

# Chapter 2

## The Fermi Method

### 2.1 Statistical Mechanics

At finite temperatures there are thermal excitations of the electronic system, i.e., in thermodynamic equilibrium not only the ground state ( $E_0^e, \Phi_0(\{\mathbf{r}_{k\sigma}\})$ ) of  $H^e$  is present, but also excited states. Thus, due to thermal fluctuations all states ( $E_\nu^e, \Phi_\nu$ ) are realized with a certain probability. Assuming that the number of particles and the temperature are determined by external conditions, we have a *canonical ensemble* and the probability  $P(E_\nu^e, T)$  for the occupation of state ( $E_\nu^e, \Phi_\nu$ ) is proportional to  $\exp(-E_\nu^e/k_B T)$ . Here  $k_B$  is the Boltzmann constant. The ensemble is described by the density operator

$$\rho = \sum_\nu P(E_\nu^e, T) |\Phi_\nu\rangle \langle \Phi_\nu| \quad . \quad (2.1)$$

Of course the ensemble of all states has to be normalized to 1 and therefore we have

$$\sum_\nu P(E_\nu^e, T) = 1 = \frac{1}{Z^e} \sum_\nu \exp(-E_\nu^e/k_B T) \quad . \quad (2.2)$$

One obtains

$$Z^e = \sum_\nu \exp(-E_\nu^e/k_B T) = \text{Tr}(\exp(-H^e/k_B T)) \quad . \quad (2.3)$$

$Z^e$  is the partition function of the electrons and is related to the Helmholtz free energy:

$$-k_B T \ln Z^e = F^e = U^e - TS^e \quad , \quad (2.4)$$

where  $U^e$  and  $S^e$  are the internal energy and the entropy of the electronic systems, i.e. of the electron-hole excitations. Below at Eq. (2.6) we will come back to this point. Consequently, the probability of a thermal occupation of a certain state ( $E_\nu, \Phi_\nu$ ) is

$$P(E_\nu^e, T) = \frac{1}{Z^e} \exp(-E_\nu^e/k_B T) = \exp[-(E_\nu^e - F^e)/k_B T] \quad . \quad (2.5)$$

At finite temperature we therefore need the full energy spectrum of the many-body Hamilton operator. Then we can calculate the partition function (Eq. (2.3)) and the free energy (Eq. (2.4)). Let us now discuss briefly, how the internal energy and the entropy can be determined separately<sup>1</sup>: The internal energy is what up to now we have called total energy at finite temperature:

$$U^e(T) = \sum_\nu E_\nu^e(T) P(E_\nu^e, T) \quad . \quad (2.6)$$

In the general case, i.e., when also atomic vibrations are excited, we have  $U = U^e + U^{\text{vib}}$ , not just  $U^e$ .

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<sup>1</sup>cf. e.g. N.D. Mermin, Phys. Rev. **137**, A 1441 (1969); M. Weinert and J.W. Davenport, Phys. Rev. B **45**, 13709 (1992); M.G. Gillan, J. Phys. Condens. Matter **1** 689 (1989); J. Neugebauer and M. Scheffler, Phys. Rev. B **46**, 16067 (1992); F. Wagner, T. Laloyaux, and M. Scheffler, Phys. Rev. B **57**, 2102 (1998).

From the laws of thermodynamics  $[(\partial u/\partial T)_V = T(\partial s/\partial T)_V]$  and from the third law of thermodynamics ( $s \rightarrow 0$  if  $T \rightarrow 0$ ) we obtain

$$s^e = \frac{S^e}{V} = -k_B \sum_i \left[ f(\epsilon_i, T) \ln f(\epsilon_i, T) + (1 - f(\epsilon_i, T)) \ln (1 - f(\epsilon_i, T)) \right] . \quad (2.7)$$

Here we used the energy and entropy per unit volume ( $u = U/V, s = S/V$ ), and  $f(\epsilon_i, T)$  is the Fermi function (see below). The derivation is particularly simple, if one assumes that we are dealing with independent particles (Eq. (2.11), (2.12), below).

From Eq. (2.4) or (2.7) we obtain the specific heat

$$c_v = \frac{1}{V} \left( \frac{\partial U}{\partial T} \right)_V \quad (2.8)$$

$$= \frac{T}{V} \left( \frac{\partial S}{\partial T} \right)_V . \quad (2.9)$$

Here we removed the superscript  $e$  and in fact mean  $U = U^e + U^{\text{vib}}$  and  $S = S^e + S^{\text{vib}}$ . The calculation of  $c_v$  of metals is an important example of the importance of Fermi-Dirac statistics of the electrons (cf. Ashcroft-Mermin p. 43, 47, 54).

## 2.2 Fermi Statistics of the Electrons

Let us assume that the  $N$  electrons of our many-body problem occupy single particle levels. Then we also know that due to the Pauli principle each single particle level can be occupied with two electrons at most (one electron with spin up and one electron with spin down). With this assumption it follows (for  $T = 0$  K) that the  $N$  lowest energy levels  $\epsilon_i$  are occupied:

$$E^e(T = 0K) = E_0^e = \sum_{i=1}^N \epsilon_i + \Delta , \quad (2.10)$$

where  $\Delta$  is a correction describing the electron-electron interaction. For independent particles  $\Delta$  is zero, but for the many-body problem it is very important (see Chapter 3).

The  $\epsilon_i$  then are eigenvalues of an *effective* single-particle Hamiltonian

$$h = \frac{-\hbar^2}{2m} \nabla^2 + V^{\text{eff}}(\mathbf{r}) .$$

Employing the above description in terms of the density matrix (cf. Marder, Chapter 6.4 and Landau-Lifshitz, Vol. IV) to a situation of independent particles gives for finite temperature the lowest energy that is compatible with the Pauli principle as

$$E^e(T) = \sum_{i=1}^{\infty} \epsilon_i f(\epsilon_i, T) + \Delta . \quad (2.11)$$

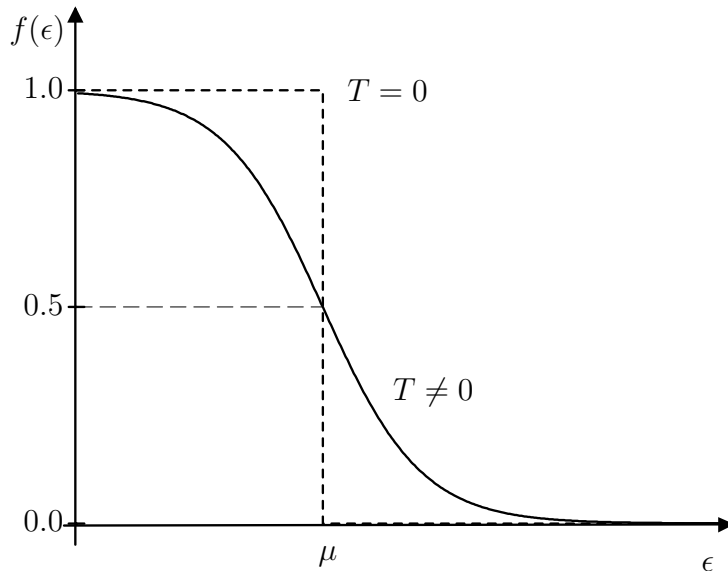


Figure 2.1: The Fermi distribution function [Equation (2.12)].

The index  $i$  is running over all single particle states.

The occupation probability (cf. e.g. Ashcroft-Mermin, Eq. (2.41) - (2.49) or Marder, Chapter 6.4) of the  $i$ th single particle level  $\epsilon_i$  is given by the Fermi function:

$$f(\epsilon, T) = \frac{1}{\exp[(\epsilon - \mu)/k_B T] + 1} \quad . \quad (2.12)$$

Here  $k_B$  is the Boltzmann constant and  $\mu$  is the chemical potential of the electrons, i.e., the lowest energy, which is required to remove a particle from the system:

$$-\mu = E^e(N - 1) - E^e(N) \quad . \quad (2.13)$$

How are  $\mu$  and its temperature dependence determined? The number of electrons is  $N$ , and it is independent of the temperature. Therefore, we have

$$N = \sum_{i=1}^{\infty} f(\epsilon_i, T; \mu) \quad . \quad (2.14)$$

For a given temperature this equation contains only one unknown quantity, the chemical potential  $\mu$ . If all  $\epsilon_i$  are known,  $\mu(T)$  can be calculated.

## 2.3 Some Definitions

We will now introduce some definitions and constrain ourselves to a so-called “jellium” system. The most simple way (i.e., the crudest approximation to the atomic structure) to investigate the Schrödinger equation of the Hamilton operator

$$H^e = T^e + V^{e-\text{Ion}} + V^{e-e} \quad (2.15)$$

is obtained when setting  $V^{e-\text{Ion}} + V^{e-e}$  as a constant function of the electron coordinates. We note that this crude approximation provides reasonable and helpful results for some problems. A system with  $V^{e-\text{Ion}} = \text{constant}$  is called “jellium”, and if  $V^{e-\text{Ion}}$  as a function of the electronic coordinates is constant, then it can easily be shown that also  $V^{e-e}$  is constant<sup>2</sup> We like to consider here a system without spin-orbit interaction. Thus spin and position coordinates can be separated.

$$\Phi(\{\mathbf{r}_k \sigma_k\}) = \Phi(\{\mathbf{r}_k\})\chi(\{\sigma_k\}) \quad . \quad (2.16)$$

Without introducing a new approximation the zero point of the energy is chosen in a way that the constant potential  $V^{e-\text{Ion}} + V^{e-e}$  vanishes. Then the Hamilton operator of the electrons has the simple form

$$H^e = T^e = \sum_{k=1}^N -\frac{\hbar^2}{2m} \nabla_{\mathbf{r}_k}^2 \quad , \quad (2.17)$$

and the many-body Schrödinger equation decomposes into a number of  $N$  single particle equations

$$-\frac{\hbar^2}{2m} \nabla^2 \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r}) \quad . \quad (2.18)$$

The solutions of Eq. (2.17) are plane waves

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \quad , \quad (2.19)$$

and the energy eigenvalues are

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad , \quad (2.20)$$

where the vectors  $\mathbf{k}$  and the components  $k_x, k_y, k_z$  have to be interpreted as quantum numbers, up to now noted as index  $j$  in  $(\epsilon_j, \varphi_j)$ : the state of an electron of the Hamilton operator (2.17) is labeled by the quantum number  $\mathbf{k}$  and the spin  $s$ . The wave length

$$\lambda = 2\pi/k \quad (2.21)$$

is called de Broglie wave length.

The wave functions in Eq. (2.19) are not normalized (or they are normalized with respect to  $\delta$  functions). In order to obtain a simpler mathematical discussion often it is useful, or helpful, to constrain the electrons to a finite volume. This volume is called the *base region*,  $V_g$ , and it shall be large enough to obtain results independent of its size.<sup>3</sup> The base region  $V_g$  shall contain  $N$  electrons and  $M$  atoms. The shape of the base region in principle is meaningless. For simplicity here we chose a box of the dimensions  $L_x, L_y, L_z$  (cf. Ashcroft,

<sup>2</sup>For systems with very low densities, however, electrons will localize themselves at  $T = 0\text{K}$  due to the Coulomb repulsion. This is called Wigner crystallization and was predicted in 1930.

<sup>3</sup>For external magnetic fields the introduction of a base region can give rise to difficulties, because then physical effects often depend significantly on the border.

Mermin: Exercise for more complex shapes). For the wave function we could chose an almost arbitrary constraint (because  $V_g$  shall be large enough). It is advantageous to use periodic boundary conditions

$$\varphi(\mathbf{r}) = \varphi(\mathbf{r} + L_x \mathbf{e}_x) = \varphi(\mathbf{r} + L_y \mathbf{e}_y) = \varphi(\mathbf{r} + L_z \mathbf{e}_z) \quad . \quad (2.22)$$

Here  $\mathbf{e}_x$ ,  $\mathbf{e}_y$ ,  $\mathbf{e}_z$  are the unit vectors in the three Cartesian directions. This is also called the Born-von Karman boundary condition.

As long as  $V_g$ , or  $L_x \times L_y \times L_z$  is large enough, all physical results do not depend on this treatment. Sometimes also anti-cyclic boundary conditions are chosen in order to check the independence of the results of the choice of the base region.

Using Eq. (2.22) and the normalization condition

$$\int_{V_g} \varphi_{\mathbf{k}}^*(\mathbf{r}) \varphi_{\mathbf{k}'}(\mathbf{r}) d^3 \mathbf{r} = \delta_{\mathbf{k}, \mathbf{k}'} \quad (2.23)$$

we obtain

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_g}} e^{i\mathbf{k}\mathbf{r}} \quad . \quad (2.24)$$

Because of Eq. (2.22), i.e., because of the periodicity, only discrete values are allowed for the quantum numbers  $\mathbf{k}$ , i.e.,  $\mathbf{k} \cdot L_i \mathbf{e}_i = 2\pi n_i$  and therefore

$$\mathbf{k} = \left( \frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right) \quad , \quad (2.25)$$

with  $n_i$  being arbitrary integer numbers. Thus, the number of vectors  $\mathbf{k}$  is countable and finite. Each  $\mathbf{k}$  point therefore has the volume

$$\frac{(2\pi)^3}{V_g} \quad (2.26)$$

in  $k$ -space.

Each state  $\varphi_{\mathbf{k}}(\mathbf{r})$  can be occupied by two electrons. In the ground state at  $T = 0$  K the  $N/2$   $\mathbf{k}$  points of lowest energy are occupied by two electrons each. Because  $\epsilon$  depends only on the absolute value of  $\mathbf{k}$ , these points fill (for non-interacting electrons) a sphere in  $\mathbf{k}$ -space of radius  $k_F$  (the ‘‘Fermi sphere’’). We have

$$N = 2 \frac{4}{3} \pi k_F^3 \frac{V_g}{(2\pi)^3} = \frac{1}{3\pi^2} k_F^3 V_g \quad . \quad (2.27)$$

Here the spin of the electron (factor 2) has been taken into account, and  $V_g/(2\pi)^3$  is the density of the  $\mathbf{k}$ -points (cf. Eq. (2.26)). The particle density of the electrons in jellium is constant:

$$n(\mathbf{r}) = n = \frac{N}{V_g} = \frac{1}{3\pi^2} k_F^3 \quad , \quad (2.28)$$

and the charge density of the electrons is  $-en$ , and  $k_F = \sqrt[3]{3\pi^2 n}$ .

For the single particle of the highest energy (in the ground state at  $T = 0$  K) we get

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad . \quad (2.29)$$

Often for jellium-like systems the electron density is given by the *density parameter*  $r_s$ . This is defined by a sphere  $\frac{4\pi}{3} r_s^3$ , which contains exactly one electron. One obtains

$$\frac{4\pi}{3} r_s^3 = V_g/N = 1/n \quad . \quad (2.30)$$

The density parameter  $r_s$  is typically given in bohr units.

For metals  $r_s$  is typically around 2 bohr (remember: this only refers to the valence electrons), and therefore  $k_F$  is approximately 1 bohr $^{-1}$ , or 2 Å $^{-1}$ , respectively.

Later, we will often apply Eq. (2.29) and (2.30) because some formulas can be presented and interpreted more easily, if  $\epsilon_F$ ,  $k_F$  and  $n(\mathbf{r})$  are expressed in this way.

Now we introduce the (electronic) density of states:

$$N(\epsilon)d\epsilon = \text{number of states in the energy interval } [\epsilon, \epsilon + d\epsilon] \quad .$$

For the total number of electrons in the base region we have:

$$N = \int_{-\infty}^{+\infty} N(\epsilon) f(\epsilon, T) d\epsilon \quad . \quad (2.31)$$

For free electrons (jellium) we have for the density of states:

$$\begin{aligned} N(\epsilon) &= 2 \frac{V_g}{(2\pi)^3} \int d^3\mathbf{k} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{2V_g 4\pi}{(2\pi)^3} \int k^2 dk \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{V_g}{\pi^2} \int \frac{d\epsilon_{\mathbf{k}}}{|\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}|} \frac{2m\epsilon_{\mathbf{k}}}{\hbar^2} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{V_g}{\pi^2} \int d\epsilon_{\mathbf{k}} \frac{\sqrt{m}}{\hbar\sqrt{2\epsilon_{\mathbf{k}}}} \frac{2m\epsilon_{\mathbf{k}}}{\hbar^2} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{mV_g}{\pi^2 \hbar^3} \sqrt{2m\epsilon} \quad . \end{aligned} \quad (2.32)$$

For  $\epsilon < 0$  we have  $N(\epsilon) = 0$ . The density of states for two- and one dimensional systems is discussed in the exercises (cf. also Marder).

Figure 2.2 shows the density of states and the occupation at  $T = 0$  K and at finite temperature. The density of states at the Fermi level is

$$\frac{N(\epsilon_F)}{V_g} = \frac{3}{2} \frac{N}{V_g} \frac{1}{\epsilon_F} = \frac{m}{\hbar^2 \pi^2} k_F \quad (2.33)$$

The figure shows that at finite temperature holes below  $\mu$  and electrons above  $\mu$  are generated.

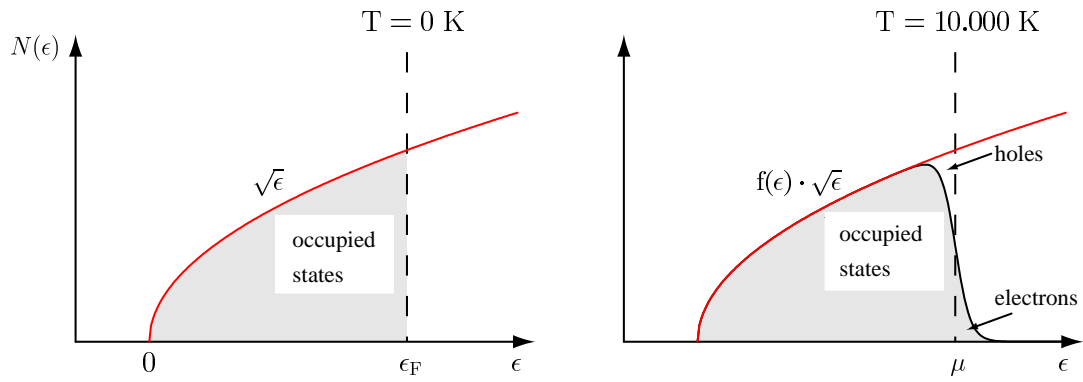


Figure 2.2: Density of states of free electrons  $\sqrt{\epsilon}f(\epsilon, T)$  and the separation in occupied and unoccupied states for two temperatures.