6 “Free” Electrons in Solids

To a good approximation, the properties of solids can be divided into vibrational dynamics and electronic properties. This so-called *adiabatic approximation* (Chap. 4) is based on the fact that for the dynamics of the heavy nuclei, or of the nuclei together with their strongly bound core electrons (this combination is known as the “atomic core”), the energy can be expressed as a function of the nuclear or core coordinates in terms of a time-independent potential: the electron system, because of its very much smaller mass, follows the motion of the nuclei or cores almost instantaneously. From the viewpoint of the electron system this also means that for the electron dynamics one can regard the nuclear or core motion as extremely slow and, in the limiting case, as nonexistent. Within the adiabatic approximation one can then determine the excitation states of the electron system in the static potential of the positively charged, periodically arranged nuclei or atomic cores. In doing so, one neglects any interactions between the moving atomic cores and the remaining electrons of the crystal. In order to treat electronic transport phenomena (Sects. 9.3–9.5) in crystals, one has to reintroduce these so-called electron-lattice interactions in the form of a perturbation.

Even the adiabatic approximation of stationary nuclei or cores does not enable a quantitative treatment of the excitation states of electrons; one would still have to solve the Schrödinger equation for about 10^{23} electrons (which also interact with one another) in a periodic, static core potential. The problem must therefore be further simplified:

One considers just a simple electron in an effective periodic and time-independent potential. This potential is the one produced by the stationary nuclei in their equilibrium positions and by all the other electrons. These electrons shield the nuclear charge to a large extent and one obtains a potential which, in a section through an atomic row of the crystal, appears qualitatively as shown in Fig. 6.1 (full line). In this so-called *one electron approximation* one neglects all electron-electron interactions that cannot be represented as a local potential for the single electron under consideration, for example interactions arising from the exchange of two electrons. However, such correlations between electrons are important, for example, for understanding magnetism and superconductivity. We will thus be returning later to the subject of electron correlations. For the time being, however, we shall confine ourselves to the assumption of a local periodic potential and will solve the Schrödinger equation for a single electron in this potential. For this electron we shall find

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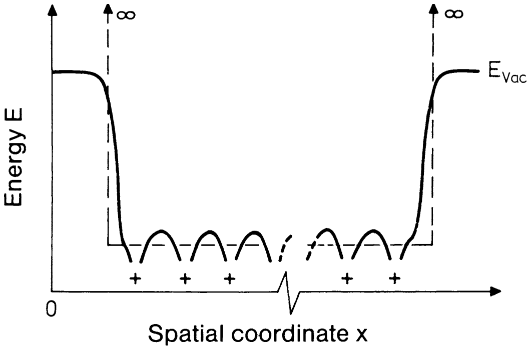

Fig. 6.1. Qualitative form of the potential for an electron in a periodic lattice of positive cores (+). The vacuum level E_{vac} is the level to which the electron must be promoted in order for it to leave the crystal and escape to infinity. The simplest approximation to describe this system is that of the square well potential (– – –) with infinitely high walls at the surfaces of the crystal

a series of one electron quantum states that will be successively filled with the available electrons. In this procedure the Pauli principle demands that each state contains only a single electron.

6.1 The Free-Electron Gas in an Infinite Square-Well Potential

An even simpler model, first considered by *Sommerfeld* and *Bethe* in 1933 [6.1], also ignores the periodic potential within the crystal. Despite its simplicity, this model yielded a much improved understanding of many of the electronic properties of solids, in particular those of metals. In this model a metal crystal (a cube of side L) is described by a three-dimensional potential box with an infinite barrier at the surfaces (Fig. 6.1); in other words, the electrons are unable to leave the crystal, which is clearly a gross over-simplification given that work function values lie in the region of 5 eV (Sect. 6.6). The time-independent Schrödinger equation for the electron in the one-electron approximation in the infinite square well is

$$-\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{r}) + V(\boldsymbol{r})\,\psi(\boldsymbol{r}) = E'\,\psi(\boldsymbol{r})\ , \tag{6.1}$$

where the potential $V(\boldsymbol{r})$ is given by

$$V(x,y,z) = \begin{cases} V_0 = \text{const} & \text{for} \quad 0 \leqq x,y,z \leqq L \\ \infty \ \text{otherwise}\ . \end{cases} \tag{6.2}$$

With $E = E' - V_0$ this yields

$$-\frac{\hbar^2}{2m}\Delta\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})\ . \tag{6.3}$$

Since the electrons, due to the infinite barrier at the surfaces ($x, y, z = 0$ and L), cannot leave the crystal, we have so-called *fixed boundary conditions* (cf. the periodic boundary conditions adopted in Sect. 5.1). These read

$$\begin{aligned} \psi = 0 \quad \text{for} \quad & x = 0 \text{ and } L\,; \quad \text{for} \quad y, z \text{ between } 0 \text{ and } L\,; \\ & y = 0 \text{ and } L\,; \quad \text{for} \quad x, z \text{ between } 0 \text{ and } L\,; \\ & z = 0 \text{ and } L\,; \quad \text{for} \quad x, y \text{ between } 0 \text{ and } L\,. \end{aligned} \tag{6.4}$$

The electron is certain to be found somewhere within the potential box and thus the normalization condition for $\psi(\boldsymbol{r})$ is written

$$\int_{\text{box}} d\boldsymbol{r}\psi^*(\boldsymbol{r})\psi(\boldsymbol{r}) = 1\,. \tag{6.5}$$

The Schrödinger equation (6.3) together with the boundary conditions (6.4) yield the solution

$$\psi(\boldsymbol{r}) = \left(\frac{2}{L}\right)^{3/2} \sin k_x x \sin k_y y \sin k_z z\,. \tag{6.6}$$

The possible energy states are found by substituting (6.6) into (6.3) as

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)\,. \tag{6.7}$$

The energies are, as expected, those of a free electron (de Broglie relation), where, however, the condition $\psi = 0$ at $x, y, z = L$ (6.4) leads to the following constraints on the wave vector k_x, k_y, k_z:

$$\begin{aligned} k_x &= \frac{\pi}{L} n_x\,, \\ k_y &= \frac{\pi}{L} n_y\,, \\ k_z &= \frac{\pi}{L} n_z \quad \text{with} \quad n_x, n_y, n_z = 1, 2, 3, \ldots\,. \end{aligned} \tag{6.8}$$

Solutions with n_x, n_y or $n_z = 0$ cannot be normalized over the volume of the box and must therefore be excluded. Negative wave vectors give no new linearly independent solutions in (6.6). The possible states of an electron in a three-dimensional infinite square well (standing waves, Fig. 6.2) can be listed according to their quantum numbers (n_x, n_y, n_z) or (k_x, k_y, k_z). A representation of the allowed values in three-dimensional wave-vector space yields constant energy surfaces, $E = \hbar^2 k^2/2m = \text{const}$, that are spherical.

For the fixed boundary conditions described here, the possible $\boldsymbol{k}$-values are confined to the positive octant of $\boldsymbol{k}$-space. In comparison with the case of periodic boundary conditions (Sect. 5.1), however, the states are twice as dense in every axis direction. Thus every state corresponds to a volume $V_k = (\pi/L)^3$. For macroscopic dimensions L one can again consider the states to be quasi-continuous, so that for many purposes one can replace sums over $\boldsymbol{k}$-space by integrals.

As in the case of phonons, we can calculate a density of states. We simply take the volume of a thin shell of the octant bounded by the energy

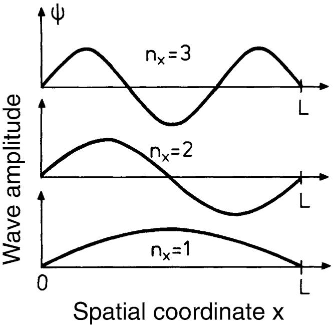

Fig. 6.2. Spatial form of the first three wavefunctions of a free electron in a square well potential of length L in the x-direction. The wavelengths corresponding to the quantum numbers $n_x = 1, 2, 3, \ldots$ are $\lambda = 2L, L, 2L/3, \ldots$ The states with low quantum numbers as shown here play no role for macroscopic bodies as they are buried in the quasi-continuum of the many other states with higher quantum numbers. This is different in nanostructures where L is in the range of 5–100nm ((12.93), Sect. 9.9).

surfaces $E(\boldsymbol{k})$ and $E(\boldsymbol{k})+dE$ and divide this by the volume V_k associated with a single $\boldsymbol{k}$-point:

$$dZ' = \frac{1}{8} 4\pi k^2 dk/(\pi/L)^3 \,. \tag{6.9}$$

Since $dE = (\hbar^2 k/m)dk$, we have for the number of states per unit volume of the crystal:

$$dZ = \frac{(2m)^{3/2}}{4\pi^2\hbar^3} E^{1/2} dE \,. \tag{6.10}$$

In Schrödinger's wave mechanics as used up to now, no provision has been made for the intrinsic angular momentum, i.e. the spin, of the electron. As can be seen from the construction of the periodic table (Sect. 1.1), one must attribute a spin to the electron, such that it has two possible orientations in an external magnetic field. In the absence of an external field, the energy levels of these two orientations are degenerate. This means that every $\boldsymbol{k}$-space point in Fig. 6.3 describes two possible electron states when one takes the electron spin into account. Thus, for the density of states $D(E) = dZ/dE$ of the free electron gas in the infinite potential well, we finally obtain

$$D(E) = \frac{(2m)^{3/2}}{2\pi^2\hbar^3} E^{1/2} \,. \tag{6.11}$$

$D(E)$ is usually expressed in units of $\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}$. The same density of states (Fig. 6.4), and thus the same expressions for the macroscopic properties of the crystal, are obtained if one uses periodic boundary conditions:

$$\psi(x+L, y+L, z+L) = \psi(x,y,z) \,. \tag{6.12}$$

These conditions yield propagating electron waves as the solutions of (6.3):

$$\psi(\boldsymbol{r}) = \left(\frac{1}{L}\right)^{3/2} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \,.$$

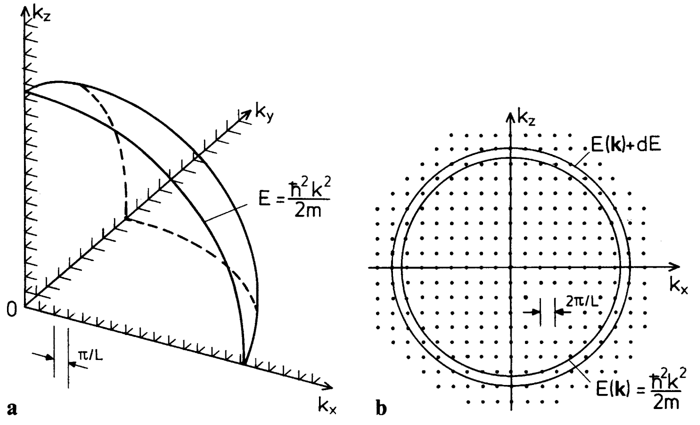

Fig. 6.3 a, b. Representation of the states of an electron in an infinite square well by means of a lattice of allowed wave vector values in $\boldsymbol{k}$-space. Because of the two possible spin orientations, each point corresponds to two states. (**a**) For fixed boundary conditions the states all lie in one octant and have a linear separation of π/L. (**b**) For periodic boundary conditions the allowed states span the whole of $\boldsymbol{k}$-space, but with a linear separation that is now $2\pi/L$. The figure shows a cross-section perpendicular to k_y (cf. Fig. 5.1). For both (**a**) and (**b**) spherical surfaces of constant energy $E(\boldsymbol{k})$ are also shown

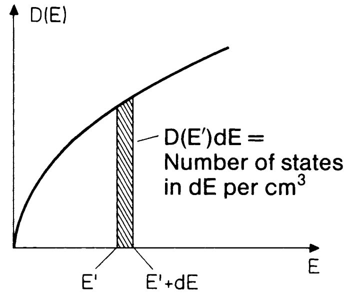

Fig. 6.4. Density of one-particle states $D(E)$ for a free electron gas in three dimensions

In this case, positive and negative $\boldsymbol{k}$-values represent linearly independent solutions and, furthermore, the solution with $\boldsymbol{k}=0$ can be normalized. Thus the possible states now extend throughout $\boldsymbol{k}$-space and possess the k-values

$$\begin{aligned}
&k_x = 0, \;\; \pm 2\pi/L, \;\; \pm 4\pi/L, \ldots, \;\; \pm 2\pi n_x/L, \ldots \\
&k_y = 0, \;\; \pm 2\pi/L, \ldots, \;\; \pm 2\pi n_y/L, \ldots \\
&k_z = 0, \;\; \pm 2\pi/L, \ldots, \;\; \pm 2\pi n_z/L, \ldots \, .
\end{aligned} \tag{6.13}$$

The separation of neighboring points is now $2\pi/L$, and the volume associated with each point (= two electron states because of spin) is

$$(2\pi/L)^3 = 8V_k \, .$$

However, instead of an octant in $\boldsymbol{k}$-space we must now consider the full solid angle of 4π when calculating the density of states. This leads to the same expression, (6.11), for $D(E)$ as was obtained for the case of fixed boundary conditions.

If the model is modified to allow for a finite potential barrier at the crystal surface (finite work function), the resulting expressions are also modified: the electron waves now decay exponentially outside the crystal, i.e., there is a nonvanishing probability of finding electrons in the vacuum just outside the crystal surface. It is also possible for certain localized surface states to occur. Here, however, we are interested in the bulk properties of relatively large crystals, and for these one may neglect such surface effects.

6.2 The Fermi Gas at $T = 0$ K

The states that an electron can occupy within the one-electron approximation for the square well potential are distributed along the energy axis according to the density of states $D(E)$. The occupation of these states by the available electrons of the crystal must be such that their total energy corresponds to the mean thermal energy of the system. In other words there has to be a temperature-dependent occupation probability $f(T, E)$ that governs the distribution of the available electrons among the possible states. The electron density per unit volume can therefore be expressed as

$$n = \int_0^\infty D(E) f(T, E) dE \, . \tag{6.14}$$

For a gas of classical particles this distribution function $f(T, E)$ would be the familiar Boltzmann exponential, which would require that at temperatures $T \to 0$ K all electrons should occupy the lowest available states.

However, for all fermions, i.e., particles with half-integral spin such as electrons, the Pauli principle applies. Within the one-particle approximation for noninteracting particles this can be formulated as follows: in an atomic system no two fermions may possess identical sets of quantum numbers. This exclusion principle therefore demands that in the lowest energy state, i.e., for $T \to 0$ K, the available electrons occupy successive energy levels starting with the lowest and ending at some upper limit. This limiting energy, which, at $T \to 0$ K, separates occupied from unoccupied states, is known as the Fermi energy E_F^0 for zero temperature. In the free-electron-gas model with a square-well potential, this energy corresponds to the spherical surface $E_F^0(\boldsymbol{k}_F) = \hbar^2 k_F^2 / 2m$ in $\boldsymbol{k}$-space with the Fermi wave vector k_F as its radius.

The occupation probability for electrons in the potential well at $T = 0$ K is a step function with $f = 1$ for $E < E_F^0$ and $f = 0$ for $E > E_F^0$ (Fig. 6.5). The spherical form of the Fermi surface $E_F^0(\boldsymbol{k})$ at $T \to 0$ K leads immediately to a simple relationship between the electronic density n and the Fermi radius k_F or Fermi energy E_F^0:

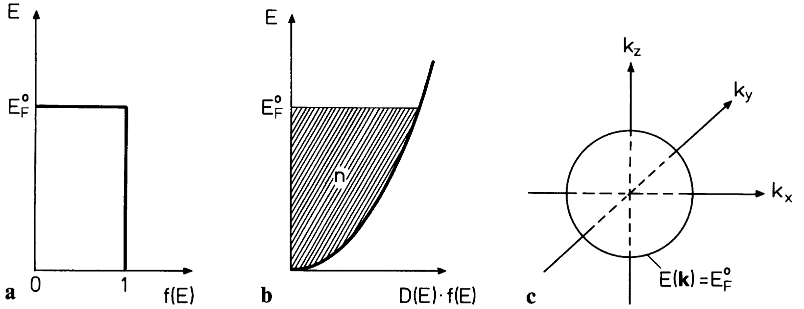

Fig. 6.5 a–c. Description of the quasi-free valence electrons of a metal at $T = 0$. (**a**) $f(E)$ is a step function. (**b**) The concentration n of valence electrons is given by the area under the density of states curve up to the Fermi energy E_F^0. (**c**) In $\boldsymbol{k}$-space the Fermi sphere $E(\boldsymbol{k}) = E_F^0$ separates occupied from unoccupied states

$$nL^3 = \frac{L^3 k_F^3}{3\pi^2} \,, \tag{6.15}$$

$$E_F^0 = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3} \,. \tag{6.16}$$

The magnitude of the Fermi energy can thus be estimated by using the number of valence electrons per atom to determine the electron concentration n. A few values of E_F^0 are listed in Table 6.1. From these we see that at normal temperatures the Fermi energy is always very large compared to $k T$. To make this more obvious one can define a Fermi temperature $T_F = E_F^0/k$; this temperature lies about two orders of magnitude above the melting point of the metals.

Table 6.1. Fermi energy E_F^0, radius of the Fermi sphere in k-space k_F, Fermi velocity $v_F = \hbar k_F/m$, and Fermi temperature $T_F = E_F^0/k$ for a few typical metals. n is the concentration of conduction electrons deduced from the structural data of the elements [6.2]. It should be noted that the electron configuration of Cu, Ag and Au is $3d^{10}\,4s^1$ and so every atom contributes one free electron (Fig. 7.12). The characteristic radius r_s is also often used in this context. It is defined via the volume of a hypothetical sphere containing one electron, $4\pi r_s^3/3 = a_0^{-3} n^{-1}$, where a_0 is the Bohr radius so that r_s is dimensionless. Values for r_s lie between 2 and 6 for typical metals

Metal	n (10^{22} cm^{-3})	r_s	k_F (10^8 cm^{-1})	v_F (10^8 cm/s)	E_F^0 (eV)	T_F (10^4 K)
Li	4.62	3.27	1.11	1.29	4.70	5.45
Na	2.53	3.99	0.91	1.05	3.14	3.64
Cs	0.86	5.71	0.63	0.74	1.53	1.78
Al	18.07	2.07	1.75	2.03	11.65	13.52
Cu	8.47	2.67	1.36	1.57	7.03	8.16
Ag	5.86	3.02	1.20	1.39	5.50	6.38
Au	5.9	3.01	1.20	1.39	5.52	6.41

An interesting consequence of the Pauli exclusion principle is that the Fermi gas, in contrast to a classical gas, has a nonvanishing internal energy at $T = 0\,\mathrm{K}$. It is well known that the internal energy density U of a system is the average value over all states; thus at $T = 0\,\mathrm{K}$ we obtain

$$\begin{aligned} U &= \int_0^{E_\mathrm{F}^0} D(E)E\,dE \\ &= \frac{3}{5}nE_\mathrm{F}^0 \,. \end{aligned} \tag{6.17}$$

As has already been established, this value lies many orders of magnitude above the internal energy of a classical gas at $T = 300\,\mathrm{K}$. In order to treat the conduction electrons in a metal it is therefore sufficient for many purposes to use a zero-temperature description (Fig. 6.5).

6.3 Fermi Statistics

We now move on to consider the Fermi gas at finite temperatures. We shall need to derive the distribution function or occupation probability $f(E, T)$ for non-zero temperatures. This is a thermodynamical problem, since we are inquiring about the distribution that arises when various quantum mechanical states are in equilibrium with one another. To derive the distribution $f(E, T)$ we must therefore apply some basic concepts of thermodynamics.

We consider an atomic system with single-particle energy levels E_j. We assume that the energy levels E_j lie very close to one another as in a solid. We can then consider new energy levels E_i each of which consists of many E_j. The degeneracy of these new levels is denoted by g_i and their occupation number by n_i where both g_i and n_i are large numbers. On account of the Pauli principle we must have $n_i \leq g_i$. From thermodynamics we know the conditions that the system must fulfill in order for all energy levels to be in equilibrium: the free energy F of the total system must be stationary with respect to a variation in the relative occupation numbers of the levels. In other words we must have

$$\delta F = \sum_i \frac{\partial F}{\partial n_i}\delta n_i = 0 \tag{6.18}$$

with the subsidiary condition of conservation of particle number

$$\sum_i \delta n_i = 0 \,. \tag{6.19}$$

For the specific case of exchange of electrons between two arbitrary levels k and l the equilibrium conditions read

$$\frac{\partial F}{\partial n_k}\delta n_k + \frac{\partial F}{\partial n_l}\delta n_l = 0 \,, \tag{6.20}$$

$$\delta n_k + \delta n_l = 0 \,. \tag{6.21}$$

From this it follows immediately that the derivatives of the free energy with respect to the occupation numbers must be equal

$$\frac{\partial F}{\partial n_k} = \frac{\partial F}{\partial n_l} \,. \tag{6.22}$$

Since the two levels were selected at random, at equilibrium all $\partial F/\partial n_i$ must be equal and we denote this quantity by a new constant, μ, defined as the "chemical potential" of the electrons.

We will now calculate the free energy of the system of electrons. From thermodynamics we have the relation

$$F = U - TS \tag{6.23}$$

with the internal energy U

$$U = \sum_i n_i E_i \tag{6.24}$$

and the entropy S. The entropy is given by

$$S = k \ln P \,, \tag{6.25}$$

where P represents the number of possible ways of distributing the electrons among the states. The number of ways of accommodating one electron in the level E_i is g_i. For a second electron, also in level E_i, the number of possibilities is g_i–1, and so on. There would therefore be

$$g_i(g_i - 1)(g_i - 2)\ldots(g_i - n_i + 1) = \frac{g_i!}{(g_i - n_i)!} \tag{6.26}$$

possible ways of accommodating n_i electrons at definite positions within the energy level E_i. However, arrangements which differ only in the exchange of electrons within the energy level are not distinguishable. Since there are $n_i!$ such possibilities, the total number of distinguishable ways of accommodating n_i electrons in the level E_i is given by

$$\frac{g_i!}{n_i!(g_i - n_i)!} \,. \tag{6.27}$$

The number of ways P of realizing the total system is then the product over all possibilities for occupying each level:

$$P = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \,. \tag{6.28}$$

Thus the entropy can be expressed as

$$S = k \sum_i [\ln g_i! - \ln n_i! - \ln(g_i - n_i)!] \ , \tag{6.29}$$

where the factorials can be replaced by using Stirling's approximate formula

$$\ln n! \approx n \ln n - n \quad \text{(for large } n) \ . \tag{6.30}$$

It now becomes a straightforward matter to calculate the chemical potential, i.e., the derivative of the free energy F with respect to the occupation number of an arbitrary level i:

$$\mu = \frac{\partial F}{\partial n_i} = E_i + kT \ln \frac{n_i}{g_i - n_i} \ . \tag{6.31}$$

We can rearrange this expression to obtain the occupation number n_i:

$$n_i = g_i (e^{(E_i - \mu)/kT} + 1)^{-1} \ . \tag{6.32}$$

The probability that a quantum mechanical state (degenerate states are also considered distinct here) is occupied is given by the distribution function $f(E, T)$, which, from (6.32), can be seen to be (Fig. 6.6)

$$f(E, T) = \frac{1}{e^{(E-\mu)/kT} + 1} \ . \tag{6.33}$$

This function is also known as the Fermi distribution. It is the distribution function for particles, only one of which may occupy each quantum state. For electrons and all particles with half-integral spin, i.e., fermions, this distribution function guarantees that the Pauli principle is obeyed. However, it

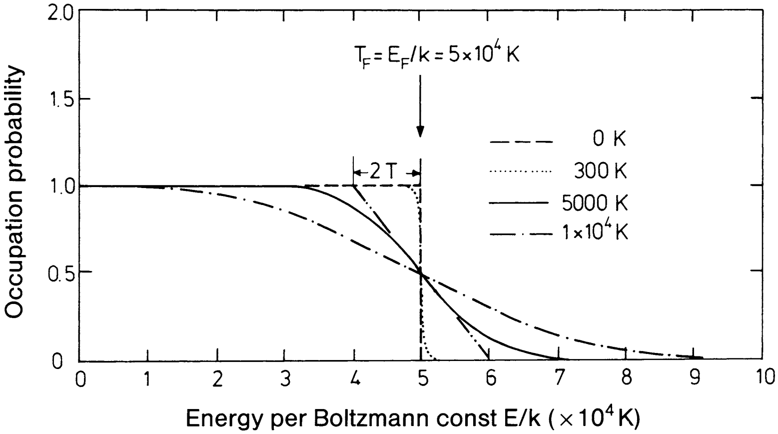

Fig. 6.6. The Fermi distribution function at various temperatures. The Fermi temperature $T_F = E_F^0/k$ has been taken as 5×10^4 K. The tangent at the point of inflection (–··–) intersects the energy axis at $2kT$ above E_F^0 at all temperatures

would be wrong to claim that the Fermi distribution is only valid for particles with spin $\frac{1}{2}$; it is equally valid for atoms or molecules that are distributed among predetermined fixed positions, whenever only one atom or molecule can occupy such a position. Corresponding situations arise in the thermodynamics of defects (Sect. 2.7), the solubility of gases in solids, and adsorption processes.

The significance of the chemical potential μ in the Fermi distribution is most readily seen in the limiting case of $T = 0\,\text{K}$. At zero temperature the Fermi function becomes identical with the step function introduced previously. It has a value of 1 for $E < \mu$ and of 0 for $E > \mu$. Thus at $T = 0\,\text{K}$ the chemical potential of the electrons is equal to the Fermi energy:

$$\mu(T = 0\,\text{K}) = E_\text{F}^0 \, . \tag{6.34}$$

Because of this equality, one often speaks of the "Fermi level" in place of the chemical potential and uses the symbol E_F. This Fermi level, however, is then a temperature-dependent quantity!

At higher temperatures the sharp edge of the Fermi distribution becomes more rounded; states below E_F have a finite probability of being unoccupied, while those slightly above E_F may be occupied (Fig. 6.6). The size of the region, over which the Fermi function deviates significantly from the step function, is of the order of $2kT$ to each side, as shown by the tangent to $f(T, E)$ at E_F drawn in Fig. 6.6. One sees that as the temperature is raised, only a small fraction of the electrons is able to gain energy. This has important consequences, e.g., for the specific heat capacity of the electron gas (Sect. 6.4).

If one is interested in the occupation probability for energies or temperatures in the range $|E–E_\text{F}| \gg 2kT$, it is possible to use approximations to the Fermi function (6.33).

The condition $E–E_\text{F} \gg 2kT$ is often fulfilled, for example for the conduction electrons in semiconductors (Sect. 12.2). In this regime, with energies E far above the Fermi edge, the Fermi function $f(E, T)$ can be approximated by the classical Boltzmann distribution, $f(E, T) \sim \exp(E_\text{F} - E)/kT$; see (12.5).

6.4 The Specific Heat Capacity of Electrons in Metals

The application of the square-well potential model to the conduction electrons allows a very simple description of the specific heat capacity c_v of these metal electrons. In fact this is an age-old problem, and one which seemed insoluble prior to the development of quantum mechanics. For a typical conduction electron density of $n = 10^{22}\,\text{cm}^{-3}$ one would have expected, in addition to the lattice specific heat, an electronic contribution according to the equidistribution law of $c = 3nk/2$, at least at elevated temperatures. Experiments on metals, however, showed no deviation from the Dulong-Petit value. The reason is simple: electrons, in contrast to a classical gas, can only gain energy if they can move into free states in their energetic neighborhood. The number of such electrons, expressed as a fraction of the total density n, is only of the order of 1/100, as demonstrated by the following simple estimate:

The “smeared out” region of the Fermi function has a width on the order of $4kT$, i.e., according to Fig. 6.7, the Pauli principle dictates that only a fraction of about $4kT/E_F$ of all “free” electrons (density n) can absorb thermal energy. The energy per electron is around kT and so the total energy of these thermally excited electrons is on the order of

$$U \sim 4(kT)^2 n/E_F \ . \tag{6.35}$$

With $T_F = E_F/k$ as the Fermi temperature, one obtains the following order of magnitude estimate for the specific heat of the electrons

$$c_V = \partial U/\partial T \sim 8knT/T_F \ . \tag{6.36}$$

As seen in Table 6.1, the Fermi temperatures are typically on the order of 10^5 K and this, on account of the factor T/T_F in (6.36), explains the vanishingly small contribution of the conduction electrons to the specific heat capacity.

The exact calculation to determine the specific heat capacity of the gas of free electrons is as follows:

Upon heating the Fermi electron gas from 0 K to a temperature T, the internal energy per unit volume is increased by an amount U given by

$$U(T) = \int_0^\infty dE \cdot ED(E) f(E,T) - \int_0^{E_F^0} dE \cdot ED(E) \ . \tag{6.37}$$

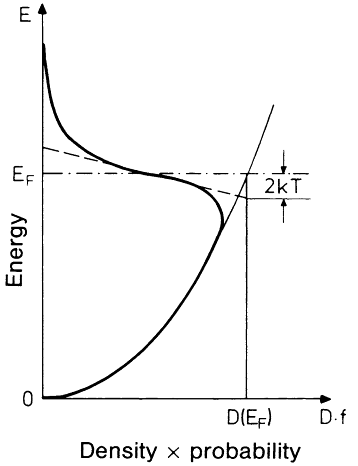

Fig. 6.7. Explanation of the specific heat capacity of quasi-free metal electrons. The effect of raising the temperature from 0 K to T is to allow electrons from $\leq 2kT$ below the Fermi energy to be promoted to $\leq 2kT$ above E_F. The tangent (– – –) intersects the energy axis at $E_F + 2kT$

We also have the relation

$$E_F \cdot n = E_F \int_0^\infty dE\, D(E) f(E,T)\ , \tag{6.38}$$

where n is the total concentration of free electrons. Differentiating (6.37) and (6.38) yields

$$c_v = \partial U/\partial T = \int_0^\infty E\, D(E)(\partial f/\partial T)dE\ , \tag{6.39}$$

$$0 = E_F(\partial n/\partial T) = \int_0^\infty E_F D(E)(\partial f/\partial T)dE\ . \tag{6.40}$$

Subtracting (6.40) from (6.39), the specific heat capacity c_v of the electrons is obtained as

$$c_v = \partial U/\partial T = \int_0^\infty dE(E - E_F)D(E)(\partial f/\partial T)\ . \tag{6.41}$$

The derivative $\partial f/\partial T$ (Fig. 6.7) has significant values only in the "smeared out" region of $\pm\, 2\ell\!\!\!/\, T$ about E_F. The density of states $D(E)$ does not vary a great deal in this region and may be approximated by $D(E_F)$, i.e.,

$$c_v \approx D(E_F) \int_0^\infty dE(E - E_F)(\partial f/\partial T)\ , \tag{6.42}$$

where the temperature derivative of the Fermi function (6.33) is given by

$$\frac{\partial f}{\partial T} = \frac{E - E_F}{\ell\!\!\!/ T^2}\, \frac{\exp[(E - E_F)/\ell\!\!\!/ T]}{\{\exp[(E - E_F)/\ell\!\!\!/ T] + 1\}^2}\ . \tag{6.43}$$

With the abbreviation $x = (E - E_F)/\ell\!\!\!/ T$ we then have

$$c_v \approx \ell\!\!\!/^2\, T D(E_F) \int_{-E_F/\ell\!\!\!/ T}^{\infty} dx\, x^2 \exp x(\exp x + 1)^{-2}\ . \tag{6.44}$$

Since the factor of $\exp x$ in the integrand is negligible for $x \leq -E_F/\ell\!\!\!/ T$, the lower integration limit can be extended to minus infinity. The resulting integral

$$\int_{-\infty}^{\infty} dx\, x^2 \exp x(\exp x + 1)^{-2} = \pi^2/3 \tag{6.45}$$

is a standard integral whose value can be found in tables.

One thus has the following general result for the specific heat capacity of the "free" electrons in metals:

$$c_V \approx \frac{\pi^2}{3} D(E_F) k^2 T \, . \tag{6.46}$$

In deriving (6.46) no use has been made of the explicit form of the density of states $D(E)$. Equation (6.46) is therefore also valid for cases where the density of states deviates from that of the free electron gas, as indeed is expected in the majority of cases. For metals, measurements of the electronic heat capacity are therefore used as a method of determining the density of states $D(E_F)$ at the Fermi level.

In the free electron gas model $D(E_F)$ can be very simply expressed in terms of the electron concentration. In the case of metals, the validity of the relation $T \ll T_F$ implies

$$n = \int_0^{E_F} D(E) dE \, , \tag{6.47}$$

and the density of states for this case can be written

$$D(E) = D(E_F)(E/E_F)^{1/2} \, . \tag{6.48}$$

It follows that

$$n = \frac{2}{3} D(E_F) E_F \, , \tag{6.49}$$

and from (6.46) we have

$$c_V \approx \frac{\pi^2}{2} n k \frac{kT}{E_F} = \frac{\pi^2}{2} n k \frac{T}{T_F} \, . \tag{6.50}$$

Thus the only difference between this exact calculation and the previous rough estimate (6.36) is the appearance of the factor $\pi^2/2$ in place of the factor 8.

The predicted linear dependence of the electronic specific heat capacity on temperature is well confirmed experimentally. For low temperatures, where the phonon contribution to c_V displays the Debye T^3 dependence, one expects to observe

$$c_V = \gamma T + \beta T^3 \, , \quad \gamma, \beta = \text{const.} \tag{6.51}$$

The experimental results in Fig. 6.8 show the linear dependence expected from (6.51) for a plot of c_V/T against T^2.

For the transition metals in particular, the experimentally determined values of γ bear little resemblance to those calculated from the electron gas model, as is seen in Table 6.2.

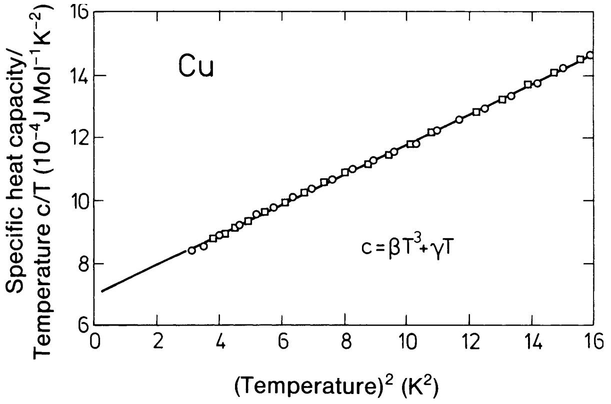

Fig. 6.8. Plot of c_V/T against T^2 for copper. The experimental points (○ and □) stem from two separate measurements [6.3]

Table 6.2. Comparison of experimentally determined values of the coefficient γ of electronic specific heat with values calculated using the free-electron-gas model. At low temperatures one has $c_V = \gamma T + \beta T^3$ for the combined electronic ($\propto T$) and ($\propto T^3$) contributions to the specific heat

Metal	γ_{exp} (10^{-3} J/Mol K^2)	$\gamma_{exp}/\gamma_{theo}$
Li	1.7	2.3
Na	1.7	1.5
K	2.0	1.1
Cu	0.69	1.37
Ag	0.66	1.02
Al	1.35	1.6
Fe	4.98	10.0
Co	4.98	10.3
Ni	7.02	15.3

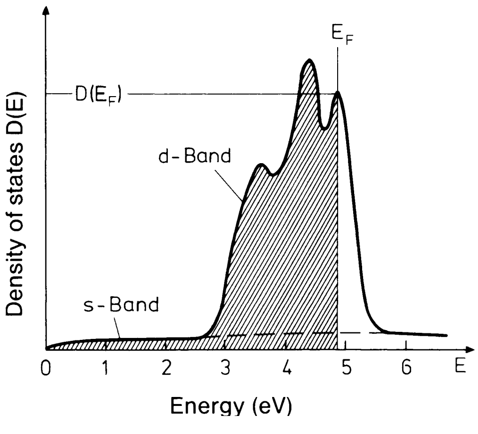

Fig. 6.9. Qualitative behavior of the density of states $D(E)$ for the conduction band of a transition metal. The strong contribution of the d-electrons in the vicinity of the Fermi level lies on top of that of the s-band (*partially dashed*)

The large deviations for Fe, Co, and Ni are attributed to the partially filled *d*-shells of these transition metals, whose *d*-bands thus lie at the Fermi energy. Because of the strong localization of the *d*-electrons at the atoms, the overlap of their wavefunctions is small. This means that the corresponding energy band is relatively narrow and therefore yields a large contribution to the density of states as shown in Fig. 6.9.

6.5 Electrostatic Screening in a Fermi Gas – The Mott Transition

If an electric charge is introduced into a metal, e.g. by the inclusion of a charged defect, then in the vicinity of this charge there is a perturbation in the otherwise homogeneous electron concentration which compensates or screens the electric field of the charge.

This problem can be treated approximately using the model of a quasi-free electron gas in a potential well:

A local perturbation potential δU (assumed to obey $|e\delta U| \ll E_{\mathrm{F}}$) produces a local raising of the density of states parabola $D(E)$ by an amount $e\delta U$ (Fig. 6.10). If one imagines the perturbation potential to be switched on, it is clear that some electrons must immediately leave this region in order for the Fermi level to remain constant throughout the crystal. This homogeneity is necessary since the Fermi level is a thermodynamic function of state (equal to the electrochemical potential). For not too large δU the change in the electron concentration is given in terms of the density of states at the Fermi level (in analogy to the specific heat capacity) by

$$\delta n(\boldsymbol{r}) = D(E_{\mathrm{F}})|e|\delta U(\boldsymbol{r}) \,. \tag{6.52}$$

Except in the immediate vicinity of the perturbation charge, one can assume that $\delta U(\boldsymbol{r})$ is caused essentially by the induced space charge. Thus $\delta n(\boldsymbol{r})$ is related to δU via the Poisson equation:

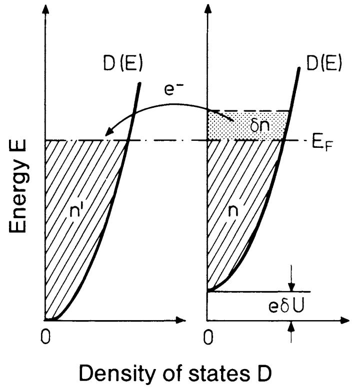

Fig. 6.10. Effect of a local perturbation potential δU on the Fermi gas of “free” electrons. Immediately after the perturbation is switched on, δn electrons must move away such that the Fermi level E_{F} is homogeneous throughout the crystal in thermal equilibrium

$$\nabla^2(\delta U) = \frac{-\delta\varrho}{\varepsilon_0} = \frac{e}{\varepsilon_0}\delta n = \frac{e^2}{\varepsilon_0} D(E_\mathrm{F})\delta U\,, \tag{6.53}$$

where ε_0 is the dielectric constant.

With $\lambda^2 = e^2 D\,(E_\mathrm{F})/\varepsilon_0$, this differential equation for the screening potential δU has a nontrivial solution in spherical coordinates

$$\left(\nabla^2(\delta U) \equiv \frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r}(\delta U)\right):$$

$$\delta U(r) = \alpha\, e^{-\lambda r}/r\,. \tag{6.54}$$

Spherical coordinates are the obvious choice when dealing with a point-like defect. For a point charge e one would have $\alpha = e/(4\pi\varepsilon_0)$ since for $\lambda \to 0$ the screening effect would disappear and one must obtain the Coulomb potential of this point charge (Fig. 6.11). The quantity $r_\mathrm{TF} = 1/\lambda$ is known as the Thomas-Fermi screening length:

$$r_\mathrm{TF} = \left[e^2 D(E_\mathrm{F})/\varepsilon_0\right]^{-1/2}\,. \tag{6.55}$$

For the special case of the free electron gas model, (6.49) and (6.16) give

$$D(E_\mathrm{F}) = \frac{3}{2} n/E_\mathrm{F} \quad \text{and} \quad E_\mathrm{F} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}\,,$$

i.e.

$$D(E_\mathrm{F}) = \frac{1}{2\pi^2}\frac{2m}{\hbar^2}(3\pi^2 n)^{1/3}\,. \tag{6.56}$$

For the Thomas-Fermi screening length in the square-well model it follows that

$$\frac{1}{r_\mathrm{TF}^2} = \lambda^2 = \frac{me^2}{\pi^2\hbar^2\varepsilon_0}(3\pi^2 n)^{1/3} = \frac{4}{\pi}\,(3\pi^2)^{1/3}\,\frac{n^{1/3}}{a_0}\,, \tag{6.57}$$

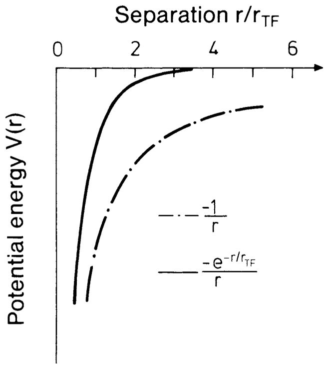

Fig. 6.11. Screened (——) and unscreened (–·–) Coulomb potential of a positive unit charge in a Fermi gas of free electrons. The distance r is given as a multiple of the Thomas-Fermi screening length r_TF

$$\frac{1}{r_{\mathrm{TF}}} \simeq 2\frac{n^{1/6}}{a_0^{1/2}} \quad \text{or} \quad r_{\mathrm{TF}} \simeq 0.5\left(\frac{n}{a_0^3}\right)^{-1/6} , \tag{6.58}$$

where $a_0 = 4\pi\hbar^2\varepsilon_0/(m e^2)$ is the Bohr radius. Copper, for example, with an electron concentration of $n = 8.5 \times 10^{22}\,\mathrm{cm}^{-3}$, has a screening length of $r_{\mathrm{TF}} = 0.55\,\mathrm{\AA}$.

The screening process described here is responsible for the fact that the highest energy valence electrons of a metal are not localized. These electrons cannot be held in the field of the ion core potential. As the electron density decreases, the screening length r_{TF} becomes even larger.

Using arguments related to screening, it is possible to understand the sharp transition between metallic and insulating or semiconducting properties known as the *Mott transition* [6.4].

Above a certain critical electron density n_c the screening length r_{TF} becomes so small that electrons can no longer remain in a bound state; this produces metallic behavior. Below this critical electron concentration the potential well of the screened field extends far enough for a bound state to be possible. The electron is then localized in a covalent or ionic bond. Such localized states correspond, by definition, to insulating properties where the highest occupied states form localized bonds. To make a simple estimate of when a bound state becomes possible in a screened potential, we assume that the screening length must be significantly larger than the Bohr radius a_0, i.e., that the potential well of a positive center extends sufficiently far to bind an electron:

$$r_{\mathrm{TF}}^2 \simeq \frac{1}{4}\frac{a_0}{n^{1/3}} \gg a_0^2 , \tag{6.59}$$

i.e.

$$n^{-1/3} \gg 4a_0 . \tag{6.60}$$

This estimate, originally proposed by Mott, predicts that a solid will lose its metallic character when the average electron separation $n^{-1/3}$ becomes significantly larger than four Bohr radii. One then expects an abrupt transition to insulating properties.

It is today believed that sharp jumps observed in the conductivity of transition metal oxides, glasses, and amorphous semiconductors, may be explicable in terms of the above mechanism.

6.6 Thermionic Emission of Electrons from Metals

If a metal is made sufficiently hot it is found to emit electrons. This phenomenon is exploited in all electron tubes.

In the circuit shown in Fig. 6.12a one observes a saturation current j_s in the current-voltage characteristic (Fig. 6.12b) that is dependent on the cathode temperature T.

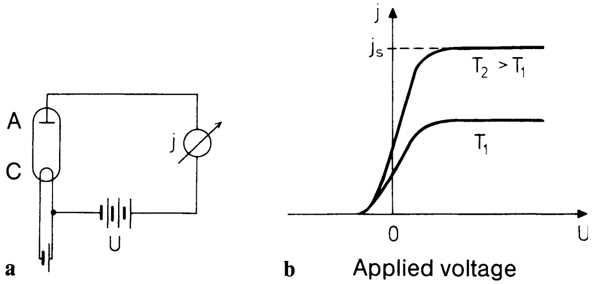

Fig. 6.12. (**a**) Schematic drawing of a diode circuit for observing thermionic emission of electrons from the heated cathode C (A = anode). (**b**) Qualitative behavior of the current-voltage curve at two different temperatures T_1 and $T_2 > T_1$. As a consequence of their thermal energy, electrons can even overcome a countervoltage (A negative with respect to C)

The existence of this effect demonstrates that the assumption of an infinite square well to describe metal electrons is too simple. The potential well clearly has only a finite barrier height. The energy difference $E_{\text{vac}}–E_{\text{F}} = \Phi$ is known as the work function. This is the energy barrier that an electron must overcome in order to reach the energy level of the vacuum (far away from the metal) from the "Fermi sea". If the electron also possesses a sufficient momentum perpendicular to the surface, it can leave the metal and will contribute to the saturation current j_s.

We will calculate the temperature-dependent saturation current for the free-electron-gas model. If the drift velocity v of the charge carriers is homogeneous, the current density is given by $\boldsymbol{j} = n\,e\,v$, where n is the concentration of charge carriers. (Strictly speaking a minus sign is also required, but this can be omitted for our present purposes.) We can generalize this expression to the case where the electron velocity is a function of the wave vector $\boldsymbol{k}$:

$$j_x = \frac{e}{V}\sum_{\boldsymbol{k}} v_x(\boldsymbol{k}) = \frac{e}{(2\pi)^3}\int\limits_{\substack{E>E_{\text{F}}+\Phi \\ v_x(\boldsymbol{k})>0}} v_x(\boldsymbol{k})\,d\boldsymbol{k}\,. \tag{6.61}$$

This form includes the fact that the density of states in $\boldsymbol{k}$-space is $V/(2\pi)^3$. Both the summation and the integral extend only over occupied states, as dictated by Fermi statistics. This condition can be included explicitly by multiplying by the occupation probability given in (6.33). Thus

$$j_x = \frac{2e\hbar}{(2\pi)^3 m}\int\limits_{-\infty}^{\infty} dk_y dk_z \int\limits_{k_{x\,\text{min}}}^{\infty} dk_x k_x f(E(\boldsymbol{k}), T)\,. \tag{6.62}$$

Here we have written $mv_x = \hbar k_x$, and have taken into account that for a free-electron gas all states are doubly degenerate. Since the work function Φ is large compared to kT, we can approximate the Fermi statistics by Boltzmann statistics:

$$\begin{aligned} j_x = \frac{e\hbar}{4\pi^3 m} & \int\limits_{-\infty}^{\infty} dk_y \mathrm{e}^{-\hbar^2 k_y^2/2mkT} \int\limits_{-\infty}^{\infty} dk_z \mathrm{e}^{-\hbar^2 k_z^2/2mkT} \\ & \times \int\limits_{k_{x\,\min}}^{\infty} dk_x k_x \mathrm{e}^{-\hbar^2 k_x^2/2mkT} \mathrm{e}^{E_\mathrm{F}/kT} \, . \end{aligned} \tag{6.63}$$

The integrals are thus factorized and can be readily evaluated. In the third integral we must also take into account that the kinetic energy in the $+x$-direction must be greater than $E_\mathrm{F} + \varPhi$:

$$\begin{aligned} \int\limits_{k_{x\,\min}}^{\infty} dk_x k_x \mathrm{e}^{-\hbar^2 k_x^2/2mkT} \mathrm{e}^{E_\mathrm{F}/kT} & = \int\limits_{(E_\mathrm{F}+\varPhi)2m/\hbar^2}^{\infty} \frac{1}{2} dk_x^2 \mathrm{e}^{-\hbar^2 k_x^2/2mkT} \mathrm{e}^{E_\mathrm{F}/kT} \\ & = \frac{mkT}{\hbar^2} \mathrm{e}^{-\varPhi/kT} \, . \end{aligned} \tag{6.64}$$

One thus arrives at the so-called Richardson-Dushman formula for the saturation current density:

$$j_\mathrm{s} = \frac{4\pi m e}{h^3} (kT)^2 \mathrm{e}^{-\varPhi/kT} \, . \tag{6.65}$$

The universal factor $4\pi m e k^2/h^3$ has the value 120 $\mathrm{A}/(\mathrm{K}^2\,\mathrm{cm}^2)$. In this derivation we have made the simplifying assumption that electrons arriving at the surface with an energy $\hbar^2 k_x^2/2m \geqslant E_\mathrm{F} + \varPhi$ have a 100% probability of escaping from the solid. Even in the free-electron-gas model this assumption is not correct. The well-known quantum mechanical treatment of the reflection and transmission of electrons at a potential step tells us that electrons whose energy exactly equals the energy of the potential step have zero probability of transmission. The effect of the potential step can be included by introducing a factor $\sqrt{\pi kT/(E_\mathrm{F} + \varPhi)}$, which significantly reduces the saturation current density. The Richardson-Dushman formula can also be applied to the ballistic transport of charge carriers in semiconductor multilayer structures (cf. Sect. 12.7).

In the particular case of thermionic emission, it is also necessary to consider the dependence of the work function on the external field $\mathcal{E}$.

The appropriate correction is the replacement of the constant $\varPhi$ in the exponent by the field-dependent quantity

$$\varPhi' = \varPhi - \sqrt{\frac{e^3 \mathcal{E}}{4\pi\varepsilon_0}} = \varPhi - \Delta\varPhi \, . \tag{6.66}$$

The correction term $\Delta\varPhi$ is derived simply by assuming that essential contributions to the work function stem from the Coulomb force due to the image charge of an electron lying outside the surface and the effect of the external

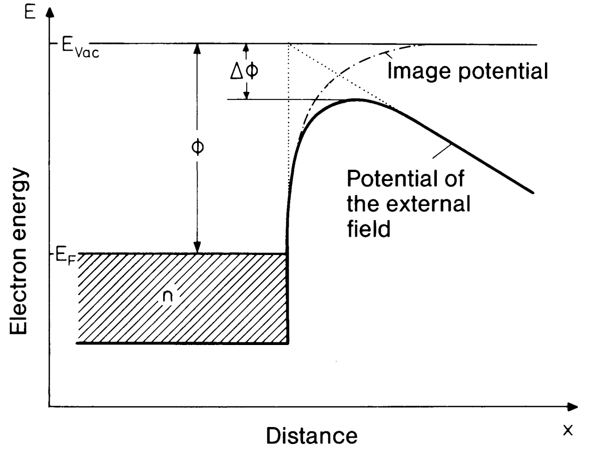

Fig. 6.13. Schematic representation of the thermionic emission of free electrons (density n) from a metal. An electron in the potential well must overcome the work function barrier $\Phi = E_{\mathrm{vac}} - E_{\mathrm{F}}$ in order to reach the energy level E_{vac} of the vacuum and escape from the crystal. An important part of the work function is assumed to be the Coulomb potential between the escaping electron and its positive image charge in the metal (image potential –·–). If an external electric field is applied, then Φ is reduced by an amount $\Delta\Phi$. Reductions of the work function of ~ 1 eV as shown here can only be achieved with extremely strong external fields of 10^7–10^8 V/cm

field in reducing the potential barrier. This is illustrated by the superposition of the external applied potential $\mathscr{E}x$ and the Coulomb image potential as shown in Fig. 6.13.

The Richardson-Dushman formula can be used in this extended form to determine the work functions of metals. In order to do this, one must first determine the saturation emission current $j_{\mathrm{s}0}$ for $\mathscr{E} = 0$ by extrapolating the measured current j_{s} at finite fields $\mathscr{E}$. A semi-log plot of $j_{\mathrm{s}0}/T^2$ against $1/T$ yields the work function.

Work functions of the elements (polycrystalline) are listed in Table 6.3.

Table 6.3. Work functions of elements in eV (polycrystalline samples, after Michaelson [6.5])

Li	Be											B	C		
2.9	4.98											4.45	5.0		
Na	Mg											Al	Si	P	S
2.75	3.66											4.28	4.85	–	–
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
2.30	2.87	3.5	4.33	4.3	4.5	4.1	4.5	5.0	5.15	4.65	4.33	4.2	5.0	3.75	5.9
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
2.16	2.59	3.1	4.05	4.3	4.6	–	4.71	4.98	5.12	4.26	4.22	4.12	4.42	4.55	4.95
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
2.14	2.7	3.5	3.9	4.25	4.55	4.96	4.83	5.27	5.65	5.1	4.49	3.84	4.25	4.22	–

As a concluding remark we note that the work function depends strongly on the crystallographic orientation of the surface and on the degree of contamination.

Problems

6.1 a) Calculate the density of states for a two-dimensional gas of free electrons in a so-called quantum well. The boundary conditions for the electronic wavefunction are: $\psi(x,y,z) = 0$ for $|x| > a$, where a is of atomic dimensions.

b) Calculate the density of states for a one-dimensional gas of free electrons in a so-called quantum wire with the boundary conditions: $\psi(x,y,z) = 0$ for $|x| > a$ and $|y| > b$, where a and b are of atomic dimensions.

c) Can such electron gases be realized physically?

6.2 Calculate to lowest order the temperature dependence of the chemical potential for a gas of free electrons whose electron concentration remains constant.

Hint: Write down an expression for the electron concentration at finite temperature. You will encounter an integral

$$F(x) = \int_0^\infty \frac{\sqrt{y}\,dy}{1 + \mathrm{e}^{y-x}} \, .$$

For $x \geq 1.5$

$$F(x) \cong 2/3x^{3/2}\left(1 + \frac{\pi^2}{8x^2}\right)$$

is a good approximation.

6.3 The bulk modulus κ is given by the second derivative of the total energy E_{tot} with respect to the volume: $\kappa = V^{-1}\partial^2 E_{\text{tot}}/\partial V^2$. Estimate the bulk moduli of alkali metals by assuming that the total energy is equivalent to the kinetic energy of the Fermi gas. What has been neglected in this estimate?

6.4 At what temperature T_0 does the specific heat of the free electrons become larger than the specific heat of the lattice. Express this temperature in terms of the Debye temperature Θ and the electron concentration. Calculate T_0 for copper.

6.5 The benzene molecule C_6H_6 exhibits characteristic optical absorption bands near to the wavelengths 180, 200 and 256 nm. These are explained in terms of $\pi \rightarrow \pi^*$ transitions of the carbon ring skeleton. The occupied π orbitals in the LCAO picture have, respectively: one and the same sign around the C-ring (1st π orbital); one node line through two opposite C–C bonds (2nd π orbital); and one node line through two opposite C atoms (3rd π orbital). From the equal C–C bond length around the ring (~ 1.39 Å) it is inferred that the 6π electrons are not localized in a particular bond but delocalized around the ring. As a simple model for the electronic properties of the π-system a closed, ring-like, one-dimensional electron gas consisting of the 6π electrons is assumed (periodic boundary conditions). Calculate the possible energy eigenvalues E_n for this π system.

a) Successively fill the states with six electrons and determine the optical absorption as the transition between the highest occupied and the lowest unoccupied state. Compare the result with the experimental absorption bands.
b) Sketch the wavefunctions of the free electrons in the π-orbitals and match these to the LCAO orbitals.
c) Discuss reasons why the calculated optical absorption deviates from experimental values.

6.6 A free electron plasma fills the half-space ($z < 0$) up to the surface $z = 0$, where it is bounded by vacuum. Show that the surface wave

$$\phi = \phi_0 \exp(-k|z|) \exp\left[\mathrm{i}\,(kx - \omega t)\right]$$

is a solution of the Laplace equation $\Delta\phi = 0$ and that the Maxwell boundary conditions for the $\mathscr{E}$ and D fields can be fulfilled at the surface $z = 0$, thus giving the condition $\varepsilon(\omega_{\mathrm{sp}}) = -1$ for the existence of the surface plasma wave with frequency ω_{sp}. Derive the dielectric function $\varepsilon(\omega)$ for the undamped free electron plasma and find a relation between the frequencies ω_{p} and ω_{sp} of the bulk and surface plasmons.

6.7 Normal (main sequence) stars are stabilized by a balance between gravitational pressure and radiation pressure arising from nuclear fusion processes occurring in the interior. After burn out and exhaustion of the nuclear fuel a new equilibrium state, that of a white dwarf, can be reached following some loss of mass and a gravitational contraction of the residual star. This contraction is accompanied by the production of a large amount of heat, which causes disintegration of atoms. A plasma of free electrons and positive H and He nuclei is formed whose internal (Fermi) pressure counteracts further gravitational contraction.

a) Calculate in the non-relativistic limit (electron velocity $\ll c$) the average energy of an electron and the average pressure in the electron plasma as a function of electron density n.
b) Making use of the equilibrium between Fermi pressure and gravitational pressure, calculate for the non-relativistic case the mass spectrum $M(\varrho)$ of possible white dwarfs (ϱ is the density of the star).

Hint: It is easy to see that the gravitational energy is proportional to GM^2/R where G is the gravitation constant. However, since the distribution of density in a star is very inhomogeneous, a better approximation for the gravitational pressure at the center of the star is $p_{\mathrm{GR}}(R=0) \simeq 2^{-1/3} G M^{2/3} \varrho^{4/3}$.

c) Investigate whether white dwarfs for which the mass-density relationship of part (b) holds are stable. Plot the total energy for a fixed mass and particle-number against the radius. At which masses is the white dwarf stable?

d) With decreasing radius, the Fermi velocity of the electrons increases. For the relativistic case ($v \cong c$) calculate the average energy per electron and the pressure of the electron plasma as a function of the electron density.

Hint: When the kinetic energy becomes significantly larger than the rest-mass energy, then $E \cong pc = \hbar k c$.

e) For the relativistic case calculate, in analogy to part (b), the equilibrium between Fermi pressure and gravitational pressure and determine the mass M_{crit} for which this is possible. How does M_{crit} compare to the mass of the sun $M_{\mathrm{s}} = 2 \times 10^{30}$ kg?

f) Describe explicitly what happens to stars that have masses $M > M_{\mathrm{crit}}$, $M = M_{\mathrm{crit}}$, and $M < M_{\mathrm{crit}}$. For each of the three cases plot the total energy at fixed mass and particle number as a function of the radius.

g) Calculate the electron density n_{c} at which the non-relativistic approximation must be replaced by the relativistic. This can be achieved with good accuracy by equating the relativistic and non-relativistic electron momenta at the Fermi edge:

$$p_{\mathrm{F}}^{\mathrm{rel}}(n_{\mathrm{c}}) \cong p_{\mathrm{F}}^{\text{non-rel}}(n_{\mathrm{c}}) \; .$$

Compare the mean separation of electrons at this density with their compton wavelength $\lambda_{\mathrm{c}} = \hbar/mc$. What star mass (expressed as a multiple of the sun's mass, M_{s}) corresponds to this density?

Remark: Realistic calculations give an upper limit for the mass of white dwarfs of $M_{\mathrm{crit}} \approx 1.4 M_{\mathrm{s}}$. This upper limit is named the Chandrasekhar limit after the Indian-American astrophysicist Subrahmanyon Chandrasekhar (Nobel prize 1984).

6.8 When the gravitational collapse of a burnt out star leads to even higher interior temperatures, inverse β decay processes ($e + p \rightarrow n$) cause the generation of neutrons (n). In its final state such a star consists only of neutrons (mass m_n). These form a Fermi gas similar to that of the electrons in a white dwarf. Apply the stability criterion derived in Problem 6.7 (Chandrasekhar limit) to the neutron Fermi gas of a neutron star and estimate the critical mass M_{crit}, the critical density ϱ_{crit}, and the critical radius R_{crit} of a neutron star. Compare these with the values for the sun.