

5.2: Quantum and Classical Statistics

Types of Permutation Symmetry

Classical particles are either distinguishable or non-distinguishable, a difference that influences the relation between the system partition function and the molecular partition function (Section [s_from_z]). Quantum particles are special. They are always indistinguishable, but there exist two types that behave differently when two particles are permuted. For *bosons*, the wavefunction is unchanged on such permutation, whereas for *fermions* the wavefunction changes sign. This sign change does not make the particles distinguishable, as absolute phase of the wavefunction does not correspond to an observable. However, it has important consequences for the population of microstates. Two (or more) bosons can occupy the same energy level. In the limit $T \rightarrow 0$ they will all occupy the ground state and form a *Bose-Einstein condensate*. Bosons are particles with integer spin, with the composite boson ${}^4\text{He}$ (two protons, two neutrons, two electrons) probably being the most famous example. In contrast, two fermions (particles with half-integer spin) cannot occupy the same state, a fact that is known as *Pauli exclusion principle*. Protons, neutrons, and electrons are fermions (spin 1/2), whereas photons are bosons (spin 1).

This difference in permutation symmetry influences the distribution of particles over energy levels. The simplest example is the distribution of two particles to two energy levels ϵ_l (for 'left') and ϵ_r (for 'right') . For distinguishable classical particles four possible configurations exist:

1. ϵ_l is doubly occupied
2. ϵ_l is occupied by particle A and ϵ_r is occupied by particle B
3. ϵ_l is occupied by particle B and ϵ_r is occupied by particle A
4. ϵ_r is doubly occupied.

For bosons and for indistinguishable classical particles as well, the second and third configuration above cannot be distinguished. Only three configurations exist:

1. ϵ_l is doubly occupied
2. ϵ_l is occupied by one particle and ϵ_r is occupied by one particle
3. ϵ_r is doubly occupied.

For fermions, the first and third configuration of the boson case are excluded by the Pauli principle. Only one configuration is left:

1. ϵ_l is occupied by one particle and ϵ_r is occupied by one particle.

Since the number of configurations enters into all probability considerations, we shall find different probability distributions for systems composed of bosons, fermions, or distinguishable classical particles. The situation is most transparent for an ideal gas, i.e. N non-interacting point particles that have only translational degrees of freedom . For such a system the spectrum of energy levels is continuous.

Bose-Einstein Statistics

We want to derive the probability distribution for the occupation of energy levels by bosons. To that end, we first pose the question how many configurations exist for distributing N_i particles to A_i energy levels in the interval between ϵ_i and $\epsilon_i + d\epsilon$. Each level can be occupied by an arbitrary number of particles. We picture the problem as a common set of particles P_k ($k = 1 \dots N_i$) and levels L_k ($k = 1 \dots A_i$) that has $N_i + A_i$ elements. Now we consider all permutations in this set and use the convention that particles that stand left from a level are assigned to this level. For instance, the permutation $\{P_1, P_2, L_1, P_3, L_2, L_3\}$ for three particles and three levels denotes a state where level L_1 is occupied by particles P_1 and P_2 , level L_2 is occupied by particle P_3 and level L_3 is empty. With this convention the last energy level is necessarily the last element of the set (any particle standing right from it would not have an associated level), hence only $(N_i + A_i - 1)!$ such permutations exist. Each permutation also encodes a sequence of particles, but the particles are indistinguishable. Thus we have to divide by $N_i!$ in order to not double count configurations that we cannot distinguish. It also does not matter in which sequence we order the levels with their associated subsets of particles. Without losing generality, we can thus consider only the sequence with increasing level energy, so that the level standing right (not included in the number of permutations $(N_i + A_i - 1)!$) is the level with the highest energy. For the remaining $A_i - 1$ lower levels we have counted $(A_i - 1)!$ permutations, but should have counted only the properly ordered one. Hence, we also have to divide by $(A_i - 1)!$. Therefore, the number of configurations and thus the number of microstates in the interval between ϵ_i and $\epsilon_i + d\epsilon$ is

$$C_i = \frac{(N_i + A_i - 1)!}{N_i! (A_i - 1)!} . \quad (5.2.1)$$

The configurations in energy intervals with different indices i are independent of each other. Hence, the statistical weight of a macrostate is

$$\Omega = \prod_i \frac{(N_i + A_i - 1)!}{N_i! (A_i - 1)!} \quad (5.2.2)$$

As the number of energy levels is, in practice, infinite, we can choose the A_i sufficiently large for neglecting the 1 in $A_i - 1$. In an exceedingly good approximation we can thus write

$$\Omega = \prod_i \frac{(N_i + A_i)!}{N_i! A_i!} . \quad (5.2.3)$$

The next part of the derivation is the same as for the Boltzmann distribution in Section [subsection:Boltzmann], i.e., it relies on maximization of $\ln \Omega$ using the Stirling formula and considering the constraints of conserved total particle number $N = \sum_i N_i$ and conserved total energy of the system. The initial result is of the form

$$\frac{N_i}{A_i} = \frac{1}{B e^{-\beta \epsilon_i} - 1} , \quad (5.2.4)$$

where B is related to the Lagrange multiplier α by $B = e^{-\alpha}$ and thus to the chemical potential by $B = e^{-\mu/(k_B T)}$. After a rather tedious derivation using the definitions of Boltzmann entropy and $(\partial u / \partial s)_V = T$ we can identify β with $-1/k_B T$. We refrain from reproducing this derivation here, as the argument is circular: It uses the identification of k with k_B in the definition of Boltzmann entropy that we had made earlier on somewhat shaky grounds. We accept the identification of $|\beta|$ with $1/k_B T$ as general for this type of derivations, so that we finally have

$$\frac{N_i}{A_i} = \frac{1}{B e^{\epsilon_i/k_B T} - 1} . \quad (5.2.5)$$

Up to this point we have supposed nothing else than a continuous, or at least sufficiently dense, energy spectrum and identical bosons. To identify B we must have information on this energy spectrum and thus specify a concrete physical problem. When using the *density of states* for an ideal gas consisting of quantum particles with mass m in a box with volume V (see Section [section:gas_translation] for derivation),

$$D(\epsilon) = 4\sqrt{2}\pi \frac{V}{h^3} m^{3/2} \epsilon^{1/2} , \quad (5.2.6)$$

we find, for the special case $B e^{\epsilon_i/k_B T} \gg 1$,

$$B = \frac{(2\pi m k_B T)^{3/2}}{h^3} \cdot \frac{V}{N} . \quad (5.2.7)$$

Fermi-Dirac Statistics

The number N_i of fermions in an energy interval with A_i levels cannot exceed A_i . The number of allowed configurations is now given by the number of possibilities to select N_i out of A_i levels that are populated, whereas the remaining levels remain empty. As each level can exist in only one of two conditions, populated or empty, this is a binomial distribution problem as we have solved in Section [binomial_distribution]. In Equation ???) we need to substitute N by A_i and n by N_i . Hence, the number of allowed configurations in the energy interval between ϵ_i and $\epsilon_i + \Delta\epsilon_i$ is given by

$$C_i = \frac{A_i!}{N_i! (A_i - N_i)!} \quad (5.2.8)$$

and, considering mutual independence of the configurations in the individual energy intervals, the statistical weight of a macrostate for fermions is

$$\Omega = \prod_i \frac{A_i!}{N_i! (A_i - N_i)!} . \quad (5.2.9)$$

Again, the next step of the derivation is analogous to derivation of the Boltzmann distribution in Section [subsection:Boltzmann]. We find

$$\frac{N_i}{A_i} = \frac{1}{Be^{\epsilon_i/k_B T} + 1} \quad (5.2.10)$$

For the special case $Be^{\epsilon_i/k_B T} \gg 1$, B is again given by Equation 5.2.7. Comparison of Equation 5.2.10 with Equation 5.2.5 reveals as the only difference the sign of the additional number 1 in the denominator on the right-hand side of the equations. In the regime $Be^{\epsilon_i/k_B T} \gg 1$, for which we have specified B , this difference is negligible.

It is therefore of interest when this regime applies. As $\epsilon_i \geq 0$ in the ideal gas problem, we have $e^{\epsilon_i/k_B T} \geq 1$, so that $B \gg 1$ is sufficient for the regime to apply. Wedler and Freund have computed values of B according to Equation 5.2.7 for the lightest ideal gas, H_2 , and have found $B \gg 1$ for $p = 1$ bar down to $T = 20$ K and at ambient temperature for pressures up to $p = 100$ bar. For heavier molecules, B is larger under otherwise identical conditions. Whether a gas atom or molecule is a composite boson or fermion thus does not matter, except at very low temperatures and very high pressures. However, if conduction electrons in a metal, for instance in sodium, are considered as a gas, their much lower mass and higher number density N/V leads to $B \ll 1$ at ambient temperature and even at temperatures as high as 1000 K. Therefore, a gas model for conduction electrons (spin 1/2) must be set up with Fermi-Dirac statistics.

Maxwell-Boltzmann Statistics

In principle, atoms and molecules are quantum objects and not classical particles. This would suggest that the kinetic theory of gases developed by Maxwell before the advent of quantum mechanics is deficient. However, we have already seen that for particles as heavy as atoms and molecules and number densities as low as in gases at atmospheric pressure or a bit higher, the difference between Bose-Einstein and Fermi-Dirac statistics vanishes, unless temperature is very low. This suggests that, perhaps, classical Maxwell-Boltzmann statistics is indeed adequate for describing gases under common experimental conditions.

We assume distinguishable particles. Each of the N_i particles can be freely assigned to one of the A_i energy levels. All these configurations can be distinguished from each other, as we can picture each of the particles to have an individual tag. Therefore,

$$C_i = (A_i)^{N_i} \quad (5.2.11)$$

configurations can be distinguished in the energy interval between ϵ_i and $\epsilon_i + \Delta\epsilon_i$. Because the particles are distinguishable ('tagged'), the configurations in the individual intervals are generally not independent from each other, i.e. the total number of microstates does not factorize into the individual numbers of microstates in the intervals. We obtain *more* configurations than that because we have the additional choice of distributing the N 'tagged' particles to r intervals. We have already solved this problem in Section [subsection:Boltzmann], the solution is Equation ????. By considering the additional number of choices, which enters multiplicatively, we find for the statistical weight of a macrostate

$$\Omega = \frac{N!}{N_0! N_1! \dots N_{r-1}!} \cdot A_0^{N_0} \cdot A_1^{N_1} \cdot \dots \cdot A_{r-1}^{N_{r-1}} \quad (5.2.12)$$

$$= N! \prod_i \frac{A_i^{N_i}}{N_i!} \quad (5.2.13)$$

It appears that we have assumed a countable number r of intervals, but as in the derivations for the Bose-Einstein and Fermi-Dirac statistics, nothing prevents us from making the intervals arbitrarily narrow and their number arbitrarily large.

Again, the next step in the derivation is analogous to derivation of the Boltzmann distribution in Section [subsection:Boltzmann]. All the different statistics differ only in the expressions for Ω , constrained maximization of $\ln \Omega$ uses the same Lagrange ansatz. We end up with

$$\frac{N_i}{A_i} = \frac{1}{Be^{\epsilon_i/k_B T}} \quad (5.2.14)$$

Comparison of Equation 5.2.14 with Equation 5.2.5 and 5.2.10 reveals that, again, only the 1 in the denominator on the right-hand side makes the difference, now it is missing. In the regime, where Bose-Einstein and Fermi-Dirac statistics coincide to a good approximation, both of them also coincide with Maxwell-Boltzmann statistics.

There exist two caveats. First, we already know that the assumption of distinguishable particles leads to an artificial mixing entropy for two subsystems consisting of the same ideal gas or, in other words, to entropy not being extensive. This problem does not, however, influence the probability distribution, it only influences scaling of entropy with system size. We can solve it by an *ad hoc* correction when computing the system partition function from the molecular partition function. Second, to be consistent we should not use the previous expression for B , because it was derived under explicit consideration of quantization of momentum.¹⁷ However, for Maxwell-Boltzmann statistics B can be eliminated easily. With $\sum_i N_i = N$ we have from Equation 5.2.14

$$N = \frac{1}{B} \sum_i A_i e^{-\epsilon_i/k_B T}, \quad (5.2.15)$$

which gives

$$\frac{1}{B} = \frac{N}{\sum_i A_i e^{-\epsilon_i/k_B T}}. \quad (5.2.16)$$

With this, we can express the distribution function as

$$P_i = \frac{N_i}{N} = \frac{A_i e^{-\epsilon_i/k_B T}}{\sum_i A_i e^{-\epsilon_i/k_B T}}. \quad (5.2.17)$$

Comparison of Equation 5.2.17 with the Boltzmann distribution given by Equation ??? reveals the factors A_i as the only difference. Thus, the probability distribution for Maxwell-Boltzmann statistics deviates from the most common form by the **degree of degeneracy** A_i of the individual levels. This degeneracy entered the derivation because we assumed that within the intervals between ϵ_i and $\epsilon_i + \Delta\epsilon_i$ several levels exist. If $\Delta\epsilon_i$ is finite, we speak of *near degeneracy*. For quantum systems, degeneracy of energy levels is a quite common phenomenon even in small systems where the energy spectrum is discrete. In order to describe such systems, the influence of degeneracy on the probability distribution must be taken into account.

Concept 5.2.1: Degeneracy

In quantum systems with discrete energy levels there may exist g_i quantum states with the same energy ϵ_i that do not coincide in all their quantum numbers. This phenomenon is called *degeneracy* and g_i the *degree of degeneracy*. A set of g_i degenerate levels can be populated by up to g_i fermions. In the regime, where Boltzmann statistics is applicable to the quantum system, the probability distribution considering such degeneracy is given by

$$P_i = \frac{N_i}{N} = \frac{g_i e^{-\epsilon_i/k_B T}}{\sum_i g_i e^{-\epsilon_i/k_B T}} \quad (5.2.18)$$

and the molecular partition function by

$$Z = \sum_i g_i e^{-\epsilon_i/k_B T}. \quad (5.2.19)$$

The condition that degenerate levels do not coincide in all quantum numbers makes sure that the Pauli exclusion principle does not prevent their simultaneous population with fermions.

At this point we can summarize the expected number of particles with chemical potential μ at level i with energy ϵ_i and arbitrary degeneracy g_i for Bose-Einstein, Fermi-Dirac, and Boltzmann statistics:

$$N_i = \frac{g_i}{e^{(\epsilon_i - \mu)/(k_B T)} - 1} \quad \text{Bose - Einstein statistics} \quad (5.2.20)$$

$$N_i = \frac{g_i}{e^{(\epsilon_i - \mu)/(k_B T)} + 1} \quad \text{Fermi - Dirac statistics} \quad (5.2.21)$$

$$N_i = \frac{g_i}{e^{(\epsilon_i - \mu)/(k_B T)}} \quad \text{Boltzmann statistics.} \quad (5.2.22)$$

Note that the chemical potential μ in these equations is determined by the condition $N = \sum_i N_i$. The constant B in the derivations above is given by $B = e^{-\mu/(k_B T)}$. If N is not constant, we have $\mu = 0$ and thus $B = 1$.

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