

Statistical Physics, Electromagnetic Theory and RelativityUNIT - IStatistical Basis and Thermodynamics* Statistical Basis

A study of thermodynamics gives us various macroscopic properties that are related through an equation of state having only two independent parameters. But the equation of state can not be deduced from the laws of thermodynamics. It has to be obtained experimentally. Up to 17th century, the ordinary laws of mechanics was the only tool to explain physical phenomenon. But ordinary laws of mechanics could not be used where the system contains a large number of particles, particularly electrons. Such problems are successfully solved by statistical mechanics. The larger is the number of particles in the physical system considered, the more nearly correct are the statistical predictions. Before the advent of quantum theory, Maxwell, Boltzmann, Gibbs etc. applied the statistical method making the use of classical physics. These methods are known as classical statistics or Maxwell-Boltzmann statistics. The classical statistics successfully explained the phenomena like temperature, pressure, energy etc. but failed to explain other observed phenomenon like black body radiation, specific heat at low temperature etc. For this new approach was introduced by Bose, Einstein, Fermi and Dirac. The Planck's quantum concept of discrete exchange of energy between systems was used. The new statistics was subdivided into two categories

(i) Bose-Einstein statistics.

(ii) Fermi-Dirac statistics.

Thus, there are three statistics depending upon three different kinds of particles:

(I) Maxwell-Boltzmann statistics -

• This is applicable to the identical, indistinguishable particles of any spin. The molecules of a gas are the particles of this kind.

(II) Bose-Einstein statistics

This is applicable to the identical, indistinguishable particles of zero spin or integral spin. These particles are called bosons. The examples of bosons are helium atom at low temperature and the photons.

(III) Fermi-Dirac statistics :-

This is applicable to the identical, indistinguishable particles of half-integral spin. These particles obey Pauli exclusion principle and are called fermions. The examples of fermions are electrons, protons, neutrons etc.

* Probability

The probability of an event may be defined as the ratio of the number of cases in which the event occurs to the total number of cases. Thus,

The probability of an event = $\frac{\text{No. of cases in which event occurs}}{\text{Total number of cases}}$

suppose an event can happen in a ways and fails to happen in b ways, then the probability of happening

the event = $\frac{a}{a+b}$

and the probability of failing the event = $\frac{b}{a+b}$

Here $(a+b)$ represents the total number of equally likely possible ways. It should be noted that the sum of these two probabilities is always 1.

An event is called 'sure' event if it occurs in an

• Maxwell-Boltzmann statistics

Die - A die is a homogeneous, regular and balanced cube with six faces marked number of dots from 1 to 6.

experiment. Thus, the probability of a 'sure' event is always 1 and that of an impossible event to be equal to zero. Thus, the probability P of a random event lies between 0 and 1 i.e. $0 \leq P \leq 1$.

Zero Probability - The die has only six faces marked serially from 1 to 6. If we want to know the probability of the die coming up with a face marked with a number 7. There is no face marked as 7. Therefore, probability of appearing a number 7 is zero, i.e.

$$\therefore P(\text{number } 7) = 0/6 = 0$$

so, the probability of impossible event is always zero.

Probability one - The probability of appearing any number less than 7 is one. This is because all the six faces of the die are marked from 1 to 6, i.e. the number less than 7.

$$\therefore P(\text{number } < 7) = 6/6 = 1$$

* Probability and Frequency

Suppose we toss a coin, say N times and we find that 'Head' appears M times. Here we introduce a term frequency of an event F as

$$F = \frac{\text{No. of trials in which head occurs}}{\text{Total number of trials}} = \frac{M}{N}$$

Thus, if a coin is tossed 50 times and in 10 of them the coin shows Heads, the frequency of this event is ~~10/50~~

$$= \frac{10}{50} = 0.2$$

From the classical definitions of probability, the probability of occurrence of Head is 0.5 or 50%. Hence, we conclude that frequency is not the same as probability. There must be a relationship between frequency and probability. As the number of trials is increased, the frequency of the event progressively tends to stabi-

size and gradually approaches a constant value, known as the probability of the event. we define probability in terms of frequency as

$$p = \lim_{N \rightarrow \infty} \frac{M}{N}$$

* Permutations and Combinations -

The word permutation means arrangement and combination means formation of groups.

Permutations - consider four distinguishable objects marked a, b, c and d. Take any two objects at a time, the possible arrangements are

- ab, ba, ac, ca, ad, da, bc, cb, bd, db, cd, dc.

These are total 12 possible arrangements. In arranging these objects the order of their placing is also taken into consideration. Thus, ab and ba are two different permutations. Thus, 4 objects can be arranged in 12 ways by taking 2 objects at a time i.e the number of permutations is 12.

symbolically, $4P_2 = 12$

If three objects are taken at a time out of 4 objects a, b, c and d the various arrangements are

- abc abd acd bcd
- acb adb adc bdc
- bca bad cda cbd
- bac bda cad cdb
- cab dab dac dbc
- cba dba dca dcg

Thus, 4 objects can be arranged in 24 different ways by taking 3 at a time out of 4 objects.

symbolically, $4P_3 = 24$

In general, the number of arrangements of n distinguishable objects by taking r at a time is given

by
$$\boxed{{}^n P_r = \frac{n!}{(n-r)!}} \quad (1)$$

Thus,

$${}^4 P_2 = \frac{4!}{(4-2)!} = \frac{4!}{2!} = \frac{4 \times 3 \times 2 \times 1}{2 \times 1} = 12$$

and
$${}^4 P_3 = \frac{4!}{(4-3)!} = \frac{4!}{1!} = \frac{4 \times 3 \times 2 \times 1}{1} = 24$$

This includes all types of arrangements, meaningful as well as meaningless.

Combinations - In combinations i.e. groups we consider only meaningful combinations. The groups without considering the order of their placement is combinations.

The combinations of 4 objects a, b, c and d taking two at a time are

ab, ac, ad, bc, bd, cd
i.e. only six combinations.

symbolically, ${}^4 C_2 = 6$

Similarly, combinations of 4 objects a, b, c and d taking three at a time are

abc, abd, acd, bcd

i.e. only four combinations.

symbolically, ${}^4 C_3 = 4$

In general, the combinations of n distinguishable objects by taking r at a time is given by

$$\boxed{{}^n C_r = \frac{n!}{r!(n-r)!}} \quad (2)$$

But
$${}^n P_r = \frac{n!}{(n-r)!}$$

$$\therefore {}^n C_r = \frac{{}^n P_r}{r!}$$

$${}^2P_2 = 2! {}^2C_2 \quad \text{--- (3)}$$

From equation (1)

$${}^nP_n = \frac{n!}{(n-n)!} = \frac{n!}{0!} = n! \quad (\because 0! = 1)$$

From equation (2)

$${}^nC_n = \frac{n!}{n!(n-n)!} = \frac{n!}{n!0!} = \frac{n!}{n!} = 1 \quad (\because 0! = 1)$$

* Macrostate and Microstate

Macrostate

Consider 4 distinguishable particles. Let distribute them into two exactly similar compartments in an open box. Let the particles be a, b, c and d. When any particle thrown into the box, it must fall into one of the two compartments. Since the ~~particles~~ compartments are same, the particles have the same probability of going into either of them and will be $\frac{1}{2}$. The possible ways in which 4 particles can be distributed in two compartments is shown in below table 1.

Table 1

Compartment	No. of particles				
	Distribution 1	Distribution 2	Distribution 3	Distribution 4	Distribution 5
1	0	1	2	3	4
2	4	3	2	1	0

Thus, there are 5 different distributions (0, 4), (1, 3), (2, 2), (3, 1) and (4, 0). Each compartmentwise distribution of a system of particles is known as a macrostate. In general, for a system of n particles to be distributed in two similar compartments,

the various macrostates are $(0, n)$, $(1, n-1)$, $(2, n-2)$, ... $(n-1, 1)$ and $(n, 0)$. Therefore, the total no. of macrostates for n particles is $(n+1)$.

Microstates

Since the particles are distinguishable, the number of different possible arrangements in each compartment is shown in below table 2.

Macrostate	Possible arrangements		No. of microstates Ω (Thermodynamic probability)
	compartment 1	compartment 2	
0, 4	0	abcd	1
1, 3	a	bcd	4
	b	cda	
	c	dab	
	d	abc	
2, 2	ab	cd	6
	ac	bd	
	ad	bc	
	bc	ad	
	bd	ac	
	cd	ab	
3, 1	bcd	a	4
	cda	b	
	dab	c	
4, 0	abc	d	1
	abcd	0	

Each distinct arrangement is known as the microstate of the system. The distribution $(0, 4)$ can have only one arrangement, distribution $(1, 3)$ can have 4 distinct arrangements, distribution $(2, 2)$ can have 6, distribution $(3, 1)$ have 4 and distribution $(4, 0)$ have

only one. Thus, a given macrostate may consist of a number of microstates. For 4 particles, the total number of microstates are $16 = 2^4$.

In general, for a system of n particles, the total number of microstates are 2^n .

* Thermodynamic Probability

"The number of microstates corresponding to any given macrostate is called its thermodynamic probability."

In other words, the thermodynamic probability of a particular macrostate is defined as the number of microstates corresponding to that macrostate. This is very large number and is represented by W (or Ω).

The number of microstates corresponding to a given macrostate is equal to the number of meaningful arrangements or permutations of various particles in the macrostate. Consider n particles and two compartments. If z is the number of particles in the compartment No. 1 and the remaining $(n-z)$ are in a compartment No. 2 then,

$$\begin{aligned} \text{No. of meaningful arrangements} &= \frac{n!}{z!(n-z)!} \\ &= {}^n C_z \end{aligned}$$

Therefore, the total number of microstates in a macrostate $(z, n-z)$ or thermodynamic probability

$$W_{(z, n-z)} = \frac{n!}{z!(n-z)!} = {}^n C_z$$

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The probability of a macrostate is defined as the ratio of the number of microstates (i.e. thermodynamic probability W) in it to the total number of possible microstates of the system.

$$\text{Thus, } p_{\text{macro}} = \frac{\text{No. of microstates in the macrostate}}{\text{Total No. of microstates of the system}}$$

The total number of ways of arranging n distinguishable particles in c numbered compartments = c^n

$$\therefore p_{\text{macro}} = \frac{W}{c^n}$$

* Entropy and Probability

When an isolated system undergoes an irreversible process, there is a net increase of the entropy of the system. Spontaneous process, such as spontaneous expansion of a gas into an evacuated space, diffusion of one gas into another, etc., are all irreversible processes. Hence, in all irreversible processes, there is a net increase of entropy.

In general, all spontaneous processes represent changes from less probable to a more probable state and since in such processes the entropy increases, there should be relation between the entropy S of the system in a given state and the probability of that state.

Boltzmann, in 1896 derived a relation between entropy (a thermodynamical quantity) and probability (a statistical quantity).

According to thermodynamics, the function entropy S of a system is related with temperature T by the rel.ⁿ

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad \text{--- (1)}$$

According to the approach of statistical mechanics,

we have $\frac{1}{T} = k\beta = k \frac{\partial \log W}{\partial E}$ (2)

Equating (1) and (2), we have

$$\frac{\partial S}{\partial E} = k \frac{\partial \log W}{\partial E} \quad (3)$$

Integrating above eqⁿ we get

$$S = k \log W$$

$$\therefore \boxed{S = k \log W} \quad (4)$$

This is the required relation between entropy and thermodynamic probability and is called as Boltzmann's entropy relation. Here k is universal constant known as Boltzmann's constant.