5.4.3 The Most Probable Configuration

In thermal equilibrium, we are searching for the *most probable configuration* (N_1, N_2, …, N_n, …) i.e. the one that can be achieved in the largest number of ways i.e. such that $Q(N_1, N_2, \ldots, N_n, \ldots)$ is the largest.

The catch is that there are **constraints**:

$$\sum_{n=1}^{\infty} N_n = N \qquad \sum_{n=1}^{\infty} N_n E_n = E$$

Maximizations with **constraints** are handled via a method called **Lagrange Multipliers**:

The general problem is that of maximizing a function of many variables $F(x_1, x_2, x_3, \ldots)$ subject to constraints such as

$$f_1(x_1, x_2, x_3, \ldots) = 0, \; f_2(x_1, x_2, x_3, \ldots) = 0, \text{ etc.}$$

The address this problem we introduce a bigger function with Lagrange multipliers $G(x_1, x_2, x_3, \ldots, \lambda_1, \lambda_2, \ldots) \equiv F + \lambda_1 f_1 + \lambda_2 f_2 + \cdots$

Lagrange multipliers

And request: $\frac{\partial G}{\partial x_n} = 0 \quad \frac{\partial G}{\partial \lambda_n} = 0$

Better to work with lnQ instead of Q since they have maxima at same point, but lnQ is easier

$$G \equiv \ln(Q) + \alpha\left[N - \sum_{n=1}^{\infty} N_n\right] + \beta\left[E - \sum_{n=1}^{\infty} N_n E_n\right]$$

Use Sterling formula: $\ln(z!) \approx z\ln(z) - z \quad \text{for } z \gg 1$

Again, only results will be given here, for the most probable configuration. For distinguishable particles:

$$\ln(Q) = \ln(N!) + \sum_{n=1}^{\infty} [N_n \ln(d_n) - \ln(N_n!)]$$

$$N_n = d_n e^{-(\alpha+\beta E_n)}$$

For identical fermions:

$$\ln(Q) = \sum_{n=1}^{\infty} \{\ln(d_n!) - \ln(N_n!) - \ln[(d_n - N_n)!]\}$$

$$N_n = \frac{d_n}{e^{(\alpha+\beta E_n)} + 1}$$

For identical bosons:

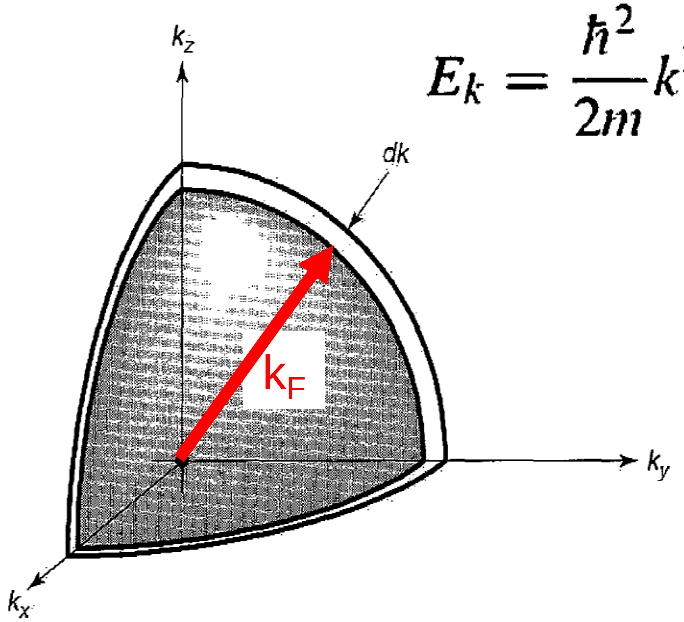
$$\ln(Q) = \sum_{n=1}^{\infty} \{\ln[(N_n + d_n - 1)!] - \ln(N_n!) - \ln[(d_n - 1)!]\}$$

$$N_n = \frac{d_n - 1}{e^{(\alpha+\beta E_n)} - 1}$$

5.4.4 Physical Significance of α and β.

Thus far, α and β are merely Lagrange multipliers, but they have an important physical meaning.

To understand the meaning, we will use the example of the ideal gas employing a 3D infinite square well.



$$E_k = \frac{\hbar^2}{2m}k^2$$

$$\mathbf{k} = \left(\frac{\pi n_x}{l_x}, \frac{\pi n_y}{l_y}, \frac{\pi n_z}{l_z}\right)$$

Vol of thin layer dk

$$d_k = \frac{1}{8}\frac{4\pi k^2\,dk}{(\pi^3/V)} = \frac{V}{2\pi^2}k^2\,dk$$

Octant — Vol. of a block

Degeneracy: all states in a thin layer have the same energy.

The first constraint is:

$$\sum_{n=1}^{\infty} N_n = N$$

For distinguishable particles:

$$N_n = d_n e^{-(\alpha+\beta E_n)}$$

$$E_k = \frac{\hbar^2}{2m}k^2$$

$$d_k = \frac{1}{8}\frac{4\pi k^2\,dk}{(\pi^3/V)} = \frac{V}{2\pi^2}k^2\,dk$$

$$N = \frac{V}{2\pi^2}e^{-\alpha}\int_0^{\infty} e^{-\beta\hbar^2k^2/2m}k^2\,dk = Ve^{-\alpha}\left(\frac{m}{2\pi\beta\hbar^2}\right)^{3/2}$$

Rearranging numbers:

$$e^{-\alpha} = \frac{N}{V}\left(\frac{2\pi\beta\hbar^2}{m}\right)^{3/2}$$

The second constraint is:

$$\sum_{n=1}^{\infty} N_n E_n = E$$

$$E_k = \frac{\hbar^2}{2m} k^2$$

Again, for distinguishable particles:

$$N_n = d_n e^{-(\alpha + \beta E_n)}$$

$$E_k = \frac{\hbar^2}{2m} k^2$$

$$d_k = \frac{1}{8} \frac{4\pi k^2 \, dk}{(\pi^3 / V)} = \frac{V}{2\pi^2} k^2 \, dk$$

$$E = \frac{V}{2\pi^2} e^{-\alpha} \frac{\hbar^2}{2m} \int_0^{\infty} e^{-\beta \hbar^2 k^2 / 2m} k^4 \, dk = \frac{3V}{2\beta} e^{-\alpha} \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2}$$

$$e^{-\alpha} = \frac{N}{V} \left(\frac{2\pi \beta \hbar^2}{m} \right)^{3/2}$$

Very simple equation arises:

$$E = \frac{3N}{2\beta} \quad \text{vs} \quad \frac{E}{N} = \frac{3}{2} k_B T$$

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

Instead of α, we will introduce a quantity called the chemical potential via a definition:

$$\mu(T) \equiv -\alpha k_B T$$

Thus, $\alpha = -\mu\beta$ which simplifies the math.

$$N_n = d_n e^{-(\alpha+\beta E_n)} \longrightarrow \frac{N_n}{d_n} = e^{-(-\mu\beta + \beta E_n)} = e^{-(\varepsilon-\mu)\beta} = n(\epsilon)$$

Most probable number of particles in a (one-particle) state with energy ε:

$$n(\epsilon) = \begin{cases} e^{-(\epsilon-\mu)/k_B T} & \text{MAXWELL-BOLTZMANN} \\ \dfrac{1}{e^{(\epsilon-\mu)/k_B T}+1} & \text{FERMI-DIRAC} \\ \dfrac{1}{e^{(\epsilon-\mu)/k_B T}-1} & \text{BOSE-EINSTEIN} \end{cases}$$

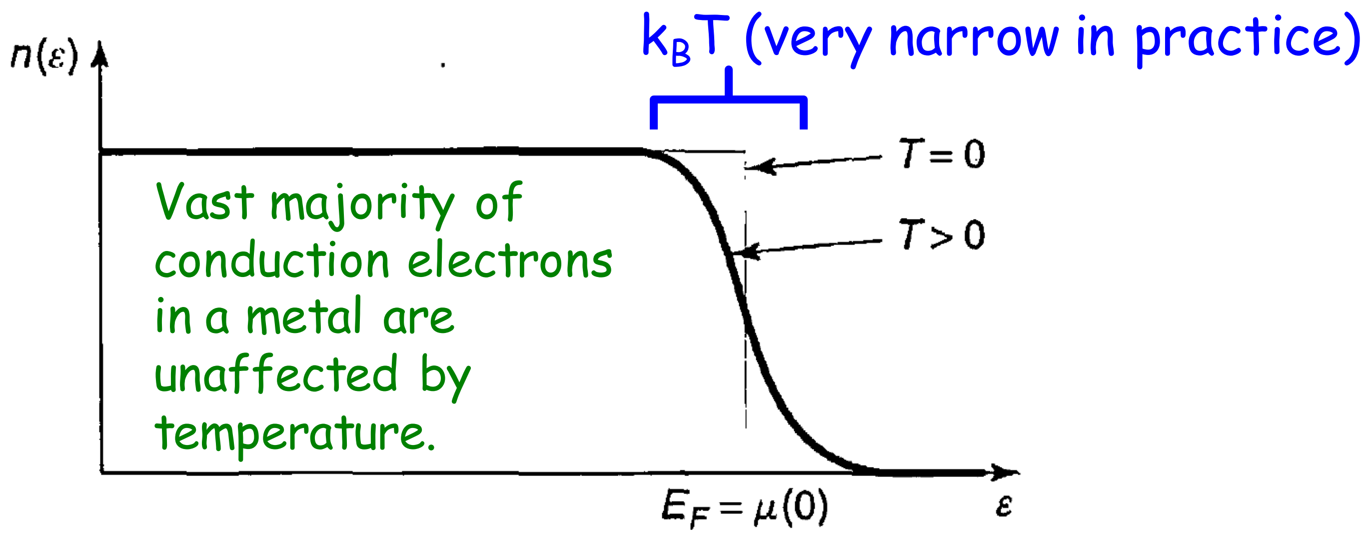
Here, we will only discuss the case of fermions where both the temperature and the chemical potential can be easily visualized. For classical and bosonic particles, T is the same as usual while μ is somewhat related to how many particles you have. μ is crucial in chemical reactions, where number of particles is not conserved.

Consider fermions: as T → 0

$$e^{(\epsilon-\mu)/k_B T} \to \begin{cases} 0, & \text{if } \epsilon < \mu(0) \\ \infty, & \text{if } \epsilon > \mu(0) \end{cases}$$

Then, the number of particles at a particular energy becomes:

$$n(\epsilon) \to \begin{cases} 1, & \text{if } \epsilon < \mu(0) \\ 0, & \text{if } \epsilon > \mu(0) \end{cases}$$



The Bose Einstein condensation and the black body radiation are left for the near future, whenever we have a chance.

We must move to Ch 6 fast …