Lecture 6 – 15/10/2025

Occupancy statistics and band filling

- Semiconductors: non-degenerate, intrinsic, degenerate, doped
- Occupancy of donor and acceptor levels
- Charge neutrality condition
- Doped semiconductors – temperature dependence

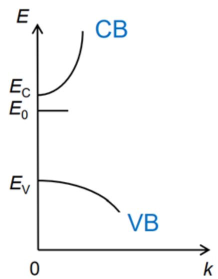
Carrier transport

- Mobility at moderate electric field

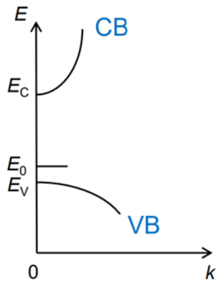
Summary of Lecture 5: donors and acceptors

Donor species: **Provide 1+ free conduction electron to the lattice → n-type**

Acceptors: **Trap 1+ valence electron of the lattice (forms free conduction holes) → p-type**



Donor level



Acceptor level

Eigenenergies: **Modification of the H atom with dielectric constant and effective mass**

$$E_n = -\frac{\hbar^2}{2m_0 a_0^2} \times \frac{\frac{m^*}{m_0}}{\varepsilon_r^2} \times \frac{1}{n^2} = -\frac{13.6}{n^2} \times \frac{\frac{m^*}{m_0}}{\varepsilon_r^2}$$

Binding energy of a donor: **difference between energy level *n*=1 and the CB level**

Binding energy of an acceptor: **difference between VB level and energy level *n*=1 of the acceptor atom**

Summary of Lecture 5: density of states and band filling

Density of States (DOS): **Number of states of different energies available for carriers**

DOS in reciprocal space per unit volume = $\frac{1}{V_k} \times \frac{1}{V}$

$k = \sqrt{2m^* (E - E_0) / \hbar^2}$

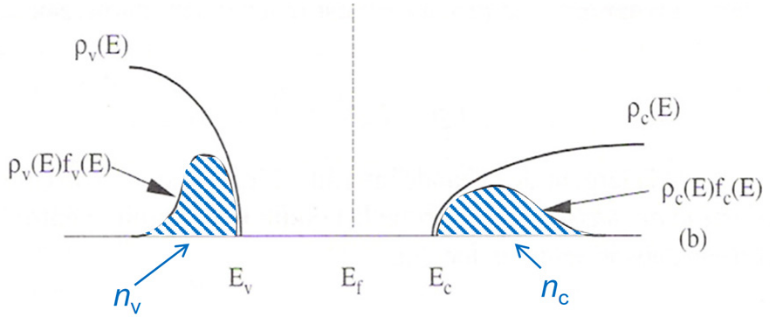
Number of states in sphere of radius k = $N_{3D}(E) = V_{sphere}$ x DOS per unit volume x 2 (spins $\pm 1/2$)

Density of states per unit energy: $\rho_{3D}(E) = \frac{dN_{3D}(E)}{dE}$

Fermi-Dirac distribution: Probability that an energy state E is filled by 1 electron $f(E) = \frac{1}{1 + e^{(E - E_F)/k_B T}}$

Fermi Level: highest energy level occupied at T = 0 K

$f(E_F) = \frac{1}{2}$ at any T



Density of electrons in CB at an energy E: $n_c(E) = f_c(E)\rho_c(E)$

Density of holes in VB at an energy E: $n_v(E) = f_v(E)\rho_v(E) = [1 - f_c(E)]\rho_v(E)$

Fermi level calculation

$$n = N_c e^{(E_F - E_c)/k_B T}$$

$$p = N_v e^{(E_v - E_F)/k_B T}$$

Remark: n and p can be experimentally measured (Hall effect, electrochemical *C-V* profiling)

$$E_F = E_c - k_B T \ln \frac{N_c}{n} = E_v + k_B T \ln \frac{N_v}{p}$$

- When n (or p) << N_c (or N_v) $\Rightarrow$ E_F lies in the bandgap (non-degenerate SC)

- When n (or p) > N_c (or N_v) $\Rightarrow$ the Fermi level lies within the CB (or VB)

$\Rightarrow$ The semiconductor is then said to be ***degenerate***

Thermodynamic equilibrium

At equilibrium ⇒ same chemical potential, i.e., same E_F, across the sample whatever the semiconducting structure (which remains true for an unbiased device whatever its complexity)

The *np* product for a non-degenerate semiconductor is then independent of the Fermi level position and is given by:

$$np = N_c N_v e^{-\frac{E_c - E_v}{k_B T}} = N_c N_v e^{-\frac{E_g}{k_B T}}$$

Product that depends on $m^{*3/2}$, $T^{3/2}$, and E_g

For a given semiconductor, ***np* is a function of temperature**. This is a **mass action law**, which expresses the thermodynamic equilibrium condition for electrons and holes.

Intrinsic semiconductors

A pure and perfect semiconductor is intrinsic

The origin of carriers present in the CB and VB is endogenous, i.e., free carriers are only due to the thermal activation process of electrons from the VB to the CB

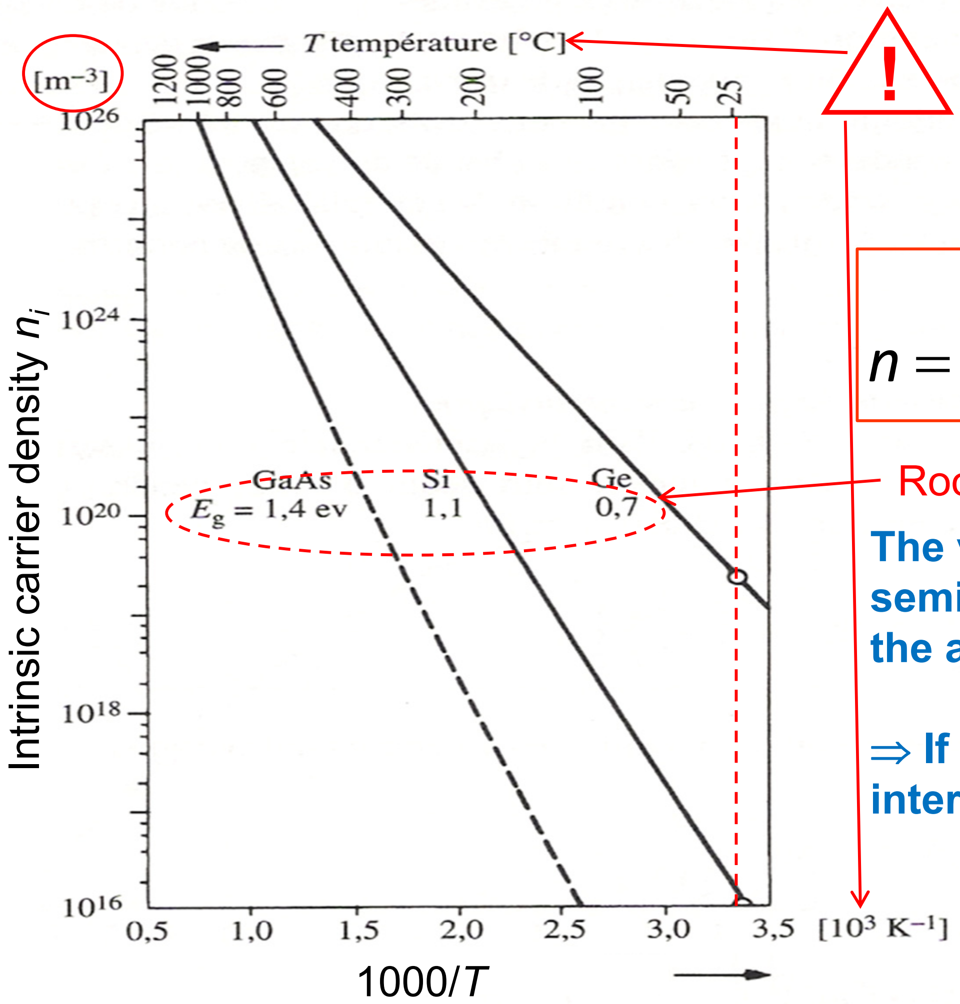
The condition for electrical neutrality throughout the crystal leads to $n = p = n_i$ at equilibrium, so that:

intrinsic

$$np = n_i^2 = N_c N_v e^{-\frac{E_c - E_v}{k_B T}} = N_c N_v e^{-\frac{E_g}{k_B T}}$$

$$n = p = n_i = \sqrt{N_c N_v} e^{-\frac{E_g}{2k_B T}}$$

Intrinsic semiconductors



$$n = p = n_i = \sqrt{N_c N_v}\, e^{-\frac{E_g}{2k_B T}}$$

Room temperature bandgap!

The value of n_i will set the sensitivity of a given semiconductor to residual impurities and hence the ability to precisely control *n*- and *p*-type doping

⇒ If the impurity concentration is < n_i, the SC of interest will preserve its intrinsic behavior!

Intrinsic semiconductors

Fermi level position in an intrinsic semiconductor

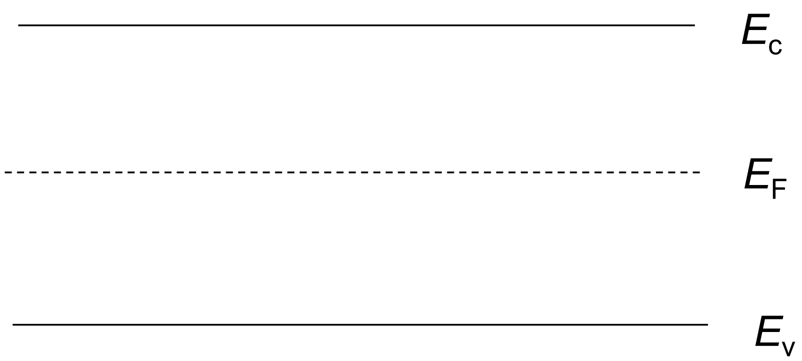
$$n = N_c e^{(E_F - E_c)/k_B T}$$

$$p = N_v e^{(E_v - E_F)/k_B T}$$

$$E_F = E_c - k_B T \ln \frac{N_c}{n} = E_v + k_B T \ln \frac{N_v}{p}$$

$$E_F = \left(\frac{E_v + E_c}{2} \right) + \frac{k_B T}{2} \ln \left(\frac{N_v}{N_c} \right)$$

N_v and N_c are comparable therefore **E_F is close to the mid-gap** (cf. slide #28, Lecture 5)



Semiconductor – degenerate case

Degenerate SC ⇒ highly doped

$$E_F = E_c - k_B T \ln \frac{N_c}{n}$$ with $n > N_c$ (case of an n-type SC)

The Fermi level lies within the CB ⇒ Boltzmann approximation is **no longer valid** (cf. slide #26, Lecture 5)

One may consider as a rough approximation a Heaviside step function to account for the occupancy statistics:

$f(E) = 1$ when $E < E_F$
$f(E) = 0$ when $E > E_F$

$$n = \int_{E_c}^{E_F} \rho_c(E)\, dE = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \int_{E_c}^{E_F} (E - E_c)^{1/2}\, dE$$

$$= \frac{1}{3\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} (E_F - E_c)^{3/2}$$

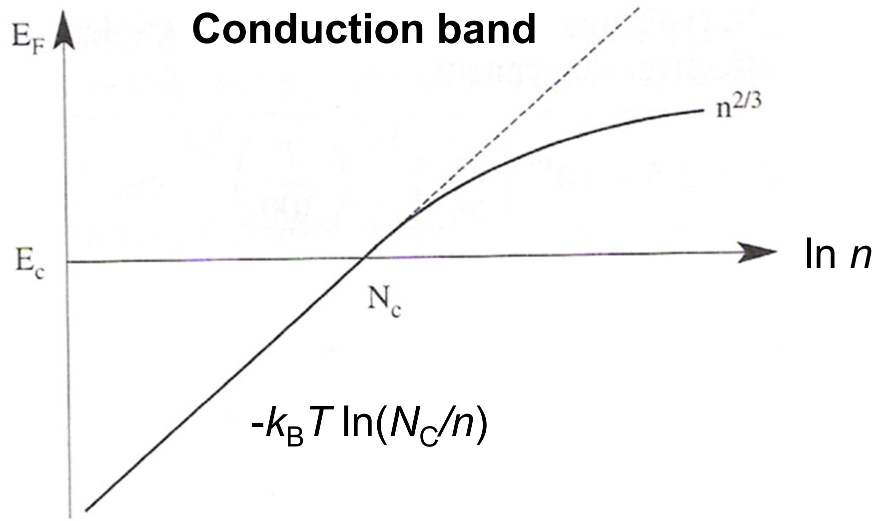
n* is independent of *T

More detailed description to be seen in the exercises !

Semiconductor – degenerate case

A degenerate SC behaves like a metal (but this is not exactly a metal, why?)

We speak about a semimetallic behavior



For $n > N_c$, the Fermi level position varies as $n^{2/3}$

⚠ The $np = n_i^2$ relationship is not valid anymore in the degenerate case!

Semiconductor – doped case

Occupancy of the donor and acceptor levels

(consideration valid only at low temperature or for deep level states)

N_D (cm^{-3}) donor concentration with an ionization energy E_D (for 1 electron)

N_D^0 Concentration of neutral donors

N_D^+ Concentration of ionized donors

Semiconductor – doped case

Occupancy of the donor (and acceptor) levels

Number of electrons in state *j*

$$\langle n \rangle = \frac{N_D^0}{N_D} = \frac{\sum N_j g_j^{-1} e^{-\beta(E_j - N_j E_F)}}{\sum g_j^{-1} e^{-\beta(E_j - N_j E_F)}} = \frac{1}{1 + g_D^{-1} e^{(E_c - E_D - E_F)/k_B T}}$$

partition function

Mean number of e- bound to donors

g_D= 2 (spin degeneracy factor) and $\beta = 1/k_B T$

(only 1 electron due to e⁻-e⁻ interaction)

$$1 - \frac{1}{1 + Ae^{\alpha}} = \frac{1}{1 + 1/Ae^{-\alpha}}$$

Thus, the density of ionized donors is

$$N_D^+ = N_D - N_D^0 = N_D \frac{1}{1 + 2e^{(E_F - E_c + E_D)/k_B T}}$$

What happens when:

- *T* increases ?
- E_D increases ?

⇒ To be seen in the exercises !
Very important concept

Charge neutrality condition

The charge neutrality condition within the crystal implies that positive and negative charges compensate themselves

$$n + N_A^- = p + N_D^+$$

Charge neutrality condition ⇒ the Fermi level is fixed at a given *T*

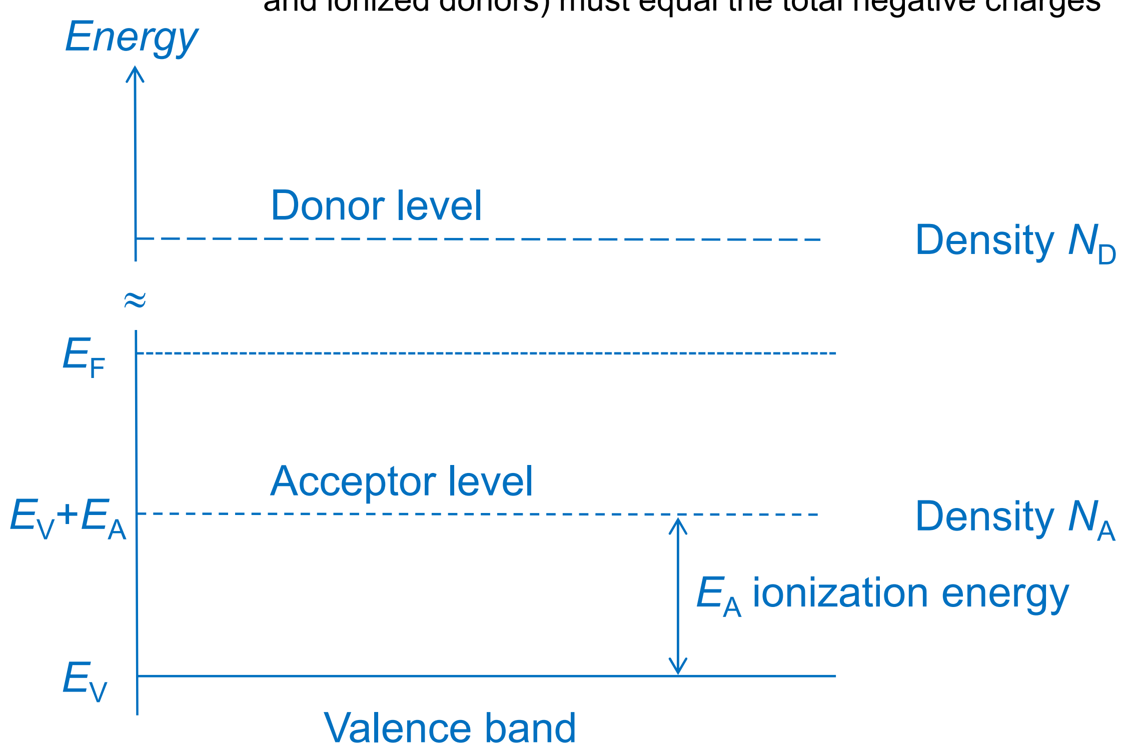
Assumption: donors and acceptors are fully ionized at 300 K:

$$n + N_A = p + N_D$$

! Always use the appropriate approximation to derive n, p, N_A and N_D!
The sign of N_A and N_D will also depend on the experimental situation.

Charge neutrality condition: an illustrative example

Diagrammatic example: case of a partially compensated *p*-type doped sample



To preserve electrical neutrality the total positive charges (holes and ionized donors) must equal the total negative charges

$$p + N_D = N_A^-$$

E_F being located above the acceptor level, all the acceptors are ionized!

$$p = N_V \exp\left(\frac{E_V - E_F}{k_B T}\right)$$

$$N_A^- = N_A f_A = N_A \left[1 + g_A \exp\left(\frac{E_V + E_A - E_F}{k_B T}\right)\right]^{-1}$$

Spin degeneracy factor

N-type semiconductor: temperature dependence

N_D donors with an ionization energy E_D and without acceptors

Intermediate temperature case:

Donors are fully ionized but no electron coming from the VB

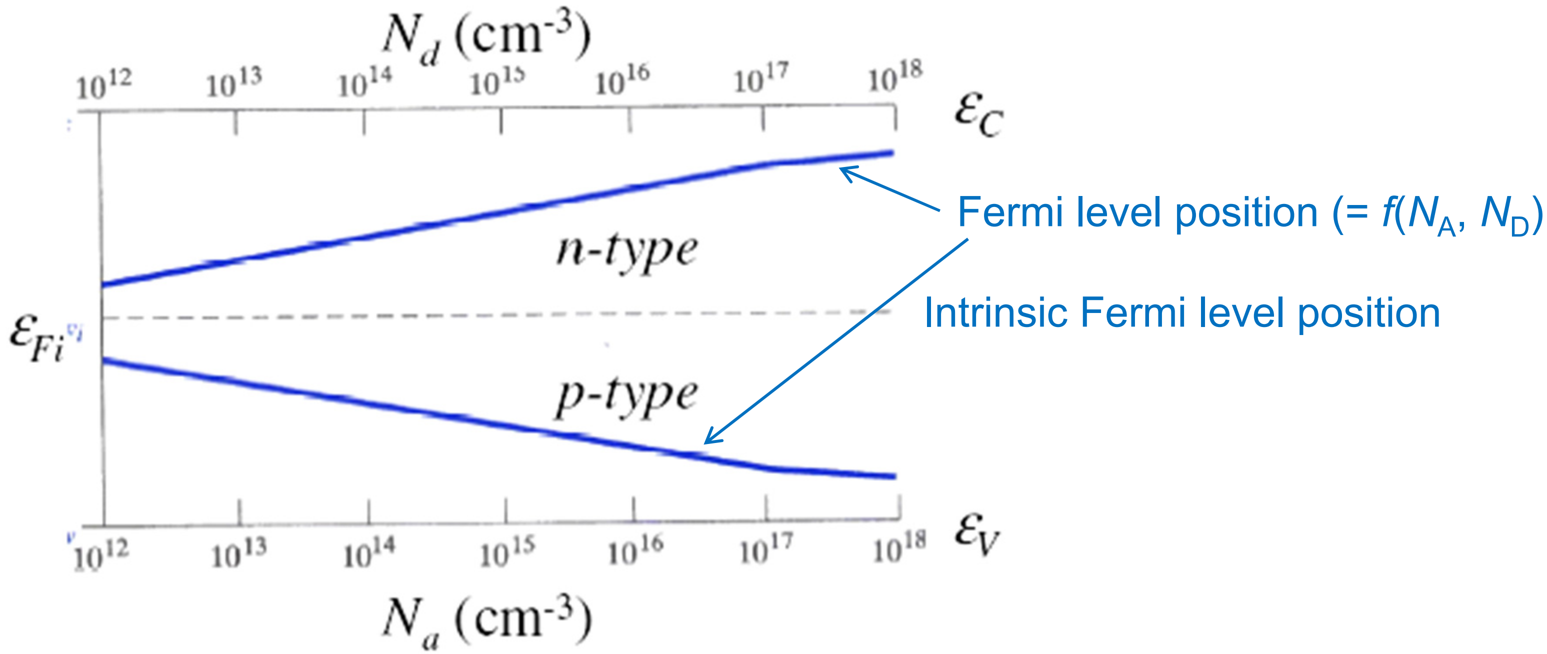
$$(p = 0) \Rightarrow n = N_D$$

Fermi level position $$E_F - E_c = k_B T \ln \frac{N_D}{N_c}$$

For a typical doping level of 10^{17} cm^{-3} in Si and at 300 K, E_F - $E_c \approx$ -145 meV

The Fermi energy is below the donor state level Whose position is given by?

Fermi level energy vs doping



N-type semiconductor: temperature dependence

Above a certain temperature, intrinsic ionization is no longer negligible.

Thus, the charge neutrality condition will write as follows:

$$n = N_\mathrm{D} + p$$

n can be expressed as a function of n_i and N_D:

$$np = n_\mathrm{i}^2 \longrightarrow n = \frac{1}{2}N_\mathrm{D} + \left(\frac{N_\mathrm{D}^2}{4} + n_\mathrm{i}^2\right)^{1/2}$$

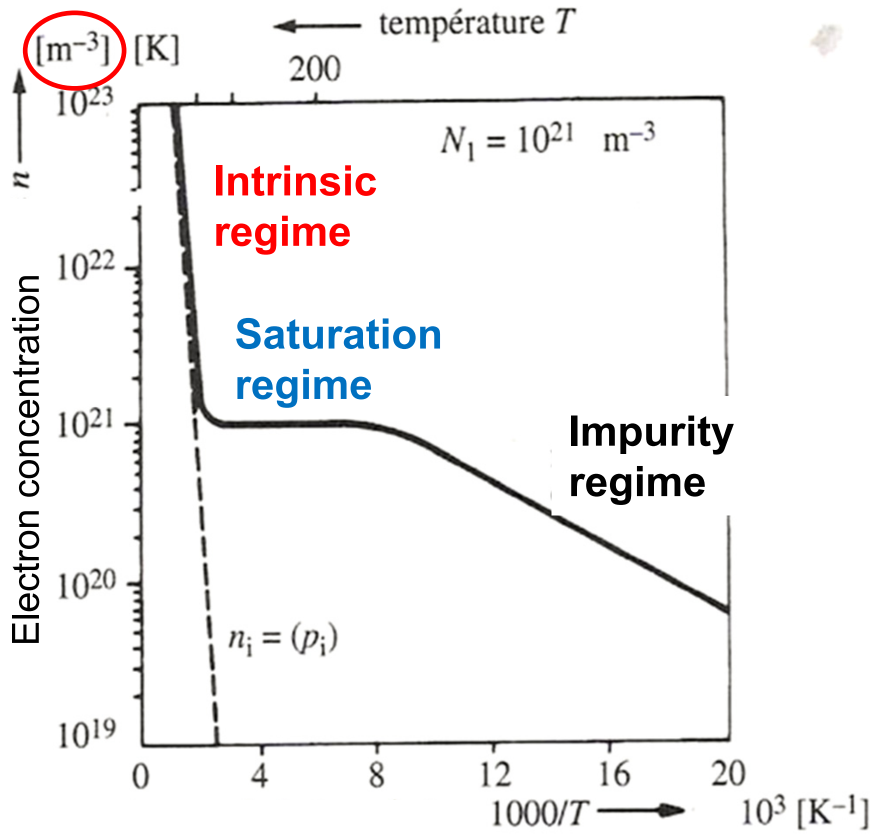
Cf. slides # 5 & 6

For the intermediate temperature range ($n_\mathrm{i} << N_\mathrm{D}$)

$$n \approx N_\mathrm{D} + \frac{n_\mathrm{i}^2}{N_\mathrm{D}} \approx N_\mathrm{D} \quad \text{and} \quad p \approx \frac{n_\mathrm{i}^2}{N_\mathrm{D}}$$

Saturation regime

N-type semiconductor: temperature dependence



N-type semiconductor: temperature dependence

- **Saturation regime:** $n \approx N_D$

- The concentration of holes is much lower than that of electrons

  - Electrons are called **majority carriers**
  - Holes are called **minority carriers**

- **The conductivity only depends on the donor concentration:**
  ⇒ extrinsic conductivity ($\sigma = ne\mu$)

  Mobility (to be defined)!

Doped semiconductor: temperature dependence

1. **High temperature range (intrinsic properties)**
   n_i much larger than N_D and N_A

   $\Rightarrow$ the charge neutrality condition is simply equal to $n = p = n_i$

2. **Intermediate temperature range (extrinsic properties)**
   Donors and acceptors are fully ionized

   $n \approx N_D - N_A \approx$ constant (n-type doping)
   and $p \approx N_A - N_D \approx$ constant (p-type doping)

3. **Low temperature range (condensation/impurity regime)**
   Partial impurity ionization

   $\Rightarrow$ the charge neutrality condition is equal to $n + N_A^- = p + N_D^+$

Doped semiconductor

Charges

Symbol	Nature	Charge
N_A^0	Neutral acceptor concentration	0
N_A^-	Ionized acceptor concentration	-e
N_D^0	Neutral donor concentration	0
N_D^+	Ionized donor concentration	+e
n	Free electron concentration	-e
p	Free hole concentration	+e

Charge neutrality condition

$$n + N_A^- = p + N_D^+$$

Very important concept !

Donors and acceptors are fully ionized at 300 K:

$N_A^- = N_A$ $\quad$ $N_D^+ = N_D$

$$n + N_A = p + N_D$$

Nota bene: When a semiconductor contains both donors and acceptors, it can be said to be compensated because, under equilibrium conditions, some of the electrons from the donors will be captured (or compensated) by the acceptors ($\Rightarrow$ a compensated sample contains both ionized donors (D^+) and acceptors (A^-)).

Carrier transport

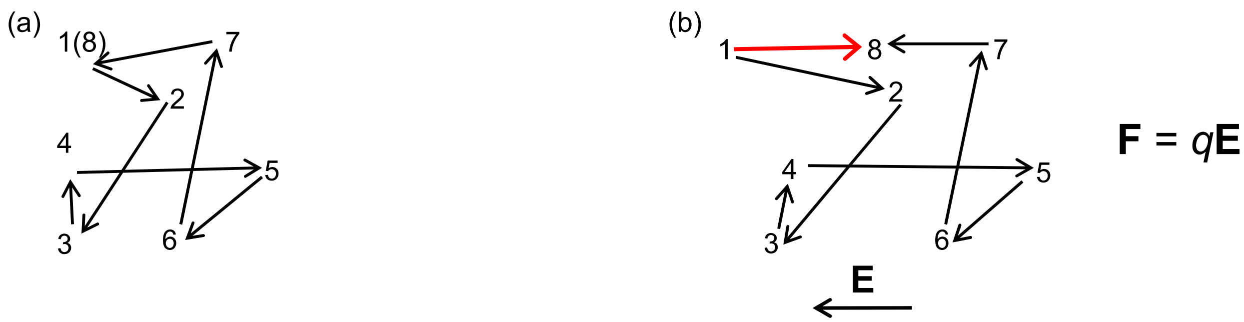
Thermal equilibrium

Thermal scattering

Origins:

- atoms
- ionized impurities
- defects
- other electrons

Isotropic scattering processes $\Rightarrow$ the net charge displacement is equal to zero



No longer the case when an electric field is applied (symmetry breaking)

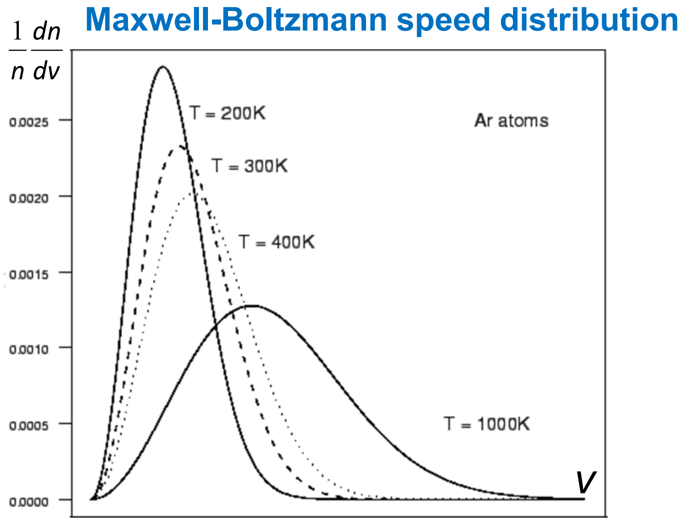
Thermal equilibrium

Nearly-free electrons ⇒ molecules in a gas

Maxwell-Boltzmann distribution law:

For an electron gas with *n* electrons per unit volume, the number of electrons with a velocity ranging between *v* and *v*+d*v* is given by:

$$dn = 4\pi v^2 n \left(\frac{m^*}{2\pi k_B T} \right)^{3/2} e^{-(m^* v^2 / 2 k_B T)} dv$$



The **root-mean-square speed** is related to temperature through

$$\frac{1}{2} m^* v_{th}^2 = \frac{3}{2} k_B T$$

Equipartition theorem (in 3D) ⇒ To be seen in the exercises!

At 300 K, the electron velocity in Si is about 10^7 cm s^{-1}

The **mean free path** λ is determined by the time between 2 collisions

τ_c is the *mean-free time*

τ_c = 0.1 - 1 ps, $\lambda = \tau_c v_{th}$ = **10 to 100 nm**

Conductivity with an electric field

Condition: moderate electric field

⇒ constant scattering rate, or velocity increase much smaller than v_{th}

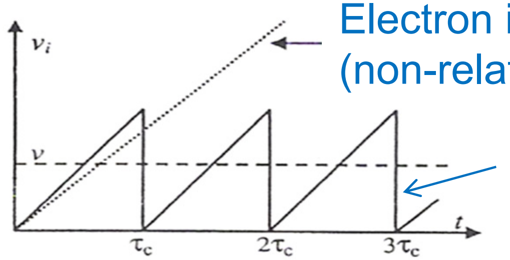
F = qE is the force induced by the electric field on the carriers

$$F = qE = m^* \frac{dv_i(t)}{dt}$$

v_i carrier velocity along the electric field

After integration between t_0 and t_0+t:

$$v_i(t) = q\frac{E}{m^*}t$$



Conductivity with an electric field

Drude model:

The average scattering time (*mean-free time*) τ_c is given by

Scattering probability per unit time

$$<t> = \int_0^\infty tP(t)\,dt = \tau_c$$

The average velocity is then equal to:

$$<v> = q\frac{<t>}{m^*}E = \frac{q\tau_c}{m^*}E$$

$$<v> = v_d = \mu E \quad \text{with} \quad \mu = \frac{q\tau_c}{m^*}$$

v_d is the drift velocity

v_d is proportional to the electric field (Ohm's law)

μ is the ***mobility***

Conductivity with an electric field

$$\mu = \frac{q\tau_c}{m^*}$$

- The mobility determines the performance of (opto)electronic devices
- It depends on the scattering rate and effective mass
- Units: $cm^2 \, V^{-1} \, s^{-1}$