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1. Learning Outcomes

After studying this module, you shall be able to

- Appreciate the need to go beyond micro-canonical ensemble in practical situations encountered in real physical problems
- See that in canonical ensemble we relax the energy constraint imposed in micro-canonical ensemble to exchange energy with the surroundings called heat bath at constant temperature
- Derive the probability of finding a system with energy $\boldsymbol{E_r}$ in two alternative ways: (i) system +heat reservoir system (ii) method of most probable state using Lagrange's undetermined multipliers
- Understand the key concept of a partition function, which implies partitioning of the members of the ensemble into a set of systems in different energy levels.
- Know interesting properties of the partition function as a function of macroscopic variables and link these to thermodynamic properties of the system.
- Know the concept of density of states and partition function in phase space
- To apply the approach of canonical ensemble via partition function to look at following physical systems to appreciate its effectiveness:
    - A two level system
    - Classical ideal gas.
    - Maxwellian distribution of speeds

2. Introduction

In the XII module we studied the micro canonical ensemble, which was a highly constrained way of looking at macroscopic systems, practically not possible to achieve because nothing can be completely isolated as envisaged in it. To have a more practical approach, instead of energy which is not only difficult to keep fixed, temperature is a better thermo-dynamical variable which can be controlled and measured easily. For this the macroscopic system can be put in a heat bath of with infinitely large heat capacity and allowed exchange of energy to keep temperature constant. Such a macroscopic system is described by the parameters $\boldsymbol{N}$, $\boldsymbol{V}$ and $\boldsymbol{T}$ and the corresponding ensemble is called canonical ensemble. In this ensemble the energy of the system is allowed to vary between zero to infinity.

We are interested in asking the question, what is the probability $\wp_{\boldsymbol{r}}$ that the macroscopic system in the ensemble is in one of the states described by energy $\boldsymbol{E_r}$ at any given instant of time. The concern in this module is to answer this question and learn how this approach can be applied to some prototype models.

3. Canonical Distribution Function: System and Heat Bath Approach

To answer the question raised in the introduction,we begin by following an approach called system and heat bath approach. We take our system (designated $\boldsymbol{A}$) and put it in a heat bath (designated $\boldsymbol{A'}$) such that system and the heat bath (designated $\boldsymbol{A_{T=}A + A'}$), Figure 1, are allowed to exchange energy,keeping system and heat bath in equilibrium at a common temperature T.Heat bath is very large having a large heat capacity. The composite system ($\boldsymbol{A_T}$) together is completely isolated, such that if at any time if system $\boldsymbol{A}$ has energy $\boldsymbol{E_r}$ and heat bath $\boldsymbol{A'}$ having energy $\boldsymbol{E_r}'$ then the total energy $\boldsymbol{E_T}$ is constant i.e.

$$\boldsymbol{E_r + E_r' = E_T = \text{Constant}} \qquad (1)$$

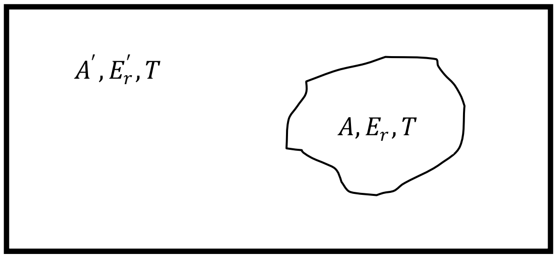

Figure 1Heat bath A' at equilibrium with system A at temperature T

Since heat bath is very large, $\boldsymbol{E_r} \ll \boldsymbol{E_T}$ i.e.

$$\boldsymbol{\frac{E_r}{E_T} = \left(1 - \frac{E_r'}{E_T}\right) \ll 1} \qquad (2)$$

Since the heat bath is very large the number of states compatible to it with energy $\boldsymbol{E_r'}$, $\boldsymbol{\Omega'(E_r')}$, is 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 $\boldsymbol{E_r}'$ and consequently the system immersed in heat bath assuming energy$\boldsymbol{E_r}$. As per the principle of equal apriori probability, different microstates in the reservoir are equally likely to occur, the probability of system $\boldsymbol{A}$occurring with energy $\boldsymbol{E_r P_r}$is proportional to the number of microstates which the reservoir has i.e. $\boldsymbol{\Omega'(E_r')}$. Therefore,

$$\boldsymbol{P_r \propto \Omega'(\mathrm{E_r'}) \equiv \Omega'(E_T - E_r)} \qquad (3)$$

Noting the inequality (2) we can expand the right hand side around $\boldsymbol{E_r' = E_T}$, which means around $\boldsymbol{E_r = 0}$. Recalling that $\boldsymbol{\Omega'}$ 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

$$\boldsymbol{\ln \Omega'(\mathrm{E_r'}) = \ln \Omega'(E_T) + \left(\frac{\partial \ln \Omega'}{\partial \mathrm{E}'}\right)_{E_r' = E_T} (\mathrm{E_r'} - E_T) + \cdots} \qquad (4)$$

Or

$$\ln \Omega'(\mathrm{E}_r') \approx \ln \Omega'(E_T) + \left(\frac{\partial \ln \Omega'}{\partial \mathrm{E}'}\right)_{E_r'=E_T} (-E_r) + \cdots \tag{5}$$

Recalling $\left(\frac{\partial \ln \Omega'}{\partial \mathrm{E}'}\right) = \beta' = \frac{1}{k_B T'}$and at equilibrium $\beta' = \frac{1}{k_B T'} = \beta = \frac{1}{k_B T}$, equation (5) can be written as

$$\ln \Omega'(\mathrm{E}_r') \approx constant - \beta E_r \tag{6}$$

From (3) and (6) we get

$$P_r \propto \mathrm{e}^{-\beta E_r} \tag{7}$$

Since sum of all probabilities must sum to 1, normalising, (7) we get

$$P_r = \frac{\mathrm{e}^{-\beta E_r}}{\sum_r \mathrm{e}^{-\beta E_r}} \tag{8}$$

Where, summation is over all the states which system A can take. Equation (8) is the canonical distribution function which provides the probability of the system in state with energy E_r.

Furthermore, since equation (8) has been derived by using very fundamental ideas of physics involving conservation of energy, extensiveness of energy $E_T = E_r + E_r'$, and slow and smooth variation of $\ln \Omega(E)$, independent of the choice of quantum mechanics or classical mechanics it is applicable very generally as we shall see later in applications.

4. Canonical Distribution Function: Most Probable Value Approach

We consider an ensemble of $\mathbb{N}$ identical systems which are allowed to share energy $\mathcal{E}$. Let $E_r(r = 0, 1, 2, 3 \ldots \ldots..)$denote the energy eigen values of the systems. If $n_r$denotes the number of systems which at any instant have the energy value E_r, then n_r and E_r together satisfy the following two conditions:

$$\sum_r \boldsymbol{n_r} = \mathbb{N} \tag{9}$$

$$\sum_r \boldsymbol{n_r E_r} = \mathcal{E} \tag{10}$$

Any set of values $\{\boldsymbol{n_r}\}$which satisfy conditions sated in equations (9) and (10) is a possible way of distributing total energy $\mathcal{E}$ among $\mathbb{N}$ members of the ensemble. There are a number of ways of distributing this total energy $\mathcal{E}$ among the members of the ensemble giving different distinct states. These different ways can be counted denoted by the symbol $\mathbb{W}\{\boldsymbol{n_r}\}$ given by

$$\mathbb{W}\{\boldsymbol{n_r}\} = \frac{\mathbb{N}!}{\boldsymbol{n_0}!\,\boldsymbol{n_1}!\,\boldsymbol{n_2}!\dots\dots\dots\dots} \tag{11}$$

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

$$\langle \boldsymbol{n_r} \rangle = \frac{\sum'_{\{\boldsymbol{n_r}\}} \boldsymbol{n_r} \mathbb{W}\{\boldsymbol{n_r}\}}{\sum'_{\{\boldsymbol{n_r}\}} \mathbb{W}\{\boldsymbol{n_r}\}} \tag{12}$$

Significance of $\boldsymbol{n_r^*}$ lies in the fact that the fraction$\frac{\boldsymbol{n_r^*}}{\mathbb{N}}$ is the canonical probability$\boldsymbol{P_r}$

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

$$\mathbf{ln}\,\mathbb{W} = \mathbf{ln}\,\mathbb{N}! - \sum_r \mathbf{ln}\,\boldsymbol{n_r}! \tag{13}$$

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

$$\begin{aligned} \mathbf{ln}\,\mathbb{W} &= \mathbb{N}\,\mathbf{ln}\,\mathbb{N} - \boldsymbol{N} - \sum_r \boldsymbol{n_r}\,\mathbf{ln}\,\boldsymbol{n_r} + \sum_r \boldsymbol{n_r} \\ &= \mathbb{N}\,\mathbf{ln}\,\mathbb{N} - \sum_r \boldsymbol{n_r}\,\mathbf{ln}\,\boldsymbol{n_r} \end{aligned} \tag{14}$$

If $\boldsymbol{n_r}$ changes by a small amount $\mathbf{ln}\, \mathbb{W}$ changes by a small amount as given below

$$\boldsymbol{\delta}(\mathbf{ln}\, \mathbb{W}) = \sum_{r} (\mathbf{ln}\, \boldsymbol{n_r} + \mathbf{1})\boldsymbol{\delta n_r} \tag{15}$$

Now for $\boldsymbol{n_r}$is to be maximum $\boldsymbol{\delta}(\mathbf{ln}\, \mathbb{W})$ should become zero, provided equations (9) and (10) also satisfy the following conditions simultaneously

$$\sum_{r} \boldsymbol{\delta n_r} = \mathbf{0} \tag{16}$$

$$\sum_{r} \boldsymbol{E_r}\, \boldsymbol{\delta n_r} = \mathbf{0} \tag{17}$$

Now to get the set $\{\boldsymbol{n_r^*}\}$, method of Lagrange's undetermined multiplier can be used according to which equations (15), (16) and (17) together yield the condition

$$\sum_{r} (-(\mathbf{ln}\, \boldsymbol{n_r} + \mathbf{1}) - \boldsymbol{\alpha} - \boldsymbol{\beta E_r})\, \boldsymbol{\delta n_r} = \mathbf{0} \tag{18}$$

Where $\boldsymbol{\alpha}$ and$\boldsymbol{\beta}$ are Lagrange's undetermined multipliers. Since $\boldsymbol{\delta n_r}$ is completely arbitrary, for equation (18) to be satisfied its coefficients must become zero, i.e. for all r

$$(-(\mathbf{ln}\, \boldsymbol{n_r^*} + \mathbf{1}) - \boldsymbol{\alpha} - \boldsymbol{\beta E_r} = \mathbf{0} \tag{19}$$

Or

$$\mathbf{ln}\, \boldsymbol{n_r^*} = -\mathbf{1} - \boldsymbol{\alpha} - \boldsymbol{\beta E_r} \tag{20}$$

Or

$$\boldsymbol{n_r^*} = \boldsymbol{e^{-(1+\alpha)} e^{-\beta E_r}} = \boldsymbol{C\, e^{-\beta E_r}} \tag{21}$$

Where now $\boldsymbol{C}$ and $\boldsymbol{\beta}$ are two undetermined parameters and (21) gives us the most probable distribution. To calculate $\boldsymbol{C}$, we note

$$\sum_r n_r^* = \mathbb{N} = C\sum_r e^{-\beta E_r} \tag{22}$$

Or

$$C = \frac{\mathbb{N}}{\sum_r e^{-\beta E_r}} \tag{23}$$

Therefore,

$$P_r = \frac{n_r^*}{\mathbb{N}} = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \tag{24}$$

Now the other Lagrange’s parameter β can be obtained from a solution of the equation

$$\langle E\rangle = \frac{\sum_r E_r\, e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial\beta}\ln\sum_r e^{-\beta E_r} \tag{25}$$

According to statistical mechanics $\langle E\rangle$ is thermodynamic energy E.

Furthermore, $= -\frac{\partial E_r}{\partial V}$, therefore,

$$\langle P\rangle = -\frac{\sum_r \left(\frac{\partial E_r}{\partial V}\right) e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \tag{26}$$

Here $\langle P\rangle$ corresponds to thermodynamic pressure.

Let us differentiate equation (25) with respect to V, remembering that E_r is a function of N, V and β, keeping N and β fixed, we have

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_{N,\beta} = -\langle P\rangle + \beta\langle EP\rangle - \beta\langle E\rangle\langle P\rangle \tag{27}$$

Now we can differentiate equation (26) with respect to β, we have

$$\left(\frac{\partial\langle E\rangle}{\partial\beta}\right)_{N,V} = \langle E\rangle\langle P\rangle - \langle EP\rangle \tag{28}$$

Multiplying (28) on both sides by $\boldsymbol{\beta}$ and adding to equation (27), we get

$$\left(\frac{\partial\langle E\rangle}{\partial V}\right)_{N,\beta} + \beta\left(\frac{\partial\langle P\rangle}{\partial\beta}\right)_{N,V} = -\langle P\rangle \tag{29}$$

Let us compare equation (29) with the well known thermodynamic relation

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} - T\left(\frac{\partial P}{\partial T}\right)_{N,V} = \left(\frac{\partial E}{\partial V}\right)_{T,N} + \left(\frac{1}{T}\right)\left(\frac{\partial P}{\partial(\frac{1}{T})}\right)_{N,V} = -P \tag{30}$$

One can easily conclude that $\boldsymbol{\beta} = \frac{constant}{T} = \frac{1}{k_B T}$, where $\boldsymbol{k_B}$ is well known Boltzmann constant.

5. Idea of Partition function

Equations (8) and (24) given above represent the canonical distribution function

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

It has a very interesting feature worth mentioning which is clear from the graph of $\boldsymbol{P_r}$versus $\boldsymbol{E_r}$ shown in figurec 2 below.

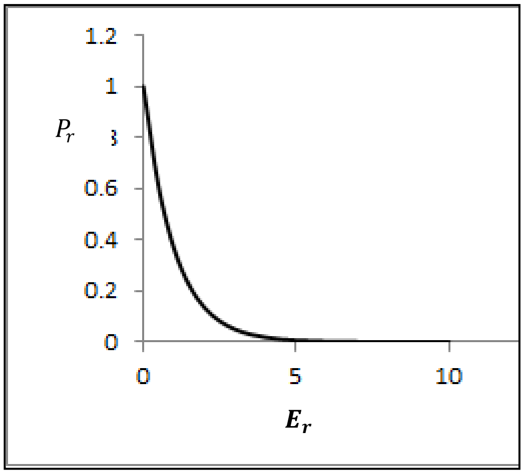

Figure 2 Canonical probability distributionof a state $\boldsymbol{E_r}$

As the energy of the state E_r increases its probability decreases exponentially compared to low energy states, clearly showing that probability distribution is not uniform unlike in micro canonical case where it is uniform with all states having equal probability.

The denominator, conventionally represented by Z, $Z = \sum_r \mathrm{e}^{-\beta E_r}$ is called the canonical partition function or canonical sum over the states. It is obviously a function of $T$and via E_r a function of $N$and V, i.e $Z(N, V, T)$. The partition function can be a function of any other parameter on which E_r depends. Knowledge of partition function is the most important result of the statistical mechanics, since once it is known than all equilibrium physical properties of the macroscopic system under consideration can be known from it. Richard Feynmann in his book on statistical mechanics described partition function as the summit of statistical mechanics. He expressed it in following words:

> *Entire subject is either the slide down from the summit, as the principle is applied to various cases, or climb up to where the fundamental law is derived and the concept of thermal equilibrium and temperature T are clarified.*

6. Partition function and Thermodynamics

In the following we discuss the

6.1 Average Energy of the thermodynamic system

Let us look at the equation (25) which represents average energy written in canonical ensemble. It can be written in terms of partition function as

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln\sum_r e^{-\beta E_r} = -\frac{\partial}{\partial\beta}\ln Z = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} \tag{31}$$

This further provides us a way to calculate the specific heat in terms of Z.

6.2 Average Pressure and Average of Other Generalised Forces

We know in general that a thermodynamic system under consideration has number of external parameters symbolic written as $X_1, X_2, X_3 \ldots\ldots\ldots\ldots\ldots X_k$. If such an external parameter is changed by an infinitesimal amount from $X_i \to X_i + dX_i$, this causes a change in its energy as

$$dE = \sum_i \frac{\partial E}{\partial X_i}\, dX_i \tag{32}$$

Here $\boldsymbol{d}$E is the amount of work done by the generalized force $\boldsymbol{F_i} = \frac{\partial \boldsymbol{E}}{\partial \boldsymbol{X_i}}$. Now if we recall $\boldsymbol{V}$ as an external parameter the generalized force corresponding to that is pressure $\boldsymbol{P} = -\frac{\partial \boldsymbol{E}}{\partial \boldsymbol{V}}$. The average of pressure can be written as

$$\langle \boldsymbol{P} \rangle = \frac{\sum_r \frac{\partial E_r}{\partial V} e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \tag{33}$$

Thus average of the generalized force $\boldsymbol{F}$ for the external parameter $\boldsymbol{X}$ can be written as

$$\langle \boldsymbol{F} \rangle = \frac{\sum_r \frac{\partial E_r}{\partial X} e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial X} \tag{34}$$

6.3Entropy

Partition function of $\boldsymbol{Z}$ is a function of $(\boldsymbol{V}, \boldsymbol{T})$ i.e. $\boldsymbol{Z} = \boldsymbol{Z}(\boldsymbol{V}, \boldsymbol{T})$ or of $(\boldsymbol{V}, \boldsymbol{\beta})$i.e. $\boldsymbol{Z} = \boldsymbol{Z}(\boldsymbol{V}, \boldsymbol{\beta})$. Thus

$$d(\ln Z) = \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial V} dV \tag{35}$$

Using equation (31) and (33), we have

$$d(\ln Z) = -E d\beta + \beta P dV + \beta dE - \beta dE \tag{36}$$

Or

$$d(\ln Z) = -\ d(E\beta) + \beta P dV + \beta dE \tag{37}$$

Or

$$d(\ln Z + E\beta) = \beta P dV + \beta dE = \frac{1}{k_B}\left(\frac{P}{T} dV + \frac{1}{T} dE\right) \tag{38}$$

Since$\frac{P}{T} dV + \frac{1}{T} dE = dS$, we have

$$S = \mathrm{k_B}(\ln Z + E\beta) \tag{39}$$

6.4Helmholtz Free Energy (F)

We know Helmholtz free energy is given by $\boldsymbol{F = E - TS}$, using equation (39) we have

$$\boldsymbol{F = E - T(\mathrm{k_B}(\ln Z + E\beta)) = -k_B T \ln Z} \tag{40}$$

7.Degenerate Energy Levels, Probability Distribution and Partition Function

In actual physical systems there is high degree of degeneracy with a set of states, $\boldsymbol{g_r}$ in number called degeneracy, having same energy $\boldsymbol{E_r}$. It is expected that these $\boldsymbol{g_r}$ states are equally likely to occur and probability is scaled up by the degeneracy $\boldsymbol{g_r}$ of the state $\boldsymbol{E_r}$. In such a case equation (8) for probability of the system to be in the state $\boldsymbol{E_r}$ becomes

$$\boldsymbol{P_r = \frac{\mathrm{g_r\, e}^{-\beta E_r}}{\sum_r \mathrm{g_r\, e}^{-\beta E_r}}} \tag{41}$$

Furthermore, in a macroscopic system the energy levels $\boldsymbol{E_i}$ of the system are bunched together very closely. One finds that in such a case, in a small interval $\boldsymbol{dE}$ of energy around $\boldsymbol{E}$, a very large number of energy levels lie, forming almost a continuum. Therefore, $\boldsymbol{E}$ can be treated as a continuous variable and define $\boldsymbol{P(E)dE}$ as the probability that the system of the canonical ensemble has the energy in the interval $\boldsymbol{dE}$ around $\boldsymbol{E}$ which is proportional to single state probability $\boldsymbol{\mathrm{e}^{-\beta E}}$ multiplied by number of energy states $\boldsymbol{g(E)dE}$ lying in the interval $\boldsymbol{dE}$, where $\boldsymbol{g(E)}$ is called density of states. Thus

$$\boldsymbol{P(E)dE \propto e^{-\beta E}\, g(E)dE} \tag{42}$$

On normalization this becomes

$$\boldsymbol{P(E)dE = \frac{e^{-\beta E}\, g(E)dE}{\int_0^\infty e^{-\beta E}\, g(E)dE}} \tag{43}$$

The partition function in this case becomes

$$\boldsymbol{Z(\beta) = \int_0^\infty e^{-\beta E}\, g(E)dE} \tag{44}$$

It is worth noting here that $\boldsymbol{Z(\beta)}$ is the laplace transform of density of state $\boldsymbol{g(E)}$ and the laplace transform can be inverted to give the density of states

$$g(E) = \frac{1}{2\pi i}\int_{\beta' - i\infty}^{\beta' + i\infty} Z(\beta)e^{\beta E}\ d\beta \quad (\beta' > 0) \tag{45}$$

The expression for the average value of a physical quantity f can be written as

$$\langle f\rangle = \frac{\int_0^\infty f(E)\, e^{-\beta E}\, g(E)dE}{\int_0^\infty e^{-\beta E}\, g(E)dE} \tag{46}$$

8. Partition Functionin Phase Space

For the sake of completeness, it is worth mentioning here that the formalism developed above can be applied to both classical as well as quantum mechanical systems. In the case of classical system this formalism can be expressedin the language of phase space. Let us recall the definition of ensemble average encountered in module XII:

$$\langle f\rangle = \frac{\int \rho(q,p)f(p,q)d^{3N}q\ d^{3N}\mathrm{p}}{\int \rho(q,p)d^{3N}q\ d^{3N}\mathrm{p}} \tag{47}$$

Here $\rho(q,p)$ is the phase space density telling us the probability of finding a representative point near (q,p) which ultimately depends on the Hamiltonian $H(q,p)$of the system. In canonical ensemble, therefore,

$$\rho(p,q) \propto e^{-\beta H(q,p)} \tag{48}$$

Thus (47) becomes

$$\langle f\rangle = \frac{\int e^{-\beta H(q,p)}f(p,q)d^{3N}q\ d^{3N}\mathrm{p}}{\int e^{-\beta H(q,p)}d^{3N}q\ d^{3N}\mathrm{p}} \tag{49}$$

Once again we note that the denominator is related to the partition function provided phase space volume is suitably modified by replacing the factor $d^{3N}q\, d^{3N}\mathrm{p} \rightarrow \frac{(d^{3N}q\, d^{3N}\mathrm{p})}{\mathrm{N!h^{3N}}}$, enumerating the distinct number of quantum states.

Therefore, partition function for classical systems is

$$\boldsymbol{Z_N(V,T) = \frac{1}{N!\,h^{3N}} \int e^{-\beta H(q,p)} d^{3N}q\; d^{3N}\mathrm{p}} \tag{50}$$

With integration extending over the whole phase space.

9. Factorability of Partition Function

Before we go over to apply the results derived above to physical systems, let us note another significant property of the partition function called factorability in the case of non interacting systems with no quantum correlations.

Let us take a system of N independent, non interacting entities (e.g. atoms/molecules in an ideal gas, small vibrational modes in a solid such as phonons etc.) such that Hamiltonian of such a system can be written as

$$\boldsymbol{H = \sum_i H_i} \tag{51}$$

Where $\boldsymbol{H_i}$ is the Hamiltonian for a single entity of the system. So the partition function of the system as given in equation (50) becomes

$$\boldsymbol{Z_N(V,T) = \frac{1}{h^{3N}N!} \int e^{-\beta \sum_i H_i(q_i,p_i)} \prod_{I=1}^{N} d^3q_i d^3\mathrm{p_i}} \tag{52}$$

Or

$$\boldsymbol{Z_N(V,T) = \frac{1}{N!}\left[\frac{1}{h^3}\int e^{-\beta H_i(q_i,p_i)} d^3q_i d^3\mathrm{p_i}\right]^N = \frac{1}{N!}[Z_1(V,T)]^N} \tag{53}$$

Where

$$\boldsymbol{Z_1(V,T) = \frac{1}{h^3}\int e^{-\beta H_i(q_i,p_i)} d^3q_i d^3\mathrm{p_i}} \tag{54}$$

Result (53) represents the factorability of the partition function for noninteracting entities in a system. This conclusion remains valid for non-interacting entities even when the entities have internal degrees of motion.

10. Applications

Now we will look at some prototype applications of canonical ensemble and simplicity with results can be obtained.

10.1 A Two Level System

Let us begin with a simple two level system, i.e. a system which has only two states accessible, consisting of Nidentical non-interacting particles, Figure 1. The lower level is the ground state of the system with zero energy and the other level is the first excited state of the system with energy $\boldsymbol{\epsilon}$. Both the states are non-degenerate. The higher energy states are not available to the system, because they exceed the total energy available to the system.

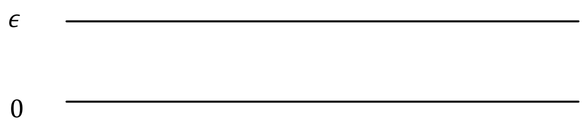

Figure 3A two non-degenerate level system

The single particle partition function can be written as

$$\boldsymbol{Z_1 = (1 + e^{-\epsilon})} \tag{55}$$

So that total partition function can be written as

$$\boldsymbol{Z = \left[1 + e^{-\beta\epsilon}\right]^N} \tag{56}$$

Using the relation of thermodynamic quantities, we can get Helmholtz free energy as

$$\boldsymbol{F = -\frac{1}{\beta}\ln Z = -\frac{N}{\beta}\ln\left[1 + e^{-\beta\epsilon}\right] = -Nk_BT\ln\left[1 + e^{-\epsilon/k_BT}\right]} \tag{57}$$

Internal energy $\boldsymbol{E}$ is given as

$$\boldsymbol{E = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{N\epsilon}{(1+e^{\beta\epsilon})}} \tag{58}$$

Entropy can be obtained as follows

$$\boldsymbol{S = \mathrm{k_B}(\ln Z + E\beta) = Nk_B\left(\ln\left(1+e^{-\frac{\epsilon}{k_BT}}\right) + \frac{\frac{\epsilon}{k_BT}}{\left(1+e^{\frac{\epsilon}{k_BT}}\right)}\right)} \tag{59}$$

10.2 Classical Ideal Gas

In module VIII we discussed at length classical ideal gas from statistical mechanics route. Here we shall revisit this from the point of view of canonical ensemble. A classical ideal gas is a system of $\boldsymbol{N}$ identical monoatomic molecules, confined in a volume $\boldsymbol{V}$ at temperature $\boldsymbol{T}$ with no interaction among the molecules. Hamiltonian of such a system is merely a sum of kinetic energies of each molecule, which can be written as

$$\boldsymbol{H(q,p) = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m}\right)} \tag{60}$$

Using (53), partition function can be written as

$$\boldsymbol{Z_N(V,T) = \frac{1}{N!}\left[\frac{1}{h^3}\int e^{-\beta\frac{p^2}{2m}} d^3\, q\, d^3\mathrm{p}\right]^N} \tag{61}$$

Or

$$\boldsymbol{Z_N(V,T) = = \frac{1}{N!}\left[\frac{1}{h^3}\int d^3\, q \int_0^\infty e^{-\beta\frac{p^2}{2m}} d^3\mathrm{p}\right]^N} \tag{62}$$

First integral in (62) is over space coordinates giving $\boldsymbol{V^N}$ giving

$$Z_N(V,T) = = \frac{V^N}{N!\,h^{3N}}\left[\int_0^\infty e^{-\beta\frac{p^2}{2m}} d^3\mathrm{p}\right]^N \tag{63}$$

Equation (63) can be further simplified by expanding in polar coordinates to give

$$Z_N(V,T) = = \frac{V^N}{N!\,h^{3N}}\left[\int_0^\infty e^{-\frac{p^2}{2mk_BT}}\, 4\pi\mathrm{p}^2 dp\right]^N \tag{64}$$

Using the standard integral $\int_0^\infty e^{-\alpha x^2} x^2 dx = \frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{\frac{1}{2}}$, we get

$$Z_N(V,T) = = \frac{1}{N!}\left[\frac{\mathrm{V}}{\mathrm{h}^3}(2\pi\, m\, k_BT)^{\frac{3}{2}}\right]^N \tag{65}$$

Now we can get thermodynamic functions using Stirling’s formula.

Helmholtz free energy is given as

$$F = -k_BT\ln Z = Nk_BT\left[\ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi m\, k_BT}\right)^{\frac{3}{2}}\right) - 1\right] \tag{66}$$

Once we have $\boldsymbol{F}$, all other thermodynamic properties can be derived immediately.

Pressure:

$$P = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \frac{Nk_BT}{V} \tag{67}$$

Equation (67) is the equation of state of an ideal gas.

Chemical potential:

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = k_BT\ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi m\, k_BT}\right)^{\frac{3}{2}}\right) \tag{68}$$

Entropy:

$$\boldsymbol{S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = Nk_B\left[\ln\left(\frac{V}{N}\left(\frac{h^2}{2\pi m\, k_B T}\right)^{\frac{3}{2}}\right) + \frac{5}{2}\right]} \tag{69}$$

Internal Energy:

We know $\boldsymbol{E = F + TS}$, using (66) and (69), we get

$$\boldsymbol{E = \frac{3}{2}Nk_BT} \tag{70}$$

10.3Maxwell Boltzmann Distribution

One of the very interesting applications of canonical distribution in classical physical systems is to obtain the distribution of velocities in a gas of an ideal gas. The aim of Maxwell Boltzmann distribution is to find the number of molecules in the phase space volume $\boldsymbol{d^3r\, d^3}$paround the representative point $(\vec{\boldsymbol{r}}, \vec{\boldsymbol{p}})$ as shown in the figure below

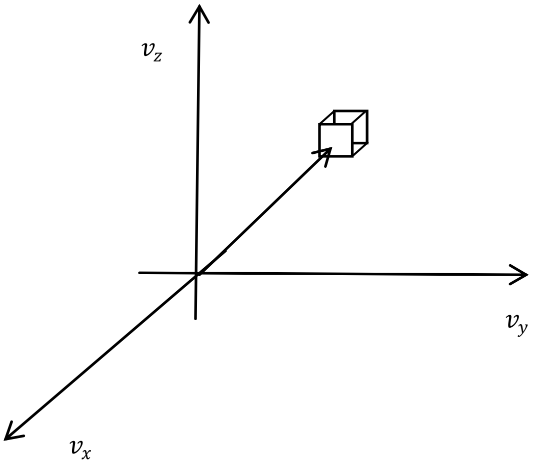

Figure 4 Infinitesimal volume in velocity space around a velocity point

The total energy of the gas, consisting of N molecules in volume $\boldsymbol{V}$ is

$$\boldsymbol{E = \sum_{i=1}^{N}\frac{p^2}{2m}} \tag{71}$$

The probability that molecule of the gas has velocity lying between $\vec{v}$and $\vec{v}+\overrightarrow{dv}$, given by canonical distribution is

$$P(\vec{r},\overrightarrow{v})d^3r\ d^3v = constant \times e^{-\frac{mv^2}{2k_BT}} d^3r\ d^3v \tag{72}$$

To get the Maxwell Boltzmann distribution, let $f(\vec{r},\vec{v})d^3r\ d^3v$be the mean number of particles in the velocity space volume $d^3r\ d^3v$where $f(\vec{r},\overrightarrow{v})$ is velocity distribution. This number is also proportional to $P(\vec{r},\overrightarrow{v})d^3r\ d^3v$i.e.

$$f(\vec{r},\vec{v})d^3r\ d^3v = \ constant \times e^{-\frac{mv^2}{2k_BT}} d^3r\ d^3v$$

This number when integrated over whole velocity space volume is equal to the total number of particles.

Thus

$$constant \iint e^{-\frac{mv^2}{2k_BT}} d^3r\ d^3v = \mathrm{N} \tag{73}$$

Or

$$Constant = \frac{N}{\int d^3r \int e^{-\frac{mv^2}{2k_BT}} d^3v} = \frac{N}{V\int e^{-\frac{mv^2}{2k_BT}}\ 4\pi v^2 dv} \tag{74}$$

Therefore,

$$constant = \frac{N}{V}\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}} \tag{75}$$

$$f(\vec{r},\vec{v}) = \frac{N}{V}\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_BT}} \tag{76}$$

Here we note that because of isotropic nature of the system, $f(\vec{r},\vec{v})$ is independent of position so that $f(\vec{r},\vec{v})$= $f(\vec{v}) \equiv f(v)$.

To find the number of molecules in the range $\boldsymbol{v}$and $\boldsymbol{v+dv}$, we multiply $\boldsymbol{f(v)}$ with the volume of the velocity shell in velocity space i.e. $\boldsymbol{4\pi v^2 dv}$ thus we get

$$\boldsymbol{4\pi v^2 f(v)dv = 4\pi n\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_BT}}\,dv} \tag{77}$$

Equation (77) gives the famous Maxwell Distribution of the speed of molecules, where $\boldsymbol{n = \frac{N}{V}}$. Figure 5 gives this distribution of speeds $\boldsymbol{\frac{4\pi v^2 f(v)}{n\left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}}}}$ against$\boldsymbol{\left(\frac{2k_BT}{m}\right)^{\frac{1}{2}}\ v}$

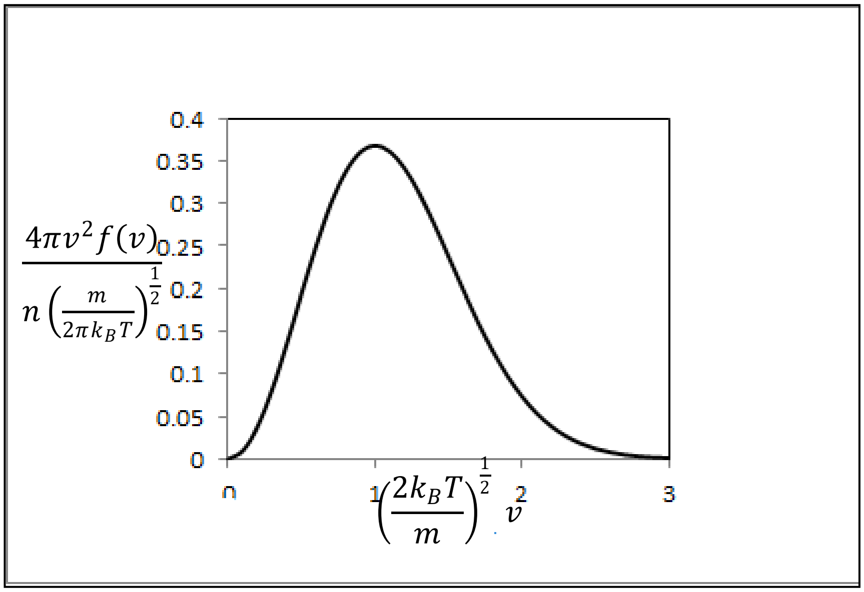

Figure 5 Maxwell Boltzmann distribution for speed of molecules in an ideal gas against v

Figure 5 and Figure 6, show that most of the molecules of an ideal gas have speed around a value which is dependent on temperature. The most provable speed can be obtained by taking

$$\boldsymbol{\frac{df(v)}{dv} = 0} \tag{78}$$

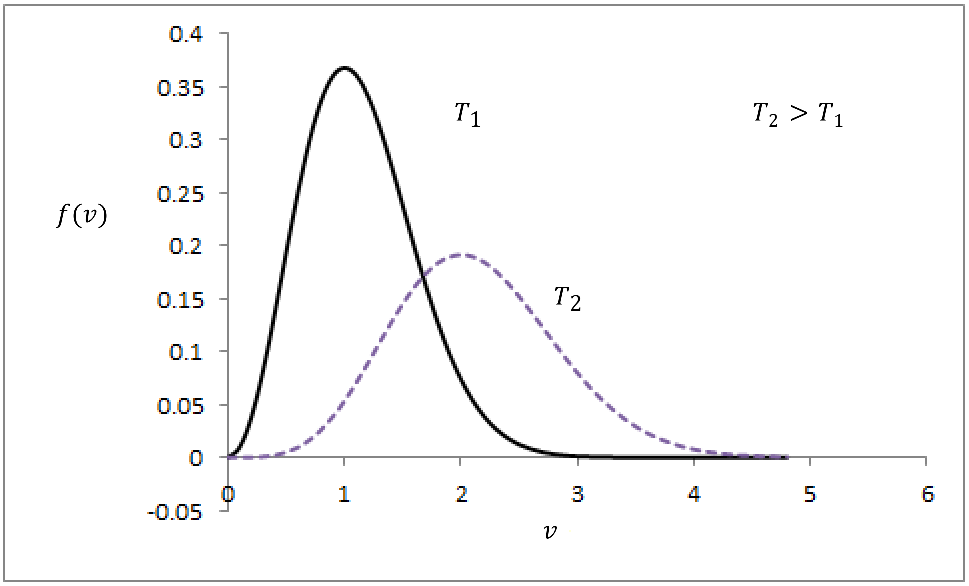

Figure 6 Maxwell distribution of speeds for two different temperatures ($\boldsymbol{T_2 = 2T_1}$)

This gives

$$\boldsymbol{v_{max} = \sqrt{\frac{2k_BT}{m}}} \tag{79}$$

Mean velocity of the gas is zero, since as many molecules move in the direction of positive axis as in the direction of negative axis. However we can find out average speed $\boldsymbol{\bar{v}}$ and root mean square speed $\boldsymbol{v_{rms}}$.

Average speed($\boldsymbol{\bar{v}}$):

$$\langle v\rangle = \frac{1}{n}\int_0^\infty v\, f(v)\ dv\ = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}}\int_0^\infty v^3 e^{-\frac{mv^2}{2k_BT}}dv$$

Putting$\boldsymbol{\frac{mv^2}{2k_BT} = \xi^2}$ such that $\boldsymbol{vdv = \frac{\xi\ \ d\xi}{\frac{m}{2k_BT}}}$ we have

$$\boldsymbol{\langle v\rangle = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}}\left(\frac{2k_BT}{m}\right)^2\int_0^\infty \xi^3 e^{-\xi^2}\ d\xi}$$

The integral appearing above is a standard integral such that $\int_0^\infty \xi^3 e^{-\alpha\xi^2}\, d\xi = \frac{1}{2\alpha^2}$, therefore, we have

$$\langle v \rangle = \sqrt{\frac{8}{\pi}\frac{k_B T}{m}} \tag{80}$$

Root mean square speed(v_{rms})

Mean square speed, i.e mean of the square of the velocity can be calculated as

$$\langle v^2 \rangle = \frac{1}{n}\int_0^\infty v^2\, f(v)\, dv \tag{81}$$

Which can be further written as,

$$4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}}\left(\frac{2k_B T}{m}\right)^{\frac{5}{2}}\int_0^\infty \xi^4 e^{-\xi^2}\, d\xi$$

The integral appearing above is a standard integral such that $\int_0^\infty \xi^4 e^{-\alpha\xi^2}\, d\xi = \frac{3}{8}\left(\frac{\pi}{\alpha^5}\right)^{\frac{1}{2}}$, therefore, we have

$$\langle v^2 \rangle = \frac{3k_B T}{m} \tag{82}$$

Thus,

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} \tag{83}$$

Here are some interesting conclusions.

- Each these three velocities are $\propto \sqrt{T}$, therby implying that these increase as temperature T increase.

- $\boldsymbol{v_{max} > \bar{v} > v_{rms}}$and are in the ratio of $\sqrt{\mathbf{2}}:\sqrt{\frac{\mathbf{8}}{\boldsymbol{\pi}}}:\sqrt{\mathbf{3}}$

5. Summary

In this module we have learnt

- That canonical ensemble corresponds to acollection of exact replicas of a systemwhere energy can be exchanged with T= $\boldsymbol{constant}$, $\boldsymbol{N = constant}$ and $\boldsymbol{V = constant}$.
- The application of *system-heat bath approach*and method of most probable values via Lagrange's undetermined multipliers to derive canonical distribution function for a system

$\boldsymbol{P_r} = \frac{\mathrm{e}^{-\beta E_r}}{\sum_r \mathrm{e}^{-\beta E_r}}$for a system with non-degenerate energy levels
$\boldsymbol{P_r} = \frac{g_r \mathrm{e}^{-\beta E_r}}{\sum_r g_r \mathrm{e}^{-\beta E_r}}$for a system with levels $\boldsymbol{E_r}$of degeneracy $\boldsymbol{g_r}$each

- That partition function is the key concept in statistical mechanics, from which all the thermodynamic properties can be derived. The canonical partition function can be written as

Type of system	Canonical Partition Function
Quantum mechanical (non-degenerate)	$\boldsymbol{Z = \sum_r \mathrm{e}^{-\beta E_r}}$
Quantum mechanical (degenerate)	$\boldsymbol{Z = \sum_r g_r \mathrm{e}^{-\beta E_r}}$
Quantum Mechanical with density of states $\boldsymbol{g(E)}$,	$\boldsymbol{Z(\beta) = \int_0^\infty e^{-\beta E}\, g(E) dE}$
Classical system in phase space	$\boldsymbol{Z_N(V,T) = \frac{1}{N!\,h^{3N}} \int e^{-\beta H(q,p)} d^{3N}q\, d^{3N}\mathrm{p}}$

- That partition function of a non-interacting system without quantum correlations is factorizable

$$\boldsymbol{Z_N(V,T) = \frac{1}{N!}\left[\frac{1}{h^3}\int e^{-\beta H_i(q_i,p_i)} d^3q_i d^3\mathrm{p_i}\right]^N = \frac{1}{N!}[Z_1(V,T)]^N}$$

- How all the thermodynamic properties can be written in terms of partition function

Average energy $\langle E\rangle$	$= -\frac{\partial}{\partial\beta}\ln\ Z = -\frac{1}{Z}\frac{\partial Z}{\partial\beta}$
Average pressure $\langle P\rangle$	$= \frac{\sum_r \frac{\partial E_r}{\partial V} e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$
Generalised Force $\langle F\rangle$	$= \frac{\sum_r \frac{\partial E_r}{\partial X} e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial X}$
Entropy S	$= \mathrm{k_B}(\ln Z + E\beta)$
Helmholtz free energy F	$= -k_B T \ln Z$

- How the properties from the knowledge of partition function of the following systems their thermodynamic properties can be obtained:

  i. A Two Level System

Partition function	$Z = Z_1^N = \left[1 + e^{-\beta\epsilon}\right]^N$
Helmholtz free energy	$F = -Nk_BT\ln\left[1 + e^{-\epsilon/k_BT}\right]$
Internal Energy	$E = \frac{N\epsilon}{(1 + e^{\beta\epsilon})}$

  ii. Classical Ideal Gas

Partition function	$Z_N(V,T) == \frac{1}{N!}\left[\frac{V}{\mathrm{h}^3}(2\pi\, m\, k_BT)^{\frac{3}{2}}\right]^N$
Helmholtz free energy	$F = Nk_BT\left[\ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi m\, k_BT}\right)^{\frac{3}{2}}\right) - 1\right]$

- How to derive Maxwell_Boltzmanndistribytion of speeds and calculate maximum speed, mean speed and root mean square speed

Maxwell --Boltzmann Distribution of speeds	$f(\,v) = \frac{N}{V}\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_BT}}$
Maximum speed	$v_{max} = \sqrt{\frac{2k_BT}{m}}$

Mean speed	$\langle v \rangle = \sqrt{\frac{8}{\pi}\frac{k_B T}{m}}$
Root mean square speed	$v_{rms} = \sqrt{\frac{3k_B T}{m}}$

Appendices

A1 Lagrange's Method of Undetermined Multipliers

In this module we used Lagrange's method of undetermined multipliers to derive canonical distribution. In this appendix a very brief mathematical basis of this method is provided. This method addresses the problem of finding extremum of a function under constraining conditions imposed by physical requirements such as particle conservation and energy conservation.

Problem can be defined as follows. Suppose we have a function $f(x_1, x_2, x_3)$ whose extremum is to be found under the conditions

$$g_i(x_1, x_2, x_3) = C_i, i = 1, 2 \tag{84}$$

Without the constraining condition, problem would have been very simply solved by requiring variation in $f(x, y, z)$ zero for small variations of the variables x, y, z on which the function depends i.e.

$$\delta f = \left(\frac{\partial f}{\partial x_1}\delta x_1 + \frac{\partial f}{\partial x_2}\delta x_2 + \frac{\partial f}{\partial x_3}\delta x_3\right) = 0 \tag{85}$$

Since there are no constraints this amounts to requiring separately

$$\frac{\partial f}{\partial x_1} = 0$$

$$\frac{\partial f}{\partial x_2} = 0$$

$$\frac{\partial f}{\partial x_3} = 0$$

However, if the constraining conditioning must be satisfied, $\delta x_1, \delta x_2$ and δx_3 can not be chosen arbitrarily and must satisfy simultaneously the conditions

$$\delta g_1 = \left(\frac{\partial g_1}{\partial x_1}\delta x_1 + \frac{\partial g_1}{\partial x_2}\delta x_2 + \frac{\partial g_1}{\partial x_3}\delta x_3\right) = 0$$

$$\delta g_2 = \left(\frac{\partial g_2}{\partial x_1}\delta x_1 + \frac{\partial g_2}{\partial x_2}\delta x_2 + \frac{\partial g_2}{\partial x_3}\delta x_3\right) = 0$$

The above two equations can be simultaneously for δx_1 and δx_2 in terms of δx_3, and substituted in equation (84) such that δx_3can be chosen arbitrarily and its coefficients must vanish identically giving the extremum condition.

An alternative way involves Lagrange's undetermined multipliers λ_1 and λ_2 and subtracting these from (87) in such a way as to require

$$\left(\frac{\partial f}{\partial x_1} - \lambda_1\frac{\partial g_1}{\partial x_1} - \lambda_2\frac{\partial g_2}{\partial x_1}\right) = 0$$

$$\left(\frac{\partial f}{\partial x_2} - \lambda_1\frac{\partial g_1}{\partial x_2} - \lambda_2\frac{\partial g_2}{\partial x_2}\right) = 0$$

$$\left(\frac{\partial f}{\partial x_3} - \lambda_1\frac{\partial g_1}{\partial x_3} - \lambda_2\frac{\partial g_2}{\partial x_3}\right) = 0$$

The above coupled equations can be solved for x_1, x_2 and x_3 in terms of λ_1 and λ_2, which when substituted in equations (84) can be solved for λ_1 and λ_2 to provide extrema corresponding to the given function.

This procedure can be extended for a function of many variables, under more than one constraint.

Example:

Let us try to find an extremum of the function $f(x, y, z) = ax + by + cz$ under the condition that $g(x, y, z) = x^2 + y^2 + z^2 = 1$

We calculate the three equations

$$\left(\frac{\partial f}{\partial\, x} - \lambda_1\frac{\partial g_1}{\partial\, x}\right) = a - 2\lambda x = 0$$

$$\left(\frac{\partial f}{\partial y} - \lambda_1\frac{\partial g_1}{\partial y}\right) = b - 2\lambda x = 0$$

$$\left(\frac{\partial f}{\partial z}-\lambda_1\frac{\partial g_1}{\partial z}\right)=c-2\lambda x=0$$

From here we obtain the values of x, y and z in terms of the undetermined multiplier λ. The undetermined multiplier can be obtained by substituting it in the condition $g(x,y,z)=x^2+y^2+z^2=1$, which gives

$$\frac{a^2}{4\lambda^2}+\frac{a^2}{4\lambda^2}+\frac{a^2}{4\lambda^2}=1$$

And hence $\lambda=\pm\frac{\sqrt{a^2+b^2+c^2}}{2}$giving extremum of $f$at $x=\pm\frac{a}{\sqrt{a^2+b^2+c^2}}, y=\pm\frac{b}{\sqrt{a^2+b^2+c^2}}$, and $z=\pm\frac{c}{\sqrt{a^2+b^2+c^2}}$. with an extremal value of $\pm\sqrt{a^2+b^2+c^2}$

A2 Some Important Integrals:

In this module we have used integrals which are of the type

$$I_\nu=\int_0^\infty x^\nu e^{-\alpha x^2}\,dx=\frac{1}{2}\frac{1}{\alpha^{\frac{\nu+1}{2}}}\Gamma\left(\frac{\nu+1}{2}\right)\ for\ \nu>-1 \qquad (86)$$

This integral has an interesting property

$$\frac{\partial I_\nu}{\partial\alpha}=-I_{\nu+2} \qquad (87)$$

Such that following integrals can be easily evaluated,using the fact that $\Gamma(\mu+1)=\mu\,\Gamma(\mu)$, where μ can be a rational number (fraction) and has a form $\Gamma(\mu+1)=\mu\,(\mu-1)(\mu-2)\ldots..(1+p)p\,\Gamma(p), where\ 0<p\leq 1$. For $\mu=n$, $\Gamma(n+1)=n!$. Also $\Gamma\left(\frac{1}{2}\right)$. Thus following useful integrals can be obtained.

$$I_0=\int_0^\infty e^{-\alpha x^2}\,dx=\frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{\frac{1}{2}}$$

$$I_1=\int_0^\infty xe^{-\alpha x^2}\,dx=\frac{1}{2\alpha}$$

$$I_2=\int_0^\infty x^2e^{-\alpha x^2}\,dx=\frac{1}{4}\left(\frac{\pi}{\alpha^3}\right)^{\frac{1}{2}}$$

$$I_3=\int_0^\infty x^3e^{-\alpha x^2}\,dx=\frac{1}{2\alpha^2}$$

$$I_4=\int_0^\infty x^4e^{-\alpha x^2}\,dx=\frac{3}{8}\left(\frac{\pi}{\alpha^5}\right)^{\frac{1}{2}}$$

A3 Excel Spreadsheet for plotting canonical distribution function and Maxwell Boltzmann distribution function