

# 1. Statistical Mechanics-I

Statistical mechanics is a formalism in the study of physical properties of matter in bulk. It makes an attempt to derive the macroscopic properties of an object from the properties of its microscopic constituents and the interactions amongst them. In statistical mechanics we try to find the answers to questions like how are the molecules distributed in space, how they are distributed in velocity.

## 1.1 Degrees of freedom

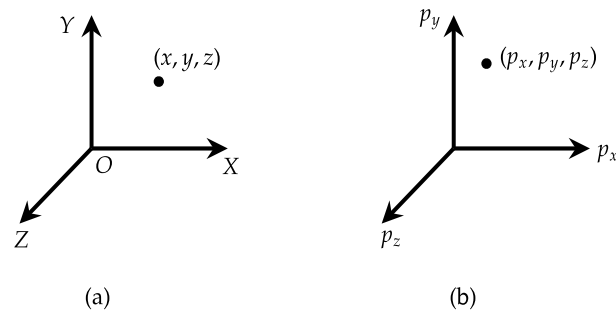
The degrees of freedom of any dynamical system is defined as the total number of independent coordinates necessary to specify the position and configuration of the system completely. For a particle in translatory motion three coordinates ( $x, y, z$ ) are needed to define its position. To describe energy of the particle three momentum coordinates ( $p_x, p_y, p_z$ ) are required. Hence to specify position and energy, 6 - coordinates are needed. We say the particle has 6 degrees of freedom.

## 1.2 Phase Space

Phase space is an imaginary space which combines the physical space and the momentum space. It is used to represent the state (phase) of each system. To specify the position and energy we require three position (space) coordinates  $x, y, z$  and three momentum coordinates  $p_x, p_y$  and  $p_z$ . We imagine a six dimensional space in which coordinates are  $x, y, z, p_x, p_y$  and  $p_z$ . It is an imaginary space and is a combination of physical space and momentum space. This six dimensional space for a single particle is called phase space or  $\mu$ -space. The instantaneous state of a particle in the phase space is denoted by a point known as phase point. An element of volume  $dx dy dz dp_x dp_y dp_z$  in six dimensional space is called a cell. A phase space can be divided into a large number of cells. A cell contains a large number of phase points. The dimensions of phase space depend upon the degrees of freedom.

### 1.2.1 More About Phase Space

A space where the three position coordinates can be represented along three mutually perpendicular axes is called the physical space. Volume of a small element in this space is  $dV = dx dy dz$ .



A space where the three momentum coordinates are represented along the three mutually perpendicular directions is called the momentum space. In Fig.(b) the point of a small element in this space  $= dp_x dp_y dp_z$ . Fig. (a) gives only the instantaneous position of a particle and Fig. (b) gives only the instantaneous momentum. Suppose we want to specify both this position and momentum at a particular instant in a single space. Such a space is called phase space. In phase space a point  $P$  has 6 coordinates,  $(x, y, z, p_x, p_y, \text{ and } p_z)$ . So it is a 6 dimensional space. Any point  $P$  in this space is called a phase point. The phase point gives a complete description of the dynamical state of the particle at any instant.

The volume of an infinitesimal element in phase space  $= d\tau$

$$d\tau = dx dy dz dp_x dp_y dp_z$$

Let us now consider a system consisting of  $N$ -particles. For one particle there are 6 coordinates. So for  $N$ -particle there are  $6N$  coordinates. This means to specify the state of the system completely we need  $3N$  position coordinates and  $3N$  momentum coordinates. The instantaneous position of a system (i.e.,  $N$ -particles) can be represented by a single point in the  $6N$ -dimensional phase space.

### 1.2.2 $\mu$ -Space and $\Gamma$ -space

The 6-dimensional phase space for a single particle is called the  $h$ -space. The  $6N$ -dimensional phase space for  $N$  particles is termed as  $\gamma$ -space ( $\gamma$ -space). Thus gamma space is built up as the product of  $N, \mu$  spaces.

Suppose a particle has  $f$  degrees of freedom. Then to specify its state,  $f$  position coordinates and  $f$  momentum coordinates are required. If there are  $N$  particles in this system then to represent the dynamical state of the system at any instant the total number of coordinates required are  $Nf$  position coordinates and  $Nf$  momentum coordinates. The phase space of the system will be a  $2Nf$  dimensional space. We can use generalised coordinates to represent a system. Let  $q_i$  represent the generalised position coordinate and  $p_j$  represent the generalised momentum coordinates. For  $N$  independent particles, in the  $6$  dimensional phase space, there will be  $3N$  position coordinates  $q_1, q_2, \dots, q_N$  and  $3N$  momentum coordinates  $p_1, p_2, \dots, p_N$ .

### 1.2.3 Phase Cell

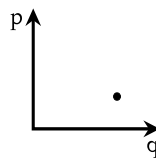


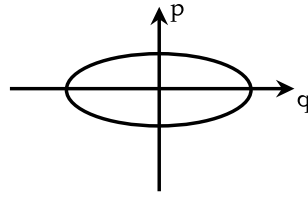
Figure 1.1

Consider a particle in one dimension. Its state can be specified using the position coordinates  $p$  and the momentum coordinates  $q$  as shown in Fig.1.1. The two coordinates change with time and the representative point moves through phase space and the line traced is called phase line or phase trajectory. Each point on the phase line represents one possible microstate.

#### Example

Consider one dimensional harmonic oscillator of mass  $m$  and spring constant  $k$ . The total energy of the oscillator

is  $E = \frac{p^2}{2m} + \frac{1}{2}kq^2$ , where  $p$  is its momentum and  $q$  its position coordinate. If  $E$  is constant then this equation represents an ellipse in the phase space.



$$\frac{q^2}{(2E/k)} + \frac{p^2}{2mE} = 1$$

The semi major axis of the ellipse is  $\sqrt{2E/k}$  and the semi minor axis is  $\sqrt{2mE}$ .

We can divide the phase space into small volumes called phase cell. In the  $\mu$ -space of a particle, the volume element  $d\tau = dx dy dz p_x p_y p_z$ .  $d\tau$  is the volume of a six dimensional cell having sides  $dx, dy, dz, dp_x, dp_y, dp_z$ . Such a cell of minimum volume is called a unit cell in the  $\mu$ -space.

$$\begin{aligned}(d\tau)_{\min} &= (dx dy dz dp_x dp_y dp_z)_{\min} \\ &= (\delta x \delta p_x)_{\min} (\delta y \delta p_y)_{\min} (\delta z \delta p_z)_{\min}\end{aligned}$$

According to classical mechanics the volume  $d\Gamma$  can take any minimum value. But in quantum mechanics, according to Heisenberg's uncertainty principle the minimum value of the products is approximately equal to the Planck's constant  $h$ .

$$\text{So } (d\tau)_{\min} = h \times h \times h = h^3$$

The minimum value of volume element of  $\mu$ -space is  $h^3$ , where 3 is the number of degrees of freedom.

Consider a system consisting of  $N$  particles having  $f$  degrees of freedom each. Then the phase space will be  $2fN$  dimensional and the volume of the cell be  $h^{Nf}$ .

The volume of one element in the  $\Gamma$  space

$$d\Gamma = (dq_1 dq_2 dq_3 \dots dq_{fN}) (dp_1 dp_2 dp_3 \dots dp_{fN})$$

The number of cells in this volume element is  $d\Omega$ .

$$d\Omega = \frac{(dq_1 dq_2 \dots dq_{fN}) (dp_1 dp_2 \dots dp_{fN})}{h^{Nf}}$$

### 1.3 Statistical Probability

Probability of a particular event is the ratio of number of cases in which the event occurs to the total number of possible events. The theory of probability is a method for making better guesses. We need this in statistics. Because, you know in statistical mechanics we deal with a very large number of particles. So nothing can be said about a particular particle with definiteness. We can only make a guess about its behaviour.

Let us toss a coin to find whether we get the head or tail. In tossing of a coin, the total number possibilities or total number of events is two. So the chance of getting a head =  $1/2$ . This chance is called probability in statistics. This means you toss a coin 100 times. Then also this chance of getting a head will be 50 out of 100. i.e., probability is  $1/2$ .

**The probability of an event is equal to the ratio of the number of favourable events to the total number of equally likely ways of happening of that event.**

$$\text{Probability of an event} = \frac{\text{Number of favourable events}}{\text{Total number of equally likely events}}$$

### 1.3.1 Probability Theorems

First let us consider an example. An opaque box contains 3 red balls, 4 blue balls and 6 black balls. If a ball is drawn from the bag what is the probability that it is either blue or black?

$$\text{Total number of balls} = 3 + 4 + 6 = 13$$

$$\text{Probability of blue balls } p_1 = \frac{4}{13}$$

$$\text{Probability of black balls } p_2 = \frac{6}{13}$$

$$\text{Total probability of white or black ball} = \frac{4}{13} + \frac{6}{13} = \frac{10}{13}$$

#### Theorem 1.3.1 Addition law of probability

If  $P_1, P_2, \dots, P_n$  be the separate probability of mutually exclusive events, then probability,  $P$  that any of these events will happen is ,

$$P = P_1 + P_2 + \dots + P_n$$

#### Theorem 1.3.2 Multiplication Law of Probability

If the probabilities of occurrence of two independent events are  $P_1$  and  $P_2$ , the probability of occurrence of the two events simultaneously is the product of  $P_1$  and  $P_2$

$$P = P_1 \times P_2$$

**Exercise 1.1** You are given four particles  $a, b, c$  and  $d$ . What are the different ways in which they can be distributed in two identical halves of a box? Also calculate the probabilities of different distributions? What is the frequency with which these distribution occur? ■

**Solution:**

Distribution	Probability
(4, 0)	1/16
(3, 1)	4/16
(2, 2)	6/16
(1, 3)	4/16
(0, 4)	1/16

Left half	Right half	Distribution	Freq.
a,b,c,d	—	4,0	1
b,c,d	a	(3,1)	4
a,c,d	b		
a,b,d	c		
a,b,c	d		
a,b	c,d	(2,2)	(6)
a,c	bd		
a,d	b,c		
c,d	a,b		
b,c	a,d		
b,d	a,c		
a	b,c,d	(1,3)	(4)
b	a,c,d		
c	a,b,d		
d	a,b,c		
—	a,b,c,d	(0,4)	1

### 1.3.2 Binomial Distribution

Suppose we carry out a series of experiments in which each experiment has only two possible outcomes. For example, experiments to evaluate the magnetic moment of a system of electrons which have spins  $\frac{1}{2}$  or  $-\frac{1}{2}$ , or

the traditionally known experiment of tossing coins in which either 'heads' or 'tails' appears. Let the probability of appearance of 'heads' be represented by  $p$  and that of 'tail' by  $q$ , where,

$$p + q = 1$$

$$\begin{aligned}\text{Total number of microstate} &= \text{No. of elements in the sample space} \\ &= (\text{Basis})^N\end{aligned}$$

$$\text{Probability of general event} = {}^nC_r(p)^{n-r}(q)^r = {}^nC_r(p)^{n-r}(1-p)^r = {}^nC_r\left(\frac{1}{2}\right)^n$$

### Tossing Coins

#### 1. Tossing a coin

$$\text{Basis} = \{H, T\}$$

$$\text{Total no of events} = 2$$

$$\text{Total number of microstate} = 2^N = 2^1 = 2$$

$$\text{equally likely probability event} = \frac{1}{2}$$

#### 2. Tossing two coins together

$$\text{Basis} = \{HH, HT, TH, TT\}$$

$$\text{Total number of microstates} = (2)^N = 2^2 = 4$$

$$\text{Equally likely Probability} = \frac{1}{4}$$

$$\text{Probability of general event} = {}^nC_r(p)^{n-r}(1-p)^r = {}^nC_r\left(\frac{1}{2}\right)^n$$

### Rolling Dice

#### 1. Rolling a Dice

$$\text{Basis} = \{1, 2, 3, 4, 5, 6, \}$$

$$\text{Total no of events} = 6$$

$$\text{Total number of microstate} = 6^N = 6^1 = 6$$

$$\text{equally likely probability event} = \frac{1}{6}$$

#### 2. Rolling two Dice together

$$\text{Basis} = \{(1, 1), (1, 2), (1, 3), \dots, (2, 1), (2, 2), \dots, (6, 6)\}$$

$$\text{Total number of microstates} = (6)^N = 6^2 = 36$$

$$\text{Equally likely Probability} = \frac{1}{36}$$

$$\text{Probability of general event} = {}^nC_r(p)^{n-r}(1-p)^r = {}^nC_r\left(\frac{1}{2}\right)^n$$

### Number of microstates in spin system

$$\text{Basis} = (2s + 1)$$

$$\text{Total number of microstate } \Omega = (2s + 1)^N$$

**Exercise 1.2** A system of 5 identical but distinguishable particles having energy  $3\varepsilon$ . The single particle states are available at energies  $0, \varepsilon, 2\varepsilon, 3\varepsilon$  find the probability of each macro state? ■

0	$\varepsilon$	$2\varepsilon$	$3\varepsilon$	$E_{\text{Total}}$	No.of Microstates
4	-	-	1	$3\varepsilon$	$\Omega = \frac{5!}{4!0!0!} = 5$
3	1	1	-	$3\varepsilon$	$\Omega = \frac{5!}{3!1!1!0!} = 20$
2	3	-	-	$3\varepsilon$	$\Omega = \frac{5!}{2!3!0!0!} = 10$

**Exercise 1.3** If two similar coins are tossed together what is the probability of getting 3 Head? ■

**Solution:**

$$\begin{aligned}
 P(3H) &= {}^{10}C_3 \left(\frac{1}{2}\right)^{10-3} \left(\frac{1}{2}\right)^3 \\
 &= {}^{10}C_3 \left(\frac{1}{2}\right)^{10} \Rightarrow \frac{10!}{3!7!} \left(\frac{1}{2}\right)^{10} \\
 &= \frac{10 \times 9 \times 8}{3 \times 2} \times \frac{1}{1024} \Rightarrow \frac{15}{128}
 \end{aligned}$$

### 1.3.3 Random Walk

The random walk problem is of considerable interest in statistical physics. We shall discuss this problem as an application of the binomial distribution. The original problem solved by Markoff can be formulated in the following way: A drunkard starts from a certain lamp post on a street. Some of the steps he takes are forward and some backward. Each step is of the same length and is completely independent of the preceding step. What is the probability that the drunkard, after taking  $N$  steps, will reach his destination, which is at a distance  $x$  from the lamp post? A particle undergoing random displacements, as in Brownian motion, forms a physical situation similar to a drunkard's totterino.

Consider a particle undergoing successive displacements each of length  $l$ , in one dimension. What is the probability that the particle, after  $N$  such displacements, will be at a distance  $x = ml$ , where  $m$  is an integer?

Let,  $N \rightarrow$  steps of equal length along a line.

$p \rightarrow$  Probability of taking a step right

$q \rightarrow$  probability of taking a step left

$n_1 \rightarrow$  no. of steps taken to right

$n_2 \rightarrow$  no. of steps taken to left.

$$p + q = 1 \quad n_1 + n_2 = N$$

**Exercise 1.4** A one dimensional random walker takes 10 steps in left and right with equal probability. Find out the probability that the random walker starting from origine is back to origine after taking 10 steps? ■

**Solution:**

$$P(5,5) = {}^{10}C_5 \left(\frac{1}{2}\right)^{10}$$

$$= \frac{10!}{5!5!} \times \frac{1}{1024}$$

## 1.4 Macroscopic and Microscopic Coordinates

A system whose size is of the order of atomic dimensions or smaller ( $< 10$ ) is called a microscopic system. Example, a molecule, an atom. If the size of the system is very large compared to size of an atom, say greater than one micron it is called a macroscopic system. A macroscopic system contains a large number of particles.

Let us consider a system, say a cylinder fitted with a frictionless weightless piston containing a gas at a pressure  $P$  and temperature  $T$ . The state of the gas can be specified by  $P, T$  and volume  $V$  of the gas. These coordinates are called macroscopic coordinates.

For the microscopic description of the state of the gas we need the position and momentum coordinates of all the  $N$  coordinates say  $(x_1, y_1, z_1), (x_2, y_2, z_2), \dots, (x_n, y_n, z_n)$  and  $(p_{x1}, p_{y1}, p_{z1}), (p_{x2}, p_{y2}, p_{z3}), \dots, (p_{xN}, p_{yN}, p_{zN})$  are called micro-coordinates.

### 1.4.1 Macrostates and Microstates

Consider a system consisting of  $N$  structureless identical weakly interacting particles, occupying a fixed volume  $V$ . Let the internal energy of the system be  $U$ . The state of the system is completely determined by  $6N$  coordinates;  $3N$  position coordinates and  $3N$  momentum coordinates. Since there are  $6N$  coordinates this phase space is  $6N$  dimensional. Let the phase space be divided into allowed discrete energy levels and all the  $N$  particles be distributed among these energy levels. Let there be  $n_1$  particles in the energy state  $E_1, n_2$  in  $E_2$  and so on. Then

$$n_1 + n_2 + n_3 + \dots = \sum_i n_i = N$$

$$n_1 E_1 + n_2 E_2 + \dots = \sum_i n_i E_i = U$$

The set of numbers,  $n_1, n_2, n_3$  of the particles represent one set of distribution of  $N$  particles corresponding to the same macrostate of the system. We can have different sets of numbers of particles in the energy levels satisfying equations above. These different sets of number of particles give different distributions corresponding to the same macrostate. Thus a macrostate is specified by just giving the number of particles in each energy state. Macrostate is a state of a system which is represented by the macro properties like pressure, volume, temperature, density etc. in the equilibrium state.

For defining a microstate we should specify to which energy state each particle of the system belongs at a particular instant. For example in solved problem each arrangement like  $(abc, d)$  or  $(acd, b)$  is a microstate. There are five macrostates in the example we have solved. The number of microstates corresponding to the given macrostate of the system is called thermodynamic probability or thermodynamic frequency.

For indistinguishable particles, each distribution of the particles among the energy levels, corresponding to the same macrostate of the system is called a microstate, or the state of a system represented by the instant positions and momenta of all the particles is called the microstate. The microstate may change continuously with time. So corresponding to a macrostate there will be a large number of microstates.

### 1.4.2 Constraints and Accessible State

Physical laws impose certain restrictions on the distribution of the molecules among various energy states in phase space and are called constraints of the system. The total number of molecules in a system remains a constant. This is a constraint. i.e.  $\sum n_i = N = \text{a constant}$ . Another constraint is that the total energy of the system is a constant.  $\sum n_i \epsilon_i = U = \text{a constant}$

Those microstates into which the molecules are permitted to go under the constraints imposed on the system are called accessible microstates. States which are not permitted by constraints are called non-accessible states.



### 1.4.3 Boltzmann Entropy

The most important relation, between the micro(scopic) and the macro(scopic) worlds is given by,

$$S = k_B \ln \Omega(E, V, N) \quad (1.1)$$

It was proposed by Boltzmann.  $S$  stands for entropy and belongs to the macro world described by thermodynamics.  $\Omega$  is the number of micro states of a macroscopic system.  $k_B$  is the Boltzmann constant that establishes correspondence of the statistical entropy of Boltzmann to the thermodynamic entropy of Clausius.

#### Classical Distribution Law

**Accessible microstate** : Microstates corresponding to a macrostate.

**Thermodynamic Probability:** Number of microstates corresponding to a macrostate.

$$\text{Probability} = \frac{\text{Number of microstates for accessible macrostate}}{\text{Total number of microstates}} \quad (1.2)$$

### 1.4.4 Thermodynamic probability

The thermodynamic probability is the number of microstates corresponding to the given macrostate of the system. As an example consider the distribution of 4 particles in the two halves of a box. There are five macrostates viz., (4,0), (3,1), (2,2), (1,3) and (0,4) are possible. The thermodynamic probability corresponding to the distribution (2,2) is 6.

The redistribution or permutation of indistinguishable particles in a cell is meaningless because it does not produce any new microstate and so it is neglected.

Consider the distribution of  $n$  similar particles in  $k$  similar boxes such that  $n_1, n_2, n_3 \dots n_k$  particles are in the boxes 1, 2, 3, ...,  $k$  respectively. Then  $n_1 + n_2 + n_3 + \dots + n_k = n$ .

It can be shown that the number of microstates corresponding to this distribution or its thermodynamic probability

$$\Omega = \frac{n!}{\prod n_i!} \quad (1.3)$$

#### Proof

The number of ways of choosing  $n_1$  particles for the first box,

$$= \frac{n!}{n_1! (n - n_1)!}$$

From the remaining particle  $(n - n_1)$  we have to choose  $n_2$  particles for the box 2.

This can be done in  $\frac{(n - n_1)!}{n_2! (n - n_1 - n_2)!}$  ways.

For the box 3,  $n_3$  particles can be chosen in  $\frac{(n - n_1 - n_2)!}{n_3! (n - n_1 - n_2 - n_3)!}$  ways and so

So the total number of meaningful ways of arranging  $n_1, n_2, n_3 \dots n_k$  particles in boxes 1, 2, 3, ...,  $k$  respectively is,

$$\Omega = \frac{n!}{n_1! (n - n_1)!} \times \frac{(n - n_1)!}{n_2! (n - n_1 - n_2)!} \times \frac{(n - n_1 - n_2)!}{n_3! (n - n_1 - n_2 - n_3)!} \times \dots, k \text{ terms}$$

$$\Omega = \frac{n!}{n_1! n_2! n_3! \dots n_k!}$$

For the  $i^{\text{th}}$  distribution then the probability  $\Omega_i = \frac{n!}{\pi n_i!}$

### 1.4.5 Statistical Ensemble

A collection of particles is called a system. A number of systems constitute an ensemble. Sometimes it is difficult to study the behaviour of a complex system. But a suitably created ensemble help us to compute the statistical behaviour of the system



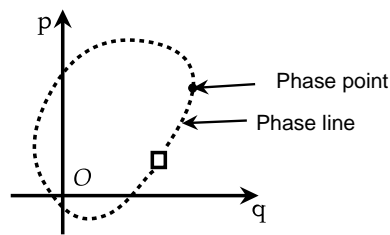


Figure 1.2

The phase line of a single system is as shown in Fig.1.2 Each phase point on the phase line emerges from the previous point, with passage of time, in accordance with the laws of mechanics. Suppose we want to compute a physical quantity of the system. Usually what we do is we find its time average over a certain interval of time. But Gibbs reduced this time dependent picture by a static picture. According to this model, the entire phase line shown by dotted line, in Fig. exists at one time. Then each phase point represents a separate system, with the same macroscopic properties ( $N, V, E$ ) but a different microscopic state where  $N$  is the total number of particles in the system,  $V$  its volume and  $E$  its total energy. i.e., we just imagine a large number, (almost infinity) of systems, which are similar in structure to the system under consideration, but placed at random in the accessible, unobservable microscopic states. Now we don't take the time average but take an average over this artificially created group of systems created simultaneously one time. This collection of replicas of similar, independent noninteracting systems is called an ensemble. Gibbs assumed that the time average of some property of a system in equilibrium is same as the instantaneous ensemble average. This is called the ergodic hypothesis. All the members of the ensemble which are identical in  $N, V, E$  are called elements.

$N, V, E$	$N, V, E$	$N, V, E$	$N, V, E$
$N, V, E$	$N, V, E$	$N, V, E$	$N, V, E$
$N, V, E$	$N, V, E$	$N, V, E$	$N, V, E$
$N, V, E$	$N, V, E$	$N, V, E$	$N, V, E$

In Fig.  $N, V, E$  represents one system. A collection of such system constitute an ensemble.

#### 1.4.6 Characteristics of an ensemble

1. The elements of an ensemble are identical in structure. i.e., they have the same macroscopic state.
2. The elements differ in their microscopic state. i.e., they differ from each other in the position coordinates and momentum coordinates.
3. The various elements do not interact each other.
4. Each element of the ensemble behaviour independently obeying the laws of mechanics.
5. The elements of the ensemble are the mental copies of the system under consideration. But the system is a physical object, whose properties are to be evaluated. The elements help us to use the probability theory.

#### 1.4.7 Ensemble average

The average value found out at a fixed time over all the elements in an ensemble is called an ensemble average. The ensemble average will be equal to the time average when the system contains a large number of particles (molecules) and the ensemble contains a large number systems (both almost infinite in number).

#### 1.4.8 Liouville's Theorem

The condition of an ensemble at any time can be specified by the density  $\rho$  with which the phase points are distributed over the phase space. It is called the density of distribution and is a function of the position coordinates

(q) and momentum coordinates (p). The dynamical state of a system at any instant of time can be represented by a point in the phase space. This point will not be stationary, but will move along a certain trajectory. The trajectory is determined by the equation of motion,

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad (1.4)$$

$$\text{and } \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (1.5)$$

Where  $H = H(q_i, p_i)$  is the Hamiltonian of the system. Due to this motion, the density  $\rho$  of the system in phase space changes with time. Liouville's theorem gives the value of  $\frac{\partial \rho}{\partial t}$  at a given point in phase space. Liouville's theorem states that the density of systems in the neighbourhood of some given system in phase space remains constant in time.

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0 \quad (1.6)$$

The sum of the two terms give the total change in density with time, Liouville's theorem states that the variation of density with time is zero i.e., the total rate of change of density  $d\rho/d\tau$  near any selected phase point of a system, as it moves through the phase space is zero. This is known as the principle of the conservation of the density in phase. This implies that the distribution of phase points move in phase space like an incompressible fluid.

#### 1.4.9 Different Types of Ensembles

Depending on the behaviour of the constituents of an ensemble with respect to the surroundings, ensembles are classified into mainly three types,

1. Microcanonical ensemble
2. Canonical ensemble
3. Grand canonical ensemble

**Note** **Uniform ensemble:** If the density in phase space is constant it is called uniform ensemble.

#### 1.4.10 Microcanonical Ensemble

Microcanonical ensemble is a collection of independent systems of constant volume separated from the neighbours with rigid impermeable adiabatic walls.  $N, V$  and  $E$  remains constant,  $N$  is the total number of particles in the system.  $V$  and  $E$  are the volume and energy of the system [See Fig. 1.3] respectively. Consider a system for which the total energy is conserved.

$$H(q, p) = E \text{ is conserved.}$$

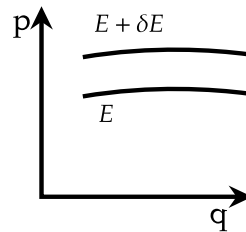
$$E[q_1, \dots, q_f, p_1, \dots, p_f] = \text{a constant.}$$

The locus of all the phase points having the same value for the energies in the phase space is called an energy surface or ergodic surface. A number of such energy surfaces can be constructed in the phase space. Each energy surface divides the phase space into two parts, one of lower energy and the other of higher energy. Since the two are of different energies they do not intersect each other.

E, V, N	E, V, N	E, V, N
E, V, N	E, V, N	E, V, N
E, V, N	E, V, N	E, V, N

Figure 1.3

Let  $E$  and  $E + \delta E$  be two neighbouring ergodic surfaces. The phase volume in between the two surfaces encloses a certain number of phase points and will be a constant. Let us assume the density to be zero for all values of energy except in a narrow range of energy between  $E$  and  $E + \delta E$ . Then the ensemble specified in terms of  $\rho$  as, is called a micro canonical ensemble.  $\rho$  is a function of energy. Here  $\rho$  is constant and hence  $E$  is also a constant. So the ensemble is in statistical equilibrium. Since  $\rho$  is a constant within the energy shell, the distribution of phase points is also uniform, by Liouville's theorem. As the ensemble is in statistical equilibrium, the average properties predicted will not change with time.



A microcanonical ensemble can be obtained from a uniform ensemble by neglecting those systems whose phase points do not lie within the phase space corresponding to the energy range between  $E$  and  $E + \delta E$ . A microcanonical ensemble is an idealised concept and hence cannot exist in practice because the systems which we come across always interact with their surroundings, either thermally or mechanically. In microcanonical ensemble there is exchange of neither energy nor particles (molecules) among the systems.

If  $\Omega$  is the number of accessible microstates, the probability that a system chosen at random from the ensemble would be in a given microstate is simply  $\frac{1}{\Omega}$ . No. of accessible microstate in phase space which has energy between  $E$  to  $E + dE$  is given by ,

$$\Omega = \sum_{\text{sates}} = \int \frac{dp \cdot dr}{h^3}$$

In terms of energy,

$$n(E)dE = 2g\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

where 'g' is degeneracy of the particle.

### Classical Ideal Gas

#### a) Non Relativistic Case

$$E = \frac{p^2}{2m} \Rightarrow p = \sqrt{2mE}$$

For  $N$  – particle : DOF =  $3N$

volume of position space =  $V^N$

$$\text{volume of momentum space} = \frac{\pi^{3N/2} p^{3N}}{(3N/2)!}$$

$$\rightarrow \Omega = \frac{V^N \cdot \pi^{3N/2} (\sqrt{2mE})^{3N}}{h^{3N} (3N/2)!}$$

$$\rightarrow E = U = \frac{3}{2} NKT = \frac{3}{2} nRT$$

$$\text{If } E \propto P^s \text{ and } d \rightarrow \text{dimension} \rightarrow P = \frac{s}{d} \left(\frac{E}{V}\right) = \frac{2}{3} \left(\frac{E}{V}\right)$$

$$\rightarrow PV^{5/3} = \text{constant}$$

$$\rightarrow S = K \ln \Omega$$

$$S = N_i k \ln v_i + \frac{3}{2} N_i k \ln \left( \frac{4\pi m_i E}{3N_i h^2} \right) + \frac{3}{2} N_i k$$

b) Relativistic case

$$E = pc$$

$$\Omega = \frac{U^N \pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} \left(\frac{E}{Ch}\right)^{3N}$$

$$P = \frac{S}{d} \left(\frac{U}{V}\right)$$

$$P = \frac{1}{3} \left(\frac{U}{V}\right)$$

$$PV^{4/3} = \text{constant}$$

## 1.5 Canonical Ensemble

Canonical ensemble is a collection of independent systems of constant volume separated from the neighbours by rigid, impermeable, diathermic walls so that the systems are in thermal equilibrium. The particles can exchange energy and hence all the systems will attain the same temperature. The systems have the same temperature  $T$  and constant volume  $V$ . The number of particles  $N$  is also a constant. In canonical ensemble systems can exchange energy and not particles.

T, V, N	T, V, N	T, V, N
T, V, N	T, V, N	T, V, N
T, V, N	T, V, N	T, V, N

### 1.5.1 Grand Canonical Ensemble

Grand Canonical ensemble is a collection of independent systems of constant volume but open and separated from its neighbours by diathermic permeable membrane so that both material and energy can be exchanged between the neighbours. Since there is exchange of energy, the energy of each system  $E$  is not a constant. Also there is exchange of particles, so the total number of particles in each system do not remain constant. The temperature  $T$ , volume  $V$  and chemical potential  $\mu$  of each system remain constant.

T, V, $\mu$	T, V, $\mu$	T, V, $\mu$
T, V, $\mu$	T, V, $\mu$	T, V, $\mu$
T, V, $\mu$	T, V, $\mu$	T, V, $\mu$

In grand Canonical ensemble there is exchange of both energy and particles (molecules) among the systems.

Micro Canonical	Canonical	Grand Canonical
E, V, N	T, V, N	$T, V, \mu$
Insulating, rigid and impermeable	Conducting, rigid and impermeable	Conducting, rigid and permeable
Isolated system	Thermal equilibrium	Thermal +Chemical equilibrium
Universe, thermal flask etc.	-	-

Table 1.1: Table of Ensembles

### 1.5.2 Statistical Equilibrium

A system of particles which does not interact with any other system so that its total energy remains constant is called an isolated system. A small part of the isolated system which is still macroscopic is called a subsystem. Subsystem interacts with other parts of the system and hence is not isolated.

If in any macroscopic subsystem of an isolated system, the average number of particles per unit volume and the average energy per particle are equal to their mean values, then the isolated system is said to be in statistical equilibrium i.e, when the mean values of macroscopic parameters like pressure, volume, temperature etc. are independent of time, the system is in equilibrium. If the system is found with equal probability in each of its possible quantum states then the isolated system is in statistical or thermodynamic equilibrium. In terms of density  $\rho$ , the condition for an ensemble to be in statistical equilibrium is  $\left(\frac{\partial \rho}{\partial t}\right)_{q,p} = 0$ , i.e,  $\rho$  is independent of time at all points in the phase space for the ensemble. For this  $\rho$  must be a function of some property of the ensemble which does not depend on time.

### 1.5.3 Postulate of Equal a priori probability

Consider an isolated 'many particle system' in equilibrium. We want to know the probability for any one particle to be in a given specified state. The answer to this is given by the a priori postulate.

**"All accessible microstates corresponding to possible macrostates are equally probable"**. This is the most fundamental postulate of statistical mechanics. This means that the probability of finding the particle in any one region is identical with that for any other region of equal volume, under similar conditions.

### 1.5.4 Canonical Ensemble

Consider a canonical system  $A$  in a microcanonical ensemble  $A'$  ( $A \ll A'$ ). The walls of  $A$  are such that  $A$  and  $A'$  free to exchange energy. The microcanonical ensemble is isolated and its total energy  $E$  is constant. As discussed before, a large number of microscopic states correspond to the macroscopic state of the microcanonical ensemble with energy  $E$ . Let  $\Omega_i$  to the total number of microstates of the microcanonical ensemble with energy  $E$ . By the postulate of equal a priori probability, all these microstates are equally probable.

Therefore, the probability microcanonical ensemble  $A'$  will give rise to different microstates of the small subsystem  $A$ . Suppose, a certain microstate of  $A'$  gives rise to a microstate of  $A$  with energy  $\epsilon_i$  ( $\epsilon_i \ll E$ ). Hence, the energy of the remaining part of the complete system is  $E - \epsilon_i$ . This is one microstate of  $A$  with energy  $\epsilon_i$  attained through the other microstates of  $A'$ . Let the number of states of the microcanonical ensemble  $A'$ , through which the states of the small system  $A$  corresponding to the energy  $\epsilon_i$  are attained, be  $\Omega_i(E - \epsilon_i)$ . Therefore, the probability that the small system  $A$  is in a state with energy  $\epsilon_i$  is

$$P_i = \frac{\Omega_i(E - \epsilon_i)}{\Omega(E)}$$

This is the Gibbs canonical distribution. It gives the probability that the small system  $A$  be in a state with energy  $\epsilon_i$ . There may be other microstates of  $A$  with the same energy  $\epsilon_i$ . According to Gibbs, the probability of finding the system in any of its  $i^{\text{th}}$  state at temperature  $T$  where energy of that state is  $\epsilon_i$  is given by,

$$P_i \propto e^{-\epsilon_i \beta} \quad \text{where, } \beta = \frac{1}{k_B T}$$

$$P_i = ce^{-\varepsilon_i \beta} \quad \text{where, } c \text{ is proportionality constant.}$$

Hence  $P_i$  is probability then

$$\sum_i P_i = \sum_i ce^{-\varepsilon_i \beta} = 1$$

$$\text{So, } c = \frac{1}{\sum_i e^{-\varepsilon_i \beta}}$$

$$\Rightarrow c = \frac{1}{\sum_i e^{-\varepsilon_i \beta}} = \frac{1}{Z}$$

The letter  $Z$  stands for the German word Zustandssumme, "sum over states" and is known as **partition function** for canonical ensemble which is given by,

$$Z = \sum_i e^{-\varepsilon_i \beta} \quad (1.7)$$

In systems with multiple quantum, we can write the partition function in terms of the contribution from energy levels ( $g_i$  degeneracy of states) as follows:

$$Z = \sum_i g_i e^{-\varepsilon_i \beta} \quad (1.8)$$

Partition Function,  $Z = \sum_i e^{-\varepsilon_i \beta}$

Probability,  $P_i = \frac{e^{-\varepsilon_i \beta}}{\sum_i e^{-\varepsilon_i \beta}}$

### 1.5.5 Average value of different thermodynamic quantities

- Average Energy:

$$\langle E \rangle = \sum \varepsilon_i P_i \Rightarrow \frac{\sum \varepsilon_i g_i e^{-\beta \varepsilon_i}}{\sum g_i e^{-\beta \varepsilon_i}}$$

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln z = +kT^2 \frac{\partial}{\partial T} \ln z$$

- Average Pressure

$$\langle P \rangle = \sum p \frac{g_i e^{-\beta \varepsilon}}{z} = \frac{1}{\beta} \frac{\partial}{\partial v} \ln z$$

- Average Chemical Potential

$$\langle \mu \rangle = \sum \mu \frac{g_i e^{-\beta \varepsilon_i}}{z} = -\frac{1}{\beta} \frac{\partial}{\partial N} \ln z$$

- Average entropy

$$\langle S \rangle = K_B \ln z + \frac{\langle E \rangle}{T} \Rightarrow K_B \ln z - \frac{1}{T} \frac{\partial}{\partial B} \ln z$$

- Average Free Energy

$$\langle A \rangle = \langle E \rangle - \langle TS \rangle \Rightarrow -K_B T \ln z$$

$$F = -K_B T \ln z$$

$$U = \sum_i \varepsilon_i P_i - \frac{\partial}{\partial \beta} \ln z$$

$$S = \frac{\partial F}{\partial T} = \frac{1}{k_B T^2} \cdot \frac{\partial F}{\partial \beta}$$

$$\frac{\partial}{\partial T} = -\frac{1}{K_B T^2} \frac{\partial}{\partial \beta}$$

$$P = \frac{-\partial F}{\partial V}$$

$$\mu = \frac{\partial F}{\partial N}$$

$$C_v = \frac{\partial U}{\partial T} = \frac{-1}{K_B T^2} \frac{\partial U}{\partial \beta}$$





## Practise set-1

1. A particle is confined to the region  $x \geq 0$  by a potential which increases linearly as  $u(x) = u_0 x$ . The mean position of the particle at temperature  $T$  is

[NET/JRF(JUNE-2011)]

- |                               |                      |
|-------------------------------|----------------------|
| a. $\frac{k_B T}{u_0}$        | b. $(k_B T)^2 / u_0$ |
| c. $\sqrt{\frac{k_B T}{u_0}}$ | d. $u_0 k_B T$       |

2. Consider a system of  $N$  non-interacting spins, each of which has classical magnetic moment of magnitude  $\mu$ . The Hamiltonian of this system in an external magnetic field  $\vec{H}$  is  $\sum_{i=1}^N \vec{\mu}_i \cdot \vec{H}$ , where  $\vec{\mu}_i$  is the magnetic moment of the  $i^{\text{th}}$  spin. The magnetization per spin at temperature  $T$  is

[NET/JRF(JUNE-2011)]

- |   |  |
|---|--|
| a. $\frac{\mu^2 H}{k_B T}$                        | b. $\mu \left[ \coth \left( \frac{\mu H}{k_B T} \right) - \frac{k_B T}{\mu H} \right]$ |
| c. $\mu \sinh \left( \frac{\mu H}{k_B T} \right)$ | d. $\mu \tanh \left( \frac{\mu H}{k_B T} \right)$                                      |

3. The internal energy  $E$  of a system is given by  $E = \frac{bS^3}{VN}$ , where  $b$  is a constant and other symbols have their usual meaning. The temperature of this system is equal to

[NET/JRF(DEC-2011)]

- |                        |                                   |
|------------------------|-----------------------------------|
| a. $\frac{bS^2}{VN}$   | b. $\frac{3bS^2}{VN}$             |
| c. $\frac{bS^3}{V^2N}$ | d. $\left( \frac{S}{N} \right)^2$ |

4. A gas of  $N$  non-interacting particles is in thermal equilibrium at temperature  $T$ . Each particle can be in any of the possible non-degenerate states of energy  $0, 2\varepsilon$  and  $4\varepsilon$ . The average energy per particle of the gas, when  $\beta\varepsilon \ll 1$ , is

[NET/JRF(DEC-2011)]

- |                     |                   |
|---------------------|-------------------|
| a. $2\varepsilon$   | b. $3\varepsilon$ |
| c. $2\varepsilon/3$ | d. $\varepsilon$  |

5. Gas molecules of mass  $m$  are confined in a cylinder of radius  $R$  and height  $L$  (with  $R > L$ ) kept vertically in the Earth's gravitational field. The average energy of the gas at low temperatures (such that  $mgL \gg k_B T$ ) is given by

[NET/JRF(DEC-2011)]

- |               |                |
|---------------|----------------|
| a. $Nk_B T/2$ | b. $3Nk_B T/2$ |
| c. $2Nk_B T$  | d. $5Nk_B T/2$ |

6. The free energy of the gas of  $N$  particles in a volume  $V$  and at a temperature  $T$  is  $F = Nk_B T \ln \left[ a_0 V (k_B T)^{5/2} / N \right]$ , where  $a_0$  is a constant and  $k_B$  denotes the Boltzmann constant. The internal energy of the gas is

[NET/JRF(JUNE-2012)]

- |   |  |
|---|--|
| a. $\frac{3}{2} Nk_B T$   | b. $\frac{5}{2} Nk_B T$                              |
| c. $Nk_B T \ln \left[ a_0 V (k_B T)^{5/2} / N \right] - \frac{3}{2} Nk_B T$ | d. $Nk_B T \ln \left[ a_0 V / (k_B T)^{5/2} \right]$ |

7. A system has two normal modes of vibration, with frequencies  $\omega_1$  and  $\omega_2 = 2\omega_1$ . What is the probability that at temperature  $T$ , the system has an energy less than  $4\hbar\omega_1$ ? [In the following  $x = e^{-\beta\hbar\omega_1}$  and  $Z$  is the partition function of the system.]

[NET/JRF(JUNE-2012)]

- a.  $x^{3/2}(x+2x^2)/Z$                       b.  $x^{3/2}(1+x+x^2)/Z$   
 c.  $x^{3/2}(1+2x^2)/Z$                       d.  $x^{3/2}(1+x+2x^2)/Z$

8. The entropy of a system, ( $S$ ), is related to the accessible phase space volume  $\Gamma$  by  $S = k_B \ln \Gamma(E, N, V)$  where  $E, N$  and  $V$  are the energy, number of particles and volume respectively. From this one can conclude that  $\Gamma$

[NET/JRF(DEC-2012)]

- a. Does not change during evolution to equilibrium  
 b. Oscillates during evolution to equilibrium  
 c. Is a maximum at equilibrium  
 d. Is a minimum at equilibrium

9. Consider a one-dimensional Ising model with  $N$  spins, at very low temperatures when almost all spins are aligned parallel to each other. There will be a few spin flips with each flip costing an energy  $2J$ . In a configuration with  $r$  spin flips, the energy of the system is  $E = -NJ + 2rJ$  and the number of configuration is  ${}^N C_r$ ;  $r$  varies from 0 to  $N$ . The partition function is

[NET/JRF(DEC-2012)]

- a.  $\left(\frac{J}{k_B T}\right)^N$                       b.  $e^{-NJ/k_B T}$   
 c.  $\left(\sinh \frac{J}{k_B T}\right)^N$                       d.  $\left(\cosh \frac{J}{k_B T}\right)^N$

10. Consider a system of three spins  $S_1, S_2$  and  $S_3$  each of which can take values  $+1$  and  $-1$ . The energy of the system is given by  $E = -J[S_1 S_2 + S_2 S_3 + S_3 S_1]$  where  $J$  is a positive constant. The minimum energy and the corresponding number of spin configuration are, respectively,

[NET/JRF(DEC-2012)]

- a.  $J$  and 1                      b.  $-3J$  and 1  
 c.  $-3J$  and 2                      d.  $-6J$  and 2

11. Consider a system of two Ising spins  $S_1$  and  $S_2$  taking values  $\pm 1$  with interaction energy given by  $\varepsilon = -JS_1 S_2$ , when it is in thermal equilibrium at temperature  $T$ . For large  $T$ , the average energy of the system varies as  $C/k_B T$ , with  $C$  given by

[NET/JRF(JUNE-2013)]

- a.  $-2J^2$                       b.  $-J^2$   
 c.  $J^2$                       d.  $4J$

12. A collection  $N$  of non-interacting spins  $S_i, i = 1, 2, \dots, N, (S_i = \pm 1)$  is kept in an external magnetic field  $B$  at a temperature  $T$ . The Hamiltonian of the system is  $H = -\mu B \sum_i S_i$ . What should be the minimum value of  $\frac{\mu B}{k_B T}$  for which the mean value  $\langle S_i \rangle \geq \frac{1}{3}$ ?

[NET/JRF(DEC-2014)]

- a.  $\frac{1}{2} N \ln 2$                       b.  $2 \ln 2$   
 c.  $\frac{1}{2} \ln 2$                       d.  $N \ln 2$

13. A system of  $N$  distinguishable particles, each of which can be in one of the two energy levels 0 and  $\epsilon$ , has a total energy  $n\epsilon$ , where  $n$  is an integer. The entropy of the system is proportional to

[NET/JRF(JUNE-2015)]

- a.  $N \ln n$                       b.  $n \ln N$   
 c.  $\ln \left(\frac{N!}{n!}\right)$                       d.  $\ln \left(\frac{N!}{n!(N-n)!}\right)$



a.  $k_B(\beta\epsilon)$

b.  $k_B e^{-\beta\epsilon}$

c.  $2k_B(\beta\epsilon)^2 e^{-\beta\epsilon}$

d.  $k_B$

20. In a thermodynamic system in equilibrium, each molecule can exist in three possible states with probabilities  $1/2$ ,  $1/3$  and  $1/6$  respectively. The entropy per molecule is

[NET/JRF(JUNE-2017)]

a.  $k_B \ln 3$

b.  $\frac{1}{2}k_B \ln 2 + \frac{2}{3}k_B \ln 3$

c.  $\frac{2}{3}k_B \ln 2 + \frac{1}{2}k_B \ln 3$

d.  $\frac{1}{2}k_B \ln 2 + \frac{1}{6}k_B \ln 3$

Answer key			
Q.No.	Answer	Q.No.	Answer
1	a	2	b
3	b	4	a
5	d	6	b
7	d	8	c
9	d	10	c
11	b	12	c
13	d	14	b
15	d	16	d
17	c	18	c
19	c	20	c

## Practise set-2

1. A system of  $N$  non-interacting classical point particles is constrained to move on the twodimensional surface of a sphere. The internal energy of the system is

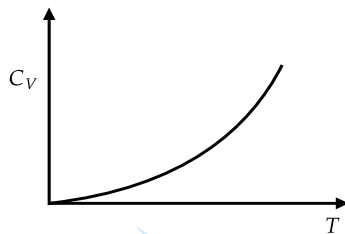
[GATE 2010]

- A.  $\frac{3}{2}Nk_B T$       B.  $\frac{1}{2}Nk_B T$       C.  $Nk_B T$       D.  $\frac{5}{2}Nk_B T$

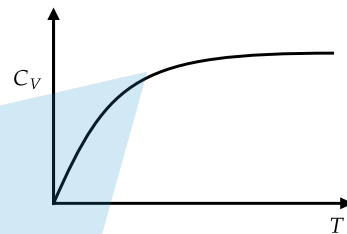
2. Partition function for a gas of photons is given as,  $\ln Z = \frac{\pi^2 V (k_B T)^3}{45 \hbar^3 C^3}$ . The specific heat of the photon gas varies with temperature as

[GATE 2010]

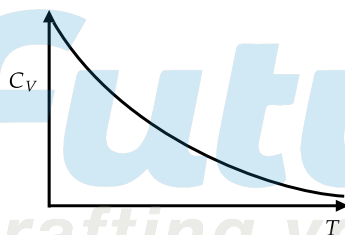
A.



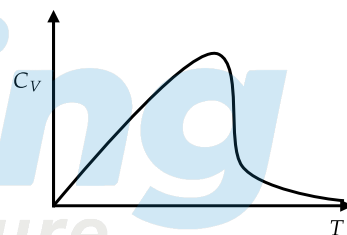
B.



C.



D.



3. From Q. no. 2, the pressure of the photon gas is

[GATE 2010]

- A.  $\frac{\pi^2 (k_B T)^3}{15 \hbar^3 C^3}$       B.  $\frac{\pi^2 (k_B T)^4}{8 \hbar^3 C^3}$       C.  $\frac{\pi^2 (k_B T)^4}{45 \hbar^3 C^3}$       D.  $\frac{\pi^2 (k_B T)^{3/2}}{45 \hbar^3 C^3}$

4. A system of  $N$  non-interacting and distinguishable particle of spin 1 is in thermodynamic equilibrium. The entropy of the system is

[GATE 2011]

- A.  $2k_B \ln N$       B.  $3k_B \ln N$       C.  $Nk_B \ln 2$       D.  $Nk_B \ln 3$

5. A system has two energy levels with energies  $\varepsilon$  and  $2\varepsilon$ . The lower level is 4 -fold degenerate while the upper level is doubly degenerate. If there are  $N$  non-interacting classical particles in the system, which is in thermodynamic equilibrium at a temperature  $T$ , the fraction of particles in the upper level is

[GATE 2011]

- A.  $\frac{1}{1+e^{\varepsilon/k_B T}}$       B.  $\frac{1}{1+2e^{\varepsilon/k_B T}}$       C.  $\frac{1}{2e^{\varepsilon/k_B T}+4e^{2\varepsilon/k_B T}}$       D.  $\frac{1}{2e^{\varepsilon/k_B T}-4e^{2\varepsilon/k_B T}}$

6. Consider a system whose three energy levels are given by 0,  $\varepsilon$  and  $2\varepsilon$ . The energy level  $\varepsilon$  is two-fold degenerate and the other two are non-degenerate. The partition function of the system with  $\beta = \frac{1}{k_B T}$  is given by

[GATE 2012]

- A.  $1 + 2e^{-\beta\epsilon}$       B.  $2e^{-\beta\epsilon} + e^{-2\beta\epsilon}$       C.  $(1 + e^{-\beta\epsilon})^2$       D.  $1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$

7. Consider a linear collection of  $N$  independent spin  $1/2$  particles, each at a fixed location. The entropy of this system is ( $k$  is the Boltzmann constant)

[GATE 2013]

- A. Zero      B.  $Nk$       C.  $\frac{1}{2}Nk$       D.  $Nk \ln(2)$

8. Consider a system of  $N$  non-interacting spin  $-\frac{1}{2}$  particles, each having a magnetic moment  $\mu$ , is in a magnetic field  $\vec{B} = B\hat{z}$ . If  $E$  is the total energy of the system, then number of accessible microstates  $\Omega$  is given by

[GATE 2015]

- A.  $\Omega = \frac{N!}{\frac{1}{2}(N - \frac{E}{\mu B})! \frac{1}{2}(N + \frac{E}{\mu B})!}$       B.  $\Omega = \frac{(N - \frac{E}{\mu B})!}{(N + \frac{E}{\mu B})!}$   
 C.  $\Omega = \frac{1}{2} \left( N - \frac{E}{\mu B} \right)! \frac{1}{2} \left( N + \frac{E}{\mu B} \right)!$       D.  $\Omega = \frac{N!}{(N + \frac{E}{\mu B})!}$

9. The average energy  $U$  of a one dimensional quantum oscillator of frequency  $\omega$  and in contact with a heat bath at temperature  $T$  is given by

[GATE 2015]

- A.  $U = \frac{1}{2}\hbar\omega \coth\left(\frac{1}{2}\beta\hbar\omega\right)$       B.  $U = \frac{1}{2}\hbar\omega \sinh\left(\frac{1}{2}\beta\hbar\omega\right)$   
 C.  $U = \frac{1}{2}\hbar\omega \tanh\left(\frac{1}{2}\beta\hbar\omega\right)$       D.  $U = \frac{1}{2}\hbar\omega \cosh\left(\frac{1}{2}\beta\hbar\omega\right)$

10. The entropy of a gas containing  $N$  particles enclosed in a volume  $V$  is given by  $S = Nk_B \ln\left(\frac{aVE^{3/2}}{N^{5/2}}\right)$ , where  $E$  is the total energy,  $a$  is a constant and  $k_B$  is the Boltzmann constant. The chemical potential  $\mu$  of the system at a temperature  $T$  is given by

[GATE 2015]

- A.  $\mu = -k_B T \left[ \ln\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - \frac{5}{2} \right]$       B.  $\mu = -k_B T \left[ \ln\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - \frac{3}{2} \right]$   
 C.  $\mu = -k_B T \left[ \ln\left(\frac{aVE^{3/2}}{N^{3/2}}\right) - \frac{5}{2} \right]$       D.  $\mu = -k_B T \left[ \ln\left(\frac{aVE^{3/2}}{N^{3/2}}\right) - \frac{3}{2} \right]$

11. entropy  $S$  of a system of  $N$  spins, which may align either in the upward or in the downward direction, is given by  $S = -k_B N [p \ln p + (1-p) \ln(1-p)]$ . Here  $k_B$  is the Boltzmann constant. The probability of alignment in the upward direction is  $p$ . The value of  $p$ , at which the entropy is maximum, is—— (Give your answer upto one decimal place)

[GATE 2016]

12.  $N$  atoms of an ideal gas are enclosed in a container of volume  $V$ . The volume of the container is changed to  $4V$ , while keeping the total energy constant. The change in the entropy of the gas, in units of  $Nk_B \ln 2$ , is—— where  $k_B$  is the Boltzmann constant.

[GATE 2016]

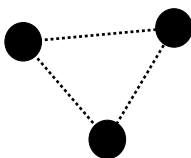
13. A two-level system has energies zero and  $E$ . The level with zero energy is nondegenerate, while the level with energy  $E$  is triply degenerate. The mean energy of a classical particle in this system at a temperature  $T$  is

[GATE 2016]

- A. (a)  $\frac{Ee^{\frac{-E}{k_B T}}}{1+3e^{\frac{-E}{k_B T}}}$       B.  $\frac{Ee^{\frac{-E}{k_B T}}}{1+e^{\frac{-E}{k_B T}}}$       C.  $\frac{3Ee^{\frac{-E}{k_B T}}}{1+e^{\frac{-E}{k_B T}}}$       D.  $\frac{3Ee^{\frac{-E}{k_B T}}}{1+3e^{\frac{-E}{k_B T}}}$

14. Consider a triatomic molecule of the shape shown in the figure in three dimensions. The heat capacity of this molecule at high temperature (temperature much higher than the vibrational and rotational energy scales of the molecule but lower than its bond dissociation energies) is:

[GATE 2017]



- A.  $\frac{3}{2}k_B$       B.  $3k_B$       C.  $\frac{9}{2}k_B$       D.  $6k_B$

15. Consider  $N$  non-interacting, distinguishable particles in a two-level system at temperature  $T$ . The energies of the levels are 0 and  $\varepsilon$ , where  $\varepsilon > 0$ . In the high temperature limit ( $k_B T > \varepsilon$ ), what is the population of particles in the level with energy  $\varepsilon$ ?

[GATE 2017]

- A.  $\frac{N}{2}$       B.  $N$       C.  $\frac{N}{4}$       D.  $\frac{3N}{4}$

16. A microcanonical ensemble consists of 12 atoms with each taking either energy 0 state, or energy  $\varepsilon$  state. Both states are non-degenerate. If the total energy of this ensemble is  $4\varepsilon$ , its entropy will be \_\_\_\_\_  $k_B$  (up to one decimal place), where  $k_B$  is the Boltzmann constant.

[GATE 2018]

17. The partition function of an ensemble at a temperature  $T$  is

$$Z = \left( 2 \cosh \frac{\varepsilon}{k_B T} \right)^N$$

where  $k_B$  is the Boltzmann constant. The heat capacity of this ensemble at  $T = \frac{\varepsilon}{k_B}$  is  $XNk_B$ , where the value of  $X$  is (up to two decimal places).

[GATE 2018]

18. A collection of  $N$  two-level systems with energies 0 and  $E > 0$  is in thermal equilibrium at temperature  $T$ . For  $T \rightarrow \infty$ , the specific heat approaches to,

[JEST 2012]

- A. 0      B.  $Nk_B$       C.  $\frac{3Nk_B}{2}$       D.  $\infty$

19. A monoatomic gas consists of atoms with two internal energy levels, ground state  $E = 0$  and an excited state  $E_1 = E$ . The specific heat of the gas is given by

[JEST 2014]

- A.  $\frac{3}{2}k$       B.  $\frac{E^2 e^{E/kT}}{kT^2 (1 + e^{E/kT})^2}$   
 C.  $\frac{3}{2}k + \frac{E^2 e^{E/kT}}{kT^2 (1 + e^{E/kT})^2}$       D.  $\frac{3}{2}k - \frac{E^2 e^{E/kT}}{kT^2 (1 + e^{E/kT})^2}$

20. Consider a system of  $2N$  non-interacting spin  $1/2$  particles each fixed in position and carrying a magnetic moment  $\mu$ . The system is immersed in a uniform magnetic field  $B$ . The number of spin up particles for which the entropy of the system will be maximum is

[JEST 2014]

- A. 0      B.  $N$       C.  $2N$       D.  $N/2$

21. For a system in thermal equilibrium with a heat bath at temperature  $T$ , which one of the following equalities is correct? ( $\beta = \frac{1}{k_B T}$ )

[JEST 2015]

- A.  $\frac{\partial}{\partial \beta} \langle E \rangle = \langle E \rangle^2 - \langle E^2 \rangle$       B.  $\frac{\partial}{\partial \beta} \langle E \rangle = \langle E^2 \rangle - \langle E \rangle^2$   
 C.  $\frac{\partial}{\partial \beta} \langle E \rangle = \langle E^2 \rangle + \langle E \rangle^2$       D.  $\frac{\partial}{\partial \beta} \langle E \rangle = -(\langle E^2 \rangle + \langle E \rangle^2)$



22. A particle in thermal equilibrium has only 3 possible states with energies  $-\epsilon, 0, \epsilon$ . If the system is maintained at a temperature,  $T \gg \frac{\epsilon}{k_B}$ , then the average energy of the particle can be approximated to, [JEST 2015]

A.  $\frac{2\epsilon^2}{3k_B T}$       B.  $\frac{-2\epsilon^2}{3k_B T}$       C.  $\frac{-\epsilon^2}{k_B T}$       D. 0

23. A collection of  $N$  interacting magnetic moments, each of magnitude  $\mu$ , is subjected to a magnetic field  $H$  along the  $z$  direction. Each magnetic moment has a doubly degenerate level of energy zero and two non-degenerate levels of energies  $-\mu H$  and  $\mu H$  respectively. The collection is in thermal equilibrium at temperature  $T$ . The total energy  $E(T, H)$  of the collection is [JEST 2018]

A.  $-\frac{\mu H N \sinh\left(\frac{\mu H}{k_B T}\right)}{1 + \cosh\left(\frac{\mu H}{k_B T}\right)}$       B.  $-\frac{\mu H N}{2\left(1 + \cosh\left(\frac{\mu H}{k_B T}\right)\right)}$

C.  $-\frac{\mu H N \cosh\left(\frac{\mu H}{k_B T}\right)}{1 + \cosh\left(\frac{\mu H}{k_B T}\right)}$       D.  $-\mu H N \frac{\sinh\left(\frac{\mu H}{k_B T}\right)}{\cosh\left(\frac{\mu H}{k_B T}\right)}$

24. Consider a system of  $N$  distinguishable particles with two energy levels for each particle, a ground state with energy zero and an excited state with energy  $\epsilon > 0$ . What is the average energy per particle as the system temperature  $T \rightarrow \infty$ ? [JEST 2019]

A. 0      B.  $\frac{\epsilon}{2}$       C.  $\epsilon$       D.  $\infty$

25. Consider a diatomic molecule with an infinite number of equally spaced non-degenerate energy levels. The spacing between any two adjacent levels is  $\epsilon$  and the ground state energy is zero. What is the single particle partition function  $Z$ ? [JEST 2019]

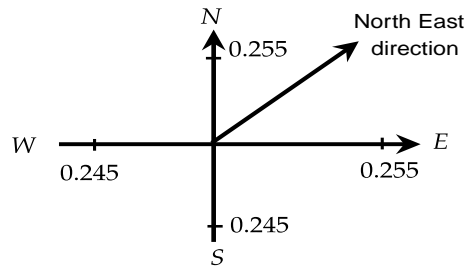
A.  $Z = \frac{1}{1 - \frac{\epsilon}{k_B T}}$       B.  $Z = \frac{1}{1 - e^{\frac{\epsilon}{k_B T}}}$

C.  $Z = \frac{1}{1 - e^{\frac{2\epsilon}{k_B T}}}$       D.  $Z = \frac{1 - \frac{\epsilon}{k_B T}}{1 + \frac{\epsilon}{k_B T}}$

Answer key			
Q.No.	Answer	Q.No.	Answer
1	<b>C</b>	2	<b>A</b>
3	<b>C</b>	4	<b>D</b>
5	<b>B</b>	6	<b>C</b>
7	<b>D</b>	8	-
9	<b>A</b>	10	<b>A</b>
11	<b>0.5</b>	12	$2Nk_B \ln 2$
13	<b>D</b>	14	<b>D</b>
15	<b>A</b>	16	$6.204k_B$
17	$0.42Nk_B$	18	<b>A</b>
19	<b>C</b>	20	<b>B</b>
21	<b>A</b>	22	<b>B</b>
23	<b>A</b>	24	<b>B</b>
25	-		

- ### Solution:





$$\begin{aligned}\langle x \rangle_N &= 0.255Na\hat{i} + 0.255Na\hat{j} - 0.245Na\hat{i} - 0.245Na\hat{j} \\ \langle x \rangle_N &= 10^{-2}(Na\hat{i} + Na\hat{j}) \\ &= 10^{-2}\sqrt{(1)^2 + (1)^2}Na \\ \langle x \rangle_N &= \sqrt{2} \times 10^{-2}Na \text{ in } N - E\end{aligned}$$

So the correct answer is **Option (a)**

8. The entropy of a system  $S$  is related to the accessible phase space volume  $\Gamma$  by

$$S = K_B \ln \Gamma(E, V, N)$$

where  $E, N$  and  $V$  are energy number of particles and volume respectively. From this one can conclude that  $\Gamma$ .

- a. Does not change during evolution to equilibrium.    b. Oscillated during evolution to equilibrium .  
c. Is a maximum in equilibrium .    d. Is a minimum in equilibrium .

**Solution:**

$$\begin{aligned}E, U, N &\rightarrow \text{micro canonical ensemble} \\ S &= K \ln T(E, V, N) \\ \text{maximum when } \Gamma &\text{ is maximum} \\ \text{In equilibrium } s &\rightarrow \text{ maximum} \\ \Rightarrow r &\rightarrow \text{ maximum}\end{aligned}$$

So the correct answer is **Option (c)**

9. In a canonical ensemble description of a system, which of the following quantities remain fixed?

- a. Energy of system    b. Square of energy  
c. Volume of system    d. Number of particles

**Solution:**

Canonical ensemble: fixed values are  $T, V, N$

So the correct answers are **Option (c) and (d)**

10. A microcanonical ensemble represents

- a. A system in contact with a heat reservoir.    b. An isolated system in equilibrium.  
c. A system can exchange particle with surroundings    d. A system under constant external pressure.

**Solution:** microcanonical:  $E, V, N$  fixed isolated system in equilibrium  
So the correct answer is **Option (b)**

11. The pressure for a non interacting fermi gas with internal energy  $U$  at temperature  $T$  is

a.  $P = \frac{3}{2} \left( \frac{U}{V} \right)$

b.  $P = \frac{2}{3} \frac{U}{V}$

c.  $P = \frac{3}{5} \frac{U}{V}$

d. none

**Solution:**

Non interacting fermi gas = ideal classical gas

$$U = \frac{3}{2} NK = \frac{3}{2} PV$$

$$P = \frac{2}{3} \left( \frac{U}{V} \right)$$

So the correct answer is **Option (b)**

12. The partition function of two base particles each of which can occupy any of the two energy levels of  $\epsilon$  is.

a.  $1 + e^{-2\epsilon/KT} + 2e^{-\epsilon/KT}$

b.  $1 + e^{-2\epsilon/KT} + e^{-\epsilon/KT}$

c.  $2 + e^{-2\epsilon/KT} + e^{-\epsilon/KT}$

d.  $e^{-2\epsilon/KT} + e^{-\epsilon/KT}$

**Solution:**

0	$\epsilon$	$E_{Total}$
aa	-	0
a	a	$\epsilon$
-	aa	$2\epsilon$

$$z = \sum g_i e^{-\beta \epsilon_i}$$

$$z = 1e^0 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}$$

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

$$g_i = 1$$

So the correct answer is **Option (b)**

13. Consider a system of two non-interacting classical particles which can occupy any of the three energy levels with energy values  $E = 0, \epsilon$  and  $2\epsilon$  having degeneracies  $g(E) = 1, 2$  and  $4$  respectively. The mean energy of the system is.

a.  $\epsilon \left( \frac{4 \exp(-\epsilon/k_B T) + 8 \exp(-2\epsilon/k_B T)}{1 + 2 \exp(-\epsilon/k_B T) + 4 \exp(-2\epsilon/k_B T)} \right)$

b.  $\epsilon \left[ \frac{2 \exp(-\epsilon/k_B T) + 8 \exp(-2\epsilon/k_B T)}{1 + 2 \exp(-\epsilon/k_B T) + 4 \exp(-2\epsilon/k_B T)} \right]$

c.  $\epsilon \left[ \frac{2 \exp(-\epsilon/k_B T) + 4 \exp(-2\epsilon/k_B T)}{1 + 2 \exp(-\epsilon/k_B T) + 4 \exp(-2\epsilon/k_B T)} \right]^2$

d.  $\epsilon \left[ \frac{\exp(-\epsilon/k_B T) + 2 \exp(-2\epsilon/k_B T)}{1 + \exp(-\epsilon/k_B T) + \exp(-2\epsilon/k_B T)} \right]^2$

**Solution:**

$$\langle \epsilon_i \rangle = \sum \epsilon_i P_i$$

$$\begin{aligned}
&= \frac{\sum \epsilon_i g_i e^{-\beta \epsilon_i}}{\sum g_i e^{-\beta \epsilon_i}} \\
&= \frac{0 + 2\epsilon e^{-\beta \epsilon} + g\epsilon^{-2\beta \epsilon}}{1e^0 + 2e^{-\beta \epsilon} + 4e^{-2\beta \epsilon}} \\
&= \epsilon \left( \frac{2e^{-\beta \epsilon} + 8e^{-2\beta \epsilon}}{1 + 2e^{-\beta \epsilon} + 4e^{-2\beta \epsilon}} \right)
\end{aligned}$$

14. The free energy of a gas,  $N$  particles in a volume  $V$  and at a temperature  $T$  is

$$F = NK_B T \ln \left( \frac{a_0 V (H_B T)^{5/2}}{N} \right)$$

where  $a_0$  is a constant and  $k_B$  denotes the Boltzmann constant. The internal energy of a gas is

a.  $\frac{3}{2} N_B T$

b.  $\frac{5}{2} N K_B T$

c.  $N K_B T \ln \left[ \frac{a_0 V (K_B T)^{5/2}}{N} \right] - \frac{3}{2} N K_B T$

d.  $N K_B T \ln \left[ \frac{a_0 V}{(K_B T)^{5/2}} \right]$

**Solution:**

$$\begin{aligned}
F &= K_B T \ln \left[ \frac{a_0 V (K_B T)^{5/2}}{N} \right]^N \\
F &= K_B + \ln z
\end{aligned}$$

compare 1 and 2, we get

$$\begin{aligned}
\ln z &= -\ln \left[ \frac{a_0 V (K_B T)^{5/2}}{N} \right]^N \\
\langle u \rangle &= -\frac{\partial}{\partial \beta} \ln z = +K T^2 \frac{\partial}{\partial T} \ln z \\
\langle u \rangle &= N K_B T^2 \frac{\partial}{\partial T} \left( -\ln \left( \frac{a_0 V (K_B T)^{5/2}}{N} \right) \right) \\
&= N K_B T^2 \frac{\partial}{\partial T} \left[ -\ln T^{5/2} - \ln \left( \frac{a_0 V K_B}{N} \right) \right] \\
&= -\frac{5}{2} N K_B T^2 \times \frac{1}{T} \\
&= -\frac{5}{2} N K_B T
\end{aligned}$$

So the correct answer is **Option (b)**

15. A system has two energy levels with energies  $\epsilon$  and  $2\epsilon$ . The lower level is 4-fold degenerate while the upper level is double degenerate. If there are  $N$  non-interacting classical particles in the system, which is in thermodynamic equilibrium at a temperature  $T$ , the fraction of particles in the upper level is

a.  $\frac{1}{1 + e^{-\epsilon/k_B T}}$

b.  $\frac{1}{1 + 2e^{\epsilon/k_B T}}$

c.  $\frac{1}{2e^{\epsilon/k_B T} + 4e^{2\epsilon/k_B T}}$

d.  $\frac{1}{2e^{\epsilon/k_B T} + 4e^{2\epsilon/k_B T}}$



**Solution:**

$$E_1 = \varepsilon \quad g_1 = 4 \quad \text{fraction of particles in upper level}$$

$$E_2 = 2\varepsilon \quad g_2 = 2$$

$$P_2 = \frac{N_2}{N} = \frac{2e^{-2\beta\varepsilon}}{4e^{-\beta\varepsilon} + 2e^{-\beta\varepsilon}}$$

$$P_\theta = \frac{1}{2e^{\beta\varepsilon} + 1}$$

So the correct answer is **Option (b)**

16. A one dimension chain consists of a set of  $N$  rods each of length  $a$ . When stretched by a load, each rod can align either parallel or antiparallel to length. The energy of a rod is  $-\varepsilon$  when aligned parallel to length of the chain is  $+\varepsilon$  when perpendicular to it. When the chain is in thermal equilibrium at temperature  $T$  its average length is,

a.  $\frac{Na}{2}$

b.  $Na$

c.  $\frac{Na}{1+e^{2\beta\varepsilon}}$

d.  $\frac{Na}{1+e^{-\varepsilon/k_B T}}$

**Solution:**

$$\langle L \rangle = \sum_i L_i P_i$$

$$= \frac{NaP_{11} + 0 \cdot P_{\perp ar}}{P_{11} + P_{\perp}} = \frac{Na e^{\beta\varepsilon}}{e^{\beta\varepsilon} + e^{-\beta\varepsilon}}$$

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

So the correct answer is **Option (c)**

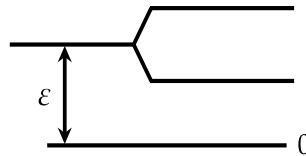
17. An atom has a non-degenerate ground state and a double degenerate excited state. The energy difference between the two states is  $\varepsilon$ . The specific heat at very low temperature ( $\beta\varepsilon \gg 1$ ) is given by

a.  $K_B(\beta\varepsilon)$

b.  $k_B e^{-\beta\varepsilon}$

c.  $2k_B(\beta\varepsilon)^2 e^{-\beta\varepsilon}$

d.  $K_B$

**Solution:**

$$z = 1e^{0\beta} + 2e^{-\beta\varepsilon}$$

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

$$\langle E \rangle = \frac{0 + 2\varepsilon e^{-\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon}} = \frac{2\varepsilon e^{-\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon}}$$

$$\begin{aligned}
C_V &= \left( \frac{\partial E}{\partial T} \right)_V & \beta &= \frac{1}{K_B T} \\
&= \frac{-1}{K_B T^2} \left( \frac{\partial E}{\partial \beta} \right)_V & \frac{\partial \beta}{\partial T} &= -\frac{1}{K_B T^2} \\
C_V &= -K_B \beta^2 \left( \frac{\partial E}{\partial \beta} \right)_V & \frac{1}{\partial T} &= -\frac{1}{K_B T^2} \frac{1}{\partial \beta} \\
c_V &= -k_B \beta^2 \frac{(1 + 2e^{-\beta \epsilon}) (-2\epsilon^2 e^{-\beta \epsilon}) - (2\epsilon e^{-\beta \epsilon}) (-2\epsilon e^{-\beta \epsilon})}{(1 + 2e^{-\beta \epsilon})^2} \\
c_V &= -k_B \beta^2 \left( -\frac{2\epsilon^2 e^{-\beta \epsilon}}{(1 + 2e^{-\beta \epsilon})^2} \right) \\
C_V &= 2k_B (\beta \epsilon)^2 e^{\beta \epsilon} \quad (\because \beta \epsilon \gg 1)
\end{aligned}$$

So the correct answer is **Option (c)**

18. Consider a system maintained at temperature  $T$ , with two available energy states  $E_1$  &  $E_2$  each with degeneracies  $g_1$  &  $g_2$ . If  $p_1$  &  $p_2$  are probabilities of occupancy of the energy states, what is the entropy of the system.

- a.**  $S = -K_B \left[ P_1 \ln \left( \frac{P_1}{g_1} \right) + P_2 \ln \left( \frac{P_2}{g_2} \right) \right]$ 
**b.**  $S = -K_B [P_1 \ln (P_1 g_1) + P_2 \ln (P_2 g_2)]$   
**c.**  $S = -K_B [P_1 \ln (p_1^{g_1}) + P_2 \ln (P_2 g_2)]$ 
**d.**  $s = -K_B \left[ \left( \frac{1}{P_1} \right) \ln \left( \frac{P_1}{g_1} \right) + \left( \frac{1}{P_2} \right) \ln \left( \frac{P_2}{g_2} \right) \right]$

**Solution:**

$$\begin{aligned}
S &= -K \sum_i P_i \ln \left( \frac{P_i}{g_i} \right) \\
s &= -k_B \left[ P_1 \ln \left( \frac{P_1}{g_1} \right) + P_2 \ln \left( \frac{P_2}{g_2} \right) \right]
\end{aligned}$$

So the correct answer is **Option (a)**



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