Lecture 10

Statistical Mechanics and Density of States Concepts

Reading:

Notes and Brennan Chapter 5

How do electrons and holes populate the bands?

Density of States Concept

In lower level courses, we state that "Quantum Mechanics" tells us that the number of available states in a cubic cm per unit of energy, the density of states, is given by:

$$g_c(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_c)}}{\pi^2 \hbar^3}, E \geq E_c$$

$$g_v(E) = \frac{m_p^* \sqrt{2m_p^*(E_v - E)}}{\pi^2 \hbar^3}, E \leq E_v$$

$$unit \equiv \left(\frac{Number\ of\ States}{cm^3} \right) \Big/ eV$$

How do electrons and holes populate the bands?

Density of States Concept

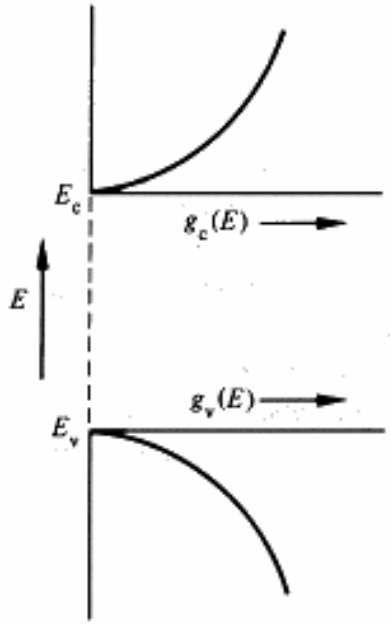


Figure 2.14 General energy dependence of $g_c(E)$ and $g_v(E)$ near the band edges. $g_c(E)$ and $g_v(E)$ are the density of states in the conduction and valence bands, respectively.

Thus, the number of states per cubic centimeter between energy E' and E'+dE is

$$g_c(E')dE \text{ if } E' \geq E_c \quad \textit{and},$$
$$g_v(E')dE \text{ if } E' \leq E_v \quad \textit{and},$$
$$0 \textit{ otherwise}$$

But previously derived this for bulk materials.

How do electrons and holes populate the bands?

Derivation of Density of States Concept

Reminder from lecture 7...

$$N = \frac{V k_f^3}{3\pi^2} = \left(\frac{V}{3\pi^2}\right)\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

Finally, we can define the density of states function:

$$G(E) \equiv \text{\# of states per energy per volume} = \left(\frac{dN}{dE}\right)\Big/ V$$

$$G(E) = \left[\frac{3}{2}\left(\frac{V}{3\pi^2}\right)\left(\frac{2mE}{\hbar^2}\right)^{1/2}\left(\frac{2m}{\hbar^2}\right)\right]\Big/ V$$

$$G(E) = \frac{m\sqrt{2m}}{\pi^2\hbar^3}\sqrt{E}$$

Applying to the semiconductor we must recognize m→ m* and since we have only considered kinetic energy (not the potential energy) we have E → E-E_c

$$\boxed{G(E) = \frac{m^*\sqrt{2m^*}}{\pi^2\hbar^3}\sqrt{E - E_c}}$$

How do electrons and holes populate the bands?

Probability of Occupation (Fermi Function) Concept

Now that we know the number of available states at each energy, how do the electrons occupy these states?

We need to know how the electrons are "distributed in energy".

Again, Quantum Mechanics tells us that the electrons follow the "Fermi-distribution function".

$$f(E) = \frac{1}{1 + e^{(E - E_F)/kT}} \quad where\ k \equiv Boltzman\ cons\tan t, T \equiv Temperature\ in\ Kelvin$$

$$and\ E_F \equiv Fermi\ energy\ (\sim average\ energy\ in\ the\ crystal)$$

f(E) is the probability that a state at energy E is *occupied*

1-f(E) is the probability that a state at energy E is *unoccupied*

How do electrons and holes populate the bands?

Probability of Occupation (Fermi Function) Concept

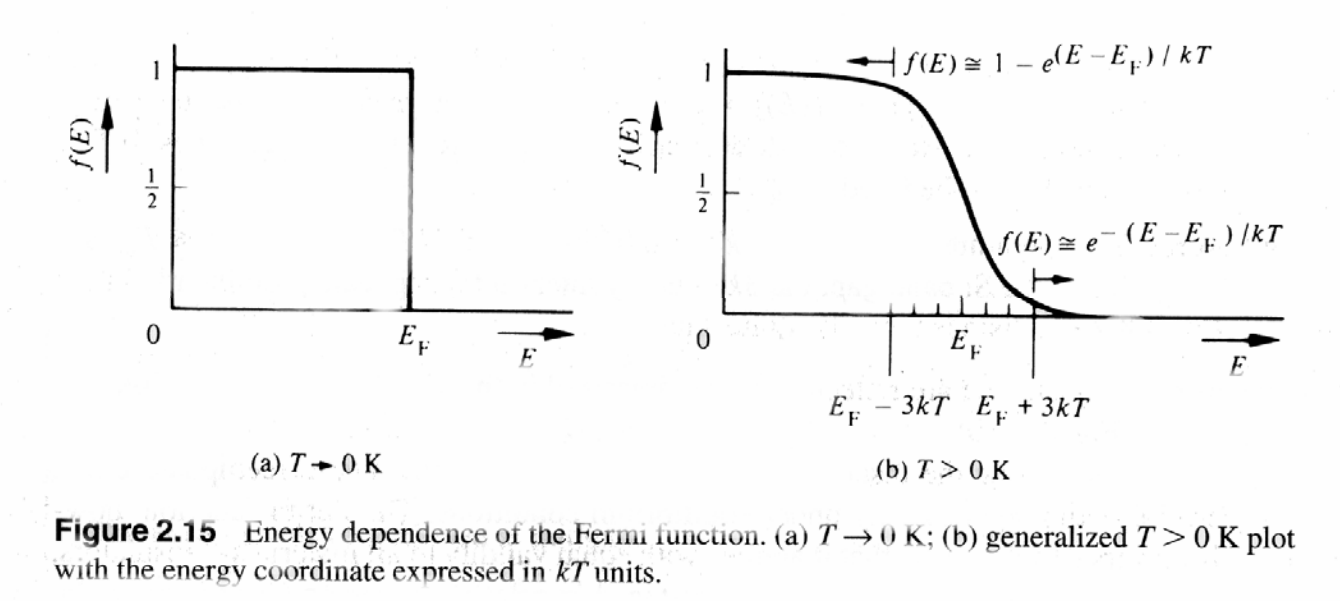


Figure 2.15 Energy dependence of the Fermi function. (a) $T \to 0$ K; (b) generalized $T > 0$ K plot with the energy coordinate expressed in kT units.

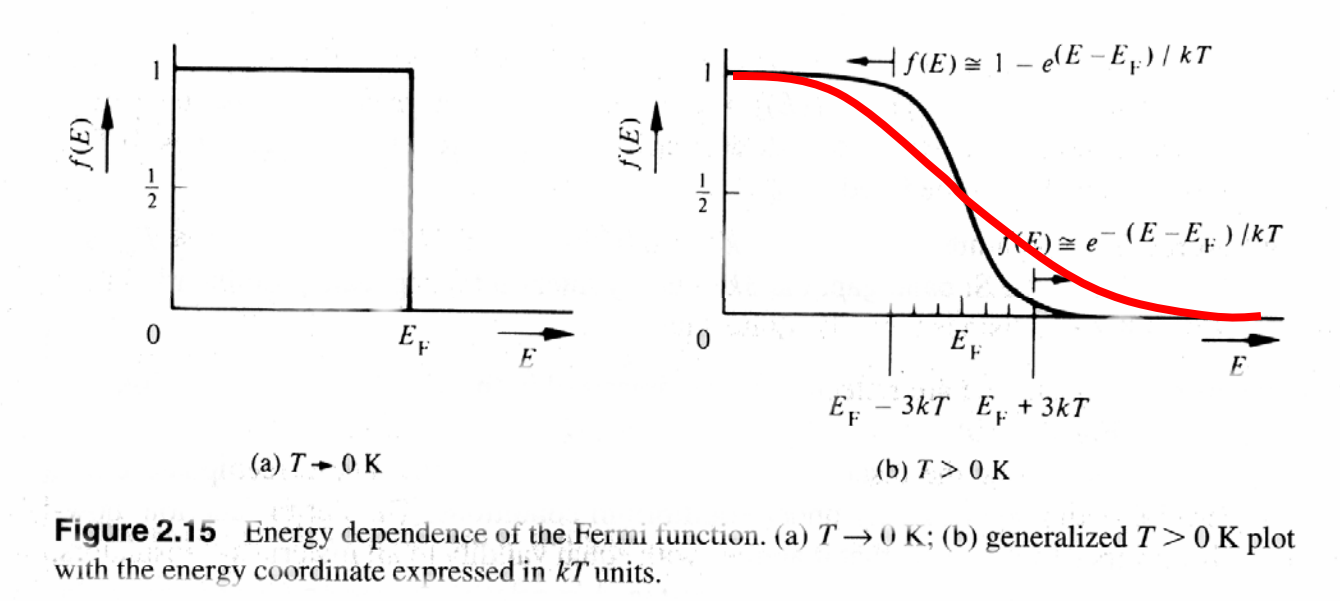
At T=0K, occupancy is "digital": No occupation of states above E_F and complete occupation of states below E_F

At T>0K, occupation probability is reduced with increasing energy.

f(E=E_F) = 1/2 regardless of temperature.

How do electrons and holes populate the bands?

Probability of Occupation (Fermi Function) Concept



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At T=0K, occupancy is "digital": No occupation of states above E_F and complete occupation of states below E_F

At T>0K, occupation probability is reduced with increasing energy.

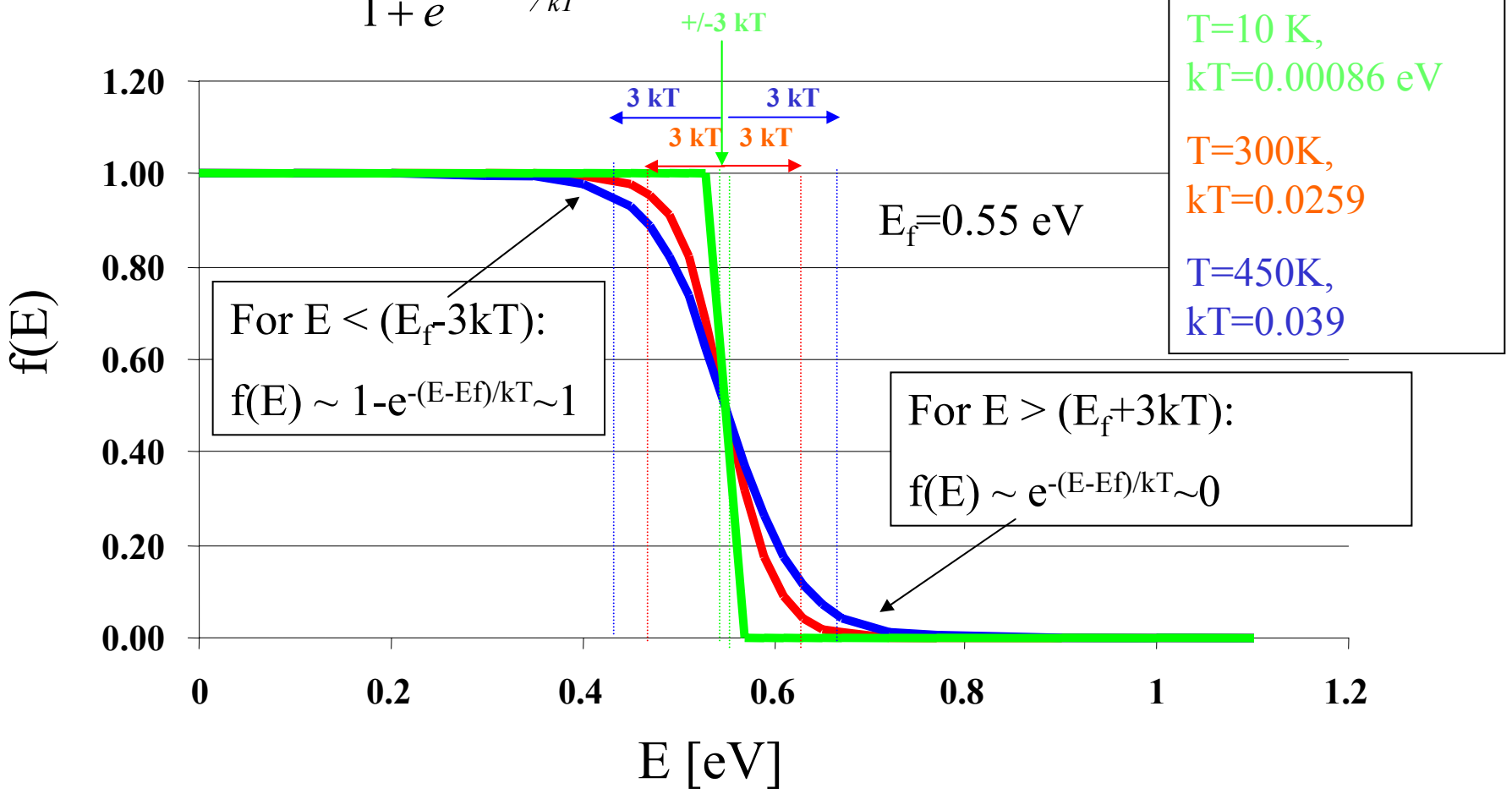
f(E=E_F) = 1/2 regardless of temperature.

At higher temperatures, higher energy states can be occupied, leaving more lower energy states unoccupied (1-f(E)).

How do electrons and holes populate the bands?

Probability of Occupation (Fermi Function) Concept

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



How do electrons and holes populate the bands?

Probability of Occupation

We now have the density of states describing the density of available states versus energy and the probability of a state being occupied or empty. Thus, the density of electrons (or holes) occupying the states in energy between E and E+dE is:

Electrons/cm^3 in the conduction band between Energy E and E+dE → $g_c(E)\,f(E)\,dE \quad \text{if} \quad E \geq E_c \quad \textit{and},$

Holes/cm^3 in the valence band between Energy E and E+dE → $g_v(E)[1-f(E)]\,dE \quad \text{if} \quad E \leq E_v \quad \textit{and},$

0 *otherwise*

How do electrons and holes populate the bands?

Band Occupation

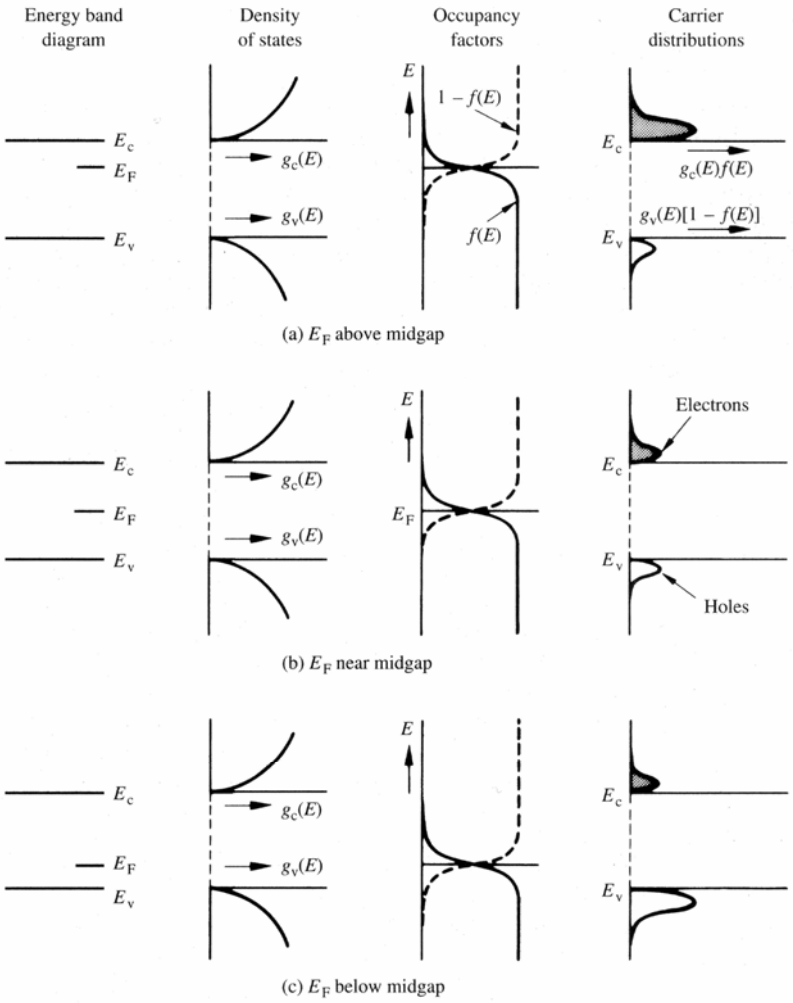
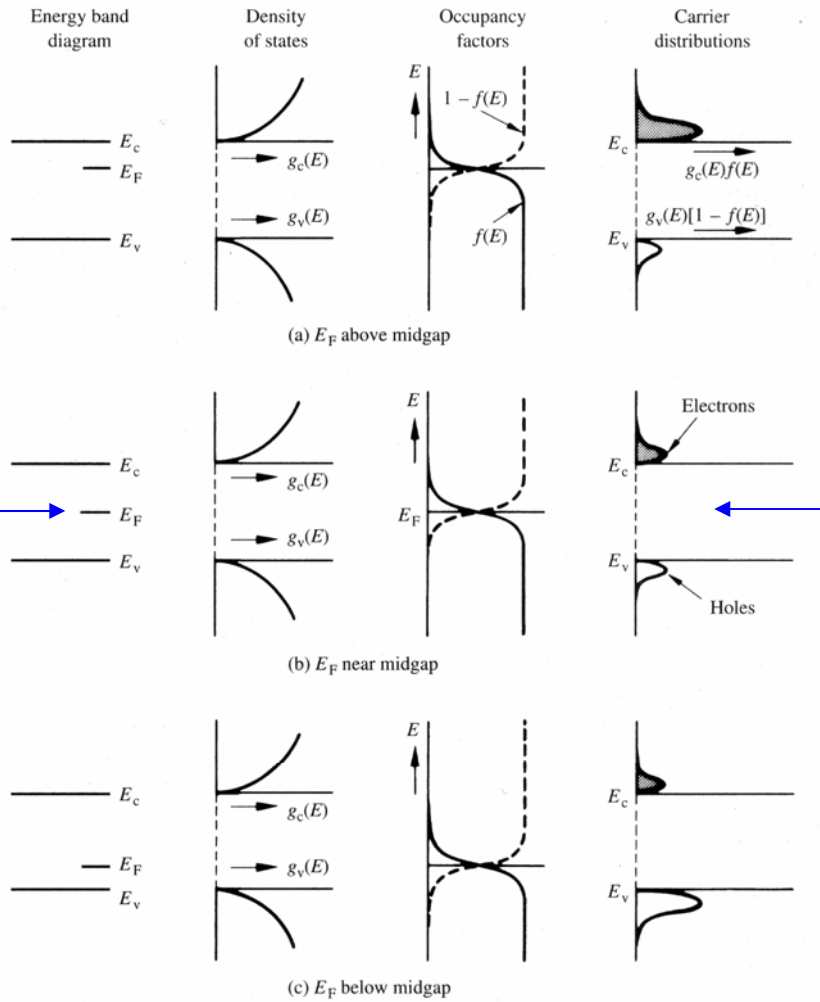


Figure 2.16 Carrier distributions (not drawn to scale) in the respective bands when the Fermi level is positioned (a) above midgap, (b) near midgap, and (c) below midgap. Also shown in each case are coordinated sketches of the energy band diagram, density of states, and the occupancy factors (the Fermi function and one minus the Fermi function).

How do electrons and holes populate the bands?

Intrinsic Energy (or Intrinsic Level)

E_f is said to equal E_i (intrinsic energy) when…



…Equal numbers of electrons and holes

Figure 2.16 Carrier distributions (not drawn to scale) in the respective bands when the Fermi level is positioned (a) above midgap, (b) near midgap, and (c) below midgap. Also shown in each case are coordinated sketches of the energy band diagram, density of states, and the occupancy factors (the Fermi function and one minus the Fermi function).

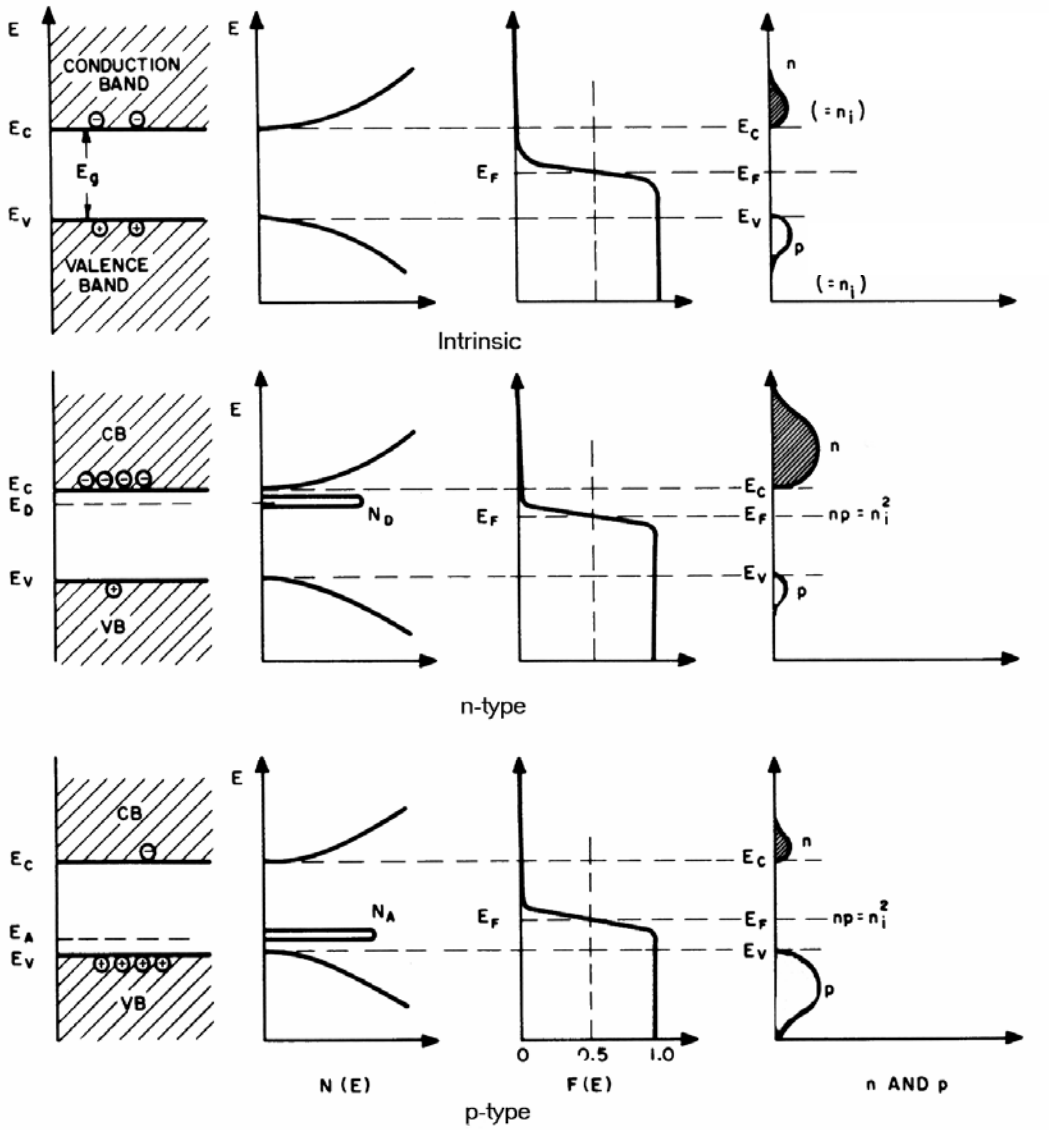
How do electrons and holes populate the bands?

Additional Dopant States

Intrinsic: Equal number of electrons and holes

n-type: more electrons than holes

p-type: more holes than electrons



1st What is an "Equilibrium Distribution"

If all possible configurations of a system are equally probable, then the most likely distribution is the distribution that has the most degeneracies. In this case, the degeneracies are not energy but the number of ways of reconfiguring the particles to arrive at the same result.

Consider a "Craps" system described by the vector |A+B> where A and B are 1-6 (dice). In small numbers, it is easy to see that the sum of dice, while most likely to be 7 (most probable combination of numbers on 2 die), many different results can occur. However, what happens for a very large number of die described by the state,

$|A^1+B^1, A^2+B2, ...A^{10,000}+B^{10,000}>$. The average pair sum is almost always ~7. Thus, 7 is the equilibrium configuration of this system – i.e the most likely arrangement of die pairs.

Entropy tells us that systems tend toward disorder. This is merely a byproduct of the fact that a disordered system has the largest number of ways the system can reconfigure itself.

An Aside: Statistical Mechanics is based on the assumption of purely random particle behavior. The Fundamental Postulate of Statistical Mechanics states that all states in a system are equally likely. This is a purely TRUE assumption in perfectly random systems. However, be careful how this assumption is applied in real systems where forces act between particles. For example, having 10^{22} neutral particles congregated in a nm^3 corner of the 1 cm^3 block is just as likely as 1 specific distribution of these particles throughout the 1 cm^3 block. However, having 10^{22} electrons congregated in a nm^3 corner of the 1 cm^3 block is not equally as likely as on configuration with electrons equally distributed throughout the block because the electrons are not random in that they exert forces on each other and thus do not congregate without added energy. Luckily, we are describing electron systems using a constant total energy constraint so this is not an issue for us. This deviation from statistical randomness is important in the formation of highly ordered materials such as crystals in that "lowest energy" configurations can override a systems natural tendency to maximize entropy.

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

Electrons, belong to a class of particles (including protons and neutrons) known as "Fermions". Fermions are characterized as quantum mechanical particles "with ½ integral spin" which thus must obey the Pauli Exclusion Principle. The number of Fermions is always conserved in a closed system and each Fermion is indistinguishable[1] from any other Fermion of like type – i.e. all electrons "look alike". No two Fermions can occupy the same quantum mechanical state.

Consider a system of N total electrons spread between S allowable states. At each energy, E_i, we have S_i available states with N_i of these S_i states filled.

As they are Fermions, electrons are indistinguishable[1] from one another.

Constraints for electrons (fermions):

(1) Each allowed quantum state can accommodate at most, only one electron

(2) $N=\Sigma N_i$=constant; the total number of electrons is fixed

(3) $E_{total}=\Sigma E_i N_i$; the total system energy is fixed

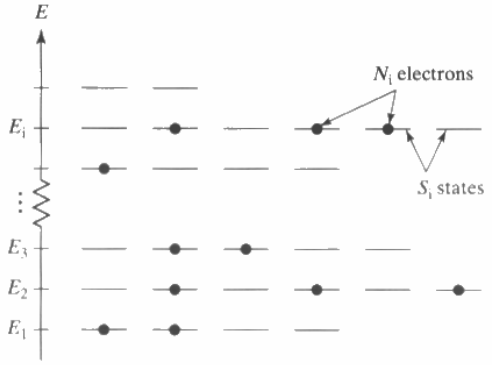


Figure 4.5 Envisioned multi-level energy system of a totally arbitrary nature which contains S_i states and N_i electrons at an energy E_i ($i = 1, 2, 3, \cdots$).

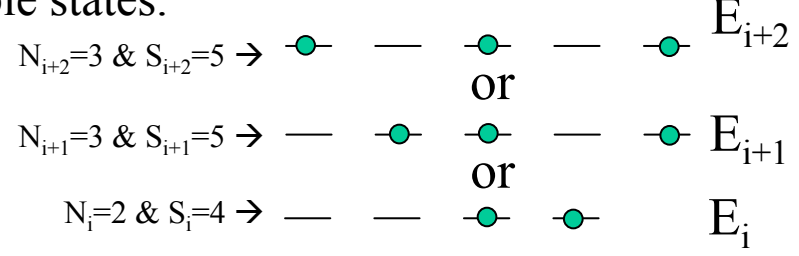
[1]A simple test as to whether a particle is indistinguishable (statistically invariant) is when two particles are interchanged, did the electronic configuration change?

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

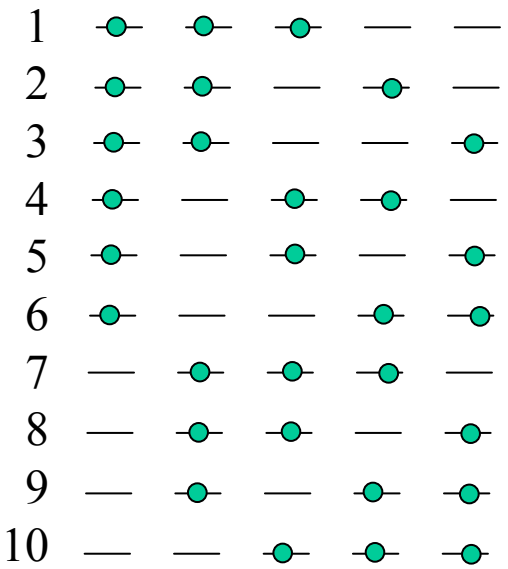
Consider only one specific energy, Ei: How many ways, W_i, can we arrange at each energy, E_i, N_i indistinguishable electrons into the S_i available states.

$$W_i = \frac{S_i!}{(S_i - N_i)!\,N_i!}$$



Example: The number of unique ways of arranging 3 electrons in 5 states at energy E_i is:
S_i=5, N_i=3

$$W_i = \frac{S_i!}{(S_i - N_i)!\,N_i!} = \frac{5!}{(5-3)!\,3_i!} = 10$$

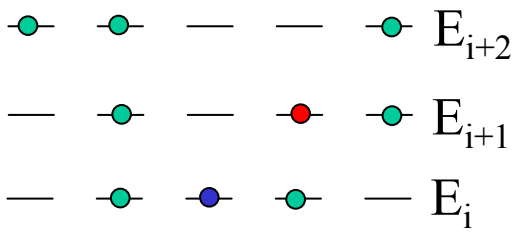


But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

When we consider more than one level (i.e. all i's) the number of ways we can arrange the electrons increases as the product of the W_i's .

$$W = \prod_i W_i = \prod_i \frac{S_i!}{(S_i - N_i)!\,N_i!}$$



If all possible distributions are equally likely, then the probability of obtaining a specific distribution is proportional to the number of ways that distribution can be constructed (in statistics, this is the distribution with the most ("complexions"). For example, interchanging the blue and red electron would result in two different ways (complexions) of obtaining the same distribution. **The most probable distribution is the one that has the most variations that repeat that distribution**. To find that maximum, we want to maximize W with respect to N_i's . Thus, we will find dW/dNi = 0. However, to eliminate the products and factorials, we will first take the natural log of the above...

$$\ln(W) = \sum_i \ln(S_i!) - \ln([S_i - N_i]!) - \ln(N_i!)$$

... then we will take $d(\ln[W])/dN_i=0$. Before we do that, we can use Stirling's Approximation to eliminate the factorials.

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

Using Stirling's Approximation, for large x, $\ln(x!) \sim (x\ln(x) - x)$ so,

$$\ln(W) = \sum_i \ln(S_i!) - \ln([S_i - N_i]!) - \ln(N_i!)$$

$$\Downarrow$$

$$\ln(W) = \sum_i S_i \ln(S_i) - S_i - (S_i - N_i)\ln([S_i - N_i]) + (S_i - N_i) - N_i \ln(N_i) + N_i$$

Collecting like terms,

$$\ln(W) = \sum_i S_i \ln(S_i) - (S_i - N_i)\ln([S_i - N_i]) - N_i \ln(N_i)$$

Now we can maximize W with respect to N_i's . Noting that S_i is independent of N_i and that since d(ln(x))/dx=1/x, then d(lnW)=dW/W when dW=0, d(ln[W])=0.

$$\frac{d\ln(W)}{dN_i} = \sum_i \frac{\partial \ln(W)}{\partial N_i}$$

$$d\ln(W) = \sum_i [\ln([S_i - N_i]) + 1 - \ln(N_i) - 1] dN_i$$

Setting the derivative equal to 0...

$$(4) \qquad d\ln(W) = 0 = \sum_i \left[\ln\left(\frac{S_i}{N_i} - 1 \right) \right] dN_i$$

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

From our original constraints, (2) and (3), we get...

$$\sum_i N_i = N, \text{a constant} \Rightarrow \sum_i d(N_i) = 0$$

$$\sum_i E_i N_i = E_{total}, \text{a constant} \Rightarrow \sum_i E_i d(N_i) = 0$$

Using the method of undetermined multipliers (Lagrange multiplier method) we multiply the above constraints by constants $-\alpha$ and $-\beta$ and add (adding zeros) to equation 4 to get ...

$$\sum_i -\alpha\, d(N_i) = 0$$

$$\sum_i -\beta\, E_i d(N_i) = 0$$

$$\Downarrow$$

$$d\ln(W) = 0 = \sum_i \left[\ln\left(\frac{S_i}{N_i} - 1\right) - \alpha - \beta E_i \right] dN_i$$

which since α and β can take on any value, requires that $\ln\left(\frac{S_i}{N_i} - 1\right) - \alpha - \beta E_i = 0$ for all i

But where did we get the fermi distribution function?

Probability of Occupation (Fermi Function) Concept

This final relationship can be solved for the ratio of filled states, N_i per states available S_i ...

$$\ln\left(\frac{S_i}{N_i}-1\right)-\alpha-\beta E_i=0$$

$$\Downarrow$$

$$f(E_i)\equiv\frac{S_i}{N_i}=\frac{1}{1+e^{\alpha+\beta E_i}}$$

in the case of of semiconductors, we have

$$\alpha=-\frac{E_F}{kT}\quad\text{and}\quad\beta=\frac{1}{kT}$$

$$\boxed{f(E_i)=\frac{S_i}{N_i}=\frac{1}{1+e^{(E_i-E_F)/kT}}}$$

What other Distributions are Possible?

Bose-Einstein Distribution- Probability of Occupation for Bosons and Planckians

Bosons are characterized as quantum mechanical particles "with integral spin" which thus DO NOT obey the Pauli Exclusion Principle. Two types of Bosons are possible and Brennan has a restrictive definition of both (note most texts describe Planckians as a subset of Bosons while Brennan adopts a separate definition for Bosons and Planckians): Brennan defines a Boson as an indistinguishable (– i.e. all Bosons "look alike") particle whose number is conserved in a closed system. He further defines a Planckian as an indistinguishable particle whose number is NOT conserved. The number of Planckians in a system is unlimited (except for total universal energy constraints). Unlike Fermions, any number of Bosons/Planckians can occupy the same quantum mechanical state. Bosons/Planckians tend to collect in the same state at low temperatures forming "Bose-Einstein Condensates".

Consider a system of N total electrons spread between S allowable states. At each energy, E_i, we have S_i available states with N_i of these S_i states filled.

As defined by Brennan, Bosons (number conserved) are important in nuclear, atomic and high energy physics while Planckians (number unlimited) are important in photonics and phononics.

<u>Constraints for Bosons</u>:

(1) Each allowed quantum state can accommodate any number of Bosons.

(2) $N=\Sigma N_i$=constant; the total number of electrons is fixed

(3) $E_{total}=\Sigma E_i N_i$; the total system energy is fixed

<u>Constraints for Planckians:</u>

(1) Each allowed quantum state can accommodate any number of Bosons.

(2) $E_{total}=\Sigma E_i N_i$; the total system energy is fixed

Bosons are named after Satyendra Nath Bose who constructed the original theory for photons in 1920 which was generalized to other particles by Einstein in 1924

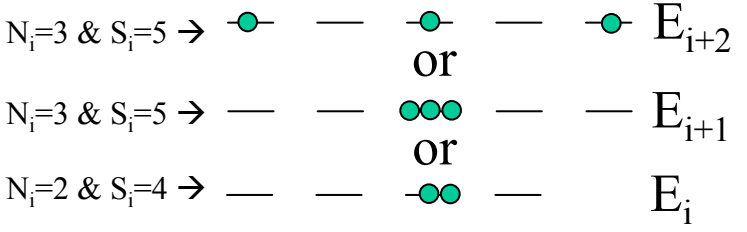
What other Distributions are Possible?

Bose-Einstein Distribution- Probability of Occupation for Bosons and Planckians

How many ways, W_i, can we arrange at each energy, E_i, N_i indistinguishable Bosons into the S_i available states.

$$W_i = \frac{\text{Total \# Permutations of Bins and Particles}}{(\text{\# Indistinguishable Permutations of Bins})(\text{\# Indistinguishable Permutations of Particles})}$$

$$W_i = \frac{(N_i + S_i - 1)!}{(S_i - 1)!\, N_i!}$$

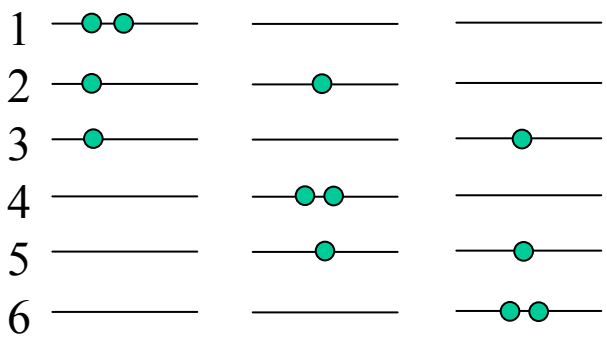


Example: The number of ways of arranging 3 Bosons in 5 states at energy E_i is: S_i=5, N_i=3

$$W_i = \frac{(N_i + S_i - 1)!}{(S_i - 1)!\, N_i!} = \frac{(3 + 5 - 1)!}{(5 - 1)!\, 3!} = 35$$

Example: The number of ways of arranging 2 Bosons in 3 states at energy E_i is: S_i=3, N_i=2

$$W_i = \frac{(N_i + S_i - 1)!}{(S_i - 1)!\, N_i!} = \frac{(2 + 3 - 1)!}{(3 - 1)!\, 2!} = 6$$



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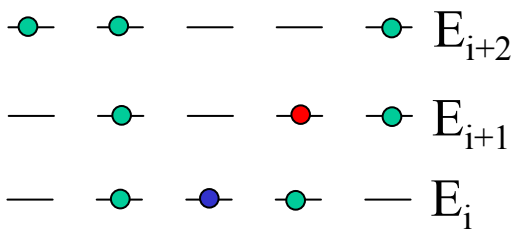

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$$\ln(W) = \sum_i \ln([N_i + S_i - 1]!) - \ln([S_i - 1]!) - \ln(N_i!)$$

... then we will take $d(\ln[W])/dN_i=0$. Before we do that, we can use Stirling's Approximation to eliminate the factorials.

What other Distributions are Possible?

Bose-Einstein Distribution- Probability of Occupation for Bosons and Planckians

Using Stirling's Approximation, for large x, $\ln(x!) \sim (x\ln(x) - x)$ so,

$$\ln(W) = \sum_i \ln([N_i + S_i - 1]!) - \ln([S_i - 1]!) - \ln(N_i!)$$

$$\Downarrow$$

$$\ln(W) = \sum_i [N_i + S_i - 1]\ln([N_i + S_i - 1]) - [N_i + S_i - 1] - (S_i - 1)\ln([S_i - 1]) + (S_i - 1) - N_i \ln(N_i) + N_i$$

Collecting like terms,

$$\ln(W) = \sum_i [N_i + S_i - 1]\ln([N_i + S_i - 1]) - (S_i - 1)\ln([S_i - 1]) - N_i \ln(N_i)$$

Now we can maximize W with respect to N_i's . Noting that S_i is independent of N_i and that since d(lnW)=dW/W when dW=0, d(ln[W])=0.

$$\frac{d\ln(W)}{dN_i} = \sum_i \frac{\partial \ln(W)}{\partial N_i}$$

$$d\ln(W) = \sum_i [\ln([S_i + N_i - 1]) + 1 - \ln(N_i) - 1]dN_i$$

Setting the derivative equal to 0...

$$(4) \qquad d\ln(W) = 0 = \sum_i \left[\ln\left(\frac{S_i + N_i - 1}{N_i}\right)\right]dN_i$$

What other Distributions are Possible?

Bose-Einstein Distribution- Probability of Occupation for Bosons and Planckians

For Bosons or Planckians we have different constraints, (2) and (3), we get...

Both Constraints for Bosons

$$\sum_i N_i = N, \text{a constant} \Rightarrow \sum_i d(N_i) = 0$$

$$\sum_i E_i N_i = E_{total}, \text{a constant} \Rightarrow \sum_i E_i d(N_i) = 0$$

Only 1 Constraint for Planckians

For Bosons: Using the method of undetermined multipliers (Lagrange multiplier method) we multiply the above constraints by constants $-\alpha$ and $-\beta$ and add (adding zeros) to equation 4 to get ...

$$\sum_i -\alpha\, d(N_i) = 0$$

$$\sum_i -\beta\, E_i d(N_i) = 0$$

$$\Downarrow$$

$$d\ln(W) = 0 = \sum_i \left[\ln\left(\frac{S_i + N_i - 1}{N_i} \right) - \alpha - \beta E_i \right] dN_i$$

which requires that $\ln\left(\frac{S_i + N_i - 1}{N_i} \right) - \alpha - \beta E_i = 0$ for all i

What other Distributions are Possible?

Bose-Einstein Distribution- Probability of Occupation for Bosons and Planckians

This final relationship can be solved for the ratio of filled states, N_i per states available S_i ...

$$\ln\left(\frac{S_i + N_i - 1}{N_i}\right) - \alpha - \beta E_i = 0$$

$$\Downarrow$$

$$f(E_i) \equiv \frac{S_i}{N_i} = \frac{1}{e^{\alpha+\beta E_i} - 1}$$

in the case of of semiconductors, we have

$$\alpha = -\frac{E_F}{kT} \text{ and } \beta = \frac{1}{kT}$$

For Bosons: $$f(E_i) = \frac{S_i}{N_i} = \frac{1}{e^{(E_i - E_F)/kT} - 1}$$

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Only 1 Constraint for Planckians

For Planckians: Using the method of undetermined multipliers (Lagrange multiplier method) we multiply the above constraints by ONLY the constant –β and add (adding zero) to equation 4 to get ...

$$\sum_i -\beta E_i d(N_i) = 0$$

$$\Downarrow$$

$$d\ln(W) = 0 = \sum_i \left[\ln\left(\frac{S_i + N_i - 1}{N_i} \right) - \beta E_i \right] dN_i$$

which requires that $\ln\left(\frac{S_i + N_i - 1}{N_i} \right) - \beta E_i = 0$ for all i

What other Distributions are Possible?

Bose-Einstein Distribution- Probability of Occupation for Bosons and Planckians

This final relationship can be solved for the ratio of filled states, N_i per states available S_i ...

$$\ln\left(\frac{S_i + N_i - 1}{N_i}\right) - \beta E_i = 0$$

$$\Downarrow$$

$$f(E_i) \equiv \frac{S_i}{N_i} = \frac{1}{e^{\beta E_i} - 1}$$

in the case of of semiconductors, we have

$$\beta = \frac{1}{\mathrm{kT}}$$

For Planckians $$f(E_i) = \frac{S_i}{N_i} = \frac{1}{e^{(E_i)/kT} - 1}$$