

## 0.1 Thermodynamic properties of the non-interacting electron gas

For the non-interacting or weakly interacting electron gas, where we assume the system is a so-called Fermi liquid and the single particle picture still holds, we can write the total energy and total electron number as a function of the density of states (DOS) as follows:

$$\mathcal{E} = \int_{-\infty}^{\infty} E \text{DOS}(E) f(E) dE \quad (1)$$

$$\mathcal{N} = \int_{-\infty}^{\infty} \text{DOS}(E) f(E) dE \quad (2)$$

$$(3)$$

where  $f(E)$  is the Fermi-Dirac occupation number of electronic states.

For metals, where there is no gap near the Fermi level and the DOS is an analytic function, we can use the following identity

$$\int_{-\infty}^{\infty} f(E) h(E) dE = \int_{-\infty}^{\infty} \left(-\frac{\partial f}{\partial E}\right) H(E) dE = H(\mu) + \frac{(\pi k_B T)^2}{6} h'(\mu) + O(T^4) \quad (4)$$

where we have assumed  $H'(E) = h(E)$ , and  $H(-\infty) = 0$ . The proof follows from an integration by parts and a Taylor expansion of the function  $H$  around  $\mu$ . The sommerfeld expansion applied to the total energy and particle number gives:

$$\mathcal{E} = \int_{-\infty}^{\mu} E \text{DOS}(E) dE + \frac{(\pi k_B T)^2}{6} [\mu \text{DOS}'(\mu) + \text{DOS}(\mu)] \quad (5)$$

$$\mathcal{N} = \int_{-\infty}^{\mu} \text{DOS}(E) dE + \frac{(\pi k_B T)^2}{6} \text{DOS}'(\mu)$$

The heat capacity is the energy increase for a temperature increase of 1 Kelvin keeping the volume and the particle number constant:  $C_V = (\partial \mathcal{E} / \partial T)_{V, N}$ .

$$\left(\frac{\partial \mathcal{E}}{\partial T}\right)_{V, N} = \frac{\partial \mu}{\partial T} [\mu \text{DOS}(\mu)] + \frac{(\pi k_B)^2 T}{3} [\mu \text{DOS}'(\mu) + \text{DOS}(\mu)] \quad (6)$$

$$\left(\frac{\partial \mathcal{N}}{\partial T}\right)_{V, \mu} = \frac{(\pi k_B)^2 T}{3} \text{DOS}'(\mu)$$

So that  $\left(\frac{\partial \mu}{\partial T}\right)_{V, N} = -\left(\frac{\partial \mathcal{N}}{\partial T}\right)_{V, \mu} / \left(\frac{\partial \mathcal{N}}{\partial \mu}\right)_{V, T} = -\frac{(\pi k_B)^2 T}{3} \text{DOS}'(\mu) / \text{DOS}(\mu)$ , to linear order in  $T$ . Substituting this expression in the formula for  $\frac{\partial \mathcal{E}}{\partial T}$ , we finally

obtain:

$$C_V = \frac{(\pi k_B)^2 T}{3} DOS(\mu) \quad (7)$$

which shows that at low temperatures, the heat capacity of a Fermi liquid varies linearly with temperature and is also proportional to the density of states at the Fermi level, regardless of the dimensionality or the atomic structure of the system. This result can also be explained using a simple counting argument: the increase in the total energy when the temperature is raised from  $T = 0\text{K}$ , is proportional to the average energy increase of the electrons which cross the Fermi level times their number. The energy increase when electrons go from below the Fermi energy to above it is of the order of  $k_B T$  since the width of the distribution is  $k_B T$ . The number of such electrons is proportional to  $DOS(\mu) k_B T$ , since these are mostly at the Fermi level, or at the order of  $k_B T$  around it. So finally, the energy increase is  $\Delta \mathcal{E} = \mathcal{E}(T) - \mathcal{E}(0) \propto k_B T \times DOS(\mu) k_B T$ , and the heat capacity is  $C_V \propto k_B T \times DOS(\mu)$ .

The relation  $\mathcal{E} = \mathcal{N}e(n, T, V)$  is called the equation of state of an electron gas. Different thermodynamic properties can be obtained by taking derivatives of this quantity. It is therefore important to be able to calculate this equation of state for a given system, from first principles. In the following chapters on Density Functional Theory, and Hartree-Fock, we will see how such equation can be calculated.

### 0.1.1 Metals and semiconductors

The difference between a metal and a semiconductor is in the position of the Fermi level. If the latter lies within a band, one is dealing with a metal, and if it is in the gap (fully filled bands), one is dealing with a semiconductor. To leading order, simple metals<sup>1</sup> despite the strong electron-electron and electron-ion interactions, can be thought of as a free electron gas with quadratic dispersion but with an effective mass. The free electrons are really **quasi-particles** with a quadratic dispersion and large lifetimes, so that they are simulated with free electrons given an effective mass reflecting the crystal potential and inter-electron interactions.

Most properties of Fermi-liquid systems depend on the density of states at the Fermi level. Indeed electrons at the Fermi level are the ones that

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<sup>1</sup>By simple we mean uncorrelated metals for which the Landau Fermi-liquid theory is a good approximation

participate in low-energy phenomena such as conduction, and in thermodynamics properties such as heat capacity, electric or magnetic susceptibility, and compressibility. In all these cases, the property involves excitations of electrons, which are in number proportional to  $\text{DOS}(\mu)$ , from states just below the Fermi level to states just above it (low-energy excitations). So the main thermodynamic properties being proportional to the DOS at the Fermi level, holds only for metals where the DOS near the Fermi level is an analytic function and expansions such as Sommerfeld's can be used. Semiconductors require a different treatment, which is simple but does not use a Sommerfeld expansion. Instead, the Fermi-Dirac function can be replaced by a Maxwell-Boltzmann one, and calculations are then simplified and can be done mostly analytically <sup>2</sup>.

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<sup>2</sup>See exercises