Chapter 4
Classical Maxwell-Boltzmann Distribution

4.1 The partition function:

The probability P_i that a system is in the micro state i with the energy E_i is given by

$$P_i \propto e^{-\beta E_i} \quad , \quad \beta = \frac{1}{kT}$$

From the normalization condition ($\sum_i P_i = 1$),

$$\therefore P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

The summation $\sum_i e^{-\beta E_i}$ is called the partition function, and it is denoted by $Z(T, V, N)$, where

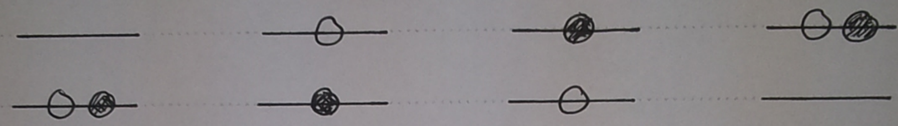
$$Z(T, V, N) = \sum_i e^{-\beta E_i}$$

* Example 1. Consider a system consists of two particles, and has two energy levels 0 and ε. Calculate the partition function in two cases: distinguishable and

indistinguishable particles.

Solution

(i) For distinguishable particles, there are four microstates:



$E_1 = 0$ $\quad E_2 = \varepsilon$ $\quad E_3 = \varepsilon$ $\quad E_4 = 2\varepsilon$

The partition function:

$$Z = \sum_{i=1}^{4} e^{-\beta E_i} = e^{-\beta E_1} + e^{-\beta E_2} + e^{-\beta E_3} + e^{-\beta E_4}$$

$$= 1 + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$

$$= (1 + e^{-\beta\varepsilon})^2$$

The partition function of a single particle

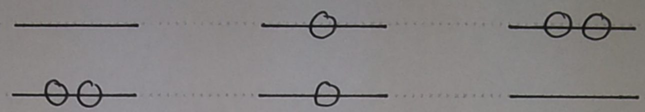
$$Z_1 = 1 + e^{-\beta\varepsilon}$$

* Note. For distinguishable particles,

$$Z = Z_1^N,$$

where N is the number of particles.

(ii) For indistinguishable particles, we have three microstates:



$E_1 = 0$ $\quad$ $E_2 = \varepsilon$ $\quad$ $E_3 = 2\varepsilon$

The partition function:

$$Z' = \sum_{i=1}^{3} e^{-\beta E_i} = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}.$$

4.2 Maxwell-Boltzmann Distribution:

Consider a system has a constant large number of identical, and distinguishable particles N. The particles are distributed to the energy levels $E_1, E_2, \ldots$, where the number of particles in the ith energy level is N_i. The Maxwell-Boltzmann distribution studies the distribution of particles to the energy levels in the most probable state.

The total number of particles:

$$N = \sum_i N_i.$$

The total internal energy:

$$U = \sum_i N_i E_i = \text{constant}.$$

The probability p_i that a system is in a microstate i with energy E_i is

$$P_i = \frac{e^{-\beta E_i}}{Z_1} = \frac{N_i}{N}$$

$$\therefore N_i = N \frac{e^{-\beta E_i}}{Z_1}$$

4.3 The Average, Variance and Standard Deviation of Energy:

* The average energy:

$$\langle E \rangle = \sum_i E_i \cdot P_i$$

$$= \frac{1}{Z_1} \sum_i E_i \, e^{-\beta E_i}$$

$$= \frac{-1}{Z_1} \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i}$$

$$= \frac{-1}{Z_1} \frac{\partial Z_1}{\partial \beta} = - \frac{\partial \ln Z_1}{\partial \beta}$$

$$\langle E^2 \rangle = \frac{1}{Z_1} \sum_i E_i^2 \, e^{-\beta E_i}$$

$$\langle E^2 \rangle = \frac{1}{Z_1} \frac{\partial^2}{\partial \beta^2} \sum_i e^{-\beta E_i}$$

$$= \frac{1}{Z_1} \frac{\partial^2 Z}{\partial \beta^2} .$$

* The variance:

$$\sigma^2 = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \frac{1}{Z_1} \frac{\partial^2 Z_1}{\partial \beta^2} - \left(\frac{\partial \ln Z_1}{\partial \beta} \right)^2$$

$$= \frac{\partial^2 \ln Z_1}{\partial \beta^2} .$$

* The standard deviation:

$$\sigma = \sqrt{\frac{\partial^2 \ln Z_1}{\partial \beta^2}} .$$

4.4 The Average Pressure:

The pressure is given by:

$$P_i = - \left(\frac{\partial E_i}{\partial V} \right)_T .$$

$\therefore$ The average pressure:

$$\langle p \rangle = \frac{1}{Z_1} \sum_i \left(- \frac{\partial E_i}{\partial V} \right)_T e^{-\beta E_i}$$

$$\therefore \langle P \rangle = \frac{1}{\beta Z_1} \sum_i \left(- \frac{\partial \beta E_i}{\partial V} \right)_T e^{-\beta E_i}$$

$$= \frac{1}{\beta Z_1} \frac{\partial}{\partial V} \left[\sum_i e^{-\beta E_i} \right]_T$$

$$= \frac{1}{\beta Z_1} \left(\frac{\partial Z_1}{\partial V} \right)_T$$

$$= \frac{1}{\beta} \left(\frac{\partial \ln Z_1}{\partial V} \right)_T .$$