5.1 Configuration, weights, and probabilities

In what follows we will discuss possible arrangements of particles in states, i.e. configurations, and the probabilities to find these arrangements. The reason for this is quite simple: **The most probable configuration(s) will be found in nature**, i.e. thermodynamic systems. This is a quite obvious statement but it is the key for understanding entropy and all properties of classical thermodynamics as discussed up to now.
Fig. 5.1 a) shows an example of different arrangements of two particles in a three level system. Some general features can be seen:

- Energy levels are labeled by integer numbers $i = 0, 1, 2$
- Each energy level has an energy ϵ_i with typically $\epsilon_0 = 0$ (by convention)
- n_i labels the occupation numbers of each energy level
- A configuration is the overall set of occupation numbers $\{n_0, n_1, n_2\}$

In our example two configuration are shown: $\{2, 0, 0\}$ vs. $\{1, 1, 0\}$. Obviously the configuration $\{1, 1, 0\}$ has a larger weight $W = 2$ (number of arrangements for occupying states in one configuration) than $\{2, 0, 0\}$ with $W = 1$. But several aspects have been neglected for the comparison of both configurations:

- Both configurations differ in the overall energy, and thus in their temperature dependence
- Particles have been assumed to be distinguishable, otherwise configuration $\{1, 1, 0\}$ would have the same weight $W = 1$ as configuration $\{2, 0, 0\}$.

Fig. 5.1 b) emphasizes the dependence of weights on the nature of particles, i.e. if they are distinguishable or indistinguishable. To be principally indistinguishable is a property of quantum mechanical particles, which is not so easy to understand and with dramatic consequences for many particle systems, some of which we will discuss as well here. For the moment is is enough to take indistinguishable as identical and distinguishable as non-identical particles.

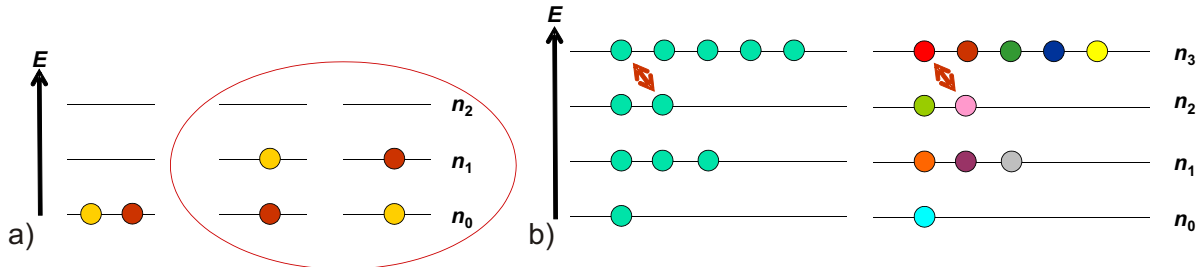


Figure 5.1: a) Dependence of occupation weights on configuration; b) Dependence of occupation weights on particles being distinguishable or indistinguishable.

Obviously for non-identical particles many more arrangements exist which for the example in Fig. 5.1 b) can be calculated easily

$$W = \frac{N!}{n_0!n_1!n_2!...} = \frac{N!}{\prod_i n_i!} = \frac{\text{total number of variations}}{\text{number of variation inside the same level}} \tag{5.1}$$

The following table shows for a four level system two configurations of 10 non-identical particles which have the same overall energy.

level i	n_i		E_i	n_iE_i	
3	0	1	4	0	4
2	0	2	3	0	6
1	10	3	2	20	6
0	0	4	1	0	4
	$\sum n_i = 10$			$\sum n_iE_i = 20$	

According to Eq. (5.1) the weight for configuration $\{0, 10, 0, 0\}$ is

$$W = \frac{10!}{10!} = 1 \quad . \tag{5.2}$$

The weight for configuration $\{4, 3, 2, 1\}$ is

$$W = \frac{10!}{1!2!3!4!} = 12600 \quad , \tag{5.3}$$

so even under the restriction of two states having the same overall energy large differences in the weights can exist. Configuration $\{0, 10, 0, 0\}$ is much less probable than configuration $\{4, 3, 2, 1\}$.
To find the full solution for weights of distinguishable particles (i.e. classical particles) we have to introduce the degeneracy of an energy level g_i. According to the above definition i indicates states with different energies, but several states may have the same energy. For example without magnetic fields states with spin up and spin down have the same energy, so the degeneracy is $g = 2$. The same is true for electrons in atomic orbitals having the same quantum number l. The degeneracy is $g = (2l + 1)2$; here the last factor 2 takes into account the two spin orientation. In summary the weight W_i to occupy energy level i for distinguishable particles can be calculated as follows:

- The weight for arranging N distinguishable particles in a configuration $\{n_0, n_1, \cdots\}$ is

$$W = \frac{N!}{\prod_i n_i!} \tag{5.4}$$

- Taking into account a possible degeneracy g_i of each energy level i the weight increases to

$$W = \frac{N! \prod_i (g_i)^{n_i}}{\prod_i n_i!} \tag{5.5}$$

- As we learned from the Gibbs paradox even classical particles must be assumed to be "somehow non distinguishable". This can be achieved by omitting $N!$ in the weight leading to

$$W = \frac{\prod_i (g_i)^{n_i}}{\prod_i n_i!} \tag{5.6}$$

- This is the weight for the famous **Maxwell-Boltzmann** distribution. It holds for classical particle at "normal" temperatures and "normal" masses.

Bosons are quantum mechanical particles, i.e. principally indistinguishable, for which each energy level can be occupied with an unlimited number of particles (because they have a symmetric quantum mechanical many particle state function). An example for the distribution of n_i bosons in one energy level E_i with a degeneracy g_i is shown in Fig. 5.2. The $g_i - 1$ vertical lines indicate the limits of the degenerate states.

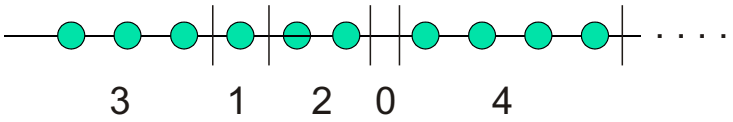


Figure 5.2: Scheme of distribution of bosons into degenerated states belonging to one energy.

The n_i circles indicate the particles being arranged into states as indicated by the vertical lines. Any arrangement of circles and vertical lines is an allowed configuration and the number of these arrangements is $(n_i + g_i - 1)!$. Interchanging the n_i particles gives always the identical state, the same is true for the $g_i - 1$ vertical lines. So the weight for occupying this state is

$$W_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad , \tag{5.7}$$

leading to the overall weight, i.e. the weight of the **Bose-Einstein distribution**,

$$W = \prod_i W_i = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!} \quad . \tag{5.8}$$

Fermions are quantum mechanical particles, i.e. principally indistinguishable, for which each energy level can only be occupied once (because they have an antisymmetric quantum mechanical many particle state function). As outlined before, e.g. the two spin states are taken into account by the degeneracy g_i. Distributing n_i fermions in one energy level E_i with a degeneracy g_i can be described as follows:
The first particle we can put into any of the g_i states. The second particle can be put into any one of the remaining $g_i - 1$ states. So the weight W_i is given by

$$W_i = g_i(g_i - 1)(g_i - 2)...(g_i - n_i + 1) = \frac{g_i!}{(g_i - n_i)!} \quad , \tag{5.9}$$

leading to the overall weight, i.e. the weight of the **Fermi-Dirac distribution**,

$$W = \prod_i W_i = \prod_i \frac{g_i!}{(g_i - n_i)!} \quad . \tag{5.10}$$