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FIP10601 – Text 5

## Thermodynamics of Bloch electrons

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### Equilibrium states for $T \neq 0$

Within the independent-electron approximation, conduction electrons of a metal do not interact with one another, but obey Pauli’s exclusion principle, thus forming a *Fermi gas*. The ground state defines a *Fermi Surface* in  $\mathbf{k}$ -space, with the enclosed volume (occupied states) usually referred to as the *Fermi sea*. But the ground-state could only be an actual state of the system strictly at zero temperature.

From Statistical Mechanics we know how to describe a Fermi gas in thermodynamic equilibrium at a given absolute temperature  $T$ . The starting point is the probability of occupation of one-particle energy states, which is given by the Fermi-Dirac distribution (also called Fermi function),

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}, \quad \text{with } \beta \equiv \frac{1}{k_B T}, \quad (1)$$

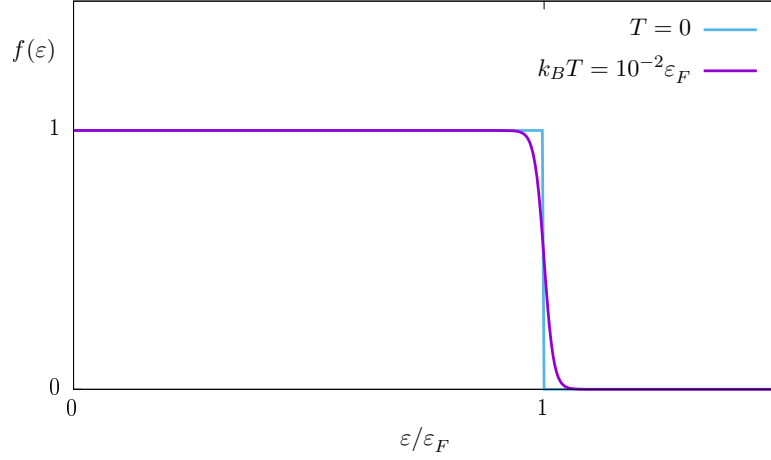
Here the chemical potential  $\mu$  plays an important role, as we are using the *grand-canonical ensemble*, and  $\mu$  must be tuned to ensure the expected number of particles, as we will see in detail below. It can be seen that

$$\lim_{T \rightarrow 0} \mu = \varepsilon_F, \quad (2)$$

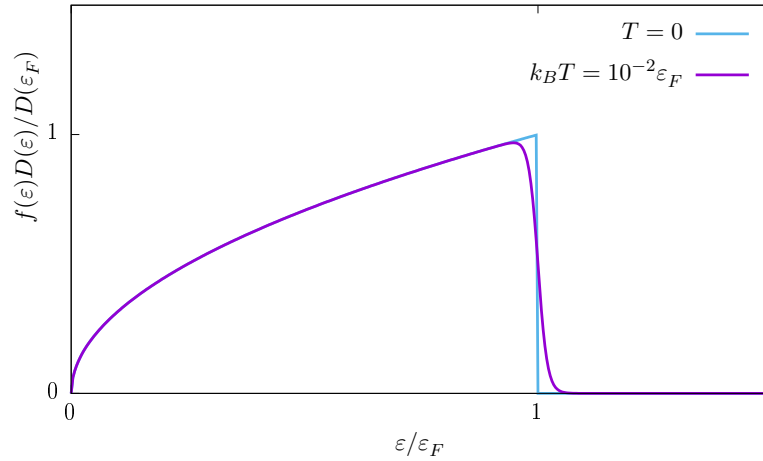
since in this limit  $f(\varepsilon)$  is either 1 or 0 depending on  $(\varepsilon - \mu)$  being, respectively, negative or positive. This is consistent with our previous definition of  $\varepsilon_F$  as the maximum energy of occupied one-electron states in the system’s ground state. Figure 1 shows plots of the Fermi-Dirac distribution for  $T = 0$  and for a non-zero temperature (expressed in terms of the Fermi energy). Note that  $f(\varepsilon)$  deviates from its zero-temperature “step” shape in a region of width  $\sim k_B T$ , roughly centered at  $\varepsilon_F$ .

The Fermi distribution can be used for Bloch electrons, since they are formally non-interacting, but the possible individual energies are constrained to those appearing in the band structure. This information can be taken into account via the density of states (discussed in Text 3), so that we can view the product  $f(\varepsilon)D(\varepsilon)$  as a *distribution of occupied states*. Figure 2 shows an example using a free-electron-like DOS (the reader should be able to verify, from the definitions in Text 3, that this DOS has a square-root shape).

The *Fermi temperature* is defined as  $T_F \equiv \varepsilon_F/k_B$ , with  $\varepsilon_F$  measured from the bottom of the band. Typically, in a metal the Fermi energy has the same order of magnitude of the conduction band width, which is generally in the range 1–10 eV. The conversion factor is



**Figure 1:** Variation of the Fermi function with energy for  $T = 0$  and a low non-zero temperature.



**Figure 2:** Distribution of **occupied** states in a free-electron band as a function of energy, for the same temperatures as in Fig. 1.

approximately  $1.16 \times 10^4 k_B$  K/eV, implying that  $T_F \sim 10^4$ – $10^5$  K. Therefore, the step deformation at room temperature is only about 1%, which reveals that real metals at room temperature are very close to their ground state. So, a zero-temperature concept as the Fermi surface is still useful, even though we expect to have a somewhat *fuzzy* surface, with part of the electrons promoted from states just below the Fermi level to states just above it. Note that the exclusion principle has a huge effect, as electrons deep down in the Fermi sea cannot gain any energy due to the lack of available states.

### Thermodynamic properties

In the absence of applied fields, the most important property of a solid that can be experimentally measured is the specific heat. The electronic contribution to this quantity is given by

$$c_{\text{el}} = \frac{1}{V} \frac{\partial E(T)}{\partial T}, \quad (3)$$

where  $E(T)$  is the total electronic energy at temperature  $T$ .

According to our discussion in the previous section, the energy per unit volume can be expressed as

$$\frac{E(T)}{V} = 2 \int_{-\infty}^{\infty} d\varepsilon D(\varepsilon) f(\varepsilon, T) \varepsilon, \quad (4)$$

with a factor 2 accounting for spin degeneracy. The integral can be over an infinite range because the relevant energy region is selected by  $D(\varepsilon)$ . We explicitly included  $T$  as an argument of the Fermi function to show where the temperature dependence appears on the right-hand side.

We also need to take into account that the average number of electrons per unit volume ( $n = \mathcal{N}/V$ ) must obey the relation

$$n = 2 \int_{-\infty}^{\infty} d\varepsilon D(\varepsilon) f(\varepsilon, T). \quad (5)$$

Since the electron density does not vary with temperature, the above equation determines the chemical potential for which the equality is verified at each chosen temperature, i.e., the function  $\mu(T)$ . We already know this function's zero-temperature limit,  $\mu(0) = \varepsilon_F$ . Considering that  $\mu$  and  $T$  appear in  $f(\varepsilon, T)$  combined in the form  $(\varepsilon - \mu)/k_B T$ , and that an increase of  $T$  alone reduces the denominator in Eq. (1), we may expect  $\mu$  to decrease with increasing  $T$  to compensate the first effect.

Equations (4) and (5) are both of the type

$$I = \int_{-\infty}^{\infty} d\varepsilon g(\varepsilon) f(\varepsilon, T), \quad (6)$$

so that a single scheme may be used to solve both. We already observed that usual experimental conditions involve temperatures that are small in the scale of the Fermi temperature  $T_F$ . We can therefore expect to evaluate thermodynamic quantities of the electron gas using a *low-temperature expansion*, that is, expressing these quantities as power series in  $T$ , or, more precisely,  $T/T_F$ . However, a direct expansion of the Fermi function in Eq. (6) is inconvenient as it would also involve temperature derivatives of the chemical potential. The workaround is as follows.

For  $T \rightarrow 0$ ,  $f(\varepsilon)$  only varies significantly with temperature for  $\varepsilon \sim \mu \sim \varepsilon_F$  (see Fig. 1). Note that  $(-\partial f/\partial \varepsilon) \rightarrow \delta(\varepsilon - \mu)$  as  $T \rightarrow 0$ . Now, integrating the right-hand side of Eq. (6) by parts gives

$$I = \int_{-\infty}^{\infty} d\varepsilon G(\varepsilon) \left( -\frac{\partial f}{\partial \varepsilon} \right), \quad (7)$$

where  $G(\varepsilon)$  is the primitive function of  $g(\varepsilon)$ , i.e.,

$$G(\varepsilon) = \int_{-\infty}^{\varepsilon} d\varepsilon' g(\varepsilon'). \quad (8)$$

The integrand in Eq. (7) contains the energy derivative of the Fermi function, which is strongly peaked at  $\varepsilon = \mu$ . So, it is convenient to expand  $G(\varepsilon)$  in powers of  $\varepsilon - \mu$  (Taylor series). After solving the integrals, we can rearrange the results as a power series in  $T/T_F$ .

The above scheme yields the formal solution

$$I = G(\mu) + G'(\mu)F_1 + G''(\mu)F_2 + \dots \quad (9)$$

where primes indicate derivatives with respect to  $\varepsilon$ , with the results evaluated at  $\varepsilon = \mu$ , and

$$\begin{aligned} F_l &\equiv \frac{1}{l!} \int_{-\infty}^{\infty} d\varepsilon (\varepsilon - \mu)^l \left( -\frac{\partial f}{\partial \varepsilon} \right) \\ &= \frac{(k_B T)^l}{l!} \int_{-\infty}^{\infty} d \left( \frac{\varepsilon - \mu}{k_B T} \right) \left( \frac{\varepsilon - \mu}{k_B T} \right)^l \frac{e^{(\varepsilon - \mu)/k_B T}}{[e^{(\varepsilon - \mu)/k_B T} + 1]^2} \\ &= \frac{(k_B T)^l}{l!} \int_{-\infty}^{\infty} \frac{x^l dx}{(e^x + 1)(1 + e^{-x})} \\ &\equiv \begin{cases} 2 c_l (k_B T)^l & \text{for even } l, \\ 0 & \text{for odd } l. \end{cases} \end{aligned} \quad (10)$$

So, we arrived at an expression explicitly containing powers of  $T$ , besides the implicit dependence through  $\mu(T)$ . The  $c_l$  coefficients can be exactly evaluated. In particular,

$$2 c_2 = \frac{\pi^2}{6}. \quad (11)$$

Therefore, to order  $T^2$ , we can write

$$\int_{-\infty}^{\infty} d\varepsilon g(\varepsilon)f(\varepsilon) = \int_{-\infty}^{\mu} d\varepsilon g(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 \left[ \frac{\partial g(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon=\mu} + \dots \quad (12)$$

This low-temperature expansion is also known as *Sommerfeld expansion*.

### Chemical potential at low temperatures

Using Eqs. (5) and (12), and the fact that  $n(t) = n(0)$ , we have

$$\int_0^{\infty} d\varepsilon D(\varepsilon)f(\varepsilon) = \int_0^{\mu} d\varepsilon D(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 D'(\mu) = \int_0^{\varepsilon_F} d\varepsilon D(\varepsilon). \quad (13)$$

From now on we chose the lower band edge at  $\varepsilon = 0$ , so that  $D(\varepsilon) = 0$  for  $\varepsilon < 0$ . The integral on the right side can be divided in two parts,

$$\int_0^{\varepsilon_F} d\varepsilon D(\varepsilon) = \int_0^{\mu} d\varepsilon D(\varepsilon) + \int_{\mu}^{\varepsilon_F} d\varepsilon D(\varepsilon). \quad (14)$$

For low temperatures  $\varepsilon_F \sim \mu$ . Besides,  $D(\varepsilon)$  is usually a smooth function of  $\varepsilon$ . Thus,

$$\int_{\mu}^{\varepsilon_F} d\varepsilon D(\varepsilon) \simeq D(\varepsilon_F)(\varepsilon_F - \mu), \quad (15)$$

from which it follows that

$$\mu = \varepsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{D'(\varepsilon_F)}{D(\varepsilon_F)} + O(T^4). \quad (16)$$

Note that we replaced  $D'(\mu)$  by  $D'(\varepsilon_F)$  in the coefficient of  $T^2$  since the difference would be of order  $T^4$ . Keeping only the first two terms, we can rewrite this equation as

$$\mu = \varepsilon_F \left[ 1 - \frac{\pi^2}{6} \Lambda_F \left( \frac{T}{T_F} \right)^2 \right], \quad \Lambda_F \equiv \frac{\varepsilon_F D'(\varepsilon_F)}{D(\varepsilon_F)}, \quad (17)$$

where  $\Lambda_F$ , as defined, is a dimensionless quantity of order one. We leave as an **EXERCISE** to show that it assumes the numerical value  $1/2$  for a free-electron DOS (independently of the effective mass  $m^*$ ). This analysis makes it clear that the relative deviations of  $\mu(T)$  with respect to  $\varepsilon_F$  are given as a power series on  $(T/T_F)$ . As expected,  $\mu < \varepsilon_F$  for  $T > 0$ . However, this reduction is negligible in most practical cases, the relative correction having an order of magnitude of  $10^{-4}$  at room temperature.

### Specific heat at low temperatures

Applying the Sommerfeld expansion up to second order to the average energy per unit volume, Eq. (4), gives us

$$\frac{E}{V} = 2 \int_0^{\mu} \varepsilon D(\varepsilon) d\varepsilon + \frac{\pi^2}{3} (k_B T)^2 [\mu D'(\mu) + D(\mu)]. \quad (18)$$

Up to order  $T^2$ , the last term above can be evaluated at  $\mu = \varepsilon_F$ . Furthermore, dividing the integration region as we did when calculating the chemical potential, we have

$$\frac{E}{V} = 2 \int_0^{\varepsilon_F} \varepsilon D(\varepsilon) d\varepsilon + 2\varepsilon_F \left[ (\mu - \varepsilon_F) D(\varepsilon_F) + \frac{\pi^2}{6} (k_B T)^2 D'(\varepsilon_F) \right] + \frac{\pi^2}{3} (k_B T)^2 D(\varepsilon_F). \quad (19)$$

The term in square brackets is equal to zero as a consequence of Eq. (16). Therefore,

$$\frac{E}{V} = \frac{E_0}{V} + \frac{\pi^2}{3} D(\varepsilon_F) (k_B T)^2. \quad (20)$$

Differentiating with respect to the temperature, we obtain the electronic specific heat as

$$c_{\text{el}} = \gamma T, \quad \gamma = 2 \frac{\pi^2}{3} k_B^2 D(\varepsilon_F). \quad (21)$$

with corrections of  $O(T^3)$ .

Once more it is possible to verify that we actually have the ratio  $T/T_F$ . To do this, we may suppose that  $D(\varepsilon)$  grows monotonically with  $\varepsilon$ . If it is not so, we should resort to a hole-band description, for which this assumption would apply. Then, we can define an average of the DOS up to the Fermi energy as

$$\bar{D} \equiv \zeta D(\varepsilon_F) \equiv \frac{1}{\varepsilon_F} \int_0^{\varepsilon_F} d\varepsilon D(\varepsilon) = \frac{n}{2\varepsilon_F}, \quad (22)$$

where  $\zeta$  is a number smaller than 1. Using the above to replace  $D(\varepsilon_F)$  in Eq. (21), we can write the specific heat as

$$c_{\text{el}} = \frac{\pi^2}{3\zeta} n k_B \frac{T}{T_F}. \quad (23)$$

Specific-heat measurements in metals confirm the linear behavior with temperature. From the second equality in Eq. (21), the experimental value of  $\gamma$  may be viewed as a measure of the DOS at the Fermi level. Since the free-electron DOS is easily evaluated, the ratio between experimental and free-electron values of  $\gamma$  may be used to judge how accurate this simplified model might be. This ratio is actually close to 1 for some “well behaved” metals like Na, K, Ag, or Au, but is larger by an order of magnitude for Fe, Nb, or Mn, for example. This may be understood by the presence of narrow (*3d*) bands near the Fermi level in the latter examples, as a narrow band must have a higher DOS in comparison to a wide band to accommodate the same number of states.

Other thermodynamic quantities are mostly related to effects of applied fields, and will be discussed in the remaining Texts of this Unit.

## Thermal properties of semiconductors

We have seen that doped semiconductors are actually conductors with a low electron (or hole) density. This means that the electronic specific heat will show essentially the same behavior, with the  $\gamma$  coefficient being affected by the electron density but also by the effective mass (which affects  $\varepsilon_F$ ).

On the other hand, thermal properties of **intrinsic** semiconductors are strongly affected by the energy gap. Since the system is insulating at zero temperature, the carrier density is due to thermal excitation of electrons from the valence band to the conduction band. Utilizing one of the usual notations, we denote by  $n_c$  the electron density in the conduction band, and by  $p_v$  the hole density in the valence band. The gap energy will be denoted as  $E_g$ , being related to the lower and upper limits of the two bands by

$$E_g = \varepsilon_c - \varepsilon_v. \quad (24)$$

From what we have seen for metals, we can write

$$n_c(T) = \int_{\varepsilon_c}^{\infty} d\varepsilon D_c(\varepsilon) f(\varepsilon) = \int_{\varepsilon_c}^{\infty} d\varepsilon D_c(\varepsilon) \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1}, \quad (25)$$

where  $D_c(\varepsilon)$  is the density of states in the conduction band. Since the probability of a state of energy  $\varepsilon$  to be occupied is given by the Fermi function  $f(\varepsilon)$ , the probability of this state empty being empty is  $1 - f(\varepsilon)$ . Then,

$$p_v(T) = \int_{-\infty}^{\varepsilon_v} d\varepsilon D_v(\varepsilon) \left[ 1 - \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} \right] = \int_{-\infty}^{\varepsilon_v} d\varepsilon D_v(\varepsilon) \frac{1}{e^{(\mu-\varepsilon)/k_B T} + 1}, \quad (26)$$

where  $D_v(\varepsilon)$  is the valence-band DOS, and the last equality derives from a simple algebraic development.

The chemical potential must be near the middle of the gap, since the occupation of states in both bands should be treated in an equal footing. Typical gap widths are of the order of 1 eV, which means that  $\varepsilon_c - \mu \sim \mu - \varepsilon_v \gg k_B T$  at room temperature. Thus, the following approximations are valid:

$$\begin{aligned} \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} &\simeq e^{-(\varepsilon-\mu)/k_B T}, & \varepsilon \geq \varepsilon_c, \\ \frac{1}{e^{(\mu-\varepsilon)/k_B T} + 1} &\simeq e^{-(\mu-\varepsilon)/k_B T}, & \varepsilon \leq \varepsilon_v. \end{aligned} \quad (27)$$

We can separate the dependence on the chemical potential, defining quantities that depend only on characteristics of the two bands,

$$\begin{aligned} N_c(T) &= \int_{\varepsilon_c}^{\infty} d\varepsilon D_c(\varepsilon) e^{-(\varepsilon-\varepsilon_c)/k_B T}, \\ P_v(T) &= \int_{-\infty}^{\varepsilon_v} d\varepsilon D_v(\varepsilon) e^{-(\varepsilon_v-\varepsilon)/k_B T}, \end{aligned} \quad (28)$$

and writing

$$\begin{aligned} n_c(T) &= N_c(T) e^{-(\varepsilon_c-\mu)/k_B T}, \\ p_v(T) &= P_v(T) e^{-(\mu-\varepsilon_v)/k_B T}. \end{aligned} \quad (29)$$

The densities of states  $D_c(\varepsilon)$  and  $D_v(\varepsilon)$  can be chosen as having the form of a free-electron DOS, but with energies measured from the respective band “bottom”, and the electron mass replaced by the corresponding effective mass.

From Eq. (29) we obtain the product

$$n_c p_v = N_c P_v e^{-E_g/k_B T}, \quad (30)$$

which is independent of the chemical potential. Since we are dealing with the intrinsic case, we must have  $n_c = p_v \equiv n_i$ , obtaining the *intrinsic* carrier density (per band)

$$n_i(T) = [N_c(T) P_v(T)]^{1/2} e^{-E_g/2k_B T}. \quad (31)$$

The chemical potential may be obtained by imposing the equality of  $n_i$ , Eq. (31), with  $p_v$  as given by Eq. (29), which yields

$$\mu = \varepsilon_v + \frac{1}{2}E_g + \frac{1}{2}k_B T \ln \left( \frac{P_v}{N_c} \right). \quad (32)$$

Using free-electron-like densities of states for both bands, with the corresponding effective masses, we have (**EXERCISE**)

$$\mu = \varepsilon_v + \frac{1}{2}E_g + \frac{3}{4}k_B T \ln \left( \frac{m_v}{m_c} \right). \quad (33)$$

Note that this result confirms that the chemical potential is near the middle of the gap, approaching this position as  $T \rightarrow 0$ .