IX. Semiconductor Statistics

Preparations (Self-read)

Fermi-Dirac Distribution $$f_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon - E_F)/kT} + 1} \quad (1)$$

Meaning: Prob. that a state at energy ε is occupied by an electron at temperature T, (if there is a state at that energy)

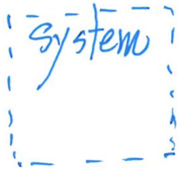
[actually, it is the mean # electron per state at ε, so $\underbrace{f_{FD}(\varepsilon) \leq 1}^{\text{Pauli Exclusion rule}}$]

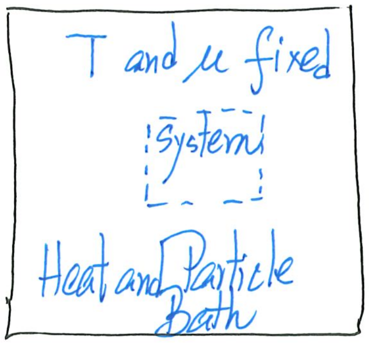
- E_F is a function of T, i.e. $E_F(T) \equiv \mu(T)$ is the chemical potential
- "states" considered are "single-particle states" (as counted by DOS)
- Usually use E_F in semiconductor physics
- Occupation of one state or not doesn't affect occupation of other states$^+$

$^+$This point is relevant to statistics of impurity states

A bit of Statistical Physics: Grand Canonical Ensemble

System can exchange energy and particles with Bath





∴ Mean Energy and Mean number of particles of system are governed by temp. T and chemical potential μ of Bath

A particle situation of the System: N_i particles, in a N_i-particle state of energy $U_i(N_i)$ (there are many possible N_i-particle states with energies labelled by U_i)

$$P_i \equiv P(N_i, U_i(N_i)) = P(U_i(N_i)) \propto e^{-\frac{U_i(N_i)}{kT}} e^{+\mu\frac{N_i}{kT}}$$

(Gibbs Distribution)

Prob. at equilibrium with bath

$$= \frac{e^{-\frac{U_i(N_i)}{kT}} e^{+\mu\frac{N_i}{kT}}}{Q(T,\mu,V)} \qquad (2)$$

Grand Partition Function → $Q(T,\mu,V)$

$$Q(T,V,\mu) = \sum_{N_i} \sum_{\text{all } U_i(N_i)} e^{-\frac{U_i(N_i)}{kT} + \frac{\mu N_i}{kT}} = \sum_{N_i} e^{\frac{\mu N_i}{kT}} \underbrace{Z(T,V,N_i)} \qquad (3)$$

all #'s particles that system can possibly have → N_i

all possible N_i-particle states of system

Partition Function of a system of N_i particle in bath of temp. T

the one in Canonical Ensemble

Mean # particles in system at equilibrium

$$\bar{N} = kT\left(\frac{\partial \ln Q}{\partial \mu}\right)_{T,V} = \frac{kT}{Q}\left(\frac{\partial Q}{\partial \mu}\right)_{T,V} \qquad (4)$$

plays the role of N in thermodynamics

- Eqs. (2), (3), (4) are general [interacting and non-interacting systems]
- As such, Eq. (3) is useful in some cases when unionized donor and acceptor states need to be considered (e.g. can't insert a second electron in a neutral donor) [one electron trapped at donor site affects occupancy of second electron]

For ideal Fermi Gas (e.g. free electrons in CB, free holes in VB)

$$Q_{\text{fermion}} = \prod_{\substack{\text{all single-particle}\\ \text{states } r}} \left(1 + e^{-\beta(\varepsilon_r - \mu)}\right) \qquad (5) \qquad [\text{ideal Fermi gas}]$$

ε_r = energy of s.p. state labelled r

$$\bar{N} = \sum_{\substack{\text{all}\\ \text{s.p. states } r}} \frac{1}{e^{\beta(\varepsilon_r - \mu)} + 1} = \sum_{\text{all s.p. states } r} \underbrace{\frac{1}{e^{(\varepsilon_r - \mu)/kT} + 1}}_{f_{FD}(\varepsilon_r)} \qquad (6) \qquad \text{using (4)}$$

$f_{FD}(\varepsilon_r)$ = mean # fermion in a s.p. state of energy ε_r

thus derived the Fermi-Dirac distribution

Taking s.p. states as densely packed in energy:

$$\bar{N} = \int_{\text{all energy}} g(\varepsilon) \frac{1}{e^{(\varepsilon - \mu)/kT} + 1}\, d\varepsilon = \int_{\text{all energy}} g(\varepsilon) \frac{1}{e^{(\varepsilon - E_F)/kT} + 1}\, d\varepsilon \qquad (7)$$

Eq.(7) invokes DOS $g(\varepsilon)d\varepsilon$ and is the starting point of discussing semiconductor statistics.

Key Messages

- Eq. (7) includes the filling of electrons into electronic states counted in $\underbrace{g(\varepsilon)d\varepsilon}_{\text{e.g. } \frac{V}{2\pi^2}\left(\frac{2m^*_{DOS}}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon - E_0}}$

  [band effect in m^*; parabolic band]

- Eq. (3) is sometimes useful in studying impurity states remained unionized (thus quite $\underbrace{\text{low temperature}}_{\text{academic (freezing out of impurities) than practical}}$)

Don't worry if you don't follow everything here. Eq. (7) can go quite far!

For more on Statistical Mechanics, see my class notes in my webpage in the department website.

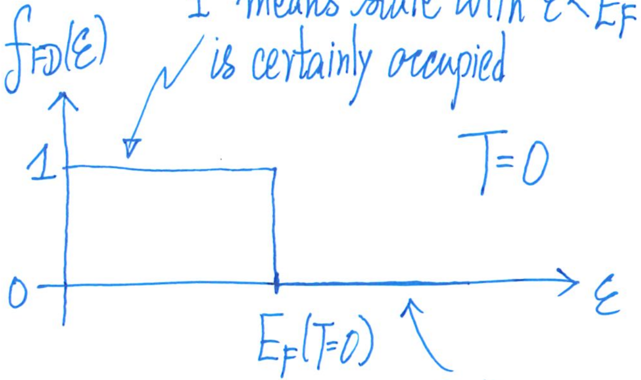
A. Knowing the Fermi-Dirac Distribution

$$f_{FD}(\varepsilon) = \frac{1}{e^{(\varepsilon - E_F)/kT} + 1} \qquad (1)$$

(i) $f_{FD}(\varepsilon = E_F) = 1/2$ (can be used to define E_F)

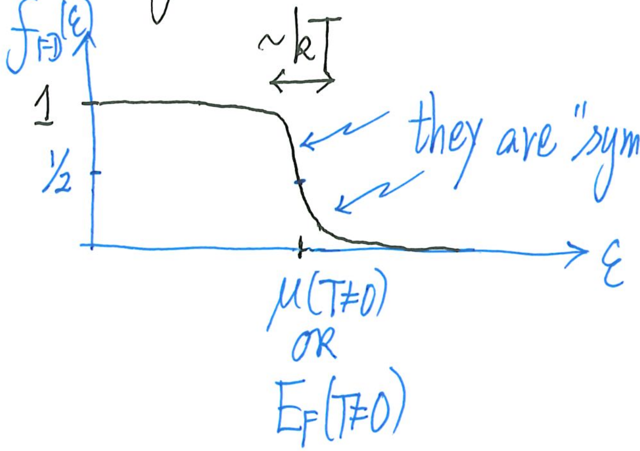
(ii) a step function at $T=0$

(iii) smearing out somewhat at $T \neq 0$



"1" means state with $\varepsilon < E_F$ is certainly occupied

"0" means certainly unoccupied



they are "symmetric" about $E_F(T)$

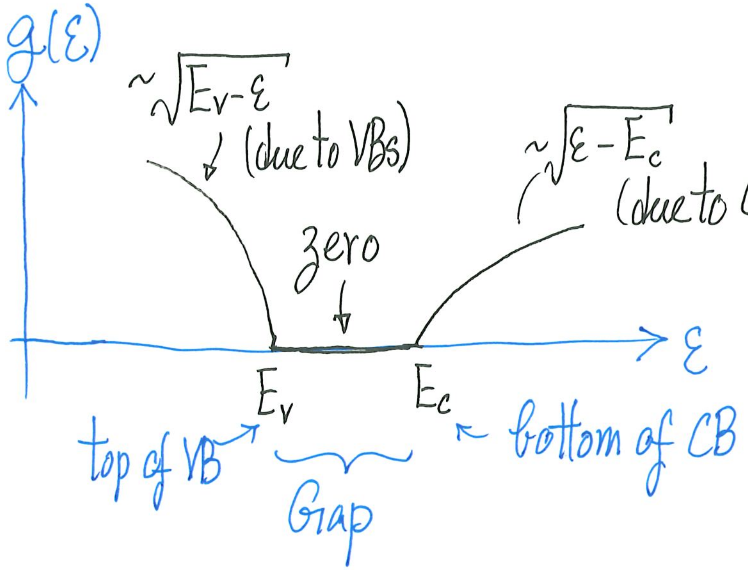
$$\boxed{\begin{array}{c}\text{how it goes to zero for } \varepsilon > E_F \\ \| \\ \text{how it goes to one for } \varepsilon < E_F\end{array}}$$

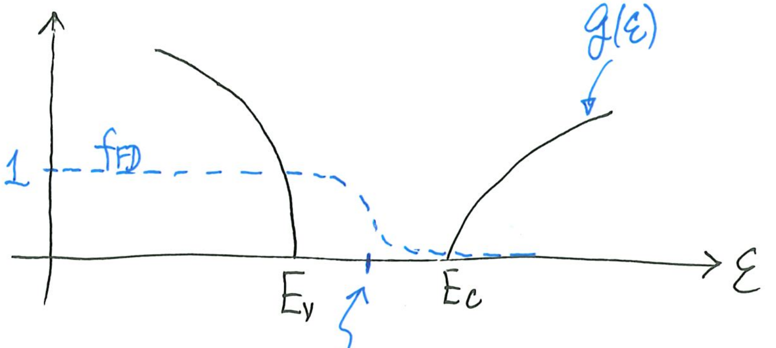
} makes analysis of electrons and holes almost the same

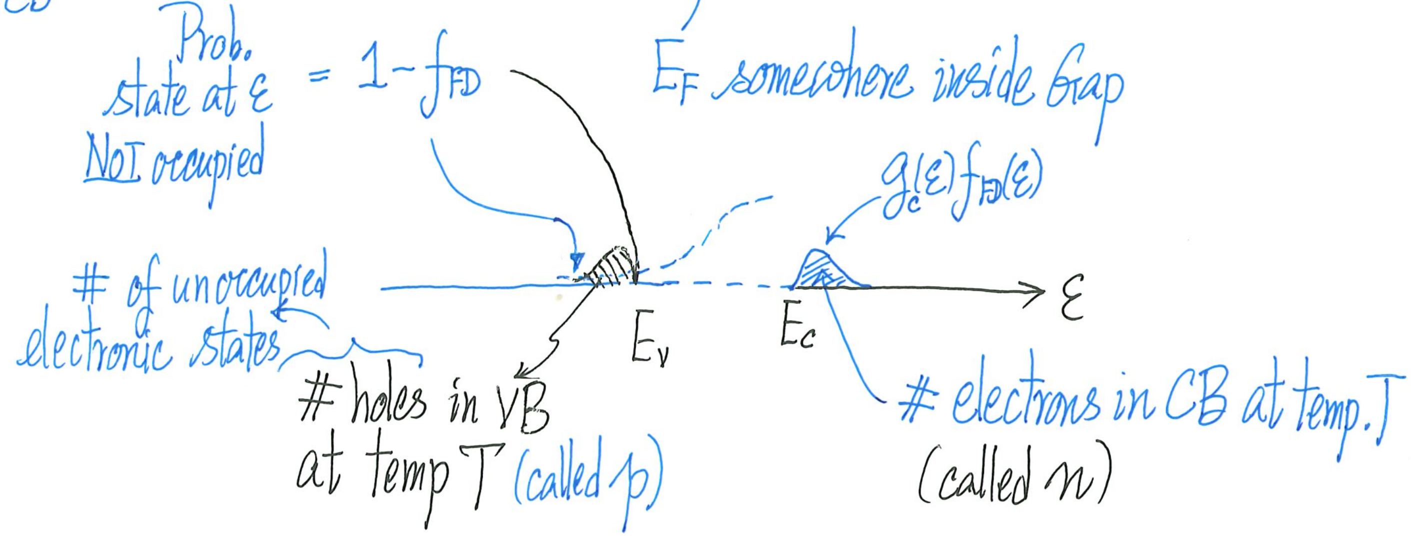
$$\boxed{\text{The smearing out range is just a few } kT} \qquad (8)$$

$$\underbrace{f_{FD}(\varepsilon)}_{\text{prob. of a state at energy }\varepsilon\text{ occupied by an electron}}\ \text{is useful when it comes together with}\ \underbrace{g(\varepsilon)d\varepsilon}_{\#\text{ electronic states in }\varepsilon\to\varepsilon+d\varepsilon}$$

$$\underbrace{f_{FD}(\varepsilon)\cdot g(\varepsilon)d\varepsilon}_{\#\text{ electrons in interval }\varepsilon\to\varepsilon+d\varepsilon}$$







$$\underbrace{1-f_{FD}(\varepsilon)}_{\substack{\text{Prob. state of energy } \varepsilon \\ \text{is } \underline{\text{NOT}} \text{ occupied}}} = 1 - \frac{1}{e^{(\varepsilon-E_F)/kT}+1} = \frac{e^{(\varepsilon-E_F)/kT}}{e^{(\varepsilon-E_F)/kT}+1} = \frac{1}{1+e^{(E_F-\varepsilon)/kT}} \equiv \underset{\substack{\uparrow \\ \text{for holes}}}{f_p(\varepsilon)} \quad (9)$$

DOS (per unit volume, spin included) of CB

$$n = \text{Number of electrons } \underline{\text{in CB}} \text{ per unit volume} = \overbrace{\int_{\text{bottom of CB}}^{\text{top of CB}}}^{\text{Count through CB}} g_{CB}(\varepsilon) \underbrace{\frac{1}{e^{(\varepsilon-E_F)/kT}+1}}_{\text{states } \underline{\text{Occupied}}} d\varepsilon \quad (10)$$

$$p = \text{Number of holes } \underline{\text{in VB}} \text{ per unit volume} = \underbrace{\int_{\text{bottom of VB}}^{\text{top of VB}}}_{\substack{\text{Count through} \\ \text{VB (VBs if} \\ \text{DOS included VB's)}}} g_{VB}(\varepsilon) \underbrace{\frac{1}{1+e^{(E_F-\varepsilon)/kT}}}_{\text{states } \underline{\text{NOT}} \text{ occupied}} d\varepsilon \quad (11)$$

Eqs. (10) and (11) are general expressions for n and p (large gap, small gap, pure/doped, any temperature)

← When approximations don't work, come back here!

B. Some Numbers to carry around

- $kT_{room} \approx 1/40\ eV \approx 0.025\ eV$

  $\uparrow$ most important temperature

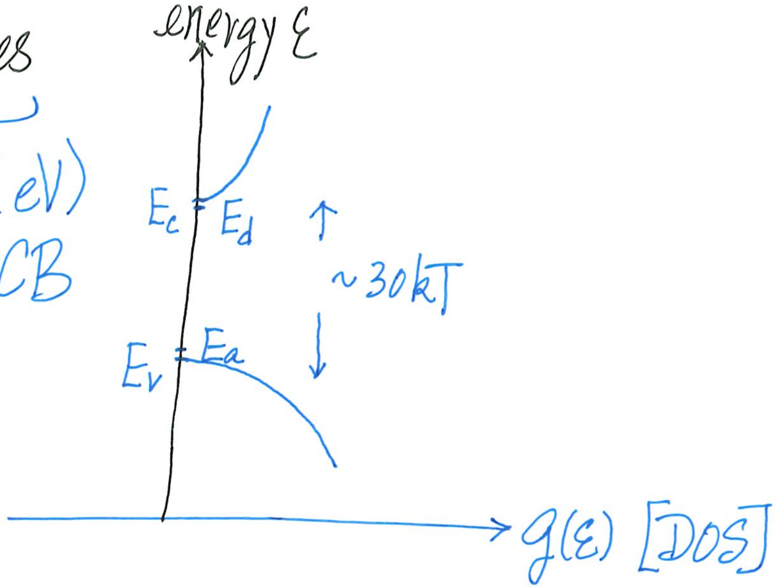
  E_g = band gap $\begin{cases} 1.1eV & (Si) \\ \sim 0.7eV & (Ge) \\ \sim 1.5eV & (GaAs) \end{cases}$

  ∴ $E_g \sim$ several tens of kT (30 kT or even more)

- Donor impurity states / Acceptor impurity states

  Donor impurity states: ~10 meV (0.01eV) below bottom of CB

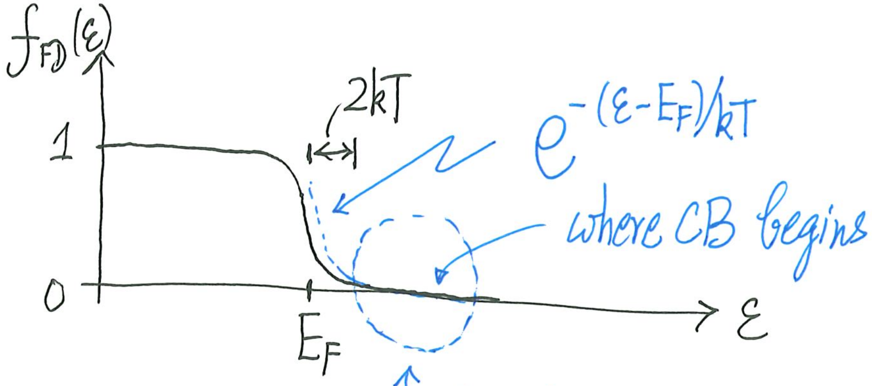
  Acceptor impurity states: ~10 meV (~0.01 eV) above top of CB



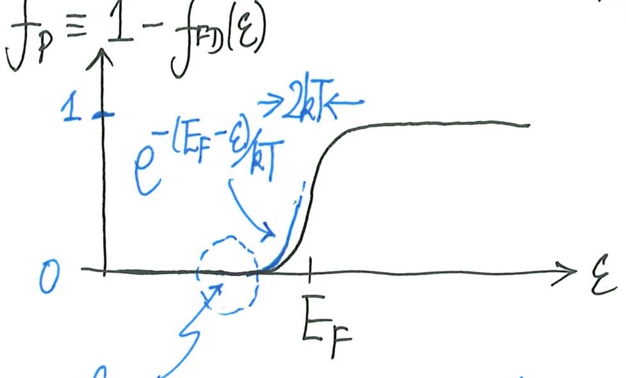
- The "2kT" range around E_F

$$\boxed{f_{FD}(\varepsilon)\ \frac{1}{e^{(\varepsilon-E_F)/kT}+1}\approx e^{-(\varepsilon-E_F)/kT}\qquad (12)\quad \text{for } (\varepsilon-E_F)>2kT}$$

OR $\dfrac{\varepsilon-E_F}{kT}>2$ (good up to ~4% for $\dfrac{\varepsilon-E_F}{kT}=2$)



for $(\varepsilon-E_F)\gtrsim 2kT$, only an exponential tail (i.e. close to zero tail) (tiny tiny chance of being occupied)

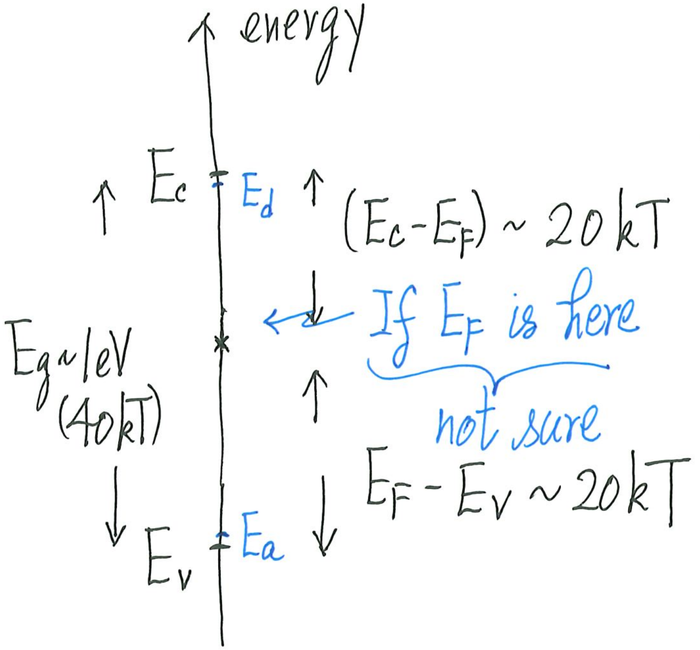


Eqs. (12), (13) are called the Classical Approximations to f_{FD} and f_p (14)

for $E_F-\varepsilon\gtrsim 2kT$, only an exponential $\underbrace{\text{tail } e^{-(E_F-\varepsilon)/kT}}_{\text{tiny tiny chance of being unoccupied}}$

$$\boxed{f_p=\frac{1}{e^{(E_F-\varepsilon)/kT}+1}\approx e^{-(E_F-\varepsilon)/kT}\qquad \text{for } E_F-\varepsilon>2kT\quad (13)}$$

Approximations (12), (13) are valid in many (most) cases



$$f_{FD} \approx e^{-(E_c-E_F)/kT} \sim \underbrace{e^{-20}\ (\text{tiny tail})}_{\text{even smaller for } \varepsilon \text{ in CB}}$$

$$f_p \approx e^{-(E_F-E_V)/kT} \sim \underbrace{e^{-20}\ (\text{tiny tail})}_{\text{even smaller for } \varepsilon \text{ in VB}}$$

Same argument works for a large range of energies within the gap where $E_F(T)$ could lie!

Only need to worry when E_F gets to 2-3 kT just below CB (or just above VB) (then use full expressions for f_{FD} and f_p)

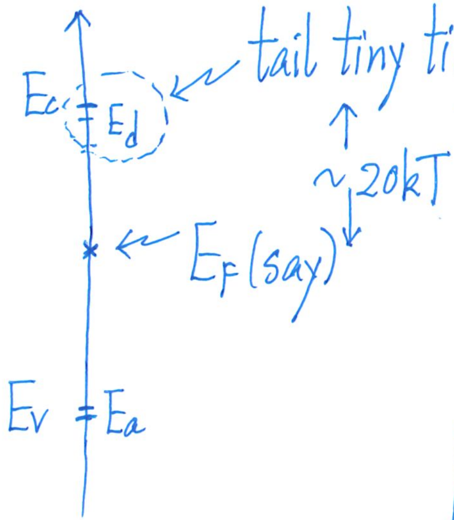
Implications

- Pure semiconductors (say E_F well within gap)
  - $\underbrace{e^{-(\varepsilon-E_F)/kT}}_{\text{CB states}}$ and $\underbrace{e^{-(E_F-\varepsilon)/kT}}_{\text{VB states}}$ are tiny $\left.\begin{matrix} n \\ p \end{matrix}\right\}$ are not big

Temperature effect: E_F shifts a bit, $\underbrace{n \text{ and } p \text{ can increase sensitivity}}_{\sim e^{-E_g/2kT}}$.

[a property that metals don't possess]
(metals have bigger n)

- Extrinsic Semiconductors

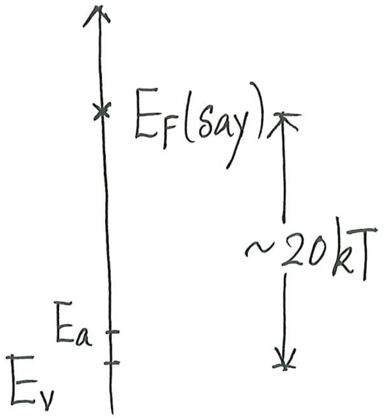


donor impurity states are highly likely unoccupied

⇒

← No electron here
(donor becomes +ve ion, e.g. P^+ in Si)

$\boxed{\text{Impurites are all ionized (electrons from donors all in CB)}}$

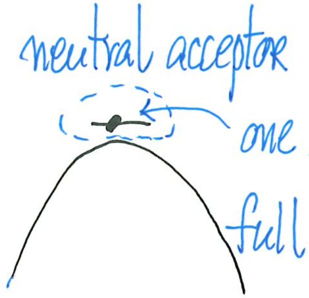


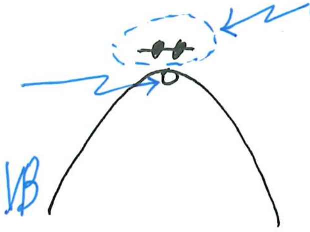
"electron picture" $f_p \sim e^{-20}$ tiny

⇒ tiny tiny chance for electron states to be unoccupied $(1-f_{FD})$

⇒ Acceptor state is Occupied

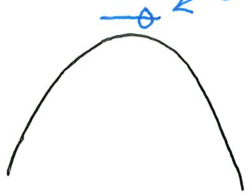
⇓

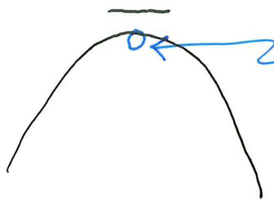




$\underbrace{\text{one empty state in VB}}_{\text{one hole in VB}}$

OR "hole picture"





↓

hole energy increases

$(E_h(\vec{k}_h) = -E_e(\vec{k}_e))$ (here band is drawn with electron energy increasing going up)

C. Statistics of Electrons and Holes: General Non-degenerate Semiconductors

DOS: $g_{CB}(\mathcal{E}) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{\mathcal{E}-E_c}$; $g_{VB}(\mathcal{E}) = \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}\sqrt{E_v-\mathcal{E}}$ (15)

$(\mathcal{E} > E_c)$ $(\mathcal{E} < E_v)$

[Recall: m_e^* could have included ellipsoidal energy surfaces and multiple valleys
m_h^* could have included effects of several (hh, lh) VBs]

- With previous argument (numbers):
  - electrons in CB are all close to bottom of CB → $e^{-(\mathcal{E}-E_F)/kT} \ll e^{-20}$
  - holes (empty states) in VB are all close to top of VB → $e^{-(E_F-\mathcal{E})/kT} \ll e^{-20}$

which is small

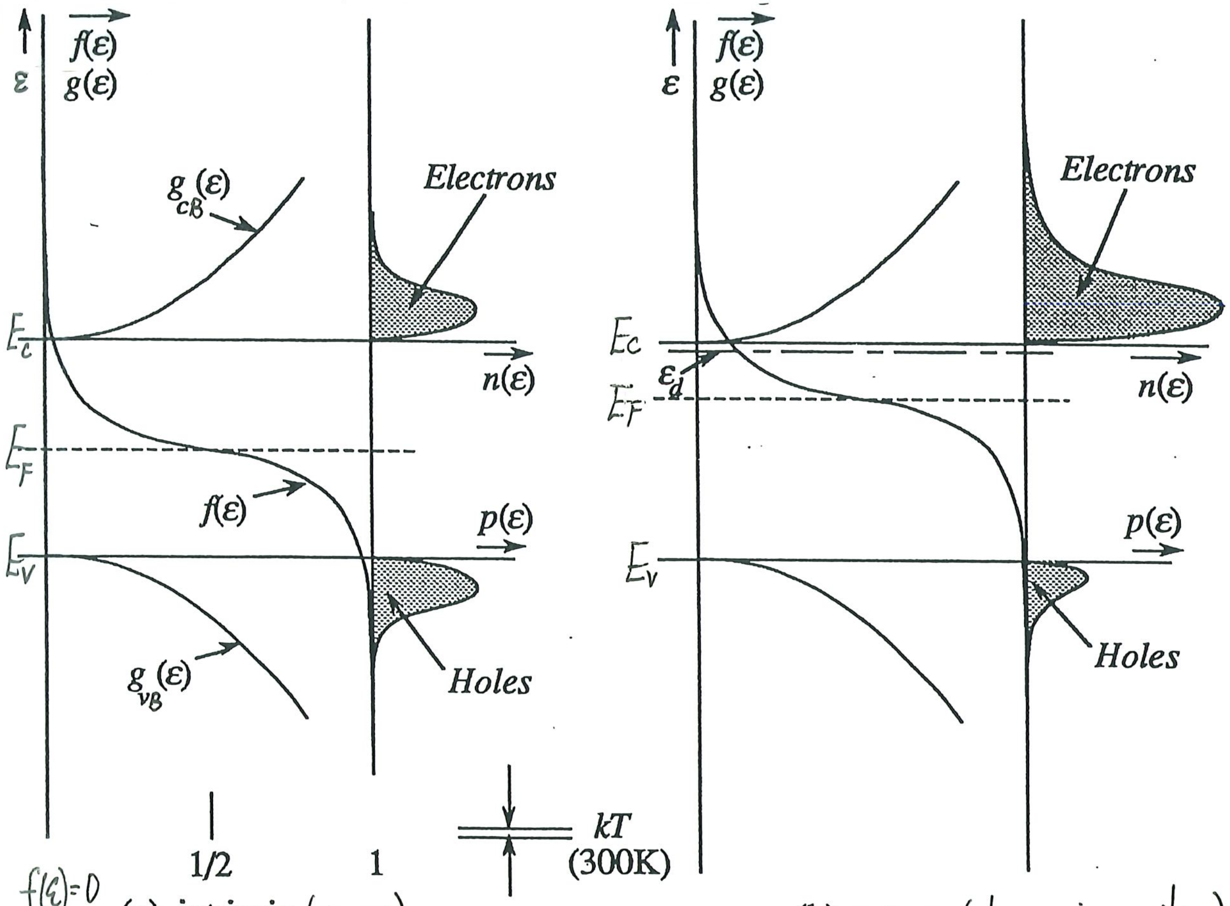
$\Downarrow$

parabolic ($\sim k^2$) parts of CB/VB

$\Downarrow$

m^* description is good

Key Physical Picture



(a) intrinsic (pure)

(b) n-type (donor impurities)
Extrinsic

Distribution functions, Fermi energy, and electron/hole populations (shown as shaded areas) for (a) an intrinsic semiconductor, and (b) an n-type semiconductor. The spread of the Fermi distribution function is grossly exaggerated for illustrative reasons; in reality it is normally much more steplike.

Possible to alter
⇐ n (electron number density)
in CB by adding
impurities (donors)

(metals can't do this)

$\boxed{\text{conductivity can be changed}}$

⇓

basis of why
semiconductors are
useful

[From McKelvey, "Solid State Physics for Engineering and Materials Science]

Using general expressions (Eqs. (10), (11)) and the Classical Approximations (Eqs. (12), (13)):

$$n_0 = \int_{E_c}^{\text{top of CB}} \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{\varepsilon - E_c}\cdot e^{-(\varepsilon - E_F)/kT}\,d\varepsilon$$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} e^{E_F/kT}\int_{E_c}^{\infty}\sqrt{\varepsilon - E_c}\; e^{-\varepsilon/kT}\,d\varepsilon$$

← no error here, as electrons are close to CB bottom

Call $x = \dfrac{\varepsilon - E_c}{kT}$

$d\varepsilon = kT\,dx$

$$= \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}(kT)^{3/2} e^{(E_F - E_c)/kT}\underbrace{\int_0^{\infty} x^{1/2} e^{-x}\,dx}_{\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{\sqrt{\pi}}{2}}$$

$$= 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2}\cdot e^{-(E_c - E_F)/kT}$$

$$= 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2}\cdot e^{-(E_c - E_F)/kT} \qquad (16a)$$

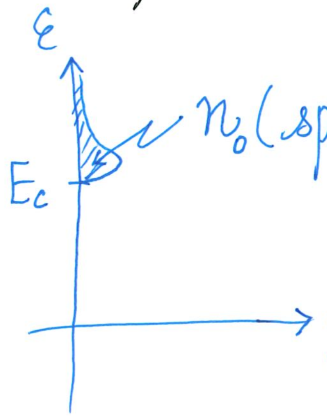
$$\equiv N_c \cdot e^{-(E_c - E_F)/kT} \qquad (16b)$$

- n_0 ~ # per unit volume
  - ↑ at equilibrium
- $N_c \equiv \left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2}\cdot 2$ has T-dependence
- $e^{-(E_c - E_F)/kT}$ dominant T-dependence

Physical Meaning

$$n_0 = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \cdot e^{-(E_c-E_F)/kT} \equiv \underbrace{N_c \cdot e^{-(E_c-E_F)/kT}}_{\text{why write in this form}}$$

this form



n_0 (spread over $\underbrace{\text{a tiny range}}_{\text{because of } \sim e^{-(E_c-E_F)/kT}}$ of energy just above E_c)

equivalent to think of it as

$\underbrace{N_c(T)}_{\sim (kT)^{3/2} \text{ (increases with T)}}$ of states ALL at $\varepsilon = E_c$ ← bottom of CB

so that

$$n_0 = \underbrace{N_c}_{\text{degeneracy at } \varepsilon = E_c} \cdot \underbrace{e^{-(E_c-E_F)/kT}}_{\text{prob. of a state being occupied (classical approximation}^{+}\text{ applied)}}$$

+ The classical approximation is also called the Boltzmann approximation.

Recall: When applied to Si (Ge), $m_e^* = \left(\eta^2 m_\ell^* m_t^2\right)^{1/3}$

Key Idea: Examine the steps

$$n_0 = N_c \cdot e^{-(E_c-E_F)/kT} = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \cdot e^{-(E_c-E_F)/kT} \qquad (16)$$

does NOT refer to where the electrons in CB came from.

∴ n_0 works for both intrinsic$^+$ and extrinsic$^+$ semiconductors

[assumed $\sim k^2$ band and classical approximation for $f_{FD}(E)$]

$^+$electrons in CB could have come from thermal excitations from VB or/and from donors.

$$p_0 = \int_{\text{bottom of VB}}^{E_v} \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}\sqrt{E_v-\varepsilon}\cdot e^{-(E_F-\varepsilon)/kT}\,d\varepsilon$$

classical approximation for $f_p(\varepsilon) = 1 - f_{FD}(\varepsilon)$

$$= \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}\int_{-\infty}^{E_v}\sqrt{E_v-\varepsilon}\;e^{-(E_F-\varepsilon)/kT}\,d\varepsilon$$

$-\infty$ ← made no error as empty states are near top of VB

[call $y = \frac{E_v-\varepsilon}{kT}$; $d\varepsilon = -kT\,dy$; $e^{-(E_F-\varepsilon)/kT} = e^{-y}\cdot e^{-(E_F-E_v)/kT}$]

$$= \frac{1}{2\pi^2}\left(\frac{2m_h^*}{\hbar^2}\right)^{3/2}(kT)^{3/2}(-)\underbrace{\int_{\infty}^{0} y^{1/2}e^{-y}\,dy}_{\Gamma(3/2)=\frac{\sqrt{\pi}}{2}}\cdot\left(e^{-(E_F-E_v)/kT}\right)$$

$$= 2\cdot\left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2}\cdot e^{-(E_F-E_v)/kT} \qquad (17a)$$

$$\equiv N_v\cdot e^{-(E_F-E_v)/kT} \qquad (17b)$$

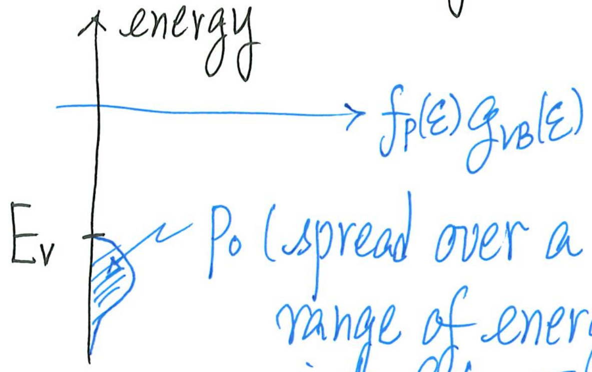
Unit: #/Volume

↑ has T-dependence

↖ dominant T-dependence

p_o ↑ indicates equilibrium

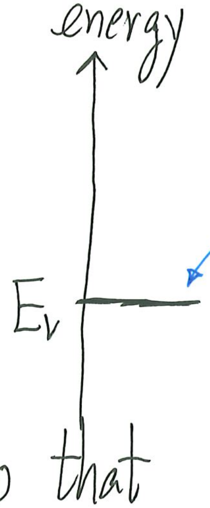
Physical Meaning



p_0 (spread over a tiny range of energy just below E_v)

Actual

equivalent to



top of VB

$\underbrace{N_v(T)}_{\sim (kT)^{3/2}}$ of states ALL at $\varepsilon = E_v$

$\sim (kT)^{3/2}$ (increases with T)

so that

$$p_0 = N_v \cdot \underbrace{e^{-(E_F - E_v)/kT}}_{}$$

prob. of a state being empty
(prob. of a hole state being occupied)
(classical approximation applied)

Recall: When applied to top of VB

$$m_h^{3/2} = m_{hh}^{*\,3/2} + m_{\ell h}^{*\,3/2}$$

(as lh and hh overlap)

Key Idea: Examine the steps

$$p_0 = N_v \cdot e^{-(E_F - E_v)/kT} = 2\left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2} \cdot e^{-(E_F - E_v)/kT} \quad (17)$$

does NOT refer to where the holes (empty states) came from

∴ p_0 works for both intrinsic$^+$ and extrinsic$^+$ semiconductors

[assumed $\sim -k^2$ VBs and classical approximation]

$^+$ Empty states in VB could have come from thermal excitations of electrons from VB to CB OR/and from VB to acceptors

(holes could have come from thermal excitations from CB to VB OR/and from acceptors to VB)

Law of Mass Action

n_0 and p_0 are general and good for intrinsic and extrinsic semiconductors

Construct $n_0 \cdot p_0$ (product of equilibrium electron and hole number densities)

$$n_0 \cdot p_0 = N_c \cdot N_c \cdot e^{-(E_c - E_F)/kT} \cdot e^{-(E_F - E_v)/kT}$$

$$= 4 \cdot \left(\frac{2\pi \sqrt{m_e^* m_h^*}\, kT}{h^2} \right)^3 \cdot e^{-(E_c - E_v)/kT}$$

$E_g = E_c - E_v$

$$= 4 \cdot \underbrace{\left(\frac{2\pi \sqrt{m_e^* m_h^*}\, kT}{h^2} \right)^3}_{\uparrow} \cdot \underbrace{e^{-E_g/kT}}_{\uparrow} \qquad (18)$$

Key Point

E_F dropped out of $n_0 \cdot p_0$

$\Downarrow$

Don't need to know value of E_F

Key Point: depends on m_e^*, m_h^*, E_g (i.e. semiconductor itself, band structure) and kT [nothing else]

Good for pure or doped semiconductors!

Define a symbol n_i as:

$$\boxed{n_0 \cdot p_0 = n_i^2 \quad , \quad n_i = 2 \cdot \left(\frac{2\pi \sqrt{m_e^* m_h^*}\, kT}{h^2} \right)^{3/2} \cdot e^{-E_g/2kT}}$$

(19)
(General)

- n_i is a Property of a semiconductor (regardless clean/doped) at a given temperature
- it has the unit of 1/volume [m_e^*, m_h^*, E_g are data; kT for a temperature]

e.g. Si at 300K

$$n_i \approx 1.5 \times \underbrace{10^{10}\ cm^{-3}}_{cm^{-3} \text{ is commonly used}} = 1.5 \times 10^{16}\ m^{-3}$$

Ge at 300K

$$n_i \approx 2.4 \times \underbrace{10^{13}\ cm^{-3}} = 2.4 \times 10^{19}\ m^{-3}$$

- n_i is called a semiconductor's intrinsic electron (hole) density
  (again, $n_0 \cdot p_0 = n_i^2$ works NOT ONLY for pure sample)
- n_i takes on an additional meaning (beyond $n_i^2 = n_0 \cdot p_0$) in an intrinsic semiconductor

When Eqs. (16), (17), (18), (19) work for a semiconductor, the semiconductor is referred to as Non-degenerate semiconductor

Stat. Physics: When only few electrons/fermions in many available states, occupation per state is low ($\ll 1$) so need not worry about Fermi-Dirac form of distribution

(non-degenerate fermi gas)

Here, depends on E_F well below CB (many kT) and well above VB (many kT)

When Fermi-Dirac Distribution is needed, degenerate semiconductor

Many electrons in CB

(e.g. heavily doped with impurity band)