Counting Microstates.

Recall that for N particles, have a large number of microstates, Ω, correspond to distributions $\{n_1, n_2, n_3, \ldots\}$. We're seeking the distribution with the largest number of microstates.

Need to find $\{n_1, n_2, \ldots\}$ with constraints

$$\sum_i n_i = N \quad \text{and} \quad \sum_i n_i \varepsilon_i = U.$$

for which $\Omega(\{n_i\}) = \dfrac{N!}{\prod_i n_i!}$ which is maximum.

What changes if energy level ε_1 has degeneracy g_1.

- there are more microstates associated with the n_1 particles in ε_1, they can be in any of the g_1 degenerate states.

$$\Omega(\{n_i\}) \rightarrow N! \frac{g_1^{n_1}}{\prod_i n_i!}$$

What about making state ε_2 degenerate with degeneracy g_2?

By the same reasoning

$$\Omega(\{n_i\}) \rightarrow N! \frac{g_1^{n_1} g_2^{n_2}}{\prod_i n_i!}$$

This is generalise with

$$\Omega(\{n_i\}) \rightarrow N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

where n_i is the number of distinguishable particles in state ε_i which is g_i-fold degenerate.

Maxwell - Boltzmann distribution - fractional occupancies - most probable distribution of fractional occupancies

$$f_{MB}(\varepsilon_i) = n_i / g_i \text{ of levels } \varepsilon_i$$

To do this we will maximise the entropy.

So: $$\frac{S}{k_B} = \ln\left[\prod_i \frac{g_i^{n_i}}{n_i!}\right] + \underbrace{\ln N!}_{\text{constant}}$$ constant, so derivative will be zero (ignore).

$$= \sum_i n_i \ln g_i - \ln n_i! \quad \text{(split with log-rules).}$$

$$\simeq \sum_i n_i \ln g_i - (n_i \ln n_i - n_i) \quad \text{(Stirling).}$$

Take constraints of constant particle number and constant internal energy into account with Lagrange multipliers.

$$\frac{S}{k_B} - \alpha N - \beta U = \sum_i \Big(n_i \ln g_i - n_i \ln n_i + n_i - \alpha n_i - \beta n_i \varepsilon_i \Big)$$

Vary the distribution, i.e. $\partial / \partial n_i \Rightarrow 0$ (find maximum by varying the occupation numbers).

$$0 = \frac{\partial}{\partial n_i} \{ \text{above} \} = \ln g_i - \ln n_i - 1 + 1 - \alpha - \beta \varepsilon_i$$

$$\Rightarrow \ln \left(g_i / n_i \right) = \alpha + \beta \varepsilon_i$$

$$\Rightarrow \frac{n_i}{g_i} = f_{MB}(\varepsilon_i) = e^{-\alpha} e^{-\beta \varepsilon_i}.$$

This is the Maxwell Boltzmann distribution function.

As we saw previously, β is inverse temperature, and α is determined by fixed N,

$$\text{i.e.} \quad \int f_{MB}(\varepsilon)\, d\varepsilon = N.$$

This is for distinguishable/classical particles.