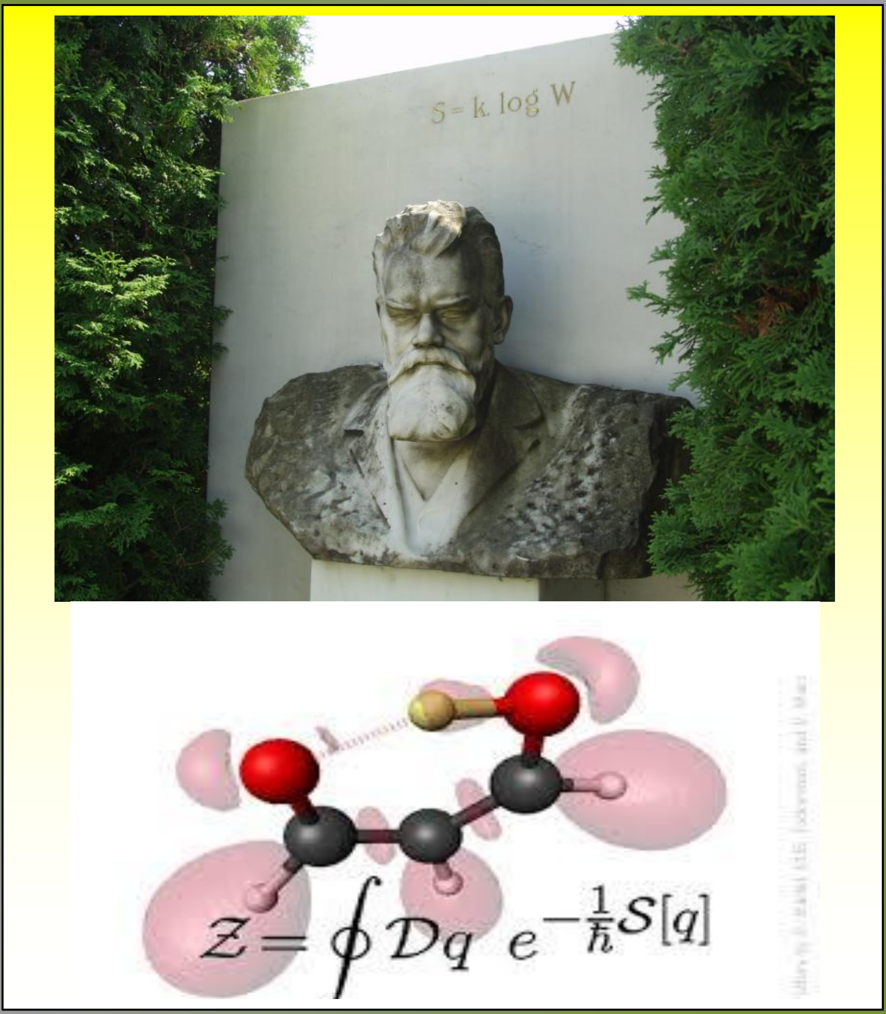
KARNATAKA STATE OPEN UNIVERSITY

Mukthagangothri, Mysore – 570 006

M.Sc. PHYSICS

(SECOND SEMESTER)



COURSE –MP 2.3

Thermal Physics and Statistical Mechanics

M.Sc. PHYSICS

SECOND SEMESTER

Course: MP 2.3

THERMAL PHYSICS & STATISTICAL MECHANICS

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PRELUDE

In this course you will learn about the basic principles and applications of Thermodynamics and Statistical Mechanics. Thermodynamics deals with properties of matter in equilibrium. It is based on empirical foundations. Here we deal mainly with transformation of heat into mechanical work or vice versa. Thermodynamics deals with equilibrium variables and thus there is no reference to the rate of approaching or deviation from equilibrium states. There are three laws of thermodynamics that have stood the test of time. Due to changes in temperature and pressure we come across changes for equilibrium phases. You shall learn about van der waals gas that exhibits phase transitions. Irreversible thermodynamics deals with processes that are slightly away from equilibrium. Basic physical quantities like mass, temperature and pressure change in space and time. We shall study transport processes that play a central role in non-equilibrium processes. Local equilibrium hypothesis plays an important role. Entropy balance is important to understand irreversible processes. In the linear region fluxes and forces are related linearly via coefficients that satisfy certain symmetry relations called Onsager relations. Various thermoelectric phenomena like Seebeck effect, Peltier effect and Thomson effect shall be discussed using the principles of non-equilibrium thermodynamics.

Statistical Mechanics deals with the average properties of large systems. It aims to provide a theoretical basis for thermodynamics. Description of micro-states is best done with the help of phase space. It is found that phase space fluid of a system moves like an incompressible fluid. Statistical mechanics makes use of different kinds of ensembles of identically prepared systems. While we normally get the most probable or mean values of various physical variables, it is found that there can be small fluctuations about the mean values. The fluctuations decrease rapidly with the number of particles in a system under consideration. Gibbs distribution reduces to Maxwell Boltzmann distribution in the limit of non interacting systems. The entropy of a system is related to the number of accessible micro-states of a large system. When mixing of gasses is considered we come across a paradoxical situation called

Gibbs paradox whose resolution requires us to treat the molecules of a gas as indistinguishable. Thus we are lead to Sackur-Tetrode formula for entropy. It is found that every quadratic degree of freedom contributes an energy of $\frac{1}{2}KT$ per particle under equilibrium conditions. This is known as equipartition theorem. It can be employed to deduce the specific heat of solids etc. We shall also study the basic postulates of quantum statics. We shall find the classical limits of quantum statistical distributions. It is found that there are two distinct quantum statistics, namely Bose-Einstein and Fermi-Dirac distributions. Correspondingly the wave functions satisfy specific symmetry properties. In quantum statics we make use of density operator to describe mixed states. Quantum version of Liouville theorem is formulated in terms of the density operator. We shall study the conditions satisfied in equilibrium. We shall deduce the distribution functions in quantum statistics making use of the grand canonical ensemble. The quantum distributions reduce to the classical expression in the limit of high temperatures and low densities. We shall evaluate partition functions of molecules at normal temperatures etc.

Fermi-Dirac distribution is applicable to Fermions, i.e., particles with half-odd integer spins. It can be applied to study of electrons in metals. Paramagnetic susceptibility can be deduced using quantum statistics. We can apply BE statistics to describe a gas of photons thus getting the famous Planck's distribution formula. Bosons have this peculiar tendency to crowd together. As the temperature of a gas is reduced below a certain value, a certain kind of clustering into the lowest possible state happens. It is called Bose-Einstein condensation. We shall study that in some detail

UNIT 1

1 Thermodynamics and its applications

1.1 Objectives

After studying this unit you will be able to

- have an overview of thermodynamics
- understand Maxwell's relations
- understand specific heats from thermodynamic relations
- know about the laws of thermodynamics
- learn about some applications of thermodynamics
- understand phase transitions
- learn about surface effects in condensation.

1.2 Introduction

In this unit you shall learn about thermodynamics. Thermodynamics happens to be a study of heat and matter transfer between equilibrium states. It is a phenomenological study based on our experiments with macroscopic systems. We make use of pressure, volume, temperature, entropy etc. to discuss properties of macroscopic systems. There are differential relations between the variations of the mentioned variables. They are called Maxwell's relations. Relations between specific heats can be established using Maxwell's relations. There are three laws of thermodynamics. They are based on careful observations of various systems around us. You shall learn about them in this unit. There are several applications of thermodynamics. We see matter in several phases and due to changes in temperature and pressure changes in phase are observed. You shall learn briefly about phase changes or transitions.

1.3 Overview of thermodynamics

Thermodynamics is mainly an empirical science based on axioms whose validity has been established by experiments. Just as in classical mechanics we begin with a small number of premises or laws and deduce other results there-from. Certain fundamental laws are inferred from experiments and various conclusions are drawn from them in thermodynamics. Pure thermodynamics is not concerned with the justification of the fundamental laws. Such an attempt is done in "Statistical Mechanics".

Thermodynamic results are generally very accurate and hence the science of thermodynamics occupies an important place in modern physics and engineering. Thermodynamics mainly deals with equilibrium variables of a macroscopic system. Here we mainly deal with the transformation of heat into mechanical work or vice versa. Sometimes electrical and magnetic agencies have to be taken into account. In thermodynamics attention is focussed on the interior of a complex system in contrast to external aspects as in mechanics. In thermodynamics one defines the interior properties by means of a few measurable quantities such as temperature, entropy etc. Such quantities are called variables of state or thermodynamic variables. Since thermodynamics deals with equilibrium variables, there is no reference to the rate of approaching or deviation from equilibrium states.

Thermodynamic equilibrium

As a system changes, the internal variables such as pressure, volume, temperature change. Such a change is called change of state. There are several types of equilibria. When there is no unbalanced force between the system and its surroundings the system is said to be in mechanical equilibrium. When forces are unbalanced time has to be brought in for the description of the system.

If the temperature in all parts of a system is uniform and equal to that of the surroundings, the system is said to be in thermal equilibrium. Additionally, if the chemical composition is uniform throughout a system, the system is said to be in chemical equilibrium. A system that is in thermal, mechanical and chemical equilibrium is said to be in thermodynamic equilibrium. It is defined by pressure, volume and temperature of the system without reference to time. These are called thermodynamic coordinates or variables of the state. In general, a thermodynamic system may be chemical, magnetic, electrical etc.

A system is said to be homogeneous if it is uniform in every portion of it. On the other hand, a heterogeneous system is composed of a number of homogeneous systems separated from one another by surfaces of discontinuity. Each separate part of the heterogeneous system is called a phase. For example water contained in a closed vessel has two phases: one liquid phase and another gaseous(vapour) phase over the liquid surface. We call a system a simple homogeneous system if its internal state can be specified by two thermodynamic variables like pressure and volume.

Zeroth law of thermodynamics

Temperature is one of the quantities that are required to specify the state of a thermodynamic system. Every thermodynamic system must possess a temperature. This postulate of the existence of temperature is sometimes called zeroth law of thermodynamics.It is observed that if A and B are two thermodynamic systems in equilibrium, then they shall possess the same temperature. If A and C are in equilibrium then B and C happen to be in equilibrium with each other. all three are then characterised by the same value of temperature. This law makes it possible to compare temperature by means of a standard device called thermometer.

The equation of state

The thermal state of a simple homogeneous substance body like a fluid or a solid is characterised by its pressure P and volume V. The temperature T of the system depends on P and V. Hence out of P, V and T only two are independent. This fact is written in the form:

$$f\left(P,V,T\right)=0 \tag{1}$$

Equation 1.1 is called the "equation of state". The function f depends on individual systems. Please note that an equation of state is not applicable to systems not in equilibrium. The equation of state of a systems has to be deduced experimentally.

The quantities P, V and T refers to gross or large scale properties of a system that can be measured. Hence they are called macroscopic coordinates. We do not care much about the internal constitution of systems in terms of microscopic entities like atoms and molecules.

Energy and work

Thermodynamics deals with energy and work. Energy can exist in several forms such as Kinetic energy, mechanical potential energy, chemical energy, electrical energy etc. It is well known in mechanics that the sum of kinetic and potential energies remains constant during motion. This result is known as the principle of conservation of energy. In a dissipative system, mechanical energy is lost due to friction. But physics tells us that there is no loss of energy as a whole. Friction leads to the production of heat, which is also a form of energy. This principle of conservation of energy can be extended to other forms of energy. For example, electrical energy can be transformed into heat or mechanical energy such that the total sum of all forms of energy remains constant.

In thermodynamics a system can interact with the surroundings by performing mechanical work or by transferring heat. Work in thermodynamics is a macroscopic concept and can be measured in macroscopic coordinates. Hence it may be called external work in contrast to internal work which is applicable to work done by one part of the system on another. It is only the external work that is being considered in thermodynamics.

Internal energy and heat

There are systems which may show no apparent mechanical energy, but may still be capable of doing work. They are said to possess internal energy. For example, a mixture of Hydrogen and Oxygen gasses has no kinetic energy if the system is not moving, but still the system can do work on explosion. It is due to the internal energy of the system. In thermodynamics we do not try to find the source of internal energy but simply take account of its existence.

When a thermodynamic system does any work it loses some of its internal energy such that

$$\Delta U = -\Delta W \tag{2}$$

where ΔU is the change in the internal energy and ΔW is the work done by the system.

It is also assumed that the internal energy of a system is a single valued function of the variables of state. The energy acquired by a system due to non-conventional ways is called heat. It can be shown that heat is the energy transferred between the system and surrounding by the virtue of temperature difference. Heat must be distinguished from work which is a transfer of energy without a temperature difference. Heat may

enter or leave a system without mechanical changes.
For a thermally insulated system

$$\Delta U + \Delta W = 0 \tag{3}$$

where ΔU is the change in the internal energy and ΔW is the work done by the system. If however, the system is not thermally insulated, some amount of heat ΔQ will enter the system and hence the net energy entering the system will be

$$\Delta U = \Delta Q - \Delta W \tag{4}$$

or

$$\Delta Q = \Delta U + \Delta W.$$

This provides a simple way of measuring heat.

The first law of thermodynamics

This is simply the law of conservation of energy applied to a thermodynamic system. It has been stated in several different ways. The increase in internal energy of a system is equal to the sum of the work done on the system and the heat added to it. The work done by a mechanical force is equal to $\int P\, dV$. If magnetic and electrical forces are present suitable terms have to be included. It should be noted that the first law of thermodynamics asserts

(a) heat is a form of internal energy

(b) energy is conserved in thermodynamic changes

The Specific heat of a body

The internal energy is a function of any two of the state variables P, V and T. Hence we can write

$$U = f\,(V, T) \tag{5}$$

Differentiating the above equation

$$dU = \left(\frac{\partial f}{\partial T}\right)_V dT + \left(\frac{\partial f}{\partial V}\right)_T dV \tag{6}$$

For perfect gases $\left(\frac{\partial f}{\partial V}\right)_T = 0$, while for a gas obeying vander waal's equation of state $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$.
Let an amount of heat δQ be added to a thermodynamic system such as a perfect gas, it expands by volume dV against pressure P. Hence

$$\Delta Q = dU + PdV \tag{7}$$

Substituting for dU from equation 1.6 we get

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P\,dV \tag{8}$$

Hence

$$\frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \tag{9}$$

But $\frac{\delta Q}{dT}$ is the specific heat. It depends on the conditions being varied. If pressure is kept constant we get $\left(\frac{\delta Q}{dT}\right)_P = C_P$. Thus

$$C_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{10}$$

But, if heat is supplied at constant volume, we get

$$\left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \tag{11}$$

by definition. Therefore equation 1.10 leads to

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \tag{12}$$

For a perfect (or ideal) gas $PV = RT$. Hence $\left(\frac{\partial U}{\partial V}\right)_T = 0$ and $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$. Therefore

$$C_P - C_V = R \tag{13}$$

The second law of thermodynamics

The second law of thermodynamics deals with the subject of direction in which any physical or chemical process involving change of energy takes place. Consider the process indicated below

$$2H_2 + O_2 \quad\longrightarrow\quad 2H_2O + \text{energy} \tag{14}$$

This indicates a chemical reaction in which one mole of O_2 combines with two moles of H_2 to produce two moles of water vapour with a release of ΔU amount of energy. The first law of thermodynamics simply indicates energy conservation in the reaction. But it can not tell us what direction the reaction takes place. If we have a mixture of H_2, O_2 and H_2O vapour in arbitrary proportions at same temperature and pressure, the first law cannot tell us whether some H_2 and O_2 will combine to form H_2, O_2 or some H_2, O_2 will dissociate into H_2 and O_2.

As another example consider two bodies A and B at two different temperatures. When they are brought into contact, the first law states that the heat lost by one body is equal to the heat gained by the other body. But it does not tell us in which direction the heat flows. However our experience tells us that heat passes from hotter body to cooler body wherein we introduce the concept of temperature to define the degree of hotness of a body. The law that arose out of Carnot's investigations about the convertibility of heat to work is generally known as second law of thermodynamics.

We know that mechanical energy and heat are different forms of energy. While mechanical energy can be completely converted into heat by a process as friction, it is not possible to convert heat completely into work. Even by using reversible engines, which are most efficient engines, only a fraction of heat can be converted into work. Otherwise it is possible to achieve perpetual motion with heat energy available in many sources such as ovens, atmosphere etc that are available to us. But perpetual motion is never attained. This leads to Kelvin-Planck statement of second law:

" It is impossible to construct a heat engine which, operating in a complete cycle, will abstract heat from a single body and convert the whole of it to work, without leaving changes in the working system".

German scientist Rodolf Clausius in 1854 stated the same law as:

"It is impossible for a self acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature, or heat cannot itself pass from a colder to a warmer body".

It is clear from our experience of producing heat by stopping a moving body with the help of friction that ordered motion can be converted into chaotic motion but it requires a lot of effort to evolve ordered motion from chaotic motion.

The second law of thermodynamics can be used to define the absolute scale of temperature. This was done in 1848 by Lord Kelvin. He found that the ratio of heat taken in and heat rejected in an ideal Carnot engine depends only on the ratio of the temperatures involved being independent of the working material. That is

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{15}$$

Here Q_1 and Q_2 are the amounts of heat taken in and rejected, respectively at temperatures T_1 and T_2.

The second law of thermodynamics also lead Clausius to the concept of entropy. He noted that in a reversible cycle

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \tag{16}$$

so far as the working substance is concerned.

In going from one thermodynamic state A to another such state B the following integral

$$\int_A^B \frac{\delta Q}{T}$$

remains independent of the path in a reversible process. It depends only on the coordinates of A and B hence the entropy S of a state represented by T, V is given by

$S - S_0 = \int_{T_0,V_0}^{T,V} \frac{\delta Q}{T}$

where S_0 denotes the entropy at T_0 and V_0 and δQ is measured along any reversible process. This definition allows us to measure entropy of equilibrium states only as non-equilibrium states cannot be connected to a reference (standard) state by a reversible process.

Equation 1.16 can also be interpreted as the constancy of entropy in a reversible process.

Example-1:

Calculate the increase in entropy of an ideal gas in an isothermal reversible expansion from volume V_1 to V_2 at temperature T.

By definition, the change in entropy is

$$\Delta S = \int_{V_1}^{V_2} \frac{dU + PdV}{T}$$

But $dV = 0$ in an isothermal process and $PV = RT$ for a mole of an ideal gas.

Hence

$$\begin{aligned}\Delta S &= \int_{V_1}^{V_2} \left(\frac{RT}{V}\right)\frac{dV}{T} \\ &= \int_{V_1}^{V_2} R\frac{dV}{V} \\ &= R\ln\left(\frac{V_2}{V_1}\right)\end{aligned}$$

However, the entropy of the universe increases as a result of irreversible process. Irreversible processes can be mechanical, thermal, chemical or other type.

Example-2:

In heat conduction the entropy of the system increases.

Heat conduction is an irreversible process where some heat, say ΔQ is transferred from a body of higher temperature T_1 to a body at a lower temperature T_2. Hence the change in entropy $(S_{\text{final}} - S_{\text{initial}})$

$$\Delta S = \frac{\Delta Q}{T_2} - \frac{\Delta Q}{T_1}$$

$$\Delta S = \Delta Q\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

As $T_1 > T_2$ in heat conduction $\Delta S > 0$

From the study of irreversible process of all kinds we arrive at the principle of increase of entropy:

The entropy of a system of bodies tends to increase in all physical and chemical process occurring in nature, if we include in the system all bodies which are affected by the change.

Only in the limiting case of a reversible process entropy remains constant. Sometimes this principle of increase of entropy is itself called the second law of thermodynamics. According to Clausius, the second law states that the entropy of the world tends to a maximum.

The third law of thermodynamics

The zero of the absolute temperature place a special role from a formal and physical point of view. One has to examine the behaviour of system as T tends to zero in order to give meaning to entropy. The properties of the systems change distinctly as approaches absolute zero. The question of whether $T = 0$ can be attained or cannot be attained is very important. Study of chemical reactions, that is to say, of the conditions which obtain at equilibrium indicates that as $T \to 0$ the entropy becomes independent of the amounts of the various chemical constituents present, so long as the total amount of matter in the system remains constant. Hence we may state the third law as : "The entropy of any given system attains the same finite least value for every state of least energy".

No system can attain temperature zero. The entropy principle clearly implies that it is impossible to reduce the absolute temperature of any system to zero. There are a number of alternative or equivalent statements of the third law. Experiments show that for any isothermal, reversible process of a condensed system the accompanying entropy change is a function of temperature that approaches zero as T approaches zero. Hence we get Nernst-Simon statement of the third law of thermodynamics: "

The entropy change associated with any isothermal, reversible process of a condensed system approaches zero as the temperature approaches zero."
Both the above mentioned statements can be shown to be equivalent.
Another way of stating the same law is: " It is impossible by any procedure, no matter how idealised, to reduce the entropy of a system to its zero point value in a finite number of operations." Many physical and chemical facts substantiate the third law.

Maxwell's Relations

These are equations relating the derivatives of thermodynamic variables such as pressure, temperature, volume and entropy.
Let us consider a few mathematical theorems. Let z be a function of x and y. Then

$$dZ = \left(\frac{\partial Z}{\partial x}\right)_y dx + \left(\frac{\partial Z}{\partial y}\right)_x dy \tag{17}$$

If we write $M(x,y) = \left(\frac{\partial Z}{\partial x}\right)_y$ and $N(x,y) = \left(\frac{\partial Z}{\partial y}\right)_x$ then

$$dZ = M(x,y)\,dx + N(x,y)\,dy \tag{18}$$

Differentiating M with respect to y and N with respect to x we get

$$\begin{aligned}\left(\frac{\partial M}{\partial y}\right)_x &= \frac{\partial^2 Z}{\partial x \partial y}\\ \left(\frac{\partial N}{\partial x}\right)_y &= \frac{\partial^2 Z}{\partial x \partial y}\end{aligned} \tag{19}$$

Since the two derivatives on the right side of equations 1.18 are equal we conclude that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{20}$$

This is known as the condition for an exact differential.
If a quantity f is a function of x, y and z and a relation exists among x, y, z and f can be regarded as a function of any two of x, y and z. Similarly any one of x, y and z may be considered to be a function of f and one other x, y and z. Therefore,

$$dx = \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy \tag{21}$$

Regarding y as a function of f and z we get

$$dy = \left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz \tag{22}$$

Substituting this in equation 1.21 we get

$$
\begin{aligned}
dx &= \left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f \left[\left(\frac{\partial y}{\partial f}\right)_z df + \left(\frac{\partial y}{\partial z}\right)_f dz\right] \qquad (23)\\
&= \left[\left(\frac{\partial x}{\partial f}\right)_y + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_z\right] df + \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f dz
\end{aligned}
$$

But

$$
dx = \left(\frac{\partial x}{\partial f}\right)_z df + \left(\frac{\partial x}{\partial z}\right)_f dz \qquad (24)
$$

Equating the dz terms in equation 1.24 and equation 1.23, we get

$$
\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f = \left(\frac{\partial x}{\partial z}\right)_f .
$$

This can also be written as

$$
\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1 \qquad (25)
$$

Let us make use of these two theorems.

A thermodynamic system in equilibrium can be described in terms of three variables (coordinates) P, V and T. For convenience we can also make use of the following functions

(1) The internal energy U

(2) The enthalpy $H = U + PV$

(3) The Helmholtz function $A = U - TS$

(4) The Gibbs function $G = H - TS$

Any one of these functions may be regarded as a function of any two of P, V and T. Suppose we are given U and S as two functions of V and T. Then we can eliminate T between them to obtain U as a function of S and V etc. Hence we may regard any of the eight quantities P, V, T, S, U, A and G may be expressed in terms of any two other quantities.

Let us consider a chemical system undergoing an infinitesimal reversible process from one equilibrium state to another. Then we will have the change in internal energy

$$
\begin{aligned}
dU &= dQ - PdV\\
&= TdS - PdV \qquad (26)
\end{aligned}
$$

Since dU is a perfect differential, by using the mathematical theorem derived earlier we get

$$
\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad (27)
$$

The change in the enthalpy in the process is

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= TdS + VdP \end{aligned} \tag{28}$$

As dH is a perfect (exact) differential we get

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_P \tag{29}$$

The change in Helmholtz function can be written as

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= -PdV - SdT \end{aligned} \tag{30}$$

using the first law of thermodynamics.
As dA is an exact differential, we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{31}$$

Finally small changes in the Gibbs potential can be written as

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= VdP - SdT \end{aligned} \tag{32}$$

Since dG is an exact differential we get

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \tag{33}$$

The equations $1.27, 1.29, 1.31$ and 1.33 are known as Maxwell's equations (or relations). They are useful in deducing some other thermodynamic equations.
As a simple application of Maxwell's relations consider the change in entropy $S\left(T, V\right)$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \tag{34}$$

But

$$T\left(\frac{\partial S}{\partial T}\right)_V = C_V$$

and Maxwell's equation 1.31 gives

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Hence,

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

This is known as the first TdS equation.

In a similar way, regarding S as a function of T and P we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \tag{35}$$

Using Maxwell's equation 1.33 we get

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P \tag{36}$$

This is sometimes known as the second TdS equation.

Difference in Heat Capacities

By equating the first and the second TdS equations we get

$$C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

Hence

$$\left(C_P - C_V\right) dT = T\left(\frac{\partial V}{\partial T}\right)_P dP + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

Therefore

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V}$$

or

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

Since

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

we get

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \tag{37}$$

Equation 1.37 leads to the conclusion that $C_P - C_V/ge0$ as for most systems $\left(\frac{\partial P}{\partial V}\right)_T <$ 0.. It tells us that $C_P - C_V$ goes to zero as $T \rightarrow 0$. that is at absolute zero temperature both C_P and C_V are equal. In fact, we generally measure C_P in the lab and so C_V

can be obtained using a modification of equation 1.37.

Since the coefficient of volume expansion

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

and the elastic modulus

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

We can rewrite equation 1.37 in terms of measurable quantities as

$$C_P - C_V = \frac{TV\beta^2}{K}$$

Phase transitions

Phase transitions are very common in nature. You are familiar with different phases of water namely, vapour, liquid and ice. Changes do occur between the phases. Changes of phase are called phase transitions. They are also useful in industry. The first microscopically-based understanding of phase transitions is due to Vanderwaals. In 1873 he presented a simple theory for gas-liquid transition.

Let us begin by understanding a phase diagram of a simple substance. A phase diagram is a representation, typically in a plane of the regions where some substance is stable in a given phase. The axes are usually intensive variables such as pressure, temperature, chemical potential etc. Density is sometimes used in the case of fluids. Different phases are separated by lines indicating phase transitions, or regions where the system is unstable. The following figure is a typical phase diagram in the pressure-temperature plane.

The three possible phases - solid, liquid and gas are separated by first order phase transition lines where two phases coexist at the same time. Phases are indicated by their names and two special points called the triple point and the critical point are also shown.

The three lines of coexistence are

(a) Sublimation line

(b) Melting line

(c) Condensation line.

Along the sublimation line the solid coexists with the gas. It exists from zero temperature to the triple point temperature A. On lowering the temperature, at constant pressure, starting from the gas side, the gas would reach the sublimation line, at which crystallites begin to form.

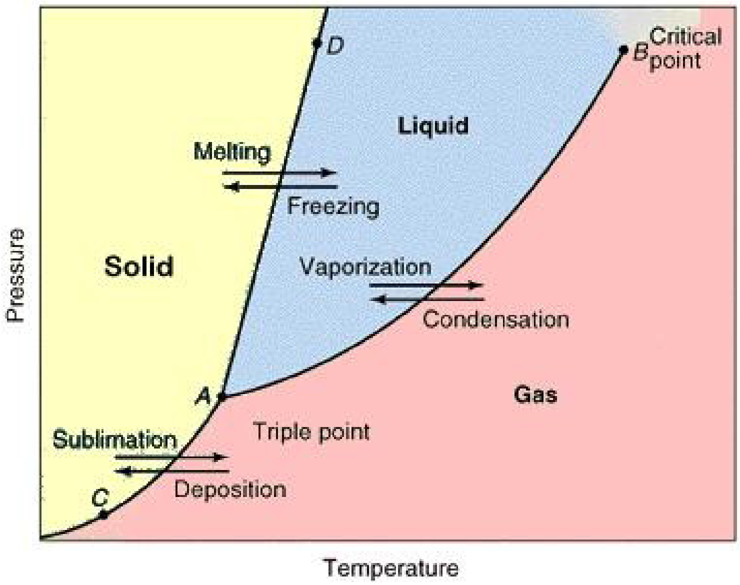


Figure 1.1: Phase diagram of water

The melting line is also called fusion line. Here the solid coexists with liquid on crossing this line from the liquid phase the system would begin to crystallise. This line exists from A upto very high temperature.
The condensation line is called vapour pressure line. Here the gas coexists with liquid. On crossing the line from the gas side of the system begins to form droplets of liquid on the condensation line. Conversely from the liquid side, gas bubbles form at the line, which grow and coalesce until all the material has transformed into gas. This is also called vapour pressure line because it gives the maximum pressure the system can stand as a gas for a given temperature.
All the above transitions are first order transitions which are accompanied by a latent heat and a change in density(or volume). On the other hand, the critical point is such that there are no discontinuities. Hence a critical point is an example of continuous phase transition.

1.4 Let us sum up

Thermodynamics deals with changes in equilibrium states due to changes in temperature and matter. It is based on our experiences with materials in nature. There are three laws of thermodynamics. The first law is nothing but a restatement of the conservation of energy. Heat is recognised as a form of energy. The second law of thermodynamics tells us about the direction of natural processes. It states that entropy in any process cannot decrease. There are several versions of the second law. The third law of thermodynamics, also called Nernst theorem states that no system can attain absolute zero temperature. The existence of temperature sometimes regarded as zeroth law of thermodynamics. From the fact that the internal energy and entropy are perfect differentials (or state variables) it is possible to derive differential relations between thermodynamic variables. They are called Maxwell's relations. A gas can have two different kinds of specific heat namely C_P and C_V. They can be related by thermodynamic relations. For an ideal gas we find $C_P - C_V = R$. Maxwell's relations can be applied to several thermodynamic processes. Changes in state or phase of a substance can be understood using the concepts of latent heats. Phase changes can be of two kinds- first order and second order.

1.5 Key words

Temperature: It is a measure of "hotness" or "coldness" of a body
Heat: It is a form of energy that is related to work and temperature
Equilibrium: It is a state that does not change with time
State variables: These are the variables like pressure, volume and temperature that are used to describe the condition of a thermodynamic system
Internal energy: It is the energy of a system by virtue of having a temperature
Specific heat: It is the amount of heat energy required to raise the temperature of unit mass of a body by one degree celsius
Entropy: Macroscopically it is related to the ratio of heat energy to the temperature of a body. It is one of the state variables of a system.
Reversible process: A process that proceeds from one equilibrium state to another very slowly is called a reversible process
Irreversible process : A process that is not retraceble or reversible is called an irreversible process
Enthalpy: It is another state variable that is equal to $(U + PV)$. It is denoted by H
Gibbs function: It is equal to $H - TS$
Helmholtz function: It is equal to $U - TS$ and denoted by A
Triple point: It is a unique state in which solid, liquid and vapour states of a substance are in equilibrium.

1.6 Questions for self study

a). What is meant by thermodynamic equilibrium?

b). State the zeroth law of thermodynamics

c). What is meant by an equation of a state?

d). Explain the nature of heat

e). State the first law of thermodynamics f). State the second law of thermodynamics

g). Explain the concept of entropy

h). State the third law of thermodynamics

i). Deduce Maxwell's relations

j). Show that $C_P - C_V = R$ for an ideal gas

k). Explain the general properties of phase transitions.

1.7 Further References

1). M.W. Zemansky, *Heat and thermodynamics*, McGraw Hill.

2). Saha and Srivastava, *A treatise on heat.*

3). C. Kittel, *Thermal Physics*

UNIT 2

2 Phase transitions and van der waals equation

2.1 Objectives

After studying this unit you should be able to

- describe phase equilibrium
- classify phase transitions
- draw phase diagrams
- derive Clausius-Clapeyron equation
- apply Clausius-Clapeyron equation
- describe vander waals equation.

2.2 Introduction

In this unit you will learn about equilibrium properties of several phases of a material. A phase of a substance is a homogeneous part of a system that exhibits distinct properties and a well defined boundary with other phases of the same substance. Examples of a two-phase system a liquid and its saturated vapour, a liquid and its crystalline form etc. In general each phase may contain several components. However, here we shall confine ourselves to a single component. A substance may pass from one phase to another by change of conditions such as temperature and pressure. Such a process is called phase transition. We shall study conditions required for equilibrium of phases. You shall learn about the classification of phase transitions. Clausius-Clapeyron equation gives the rate of change of pressure with temperature. It has several applications. Finally you will learn about a simple equation which exhibits phase transitions. It is called vander waal's equation of state.

2.3 Phase Equilibriums

Let us derive the conditions for different phases to coexist in equilibrium. Under such condition no transfer of matter takes place from one phase to another.

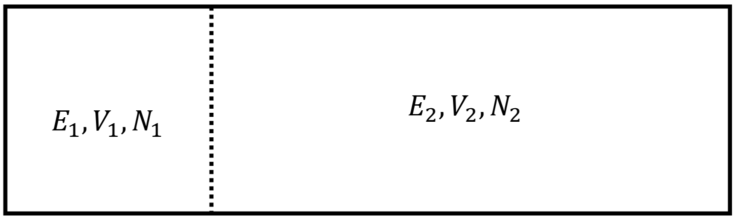


Figure 2.1: One component two phase system

Figure 2.1 shows schematically a one component system existing in two phases. The entire system is isolated from its surroundings. It has energy E, volume v particle number N. The two phases in equilibrium have energy, volume and particle numbers (E_1, V_1, N_1) and (E_2, V_2, N_2) respectively. We get

$$E = E_1 + E_2, \quad V = V_1 + V_2 \quad \text{and} \quad N = N_1 + N_2 \tag{38}$$

The entropy of the system satisfies

$$S\left(E, V, N\right) = S_1\left(E_1, V_1, N_1\right) + S_2\left(E_2, V_2, N_2\right) \tag{39}$$

From equation 2.1 it follows that

$$S\left(E, V, N\right) = S_1\left(E_1, V_1, N_1\right) + S_2\left(E - E_1, V - V_1, N - N_1\right) \tag{40}$$

Under equilibrium, the entropy of the system should be maximum. That means $dS = 0$ under first order variations in E, V and N. Therefore

$$\begin{aligned} dS = & \left(\frac{\partial S_1}{\partial E_1}\right)_{N_1, V_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1, N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{E_1, V_1} dN_1 \\ & - \left(\frac{\partial S_2}{\partial E_2}\right)_{N_2, V_2} dE_2 - \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2, N_2} dV_2 - \left(\frac{\partial S_2}{\partial N_2}\right)_{E_2, V_2} dN_2 \\ = & \, 0 \end{aligned} \tag{41}$$

This can be simplified to

$$0 = \left[\left(\frac{\partial S_1}{\partial E_1}\right) - \left(\frac{\partial S_2}{\partial E_2}\right)\right] dE_1 + \left[\left(\frac{\partial S_1}{\partial V_1}\right) - \left(\frac{\partial S_2}{\partial V_2}\right)\right] dV_1 + \left[\left(\frac{\partial S_1}{\partial N_1}\right) - \left(\frac{\partial S_2}{\partial N_2}\right)\right] dN_1 \quad (42)$$

Since E_1, V_1 and N_1 are mutually independent variables, the coefficients of dE_1, dV_1 and dN_1 are zero separately. Hence we get

$$\left(\frac{\partial S_1}{\partial E_1}\right) - \left(\frac{\partial S_2}{\partial E_2}\right) = 0 \; ; \; \left(\frac{\partial S_1}{\partial V_1}\right) - \left(\frac{\partial S_2}{\partial V_2}\right) = 0 \; ; \; \left(\frac{\partial S_1}{\partial N_1}\right) - \left(\frac{\partial S_2}{\partial N_2}\right) = 0 \quad (43)$$

As $\frac{\partial S}{\partial E} = K\beta = \frac{1}{T}$ we conclude from equation $T_1 = T_2$ in equilibrium. That means the two phases must have same temperature.
As $\frac{\partial S}{\partial V} = K\frac{\partial \ln Z}{\partial V} = \frac{P}{T}$, it follows from equation 2.6 that pressures are equal in equilibrium. Since $\frac{\partial S}{\partial N} = -\frac{\mu}{T}$, it follows that the chemical potentials are equal in equilibrium. That is

$$\mu_1 (T, P) = \mu_2 (T, P) \, .$$

These are the conditions fulfilled under equilibrium.

Classification of phase transitions

Paul Ehrenfest classified phase transitions on the basis of the behaviour of thermodynamic free energy. As Gibbs free energy $G = H - TS$, for a process that occurs at constant pressure and temperature

$$dG = \sum_i \mu_i \, dN_i \quad (44)$$

Therefore

$$\mu_i = \frac{\partial G}{\partial N_i} \quad (45)$$

Since at phase transition μ remains unchanged, the derivatives of G with respect to N must be equal. Thus

$$\frac{\partial G}{\partial N_1} = \frac{\partial G}{\partial N_2}. \quad (46)$$

However, there is no restriction on the derivatives of G with respect to P and T. Phase transitions are classified on the basis of the behaviour of these derivatives. The transition is said to be of first order if the derivatives $\left(\frac{\partial G}{\partial P}\right)_{T,N}$ and $\left(\frac{\partial G}{\partial T}\right)_{P,N}$ are discontinuous at the transition point.
If the above derivatives are continuous but higher derivatives are discontinuous at the transition point, the phase transition is said to be continuous.

The behaviour of Gibbs free energy and entropy at a transition point are shown in figure 2.2. Here T_C denotes the critical temperature.

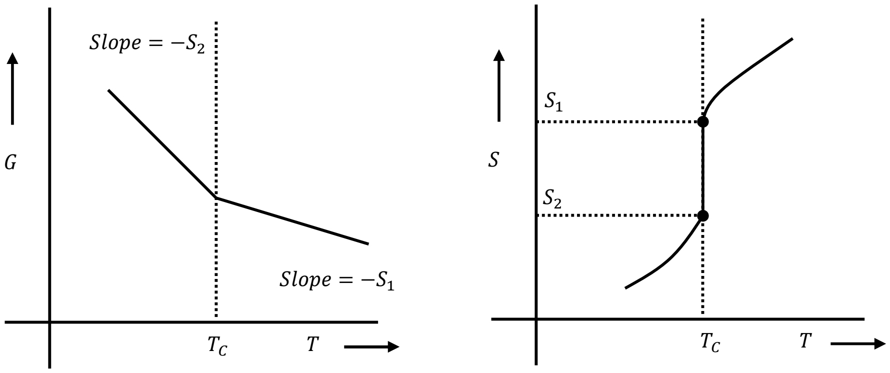


Figure 2.2: Variation of Gibbs free energy / Entropy as a function of temperature

Phase Diagrams

The phases that are realised in nature for a given set of independent variables are those having lowest free energy. The Gibbs free energy is a function of T, P and N. At constant temperature and pressure, Gibbs free energy is proportional to the number of particles. That is

$$G\left(T, P, N\right) = N\ g\left(T, P\right) \tag{47}$$

where $g\left(T, P\right)$ is Gibbs free energy per particle. Since $G = \mu\ N$ we get

$$\mu = g\left(T, P\right) \tag{48}$$

Hence the chemical potential will be Gibbs free energy per particle. The equilibrium conditions can be written as

$$g_1\left(T, P\right) = g_2\left(T, P\right) \tag{49}$$

If we have analytic expressions for the chemical potentials of both phases we can express P as a function of T. That defines a curve in $T - P$ plane. This is illustrated in figure 2.3. At any point on the curve the two phases can coexist in equilibrium. Hence such a curve is called phase equilibrium curve. For instance, if the phases are liquid and vapour, it is called vapour pressure curve. For a solid and its vapour, it is called sublimation curve. For a solid and liquid it is called fusion curve. As Gibbs free energy $G = N_1 g_1 + N_2 g_2$ and $g_1 = g_2$ in equilibrium, transfer of particles from one phase to another does not change G in equilibrium.

A single component system may also exist in three different phases namely, solid liquid and vapour. In that case

$$g_1\left(T, P\right) = g_2\left(T, P\right) = g_3\left(T, P\right) \tag{50}$$

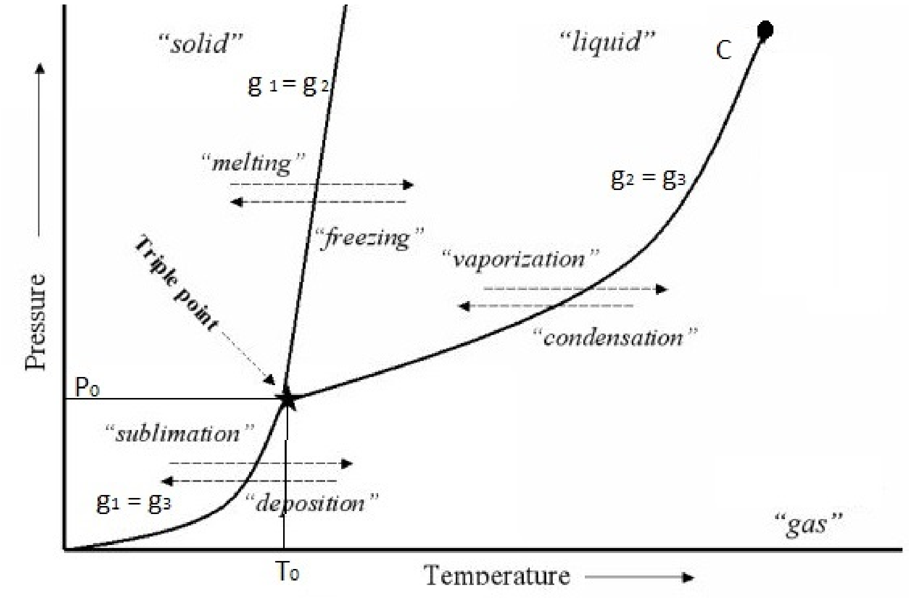


Figure 2.4: Phase diagram of water

for the three phases. Equation 2.13 defines three equilibrium curves:

$$g_1 = g_2, \quad g_2 = g_3 \ \text{ and } \ g_3 = g_1$$

which meet at a point known as triple point. It is shown in figure 2.4
Such a diagram is known as phase diagram. The three phase equilibrium curves divide the $T - P$ plane into three regions in which solid, liquid and gaseous states are in stable states. At the triple points having temperature T_0 and pressure P_0 all the three phases are in equilibrium. For water this occurs, for example, at $T_0 = 0.0078\ °C$ and $P_0 = 0.006$ atmosphere. The point C at which the vapour pressure curve terminates abruptly (i.e C in figure 2.4) is called the critical point. Above this point a substance can pass continuously from a gaseous state to liquid state without a phase transition.

Clausius-Clapeyron Equation

It has been shown that under equilibrium we have

$$\mu_1 (T, P) = \mu_2 (T, P)$$

Differentiating this with respect to temperature

$$\frac{\partial \mu_1}{\partial T} + \frac{\partial \mu_1}{\partial P} . \frac{\partial P}{\partial T} = \frac{\partial \mu_2}{\partial T} + \frac{\partial \mu_2}{\partial P} . \frac{\partial P}{\partial T} \tag{51}$$

This simplifies to

$$-S_1 + V_1 \frac{\partial P}{\partial T} = -S_2 + V_2 \frac{\partial P}{\partial T} \tag{52}$$

Hence

$$\frac{\partial P}{\partial T} = \frac{S_2 - S_1}{V_2 - V_1} \tag{53}$$

Since $\delta Q = T\left(S_2 - S_1\right)$ we get

$$\frac{\partial P}{\partial T} = \frac{\delta Q}{T\left(V_2 - V_1\right)}. \tag{54}$$

This is known as Clausius-Clapeyron equation. This equation gives the rate of change of pressure along the equilibrium curve. This equation implies a rise in temperature with pressure $\left(\text{i.e } \frac{\partial P}{\partial T} > 0\right)$ if there is absorption of heat accompanied by increase in volume as in the case of boiling point of water.

On the other hand, $V_2 < V_1$ as in the case of melting of ice, the phase transition temperature decreases with pressure. The slope $\frac{dP}{dT}$ can take positive or negative values depending on the nature of the substance.

An application of Clausius-Clapeyron equation

There are several applications of this equation. Let us consider the heat capacity of vapour in equilibrium.

Since the entropy is a function of pressure and temperature, the equilibrium heat capacity

$$\begin{aligned} C_{\text{eq}} = \left(\frac{\partial Q}{\partial T}\right)_{\text{eq}} &= T\left(\frac{\partial S}{\partial T}\right)_{\text{eq}} \\ = T\left(\frac{\partial S}{\partial T}\right)_P &+ T\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{\text{eq}} \end{aligned} \tag{55}$$

But we have $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$, the specific heat at constant pressure.

Also,

$$\begin{aligned} dE &= TdS - PdV \\ &= d\left(TS\right) - SdT - d\left(PV\right) + VdP \\ d\left(E_T S + PV\right) &= -SdT + VdP \end{aligned}$$

In other words, Gibbs function satisfies

$$dG = -SdT + VdP$$

Therefore

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

Using the relation

$$\frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P}$$

we get

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \tag{56}$$

Substituting $\left(\frac{\partial S}{\partial P}\right)_T$ into equation 2.18 we get

$$C_{\text{eq}} = C_P - T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_{\text{eq}}$$

Assuming that the vapour pressure behaves like an ideal gas and hence using the equation of state

$$PV = RT$$

we get

$$\left(\frac{\partial V}{\partial T}\right) = \frac{R}{P}.$$

Finally, we get

$$C_{\text{eq}} = C_P - T\frac{R}{P}.\frac{R\delta Q}{RT^2}.$$

$$C_{\text{eq}} = C_P - \frac{\delta Q}{T} \tag{57}$$

Van der waals equation

This equation, though simple, exhibits many essential features of the liquid-vapour phase transition. The equation is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{58}$$

It can be rewritten as

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0 \tag{59}$$

As you know, a third degree equation with real coefficients can have either

(a). one real and two complex roots, or

(b). three real roots.

Therefore an isotherm plotted on a $P-V$ plane using equation 2.22 will be a straight line parallel to V axis either at three points or at one (see figure 2.5).
From the general form of the curves (figure 2.5) it is clear that higher curves correspond to higher T. With increasing temperature the positions between humps and valleys decreases. At a particular temperature, called critical temperature T_C, the curve turns into a point of inflexion.
The maxima and minima can be obtained from the equation

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{60}$$

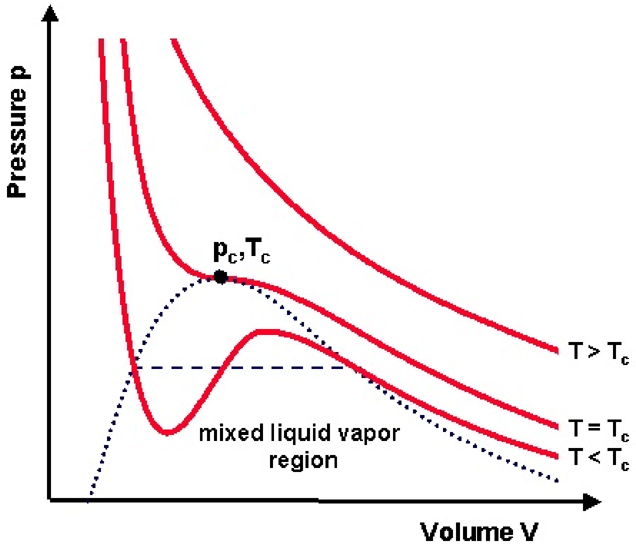


Figure 2.5: Van der Waals isotherms

by setting $\frac{dP}{dV}$ to zero.
Thus

$$\frac{\partial P}{\partial V} = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \tag{61}$$

Eliminating T between the above two equations we get

$$P = \frac{a\,(V-2b)}{V^2}. \tag{62}$$

This equation gives the locus of the maxima and minima of the family of curves obtained for different values of T. This locus is shown as the dotted curve as shown figure 2.5.

This curve $ARBQC$ divides the PV plane into three regions. The region bounded by AB and the upper point of the critical isotherm represents the liquid phase. The region located inside the dome shaped curve ABC describes two phase states-liquid and vapour. The region to the right side of curve BC gives the vapour phase. The curve ABC is called the coexistence curve. The maximum point B of ABC is obtained by equating to zero the derivative of P with respect to V in equation 2.25. On simplification we get the critical values

$$\begin{aligned} V_C &= 3b \\ P_C &= \frac{a}{27b^2} \\ T_C &= \frac{8a}{27Rb} \end{aligned} \tag{63}$$

These values belong to the critical point the curve corresponding to the critical temperature has a point of inflection. At pressures higher than P_C and temperatures above T_C, no phase difference exists. At the critical point the two phases become identical.

It is found that Van der waals equation of state provides a good fit to experiments away from the critical point. An interesting feature of Van der waals equation is that it can be expressed in a universal form using reduced pressure, volume and temperature. We define the reduced values as

$$\begin{aligned}\bar{P} &= \frac{P}{P_C}\\ \bar{V} &= \frac{V}{V_C}\\ \bar{T} &= \frac{T}{T_C}\end{aligned} \tag{64}$$

In terms of $\bar{P}, \bar{V}$ and $\bar{T}$ van der waals equation can be expressed as

$$\left(\bar{P} + \frac{3}{\bar{V}^2}\right)\left(3\bar{V} - 1\right) = 8\bar{T} \tag{65}$$

We can see that specific constants such as a and b are absent giving it an universal form. this is the statement of law of corresponding states which states that all fluids when described in terms of reduced parameters obey the same equation of state.

Example:

Given that the critical temperature is 33.2 K, its critical pressure is $1.295 \times 10^6\ Pa$ and the molar volume in critical state is $6.5 \times 10^{-5}\ m^3 mole^{-1}$ find the van der waals constants.

Solution: We have

$$\begin{aligned}T_C &= \frac{8a}{27Rb} = 33.2\ K\\ P_C &= \frac{a}{27b^2} = 1.295 \times 10^6\ Pa\\ V_C &= 3b = 6.5 \times 10^{-5}\ m^3 mole^{-1}\\ b &= \frac{6.5 \times 10^{-5}}{3} = 2.16 \times 10^{-5}\ m^3 mol^{-1}\\ a &= 27b^2 P_C = 27\left(2.16 \times 10^{-5}\right)^2\left(1.295 \times 10^6\right)\end{aligned}$$

Thus

$$a = 1.63 \times 10^{-2}\ m^6 mol^{-2}$$

2.4 Let us sum up

A phase of a substance is a homogeneous part of a system that exhibits distinct properties and has a well defined boundary with other phases of the same substance. A general phase may contain several components. passing from one phase to another is called a phase transition. For equilibrium between two phases one should have temperature, pressure and chemical potentials equal. A phase transition is said to be of first order if the derivatives $\left(\frac{\partial G}{\partial P}\right)_{T,N}$ and $\left(\frac{\partial G}{\partial T}\right)_{P,N}$ are discontinuous at the transition point. A phase transition is said to be continuous if the above derivatives are continuous but the higher derivatives are discontinuous at the transition point. Transfer of particles from one phase to another does not change Gibbs free energy in equilibrium. At a triple point three phases coexist. Clausius-Clapeyron equation gives the rate of change of pressure along the equilibrium curve. there are several applications of the equation. Van der waals equation exhibits many essential features of liquid-vapour phase transition. The equation of state has a critical point. at higher pressures and temperatures than the critical ones, no phase difference occurs. Van der waals equation is found to provide a good fit to experiments away from the critical point. It can be reduced to a universal form by suitable normalisation.

2.5 Key words

Phase of a substance: It is a homogeneous part of a substance that has distinct properties. It has a well defined boundary

Gibbs free energy: It is equal to $H - TS$

Phase equilibrium: The condition under which two phases coexist is called phase equilibrium

Triple point: The point where three phases are in equilibrium is called a triple point

Critical temperature: It is that temperature where gas and its liquid phase coexist.

2.6 Questions for self study

a) Derive the conditions for a phase equilibrium to exist

b) Draw the phase diagram for water

c) Derive Clausius-Clapeyron equation

d) Discuss the important features of Van der waals equation of state.

2.7 Further References

- B.B Laud, *Fundamentals of Statistical Mechanics*, New age international ltd. New Delhi.
- B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi.

- Allis, Herlin, *Thermodynamics and Statistical Mechanics*, McGraw-Hill, New York, 1952.
- A. Sommerfeld, *Thermodynamics and Statistical Mechanics*, Academic Press, New York, 1956.
- Chisholm, de Borde *An Introduction to Statistical Mechanics*, Pergamon, New York, 1958.
- E. Schrödinger, *Statistical Thermodynamics*, Cambridge U.P, Cambridge, 1946.
- M.W. Zemansky, *Heat and thermodynamics*, McGraw Hill.
- Saha and Srivastava, *A treatise on heat.*

UNIT 3

3 Irreversible Thermodynamics

3.1 Objectives

After studying this unit you should be able to

- understand transport equations which are important in non-equilibrium thermodynamics
- understand the local equilibrium hypothesis
- understand balance equation
- understand irreversibility and the arrow of time
- learn about entropy production
- learn about the linear flux-force relations
- understand Onsager reciprocal relations

3.2 Introduction

Irreversible Thermodynamics, also called non-equilibrium thermodynamics deals with process that are slightly away from equilibrium. Here basic physical quantities like mass, temperature, pressure etc are allowed to change from place to place as well as in time. It aims to provide a thermodynamic support to the classical transport equations of heat, mass, momentum, electric charge etc. It also provides a systematic description of the coupling between thermal, mechanical, chemical and electromagnetic effects. Another goal of irreversible thermodynamics is to study stationary non-equilibrium dissipative states, whose properties do not depend on time but are characterised by a non-homogeneous distribution of variables and non-vanishing fluxes. In this unit you shall learn about transport processes that play a central role in non-equilibrium thermodynamics just like the important role played by equations of state in equilibrium thermodynamics.

The most important hypothesis underlying irreversible thermodynamics is the local equilibrium hypothesis. You shall learn about it . Entropy balance is important under irreversible processes. Since irreversible processes take place only in one direction towards entropy increasing direction, it is necessary to understand the root cause of irreversibility.

In the linear region that we deal with we are lead to accept linear flux-force relations and work out their consequences. Fluxes and forces are related via coefficients satisfy certain equations. Their signs are restricted by the laws of thermodynamics. The said coefficients also satisfy symmetry relations first derived by Onsager in 1931. You will learn about all these in this unit.

3.3 Basic transport equations

Transport equations describe the amount of heat, mass, electrical charge or other quantities which are transferred per unit time between different systems and different regions of a system as a response to a non-homogeneity in temperature T, molar concentration C, electric potential ϕ_e. Historically their development is due to Fourier, Fick and Ohm. They proposed the following well known laws

$$\vec{q} = -\lambda \vec{\nabla} T \qquad \text{Fourier's law} \tag{66}$$

$$\vec{J} = -D \vec{\nabla} C \qquad \text{Fick's law} \tag{67}$$

$$I = \sigma_e \vec{\nabla} \phi_e \qquad \text{Ohm's law} \tag{68}$$

Here $\vec{q}$ stands for the heat flux i.e. the amount of internal energy per unit time and unit area transported by conduction. $\vec{J}$ is the diffusion flux i.e. the amount of matter expressed in moles, transported per unit time and unit area. I stands for familiar electric current i.e. electric charge transported per unit time per unit area. The coefficients λ, D and σ_e are called coefficients of thermal conductivity diffusion and electrical conductivity respectively. Knowledge of these transport coefficients in terms of temperature, pressure and mass concentrations plays an important role in material science as well as in daily life. For instance, low thermal conductivity is needed in better insulation of buildings, diffusion coefficient is crucial in biology as well as pollution dispersal problems. Electrical conductivity is vital in microelectronic devices, networks, electrical plants etc.

The physical interpretation of the transport equation is rather intuitive: heat flows from regions of higher temperature to regions at low temperatures. The heat flow is directly proportional to the temperature gradient. Similarly matter diffuses from regions with higher mass concentrations to regions with lower concentration. Electric positive charges move from regions with higher electric potential to regions with lower potential. The evolution of a system in the course of time and space requires the knowledge of the balance between incoming and outgoing fluxes. When incoming and outgoing fluxes are equal, the properties of the system do not change in the course of time and the system is said to be in non-equilibrium steady state. In equilibrium all fluxes vanish. It should be noted that the above considerations apply only for so called conserved quantities, which means absence of production or consumption inside the system.

Expressions $3.1 - 3.3$ of the classical transport laws were originally proposed either from theoretical considerations or on experimental grounds. Non-equilibrium thermodynamics aims to provide a general scheme for the derivation of transport laws by ensuring their compatibility with thermodynamic laws. For instance thermal conductivity must be positive, otherwise, heat would spontaneously flow from a lower temperature to a higher temperature in conflict with the second law of thermodynamics. When λ, D and σ_e are scalars, they must be positive.

Local equilibrium hypothesis

This is a very important hypothesis of irreversible thermodynamics. According to it, the local and instantaneous relations between thermodynamic quantities in a system out of equilibrium are the same as for a uniform system in equilibrium. Explicitly, consider a system split mentally in a series of cells, which are sufficiently large for microscopic fluctuations to be negligible but sufficiently small so that equilibrium is realised to a good approximation in each individual cell.

The local equilibrium hypothesis states that at a given instant of time, equilibrium is achieved in each individual cell (or each material point). It should be realised that the state of equilibrium is different from one cell to the other so that exchanges of mass and energy are allowed between neighbouring cells.

Another way of describing the situation is in terms of two time scales: the first τ_m, denotes the equilibrium time inside one cell. It is of the order of time interval between two successive collisions between collisions. Typically it is of the order 10^{-12} S at normal pressure and temperature. The second characteristic time τ_M is a macroscopic one whose order of magnitude is related to the duration of the experiment. Typically it is of the order of one second. The ratio between the time scales i.e. $\frac{\tau_m}{\tau_M}$ is called Deborah number. When this number is very much less than unity the local equilibrium hypothesis is fully justified.

One consequence of the local equilibrium hypothesis is that all variables defined in equilibrium such as entropy, temperature, chemical potential etc are also clearly defined outside equilibrium, but they are allowed to vary in time and space. Another consequence is that the local state variables are related by the same state equations as in equilibrium. In particular Gibbs relation between entropy and state variables remains locally valid for each value of time and position.

For example, in the case of a $n-$component fluid of total mass m, the local Gibbs equation can be written as

$$dS = T^{-1}\, dU + PT^{-1}\, dV - T^{-1}\sum_{K=1}^{n} \mu_K dC_K \tag{69}$$

Where S is the entropy per unit mass, U is the specific internal energy and T is the obsolute temperature. P stands for pressure and V is the specific volume (related to mass density ρ by $V = \frac{1}{\rho}$). $C_K = \frac{m_K}{m}$ is the mass fraction of the substance K, μ is its chemical potential.

Another consequence follows from the property that, locally, the system is stable. More generally Gibbs equation takes the form

$$dS\left(\vec{r},t\right) = \sum_i \Gamma_i\left(\vec{r},t\right)\; da_i\left(\vec{r},t\right) \tag{70}$$

where $a_i\left(\vec{r},t\right)$ is an extensive stable variable like u, v, c_K while $\Gamma_i\left(\vec{r},t\right)$ is the corresponding conjugate state variable such as T, P or μ_K. From kinetic theory point of view, local equilibrium hypothesis is justified only for conditions where Maxwellian distribution is approximately maintained.

Entropy balance

In equilibrium thermodynamics, entropy is a well defined function of state only in equilibrium states or during reversible processes. How to define entropy when a system is driven far from the equilibrium? Thanks to the local equilibrium hypothesis, entropy remains a valuable state function even in non-equilibrium situations.

Consider an arbitrary body outside equilibrium whose total entropy at time t is S. The rate of variation of this extensive quantity may be written as the sum of the rate of exchange with the exterior $\frac{dS^e}{dt}$ and the rate of internal production.n Hence

$$\frac{dS}{dt} = \frac{dS^e}{dt} + \frac{dS^i}{dt} \tag{71}$$

The quantity $T\frac{dS^i}{dt}$ is sometimes called uncompensated heat or the rate of dissipation. Let $\vec{J}^{\mathrm{s}}$ denote the entropy flux, i.e. entropy crossing the boundary surface per unit area in unit time and σ^{s} be the rate of production of entropy per unit volume and unit time inside the system. Then

$$\frac{dS^e}{dt} = -\int_{\Sigma} \vec{J}^{\mathrm{s}}.\hat{n}d\Sigma \tag{72}$$

and

$$\frac{dS^i}{dt} = \int_{V} \sigma^{\mathrm{s}}dV \tag{73}$$

where $\hat{n}$ is the unit normal pointing outwards the volume of the body.
The classical formulation of the second law due to Clausius states that, in isolated systems, possible processes are those in which the entropy of the final equilibrium state is higher than or equal to the entropy of the initial equilibrium state. In the theory of irreversible processes one introduces an even stronger restriction by requiring that the entropy of an isolated system must increase everywhere and at any time, i.e, $\frac{dS}{dt} \geq 0$. In non-isolated systems the second law takes the more general form:

$$\frac{dS^i}{dt} > 0 \quad \text{(for reversible processes)} \tag{74}$$

and

$$\frac{dS^i}{dt} = 0 \quad \text{(for reversible processes at equilibrium)} \tag{75}$$

It is worth mentioning here that the second law introduces an asymmetry in time for irreversible processes, which is often known as an arrow of time.

Irreversibility and arrow of time

The principle of entropy increase sheds new light on the concept of time. The equations of Newtonian mechanics are deterministic and reversible with respect to reversal of time. Time is considered as an external parameter, which describes the chronology of succession of events. Reversible processes do not distinguish between the future and the past. In contrast, the principle of increase of entropy makes possible the distinction between future and past as it implies an arrow of time. Irreversible processes proceed spontaneously within a given direction in time. It establishes a fundamental anisotropy in nature and provides a criterion allowing to decide whether a process is

going forwards or backwards.
At microscopic level systems are reversible. It is believed that the large number of particles in a system, makes the system evolve with irreversible dynamics due to our inability to follow each individual particle. In other words, irreversibility is an illusion raised up by our ignorance. In this way irreversibility should not be related to the system itself but to the observer.
Irreversibility is also associated with loss of information according to information theory. Accordingly, entropy is interpreted as a lack of information about the microscopic state of the system, and loss of information means higher entropy. When entropy production is large, much information is lost per unit time, but in reversible processes no information is lost. The problem of evolution of a system from reversible to irreversible is still being studied.

Entropy production

The entropy production rate σ^s depends on the thermodynamic fluxes J_α and thermodynamic forces X_α as :

$$\sigma^s = \sum J_\alpha X_\alpha \tag{76}$$

Note that the thermodynamic forces are not forces in the mechanical sense, but they are quantities generally related to the gradients of the intensive variables whereas the fluxes J_α can be identified with the fluxes of energy, mass, momentum, etc. In equation 3.11 the fluxes and forces may be scalars, vectors or tensors and the product $J_\alpha X_\alpha$ stands for the usual product between two scalars, the scalar product between two vectors and the double scalar product between two tensors as the case may be. At equilibrium or for reversible processes, the thermodynamic fluxes and forces vanish identically so that entropy production is zero in such situations, as it should.
Experience shows that thermodynamic fluxes and forces are not independent but a relationship exists between them. It has been observed for a large class of irreversible processes, the fluxes are linear functions of the forces to a good approximation. This also ensures that entropy production rate is a positive quantity. Hence we can put

$$J_\alpha = \sum L_{\alpha\beta}\, X_\beta \tag{77}$$

These flux-force relations are called phenomenological relations, constitutive or transport equations. They express the relation between causes (the forces) and their effects (the fluxes). They depend on the specific properties of the materials being studied. The phenomenological coefficients $L_{\alpha\beta}$ generally depend on the intensive variables T, P and C_K. The coefficient $L_{\alpha\alpha}$ connects a flow J_α to its conjugate X_α while $L_{\alpha\beta}$ describes the coupling between two irreversible processes denoted by α and β. For example, in thermo-electricity $L_{\alpha\alpha}$ is related to the electrical resistance and $L_{\alpha\beta}$ to the coupling between electric current and the heat flow.

Onsager reciprocity relations

According to equation 3.12 one should be allowed to couple flux to any force. However material symmetry considerations limit the number of couplings between fluxes and forces. This property is known as curies law. It reflects the property that macroscopic causes cannot have more elements of symmetry than the effects they produce. For instance, in isotropic systems and within the linear regime it is forbidden to couple fluxes and forces of different tensorial character. As an example, chemical affinity (a scalar) cannot give rise to a heat flux(a vector). similarly a temperature gradient (a vector) cannot induce a mechanical stress (a tensor of order 2).

Another restriction on the sign of the phenomenological coefficients $L_{\alpha\beta}$ arises as a direct consequence of the second law. Substituting the linear flux-force relations 3.12 into entropy production rate equation leads to the quadratic form

$$\sigma^s = \sum_{\alpha\beta} L_{\alpha\beta} X_\alpha X_\beta \geq 0 \tag{78}$$

According to standard results in algebra this implies that determinant $|L_{\alpha\beta} + L_{\beta\alpha}|$ and all its principal minors are non-negative. Therefore we get

$$L_{\alpha\alpha} \geq 0 \tag{79}$$

and

$$L_{\alpha\alpha} L_{\alpha\beta} \geq \frac{1}{4} \left(L_{\alpha\beta} + L_{\beta\alpha}\right)^2 \tag{80}$$

Due to equation 3.14 all transport coefficients like heat conductivity, diffusion coefficient and the electrical resistance are positive. In other words, heat flows from higher to lower temperature, electrical current flows from higher to lower electrical potential and neutral solutions move from higher to lower concentrations.

Another important restriction on $L_{\alpha\beta}$ was deduced by Onsager in 1931. According to him "microscopic reversibility" meaning the invariance of the microscopic equations of motion with respect to time reversal $t \longrightarrow -t$ leads to symmetry property

$$L_{\alpha\beta} = L_{\beta\alpha} \tag{81}$$

The above result holds for fluctuations of extensive state variables that are even functions of time. In the case of odd parity of one of the variables α or β for which fluctuations are odd functions of time, the coefficients $L_{\alpha\beta}$ are skew-symmetric instead of symmetric. This was shown by Casimir in 1945. Hence for odd fluctuations

$$L_{\alpha\beta} = -L_{\beta\alpha} \tag{82}$$

At first sight, Onsager-Casimir relations may appear modest. Their main merit lies in symmetry properties in coupled processes. An advantage of these reciprocal relations is their help in reducing the number of measurements. In practice the cross coefficients are usually much smaller (of the order of 10^{-3} times) the direct coupling coefficients. Onsager reciprocal relations have been widely applied in the treatment of coupled irreversible place at the macroscopic scale far from equilibrium. It is important to note that they are valid as long as the flux-force relation is linear.

3.4 Let us sum up

Irreversible thermodynamics deals with processes that are slightly away from equilibrium. The basic transport equations like Fourier's law, Fick's law and Ohm's law relate fluxes to thermodynamic forces in a linear manner. Local equilibrium hypothesis is used in irreversible thermodynamics to define variables outside equilibrium. Entropy leads to $\frac{dS}{dt} \geq 0$. Irreversibility may be thought of as arising from our lack of knowledge of all microscopic processes. It is related to lack of information about our system. Entropy production depends on fluxes and forces of thermodynamic nature. The Phenomenological coefficients $L_{\alpha\beta}$ relating fluxes and forces satisfy Curie's law. They also satisfy Onsager-Casimir reciprocal relations.

3.5 Key words

Arrow of time: Irreversible processes take place in only direction of increasing entropy. This defines a direction of time called arrow of time.

3.6 Questions for self study

a) State and explain Fourier's law, Fick's law and Ohm's law

b) Bring out the difference between a reversible process and an irreversible process

c) State and explain the local equilibrium hypothesis

d) Discuss the connection between irreversibility and arrow of time

e) Discuss the conditions satisfied by the phenomenological coefficients $L_{\alpha\beta}$

3.7 Further references

1. B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi.

2. I. Prigogine, *Introduction to thermodynamics of irreversible processes.*

3. S.R de Groot and P. Mazur, *Non-equilibrium thermodynamics.*
4. Zemonsky, *Heat and Thermodynamics*, McGraw Hill.
5. B.H. Lavenda, *Thermodynamics of irreversible processes*

UNIT 4

4 Thermoelectric Phenomena

4.1 Objectives

After studying this unit you will be able to know about

- Seebeck effect
- Joule effect
- Heat conduction
- Peltier effect
- Thomson effect

4.2 Introduction

There are five different effect that take place when two dissimilar metals are connected and the junctions are held at different temperatures. Such effects occur simultaneously. The effects are Seebeck effect, the Joule effect, the conduction of heat, the Peltier effect and the Thomson effect. In this lesson you will learn about all the mentioned effects.

4.3 Thermoelectric effects

Seebeck effect

When two junctions are maintained at different temperatures, there is a thermal emf between the junctions. The value of the emf (ϵ) depends on the materials and the the two temperatures. If the circuit is broken at any point, the two ends may be joined to wire of a third metal forming two new junctions. If these junctions are maintained at the same temperature, the thermal emf in the circuit is not altered. Then a galvanometer, a potentiometer or a motor may be inserted into the circuit.
When one junction is held at the constant temperature of melting ice, the variation of the thermal emf with temperature of the other junction is found to obey the equation

$$\epsilon = \alpha_1 t + \frac{\alpha_2}{2} t^2 + \frac{\alpha_3}{3} t^3 \tag{83}$$

where t is the temperature in celsius units and α's are constants that depend on materials.
The following diagram shows the variation of ϵ as a function of temperature for different thermocouples

To obtain the emf when the cold junction is at a temperature other than $0°C$, it is necessary to add a constant term. Therefore, it follows that the derivative $\frac{d\epsilon}{dT}$ at one junction is independent of the temperature of the other junction.

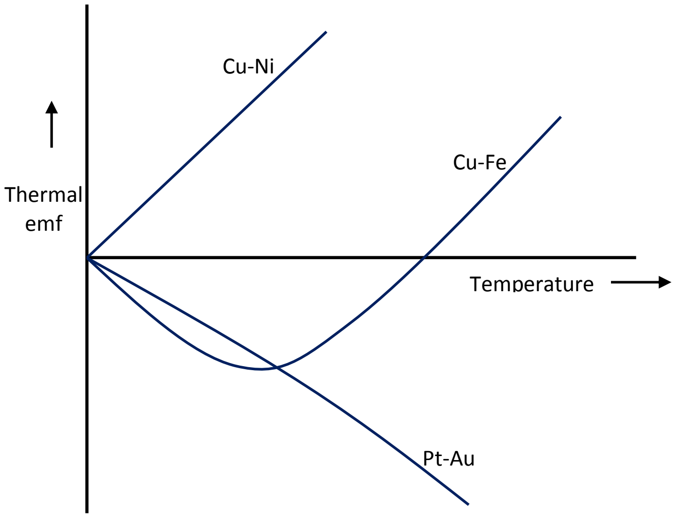


Figure 4.1: Thermoemf Versus temperature

Joule effect

This is the familiar heating effect due to electric current. If the thermal emf is not balanced by an external emf, a current I exists. Its value may be adjusted by varying the external emf. Then if there is no external circuit, all the electrical energy developed by the thermocouple is dissipated into internal energy. Then is the well known Joule effect. Then

$$\epsilon\, I = I^2 R \tag{84}$$

where R is the resistance of the thermocouple. Sometimes it is possible to convert the energy developed by the thermocouple can be converted into mechanical work.

Heat conduction

Let us say the junctions of a thermocouple are at temperatures T_1 and T_2 with $T_1 > T_2$. Break the circuit at some point, the two ends of which are maintained at temperature T by means of an insulating reservoir. Now there is no thermoelectric current and therefore no Joule effect. However, the heat lost by the reservoir at T_1 and gained by that at T_2 with no net gain or loss to the reservoir at T. The wires can be imagined to be suitably insulated so that there is no appreciable lateral transfer of heat across the surfaces of the wires. Then we obtain conducted heat for various values of the temperature difference $T_1 - T_2$.

Peltier Effect

Let us consider a thermocouple with its junctions held at the same temperature. If by means of an outside battery, a current is produced in the thermocouple, the temperatures of the junctions will be found to change by an amount that is not entirely due to the Joule effect. This additional temperature change is called Peltier effect. Allowing for Joule effect, heat that must be either supplied or extracted to restore the junction to its initial value of temperature is called the Peltier heat. The Peltier effect takes place whether the current is provided by an outside source or generated by the thermocouple itself.

The Peltier heat is measured by creating a known current in a junction initially at a known temperature and measuring the rate at which the temperature of the junction changes. The junction itself can be used as some kind of calorimeter. From the rate of change of temperature and the heat capacity of the junction, the rate at which heat is transferred is calculated. After subtracting the I^2R loss and correcting for the conducted heat, the Peltier heat is finally obtained. Detailed measurements have lead to the following results:

(a) The rate at which Peltier heat is transferred is proportional to the first power of the current. It is put equal to πI. The quantity π is called Peltier coefficient. It is equal to the heat transferred when unit quantity of electricity travels through the junction.

(b) The Peltier heat is reversible. When the direction of the current is reversed without changing the magnitude, the Peltier heat is the same, but in opposite direction.

(c) The Peltier coefficient depends on the temperature and the materials of the junction being independent of the temperature of the other junction.

Thomson Effect

The conduction of heat along the wires of a thermocouple carrying no current gives rise to a uniform temperature distribution in each wire. If a current is present, the temperature distribution in each wire is altered by an amount that is not entirely due to Joule effect. This additional change in the temperature distribution is called the Thomson effect. Allowing for Joule effect, heat must be either supplied or extracted laterally at all places along the wires to restore initial temperature distribution is called Thomson heat.

To measure the Thomson heat at a small region of any one wire, it is necessary to produce a known temperature gradient in the region and to pass a known current either up or down the temperature gradient. The rate at which Thomson heat is transferred is equal to the rate at which electrical energy is dissipated minus the rate at which heat is conducted. Since Joule effect can be calculated and the conducted heat is known from previous experiments, Thomson heat can be deduced. The following conclusions may be drawn about Thomson effect:

(a) Thomson heat is reversible

(b) The rate at which Thomson heat is transferred into a small region of wire carrying current I and supporting a temperature difference dT is equal to $\sigma\ I\ dT$, where σ is called Thomson coefficient.

(c) The Thomson coefficient depends on the material of the wire and on the mean temperature of the small region under consideration.

Thermodynamic analysis of a thermocouple

Thermodynamics has been applied to understand the working of a thermocouple. Lord Kelvin realised that the two irreversible phenomena of Joule effect and Heat conduction could not be eliminated by merely choosing wires of proper dimensions. If the wires are made very thin in order to cut down heat conduction, the electrical resistance increases. On the other hand, if the wires are made thick to reduce electrical resistance, heat conduction increases. He assumed that irreversible effects could be ignored on the ground that they seemed to be independent of the reversible Peltier and Thomson effects. Kelvin set the sum of all entropy changes to zero by considering a reversible transfer of unit amount of electricity through a thermocouple circuit. His conclusions have been checked and verified.

However, it remains that Seebeck, Peltier and Thomson effects are inextricably linked with irreversible effects. Hence it is necessary to study microscopic treatment of irreversible coupled flows developed by Onsager.

A small temperature difference ΔT established across a wire disturbs thermal equilibrium and gives rise to heat current I_Q. Since a cool reservoir at one end of the wire is gaining entropy from the wire at a greater rate than that at which a warmer reservoir at the other end is loosing it to the wire, we say that entropy produced in the wire at a rate

$$\frac{dS}{dT} = I_Q \frac{\Delta T}{T^2} = I_S \frac{\Delta T}{T} \tag{85}$$

where I_S is the entropy current equal to $\frac{I_Q}{T}$.

A small potential difference $\Delta\epsilon$ established across a wire disturbs the electric equilibrium and gives rise to an electric current I. Since a reservoir at temperature T which maintains the wire at a uniform temperature is gaining entropy and there is no entropy input to the wire, we can say that entropy is being produced in the wire at a rate

$$\frac{dS}{dT} = I \frac{\Delta\epsilon}{T} \tag{86}$$

When both temperature difference ΔT and a potential difference $\Delta\epsilon$ are present across the wire, the rate of entropy production will be their sum

$$\frac{dS}{dT} = I_S \frac{\Delta T}{T} + I \frac{\Delta\epsilon}{T} \tag{87}$$

If departures from equilibrium are too large, the entropy and electricity flow are coupled in a simple manner, both depending linearly on both $\frac{\Delta T}{T}$ and $\frac{\Delta\epsilon}{T}$. The latter are called 'generalised forces' while the former are called 'currents'. Hence,

$$I_S = L_{11} \frac{\Delta T}{T} + L_{12} \frac{\Delta\epsilon}{T} \tag{88}$$

$$I = L_{21} \frac{\Delta T}{T} + L_{22} \frac{\Delta\epsilon}{T} \tag{89}$$

In other words 'generalised currents' are linearly proportional to 'forces' or causes. Clearly L_{11} and L_{22} have simple interpretation in terms of thermal conductivity and electrical conductivity, respectively. The quantities L_{12} and L_{21} are called coupling coefficients. They represent the effect of potential difference on an entropy current and the effect of temperature difference on an electric current, respectively.

It was proved by L.Onsager (1931) that

$$L_{12} = L_{21} \tag{90}$$

which is now known as Onsager's reciprocal relation.
If ΔT is set equal to zero in 4.6 and 4.7 then we get

$$\left(\frac{I_S}{I}\right)_{\Delta T=0} = \frac{L_{12}}{L_{22}} \tag{91}$$

The ratio on the left hand side is a measure of the entropy that is carried along with electricity when the temperature is uniform. It is therefore called entropy transport parameter and denoted by S^*. Thus

$$S^* = \left(\frac{I_S}{I}\right)_{\Delta T=0} = \frac{L_{12}}{L_{22}} \tag{92}$$

S^* plays an important role in the theory of a thermocouple.
In the absence of current equation 4.7 leads to

$$(\Delta\epsilon)_{I=0} = -\frac{L_{21}}{L_{22}}\Delta T \tag{93}$$

Using Onsager reciprocal relation we get

$$(\Delta\epsilon)_{I=0} = -\frac{L_{12}}{L_{22}}\Delta T \tag{94}$$

This equation can be written in terms of entropy transport parameter S^* as

$$-(\Delta\epsilon)_{I=0} = S^*\,\Delta T \tag{95}$$

This equation can be used to calculate Seebeck emf generated in a thermocouple.
Consider a thermocouple shown in figure 4.2

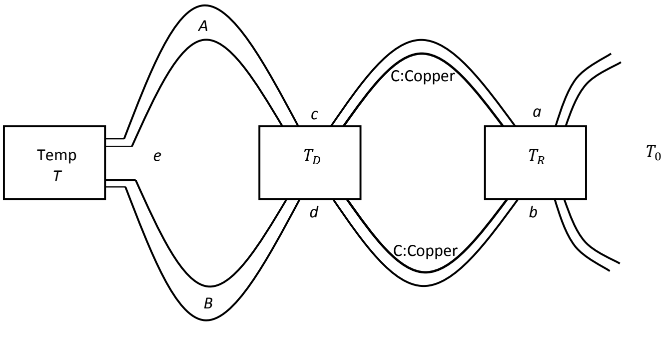


Figure 4.2: Thermocouple

The junction e of the wires A and B is maintained at temperature T while the two junctions c and d, each with copper marked C are connected to the brass binding posts of a potentiometer, forming two more junctions each of which is at room temperature T_R. The potentiometer is supposed to be balanced so that $I = 0$ and $\epsilon_a = \epsilon_b$

is the Seebeck emf denoted by ϵ_{AB}.

Applying equation 4.13 to each of the wires marked A, B and C which are supposed to have entropy transport parameters S^*_A, S^*_B and S^*_C. Replacing $\Delta\epsilon$ and ΔT by $d\epsilon$ and dT and integrating from one end of each wire to the other we get

$$\begin{aligned} \epsilon_a - \epsilon_c &= \int_{T_R}^{T_0} S^*_C \, dT \\ \epsilon_c - \epsilon_e &= \int_{T_0}^{T} S^*_A \, dT \\ \epsilon_e - \epsilon_d &= \int_{T}^{T_0} S^*_B \, dT \\ \epsilon_d - \epsilon_b &= \int_{T_0}^{T_R} S^*_C \, dT \end{aligned} \tag{96}$$

Taking the sum of the equations we get

$$\epsilon_a - \epsilon_b = \epsilon_{\ A,B} = \int_{T_0}^{T} \left(S^*_A - S^*_B\right) \, dT \tag{97}$$

Similar analysis applied to a thermo-junction of wires A and B leads to

$$\pi_{A,B} = T\left(S^*_A - S^*_B\right) \tag{98}$$

Here $\pi_{A,B}$ denotes the Peltier coefficient.

Analysis of a small wire having a small temperature difference between the ends leads us to the following famous equations:

$$\sigma_A - \sigma_B = -T\frac{d}{dt}\left(S^*_A - S^*_B\right) \tag{99}$$

$$\frac{\pi_{A,B}}{T} = \frac{d\epsilon_{A,B}}{dT} \tag{100}$$

and so

$$\sigma_A - \sigma_B = -T\,\frac{d^2\epsilon_{A,B}}{dT^2} \tag{101}$$

From these equations it is possible to calculate the Peltier coefficient of any junction and the difference of Thomson coefficients of two wires at any temperature, once the temperature difference of the thermal emf is known.

4.4 Let us sum up

Five different effects take place when two dissimilar metals are connected and the junctions are kept at different temperatures. The emf generated when the two junctions are maintained at different temperatures is called Seebeck effect. The emf produced can be expressed as

$$\epsilon = \alpha_1 t + \frac{\alpha_2}{2}t^2 + \frac{\alpha_3}{3}t^3$$

where t is the junction temperature. The constants α_1, α_2 and α_3 depend on the materials involved. Joule effect is the heating effect due to resistance of the wires. Heat conduction occurs whenever two ends are maintained at different temperatures. Changes in temperatures of the junctions due to an external current passing through the system is called Peltier effect. The rate at which Peltier heat is transferred is proportional to the first power of the current. The proportionality coefficient is called Peltier coefficient. Peltier heat is reversible. Thomson effect leads to a heating effect whenever a current is passed through a junction. It is also reversible. If both temperature difference and voltage difference are present in a rod like material there is a production of entropy. The rate of entropy production depends linearly on $\frac{\Delta T}{T}$ and $\frac{\Delta \epsilon}{T}$. When departures from equilibrium is not large thermal and electrical currents depend linearly on $\frac{\Delta T}{T}$ and $\frac{\Delta \epsilon}{T}$ which are called generalised forces. The coefficients of proportionality are found to be symmetric. That is known as Onsager reciprocal relations. Thermodynamic analysis of Seebeck and Peltier effects can be performed in terms of entropy transport parameters of the materials involved.

4.5 Key words

Entropy current: If I_R is the heat current in a material i.e, the rate of transfer of heat, $\frac{I_Q}{T}$ is said to be the entropy current due to heat

Generalised forces: The causes that lead to entropy production are called generalised forces. For heat and electricity they are equal to $\frac{\Delta T}{T}$ and $\frac{\Delta \epsilon}{T}$, respectively.

Generalised currents: These are the effects of generalised forces. They are assumed to be linearly proportional to generalised forces

Entropy transport parameter: Denoted by S^*, it is defined by $\left(\frac{I_S}{I}\right)$ at constant temperature, where I_S and I are thermal and electrical currents, respectively.

4.6 Questions for self study

a) Explain the occurrence of Seebeck effect, Joule effect, Peltier effect and Thomson effect in a thermocouple

b) State and explain Onsager reciprocal relations

c) Explain the role of entropy transport parameter in thermocouples

4.7 Further references

1. B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi, 2007.

2. B.B Laud, *Fundamentals of Statistical Mechanics*, New age international ltd. New Delhi, 2003.
3. Zemonsky, *Heat and Thermodynamics*, McGraw Hill, 1957.
4. M.N Saha and Srivastava, *A treatise on heat*, Indian Press, New Delhi, 1965.
5. K. Huang, *Statistical Mechanics*, Wiley Eastern ltd, 1975.
6. C. Kittel, *Thermal Physics*, Wiley Eastern ltd, 1969.

UNIT 5

5 Phase Space and Liouville Theorem

5.1 Objectives

After studying this unit you will be able to

- define micro states and macro states of a system
- understand the postulate of equal apriori probability
- understand phase space
- state and prove Liouville theorem.

5.2 Introduction

A thermodynamic system will be having macro states described by a few dynamical variables like pressure, volume, temperature etc. But it will have a large number of micro states corresponding to the large number of possible distribution of its small constituents. Macro states will be obtained as the resultants of large number of micro states. We shall define both micro states and macro states precisely. A commonly made postulate of equal apriori probability of micro states. You shall learn about it. Dynamic evolution of a system is represented with the help of phase space. For microscopic systems we have a μ space, while for a macroscopic system we have Γ space. The latter can be thought of as a direct product of μ spaces. A general state of a system is represented by a point in phase. A large collection of closely spaced phase points go to make up a phase fluid. Since our system has to obey Hamilton's dynamical equations, such a phase space fluid moves like an incompressible fluid. That is the essence of Liouville theorem. You shall learn the statement and proof of Liouville theorem.

5.3 Micro and Macro states

In classical mechanics the state of a particle is described in terms of its position and momentum (or velocity) as a function of time. For a system of several particles the state is specified by the set of position and momentum values of all its particles. Suppose we are interested in a thermodynamic system such as gas in a container or a solid body we have an extremely large number of particles (such as atoms or molecules) to consider. For instance one cc of normal gas may contain up to 10^{19} atoms/molecules. But the thermodynamic properties of interest such as volume, pressure, temperature are only few in number. Hence we have to find a way of relating the thermodynamic variables to the properties of the constituent particles.

Micro states

Each set of coordinate and momentum variables of the constituent particles of a system is said to specify a micro state. It is constantly changing in time due to collisions between particles. The time between collisions is extremely small compared to the time required for measuring the average or overall property of the system such as pressure. If there are N particles in a system then each micro state is specified by a set of $6N$ values of position and momenta.

Macro states

These are the states of a large system that need only a few variables for their specification. For instance, the pressure of a gas in a large container measured over some time is an example of a macroscopic variables. Hence, the macro state of normal gas is specified by three variables namely, pressure, volume and temperature. We shall be concerned here only with equilibrium values of macro states. Such variables do not change with time.

Relation between micro and macro states

As a simple example for illustrating the connection between micro and macro states, let us consider the simplified example of three particles a, b and c having micro states with energies $0, 1, 2, 3, 4$ units. We may specify the macro state by the total energy of the system. The micro states are specified by the distribution of these particles in the available energy levels.
Let us find out the number of micro states that correspond to a chosen energy level. If the total energy of the system is zero, then there is only micro state wherein all the three particles are in the zeroth energy state.
If the total energy of the system is one unit, there are three possible micro states such that only one of the three particles is in the first energy level while the other two are in the zeroth energy state.

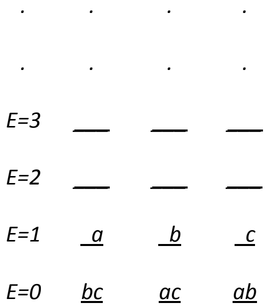


Figure 5.1: Representation of a macro state with energy one unit

The three micro states are shown in figure 5.1. Here we have assumed that a, b and c are distinguishable.
For a macro state with energy equal to two units, the number of micro states are 6 as shown in figure 5.2.

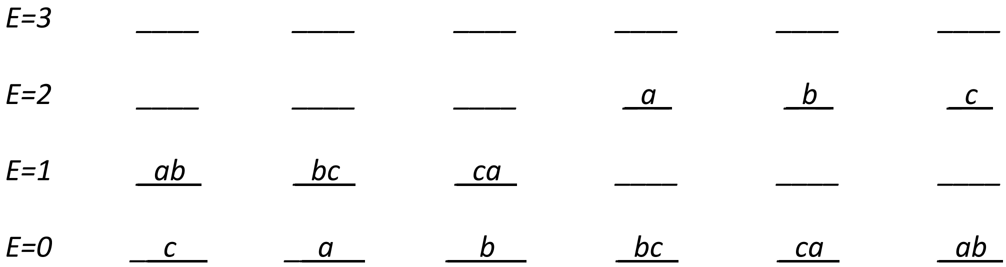
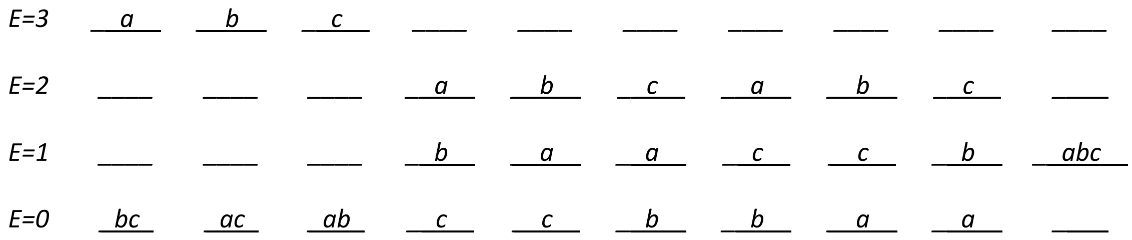


Figure 5.2: Representation of a macro state with energy two units

In case the particles are indistinguishable, the number of micro state will reduce to only two.

Similarly for a macro state with energy 3 units the number of micro states turns out to be 10. They are illustrated in figure 5.3.

The results are summarised in the table below



E=3	a	b	c							
E=2				a	b	c	a	b	c	
E=1				b	a	a	c	c	b	abc
E=0	bc	ac	ab	c	c	b	b	a	a	

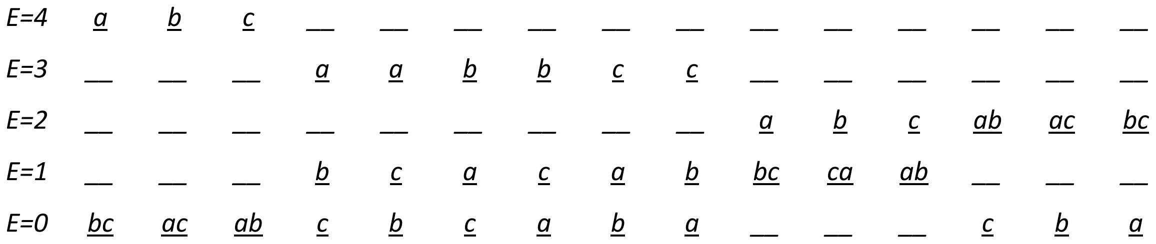
Figure 5.3: Representation of a macro state with energy three units

Macroscopic energy	Number of micro states	
E	If the particles are distinguishable	Particles are indistinguishable
0	1	1
1	3	1
2	6	2
3	10	3

Example: 5.1

If the energy of the macro system is 4 units in the above example, calculate the number of micro states when the particles are distinguishable and indistinguishable.

As you can see, as the total energy of the system of three particles increases, the



E=4	a	b	c												
E=3				a	a	b	b	c	c						
E=2										a	b	c	ab	ac	bc
E=1				b	c	a	c	a	b	bc	ca	ab			
E=0	bc	ac	ab	c	b	c	a	b	a				c	b	a

Number of states when *a,b,c* are distinguishable = 15

Number of states when *a,b,c* are indistinguishable = 04

Figure 5.4: Number of micro states with energy equal to four units

number of micro states rapidly increases. For a truly realistic system having extremely large number of particles (or constituents) the micro states increase rapidly with a macroscopic parameter such as energy. It will be seen that the number of micro states reaches a peak value for a particular distribution of particles over the possible micro states.

The postulate of equal apriori probability

You have seen that for a specified macro state there can be a large number of micro states corresponding to different distribution of the constituents over allowed micro states. It is assumed that all the allowed micro states are equally likely. This is stated in the form of a postulate. It may be stated as : A microscopic system in equilibrium is equally likely to be in any one of the micro states which are accessible to it and which fulfill the conditions of the macroscopic system. Even though there is no direct proof of this postulate, it is found to be reasonable and conformity with the laws of mechanics.

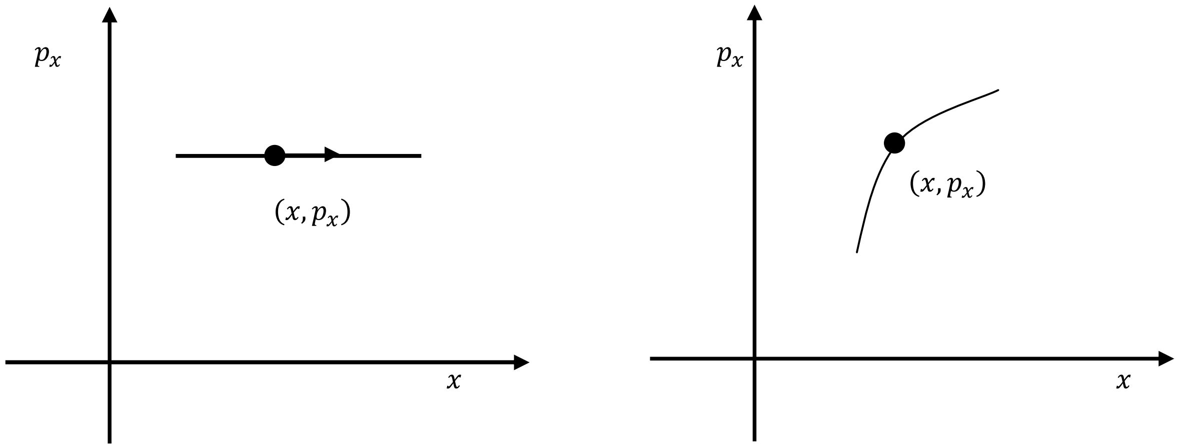
The Phase Space

Let us consider the simple example of a bead moving along a string stretched along the $X-$axis. The system has only one degree of freedom. Its state is represented by the position and velocity (or equally well by momentum) at any instant of time. The state of the bead can be represented by a point in a hypothetical two-dimensional space called phase space. The coordinates of the points are x and p_x. As the bead moves its state changes and hence its state point also moves in phase space. The state point traces a curve in phase as shown in figure 5.5.

Similarly, a molecule of an ideal gas has three translational degrees of freedom. Its phase space has has six dimensions whose Cartesian coordinates are x, y, z, p_x, p_y, p_z. Such a space is called μ space, the symbol μ standing for molecule.

For a system of N molecules (in a gas) the instantaneous state is represented by a set of N points in the μ space, one for each molecule. As done by Ehrenfest, the phase space of the collection of molecule has $6N$ dimensions with $3N$ coordinates and $3N$ momentum variables. It is called the Γ space of the system of molecules. It is spanned by $3N$ coordinate values and $3N$ momentum values. As the molecules moves the representative point in Γ space also moves. This is illustrated in figure 5.6

Since molecular motion is extremely random, the trajectory P in Γ space is expected to be highly random in nature.



Phase space trajectory of a uniformly moving bead

Phase space trajectory of an accelerated bead

Figure 5.5: Phase space representations

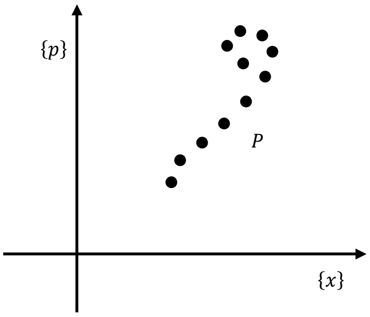


Figure 5.6: Γ space representation

Example 5.2

For a one dimensional harmonic oscillator the momentum and coordinate variables satisfy

$$\frac{p_x^2}{2m} + \frac{1}{2}Kx^2 = E = \text{constant}$$

Hence, the locus of phase space points will be an ellipse as shown in figure 5.7.

A three dimensional harmonic oscillator satisfies

$$\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + \frac{1}{2}\left(K_1x^2 + K_2y^2 + K_3z^2\right) = E = \text{constant}$$

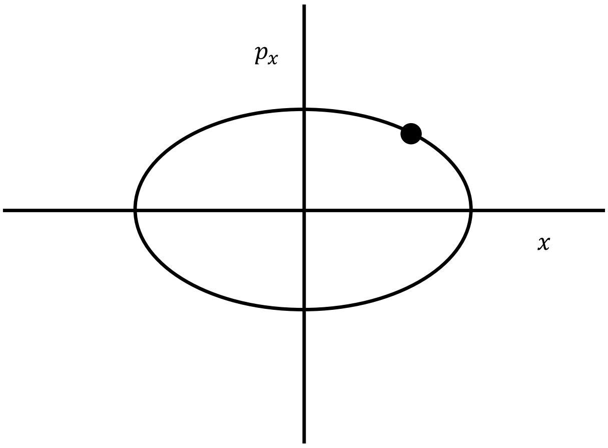


Figure 5.7: Phase space of a simple harmonic oscillator

Hence, the phase space will be the surface of an ellipsoidal figure in six dimensions.

Liouville Theorem

In 1838 Joseph Liouville showed that as a system moves in Γ space, no two trajectories ever cross each other and that the density of phase space points remains constant in time.

Consider a Γ space having f degrees of freedom. The number of phase space points in the vicinity of a point $q_1, q_2, ...q_f; p_1, p_2, ...p_f$ in Γ space will be given by

$$dN = D\left(q_i, p_i, t\right)\ dq_1.....dq_f\ dp_1.....dp_f$$

where $D\left(q_i, p_i, t\right)$ represents the density of points around $\{q_i\}, \{p_i\}$ and $dq_1.....dq_f\ dp_1.....dp_f$ denotes the hyper volume $d\Gamma$ in phase space. Due to flow of phase points this number will change with time due points entering and leaving the hyper volume under consideration.

For simplicity let us consider a two dimensional phase space spanned by q_1 and p_1 as shown in figure 5.8. Consider a rectangular region normal to q_1 and p_1 axes

The number of phase points entering the face $q_1 =$ constant in time dt is given by

$$D\left(q_1, p_1\right)\left(\dot{q}_1\ dt\right)\left(dq_2.....dq_f\right)\left(dp_1.....dp_f\right) \tag{102}$$

The number of phase points leaving the opposite face at $q_1 + dq_1$ in time dt is

$$\left(D + \frac{\partial D}{\partial q_1}dq_1\right)\left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}dq_1\right)dt\ \left(dq_2.....dq_f\right)\left(dp_1.....dp_f\right) \tag{103}$$

Subtracting 5.2 from 5.1 and neglecting second order differentials the change in the number of points in the hyper volume $d\Gamma$ in time dt is

$$-\left(D\frac{\partial \dot{q}_1}{\partial q_1} + \frac{\partial D}{\partial q_1}\dot{q}_1\right)dt\ d\Gamma \tag{104}$$

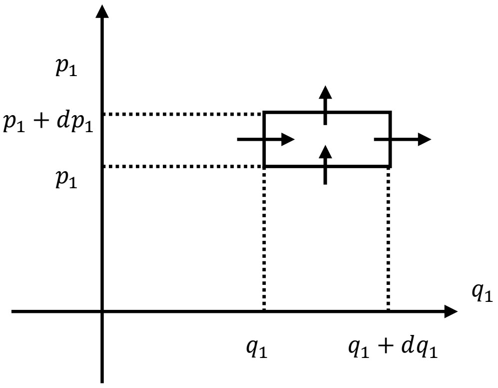


Figure 5.8

Similarly movement along p_1 leads to a change in the number of phase points by

$$-\left(D\frac{\partial \dot{p}_1}{\partial p_1} + \frac{\partial D}{\partial p_1}\dot{p}_1\right) dt\ d\Gamma \tag{105}$$

The total change in time dt of phase points in the small phase space volume $d\Gamma$ will be

$$\frac{\partial D}{\partial t} d\Gamma\ dt \tag{106}$$

It should be equal to the sum of 8.3 and 8.4 over all pairs of position and momenta:

$$-\sum_{i=1}^{3N}\left\{D\left(\frac{\partial \dot{q}_i}{\partial q_i}\right) + \frac{\partial D}{\partial q_i}\dot{q}_i + D\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial D}{\partial p_i}\dot{p}_i\right\} d\Gamma dt \tag{107}$$

Hence equating 5.5 and 5.6 we get

$$\frac{\partial D}{\partial t} + \sum_{i=1}^{3N}\left\{D\left(\frac{\partial \dot{q}_i}{\partial q_i}\right) + \frac{\partial D}{\partial q_i}\dot{q}_i + D\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial D}{\partial p_i}\dot{p}_i\right\} = 0 \tag{108}$$

Due to Hamilton's equations of motion we have

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \text{ and } \dot{p}_i = -\frac{\partial H}{\partial q_i}.$$

Hence

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} = -\frac{\partial \dot{p}_i}{\partial p_i} = -\frac{\partial^2 H}{\partial p_i \partial q_i}$$

Hence equation 5.7 reduces to

$$\frac{\partial D}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial D}{\partial q_i}\dot{q}_i + \frac{\partial D}{\partial p_i}\dot{p}_i\right) = 0 \tag{109}$$

The LHS of the above equation is nothing but the total time derivative of $D(q_i, p_i, t)$. Hence we get the equation

$$\frac{d}{dt}D(q_i, p_i, t) = 0$$

This is known as Liouville's theorem.

It may be stated as: The density of phase space points does not change in time as the system evolves in time. Hence, if any time the phase points are distributed uniformly in Γ space, they will have uniform density for ever. There will not be any crowding of phase points into any special region of Γ space.

We can use Liouville theorem to show the conservation of extension in phase space. The number of phase space points in a small region can be obtained as

$$\Delta M = D\left(\Delta\Gamma\right)$$

where D is the density and $\Delta\Gamma$ is the small volume.

Then

$$\frac{d}{dt}\Delta M = \frac{dD}{dt}\Delta\Gamma + \frac{d\Delta\Gamma}{dt}.$$

Since $\frac{dD}{dt} = 0$ from Liouville theorem, we may conclude that $\Delta\Gamma$ remains constant as it moves. The phase points on the boundary of $\Delta\Gamma$ form a skin that permanently encloses the space points in $\Delta\Gamma$. These points can be neither created nor destroyed. Consequently, the number ΔM of phase points enclosed by $\Delta\Gamma$ remains constant. Following J. Gibbs this result is called the principle of conservation of extension in phase space.

5.4 Let us sum up

A thermodynamic system will generally have few macro states which are associated with a large number of micro states. Macroscopic properties are believed to be derivable by summing over micro states. The number of micro states rapidly increases as the energy is increased. All micro states are assumed to occur with equal probability. This is known as postulate of equal apriori probability. Specification of position and momentum variables of micro states leads to the phase space. Microscopic properties can be regarded as average values over suitable phase space volume. Closely space points in phase space form what is known as phase fluid. Such a fluid behaves like an incompressible fluid. That is the gist of Liouville theorem. It is also seen that the volume in phase space is conserved.

5.5 Key words

Macro state: The state of a thermodynamic system

Micro states: The states of the small constituents of a macroscopic system

μ **space:** The phase space of a molecule or a microscopic system is called μ space

Γ **space:** The phase space of a large system is called a Γ space

Phase space fluid: A collection of very closely related set of phase space points form a phase space fluid.

5.6 Questions for self study

a). Define the micro states and macro states of a system

b). Define phase space of a molecule

c). Define Γ space

d). State and explain the postulate of equal apriori probability

e). State and prove Liouville theorem

f). Deduce the number of micro states for three particles with energy four units when the allowed energy level are $0, 1, 2, 3, 4, 5, ...$ units.

5.7 Further References

- Allis, Herlin, *Thermodynamics and Statistical Mechanics*, McGraw-Hill, New York, 1952.
- Andrews, *Equilibrium Statistical Mechanics*, John Wiley, New York, 1963.
- A. Sommerfeld, *Thermodynamics and Statistical Mechanics*, Academic Press, New York, 1956.
- B.B Laud, *Introduction to Statistical Mechanics*, Macmillan, India, 1981.
- Charles Kittel, *Elementary Statistical Physics*, John Wiley, New York, 1968.
- Chisholm, de Borde *An Introduction to Statistical Mechanics*, Pergamon, New York, 1958.
- E. Schrödinger, *Statistical Thermodynamics*, Cambridge U.P, Cambridge, 1946.
- Feynman,R.P, *Statistical Mechanics*, Benjamin, Massachusetts, 1972.
- F. Mandl, *Statistical Physics*, John Wiley, London, 1971.
- Grad, Harold, *The many faces of entropy*, Communications on Pure and Applied Mathematics 14 (3): 323,1961.
- Gibbs, Josiah Willard, *Elementary Principles in Statistical Mechanics*, Charles Scribner's Sons, New York, 1902.
- Hill, *Statistical Mechanics*, McGraw-Hill, New York, 1956.
- Huang, *Statistical Mechanics*, McGraw-Hill, John Wiley, New York, 1963.

- J. Liouville, *Journ. de Math.*, 3, 349.
- Landau, Lev Davidovich; and Lifshitz, Evgeny Mikhailovich, *Statistical Physics. Course of Theoretical Physics 5*, Oxford: Pergamon Press, Oxford, 1980.
- Philippe Denney, *An Introduction to Statistical Mechanics*, George Allen, London, 1972.
- R. Kubo, *Statistical Mechanics*,North-Holland, Amsterdam, 1965.
- Sackur, *Die Anwendung der kinetischen Theorie der Gase auf chemische Probleme (The application of the kinetic theory of gases to chemical problems)*, Annalen der Physik, 36: 958 - 980,1911.
- Tolman RC, *General Theory of Energy Partition with applications to Quantum Theory* , Physical Review 11 (4): 261275.1918.

UNIT 6

6 Ensembles, Mean values and fluctuations

6.1 Objectives

After studying this unit you will be able to

- understand ensembles and their types
- learn about micro-canonical, canonical and grand canonical ensembles
- learn about mean values
- learn about fluctuations about mean values

6.2 Introduction

To deal with statistical systems Gibbs introduced three types of ensembles of systems. They are

a) the micro-canonical ensemble

b) the canonical ensemble and

c) the grand canonical ensemble

Their classification depends on the manner in which their systems interact. Each corresponds to its own characteristic distribution. Physical systems can interact in several ways. The ensemble in which systems exchange energy but not matter is called a canonical ensemble. An ensemble in which both energy and matter are exchanged between the systems is called a grand canonical ensemble. that in which neither matter nor energy is exchanged is said to be a micro-canonical ensemble. In statistical mechanics one calculates physical quantities in equilibrium conditions. They correspond to mean values. However, one finds small fluctuations or deviations from the mean values in a physical collection of systems. The fluctuations depend on the number of constituents in a system. You will learn about all these in this unit.

6.3 Types of ensembles

Micro-canonical Ensemble

This ensemble consists of systems that are isolated from the rest of the world. Such a system is also known as 'closed isolated system'. It will have a fixed volume, fixed energy and fixed number of particles. The probability density $P(q, p)$ of such a system will be different from zero only on a constant energy hyper-surface. In reality such a surface will have a width ΔE in energy.

In phase space a micro-canonical distribution would be something like a very thin uniform cloud (see figure below)

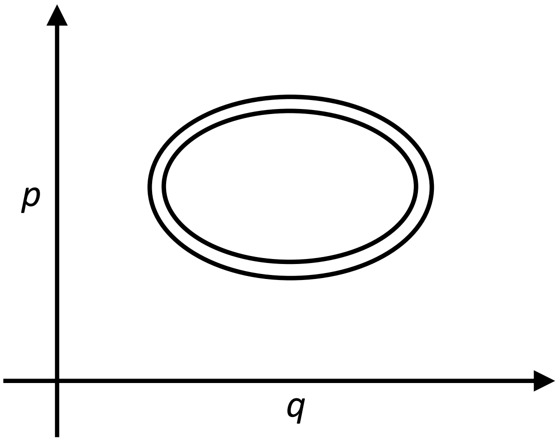


Figure 6.1: Micro-canonical ensemble

For a simple harmonic oscillator, specifically, it will be an ellipse in $p - q$ space. On the ellipse the energy remains constant.

According to fundamental postulate of equal apriori probability, the system is equally likely to be found in one of its accessible states. In the case of micro-canonical ensemble all the states between energy E and $E+\Delta E$ are equally accessible. Hence the probability of finding the system in a state X with a fixed energy will take the form

$$P_x = \begin{cases} c, \text{a constant for } \ E < E_x < E + \Delta E \\ 0, \text{otherwise} \end{cases} \tag{110}$$

The constant c can be determined by the normalisation condition: $\sum_x P_x = 1$, where the summation is taken over all accessible states.

Canonical Ensemble

A micro-canonical ensemble is not very useful in applications since isolated systems are very rare. However, it is useful in basic theory. A more realistic ensemble is one where equilibrium is achieved by exchange of energy with the surroundings. Such an ensemble is a canonical ensemble.

Suppose we want to study a thermodynamic system A. we imagine an assembly of a very large number of identical systems in contact with a huge heat reservoir. A heat reservoir is a system whose heat capacity so much greater than the subsystems in contact with it. heat flow from or to the heat reservoir does not change its temperature significantly. The assembly can be thought of as contained within a micro-canonical ensemble. Each system of the assembly is in contact with other elements of the micro-canonical ensemble, but isolated from the outside world.

What is the probability that a canonical system, in equilibrium, is in a particular state with a specific energy E_α? Consider a canonical system A in a micro-canonical ensemble A' such that $A \ll A'$. (fig 6.2)

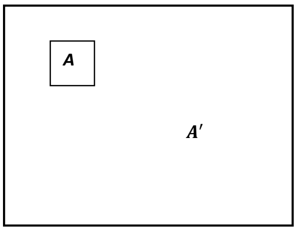


Figure 6.2

The walls of A are such that A and A' are free to exchange energy. The micro-canonical ensemble is isolated with total energy, say, E_0. A large number of microscopic states correspond to the macroscopic state of the micro-canonical ensemble with energy E_0.

Let Ω_0 be the total number of micro states of the micro-canonical ensemble with energy E_0. Using the postulate of equal apriori probability we conclude that all these micro states are equally probable with probability $\frac{1}{\Omega_0}$. Different micro states of the ensemble $A^{'}$ give rise to different micro states of the small subsystem A. Suppose a certain micro state of $A^{'}$ gives rise to a micro state of A with energy E_a(with $E_a \ll E_0$). The energy of the remaining part of the complete system is $E_0 - E_a$. Let the number of states of the micro-canonical ensemble $A^{'}$ through which the states of the small system A with energy E_a are attained be $\Omega_\alpha\left(E_0 - E_a\right)$. Therefore the probability of finding the system A in a state with energy E_a is

$$P_a = \frac{\Omega_\alpha\left(E_0 - E_a\right)}{\Omega_0} \tag{111}$$

Using $a = e^{\ln a}$ we can write this as

$$P_a = \frac{e^{\ln \Omega_\alpha (E_0 - E_a)}}{\Omega_0} \tag{112}$$

Expanding $\Omega_\alpha\left(E_0 - E_a\right)$ in Taylor series,

$$\ln \Omega_\alpha\left(E_0 - E_a\right) = \ln \Omega_\alpha\left(E_0\right) - E_a \frac{\partial}{\partial E_0} \ln\left(\Omega_\alpha\left(E_0\right)\right) + \text{higher order terms}$$

we get,

$$P_\alpha = \frac{e^{\ln \Omega_\alpha (E_0)}\ e^{-\beta\ E_a}}{\Omega_0} \tag{113}$$

where

$$\beta = \frac{\partial}{\partial E_0} \ln\left(\Omega_\alpha\left(E_0\right)\right)$$

Hence,

$$P_\alpha = (\text{constant})\ e^{-\beta\ E_a} \tag{114}$$

The constant can be found by normalisation $\sum P_\alpha = 1$.
This expression in equation 6.5 is called Gibbs canonical distribution. After normalisation, we can write for the probability of finding A in energy state E_a as Hence,

$$P_\alpha = \frac{e^{-\beta\ E_a}}{\sum e^{-\beta\ E_a}} \tag{115}$$

The denominator is usually denoted by Z and called partition function. Thus

$$Z = \sum_a e^{-\beta\ E_a} \tag{116}$$

The parameter β shall be identified with $\frac{1}{KT}$.

Alternative method for canonical distribution

Let us consider an ensemble of a large number of systems, say, N. The numbers of the ensemble are separated by 'diathermic' walls that permit the transfer of energy from one system to another. Let us suppose that there are n_1 systems in a state 1 with respect to energy E_1, n_2 systems in a state 2 with respect to energy E_2 and so on. In general there are n_i systems in state i with energy E_i. Then it is clear that

$$\sum n_i = N \text{ and } \sum n_i E_i = N \langle E \rangle \tag{117}$$

where $\langle E \rangle$ is the mean energy of the system.

Any set of numbers $(n_1, n_2 .... n_i ......)$ that satisfies equation 6.8 is a possible mode of distribution and any such mode can be realised in a number of ways by shuffling the members of the ensemble.

What is the probability of occurrence of such a distribution? Let us find the number of ways in which a distribution of n_i systems in energy state with energy E_i is possible. Out of the total N systems n_1 are to be accommodated in state 1. The total number of ways for this is

$$N(N-1)......(N-n_1+1) \tag{118}$$

or,

$$\frac{N!}{(N-n_1)!}$$

Now we are left with $N - n_1$ systems of which n_2 are in state 2. This can be done in $\frac{(N-n_1)!}{n_2!(N-n_1-n_2)!}$ different ways.

Proceeding this way we find the number of ways of choosing n_1 systems in state 1, n_2 systems in state 2 etc. is given by

$$W = \frac{N!}{n_1!\,(N-n_1)!} \times \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!} \times ..... \tag{119}$$

Note the presence of $n_1!, n_2!$ in the denominator corresponding to the number of ways of arranging n_1, n_2 etc. within themselves. Hence the factor $n_1!, n_2!$ etc in the denominator.

The probability of obtaining such a distribution is proportional to W. The most probable distribution, which will be almost equal to the n=mean distribution, is found by maximising W with respect to $n_1, n_2 .... n_i$. Now

$$W = \frac{N!}{n_1!\; n_2!\; ....} \tag{120}$$

Therefore

$$\ln W = \ln N! - \sum_i \ln n_i! \tag{121}$$

Using Stirling's formula for $\ln n$ for large n namely

$$\ln n! \simeq n\left(\ln n - 1\right)$$

we get

$$\ln W = N\left(\ln N - 1\right) - \sum_i n_i\left(\ln n_i - 1\right) \tag{122}$$

Therefore

$$\ln W = N\left(\ln N\right) - \sum_i n_i\left(\ln n_i\right) \tag{123}$$

Treating n_i to be continuous variable $\ln W$ will be maximum if $\delta \ln W = 0$ for variations in all n_i. This leads to

$$\delta \sum_i n_i\left(\ln n_i\right) = 0 \tag{124}$$

Thus

$$\sum_i \delta n_i\left(\ln n_i\right) + \delta n_i = 0 \tag{125}$$

is the condition for maximum W.
The constraint conditions 6.8 imply

$$\sum_i \delta n_i = 0 \text{ and } \sum_i E_i \delta n_i = 0 \tag{126}$$

Using Lagrange multiplier method for finding maxima under constraints the condition for maximum W is

$$\sum_i \left(\ln n_i + \alpha + \beta E_i\right)\delta n_i = 0 \tag{127}$$

where α and β are Lagrange multipliers.
Regarding δn_i are independent and arbitrary, equation 6.18 implies that the coefficient of each δn_i to vanish. Hence

$$\ln n_i + \alpha + \beta E_i = 0 \tag{128}$$

This implies

$$n_i = e^{-\alpha - \beta E_i} \tag{129}$$

as the general form for n_i. Using the normalisation condition $\sum n_i = N$ we get

$$n_i = \frac{N e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} \tag{130}$$

for the number of systems in energy state E_i. This is the well known canonical distribution.

Grand Canonical Ensemble

We consider a situation in which a subsystem A in a system $A^{'}$ is such that A and $A^{'}$ can exchange both energy and particles (matter). Such systems are called open systems. $A^{'}$ is a member of a micro-canonical ensemble. Let E_0 and N_0 be the energy and number of particles of the entire system. Then

$$E_0 = E_a + E^{'} \ \text{ and } \ N_0 = N_a + N^{'} \tag{131}$$

Here $E_a, E^{'}$ are the energies and $N_a, N^{'}$ are the number of particles in $A, A^{'}$ respectively. We adopt the same technique as in canonical distribution.
The probability that a subsystem A is in state with energy E_a and has N_a number of particles is

$$P_a = c\Omega_\alpha \left(E_0 - E_a, N_0 - N_a\right) \tag{132}$$

where c is a constant and Ω_α has the same as in th case of canonical distribution.
Let us expand $\ln\Omega_\alpha$ in powers of E_a and N_a as:

$$\ln\Omega_\alpha \left(E_0 - E_\alpha, N_0 - N_\alpha\right) = \ln\Omega_\alpha \left(E_0, N_0\right) - \frac{\partial \ln\Omega_\alpha}{\partial E_0} E_a \ \frac{\partial \ln\Omega_\alpha}{\partial N_0} N_a + \text{higher order terms} \tag{133}$$

Keeping only the first order terms in E_a and N_a and putting

$$\beta = \frac{\partial \ln\Omega_\alpha}{\partial E_0} \ \text{ and } \ -\mu = \frac{\partial \ln\Omega_\alpha}{\partial N_0}$$

we get

$$\Omega_\alpha \left(E_0 - E_\alpha, N_0 - N_\alpha\right) = \Omega_\alpha \left(E_0, N_0\right) e^{-\beta E_a + \mu N_a} \tag{134}$$

The normalisation condition gives

$$c = \frac{1}{\sum_a e^{-\beta E_a + \mu N_a}} \tag{135}$$

This distribution is called grand canonical distribution.

Mean values and fluctuations

The mean value of a function f_a is given by

$$\langle f \rangle = \sum_a f_a P_a \tag{136}$$

For a canonical distribution

$$P_a = \frac{e^{-\beta\ E_a}}{\sum e^{-\beta\ E_a}}.$$

Hence the mean value of f in a canonical ensemble is

$$\langle f \rangle = \frac{\sum_a f_a\ e^{-\beta E_a}}{\sum_a e^{-\beta E_a}} \tag{137}$$

Let us apply the formula to energy. Thus the mean energy will be

$$\langle E\rangle = \frac{\sum_a E_a\, e^{-\beta E_a}}{\sum_a e^{-\beta E_a}} \tag{138}$$

putting $Z = \sum e^{-\beta E_a}$ we can write

$$\langle E\rangle = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln Z \tag{139}$$

The mean value of the square of the energy is

$$\left\langle E^2\right\rangle = \frac{\sum_a E_a^2\, e^{-\beta E_a}}{\sum_a e^{-\beta E_a}} = -\frac{1}{Z}\frac{\partial^2}{\partial\beta^2}Z \tag{140}$$

We can define the fluctuation in energy ΔE by

$$\left(\Delta E^2\right) = \left\langle (E - \langle E\rangle)^2\right\rangle = \left\langle E^2\right\rangle - \langle E\rangle^2 \tag{141}$$

substituting the expressions in 139 and 140 we get

$$\left(\Delta E^2\right) = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2}\left(\frac{\partial Z}{\partial\beta}\right)^2 \tag{142}$$

Therefore

$$\left(\Delta E^2\right) = \frac{\partial^2}{\partial\beta^2}\left(\ln Z\right) = -\frac{\partial}{\partial\beta}\langle E\rangle \tag{143}$$

Using the equation

$$\beta = \frac{1}{KT}$$

$$\left(\Delta E^2\right) = -\frac{\partial\langle E\rangle}{\partial\beta} = -\frac{\partial\langle E\rangle}{\partial T}\frac{\partial T}{\partial\beta} = KT^2\frac{\partial\langle E\rangle}{\partial T} = KT^2 C_V \tag{144}$$

Hence, we conclude that the fluctuation in energy is proportional to the specific heat. In specific case of a perfect gas $\langle E\rangle = \frac{3}{2}NKT$.

Hence

$$\left(\Delta E^2\right) = KT^2\,\frac{3}{2}NK = \frac{3}{2}NK^2T^2$$

Therefore the mean fractional fluctuation will be

$$\left\{\frac{\left(\Delta E^2\right)}{\langle E\rangle^2}\right\}^{\frac{1}{2}} = \frac{\frac{3}{2}NK^2T^2}{\frac{9}{4}N^2K^2T^2} = \sqrt{\frac{2}{3N}} \tag{145}$$

This turns out to be extremely small for practical values of N of the order of 10^{18}. Then the fractional fluctuation will be of the order of 10^{-9}. This means the mean energy is a very sharp function of $\{x_1, x_2, ...x_i\}$. It may also be taken as the most probable value for all practical purposes.

6.4 Let us sum up

We have three different types of statistical ensembles. They are micro-canonical, canonical and grand canonical ensembles. The micro-canonical ensemble corresponds to an isolated system hence has theoretical importance only. In a canonical ensemble, the elements can exchange energy but not particles. The probability of occurrence of energy E_a is proportional to $e^{-\beta E_a}$. In a grand canonical ensemble both energy and particles are allowed to be exchanged between the elements of the ensemble. The probability of occurrence of a state with energy E_a and particle number N_a is proportional to $e^{-\beta E_a + \mu N_a}$. Statistical ensembles show fluctuations in energy around the mean value. The fractional fluctuation is typically proportional to $\frac{1}{\sqrt{N}}$ where N is the number of systems. It turns out to be negligible for practical systems having $N \simeq 10^{18}$.

6.5 Key words

partition function: It is defined by

$$Z = \sum_a e^{-\beta E_a}$$

fluctuation in f: It is defined by $(\Delta f)^2$, where $(\Delta f^2) = \left\langle (f - \langle f \rangle)^2 \right\rangle = \langle f^2 \rangle - \langle f \rangle^2$. It is a measure of deviations from the mean value

6.6 Questions for self study

a). Define canonical, micro-canonical and grand canonical ensembles

b). Derive the distribution for a canonical ensemble

c). Derive the grand canonical distribution function

d). Define mean values and fluctuations

e). Obtain the fractional fluctuation for an ideal gas

6.7 Further References

- Allis, Herlin, *Thermodynamics and Statistical Mechanics*, McGraw-Hill, New York, 1952.
- A. Sommerfeld, *Thermodynamics and Statistical Mechanics*, Academic Press, New York, 1956.

- B.B Laud, *Introduction to Statistical Mechanics*, Macmillan, India, 1981.
- Charles Kittel, *Elementary Statistical Physics*, John Wiley, New York, 1968.
- Chisholm, de Borde *An Introduction to Statistical Mechanics*, Pergamon, New York, 1958.
- E. Schrödinger, *Statistical Thermodynamics*, Cambridge U.P, Cambridge, 1946.
- Feynman,R.P, *Statistical Mechanics*, Benjamin, Massachusetts, 1972.
- Hill, *Statistical Mechanics*, McGraw-Hill, New York, 1956.
- Huang, *Statistical Mechanics*, McGraw-Hill, John Wiley, New York, 1963.
- Landau, Lev Davidovich; and Lifshitz, Evgeny Mikhailovich, *Statistical Physics. Course of Theoretical Physics 5*, Oxford: Pergamon Press, Oxford, 1980.
- Philippe Denney, *An Introduction to Statistical Mechanics*, George Allen, London, 1972.
- R. Kubo, *Statistical Mechanics*,North-Holland, Amsterdam, 1965.

UNIT 7

7 Gibbs distribution and Gibbs paradox

7.1 Objectives

After studying this unit you will be able to

- understand the reduction of Gibbs distribution to Maxwell-Boltzmann distribution
- understand the relationship between entropy and thermodynamic probability
- deduce entropy of an ideal gas
- state and explain Gibbs paradox

7.2 Introduction

Gibbs distribution was deduced from the theory of canonical ensembles can be reduced to Maxwell-Boltzmann velocity distribution law for gases by making use of the number of states in a given phase space. Entropy is a measure of disorder of a system. It can be related to the number of accessible micro states for the system. It was first deduced by Boltzmann. An ideal gas has entropy that can be worked out using its partition function. Using the expression for ideal gas entropy we get a paradoxical situation when mixing of two containers of gases are considered. The resolution of the paradox was proposed by Gibbs. We shall study all these topics in this unit.

7.3 Gibbs distribution and Gibbs paradox

Reduction of distribution to Maxwell-Boltzmann distribution

Maxwell-Boltzmann distribution function gives the probability of finding a particular molecule within a certain velocity range. The system here is a single molecule in a heat reservoir. The phase phase of a molecule is a six dimensional space.
A molecule occupies a phase space of volume h^3. Hence the number of states of a molecule contained in a phase space volume $d\Gamma$ is

$$\frac{d\Gamma}{h^3} = \frac{dxdydz\ dP_x dP_y dP_z}{h^3} \tag{146}$$

where $\hbar$ is the Planck's constant.
But according to Gibbs canonical distribution the probability of a system having a state with energy E_a is

$$\frac{g_a e^{-\beta E_a}}{\sum_a e^{-\beta E_a}} \tag{147}$$

Therefore the probability of finding the system in phase space volume $d\Gamma$ corresponding to energy E_a is

$$dP_a = \frac{e^{-\beta E_a} \frac{d\Gamma}{h^3}}{\sum_a e^{-\beta E_a}} \tag{148}$$

To find the probability that the molecule has energy E_a, we have to integrate equation 7.3 with respect to all the elements of phase space corresponding to E_a.
Since the energy does not depend on the coordinates for an ideal gas we can straight way integrate with respect to coordinates to get

$$dP_a = \frac{V}{h^3} \frac{e^{-\beta E_a}}{\sum_a e^{-\beta E_a}} dP_x dP_y dP_z \tag{149}$$

The energy depends only on the magnitude of momentum. Hence going over to spherical coordinates in $P-$ space we get

$$dP_a = \frac{V}{h^3} \frac{(4\pi P^2)\, e^{-\beta E_a}}{\sum_a e^{-\beta E_a}} dP \tag{150}$$

where $E = \frac{P^2}{2m}$ and $P = mu$. Substituting these into equation 7.5 we get

$$dP_a = \frac{4\pi V}{h^3} \frac{e^{-\beta m \frac{u^2}{2}}}{\sum_a e^{-\beta m \frac{u^2}{2}}} \left(m^2 u^2\right) (m\ du) \tag{151}$$

Normalisation condition can be expressed as

$$\int_0^\infty dP_a = 1$$

Therefore the condition becomes

$$\frac{4\pi V m^3}{h^3 \sum_a e^{-\beta m \frac{u^2}{2}}} \int_0^\infty e^{-\beta m \frac{u^2}{2}} u^2 du = 1 \tag{152}$$

Using

$$\int_0^\infty e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$

we can perform the integration to get for the LHS of equation 7.6

$$\frac{4\pi V m^3}{h^3} \frac{m^3}{\left(\frac{\beta m}{2}\right)^{\frac{3}{2}}} \frac{\sqrt{\pi}}{2} \frac{1}{\sum e^{-\beta m \frac{u^2}{2}}}$$

This gives the value of $e^{-\beta m \frac{u^2}{2}}$. Putting it back into equation 7.6 we get

$$dP_a = \frac{4}{\sqrt{\pi}} \left(\frac{\beta m}{2}\right)^{\frac{3}{2}} e^{-\beta m \frac{u^2}{2}} u^2 du \tag{153}$$

This is nothing but Maxwell-Boltzmann distribution law for gas velocities. Here $\beta = \frac{1}{KT}$.

We can use equation 7.8 to calculate the mean kinetic energy of the molecules. Hence

$$\begin{aligned}
\left\langle \frac{1}{2} m u^2 \right\rangle &= \int_0^\infty \left(\frac{1}{2} m u^2\right) \left(\frac{4}{\sqrt{\pi}} \left(\frac{\beta m}{2}\right)^{\frac{3}{2}} e^{-\beta m \frac{u^2}{2}} u^2 \right) du \\
&= \frac{2m}{\sqrt{\pi}} \left(\frac{\beta m}{2}\right)^{\frac{3}{2}} \int_0^\infty u^4 e^{-\beta m \frac{u^2}{2}} du \\
&= \frac{3}{2\beta} = \frac{3}{2} KT
\end{aligned} \tag{154}$$

Hence we get Maxwell-Boltzmann distribution law

$$dP(u) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2KT}\right)^{\frac{3}{2}} e^{-\frac{m}{2KT} u^2} du \tag{155}$$

which is same as the standard M-B distribution law for gases.

Entropy and Thermodynamic probability

Entropy in thermodynamics is defined by

$$dS = \frac{\delta Q}{T} \tag{156}$$

where

$$\delta Q = d\langle E\rangle + \langle dW\rangle .$$

The partition function Z is a function of β and energy E, which in turn is a function of external parameters denoted by x

Therefore

$$\begin{aligned} d\left(\ln Z\right) &= \frac{\partial\left(\ln Z\right)}{\partial \beta} d\beta + \frac{\partial\left(\ln Z\right)}{\partial x} dx \\ &= -\left\langle E\right\rangle d\beta + \beta\left\langle dW\right\rangle \end{aligned} \tag{157}$$

Therefore

$$d\left(\ln Z\right) = -d\left(\beta\left\langle E\right\rangle\right) + \beta d\left\langle E\right\rangle + \beta\left\langle dW\right\rangle \tag{158}$$

Therefore

$$d\left(\ln Z + \beta\left\langle E\right\rangle\right) = \beta d\left\langle E\right\rangle + \beta\left\langle dW\right\rangle \tag{159}$$

$$d\left(\ln Z + \beta\left\langle E\right\rangle\right) = \beta\delta Q = \frac{1}{K} dS \tag{160}$$

This leads us to

$$K\ d\left(\ln Z + \beta\left\langle E\right\rangle\right) = dS \tag{161}$$

Therefore entropy can be expressed as

$$S = K\left(\ln Z + \beta\left\langle E\right\rangle\right)$$

but for an additive constant.

Entropy plays an important role in thermodynamics. Its statistical interpretation makes us understand it in a better way.

We know that the most probable state is more probable than any other state. Important contribution to the partition function comes from most probable energy, which in turn is equal to the mean energy for all practical purposes. Hence, we can write for Z

$$Z = e^{-\beta\langle E\rangle}\Omega\left(\left\langle E\right\rangle\right) \tag{162}$$

where $\Omega\left(\left\langle E\right\rangle\right)$ is the number of states with mean energy $\left\langle E\right\rangle$. Using this equation 7.16 we get

$$S = K\left\{-\beta\left\langle E\right\rangle + \ln\left(\left\langle E\right\rangle\right) + \beta\left\langle E\right\rangle\right\}$$

$$S = K\ln\Omega\left(\left\langle E\right\rangle\right) \tag{163}$$

Hence the entropy is essentially determined by the logarithm of the number of micro states corresponding to the energy $\left\langle E\right\rangle$.

Even though equation 7.18 has been derived for an ideal gas, it is valid in general for all systems. It provides a clear interpretation of entropy. The more ordered a system is, lower is the number of micro states through which the micro state is realised. Hence more ordered system will have lower entropy.

For instance, if all the particles in a system are having a fixed position, there is only one micro state leading to zero entropy. It may be noted that increasing the number of accessible micro states, the system becomes more disordered leading to increase in entropy. Hence entropy is a measure of disorder or chaotic state of the system.

The equilibrium state of a system is the most probable state under given conditions and it is attained through the largest number of microscopic states. The entropy of the system attains its maximum value in this state. Also a system always tends to move towards equilibrium state. i.e., in the direction of increasing entropy. This, incidentally, can be taken as another statement of the second law of thermodynamics.

In practical terms, it is more difficult to calculate $\Omega\left(\langle E\rangle\right)$ but easier to calculate the partition function and the mean energy. Therefore, the definition for entropy is given by 7.18 has lesser practical value.

Entropy of an ideal gas

As you know an ideal gas is one in which mutual interaction between molecules of the gas is negligible. It is a good approximation for low density noble gases.

The total energy of an ideal gas having N molecules is

$$E = \sum \frac{p_i^2}{2m} \tag{164}$$

where n is the mass of each molecule.

It has been shown that almost all macroscopic properties of the system can be calculated from its partition function

$$Z = \sum_s e^{-\beta E_s}.$$

The summation is over all discrete states denoted by S. If the states are not discrete, as in the case classically, the sums must be replaced by integrals. How does one go from summation to integration? The sum is over states has to be replaced by an integration over phase space.

Consider the phase space divided into cells of volume h^f each, where f is the number of degrees of freedom. Let $dV = dq_1, ..., dq_f,\ \ dp_1, ..., dp_f$ be a volume element in the phase space at the point $(q_1, ...q_f,\ p_1, ...p_f)$, the energy throughout it being the same, the number of cells in this volume element is

$$\frac{dV = dq_1, ..., dq_f,\ \ dp_1, ..., dp_f}{h^f}.$$

The partition function is found by summing over all these cells and then integrating over all elements of volume. Thus

$$Z = \int ...... \int e^{-\beta E} \frac{dV = dq_1, ..., dq_f,\ \ dp_1, ..., dp_f}{h^f} \tag{165}$$

For an ideal gas with N molecules $f = 3N$ and so

$$Z = \frac{1}{h^{3N}} \int ....\int e^{-\beta\left(\frac{p_1^2}{2m}+\frac{p_2^2}{2m}+.........\right)} dq_1, ..., dq_{3N}, \quad dp_1, ..., dp_{3N} \tag{166}$$

Now

$$\int .... \int dq_1, ..., dq_{3N} = \int d^3q_1 \int d^3q_2 ...... \int d^3q_N = V^N \tag{167}$$

where V is the volume of the container.

Therefore

$$Z = \frac{V^N}{h^{3N}} \int ..... \int e^{-\beta\left(\frac{p_1^2}{2m}+\frac{p_2^2}{2m}+.........\right)} dp_1 dp_2 .....dp_{3N}$$

$$Z = \frac{V^N}{h^{3N}} \int e^{-\beta\left(\frac{p^2}{2m}\right)} d^3p \tag{168}$$

The integral in equation 7.23 is

$$\begin{aligned}\int e^{-\beta\left(\frac{p^2}{2m}\right)} d^3p &= \int_{-\infty}^{+\infty} e^{-\beta\left(\frac{p_x^2}{2m}\right)} dp_x \int_{-\infty}^{+\infty} e^{-\beta\left(\frac{p_y^2}{2m}\right)} dp_y \int_{-\infty}^{+\infty} e^{-\beta\left(\frac{p_z^2}{2m}\right)} dp_z \\ &= \left[\int_{-\infty}^{+\infty} e^{-\beta\left(\frac{p^2}{2m}\right)} dp\right]^3 \\ &= \left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}} \end{aligned} \tag{169}$$

Hence

$$Z = \frac{V^N}{h^{3N}} \left(\frac{2m\pi}{\beta}\right)^{\frac{3}{2}} = \left[\left(\frac{2mKT}{h^2}\right)^{\frac{3}{2}} V\right]^N \tag{170}$$

Using this Z various thermodynamic quantities can be deduced. For example,

$$\langle P \rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{N}{\beta V} = \frac{NKT}{V} \tag{171}$$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{3N}{2\beta} = \frac{3}{2}NKT \tag{172}$$

give the mean pressure and energy.

The entropy is given by the formula

$$\begin{aligned} S &= K\left(\ln Z + \beta\langle E\rangle\right) \\ &= NK\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi m}{h^2}\right) - \frac{3}{2}\ln\beta + \frac{3}{2}\right] \\ &= NK\left[\ln V + \frac{3}{2}\ln T + \sigma\right] \end{aligned} \tag{173}$$

where $\sigma = \frac{3}{2}\left[\ln\left(\frac{2\pi mK}{h^2}\right) + 1\right]$, a constant.

Note that classically h is arbitrary and thus the expression σ is indeterminate. Hence absolute value of entropy is not defined, only its changes are physically meaningful. We have derived the above expression on the basis of distinguishable particles of the gas. It leads to paradoxical result when mixing of gases is considered.

Gibbs paradox

Let us consider two boxes of ideal gas, one composed of N_1 molecules in volume V_1 and the other having N_2 molecules in volume V_2. Let them be at a temperature T. See figure below

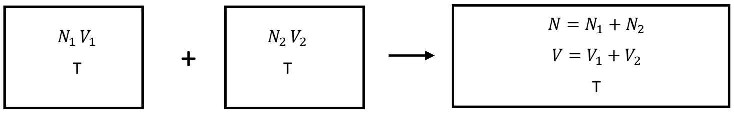


Figure 7.1: Mixing of Ideal gases

The entropies of the two systems (boxes) before mixing are

$$S_1 = N_1 K \ln V_1 + N_1 K \frac{3}{2} \ln T + N_1 K \sigma \tag{174}$$

$$S_2 = N_2 K \ln V_2 + N_2 K \frac{3}{2} \ln T + N_2 K \sigma \tag{175}$$

When the two boxes are brought in contact forming one enclosure of volume $V_1 + V_2$ the entropy of the combined system is

$$S_{12} = (N_1 + N_2)\, K \ln (V_1 + V_2) + (N_1 + N_2)\, K \frac{3}{2} \ln T + (N_1 + N_2)\, K \sigma \tag{176}$$

The change in entropy after mixing is

$$\begin{aligned} \Delta S &= S_{12} - S_1 - S_2 \\ &= N_1 K \ln \frac{V_1 + V_2}{V_1} + N_2 K \ln \frac{V_1 + V_2}{V_1} \end{aligned} \tag{177}$$

Clearly ΔS is positive and is known as entropy of mixing. This is understandable, the process of mixing is irreversible etc.

A paradoxical situation arises when we consider the mixing of two identical volumes of gas. In that case $N_1 = N_2$ and $V_1 = V_2$. Using equation 7.32 we get

$$\Delta S = 2 N_1 K \ln 2 \tag{178}$$

This is totally non-physical. We can imagine the present state of gas as coming from removal of imaginary partitions/compartments. Since there will be increase in entropy with the removal of every partition, the entropy could be larger than any finite value! This is known as Gibbs paradox since it was first pointed out by Gibbs.

The paradox can be removed only within the frame work of quantum mechanics. The molecules of a gas are to be treated as indistinguishable. The treatment of classical ideal gas discussed so far has over counted the states by assuming the molecules as

distinguishable by a factor $N!$ which is the number of permutations of N identical particles.
The correct partition function must be

$$Z_c = \frac{V^N}{N!h^{3N}} \left(\frac{2m\pi}{\beta}\right)^{\frac{3N}{2}} \tag{179}$$

This leads to

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

Using Stirling's approximation for $\ln N!$:

$$\ln N! \simeq N \left(\ln N - N\right)$$

We get

$$\ln Z_c = N \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + 1\right] \tag{180}$$

With this expression for Z_c the entropy becomes

$$S_c = NK \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + \frac{5}{2}\right] \tag{181}$$

This is known as Sackur-Tetrode formula for entropy. This entropy behaves like an extensive quantity. With this S_c the entropies of the gases considered earlier becomes

$$\begin{aligned} S_{c1} &= N_1 K \left[\ln \frac{V_1}{N_1} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + \frac{5}{2}\right] \\ S_{c2} &= N_2 K \left[\ln \frac{V_2}{N_2} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + \frac{5}{2}\right] \\ S_{c12} &= \left(N_1 + N_2\right) K \left[\ln \frac{(V_1 + V_2)}{(N_1 + N_2)} + \frac{3}{2} \ln \frac{2m\pi}{h^2\beta} + \frac{5}{2}\right] \end{aligned} \tag{182}$$

It is clear that $S_{c\,12} = S_{c\,1} + S_{c\,2}$ when $V_1 = V_2$ and $N_1 = N_2$ thus leading to no change in entropy on the mixing of identical boxes of gases. The paradox has been resolved.

7.4 Let us sum up

Gibbs canonical distribution leads to Maxwell-Boltzmann distribution law for velocities of an ideal gas when the phase space volume of gas molecules is considered. Entropy is related to the degree of disorder present in a system. It equals $K \ln \Omega \left(\langle E \rangle\right)$, the famous formula of Boltzmann. The correct entropy of a classical ideal gas is given by Sackur-Tetrode equation. If classical particles/molecules of a gas are treated as distinguishable, we are lead to a paradoxical result called Gibbs paradox. The paradox is resolved by assuming the particles as indistinguishable. The resolution was proposed by Gibbs even before the arrival of quantum mechanics.

7.5 Key words

partition function: Denoted by Z, it is equal to $\sum_s e^{-\beta E_s}$ where the sum is over all the states of the system

Entropy: Thermodynamically differential entropy is defined by $dS = \frac{\delta Q}{T}$ where δQ is the heat transferred at temperature T. Statistically it is defined by $S = K \ln \Omega(E)$, where Ω is the number of micro states corresponding to energy E.

7.6 Questions for self study

a) Deduce Maxwell-Boltzmann velocity distribution using Gibbs canonical distribution

b) Explain the relationship between entropy and thermodynamic probability

c) Derive the partition function for an ideal gas and hence its entropy

d) State and explain Gibbs paradox. How it is restored?

7.7 Further references

1. B.B Laud, *Fundamentals of Statistical Mechanics*, New age international ltd. New Delhi.
2. B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi.
3. K. Huang, *Statistical Mechanics*, Wiley Eastern ltd., 1975.
4. Gopal ESR, *Statistical Mechanics and properties of matter*, McMillan India ltd. New Delhi.
5. C. Kittel, *Thermal Physics*, Wiley Eastern ltd, 1969.
6. Landau and Lifshitz, *Statistical Mechanics*, Pergamon press.

UNIT 8

8 Equipartition theorem and Chemical Equilibrium

8.1 Objectives

After studying this unit you will be able to

- state and derive equipartition theorem
- apply equipartition to solids
- understand some properties of chemical equilibrium

8.2 Introduction

In statistical mechanics the mean energy due to every particular type of motion or degree of freedom is important. In a canonical distribution it is found that the mean energy takes the same values of each quadratic degree of freedom. Such a result is know as equipartition theorem. We shall state and derive it. In the classical model of a solid one has atoms or molecules of a solid executing vibrational motion about their stable rest position. That leads to certain energy and form the equipartition theorem to a specific value of specific heat. We shall consider that problem here. Finally under equilibrium conditions we get equal chemical potentials. We shall study all these topics in this unit.

8.3 The equipartition theorem

The mean energy due to a particular motion or degree of freedom is very important in statistical treatments of a macroscopic system. The treatment of mean energy became specially simple when we can express the energy function as a sum of quadratic functions of coordinates or generalised momenta.

Let the energy of a system due to motion in one particular degree of freedom depend quadratically on the momentum, say p_i. That is $E_i = \alpha p_i^2$. The total energy can be written as

$$E = \alpha p_i^2 + E^{'} \tag{183}$$

where $E^{'}$ is a function of coordinates and momenta which do not depend on p_i. When the system is in thermal equilibrium, the mean value of E_i at a particular temperature is given by the canonical distribution. It can be written as

$$\langle E_i \rangle = \frac{\int .... \int e^{-\beta E} \left(\alpha p_i^2\right) \ dq_1.......dp_f}{\int .... \int e^{-\beta E} \ dq_1.......dp_f} \tag{184}$$

Here the integration is performed over all coordinates and momenta from q_1 to p_f. let us split E into two points, one depending on p_i and the other independent of it. Hence equation 184 can be written as

$$\langle E_i \rangle = \frac{\int e^{-\beta\alpha p_i^2} \left(\alpha p_i^2\right) dp_i \int ..... \int e^{-\beta E^{'}} \ dq_1.......dp_f}{\int e^{-\beta\alpha p_i^2} dp_i \int ..... \int e^{-\beta E^{'}} \ dq_1.......dp_f} \tag{185}$$

The last factors in the numerator and denominator cancel each other and thus we get

$$\langle E_i \rangle = \frac{\int_{-\infty}^{+\infty} e^{-\beta\alpha p_i^2} \left(\alpha p_i^2\right) dp_i}{\int_{-\infty}^{+\infty} e^{-\beta\alpha p_i^2} dp_i} \tag{186}$$

This can be evaluated easily since

$$\langle E_i \rangle = -\frac{\partial}{\partial\beta} \ln \int_{-\infty}^{+\infty} e^{-\beta\alpha p_i^2} dp_i \tag{187}$$

Using the standard integral

$$\int_{-\infty}^{+\infty} e^{-x^2} dx = \sqrt{\pi}$$

we can evaluate

$$\int_{-\infty}^{+\infty} e^{-\beta\alpha p_i^2} dp_i$$

by using the simple substitution $x^2 = \beta\alpha p_i^2$. Then $dx = \sqrt{\beta\alpha}\ dp_i$. Hence

$$\int_{-\infty}^{+\infty} e^{-\beta\alpha p_i^2} dp_i = \int_{-\infty}^{+\infty} e^{-x^2} \frac{dx}{\sqrt{\beta\alpha}} = \sqrt{\frac{\pi}{\beta\alpha}} \tag{188}$$

Therefore

$$\langle E_i \rangle = -\frac{\partial}{\partial\beta} \ln \sqrt{\frac{\pi}{\beta\alpha}} = \frac{1}{2\beta} \tag{189}$$

As $\beta = \frac{1}{Kt}$ we conclude that $\langle E_i \rangle = \frac{1}{2}KT$. This is known as equipartition theorem. Note that it is independent of α. It gives the same value whether we consider a coordinate or momentum as long as energy dependence is a quadratic function of either coordinate or momentum. The total energy is equally partitioned or divided into various quadratic degrees of freedom. Hence the name-equipartition theorem.
Tolman has generalised this theorem. It is stated as:

$$\left\langle q_i \frac{\partial E}{\partial q_i} \right\rangle = \left\langle p_i \frac{\partial E}{\partial p_i} \right\rangle = KT \tag{190}$$

We can check easily that this general form reduces to the equipartition theorem whenever the energy depends quadratically on coordinates or momenta.
For example, in the case of ideal gas the total energy depends on the momenta only as

$$E = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \tag{191}$$

Then the mean energy per molecule of the gas will be

$$\langle E \rangle = 3 \times \frac{1}{2}KT = \frac{3}{2}KT$$

per molecule.
For a three dimensional harmonic oscillator

$$E = \sum_{i=1}^{3} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i=1}^{3} K_i q_i^2 \tag{192}$$

Then mean energy per molecule comes from both p_i and q_i. From equipartition theorem

$$\langle E \rangle = 3 \times \left(\frac{1}{2}KT\right) + 3 \times \left(\frac{1}{2}KT\right) = 3KT$$

per molecule.

Specific heat of Solids

In a simple three dimensional model of solid we consider molecules located at fixed locations (sites) forming bonds with the neighbouring molecules. But the molecules are assumed to be capable of vibrations about their mean positions. The vibrations will have higher amplitudes at higher temperatures.
Let us consider a gram atom of a solid containing N_0 (Avogadro number) non-interacting atoms harmonically bound to centres of forces. The Hamiltonian of each atom can be

$$H = \sum_{i} \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i} K_i q_i^2 \tag{193}$$

Note that K_i are force constants that can be different along three orthogonal directions. The total energy will be the sum of the energies of non-interacting N_0 atoms. From equipartition theorem, we can deduce the mean energy of the solid as

$$\langle E\rangle = N_0\left(3\times\left(\frac{1}{2}KT\right)\right) + N_0\left(3\times\left(\frac{1}{2}KT\right)\right) \tag{194}$$

That is $\langle E\rangle = 3N_0KT = 3RT$ where R is the gas constant. Hence the specific heat of the solid due to vibrations of its atoms is

$$C_V = \frac{\partial\langle E\rangle}{\partial T} = 3R \tag{195}$$

This is known as Dulong-Petit law. Note that the specific heat is independent of temperature. This law is not empirically satisfied by solids. It is valid at very high temperatures only. The discrepancy can be explained in a quantum theory of solids where it is shown that not all vibrations are excited at low temperatures. We are then lead to Einstein model for the specific heat of a solid.

Chemical potentials in the Equilibrium state

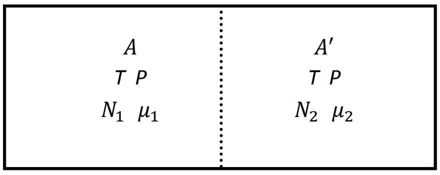


Figure 8.1

Consider two systems A and $A^{'}$ with particles N_1 and N_2 and chemical potentials μ_1 and μ_2. Suppose they are in equilibrium. Then their temperatures and pressures will be equal. When they are in contact being separated by a permeable partition (see figure 8.1) we wish to consider their free energies. The free energy is given by

$$F = U - TS$$

Therefore

$$dF = dU - TdS - SdT \tag{196}$$

But

$$dU = TdS - PdV + \sum \mu_i \delta N_i \tag{197}$$

Therefore

$$dF = -SdT - PdV + \sum \mu_i \delta N_i \tag{198}$$

When T and V are maintained constant

$$dF = \sum \mu_i \delta N_i \tag{199}$$

In the system under consideration

$$dF = \mu_1 dN_1 + \mu_2 dN_2 \tag{200}$$

Where dN_1 and dN_2 are the changes in the number of particles on the two sides of the partition. If the composite system is closed then $N_1 + N_2$ is constant. Therefore

$$d\left(N_1 + N_2\right) = dN_1 + dN_2 = 0 \tag{201}$$

Hence

$$dF = \left(\mu_1 + \mu_2\right) dN_1 \tag{202}$$

Under equilibrium conditions

$$\frac{\partial F}{\partial N_1} = 0 = \frac{\partial F}{\partial N_2} \tag{203}$$

Applying this rule to equation 202 we get

$$\mu_1 - \mu_2 = 0 \ \text{ or } \ \mu_1 = \mu_2 \tag{204}$$

Therefore, we conclude that for a system to be in equilibrium state, temperature, pressure and chemical potential must be constant throughout the system.

8.4 Let us sum up

The canonical distribution function leads to the result that energy is equally partitioned between various quadratic degrees of freedom in thermal equilibrium. Each degree of freedom will have energy of $\frac{1}{2}KT$ per molecule. Assuming a solid to be made of classical vibrations we come to conclusion that the specific heat of a solid is equal to $3R$ per mole at all temperatures.

From considerations of equilibrium we conclude that chemical potential remains constant throughout the system when different parts of it are in equilibrium.

8.5 Key words

Equipartition of energy: The process of dividing the total energy equally for each degree of freedom is known as equipartition of energy

Molar specific heat: The specific heat per mole of a substance is called molar specific heat

8.6 Questions for self study

a) State and prove the equipartition theorem of energy

b) Derive the specific heat for a gas made of rotating diatomic molecules

c) Show that chemical potential is constant throughout a system in equilibrium.

8.7 Further references

1. B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi, 2007.
2. B.B Laud, *Fundamentals of Statistical Mechanics*, New age international ltd. New Delhi, 2003.
3. Zemonsky, *Heat and Thermodynamics*, McGraw Hill, 1957.
4. M.N Saha and Srivastava, *A treatise on heat*, Indian Press, New Delhi, 1965.
5. K. Huang, *Statistical Mechanics*, Wiley Eastern ltd, 1975.
6. C. Kittel, *Thermal Physics*, Wiley Eastern ltd, 1969.

UNIT 9

9 Quantum Statistical Mechanics

9.1 Objectives

After studying this unit you will be able to

- understand quantum micro-canonical ensemble
- understand the basic postulates of quantum statistics
- know the classical limit
- know the symmetry of the wave functions

9.2 Introduction

Quantum mechanics provides the correct description of systems both small and large. Classical statistical mechanics is useful approximation to quantum statistical mechanics in the limit of low densities and high temperatures. Heisenberg uncertainty relation is another reason for using quantum considerations. According to that principle, it is not possible to specify both position and momentum simultaneously which are needed for a classical description. We use methods based on probabilities and averages in quantum mechanics. The classical notion of phase space cannot be used in quantum statistical mechanics. You will learn how quantum micro-canonical ensemble is defined and used. You will learn the basic postulates of quantum statistical mechanics. It reduces to the classical description in the limit of low densities and high temperatures. Due to the indistinguishability of quantum particles, it becomes necessary to use suitably symmetrised wave functions in quantum statistics. All these matters are discussed in this unit.

9.3 Micro-canonical ensemble

For a system of N particles in volume V, the quantum states are determined by Schrödinger eigenvalue equation

$$H_N \Psi_i\left(\{q_i\}\right) = E_i \Psi_i\left(\{q_i\}\right) \tag{205}$$

Where H_N is the Hamiltonian operator of the $N-$ particle system $\Psi_i\left(\{q_i\}\right)$ is the wave function for the system in the quantum state i having energy E_i. Therefore the set of microscopic states in quantum statistical mechanics is a discrete denumerable set denoted by the quantum number i. The system has to be in one or the another of these states.

We construct mentally an ensemble to represent what we know about the physical system of interest. Each element of the ensemble can be in one of the discrete quantum states allowed by the system. The number of different quantum states which have a given energy is called the degeneracy g of the energy level. Energy levels can have degeneracies while quantum states do not.

A fundamental assumption of equilibrium statistical mechanics is that the probability P_i of occupation of the i^{th} level is a function of E_i only. Thus

$$P_i = P_i\left(E_i\right) \tag{206}$$

In addition, all quantum states with the same energy have the same probability. Thus the probabilities of all degenerate quantum states in one level are equal. Therefore we say that in a state of microscopic equilibrium, all stationary quantum states of equal energy have equal apriori probability. This replaces the familiar equal apriori probability hypothesis of classical phase space.

For an isolated system the energy is constant. Then the probability P_i should be such that it is zero for all states unless $E_i = E_{\text{system}}$. If Ω is the degeneracy of the energy level E_{system} then only these states are present in the ensemble. Each such state has equal probability,

$$P_i = \text{constant} = a \;\; (\text{say}) \tag{207}$$

Then

$$\sum_{i=1}^{g} P_i = \sum_{i=1}^{g} a = ga = 1 \tag{208}$$

This defines the micro-canonical ensemble with probability distribution

$$P_i = \begin{cases} \frac{1}{\Omega} \text{ if } E_i = E_{\text{system}} \\ 0 \text{ if } E_i \neq E_{\text{system}} \end{cases} \tag{209}$$

Note that as the energy of the microscopic system increases, the degeneracies of the different energy levels increase rapidly. Hence if the system energy is large, more quantum states are available to the system and the probability of any one state being occupied decreases. E_{system} may lie between E and $E + \Delta E$ where ΔE is large compared with $\frac{h}{\delta t}$, δt being the time available for observation and h is Planck's constant.

Basic postulates of quantum statistical mechanics

Let Ψ_n be the state function of the n^{th} element in an arbitrary ensemble A. The expectation value of energy in the quantum mechanical average of the Hamiltonian operator. It is

$$\langle H \rangle_n = \int \Psi_n^* H \Psi_n \, d\tau = H_{nn} \tag{210}$$

with

$$\int \Psi_n^* \Psi_m \, d\tau = \langle \Psi_n | \Psi_m \rangle = \delta_{mn}$$

The ensemble average is defined by

$$\langle \bar{H} \rangle_A = \frac{1}{M} \sum_{n=1}^{M} \langle H \rangle_n = \frac{1}{M} \sum_{n=1}^{M} H_{nn} \tag{211}$$

In the case of an ideal micro-canonical ensemble I representing an isolated system in equilibrium, the elements are all in one of the energy eigenstates Ψ_i such that

$$H_N \Psi_i = E_i \Psi_i \text{ and } \Psi_n = \Psi_{in} \tag{212}$$

Therefore in this ensemble

$$\langle \bar{H} \rangle_I = \frac{1}{M} \sum_{n=1}^{M} \langle \Psi_{in} | H | \Psi_{in} \rangle = \frac{1}{M} \sum_{n=1}^{M} E_{in} = \sum P_i E_i \tag{213}$$

where P_i is the probability that an element in ensemble I is in the state Ψ_i. This is also the definition of quantum mechanical average energy. This situation has no classical analogue because in spite of the maximal knowledge given by the wave function we must use quantum mechanical averaging procedure. For an arbitrary ensemble we expand Ψ_n as

$$\Psi_n = \sum_j a_{nj}\Psi_j \text{ with } \langle\Psi_j|\Psi_k\rangle = \delta_{jk} \tag{214}$$

This is satisfied by systems of interest that interact weakly with surroundings.
The system would not be in a stationary state as this is a mixed case. Its state is a superposition of pure states. We do not possess such complete knowledge, as in the pure case, about the quantum mechanical description of the system. There may exist many wave functions compatible with the incomplete information about the system. The effect of these must be suitably averaged. Hence

$$\begin{aligned}\langle\bar{H}\rangle_A &= \frac{1}{M}\sum_{n=1}^{M}\left\langle \sum_j a_{nj}\Psi_j \,|H|\sum a_{nk}\Psi_k\right\rangle \\ &= \frac{1}{M}\sum_{n=1}^{M}\sum_j a^*_{nj}E_j \end{aligned}\tag{215}$$

If we choose

$$P_i = \frac{1}{M}\sum_{n=1}^{M} a^*_{ni}a_{ni} = \overline{a^*_{ni}a_{ni}} \tag{216}$$

we get

$$\overline{\langle H\rangle}_I = \overline{\langle H\rangle}_A.$$

In terms of a_{nj} we can state the postulates of statistical mechanics as:

(a) postulate of equal apriori probabilities:
ie.

$$P_i = \overline{a^*_{ni}a_{ni}} = \begin{cases}\frac{1}{\Omega} \text{ if } E < E_i < E+\Delta E \\ 0 \text{ otherwise}\end{cases} \tag{217}$$

(b) postulate of random phases:

$$\overline{a^*_{nj}a_{nk}} = 0 \text{ for } j \neq k \tag{218}$$

Here the bar denotes ensemble average. The constant $\frac{1}{\Omega}$ follows from the normalisation :

$$\overline{a^*_{ni}a_{ni}} = 1.$$

For the mixed case we need both the quantum mechanical and ensemble average. For the micro-canonical ensemble only 217 is required.
We need equation 218 for systems interacting with surroundings (like in canonical ensemble). It ensures that the relevant probability amplitudes do not interfere. We have an incoherent superposition of states. In the absence of interference we can

assume that the elements are in definite energy eigenstates.

In the classical limit, under Bohr's correspondence principle, it is found that these allowed eigenstates divide the phase space into cells of equal size. We can replace the eigenstates by equal regions in phase space. The equal regions in phase space are assigned equal apriori probabilities. In the classical case there is no analogue to the postulate of random phases because unknown phases arise solely in quantum mechanics.

For the purpose of calculations we can formulate the statistical hypothesis in terms of the following postulates:

(a) Postulate of ensemble average: The average behaviour of a macroscopic system in equilibrium is given by the average taken over a suitable ensemble consisting of an infinite number of randomised metal copies of the system of interest.

(b) Postulate of equal apriori probabilities: In a state of microscopic equilibrium, all stationary states of quantum states of equal energy have equal apriori probability.

(c) Postulate of equilibrium state: Equilibrium state is the one which occupies maximum volume in Γ space (classical or quantum mechanical cellular space).

The following are some implications of the postulates. The method of calculation is statistical in nature. The predictions are to be regarded as true on the average. The equilibrium state is the state of maximum probability.

The classical limit

In classical mechanics we can specify simultaneously both q_i and P_i for a particle. In quantum mechanics the uncertainty principle forbids this. A classical description is a reasonable approximation only when the effects of h are negligible. That is

$$\delta q.\delta P \gg h \tag{219}$$

Consider molecular motion in a gas. If P_{av} denotes the mean momentum and γ_{av} its mean separation from other identical molecules, a classical description is valid when

$$\gamma_{av}.P_{av} \gg h \tag{220}$$

Using deBroglie wavelength $\lambda = \frac{h}{P}$ this means

$$\gamma_{av} \gg \lambda_{av} \tag{221}$$

is satisfied by the classical limit.

As λ_{av} is a measure of the spread of a molecule in space, it means that when 221 is satisfied molecular wave-functions do not overlap and they are distinguished by their position.

Let us imagine that each particle occupies a tiny cube of side γ_{av} and these cubes fill a volume V. Then

$$\gamma_{av}^3 N = V \text{ or } \gamma_{av} = \left(\frac{V}{N}\right)^{\frac{1}{3}} \tag{222}$$

For a temperature T the average energy is given by

$$\frac{P_{av}^2}{2m} = \bar{\epsilon} = \frac{3}{2}KT \text{ or } P_{av} = (3mKT)^{\frac{1}{2}} \tag{223}$$

Hence

$$\lambda_{av} \simeq \frac{h}{(3mKT)^{\frac{1}{2}}} \tag{224}$$

Condition 221 then implies

$$\left(\frac{V}{N}\right)^{\frac{1}{3}} \gg \frac{h}{(3mKT)^{\frac{1}{2}}} \quad \text{(classical limit)} \tag{225}$$

From this we can clearly see that classical description is valid for small N (dilute gas) and T is large (high temperature). This is clearly satisfied by ordinary gases at room temperature. For electrons in a metal at normal temperatures it is not fulfilled. Therefore quantum statistics has to be applied to electrons in a metal.

Symmetry of wave functions

Let us consider a two-particle system described by a wave function $\Psi(1,2)$. In the quantum region it is not possible to distinguish the two identical particles. If we exchange the two particles, there should be no change in observable effects. That means $\Psi(2,1)$ should be proportional to $\Psi(1,2)$. By repeating the interchange once more we conclude that

$$\Psi(1,2) = \pm\Psi(2,1).$$

Hence only two possibilities exist in nature

$$\begin{aligned} \Psi(1,2) &= +\Psi(2,1) \text{ symmetric} \\ \Psi(1,2) &= -\Psi(2,1) \text{ antisymmetric} \end{aligned} \tag{226}$$

It is found in nature that the symmetry or antisymmetry property under interchange of two particles is an intrinsic property of the particles themselves. It is found that

(a) Systems consisting of identical particles of integral spin: $0, \hbar, 2\hbar, ...$ are described by symmetric wave functions, Ψ^{S}.

(b) Systems consisting of identical particles of half odd-integral spin: $0, \frac{\hbar}{2}, \frac{3\hbar}{2}, ...$ are described by antisymmetric wave functions, Ψ^{A}.

Particles of type (a) are called Bosons while those of type (b) are called Fermions. Thus there is a deep lying connection between spin of particles and their quantum statistics.

For quantum statistics, the simple product type wave functions have to be suitably symmetrised. For example if Ψ_a and Ψ_b are two single particle states for two particles 1 and 2 Bosons would require the wave function

$$\Psi^{\mathrm{S}}(1,2) = \frac{1}{\sqrt{2}}\left(\Psi_a(1)\,\Psi_b(2) + \Psi_b(1)\,\Psi_a(2)\right) \tag{227}$$

while Fermions would require

$$\Psi^{\mathrm{A}}(1,2) = \frac{1}{\sqrt{2}}\left(\Psi_a(1)\,\Psi_b(2) - \Psi_b(1)\,\Psi_a(2)\right) \tag{228}$$

for their description.

For a collection of more than two bosons or Fermions we have to form totally symmetric or antisymmetric wave functions from the single particle wave functions.

The statement that no two Fermions can be in the same quantum state is called Pauli's exclusion principle. Hence the occupation number for a Fermionic state is 0 or 1. Similarly the occupation number for a Boson state can be $0, 1, 2, \ldots\ldots$

9.4 Let us sum up

The classical notion of phase space cannot be used in quantum statistical mechanics. Quantum description reduces to the classical one in the limit of low densities and high temperatures. The probability of occupation of i^{th} energy level is a function of E_i only. In macroscopic equilibrium all stationary states of equal energy have equal apriori probability and random phases in quantum statistics. The equilibrium state is that which occupies maximum volume in Γ space. Classical limit is obtained when the mean separation between molecules is greater than their de Broglie wavelength. The wave functions of identical quantum particles obey specific symmetry properties. Wave functions of bosons have to be symmetric under exchange of particles while those of Fermions have to be antisymmetric under exchange.

9.5 Key words

Ensemble: A large collection of macroscopically identical but microscopically different systems constitute an ensemble

Degeneracy of a level: The number of independent quantum states that correspond to the same energy is said to be the degeneracy of that level

Bosons: Particles that have spin integer multiple of $\hbar$ including zero are said to be Bosons

Fermions: Particles that have half odd integer multiple of $\hbar$ as their spin angular momentum are said to be Fermions

9.6 Questions for self study

a) State and explain the basic postulates of quantum statistical mechanics

b) Under what conditions does one get the classical limit of quantum description?

c) Show that electrons with density of $10^{22}\ cm^{-3}$ and mean energy of $1\ eV$ constitute a quantum mechanical gas

d) Obtain the symmetric and antisymmetric wave functions for a collection of three independent quantum particles

9.7 Further references

1. B.B Laud, *Fundamentals of Statistical Mechanics*, New age international ltd. New Delhi.

2. B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi.

3. K. Huang, *Statistical Mechanics*, Wiley Eastern ltd., 1975.

4. Gopal ESR, *Statistical Mechanics and properties of matter*, McMillan India ltd. New Delhi.

5. C. Kittel, *Thermal Physics*, Wiley Eastern ltd, 1969.

6. Landau and Lifshitz, *Statistical Mechanics*, Pergamon press.

7. F. Reif, *Statistical Physics*, McGraw Hill.

UNIT 10

10 Density Matrix, Liouville theorem and Statistical equilibrium

10.1 Objectives

After studying this unit you will be able to

- know the definition and properties of density matrix
- state and prove Liouville theorem
- understand the condition for statistical equilibrium

10.2 Introduction

Quantum mechanical systems are comprised of indistinguishable components. The micro particles of the same species are indistinguishable from one another. For example, all electrons are identical. Hence if two electrons are exchanged the physical situation do not change. Hence the rules of counting states must be different from that used in classical Maxwell-Boltzmann model. It is therefore necessary to treat the theory in terms of quantum mechanical wave functions and operators. The treatment is different from the classical one. However in the limit of high temperatures and low densities the quantum treatment reduces to the classical one. Quantum mechanical mixed states are best described in terms of the density matrix of states. You shall learn about it. Liouville theorem can be formulated in terms of density matrix. The condition to be satisfied by statistical equilibrium shall also be discussed.

10.3 The Density Matrix

In classical statistical mechanical we specify the state of a system by a point in phase space and an ensemble by a cloud in phase space. The mean value of any function $F\left(q_i, P_i\right)$ is given by

$$\langle F\rangle = \int .....\int F\left(q_i, P_i\right)\rho\left(q_i, P_i\right)\ dq_i.......dP_f \tag{229}$$

where ρ is the density distribution of phase points and f is the number of degrees of freedom. It has been shown by Von Neumann that a quantity called density matrix in quantum statistics takes the place of distribution function in classical statistics. By knowing this matrix it is possible to calculate the mean values of any quantity describing a property of the system as well as the probabilities of various values of such quantities.

In quantum statistics the concept of uncertainty enters in two different ways

(1) If one try to assess the value of a dynamical variable corresponding to an operator $\hat{O}$ by performing measurements, then each system will respond by jumping into one of the eigenstates of $\hat{O}$. It is impossible to predict in advance which eigenstate it is going to be. Consequently quantum measurements can only provide us with probabilities of getting different eigenvalues of the operator $\hat{O}$. This type of uncertainty forms an integral part of quantum mechanics and cannot be overcome by any refinement in the techniques of measurement.

The variation of a wave function in time t is determined by Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\Psi\left(q,t\right) = \hat{H}\Psi\left(q,t\right) \tag{230}$$

Let $\{\phi_n\left(q\right)\}$ be a complete set of orthonormal functions of the system. Here the suffix n denotes the set of all quantum numbers which distinguish various stationary states. Then Ψ can be expressed as a linear combination of $\phi_n\left(q\right)$. Thus

$$\Psi\left(q,t\right) = \sum_n C_n\left(t\right)\phi_n\left(q\right) \tag{231}$$

where $C_n\left(t\right)$ are the probability amplitudes for the system. Hence $\left|C_n\left(t\right)\right|^2$ is the probability that the system at time t is in the state $\phi_n\left(q\right)$.

It is clear from conservation of probability that

$$\sum_n C_n^* (t) \, C_n (t) = \sum_n |C_n (t)|^2 = 1 \tag{232}$$

The average value (expectation value) of an observable F for the system is given by

$$\langle F \rangle = \int \Psi^* (q,t) \, \hat{F} \, \Psi (q,t) \ dq \tag{233}$$

where $\hat{F}$ is the operator corresponding to the observable. Using equation 231 we get

$$\begin{aligned} \langle F \rangle &= \int \sum_n C_n^* (t) \, \phi_n^* (q) \, \hat{F} \ \sum_m C_m (t) \, \phi_m (q) \, dq \\ &= \sum_m \sum_n C_n^* (t) \, C_m (t) \int \phi_n^* (q) \, \hat{F} \ \phi_m (q) \, dq \\ &= \sum_m \sum_n C_n^* (t) \, C_m (t) \, F_{nm} \end{aligned} \tag{234}$$

where

$$F_{nm} = \int \phi_n^* (q) \, \hat{F} \ \phi_m (q) \, dq \tag{235}$$

(2) There is another kind of uncertainty which is used in both classical and quantum statistical mechanics. It arises from the lack of accurate knowledge of the system. Imagine a system which has a number of degrees of freedom. It is impossible to carry out experiments to measure the values of each variable and thus determine the state of the system completely. The system then is described approximately by specifying the mean values and corresponding probability distributions of each variable.

If $\langle F_\alpha \rangle$ is the mean value of the observable for the α^{th} system, the mean of this observable for N systems $\alpha = 1, 2, ...N$ is

$$\begin{aligned} \overline{\langle F \rangle} &= \frac{1}{N} \sum_{\alpha=1}^{N} \langle F_\alpha \rangle \\ &= \frac{1}{N} \sum_{\alpha=1}^{N} \left[\sum_{m,n} \sum C_n^{\alpha \, *} (t) \, C_m^\alpha (t) \, F_{nm} \right] \end{aligned} \tag{236}$$

Here we have two fold averaging. It comprises averaging due to the probabilistic nature of the quantum description as well as statistical averaging. It should be noted the averaging process has to be carried out as a single operation without separating its constituents.

Consider α^{th} system whose state can be described in terms of probability amplitude $C_n^\alpha (t)$. Then

$$\overline{C_n^* (t) \, C_m (t)} = \frac{1}{N} \sum_{\alpha=1}^{N} C_n^{\alpha \, *} (t) \, C_m^\alpha (t) = \rho_{mn} \tag{237}$$

would give the statistical mean value of the quantity $C_n^*(t)\, C_m(t)$ over all the systems in the ensemble. Here ρ_{nm} is considered as the matrix element of a statistical operator called density operator $\hat{\rho}(t)$.The term density refers to the fact that the diagonal element $\rho_{mm}(t) = |C_{mm}|^2$ of the matrix represents the probability that the state function $\phi_n(q)$. the elements of the density matrix depend on the representation. The final observable results, however, must be independent of the representation.

Let us see how the density matrix can be used to calculate the mean value of an observable F for the systems of an ensemble.

For a single system, the quantum mechanical mean value of F is

$$\overline{\langle F\rangle} = \sum_{n,m}\sum F_{nm}\; C_n^*(t)\, C_m(t)\,.$$

Therefore the mean value of F for all systems in the ensemble is

$$\overline{\langle F\rangle} = \sum_n \sum_m F_{nm}\; \overline{C_n^*(t)\, C_m(t)}$$

Thus

$$\overline{\langle F\rangle} = \sum_n \sum_m F_{nm}\; \rho_{mn} \tag{238}$$

This is the quantum mechanical analogue of the classical expression given by equation 229.

Following the rules of matrix multiplication,

$$\overline{\langle F\rangle} = \sum_n [F\rho]_{nn} = \text{trace}\,[F\rho] \tag{239}$$

Hence, the integral over all phase space of a classical quantity is replaced in quantum mechanics by the trace of the corresponding quantum mechanical matrix.

This formula has the advantage that we can use any set of complete states for evaluating the trace.

Liouville's theorem in Quantum Statistical Mechanics

Let us investigate the rate of change of the elements of the density matrix

As

$$\rho_{mn} = \frac{1}{N}\sum_{\alpha=1}^{N} C_n^{\alpha\,*}(t)\, C_m^{\alpha}(t)$$

we get

$$\frac{d\rho_{mn}}{dt} = \frac{1}{N}\sum_{\alpha=1}^{N}\left(\dot{C}_n^{\alpha\,*}(t)\, C_m^{\alpha}(t) + C_n^{\alpha\,*}(t)\, \dot{C}_m^{\alpha}(t)\right) \tag{240}$$

As

$$\Psi^{\alpha}(q,t) = \sum_{l} C_{l}^{\alpha}(t)\,\phi_{l}(q)$$

multiplying Ψ^{α} with $\phi_{n}^{*}(q)$ and integrating with respect to q we get

$$\int \phi_{n}^{*}(q)\,\Psi^{\alpha}(q,t)\,dq = \sum_{l} C_{l}^{\alpha}(t) \int \phi_{n}^{*}(q)\,\phi_{l}(q)\,dq \tag{241}$$

From the orthonormality of $\phi_{n}(q)$ it follows that

$$C_{n}^{\alpha}(t) = \int \phi_{n}^{*}(q)\,\Psi^{\alpha}(q,t)\,dq$$

Now

$$\frac{d}{dt}\left(C_{n}^{\alpha}(t)\right) = \int \phi_{n}^{*}(q)\,\frac{\partial}{\partial t}\left(\Psi^{\alpha}(q,t)\right)dq$$

$$\frac{d}{dt}\left(C_{n}^{\alpha}(t)\right) = \frac{1}{i\hbar}\int \phi_{n}^{*}(q)\,\hat{H}\Psi^{\alpha}(q,t)\,dq$$

from the Schrödinger equation for $\Psi^{\alpha}(q,t)$.

Therefore

$$\dot{C}_{n}^{\alpha}(t) = \frac{1}{i\hbar}\int \phi_{n}^{*}(q)\,\hat{H}\sum C_{l}^{\alpha}(t)\,\phi_{l}(q)$$

$$\dot{C}_{n}^{\alpha}(t) = \frac{1}{i\hbar}\sum_{l} H_{nl}\,C_{l}^{\alpha}(t) \tag{242}$$

Similarly we get

$$\dot{C}_{n}^{\alpha\,*}(t) = -\frac{1}{i\hbar}\sum_{l} H_{nl}^{*}\,C_{l}^{\alpha\,*}(t) \tag{243}$$

Substituting these expressions in 240 we get

$$\dot{\rho}_{mn} = \frac{1}{N}\sum_{\alpha=1}^{N}\left[-\frac{1}{i\hbar}\sum_{l} H_{nl}^{*}\,C_{l}^{\alpha\,*}(t)\;C_{m}^{\alpha}(t) + \frac{1}{i\hbar}C_{n}^{\alpha\,*}\sum_{l} H_{nl}\,C_{l}^{\alpha}(t)\right]$$

Since $H_{ln} = H_{nl}^{*}$ as H is Hermitian, we get

$$\dot{\rho}_{mn} = \frac{1}{i\hbar}\left[\sum_{l} H_{ml}\,\rho_{ln} - \sum_{l}\rho_{ml}\,H_{ln}\right] \tag{244}$$

$$\dot{\rho}_{mn} = \frac{1}{i\hbar}\left[(H\,\rho)_{mn} - (\rho\,H)_{mn}\right]$$

Therefore

$$i\hbar\,\dot{\hat{\rho}} = \left[\hat{H},\hat{\rho}\right] \tag{245}$$

in the operator form.

This is the quantum analogue of classical Liouville theorem.

Condition for Statistical Equilibrium

For a system in equilibrium, the corresponding ensemble must be stationary. That is $\dot{\rho}_{mn} = 0$. This would be possible under the following conditions:

(a) when the density matrix is constant, or

(b) when the density matrix is a function of a constant of motion.

If the density matrix is constant, its elements will be given by

$$\rho_{mn} = \rho_0 \, \delta_{mn} \tag{246}$$

That means all non-diagonal elements of the matrix will be equal to zero and all the diagonal elements will be equal to a constant ρ_0.
In the energy representation, the basic functions ϕ_n are eigenfunctions of the Hamiltonian $\hat{H}$ and hence the matrices H and ρ are diagonal

$$\text{i.e.} \quad \rho_{mn} = \rho_n \, \delta_{mn}$$

In this representation the density operator $\hat{\rho}$ may be formally written as

$$\hat{\rho} = \sum |\phi_n\rangle \, \rho_n \, \langle\phi_n| \tag{247}$$

To verify this consider an element ρ_{kl}

$$\rho_{kl} = \langle\phi_k \,|\hat{\rho}|\, \phi_l\rangle$$

$$\rho_{kl} = \sum_n \langle\phi_k \,|\phi_n\rangle \, \rho_n \, \langle\phi_n| \, \phi_l\rangle$$

$$\rho_{kl} = \sum_n \delta_{kn} \, \rho_n \, \delta_{nl} = \delta_{kl} \, \rho_k$$

which agrees with 246.
Therefore

$$i\hbar \, \dot{\rho_{mn}} = \sum_l (H_{ml} \, \rho_{ln} - \rho_{ml} \, H_{ln})$$

$$i\hbar \, \dot{\rho_{mn}} = \sum_l (\rho_0 \, H_{ml} \, \delta_{ln} - \rho_0 \, \delta_{ml} \, H_{ln})$$

$$i\hbar \, \dot{\rho_{mn}} = \rho_0 \, (H_{mn} - H_{mn}) = 0$$

That means the distribution does not change with time and therefore the system is in equilibrium under this condition.
So far as the condition (b) is concerned, if the time derivative of the statistical matrix vanishes, the operator $\hat{\rho}$ must commute with $\hat{H}$. That means ρ is a function of a constant of motion.

10.4 Let us sum up

In quantum mechanics mixed states are best described in terms of the density matrix. in quantum statistics the concept of uncertainty enters in two different ways. In the first instance, quantum mechanical state functions lead to a probabilistic interpretation for single systems. When we have an ensemble of states there is further uncertainty due to the randomness of the elements of the ensemble. this double averaging process leads to trace $\left(\hat{F}\hat{\rho}\right)$ as the mean value of an observable F in a statistical state. There is a quantum analogue of classical Liouville theorem. It can be stated as $i\hbar\,\dot{\hat{\rho}} = \left[\hat{H},\ \hat{\rho}\right]$. in equilibrium conditions the density matrix takes a diagonal form.

10.5 Key words

the density operator: It is defined as having matrix elements

$$\rho_{mn} = \frac{1}{N}\sum C_n^{\alpha\,*} C_m^{\alpha}$$

Ensemble: A collection of systems having a wide range of values of observables is called an ensemble

10.6 Questions for self study

a) State and prove quantum Liouville theorem

b) Express the average value of an observable using density matrix formalism

10.7 Further references

1. B.B Laud, *Fundamentals of Statistical Mechanics*, New age international ltd. New Delhi.
2. B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi.
3. K. Huang, *Statistical Mechanics*, Wiley Eastern ltd., 1975.
4. Gopal ESR, *Statistical Mechanics and properties of matter*, McMillan India ltd. New Delhi.
5. C. Kittel, *Thermal Physics*, Wiley Eastern ltd, 1969.
6. Landau and Lifshitz, *Statistical Mechanics*, Pergamon press.
7. F. Reif, *Statistical Physics*, McGraw Hill.

UNIT 11

11 Ensembles and Distribution Functions

11.1 Objectives

After studying this unit you will be able to

- understand ensembles in quantum mechanics
- deduce quantum distribution functions

11.2 Introduction

There are three kinds of ensembles in quantum mechanics- micro-canonical, canonical and grand canonical. They correspond to isolated systems and systems that can exchange energy as well as well as particles namely, Fermions and Bosons. Correspondingly there are two different distribution function, called FD and BE distributions.

11.3 Types of ensembles

The micro-canonical ensemble

In this ensemble we shall have system that are characterised by a fixed number of particles, fixed volume and energy between E and $E + \delta E$. Let the total number of states accessible to the system be $\Omega\left(E\right)$. The density matrix will be diagonal in the energy representation. Hence

$$\rho_{mn} = \begin{cases} \rho_0\, \delta_{mn} & \text{for states in } (E, E + \delta E) \\ 0 & \text{otherwise} \end{cases} \tag{248}$$

The trace of ρ is equal to the number of states whose energy lies between E and $E + \delta E$. That is

$$\text{Trace } \hat{\rho} = \sum_n \rho_0 = \Omega\left(E\right) \tag{249}$$

The entropy, which determines the thermodynamics of the system, is given by

$$S = K \ln \Omega\left(E\right) \tag{250}$$

Gibbs paradox does not arise here as $\frac{\partial \Omega}{\partial E}$ is computed correctly by considering the indistinguishability of the particles.

If $\Omega\left(E\right) = 1$ then $S = 0$. It is consistent with Nernst theorem or the third law of thermodynamics which states: "The entropy of a system at absolute zero temperature is a universal constant which may be taken to be zero". At absolute zero temperature the system will be in its ground state. If this is unique, $\Omega = 1$ and the system is going to be found in the state. Complete order prevails and hence $S = 0$.

If $\Omega = 1$ every system in the ensemble has got to be in one and the same state. Then we say the ensemble is in a pure state. If $\Omega > 1$ complete specification of the systems is not possible and then the system is said to be in a mixed state.

If the ensemble is in the pure state, in the energy representation, there is only one diagonal element ρ_{nn} and that is equal to 1, all other elements being zero. Then the matrix satisfies

$$\rho^2 = \rho \tag{251}$$

In any other representation

$$\begin{aligned} \rho_{mn} &= \frac{1}{N} \sum_\alpha C_n^{\alpha\,*}\left(t\right) C_m^\alpha\left(t\right) \\ &= \overline{C_n^*\left(t\right) C_m\left(t\right)} \end{aligned} \tag{252}$$

Therefore

$$\begin{aligned} \rho_{mn}^2 = \sum_l \rho_{ml}\, \rho_{ln} &= \sum_l \overline{C_l^*\left(t\right) C_m\left(t\right) C_n^*\left(t\right) C_l\left(t\right)} \\ &= \overline{C_n^*\left(t\right) C_m\left(t\right)} = \rho_{mn} \end{aligned} \tag{253}$$

Therefore $\rho^2 = \rho$ is a necessary requirement for a pure state.

The Canonical Ensemble

In this ensemble N and V are fixed but E is a variable quantity. The considerations of classical statistics are applicable here in quantum statistics. The probability that a system will possess energy E_n is given by $P_n = Ce^{-\beta E_n}$. Therefore the density matrix in the energy representation is taken to be

$$\rho_{mn} = \rho_n \, \delta_{mn} \tag{254}$$

Since

$$\text{Trace } \hat{\rho} = 1$$

We will have

$$\sum C \, e^{-\beta E_n} = 1.$$

Therefore

$$C = \frac{1}{\sum e^{-\beta E_n}} = \frac{1}{Z(\beta)} \quad \text{and} \quad \rho_n = \frac{e^{-\beta E_n}}{Z(\beta)} \tag{255}$$

Where $Z(\beta) = \sum e^{-\beta E_n} = \text{Trace}\left(e^{-\beta \hat{H}}\right)$ is the partition function of the system. Note that summation is over the states and not over the energy eigenvalues. $\hat{H}$ is the Hamiltonian operator.
thus the density operator in this ensemble is

$$\begin{aligned}
\hat{\rho} &= \sum_n |\phi_n\rangle \, \frac{e^{-\beta E_n}}{Z(\beta)} \, \langle\phi_n| \\
&= \frac{e^{-\beta \hat{H}}}{Z(\beta)} \sum_n |\phi_n\rangle \, \langle\phi_n| \\
&= \frac{1}{Z(\beta)} \, e^{-\beta \hat{H}}
\end{aligned} \tag{256}$$

The ensemble average of a physical quantity G is given in terms of its operator $\hat{G}$ as

$$\overline{\langle G\rangle} = \text{Tr}\left(\hat{\rho}\,\hat{G}\right) = \frac{\text{Tr}\left(\hat{G}\, e^{-\beta\hat{H}}\right)}{\text{Tr}\left(e^{-\beta\hat{H}}\right)} \tag{257}$$

The other thermodynamic variables are given by

$$\overline{\langle E\rangle} = \text{Tr}\left(\hat{\rho}\,\hat{H}\right)$$

and

$$\overline{\langle F\rangle} = -KT \, \ln\left(\text{Tr}\left(e^{-\beta\hat{H}}\right)\right)$$

As a simple example consider a beam of photons with various polarisations travelling along z axis. Let us determine the probability that the photon is found with polarization along

(a) x axis and

(b) y axis.

Let the state of polarisation in the $x-$ direction be denoted by

$$|\alpha\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

and the state of polarisation in the y direction by

$$|\beta\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}.$$

Then the state with polarisation angle ϕ with the $x-$axis will be given by

$$|\psi\rangle = e^{ia}\left[\cos\phi\,|\alpha\rangle + \sin\phi\,|\beta\rangle\right]$$

$$|\psi\rangle = e^{ia}\left[\cos\phi\begin{pmatrix} 1 \\ 0 \end{pmatrix} + \sin\phi\begin{pmatrix} 0 \\ 1 \end{pmatrix}\right]$$

where a is a phase factor.
The density matrix for the pure state is

$$\hat{\rho} = \begin{pmatrix} \cos\phi \\ \sin\phi \end{pmatrix}\begin{pmatrix} \cos\phi & \sin\phi \end{pmatrix} = \begin{pmatrix} \cos^2\phi & \cos\phi\sin\phi \\ \sin\phi\cos\phi & \sin^2\phi \end{pmatrix} \tag{258}$$

Therefore the probability of finding the photon polarised in the $x-$direction is

$$\langle\alpha\,|\hat{\rho}|\,\alpha\rangle = \cos^2\phi \tag{259}$$

Similarly the probability of polarisation in the $y-$direction is

$$\langle\beta\,|\hat{\rho}|\,\beta\rangle = \sin^2\phi.$$

The Grand Canonical Ensemble

In this ensemble both N and E are variables. By generalising the canonical ensemble case, we can write for the density operator

$$\hat{\rho} = \frac{1}{Z(\beta,\mu)}e^{-\beta\left(\hat{H}-\mu\hat{n}\right)} \tag{260}$$

Where μ is the chemical potential, $\hat{n}$ is the number operator with eigenvalues $0, 1, 2, ...$ and $Z(\beta,\mu)$ is the grand partition function given by

$$\begin{aligned} Z(\beta,\mu) &= \sum_r e^{-\beta(E_r-\mu n_r)} \\ &= \mathrm{Tr}\left\{e^{-\beta\left(\hat{H}-\mu\hat{n}\right)}\right\} \end{aligned} \tag{261}$$

The ensemble average of a physical variable G in the grand canonical ensemble is given by

$$\begin{aligned}\overline{\langle G\rangle} &= \mathrm{Tr}\left(\hat{\rho}\,\hat{G}\right)\\ &= \frac{\mathrm{Tr}\left\{\hat{G}\,e^{-\beta\left(\hat{H}-\mu\hat{n}\right)}\right\}}{\mathrm{Tr}\left\{e^{-\beta\left(\hat{H}-\mu\hat{n}\right)}\right\}}\end{aligned} \tag{262}$$

The Quantum distribution functions

We have seen earlier the connection between symmetry of wave functions and the types of particles. For Bosons the total wave function must be symmetric under exchange of any two Bosons while for Fermions the wave function must be antisymmetric under particle exchange. As a consequence any number of Bosons can occupy a given quantum state while only Fermion can occupy one quantum state.

Let us consider an ideal gas of N identical particles. Let s represent the state of a single particle and S the state of the whole gas. Suppose that when the gas is in state S, n_1 particles are in state $s = 1$ with energy ϵ_1, n_2 particles are in state $s = 2$ with energy ϵ_2 etc. Then the total energy of the gas will be

$$E_s = \sum_s n_s \epsilon_s \tag{263}$$

and the total number of particles will be

$$N = \sum_s n_s \tag{264}$$

The partition function helps us in calculating physical quantities. It is given by

$$Z = \sum_s e^{-\beta E_s}$$

the summation is over all possible states. While summing over states we have to keep in mind the statistics obeyed by the particles.

Let us consider the cases separately

(a) MB Statistics

In this case the particles are distinguishable. The partition function is

$$Z = \sum_s e^{-\beta \sum n_s \epsilon_s} \tag{265}$$

The summation is extended over all possible n_s values.

The mean number of particles in the state S is

$$\langle n_s\rangle = \frac{\sum_s n_s e^{-\beta\sum n_s\epsilon_s}}{\sum_s e^{-\beta\sum n_s\epsilon_s}} \tag{266}$$

$$\langle n_s \rangle = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_s}(\ln Z) \tag{267}$$

The partition function can be written as

$$Z = \sum_s e^{-\beta\left(\epsilon_{s_1}+\epsilon_{s_2}+........+\epsilon_{s_n}\right)} \tag{268}$$

where the summation is over all possible states of each individual particles s_1, s_2.......etc. We can see that the summation is carried out in this manner takes into account the distinguishability of of particles.
It can therefore be written as

$$\begin{aligned} Z &= \sum_{s_1,s_2.....} e^{-\beta\epsilon_{s_1}} e^{-\beta\epsilon_{s_2}}....... \\ &= \left(\sum_{s_1} e^{-\beta\epsilon_{s_1}}\right)\left(\sum_{s_2} e^{-\beta\epsilon_{s_2}}\right)......... \\ &= \left[\sum_{s_1} e^{-\beta\epsilon_{s_1}}\right]^N \end{aligned} \tag{269}$$

Thus

$$\ln Z = N \ln\left(\sum_{s_1} e^{-\beta\epsilon_{s_1}}\right) \tag{270}$$

With this Z we get

$$\langle n_s \rangle = \frac{N e^{-\beta\epsilon_s}}{\sum_s e^{-\beta\epsilon_s}}$$

Clearly this corresponds to the earlier MB distribution.

(b) BE Statistics

Here the particles are indistinguishable. Grand canonical ensemble is most suited for its study as the number of particles is not fixed. The grand partition function is given by

$$\mathcal{Z} = \sum_s e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+.....)+\mu\beta(n_1+n_2+......)} \tag{271}$$

where the summation is over all possible states, hence over all possible number of particles in each single particle state. The number of particles n_i in each state i will be $0, 1, 2,$ ...... subject to the condition $\sum n_i = N$.
Therefore

$$\mathcal{Z} = \left(\sum_{n_1} e^{-\beta(\epsilon_1-\mu)n_1}\right)\left(\sum_{n_2} e^{-\beta(\epsilon_2-\mu)n_2}\right)........$$

But

$$\sum_{n_1} e^{-\beta(\epsilon_1-\mu)n_1} = 1 + e^{-\beta(\epsilon_1-\mu)} + e^{-2\beta(\epsilon_1-\mu)} + ... \tag{272}$$

This is a geometric whose sum can be found as

$$\sum_{n_1} e^{-\beta(\epsilon_1-\mu)n_1} = \frac{1}{1-e^{-\beta(\epsilon_1-\mu)}}.$$

Therefore

$$Z = \Pi_i \frac{1}{1-e^{-\beta(\epsilon_i-\mu)}} \tag{273}$$

with

$$\ln Z = -\sum_s \ln\left(1-e^{-\beta(\epsilon_i-\mu)}\right) \tag{274}$$

As

$$N = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mu}$$

we get

$$N = \frac{1}{\beta}\frac{\partial}{\partial \mu}\sum_s \ln\left(1-e^{-\beta(\epsilon_s-\mu)}\right)$$

Hence

$$N = \sum \langle n_s \rangle$$

Therefore the average number of particles in the s^{th} level is

$$\begin{aligned}\sum \langle n_s \rangle &= -\frac{1}{\beta}\frac{\partial}{\partial \mu}\ln\left(1-e^{-\beta(\epsilon_s-\mu)}\right)\\ &= \frac{e^{-\beta(\epsilon_s-\mu)}}{1-e^{-\beta(\epsilon_s-\mu)}}\\ &= \frac{1}{e^{\beta(\epsilon_s-\mu)}-1}\end{aligned} \tag{275}$$

The last expression gives the BE distribution function, i.e the number of particles in the s^{th} energy level.

Since the number of Bosons in any state cannot be negative $e^{\beta(\epsilon_s-\mu)}$ must be greater than unity for ϵ_s. The lowest energy for a single particle state of a Boson gas is zero. Hence μ for an ideal Boson gas must be always negative.

For photons, when $\sum n_s = N$ is not satisfied, the distribution formula can be obtained by taking $\mu = 0$. Then we get for photons

$$\langle n_s \rangle = \frac{1}{e^{\beta\epsilon_s}-1} \tag{276}$$

(c) FD Statistics

For an FD gas the number of particles per energy state can be zero or one. Therefore

$$Z = \left(1+e^{\beta(\mu-\epsilon_1)}\right)\left(1+e^{\beta(\mu-\epsilon_2)}\right)........$$

and so

$$\ln Z = \sum_s \ln\left(1+e^{\beta(\mu-\epsilon_s)}\right) \tag{277}$$

Hence the total number of particles

$$N = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mu} = \sum_s \langle n_s \rangle = \frac{e^{\beta(\mu-\epsilon_s)}}{1+e^{\beta(\mu-\epsilon_s)}} \tag{278}$$

Simplifying we get

$$\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s-\mu)}+1} \tag{279}$$

as the distribution function for the s^{th} state. Therefore we notice that $\langle n_s \rangle \leq 1$ for all energies.

The behaviour of the gas obeying FD statistics is different from that obeying BE statistics. This difference becomes strikingly different as T tends to zero, when the gas is in the lowest energy. In the case of BE statistics, since there is no restriction on the number of particle state, the gas will have the lowest possible energy state. But in the case of FD statistics, since we can place only one particle in any single state, even though the gas has lowest energy, one is forced to populate higher energy states with one particle each. Therefore the lowest energy of an FD gas will be higher than that of BE gas at the same temperature. It leads to observable consequences like higher pressure etc.

11.4 Let us sum up

The density for a micro-canonical ensemble satisfies $\rho^2 = \rho$. For a canonical ensemble the density matrix takes the form $Z\ e^{-\beta\hat{H}}$. The partition function for a grand canonical ensemble can be written as $\text{Tr}\left\{e^{-\beta\left(\hat{H}-\mu\hat{n}\right)}\right\}$. Using the grand canonical ensemble, it is most convenient to deduce the familiar distribution laws for BE and FD gases. For a BE gas μ has to be negative at all energies. For a photon gas $\mu = 0$ and we get the familiar Planck distribution function for the number of particles occupying a given energy

11.5 Key words

The density matrix: Its matrix elements are given by

$$\rho_{mn} = \frac{1}{N}\sum_{\alpha=1}^{N} C_n^{\alpha\,*}\, C_m^{\alpha}$$

where the summation is over the elements of an ensemble

Partition function: It is denoted by Z, it is equal to

$$\sum_s e^{-\beta\left(\epsilon_{s_1}+\epsilon_{s_2}+........+\epsilon_{s_n}\right)}$$

11.6 Questions for self study

a) Explain the features of a micro-canonical ensemble

b) Show that

$$\overline{\langle F\rangle} = -KT\ \ln\left(\mathrm{Tr}\left(e^{-\beta\hat{H}}\right)\right)$$

for a canonical ensemble

c) Deduce BE and FD distributions starting with a grand canonical ensemble.

d) Compare $\langle n_s\rangle$ for BE and FD gases.

e) Comment on the properties of BE and FD gases at low temperatures.

11.7 Further references

1. B.B Laud, *Fundamentals of Statistical Mechanics*, New age international ltd. New Delhi.

2. B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi.

3. K. Huang, *Statistical Mechanics*, Wiley Eastern ltd., 1975.

4. Gopal ESR, *Statistical Mechanics and properties of matter*, McMillan India ltd. New Delhi.

5. C. Kittel, *Thermal Physics*, Wiley Eastern ltd, 1969.

6. Landau and Lifshitz, *Statistical Mechanics*, Pergamon press.

7. F. Reif, *Statistical Physics*, McGraw Hill.

UNIT 12

12 The Boltzmann limit and Partition Functions

12.1 Objectives

After studying this unit you will be able to

- understand the Boltzmann limit of Boson and Fermion gases
- know the partition function for ideal gas
- know the rotational partition function for a diatomic molecule
- know the vibrational partition function of a molecule
- know the electronic partition function for a molecule

12.2 Introduction

In the limit of high temperature and low densities we get Boltzmann distribution. It is the same as the classical limit. The partition function of a molecule can be written as a product of translational, rotational, vibrational and electronic functions. Let us understand how these different partition functions are evaluated.

12.3 The Boltzmann limit

We have seen that the occupation number of particles in an energy state ϵ_s is given by

$$\langle n_s \rangle = \frac{1}{e^{\beta(\epsilon_s - \mu)} \pm 1} \tag{280}$$

where the upper sign (+ sign) refers to FD statistics and the lower sign (− sign) refers to BE statistics.
Let us suppose $e^{-\beta\mu} \gg 1$ i.e $e^{\beta(\epsilon_s-\mu)} \gg 1$ for all energy levels. Then

$$\langle n_s \rangle \simeq \frac{1}{e^{\beta(\epsilon_s - \mu)}} = e^{\beta\mu} e^{-\beta\epsilon_s} \tag{281}$$

Since $\langle n_s \rangle = N$, the total number of particles

$$e^{\beta\mu} \sum_s e^{-\beta\epsilon_s} = N \tag{282}$$

Therefore

$$e^{\beta\mu} = \frac{N}{\sum_s e^{-\beta\epsilon_s}} \tag{283}$$

Substituting this into 282 we get

$$\langle n_s \rangle = \frac{N\ e^{-\beta\epsilon_s}}{\sum_s e^{-\beta\epsilon_s}} \tag{284}$$

Which is nothing but MB distribution. Therefore quantum statistics leads to Boltzmann distribution in the limit $e^{-\beta\mu} \gg 1$.
Since

$$\mu = -KT \ln \left[\left(\frac{2\pi m}{h^2 \beta} \right)^{\frac{3}{2}} \frac{V}{N} \right]$$

we can express this limiting case as

$$\left(\frac{2\pi m K T}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} \gg 1 \tag{285}$$

This condition is clearly satisfied for high temperatures and low number densities.
The variation of the occupation number $\langle n_s \rangle$ with $\beta\,(\epsilon - \mu)$ in the three cases is shown in figure 12.1.

As in the figure, for large values of $\beta\,(\epsilon - \mu)$ the quantum curves (FD and BE) merge into the classical curve (MB). For high T, $\frac{\epsilon-\mu}{KT}$ will be large only if μ is large and negative. The classical limit can also be written as

$$\frac{1}{\lambda_T^3} \frac{V}{N} \gg 1 \tag{286}$$

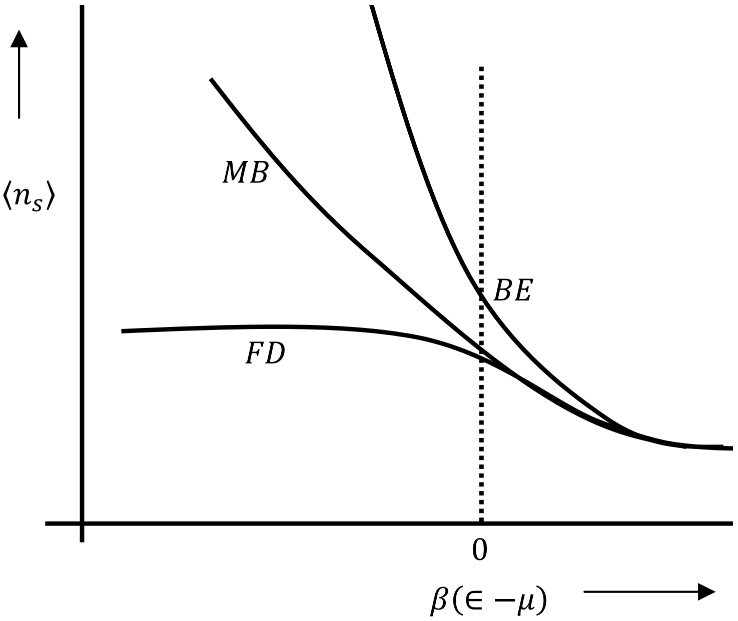


Figure 12.1

where λ_T is the de Broglie wavelength at temperature T, i.e

$$\lambda_T = \frac{h}{(2\pi m KT)^{\frac{3}{2}}}.$$

λ_T is a measure of the spread in the wave functions of the particles. As long as λ_T is much smaller than the average spacing $\left(\left(\frac{V}{N}\right)^{\frac{1}{3}}\right)$ between particles, the statistics will be classical.

A gas which can be treated classically is said to be non-degenerate. On the other hand, quantum statistical distributions have to be used if the gas is degenerate. The condition for a degenerate gas can be written as

$$\left[\frac{h^2}{2\pi m KT}\right]^{\frac{3}{2}} \frac{N}{V} \gg 1 \tag{287}$$

This is sometimes called degeneracy criterion.

For instance electron gas in copper at room temperature is degenerate for typical concentrations of electrons of the order $10^{28}\ m^{-3}$. On the other hand, atmospheric gases at room temperature and normal pressures can be seen to be non degenerate.

The partition function for a gas

Let us consider an ideal gas having a large number of molecules (N) enclosed in a volume V. The molecules can have translational, rotational, vibrational and electronic energies. As a first approximation, we assume that the gas molecules do not have any intermolecular forces. Hence the total energy can be written as

$$E_{\text{tot}} = E_{\text{trans}} + E_{\text{vibr}} + E_{\text{rot}} + E_{\text{ele}} \tag{288}$$

and hence the canonical partition function can be expressed as a product

$$Z = Z_{\text{trans}} \,.\, Z_{\text{vibr}} \,.\, Z_{\text{rot}} \,.\, Z_{\text{ele}} \tag{289}$$

where the subscripts stand for translational, vibrational, rotational and electronic types of partition functions, respectively.
For a monochromatic gas, there is no vibration or rotation and

$$E_{\text{mol}} = E_{\text{trans}} + E_{\text{ele}}$$

The translational partition function is calculated as follows. Let us assume that the gas is enclosed in a rectangular box of dimensions L_x, L_y and L_z so that $V = L_xL_yL_z$. The energy levels of a particle in a box are given by

$$\epsilon = \frac{\hbar^2}{2m}\left(K_x^2 + K_y^2 + K_z^2\right) \tag{290}$$

where

$$K_x = \frac{n_x\pi}{L_x},\; K_y = \frac{n_y\pi}{L_y} \text{ and } K_z = \frac{n_z\pi}{L_z}.$$

Hence

$$\epsilon = \frac{\hbar^2\pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \tag{291}$$

The partition function is given by $\sum_s e^{-\beta\epsilon_s}$. For large L_x, L_y and L_z the energy levels are closely spaces and therefore the quantisation of the energy levels can be neglected. Hence the summation in $\sum_s e^{-\beta\epsilon_s}$ can be replaced by integration of the differential $\frac{1}{h^3}\sum_s e^{-\beta\epsilon_s} d^3q\; d^3P$.
Therefore the partition function can be expressed as

$$Z_{\text{trans}} = \frac{1}{h^3}\int \dots\dots \int e^{-\beta\frac{P^2}{2m}} d^3q\; d^3P \tag{292}$$

Clearly integration over d^3q gives the volume V of the enclosure. Hence

$$\begin{aligned} Z_{\text{trans}} &= \frac{V}{h^3}\int\int\int e^{-\beta\frac{P^2}{2m}} dP_xdP_ydP_z \\ &= \frac{V}{h^3}\left(2\pi mKT\right)^{\frac{3}{2}} \end{aligned} \tag{293}$$

For N particles the correct partition function is

$$Z_{\text{trans}} = \left(\frac{V}{h^3}\right)^N \left(2\pi mKT\right)^{\frac{3}{2}} \tag{294}$$

This result is the same as the classical result but for the fact that the Planck's constant h replaces the arbitrary cell volume assumed in the classical gas.
For a diatomic molecule we simply replace m by the sum of the masses of the atoms involved. Thus

$$Z_{\text{trans}} = \left(\frac{V}{h^3}\right)\left[2\pi\left(m_1 + m_2\right)KT\right]^{\frac{3}{2}} \tag{295}$$

gives the diatomic translatory partition function.

The Rotational partition function

In the first approximation, we may treat a diatomic molecule as consisting of a pair of atoms with masses m_1 and m_2 separated by a fixed distance r_0.
The energy levels of such a rotator is given by quantum mechanics as

$$E_{\text{rot}} = \left(\frac{\hbar^2}{2I}\right) J\left(J+1\right) \tag{296}$$

where

$$I = \mu r_0^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

is the moment of inertia and J is the rotational quantum number that can take values $0, 1, 2, 3, ...$
As $(2J+1)$ is the degeneracy of the J^{th} energy level

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} \left(2J+1\right) e^{-\beta\left(\frac{\hbar^2}{2I}\right)J(J+1)} \tag{297}$$

Using $\theta_r = \frac{\hbar^2}{2KI}$ called the rotational characteristic temperature we can write

$$Z_{\text{rot}} = \sum_{J=0}^{\infty} \left(2J+1\right) e^{-\left(\frac{\theta_r}{T}\right)J(J+1)} \tag{298}$$

We may consider two special cases depending on the temperature or moment of inertia.

a) For very small T or I_m

$$Z_{\text{rot}} \simeq 1 + 3e^{-\frac{2\theta_r}{T}} + 5e^{-\frac{6\theta_r}{T}} + ... \tag{299}$$

In this case, the thermal energy of the order of KT is not sufficient to populate the higher rotational levels, almost all the molecules will be in the lowest rotational state and hence all terms beyond the first few can be neglected.

b) For high temperature and not so small I.
In this case, the the spacing between consecutive levels is small compared to KT. Therefore ϵ may be considered as a continuous variable in J. Thus summation over J can be replaced by integration.
Putting $x = J\left(J+1\right)$ we get

$$Z_{\text{rot}} = \int_0^{\infty} e^{-\left(\frac{\beta\hbar^2 u}{2I}\right)} du = \frac{2I}{\beta\hbar^2} = \frac{2IKT}{\hbar^2} \tag{300}$$

Hence the mean rotational energy

$$\langle E\rangle = -N\frac{\partial \ln Z_{\text{rot}}}{\partial\beta} = NKT \tag{301}$$

Therefore the contribution of rotational energy to the specific heat is

$$(C_V) = NK \tag{302}$$

At lower temperature, the rotational states have to be treated as discrete. Then

$$Z_{\text{rot}} = \sum (2J+1)\, e^{\frac{-J(J+1)\theta_r}{T}}$$

has to be evaluated taking into account the symmetry character of nuclear wave function.

Vibrational partition function

To a good approximation, the vibrational motion of a molecule may be taken to be the simple harmonic type. the energy values of a simple harmonic oscillator are given by

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{303}$$

Therefore the vibrational partition function

$$Z_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} \tag{304}$$

This can be easily evaluated.

$$\begin{aligned} Z_{\text{vib}} = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} \\ = \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1 - e^{-\beta\hbar\omega}} \end{aligned} \tag{305}$$

In terms of a vibrational characteristic temperature $\theta_r = \frac{\hbar\omega}{K}$ this can be written as

$$Z_{\text{vib}} = \frac{e^{-\frac{\theta_V}{2T}}}{1 - e^{-\frac{\theta_V}{T}}} \tag{306}$$

Therefore the mean vibrational contribution to the energy

$$\begin{aligned} \langle E_V \rangle = -N\frac{\partial \ln Z_{\text{vib}}}{\partial \beta} = NKT^2 \frac{\partial \ln Z_{\text{vib}}}{\partial T} \\ = NKT^2 \frac{\partial}{\partial T}\left[-\frac{\theta_V}{2T} - \ln\left(1 - e^{-\frac{\theta_V}{T}}\right)\right] \\ = NKT^2\left[\frac{\theta_V}{2T^2} + \frac{e^{-\frac{\theta_V}{T}}}{1 - e^{-\frac{\theta_V}{T}}}\frac{\theta_V}{T^2}\right] \\ = NK\left[\frac{\theta_V}{2} + \frac{\theta_V}{e^{\frac{\theta_V}{T}} - 1}\right] \end{aligned} \tag{307}$$

Hence the specific heat

$$(C_V)_{\text{vib}} = \frac{\partial \langle E_V \rangle}{\partial T} = NK \left(\frac{\theta_V}{T}\right)^2 \frac{e^{\frac{\theta_V}{T}}}{\left(e^{\frac{\theta_V}{T}} - 1\right)^2} \tag{308}$$

At high temperatures $\frac{\theta_V}{T} \ll 1$ and using the expansion

$$e^{\frac{\theta_V}{T}} \simeq 1 + \frac{\theta_V}{T} + \frac{1}{2}\left(\frac{\theta_V}{T}\right)^2$$

upto second order terms.
For high temperatures

$$\begin{aligned}\langle E_V \rangle &\simeq NK\theta_V \left[\frac{1}{2} + \frac{1}{\frac{\theta_V}{T} + \frac{1}{2}\left(\frac{\theta_V}{T}\right)^2}\right] \\ &\simeq N\hbar\omega \left[\frac{1}{2} + \frac{T}{\theta_V}\left(1 - \frac{\theta_V}{2T}\right)\right] \\ &\simeq NKT + \frac{N\hbar\omega}{2} \end{aligned} \tag{309}$$

This leads to

$$C_V = NK \tag{310}$$

Electronic partition function

The electronic partition function is given by

$$Z_{\text{el}} = g_0 + g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} + ... \tag{311}$$

where $\epsilon_1, \epsilon_2.....$ are the excitation energy levels and $g_1, g_2.....$ are the respective degeneracies.
The values of energies $\epsilon_1, \epsilon_2.....$ being generally much larger than the thermal energy KT at room temperature, the molecules of most gases are hardly excited to higher electronic states. Hence the electronic partition function can be represented with sufficient accuracy by the first two terms in equation 311.
Thus

$$Z_{\text{el}} \simeq g_0 + g_1 e^{-\beta\epsilon_1} \tag{312}$$

This leads to

$$\begin{aligned}\langle E_{\text{el}} \rangle &\simeq NKT^2 \frac{g_1 e^{-\beta\epsilon_1}}{g_0 + g_1 e^{-\beta\epsilon_1}} \left(\frac{\epsilon_1}{KT^2}\right) \\ &\simeq N\epsilon_1 \left(\frac{g_0}{g_1} e^{\beta\epsilon_1} + 1\right)^{-1} \end{aligned} \tag{313}$$

and

$$(C_V)_{\text{el}} \simeq \frac{N\epsilon_1^2}{KT^2} \frac{g_0}{g_1} e^{\beta\epsilon_1} \left[1 + \frac{g_0}{g_1} e^{\beta\epsilon_1}\right]^{-2} \tag{314}$$

As there is no significant contribution from the electronic energy to the specific heat at ordinary tempeatures, the total temperature dependent energy of the gas is given by

$$\begin{aligned} E &= \frac{3}{2}NKT_{\text{trans}} + NKT_{\text{rot}} + NKT_{\text{vib}} \\ &= \frac{7}{2}NKT \end{aligned} \tag{315}$$

Therefore, at ordinary temperatures the specific heat becomes

$$C_V \simeq \frac{7}{2}NK \tag{316}$$

12.4 Let us sum up

Boltzmann limit (classical gas limit) of gases is obtained at high temperatures and low densities. It also means the de Broglie wavelength of molecules is much smaller than the mean separation between molecules.

The partition function for a non-interacting gas can be written as a product of translational, vibrational, rotational and electronic partition functions. Z_{trans} is the same as the classical expression. The specific heat due to rotations at high temperatures is equal to NK. The vibrational specific heat at high temperatures is also equal to NK. The electronic contribution to specific heat is negligible at normal temperatures. Hence the total specific heat is equal to $\frac{7}{2}NK$.

12.5 Key words

de Broglie thermal wavelength: denoted by λ_T it is equal to

$$\frac{h}{(2\pi mKT)^{\frac{1}{2}}}.$$

Rotational characteristic temperature: It is given by

$$\theta_r = \frac{\hbar^2}{2KI}$$

where I is the moment of inertia of the molecule

Vibrational characteristic temperature: It is given by

$$\theta_V = \frac{\hbar\omega}{K}$$

where ω is the oscillatory frequency of the molecule

12.6 Questions for self study

a) Obtain the Boltzmann limit of quantum distribution functions

b) State and explain degeneracy criterion

c) Deduce the vibrational contribution to the specific heat

d) Obtain the rotational contribution to the specific heat at high temperatures.

12.7 Further references

1. B.B Laud, *Fundamentals of Statistical Mechanics*, New age international ltd. New Delhi.

2. B.K. Agarwal and M.Eisner, *Statistical Mechanics*, New age international ltd. New Delhi.

3. K. Huang, *Statistical Mechanics*, Wiley Eastern ltd., 1975.

4. Gopal ESR, *Statistical Mechanics and properties of matter*, McMillan India ltd. New Delhi.

5. C. Kittel, *Thermal Physics*, Wiley Eastern ltd, 1969.

6. F. Reif, *Statistical Physics*, McGraw Hill.

Unit-13: The equation of state of an ideal Fermi gas Application of Fermi Dirac statistics to the theory of free electron in metals.

13.1 Objectives

After studying this unit you will be able to understand the following aspects;

- Equation of state of an ideal Fermi gas
- Application of Fermi -Dirac statistics to the theory of free electrons in metals

13.2 Introduction:

Thermodynamics of an ideal gas is important in metals, in white dwarfs in simplified models of neutrons and quark stars in speculation about cosmological neutrinos, and in many parts of stellar structure and stellar atmosphere. In this unit we study the various examples of Fermions. The dominant common characteristic is the existence of Fermions, which is direct consequence of the Pauli Exclusion Principle. Free electron model for the physical properties of metals. It is the simplest theory for these materials, but still gives a very good description of many properties of metals which depend on the dynamics of the electrons.

The equation of state of a spineless ideal Fermi gas is obtained by eliminating Z from the following equation

$$\left.\begin{aligned}\frac{\rho}{kT}&=\frac{4\pi}{h^3}\int_0^\infty dp\, p^2\log\left(1+ze^{-\beta p^2/2m}\right)\\ \frac{1}{V}&=\frac{4\pi}{h^3}\int_0^\infty dp\, p^2\,\frac{1}{Z^{-1}e^{-\beta p^2/2m}+1}\end{aligned}\right\}------------(1)$$

First we study the behaviour of Z determined by the second equation (above) namely

$$\frac{\lambda^3}{v}=f_{3/2}(Z)---------------(2)$$

$$\textit{Where}\quad v=\frac{V}{N}\quad \lambda=\sqrt{2\pi\hbar^2/mkT}\ \textit{ is the thermal wavelength and}$$

$$f_{3/2}(Z)=\frac{4}{\sqrt{\pi}}\int_0^\infty dx\,\frac{x^2}{Z^{-1}e^{x^2}+1}$$

It is monotonically increasing function of Z. We have the power series expansion

$$f_{3/2}(Z)=Z-\frac{Z^2}{2^{3/2}}+\frac{Z^3}{3^{3/2}}+\frac{Z^4}{4^{3/2}}+----------------(3)$$

For a large Z, an asymptotic expansion may be obtained through a method due to the Summerfield as follows:

For convenience put $Z=e^\gamma$ so that γ is related to the chemical potential μ by

$$\gamma=\log Z=\mu/kT$$

$$f_{3/2}(Z)=\frac{4}{\sqrt{\pi}}\int_0^\infty dx\,\frac{x^2}{e^{x^2-\gamma}+1}=\frac{2}{\sqrt{\pi}}\int_0^\infty dy\,\frac{\sqrt{y}}{e^{y-\gamma}+1}$$

$$=\frac{4}{3\sqrt{\pi}}\int_0^\infty dy\,\frac{y^{3/2}e^{y-\gamma}}{\left(e^{y-\gamma}+1\right)^2}$$

The last step is obtained through a partial integration. Expanding $y^{3/2}$ in a Taylor series about γ we obtain

$$f_{3/2}(Z)=\frac{4}{3\sqrt{\pi}}\int_0^\infty dy\,\frac{e^{y-\gamma}}{\left(e^{y-\gamma}+1\right)^2}\times\left[\gamma^{3/2}+\frac{3}{2}\gamma^{1/2}(y-\gamma)+\frac{3}{8}\gamma^{-1/2}(y-\gamma)^2+------\right]$$

$$\Rightarrow\frac{4}{3\sqrt{\pi}}\int_{-\gamma}^\infty dt\,\frac{e^t}{\left(e^t+1\right)^2}\left(\gamma^{3/2}+\frac{3}{2}\gamma^{1/2}t+\frac{3}{8}\gamma^{-1/2}t^2+----\right)$$

Now we write

$$\int_{-\gamma}^\infty=\int_{-\infty}^{+\infty}-\int_{-\infty}^{-\gamma}$$

The second integral is of the order $e^{-\gamma}$, Therefore

$$f_{3/2}(z)=\frac{4}{3\sqrt{\pi}}\int_{-\infty}^{\infty}dt\,\frac{e^{t}}{\left(e^{t}+1\right)^{2}}\left(\gamma^{3/2}+\frac{3}{2}\gamma^{1/2}t+\frac{3}{8}\gamma^{-1/2}t^{2}+----\right)+O\left(e^{-\gamma}\right)$$

$$\Rightarrow\frac{4}{3\sqrt{\pi}}\left(I_0\gamma^{3/2}+\frac{3}{2}I_1\gamma^{1/2}+\frac{3}{8}I_2\gamma^{-1/2}+----\right)+O\left(e^{-\gamma}\right)$$

$$Where\quad I_n=\int_{-\infty}^{+\infty}dt\,\frac{t^{n}e^{t}}{\left(e^{t}+1\right)^{2}}$$

Apart from the factor ***t^n*,** the integrand is an even function of *t* Hence $I_n=0$ for odd *n*. For *n=0.* We have

$$I_0=-2\int_0^{\infty}dt\,\frac{d}{dt}\frac{1}{\left(e^{t}+1\right)}=1$$

and for even $n(>0)$

$$I_n=-2\left[\frac{\partial}{\partial\lambda}\int_0^{\infty}dt\,\frac{t^{n-1}}{e^{\lambda t}+1}\right]_{\lambda=1}=2n\int_0^{\infty}du\,\frac{u^{n-1}}{e^{u}+1}$$

$$=(n-1)!(2n)\left(1-2^{1-n}\right)\xi(n)$$

where ξ(n) is the Riemann Zeta function. Some special values of which are

$$\xi(2)=\frac{\pi^2}{6};\ \xi(4)=\frac{\pi^4}{90};\ \xi(6)=\frac{\pi^6}{945}$$

Hence

$$f_{3/2}(z)=\frac{4}{3\sqrt{\pi}}\left[(\log z)^{3/2}+\frac{\pi^2}{8}(\log z)^{-1/2}+----\right]+O\left(z^{-1}\right)\text{.............................}(4)$$

A graph of $f_{3/2}(Z)$ versus Z is shown in following fig, any given +ve values of Z determined by eqn(2) can be read off such a graph. It is seen that Z increases monotonically as λ^3/v increases. For fixed *v*, Z increases monotonically as the temperature decreases.

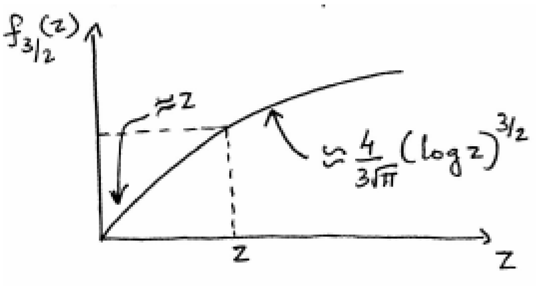


Fig 1: The function $f_{3/2}(z)$

(i) ***High Temperature and low Densities*** $\left(\lambda^3/v << 1\right)$:

For $\left(\lambda^3/v << 1\right)$ the average inter-particle separation $v^{1/3}$ is much larger than thermal wave length λ. We expect quantum effects to be negligible. From equation (2) and (3)

$$\frac{\lambda^3}{v} = Z - \frac{Z^2}{2^{3/2}} + ------$$

$$which\ \ may\ \ be\ \ solved\ to\ give$$

$$Z = \frac{\lambda^3}{v} + \frac{1}{2^{3/2}}\left(\frac{\lambda^3}{v}\right)^2 + ------$$

Thus, Z reduces to that of the Boltzmann gas equation $\left(z = \frac{\lambda^3}{v}\right)$ when $\lambda^3 \to 0\left(T \to \infty\right)$. The average occupation number $\left(\left\langle n_p \right\rangle = \frac{ze^{-\beta\varepsilon_p}}{1 \pm ze^{-\beta\varepsilon_p}}\right)$reduces to Maxwell- Boltzmann form.

$$\left\langle n_p \right\rangle \simeq \frac{\lambda^3}{v} e^{-\beta\varepsilon_p}$$

$$The\, eqn\ of\ \ state\ \ \left(eqn(1)\right)\ \ then\ becomes$$

$$\frac{\rho v}{kT} = \frac{v}{\lambda^3}\left(Z - \frac{Z^2}{2^{5/2}} + -----\right) = 1 + \frac{1}{2^{5/2}}\frac{\lambda^3}{v} + -------$$

This is the form of Virial expansion. The corrections to the ideal gas law, however, are not due to the molecular interactions, but to quantum effects. The second Virial co efficient in this case is

$$\frac{\lambda^3}{2^{5/2}} = \frac{1}{2}\left(\frac{\pi\hbar^2}{mkT}\right)^{3/2}$$

All other thermodynamic function reduce to those for a classical ideal gas plus small corrections.

(ii) **Low Temperature and High Densities** $\left(\lambda^3/v >> 1\right)$:

For $\lambda^3/v >> 1$, the average de-Broglie wavelength of a particle is much greater than the average inter particle separation. Thus, quantum effects, in particular, the effects of the Pauli's Exclusion principle become all important.

In the neighbourhood of absolute zero, we have from equation (2) and equation (4)

$$\frac{1}{v}\left[\frac{2\pi\hbar^2}{2mkT}\right]^{3/2} \approx \frac{4}{3\sqrt{\pi}}\left(\log Z\right)^{3/2}$$

where ε_F, the chemical potential at absolute zero, is called the Fermi energy

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{v}\right)^{2/3} \text{---------------}(5)$$

To study its physical significance, let us examine $\langle n_p \rangle$ near absolute zero

$$\langle n_p \rangle \approx \frac{1}{e^{\beta(\varepsilon_p - \varepsilon_F)+1}}$$

if $\varepsilon_p < \varepsilon_F$, then the exponential in the denominator vanishes as T→0 (β→∞). Hence $\langle n_p \rangle$=1. Otherwise $\langle n_p \rangle$=0 thus

$$\langle n_p \rangle_{T=0} = \begin{cases} 1 & (\varepsilon_p < \varepsilon_F) \\ 0 & (\varepsilon_p > \varepsilon_F) \end{cases} \text{-------------}(6)$$

The physical meaning of this formula is clear. Because of the Pauli's Exclusion principle, no two particles can be in the same state. Therefore, in the ground state of the system, the particles occupy the lowest possible levels and fill the levels up to the finite energy ε_F. Thus ε_F is simple the single particle energy level below which there are exactly N states. In momentum space, the particles fill a sphere of radius $P_{F,}$ the surface of which is called the Fermi Surface. With the interpretation, let us now calculate the Fermi energy independently under more general conditions. Suppose all single particle energy levels are g-fold degenerate. For example, g=2s+1 for a particle of spin S. The condition determining ε_F is then

$$g\sum_p \langle n_p \rangle_{T=0} = N \text{--------------}(7)$$

In view of equation (6) this states that there are N states with energy below the Fermi energy. Putting, $\varepsilon_F = P_F^2 / 2m$. We find,

$$\frac{g}{(2\pi\hbar)^3}\frac{4\pi}{3}P_F^3 = \frac{N}{V}$$

Hence

$$\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{gv}\right)^{2/3}$$

which reduces to equation (5) when *g=1*. We can also interpret equation (7) as follows: Particles with different Quantum numbers are not constrained by any symmetry requirement with respect to the interchange of these positions. Thus we may consider a system of N Fermions, each with degeneracy *g*, to be made up of *g* independent Fermi gases each with N/g particles whose energies are non-degenerate.

To obtain the thermodynamic function for low temperatures and high densities, we first obtain the expansion for the chemical potential. From equation (1) and equation (4)

$$kT_\gamma = kT\log Z = \varepsilon_F\left[1-\frac{\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2+\ldots\ldots\ldots\ldots\ldots\ldots\right]-----(8)$$

The expansion parameter is $\frac{kT}{\varepsilon_F}$. If we define the Fermi temperature T_F, which is a function of density by

$$kT_F = \varepsilon_F$$

then low temperature and high density means $T \ll T_F$. In this domain, the gas is said to be degenerate because the particles tend to go to the energy levels possible. For this reason, T_F is also called the '***degeneracy temperature***'.

The average occupation number is

$$\langle n_p\rangle = \frac{1}{e^{\beta\varepsilon_p-\gamma}+1}$$

where γ is given by (8). Since $\varepsilon_p = P^2/2m$, n_p depends on *p* only through P^2. A sketch of n_p is shown in fig (2).

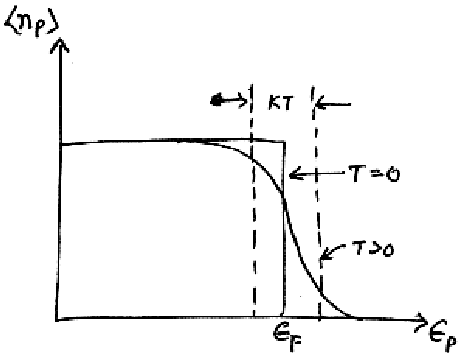


Fig 2: Average occupation number in an ideal Fermi gas

The internal energy is

$$U = \sum_p \varepsilon_p \left\langle n_p \right\rangle = \frac{V}{h^3}\frac{4\pi}{2m}\int_0^\infty dp\, p^4 \left\langle n_p \right\rangle$$

After the partial integration we obtain

$$U = \frac{V}{4\pi^2 m\hbar^3}\int_0^\infty dp \frac{P^5}{5}\left(-\frac{\partial}{\partial p}\left\langle n_p \right\rangle\right) = \frac{\beta V}{20\pi^2 m^2 \hbar^3}\int_0^\infty dp \frac{p^6 e^{\beta\varepsilon_p-\gamma}}{\left(e^{\beta\varepsilon_p-\gamma}+1\right)^2} \text{---------}(9)$$

It is apparent from fig that $\frac{\partial\left\langle n_p \right\rangle}{\partial p}$ is sharply peaked at p=P$_F$. In fact, at absolute zero it is a δ(delta) function at p=P$_F$. Therefore the integral in equation (9) can be evaluated by expanding the factor P^6 about p=P$_F$. The procedure is similar to that used in obtaining equation (4) . After inserting γ from equation (8), we obtain the asymptotic expansion

$$U = \frac{3}{5}N\varepsilon_F\left[1+\frac{5}{12}\pi^2\left(\frac{kT}{\varepsilon_F}\right)^2+.................\right]\text{------}(10)$$

The first term is the ground state energy of the Fermi gas at the given density, as we can verify by showing the following

$$\sum_{|p|<P_F}\frac{p^2}{2m} = \frac{3}{5}N\varepsilon_F$$

The specific heat at constant volume can be immediately obtained from equation (10)

$$\frac{C_v}{Nk} = \frac{\pi^2}{2}\frac{kT}{\varepsilon_F}$$

It vanishes linearly as T→0, thus verifying the third law of thermodynamics. We know that $\frac{C_v}{Nk}$ approaches 3/2 as T→∞. Thus a rough sketch of $\frac{C_v}{Nk}$ can be made as shown in fig 3. The fact that it is proportional to T at these low temperatures can be understood as follows. At a temperature t>0, $\left\langle n_p \right\rangle$ differs from that at T=0 because a certain number of particles are excited to energy levels $\varepsilon_p > \varepsilon_F$. Roughly speaking, particles with energies of order kT below ε_F (see fig 2). The number of particles excited is therefore of the order of $\left(kT/\varepsilon_F\right)N$ therefore the total excitation energy above the ground state $\Delta U = \left({kT}/{\varepsilon_F}\right)NkT$ from which it follows

$$C_V = \left(KT/\in_F\right)NK$$

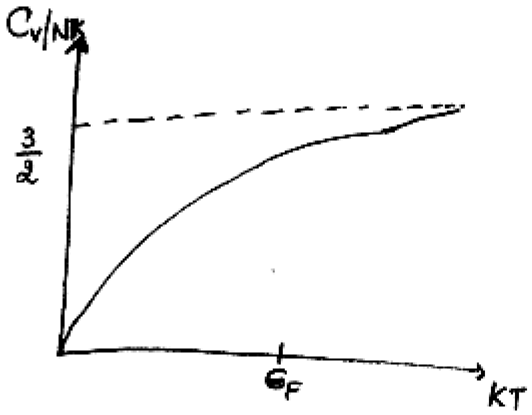


Fig 3: Specific heat of an ideal Fermi gas

From (equation $U = \frac{3}{2}PV$) and (equation 10) follows the equation of state

$$P = \frac{2}{3}\frac{U}{V} = \frac{2}{5}\frac{\varepsilon_F}{v}\left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2 + - - - -\right]$$

This shows that even at absolute zero, it is necessary to contain the ideal Fermi gas with externally fixed walls because the pressure does not vanish. This is a manifestation of the Pauli’s Exclusion principle which allows only one particle to have zero momentum. All other particles must have finite momentum and give rise to the zero point pressure.

To obtain the thermodynamic function for arbitrary values of λ^3/v numerical methods must be employed to calculate the functions $f_{3/2}(Z)\, and\; f_{5/2}(Z)$

13.3 Electron gas in Metals

A metal can be considered to be composed of a system of fixed positive nuclei and a number of mobile electrons. These mobile electrons are assumed to move freely in the metal like the particles of a gas and constitute a perfect gas known as electron gas. On this assumption the classical statistics could explain to a certain extent the various properties of metals depending on the motion of free electrons in metal such as electrical and thermal conductivities, thermo electricity, thermionic emission, magnetic properties of metals and photoelectric effect etc. But in certain cases, the chief among them being specific heat of metals, very serious difficulties encountered in the use of Classical Statistics. That is why the theory of electron gas was discredited to some extent.

Sommerfield, in 1928, however explained the electron theory of metals on the basis of new quantum statistics. According to him, the electrons in metals are not completely free but only partially, in the sense that though they are not bound to any particular atomic system. Yet they are bound to the metal as a whole. Therefore the interior of the metal is to be conceived as a region of uniform potential, positive relative to free space, so that work is required to be done to extract an electron from the metal. Th electrons in metals cannot therefore be compared to the free particles of a gas obeying the classical statistics. More over due to their light mass and dense packing, the electrons in the metals should be assimilated to the particles of a gas under very high compression, hence to a degenerate gas. Further these electrons are assumed to obey Pauli's Exclusion principle; hence they should obey the Fermi Dirac statistics. Therefore to study the properties of the electron in metals at low temperature, we shall make use of the last section.

For electron $S = 1/2 \quad so\ that\ \ g_s = 2S + 1 = 2$

$$\therefore the\ \ eqn:\ \ \varepsilon_F(0) = \frac{h^2}{2m}\left[\frac{3n}{4\pi V g_s}\right]^{2/3} = \mu_F$$; the Fermi energy at 0K.

$$\varepsilon_F = \frac{h^2}{2m}\left[\frac{3n}{4\pi V g_s}\right]^{2/3} = \frac{h^2}{2m}\left[\frac{3n}{4\pi V \times 2}\right]^{2/3}$$

$$= \frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{2/3} = 0.625\times10^{-17}\rho^{2/3} joule\ (or)\ 39\rho^{2/3}\ eV$$

$where$

$$\rho = \left(\frac{mn}{V}\right)^{2/3} kg/m^3\ \ is\ \ the\ \ density\ \ of\ \ the\ \ electron\ \ gas$$

For conduction electrons in metals $\rho = 0.1 kg/m^3$

The Fermi Temperature T_F for electron gas is

$$T_F = \frac{\varepsilon_F(0)}{K} = \frac{h^2}{8\pi mk}\left(\frac{3n}{\pi V}\right)^{2/3} = \left(4.52\times10^5\rho^{3/2}\right)K$$

$$for\ \rho = 0.1 kg/m^3\ T_F = 10^5 K.$$

Thus electron gas below 10^5 K temperature is degenerate

The degeneracy factor of an electron gas from equation (1)

$$= \frac{1}{g_s}.\frac{n}{v}.\frac{h^3}{(2\pi mkT)^{3/2}}$$

$$A = \frac{1}{g_s}.\frac{n}{v}.\frac{h^3}{(2\pi mkT)^{3/2}} = \frac{1}{2}.\frac{n}{v}.\frac{h^3}{(2\pi mkT)^{3/2}}$$

$$As\,T \to 0, A \to \infty$$

$$therefore\ \frac{1}{e^{\alpha+x}+1} = \frac{1}{\frac{1}{A}\left(e^x+1\right)} ------------(11)$$

and that for low temperatures

$$n = g_s.\frac{v}{h^3}(2\pi mkT)^{3/2}.\frac{1}{\sqrt{\pi}}\int_0^\infty x^{1/2}dx$$

$$= \frac{4V}{\sqrt{\pi}}\frac{(2\pi mkT)^{3/2}}{h^3}\int_0^A x^{1/2}\,dx$$

Here we have $g_s = 2$ and have replaced its upper limit by A at low temperature near absolute zero. Since A→∞, when T→0

$$n = \frac{4V}{\sqrt{\pi}}\frac{(2\pi mkT)^{3/2}}{h^3}\frac{A^{3/2}}{3/2}$$

$$A = \frac{h^2}{2mKT}\left(\frac{3n}{8\pi V}\right)^{2/3} = \frac{h^2}{2m^{5/2}.KT}\left(\frac{3\rho}{8\pi}\right)^{2/3}$$

This equation represents the degeneracy factor of electron gas at low temperature near absolute zero. Now substituting $h=6.6X10^{-34}$ joule-sec, $m=9X10^{-31}$ kg, $k=1.38X10^{-23}$ Joule/Kelvin and $\rho=0.1$ kg/m^3

$$A = \frac{4.56\times10^5}{T}$$

This means that at low temperature the electron gas is strong

Zero point energy of the electron gas

$$E_0 = \frac{3nh^2}{10m}\left(\frac{3n}{4\pi Vg_s}\right)^{2/3} = \frac{3nh^2}{10m}\left(\frac{3n}{4\pi V.2}\right)^{2/3} = \frac{3nh^2}{40m}\left(\frac{3n}{\pi V}\right)^{2/3} = \frac{3}{5}n\varepsilon_P(0)$$

Zero point pressure of the electron gas

$$P_0 = \frac{1}{5}\frac{n}{V}.\frac{h^2}{m}\left(\frac{3n}{4\pi Vg_s}\right)^{2/3} = \frac{1}{5}\frac{n}{V}.\frac{h^2}{m}\left(\frac{3n}{8\pi V}\right)^{2/3}$$

$$= \frac{nh^2}{20mV}\left(\frac{3n}{\pi V}\right)^{2/3}$$

At normal temperature, the pressure of the electron gas comes out to be sufficiently high of the order $=10^5$ atmosphere.

The electronic contribution to the specific heat of metals at low temperature is given by

$$C_v = \left[\frac{\partial E}{\partial T}\right]_V = \frac{\partial}{\partial T}\left[\frac{3}{5} n\varepsilon_p(o)\left\{1+\frac{5}{12}\left(\frac{nkT^2}{\varepsilon_F(0)}\right)\right\}\right]_V$$

$$\Rightarrow \frac{1}{2} nk\pi^2\left(\frac{kT}{\varepsilon_F(0)}\right)$$

$$= \lambda T$$

Where $\lambda = \dfrac{nK^2\pi^2}{2\varepsilon_F(0)}$ is constant quantity independent of temperature i.e., $C_v \propto T$

Thus the electronic contribution to the specific heat is proportional to the absolute temperature and vanishes at the absolute zero.

13.4 Let us sum up

In this unit we have understood

- Equation of state of an ideal Fermi gas
- Application of Fermi -Dirac statistics to the theory of free electrons in metals
- Degenerate level Low temperatures and high densities
- Degenerate level high temperatures and low densities
- Electron gas in metal

13.5 Key words: Fermi gas; specific heat; Fermi Dirac; Fermions.

13.6 Questions for self study:

- Obtain an expression for Fermi energy in case of metals using FD statistics.

13.7 Problems:

1. Calculate the Fermi energy in electron Volt for Sodium, assuming that it has one free electron per atom. Given density of Sodium =0.97 g cm^{-3}, atomic weight of Sodium is 23.

Solution: The Fermi energy is given by

$$\varepsilon_F(0) = \frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{\left(2/3\right)}$$

Assuming one electron per Sodium atom, the electron density $\frac{n}{V}$ is given by

$$\frac{n}{V}=\frac{N_0\rho}{W}$$

But,

density of Sodium $\rho = 0.97\times10^{3}\,kgm^{-3}$, atomic weight of Sodium = W=23,

Avogadro number N_0= 6 X 10^{26} atoms/kg-mol.

$$\frac{n}{V}=2.53\times10^{28}\,electrons/m^{3}$$

The Fermi energy $\varepsilon_F(0)$ is given by,

$$\varepsilon_F(0)=\frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{\left(2/3\right)}$$

$$where \quad m = mass\ of\ electron = 9.1\times10^{-31}\,kg$$

$$After\ substituting\ the\ values\ we\ get$$

$$\varepsilon_F(0)=3.145\,eV$$

2. Show that the average energy at 0K will be $\frac{3}{5}$ times the Fermi energy.

Solution: The number of electrons in an electron gas having energies between $\varepsilon\ \ and\ \ \varepsilon+d\varepsilon$ is given by

$$n(\varepsilon)d\varepsilon=\frac{8\pi mV}{h^3}\sqrt{2m}\,\frac{\varepsilon^{1/2}d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1} \qquad (1)$$

where m is the mass of electron.

But, the Fermi energy $\varepsilon_F(0)$ is given by

$$\varepsilon_F(0)=\frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{\left(2/3\right)}$$

$$\frac{V}{h^3}=\frac{3N}{8\pi m}\frac{1}{2\sqrt{2m}}\times\left[\varepsilon_F(0)\right]^{-3/2}$$

Substituting this in equation (1), we get

$$n(\varepsilon)d\varepsilon=\frac{3}{2}N\left[\varepsilon_F(0)\right]^{-3/2}\frac{\varepsilon^{1/2}d\varepsilon}{e^{(\varepsilon-\varepsilon_F)/kT}+1}$$

At T = 0 all of the electrons have energies less than or equal to $\varepsilon_F(0)$ (i.e., $\varepsilon \le \varepsilon_F$) . So that at T = 0 we have

$$e^{(\varepsilon-\varepsilon_F)/kT} = e^{-\infty} = 0$$

Therefore, at absolute zero

$$n(\varepsilon)d\varepsilon = \frac{3N}{2}\left[\varepsilon_F(0)\right]^{-3/2} \varepsilon^{1/2} d\varepsilon$$

Total energy at absolute zero is

$$E_0 = \int_0^{\varepsilon_F(0)} \varepsilon\, n(\varepsilon)\, d\varepsilon$$

$$= \frac{3N}{2}\left[\varepsilon_F(0)\right]^{-3/2} \int_0^{\varepsilon_F(0)} \varepsilon^{3/2}\, d\varepsilon$$

$$= \frac{3}{5} N\varepsilon_F(0)$$

Hence, the average energy at absolute zero

$$\bar{E}_0 = \frac{E_0}{N} = \frac{3}{5}\varepsilon_F(0)$$

13.8 References for further study:

- Statistical mechanics: **Kerson Haung**. Massachusetts, Institute of technology, John Wiley and sons Singapore.
- Thermodynamic and Statistical Physics: **J.P Agarwal.**
- Statistical Physics-A survival Guide, by **A.M.Glazer and J.S.Wark,** 2001, Oxford University Press, New York.)

UNIT 14: Degeneracy and magnetic susceptibility.

14.1 Objectives

After studying this unit you will be able to understand the following aspects;

- The single- Particle Partition Function
- Degeneracy
- The Partition Function of a System
- Landau Diamagnetism
- Flux Quantization
- Magnetic susceptibility

14.2 Introduction

In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium. They are functions of temperature and other parameters, such as the volume enclosing a gas. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives. A microstate is a full specification of all degrees of freedom of a system. A system may be conveniently defined as having N degrees of freedom confined to a volume V. In general, microscopic degrees of freedom are quantum numbers.

14.3 The single- Particle Partition Function

If we look at the equation above we notice that the particular term $\sum_i \exp\left(-\varepsilon_i / k_B T\right)$ keeps turning up. We give it a special name- the Partition function denoted by the letter Z, which stands for the German 'Zustandsumme' meaning 'sum over states'. We define,

$$Z = \sum_i \exp\left(-\varepsilon_i \big/ k_B T\right) ----------(1)$$

Strictly speaking, the partition function we have written down is called the single partition function, Z_{sp}, as it is independent of the total number of particles more of this later. For now, let us note an extremely important point: if we know the partition function for a particular system, we then know all of the thermodynamic functions. It is difficult to overstress the importance of this. If you know the formula for the partition function you know everything about the thermodynamics of the system. Consider, to take an example, an ideal gas if we knew the partition function of the gas we could immediately deduce the equation of state and the heat capacity. Lets say we told you that we had an ideal gas, with equation of state PV=RT. Given that information, what is its heat capacity? You might say 3R/2 (if you already knew the heat capacity of a monatomic gas) so the heat capacity (and vice versa); on the other hand as we shall show as we proceed, armed with the partition function of a system. We know everything about it the equation of state, heat capacity, formula for adiabatic expansion etc. The partition function contains all of the thermodynamics. Whilst this is truly remarkable, there is a sense in which we should not be too surprised. In order to construct the partition function we need to know the quantum levels of the system in question and clearly that piece of information must contain all of the pertinent physics. To put it another way, what else is there to know apart from the spectrum of the energy levels?

Let's now write down our thermodynamic function in terms of the single- particle partition function - these are extremely important as they tell us how to get any thermodynamic potential from Z_{sp}.

$$N = AZ_{sp} --------------------(2)$$

$$U = Nk_B T^2 \frac{\partial \ln Z_{sp}}{\partial T} ----------------(3)$$

$$S = Nk_B \ln Z_{sp} + Nk_B T \frac{\partial \ln Z_{sp}}{\partial T} ----------(4)$$

$$F = -Nk_B T \ln Z_{sp} ----------------(5)$$

Note the comparatively simple form of F in terms of Z_{sp}. This is one of the beauties of F, the other main one being that it naturally leads us to the equation of state of the system as we shall see shortly.

14.4 Degeneracy.

Let us make our definition of the single particle partition function a little bit more general. You will recall that when we started out, we made the assumption that each energy level was associated with a different quantum state and on that basis was equally weighted. However we know from our knowledge of Quantum Mechanics that situations can arise when different quantum states both have the same energy: this is known as degeneracy. How do we deal with this? Consider fig (1) where we show an arbitrary system which has three different energy levels. In Fig 1(a) we assume that each energy level has one state associated with it- i.e., is non- degenerate. The partition function is clearly

$$Z_{sp} = \exp\left(-{}^{\varepsilon_1}\!/_{k_B T}\right) + \exp\left(-{}^{\varepsilon_2}\!/_{k_B T}\right) + \exp\left(-{}^{\varepsilon_3}\!/_{k_B T}\right) ---------(6)$$

If we let the second and third energy levels get closer and closer together as shown in Fig 1 (b) they would eventually have same energy. And it would look as though we only had two energy levels, but there would still be three quantum states. The upper level would need to be counted twice as it has two states associated with it (it is now degenerate). This is the important point- it is the quantum states that are the entities that are given equal statistical weight, not the levels. So the partition function would in this case where the upper state is now doubly degenerate and $\varepsilon_2 = \varepsilon_3$, be

$$Z_{sp} = \exp\left(-{}^{\varepsilon_1}\!/_{k_B T}\right) + 2\exp\left(-{}^{\varepsilon_2}\!/_{k_B T}\right) ---------(7)$$

In general, if the energy level ε_i has g_i quantum states associated with it (that is to say it is g_i degenerate) then the single particle partition function is given by

$$Z_{sp} = \sum_i g_i \exp\left(-{}^{\varepsilon_1}\!/_{k_B T}\right) -----------(8)$$

where the sum is over the levels.

It is this form of Z_{sp} that should be used in equation (2) through (5). It should also be obvious that in the presence of degeneracy, the number of particles n_i with energy ε_i is now

$$n_i = A g_i \exp\left(-{}^{\varepsilon_i}\!/_{k_B T}\right) -----------(9)$$

14.5 The Partition Function of a System.

Thus far we have considered the so called single particle partition function, defined as $Z_{sp} = \sum_i g_i \exp\left(-\varepsilon_i / k_B T\right)$ and then worked out thermodynamic potential such as $F = -Nk_B T \ln Z_{sp}$. However it is also possible to define a partition function for the whole system which we denote by Z_N. We assume that the energy level occupied by each of the N particles in the.

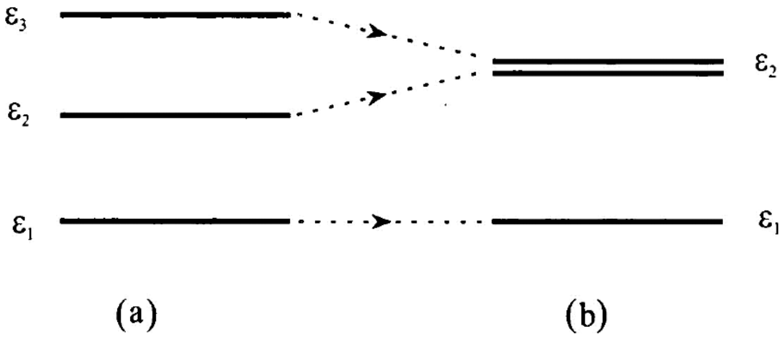


Fig 1(a). Three non-degenerate energy levels. Giving rise to the partition function in equation (6) (b) two of the quantum states now have the same energy, and thus if we sum over energy levels the partition function is now given by equation(7)

system is independent of all the other particles, so that one particles is in say energy level ε_i (which is g_i degenerate), and so on. We can then think of the whole system of N particles being in some energy state, E_m, where

$$E_m = \varepsilon_i + \varepsilon_j + \varepsilon_k + -----,$$

with a degeneracy g_m

$$g_m = g_i \times g_j \times g_k ....,$$

The partition function of the system is therefore

$$Z_N = \sum_m g_m \exp\left(-E_m / k_B T\right)$$

$$Z_N = \sum_i g_i \exp\left(-\varepsilon_i / k_B T\right) \times \sum_j g_j \exp\left(-\varepsilon_j / k_B T\right) \times .... = \left(Z_{sp}\right)^N$$

as there is a total of N terms.

We now can write $F = -Nk_BT\ln Z_N$. Similarly U and S are the same as before apart from the factor of N. Thus, for distinguishable particles

$$Z_N = \left(Z_{sp}\right)^N --------(10)$$
$$U = k_BT^2\frac{\partial \ln Z_N}{\partial T}-----(11)$$
$$S = k_B\ln Z_N + k_BT\frac{\partial \ln Z_N}{\partial T}----(12)$$
$$F = -k_BT\ln Z_N -----------(13)$$

You are probably asking yourself why we bothered to do this. What was wrong with the previous formulae: equations (2) and (5). Well, nothing really: they are totally equivalent to those given above. Whether we use the equation for the single-particle partition function or those for the partition function of the whole system, we will still obtain the same results. However in many ways it is more useful to remember the equation for the partition function for a system. When we go on to deal with indistinguishable (rather than distinguishable) particles that obey Boltzmann statistics we will find that they also obey (11) to (13) and thus we only need to remember one set of equations. However, for indistinguishable particles, there is a difference relationship between the single particle partition function and that for the whole system- i.e., equation (10) does not hold for the indistinguishable particles. Finally even though we have assumed that each particle can occupy different quantized energy levels, this type of statistics is usually referred to as classical statistics. This admittedly somewhat confusing convention is used because even though the particles occupy quantized levels, the way in which we do the counting of number of arrangements is purely classical, because we can tell the particles apart just as we can tell classical billiard balls apart.

14.6 Landau Diamagnetism

Van Leeuwen’s theorem states that the phenomenon of diamagnetism is absent in classical statistical mechanics. Landau first showed how diamagnetism arises from the quantization of the orbits of charged particles in a magnetic field.

The magnetic susceptibility per unit volume of a system is defined to be

$$\chi = \frac{\partial M}{\partial H}----------(14)$$

Where M is the average induced magnetic moment per unit volume of the system along the direction of an external magnetic field ***H***:

$$M=\frac{1}{V}\left\langle -\frac{\partial \mathrm{H}}{\partial H}\right\rangle ------------(15)$$

where H is the Hamiltonian of the system in the presence of an external magnetic field ***H***. for weak field, the Hamiltonian H depends on ***H*** linearly. In the canonical ensemble we have

$$M=kT\frac{\partial}{\partial H}\frac{\log Q_N}{V}---------(16)$$

and in the grand canonical ensemble we have

$$M=kT\frac{\partial}{\partial H}\left(\frac{\log \mathbb{Z}}{V}\right)_{T,V,z}--------(17)$$

where Z is to be eliminated in terms of N by the usual procedure.

A system is said to be diamagnetic if $\chi<0$; paramagnetic if $\chi>0$. To understand diamagnetism in the simplest possible terms, we construct an idealized model of a physical substance that exhibits diamagnetism. The magnetic properties of a physical substance are mainly due to the electrons in the substance. These electrons are either bound to atoms or nearly free. In the presence of an external magnetic field two effects are important for the magnetic properties of the substance (a) the electrons free or bound move in quantized orbits in the magnetic field. (b) the spin of the electrons tend to be aligned parallel to the magnetic field. The atomic nuclei contribute little to the magnetic properties except through their influence on the wave functions of the electrons. They are too massive to have significant orbital magnetic moments, and their intrinsic magnetic moments are about 10^{-3} times smaller than the electron's. The alignment of the electron spin with the external magnetic field gives rise to paramagnetism, whereas the orbital motions of the electrons give rise to diamagnetism. In a physical substance, these two effects compete. We completely ignore paramagnetism for the present, however. The effect of atomic binding on the electrons is also ignored. Thus we consider the idealized problem of a free spinless electron gas in an external magnetic field.

Landau Levels:

The Hamiltonian of a non-relativistic electron in an external magnetic field is

$$H=\frac{1}{2m}\left(\vec{p}+\frac{e}{c}\vec{A}\right)^2-------------------(18)$$

where *e* is positive (i.e., the charge of the electron is –e). The Schrödinger equation $H\psi=\varepsilon\psi$ is invariant under the gauge transformation.

$$\vec{A}(r) \to \vec{A}(r) - \vec{\nabla}\omega(\vec{r})$$
$$\psi(\vec{r}) \to \exp\left[-\frac{ie}{\hbar c}\omega(\vec{r})\right]\psi(\vec{r}) ----------------- (19)$$

where $\omega(\vec{r})$ is an arbitrary continuous function. We consider a uniform external magnetic field ***H*** pointing along the z-axis and choose the vector potential via a gauge transformation if necessary, such that

$$A_x = -Hy, \qquad A_y = A_z = 0 ------------- (20)$$

This is called “choosing the gauge”. The Hamiltonian then reads

$$H = \frac{1}{2m}\left\{\left[p_x - (eH/c)\right]^2 + p_y^2 + p_z^2\right\} ------------- (21)$$

We solve the Schrödinger equation by assuming a wave function of the form

$$\psi(x,y,z) = e^{i(k_x x + k_z z)} f(y) ------------------- (22)$$

where f(y) satisfies the equation for a harmonic oscillator:

$$\left[\frac{1}{2m}p_y^2 + \frac{1}{2}m\omega_0^2(y - y_o)^2\right] f(y) = \varepsilon_0' f(y)$$
$$\omega_o = {}^{eH}\!/_{mc}, \; y_0 = (\hbar c/eH)k_x ----------------- (23)$$

where $\varepsilon' = \varepsilon - {}^{\hbar^2 k_z^2}\!/_{2m}$.The natural frequency of the harmonic oscillator ω_o is the “cyclotron frequency”, that of a classical charge moving in a circular orbit normal to a uniform magnetic field. The energy eigenvalues are thus

$$\varepsilon(p_z, j) = \frac{p_z^2}{2m} + \hbar\omega_0\left(j + \frac{1}{2}\right), \quad (j = 0,1,2..........) ---------- (24)$$

where $p_z = \hbar k_z$.These are the Landau energy levels. Since they are independent of k_x , they have a degeneracy equal to the number of allowed values of k_x such that y_0 lies within the container of the system.

Let us put the system in a large cube of size *L*, and impose periodic boundary conditions. The allowed values of k_x are of the $2\pi n_x/L$, where $n_x = 0, \pm 1, \pm 2, ...$ For y_o to lie between 0 and L, the values of n_x must be positive and bounded by

$$g = (eH/hc)L^2 ----------------(25)$$

which is the degeneracy of a Landau level. The proportionality to L^2 reflects the fact that the projection of the electron orbit onto the *xy* plane can be centered anywhere in the plane without changing the energy. Thus when the external field is turned on, the energy spectrum associated with the motion in the *xy* plane changes from a continuous spectrum to a discrete one and the level spacing and degeneracy increase with the external field. This is illustrated in fig (2)

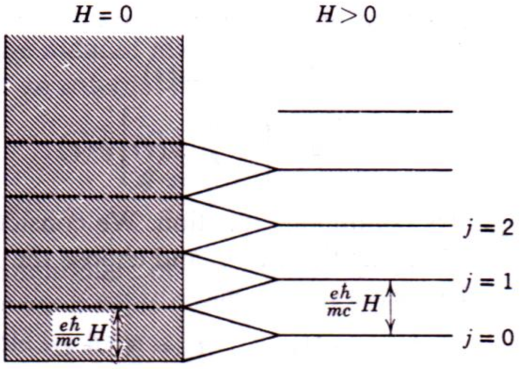


Fig 2: Comparison of the energy spectra of a charged particle with and without magnetic field

14.7 Flux Quantization.

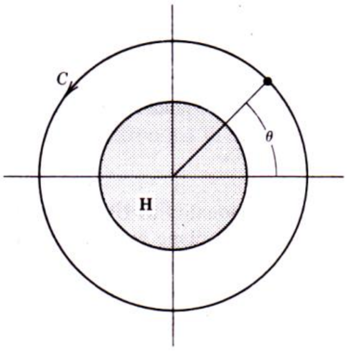
The Landau levels and the degeneracies derived above are all we need to calculate the partition function. However we take the opportunity to discuss flux quantization briefly to help us better understand the wave functions.

Consider a plane with a hole in it, which contains a certain amount of magnetic flux Φ, as shown in fig (3). Suppose there is no magnetic field anywhere else. Then the vector potential in the plane must be “pure gauge”, i.e., of the form.

$$\vec{A} = \vec{\nabla}\omega$$

We cannot transform this to zero through any continuous gauge transformation because necessarily

$$\int_C d\vec{S}.\vec{A} = \Phi ----------(26)$$



Fig(3) charged particle moving in plane with a hole containing magnetic flux. The particle will not notice the flux if either (a) is in a localized state or (b) the flux is quantized in units of hc/e

where the close path C encloses the hole, as indicated in Fig(2). A solution to (26) is

$$\omega = \Phi\theta/2\pi \text{ ---------- } (27)$$

where θ is the angle around the hole measured from some arbitrary axis.

Now consider an electron moving in the plane with the boundary condition that its wave function vanish in the hole. In general it is affected by the flux because the Schrödinger equation involves A**,** which is non zero where the electron moves. But since **A** is pure gauge, we are tempted to try to remove it from the Schrödinger equation through the gauge transformation.

$$\vec{A}(r) \to \vec{A}(r) - \vec{\nabla}\omega(\vec{r})$$

In so doing, the wave function of the electron acquires the phase factor

$$\exp\left(-\frac{ie\omega}{\hbar c}\right) = \exp\left[-i\theta\left(\frac{e\Phi}{hc}\right)\right] \text{ -------- } (28)$$

which is generally unacceptable because it will render the wave function discontinuous in space (for θ increases by 2π each time we go around the hole). The objection is circumvented under either of the following circumstance.

(a) The electron is "localized" i.e., its wave function is non-vanishing only in the neighborhood of some point. In this case where (28) might lead to a discontinuity, the wave function vanishes anyway. This is not relevant to free electrons. But may be relevant, for example, for an electron trapped by an impurity in a metal.

(b) The electron is "extended" with a wave function that is phase-coherent around a closed path about the hole but the flux is quantized in integer multiples of the flux quantum.

$$\Phi_0 = hc/e \text{ ------------ } (29)$$

In this case, (28) becomes a periodic function of θ and represents a legitimate gauge transformation. Thus the vector potential can be transformed away, and the electron does not "know" there is flux through the hole. This is the basis of the Aharanov-Bohm effect and the flux quantization in superconductivity which have been experimentally verified.

The relevance of flux quantization to the Landau levels lies in the fact that the degeneracy (25) is just the total magnetic flux measured in units of the flux quantum:

$$g = \Phi/\Phi_0 \quad ----------(30)$$

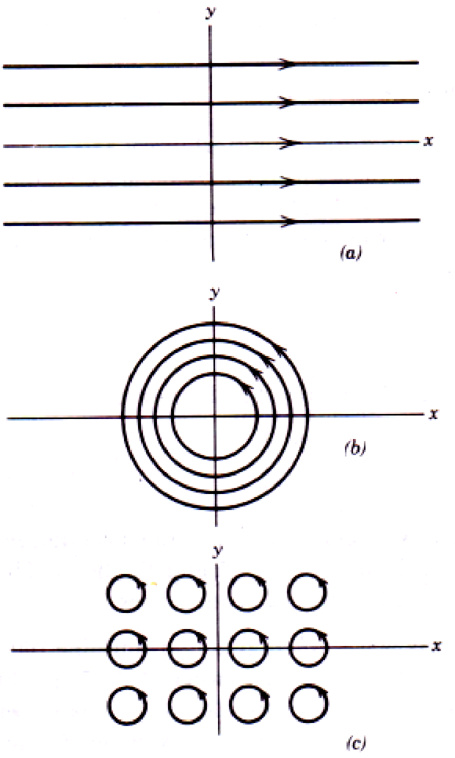


Fig (4) different bases for electron states in a Landau level, which is highly degenerate: (a) member wave functions are peaked at different elevations (y direction) and are eigen states of momentum in the *x* direction (b) member wave functions are eigen states of orbital angular momentum. They are peaked at concentric circles, with equal areas between successive circles. Each ring between circles supports one magnetic flux quantum. (c) Member wave functions are "vortices" of flux quanta forming a lattice.

We have been working in a gauge in which the wave functions have definite linear momentum in the *x* direction. Thus the probability densities are independent of *x* and peaked about parallel ridges at $y=y_0$. The spacing between successive values of y_0 is hc/eHL , and hence the area of the strip in the *xy* plane between two neighboring ridges is hc/eH. Thus exactly one flux quantum hc/e goes through the strip.

Since the energy levels are highly degenerate, we can make linear transformation on the wave functions belonging to the same Landau level to obtain equivalent sets. Such transformations are equivalent to gauge transformations. We can make them Eigen functions of angular momentum about z axis in which case the probability distributions will be peaked about circles in the *xy* plane about the z axis with exactly one quantum of flux going through the annular ring between two successive circles. We can also make them into individual orbitals whose centers form a regular lattice in the *xy* plane. In this case each orbital will link exactly one flux quantum (a “vortex”). These different bases are illustrated in fig (4)

The qualitative fact relevant to our immediate purpose is that the flux quantum sets a finite minimum size of an orbit, and thereby provides the escape from Van Leeuwen’s theorem.

14.8 Magnetic susceptibility:

The grand partition function is

$$\mathbb{Z}=\prod_{\lambda}\left(1+ze^{-\beta\varepsilon_\lambda}\right)------------(31)$$

where λ denotes the set of quantum numbers $\{p_z, j, \alpha\}$ with $\alpha=1\ldots\ldots g$. Thus

$$\log\mathbb{Z}=\sum_{\alpha=1}^{g}\sum_{j=0}^{\infty}\sum_{p_z}\log\left[1+ze^{-\beta\varepsilon\left(p_z,j\right)}\right]$$

$$=\frac{2gL}{h}\sum_{j=0}^{\infty}\int_0^\infty dp\log\left[1+ze^{-\beta\varepsilon(p,j)}\right]--------------(32)$$

The average number of electron is

$$N=\frac{2gL}{h}\sum_{j=0}^{\infty}\int_0^\infty dp\frac{1}{z^{-1}e^{\beta\varepsilon(p,j)}+1}----------------(33)$$

To calculate the magnetization in the classical domain we take the high temperature limit. The condition (32) requires that z→0 to keep N finite. Thus we expand the above equations in powers of z, and retain only the first order term:

$$\log\mathbb{Z}\approx\frac{2zgL}{h}\sum_{j=0}^{\infty}\int_0^\infty dp\,e^{-\beta\left[p^2/2m+\hbar\omega_0(j+1/2)\right]}$$

$$=\frac{zgL}{\lambda}\frac{e^{-x}}{1-e^{-2x}}--------------------(34)$$

where $\lambda=\sqrt{2\pi\hbar^2/mkT}$ *and* $x=\hbar\omega_0/2kT$. We keep only the lowest-order contribution in *x*:

$$\log\mathbb{Z}\approx\frac{zgL}{\lambda}\frac{1}{2x}\left(1-\frac{x^2}{6}\right)=\frac{zV}{\lambda^3}\left[1-\frac{1}{24}\left(\frac{\hbar\omega_0}{kT}\right)^2\right]--------(35)$$

from which follows

$$\chi\approx-\frac{z}{3kT\lambda^3}\left(\frac{e\hbar}{2mc}\right)^2---------------------(36)$$

To eliminate *z*, we note from (33) that to first order in *z*, N is the same as $\log \mathbb{Z}$. Hence

$$\frac{N}{V} \approx \frac{z}{\lambda^3} ------------(37)$$

Solving for *z* and substituting the result into (36), we obtain the final answer

$$\chi \approx -\frac{1}{3kTv}\left(\frac{e\hbar}{2mc}\right)^2 --------------(38)$$

14.9 Let us sum up

After studying this unit we have understand the following aspects;

- The single- Particle Partition Function
- Degeneracy
- The Partition Function of a System
- Landau Diamagnetism
- Flux Quantization
- Magnetic susceptibility

14.10 Key words

Partition function, Degeneracy, Diamagnetism, Flux quantization, Magnetic susceptibility

14.11 Questions for self study

- Define Magnetic susceptibility. Arrive at an expression for the same.
- Write a note on flux quantization.
- Describe Landau Levels in Diamagnetism.
- Discuss the Partition Function of a System of micro particles.
- Write a note on degeneracy.

14.12 Problems:

1. The energy of non-relativistic electrons in a small magnetic field is given by $\varepsilon_{\vec{p},s} = \frac{p^2}{2m} - s\mu_0 B$ where $s = \pm 1$ and μ_0 is the magnetic moment of the electron. Assume $\mu_0 B \ll \varepsilon_F$. Note that in this problem we ignore the effect of the magnetic field on the orbit

of the electron, that turns out to be 0K in first approximation. Evaluate the magnetic susceptibility χ in the following four cases:

a. For T = 0.

b. For $k_B T \ll \varepsilon_F$, one more term beyond (A).

c. For $T = \infty$. (Note: this one you can get without any detailed calculation).

d. For $k_B T \gg \varepsilon_F$, one more term beyond (C).

Solution:

$$N = V\hbar^{-3} \sum_s \int d^3p f_{FD}(\epsilon_{\vec{p},s})$$

$$M = V\hbar^{-3}\mu_0 \sum_s \int d^3p s f_{FD}(\epsilon_{\vec{p},s})$$

We use the first integral to find $\mu(N,V,T)$ *and then the second to find* $M(N,V,T)$. *For low temperature we write the integrals in the following way:*

$$I(T,\mu) = V\hbar^{-3} \int d^3p f_{FD}(\frac{p^2}{2m}, T, \mu)$$

Since the argument of the Fermi-Dirac distribution is given by $\mu - \epsilon = \mu - \frac{p^2}{2m} + s\mu_0 B$, *we can rewrite the expressions for* N *and* M *as:*

$$N = I(T, \mu + \mu_0 B) + I(T, \mu - \mu_0 B)$$

$$M = \mu_0 (I(T, \mu + \mu_0 B) - I(T, \mu - \mu_0 B))$$

Using the fact that B is very small we find up to first order:

$$N = 2I(T,\mu)$$

$$M = 2\mu_0^2 B \left(\frac{\partial I}{\partial \mu}\right)_T (T,\mu)$$

$$\chi = 2\mu_0^2 \left(\frac{\partial I}{\partial \mu}\right)_T (T,\mu)$$

$$\chi = N\mu_0^2 \left(\frac{\partial \log I}{\partial \mu}\right)_T (T,\mu)$$

At $T = 0$ the integral is easy, since $\mu(T=0) = \epsilon_F$:

$$I(T=0,\epsilon_F) = V\hbar^{-3}\frac{4\pi}{3}p_F^3 = V\hbar^{-3}\frac{4\pi}{3}(2m\epsilon_F)^{\frac{3}{2}}$$

with $\epsilon_F = \frac{p_F^2}{2m}$. Hence

$$\chi(T=0) = N\mu_0^2\frac{3}{2}\frac{1}{\epsilon_F}$$

For small T we use $\mu = \epsilon_F - \frac{\pi^2}{12}\frac{k_B^2T^2}{\epsilon_F}$ which was obtained from:

$$N = 2I(T,\epsilon_F - \frac{\pi^2}{12}\frac{k_B^2T^2}{\epsilon_F})$$

Therefore, we have at low temperature:

$$I(T,\epsilon_F - \frac{\pi^2}{12}\frac{k_B^2T^2}{\epsilon_F}) = I(T=0,\epsilon_F) = V\hbar^{-3}\frac{4\pi}{3}(2m\epsilon_F)^{\frac{3}{2}}$$

and taking the derivative with ϵ_F:

$$\left(\frac{\partial I}{\partial \mu}\right)_T (T,\epsilon_F - \frac{\pi^2}{12}\frac{k_B^2T^2}{\epsilon_F})(1 + \frac{\pi^2}{12}\frac{k_B^2T^2}{\epsilon_F^2}) = V\hbar^{-3}\frac{4\pi}{3}(2m\epsilon_F)^{\frac{3}{2}}\frac{3}{2}\frac{1}{\epsilon_F}$$

which gives

$$\chi(T)(1 + \frac{\pi^2}{12}\frac{k_B^2T^2}{\epsilon_F^2}) = \chi(T=0)$$

or

$$\chi(T) = \chi(T=0)(1 - \frac{\pi^2}{12}\frac{k_B^2T^2}{\epsilon_F^2})$$

Large T, looks like Maxwell-Boltzmann

$$N = V\hbar^{-3}\sum_s \int d^3p e^{\frac{1}{k_BT}(\mu - \frac{p^2}{2m} + s\mu_0 B)}$$

$$M = V\hbar^{-3}\mu_0 \sum_s \int d^3p\, s e^{\frac{1}{k_BT}(\mu - \frac{p^2}{2m} + s\mu_0 B)}$$

$$\frac{M}{N} = \mu_0 \frac{\sinh(\frac{\mu_0 B}{k_BT})}{\cosh(\frac{\mu_0 B}{k_BT})}$$

For $T \to \infty$ this is zero. That makes sense, all states are equally probable, independent of B, and hence there is no M as a function of B. Therefore $\chi = 0$. The next order term is:

$$\frac{M}{N} = \mu_0 \frac{\mu_0 B}{k_BT}$$

$$\chi = \frac{N\mu_0^2}{k_BT}$$

14.13 References for further study

- Statistical mechanics: **Kerson Haung**. Massachusetts, Institute of technology, John Wiley and sons Singapore.
- Thermodynamic and Statistical Physics: **J.P Agarwal.**
- Statistical Physics-A survival Guide, by **A.M.Glazer and J.S.Wark,** 2001, Oxford University Press, New York.)

Unit-15: Application of Bose statistics to the photon gas, Derivation of Plank's Law, comments on the rest mass of photon.

15.1 Objectives

After studying this unit you will be able to understand the following aspects;

- Application of Bose statistics to the photon gas
- Deviation of Plank's Law
- Rest mass of photon

15.2 Introduction:

Here we give a brief derivation of thermodynamic properties of electromagnetic radiation thermal equilibrium, which we regarded as gas of photons. We consider photons to be in a container of volume with heat insulating and perfectly reflecting inside walls. Thus the system is isolated and has a definite energy E. because photons do not interact with each other, a very small black body is assumed to be present in the container to absorb and emit photons, thus making thermal equilibrium possible. Photons absorbed at one frequency might be emitted at another and in different numbers to conserve energy, the total number N of photons in the system is not fixed, even thought the system is isolated.

There are two essential respects, then, in which a photon gas differs from a gas of particles with non-zero rest mass. The photons do not interact with each other; so that in the photon gas no approximation is made by neglecting inter particle interaction. The number particle is an isolated system is not conserved.

Every physical body spontaneously and continuously emits electromagnetic radiation. Near thermodynamic equilibrium, the emitted radiation is nearly described by Planck's law. Because of its dependence on temperature, Planck radiation is said to be thermal. The higher the temperature of a body the more radiation it emits at every wavelength. Planck radiation has a maximum intensity at a specific wavelength that depends on the temperature.

Classical physics (statistical thermodynamics) cannot explain the experimentally observed spectra of radiation. Classical physics assumed that radiation is emitted continuously by the matter with smooth continuous spectrum of all possible energy levels.)

Particle or wave: The dual nature allows another description of the electromagnetic waves in terms of particles called photons. As a particle the photon can have a ≥rest mass≤, it can carry energy and momentum. The photon mass is considered to be zero. This conception turns out to be very powerful in building the most significant theory in physics in the same way like so many laws are established on the foundation of a point charge or a point body. In reality we may ask if the mass of proton in rest is really zero, or at least zero within the uncertainties of a real experiment.

Recently, one of the most discussing problems concerns the question about the mass of neutrino. Although the interactions involved are different and therefore totally different experiments are performed, the approach to the answer is the same: looking for evidence that can occur in the case of non-zero mass. As far as the future physics can learn from its history it is important to see how the problem of the photon mass was approached.

Some experiments are made, which results are equivalent to the catching and weighing of a proton. None of them has proved the rest mass to be zero, and indeed such a proof may be impossible. An experiment that fails to find a photon mass does not prove the mass is zero; it merely shows that the mass is less than the limit of accuracy of the experiment. These limits have approached so close to zero, and the most recent values are exceedingly small. One can hope that the next experiments will reveal evidence of a definite, nonzero mass.

` The distribution of energy with wavelength or frequency in case of Black Body Radiation was investigated by Wein, Rayleigh, Jeans and Planck.

Wein's law is based on Classical Thermodynamics and Rayleigh- Jean's law is based on Classical Electromagnetic theory with the application of statistical mechanism.

Now we shall derive Planck's law for distribution of energy with wavelength in case of blackbody radiation on the basis of Bose- Einstein statistics. If we have a hollow enclosure and the walls of which are maintained at a constant temperature T and a small hole is made on the wall of the enclosure. Radiation emitting out will be those which a perfect black body will emit at a Temperature T. These radiations carry energy in discrete units or quanta.

According to quantum theory, radiation of frequency ν has a quantum of energy $h\nu$ where h is Planck's constant and momentum $h\nu/c$ where c is the velocity of light. These quanta are known as photons and can be treated as particles. The radiation inside the hollow enclosure consists of a very large number of photons with different energies as these have different wavelengths or frequencies and supposed to form a photon gas. The distribution of energy among these photons inside the enclosure obeys the laws of statistics. Since the photons have integral spin angular momentum, they obey Bose-Einstein statistics.

Although the total energy of the photons inside the hollow enclosure at a particular temperature T remains constant, the total number of photons within the enclosure may not remain constant. It is impossible that a photon of energy of $2h\nu$ may be dissociated and two photons each of energy $h\nu$ may be emitted. i.e., photons may be created or destroyed. In other words, for a photon gas system

$$\sum_{i=1}^{k} dn_i = 0$$

Therefore the system has to satisfy only one condition, namely- the total energy of system remains constant (or)

$E = n_i\varepsilon_i =$ constant

Or

$$dE = \sum_{i=1}^{k} \varepsilon_i dn_i = 0$$

Now we can say that the black body is the one which absorbs all the radiations falling on it irrespective of the wavelength. Black body appears always black because it neither reflects nor transmits any radiation on its own. But upon heating it to certain temperature T, it emits the radiation which is the characteristics of the temperature T. This radiation is quantised according to quantum theory.

Here the black body may absorb the low energy photons and emit the high energy photons or vice versa implying the total number of particles (or) photons has no relationship with free energy of the system of the system i.e., μ=0

Consider grand canonical partition function and keep μ=0 in it, we get

$$Q_g = \prod_i \left[\sum_{n_i=0}^{\infty} \exp\left(-\frac{\varepsilon_i n_i}{kT} \right) \right] \qquad E_i = \varepsilon_i n_i$$

We know that

$$\sum_{n_i=0}^{\infty} x^n = (1-x)^{-1}$$

$$Q_g = \prod_i \left[1 - \exp\left(\frac{-\varepsilon_i}{kT} \right) \right]^{-1} \qquad -------(1)$$

$$\ln Q_g = \sum_i \ln \left[1 - \exp\left(\frac{-\varepsilon_i}{kT} \right) \right]^{-1}$$

$$\ln Q_g = \sum_i -\ln \left[1 - \exp\left(\frac{-\varepsilon_i}{kT} \right) \right] --------(2)$$

We know that the number of particles in the phase space in the momentum interval between *p* and *p+dp* given by

$$\frac{4\pi V}{h^3} p^2 dp \qquad p = \frac{h\gamma}{c}$$

$$\Rightarrow dp = \frac{h}{c} d\gamma$$

$$\Rightarrow \frac{4\pi V}{h^3} \frac{h^2\gamma^2}{c^2} \frac{h}{c} d\gamma$$

$$\Rightarrow \frac{4\pi}{c^3} \gamma^2 d\gamma ------------(3)$$

The above equation (3) holds well in case of gas molecules obeying Maxwell -Boltzmann statistics.

In case of photon obeying BE statistics, the property of polarization of photons due to their wave character must be taken into account. The photons inside the constant temperature enclosure are of two types.

1) Those having a left-handed polarization

2) Those having a right-handed polarization.

The photons of the first type are indistinguishable among themselves, but can be distinguished from those of the second type on amount of different polarization, similarly for second type of particles. In other words the whole system can be considered to be made up of two subsystems one having photon with left-handed polarization and other having an equal number of photons with right handed polarization. Here is multiplying, because for energy E. There will be two transition modes.

$$\therefore \left.\begin{matrix} the\, number\, of\;\; particles \\ in\;\; p\;\; and\;\; p+dp \end{matrix}\right\} = \int_0^\infty \frac{8\pi V}{c^3}\gamma^2 d\gamma --------(4)$$

$$Also,\ we\ know\ \ \varepsilon_i = h\gamma_i -----------------(5)$$

Substituting equation (4) and (5) in equation (2), we get

$$\ln Q_G = -\frac{8\pi V}{h^3}\int_0^\infty \gamma^2 \ln\left[1-\exp\left(\frac{-h\gamma}{KT}\right)\right]d\gamma --------(6)$$

We know that, the total energy of the system

$$E = kT^2\frac{d}{dt}\left(\ln Q_G\right)$$

$$E = -kT^2\frac{8\pi V}{c^3}\frac{d}{dt}\int_0^\infty \gamma^2 \ln\left[1-\exp\left(\frac{-h\gamma}{kT}\right)\right]d\gamma ------(7)$$

The spectral density of radiation is defined through

$$E = V\int_o^\infty \rho(\gamma,T)d\gamma -------------(8)$$

Here $\rho(\gamma,T)$ is called the spectral density.

From eqn (7) and (8) we can get

$$\rho(\gamma,T) = KT^2\left[-\frac{8\pi V}{c^3}\gamma^2\frac{1}{1-\exp\left(\frac{-h\gamma}{kT}\right)}\times\exp^{\left(\frac{-h\gamma}{kT}\right)}\left(\frac{-h\gamma}{kT}\right)\right]$$

$$= \frac{8\pi}{c^3}\frac{h\gamma^3}{\left(e^{\left({}^{1}\!/\!\left({}^{-h\gamma}\!/\!{}_{kT}\right)\right)}-1\right)}$$

$$\rho(\gamma,T) = \frac{8\pi}{c^3}\frac{h\gamma^3}{e^{{}^{h\gamma}\!/\!{}_{kT}}-1}$$

This equation is Planck’s distribution law

15.3 Quantum to Classical Transition:

Conversion of Quantum to classical equation can be done using Planck's distribution law

Case (i):

$$if \quad \frac{h\gamma}{kT} << 1, \quad e^{\frac{h\gamma}{kT}-1} = \frac{-h\gamma}{kT}$$

$$\rho(\gamma, T) = \frac{8\pi\gamma^2}{c^3} kT --------(9)$$

This is Rayleigh-Jeans formula

Case(ii):

$$if \ \frac{h\gamma}{kT} >> 1, \ e^{h\gamma/kT} - 1 = e^{h\gamma/kT}$$

$$\rho(\gamma, T) = \frac{8\pi}{c^3} h\gamma^3 ----------(10)$$

Equation (10) is found to reach maximum value at a frequency given through the relation

$$\frac{h\gamma_{\max}}{kT} = 2.822 \ \ where \ \ \gamma = \frac{c}{\lambda}$$

$$\frac{hc}{kT\lambda_{\min}} = 2.822 \ or \ \lambda_{\min}T = \frac{hc}{k(2.822)} = constant$$

$$\lambda_{\min}T = constant$$

This is Wein's displacement law

If e(γ,T) is emissivity i.e., the amount of energy coming out per unit area per unit time from the cavity in the black body

$$e(\gamma, T) = \frac{1}{4}\rho(\gamma, T)$$

$$= \frac{1}{4}\frac{8\pi h\gamma^3}{c^3}\frac{1}{e^{h\gamma/KT} - 1}$$

$$e(\gamma, T) = \frac{2\pi h\gamma^3}{c^3}\frac{1}{e^{h\gamma/KT} - 1}$$

The average energy coming out from the black body per unit area per unit time is

$$e(T) = \int_0^\infty e(\gamma, T) d\gamma$$

$$= \int_0^\infty \frac{2\pi h\gamma^3}{c^3}\frac{1}{e^{h\gamma/KT} - 1} d\gamma$$

$$\Rightarrow \frac{2\pi h}{c^3}\int_0^\infty \left(\frac{kT}{h}\right)^3 x^3\left(e^x-1\right)^{-1}\left(\frac{kT}{h}\right)dx$$

$$\Rightarrow \frac{2\pi h}{c^3}\int_0^\infty \frac{x^3}{e^x-1}\left(\frac{kT}{h}\right)^4 dx$$

$$\Rightarrow \frac{\pi^4}{15}\frac{2\pi h}{c^3}\left(\frac{kT}{h}\right)^4$$

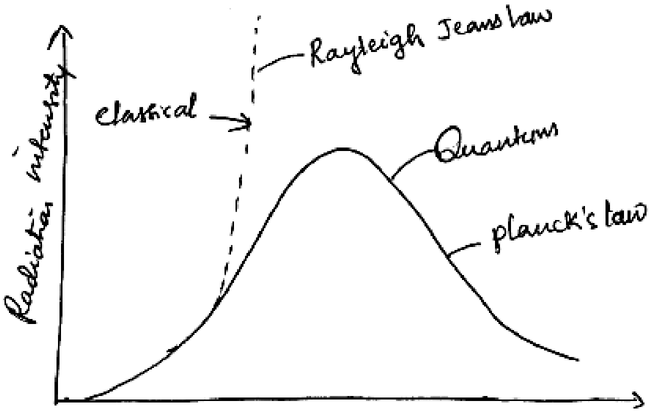
$$e(T)=\frac{2\pi^5k^4T^4}{15h^3c^3}$$

$$or\ e(T)=\sigma T^4 \Rightarrow Stefan's\, law$$

It states that the emissivity of black body is directly proportional to the fourth power of the absolute temperature where

$\sigma=\frac{2\pi^5K^4}{15h^3c^3}$ is called Stefan’s constant

The above equation represents the conversion of quantum to classical statistics equation. The expression from Planck’s radiation law to Stefan-Boltzmann law clearly explains the Quantum to classical transitions.



What is the rest mass of photon? Apply E= γmc^2 to photons (v= c)

$$m=\frac{E}{\gamma c^2}=\frac{E}{c^2}\sqrt{1-\left(\frac{v}{c}\right)^2}=0$$

For a particle with zero rest mass the energy momentum relationship

$$E^2=P^2C^2=\left(mc^2\right)^2\ becomes\ \ E=PC$$

The momentum of the photon is then $P = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda}$

- Meaningless Question since a photon cannot be brought to rest.
- Zero
- $E=mc^2$ and $E=hf$, so $m = {hf}/{c^2}$
- The same as its relativistic mass.
- It must be non zero, since “the Higgs particle gives mass to all particles”

15.4 Let us sum up

In this unit we have understood

- Black body radiation
- Photon gas,
- Planck law
- Wein’s displacement law
- Quantum classical transition
- Rest mass of photons,

15.5 Key words: Photon gas, Planck law Rest mass of photons

15.6 Questions for self study:

- Using BE Statistics derive Planck’s law of black body radiation.
- Show that in the long wavelength limits the Planck’s law leads to Rayleigh-Jean’s law

15.7 Problems:

1. Find the number of photons per mm^3 in a cavity containing black body radiation at 300K.

Solution: Number of photons in a volume V is given by

$$
\begin{aligned}
&N = 2.405 \times 8\pi \left(\frac{kT}{hc} \right)^3 \times V \\
&with, \\
&k = 1.38 \times 10^{-23} J/K,\ T = 300K,\ h = 6.625 \times 10^{-34} Js,\ c = 3 \times 10^8 m/s, \\
&we\,get \\
&N = 546027.26
\end{aligned}
$$

2. How many photons are there in 1cc of radiation at 727^0C temperature? Find their average energy.

given : $\int_0^\infty \frac{x^2}{\left(e^x - 1\right)} dx = 2.405$

Solution: Number of photons per unit volume in the frequency interval $\gamma\ and\ \gamma + d\gamma$ is

$$n(\gamma)d\gamma = \frac{8\pi}{c^3} \frac{\gamma^2 d\gamma}{\left(e^{h\gamma / kT} - 1\right)}$$

Therefore, the total number of photons/unit volume having all frequencies is:

$$N = \int_0^\infty n(\gamma)d\gamma = \frac{8\pi}{c^3} \int_0^\infty \frac{\gamma^2 d\gamma}{\left(e^{h\gamma / kT} - 1\right)}$$

put $x = \frac{h\gamma}{kT}$

$$N = 8\pi \times \left(\frac{kT}{hc}\right)^3 \times 2.405 \times \nabla$$

$$= 8\pi \times \left[\frac{1.38 \times 10^{-23} \times 1000}{6.625 \times 10^{-34} \times 3 \times 10^8}\right]^3 \times 2.405 \times (1 \times 10^{-2})^3$$

$$= 2.017 \times 10^{10}\ photons$$

Also,

Total energy/unit volume $\left[E\right] = \frac{8\pi^5 k^4}{15 c^3 h^3} T^4$

Number of photons per unit volume, $N = 8\pi \times \left(\frac{kT}{hc}\right)^3 \times 2.405$

$$\bar{E} = \frac{E}{N}$$

Now, the average energy of each photon $= \frac{8.96 \times 10^{-13}}{1.6 \times 10^{-12}}$

$$= 0.56\,eV$$

15.8 References for further study:

- Introduction to Statistical Physics: **S.R.A.Salinas.** 2001, Springer, New York.
- Thermodynamic and Statistical Physics: **J.P Agarwal**.
- Statistical Physics-A :**A.M.Glazer** and **J.S.Wark**. 2001, Oxford University Press, New York.

UNIT 16: thermodynamics of black body radiation, Bose-Einstein condensation.

16.1 Objectives

After studying this unit you will be able to understand the following aspects;

- thermodynamics of black body radiation
- Bose-Einstein condensation.

16.2 Introduction:

Thermodynamics of Black body Radiation

A blackbody (sometimes spelled "black body") is a theoretically ideal radiator and absorber of energy at all electromagnetic wavelength s. The term comes from the fact that a cold blackbody appears visually black.

The energy emitted by a blackbody is called blackbody radiation. This takes the form of an electromagnetic field having an intensity-versus-wavelength relation whose graph looks like a skewed, bell-shaped statistical curve. The maximum point on the curve shows the wavelength at which the radiation intensity is greatest. This wavelength depends on the thermodynamic temperature, in Kelvin’s, of the object. The higher the temperature, the shorter the wavelength at which the radiation is most intense. The wavelength and temperature are related by a function involving Wien's constant.

Scientists attempt to determine the temperatures of distant objects in space by observing their blackbody radiation. The calculations are made by assuming that celestial objects behave as perfect blackbodies. A blackbody is a theoretical ideal, but many astronomical objects come reasonably close to this ideal.

Bose-Einstein condensate (BEC), a state of matter in which separate atoms or subatomic particles, cooled to near absolute zero (0 K= -273.15 °C, or − 459.67 °F; K = Kelvin), coalesce into a single quantum mechanical entity—that is, one that can be described by a wave function—on a near-macroscopic scale. This form of matter was predicted in 1924 by Albert Einstein on the basis of the quantum formulations of the Indian physicist Satyendra Nath Bose.

We have already known the various distribution functions of black body radiation, the Planck's distribution, Rayleigh-Jeans formula and Wien's displacement law. Now we calculate the thermodynamic quantities of black body radiation for μ=0(the zero chemical potential makes the free energy F equal to the thermodynamic potentialΩ). The thermodynamic potential Ω_k of the Kth state is:

$$\Omega_k = kT\ln\left(1-e^{(\mu-\varepsilon_k)/kT}\right)$$

Taking μ=0 and summing over all quantum states, we have

$$\Omega = kT\sum_k \ln\left(1-e^{(\mu-\varepsilon_k)/kT}\right)$$

The number of quantum states of the photons with frequency between

$\omega \,\&\, \omega + d\omega \quad is \quad \frac{V\omega^2 d\omega}{\pi^2 c^3}$. Hence the free energy F is

$$F = kT\frac{V}{\pi^2 c^3}\int_0^\infty \omega^2 \ln\left(1-e^{(\mu-\varepsilon_k)/kT}\right)d\omega$$

Putting $x = \hbar\omega/kT$ as a variable of integration, we obtain,

$$F = -V\frac{(kT)^4}{3\pi^2\hbar^3c^3}\int_0^\infty \frac{x^3dx}{e^x-1}$$

This integral can be evaluated with the help of ξ-function and is equal to $\pi^4/15$. Thus,

$$F = -V\frac{\pi^2(kT)^4}{45(\hbar c)^3} = -\frac{4\sigma}{3c}VT^4$$

where,

$$\sigma = \frac{\pi^2 k^4}{60\hbar^3 c^2} = 5.67\times10^{-5}\, {gm}\!\!\diagup\!_{\sec} \quad \deg^4$$

is called the Stefan- Boltzmann constant. The entropy S is

$$S = \frac{\partial F}{\partial T} = \frac{16\sigma}{3c} VT^3$$

Thus entropy is proportional to the cube of the temperature

The total energy of the radiation

E=F+TS

From equation

$$E = \frac{4\sigma}{c} VT^4 = -3F$$

Thus, the total energy of the black body radiation is proportional to the 4th power of temperature.

Boltzmann law the specific heat of the radiation

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{16\sigma}{c} T^3 V$$

C_v is also proportional to the cube Temperature the pressure

$$P = -\left(\frac{\partial E}{\partial V}\right)_T = \frac{4\sigma}{3c} T^4$$

or

$$PV = \frac{E}{3}$$

The total number of photons in the black body radiation is

$$N = \frac{V}{\pi^2 c^3}\int_0^\infty \frac{\omega^2 d\omega}{e^{\hbar\omega/kT} - 1} = \frac{V\left(kT\right)^3}{\pi^2 c^3 \hbar^3}\int_0^\infty \frac{x^2 dx}{e^x - 1}$$

With the help of ξ function given

We have ξ(3) =1.202

$$N = \frac{2\xi(3)}{\pi^2} . \left[\frac{kT}{\hbar c}\right]^3 V = 0.244\left[\frac{kT}{\hbar c}\right]^3 V$$

or

$$N = \frac{\gamma V}{2\pi^2\hbar^3}\int_0^{p_0} p^2 dp = \frac{\gamma V P_0^3}{6\pi^2\hbar^3}$$

$$where \quad \gamma = 2S + 1$$

S is the spin of the electron and hence

$$P_0 = \left(\frac{6\pi^2}{\gamma}\right)^{1/3} \left(\frac{N}{V}\right)^{1/3} \hbar$$

And the limiting energy is $\varepsilon_0 = \frac{P_0^2}{2m} = \left[\frac{6\pi^2}{\gamma}\right]^{2/3} \frac{\hbar^2}{2m}\left[\frac{N}{V}\right]^{2/3}$. This energy has a simple thermodynamic meaning.

The Fermi-Dirac distribution function is

$$f = \frac{1}{e^{(\varepsilon-\mu)/kT} + 1}$$

This tends to zero for $\varepsilon > \mu$ as T→0. The total energy of the gas is obtained by multiplying the number of states $\frac{\gamma V P^2 dp}{2\pi^2\hbar^3}$ *by* $\frac{P^2}{2m}$ *and*

Integrating over all momenta $E = \frac{\gamma V}{4m\pi^2\hbar^3}\int_0^{P_0} P^4 dp = \frac{\gamma V P_0^5}{20m\pi^2\hbar^3}$

Substituting the value of P_0 we have

$$E = \frac{3}{10}\left(\frac{6\pi^2}{\gamma}\right)^{2/3} \frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3} N$$

Now we use the ideal gas relation of pressure P and volume V with energy E, $PV = \frac{2}{3}E$.

This gives

$$P = \frac{1}{5}\left[\frac{6\pi^2}{\gamma}\right]^{2/3} \frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{5/3}$$

These equations are used as approximations for temperature sufficiently close to absolute zero(for given density of gas). The condition of strong degeneracy of the gas requires kT to be small compared with the lowest energy ε_0

$$kT << \frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3}$$

This condition is the condition opposite to the Boltzmann statistics and should be appreciable. The temperature $kT_0 = \varepsilon_0$ is called the degeneracy temperature.

16.3 Bose Einstein Condensation

In 1924 Einstein pointed out that bosons should condense unlimited numbers into a single ground state, since they are governed by Bose- Einstein statistics. For an ideal Bose Einstein gas transitions occur at a certain low temperature above which the atoms distribute themselves on the various energy levels in the usual way but below which a certain fraction of atoms fall into the ground state. This fraction increases from 0 at the transition temperature to unity as temperature approaches absolute zero. This phase transition is known as Bose–Einstein condensation.

When Helium is cooled to a critical temperature of 217K, a remarkable discontinuity in heat capacity occurs. The liquid density drops and a fraction of the liquid becomes a zero viscosity super fluid.

A condensation effect is also credited with producing super conductivity. In the B.C.S theory, the pairs of electron are coupled by lattice interactions and the pairs (cooper pairs) act like Bose and can condense into a state of zero electrical resistance.

The condition for achieving a Bose Einstein condensation is quite extreme. The participating particles must be considered to be identical and this is a condition that is difficult to achieve for whole atoms. The condition of indistinguishability requires that the de- Broglie wavelength of the particles shall overlap significantly and this requires extremely low temperature and also requires fairly high particle density to narrow the gap between the particles.

In general, for fermions and classical gas, the excitation of the particles will be coming down to the ground state gradually when we decrease the temperature of the system. But in the case of Bosons, because the condensation observed, this change takes place very fast.

The average number of particles with energy E_i is given by

$$\overline{n}_i = \left[e^{\frac{E_i - \mu}{kT}} - 1 \right]^{-1} ----------(1) \quad where \ \sum_i n_i = N$$

Replace the summation by integration to know the number of particles whose momentum lies between p and $p+dp$ in phase space

$$\therefore N = \frac{4\pi V}{h^3}\int_0^\infty \left[e^{\frac{\frac{p^2}{2m}-\mu}{kT}} - 1 \right]^{-1} p^2 dp -------(2)$$

where h^3 is the phase cell size

Set μ=0 in equation (2) to find T$_c$

$$\therefore N = \frac{4\pi V}{h^3}\int_0^\infty \left[\exp\left(\frac{\frac{p^2}{2m}-\mu}{kT} \right) - 1 \right]^{-1} p^2 dp -------(3)$$

$$Put, \quad \frac{p^2}{2mkT_c} = x^2 \;\; \& \quad p^2 dp = (2mkT_c)^{3/2} x^2 dx$$

$$\therefore N = \frac{4\pi V}{h^3}\int_0^\infty \left(\frac{1}{e^{x^2}-1} \right) (2mkT_c)^{3/2} x^2 dx$$

$$N = \frac{4\pi V}{h^3}(2mkT_c)^{3/2} \times 2.612 \frac{\sqrt{\pi}}{4}$$

or

$$2mkT_c = \frac{h^2}{\pi}\left(\frac{N}{V \times 2.612} \right)^{2/3}$$

or

$$T_c = \frac{h^2}{2\pi mk}\left(\frac{N}{V \times 2.612} \right)^{2/3} ------(4)$$

Equation (4) is obtained by assuming μ=0 at T=T$_c$.

Now let us consider

$$\varepsilon_i = 0 \, and \, \mu = 0$$

$$N = \int \left[\exp\left(\frac{E_i - \mu}{kT} \right) - 1 \right]^{-1}$$

Because in equation (3) we have included the ground state term, which is to be separate

Consider the integral in equation (3)

$$\int \frac{4\pi V}{h^3}\left[\exp\frac{p^2}{2mkT_c} - 1 \right]^{-1} p^2 dp = 0 ------I$$

$$Here \, E_i = \frac{P^2}{2m} = 0 \;\Rightarrow I = 0$$

$$N = n_0 + \int \frac{4\pi V}{h^3}\left[\exp\left(\frac{\frac{p^2}{2m} - \mu}{KT}\right) - 1\right]^{-1} p^2 dp ----------(5)$$

$$put \quad \mu = 0 \quad in \quad equation\,(5)$$

$$N = n_0 + \int \frac{4\pi V}{h^3}\left[\left(\frac{p^2}{2mkT}\right) - 1\right]^{-1} p^2 dp$$

$$N = n_0 + \frac{4\pi V}{h^3}\left(2mkT\right)^{3/2} \frac{2.612}{4}\sqrt{\pi} ----------------(6)$$

$$But \quad w.k.t \quad from \quad equation\,(4)$$

$$T_c = \frac{h^2}{2\pi mk}\left(\frac{N}{2.612V}\right)^{2/3}$$

$$V = \frac{N}{2.612}\left(\frac{2\pi mkT_C}{h^2}\right)^{-3/2}$$

$$N = n_0 + \frac{4\pi}{h^3}\left(2\pi mkT_C\right)^{3/2} \frac{2.612}{4}\sqrt{\pi} \times \frac{N}{2.612}\left(\frac{2\pi mkT_C}{h^2}\right)^{-3/2}$$

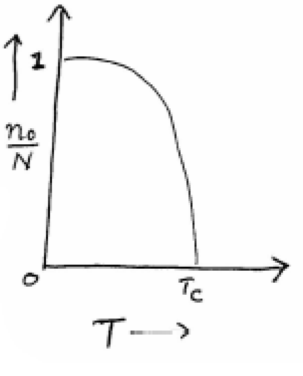
$$N = n_o + N\left(\frac{T}{T_C}\right)^{3/2}$$

$$n_0 = N\left\{1 - \left(\frac{T}{T_C}\right)^{3/2}\right\} --------------(7)$$

$$At\,T = 0; n_0 = N$$

$$At\,T = T_c\,; n_0 = 0$$

Here we see that in the range of temperature $T \ll T_c$ there is a rush of particles towards the ground state and at T=0 the total number of particles will be present at ground state only. This type of phase change in momentum space i.e., from finite to zero momentum state is called Bose-Einstein condensation.



16.4 Let us sum up

In this unit we have understood

- Thermodynamic Black body radiation
- Bose-Einstein condensation

16.5 Key words: Black body radiation, Planck distribution Wein's displacement law, Chemical potential, Fermi Dirac distribution, Bosons

16.6 Questions for self study:

- Explain thermodynamic black body radiation.
- Discuss the Bose-condensation of a system of N bosons occupying a volume V.
- Obtain expression for the transition temperature TBE below which condensation occurs.

16.7 Problems:

1. Black body radiation in a box of volume V and at a temperature T has internal energy $U = \alpha V T^4$ and pressure $P = \frac{1}{3}\alpha T^4$, where α is Stefan- Boltzmann constant

   a) What is the fundamental equation for the black body radiation (entropy)

   b) Compute the chemical potential

Solution:

a) Let us first find the Helmholtz free energy:

From the relation, $P = -\left(\frac{\partial A}{\partial V}\right)_T$ we get ,

A = $-PV = -\frac{1}{3}\alpha V T^4 = -\frac{1}{3}U$

Consequently, $S = -\left(\frac{\partial A}{\partial T}\right)_V = \frac{4}{3}\alpha V T^3 = \frac{4}{3}\frac{U}{T}$

As a result,

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{\partial(S,V)}{\partial(U,V)} = \frac{\partial(S,V)}{\partial(T,V)} \frac{\partial(T,V)}{\partial(U,V)}$$

$$= \left(\frac{\partial S}{\partial T}\right)_V \Big/ \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{T}$$

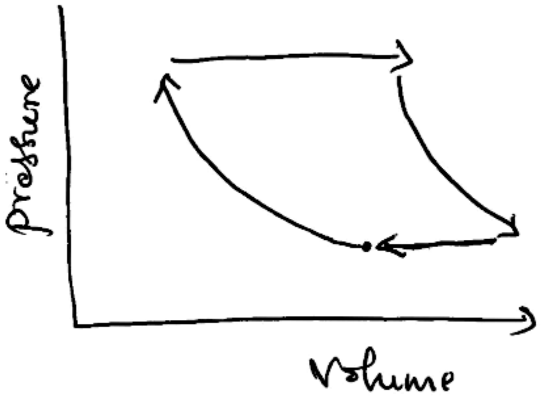
b) Since A is N- independent, $\mu = 0$.

2. Electromagnetic radiation in an evacuated vessel of volume V at equilibrium with the walls at temperature T (black body radiation) behaves like agas of photons having an internal energy $U = \alpha V T^4$ and pressure $P = \frac{1}{3}\alpha T^4$, where α is Stefan- Boltzmann constant

a) Plot a closed curve in the P-V plane for a Carnot cycle using black body radiation
b) Derive explicitly the efficiency of Carnot engine which uses a black body radiation as its working substance

Solution:

a) The plot of Carnot cycle with black body radiation is:



b) Let us start with isotherms. At the isotherm, the pressure is V-independent. Thus the isotherms are horizontal. See the figure. Along the first isotherm path

$$Q_{1\to 2} = \Delta U + P\Delta V = \frac{4}{3}\alpha T_h^4 (V_2 - V_1)$$

$$= \frac{4}{3}\alpha T_h^4 V_1 \left[\frac{V_2}{V_1} - 1\right] \qquad (1)$$

In a similar way,

$$Q_{3\to 4} = \frac{4}{3}\alpha T_h^4 V_4 \left[1 - \frac{V_3}{V_4}\right] \qquad (2)$$

Now, let us consider an adiabatic path. Along an adiabatic path,

$$dQ = 0 = dU + PdV = 4\alpha VT^3 dT + \alpha T^4 dV + \frac{1}{3}\alpha T^4 dV$$

$$= 4\alpha VT^3 dT + \frac{4}{3}\alpha T^4 dV$$

Consequently,

$$\frac{dT}{T} = -\frac{1}{3}\frac{dV}{V} \rightarrow VT^3 = \text{constant}, \ PV^{4/3} = \text{constant}.$$

Let us start from the point 2 characterised by the values P_1, P_2 and adiabatically expand the gas to the point 3 characterised by the volume V_3. We have,

$$V_2 T_h^3 = V_3 T_c^3; \ \textit{and} \ V_1 T_h^3 = V_4 T_c^3$$

$$\Rightarrow \frac{V_2}{V} = \frac{V_1}{V_4} = \frac{T_c^3}{T_h^3} \qquad (3)$$

Combining (1), (2) and (3), we get

$$\Delta W = \Delta Q_{1\to 2} + Q_{3\to 4} = \frac{4}{3}\alpha T_h^4 V_1 \left(\frac{V_3}{V_4} - 1\right)\left(1 - \frac{T_c}{T_h}\right)$$

Remember: along a closed path $\Delta U = 0$ and the total heat consumption is equal to mechanical work on the

$$Q_{1\to 2} = \frac{4}{3}\alpha T_h^4 V_1 \left[\frac{V_2}{V_1} - 1\right]$$

As a result:

$$\eta = \frac{\Delta W}{\Delta Q_{1\to 2}} = \frac{T_h - T_c}{T_h}$$

16.8 References for further study:

- Thermodynamics, kinetic theory and statistical mechanics, 3rd Ed., by **F.W. Sears and G.L. Salinger**, 1986, Narosa, New Delhi .
- Statistical mechanics, **K.Huang,** Wiley-Eastern, 1975, New Delhi.
- Thermodynamic and Statistical Physics- **J.P Agarwal**.
- Statistical Physics-A survival Guide, by **A.M.Glazer and J.S.Wark,** 2001, Oxford University Press, New York.).
- Statistical Physics : Berkeley Physics Course Volume 5. **F Reif** (Tata McGraw-Hill Company Ltd, 2008