5.2 Distribution functions

Having calculated the three overall weight functions for the Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac distribution we now have to calculate the distribution functions themselves. For this we have to answer the question: **What is the most probable configuration?**
This question we have to answer taking into account possible restrictions like conserving the overall energy and/or particle number. Both restrictions represent extensive parameters (i.e. they scale with the size of the system), which is not true for the weight functions W (here the $\prod_i$ shows up and not $\sum_i$). This we can cure by not maximizing W but $\ln(W)$. Further justification will be given in the subsequent sections; here it is enough to state that the entropy $S := k\ln(W)$ becomes an extensive parameter, i.e. for two independent occupation weights W_1 and W_2, having a combined weight $W = W_1W_2$, we find the overall entropy

$$S = S_1 + S_2 = k\ln(W_1) + k\ln(W_2) = k\ln(W_1W_2) = k\ln(W) \quad . \tag{5.11}$$

Our mathematical task is thus

- Maximize $k\,\ln(W)$, i.e. $k\,d\,\ln(W) = 0 = \sum_i \left(\frac{\partial\ln(W)}{\partial n_i}\right) dn_i$
- Under **restriction 1**: Number of particles $N = \sum_i n_i$ is constant, i.e. $\sum_i dn_i = 0$
- Under **restriction 2**: Overall energy $\epsilon = \sum_i n_i\epsilon_i$ is constant, i.e. $\sum_i \epsilon_i dn_i = 0$

To incorporate the restrictions into the optimization problem we will introduce Lagrange parameters β and γ, leading to the final mathematical problem

$$\max\left[k\,\ln(W) - k\,\gamma\left(\sum_i n_i - N\right) - k\,\beta\left(\sum_i \epsilon_i n_i - \epsilon\right)\right] \quad . \tag{5.12}$$

In order to find an explicit solution we now have to specify W, which in our example will be the Maxwell-Boltzmann weight of Eq. (5.6). Using the Stirling formula $\ln(x!) \approx x\ln(x) - x$ we get

$$\begin{aligned} \ln(W) &= n_1\ln(g_1) + n_2\ln(g_2) + n_3\ln(g_3) + \ldots \\ &\quad - \ln(n_1!) - \ln(n_2!) - \ln(n_3!) - \ldots \\ &\approx n_1\ln(g_1) + n_2\ln(g_2) + n_3\ln(g_3) + \ldots \\ &\quad - (n_1\ln(n_1) - n_1) - (n_2\ln(n_2) - n_2) - (n_3\ln(n_3) - n_3) - \ldots \\ &= -(n_1\ln(n_1/g_1)) - (n_2\ln(n_2/g_2)) - \ldots + (n_1 + n_2 + \ldots) \\ &= \sum_i n_i - \sum_i n_i\ln(n_i/g_i) \quad . \end{aligned} \tag{5.13}$$

For the total derivative we find

$$\begin{aligned} d\ln(W) &= \sum_i dn_i - \sum_i dn_i\ln(n_i/g_i) - \sum_i n_i d\ln(n_i/g_i) \\ &= \sum_i dn_i - \sum_i dn_i\ln(n_i/g_i) - \sum_i n_i(dn_i)/n_i \\ &= \sum_i dn_i - \sum_i dn_i\ln(n_i/g_i) - \sum_i dn_i \\ &= -\sum_i dn_i\ln(n_i/g_i) \quad , \end{aligned} \tag{5.14}$$

Inserting Eq. (5.14) into the independent variation for all dn_i of Eq. (5.12) we finally get

$$\ln(n_i/g_i) + \gamma + \beta\epsilon_i = 0 \quad \text{for all } i, \tag{5.15}$$

leading to

$$n_i = g_i e^{-\gamma-\beta\epsilon_i} \quad . \tag{5.16}$$

The physical meaning of the two Lagrange parameters can now easily be extracted by including Eq. (5.16) into Eq. (5.14). We get

$$\begin{aligned} \frac{dS}{k} &= d\ln(W) = -\sum_i dn_i \ln(n_i/g_i) \\ &= -\sum_i dn_i(-\gamma - \beta\epsilon_i) \\ &= \gamma dN + \beta d\epsilon \end{aligned} \tag{5.17}$$

From classical thermodynamics we know

$$d\epsilon = dU = \mu dN + TdS - pdV \quad \text{, so} \quad \frac{\partial S}{\partial N} = -\frac{\mu}{T} \quad \text{and} \quad \frac{\partial S}{\partial \epsilon} = \frac{1}{T} \quad . \tag{5.18}$$

Comparison with Eq. (5.17) gives

$$\gamma = -\frac{\mu}{kT} \quad \text{and} \quad \beta = \frac{1}{kT} \quad , \tag{5.19}$$

leading to the well known Maxwell-Boltzmann distribution function

$$n_i = g_i e^{-\frac{\epsilon_i - \mu}{kT}} \quad . \tag{5.20}$$

The two Lagrange parameter can now be determined by fulfilling the restrictions. From restriction 1 we get

$$N = \sum_i n_i = \sum_i g_i e^{-\gamma - \beta\epsilon_i} = e^{-\gamma} \sum_i g_i e^{-\beta\epsilon_i} = e^{-\gamma} Z \quad . \tag{5.21}$$

So by introducing the partition function

$$Z = \sum_i g_i e^{-\beta\epsilon_i} \tag{5.22}$$

we get

$$n_i = \frac{N}{Z} g_i e^{-\beta\epsilon_i} \quad . \tag{5.23}$$

Note: That γ (and thus μ) does not show up in the final results is a common feature of the Maxwell-Boltzmann distribution function and thus of classical particles. Consequently the canonical ensemble (cf. section 5.4) is typically used to describe systems of classical particles.
From restriction 2 we get

$$\epsilon = \frac{N}{Z} \sum_i g_i e^{-\beta\epsilon_i} \epsilon_i \tag{5.24}$$

which in an alternative form can be written as

$$\epsilon = -\frac{N}{Z}\frac{dZ}{d\beta} = -N \frac{d}{d\beta} \ln(Z) \tag{5.25}$$

So having calculated the partition function Z, the entropy of the system can be calculated. The fundamental meaning of $\ln(Z)$ will be discussed in larger detail in the remaining sections. There entropy will be discussed from a more general point of view and makes it unnecessary to solve the maximization problem for the entropy for the Bose-Einstein and Fermi-Dirac distributions separately. Here we will just state the final results:

$$\text{Bose-Einstein distribution:} \quad n_i = \frac{g_i}{e^{\frac{\epsilon_i - \mu}{kT}} - 1} \quad . \tag{5.26}$$

$$\text{Fermi-Dirac distribution:} \quad n_i = \frac{g_i}{e^{\frac{\epsilon_i - \mu}{kT}} + 1} \quad . \tag{5.27}$$