ECE-656: Fall 2011

Lecture 9: Thermoelectric Effects: charge flow

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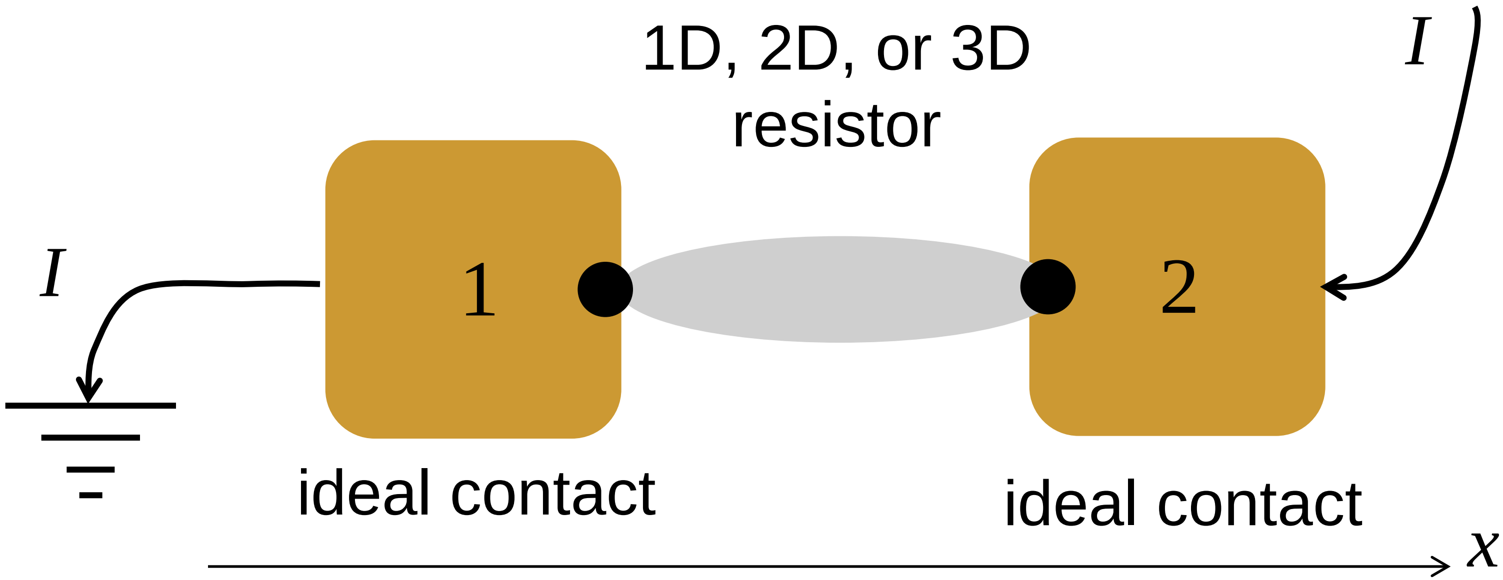
review



$$G = \frac{2q^2}{h}\int T(E)M(E)\left(-\frac{\partial f_0}{\partial E}\right)dE$$

$$G = \frac{2q^2}{h}\langle\langle T(E)\rangle\rangle\langle M(E)\rangle$$

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

$$G'(E) = \frac{2q^2}{h}T(E)M(E)\left(-\frac{\partial f_0}{\partial E}\right)$$

"differential conductance"

transport in the bulk (3D)

$$G = \frac{2q^2}{h}\int T(E)M(E)\left(-\frac{\partial f_0}{\partial E}\right)dE$$

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

$$G = \frac{2q^2}{h}\langle\langle T(E)\rangle\rangle\langle M(E)\rangle$$

$$G'(E) = \frac{2q^2}{h}T(E)M(E)\left(-\frac{\partial f_0}{\partial E}\right)$$

differential conductance

$$T(E) \rightarrow \lambda(E)/L$$

$$G = \sigma A/L$$

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

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

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

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

mathematical description of bulk transport

In Lecture 6 we saw that the electrical current in the bulk is:

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

Alternatively, we could write this equation in the inverted form as:

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

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

mathematical description

The answer is:

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

S_n is the Seebeck coefficient in V/K.

Alternatively, we can write this equation as:

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

(inverted form of the equations)

in this lecture…

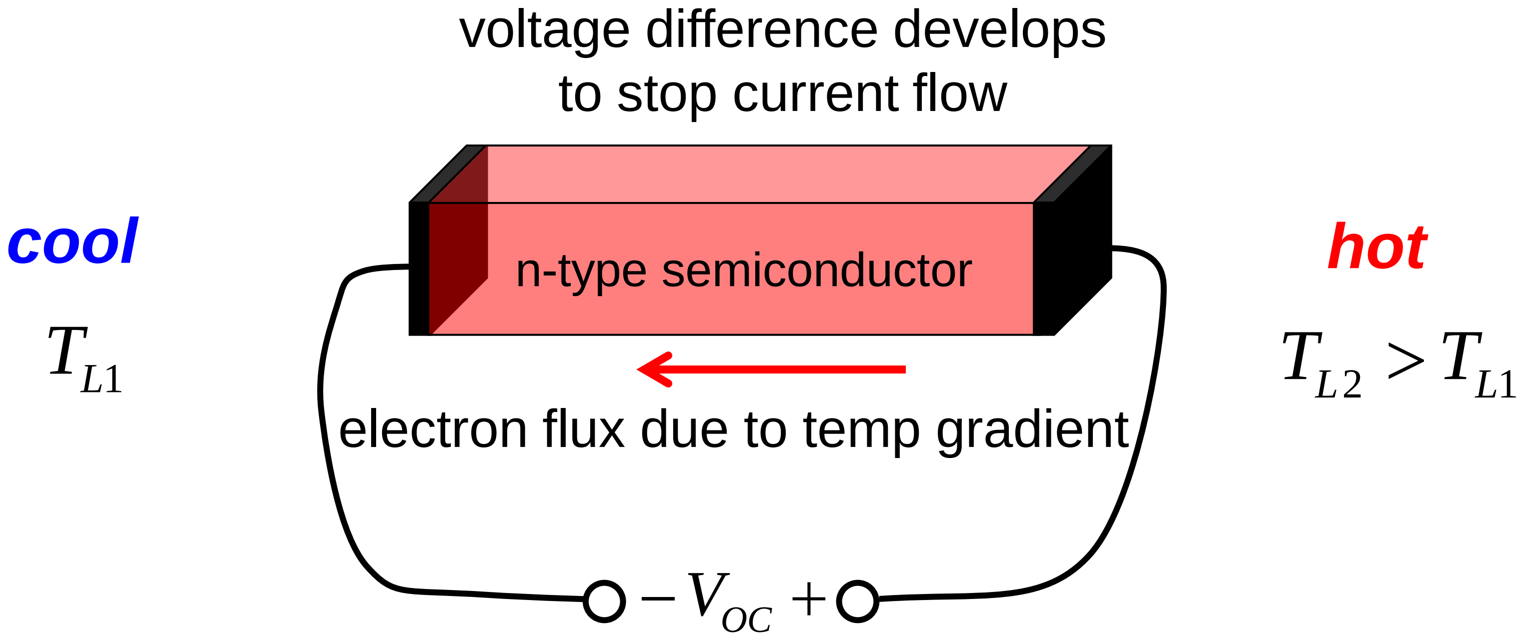
Our goal is to understand the physical origin of the **Seebeck coefficient** (which is also called the **thermopower**) and how it is mathematically related to the properties of the semiconductor.

outline

1) Introduction
2) **Charge transport in a temperature gradient**
3) Mathematical formulation
4) Discussion
5) Summary

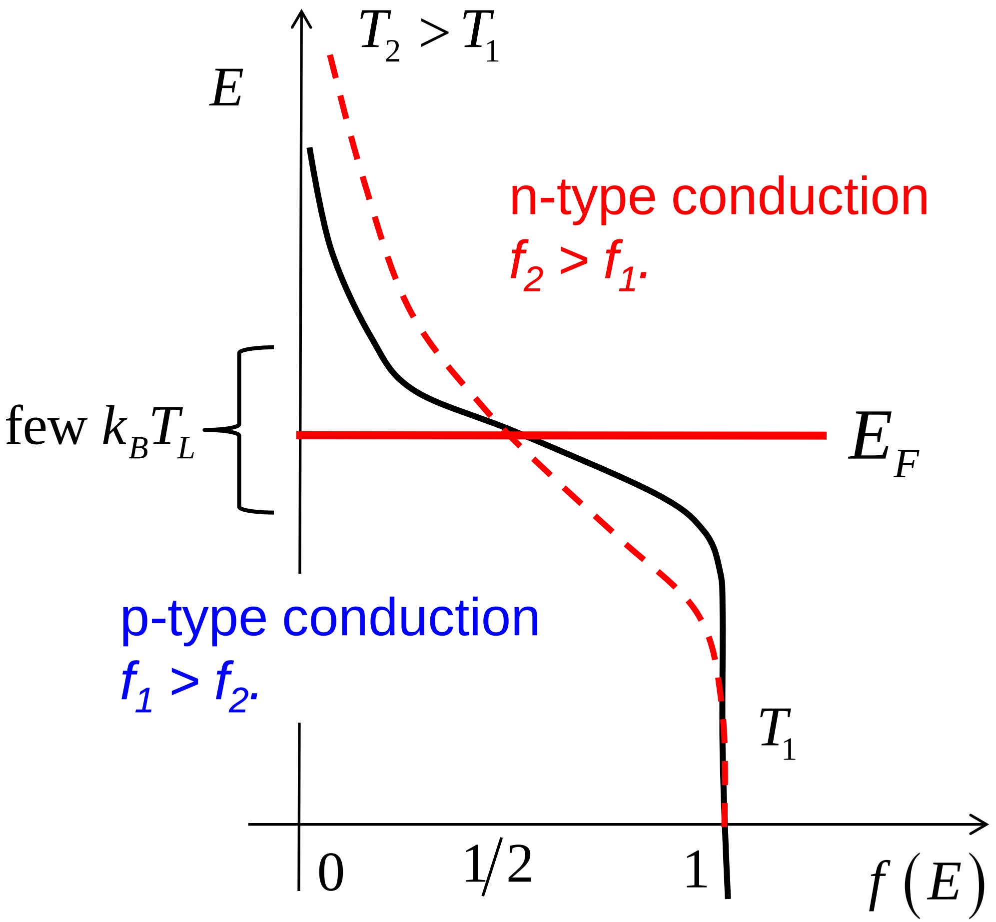
We will use an approach similar to that of Prof. Supriyo Datta,
Lessons from Nanoscience: A new approach to transport, World Scientific, 2011

temperature gradients and voltage



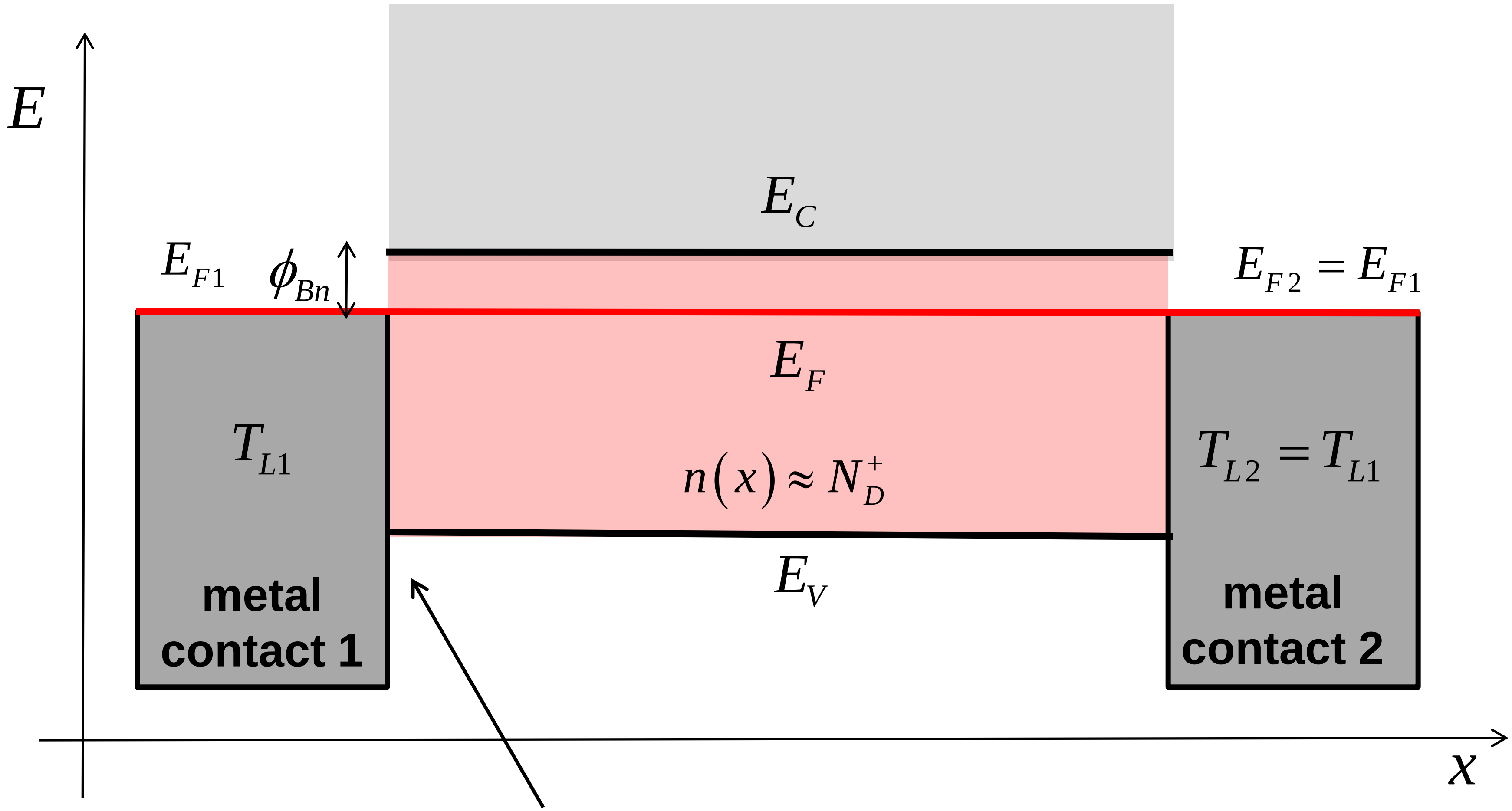
Temperature gradients give rise to an open circuit voltage, which is known as the Seebeck effect. We expect a **positive** voltage for an n-type semiconductor (and **negative** voltage for a p-type semiconductor.)

current is proportional to ($f_1 - f_2$)



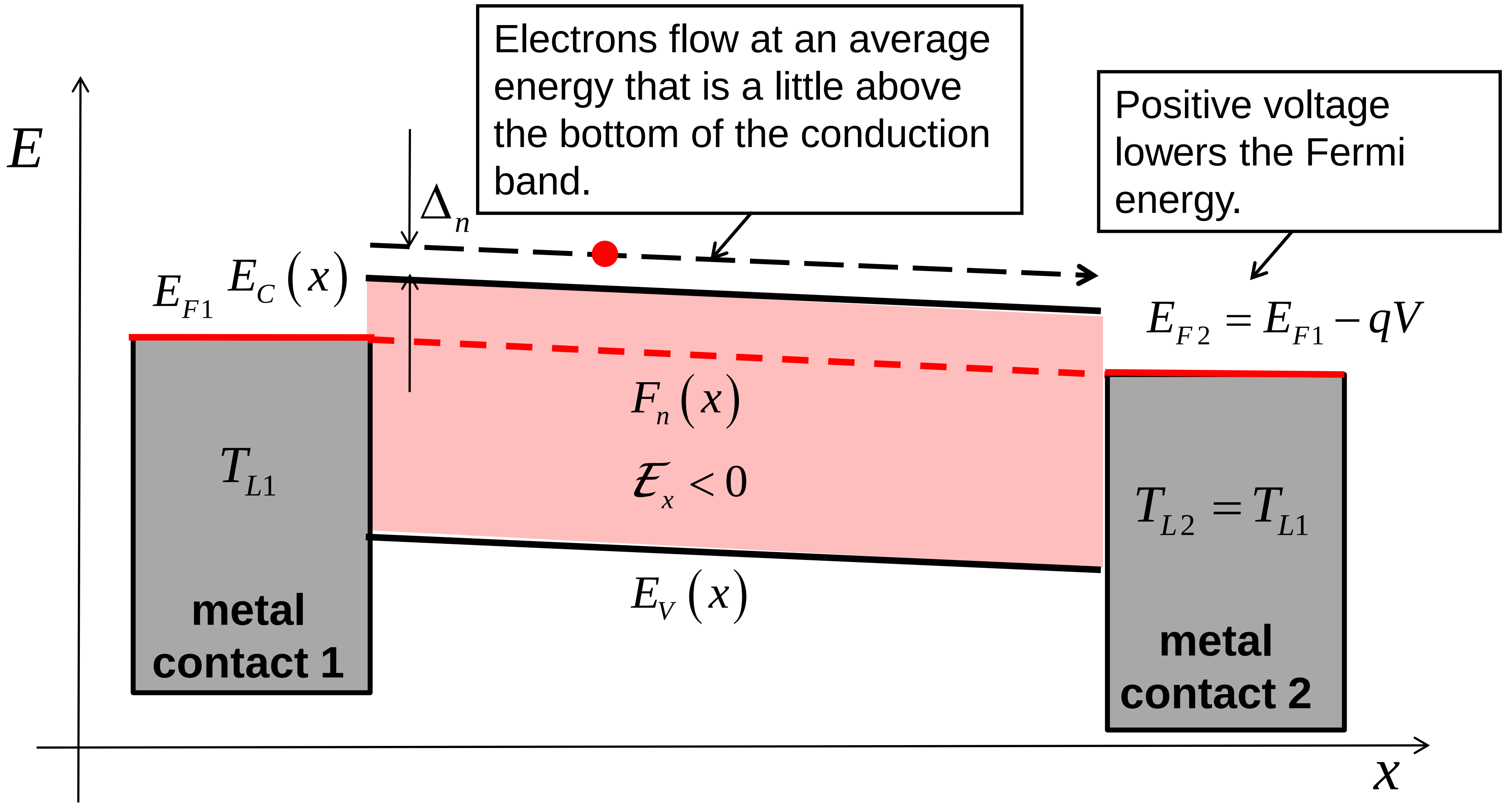
$$f(E) = \frac{1}{1 + e^{(E - E_F)/k_B T_L}}$$

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

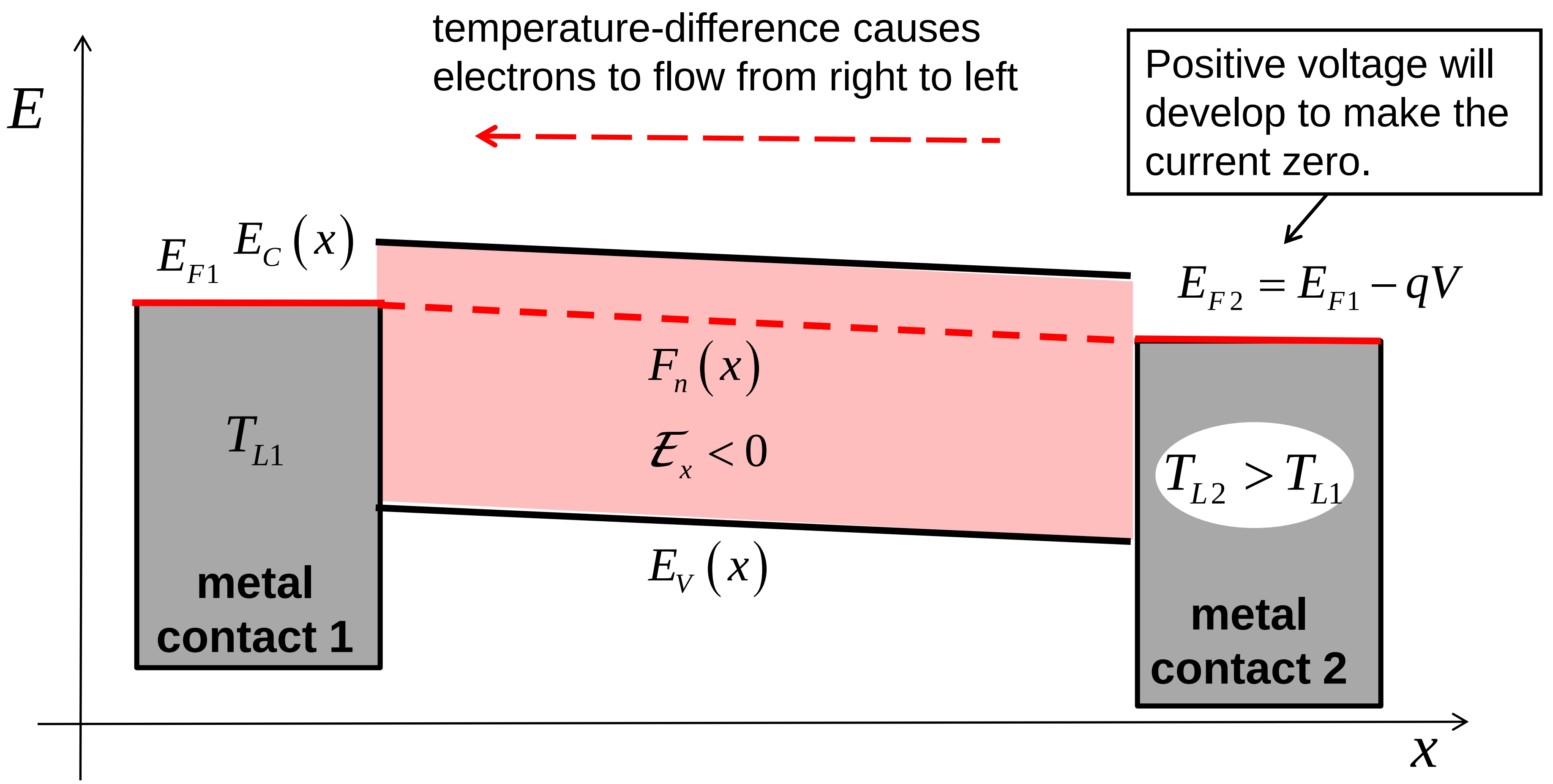


ideal contacts (no band bending)

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

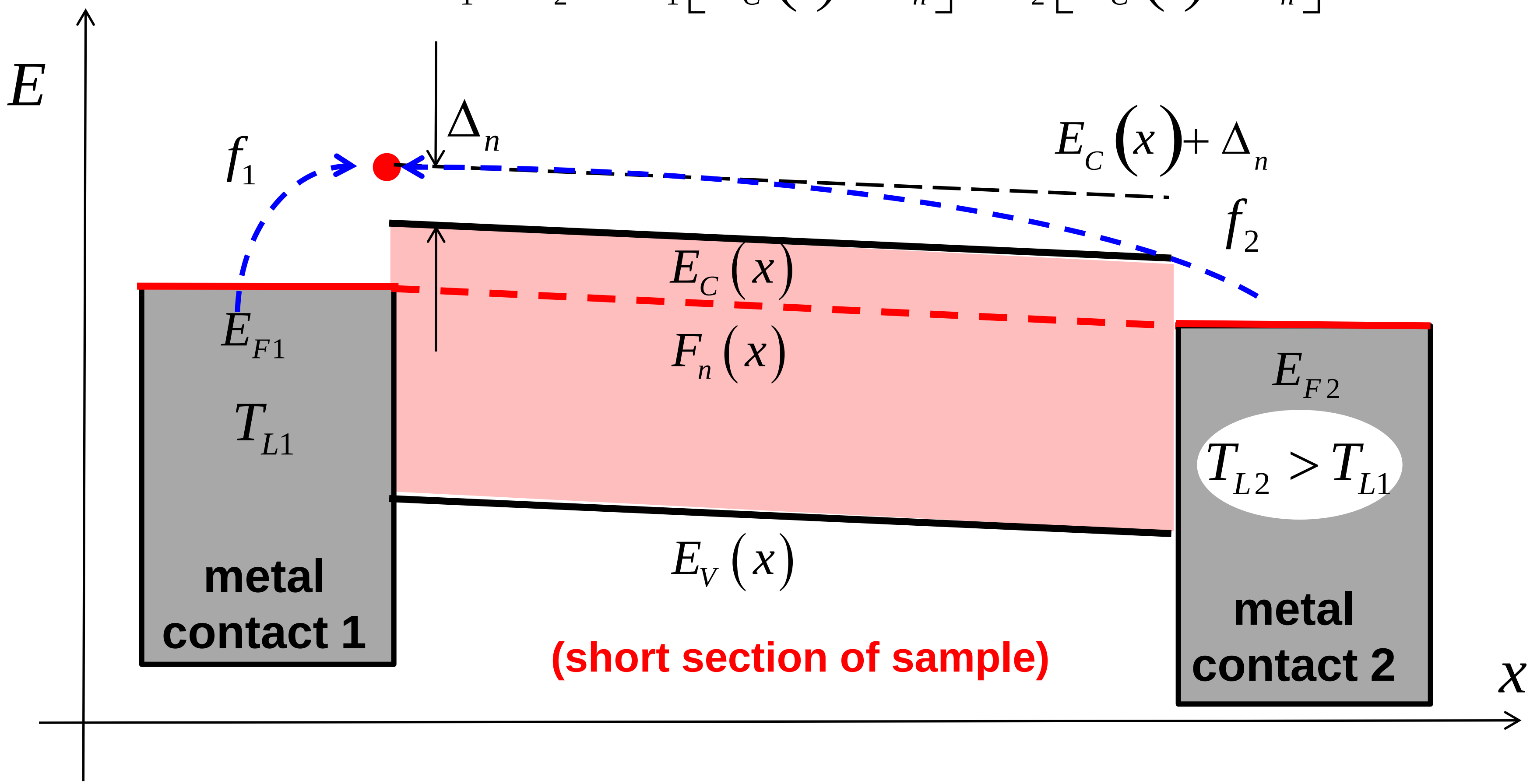


Seebeck effect



Seebeck effect (ii)

$$I = 0 \Rightarrow f_1 = f_2 \Rightarrow f_1\left[E_C(0) + \Delta_n\right] = f_2\left[E_C(0) + \Delta_n\right]$$



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

Seebeck coefficient

$$I = 0 \Rightarrow f_1\left[E_C(0) + \Delta_n\right] = f_2\left[E_C(0) + \Delta_n\right] \qquad E_{F2} = E_{F1} - q\delta V$$

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

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

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

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

$$S_n = -\frac{\left[E_C(0) + \Delta_n - E_{F1}\right]}{q T_{L1}}$$

$$S_n = -\frac{\left[E_J - E_{F1}\right]}{q T_{L1}}$$

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

Lundstrom 2011

Seebeck coefficient: recap

$$V = RI - S\delta T_L$$

$$S = -\frac{\left(E_J - E_F\right)}{qT_L}$$

S is negative for *n*-type semiconductors and positive for p-type.)

$$E_J = E_C + \Delta_n$$

$$\Delta_n = \frac{\int \left(E - E_C\right)\sigma'\left(E\right)dE}{\int \sigma'\left(E\right)dE}$$

$$I = GV + \left(SG\right)\delta T_L$$

S is proportional to the average energy of current flow (with respect to the Fermi level).

outline

1) Introduction
2) Charge transport in a temperature gradient
3) **Mathematical formulation**
4) Discussion
5) Summary

driving "forces" for transport

$$I = \frac{2q}{h}\int T(E)M(E)(f_1 - f_2)\,dE$$

Differences in occupation, *f*, produce current.

$$(f_1 - f_2) \approx -\frac{\partial f_1}{\partial E}\Delta E_F$$

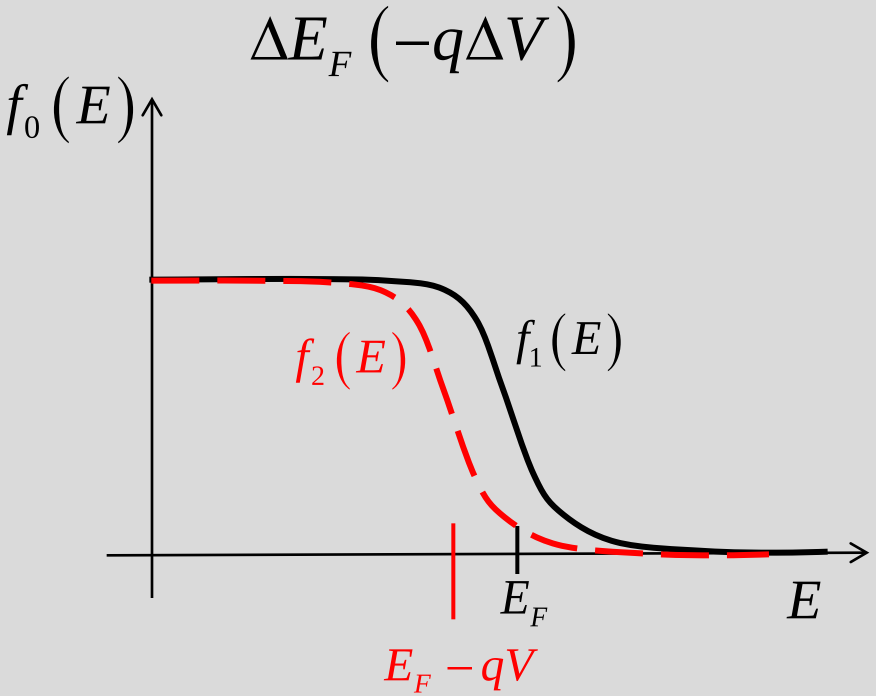
Assumes $T_{L1} = T_{L2}$.

but differences in temperature also produce differences in *f* and can, therefore, drive current (thermoelectric effects).

$$\Delta E_F = -q\Delta V = -q(V_2 - V_1)$$

$$\Delta T_L = T_{L2} - T_{L1}$$

when ⊗T = 0, the driving force is: ΔE_F

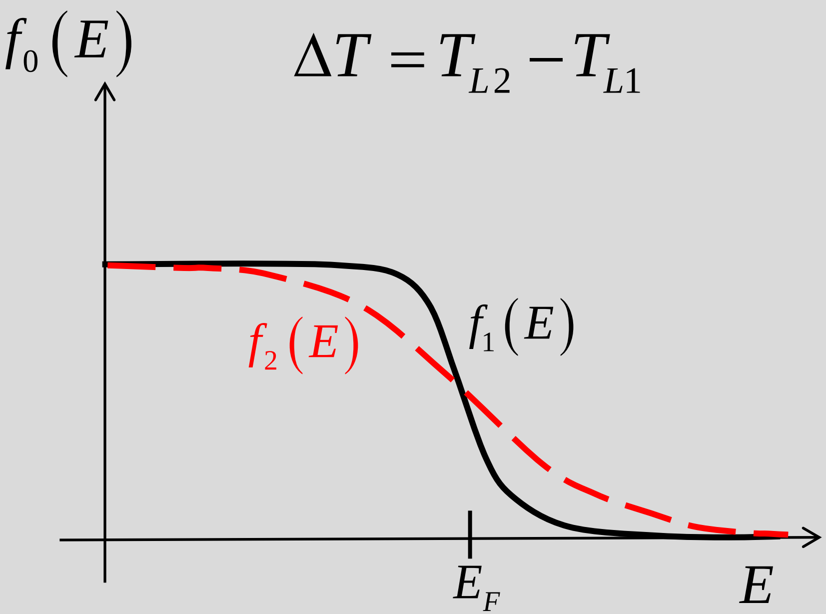


$f_1 > f_2$ and current flows

$$\left(f_1 - f_2\right) \approx \left(-\frac{\partial f_0}{\partial E}\right) q\Delta V$$

$$\left(f_1 \approx f_2 \approx f_0\right)$$

driving force: differences in temperature



$|f_1 - f_2| > 0$ so current flows.

$$\left(f_1 - f_2\right) \approx f_1 - \left(f_1 + \frac{\partial f_1}{\partial T_L}\Delta T\right)$$

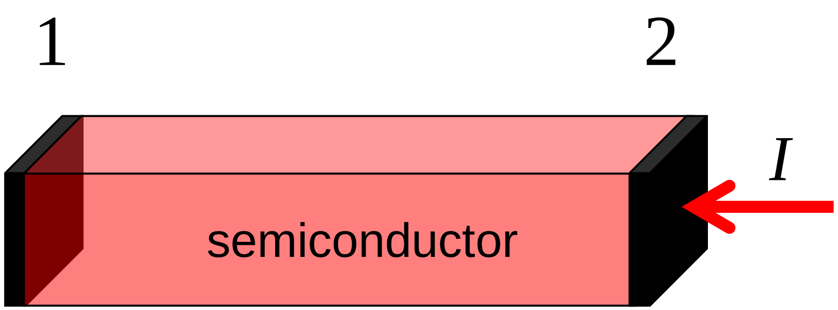
$$= -\frac{\partial f_1}{\partial T_L}\Delta T$$

$$\frac{\partial f_1}{\partial T_L} = -\frac{\left(E - E_F\right)}{T_L}\left(\frac{\partial f_0}{\partial E}\right)$$

$$\boxed{\left(f_1 - f_2\right) \approx -\left(-\frac{\partial f_0}{\partial E}\right)\frac{\left(E - E_F\right)}{T_L}\Delta T}$$

$$\left(f_1 \approx f_2 \approx f_0\right)$$

n-type vs. p-type…

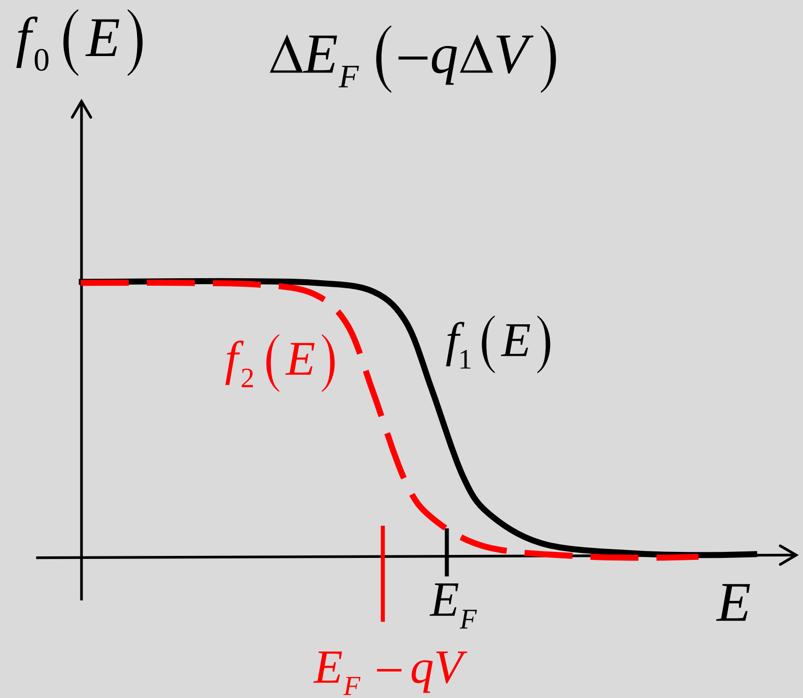


$$I = \frac{2q^2}{h}\int T(E)M(E)\left(f_1 - f_2\right)dE$$

The same answer for both n-type and p-type semiconductors!

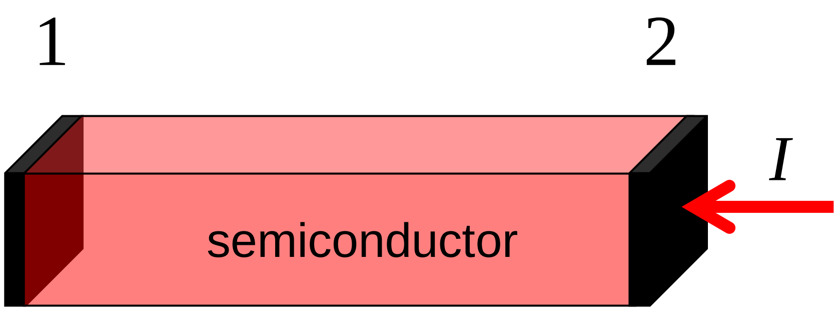
This occurs because $f_1 > f_2$ for states above and below the Fermi energy.

$V_2 > V_1 \quad T_{L2} = T_{L1}$



$f_1 > f_2 \quad I > 0$

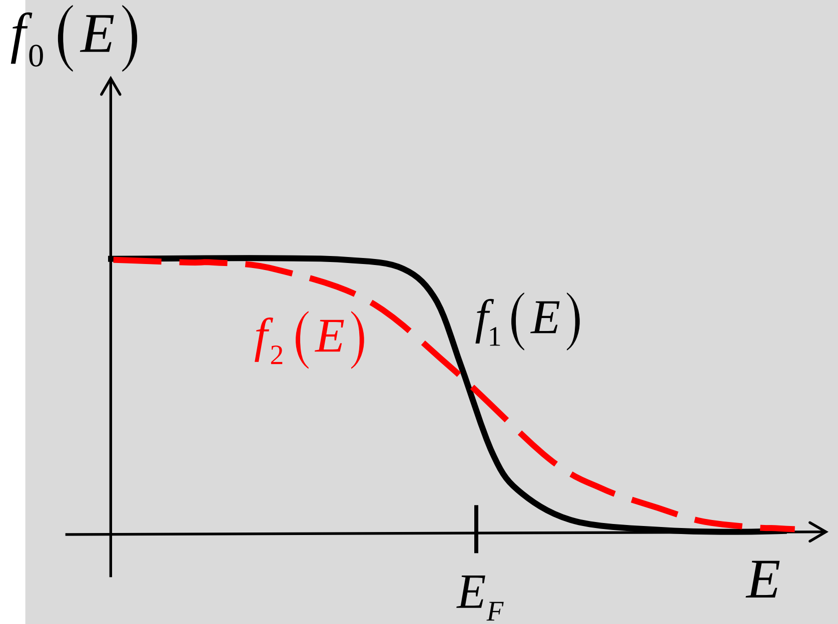
n-type vs. p-type (ii)…



$$I = \frac{2q}{h}\int T(E)M(E)\left(f_1 - f_2\right)dE$$

n-type: I < 0
p-type: I > 0

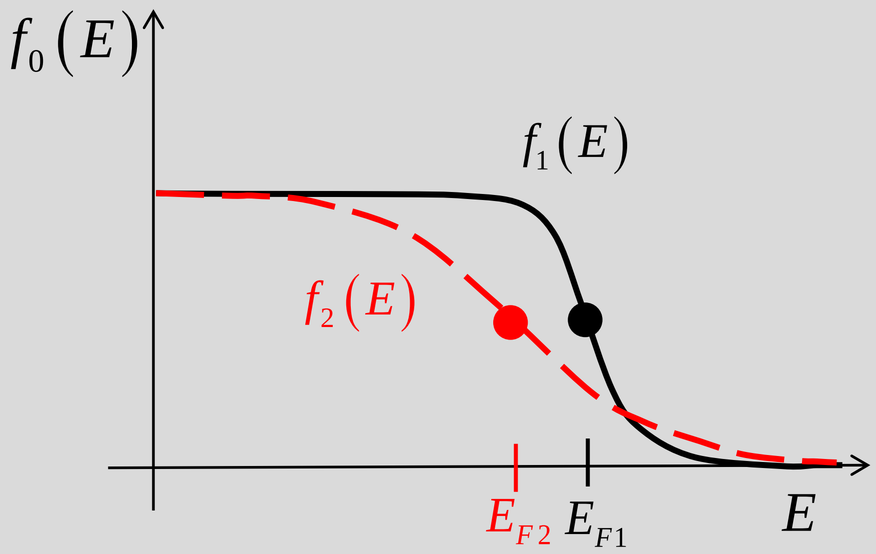
$$V_2 = V_1 \quad T_{L2} > T_{L1}$$



n-type: $E > E_F: \quad f_2 > f_1$

p-type: $E < E_F: \quad f_1 > f_2$

finally: differences in **both** E_F **and** T



$$\left(f_1 - f_2\right) \approx \left(-\frac{\partial f_0}{\partial E}\right) q\Delta V - \left(-\frac{\partial f_0}{\partial E}\right) \frac{\left(E - E_F\right)}{T_L} \Delta T_L$$

the math…

$$I'(E) = \frac{2q}{h} T(E) M(E)\left(f_1 - f_2\right) \qquad I = \int I'(E)\, dE$$

$$\left(f_1 - f_2\right) \approx \left(-\frac{\partial f_0}{\partial E}\right) q\Delta V - \left(-\frac{\partial f_0}{\partial E}\right) \frac{\left(E - E_F\right)}{T_L} \Delta T$$

$$\boxed{I'(E) = G'(E)\Delta V + S_T'(E)\Delta T}$$

S_T is related to the “Soret coefficient” for electro-thermal diffusion

the math…

$$I'(E) = G'(E)\Delta V + S_T'(E)\Delta T$$

$$S_T'(E) = -\frac{2q}{h}T(E)M(E)\left(-\frac{\partial f_0}{\partial E}\right)\frac{(E-E_F)}{T_L}$$

$$S_T'(E) = -G'(E)\frac{(E-E_F)}{qT_L}$$

$$S_T = \int S_T'(E)\,dE = -\int \frac{(E-E_F)}{qT_L}G'(E)\,dE$$

S_T is negative for n-type and positive for p-type.

re-cap

$$I = G\Delta V + S_T \Delta T$$

$$G = \frac{2q^2}{h}\int T(E)M(E)\left(-\frac{\partial f_0}{\partial E}\right) dE = \int G'(E)dE$$

$$S_T = -\int \frac{(E - E_F)}{qT_L} G'(E)dE = \int S_T(E)dE$$

Valid near equilibrium for 1D, 2D, or 3D and from ballistic to diffusive transport.

inverted form

$$\Delta V = \frac{1}{G} I - \frac{S_T}{G} \Delta T = RI - S\Delta T$$

$$S = \frac{S_T}{G} = -\frac{1}{qT_L} \frac{\int (E - E_F) G'(E) dE}{\int G'(E) dE} = -\frac{E_J - E_F}{qT_L}$$

$$E_J = E_C + \Delta_n \qquad \Delta_n == \frac{\int (E - E_C) G'(E) dE}{\int G'(E) dE}$$

Valid near equilibrium for 1D, 2D, or 3D and from ballistic to diffusive transport.

outline

1) Introduction
2) Charge transport in a temperature gradient
3) Mathematical formulation
4) **Discussion**
5) Summary

current equation in the bulk

Develop a diffusive transport equation that describes bulk transport in the presence of gradients in the electrochemical potential ***and*** temperature.

$$J_{nx} = \sigma_n \frac{dF_n/q}{dx} \rightarrow ?$$

$$J_{nx} = \sigma_n \frac{dF_n/q}{dx} - s_T \frac{dT_L}{dx}$$

$$I = -I_x = G\Delta V + S_T \Delta T$$

$$I_x = J_{nx} A = -G\Delta V - S_T \Delta T$$

$$J_{nx} = -\frac{G}{A}\Delta V - \frac{S_T}{A}\Delta T$$

$$J_{nx} = -G\frac{L}{A}\frac{\Delta V}{L} - S_T \frac{L}{A}\frac{\Delta T}{L}$$

$$G = \sigma_n A/L$$

$$S_T = s_T A/L$$

$$\Delta V = -\Delta F_n/q$$

current equation in the bulk (ii)

$$J_{nx} = \sigma_n \frac{dF_n/q}{dx} - s_T \frac{dT_L}{dx}$$

$$S_T = s_T \frac{A}{L} \qquad G = \sigma \frac{A}{L}$$

$$s_T = -\int \frac{(E - E_F)}{qT_L} \sigma'(E) dE$$

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

inverted form of the current equation

$$J_{nx} = \sigma_n \frac{dF_n/q}{dx} - s_T \frac{dT_L}{dx}$$

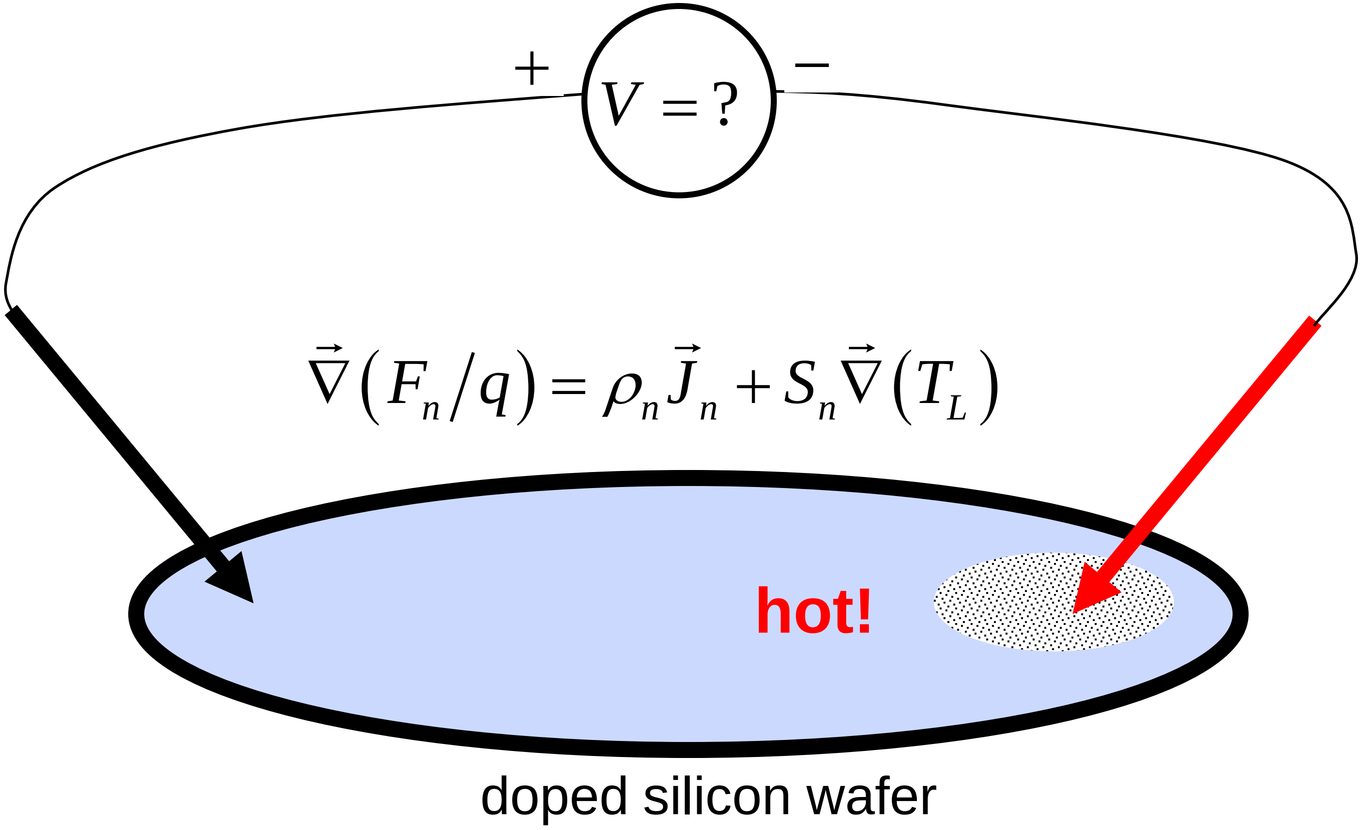
$$\frac{dF_n/q}{dx} = \rho_n J_{nx} + \rho_n s_T \frac{dT_L}{dx}$$

$$\frac{dF_n/q}{dx} = \rho_n J_{nx} + S_n \frac{dT_L}{dx}$$

$$S_n = \frac{s_T}{\sigma_n}$$

$$S_n = \left(-\frac{1}{qT_L}\right) \frac{\int (E - E_F)\sigma'(E) dE}{\int \sigma'(E) dE}$$

hot point probe



basic equation

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

(Uniform semiconductor assumed, so $d\left(F_n/q\right)/dx = \mathcal{E}_x$)

Two transport coefficients:

1) resistivity (Ω-cm) = 1/conductivity (S/cm)
2) Seebeck coefficient (V/K)

Seebeck coefficient

$$S_n(T_L) = -\frac{1}{qT_L}(E_J - E_F)$$

$$S_n(T_L) = -\frac{1}{qT_L}(E_C + \Delta_n - E_F)$$

$$\Delta_n = \frac{\int (E - E_c)\sigma_n'(E)dE}{\int \sigma_n'(E)dE}$$

The parameter, Δ_n, depends on bandstructure and scattering.

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

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

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

$\delta_n \approx 2$ (3D, non-degenerate)

Example: transport parameters of n-Ge

ρ_n $\quad \Omega\text{-m}$

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

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

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

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

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

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

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

TE transport parameters of n-Ge: resistivity

ρ_n Ω-m

S_n V/K

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

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

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

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

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

TE transport parameters of n-Ge: Seebeck coeff.

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

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

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

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

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

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

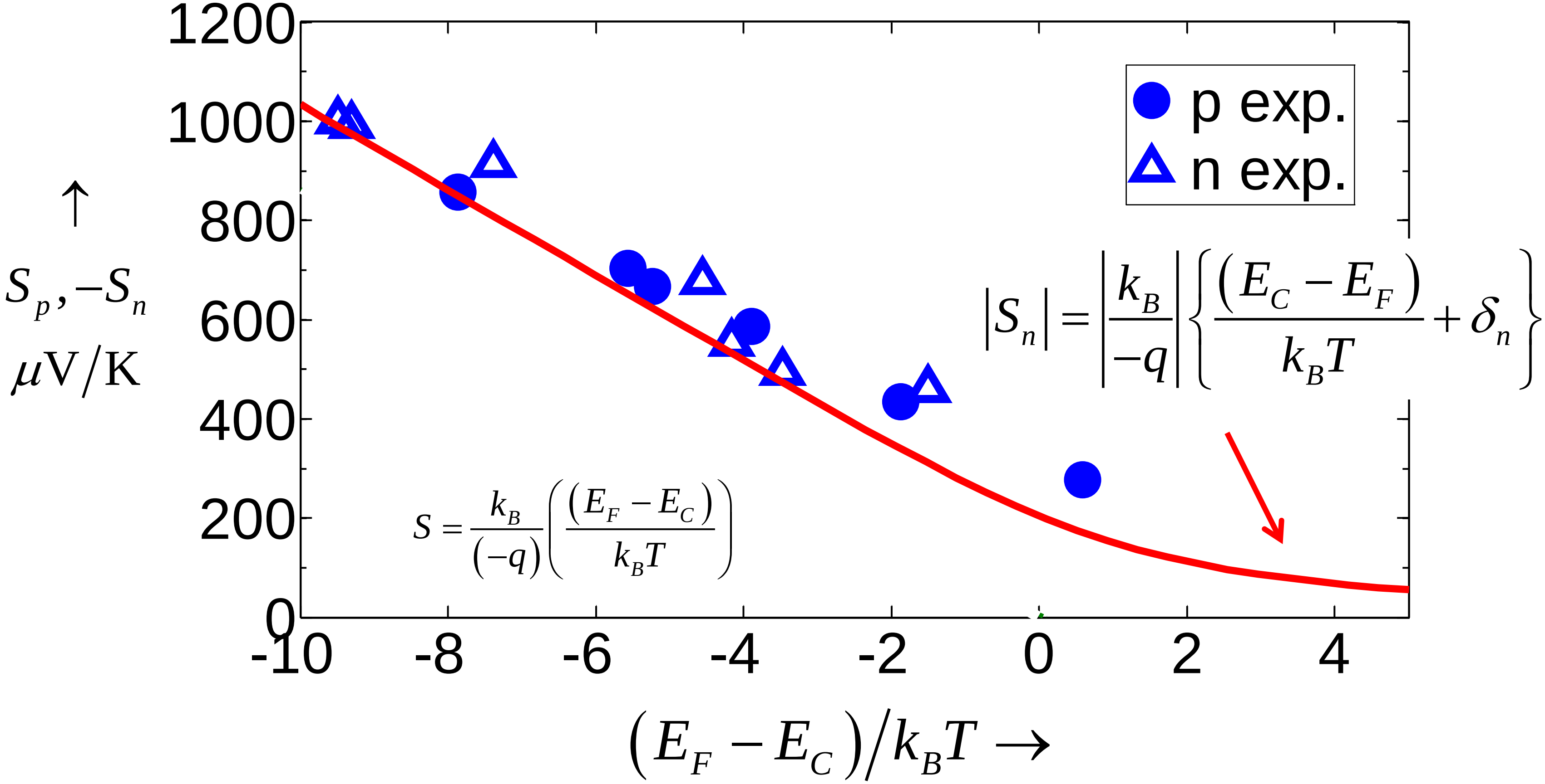
$T_L = 300\ \mathrm{K}$

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

$\delta_n \approx 2$ (non-degenerate, 3D)

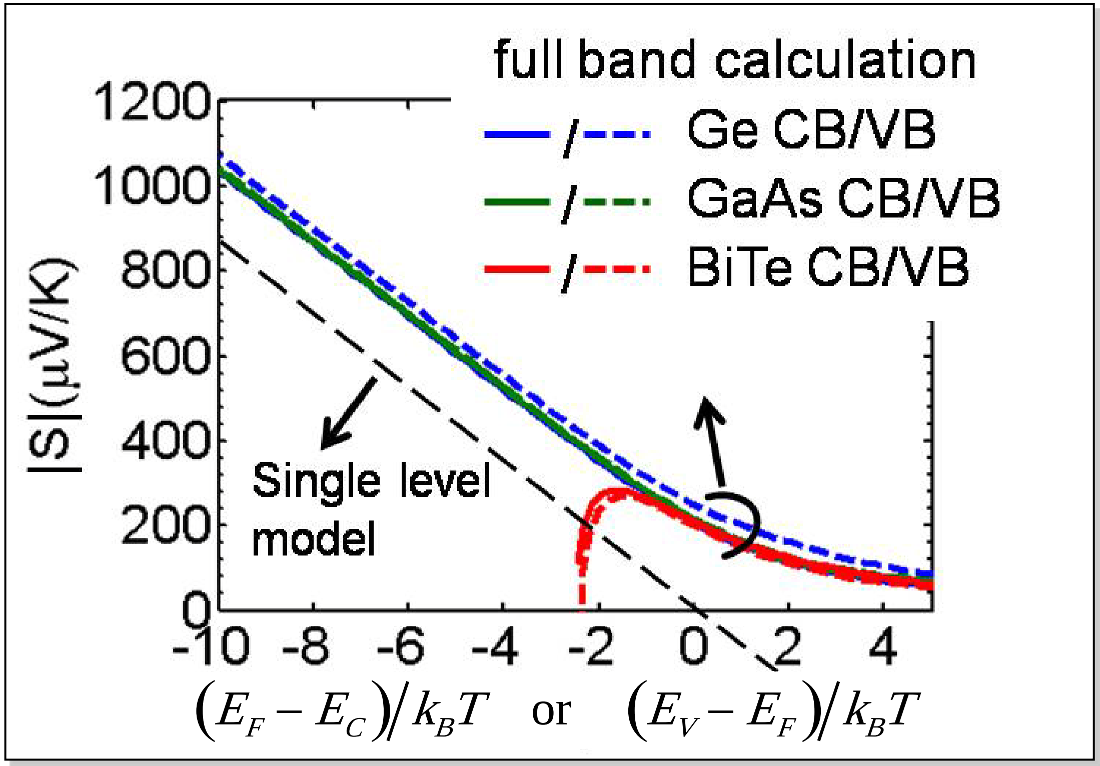
$$S_n = \left(\frac{k_B}{-q}\right)\left\{\frac{(E_c - E_F)}{k_B T_L} + \delta_n\right\} \approx -970\ \mu\mathrm{V/K}$$

Seebeck coefficient of Ge



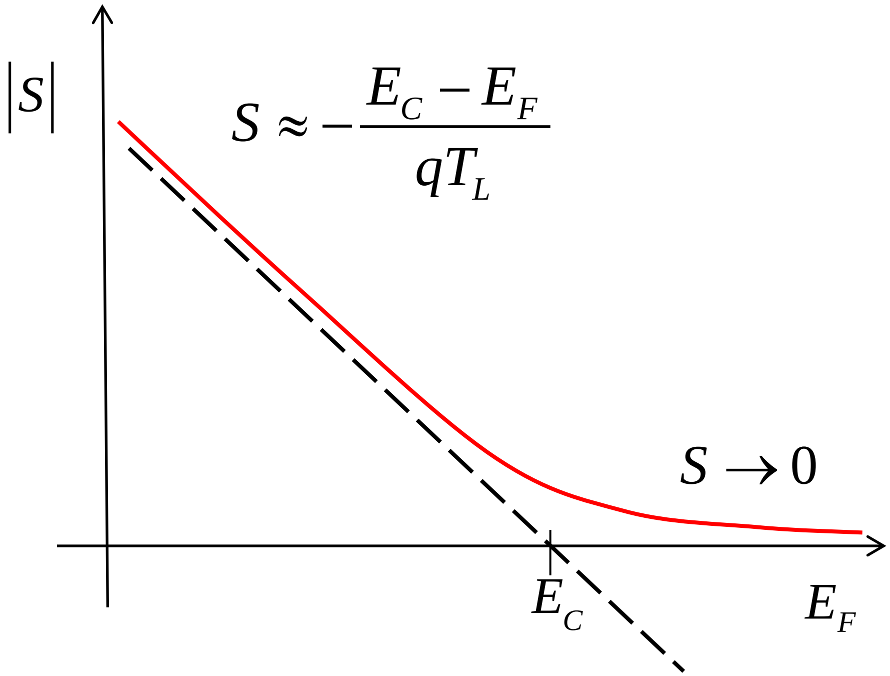
Exp. data: T.H. Geballe and G.W. Hull, “Seebeck Effect in Germanium,” *Physical Review*, **94**, 1134, 1954.

“full band” Seebeck coefficient



Changwook Jeong, et al., “On Landauer vs. Boltzmann and Full Band vs. Effective Mass Evaluation of Thermoelectric Transport Coefficients,” *J. Appl. Phys*., **107**, 023707, 2010.

understanding Seebeck coefficients



$$S_n = -\frac{E_J - F_n}{qT_L}$$

1) |S| is large for a non-degenerate semiconductor because the current carrying channels are way above (below) the Fermi level.

2) |S| is small for a degenerate semiconductor (or metal) because the current flows near the Fermi energy.

outline

1) Introduction
2) Charge transport in a temperature gradient
3) Mathematical formulation
4) Discussion
5) **Summary**

mathematical description

The answer is:

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

S_n is the Seebeck coefficient in V/K.

Alternatively, we can write this equation as:

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

(inverted form of the equations)

transport parameters

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

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

$$S_n = \left(-\frac{1}{qT_L}\right)(E_J - E_F)$$

$$S_n = \left(-\frac{1}{qT_L}\right)\frac{\int (E - E_F)\sigma'_n(E)dE}{\int \sigma'_n(E)dE}$$

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

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

questions

1) Introduction
2) Charge transport in a temperature gradient
3) Mathematical formulation
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