Section 4: Carrier Concentration

Sunday, October 10, 2021 8:00 PM

(I.) Fermi Energy

Consider free electrons confined to a box (approximation for metal):

$$V(x,y,z) = \begin{cases} 0 & 0<x<L,\ 0<y<L,\ 0<z<L \\ \infty & \text{otherwise} \end{cases}$$

$$H\psi = E\psi$$

$$\Rightarrow -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi = E\psi$$

1D potential well:

$$E = \frac{\hbar^2 k^2}{2m} \quad \text{where} \quad k = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{L},$$

$$n = 1, 2, 3 \ldots$$

3D:

$$E(\vec{k}) = \frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right) = \frac{\hbar^2|\vec{k}|^2}{2m}$$

$$k_x = \frac{n_x\pi}{L}, \quad n_x = 1, 2, 3 \ldots$$

$$k_y = \frac{n_y\pi}{L}, \quad n_y = 1, 2, 3 \ldots$$

$$k_z = \frac{n_z\pi}{L}, \quad n_z = 1, 2, 3 \ldots$$

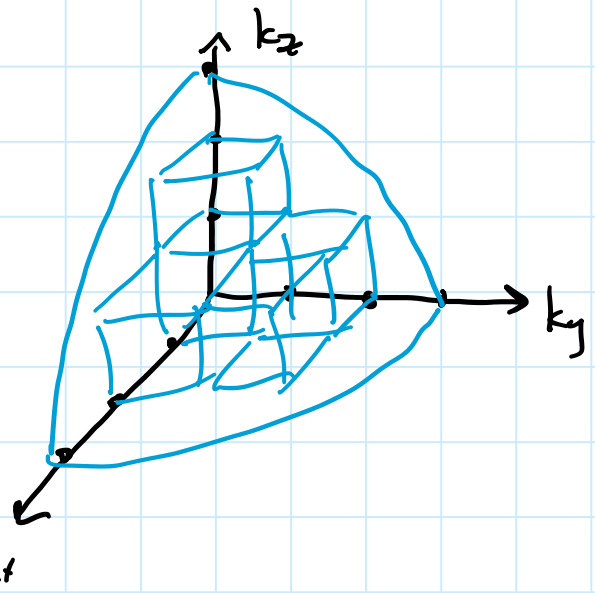
Pauli Exclusion Principle: only one fermion (e.g. an electron) can occupy a given state.

can occupy a given state.

⇓

Here, this means 2 electrons for a given value of k (factor of 2 from 2 spin states, not important)

Can look at states as points in "k-space", i.e. coordinates where the axes are k_x, k_y, k_z.

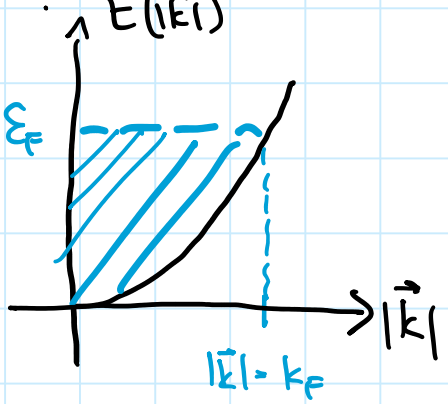


The electrons fill up k-space, starting from the center and settling into the next-lowest energy state (combination of k_x, k_y, k_z that's not already taken and has the next lowest energy). This forms an octant of a sphere — the outer surface is called the Fermi surface, and corresponds to the Fermi energy $\mathcal{E}_F$.

$$\mathcal{E} = \frac{\hbar^2 k_F^2}{2m}$$

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$$

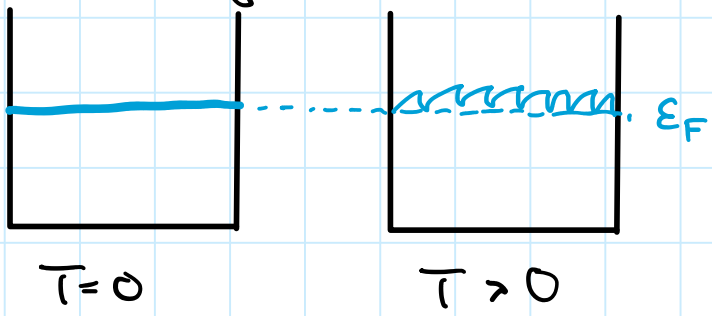
If it helps, you can just look at the magnitude of $\vec{k}$, $|k|$:



A semiconductor is not well modeled by a free electron gas (there is the potential from the atoms in the lattice, after all) but the intuition is similar.

Intuition: at $T=0$ the Fermi energy is "sea-level", everything below is filled with electrons and everything above is empty.

At $T>0$ the additional energy smears out the distribution — still, everything below ε_F is mostly filled and everything above ε_F is mostly empty.



"real space"

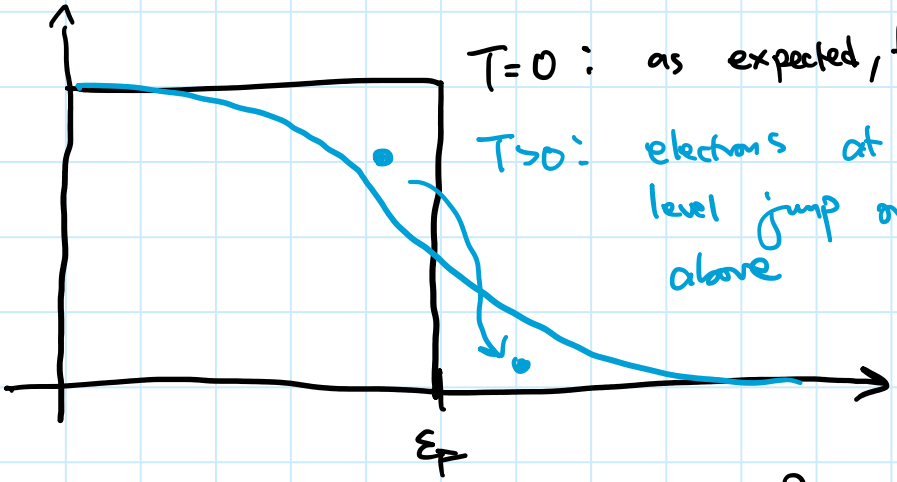
(II.) Fermi-Dirac Distribution

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

"Probability state at ε is occupied by an electron"

Note: $\lim_{\varepsilon - \varepsilon_F \gg k_B T} f(\varepsilon) \sim e^{-(\varepsilon - \varepsilon_F)/k_B T}$

Boltzmann statistics recovered in high energy limit!



$T = 0$: as expected, follows intuition!

$T > 0$: electrons at edge of Fermi level jump over to slightly above

Q: Probability of hole occupation?

A: "Probability ε not occupied by electron"

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"probability ε occupied by hole"

$\Rightarrow 1 - f(\varepsilon)$

Bonus: derivation of Fermi-Dirac distribution

If the fermions are non-interacting, we can just consider each energy level ε on its own. There are two possible states:

$N = 0$ electrons: $E(N=0) = 0$

$N = 1$ electrons: $E(N=1) = \varepsilon$

If you take statistical mechanics, you will learn that one of most useful functions to calculate is the partition function (essentially a normalizing factor when deriving the probability distribution that maximizes the entropy for a given system).

For a system that can vary the number of particles N and the energy ε (fixed T):

$$\mathcal{Z} = \sum_i \exp\left(\frac{N_i\mu - \varepsilon_i}{k_B T}\right) \leftarrow \text{partition function}$$

$$p_i = \frac{\exp\left(\frac{N_i\mu - \varepsilon_i}{k_B T}\right)}{\mathcal{Z}} \leftarrow \text{prob. of state } i$$

$\Rightarrow$ For us, $\mathcal{Z} = e^{\frac{0\cdot\mu - 0}{k_B T}} + e^{\frac{\mu - \varepsilon}{k_B T}}$

$\Rightarrow$ $\langle N \rangle = p_0 N_0 + p_1 N_1$

$$= \frac{e^{\frac{\mu-\varepsilon}{k_B T}}}{1 + e^{\frac{\mu-\varepsilon}{k_B T}}} \cdot \frac{e^{(\varepsilon-\mu)/k_B T}}{e^{(\varepsilon-\mu)/k_B T}}$$

$$= \frac{e^{\frac{\mu}{k_B T}}}{1 + e^{\frac{\mu - \varepsilon}{k_B T}}} \cdot \frac{e^{-\mu/k_B T}}{e^{-\mu/k_B T}}$$

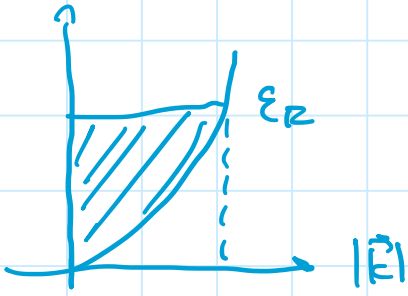
$$= \frac{1}{1 + e^{(\varepsilon - \mu)/k_B T}}$$

Fermi – Dirac distribution!

But what is μ?

→ "Chemical potential": energy associated with adding a particle

Recall for fermions, they "fill to the top":



To add another particle, it will essentially be at the top ⟹ μ essentially ε_F

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

III. Carrier Concentration

Method: # electrons = probability × # states

Method: # electrons at E = probability E is occupied × # states at E

$$\text{total \# electrons} = \sum_{\text{all } E} \#\text{ electrons at } E$$

In practice, more useful to think of <u>densities</u> so volume independent,

electrons at E per unit vol. = probability E is occupied × # states at E per unit vol.

$$\text{total \# electrons per unit vol.} = \sum_{\text{all } E} \#\text{ electrons at } E \text{ per unit vol.}$$

And as we know, the band structure is essentially continuous → sum becomes integral

$$n = \int dE\, f(E)\, D(E)$$

$f(E)$: F-D dist. $D(E)$: density of states

Q: if we want the number of conduction electrons in the conduction band, what should our integration bounds be?

$$E \in [E_c, \infty)$$

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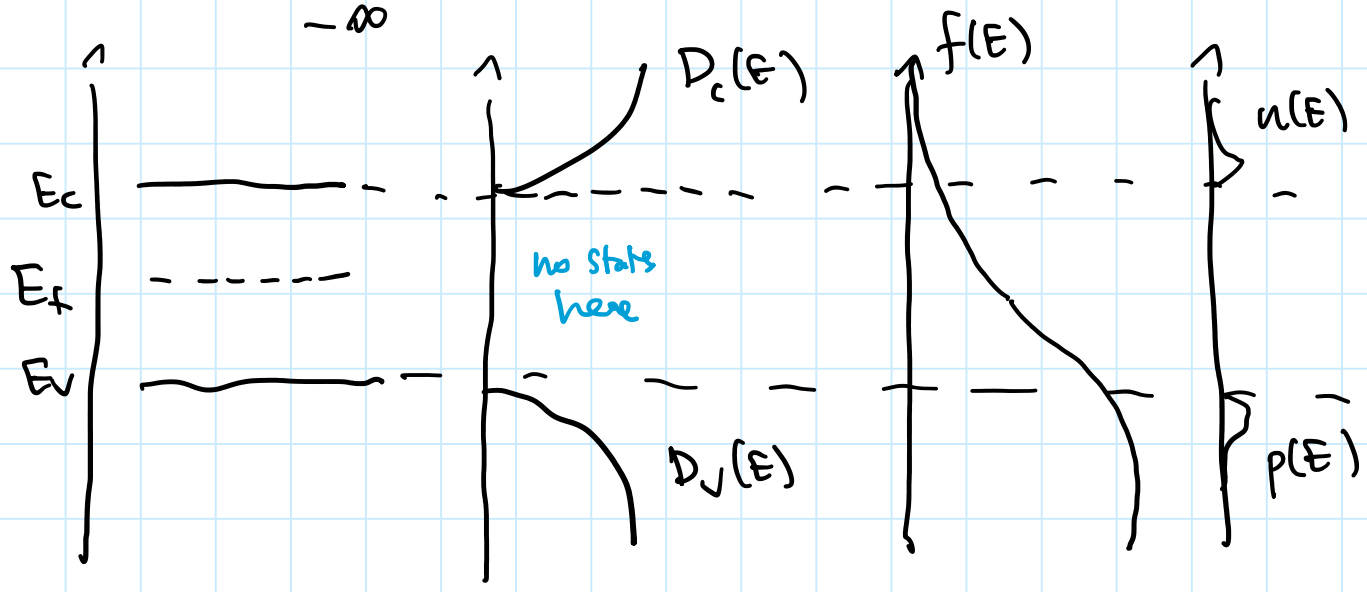
$$\Rightarrow n = \int_{E_c}^{\infty} dE\, f(E)\, D_c(E)$$

Conduction electron concentration

Similarly,

$$p = \int_{-\infty}^{E_v} dE\, (1 - f(E))\, D_v(E)$$

Conduction hole concentration



The actual integral is annoying (Fermi-Dirac integral $\Rightarrow$ Sommerfeld expansion). The end result is:

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

$$N_c = 2\left(\frac{2\pi m_n k_B T}{h^2}\right)^{3/2} \quad [cm^{-3}]$$

m_n, m_p "effective masses"

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

$$N_v = 2\left(\frac{2\pi m_p k_B T}{h^2}\right)^{3/2} \quad [cm^{-3}]$$

Q: What is meaning of N_c, N_v?

A: looks like Boltzmann factor (probability) times a concentration. N_c, N_v are "effective density of states of the [CB, VB]"

— as if all the CB, VB squished into a single energy level that we plug into our naive formula from the very beginning.

$$\#\text{ electrons at } E \text{ per unit vol} = \text{probability } E \text{ is occupied} \times \#\text{ states at } E \text{ per unit vol}$$

Q: How are n, p related if "intrinsic" material — n doesn't

Q: How are n, p related if intrinsic material — no doping.

A: Each promoted electron to the CB corresponds to a hole in the VB.

$$n = p$$

By convention, say $n = p = n_i$ ("intrinsic carrier concentration")

Q: Find n_i in terms of $E_g, k_B T, N_c, N_v$

A: $$np = n_i^2 = N_c N_v e^{-E_g / k_B T}$$

$$\Rightarrow \boxed{n_i = \sqrt{N_c N_v}\, e^{-E_g/2k_B T}}$$ ✱✱✱

Q: Where is the Fermi level if the material is intrinsic?

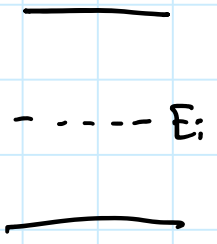
A: Guess might be $E_f = E_i$ is in the middle of the bandgap ("unbiased" toward n or p)

This is essentially true.

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

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

$$\Rightarrow \boxed{E_i = E_c - \frac{E_g}{2} - k_B T \ln\sqrt{\frac{N_c}{N_v}} \approx E_c - \frac{E_g}{2}}$$



Remarks:

- n_i depends on material properties and temperature: E_g, $k_B T$
- $np = n_i^2$ is always true in equilibrium, even if $n \neq n_i$, $p \neq n_i$

(IV.) Carrier Concentration with Doping

Q: What is the charge of a doped semiconductor? Say N_D, N_A with $N_D > N_A$

A: overall neutral (donor gives up an electron and becomes a positive ion, but electron is negative ... similar for acceptors).

$q = 0$

→ Charge neutrality: $n + N_A^- = p + N_D^+$

Plus, np product: $np = n_i^2$

⇒ Two unknowns, two equations:

$$n = \frac{N_D - N_A}{2} + \left[\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2\right]^{1/2}$$

$$p = \frac{N_A - N_D}{2} + \left[\left(\frac{N_A - N_D}{2}\right)^2 + n_i^2\right]^{1/2}$$

Q: What have I assumed here?

A: T high enough that all dopants ionized!

Interesting consideration to see temperature effects on N_A, N_D vs n_i —— see HW 3.

In practice, usually $|N_D - N_A| \gg n_i$

N-type material: $N_D - N_A \gg n_i$

$$n = N_D - N_A$$

$$p = n_i^2 / n$$

P-type material: $N_A - N_D \gg n_i$

$$p = N_A - N_D$$

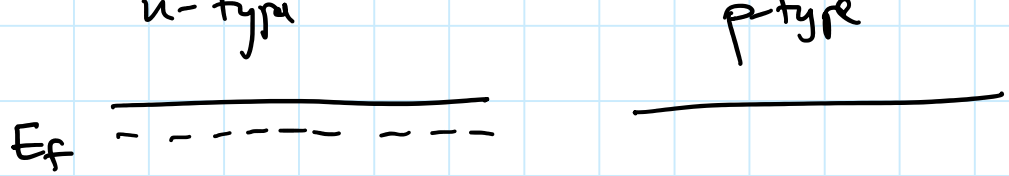
$$n = n_i^2 / p$$

Q: Where is E_f for n-type material? p-type?

A: Can do the math (exercise for reader).

But using our intuition all the way from section I, if n-type we expect E_f to be close to the CB edge so many electrons "spill over" into CB.

Similarly, if p-type we expect E_f to be close to the VB edge.




Ef