

## 0.1 Required Classical Mechanics

The subject of statistical mechanics deals with macroscopic (large sized systems consisting of  $10^{23}$  particles) systems. As a result, they have a huge number of degrees of freedom. These degrees of freedom evolve obeying Newton's laws of motion, when we are considering a classical statistical mechanical system. These systems have a very large number of micro-states defined by the position coordinates and the momenta of each particle making up the system. All the micro-states which are consistent to an externally imposed constraint (like constant energy of the system when it is isolated from the rest of the universe) actually makes the macro-state of the system. The equilibrium situation which we will be concerned with in the present course requires that the probability distribution of the system over these accessible (consistent with the constraint) micro-states is stationary over time.

### 0.1.1 Hamilton's equations

Considering a system of  $N$  particles ( $N \sim 10^{23}$ ), the  $3N$  position coordinates of the system are denoted by  $q_i$ s, where the suffix  $i$  runs over  $1-3N$ , and the  $3N$  momenta  $p_i$ s. We consider here the system consisting of particles which do not have other degrees of freedom than translations. These  $6N$  coordinates at a time  $t$  (actually within an interval  $\Delta t$  at the instant  $t$  where  $\Delta t$  is arbitrarily small) defines the micro-state of the system at that time  $t$ . So, to look at the evolution of the micro-state we will consider the  $6N$  Hamilton's equations of the system

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (1)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad (2)$$

where the dot indicates derivative with respect to time. The Hamiltonian is a function of  $p_i$  and  $q_i$  and gives the total energy ( $T+V$ ) of the system in a micro-state. The existence of the Hamilton's equations makes the Hamiltonian stationary in this case i.e.  $\frac{dH}{dt} = 0$ .

- Prove that the Hamilton's equations conserve the Hamiltonian when it is not an explicit function of time i.e.  $\frac{dH}{dt} = 0$ .

## 0.1.2 Liouville's Equation

The micro-state of a system of  $N$  particles can be represented by a point in a  $6N$  dimensional space. The position vector to this phase point  $\mathbf{X}$  has  $6N$  coordinates (in  $p_i$  and  $q_i$ ) and thus, has all the information about the micro-state under consideration. This space is called the phase space or the  $\Gamma$ -space of the system.

Let us consider the density of the phase points at  $\mathbf{X}$  in the  $\Gamma$ -space is given by  $f(\mathbf{X}, t)$ . This  $f(\mathbf{X}, t)$  gives a measure of the probability of the system to be at the micro-state  $\mathbf{X}$ , since, having more phase point around the point at  $\mathbf{X}$  enhances the possibility of the system to visit this point more often keeping the system at its neighbourhood for relatively longer time. The velocity of the phase points at  $\mathbf{X}$  is  $\dot{\mathbf{X}}$  (remember that the system evolves according to the Hamilton's equations and one can move along a trajectory passing through the phase point  $\mathbf{X}$  given by this dynamics). The elementary flux through a surface area  $d\mathbf{s}$  at  $\mathbf{X}$  is  $d\mathbf{F} = d\mathbf{s} \cdot (\dot{\mathbf{X}}f(\mathbf{X}, t))$ . The total flux (outward by convention) through an arbitrary closed surface  $S$  enclosing the volume  $V$  is

$$F = \int d\mathbf{F} = \int_S d\mathbf{s} \cdot (\dot{\mathbf{X}}f(\mathbf{X}, t)). \quad (3)$$

This flux has to match the time rate of decrease of the total phase points inside the volume  $V$  which is  $\frac{\partial}{\partial t} \int_V dv_X f(\mathbf{X}, t)$ . Equating these two quantities and applying the Gauss's theorem  $\int_S d\mathbf{s} \cdot \mathbf{A} = \int_V dv \nabla \cdot \mathbf{A}$  for an arbitrary vector field  $\mathbf{A}$

$$\int_V dv_X \left( \frac{\partial f}{\partial t} + \nabla \cdot \dot{\mathbf{X}}f \right) = 0. \quad (4)$$

Since, the integration is over arbitrary volume, the integrand must vanish to make the relationship hold good for all  $V$  and that gives

$$\frac{\partial f}{\partial t} + \nabla \cdot \dot{\mathbf{X}}f = 0. \quad (5)$$

Now,  $\nabla \cdot \dot{\mathbf{X}}f = f\nabla \cdot \dot{\mathbf{X}} + \dot{\mathbf{X}} \cdot \nabla f$  and it can be shown that  $\nabla \cdot \dot{\mathbf{X}} = 0$  when the components of  $\mathbf{X}$  evolves according to Hamilton's equations. This divergence less flow is a signature of a Hamiltonian system and it can also be shown from the consideration of a divergence less flow that the phase space volume of such a Hamiltonian system remains conserved over time. Imagine that a phase space volume  $dv_X$  is evolving in time along the trajectory of the phase points in it towards its later configuration  $dv_X^f$ . The divergence free

velocity field of the phase points motion ensures that  $dv_X = dv_X^f$ . Contrary to the Hamiltonian systems, in dissipative systems the phase space volume can change and that is why in dissipative dynamical systems we talk about the attractors in phase space which can be nodes, limit cycles or strange attractors to which an initial volume of the phase space (basin of attraction) converges to (by getting contracted) at large time.

- Show that  $\nabla \cdot \dot{\mathbf{X}} = 0$  when the system evolves along a Hamiltonian trajectory.

Thus, the Liouville's equation for the hamiltonian flow is

$$\frac{\partial f}{\partial t} + \dot{\mathbf{X}} \cdot \nabla f = 0. \quad (6)$$

### 0.1.3 Equilibrium and Ensemble

The equilibrium of the system demands no explicit time dependence of the phase space density. Considering  $\frac{\partial f}{\partial t} = 0$  modifies eq.6 as  $\dot{\mathbf{X}} \cdot \nabla f = 0$  which can be rewritten in the form of Poisson's bracket as  $\{f, H\} = 0$ . Poisson's bracket of two functions A and B of  $p_i$  and  $q_i$  is the expression

$$\{A, B\} = \sum_i \left( \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right) \quad (7)$$

- Prove that  $\dot{\mathbf{X}} \cdot \nabla f = \{f, H\}$

The relation  $\{f, H\} = 0$  ensures that  $f = f(H(q_i, p_i))$ . So, in the context of equilibrium statistical mechanics we would always get the probability distribution over the micro-states as a function of the hamiltonian. While the probability of the system to be at a micro-state is given by  $f(H)$ ,  $\int_V dv_X f(H) = Z$  over the whole accessible phase space is called the partition function and the average of any quantity A is given as

$$\langle A \rangle = \frac{\int_V dv_X A f(H)}{Z} \quad (8)$$

which indicates that the average would not change even if  $f(H) = C f(H)$  where C is an arbitrary constant.

At equilibrium, the system under consideration generally satisfies certain macroscopic constraints like the total energy of the system is a constant or the

temperature of the system is constant etc. which actually defines the macro-state. The stationarity of the probability distribution over the phase space  $f(H)$  ensures that if we prepare a large number of similar systems, called an ensemble, which are subject to the same macroscopic constraint, then, the micro-states of these systems at an instant of time will be distributed over the phase space according to the probability distribution on it. Thus, averaging over these collection of systems at an instant is equivalent to time averaging over a larger period of time, since, given that time the system would visit all the points in phase space where the ensemble is sitting at an instant in accordance with the same probability distribution.

## 0.2 Micro-canonical Ensemble

In micro-canonical ensemble we consider an isolated system. The relevant constraint on the system is its total energy  $E$  which is practically a constant due to lack of interactions and we generally take the energy to remain within a very small range  $\delta E$  at  $E$  so that  $E \leq H(p_i, q_i) \leq (E + \delta E)$ . Let us have an estimate of the phase space volume accessible to a system of  $N$  non interacting classical particles. If we consider that all of those  $N$  particles are identical then a transformation that exchanges the positions of any pair of particles will produce a new phase point in the  $\Gamma$ -space (because particle identifying indices are included in the suffix of  $ps$  and  $qs$ ), but the actual micro-state will be identical to the previous one. Consequently, we actually have to alter the phase space density  $f(H)$  to  $f(H) = C' \frac{f(H)}{N!}$  to correct the over counting of the actual micro-states<sup>1</sup>. Here  $C'$  is an arbitrary constant taking care of all other relevant things.

The probability distribution function for micro-canonical ensemble we consider is in the form  $f(H) = C\delta(E - H)$  where  $\delta(E - H)$  is a Dirac delta function and the  $N!$  term has been absorbed in the new constant  $C$ . We want to find the partition function of an isolated system of classical particles which

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<sup>1</sup>The  $N!$  takes care of so called Gibb's Paradox (see Pathria)

are non interacting (classical ideal gas).

$$\begin{aligned}
Z &= C \int dv_X \delta(E - H(p, q)) \\
&= C \int \prod_{i=1}^{3N} dq_i \prod_{j=1}^{3N} dp_j \delta(E - H(p_j, q_i)) \\
&= CV^N \int_{R=2m\sqrt{E}} \prod_{j=1}^{3N-1} dp'_j. \tag{9}
\end{aligned}$$

In the above expression  $V$  is the volume of the container and the volume term originates from the integration over  $q_i$ s. Since, the constraint here is on the kinetic energy (potential energy is zero by consideration), the constraint will actually be felt on the momentum space. The removal of the delta function from the integral is justified by adjustment of the integration limits which takes care of the energy constancy. To do that we have moved to a coordinate system which is a spherical polar analogue of 3-D in 3N-D and the radial coordinate of such a system  $R$  will be given generally as  $R^2 = \sum_{j=1}^{3N} p_j^2$ . But,  $E = \frac{\sum_{j=1}^{3N} p_j^2}{2m}$  where  $m$  is the mass of each particle, readily produces the radius of the constant energy surface  $R = 2m\sqrt{E}$  on which all the momentum micro-states of the system should fall. A 'r' to the  $p_j$  coordinates in the last line of eq.9 indicates that they are now different coordinates (angle like) than those in the previous line. So, the result of the remaining integration in the eq.9 is the surface area of the (3N-1) dimensional sphere. General formula for the surface area of an n-1 dimensional sphere is  $A_n = 2 \frac{\pi^{n/2}}{\Gamma(n/2)} R^{(n-1)}$ . So, in the present case the value of the momentum integral is  $2 \frac{\pi^{3N/2}}{\Gamma(3N/2)} (2m)^{3N-1} E^{\frac{3N-1}{2}}$ .

$$Z = CV^N (2m)^{3N-1} E^{\frac{3N-1}{2}} \tag{10}$$

where all the constants have now been absorbed in the constant  $C$ .

Let us look at the calculation of the partition function more closely. It involved calculating the accessible phase space volume  $\Omega$  to the system under consideration and  $Z$  is actually proportional to the  $\Omega$ . The constant of proportionality which enters via the presence of  $C$  is at most a function of the particle number  $N$  and not of  $E$  and  $V$ . So, from the calculation of  $Z$  we can easily conclude that  $\Omega = \Omega(E, V, N)$ . A measure of entropy due to Boltzmann is  $S = k_B \log(\Omega)$  where  $k_B$  is Boltzmann constant which has a

value  $1.38 \times 10^{-16}$  erg/K. This definition of entropy is a bridge between the microscopic and the macroscopic domains and using this definition we can actually get to the macroscopic thermodynamic relations from the knowledge of the microscopic evolution of the system.

$\Omega$  being a function of E, N and V makes S a function of the same variables in the micro-canonical case. Consider a variation of S

$$dS = \left( \frac{\partial S}{\partial E} \right)_{V,N} \delta E + \left( \frac{\partial S}{\partial V} \right)_{N,E} \delta V + \left( \frac{\partial S}{\partial N} \right)_{E,V} \delta N. \quad (11)$$

The conservation of energy requires the increase in energy of a system  $\delta E$  be equal to the amount of heat given to it  $\delta Q$  and the work done on it  $\delta W$ . Thermodynamic definition of entropy gives us  $\delta Q = TdS$  where T is the temperature of the system.  $\delta W = -P\delta V + \mu\delta N$ , where  $-P\delta V$  is the work done on the system and  $\mu\delta N$  is the work done on the system by addition of particles where  $\mu$  is the chemical potential of the system. Thus, the conservation of energy expresses the increment in entropy as

$$dS = \left( \frac{1}{T} \right) \delta E + \left( \frac{P}{T} \right) \delta V - \left( \frac{\mu}{T} \right) \delta N. \quad (12)$$

Equating the coefficients of Eq.11 and Eq.12 we get the thermodynamic relations as

$$\begin{aligned} \left( \frac{\partial S}{\partial E} \right)_{V,N} &= \frac{1}{T} \\ \left( \frac{\partial S}{\partial V} \right)_{N,E} &= \frac{P}{T} \\ \left( \frac{\partial S}{\partial N} \right)_{E,V} &= -\frac{\mu}{T} \end{aligned}$$

Its interesting to note that  $\Omega$  being the phase space volume of the system in  $6N-1$  dimensional space (constant energy constraint  $H = E$  reduces one dimension) is actually a constant energy surface (spherical since R is a function of E) in  $3N$  dimensions. Now, consider that  $E \leq H \leq (E + \Delta)$ . In this case, the phase volume accessible to the system (spatial part is fixed by fixing the volume of the system) falls within the annular region between the two constant-energy surfaces giving us

$$\Omega \times \Delta = \Sigma(E + \Delta) - \Sigma(E) \quad (13)$$

where  $\Sigma(E)$  is the phase volume accessible to the system for all energies less than equal to  $E$ . Now, taking the limit  $\Delta \rightarrow 0$ ,  $\Omega$  is recognized as the density of states at the energy  $E$  with an expression  $\Omega = \frac{\partial \Sigma(E)}{\partial E}$ . Since,  $\log(\Omega)$  differs from  $\log(\Sigma(E))$  by an additive function of  $N$  the definition of the entropy as  $S = k_B \log(\Sigma)$  is equivalent to that with respect to  $\Omega$ . Both of these entropies give the same temperature and retains the extensive property of it.

- Show that  $\log(\Omega)$  differs from  $\log(\Sigma(E))$  by an additive function of  $N$  in the case of classical ideal gas.

### 0.2.1 Micro-canonical derivation of virial theorem

The mathematical statement of the virial theorem states that  $\langle x_i \frac{\partial H}{\partial x_j} \rangle = \delta_{ij} k_B T$ . The average here is done on micro-canonical ensemble

$$\begin{aligned}
\langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{1}{\Omega} \int \prod_i dp_i dq_i \left( x_i \frac{\partial H}{\partial x_j} \right) \delta(E - H) \\
&= \frac{1}{\Omega} \frac{\partial}{\partial E} \int_{H < E} \prod_i dp_i dq_i \left( x_i \frac{\partial H}{\partial x_j} \right) \\
&= \frac{1}{\Omega} \frac{\partial}{\partial E} \int_{H < E} \prod_i dp_i dq_i \left( \frac{\partial x_i (H - E)}{\partial x_j} - \delta_{ij} (H - E) \right) \\
&= \frac{1}{\Omega} \frac{\partial}{\partial E} \left( \int_{H \sim E}^{surface} dp'_i dq'_i x_i (H - E) - \int_{H < E} \prod_i dp_i dq_i \delta_{ij} (H - E) \right)
\end{aligned} \tag{14}$$

In the last line of the above expressions, the first integral is now the one which is an integration over the surface of  $6N-1$  dimensions. This we get by integrating over the  $x_j$  coordinate on a spherical polar frame and the rest of the coordinates are now like angles (effectively) which define the constant energy surface  $(H - E)$ . The prime on the coordinates  $p_i$  and  $q_i$  actually indicates of the fact that they are different in nature than those in the previous line<sup>2</sup>. The first integral (surface one) actually vanishes since  $(H=E)$

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<sup>2</sup>this is not at all necessary if we keep in mind that from the very beginning we are on a polar frame

on it. So,

$$\begin{aligned} \langle x_i \frac{\partial H}{\partial x_j} \rangle &= \frac{1}{\Omega} \frac{\partial}{\partial E} \int_{H < E} \prod_i dp_i dq_i \delta_{ij} (H - E) \\ &= \frac{1}{\Omega} \delta_{ij} \int_{H < E} \prod_i dp_i dq_i. \end{aligned}$$

Thus,

$$\langle x_i \frac{\partial H}{\partial x_j} \rangle = \delta_{ij} \frac{\Sigma(E)}{\Omega} = \delta_{ij} \frac{k_B}{\frac{k_B \partial \ln(\Sigma(E))}{\partial E}} = \delta_{ij} \frac{k_B}{\frac{\partial S}{\partial E}} = \delta_{ij} k_B T \quad (15)$$

The measure of average K.E. per degrees of freedom can readily be got from the expression  $\langle x_i \frac{\partial H}{\partial x_j} \rangle = \delta_{ij} k_B T$  which shows  $\langle \frac{p_i \dot{q}_i}{2} \rangle = \frac{1}{2} k_B T$  which is the average K.E. per degree of freedom.

### 0.3 Canonical Ensemble

In canonical ensemble we take into consideration the statistical mechanics of a system which is in thermal contact with a reservoir of heat. The heat reservoir is much much bigger than the system itself so that exchange of heat to the system does not alter the temperature of the reservoir. The system being in thermal equilibrium shares the same temperature with its reservoir. Let the system be denoted by A and the reservoir by A' and together they make a micro-canonical system  $A_0 = A + A'$ . Given the total energy of the  $A_0$  as  $E_0$ , the individual energies of the system and its reservoir  $E$  and  $E'$  respectively add up to give  $E_0$ . When the system is at an energy  $E$ , the probability of the system to be at this state is proportional to the compatible micro-states available in its environment to keep it stay at this energy E i.e.  $\Omega(E')$ . Expanding  $\ln(\Omega(E')) = \ln(\Omega(E_0 - E))$  about  $E_0$  we get

$$\ln(\Omega(E_0 - E)) = \ln(\Omega(E_0)) - \left( \frac{\partial \ln(\Omega(E'))}{\partial E} \right) E = \ln(\Omega(E_0)) - \frac{E}{k_B T}. \quad (16)$$

Thus the probability of the system to be at the energy state E,  $P(E)$  is proportional to  $e^{-\beta E}$  where  $\beta = 1/k_B T$  (T is the temperature of the reservoir which is also the temperature of the system when it is in thermal equilibrium with the reservoir). So, from now on we will take  $P(E) = e^{-\beta E} / \Sigma_E e^{-\beta E}$ , the



constant of proportionality is taken care of by the normalization. The normalization constant  $\sum_E e^{-\beta E}$  is generally known as the partition function of the system (exactly as in the micro-canonical case). Let us get a few points cleared in the beginning. The energy  $E$  actually contains the kinetic and the potential parts. But equipartition of energy, where applicable, makes the average energy per degrees of freedom a function of temperature only. Temperature of a system being in canonical equilibrium (classical) is a constant and as a result gets cancelled by normalization. Its only the potential energy of the system which features in the expression of the probability. Consider the state of the system at energy  $E$  to be degenerate. If there are  $n_E$  states at the energy  $E$  then the probability of the system to be at energy must get  $n_E$  fold raised. So the probability will now be  $P(E) = n_E e^{-\beta E} / \sum_E n_E e^{-\beta E}$ . In the continuum, its the density of states  $\Omega(E)$  that gives you the measure of the  $n_E$  because by definition density of states is the number of states at the energy  $E$ . Thus, in continuum, the probability is  $P(E) = \Omega(E) e^{-\beta E} / \int dE \Omega(E) e^{-\beta E}$ .

The relation which is used to bridge the statistical mechanics to the thermodynamics in the canonical ensemble case is the partition function  $Z = e^{-\beta F}$  where  $F$  is the Helmholtz free energy (relevant thermodynamic potential in the canonical case) and thermodynamically  $F = \langle E \rangle - TS$ . The  $\langle E \rangle$  in the expression of  $F$  is canonical average energy defined as

$$\langle E \rangle = \frac{\sum E e^{-\beta E}}{Z}. \quad (17)$$

Taking the derivative with respect to  $\beta$  the average energy is given by  $\langle E \rangle = -\frac{\partial \ln(Z)}{\partial \beta}$ . The dispersion of the system  $\langle \Delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$  is given by  $-\frac{\partial \langle E \rangle}{\partial \beta}$  indicates that the average energy always increases with temperature to keep the dispersion positive definite. To get to the expression of the dispersion let us consider

$$\langle E^2 \rangle = \frac{1}{Z} \sum \frac{\partial^2}{\partial \beta^2} e^{-\beta E} = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \sum \frac{\partial}{\partial \beta} e^{-\beta E} \right) + \frac{\left( \sum \frac{\partial}{\partial \beta} e^{-\beta E} \right)^2}{Z^2} \quad (18)$$

So, using the expression of  $\langle E \rangle$ ,

$$\langle \Delta E^2 \rangle = -\frac{\partial \langle E \rangle}{\partial \beta}. \quad (19)$$

The generalized force of a system is negative gradient of energy and following this rule, the generalize force corresponding to the thermodynamic

coordinate  $x$  (also called parameter) is  $-\frac{\partial E}{\partial x}$ . so the work done by the system under the action of this force to achieve a displacement of  $dx$  is

$$dw = -\frac{\sum \frac{\partial}{\partial x} e^{-\beta E}}{Z} \times dx = \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial x} \times dx. \quad (20)$$

Now, consider the partition function to be a function of the coordinate  $x$  and temperature  $\beta$ . Given that, an increment of  $\ln(z)$  is written as

$$d(\ln(Z)) = \frac{\partial \ln(Z)}{\partial x} dx + \frac{\partial \ln(z)}{\partial \beta} d\beta = \beta dw - d(\langle E \rangle \beta) + \beta d \langle E \rangle \quad (21)$$

or

$$d(\ln(Z) + \beta \langle E \rangle) = \frac{dS}{k_B} \quad (22)$$

Thus, we arrive at the relation which combines canonical stat. mech. to the thermodynamics and the relation is  $Z = e^{-\beta F}$  where  $F = \langle E \rangle - TS$  is the Helmholtz free energy.

### 0.3.1 Gaussian form

As we know the probability distribution of a system over an energy scale (continuum) is given by  $P(E) = \Omega(E)e^{-\beta E}$ , the  $\Omega(E)$  part of the probability is a very rapidly increasing quantity of energy whereas the  $e^{-\beta E}$  is a rapidly decreasing function of  $E$ . A combination of rapidly increasing and rapidly decreasing parts make the probability  $P(E)$  have a peak at some  $E_m$  on the scale where  $E_m$  is the most probable energy of the system. Since  $E_m$  is the maximum of the distribution the following relation holds.

$$\left[ \frac{\partial}{\partial E} (e^{-\beta E} \Omega(E)) \right]_{E=E_m} = 0, \quad (23)$$

which immediately gives

$$\left[ \frac{\partial \ln \Omega(E)}{\partial E} \right]_{E=E_m} = \beta. \quad (24)$$

Now, from the Eq.22 and considering the relation  $s = k_b \ln \Omega(E)$  we get

$$\frac{1}{k_B} \left[ \frac{\partial S}{\partial E} \right]_{E=\langle E \rangle} = \beta = \left[ \frac{\partial \ln \Omega(E)}{\partial E} \right]_{E=\langle E \rangle} \quad (25)$$

Eq.24 and 25 are the same relations but derived at  $E = E_m$  and  $E = \langle E \rangle$ , which indicated that  $E_m = \langle E \rangle$  and the  $P(E)$  is a symmetric distribution about the most probable value of it which is the same as the average of the distribution i.e.  $\langle E \rangle$ .

Having know that the  $P(E)$  is symmetric, let us try to find its actual shape. To that end, consider the  $\ln P(E)$  and expand it on a Taylor series about  $\langle E \rangle$ .

$$\begin{aligned} \ln (\Omega(E)e^{-\beta E}) &= \ln (\Omega(\langle E \rangle)e^{-\beta \langle E \rangle}) \\ &+ \frac{1}{2} \left[ \frac{\partial^2 \Omega(E)e^{-\beta E}}{\partial E^2} \right]_{E=\langle E \rangle} (E - \langle E \rangle)^2 + \text{higher order terms.} \end{aligned} \quad (26)$$

The first derivative does not appear in the above expression due to the fact that  $\langle E \rangle$  coincides with  $E_m$  and consequently the first derivative is zero at  $E = \langle E \rangle$ . Now, using the thermodynamics relations we have encountered so far, one can easily show that the first (constant) term on the r.h.s. of the above equation can be write as  $-\beta(\langle E \rangle - TS)$ , and, the coefficient of the second term in  $(E - \langle E \rangle)^2$  can be expressed as  $-1/2k_B T^2 C_V$ . Using these thermodynamic expressions one can write the form of  $P(E)$  down as

$$P(E) = e^{-\beta F} \times e^{-\frac{(E - \langle E \rangle)^2}{2k_B T^2 C_V}} \quad (27)$$

- Arrive at Eq.27 starting from Eq.26 using required thermodynamic relations.

Equation 27 manifests a Gaussian form for the probability distribution function  $P(E)$  which has a width or standard deviation  $\sigma = T\sqrt{k_B C_V}$  where  $C_V$  is the specific heat of the system at constant volume. The  $C_V$  is an extensive quantity i.e. it scales as the number of particles (molecules)  $N$  in the system. This can easily be understood from the definition of  $C_V$  which is the amount of heat required to raise the temperature of the system by one degree. Since the temperature is a measure of the average K.E. of the particles in the system  $C_V$  should scale as  $N$ . The energy of the system  $\langle E \rangle$  is also an extensive quantity i.e. proportional to  $N$ . So,  $\sigma / \langle E \rangle \sim N^{-\frac{1}{2}}$ . In the thermodynamic limit, as  $N \rightarrow \infty$  the distribution becomes infinitely sharp on the scale of  $\langle E \rangle$ .

### 0.3.2 Correspondence between micro-canonical and canonical ensembles

At the thermodynamic limit, considering the probability distribution to be a delta function about its average energy, the partition function, which is the area under the probability distribution curve on energy scale, can be written as

$$\begin{aligned} Z &\simeq \Omega(\langle E \rangle) e^{-\beta \langle E \rangle} \times \delta E \\ \ln Z &= \ln \Omega(\langle E \rangle) - \beta \langle E \rangle \quad (\text{neglecting } \ln \delta E). \end{aligned} \quad (28)$$

The above expression of  $\ln Z$  when combined to the other expression  $Z = e^{-\beta F}$  immediately leads us to the relation

$$S = k_B \ln \Omega(\langle E \rangle). \quad (29)$$

But, this is the definition of micro-canonical entropy which we have arrived at from the canonical distribution at thermodynamic limit. This observation implies the correspondence or equivalence of canonical and micro-canonical ensembles at the thermodynamic limit and one may use either of them depending upon the amount of ease it provides in dealing with the mathematics. Generally, using canonical ensemble makes life simple by not putting any restriction on the integration limits and one can integrate up to the extreme limits of the phase space variables (degrees of freedom) or the energy where the canonical distribution function takes care of the irrelevant extensions over these scales with the help of some useful potential functions (or functionals) of the degrees of freedom.

### 0.3.3 Alternative expression of entropy

Let us derive an expression of entropy, useful in the context of canonical ensemble, starting from the expression of the canonical partition function

$$\ln Z = -\beta(\langle E \rangle - TS).$$

$$\begin{aligned} S &= k_B \left[ \ln Z + \beta \sum_i P_i E_i \right] \\ &= k_B \left[ \ln Z - \sum_i P_i \ln(Z P_i) \right] \\ &= k_B \left[ \ln Z - \ln Z \sum_i P_i - \sum_i P_i \ln P_i \right] \end{aligned}$$

Since,  $\sum_i P_i = 1$ , we get

$$S = -k_B \sum_i P_i \ln P_i \quad (30)$$

This is the expression of entropy for a canonical ensemble which is positive on account of the fact that  $P_i$  is a fraction.

### 0.3.4 Canonical distribution by entropy maximization

Let us have a look at an alternative derivation of canonical distribution function to correlate the equilibrium distribution with the maximization of entropy of the system. Consider a large number 'a' of similarly prepared systems which are in contact with a heat reservoir and the average energy over all these systems is  $\langle E \rangle$  a constant. Thus,

$$\begin{aligned} \sum_i a_i &= a = \text{constant} \\ \sum_i \delta a_i &= 0 \end{aligned} \quad (31)$$

and

$$\begin{aligned} \sum_i a_i E_i &= \langle E \rangle = \text{constant} \\ \sum_i \delta a_i E_i &= 0 \end{aligned} \quad (32)$$

Eq.31 and 32 are the two constraints on the variation of number of elements of the ensemble at an energy  $E_i$ . Consider the number  $\Gamma(a_1, a_2, \dots, a_n)$  in

which a particular distribution such that -  $a_1$  systems of  $a$  are at energy  $E_1$ ,  $a_2$  in  $E_2$  and so on - can be achieved for all distinct  $a_i$ s and  $E_i$ s keeping the  $\langle E \rangle$  constant and  $\sum a_i = a$ . The number  $\Gamma$  corresponding to a particular set  $\{a_i\}$  is

$$\Gamma(a_1, a_2, \dots, a_n) = \frac{a!}{a_1! a_2! \dots a_n!}. \quad (33)$$

So,

$$\ln \Gamma(a_1, a_2, \dots, a_n) = \ln a! - \sum_i \ln a_i!. \quad (34)$$

Since,  $a$  is very large, presumably so are all  $a_i$ s and that helps apply Stirling's formula as

$$\ln a_i! = a_i \ln a_i - a_i \quad (35)$$

By the use of Stirling's formula

$$\ln \Gamma = a \ln a - \sum_i a_i \ln a_i \quad (36)$$

Let us consider that  $\Gamma(\{a_i\}) = \Gamma'$  which is a maximum. Thus,

$$\delta \Gamma' = 0 = \sum_i \ln a_i \delta a_i. \quad (37)$$

Equation 37 is the third equation of constraint we have corresponding to the maximization of  $\Gamma$ . The situation in which Eq.31, 32 and 37 apply can be mathematically captured by the use of Lagrange multipliers

$$\sum_i (\ln a_i^m + \alpha + \beta E_i) \delta a_i^m = 0 \quad (38)$$

where  $\alpha$  and  $\beta$  are Lagrange multipliers which has to be determined and  $a_i^m$  explicitly mentions the set  $\{a_i\}$  corresponding to the maximum  $\Gamma$ . Considering  $\delta a_i^m$  arbitrary, the validity of Eq.38 demands

$$\ln a_i^m + \alpha + \beta E_i = 0 \quad (39)$$

or

$$a_i^m = e^{-\alpha} e^{-\beta E_i} \quad (40)$$

and by normalization

$$e^{-\alpha} = a \left( \sum_i e^{-\beta E_i} \right)^{-1}. \quad (41)$$

Once we know the expression of  $a_i^m$  we can readily find out the corresponding probability distribution function and average energy

$$P_i = \frac{a_i^m}{a} = \frac{e^{-\beta E_i}}{e^{-\beta E_i}} \quad (42)$$

$$\langle E \rangle = \frac{\sum_i e^{-\beta E_i} E_i}{e^{-\beta E_i}} \quad (43)$$

Eq.42 is the canonical distribution we have already got. Since, all the elements of the ensemble are in contact with the same heat bath the other Lagrange multiplier  $\beta$  is equal to  $1/k_B T$ , where  $T$  is the temperature of the bath, from analogy. Thus, the canonical distribution function is arrived at on maximization of the number  $\Gamma$  at a constant average energy of a fixed sized ensemble. To relate  $\Gamma$  to the entropy of the system rewrite Eq.36 as

$$\begin{aligned} \ln \Gamma &= a \ln a - \sum_i a P_i \ln a P_i \\ &= a \ln a - a \sum_i P_i (\ln a + \ln P_i) \\ &= a \ln a - a \ln a \left( \sum_i P_i \right) - a \sum_i P_i \ln P_i \\ \ln \Gamma &= -a \sum_i P_i \ln P_i \end{aligned}$$

Thus,  $\ln \Gamma$  is proportional to the canonical entropy  $\ln \Gamma = \frac{a}{k_B} S$  and maximization of  $\Gamma$  is equivalent to the maximization of the entropy of the system. So, in canonical equilibrium the entropy of the system is a maximum corresponding to a constant average energy and temperature of the system. The Helmholtz free energy of the system  $F = \langle E \rangle - TS$  would definitely be a minimum when entropy is a maximum at constant  $\langle E \rangle$  and  $T$  and the equilibrium thermodynamic relations are subject to these extremum conditions. The maximization of entropy can be understood as a consequence of maximizing the symmetry of the system at the microscopic level where the thermal equilibrium would ensure no further evolution of the probability distribution of the system towards any more symmetric situations. The requirement of the highest symmetry is a consequence of thermalization of the system and corresponding disorder. The level of microscopic disorder is similar to the level of symmetry of the system at the microscopic level and it comes out that the system tries to remain maximally disordered to fix the probability distribution to a stationary profile.

## 0.4 Grand canonical ensemble

The grand canonical ensemble represents systems which are in contact with an environment with which it can exchange heat and particles as well. So, unlike canonical ensemble the total number of particles is not a constant for such systems, rather the energy and particle numbers both can vary. Following a similar treatment as the one used to arrive at the canonical distribution function we can derive the probability distribution function for the grand canonical system i.e. the probability of the system to be at an energy  $E_i$  with number of particles  $N_j$  as

$$P_{ij} = e^{-\beta(E_i - \mu N_j)} / Z_G. \quad (44)$$

The  $Z_G = \sum_{ij} e^{-\beta(E_i - \mu N_j)}$  is grand partition function and is related to the thermodynamics of the system through the relation

$$\ln Z_G = \frac{PV}{k_B T} \quad (45)$$

which basically is equation of states. The Gibbs potential  $G = F + PV$  is the relevant thermodynamic potential in the grand canonical case. The use of it we will come across at the time of discussing phase co-existence of systems. Gibbs potential is a function of temperature, pressure and number of particles of the system i.e.  $G = G(T, P, N)$ . Take the definition of  $G$  as  $F + PV$ . A variation in it is then expressed as

$$dG = dF + PdV + VdP = d \langle E \rangle - TdS - SdT + PdV + VdP, \quad (46)$$

the last equality follows from the definition of the Helmholtz potential  $F = \langle E \rangle - TS$ . Now, consider the conservation of energy as

$$d \langle E \rangle = dQ - PdV + \mu dN \quad (47)$$

where the change in internal energy of the system is equal to the sum of heat given to it, mechanical work done on it, and the rise in energy of it due to addition of particles to it. This immediately gives

$$d \langle E \rangle + PdV - dQ = d \langle E \rangle + PdV - TdS = \mu dN. \quad (48)$$

Using Eq.48 and Eq.46

$$dG = \mu dN - SdT + VdP, \quad (49)$$

which clearly shows that  $G = G(T, P, N)$ .



## 0.5 Application of Boltzmann statistics: Maxwell velocity distribution

Consider a classical gas of noninteracting distinguishable particles. Such a classical gas limit can be achieved at a high temperature and a very dilute conditions. Since the particles are noninteracting, they only have the K.E. which is equal to  $p^2/2m$  for the particle having momentum  $p$  and the mass  $m$ . In what follows we will consider the all the particles of mass  $m$ . From the knowledge of the Boltzmann distribution function for a system of particles at a constant temperature  $T$ , we can say that the probability for the particle under consideration to remain at a momentum  $p$  within the range  $dp$  and a position  $r$  within a range  $dr$  is  $f(p, r)d\vec{p}d\vec{r} \propto e^{-\beta p^2/2m}d\vec{p}d\vec{r}$ . So, the total number of particles at the momentum  $p$  and position  $r$  within the ranges  $dp$  and  $dr$  respectively is

$$n(p, r)d\vec{p}d\vec{r} = C e^{-\beta p^2/2m} d\vec{p}d\vec{r} \quad (50)$$

where the proportionality constant would be found out from the consideration of the constraint that the system has  $N$  number of particles in a volume  $V$ . If one integrates either sides of the above equation, one gets  $N$ ; thus,

$$N = CV \int e^{-\beta p^2/2m} d\vec{p}. \quad (51)$$

Taking into account  $p^2 = m^2(v_x^2 + v_y^2 + v_z^2)$ , we can make the change of variables by absorbing some constants into the constant  $C$  (which has to be determined).

$$\frac{N}{V} = n = C \int e^{-\frac{\beta m(v_x^2 + v_y^2 + v_z^2)}{2}} dv_x dv_y dv_z \quad (52)$$

Utilizing the symmetry along the x, y, and the z directions one can easily show that the integral in the above equation is actually equal to  $\left( \int e^{-\frac{\beta m v_x^2}{2}} dv_x \right)^3 = \left( \frac{2\pi}{\beta m} \right)^{\frac{3}{2}}$  and thus,  $C = n \left( \frac{\beta m}{2\pi} \right)^{\frac{3}{2}}$ . Finally, the Maxwell velocity distribution for distinguishable non-interacting classical particles i.e. number of particles at velocity  $\vec{v}$  and within a range  $d\vec{v}$  reads as

$$f(\vec{v}, r)d\vec{r}d\vec{v} = n \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-mv^2/2k_B T} d\vec{v}d\vec{r} \quad (53)$$

Eq.53 gives a Gaussian distribution with zero mean. If one is interested in the distribution of speed one has to write the  $d\vec{v}$  as  $4\pi v^2 dv$ , because in spherical polar coordinate we are effectively, in this way, considering all the velocities of magnitude  $v$  irrespective of their directions. Using this differential form of volume element in the spherical polar coordinates we get the speed distribution function

$$f(v) = N4\pi v^2 \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-mv^2/2k_B T}. \quad (54)$$

These speed distribution function is clearly not a Gaussian due to the presence of the  $v^2$  term in the coefficient of the exponential part. One can calculate all the average quantities for such systems considering either of the two distribution functions shown above.

### 0.5.1 Equation of state for ideal classical gas

The momentum transferred per unit time in positive x-direction cross the area  $dA$  held perpendicular to the x-direction, in a gas is

$$F^+ = \int_{v_x > 0} d\vec{v} f(\vec{v}) dA (|\vec{v}| \cos \theta) (m\vec{v}) \quad (55)$$

where  $dA|\vec{v}| \cos \theta$  is the volume on the left hand side of the area  $dA$  from which the particles can impinge on the surface  $dA$  within one seconds time where  $|\vec{v}| \cos \theta = v_x$  i.e. x-component of the velocity. Similarly, considering particles falling on the area  $dA$  moving in the negative x directions (from the right hand side of the surface) would transfer a momentum

$$F^- = - \int_{v_x > 0} d\vec{v} f(\vec{v}) dA (|\vec{v}| \cos \theta) (m\vec{v}). \quad (56)$$

The negative sign comes from the  $\cos \theta$  part. Now the pressure on the surface perpendicular to the x-direction is the resultant force per unit area on this surface and is given by

$$P_x = P = F^+ - F^- = \int d\vec{v} f(\vec{v}) (|\vec{v}| \cos \theta) (m\vec{v}) = \int d\vec{v} f(\vec{v}) v_x (m\vec{v}) \quad (57)$$

where the integration is now on all  $v_x$  from  $-\infty$  to  $+\infty$ . The  $P_x = P$  is there because of the fact that the x-direction is completely arbitrary an

that also reflects the scalar nature of the pressure. The above expression of pressure is a general expression irrespective of the equilibrium or non-equilibrium situations of the system. The problem in the non-equilibrium case is due to mostly not having known an expression of  $f(\vec{v})$  because of the failing of the symmetry arguments we made for the system in equilibrium. Considering the Maxwell velocity distribution one can readily show that the integral in Eq.57 is equal to  $nm\bar{v}_x^2$  ( $n$  is the number density of particles) where the integral consisting of the cross terms like  $v_x v_y$  will vanish due to the zero mean Gaussian nature of the velocity distribution function which means that there is no resultant tangential force on any surface in the gas. Now, again considering the symmetry along the x, y and z-directions we can write  $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = \frac{\bar{v}^2}{3}$  which immediately gives

$$P = \frac{1}{3}mn\bar{v}^2 \quad (58)$$

From equipartition of energy we know that  $k_B T = \frac{1}{2}m\bar{v}^2$  and  $n = \frac{N}{V}$  ( $N$ =total number of particles in the system and  $V$  is the volume), leading to the equation of states of the gas

$$PV = \frac{2}{3}Nk_B T \quad (59)$$

## 0.6 quantum statistics: Bose-Einstein (BE) and Fermi-Dirac (FD)

The semi classical treatment of quantum gases is done in such a way that a. particles of a gas are loaded onto the quantum energy levels of a single particle bounded by the potential well of the same size of that binding the whole system, b. particles are considered indistinguishable unlike the classical ones which obey Maxwell-Boltzmann (MB) distribution, c. symmetry of the many particle wave function under the interchange of particle energies are taken care of.

To illustrate the last point (c.), consider the wave function (function in which all the dynamical information of the system of particles are contained) representing the particles as  $\psi_b = \psi(q_1, q_2, \dots, q_N)$ . Here, the suffix  $b$  mentions of the Bose-particles, that is particles with integral spin quantum numbers such as 0,1,2,...etc. Spin is a degree of freedom of particles of entirely quantum origin. Thus, its difficult to visualize it as classical rotational motion of a

particle, since, particle is structureless. But, its something of similar kind and is measured by a set of quantum numbers. In fact, there are quantum numbers associated to each degrees of freedom of a quantum particle. The existence of spin degrees of freedom and like that many others have actually been discovered from the requirement of existence of new quantum numbers to make the theory consistent. One of the consequences of particles having integral spin is that  $\psi_b$  is that interchange of the  $q_i$  and  $q_j$  of two particles does not change  $\psi_b$ , where  $q_i$ s are the set of quantum numbers of the  $i$  th particle in the system. Explicitly,

$$\psi_b(q_1, q_2, \dots, q_i, \dots, q_j, \dots, q_N) = \psi_b(q_1, q_2, \dots, q_j, \dots, q_i, \dots, q_N). \quad (60)$$

Fermi particles which are characterized by half integral spin ( $1/2, 3/2, 5/2 \dots$  etc.) have anti-symmetric many body wave function. In explicit forms

$$\psi_f(q_1, q_2, \dots, q_i, \dots, q_j, \dots, q_N) = -\psi_f(q_1, q_2, \dots, q_j, \dots, q_i, \dots, q_N). \quad (61)$$

Now, if two fermions are at the same energy and are indistinguishable, interchanging the set of quantum numbers of them would not be any physically noticeable change in the system, but, according to the relation mentioned above the wave function will change sign. Since, identical physical situations cannot have different theoretical representations, two fermions are not allowed to be in the same energy state. Unlike fermions, bosons can be in an energy state in as many number as allowed by the temperature related constraints of the system, because, the Bosonic wave function is symmetric.

### 0.6.1 Quantum distribution functions

The expression of the average number of particles in the  $i$  th energy level of a quantum gas is called the quantum distribution function. The expression of it is

$$\langle n_i \rangle = \frac{1}{e^{\beta\epsilon_i + \alpha} \pm 1}, \quad (62)$$

where the - sign corresponds to the BE case and the + sign corresponds to the FD statistics. The constant  $\alpha = -\beta\mu$  where  $\mu$  is the chemical potential given by

$$\mu = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial N}. \quad (63)$$

The  $\mu$  is negative for large  $N$  since  $Z(N)$  is a rapidly increasing function of  $N$ . We will utilize this property of  $\mu$  to derive the quantum distribution functions.

The partition function  $Z(N) = \sum_{\{n_i\}} e^{-\beta(\sum_i n_i \epsilon_i)}$ , is a rapidly increasing function of total number of particles  $N = \sum_i n_i$  where  $n_i$  the number of particles at an instant of time at the  $i$ th energy level is an integer between 0 and  $N$ . The expression of  $N$  as a sum of individual particle numbers at different energy levels is a constraint on the system which makes general calculations difficult and the derivation proceeds by getting rid of this constraint. Consider a rapidly increasing functional form  $e^{-\alpha N'}$  of  $N'$  where  $N'$  is any integral number. Since,  $Z(N')$  is a rapidly increasing form with  $N'$  the product  $Z(N')e^{-\alpha N'}$  will have a sharp peak at some point on the  $N'$  scale, lets call this point or number  $N$ . Considering the peak to be very sharp, the area under the graph is approximated as

$$\sum_{N'} Z(N')e^{-\alpha N'} = Z(N)e^{-\alpha N} \Delta N, \quad (64)$$

where  $\Delta N$  is the width of the peak. Take the grand partition function as  $\mathcal{Z} = \sum_{N'} Z(N')e^{-\alpha N'}$ , and log on both sides of above equations to get

$$\ln Z(N) = \alpha N + \mathcal{Z} \quad (65)$$

Now, the grand partition function can be expanded, keeping in mind that  $\sum_i n_i = N'$  and  $N'$  varies from 0 to  $+\infty$ , as

$$\begin{aligned} \mathcal{Z} &= \sum_{\{n_i\}} e^{-(\alpha + \beta \epsilon_i)n_i} \\ &= \left( \sum_{n_1=0}^{\infty} e^{-() \alpha + \beta \epsilon_1 n_1} \right) \left( \sum_{n_2=0}^{\infty} e^{-() \alpha + \beta \epsilon_1 n_2} \right) \dots \end{aligned} \quad (66)$$

### BE Case

Due to  $\infty$  being the maximum limit on the number of particles  $n_i$  that can remain at an energy level  $\epsilon_i$  for Bosons, the sums in each perenthesis can be done readily and the above expression for  $\mathcal{Z}$  can be simplified as

$$\mathcal{Z} = \left( \frac{1}{1 - e^{-(\beta \epsilon_1 + \alpha)n_1}} \right) \left( \frac{1}{1 - e^{-(\beta \epsilon_2 + \alpha)n_2}} \right) \dots \quad (67)$$

$$\ln \mathcal{Z} = - \sum_i \ln (1 - e^{-(\beta \epsilon_i + \alpha)}) \quad (68)$$

Thus, one gets

$$\ln Z = \alpha N - \sum_i \ln(1 - e^{-(\beta\epsilon_i + \alpha)}). \quad (69)$$

The average number of particles in the state  $\epsilon_i$  (energy determines the state) is given by

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_i} = \frac{1}{\beta} \times \frac{\beta e^{-(\beta\epsilon_i + \alpha)}}{1 - e^{-(\beta\epsilon_i + \alpha)}} = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \quad (70)$$

where  $\alpha = -\beta\mu$ .

### FD Case

In the FD case, since an energy state can only have either 1 or 0 particles the  $\mathcal{Z}$  can be written as

$$\mathcal{Z} = \sum_{\{n_i\}} e^{-\sum_i -(\beta\epsilon_i + \alpha)n_i} \quad (71)$$

$$= \left( \sum_{n_1=0}^1 e^{-() \alpha + \beta\epsilon_1 n_1} \right) \left( \sum_{n_2=0}^1 e^{-() \alpha + \beta\epsilon_1 n_2} \right) \dots \quad (72)$$

Each sum in the above expression can be easily done, since there are only two terms, and it immediately follow that,

$$\ln Z = \alpha N + \sum_i \ln(1 + e^{-(\beta\epsilon_i + \alpha)}). \quad (73)$$

Upon applying the usual definition of average number of particles in the energy level  $\epsilon_i$  as

$$\langle n_i \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_i} = \frac{1}{e^{\beta\epsilon_i + \alpha} + 1} = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1} \quad (74)$$

### Maxwell-Boltzmann

In contrast to the BE and FD distributions the MB distribution is obtained straightforwardly considering  $\frac{e^{-\beta\epsilon_i}}{\sum_i e^{-\beta\epsilon_i}}$  to be the probability of the system to be at state  $\epsilon_1$  and there are  $N$  distinguishable particles in the system as

$$\langle n_i \rangle = N \frac{e^{-\beta\epsilon_i}}{\sum_i e^{-\beta\epsilon_i}}. \quad (75)$$

## 0.6.2 Classical limit of the quantum statistics

For very low concentration of a gas or the gas at very high temperature, the  $\alpha$  must be so large that  $e^{\alpha+\beta\epsilon_i} \gg 1$  for all  $i$ , so that the statistics remains consistent. So, for  $e^{\alpha+\beta\epsilon_i} \gg 1$ , both the FB and BE statistics reduces to

$$\langle n_i \rangle = \sum_i e^{-(\alpha+\beta\epsilon_i)} \quad (76)$$

Thus,

$$N = e^{-\alpha} \sum_i e^{-\beta\epsilon_i}, \quad (77)$$

replacing the  $e^{-\alpha}$ , in the expression of  $\langle n_i \rangle$  we get

$$\langle n_i \rangle = N \frac{e^{-\beta\epsilon_i}}{\sum_i e^{-\beta\epsilon_i}} \quad (78)$$

which basically is the MB statistics. Thus, very dilute and high temperature phase of a quantum gas would practically show the classical behavior.