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Content Writer	Prof. P.K. Ahluwalia Physics Department Himachal Pradesh University Shimla 171 005

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1. Learning Outcomes

After studying this module, you shall be able to

- Appreciate the need to further relax the constraints to not only allow exchange of energy but allow exchange of particles between the system and the surroundings
- Derive the probability of finding a system with energy E_r and number of particles N_r in two alternative ways in Grand Canonical Ensemble: (i) system +heat reservoir system (ii) method of most probable state using Lagrange's undetermined multipliers.
- Identify Grand Partition function and know interesting properties of the Grand partition function as a function of macroscopic variables and link these to thermodynamic properties of the system such as Grand potential or thermodynamic potential..
- Relate grand canonical partition function to canonical partition function studied in last two modules.
- Express Grand partition function as product of single orbital partition functions
- Apply the approach of the Grand canonical ensemble via Grand canonical partition function to study the following :
  - o Classical ideal gas
  - o Derivation of Fermi and Bose distributions
- Compare the occupation number of single particle Fermi-Dirac, Bose-Einstein and Maxwell-Boltzmann distributions

2. Introduction

In modules XII, XIII and XIV we introduced the microcanonical and canonical ensembles and the idea of partition function and laid down a systematic procedure to derive thermodynamic properties and applied theses to study a variety of interesting physical macroscopic systems. In going from microcanonical ensemble to canonical ensemble we relaxed the constraint from complete isolation to allow exchange of energy with the surroundings, making E a variable. Such a system is now a closed system . However, to be more realistic, it is desirable to also allow exchange of matter or more precisely particles constituting the system, making N another variable of the system. System is then said to be an open system. In equilibrium system has an average energy, $\langle E \rangle$ and an average number of particles $\langle N \rangle$. This open system is then described by a Grand Canonical Ensemble the subject matter of this module. This ensemble deals with microstates of a system kept at constant temperature (T), constant chemical potential (μ) in a given volume V. As was seen in the case of canonical ensemble we will now have a new partition function called Grand partition function. This shall be used to define grand potential followed by derivation of thermodynamic properties. We shall apply this approach to study once again the classical ideal gas. At the end of this module we shall also use Grand potential to derive Fermi and Bose distribution from the knowledge of the fact that in Fermi distribution each state can have either zero or one number of particles and in Bose distribution each state can have number of particles from zero to infinity. In later modules we will have a re-derivation of these from a quantum mechanical perspective by actually counting the states.

3. Grand Canonical Distribution Function: System and Heat Bath Approach

We follow the same approach followed for canonical ensemble system and heat bath approach. We take our system (designated A) and put it in a heat bath (designated A') such that system and the heat bath (designated $A_{T=}A + A'$), Figure 1, are allowed to now exchange both energy and particles, keeping system and heat bath in equilibrium at a common temperature T and common chemical potential μ. Heat bath is very large having a large heat capacity. The composite system (A_T) together is completely isolated, such that if at any time if system A has energy E_r and number of particles N_r and heat bath A' having energy E_r' and number of particles N_r' then the total energy E_T and total number of particles N_T are constant i.e.

$$E_s + E_s' = E_T = \text{Constant} \tag{1}$$

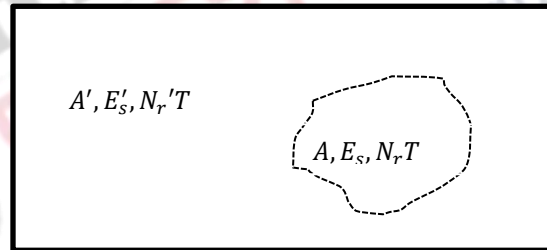$$N_r + N_r' = N_T = \text{Constant} \tag{2}$$

Figure 1 Heat bath A' at equilibrium with system A at temperature T and chemical potential μ

Since heat bath is very large, $E_s \ll E_T$ and $N_s \ll N_T$ i.e.

$$\frac{E_s}{E_T} = \left(1 - \frac{E_s'}{E_T}\right) \ll 1 \tag{3}$$

$$\frac{N_r}{N_T} = \left(1 - \frac{N_r'}{N_T}\right) \ll 1 \tag{4}$$

Since the heat bath is very large the number of states compatible to it with energy E_s' and particles N_r', $\Omega'(E_s', N_r')$, is also very large independent of the nature of the reservoir. It is worth noting that larger the number of states available to the reservoir larger is the

probability of it assuming energy E_s' and having particles N_r' and consequently the system immersed in heat bath assuming energy E_s and having number of particles N_r. As per the principle of equal apriori probability, different microstates in the reservoir are equally likely to occur, the probability P_r of system A, occurring with energy E_s and number of particles N_r, is proportional to the number of microstates which the reservoir has i.e. $\Omega'(E_s', N_r')$. Therefore,

$$P_{s,r} \propto \Omega'(E_s', N_r') \equiv \Omega'(E_T - E_s, N_T - N_r) \tag{5}$$

Noting the inequalities (3) and (4) we can expand the right hand side around $E_s' = E_T$ and $N_r' = N_T$, which means around $E_s = 0$ and $N_r = 0$ Recalling that Ω' is a very large number which varies very rapidly, it is therefore, more convenient to deal with logarithm of this function which is a slowly varying function. So

$$\ln \Omega'(E_s', N_r') = \ln \Omega'(E_T, N_T) + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E_r' = E_T} (E_s' - E_T) \tag{6}$$
$$+ \left(\frac{\partial \ln \Omega'}{\partial N'}\right)_{E_s' = E_T} (N_r' - N_T) + \cdots$$

Or

$$\ln \Omega'(E_r', N_r') \approx \ln \Omega'(E_T, N_T) + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E_s' = E_T} (-E_s) \tag{7}$$
$$+ \left(\frac{\partial \ln \Omega'}{\partial N'}\right)_{N_r' = N_T} (-N_r) \ldots$$

Recalling $\left(\frac{\partial \ln \Omega'}{\partial E'}\right) = \beta' = \frac{1}{k_B T'}$ and at equilibrium $\beta' = \frac{1}{k_B T'} = \beta = \frac{1}{k_B T}$, $\left(\frac{\partial \ln \Omega'}{\partial N'}\right) = \alpha' = -\frac{\mu'}{k_B T'} = \alpha = -\frac{\mu}{k_B T}$ equation (6) can be written as

$$\ln \Omega'(E_s', N_r') \approx constant - \beta E_s - \alpha N_r \tag{8}$$

Or

$$\Omega'(E_s', N_r') \approx Constant\ e^{\beta E_s - \alpha N_r} \tag{9}$$

From (4) and (9) we get

$$P_{s,r} \propto e^{-\beta(E_s - \mu N_r)} \tag{10}$$

Since sum of all probabilities must sum to 1, normalising, () we get

$$P_{s,r} = \frac{e^{-\beta(E_s - \mu N_r)}}{\sum_{s,r} e^{-\beta(E_s - \mu N_r)}} \tag{11}$$

Where, summation is over all the (E_s, N_r)states which system A can take. Equation (11) is the Grand canonical distribution function which provides the probability of the system in state with energy E_s and number of particles N_r.

Furthermore, since equation (11) has been derived by using very fundamental ideas of physics involving conservation of energy, extensiveness of energy $E_T = E_r + E'_r$, conservation of number of particles, extensiveness of number of particles and slow and smooth variation of $\ln \Omega(E, N)$, independent of the choice of quantum mechanics or classical mechanics, it is applicable very generally as we shall see later in applications.

4. Grand Canonical Distribution Function: Most Probable Value Approach

We consider an ensemble of $\mathbb{N}$ identical systems which are allowed to mutually share total energy $\mathbb{N} < E >$ and a total number of particles $\mathbb{N} < N >$. Let n_{sr} denote the number of system which have at any instant t an amount of energy E_s and number of particles N_r then these together satisfy the following three conditions:

$$\sum_{s,r} n_{sr} = \mathbb{N} \tag{12}$$

$$\sum_r n_{sr} E_s = \mathbb{N} < E > \tag{13}$$

$$\sum_r n_{sr} N_r = \mathbb{N} < N > \tag{14}$$

Any set of values $\{n_{sr}\}$which satisfy conditions stated in equations (12), (13) and (14) is a possible way of distributing energy and particles among the members of the ensemble. Number of such possible ways $\mathbb{W}\{n_{rs}\}$, of distributing energy and particles among the members of the ensemble is given by

$$\mathbb{W}\{n_{sr}\} = \frac{\mathbb{N}!}{\prod_{n_{sr}}(n_{sr}!)} \tag{15}$$

According to principle of equal apriori probability, all possible distribution of energy and particles among the members of the ensemble are equally likely, the frequency of achieving a given set $\{n_{rs}\}$ is directly proportional to the number $\mathbb{W}\{n_{rs}\}$. Out of all these sets the most probable set shall be the one for which $\mathbb{W}\{n_{rs}\}$ is maximum. Once we have identified this set say $\{n_{rs}^*\}$, we shall be physically interested in this distribution. However statistically we can not ignore other $\{n_{rs}\}'s$ with their corresponding weights or frequencies to calculate the expectation values or mean values of the numbers n_r as given below

$$\langle n_{rs}\rangle = \frac{\sum'_{\{n_{sr}\}} n_r \mathbb{W}\{n_{sr}\}}{\sum'_{\{n_{sr}\}} \mathbb{W}\{n_{sr}\}} \tag{16}$$

Significance of n_{sr}^* lies in the fact that the fraction $\frac{n_{sr}^*}{\mathbb{N}}$ is the grand canonical probability P_{sr}

Let us now calculate the desirable numbers $\{n_{sr}^*\}$ and $\langle n_{sr}\rangle$. Again for the reasons stated earlier $\ln \mathbb{W}$ is a slowly varying function and we shall use it to proceed further, which implies

$$\ln \mathbb{W} = \ln \mathbb{N}! - \sum_{sr} \ln n_{sr}! \tag{17}$$

In thermodynamic limit apply Stirlings formula and equation (13) becomes

$$\ln \mathbb{W} = \mathbb{N} \ln \mathbb{N} - N - \sum_{sr} n_{sr} \ln n_{sr} + \sum_{sr} n_{sr} \tag{18}$$
$$= \mathbb{N} \ln \mathbb{N} - \sum_{r} n_{sr} \ln n_{sr}$$

If n_{sr} changes by a small amount $\ln \mathbb{W}$ also changes by a small amount as given below

$$\delta(\ln \mathbb{W}) = \sum_{r} (\ln n_{sr} + 1)\delta n_{sr} \tag{19}$$

Now for n_{sr} to be maximum $\delta(\ln \mathbb{W})$ should become zero, provided equations (12) and (13) and (14) also satisfy the following conditions simultaneously

$$\sum_{r} \delta n_{sr} = 0 \tag{20}$$

$$\sum_{sr} E_s \, \delta n_{sr} = 0 \tag{21}$$

$$\sum_{r} N_r \, \delta n_{sr} = 0 \tag{22}$$

Now to get the set $\{n_r^*\}$, method of Lagrange's undetermined multiplier can be used according to which equations (20), (21) and (23) together yield the condition

$$\sum_{r} \left(-(\ln n_{sr} + 1) - \alpha N_r - \beta E_s - \gamma\right) \delta n_{sr} = 0 \tag{23}$$

Where α, β and γ are Lagrange's undetermined multipliers. Since δn_r is completely arbitrary, for equation (18) to be satisfied its coefficients must become zero, i.e. for all r

$$\left(-(\ln n_r^* + 1) - \alpha N_r - \beta E_s - \gamma\right) = 0 \tag{24}$$

Or

$$\ln n_{sr}^* = -1 - \alpha N_r - \beta E_s - \gamma \tag{25}$$

Or

$$n_{sr}^* = e^{-(1+\gamma)} e^{-\beta E_r - \alpha N_r} = C \, e^{-\beta E_r - \alpha N_r} \tag{26}$$

Where now C, α and β are two undetermined parameters and (26) gives us the most probable distribution. To calculate C, we note

$$\sum_{r} n_{sr}^* = \mathbb{N} = C \sum_{sr} e^{-\beta E_s - \alpha N_r} \tag{27}$$

Or

$$C = \frac{\mathbb{N}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}} \tag{28}$$

Therefore,

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$$P_{sr} = \frac{n_{sr}^*}{\mathbb{N}} = \frac{e^{-\beta E_s - \alpha N_r}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}} \tag{29}$$

In Thermodynamic limit at equilibrium $\frac{n_{sr}^*}{\mathbb{N}} \approx \frac{\langle n_{sr} \rangle}{\mathbb{N}}$, therefore,

$$\frac{\langle n_{sr} \rangle}{\mathbb{N}} \approx \frac{n_{sr}^*}{\mathbb{N}} = \frac{e^{-\beta E_s - \alpha N_r}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}} \tag{30}$$

The undetermined parameters α and β are determined by the equations for average number of particles $\langle N \rangle$ and average energy $\langle E \rangle$ in each system of the ensemble with prior knowledge of their values:

$$\langle N \rangle = \frac{\sum_{sr} N_r e^{-\beta E_s - \alpha N_r}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}} = -\frac{\partial}{\partial \alpha} \left\{ \ln \sum_{sr} N_r e^{-\beta E_s - \alpha N_r} \right\} \tag{31}$$

$$\langle E \rangle = \frac{\sum_{sr} E_s e^{-\beta s - \alpha N_r}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}} == -\frac{\partial}{\partial \beta} \left\{ \ln \sum_{sr} E_r e^{-\beta E_s - \alpha N_r} \right\} \tag{32}$$

5. Link between Grand Canonical Ensemble and Thermodynamics : Thermodynamic potential

To establish a link between the Grand canonical ensemble and thermodynamics, we introduce a quantity q, called q potential as follows:

$$q = \ln \left\{ \sum_{sr} e^{-\beta E_s - \alpha N_r} \right\} \tag{33}$$

q is a function of α, β and all the energy states E_s. Taking the differential of q, we have

$$dq = -\frac{\sum_{sr} N_r e^{-\beta E_s - \alpha N_r}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}} d\alpha - \frac{\sum_{sr} E_s e^{-\beta E_s - \alpha N_r}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}} d\beta \tag{34}$$
$$- \beta \sum_{sr} \frac{e^{-\beta E_s - \alpha N_r}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}} dE_s$$

Or using equations (30), (31) and (32), we have

$$dq = -\langle N \rangle d\alpha - \langle E \rangle d\beta - \frac{\beta}{\mathbb{N}} \sum_{sr} \langle n_{sr} \rangle dE_s$$

Which can be further written as

$$d(q + \alpha\langle N \rangle + \beta\langle E \rangle) = \beta\left(-\frac{\alpha}{\beta} d\langle N \rangle - d\langle E \rangle - \frac{1}{\mathbb{N}} \sum_{sr} \langle n_{sr} \rangle dE_s \right) \qquad (35)$$

Now if we compare the expression with in the parenthesis with the first law of thermodynamics:

$$\delta Q = -\frac{\alpha}{\beta} d\langle N \rangle - d\langle E \rangle + \delta W \qquad (36)$$

We can arrive at the following correspondence

$$\mu = -\frac{\alpha}{\beta} \qquad (37)$$

$$\delta W = -\frac{1}{\mathbb{N}} \sum_{sr} \langle n_{sr} \rangle dE_s \qquad (38)$$

So that

$$d(q + \alpha\langle N \rangle + \beta\langle E \rangle) = \beta\,\delta Q \qquad (39)$$

A closer look at equation (39) and comparing it with $dS = \frac{\delta Q}{T}$ tells us that the coefficient β on the right hand side should correspond to reciprocal of temperature T, so that

$$\beta = \frac{1}{k_B T} \qquad (40)$$

From equation (37), it immediately follows that

$$\alpha = -\frac{\mu}{k_B T} \qquad (41)$$

Left hand side of equation (39), then provides correspondence of the quantity $q + \alpha\langle N \rangle + \beta\langle E \rangle$ with entropy, such that

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$$\frac{S}{k_B} = q + \alpha\langle N\rangle + \beta\langle E\rangle$$

Or

$$q = \frac{S}{k_B} - \alpha\langle N\rangle - \beta\langle E\rangle = \frac{S}{k_B} - \frac{\mu\langle N\rangle}{k_B T} - \frac{\langle E\rangle}{k_B T} = \frac{TS + \mu\langle N\rangle - \langle E\rangle}{k_B T} \qquad (42)$$

The function $k_B T\, q = TS + \mu\langle N\rangle - \langle E\rangle$ is the well known Thermodynamic Potential Φ which describes an open, isochoric and isothermal collection

$$\Phi(T, \mu, V) = TS + \mu\langle N\rangle - \langle E\rangle = q k_B T$$

Recalling that Gibbs free energy $G = \mu\langle N\rangle = \langle E\rangle - TS + PV$, equation (42) becomes

$$q = \ln\left\{\sum_{sr} e^{-\beta E_s - \alpha N_r}\right\} = \frac{PV}{k_B T} \qquad (43)$$

Equation (43) provides a bridge between thermodynamics and grand canonical ensemble.

6. Grand Canonical Partition Function and Thermodynamic Functions

We can define grand canonical partition function $\mathbb{Z}$,

$$\mathbb{Z} = \left\{\sum_{sr} e^{-\frac{E_s}{k_B T} + \frac{\mu N_r}{k_B T}}\right\} \qquad (44)$$

Defining $e^{\frac{\mu}{k_B T}} = f$ called fugacity equation (44) can be written as

$$\mathbb{Z} = \left\{\sum_{sr} (f)^{N_r}\, e^{-\frac{E_s}{k_B T}}\right\} = \left\{\sum_{r} (f)^{N_r} \left(\sum_{s} e^{-\frac{E_s}{k_B T}}\right)\right\} \qquad (45)$$

The expression $Z_{N_r}(V,T) = \left(\sum_s e^{-\frac{E_s}{k_BT}} \right)$ is the canonical partition function for a fixed N_r and has in it via energy, dependence on volume. Therefore, Grand canonical partition function can be written as

$$\mathbb{Z} = \left\{ \sum_{N_r=0}^{\infty} (f)^{N_r} Z_{N_r}(V,T) \right\} \tag{46}$$

Hence q is related to the partition function via the relation

$$q = \ln \mathbb{Z}(f,V,T) = \frac{PV}{k_BT} \tag{47}$$

Now we are in a position to write down the thermodynamic functions of interest in terms of q or $\mathbb{Z}$

Pressure:

$$P = \frac{k_BT}{V} q(f,V,T) = \ln \mathbb{Z}(f,V,T) \tag{48}$$

Average number of particles in equilibrium

$$N = \langle N \rangle = k_BT \left[\frac{\partial q(\mu,V,T)}{\partial \mu} \right]_{V,T} = \left[f \frac{\partial q(f,V,T)}{\partial f} \right]_{V,T} \tag{49}$$

Internal Energy

$$E = \langle E \rangle = - \left[\frac{\partial q(f,V,T)}{\partial \beta} \right]_{V,f} = k_BT^2 \left[\frac{\partial q(f,V,T)}{\partial T} \right]_{V,f} \tag{50}$$

One can get E as a function of N, V, T by eliminating f between equations (49) and (50). Using this functional form, taking derivative with respect to T gives specific heat at constant volume.

Equation of state: It is a relationship between P, V, T and can be obtained by eliminating f between equations (48) and (49)

Helmholtz free energy:

$$F = E - TS + PV - PV = G - PV = N\mu - PV \tag{51}$$
$$= Nk_BT \ln f - k_BT \ln \mathbb{Z}(f,V,T) = -k_BT \ln \frac{\mathbb{Z}(f,V,T)}{f^N}$$

Interestingly, argument of the logarithm is canonical distribution function.

Entropy:

$$S = \frac{E-F}{T} = k_B T \left[\frac{\partial q(f,V,T)}{\partial T}\right] - N k_B \ln f + k_B q(f,V,T) \tag{52}$$

7. Grand Canonical Partition Function and Single Orbital Partition Functions

Keeping equation (13) in mind the grand partition function (46)

$$\mathbb{Z} = = \left\{\sum_{N_r=0}^{\infty} (f)^{N_r} Z_{N_r}(V,T)\right\}$$

By recalling that

$$Z_{N_r}(V,T) = \left(\sum_s e^{-\frac{E_s}{k_B T}}\right) = \left(\sum_{\{N_r\}} e^{-\sum_r \frac{N_r E_r}{k_B T}}\right)$$

With $\sum_{\{N_r\}} N_r = N,$ can be written as

$$\mathbb{Z} = = \left\{\sum_{N_r=0}^{\infty} (f)^{N_r} \sum_{\{N_r\}} \left(e^{-\sum_r \frac{N_r E_r}{k_B T}}\right)\right\} \tag{53}$$

Or

$$\mathbb{Z} = = \left\{\sum_{N_r=0}^{\infty} \sum_{\{N_r\}} (f)^{\sum_r N_r} \left(e^{-\sum_r \frac{N_r E_r}{k_B T}}\right)\right\} \tag{54}$$

Or

$$\mathbb{Z} = \left\{\sum_{N_r=0}^{\infty} \sum_{\{N_r\}} \prod_r \left(f e^{-\frac{E_r}{k_B T}}\right)^{N_r}\right\} \tag{55}$$

This can be further written as

$$\mathbb{Z} = \left\{ \prod_r \sum_{N_r=0}^{\infty} \left(f e^{-\frac{E_r}{k_B T}} \right)^{N_r} \right\} \tag{56}$$

Here the product is over the partition function for a single orbital only with all possible number of particles. In this form grand particle function becomes a very useful result providing us to find the grand partition function from one orbital partition function. We shall see its utility later in deriving Fermi-Dirac and Bose-Einstein distribution function which is decided the number of particles allowed in an orbital or state.

8. Applications

Here we discuss two applications of Grand canonical ensemble. First one is our prototype example of an ideal gas and second one is to derive Fermi-Dirac and Bose-Einstein distribution function. The real effectiveness of grand canonical ensemble becomes useful when one applies it to systems involving interparticle interaction and systems having quantum statistical effect.

8.1 Classical Ideal Gas

The grand partition function for a macroscopic system is given by

$$\mathbb{Z} = = \left\{ \sum_{N=0}^{\infty} (f)^N Z_N(V,T) \right\}$$

Where $Z_N(V,T)$ is the canonical partition function and $f = e^{\frac{\mu}{k_B T}}$ is fugacity. For an ideal gas the partition function of such a system can be written as made up single particle partition function $Z_1(V,T)$:

$$Z_N(V,T) = \frac{[Z_1(V,T)]^N}{N!} \tag{57}$$

Here factor $N!$ in the denominator takes care of indistinguishability of particles. Once again recalling that since particles in the system are free to be anywhere in the volume in which they are enclosed, therefore, $Z_1(V,T)$ shall be proportional to V and a function of T, so that

$$Z_1(V,T) = V g(T) \tag{58}$$

Where $g(T)$ is a function of T alone. You may recall for earlier discussion of the classical ideal gas in canonical ensemble $g(T) = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$

Thus the grand partition function of the ideal gas can be written as

$$\mathbb{Z} = \sum_{N=0}^{\infty} \frac{[fVg(T)]^N}{N!} = e^{fVg(T)} \tag{59}$$

Hence the q potential for the ideal gas can be written as

$$q(f, V, T) = \ln \mathbb{Z}(f, V, T) = fVg(T) \tag{60}$$

Pressure:

From equation (48) we have Pressure **P**

$$P = \frac{k_B T}{V} q(f, V, T) = k_B T f g(T) \tag{61}$$

Average number of particles:

From equation (49) we have average number of particles **N**

$$N = \left[f \frac{\partial q(f, V, T)}{\partial f} \right]_{V,T} = fVg(T) \tag{62}$$

Internal Energy, Helmholtz Free Energy, Entropy:

From equation (50) we have the Internal Energy E

$$E = fVk_B T^2 \left[\frac{\partial g(T)}{\partial T} \right]_{V,f} \tag{63}$$

From equation (51), we have Helmholtz free energy

$$F = Nk_B T \ln f - k_B T \ln \mathbb{Z}(f, V, T) = Nk_B T \ln f - k_B T fVg(T) \tag{64}$$

And finally from equation (52) we have entropy

$$S = k_B fV \left[T \left[\frac{\partial g(T)}{\partial T} \right] + g(T) \right] - Nk_B \ln f \tag{65}$$

Equation of State:

Eliminating **f** from equation (60 and (61), we get

$$PV = Nk_B T \tag{66}$$

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Equation of state is independent of the functional form of $g(T)$.

Internal energy:

Eliminating f between equation (62) and (63)

$$\mathbf{E} = fVk_BT^2\left[\frac{\partial g(T)}{\partial T}\right]_{V,f} = \frac{N\,k_BT^2}{g(T)}\left[\frac{\partial g(T)}{\partial T}\right]_{V,f} \tag{67}$$

Specific heat at constant volume:

Taking the derivative of equation (67) with respect to temperature T, specific heat at constant volume is given by

$$C_V = \frac{N\,k_B\left[-T^2\left[\frac{\partial g(T)}{\partial T}\right]_{V,f}^2 + g(T)T^2\frac{\partial^2 g(T)}{\partial T^2} + 2Tg(T)\frac{\partial g(T)}{\partial T}\right]}{[g(T)]^2} \tag{68}$$

To see whether E and C_V indeed are well known results for classical ideal gas, we require explicit temperature dependence of $g(T)$ which is known to be proportional to some power of T. If we suppose this to be $g(T) \propto T^n$, we get

$$E = \frac{N\,k_BT^2}{g(T)}\left[\frac{\partial g(T)}{\partial T}\right]_{V,f} = n\frac{N\,k_BT^2}{T^n}\,T^{n-1} = nNk_BT \tag{69}$$

For an ideal gas n=3/2 which gives us the well known result.

$$C_V = \frac{N\,k_B\left[-T^2\left[\frac{\partial g(T)}{\partial T}\right]_{V,f}^2 + g(T)T^2\frac{\partial^2 g(T)}{\partial T^2} + 2Tg(T)\frac{\partial g(T)}{\partial T}\right]}{[g(T)]^2}$$

$$C_V = nN\,k_B \tag{70}$$

Entropy:

Eliminating f from (65) and (62), we get

$$S = \frac{k_BN}{g(T)}\left[T\left[\frac{\partial g(T)}{\partial T}\right] + g(T)\right] - Nk_B\ln\frac{N}{Vg(T)} \tag{71}$$

One can see that it is an extensive quantity.

Helmholtz free energy:

Eliminating f from (64) and (62) we get

$$F = Nk_BT \left[\ln \frac{N}{Vg(T)} - 1 \right] \tag{72}$$

Once again one can notice that it is an extensive quantity.

8.1 Derivation of Bose and Fermi Distribution Functions

Writing Grand canonical partition function in terms of single orbital partition functions offers a very interesting way to derive Bose and Fermi distributions.

According to equation (56), single orbital partition function can be written as

$$Z_1 = \sum_{N_r} \left(f e^{-\frac{E_r}{k_BT}} \right)^{N_r} \tag{73}$$

The summation in equation (37) has two possibilities to choose N_r while taking the summation. In the case of Fermi-Dirac distribution N_r can take only two values $N_r = 0$ and 1, where as in the case of Bose Einstein Distribution N_r can take values from 0 to ∞. These two possible choices lead to two different results for the two distributions as discussed below:

Fermi-Dirac Distribution:

$$Z_1 = \left(f e^{-\frac{E_r}{k_BT}} \right)^0 + \left(f e^{-\frac{E_r}{k_BT}} \right)^1 = 1 + e^{\frac{\mu - E_r}{k_BT}} \tag{74}$$

Thus the grand partition function for the Fermi-Dirac Distribution becomes

$$\mathbb{Z} = \left\{ \prod_r \left(1 + e^{\frac{\mu - E_r}{k_BT}} \right) \right\} \tag{75}$$

Therefore, q-potential can be obtained as

$$q = \ln \mathbb{Z} = \sum_r \ln \left(1 + e^{\frac{\mu - E_r}{k_BT}} \right) \tag{76}$$

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Bose-Einstein:

$$Z_1 = \sum_{N_r=0}^{\infty} \left(f e^{-\frac{E_r}{k_B T}} \right)^{N_r} = 1 + e^{\frac{\mu-E_r}{k_B T}} + \left(e^{\frac{\mu-E_r}{k_B T}} \right)^2 + \cdots \tag{77}$$

This is a geometrical progression (G.P.) and is convergent provided $e^{\frac{\mu-E_r}{k_B T}} < 1$ for every E_r. This is possible only if $\mu < 0$, which is a very important result that for a bose system chemical potential is always negative. Thus (77), which is a sum of a convergent series can be written as

$$Z_1 = \frac{1}{\left(1 - e^{\frac{\mu-E_r}{k_B T}} \right)} \tag{78}$$

Thus the grand partition function for the Bose-Einstein Distribution becomes

$$\mathbb{Z} = \left\{ \prod_r \left(1 - e^{\frac{\mu-E_r}{k_B T}} \right)^{-1} \right\} \tag{79}$$

Therefore, q-potential can be obtained as

$$q = \ln \mathbb{Z} = -\sum_r \ln \left(1 - e^{\frac{\mu-E_r}{k_B T}} \right) \tag{80}$$

For Fermi-Dirac distribution and Bose-Einstein distribution together the q-potential can be written as

$$q = \pm \sum_r \ln \left(1 \pm e^{\frac{\mu-E_r}{k_B T}} \right) \tag{81}$$

(+) sign gives Fermi-Dirac distribution and (-) gives Bose-Einstein distribution.

Since $q(f, V, T) = \frac{PV}{k_B T}$

For the two distributions pressure can be obtained as

$$P = \pm \frac{k_B T}{V} \sum_r \ln \left(1 \pm e^{\frac{\mu-E_r}{k_B T}} \right) = \pm \frac{k_B T}{V} \sum_r \ln \left(1 \pm f e^{\frac{-E_r}{k_B T}} \right) \tag{82}$$

Mean energy can be obtained from equation (50)

$$\langle E \rangle = -k_B T^2 \left[\frac{\partial q(f,V,T)}{\partial T} \right]_{V,f} = \mp k_B T^2 \left[\frac{\partial \sum_r \ln \left(1 \pm e^{\frac{\mu - E_r}{k_B T}} \right)}{\partial T} \right]_{V,f}$$

$$= \sum_r \frac{E_r}{\left(e^{\frac{E_r - \mu}{k_B T}} \pm 1 \right)}$$

Average number of particles can be obtained from equation (51):

$$\langle N \rangle = \left[f \frac{\partial q(f,V,T)}{\partial f} \right]_{V,T} = \sum_r \frac{1}{\left(f^{-1} e^{\frac{E_r}{k_B T}} \pm 1 \right)} = \sum_r \frac{1}{\left(e^{\frac{E_r - \mu}{k_B T}} \pm 1 \right)} \quad (83)$$

Mean occupation number of an orbital or level E_r

$$\langle n_{E_r} \rangle = \left[f \frac{\partial q(f,V,T)}{\partial f} \right]_{V,T,all\ other\ E_r} = \frac{1}{\left(f^{-1} e^{\frac{E_r}{k_B T}} \pm 1 \right)} \quad (84)$$

$$= \frac{1}{\left(e^{\frac{E_r - \mu}{k_B T}} \pm 1 \right)}$$

In the Maxwell Boltzmann case $e^{\frac{E_r - \mu}{k_B T}} \gg 1$ for all values of single orbital energies including $E_r = 0$ which essential implies $e^{\frac{-\mu}{k_B T}} \gg 1$ and μ must be negative and $|\mu| \gg k_B T$. The Bose-Einstein Distribution and Fermi Dirac Distribution tend to so called Maxwell-Boltzmann

$$\langle n_{E_r} \rangle = e^{\frac{\mu - E_r}{k_B T}} \propto e^{\frac{-E_r}{k_B T}} \quad (85)$$

Also mean occupation per orbital in Maxwell-Boltzmann reduces to the fact that $\langle n_{E_r} \rangle \ll 1$, i.e. probability of occupation to be greater than 1 is negligible. Figure 2 below shows occupation number per orbital state $\langle n_{E_r} \rangle$ for the three cases. It is clear in the figure that for large value of $\frac{E_r - \mu}{k_B T}$ the Fermi-Dirac distribution curve (a) and Bose-Einstein distribution curve (b) merges with the Maxwell-Boltzmann distribution curve (b). In the case of Fermi-Dirac distribution occupation number is never goes higher than 1. In the case of Bose-Einstein distribution as $E_r = \mu$, occupancy of that level becomes infinite leading to the phenomenon of Bose-Einstein Condensation.
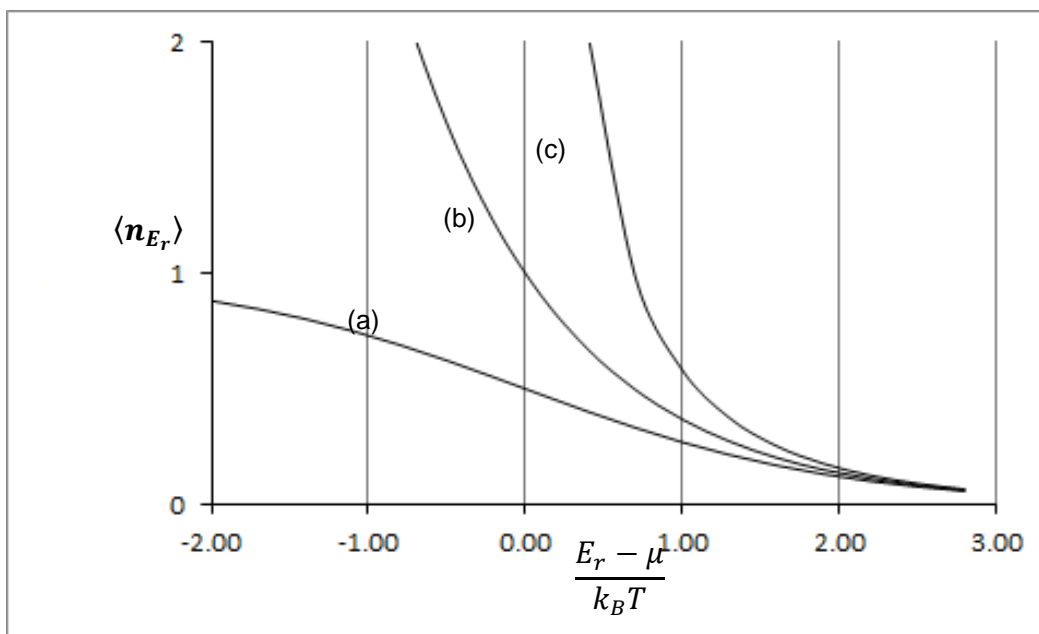
Figure 2 (a) Fermi Dirac Distribution (b) Maxwell Boltzmann Distribution (c) Bose Einstein Distribution for a non-interacting system

7. Summary

In this module we have learnt

- That Grand canonical ensemble corresponds to an open, isochoric, isothermal system; which allows exchange of energy and exchange of particles with the surroundings unlike micro canonical ensemble which corresponds to a completely isolated system and canonical ensemble which allows exchange of energy but does not allow exchange of particles.

- That Grand canonical probability distribution function can be derived by two two distinct approaches (i) System and Heat Bath approach (ii) most probable approach. First approach treats system in equilibrium with the heat bath at a common temperature T and the other involves regarding the system being studied as a member of collection of large number of exact replicas of the system, in all possible microstates, called an ensemble. Both approaches provide us dependence of probability of finding a system with energy E_s and number of particles N_r given by

$$P_{sr} = \frac{e^{-\beta E_s - \alpha N_r}}{\sum_{sr} e^{-\beta E_s - \alpha N_r}}$$

Where $\beta = \frac{1}{K_B T}$ and $\alpha = -\frac{\mu}{k_B T}$.

- That the probability so defined is linked with thermodynamics via q potential $q(\mu, V, T) = \ln\{\sum_{sr} e^{-\beta E_s - \alpha N_r}\}$, which is linked with thermodynamic potential, describing an open, isochoric and isothermal system such that

$$\Phi(T, \mu, V) = TS + \mu\langle N\rangle - \langle E\rangle = q k_B T$$

- That we can define Grand Partition function $\mathbb{Z}$ from the knowledge of P_{sr} in the following forms

$$\mathbb{Z} = \left\{\sum_{sr} e^{-\frac{E_s}{k_B T} + \frac{\mu N_r}{k_B T}}\right\}$$

Or

$$\left\{\sum_r (f)^{N_r} \left(\sum_s e^{-\frac{E_s}{k_B T}}\right)\right\}$$

Or

$$\mathbb{Z} = = \left\{\sum_{N_r=0}^{\infty} (f)^{N_r} Z_{N_r}(V, T)\right\}$$

Where $Z_{N_r}(V, T) = \left(\sum_s e^{-\frac{E_s}{k_B T}}\right)$ for a given N_r that is

$Z_{N_r} = \left(\sum_{\{N_r\}} e^{-\sum_r \frac{N_r E_r}{k_B T}}\right)$ is the canonical distribution function and $f = e^{\frac{\mu}{k_B T}}$ is fugacity.

- Knowing $\mathbb{Z}$ and q- potential the other thermodynamic functions can easily be obtained by using following formulae

Pressure	$P = \dfrac{k_B T}{V} q(f, V, T) = \ln \mathbb{Z}(f, V, T)$
Average number of particles	$N = \langle N\rangle = k_B T \left[\dfrac{\partial q(\mu, V, T)}{\partial \mu}\right]_{V,T} = \left[f\dfrac{\partial q(f, V, T)}{\partial f}\right]_{V,T}$
Internal Energy	$E = \langle E\rangle = -\left[\dfrac{\partial q(f, V, T)}{\partial \beta}\right]_{V,f} = k_B T^2 \left[\dfrac{\partial q(f, V, T)}{\partial T}\right]_{V,f}$
Helmholtz free energy	$F = -k_B T \ln \dfrac{\mathbb{Z}(f, V, T)}{f^N}$

Entropy	$S = k_B T \left[\dfrac{\partial q(f, V, T)}{\partial T} \right] - N k_B \ln f + k_B q(f, V, T)$

- How Grand canonical partition function can be written in terms of single orbital partition functions as

$$\mathbb{Z} = = \left\{ \prod_r \sum_{N_r=0}^{\infty} \left(f e^{-\frac{E_r}{k_B T}} \right)^{N_r} \right\}$$

Where $Z_1 = \sum_{N_r}^{\infty} \left(f e^{-\frac{E_r}{k_B T}} \right)^{N_r}$ is the single orbital partition function.

- That using Grand canonical partition function can be used to derive the thermodynamic properties of a classical ideal gas by the same recipe which was used in the case of canonical ensemble.
- That Fermi Dirac distribution function and Bose-Einstein distribution functions can be derived from single orbital partition function by using the fact that for Fermi-Dirac distribution an orbital can have either zero or one particles and for Bose-Einstein distribution function number of particles can take values from zero to infinity, paving way for calculating various thermodynamic properties.
- The Grand partition function for Fermi-Dirac and Bose Einstein case are respectively $\mathbb{Z} = \left\{ \prod_r \left(1 + e^{\frac{\mu - E_r}{k_B T}} \right) \right\}$ and $\mathbb{Z} = \left\{ \prod_r \left(1 - e^{\frac{\mu - E_r}{k_B T}} \right)^{-1} \right\}$
- The various thermodynamic properties for the Fermi Dirac and Bose Einstein cases can obtained from the knowledge of respective partition functions (+ sign for Fermi-Dirac and – sign for Bose Einstein cases respectively)

q-potential	$q = \pm \sum_r \ln \left(1 \pm e^{\frac{\mu - E_r}{k_B T}} \right)$
Pressure	$P = \pm \dfrac{k_B T}{V} \sum_r \ln \left(1 \pm e^{\frac{\mu - E_r}{k_B T}} \right)$
Average energy	$\langle E \rangle = \sum_r \dfrac{E_r}{\left(e^{\frac{E_r - \mu}{k_B T}} \pm 1 \right)}$
Average number of particles	$\langle N \rangle = \sum_r \dfrac{1}{\left(e^{\frac{E_r - \mu}{k_B T}} \pm 1 \right)}$
Mean occupation number	$\langle n_{E_r} \rangle = \dfrac{1}{\left(e^{\frac{E_r - \mu}{k_B T}} \pm 1 \right)}$

- That under the condition $e^{\frac{E_r - \mu}{k_B T}} \gg 1$ the mean occupation numbers of both Bose-Einstein and Fermi Dirac Distributions reduce to Maxwell Boltzmann distribution

$$\langle n_{E_r} \rangle = e^{\frac{\mu - E_r}{k_B T}} \propto e^{\frac{-E_r}{k_B T}}$$

- From the plot of occupation number of Fermi Dirac Distribution that it never goes higher than 1.
- That the occupation number curves for the three distributions merge for large values of $\frac{E_r - \mu}{k_B T}$.
- At $E_r = \mu$ occupation number corresponding to Bose-Einstein distribution goes to infinity leading to Bose Einstein condensation.

Appendices

A1 Some Intermediate Results

To prove (55) is same as (56)

$$\left\{ \sum_{N_r=0}^{\infty} \sum_{\{N_r\}} \prod_r \left(f e^{-\frac{E_r}{k_B T}} \right)^{N_r} \right\} = \left\{ \prod_r \sum_{N_r=0}^{\infty} \left(f e^{-\frac{E_r}{k_B T}} \right)^{N_r} \right\}$$

Let us put $f e^{-\frac{E_r}{k_B T}} = x_r$, this means we have to prove

$$\left\{ \sum_{N_r=0}^{\infty} \sum_{\{N_r\}} \prod_r (x_r)^{N_r} \right\} = \left\{ \prod_r \sum_{N_r=0}^{\infty} (x_r)^{N_r} \right\}$$

Let us choose two sets $\{N_1\}$ **and** $\{N_2\}$ such that each N_1 and N_2 take values 0, 1, 2 and directly expand the left hand side

$$\sum_{N_r=0}^{2} \sum_{\{N_r\}} \prod_r (x_r)^{N_r} = \sum_{N_r=0}^{2} \sum_{\{N_r\}} (x_r)^{N_1} (x_r)^{N_2}$$

$$= \sum_{N_r=0}^{2} \{ (x_1)^0 (x_2)^0 + (x_1)^0 (x_2)^1 + (x_1)^1 (x_2)^0 + (x_1)^1 (x_2)^1 + (x_1)^0 (x_2)^2$$

$$+ (x_1)^2 (x_2)^0 + (x_1)^1 (x_2)^2 + (x_1)^2 (x_2)^1 + (x_1)^2 (x_2)^2 =$$

$$= \sum_{N_r=0}^{2} \{1 + (x_2)^1 + (x_1)^1 + (x_1)^1(x_2)^1 + (x_2)^2 + (x_1)^2$$
$$+ (x_1)^1(x_2)^2 + (x_1)^2(x_2)^1 + (x_1)^2(x_2)^2\}$$

$$= \sum_{N_r=0}^{2} \{(1 + x_1 + x_1^2)(1 + x_2 + x_2^2)\}$$

$$= \prod_{r} \sum_{N_r=0}^{2} (x_r)^{N_r}$$

$= $ L.H.S.

This can be extended further to see that this is true in general.

A2 Spreadsheet for plotting Occupation number distribution

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