

# 5

## Closed System : Canonical Ensemble

### 5.1 What is a Closed System ?

A closed system is one which does not exchange material with the surroundings. However, it does exchange energy. It is in thermal contact with the surroundings. We idealize the surroundings as a "heat bath"<sup>1</sup>.

Thus, a closed system in thermal equilibrium, is characterized by  $T$ ,  $V$  and  $N$ . The system is not isolated. Hence its micro states are not all equally probable.

### 5.2 Toy Model à la H B Callen

Consider<sup>2</sup> a fair red die representing the system and two fair white dice representing the surroundings. A string of three numbers, each lying between 1 and 6 constitutes a micro state of the three dice system. There are  $6^3 = 216$  micro states and they are all equally probable<sup>3</sup>. In particular the system-dice (the red one) shall be in one of its six micro states with equal probability.

Let us now impose the condition that the three dice add to 6. Under this condition, let us enquire if the six micro states of the dice are equally probable.

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<sup>1</sup>A "heat bath" transacts energy with the system, but its temperature does not change.

<sup>2</sup>Herbert B Callen, *Thermodynamics and an Introduction to Thermostatistics*, Second Edition, Wiley (2006)

<sup>3</sup>All micro states are equally probable : Ergodicity.

Let  $P(k)$  denote the probability that the red die shows up  $k$  given the three dice add to 6. Because of the condition imposed, the red die can be in any one of the four states,  $\{1, 2, 3, 4\}$  only; and these four micro states are not equally probable. The probabilities can be calculated as follows.

We find that for the three-dice system, there are 10 micro states with the property that the three dice add to 6. These are listed in Table(1).

No.	W	R	W	No	W	R	W
1	1	1	4	6	2	2	2
2	2	1	3	7	3	2	1
3	3	1	2	8	1	3	2
4	4	1	1	9	2	3	1
5	1	2	3	10	1	4	1

The ten micro states are equally probable. These are the micro states of the universe - which consists of the system and its surroundings. The universe constitutes an isolated system.

Of these ten micro states of the universe, there are four micro states for which the system die shows up 1; therefore  $P(1) = 0.4$ . Similarly we can calculate the other probabilities :

$$P(2) = 0.3; P(3) = 0.2; P(4) = 0.1; P(5) = P(6) = 0.0$$

The important point is that the micro states of the system are not equally probable.

From the above toy model, we can say that if we consider the system and its surroundings together to constitute the universe and demand that the universe has a fixed energy, then the system will not be in its micro states with equal probability.

What is the probability of a micro state of a closed system ? We shall calculate the probability in the next section employing two different methods. The first involves Taylor expansion of  $S(E)$ . I learnt of this, from the book of Balescu<sup>4</sup>. The second is based on the method of most probable distribution, described in several books<sup>5</sup>.

<sup>4</sup>R Balescu, *Equilibrium and non-equilibrium statistical mechanics*, Wiley (1975).

<sup>5</sup>see e.g. R. K. Pathria, *Statistical Mechanics*, Second Edition Butterworth Heinemann (2001)p.45

## 5.3 Canonical Partition Function

### 5.3.1 Derivation à la Balescu

A closed system, its boundary and the bath - constitute the universe; the universe is an isolated system. We know for an isolated system, all micro states are equally probable. Let  $\mathcal{E}$  denote the energy of the universe. It remains a constant.

Now consider a particular micro state of the closed system. Let us label it as  $C$ . Let its energy be  $E(C)$ . Note that  $E(C) \ll \mathcal{E}$ . When the closed system is in its micro state  $C$ , the surroundings can be in any one of  $\hat{\Omega}(\mathcal{E} - E(C))$  micro states of the universe<sup>6</sup>.

For the universe, which is an isolated system, all the micro states are equally probable. Thus we can say that the probability of finding the closed system in its micro state  $C$  is given by,

$$P(C) = \frac{\hat{\Omega}(\mathcal{E} - E(C))}{\hat{\Omega}_t}, \quad (5.1)$$

where we have denoted the total number of micro states of the universe as  $\hat{\Omega}_t$ .

We have  $S(\mathcal{E} - E(C)) = k_B \ln \hat{\Omega}(\mathcal{E} - E(C))$ . Therefore

$$\hat{\Omega}(\mathcal{E} - E(C)) = \exp \left[ \frac{1}{k_B} S(\mathcal{E} - E(C)) \right]. \quad (5.2)$$

Also since  $E(C) \ll \mathcal{E}$ , we can Taylor expand  $S(\mathcal{E} - E(C))$  around  $\mathcal{E}$  retaining only the first two terms. We get,

$$\begin{aligned} S(\mathcal{E} - E(C)) &= S(\mathcal{E}) - E(C) \left( \frac{\partial S}{\partial E} \right)_{E=\mathcal{E}}, \\ &= S(\mathcal{E}) - \frac{1}{T} E(C). \end{aligned} \quad (5.3)$$

Substituting the above in the expression for  $P(C)$ , we get,

$$\begin{aligned} P(C) &= \frac{\exp [S(\mathcal{E})/k_B]}{\hat{\Omega}_t} \exp \left[ -\frac{E(C)}{k_B T} \right], \\ &= \alpha \exp [-\beta E(C)], \end{aligned} \quad (5.4)$$

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<sup>6</sup>I am considering that a micro state of the universe can be thought of as a simple juxtaposition of the micro state of closed system and the micro state of the surroundings. The system and the surroundings interact at the boundaries and hence there shall exist micro states of the isolated system which can not be neatly viewed as the system micro state juxtaposed with the surroundings micro state. Such micro states are so few in number we shall ignore them.

where  $\alpha$  is a constant and  $\beta = 1/(k_B T)$ . We can evaluate  $\alpha$  completely in terms of the properties of the closed system by the normalization condition for the probabilities, see below.

$$\sum_C P(C) = 1, \quad (5.5)$$

$$\alpha \sum_C \exp[-\beta E(C)] = 1, \quad (5.6)$$

$$Q(T, V, N) = \frac{1}{\alpha} = \sum_C \exp[-\beta E(C)]. \quad (5.7)$$

where  $Q(T, V, N)$  is called the **canonical partition function**.

### 5.3.2 Canonical Partition Function : Transform of Density of States

We start with

$$Q(\beta, V, N) = \sum_i \exp[-\beta E_i(V, N)], \quad (5.8)$$

where,  $\beta = 1/[k_B T]$ , and the sum runs over all the micro states of a closed system at temperature  $T$ , volume  $V$  and number of particles  $N$ . Let  $\hat{\Omega}(E, V, N)$  denote the density of (energy) states. In other words  $\hat{\Omega}(E, V, N)dE$  is the number of micro states having energy between  $E$  and  $E + dE$ . The canonical partition function, see Eq. (5.8), can be written as an integral over energy,

$$Q(\beta, V, N) = \int_0^\infty dE \hat{\Omega}(E, V, N) \exp[-\beta E(V, N)]. \quad (5.9)$$

We see that the canonical partition function is a 'transform' of the density of states. The "variable" energy is transformed to the "variable" temperature. The transform helps us go from a micro canonical (ensemble) description (of an isolated system) with independent variables  $E$ , ( $V$  and  $N$ ) to a canonical (ensemble) description (of a closed system) with independent variables  $T$ , ( $V$ , and  $N$ ). The density of states is a steeply increasing function of  $E$ . The exponential function  $\exp(-\beta E)$  decays with  $E$  for any finite value of  $\beta$ . The decay is steeper at higher value of  $\beta$  or equivalently at lower temperatures. The product shall be, in general, sharply peaked at a value of  $E$  determined by  $\beta$ .

When  $\beta$  is small (or temperature is large) the integrand would peak at a large value of  $E$ . When  $\beta$  is high (at low temperatures) it would peak at a low value of  $E$ .

## 5.4 Helmholtz Free Energy

The internal energy  $U$  of thermodynamics is obtained by averaging the statistical energy  $E$  over a canonical ensemble. A closed system will invariably be found with an energy  $U = \langle E \rangle$  but for extremely small (relative) fluctuations around  $U$ ; these fluctuations are proportional to the inverse of the square root of the number of molecules. Consider,

$$Q(\beta, V, N) = \int_0^\infty dE \hat{\Omega}(E, V, N) \exp[-\beta E(V, N)]. \quad (5.10)$$

In the above replace the integral over  $E$  by the value of the integrand, evaluated at  $E = \langle E \rangle = U$ . We get,

$$\begin{aligned} Q &= \hat{\Omega}(E = U, V, N) \exp(-\beta U) ; \ln Q = \ln \hat{\Omega}(U, V, N) - \beta U, \\ -k_B T \ln Q &= U - T k_B \ln \hat{\Omega}(U, V, N) \\ &= U - TS(U, V, N). \end{aligned} \quad (5.11)$$

We identify the right hand side of the above as (Helmholtz) free energy <sup>7</sup> :

$$F(T, V, N) = U - TS(U, V, N) ; \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V, N}. \quad (5.12)$$

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<sup>7</sup> Legendre Transform : Start with  $U(S, V, N)$ . Concentrate on the dependence of  $U$  on  $S$ . Can this dependence be described in an alternate but equivalent way ?

Take the slope of the curve  $U(S)$  at  $S$ . We have

$$T(S, V, N) = \left( \frac{\partial U}{\partial S} \right)_{V, N}.$$

We can plot  $T$  against  $S$ ; but then it will not uniquely correspond to the given curve  $U(S)$ . All parallel curves in the  $U$ - $S$  plane shall lead to the same  $T(S)$ . It is the intercept that will tell one curve from the other, in the family. Let us denote the intercept by the symbol  $F$ . We have

$$\frac{U(S, V, N) - F}{S} = T ; F(T, V, N) = U(S, V, N) - TS ; T = \left( \frac{\partial U}{\partial S} \right)_{V, N}.$$

The equation for micro canonical temperature, is inverted and entropy is expressed as a function of  $T$ ,  $V$ , and  $N$ . Employing the function  $S(T, V, N)$  we get  $U(T, V, N)$  and  $F(T, V, N)$ . The above is called Legendre transform.  $S$  transforms to 'slope'  $T$  and  $U(S)$  transforms to the intercept  $F(T)$ . We call  $F(T, V, N)$  as Helmholtz free energy.

Example: Consider  $U$  expressed as a function of  $S$ ,  $V$ , and  $N$  :

$$U(S, V, N) = \alpha \frac{S^3}{NV}.$$

Thus we get a relation between (the microscopic description enshrined in) the canonical partition function (of statistical mechanics) and (the macroscopic description given in terms of) (Helmholtz) free energy (of thermodynamics) :  $F(T, V, N) = -k_B T \ln Q(T, V, N)$ . Statistical mechanics aims to connect the micro world (of say atoms and molecules) to the macro world (of solids and liquids). In other words it helps you calculate the macroscopic properties of a system say a solid, in terms of the properties of its microscopic constituents (atoms and molecules) and their interactions.

Boltzmann started the game of statistical mechanics by first proposing a micro - macro connection for an isolated system, in the famous formula

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We get

$$T = \left( \frac{\partial U}{\partial S} \right)_{V,N} = \alpha \frac{3S^2}{NV} .$$

Inverting, we get,

$$S = \sqrt{\frac{NVT}{3\alpha}} .$$

We then get internal energy as a function of temperature,

$$U = \sqrt{\frac{NV}{3\alpha}} \left( \frac{T}{3} \right)^{3/2} .$$

The Helmholtz free energy is then expressed as

$$F = U - TS = -2 \left( \frac{NV}{\alpha} \right)^{1/2} \left( \frac{T}{3} \right)^{3/4} .$$

ENTHALPY :  $H(S, P, N)$ . Start with  $U(S, V, N)$ . Carry out the Legendre transform of  $V \rightarrow -P$  and  $U(S, V, N) \rightarrow H(S, P, N)$ .

$$H(S, P, N) = U + PV ; P = \left( \frac{\partial U}{\partial V} \right)_{S,N} .$$

GIBBS FREE ENERGY :  $G(T, P, N)$ . Start with  $U(S, V, N)$ . Transform  $S \rightarrow T$ ,  $V \rightarrow -P$ , and  $U \rightarrow G(T, P, N)$ .

$$G(S, P, N) = U - TS + PV ; T = \left( \frac{\partial U}{\partial S} \right)_{V,N} ; P = \left( \frac{\partial U}{\partial V} \right)_{S,N} .$$

GRAND POTENTIAL :  $\mathcal{G}(T, V, \mu)$ . Start with  $U(S, V, N)$ . Transform  $S \rightarrow T$ ,  $N \rightarrow \mu$ , and  $U \rightarrow \mathcal{G}(T, P, N)$ .

$$\mathcal{G}(T, V, \mu) = U - TS - \mu N , T = \left( \frac{\partial U}{\partial S} \right)_{V,N} , \mu = \left( \frac{\partial U}{\partial N} \right)_{S,N} .$$

engraved on his tomb:  $S = k_B \ln \hat{\Omega}$ . You will come across several micro-macro connections in this course on statistical mechanics. The formula,  $F(T, V, N) = -k_B T \ln Q(T, V, N)$ , provides another important micro - macro connection.

## 5.5 Energy Fluctuations and Heat Capacity

The average energy of a system is formally given by,  $\langle E \rangle = \sum_i E_i p_i$ , where  $p_i$  is the probability of the micro state  $i$  and  $E_i$  is the energy of the system when in micro state  $i$ . For a closed system,  $p_i = Q^{-1} \exp(-\beta E_i)$ , where  $Q(T, V, N)$  is the (canonical) partition function given by

$$Q = \sum_i \exp(-\beta E_i).$$

We have,

$$\begin{aligned} \langle E \rangle &= \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}, \\ &= \frac{1}{Q} \sum_i E_i \exp(-\beta E_i), \\ &= -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta}. \end{aligned} \quad (5.13)$$

We identify  $\langle E \rangle$  with the internal energy, usually denoted by the symbol  $U$  in thermodynamics.

We have,

$$U = -\frac{1}{Q} \frac{\partial Q}{\partial \beta}, \quad (5.14)$$

$$\left( \frac{\partial U}{\partial \beta} \right)_V = -\frac{1}{Q} \frac{\partial^2 Q}{\partial \beta^2} + \left( \frac{1}{Q} \frac{\partial Q}{\partial \beta} \right)^2 = -[\langle E^2 \rangle - \langle E \rangle^2] = -\sigma_E^2. \quad (5.15)$$

Now write,

$$\frac{\partial U}{\partial \beta} = \frac{\partial U}{\partial T} \times \frac{\partial T}{\partial \beta} = C_V (-k_B T^2). \quad (5.16)$$

We get the relation between the fluctuations of energy of an equilibrium system and the reversible heat required to raise the temperature of the system by one degree Kelvin :

$$\sigma_E^2 = k_B T^2 C_V. \quad (5.17)$$

The left hand side of the above equation represents the fluctuations of energy when the system is in equilibrium. The right hand side is about how the system would respond when you heat it<sup>8</sup>. Note  $C_V$  is the amount of reversible heat you have to supply to the system at constant volume to raise its temperature by one degree Kelvin. The equilibrium fluctuations in energy are related to the linear response; *i.e.* the response of the system to small perturbation<sup>9</sup>.

## 5.6 Canonical Partition Function : Ideal Gas

I shall derive an expression for the canonical partition function of an ideal gas of  $N$  molecules confined to a volume  $V$  and at temperature  $T$ . I shall do the derivation by a method that involves the density of states

We first derive an expression for the density of (energy) states, denoted by  $g(E)$  from micro canonical ensemble.  $g(E)dE$  is the number of micro states of an isolated system with energy between  $E$  and  $E + dE$ . Formally, we have

$$g(E) = \frac{\partial \hat{\Omega}}{\partial E} \quad (5.18)$$

$$\hat{\Omega} = \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m E)^{3N/2}}{\Gamma(\frac{3N}{2} + 1)}. \quad (5.19)$$

Therefore the density of (energy) states is given by,

$$\begin{aligned} g(E) = \frac{\partial \hat{\Omega}}{\partial E} &= \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m)^{3N/2}}{\Gamma(\frac{3N}{2} + 1)} \frac{3N}{2} E^{\frac{3N}{2}-1}, \\ &= \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m)^{3N/2}}{\Gamma(\frac{3N}{2})} E^{\frac{3N}{2}-1} \end{aligned} \quad (5.20)$$

where we have made use of the relation

$$\Gamma\left(\frac{3N}{2} + 1\right) = \left(\frac{3N}{2}\right) \Gamma\left(\frac{3N}{2}\right). \quad (5.21)$$

The partition function is obtained as a "transform" of the density of states where the variable  $E$  transformed to the variable  $\beta$ .

$$Q(\beta, V, N) = \frac{V^N}{N!} \frac{1}{h^{3N}} \frac{(2\pi m)^{3N/2}}{\Gamma(\frac{3N}{2})} \int_0^\infty dE \exp(-\beta E) E^{\frac{3N}{2}-1}. \quad (5.22)$$

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<sup>8</sup>Notice that  $\sigma^2$  is expressed in units of Joule<sup>2</sup>. The quantity  $k_B T^2$  is expressed in units of Joule-Kelvin.  $C_V$  is in Joule/Kelvin. Thus  $k_B T^2 C_V$  has units of Joule<sup>2</sup>.

<sup>9</sup>first order perturbation.



Consider the integral,

$$I = \int_0^\infty dE \exp(-\beta E) E^{\frac{3N}{2}-1}. \quad (5.23)$$

Let,

$$x = \beta E \text{ then } dx = \beta dE, \quad (5.24)$$

$$I = \frac{1}{\beta^{3N/2}} \int_0^\infty dx x^{\frac{3N}{2}-1} \exp(-x), \quad (5.25)$$

$$= \frac{\Gamma(\frac{3N}{2})}{\beta^{3N/2}}. \quad (5.26)$$

Substituting the above in the expression for the partition function we get,

$$Q(T, V, N) = \frac{V^N}{N!} \frac{1}{h^{3N}} (2\pi m k_B T)^{3N/2} = \frac{V^N}{N!} \frac{1}{\Lambda^{3N}}, \quad (5.27)$$

where

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}. \quad (5.28)$$

First check that  $\Lambda$  has the dimension of length.  $\Lambda$  is called thermal wavelength or quantum wavelength. It is approximately the de Broglie wavelength of a particle with energy  $p^2/2m = k_B T$ . We have  $p = \sqrt{2mk_B T}$ . Therefore

$$\Lambda = \frac{h}{p} = \frac{h}{\sqrt{2mk_B T}} \approx \frac{h}{\sqrt{2\pi m k_B T}}.$$

A wave packet can be constructed by superimposing plane waves of wavelengths in the neighbourhood of  $\Lambda$ . Thus a wave is spatially localized in a volume of the order of  $\Lambda^3$ . Consider a gas with number density  $\rho$ . The inter particle distance is of the order of  $\rho^{1/3}$ . Consider the situation  $\rho\Lambda^3 \ll 1$ . The particles are far apart. The wave packets do not overlap. Classical description will suffice. Quantum effects manifest when  $\rho\Lambda^3 \gg 1$ : when density is large and temperature is low.

## 5.7 Method of Most Probable Distribution

Let us now derive an expression for the canonical partition function employing the **method of most probable distribution**. Consider an isolated system

representing the universe. For convenience we imagine it to be a big cube. It contains molecules moving around here and there, hitting against each other and hitting against the wall. The universe is in equilibrium<sup>10</sup>. Let the temperature be  $T$ . The universe attains that temperature for which its entropy is maximum, under the constraints of energy, volume and number of particles, imposed on it.

Let us imagine that the universe, represented by a big cube, is divided into a set of small cubes of equal volumes by means of imaginary walls. Each cube represents a macroscopic part of the universe.

Each small cube is, in its own right, a macroscopic object with a volume  $V$ . Since the walls of a small cube permits molecules and energy to move across, the number of molecules in a cube, is not a constant. It shall fluctuate around a mean value; the fluctuations, however, are extremely small. What remains constant is the chemical potential,  $\mu$ .

The above observations hold good for energy also. Energy is not a constant. It fluctuates around a mean value; the fluctuations are small; what remains fixed is the temperature,  $T$ .

Let  $\mathcal{A}$  denote the number of cubes contained in the big cube.

The universe - the big cube, has a certain amount energy say  $\mathcal{E}$  and certain number of molecules  $\mathcal{N}$  and a certain volume  $\mathcal{V}$  and these quantities are constants.

You can immediately see that what we have is Gibbs' grand canonical ensemble of open systems : each small cube represents an open system. and is a member of a grand canonical ensemble. All the members are identical as far as their macroscopic properties are concerned. This is to say the volume  $V$ , the temperature  $T$  and chemical potential  $\mu$  are all the same for all the members.

Now, let us imagine that the walls are made impermeable to movement of molecules across. A cube **can not** exchange matter with its neighbouring cubes. Let us also assume that each cube contains exactly  $N$  molecules. However energy in a cube is not fixed. Energy can flow from one cube to its neighbouring cubes. This constitutes a canonical ensemble<sup>11</sup>.

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<sup>10</sup> Remember that an isolated system left to itself will eventually reach a state of equilibrium whence all its macroscopic properties are y unchanging with time; also a macroscopic (intensive) property shall be the same at all regions in the system.

<sup>11</sup> Usually, canonical ensemble is constructed by taking a system with a fixed value of  $V$  and  $N$  and assembling a large number of them in such a way that each is in thermal contact with its neighbours. Usually these are called mental copies of the system. The system and its mental copies are then isolated. The isolated system constitutes the universe. All the mental copies are identical macroscopically in the sense they all have the same value of  $T$ ,

Aim :

To find the probability for the closed system to be in **its** micro state  $i$ .

First, we list down all the micro states of the system. Let us denote the micro states as  $\{1, 2, \dots\}$ . Note that the macroscopic properties  $T$ ,  $V$ , and  $N$  are the same for all the micro states. In fact the system switches from one micro state to another, incessantly. Let  $E_i$  denote the energy of the system when it is in micro state  $i$ . The energy can vary from one micro state to another.

To each cube, we can attach an index  $i$ . The index  $i$  denotes the micro state of the closed system with fixed  $T$ ,  $V$  and  $N$ . An ordered set of  $\mathcal{A}$  indices uniquely specifies a micro state of the universe.

Let us take an example. Let the micro states of the closed system be denoted by the indices  $\{1, 2, 3\}$ . There are only three micro states. Let us represent the isolated system by a big square and construct nine small squares, each of which represents a member of the ensemble. Each square is attached with an index which can be 1, 2 or 3. Thus we have a micro state of the universe represented by

3	1	2
2	3	3
2	3	1

Table 5.1: A micro state with occupation number representation (2, 3, 4)

In the above micro state, there are two squares with index 1, three with index 2 and four with index 3. Let  $\{a_1 = 2, a_2 = 3, a_3 = 4\}$  be the occupation number string of the micro state. There are several micro states having the same occupation number string. I have given below a few of them.

Notice that all the micro states given above have the same occupation number string  $\{2, 3, 4\}$ . How many micro states are there with this occupation number string ? We have

$$\hat{\Omega}(2, 3, 4) = \frac{9!}{2!3!4!} = 1260 \quad (5.29)$$

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$V$  and  $N$ . Also other macroscopic properties defined as averages of a stochastic variable *e.g.* energy are also the same for all the mental copies. But these mental copies will often differ, one from the other, in their microscopic properties.

1	3	3
2	1	2
3	2	3

2	3	3
3	1	2
3	2	1

1	2	1
2	3	2
2	3	2

1	1	2
2	2	3
3	3	3

1	2	3
1	2	3
2	3	3

Table 5.2: A few micro states with the same occupation number representation of  $(2, 3, 4)$ . There are 1260 micro states with the same occupation number representation

I am not going to list all the 1260 of the microstates belonging to the occupation number string  $\{2, 3, 4\}$

Let me generalize and say that a string of occupation numbers is denoted by the symbol  $\tilde{a} = \{a_1, a_2, \dots\}$ , where  $a_1 + a_2 + \dots = \mathcal{A}$ . We also have an additional constraint namely  $a_1 E_1 + a_2 E_2 + \dots = \mathcal{E}$ .

Let  $\hat{\Omega}(\tilde{a}) = \hat{\Omega}(a_1, a_2, \dots)$  denote the number of micro states of the universe belonging to the string  $\tilde{a}$ . For a given string, we can define the probability for the closed system to be in its micro state indexed by  $i$  as

$$p_i(\tilde{a}) = \frac{a_i(\tilde{a})}{\mathcal{A}} \quad (5.30)$$

Note, the string  $\tilde{a} = \{a_1, a_2, \dots\}$  obeys the following constraints.

$$\sum_{i=1}^{\mathcal{A}} a_i(\tilde{a}) = \mathcal{A} \quad \forall \text{ strings } \tilde{a} \quad (5.31)$$

$$\sum_{i=1}^{\mathcal{A}} a_i(\tilde{a}) E_i = \mathcal{E} \quad \forall \text{ strings } \tilde{a} \quad (5.32)$$

Note that the value of  $p_i$  varies from one string to another. It is reasonable to obtain the average value of  $p_i$  over all possible strings  $\tilde{a}$ . We have

$$P_i = \sum_{\tilde{a}} \left( \frac{a_i(\tilde{a})}{\mathcal{A}} \right) \mathcal{P}(\tilde{a}) \quad (5.33)$$

where

$$\mathcal{P}(\tilde{a}) = \frac{\hat{\Omega}(\tilde{a})}{\sum_{\tilde{a}} \hat{\Omega}(\tilde{a})}. \quad (5.34)$$

We are able to write the above because all the elements of an an ensemble have the same probability given by inverse of the size of the ensemble. In the

above,

$$\hat{\Omega}(\tilde{a}) = \frac{\mathcal{A}!}{a_1!a_2!\dots}, \quad (5.35)$$

where we have used a simple notation  $a_i = a_i(\tilde{a}) \forall i = 1, 2, \dots$ .

Let us take a look at  $\hat{\Omega}(\tilde{a})$  for various strings  $\tilde{a}$ . For large  $\mathcal{A}$  the number  $\hat{\Omega}(\tilde{a})$  will be overwhelmingly large for a particular string, which we shall denote as  $\tilde{a}^*$ . We can ensure this by taking  $\mathcal{A} \rightarrow \infty$ . Note that  $\mathcal{A}$  should be large enough so that even a micro state of smallest probability is present in the ensemble atleast once.

Thus we can write

$$\begin{aligned} P_i &= \frac{a_i(\tilde{a}^*)}{\mathcal{A}} \frac{\hat{\Omega}(\tilde{a}^*)}{\hat{\Omega}(\tilde{a}^*)}, \\ &= \frac{a_i(\tilde{a}^*)}{\mathcal{A}}, \\ &= \frac{a_i^*}{\mathcal{A}} \end{aligned} \quad (5.36)$$

Thus the problem reduces to finding that string  $\tilde{a}^*$  for which  $\hat{\Omega}(\tilde{a})$  is a maximum. Of course there are two constraints on the string. They are

$$\sum_j a_j(\tilde{a}) = \mathcal{A} \forall \tilde{a}; \quad (5.37)$$

$$\sum_j a_j(\tilde{a}) E_j = \mathcal{E} \forall \tilde{a}. \quad (5.38)$$

We need to find the maximum (or minimum) of a function of a many variable under one or several constraints on the variables. In the above example there are two constraints. We shall tackle this problem employing the Lagrange method of undetermined multipliers and to this we turn our attention below.

## 5.8 Lagrange and his Method

Let me pose the problem through a simple example.

A mountain be described by  $h(x, y)$  where  $h$  is a function of the variable  $x$  and  $y$ .  $h$  is the elevation of the mountain at a point  $(x, y)$  on the plane.

I want to find out  $(x^*, y^*)$  at which  $h$  is maximum.

We write

$$dh = \frac{\partial h}{\partial x} dx + \frac{\partial h}{\partial y} dy = 0 \quad (5.39)$$

If  $dx$  and  $dy$  are independent then  $dh = 0$  if and only if

$$\frac{\partial h}{\partial x} = 0 \quad (5.40)$$

$$\frac{\partial h}{\partial y} = 0 \quad (5.41)$$

We have two equations and two unknowns. In principle we can solve the above two equations and obtain  $(x^*, y^*)$  at which  $h$  is maximum.

Now imagine there is a road on the mountain which does not necessarily pass through the peak of the mountain. If you are travelling on the road, then what is the highest point you will pass through ? In the equation

$$dh = \frac{\partial h}{\partial x} dx + \frac{\partial h}{\partial y} dy = 0 \quad (5.42)$$

the infinitesimals  $dx$  and  $dy$  are not independent. You can choose only one of them independently. The other is determined by the constraint which says that you have to be on the road.

Let the projection of the mountain-road on the plane be described by the curve

$$g(x, y) = 0.$$

This gives us a constraint

$$\frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial y} dy = 0 \quad (5.43)$$

From the above we get,

$$dy = -\frac{\left(\frac{\partial g}{\partial x}\right)}{\left(\frac{\partial g}{\partial y}\right)} dx \quad (5.44)$$

We then have,

$$dh = \frac{\partial h}{\partial x}dx + \frac{\partial h}{\partial y}dy = 0 \quad (5.45)$$

$$= \frac{\partial h}{\partial x}dx + \frac{\partial h}{\partial y} \left[ -\frac{\left(\frac{\partial g}{\partial x}\right)}{\left(\frac{\partial g}{\partial y}\right)} \right] dx = 0, \quad (5.46)$$

$$= \left[ \frac{\partial h}{\partial x} - \left\{ \frac{\left(\frac{\partial h}{\partial y}\right)}{\left(\frac{\partial g}{\partial y}\right)} \right\} \frac{\partial g}{\partial x} \right] dx = 0. \quad (5.47)$$

In the above  $dx$  is an arbitrary non-zero infinitesimal. Hence the above equality holds good if and only if the terms inside the square bracket is zero. We have,

$$\frac{\partial h}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0, \quad (5.48)$$

where we have set,

$$\lambda = \frac{\left(\frac{\partial h}{\partial y}\right)}{\left(\frac{\partial g}{\partial y}\right)}. \quad (5.49)$$

We have an equation similar to Eq. (5.48) involving partial derivative with respect to the variable  $y$ , which follows from the definition, see Eq. (5.49), of the Lagrange undetermined multiplier,  $\lambda$ .

Thus we have two independent equations,

$$\frac{\partial h}{\partial x} - \lambda \frac{\partial g}{\partial x} = 0, \quad (5.50)$$

$$\frac{\partial h}{\partial y} - \lambda \frac{\partial g}{\partial y} = 0. \quad (5.51)$$

We can solve and get  $x^* \equiv x^*(\lambda)$  and  $y^* = y^*(\lambda)$ . The value of  $x$  and  $y$  at which  $h(x, y)$  is maximum under constraint  $g(x, y) = 0$  can be found in terms of the unknown Lagrange multiplier  $\lambda$ .

Of course we can determine the value of  $\lambda$  by substituting the solution  $(x^*(\lambda), y^*(\lambda))$  in the constraint equation :  $g(x^*(\lambda), y^*(\lambda)) = 0$ .

## 5.9 Generalisation to $N$ Variables

Let  $f(x_1, x_2, \dots, x_N)$  be a function of  $N$  variables. The aim is to maximize  $f$  under one constraint  $g(x_1, x_2, \dots, x_N) = 0$ .

We start with

$$df = \sum_{i=1}^N \frac{\partial f}{\partial x_i} dx_i = 0 \quad (5.52)$$

for maximum. In the set  $\{dx_1, dx_2, \dots, dx_\mu, \dots, dx_N\}$ , not all are independent. They are related by the constraint

$$\sum_{i=1}^N \frac{\partial g}{\partial x_i} dx_i = 0 \quad (5.53)$$

We pick up one of the variable, say  $x_\mu$  and write

$$dx_\mu = - \sum_{i=1, i \neq \mu}^N \frac{\left( \frac{\partial g}{\partial x_i} \right)}{\left( \frac{\partial g}{\partial x_\mu} \right)} dx_i \quad (5.54)$$

Substitute the above in the expression for  $df$ . We get,

$$\sum_{i=1, i \neq \mu}^N \left[ \frac{\partial f}{\partial x_i} - \lambda \frac{\partial g}{\partial x_i} \right] dx_i = 0 \quad (5.55)$$

where

$$\lambda = \frac{\left( \frac{\partial f}{\partial x_\mu} \right)}{\left( \frac{\partial g}{\partial x_\mu} \right)} \quad (5.56)$$

There are only  $N - 1$  values of  $dx_i$ . We have eliminated  $dx_\mu$ . Instead we have the undetermined multiplier  $\lambda$ . Since  $dx_i : i = 1, N$  and  $i \neq \mu$  are all independent of each other we can set each term in the sum to zero. Therefore

$$\frac{\partial f}{\partial x_i} - \lambda \frac{\partial g}{\partial x_i} = 0 \quad \forall i \neq \mu \quad (5.57)$$

From the definition of  $\lambda$  we get

$$\frac{\partial f}{\partial x_\mu} - \lambda \frac{\partial g}{\partial x_\mu} = 0 \quad (5.58)$$

Thus we have a set of  $N$  equations

$$\frac{\partial f}{\partial x_i} - \lambda \frac{\partial g}{\partial x_i} = 0 \quad \forall i = 1, N \quad (5.59)$$



There are  $N$  equations and  $N$  unknowns. In principle we can solve the equation and get

$$x_i^* \equiv x_i^*(\lambda) \quad \forall i = 1, N,$$

where the function  $h$  is maximum under constraint

$$g(x_1, x_2, \dots, x_N) = 0.$$

The value of the undetermined multiplier  $\lambda$  can be obtained by substituting the solution in the constraint equation.

If we have more than one constraints we introduce separate Lagrange multipliers for each constraint. Let there be  $m \leq N$  constraints. Let these constraints be given by

$$g_i(x_1, x_2, \dots, x_N) = 0 \quad \forall i = 1, m.$$

We introduce  $m$  number of Lagrange multipliers,  $\lambda_i : i = 1, m$  and write

$$\frac{\partial f}{\partial x_i} - \lambda_1 \frac{\partial g_1}{\partial x_i} - \lambda_2 \frac{\partial g_2}{\partial x_i} \dots - \lambda_m \frac{\partial g_m}{\partial x_i} = 0 \quad \forall i = 1, N \quad (5.60)$$

where the  $m \leq N$ .

## 5.10 Derivation of Boltzmann Weight

Let us return to our problem of finding  $P_i$  - the probability that a closed equilibrium system (with macroscopic properties  $T, V, N$ ) will be found in its micro state  $i$  with energy  $E_i$ . Employing the method of most probable distribution, we have found that,

$$P_i = \frac{a_i^*}{\mathcal{A}} \quad (5.61)$$

where  $\mathcal{A}$  is the number of elements of the canonical ensemble and  $a_j^* = a_j(\tilde{a}^*)$ .

$\tilde{a}^*$  is that string for which  $\hat{\Omega}(\tilde{a})$  is maximum, under two constraints.

$$\hat{\Omega}(\tilde{a}) = \frac{\mathcal{A}!}{a_1! a_2! \dots} \quad (5.62)$$

The two constraints are

$$\sum_j a_j(\tilde{a}) = \mathcal{A} \quad (5.63)$$

$$\sum_j a_j(\tilde{a}) E_j = \mathcal{E} \quad (5.64)$$

We extremize entropy given by  $\ln \hat{\Omega}(\tilde{a})$ .

$$\ln \hat{\Omega}(a_1, a_2, \dots) = \ln \mathcal{A}! - \sum_j a_j \ln a_j + \sum_j a_j \quad (5.65)$$

We introduce two Lagrange multipliers  $\alpha$  and  $\beta$  and write

$$\begin{aligned} \frac{\partial \ln \hat{\Omega}(a_1, a_2, \dots)}{\partial a_i} &= \alpha \frac{\partial (a_1 + a_2 + \dots - \mathcal{A})}{\partial a_i} \\ &- \beta \frac{\partial (a_1 E_1 + a_2 E_2 + \dots - \mathcal{E})}{\partial a_i} = 0 \end{aligned} \quad (5.66)$$

Let  $a_j^*$  denote the solution of the above equation. We get,

$$-\ln a_j^* - \alpha - 1 - \beta E_j = 0 \quad \forall j = 1, 2, \dots \quad (5.67)$$

The above can be written in a convenient form

$$a_j^* = \gamma \exp(-\beta E_j) \quad (5.68)$$

where  $\gamma = \exp(-\alpha - 1)$ . We thus have,

$$P_j = \eta \exp(-\beta E_j)$$

where  $\eta = \gamma/\mathcal{A}$ .

Thus we get the probability that a closed system shall be found in its micro state  $j$  in terms of the constants  $\eta$  (which can be expressed as a function of the Lagrange multiplier  $\alpha$ ) and  $\beta$  (which is the Lagrange multiplier for the constraint on the total energy of the isolated system).

The task now is to evaluate the constants  $\eta$  and  $\beta$ . The constant  $\eta$  can be evaluated by imposing the normalization condition :  $\sum_j P_j = 1$ . The closed system has to be in one of its micro state with unit probability. Thus we have,

$$P_j = \frac{1}{Q} \exp(-\beta E_j) \quad (5.69)$$

$$Q(\beta, V, N) = \sum_j \exp(-\beta E_j) \quad (5.70)$$

We call  $Q$  the canonical partition function.

What is the nature of the Lagrange multiplier  $\beta$  ? On physical ground we identify

$$\beta = \frac{1}{k_B T}.$$

This we do by making a correspondence to thermodynamics. I shall refer you to

- Donald A McQuairrie, *Statistical Mechanics*, Harper and Row (1976)pp.35-44, for this.

## 5.11 Mechanical and Thermal Properties

In statistical mechanics, we have a random variable corresponding to a property *e.g.* energy,  $E$ . We take an average of this random variable over a canonical ensemble and denote it by  $\langle E \rangle$ . This quantity corresponds to the internal energy, usually denoted by the symbol  $U$ , of thermodynamics :  $U = \langle E \rangle$ . This establishes a micro-macro connection.

Energy of a closed system varies, in general, from one micro state to another. An equilibrium system visits a sequence of micro states dictated by Newtonian dynamics. Averaging over the visited microstates during the observation time gives us the time average. Instead, invoking 'ergodicity', we average over a Gibbs' ensemble and equate it to the thermodynamics property. Thus, energy averaged over a canonical ensemble, gives internal energy of thermodynamics, see below.

$$p_i = \frac{\exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \quad (5.71)$$

$$\langle E \rangle = \sum_i E_i p_i = \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)} \quad (5.72)$$

We are able to establish a connection between statistical mechanics and thermodynamics for a mechanical property like energy; notice energy is a 'private' property of a micro state; in other words I can attach a numerical value for the property called energy to each microstate. Hence we are able to average this property over a canonical ensemble and get the internal energy.

How do we calculate a thermal property like entropy ? First we notice, entropy is not a 'private' property of a micro state. We can not attach a numerical value for entropy to a microstate. Entropy is a "social" property or a 'collective' property. Hence entropy can not be easily calculated the way we calculated energy. For an isolated system, we could write an expression for entropy as  $S = k_B \ln \hat{\Omega}(E, V, N)$  since all the micro states are equally probable<sup>12</sup>

What is the expression for entropy of a closed system ? To this issue we turn our attention below.

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<sup>12</sup>The probability of a microstate in a micro canonical ensemble is  $p_i = 1/\hat{\Omega}(E, V, N) \forall i$ . Hence  $k_B \ln \hat{\Omega} = -k_B \sum_i p_i \ln p_i$

## 5.12 Entropy of a Closed System

Consider the expression  $-\sum_i p_i \ln p_i$  in the context of canonical ensemble. In an earlier lecture we talked of the number of micro states of an isolated system. The isolated system is constructed as follows : Assemble a large number of closed systems. Each closed system is in thermal contact with its neighbouring closed systems. Let  $\eta = \{i : i = 1, 2, \dots\}$  label the micro states of a closed system. Let  $\mathcal{A}$  denote the number of closed systems in the ensemble. The ensemble is isolated. We have thus an isolated system. We call it the universe. We describe a micro state of the universe by specifying the index  $i$  for each of its members. The index comes from the set  $\eta$  defined earlier. The micro states of the universe system are all equally probable; we group them and denote a group by specifying the string  $\{a_1, a_2, \dots\}$  where  $a_i$  is the number of elements of the ensemble, having the index  $i$ . We have

$$\hat{\Omega}(a_1, a_2, \dots) = \frac{\mathcal{A}!}{a_1! a_2! \dots} \quad (5.73)$$

The aim is to find  $\{a_i^* : i = 1, 2, \dots\}$  that maximizes  $\hat{\Omega}$ . For convenience we maximize  $\ln \hat{\Omega}$ . Let us consider the limit  $a_i \rightarrow \infty \forall i$ . Also consider the variables  $p_i = a_i/\mathcal{A}$ . Then

$$\ln \hat{\Omega} = \mathcal{A} \ln \mathcal{A} - \mathcal{A} - \sum_i a_i \ln a_i + \sum_i a_i \quad (5.74)$$

$$= \sum_i a_i \ln \mathcal{A} - \sum_i a_i \ln a_i \quad (5.75)$$

$$= - \sum_i a_i \ln \left( \frac{a_i}{\mathcal{A}} \right) \quad (5.76)$$

$$= -\mathcal{A} \sum_i p_i \ln p_i \quad (5.77)$$

$$\frac{\ln \hat{\Omega}}{\mathcal{A}} = - \sum_i p_i \ln p_i \quad (5.78)$$

The above is the entropy of one of the  $\mathcal{A}$  number of closed systems constituting the the universe. Thus,  $-\sum_i p_i \ln p_i$  provides a natural formula for the entropy of a system whose micro states are not equi-probable.

Physicists would prefer to measure entropy in units of Joules per Kelvin. For, that is what they have learnt from Clausius, who defined

$$dS = \frac{q}{T},$$

where  $dS$  is the entropy gained by a system when it receives an energy of  $q$  Joules by heat in a reversible process at a constant temperature of  $T$  Kelvin. Hence we define,

$$S = -k_B \sum_i p_i \ln p_i. \quad (5.79)$$

This expression for entropy is natural for a closed system described by a canonical ensemble. We call it Boltzmann-Gibbs-Shannon entropy.

### 5.13 Microscopic View : Heat and Work

The thermodynamic energy  $U$  is identified with statistical energy  $E$  averaged over a suitable Gibbs' ensemble. We use micro canonical ensemble for isolated system, canonical ensemble for closed system, and grand canonical ensemble for open system. Let  $p_i : i = 1, 2, \dots$  denote formally an ensemble.  $p_i$  is the probability of a micro state of the system under consideration.

For example if the system is isolated, then all micro states are equally probable. We simply count the number of micro states of the system; let us say there are  $\hat{\Omega}$  micro states. Inverse of this shall be the probability of a micro state.

For an isolated system  $p_i = 1/\hat{\Omega}$ .

For a closed system,  $p_i = \frac{1}{Q} \exp(-\beta E_i)$ .

For an open system  $p_i = \frac{1}{Q} \exp(-\beta E_i + \beta \mu N_i)$

We can write, in general,  $U = \sum_i p_i E_i$ . This equation suggests that the internal energy of a closed system can be changed by two ways.

1. change  $\{E_i : i = 1, 2, \dots\}$  keeping  $\{p_i : i = 1, 2, \dots\}$  the same. This we call as work. Note that the energy eigenvalue change when we change the boundary condition, *i.e.* when we move the boundary thereby changing the volume.
2. change  $\{p_i : i = 1, 2, \dots\}$  keeping  $\{E_i : i = 1, 2, \dots\}$  the same. The changes in  $p_i$  should be done in such way that  $\sum_i p_i = 1$ . This we call as heat.

Thus we have,

$$dU = \sum_i p_i dE_i + \sum_i^* E_i dp_i \quad (5.80)$$

where the superscript  $*$  in the second sum should remind us that all  $dp_i$ s are not independent and that they should add to zero.

In the first sum we change  $E_i$  by  $dE_i \forall i$  keeping  $p_i \forall i$  unchanged.

In the second sum we change  $p_i$  by  $dp_i \forall i$  keeping  $E_i$  unchanged for all  $i$  and ensuring  $\sum_i dp_i = 0$ .

### 5.13.1 Work in Statistical Mechanics : $W = \sum_i p_i dE_i$

We have

$$\begin{aligned}
 \sum_i p_i dE_i &= \sum_i p_i \frac{\partial E_i}{\partial V} dV \\
 &= \frac{\partial (\sum_i p_i E_i)}{\partial V} dV \\
 &= \frac{\partial \langle E \rangle}{\partial V} dV \\
 &= \frac{\partial U}{\partial V} dV \\
 &= -PdV = W
 \end{aligned} \tag{5.81}$$

### 5.13.2 Heat in Statistical Mechanics : $q = \sum_i E_i dp_i$

#### Method-1

We start with the first term on the right hand side of Eq. (5.80).

$$S = -k_B \sum_i p_i \ln p_i, \tag{5.82}$$

$$dS = -k_B \sum_i^* [1 + \ln p_i] dp_i, \tag{5.83}$$

$$TdS = \delta q = -k_B T \sum_i^* \ln p_i dp_i, \tag{5.84}$$

$$= -k_B T \sum_i^* [-\beta E_i - \ln Q] dp_i \text{ since } p_i = \frac{e^{-\beta E_i}}{Q} \tag{5.85}$$

$$= \sum_i^* E_i dp_i \tag{5.86}$$

Method-2

Alternately, we recognize that change of entropy is brought about by change of probabilities of microstates and *vice versa*, keeping their respective energies the same. Thus,

$$\sum_i E_i dp_i = \sum_i E_i \frac{\partial p_i}{\partial S} dS \quad (5.87)$$

$$= \frac{\partial (\sum_i E_i p_i)}{\partial S} dS = \frac{\partial \langle E \rangle}{\partial S} dS = \frac{\partial U}{\partial S} dS = T dS = q \quad (5.88)$$

## 5.14 Adiabatic Process - a Microscopic View

In an adiabatic process, the system does not transact energy by heat. Hence the probabilities  $\{p_i\}$  of the micro states do not change during an adiabatic process. The only way the internal energy can change is through change of  $\{\epsilon_i : i = 1, 2, \dots\}$ . For a particle confined to a box, quantum mechanics tells us that the energy eigenvalue is inversely proportional to the square of the length of the box.

$$\epsilon_i \sim \frac{1}{L^2} \quad (5.89)$$

$$\sim V^{-2/3} \quad (5.90)$$

$$\frac{\partial \epsilon_i}{\partial V} \sim V^{-5/3} \quad (5.91)$$

First law of thermodynamics tells us  $dU = \delta Q + \delta W$ ; For an adiabatic process  $\delta Q = 0$ ; if the process is reversible then  $\delta W = -PdV$ . Thus, for an adiabatic process  $dU = -PdV$ . Therefore,

$$dU = \sum_i p_i \frac{\partial \epsilon_i}{\partial V} dV \quad (5.92)$$

$$-PdV \sim V^{-5/3} dV \quad (5.93)$$

$$PV^{5/3} = \Theta, \text{ a constant.} \quad (5.94)$$

## 5.15 Ideal Gas

I shall derive an expression for the canonical partition function of an ideal gas of  $N$  molecules confined to a volume  $V$  and at temperature  $T$ .

Formally the partition function is given by,

$$Q(T, V, N) = \frac{V^N}{N!} \frac{1}{h^{3N}} \int_{-\infty}^{+\infty} dp_1 \int_{-\infty}^{+\infty} dp_2 \cdots \cdots \int_{-\infty}^{+\infty} dp_{3N} \exp \left[ -\frac{\beta}{2m} (p_1^2 + p_2^2 \cdots + p_{3N}^2) \right] \quad (5.95)$$

$$= \frac{V^N}{N!} \frac{1}{h^{3N}} \left[ \int_{-\infty}^{+\infty} dp \exp \left( -\frac{\beta}{2m} p^2 \right) \right]^{3N} \quad (5.96)$$

$$= \frac{V^N}{N!} \frac{1}{h^{3N}} \left[ \int_{-\infty}^{+\infty} dp \exp \left( -\frac{1}{2} \frac{p^2}{mk_B T} \right) \right]^{3N} \quad (5.97)$$

Consider the integral

$$I = \int_{-\infty}^{+\infty} dp \exp \left( -\frac{1}{2} \frac{p^2}{mk_B T} \right) \quad (5.98)$$

since the integrand is an even function, we can write the above as

$$I = 2 \int_0^{+\infty} dp \exp \left( -\frac{1}{2} \frac{p^2}{mk_B T} \right) \quad (5.99)$$

Let

$$x = \frac{p^2}{2mk_B T} \quad (5.100)$$

Therefore,

$$dx = \frac{p}{mk_B T} dp \quad (5.101)$$

$$dp = \sqrt{\frac{mk_B T}{2}} \frac{1}{x^{1/2}} dx \quad (5.102)$$



The integral can now expressed as

$$\begin{aligned}
 I &= \sqrt{2mk_B T} \int_0^\infty dx x^{-1/2} \exp(-x) \\
 &= \sqrt{2mk_B T} \int_0^\infty dx x^{(1/2)-1} \exp(-x) \\
 &= \sqrt{2mk_B T} \Gamma\left(\frac{1}{2}\right) \\
 &= \sqrt{2\pi mk_B T} \quad \text{since } \Gamma(1/2) = \sqrt{\pi}
 \end{aligned} \tag{5.103}$$

The canonical partition function is thus given by,

$$Q(\beta, V, N) = \frac{V^N}{N!} \frac{1}{h^{3N}} (2\pi mk_B T)^{3N/2} \tag{5.104}$$

We write the above as

$$Q(T, V, N) = \frac{V^N}{N!} \frac{1}{\Lambda^{3N}} \tag{5.105}$$

$$\Lambda(T) = \frac{h}{\sqrt{2\pi mk_B T}}. \tag{5.106}$$

### 5.15.1 Energy

$$\ln Q = N \ln\left(\frac{V}{N}\right) + N - 3N \ln(\Lambda) \tag{5.107}$$

$$-\langle E \rangle = \frac{\partial \ln Q}{\partial \beta} = -3N \frac{\partial \ln \Lambda}{\partial \beta} \tag{5.108}$$

$$\ln \Lambda = \ln(h/\sqrt{2\pi m}) + (1/2) \ln \beta \tag{5.109}$$

$$U = \langle E \rangle = \frac{3Nk_B T}{2} \tag{5.110}$$

The above shows that energy is equi-partitioned amongst the  $3N$  degrees of freedom; each degree of freedom carries  $k_B T/2$  of energy.

### 5.15.2 Heat capacity

The heat capacity is given by

$$C_V = \frac{\partial U}{\partial T} = \frac{3Nk_B}{2}$$

We have  $nR = Nk_B$ , where  $n$  is the number of moles and  $R$  the universal gas constant. Thus heat capacity per mole of the substance - the so-called molar specific heat is given by,

$$\frac{C_V}{n} = \frac{3R}{2} \quad (5.111)$$

$R = 8.315 \text{ joule } (mol)^{-1} \text{ kelvin}^{-1} = 1.9873 \text{ Calories } (mol)^{-1} \text{ kelvin}^{-1}$ ;  $3R/2 = 2.9809 \approx \text{calories } (mol)^{-1} \text{ kelvin}^{-1}$ . The heat capacity is independent of temperature.

### 5.15.3 Entropy

The entropy of an ideal gas is obtained from the following relation:

$$S = \frac{U - F}{T} \quad (5.112)$$

where,

$$U = \frac{3Nk_B T}{2} \quad (5.113)$$

$$F = -k_B T \ln Q \quad (5.114)$$

We get,

$$S(\Lambda, V, N) = \frac{5Nk_B}{2} + Nk_B \ln \left( \frac{V}{N} \right) - 3Nk_B \ln \Lambda \quad (5.115)$$

Substituting in the above the expression for  $\Lambda$  we get,

$$S(T, V, N) = Nk_B \left[ \ln \left( \frac{V}{N} \right) + \frac{3}{2} \ln \left( \frac{2\pi m k_B T}{h^2} \right) + \frac{5}{2} \right] \quad (5.116)$$

In the above if we replace  $T$  by  $E$  employing the relation  $E = 3Nk_B/2$ , we get an expression for entropy consistent with the Sackur-Tetrode equation, see Section 4.14.

### 5.15.4 Canonical Ensemble Formalism and Adiabatic Process

For a fixed  $N$ , change in entropy can be brought about by changing temperature and / or volume. We have,

$$dS = \left( \frac{\partial S}{\partial V} \right)_{T,N} dV + \left( \frac{\partial S}{\partial T} \right)_{V,N} dT \quad (5.117)$$

$$= Nk_B \left[ \frac{dV}{V} + \frac{3}{2} \frac{dT}{T} \right] \quad (5.118)$$

In an quasi-static reversible adiabatic process,  $dS = 0$ . Therefore for a reversible adiabat,

$$\frac{dV}{V} + \frac{3}{2} \frac{dT}{T} = 0 \quad (5.119)$$

$$\ln V + \ln T^{3/2} = \Theta \quad (\text{a constant}) \quad (5.120)$$

$$VT^{3/2} = \Theta_1 \quad (5.121)$$

$$TV^{2/3} = \Theta_2 \quad (5.122)$$

For an ideal gas  $PV = Nk_B T$ . Eliminating  $T$  in favour of  $P$  and  $V$ , we get the familiar expression  $PV^\gamma$  with  $\gamma = 5/3$ , that describes an adiabatic process in an ideal gas containing mono-atomic spherically symmetric molecules.