



Part 3: Equilibrium Carrier Statistics

Q: How many carriers are available for conduction?

Topics: Density of states, Fermi-Dirac Statistics, Carrier concentration in semiconductors.

EE5181: Semiconductor devices

EE, IIT Hyderabad

Shubhadeep B (shubhadeep@ee at iith)

Understanding n (available free carriers)

↑ Imp!

$$\sigma = n q \mu \rightarrow E-K \text{ diagram} \quad n \rightarrow \# \text{ of carriers avail for conduction}$$

??

A CLASS ROOM ANALOGY!

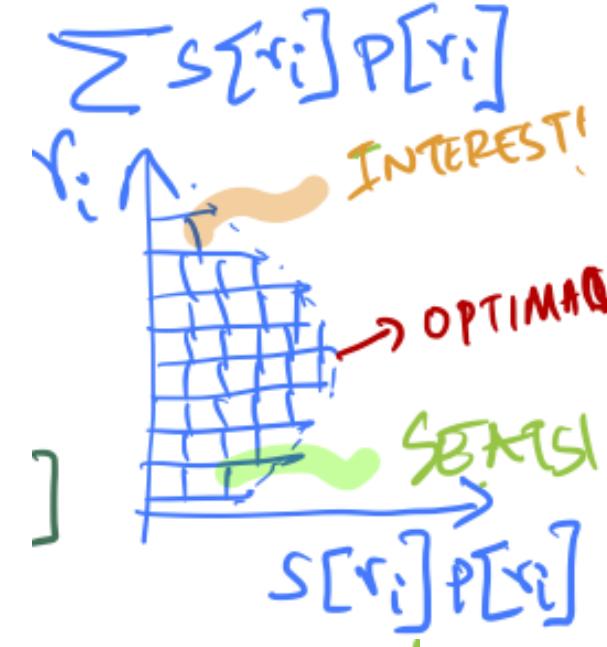
volume

Shape of
class room

Seats, $S[r_i]$



Interest in the
course &
probabilis to occupy
seats near me



D.O.S $\frac{\text{available states } e^- \text{ can occupy}}{\text{VOLUME}}$ proof that $\frac{\text{F-D distrib}}{\text{State is filled}} = \frac{\# \text{ of } e^-}{\text{Volume}}$ (n)



Equilibrium carrier concentration

$$n = \int_{E_{\min}}^{E_{\max}} N(E) dE ; \quad N(E) = g(\bar{E}) f(E)$$

$n \equiv$ no. of free carriers per unit volume (cm^{-3})

$N(E) \equiv$ no. of available carriers per unit energy per unit vol. [$\text{cm}^{-3} \text{eV}^{-1}$]

$g(\bar{E}) \equiv$ no. of available states carrier can occupy
 [Density of states (DOS)] per unit energy per unit vol. [$\text{cm}^{-3} \text{eV}^{-1}$]

Occupation Probability

$f(\bar{E}) =$ probability of finding an e^- @ Energy ' \bar{E} ' {from 0-1, dimensionless}
 OR probability that an "allowable state" is filled (or empty)

→ Fermi-Dirac [F-D] Distribution.

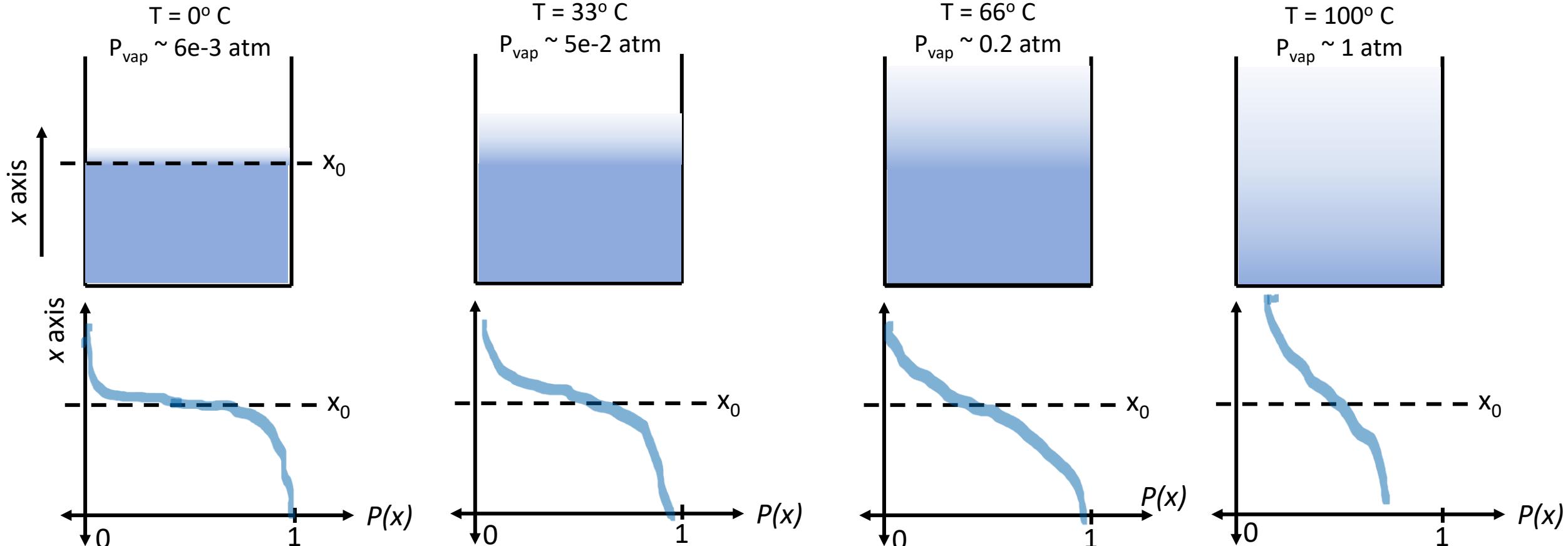
Normally Textbooks start with DOS, but we will start with F-D Distribution



Understanding Fermi Dirac Statistics with an intuitive example

Let's not derive F-D statistics but understand it intuitively.

Take a beaker of water and track the probability of finding a H₂O molecule



Probability of finding
a water molecule at 'x'

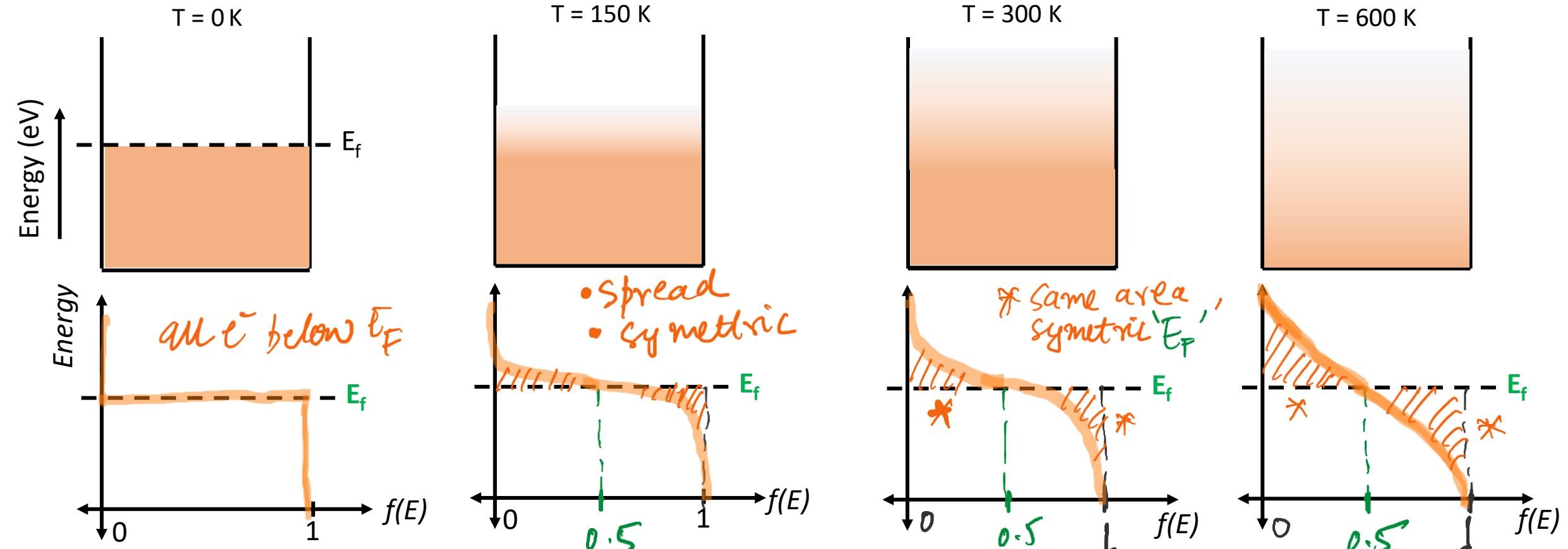
Insights:

- T increasing H₂O molecule energy increasing – vaporizes
 - Spread in $P(x)$, with Temp
- Notice $P_{\text{vap}} \propto \exp(a - b/T)$ – Maxwell Boltzmann-like statistics!



Understanding Fermi Dirac Statistics – Now with fermions (electrons)!

Note following changes: 1) $T_0 = 0$ Kelvin 2) x axis replaced with Energy (E) axis
3) $f(E)$ – probability of finding e^- @Energy (E)



$f(E)$ – prob of finding e^-
@ Energy, E

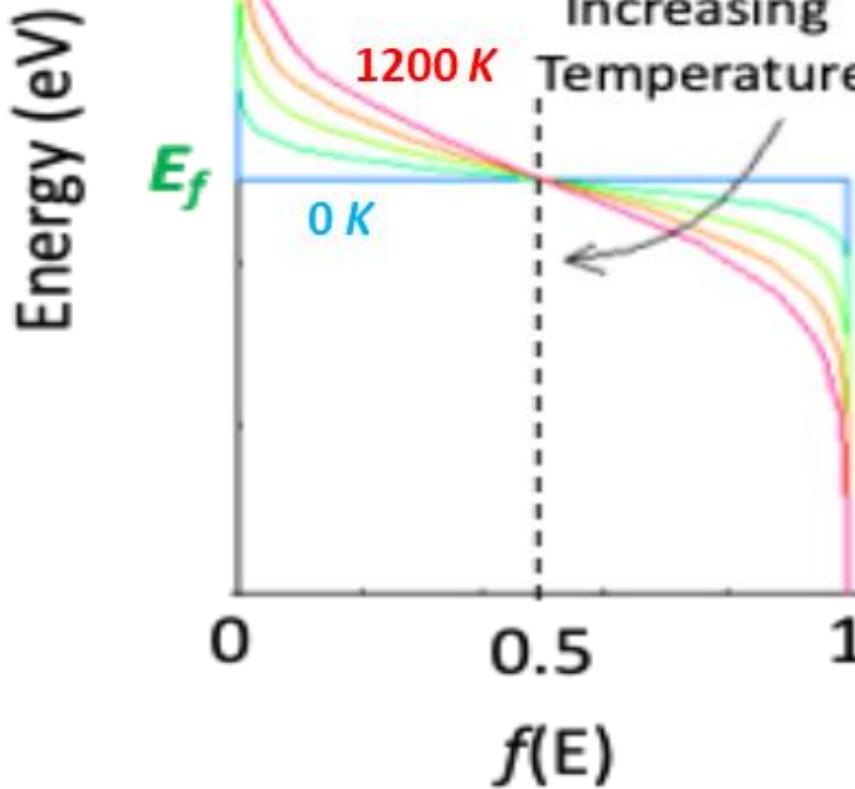
Insights:

- T increasing some electrons get excited- thermal energy $k_B T$
 - Smearing in Probability of finding electron, $f(E)$
 - $f(E) \propto \exp(-1/T)$ – Fermi- Dirac Distribution, E_f next slide



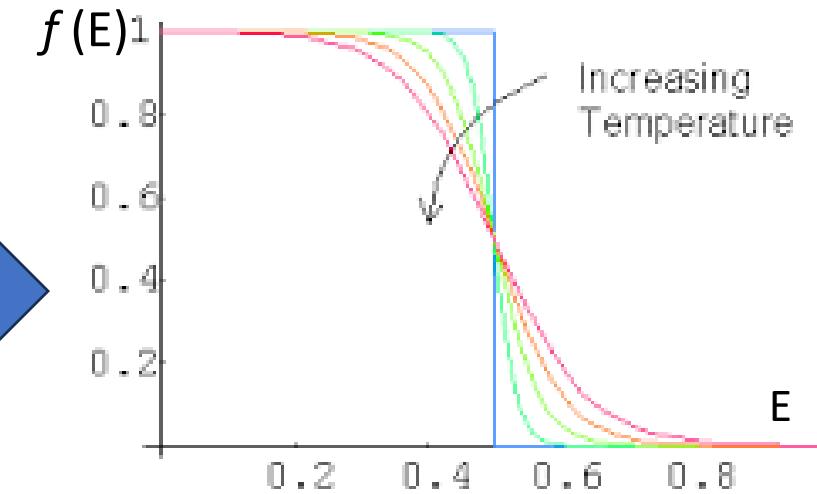
Fermi Dirac distribution/statistics - 1

Combining different T
(from prev slide)



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

Derived from stat mech,
indistinguishable particles
(Pauli's exclusion principle)



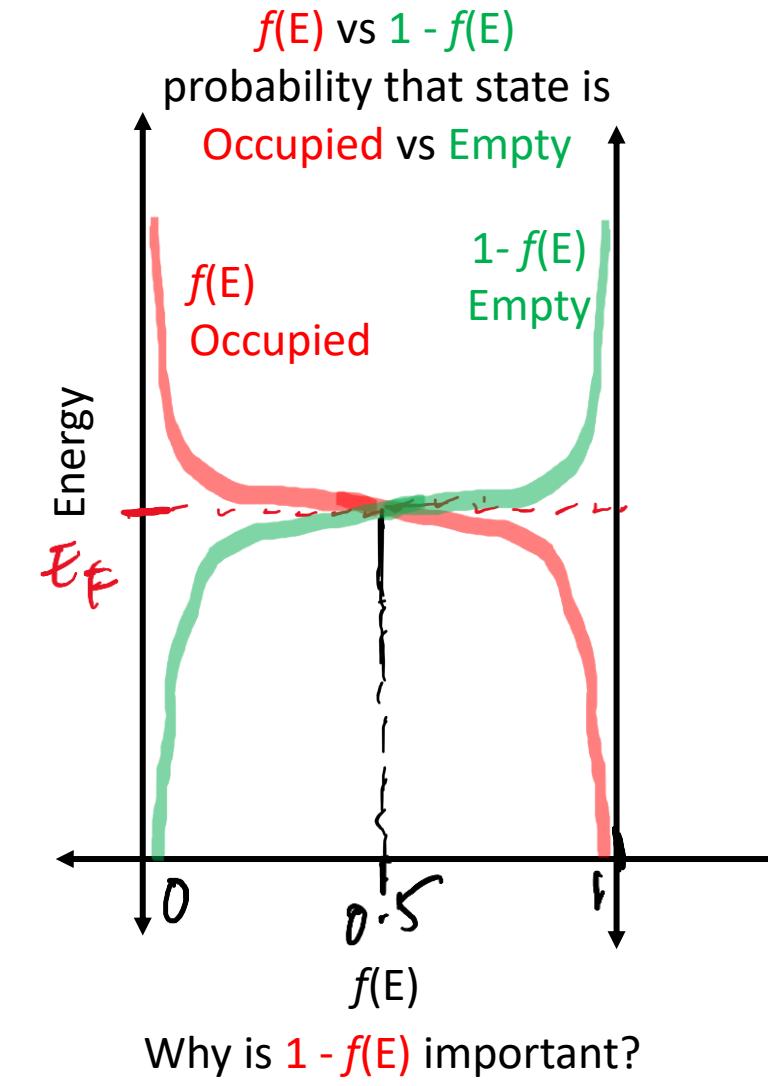
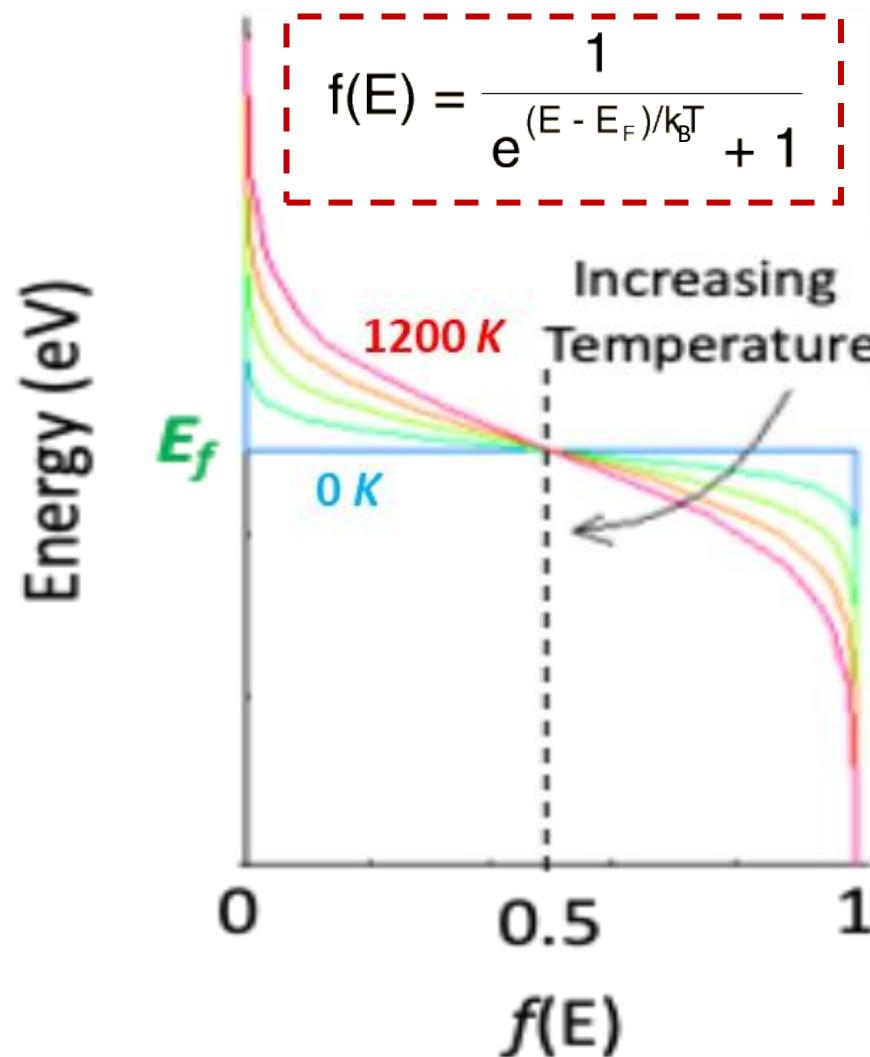
Text books plot E in x axis and $f(E)$ in y
In this course we will flip axis (E in y
axis ex: $E-k$) – Don't be confused ☺

- Imp points:
1. $k_B T$ – Thermal Energy, k_B = Boltzmann const
 2. $k_B T = 25.9$ meV @ 300K, $E_{g, Si} \sim 1.1$ eV
 3. $T = 0$ highest Energy is E_f
 4. E_f Fermi Energy $f(E_f) = 0.5$
 $T > 0$
 5. $E \gg E_f \Rightarrow f(E) \rightarrow 0$;
 $E \ll E_f \Rightarrow f(E) \rightarrow 1$
 6. $|E - E_f| > 3 k_B T$, then
 $f(E) = e^{-(E-E_f)/k_B T}$ {Maxwell-Boltzmann distr}

Simply describes occupation probability of electrons due $k_B T$ (Thermal smearing)
(nothing to do with 'band theory': common confusion in students)

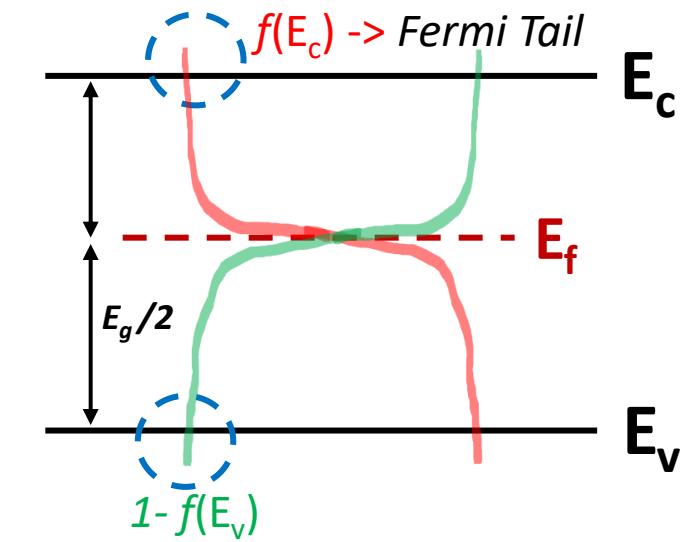


Fermi Dirac distribution/statistics - 2



Empty state: Occupation probability of Holes in Valence band!

Feel With Numbers:
Ex: Silicon ($E_g = 1.1$ eV) and E_f in middle of gap,
How many filled states in E_c ?
How many vacant states in E_v ?



$$f(E_c) = \exp(-0.55/0.026) = 6.5 \times 10^{-10} !!$$

$$1-f(E_v) = 6.5 \times 10^{-10} !!$$

Almost no occupation,
But $n_i \sim 1.5 \times 10^{10}$

Density of States very large
offsets tiny $f(E)$!



Equilibrium carrier concentration

$$n = \int_{E_{\min}}^{E_{\max}} N(E) dE ; N(E) = g(\bar{E}) f(E)$$

$n \equiv$ no. of free carriers per unit volume (cm^{-3})

$N(E) \equiv$ no. of available carriers per unit energy per unit vol. [$\text{cm}^{-3}\text{eV}^{-1}$]

$g(\bar{E}) \equiv$ no. of available states carrier can occupy
[\rightarrow Density of states (DOS)] per unit energy per unit vol. [$\text{cm}^{-3}\text{eV}^{-1}$]

$f(\bar{E}) =$ ~~probability of finding an e^- @ Energy ' \bar{E} ' {from 0-1, dimensionless}~~
Occupation Probability
OR probability that an "allowable state" is filled (or empty)
[\rightarrow Fermi-Dirac (F-D) Distribution]

Density of states (DOS) $g(E)$ - BAND STRUCTURE!

Q: How many 'states' (NOT Carriers!) per unit volume per unit energy

Reminder: What are States (analogous to seats in the previous example): Solution to the Schrodinger equation that particle **CAN** occupy (allowed energy levels)

Large but finite no. of states that e- can occupy.

- E_c @ 0 K: many states – but none are occupied.
- E_v @ 0 K: many states – all are occupied.
- Band gap: no allowable energy states.

$$g_{3D}(E) \rightarrow \frac{\text{no. of states}}{\text{Volume } dE} \quad \left. \begin{array}{l} \text{WISH TO} \\ \text{DERIVE} \end{array} \right\}$$

much easier and more useful

$$g_{3D}(E) dE = \frac{\# \text{ states b/w } E \& E+dE}{\text{VOLUME}}$$

Another simplification:- Since $E - k$ is parabolic related



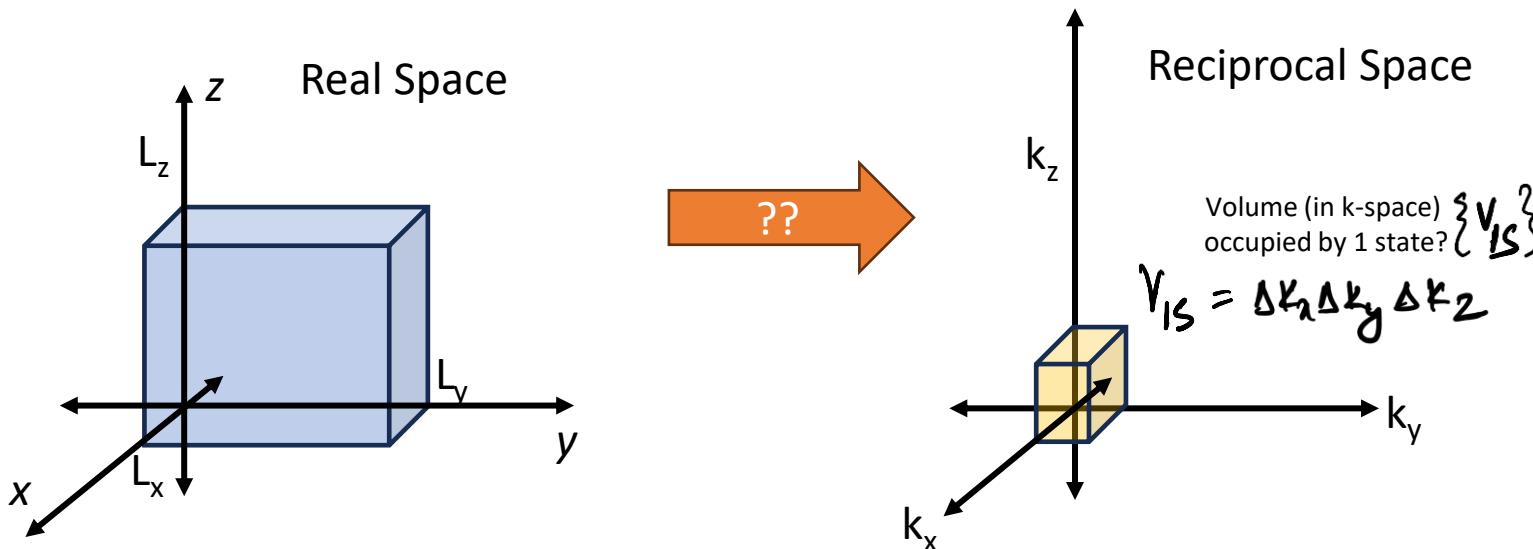
$$\begin{aligned} g(E) dE &\equiv g(k) dk \\ \text{no. of states} &= \text{no. of states} \\ \text{b/w } E \& dE &\equiv \text{b/w } k \& dk \\ \text{per Volume} &\text{ per Volume} \end{aligned}$$

$g_3(k) dk$ - straightforward to derive.

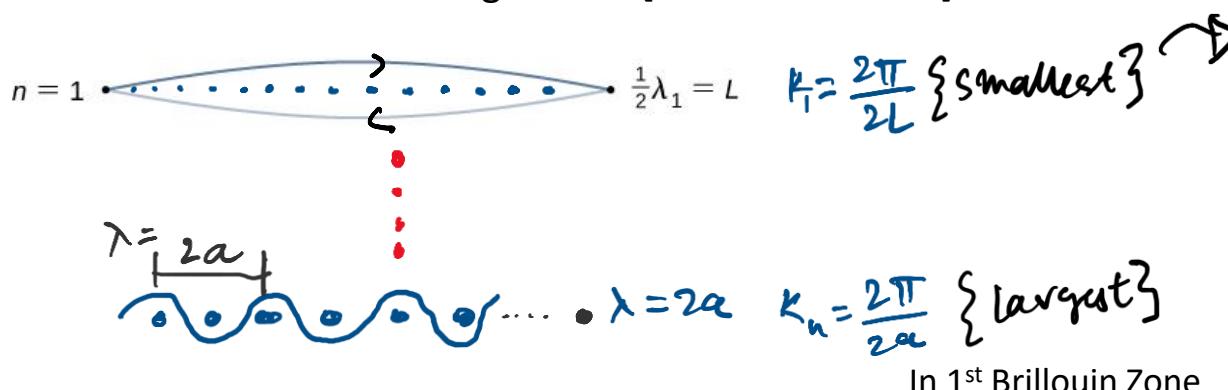
$$g_{3D}(k) dk = \frac{\text{Volume in k-space b/w } k \text{ and } k+dk}{\text{Volume in k-space occupied by 1 state}}$$

Derivation for DOS (Vol of 1 state)

Let's consider a piece of material with dimensions L_x , L_y and L_z and convert to k-space



Recap: Solution to SCE $|\Psi|$ periodic and confined to L : standing waves! [Bloch's Theorem]



Since k_x, k_y, k_z are orthogonal:

$$\Delta k_x = \frac{\pi}{L_x}; \Delta k_y = \frac{\pi}{L_y}; \Delta k_z = \frac{\pi}{L_z}$$

$\nabla_{\Delta k} = \Delta k_x \Delta k_y \Delta k_z$

$$= \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{\text{Vol}}$$

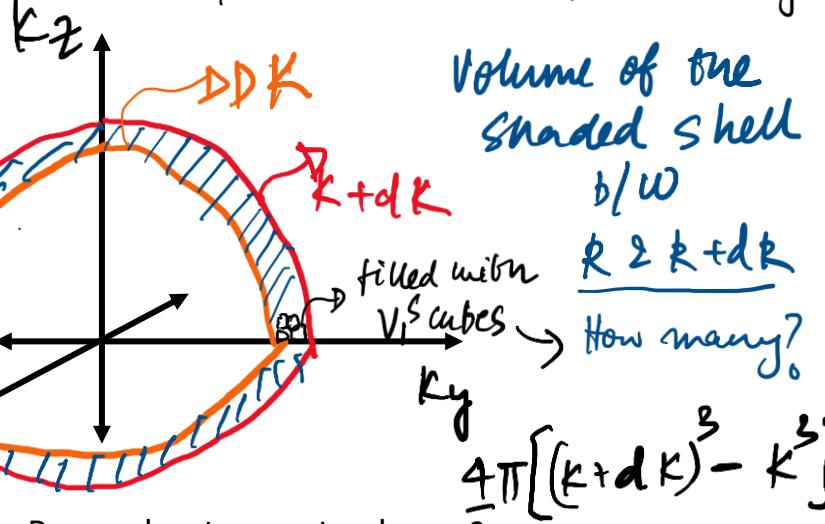
This considers STANDING WAVE \rightarrow BOTH $\pm k_x$

{NOTE:- some text books consider $\frac{2\pi}{L_x} \rightarrow$ only $+k_x$ }

Derivation for DOS (Vol b/w k and $k+dk$)

What is the Volume between k and $k+dk$

Assumption:- Isotropic medium :- Spherical Symm.



Remember to count only positive $k_x k_y k_z$ i.e. first octant

$$V_{k+k+dk} = \frac{1}{8} \times \frac{1}{8} \times 4\pi k^2 dk$$

$\uparrow \downarrow$
 {Spin} Octant

$$g_{3D}(k) dk = \frac{\text{Volume in k-space b/w } k \text{ and } dk}{\text{Volume in k-space occupied by 1 state}}$$

$$g_{3D}(k) dk = \frac{\pi k^2}{\pi^3} dk = \frac{k^2}{\pi^2} dk \quad \textcircled{1}$$

To convert $g(k) dk \rightarrow g(E) dE$, we use the free particle approx $\rightarrow E = (\hbar^2 k^2)/2m^*$

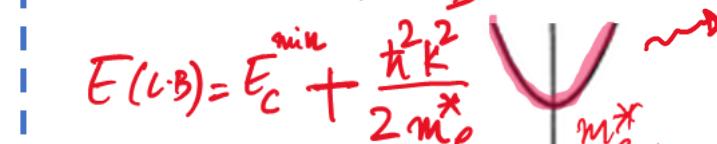
Substituting in ① R^2 and $\frac{dE}{dk} = \frac{\hbar^2 k}{m^*}$

$$g_{3D}(E) dE = \frac{4\pi}{\hbar^3} (2m^*)^{3/2} E^{1/2} dE$$

This is generic expression in E ,
 But we care about DOS in CB and VB;
 Simply Substitute $E_{CB}(k)$ and $E_{VB}(k)$

Recap:

$$E(CB) = E_C + \frac{\hbar^2 k^2}{2m_e^*} \quad \rightsquigarrow g_C(E) = \frac{4\pi}{\hbar^3} (2m_e^*)^{3/2} [E - E_C]^{1/2} \quad \text{for } E > E_C$$



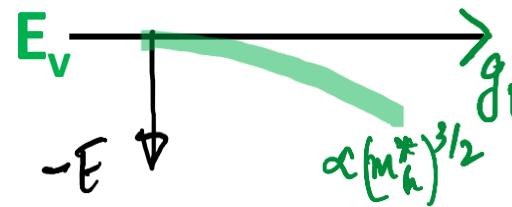
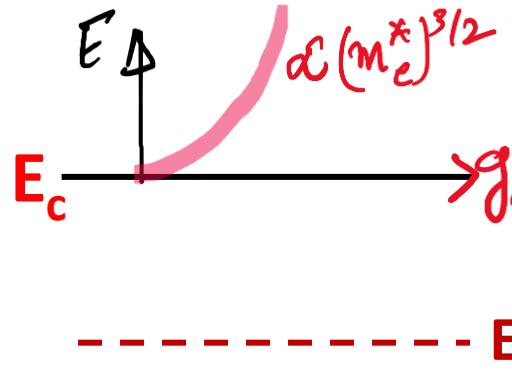
$$\rightsquigarrow g_{\text{Band gap}} = 0$$

$$E(VB) = E_V - \frac{\hbar^2 k^2}{2m_h^*} \quad \rightsquigarrow g_V(E) = \frac{4\pi}{\hbar^3} (2m_h^*)^{3/2} [E_V - E]^{1/2} \quad \text{for } E < E_V$$

DOS Depends only (a) Dimensionality (b) Band Structure!

Density of states in real materials

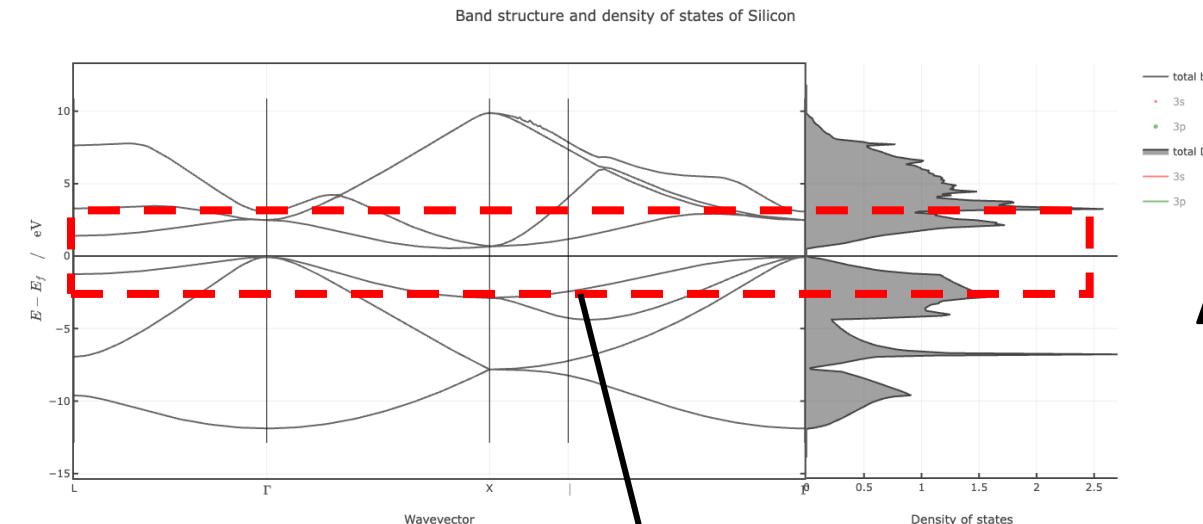
Density of States **near E_c** and E_v
(Parabolic band approx.)



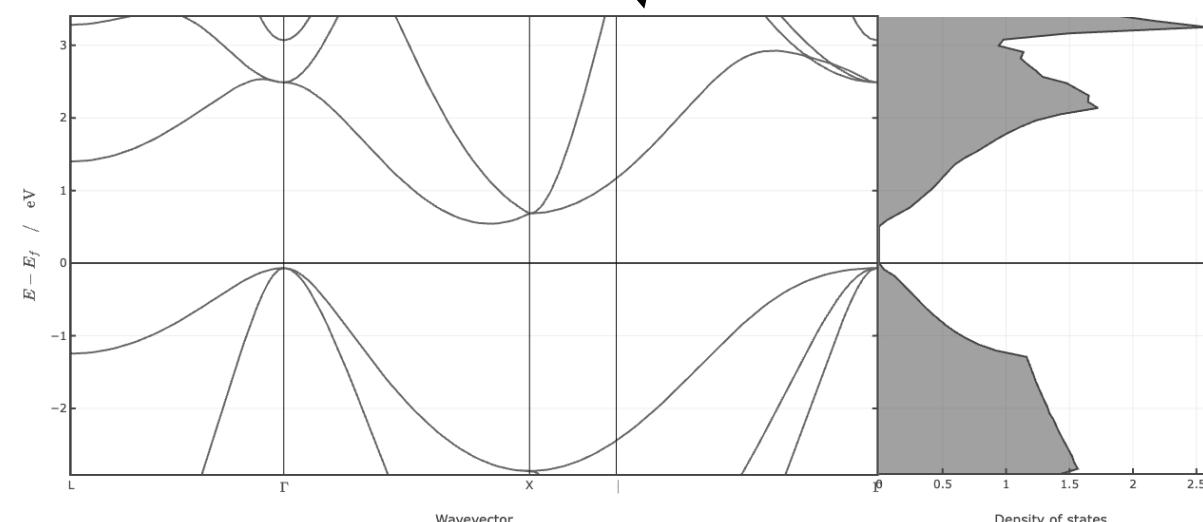
$$g_c^{3D}(E) = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} [E - E_c]^{1/2}$$

$$g_v^{3D}(E) = \frac{4\pi}{h^3} (2m_h^*)^{\frac{3}{2}} [E_v - E]^{1/2}$$

Source (go check it out): <https://plotly.com/~annemarietan/30.embed>



DOS @ Silicon:
Complicated
Away from E_c E_v

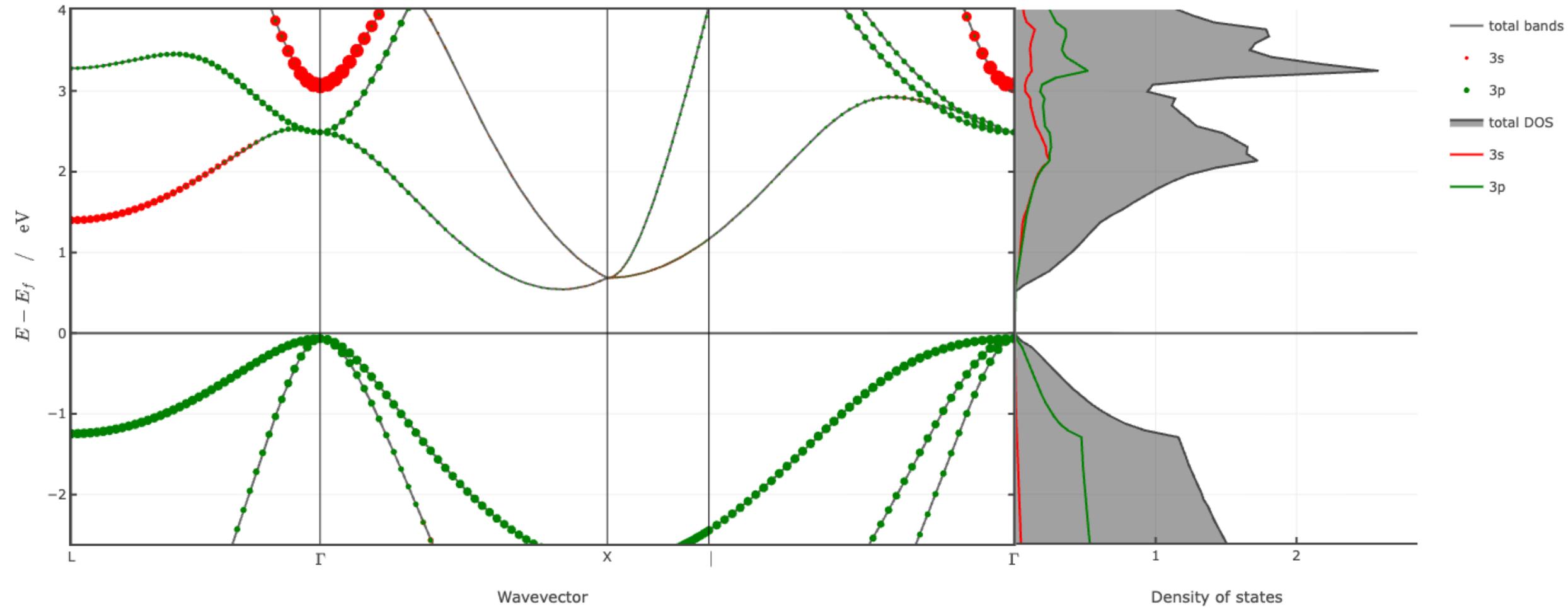


* Notice: DOS depends on m^* (exaggerated in this diag for the case $m_e^* < m_h^*$)



3s and 3p Orbitals picture.

Band structure and density of states of Silicon





Equilibrium carrier concentration

$$n = \int_{E_{\min}}^{E_{\max}} N(E) dE ; N(E) = g(\bar{E}) f(E)$$

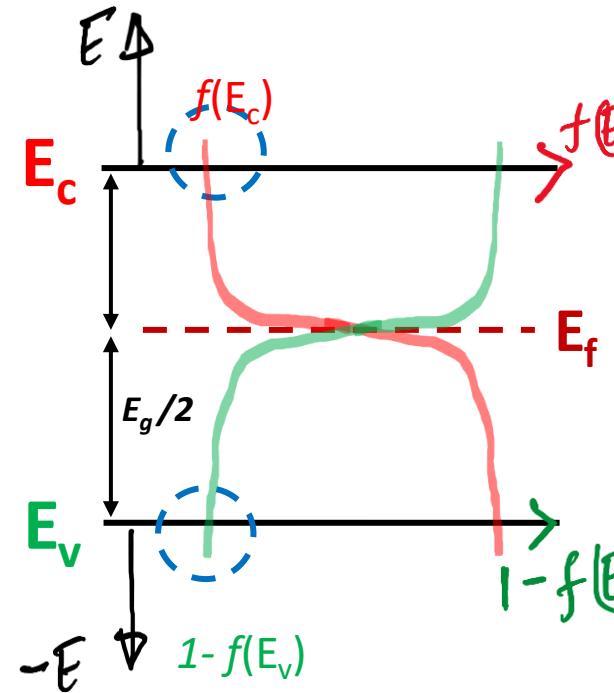
$n \equiv$ no. of free carriers per unit volume (cm^{-3})

$N(E) \equiv$ no. of available carriers per unit energy per unit vol. [$\text{cm}^{-3} \text{eV}^{-1}$]

$g(\bar{E}) \equiv$ no. of available states carrier can occupy
[\rightarrow Density of states (DOS)] per unit energy per unit vol. [$\text{cm}^{-3} \text{eV}^{-1}$]

$f(\bar{E}) =$ ~~probability of finding an e^- @ Energy ' \bar{E} ' {from 0-1, dimensionless}~~
Occupation Probability
OR probability that an "allowable state" is filled (or empty)
→ Fermi-Dirac [F-D] Distribution.

Revisit Si example with E_f in mid gap



$$f(E_c) = 1 / \left(1 + e^{\frac{(E - E_F)}{k_B T}} \right)$$

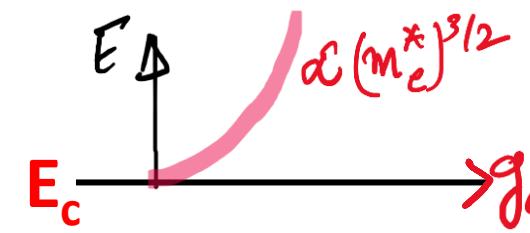
$$\approx \exp \left(-\frac{(E - E_F)}{k_B T} \right) \quad \{ E \gg E_F \}$$

$$\sim 6.5 \times 10^{-10}$$

$$1 - f(E_v)$$

F-D Function
(occupation probability)

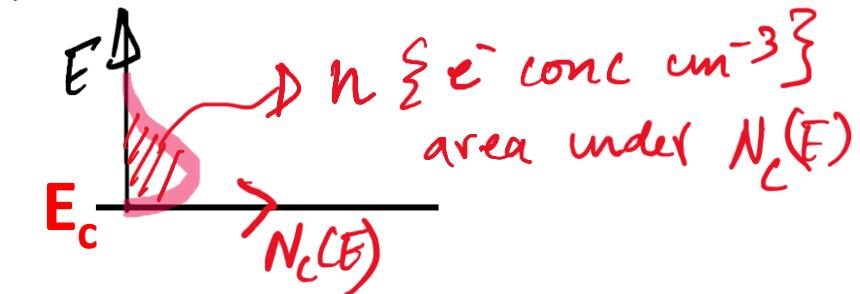
\times



$$g_c^{3D}(E) = \frac{4\pi}{h^3} (2m_e^*)^{\frac{3}{2}} [E - E_c]^{1/2}$$

$$g_v^{3D}(E) = \frac{4\pi}{h^3} (2m_h^*)^{\frac{3}{2}} [E_v - E]^{1/2}$$

Density of States



$$N_c(E) = f(E_c) g_c(E) \rightsquigarrow n(\text{cm}^{-3}) = \int_{E_c}^{+\infty} N_c(E) dE$$

$$N_v(E) = [1 - f(E_v)] g_v(E) \rightsquigarrow p(\text{cm}^{-3}) = \int_{-\infty}^{E_v} N_v(E) dE$$

= Supply Function $\rightarrow \int = n, p$ {carr conc.}

Doping, E_F position and carrier concentration

Insights from previous slide

E_F in mid gap \rightarrow Intrinsic carrier conc (n_i)

WRONG!! Why?

Case1: E_F in mid gap (prev slide)

- occupation probability of e- and h+ is equal
- But DOS entirely different.
- $n \neq p$

Case 2: Intrinsic Carrier conc. (this slide)

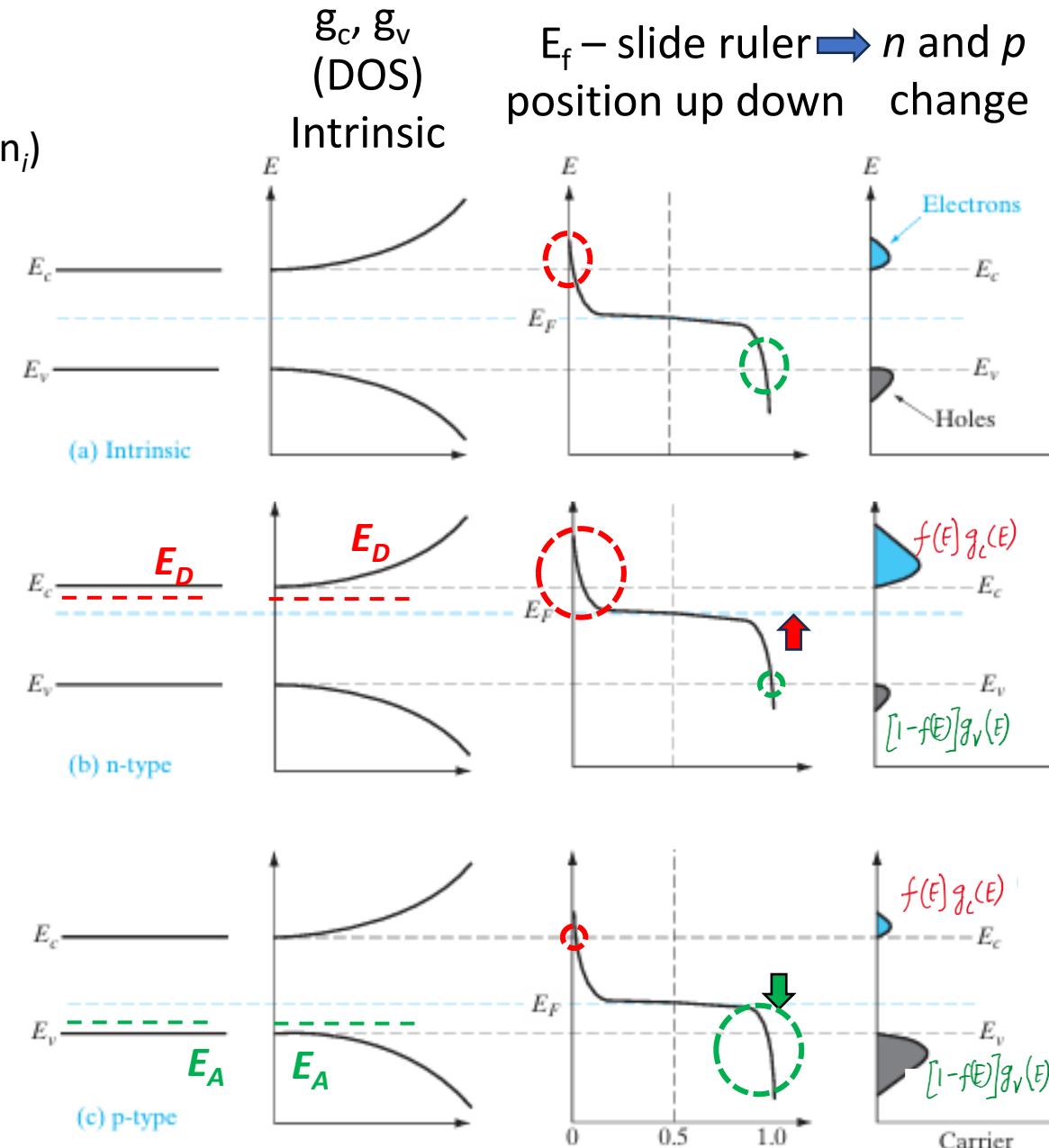
$(n_i = n = p)$ (No doping)

E_F is close to midgap

Why are semiconductors useful?

n, p can be tuned (chemical doping)

How do we represent this in Band diagrams?



Insights:

Doping $\rightarrow E_F$ closer to E_c or E_v \rightarrow Occupation probability e-/h+ {DOS Unchanged}

Open Questions:

1) How does doping happen practically (E_D and E_A , next slide)

Common Confusion: E_F representation of doping NOT cause, Cause is E_A, E_D

2) Notice when E_F moves up(down) n increases (decreases) and p proportionally decreases (increases)

- Is there a relationship n and p (slide after that)?

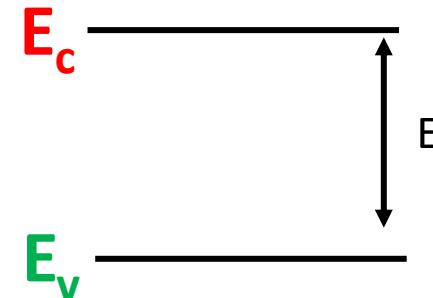
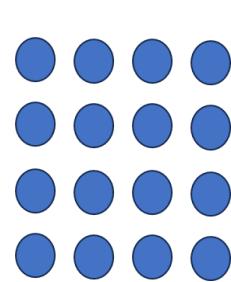


What does doping physically mean? (Si example)

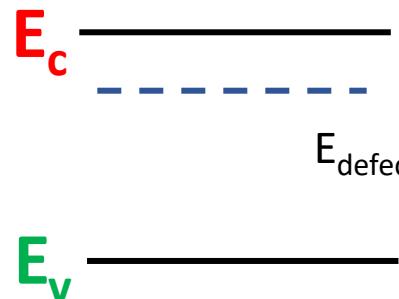
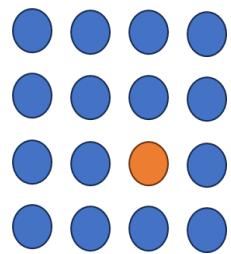
Perfect lattice



Band Diagram



Defect:
(ex. substitutional)

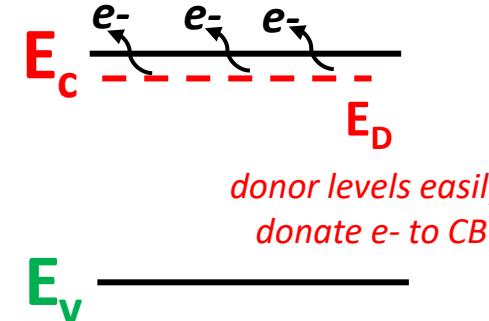


How to account for this defect in Band Diag?

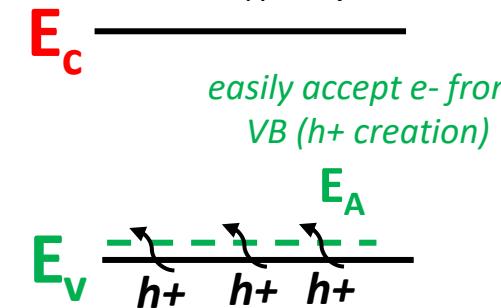
- States in CB/VB: little/no impact
- States within the Bang-gap: huge impact (+ve and -ve) – How to represent?
A: Dashed lines indicating not continuous

Position of Defect state in Band gap makes all the difference!

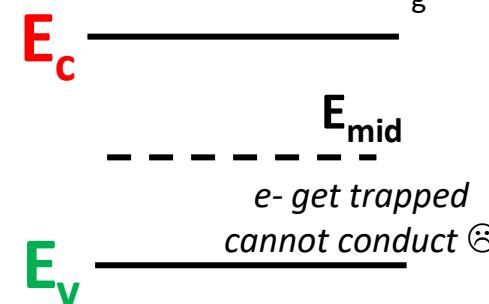
Case 1: Near CB: $E_c - E_D \sim \text{few } k_B T$



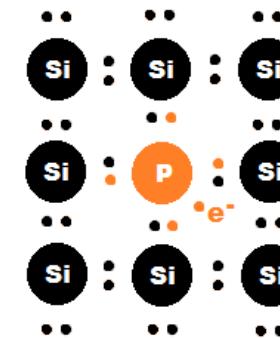
Case 2: Near VB: $E_A - E_v \sim \text{few } k_B T$



Case 3: Middle of E_g



example: P doping in Si



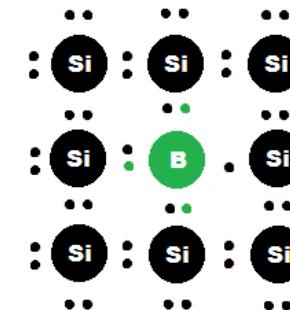
$$E_c - E_D = 46 \text{ meV}$$

$$N_D (\text{cm}^{-3})$$

Donor atom conc.

$$\bar{n} = N_D^{+} \left\{ \begin{array}{l} 100\% \\ \text{IONISATION APPR.} \end{array} \right.$$

example: B doping in Si



$$E_A - E_V = 44 \text{ meV}$$

$$N_A (\text{cm}^{-3})$$

Acceptor conc.

$$P^+ = N_A^- \left\{ \begin{array}{l} 100\% \\ \text{IONISATION APPR.} \end{array} \right.$$

example: Au/Cu in Si

$$E_{mid} \sim E_g / 2$$

Terrible for electronic and photonic properties: must be avoided.

Simplified expression for Carrier Conc/Effective DOS

$$n = \int N_c(E) dE = \int_{E_C}^{\infty} g_c(E) f(E) dE = \int_{E_C}^{\infty} \frac{4\pi}{h^3} (2m_e^*)^{3/2} [E - E_C]^{1/2} \frac{1}{1 + \exp \frac{[E - E_F]}{k_B T}} dE$$

Very difficult to solve analytically
 → Simplifying assumptions $E_C - E_F > 3k_B T$

? light, non-degenerate doping.
NOT degenerate doping \Rightarrow JOYCE-DIXON APPROX.

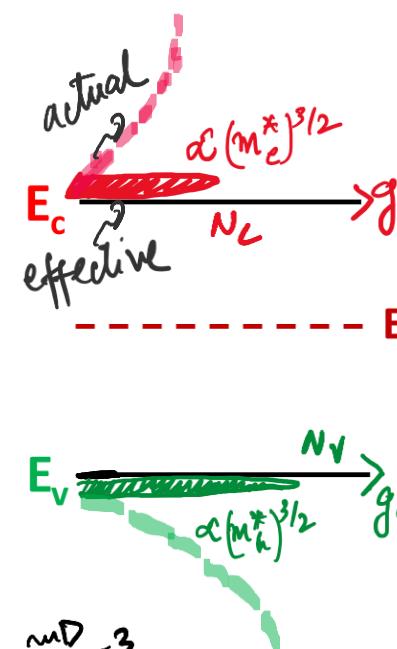
$n = N_c^{\text{eff}} \exp \left[-\frac{(E_C - E_F)}{k_B T} \right]; E_C - E_F > 3k_B T$

where $N_c^{\text{eff}} = 2 \left(\frac{2\pi m_e^* k_B T}{h^2} \right)^{3/2} \equiv \text{EDOS @ C.B}$

$p = N_v^{\text{eff}} \exp \left[-\frac{(E_F - E_V)}{k_B T} \right]; E_F - E_V > 3k_B T$

where $N_v^{\text{eff}} = 2 \left(\frac{2\pi m_h^* k_B T}{h^2} \right)^{3/2} \Rightarrow \text{EFFECTIVE DOS @ V.B}$

Caution: Don't confuse between (Effective DOS) $N_{c/v}^{\text{eff}}$ or $N'_{c/v} \text{ cm}^{-3}$
 and Supply Function $N_{c/v}(E) \text{ cm}^{-3} \text{ eV}^{-1}$



What does effective DOS mean?

No physical meaning: As if all DOS are concentrated @ E_c and E_v

Of course, mathematical convenience actual DOS = 0 at E_c and E_v

$$\begin{aligned} n &= N_c^{\text{eff}} f(E_C) \\ p &= N_v^{\text{eff}} [1 - f(E_V)] \end{aligned}$$

{ No Integration! }

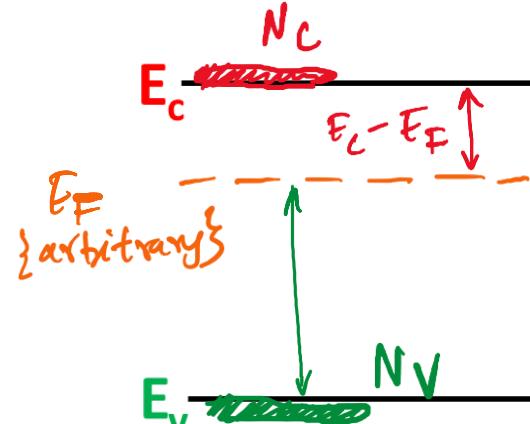
	$N_c (\text{cm}^{-3})$	$N_v (\text{cm}^{-3})$
Silicon	2.8×10^{19}	1.04×10^{19}
Gallium arsenide	4.7×10^{17}	7.0×10^{18}
Germanium	1.04×10^{19}	6.0×10^{18}

Some numbers for EDOS

Q: Why is $N'_c > N'_v$ for Si despite $m_e^* < m_h^*$

$n_0 p_0$ and n_i @ Thermal equilibrium

Thermal equilibrium:— **no NET** flow of charges.



General Case { Abbreviating $(N_c^{ch} + D N_c')$

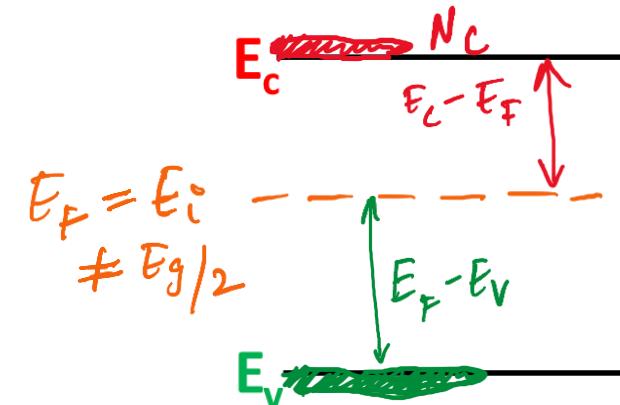
$$n_0 = N'_c \exp \left[-\frac{(E_c - E_f)}{k_B T} \right] - ①$$

$$p_0 = N'_v \exp \left[-\frac{(E_f - E_v)}{k_B T} \right] - ②$$

$$n_0 p_0 = N'_c N'_v \exp \left[-\frac{E_c + E_f - E_f + E_v}{k_B T} \right]$$

$$= N'_c N'_v \exp \left[-\frac{E_g}{k_B T} \right]$$

all constants



Intrinsic Case { No doping }

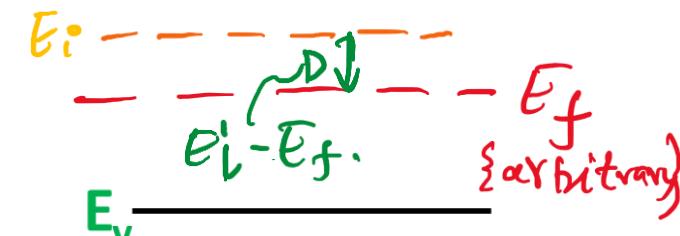
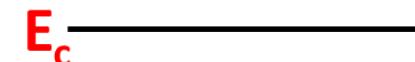
$$BUT \text{ such that } n_i = p_i \\ n_i^2 = h_i = N'_c N'_v \exp \left[\frac{E_g}{k_B T} \right]$$

$$n_i = \sqrt{N'_c N'_v} \exp \left[-\frac{E_g}{2k_B T} \right]$$

therefore $n_0 p_0 = h_i^2$ { Only in thermal equilibrium }

Mass action law

n_0, p_0 from n_i, E_i perspective



general Case :— $n_0, p_0 (n_i, E_i)$

$$n_0 = n_i \exp \left[\frac{E_f - E_i}{k_B T} \right]$$

$$p_0 = n_i \exp \left[\frac{E_i - E_f}{k_B T} \right]$$

* For $n_0 \text{ OR } p_0 \rightarrow 10^x n_i$
 $\rightarrow |E_f - E_i| \rightarrow x \times 60mV$

E_g (eV)	N'_c (cm^{-3})	N'_v (cm^{-3})	n_i (cm^{-3})
---------------	--------------------------------	--------------------------------	-------------------------------

Ge	0.66	1.04×10^{19}	6.0×10^{18}	2.3×10^{13}
Si	1.10	2.8×10^{19}	1.2×10^{19}	1.0×10^{10}
GaAs	1.42	4.7×10^{17}	7.0×10^{18}	2.1×10^6



From qualitative understanding to quantitative models

Good to have Qualitative understanding about physical reality,
But as Electrical Engineers all we care: Apply V/E what is the I/J

$$J = \sigma E$$

{Drude's law}

$$\sigma \{conductivity\} = q N \mu$$

of carriers
mobility

Q: Can we get
quantitative estimates

YES!

Next!
Transport

$$\mu$$

"E-k" \Rightarrow
Band-structure
{Intrinsic property}
{This section}

$$\#2 \mu \quad \{Next section\}$$

Energy $n(E) = \int g(E) f(E) dE$
{intrinsic}
no. of states an e^- can occupy [Energy] \times {TUNABLE}
probability of finding an $e^-[E]$

Done! ☺

Done! ☺

Summary – Equilibrium Carrier Statistics

Q: How many carriers are available for conduction in VB and CB?

#1) $n = \int_{E_{\min}}^{E_{\max}} N(E) dE$ = $\int_{E_{\min}}^{E_{\max}} g(E) f(E) dE$

Total no. of carriers available for conduction $\#(\text{cm}^{-3})$

Supply function $\{ \text{filled states per unit } E \rightarrow (\text{cm}^{-3}\text{eV}^{-1}) \}$

D.O.S $\{ \text{how many avl. states} \}$ $(\text{cm}^{-3}\text{eV}^{-1})$

F.D statistics $\{ \text{occupation probability} \}$ $\{ 0 \rightarrow 1 \}$

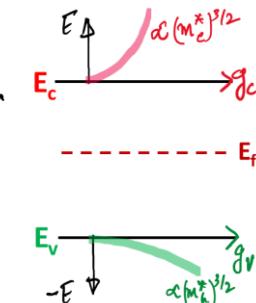
Classroom analogy

$n = \sum_{i=1}^n N[i] = \sum_{\substack{\text{row}=1 \\ \text{# students/ row}}}^N \text{Seats}[i] P_i[i]$

\uparrow Seats/ row \uparrow OCC prob/ row.

#2) $f(E) = \frac{1}{1 + \exp \left[\frac{E - E_F}{k_B T} \right]}$ $\approx \exp \left[\frac{-(E - E_F)}{k_B T} \right]$ $\rightarrow E_F \{ \text{Fermi Energy} \} \rightarrow f(E_F) = \frac{1}{2}$; $f(E_C) \rightarrow e^-$ and $1 - f(E_V) \rightarrow h^+$

$\{ \text{occupation probability} \}$ $\{ \text{for } E \gg E_F \}$



INDEPENDENT!

#3 $g_{3D}(E) dE = g_{3D}(K) dK = \frac{\text{Vol in } k' \text{ b/w } K + dK}{\text{Vol in } k' \text{ for one state}} = \frac{k^2}{\pi^2} dK = \frac{4\pi}{h^3} (2m^*)^{3/2} E^{1/2} dE$;

density of states

#4) DOPING E_A , E_D and simplified

$n_0 = \frac{N_C}{\text{effective DOS}} f(E_C)$; $P_0 = \frac{N_V}{\text{effective DOS}} [1 - f(E_V)]$

} for low doping only!

#5) $n_0 P_0 = n_i^2$ @ Thermal Equl. $n_0 = n_i \exp \left[\frac{E_F - E_i}{k_B T} \right]$; $P_0 = n_i \exp \left[\frac{E_i - E_F}{k_B T} \right]$