"Complementi di Fisica" Lectures 18 - 20

Livio Lanceri
Università di Trieste

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In these lectures

- Contents (1)
  - Insulators, semiconductors, conductors
  - Semiconductor materials: resistivity and conductivity
  - Crystal structure of solids
- Reference textbooks
  - D.A. Neamen, Semiconductor Physics and Devices, McGraw-Hill, 3rd ed., 2003, p.1-16 (Crystal structure of solids)
  - R.F.Pierret, Advanced Semiconductor Fundamentals, Prentice Hall, 2003, 2nd ed.
  - S.M.Sze, Semiconductor Devices - Physics and Technology, J.Wiley & Sons, 2nd ed., 1985.

In these lectures

- **Contents (2)**
  - **Models for charge carriers: electrons and holes**
  - **Pure ("*intrinsic*") semiconductors *at equilibrium***

- **Reference textbooks**
  - **D.A. Neamen, Semiconductor Physics and Devices, McGraw-Hill, 3rd ed., 2003, p.83-96 (Density of states, Fermi-Dirac), p. 103-114 (Charge carriers in semiconductors)**
  - **R.F.Pierret, Advanced Semiconductor Fundamentals, Prentice Hall, 2003, 2nd ed.**
  - **S.M.Sze, Semiconductor Devices - Physics and Technology, J.Wiley & Sons, 2nd ed., 1985.**

Insulators, semiconductors, conductors

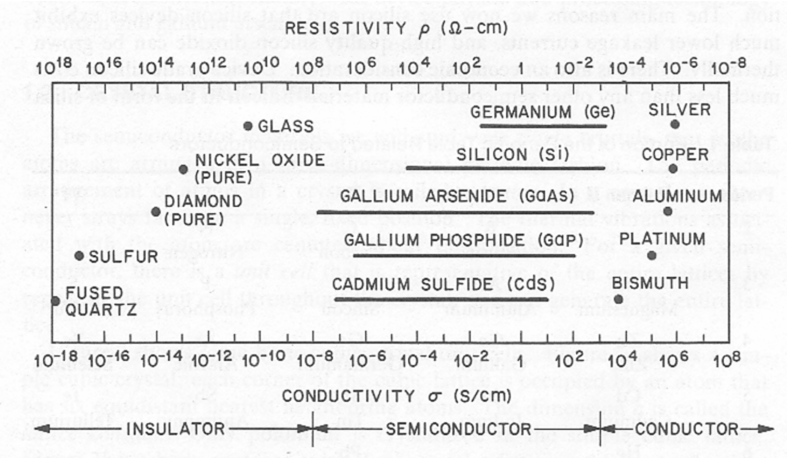


Fig. 1 Typical range of conductivities for insulators, semiconductors, and conductors.

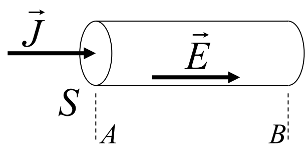
(from SZE, fig.1-1)

Semiconductor materials

Resistivity ρ, conductivity σ

Recall the definitions:

$$\boxed{\vec{J} = \sigma \vec{E}}$$



$$I = \frac{\Delta V}{R} \qquad \Delta V = RI$$

$$R = \rho \frac{\Delta x}{S}, \quad I = \left(\vec{J} \bullet \hat{n}\right) S = JS$$

$$\Rightarrow \Delta V = \rho \frac{\Delta x}{S} JS = \rho J \Delta x$$

$$|J| = \frac{1}{\rho}\left|\frac{\Delta V}{\Delta x}\right| = \frac{1}{\rho}|E| = \sigma |E|$$

Current Density J

Electric Field E

Resistivity Ω cm

Conductivity S cm^{-1}

$$\Delta V = V_B - V_A < 0$$

$$\Delta x = x_B - x_A > 0$$

$$\vec{E} = -\vec{\nabla} V$$

$$E_x = -\frac{dV}{dx}$$

Electric Potential V

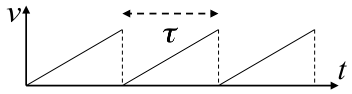
Ohm's law (for "ohmic materials")

R is a constant (at fixed T)

Naïve microscopic interpretation

- **Classical interpretation of Ohm's law (Drude Model):**
  - Some electrons move "almost freely" in conductors
  - They are subject to some sort of "collision" on atoms (not clear how!): "dissipative" effect on the electron energy…
  - Simplified picture:
    - electrons are accelerated by the external field E_x
    - on average, at *time intervals* τ electrons collide and "stop"
    - the kinetic energy gained due to E_x is dissipated as "heat"
    - The net resulting motion is a "drift" with *average velocity v*

$$q_e = -|q|$$



average drift velocity

mobility μ cm^2 / (V s)

$$v_x = a_x\tau = -\frac{|q|E_x}{m}\tau = -\boxed{\frac{|q|\tau}{m}}E_x = -\mu E_x \quad \Rightarrow \quad \tau = \frac{\mu m}{q}$$

$$J_x = -|q|nv_x = \boxed{|q|n\mu}E_x = \sigma E_x \quad \Rightarrow \quad \mu = \frac{\sigma}{|q|n} \quad \Rightarrow \quad \tau = \frac{\sigma m}{q^2 n}$$

Exercise: check dimensions and units for resistivity, conductivity, mobility

Several problems…

- **The simplified picture is appealing and defines quantities (drift velocity, mobility) that can be indirectly measured and used to characterize materials, but:**
  - Why do different materials behave differently?
  - Dependence on temperature in this model: completely wrong!
  - Computing the *"mean free path"* λ of electrons: surprise! much larger than the *average distance d* between atoms!
  - NB: use "thermal velocity" rather than "drift velocity"…

$$\lambda = v\tau_{collision}; \quad v = v_{drift} \quad \text{or} \quad v = v_{therm} = \sqrt{\frac{3kT}{m}} \; ?$$

NB: different physical meaning!

⇒ We will introduce also the "Fermi velocity", still larger

Periodic table of the elements

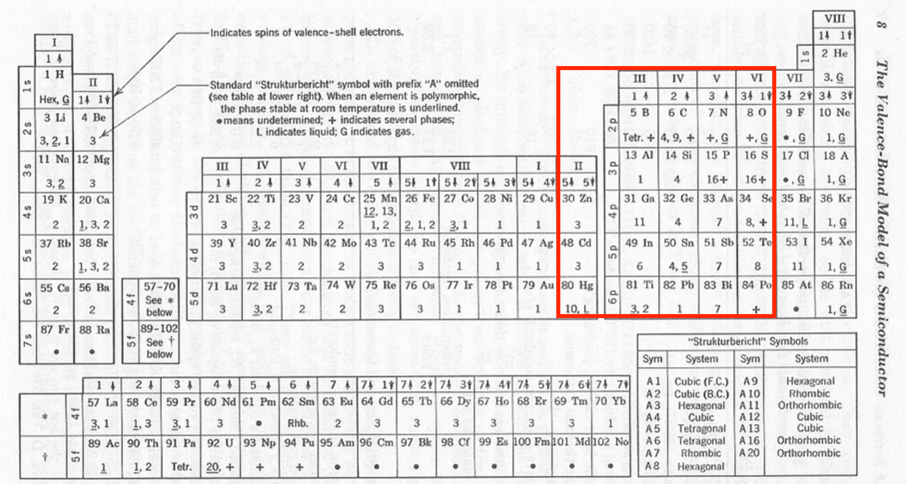


Fig. 1.3. Periodic table of the elements, showing configuration of outer electrons and crystal structures. (Table prepared at Westinghouse Research Laboratories, Pittsburgh, Pa., by A. J. Cornish.)

(from ADL, Fig1-3)

Periodic table and semiconductors

Table 1 Portion of the Periodic Table Related to Semiconductors

Period	Column II	III	IV	V	VI
2		B Boron	C Carbon	N Nitrogen	
3	Mg Magnesium	Al Aluminum	→ Si Silicon	P Phosphorus	S Sulfur
4	Zn Zinc	Ga Gallium	→ Ge Germanium	As Arsenic	Se Selenium
5	Cd Cadmium	In Indium	Sn Tin	Sb Antimony	Te Tellurium
6	Hg Mercury		Pb Lead		

† The international system of units is presented in Appendix B.

(from SZE, Table1-1)

Element and compound semiconductors

Practical considerations: most frequently used in standard devices:

- **(Ge)… Si, GaAs**

Table 2 Element and Compound Semiconductors

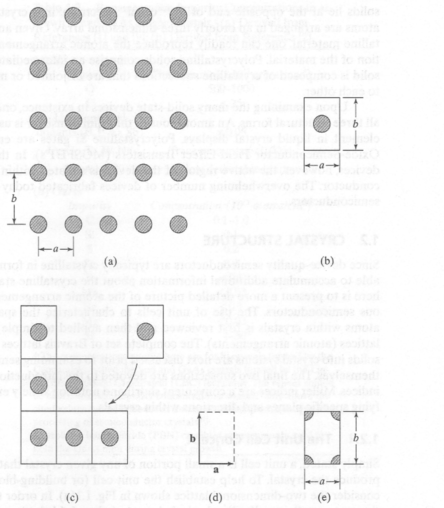
Element	IV–IV Compounds	III–V Compounds	II–VI Compounds	IV–VI Compounds
Si	SiC	AlAs	CdS	PbS
Ge		AlSb	CdSe	PbTe
		BN	CdTe	
		GaAs	ZnS	
		GaP	ZnSe	
		GaSb	ZnTe	
		InAs		
		InP		
		InSb		

(from SZE, Table1-2)

Crystal structure

Crystal lattice and unit cell

- Two-dimensional periodic arrangement of atoms



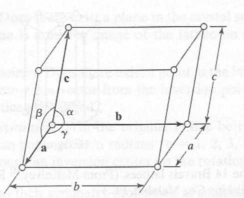
(from PIER, Fig.1-1)

Figure 1.1 Introduction to the unit cell method of describing atom arrangements within crystals. (a) Sample two-dimensional lattice. (b) Unit cell corresponding to the part (a) lattice. (c) Reproduction of the original lattice. (d) Basis vectors. (e) An alternative unit cell.

Crystal lattice and unit cell

Three-dimensional periodic arrangement of atoms; an example

Crystallography: classification of all possible configurations (14 Bravais cells, 230 possible patterns)



(from PIER, Fig.1-4)

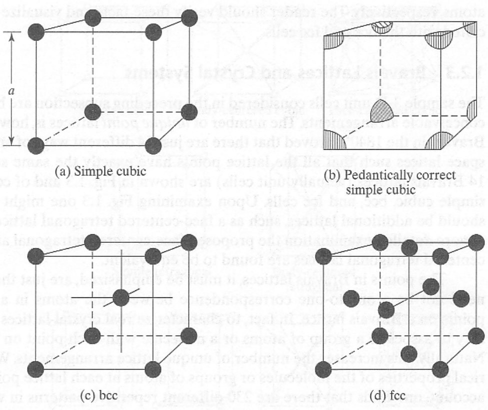


Figure 1.2 Simple three-dimensional unit cells. (a) Simple cubic unit cell. (b) Pedantically correct simple cubic unit cell including only the fractional portion (1/8) of each corner atom actually within the cell cube. (c) Body-centered cubic unit cell. (d) Face-centered cubic unit cell (After Pierret.[3])

(from PIER, Fig.1-2)

Si and GaAs unit cells

"Diamond lattice": Si, Ge

Lattice constant: a = 5.43 Å (Si)
a = 5.64 Å (Ge)

Exercise:
What is the distance between nearest neighbours in Si crystals?

"Zincblende lattice": GaAs

Lattice constant: a = 5.63 Å (GaAs)

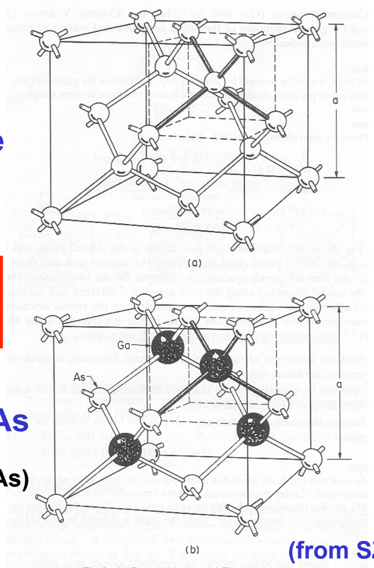
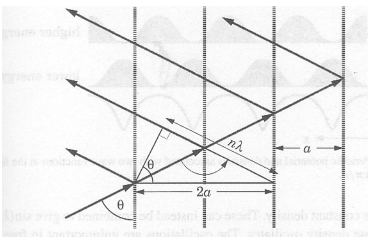


Fig. 3 (a) Diamond lattice. (b) Zincblende lattice.

(from SZE, fig.1-3)

3. Bragg, "reciprocal lattice", Brillouin



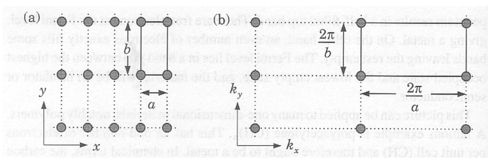


FIGURE 2.8. Two-dimensional rectangular lattices in (a) real and (b) reciprocal space.

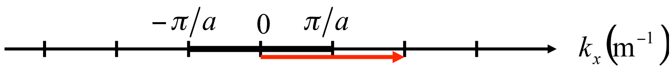
"real" space (x, y, z) "reciprocal" space (k_x, k_y, k_z)

Constructive interference (Bragg) if:

$$n\lambda = 2a\sin\theta \qquad (\lambda = 2\pi/k)$$

One-dimensional lattice reflections:

$$\theta = \pi/2 \;\Rightarrow\; \sin\theta = 1 \;\Rightarrow\; n\frac{2\pi}{k} = 2a \;\Rightarrow\; k = \frac{n\pi}{a}$$



One-dimensional "reciprocal lattice": "first Brillouin zone" and "basis vector"

Miller indices

- Miller indices (i j k)
  - Intercepts of the plane on the three cartesian axes, in units of lattice constants
  - Reciprocals, reduced to the smallest integers having the same ratio
- Other conventions and "Wafer flats"
  - See "advanced" topics

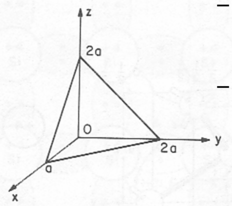


Fig. 4 A (211)-crystal plane.

- On planes of different orientation in the crystal:
  - Different number of atoms and atom spacing
  - Different crystal properties (mechanical, electrical)

Exercise: If a plane has intercepts 2a, 3a, 4a along the three axes, find its Miller indices

Exercise: Find the number of atoms Per cm^2 in Si in the (100), (110), and (111) planes

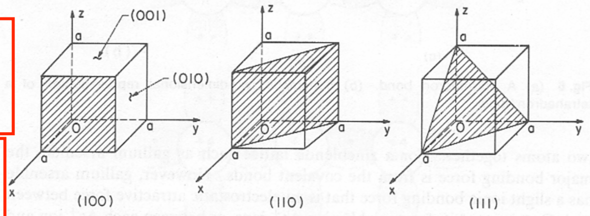
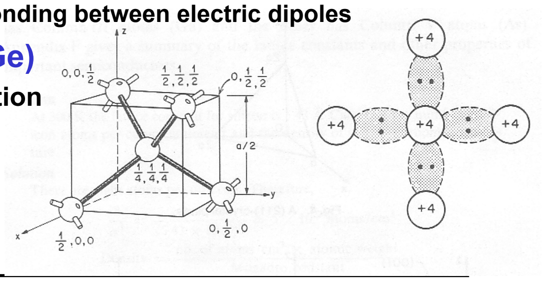


Fig. 5 Miller indices of some important planes in a cubic crystal.

Valence bonds model

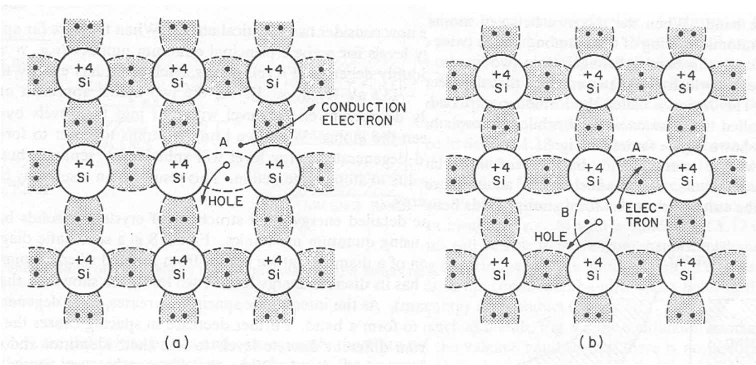
Atoms bonding

- **Classification (recall from Chemistry courses?)**
  - Ionic: "**low affinity": lose electrons, "high affinity": absorb electrons; negatively and positively charged ions attract each other**
  - Metallic: **"sea" of loosely bound (almost free) outer electrons keep together the positive ions left behind (found in good *conductors*)**
  - Covalent: **energetically stable configuration with outer electrons "shared" between neighbour atoms, when "shells" fully occupied (very stable, found in *semiconductors* and *insulators*)**
  - Van der Waals: **weak bonding between electric dipoles**
- **Covalent bonds (Si, Ge)**
  - **Schematic representation**



Broken bonds: electrons and holes

Basic bond model of "intrinsic" (= "pure") Silicon



a broken bond at position A, resulting in a conduction electron and a "hole"

deficiency filled by one of the neighboring electrons (in B), resulting in a shift of the "hole" from A to B

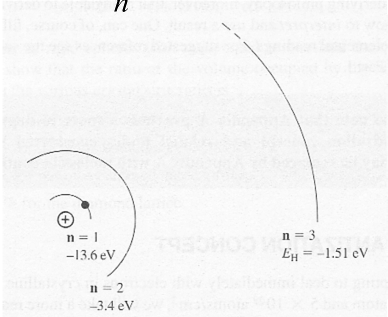
Energy band model

Isolated atoms: energy levels

Hydrogen atom (Z=1)

Idealized representation of the first three allowed Bohr orbits and their quantized energy levels

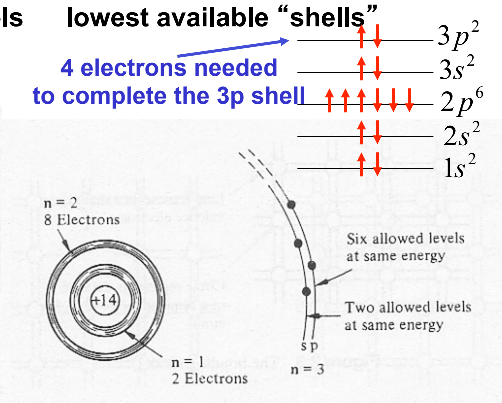
$$E_n = -\frac{13.6\,\text{eV}}{n^2}$$



Silicon atom (Z=14)

Schematic representation of how the 14 electrons fill the lowest available "shells"

4 electrons needed to complete the 3p shell

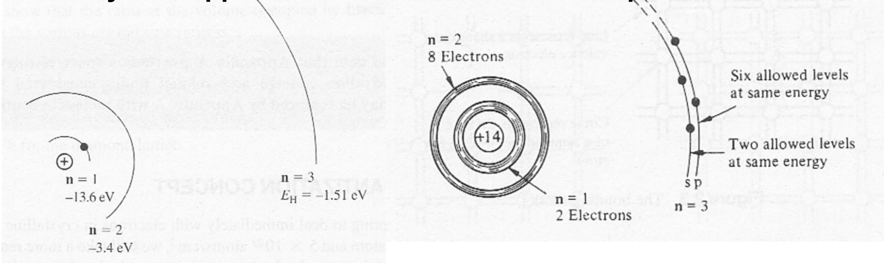


Isolated atoms: energy levels

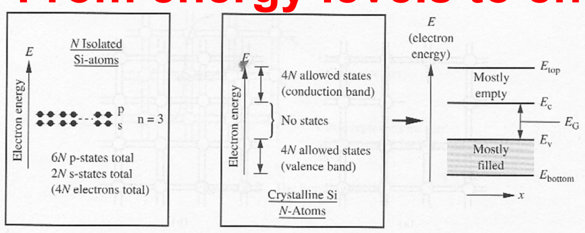
Naive pictures! (available electron states as circular Bohr orbits)
QM: 3-d Schrödinger equation for electrons in the electrostatic field
- H atom (Z=1 electron): exact solutions (Bohr energies are OK!)
- (Z≠1)-electron atoms: approximate solutions (shell method)

More information:
- J.Bernstein et al, Chapters 9, 10, 11
- D.J.Griffiths, Chapters 4, 5.1, 5.2

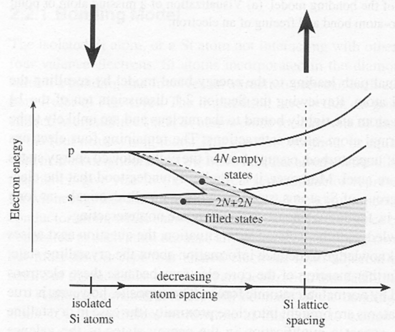
Qualitatively: see applet with H wave functions and quantum numbers!



From energy levels to energy bands



"Conduction Band"
"Gap"
"Valence Band"



Somehow (quantum mechanics !), when many atoms get close together their quantized energy levels split and turn into many states grouped in "energy bands", see diagrams

Conduction only happens if electrons have empty "states" available at nearby energy !

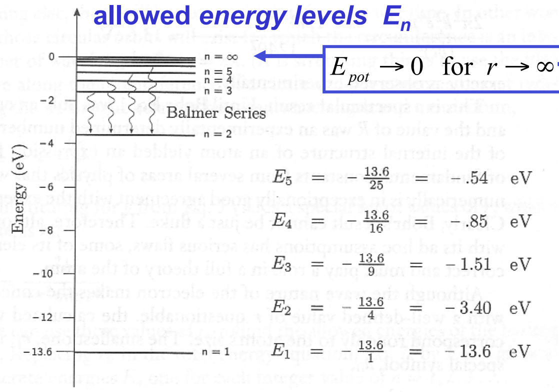
Energy levels and energy bands diagrams

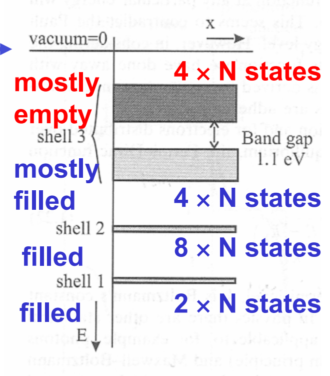
$$E = E_{pot} + E_{kin} < 0 \quad \text{for bound electrons}$$
$$E_{pot} < 0, \quad E_{kin} > 0$$

Isolated hydrogen atom, only one electron: allowed *energy levels* E_n

$$E_{pot} \to 0 \quad \text{for } r \to \infty$$

N Silicon atoms, 14 × N electrons: allowed states grouped in *energy bands*, filled according to Pauli Principle





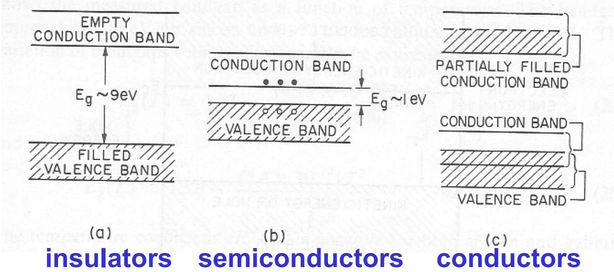
mostly empty — **4 × N states**

mostly filled — **4 × N states**

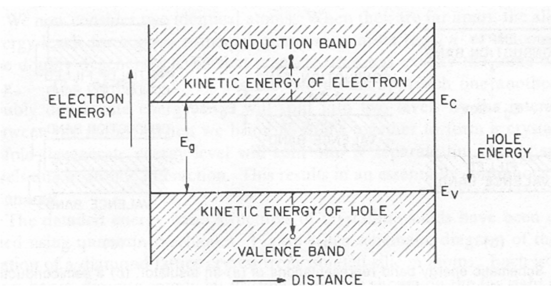
filled — **8 × N states**

filled — **2 × N states**

Energy band representations

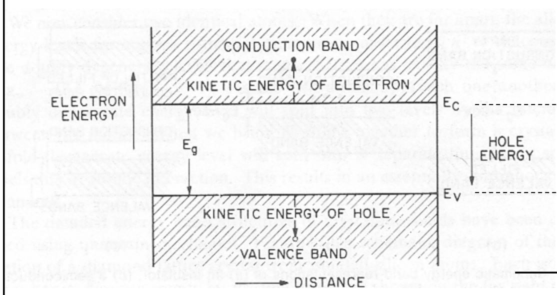


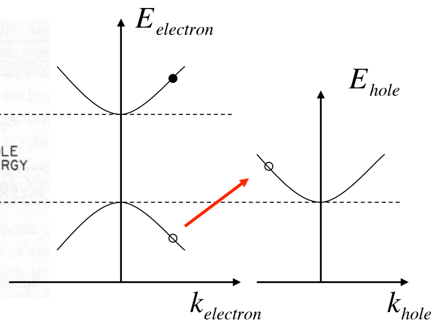
insulators **semiconductors** **conductors**



kinetic energy and potential energy for electrons and holes (= for "carriers"): Why? See next slide…

Energy band representations





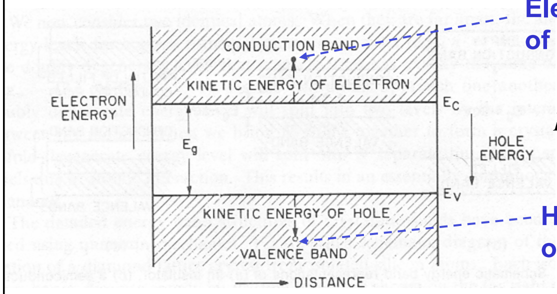
Close to the band edges, the E:k diagram is approximately parabolic, similar to that of a free particle, with effective mass m*…

bottom of conduction band: $E_e - E_C \approx \dfrac{\hbar^2 k_e^2}{2m_e^*} \quad m_e^* > 0$ $\qquad k_h = -k_e \quad m_h^* = -m_e^*$

top of valence band: $E_e - E_V \approx \dfrac{\hbar^2 k_e^2}{2m_e^*} \quad m_e^* < 0 \qquad E_h - E_V = -(E_e - E_V) \approx \dfrac{\hbar^2 k_h^2}{2m_h^*} \quad m_h^* > 0$

Crystal momentum and effective mass

From the practical point of view:
electrons and holes in a crystal as classical particles characterized by "effective mass", kinetic energy, and "crystal momentum":



Free electron:

$$E = \frac{p^2}{2m_0} \qquad p = m_0 v = \hbar k$$

Electrons close to the bottom of the conduction band ($E>E_c$):

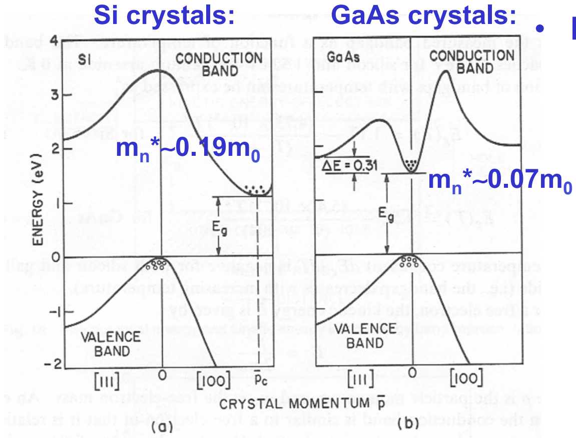
$$E = E_c + \frac{\overline{p}^2}{2m_e^*} \qquad \overline{p} = m_e^* v = \hbar k_e$$

Holes close to the top of the valence band:

$$E_{hole} = \frac{\overline{p}^2}{2m_h^*} \qquad \overline{p} = m_h^* v = \hbar k_h$$

Energy-momentum in three dimensions

Si crystals: **GaAs crystals:**

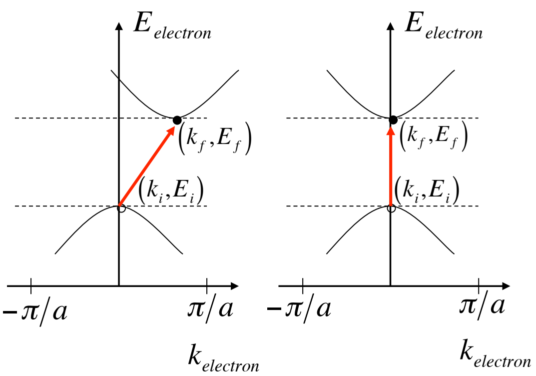


"indirect" semiconductor

"direct" semiconductor

- **More complications:**
  - **Different E-p relations in different space directions**
  - **Usually only [111] and [100] are shown**
  - **Minimum E in conduction band and maximum E in valence band may occur for different crystal momenta ! ("indirect" semiconductors)**
  - **Practical consequences, see later (for instance: optoelectronic devices)**

Indirect and direct semiconductors - 1



"indirect" semiconductor

"direct" semiconductor

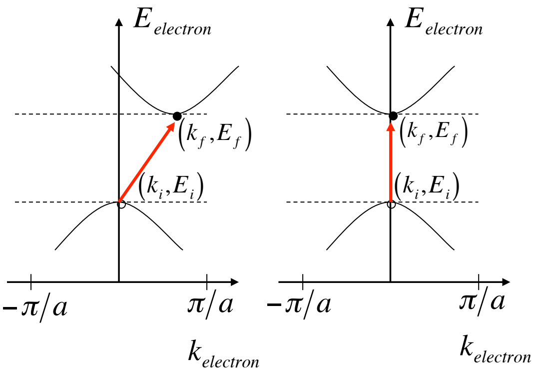
Photon-induced transitions:

"direct" (2-body)
electron - photon
more probable, for the same *ΔE*

"indirect" (3-body)
electron - photon - phonon
less probable, for the same *ΔE*

Different optical properties!

Indirect and direct semiconductors -2



"indirect" semiconductor

"direct" semiconductor

Energy and crystal momentum "jumps" for electrons in Silicon (typical):

$$\Delta p = \hbar \Delta k = \hbar k_f - \hbar k_i \approx 0 \div \hbar\pi/a$$
$$\approx 3 \times 10^{-8} \text{ eV s cm}^{-1} \text{ (Si)}$$
$$\Delta E = E_f - E_i \approx E_g$$
$$\approx 1.1 \text{ eV (Si)}$$

Photons carry *energy*, but small *momentum*

$$\text{photons}: E \approx 1 \text{ eV} \Rightarrow$$
$$\Rightarrow p = E/c \approx 3 \times 10^{-11} \text{ eV s cm}^{-1}$$

Phonons carry *momentum*, but small *energy*

$$\text{phonons}: p \approx 3 \times 10^{-8} \text{ eV s cm}^{-1} \Rightarrow$$
$$\Rightarrow E = pv_{phase} \approx 0.02 \text{ eV}$$

A "real life" example (Ge)

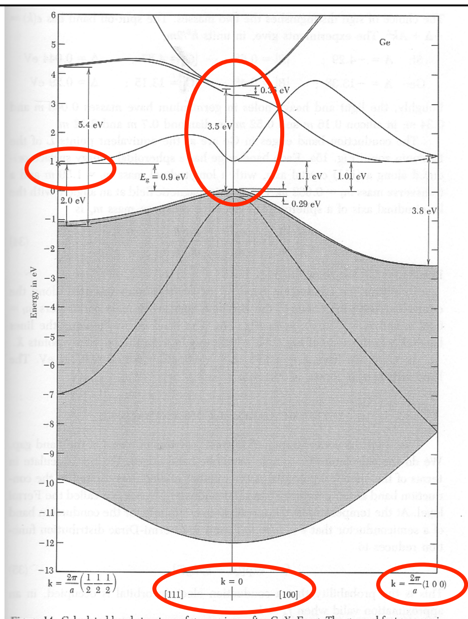


Figure 14 Calculated band structure of germanium, after C. Y. Fong. The general features are in good agreement with experiment. The four valence bands are shown in gray. The fine structure of the valence band edge is caused by spin-orbit splitting. The energy gap is indirect; the conduction band edge is at the point $(2\pi/a)(\frac{1}{2}\frac{1}{2}\frac{1}{2})$. The constant energy surfaces around this point are ellipsoidal.

Theoretical computation of the "band structure of Ge", in good agreement with experimental data (not shown)

From:
C.Kittel,
Introduction to Solid State Physics

Intrinsic semiconductors at equilibrium

We need to know:
charge carriers concentration
(n electrons/cm^3, p holes/cm^3)

↓

Outline of ingredients and final results

Thermal equilibrium

- **Thermal equilibrium = ?**
  - **Between two bodies or systems in "thermal equilibrium" there can be *no net transfer of any sort* (law of detailed balancing).**
- **Thermal equilibrium: static, endless, useless… why do we care?**
  - **Systems near thermal equilibrium tend to come to equilibrium in predictable ways**
  - **The predictable behavior of systems not quite in equilibrium allows us to design and construct useful devices!**
- **From the statistical point of view:**
  - **Thermal equilibrium represents the distribution of maximum probability, achieved when the detailed balancing between the possible processes is reached.**

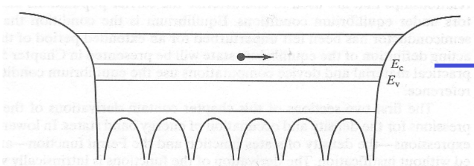
Finding the maximum probability

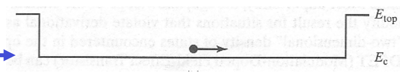
- *First part:* specify all possible "states" (solutions to the S. equation) and a set of appropriate boundary conditions
  - Possible eigenstates of the system (in our case *E-k* plot!)
  - Total internal energy of the system
  - Rules about filling states (in our case the Pauli principle)
  - Rules about conservation of particles
- *Second part:* procedure to find the most likely distribution of particles among the states, that does not violate any of the rules
  - Finding a maximum (prob.) subject to constraints ("rules"): Lagrange's method of undetermined multipliers
  - Or, alternatively, apply thermodynamics (min. free energy)
- Let's start with the "density of states" (step 1)

Step 1: density of states

Density of states …

- **Density of states *g(E)***
  - ***g(E)* = number of allowed states for electrons in the energy range (*E, E+dE*), per unit volume of the crystal**
  - **For a general solution (any *E*) we should use the full machinery of band theory… (possible, but complicated!)**
  - **but we are mainly interested in the band edges, normally populated by carriers: much simpler! Shortcut:**
    - **Equivalent problem: density of states for electrons in a 3-d box, provided we finally modify the solution, taking into account the "effective mass" m* and the band structure**





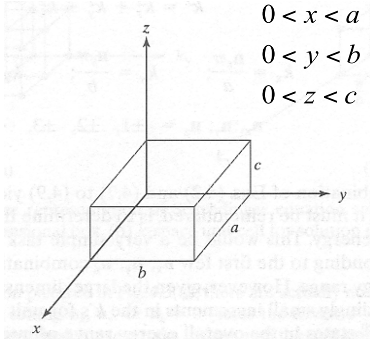
"Equivalent" problem: electrons in a box

Electrons in a box

$0 < x < a$

$0 < y < b$

$0 < z < c$



- **Infinitely deep 3-d potential well:**

Time-independent Schrödinger equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+k^2\psi = 0$$

$$k \equiv \sqrt{2mE/\hbar^2} \quad \text{or}: \quad E = \frac{\hbar^2 k^2}{2m}$$

Separation of variables

$$\psi(x,y,z) = \psi_x(x)\psi_y(y)\psi_z(z)$$

substituting and dividing by: $\psi = \psi_x\psi_y\psi_z$

$$\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2}+\frac{1}{\psi_y}\frac{\partial^2\psi_y}{\partial y^2}+\frac{1}{\psi_z}\frac{\partial^2\psi_z}{\partial z^2}+k^2 = 0$$

For each of the three functions:

$$\frac{1}{\psi_x}\frac{\partial^2\psi_x}{\partial x^2} = \text{constant} = -k_x^2$$

$$\frac{\partial^2\psi_x}{\partial x^2}+k_x^2\psi_x = 0 \quad 0 < x < a$$

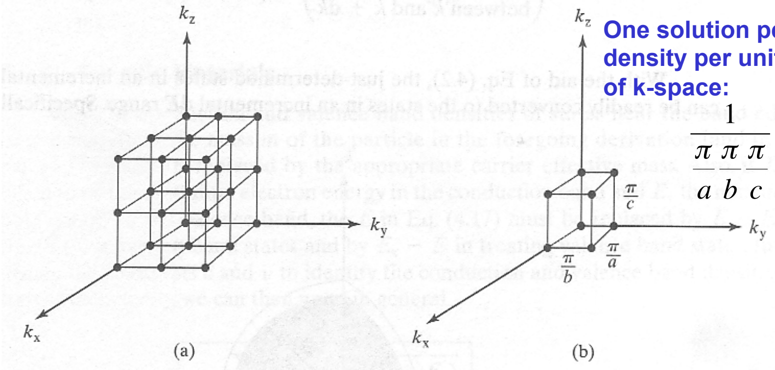
(similar for the other two)

Energy eigenstates and eigenvalues

Each solution is associated with a 3-d *k*-space vector:

$$\psi_E(x,y,z) = A\sin(k_x x)\sin(k_y y)\sin(k_z z) \qquad k_x = \frac{n_x\pi}{a}, \quad k_y = \frac{n_y\pi}{b}, \quad k_z = \frac{n_z\pi}{c}$$

$$E = \frac{\hbar^2 k^2}{2m} \qquad k^2 = k_x^2 + k_y^2 + k_z^2 \qquad n_x, n_y, n_z = 1, 2, 3, 4, \ldots$$



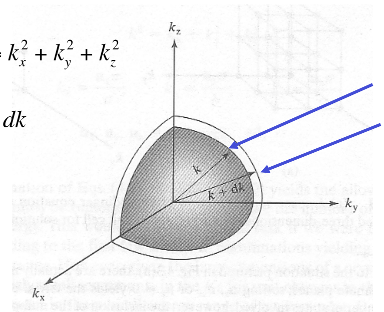
One solution per "cell": density per unit volume of k-space:

$$\frac{1}{\frac{\pi}{a}\frac{\pi}{b}\frac{\pi}{c}} = \frac{abc}{\pi^3}$$

E intervals in *k*-space

$$E = \frac{\hbar^2 k^2}{2m} \qquad k^2 = k_x^2 + k_y^2 + k_z^2$$

$$dE = \frac{dE}{dk}dk = \frac{\hbar^2 k}{m}dk$$



$k, \quad E$

$k + dk, \quad E + dE$

Counting the density of states in the interval (*E*, *E* + *dE*) or (*k*, *k* + *dk*) can be done in two steps:
- **computing the spherical shell volume of k-space (see figure)**
- **multiplying it by the density of states in k-space (see previous slide)**

Counting the solutions in *E* intervals

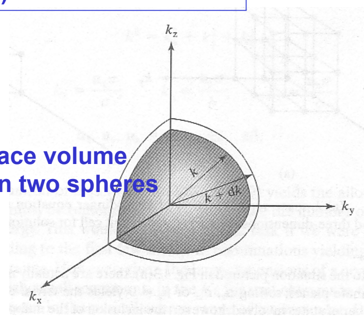
Only the 1st octant in k-space corresponds to independent solutions

Each state can be occupied by two electrons with opposite spin (Pauli principle)

$$\left(\frac{\text{allowed energy states}}{\text{unit volume in } k\text{ - space}}\right) = \frac{1}{8} \times 2 \times \frac{abc}{\pi^3} = \frac{abc}{4\pi^3}$$

$$\left(\begin{matrix}\text{energy states with} \\ k < k' < k + dk\end{matrix}\right) = \frac{abc}{4\pi^3} 4\pi k^2 dk$$

k-space volume between two spheres



$$k^2 = \frac{2mE}{\hbar^2} \qquad dk = \frac{\sqrt{2m}}{\hbar}\frac{1}{2}\frac{dE}{\sqrt{E}}$$

Density of states

$$\left(\begin{matrix}\text{energy states with} \\ E < E' < E + dE\end{matrix}\right) \equiv \gamma(E)dE = abc\frac{m\sqrt{2mE}}{\pi^2\hbar^3}dE \Rightarrow \boxed{g(E) \equiv \frac{\gamma(E)}{V} = \frac{m\sqrt{2mE}}{\pi^2\hbar^3}}$$

Crystal volume V = abc

… density of states …

- **Density of states, simplified model (box with infinitely deep walls)**

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

- **But: bands? Interaction with the crystal periodic potential? No problem:**
  - **the "average effective mass" *m** and the "crystal wave number" *k* describe the interactions with the crystal**
  - **for *E* close to E_C :**

$$E - E_C \cong \frac{\hbar^2 k^2}{2m_n^*} \Rightarrow \boxed{g_C(E) = \frac{m_n^*\sqrt{2m_n^*(E - E_C)}}{\pi^2\hbar^3}} \qquad E \geq E_C$$

  - **Similarly for holes:**

$$E_V - E \cong \frac{\hbar^2 k^2}{2m_n^*} \Rightarrow \boxed{g_V(E) = \frac{m_p^*\sqrt{2m_p^*(E_V - E)}}{\pi^2\hbar^3}} \qquad E \leq E_V$$

… with "average" effective masses

- The effective masses appearing in the density of states for some useful semiconductors (Si, Ge, GaAs) are averaged over crystal directions

Table 4.1 Density of States Effective Masses for Ge, Si, and GaAs

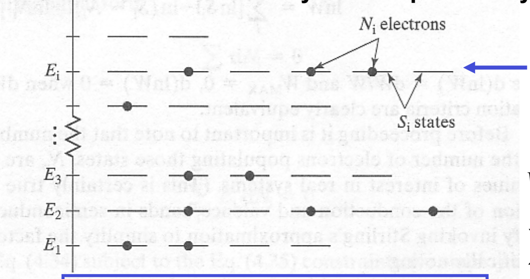
Effective Mass		Ge	Si	GaAs
m_n^*/m_0	T = 4 K	0.553	1.062	0.067
	T = 300 K	....	1.182	0.0655[†]
m_p^*/m_0	T = 4 K	0.357	0.590	0.532
	T = 300 K	....	0.81	0.524

- only GaAs is approximately isotropic
- See R.F.Pierret, section 4.1.2, p.94, for details on Si and Ge

Step 2: probability distribution function (Fermi-Dirac)

F.-D. probability distribution function

- **From thermodynamics:**
  - The most likely "macroscopic" state is the one corresponding to the largest number W of *equivalent* "microscopic" states, compatible with a given total number N of electrons and a fixed total energy E_{TOT}
  - W = "thermodynamical probability"; "entropy" = $\ln(W)$



S_i available states at energy E_i (partially) filled by N_i electrons according to Pauli principle

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

$$\sum_i N_i = N = \text{const.}$$

$$\sum_i E_i N_i = E_{TOT} = \text{const.}$$

Probability distribution function at thermal equilibrium:
N_i / S_i = ??? (at energy E_i)

Maximization procedure to find N_i/S_i

- Take the logarithm $\ln W$, use Stirling's approximation, and set the differential to zero (S_i are constant, N_i variable: see back-up slides for details) to find N_i/S_i that maximizes W or $\ln W$

  Introducing the undetermined Lagrange multipliers α and β to express the constraints on total N and E (constant) one finds:

$$f(E_i) = \frac{N_i}{S_i} = \frac{1}{1 + e^{\alpha + \beta E_i}} \quad \rightarrow \quad \boxed{f(E) = \frac{1}{1 + e^{\alpha + \beta E}}}$$

For closely spaced levels, $E_i \rightarrow E$

- α and β: from thermo-dynamical arguments $\Rightarrow$ for fermions, Fermi distribution:

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

$k_B = 8.617 \times 10^{-5}$ eV/K

T = absolute temperature

E_F "chemical potential" or "Fermi level"

Alternative method - 1

E_i	energy levels
S_i	"degeneracy" (# available states for each level)
N_i	occupation number (# occupied states) $N_i \le S_i$
$N_i/S_i\left(E_i\right)$	probability distribution function (pdf)

$F = U - TS$	free energy
$U = \sum_i N_i E_i$	total energy
$S = k_B \ln W$	entropy
$W = \prod_i \frac{S_i!}{N_i!(S_i - N_i)!}$	number of microstates

Alternative method - 2

equilibrium condition: conservation of particle number:

$$\delta F = \sum_i \frac{\partial F}{\partial N_i}\delta N_i = 0 \qquad \sum_i \delta N_i = 0$$

at equilibrium, exchange of electrons between levels k and l :

$$\frac{\partial F}{\partial N_k}\delta N_k + \frac{\partial F}{\partial N_l}\delta N_l = 0 \qquad \delta N_k + \delta N_l = 0$$

$$\Leftrightarrow \forall\, k,l: \quad \frac{\partial F}{\partial N_k} = \frac{\partial F}{\partial N_l} = \mu \quad \text{"chemical potential"}$$

At equilibrium, the chemical potential (defined as the rate of change of the free energy F for a change δN of the number of particles) is the same for all the energy levels, constant across the system

Alternative method - 3

$$F = U - TS = \sum_j N_j E_j - k_B T \ln \prod_j \frac{S_j!}{N_j!\left(S_j - N_j\right)!} =$$

$$= \sum_j N_j E_j - k_B T \sum_j \left[\ln S_j! - \ln N_j! - \ln\left(S_j - N_j\right)!\right]$$

$\ln N! \approx N \ln N - N$ Stirling's approximation (large N)

$$F = \sum_j N_j E_j - k_B T \sum_j \left[S_j \ln S_j - N_j \ln N_j - \left(S_j - N_j\right)\ln\left(S_j - N_j\right)\right]$$

Alternative method - 4

Chemical potential:

$$\mu \equiv \frac{\partial F}{\partial N_i} = E_i - k_B T \frac{\partial}{\partial N_i}\left[-N_i \ln N_i - \left(S_i - N_i\right)\ln\left(S_i - N_i\right)\right] =$$

$$= E_i - k_B T\left[-\ln N_i - 1 + \ln\left(S_i - N_i\right) + 1\right] = E_i - k_B T \ln\left(\frac{S_i}{N_i} - 1\right)$$

Relation with the occupancy of the available states:

$$\frac{E_i - \mu}{k_B T} = \ln\left(\frac{S_i}{N_i} - 1\right) \quad \Rightarrow \quad \exp\left(\frac{E_i - \mu}{k_B T}\right) = \frac{S_i}{N_i} - 1$$

Fermi-Dirac probability distribution function (pdf):

$$\boxed{f\left(E_i\right) \equiv \frac{N_i}{S_i} = \left[1 + \exp\left(\frac{E_i - \mu}{k_B T}\right)\right]^{-1} = \frac{1}{1 + \exp\left(\frac{E_i - \mu}{k_B T}\right)}}$$

"Fermi energy": $\mu\left(T = 0K\right) \equiv E_F$

Fermi-Dirac pdf

For fermions, obeying the Pauli principle:

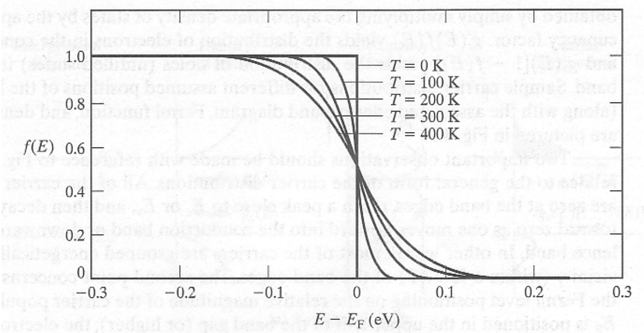
$$f(E) = \frac{1}{1 + e^{(E-E_F)/k_B T}}$$

(what about bosons? See next slide)

k_B = 8.617 × 10^{-5} eV/K

***T* = absolute temperature**

μ "chemical potential"
"Fermi level" $E_F \equiv \mu(T=0K)$



Fermions, bosons and classical limit

- **Fermions: Fermi-Dirac distribution (at most one fermion per state):**

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

- **Bosons: Bose-Einstein distribution (any number of bosons per state)**

$$f_{BE}(E) = \frac{1}{e^{(E-\mu)/k_B T} - 1}$$

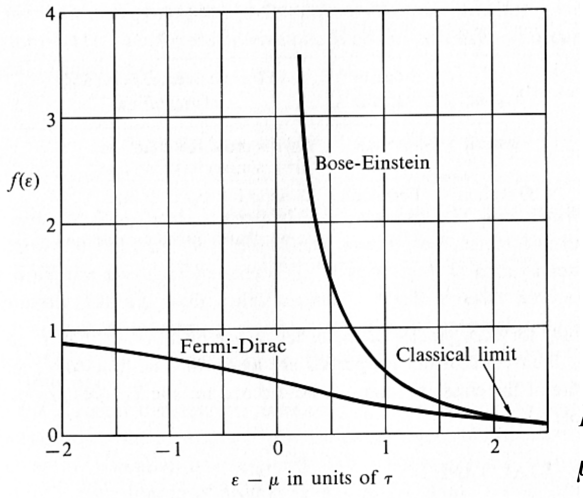
This sign makes a LARGE difference!

- **Classical: Maxwell-Boltzmann (good limit of quantum statistics when: few particles / high temperature, small filling probability per state)**

$$f_{MB}(E) = \frac{1}{e^{(E-\mu)/k_B T}} = e^{-(E-\mu)/k_B T}$$

Fermions, bosons and classical limit

Comparison of the 3 pdfs:



$$f_{FD}(E) = \frac{1}{e^{(E-\mu)/k_BT} + 1}$$

$$f_{BE}(E) = \frac{1}{e^{(E-\mu)/k_BT} - 1}$$

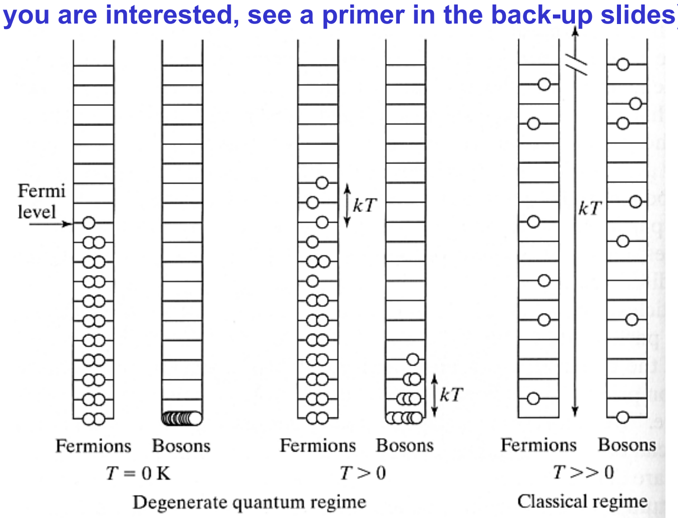
$$f_{MB}(E) = e^{-(E-\mu)/k_BT}$$

$E - \mu$ in units of k_BT

$\mu =$ "chemical potential"

Fermions, bosons and classical limit

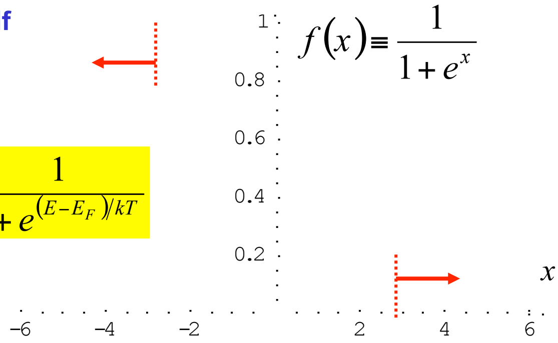
Analysis performed in statistical quantum mechanics
(if you are interested, see a primer in the back-up slides):



Fermi pdf: Boltzmann approximation

- Fermi pdf

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



$$f(x) \equiv \frac{1}{1+e^{x}}$$

$$x = \frac{E-E_F}{kT}$$

- approximate expressions for energies far enough from E_F:

$$E - E_F > 3kT \Rightarrow F(E) \approx e^{-(E-E_F)/kT} \qquad \left(\boxed{x > 3} \Rightarrow \frac{1}{1+e^{x}} \approx e^{-x} \right)$$

$$E - E_F < -3kT \Rightarrow F(E) \approx 1 - e^{-(E_F-E)/kT} \qquad \left(\boxed{x < -3} \Rightarrow \frac{1}{1+e^{x}} \approx 1 - e^{x} \right)$$

Number of carriers at band edges (Boltzmann approximation)

– We have now “understood” all the ingredients needed to obtain *carrier concentrations* in *intrinsic and extrinsic semiconductors at equilibrium*
  - allowed and forbidden energy bands
  - density of available states
  - Fermi probability density function

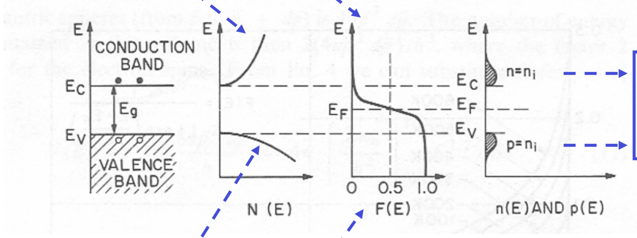
Intrinsic carrier concentrations *n, p*

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

$$F(E) \cong e^{-(E-E_F)/kT}$$

"Effective density of states" in the conduction band

$$N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$$



$$n \cong N_C e^{-(E_C-E_F)/kT}$$

$$p \cong N_V e^{-(E_F-E_V)/kT}$$

$$N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$$

$$1-F(E) \cong e^{-(E_F-E)/kT}$$

"Effective density of states" in the valence band

$$g_V(E) = \frac{m_p^* \sqrt{2m_p^*(E_V-E)}}{\pi^2\hbar^3}$$

Exercise Integrate *g(E)F(E)* to obtain *n* and *p*

Intrinsic electron concentration *n*

- **Explicit computation for electrons:**

$$n = \int_{E_C}^{\infty} g_C(E)F(E)dE =$$

$$= 4\pi\left(\frac{2m_n^*}{h^2}\right)^{3/2} \int_{E_C}^{\infty} (E-E_C)^{1/2} e^{-(E-E_F)/kT} dE =$$

$$= 4\pi\left(\frac{2m_n^*}{h^2}\right)^{3/2} \int_{0}^{\infty} E'^{1/2} e^{-(E'+E_C-E_F)/kT} dE' =$$

$$= 4\pi\left(\frac{2m_n^*}{h^2}\right)^{3/2} (kT)^{3/2} \exp\left(-\frac{E_C-E_F}{kT}\right) \int_0^\infty x^{1/2} e^{-x}\, dx =$$

$$= 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} \exp\left(-\frac{E_C-E_F}{kT}\right)$$

$g_C(E)$ state density

Fermi f. for $E - E_F > 3kT$

$F(E) \approx e^{-(E-E_F)/kT}$

change variables:

$E' = E - E_C \quad dE' = dE$

$x = \dfrac{E'}{kT} \quad dE' = kT dx$

$$\int_0^\infty x^{1/2} e^{-x}\, dx = \frac{\sqrt{\pi}}{2}$$

Intrinsic hole concentration *p*

- **Explicit computation for holes:**

$$p = \int_{-\infty}^{E_V} g_V(E)\left(1-F(E)\right)dE =$$

$$= 4\pi\left(\frac{2m_p^*}{h^2}\right)^{3/2}\int_{-\infty}^{E_V}\left(E_V-E\right)^{1/2}e^{-(E_F-E)/kT}dE =$$

$$= 4\pi\left(\frac{2m_p^*}{h^2}\right)^{3/2}\int_{0}^{\infty}E'^{1/2}e^{-(E'+E_F-E_V)/kT}dE' =$$

$$= 4\pi\left(\frac{2m_p^*}{h^2}\right)^{3/2}(kT)^{3/2}\exp\left(-\frac{E_F-E_V}{kT}\right)\int_0^\infty x^{1/2}e^{-x}\,dx =$$

$$= 2\left(\frac{2\pi m_p kT}{h^2}\right)^{3/2}\exp\left(-\frac{E_F-E_V}{kT}\right)$$

$g_V(E)$ state density

$1-F(E)$ for $E-E_F < -3kT$

$1-F(E) \approx e^{-(E_F-E)/kT}$

change variables:

$E' = E_V - E \quad dE' = -dE$

$x = \dfrac{E'}{kT} \qquad dE' = kTdx$

$$\int_0^\infty x^{1/2}e^{-x}\,dx = \frac{\sqrt{\pi}}{2}$$

Intrinsic carrier densites

$$n \cong N_C e^{-(E_C-E_F)/kT}$$
$$p \cong N_V e^{-(E_F-E_V)/kT}$$

For an intrinsic semiconductor: $\boxed{n = p = n_i}$ **Intrinsic carrier density**

N_C : "Effective density" of states in the conduction band

$$N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$$

$\cong 2.8\times10^{19}cm^{-3}$ (Si), $4.7\times10^{17}cm^{-3}$ (GaAs)

N_V : "Effective density" of states in the valence band

$$N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$$

$\cong 1.04\times10^{19}cm^{-3}$ (Si), $7.0\times10^{18}cm^{-3}$ (GaAs)

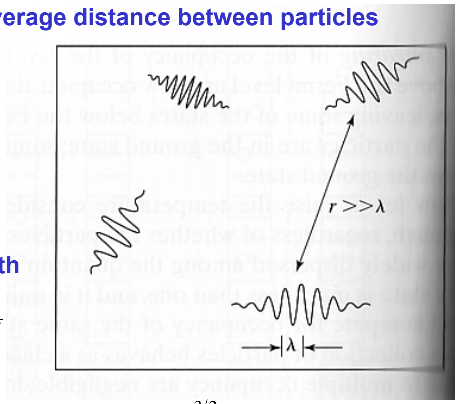
@ T~300K

N_C, N_V : also called "quantum concentrations" in statistical mechanics
physical meaning: in the Boltzmann approx. ("non-degenerate" semiconductors)
n << N_C , p << N_V : low occupancy of states, behaviour similar to classical gas

“effective densities” or “quantum concentrations”

N_C, N_V : physical meaning: density corresponding to the transition from the classical to the quantum behaviour of a gas

particles concentration $n \approx \dfrac{1}{r^3}$ $\quad r$ average distance between particles



de Broglie $E = \dfrac{p^2}{2m} = \dfrac{h^2}{2m\lambda^2}$

equipartition $E = \dfrac{1}{2}mv^2 = \dfrac{3}{2}k_B T$

“thermal” de Broglie wavelength

$$\frac{h^2}{2m\lambda^2} = \frac{3}{2}k_B T \quad \Rightarrow \quad \lambda = \frac{h}{\sqrt{3mk_B T}}$$

Classical gas condition

$$r >> \lambda \quad \Leftrightarrow \quad \frac{1}{n^{1/3}} >> \frac{h}{\sqrt{3mk_B T}} \quad \Leftrightarrow \quad n << \left(\frac{3mk_B T}{h^2}\right)^{3/2} = n_q$$

“quantum concentration”

Intrinsic Fermi level

$$\boxed{\begin{array}{l} n \cong N_C e^{-(E_C - E_F)/kT} \\ p \cong N_V e^{-(E_F - E_V)/kT} \end{array}}$$

For an intrinsic semiconductor: $\boxed{n = p = n_i}$ Intrinsic carrier density

$$n = p$$

$$\Rightarrow E_i = E_F = \frac{E_C + E_V}{2} + \frac{kT}{2}\ln\left(\frac{N_V}{N_C}\right) = \frac{E_C + E_V}{2} + \frac{3kT}{4}\ln\left(\frac{m_p}{m_n}\right)$$

$$\Rightarrow \boxed{E_i \cong \frac{E_C + E_V}{2}}$$

Intrinsic Fermi level: in the limit of equal effective mass for electrons and holes, approximately in the middle of the forbidden energy gap

Mass action law

$$\boxed{\begin{array}{l} n \cong N_C e^{-(E_C - E_F)/kT} \\ p \cong N_V e^{-(E_F - E_V)/kT} \end{array}}$$

For an intrinsic semiconductor: $\boxed{n = p = n_i}$ Intrinsic carrier density

↓

"mass action law": at thermal equilibrium:

$$\boxed{np = n_i^2 = N_C N_V e^{-E_g/kT} \qquad n_i = \sqrt{N_C N_V}\, e^{-E_g/2kT}}$$

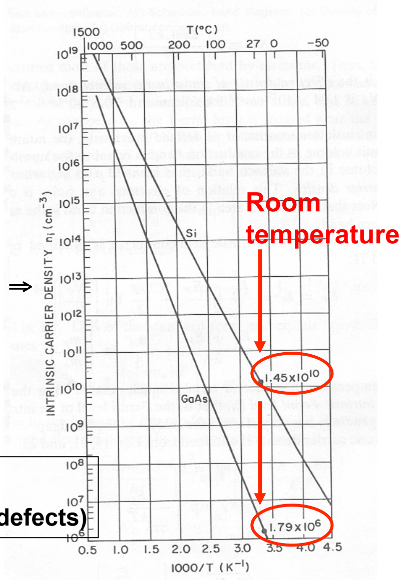
Typical values at room temperature ($T = 300$ K, $kT = 0.0259$ eV):

	N_C [cm^{-3}]	N_V [cm^{-3}]	m_n^*/m_0	m_p^*/m_0	E_g [eV]	n_i [cm^{-3}]
Si	2.8×10^{19}	1.04×10^{19}	1.08	0.56	1.11	1.5×10^{10}
GaAs	4.7×10^{17}	7.0×10^{18}	0.067	0.48	0.66	1.8×10^{6}
Ge	1.04×10^{19}	6.0×10^{18}	0.55	0.55	1.43	2.4×10^{13}

Intrinsic carrier densities

- **Temperature dependence**
  - increase with temperature
  - smaller with larger E_g
- **Caveats:**
  - Pure Si: very low conductivity: $\sigma \approx 10^{-6}\,(\Omega\ \mathrm{cm})^{-1}$ at $T \approx 300$ K
  - However, in practice dominated by defects (Kowalski method: typically $10^{11}/\mathrm{cm}^2$) $\sigma \approx 10^{-5}\,(\Omega\ \mathrm{cm})^{-1}$
  - Doping is needed in practice, to control conductivity!

⇒



Exercise Estimate orders of magnitude for the conductivity of Si (pure and with realistic defects)

Lectures 24-26 - summary

- Using results from quantum mechanics in 1-d (periodic potential, infinite potential well) and in 3-d (hydrogen and hydrogen-like atoms, angular momentum and spin) we moved from single particle (electron) to many (weakly or non-interacting) particles (electrons), filling one-particle states ("orbitals") according to the Pauli exclusion principle for identical fermions.
- We qualitatively described the "band model" for conductors, insulators and semiconductors, linking it to the results obtained in the 1-d simple Kronig-Penney model (periodic potential), (E:k) dispersion relations and effective mass for electrons and holes
- We considered *equilibrium* statistics and obtained both the density of states and the Fermi-Dirac probability distribution functions, essential ingredients to predict equilibrium carrier concentrations.
- We finally computed the charge-carrier concentrations in *intrinsic* (pure) semiconductors at thermal equilibrium, evaluated the Fermi level, and formulated the "mass action law"

Lecture 24-26 - exercises

- Exercise 1: **Consider a simplified model of a conductor with non-interacting conduction electrons in a 3-d infinite well. Find the Fermi energy and the average inter-electron spacing. Apply the results to the case of aluminum (A=27), assuming: density ρ = 2.7×10^3 kg/m^3, and three free atoms per electron (hint: see Bernstein, par.10-5 and example 10-5).**
- Exercise 2: **Explain the reason for introducing the effective mass in the density of states as obtained from the "infinite well" box model.**

Back-up slides

Quantum statistics primer

Entropy

Thermal contact and thermal equilibrium

Temperature and Boltzmann factor

Diffusive contact and diffusive equilibrium

Chemical potential and Gibbs factor

Fermi-Dirac and Bose-Einstein statistics

distribution functions and classical limit

Entropy

Quantum states **are either** ***accessible*** **or** ***not accessible*** **to a system**

All accessible states are ***equally probable*** **(fundamental assumption)**

$$S = k_B \sigma \qquad \sigma = \log g$$

g : number of accessible quantum states

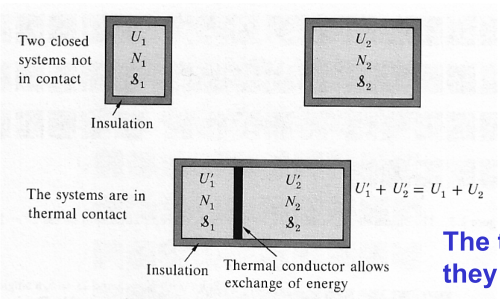
Entropy S **measures the number of accessible states**

Example: system of 3 elementary magnets, each with magnetic moment +*m* (up) or -*m* (down).

If the total magnetic moment is *M = 2m*, there are *g = 3* accessible states

Three magnets up:		$\uparrow_1\uparrow_2\uparrow_3$	
Two magnets up:	$\uparrow_1\uparrow_2\downarrow_3$	$\uparrow_1\downarrow_2\uparrow_3$	$\downarrow_1\uparrow_2\uparrow_3$
One magnet up:	$\uparrow_1\downarrow_2\downarrow_3$	$\downarrow_1\uparrow_2\downarrow_3$	$\downarrow_1\downarrow_2\uparrow_3$
None up:		$\downarrow_1\downarrow_2\downarrow_3$.	

Thermal contact and equilibrium



Two insulated systems:

$$U_1, U_2 \quad \text{energies} \quad U = U_1 + U_2$$

$$N_1, N_2 \quad \text{particles} \quad N = N_1 + N_2$$

$$g(N,U) = \sum_{U_1} g_1(N_1,U_1)\, g_2(N_2,U-U_1)$$

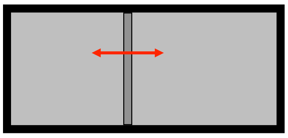
The two systems in thermal contact: they exchange energy, not particles

Energy is exchanged maximizing entropy (⇔ *g*) to reach equilibrium

$$dg = \left(\frac{\partial g}{\partial U_1}\right)_{N_1} g_2 dU_1 + g_1 \left(\frac{\partial g}{\partial U_2}\right)_{N_2} dU_2 = 0\,, \qquad dU_1 + dU_2 = 0$$

$$\Leftrightarrow \frac{1}{g_1}\left(\frac{\partial g}{\partial U_1}\right)_{N_1} = \frac{1}{g_2}\left(\frac{\partial g}{\partial U_2}\right)_{N_2} \quad \Leftrightarrow \quad \left(\frac{\partial \log g}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \log g}{\partial U_2}\right)_{N_2} \quad \Leftrightarrow \quad \left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2}$$

Temperature



U_1, N_1 $\quad$ U_2, N_2

σ_1 $\quad$ σ_2

Thermal equilibrium condition: no net energy transfer, maximum entropy

$$\frac{1}{\tau_1} \equiv \left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial \sigma_2}{\partial U_2}\right)_{N_2} \equiv \frac{1}{\tau_2}$$

corresponding to equal "absolute (Kelvin) temperature" *T*:

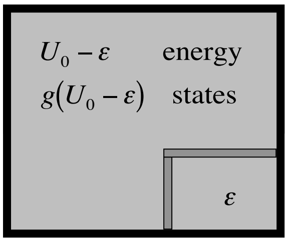
$$\tau \equiv k_B T, \qquad \frac{1}{T_1} \equiv k_B\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1} = \left(\frac{\partial S_2}{\partial U_2}\right)_{N_2} = k_B\left(\frac{\partial \sigma_1}{\partial U_1}\right)_{N_1} \equiv \frac{1}{T_2}$$

$$\Rightarrow \boxed{\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_N}$$

Definition of absolute (Kelvin) temperature *T*

Temperature regulates the *energy* transfer !

Boltzmann factor



Small *system*, with only two states, in thermal contact with a large system called *reservoir* ; total energy U_0

	System	*Reservoir*	
state 1	0	U_0	$g(U_0)$
state 2	ε	$U_0 - \varepsilon$	$g(U_0 - \varepsilon)$
	energy	***energy***	***accessible states***

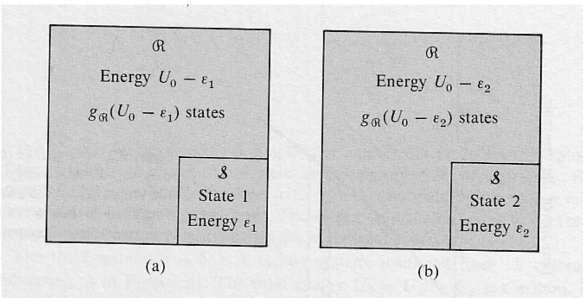
The ratio of probabilities for the two states of the small system depends on the corresponding multiplicities *g* for the reservoir

$$\boxed{\frac{P(\varepsilon)}{P(0)}} = \frac{g(U_0 - \varepsilon)}{g(U_0)} = \frac{\exp[\sigma(U_0 - \varepsilon)]}{\exp[\sigma(U_0)]} = \boxed{\exp\left(-\frac{\varepsilon}{k_B T}\right)}$$

"Boltzmann factor"

$$\sigma(U_0 - \varepsilon) \approx \sigma(U_0) - \varepsilon\left(\frac{\partial \sigma}{\partial U_0}\right)_N = \sigma(U_0) - \frac{\varepsilon}{k_B T}$$

Partition function, etc.



Generalization to systems with any number of states (*s*), with energies ε_s

Ratio of probabilities for two of the states of the system :

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{\exp[-\varepsilon_1/k_B T]}{\exp[-\varepsilon_2/k_B T]}$$

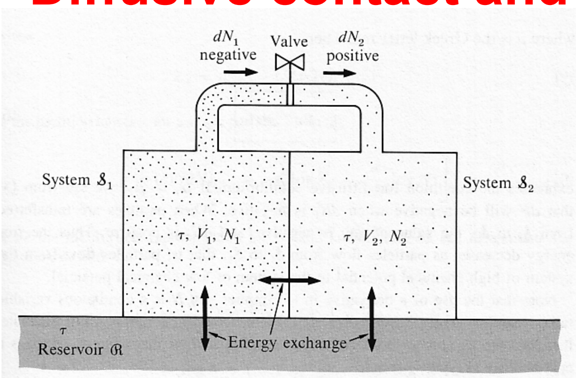
Basic ingredients for all computations (average macroscopic quantities, etc.)

Probability of a given state *s* of the system:

$$P(\varepsilon_s) = \frac{\exp(-\varepsilon_s/k_B T)}{Z} \qquad \boxed{Z \equiv \sum_j \exp(-\varepsilon_j/k_B T)}$$

"Partition function"

Diffusive contact and equilibrium



"Helmoltz free energy"

$$F \equiv U - TS = U - \tau\sigma$$

is minimum for systems in thermal contact with a reservoir, with constant volume

Balance of conflicting requirements (minimum *U*, maximum "disorder" *S*)

$$F = F_1 + F_2 = U_1 + U_2 - \tau(\sigma_1 + \sigma_2) \qquad N = N_1 + N_2 = \text{constant}$$

"diffusive equilibrium" (zero net particle transfer) if F is a minimum with respect to variations $dN_1 = -dN_2$

$$dF = \left(\frac{\partial F}{dN_1}\right)_\tau dN_1 + \left(\frac{\partial F}{dN_2}\right)_\tau dN_2 = \left[\left(\frac{\partial F}{dN_1}\right)_\tau - \left(\frac{\partial F}{dN_2}\right)_\tau\right] dN_1 = 0 \quad \Leftrightarrow \quad \boxed{\left(\frac{\partial F}{dN_1}\right)_\tau = \left(\frac{\partial F}{dN_2}\right)_\tau}$$

Chemical potential

"chemical potential": definition

$$\boxed{\mu(\tau,N,V) \equiv \left(\frac{\partial F}{dN}\right)_{\tau,V}}$$

Two systems 1, 2:

diffusive equilibrium $\mu_1 = \mu_2$

thermal equilibrium $\tau_1 = \tau_2$

Chemical potential: guides the flow of particles $\mu_1 > \mu_2 \quad \Rightarrow \quad dN_1 = -dN_2 < 0$

Particles: net flow from 1 to 2

Temperature: guides the flow of energy $\tau_1 > \tau_2 \quad \Rightarrow \quad dU_1 = -dU_2 < 0$

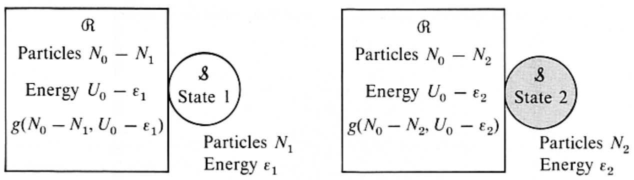
Energy: net flow from 1 to 2

$\mu = \mu_{\text{tot}} = \mu_{\text{int}} + \mu_{\text{ext}}$ "internal" (thermal origin) + "external" (gravitational, electrostatic, magnetic, etc.) contributions

$$\mu(U,N,V) = -\tau\left(\frac{\partial \sigma}{dN}\right)_{U,V} = -T\left(\frac{\partial S}{dN}\right)_{U,V}$$

Relation with entropy (can be derived)

Gibbs factor



System in thermal and diffusive contact with a reservoir

Ratio of probabilities for two of the states of the system (generalization of the Boltzmann factor: it can be shown that…):

$$\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = \frac{\exp\left[(N_1\mu - \varepsilon_1)/k_B T\right]}{\exp\left[(N_2\mu - \varepsilon_2)/k_B T\right]}$$

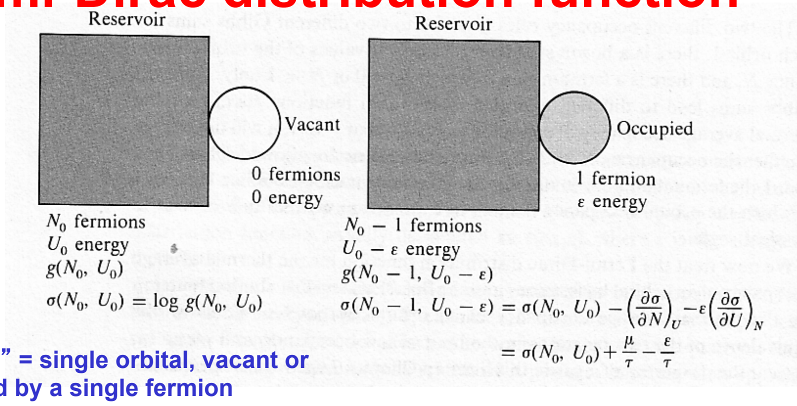
"Gibbs factor"

Probability of a given state *s* of the system:

$$P(N_s,\varepsilon_s) = \frac{\exp\left[(N_s\mu - \varepsilon_s)/k_B T\right]}{Z} \qquad Z \equiv \sum_{N,s} \exp\left[\left(N\mu - \varepsilon_{s(N)}\right)/k_B T\right]$$

"Gibbs sum"

Fermi-Dirac distribution function

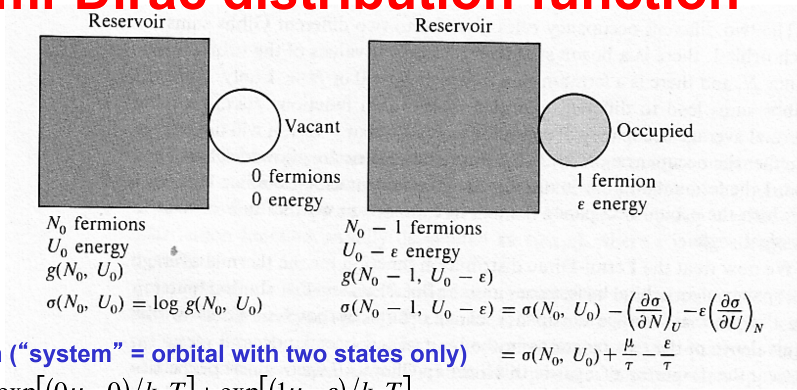


"System" = single orbital, vacant or occupied by a single fermion

Reservoir = all other orbitals

Problem: find the average thermal occupancy of the orbital thus singled out

Fermi-Dirac distribution function



Gibbs sum ("system" = orbital with two states only)

$$Z = \exp\left[(0\mu - 0)/k_B T\right] + \exp\left[(1\mu - \varepsilon)/k_B T\right] =$$

$$= 1 + \exp\left[(\mu - \varepsilon)/k_B T\right]$$

Average orbital occupancy:

$$\langle N(\varepsilon)\rangle = \frac{\exp\left[(\mu - \varepsilon)/k_B T\right]}{1 + \exp\left[(\mu - \varepsilon)/k_B T\right]} = \boxed{\frac{1}{\exp\left[(\varepsilon - \mu)/k_B T\right] + 1} \equiv f(\varepsilon)}$$

Fermi-Dirac pdf

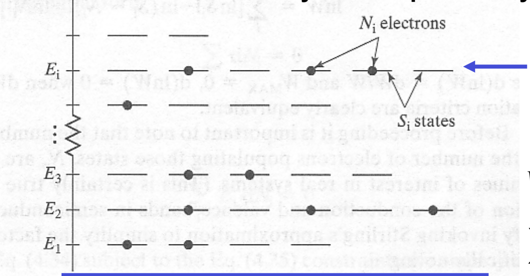
probability distribution function (Fermi-Dirac)

Detailed calculations

(Combinatorial approach)

F.-D. probability distribution function

- **From thermodynamics:**
  - **The most likely "macroscopic" state is the one corresponding to the largest number W of *equivalent* "microscopic" states, compatible with a given total number N of electrons and a fixed total energy E_{TOT}**
  - **W = "thermodynamical probability"; "entropy" = $\ln(W)$**



S_i available states at energy E_i (partially) filled by N_i electrons

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

$$\sum_i N_i = N = \text{const.}$$

$$\sum_i E_i N_i = E_{TOT} = \text{const.}$$

Probability distribution function at thermal equilibrium:
N_i / S_i = ??? (at energy E_i)

Maximization procedure to find N_i/S_i

- Take the logarithm, use Stirling's approximation, and set the differential to zero (S_i are constant, N_i variable):

$$\ln W = \sum_i \left(\ln S_i! - \ln(S_i - N_i)! - \ln N_i!\right)$$

$$\ln x! \cong x\ln x - x \qquad (x \text{ large})$$

$$\ln W \cong \sum_i \left[S_i \ln S_i - S_i - (S_i - N_i)\ln(S_i - N_i) + (S_i - N_i) - N_i \ln N_i + N_i\right]$$

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

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

$$= \sum_i \left[\ln(S_i - N_i) + 1 - \ln N_i - 1\right] dN_i$$

$$= \sum_i \ln(S_i/N_i - 1)\, dN_i = 0$$

Constraints: Lagrange multipliers

$$d(\ln W) = 0. \quad \Rightarrow \quad \sum_i \ln(S_i/N_i - 1)\, dN_i = 0$$

$$\sum_i N_i = N. \quad \Rightarrow \quad \sum_i dN_i = 0$$

$$\sum_i E_i N_i = E_{TOT}. \quad \Rightarrow \quad \sum_i E_i dN_i = 0$$

Introducing the undetermined Lagrange multipliers α and β :

$$\sum_i \left[\ln(S_i/N_i - 1) - \alpha - \beta E_i\right] dN_i = 0$$

$$\ln(S_i/N_i - 1) - \alpha - \beta E_i = 0$$

$$S_i/N_i - 1 = e^{\alpha + \beta E_i}$$

$$f(E_i) = \frac{N_i}{S_i} = \frac{1}{1 + e^{\alpha + \beta E_i}} \quad \rightarrow \quad \boxed{f(E) = \frac{1}{1 + e^{\alpha + \beta E}}}$$

For closely spaced levels, $E_i \rightarrow E$

Number of carriers at band edges (Boltzmann approximation)

- Summary of results for "intrinsic" semiconductors
  - "Intrinsic" density of carriers
  - "effective density of states"
  - "Intrinsic" Fermi level
  - "Mass action" law

Intrinsic Fermi level and carrier density

N_C : "Effective density" of states in the conduction band

$$N_C \equiv 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} \cong 2.8\times10^{19}\,cm^{-3}\ (\mathrm{Si}),\ 4.7\times10^{17}\,cm^{-3}\ (\mathrm{GaAs})$$

N_V : "Effective density" of states in the valence band

$$N_V \equiv 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2} \cong 1.04\times10^{19}\,cm^{-3}\ (\mathrm{Si}),\ 7.0\times10^{18}\,cm^{-3}\ (\mathrm{GaAs})$$

@ T~300K

$$\boxed{\begin{aligned} n &\cong N_C e^{-(E_C-E_F)/kT} \\ p &\cong N_V e^{-(E_F-E_V)/kT} \end{aligned}}$$

For an intrinsic semiconductor: $\boxed{n = p = n_i}$ Intrinsic carrier density

$$n = p \Rightarrow E_i = E_F = \frac{E_C+E_V}{2} + \frac{kT}{2}\ln\left(\frac{N_V}{N_C}\right) = \frac{E_C+E_V}{2} + \frac{3kT}{4}\ln\left(\frac{m_p}{m_n}\right) \Rightarrow \boxed{E_i \cong \frac{E_C+E_V}{2}}$$

Intrinsic Fermi level

"mass action law": at thermal equilibrium:

$$\boxed{np = n_i^2 = N_C N_V e^{-E_g/kT} \qquad n_i = \sqrt{N_C N_V}\, e^{-E_g/2kT}}$$