

**STATISTICAL THERMODYNAMICS**  
**BOLTZMANN'S DISTRIBUTION**

It is our goal to determine the equilibrium configuration for a closed system, an assembly, of  $N$  distinguishable noninteracting particles subject to the constraints:  $N = \sum_i N_i$ , and  $U = \sum_i N_i \varepsilon_i$ . Here,  $N_i$  is the number of particles with energy  $\varepsilon_i$ , and  $N$  and  $U$  are assumed to be fixed quantities. Also, at equilibrium, the values of the energy levels will not alter, i.e.  $d\varepsilon_i = 0$ .

**Non-Degenerate Case:**

$$N = \sum_i N_i \Rightarrow \alpha \sum_i \delta N_i = 0, \quad (i)$$

$$U = \sum_i N_i \varepsilon_i \Rightarrow \beta \sum_i \varepsilon_i \delta N_i = 0 \quad (ii)$$

$$w = \frac{N!}{\prod_{i=1}^r N_i!} \Rightarrow \delta \ln(w) = -\sum_i \ln N_i \delta N_i = 0. \quad (iii)$$

where  $\alpha$  and  $\beta$  are the Lagrangian undetermined multipliers and are related to the physical prosperities of the assembly. Adding (i), (ii) and (iii) implies:

$$\left[ \sum_i \ln N_i + \alpha + \beta \varepsilon_i \right] dN_i = 0.$$

It is possible to select values of  $\alpha$  and  $\beta$  such that one of the terms in the sum (i.e.  $i=1$ ) is zero, the value of  $dN_1$  being immaterial. The remaining  $dN_i$  terms are then independent of one another (since  $dN_1$  may be obtained from equation (i)). It is now possible to set each of the coefficients of  $dN_i$  to zero in the last equation and this gives:

$$N_i = e^{-\alpha - \beta \varepsilon_i}.$$

Which gives the distribution for the most probable distribution.

**Degenerate Case :**

The only difference will be in equation (iii), which will be replaced by:

$$w = N! \prod_{i=1}^r \frac{g_i^{N_i}}{N_i!} \Rightarrow \delta \ln(w) = \sum_i \ln g_i \delta N_i - \sum_i \ln N_i \delta N_i. \quad (iv)$$

The new distribution will be

$$N_i = g_i e^{-\alpha - \beta \varepsilon_i}.$$

We must now identify the two constants  $\alpha$  and  $\beta$  in this distribution equation.

**Identification of  $\alpha$  :**

Now we have

$$\sum_i N_i = N \Rightarrow \sum_i g_i e^{-\alpha - \beta \varepsilon_i} = N \Rightarrow e^{-\alpha} = \frac{N}{\sum_i g_i e^{-\beta \varepsilon_i}} = \frac{N}{Z},$$

where  $Z = \sum_i g_i e^{-\beta \varepsilon_i}$  is known as the molecular partition function and is of the utmost importance in statistical thermodynamics. The Maxwell-Boltzmann distribution is therefore:

$$N_i = \frac{N g_i e^{-\beta \varepsilon_i}}{Z} \Rightarrow f(\varepsilon_i) = \frac{N_i}{N} = \frac{g_i e^{-\beta \varepsilon_i}}{Z}$$

Where  $f(\varepsilon_i)$  is the probability of occupation of a single state belonging to the  $i$ th energy level. We can also define  $P_i = \frac{N_i}{N} = \frac{g_i e^{-\beta \varepsilon_i}}{Z}$ , with  $N \rightarrow \infty$  as the probability that a particle is chosen at random is in the state  $i$ , with the conditions:

$$\sum_i P_i = 1 \quad \text{and} \quad \sum_i \varepsilon_i P_i = u,$$

➤ The average value of a physical quantity will be expressed as:

$$\bar{f} = \frac{1}{N} \sum_i n_i f(\varepsilon_i) = \frac{1}{Z} \sum_i g_i f(\varepsilon_i) e^{-\beta \varepsilon_i}.$$

**Example 1:** If the particles of a system can be in only two states of energy  $\varepsilon_1 = +\varepsilon$  and  $\varepsilon_2 = -\varepsilon$ , both with the same probability ( $g_1 = g_2 = 1$ ), then

$$Z = e^{-\beta \varepsilon_1} + e^{\beta \varepsilon_2} = e^{-\beta \varepsilon} + e^{\beta \varepsilon} = 2 \cosh(\beta \varepsilon)$$

$$\bar{U} = \frac{1}{Z} \left( \varepsilon_1 e^{-\beta \varepsilon_1} + \varepsilon_2 e^{\beta \varepsilon_2} \right) = \frac{\varepsilon e^{-\beta \varepsilon} - \varepsilon e^{\beta \varepsilon}}{2 \cosh(\beta \varepsilon)} = -\varepsilon \tanh(\beta \varepsilon)$$

and the total energy

$$U = N \bar{U} = -N \varepsilon \tanh(\beta \varepsilon)$$

which allows us to find  $\beta$  in terms of  $U$ .

**Identification of  $\beta$ :**

$$N_i = \frac{N g_i e^{-\beta \varepsilon_i}}{Z}$$

$$\Rightarrow \ln(N_i) = \ln(N) - \ln(Z) + \ln(g_i) - \beta \varepsilon_i$$

$$U = \sum_i N_i \varepsilon_i$$

$$\Rightarrow U = \frac{N}{Z} \sum_i \varepsilon_i g_i e^{-\beta \varepsilon_i} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} [\ln(Z)]$$

$$w = N! \prod_{i=1}^r \frac{g_i^{N_i}}{N_i!}$$

$$\Rightarrow \ln(w) = N \ln(N) + \sum_i N_i \ln g_i - \sum_i N_i \ln N_i = N \ln Z + \beta U .$$

$$S = k \ln W = kN \ln Z + k\beta U .$$

$$\Rightarrow \left( \frac{\partial S}{\partial U} \right)_V = \frac{Nk}{Z} \frac{dZ}{d\beta} \left( \frac{\partial \beta}{\partial U} \right)_V + k\beta + kU \left( \frac{\partial \beta}{\partial U} \right)_V = \beta k .$$

$$Z = \sum_i g_i e^{-\beta \epsilon_i}$$

$$\Rightarrow \frac{\partial Z}{\partial \beta} = - \sum_i \epsilon_i g_i e^{-\beta \epsilon_i} = - \frac{UZ}{N} .$$

$$\text{Then Maxwell's law gives } \left( \frac{\partial S}{\partial U} \right)_V = \frac{1}{T} = \beta k$$

**Example 2:** A system has three energy levels of energy 0, 100 k, and 200 k, with degeneracy of 1, 3, and 5 respectively. Calculate the partition function, the relative population of each level, and the average energy at a temperature of 100 K.

$$Z = 1 + 3e^{-1} + 5e^{-2} = 2.78$$

The probability is given by

$$P_i = \frac{N_i}{N} = g_i \frac{e^{-\beta \epsilon_i}}{Z}$$

So, the probability of the particles being in the lowest, first and second states are:

$$p_0 = \frac{1}{Z} = 0.360, p_1 = \frac{3e^{-1}}{Z} = 0.397, p_2 = \frac{5e^{-2}}{Z} = 0.243$$

$$\text{Note that: } p_0 + p_1 + p_2 = 1$$

The average energy is

$$\bar{U} = (0 \times p_0 + 100 \times p_1 + 200 \times p_2)k = 88.3k$$

## Appendix

**Lemma I:** The number of permutation of  $N$  distinguishable particles is  $N!$ .

**Lemma II:** The number of ways of assigning  $N$  distinguishable particles into  $r$  distinguishable cells so that there are  $N_1, \dots, N_r$  particles in the respective cells is

$$\frac{N!}{\prod_{i=1}^r N_i!}.$$

**Comment 1:** Use  $w = \frac{N!}{\prod_{i=1}^r N_i!}$  to prove that  $\ln(w) = N \ln N - \sum_i N_i \ln N_i$ .

**Answer:**

$$\begin{aligned} \ln(w) &= \ln\left(\frac{N!}{\prod_{i=1}^r N_i!}\right) = \ln(N!) - \ln\left(\prod_{i=1}^r N_i!\right) = \ln(N!) - \ln[(N_1!)(N_2!) \dots] \\ &= \ln(N!) - [\ln(N_1!) + \ln(N_2!) + \dots] = \ln(N!) - \sum_i \ln(N_i!) \end{aligned}$$

Apply Stirling's approximation in the form  $\ln(N!) = N \ln(N) - N$ , we can then approximate the expression for the number of microstates as

$$\begin{aligned} \ln(w) &= N \ln N - N - \sum_i (N_i \ln N_i - N_i) \\ &= N \ln N - N - \sum_i N_i \ln N_i - \underbrace{\sum_i N_i}_N = N \ln N - \sum_i N_i \ln N_i. \end{aligned}$$

➤ By differentiation with respect to  $N_i$ , we can get

$$\begin{aligned} \delta \ln(w) &= \delta(N \ln N) - \sum_i \ln N_i \delta N_i - \sum_i N_i \delta(\ln N_i) \\ &= 0 - \sum_i \ln N_i \delta N_i - \underbrace{\sum_i \delta N_i}_{=0} = - \sum_i \ln N_i \delta N_i. \end{aligned}$$

The last equation gives the change in  $\ln(w)$  as the number of particles in each level is varied.

➤ In degenerate case, we can use  $w = N! \prod_{i=1}^r \frac{g_i^{N_i}}{N_i!}$ , where  $g_i$  is the degeneracy of the  $i$ th energy level, so that  $\delta \ln(w) = \sum_i \ln g_i \delta N_i - \sum_i \ln N_i \delta N_i$ .

## DISTRIBUTION OF THE MOLECULAR SPEED

Use the definition  $f(\varepsilon_i) = \frac{N_i}{g_i} = N \frac{e^{-\beta \varepsilon_i}}{Z}$ , to define the number of particles having energies between  $\varepsilon$  and  $\varepsilon + d\varepsilon$  as:  $N(\varepsilon)d\varepsilon = f(\varepsilon)g(\varepsilon)d\varepsilon$ . For ideal gas,

$$z = V \left( \frac{2\pi mkT}{h^2} \right)^{3/2} = V \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \quad \text{and} \quad g(\varepsilon) = \frac{4\pi V \sqrt{2}}{h^3} m^{3/2} \varepsilon^{1/2} \text{ is the density of states.}$$

Combined the above equations, one can have

$$N(\varepsilon)d\varepsilon = \frac{2\pi N}{(\pi kT)^{3/2}} \varepsilon^{1/2} e^{-\beta \varepsilon} d\varepsilon, \quad \varepsilon = \frac{1}{2} m v^2, \quad d\varepsilon = m v dv.$$

Here is the single particle K.E. Thus  $\varepsilon = \frac{1}{2} m v^2$ ,  $d\varepsilon = m v dv$ ,  $\varepsilon^{1/2} d\varepsilon = \frac{1}{\sqrt{2}} m^{3/2} v^2 dv$ .

Convert the K.E. to speed, such that  $N(\varepsilon)d\varepsilon = N(v)dv$ , where  $N(v)dv$  is the number of particles having speed between  $v$  and  $v + dv$ . Finally the Maxwell speed distribution is:

$$N(v)dv = 4\pi N \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-\beta m v^2 / 2} dv.$$

Such formula has been derived using the Kinetic theory.

**Mean speed:**

$$\bar{v} = \frac{1}{N} \int_0^{\infty} v N(v) dv = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^3 e^{-av^2} dv = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = 1.596 \sqrt{\frac{RT}{M}}.$$

**Root mean square speed:**

$$v^2 = \frac{1}{N} \int_0^{\infty} v^2 N(v) dv = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} \int_0^{\infty} v^4 e^{-av^2} dv = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

$$v_{rms} = \sqrt{v^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = 1.732 \sqrt{\frac{RT}{M}}$$

**Most probable speed:**

$$\frac{d}{dv} (v^2 e^{-av}) = 0 \Rightarrow v_{mps} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} = 1.414 \sqrt{\frac{RT}{M}}$$

$$\text{Standard integral } \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}, \quad \int_{-\infty}^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}, \quad n = 0, 1, 2, \dots$$

**Equipartition theorem:** For every degree of freedom for which the energy is a quadratic function, the mean energy per particle of a system in equilibrium at temperature  $T$  is  $kT/2$ .

$$\bar{\varepsilon}(z) = \frac{\int \varepsilon(z)N(z)dz}{\int N(z)dz} = \frac{\int az^2 e^{-az^2/kT} dz}{\int N(z)dz} = \frac{1}{2}kT$$

Using the standard integral  $\int_{-\infty}^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$ ,  $n = 0,1,2,\dots$

Q1- Calculate the average speed, root mean square speed and the most probable speed of nitrogen at 1000 K.

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 1000}{\pi \times 28 \times 10^{-3}}} \approx 870 \text{ m/s}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} \approx 944 \text{ m/s}$$

$$v_{mp} = \sqrt{\frac{2RT}{M}} \approx 771 \text{ m/s}$$

Q2- Determine the fraction of molecules of the X-component velocities in the range  $v_{mp}$  and  $1.6 v_{mp}$ .

The fraction F is given as:

$$F = \int_{v_{mp}}^{1.6v_{mp}} \frac{f(v_x)dv_x}{N}, \quad f(v_x)dv_x = \frac{N}{\sqrt{\pi}} \left( \frac{m}{2kT} \right)^{1/2} e^{-m\beta v_x^2/2} dv_x$$

Change the variable  $X = \frac{v_x}{v_{mp}} \Rightarrow dv_x = v_{mp} dx$ , then

$$F = \frac{1}{\sqrt{\pi}} \int_1^{1.6} e^{-X^2} dX = \frac{1}{2} \left[ \frac{2}{\sqrt{\pi}} \int_0^{1.6} e^{-X^2} dX - \frac{2}{\sqrt{\pi}} \int_0^1 e^{-X^2} dX \right]$$

$$= \frac{1}{2} [erf(1.6) - erf(1)] = \frac{1}{2} [0.9763 - 0.8427] = 0.0668$$

Note that:  $erf(X) = \frac{2}{\sqrt{\pi}} \int_0^X e^{-X^2} dX$