

2 Some Definitions and Reminders, incl. Fermi Statistics of Electrons

2.1 Statistical Mechanics

We had introduced the Hamiltonian of the electrons H^e in Eqs. (1.11) and (1.12). We now like to elaborate on the physical (thermodynamic) meaning of its eigenvalues. At finite temperatures a solid is not just in its electronic ground state $(E_0^e, \Phi_0(\{\mathbf{r}_{k\sigma}\}))$, but higher-energy states $(E_\nu^e, \Phi_\nu(\{\mathbf{r}_{k\sigma}\}))_{\nu \neq 0}$ are thermally excited with a certain probability. In principle, there are also vibrations of the nuclei above the zero-point level, but those we will consider later [see the discussion of Eq. (2.6) below]. For the moment, we solely focus on electronic electron-hole excitations. Assuming that the volume, the number of particles in this volume, and the temperature are fixed, we have a *canonical ensemble*, and the probability $P(E_\nu^e, T)$ for the occurrence of state $(E_\nu^e, \Phi_\nu(\{\mathbf{r}_{k\sigma}\}))$ is proportional to $\exp(-E_\nu^e/k_B T)$. Here, k_B is the Boltzmann constant and T the absolute temperature. 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. Therefore we have

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

This yields the partition function of the electrons Z^e :

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

Z^e is directly related to the Helmholtz free energy F^e :

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

where U^e and S^e are the internal energy and the entropy of the electronic system, respectively. Consequently, the probability of a thermal excitation of a certain state (E_ν, Φ_ν) is

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

At finite temperatures, we thus need to know the full energy spectrum of the many-body Hamilton operator, i.e., E_ν^e for all values of ν . Then we can calculate the partition function

and the free energy defined in Eqs. (2.3) and (2.4), respectively.

Let us now briefly discuss, how the internal energy and the entropy can be determined¹: The internal energy is what is often also called the “total energy at finite temperature”:

$$U^e(\{\mathbf{R}_I\}, T) = \sum_{\nu} E_{\nu}^e(\{\mathbf{R}_I\}, T) P(E_{\nu}^e, T) + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{\substack{I, J \\ I \neq J}}^{M, M} \frac{e^2}{|\mathbf{R}_I - \mathbf{R}_J|} Z_I Z_J \quad . \quad (2.6)$$

It is important to keep in mind that in the general case, i.e., when also atomic vibrations are excited, we have $U = U^e + U^{\text{vib}}$, not just U^e .

From Eq.(2.4) we obtain the specific heat

$$c_v = \frac{1}{V} \left(\frac{\partial U}{\partial T} \right)_V = \frac{T}{V} \left(\frac{\partial S}{\partial T} \right)_V \quad . \quad (2.7)$$

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 for metals (cf. Ashcroft-Mermin p. 43, 47, 54) is an instructive example for the importance of the Fermi statistics for electrons that will be introduced below.

2.2 Fermi Statistics of the Electrons

To inspect the statistical mechanics of electrons, we have to introduce some concepts that will be justified and discussed in a more formal way in Chap. 3. For the start, we note that the full many-problem for N electrons is given by Eqs. (1.11) and (1.12):

$$H^e(\{\mathbf{R}_I\}) \Phi_{\nu}(\{\mathbf{R}_I\}, \{\mathbf{r}_k \sigma_k\}) = E_{\nu}^e \Phi_{\nu} \quad \text{with} \quad H^e = T^e + V^{e-\text{Nuc}} + V^{e-e} \quad . \quad (2.8)$$

If the electron-electron interaction V^{e-e} is neglected by assuming $H^{\text{ind},e} = T^e + V^{e-\text{Nuc}}$, the problem separates and one gets N independent Hamiltonians h_j :

$$H^{\text{ind},e} = \sum_{j=1}^N h_j \quad \text{with} \quad h_j = -\frac{\hbar^2}{2m} \nabla_j^2 + V^{e-\text{Nuc}}(\mathbf{r}_j) \quad . \quad (2.9)$$

Since the Hamiltonians $h = h_j = h_i$ are identical for all electrons, it is sufficient to solve

$$h \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad (2.10)$$

once. Each of these single-particle levels can be occupied with two electrons at most (one electron with spin up and one electron with spin down) due to the Pauli principle. In the absence of thermal excitations, i. e., at $T = 0$ K, only the lowest N energy levels ϵ_i are

¹cf. 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).

occupied, so that the ground-state total energy (internal energy at 0K) of this electronic system is given by:

$$U^{e,\text{ind}}(T = 0\text{K}) = E_0^{e,\text{ind}} = \sum_{i=1}^N \epsilon_i \quad . \quad (2.11)$$

This *independent electron approximation* is very strong and thus not particularly useful by itself. However, it is very instructive: As will be discussed in Chap. 3, also the full many-body problem can be rewritten in terms of an *effective single-particle* Hamiltonian

$$h = \frac{-\hbar^2}{2m} \nabla^2 + V^{\text{eff}}(\mathbf{r}) \quad (2.12)$$

with *effective* “single-particle” levels² given by

$$h \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}) \quad . \quad (2.13)$$

Please note that in this formalism the electrons are only described by an *effective* single-particle Hamiltonian, but they are in fact not independent (see Chapter 3). As a consequence, the ground-state total energy (internal energy at 0K) is given by

$$U^e(T = 0\text{K}) = E_0^e = \sum_{i=1}^N \epsilon_i + \Delta \quad , \quad (2.14)$$

where Δ is a correction accounting for the electron-electron interaction. For independent particles Δ is zero, but for the true, fully interacting many-body problem it is very important (see Chapter 3).

We now apply the density matrix formalism introduced in the previous section to the electronic system described by Eq. (2.12), see for instance Marder, Chapter 6.4 or Landau-Lifshitz, Vol. IV. In this case, the lowest internal energy that is compatible with the Pauli principle at finite temperatures is given by

$$U^e(T) = \sum_{i=1}^{\infty} \epsilon_i f(\epsilon_i, T) + \Delta(T) + U^{\text{vib}}(T) \quad . \quad (2.15)$$

The index i is running over all single particle states and the occupation probability of the i th single particle level ϵ_i is given by the Fermi function (cf. e.g. Ashcroft-Mermin, Eq. (2.41) - (2.49) or Marder, Chapter 6.4, and the plot in Fig. 2.1):

$$f(\epsilon_i, T) = \frac{1}{\exp[(\epsilon_i - \mu)/k_B T] + 1} \quad . \quad (2.16)$$

Here, k_B is again the Boltzmann constant and μ is the chemical potential of the electrons, i.e., the lowest energy required to remove an electron from the system. At $T = 0\text{K}$ this is

$$-\mu = E_0^e(N - 1) - E_0^e(N) \quad . \quad (2.17)$$

At finite temperature this should be replaced by the difference of the corresponding free energies.

²The justification and meaning of the term “single-particle level” will be discussed in Chapter 3.

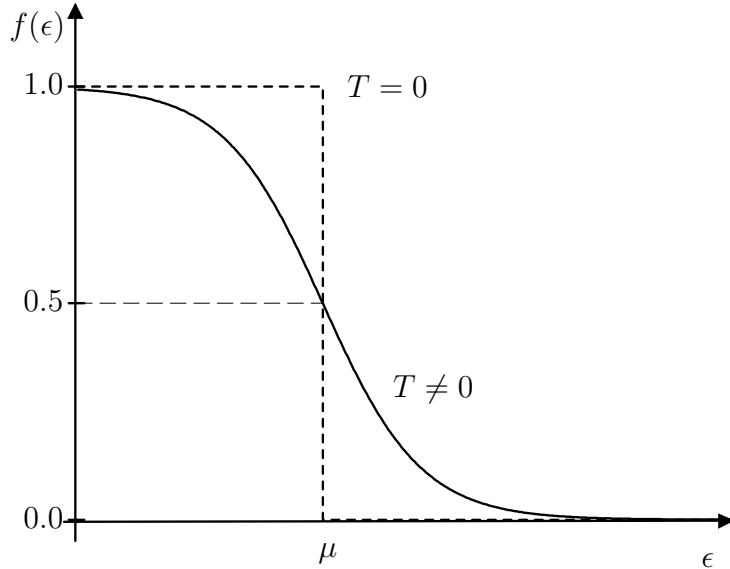


Figure 2.1: The Fermi-distribution function [Eq. (2.16)].

Obviously, the number of electrons N is independent of temperature. Therefore, we have

$$N = \sum_{i=1}^{\infty} f(\epsilon_i, T; \mu) \quad . \quad (2.18)$$

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

By introducing the energy and entropy per unit volume ($u = U/V$, $s = S/V$) and using the laws of thermodynamics [$(\partial u / \partial T)_V = T(\partial s / \partial T)_V$, and $s \rightarrow 0$ if $T \rightarrow 0$], we obtain

$$s^e = \frac{S^e}{V} = -k_B \sum_i \left[f(\epsilon_i, T) \ln f(\epsilon_i, T) + (1 - f(\epsilon_i, T)) \ln (1 - f(\epsilon_i, T)) \right] \quad . \quad (2.19)$$

The derivation of Eq. (2.19) is particularly simple if one is dealing with independent particles as described by Eq. (2.15) with $\Delta(T) = 0$.

2.3 Some Definitions

We will now introduce some definitions and constraints that are particularly useful in the description of solids. First, we like to consider a system without spin-orbit interaction. Thus spin and position coordinates separate:

$$\Phi(\{\mathbf{r}_k \sigma_k\}) = \Phi(\{\mathbf{r}_k\}) \cdot \chi(\{\sigma_k\}) \quad . \quad (2.20)$$

Second, we simplify the Hamiltonian H^e : One possibility consists in approximating the electron-nuclear interaction with a constant C^{jellium}

$$H^e = T^e + V^{e-\text{Nuc}} + V^{e-e} \approx T^e + C^{\text{jellium}} + V^{e-e} \quad . \quad (2.21)$$

In this so called “jellium” model, the potential of the nuclei is smeared out to a constant value. We note in passing that for different electron numbers N this constant is different and that at not too low electron densities, this is an exact description (see Sec. 3.8 for details).³

Since the “jellium” model defined in Eq. (2.21) is not tractable analytically, we switch to an ever cruder approximation, in which also the electron-electron interaction is neglected:

$$H^e \approx T^e + C^{\text{jellium}} \quad . \quad (2.22)$$

For $C^{\text{jellium}} = 0$, this is the *free electron* problem that will be analysed in detail below. At this stage, you might ask yourself why it is helpful to discuss such a harsh approximation at all. As already mentioned in the discussion of Eq. (2.12) and discussed in detail in Chap. 3, the full many-body Schrödinger equation can be addressed using Density-Functional Theory (see Sec. 3.8) via an *effective* single-particle equation

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V^{\text{eff}}(\mathbf{r}) \right) \varphi_j(\mathbf{r}) = \epsilon_j \varphi_j(\mathbf{r}) \quad . \quad (2.23)$$

In such a formalism, the “jellium” and the “free-electron” problem would just differ in the *effective* potential $V^{\text{eff}}(\mathbf{r})$: For the “free-electron” problem, $V^{\text{eff}}(\mathbf{r})$ is zero. For the “jellium” model in the limit of not too low densities, $V^{\text{eff}}(\mathbf{r})$ becomes a constant that depends on C^{jellium} in a non-trivial way. We will discuss the details in Chap. 3.8. In the following, we will thus discuss the *free electron* problem and then use the derived formalism to find interpretations to the more complex theories discussed in the later chapters.

The eigenfunctions of Eq. (2.23) are plane waves

$$\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} \quad , \quad (2.24)$$

and choosing the energy zero such that $C^{\text{jellium}} = 0$ the energy eigenvalues are

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 \mathbf{k}^2}{2m} \quad . \quad (2.25)$$

The vectors \mathbf{k} , or its components k_x, k_y, k_z , are interpreted as quantum numbers. Thus, they replace what so far was noted as index j . Including the spin, the quantum numbers are \mathbf{k} and s , where the latter can assume one of the two values: $+1/2$ and $-1/2$ (up and down).

The wave functions in Eq. (2.24) are not normalized (or they are normalized with respect to δ functions). In order to obtain a simpler mathematical description, it is often useful and helpful to constrain the electrons to a finite volume. This volume is called the *base region* V_g and it shall be large enough, so that the obtained results are independent of its size and shape.⁴ The base region V_g shall contain N valence electrons and M ions, and for simplicity we chose a box of the dimensions L_x, L_y, L_z (cf. Ashcroft, Mermin:

³For systems with very low densities, electrons will localize themselves at $T = 0$ K due to the Coulomb repulsion. This is called Wigner crystallization and was predicted in 1930.

⁴For external magnetic fields the introduction of a base region can give rise to difficulties, because then physical effects often depend significantly on the border.

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

$$\varphi(\mathbf{r}) = \varphi(\mathbf{r} + L_x \mathbf{e}_x) = \varphi(\mathbf{r} + L_y \mathbf{e}_y) = \varphi(\mathbf{r} + L_z \mathbf{e}_z) \quad . \quad (2.26)$$

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 Kármán boundary condition. As long as L_x, L_y, L_z , and thus also V_g are large enough, the physical results do not depend on this treatment. Sometimes also anti-cyclic boundary conditions are chosen in order to check that the results are independent of the chosen base region.

By introducing such a base region, the wave functions can be normalized to the Kronecker delta. Using Eq. (2.26) and the normalization condition

$$\int_{V_g} \varphi_{\mathbf{k}}^*(\mathbf{r}) \varphi_{\mathbf{k}'}(\mathbf{r}) d^3 \mathbf{r} = \delta_{\mathbf{k}, \mathbf{k}'} \quad (2.27)$$

we obtain

$$\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{V_g}} e^{i\mathbf{k}\mathbf{r}} \quad . \quad (2.28)$$

Because of Eq. (2.26), 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

$$\mathbf{k} = \left(\frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right) \quad , \quad (2.29)$$

with n_i being arbitrary integer numbers. Thus, the number of vectors \mathbf{k} is countable, and each \mathbf{k} point is associated with the volume $(2\pi)^3/V_g$.

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 ϵ depends only on the absolute value of \mathbf{k} , these points fill (for non-interacting electrons) a sphere in \mathbf{k} -space (the ‘‘Fermi sphere’’) of radius k_F (the ‘‘Fermi radius’’). We have

$$N = 2 \frac{4}{3} \pi k_F^3 \frac{V_g}{(2\pi)^3} = \frac{1}{3\pi^2} k_F^3 V_g \quad . \quad (2.30)$$

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. (2.25)]. The particle density of the electrons in jellium is constant:

$$n(\mathbf{r}) = n = \frac{N}{V_g} = \frac{1}{3\pi^2} k_F^3 \quad , \quad (2.31)$$

the charge density of the electrons is $-en$, and the highest occupied state has the ‘‘quantum number’’, or \mathbf{k} -vector with radius $k_F = \sqrt[3]{3\pi^2 n}$.

The energy of this single-particle state $|k_F\rangle$ is

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2 = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \quad . \quad (2.32)$$

For jellium-like systems (e.g, metals), the electron density is often noted in terms of 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

$$\frac{4\pi}{3} r_s^3 = V_g/N = 1/n \quad . \quad (2.33)$$

The density parameter r_s is typically given in bohr units. For the valence electrons of metals r_s is typically around 2 bohr , and therefore k_F is approximately 1 bohr^{-1} , or 2 \AA^{-1} , respectively.

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:

$$N = \int_{-\infty}^{+\infty} N(\epsilon) f(\epsilon, T) d\epsilon \quad . \quad (2.34)$$

For free electrons (jellium), we get the density of states:

$$\begin{aligned} N(\epsilon) &= \frac{2V_g}{(2\pi)^3} \int d^3\mathbf{k} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{2V_g 4\pi}{(2\pi)^3} \int k^2 dk \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{V_g}{\pi^2} \int \frac{d\epsilon_{\mathbf{k}}}{(d\epsilon_{\mathbf{k}}/d\mathbf{k})} \frac{2m\epsilon_{\mathbf{k}}}{\hbar^2} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{V_g}{\pi^2} \int d\epsilon_{\mathbf{k}} \frac{2m}{\hbar 2\mathbf{k}} \frac{2m\epsilon_{\mathbf{k}}}{\hbar^2} \delta(\epsilon - \epsilon_{\mathbf{k}}) \\ &= \frac{mV_g}{\pi^2 \hbar^3} \sqrt{2m\epsilon} \quad . \end{aligned} \quad (2.35)$$

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 $T = 0 \text{ K}$ and at finite temperature. The density of states at the Fermi level is

$$\frac{N(\epsilon_F)}{V_g} = \frac{3}{2} \frac{N}{V_g} \frac{1}{\epsilon_F} = \frac{m}{\hbar^2 \pi^2} k_F \quad . \quad (2.36)$$

The figure shows that at finite temperatures holes below μ and electrons above μ are generated.

Later, we will often apply Eqs. (2.32)-(2.35) and the underlying concepts, because some formulas can be presented and interpreted more easily, if ϵ_F , k_F , and $n(\mathbf{r})$ are expressed in this way.

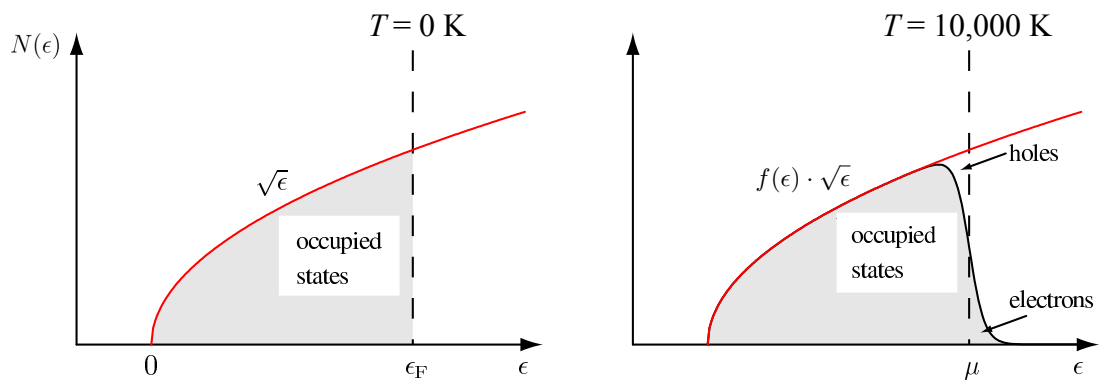


Figure 2.2: Density of states of free electrons $\sqrt{\epsilon}f(\epsilon, T)$ and the separation in occupied and unoccupied states for two temperatures.