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Element of Statistical Physics

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Forward

The book Elements of Statistical Physics is a textbook intended for undergraduates and graduates. Statistical Physics is a very important part of Physics that is intellectually and mathematically demanding. The conceptual and mathematical problems associated with statistical Physics were tackled by the authors by scaling down the mathematical expressions used. Numerous worked examples were provided in the text to enhance appreciation of the subject matter. The book will also serve as a quick reference material for higher level and postgraduate courses in Statistical Physics.

Prof. P.N. Okeke, FAS

PREFACE

Statistical physics with classical and quantum mechanics forms the present day theoretical training for undergraduate and graduate physicists. A thorough grounding in these subjects is a requirement for more advance or specialized training. The mathematical tools utilized include statistics, ordinary and partial differential equations.

The book is intended for both under graduates and beginning foundation for graduates.

The book begins in the traditional manner with the concept of thermodynamics coupled with involvement of partial derivatives necessary to handle thermodynamic variables. Chapter 2 and 3 are continuation of thermodynamics chapter 4 introduces the statistical physics bringing into focus the basic concept of statistical distributions and theory identical particles is presented chapter 6 and 7 illustrate Bose-Einstein condensation and Liouville's theorem and finally chapter 8 where the application of statistical physics to information theory is presented. This book is the outgrowth of an undergraduate and graduate lecture notes which I have used in teaching for over nine years at Ebonyi State University. I wish to especially thank those whose have always encouraged me to keep on working hard.

E.I. Ugwu
Ebonyi State University, 2018.

CONTENTS

CHAPTER ONE

CONCEPT OF THERMODYNAMICS

A physical system under study here usually consist of a large number of atoms or molecules of order 10^{23} and 50 has a large number of dynamical

variables involved this we combine the atomic and the molecular concept with the method of mathematical statistics and probability theory to obtain average values of measurable quantities of the system. In statistics, we are familiar with the concept of distribution function [F]. Thus if T_i represents

the number of times an items xi occurs in the system, then the mean $\bar{x}$ is

given by

$$\bar{x} = \frac{\sum T_i x_i}{\sum T_i} \qquad 1.1$$

This idea of distribution function is used in statistical mechanic to obtain the average values of measurable quantities usually done by replacing $\sum$ sign with integral sign.

The statistical mechanics is based on classical statistics and is thus called classical statistical mechanic. The energy of the system in this case is constant, but is a continuous function of position, x and momentum, p.that

is

$$\left.\begin{array}{l} H(x,p) = E \text{ or} \\ H(q,p) = E \end{array}\right\} \qquad 1.2$$

Where q is a generalised position vector and H is the total Harmiltonian

[total energy] of the system is momentum. The energy quantized and is

usually obtained by solving Schrödunger equation.

$HV_i = \varepsilon_i \Psi_i$ where $i = 1,2,3,4 \cdots N$ of the system. For any observable physical quantities $A$the quanties mechanical values of Acan be expressed by using the equation.

$$Aobs = \int \phi_i^* A\phi_i dT \qquad 1.3$$

In statistical mechanics, $\bar{n}$s the distribution. The normalised form of the expression is

$$Aobs = \bar{A} = \sum A_i T_i = \int A(P)\ dT \qquad 1.4$$

Where P is the phase space variable with co-ordinate $[x, p]$ or $[q, p]$ where $[x, y, z]$

The subject thermal physics introduces one more fundamental quantity in mechanic which is temperature. The temperature is given as the degree of hotness and coldness of a body. The temperature of a body is usually measure with thermometer. Thus the quantity of temperature is a necessary conditions two systems. A body which is in thermal equilibrium has the same temperature everywhere. Two bodies which are maintained in thermal contact for a long time will achieve temperature. So this has led R H. Fowler to propose the so called Zeroth law of thermodynamic. This law can be stated as follows: there exist property called temperature which defines the thermodynamics state of a body and equality of temperature is a condition for thermal equilibrium between two system or between 2 parts of a single all the bulk physical properties of the system are uniform throughout the system and do not change with temperature.

Definition. If each of two systems is in thermal equilibrium with a third, they are in thermal equilibrium with one another.

Generalized concept of work

In thermodynamic, work done $\delta\omega$ is always formulated as the product of two

terms, namely an intensive variable or properties which is a generalized force and as an extensive variable or property which is a generalised displacement. Such a formulation will include non-mechanical system e.g chemical, electrical and magnetic system etc. A property that is independent of mass is called on intensive property or variable. Examples are Temperature, pressure and density. An extensive variable or property is a variable that is proportional to the mass of the system example total energy of the system, volume, vNow for mechanical system of element of work

$$\delta\omega = f\delta x$$

But pressure, $p = {}^{F}/_{A}$

$\therefore d\omega = Pdv$ 1.5

Fig 1.1 Work done on by a mechanical system

In thermodynamics, work done by the system correspondent to an expression of gas or fluid and is given a positive sign by convection. Note that in this case pressure p and volume expansion $du$are in opposite direction. However work done on the system to the system correspond to a compression and is given a negative sign by convection. Note that pressure p and volume v expansion are in the same direction

$d\omega_{by} = PdV$ 1.6

$d\omega_{on} = -PdV$ 1.7

On the other hand, other forms of work in thermodynamic are

(i) Surface tension in which case

$d\omega = -TdA$ 1.8

where both T and dA are acting in the same direction and hence it has a negative sign

(ii) Electrical type of work, which case $d\omega = -\varepsilon dq$ where $\varepsilon \sim f$ and dq is element of change.

(iii) Magnetic type of work $dw = -HdM$ $H =$ magnetic filed, $dm =$ element magnetic moment.

Heat capacity

An important quantity in the thermodynamics is the heat capacity of a body. It is defined as quantity of heat absorbed by the body divided by the corresponding increase in the temperature ΔT

$$C = \lim_{\Delta T \to o} \left(\frac{\Delta Q}{\Delta T}\right) = \frac{dQ}{dT} \qquad 1.9$$

The specific heat capacity is the heat capacity per unit mass

$$c = \frac{C}{M} = \frac{I}{M}\frac{dQ}{dT} \qquad 1.10$$

However, specific heat capacity of a gas or fluid has unique value only the volume and pressure are specified. There we define the specific heat capacity at constant pressure as

$$C_v = \left(\frac{dQ}{dT}\right)_V \qquad 1.11$$

And that at a constant pressure as

$$C_p = \left(\frac{dQ}{dT}\right)_p \qquad 1.12$$

NB we have avoided the use of partial derivate in these definitions because dQ is not a function of state like in the internal energy u.

1.2.1 Equation of States

An equation of states in thermal physics is a functional relationship between pressure p, volume v and temperature T which exist for any solid, liquid or gas e.g Real gas equation. By rearrangement, we can always write equation of state as $f(P,V,T) = 0$. Thus if you know or measure any of the two variables, can determine the third variable with the equation of the state e.g from

$$F(P,V,T) = 0 \qquad 1.13$$

We can get $P = f(VT), V = f(P, P) = 0$ more generally on equation of state include the mass M as a variable i.e

$$f(P, V, T, M) = 0 \qquad 1.14$$

Equation of state are usually obtained experimentally, theoretically or semi empirically for example of state for an ideal gas

$$PV = RT = \cap RT \qquad 1.15$$

ii. Vander weal equation of state which was obtained semi empirically.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad 1.16$$

These are attempting to get equation of state that fit real gas behaviour. The real gas equation is good for low pressure regions while Vander weal equation is good for high pressure region especially near the critical point. Diotericis is satisfactory for moderate pressure while Berthelot's equation agrees better with the experiment at ordinary pressure, but fails for high pressure.

1.2.3 First law of thermodynamics

The first law of thermodynamics is just a generalization of principle of conservation of energy to embrace heat which gives the idea that

1. Total energy of a closed system always remains constant.
2. It can be state in another form, i.e when Q is supplied to a system, it increases the internal energy [] of the system and in addition; work is done by the system [] i.e

= increase in internal energy + work done by the system.

$$= [\ -\ ] + \qquad 1.17$$

Where all the quantities are of the same unit. Internal energy means the kinetic energy of the system and the potential energy due to attraction between the molecules. Also this quantity, work done can be mechanical or any other form of work including electrical, magnetic etc.

In differential form, the first law can be written as $= +$. this expression

implies the quantity is not perfect differential and depends on the part taken.Thequantities

And are path variable i.e is a function that depends on the path taken, whereas a function

which is a perfect differential is called a state variable because it is a function that only depend on initial and final stages of the system and is independent of the path through which the process occur. Other quantities that have similar behaviour in terms of path independent are temperature, ,

pressure, and volume, .

1.3.3 .0 Partial Derivative

For a better understanding of some of the thermodynamic variables, such as state variable , knowledge of partial derivatives that will bring a clear picture of some useful relation involve partial derivative the understanding for instance, we can analogously of the concept of source relations between the partial derivatives of three variables satisfying the relation $(,,) = 0$.

Now,

Suppose solve for and for obtaining $= {}_1(,), = {}_2(,)$

Then $f_1(y, z)$ and $f_2(x,z)$ 1.13

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz, \quad \cdots \qquad 1.14$$

Eliminating

by equation 1,13 1,14

From (1.13) $dx = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial x}{\partial z}\right)_x dz\right] + \left(\frac{\partial x}{\partial z}\right)_y dz$

$$dx - \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx = \left(\frac{\partial x}{\partial z}\right)_x \left(\frac{\partial y}{\partial y}\right)_z dz + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$dx = \left[1 - \left(\frac{\partial x}{\partial y}\right) z \left(\frac{\partial y}{\partial x}\right)_z\right] = \left[\left(\frac{\partial y}{\partial z}\right) z \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y\right] dz$$

Suppose $dz = 0, dx \neq 0$

$$1 - \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 0 \qquad 1.15$$

$$\therefore \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\partial y / \partial x\right)_z} \qquad (1.16)$$

Similarly when $dx = 0, dz \neq 0$

$$\left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y = 0, \qquad 1.17$$

From (4) $\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)^y / \left(\frac{\partial y}{\partial z}\right)_x$

Putting it in equation (1.15)

$$-\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial y}{\partial x}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_x} \Rightarrow -\left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_z = 1.$$

$$\Rightarrow \left(\frac{\partial x}{\partial z}\right)_y\left(\frac{\partial z}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_z = 1 \qquad 1.18$$

These equations are readily verified for an ideal gas. Let $x = p, y = v\ z = T$

$$F(P,V,T] = 0\ i.e\ f(x,y,z) = 0$$

Then

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial T}{\partial P}\right)_V = \left[\frac{\partial}{\partial P}\left(\frac{PV}{V}\right)\right]_V = \frac{V}{R}, \qquad 1.20$$

$$\left(\frac{\partial x}{\partial z}\right)_y = \left(\frac{\partial P}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\left(\frac{RT}{V}\right)\right]_V = \frac{R}{V} \qquad 1.21$$

$$\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{RT}{V}\right)\right]_V = -\frac{RT}{V^2} \qquad 1.22$$

$$\left(\frac{\partial y}{\partial z}\right)_x = \left(\frac{\partial V}{\partial T}\right)_p = \left[\frac{\partial}{\partial T}\left(\frac{RT}{P}\right)\right]_p = \frac{R}{P}$$

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{R}\cdot\frac{RT}{V^2}\cdot\frac{R}{P} = -1$$

$$= -\frac{RT}{PV} = -1 \qquad 1.23$$

$$\Rightarrow \frac{RT}{PV} = 1$$

To prove that $\frac{PV}{RT} = 1$

Since

$f[T,P,V] = 0,$

we differentiate partially.

$$\left(\frac{\partial T}{\partial P}\right)_V = \left[\frac{\partial}{\partial P}\left(\frac{PV}{R}\right)\right]_V = \frac{V}{R}, \qquad (1.24)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left[\frac{\partial}{\partial T}\left(\frac{RT}{V}\right)\right]_V = \frac{R}{V} \qquad (1.25)$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(\frac{RT}{V}\right)\right]_T = -\frac{RT}{V^2} \qquad (1.26)$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \left[\frac{\partial}{\partial T}\left(\frac{RT}{P}\right)\right]_p = \frac{R}{P} \qquad (1.27)$$

Since

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

$$\therefore \frac{V}{R} \times -\frac{RT}{V^2} \times \frac{R}{P} = -1$$

$$\frac{RT}{VP} = 1$$

$$\therefore \frac{PV}{RT} = 1$$

Compare the $T - S$ curve and $P - V$ curve

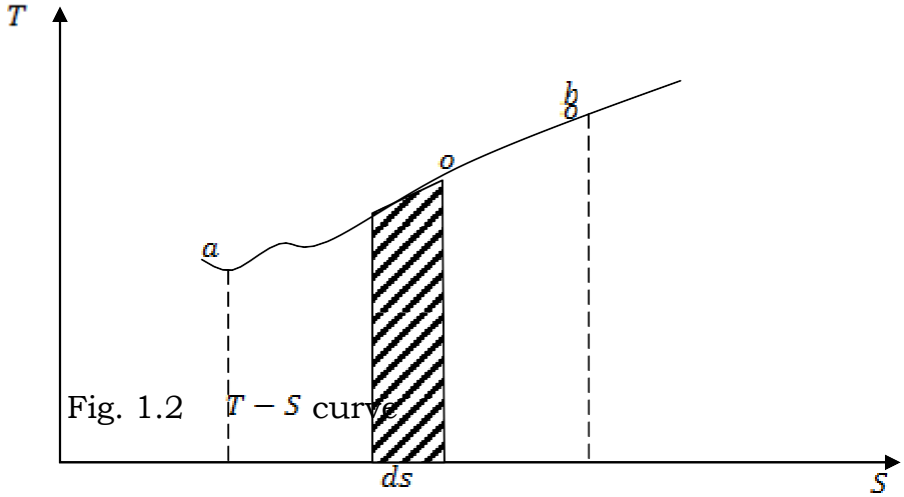


Fig. 1.2 $T - S$ curve

From second law, $\eth\theta = du + pdv$ where the work done is $\partial Q = PdV$ From entropy view point as a state function; $\eth Q = TdS$ which is the shaded area in equal to the heat taken during the process.

$$\therefore \int dQ = \int_a^b T\partial S \Rightarrow Q = \int_a^b TdS = \frac{Q}{T} = S_b S_a \qquad 1.28$$

Where the integral limit from a to b is the total area under the curve. From $P - V$ diagram

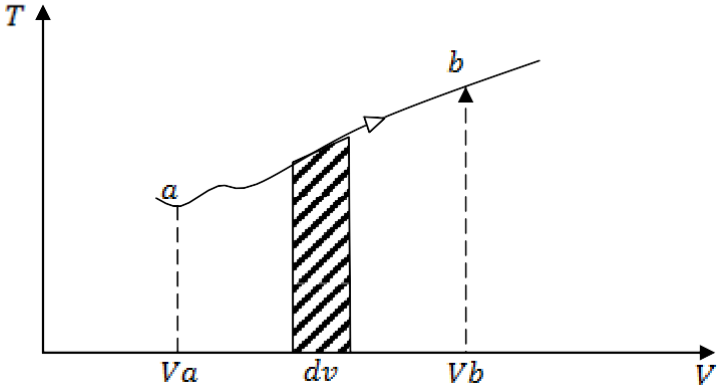


Fig.1.3 $P-V$ diagram

Similarly, the work done in the system or process

$$\partial w = PdV \text{ or}$$

$\partial Q = PdV$

$\therefore w = \int PdV$

$\Rightarrow w = \int_{V^a}^{V_b} PdV = \int_{V_a}^{V_b} \frac{RT}{V} dV = RT \ln\left(\frac{V_b}{V_a}\right)$ 1,29

Here also the work done by the system or during the process in the integral over the volume from a to b. Hence they compares with each other.

Taking T and V as an independent variable let $u = u(T,V)$

$$du = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV \qquad 1.30$$

From the 1st law of THD

$$\partial Q = du + PdV \qquad 1.31$$

$$\partial Q = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dv + PdV \qquad 1.32$$

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

At a constant volume

$$du = 0, \partial Q = c_v dT$$

$$\therefore c_v dT = \left(\frac{\partial u}{\partial T}\right)_V dT \Rightarrow c_v = \left(\frac{\partial u}{\partial T}\right)_T \qquad 1.33$$

Substituting in (1.13)

$$\partial Q = c_v dT + \left[\left(\frac{\partial u}{\partial V}\right)_T + P\right] dV \qquad (1.34a)$$

considering next the process at a constant pressure

$$CpdT_p = c_v dT_p + \left[\left(\frac{\partial u}{\partial V}\right)_T + P\right] dVp$$

$$Cp = c_v + \left[\left(\frac{\partial u}{\partial V}\right)_T + P\right]\left(\frac{\partial u}{\partial T}\right)_p \qquad (1.34b)$$

For a reversible adiabatic process $\eth Q = 0$ hence equation (2) becomes

$$CvdT = -\left[\left(\frac{\partial u}{\partial V}\right)_T + P\right] dV \qquad (1.35)$$

The change in the state variable in such a process will be designated by subscript because the change in entropy for such process remains constant

$$CvdTs = -\left[\left(\frac{\partial u}{\partial V}\right)_T + P\right] dV$$

$$cv\left(\frac{\partial u}{\partial V}\right)_S = \left[\left(\frac{\partial u}{\partial T}\right)_T + P\right] \qquad (1.36)$$

Using expansively and compressibility $\beta \& K$

Where $\left(\frac{\partial u}{\partial T}\right)_p = \beta V$ and $\left(\frac{\partial u}{\partial T}\right)_T = UK$ from equation ()

$$Cp - Cv = \left[\left(\frac{\partial u}{\partial V}\right)_T + P\right]\left(\frac{\partial u}{\partial T}\right)_p$$

$$\frac{Cp - Cv}{\left(\frac{\partial u}{\partial T}\right)_T} = \left(\frac{\partial u}{\partial V}\right)_T + P$$

$$\left(\frac{\partial u}{\partial V}\right)_T = \frac{Cp - Cv}{\beta V} - P$$

From equation (1.36)

$$Cv\left(\frac{\partial T}{\partial V}\right)_S = -\left[\left(\frac{\partial u}{\partial V}\right)_T + P\right]$$

$$Cv\left(\frac{\partial T}{\partial V}\right)_S = \frac{Cp - Cv}{\beta V} - P + P$$

$$Cv\left(\frac{\partial T}{\partial V}\right)_S = \frac{Cp - Cv}{\beta V}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = \left[\frac{Cp - Cv}{BVCv}\right] \quad 1.37$$

Taking T and P as an independent A_2 variable

$$u = u[T,P], V = V[T,P]$$

$$du = \left(\frac{\partial u}{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T + dP \quad ; \quad dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T + dP$$

$$\partial Q = \left(\frac{\partial u}{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T + P\left[\left(\frac{\partial u}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial P}\right)_T\right] dP$$

Collecting terms

$$\partial Q = \left(\frac{\partial u}{\partial T}\right)_P dT + P\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial P}\right)_T dP \quad 1.38$$

$$Q = \left[\left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left[\left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP \quad (1.39a)$$

for isobaric process $dP = 0$

$$\partial Q = \left[\left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT \quad (1.39b)$$

also $CpdT = \partial Q$

$$\therefore CpdT = \left[\left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT \Rightarrow Cp = \left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \quad (1.40)$$

From equation (1.39)

$$\partial Q = CpdT + \left[\left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP \quad (1.41)$$

$\Rightarrow CvdT = CpdT + \left[\left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP$ at a constant volume.

$$\therefore c_v - c_p = \left[\left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V \quad (1.42)$$

For adiabatic process $\partial Q = 0$ hence from (1.40)

$$CpdT = -\left[\left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]dP$$

$$Cp = -\left[\left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V \qquad (1.43)$$

$$= -\left[\left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]\frac{\partial P}{\partial T}$$

From equation (1.42)

$$Cp = \left(\frac{\partial u}{\partial P}\right)_T + P\beta V \Rightarrow \left(\frac{\partial u}{\partial T}\right)_p = Cp - P\beta V \qquad (1.44)$$

From equation (1.43) $\left(\frac{\partial u}{\partial P}\right)_T = \frac{CV-CP}{dP/_{dT}} - P\left(\frac{\partial V}{\partial P}\right)_T$

$$\left(\frac{\partial u}{\partial P}\right)_T = \frac{c_v - c_p}{\left(\partial P/_{dT}\right)_V} - PKV \qquad (1.45)$$

From the relation

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

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p / \left(\frac{\partial V}{\partial P}\right)_T = +\frac{K}{B}$$

Hence substituting in equation 6 for the value of $\left(\frac{\partial P}{\partial T}\right)_V$.

$$\left(\frac{\partial u}{\partial P}\right)_T = \frac{c_v - c_p}{-B/_K} - PKV \Rightarrow \frac{K}{B}(c_p - c_v) - PKV$$

From equation (1.43)

$$c_p\left(\frac{dT}{dP}\right)_S = -\left(\frac{\partial U}{\partial P}\right)_p + P\left(\frac{\partial V}{\partial P}\right)_T$$

$$c_p\left(\frac{\partial T}{dP}\right)_S = -\left[\left\{\frac{K}{\beta}(c_v - c_p\ ) - PKV\right\} + PKV\right]$$

$$= \frac{K}{\beta}(c_v - c_p) \Rightarrow \left(\frac{\partial T}{dP}\right)_S = K\frac{c_v - c_p}{\beta c_p}$$

Taking $P\ and\ V$ as an independent variable

$U = U(P,V)$

$$du = \left(\frac{\partial u}{\partial P}\right)_V dP + \left(\frac{\partial u}{\partial V}\right)_p dV$$

From first law of THD.

$$\partial Q = du + PdV \quad 1.45$$

$$\partial Q = \left(\frac{\partial u}{\partial P}\right)_V dP + \left(\frac{\partial u}{\partial V}\right)_p dV + PdV$$

$$\partial Q = \left(\frac{\partial u}{\partial P}\right)_V dP + \left[\left(\frac{\partial u}{\partial V}\right)_p + P\right] dV \qquad (1.46)$$

for a constant volume process

$$\partial Q = \left(\frac{\partial u}{\partial P}\right)_V dP \qquad c_v dT = \partial Q \qquad 1.47$$

$$\partial Q = c_v dT + \left[\left(\frac{\partial U}{\partial V}\right)_p + P\right] dV$$

$$CvdT = \left(\frac{\partial U}{\partial P}\right)_V dP$$

$$c_v = \left(\frac{\partial U}{\partial P}\right)_V \left(\frac{\partial P}{\partial T}\right)_V$$

So that

$$\left(\frac{\partial U}{\partial P}\right)_V = \frac{c_v}{\left(\frac{\partial P}{\partial T}\right)_V} \qquad 1.48$$

Where $\left(\frac{\partial P}{\partial T}\right)_V = {}^{B}/_{K}$

$$\left(\frac{\partial U}{\partial P}\right)_V = \frac{c_v}{{}^{B}/_{K}} = \frac{Kc_v}{B}$$

$$\left(\frac{\partial U}{\partial P}\right)_V = \frac{Kc_v}{B}$$

At a constant pressure,

$$\partial Q = \left[\left(\frac{\partial u}{\partial V}\right)_p + P\right] dV$$

$$CpdT = \left[\left(\frac{\partial u}{\partial P}\right)_p + P\right] dV$$

$$Cp = \left[\left(\frac{\partial u}{\partial V}\right)_p + P\right]\left(\frac{\partial V}{\partial T}\right)_p$$

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

$$\frac{Cp}{BV}\left(\frac{\partial u}{\partial V}\right)_p + P$$

$$\left(\frac{\partial u}{\partial V}\right)_p = \frac{Cp}{\beta v} - P \Rightarrow \frac{Cp - p\beta v}{\beta V} \qquad 1.49$$

At a constant volume as from the previous equation

$$\partial Q = \left(\frac{\partial u}{\partial P}\right)_V + dP$$

$$and\ cPdT = \partial Q$$

$$\therefore CpdTs = \left(\frac{\partial u}{\partial P}\right)_V dPs$$

$$Cp = \left(\frac{\partial u}{\partial P}\right)_V \left(\frac{\partial P}{\partial T}\right)_S$$

$$\left(\frac{\partial u}{\partial P}\right)_V = {Cp}\Big/{\left(\frac{\partial T}{\partial P}\right)_S} \qquad (1.50)$$

From the relation

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

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{-1}{\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p} \qquad (1.51)$$

Putting equation (1.51) in (1.50)

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-1}{\left({\partial V}/{\partial P}\right)_V \Big/ {c_p}\left(\frac{\partial V}{\partial T}\right)_p}$$

But $\left(\frac{\partial U}{\partial P}\right)_V = \frac{Kc_v}{\beta}$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-c_p}{\frac{Kc_v}{\beta} \times \beta V}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-c_p}{Kc_v V}$$

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

Example 1

For the system A, the increase in entropy of $1ky$ of water when heat from 273^0K to 323^0K is $S_2 - S_1 = MC \lim \left({}^{T_2}/_{T_1} \right)$

$$= 1 \times 4.19 \times 10^3 \ln\left(\frac{323}{273}\right)$$

$$= 4.19 \times 10^3 \times 0.16818052$$

$$A \quad = 70531^0C$$

For system B, the entropy change is

$$S_2' - S_1' = MC \ln\left(\frac{323}{273}\right)$$

$$= 1 \times 4.19 \times 10^3 \ln(0.8659512)$$

$$B \quad = -603.131^0C$$

The entropy decreases the net change in entropy $= A + B$

$$= 705 - 603.1 = 101.931^0C$$

i For ice, change in entropy

$$S_2 - S_1 = \frac{ML}{T} = \frac{20 \times 80}{273} = 5.861 cal/0_C$$

ii For the water the entropy change is

$$S_2' - S_1' = MC \ln\left(\frac{T_2}{T_1}\right)$$

Since the temperature finally remained unchanged, the entropy change is zero

$i.e\ S_2' - S_1' = 0$

∴ Net gain in entropy is $5.861 calorie$

Example 2

Show the between (P, V)

From equation of state,

$PV = RT$

$PdV + VdP = RdT$ (1)

From the equation of state $ðQ = du + PdU$ for an adiabatic procen,

$dQ = 0$

$\therefore du = -pdv$

Where $du = CvdT$

$\therefore CvdT = -PdV$ (2)

$\therefore CvdT = VdP$ (3)

Therefore dividing equation (3) by (2)

$$\frac{CpdT}{CvdT} = \frac{-VdP}{PdV}$$

$$\frac{CP}{CV} = \frac{-V}{P}\frac{dP}{dV}$$

$$\gamma \int \frac{dV}{V} = -\int \frac{dP}{P}$$

$\gamma \ln V + \ln P = costant$

$\ln(v^{\gamma} P) = costant$

$P_1 v^{\gamma} = costant$

$P_v V_1 = P_2 V_2^{r}$

Example 3

Show the relation between $P\ and\ V$

Solution

From law, $\eth Q = du + PdV$ using U as a function of state, i.e $U = U(V,T)$

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

But $\left(\frac{\partial u}{\partial T}\right)_V = c_v dT$, defined

$$\because \partial u = c_v dT + \left(\frac{\partial u}{\partial V}\right)_T dV$$

Therefore substituting in equation of 1st law

$$dQ = CvdT + \left[\left(\frac{\partial u}{\partial V}\right)_T + P\right] dV$$

For adiabatic expansion

$\partial Q = 0$ and for a perfect gas, u is a function of T and $\left({}^{\partial u}/_{\partial V}\right)_T = 0$

$$\therefore 0 = CvdT + PdV$$

Eliminating dT from equation of state $PV = RT$

$$PdV + VdP = RdT$$

$$Cv[PdV + VdP] + RPdV = 0$$

Since $Cp - Cv = R$

$$CvdP = -CpPdV$$

$$\frac{dP}{P} = -\frac{C_p}{C_V}\frac{dV}{V}$$

$$\int \frac{dP}{P} = -\int \frac{dV}{V}$$

$$\ln P + r \ln V = constant$$

$$\ln P \times r \ln V^r = constant$$

$$\ln(Pv^\gamma) = constant$$

$$Pv^\gamma = constant$$

Example 4

Refrigeration cycles have been developed for heating buildings. Heat is absorbed from the earth by fluid circulating in buried pipes and heat is

delivered at a higher temperature to the interior of the building. If a Carnot refrigerator were available for use in this way, operating between on outside temperature$0^{o}C$ and an interior temperature of 25^{0}C, how many kilowatt- hours of heat would be supplied to the building for every kilowatt-hour of electrical energy needed to operate the refrigerator?

Solution;

$T_1 = (273 - 0.25)0_K$

$T_2 = (273 + 24.25)$

$$Q_2 = Q_1\left(\frac{T_1}{T_2 - T_1}\right) = 272.75$$

Example 5

A Carnot engine absorbs heat from a reservoir at a temperature of 100^{0}C and rejects heat to a reservoir at a temperature of ℃. If the engine absorbs 1000J from the high temperature reservoir, find the work done, the heat rejected and the efficiency.

<u>Solution</u>

Work done, $W = Q_1 - Q_2$ work done w

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}\begin{bmatrix} T_2 = 273 \\ T_1 = 373 \end{bmatrix} = 1000 - 732 \\ = 268J$$

$$Q_2 = \frac{T_2 \times Q_1}{T_1} \quad efficiency\ n = 1 - \frac{T_1}{T_2}$$

$$Q_2 = \frac{(273 + 0) \times 100}{(373)} \eta = \left(1 - \frac{273}{373}\right) \times 100$$

$= 732 = 26.81\%$

Example6

Which is the more effective way to increase the efficiency of a Carnot engine, to increase the temperature T_2 keeping T_1fixed or to decrease the temperature T_1 keeping T_2 fixed?

<u>Solution:</u> Using $T_1 = T_2\left(1 - \frac{W}{Q_2}\right)$, a greater work is done with a decrease in T_2 hence efficiency is equally greater if T_1 is lowered.

Example 6

A refrigerator having a coefficient of performance one half as great as that of a Carnot refrigerator is operated between reservoirs at temperatures of

200^oK and 400^oK and it absorbs $600J$ from the low temp reservoir. How much heat is rejected to the high temperature reservoir?

Solution:

$$\frac{1}{2}\eta = \frac{Q_1}{Q_2 - Q_1} = \frac{T_1}{T_2 - T_1}$$

$$\frac{1}{2}\left[\frac{T_1}{T_2 - T_2}\right)\frac{Q_1}{Q_2 - Q_1}$$

$$\frac{1}{2}\left(\frac{200}{400 - 200}\right) = \frac{600}{Q_2 - 600}$$

$$\frac{1}{2} = \frac{600}{Q_2 - 600}$$

$$Q_2 = 600 + 1200$$

$$= 1800J$$

Example 7

A Carnot refrigerator or heat pump is operated between reservoir at $0°C$ and $100°C$ (a) if $1000J$ are absorbed from the low temperature reservoir, how many joule are rejected to the high temperature reservoir (b) what is the co-efficient of performance?

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \Rightarrow \frac{373 \times 1000}{273}$$

$$Q_2 = \frac{Q_1 T_2}{T_1} \Rightarrow 1366.35$$

$$(b)\eta = \frac{T_1}{T_2 - T_1} = \frac{273}{373.273}$$

$$= 2.73$$

1.2.3.1 Consequences of first law of thermodynamic

The first law of thermodynamic in the differential form given as

$$\partial Q = du + \partial\omega$$

for mechanical type of work, $\partial\omega = PdV$

$$\therefore \partial Q = du + PdV \qquad 1.52$$

Since internal energy u is a state function, we can variable P, V and T.Only

two independent variable are required to be determined in order to specify the state of a system while the third can be determined by the equation of state. Therefore we can write

$U = U(T,V) U = U(T,P)$

$$U = U(P,V) \qquad 1.53$$

Taking T and U as independent variable, we can write

$U = U[T,V]$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad 1.54$$

Putting equation 1.20 into equation 1.18 we obtain.

$$\partial Q = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV + PdV \qquad 1.55$$

$$\partial Q = \left(\frac{\partial u}{\partial T}\right)_V dT + \left[\left(\frac{\partial u}{\partial V}\right)_T + P\right] dV \qquad 1.56$$

For a process at a constant volume, $dV = 0$

Hence

$$\partial Q = \left(\frac{\partial u}{\partial T}\right)_V dT \qquad 1.57$$

By definition, specific heat at constant volume

$$C_p = \left(\frac{\partial U}{dT}\right)_V = \left(\frac{\partial u}{\partial T}\right)_V \qquad 1.58$$

Putting equation 1.24 into 1.22 above

$$\partial Q = c_v dT + \left[\left(\frac{\partial u}{\partial V}\right)_T + P\right] dV \qquad 1.59$$

For a process at constant pressure $dP = 0$ and $C_P = \left(\partial Q/_{dT}\right)P$,

$\partial Q = C_P dT$, substituting this in equation 1.25 $C_P dT = C_V dT + \left[P + \left(\partial u/_{\partial V}\right)_T\right] dV$

$$C_P - C_V = \left[\left(\frac{\partial u}{\partial V}\right)_T\right] \partial V/_{dT} \qquad 1.60$$

Taking T and P as independent variable i.e $U = U[T,P]$, then

$$dV = \left(\partial u/_{\partial T}\right)_P + \left(\frac{\partial u}{\partial P}\right)_T dP \qquad 1.61$$

From the first law of thermodynamics, we substitute for dU and dV. First we take $V = V[T,P]$

$$dV = \left(\partial u/_{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T dP \qquad 1.62$$

Substituting equations 1.27 and 1.28 in equation 2, we obtain

$$\partial Q = \left(\frac{\partial u}{\partial T}\right)_P dT + \left(\frac{\partial u}{\partial P}\right)_T dP + P\left[\left(\frac{\partial V}{\partial T}\right)_P + dP + \left(\frac{\partial V}{\partial T}\right)_T dP\right]$$

$$\partial Q = \left[\left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left[\left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP \qquad 1.63$$

For isobaric process, $dP = 0$

$$\therefore \partial Q = \left[\left(\frac{\partial u}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT = C_P dT$$

$$c_p = \left(\frac{\partial u}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p$$

Therefore $\partial Q = C_p\, dT + \left[\left(\partial u/_{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP$ 1.30

For isochoric process, equation 1.29 become

$$c_v dT = c_p dT + \left[\left(\partial u/_{\partial P}\right)_p + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP$$

$$C_V - C_P = \left[\left(\partial u/_{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right]\left(\partial P/_{\partial T}\right)_V \qquad 1.64$$

Finally taking P and V as independent variable; we have now

$$U = U[P,V]$$

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV$$

Substituting this an equation 2, we have

$$\partial Q = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV + PdV \qquad 1.65$$

Isochoric process, $dV = 0$

Thus,

$$\partial Q = \left(\frac{\partial U}{\partial P}\right)_V dP$$

Then

$$C_p dT = \left(\frac{\partial U}{\partial P}\right)_V dP$$

$$\therefore C_p = \left(\frac{\partial U}{\partial P}\right)_V \partial Q = \left(\frac{\partial P}{\partial T}\right)_V \qquad 1.66$$

Equation 1.65 thus becomes

$$\partial Q = C_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_p\right] dV \qquad 1.67$$

For a process at constant pressure

$dP = 0$

$\therefore \partial Q = c_p \, dT$

$$C_p - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_p\right]\left[\left(\frac{\partial V}{\partial T}\right)_p\right] \qquad 1.68$$

Equations 1.65, 1.66 and 1.68 are the consequence of the first law of thermodynamics. The importance of these results is that they give us the variation internal energy, Uin terms of Cv, CP which measureable quantities and also variations are in P, V and T which are obtainable form equation of state.

$i.e \left(\frac{\partial U}{\partial V}\right)_p, \left(\frac{\partial U}{\partial P}\right)_V \; and \left(\frac{\partial U}{\partial T}\right)_p$

If the apply the first law of thermodynamics to an ideal gas i.e

$\partial Q = dU + PdV$

For a process at constant volume in which $dV = 0$

Hence $C_V dT = dU$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad 1.36$$

But $U = U(T)$

$$\therefore dU = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial U}{\partial T}$$

$$c_v = \frac{\partial U}{\partial T} \; and \; dU = c_v \, dT$$

Therefore the first law becomes

$$\partial Q = c_v \, dT + PdV$$

from equation of state of an ideal gas

$PV = RT, we \; differentiate$

$$PdV + VdP = RdT \qquad 1.37$$

Replacing PdV in equation of state we have

$$\partial Q = C_p dT + RdT - VdP \qquad 1.38$$

for a process at constant volume, $dV = 0$

$$dQ = C_V dT + RdT$$

Also for $P = constant, dP = 0$

$$\therefore C_V = \left(\frac{\partial Q}{\partial T}\right)_P ; dQ = c_v dT$$

This implies that

$$C_p dT = C_V dT + RdT$$

$$\therefore C_p - C_V = R \qquad 1.39$$

For an adiabatic change, $dQ = 0$, thus equation 1.37 becomes

$$(C_V + R)\,dT = vdP$$

WHERE $dP = 0$ for adiabatic process,

$$O = c_p dT - VdP \text{ and } c_v dT = -PdV$$

Then $\frac{c_p dT}{c_v\, dT} = -\frac{VdP}{PdV} = r$

$$\frac{c_p}{c_v} = -\frac{V}{P}\left(\frac{dP}{dV}\right)$$

$$\gamma = \frac{VdP}{PdV}$$

$$\int \frac{dP}{P} = -\gamma \int \frac{dV}{V}$$

$$\ln P = -\gamma \ln V + constant$$

$$\ln P + \ln V^{\gamma} = constant$$

$$PV^{\gamma} = constant$$

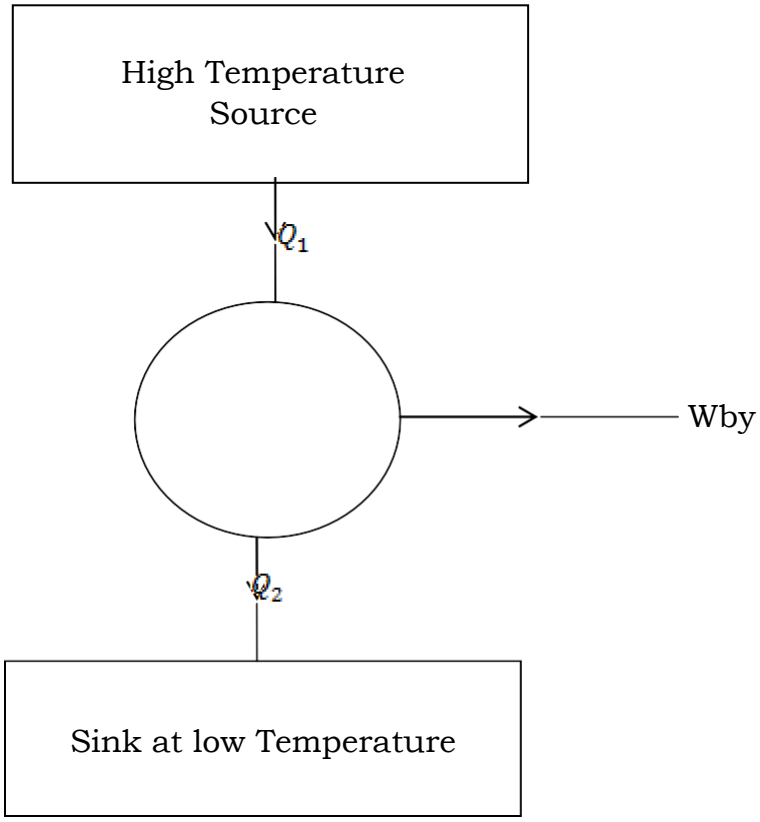
$$P_1 V_1^{\gamma} = constant \qquad 1.40$$

The students can find the relationship between $P and\ T\ and\ V\ and\ T$

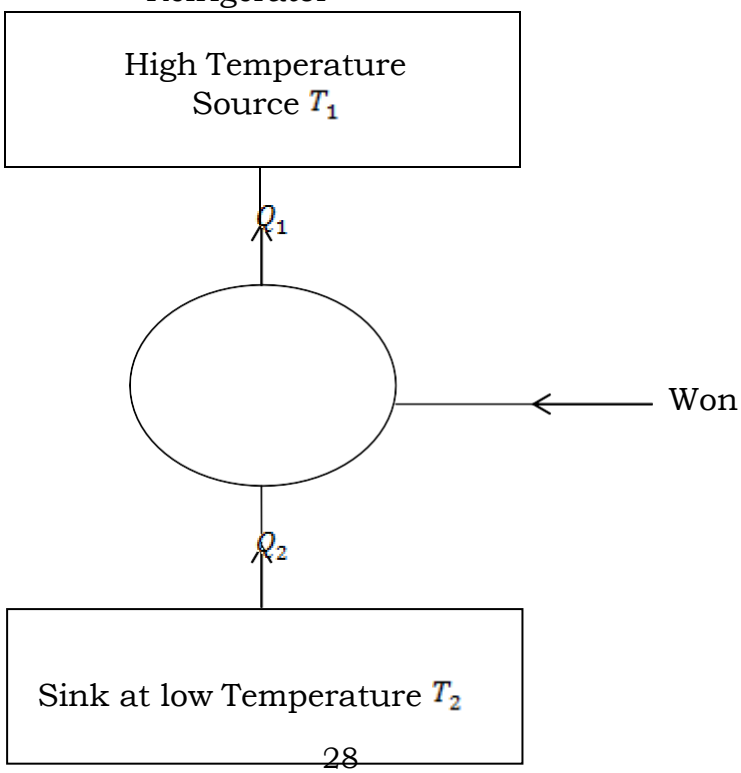
CHAPTER TWO

SECOND LAW OF THERMODYNAMICS

Heat Engine



Refrigerator



So many device and scheme have been conceived to transform one form of energy form one form to another. For examples are in the case of transformation of electrical to heat or chemical energy to heat energy. In heat engine, thermal energy is converted to mechanical energy. In general, heat energy Q_1 is taken from a high temperature source at temperature T_1 and some of them is converted into work; W_{by} and the remainder Q_2 (apart from heat losses) is rejected into a sink at lower temperature. T_2 This cycle is repeated severally. In refrigerator, the process is reversed. Heat Q_2 is removed from a cooler reservoir T_2 and work is done on the system to extract this heat while the remainder Q_1 is rejected into reservoir or the surrounding at high temperature. T_1. In all heat engine, there are basically 4 steps as shown in $P - V$ diagram bellow.

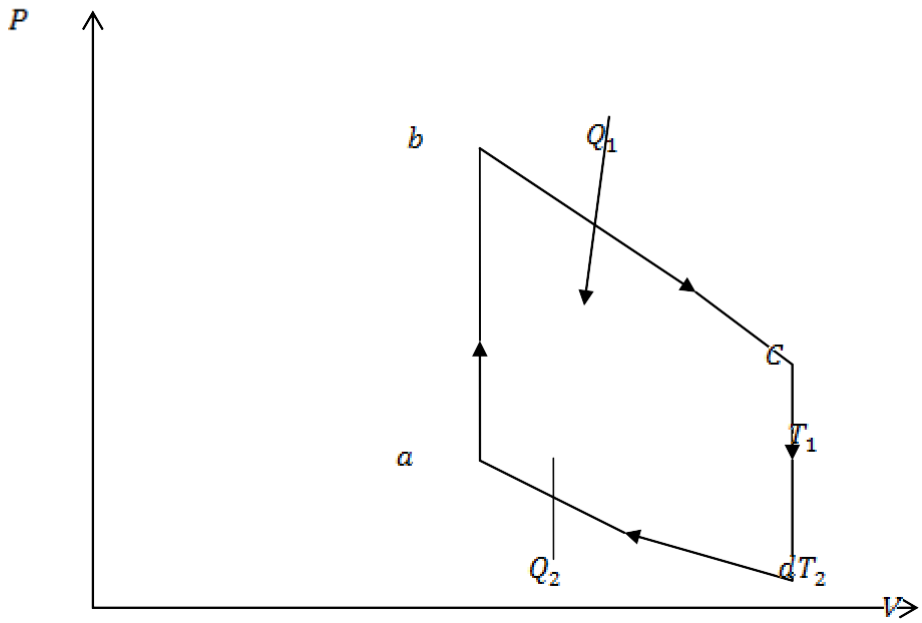


Fig2.1 $P - V$ diagram

i. An adiabatic compression from $a - b$

ii. An adiabatic expansion from $c - d$

iii. An isothermal expansion $b - c$

iv. An isothermal compression $d - a$

For this purpose, we device a Carnot cycle which is an ideal engine where heat Q_1 is taken in from the source temperature T_1 while the working substance expands isothermally [i.e from $b - c$], then the working gas is allowed to expand adiabatically doing useful work. Then the gas compresses isothermally while giving up heat Q_2. Finally the gas is compressed adiabatically from $a - b$ and the cycle is repeated over and over again.

The efficient of Carnot cycle η_j

$$\eta = \frac{Output}{Input} = \frac{work\ done}{Heat\ Input}$$

$$\frac{W_{by}}{Q} = \frac{Q_1 - Q_2}{Q_1} \qquad 2.1$$

Where $W.D = heat\ extracted\ Q_1 - Q_2$

$$\eta = 1 - \frac{Q_2}{Q_1}$$

This is an ideal engine because all the heat extracted $(Q_1 - Q_2)$ is assumed to have been converted into useful work is not a fact. Thus the efficient of Carnot cycle represents the maximum efficient of an ideal engine. We note that the heats $Q_1 and\ Q_2$ taken in and rejected are proportional to the absolute temperature of the source and the sinks.

$$\therefore \eta = 1 - \frac{T_2}{T_1} \qquad 2.2$$

However, in real engine:

i. P-V diagram is not exactly pure isothermal or adiabatic curve.

ii. Also the working gas used can change state [i.e evaporation and condensation may occur]

iii. Efficiency are lower than at that of the ideal Carnot engine.

iv. The cycles are not truly reversible

A reversible process for any system is a process which having taken place can be reversed without irrecoverable heat losses to the environment or surrounding. There are factor that render a process irreversible such as:

i. Rapid contraction and expansion which lead to heat losses

ii. Heat transfer out of a system due to poor lagging

iii. Hysteresis losses

iv. Eddy current losses

v. Power losses I^2R

vi. Mixing of substances

vii. Combustion process leading to degradation of material etc.

An example of real engine is the internal combustion engine as used in automobile combustion engine.

The working substance is a mixture of fuel and gas. The $P-V$ diagram the depict auto-cycle is shown below:

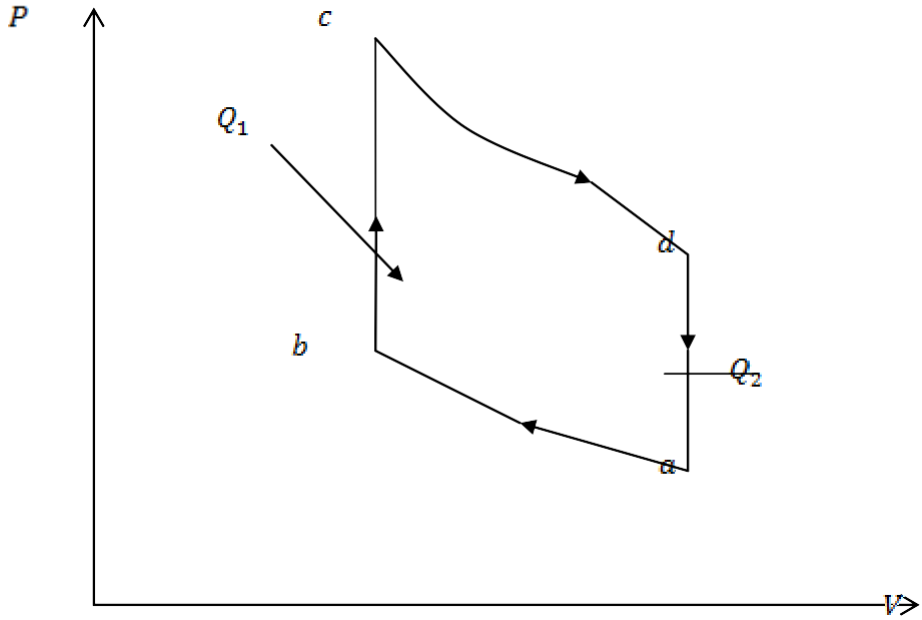


Fig 2.2 $P-V$ *diagram of auto – cylce*

1: The principle

The air fuel mixture is taken into the value via the inlet value; the piston then compresses the mixture along the path ab while closing the value.

Secondly, the fuel is ignited by a spark plug and an explosion occurs while the temperature and pressure of the mixture rises leading to the part be during which heat Q_1 is taken in. Finally the exhaust value is opened to release the combustion product while pressure drops along da and the Q_2 is given out. The cycle is completed and is ready to be repeated.

There are so many types of real heat engines. Whose Carnot cycle could be drawn, but we limit our work to the one we have discussed above.

In the case of refrigerator, the working substance is NH_2 and CO_2 or C_2H_5CL.

The compressor in its downward stoke, compresses the vapour and forces it into the pipe in the right hand side of system. As the vapour is compressed into the pipe, it is cooled by the flowing cool water and as liquefied. The circulating cold water (or air as in the case of domestic refrigerator) absorbs the latent heat of condensation Q_1 and carries it away. As the liquid passes through the value, it expands and evaporates. The latent heat needed for evaporation is extracted from the brime solution or air in the case of domestic one thereby cooling the compartment. Finally the compressor expands and draws in the vapour back into, its original chamber having lost heat Q_2.

The co-efficient of performance of refrigerator is defined as the ratio of heat extracted from the freezer compartment to the work done by compression on the working substance

$$C.P = \frac{Q_2}{W_{on}}$$

But $\eth Q = du + \eth W$, but $du = 0$ because u is a function of state and the process stated at point a and ended at point a

$$\therefore \partial Q = \eth W$$

$$\therefore Q_1 - Q_2 = W_{on}$$

$$C.P = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} \qquad 2.3$$

Statement of Second Law of Thermodynamics

While the first law of thermodynamics is a statement of law conservation of energy. The second law of thermodynamics deals with heat engine due to the fact that no known process can convert all energy from one to another without heat loss. Thus in heat engine, all the available heat cannot be converted into available work without some losses.

In Kelvin's statement of thermodynamics, he made it clear that it is impossible to remove heat from a hot body and convert it into useful work without rejecting a certain amount of heat to a reservoir or sink. That of Clausius statement says that it is impossible to convey heat from a colder to hotter body without the aid of an external agency doing work on the system, ie heat cannot of itself pass from a colder to a hotter body. This law expresses the fact that no heat engine can be 100% efficient. And the most efficient working between two temperature is a

Kelvin Thermodynamic Scale of Temperature

Kelvin was the first to note that if in a depends on the temperature and

$$\frac{T}{T_2} = \frac{Q}{Q_i} \qquad 2.4$$

Then a scale of temperature can be defined which is independent of the properties of working substance, but depends only on the heat Q_1 absorbed and the heat Q_2 rejected. Supposed ice point of water and the sink is at the triple point T_i and the source at unknown temperature T then

$$\frac{T}{T_2} = \frac{Q}{Q_i}$$

2.5

If $T_i = 273.16K$, then

$$T = 273.16\frac{Q}{Q_i}K$$

Further if the source is placed at stream temperature T_s and sink at ice point T_i and subdivide the interval into 100, then $T_S - T_i = 100$

Since $T_i = 273.^o K$, then $T_S = 373.^o K$

Entropy

Before we look at entropy which is the consequence of the second law of thermodynamic, we make a general reference to the first law of thermodynamics which is based on the low of energy conservation. The second law on its own deals with the limitation of practical heat engine in which it is not possible for a process to convert all energy from one form to another without heat loss, thus in heat engine, the available heat cannot be converted to available work without heat losses. In continuation with this same discussion, Kelvin stated that it is impossible to remove heat from a hot body and convert it into useful without rejecting certain amount heat to a reservoir sink. To cap it up clauses stated that it is impossible to convey heat from a colder to a hotter body without the aid of an external agency doing work on the system i.e heat cannot of itself pass from colder to a hotter body. This law the expresses the fact that no heat engine can be 100% efficient and that the most efficient working system between two temperature reversible Carnot engine has efficiency of $h = \left(1 - \frac{T_1}{T_2}\right) x100$

This is known Carnot theory.

The consequence of the second law of thermodynamic is the introduction of the new state function known as entropy of a system s defined as

$$dS = \frac{dQ}{T}$$

where ~~dQ~~ is the heat absorbed loss by the system reversibly at the absolute temperature T . This quantity enables one to deal with second law quantitatively rather than qualitatively. Therefore, clear explanation, if heat dQ is absorbed by the working system at temperature T the gain in entropy is given by

$$dS = \frac{dQ}{T}$$

Similarly, if heat is removed from the system, at the temperature, T then the loss in entropy is

$$dS = -\frac{dQ}{T}$$

Therefore, if a carnet cycle absorbs heat Q_1 at temperature T_1 and reject it Q_2 at temperature T_2 while the loss in entropy is $-\frac{Q_2}{T_2}$.

The net gain in entropy is $\frac{Q_1}{T_1} - \frac{Q_2}{T_2}$

Thus,

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

Thus there is no net gain for reversible carnet cycle; Clausius therefore concluded that in reversible process, the total change in entropy is zero. i.e

$$\int_R dS = \int_R \frac{dQ}{dT}$$

$$\sum \frac{dQ}{T} = 0$$

⇨ This implies that for reversible process,

$$\int_A^B \frac{dQ}{T} = \int_A^B dS = S_B - S_A$$

Thus, entropy is a function of state only.

$$ds = \frac{dQ}{T}$$

Similarly, if heat is removed from the working substance at the temperature$T$, then the less in entropy is

$$ds = -\frac{dQ}{T}$$

To see how entropy is a consequence of second law of thermodynamics, we considers a carnet cycle which absorbs heat Q_1 at temperature T_1 and reject heat Q_2 at temperatuure T_2.

Therefore gain in entropy $= \frac{Q_1}{T_1}$

Then loss is entreply $= -\frac{Q_2}{T_2}$

Net gain in entropy is

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

But $\frac{Q_2}{Q_2} = \frac{T_2}{T_2}$

$$\Rightarrow \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

There is no net gain for reversible Carnot cycle. Cleanses concluded that in reversible process, total change in entropy must be zero.

$$\oint_R dS = \int_R \frac{dQ}{T} = 0 \qquad 2.8$$

This becomes what is known a Clause theory of thermodynamics.

For car not

$$\sum \frac{dQ}{T} = 0$$

for many other reversible cycle which is not a car not cycle we can also write

$$\sum_i \frac{dQ_2}{T_1} = \oint_R \frac{dQ}{T} = 0$$

Now since $\oint_R \frac{dQ}{T} = 0$, it follows that

$$\oint_{R_1} {}_A \frac{dQ}{T} + \int_{R_2} {}_B \frac{dQ}{T} = 0 \qquad 2.9$$

As below

$$\therefore \oint_A^B \frac{dQ}{T} = -\oint_A^B d$$

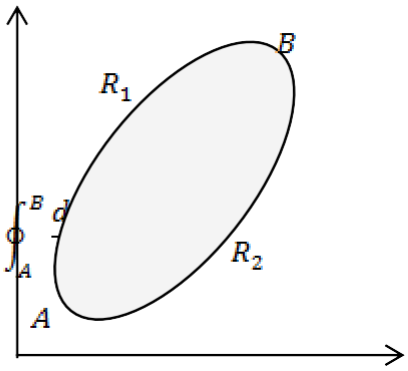


Fig 2.1 Independent path integral

Therefore $\oint_A^B \frac{dQ}{T}$ is independent of path taken provided that the path is reversible.

$$\therefore \oint_A^B \frac{dQ}{T} = -\oint_A^B \frac{dQ}{T} = S_B - S_A$$

2.10

Entropy S is an extensive variably, a function of state only, independent of path

with a perfect differential.

$$ds = \frac{dQ}{T}$$

We can define a term called specific entropy which is entropy per unit incase and is denoted with s

$$S = \frac{S}{M} \qquad 2.11$$

Some Important Points to Note in Calculation Involving Entropy

i. In a reversible adiabatic process $dQ = 0$
$\therefore dS = \frac{dQ}{T} = 0$
This is called an isentropic process or constant entropy process.

ii. For a reversible isothermal process $\Delta S = S_2 - S_1 = \int ds = \int \frac{dQ}{T} = \frac{Q}{T}$ as a change of phase where $Q = ML$.

iii. For a reversible process at a constant volume
$\Delta S = S_2 - S_1 = \int ds = Mcv\frac{Q}{T}$ .WhereC_v is not a constant unless otherwise state?

iv. For a reversible process at a constant pressure$\Delta S = S_2 - S_1 = \int ds = Mcp\int \frac{Q}{T}$.

v. When a system undergoes a reversible change of state although entropy is not defined for irreversible path, we can still calculate the change in entropy between the two states and assume that we can select and arbitrary reversible path between the two state and calculate $\Delta S = S_2 - S_1 = \int ds = \int \frac{Q}{T}$ for the path.

vi. By the term universe in the thermodynamics we mean a system plus its surrounding. Thus in a problem where we have one system into another like when ice is in beaker water the ice can be regarded as the system and the beaker of water an its surrounding. Therefore we have to calculate the net gain of the universe. Scientists head postulated that net gain of a unive4rse is always zero or greater than zero $\Delta S \geq 0$for universe.

a. For reversible process, ΔSr of the system is equal and opposite to the ΔSr of the surrounding. So that

$$\Delta S \text{ universe} = 0$$

b. For an irreversible process, $\Delta Sr$is greater than ΔSs

$$\therefore \Delta Sr > \Delta Ss.$$

Since increase in entropy corresponds to a gain in it, entropy leads to increase in disorder of the system. Therefore occurrence of irreversible process leads to more disorderly system. Thus clauses therefore states that the entropy of a universe tends to a maximum due to irreversible processes which leads to increase in disorder of the universe.

2.2.1 Combination Of First Law And Second Law Of Thermodynamics

From the first law $dQ = du + dw$ and from the second law, $Tds = dQ$ combming the two laws, we obtain that $Tds = du + dw$ and for the system in which $dw = pdv$,

$$Tds = du + pdv \qquad 2.12$$

Here all the variables are now state. Here all the variables are now state function.

i. Using T and V as independent variables

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

Substituting in equation above

$$T\left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\right] = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdv \qquad 2.13$$

Equating co-efficient of the ∂T and dv on both sides,

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

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

This is another development of combining the two laws.

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

ii. Similarly taking $T$and P as independent variables, then

$$S = S(T,P) \qquad 2.14$$
$$U = U(T,P) \text{ and } V = V(T,p)$$
$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T + dP$$
$$du = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T + dP$$

Substituting these in the combined law, we have

$$T\left[\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T\right] = T\left(\frac{\partial U}{\partial T}\right)_T dT \left(\frac{\partial U}{\partial P}\right)_T dP + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial P}\right)_T dT$$

2.15

Equating the terms with the same co-efficient on both sides

$$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \qquad 2.16$$

But $C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$

$$= T\left(\frac{\partial S}{\partial P}\right)_T \Rightarrow T\left(\frac{\partial S}{\partial T}\right)_P = {}^{C_P}/_{T} \qquad 2.17$$

Also $T\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T$ 2.18

Again, if we take P and V as an independent variable and then show that

$$T\left(\frac{\partial s}{\partial p}\right)_V = \frac{C_v K}{B} \text{ and } T\left(\frac{\partial s}{\partial v}\right)_p = {}^{C_P}/_{V_B} \qquad 2.19$$

Maxwell's First Relation In Thermodynamics

a. This can be obtained from the combined laws of thermodynamic and can be expressed as

$$\left(\frac{\partial T}{\partial v}\right)_p = T\left(\frac{-\partial P}{\partial s}\right)_V$$

2.20

b. Maxwell's second relation

From $F = U - TS$, all the quantities in the right hand side are state function, F is also function of state and a perfect differential of F is known as Helmholtz's free energy.

$$dF = dU - Tds - sdT \qquad 2.21$$

But $dU = Tds - Pdv$

$\Rightarrow dF - Pdv - SdT$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \text{ and } \left(\frac{\partial F}{\partial T}\right)_V = -S.$$

Since F is a perfect differential, order of differentiation is relevant.

$$\therefore \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V = \left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right]_T$$

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

2.22

This is Maxwell's second relation derived from Helmholtz's free energy.

Maxwell's Third Relation

Let $G = U - TS + PdV$ where all the quantities at the right hand side are state function. G is therefore state function. The differential of G is called the Gibb's function.

$$dG = dU - Tds - SdT + PdV + VdP \qquad 2.23$$

But $dU = TdS - PdV$

$$\therefore dG = -SdT + VdP$$

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

Since dG is a perfect differential, the order of differential is relevant.

$$\therefore \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P$$

$$\therefore \left(\frac{-\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_T = 0$$

2.25

Uusing $H = U + PV$ where H = enthalpy

$$dH = dU + Pdv + vdP$$

2.26

But $du + Pdv = TdS$

$\Longrightarrow dH = Tds + VdP.$

$$\left(\frac{\partial H}{\partial S}\right)_P = 1, \left(\frac{\partial H}{\partial P}\right)_S = V$$

Differentiating twice

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)\right]_P \qquad 2.27$$

$$\therefore \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad 2.28$$

These Maxwell's relations are useful because they provide expression for changers in entropy write respect to P, V and T which are difficult to measure in terms of variation of P and V which are easily measurable or can be obtained from the appropriate equation of state.

An expression for the relation between C_P and C_V for all substance can be derived using TdS.

Starting from Tds equation

$$Tds = CvdT + T\left(\frac{\partial P}{\partial T}\right)_V dv \qquad 2.29$$

$$Tds = CpdT - T\left(\frac{\partial V}{\partial T}\right)_P dp \qquad 2.30$$

Solving equations 2.29 and 2.30 simultaneously

$$CvdT + T\left(\frac{\partial P}{\partial T}\right)_V dv = CpdT - T\left(\frac{\partial V}{\partial T}\right)_P dp$$

$$(c_p - Cv)dT = T\left(\frac{\partial P}{\partial T}\right)_V dv + T\left(\frac{\partial V}{\partial T}\right)_P dp$$

For a process at a constant volume $dv = 0$,

$$T\left(\frac{\partial P}{\partial T}\right)_V dv = 0$$

$$\therefore (c_p - Cv)dT = T\left(\frac{\partial V}{\partial T}\right)_T dp$$

$$Cp - Cv = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P}{\partial T}\right)_V dp \qquad 2.31$$

But $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial P}\right)_T = -1$

Then $\left(\frac{\partial P}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T$

Therefore

$$Cp - Cv = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \Big/ \left(\frac{\partial V}{\partial P}\right)_T$$

The co-efficient of heat expansion is $B = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and Bulk modulus $-K = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$Cp - Cv = \frac{TVB^2}{K} \qquad 2.32$$

Thus with this equation, $Cp - Cv$ can be calculated for any susbstance in which the value of B and K are known. Since T and K are positive and $B < 0 < B$, B^2 is all positive in all cases, thus the right hand side is positive always.

$$\therefore Cp > Cv. \qquad 2,33$$

An expression for the calculation of the entropy of an ideal gas can be obtained from the relation.

$$dQ = CvdT + pdv \qquad 2.34$$

Since $\frac{dQ}{T} = dS$

$$dS = \frac{CvdT}{T} + \frac{Pdv}{T}$$

$$S = \int \frac{dQ}{T} = \int \frac{CvdT}{T} + \int \frac{Pdv}{T}$$

From the equation of state $PV = RT$ and $P = \frac{RT}{V}$

$$\therefore S = \int \frac{CvdT}{T} + \int \frac{Rdv}{V}$$

$$S = Cv/nT + R/nV + C. \qquad 2.35$$

Similarly if we know Cp, we start from

$$dQ = CpdT - Vdp \qquad 2.36$$

$$dS = \frac{dQ}{T} = \frac{CpdT}{T} + \frac{Vdp}{T}$$

From $PV = RT; V = {}^{RT}/_{P}$

$$\therefore \int dS = \int \frac{CpdT}{T} \int R\frac{dP}{P}$$

$$\therefore = Cp/nT - R/nP + C \qquad 2.37$$

Joule-Kelvin Effect

Joule-kelvin effect refers to a change in temperature of a gas in passing from a region of high pressure to a region of low pressure [usually through porous play or value]. This may be an increase [in heating effect] or decrease [in cooling effect] in temperature.

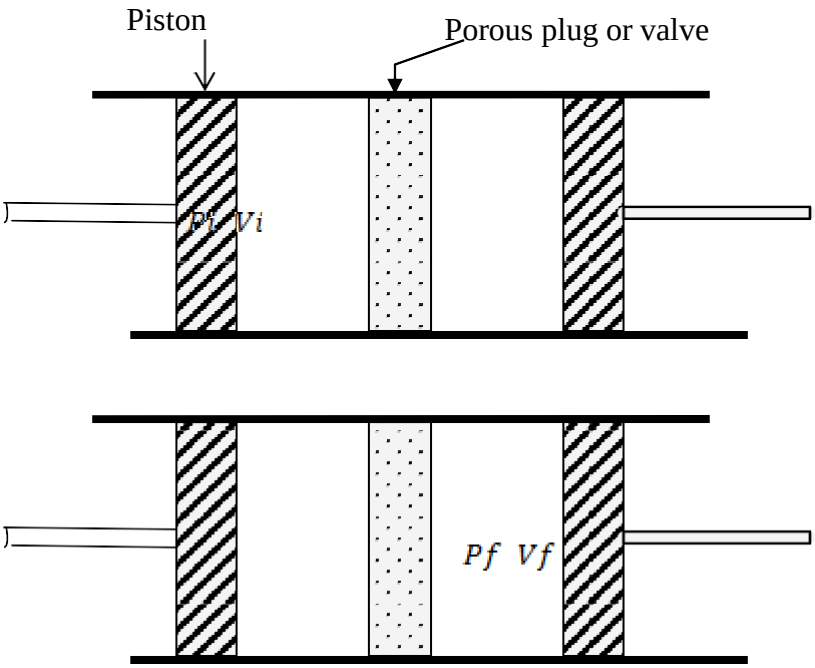


Fig 2.2 Diagram of throttling process

To derive throttling process condition, we start with enthalpy equation

$$H = U + PV. \qquad 2.38$$

Applying the first law of thermodynamics

$$i.e \qquad Q = Uf - Ui + W \qquad 2.39$$

And since the system is insulated no heat is gained and $W = PdV$. Where $U = 0$ and work done.

$$W = \int_{V_i}^{0} P_i dV + \int_{0}^{V_f} P_f dV$$

$$W = -P_i\ V_i + P_f V_f \qquad 2.40$$

Since $Q = 0$

$$\therefore 0 = U_f - V_i \neq P_f V_f - P_i V_i$$

$$U_i + P_i V_i = U_f + P_f V_f$$

Therefore for a throttling process

$$H_i = H_f \qquad 2.41$$

This means that for throttling process, the initial and final enthalpy must be equal and the process is said to isenthalpic process.

Worked Examples 2.1

a. The equation of state of a certain gas is given by $(P + b)V = RT$ and its internal energy is given by $u = aT + bv - uo$, determine Cv and $Cp = Cv$.

Solution

$PV + bV = RT \cdots (1)$

$U = aT + bV - U0 \ \cdots (2)$

Differentiating both equations

$PdV + VdP + bdv + RdT \ \cdots (3)$

$du = adT + bdv \ \cdots (4)$

From the first law of Thd

$dQ = du + PdV \quad \cdots (5)$

From (3) $Pdv = RdT - VdP - bdv$

Therefore substituting for du and Pdv $dQ = adT + bdv + RdT - VdP - bdv$

$dQ = adT + dT - VdP$ at a constant pressure $dP = 0$ and $dQ = adT + RdT$

$$\left(\frac{dQ}{dT}\right)_p = a + R$$

But

$$\left(\frac{dQ}{dT}\right)_p = cP$$

$$C_p = \left(\frac{dQ}{dT}\right)_p C_p = a + R \cdots (6)$$

From $(5) dQ = adT + bdv + pdv$ at a constant volume $dv = 0$

$dQ = adT$

$$\left(\frac{dQ}{dT}\right)_V = a$$

$C_v = a \quad \cdots (7)$

$C_p = a = R$

$\Rightarrow C_p = C_v + R$

$C_p = C_v = R$

Work example 2.2

Vandar wall gas equation is given as $\left(P + \frac{a}{V^2}\right)(V - b) = RT$, derive an expression B.

Solution

$$P = \frac{RT}{V - L} - \frac{a}{V^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{(V - L)^3} + \frac{20a}{V3} = \frac{-RTV^3 + 2a(V - b)^2}{RV^3(V - b)^2}$$

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

$$\therefore \frac{\left(\frac{\partial P}{\partial V}\right)_T}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{-RTV^3 - 2a(V-b)^2}{RV^3(V-b)}$$

But from

$$\left(\frac{\partial P}{\partial T}\right)_p \cdot \left(\frac{\partial P}{\partial V}\right)_V \cdot \left(\frac{\partial P}{\partial V}\right)_T = 1$$

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

$$-\left(\frac{\partial P}{\partial V}\right)_T / \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P}{\partial V}\right)_V = \frac{-RTV^3 + 2a(V-b)^2}{RV^3(V-b)}$$

$$\frac{-1}{\left(\frac{\partial V}{\partial T}\right)_p} = -\frac{-RTV^3 + 2a(V-b)^2}{RV^3(V-b)}$$

$$\frac{-1}{BV} = \frac{-RTV^3 + 2a(V-b)^2}{RV^3(V-b)}$$

$$B = \frac{RTV^3 + 2a(V-b)}{RTV^3 - 2a(V-b)^2}$$

Example 2.3

b. A gas obeys the Dietetics equation of state $P = \frac{RT}{V-b} e^{\left(-\frac{a}{vRT}\right)}$

i. Obtain the expression for B.

ii. Obtain also the expression for the isothermal Bulk modulus K

Solution

$$P = \frac{RT}{V-b} e^{-\frac{a}{vRT}}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left[\frac{R}{V-b}\right] e^{-\frac{a}{vRT}} + \left(\frac{RT}{V-b}\right)\left[\frac{-a}{VR}\right] e^{-\frac{-a}{RvT}}$$

$$= \left[\frac{R}{V-b} - \frac{aT}{V[V-b]}\right] e^{-\frac{a}{RvT}}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{-RT}{V-b} - \frac{a}{V-b}\right] e^{-\frac{-a}{RTV}}$$

$$\left(\frac{\partial P}{\partial V}\right)_T / \left(\frac{\partial P}{\partial T}\right)_V = \frac{V[RT + a[V = -b]}{(V-b)(RV - aT)}$$

But $\left(\frac{\partial P}{\partial V}\right)_V / -\left(\frac{\partial V}{\partial T}\right)_T \left(\frac{\partial P}{\partial V}\right)_V = \frac{V[RT+a[V=-b]}{(V-b)(RV-aT)}$

$$-\left(\frac{\partial V}{\partial T}\right)_p = \frac{-(V-b)(RV-aT)}{V[RT+a[V=-b]}$$

$$\therefore B = \frac{(V-b)(VR-aT)}{V^2[RT+a[V=-b]}$$

Deduce for K using this idea

$$K = \frac{(V-b)^2}{V[RT+a[V=-b]} e^{+-\frac{a}{RTV}}$$

Example 2.4

1kg of water at 273k (system A) is mixed with 1kg of water at 373^0k (system B) such that the final temperature is 323^0k. Calculate the gain an entropy of system A and the loss in entropy o system B and the net gain in entropy of the system combined. $[C = 4.19410^3 J/kg\ 0_C]$

Solution

For a system A $T_1 = 373k$, and gain in temperature $323k$. Where mixed with another water of the same quantity at $323k. T_2$=323k

Entropy gain in A

$$\Rightarrow S_2 - S_1 = \Delta S_A = MC/n\frac{T_2}{T_1}$$

$$= 1 \times 4.19 \times 10^3/n\left(\frac{323}{273}\right)$$

$$\Delta S_A = 705J/0_C$$

For system $B, T_1 = 373k$, heat the water lost temperature when mixed the other water of colder temperature hence dropped to $323^0k = T_2$

Entropy loss is

$$S_2 - S_1 = \Delta S_R = MC/n\frac{T_2}{T_1}$$

$$= 1 \times 4.9 \times 10^3 \times MC/n\frac{T_2}{T_1}$$

$$= -603./J/0_C$$

net change in entropy of the water is

$\Delta S_R + \Delta S_E \Rightarrow 705 - 603.1$

$= 101.9 J/0_C$Example 5

a. One kg of water at 0^0C is brought into contact with a large heat reservoir 100^0C. When the water has 100^0C what has been the change in entropy of the water? Of the heat reservoirs? Of the universe.

b. If the water had been heated from 0^0C to100^0C by first bringing it in contact with a reserve at 50^0C and then with a reservoir at 100^0C, what would have been the change in the entropy of the universe?

c. Explain how the water might be heated from 0^0C to 100^0C with no change in the entropy of the universe.
$C_p = 41/80 J/kgk$

Solution

a. (i) $\Delta S = \frac{C_p}{n\left(\frac{T_2}{T_1}\right)} = 4180/n\left(\frac{373}{273}\right)$
$= 1305 J/k$

(ii) $\Delta Sre = -C_p\left[\frac{T_f - T_i}{T_f}\right]$
$= -4180\left[\frac{373-273}{393}\right] = -1121 J/k$

(iii) $\Delta Sun = C_p\left[/n\left(\frac{T_f}{T_i}\right)\right] - \frac{T_f - T_i}{T_f}$
$= 4180\left[in\frac{373}{273} - \frac{373-273}{373}\right]$
$= 183.976\ J/k$

b. If the heat has been taken stage by say from 0^0C to $T =^0 C$ and finally to 100^0C

$\Delta Sun = C_p\left[/n\left(\frac{T_f}{T_i}\right) - \left(\frac{T_z}{273+T_z}\right) - \frac{373-323}{T_f}\right]$
$= 4180\left[/n\left(\frac{373}{273}\right) - \frac{323}{323} - \frac{50}{373}\right]$
$= 97 J/K.$

c. The water can be heated using a series of reservoirs with various value of temperature between $273k$ to $373\ k$.
A Carnot engine absorbs heat from a reservoir at a temperature of 100^0C and rejects the heat to reservoir at a temperature of 0^0C. If theengine absorbed $1000J$ from the high temperature reservoir, find the work done, the heat rejected and the efficiency.

Solution

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

$$Q_2 = \frac{Q_2 Q_1}{T_1}$$

Q_2 =heat rejected.

$$Q_2 = \frac{273 \times 1000}{373} = 732J$$

$$\therefore work\ done = Q_1 - Q_2$$

$$= 1000 - 723 = 268J$$

The efficiency $\eta = \left(1 - \frac{T_1}{T2}\right) \times 100$

$$= \left(1 - \frac{273}{373}\right) \times 100 = 26.81$$

6. A refrigerator having a co-efficient of performance one-half as great as that of a Carnot refrigerator is operated between reservoirs at temperature of 400^0K and it absorbs J from the low temperature reservoir. How much heat is rejected to the high temperature reservoir?

Solution

$$\frac{Q_1}{Q_2 - Q_1} = \frac{T_1}{T2 - T_1}$$

$$\frac{1}{2}\left[\frac{200}{400 - 200}\right] = \frac{600}{Q_2 - 600}$$

$$Q_2 = 1800J$$

CHAPTER 3

Change of Phase

There exists for every real substance a relation between the pressure, specific volume (or density) and temperature. That is equation of state of the substance. Therefore all possible equilibrium state of the substance lies on a PVT surface. However, real substances can exist in the gas phase only at sufficiently light temperatures and low pressure. At low temperatures and high pressure, transitions occur to the liquid phase and solid phase. $P - V - T,$ surfaces include those phases as well as the gas phase.

Heat of Transformation

Heat is absorbed or liberated during a change of phase. Consider a portion in an isothermal process in either the solid-liquid-vapour region, and let the process proceed in such a direction that a mass m is converted from solid to liquid, from liquid to vapour or solid to vapour, the system absorbs heat say, $l.$ It is defined as the ratio of the heat absorbed $Q,$ to the mass undergoing a change of phase. One can also define the molar latent heat of transformation as the ratio of the heat absorbed to the number of mole n undergoing a change.

$$L = \frac{Q}{m} or\ l = \frac{Q}{n} \qquad 3.1$$

The unit is $J/_{Kg}$.

If L_{12}, L_{13} are called latent heat of fusion, of vaporization, of sublimation and the change proceeds in the opposite direction, the same quantity of heat is liberated. Change of phase is always associated with changes in volume so that work is done always on or by a system in a phase change, except at critical point where the specific volume of liquid and vapour are equal.

$$W = P[V_2 - V_1] \qquad 3.2$$

$U_2 - U_1 = 9 - W$

$\Rightarrow U_2 - U_1 = L - P[V_2 - V_1]$

$L = (U_2 + PV_2) - (U_1 + PV_1)$

Or from the definition of enthalpy,

$$L = h_2 - h_1 \qquad 3.3$$

The heat of transformation in any change of phase is therefore equal to the difference between the enthalpies of the system in the two phases.

At triple $L_{13} = L_{12} \times L_{23}$ i.e the heat of sublimation equals the sum of the heat of fusion and the heat of vaporization.

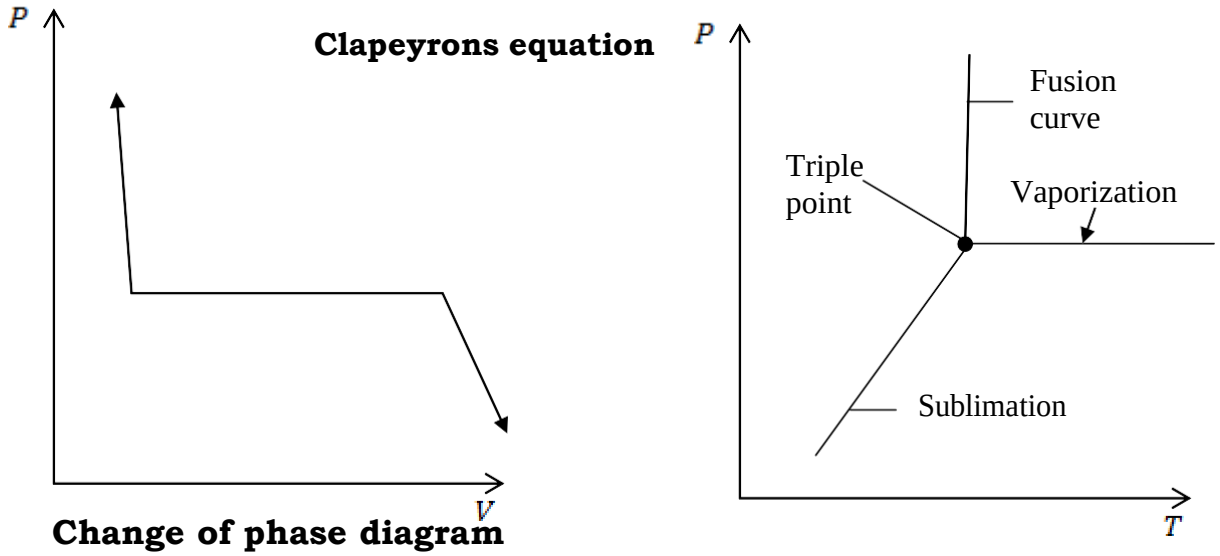


Fig 3.1 **Change of phase diagram**

As already explained, change of phase usually occurs at constant temperature and pressure. During change of phase, the specific Gibb's function remains constant.

That is $g = u - Ts + PV$

Or $g_1 = g_2$

Where $g_1$the specific Gibb's is function for the liquid phase and g_2 is that for the solid phase. This can be shown by applying the first law of thermodynamics to the system and as indicated in the previous page;

$du = \partial Q = T[S_2 S_1] = L \qquad 3.4$

$\partial W = P[V_2 - V_1]$

$du = U_2 - U_1$

$U_2 - U_1 = T[S_2 - S_1] - T[U_2 - U_1]$

$$U_1 - TS_1 + PV_1 = U_2 - TS_2 + PV_2 \qquad 3.5$$

Which explain that

$$g_1 = g_2 \qquad 3.6$$

Clapeyron's equation is an equation that gives

$$\frac{dP}{dT} \qquad 3.7$$

i.e the scope of the change of phase given that

$$g = U - TS + PV$$

$$dg = du - TdS - AdT + PdV + VdP \qquad 3.8$$

But $du = TdS - PdV$

$$\therefore dg = -SdT + VdP \qquad 3.9$$

and $dg_1 = dg_2$

$$\Rightarrow -S_1 dT + V_1 dP = -S_2 dT + V_2 dP$$

$$(S_2 - S_1)dT = (V_2 - V_1)dP$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \qquad 3.10$$

But earlier we had obtained that

$$T[S_2 - S_1] = \partial Q = L$$

$$\therefore \frac{dP}{dT} = \frac{L}{T[V_2 - V_1]}$$

$$\frac{\Delta P}{\Delta T} = \frac{L}{T[V_2 - V_1]}$$

$$\Delta T = \frac{T[V_2 - V_1]}{L}\Delta P \qquad 3.11$$

Therefore if $\Delta P > 0$, then $\Delta T > 0$ ie increase in pressure ΔP raises the boiling point. For example, at mountain top, there is a decrease in pressure which decrease the boiling point there.

3.2.1 Phase space

The concept on phase space is needed in the study of statistical physics because ordinarily, the state of a system of particles is completely needed to be specified classically at a position in a particular instant in order to enable one develop statistical mechanics in geometrical frame work, thereby permitting a simpler and more straightforward methods of analysis than equivalent one which looks more abstract in nature.

A point in phase space corresponds to momentum and position while a point in ordinary space corresponds to a position only.

Thus every particle is completely specified by a point in phase space and the state of the system of a particle corresponds to certain distribution of point in the phase space. By this, we can now divide the phase space into 6 dimensional cells whose sides are $dx, dy, dz, dp_x, dp_y dp_z$

As we reduce the size of the cells we approach more and more closely tp the limit of a point in the phase space.

If the volume of each of these cell is $\tau = dxdydzdP_x dp_y dp_z$ $\tau = dxdydzdP_x dp_y dp_z$,and and according to the uncertainty principle, $dxdp_x \geq h, dydp_y \geq h, dzdp_z \geq h$

It means that $\tau = h^3$ that tells that points in phase space is actually a cell whose minimum volume is of the order $h^{3.}$

The state of a system of particles is completely specified classically at a particular instant if the position and momentum of each of its constituent particles were known. Since position and momentum are vectors with three components apiece, we must know six quantities,

$x, y, z, p_x p_y, p_z$ for each particle.

The position of a particle is a point having the co-ordinate x, y, z in ordinary three-dimensional space. It is convenient to generalized this conception by imagining a six- co-ordinates x, y, z, p_x, p_y, p_z.

The combined position and momentum space is called phase space. The idea of phase space is introduced to enable one develop-statistical mechanics in geometrical frame-work thereby permitting a simpler and more straightforward method and technique of analysis than an equivalent one wholly abstract in character. A point in phase space corresponds to a particular position only. Thus every particle is completely specified by a point in phase, and the state of a system of particles corresponds to a certain distribution of points to phase space.

It is off course the task of statistical mechanics to determine the state of a system by investigating how the particles constituting the system distribute themselves in phase space. If we can find the probabilities of

finding all possible distributions that are permitted by the nature of the system, we can select the correct and most probable one and assert that the system tends to behave according to this distribution of particle positions and momenta. That is, we assert that the sate of a system when it is in thermal equilibrium corresponds to the most probable distribution of particles in phase space. Mole, C_V, is

$$C_V = \frac{1}{n}\left(\frac{dE}{dE}\right) = 3\left(\frac{N}{n}\right)K = 3N_A K = 3R$$

Where the number of moles is n, N_A is Avogadro's number, and R is the constant of the general gas law. This classical relation is known as the Dulong-petiti law. The equation, predicting that the molar specific heat of any solid is the same constant, $3R$, independent of the material and of the temperature, is in agreement with experiment at high temperatures. The classical theory is however, incapable of explaining the observed decrease in the specific heat at low temperature will be shown in section.

The first successful theoretical treatment of the lattice specific heat for all temperature was improved upon by p Debye and is usually referred to as the Debye theory of specific heats.

The observed temperature dependence of the specific heats of solids, whether insulators or conductors, are found to be in good agreement with the Debye theory, in fig. this is at first sight, rather surprising, in much as the Debye takes into account the internal energy arising from lattice vibrations but not the contribution to the specific heat of the conduction elections. An electric or thermal insulator is a material in which there are essentially no free electrons. It is to be expected, then that the specific heat of an insulator would have contributions from the lattice vibrations alone, in agreement with experiment and the Debye theory, but that a conductor would have in addition a contribution to the specific heat from the free electrons. Let us compute the electronic specific heat of solid under the assumption that each of the N atoms of the solid has one free, or conduction, election and that the N free electrons may be regard as classical particles of a Maxwell-Boltzmann gas. Three degree of freedom are associated with the translational motion of each particle and, if these free electrons are regarded as classical particles wandering throughout the solid conductor, much as molecules in a gas then the total electronic is $E_e = N(3/2KT)$. The electronic contribution to the molar specific heat would be $C_{ve} = (1/n)\left(dE_e/dT\right) = \frac{3}{2}(NK/n) = 3/2\,R$. But at the high-temperatures classical limit of the Debye theory that lattice specific heat is $3R$. Thus, if the conduction electrons of a conductor were to behave as classical free particles, the conductor's total molar specific heat at relatively high temperatures would be $3R + 3/2\,R\ a/2\,R$, whereas the observed value of C_v for both insulators and conductors is $3R$ for $T > T_D$

Blackbody radiation

The term blackbody is a material that absorbs all radiation, reflecting none, of the incident from the point of view. At the quantum theory, a blackbody is then a material that has so many quantized energy levels, spaced over so wide a range of energy differences that nay photon whatever its energy or frequency, is absorb when incident on it. A physical system illustrating the Bose-Einstein distribution law is that of a blackbody and its radiation. This is because the interpretation of the radiation from solid materials involves not only the quantum theory but also the statistical distribution of particles in a many-particle system as solid material represents a complex radiator or absorber which may be regarded in some ways as an enormous molecule with a corresponding increased number of degrees of freedom. This is the more reason why in the next chapter we shall look at element of statistical physics. The radiation emitted by solid consists of a continuous spectrum since all frequencies or wavelengths are radiated. An adequate theory of blackbody radiation must account for how the radiation is distribution among the various frequency components and how it varies with the temperature of the emitting surface. Based on this relation, the energy distribution of blackbody can be derived using. Bose Einstein statistics. In order to achieve this we require the distribution of a single photon state using the mean occupation number

$$\bar{n} = \frac{1}{\exp BE_{i-1}}$$

Now the photon state for which the frequency range is from $w + dw$ has the relation

$$f(\rho)d\rho = \frac{4\pi \vee \rho^2 d\rho}{\hbar^3}$$

The momentum of a photon with this energy is of magnitude

$$P = \frac{\hbar\omega}{C}$$

Since photon has zero mass, the number of photon states in which the photon has frequency in the range sated above is

$$f(\omega)d\omega = \frac{2V\,4\pi\left(\frac{\hbar\omega}{C}\right)^2}{\hbar^3}\hbar dw/C$$

Combining this equation with the first one that depicts the occupation number, we obtain the number of photons in the frequency range as

$$dNw = \frac{8\pi V_{\hbar}{}^3 w^2 dw}{8\pi^3 C^3 \hbar^3} = \frac{Vw^2 dw}{\pi C^3}$$

Hence the total energy of the radiation in this frequency range is

$$dEw = \hbar w dw = \frac{V\ \hbar^3}{\pi^2 C^3}\ \frac{w^3 dw}{e^{\beta\hbar w}{}_{-1}}$$

which energy density is

$$\frac{dEw}{V} = \frac{\hbar w^3 dw}{\pi C^3 \left[e^{\beta \hbar w} - 1 \right]}$$

Question on Thermodynamics

1. Show that the relationship between T, V is
$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$
2. explain the following terms
   i.Thermodynamics efficiency
   ii.Internal energy
   iii.Isothermal process
   iv.Adiabatic process
   v.Adiabatic process
3. The thermodynamic efficiency of an ideal-gas Carnot engine which reject heat to sink at $15°C$ is 30 percent. What is the temperature of the source?
4. A Carnot refrigerator or heat pump is operated between reservoir at $0°C$ and $100°C$
   a) If $1000J$ are absorbed from the low temperature reservoir, how many joule are rejected to the high temperature reservoir?
   b) What is the co-efficient of performance

$(a) = 1366.35$

(b) 2.73

5. Explain the implication of Kelvin's and Clacisuis statement of second law of thermodynamics.
6. Explain the term "entropy". Hence show that the entropy of a reversible Carnot cycle is zero.
7. Show that the entropy of an ideal gas can be expressed as
   i. $S = Cv \ln T + R \ln V + C$
   ii. $S = Cp \ln T - R \ln P + C$
8. State 3 important Maxwell's relations in thermodynamics
9. A piece of hot steel at temperature $500°C$ is thrown into an isolated oil bath at $20°C$ If the constant thermal capacity of the steel and oil are 60 and $200\ calC^{-1}$ respectively. Calculate
   i. The entropy change of the steel
   ii. The entropy change of the oil bath
   iii. The entropy change of the universe
   iv. Show that the relationship between (P, T) is

10a $\quad {}^{T}/_{P^{(\gamma-1)/\gamma}} = constant$

Hint first finds the equilibrium temperature

i. $-12.8\ Cal/C.$

ii. $55\ Cal/C.$
iii. $9.3\ Cal/C.$

If $2kg$ of liquid H_2O at $363k$ are mixed adiabatically and at constant p with $3kg$ of liquid water at $287k$, what is the total entropy change resulting from this process 3 $C_p = \frac{4}{84J}/kgK.$

Hint: Obtain the equilibrium temperature $157.4\ J/K.$

10b Explain the Joule-Kelvin effect when a gas expands from initial condition P_iV_i to a final condition P_fV_f through a porous plug.

11 Derive the Clapeyron's equations for a change of state [ie first latent heat equation. Show that the change in melting ΔT produced by a change in pressure Δ is given by $\Delta T = \frac{T}{L}(V_2V_1)\Delta P.$

12 A quantity of ice exist at temperature of $-30°C$ find the rate of change of pressure with respect to temperature $dP/_{dT}$ for the ice to melt; give that $L = 336Jgm^{-1}$ $V_1 = 1.091cm^3gm^{-1}, V_2 1.00cm^3gm^{-1}$

13 The internal energy of a certain gas may be presented by an empirical equation $u = aT - bP$ where a and b are constant and compressibility are respectively $1/T$ and $\frac{1}{P}$, find the heat capacity at constant volume C_V in terms of a, b, p and T.

CHAPTER 4

INTRODUCTION

4.1.0 Statistical physics

In This case, we look at the laws which govern the behavior and properties of macroscopic bodies, [that is bodies formed of a very large number of individual particles, ,such as atoms and molecules],to a considerable extent the general character of these laws does not depend on the mechanics[classical or quantum] which describes the motion of the individual particles in a body, but their substantiation demands a different argument in the two cases. For convenience of exposition, we shall begin by assuming that classical mechanics is everywhere valid.

In principle, we can obtain complete information concerning the motion of mechanical system by constructing and integrating the equations of motion of the system, which are equal in number to its degree of freedom. But if we are concerned with a system which though it obeys the laws of classical mechanics, has a very large number of degrees of freedom, the actual application of the method of mechanics involves the necessity of setting up and solving the same number of differential equations, which in general is impossible.

In fact even if one could integrate these equations in general form, it would be completely impossible to substitute in general solution the initial conditions for the velocities and the coordinate of the particles. This implies that as the number of particles increase, so also the complexity and the intricacy of the properties of the mechanical system become and thus the trace of regularity of the behavior of a macroscopic body becomes elusive. Therefore as number of particle become large, new types of regularity appear which is known as the statistical laws resulting from the very presence of large number of particles forming the body can not in any way be reduced to purely mechanical laws. It is observed that one of their distinctive features is that they cease to have meaning when applied to mechanical systems with a small degree number of degree of freedom. Although the motion of the system with large number of degree of freedom still obeys the same laws of mechanics as that of the systems consisting of a small number of particles but the existence of many degrees of freedom results in different kind of laws that leads to statistical laws. The importance of statistical Physics in many other branches of theoretical physics is due to the fact in nature, we continually encounter macroscopic bodies whose behviour cannot be fully described by the methods of mechanics alone, but obeys the statistical laws.

However, in anticipation to formulate the fundamental problems classical statistics, we need the preamble which is first of all the concept of phase space

Basic Concept of Statistical Distribution

Statistical distribution is important concept in statistical physics. They comprise (i) Maxwell-Bose distribution (ii) Bose-Einstein's statistical

distribution (ii) Fermi-Dirac distribution. Any of this distribution as mentioned above has unique characteristics as may be discussed later in the subsequent sections.

Maxwell-Bose Distribution

This is a classical distribution is applied to any system of identical particles which are nevertheless, distinguishable from one another. The system that obeys $M-B$ statistics are all gases at all temperature. The distribution can be derived by first considering N phase point within a cell where all permutation within the cells are allowed. Under this condition, the thermodynamic probability is given by

$$W = \frac{N!}{n_1!\,n_2!\cdot\cdot n_i!} = \pi\,\frac{N!}{n_i!} \qquad 3.32$$

$$\ln W = \ln N! - \sum \ln N! \qquad 3.33$$

Using sterling's approximation

$\therefore \ln W = N\ln N - N; \ln n_1' = n_i \ln n_i - n_i$

$\Rightarrow \ln W = N\ln N - N - \sum (n_i \ln n_i - n_i)$

where $N = \sum n_i$

$$\ln W = N\ln N - \sum n_i \ln n_i - n_i \qquad 3.34$$

For small change in the quantities, equation 3.34 can be differentiated

$\partial \ln W = \partial[\eth N \ln N] - \sum \partial n_i \ln n_i$ and at $Wmax$

$\partial \ln W = \partial N \ln N - \sum \partial n_i \ln n_i = 0$

Considering $\partial N \ln N = 0$,

Then

$$-\sum \partial n_i \ln n_i = 0 \qquad 3.35$$

$$\therefore \sum n_i\,\partial \ln n_i = 0 \qquad 3.36$$

But ∂n_i is conditionally zero for an isolated system, the internal energy u is given by

$$U = \sum_i^n \epsilon_i n_i$$

$$\partial u = \sum \epsilon_i \, \partial n_i \qquad 3.37$$

Multiplying equation's 3.36 and 3.37 by Lagrange multipliers $\propto$ and B and adding then to equation 3.35

$$\sum n_i \partial \ln n_i + \sum \propto \partial n_i + \sum B \, \epsilon_i \, \partial n_i = 0$$

$$\sum \ln n_i \, \partial n_i + \sum \propto \partial n_i + \sum B \, \epsilon_i \, \partial n_i = 0$$

$$\left[\sum \ln n_i \propto + B \, \epsilon_i\right] \partial n_i = 0 \qquad 3.38$$

If we assume that in equation 3.38 $\partial n_i \neq 0$,

Therefore,

$$\ln n_i + \propto + B \, \epsilon_i = 0$$

Thus

$$n_i = e^{-\propto} e^{-B\epsilon_i} = e^{-[\propto + B\epsilon_i]} \qquad 3.39$$

The graph of the distribution looks thus

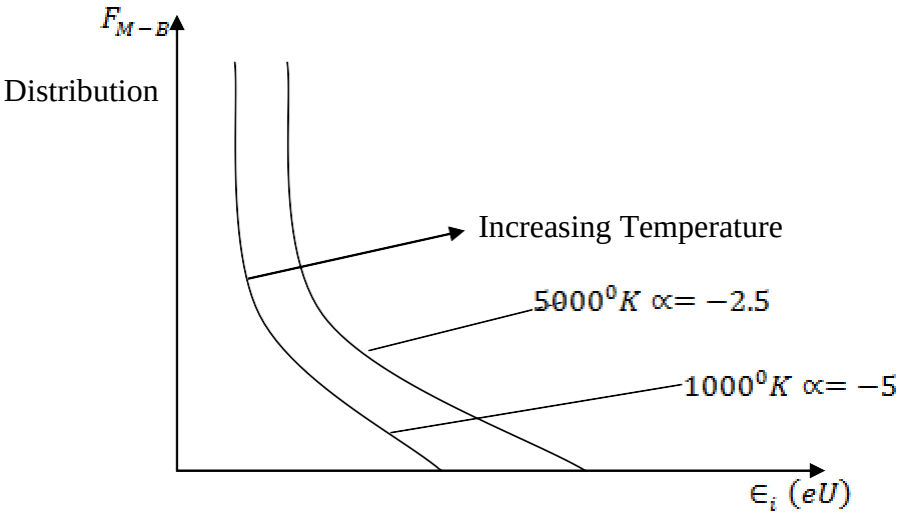


Fig. 3.4: The occupation indexes for $2M - B$ distributions

Bose-Einstein's Statistical Distribution

In this case we consider possibly identical particles n_i which are indistinguishable in g_i cells. These particles are identical, indistinguishable with integral spin and are popular referred to as **BOSONS.**

Examples are liquid helium, with $spin = 0$ photon gas with $spin = 1$ and phonon gas with $spin = 0$. Since these particles, n_i occupy energy $\in_i$ with energy density g_i, The arrangement of the system is equivalent to $(g_i - 1)$. Therefore total number of items is given by

$$\frac{(n_i + g_i - 1)!}{n_i(g_i - 1)!} \qquad 3.40$$

$$W = \frac{\pi(n_i + g_i - 1)!}{n_i!\,(g_i - 1)} \qquad 3.41$$

Defines the number of ways in which the n_i particles can be distinguished if $n_i + g_i \gg 1$, then equation 3.41 becomes.

$$\Rightarrow W = \frac{\pi(n_i + g_i)!}{n_i!\,(g_i - 1)!} \qquad 3.42$$

From equation 3.42, we obtain that $\ln W = \sum[\ln(n_i + g_i)! - \ln n_i - \ln(g_i - 1)!]$ and treated in $M - B$ distribution using sterling's approximation.

$$\ln W = \sum[(n_i + g_i)\ln(n_i + g_i) - n_i \ln n_i - \ln(g_i - 1)! - g_i] \qquad 3.43$$

Taking $\partial \ln Wmax = 0$ and neglecting $\ln(g_i - 1)! - g_i)$

$$\partial \ln Wmax = \sum[\ln(n_i + g_i) - \ln n_i]\,\partial n_i = 0$$

$$where\ \partial \ln \pi = \frac{1}{n}\partial n \qquad 3.44$$

For particle conservation,

$$\sum \partial n_i = 0 \qquad 3.45$$

If the internal energy $u = \sum \in_i n_i$

$$\partial u = \sum \in_i \partial n_i \qquad 3.46$$

Multiplying equations 3.45 and 3.46 by $-\propto\ and - B$ and adding them to equation 3.44

$$\sum[\ln(n_i + g_i) - \ln n_i] + \sum(-\propto \partial n_i + \sum -B \in_i \partial n_i = 0 \qquad 3.47$$

$$\sum\left[\ln\left(\frac{n_i + g_i}{n_i}\right) - \propto - B \in_i\right]\partial n_i = 0$$

But $\partial n_i \neq 0$

$$\ln\left(\frac{n_i + g_i}{n_i}\right) - \propto - B \in_i = 0$$

$$n_i = \frac{g_i}{e^{\propto} e^{-B\epsilon_i} - 1} \qquad 3.48$$

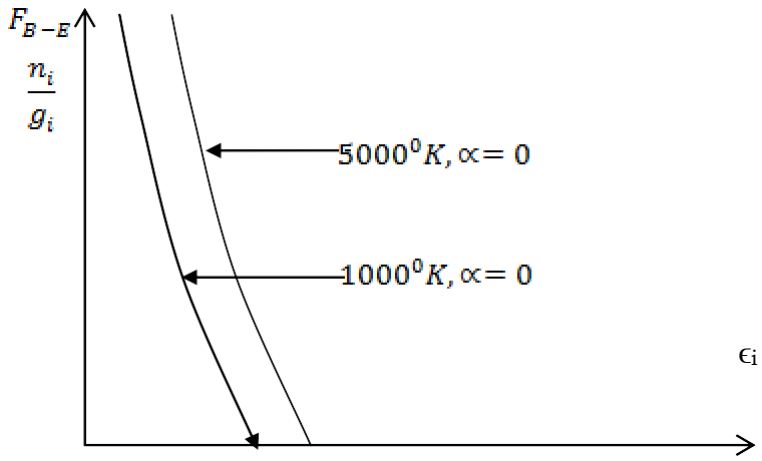


Fig. 3.5. The occupation indexes for $\in_i$ $(eU)B - E$ distributions.

Fermi-Dirac Statistical Distribution

Fermi-Dirac Statistics apply to indistinguishable particles which are controlled by the exclusion principle. The derivation of this distribution law will run parallel to that of the $B - E$ distribution law except that now each cell [i.e quantum state) can be occupied by at most one particle. If there are g_i cell having the same energy u and n_i particles, n_i cells are filled arg are $(g_i - n_i)$ unoccupied. The g_i cell can be arranged in $g_i!$ different ways. The number of distinguishable arrangements of the particles among the cells therefore

$$\frac{g_i!}{n_i!\,(g_i - n_i)!}$$

The particles here obey Paul, exclusion principle and have half integral spin.

The example is electron gas the probability, W of the entire distribution of the particles is given as

$$W = \frac{\pi g_i!}{n_i!\,(g_i - n_i)!} \qquad 3.49$$

$$\ln W = \sum [\ln g_i! - \ln n_i! - \ln(g_i - n_i)!] \qquad 3.50$$

Using sterling's approximation

$$\ln W = \sum [g_i \ln g_i - n_i \ln n_i - (g_i - n_i)\ln(g_i - n_i)] \qquad 3.51$$

For small change in ∂n_i in any of the individual $n_i's$ must not change W. Thus

$$\partial \ln Wmax = \sum [-\ln n_i + \ln(g_i - n_i)]\partial n_i = 0 \qquad 3.52$$

Since particles and energy are conserved and multiplying Langrage multiplier, we obtain

$$\left.\begin{aligned} -\propto \sum \partial n_i &= 0 \\ -B \sum \in_i \partial n_i &= 0 \end{aligned}\right\} \qquad 3.53$$

Adding these to equation 3.52, we have

$$\sum [-\ln n_i + \ln(g_i - n_i) - \propto \partial n_i - B \in \partial n_i] = 0$$

$$\sum \left[\ln\left(\frac{g_i - n_i}{n_i}\right) - \propto - B \in_i \partial n_i\right] \partial n_i = 0$$

Since

$\partial n_i \neq 0,$

$$\frac{g_i - n_i}{n_i} = e^{\propto} e^{B\epsilon_i} \qquad 3.54$$

$$n_i = \frac{g_i}{e^{\propto} e^{B\epsilon_i} + 1} \qquad 3.55$$

$$= \frac{g_i}{e^{[\propto + B\epsilon_i]} + 1}$$

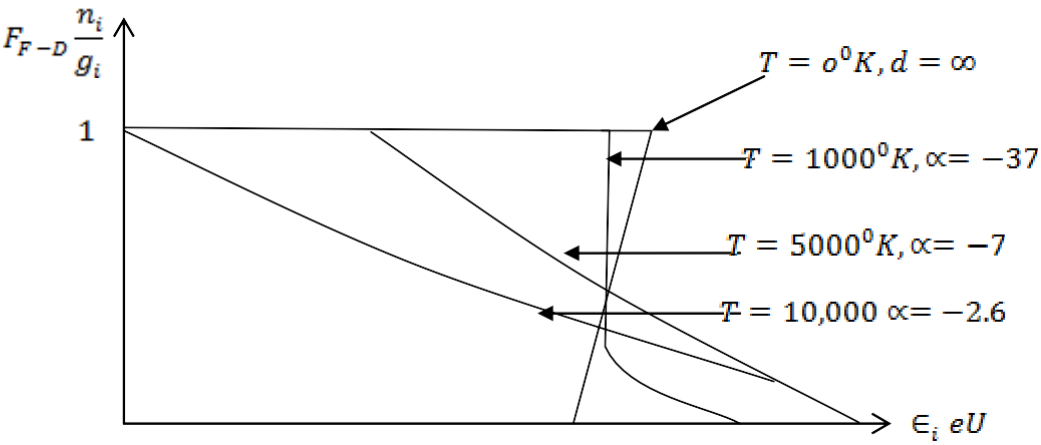


Fig. 3.6. A sketch of occupation $\in_i eU$ indices for 3 Fermi-Dirac distributions

The three statistical distribution laws are derived as written in equations 3.39,3.48 and 3.55. In these three formulas, n_i is the number of particles whose energy is ϵ_i and g_i s the number of states that have the same energy ϵ_i. The quantity n_i/g_i is called the occupation index of the state of energy ϵ_i which is the average number of particles in each of the states of that energy. The occupation index is independent upon how the energy levels of a system of particles are distributed and hence provides a good way of comparing the essential natures and features of these three distributions.

$B\beta$ is defined as $1/KT$ The $Max\ well\ Boltzmann$ occupation index ϵ_i is sketched in fig 3. For 2 different values of T. This is purely exponential dropping by a factor $1/e$ for each increase in ϵ_i of KT. While $f(\epsilon_i)$ depends upon the parameter $\propto$, the ratio between the occupation indices $f(\epsilon_i)$
and $f(\epsilon_j)$ of the two energy levels ϵ_i and ϵ_j does not.

That is

$$\frac{f(\epsilon_i)}{f(\epsilon_j)} = e^{(\epsilon_j - \epsilon_i)/KT} \qquad 3.56$$

The formula is useful since under certain conditions, the $B-E$ and $F-D$ distribution resemble the $M-B$ distribution, and it then permits one to determine the relative degrees of occupancy of two energy state the $B-E$ occupation index is sketched in fig 3. For temperatures of 1000^0k and 5000^0k ,in each case for $\propto = 0$ corresponding to a "gas" of photons), when $\epsilon_i \gg KT$, the $B-E$ distribution approaches the $M-B$ distribution. When $\epsilon_i \ll KT$, the minus 1 term in the denominator of the equation 3.48 causes the occupation index of the former distribution to be much great

The $F-D$ occupation index is sketched in fig 3.6 for four values of T and . The occupation index never goes above 1, showing one particle per state, which is a consequence of the obedience of the Fermi particles to the exclusion principle. At low temperature virtually all the lower energy states are filled, with the occupation index dropping rapidly near a certain critical energy known as the Fermi energy. At high temperatures the occupation index is sufficiently small at all energies for the effects of the exclusion principle to be important, and the Fermi-Dirac $F-D$ distribution becomes similar to the Maxwell-Boltzmann distribution.

0 THEORY OF ENSEMBLE

Gibb's formulation of statistical mechanics was faced by the problem of introducing a more abstract theory which would cover assemblages of particles much more complicated than gas molecules-in particular, microscopic objects. Visualizing "ensemble - collections of very large numbers of identical system, which could be microscopic or macroscopic in nature; again in considering the probabilistic calculations of predicting the most probable behaviour of the ensemble was the same as the long-time average behaviour of a single system of the type under condition. To carry out this calculation, he introduced 3 standard or canonical, ensembles to

which real experiments could be approximated. However, before any mathematical manipulation/concept are introduced here, we first of all give brief discussion of the physical ideas behind the ensembles.

First, definition of "microcanonical ensemble", physically the microcanonical ensemble can be considered as a large heat bath, very carefully insulated from the surrounding object so that the temperature [and therefore the total energy] is hold as nearly constant as possible.

Somewhat, the canonical ensemble ought to be thought of as an ensemble contained within the microcanonical ensemble and is otherwise completely isolated from the rest of the world. The container which separates the canonical from the microcanonical ensemble is such that it allows the exchange of heat between the two ensembles but not the exchange of particles or system. Thus the number of systems or microparticles in the canonical ensemble is constant, while the energy of the whole heat bath, but not that of the (small) volume representing the canonical ensemble remains constant.

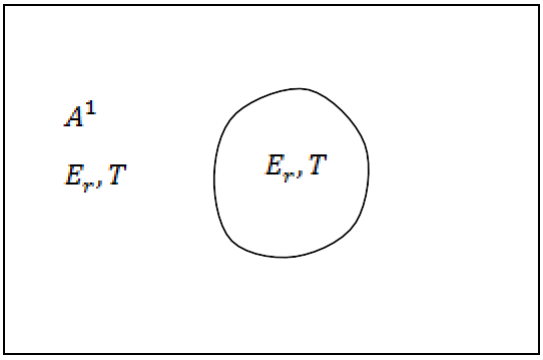


Fig:4.1 A given system A immersed in a heat reservoir $\boldsymbol{A^1}$; in equilibrium, they have a common temperature $\boldsymbol{T}$.

Lastly, Grand canonical ensemble was defined. Here the situation is exactly the same as in the canonical ensemble except that the wall separating the grand canonical ensemble from the microcanonical ensemble allows the passage of both heat and particles in the ensemble can change. From the mathematical view point, the grand canonical ensemble is the most useful and flexible of the three.

The description of a system by means of microcanonical distribution is equivalent to neglecting the fluctuation of its total energy the canonical distribution takes into account these fluctuations. The later form; in turn neglects the fluctuation's in the number of particles may be said to be microcanonical with respect to the number of particles. The grand canonical ensemble is "canonical" both with respect to the energy and to the number of particles. Thus all the three distribution are in principle, suitable for determining thermodynamics properties of the body. The difference from lies only in the degree of mathematical convenience, in reality, the

microcanonical distribution is the least convenient and is rarely used for this purpose.

Microcanonical Ensemble

To introduce this concept, consider the ensemble which consist of system which are isolated from the rest of the world or we suppose an ensemble of adiabatic systems which had been set up. Already from what has been said, we can not achieve complete isolation or a completely adiabatic system; we can only achieve conditions in which the interaction energy ΔE is very small by any comparison with all the other energies of all the elements of the adiabatic system are in the range $E_o \rightarrow E_o + \Delta E_L \cdots\cdots$

In an ensemble of microparticles we there conclude that no matter how small the interaction energy ΔE_i, vast numbers of state will be accessible to the particles of the ensemble. Then as there is no reason why a particular state with a certain energy, we must conclude that probability of finding a particular state is a constant provided the state is one which has an energy in ΔE_i, at E.

If we now denote probabilities by the symbol W, we can write down the mathematical expression for the probabilities. If we let $\partial(E)dE$ be the number of quantum state in dE at E, then oL is clearly a function of E and depends on the system.

Then $W(E_i) \alpha \partial(E_i)$ 4.0

$W(E_i) = cons\tan t \partial(E_i)$ 4.1

This constant in equation is to be obtained by the condition that

$$\sum_{i=1}^{\infty} W(E_i) = 0.$$

Equation (1) represents the mathematical expression of Gibbs microcanonical ensemble.

Canonical Ensemble

Here, as already presented, we visualize a very large isolated system which is usually called the reservoir, in which a much smaller system is immersed, but which still involves an enormous number of degrees of freedom. An

example, a small hot metal dropped into a large tank of cooling water. The question is what is the probability of finding the small system with a specified energy value? We note that the probability found relates only to the whole system of cooling water and hot metal after equilibrium has been established; the transient process is much more difficult and is considered later.

Let E_r = energy of reservoir in the rth state.

E_i = energy of object in the ith state

Then $E = E_r + E_i$ = constant $+ \partial E$

$\partial E =$ Interaction energy which we have earlier noted not to be identically zero.

However, under our presentation, we assume that for large reservoir]; $\delta E \ll E_i \ll E_r$ so δE is negligible from a numerical view point. After equilibrium is reached, the ensemble as a whole is isolated and can be considered as a microcanonical ensemble.

Thus using equation (1)

$$W_i \propto \Pi(E_r)$$

$$W_i \propto \Pi(E_r + E_i)$$

$$W_i = \Pi(E_r + E_i) \qquad 4.2$$

From $E = E_r + E_i \Rightarrow E_r = E - E_i$

W_i is the probability that the state is one in which the energy of the object is E_i and that of the reservoir is E_r. But the number of states $OL(E_r + E_i)$ must equal the product $\Pi(E_r).\ \Pi(E_i)$, according to the law of multiplication of probability of independent events or which is precisely equivalent to equation 3.2

$\therefore W_i = C\Pi(E - E_i).\Pi(E_i)$ 4.3

Expending equation 3 in power series $\ln \Pi\,(E - E_i) = \ln \delta C\,(E) - [\partial \ln OL\,/\partial E]_O E + etc$ but $[\partial \ln OL\,/\partial E]_O = \beta = 1/KT$

$\Rightarrow In\Pi\ (E - E_i) = \ln In\Pi\ \ E - \beta E_i$

$In\Pi(E - E_i) = Ce^{-\beta E_i}$

$W_i = C' e^{-\beta E_i} \delta L(E_i)$ 4.4

To find the value of C', we consider the fact that the sum of the probability of the whole event is unity.

i.e we consider the fact that the sum of the probability of the whole event is unity.

i.e $\sum C'\ C' e^{-\beta E_i}(E_i) = 1$

$$C' = \sum \frac{1}{e^{-\beta E_i}\ \Pi(E_i)} \qquad 4.5$$

Hence

$$W_i = \sum \frac{1}{e^{-\beta E_i}\ \delta L(E_i)} \frac{}{e^{-\beta E_i}} \Pi(E_i) \qquad 4.6$$

Equation 6 defines the probability distribution which is called the "Gibbs distribution" or the canonical (standard) distribution" The denominator of equation 6 can be denoted with letter $z$called partition function or the sum over all state

$$z = \sum_r e^{-\beta E_i}\ \Pi(E_i) \qquad 4.7$$

The partition function has a rule to play in calculation and derivation of the system.

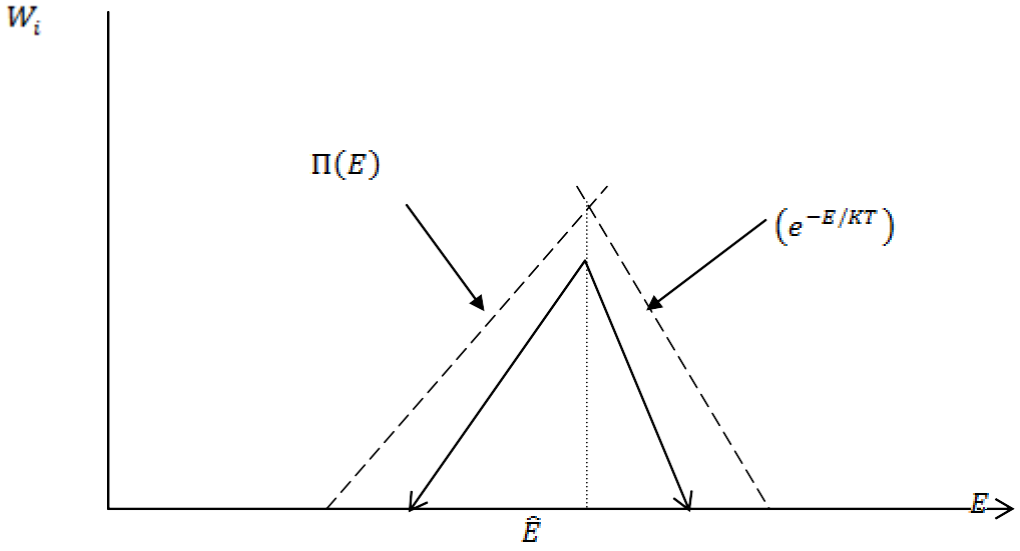


Fig: 4.2. The probability distribution over small range of energies.

W_i is sharply pealed over a particular small range of energies as shown in fig4.2, where $\hat{E}$ is the energy for which W_i has its maximum value. It should be noted that W_i will be negligible when E_i lies outside the range $\hat{E} + \frac{\partial E}{2}$ which assures us that the Gibb's distribution will predict average quantities with sharply defined means and small fluctuation.

Mean Value in Canonical Ensemble

When a system A is in thermal contact with a heat reservoir as in fig. 1 or when only its mean energy is known, the system in the representative of statistical ensemble are distributed over their accessible state in accordance with the canonical distribution.

$$W_i = \frac{e^{-BE_i}}{\sum_r e^{-BE_i}}$$

In these physical situations the energy of the system is not precisely specified and the solution of the mean value becomes particularly simple.

The mean energy is given by

$$\overline{E} = \frac{\sum_r e^{-BE_i}\ E_r}{\sum_r e^{-BE_i}} = W_i\ E_r. \qquad 4.8$$

Where the sums are over all accessible states v of the system irrespective of their energy. The last relation can be reduced to much simple form by noting that the expression in the numerator can write as in equation 7 thus

$$z = \sum_r e^{-BE_i}$$

$$E = \frac{\sum_r \frac{\partial}{\partial B}(e^{-BE_i})}{z} = \frac{-1}{z}\frac{\partial}{\partial B} = -\frac{\partial \ln z}{\partial B} \qquad 4.9$$

Application of canonical distribution

(1) Mean pressure of an ideal gas and mean energy in thermodynamic system

(2) Investigation of the magnetic properties of a substance

PARAMAGNETISM

The canonical distribution can be used to discuss a large number of situations of great physical interest. As a first application we shall investigate the magnetic properties of a substance which contains no magnetic atoms per unit volume and which is placed in a external magnetic filed B. we consider the particularly simple case where each magnetic atom has spin ½ and an associated magnetic moment μ_0. In a quantum-mechanical description the magnetic moment of each atom can then point either "up" (i.e parallel to the external field). The substance is said to be paramagnetic since its magnetic properties are due to the orientation of individual magnetic moments. Suppose that the substance is at an absolute temperature T. What then is μ_1 the mean component of the magnetic moment of one of its atoms along the direction of the magnetic field B?

We assume that each magnetic atom *interacts only weakly* with all the other atoms of the substance. In particular, we assume that the magnetic atoms are sufficiently for separated from each other so that we can neglect the magnetic field produced at the position of one magnetic atom by a neighboring magnetic atom. It is then small system under consideration and to regard all the other atoms of the substance as constituting a heat reservoir at the absolute temperature T of interest.

Each atom can be in 2 possible states, $\rightarrow$ the state $\oplus$ where its magnetic moment points up, and the state $(-)$ where its magnetic montenta points down. Let us discuss their states in turn.

In the state $\oplus$, the atomic magnetic moment in parallel to field so that $\mu = \mu_0$. The corresponding magnetic energy of the atom in then $E_+ = -\mu_0 B$. The canonical distribution thus yields for probability P_+ of finding the atom in this state the result.

$$P_+ = Ce^{-BE_+} = Ce^{B\mu_0 B} \cdots \qquad (54) \quad 4.10$$

where C in a constant of proportionality and $B = (KT)^{-1}$. This is the state of lower energy and thus is the state in which the atom is more likely to be found.

In the state $(-)$ the atomic magnetic moment is *antiparallel* to the field so that $\mu = \mu_0$. The corresponding energy of the atom is then $E_- = +\mu_0 B$. The probability

$$P_{-} = Ce^{-BE_{-}} = Ce^{-BE_{-}B} \cdots \qquad (55) \quad 4.11$$

This is the state of higher energy and thus is the sates in which the atom is likely to be found.

The constant C is immediately determined by the normalization requirement that the probability of finding the atom in either one of this states must be unity.

$$P_{+} + P_{-} = C\left[e^{B\mu_0 B} + e^{-B\mu_0 B}\right] = 1$$

$$C = \frac{1}{e^{B\mu_o B} + e^{-B\mu_o B}} \cdots \qquad (56) \quad 4.12$$

Since the atom in more likely to be in the state $\oplus$ where its magnetic moment is llel to the filed B, the mean magnetic moment μ must point in eh direction of the filed B. By virtue of (54) and (55), the significant parameter characterizing the orientation of the magnetic moment in the quantity.

$$w \equiv B\mu_0 B = \frac{\mu_0 B}{KT} \cdots \qquad (57) \quad 4.13$$

which measures the ratio of the magnetic energy $\mu_o B$ to the chrematistic thermal energy KT . It is apparent that if T is very large [i.e if $w << 1$] the probability that the magnetic moment is parallel to the field in almost the same as that it is antiparallel. In this case the magnetic moment is almost completely randomly oriented so that $\mu \square 0$. On the other hand, if T is very small (i.e if $w >> 1$), it is much more probable that the magnetic moment is parallel to the field than antiparallel to it. In this case $\mu \square \mu_0$

All these quantitative conclusion can readily be made quantitative by actually calculating the mean value u . Thus we find

$$\mu \equiv P_1(\mu_0) + P_1(-\mu_0) = \frac{\mu_0}{\left(e^{B\mu_0 B} + e^{-B\mu_0 B}\right)} \left(e^{B\mu_0 B} - e^{-B\mu_0 B}\right) \cdots \qquad (58) \quad 4.14$$

But

$$\mu = \mu_0 \tan h\left(\frac{\mu_0 B}{KT}\right) \cdots \qquad (59) \quad 4.15$$

$$\tan\theta = \frac{e^{\theta} - e^{-\theta}}{e^{\theta} + e_{-\theta}} \cdots \qquad (60) \quad 4.16$$

$$\therefore \mu_0 \frac{\left(e^{B\mu_0 B} - e^{-B\mu_0 B}\right)}{e^{B\mu_0 B} + e^{-B\mu_0 B}} = \mu_0 \tan hB\mu_0 B$$

Here, we have used the definition of the hyperbolic tangent.

The mean magnetic moment per unit volume of the substance (i.e its magnetization) power in the direction of the magnetic field has Its magnitude as $\bar{M}_o$ is simply given

By

$$\bar{M}_o = N_o \mu \cdots \qquad (61) \quad 4.17$$

If there are No magnetic atoms per unit volume.

We can easily verify that μ exhibits the behavior discussed previously in quantitative terms if $w<<1$ then $e^{w}=1+w\cdots$ and $e^{w}=1+\cdots$ hence, for

$$w << 1, \tan hw = \frac{(1+w+\cdots)-(1-w+\cdots)}{2}$$

$$= \underline{\underline{w}}\cdots$$

On the other hand, if $w>>1$, then $e^{w} >> e^{w}\cdot$

Hence, for $w >> 1$, tan $hw = 1$

The relation (59) predicts thus the following limiting behavior:

for $\mu_o B << KT$

$$\mu = \mu_o \left(\frac{\mu_o B}{KT}\right) = \frac{\mu_o^2 B}{KT} \qquad 4.18$$

for $\mu_o B << KT$,

$$\mu = \mu_o$$

when $\mu_o B << KT$, the value of μ is rather small. By (62), μ is then less than its maximum possible value μ_0 by the ratio μ_0/KT. Note that μ is this limit is simply proportional to the magnetic field B and inversely proportional to the absolute temperature, T.

using (61) and (62), the magnetization then becomes,

$\mu_o B << KT$,

for $\bar{M}_o = N_o \mu$,

$$\chi^{\beta} = \frac{\mu_o^2 B}{KT} \qquad 4.19$$

where is a constant of proportionalities independent of B. This parameter x is called the magnetic susceptibility of the substance.

Conventional definition of $\chi = m_o/H$. Equation 4.19 thus provides the following explicit expression for x in terms of microscopic quantities.

$$\chi = \frac{N_o \mu_0^2}{KT} \qquad 4.20$$

The fact that x is inversely proportional to the absolute temperature is known as curies law.

When $\mu_o B >> KT$, the mean magnetic moment μ attains its maximum possible value μ correspondingly the magnetization becomes for

$$\mu_o B >> KT , \bar{m}_o = N_o \mu_o$$

which is its maximum possible (or saturation) value and is thus independent of B or T . The complete dependence of the magnification $\bar{M}_o$ on the absolute temperature T and magnetic field B .

MEAN PRESSURE OF AN IDEAL GAS

It is experimentally quite easy to measure the mean pressure (i.e; the mean force per unit area) exerted by a gas on the walls of the container within which it is confined. Hence it is of pressure exerted by an ideal gas.

Let us denote by F the force in the mean pressure exerted by a single molecule on the right wall (i.e; the wall $x = L_x$) of the box containing the gas. Let us denote by F_r the value of this force when the molecule is in a particular quantum state r where its energy is $\in_r$. The force F_r can be readily related to the energy $\in_r$. Indeed, suppose that the right wall of the box were displaced very slowly to the right by an amount dL_x In this process the molecule would do on the wall an amount of work $F_x dL_x$ which must me equal to the decrease $-d \in_r$ of the energy of the molecule

Hence, $F_x dL_x = -d \in_r$

$$F_r = \frac{-t_r}{\partial L_x} \qquad 4.21$$

Here we have written a partial derivative to indicate that the other dimension L_y and L_z were supposed to remain constant in the argument leading to (87).

The mean force $\bar{F}$ exerted by a molecule on the wall is then given by averaging the force F_r over all possible states r of the molecule.

Thus,

$$\bar{F} = \sum_r P_r F_r = \sum_r \frac{e^{-B\in_r} \frac{(-\partial \in_r)}{\partial L_x}}{\sum_r e^{-B\in_r}} \qquad 4.22$$

where we have used the expression (67) for the probability P_r of finding the molecule in any state r. The relation (88) can be simplified since the sum in the numerator can again be expressed in terms of the sum in the denominator. Thus the numerator can be written

$$-\sum_r e^{-B\in_r} \frac{\partial \in_r}{\partial L_x} = -\sum_r \left(-\frac{1}{B}\right) \frac{\partial\left(e^{-\partial\in_r}\right)}{\partial L_x}$$

$$= \frac{1}{B}\frac{\partial}{\partial L_x}\left(\sum_r e^{-B\in_r}\right) \qquad 4.23$$

Using again the abbreviation Z of (73) the expression (88) becomes:-

$$\bar{F} = \frac{\frac{1}{B}\frac{\partial Z}{\partial ZL_x}}{Z} = \frac{1}{B}\frac{1}{Z}\frac{\partial Z}{\partial ZL_x}$$

$$\bar{F} = \frac{1}{B}\frac{\partial InZ}{\partial ZL_x}$$

But

$Z = V\alpha^3 B^{3/2} \Rightarrow InZ = InV + 3In\alpha - 3/2\, InB$

This general relation can be applied to the result (82) already obtained for In Z in the case of a monatomic molecule. Remembering that $V = L_x L_y L_z$, the partial differentiation yields immediately

$$\bar{F} = \frac{1}{B}\frac{\partial In\bar{Z}}{\partial \cancel{Z}L_x} = \frac{1}{B}\frac{\partial InV}{\partial \cancel{Z}L_x} = \frac{1}{BL_x}.$$

$$\bar{F} = \frac{KT}{L_x}$$

If the molecule is not monatomic the expression (87) for the force F_r becomes

$$F_r = \frac{-\partial}{\partial L_x}\left(\in_r^{(k)} + \in_r^{(i)}\right) = -\frac{\partial \in_r^{(k)}}{\partial L\cancel{z}}. \quad 4.24$$

where $\in_r^i$ does not depend the dimension L_z of the box. Hence the force, F_r,as it is only calculable from the centre-of-mass translational energy alone The preceding computation, which was based on this translational energy; remains therefore equally valid for polyatomic molecule.

Since the gas is ideal, the molecules move about without influencing each other appreciably. Hence the total mean normal force (i.e force in the x direction) exerted on the right wall by all the molecules of the gas is simply obtained by multiplying (the mean force $\bar{F}$ exerted by one molecule) by (the total number N of molecules in the gas). Dividing this result by the area $L_y L_z$, of the wall give then the mean pressure $\bar{P}$ exerted by the gas on this all. The relation (90) thus leads to the result.

$$\bar{P} = \frac{NF}{L_y L_z} = \frac{N}{L_y L_z}\frac{KT}{L_x} = \frac{N}{V}KT$$

$$\bar{P}V = NKT$$

But $n = N/V$

$$\therefore \bar{P} = nKT \quad 4.25$$

Where $V = L_x L_y L_z$ is the volume of the container and where $n \equiv N/V$ is the number of molecules per unit volume.

Fluctuation

However, the heat bath of out system will definitely have fluctuation in its actual energy. Hence we want to examine how large these fluctuations are the magnitude of the fluctuations is measured by the standard deviation ΔE. The mean square fluctuation of the energy is found by using the general statistical result.

$$\overline{(x-\bar{x})^2} = \overline{x^2(\bar{x})^2 - 2x\bar{x}} = \bar{x}^2 - \bar{x}^2 \quad 4.26$$

The standard *deviation* ΔE is defined by $(\Delta E)^2 = \left(E - \bar{E}\right)^2 = \overline{E^2} - \bar{E}^2$ 4.27

From equation 4.27

$$(\Delta E)^2 = \frac{\sum_r E_1^2 e^{-\beta E_r}}{z} = \left(\frac{\sum_r e^{-\beta E_i}}{z}\right)^2 \qquad 4.28$$

but

$$\sum_i e^{-\beta E_i} E_1^2 = \frac{-\partial}{\partial\beta}\left(\sum e^{-\beta E_i} E_i\right) \qquad 4.29a$$

$$= \left(\frac{-\partial}{\partial\beta}\right)^2 \sum e^{\beta E_i} \qquad 4.29b$$

Hence

$$\bar{E}^2 = \frac{1}{z}\left(\frac{\partial^2 Z}{\partial\beta^2}\right)_V \qquad 4.30$$

or

$$\bar{E}^2 = \frac{\partial}{\partial\beta}\left(-\frac{1}{Z}\frac{\partial^2}{\partial\beta^2}\right)_V + \frac{1}{Z}\left(\frac{\partial Z}{\partial\beta}\right)_V \qquad 4.31$$

Differentiate mean energy with respect to B at constant volume

Note the derivative is taken with respect to β rather that temperature; the temperature derivative can of course be obtained from

$$\beta = \frac{1}{KT}\frac{\partial\beta}{\partial T} = \frac{1}{KT} = K\beta^2 \qquad 4.32$$

But

$$\Delta(E)^2 = \bar{E}^2 - E^2 \qquad 4.33$$

Substituting the equations in their respective positions, we obtain

$$(\Delta E)^2 = \frac{1}{z}\left(\frac{\partial^2 Z}{\partial\beta^2}\right)_V - \frac{1}{Z}\left(\frac{\partial Z}{\partial\beta}\right)_V^2 \qquad 4.34$$

Comparing this with equations4.330 and(4.34) we obtain

$$E^2 - \bar{E}^2 = (\Delta E)^2 = -\left(\frac{\partial E}{\partial\beta}\right)_V \qquad 4.35$$

The right hand side of equation is related to the heat capacity of the system at constant volume since.

$$C_V = \left(\frac{\partial u}{\partial T}\right)_V = \left(\frac{\partial E}{\partial \beta}\right)_V$$

4.36

$$\left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial \beta}\right)_V \frac{\partial E}{\partial T}$$

4.37

$$C_V = \left(\frac{\partial u}{\partial T}\right)_V = \left(\frac{\partial E}{\partial \beta}\right)_V \frac{1}{KT^2}$$

4.38

From equation 4.32, we obtain

$$C_V = \overline{\overline{(E - \bar{E})}}^2 / KT^2$$

4.39

$$\overline{\overline{E - \bar{E}^2}} = KT^2 C_v$$

4.40

The importance of the energy fluctuations depends upon the ratio of the square root of the equation as in the equation below

$$\frac{\Delta E}{\bar{E}} = \frac{\sqrt{KTC_V}}{\bar{E}}$$

4.41

In this equation 16 C_V and E are extensive quantities 1 i.e they are proportional to the number of molecules N in the systems, where KT^2 is independent of N. Hence the dependence of $\Delta E / \bar{E}$ on the size of the system is given by:

$$\frac{\Delta E}{\bar{E}} = \frac{\sqrt{KTC_V}}{\bar{E}}$$

4.42

$$\frac{\Delta E}{E} \sqsubset \frac{1}{\sqrt{N}}$$

4.43

Equation 17 tells us that the relative fluctuation of the energy of a system in a heat bath is inversely proportional to square root of its size. For a

macroscopic system where $N \simeq 10^{23}, \frac{\Delta E}{E} \simeq 10^{-11}$; the fluctuation are extremely small; the energy of a macroscopic body in a heat bath is, for practical purposes completely determined. The above equation contains the reason why statistical physics can make definite quantitative statements about macroscopic system,

The fact that usually $\frac{\Delta E}{E}$ is so small for macroscopic systems means that the probability, distribution.

$P(E_i) = \frac{1}{z} g(E_i) e^{-BE_i}$ has an extremely sharp maximum at energy $\bar{E}$. This is because for a macroscopic body, the density of energy level E_i. i.e the number of such state per unit energy interval is very large.

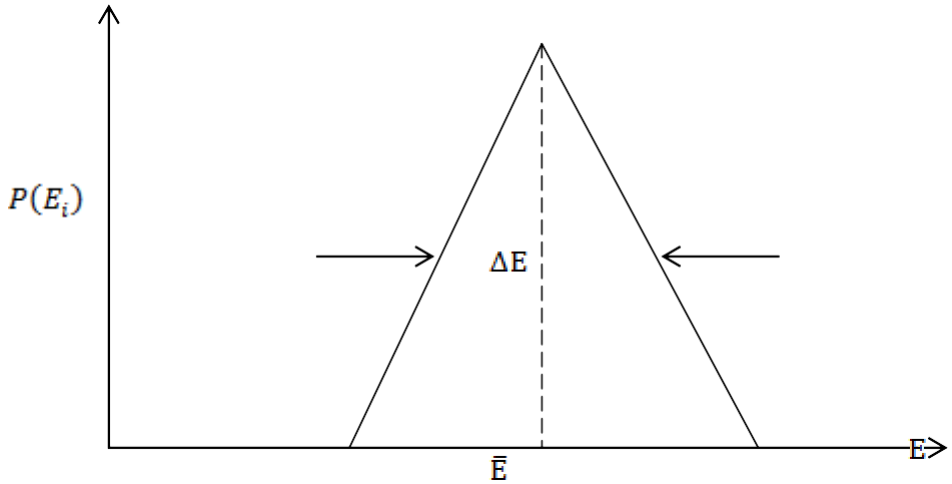


Fig 4.3 Schematic picture of the energy distribution $P(E_i)$ for a macroscopic body; The width of the peak is the standard deviation.

Example (1) derive an expression for the mean energy using the partition function z for monatomic gas in which only translational energy is considered.

Solution

Considering a gas molecules in a box with energy $E_{nx} n_z = \frac{\pi^2 \hbar^2}{2m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right]$

and the partition function

$$z = \sum_i e^{-BE_i}$$

Where $i = nx\ ny\ and\ nz$

$$z = \sum_{nx\ ny\ nz} Exp\left[\frac{-B\pi^2\hbar^2}{2m}\left\{\frac{n_x^2}{L_x^2}+\frac{n_y^2}{L_y^2}+\frac{n_z^2}{L_z^2}\right\}\right]$$

$$= \sum_{nx} Exp\left(\frac{-B\pi^2\hbar^2}{2m}\frac{n_x^2}{L_x^2}\right) \times \sum_{ny} Exp\left(\frac{-B\pi^2\hbar^2}{2m}\frac{n_y^2}{L_y^2}\right) \times \sum_{nz} Exp\left(\frac{-B\pi^2\hbar^2}{2m}\frac{n_z^2}{L_z^2}\right)$$

$$z = Z_x\, Z_y\, Z_z$$

Since Z_x is similar to Z_y and Z_z, we solve for Z_x and generalize for Z_y and Z_z.

Therefore,

$$Z_x = \sum_{nx} Exp\left(-\frac{B\pi^2\hbar^2}{2m}\frac{n_x^2}{L_x^2}\right)$$

If m is very small along with T, B is very large such that

$\frac{B\pi^2\hbar^2}{2m} \gg \frac{n_x^2}{L_x^2}$, the $\frac{n_x^2}{L_2^x}$ changes continuously.

$\therefore Z_x = \int_{\frac{1}{2}}^{\infty} exp\left[-\frac{B\pi^2\hbar^2}{2m}\frac{n_x^2}{L_x^2}\right] dnx \ldots\ldots\ A_1$ for a large number of count, the limit of integration can be changed. Thus,

$$Z_x = \int_0^{\infty} exp\left[-\frac{B\pi^2\hbar^2}{2m}\frac{n_x^2}{L_x^2}\right] dnx$$

To solve for Z_x, we let

$$U = \left(\frac{B}{2m}\right)^{1/2}\left(\frac{\pi\hbar}{L_x}\right) n_x$$

$$n_x = \left(\frac{2m}{B}\right)^{1/2}\left(\frac{L}{\pi\hbar}\right) U$$

$$Z_x = \left(\frac{2m}{B}\right)^{1/2}\left(\frac{Lx}{\pi\hbar}\right)\int_0^{\infty} exp\,(-u^2)du$$

The integration of $exp(-u^2)du$ is a standard integral which gives a constant value $\sqrt{\pi/4}$

$$\therefore Z_x = \left[(2m)^{1/2}\frac{\sqrt{\pi}}{4\pi\hbar}\right]\frac{Lx}{B^{1/2}} = d\,\frac{Lx}{B^{1/2}}$$

Where $\propto = \left[(2m)^{1/2}\frac{\sqrt{\pi}}{4\pi\hbar}\right]$

If for Z_y we have $\propto \frac{Ly}{B^{1/2}}$ and $Z_z = \propto \frac{Lz}{B^{1/2}}$

Then $Z = \frac{\propto Lx}{B^{1/2}} \times d\frac{\propto Ly}{B^{1/2}} \times \frac{\propto Lz}{B^{1/2}} = \frac{\propto 3V}{B^{3/2}}$

$\ln Z = 3\ln \propto + \ln V - 3/2 \ln B$

$$E = \frac{-\partial \ln Z}{\partial B} = -\frac{3}{2}\frac{1}{B} = \frac{3}{2}KT$$

Using $K = nR$

$E = {}^{3}/_{2}\, nRT$

Molar specific heat capacity at constant volume is

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}nR$$

4.3.8 The Grand Canonical Ensemble

In the proceeding sections, we developed the formalism of the canonical ensemble and established a scheme of operations for deriving the various thermodynamics properties of a given physical system. The effectiveness of the approach because clear from the examples solved, it will became more vivid in the subsequent studies carried out in this text. However, for a number of problems, both physical and chemical, the usefulness of the canonical ensemble formalism turns out to be severely limited and it appear that a further generalization of the formalism needs to be evolved.

The motivation that brings about this generalization is physically of the same nature as the one that led us form the microcanonical to the canonical ensemble-it is only the next natural step from there. It becomes important that not only the energy of a system but the number of the particles as well are considered in probing into our system. Consequently, there we may regard N and E as variables of the system.

The procedure for studying the statistics of the variables N and E is self-evident we may either (i) consider the given system A to immersed in a large reservoir A' with which it can exchange both energy and particles or (ii) regard it as a number of what we may call a grand canonical ensemble.

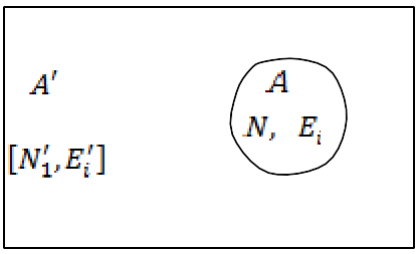


Fig 3.3 A Statistical system immersed in a particle-energy reservoir.

For obvious reason, the grand canonical ensemble is often called the "Gibbs ensembles for a variable number of particles". Here we must have to describe a system of constant volume which can exchange both heat and particle with the surrounding heat bath as shown in the fig 3. If the problem were merely that the numbers of particles in the volume V were not constant, it would be readily soluble. However, we must remember instead that the number of energy levels, depending on the quantum numbers or generalized co-ordinates n and also on N, the number of particles at a given time [i.e N is the instantaneous number of particles in V] The total number of particles present inside the reservoir, or microcanonical ensemble, is constant, symbol No, and E_i is large, constant energy of the reservoir and N_i is the number of particles in the reservoir.Now we want to consider a situation where a system A of a fixed volume is in contact with a large reservoir A' with which it can exchange not only energy but particles. Then neither the energy in A nor the particles N in the system are fixed,but the total energy $E^{(o)}$ and the total number of particles $N^{(o)}$ of the combined system $A^{o)} = A + A'$ are fixed ie

$E^{(o)} = E + E'$ is constant $N^{(o)} = N + N'$ is constant where $E' and N'$ denote the energy and the number of particles in the reservoir A' .

The probability, P_r in the ensemble of finding any of the particle state in the system where it contains N particles with energy E_r can be deduced by the procedure to be followed below;

Let $\Omega'(E', N')$ denote the number of states ascribed to the reservoir A' which contains N' particles and energy in the range near E' ,

The probability, $P_r(E_r, N_r) \alpha \Omega'(N^o - E_r, N^o - N_r)$ 4.44

Here, we use conservation equation for energy and number of particles since A is very small as compared to A'

Now we consider $E_r \square E^{(o)} and N_r \square N^{(o)}$ and take log of equation 4.44 and expand $In\Omega'(E^{(o)} - E_r, N^{(o)} - N_r)$

$$In\Omega'(E^{(o)}, N^{(o)}) = \left[\frac{\partial In\Omega'}{\partial E'}\right]_o E_r - \left[\frac{\partial In}{\partial N'}\right]_o N_r \qquad 4.45$$

Note that the left hand does not change because they are constants since they are fixed as such that in the derivation, we evaluate in terms of $E' = E^{(o)} and N' = N^{(o)}$ which reminds us that they are constant that

characterizes the reservoir A'. The two terms containing differential coefficients can be assigned values $\beta = \left[\frac{\partial ln\Omega'}{\partial E'}\right]$ $and \alpha = \left[\frac{\partial ln\Omega'}{\partial N'}\right]$

Therefore $P_r \infty e^{-\beta E_r - \alpha N_r}$ 4.46

The expression in 4.46 is the grand canonical ensemble distribution; the parameters of the reservoir are the temperature and the chemical potential.

$T = (k\beta)^{-1}$ is the absolute temperature of the reservoir while $\mu = -kT\alpha$ where μ is the chemical potential of the reservoir.

If one considers a physical situation where only the mean energy and mean number of particles $\overline{E} and \overline{N}$ of the system are invoked the distribution can be written in term of then respectively as

$$\overline{E} = \frac{e^{-\beta E_r - \alpha N_r}}{\sum_r \left(e^{-\beta E_r - \alpha N_r}\right)} \qquad 4.47$$

and

$$\overline{N} = \frac{e^{-\beta E_r - \alpha N_r}}{\sum_r e^{-\beta E_r} - \alpha N_r} \qquad 4.48$$

The denominator of equations 4.47 and 4.48 signifies the grand partition function which implies sum over all particles state of the particles in the system A irrespective of the energy of the particle. One of the beauty of this is that Bose- Einstein and Fermi Dirac statistical distribution can be deduced from this relation

CHAPTER 5

SYSTEM OF IDENTICAL PARTICLES

According to quantum Mechanics, the Schrodinger wave equation of a system contains all the information available about that system. This information may however be less than would be expected from the classical physics of macroscopic bodies. For instance the 2 electrons in $^{4}_{2}$He atom are considered to be insisting washable by experiment whereas moon of a planet are certainly distinguishable.

An independent solution of the wave equation using the time-independent of the system or a microstate if is considered necessary do distinguish it from the thermodynamics state [Microstate] Generally a number of independent solutions of the wave equation have the same energy (En). The energy level n is then said to be g −gold degenerate. If splitting of the energy levels. Is not considered and if the separation between the thermal energy (KT) they, degenerated level. The wave function of a free particle in space has the form.

$$\psi = Ae^{k.r} \qquad (5.1)$$

If the particle is considered to be confined to a box of volume v, the energy levels become quantized. The energy levels are closely related to the thermal energy KT. The allowed energy states may then be treated as a continuous function [density of states] such $D(E)dE =$ number of allowed state in the energy range $E \ \ to \ \ E + dE$.

The density of states function for the molecule of a gas in fact provides the link between the quantum and classical theories of perfect gases.

When the system consists of more than one identical partied, there will be the wave function overlapping in of the individual particles and the interaction of allowed energy levels of the whole system will become quite different from the energy levels in the individual particles. Consider for

simplicity a system of two identical particles in a no degenerate state. Then if the co-ordinates of the two particles are written A and B respectively, then the co-ordinates are in three special dimensions plus the spin of the particle.

$$\psi(A,B) = \pm\,\psi(B,A) \qquad 5.2$$

When the sign is positive the wave function is called symmetrical, when negative anti-symmetrical. The restriction imposed on the wave function by the equation.

$$f_0(V)\,d^3V = \frac{N}{V}\left(\frac{M}{2\pi\,KT}\right)^{3/2}\exp\left(-\frac{MV^2}{2KT}\right)d^3V$$

was because it is not possible to distinguish between the two particles. The probability that one particle is in a volume $d\,V_a$ at A and the other in a volume $d\,V_B$ at B is given by

$$|\psi(A,B)|^2\,dV_n\,dV_B \qquad 5.3$$

Since it is not possible to say which of the particles is at A and which at B the interchange of the two particles does not lead to a new state of the system and

$$|\psi(A,B)|^2 = |\psi(B,A)|^2 \qquad 5.4$$

Derivation of the Bose-Einstein distribution properties of an Ideal gas System from Grand Partition Function

We may now use the grand canonical approach to obtain the properties of ideal gases of identical –Bose–Einstein and –Dirac statistics. The first thing we would like is the occupancy of any single particle state and this is now very easy to work out. Let the single particle energy level have single particle energy E and this single particle level is to be our system in thermal contact with the rest of gas. The system energy is NE, where N is the occupancy which is clearly not fixed. Our general probability distribution for a system for a system is given by

$$W_1 = \frac{e^{MN/KT-EN/KT}}{\sum_i e^{MN/KT-EN/EJ}} \qquad 5.5$$

where the denominator is the grand partition $, z_g$. For our system consisting of just one sung particle energy level with variable occupancy$E(N) = NE$ Thus

$$w = \frac{e^{N(\mu-E)/KT}}{\sum_N e^{N(\mu-E)/KT}} \qquad 5.6$$

In this case $Z_g = \sum_N e^{N(\mu-E)/KT}$

We note that for integral spin particle any numbers of identical particles are permitted in any level. So we take from zero to infinity (∞)

$$Z_{B-E} = \sum_{N=0}^{\infty} e^{-(E-M)^N/KT} \qquad 5.7$$

Where N may be $N = 0, 1, 2 \cdots$

$$z_{B-E} = 1 + -e^{-[E-\mu]/KT} + e^{-[E-\mu]\,2/K} \cdots\cdots e^{-[E-\mu]\,\alpha/KT}$$

5.8

The increment is geometrical

$$\sum_0^{\infty} x^n = \frac{1}{1-x} \qquad 5.9$$

If $x < 1$ and $e^{-[E-\mu]/KT} < 1$

When $Z_{B-E,}$ N are to be averaged and < 1 then

$$Z_{B-E} = \frac{1}{1-e^{-[E-\mu]/KT}} \qquad 5.10$$

$$\bar{N} = \sum_0^{\infty} \frac{Ne^{-[E-\mu]N/KT}}{Z_{B-E}} \qquad 5.11$$

Evaluating the numerator

$$\sum_{0}^{\infty} nx^n = d\frac{d}{dx}\sum_{0}^{\infty} x^n = x\frac{d}{dx}\frac{1}{(1-x)} = \frac{x}{(1-x)^2} \qquad 5.12$$

Therefore$x = e^{-[E-N]/KT}$, then the numerator becomes $\frac{e^{-[E-N]/KT}}{1-e^{-[E-\mu]KT]^2}}$

Substituting in equation, we obtain

$$\bar{N} = \frac{e^{-[E-\mu]/KT}}{1-e^{-[E-\mu]KT]^2}} \qquad 5.13$$

$$\bar{N}_{BE} = \frac{1}{e^{-[E-\mu]KT]^2}} \qquad 5.14$$

This is called Base-Einstein distribution

5.1.4 Derivation of Ideal Fermi System from Grand Partition Function

For F-Dirac distribution, the spin is $^1/_2$,indistingwhableparticles with half-integral spin. It obeys the levels exclusion principle e.g. is electron gas.

This is called fermions, since the only possible occupation numbers zero our one, for $N = 0$, or for $1, N = 1$, we obtain.

$$Z_f a = 1 + e^{-[E-N]/KT} \qquad 5.15$$

From the partition function.

$$\text{As } \bar{N} = \sum NWi, \qquad 5.6$$

the mean occupation number $\frac{e^{-[E-\mu]/KT}}{1+e^{-[E-\mu]/KT}}$

This can be written as

$$N_{F-D} = \frac{1}{e^{[E-\mu]/KT}+1} \qquad 5.7$$

This is called the Fermi-Dirac distribution.

μ is h0wever considered to be common to many energy levels. Bose-Einstein distribution was obtained using the micro canonical ensemble. The distinguishability of the particles has been taken into account quite painlessly because our state was specified only by saying that occupancy of a given single particle level was N

The Quantum Theory of Specific Heats of Solid

Another application of the quantum statistics is to the specific heat of solids. In this section we first review the partially successful classical theory and then give the quantum theory, again utilizing the Bose-Einstein statistics.

Consider a crystalline solid composed of N atoms, each atom bound in the crystal lattice by forces arising from its neighbouring atoms. When any one atom is displaced from its equilibrium position, it is subject in a first approximation, to a restoring force proportional to its displacement. Thus, any atom displaced from its equilibrium position will undergo simple harmonic motion. However, when one atom is displaced from its equilibrium position, so too are the neighbours with which it is coupled by interatomic binding forces. Consequently, if one atom undergoes simple harmonic motion, it causes neighbouring atoms also to oscillate and the disturbance or deformation to be propagated through the crystal as an elastic wave.

At temperatures below the melting point the total energy content of the solid which may change with temperature consists of the following contributions from each atom: the kinetic energy of the essentially free, outer, valence electrons and the energy of vibration of the remainder of the atom, namely the nucleus plus the tightly bound, inner electrons. At all moderate temperatures the quantum state of any of the bound electrons is unchanged. For this reason the nucleus plus the bound electrons may be treated as a single, inert, vibrating particle. If the internal energy of the solid changes, so too does the temperature, and the change in the internal energy of the crystal per unit change in temperature is the specific heat of the solid. The total specific heat of the solid consists of the electronic specific heat and the lattice (vibrational) specific heat for all temperatures except the very lowest the electronic specific heat is negligible in this section we shall discuss the contributions arising from the lattice vibrations only.

We first compute the specific heat of a solid by using the classical theory, attributing the lattice energy content to N simple harmonic oscillators. For each degree of freedom of a simple harmonic oscillator there is $\frac{1}{2}KT$ of energy associated with potential energy and $\frac{1}{2}KT$associated with

kinetic energy (see also section 12 – 5) Therefore, for oscillations in three dimensions the total vibrational energy E is the number of degree of

freedom, 3N, time the energy of degree of freedom, KT,

$$= (3N)(KT) = 3NKT$$

5.8

And the classical lattice specific heat per the distribution functions is derived from the fundamental postulate of statistical mechanics.

Any particle among the various available states of a system is just as any other distribution.

Maxwell-Boltzmann Statistics Applied to the Specific Heat of a Diatomic Gas

The specific heat of constant volume of a classical ideal gas imagined to consist of point masses was computed to be $\frac{3}{2}NK = \frac{3}{2}R$, in a good agreement with the measured values of monoatomic gases. Of course, the atoms of a monatomic gas are not simple point masses; they have a complicated internal structure and follow the laws of the quantum theory. Their translational kinetic energy, however, is not quantized, and for moderate temperatures the electron configuration is always that of the ground state.

Thus, the atoms of a monatomic gas behave as if they were point masses.

Now consider the specific heat of a gas of diatomic molecules. There are three contributions to the total energy of such molecules: the translational kinetic energy of the centre of mass (unquantised), the rotational kinetic energy of the molecule as a whole about the centre of mass (quantised) and the (quantised) vibrational energy of the atoms of the molecule.

The molecules' translational kinetic energy contributes to the total energy of the gas at all finite temperatures, but there are contributions to the total energy from rotation and vibration only if an appreciable fraction of the molecules exist in excited rotational or vibrational states.

If all molecules were in the lowest rotational state (J = 0), the rotational kinetic energy would be zero, and if all molecules were in the lowest vibrational state (V = 0) , there would be no contribution form vibrational energy (except for the ever-present zero-point vibration). We can determine under what circumstances molecular rotation and vibration make significant contributions to the total energy of a diatomic gas by applying the Maxwell-Boltzmann statistics to find the temperatures for which excited rotational and vibrational states are appreciably occupied.

Atoms vibrate in $3-$dimension taken independently and hence each atom can be regarded as 3 oscillators. That is each atom has 3 degrees of oscillations. Therefore fro Natoms, the vibration is $3N$.

Einstein's assumed that atom vibrates with the same frequency, but it is only correct for a certain values of frequency. It was only correct when the energy of an oscillator is given as

From the mean energy E of oscillator which is given as

We derive an expression for the specific heat capacity by neglecting $\frac{1}{2}\ h\omega$ in which the average energy becomes

$$\bar{E} = \frac{h\omega}{exp - h_{\omega_E}\ \beta} \qquad 5.57$$

ω= ω_E $\Theta = {}^{h\omega_E}/_{K}$ is assumed to be Einstein's temperature, then

$$\bar{E}_T = 3N\frac{h\omega_E}{e^{h\omega_E\beta}-1} \qquad 5.58$$

$$C_r = \left(\frac{\partial E_T}{\partial T}\right)_v = \left(\frac{\partial \bar{E}_T}{\partial \beta}\right)_v \frac{\partial \beta}{\partial T} = -K\beta^2$$

$$\left(\frac{\partial \bar{E}_T}{\partial \beta}\right)_v = 3N\frac{h\omega_E}{[e^{h\omega_E B}-1]^2}, \frac{\partial B}{\partial T} = -K\beta^2$$

$$C_r = 3KN\frac{(h\omega_E\ \beta)^2}{[e^{hw_E\beta}-1]^2}e^{h\omega_E\beta}$$

$$3NK\left(\frac{h\omega_E}{KT}\right)^2\frac{e^{h\omega_E/KT}}{[e^{h\omega_E/KT}-1]^2}$$

But $\frac{\theta}{T} = \frac{h\omega_E}{KT}$

$$C_V = 3NK\left(\frac{\Theta_E}{T}\right)^2\frac{e^{\Theta_E/T}}{\left[e^{\Theta_E/T-1}\right]^2}$$

5.59

When $\Theta >> T, e^{\Theta/T} >> 1$

$$\therefore V_v = 3NK \frac{e^{\theta/T}}{e^{2\,\theta/T}}$$

$$= 3NK \left(\frac{\theta}{T}\right)^2 e^{-\theta/T}$$

When $\Theta_E << T$

$$C_V = 3NK = 3R$$

5.60

DEBYE'S SPECIFIC HEAT

Debye's assumes that all atoms do not vibrate at the same frequency because of dispersion of lattice wave in solid. The idea is contrary to Einstein's assumption. Also due to the fact that there is a finite number of atoms not all wave number are allowed.

If K_θ is the minimum allowed wave number of an atom can have, we obtain from the density of state an follows

$$g_k = \frac{3V}{(2\pi)^3} d^3k = \frac{3V}{(2\pi)^3} 4\pi\, K^2 dk \qquad 5,61$$

Where 3 is number of polarization modes with the $3N$ degree of freedom in a sphere in k −space of radius k_0

$$3N = \sum_K g_k = \int_0^{k_0} \frac{3V}{(2\pi)^3} 4\pi k^2 dk.$$

5.62

$$3N = \frac{3V}{(2\pi)^3} 4\pi \frac{K_\theta^3}{3}$$

$$\frac{N}{V} = \frac{3V}{(2\pi)^3} 4\pi \frac{K_\theta^3}{3}$$

$$\frac{N}{V} = \frac{1}{(2\pi)^3} \frac{4\pi K_\theta^3}{6\pi^2}$$

$$K_\theta = \left[6\pi^2 \frac{N}{V}\right]^{1/3}$$

If $N/V = 10^{25}$ atoms/cm^3, then

$$K_D = \frac{2 \times 10^3}{2\pi}$$

That is the or advent $\lambda_D = \frac{2\pi}{K_D} = 10^{-8} cm$ of the order of inter atomic or lattice spaing Debye's assumption for the dispersion relation $i.e w_k v_s k$ is given by the classical relation, $\omega = ck$.

$$i.e. g_k = d\omega_k = \frac{3V}{(2\pi)^3} \frac{4\pi k^2 dk}{C^3} \qquad 5.63$$

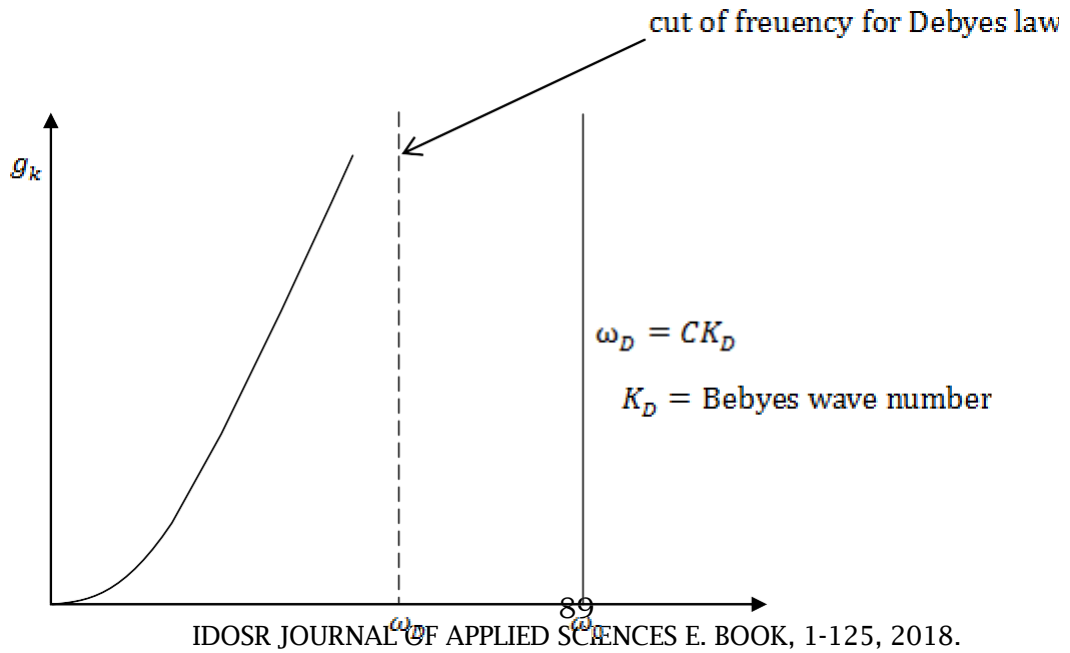
$$g_k = A\omega^2$$

$$\text{where} \quad A = \frac{3V}{(2\pi)^3} \frac{4\pi k^2}{C^3} \qquad 5,64$$

For $\omega \leq \omega_D$

When $g_k = 0, \omega > \omega_D$

The graph of g_k against ω is sketched



ω

Fig. 5,1 g_k against ω showing frequency distribution

Therefore total energy U is given by

$$U = \int_0^{\omega_D} \frac{3V}{(2\pi)^3} \frac{4\pi k^2}{C^3} . \frac{h\omega}{e^{\beta h\omega} - 1} d\omega \qquad 5.65$$

If we let $x = \frac{h\omega}{KT}$ and

$\frac{\theta_D}{T}$ implies that $\theta_D = \frac{h\omega}{K}$

$d\omega = \frac{KT}{h} dx$ and from

$$3N = \frac{3V}{(2\pi)^3} \frac{4\pi k^3 D}{3}$$

5.66

$$N = \frac{3V}{C\pi^3} K_D^3$$

Substituting these in equation

$$U = 9NK\,T \left(\frac{T}{\theta_D}\right)^2 \int_0^{x_D} \frac{x^3}{e^x - 1} dx \qquad 6.13$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 9NK \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

At low temperature $x_D \to \infty$; and $T << \theta_D$

$$C_V = 9NK \left(\frac{T}{\theta_D}\right)^3 \frac{4\pi^4}{15} \qquad 6.14$$

$$C_V = \left(\frac{12\pi 4\,NK}{5\theta_{dS}^3}\right) T^3$$

$C_v \propto T^3$

This expression indicates the relationship between the specific heat capacity and the Debye temperature.

One can also use Debye's approximation to derive the relation that the specific heat capacity at a constant volume agrees with that of classical theory of specific heat capacity.

Here $E = \frac{1}{2}\, h\omega + {h\omega}/{(e^{h\omega/KT} - 1)}$ over frequency weighted according to the density of states $g(w)$

$$E = \int_0^{\infty} \left[\frac{1}{2} h\omega + {h\omega}\Big/{\left(e^{\frac{h\omega}{KT}} - 1\right)} \right] g(\omega) d\omega \qquad 5.67$$

$$g(\omega) = \frac{V\omega^2}{2\pi^2 K_D^3} = \frac{V\omega^2}{2\pi^2}\left[\frac{1}{v_l^3 - v_T^3}\right]$$

Imposing A ω_T off ω_c such that

$$\int_0^{\omega_c} g(\omega) d\omega \quad = \quad 3N \qquad 5.68$$

We have that

$$\int_0^{\omega_c} \frac{\omega_c}{2\pi^2 K_D^3} d\omega = \frac{V\omega_c^2}{2\pi^2}\left[\frac{1}{v_l^3 - v_T^3}\right] = 3N \qquad 5.69$$

$$\Rightarrow \frac{V}{2\pi^2}\left[\frac{1}{v_l^3} + \frac{2}{v_T^3}\right] = \frac{\frac{gN}{\omega_C^3}}{g(\omega)} = \frac{g\omega^2}{\omega_c^2} \qquad 5.70$$

Substituting thus in equation the energy becomes

$$E = \frac{9N}{2\omega_c^3}\int_0^{\omega_c} \omega^3 d\omega + \frac{9N}{\omega_l^3}\int_0^{w_c} \frac{\omega^3}{e^{h\omega/KT} - 1} d\omega$$

$$\frac{9N\hbar\omega_c}{8} + 9NKT\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} \frac{x^3}{e^x - 1} dx \qquad 5.71$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = 9NK\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

At low temperature x_D>>1, $\Theta >> T$ considering the conditions given above, equation yields

$$C_v = \frac{12\pi^4 NK}{5}\left(\frac{T}{\theta}\right)^3 \qquad 5.72$$

At high temperature $x_D << 1,\ T >> \Theta$

$$C_v = 9NK\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} \frac{x^4}{2(coshx - 1)} dx \qquad 5.73$$

$$= 9NK\left(\frac{T}{\theta}\right)^3 \int_0^{x_D} \frac{x^4}{2\left(\frac{x^2}{2!} + \frac{x^4}{4!} + \cdots\right)}$$

Considering only the first term in the expansion and integrating, we have

$$V_v = 9NK\left(\frac{T}{\theta}\right)^3 \frac{1}{3} x_D^3 \qquad 5.74$$

But since $x_D = \frac{\Theta}{T}$

$$V_v = 9NK\left(\frac{T}{\Theta}\right)^3 \frac{1}{3}\left(\frac{T}{\Theta}\right)^3$$

$$C_v = 3NK$$

$$C_v = 3R \qquad 5.75$$

It should be noted that μ must be common to many energy level. Bose-Einstein distribution is obtained using the micro canonical ensemble. The distinguishability of the particles has been taken into account quite

painlessly because our state was specified only by saying that occupancy of a given single particle level was N.

Chapter 6

6.1.1 BOSE-EINSTEIN CONDENSATION

We shall now study the properties of a perfect gas of bosons of non-zero mass.

The Pauli's principle does not apply in this case and the low temperature properties of such a gas are very different from those of the fermions. $A\ B-E$ gas display most remarkable quintal feature.

At low temperature a phase change occurs in some respect reminiscent of the condensation of vapour. This phenomenon is known as Bose Einstein condensation which was predicted first by Einstein in 1925. It's study is of interest become it is a case of phase transaction which admits an exact mathematical treatment –liquid helium $4\ (4H_e)$ displays phenomenon similar to the $B-E$ condensation of a perfect $B-E$ gas.

In this section we shall briefly discuss the properties of a perfect $B-E$ gas and shall then point out the similarities which exist $4H_e$ problem.

The properties of a $B-E$ gas follows from the expression of for the mean occupation number n_s of the angle particle states and for the chemical potential, μ. Using equation

$$n_S = \frac{1}{e^{\beta}(\varepsilon_S - \mu) - 1} \qquad 6.1$$

If call the total number of particles N and substitute $\alpha = -{}^{\mu}/_{KT}$, the equation becomes

$$n_S = \frac{1}{e^{\beta}(\varepsilon_S - \mu) - 1} \qquad 6.2$$

$$N = \sum_S \frac{1}{e^{\beta}(\varepsilon_S - \mu) - 1} \qquad 6.3$$

The mean occupation numbers n_S must be tre of zero; they cannot be $-ve$ from equation –this implies that we must always $\varepsilon_S > U$. We are taking the zero of the energy scale so that the single particle ground state t_1 in zero, $t_1 = 0$ it's follows the chemical potential U of a $B-E$ gas must always be negative < 0.

Writing equation – as an integral where density of state is

$$f(\varepsilon)d\varepsilon = {}^{V4\pi P^2}/_{h^3} \quad {}^{dp}/_{d\varepsilon} \quad d\varepsilon \qquad 6.4$$

$$\varepsilon = P^2/_{2m}$$

$$\Longrightarrow P^2 = 2m\varepsilon$$

$$P = (2m\varepsilon)^{1/2}$$

Substituting $f(\varepsilon)d\varepsilon = \frac{V4\pi\,(2m\varepsilon).M(2m\varepsilon)^{-1/2}}{h^3}d\varepsilon$

$$f(\varepsilon)d\varepsilon = \frac{V2\pi.2.2^{1/2}\,M^{3/2}\varepsilon^{1/2}}{h^3}\,d\varepsilon \qquad 6.5$$

Using equation6.28 and6.30

$$N/_V = \frac{2\pi(2m)^{1/2}}{h^3}\int_0^\infty \frac{1}{e^B(\varepsilon_S-\mu)-1}d\varepsilon \qquad 6.6$$

Let us vary the temperature of the gas keeping N, V and hence the particles density $N/_V$ constant in equation – the left hand side, and hence the right hand side also are constant. This implies that as T is lowered U, which is $-Ve$, increases $i.e\ |U|$ decrease. The integral in equation –then defines a minimum temperature T_C such that for $T = T_C$ the chemical potential vanishes.

$U_0 = 0$ this temperature T_C is given thus

$$N/_V = \frac{2\pi(2m)^{1/2}}{h^3}\int_0^\infty \frac{\varepsilon^{1/2}d\varepsilon}{e^{\varepsilon/KTC}-1} \qquad 6.7$$

Changing the variable of integration of $Z = \varepsilon/_{KT_c}$ in equation –we have

$$N/_V = \left(\frac{2\pi KTc}{h^2}\right)^{3/2}\left[2/_{\sqrt{\pi}}\int_0^\infty \frac{z^{1/2}\,dz}{e^z-1}\right] \qquad 6.8a$$

$$= \left[\frac{2\pi\ mKTc}{h^2}\right]^{3/2} \qquad 6.8b$$

Following the evacuation of the integral in the bracket now there is clearly something wrong with this argument which says that there exist a temperature T_C below which $B-E$ gas cannot be cooled at constant density equation –only holds for $T \geq T_C$, but for $T < T_C$ this equation must be modified. The trouble stems from the replacement of the discrete sum single particles state in equation –by the integral in equation –.

As the temperature of the gas is lowered sufficiently, particles with begin to crowd into the single particle ground state with zero energy; $\varepsilon_1 = 0$. Just this state is completely neglected in equatio0n – Because of the factor

$\varepsilon^{1/2}$ in the integrand it is given zero weight. At higher temperatures this does not introduce an error but at low temperature we must not simply omits this state, since it will contain an appreciable number of particles.

In replacing equation –by an integral we must explicitly retain the 1st term $n_S = (e^{-B\mu} - 1)$ which gives the number of particles in the ground state and replacing only the remaining terms by an integral. Instead of equation – we have

$$N = \frac{1}{e^{-B\mu} - 1} + V\frac{2\pi(2m)^{1/2}}{h^3}\int_0^\infty \frac{\varepsilon^{1/2}d\varepsilon}{e^{B(\varepsilon-\mu)} - 1} \qquad 6.9$$

Here $N_1 = e^{-B\mu} - 1$ is the number of particles in the ground state with zero energy and zero momentum, $\varepsilon = 0, P = 0$ while

$N_\varepsilon > 0 = V\frac{2\pi(2m)^{1/2}}{h^3}\int_0^\infty \frac{\varepsilon^{1/2}d\varepsilon}{e^{B(\varepsilon-\mu)-1}}$ is the number of particles whose energy and momentum is non-zero, $\varepsilon > 0, P > 0$.

Above the temperature, T_C the number of particle in the ground state in quite negligible the 1st term equation –can be omitted and the chemical potential is given by the original equation –

Below the temperature T_C the chemical potential stays extremely close to zero.

For $T < T_C$, the number of particles with non-zero energy in them given by equation – with $\mu = 0$. If in the integral in this equation we introduce a new variable of integration $Z = B\varepsilon$ and use equation – to evaluate the resulting integral from equation –

$\mu = 0, Z = B\varepsilon$

$$N_{\varepsilon>0} = \frac{2\pi(2KTm)^{1/2}}{h^3}\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{z^{1/2}}{e^{z-1}}dz \qquad 6.10$$

$$N_{\varepsilon>0} = \left(\frac{2\pi\, MKT}{h^2}\right)^{3/2} \times 2.61$$

Equation 6.8 divides 6.10 to give

$$\frac{N_{\varepsilon>0}}{V}\, N/_V \frac{(2\pi\, mKT.)^{3/2} \times 2.61}{(2\pi\, mKT_c) \times 2.61}$$

$$\frac{N_{\varepsilon>0}}{N} = \left(T/_{T_C}\right)^{3/2}$$

$$N_{\varepsilon>0} = N\left({}^{T}/_{T_C}\right)^{3/2} \qquad 6.11$$

This equation gives the fraction of particles $\frac{N_{\varepsilon>0}}{N}$ in state with energy $\varepsilon > 0$. The remaining particles $i.e.$

${}^{N_1}/_{N} = 1 - \left({}^{T}/_{T_C}\right)^{3/2}$ are in the ground state with zero energy $(\varepsilon = 0)$ and zero momentum for equation – as $T > T_C$, the no of particles in the ground state in negligible.

As T decrease below, T_C the number of such particles increases rapacity. These particles posses zero energy and zero momentum. Because of the latter, they contribute neither to the pressure nor do they posses viscosity (Since viscosity is related to transport momentum).

The process of concentrating particles into the zero energy ground state is known as Bose Einstein condensation. It differs from the condensation of vapour into a liquid in that no spatial separations into phases with different properties occur in $B - E$ condensation. Never the less many similar features occur in both kinds of condensation.

Show that the relationship between (P, T) is

$${}^{T}/_{P^{(\gamma-1)/\gamma}} = constant$$

For eg, the pressure of a BE gas at $T < T_C$, just like the pressure of a saturated vapour, its volume. A $B - E$ gas at temperature below T_C is called degenerate. T_C is known as the degeneracy temperature or the condensation temperature.

We next consider the energy of the $B.E$ gas for $T < T_C$ only the normal particles posses energy. There are $N_{\varepsilon>0}$ such particles and the energy of each is the order of magnitude of KT, hence it follows from equation – that the energy of the $B - E$ gas is given by

$$E = N_{\varepsilon>0}KT = N\left({}^{T}/_{T_C}\right)^{3/2}.KT \qquad 6.12$$

$$= NK\frac{(T)^{5/2}}{{T_C}^{3/2}}$$

$T < T_C$ and hence the molar heat capacity at constant volume by

$$C = {}^{5}/_{2}\left({}^{T}/_{T_C}\right)^{3/2}$$

$$= T < T_C \qquad 6{,}38$$

The exact calculation from the $B\ E$ distribution function gives $C_V = 1.93R$ $\left({}^{T}/_{T_C}\right)^{3/2}$

$= T < T_C$

From equation

$$E = V\frac{2\pi(2m)^{1/2}}{h^3}\int_0^\infty \frac{\varepsilon^{1/2}}{e^{B\varepsilon}-1}d\varepsilon \quad T < T_C \qquad 6.13$$

Let $z = B\varepsilon \Longrightarrow \frac{dz}{d\varepsilon} = B$

$$E = V\frac{2\pi(2m)^{1/2}}{h^3\ B^{5/2}}\left[{}^{2}/_{\sqrt{\pi}}\int_0^\infty \frac{e^{3/2}}{e^z-1}dz\right.$$

$$E = V\frac{2\pi(2m)^{1/2}}{h^3}\int_0^\infty \frac{e^{3/2}}{e^{B\varepsilon}-1}d\varepsilon \quad T < T_C$$

$=$ let $z = \beta\varepsilon \Longrightarrow {}^{dz}/_{d\varepsilon} = \beta$

${}^{z}/_{\beta} = \varepsilon, {}^{dz}/_{\beta} = d\varepsilon$

$$V.\frac{2\pi(2m)^{1/2}}{h^3}\ \frac{1}{\beta^{3/2}\beta}\int_0^\infty \frac{z^{1/2}}{(e^z-1)}dz$$

$$.V\frac{2^{5/2}m^{3/2}\ (KT)^{5/2}(\pi)^{1/2}}{h^3} = \frac{V\,m^{3/2}(KT)^{5/2}\ \ 31.5}{h^3}$$

6.15

$$E = {}^{N}/_{m^{3/2}}$$

To conclude this section, we briefly discuss the relevance of BE condensation for the low temperature properties of helium $4(4_{He})$ which has spin zero and therefore satisfies BE statistics.

a. We note first of all that under its own vapour pressure 4_{He} remains liquid down to the absolute zero of temperature. Large pressures, about 25 atoms are required to solidify it under these conditions.
b. The normal boiling point of 4_{He} 4.2^0k, as liquid 4_{He} in contact with it's vapour is cooled it's properties change chromatically at a sharply define temperature of 2.17^0k.

Above this temperature it's behave as normal liquid and is known as helium I.

Below this temperature it's has almost remarkable properties, such as flowing rapidly through fine capillaries with apparently no viscosity. This peculiar form of helium is called helium II.

Many of the properties of helium II are described well by a two fluid model. This model assumes that helium II behaves likes a mixture of two fluids, the normal fluid and the super fluid, and the there is no viscous interaction between these two fluids. The normal fluid possesses all the usual properties of a fluid. The super fluid has curious properties. It has zero entropy and experience no resistance to it's flow, i.e. it has no viscosity.

CHAPTER 7

LIOUVILLE'S THEOREM

Suppose that we have a large collection of identical, non-iterating systems. The state of each system can be represented by a point in phase space. The state of the collection of systems can be represented by a set of points in phase space, each points representing one system. We will now show that this collection of points move through phase space in the same manner as an incompressible fluid.

First consider an arbitrary fluid flowing in three dimensions. Let $p(x,t)$ be its density and $v(x,t)$ its velocity. Imogene an observer moving through the fluid along an arbitrary path $x_i = x_i(t)$ . .(1)

The observer will note a change in density as he moves through the fluid, given by

$$dp/dt = \sum_{i=1}^{3} \frac{dp}{dx_i} \frac{dx_i}{dt} + \frac{\partial p}{\partial t} \quad 7.1)$$

Now suppose the observer stations himself on an element of the fluid and allows himself to be transported along with the element. Then his velocity corresponds with the velocity of the fluid and thus

$$\frac{dx_i}{dt} = V_i \qquad 7.2$$

Substituting (3) and (2)

$$\frac{dp}{dt} = \sum_i \frac{\partial p}{\partial x_i} V_i + \frac{\partial p}{\partial t} \quad 7.3$$

If the fluid is incompressible, then the observer waving with the fluid will always observe the same density in his immediate neighborhood $i.e$

$$\frac{\partial p}{\partial t} + \sum \frac{dp}{dx_i} V_i = \qquad 7.4$$

If equation 5 is always satisfied, the fluid is incompressible. It should be noted that an incompressible fluid is not necessarily a fluid of constant density. Imagine can incompressible and immiscible bolob of oil, flowing along in a volume of water. The combined system of oil and water would constitute an incompressible fluid and equation (5) would be satisfied. However, since the density of the oil and water are different, the density of the combined system would not be constant. It would vary with position and with time.

We are now in a position to consider the collation of representative points in the phase space discussed above. Let (q, p, t) be the density of such point. Consider a point whose ith position co-ordinate in q_i and whose jth momentum co-ordinate in P_j the velocity of this point in the q_i direction in the phase space will be q_i and the component of the flux in the q_i direction will be $\emptyset q_i$. The velocity of the point in the p_i direction will be with flux $\emptyset p_j$.

Applying the equation of continently to the points in phase space, we then have

$$\frac{\partial \emptyset}{\partial t} + \sum_i \frac{\partial}{\partial q_i}(Q, q_i) + \sum_i \frac{\partial}{\partial p_j}(Q, q_j) = 0 \qquad 7.5$$

Differentiating

$$\frac{\partial \emptyset}{\partial t} = \sum_i P_i \frac{\partial \emptyset}{\partial P_t} + q_i \frac{\partial \emptyset}{\partial q_i} + \sum_i \emptyset \left(\frac{\partial q_i}{\partial q_i} + \frac{\partial p_i}{\partial p_i}\right) = 0 \qquad 7.6$$

From Hamiltonian's equation, of motion

$$q_i = \frac{\partial H}{\partial P_t} + P_i = \frac{-\partial H}{\partial P_i} \qquad 7.7$$

Substituting this in equation (7) the 3rd term disappears. Thus

$$\frac{\partial \emptyset}{\partial t} + \sum_i P_i \frac{\partial \emptyset}{\partial t} + q_i \frac{\partial \emptyset}{\partial q_i} = 0 \qquad 7.8$$

Lowville's equation governs the motion of the points in phase space representing the dynastical state of a collection of now interacting system. It represents the flow of an incompressible fluid in the 25 direction phase space as compare with the $3-$ dimensional case revealed. The theory can be under to derive the distribution function which are independent of time $i.e.$ to represent the equilibrium microstates.

CLASSICAL DISTRIBUTION FUNCTION

Considering he probability of finding a particle in one cell. Assume that the probability of finding particle in one cell is the same

N_1 is the particle in cell S_1

N_2 is the particle in cell S_2

N_3 is the particle in cell S_3

N_k is the particle in cell S_k

These are proportional to the number of ways

$$W(N_1, N_2 \cdots N_k) = \frac{C\ \ N}{N_1!\, N_2! \cdots N_k!} \qquad 7.9$$

In thermal equilibrium, the system will be nearly in a state obtained by maximizing w subject to constraint of conservation of U and N using the langrangian

$$f(x,t) = ax + b = 0 \qquad 7.9$$

$$ax^2 + b = 0$$

It we use $f(x,t) + \lambda(ax^2 + b)$ 7.10

$\partial f / \partial x = 0$ Maximizes the function

$\lambda =$ Langrangian multiplies

In $w = In\ N! - \sum_{i=1}^{k} In\ \ N_i!$ +const.

For large N_i, we use starlings approximating

$x! = \sqrt{2\pi}\ x^{x+1/2}\ e^{-x}$

$in(x!) = const - + \left(x + \frac{1}{2}\right) in\ x - x$

$= \text{const} + x\ in - x$

Applying this

In $w = \frac{N}{n} N - N - \sum_{i=1}^{k} \left(\frac{N_i}{nN_i} - N_i\right) + \text{const}$ 7.11

In $w = N/nN - \sum_{i-1}^{k} N_i/nN_i + \text{const}$ 7.12

To W

$$\partial / \partial\ N(Inw) = 0 = \partial(NIn\ N) - \partial \sum_{i=1}^{k} (N_i In\ N_i) \qquad 7.13$$

But $\partial N = 0 = \lambda \sum \partial N_i$

$\partial u = 0 = \beta \sum N_i\ E_i$

Where λ and β are Langrangian multiplier summing up, we obtain.

$$\sum[(In\ N_i + 1 + \lambda B\ \in_i)\partial N_i] = 0$$

$$InN_i = -1 - \lambda - \beta \in_i$$

$$N_i = e^{-1} e^{-\lambda}\ e^{\beta \epsilon_i}$$

$$N_i = \propto\ e^{-\beta \epsilon_i} \qquad 7.14$$

This is the thermal equilibrium for state of the most probable distribution.

Considering classical ideal gas

Take cells in the range $U, U + du, V + dv$ and

$w, w + dw$ in ith cell

$$N_i = f(u, v, w) du\ dv\ dw \qquad 7.15$$

Where $f(u, v, w) = Ae^{-\beta \epsilon_i}$ and energy in each particle is

$$\in_i = \frac{1}{2}\ M(U^2 + V^2 + W^2)$$

$$F(U, V, W) = Ae^{-B^1/2}\ (u^2 + v^2 + w^2) \qquad 7.15$$

If we look at microscopic particle,

$$\sum_i N_i = \iiint du\ \ dv\ \ dw \qquad 7.16$$

$F(u, v, w)$ is the Maxwell distribution law and the constant $\sum N_i = N$ such that

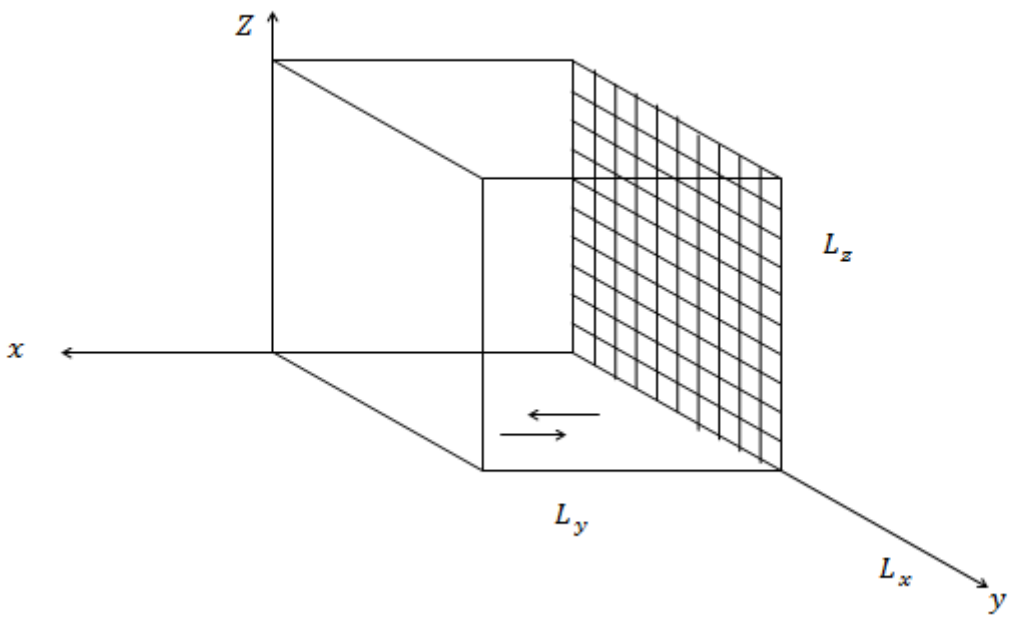
$$\int \int_{-}^{+} \int_{\infty}^{\infty} f(U, V, W) du\ dv\ \ dw = N \qquad 7.17$$

$$A = N\left(\frac{m\beta}{2\pi}\right)^{3/2} \qquad 7.18$$

$$\Rightarrow\ f(u, v, w) = N\left(\frac{M}{2\pi\ KT}\right)^{3/2} e^{-m/2} \frac{(u^2 + v^2 + w^2)}{KT} \qquad 7.19$$

This is the

For ideal gas case



Area of side of the cub parallel to $x -$ axis is $Lx\ Lz$. Force on this area

$$f = \frac{change\ in\ monertum}{time}$$

$$= \frac{2mu}{L_y/U} \qquad 7.20$$

Pressure, $P = \frac{F_x}{L_x\ L_z} = \frac{2MU^2}{L_x\ L_z\ L_y} = \frac{2MU}{Vol}$ 7.21

$$\bar{P} = \iiint A^{e^{-1/2}}\, m\beta\,(u^2 + v^2 + w^2) fx\ du\ dv\ dw \qquad 7.22$$

$i.e.$ Average pressure

$$\vec{P} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} A^{e^{-\frac{\beta}{2KT}}}\,(u^2 + v^2 + w^2)\frac{2mU^2}{Vol}\ du\ dv\ dw \qquad 7.23$$

Where $A = N\left(\frac{m}{2\pi\ KT}\right)^{3/2}$

The integration over U is only over $+Ve$ velocity because only such particle strike the wall. In this case, we obtain

$$\vec{P} = \frac{2m}{Vol} A\left(\frac{2\ KT}{m}\right)\pi\ \frac{\sqrt{\pi}}{4}\left(\frac{2\ KT}{m}\right)^{3/2}$$

$$\bar{p} = \frac{N\bar{U}}{Vol} = nkT \qquad 7.24$$

Consider a particle confined within a box in the shape of cube of edge $L_x = L_y = L_z$ possible energy level in given by

$$E = \frac{h^2}{2m}\pi^2\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right] \qquad 7.25$$

a. Suppose that the particle is on a given state specified by a particular value of the 3 integer n_x, n_y and n_z by considering how the energy of this state might change when the length L_x is changed quasi statistically by small d_x. Blow that the force exerted by the particle in this state on the wall plar to the x −axis is given $f(x) = -{}^{\partial E}/_{\partial L_x}$.

Calculate explicitly the force per unit area, (Pressure on this wall).

Classical limit

An expression for the no of particles N is given as

$$N = \int_0^\infty \left[\frac{4\pi\, V_g\, M}{h^3}\sqrt{2ME}\right. \frac{dE}{e^{\lambda+BE}+1} \qquad 7.26$$

Where $\frac{4\pi\, V_g\, M}{h}\sqrt{2ME}$ is the density of state

$$2\pi\, V_g \frac{(2\,MKT)^{3/2}}{h^3}\int_0^\infty \frac{Z^{1/2}}{e^{\lambda+Z}+1}\, dz$$

Where total energy $E = ZKT\ i.e. Z = BE$

$$U = \int_0^\infty E d\,N = \frac{4\pi\, V_g}{h^3}\frac{E^{3/2}}{e^{\lambda+BE}\pm 1}dE$$

$$= NKT2\pi\, Vg_o \frac{(2MKT)^{3/2}}{h^3}\int_0^N \frac{Z^{1/2}}{e^{\lambda+Z}+1}dZ \qquad 7.27$$

$$N \simeq \frac{2\pi\ V_g}{h^3}(2MKT)^{3/2}\int_0^\infty Z^{1/2}\quad e^{-\lambda-Z}dz$$

$$N = \frac{Vg_0(2MKT)^{3/2}}{h^3}e^{-\lambda}\left(\int_0^\infty Z^{1/2}\quad e^{-Z}dz\right. \qquad 7.28$$

$$= {}^{\sqrt{\pi}}/_{2}$$

$$e^{-\lambda} = \frac{N\ h^3}{Vg_0(2\pi\ MKT)^{3/2}} << 1 \qquad 7.29$$

$\frac{N}{V}$ = density of particle

$(2\pi\ MKT)^{3/2}$ average momentum $\bar{P}$

$$\Rightarrow e^{-\lambda} \simeq \frac{\left(\frac{N}{V_0}\right)^{h^3}}{\bar{P}3} < 1 \qquad 7.30$$

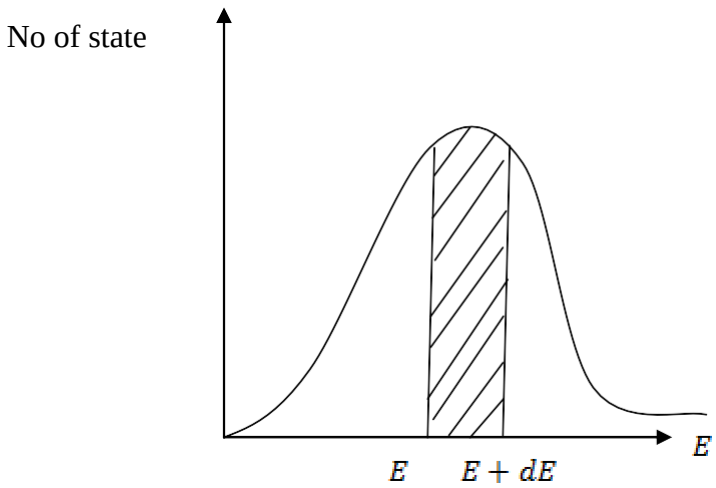
$$h^3/_{\bar{P}3} << r_0^3 \quad \left(r_0^3 = \frac{V_0}{N}\right)$$

$$\boxed{h/_p << r_0}$$

$h/_p$ is the de −Broglie wavelength of classical particle and r_0 is the inter particle separation.

ENTROPY AND DENSITY OF STATE

The number of state in the system is denoted by $\Gamma(E)$; $\Gamma(E) << E$

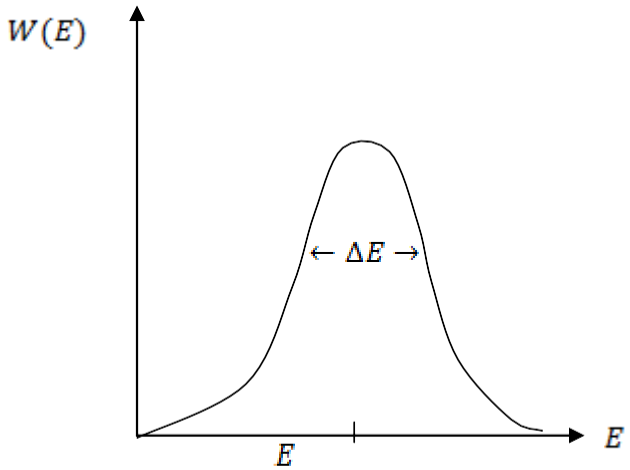


The energy is in the range $E < E_n < E + dE$ is $d\Gamma(E)d^E/_{dE}$

Distribution of probability over the no of states function

$$W(E) = \frac{d\Gamma(E)}{dE} \quad W(E) \qquad 7.31$$

Where $W(E)$ =density matrix.



E has sharp maximum at $E = E$

$W(E)\Delta E = 1 \equiv W(E)\Delta\Gamma(E) = 1$

Where $\Delta\Gamma = \frac{d\Gamma(E)}{dE} dE$

Entropy $S = K/n\ \Delta\Gamma$

This is the relationship between the entropy and density of state.

The connection between $\Delta\Gamma$ and $\Delta q\ \Delta p$ is obtained by viewing classical theory as a limiting case of quantum theory

$$\therefore \quad \Delta\Gamma = \frac{\Delta q\ \Delta p}{(2\pi\ h)^3} \qquad 7.32$$

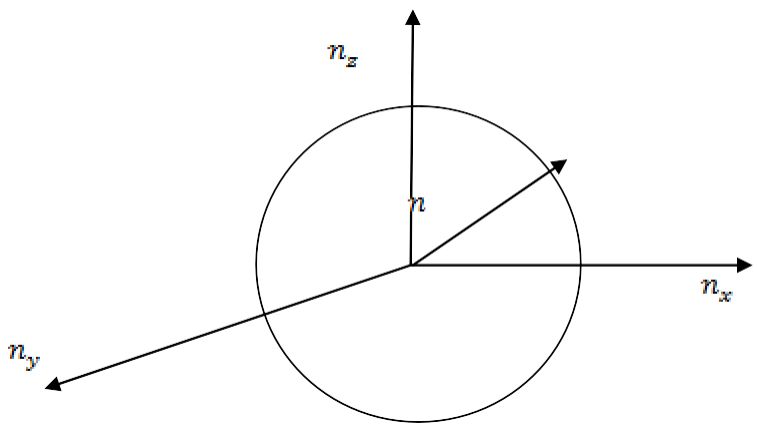
Density of state

$$E_k = \frac{h^2 K^2}{2m} \ is \text{ Quantized}$$

$$K_r = \frac{2\pi\ n_r}{L} \Rightarrow K_x\ \frac{2\pi\ \ n_x}{L}, k_y = \frac{2\pi\ \ n_y}{L}$$

$$K_z = \frac{2\pi\ \ n_z}{L}$$

$$E = \frac{h^2}{2m}\ \frac{4\pi^2\ n^2}{L} \qquad 7.33$$



Consider the number of state Γ with energy $< E$ given that $\Gamma = \frac{1}{8}\,\frac{4}{3}\pi\, n^3$

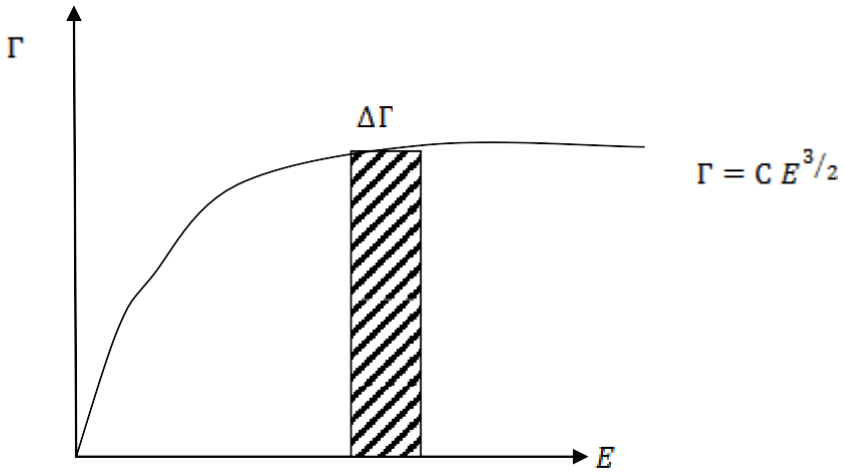
$$\Gamma = \frac{1}{8}.\frac{7}{3}\pi\left(\frac{2m\,E\,L^2}{4\,\pi^2\;h^3}\right)^{3/2} = \frac{\pi V}{6\,\pi^2\;h^3}\left(\frac{1}{2}ME\right)^{3/2}$$

$$\Gamma \propto E^{3/2} \text{ where } C = \frac{V}{6\,\pi^2\;h^3}\left(\frac{1}{2}M\right)^{3/2}$$

$$\Gamma = CE^{3/2}$$

The density of state is given by

$$g(E) = \frac{d\Gamma}{dE} = {}^{3}/_{2}\;C\,E^{3/2} \qquad 7.34$$



The probability, $W(E)\overset{dE}{=} g(E)$

Application of $B-E$ statistic (Blackbody Radiation)

The most important application of $B-E$ statistics relates to electromagnetic radiation witch is thermal equilibrium called Blackbody radiation as already mentioned in previous chapter 3.

Such a radiation may be regarded as a gas consisting of photon. The E-M field can be characterized by a vector potential $A\left(\vec{\gamma},\ t\right)$. given by

$$\nabla^2 A - \frac{1}{C^2}\frac{\partial^2 A}{\partial\ t^2} = 0 \ \ and\ \nabla.A = 0 \qquad 7.37$$

If $\vec{A}(\vec{\gamma},t) = A_k(r)e^{iwkt}$.

$$\nabla^2 An + \frac{wic}{C^2}An = 0$$

Let $k_{n=\frac{wk}{C}}$, $A_{n=Ae^{-ik\vec{r}}}$

Applying the boundary condition that the amplitude vanities at the side of the cavity box $L, A_n = 0$

Also, $k_{nx} = \frac{2\pi n_y}{L}, k_{nz} = \frac{2\pi n_z}{L}$ and $\nabla.A = 0$ given that.

$A.k_n = 0$ shows that there are 2 direction Q polarization of the filed.

Total energy $U = \sum n_k\ \hbar\ w_k$

No of photons (no of normal modes of vibration in the field in element d^3k of $k-$ space is

$$g_k dw_k = \Delta n_x \Delta n_y \Delta n_z = \frac{2L^3\ d^3K}{(2\pi)^2} \rightarrow (Polarization\ factor$$

$$g_k dw_k = \frac{2L^3}{(2\pi)^3}4\pi k^2 dk. \qquad 7.39$$

But $k = \frac{w}{c}, L^3 = V.$

$g_k dw_k = \frac{2V}{(2\pi)^3}\frac{4\pi}{C^3}W_K^2\, dw_k$ is density of state in deriving plaetcle's Radiation law, we consider the energy density in the frequency range $w_k = w_k + dw_k$.

$$Udw_k = n_k \hbar w_k = \frac{g_k \hbar w_k}{V}\frac{dw_k}{(e^{B\hbar w} - 1)}$$

Since w_k is independent of k.

$$U = \frac{\left[\frac{2V}{(2\pi)^3}\frac{4\pi}{C^3}\omega^2\right]\hbar\omega}{V(e^{\hbar\omega_k B} - 1)} = \frac{1}{2\pi^3 C^3}\frac{\hbar\ \omega^3}{(e^{B\hbar\omega} - 1)}$$

Let $\omega = 2\pi v, \quad \hbar = \frac{h}{2\pi}$ $\qquad U(v,T)dv = \frac{8\pi h}{C^3}\frac{V^3 dv}{e^{Bhv}-1}$ *planck radiation law* 7.40

STEFAN-BOLTZMANN LAW

The total energy per unit volume

$$U(T) = \int_0^\infty U(V,T)dv = \frac{8\pi h}{C^3}\int_0^\infty \frac{V^3 dv}{e^{Bhv}-1} \qquad 7.41$$

Let $x = BhV, V = \frac{x}{Bh}; dv = \frac{dx}{Bh}$

Then $U(T) = \frac{8\pi h}{C^3}\left(\frac{1}{Bh}\right)^2 . \frac{1}{Bh}\int_0^\infty \frac{x^3}{e^X-1}dx$

$$\int_0^\infty \frac{x^3}{e^X-1}dx = \frac{\pi^4}{15}$$

$$\Rightarrow U(T) = \frac{8\pi h}{C^3}\left(\frac{1}{Bh}\right)^4 \frac{\pi^4}{15} = \frac{8\pi^4 k^3}{C^3 h^3 15}T^4 \qquad 7.42$$

$$\propto = \frac{8\pi^5 k^4}{15C^3h^3} = Stefans - Boltzamann\ const.$$

$$U(T) = \propto T^4. \qquad 7.43$$

PHONON INN SOLIDS

The heat content of a solid react entirely on a system of oscillator or quantized modes of atom vibration. Such oscillation of frequency of w_k with wave vector $\vec{k}$ and 3 normal mode of polarization carries a quantum of energy $E = \hbar w_{k\lambda}$. The energy per mode is

$$U_{k\lambda} = n_k h\,\omega_{k\lambda} = \frac{\hbar\omega_{k\lambda}}{e^{B\hbar\omega_{k\lambda}}-1} \qquad 7.44$$

The total energy $\qquad U = \sum U_{k\lambda}. \qquad 7.45$

The specific heat at constant volume is

$$C_v = \left(\frac{\partial U}{\partial T}\right)_C \qquad 7.46$$

Specific Heat Model

1) Einstein model of specific heat
2) Debye specific model which has been treated.

$\Rightarrow (1)(a)$ He assumed that all atoms vibrate with the same frequency called Einstein's frequency w_o (b) atoms are vibrating independently and are assumed to be harmonic, Total energy per unit volume

$$U = 3N\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$$

$3N$ is the no of degree of freedom or the normal mode,

$$C_V = (\partial U/\partial T)_V = \frac{3NK(B\hbar\omega_o)}{e^{B\hbar\omega_o} - 1} e^{B\hbar\omega_o} \qquad 7.47$$

Thus we define $\theta_E = \frac{\hbar w}{k} = Einstein\ Temp.$

$$y = \frac{\hbar\omega}{kT} \Rightarrow Y = \frac{\theta_E}{T}$$

We have

$$C_V = \frac{3NKy^2e^y}{(e^y - 1)^2} \qquad 7.48$$

At high temp, $T \gg \theta_E, Y \ll 1$

$C_V = 3NK.$ This is equivalent to Dulong and petit law.

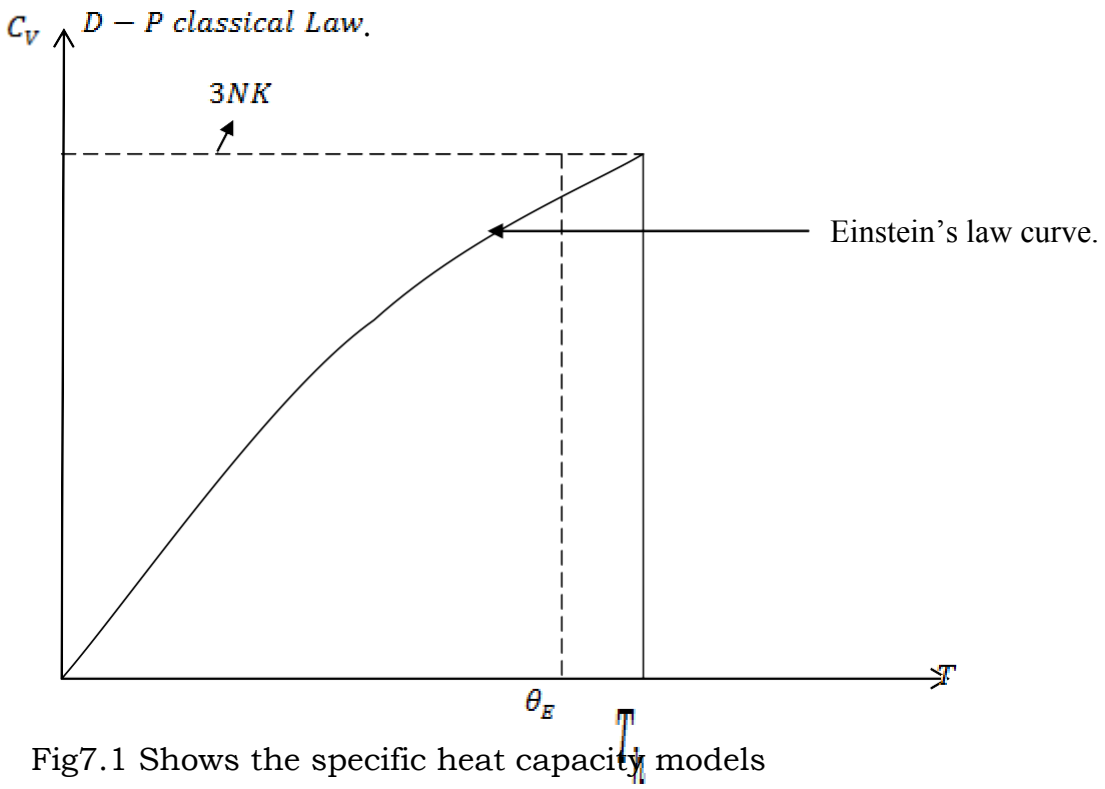


Fig7.1 Shows the specific heat capacity models

At high temperature $D - P$ law corresponds to the Einstein law.

At low temperature $T \ll \theta_E$

$$C_V \simeq 3NKe^{-y}. \qquad 7.49$$

The Einstein's experimental curve shows good fit for many substances diamond and some metals for $T > 300k$, but breaks down at low temperature $\hbar w_o \gg KT$ because all atoms do not vibrate at the same frequency as assumed by Einstein.

Electron Gas

The electron gas is one of the application of the Fermi statistic consider an electron gas of a temperature of absolute zero. In such a gas electron would be distributed among the quantum state such that the total energy of the gas would be minimum. Since no more than one electron can be in each quantum state, the electron will occupy all state with energy ranging from $0 + 0$ a value that depending on the number of electron gas.

If the volume is $Vg = 2$
Spin degeneracy, then momentum form P to $P + dp$ becomes

$$2\frac{4\pi p^2 dp}{(2\pi\hbar)^3} = \frac{Vp^2 dp}{\pi^2\hbar^3} \qquad (7.50)$$

The electron occupy all state with moment from p to p_f.

$$N = \frac{V}{\pi^2\hbar^3}\int_0^{p_f} p^2 dp = \frac{VP_f^3}{3\pi^2\hbar^3} \qquad 7.51$$

$p_f = \left(3\pi^2\frac{N}{V}\right)^{1/3}\hbar$ is the limiting momentum similarly, the limiting energy will be $E_f = \frac{P_f^3}{2M} = \frac{\hbar^2}{2M}\left(3\pi^2\frac{N}{V}\right)^{2/3}$

But the Fermi distribution function over quantum state with fixed value of momentum is $n_p = \frac{1}{e^{(\varepsilon-m)/KT}+1}$

At $T \to 0$, the function becomes a step function for $\varepsilon - M, I$
$\varepsilon = I, O$

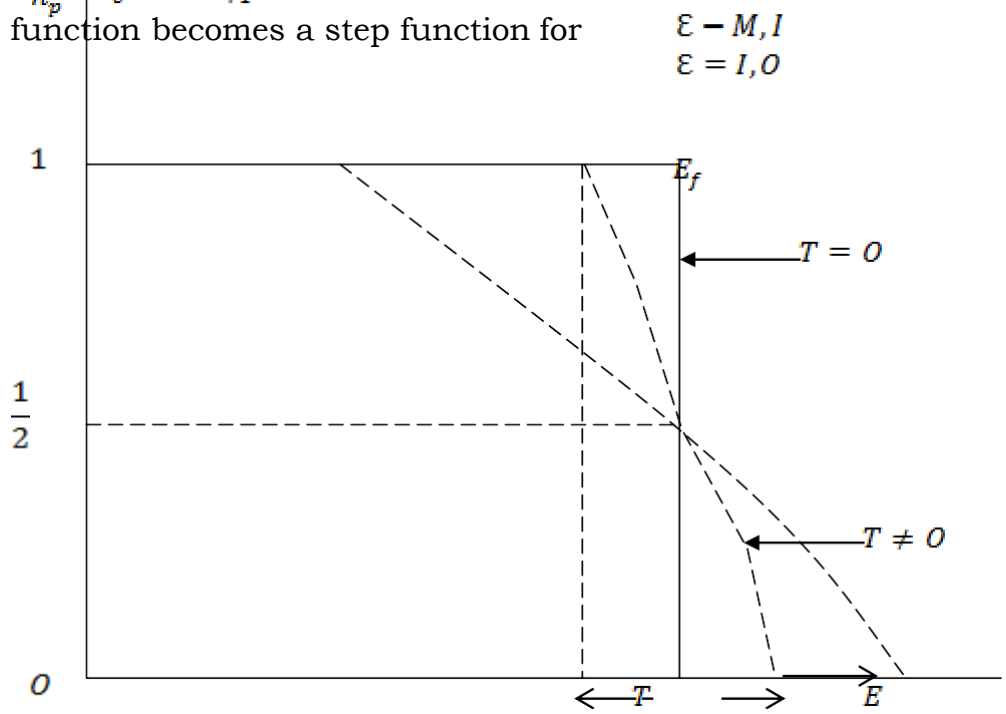


Fig 7.2 Shows Fermi distribution function

At absolute zero, the chemical potential, μ of the gas coincides with the limiting of the gas or electron.

$$E_f = -\lambda/_B$$

$$E_f = \frac{\hbar^2 k_f^2}{2m}, N = \frac{2V}{(2\pi)^2}\frac{4\pi k_f^2}{3} \qquad 7.51$$

$$E_f = \left(3\pi^2\frac{N}{V}\right)^{1/3} = (3\pi^2 n)^{1/3}$$

Maxwell Distribution Law

The maxwellian law of distribution of velocities provides an expression for the number of molecules with speeds between V and $v + dv$.

If we have a system of N molecules, the molecules will have no preferred direction of velocity at equilibrium. The fraction dN/dN have velocity lying between V_x and $V_x + dV_x$.
The fraction V_y and $V_y + V_y$

$\frac{dNV_z}{dN}$ V_z and $V_z + dV_z$

If is the probability for a molecule to have a velocity V_x, the

$$\frac{dNV_x}{dN} = f(V_x)dV_x \qquad 7.52$$

$$\frac{dNV_y}{dN} = f(V_y)dV_y$$

$$\frac{dNV_z}{dN} = f(V_z)dV_z$$

Fraction of the dNV_x molecules whose y components of velocity lie in the range V_y and $V_y + dV_y$ is

$$\frac{d^2NV_xV_y}{dN} = f(V_x)f(V_y)dV_xdV_y$$

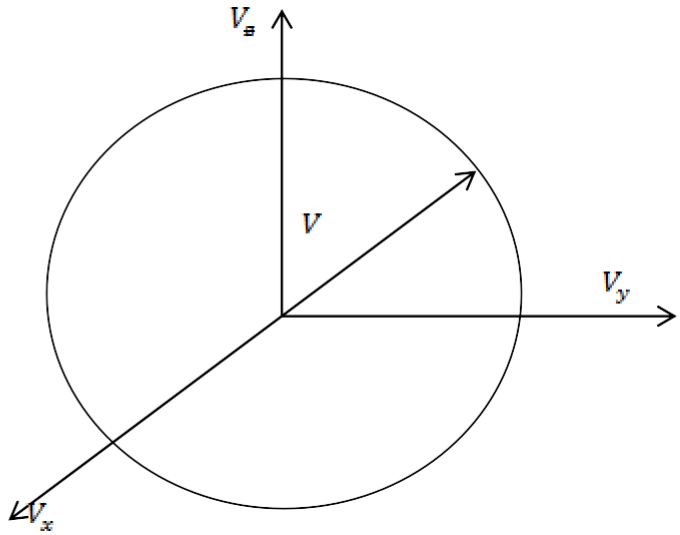
Fraction of molecules having velocities in the range $(V_x; V_x + dV_x; V_y, V_y + dV_y; V_z, V_z + dV_z)$ is

$$\frac{d^3NV_xV_yV_z}{N} = f(V_x)f(V_y)dV_xdV_ydV_z \qquad 7.53$$

The density of molecules the velocity space is

$$P = \frac{d^3NV_xV_yV_z}{dV_xdV_ydV_z} = Nf(V_x)f(V_y)f(V_z) \qquad 7.54$$

Since there is no preferred direction foe the velocities, the velocity space is isotropic, ie the density must be constant or $V^2 = V_x^2 + V_y^2 + V_z^2 = const.$



Thus

$Nf(V_x)f(V_y)f(V_z) = const$

When

$V_x^2 + V_y^2 + V_z^2 = const$

Equations velocity and given above must be satisfied simultaneously

Differentiating both Equation

$$f(V_y)f(V_z)\frac{\partial f(V_x)}{\partial V_x}dV_x + f(V_x)f(V_z)\frac{\partial f(V_y)}{\partial V_y}dV_y + (V_x)f(V_y)\frac{\partial f(V_z)}{\partial V_z}dV_z = 0 \qquad 7.55$$

$and\ 2V_x dV_x + 2V_y dV_y + 2V_z + dV_z$

Multiplying (a) by $\frac{1}{f(V_x)f(V_y)f(V_z)}$, we get

$$\frac{1}{f(V_x)}\frac{\partial f(V_x)}{\partial V_x}dV_x + \frac{1}{f(V_y)}\frac{\partial f(V_y)}{\partial V_y}dV_y + \frac{1}{f(V_z)}\frac{\partial f(V_z)}{\partial V_z}dV_z = 0 \qquad 7.56$$

$$and\ V_x dV_x + V_y dV_y + V_z + dV_z = 0$$

Using Lagrange undetermined multiplier method, we can multiply (12) with the constant B and add to (11).

$$\left[\frac{1}{f(V_x)}\frac{\partial f(V_x)}{\partial V_x} + BV_x\right]dV_x + \left[\frac{1}{f(V_y)}\frac{\partial f(V_y)}{\partial V_y} + \beta V_y\right]dV_y +$$

$$\left[\frac{1}{f(V_z)}\frac{\partial f(V_z)}{\partial V_z} + \beta V_z\right]dV_z = 0 \qquad 7.57$$

Taking

$$\frac{1}{f(V_x)}\frac{\partial f(V_x)}{\partial V_x} = -\beta V_x$$

Which symmetrical with other terms; solve and obtain

$$f(V_x) = k_1 e^{-\beta\frac{V_x^2}{2}} \qquad 7.58$$

$$Similarly\ f(V_y) = k_2\, e^{-\beta\frac{V_y^2}{2}}$$

$$f(V_z) = k_3\, e^{-\beta\frac{V_z^2}{2}}$$

The probability that a molecule will have x, y, z components of velocity in the range V_z, $V_z + dV_z$ where

$$f(v) = f(vx)f(vy)f(vz) = ke^{-\beta/2}(v_x^2 + v_1^2 + v_z^2) \qquad 7.59$$

Where k and β are constants.

.

$$P = Nke^{-B/2}V^2 \qquad (7.60)$$

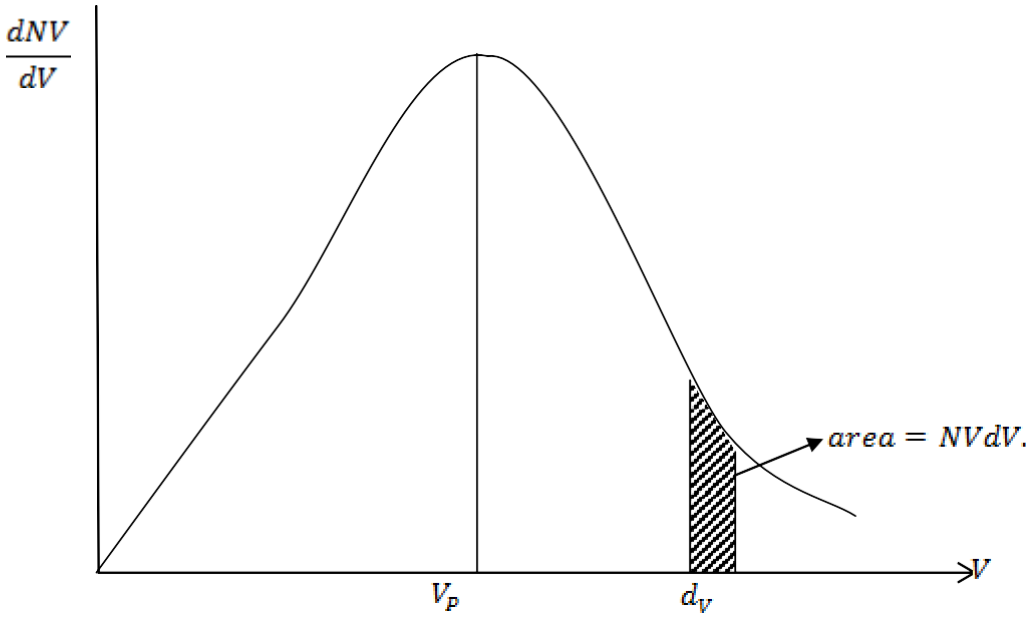
By equation (7.54), the infinitesimal spherical shell lying between radii v and $v + dv$ has volume $4\pi V^2 dV$ and contains dNv molecules, Thus

$$P = \frac{dNv}{4\pi V^2 dV} \qquad 7.61$$

It then follows from 7.60 that

$$P = \frac{dNv}{dV} = 4\pi NKV^2 e^{-B/2}V^2 \qquad 7.62$$

representing the equation for the maxwellian distribution of velocities



Graph of maxwellian velocity distribution to evaluate k and B, we continue from equation 7.62

$dN_v 4\pi NKV^2 e^{-B/2} V^2 dV$

where B is undetermined multiplier

and k is an integration constant;

$$4\pi k = \int_o^\infty e^{-B/2} V^2 dV \qquad 7.63$$

where In $= \int_o^\infty x^n e^{-ax^2 2} dx$

where $n = 2$

$$\int_o^\infty x^2 e^{-ax^2 2} dx = \sqrt{\frac{\pi}{a^3}}$$

Comparing this with equation 7.63

$$\frac{1}{4\pi k} = \frac{1/4\pi^{1/2}}{\left(\frac{1}{2}\beta\right)^{3/2}}$$

$$K = (B/2\pi)^{3/2} \qquad 7.64$$

To evaluate β,

$$< V^2 >= \frac{1}{N}\int_O^\infty V^2 dN_V$$

Substituting for dN_V, we get

$$< V^2 >= 4\pi k \int_O^\infty V^4 e^{-\beta/2} V^2 dV$$

Similarly $I_4 = \int_O^\infty x^4 e^{-ax^2} dx = 3/8\sqrt{\frac{\pi}{a^5}}$

$$\therefore < V^2 >= 4\pi \left(\beta/_\pi\right)^{3/2} \frac{3}{2}\pi^{1/2}\left(\frac{2}{\beta}\right)^{5/2} = 3/\beta$$

But $< K.E. \geq \frac{3}{2}KT$ from experiment

$$\therefore \frac{1}{2}M < V^2 >= \frac{1}{2}M\, {}^3/_\beta \frac{3}{2}KT \text{ or } \frac{M}{\beta} = KT \qquad 7.65$$

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

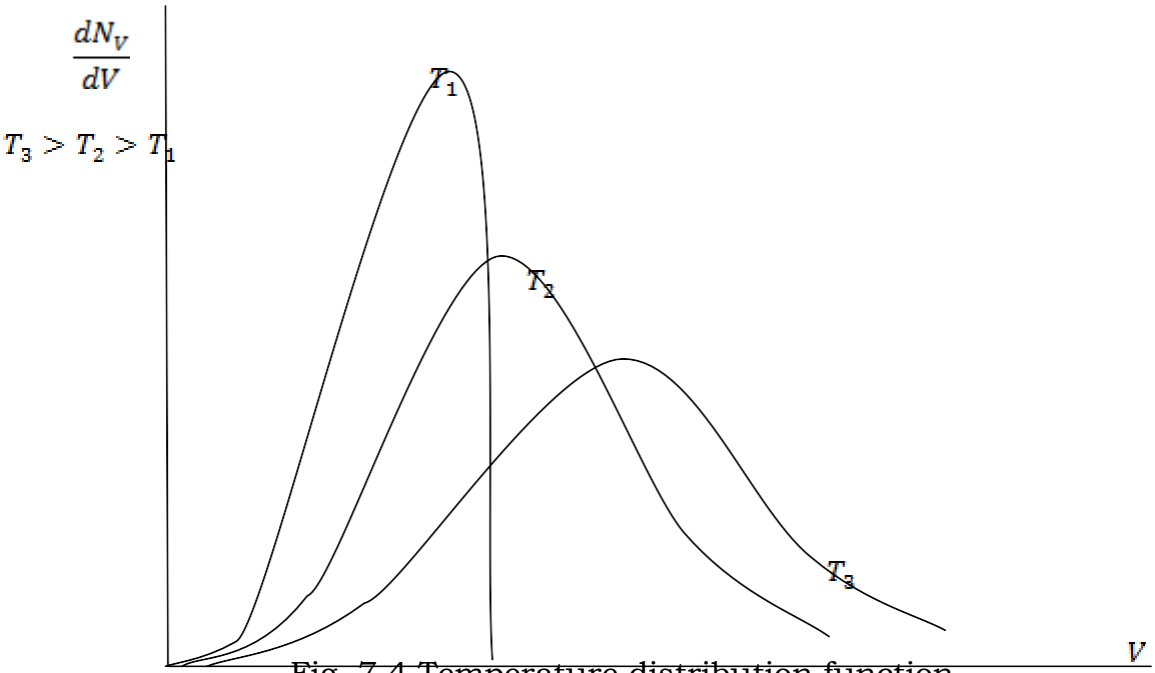


Fig. 7.4 Temperature distribution function

Example 7,1

Show that average kinetic energy $< KE >$ for an ideal gas is $^3/_2\, KT$.

Solution:

$$d^3V_xV_yV_z = N\left(^B/_{2\pi}\right)^{3/2} e^{-B/_2 V^2}\, dV_x dV_y dV_z$$

$$\therefore < KE > = \int_0^\infty \frac{1}{2} MV^2 \left(^B/_{2\pi}\right)^{3/2} e^{-B/_2 V^2}\, dV$$

$$\int_0^\infty \frac{1}{2} MV^4 4\pi \left(^B/_{2\pi}\right)^{3/2} e^{-B/_2 V^2}\, dV.$$

$$= M/2\left(^B/_{2\pi}\right)^{3/2}.4\pi.3/8\sqrt{\frac{\pi}{\left(^B/_2\right)^5}}$$

$$= \frac{M}{2} B^{3/2} 2\pi^{-3/2}.4\pi\ ^3/_8\, \pi^{1/2}\, 2^{5/2}\, B^{-5/2}$$

$$= ^3/_2\ MB^{-1}$$

$$^3/_2\, ^M/_B = ^3/_2 KT.$$

Chapter 8

8.1.1 INTRODUCTION TO INFORMATION THEORY APROACH FROM STATISTICAL PHYSICS

Relationship between information theory and statistical physics has extensively been of interest, and as a result has been recognized over the last few decades and they are drawn from many different aspects.

One of such aspect is characterized by identifying structures of optimization problems pertaining to certain information-theoretic settings as being analogous to parallel structures that arises in statistical physics, and the borrowing statistical-mechanical insights, as well as powerful analysis techniques (like the replica method) from statistical Physics to the dual information-theoretic setting of interest.

Another aspect pertains to the philosophy and the application of the maximum entropy principle, which emerged from statistical physics coupled with the guiding principle of statistical physics in the areas of signal processing in particular speech coding, spectrum estimation. Also great ideas that underlies the relation between information bits and energy or heats and that is why it has been argued according to Landover's principle that the erasure of every bit of information increases the thermodynamics entropy of the world by $k \ln 2$ where k Boltzmann's constant. As a matter of fact, there are close parallels between the mathematical expressions for thermodynamic entropy, usually denoted by $s,$ of a physical system in statistical thermodynamics established by Boltzmann and Gibbs; the information-theoretic entropy usually expressed as $H.$ The information entropy H can be calculated for any probability distribution (if the "message" is taken to be that of the event i which had probability p_i occurred, out of the space of events possible). However in the context of thermodynamics, entropy S refers to thermodynamics probabilities p_i which described the different arrangements of the system and in particular its energy that are possible on a molecular scale.

ENTROPY IN THERMODYNAMICS INFORMATION THEORY

We note that thermodynamics and statistical physics describe all systems comprising a large number of microscopic constituents. Mostly, one studies gases, solids etc. where the constituents are atoms and molecules also one can consider various astrophysical examples, for example neutron stars, and modern applications of statistical physics to a whole gamut of systems including traffic flow, economics, neural networks etc.

In the previous chapters, we were introduced to statistical physics by considering assemblies (i.e. systems) of microscopic constituents where by one established the entropy as corresponding to the statistical weight Type equation here. of a microstate through the relation.

$$S = K_B \ln = -K_B \sum_i P_i \log P_i \qquad 7.1$$

This is the Boltzmann entropy which is the expression that resulted from the derivation of key distributions such as Boltzmann, Fermi-Dirac and Bose-Einstein statistics when a system is placed in a reservoir of energy especially where there is demand that the entropy of the assembly + the bath is to be maximized.

Probability

The information theory as developed by Shannon, is a fundamental theory behind all the digital communications. On the use of the probabilities concept Shannon asked whether he could define a quantity which would measure how much information was produced by a discrete information source. He supposed that he had a set of possible events whose probabilities of occurrence were $P_1, P_2 \;\; P_n$. These probabilities were known but that was all he assumed to know concerning which event will occur. The next was whether there could be a measure of how much choice is involved in the selection of event or how much uncertain is the outcome.

Therefore in continuation of this discussion we introduce some important notation in which we use capital letters to indicate a discrete random variable and lowercase letters to indicate a particular variable. For instance, let X be a random variable. The variable X may take on the value $x \in x$. Here x is the finite set of all possible values for X and is referred to as the alphabet of X.

The probability that X takes on the particular value x is written $P_r.(X = x)$ or just $P_r(x)$ in some case some books use H in the definition instead of P_r.

We may also form joint probability and conditional probability. First all let y be another random variable with $y = y \in \gamma$.

The probability that $X = x$ and $Y = y$ is written $P_r(X = x, Y = y\,)\; or P_r x, y)$ which is referred to as conditional probability. The conditional probability that $X = x$ give $Y = y$ is written $P_r(X = x/Y = y\,) or P_{r(x/y)}$. There are some reasonable properties which Shannon considered in measuring or making selection of event. These are:

1. H should be continuous in the P_i in a measure given as $H(P_1, P_2, P_3, \cdots P_n)$
2. If all the P_i are equal $P_i = n$, then H should be a monotomonically increasing function of n.
3. If a choice be broken down into two successive choice, the original H should be the weighted sum of the individual value H Shannon showed that the only function satisfying the three above assumption is of the form.

$$S = K_B \ln = -K_B \sum_i P_i \log P_i \qquad 7.1$$

Where k is a positive constant. The form of H is the same as that of the entropy in statistical physics where the probability of the system in being in cell i of its phase space. This is by no means a coincidence, as Boltzmann expression.

Shannon entropy of discrete random variable X and probability distribution is defined as

$$(X) = -\sum_{x \in x} P_{(X)} \log P_{(X)}$$

7.3

This measures the uncertainty in a random variable. It is a measure of surprise when looking at an out come of the random variable. For instant if $/toss$ a fair $coin,$ I don't know what the out come will be I can, however describe the situation with probability distribution:

$$\left\{P_r(coin = Head) = \frac{1}{2}, P_r coin = tail = \frac{1}{2}\right\}. \qquad 7.4$$

If the coin is biased, there is a different distribution:

$$P_r(Biased\ coin = Head) = 0.9 \qquad 7.5$$

$$P_r(Based\ coin = tails) = 0.6 \qquad 7.6$$

It is important to note that will probability distributions are not created equal. Some distributions indicate more uncertainty than others; it is clear that we are more in double about the outcome of the fair $coin$ that the $biazed\ coin$. Now there arises a question of the possibility of making this notation of uncertainty or double quantitative?

However in the context of this book we didn't in the intricacy of such concept.

Joint entropy presents a pair of discrete random variables (x, y) and joint probability distribution $P(X, Y)$, The joint entropy is defined as

$$H(X, Y) = \sum_{x \in X, y \in Y} P_{(x,y)} \log P_{(x,y)} \qquad 7.7$$

The entropy of the amount of information revealed by evaluating (X, Y) that is evaluating X and Y simultaneously is equal to the information revealed by conducting two consecutive experiment first evaluating the evalue of $Y,$ the revealing the value of X given that you know the value of Y as written above.

$$H(X, Y) = H(X/Y) + H(Y) \qquad 7.8$$

However, if X and Y are two independent experiment, then knowing the value of y does not influence our knowledge of the value of X (since the two do not influence each other by independence);

$H(X/Y) + H(X)$ 7.9

Conditional entropy for a pair discrete random, variable (X,Y) and joint probability distribution $P(X,Y)$,is defined in term of conditional entropy as $H(X,Y) = -\sum_{x\in X, y\in Y} P_{(x,y)} \log P_{(x/y)}$ 7.10

Where the chain value of entropy specifies that $H(X,Y) = H(X) + H(Y/X)$ 7.11

$H(X)$ is sub-additive, which means that for random variables X, Y

$H(X,Y) \leq H(X) + H(Y)$ 7.12

With equality $H\ X\ and\ Y$ are independent. There since Relative Entropy: The relative entropy or Kulback-Leibler distance between two probability distribution $P_{(X)}$ and $Q(X)$ is defined as

$$D(P\|Q) = -\sum_{x\in X} P_{(x)} \log \frac{P_{(x)}}{q_{(x)}} \qquad 7.13$$

Where $D(P\|Q)$ is not a "true" distance since it is not symmetric and does not obey the triangular inequality. The relative entropy is a measure of "distance" between two probability distributions. It is a measure of inefficiency of assuming that you have distribution $Q(X)$ when really you have distribution $P(X)$.

Mutual information: Given joint probability distribution $P(X,Y)$ the mutual information between $X\ and\ Y$ is defined as

$$I(X,Y) = -\sum_{x,y} P_{(x,y)} \log \frac{P_{(x,y)}}{P_{(x)}P_{(y)}} \qquad 7.14$$

$= DP(X,Y)\|P(X)P(y).$ 7.15

The mutual information is a measure of how much information one random variable contains about another. Equivalent expressions for the mutual information are:

$I(X;Y) = H(X) + H(Y) - H(X,Y)$ 7.16

$= H(X) - H(X/Y)$

Mutual information is symmetric,

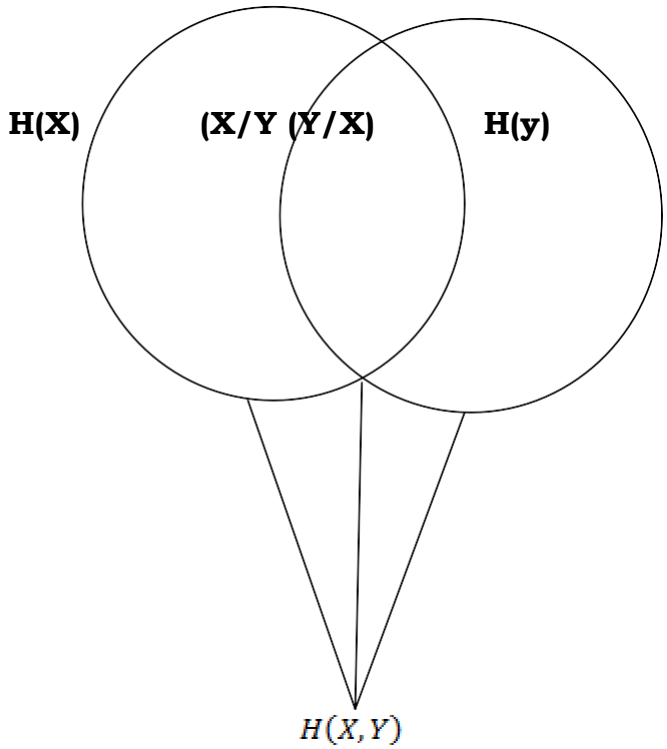
$I(X;Y) = I(Y;X)$ 7.17

$I(X;Y) \geq 0$

With equality $|HP(X) = P(Y)$.

A true distance of information is defined as

$d(X,Y) = H(X/Y) + H(Y/X)$



This diagram shows special relationship between various entropy measures.

1) Continuity meaning that the measure should be continuous so that changing the values of the probabilities by a very small amount should only change the entropy by small amount.
2) Symmetry which explains that the measure should be unchanged if the out comes xi are reordered i.e $H_n(P_1P_2) = H_n(P_2P_1 \cdots)$ etc.
3) Maximum: The measure should be maximal if the outcomes are equally likely (uncertainty is highest when all possible events are equiprobable) while for equiprobable events, the entropy should be increased with number of outcomes.
4) Additively: This explains the fact that the amount of entropy should be independent of hoe the process is regarded as being divided into parts relationship. This functional relationship characterizes the entropy of a system with subsystems which demands that the entropy of a system can be calculated from the entropies of its subsystems if the interactions between the subsystems are know.

Summary of the Properties

The Shannon entropy satisfies all the above mentioned properties out lined in the above mathematical expression

Differential Entropy

The Shannon entropy is restricted to random variables taking discrete values.

The formula.

$$h[f] = -\int_{-\infty}^{\infty} f(x)\log f(x)\,dx \qquad 7.17$$

where $f$denotes a probability density function on the real line, is analogous to the Shannon entropy and could thus be viewed an extension of the Shannon entropy. To the domain of real number, the above expression is related to the function H in Boltzmann's theorem. This above formula is usually referred to as the **continuous entropy,** or differential entropy. Although there is analogy between differential entropy is viewed as an extension of the Shannon discrete entropy, differential entropy lacks a number of properties that the discrete points. However the two functions we favourably connected. This was done by generally obtaining the finite measure as the bin size goes to zero of which in the case of the discrete types, the bin size is the (implicit) width of each of the n (finite or infinite) bins whose probabilities are denoted by p_n. Now as we generalize to the continuous domain, we must ensure that this width is explicit. To do this, start with a continuous function f which is discretized Δ in which we indicates that there exist $x_i$in each bin such that

$$f(x_i)\Delta = \int_{i\Delta}^{(i+1)\Delta} f(x)dx \qquad 7.18$$

The mean-value theory was applied though was not discussed here in this book. This integral of the function f can be approximated (in Riemannian sense by

$$\int_{-\infty}^{\infty} f(x)dx \lim_{\Delta\to 0}\sum_{i=-\infty}^{\infty} f(x_i)\Delta \qquad 7.19$$

where we expect that the limit and "bin size goes to zero" are equivalent.

Now, we denote

$$H^{\Delta} = -\sum_{i=-\infty}^{\infty} \Delta f(x_i)\log f(x_i) - \sum_{i=-\infty}^{\infty} f(x_i)\Delta\log\Delta$$

As $\Delta\to 0$, we have

$$\sum_{i=-\infty}^{\infty} f(x_i)\Delta \to \int f(x)dx = 1 \qquad 7.20$$

And also

$$\sum_{i=-\infty}^{\infty} \Delta f(x_i)\log f(x_i) \to \int f(x)\log f(x)\,dx \qquad 7.21$$

Already we should take note that

$\log\Delta \to -\infty\ as\ \Delta\to 0$, there exists a special definition for differential or continuous entropy.

Thus we have

$$h[f] = [H^{\Delta} + \log\Delta] = \int_{-\infty}^{\infty} f(x_i) f(x) dx \qquad 7.23$$

from all these derivation it is observed that unlike Shannon entropy, the differential entropy is not in general a good measure of uncertainty or information as it can be negative and is not invariant under continuous co-ordinate transformations.

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