2.5.5. Derivation of the Fermi-Dirac distribution function

To derive the Fermi-Dirac distribution function, we start from a series of possible energies, labeled E_i. At each energy, we can have g_i possible states and the number of states that are occupied equals $g_i f_i$, where f_i is the probability of occupying a state at energy E_i. We also assume that the number of possible states is very large, so that the discrete nature of the states can be ignored.

The number of possible ways - called configurations - to fit $g_i f_i$ electrons in g_i states, given the restriction that only one electron can occupy each state, equals:

$$W_i = \frac{g_i!}{(g_i - g_i f_i)! g_i f_i!} \tag{2.5.6}$$

This equation is obtained by numbering the individual states and exchanging the states rather than the electrons. This yields a total number of $g_i!$ possible configurations. However since the empty states are all identical, we need to divide by the number of permutations between the empty states, as all permutations cannot be distinguished from each other and can therefore only be counted once. In addition, all the filled states are indistinguishable from each other, so we need to divide also by all permutations between the filled states, namely $g_i f_i!$.

The number of possible ways to fit the electrons in the number of available states is called the multiplicity function.

The multiplicity function for the whole system is the product of the multiplicity functions for each energy E_i:

$$W = \prod_i W_i = \prod_i \frac{g_i!}{(g_i - g_i f_i)! g_i f_i!} \tag{2.5.7}$$

Using Stirling's approximation[#], one can eliminate the factorial signs, yielding:

$$\ln W = \sum_i \ln W_i = \sum_i [g_i \ln g_i - g_i (1 - f_i) \ln(g_i - g_i f_i) - g_i f_i \ln g_i f_i] \tag{2.5.8}$$

The total number of electrons in the system equals N and the total energy of those N electrons equals U. These system parameters are related to the number of states at each energy, g_i, and the probability of occupancy of each state, f_i, by:

$$N = \sum_i g_i f_i \tag{2.5.9}$$

and

$$U = \sum_i E_i g_i f_i \tag{2.5.10}$$

[#] See appendix 14.

According to the basic assumption of statistical thermodynamics, all possible configurations are equally probable. The multiplicity function provides the number of configurations for a specific set of occupancy probabilities, f_i. The multiplicity function sharply peaks at the thermal equilibrium distribution since this is the most likely distribution of the system and must therefore be associated with the largest number of - equally probable - configurations. The occupancy probability in thermal equilibrium is therefore obtained by finding the maximum of the multiplicity function, *W*, while keeping the total energy and the number of electrons constant.

For convenience, we maximize the logarithm of the multiplicity function instead of the multiplicity function itself. According to the Lagrange method of undetermined multipliers, we must maximize the following function:

$$\ln W - a\sum_j g_j f_j - b\sum_j E_j g_j f_j \tag{2.5.11}$$

where *a* and *b* need to be determined. The maximum of the multiplicity function, *W*, is obtained from:

$$\frac{\P}{\P(g_i f_i)}\left[\ln W - a\sum_j g_j f_j - b\sum_j E_j g_j f_j\right] = 0 \tag{2.5.12}$$

which can be solved, yielding:

$$\ln\frac{g_i - g_i f_i}{g_i f_i} - a - bE_i = 0 \tag{2.5.13}$$

or

$$f_i = f_{FD}(E_i) = \frac{1}{1 + \exp(a + bE_i)} \tag{2.5.14}$$

which can be written in the following form

$$f_{FD}(E_i) = \frac{1}{1 + \exp(\frac{E_i - E_F}{b})} \tag{2.5.15}$$

with $b = 1/b$ and $E_F = -a/b$. The symbol E_F was chosen since this constant has units of energy and will be the constant associated with this probability distribution.

Taking the derivative of the total energy, one obtains:

$$dU = \sum_i E_i\, d(g_i f_i) + \sum_i g_i f_i\, dE_i \tag{2.5.16}$$

Using the Lagrange equation, this can be rewritten as:

$$dU = b\,d(\ln W) + \sum_i g_i f_i dE_i + E_F dN \tag{2.5.17}$$

Any variation of the energies, E_i, can only be caused by a change in volume, so that the middle term can be linked to a volume variation dV.

$$dU = b\,d(\ln W) + \left[\sum_i g_i f_i \frac{dE_i}{dV}\right] dV + E_F dN \tag{2.5.18}$$

Comparing this to the thermodynamic identity:

$$dU = TdS - pdV + m\,dN \tag{2.5.19}$$

one finds that $b = kT$ and $S = k$ ln$W$, where k is a constant that must be determined . The energy, E_F, equals the energy associated with the particles, namely the electro-chemical potential, m.

The comparison also identifies the entropy, S, as being proportional to the logarithm of the multiplicity function, W. The proportionality constant, k, is known as Boltzmann's constant.

The Fermi-Dirac distribution function then becomes:

$$f_{FD}(E) = \frac{1}{1 + \exp(\frac{E - E_F}{kT})} \tag{2.5.20}$$

Note that this derivation can only truly be followed if one has prior knowledge of statistical thermodynamics. Those who are well versed in this field can quickly derive the Fermi-Dirac and other distribution functions using the Gibbs sum. A more complete description can be found in reference 8 listed in the bibliography at the end of Chapter 2.