STATISTICAL MECHANICS

Lecture Three

Thermodynamic Probability and Entropy

Phase Space

In dynamical system theory, a phase space in which all possible states of a system are represented, with each possible state corresponding to one unique point in the phase space. For mechanical systems, the phase space usually consists of all possible values of position and momentum variables values of position.

To described both the position and the state of motion of a point in space, it is customary to set up a six-dimensional space, called the phase space, in which the six co-ordinates, $x,\ y,\ z,\ p_x, p_y, p_z$ are marked out along six mutually perpendicular axes.

For mechanical systems, the phase space usually consists of all possible values of position and momentum variables.

Molecules as appoint in space.

In thermodynamics and statistical mechanics, the term phase space has the same meaning as in classical mechanics. *If a system consists of N particles, then a point in the 6N-dimensional phase space describes the dynamic state of every particle in that system, as each particle is associated with three position and three momentum variables. A point in phase space is said to be a microsate of the system.*

3 positional $\longrightarrow$ $x,\ y,\ z$

3 conjugate momenta coordinate ⟶ p_x, p_y, p_z

Every molecules of the gas represented in phase space as,

$dxdydzdp_x dp_y dp_z$

Molecules as a point in space

or the phase space in terms of velocity coordinate

$x, y, z, and\ v_x, v_y, v_z$ $where\ p=mv$

In statistical method for large number of molecules, it is possible to subdivided phase space in to small six-dimensional elements of volume, which is called *Cells*, with sides of length. (Element of volume in space called cells).

$dx, dy, dz, dv_x,\ dv_y,\ dv_z$

The volume in phase space can be written as,

$dV_x dV_y dV_z = d^3 r d^3 c = dxdydzdp_x dp_y dp_z$

Where $r \rightarrow position\ vector, and\ \ c \rightarrow velocity\ vectors$
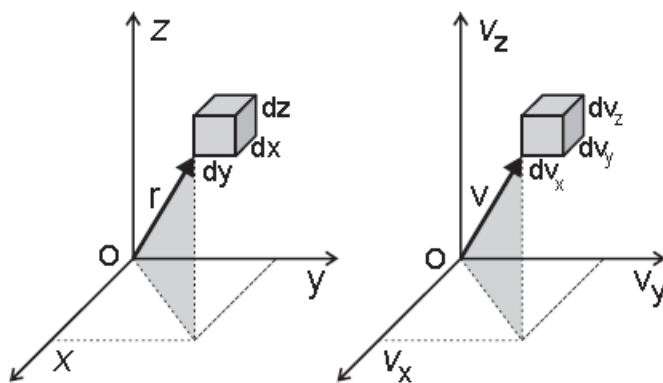
$$H = h^3$$

The volume of the smallest cell in the phase space The number of the phase point per unit volume or the density in phase space, is

$$\rho = \frac{N_i}{H} \qquad or \quad \rho = \frac{N_i}{h^3}$$

The three dimensional space in which the location of a particle is completely specified by the three position co-ordinate, is known as **_position space._**

Small volume in position space is dV= *dx dy dz*

The three dimensional space in which the momentum of a particle is completely specified by three momentum co-ordinate p_x p_y and p_z is known as **_Momentum space_** small volume in momentum space is p_x p_y p_z .

Thermodynamic Probability

How many microstate correspond to a given macrostate ? How many ways there are of putting N distinguishable particles in to cells?.

In general, there are many different microstates corresponding to a given macrostates.

The number of microstates leading to a given macrostate is called

Thermodynamic probability.

The number of ways in which is given macrostate Can be achieved It is denoted by W.

The thermodynamic probability is an unnormalized probability, an integer between one and infinity, rather than a number between zero and one. 1 $\longrightarrow$ ∞

Example:

Assuming that there are three Bolls to be assigned into two boxes, how many possibilities to split them. The possible microstate

If the bolls indistinguishable

	Bolls in box 1	Bolls in box 2
Case 1	3	0
Case 2	2	1
Case 3	1	2
Case 4	0	3

There are 4 distributions (4 macrostate).

Using R, G, and B to represent the identity of these 3Bolls, there will be many different combinations for each case (i.e. macrostate).

If they are distinguishable

	Bolls in Box1	Bolls in Box1	Total
Case 1	R, G, B	0	1
Case 2	G,B R,B R,G	R G B	 3
Case 3	R G B	G,B R,B R,G	 3
Case 4	0	R,G,B	1

In this example, the macrostate corresponds to the case (i.e. the Bolls can be found in each Boxes), whereas the number of possible arrangements for each case is viewed as the corresponding ***Thermodynamic probability.***

More specifically, For the macrostate 2,3 (i.e. case 2,3), the thermodynamics probability is 3.

The number of microstate corresponding to a given macrostate can be computed by different arrangements of the phase points.

In the general case of N phase points and the arrangements within more than one cell are possible.

The number of combinations for having N_1 student in a room can be calculated from

$$W_{N1} = \frac{N!}{N_1!(N-N_1)!}$$

Now, the macrostate will be defined by the number of students in each room, say: $N_1, N_2, \ldots.. N_n$

Note that

$$N_1 + N_2 + N_3 + \cdots + N_{n-1} + N_n = N$$

The number of microstate for the above macrostate can be calculated from,

$$W = \frac{N!}{N_1!(N-N_1)!} \times \frac{(N-N_1)!}{N_2!(N-N_1-N_2)!} \times \ldots.\times \frac{(N\ N_1\ N_2\ldots..-N_{n-2}\ )!}{N_{n-1}!(N-N_1-N_2-N_{n-1})!}$$

$$W = \frac{N!}{N_1!N_2!N_3!\ldots\ldots.N_n!} \text{ or}$$

$$W = \frac{N!}{\prod N_j!} \qquad \text{or}$$

$$W = \frac{N!}{\sum N_j!} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

Assembly of distinguishable particles

- An isolated system consists of N distinguishable particles.
- The macrostate of the system is defined by (N, V, U).
- Particles interact sufficiently, despite very weakly, so that the system is in thermal equilibrium.
- Two restrictive conditions apply here

$$\sum_{j=1}^{n} N_j = N \quad \text{(conservation of particles)}$$

$$\sum_{j=1}^{n} N_j E_j = U \quad \text{(conservation of energy)}$$

Where N_j is the number of particles on the energy level j with the energy E_j .

1. N! different ways arrange N molecules;
2. N_j arrangements of N_j molecules with energy ε_j correspond to the same configuration.

Example:

Four distinguishable particles distributed in to two cells i and j. Compute, 1. The possible macrostate.

2. The thermodynamic probability.

N_i	4	3	2	1	0
N_j	0	1	2	3	4

1- The number of macrostates are only 5.

2- The number of microstates are;

For $N_i = 4, \ N_j = 0$

$$W(N_i, N_j) = \frac{N!}{N_i! N_j!}$$

$$W(N_i = 4, N_j = 0) = \frac{N!}{N_i! N_j!} = \frac{4!}{4! 0!}$$

$$= \frac{1 \times 2 \times 3 \times 4}{1 \times 2 \times 3 \times 4 \times 1} = 1$$

For $N_i = 3, \ N_j = 1$

$$W(N_i = 3, N_j = 1) = \frac{4!}{3!1!} = \frac{1 \times 2 \times 3 \times 4}{1 \times 2 \times 3 \times 1} = 4$$

For $N_i = 2, \ N_j = 2$

$$W(N_i = 2, N_j = 2) = \frac{4!}{2!2!} = \frac{1 \times 2 \times 3 \times 4}{1 \times 2 \times 1 \times 2} = 6$$

For $N_i = 1, \ N_j = 3$

$$W\left(N_i = 1, N_j = 3\right) = \frac{4!}{1!3!} = \frac{1 \times 2 \times 3 \times 4}{1 \times 1 \times 2 \times 3} = 4$$

For $N_i = 0, \ N_j = 4$

$$W(N_i = 0, N_j = 4) = \frac{4!}{0!4!} = \frac{1 \times 2 \times 3 \times 4}{1 \times 1 \times 2 \times 3 \times 4} = 1$$

*There are (16) microstate corresponds to the five macrostate.

*The maximum thermodynamic probability is that with two phase points in each cell $N_i = 2, \ N_j = 2$.

Note:

- The most disordered macrostate is the state with the highest probability.
- The macrostate with the highest thermodynamic probability will be the observed equilibrium state of the system.
- The statistical model suggests that systems tend to change spontaneously from states with low thermodynamic probability to states with high thermodynamic probability.
- A state of high order = Low probability

- A state of low order = High probability
- Each macrostate contains a large number of microstate.
- <u>Fundamental assumption of statistical mechanics; *All microstate are equally probable.*</u>

H.W:

Three distinguishable particles distributed in to two cells Compute,

1. The possible macrostate.

2. The thermodynamic probability.

Thermodynamic Probability and Entropy

In classical thermodynamic: as a system proceeds toward a state of equilibrium the entropy increase, and at equilibrium the entropy attains its maximum.

In statistical thermodynamic; system tends to change spontaneously from states with low thermodynamic probability to states with high thermodynamic probability (large number of microstate).

Entropy $\longrightarrow$ a measure of the disorder of a system.

Microstate: a description of a system that specifies the properties (position and / or momentum) of each individual particle.

Macrostate: description of the system in terms of macroscopic quantities (such as P and V…..).

<u>Disorder Number, Ω is defined as the number of microstate available to a macrostate.</u>

Luding Boltzmann made many important contributions to thermodynamics. His most important contribution, to physics is the relation ship between thermodynamic probability W and the classical concept of entropy.

His argument was as follows.

Consider an isolated assembly which undergoes a spontaneous, irreversible process. At equilibrium S has its maximum value consistent with U and V. But W also increases and approaches a maximum when equilibrium is achieved.

Boltzmann therefore assumed that there must be some connection between W and S. Therefore *S= f(W),* and S and W are state variables. To be physically meaningful *f(W)* must be asingle-valued monotonically increasing function.

Boltzmann showed that for an isolated system the entropy must be proportional to $\ln \Omega$ i.e.

$$S = k \ln \Omega \quad \text{................................(2)}$$

Where k is Boltzmann constant

$$S = k \ln W \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

In the equilibrium state both entropy and thermodynamic probability have their maximum values.

The greater the disorder $\longrightarrow$ greater thermodynamic
probability $\longrightarrow$ grater the entropy.

To prove this;

Let us consider two isolated system A and B, in thermal contact.

Entropy is an extensive property and so S for the composite system is the sum of the individual entropies:

System 1	System 2
$W_1,\ \mathbf{\Omega_1},\ S_1$	$W_2,\ \mathbf{\Omega_2},\ S_2$
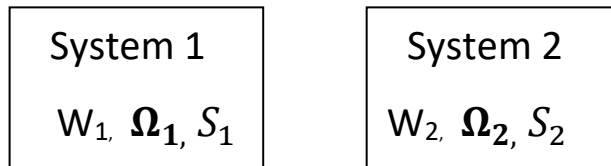
The (disorder number Ω) of such realization is given by;

$$\Omega = \Omega_1 \Omega_2 \quad and \quad W = W_1 W_2 \ \ldots\ldots\ldots\ldots..(4)$$

$S1 = f(\Omega 1)$ and $S1 = f(W1)$

$S2 = f(\Omega 2)$ and $S2 = f(W2)$

The entropy of the combined system is
$$S_{tot} = S_1 + S_2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(5)$$

$f(\Omega_{tot}) = f(\Omega_1) + f(\Omega_2)$

$f(W_{tot}) = f(W_1) + f(W_2)$

The only function for which the above relationship is true is the logaretim. Therefor;

$$S_1 = k \ln \Omega_1 \quad \text{and} \quad S_2 = k \ln \Omega_2 \quad \dots\dots\dots(6) \quad \text{Therefore,}$$
$$S_1 + S_2 = k \ln \Omega_1 + k \ln \Omega_2$$

$$S_1 + S_2 = k \ln \Omega_1 \Omega_2 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots(7)$$

$$S = k \ln \Omega \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(8)$$

The unit of entropy is J/K.

The units of entropy are **J/K**. The temperature in this equation must be measured on the absolute, or Kelvin temperature scale. On this scale, zero is the theoretically lowest possible temperature that any substance can reach.

Processes that decrease entropy

 *Freezing, and condensation.
 *Reactions that combine two molecules into one (addition)
 *Reactions that reduce the number of gas molecules.
 *Reactions that make a molecule more rigid (going from long chains to inflexible rings