Macrostates and Microstates and their relations with Thermodynamic Probability

In this article we will define what are Macrostates and Microstates in Statistical Physics with examples and illustrations.

Consider some (4, say) distinguishable particles. If we wish to distribute them into two exactly similar compartments in an open box, then the priori probability for a particle of going into any one of the compartments will be exactly 1/2 as both compartments are identical. If the four particles are named as a , b, c and d and the compartments as compartment (1) and compartment (2), then the following table can be made listing all the possible arrangements.

	Compartment (1) ↓		Compartment (2) ↓		
Distribution	Number of Particles	Name(Type) of particles	Number of Particles	Name(Type) of Particles	Total Number of Arrangements
Distribution (1)	0	–	4	{a,b,c,d}	1
Distribution (2)	1	{a} {b}	3	{b,c,d} {c,d,a}	4

		{c} {d}		{d,a,b} {a,b,c}	
Distribution (3)	2	{a,b} {b,c} {c,d} {a,c} {b,d} {a,d}	2	{c,d} {a,d} {a,b} {b,d} {a,c} {b,c}	6
Distribution (4)	3	{b,c,d} {c,d,a}	1	{a} {b}	4

		{d,a,b} {a,b,c}		{c} {d}	
Distribution (5)	4	{a,b,c,d}	0	–	1

[Download this table in PDF for better view.]

Now in the second distribution, only one particle is chosen to be inside compartment (1) and all others in Compartment (2). There are exactly $\binom{4}{1}$ = 4 ways to do so. All four arrangements are shown in the table above.

Similarly, in the distribution (3) exactly two particles enter in each of the compartment (1) and (2) , i.e., if a and b are placed in the compartment (1), c and d must take place in Compartment (2).

There are exactly $\binom{4}{2}$=6 ways to do so. Following the same procedure to complete table by increasing the number of particles one by one in Compartment (1) and decreasing them one by one in Compartment (2).

We have following 5 different distributions for the system of four particles:

> Distribution (1) = d_1 = (0,4)
> Distribution (2) = d_2 = (1,3)
> Distribution (3) = d_3 = (2,2)
> Distribution (4) = d_4 = (3,1)
> Distribution (5) = d_1 = (4,0)

These compartment-wise distributions of a system of particles are known as macrostates of the system. There are five macrostates observed corresponding to a system of four particles. In general, for a system of n particles, there are exactly $n+1$ macrostates (for the system of n particles to be distributed in two identical compartments). These macrostates are the following distribution of particles:

> $$\begin{aligned} &d_1 = (0, n) \\ &d_2 = (1, n-1) \\ &d_3 = (2, n-2) \\ &\ldots \\ &d_k = (k-1, n-k+1) \\ &\ldots \\ &d_{n+1} = (n, 0). \end{aligned}$$

Now, the different possible arrangements for each macrostate are in their own 'a distribution', called microstates.

For example {{a}, {b,c,d}} is a microstate of macrostate d_2 (distribution 2) in the table of system of four particles. From the table, it can be observed that a macrostate may have many corresponding microstates.

The distribution $d_1 = (0, 4)$ has one microstate {{ }{a,b,c,d}}, while the distribution $d_2 = (1, 3)$ has four, d_3 has six , d_4 has four and d_5 has one.

The total number of microstates for the system of four particles is, therefore, $1+4+6+4+1 = 16 = 2^4$.

In general, the total number of microstates for the system of n-particles in 'two compartment' composition is 2^n. And also, the number of microstates corresponding to a single macrostate with $(r, n-r)$ distribution among n particles is $\binom{n}{r}$.

Thermodynamic Probability

In statistical physics, the number of microstates plays very important role at quantum level. The number of microstates corresponding to any macrostate is called the thermodynamic probability of the macrostate, represented by W or Ω.

Since, for the macrostate $(r, n-r)$ the number of microstates is

$$\binom{n}{r} = \frac{n!}{r! \cdot (n-r)!}$$

. Thus, the thermodynamic probability of this macrostate:

$$W_{(r,n-r)} = \binom{n}{r} = \frac{n!}{r! \cdot (n-r)!}$$

.

In mathematics, we know that

$$\binom{n}{r} = \binom{n}{n-r} = \frac{n!}{r! \cdot (n-r)!}$$

. Therefore,

$$W_{(r,n-r)} = W_{(n-r,r)}$$

.

Or,

$$W_{(r,n-r)} = \binom{n}{r} = \frac{n!}{r! \cdot (n-r)!} = W_{(n-r,r)}$$

.

That is, for a system of four distinguishable particles, $n = 4$, $r = 0, 1, 2, 3, 4$, provided

$$W_{(0,4)} = \binom{4}{0} = \frac{4!}{0! \cdot (4)!} = W_{(4,0)} = 1$$

$$W_{(1,3)} = \binom{4}{1} = \frac{4!}{1! \cdot (3)!} = W_{(3,1)} = 4$$

$$W_{(2,2)} = \binom{4}{2} = \frac{4!}{2! \cdot (2)!} = W_{(2,2)} = 6$$

All agree with the table.

Thermodynamic probability is not identical to ‘probability’ in mathematics and statistics, but it gives rise to that.

Probability of a Macrostate

The probability of macrostate (i.e., availability of a macrostate) in a system is given by

$$P_m = \frac{\text{No. of such microstates in the macrostate}}{\text{Total no. of microstates in the system}}$$

Thus,

$$P_m = \frac{W}{2^n}$$

Or,

$$P_{(r,n-r)} = \frac{W_{(r,n-r)}}{2^n} = \binom{n}{r} \times \frac{1}{2^n} = P_{(n-r,r)}$$

Practically, the probability of finding the macrostate (0,4) in a system of four particles is

$$P_{(0,4)} = \frac{W_{(0,4)}}{2^4} = \binom{4}{0} \times \frac{1}{2^4} = \frac{1}{16}$$

Similarly, $P_{(1,3)} = \frac{1}{4}$.

Macrostate with highest probability

The macrostate (r, n-r) has the highest probability only if

$$r = \frac{n}{2} \text{ when n is even}$$

and

$$r = \frac{n+1}{2} \text{ or} \frac{n-1}{2} \text{ when n is odd}$$

. Then the highest probability is given by:

$$P_{max} = \frac{n!}{\frac{n}{2}! \cdot \frac{n}{2}!} \times \frac{1}{2^n}$$

(n is even)

$$P_{max} = \frac{n!}{\frac{n-1}{2}! \frac{n+1}{2}!} \times \frac{1}{2^n}$$

(n is odd)

Macrostate with least probability

The macrostate (r, n-r) is least probable when r is either zero or n.

$$P_{min} = \frac{n!}{0! \cdot n!} \times \frac{1}{2^n}$$

.

Thus, least probability for a macrostate is $\frac{1}{2^n}$. $\square$

> Remark: The probability of a macrostate (P) is directly proportional to the thermodynamic probability (W).