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> *Director* : J. K. Bhattacharjee *Secretary* : S. K. Sarkar

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FOREWORD TO THE SPECIAL ISSUE

Satyendra Nath Bose was born on January 1, 1894. To celebrate his 125th birth anniversary, a large number of conferences and meetings were held throughout the country. The Calcutta Institute of Theoretical Physics marked the happy occasion by holding a one day meeting in collaboration with St. Paul's College, Kolkata, on 28th July, 2018. This special issue containing three articles is a mark of our continued effort to remember the contribution of one of our country's foremost physicists.

Ever since the prediction of an exotic phase (1925) through a process known as Bose -Einstein condensation, experimentalists the world over had been trying to create this unusual phase in the laboratory. It took seventy years for that effort to succeed! In the physics department of Calcutta University, Prof. Pradip Narayan Ghosh and his collaborators put in a huge amount of effort towards the end of the previous century and the beginning of the present to attain the ultra- low temperatures needed to see this exotic phase. While they succeeded in cooling the alkali vapours well towards the final goal, the facility had to be abandoned before the final frontier could be breached. In this memorial issue Prof. Ghosh describes the phenomenon of Bose-Einstein condensation and discusses in detail the technique of evaporative cooling - the process that leads to temperatures low enough to observe the condensate.

We round out this special issue with two more articles - one a discussion of the important process of thermoluminescence which has to do with the emission of visible or invisible light by matter. In this process, certain crystalline materials absorb electromagnetic radiation and later emit them on heating. The process has important applications on the dating of materials. In the other article a brief historical overview of statistical physics has been given from the vantage point of the ideal gas.

Jayanta K Bhattacharjee School of Physical Sciences IACS, Kolkata. & Director of Calcutta Institute of Theoretical Physics 4/1, Mohan Bagan Lane, Kolkata.

CONTENTS

1.	Bose Einstein Condensation –Pradip N Ghosh	Page
		101
2.	Thermoluminescence and its applications -Tapan Ganguly	113
3.	A Random Walk Through Statistical Physics on the Crutches of the Ideal Gas –Jayanta K Bhattacharjee	123

Bose Einstein Condensation

Pradip N Ghosh Physics Department, University of Calcutta

1. Condensation of Boson

Bose's significalt paper was introduced as a new statistics that was published in 1924. Einstein tranlated it into German language for publication with a note that in English is:

"Bose's work signifies an important step forward. The method used here also yields the quantum theory of an ideal gas as I shall work out elsewhere".

The statement was very significant. Bose statistics was developed while deriving Planck distribution law for radiation. It was applicable to *photons*. Einstein showed that it can be applied to ideal gases as well and he wrote that in future he would show that it could be used to develop the **quantum theory of an ideal gas**. As per his promise he published a paper in the next year and showed that gas phase atoms obeying Bose statistics could be cooled to very low temperature so that they would all condense to the ground state. *Dilute gas of atoms collected in the ground state would form a new phase*. The proposal of Einstein led scientists to understand the theoretical implications and to attempt the new phase experimentally. After many failures and some misinterpretaions, it was experimentally achieved in 1995 after long seventy years.

We shall try to understand what this new phase is and also the problems for achiving the new phase.

2. Boson and Fermion

Bosons have integral spins, for example, photon, phonon or atoms like ${}^{87}Rb$ that have an even number of Fermions. On the other hand Fermions have half-integral spins like electrons, protons or ${}^{3}He$ or similar atoms. Bosons allow any number of particles in a quantum state; so they are Gregarious in nature. In contrast, Fermi statistics allows only one particle in a state; so they are Loners in nature.

PRADIP N GHOSH

3. Cold Atom as a de Broglie Wave

Cold atoms have low momentum p so the wavelength $\lambda_{dB} = h/p$ becomes large.

$$\lambda_{dB} = h / (2 \pi kT)^{1/2}$$
.



Fig. 1 Atom as a de Broglie wave. Atomic spin is shown as a line.

Hence at low temperature, the average wavelength is much larger (Fig. 1) and may become comparable to the average distance between the atoms (Fig. 2). This picture can be extended to the three dimensional case. The increase in de Broglie wavelength will mean that the probability distribution of the atom will be over a larger space or the atom itself will occupy more space. Since the distance between the atoms is fixed for a certain gas pressure, the average distance between the



The wavelength increases with lowering of temperature. Finally, at very low temperature one-dimensional *BEC* is formed.

atoms decreases with lowering of temperature. Thus at a ceratin low temperature, there will be no space between the atoms. The waves will join each other. Thus the atome are tightly packed in the coordinate space (Fig. 3). The atoms are "inflated". The dilute gas system becomes dense, The gas atoms are at low temperature and

BOSE EINSTEIN CONDENSATION

high density, a significant fraction of all the atoms will condense into a single ground state, since the Boltzman law states that the atoms will fall down to the lower state and Bose statistics allows accumulation of any number of atoms in a single state.

4. Quantum Identity Crisis

In this case, single atoms cannot be identified. The atoms are absolutely identical. No measurement can separate them. One cannot separate one atom from another; they are all in the same place. Now we can realize why it took so long before people could understand what *BEC* really meant. At the exceptionally low temperature needed for *BEC* the atoms lose their individual quantum identities and coalesce into a single blob (Fig. 3). It may be called a "super atom" for that reason. All the atoms move in phase. They all dance in tune. Hence their dynamics cannot be described by a single Schroedinger equation. The system of all atoms that participate in the formation of the *BEC* is to be described by one equation of motion. Thus individual atoms are not be described by one wave function. We have to develop the wave function describing the set of atoms that form *BEC*.



Fig. 3 Picture shows atoms confined in a Bose Einstein Condensate.

If we put an atom in a box, it can only have certain particular energies. It has to choose from a particular set of allowed energies. What Einstein's equations predicted was that at normal temperatures the atoms would be in many different energy levels. However, at very low temperature, a large fraction of the atoms would suddenly go down into the very lowest energy level. The atoms collected in the bottom is what we call Bose-Einstein condensation.

PRADIP N GHOSH

5. Theoretical aspects of condensation

Bose Einstein Statistics for a Perfect Quantum Gas :

In a perfect quantum gas, the total Hamiltonian of a set of *N* non-interacting particles is

$$H = \sum_{i=1}^{N} h_i \qquad \dots \qquad (1)$$

 h_i are the one particle Hamiltonians. In terms of creation and annihilation operators, we can write the Hamiltonian and the number operator as

$$H = \sum_{\mu} \mathcal{E}_{\mu} a_{\mu}^{\dagger} a_{\mu}, \qquad N_{op} = \sum_{\mu} a_{\mu}^{\dagger} a_{\mu} \qquad \dots \qquad (2)$$

For a multimode radiation field we can define the eigenstates in the Fock space as $|n_1, n_2, \dots, n_s \dots \rangle$

For a given set of values of $n_1, n_2, \dots, n_s \dots$ we can use a notation *j*, then

$$H|j\rangle = E_j|j\rangle, \qquad E_j = \sum_s n_s \,\mathcal{E}_s \qquad \dots \qquad (3)$$

$$N_{op}|j\rangle = N_j|j\rangle, \qquad N_j = \sum_s n_s \qquad \dots \qquad (4)$$

 $n_{\rm s}$ is the occupation number of the individual quantum states and it can have any positive integer value including zero. The Bose Einstein distribution for the mean occupation number of the particles in the *j*-th state is

$$N_j = \frac{1}{e^{-(\mu - E_j)/k_B T} - 1}, \qquad \dots \qquad (5)$$

where μ is the chemical potential determined by the condition that the total number of particles is $N = \sum_{j} N_{j}$.

The Grand canonical partition function is

$$Z = \sum_{j} e^{(\mu - E_{j})N_{j}/k_{B}T} = \prod_{s} Z_{s} \qquad ... \quad (6)$$

where,

$$Z_{s} = \sum_{n_{s}} e^{(\mu - \varepsilon_{s})n_{s}/k_{B}T} \qquad ... \tag{7}$$

is the grand canonical partition function for each single particle state s. This leads to a factoriztion of the partition function into a product of terms for individual quantum states.

For the Free energy, $F = -k_B T in Z$, we can write

$$F = \sum_{s} F_{s}, \quad F_{s} = -k_{B}T ln Z_{s}. \quad \dots \quad (8)$$

For Bosons the summation in Z leads to a geometrical series since n_s can have values $0, 1, 2, \dots$. Hence

$$Z_{s} = \sum_{n_{s}} e^{(\mu - \mathcal{E}_{s})n_{s}/k_{B}T} = \frac{1}{1 - e^{(\mu - \mathcal{E}_{s})/k_{B}T}}.$$
 (9)

The partition function satisfies the condition

$$lnZ = \sum_{s} ln \frac{1}{1 - e^{(\mu - \varepsilon_s/k_B T)}} \qquad ... (10)$$

Hence we get

$$F = k_B T \sum_{s} ln(1 - e^{(\mu - \varepsilon_s)/k_B T}) \qquad ... (11)$$

In case of a large system we have to know the number of particles *N*. For the chemical potential, we can write

$$\mu = -\left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

Bose Einstein Condensation in a cubical box :

For the non-interacting particles, we must have $\mu < 0$, this is necessary since the number of particles in a state should be positive. If *E* is the energy of the particles of mass *M* confined in a box of volume $V=L^3$ we can write the particle eigenfunctions and energies as

PRADIP N GHOSH

$$\psi(x, y, z) = \frac{1}{v} e^{i(p_x x + p_y y + p_z z)/\hbar}, \qquad ... (12)$$

$$E = \frac{p^2}{2M} = \frac{p_x^2 + p_y^2 + p_z^2}{2M}, \qquad \dots (13)$$

the allowed values of momenta are

$$p_x = \frac{2\pi\hbar}{L}n_{1}, \ p_x = \frac{2\pi\hbar}{L}n_{2}, \ p_x = \frac{2\pi\hbar}{L}n_{3}, \ \dots \ (14)$$

where n_1 , n_2 , n_3 are integers (0,1,2,3....). For a large box $(L \rightarrow \infty)$, the momentum is quasi-continuous. In momentum space in a volume $dp_x dp_y dp_z$, the number of eigenstates is $Vdp_x dp_y dp_z/(2\pi h)^3$. Assuming continuous distribution of momentum the number of states with momentum below a certain value of $p = \sqrt{2\text{ME}}$ is

$$N(E) = \frac{V}{(2\pi\hbar)^3} \int_0^p 4\pi p^2 dp$$
$$= \frac{4\pi V}{3(2\pi\hbar)^3} (2ME)^{3/2}.$$
 ... (15)

The density of states is

$$\rho(E) = \frac{dN(E)}{dE} = \frac{4\pi V}{(2\pi\hbar)^3} M^{3/2} (2E)^{1/2} . \qquad \dots (16)$$

It must be mentioned here that the number of states and also the density of states as calculated in this approximation is zero if the nergy is zero. Hence the density does not include the particles in the zero energy state.

The total number of particles is

$$N = N_0 + \int_0^\infty dE \rho(E) \frac{1}{e^{-(\mu - E)/k_B T} - 1} \quad \dots \quad (17)$$

where N_0 is the number of particles in the ground or zero-energy state. The chemical potential can be determined from the total number of particles. But it has to be done numerically and analytical solution is complicated. For this purpose we define a few parameters and follow the standard nomenclature of statistical mechanics.

$$\beta = 1/k_B T, \qquad x = \beta E \qquad \dots (18)$$

and define fugacity as

$$\mathbf{Z} = e^{\beta \mu} \quad \dots \quad (19)$$

Using the expression of density of states and the number of particles (Eq. (15) and (16)), we can write

$$\frac{N(2\pi\hbar)^3}{4\pi V} (M/\beta)^{-3/2} = \int_0^\infty dx \frac{\sqrt{2x}}{e^x/z-1} = I(z). \qquad \dots (20)$$

The ground state number of particles are omitted in deriving this expression. The integral is a function of fugacity and hence the chemical potential. Since $\mu < 0$, we should have



In order to solve the above equation we can use a geometric method by plotting the curve (Fig. 4) of the integral I(z) against z and the intersection of a horizontal line for a fixed density and temperature with this curve will lead to a value of z. We need

PRADIP N GHOSH

a value for the right hand side of the above equation when the horizontal line intersects the curve at z < 1. The integral has a value of approximately 3.274 when z = 1. Hence we need a solution when

$$\frac{N2\pi^2}{V} (M/\hbar^2 \beta)^{-3/2} < I(1) \cong 3.274 \qquad \dots (22)$$

There is no solution, if the above is not satisfied. Hence for a fixed density $\frac{N}{V}$ we can define a critical temperature above which there can be a positive density for chemical potential satisfying the condition $\mu < 0$.

$$T_c = 3.308 \ \frac{\hbar^2}{k_B M} (\frac{N}{V})^{2/3}.$$
 ... (23)

Thus the above condition requires that $T > T_c$. It may be noted that the above relation is valid for the case when the ground state population is zero. If we consider the ground state population we need the situation is valid when $T < T_c$.

According to Bose Einstein distribution

$$N_0 = \frac{1}{e^{-\beta\mu} - 1} . (24)$$

The chemical potential approaches the value zero from a negative value, hence the figacity approaches unity as $\mu \rightarrow 0$. Hence

$$N_0 = \frac{1}{e^{-\beta\mu} - 1} = -\frac{1}{\beta\mu}.$$
 (25)

Since $\beta\mu$ is a small negative quantity, the population of the ground level can be very large. If the energy of the first excited state is higher than the ground state energy by $k_B T$ or larger,

$$N_1 = \frac{1}{e^{\beta(E_1 - \mu)} - 1} < 1.$$
 (26)

The above is true because $\beta(E_1 - \mu)$ is a positive quantity with magnitude more than unity. If the first excited state energy is less than $k_B T$, $\beta(E_1 - \mu) \ll 1$, so we can write

$$N_1 = \frac{1}{\beta(E_1 - \mu)} = \frac{1}{\beta E_1 + 1/N_0} . \qquad ... (27)$$

BOSE EINSTEIN CONDENSATION

Hence,

$$\frac{N_1}{N_0} = \frac{1}{N_0 \beta E_1 + 1} = \frac{\mu}{\mu - E_1} \cong -\frac{\mu}{E_1} . \qquad ... (28)$$

Thus $N_1 \ll N_0$ as $\mu \to 0$. Hence the ground state population is larger than that of any of the excited states. This leads to a transition to a state in which the population is mostly concentrated in the ground level at a temperature lower than the critical temperature. This exhibits *Bose Einstein Condensation below the critical temperature* T_c .

Since $\mu = -\frac{1}{\beta N_0}$ and N_0 is very large below T_c , the chemical potential is practically zero and hence the fugacity is nearly 1. Using the integral in the definition of the number of particles, N (Eq.20) and also the expression of temperature (Eq. 23), it can easily be shown that

$$N_0 = N[1 - (T/T_c)^{\frac{3}{2}}] \qquad \dots (29)$$

Hence, as the temperature approaches the critical temperature the entire population collapses to the ground state.

6. Evaporative Cooling

Laser cooling in a *MOT* can cool the atoms down to a temperature of neraly 100 μK which is much higher than the temperature needed for observation of *BEC*. Hence the formation of *BEC* needs a low temperature and high density.

A more efficient method of atom cooling is Evaporative Cooling applied to atoms. It happens in the same principle as it happens in the cooling of a cup of hot tea. In the case hot tea at a temperature of 373 K, the molecules of tea, water etc have higher energy at the surface of the cup of tea than those at the lower part. When there is evaporation these molecules with higher kinetic energy and higher velocity will first leave the cup. The remaining molecules thermalize in a continuous process.

Thus the average energy of the cup of tea is lower leading to lowering of temperature. This simple explanation is known from the school level physics. But the point to be noted here is that the number of molecules lost is very small. The loss can be easily measured by noting lowering of the height of the liquid tea in the cup that is allowed to cool by evaporation. When it cools down to room

PRADIP N GHOSH

temperature (300K), there is decrease of temperature by more than 20%, though the number of molecules lost is not more than 2%. Hence the process is efficient.

The same physics of cooling a cup of tea is used to cold atoms in a magnetic trap. The cold atoms in the *MOT* are driven to a magnetic trap produced by a magnetic field. The atoms with magnetc moments align themselves parallel to the direction of the field and the magnetic field interaction energy is $-\vec{\mu}.\vec{H}$, where $\vec{\mu}$ is the magnetic moment of the atom and \vec{H} is the magnetic field. The interaction is attractive and produces a potential well trapping the atoms, if the atomic moments and the magnetic field are in the same direction. Atoms within the trap have different velocities and the higher velocity or higher energy atoms are near the top of the trap. If the atoms have a magnetic moment in the reverse direction the interaction energy will be $+\vec{\mu}.\vec{H}$ and hence it produces a repulsive interaction. Thus if a mechanism can invert the moment of the atoms they will escape the well.

This is achieved by using a radio frequency field with a frequency v_{RF} such that $hv_{RF} = 2 \overrightarrow{\mu} \cdot \overrightarrow{H}$. This frequency can be tuned to coincide with some particular trap depth. If the frequency is set to a value that corresponds to the top of the well, then the atoms near the surface of the potential well will move out of the top as they have a reversal of the moment with gain of energy.

This process may be continued and the RF frequency can be tuned and slowly lowered to remove more atoms from the top of the trap. In practice, the tuning of the frequency is stopped at a certain depth of the well. The well will contain the atoms that will retharmalize after atoms with higher velocity have been driven out.

7. Observation

The observation of *BEC* is mostly destructive. Any laser beam incident on the *BEC* may evaporate out the atoms and completely destroy the condensed state.

In the destructive method of observation, we can only get the velocity distribution of the atoms giving a signature that the *BEC* was formed. In this method as soon as the cooling lasers are switched off, the cold atoms start flying out with their residual velocities. They are recorded by a *CCD* camera kept fixed near the *BEC* cell after a few *msec* from the moment of switching off the lasers. The atoms with larger initial velocity will traverse a longer path and the slower atoms will travel a shorter distance. So a velocity distribution can be observed in the coordinate space. This will give a signature of *BEC* (Fig. 5). Before the formation of *BEC* ($T > T_c$) the atomic velocity

distribution can be described by a Gaussian describing the cold atoms. As the condensation begins ($T \approx T_c$) we can see a much narrower and sharper peak sitting on a Gaussian pedestal. The sharp peak describes the *BEC* atoms and the broader background represents the atoms that have not yet been condensed. With further lowering of temperature ($T < T_c$) we can get a single narrow Gaussian describing all the condensed atoms. The condensation was observed for *Na* atom at *MIT* and *Rb* atom (Fig 5).



Fig. 5

The velocity distribution of atoms recorded as a function of distance traversed measured from the source after a fixed time interval of a few *msec* from the moment of switching off the cooling laser.

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Thermoluminescence and its applications

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1. Introduction

It is well-known that Photoluminescence causes due to absorption of photons. It is mainly of two kinds: Fluorescence and Phosphorescence. Fluorescence is a kind of photoluminescence as a result of singlet-singlet electronic relaxation (typical lifetime: nanoseconds) whereas Phosphorescence represents photoluminescence as a result of triplet-singlet electronic relaxation whose typical lifetime is of milliseconds to seconds. Luminescence is the emission of optical radiation (infrared, visible, or ultraviolet light) by matter. This phenomenon differs from incandescence, which is the emission of radiation by a substance by virtue of its being at a high temperature (>5000°*C*) (Black body radiation). Luminescence can occur in a wide variety of matter and under many different circumstances. Thus, atoms, polymers, inorganic, organic or organometallic molecules, organic or inorganic crystals, and amorphous substances all emit luminescence under various conditions.

Thermoluminescence process is one of the processes in Thermally Stimulated Phenomena^{1,2}. Thermoluminescence is a temperature stimulated light emission from a crystal which occurs after removal of excitation. Thermoluminescence is a complicated phenomenon. With the advancement of technology, thermoluminescence possesses various applications such as, radiation dosimetry, age determination and geology.

In seventeenth century Robert Boyle and Henry Oldenburg conducted

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TAPAN GANGULY

experiments on minerals to examine their radiation due to heating. Dufay is the first to be acknowledged for his findings on thermoluminescence. He referred to lighting as a kind of burning. He worked on many materials, primarily chlorophane, and found out that too much heating would lead to loss of thermoluminescence of the material. A famous scientist, Canton brought Dufay's studies to a new level, by raising the temperature of phosphorus even further and discovering a new type of light, which he referred to as the thermoluminescence of artificial phosphorus.

The scientists Saussure and Wedgwood studied thermoluminescence in the eighteenth century. The former recognized three types of stones which emit luminescence on heating. They are : (*i*) those containing sulphur, (*ii*) those which absorb the light and then emit it, like the diamond, and (*iii*) those which do not require air and will luminesce under hot water, like dolomite and fluorspar. He further showed that the intensity of the colour of the fluorspar is an indicator for the level of thermoluminescence. The latter conducted a study on the thermoluminescence and triboluminescence, lighting as a result of friction. Studies on thermoluminescence continued in the nineteenth century. Researcher Heinrich claimed that almost all substances could emit light, provided that they are in powder form and subject to moderate heating.

Wiedmann and Schmitt attributed the thermoluminescence characteristic to cathode rays³.

Thermoluminescence can be described by two stages. First stage is the change of the system from equilibrium to metastable state by absorption of energy from UV or ionizing radiation. Then the second stage is relaxation of the system back to the equilibrium by energy release such as light with the help of thermal stimulation. Thus, thermoluminescence (TL) is the thermally stimulated emission of light following the previous absorption of energy from radiation.

2. A-Energy Storage

There are two ways for the stabilization of this absorbed energy: electronic excitation and displacement damage. At the end of both processes, radiation-induced defects are formed in the material structure. Radiation-induced defects are localized electronic states occupied by non-equilibrium concentration of electrons. Before irradiation, materials have localized electronic energy states and after irradiation, some of these states are occupied by a non-equilibrium concentration of electrons.

Therefore, these occupied states are called radiation-induced defects. They showed that the cause of defect creation is electronic excitation rather than non-ionizing displacement damage.

Energy storage caused by electronic excitation takes place by the electron-hole pair production and excitation creation. Electron-hole pair production is the formation of mobile holes and electrons in the crystal structure of the material after radiation. In addition, there exists a mid gap state caused by defects which may be created by preexisting impurities or radiation induced defects. This gap is found between the two energy bands; called conduction band and valence band. The valence band is the outer most energy level and contains electron-hole pairs in ground state of the solid. On the other hand; in the conduction band, electrons are free to move and have ability to produce electric current.

According to thermoluminescence phenomena it is assumed that there are two kinds of imperfections called electron trap and hole trap in the crystal which are localized at mid gap states . In the mid gap, the electron trap is believed close to the conduction band and the hole trap is far from the valence band.

Scheme 1a reproduces the energy storage mechanism. After irradiation, the electrons pass from valence band to conduction band and hole becomes positively charged area in the valence band. When electron reaches the conduction band, electron find its way into an electron trap and hole occupies its associated trap. Hole traps are called luminescence center in this process ^{4,5}.



TAPAN GANGULY

3. B-Energy Release

Excitation with an increase in temperature or giving light, results in release of the stored energy. Furthermore, state of the material changes from metastable to ground. When heat is increased, the electron trapped in the electron trap is released to conduction band. After that electron is free to retrap or recombine with the hole found in the hole trap. The recombination of the electron with the hole in hole trap results in the emission of photons. In this case hole trap is called as recombination center ². This process is explained in the **Scheme 1b**.



After the energy release, the output of the emitted light as a function of temperature is called thermoluminescence glow curve². Shape of the glow curves is one or more peaks of emitted light and some of them may overlap. Magnitudes and looks of the glow curves may change depending on the spectral response of the light sensitive device.

4. Applications of Thermoluminescence

One of the important applications of Thermoluminescence is Thermoluminescent dosimetry (*TLD*). *TLD* is used in many scientific and applied fields such as radiation protection, radiotherapy clinic, industry, and environmental and space research, using

many different materials. The basic demands of *TLD* are good reproducibility, low hygroscopicity, and high sensitivity for very low dose measurements or good response at high doses in radiotherapy and in mixed radiation fields.

LiF is used for dose measurements in radiotherapy since the effective atomic number of 8.3 is close to that of water or tissue. Lithium tetraborate is more tissue-equivalent than *LiF*, but it is deliquescent (absorbs moisture from the atmosphere) and its stored signals fade rapidly. Its use is therefore only worthwhile for *x*-rays, where the closeness of its effective atomic number of 7.3 to tissue outweighs the disadvantages⁶. Calcium sulphate has an effective atomic number of 15.6 and is therefore much less tissue-equivalent, but its effective atomic number of protection dosimetry. Calcium fluoride has an effective atomic number of 16.9 and is also used for protection dosimetry, as it is also very sensitive. *TLDs* are relative dosimeters and therefore have to be calibrated against absolute dosimetry systems such as a calibrated ion chamber. A 60 *Co* gamma source is generally used. Due to their small size, *TLDs* are convenient for dose-distribution measurements in medicineand biology.

The *TLDs* most commonly used in medical applications are *LiF*: *Mg*,*Ti*, LiF: Mg, Cu, P and Li2B407: Mn, because of their tissue equivalence. Other TLDs, used because of their high sensitivity, are CaSO4: Dy, Al2O3: C and *CaF2*: *Mn*. *TLDs* are available in various forms (*e.g.* powder, chips, rods and ribbons). Before they are used, *TLDs* need to be annealed to erase the residual signal. Well established and reproducible annealing cycles, including the heating and cooling rates, should be used. A basic TLD reader system consists of a planchet for placing and heating the TLD, a PMT to detect the thermoluminescence light emission and convert it into an electrical signal linearly proportional to the detected photon fluence and an electrometer for recording the PMT signal as a charge or current. The thermoluminescence intensity emission is a function of the TLD temperature T. Keeping the heating rate constant makes the temperature T proportional to time t, and so the thermoluminescence intensity can be plotted as a function of t if a recorder output is available with the *TLD* measuring system. The resulting curve is called the *TLD* glow curve. In general, if the emitted light is plotted against the crystal temperature one obtains a thermoluminescence thermogram. The peaks in the glow curve may be correlated with trap depths responsible for thermoluminescence emission. The main dosimetric peak of the

TAPAN GANGULY

LiF: Mg, Ti glow curve between 180°C and 260°C is used for dosimetry. The peak temperature is high enough so as not to be affected by room temperature and still low enough so as not to interfere with black body emission from the heating planchet. The total thermoluminescence signal emitted (*i.e.* the area under the appropriate portion of the glow curve) can be correlated to dose through proper calibration. Good reproducibility of heating cycles during the readout is important for accurate dosimetry. The thermoluminescence signal decreases in time after the irradiation due to spontaneous emission of light at room temperature. This process is called fading. Typically, for LiF: Mg, Ti, the fading of the dosimetric peak does not exceed a few percent in the months after irradiation. Good reproducibility of heating cycles during the readout is important for accurate dosimetry. The thermoluminescence dose response is linear over a wide range of doses used in radiotherapy, although it increases in the higher dose region, exhibiting superlinear behavior before it saturates at even higher doses. TLDs need to be calibrated before they are used (thus they serve as relative dosimeters). To derive the absorbed dose from the thermoluminescence reading a few correction factors have to be applied, such as those for energy, fading and dose response nonlinearity. Typical applications of TLDs in radiotherapy are: in vivo dosimetry on patients (either as a routine quality assurance procedure or for dose monitoring in special cases, for example complicated geometries, dose to critical organs, total body irradiation (TBI), brachytherapy); verification of treatment techniques in various phantoms (e.g. anthropomorphic phantoms); dosimetry audits (such as the IAEA-World Health Organization (WHO) TLD postal dose audit programme); and comparisons among hospitals.

The thermoluminescent materials used in the industry⁷⁻¹¹ have three major areas; radiation dosimetry, age determining and geology. The radiation dosimetry measures the dose that is absorbed by the sample that is exposed to irradiation. Radiation dosimetry has three subgroups; personnel dosimetry, medical dosimetry and environmental dosimetry. The first one focuses on body parts that are exposed to radiation such as hands, arms or feet while the whole-body focuses on the tissue below the surface of the body or the critical organs. It measures the dose absorbed in these parts of the body by dealing with gamma and *X*- rays (greater than 15 *keV*) and neutrons which are penetrating rays. Tissue dosimetry, which is also called skin dose, measures the dose absorbed by skin. However rather than dealing with penetrating radiation, it focuses on non-penetrating radiation such as

beta particles or <15 *KeV* Xrays. In order for these measurements to be done, a *TLD* material that is equivalent to the human tissue is needed. The *TLD* material should absorb the same dose or amount of radiation as the human tissue would do in the same area within the same radiation levels.

5. Development of luminescence dating

A major development in luminescence studies occurred when TL dating was extended to determining burial ages of unheated sediments. The evolution appears to have followed two parallel paths, one in the West and another in former Eastern Bloc countries. However, it seems there was minimal interaction between the two geographical regions, especially in the early stages. In the West, some of the earliest work includes a study that looked at TL signals of deep-sea sediment that mostly comprised for a miniferal shells. The investigators considered the signals to be from calcite and noticed that the TL intensity increased with depth. Later, another study investigated a deep-sea sediment core that comprised predominantly siliceous plankton and reported results similar to those presented earlier^{12,13}.

Thermally stimulated luminescence (*TSL*), also known as *TL*, is considered to be a reliable technique used in radiation dosimetry. Detection of defects and impurities, even in ppm level of solids, is possible with this method. A powder sample is irradiated by a known strength of light radiation for different time periods and then removed. The irradiated material is then heated at a constant heating rate so that it starts emitting thermal radiation. The intensity of the emitted radiation is measured as a function of temperature of the sample, and a *TSL* glow curve was plotted. The position of the peaks on the temperature scale is a measure of the energy depth of the trapped electrons in the solid, whereas the area under the peak indicates the number of electrons transferred into these traps by exciting radiation. The knowledge of traps with their distribution in the band gap of solids is essential to understand the luminescence process that can be obtained by *TSL* studies. With the advent of nanotechnology, there is a considerable amount of research for new nanocrystalline phosphor materials with better *TSL* and dosimetric properties¹⁴.

Thermoluminescence (*TL*) is a technique to measure the intensity of luminescence of a sample when it is irradiated by *UV* radiation, *X*-rays, γ -rays, or an electron beam as a function of temperature. This technique is widely used in mineralogy and geology, and for dating anthropological and archaeological samples. It is a

TAPAN GANGULY

stimulated emission process occurring when the thermally excited emission of light follows the previous absorption of energy from radiation. Energy absorbed from ionizing radiation (alpha, beta, gamma, cosmic rays) frees electrons to move through the crystal lattice, and some are trapped in imperfections in the lattice. Subsequent heating of the crystal can release some of these trapped electrons with an associated emission of light.

The *TL* technique has been found to be useful in dating specimens of geologically recent origin where all other conventional methods fail. It has been found to be highly successful in dating ancient pottery samples. The main basis in the Thermoluminescence Dosimetry (*TLD*) is that *TL* output is directly proportional to the radiation dose received by the phosphor and hence provides the means of estimating the dose from unknown irradiations. The *TL* dosimeters are being used in personnel, environmental and medical dosimetry. During the last two decades, *OSL* based dosimeters have also been used for various applications. Natural and induced *TL* signals can be used to explore mineral, oil and natural gas.

In many parts of the world there are deposits of wind-blown silt, known as loess, which has been transported long distances high up in the atmosphere. These deposits are usually associated with different phases of glacial history so that their dating is of considerable importance to geologists. Another application has been to sand dunes, by the research group of Singhvi at Ahmedabad¹⁵ where they successfully computed the dating of dust extracted from glaciers. Successful attempts were made to obtain the results from deep-sea material and from a variety of glacial sediments. Throughout the world this field is under very active investigation.

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A Random walk Through Statistical Physics on the Crutches of the Ideal Gas

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The physical science that attracted a lot of attention since the beginning of modern civilization was dynamics-primarily dynamics of the sun, the moon and the stars. Centuries of continuous efforts culminated in a very reasonable understanding reflected in Galilean relativity¹ and Newton's laws of motion and gravitation² in the seventeenth century, Galilean relativity asserted that all observers moving with constant velocity relative to each other (inertial observers) would see the same laws of dynamics. Newton's law expressed this in a quantitative form by the statement that if the velocity (we are assuming that the motion is in a *D*-dimensional space with D = 1 a straight line, D = 2 a plane and D = 3 our usual visible space) of a point particle (meaning usually the centre of mass a rigid body) of mass 'm' is v in an inertial frame and the external force (net) on it is \vec{F} (the components of any vector \vec{X} will be denoted by X_i , where i = 1, 2, ...D as the case may be), then in terms of the momentum $\vec{p} = m\vec{v}$, one has

$$\dot{p}_i = m\dot{v}_i = F_i \qquad \dots (1)$$

if one considers a set of point particles which are subject to an external force \vec{F} and interact with each other through a pairwise interaction \vec{F}_{ij} (this is the force on the *i*-th particle due to the *j*-th one and the sign is reversed if the ordering of the subscript is interchanged unless one has velocity dependent forces), the above equation becomes

$$m\dot{v}_i = F_i + F_{ij} \qquad \dots \qquad (2)$$

^{*} An essay in the honour of Satyendranath Bose whose 125th birth anniversary was celebrated by CITP in 2019

An example of a pairwise force is the gravitational force between two masses m_1 and m_2 located at positions $\vec{r_1}$ and $\vec{r_2}$. This force is attractive and given by $Gm_1m_2(\vec{r_1}-\vec{r_2})/|\vec{r_1}-\vec{r_2}|^3$. Historically this was the first step in sorting out the planetary motions.

In a different setting altogether, the seventeenth century saw a different kind of advancement. Experiments by Boyle³ (1662), Charles⁴ (1783), Gay-Lussac (1802) and Dalton⁵ (1802) established certain quantitative facts about qualitative relations between the pressure, volume and temperature of a gas. Boyle established that at a constant temperature the pressure of a fixed amount of gas (let us say one mole for convenience) is inversely proportional to its volume. This means if *P* is the pressure of one mole of a gas occupying a volume *V*, then at a fixed temperature *T*,

$$PV = C (a \text{ constant}) \qquad \dots \qquad (3)$$

Charles and a little later Gay-Lussac studied the volume expansion of a fixed mass of gas at fixed pressure with increasing temperature and found that for all gases a single degree centigrade rise in temperature causes a fractional change of nearly 1/273 in the volume of the gas. This means that if the gas occupies a volume V_0 at zero degree centigrade, then its volume at 't' degrees centigrade is

$$V_t = V_0 \left(1 + \frac{t}{273} \right)$$
 ... (4)

For two different temperatures t_1 and t_2 , we have

$$V_{1,2} = V_0 \left(1 + \frac{t_{1,2}}{273} \right) \qquad \dots \tag{5}$$

leading to

$$\frac{V_1}{V_2} = \frac{273 + t_1}{273 + t_2} \qquad \dots \tag{6}$$

if we now define a new temperature scale (absolute temperature) T as (273 + t) degree absolute when t is in degree centigrade, then clearly Eq. (6) can be written as

$$V_1/V_2 = T_1/T_2$$
 ... (7)

or V/T = constant if the pressure is held fixed. It should be noted that the definition of absolute temperature makes it clear that there can be no temperature lower than T = 0 and hence no temperature lower than-273 degree centigrade. Thus we learn that for a given mass (or moles) of a gas the volume V is inversely proportional to the pressure P at constant temperature T and directly proportional to the temperature T at constant pressure, leading to the relation $V \propto T / P$ for a given mass of gas. If the given mass 'm' corresponds to 'n' moles (n=m/M, M being the molecular weight of the gas), then one has

$$PV = nRT \qquad \qquad \dots \qquad (8)$$

where '*R*' is a universal constant (*i.e.* same for all gases). Relations between *P*, *V* and *T* are called equations of state and at this stage such relations are the result of experimentations.

Experiments with gases gave rise to the study of 'processes' since changing the volume at constant temperature (Boyles law) is not easy to achieve experimentally since an attempt to change the volume should change the temperature. Care has to be taken to ensure that the system has enough opportunity to exchange heat with the surroundings and recovers its original temperature at every moment to the expansion 'process'. We will return to this issue a little later in the narrative. Now, we jump to the beginning of the nineteenth century when Dalton⁵, standing on the shoulders of Democritus⁶, put forward thye atomic structure of matter where a mole of gas was supposed to contain a definite number of smaller units called atoms (this for a monotonic gas, for a diatomic gas like oxygen the unit would be a molecule which would have an internal structure made up of two atoms). Accordingly, the constant R can be written as R = kN where N is the number of molecules in one mole (universal number *i.e.* same for all gases) and the constant 'K' has been named Boltzmann's constant). The constant N is approximately $6x10^{23}$ At this point it is legitimate to ask if the pressure P exerted by the gas on the surfaces of the container of volume Vin which it is enclosed can be calculated using Newton's law².

We consider one mole (N molecules) of the gas enclosed in a cube of volume V. In the simplest model we ignore the mutual interaction between the molecules. One still has to address the problem associated with the large (virtually infinite) number of molecules. To calculate the pressure using Newton's, we have to follow the dynamics of each of the individual molecule and find out how many collisions occur in an unit time interval between the molecules and an elementary area dA of any chosen wall. Since the pressure is uniform, this number is independent of the position of the element dA. the collisions with the wall can be taken to be elastic and hence the momentum transferred to the area per unit time can be calculated. This yields the

normal force dF on the area dA leading to the pressure $P = \frac{dF}{dA}$, The calculation involves a number of assumptions which lead to a simplified but logically consistent picture.

While we adopt the simplification of ignoring the interaction forces between the molecules we still have the problem of dealing with virtually an infinite number of them and each trajectory has to be monitored separately. This is also insurmountable and hence comes another reasonable proposition; at any instant all velocities will be there since there will be some molecules travelling slowly, there will be a larger number with intermediate speeds and there will be a few with high velocities. This means we can adopt a probabilistic picture where we specify only the number dn(v) of molecules having velocities between v and v + dv where by 'v' we mean any of the three components v_x , v_y or v_z . Thus we specify the number of particles per unit volume $n(v_x)dv_x$ which have the x-component of velocity lying between v_x and $v_x + dv_x$ and similarly specify $n(v_y)dv_y$ and $n(v_z)dv_z$. We have by this procedure surreptitiously shifted from a deterministic to a probabilistic description where what we specify is $n(v_x) = Np(v_x)/V$, where N is the total number of particles in volume V and $p(v_x)$ is the probability (normalized to unity) of the x-component to the velocity lying between v_x and dv_x .

We need another plausible assumption- the number $n(v_x)$ does not change with time. One can appreciate this by considering the range of reasonable velocities for

these virtually point particles lowest being around 10 cms/sec (this is already impossibly low) and the highest around ten killometres per sec (impossibly high) in a given direction. If we break up the available velocity space into millions of small units (10^{10} say) then each unit (a box in velocity space) would have a lateral dimension of 0.0001 cm/sec which is a very small box alright in velocity space. The number of particles in this small unit for an even distribution is 10^{10} assuming a total of 10^{20} particles present. This is still a very large number and one can imagine that in a given time interval only the particle near the edges can move in or out and the particles at the edges will be a very small number compared to the large total number in the box. Hence it would be very difficult to change the occupation number in a box and we will find $n(v_x)$ virtually independent of time. We choose the area dA to lie on one of the surfaces of the cube parallel to the y-z plane. The number of particles with xcomponent of velocities lying between v_x and $v_x + dv_x$ (independent of values of v_{y} and v_{z}) and striking the area dA in unit time is half the number of particles contained in the volume $v_x dA$ (the other half travels in the opposite direction). The elastic collision reverses the sign of the velocity and the momentum transferred by the wall to the molecules in unit time in the x-direction is $Nmv_x^2 p(v_x) dA dv_x / V$. We now need to integrate over all possible values of v_r to find the total momentum transferred in unit time due to collisions with dA and hence the force dF exerted (Newton's third law) on the element dA is given by

$$dF = \int \frac{mN}{V} v_x^2 p(v_x) dv_x dA = \frac{mN}{V} \left\langle v_x^2 \right\rangle dA \qquad \dots \qquad (9)$$

where $\langle v_x^2 \rangle$ is the average value over the probability distribution. The fact that there is complete isotropy (all direction *x*, *y* and *z* equivalent) implies $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} \langle v_x^2 + v_y^2 + v_z^2 \rangle = \frac{1}{3} \langle v^2 \rangle.$

Hence,

$$dF = dA \frac{mN}{3V} \left\langle v^2 \right\rangle = \frac{2}{3} dA \frac{N}{V} \frac{1}{2} m \left\langle v^2 \right\rangle = \frac{2}{3} dA \frac{E}{V} \qquad \dots \tag{10}$$

where $E = N \frac{1}{2} m \langle v^2 \rangle$ is the total energy (in this case only kinetic energy) of the N particle gas Consequently the pressure everted by the gas is given by

N particle gas. Consequently the pressure exerted by the gas is given by

$$P = \frac{dF}{dA} = \frac{2}{3} \frac{E}{V} \qquad \qquad \dots \qquad (11)$$

The above equation could be identified with Eq. (8) for the mole of gas if

$$E = \frac{3}{2}RT = \frac{3}{2}NkT \qquad ... (12)$$

(for an arbitrary number 'n' moles of the gas N instead of being the Avogadro number would be the actual number of particles which is nN). This implies that the average kinetic energy per particle has to be identified as 3kT/2. This is certainly a property of the distribution of velocities which leads to the question : what is the probability distribution $p(\vec{v})$ of velocities of molecules.

The first thing that one can say is that $p(\vec{v}) = p(-\vec{v})$ and hence p(v) is a function of v^2 alone. For a given v^2 , we have the three independent components, v_x , v_y , v_z with the constaint

$$v_x^2 + v_y^2 + v_z^2 = v^2 \qquad \dots (13)$$

Written in terms of v_x , v_y and v_z , we must have

$$p(v^2) = f(v_x^2) f(v_y^2) f(v_z^2) \qquad \dots \qquad (14)$$

since all the velocity components are independent of each other and isotropy ensures the same function f(v) for each component. We now need a criterion for determing the function p(v). We need the function to be stable against small perturbations in the agruments v_x , v_y and v_z . Hence for small variations in the agruments the change in p(v) must be zero. The variation in the arguments have to be subject to the condition of Eq. (13). From Eq. (14).

$$\ln p(v) = \ln f(v_x^2) + \ln f(v_y^2) + \ln f(v_z^2) \qquad \dots \qquad (15)$$

If we vary v_x, v_y, v_z and p(v) does not vary, then we get

$$\frac{1}{f\left(v_x^2\right)}\frac{\partial f}{\partial v_x}\delta v_x + \frac{1}{f\left(v_y^2\right)}\frac{\partial f}{\partial v_y}\delta v_y + \frac{1}{f\left(v_z^2\right)}\frac{\partial f}{\partial v_z}\delta v_z = 0 \qquad \dots (16)$$

subject to

$$v_x \delta v_x + v_y \delta v_y + v_z \delta v_z = 0 \qquad \dots (17)$$

To make the variation in the three variables independent of each other, we use a Lagrangian multiplier λ to write

$$\left(\frac{1}{f}\frac{\partial f}{\partial v_x} + \lambda v_x\right)\delta v_x + \left(\frac{1}{f}\frac{\partial f}{\partial v_y} + \lambda v_y\right)\delta v_y + \left(\frac{1}{f}\frac{\partial f}{\partial v_z} + \lambda v_z\right)\delta v_z = 0$$
... (18)

We choose the multiplier to write

$$\frac{1}{f(v_x)}\frac{\partial f}{\partial v_x} + \lambda v_x = 0 \qquad \qquad \dots \qquad (19)$$

With the *x*-component gone, the other two components can be independently varied and hence each of the remaining two bracketed terms in Eq. (18) must be separately zero. Thus we have relations idential to Eq. (19) for the *y* and *z* components. Integrating Eq. (19), we get

$$f(v_x) = C_1 e^{-\frac{\lambda v_x^2}{2}}$$
 ... (20)

where C_1 is a constant. The corresponding results for $f(v_y)$ and $f(v_z)$ are given by

$$f(v_x) = C_2 e^{-\frac{\lambda v_y^2}{2}}$$
 ... (21a)

$$f(v_z) = C_3 e^{-\frac{\lambda v_z^2}{2}}$$
 ... (21b)

From Eq. (14), we get the distribution p(v) as

$$p(v) = Ce^{-\frac{\lambda v^2}{2}} \qquad \qquad \dots \qquad (22)$$

where *C* is a constant. The constant is evaluated from the fact that the probability distribution needs to be nomalized which means we must have $\int_{0}^{\infty} 4\pi v^2 p(v) dv = 1.$ This yields

$$C = \left(\frac{\lambda}{2\pi}\right)^{3/2} \qquad \dots \qquad (23)$$

The average value of v^2 works out to be

$$\left\langle v^2 \right\rangle = \frac{3}{\lambda}$$
 ... (24)

For this average value to be consistent with the experimental equation of state PV=NkT, we need $\lambda = m / kT$ and this leads to he distribution function

$$p(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kt}} \qquad \dots \quad (25)$$

This distribution of velocities is generally known as the Maxwell-Boltzmann distribution^{8,9}.

We now have a picture of what is called an ideal monatomic gas. This gas is characterized (as gases always are) by its pressure P, occupying volume V and temperature T. However these macroscopic quantities that characterize a gas are not independent. They are related by the equation of state PV=nRT (n is the number of moles). The temperature is related to the energy of the gas by the relation E=3nRT/2. Ideal gas means that there is no interation between the molecules and E refers only to the kinetic energy. The monatomic gas is structure-less and ideal point particles. Adiatomic molecule on the other hand would have an axis connecting the two atoms which constitute the molecule. The axis would be capable of rotating

in space and also there could be stretching and contracting along the axis. This would change the energy expression (Eq. (12)) but would not change the equation of state (Eq. (18)).

The macroscopic or thermodynamic state of the system is characterized by only two independent variables because of the equation of state and we shall use a (V,T)space for the macroscopic space of the gas for our convenience (Fig. 1). We not ask the question : how does one change the thermodynamic state of the gas. The usual answer is by heating it. Heating makes the gas hotter (changes its energy)



but can also make the gas expand.

The expansion can be viewed as work done by the gas (Fig 2). The gas is kept in a cylinder with a movable piston. Heating the gas moves the piston up



Fig. 2 The work done by a gas as it exands on heating.

from the initial position (volume V_1) to the final position (V_2). At any instant when the volume of the gas is V and its pressure P, the force exterted on the piston is PA, where A is the cross sectional area of the piston. If the piston now moves up an infinitesimal distance dz (pushed up by the gas), the work done by the gas is PAdz = PdV(dV) is the change in volume). If the infinitesimal work done is dW then

$$dW = PdV \qquad \dots (26)$$

and the total work done in the process is

$$W = \int_{V_1}^{V_2} P dV \qquad ... (27)$$

The integral cannot be evaluated in general since pressure P cannot be expressed as a function V alone in general. In the expansion process when the gas does an infinitesimal amount of work dW, its internal energy changes by an amount dE as well. In this case of the ideal gas it happens because we are heating the gas and changing its temperature, for a real gas where inter-particle interactions are nonnegligible the change in volume alone can induce a change in energy. The work done and energy change are occuring because the gas is being heated and hence the infinitesimal heating process can be quantified by a "heat energy" dQ and a global energy conservation required

$$dQ = dE + dW \qquad \dots (27)$$

which is the first law of thermodynamics.

It is clear from Eq. (27) that the integral of dW will depend on the path that connects the two end points in Fig 1. This can easily be checked by taking a path from (V_1, T_1) to (V_1, T_2) and then from (V_1, T_2) to (V_2, T_2) as path 1 (work done is $nRT_2 ln\left(\frac{V_2}{V_1}\right)$ and as path 2 from (V_1, T_1) to (V_2, T_1) followed by (V_2, T_1) to

 (V_2, T_2) (work done is $nRT_1 In\left(\frac{V_2}{V_1}\right)$). The integral of *dE* between the two end

points is not dependent on the path and is simply given by $E(T_2, V_2) - E(T_1, V_1)$. The integral of dQ is path dependent because of the path dependence of the integral of dW.

We now divide out Eq. (28) by T and get (using the energy expression for the ideal gas and its equation of state)

$$\frac{dQ}{T} = \frac{dE}{T} + \frac{PdV}{T} = \frac{3}{2}nR\frac{dT}{T} + nR\frac{dV}{V} \qquad \dots (29)$$

where the right hand side can easily be integrated from the initial to the final point without any dependence on the path used. We have

$$\int_{1}^{2} \frac{dQ}{T} = \frac{3nR}{2} ln \frac{T_2}{T_1} + nR ln \frac{V_2}{V_1} \qquad \dots (30)$$

independent of the path taken between the initial and final points. The quantity dQ/T which we denote by dS is thus a perfect differential and S is known as the entropy of the system. For *n* moles of an ideal gas at temperature *T* and occupying volume *V*, the entropy *S* is

$$S = nR \left[ln T^{3/2} + ln V \right] + S_0 \qquad ... (31)$$

The constant S_0 can depend on the number of particles in the gas considered sine the particle number is constant during the process. This is necessary for the entropy to have the desired extensive property (*i.e.* if the number of particles are increased keeping temperature and density fixed then the entropy must increase proportionately)

We now return to the molecular picture of the ideal gas and see how the entropy is related to that. To do this we need to return to Newton's laws and understand how to visualize the dynamics. It is a common misconception that how a particle moves in time can be understood by knowing the position 'x' as a function time 't' (assuming one dimensional motion to begin with). But this is only half the story since if you were given the force F(x) acting on the particle and the position of the particle

at t=0, you would not be able to find x(t). You need to be given \dot{x} as well at t=0 before you can find x(t) and hence solving Newton's law entails finding x(t) and $\dot{x}(t)$ at every instant after you have been given their values at t = 0. The Newtonian "state of a particle" of mass 'm" moving in one dimension is specified by its position and velocity (for technical reasons it is the "conjugate" momentum rather than the velocity) and the most convenient form of Newton's law for this one dimensional motion is $\dot{x} = p / m$ and $\dot{p} = F / m$. These are two first order coupled differential equations and constitute what is known as a dynamical system (two dimensional in this case because there are two variables). In three dimensions, Newtonian dynamics is describe by a six dimensional dynamical system. The "state" is a set of six variables x, y, z and the corresponding components p_x , p_y , p_z and the dynamics needs to be visualized as the motion of a point in a six dimensional state space more **commonly known as phase space.** There is a technical complication in that it is very often impractical to use Cartesian co-ordinates. One uses what are called generalized co-ordinates (co-ordinates of convenience). For motion of a particle in a plane caused by the pull of a very massive gravitational object (approximated stationary let us say) one would rather use the polar co-ordinates 'r' and θ . Denoting the generalized co-ordinates by a set of 'q's $(q_1, q_2, q_3,...)$ and defining an object called a Lagrangian L defined as "kinetic energy potential energy" (written in terms of the q's and their time derivatives), one constructs the conjugate momentum as

 $p_i = \frac{\partial L}{\partial \dot{q}_i}$ and in terms of the 'q' and 'p', Newton's laws can be written as a set of first order differential equation

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \qquad \dots \quad (32a)$$

and

$$\dot{p}_i = \frac{\partial H}{-\partial q_i} \qquad \dots \quad (32b)$$

where $H = p_i \dot{q}_i - L$ is called the Hamiltonian of the system. For a single particle in a three dimensional space (D=3) *i*=1, 2 and 3. For two particle in D=3, we will label the co-ordinates as *i*=1, 2, 3, 4, 5 and 6. The dynamics needs to be visualized in a six dimensional space where it is pictured as the motion of a point (the state) in

the six dimensional space. For N particles in D=3 the phase space is 6N dimensional. When one is discussing thermodynamic system 'N' is very large but the **simplification** of this description is that one is simply tracking the evolution of a point.

The complication and simplification of statistical mechanics comes from the picture of the evolution of the phase point. This complication was noticed for a single particle (started off from some point with a velocity in the arbitrary direction) for a motion in a stadium¹⁰⁻¹² where the particle simply reflects elastically off the walls of the stadium (Sinai billiard). The motion of the particle is restricted in a finite part of the four dimensional phase space but does not ever settle down. As time goes on the trajectory starts filling the available phase space volume more and more densely. The motion is ergodic at long times meaning that if one watches the trajectory for a time T, the fraction of time that the trajectory spends inside a given elementary volume of phase space is asymptotically the same as the fraction of points of the trajectory in that elementary volume when compared to the total number of observations of the state made in the time T. Focussing on a particular volume $dq_1 dq_2 dp_1 dp_2$ of phase space, one observes the motion for a time T making observation of the "state" of the particle at definite intrvals so that a total of N points are obtained in time T. If 'dt' is the time that the particle spends in the designated box during the observation period and 'dn' is the number of observed points of the trajectory in that box over that period T, then for $T \rightarrow \infty$, the fraction dt/T and dn/N tend to become equal according to the ergodicity requirement. The motion in the 6N dimensional phase space for the thermodynamic system is assumed to be ergodic and that sets up the statistical description where instead of talking about the position and moments of each individual particle one talks about the probability of its being in a certain region of the large dimensional phase space.

Statistical mechanics emerges then as the microscopic pictre behind the thermodynamics. The thermodynamic description is macroscopic and uses a few variables like pressure, volume and temperature. The number of particles (*N*) involved is huge and of the order of 10 and their dynamics would be described by the evolution of a point in a 6*N* dimensional space denoted by Γ . The infinitesimal volume element in this space is

$$d\Gamma = \prod_{i=1}^{3N} dq_i \prod_{i=1}^{3N} dp_i \qquad \dots \qquad (33)$$

in this system with large number of particles bouncing elastically off the walls of the enclosure in the simplest possible situation of free particles (ideal gas) the dynamics has the ergodic property discussed in the context of Sinai billiard in the previous paragraph and eventually fills the entire allowed volume of the 6N dimensional phase space. In the large time limit one adopts the point of view that the system will be

described by the time independent density $\rho_{eq}(\{q_i\}, \{p_i\})$ which describes what is the probability of finding the system in the phase space volume $d\Gamma$. This is the basic set-up of the science of statistical mechanics- a statistical description of microscopic states corresponding to a given thermodynamic or macroscopic) state. The microscopic evolution of the system of 6N particle is finally described by a time independent distribution

$$\lim_{i \to \infty} \rho(\lbrace q_i \rbrace, \lbrace p_i \rbrace, t) = \rho_{eq}(\lbrace q_i \rbrace, \lbrace p_i \rbrace) \qquad \dots \quad (34)$$

Instead of following the individual particles we have taken a coarse grained (statistical) view but one is not yet out of the woods since who will calculate ρ_{eq} . This is handled by the single most important postulate of statistical mechanics : **all microstates corresponding to a given macrostate are equally probable.** Hence if the total accessible volume of phase space corresponding to a given macrostate is Γ , then

$$\rho_{eq}\left(\left\{q_i\right\}, \left\{p_i\right\}\right) = \text{constant} = \frac{1}{\Gamma} \qquad \dots \quad (35)$$

The normalisation of the distribution is ensured by the above assertion.

We now return to the ideal gas of *N* particles confined in a volume *V* and having a total energy *E*. We want to calculate $\Gamma(E,V)$ the total volume occupied by the gas in phase space. Since the particles are all independent, each can occupy the whole available physical volume *V* independent of the other particles, Hence

$$\int d^3 r_1 \int d^3 r_2 \dots \int d^3 r_N = V^N \qquad \dots (36a)$$

The momenta $\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N$ satisfy the constraint $\sum_i p_i^2 = 2mE$ and hence

$$\int d^3 p_1 \int d^3 p_2 \dots \int d^3 p_N = \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2mE)^{(3N-1)/2} \dots (36b)$$

which is the volume of a 3N dimensional sphere of radius $\sqrt{2mE}$. Consequently from Eq. (33)

$$\Gamma(E, N, V) = V^{N} (2mE)^{3N/2} / \Gamma(3N/2) \qquad ... (37a)$$

Note that the Γ 's on the right hand side of Eqs. (36*b*) and (37*a*) are gamma function. Taking logs in Eq. (37*a*), we get (*n* is the number of moles)

$$k \ln \Gamma(E, N, V) = nR \left[ln V + \frac{3}{2} ln \frac{2E}{3N} \right] + \text{constant} \qquad \dots \quad (37b)$$

Using the fact that for an ideal gas E=3nRT/2 and remembering the expression of entropy from Eq. (31), we get

$$k \ln \Gamma = nR \left[\ln T^{3/2} + \ln V \right] + S_0 = S(V,T) \qquad \dots (38)$$

This is the connector between the macroscopic (rith hand side) and microscopic (left hand side) pictures of the ideal gas. We will tacitly assume in this article that this equality holds for interacting systems as well. But Eq. (25) had an even greater insight. It says that in equilibrium the number of gas molecules having an energy $\varepsilon = mv^2/2$, is proportional to $\exp(-\varepsilon/kT)$. The connection between Eq. (25) and the tenets of statistical mechanics as discussed till now requires a little embellishment to make Eq. (25) accessible. To begin with re-write Eq. (25) in terms of the energy ε . To this end we define the number of particles having energy between ε and $\varepsilon + d\varepsilon$ in the physical volume d^3r as $n(\varepsilon)$ and obtain from Eq. (25)

$$n(\varepsilon)d\varepsilon = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} 4\pi v^2 dv$$

$$= 2n\pi^{-1/2} \left(\frac{1}{kT}\right)^{3/2} \varepsilon^{1/2} e^{-\frac{\varepsilon}{kT}} d\varepsilon$$
$$= e^{-\varepsilon/kT} g(\varepsilon) d\varepsilon \qquad \dots \quad (39)$$

We now consider the above formula in a discrete picture. If we consider the energies accessible to a single molecule as a discrete set of numbers ε_i and think of $g(\varepsilon)d\varepsilon$ as the number of available states g, in the immediate vicinity of the energy ε_i , then Eq. (39) reads

$$n_i = g_i e^{-\varepsilon_i/kT} \qquad \dots \qquad (40)$$

The total number of particles N is expressed as

$$N = \sum_{i} n_i \qquad \dots \quad (41a)$$

and the total energy is given by

$$E = \sum_{i} n_i \varepsilon_i \qquad \dots \quad (41b)$$

The final task is to calculate the volume of phase space. This translates to solving the combinatoric problem of finding the number of ways in which the *N* particles can be distributed in the available energy states. For the i-th level we can take the first particle and put it in any of the g_i slots. This can be gone in g_i ways. We now take the second particle and for every position of the first particle, this can be accommodate in g_i ways. The number of possible arrangements now become g_i^2 . This can be continued for all the n_i particles and so we can put the n_i particle in g_i boxes in $g_i^{n_i}$ ways. The particles are all identical and hence the number of **recognizable** possibilities is $g_i^{n_i} / n_i$!. [**There is a very important caveat to be noted at this state-** n_i **and** g_i **are assumed to be large numbers with** $g_i >> n_i$. **The formula would not work for** $n_i = 2$, $g_i = 3$ **as an example. The correct answer can be found in Eq. (81).**] For a specific arrangement for a specific value of 'i', we can

have all the recognizable possibilities for another value of 'i' and hence the total number of configurations which is the total available volume of phase space is

$$\Gamma(N,E) = \prod \frac{g_i^{n_i}}{n_i!} \qquad \dots \qquad (42)$$

with the constraints shown in Eqs (41*a*, *b*). The problem is what is Γ in equilibrium. We imagine as the system evolves in time the occupation numbers n_i change and when we have reached equilibrium they do not change anymore or more correctly the small changes that may occur in them do not change the value of Γ anymore. It reaches a stationary value which is obviously a maximum. It should be noted that we are assuming that the occupation number of the small interval around the energy ε_i is capable of changing and in equilibrium assumes a constant value on the average. In principle small fluctuations around the average is allowed and also the n_i that we consider here are the average occupancies in the intervals. This particular set of g_i states are capable of exchanging energy and particles with the other sets and eventually settle down to a situation where there are n_i particles on the average each with an energy ε_i . Hence, for equilibrium, we maximize Γ or rather for convenience $\ln \Gamma$ subject to the constraints of Eqs (41a, b). Using Stirling's approximation for gamma function we have

$$\ln \Gamma(N, E) = \sum_{i} \left(n_i \ln g_i - n_i \ln n_i + n_i \right) \qquad \dots \quad (43)$$

with

$$\delta \ln \Gamma = \sum_{i} \ln \left(g_i / n_i \right) \delta n_i \qquad \dots \quad (44)$$

subject to

(

$$\sum_{i} \delta n_{i} = 0 \quad \text{and} \quad \sum_{i} \varepsilon_{i} \delta n_{i} = 0 \qquad \dots \quad (45)$$

Using two Lagrange multipliers α and β , we have

Appropriately choosing α and β , one makes all the $\delta n_i = 0$ independently and hence

$$n_i = g_i e^{-\alpha} e^{-\beta \varepsilon_i} \qquad \dots \qquad (47)$$

which agrees with Eq. (40) for $e^{-\alpha} = 1$ and $\beta^{-1} = kT$. Of course the constants α and β need not be determined by comparison with Eq. (40). We can use Eq. (47) to calculate the total number of particles and the average energy. To do so, we recognize that for free particles the number of available states near a given momentum \vec{p} is proportional to the phase space volume d^3rd^3p . The number of states should be dimensionless and it is customary to make this element dimensionless by dividing by h^3 where 'h' is Planck's constant. Thus,

$$dn = \frac{d^3 r d^3 p}{h^3} e^{-\alpha} e^{-\frac{\beta p^2}{2m}} \qquad ... (48)$$

Integrating,

$$N = \frac{Ve^{-\alpha}}{h^3} \int_0^\infty 4\pi p^2 e^{-\frac{\beta p^2}{2m}} dp$$
$$= \frac{2V}{h^3} e^{-\alpha} \left(\frac{2\pi m}{\beta}\right)^{3/2} \qquad \dots (49)$$

The total average energy is

$$E = \frac{Ve^{-\alpha}}{h^3} \int_0^\infty 4\pi p^2 \frac{p^2}{2m} e^{-\frac{\beta p^2}{2m}} dp$$

= $3 \frac{Ve^{-\alpha}}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2} \frac{1}{\beta} = \frac{3N}{2\beta}$... (50)

This identifies $\beta^{-1} = kT$ since E=3NkT/2 and from Eq. (49), it follow that

$$e^{-\alpha} = \frac{N}{2V} \left(\frac{h^2}{2\pi m kT}\right)^{3/2}$$
 ... (51)

Hence the number of non-interacting particles with energy between ε and $\varepsilon + d\varepsilon \left(\varepsilon = p^2 / 2m\right)$ and located in the elementary volume d^3r is

$$n(\varepsilon)d\varepsilon = \frac{N}{2V} \left(\frac{h^2}{2\pi m kT}\right)^{3/2} e^{-\varepsilon/kT} \frac{d^3 r d^3 p}{h^3} \qquad \dots \quad (52)$$

with this we regain the Mxwell-Boltzmann distribution. With the energy given by Eq. (50) and the entropy by $S = k \ln \Gamma(E, V)$, the thermodynamic free energy *F* is obtained as F = E - TS and all other thermodynamic properties follow.

We now turn to another interesting system of the mid-nineteenth century and see how it can be thought of as an ideal gas as well! This is the issue of black-body radiation. Radiation from a body at temperature T was extensively studied in the second half of the nineteenth century. If the radiating body remained at a definite temperature T, then clearly it was absorbing as much radiation per unit time as it was emitting and hence was in thermal equilibrium. The total energy emitted was found to be proportional to T^4 and one could write the energy emitted (*E*) per unit time as

 $E = \sigma T^4$, where the proportionality constant σ is known as Stefan's constant¹³. Of particular interest was the spectral decomposition of the energy (it gave the amount of energy associated with a given frequency ω). Denoting by $g(\omega)d\omega$ the number of modes of vibration corresponding to the frequency range ω to $\omega + d\omega$, we can define the spectral density of the energy in two different ways by

$$E = \int E(\omega)g(\omega)d\omega = \int \overline{E}(\omega)d\omega \qquad \dots \tag{53}$$

The challenge was to find $E(\omega)$. That the radiation was a wave (light wave) was known and hence if one considered a box shaped enclosure for the radiation with

sides of length L_1 , L_2 , L_3 , then for the radiation to 'fit' into the box one would need to have an integer number of wavelengths in each direction *i.e.*

$$L_i = n_i \lambda$$
 (*i* = 1, 2, 3) ... (54)

The integers n_i would have to be very large since $L \gg \lambda$. The frequency ω is related to the speed of light by the usual relation $\omega = ck = 2\pi c / \lambda$. A particular mode of vibration is characterized by the three integers n_i . A change in the set implies a change in wavelength (consequently frequency as well) and corresponds to a different mode of vibration. An elementary unit for the mode of vibration is given by

$$dn_1 dn_2 dn_3 = \frac{L_1 L_2 L_3}{8\pi^3 c^3} 4\pi \omega^2 d\omega = \frac{V\omega^2}{2\pi^2 c^3} d\omega \qquad \dots \tag{55}$$

and hence (including a factor of 2 for the modes of vibration of a transverse wave)

$$E = \frac{V}{\pi^2 c^3} \int E(\omega) \omega^2 d\omega \qquad \dots \tag{56}$$

What could be the origin of this energy? The assumption made by Rayleigh and Jeans¹⁴ was that it came from the vibration of the charged particles responsible for the radiation. Each mode of vibration is associated with an energy kT (half from the kinetic energy as we have seen for the ideal gas and half from the potential energy which all vibrators have and the virial theorem ensures the equality of the two energies for low amplitude oscillations) and hence (the history of this is rather confusing and best discussed in Kuhn)

$$E = \frac{VkT}{\pi^2 c^3} \int \omega^2 d\omega \qquad \dots \tag{57}$$

The integral runs from zero to infinity and is infinitely big showing that the Rayleigh Jeans idea is incorrect. The experimental curve of $E(\omega)$ vs ω was accurately known and Planck¹⁵ (1900) developed a heuristic picture of the energy generation process to arrive at

$$E(\omega) = \frac{\hbar\omega}{e^{\frac{\hbar\omega}{kT}} - 1} \qquad \dots \tag{58}$$

which fit the experimental data perfectly. For high temperatures, $kT \gg \hbar\omega$ ($\hbar = h/2\pi$), $E(\omega) \Box kT$ and agrees with the picture proposed by Rayleigh and Jeans. For low temperatures ($kT \ll \hbar\omega$) Eq. (58) reduces to

$$\overline{E}(\omega) = \omega^2 E(\omega) = \frac{V\hbar\omega^3}{\pi^2 c^3} e^{-\frac{\hbar\omega}{kT}} \qquad \dots \tag{59}$$

and could not be understood on the basis of anything known in 1900. The relevant picture came in 1905. The key idea was to look at thermodynamics and in particular the entropy–the connector between thermodynamics and the microscopic world. The entropy would be determined by the energy E and volume V. Since we will keep the volume fixed, we need to worry about the energy only. If one carries out a spectral decomposition of the entropy

$$S = \int \phi(\overline{E}, \omega) d\omega \qquad \dots \tag{60}$$

For equilibrium, we have learnt that entropy needs to be stationary (maximum) and hence maximize the entropy subject to constant energy *i.e.*

$$\delta S = \int \delta \phi d\omega = 0 \qquad \qquad \dots \tag{61}$$

subject to

$$\delta E = \int \delta \overline{E}(\omega) d\omega = 0 \qquad \qquad \dots \tag{62}$$

Using a Lagrange multiplier λ

$$\int \left(\delta\phi - \lambda\delta\overline{E}\right)d\omega = 0 \qquad \qquad \dots \tag{63}$$

leading to $\lambda = \frac{\partial \phi}{\partial \overline{E}}$ independent of ω . Since we are considering a constant volume process we have $T \delta S = \delta E$. Using Eq. (60).

$$\delta S = \int \frac{\partial \phi}{\partial \overline{E}} \delta \overline{E} d\omega = \lambda \int \delta \overline{E} d\omega = \lambda \delta \overline{E} \qquad \dots \tag{64}$$

identifying λ as T^{-1} . We note from Eqs. (59) and (63) that

Integrating,

$$\phi(\omega) = \frac{k}{\hbar\omega} \left[\left(ln \, \frac{V\hbar\omega^3}{\pi^2 c^3} \right) \overline{E} - \overline{E} \, ln \, \overline{E} \right] = \frac{k\overline{E}}{\hbar\omega} \left(ln \, \frac{V\hbar\omega^3}{\pi^2 c^3 \overline{E}} \right)$$
$$= k \, ln \left(\frac{V\hbar\omega^3}{\pi^2 c^3 \overline{E}(\omega)} \right)^{\frac{\overline{E}}{\hbar\omega}} \qquad \dots \quad (66)$$

If we now consider a process in which the volume of the box enclosing the radiation is changed from V_1 to V_2 keeping \overline{E} fixed, then the change in entropy at frequency ω is

$$\Delta S(\omega) = k \frac{\overline{E}(\omega)}{\hbar \omega} \ln \frac{V_2}{V_1} \qquad \dots \tag{67}$$

Comparing with Eq. (38) for an ideal gas, we infer that if $\overline{E} / \hbar \omega$ is identified as the "number of particles $N(\omega)$ " at frequency ω then on integrating Eq. (67) over all frequencies one regains the thermodynamic relationship

$$\Delta S = kN \ln \left(V_2 / V_1 \right) \qquad \dots \tag{68}$$

at constant energy. Hence we say that

$$\frac{E(\omega)}{\hbar\omega} = N(\omega) \qquad \qquad \dots \tag{69}$$

can be interpreted as saying that radiation at frequency ω can be thought of as consisting of "quanta" (generalized notion of particle) each carrying an elementary

energy unit $\hbar\omega$ (Einstein¹⁶ 1905). This explained the photo-electric effect and the quanta came to be known as photons (the real meaning emerged thirty years later) Clearly the photons have no "number conservation". They can be absorbed or emitted by any material (ignoring niceties like vacuum fluctuations). A year later Einstein¹⁷ invoked (1906) an identical picture for the vibrations in a solid to explain why the specific heat of a solid vanishes as $T \rightarrow 0$.

We now skip twenty years to a period where it became well established that if one wanted to describe particle which are very small, then Newtonian dynamics was not adequate. "Very small" had a quatitative meaning and it meant that if for a particle of mass 'm' moving with a momentum 'p' one constructed the length scale $\lambda = h / p$, then this length would be of the order of the other relevant length scales like the size of the particle or the separation between two particles...etc. Since at a temperature T, the momentum of the particle is of the order of \sqrt{mkT} , the scale λ can be estimated as h/\sqrt{mkT} which can clearly be very big for very small 'm' or very low temperatures. As for the length scales relevant for the particles, it could be their size l or if the number density of the particles is n=N/V, then it could be the quantity $n^{-1/3}$. This length scale could become very small for n >>1. Thus, the new world order of dynamics would become absolutely relevant at very low temperatures or at very high densities. This length scale (postulated de Broglie in 1924 in a bid to construct a 'dual' to the Einstein picture of particle like properties of radiation) was the wavelength associated with every material particle which could also be thought of as a wave.

The breakdown of Newtonian dynamics was supported by theoretical developments employing the wave picture and a host of experimental findings which established that under the appropriate circumstance a single particle could have wave like properties¹⁸⁻²⁰ that exhibit interference, diffraction etc. Hence the meaning of the 'state' of a particle had to change. The Newtonian picture described the particle by its position and momentum. If one had to admit the possibility of a particle being capable of showig interference, it's 'state' had to have a phase (wave like property) and hence the state had to be a complex number. Thus the 'state' of a particle in quantum mechanics is described by a function $\psi(\vec{r}.t)$ (wave function)²¹

which has the physical interpretation that $|\psi(\vec{r},t)|^2 d^D r$ is the probability of finding the particle between \vec{r} and $\vec{r} + d\vec{r}$ in a *D*-dimensional space²². This probabilistic description was forced by an examination of the process of locating the position of a particle in the new mechanics and led to the conclusion (Heisenberg) that determining precisely the position co-ordinate and the corresponding momentum co-ordinate (corresponding means canonically conjugate) of a particle simultaneously is not possible. Quantitatively, the errors Δx and Δp_x (the *x* co-ordinate is being considered) follow the constraint²³.

$$\Delta x \Delta p_x \ge \hbar / 2 \qquad \qquad \dots \tag{70}$$

Similar relations hold for the y and z co-ordinates and for other conjugate variables like angle and angular momentum etc.

We will restrict ourselves to equilibrium situations where there is no time dependence and hence we will talk about position dependent wave function $(\psi(\vec{r}))$ alone. Since free particles are all we are interested in, the wave function of a free

particle in a *D*-dimensional space is $\psi(\vec{r}) = \frac{1}{(2\pi)^{D/2}} e^{i\vec{k}.\vec{r}}$ and a measurement of

the momentum of the particle when it is in such a state yields $\vec{p} = \hbar \vec{k}$.

If we are to do statistical mechanics then we need to deal with a large number (N) of identical particles and the important quantity that we need to deal with is the N-component wave function $\psi(\vec{r_1}, \vec{r_2}, ..., \vec{r_N})$. This function of N position variables describes the wave-function of the N-particle system. If $\phi_{\alpha}(\vec{r})$ is the single particle state (wave-function) labelled by some physical quantity α (momentum vector for a free particle) then the N particle state will be assumed to be given by

$$\psi(\vec{r}_1, \vec{r}_2, ... \vec{r}_N) = \prod_{i=1}^N \phi_{\alpha_i}(\vec{r}_i)$$
 ... (71)

We will drop the subscript α from now on since we will be talking about free particle states only in this article and $\phi_i(\vec{r})$ will denote a free particle state with

momentum $\hbar \vec{k}_n$. Now comes an important constraint. Let us consider N=2 and consider the two particle state $\psi(\vec{r_1}, \vec{r_2}) = \phi_1(\vec{r_1})\phi_2(\vec{r_2})$. If we define an exchage operator P with the property

$$P\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_2, \vec{r}_1) \qquad \dots (72)$$

then clearly

$$P^{2}\psi(\vec{r}_{1},\vec{r}_{2}) = P\psi(\vec{r}_{2},\vec{r}_{1}) = \psi(\vec{r}_{1},\vec{r}_{2}) \qquad \dots (73)$$

The possible eigenvalues of the operator P are ± 1 . For every pair denoted by 1 and 2, we have the possible $\psi(\vec{r_1}, \vec{r_2})$ are either (P = 1)

$$\psi(\vec{r}_1, \vec{r}_2) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_2(\vec{r}_1)\phi_1(\vec{r}_2) \qquad \dots \quad (74)$$

or (P = -1)

$$\psi(\vec{r_1}, \vec{r_2}) = \phi_1(\vec{r_1})\phi(\vec{r_2}) - \phi_2(\vec{r_1})\phi_1(\vec{r_2}) \qquad \dots (75)$$

If the two states ϕ_1 and ϕ_2 are identical then the P = -1 wave function is identically zero and hence for particles which correspond to the netgative eigenvalue of the exchange operator, there cannot be two particles in the same quantum state. For particles corresponding to the positive eigenvalue of P there is no constraint on the occupancy of any state. The particles which cannot have more than one particle in a given quantum state are called fermions while the particles which can have arbitrary number of particles in a given quantum state are called bosons.

We are now ready to tackle the quantum ideal gas where the N particle wave function factors as shown in Eq. (71). We need to keep in mind that for the fermions in the string of single particle wave functions of Eq. (71), all the states have to be different. For the bosons it is possible to have the single particle state the same for all the particles. Since these are free particles the momentum eigenstates are also the energy eigenstates and for an eigenfunction $e^{i\vec{k}\cdot\vec{r}}$ the energy eigenvalue is $\varepsilon(k) = \hbar^2 k^2 / 2m$. As before instead of a continuum of k-values we will consider a discretized version and energies will be written as ε_i ad the number of available

states around this particular energy will be denoted by g_i . If there n_i particles in these states, then we have the constraints

$$\sum_{i} n_i = N \qquad \dots (76a)$$

$$\sum_{i} n_i \varepsilon_i = E \qquad \dots (76b)$$

Our goal will be to construct the total number of states available to the system (the exact analogue of Eq. (42)). Each 'i' is filled independently of the others and so we need to calculate the number of ways of occupying the n_i states at any 'i' and multiply over 'i'. However, the calculation will be different for fermions and bosons and needs to be done separately :

(A) *Fermions*: Each state can have only one particle and hence out of the g_i states available only n_i will be occupied. The number of ways this can be done is the number of ways in which n_i slots can be chosen from g_i and this is just the g_i !

number $\frac{g_i!}{n_i!(g_i - n_i)!}$. Hence the total number of arrangement is

$$\Gamma_F = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!} \qquad ... \tag{77}$$

It has to be brne in mind that as in the Maxwell-Boltzmann situation n_i and g_i are very large numbers and hence Stirling's approximation can be used for them including the difference $g_i - n_i$ since the momenta are very very closely spaced and the number of states available is much greater than the particles that will occupy them. We work with $\ln \Gamma_F$ as before to make use of the Stirling approximation and get

$$\ln \Gamma_{i} = \sum_{i} [g_{i} \ln g_{i} - n_{i} \ln n_{i} - (g_{i} - n_{i}) \ln (g_{i} - n_{i})] \qquad \dots (78)$$

As before our picture is that for the equilibrium distribution, the total volume occupied has to be insensitive to small variations in the individual occupation numbers and hence we set the small variation $\delta \ln \Gamma_F = 0$ under the constraints of δN and δE set equal to zero. We find

$$\delta \ln \Gamma_F = \left[ln \frac{g_i - n_i}{n_i} \right] \delta n_i \qquad \dots \quad (79a)$$

and if this is zero subject to $\sum_{i} \delta n_i = 0$ and $\sum_{i} \varepsilon_i \delta n_i = 0$, then using the Lagrange multipliers α and β , we get

$$\sum_{i} \left[ln \frac{g_i - n_i}{n_i} - (\alpha + \beta \varepsilon_i) \right] \delta n_i = 0 \qquad \dots \quad (79b)$$

The constants can be chosen to make all the δn_i independent and hence each coefficient vanishes in the above equation to give [24m 25]

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + 1} \qquad \dots \tag{80}$$

(B) Bosons: We now have no restrictions in putting n_i identical particles in g_i idential boxes. The number of ways this can be done is exactly the number of ways in which 'n' identical letters can be put in 'g' identical letter boxes. This is solved by drawing 'g-1' lines and treating the 'g' spaces thus created a 'g' boxes. We draw the 'n' particles as 'n' dots and for g = 5 and n = 3 we show a typical arrangement in Fig. 3

If we now treat te bars and dots as a total of n + g - 1 objects and simply permute them then we have (n + g - 1)! arrangements of lines and dots and that accounts for all the possible ways in which 'n' objects can be put in 'g' boxes. But the dots are identical and so are the lines. Hence the dots can be arranged in *nl* ways

which cannot be distinguished and the g-1 lines can be arranged in (g-1)! ways which cannot be distinguished. Hence the total umber of recognizable independent

arrangements are $\frac{(n+g-1)!}{n!(g-1)!}$. This allows us to write the total number of

configurations Γ_B for the bosons as

$$\Gamma_B = \prod_i \frac{(n_i + g_i - 1)!}{n_i ! (g_i - 1)!}.$$
(81)

To find the equilibrium distribution it is convenient to maximize $ln \Gamma_B$ instead. Remembering n_i and g_i are both much greater than unity and one can always drop it when working with the above expression for Γ_B , we get

$$\ln \Gamma_B = \sum_i \left[\left(g_i + n_i \right) \ln \left(g_i + n_i \right) - g_i \ln g_i - n_i \ln n_i \right] \qquad \dots \qquad (82)$$

Following identical steps as for the fermions,

$$\delta \ln \Gamma_B = \sum_i \left[\ln \frac{g_i + n_i}{n_i} \right] \delta n_i \qquad \dots \qquad (83)$$

and maximizing $ln \Gamma_B$ with the constraints on the total number of particles and total energy (as in the case of fermions), we get²⁶

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} - 1} \qquad \dots \qquad (84)$$

If we do not have the constraint of fixed number (that is creation and annihilation of particles is allowed –they can be absorbed or emitted by any medium including vacuum) then the constant α does not appear and we have

$$n_i = \frac{g_i}{e^{\beta \varepsilon_i} - 1}$$
 (no number conservation) ... (85)

For a continuous distribution of energies, Eqs. (80), (84) and (85) become after defining the chemical potential by the relation $\alpha = -\beta\mu$

Fermions :

$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1} \qquad \dots \qquad (86)$$

Bosons :

With number conservation :
$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)}-1}$$
 ... (87)

Without number coservation:
$$n(\varepsilon)d\varepsilon = \frac{g(\varepsilon)d\varepsilon}{e^{\beta\varepsilon} - 1}$$
 ... (88)

The first thing to note is that if we drop ± 1 in the above equations we have the classical Maxwell Botzmann answer. Clearly this happens if $e^{-\beta m} >> 1$. To check when this occurs we assume that this is indeed so and calculate the total number of particles from Eqs. (86) and (87) by using the $g(\varepsilon)d\varepsilon$ written down in Eq. (39). We ignore the spin degeneracy factor of 2s + 1 which can be put back whenever one so desires, Integrating,

$$N = V e^{\beta \mu} \left(\frac{2\pi m kT}{h^2}\right)^{3/2} \qquad \dots \tag{89}$$

yielding

$$e^{-\beta\mu} = \frac{V}{N} \left(\frac{2\pi mkT}{h^2}\right)^{3/2}$$
 ... (90)

Clearly the classical limit holds if $N/V \ll 1$ at moderate temperatures and $kT \gg h^2/2\pi m$ at moderate densities. Hence we have established that the qantum effects are vital at low temperatures and high densities as discussed between Eqs. (69) and (70). For the case of no number conservation there is no classical limit.

Looking back at Eq. (69), we now see that the ε of Eq. (88) is the single photon energy of $\hbar\omega$ and $g(\varepsilon)d\varepsilon$ in the number of modes of vibration between ω and $\omega + d\omega$. Consequently the distribution of energy associated with Eq. (88) can be written as

$$E = \frac{2V}{\pi^2 c^3} \int_0^\infty \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \omega^2 d\omega \qquad \dots \qquad (91)$$

which is exactly Planck's law of radiation. This result was obtained by Bose²⁷ (1924) by a different procedure. It should be noted that integrating Eq. (91) yields $E = \sigma T^4$, which is Stefan's law of radiation.

If we were considering the sound waves in a solid (the result of any disturbance affecting the interior of the solid), then the modes of vibration is very similar to Eq. (55) if we take note of the fact that there are two transverse vibrations (velocity c_T) and one longitudinal vibration (velocity c_L) and hence Eq. (55) with all the modes

accounted for would have a right hand side given by $\frac{V}{2\pi^2} \left(\frac{2}{c_T^3} + \frac{1}{c_L^3}\right) \omega^2 d\omega$. Just

as light vibrations are quantized in the form of photons (no number conservation), the sound vibration can be quantized in the form of phonons (no number conservation) and Eq. (91) would hold with the appropriate changes in $g(\omega)$. The frequency integral for vibrations in a solid would have an upper cut off but at very low temperatures that cut off could be considered infinitely large. Consequently the total energy associated with the vibrations in a solid at very low temperatures (extreme quantum limit) will be proportional to T^4 and the specific heat proportional to T^3 (Debye²⁸. This behaviour of the specific heat is completely consistent with experimental results and a big improvement on Einstein (1906). It should, however, be clearly understood that a proper understanding of the 'photon' and the 'phonon'' comes only from quantum field theory and many body quantum mechanies respectively.

We now end this essay with a discussion of two cases where the quantum gases with number conservation ($\mu \neq 0$) are strongly quantum mechanical and the ±1 in

the denominators of Eqs. (86) and (87) play a dominant role. We treat fermions and bosons separately.

Bosons: We fix the volume V and the number of particles N and start from high temperatures where the chemical potential term is dominant. As we lower the temperature the chemical potential starts increasing from the large negative values that it has at very temperatures. But the maximum possible value of μ is zero since for $\mu > 0$, the distribution of Eq. (87) is not defined for energies lower than μ . The temperature at which $\mu = 0$ is denoted by T_c and is defined by the relation

For temperatures $T < T_c$, the chemical potential remains at zero but the number of particles as obtained by an integral of the form in Eq. (92) with T replacing T_c , will be less than N since $e^{\varepsilon/kT} > e^{g/kT_c}$ for all energies. If the integral at $T < T_c$ yields N' < N, then what happens to the N - N' particles. They all settle in the ground state $\varepsilon = 0$. Thus for temperatures $T < T_c$, the ground state has a macrossopic occupation *i.e.* the occupation is proportional to V however large V may be. This number increases as the tee temperature decreases and as T becomes almost zero, all the gas molecules settle in the ground state. This phenomenon is known as the Bose-Einstein condensation (BEC) [Einstein 1925]. It should be realized that this was a very unusual prediction. A real phase transition is supposed to occur in a system which consisted entirely of non-interacting particles. But here is a situation where there is a single phase of a normal quantum gas above T_c and below it two co-existing phases, one of which has a macroscopic number of particles condensed in the ground state. This was such an unusual happening that it prompted a wide search for a system of this kind. The phenomenon of superfluidity was one of the early candidates (a combination of superfluid and normal fluid below the transition point) but it beecame clear that superfluidity does require interactions. The quest for observing the BEC ended in its experimental realization^{29,30} in 1995 fifty years after the prediction.

Fermions: We consider ultra-low temperatures at which the ratio $(\varepsilon - \mu)/kT$ is extremely big if $\varepsilon > \mu$ and very close to zero if $\varepsilon < \mu$. This makes the number $n(\varepsilon)n$ egligibly small for $\varepsilon > \mu$ and $n(\varepsilon) = g(\varepsilon)$ if $\varepsilon < \mu$. The μ cocerned is the chemical potential corresponding to T = 0. This particular μ is called the Fermi energy and denoted by ε_F . If the fermion that one is talking about is an electron or a nucleon then the spin is $\frac{1}{2}$ and hence the spin degeneracy is 2. In that case the volume element in phase space is $2\frac{d^3rd^3p}{h^3}$ and is our factor $g(\varepsilon)d\varepsilon$. The integration in momentum extends to the Fermi momentum p_F defined as $p_F = \sqrt{2m\varepsilon_F}$. The total number of particles is

$$N = \frac{2V}{h^3} \int_0^{p_F} 4\pi p^2 dp = \frac{8\pi V}{3} \left(\frac{2m\varepsilon_F}{h^2}\right)^{3/2}$$

leading to

$$\varepsilon_F = \frac{h^2}{2m} \left(\frac{3N}{8\pi V}\right)^{2/3} \qquad \dots \qquad (93)$$

High densities make the Fermi energy very high. The energy of the Fermi gas is obtained from the integral

$$E = \frac{2V}{h^3} \int_0^{p_F} \frac{p^2}{2m} 4\pi p^2 dp = \frac{8\pi}{5} \frac{V}{h^3} \frac{p_F^2}{2m} p_F^3 = \frac{3}{5} N \varepsilon_F \qquad \dots \qquad (94)$$

Using the ideal gas relationship PV = 2E/3, the pressure exerted by a Fermi gas is seen to be

$$P = \frac{2N}{5V} \varepsilon_F = \left(\frac{3}{8\pi}\right)^{2/3} \frac{h^2}{5m} \left(\frac{N}{V}\right)^{5/3} \qquad \dots \qquad (95)$$

For high values of number density, this can be a very high pressure. It must be noted that this pressure is not coming from the random motion of the molecules that happens at finite temperatures. This is an essentially zero temperature pressure and stems from the fact that two fermions cannot occupy the same state and hence there is an inherent repulsion in an ideal Fermi gas leading to this enormous pressure.

An application of this pressure can be found in stars called white dwarfs. These are stars which have run out of the fuel required to maintain the fusion reactions and hence tend to cool off. The cooling reduces the pressure and gravitational forces tend to shrink the volume of such stars which are called white dwarfs. An important issue is whether such stars will hold their own as dim stars or shrink sufficiently to become a white dwart. When the star has shrunk sufficiently the density will become high and it is possible that the resulting Fermi pressure effects.

First we need to know which particles in the star provide the largest pressure. The helium atoms (primary constituents) in the star are dissociated and the nucleons which are heavy are virtually static and provide the mass while the electrons which are light and moving around fast provide the pressure. The mass of the star can be written as $M = 2Nm_n$ where N is the number of protons (equal to the number of electrons) and the factor of two arises as in helium the number of neutrons equal the number of protons (masses are nearly the same). From now on we will disregard all numerical factors, if the radius of the star is R, then according to Eq. (95), the Fermi

pressure of the electrons (mass 'm') is $P \Box \frac{h^2}{m} \left(\frac{M}{m_n}\right)^{5/3} R^{-5}$. The gravidational

force causing the collapse of the star is GM^2 / R^2 . The force arising from the Fermi pressure is obtained from PR^2 and for a balance at radius *R* we need the gravitational force and Fermi force to balance. This gives

$$G\frac{M^2}{R^2} = \frac{h^2}{m} \left(\frac{M}{m_n}\right)^{5/3} \frac{1}{R^3} \qquad \dots \qquad (96)$$

The critical mass M_c for balance at radius 'R' is consequently obtained as

$$\left(\frac{M_c}{m_n}\right)^{1/3} = \frac{h^2}{Gm_n^2} \frac{1}{R} \qquad ... \tag{97}$$

The above result says that the radius '*R*' and the corresponding critical mass of the white dwarf are related as $M_c \propto R^{-3}$ *i.e.* larger the mass, smaller the rdius. But there is a catch!

The thermodynamic relation of Eqs. (94) and (95), assume that the electrons are non-relativistic. However, if we calculate the Fermi energy for a typical white dwarf parameters from Eq. (93) and use it to find the equivalent Fermi temperature T_F through the relation $\varepsilon_F = kT_F$, then typical Fermi te4mperatures are $10^{11}K$. The temperature of a white dwarf is typically $10^7 K$ and hence the energies of individual electrons are in general much higher than the rest mass energy which makes the electrons strongly relativistic. The relativistic dispersion relation is $\varepsilon = \sqrt{p^2c^2 + m^2c^4}$ which becomes $\varepsilon \square pc$ when the rest mass contribution to energy is smaller than the motional contribution. The total energy is now found as

$$E = \frac{Vc}{h^3} \int_0^{p_F} 4\pi p^3 dp = \frac{\pi c V}{h^3} \left(\frac{3}{8\pi} \frac{N}{V} h^3\right)^{4/3} \qquad \dots \qquad (98)$$

it can easily be checked that the ultra-relativistic ideal gas has a pressure volume relationship given by PV = E/3. The pressure, consequently, works out to be

$$P = \frac{3c}{8h^3} \left(\frac{Nh^3}{V}\right)^{4/3} ...$$
(99)

Once again dropping all numerical factors the pressure is estimated as

$$P \Box \left(\frac{M}{m_n}\right)^{4/3} \frac{hc}{R^4}$$
 which leads to a repulsive force proportional to $\left(\frac{M}{m_n}\right)^{4/3} \frac{hc}{R^2}$.

Balancing this force against the gravitational collapse inducing force GM^2 / R^2 , the critical mass M_c for balance is found as

$$\left(\frac{M_c}{m_n}\right)^{2/3} \approx \frac{hc}{Gm_n^2} \qquad \qquad \dots \qquad (100)$$

The critical mass is independent of radius of the star !! The interpretation is that no matter what the radius, if the mass of the star is greater than M_c , then the gravitational forces will always win and the star will collapse to become a black hole. For a white dwarf star to be founed we must have $M < M_c$. This critical mass was found by Chandrasekhar³¹ and a called the Chandrasekhar limit – another great result found by an Indian scientist.

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CONTENTS

JANUARY – JUNE, 2018

	Page
On the determination of activation energy of thermoluminescence peaks recorded under hyperbolic heating scheme and obeying mixed order kinetics	
–Ananda Sarkar	1
Analytical study of diffusivity and shear viscosity of liquid semiconductor	
–Lalit Kumar Mishra, Gyanesh and Tarun Kumar Dey	9
Causality analysis between solar irradiance and Forbush decrease indices	
–Sankar Narayan, Amrita Prasad, Soumya Roy, Gautam Bhattacharya, Subhash Chandra Panja and Koushik Ghosh	17
A cable-connected satellites system : stability in elliptical orbit of centre of mass of the system	
– Sangam Kumar and Santosh Kumar	35
Effect of induced magnetic field and thermal radiation of visco- elastic fluid flow past an infinite vertical porous plate with constant heat flux	
–Paban Dhar and Rita Choudhury	43
Development of a self controlled interferometer using optical Kerr medium as switching element –Agnijita Chatterjee and Sourangshu Mukhopadhyay	
Numerical analysis of hetrostructure semiconductor devices –Mukesh Kumar, Archana Kumari, Bidyanand Mahto and Tarun Kumar Dey	71
Analysis of memory and self affinity and identification of governing process in solar flare index signal	
–Shankhachur Mukherjee, Kausik Rakshit and Koushik Ghosh	79

JULY – DECEMBER, 2018

Bose Einstein Condensation				
–Pradip N Ghosh	101			
Thermoluminescence and its application				
–Tapan Ganguly	113			
A Random Walk Through Statistical Physics on the				
Crutches of the Ideal Gas				
Jayanta K Bhattacharjee	123			

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