A derivation of statistical distributions for various types of particles

In the following text I will derive statistical distributions for indistinguishable particles directly using combinatorics. This leads initially to the Bose-Einstein and the Fermi-Dirac distribution. Then I show how the Boltzmann distribution emerges under low occupancy conditions. By identifying statistical entropy (the Boltzmann formula) with thermodynamic entropy it is then possible to give all undetermined parameters (the Lagrange multipliers) physical meaning without considering a specific system (such as an ideal gas). Finally I apply these results to the ideal gas and derive the Sackur-Tetrode equation for statistical entropy and the Maxwell-Boltzmann distribution for kinetic energies in an ideal gas. For this last step I borrow the methods involving the partition function from textbook literature.

At the end of the text I also consider systems of distinguishable particles, both bosonic and fermionic, without further discussing a possible relevance for real systems. For this discussion I refer to publications by Robert Swendsen and others.

Initially the analysis considers a system of particles that can have discrete values of energy. I don't specify what kind of energy this is, for example kinetic or binding energy. I simply assign particles to generic "energy levels". Every energy level i has g_i states which can be occupied by 0 or 1 particles each in the case of fermions or any number of particles in the case of bosons. There are n_i particles in energy level i and the number of energy levels is k, which is finite. Obviously, for fermions the number of states g_i on every energy level cannot be smaller than the number of particles n_i. Each distribution of particles among energy levels can be realized in, usually, a large number of ways denoted by W. It is reasonable to assume that a system of particles that can freely change energy levels will eventually be found in a distribution close to that with the largest value for W. This most likely distribution will also be the average distribution over an extended time once the system is in equilibrium.

1. Bosons: Indistinguishable particles, any number of particles per state

The combinatorics of this case is known as "combinations of size n_i with unrestricted repetitions, taken from a set of size g_i".
The number of different ways to place n_i 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 lines 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 lines 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 lines among themselves and +-signs among themselves doesn't lead to a different expression, thus the denominator.

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

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

To find the most probable distribution of particles among energy levels (that with the largest W) we calculate the maximum of ln W:

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

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

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

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

For the maximum of ln W under the constraints of constant particle number and energy we get:

$$\ln(n_i + g_i - 1) - \ln n_i - \alpha - \beta u_i = 0$$

$$\frac{g_i - 1}{n_i} + 1 = e^{\alpha} e^{\beta u_i}$$

$$\frac{n_i}{g_i} \approx \frac{n_i}{g_i - 1} = \frac{1}{e^{\alpha} e^{\beta u_i} - 1}$$

In the last step we assumed that $g_i >> 1$.

This is the Bose-Einstein distribution for indistinguishable particles, constant particle number.

If the number of particles is not constant we get:

$$\frac{n_i}{g_i} \approx \frac{n_i}{g_i - 1} = \frac{1}{e^{\beta u_i} - 1}$$

This is the Bose-Einstein distribution for indistinguishable particles, non-constant particle number.

Examples: photon gas, phonon gas

2. Fermions: Indistinguishable particles, maximum one particle per state

The total number of arrangements becomes:

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

The same procedure as before gives us:

$$\begin{aligned}
\ln W &= \sum_{i=1}^{k} [\ln g_i! - \ln(g_i - n_i)! - \ln n_i!] \\
&\approx \sum_{i=1}^{k} [g_i \ln g_i - g_i - (g_i - n_i)\ln(g_i - n_i) + (g_i - n_i) - n_i \ln n_i + n_i] \\
&= \sum_{i=1}^{k} [g_i \ln g_i - g_i \ln(g_i - n_i) + n_i \ln(g_i - n_i) - n_i \ln n_i]
\end{aligned}$$

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

To find the maximum of ln W under the constraints of constant number of particles and constant energy we solve the following equation:

$$\ln(g_i - n_i) - \ln n_i - \alpha - \beta\, u_i = 0$$

This gives us

$$\frac{g_i}{n_i} - 1 = e^{\alpha} e^{\beta u_i}$$

And further

$$\frac{n_i}{g_i} = \frac{1}{e^{\alpha} e^{\beta u_i} + 1}$$

This is the Fermi-Dirac distribution for indistinguishable particles, constant particle number.

Examples: valence electrons in a metal

If we don't require a constant number of particles we simply leave out the Lagrange multiplier α and get:

$$\frac{n_i}{g_i} = \frac{1}{e^{\beta u_i} + 1}$$

This is the Fermi-Dirac distribution for indistinguishable particles, non-constant particle number.

Examples: ?

3. The "correct" Boltzmann distribution for indistinguishable particles as a limiting case of the Bose-Einstein and the Fermi-Dirac distribution for low occupancy

From Bose-Einstein to "correct Boltzmann counting" at low occupancy

The total number of arrangements of indistinguishable bosons among k energy levels is:

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

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 $\ln x! \approx x \ln x - x$ 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 $(n + g)/g \approx 1$, since g >> n.

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

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

From Fermi-Dirac to "correct Boltzmann counting" at low occupancy

The total number of arrangements of indistinguishable fermions among k energy levels is:

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

We again take the limiting case of $1 \ll n_i \ll g_i$ for all i.

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

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

Using Stirling's approximation $\ln x! \approx x \ln x - x$ in the form $x! \approx x^x e^{-x}$ a few times, approximating $(g - n)^n$ as g^n and using $e^{-x} \approx 1 - x$ once gives:

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

After inserting W' into the product for every i we get W for "correct Boltzmann counting" even in this case:

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

The Boltzmann distribution for indistinguishable particles

With this expression for W the usual procedure gives:

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

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

Therefore we get, for constant N:

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

For non-constant N we get:

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

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

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:

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

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

5. An expression for entropy of indistinguishable Boltzmann particles

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

Inserting the 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. An expression for the entropy of an ideal gas

The one particle partition function (see Blundell equation 21.19) is given by

$$Z_1 = \frac{V}{\lambda^3}$$

where λ is the thermal wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

The N-particle partition function for indistinguishable particles (see Blundell equation 21.29) then becomes

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

The natural logarithm of the N-particle partition function for indistinguishable particles (see Blundell equation 21.35) then becomes (using Stirling's approximation for ln N!)

$$\ln Z_N = N \ln V - 3N \ln \lambda - N \ln N + N$$

The Helmholtz free energy is given by

$$F = -k_B T \ln Z_N$$

For the chemical potential we then get

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -k_B T\left(\ln V - 3\ln \lambda - N\frac{1}{N} - \ln N + 1\right) = k_B T\, ln \frac{\lambda^3 N}{V}$$

We also have the following expression for U

$$U = \frac{3}{2} N k_B T$$

Inserting these expressions into the entropy for indistinguishable particles gives

$$S = k_B N - \mu \frac{N}{T} + \frac{U}{T} = k_B N - k_B T \ln\left(\frac{\lambda^3 N}{V}\right)\frac{N}{T} + \frac{3}{2} N k_B = \frac{5}{2} N k_B - N k_B \ln\left(\frac{\lambda^3 N}{V}\right)$$

which is the (extensive) Sackur-Tetrode equation.

7. The Maxwell-Boltzmann distribution for indistinguishable particles

We have the following expressions for indistinguishable particles

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

$$\mu = k_B T \ln\left(\frac{\lambda^3 N}{V}\right)$$

$$\beta = \frac{1}{k_B T}$$

$$\alpha = -\frac{\mu}{k_B T}$$

Inserting the chemical potential for distinguishable particles into the probability distribution for distinguishable particles gives:

$$\frac{n_i}{g_i} = e^{\frac{\mu}{k_B T}}\, e^{-\frac{u_i}{k_B T}} = N\frac{\lambda^3}{V} e^{-\frac{u_i}{k_B T}} = \frac{N}{V}\frac{h^3}{(2\pi m k_B T)^{\frac{3}{2}}} e^{-\frac{u_i}{k_B T}}$$

Writing this as a probability distribution gives:

$$f_i = \frac{n_i}{N} = \frac{g_i}{V}\frac{h^3}{(2\pi m k_B T)^{\frac{3}{2}}} e^{-\frac{u_i}{k_B T}}$$

Finally we write this distribution for a continuum of energy levels and insert an expression for the density of states g(u)du (see Blundell):

$$g(k)dk = \frac{Vk^2 dk}{2\pi^2}$$

$$u = \frac{p^2}{2m} = \frac{h^2\, k^2}{8\pi^2 m}$$

$$k^2 = \frac{8\pi^2 m u}{h^2}$$

$$k = \frac{2\pi\sqrt{2mu}}{h}$$

$$k\, dk = \frac{4\pi^2 m\, du}{h^2}$$

$$g(u)du = \frac{V}{2\,\pi^2}\frac{2\pi\sqrt{2mu}}{h}\frac{4\pi^2 m\,du}{h^2} = \frac{4\,\pi V m\sqrt{2mu}\,du}{h^3} = 4\sqrt{2}\pi m^{\frac{3}{2}}\,h^{-3}V\sqrt{u}\,du$$

$$f(u)du = \frac{g(u)}{V}\frac{h^3}{(2\pi m k_B T)^{\frac{3}{2}}}e^{-\frac{u}{k_B T}}du = \frac{2\,\sqrt{u}}{\sqrt{\pi}\,(k_B T)^{\frac{3}{2}}}\;e^{-\frac{u}{k_B T}}du$$

We thus get the Maxwell-Boltzmann distribution for the kinetic energies of indistinguishable particles in an ideal gas:

$$f(u)du = \frac{2\,\sqrt{u}}{\sqrt{\pi}\,(k_B T)^{\frac{3}{2}}}\;e^{-\frac{u}{k_B T}}du$$

An excursion to distinguishable particles

8. Distinguishable particles, any number of particles per state

The number of possible arrangements of n_i particles in the g_i states of level i is given by:

$$W_i = {g_i}^{n_i}$$

In this number all possible permutations involving particles in different states of the same level are accounted for.

Taking into account for permutations of particles on different levels the total number of arrangements is:

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

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

$$\delta \ln W = \sum_{i=1}^{k}\left[\ln N\,\delta n_i + \delta n_i \ln g_i - \delta n_i \ln n_i - n_i\frac{\delta n_i}{n_i} + \delta n_i\right]$$
$$= \sum_{i=1}^{k}[\ln N + \ln g_i - \ln n_i]\delta n_i$$

To find the maximum for constant energy and particle number:

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

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

This is the Boltzmann distribution for distinguishable particles, constant particle number.

For non-constant N we leave out the first Lagrange multiplier and get:

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

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

This is the Boltzmann distribution for distinguishable particles, non-constant particle number.

9. An expression for entropy of distinguishable Boltzmann particles

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.

Inserting the Boltzmann distribution

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

for distinguishable 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

$$U = TS + \mu N$$

10.Inserting expressions for the chemical potential into S

For distinguishable particles

The one particle partition function (see Blundell equation 21.19) is given by

$$Z_1 = \frac{V}{\lambda^3}$$

where λ is the thermal wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

The N-particle partition function then becomes (since the particles are distinguishable)

$$Z_N = \left(\frac{V}{\lambda^3}\right)^N$$

The Helmholtz free energy is given by

$$F = -k_B T \ln Z_N = -k_B T\ N\ ln \frac{V}{\lambda^3}$$

For the chemical potential we then get

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = k_B T\ ln \frac{\lambda^3}{V}$$

With the following expression for U

$$U = \frac{3}{2} N k_B T$$

we then get the following non-extensive expression for the entropy of an ideal gas of distinguishable particles

$$S = \frac{U}{T} - \mu \frac{N}{T} = \frac{3}{2} N k_B - N\ k_B \ln \frac{\lambda^3}{V}$$

11.The Maxwell-Boltzmann distribution for distinguishable particles

Inserting the chemical potential for distinguishable particles into the probability distribution for distinguishable particles gives:

$$\frac{n_i}{g_i} = N\, e^{\frac{\mu}{k_B T}}\, e^{-\frac{u_i}{k_B T}} = N\frac{\lambda^3}{V} e^{-\frac{u_i}{k_B T}} = \frac{N}{V}\frac{h^3}{(2\pi m k_B T)^{\frac{3}{2}}} e^{-\frac{u_i}{k_B T}}$$

Writing this as a probability distribution gives:

$$f_i = \frac{n_i}{N} = \frac{g_i}{V}\frac{h^3}{(2\pi m k_B T)^{\frac{3}{2}}} e^{-\frac{u_i}{k_B T}}$$

Finally we write this distribution for a continuum of energy levels and insert an expression for the density of states g(u)du (see Blundell):

$$g(k)dk = \frac{Vk^2 dk}{2\pi^2}$$

$$u = \frac{p^2}{2m} = \frac{h^2\, k^2}{8\pi^2 m}$$

$$k^2 = \frac{8\pi^2 mu}{h^2}$$

$$k = \frac{2\pi\sqrt{2mu}}{h}$$

$$k\; dk = \frac{4\pi^2 m\; du}{h^2}$$

$$g(u)du = \frac{V}{2\;\pi^2}\frac{2\pi\sqrt{2mu}}{h}\frac{4\pi^2 m\; du}{h^2} = \frac{4\;\pi V m\sqrt{2mu}\; du}{h^3} = 4\sqrt{2}\pi m^{\frac{3}{2}}\, h^{-3} V\sqrt{u}\; du$$

$$f(u)du = \frac{g(u)}{V}\frac{h^3}{(2\pi m k_B T)^{\frac{3}{2}}} e^{-\frac{u}{k_B T}} du = \frac{2\,\sqrt{u}}{\sqrt{\pi}\,(k_B T)^{\frac{3}{2}}}\; e^{-\frac{u}{k_B T}} du$$

This is the Maxwell-Boltzmann probability distribution for energies and turns out to be identical to the result we arrived at for indistinguishable particles.

12.Distinguishable particles, maximum one particle per state

The number of arrangements of n_i particles among the g_i states of level i is:

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

This number takes into account all permutations of particles within level i.

To get the total number of arrangements of particles among the k levels with n_i particles in level i we have to multiply all the W_i and then account for permutations of particles in different levels without counting permutations within the same level again. One way to do this is to first remove the permutations within in each level by dividing by $n_i!$ and then multiplying the whole product by N!, which is the total permutations of all particles.

The number of arrangements of all particles among all k levels is therefore:

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

To find the most probable distribution we take the logarithm of this expression and use Stirling's formula to simplify it.

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

Assuming that N, n_i, g_i and (g_i - n_i) are very large numbers we use Stirling's formula to approximate this expression as:

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

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

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:

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

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

This result makes it easy to calculate δW in the following.

Varying the first two terms (containing only N) gives:

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

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

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

In total we get:

$$\delta \ln W =$$

$$= \ln N \sum_{i=1}^{k} \delta n_i + \sum_{i=1}^{k}\left[-g_i \frac{-\delta n_i}{g_i - n_i} + \ln(g_i - n_i)\,\delta n_i + n_i \frac{-\delta n_i}{g_i - n_i} - \delta n_i \ln n_i - n_i \frac{\delta n_i}{n_i}\right] =$$

$$= \ln N \sum_{i=1}^{k} \delta n_i + \sum_{i=1}^{k}\left[\frac{g_i - n_i}{g_i - n_i} + \ln(g_i - n_i) - \ln n_i - 1\right]\delta n_i =$$

$$= \sum_{i=1}^{k}[\ln N + \ln(g_i - n_i) - \ln n_i]\delta n_i$$

To find the maximum for constant N we vary the n_i under the constraint that their sum is constant or in other words: $\sum_{i=1}^{k} \delta n_i = 0$.

Additionally we assume that the total inner energy of our system is constant:

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

Using the method of Lagrange multipliers we can now maximize ln W under the constraints of constant particle number and energy, which leads to the following equation for each energy level i:

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

The solution of this equation is:

$$\frac{g_i - n_i}{n_i} = \tfrac{1}{N} e^{\alpha} e^{\beta u_i}$$

$$\frac{n_i}{g_i} = \frac{1}{\frac{1}{N} e^{\alpha} e^{\beta u_i + 1}}$$

With energy conservation, but without particle conservation we get:

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

The solution of this equation is:

$$\frac{g_i - n_i}{n_i} = \frac{g_i}{n_i} - 1 = \frac{e^{\beta u_i}}{N}$$

$$\frac{n_i}{g_i} = \frac{1}{\frac{1}{N} e^{\beta u_i + 1}}$$