

The Boltzmann distribution

Distributions

In statistical physics a **distribution** is a certain arrangement of particles on available states (the mathematical meaning in probabilities is a little different). Simple examples from everyday life:

1. Particles are $N=2$ different coins; states are two pockets.

The possible arrangements are:



This is the distribution of 2 coins in the 2 pockets.

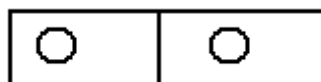
The probability that the two coins would be in the same pocket is $2/4=0.5$, because there are two “good” states (the far left and the far right) from 4 possible.

2. Particles are $N=2$ *indistinguishable* microparticles which may be in two different states: Such particles are e.g. photons.



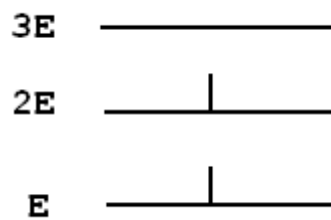
The probability that the two coins would be in the same pocket is $2/3=0.67$, so it's bigger than before. This type of *indistinguishable* microparticles is called **bosons**. They like to be together. Indeed, the probability that the two coins would be in the same pocket is $2/3=0.67$, because there are two “good” states (the far left and the far right) from 3 possible.

3. Particles are $N=2$ *indistinguishable* microparticles which may be in two different states, but this time we may have at most one particle in a state:

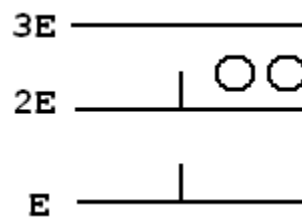
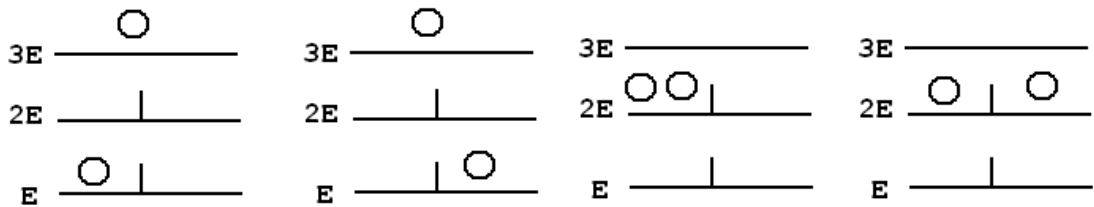


There is just one possible state. This type of *indistinguishable* microparticles is called **fermions**. They don't like to be together. Such particles are e.g. electrons.

In the above examples we didn't care about physics, but in physics we are interested in distributions with certain limiting conditions (constraints): constant temperature, constant energy, etc. Assume we want to find all the possible states of $N=2$ particles which may have three different states with energies E , $2E$ or $3E$; state with energy E has two substates (one says its **degeneracy** $g=2$ and state with energy $2E$ has the same double degeneracy. The sketch of the possible states is given below (without particles)



We want the possible states with the total energy $U=4E$. They are shown below for bosons:



We may say the system has one macrostate with energy $U=4E$ and 5 compatible microstates, so the statistical weight is $\Omega=5$. These 5 microstates may be classified in two families (they are known as complexities, but we shall not use this name): the first two and the other three. What is the criterion?

The probability that the two particles would have the same energy is $3/5=0.6$.

Exercices. 1. Draw the possible states for the same problem if the particles are fermions.

2. Draw the possible states for the same problem if the particles are classical.
3. Draw the possible states for the same problem if the total energy is $U=5E$.

Stirling approximation

We'll need to compute an approximation of $\text{Log}(n!)$, when $n \gg 1$ (Log is the natural logarithm). What follows is but a rough justification of the result. Write:

$$\text{Log}(n!) = \text{Log}(n \cdot (n-1) \cdot (n-2) \dots 3 \cdot 2 \cdot 1) = \text{Log}(n) + \text{Log}(n-1) + \dots \text{Log}3 + \text{Log}2 + \text{Log}1$$

As $n \gg 1$ the difference between two adjacent arguments is much smaller than the arguments themselves for many terms. This difference is equal to 1. As it is small, we may (horrible mathematical thing) go from sum to integral putting $dx = 1$:

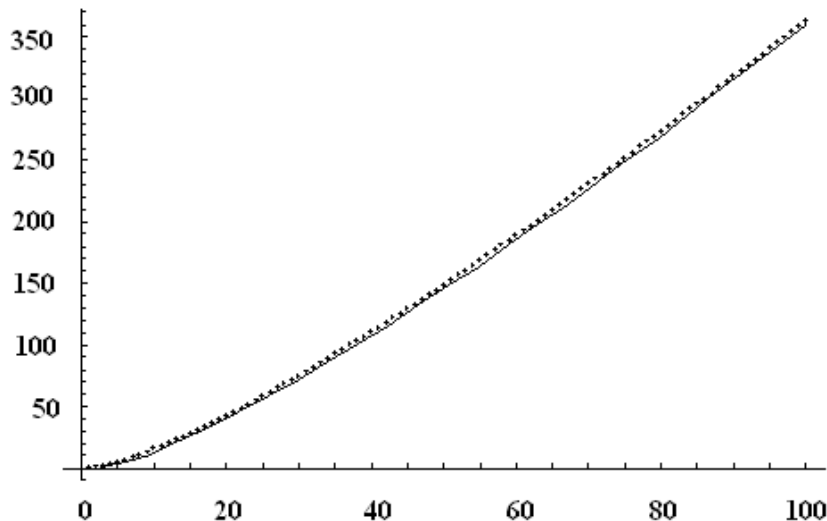
$$\text{Log}(n!) = \text{Log}(n) + \text{Log}(n-1) + \dots \text{Log}3 + \text{Log}2 + \text{Log}1 \cong$$

$$\int_1^n \text{Log}(x) dx = \left[x \text{Log}(x) - x \right]_1^n \cong n \text{Log}n - n$$

We have neglected 1 in the last approximation. This is the Stirling approximation:

$$\text{Log}(n!) \cong n \text{Log}n - n \quad \text{for } n \gg 1$$

The following graph shows calculated points $\text{Log}(n!)$ and the Stirling approximation for $1 < x < 100$.



The general problem is: **find the equilibrium distribution of N identical particles on states with energies $\varepsilon_1, \varepsilon_2, \varepsilon_3, \dots, \varepsilon_s$, states having degeneracies $g_1, g_2, g_3, \dots, g_s$. The**

total energy $U = \sum_{i=1}^s n_i \varepsilon_i$ is constant, as well as the total number of particles $N = \sum_{i=1}^s n_i$.

We have to find the number of particles on each state, that is the numbers n_1, n_2, \dots, n_s .

The equilibrium distribution is the most disordered one. That means it is the most probable distribution, the distribution with the biggest statistical weight.

Assumptions:

- the temperature is constant, as is the energy (strictly speaking the two conditions are different, but the difference is very small)
- the particles are independent, in the sense that we may put any number of particles in any state, if the two conditions

$$N = \sum_{i=1}^s n_i \quad (1)$$

$$U = \sum_{i=1}^s n_i \varepsilon_i \quad (2)$$

are satisfied.

Let's compute the statistical weight Ω for a certain distribution of particles among the s states, i.e. the number of ways we obtain certain values of n_i s. It's clear that we obtain the same distribution if we permute the particles. The number of such equivalent distributions is $N!$. But here we add in all the cases where particles in one cell are permuted and that doesn't give new states. So we have to divide by $n_1!n_2!n_3!\dots n_s!$ to get the number of different ways to get a certain family of values n_1, n_2, \dots, n_s :

$$\frac{N!}{n_1!n_2!\dots n_s!}$$

To get the probability of such a distribution we have to multiply this number by the *a priori* probability to have one of these distributions.

The probability that one particle is in the first state is g_1 ; the probability to have n_1 particles in this state is $g_1^{n_1}$

The probability that one particle is in the second state is g_2 ; the probability to have n_2 particles in this state is $g_2^{n_2}$

.....

The probability that one particle is in the s 's state is g_s ; the probability to have n_s particles in this state is $g_s^{n_s}$

The probability to have n_1 particles in the first state, n_2 in the second, ..., n_s in the s 's is the product of the individual probabilities, i.e. $g_1^{n_1} g_2^{n_2} \dots g_s^{n_s}$. The statistical weight is eventually:

$$\Omega = \frac{N!}{n_1! n_2! \dots n_s!} g_1^{n_1} g_2^{n_2} \dots g_s^{n_s} \quad (3)$$

We want the maximum of this number. It's easier to compute the maximum of its logarithm:

$$\text{Log}\Omega = \text{Log}\left(\frac{N!}{n_1! n_2! \dots n_s!} g_1^{n_1} g_2^{n_2} \dots g_s^{n_s}\right) = N(\text{Log}N - 1) - \sum_{i=1}^s n_i(\text{Log}n_i - 1) + \sum_{i=1}^s n_i(\text{Log}g_i)$$

To find the maximum we compute the derivative and make it zero:

$$d\text{Log}\Omega = \sum_{i=1}^s (\text{Log} \frac{g_i}{n_i} - 1) dn_i = 0 \quad (4)$$

Differentiation of the two conditions (1) and (2) gives two new conditions:

$$\sum_{i=1}^s dn_i = 0 \quad (5)$$

$$\sum_{i=1}^s \varepsilon_i dn_i = 0 \quad (6)$$

Multiply (5) by λ and (6) by $-\beta$ (Lagrange) and add all together to find the conditions:

$$\sum_{i=1}^s (\text{Log} \frac{g_i}{n_i} - 1 + \lambda - \beta \varepsilon_i) dn_i = 0 \quad (7)$$

Here all the variations are independent so each bracket is zero and we get:

$$\boxed{n_i = Ag_i \exp[-\beta\varepsilon_i]} \quad (8)$$

which is the Boltzmann distribution. One can demonstrate that $\beta = 1/k_B T$. Note the exponential behavior.

The constant A is obtained from the normalization condition

$$\sum_{i=1}^s n_i = N \quad \text{or} \quad \sum_{i=1}^s \frac{n_i}{N} = \sum_{i=1}^s P_i = 1 \quad (9)$$

where P_i is the probability to have n_i particles with energy ε_i . Using (8) we find:

$$\frac{1}{N} \sum_{i=1}^s Ag_i \exp[-\beta\varepsilon_i] = 1 \quad \text{hence} \quad A = \frac{N}{\sum_{i=1}^s Ag_i \exp[-\beta\varepsilon_i]} \quad (10)$$

Remark 1. We have assumed energy has a **discrete spectrum**, it does not vary continuously. This is a quantum picture, used because it is easier to think of numbers instead of continuous varying functions. Anyway, each measurement apparatus has a lower value it can measure, the so-called resolution. We can't measure energy values with accuracy superior than the resolution. So we may assume we measure the energy in discrete portions.

Remark 2. It's easier to think of numbers but harder to do sums than integrals, so in many cases we go from sums to integrals. (9) becomes

$$\sum_{i=1}^s P_i \rightarrow \int_{\text{allvalues}} G(E) dP(E) = \int_{\text{allvalues}} G(E) \mathfrak{P}(E) dE = 1 \quad (11)$$

$G(E)$ is the number of states with energy between E and $E+dE$, the spectral number of states. If you want to use the number of states per dE and per dV you introduce the spectral density of states $g(E)$. $\mathfrak{P}(E)$ is the density of probability (per unit of energy and of volume).