A micro-canonical derivation of the Boltzmann for distinguishable and the "correct" Boltzmann distribution for indistinguishable particles

1. General assumptions

In the following text I will derive the most probable distribution of N particles among k energy levels from combinatorics and some classical thermodynamics. Each energy level i is assumed to have g_i different states. I will restrict the analysis to systems where each state can accommodate an unlimited number of particles. As examples one can think of an ideal gas of atoms or molecules I will discuss two cases, distinguishable and indistinguishable particles and within each case I will assume the total number of particles to be constant.

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2. Distinguishable particles, any number of particles per state: The Boltzmann distribution

The number of possible arrangements of N particles among k energy levels such that n_i particles are on level i, which consists of g_i states, is given by:

$$W = N!\prod_{i=1}^{k}\frac{{g_i}^{n_i}}{n_i!}$$

Taking the logarithm and applying Stirling's approximation gives:

$$\ln W = \ln N! + \sum_{i=1}^{k} n_i \ln g_i - \sum_{i=1}^{k} n_i! \approx Nln\, N - N + \sum_{i=1}^{k} n_i \ln g_i - \sum_{i=1}^{k}(n_i \ln n_i - n_i)$$

$$= Nln\, N + \sum_{i=1}^{k} n_i \ln g_i - \sum_{i=1}^{k} n_i \ln n_i$$

Obviously W is a maximum when ln W is a maximum.
To find this maximum we vary n_i and then set the resulting expression equal to zero with constraints included using Lagrange multipliers.
It is useful to first investigate how an individual term in ln W varies when we vary the n_i.
All terms of ln W apart from the first can be written as follows:

$$T = \sum_{j=1}^{k} f(n_j)$$

When we vary the n_i we get:

$$\delta T = \sum_{i=1}^{k} \frac{\partial T}{\partial n_i} \delta n_i = \sum_{i=1}^{k} \frac{\partial}{\partial n_i} \left(\sum_{j=1}^{k} f(n_j) \right) \delta n_i = \sum_{i=1}^{k} \left(\sum_{j=1}^{k} f'(n_j) \frac{\partial n_j}{\partial n_i} \right) \delta n_i$$

$$= \sum_{i=1}^{k} \left(\sum_{j=1}^{k} f'(n_j) \delta_{ij} \right) \delta n_i = \sum_{i=1}^{k} f'(n_i) \delta n_i$$

Varying the first term (containing only N) gives:

$$\delta(N ln\, N) = \delta \left(\left(\sum_{i=1}^{k} n_i \right) \ln \left(\sum_{j=1}^{k} n_j \right) \right) = \left(\sum_{i=1}^{k} \delta n_i \right) \ln \left(\sum_{j=1}^{k} n_j \right) + \frac{\left(\sum_{i=1}^{k} n_i \right) \left(\sum_{i=1}^{k} \delta n_i \right)}{\sum_{j=1}^{k} n_j}$$

$$= \left(\sum_{i=1}^{k} \delta n_i \right) \ln \left(\sum_{j=1}^{k} n_j \right) + \left(\sum_{i=1}^{k} \delta n_i \right) = (\ln N + 1) \sum_{i=1}^{k} \delta n_i$$

$$\delta \ln W \approx (\ln N + 1) \sum_{i=1}^{k} \delta n_i - \sum_{i=1}^{k} \ln n_i \, \delta n_i - \sum_{i=1}^{k} n_i \frac{\delta n_i}{n_i} + \sum_{i=1}^{k} \ln g_i \, \delta n_i$$

$$= \ln N \sum_{i=1}^{k} \delta n_i - \sum_{i=1}^{k} \ln n_i \, \delta n_i + \sum_{i=1}^{k} \ln g_i \, \delta n_i$$

We want to apply constraints for total inner energy and constant particle number to our system:

$\sum_{i=1}^{k} n_i = N$, which implies that $\sum_{i=1}^{k} \delta n_i = 0$

and

$\sum_{i=1}^{k} n_i u_i = U$, which implies that $\sum_{i=1}^{k} u_i \delta n_i = 0$

Using the method of Lagrange multipliers we can now find the maximum of ln W under the constraints of constant particle number and energy by adding two extra terms for the constraints to the expression for δ lnW and solving the following equation for each n_i (see your favorite text on calculus of variations):

$$\ln N - \ln n_i + \ln g_i - \alpha - \beta u_i = 0$$

The solution of this equation is:

$$\frac{n_i}{g_i} = N e^{-\alpha} e^{-\beta u_i}$$

3. Indistinguishable particles, any number of particles per state, low occupation number: The "correct" Boltzmann distribution as a limiting case of the Bose-Einstein distribution

We start with the Bose-Einstein and then take the limiting case of $1 << n_i << g_i$ for all i.
The Bose-Einstein distribution can be derived from "combinations of size n_i with unrestricted repetitions, taken from a set of size g_i" as follows.
The number of different ways to place n_i indistinguishable particles in the g_i states of energy level i is the same as the number of integer solutions of the equation:

$$\sum_{j=1}^{g_i} k_j = n_i$$

Here the k_j are the numbers of particles in the states numbered from j = 1 to g_i.

If we write this equation for a particular distribution among the states using sticks rather than numbers we get something like this:

$$III + II + IIIII + I + +II + \cdots = n_i$$

Note that we leave the space between two +-signs empty to denote a state that didn't receive a particle. Clearly we can permute this row of sticks and plusses without changing the sum and therefore the total number of possibilities is:

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

Here the numerator gives the total number of permutations of the row of sticks and +-signs. We've also taken into account that swapping sticks among themselves and +-signs among themselves doesn't lead to a different expression, thus the denominator.

The total number of arrangements then becomes, again not accounting for permutations of particles in different energy levels since we assume indistinguishability:

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

From Bose-Einstein to "correct Boltzmann counting" for indistinguishable particles

A single factor in W can be written without index as:

$$W' = \frac{(n + g - 1)!}{n!\,(g - 1)!}$$

Assuming g >> n >> 1, which means that the number of particles in each energy level is large, but the number of possible states is still much larger (low occupancy), and using Stirling's approximation ln x! ≈ x ln x – x in the form $x! \approx x^x e^{-x}$ a few times, approximating $(n + g)^n$ as g^n and using $e^x \approx 1 + x$ once gives:

$$W' = \frac{(n+g-1)!}{n!\,(g-1)!} \approx \frac{(n+g)!}{n!\,g!} \approx \frac{(n+g)^{n+g}\,e^{-(n+g)}}{n^n e^{-n}\,g^g e^{-g}} = \frac{(n+g)^n (n+g)^g}{n^n\,g^g} \approx \frac{g^n (n+g)^g}{n^n\,g^g}$$

$$= \frac{g^n \left(\frac{n}{g}+1\right)^g}{n^n} \approx \frac{g^n \left(e^{\frac{n}{g}}\right)^g}{n^n} = \frac{g^n e^n}{n^n} = \frac{g^n}{n^n\,e^{-n}} \approx \frac{g^n}{n!}$$

In the very first step above we simply used that (n + g)/g ≈ 1, since g >> n.

After inserting W' back into the product for every i we get W for "correct Boltzmann counting":

$$W = \prod_{i=1}^{k} \frac{{g_i}^{n_i}}{n_i!}$$

In analogy to the Boltzmann distribution for distinguishable particles we therefore arrive at:

$$\ln W = \sum_{i=1}^{k} n_i \ln g_i - \sum_{i=1}^{k} n_i! \approx \sum_{i=1}^{k} n_i \ln g_i - \sum_{i=1}^{k} (n_i \ln n_i - n_i) = \sum_{i=1}^{k} n_i \ln g_i - n_i \ln n_i + n_i$$

$$\delta \ln W \approx \sum_{i=1}^{k} \ln g_i\,\delta n_i - \sum_{i=1}^{k} \ln n_i\,\delta n_i - \sum_{i=1}^{k} n_i \frac{\delta n_i}{n_i} + \sum_{i=1}^{k} \delta n_i = \sum_{i=1}^{k} \ln g_i\,\delta n_i - \sum_{i=1}^{k} \ln n_i\,\delta n_i$$

Therefore we get, for constant N:

$$\frac{n_i}{g_i} = e^{-\alpha} e^{-\beta u_i}$$

4. Interpretation of the Lagrange multipliers

To give the Lagrange multipliers physical meaning we start with a general method of determining Lagrange multipliers (see any text on calculus of variations) and then use Boltzmann's definition of entropy and results from classical thermodynamics.
The multiplier α is given by:

$$\alpha = \left(\frac{\partial \ln W}{\partial N}\right)_{U,V} = \frac{1}{k_B}\left(\frac{\partial (k_B \ln W)}{\partial N}\right)_{U,V} = \frac{1}{k_B}\left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{k_B T}$$

Here μ is the chemical potential and T the absolute temperature.
The entropy S is defined as k_B ln W.

The last step in the above derivation can be found by applying the triple product rule to the definitions of temperature and chemical potential as follows:

Definitions: $\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$ $\qquad$ $\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$

Triple product: $\left(\frac{\partial S}{\partial U}\right)_{N,V} \left(\frac{\partial U}{\partial N}\right)_{S,V} \left(\frac{\partial N}{\partial S}\right)_{U,V} = -1$

After inserting the definitions: $\frac{1}{T}\mu \left(\frac{\partial N}{\partial S}\right)_{U,V} = -1$

And therefore: $\left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\partial (S+const.)}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$

U stands for the total inner energy of the system.

Similarly we get the multiplier β:

$$\beta = \left(\frac{\partial \ln W}{\partial U}\right)_{N,V} = \frac{1}{k_B}\left(\frac{\partial (k_B \ln W)}{\partial U}\right)_{N,V} = \frac{1}{k_B}\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{k_B T}$$

Here the last step simply follows from the definition of temperature.

5. Expressions for entropy

Inserting the results for the distribution functions back into the corresponding expressions for ln W and using Boltzmann's definition for entropy as in section 4, leads to expressions for entropy in terms of macroscopic variables after some simplifications.

For distinguishable particles

Inserting the Boltzmann distribution

$$\frac{n_i}{g_i} = Ne^{-\alpha}e^{-\beta u_i}$$

for indistinguishable particles, constant N, into the corresponding expression for ln W gives:

$$\ln W \approx Nln\, N + \sum_{i=1}^{k} n_i \ln g_i - \sum_{i=1}^{k} n_i \ln n_i = Nln\, N - \sum_{i=1}^{k} n_i \ln \frac{n_i}{g_i}$$
$$= Nln\, N - \sum_{i=1}^{k} n_i (\ln N - \alpha - \beta u_i) = \alpha N + \beta U$$

Using Boltzmann's definition of entropy, S = k_B ln W, and the expressions for α and β derived in the previous section we get:

$$S = -\mu\frac{N}{T} + \frac{U}{T}$$

or

$$U = TS + \mu N$$

For indistinguishable particles

Inserting the "correct Boltzmann distribution"

$$\frac{n_i}{g_i} = e^{-\alpha}e^{-\beta u_i}$$

for indistinguishable particles, constant N, into the corresponding expression for ln W gives:

$$\ln W \approx \sum_{i=1}^{k} n_i \ln g_i - n_i \ln n_i + n_i = N - \sum_{i=1}^{k} n_i \ln\frac{n_i}{g_i} = N - \sum_{i=1}^{k} n_i(-\alpha - \beta u_i)$$
$$= N + \alpha N + \beta U$$

Using Boltzmann's definition of entropy, S = k_B ln W, and the expressions for α and β derived in the previous section we get:

$$S = k_B N - \mu\frac{N}{T} + \frac{U}{T}$$

or

$$U = TS - k_B NT + \mu N$$

For an ideal gas this becomes:

$$U = TS - pV + \mu N$$

6. Conclusions

We see that a purely combinatorial approach gives us the Boltzmann distribution for distinguishable particles, whereas it gives us a distribution without the factor N for the correct Boltzmann counting following from Bose-Einstein counting for indistinguishable particles in the limiting case $g_i \gg n_i$.

The results can be summarized as following:

Distinguishable particles, constant N:

$$\frac{n_i}{g_i} = Ne^{-\alpha}e^{-\beta u_i}$$

$$S = -\mu\frac{N}{T} + \frac{U}{T}$$

$$U = TS + \mu N$$

Indistinguishable particles, constant N, $g_i \gg n_i$:

$$\frac{n_i}{g_i} = e^{-\alpha}e^{-\beta u_i}$$

$$S = k_B N - \mu\frac{N}{T} + \frac{U}{T}$$

$$U = TS - k_B NT + \mu N$$

with the following expressions for the Lagrange multipliers:

$\alpha = -\frac{\mu}{k_B T}$ $\qquad$ $\beta = \frac{1}{k_B T}$

Observe that in both cases the expression for entropy is extensive!