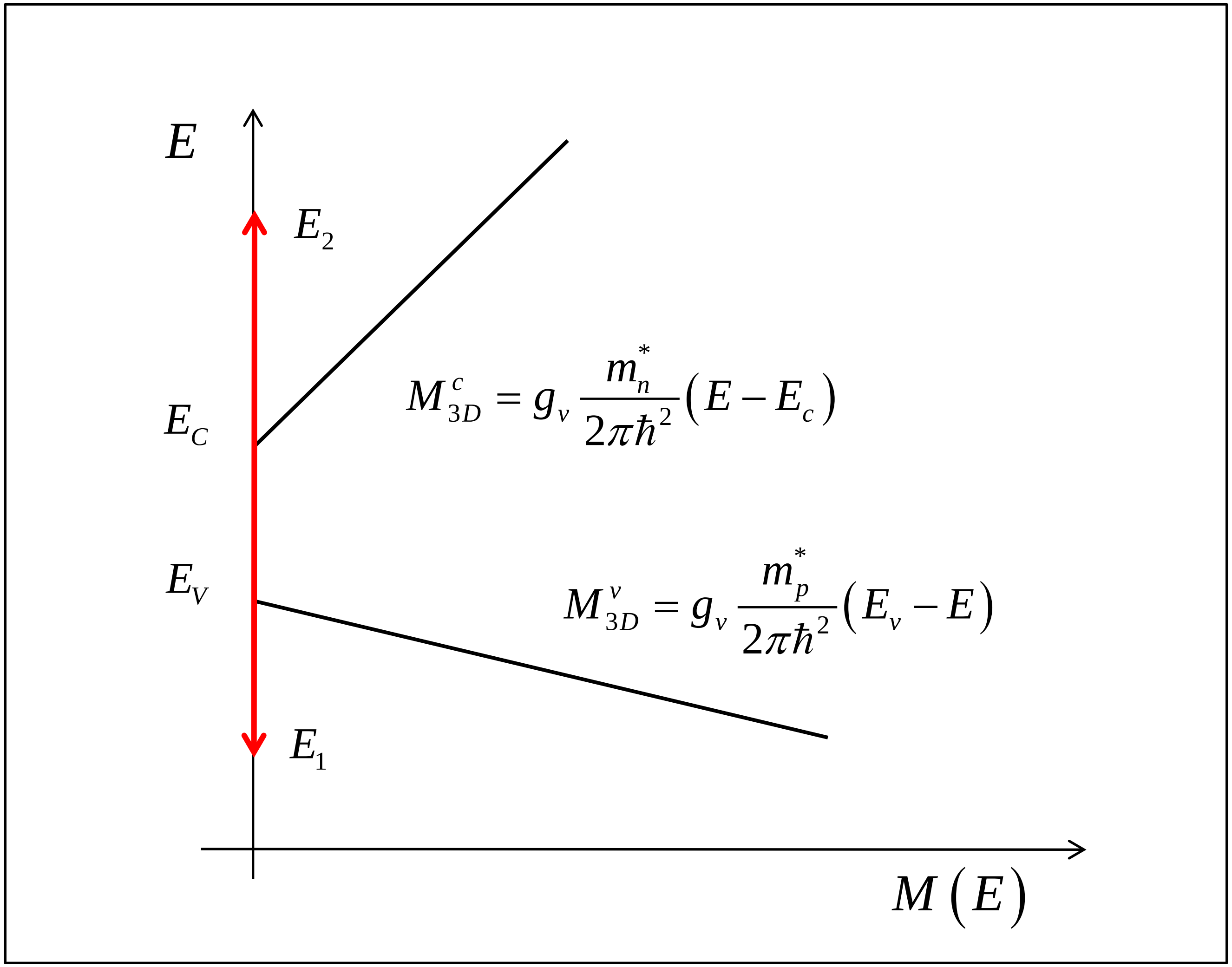
$$V_{meas} = -\left(S_s - S_l\right)\Delta T$$

what about the valence band?

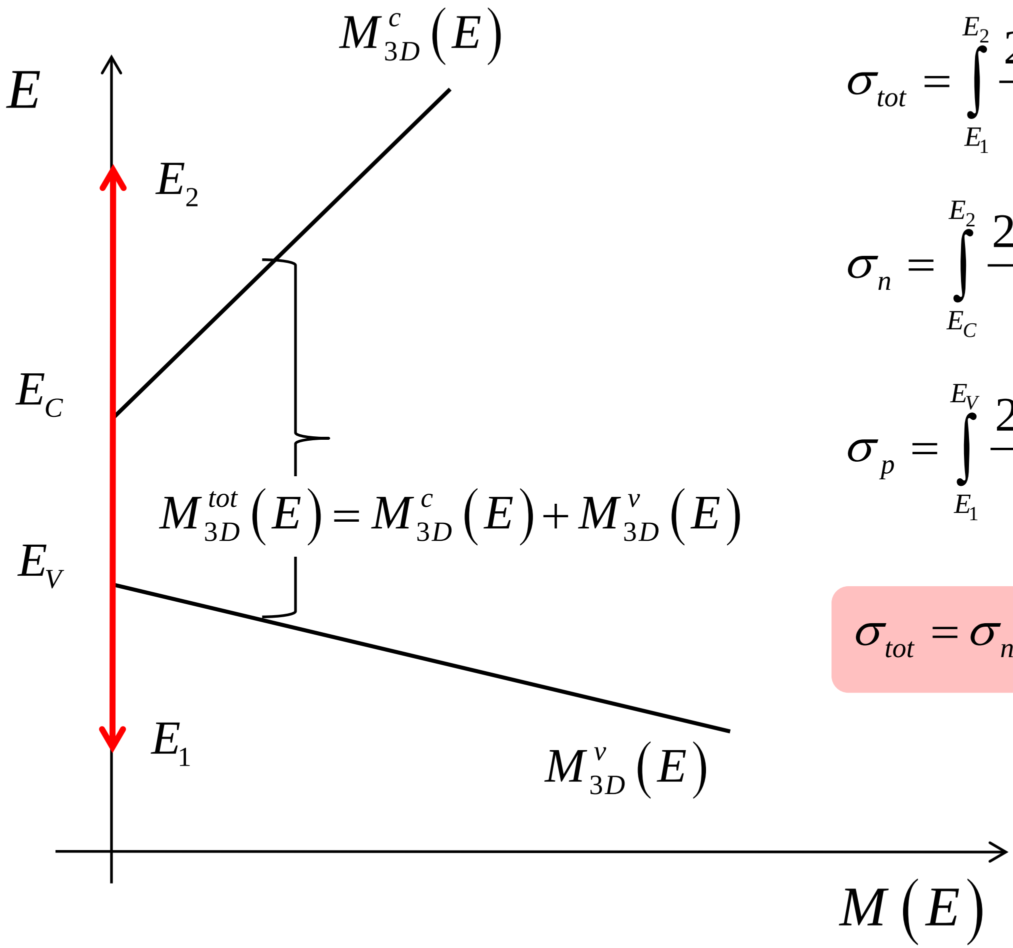
$$\mathcal{E}_i = \rho_{ij} J_j + S_{ij} \partial_j T$$

$$J_i^q = \pi_{ij} J_j - \kappa_{ij}^e \partial_j T$$

what about the valence band?



treating both bands: conductivity



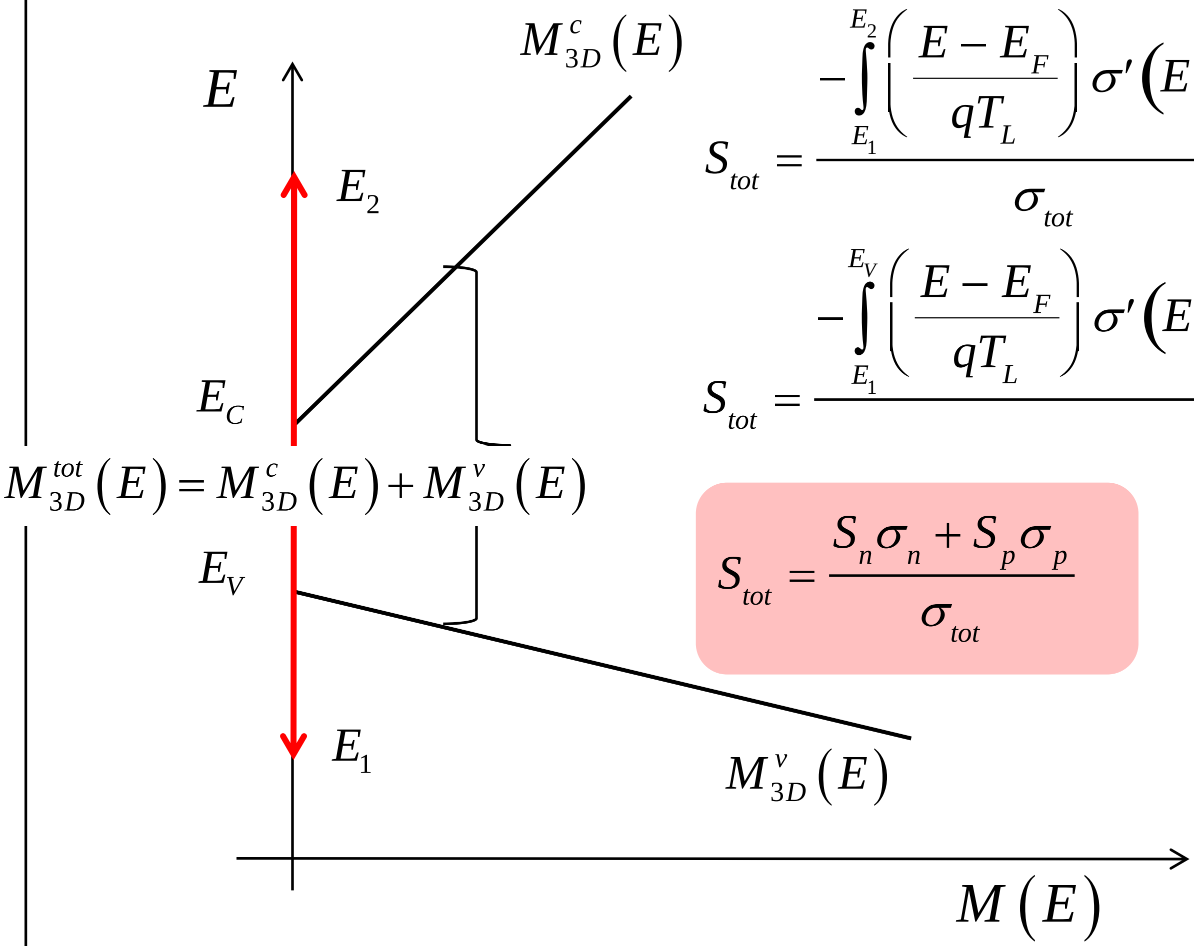
$$\sigma_{tot} = \int_{E_1}^{E_2} \frac{2q^2}{h} M_{3D}^{tot}(E)\lambda(E)\left(-\frac{\partial f_0}{\partial E}\right)dE$$

$$\sigma_n = \int_{E_C}^{E_2} \frac{2q^2}{h} M_{3D}^{c}(E)\lambda(E)\left(-\frac{\partial f_0}{\partial E}\right)dE$$

$$\sigma_p = \int_{E_1}^{E_V} \frac{2q^2}{h} M_{3D}^{v}(E)\lambda(E)\left(-\frac{\partial f_0}{\partial E}\right)dE$$

$$\sigma_{tot} = \sigma_n + \sigma_p$$

treating both bands: *S*

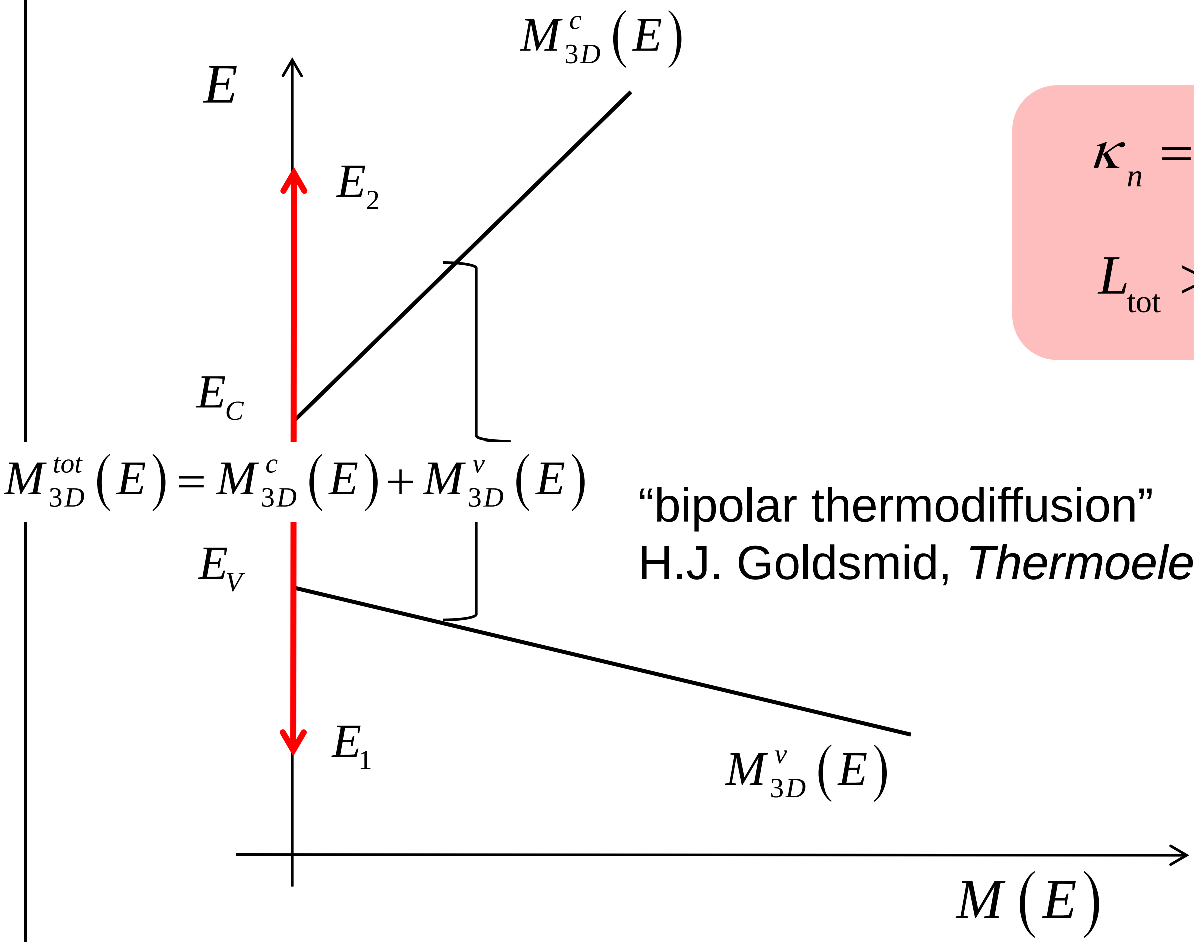


$$S_{tot} = \frac{-\int_{E_1}^{E_2} \left(\frac{E-E_F}{qT_L}\right) \sigma'(E)\,dE}{\sigma_{tot}}$$

$$S_{tot} = \frac{-\int_{E_1}^{E_V} \left(\frac{E-E_F}{qT_L}\right) \sigma'(E)\,dE - \int_{E_C}^{E_2} \left(\frac{E-E_F}{qT_L}\right) \sigma'(E)\,dE}{\sigma_{tot}}$$

$$S_{tot} = \frac{S_n\sigma_n + S_p\sigma_p}{\sigma_{tot}}$$

treating both bands: κ



$$\kappa_n = \sigma_{tot} T_L L_{\text{tot}}$$

$$L_{\text{tot}} >> L_n + L_p$$

“bipolar thermodiffusion”
H.J. Goldsmid, *Thermoelectric Refrigeration*, 1964.

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summary

$$\mathcal{E}_i = \rho_{ij} J_j + S_{ij} \partial_j T$$

$$J_i^q = \pi_{ij} J_j - \kappa_{ij}^e \partial_j T$$

questions

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