Fermions

1. Indistinguishable particles, maximum one particle per state

Now we assume that particles (no matter whether in the same energy level or in different ones) are indistinguishable from each other. We take this into account by dividing by the number of permutations of n_i when we calculate the different arrangements of particles in each energy level. We then simply multiply the number of arrangements in every level without taking into account permutations of particles in different levels.
The total number of arrangements with n_i particles in state i, which has g_i states, 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.

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.

2. 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:

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

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

3. 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 leads to expressions for entropy in terms of macroscopic variables after some simplifications, or maybe not?

The distribution

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

for indistinguishable particles, constant N, can be rewritten as

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

And also as

$$g_i = n_i\left(e^{\alpha} e^{\beta u_i} + 1\right)$$

The expression for ln W for indistinguishable particles is:

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

This gives

$$\begin{aligned}
\ln W &\approx \sum_{i=1}^{k} \left[-g_i \ln\left(1 - \frac{1}{e^{\alpha} e^{\beta u_i} + 1}\right) + n_i \ln\left(e^{\alpha} e^{\beta u_i}\right)\right] \\
&= \sum_{i=1}^{k} \left[-g_i \ln\left(\frac{e^{\alpha} e^{\beta u_i}}{e^{\alpha} e^{\beta u_i} + 1}\right) + n_i \ln\left(e^{\alpha} e^{\beta u_i}\right)\right] \\
&= \sum_{i=1}^{k} \left[g_i \ln\left(\frac{e^{\alpha} e^{\beta u_i} + 1}{e^{\alpha} e^{\beta u_i}}\right) + n_i(\alpha + \beta u_i)\right] \\
&= \sum_{i=1}^{k} \left[n_i\left(e^{\alpha} e^{\beta u_i} + 1\right) \ln\left(\frac{e^{\alpha} e^{\beta u_i} + 1}{e^{\alpha} e^{\beta u_i}}\right) + n_i(\alpha + \beta u_i)\right] \approx ??? + N\alpha + U\beta
\end{aligned}$$

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:

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