

NCN Summer School: July 2011

# Near-equilibrium Transport: Fundamentals and Applications

## Lecture 4: Thermoelectric Effects: Physical Approach

**Mark Lundstrom**

Electrical and Computer Engineering  
and  
Network for Computational Nanotechnology  
Birck Nanotechnology Center  
Purdue University, West Lafayette, Indiana USA

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# about thermoelectricity

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Thermoelectric (TE) devices convert heat into electricity or electric power into cooling (or heating) power.

This lecture is about the physics and the mathematical description of thermoelectricity.

We concentrate in this lecture on the physics and use heuristic mathematical arguments.

In Lecture 5, we present a formal, mathematical derivation.

# mathematical description

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In Lecture 2 we saw that the electrical current in the bulk is:

$$J_{nx} = \sigma_n d(F_n/q)/dx \quad \sigma_n = \text{conductivity} = 1/\rho_n \quad (1/\Omega\text{-m})$$

Alternatively, we could write this equation as:

$$d(F_n/q)/dx = \rho_n J_{nx}$$

How do these equations change when there is a temperature gradient?

# mathematical description

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The answer is:

$$J_{nx} = \sigma_n \frac{d(F_n/q)}{dx} - S_n \sigma_n \frac{dT_L}{dx}$$

$S_n$  is the Seebeck coefficient in V/K.

Alternatively, we can write this equation as:

$$\frac{d(F_n/q)}{dx} = \rho_n J_{nx} + S_n \frac{dT_L}{dx}$$

# mathematical description

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Thermoelectricity involves the flow of charge and heat, so in addition to the equation for the charge current, we need an equation for the heat current:

$$J_{Qx} = -\kappa_0 dT/dx \quad W/m^2$$

How does this equation change when there is a current flow?

# mathematical description

The answer is:

$$J_{Qx} = (S_n \sigma_n T_L) \frac{d(F_n/q)}{dx} - \kappa_0 \frac{dT_L}{dx} \quad \text{W/m}^2$$

Alternatively, we can write this equation as:

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

$$\pi_n = S_n T_L$$

$$\kappa_n = \kappa_0 - S_n^2 \sigma_n T_L$$

$\pi$  is the Peltier coefficient in W/A

**Important point:** Both electrons and the lattice (phonons) carry heat. These equations refer only to the portion of the heat carried by the electrons.

## in this lecture...

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Our goal is to understand the physical origin of the Seebeck coefficient (which is also called the thermopower) and the Peltier coefficient and how they are related to the properties of the semiconductor.



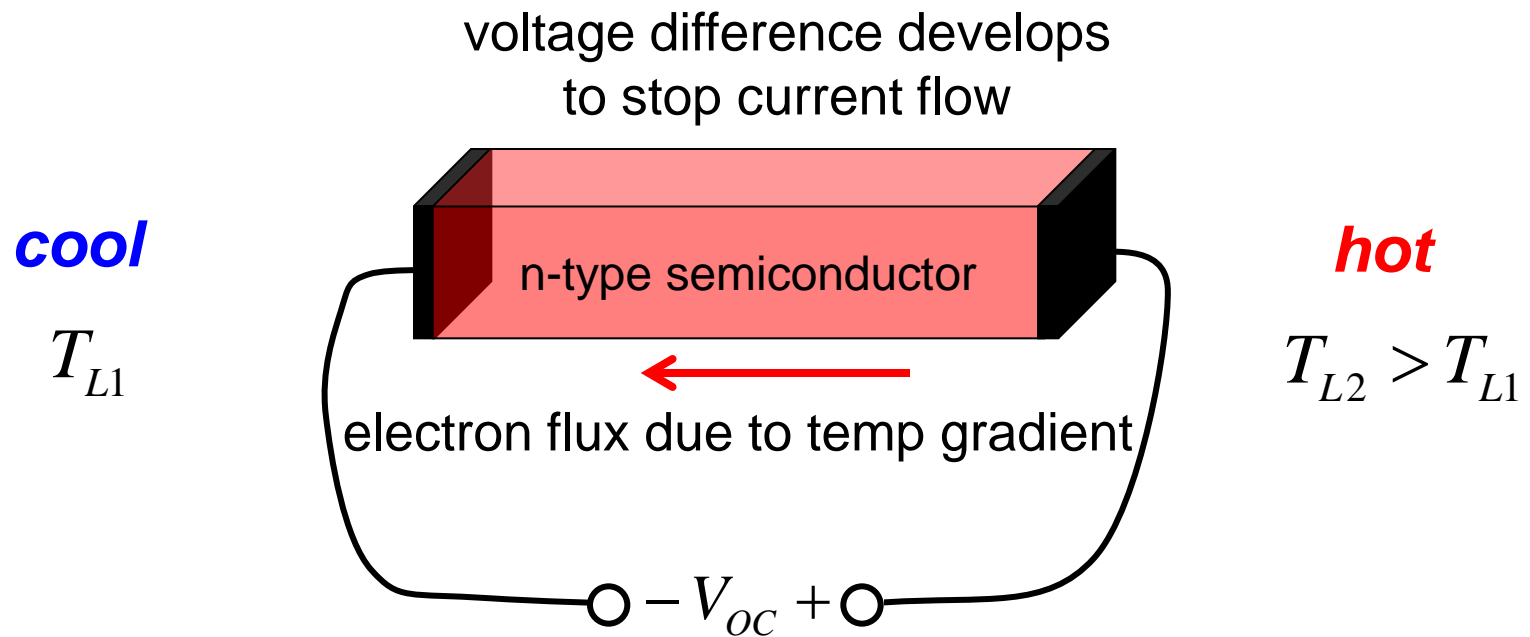
# outline

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- 1) Introduction
- 2) Current flow**
- 3) Heat flow
- 4) Coupled flows
- 5) Thermoelectric devices
- 6) Discussion
- 7) Summary

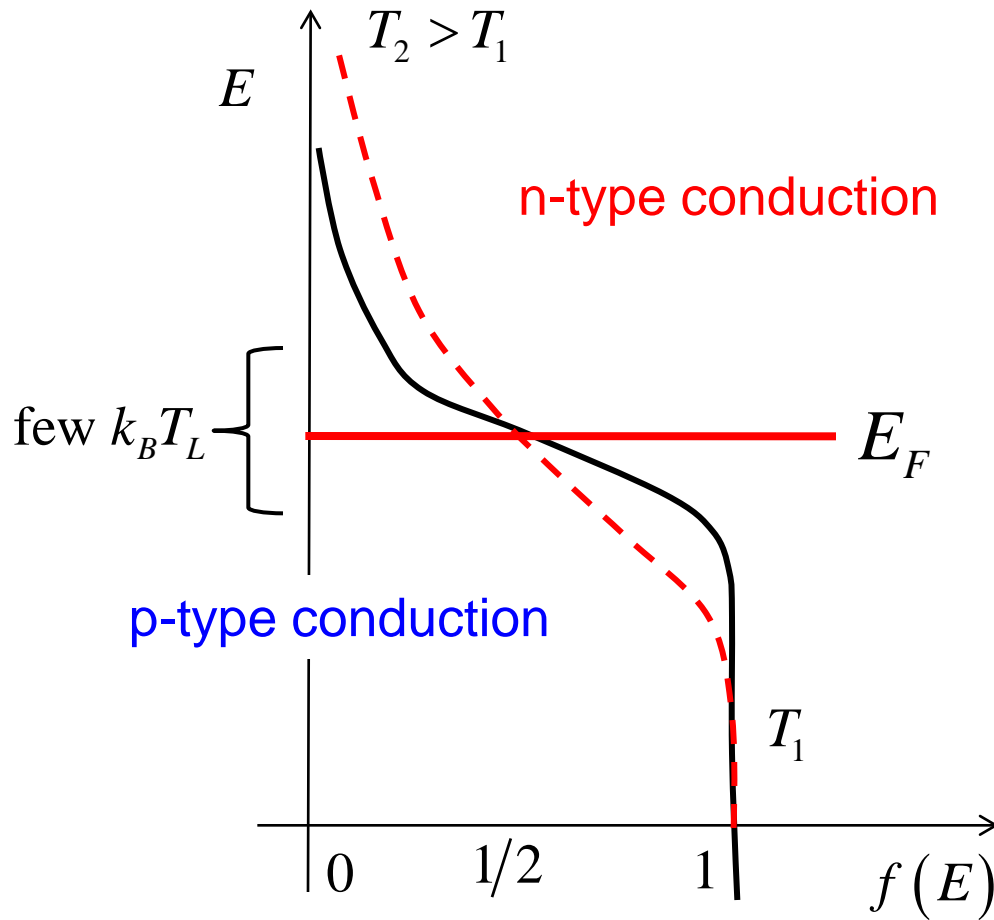
We will use an approach similar to that of Prof. Supriyo Datta.

# temperature gradients and voltage



Temperature gradients give rise to an open circuit voltage, which is known as the Seebeck effect. Expect a positive voltage for an n-type semiconductor (and negative voltage for a p-type semiconductor.)

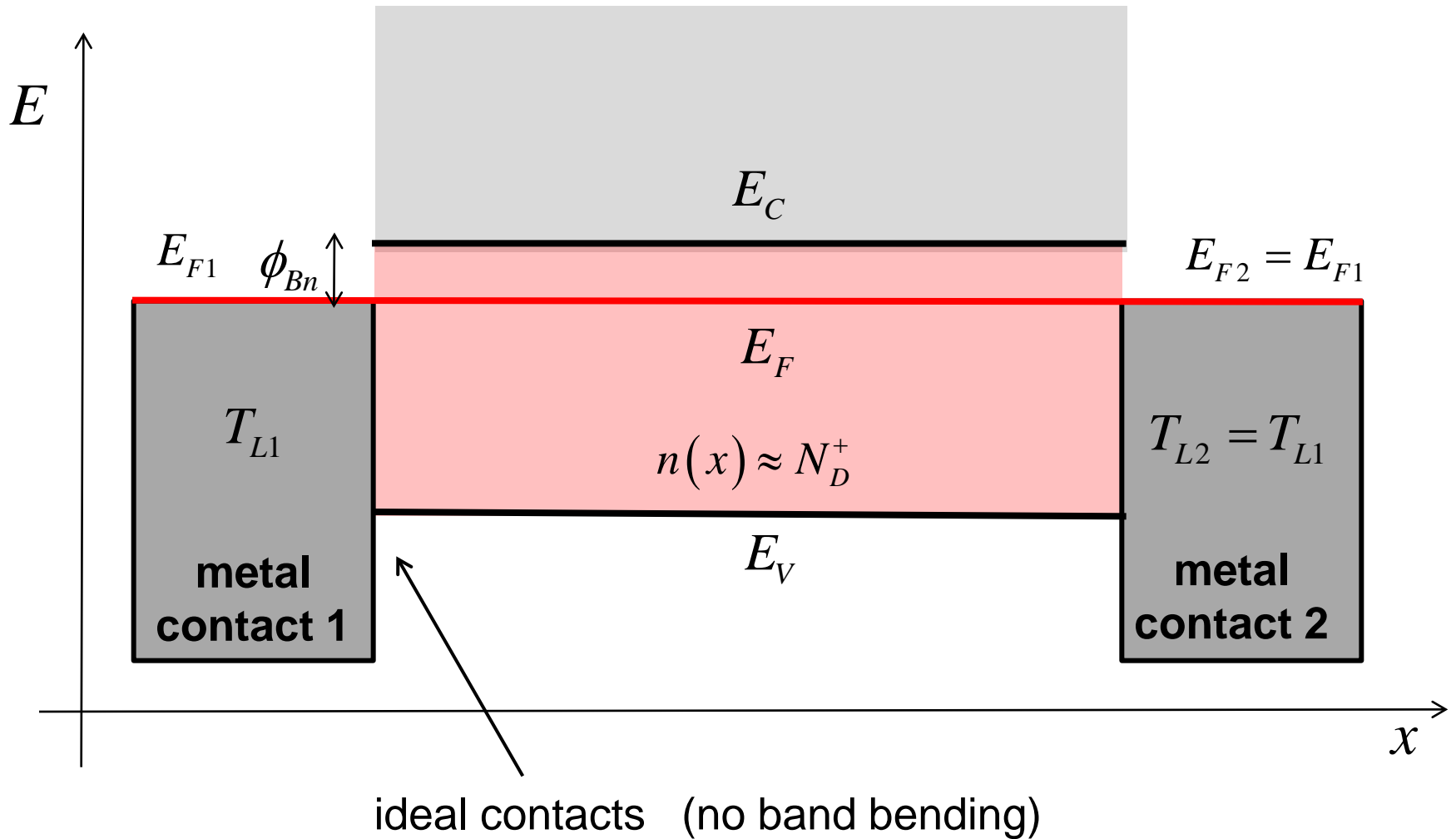
current is proportional to  $(f_1 - f_2)$



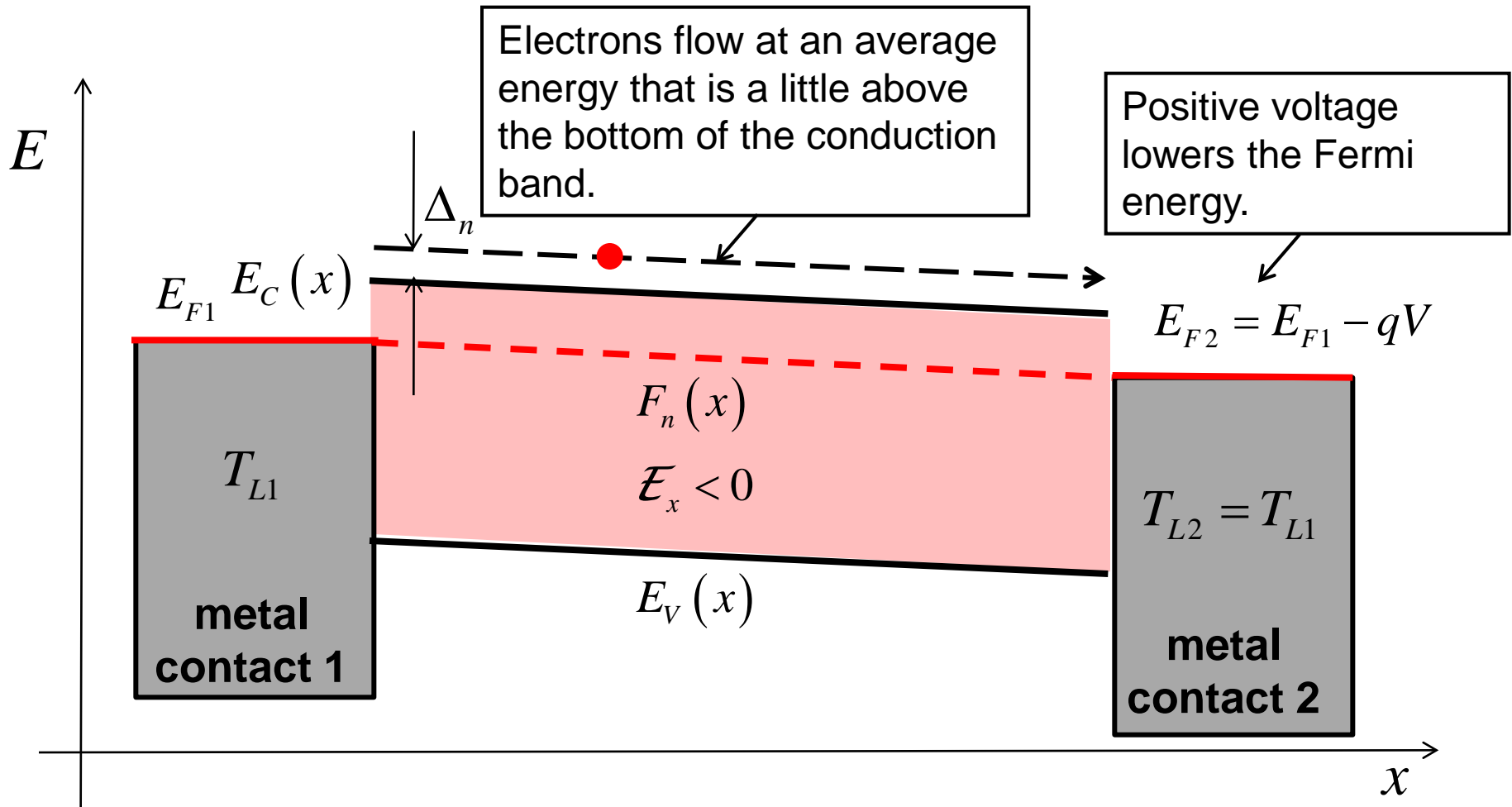
$$f(E) = \frac{1}{1 + e^{(E - E_F)/k_B T_L}}$$

Fermi-Dirac statistics

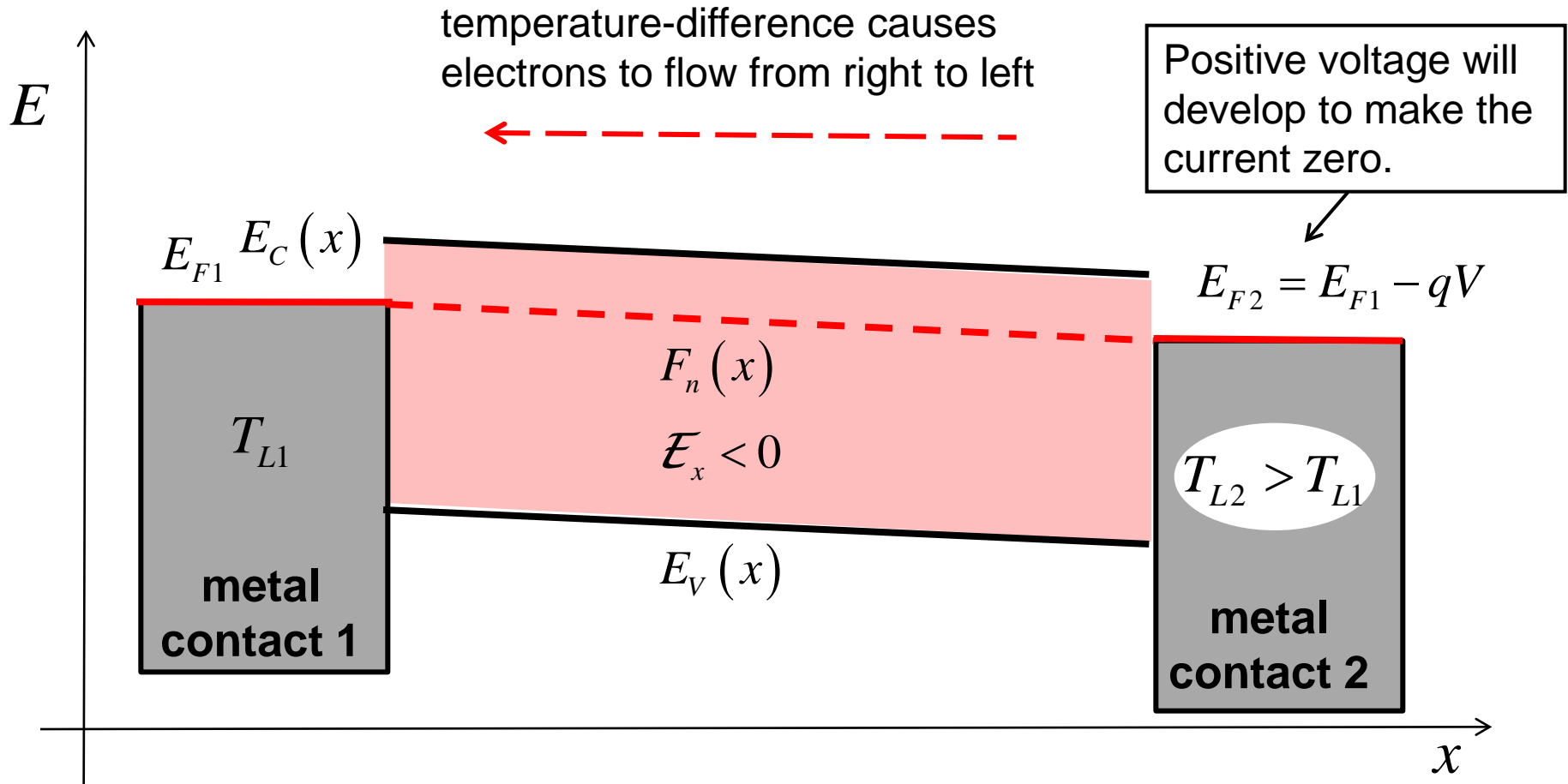
# n-type semiconductor: equilibrium, $V = 0$



# n-type semiconductor: isothermal, $V > 0$

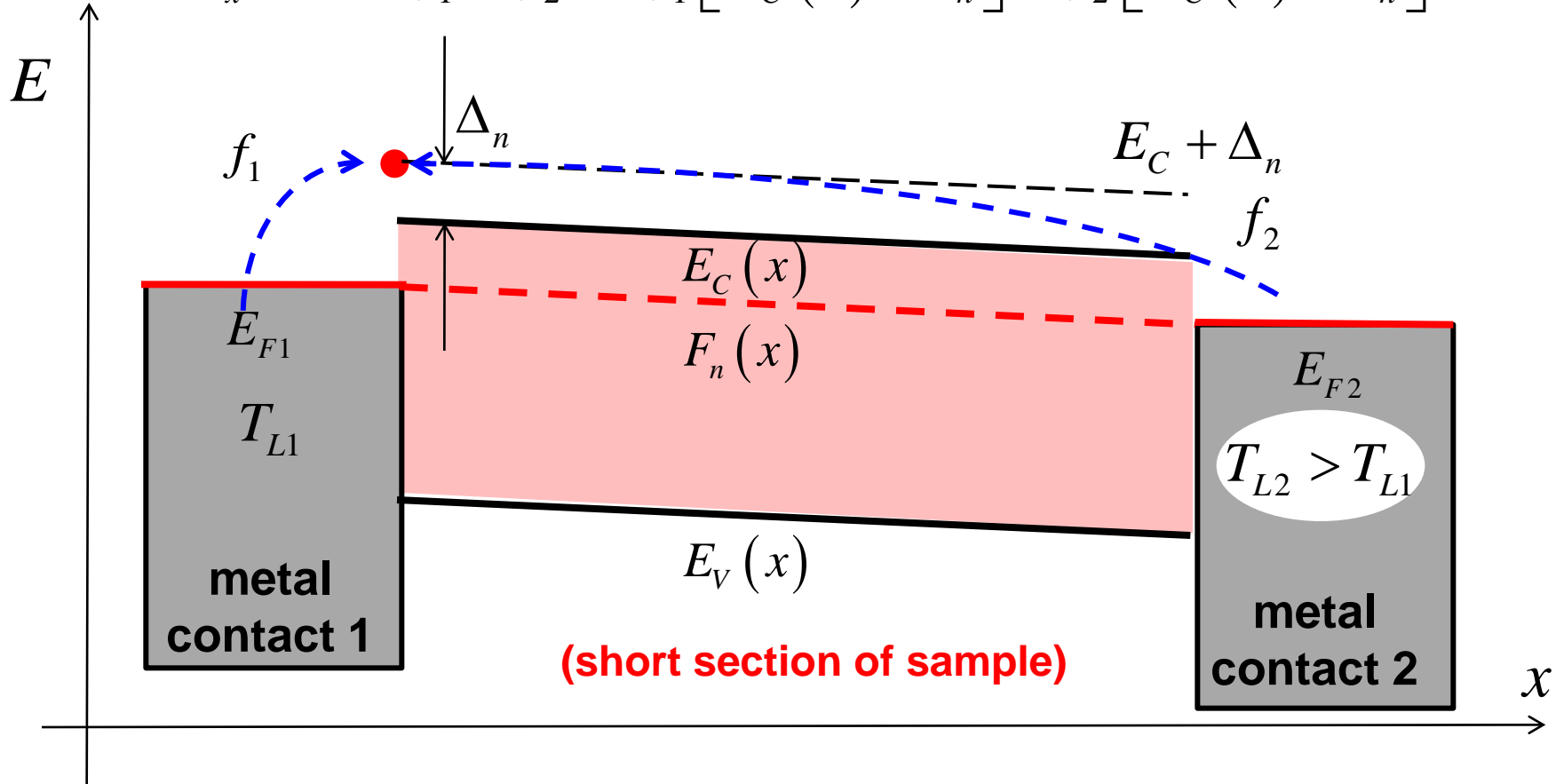


# Seebeck effect



# Seebeck effect (ii)

$$J_x = 0 \Rightarrow f_1 = f_2 \Rightarrow f_1 [E_C(0) + \Delta_n] = f_2 [E_C(0) + \Delta_n]$$



$$E_{F2} = E_{F1} - q\delta V$$

# Seebeck coefficient

$$J_x = 0 \Rightarrow f_1 [E_C(0) + \Delta_n] = f_2 [E_C(0) + \Delta_n] \quad E_{F2} = E_{F1} - q\delta V$$

$$\frac{1}{1 + e^{(E_C + \Delta_n - E_{F1})/k_B T_{L1}}} = \frac{1}{1 + e^{(E_C + \Delta_n - E_{F1} + q\delta V)/k_B T_{L2}}}$$

$$\frac{(E_C + \Delta_n - E_{F1})}{k_B T_{L1}} = \frac{(E_C + \Delta_n - E_{F1} + q\delta V)}{k_B T_{L2}}$$

$$\delta V = \frac{E_C(0) + \Delta_n - E_{F1}}{qT_{L1}} \delta T_L = -S_n \delta T_L$$

$$\delta V = -S_n \delta T_L$$

$$S_n = -\frac{[E_C(0) + \Delta_n - E_{F1}]}{qT_{L1}}$$

$$S_n = -\frac{[\langle E_J \rangle - E_{F1}]}{qT_{L1}}$$

(by convention, S is negative for *n*-type semiconductors.)



# Seebeck coefficient summary

$$\delta V = -S_n \delta T_L$$

$$S_n = -\frac{(E_C + \Delta_n - E_F)}{qT_{L1}} = -\frac{\langle E_J \rangle - E_F}{qT_{L1}}$$

$$S_n = \left( \frac{k_B}{-q} \right) \left\{ \frac{(E_C - E_F)}{k_B T_{L1}} + \delta_n \right\}$$

$$\delta_n = \Delta_n / k_B T_{L1} \quad (\text{bandstructure / scattering})$$

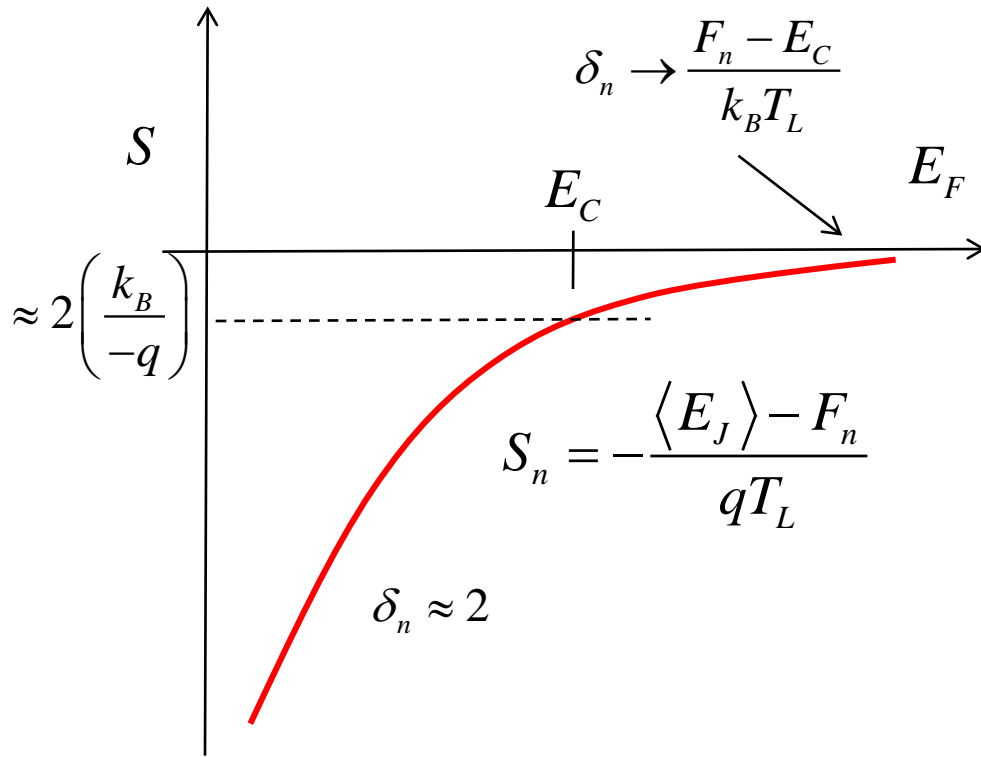
(by convention, S is negative for n-type semiconductors.)

$$\left( \frac{k_B}{q} \right) = 86 \mu\text{V/K}$$

$$\delta_n \approx 2 \quad (\text{3D, non-degenerate})$$

$$\delta_n \rightarrow \frac{E_F - E_C}{k_B T_L} \quad (\text{degenerate})$$

# Seebeck coefficient summary



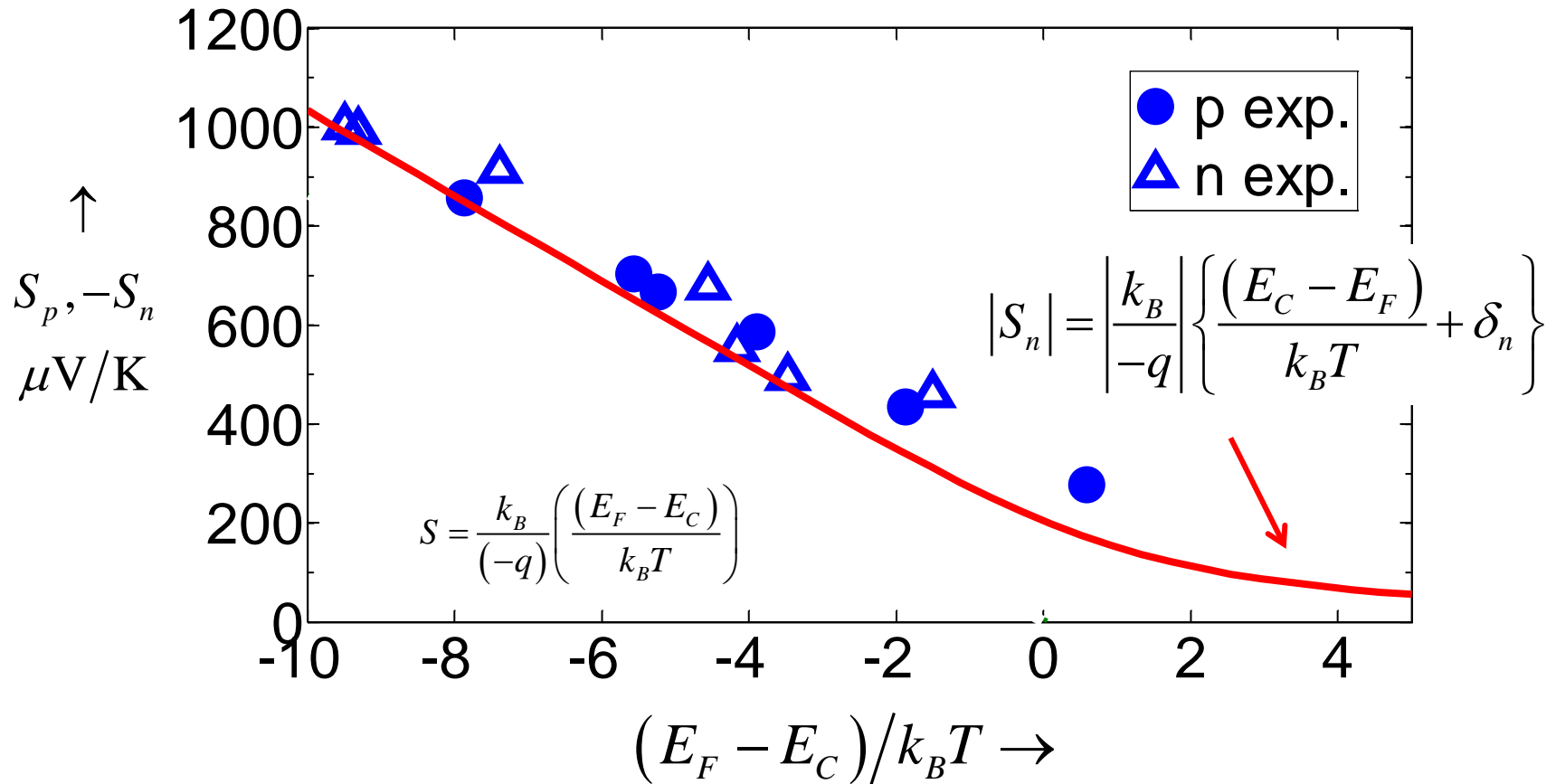
$$\frac{d(F_n/q)}{dx} = \rho_n J_{nx} + S_n(T_L) \frac{dT_L}{dx}$$

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

$$\Delta V = \int_{T_{L1}}^{T_{L2}} S_n(T_L) dT_L \quad (J_{nx} = 0)$$

The Seebeck coefficient (or “thermopower”) is proportional to the difference between the energy at which current flows and the Fermi energy.

# Seebeck coefficient of Ge



Exp. data: T.H. Geballe and G.W. Hull, "Seebeck Effect in Germanium," *Physical Review*, **94**, 1134, 1954.

# outline

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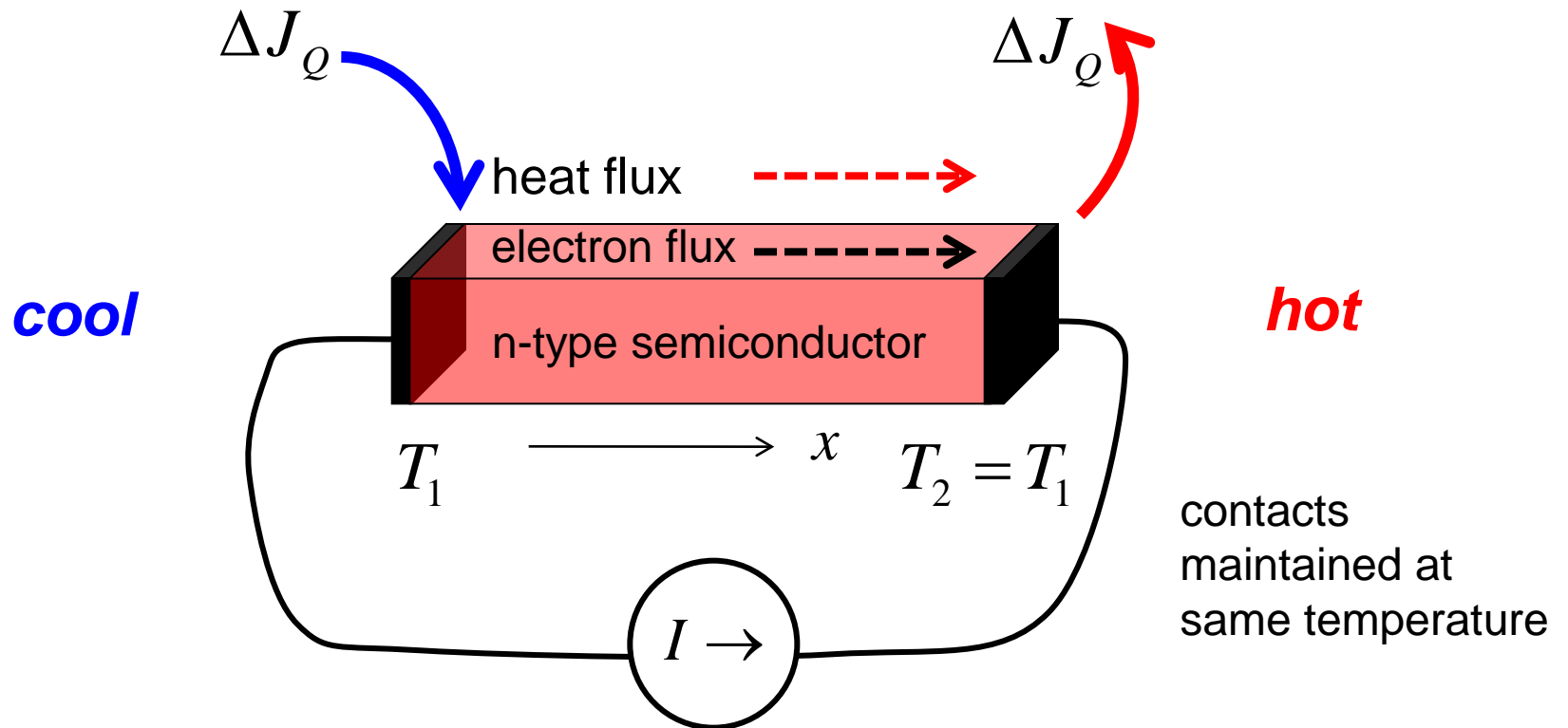
- 1) Introduction
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# the Peltier effect

$$J_n < 0$$

$$J_n / (-q) > 0$$

$$J_Q = \pi_n J_n > 0$$



# understanding the Peltier effect

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## Questions:

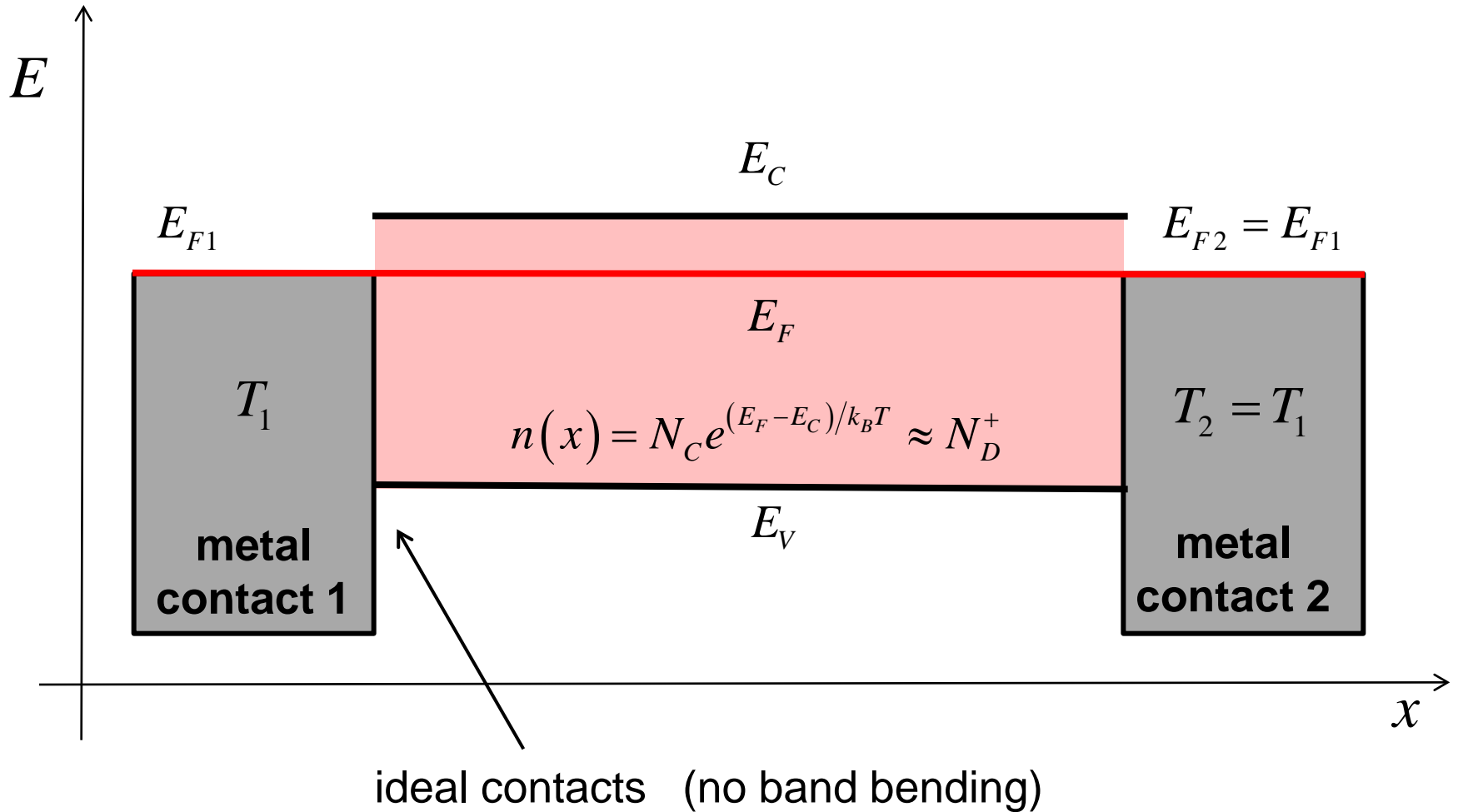
Why does  $J_Q = \pi_n J_n$  ?

(when the two contacts are at the same temperature)

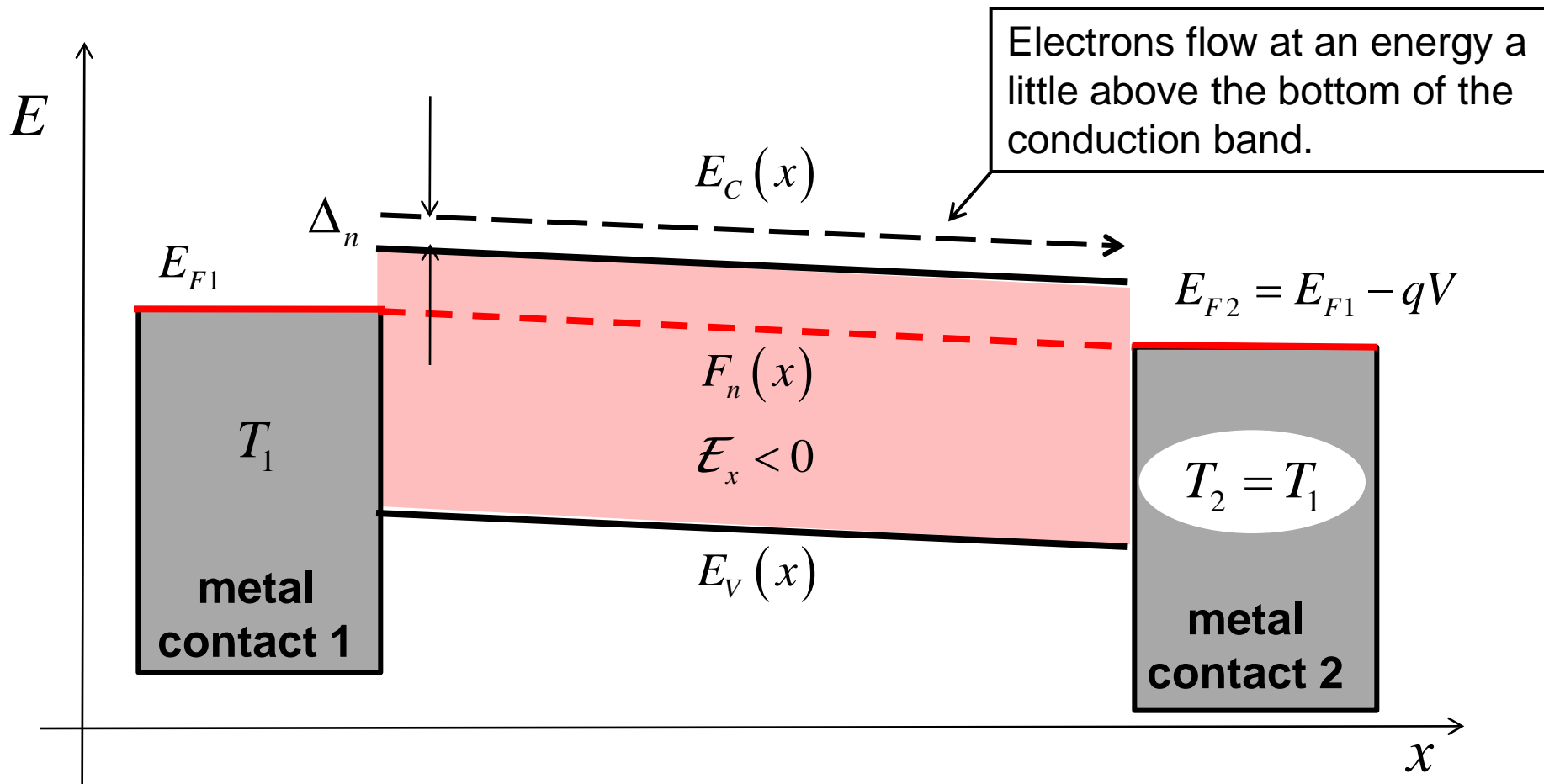
What determines the Peltier coefficient,  $\pi_n$  ?

**Answer:** We should draw an energy band diagram.

# N-type semiconductor: equilibrium, $V = 0$

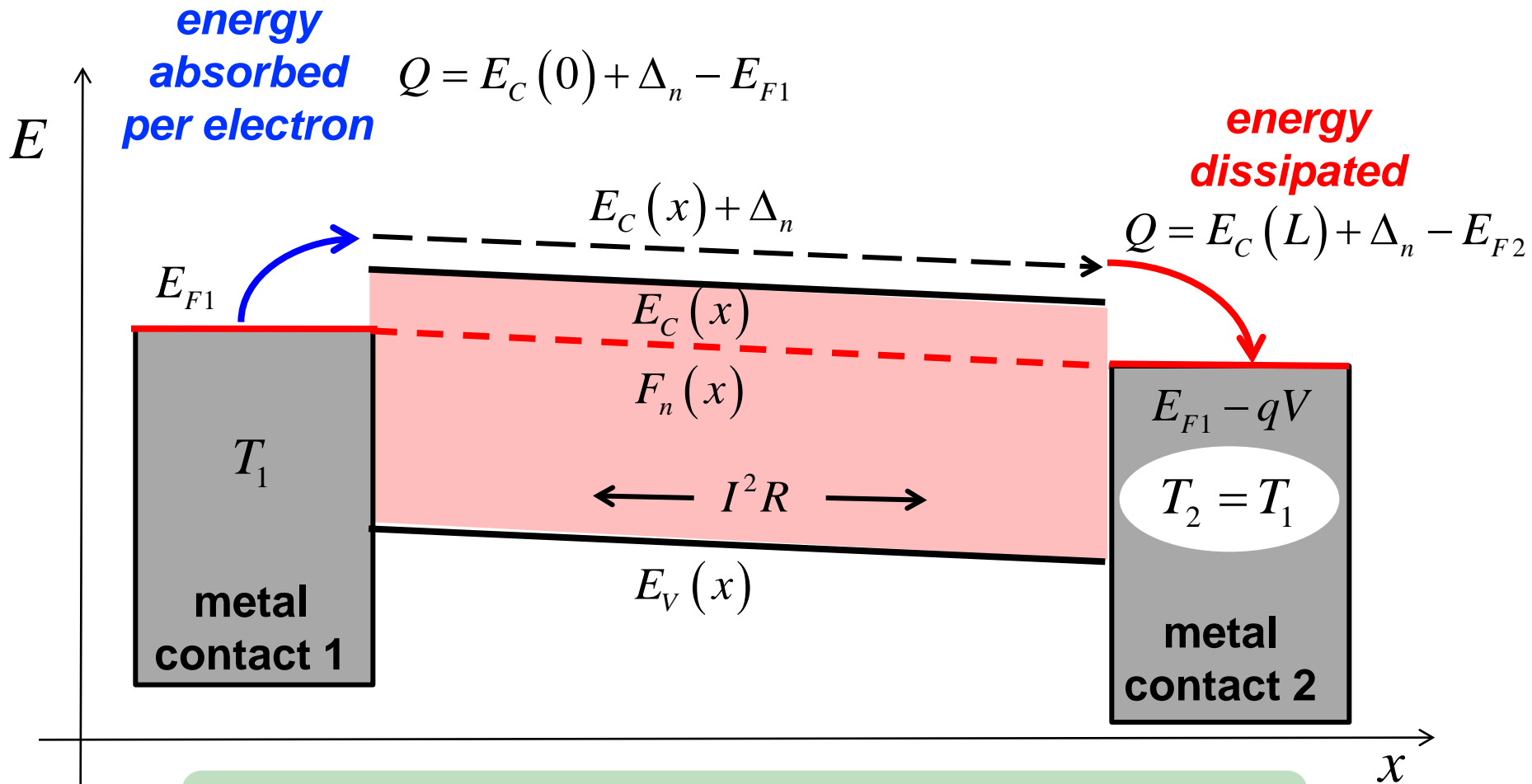


# N-type semiconductor: isothermal, $V > 0$





# N-type semiconductor: isothermal, $V > 0$



heat is absorbed (emitted) when the average energy at which the heat current flows increases (decreases)

# Peltier coefficient

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- 1) Electrons flow from left to right when  $V_2 > V_1$ .
- 2) The flux of electrons from left to right is  $J_{nx}/(-q)$
- 3) Each electron absorbs and then carries an amount of heat:  $Q = E_C(0) + \Delta_n - E_{F1}$
- 4) So the heat flux from left to right is:

$$J_{Q1} = [E_C(0) + \Delta_n - E_{F1}] \times J_{nx}/(-q) = \pi_n J_{nx}$$

$$\pi_n = -\frac{[E_C(0) + \Delta_n - E_{F1}]}{q} \quad (\text{less than zero for an n-type semiconductor})$$

## a remarkable result

$$\pi_n = -\frac{(E_C + \Delta_n - E_F)}{q}$$

$$\pi_n = T_L \left( \frac{k_B}{-q} \right) \left\{ \frac{(E_C - E_F)}{k_B T_L} + \frac{\Delta_n}{k_B T_L} \right\}$$

$$S_n = \left( \frac{k_B}{-q} \right) \left\{ \frac{(E_C - E_F)}{k_B T} + \frac{\Delta_n}{k_B T} \right\}$$

$$\pi_n = T_L S_n \quad \text{“Kelvin relation”}$$

The Peltier coefficient is proportional to the difference between the energy at which current flows and the Fermi energy – just as the Seebeck coefficient was.

# outline

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# basic equations of thermoelectricity

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

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

Four transport coefficients:

- 1) resistivity ( $\Omega\text{-cm}$ ) = 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. Phonons also carry heat.

# electrical conductivity

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

$$\sigma'_n(E) = \frac{2q^2}{h} M_{3D}(E) \lambda(E) \left( -\frac{\partial f_0}{\partial E} \right)$$

The Units of the differential conductivity are S/m-J

$M_{3D}(E)$  is the number of channel per cross-sectional area at energy,  $E$ .

# Seebeck coefficient

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

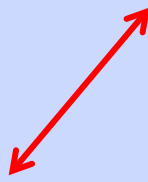
$$\delta_n = \frac{E_J - E_C}{k_B T_L}$$

$$\delta_n = \frac{\int \left( \frac{E - E_c}{k_B T_L} \right) \sigma'_n(E) dE}{\int \sigma'_n(E) dE}$$

# Peltier coefficient

$$\pi_n = T_L S_n (T_L) \quad \text{Kelvin relation}$$

*Onsager*  
relations for  
coupled flows

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




# electronic heat conductivity

$$\kappa_n = T_L \sigma_n L \quad L \text{ is the "Lorenz number"}$$

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

# lattice thermal conductivity

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$$J_q = \pi_n J_n - \kappa \frac{dT}{dx} \quad \kappa = \kappa_n + \kappa_L$$

Both electrons and lattice vibrations carry heat – we have been discussing the electronic part.

In metals, heat conduction by electrons dominates:  $\kappa_e \gg \kappa_L$

In semiconductors, lattice vibrations dominate:  $\kappa_L \gg \kappa_e$

# Example: TE transport parameters of n-Ge

$$\rho_n \quad \Omega\text{-m}$$

$$S_n \quad \text{V/K}$$

$$\pi_n \quad \text{W/A} = \text{V}$$

$$\kappa_n \quad \text{W/m-K}$$

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left( \frac{\text{V}}{\text{m}} \right)$$

$$J_{Qx} = \pi_n J_{nx} - \kappa \frac{dT_L}{dx} \quad (\text{W})$$

$$N_D = 10^{15} \text{ cm}^{-3}$$

$$T_L = 300 \text{ K}$$

$$\mu_n = 3200 \text{ cm}^2/\text{V-s}$$

$$n_0 = N_C e^{(E_F - E_c)/k_B T_L} \approx N_D$$

$$N_C = 1.04 \times 10^{19} \text{ cm}^{-3}$$

# TE transport parameters of n-Ge: resistivity

$$\rho_n \quad \Omega\text{-m}$$

$$S_n \quad \text{V/K}$$

$$\pi_n \quad \text{W/A} = \text{V}$$

$$\kappa_n \quad \text{W/m-K}$$

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left( \frac{\text{V}}{\text{m}} \right)$$

$$J_{Qx} = \pi_n J_{nx} - \kappa_n \frac{dT_L}{dx} \quad (\text{W})$$

$$N_D = 10^{15} \text{ cm}^{-3} \approx n_0$$

$$\mu_n = 3200 \text{ cm}^2/\text{V-s}$$

$$\sigma_n = n_0 q \mu_n \quad \text{S/cm}$$

$$\rho_n = 1/n_0 q \mu_n \approx 2 \text{ } \Omega\text{-cm}$$

# TE transport parameters of n-Ge: Seebeck coeff.

$$\rho_n = 2\Omega\text{-m}$$

$$S_n \quad \text{V/K}$$

$$\pi_n \quad \text{W/A} = \text{V}$$

$$\kappa_n \quad \text{W/m-K}$$

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left( \frac{\text{V}}{\text{m}} \right)$$

$$J_{Qx} = \pi_n J_{nx} - \kappa_n \frac{dT_L}{dx} \quad (\text{W})$$

$$N_D = 10^{15} \text{ cm}^{-3} \approx n_0$$

$$n_0 = N_C e^{(E_F - E_c)/k_B T_L}$$

$$N_C = 1.04 \times 10^{19} \text{ cm}^{-3}$$

$$T_L = 300 \text{ K}$$

$$(E_c - E_F)/k_B T_L \approx \ln(N_C/n_0) \approx 9.3$$

$$\delta_n \approx 2 \quad (\text{non-degenerate, 3D})$$

$$S_n = \left( \frac{k_B}{-q} \right) \left\{ \frac{(E_c - E_F)}{k_B T_L} + \delta_n \right\} \approx -970 \mu\text{V/K}$$

# TE transport parameters of n-Ge: Peltier coeff.

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$$\rho_n = 2\Omega\text{-m}$$

$$S_n = -970 \text{ V/K}$$

$$\pi_n \quad \text{W/A} = \text{V}$$

$$\kappa_n \quad \text{W/m-K}$$

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left( \frac{\text{V}}{\text{m}} \right)$$

$$J_{Qx} = \pi_n J_{nx} - \kappa \frac{dT_L}{dx} \quad (\text{W})$$



$$\pi_n = T_L S_n \approx -0.3 \text{ V}$$

# TE transport parameters of n-Ge: Peltier coeff.

$$\rho_n = 2\Omega\text{-m}$$

$$S_n = -970 \text{ V/K}$$

$$\pi_n = -0.3 \text{ W/A} = \text{V}$$

$$\kappa_n \text{ W/m-K}$$

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left( \frac{\text{V}}{\text{m}} \right)$$

$$J_{Qx} = \pi_n J_{nx} - \kappa_n \frac{dT_L}{dx} \quad (\text{W})$$



$$\frac{\kappa_n}{T_L \sigma_n} = L \quad (\text{Lorenz number})$$

$$L \approx 2(k_B/q)^2 \quad (\text{non-degenerate, 3D})$$

$$\sigma_n = 1/\rho_n$$

$$\kappa_n = 2.2 \times 10^{-4} \text{ W/m-K}$$

# TE transport parameters of n-Ge:

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$$\rho_n = 2\Omega\text{-m}$$

$$S_n = -970 \text{ V/K}$$

$$\pi_n = -0.3 \text{ W/A} = \text{V}$$

$$\kappa_n = 2.2 \times 10^{-4} \text{ W/m-K}$$

$$\mathcal{E}_x = \rho_n J_{nx} + S_n \frac{dT_L}{dx} \quad \left( \frac{\text{V}}{\text{m}} \right)$$

$$J_{Qx} = \pi_n J_{nx} - \kappa \frac{dT_L}{dx} \quad (\text{W})$$

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All of these parameters depend on the temperature and carrier concentration (Fermi level).

Note also:

$$\kappa_L = 58 \text{ W/m-K} \gg \kappa_n$$

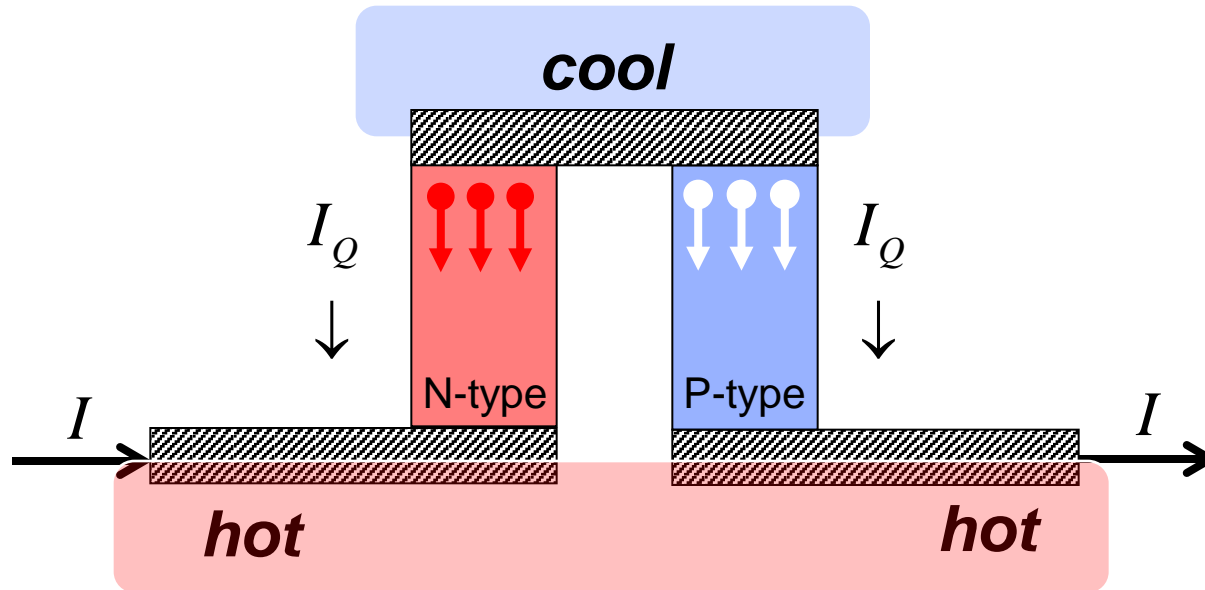


# outline

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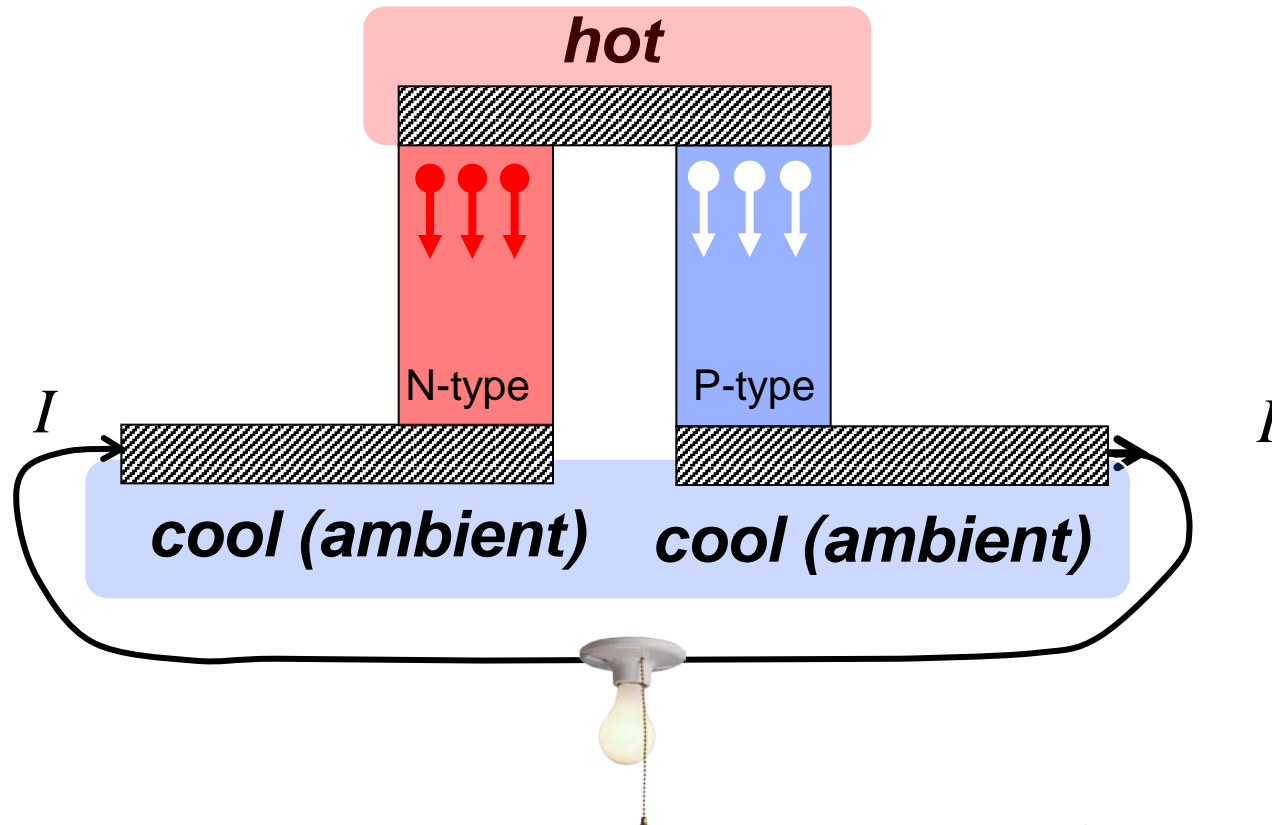
- 1) Introduction
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# thermoelectric cooling



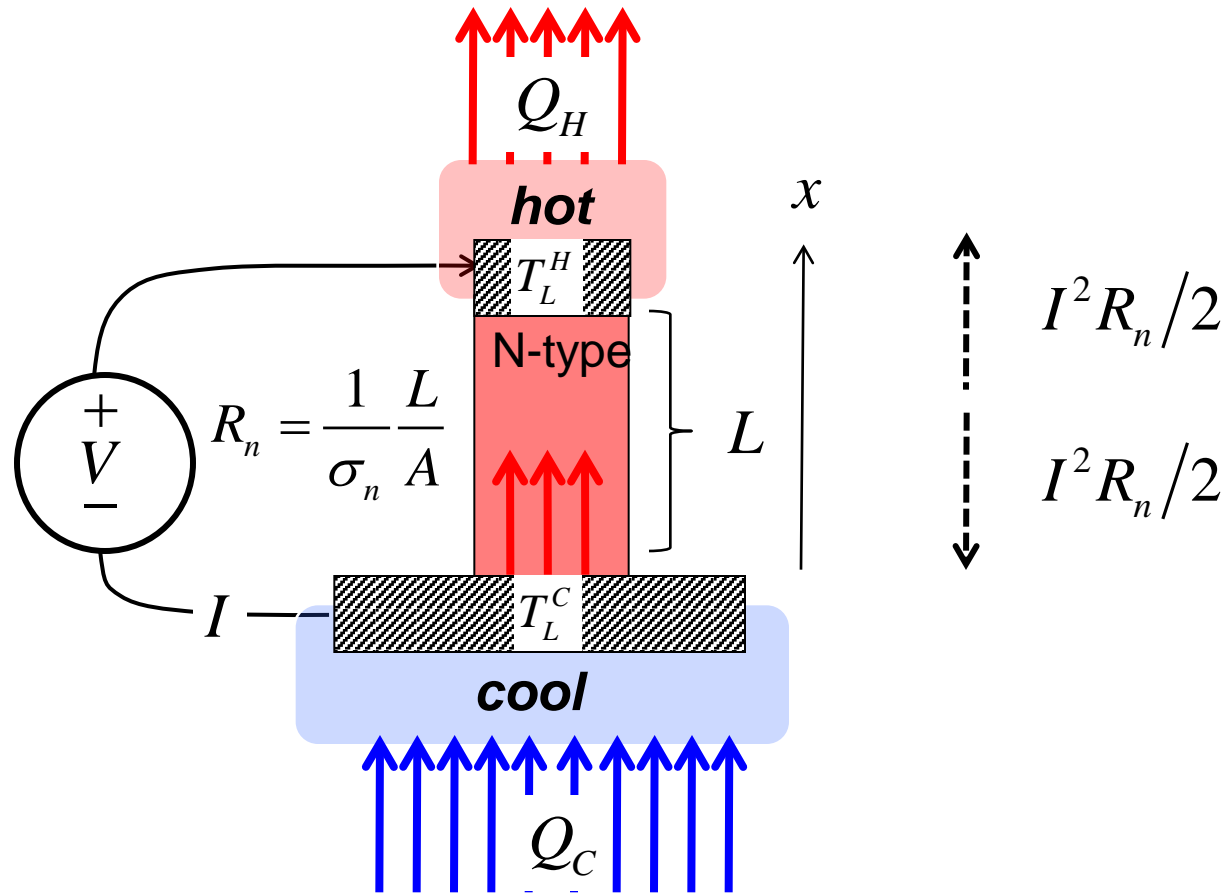
- 1) What determines the maximum temperature difference?
- 2) How much heat can be pumped?
- 3) What is the coefficient of performance?

# thermoelectric power generation

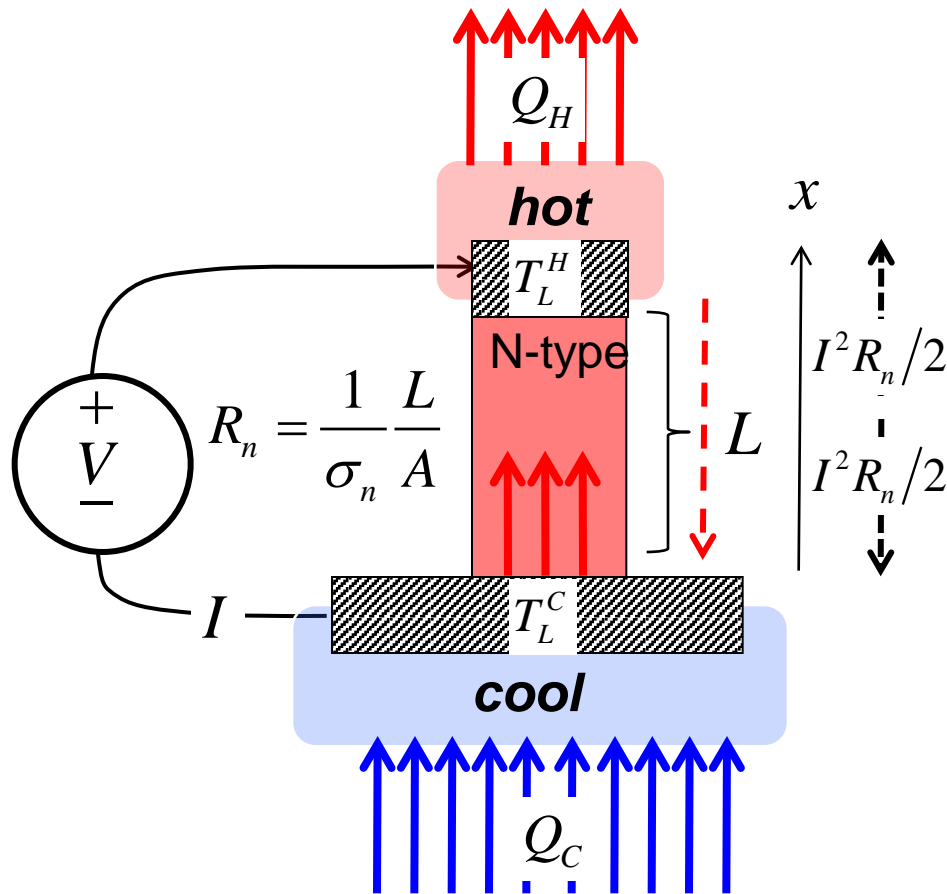


- 1) How much heat can be converted into electricity?  
(what determines the efficiency?)

# simplified TE device (one leg)



# simplified TE cooling device (one leg)



1) heat extracted from the cold side

=

2) heat pumped by Peltier effect

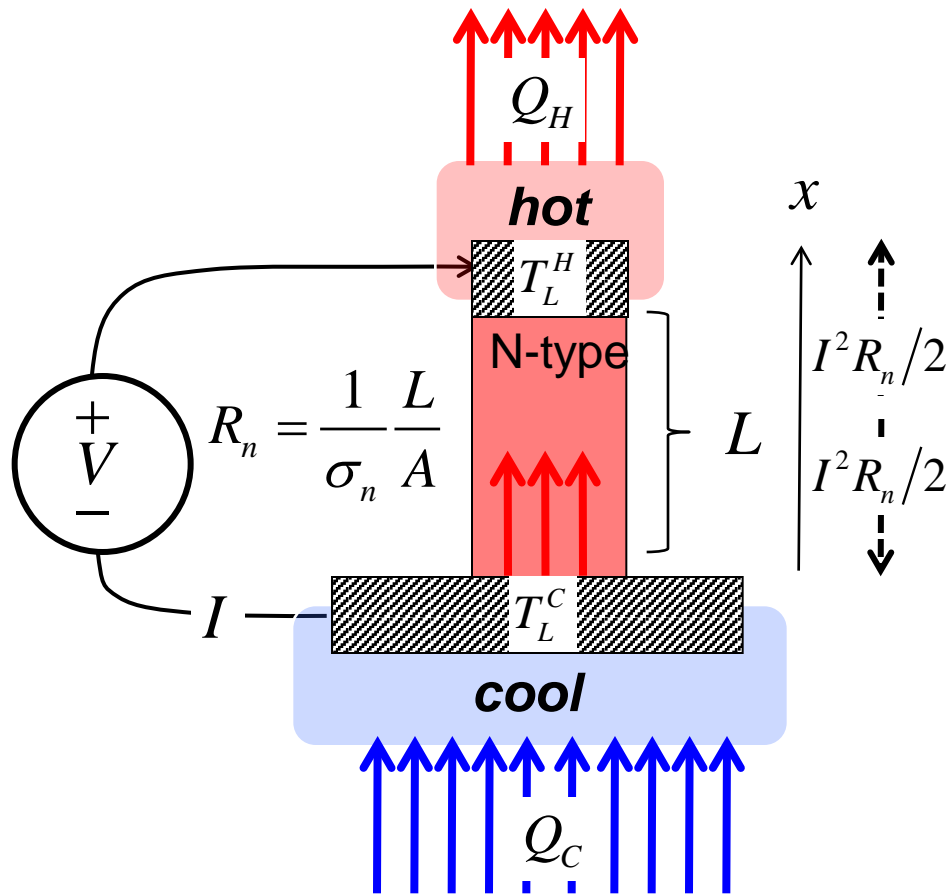
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3) heat diffusing down the thermal gradient

-

4) heat generated by Joule heating

# simplified TE cooling device (one leg)



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

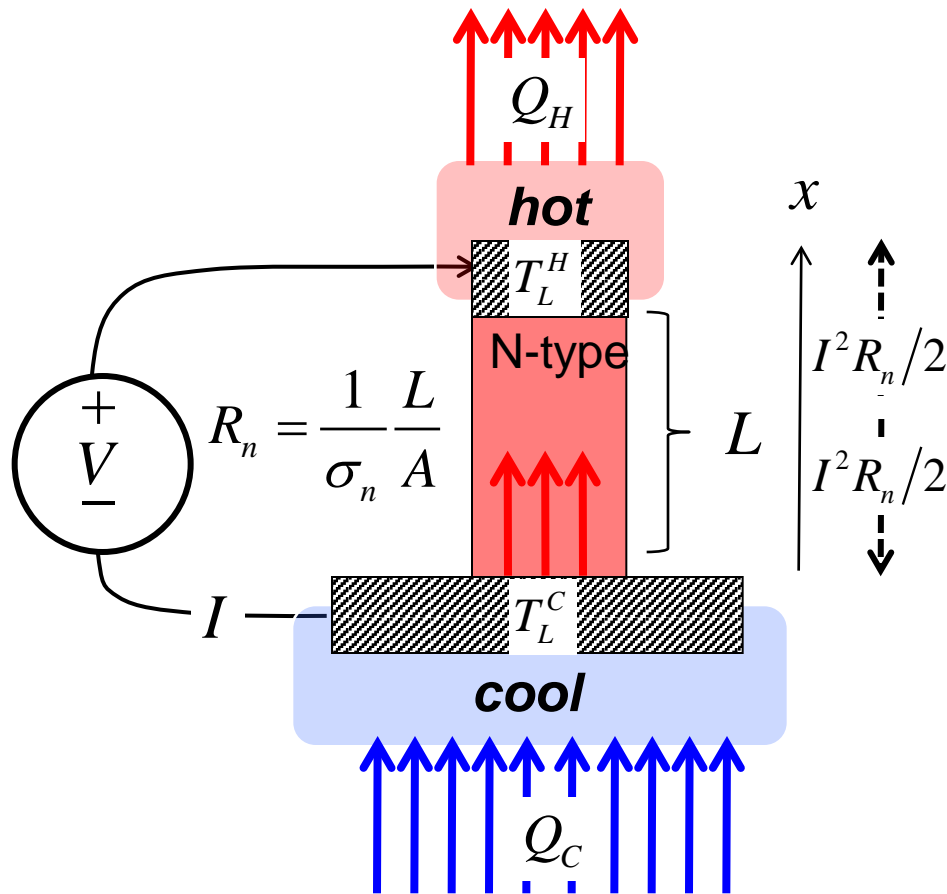
$$\frac{dQ_C}{dI} = 0 \rightarrow I_{\max}, Q_{C\max}$$

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

$$\Delta T_{\max} = \frac{1}{2} Z (T_L^C)^2 \quad Z = \frac{S_n^2 \sigma_n}{\kappa}$$

TE figure of merit (FOM)

# cooling efficiency (COP)



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

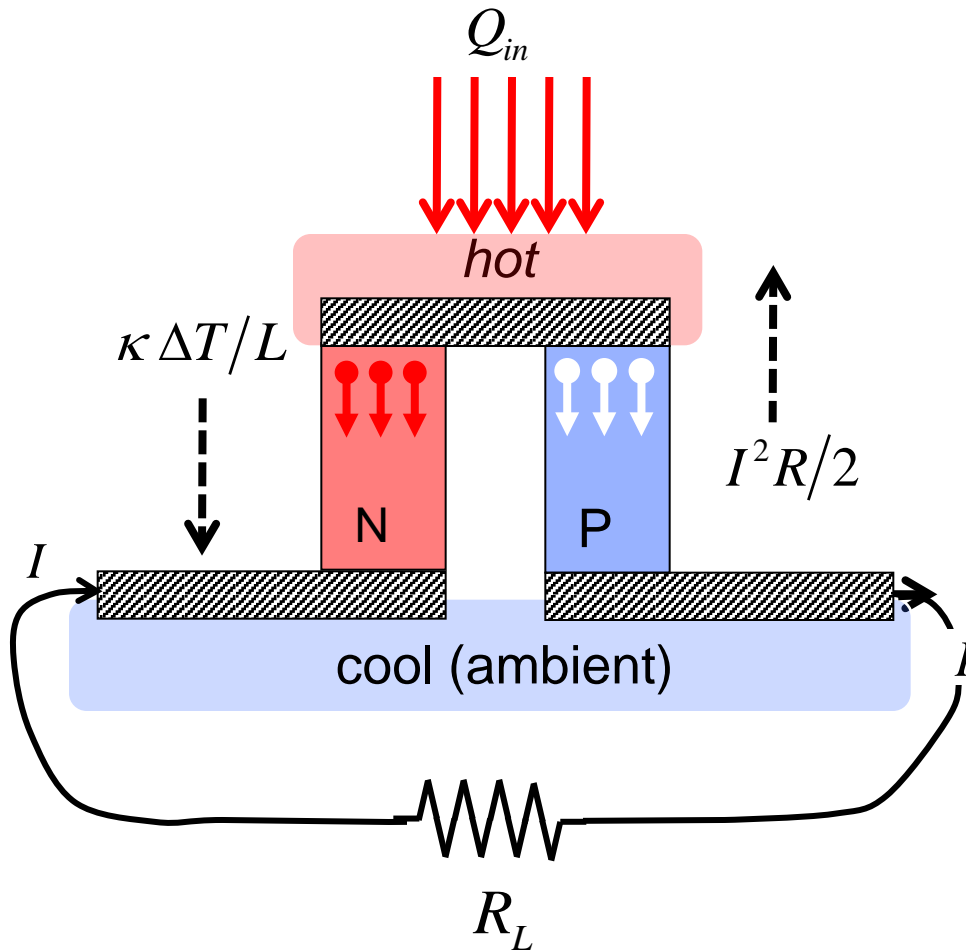
$$\frac{dQ_C}{dI} = 0 \rightarrow I_{\max}, Q_{C\max}$$

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

COP at maximum cooling power:

$$\eta = \frac{Q_{C\max}}{P_{in}} = f(T_L^C, T_L^H, Z)$$

# 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,  $Z$ .



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# FOM

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

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

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:

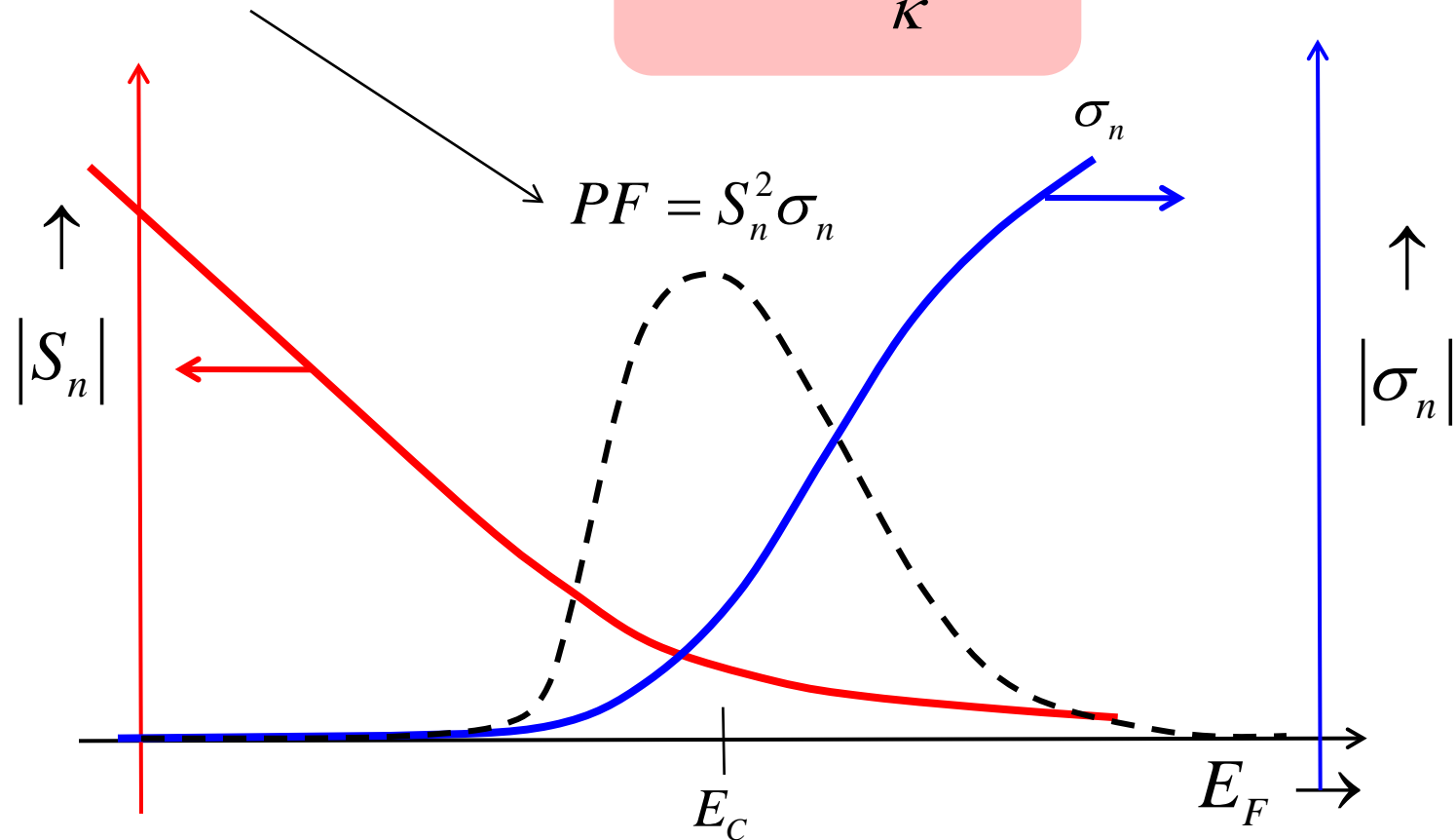
$$\kappa_L \gg \kappa_n$$

Mostly determined by lattice thermal conductivity. (Lecture 9)

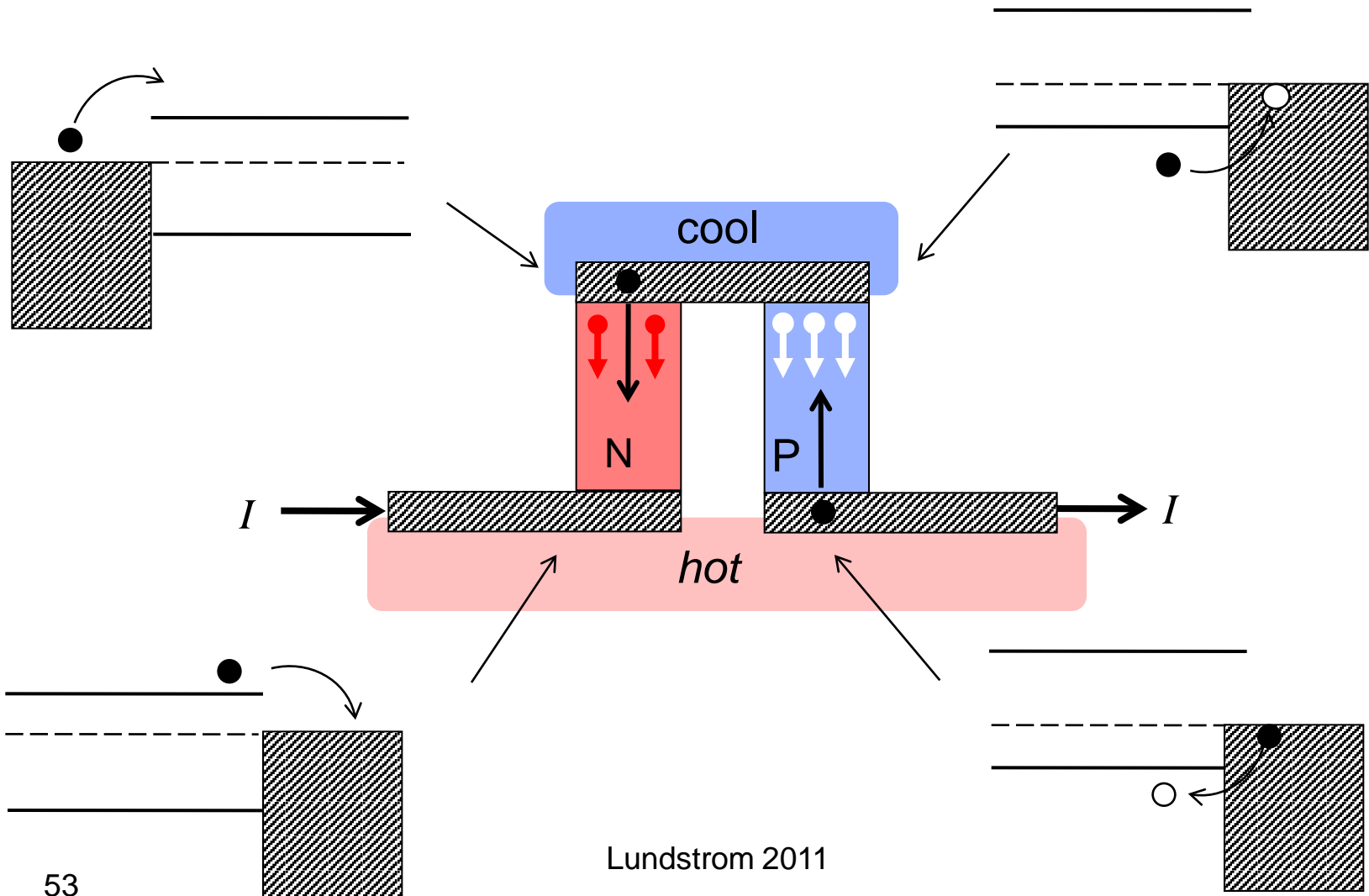
# FOM: PF vs. Fermi level

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

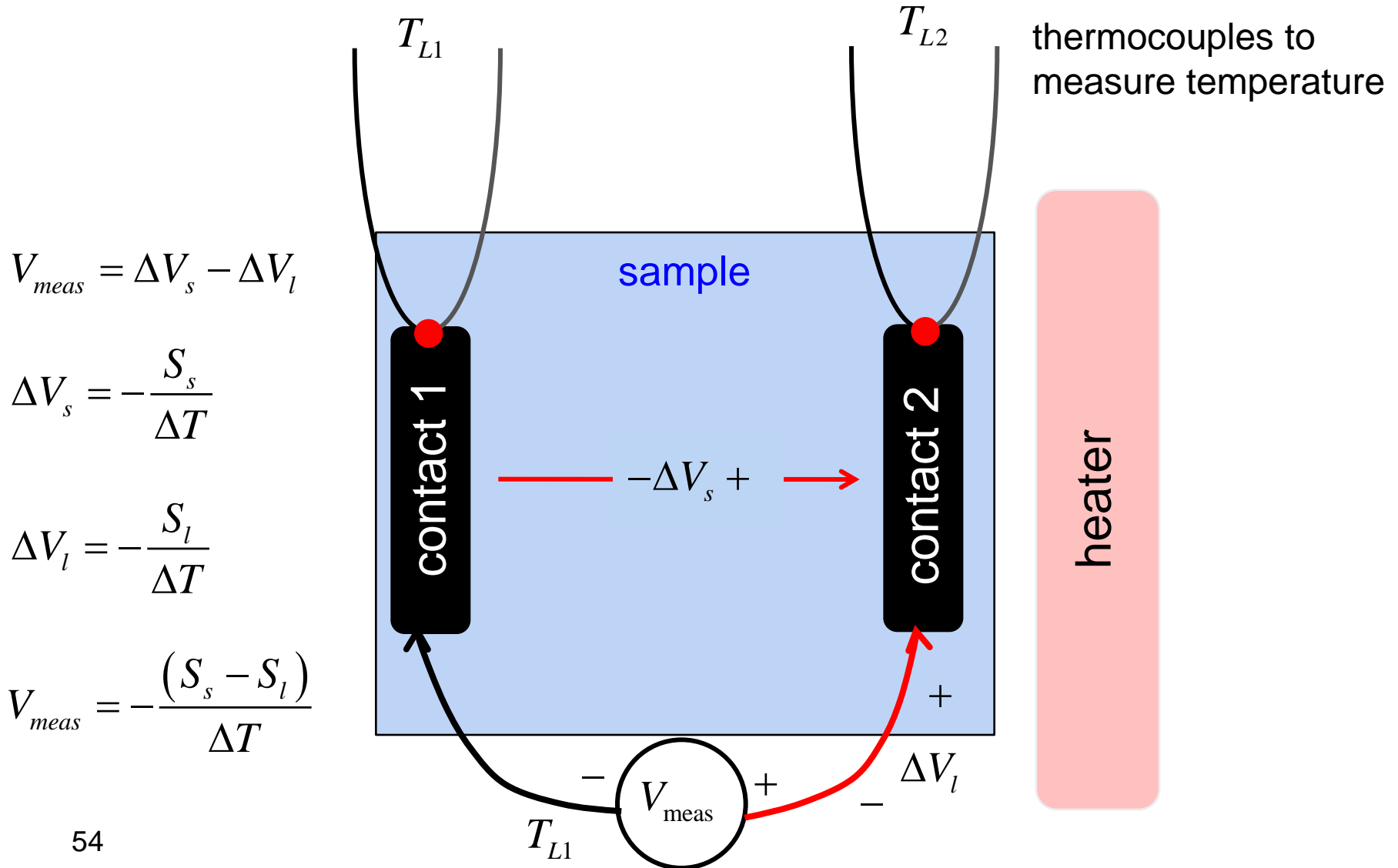
$$ZT = \frac{S_n^2 \sigma_n T_L}{\kappa}$$



# inside view of heat absorbtion/emission



# measuring S



# outline

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- 5) Discussion
- 6) **Summary**

# summary

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- 1) We have discussed the physics of thermoelectricity – the Seebeck and Peltier effects.
- 2) We have developed the basic equations that describe thermoelectricity.
- 3) We have discussed the four TE parameters
- 4) And we have introduced TE devices and the FOM



# questions

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- 1) Introduction
- 2) Current flow
- 3) Heat flow
- 4) Coupled flows
- 5) Discussion
- 6) Summary

