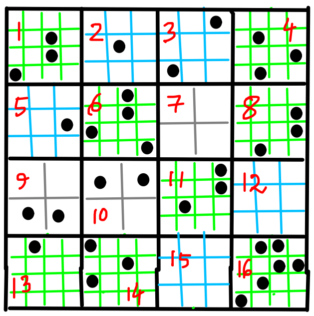
Systems of identical non-interacting particles (ideal gases)

We consider a system of N particles. These can be in K cells in **phase space**. The energy of the r^{th} cell is ϵ_r, the number of particles in the r^{th} cell is n_r and the number of subcells in the r^{th} cell is g_r. We will set g_r to 1 later.



r	1	2	3	4	5	6	7	8	...	16
g_r	16	9	9	16	9	16	4	16	...	16
n_r	3	1	2	3	1	4	0	3	...	6

We will consider states for which the total energy and the total number of particles are fixed — the microcanonical ensemble.

$$\sum_r n_r = N \quad \text{and} \quad \sum_r n_r \epsilon_r = E_R , \qquad \text{--- (1)}$$

where $R = \{n_1, n_2, \dots, n_K\}$

The number of states that correspond the state R is given by

$$\Omega_R = \frac{N!}{n_1!\, n_2! \dots n_K!} \, g_1^{n_1} g_2^{n_2} \dots g_K^{n_K} \qquad \text{--- (2)}$$

$$\ln \Omega_R = \ln N! - \sum_r \ln n_r! + \sum_r n_r \ln g_r$$

$$\simeq \ln N! - \sum_r (n_r \ln n_r - n_r) + \sum_r n_r \ln g_r$$

(Using Stirling's approximation $\rightarrow \ln x! \sim x \ln x - x$ as $x \to \infty$)

We would like to maximize $\ln \Omega_R$ with the constraints (1).

We use Lagrange multipliers α and β with the constraints and get,

$$\left[\delta \ln \Omega_R - \alpha\,\delta\left(\sum_r n_r\right) - \beta\,\delta\left(\sum_r n_r \mathcal{E}_r\right)\right]_{\{n_r\}=\{\bar{n}_r\}} = 0$$

where the occupation numbers $\{\bar{n}_r\}$ maximize Ω_R.

$$\Rightarrow \quad \sum_r \left[-\ln \bar{n}_r - 1 + 1 + \ln g_r - \alpha - \beta \mathcal{E}_r\right] \delta n_r = 0$$

Since the variations $\{\delta n_r\}$ are independent, we require

$$-\ln \bar{n}_r + \ln g_r - \alpha - \beta \mathcal{E}_r = 0 \quad \text{for each } r,$$

$$\Rightarrow \quad \bar{n}_r = g_r\, e^{-\alpha - \beta \mathcal{E}_r} \quad \Rightarrow \quad \bar{n}_r \propto g_r\, e^{-\beta \mathcal{E}_r}$$

We can choose our cells so that $g_r = 1$.

In that case, we get, $\bar{n}_r \propto e^{-\beta \mathcal{E}_r}$ --- (3)

The values of α and β are obtained from the two constraint equations.

Eq. (3) gives the Maxwell-Boltzmann distribution law.

Method of Lagrange multipliers.

Maximize the area of a rectangle with perimeter equal to 4 units.

If the length of the rectangle is x and width is y, we have,

$$A = xy$$

$$4 = 2(x+y) \quad \text{--- Constraint}$$

$$\delta A - \lambda\,\delta\left[2(x+y)\right] = 0 \qquad \text{using Lagrange multiplier } \lambda.$$

$$\Rightarrow x\,\delta y + y\,\delta x - 2\lambda\,\delta x - 2\lambda\,\delta y = 0$$

$$\Rightarrow (y - 2\lambda)\,\delta x + (x - 2\lambda)\,\delta y = 0$$

Since the variations of x and y are independent,

$$y - 2\lambda = 0 \quad \text{and} \quad x - 2\lambda = 0$$

$$\Rightarrow x = y \quad \therefore \ \delta y \text{ is arbitrary.}$$

$$\therefore \ x = y = 1 \Rightarrow A = 1.$$

Quantum identical particles are indistinguishable.
In this case let us assume that the subcells represent single particle states. For bosons, there is no restriction on the number of particles that occupy the single particle states. For fermions, at most one particle can occupy a single particle level — Pauli's exclusion principle.
Since the particles are indistinguishable, the combinatorial factor of $\left(\frac{N!}{n_1! n_2! \ldots}\right)$ in Eq. (2), is not required.

For bosons, $\Omega_R = \omega_1 \omega_2 \ldots \omega_K$

where ω_r is the number of ways of filling g_r single particle states with n_r particles.

$$1 \ 2 \ | \ 3 \ | \ 4 \ 5 \ 6 \ | \ \cdots \ | \ n_r \qquad \rightarrow g_r - 1 \text{ partitions}$$

The particles are indistinguishable and so are the partitions.

$$\therefore \ \omega_r = \frac{(n_r + g_r - 1)!}{n_r! \, (g_r - 1)!}$$

$$\ln \Omega_R \approx \sum_r \Big[(n_r + g_r - 1) \ln (n_r + g_r - 1) - (\cancel{n_r} + g_r - 1) - n_r \ln n_r + \cancel{n_r} - \ln (g_r - 1)! \Big]$$

$\therefore$ Using the Lagrange multipliers α & β for the constraints, (1), we get,

$$\sum_r \left[\ln(\bar{n}_r + g_r - 1) + 1 - \ln \bar{n}_r - 1 - \alpha - \beta \varepsilon_r \right] \delta n_r = 0$$

$\bar{n}_r \gg 1$
$\Rightarrow \bar{n}_r + g_r - 1 \sim n_r + g_r$

$$\Rightarrow \frac{\bar{n}_r + g_r}{\bar{n}_r} = e^{\alpha + \beta \varepsilon_r} \Rightarrow \left(e^{\alpha+\beta\varepsilon_r} - 1\right)\bar{n}_r = g_r$$

$$\Rightarrow \bar{n}_r = \frac{g_r}{e^{\alpha+\beta\varepsilon_r} - 1}$$

Again, choosing $g_r = 1$,

$$\bar{n}_r = \frac{1}{e^{\alpha+\beta\varepsilon_r} - 1}$$

The parameters α and β can be determined from the constraints.

$\beta = 1/k_B T$ and $\alpha = -\beta\mu$

$$\bar{n}_r = \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1}$$ --- The Bose-Einstein distribution formula.

For fermions, $\Omega_R = \omega_1 \omega_2 \cdots \omega_K$

where ω_r is the number of ways of choosing n_r single particle states from the g_r states.

$$\Rightarrow \omega_r = \binom{g_r}{n_r} = \frac{g_r!}{n_r!(g_r - n_r)!}$$

$$\Rightarrow \ln \omega_r \sim \ln g_r! - n_r \ln n_r + \cancel{n_r} - (g_r - n_r)\ln(g_r - n_r) + g_r - \cancel{n_r}$$

$$\Rightarrow \ln \Omega_R \sim \sum_r \left[-n_r \ln n_r - (g_r - n_r)\ln(g_r - n_r) \right] + \text{constant}$$

$\therefore$ Using the Lagrange multipliers α & β for the constraints, (1),

we get,

$$\sum_r \left[-\ln \bar{n}_r - 1 + 1 + \ln (g_r - \bar{n}_r) - \alpha - \beta \varepsilon_r \right] \delta n_r = 0$$

$$\Rightarrow \quad -\ln \bar{n}_r + \ln (g_r - \bar{n}_r) - \alpha - \beta \varepsilon_r = 0$$

$$\Rightarrow \quad \frac{g_r - \bar{n}_r}{\bar{n}_r} = e^{\alpha + \beta \varepsilon_r} \quad \Rightarrow \quad \frac{g_r}{\bar{n}_r} = 1 + e^{\alpha + \beta \varepsilon_r}$$

$$\Rightarrow \quad \bar{n}_r = \frac{g_r}{e^{\alpha + \beta \varepsilon_r} + 1}$$

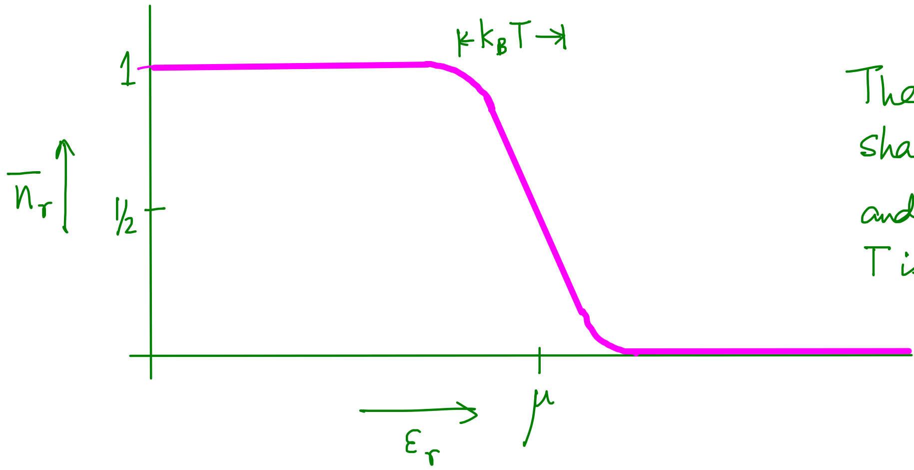
We can choose $g_r = 1$,

$$\Rightarrow \quad \bar{n}_r = \frac{1}{e^{\alpha + \beta \varepsilon_r} + 1}$$

Again, the Lagrange multipliers can be determined from the constraints.

$\alpha = -\beta \mu$ and $\beta = 1/k_B T$

$$\bar{n}_r = \frac{1}{e^{\beta(\varepsilon_r - \mu)} + 1}$$ --- The Fermi-Dirac distribution formula.



The step becomes sharp at $T=0$ and flattens as T is increased.