2. THERMODYNAMICS and ENSEMBLES
(Part B)

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2.4 Ensembles

An ensemble is a collection of replicas of member systems which have identical macroscopic parameters, but whose microscopic descriptions of these members can be and are quite different. Different ensembles are described below.

2.4.1 Isolated System (The micronomical Ensemble)

In trying to give statistical description to a system, one always has some information available about the physical system under consideration. A representative statistical ensemble is then constructed in such a way that all the systems in the ensemble satisfy conditions consistent with one's information about the system.
An isolated system is clearly an important example for consideration. Whenever one is dealing with a system that interacting with another, it is always possible to reduce the situation to the case of an isolated system by considering the combined system.
If V is the only relevant external parameter, then an isolated system consists of a given number of N particles in a specified volume V, the constant energy of the system lying in the range [E, E + δE]. Probability statements are then made with reference to an ensemble which consists of many such systems. At equilibrium, the system is equally likely to be found in any one of its accessible states. Then if the energy of system in a state r is E_r, the probability P_r of finding the system in this state is

$$P_r = C \;,\; E < E_r < E + \delta E \;\text{ and }\; P_r = 0 \;\text{ otherwise} \qquad (2.113)$$

An isolated system in equilibrium can be represented by an ensemble of systems distributed according to the above prescription. This is called a **microcanonical ensemble** .
Example: <u>Ideal Gas in the Classical Limit</u> :
For a collection of N particles which are non-interacting,

$$H = \frac{1}{2m}\sum_{i=1}^{N} \vec{p}_i^{\,2} = E \qquad (2.114)$$

The number of states Ω(E) lying between the energies E and E + δE is equal to the number of cells in phase space contained between these energies.

$$\begin{aligned}\Omega(E) &= \frac{1}{h^{3N}}\int_E^{E+\delta E}\ldots\int d^3p_1\ldots d^3p_N \;\; d^3q_1\ldots d^3q_N \\ &= \frac{V^N}{h^{3N}}\int_E^{E+\delta E}\ldots\int \; d^3p_1\ldots d^3p_N\end{aligned} \qquad (2.115)$$

since E is independent of the co-ordinates of the molecules.

$$\begin{aligned}&or \quad \Omega(E) = \frac{V^N}{h^{3N}}\chi(E) \\ &where \quad \chi(E) = \int_E^{E+\delta E}\ldots\int d^3p_1\ldots d^3p_N .\end{aligned} \qquad (2.116)$$

From Eq. (2.114), we have,

$$2mE = \sum_{i=1}^{N} \vec{p}_i^{\,2} \tag{2.117}$$

The sum contains 3N terms. In 3N dimensional (p) space this describes a sphere of radius $(2mE)^{1/2}$. $\chi(E)$ is then equal to the volume of phase space lying in the spherical shell between the radii $R(E)$ and $R(E + \delta E)$. Consider first how to calculate the volume of an 'n-sphere' of radius R, i.e.,

$$\Gamma_n(R) = \int_{\sum x_i^2 < R^2} dx_1 ....dx_n \tag{2.118}$$

Then,

$$\Gamma_n(R) = C_n R^n \tag{2.119}$$

To find C_n, consider

$$\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dx_2 .... \int_{-\infty}^{+\infty} dx_n \; e^{(-x_x^2 + x_2^2 + ...+ x_n^2)} \tag{2.120}$$

$$= \left(\int_{-\infty}^{+\infty} dx \; e^{-x^2} \right)^n = \pi^{n/2} \tag{2.121}$$

But Eq. (2.120) is also equal to

$$= \int_0^{\infty} dR \, S_n(R) \; e^{-R^2} \tag{1.122}$$

Where, $S_n(R) = \dfrac{d\Gamma_n(R)}{dr}$ = the surface area of an n-sphere of radius R. Therefore,

$$= nC_n \int_0^{\infty} dR \; R^{n-1} e^{-R^2} = \frac{nC_n}{2} \int_0^{\infty} dt \; t^{\frac{n}{2}-1} \; e^{-t} = \frac{n}{2} C_n \left(\frac{n}{2} - 1 \right) \tag{2.123}$$

$$\therefore C_n = \frac{\pi^{n/2}}{(n/2)!} \tag{2.124}$$

Therefore, the volume of a shell of thickness *s* is

$$V_s = V_n(R) - V_n(R-s) = C_n[R^n - (R-s)^n] = C_n R^n [1 - (1 - s/R)^n] \tag{2.125}$$

If $sn >> R$, $V_s \sim R^n$ (for n ~10^{23}, this approximation is good).
Therefore,

$$\chi(E) \; \alpha \; (2mE)^{3N/2} \tag{2.126}$$

And
$$\Omega(E) \; \alpha \; V^N (2mE)^{3N/2} \;\; \alpha \;\; V^N E^{3N/2} \tag{2.127}$$

$$\therefore \ln \Omega(E) = const + N \ln V + (3N/2) \ln E \tag{2.128}$$

$$\beta p = \frac{\partial}{\partial V} \ln \Omega = N/V \tag{2.129}$$

Or $pV = NkT$ and $\beta = \dfrac{\partial}{\partial E} \ln \Omega(E) = \dfrac{3N}{2} \dfrac{1}{E}$ so that $E = 3NkT/2$. The entropy is given by

$$S = S(E, V) = k \ln \Omega(E)$$

$$= k[\ln C_{3N} + N\ln\frac{V}{h^3} + \frac{3N}{2}\ln(2mE) \tag{2.130}$$

Now, $C_{3N} = \dfrac{\pi^{3N}}{(3N/2)!}$ .Using Stirling's approximation, *ln L! = L ln L – L*, we get

$$\ln C_{3N} = \ln\pi^{3N/2} - \frac{3N}{2}\ln(3N/2) + 3N/2 \tag{2.130}$$

$$\therefore\ S = Nk[\ln\pi^{3N/2} + \ln(V/h^3) + (3/2)\ln(2mE) - \frac{3N}{2}\ln(3N/2)] + 3Nk/2$$

(2.131)

$$= Nk\ \ln\left(V\left(\pi\frac{2}{3N}\frac{1}{h^2}2mE\right)^{3/2}\right) + Nk/2 \tag{2.122}$$

$$= Nk\ \ln\left(V\left(\frac{4\pi m}{3h^2}\frac{E}{N}\right)^{3/2}\right) + Nk/2$$

(2.133)

Or $$E(S,V) = \left(\frac{3}{4\pi}\frac{h^2}{m}\right)\frac{N}{V^{3/2}}\exp\left(\frac{2}{3}\frac{S}{Nk} - 1\right) \tag{2.134}$$

$$T = \left(\frac{\partial E}{\partial S}\right)_V = \frac{2}{3}\frac{E}{Nk},\ C_v = \frac{3}{2}Nk,\ p = -\left(\frac{\partial E}{\partial V}\right)_s = \frac{2}{3}\frac{E}{V} = \frac{NkT}{V} \tag{2.135}$$

Therefore,

$$S = Nk\ \ln\left(Vu^{3/2}\right) + NS_0, where,\ u = 3/2\,kT\ and\ S_0 = \frac{3k}{2}\left(1 + \ln\frac{4\pi m}{3h^2}\right) \tag{2.136}$$

Consider two ideal gases with N_1 and N_2 particles occupying volumes V_1 and V_2 at the same temperature. Consider the change in entropy when the gases are allowed to mix in a volume $V = V_1 + V_2$. The final temperature is the same. Thus u is unchanged. The change in entropy is given by

$$\therefore\ S = (N_1 + N_2)\ln V - N_1\ln V_1 - N_2\ln V_2 = N_1\ln\frac{V}{V_1} + N_2\ln\frac{V}{V_2} > 0 \tag{2.137}$$

If two gases are different, the result is correct. However, if the two gases are identical, we would get the same increase in entropy (Gibbs' paradox). This is clearly wrong because we can increase entropy indefinitely by pulling off a large number of partitions in a gas. The resolution of the paradox lies in the introduction of the factor (1/N!) in the gas phase volume. Thus, in S, we get additionally, - *ln N ! = N ln N – N*.

$$= Nk\ \ln\left(\frac{V}{N}u^{3/2}\right) + \frac{3Nk}{2}\left(1 + \ln\frac{4\pi m}{3h^2}\right) \tag{2.138}$$

This removes the paradox and makes the entropy additive.

2.4.2 System in Contact with a heat reservoir, The Canonical Distribution

We have already considered the interaction of a system A with a system A′ where A<< A′. Thus A may be a relatively small **macroscopic** system. We ask the question: Under the conditions of equilibrium, what is the probability P_r of finding the system A in any one particular microstate r of energy E_r?

The total energy of the system is, of course, fixed and is given by

$$E^{(0)} = E_r + E' \tag{2.139}$$

Where E_r is the energy of A and E' is the energy of A′. Thus, if A is in the energy state r, the number of states accessible to the combined system is just the number of states accessible to A′ when it has an energy $E' = E^{(0)} - E_r$. Thus the probability of occurunce of the state r for A is given by

$$P_r \;\alpha\; \Omega'(E^{(0)} - E_r) \tag{2.140}$$

$$\text{or}\quad P_r = C\;\Omega'(E^{(0)} - E_r) \tag{2.141}$$

C cab be determined from the condition $\sum_r P_r = 1$. Since A<< A′, $E_r << E^{(0)}$ and we can expand $\ln\,\Omega'(E^{(0)} - E_r)$ about $E^{(0)}$. Thus we get,

$$\ln\,\Omega'(E^{(0)} - E_r) = \ln\Omega'(E^{(0)}) - E_r \frac{\partial}{\partial E'}\ln\Omega' \;\Big|_{E'=E^{(0)}} + ... \tag{2.142}$$

We have neglected higher order terms in E_r as $E_r << E^{(0)}$. But,

$$\frac{\partial}{\partial E'}\ln\Omega' \;\Big|_{E'=E^{(0)}} \equiv \beta \tag{2.143}$$

And this is a constant independent of E_r. β = 1/kT, where, T is the temperature of the heat bath A′. Or,

$$\ln\,\Omega'(E^{(0)} - E_r) = \ln\Omega'(E^{(0)}) - \beta E_r$$

$$\text{or,}\quad \Omega'(E^{(0)} - E_r) = \ln\Omega'(E^{(0)})\, e^{-\beta E_r} \tag{2.144}$$

$$\text{Or,}\quad P_r = C\, e^{-\beta E_r} \tag{2.145}$$

Since, $\sum P_r = 1,\; C^{-1} = \sum_r e^{-\beta E_r}$, and

$$P_r = \frac{e^{-\beta E_r}}{Z} \quad \text{where,} \quad C^{-1} = Z = \sum_r e^{-\beta E_r} \tag{2.146}$$

The probability distribution is called the canonical distribution, and the ensemble of systems all of which are distributed over states according to this distribution is called a **canonical ensemble**. Z is called the canonical partition function.

Before we try to point out the differences between the canonical and the microcanonical distributions, let us take a look at two simple examples of the canonical distribution. The probability of finding A in one particular state of energy is $P_r = C\, e^{-\beta E_r}$. The probability that A has in the range lying between E and E + δE is then given by summing P_r for all the states whose energy lies in this range. Therefore,

$$P(E) = \sum_r P_r \text{ (for } E < E_r < E + \delta E) = C\,\Omega(E)\,e^{-\beta E} \tag{2.147}$$

Where, $\Omega(E)$ is the number of states of A in the energy range E + δE.

Example 2.5 Molecule in an ideal gas

Consider a monatomic gas at temperature T confined in a volume V. If the number density of the molecules is small, then the interaction between them may be neglected. Thus the total energy equals the sum of the energies of all the molecules. Treating the problem classically, we can concentrate on a single molecule. The remaining molecules then constitute a heat reserviour at a temperature T.

$$\therefore E = \frac{p^2}{2m} \tag{2.148}$$

If the position of the molecule lies between r and $r + dr$ and its momentum between p and $p + dp$, then the volume in phase space is $d^3r\, d^3p$. Thus the probability that the molecule has a position between r and $r + dr$ and momentum between p and $p + dp$ is given by multiplying the number of cells in phase space, i.e., $\frac{d^3r\, d^3p}{h^3}$ by the canonical probability distribution. Thus,

$$P(\vec{r}, \vec{p})\, d^3r\, d^3p \propto \frac{d^3r\, d^3p}{h^3} e^{-\beta p^2/2m} \tag{2.149}$$

Since the probability density is independent of r ,

$$P(\vec{p})\; d^3p \propto \int \frac{d^3r\, d^3p}{h^3} e^{-\beta p^2/2m} \propto e^{-\beta p^2/2m}\, d^3p \tag{2.150}$$

$$P'(v)\; d^3v = P(p)\, d^3p = C\; e^{-\beta m v^2/2}\; d^3v \tag{2.151}$$

This is the Maxwell distribution.

Example 2.6 Paramagnetism

Consider N_0 magnetic atoms per unit volume, each with magnetic moment μ and spin half placed in a magnetic field H. Each atom has two sites + and – corresponding to energies $\varepsilon_+ = -\mu H$ and $\varepsilon_- = +\mu H$. Concentrating again on a single atom,

$$P_+ = C e^{-\beta\varepsilon_+} = C e^{\beta\mu H};\; P_- = C e^{-\beta\varepsilon_-} = C e^{-\beta\mu H} \tag{2.152}$$

$$\therefore \qquad \bar{\mu} = \frac{P_+\mu + P_-(-\mu)}{P_+ + P_-} = \mu\frac{e^{\beta\mu H} - e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}} = \mu \tanh\frac{\mu H}{kT} \tag{2.152}$$

Now, tanh y = y for y << 1 and ≈ 1 for y >> 1.

$$\therefore\ \bar{\mu} = \frac{\mu^2 H}{kT}\ for\ \frac{\mu H}{kT} << 1 \quad and \quad \bar{\mu} = \mu\ for\ \frac{\mu H}{kT} >> 1 \tag{2.153}$$

The susceptibility χ is given by $M = \chi H$, where *M* is the magnetic moment per unit volume.

$$\therefore \; \chi = \frac{N_0 \mu^2}{kT}; \quad \frac{\mu H}{kT} << 1 \quad \text{(Curie's Law); and} \quad \chi = N_0 \mu; \quad \frac{\mu H}{kT} >> 1 \qquad (2.154)$$

2.4.4 Mean Value in a Canonical Ensemble

Using P_r from Eq. (2.146), we get for the mean value of energy,

$$\bar{E} = \frac{\sum_r E_r \, e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \qquad (2.155)$$

But, $\sum E_r e^{-\beta E_r} = -\sum \frac{\partial}{\partial \beta} e^{-\beta E_r} = (-\frac{\partial}{\partial \beta}) \sum e^{-\beta E_r} = -\frac{\partial Z}{\partial \beta}$

where, $\quad Z = \sum_r e^{-\beta E_r}. \qquad (2.156)$

Z is the partition function and is a function of temperature.

$$\therefore \quad \bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z \qquad (2.157)$$

Consider now the fluctuations in the energy.

$$\overline{\Delta E^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - (\bar{E})^2 \qquad (2.158)$$

$$\overline{E^2} = \frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}, \text{ since } \sum E_r^2 e^{-\beta E_r} = \left(-\frac{\partial}{\partial \beta}\right)^2 \left(\sum e^{-\beta E_r}\right) \qquad (2.159)$$

We can also write

$$\overline{\Delta E^2} + \bar{E}^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2 \qquad (2.160)$$

$$\overline{\Delta E^2} = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2}{\partial \beta^2}\ln Z \geq 0 \qquad (2.161)$$

$$\text{And } \frac{\partial \bar{E}}{\partial \beta} \leq 0 \quad \text{or} \quad \frac{\partial \bar{E}}{\partial T} \geq 0 \qquad (2.162)$$

Pressure

Suppose that the system is parametrized by a single external parameter x. Consider a quasi-static change in the external parameter from x to x + dx. Then the energy changes by an amount

$$\Delta_x E_r = -\frac{\partial E_r}{\partial x} dx = F_x dx \qquad (2.162)$$

The macroscopic work done by the system as a result of this change is

$$dW = \frac{\sum_r e^{-\beta E_r}\left(-\frac{\partial E_r}{\partial x}\right) dx}{Z} \qquad (2.163)$$

$$\text{But, } \sum e^{-\beta E_r}\frac{\partial E_r}{\partial x} = (-\frac{1}{\beta})\frac{\partial}{\partial x}\left(\sum e^{-\beta E_r}\right) = -\left(\frac{1}{\beta}\right)\frac{\partial Z}{\partial x} \qquad (2.164)$$

$$\text{Or, } đW = \frac{1}{\beta Z}\frac{\partial Z}{\partial x}dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}dx \tag{2.165}$$

If the mean generalised force is $\overline{X}$, then,

$$đW = \overline{X}\,dx\,,\quad \overline{X} = -\frac{\overline{\partial E_r}}{\partial x} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x} \tag{2.166}$$

Thus, if x = V, the volume, and p the pressure, then

$$đW = p\,dV = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}dV \tag{2.167}$$

And

$$p = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V}$$

(2.168)

which is the equation of state for the system.

Connection with thermodynamics

All important quantities can be expressed in terms of the partition function Z or ln Z. Considering $E = E(V)$, we have $Z = Z(\beta, V)$ and

$$d\ln Z = \frac{\partial \ln Z}{\partial V}dV + \frac{\partial \ln Z}{\partial \beta}d\beta = \beta đW - \overline{E}d\beta = \beta đW - d(\overline{E}\beta) + \beta d\overline{E} \tag{2.169}$$

$$d\ln(Z + \beta\overline{E}) = \beta(đW + d\overline{E}) = \beta đQ \tag{2.170}$$

Where, $đQ$ is the heat absorbed by the system. But $dS = đQ\,/T$. Therefore,

$$S = k\ln(Z + \beta\overline{E}) \tag{2.171}$$

or

$$TS = kT\ln(Z + \beta\overline{E})$$

(2.172)

or

$$F = \overline{E} - TS = kT\ln Z \tag{2.173}$$

which is the free energy. Now,

$$dF = d\overline{E} - TdS - SdT \quad = d\overline{E} - pdV - dE - SdT \quad = -pdV - SdT \tag{2.174}$$

$$\therefore \quad p = -\left(\frac{\partial F}{\partial V}\right)_T; \quad \text{and} \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{2.175}$$

Where, $\overline{E} = F + TS$. Thus one can get all the thermodynamic quantities from the partition function.

The Entropy

We have $Z = \sum_r e^{-\beta E_r} = \sum_E \Omega(E)\,e^{-\beta E}$ where $\Omega(E)$ is the number of states between E and E + δE. The right hand side has a sharp maximum at some value $\widetilde{E}$ of energy. The mean value of energy is then $\overline{E} = \widetilde{E}$ and the summand is appreciable only in some narrow range of ΔE around the maximum. Therefore,

$$Z = \Omega(\overline{E})\,e^{\beta\overline{E}}\,\frac{\Delta E}{\delta E} \tag{2.176}$$

Or

$$\ln Z = \ln\Omega(\overline{E}) - \beta E + \ln\frac{\Delta E}{\delta E}$$

(2.177)

But $\ln\frac{\Delta E}{\delta E}$ is at most of the order of ln s, where, s is the number of degrees of freedom and $\ln\Omega(\overline{E})$ is O(s). Then,

$$k\ln(Z+\beta\overline{E})+k\ln\Omega(\overline{E})=S \tag{2.178}$$

2.4.5 Weakly Interacting Systems

Consider again a system $A^{(0)}$ divided into two parts that are weakly interacting at the same temperature.

$$A^{(0)}=A+A',\ E_{rs}^{(0)}=E_r+E_s' \tag{2.179}$$

Then,

$$Z^{(0)}=\sum_{r,s} e^{-\beta(E_r+E_s')}=\sum_r e^{-\beta E_r}\sum_s e^{-\beta E_s}=Z\,Z' \tag{2.180}$$

$$\ln Z^{(0)}=\ln Z+\ln Z',\quad \overline{E}^{(0)}=\overline{E}+\overline{E}' \tag{2.181}$$

And hence,

$$S^{(0)}=k\ln(Z^{(0)}+\beta\overline{E}^{(0)})=S+S' \tag{2.182}$$

The Ideal Gas (Canonical Distribution)

We have again,

$$E=\sum_i\frac{p_i^2}{2m} \tag{2.183}$$

$$Z=\frac{1}{N!\,h^{3N}}\int d^3r_1\,d^3r_2......d^3r_N\,d^3p_1......d^3p_N\;e^{-\beta\sum_i p_i^2/2m} \tag{2.184}$$

$$=\frac{V^N}{N!\,h^{3N}}\left[\int_{-\infty}^{+\infty}e^{-\beta p^2/2m}\right]^{3N}=\frac{V^N}{N!h^{3N}}\left[\sqrt{\frac{2\pi m}{\beta}}\right]^{3N} \tag{2.185}$$

$$\ln Z=N\left[\ln V-\frac{3}{2}\ln\beta+\frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right)\right]-\ln N! \tag{2.186}$$

$$p=\frac{1}{\beta}\frac{\partial\ln Z}{\partial V}=\frac{1}{\beta}\frac{N}{V},\quad pV=NkT \tag{2.187}$$

And $S=k\ln(Z+\beta\overline{E})$

$$=Nk\left[\ln V-\frac{3}{2}\ln\beta+\frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right)+\frac{3}{2}\right]-Nk\ln N \tag{2.188}$$

$$=Nk\left[\ln\frac{V}{N}+\frac{3}{2}\ln kT+\frac{3}{2}\ln\frac{3}{2}-\frac{3}{2}\ln\frac{3}{2}+\frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right)+\frac{3}{2}\right] \tag{2.189}$$

$$=Nk\left[\ln\frac{Vu^{3/2}}{N}+\frac{3}{2}\ln\left(\frac{4\pi m}{3h^2}\right)+\frac{3}{2}\right] \tag{2.190}$$

$$= Nk\left[\ln\frac{Vu^{3/2}}{N}\right] + NS_0\text{, where, } u = \frac{3}{2}kT,\ S_0 = \frac{3k}{2}\left[1 + \ln\left(\frac{4\pi m}{3h^2}\right)\right] \quad (2.191)$$

2.4.6 Equivalence of the Canonical and the Microcanonical Distributions

We have seen that the entropy obtained from either distributions gives the same result. Instead of arguing mathematically, we can also argue physically to show the equivalence of the distributions. A microcanonical distribution is the description that is the appropriate one for an isolated system with a given energy. A canonical distribution describes a system interacting a reserviour, and hence the system does not have a fixed energy. However, since the probability that the system has an energy between E and E + δE is,

$$P(E) = \Omega(E)\, e^{-\beta E} \quad (2.192)$$

This probability has a sharp maximum at some value of E = $\bar{E}$, the mean energy of the system. One can approximate even an isolated system by a canonical distribution by choosing a β in such a way that the maximum occurs at the desired value of energy. Though the energy is not strictly a constant, it varies from $\bar{E}$ negligibly because of the sharpness of the distribution. The advantage of the canonical distribution is that there is no restriction on the value of energy and all the quantities of interest are much easier to evaluate.

2.4.7 The Grand Canonical Distribution

Consider now a system A of fixed volume in contact with a reserviour A' with which it can interchange not only energy, but also particles. Then neither the energy of A nor its number of particles N are fixed. The total energy of the system $A^{(0)} = A + A'$ and its total number of particles are fixed.

$$E^{(0)} = E + E' = \text{constant} \quad (2.193)$$

$$N^{(0)} = N + N' = \text{constant} \quad (2.194)$$

We now ask for the probability of finding the system A in a given state r where it has an energy E_r and contains N_r particles.

The argument is similar to the one used before. Let *Ω'(E', N')* denote the number of states accessible to *A'* when it contains *N'* number of particles in the energy range near *E'*. If A is in state r, then the number of states accessible to the entire system is simply Ω' . Therefore,

$$P_r(E_r, N_r) = \Omega'(E^{(0)} - E_r, N^{(0)} - N_r) \quad (2.195)$$

If $A \ll A'$, then, $E_r \ll E^{(0)}$, $N_r \ll N^{(0)}$.Then,

$$\ln \Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \Omega'(E^{(0)}, N^{(0)}) - \beta E_r - \alpha N_r + \ldots\ldots\ldots \quad (2.196)$$

Where,

$$\beta \equiv \frac{\partial}{\partial E'}\ln\Omega'\Big|_{E'=E^{(0)}} \text{ and } \alpha \equiv \frac{\partial}{\partial N'}\ln\Omega'\Big|_{N'=N^{(0)}} \quad (2.197)$$

We have neglected the higher derivatives as well as the cross terms between E_r and N_r.

Then, $\Omega'(E^{(0)} - E_r, N^{(0)} - N_r) = \Omega'(E^{(0)}, N^{(0)})\ e^{-\beta E_r - \alpha N_r}$ and (2.198)

$$P_r = C^{-1}\, e^{-\beta E_r - \alpha N_r} \quad (2.199)$$

Where, $C = \mathcal{Z} = \sum_{r,N_r} e^{-\beta E_r - \alpha N_r}$ (2.200)

$\mathcal{Z}$ is called the grand partition function. It involves the sum over energies as well as the numbers of particles. The average energy and the average particle number in the system is

$$\bar{E} = \frac{1}{\mathcal{Z}} \sum_{r,N_r} E_r e^{-\beta E_r - \alpha N_r} \text{ and } \bar{N} = \frac{1}{\mathcal{Z}} \sum_{r,N_r} N_r e^{-\beta E_r - \alpha N_r} . \quad (2.201)$$

As in the earlier case of the canonical partition function, we have,

$$\bar{E} = -\frac{1}{Z}\frac{\partial \mathcal{Z}}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln \mathcal{Z} \quad (2.202)$$

The average number of particles is given by

$$\bar{N} = \frac{1}{\mathcal{Z}}\left(-\frac{\partial}{\partial \alpha}\right)\sum_{r,N_r} e^{-\beta E_r - \alpha N_r} = -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \alpha} = -\frac{\partial}{\partial \alpha}\ln \mathcal{Z} \quad (2.203)$$

Writing $\mathcal{Z} = \bar{Z}(\alpha, \beta, V)$ and $\alpha = -\beta\mu = \mu / kT$, we get,

$$d \ln \mathcal{Z} = \frac{\partial \ln \mathcal{Z}}{\partial \alpha} d\alpha + \frac{\partial \ln \mathcal{Z}}{\partial \beta} d\beta + \frac{\partial \ln \mathcal{Z}}{\partial V} dV \quad (2.204)$$

$$= -\bar{N}\, d\alpha - \bar{E} d\beta + \beta p\, dV = \beta \bar{N}\, d\mu - \bar{E}\, d\beta + \beta p\, dV \quad (2.205)$$

$$= \beta d(\mu \bar{N}) - \beta\mu d\bar{N} - d(\bar{E}\beta) + \beta d\bar{E} + \beta p\, dV \quad (2.206)$$

$$\therefore d\ (\ln \mathcal{Z} + \bar{E}\beta - \beta\,\mu\,\bar{N}) = \beta\ d\bar{E} - \beta\,\mu\, d\bar{N} + \beta\, p\, dV$$

Recalling that

$$đQ = T\, dS = dE + p\, dV - \mu dN \ , \quad (2.207)$$

we have, $dE + pdV - \mu dN = k T d(\ln \mathcal{Z} + \bar{E}\beta - \beta\mu\bar{N}) = TdS$.
(2.208)

Or, $S = k\ (\ln \mathcal{Z} + \bar{E}\beta - \beta\mu\bar{N})$
(2.209)

$$k\, T \ln \mathcal{Z} = TS - kT\ \beta\bar{E} + kT\beta\mu\bar{N}) = TS - \bar{E} + \mu\bar{N} = -\Phi \quad (2.210)$$

Where, $\Phi = \bar{E} - TS - \mu\bar{N} = F - \mu\bar{N}$
(2.211)

In terms of this new potential Φ, the ensemble averages are given by

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{V,\,T} ; \quad p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\,\mu} ; \quad S = -\left(\frac{\partial \Phi}{\partial T}\right)_{V,\,\mu} \quad (2.212)$$

Ideal gas in the grand-canonical distribution

The grand partition function may be written as

$$\mathcal{Z} = \sum_{r,N_r} e^{-\beta E_r - \alpha N_r} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N \quad (2.213)$$

Where Z_N is the canonical partition function for N particles, given by (2.185) may be rewritten as

$$Z_N = \frac{V^N}{N! h^{3N}}\left[\sqrt{\frac{2\pi m}{\beta}}\right]^{3N} = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^{3N}, \text{ where, } \lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} = \frac{h}{\sqrt{2\pi mkT}} \quad (2.214)$$

$$Z = \sum_{N=0}^{\infty}\left(\frac{Ve^{\beta\mu}}{\lambda^3}\right)^N \frac{1}{N!} = \exp\left(e^{\beta\mu}\frac{V}{\lambda^3}\right) \tag{2.215}$$

Therefore,

$$\Phi = -kT\ln Z = -kT\,e^{\beta\mu}\frac{V}{\lambda^3} \tag{2.216}$$

$$\text{And } \overline{N} = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{V,T} = e^{\beta\mu}\frac{V}{\lambda^3} \tag{2.217}$$

$$\text{Or } \mu = kT\ln\left(\frac{\overline{N}\lambda^3}{V}\right), \text{ and } p = -\left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu} = \frac{kTe^{\beta\mu}}{\lambda^3} = kT\frac{\overline{N}}{V} \tag{2.218}$$

2.5 Quantum Statistics of Ideal Gases

Consider a gas of N structureless particles within a container of volume V. The state of the gas may be described by the wavefunction

$$\Psi = \Psi_{\{s_1,\ldots\ldots s_N\}}(Q_1, Q_2\ldots\ldots\ldots\ldots Q_N) \tag{2.219}$$

Here, Q_i denotes collectively all the coordinates of the i^{th} particle (i.e. its position and spin coordinates if any). The possible quantum states are labelled by the indices s_i.

Two cases need to be considered. In the **classical case** (Maxwell-Boltzmann statistics), the particles are considered distinguishable and any number particles can be in the same state s. The 'classical' case imposes no symmetry requirements on the wavefunction. In the **quantum mechanical case**, quantum mechanics imposes definite symmetry requirements on the wavefunction under the exchange or interchange of identical particles. When the particles are indistinguishable, one does not get a new state by interchanging two particles. When counting the distinct possible states of the system, the relevant consideration is how many particles are in each state s rather than which particle is in which state. Moreover, the symmetry properties are different for particles with integral or half-integral spins (in units of ħ).

(a) Bosons are particles with integral spin. For bosons, Ψ is symmetric under the interchange of two particles, i.e.,

$$\Psi(Q_1, Q_2\ldots Q_i\ldots Q_j\ldots\ldots Q_N) = \Psi(Q_1, Q_2\ldots Q_j\ldots Q_i\ldots\ldots Q_N) \tag{2.220}$$

Exampled of bosons are photons, pions, kaons and He^4 atoms.

(b) Fermions are particles with half-integral spins. Examples are electrons, protons, He^3 atoms, Δ^{++} and so on. The requirement that Ψ is anti-symmetric under the interchange of two particles.

$$\Psi(Q_1, Q_2\ldots Q_i\ldots Q_j\ldots\ldots Q_N) = -\Psi(Q_1, Q_2\ldots Q_j\ldots Q_i\ldots\ldots Q_N) \tag{2.221}$$

If two particles are in the same state, then clearly, Ψ = 0. This is the familiar Pauli exclusion principle.

Example 2.7

Consider the different ways distribution of two particles in three quantum states in the different cases.

(i) Maxwell-Boltzmann statistics: The particles A and B are considered distinguishable, and any number can be in a given state. The distribution can be seen in the first section of the following table (2.2).

Table 2.2 Particle occupancies of two particles in three states in the three cases.

Maxwell Boltzmann			Bose-Einstein			Fermi-Dirac		
1	2	3	1	2	3	1	2	3
AB	--	--	AA	--	--	A	A	--
--	AB	--	--	AA	--	--	A	A
--	--	AB	--	--	AA	A	--	A
A	B	--	A	A	--			
B	A	--	A	--	A			
A	--	B	--	A	A			
B	--	A						
--	A	B						
--	B	A						

(ii) Bose-Einstein statistics: Particles are indistinguishable, and one or more can be in the same state.
(iii) Fermi-Dirac statistics: Particles are indistinguishable and no two can be in the state. Thus in the Bose-Einstein case, there is a greater relative tendency for the particles to bunch together. This phenomenon is called Boson condensation and was proposed in 1921 and experimentally verified in 1996.
Now we turn to the formulation of the problem in quantum statistics. Consider a system of N particles in volume V in equilibrium at temperature T. Let ε_r be the energy of a particle in state r and n_r be the number of particles in state r. If R denotes some state of the system, and assuming no interaction between particles

$$E_R = n_1\varepsilon_1 + n_2\varepsilon_2 + ... = \sum_r n_r\varepsilon_r \tag{2.222}$$

$$N = n_1 + n_2 + ... = \sum_r n_r \tag{2.223}$$

The partition function is then

$$Z = \sum_R e^{-\beta E_R} = \sum_R e^{-\beta\sum n_r\varepsilon_r} \tag{2.224}$$

This has to be evaluated keeping in mind $\sum_r n_r = N$. In general this is a difficult thing to do, and it is more convenient to work with the grand canonical distribution for which this condition does not apply. The grand partition function is

$$\mathcal{Z} = \sum_{,N_r} E_r e^{-\beta E_r + \beta\mu N_r} = \sum_{n_1, n_2, n_2 ...} e^{\beta\mu(n_1 + n_2 + n_3.....)} e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + ...)} \tag{2.225}$$

$$= \sum_{n_1} e^{\beta(\mu-\varepsilon_1)n_1} \sum_{n_2} e^{\beta(\mu-\varepsilon_2)n_2} .... \tag{2.226}$$

$$\therefore \ln \mathcal{Z} = \ln \mathcal{Z}_1 + \ln \mathcal{Z}_2 + \ldots\ldots\ldots \quad \text{where,} \quad \mathcal{Z}_i = \sum_{n_i} e^{\beta(\mu-\varepsilon_i) n_i} \tag{2.227}$$

But $\Phi = -kT \ln \mathcal{Z}$. Therefore,

$$\Phi = \sum_i \Phi_i; \qquad \Phi_i = -kT \ln \sum_{n_i} e^{-\beta(\mu-\varepsilon_i)\, n_i} \tag{2.228}$$

For n_i particles in a given state i with energy ε_i.

2.5.1 Fermi-Dirac Statistics

The n_i are called the occupation numbers for the states i. According to the Pauli's principle, the occupation numbers for fermions is either 0 or 1. We have, therefore,

$$\Phi_i = -kT \ln \sum_{n_i} e^{-\beta(\mu-\varepsilon_i)\, n_i} = -kT \ln (1 + e^{\beta(\mu-\varepsilon_i)}) \tag{2.229}$$

The mean number of particles in the ith quantum state is therefore given by

$$\bar{n}_i = -\frac{\partial \Phi_i}{\partial \mu} = \frac{e^{\beta(\mu-\varepsilon_i})}{1+e^{\beta(\mu-\varepsilon_i)}} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}+1} \tag{2.230}$$

This is the Fermi-Dirac distribution for the mean number of particles in a given quantum state at temperature T. If we have a system with a total number of particles N, then we must have,

$$\sum_i \bar{n}_i = N; \quad \text{or} \quad \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)}+1} = N \tag{2.231}$$

This implicitly determines the chemical potential μ in terms of T and N. The thermodynamic potential for the whole system is given by

$$\Phi = \sum_i \Phi_i; \qquad \Phi_i = -kT \sum_i \ln\left(1 + e^{\beta(\mu-\varepsilon_i)}\right) \tag{2.232}$$

2.5.2 Bose Statistics

For an ideal system of bosons, the occupation numbers of the quantum states are unrestricted and can take any values. Therefore

$$\Phi_i = -kT \ \ln \sum_{n_i=0}^{\infty} \left(1 + e^{+\beta(\mu-\varepsilon_i) n_i}\right) \tag{2.233}$$

The series $\sum_{n_i=0}^{\infty} \left(1 + e^{+\beta(\mu-\varepsilon_i) n_i}\right)$ is a geometric series that is convergent provided $\left(e^{+\beta(\mu-\varepsilon_i) n_i}\right)$ <1. Since this must be satisfied for all ε_i including $\varepsilon_i = 0$, we must have $\mu < 0$. Then,

$$\Phi_i = -kT \ \ln \frac{1}{1-e^{\beta(\mu-\varepsilon_i)}} = kT \ln (1 - e^{\beta(\mu-\varepsilon_i)}) \tag{2.234}$$

$$\bar{n}_i = -\frac{\partial \Phi_i}{\partial \mu} = \frac{e^{\beta(\mu-\varepsilon_i})}{1-e^{\beta(\mu-\varepsilon_i)}} = \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1} \tag{2.235}$$

This is the Bose (or the Bose-Einstein) distribution. Again,

$$\sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)}-1} = N \tag{2.236}$$

And $$\Phi = \sum_i \Phi_i = -kT\sum_i \ln\left(1-e^{\beta(\mu-\varepsilon_i)}\right) \tag{2.236}$$

2.5.3 Thermodynamics of Boson and Fermion Systems

We can use the relations we have derived to discuss the thermodynamics of system of noninteracting bosons and fermions. The energy of a particle is

$$E = \frac{1}{2m}\left(p_x^2+p_y^2+p_z^2\right) \tag{2.237}$$

In the distribution function, we make the usual change to the distribution in the phase of the particle. For a given position and momentum, the state of the system depends on the spin. Hence the number of particles in a given volume d^3p dV of phase space is found by multiplying the Fermi or the Bose distribution by g d^3p dV/h^3 where g = 2s + 1 and s is the spin of the particle. Therefore,

$$dN = \frac{g}{h^3}\frac{d^3p\,dV}{e^{\beta(\varepsilon-\mu)}\pm 1} \qquad \text{(+ for F.D. and – for B.E.)} \tag{2.238}$$

The number of particles with magnitude of momentum between p and p and p +dp is

$$dN_p = \frac{4\pi g\,dV}{h^3}\frac{p^2dp}{e^{\beta(\varepsilon-\mu)}\pm 1} \tag{2.139}$$

The energy distribution is

$$dN_\varepsilon = \frac{4\pi g d V}{h^3}\frac{1}{e^{\beta(\varepsilon-\mu)}\pm 1}\sqrt{2}\,m^{3/2}\sqrt{\varepsilon}\,d\varepsilon \tag{2.240}$$

Since $\varepsilon = \dfrac{p^2}{2m},\ d\varepsilon = \dfrac{p\,dp}{m},\ dp = \dfrac{m\,d\varepsilon}{p} = \dfrac{m\,d\varepsilon}{\sqrt{2m\varepsilon}}$

i.e., $$p^2dp = \frac{2m\varepsilon\,m\,d\varepsilon}{\sqrt{2m\varepsilon}} = \sqrt{2}m^{3/2}\sqrt{\varepsilon}d\varepsilon \tag{2.141}$$

The total number of particles is given by

$$N = \frac{4\pi g\sqrt{2}\,m^{3/2}V}{h^3}\int_0^\infty \frac{1}{e^{\beta(\varepsilon-\mu)}\pm 1}\sqrt{\varepsilon}\,d\varepsilon \tag{2.242}$$

Or, $$\frac{N}{V} = \frac{g\left(mkT\right)^{3/2}}{\sqrt{2}\pi^2h^3}\int_0^\infty \frac{\sqrt{z}\,dz}{e^{z-\beta\mu}\pm 1} \qquad \text{where } z = \beta\varepsilon \tag{2.243}$$

Similarly,

$$\Omega = \mp\frac{VgkT\,m^{3/2}}{\sqrt{2}\pi^2h^3}\int_0^\infty \sqrt{\varepsilon}\ln\left[1\pm e^{\beta(\mu-\varepsilon\varepsilon)}\right]d\varepsilon \tag{2.244}$$

Upper sign for F.D. and lower sign for B. E. Integrating by parts,

$$\Omega = -\frac{2}{3}\frac{Vg\,m^{3/2}}{\sqrt{2}\pi^2h^3}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)}\pm 1}d\varepsilon \tag{2.245}$$

Finally,

$$E = \int_0^\infty \varepsilon \, dN_\varepsilon = \frac{Vg\, m^{3/2}}{\sqrt{2}\pi^2 h^3} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} \pm 1} d\varepsilon \qquad (2.246)$$

These relations allow us to study thermodynamics.

2.5.4 Fermi and Bose Gases not in Equilibrium

We can derive the entropy of the Fermi and the Bose gases not in equilibrium and get the Fermi and Bose distribution functions from the condition that the entropy is maximum at equilibrium.

Let us distribute the single particle quantum states of an ideal gas among groups containing neighbouring states or 'cells' as shown. Let the cells be numbered j = 1,2,… and let the number of states in each cell be G_j and the number of particles in each cell be N_j .

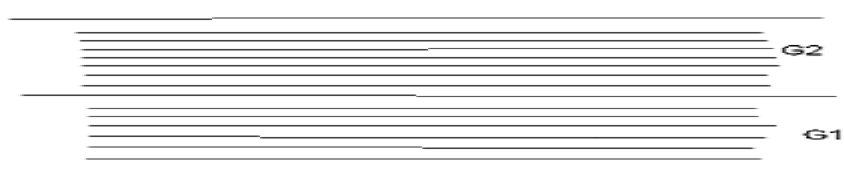

Figure 2.6 Distribution of quantum particles in cells.

The entropy of the gas can be calculated from the number of accessible states Ω of a given microscopic state. This is the number of ways in which the given state can be realised. Regarding each group of particles N_j as independent,

$$\Omega = \prod_j \Omega_j \qquad (2.247)$$

Where Ω_j is the number of ways of distributing N_j particles in G_j states.

2.5.5 Fermi gas

Here, Ω_j is given by the number of ways of distributing N_j particles in G_j states with not more than one particle in each state. This is simply equal to the ways of picking N_j objects out of G_j objects. Thus,

$$\Omega_j = {}^{G_j}C_{N_j} = \frac{G_j!}{N_j!(G_j - N_j)!} \qquad (2.248)$$

Therefore,

$$S = k \ln \Omega = k \sum_j \ln \Omega_j = k \sum_j \left(\ln G_j! - \ln N_j! - \ln (N_j - G_j)! \right)$$

Using Stirling's approximation, ln N! = N ln N – N, we have,

$$S = k \sum_j \left(G_j \ln G_j - G_j - N_j \ln N_j + N_j - (G_j - N_j) \ln (G_j - N_j) + G_j - N_j \right) \qquad (2.249)$$

$$= k \sum_j \left(G_j \ln G_j - N_j \ln N_j + N_j - (G_j - N_j) \ln (G_j - N_j) \right) \qquad (2.250)$$

The mean occupation number of the quantum state j is $\overline{n}_j = N_j / G_j$. This gives

$$= - k\ln\sum_{j} G_j\left(\bar{n}_j \ln\bar{n}_j - (1-\bar{n}_j)\ln(1-\bar{n}_j)\right) \tag{2.251}$$

This must be maximised subject to

$$\sum_j N_j = \sum G_j \bar{n}_j = N \text{, and } \sum_j \varepsilon_j N_j = \sum \varepsilon_j G_j \bar{n}_j = E \tag{2.252}$$

This gives

$$\frac{\partial}{\partial \bar{n}_j}\left(S + \alpha N + \beta E\right) = 0 \tag{2.253}$$

Or,

$$G_j\left(\alpha - \beta\varepsilon_j + \ln\frac{\bar{n}_j}{1-\bar{n}_j}\right) = 0 \tag{2.254}$$

Or,

$$\frac{1-\bar{n}_j}{n_j} = e^{\alpha+\beta\varepsilon_j}$$

(2.255)

Or,

$$\bar{n}_j = \frac{1}{e^{\alpha+\beta\varepsilon_j} + 1}$$

(2.256)

This is the Fermi distribution with β=1/kT and α = - μ/kT,

2.5.6 Bose Gas

Here each state may contain any number of particles. The number of ways of distributing N_j particles in G_j states is simply given by referring to the following figure.

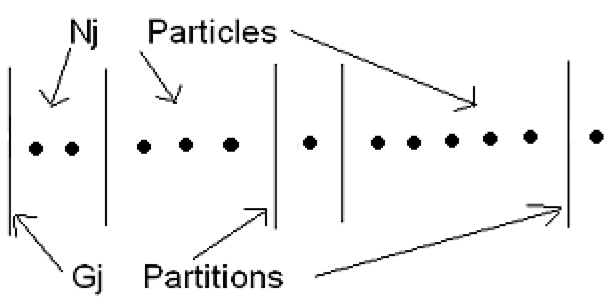

Figure 2.7: N_j Particles in G_j Partitions

Thus,

$$\Omega_j = \frac{(N_j - G_j - 1)!}{N_j!\,(G_j - 1)!} \tag{2.257}$$

This gives

$$= \sum_j G_j \left((1+\bar{n}_j)\ \ln(1+\bar{n}_j) - n_j\ \ln \bar{n}_j\right) \tag{2.258}$$

Maximizing S with the conditions,

$$\sum_j N_j = N \text{, and } \sum_j \varepsilon_j N_j = E \tag{2.259}$$

gives $$\bar{n}_j = \frac{1}{e^{\alpha+\beta\,\varepsilon_j} - 1} = \frac{1}{e^{\beta\,(\varepsilon_j-\mu)} - 1} \quad .$$

(2.260)

This is the Bose distribution.

2.5.7 The Classical Limit

The Fermi and the Bose distributions are given by

$$\bar{n}_j = \frac{1}{e^{\beta\,(\varepsilon_j-\mu)} \pm 1} \tag{2.261}$$

Both reduce to the Maxwell-Boltzmann distribution when $e^{\beta(\varepsilon_j - \mu)} >> 1$. In that case,

$$\bar{n}_j = e^{\beta\mu} e^{-\beta\varepsilon_j} \tag{2.262}$$

The Boltzmann distribution applies when $\bar{n}_j << 1$. This corresponds to an extremely rarefied gas. We had from the grand canonical distribution for the probability that there are $\bar{n}_j$ particles in state j with energy ε_j,

$$P_{\bar{n}_j} = Ce^{\beta(\mu-\varepsilon_j)\varepsilon_j} \tag{2.263}$$

Then $P_0 = C$ = the probability that there are no particles in the state j. Since $n_j << 1$, C = 1. Also, $P_1 = e^{\beta(\mu - \varepsilon_j)}$. The probabilities $P_2, P_3, \ldots$. i.e., that of finding more than one particle in the same state can be taken to be zero. Therefore,

$$\bar{n}_j = \sum_j P_{n_j} n_j = P_1 .1 = e^{\beta(\mu-\varepsilon_j)} \tag{2.264}$$

This is the Boltzmann distribution. Thus the classical limit corresponds to ($\varepsilon_j - \mu$) >>kT.

2.6 Summary

In this chapter, the behaviour of a large collection of particles is studied using the methods of thermodynamics as well as that of different ensembles. The chapter begins with probability and the random walk problem and the associated and limiting distributions. Equilibrium and approaches to equilibrium are considered next using the methods of probability and by maximising the number of accessible states. Properties of the absolute temperature, directions of heat flow, quasi static processes, the limiting behaviour of entropy and the laws of thermodynamics are then considered. Different ensembles, the mean values in these ensembles and the equivalence of ensembles is considered in the following sections. Quantum statistics of ideal gases is then studied using the grand canonical distribution function. The Fermi and Bose statistics are considered and their approach to the classical limit at high temperature is shown at the end of the chapter.

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Problems

1) de Mere's Paradox: A French gambler, de Mere observed that when 3 dice are thrown simultaneously, the probability of the total number on the three faces turning out to be 11 (event 1) is slightly greater than the total number 12 (event 2). From a common probability argument, both events should occur with the same probability. Event 1 can occur in 6 ways through the outcomes 6,4,1; 6,3,2; 5,5,1; 5,4,2; 5,3,3 and 4,4,3. Event 2 can also occur in 6 ways as 6,5,1; 6,4,2; 6,3,3; 5,5,2; 5,4,3; 4,4,4. Therefore, the probability of event 1 should be equal to the probability of event 2. Pascal found out the error in this argument and showed that P(1) was indeed greater than P(2). Prove Pascal's assertion. (Hint: Think of the degeneracies of each of the outcomes listed above and calculate the probabilities of events 1 and 2 considering the total number of 216 possibilities when 3 dice are thrown).

2) In an experiment, there are N equally likely outcomes. Consider two events A and B. The number outcomes in which the event A occurs in N_A and the number of outcomes in which B occurs in N_B. N_{AB} is the number of occurrences in which both A and B occur and N_- is the number of occurrences in which neither A nor B occur. Then, show that
(a) (i) $N = N_A + N_B + N_{AB} + N_-$ (ii) $P(A) = (N_A + N_{AB})/N$ and (iii) $P(B) = (N_B + N_{AB})/N$ where P(A) and P(B) are the probabilities of the occurrences of A and B respecticely.
(b) Calculate P(A+B), the probability of the occurrence of either A or B.
(c) Calculate the probability P(AB), the probability of the occurrence of both A and B.
(d) Calculate the conditional probability P(A|B), the probability of the occurrence of A given that B has occurred. Similarly, calculate P(B|A).
(e) Show that P(A+B) = P(A) + P(B) - P(AB) and that P(AB) = P(B)P(A|B)=P(A)P(B|A)
(f) Prove Bayes' theorem, which states that

$$\frac{P(B\,|\,A)}{P(C\,|\,A)} = \frac{P(B)}{P(C)}\frac{P(A\,|\,B)}{P(A\,|\,C)}$$

A simple introduction on Bayes' theorem and its application is found in Wikipedia.

3) In a binomial distribution, the probability of *n* occurrences of an event with probability *p* among a total of *N* trails is given by

$$W_N(n) = \frac{N!}{n!(N-n)!}\,p^n\,(1-p)^{N-n}$$

For small p (p << 1), $W_N(n)$ is very small, except when n << N. In this small n limit, show that the distribution $W_N(n)$ becomes the Poisson distribution given by

$$W_N(n) \to P(n) = \frac{\lambda^n}{n!} e^{-\lambda}$$

Where, $\lambda = n\,p$, the mean number of events. Is $P(n)$ normalised? Calculate $< n >$ and $<\Delta n^2>$ for the Poisson distribution. What are some examples of a Poisson distribution?

1) In a random walk in one dimension, let s_j be the displacement per step. After N steps from the origin, the displacement $x = \sum_{j=1}^{N} s_j$. If s_j s are obtained from a Lorentzian distribution $w(s) = \frac{1}{\pi}\frac{a}{s^2+a^2}$, where a > 0, obtain the probability distribution associated with the variable x. For large N, does the distribution for x approach the Gaussian limit?

2) In an ideal gas mixture containing N_A molecules of A and N_B molecules of B in volume V, how does the number of states Ω(E) in the range between E and E + δE depend on the volume of the system? Compare this with the result of a one component system.

3) A small mass m is suspended on a spring with spring constant k. The mass is acted on by the restoring force due to the spring – k x and the force due to gravity with the acceleration g. What is the mean position < x > of the mass and the mean thermal fluctuation $[x - < x >]^2$?

4) Consider a similar problem, where the external filed is a magnetic field varying linearly with the vertical distance z. A dilution solution of atoms which can have either a spin of +1/2 or -1/2 is placed in such a field. Let the height of the container in which the solution is placed be z. The magnetic field is H(z) and let H(0) be 0. Calculate the values of $n_+(z)$ and $n_-(z)$), where n_+ and n_- are the mean number of spins in the +z and –z direction.

5) Among N molecules, if there are n_1 molecules with energy ε_1, n_2 molecules with energy ε_2,.. then the weight of this configuration (i.e., the number of ways in which it can be accomplished) is given by $W(n_1,n_2,...) = \frac{N!}{n_1!\,n_2!}$ Since W is quite large, it is best to consider ln W. We are interested in the maximum of W subject to the constraints that the total number of molecules N = $\sum n_i$ and the total energy E = $\sum \varepsilon_i n_i$ is conserved. In the method of Lagrange undetermined multipliers, The constrained maximum is found by solving for the multipliers α and β in the equation $d\ln W = \sum_i \frac{\partial \ln W}{\partial n_i} dn_i + \alpha \sum_i n_i - \beta \sum_i \varepsilon_i dn_i = 0$ Setting this equation to 0 for each i and using the Stirling's approximation for ln W (i.e, ln N! = N ln N – N), show that in the optimal or the most probable distribution, $n_i/N = e^{\alpha - \beta\varepsilon_i}, e^{-\alpha} = q = \sum_i e^{-\beta\varepsilon_i}$, where q is the partition function.

6) Defining S = - k$\sum_i P_i \ln P_i$ subject to the constraint $\sum_i P_i = 1$, use the method of Lagrange undetermined multipliers to show that S is a maximum when all P_is are equal to a constant. Similarly, maximise S = - k$\sum_i P_i \ln P_i$ when it is subject to two constraints, $\sum_i P_i = 1$ and $\sum_i P_i E_i = E$ = constant.

7) For a free particle confined to a volume V in three dimensions, the number of microstates with momentum p less than P is given by

$$\Sigma(P) \approx \tfrac{1}{h^3} \int_{p \le P} ..\int d^3q\, d^3p = \frac{V}{h^3}\frac{4\pi}{3}P^3$$

The number of microstates lying between p and p+dp, g(p)dp is given by $\frac{d\Sigma(p)}{dp}dp$. This can be expressed in terms of energy as well by noting that E = p^2/2m. Show that the density of states g(p) is given by $\frac{V}{h^3}4\pi p^2$ and, expressed in terms of energy, it is equal to $\frac{V}{h^3}2\pi(2m)^{3/2}E^{1/2}$

11) In this problem, you are asked to derive the equation of motion for the density matrix. The matrix element of the density operator $\hat{\rho}(t)$ is defined by $\rho_{mn}(t) = \frac{1}{\text{¥}}\sum_{k=1}^{\text{¥}}\{a_m^k(t)\, a_n^{k*}(t)\}$. The summation of k is over the ensemble of systems ¥ . Here, $a_n^k(t)$ are the coefficients of the time dependent wavefunction $\psi^k(t)$ when it is expressed as a linear combination of a complete set of orthonormal basis functions ϕ_n (time independent); i.e., $\psi^k(t)$ is expressed as $\psi^k(t) = \sum_{n=1} a_n^k(t)\phi_n$. The time dependence is through the coefficients and not through ϕ_n s. The time dependence of $\psi^k(t)$ is naturally through the time dependent Schrödinger equation, $\hat{H}\psi^k(t) = i\mathrm{h}\dot{\psi}^k(t)$. Note the dot on $\psi^k(t)$. The coefficient $a_n^k(t)$ is given by $\int \phi_n^* \psi^k(t)\, d\tau$. Show that $i\mathrm{h}\dot{a}_n^k(t) = \sum_m H_{nm} a_m^k(t)$. For this use the definitions of $\dot{\psi}^k(t)$ and $\psi^k(t)$. The matrix element H_{nm} is defined as $\int \phi_n^*\, H\, \phi_m\, d\tau$.

Note that the density matrix (element) is an ensemble average and also that $\sum_n \rho_{nn} = 1$. Now, $i\mathrm{h}\dot{\rho}_{mn}(t) = \frac{1}{\text{¥}}\sum_{k=1}^{\text{¥}}\{\, \dot{a}_m^k(t)\ a_n^{k*}(t) + a_m^k(t)\,\dot{a}_n^{k*}(t)\}$. Now, substituting for the values of $\dot{a}_m^k(t)$ and $\dot{a}_n^{k*}(t)$ from the earlier above equation, show that $i\mathrm{h}\dot{\rho}_{mn}(t) =$ $(\hat{H}\hat{\rho} - \hat{\rho}\hat{H})_{mn}$ or $i\mathrm{h}\dot{\hat{\rho}} = [\hat{H}, \hat{\rho}]_-$. This is the quantum mechanical analogue of the classical equation of Liouville. Note also that the Poisson bracket $[\hat{H}, \hat{\rho}]_-$ has been replaced by the commutator $(\hat{H}\hat{\rho} - \hat{\rho}\hat{H})_{mn}/i\mathrm{h}$.