Theory of Semiconductor Devices
(반도체 소자 이론)

Lecture 12

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Equilibrium Distributions

-In Section 2.6 the distribution of electrons among conduction and valence bands in a semiconductor was considered *briefly*.

- We used the tight-binding approach to follow the banding of atomic states as the atoms were brought together to form a crystal. From the known electronic configuration of the atoms, the total number of electrons available to occupy the energy bands of the crystal was obtained.

- ***Qualitatively***, we found that all of these available electrons were used to form the bonds of the crystal at 0 K, so that, in the band picture, the valence bands were completely full and the conduction bands were completely empty.

- When we abandon the concept of a *perfect* crystal and introduce ***imperfections*** in a crystal, such as impurities and lattice vibrations, the distribution of electrons among available states has to be considered in more detail. This is the purpose of the present chapter.

Contents

Equilibrium Distributions

Statistics

- Let us consider the number of electronic energy levels and states in a band. For a crystal with ***N*** primitive unit cells there are ***N*** energy levels per energy band.
- In the *general* case of a semiconductor with donors and acceptors and their associated energy bands ,

$$W = \frac{g_d^{N_d^0} N_d!}{N_d^0!\,(N_d - N_d^0)!} \frac{g_a^{(N_a - N_a^-)} N_a!}{N_a^-!\,(N_a - N_a^-)!} \prod_k \frac{g_k!}{n_k!\,(g_k - n_k)!} \qquad (4.10)$$

- Equation (4.10) gives the total number of ways all of the donor, acceptor, and band states can be ***occupied by n' electrons***, assuming that each state has an equal probability of being occupied.
- From this we must now determine the ***most probable*** distribution of electrons among all the states.
- Constraints are given as below,

$$n' = N_d^0 + N_a^- + \sum_k n_k \qquad (4.17)$$

$$\mathscr{E}' = N_d^0 \mathscr{E}_d + N_a^- \mathscr{E}_a + \sum_k n_k \mathscr{E}_k \qquad (4.18)$$

where ***n'*** is the total number of electrons in the crystal and $\mathscr{E}'$ is the total internal electron energy.

Statistics – Variables

$$W = \frac{g_d^{N_d^0} N_d!}{N_d^0!\,(N_d - N_d^0)!} \frac{g_a^{(N_a - N_a^-)} N_a!}{N_a^-!\,(N_a - N_a^-)!} \prod_k \frac{g_k!}{n_k!\,(g_k - n_k)!} \qquad (4.10)$$

$$n' = N_d^0 + N_a^- + \sum_k n_k \qquad (4.17)$$

$$\mathscr{E}' = N_d^0 \mathscr{E}_d + N_a^- \mathscr{E}_a + \sum_k n_k \mathscr{E}_k \qquad (4.18)$$

- $\mathscr{E}_k$ **:** each of these energy levels can be uniquely indexed by the wavevector k when we use only values of **k** in the first Brillouin zone.

- $\boldsymbol{g}_k$: degeneracy or multiple states per energy level $\mathscr{E}_k$

- $\boldsymbol{n_k}$: number of ***occupied*** electrons in the $\boldsymbol{g}_k$ states. n_k is less than or equal to $\boldsymbol{g}_k$.

- For N_d (= $N^0{}_d$ + $N^+{}_d$) total donor atoms there are $2N_d$ states, including spin.

- For $N_a = N^0{}_a$ + $N^-{}_a$ total acceptor atoms there are $2N_a$ states, including spin.

Statistics

- We obtain the most probable distributions,

$$\frac{n_k}{g_k} = \frac{1}{1 + \exp\left[\beta(\mathscr{E}_k - \mathscr{E}_f)\right]} \tag{4.24}$$

$$\frac{N_d^0}{N_d} = \frac{1}{1 + \frac{1}{g_d}\exp\left[\beta(\mathscr{E}_d - \mathscr{E}_f)\right]} \tag{4.25}$$

$$\frac{N_a^-}{N_a} = \frac{1}{1 + g_a \exp\left[\beta(\mathscr{E}_a - \mathscr{E}_f)\right]} \tag{4.26}$$

respectively, where we have defined a ***Fermi energy*** as

$$\mathscr{E}_f \equiv \frac{-\alpha}{\beta} \tag{4.27}$$

- Equations (4.24), (4.25), and (4.26) are the ***Fermi-Dirac distribution functions*** for band, donor, and acceptor states, respectively. When the exponentials in the denominators of these equations are much greater than 1, the distribution of electrons can be approximated by the classical ***Maxwell Boltzmann*** functions.
- The ***undetermined*** multiplier $\mathscr{E}_f$ is evaluated from the ***constraint*** (4.17) that the total number of electrons in the system remain constant. Thus there is an ***intimate*** relationship between the Fermi energy and the number of electrons.

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Equilibrium Distributions

4.1 STATISTICS

4.2 **THERMODYNAMICS**

4.3 DENSITY OF STATES

4.4 ELECTRON AND HOLE DISTRIBUTIONS

4.5 IMPURITY AND DEFECT DISTRIBUTIONS

Thermodynamics

- The first and second laws of thermodynamics can be represented by Euler's equation,

$$\mathscr{E}' = TS - PV + \sum_i \mu_i n_i + \psi Q \qquad (4.28)$$

which relates the internal energy of a system, $\mathscr{E}'$, to the intensive variables of temperature (T) , pressure (P) , *chemical* potential (μ_i) , and internal *electrostatic* potential (ψ); and the extensive variables of entropy (S), volume (V), particle number (n_i), and total electric charge (Q).
-***Extensive*** variables are those which depend on concentration, while ***intensive*** variables are those which do not. Equation (4.28) can be taken as the basic law of thermodynamics. From it we can define the Helmholtz function,

$$F \equiv \mathscr{E}' - TS \qquad (4.29)$$

and the Gibbs function as

$$G \equiv \mathscr{E}' - TS + PV \qquad (4.30)$$

both of which have minimal properties .

- The ***Helmholtz function*** , F , is a ***minimum*** at thermal equilibrium for systems in which T, ***V***, n_i, and Q are constant.
- The ***Gibbs function*** , G, is a ***minimum*** at thermal equilibrium for systems in which T, ***P***, n_i , and Q are constant.

Thermodynamics

$$\left(\frac{\partial F}{\partial n'}\right)_{T,V} = \mathscr{E}_f \qquad (4.36)$$

the ***Fermi energy*** is the change in free energy of the crystal when an electron is added or taken away

- For our purposes (4.28) is $$\mathscr{E}' = TS - PV + \mu n' + \psi Q \qquad (4.37)$$

since we are considering *only* ***electrons***. In this case the total charge, Q, is equal to - qn'. Using this in (4.37) and (4.37) in (4.29), we have the Helmholtz function in the form

$$F = -PV + (\mu - q\psi)n' \qquad (4.38)$$

so that

$$\left(\frac{\partial F}{\partial n'}\right)_{T,V} = \mathscr{E}_f = (\mu - q\psi) \qquad (4.39)$$

- Thus, the ***Fermi energy*** is equal to the **sum** of the ***chemical potential*** and the internal ***electrostatic potential*** energy. Since the ***electrochemical*** potential for electrons is

$$\zeta \equiv \mu - q\psi \qquad (4.40)$$

we see that the ***Fermi energy*** in general is **equal** to the ***electrochemical potential***.

- For the energy band states (4.24), the ***equilibrium Fermi-Dirac*** distribution function has the form

$$f_0(\mathscr{E}, T) = \frac{1}{1 + \exp\left[(\mathscr{E} - \mathscr{E}_f)/kT\right]} \qquad (4.41)$$

Thermodynamics

- Equation (4.41) gives the ***probability*** that a band state of energy $\mathscr{E}$ is occupied by an electron at temperature *T*.
- We can see that ***at 0 K*** all states with energy below $\mathscr{E}_f$ are occupied while all states above $\mathscr{E}_f$ are empty (Fig. 4.2). For a state at 0 K with energy $\mathscr{E}_f$ the occupation probability is not defined and the derivative with respect to energy is a delta function.

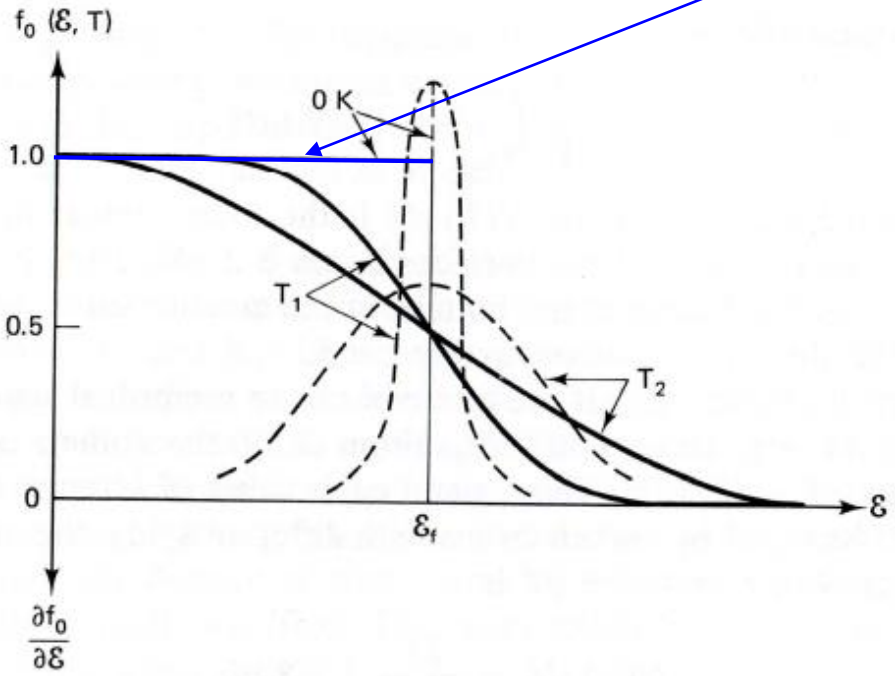

Figure 4.2 The equilibrium Fermi–Dirac distribution function and its energy derivative (dashed lines) for $0 < T_1 < T_2$. The derivative at 0 K is a delta function.

- For a state at ***finite*** temperatures with energy $\mathscr{E}_f$, the occupation probability is 0.5 and the derivative is finite . Equation (4.41) will be used to *determine* the occupancy of conduction bands with electrons.

- When the exponential factor is *sufficiently large*, the Fermi-Dirac distribution function can be approximated, in each case, by a classical ***Maxwell-Boltzmann*** distribution.

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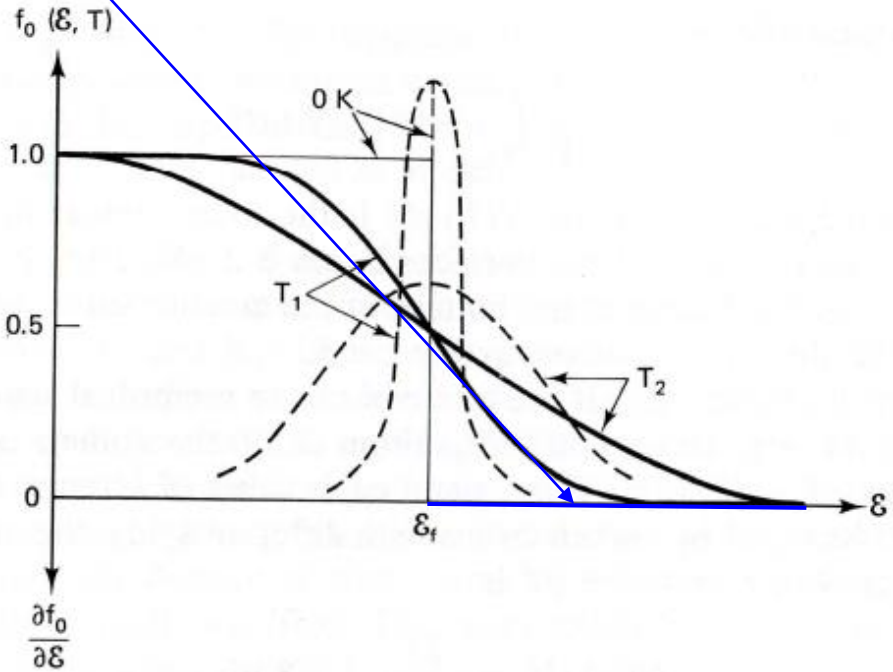

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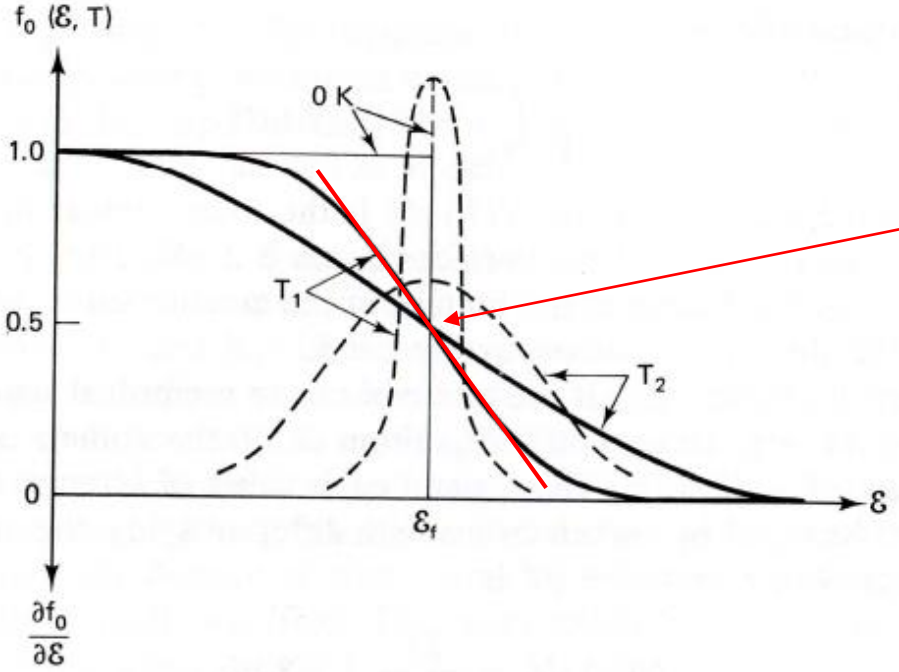

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Equilibrium Distributions

Density of States

the **density of states** (**DOS**) of a system describes the number of states per interval of energy at each energy level that are available to be occupied by electrons (Wikipedia)

- To determine the ***relationship*** between the total number of electrons in a band and the Fermi energy, we must first evaluate the density of states in the first Brillouin zone.
- From (4.24) and (4.41) the number of electrons in each state indexed by k is

$$n_k = g_k f_0(\mathscr{E}_k) \qquad (4.43)$$

- The total number of electrons, n' , is found by summing (4.43) over all $\boldsymbol{k}$. When g_k is *sufficiently large*, the summation can be replaced by an integral over all energies and

$$n' = \int_{-\infty}^{+\infty} g(\mathscr{E}) f_0(\mathscr{E})\, d\mathscr{E} \qquad (4.44)$$

The factor $g(\mathscr{E})$ contains the spin degeneracy and the total density of energy levels in the crystal. The ***concentration*** of electrons in the conduction band can be calculated from

$$n = \frac{1}{V} \int_{\mathscr{E}_C}^{\mathscr{E}_T} N(\mathscr{E}) f_0(\mathscr{E})\, d\mathscr{E} \qquad (4.45)$$

where V is the crystal volume, $N(\mathscr{E})\, d\mathscr{E}$ is the total number of states that lie between the constant energy surfaces $\mathscr{E}$ and $\mathscr{E} + d\mathscr{E}$, $N(\mathscr{E})$ is the density of states , $\mathscr{E}_C$ is the energy at the bottom of the conduction band, and $\mathscr{E}_T$ is the energy at the top of the conduction band.

Density of States

- Figure 4.3 indicates that the total volume in reciprocal space between $\mathscr{E}$ and $\mathscr{E} + d\mathscr{E}$ is given by $\int_s dS\, dk_n$. From (2 .29) the volume occupied by each value of k is $(2\pi)^3/V$. Thus, since each value of k represents a state that can be occupied by two electrons with different spins, the *total* number of states between $\mathscr{E}$ and $\mathscr{E} + d\mathscr{E}$ *is*

$$N(\mathscr{E})\, d\mathscr{E} = \frac{2V}{(2\pi)^3} \int_s dS\, dk_n \qquad (4.46)$$

where dk_n is the component of $d\mathbf{k}$ normal to the constant-energy surfaces and dS is the differential surface area for the constant -energy surface, ***S***.

The total derivative of energy is

$$d\mathscr{E} = \nabla_k \mathscr{E} \cdot d\mathbf{k} = |\nabla_k \mathscr{E}|\, dk_n \qquad (4.47)$$

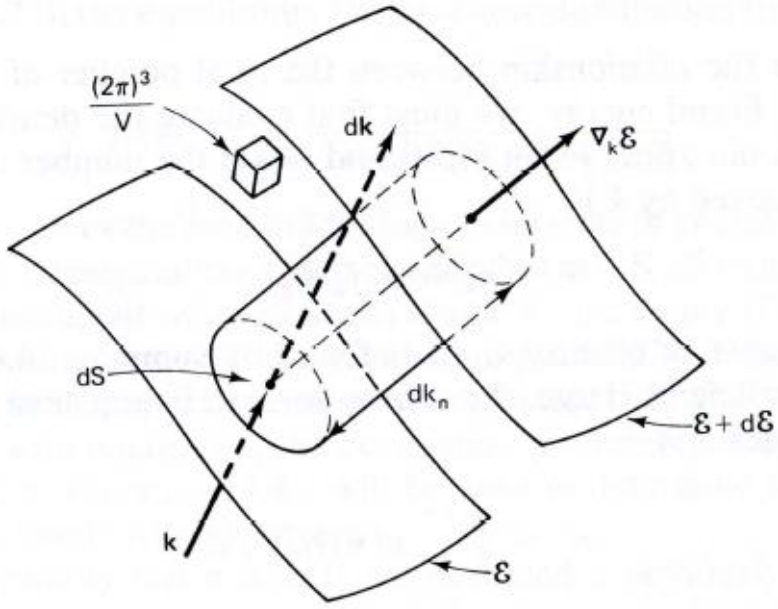


Figure 4.3 Diagram of the vectors and differential volume used to determine the density of states in the first Brillouin zone.

Density of States

- Using (4.47) in (4.46), the density of states is

$$N(\mathscr{E}) = \frac{2V}{(2\pi)^3} \int_s \frac{dS}{|\nabla_k \mathscr{E}|} \qquad (4.48)$$

-This equation can be used to determine the density of states for an energy band with any *general* dispersion relationship , including a nonquadratic one.
- We note in passing that the integrand in (4.48) diverges when $\nabla_k \mathscr{E} = 0$.
Although the resulting density of states remains *finite* at these points, discontinuities in the slope of $N(\mathscr{E})$ versus $\mathscr{E}$ are produced. These commonly occur at band extrema, as well as at other points, and are referred to as van Hove singularities.

- Let us determine the density of states for ***ellipsoidal*** energy band extrema with a *quadratic* dispersion relationship as given by (2.123) . For (2 .123) the coordinate system has been rotated to diagonalize the effective mass tensor.

$$\Delta\mathscr{E} = \frac{\hbar^2(\Delta k)^2}{2m^*} \simeq kT \qquad (2.123)$$

- In general, these extrema can occur at any point $\mathbf{k}_0$ in the first Brillouin zone, and there will be equivalent conduction band minima at each equivalent point $\mathbf{k}_0$ in the first Brillouin zone ..
- To simplify the mathematics, consider just one of the equivalent minima and translate coordinates so that $\mathbf{k}_0 = \mathbf{0}$.

Density of States

- Since the density of states must be ***independent*** of the coordinate system, this is easily justified. The relationship between $\mathscr{E}$ and **k** for the minimum at the origin is then

$$\mathscr{E} - \mathscr{E}_0 = \pm \frac{\hbar^2}{2} \sum_i \frac{\mathbf{k}_i^2}{m_i^*} \tag{4.49}$$

where the + and - refer to conduction band and valence band extrema, respectively. Equation (4.49) can be put in the form

$$\sum_i \left(\frac{k_i}{a_i}\right)^2 = 1, \qquad i = 1, 2, 3 \tag{4.50}$$

where the axes of the ellipsoid are

$$a_i = \left(\frac{2m_i^* \mid \mathscr{E} - \mathscr{E}_0 \mid}{\hbar^2}\right)^{1/2} \tag{4.51}$$

Since the volume of an ellipsoid with axes a_i is

$$\frac{4}{3}\pi \prod_i a_i = \frac{4\pi}{3\hbar^3} (8m_1^* m_2^* m_3^*)^{1/2} \mid \mathscr{E} - \mathscr{E}_0 \mid^{3/2} \tag{4.52}$$

the differential volume between the constant energy surfaces $\mathscr{E}$ and $\mathscr{E} + d\mathscr{E}$ is

$$\frac{2\pi}{\hbar^3} (8m_1^* m_2^* m_3^*)^{1/2} \mid \mathscr{E} - \mathscr{E}_0 \mid^{1/2} d\mathscr{E} \tag{4.53}$$

Density of States

- Dividing (4.53) by $(2\pi)^3/V$, the volume occupied by each energy level indexed by **k**, and multiplying by 2 because each energy level can be occupied by *two* electrons of opposite spin and thus actually represents *two* electron states, the density of states for electrons is

$$N(\mathscr{E}) = \frac{4\pi V}{h^3}(8m_1^* m_2^* m_3^*)^{1/2} \mid \mathscr{E} - \mathscr{E}_0 \mid^{1/2} \qquad (4.54)$$

where identity $h = \hbar 2\pi$ has been used. Equation (4.54) gives the density of states for any ***single*** energy band extremum which can be represented by a *quadratic* dispersion relationship.

- The density of states of a band with ***multiple*** equivalent minima can be expressed in the same form as

$$N(\mathscr{E}) = \frac{4\pi V}{h^3}(2m_d)^{3/2} \mid \mathscr{E} - \mathscr{E}_0 \mid^{1/2} \qquad (4.55)$$

where

$$m_d \equiv g^{2/3}(m_1^* m_2^* m_3^*)^{1/3} = (g^2 m_1^* m_2^* m_3^*)^{1/3} \qquad (4.56)$$

is the density-of-states effective mass.

- For band extrema with cylindrical symmetry,

$$m_d = (g^2 m_l m_t^2)^{1/3} \qquad (4.57)$$

where m_l and m_t are the effective masses longitudinal and transverse to the principal axis of revolution.

Density of States

- For a *single* extremum with *spherical* symmetry,

$$m_d = m^* \qquad (4.58)$$

and the density-of-states effective mass is just the electron effective mass.

For Impurities

- The density of states for localized levels in the energy gap between bands can also be easily determined.
- If we consider the ground states of hydrogenic impurities, the total number including spin is $2N_i$. However, both spin states cannot be occupied at the same time so the effective number of states is N_i. When the states are *discrete*, the ***density*** of states at $\mathscr{E}_i$ is ***infinite***. The integral over all possible states, however, must be N_i .
- Therefore, the density of states can be represented as

$$N_i(\mathscr{E}) = N_i\delta(\mathscr{E} - \mathscr{E}_i) \qquad (4.62)$$

where $\delta(\mathscr{E} - \mathscr{E}_i)$ is the Dirac ***delta*** function.

Density of States – 3D → 0D

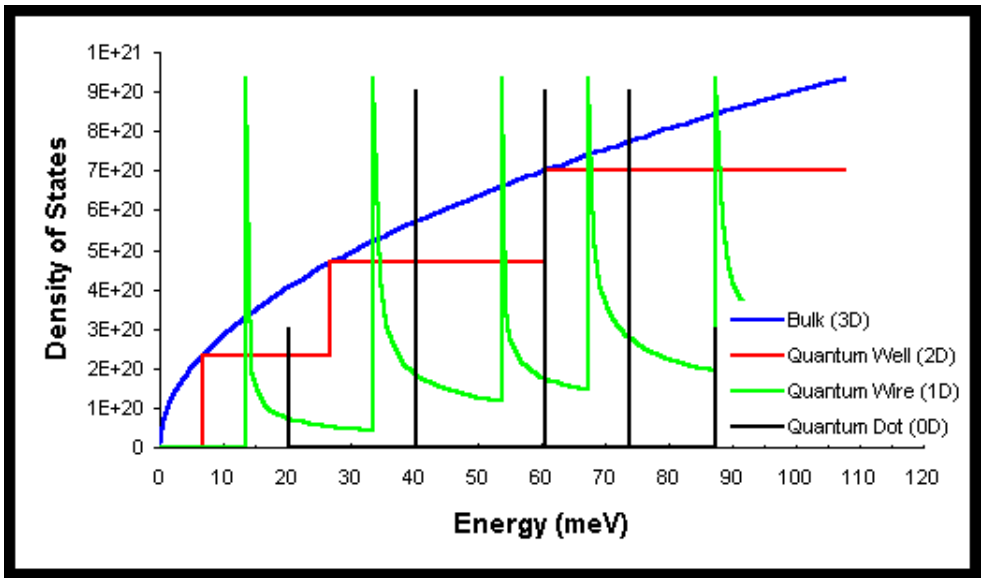
Density of States in *n*-Dimension

3D: $$g(E)_{3D}\,\mathrm{d}E = \frac{k^2\,\mathrm{d}k}{\pi^2} = \frac{2mE}{\pi^2\hbar^2}\cdot\left(\frac{2mE}{\hbar^2}\right)^{-1/2}\frac{m}{\hbar^2}\,\mathrm{d}E = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{1/2}\,\mathrm{d}E$$

2D: $$g(E)_{2D}\,\mathrm{d}E = \frac{m}{\pi\hbar^2}\sum_i H(E-E_i)\,\mathrm{d}E$$

1D: $$g(E)_{1D}\,\mathrm{d}E = \frac{1}{\pi}\left(\frac{2m}{\hbar^2}\right)^{1/2}\sum_i\left(\frac{n_i H(E-E_i)}{(E-E_i)^{1/2}}\right)\mathrm{d}E$$

0D: $$g(E)_{0D} = 2\delta(E-E_c)$$



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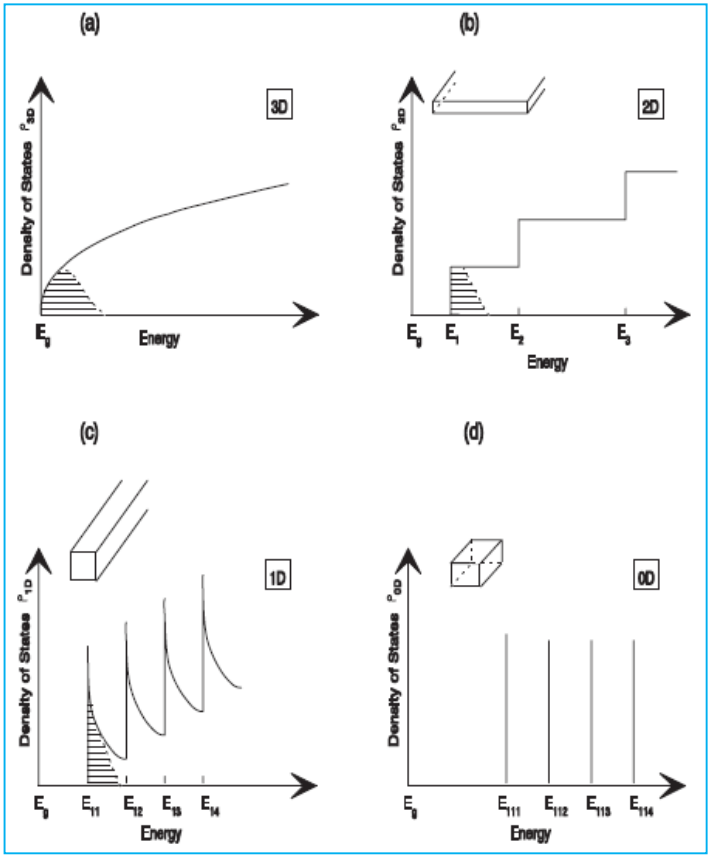

http://www.pi4.uni-stuttgart.de/NeueSeite/Lehre/FKPh2007/files/density_of_states.pdf

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Equilibrium Distributions

Effective Density of States

- Having determined the density of states in various situations, we are now in a position to examine the distribution of the total number of electrons, n' , among the different bands and levels. Let us first look at the concentration of ***electrons*** in the lowest-lying ***conduction bands***. From (4.45) the concentration or number of electrons per unit volume in these conduction band minima is

$$n = \frac{1}{V}\int_{\mathscr{E}_c}^{\mathscr{E}_t} f_0(\mathscr{E})N_c(\mathscr{E})\,d\mathscr{E} \qquad (4.63)$$

where $\mathscr{E}_t$ is the energy at the top of the bands. From Fig. 4.2 we see that $f_o(\mathscr{E})$ approaches zero at high energies, so that we can, to a good approximation, replace $\mathscr{E}_t$ with ∞ in (4.63). Using (4.41) for $f_o(\mathscr{E})$ and (4.55) for $N_c(\mathscr{E})$, we have

$$n = 4\pi\left(\frac{2m_{de}}{h^2}\right)^{3/2}\int_{\mathscr{E}_c}^{\infty}\frac{(\mathscr{E}-\mathscr{E}_c)^{1/2}\,d\mathscr{E}}{1+\exp\left[(\mathscr{E}-\mathscr{E}_f)/kT\right]} \qquad (4.64)$$

$N_c(\mathscr{E})$

$f_o(\mathscr{E})$

for ellipsoidal minima. When we introduce the dimensionless variables,

$$x = \frac{\mathscr{E}-\mathscr{E}_c}{kT} \quad \text{and} \quad \eta = \frac{\mathscr{E}_f-\mathscr{E}_c}{kT} \qquad (4.65)$$

(4 .64) becomes

$$n = 4\pi\left(\frac{2kTm_{de}}{h^2}\right)^{3/2}\int_0^{\infty}\frac{x^{1/2}\,dx}{1+\exp(x-\eta)} \qquad (4.66)$$

Effective Density of States

- The Fermi-Dirac integral of order $\frac{1}{2}$ is defined as

$$F_{1/2}(\eta) \equiv \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}\, dx}{1 + \exp(x - \eta)} \qquad (4.67)$$

With this expression the electron **concentration** in the ***conduction band minima*** is

$$n = 2\left(\frac{2\pi k T m_{de}}{h^2}\right)^{3/2} F_{1/2}(\eta) \qquad (4.68)$$

Values for $F_{1/2}(\eta)$ are tabulated in Appendix B.

- **When $\mathscr{E}_f$ is less than about $\mathscr{E}_c$ - 4*k*T**, the Fermi-Dirac distribution can be ***approximated*** by the **Maxwell-Boltzmann** distribution. In this case (4 .66) becomes

$$n = 4\pi\left(\frac{2kTm_{de}}{h^2}\right)^{3/2} \exp(\eta) \int_0^\infty \exp(-x) x^{1/2}\, dx \qquad (4.69)$$

But

$$\int_0^\infty \exp(-x) x^{1/2}\, dx = \frac{\sqrt{\pi}}{2} \qquad (4.70)$$

and (4.69) is therefore

$$n = 2\left(\frac{2\pi k T m_{de}}{h^2}\right)^{3/2} \exp\left(\frac{\mathscr{E}_f - \mathscr{E}_c}{kT}\right) \qquad (4.71)$$

Effective Density of States

- Notice that the pre-exponential factor in (4.71) is the same as in the more general case of (4.68). This factor,

$$N_c = 2\left(\frac{2\pi kTm_{de}}{h^2}\right)^{3/2} \qquad (4.72)$$

is referred to as the ***effective*** conduction band density of states. This terminology reflects the fact that, in this classical approximation, the conduction band can be regarded as a ***single*** level with degeneracy N_c at the energy level $\mathscr{E}_c$.

- Using N_c from (4.72), (4.71) has the simple form

$$n = N_c \exp\left(\frac{\mathscr{E}_f - \mathscr{E}_c}{kT}\right) \qquad (4.73)$$

where ($\mathscr{E}_f$ - $\mathscr{E}_c$)/kT is negative.

- A similar approach can be taken for the concentration of ***holes*** in the highest-lying valence bands. The hole concentration is given by

$$p = N_v \exp\left(\frac{\mathscr{E}_v - \mathscr{E}_f}{kT}\right) \qquad (4.79)$$

Effective Density of States

- The ***effective*** valence band density of states is

$$N_v = 2\left(\frac{2\pi kTm_{dh}}{h^2}\right)^{3/2} \qquad (4.80)$$

- Let us determine the value of the Fermi energy in the situation where the number of electrons in the conduction band is **equal** to the number of holes in the valence band. Since this equality would apply ① when there were no impurity or defect levels in the energy gap or ② when thermal excitation would produce a much larger number of electrons and holes than the impurities, it is called the ***intrinsic*** case. Here we have

$$n = p = n_i \qquad (4.81)$$

where n_i is the intrinsic carrier concentration. From the classical approximation (4.73) and (4 .79),

$$\mathscr{E}_f = \frac{\mathscr{E}_c + \mathscr{E}_v}{2} + \frac{kT}{2}\ln\frac{N_v}{N_c} \qquad (4.82)$$

Equation (4.82) indicates that in the intrinsic case and at finite temperatures, the Fermi level is displaced from the center of the energy gap, toward the conduction band if N_v is greater than N_c, or toward the valence band if N_c is greater than N_v .

Effective Density of States

- The ***effective*** valence band density of states is

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