CHAPTER

3

Statistical Physics P313

Statistical thermodynamics of microstates

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Statistical thermodynamics of microstates

- **We had previously defined entropy as a measure of the randomness of a system.**
- **We would like to note here that the previous explanation is a qualitative explanation and not a quantitative one, meaning that it was not produced by means of mathematical calculations or derivative equations.**
- **Therefore, we hope to find a reliable mathematical model (or mathematical equation) for explaining entropy in a way that is easy to deal with and can be applied in different studies.**
- **Boltzmann was the first to suggest a link between the thermodynamic entropy (S) and the total number of microstates of the system as:**

$$S = k_B \ln \Omega,$$

Ω is the number of available microscopic states corresponding to a macrostate of a system in equilibrium.

Microstates of a system

System state: is defined as how to fill in the energy levels of this system.

To illustrate the picture, let us consider a simple system, as in Figure (1), consisting of three energy levels ε_i, $i = 0, 1, 2$, and two distinct particles. In this system, let us know the state of the system with the numbers (1,1,0) and these numbers indicate that there is a particle in the first level (ε_0), a particle in the second level (ε_1) and the third level (ε_2) empty. In the event that one of the particles is excited, we obtain the states of the system with numbers (1,0,1) or (0,1,1)

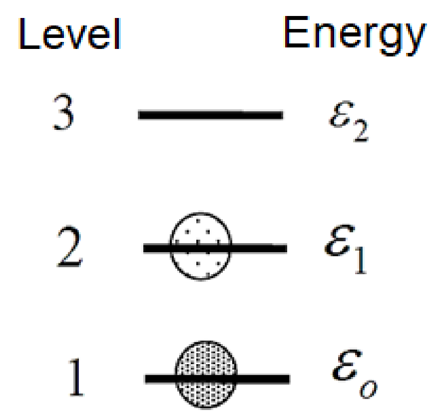
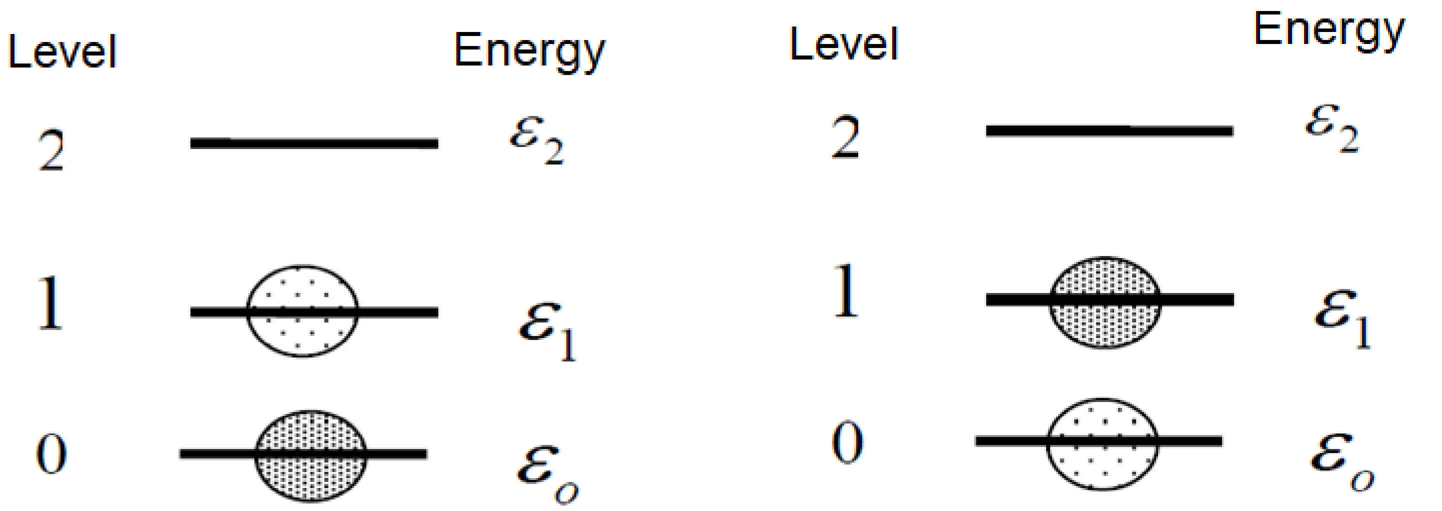


Figure (1): A simple system consisting of three energy levels and two distinct bodies



As shown in the figure, the system consists of two microstates, which are the possible states resulting from the exchange of the two particles at the first and second levels of this system.

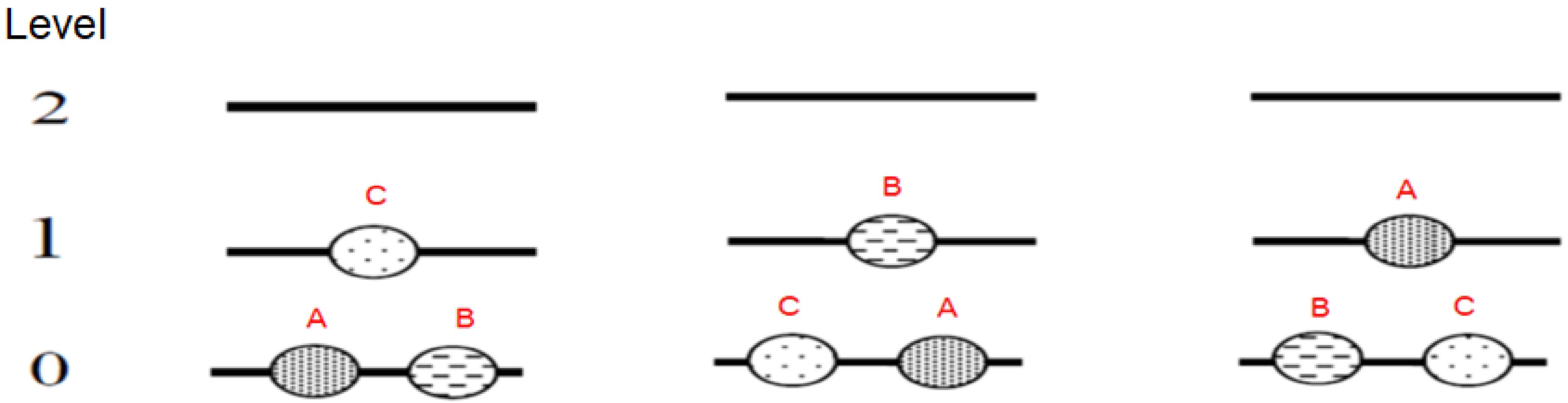
Microstate (Microscopic state): **It is the arrangement of the distinctive particles during a defined (given) state of the system.**

Therefore, the number of microstates (Ω) is the number of clear ways for arranging a group of distinctive particles to achieve a specific state.

Example **What is the number of microstates of the state of the system (2,1,0) that consists of three energy levels and three distinct particles?**

Solution:

The required here is that we place two particles at the first level and one particle at the second level and leave the third level empty. By switching the three bodies at only the first and second energy levels, as in the figure, we find that we will get only three microstates. This is while neglecting the arrangement of particles at each level.



Theory:

With the condition $N = \sum_i n_i$ **. The number of ways to distribute *N* particles in *j* levels, where, n_1 of the particles is placed in the first level, and n_2 of the particles in the second level, and so on until we reach the position of n_j particles in the last level *j* is:**

$$\omega\{n_i\} = \frac{N\,!}{n_1!\,n_2!\cdots n_j\,!} = \frac{N\,!}{\prod_{i=1}^{j} n_i\,!}$$

where,

$$\prod_{i=1}^{r} n_i\,! = n_1! \times n_2! \cdots\cdots \times n_r\,!$$

Important note: **In our study, the value ω_i , which expresses the number of different microscopic methods for a given sample situation, is defined as the "thermodynamic probability", and ω_i takes the values from zero to astronomical values. Therefore, it differs from the true probability p_i , which is known as the relationship:**

$$p_i = \frac{\omega_i}{\sum_{i=1}^{j} \omega_i}, \qquad 0 \le p_i \le 1$$

And total probability gives:

$$\sum_{i=1}^{j} p_i = \sum_{i=1}^{j} \frac{\omega_i}{\sum_{i=1}^{j} \omega_i} = \frac{\sum_{i=1}^{j} \omega_i}{\sum_{i=1}^{j} \omega_i} = 1$$

Example **What is the number of microscopic cases of the system state (4,3,2,1,0)? Then calculate the entropy of the example.**

Solution:

From the case (4,3,2,1,0), we find that the number of levels is 5, and the number of "N" particles is calculated from the given order, which is:

$$N = \sum_{n_i=1}^{5} n_i = 4+3+2+1+0 = 10$$

Using the statistical law, we find that the number of microscopic cases of this case are:

$$\omega\{n_i\} = \frac{N!}{n_1!n_2!n_3!n_4!n_5!} = \frac{10!}{4!3!2!1!0!} = 12600$$

To calculate entropy we use the formula:

$$S = k_B \ln\Omega$$
$$= \left(1.38\times10^{-23}\,\mathrm{Jk^{-1}}\right)\times\ln(12600) = 1.30\times10^{-22}\ \mathrm{Jk^{-1}}$$

Boltzmann's assumption of entropy

Assumption (*I*)

$$\lim_{T \to 0} S = 0$$

It is known that at low temperatures, which approach absolute zero $T \to 0$, we find that all the particles clump together at the ground level. And when the particles are only in one level, the number of microstates becomes 1. Therefore:

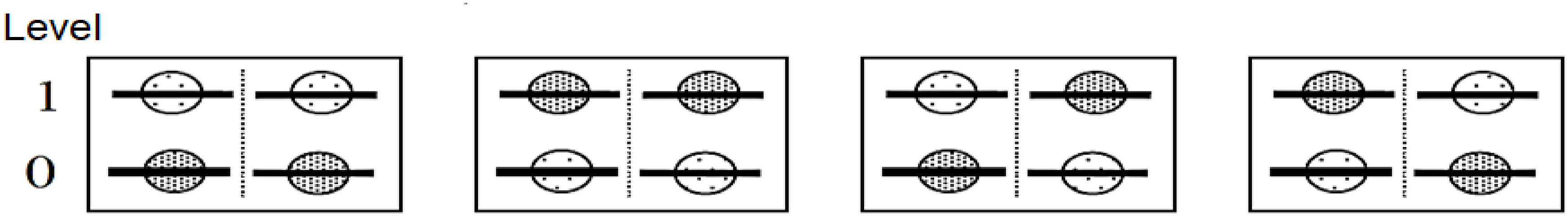
$$\lim_{T \to 0} S = k_B \ln \Omega = k_B \ln 1 = 0$$

- **This shows that the statistical definition is compatible with the third law of thermodynamics.**

Assumption (*II*)

<u>The colligative property of entropy:</u> It means that if the volume of the system doubles, the entropy is also multiplied by the same value.

To study this property, let us double the simple system state (1,1,0), which consists of three distinct planes and two bodies. We will suffice to use only two levels, as the third level is empty.



For two particles, we find that entropy: $S = k_B \ln 2$

For four particles, we find that entropy: $S = k_B \ln 4 = k_B \ln 2^2 = 2k_B \ln 2$

For N copies, we find: $S = k_B \ln 2^N = Nk_B \ln 2$

From this example, the multiplication property of the microstates and the colligative property of entropy are evident,

$$\Omega_{total} = \Omega_1 \times \Omega_2$$
$$S_{total} = S_1 + S_2,$$