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Statistical Thermodynamics

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Chapter 1

CLASSICAL MAXWELL-BOLTZMANN STATISTICS

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A Modeling a Gas in an Enclosure

To model a gas in an enclosure, imagine a closed opaque box containing N balls randomly distributed on a shelf with k levels:

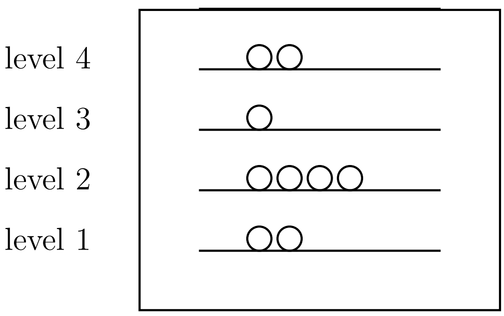


FIG. 1.1. N balls on k levels. $N = 9$ and $k = 4$.

Let n_i be the number of balls on level i: $n_1 = 2, \quad n_2 = 4, \quad n_3 = 1, \quad n_4 = 2.$

We assume that the potential energy levels ε_i of the different levels model the kinetic energy levels of translation of the gas particles.

In the following example, we determine the set $\{n_1, n_2, \ldots, n_k\}$ of the k numbers of balls on the shelf using the initial assumptions on the total number N of balls and the internal energy U of the gas in the enclosure.

Notation 1.1: Most Probable Set

The most probable set will be denoted $\{n_1^0, n_2^0, \ldots, n_k^0\}$.

This amounts to finding the distribution of balls that one would most likely see if the box were opened.

Example A.1. Initial assumptions:

- the total number of balls is $N = 2$
- the internal energy (in joules) of the system is $U = \sum_{i=1}^{N} \varepsilon_i n_i = 2$ J
- the potential energies of each level are as follows:

$$\varepsilon_1 = 0 \text{ J}, \quad \varepsilon_2 = 1 \text{ J}, \quad \varepsilon_3 = 2 \text{ J}$$

There are three energy levels, corresponding to three possible shelves. We seek the set of three numbers $\{n_1^0, n_2^0, n_3^0\}$.

Here are the different possibilities for distributing the two balls A and B in the box:

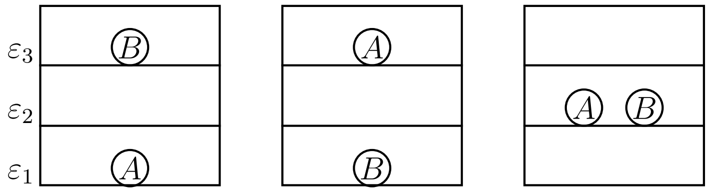


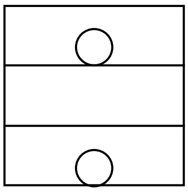
Fig. 1.2. Distribution of the two balls A and B in the box

We have twice as much chance of having one ball on level ε_1 and one on level ε_3, than two balls on level ε_2. The sought set is therefore $n_1^0 = 1$, $n_2^0 = 0$, $n_3^0 = 1$.

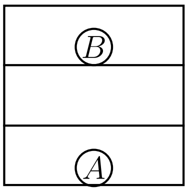
Definition 1.1: Macroscopic State

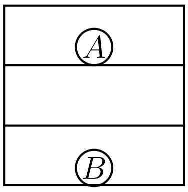
The specification of the set of k particle numbers $\{n_1, n_2, \ldots, n_k\}$ where a number n_i of particles is associated with each energy level $\varepsilon_{i=1\ldots k}$, defines a macroscopic state.

The most probable macroscopic state is this one

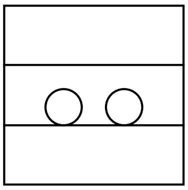


because it is realized by two microstates (two distributions):

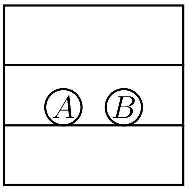




The other macroscopic state,



is realized by only one microstate:



The total number of microstates is:

$$\begin{aligned} W_T &= W(1,0,1) + W(0,2,0) \\ &= 3 \end{aligned}$$

The thermodynamic probabilities $P(n_1, n_2, n_3)$ of the different macroscopic states are given by their numbers of microstates $W(n_1, n_2, n_3)$ divided by the total number of microstates W_T:

$$P(1,0,1) = 2/3$$

$$P(0,2,0) = 1/3$$

Consequently, the most probable macroscopic state $\{n_1, n_2, \dots, n_k\}$ (denoted $\{n_1^0, n_2^0, \dots, n_k^0\}$) is the one with the highest number of microstates $W(n_1, n_2, \dots, n_k)$.

Notation 1.2: Number of Microstates of the Most Probable Macroscopic State

The number of microstates of the most probable macroscopic state $\{n_1^0, n_2^0, \dots, n_k^0\}$ is denoted $W^0(n_1^0, n_2^0, \dots, n_k^0)$.

By abuse of language, we will confuse thermodynamic probability and number of microstates.

Notation 1.3: Thermodynamic Probability

We will denote $W(n_1, n_2, n_3)$ the thermodynamic probability.

B Boltzmann's Assumptions

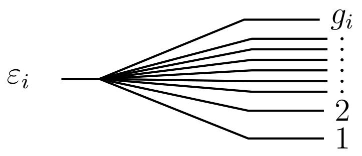
- the microstates are equally probable
- the probability of a macroscopic state is equal to the number of microstates that realize it divided by the total number of microstates
- the thermodynamic equilibrium state corresponds to the most probable macroscopic state

C Degeneracy

It often happens that an energy level ε_i is composed of g_i degenerate sub-levels. This degeneracy confers different statistical weights g_i to the various energy levels. For example, for an atom, when several atomic orbitals correspond to the same energy level, this energy level is said to be degenerate. This degeneracy can be lifted by a magnetic field.

Definition 1.2: Degeneracy

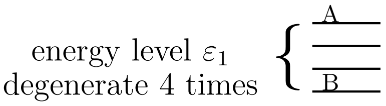
The degeneracy or statistical weight of the energy level ε_i, is the number g_i of sub-levels contained in this energy level.

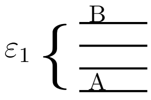


Definition 1.3: Microscopic State

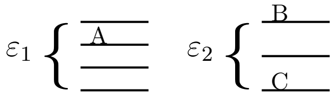
The specification of the g_i numbers of particles per energy sub-level, for each of the k energy levels ε_i, defines a microscopic state.

Determining a microscopic state is experimentally impossible. For example, the following microstates constitute one and the same microscopic state:

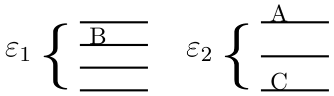




Similarly, the following microstates



and



are one and the same microscopic state.

D Classical Maxwell-Boltzmann Statistics

Initial assumptions:

- the number of particles: N
- the internal energy of the system: U
- the energy of each level i: $\varepsilon_{i=1,\dots,k}$
- the degeneracy of each level i: $g_{i=1,\dots,k}$

The problem is to determine the most probable macroscopic state $\{n_1, n_2, \dots, n_k\}$, the one whose associated number of microstates is the highest.

Suppose there are n_1 distinguishable particles on ε_1, n_2 on $\varepsilon_2, \dots, n_k$ on ε_k. The particles being assumed distinguishable here, they can be interchanged. In how many ways can this distribution be realized? In other words, what is its number of microstates W? Let's proceed step by step:

a) What is the number of ways to place one distinguishable particle on the energy level ε_1 degenerate g_1 times?

   The answer is g_1.

b) What is the number of ways to place two distinguishable particles on the energy level ε_1 degenerate g_1 times?

   g_1 possibilities for the first particle and g_1 for the second, so $g_1 \times g_1 = g_1^2$.

c) What is the number of ways to place n_1 distinguishable particles on the energy level ε_1 degenerate g_1 times?

   $g_1 \times g_1 \times \cdots \times g_1 = g_1^{n_1}$.

d) What is the number of ways to place n_2 distinguishable particles on the energy level ε_2 degenerate g_2 times?

   $g_2 \times g_2 \times \cdots \times g_2 = g_2^{n_2}$.

e) What is the number of ways to place n_1 distinguishable particles on the energy level ε_1 degenerate g_1 times and n_2 particles on the energy level ε_2 degenerate g_2 times?

$g_1^{n_1}\, g_2^{n_2}$

f) What is the number of ways to choose 2 distinguishable particles among N?

N choices for the first "A" and $N-1$ choices for the second "B". But choosing A first then B second is equivalent to choosing B first then A second, because the order in which they are chosen does not matter. The 2! ways to choose the particles are equivalent. The answer is therefore: $N(N-1)/2!$

g) What is the number of ways to choose n_1 distinguishable particles among N?

$\frac{N\times(N-1)\times\cdots\times(N-n_1+1)}{n_1!}$

h) Setting $N = n_1+n_2$, what is the number of ways to choose n_1 distinguishable particles among N?

$$\begin{aligned}&\frac{N\times(N-1)\times\cdots\times(N-n_1+1)}{n_1!}\\ &=\frac{N\times(N-1)\times\cdots\times(N-n_1+1)}{n_1!}\times\frac{(N-n_1)\times\cdots\times 1}{(N-n_1)\times\cdots\times 1}\\ &=\frac{N!}{n_1!\,n_2!}\end{aligned}$$

Remark 1.1

nother way to obtain the number of possible distributions is to start from one distribution and consider that another is obtained by permuting 2 particles that are not on the same level ε_1 or ε_2. So we start from one of the distributions, permute all the particles, i.e. $N!$ permutations, and do not take into account the $n_1!$ and $n_2!$ permutations that occur in the same set n_1 or n_2: $N!/(n_1!\,n_2!)$

i) What is the number of ways to place N distinguishable particles by putting n_1 on the energy level ε_1 degenerate g_1 times, and n_2 on the energy level ε_2 degenerate g_2 times?

$\frac{N!}{n_1!\,n_2!}\, g_1^{n_1} g_2^{n_2}$

j) What is the number of ways to place N distinguishable particles on k degenerate energy levels?

$$W_{M.B.} = \frac{N!}{n_1!\,n_2!\ldots n_k!}\, g_1^{n_1} g_2^{n_2}\ldots g_k^{n_k}$$

The *classical Maxwell-Boltzmann statistics* is:

$$\boxed{W_{M.B.} = N!\prod_{i=1}^{k}\frac{g_i^{n_i}}{n_i!}} \qquad (1.1)$$

E Most Probable Distribution in Classical M-B Statistics

Let us determine the most probable distribution $\{n_1, n_2, \ldots, n_k\}$ of the particles on the k energy levels, for Maxwell-Boltzmann statistics.

The thermodynamic probability $W(n_1, n_2, \ldots, n_k)$ is an integer-valued function of k integer-valued variables. Given the very large value taken by each variable n_i and the fact that they vary in steps of one unit, we can consider that these variables vary continuously. Under this assumption, the thermodynamic probability $W(n_1, n_2, \ldots, n_k)$ can be considered continuous, and we can use differential calculus to find its maximum. We seek the values n_i^0 that make the function $W_{M.B.}(n_i)$ maximal, in other words the values n_i^0 of the n_i such that,

$$\begin{aligned}
&\mathrm{d}W(n_1, n_2, \ldots, n_k) = 0 \\
&\mathrm{d}\left(N! \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i!}\right) = 0 \\
&\mathrm{d}N! \times \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i!} + N! \times \mathrm{d} \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i!} = 0
\end{aligned}$$

$N!$ being constant, its differential is zero, leaving

$$\begin{aligned}
\mathrm{d} \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i} &= 0 \\
\mathrm{d} \ln \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i} &= 0 \qquad \text{(since the logarithm function is increasing)} \\
\mathrm{d} \sum_{i=1}^{k} \ln \frac{g_i^{n_i}}{n_i} &= 0 \\
\mathrm{d} \sum_{i=1}^{k} (n_i \ln g_i - \ln n_i) &= 0
\end{aligned}$$

We assumed that on each energy level ε_i, the number of particles n_i is very large. This allows us to use Stirling's approximation (see appendix A p. 43):

$$\ln n_i! \approx n_i \ln n_i - n_i \qquad \text{for } n_i \gg 0$$

We obtain

$$\mathrm{d} \sum_{i=1}^{k} (n_i \ln g_i - n_i \ln n_i + n_i) \approx 0$$

Recalling that g_i is not a variable of W, we have $\mathrm{d}g_i = 0$, and

$$\begin{aligned}
&\sum_{i=1}^{k} \left[\ln(g_i)\,\mathrm{d}n_i - \ln(n_i)\,\mathrm{d}n_i - n_i\,\mathrm{d}\ln n_i + \mathrm{d}n_i\right] \approx 0 \\
&\sum_{i=1}^{k} \left[\ln\left(\frac{g_i}{n_i}\right)\mathrm{d}n_i - n_i \frac{\mathrm{d}n_i}{n_i} + \mathrm{d}n_i\right] \approx 0 \\
&\sum_{i=1}^{k} \ln\left(\frac{g_i}{n_i}\right)\mathrm{d}n_i \approx 0 \qquad (1.2)
\end{aligned}$$

The $\mathrm{d}n_i$ are not independent. Indeed, if for example n_j varies, then the number of particles on other levels will have to vary as well. This is due to two constraints:

The number of particles N is fixed:

$$\sum_{i=1}^{k} n_i = N$$

$$\sum_{i=1}^{k} \mathrm{d}n_i = 0 \tag{1.3}$$

The internal energy U is fixed, as well as the energy levels ($\mathrm{d}\varepsilon_i = 0$):

$$\sum_{i=1}^{k} \varepsilon_i \, n_i = U$$

$$\sum_{i=1}^{k} (\varepsilon_i \, \mathrm{d}n_i + n_i \, \mathrm{d}\varepsilon_i) = 0$$

$$\sum_{i=1}^{k} \varepsilon_i \, \mathrm{d}n_i = 0 \tag{1.4}$$

We thus have three equations for the $\mathrm{d}n_i$. We use the method of Lagrange multipliers (see appendix B p. 44). By introducing two temporarily undetermined parameters, called Lagrange multipliers, these three equations can form only one:

$$\sum_{i=1}^{k} \ln\left(\frac{g_i}{n_i}\right) \mathrm{d}n_i - \alpha \sum_{i=1}^{k} \mathrm{d}n_i - \beta \sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i = 0$$

$$\sum_{i=1}^{k} \left[\ln\left(\frac{g_i}{n_i}\right) - \alpha - \beta\varepsilon_i\right] \mathrm{d}n_i = 0$$

The two constraints on the n_i being taken into account, the coefficients in front of the $\mathrm{d}n_i$ must cancel:

$$\ln\left(\frac{g_i}{n_i}\right) - \alpha - \beta\varepsilon_i = 0$$

$$\ln\left(\frac{g_i}{n_i}\right) = \alpha + \beta\varepsilon_i$$

$$\frac{g_i}{n_i} = e^{\alpha} \, e^{\beta\varepsilon_i}$$

$$\boxed{n_i^0 = g_i \, e^{-\alpha} \, e^{-\beta\varepsilon_i}} \tag{1.5}$$

n_i^0 is called the *Boltzmann distribution function.*

F Parameter α of the Boltzmann Distribution

To determine the parameter α we use the constraint on N. With (1.5) p. 8:

$$\sum_{i=1}^{k} n_i^0 = N$$

$$\sum_{i=1}^{k} g_i \, e^{-\alpha} \, e^{-\beta\varepsilon_i} = N$$

$$e^{-\alpha} = \frac{N}{\sum_{i=1}^{k} g_i \, e^{-\beta\varepsilon_i}}$$

It is not necessary to further explicit the expression of α.

We inject the expression of α into (1.5) p. 8 giving n_i^0:

$$n_i^0 = \frac{N \, g_i \, e^{-\beta\varepsilon_i}}{\sum_{i=1}^{k} g_i \, e^{-\beta\varepsilon_i}}$$

Definition 1.4: Partition Function

We define the partition function Z, by

$$Z \overset{\text{def}}{=} \sum_{i=1}^{k} g_i \, e^{-\beta\varepsilon_i}$$

we then have,

$$\boxed{n_i^0 = \frac{N}{Z} \, g_i \, e^{-\beta\varepsilon_i}} \tag{1.6}$$

G Parameter β of the Boltzmann Distribution

Let's start by showing that the energy levels ε_i are a function only of the volume V of the enclosure containing the gas. Until now, we have modeled the quanta constituting the gas as particles obeying the laws of point mechanics. We will change representation and model the quanta as waves, and describe the behavior of these waves using wave mechanics. In this mechanics, the equivalent of the fundamental relation of dynamics is the Schrödinger equation[1]:

$$\frac{-\hbar^2}{2m} \, \Delta\psi_i + V_i(\mathbf{r}, t) \, \psi_i = i\hbar \, \frac{\partial \psi_i}{\partial t}$$

where $\psi_i(\mathbf{r}, t)$ is the wave function associated with the i-th particle, $\hbar$ is Planck's constant h divided by 2π, and Δ is the Laplacian operator, such that in rectangular coordinates $\Delta = \partial_x^2 + \partial_y^2 + \partial_z^2$.

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[1] See Schrödinger Equation.pdf

Definition 1.5: Hamiltonian Operator

From the classical Hamilton function H, we define the Hamiltonian operator $\hat{H}$ that applies to ψ, by

$$\hat{H} \overset{\text{def}}{=} \frac{-\hbar^2}{2m}\,\Delta + V_i(\mathbf{r},t)$$

and the Schrödinger equation is:

$$\hat{H}\psi_i = i\hbar\,\frac{\partial \psi_i}{\partial t}$$

$V_i(\mathbf{r},t)$ is the potential energy of the wave, and as in point mechanics, it will need to be replaced by a model suited to the problem. This potential energy is due to the interaction of the i-th particle with the other particles, to any external fields in which the i-th particle is immersed, and to any potential barriers.

We will use the ideal gas model, where the potential energy of interaction is neglected, and the particles are considered free. This is an approximation because without interaction between the particles, the gas could not evolve over time, and tend toward thermodynamic equilibrium. The gas is in a parallelepiped enclosure with sides a, b, c, whose walls are modeled by infinite potential barriers. Here we have our potential energy model, a flat three-dimensional well of infinite depth

$$V_i(\mathbf{r},t) = 0 \text{ if } \begin{cases} a > x > 0 \\ b > y > 0 \\ c > z > 0 \end{cases} \qquad V_i(\mathbf{r},t) = +\infty \text{ otherwise} \tag{1.7}$$

If in addition we neglect the gravitational potential energy in front of the kinetic energy, then the potential energy is zero in the enclosure and the Schrödinger equation for the quantum in the enclosure is

$$\frac{-\hbar^2}{2m}\,\Delta\psi_i = i\hbar\,\frac{\partial \psi_i}{\partial t}$$

If the space and time variables are linked, they are only in the expression of the potential energy. When the interaction potential energy V is independent of time and depends only on space, which is the case here since it is zero, the Schrödinger equation can be solved by the method of separation of space variables $\mathbf{r}$ and time t. We then seek a solution of the form

$$\psi_i(\mathbf{r},t) = \varphi_i(\mathbf{r})\, f_i(t)$$

The Laplacian Δ applying only to space variables, the Schrödinger equation becomes

$$\frac{-\hbar^2}{2m}\, f_i(t)\,\Delta\varphi_i(\mathbf{r}) = i\hbar\,\varphi_i(\mathbf{r})\,\frac{\mathrm{d}f_i(t)}{\mathrm{d}t}$$

dividing by $\varphi_i(\mathbf{r})\, f_i(t)$

$$-\frac{\hbar^2}{2m}\,\frac{\Delta\varphi_i(\mathbf{r})}{\varphi_i(\mathbf{r})} = i\hbar\,\frac{1}{f_i(t)}\,\frac{\mathrm{d}f_i(t)}{\mathrm{d}t}$$

We have a function of $\mathbf{r}$ equal to a function of t. The only possibility is that they are equal to the same constant in space and time. Dimensional analysis shows that this constant is an energy, which can only be the internal energy ε_i of the quantum. For the temporal part we have

$$\begin{aligned} i\hbar \frac{1}{f_i(t)} \frac{\mathrm{d}f_i(t)}{\mathrm{d}t} &= \varepsilon_i \\ \frac{\mathrm{d}f_i(t)}{f_i(t)} &= -\frac{i}{\hbar}\,\varepsilon_i \mathrm{d}t \\ f_i(t) &= Ce^{-i\varepsilon_i t/\hbar} \end{aligned}$$

and for the spatial part,

$$-\frac{\hbar^2}{2m}\frac{\Delta\varphi_i(\mathbf{r})}{\varphi_i(\mathbf{r})} = \varepsilon_i$$

which is called the time-independent Schrödinger equation. The Laplacian being the sum of three operators each acting on a single space coordinate, we seek a solution with separated space variables:

$$\varphi_i(\mathbf{r}) = \varphi_{i1}(x)\,\varphi_{i2}(y)\,\varphi_{i3}(z)$$

so that,

$$\begin{aligned} \Delta\varphi_i(\mathbf{r}) = \varphi''_{i1}(x)\,\varphi_{i2}(y)\,\varphi_{i3}(z) \\ + \varphi_{i1}(x)\,\varphi''_{i2}(y)\,\varphi_{i3}(z) \\ + \varphi_{i1}(x)\,\varphi_{i2}(y)\,\varphi''_{i3}(z) \end{aligned}$$

and thus,

$$-\frac{\hbar^2}{2m}\left(\frac{\varphi''_{i1}(x)}{\varphi_{i1}(x)} + \frac{\varphi''_{i2}(y)}{\varphi_{i2}(y)} + \frac{\varphi''_{i3}(z)}{\varphi_{i3}(z)}\right) = \varepsilon_i$$

The space coordinates being independent,

$$-\frac{\hbar^2}{2m}\frac{\varphi''_{i1}(x)}{\varphi_{i1}(x)} = \varepsilon_{ix} \qquad -\frac{\hbar^2}{2m}\frac{\varphi''_{i2}(y)}{\varphi_{i2}(y)} = \varepsilon_{iy} \qquad -\frac{\hbar^2}{2m}\frac{\varphi''_{i3}(z)}{\varphi_{i3}(z)} = \varepsilon_{iz}$$

and,

$$\varepsilon_i = \varepsilon_{ix} + \varepsilon_{iy} + \varepsilon_{iz}$$

Setting

$$k_{ix}^2 = 2m\varepsilon_{ix}/\hbar^2 \qquad k_{iy}^2 = 2m\varepsilon_{iy}/\hbar^2 \qquad k_{iz}^2 = 2m\varepsilon_{iz}/\hbar^2$$

we have

$$\frac{\varphi''_{i1}(x)}{\varphi_{i1}(x)} = -k_{ix}^2 \qquad \frac{\varphi''_{i2}(y)}{\varphi_{i2}(y)} = -k_{iy}^2 \qquad \frac{\varphi''_{i3}(z)}{\varphi_{i3}(z)} = -k_{iz}^2$$

whose solutions are,

$$\begin{aligned} \varphi_{i1}(x) &= A_1 \sin(k_{ix}x + \alpha_{ix}) \\ \varphi_{i2}(y) &= A_2 \sin(k_{iy}y + \alpha_{iy}) \\ \varphi_{i3}(z) &= A_3 \sin(k_{iz}z + \alpha_{iz}) \end{aligned}$$

We make the non-trivial assumption that the wave function is zero on the walls of the enclosure:

$$\begin{cases} \varphi_{i1}(0) = \varphi_{i2}(0) = \varphi_{i3}(0) = 0 \\ \varphi_{i1}(a) = \varphi_{i2}(a) = \varphi_{i3}(a) = 0 \end{cases}$$

For the first relation, the boundary condition at $x = 0$ is written as:

$$\begin{gathered} A_1 \sin\alpha_{ix} = 0 \\ \forall p_{ix} \in \mathbb{Z}, \quad \alpha_{ix} = p_{ix}\pi \end{gathered}$$

and, at $x = a$:

$$A_1 \sin(k_{ix} a + p_{ix}\pi) = 0$$

$$k_{ix} = n_{ix}, \frac{\pi}{a}$$

where n_{ix} is an integer such that:

$$\begin{aligned} n_{ix} &= \frac{a}{\pi}, k_{ix} \\ &= \frac{a}{\pi\hbar}\sqrt{2m\varepsilon_{ix}} \end{aligned}$$

Consequently, n is positive or zero. Moreover,

$$\forall n_{ix} \in \mathbb{N}, \quad n_{ix} \leqslant \frac{2a}{h}\sqrt{2m\varepsilon_i} \tag{1.8}$$

n_{ix} has a maximum value of $2a\sqrt{2m\varepsilon_i}/h$. For the three relations, we obtain:

$$k_{ix} = n_{ix}, \frac{\pi}{a} \qquad k_{iy} = n_{iy}, \frac{\pi}{b} \qquad k_{iz} = n_{iz}, \frac{\pi}{c}$$

The energy ε_i of the i-th quantum is therefore quantized, and has the expression:

$$\begin{aligned} \varepsilon_i &= \varepsilon_{ix} + \varepsilon_{iy} + \varepsilon_{iz} \\ &= \frac{\hbar^2}{2m}\left(k_{ix}^2 + k_{iy}^2 + k_{iz}^2\right) \\ &= \frac{\hbar^2\pi^2}{2m}\left(\frac{\mathrm{n}_{\mathrm{ix}}^2}{a^2} + \frac{\mathrm{n}_{\mathrm{iy}}^2}{b^2} + \frac{\mathrm{n}_{\mathrm{iz}}^2}{c^2}\right) \\ &= \frac{h^2}{8m}\left(\frac{\mathrm{n}_{\mathrm{ix}}^2}{a^2} + \frac{\mathrm{n}_{\mathrm{iy}}^2}{b^2} + \frac{\mathrm{n}_{\mathrm{iz}}^2}{c^2}\right) \end{aligned} \tag{1.9}$$

In the particular case where the enclosure is a cube,

$$a = b = c = V^{1/3}$$

the energy is written as:

$$\varepsilon_i = \frac{h^2}{8mV^{2/3}}\left(n_{ix}^2 + n_{iy}^2 + n_{iz}^2\right)$$

A set of three integers n_{ix}, n_{iy}, n_{iz} defines a quantum state for the quantum. We see that the energy levels depend only on one thermodynamic variable, the volume V. Now let's write the differential of the internal energy:

$$\begin{aligned} U &= \sum_{i=1}^{k} \varepsilon_i n_i \\ \mathrm{d}U &= \sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i + \sum_{i=1}^{k} n_i \mathrm{d}\varepsilon_i \end{aligned}$$

The internal energy can therefore vary in two ways, by redistribution of particles over the energy levels or by shifting these energy levels. We know that the ε_i are a function only of the volume

$$\mathrm{d}U = \sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i + \sum_{i=1}^{k} n_i \left(\frac{\mathrm{d}\varepsilon_i}{dV}\right) dV$$

however,

$$\begin{aligned} \mathrm{d}U &= \delta Q + \delta W \\ &= T\mathrm{d}S - P dV \end{aligned}$$

so

$$\sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i = T\mathrm{d}S \qquad \text{and} \qquad \sum_{i=1}^{k} n_i \left(\frac{\mathrm{d}\varepsilon_i}{dV}\right) = -P$$

using the expression of $\mathrm{d}\ln W$ given by (1.2) p. 7:

$$\begin{aligned}\sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i &= Tk, \mathrm{d}\ln W \\ &= Tk \sum_{i=1}^{k} \ln\left(\frac{g_i}{n_i}\right) \mathrm{d}n_i\end{aligned}$$

Now, according to (1.6) p. 9, at thermodynamic equilibrium

$$n_i^0 = (N/Z), g_i e^{-\beta\varepsilon_i}$$

so that:

$$\begin{aligned}\sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i &= Tk \sum_{i=1}^{k} \ln\left(\frac{Z}{N}, e^{\beta\varepsilon_i}\right) \mathrm{d}n_i \\ &= Tk \sum_{i=1}^{k} \left(\beta\varepsilon_i + \ln\frac{Z}{N}\right) \mathrm{d}n_i \\ &= Tk\beta \sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i + Tk \ln\left(\frac{Z}{N}\right) \sum_{i=1}^{k} \mathrm{d}n_i\end{aligned}$$

Recalling (1.3) p. 8, $\sum_{i=1}^{k} \mathrm{d}n_i = 0$

$$\sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i = Tk\beta \sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i$$

consequently

$$\boxed{\beta = \frac{1}{kT}} \tag{1.10}$$

and at equilibrium, the number n_i^0 of particles having the energy level ε_i degenerate g_i times has the expression:

$$n_i^0 = \frac{N}{Z} g_i \, e^{-\varepsilon_i/(kT)} \tag{1.11}$$

Chapter 2

EXPRESSION OF THE PARTITION FUNCTION Z

Contents

With def. 1.4 p. 9 of the partition function and the value of β, (1.10) p. 13, the partition function is written as

$$\boxed{Z = \sum_{i=1}^{k} g_i, e^{-\varepsilon_i/(kT)}} \tag{2.1}$$

Consider the simplest gas, a monatomic ideal gas with zero electric charge. If we neglect the gravitational potential energy mgz in front of the translational kinetic energy, the energy of the particles of this gas is written as

$$\begin{aligned} \varepsilon_i &= \frac{1}{2}, mv_i^2 \\ &= \frac{p_i^2}{2m} \end{aligned}$$

where the magnitude of the velocity v_i of each particle varies from 0 to $+\infty$.

A Expression of the Degeneracy Factor g_i

The relation (1.9) p. 12 giving the set of quantum states accessible to a quantum of energy ε_i, can also be written as

$$\frac{h^2}{8m}\left(\frac{n_{ix}^2}{a^2\varepsilon_i} + \frac{n_{iy}^2}{b^2\varepsilon_i} + \frac{n_{iz}^2}{c^2\varepsilon_i}\right) = 1$$

which is of the form

$$\frac{x^2}{A^2} + \frac{y^2}{B^2} + \frac{z^2}{C^2} = 1$$

with

$$x = n_{ix}, \quad y = n_{iy}, \quad z = n_{iz}, \quad A^2 = \frac{8ma^2, \varepsilon_i}{h^2}, \quad B^2 = \frac{8mb^2, \varepsilon_i}{h^2}, \quad C^2 = \frac{8mc^2, \varepsilon_i}{h^2}$$

This is the equation of an ellipsoid with parameters A, B, C (lengths of the three semi-axes). Each point with integer coordinates (n_{ix}, n_{iy}, n_{iz}) inside this ellipsoid represents a quantum state accessible to a quantum of energy ε_i. According to (1.8) p. 12, the quantum numbers n_{ix}, n_{iy} and n_{iz} are positive. We must take into account only the positive part of the ellipsoid, half along each axis, i.e., one-eighth $(\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2})$ of its volume. The degeneracy factor (the number of quantum states accessible for the same energy, or the same momentum, of a quantum) is given by:

$$\begin{aligned} g_i &= \frac{1}{8} \times \frac{4}{3}, \pi, ABC \\ &= \frac{\pi}{6} \times \frac{a}{h}, \sqrt{8m\varepsilon_i} \times \frac{b}{h}, \sqrt{8m\varepsilon_i} \times \frac{c}{h}, \sqrt{8m\varepsilon_i} \\ &= \frac{1}{h^3} \times V \times \frac{4}{3}\pi p_i^3 \end{aligned}$$

Let's interpret this result. Consider the 6-dimensional space $(\mathbf{r}, \mathbf{p})$, called phase space. The hyper-volume of this space is the multiplication of the volume V of the ordinary space accessible to the quantum and the volume of its momentum space $4/3 \times \pi\, p_i^3$. It is not possible to locate a quantum in a hyper-volume less than h^3 because $g_i \geqslant 1$. This leads us to consider that the phase space is divided into cells of hyper-volume h^3, each corresponding to a quantum state, i.e., to the energy sub-levels of § C p. 4. For fermions, an additional degeneracy factor due to spin intervenes in g_i. A phase space cell can contain several fermions of the same species, provided that their spins are different. This factor is $2(S/\hbar) + 1$, where S is the spin angular momentum of the particle. For electrons, neutrons, and protons, whose spin angular momentum is $\hbar/2$, this factor is 2. Photons also have an additional degeneracy factor of 2, due to their two right and left polarization states. In rectangular coordinates, the degeneracy factor is written as:

$$g_i = \frac{1}{h^3} \int_x \int_y \int_z \int_{p_x} \int_{p_y} \int_{p_z} \mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \tag{2.2}$$

Let's return to the partition function (2.1) p. 15:

$$\begin{aligned} Z &= \frac{1}{h^3} \int_x \int_y \int_z \int_{p_x} \int_{p_y} \int_{p_z}, e^{-\varepsilon_i/(kT)} \mathrm{d}x\mathrm{d}y\mathrm{d}z\mathrm{d}p_x\mathrm{d}p_y\mathrm{d}p_z \\ &= \frac{m^3 V}{h^3} \int_{v_x} \int_{v_y} \int_{v_z} e^{-m(v_x^2+v_y^2+v_z^2)/(2kT)} \mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z \\ &= \frac{m^3 V}{h^3} \int_{v_x} e^{-m(v_x^2+v_y^2+v_z^2)/(2kT)} \mathrm{d}v_x \int_{v_y} e^{-m(v_x^2+v_y^2+v_z^2)/(2kT)} \mathrm{d}v_y \int_{v_z} e^{-m(v_x^2+v_y^2+v_z^2)/(2kT)} \mathrm{d}v_z \end{aligned}$$

v_x, v_y and v_z vary from $-\infty$ to $+\infty$, and by symmetry:

$$\begin{aligned} Z &= \frac{m^3 V}{h^3} \left[\int_{-\infty}^{+\infty} !e^{-mv_x^2/(2kT)} \mathrm{d}v_x \right]^3 \\ &= \frac{m^3 V}{h^3} \left(\int_{-\infty}^{+\infty} !e^{-\mathrm{a}v_x^2} \mathrm{d}v_x \right)^3 \end{aligned}$$

where $\mathrm{a} = m/(2kT)$. With the Gaussian integral (see appendix C p. 45) $\int_{-\infty}^{+\infty} e^{-\mathrm{a}x^2}\mathrm{d}x = \sqrt{\pi/\mathrm{a}}$

$$\begin{aligned} Z &= \frac{m^3 V}{h^3} \left(\sqrt{\frac{2kT\pi}{m}} \right)^3 \\ &= \frac{V}{h^3} (2\pi mkT)^{3/2} \end{aligned} \tag{2.3}$$

Z is therefore a function of temperature and volume $Z = Z(T, V)$.

B Expression of the Internal Energy U

The internal energy U can be expressed using the partition function Z. At thermodynamic equilibrium, (1.11) p. 13 gives

$$\begin{aligned} U &= \sum_{i=1}^{k} \varepsilon_i, n_i^0 \\ &= \frac{N}{Z} \sum_{i=1}^{k} \varepsilon_i, g_i, e^{-\varepsilon_i/(kT)} \end{aligned}$$

Let's derive the partition function with respect to T at constant volume. According to (2.1) p. 15:

$$\begin{aligned} Z(T,V) &= \sum_{i=1}^{k} g_i, e^{-\varepsilon_i/(kT)} \\ \left(\frac{\partial Z}{\partial T}\right) V &= \sum i = 1^k g_i, \frac{\varepsilon_i}{kT^2}, e^{-\varepsilon_i/(kT)} \\ &= \frac{1}{kT^2} \sum_{i=1}^{k} \varepsilon_i, g_i, e^{-\varepsilon_i/(kT)} \end{aligned}$$

So

$$\begin{aligned} U &= \frac{NkT^2}{Z} \left(\frac{\partial Z}{\partial T}\right) V \\ &= NkT^2 \left(\frac{\partial \ln Z}{\partial T}\right) V \end{aligned}$$

For the translational internal energy, take the natural logarithm of (2.3) p. 16:

$$\begin{aligned} \ln Z &= \ln \frac{V}{h^3} + \frac{3}{2}, \ln(2\pi m k T) \\ &= \ln \frac{V}{h^3} + \frac{3}{2}, \ln(2\pi m k) + \frac{3}{2}, \ln T \\ \left(\frac{\partial \ln Z}{\partial T}\right) V &= \frac{3}{2T} \end{aligned}$$

hence

$$\boxed{U = \frac{3}{2}, NkT} \tag{2.4}$$

Chapter 3

ENTROPY

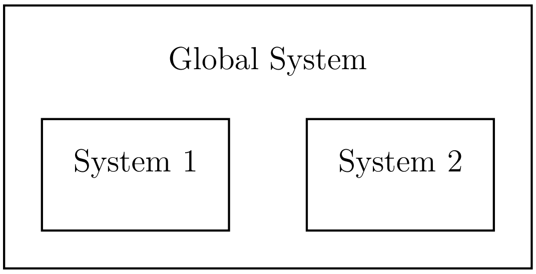
Contents

A Relation Between Entropy and Number of Microstates

When a gas is at equilibrium we have both:

- in general thermodynamics the entropy S is maximal
- in statistical thermodynamics the number of microstates W is maximal

Ludwig Boltzmann assumed that there existed an increasing function f such that $S = f(W)$ so that when W is maximal, S is also maximal. We can determine this function by considering an isolated system, at equilibrium, consisting of two isolated subsystems:



The entropy of the global system is $S = S_1 + S_2$. The number of microstates of system 1 is W_1, that of system 2 is W_2. For each microstate of system 1 there corresponds a microstate of system 2. The global system therefore has

$$W = W_1, W_2$$

possible microstates. Consequently, the function f is a logarithm, because under this assumption we have $S_1 = \log_a W_1$ and $S_2 = \log_a W_2$, and the entropies of the subsystems add up while their numbers of microstates multiply:

$$\begin{aligned} S_1 + S_2 &= \log aW_1 + \log_a W_2 \\ S &= \log_a(W_1, W_2) \\ &= \log_a W \end{aligned}$$

The base a of the logarithm being undetermined, we write

$$\begin{aligned} \log_a W &= \frac{\ln W}{\ln a} \\ &= k_B \ln W \end{aligned}$$

where the value of Boltzmann's constant k_B is determined experimentally:

$$k_B \approx 1.381 \times 10^{-23} \text{ J K}^{-1}$$

The *Boltzmann formula* is written as:

$$\boxed{S = k_B \ln W} \tag{3.1}$$

Thus, when a gas tends toward its equilibrium state, W tends toward its maximum value W^0, and the entropy increases.

B Entropy in Classical Maxwell-Boltzmann Statistics

In Boltzmann's formula (3.1) p. 20, (1.1) p. 6 gives the expression of $W_{M.B.}$:

$$\begin{aligned} S &= k \ln W_{M.B.} \\ &= k \ln \left(N! \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i!} \right) \\ &= k \left[\ln N! + \sum_{i=1}^{k} \ln \left(\frac{g_i^{n_i}}{n_i!} \right) \right] \end{aligned}$$

Using Stirling's approximation (see appendix A p. 43) for $n_i \gg 1$:

$$\begin{aligned} S &= k \left[N \ln N - N + \sum_{i=1}^{k} (n_i \ln g_i - n_i \ln n_i + n_i) \right] \\ &= k \left(N \ln N + \sum_{i=1}^{k} n_i \ln \frac{g_i}{n_i} \right) \end{aligned}$$

We seek the entropy at thermodynamic equilibrium, so with $n_i = n_i^0$. Using (1.6) p. 9,

$$\begin{aligned} n_i^0 &= \frac{N}{Z}, g_i, e^{-\varepsilon_i/(kT)} \\ \frac{g_i}{n_i^0} &= \frac{Z}{N}, e^{\varepsilon_i/(kT)} \\ \ln \left(\frac{g_i}{n_i^0} \right) &= \ln \frac{Z}{N} + \frac{\varepsilon_i}{kT} \end{aligned}$$

consequently,

$$\begin{aligned} S &= k\left[N\ln N + \sum_{i=1}^{k} n_i\left(\ln\frac{Z}{N} + \frac{\varepsilon_i}{kT}\right)\right] \\ &= k\left(N\ln N + N\ln\frac{Z}{N} + \frac{U}{kT}\right) \end{aligned}$$

The entropy in classical Maxwell-Boltzmann statistics is written as:

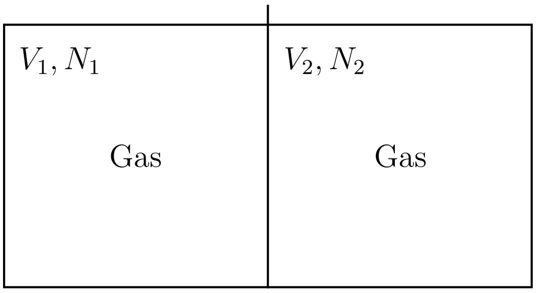
$$\boxed{S = kN\ln Z + \frac{U}{T}}$$

C The Gibbs Paradox

Let's calculate the entropy for a monatomic ideal gas. In the previous relation, inject relations (2.3) p. 16 and (2.4) p. 17:

$$\begin{aligned} S &= kN\ln\left[\frac{V}{h^3}(2\pi mkT)^{3/2}\right] + \frac{(3/2)\,NkT}{T} \\ &= kN\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right] \qquad (3.2) \end{aligned}$$

Consider an enclosure containing a monatomic ideal gas at temperature T. Separate the enclosure into two volumes V_1 and V_2 using a removable partition:



Calculate the entropy variation when the partition is removed. The initial entropy is the sum of the entropies of the two gases in their respective volumes, V_1 and V_2:

$$S_{initial} = kN_1\left[\ln V_1 + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right] + kN_2\left[\ln V_2 + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right]$$

The final entropy is the sum of the entropies of the gases in the final volume $V_1 + V_2$

$$S_{final} = kN_1\left[\ln(V_1+V_2) + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right] + kN_2\left[\ln(V_1+V_2) + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right]$$

The entropy variation ΔS is written as:

$$S_{final} - S_{initial} = kN_1\ln\left(\frac{V_1+V_2}{V_1}\right) + kN_2\ln\left(\frac{V_1+V_2}{V_2}\right)$$

This entropy variation is positive, which means that every time the partition is replaced and removed, the entropy increases! Yet we know that from a macroscopic point of view nothing happens when this operation is performed. The system returns to its initial configuration, the process is reversible and we should have $\Delta S = 0$. In classical thermodynamics, entropy is an extensive variable. If we double the extensive variables, the number of particles N at the same time as the volume V, the entropy must double in value. However, we see that this is not the case if we use (3.2) p. 21. To solve this problem, we must consider that the gas particles are indistinguishable, because under this assumption we ensure that absolutely nothing happens when the partition is removed. Indistinguishability is a purely quantum property that has no classical equivalent. Statistics with indistinguishable particles are called "quantum statistics".

Chapter 4

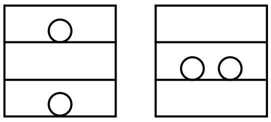
QUANTUM STATISTICS

Contents

Example .1. We take the same initial assumptions as in ex. A.1 p. 2, but with indistinguishable balls.

- $N = 2$
- $U = 2$ J
- $\varepsilon_1 = 0$ J, $\varepsilon_2 = 1$ J, $\varepsilon_3 = 2$ J
- the balls are indistinguishable

The different possible distributions are then:

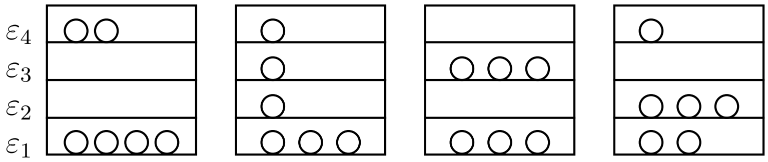


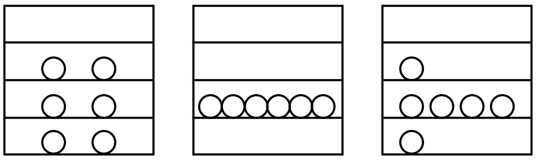
There are therefore two equiprobable macroscopic states, since each is realized by a single microstate.

Example .2. Initial assumptions:

- $N = 6$
- $U = 6$ J
- $\varepsilon_1 = 0$ J, $\varepsilon_2 = 1$ J, $\varepsilon_3 = 2$ J, $\varepsilon_4 = 3$ J
- the balls are indistinguishable

The different possible distributions are as follows:





The macroscopic states are each realized by a single microstate since the balls are indistinguishable. They are therefore equiprobable. The two previous examples show that the distinguishability or indistinguishability of particles changes the probabilities of realization of macroscopic states.

A Corrected Maxwell-Boltzmann Statistics

We resume the reasoning of the classical Maxwell-Boltzmann statistics from § D p. 5, but with indistinguishable particles.

a) What is the number of ways to place n_1 indistinguishable particles on an energy level ε_1 degenerate g_1 times? Compared to the result obtained when the particles are distinguishable, $g_1^{n_1}$, all permutations of particles on the energy level ε_1 are identical configurations, since the particles are now indistinguishable. The answer is therefore $g_1^{n_1}/n_1!$ We will see in the following § B p. 25, that this reasoning is not entirely exact, and is valid only when $g_1 \gg n_1$.

b) What is the number of ways to place n_2 indistinguishable particles on an energy level ε_2 degenerate g_2 times? $g_2^{n_2}/n_2!$

c) What is the number of ways to place n_1 indistinguishable particles on the energy level ε_1 degenerate g_1 times, and n_2 particles on the energy level ε_2 degenerate g_2 times? $g_1^{n_1}/n_1! \times g_2^{n_2}/n_2!$

d) What is the number of ways to place N indistinguishable particles on k degenerate energy levels?

The corrected Maxwell-Boltzmann statistics is written as:

$$\boxed{W_{M.B.C.} = \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i!}} \tag{4.1}$$

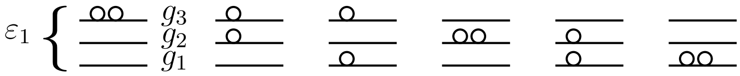
Indeed, compared to the Maxwell-Boltzmann statistics (1.1) p. 6, there is no longer any question here of permuting the particles of the energy level ε_1 with those of the energy level ε_2 since they are indistinguishable.

B This Reasoning is Not Entirely Exact

Let's take a simple case, for which there is only one energy level ε_1, degenerate three times. The initial assumptions are as follows:

- $n_1 = 2$
- $U = 2$ J
- $\varepsilon_1 = 1$ J
- $g_1 = 3$

The different distributions on the three sub-levels of the energy level ε_1 are as follows:

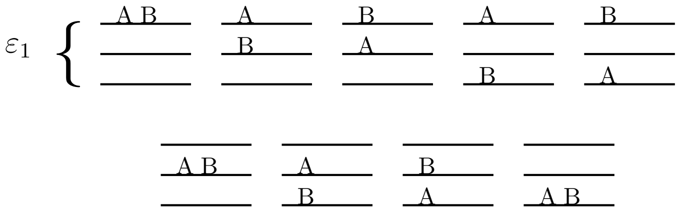


There is only one possible macroscopic state, and its number of microstates is W=6.

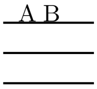
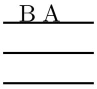
Let us apply the Maxwell-Boltzmann statistics for indistinguishable particles:

$$W_{M.B.C.} = \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i!}$$
$$= \frac{g_1^{n_1}}{n_1!} = \frac{3^2}{2!} = 4.5$$

This is not the correct result, and moreover it is non-integer, which is impossible. Let us resume the reasoning and show that there is an approximation. Suppose that the two particles are distinguishable, the different possible distributions on the energy sub-levels of ε_1 are the following:



We therefore have $W = 9$. Then we assume that each microscopic state appears as many times as there are possible permutations between the starting particles, i.e., 2! times. However, as we can see, this is false when the particles are on the same energy sub-level. Indeed,

nous avons  mais pas 

because these microstates are equivalent, whether the particles are distinguishable or indistinguishable. Similarly,

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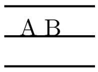

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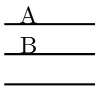
while we do have:



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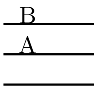


However, when g_1 is much greater than n_1, the cases where the particles are on the same sub-level become minority compared to the case where they are on different sub-levels. The gas is weakly degenerate and the Maxwell-Boltzmann formula tends toward the correct value because the different microscopic states appear almost all $n_1!$ times. We can then go from the distinguishable case to the indistinguishable case by dividing by $n_1!$ Note well that the condition $g_1 \gg 1$ is not sufficient since we need $g_1 \gg n_1$.

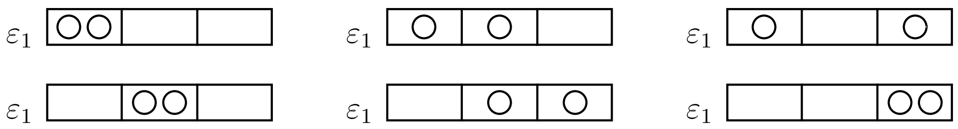
C Bose-Einstein Statistics

To avoid the approximation of the corrected Maxwell-Boltzmann statistics, we can use an advantageous representation. In what follows, the energy levels are represented by boxes. The energy sub-levels, corresponding to the cells of the phase space, are the compartments of these boxes, and are separated by partitions. To obtain the number of microstates of an energy level we permute the particles and the partitions of this level.

Example C.1. Let us resume the same initial assumptions as in § B p. 25. There is only one energy level ε_1, degenerate three times.

- $n_1 = 2$
- $U = 2$ J
- $\varepsilon_1 = 1$ J
- $g_1 = 3$

Using the Bose-Einstein representation, we have:



So $W = 6$. This indeed amounts to permuting the two internal partitions and the two particles, like this:

○○| | ○ | ○ | ○ | | ○

|○○| | ○ | ○ | |○○

For the energy level ε_1, the result is obtained by permutation of the n_1 particles and the $g_1 - 1$ partitions, then division by the permutations that give the same microstate, i.e., the internal partitions among themselves and the particles among themselves, since they are indistinguishable. The number of microstates W_1 for the energy level ε_1 is therefore:

$$\begin{aligned} W_1 &= \frac{(n_1 + g_1 - 1)!}{n_1!(g_1 - 1)!} \\ &= \frac{4!}{2!2!} = 6 \end{aligned}$$

For several degenerate energy levels, the final result is the product of the different microstates W_i, hence the expression of Bose-Einstein statistics:

$$\boxed{W_{B.E.} = \prod_{i=1}^{k} \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}} \tag{4.2}$$

Particles that obey Bose-Einstein statistics are called bosons; they are interaction particles. The boson of the electromagnetic field is the photon, that of the strong interaction is the gluon, those of the weak interaction are the W^+, the W^-, and the Z^0. Mesons (pion, kaon, ρ, B^0, η_c) and phonons are also bosons. The graviton, which remains to be evidenced, would be the boson of gravitational interaction. Bosons can be several in the same quantum state, in other words, several on the same energy sub-level.

D Fermi-Dirac Statistics

In this statistics, the quanta obey the Pauli exclusion principle: at most $2(S/\hbar) + 1$ quanta can occupy the same energy sub-level, where S is the spin angular momentum of the particle. Consequently, in this statistics we will always have:

$$g_i \geqslant N_i$$

These quanta are called fermions and constitute matter. The proton, neutron, leptons (electron, neutrinos, muons, tauons), and quarks (up, down, top, bottom, charm, strange) are fermions. Baryons are fermions but are not elementary particles.

In § F p. 9, we saw that in wave mechanics, a complex wave function ψ is associated with each quantum, solution of the Schrödinger equation. The German physicist Max Born gave without demonstration the physical interpretation of the wave function ψ: the probability $\mathrm{d}P$ that a quantum is at time t in a volume element $\mathrm{d}\mathbf{r} = \mathrm{d}x\mathrm{d}y\mathrm{d}z$, is given by

$$\mathrm{d}P = \|\psi(\mathbf{r}, t)\|^2 \mathrm{d}\mathbf{r}$$

The square of the modulus of the complex wave function ψ associated with the quantum is therefore equal to the probability density of presence of the quantum. The wave function of a system of two quanta in interaction is $\psi(\mathbf{r}_1, \mathbf{r}_2, t)$, and the probability that quantum 1 is in the volume $\mathrm{d}\mathbf{r}_1$ centered at $\mathbf{r}_1$, and quantum 2 in the volume $\mathrm{d}\mathbf{r}_2$ centered at $\mathbf{r}_2$, is given by

$$\mathrm{d}P = \|\psi(\mathbf{r}_1, \mathbf{r}_2, t)\|^2 \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2$$

This last equality can be generalized to any number of quanta. In § C p. 21, we saw that we must consider that the quanta are indistinguishable, in other words, that

$$\|\psi(\mathbf{r}_1, \mathbf{r}_2, t)\|^2 = \|\psi(\mathbf{r}_2, \mathbf{r}_1, t)\|^2$$

from which we deduce the two possibilities:

$$\begin{cases} \psi(\mathbf{r}_1, \mathbf{r}_2, t) = +\psi(\mathbf{r}_2, \mathbf{r}_1, t) & (4.3a) \\ \psi(\mathbf{r}_1, \mathbf{r}_2, t) = -\psi(\mathbf{r}_2, \mathbf{r}_1, t) & (4.3b) \end{cases}$$

We will show that

- when the sign is positive the quanta are bosons and they obey the Bose-Einstein statistics
- when the sign is negative, the quanta are fermions and they obey the Fermi-Dirac statistics and the Pauli exclusion principle

In the case where the interaction between the quanta can be neglected, the Hamiltonian H of the wave function ψ of the system formed by the two quanta is simply the sum of the Hamiltonians H_1 and H_2 of each wave function φ. We can then apply the separation of variables method and seek the wave function ψ in the form of the product of the wave functions φ of the two quanta. We thus have:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t) = \varphi_1(\mathbf{r}_1, t)\, \varphi_2(\mathbf{r}_2, t)$$

For bosons the wave function ψ must be symmetric to respect property (4.3a):

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t) = C\,[\varphi_1(\mathbf{r}_1, t)\, \varphi_2(\mathbf{r}_2, t) + \varphi_1(\mathbf{r}_2, t)\, \varphi_2(\mathbf{r}_1, t)]$$

where C is a real number, called normalization factor, which ensures that the probability of finding the two quanta somewhere in space is unity. For fermions the wave function ψ must be antisymmetric to respect property (4.3b):

$$\psi(\mathbf{r}_1, \mathbf{r}_2, t) = C\,[\varphi_1(\mathbf{r}_1, t)\, \varphi_2(\mathbf{r}_2, t) - \varphi_1(\mathbf{r}_2, t)\, \varphi_2(\mathbf{r}_1, t)]$$

We then notice that if the quanta are at the same place, $\mathbf{r}_1 = \mathbf{r}_2$, the wave function ψ of the two fermions is zero. This making no sense, we conclude that two fermions cannot occupy the same quantum state, which constitutes *the Pauli exclusion principle.* More precisely, *two fermions cannot approach a distance less than the de Broglie wavelength λ associated with these particles.*

Consider the distribution of n_1 particles on the energy level ε_1 degenerate g_1 times. Its number of microstates W_1 is given by the permutations of the set of occupied places and empty places. If we permute everything in the g_1 sub-levels, i.e. $g_1!$ permutations, we will also have permuted the indistinguishable particles among themselves and the empty places among themselves. We must therefore divide $g_1!$ by $n_1!$ and by $(g_1 - n_1)!$

$$W_1 = \frac{g_1!}{n_1!\,(g_1 - n_1)!}$$

For several degenerate energy levels, we perform the product of the different microstates W_i to obtain the Fermi-Dirac statistics:

$$\boxed{W_{F.D.} = \prod_{i=1}^{k} \frac{g_i!}{n_i!\,(g_i - n_i)!}} \tag{4.4}$$

In cases of low degeneracy, $g_i \gg n_i$, this statistics also tends toward the Maxwell-Boltzmann statistics of indistinguishable particles. Indeed, the cases where particles group on the same sub-level become minority and the Pauli exclusion principle then loses its importance.

E Entropy in Corrected Maxwell-Boltzmann Statistics

In Boltzmann's formula (3.1) p. 20, replace $W_{M.B.C}$ using (4.1) p. 24:

$$\begin{aligned}
S &= k \ln W_{M.B.C.} \\
&= k \ln \prod_{i=1}^{k} \frac{g_i^{n_i}}{n_i!} \\
&= k \sum_{i=1}^{k} (n_i \ln g_i - n_i \ln n_i + n_i) \\
&= k \left(N + \sum_{i=1}^{k} n_i \ln \frac{g_i}{n_i} \right)
\end{aligned}$$

We seek the entropy at thermodynamic equilibrium, so with $n_i = n_i^0$. From (1.11) p. 13:

$$\begin{aligned}
n_i^0 &= \frac{N}{Z}\, g_i\, e^{-\varepsilon_i/(kT)} \\
\frac{g_i}{n_i^0} &= \frac{Z}{N}\, e^{\varepsilon_i/(kT)} \\
\ln\left(\frac{g_i}{n_i^0}\right) &= \ln \frac{Z}{N} + \frac{\varepsilon_i}{kT}
\end{aligned}$$

Consequently:

$$\begin{aligned}
S &= k \left[N + \sum_{i=1}^{k} n_i \left(\ln \frac{Z}{N} + \frac{\varepsilon_i}{kT} \right) \right] \\
&= k \left(N + N \ln \frac{Z}{N} + \frac{U}{kT} \right) \\
&= kN \left(\ln \frac{Z}{N} + 1 \right) + \frac{U}{T}
\end{aligned}$$

Let's calculate the entropy for a monatomic ideal gas from the expression of the partition function Z, relation (2.3) p. 16, and the expression of the internal energy U, relation (2.4) p. 17

$$\begin{aligned}
S &= kN \left\{ \ln \left[\frac{V}{Nh^3} (2\pi mkT)^{3/2} \right] + 1 \right\} + \frac{(3/2)\, NkT}{T} \\
&= kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + 1 \right] + \frac{3}{2} kN
\end{aligned}$$

The entropy in corrected Maxwell-Boltzmann statistics is:

$$\boxed{S = kN\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2}\right]}$$

which is the *Sackur-Tetrode formula*. We can verify that the entropy is indeed an extensive variable in corrected Maxwell-Boltzmann statistics: its value is doubled when both the number of particles N and the volume V are doubled. It respects the additive character attributed to it by macroscopic thermodynamics.

Chapter 5

MOST PROBABLE DISTRIBUTION

Contents

A In Bose-Einstein Statistics

It involves finding the maximum of the function $W_{B.E.}(n_i)$ given by (4.2) p. 27:

$$\mathrm{d}\prod_{i=1}^{k}\frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}=0$$

$$\mathrm{d}\ln\prod_{i=1}^{k}\frac{(n_i+g_i-1)!}{n_i!\,(g_i-1)!}=0$$

$$\mathrm{d}\sum_{i=1}^{k}\{\ln\left[(n_i+g_i-1)!\right]-\ln(n_i!)-\ln\left[(g_i-1)!\right]\}=0$$

If we assume $n_i \gg 0$ we can use Stirling's approximation (see appendix A p. 43):

$$\mathrm{d}\sum_{i=1}^{k}\{(n_i+g_i-1)\ln(n_i+g_i-1)-(n_i+g_i-1)-n_i\ln n_i+n_i-\ln\left[(g_i-1)!\right]\}\approx 0$$

$$\sum_{i=1}^{k}\left[\ln(n_i+g_i-1)\mathrm{d}n_i+(n_i+g_i-1)\frac{\mathrm{d}n_i}{n_i+g_i-1}-\ln n_i\mathrm{d}n_i-n_i\frac{\mathrm{d}n_i}{n_i}\right]\approx 0$$

$$\sum_{i=1}^{k}\ln\left(\frac{n_i+g_i-1}{n_i}\right)\mathrm{d}n_i\approx 0$$

$$\sum_{i=1}^{k}\ln\left(\frac{n_i+g_i}{n_i}\right)\mathrm{d}n_i\approx 0$$

As in § E p. 7, to account for the constraints on the number N of particles and on the internal energy U we introduce relations (1.3) and (1.4) p. 8 with the two Lagrange multipliers, α' and

β':

$$\begin{aligned}
&\sum_{i=1}^{k} \ln\left(\frac{n_i+g_i}{n_i}\right) \mathrm{d}n_i - \alpha' \sum_{i=1}^{k} \mathrm{d}n_i - \beta' \sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i = 0 \\
&\sum_{i=1}^{k} \left[\ln\left(\frac{n_i+g_i}{n_i}\right) - \alpha' - \beta'\varepsilon_i\right] \mathrm{d}n_i = 0 \\
\forall i = 1,\dots,k \quad &\ln\left(\frac{n_i+g_i}{n_i}\right) - \alpha' - \beta'\varepsilon_i = 0
\end{aligned}$$

We isolate the number of quanta n_i per energy level:

$$\begin{aligned}
1 + \frac{g_i}{n_i} &= e^{(\alpha'+\beta'\varepsilon_i)} \\
g_i &= n_i(e^{\alpha'}\, e^{\beta'\varepsilon_i} - 1)
\end{aligned}$$

The most probable distribution in Bose-Einstein statistics for $n_i^0 \gg 0$ is:

$$\boxed{n_i^0 = \frac{g_i}{e^{\alpha'}\, e^{\beta'\varepsilon_i} - 1}} \tag{5.1}$$

The Lagrange multipliers α' and β' are determined in § 6 p. 35.

B In Fermi-Dirac Statistics

It involves finding the maximum of the function $W_{F.D.}(n_i)$ given by (4.4) p. 29.

$$\begin{aligned}
&\mathrm{d} \prod_{i=1}^{k} \frac{g_i!}{n_i!\,(g_i-n_i)!} = 0 \\
&\mathrm{d} \ln \prod_{i=1}^{k} \frac{g_i!}{n_i!\,(g_i-n_i)!} = 0 \\
&\mathrm{d} \sum_{i=1}^{k} \{\ln(g_i!) - \ln(n_i!) - \ln[(g_i-n_i)!]\} = 0
\end{aligned}$$

To use Stirling's approximation for the term $\ln[(g_i-n_i)!]$, we place ourselves in the general case of a low-degeneracy gas, for which $g_i \gg n_i$. In addition, we also use Stirling's approximation for $n_i \gg 0$.

$$\begin{aligned}
&\mathrm{d} \sum_{i=1}^{k} [g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i-n_i)\ln(g_i-n_i) + (g_i-n_i)] \approx 0 \\
&\sum_{i=1}^{k} \left[-\ln n_i\, \mathrm{d}n_i - n_i \frac{\mathrm{d}n_i}{n_i} + \ln(g_i-n_i)\, \mathrm{d}n_i + (g_i-n_i) \frac{\mathrm{d}n_i}{g_i-n_i}\right] \approx 0 \\
&\sum_{i=1}^{k} \ln\left(\frac{g_i-n_i}{n_i}\right) \mathrm{d}n_i \approx 0
\end{aligned}$$

As in Bose-Einstein statistics, to account for the constraints on the number of particles and on the internal energy we introduce two Lagrange multipliers, α'' and β'':

$$\sum_{i=1}^{k} \ln\left(\frac{g_i - n_i}{n_i}\right) \mathrm{d}n_i - \alpha'' \sum_{i=1}^{k} \mathrm{d}n_i - \beta'' \sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i = 0$$

$$\sum_{i=1}^{k} \left[\ln\left(\frac{g_i - n_i}{n_i}\right) - \alpha'' - \beta''\varepsilon_i\right] \mathrm{d}n_i = 0$$

$$\forall i = 1, \ldots, k \quad \ln\left(\frac{g_i - n_i}{n_i}\right) - \alpha'' - \beta''\varepsilon_i = 0$$

We isolate the number of quanta n_i per energy level,

$$\frac{g_i}{n_i} - 1 = e^{(\alpha'' + \beta'')\varepsilon_i}$$

$$g_i = n_i(e^{\alpha''}\, e^{\beta''\varepsilon_i} + 1)$$

$$\boxed{n_i^0 = \frac{g_i}{e^{\alpha''}\, e^{\beta''\varepsilon_i} + 1}} \tag{5.2}$$

which is the most probable distribution in Fermi-Dirac statistics, for $g_i \gg n_i^0 \gg 0$, in other words for a low-degeneracy gas. The Lagrange multipliers, α'' and β'', are determined in § 6 p. 35.

Chapter 6

PARAMETERS OF QUANTUM STATISTICS

Contents

We start with the parameters β' and β'' which are simpler to determine than α' and α''.

A Parameters β' and β'' of Quantum Statistics

Let us show that the parameters β' and β'' are independent of the statistics considered, and therefore constitute a unique parameter β. To do this, consider a mixture of particles obeying two different statistics. The total number of microstates is the product of the two microstates:

$$W = W_1(n_i)\, W_2(n'_j)$$
$$\ln W = \ln W_1(n_i) + \ln W_2(n'_j)$$

W must be maximal, so $\ln W$ too:

$$\mathrm{d}\ln W = 0$$
$$\sum_{i=1}^{k} \frac{\partial \ln W_1}{\partial n_i}\,\mathrm{d}n_i + \sum_{j=1}^{k'} \frac{\partial \ln W_2}{\partial n'_j}\,\mathrm{d}n'_j = 0$$

In addition, there are three constraints, the numbers N_1 and N_2 of particles are fixed, as well as the internal energy U:

$$\sum_{i=1}^{k} n_i = N_1 \qquad \Rightarrow \qquad \sum_{i=1}^{k} \mathrm{d}n_i = 0$$
$$\sum_{j=1}^{k'} n'_j = N_2 \qquad \Rightarrow \qquad \sum_{j=1}^{k'} \mathrm{d}n'_j = 0$$
$$\sum_{i=1}^{k} \varepsilon_i n_i + \sum_{j=1}^{k'} \varepsilon'_j n'_j = U \qquad \Rightarrow \qquad \sum_{i=1}^{k} \varepsilon_i \mathrm{d}n_i + \sum_{j=1}^{k'} \varepsilon'_j \mathrm{d}n'_j = 0$$

Having only one constraint on the internal energy, we introduce only the parameter β. We link the four previous equations using three Lagrange multipliers, α, α', and β

$$\sum_{i=1}^{k}\frac{\partial \ln W_1}{\partial n_i}\,\mathrm{d}n_i+\sum_{j=1}^{k'}\frac{\partial \ln W_2}{\partial n'_j}\,\mathrm{d}n'_j+\alpha\sum_{i=1}^{k}\mathrm{d}n_i+\alpha'\sum_{j=1}^{k'}\mathrm{d}n'_j+\beta\left[\sum_{i=1}^{k}\varepsilon_i\,\mathrm{d}n_i+\sum_{j=1}^{k'}\varepsilon'_j\,\mathrm{d}n'_j\right]=0$$

$$\sum_{i=1}^{k}\left(\frac{\partial \ln W_1}{\partial n_i}+\alpha+\beta\varepsilon_i\right)\mathrm{d}n_i+\sum_{j=1}^{k'}\left(\frac{\partial \ln W_2}{\partial n'_j}+\alpha'+\beta\varepsilon'_j\right)\mathrm{d}n'_j=0$$

The n_i being independent of the n'_j

$$\begin{cases}\displaystyle\sum_{i=1}^{k}\left(\frac{\partial \ln W_1}{\partial n_i}+\alpha+\beta\varepsilon_i\right)\mathrm{d}n_i=0\\ \displaystyle\sum_{j=1}^{k'}\left(\frac{\partial \ln W_2}{\partial n'_j}+\alpha'+\beta\varepsilon'_j\right)\mathrm{d}n'_j=0\end{cases}$$

so that:

$$\begin{cases}\forall i=1,\dots,k\quad \displaystyle\sum_{i=1}^{k}\frac{\partial \ln W_1}{\partial n_i}+\alpha+\beta\sum_{i=1}^{k}\varepsilon_i=0\\ \forall j=1,\dots,k'\quad \displaystyle\sum_{j=1}^{k'}\frac{\partial \ln W_2}{\partial n'_j}+\alpha'+\beta\sum_{j=1}^{k'}\varepsilon'_j=0\end{cases}$$

If we solve by replacing the statistics W_1 and W_2 with their respective expressions, we will have the same parameter β. Consequently, regardless of the statistics considered:

$$\boxed{\beta=\frac{1}{kT}}\tag{6.1}$$

B Parameters α' and α'' of Quantum Statistics

To determine the parameters α' and α'' we use the constraint on N,

$$N=\sum_{i=1}^{k}n_i^0$$

and the expressions of the most probable distributions in Bose-Einstein statistics, relation (5.1) p. 32, and Fermi-Dirac, relation (5.2) p. 33:

$$N=\sum_{i=1}^{k}\frac{g_i}{e^{\alpha}\,e^{\beta\varepsilon_i}\pm 1\,{}^{F.D.}_{B.E.}}$$

where $\alpha=\alpha'$ or $\alpha=\alpha''$ depending on the statistics considered. To account for the spherical symmetry of the problem we traverse the phase space in spherical coordinates of position ρ, θ, φ, and momentum p_ρ, p_θ, p_φ. Starting from (2.2) p. 16, the degeneracy factor is:

$$\begin{aligned}g_i&=\frac{1}{h^3}\int_\rho\int_\theta\int_\varphi\int_{p_\rho}\int_{p_\theta}\int_{p_\varphi}p_\rho^2\sin p_\theta\mathrm{d}p_\varphi\mathrm{d}p_\theta\mathrm{d}p_\rho\,\rho^2\sin\theta\,\mathrm{d}\varphi\,\mathrm{d}\theta\,\mathrm{d}\rho\\&=\frac{V4\pi}{h^3}\int_0^{+\infty}p_\rho^2\mathrm{d}p_\rho\end{aligned}$$

The energy ε_i of the particles can be expressed in terms of their momentum p_i

$$\varepsilon_i = \frac{p_i^2}{2m}$$

hence

$$\begin{aligned} N &= \frac{V4\pi}{h^3} \int_0^{+\infty} p_\rho^2 \mathrm{d}p_\rho \sum_{i=1}^{k} \frac{1}{e^\alpha e^{\beta p_i^2/(2m)} \pm 1 \, {}^{F.D.}_{B.E.}} \\ &= \frac{V4\pi}{h^3} \int_0^{+\infty} \frac{p_\rho^2 \mathrm{d}p_\rho}{e^\alpha e^{\beta p^2/(2m)} \pm 1 \, {}^{F.D.}_{B.E.}} \end{aligned}$$

and we have passed to a continuous representation.

We set,

$$\begin{aligned} x &= \frac{\beta\, p_\rho^2}{2m} \qquad \Rightarrow \qquad p_\rho = \sqrt{\frac{2mx}{\beta}} \\ \mathrm{d}x &= \frac{\beta}{m} p_\rho \mathrm{d}p_\rho \qquad \Rightarrow \qquad p_\rho \mathrm{d}p_\rho = \frac{m\mathrm{d}x}{\beta} \end{aligned}$$

$$\begin{aligned} p_\rho^2 \mathrm{d}p_\rho &= p_\rho \times p_\rho \mathrm{d}p_\rho \\ &= \sqrt{\frac{2mx}{\beta}}\, \frac{m\mathrm{d}x}{\beta} \\ &= \sqrt{2} \left(\frac{m}{\beta}\right)^{3/2} \sqrt{x}\mathrm{d}x \end{aligned}$$

The total number of particles is therefore:

$$\begin{aligned} N &= \frac{V4\pi}{h^3} \sqrt{2} \left(\frac{m}{\beta}\right)^{3/2} \int_0^{+\infty} \frac{\sqrt{x}\mathrm{d}x}{e^\alpha e^x \pm 1 \, {}^{F.D.}_{B.E.}} \\ &= \frac{2}{\sqrt{\pi}} V \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \int_0^{+\infty} \frac{\sqrt{x}\mathrm{d}x}{e^\alpha e^x \pm 1 \, {}^{F.D.}_{B.E.}} \end{aligned}$$

With (2.3) p. 16 giving Z:

$$N = \frac{2}{\sqrt{\pi}} Z \int_0^{+\infty} \frac{\sqrt{x}\mathrm{d}x}{e^{(\alpha+x)} \pm 1 \, {}^{F.D.}_{B.E.}} \tag{6.2}$$

This integral is not analytically solvable. We will seek approximate solutions.

Chapter 7

ANALYTICAL EXPRESSIONS OF THE PARAMETERS α' AND α''

Contents

A Parameters of Bose-Einstein and Fermi-Dirac Statistics

Let us seek the constraints we have on these parameters. In § A p. 31, we assumed $n_i^0 \gg 0$. In addition, the number of energy sub-levels is a positive number, $g_i > 0$, which implies for Bose-Einstein statistics

$$\frac{n_i^0}{g_i} > 0$$

With (5.1) p. 32,

$$\begin{aligned}\frac{1}{e^{\alpha'}\, e^{\beta\varepsilon_i} - 1} &> 0\\ e^{\alpha'} e^{x} - 1 &> 0\\ e^{(\alpha' + x)} &> 1\\ \alpha' + x &> 0\end{aligned}$$

where we set $x = \beta\varepsilon_i$. For Fermi-Dirac statistics we have the additional constraint set in § B p. 32,

$$\begin{aligned} g_i \gg n_i^0 &\gg 0\\ 1 \gg \frac{n_i^0}{g_i} &> 0\end{aligned}$$

With (5.2) p. 33,

$$\begin{aligned} 1 \gg \frac{1}{e^{\alpha''}\, e^{\beta\varepsilon_i}+1} &> 0 \\ e^{\alpha''} e^{x}+1 &\gg 1 \\ e^{(\alpha''+x)} &\gg 0 \\ \alpha''+x &\gg 0 \end{aligned}$$

In (6.2) p. 37, we expand in series the term $[e^{(\alpha+x)} \pm 1]^{-1}$ using the following series expansion:

$$(1 \pm y)^{-1} = \sum_{m=0}^{+\infty} (\mp 1)^m y^m$$

This series converges only for $y < 1$. We have $\alpha + x > 0$ so $e^{-(\alpha+x)} < 1$.

$$\begin{aligned} \frac{1}{e^{(\alpha+x)} \pm 1 \, {}^{F.D.}_{B.E.}} &= \frac{1}{e^{(\alpha+x)}} \times \frac{e^{(\alpha+x)}}{e^{(\alpha+x)} \pm 1 \, {}^{F.D.}_{B.E.}} \\ &= e^{-(\alpha+x)} \times \frac{1}{1 \pm e^{-(\alpha+x)} \, {}^{F.D.}_{B.E.}} \\ &= e^{-(\alpha+x)} \times \sum_{m=0}^{+\infty} (\mp 1)^m \, e^{-m(\alpha+x)} \, {}^{F.D.}_{B.E.} \\ &= \sum_{m=0}^{+\infty} (\mp 1)^m \, e^{-(m+1)(\alpha+x)} \, {}^{F.D.}_{B.E.} \end{aligned}$$

Setting $n = m + 1$

$$\frac{1}{e^{(\alpha+x)} \pm 1 \, {}^{F.D.}_{B.E.}} = \sum_{n=1}^{+\infty} (\mp 1)^{n-1} \, e^{-n(\alpha+x)} \, {}^{F.D.}_{B.E.}$$

We inject the series expansion into the expression of the total number N of particles given by (6.2) p. 37:

$$\begin{aligned} N &= \frac{2}{\sqrt{\pi}} Z \int_0^{+\infty} \frac{\sqrt{x}\mathrm{d}x}{e^{(\alpha+x)} \pm 1 \, {}^{F.D.}_{B.E.}} \\ &= \frac{2}{\sqrt{\pi}} Z \int_0^{+\infty} \sum_{n=1}^{+\infty} (\mp 1)^{n-1} e^{-n(\alpha+x)} \sqrt{x}\mathrm{d}x \, {}^{F.D.}_{B.E.} \\ &= \frac{2}{\sqrt{\pi}} Z \sum_{n=1}^{+\infty} (\mp 1)^{n-1} e^{-n\alpha} \int_0^{+\infty} e^{-nx} \sqrt{x}\mathrm{d}x \, {}^{F.D.}_{B.E.} \end{aligned}$$

We set

$$u = nx \quad \Rightarrow \quad x = \frac{u}{n} \quad \Rightarrow \quad \sqrt{x} = \sqrt{\frac{u}{n}} \quad \text{and} \quad \mathrm{d}x = \frac{du}{n} \quad \Rightarrow \quad \sqrt{x}\mathrm{d}x = \frac{\sqrt{u}du}{n^{3/2}}$$

$$N = \frac{2}{\sqrt{\pi}} Z \sum_{n=1}^{+\infty} (\mp 1)^{n-1} e^{-n\alpha} \int_0^{+\infty} \frac{1}{n^{3/2}} \, e^{-u} \sqrt{u}du \, {}^{F.D.}_{B.E.}$$

This integral is calculated using Euler's Gamma function (see appendix D p. 46):

$$\begin{aligned}\int_0^{+\infty} e^{-u}\sqrt{u}du &= \Gamma\left(\tfrac{3}{2}\right)\\ &= \frac{1}{2}\Gamma\left(\tfrac{1}{2}\right)\\ &= \frac{\sqrt{\pi}}{2}\end{aligned}$$

N now is,

$$\begin{aligned}N &= \frac{2}{\sqrt{\pi}}\,Z\sum_{n=1}^{+\infty}(\mp 1)^{n-1}e^{-n\alpha}\frac{1}{n^{3/2}}\frac{\sqrt{\pi}}{2}\ {\scriptstyle\substack{F.D.\\ B.E.}}\\ \frac{N}{Z} &= \sum_{n=1}^{+\infty}(\mp 1)^{n-1}\,\frac{e^{-n\alpha}}{n^{3/2}}\ {\scriptstyle\substack{F.D.\\ B.E.}}\\ &= e^{-\alpha} \mp \frac{1}{2^{3/2}}\,e^{-2\alpha} + \frac{1}{3^{3/2}}\,e^{-3\alpha} \mp \ldots\ {\scriptstyle\substack{F.D.\\ B.E.}}\end{aligned} \tag{7.1}$$

It remains to invert this relation, in other words to express α in terms of N/Z. We seek the expression of $e^{-\alpha}$ in the form of a power series of N/Z

$$e^{-\alpha} = a_0 + a_1\frac{N}{Z} + a_2\left(\frac{N}{Z}\right)^2 + a_3\left(\frac{N}{Z}\right)^3 + \ldots$$

which we replace in (7.1) p. 41:

$$\begin{aligned}\frac{N}{Z} = &\left[a_0 + a_1\frac{N}{Z} + a_2\left(\frac{N}{Z}\right)^2 + a_3\left(\frac{N}{Z}\right)^3 + \ldots\right]\\ &\mp \frac{1}{2^{3/2}}\left[a_0 + a_1\frac{N}{Z} + a_2\left(\frac{N}{Z}\right)^2 + a_3\left(\frac{N}{Z}\right)^3 + \ldots\right]^2\\ &+ \frac{1}{3^{3/2}}\left[a_0 + a_1\frac{N}{Z} + a_2\left(\frac{N}{Z}\right)^2 + a_3\left(\frac{N}{Z}\right)^3 + \ldots\right]^3\\ &\mp \ldots\ {\scriptstyle\substack{F.D.\\ B.E.}}\end{aligned}$$

We find directly

$$a_0 = 0 \quad , \quad a_1 = 1$$

It remains

$$\frac{N}{Z} = \frac{N}{Z} + \left(a_2 \mp \frac{1}{2^{3/2}}\right)\left(\frac{N}{Z}\right)^2 + \left(a_3 \mp \frac{2a_2}{2^{3/2}} + \frac{1}{3^{3/2}}\right)\left(\frac{N}{Z}\right)^3 + \ldots\ {\scriptstyle\substack{F.D.\\ B.E.}}$$

To cancel the coefficients, we must set

$$\begin{aligned}a_2 &= \pm\frac{1}{2^{3/2}}\ {\scriptstyle\substack{F.D.\\ B.E.}}\\ a_3 &= \pm\frac{2a_2}{2^{3/2}} - \frac{1}{3^{3/2}}\\ &= \pm\frac{2}{2^{3/2}}\left(\pm\frac{1}{2^{3/2}}\right) - \frac{1}{3^{3/2}}\\ &= \frac{1}{4} - \frac{1}{3^{3/2}}\end{aligned}$$

hence

$$e^{-\alpha} = \left(\frac{N}{Z}\right) \pm \frac{1}{2^{3/2}}\left(\frac{N}{Z}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)\left(\frac{N}{Z}\right)^3 + \ldots\ {\scriptstyle\substack{F.D.\\ B.E.}}$$

which we inject into (5.1) p. 32, to obtain the expression of the most probable distribution in B-E statistics, for $n_i^0 \gg 0$

$$n_i^0 = \frac{g_i}{\left[\left(\frac{N}{Z}\right) - \frac{1}{2^{3/2}}\left(\frac{N}{Z}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)\left(\frac{N}{Z}\right)^3 + \dots\right]^{-1} e^{\varepsilon_i/(kT)} - 1}$$

Injected into (5.2) p. 33, we obtain the most probable distribution in Fermi-Dirac statistics, for $g_i \gg n_i^0 \gg 0$

$$n_i^0 = \frac{g_i}{\left[\left(\frac{N}{Z}\right) + \frac{1}{2^{3/2}}\left(\frac{N}{Z}\right)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}}\right)\left(\frac{N}{Z}\right)^3 + \dots\right]^{-1} e^{\varepsilon_i/(kT)} + 1}$$

B Case of Completely Degenerate Bosons

$$\begin{aligned}
n_i^0 &\gg g_i \\
\frac{n_i^0}{g_i} &\gg 1 \\
\frac{1}{e^{\alpha'}\, e^{\beta\varepsilon_i} - 1} &\gg 1 \\
e^{\alpha'} e^{x} - 1 &\ll 1 \\
e^{(\alpha' + x)} &\ll 2 \\
\alpha' + x &\ll \ln 2
\end{aligned}$$

Now, α' and x are positive, so

$$\begin{aligned}
\alpha' &\approx 0 \\
e^{\alpha'} &\approx 1
\end{aligned}$$

Using (7.1) p. 41:

$$\begin{aligned}
\frac{N}{Z} &\approx 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \frac{1}{4^{3/2}} + \dots \\
&\approx \sum_{n=1}^{+\infty} \frac{1}{n^{3/2}} \\
&\approx 2,612
\end{aligned}$$

Chapter 8

APPENDICES

Contents

A Stirling's Approximation

Let's start by calculating the integral of $\ln x$

$$\int_1^n \ln x \mathrm{d}x$$

by integrating by parts

$$\begin{cases} u' = 1 \quad \Rightarrow \quad u = x \\ v = \ln x \quad \Rightarrow \quad v' = \dfrac{1}{x} \end{cases}$$

We have:

$$\begin{aligned} \int_1^n \ln x \mathrm{d}x &= [x \ln x]_1^n - \int_1^n \mathrm{d}x \\ &= n \ln n - n + 1 \end{aligned}$$

The rectangle method, with unit width, gives an approximation of this integral when n tends to infinity

$$\begin{aligned} \int_1^n \ln x \mathrm{d}x &\approx \frac{\ln 1 + \ln 2}{2} + \frac{\ln 2 + \ln 3}{2} + \cdots + \frac{\ln(n-1) + \ln n}{2} \\ &\approx \ln 2 + \ln 3 + \cdots + \ln(n-1) + \frac{1}{2} \ln n \\ &\approx \ln(n!) - \frac{1}{2} \ln n \end{aligned}$$

Equating the two results, we have

$$
\begin{aligned}
\ln(n!) - \frac{1}{2}\ln n &\approx n\ln n - n + 1 \\
\ln(n!) &\approx n\ln n - n + \frac{1}{2}\ln n + 1 \\
&\boxed{\ln(n!) \approx n\ln n - n}
\end{aligned}
$$

B Method of Lagrange Multipliers

Suppose we seek the extremum of a function f of k variables $n_{i=1,\dots,k}$. At the extremum point with coordinates $\{n_1^0, \dots, n_k^0\}$, the total differential of f is zero:

$$
\begin{aligned}
\mathrm{d}f(n_1, n_2, \dots, n_k) &= 0 \\
\frac{\partial f}{\mathrm{d}n_1}\mathrm{d}n_1 + \frac{\partial f}{\mathrm{d}n_2}\mathrm{d}n_2 + \dots + \frac{\partial f}{\mathrm{d}n_k}\mathrm{d}n_k &= 0 \qquad (8.1)
\end{aligned}
$$

If the variables $n_{i=1,\dots,k}$ are independent, we have directly,

$$\forall i = 1, \dots, k \qquad \frac{\partial f}{\partial n_i} = 0 \qquad (8.2)$$

because the $\mathrm{d}n_i$ vary independently, their respective coefficients must be canceled. When the variables are dependent, they are linked by a constraint

$$h(n_1, n_2, \dots, n_k) = 0 \qquad (8.3)$$

which is valid at every point, so also at the extremum point. Consequently, h being constant and zero, its total differential is zero everywhere, so also at the extremum point:

$$\frac{\partial h}{\mathrm{d}n_1}\mathrm{d}n_1 + \frac{\partial h}{\mathrm{d}n_2}\mathrm{d}n_2 + \dots + \frac{\partial h}{\mathrm{d}n_k}\mathrm{d}n_k = 0 \qquad (8.4)$$

At this stage, we could isolate for example $\mathrm{d}n_k$ in the previous relation and replace its expression in (8.1). By choosing to express one of the coordinates in terms of the others we break the symmetry, which makes the problem more difficult to solve. The Lagrange method is as follows:

We multiply (8.4) by λ and add it to (8.1):

$$\left(\frac{\partial f}{\partial n_1} + \lambda\frac{\partial h}{\partial n_1}\right)\mathrm{d}n_1 + \dots + \left(\frac{\partial f}{\partial n_k} + \lambda\frac{\partial h}{\partial n_k}\right)\mathrm{d}n_k = 0$$

Among the k variables, $k-1$ are independent since in this example we have only one constraint equation. Suppose these are the first $k-1$ variables that are independent. We can choose λ so as to eliminate the last coefficient, that of $\mathrm{d}n_k$:

$$\frac{\partial f}{\partial n_k} + \lambda\frac{\partial h}{\partial n_k} = 0$$

Then only the differentials of the $k-1$ independent variables remain:

$$\left(\frac{\partial f}{\partial n_1} + \lambda\frac{\partial h}{\partial n_1}\right)\mathrm{d}n_1 + \dots + \left(\frac{\partial f}{\partial n_{k-1}} + \lambda\frac{\partial h}{\partial n_{k-1}}\right)\mathrm{d}n_{k-1} = 0$$

Consequently, as for (8.2), we have directly

$$\forall i = 1, \dots, k-1 \qquad \frac{\partial f}{\partial n_i} + \lambda \frac{\partial h}{\partial n_i} = 0$$

which means that after introducing the parameter λ, all variables can be considered independent since

$$\forall i = 1, \dots, k \qquad \frac{\partial f}{\partial n_i} + \lambda \frac{\partial h}{\partial n_i} = 0$$

The solution to the problem will be given in terms of λ, which will be determined subsequently using the constraint equation (8.3).

C Calculation of the Gaussian Integral

$$\begin{aligned} I &= \int_{-\infty}^{+\infty} e^{-\mathrm{a}x^2} \mathrm{d}x \\ I^2 &= \int_{-\infty}^{+\infty} e^{-\mathrm{a}x^2} \mathrm{d}x \times \int_{-\infty}^{+\infty} e^{-\mathrm{a}y^2} \mathrm{d}y \\ &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\mathrm{a}(x^2+y^2)} \mathrm{d}x \mathrm{d}y \end{aligned}$$

traversing space in polar coordinates

$$\begin{aligned} I^2 &= \int_{0}^{2\pi} \int_{0}^{+\infty} e^{-\mathrm{a}r^2} dr \times r\mathrm{d}\theta \\ &= 2\pi \int_{0}^{+\infty} r e^{-\mathrm{a}r^2} dr \\ &= 2\pi \left[-\frac{1}{2a} e^{-\mathrm{a}r^2} \right]_{0}^{+\infty} \\ &= \frac{\pi}{\mathrm{a}} \end{aligned}$$

hence

$$\boxed{I = \sqrt{\frac{\pi}{\mathrm{a}}}}$$

D Euler's Gamma Function

It is defined as follows

$$\forall z \in \mathbb{C}/Re(z) > 0 \qquad \mathit{\Gamma} : z \mapsto \int_0^{+\infty} t^{z-1}\, e^{-t} \mathrm{d}t$$

We find its main property by integrating by parts:

$$\begin{cases} u' = t^{z-1} & \Rightarrow \quad u = \dfrac{1}{z}\, t^z \\ v = e^{-t} & \Rightarrow \quad v' = -e^{-t} \end{cases}$$

We have:

$$\begin{aligned} \mathit{\Gamma}(z) &= \left[-\frac{1}{z}\, t^z\, e^{-t} \right]_0^{+\infty} + \int_0^{+\infty} \frac{1}{z}\, t^z\, e^{-t} \mathrm{d}t \\ &= \frac{1}{z} \int_0^{+\infty} t^z\, e^{-t} \mathrm{d}t \\ &= \frac{1}{z}\, \mathit{\Gamma}(z+1) \end{aligned}$$

Consequently we have the property

$$\mathit{\Gamma}(z+1) = z\, \mathit{\Gamma}(z)$$

We see that Euler's Gamma function extends the factorial function to the set of complex numbers, except for negative or zero integers.

$$\mathit{\Gamma}\left(\tfrac{3}{2}\right) = \frac{1}{2}\, \mathit{\Gamma}\left(\tfrac{1}{2}\right)$$

We now need to find the expression of $\mathit{\Gamma}\left(\tfrac{1}{2}\right)$

$$\mathit{\Gamma}\left(\tfrac{1}{2}\right) = \int_0^{+\infty} t^{-1/2}\, e^{-t} \mathrm{d}t$$

We perform the change of variable

$$t = x^2 \quad \Rightarrow \quad \mathrm{d}t = 2x\mathrm{d}x$$

to have:

$$\begin{aligned} \mathit{\Gamma}\left(\tfrac{1}{2}\right) &= \int_0^{+\infty} x^{-1}\, e^{-x^2}\, 2x\mathrm{d}x \\ &= 2 \int_0^{+\infty} e^{-x^2} \mathrm{d}x \end{aligned}$$

We recover the Gaussian integral (see appendix C p. 45), with a = 1:

$$\begin{aligned} \left[\mathit{\Gamma}\left(\tfrac{1}{2}\right)\right]^2 &= 2 \int_0^{\pi} \int_0^{+\infty} e^{-r^2} dr \times r\mathrm{d}\theta \\ &= \pi \end{aligned}$$

So

$$\boxed{\mathit{\Gamma}\left(\tfrac{1}{2}\right) = \sqrt{\pi}}$$