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OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

I YEAR

M.Sc. Physics

Course Material

STATISTICAL MECHANICS

Prepared

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STATISTICAL MECHANICS

UNIT I

PHASE TRANSITIONS

Thermodynamic potentials - Phase Equilibrium - Gibb's phase rule - Phase transitions and Ehrenfest's classifications –Third law of Thermodynamics. Order parameters – Landau's theory of phase transition - Critical indices - Scale transformations and dimensional analysis.

UNIT II

STATISTICAL MECHANICS AND THERMODYNAMICS

Foundations of statistical mechanics - Specification of states of a system - Micro canonical ensemble - Phase space – Entropy -Connection between statistics and thermodynamics – Entropy of an ideal gas using the micro canonical ensemble - Entropy of mixing and Gibb's paradox.

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CANONICAL AND GRAND CANONICAL ENSEMBLES

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Cluster expansion for a classical gas - Virial equation of state – Calculation of the first Virial coefficient in the cluster expansion - Ising model – Mean - field theories of the Ising model in three, two and one dimensions - Exact solutions in one dimension. Correlation of space-time dependent fluctuations - Fluctuations and transport phenomena - Brownian motion - Langevin's theory - Fluctuation-dissipation theorem - The Fokker-Planck equation

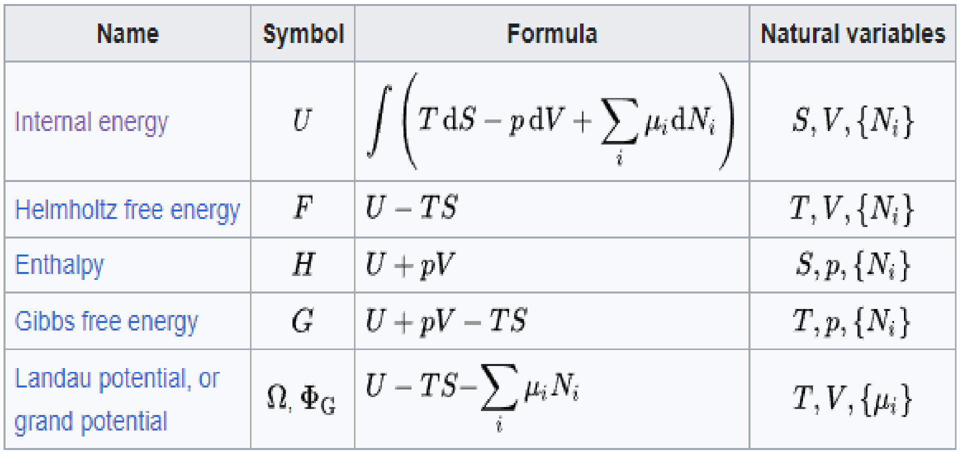
UNIT I

PHASE TRANSITIONS

Thermodynamic potentials - Phase Equilibrium - Gibb's phase rule - Phase transitions and Ehrenfest's classifications –Third law of Thermodynamics. Order parameters – Landau's theory of phase transition - Critical indices - Scale transformations and dimensional analysis.

1.1 Thermodynamic potentials

The chemical potential μ_i of species *i* (atomic, molecular or nuclear) is defined, as all intensive quantities are, by the phenomenological fundamental equation of thermodynamics. This holds for both reversible and irreversible infinitesimal processes:



Name	Symbol	Formula	Natural variables
Internal energy	U	$\int \left(T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i \right)$	$S, V, \{N_i\}$
Helmholtz free energy	F	$U - TS$	$T, V, \{N_i\}$
Enthalpy	H	$U + pV$	$S, p, \{N_i\}$
Gibbs free energy	G	$U + pV - TS$	$T, p, \{N_i\}$
Landau potential, or grand potential	Ω, Φ_G	$U - TS - \sum_i \mu_i N_i$	$T, V, \{\mu_i\}$

1.2 Gibb's phase rule

The Gibbs phase rule sate that in a system with r component and M coexistent phases u is possible arbitrarily to preassign

$$r - M + 2$$

variables from the set (T, P, $x_1{}^I, x_2{}^I, \ldots x_r{}^M$) or from the set (T, P, $\mu_1, \mu_2, \ldots \ldots \mu_r$).

The Gibbs phase rule gives the same results for single – component and two – component system. For single – component systems

$$r = 1 \text{ and } f = 0 \text{ if } M = 3.$$

For two – component systems

$$f = 0,\ r = 2\ ,\ M = 4.$$

That the temperature could be arbitrarily assigned for the three-phase system (f = 1, r = 2 , M = 3) and the both T and P could be arbitrarily assigned for the two – phase system(f = 2, r = 2 , M = 2).

1.3 Phase transitions and Ehrenfest's classifications

Phase transitions can be classified according to the type of change of state variables at the transition temperature . The first variant of this classification has been introduced by Ehrenfest:

1. For 1st order transitions: the first derivative of the chemical potential μ changes discontinuously. At $Ttrans$ the parameters $V, H,$ and S change discontinuously, while Cp becomes infinite.
2. For 2nd order: the second derivative of the chemical potential μ changes discontinuously. At $Ttrans$ the parameters $V, H,$ and S do not change discontinuously, while Cp remains finite and changes discontinuously.

The Ehrenfest classification is equivalent to a more modern classification:

First-order phase transitions involve latent heat. Latent heat is the heat released or absorbed by a chemical substance or a thermodynamic system during a change of state that occurs without a change in temperature.

Second-order transitions are continuous.So the Cp-curves allow for an easy and rapid identification of the transition order

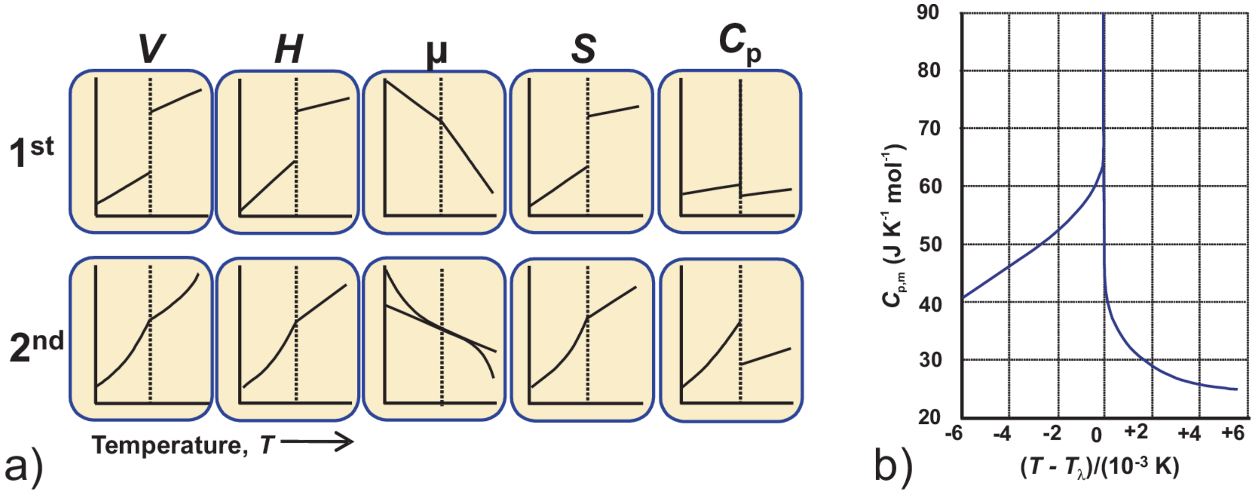


Figure 1.1 a) Ehrenfest classification of 1st and 2nd order phase transitions; b) $T{-}Cp$ diagram illustrating a so-called transition.

1.4 Third law of Thermodynamics

Entropy is a physical quantity that indicates the molecular disorder of a system or else stated as the randomness of a system. Mathematically, it is the amount of thermal energy of a system that is unavailable for doing useful work. This is because work is derived from the ordered movement of molecules of a system.

Entropy as a concept helps to understand the spontaneity of any process to come to a conclusion that which processes are thermally possible or impossible. This explains the phenomenon of the irreversibility of reactions. The entropy of a system depends on temperature. It increases with the increase in temperature and decreases with a decrease in temperature.

$$\Delta S = QT$$

where

ΔS is the entropy change in the system

Q is the heat absorbed

T is the temperature

Statement of the Third Law

This law deals with the concept of “absolute zero”. Absolute zero is the lowest temperature on the Kelvin Scale which is zero. This is equal to -273.15 on a Celsius scale and -459.7 on a Fahrenheit scale.

The third law of thermodynamics states that when the temperature of a system approaches absolute zero, the entropy of that system approaches a constant value. This suggests that there is a minimum measure of randomness of a system and that occurs when the temperature reaches absolute zero. If an isolated system is constituted by the combination of two thermodynamic systems, then any energy exchange in any form between those two systems is bounded. This can also be explained by seeing that at absolute zero, the system does not contain any heat which tells the presence of all the molecules at their lowest energy points.

the temperature decreases, the heat of a system which is just a collection of kinetic energies of the system also decreases. Thus, at some point, the kinetic energy reduces to a complete stop which means no randomness.

1.5 Order parameters

An order parameter is generically defined as a quantity – the statistical average of an observable – that typically vanishes in one phase and is different from zero in another one (or other ones). One must notice though that the order parameter is not unique (e.g., any power of an order parameter is itself an order parameter) and that there can exist transitions without an order parameter as the topological Kosterlitz-Thouless transition in the 2d XY model that we will study later.

In the ferromagnetic Ising model the order parameter is the global magnetisation density

$$\mathrm{M} = \frac{1}{N}\sum_{i=1}^{N}\langle s_i\rangle$$

$$\langle s_i\rangle = z^{-1}\sum_c s_i e^{-\beta H(c)}$$

where N is the total number of spins and the angular brackets represent the thermal average in the canonical ensemble (that we adopt henceforth unless otherwise stated) as indicated in the second equation.

The sum over configurations C is just a sum over all $s_i = \pm 1$ in this example. In Ising antiferromagnetic models one can define staggered magnetizations that take into account the periodicity between two possible orientations of the local spins.

Generalisation to systems with different internal dimension of the spins (n > 1) are straightforward.

1.6 Landau's theory of phase transition

The free energy is given by

$$e^{-F/k_BT} = \sum_\mu e^{-H(\mu)/k_BT} \qquad \text{-------(1)}$$

Landau's assumption is that we can replace the entire partition function by the following,

$$e^{-F/k_BT} \approx e^{-F_0/k_BT} \int D\psi\, e^{-F_L[T,\psi]/k_BT} \qquad \text{-----(2)}$$

where the integral $\int D\psi$ is a functional integral over all degrees of freedom associated with ψ, instead of an integral over all microstates.

For example, if ψ is the mean magnetization, a given value for the magnetization can be determined by many different microstates. It is assumed that all of this information is contained in F_L. This is a non-trivial assumption which can nonetheless be proven for certain systems.

The conversion of the degree of freedom from μ to ψ is known as coarse-graining, and is at the heart of the relationship between statistical mechanics and thermodynamics.

The next step is to minimize $F_L[T, \psi]$,

$$e^{-F/k_BT} \approx e^{-F_0/k_BT} e^{\min\{\psi\} F_L[T,\psi]/k_BT} \qquad \text{-------(3)}$$

This is tantamount to performing a saddle point approximation to the function integral in Equation. (2).

Here’s a more formal rationalization:

$$e^{-F/k_BT} = \sum_\mu e^{-H(\mu)/k_BT} \quad \text{exact partition function} \qquad \text{------(4a)}$$

$$= \sum_\mu \int D\psi\, \delta[\psi - \langle\mu\rangle] e^{-H(\mu)/k_BT} \quad \text{introduce } \psi \text{ as an average over } \mu \qquad \text{----------(4b)}$$

$$= \int D\psi \sum_\mu \delta[\psi - \langle\mu\rangle]\, e^{-H(\mu)/k_BT} \quad \text{interchange limits} \quad \text{--------(4c)}$$

$$= \int D\psi\, g(\psi)\, e^{-H(\mu)/k_BT} \qquad \text{--------(4d)}$$

$g(\psi)$ represent the degeneracy of ψ

$H(\mu) \rightarrow H(\psi)$ is generally incorrect, but illustrate the idea

$$= \int D\psi\, g(\psi)\, e^{-[\frac{H(\mu)}{k_BT} \ln g(\psi)]/k_BT} \qquad \text{--------(4e)}$$

$$F \approx \min H(\psi) - k_BT \ln g(\psi) \quad \text{saddle point approximation} \qquad \text{-------(4f)}$$

the free energy of a system is given by

$$F = E - T\,S \qquad \text{----------(5)}$$

ln g(ψ) is essentially the entropy of the system. To rationalize the assumed form of the temperature dependence of $F_L[T, \psi]$, we write:

$$\frac{F}{\text{Volume}} \simeq E_0 \underbrace{-E_*\psi^2}_{\text{attraction}} + \ldots - T[S_0 \quad \underbrace{-a\psi^2 + \ldots}_{\text{reduction due to ordering}} \quad] \qquad \text{--------(6)}$$

$$= F_0 + a(T - \frac{E}{a})\psi^2 + \ldots.. \qquad \text{---------(7)}$$

We assume there is some "attraction" necessary to induce order in the system, but this occurs at the expense of reducing the entropy; this, in principle, is contained in the degeneracy g(ψ). The competition of these effects leads to a phase transition

Scale transformations and dimensional analysis

In statistical mechanics, scale invariance is a feature of phase transitions. The key observation is that near a phase transition or critical point, fluctuations occur at all length scales, and thus one should look for an explicitly scale-invariant theory to describe the phenomena. such theories are scale-invariant statistical field theories, and are formally very similar to scale-invariant quantum field theories. second order phase transitions was the divergence of the correlation length

$$\xi\,(T \to T_c) \to \infty \qquad \text{----------(1)}$$

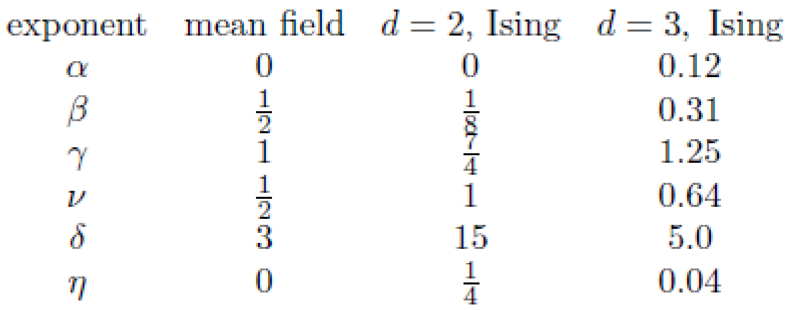
This divergency implies that at the critical point no characteristic length scale exists, which is in fact an important reason for the emergence of the various power laws. Using h as a dimensionless number proportional to an external field and

$$t = \frac{T - T_c}{T_c} \qquad \text{----------(2)}$$

as dimensionless measure of the distance to the critical point the various critical exponents are:

$$\begin{aligned}
\xi\,(t, h=0) &\sim t^{-\nu} \\
\phi\,(t, h=0) &\sim |t|^{\beta} \\
\phi\,(t=0, h) &\sim h^{1/\delta} \\
\chi\,(t, h=0) &\sim t^{-\gamma} \\
c\,(t, h=0) &\sim t^{-\alpha} \\
\chi\,(x \to \infty, t=0) &\sim x^{2-d-\eta}.
\end{aligned} \qquad \text{---(3)}$$

where D is the spatial dimensionality. The values of the critical exponents for a number of systems are given in the following table



exponent	mean field	$d = 2$, Ising	$d = 3$, Ising
α	0	0	0.12
β	$\frac{1}{2}$	$\frac{1}{8}$	0.31
γ	1	$\frac{7}{4}$	1.25
ν	$\frac{1}{2}$	1	0.64
δ	3	15	5.0
η	0	$\frac{1}{4}$	0.04

It turn out that a few very general assumptions about the scaling behavior of the correlation function χ(q) and the free energy are sufficient to derive very general relations between these various exponents.

Those relations are called scaling laws. there is no typical length scale characterizing the behavior close to a second order phase transition leads to a power-law behavior of the singular contributions to the free energy and correlation function.

For example, consider the result obtained within Landau theory

$$\chi(q, t) = \frac{1}{t + q^2} \qquad \text{--------(4)}$$

according to x → x/b, where b is an arbitrary dimensionless number, leads to

k → kb. Obviously, the mean field correlation function obeys

$$\chi(q, t) = b^2 \, \chi(bq, tb^2) \qquad \text{-----(5)}$$

Thus, upon rescaling (k → kb), the system is characterized by a correlation function which is the same up to a pre-factor and a readjustment of the distance from the critical point.

the mean field theory of Landau a similar relationship holds

$$\chi(q, t) = b^{2-\eta} \, \chi(b\,q, tb^{y}) \qquad \text{-----(6)}$$

if y = 2 and $\eta = 0$. Since b is arbitrary, we can for example chose t $b^y = 1$ implying b = $t^{-1/y}$ y and we obtain directly from our above equation

$$\chi(q, t) = t^{-(2-\eta)/y} \, \chi(qt^{-1/y}, 1) \qquad \text{-----(7)}$$

$$V = y^{-1} \qquad \text{-------(8)}$$

consider t = 0 and chose bq = 1 such that

$$\chi(q, t{=}0) = \frac{1}{q^{2-\eta}} \, \chi(1,0) \qquad \text{-------(9)}$$

Which gives

$$\chi(\text{x, t=0}) = \int \frac{d^d q}{(2\pi)^d}\ \chi\ (\text{x, t=0})\ e^{ikx}$$

$$\sim \int dq e^{ikx} \frac{q^{d-1}}{q^{2-\eta}} \qquad \text{-------(10)}$$

substituting z = k x gives

$$\chi(\text{r, t=0}) = x^{2-d-\eta} \qquad \text{----------(11)}$$

Thus, the exponent of Equation (5) is indeed the same exponent as the one given above.

This exponent is often called anomalous dimension and characterizes the change in the power-law decay of correlations at the critical point (and more generally for length scales smaller than). Thus we can write

$$\chi(\text{q, t}) = b^{2-\eta}\ \chi(\text{b q, t}b^{\frac{1}{v}}) \qquad \text{--------(12)}$$

$$F(\text{t, h}) = b^{-D}\ F(\text{t}b^{y}, \text{h}b^{y_h}) \qquad \text{--------(13)}$$

$$F(\text{t, h}) = t^{-Dv}\ F(1, \text{h}t^{-vy_h}) \qquad \text{--------(14)}$$

This enables us to analyze the specific heat at h = 0 as

$$\text{C} \sim \frac{\partial^2 F(t,0)}{\partial t^2} \sim t^{dv-2} \qquad \text{--------(15)}$$

Which leads to

$$dv - 2 = -\alpha \qquad \text{----------(16)}$$

The temperature variation of the order parameter is given as

$$\phi(t) \sim \left.\frac{\partial F(t,h)}{\partial h}\right|_{h\to 0} \sim t^{\nu(d-y_h)} \qquad \text{---------(17)}$$

Which gives

$$\beta = v(d - y_h) = 2 - \alpha - v y_h \qquad \text{-------(18)}$$

This relationship makes a relation between y_h and the critical exponents just like y was related to the exponent v . Within mean field

$$y_h = 3$$

$$\text{h b}y_h = 1$$

$$F(\mathrm{t},\, \mathrm{h}) \;=\; h^{\frac{d}{y_h}}\, F(\mathrm{t}h^{-\frac{1}{y_h}},\, 0\,)$$ --------(19)

This gives for the order parameter at the critical point

$$\varphi(t=0,h) \sim \frac{\partial F(t=0,h)}{\partial h} \sim \;\; h^{-\frac{1}{y_h}}$$ ------(20)

$$\frac{1}{\delta} = \frac{d}{y_h} - \;1.$$

$$\delta \;=\; \frac{y_h}{d-y_h}$$

$$= \frac{2-\alpha-\beta}{\beta}$$ ------(21)

The free energy is given by

$$F(\mathrm{t},\, \mathrm{h}) \;=\; b^{(2-\alpha)v^{-1}}\; F(\mathrm{t}b^{-\frac{1}{y_h}},\, \mathrm{h}b^{\frac{\beta\delta}{v}},\;)$$ --------(19)

$$\mathrm{t}b^{-\frac{1}{y_h}} \;=\; 1$$

$$F(\mathrm{t},\, \mathrm{h}) \;=\; t^{(2-\alpha)}\; F(\mathrm{t}1,\, \mathrm{h}b^{\frac{\beta\delta}{v}},\;)$$

Susceptibility diverges at the critical point

$$\chi \sim \left.\frac{\partial^2 F\,(t,h)}{\partial h^2}\right|_{h\to 0} \sim t^{2-\alpha-2\beta\delta}$$

-----------(20)

Which leads to

$$\gamma = \;\alpha - 2 + 2\beta\delta$$

UNIT II

STATISTICAL MECHANICS AND THERMODYNAMICS

Foundations of statistical mechanics - Specification of states of a system - Micro canonical ensemble - Phase space – Entropy -Connection between statistics and thermodynamics – Entropy of an ideal gas using the micro canonical ensemble - Entropy of mixing and Gibb’s paradox.

2.1 FOUNTATIONS OF STATISTICAL MECHANICS:

Statistical mechanics is the branch of science which gives the interpretation of the macroscopic behavior of a system in terms of its microscopic properties. Statistical mechanics is not concerned with the actual motion of individual particle

but investigates average or most probable or statistical properties of the system.

The larger is the number of particles in the physical system considered, the more nearly correct are the statistical predictions. The smaller is the number of particles in the mechanical system, statistical mechanics cease to have meaning.

Statistical mechanics is applicable for a system consisting large number of particles.

There are two statistical methods known as classical statistics and Quantum statistics.

- Classical statistics explained many observed physical phenomenon like temperature , pressure ,energy etc., but could not explain several experimentally observed phenomenon like black body radiation, specific heat at low temperature etc.
- For explaining such phenomenon Bose-Einstein and Fermi-Dirac made new approach known as quantum statistics.
- Quantum statistic can be classified as,
    i. Bose-Einstein statistics
    ii. Fermi-Dirac statistics

2.2 ENSEMBLE THEORY: CONCEPT OF ENSEMBLES

A system is defined as a collection of identical particles. An ensemble is defined as a collection of macroscopically identical, but essentially independent systems. Macroscopically identical means each system satisfies the same macroscopic conditions ex: volume, energy, pressure etc. Independent systems mean the systems are non interacting.

There are three most commonly used ensembles namely,

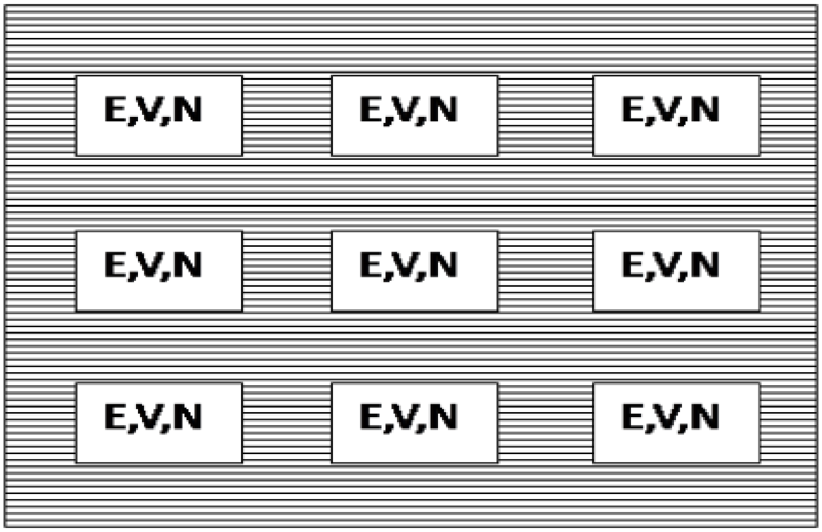
(i) micro canonical ensemble
(ii) canonical ensemble
(iii) grand canonical ensemble.

2.3 Micro canonical ensemble

Collection of large number of essentially independent systems with same energy E, volume V, and the number of particles N. All the particles are identical.

The individual systems are separated by rigid , impermeable and well insulated walls.

No exchange of heat energy as well as the number of particles between the systems takes place.



2.4 PHASE SPACE

The instantaneous position of a single particle is described by three independent co-ordinates $x, y\ and\ z$. The instantaneous motion of a particle is described by momentum co-ordinates $, p_y , p_z$.

Thus the state of a single particle is completely specified by position co-ordinates x, y, z and momentum co-ordinates p_x , p_y , p_z

We may imagine a six dimensional space with volume $d_x\, d_y\, d_z\, dp_x\, dp$.

The position of a point particle in this space can be described by a set of 6 coordinates $x\ y$, p , p_z. This 6 dimensional space for a single particle is damped as phase space.(μ=space)

If the system contains a large number of particles such that f independent position co-ordinates $q_1, q_2, \dots \dots \dots, q_f$ and f momentum co-ordinates $p_1, p_2, \dots \dots, p_f$, then 2f combined position, momentum co-ordinates may be allowed to define 2fdimensional space called phase space(Γ-space)

The Γ-space is considered to be a conceptual Euclidean space having 2f rectangular axes and an element of volume represented by

$$dq_1, dq_2, \dots \dots, dq_f\, dp_1, dp_2, \dots \dots, dp_f$$

The instantaneous state of a particle in the phase-space is represented by a point known as phase point (or) representative point. The number of phase points per unit volume is known as phase density.

2.5 CONTACT BETWEEN STATISTICS AND THERMODYNAMICS

Boltzmann used the idea that the probability of the system in equilibrium state is maximum. Thus in equilibrium state both the entropy and thermodynamical probability have their maximum values.

Boltzmann concluded that the entropy 'S' is a function of thermodynamic probability Ω.

ie, $$S = f(\Omega) \qquad \dots.(1)$$

Consider two independent systems A and B having entropies S_1 and S_2 and thermodynamic probabilities Ω_1 and Ω_2 Entropy is an additive quantity and hence the entropy of systems together must be equal to the sum of their individual entropies.

$$S = S_1 + S_2 \qquad \dots.(2)$$

The probability Ω of finding both systems will be the product of the two probabilities Ω_1 and Ω_2.

ie $$\Omega = \Omega_1\Omega_2 \qquad \dots.(3)$$

Substituting equations (2) and (3) in equation (1) we get,

$$S = f(\Omega)$$

$$= (\Omega_1\Omega_2) \qquad \dots.(4)$$

$$S = S_1 + S_2$$

$$f\ (\Omega_1\Omega_2) = f(\ \Omega_1)(\Omega_2) \qquad \dots..(5)$$

Differentiating with respect to Ω_1 we get,

$$\Omega_2 f'\,\Omega_1\Omega_2\, f'\,\Omega_1 \qquad \text{....(6)}$$

Differentiating with respect to Ω_2 we get,

$$\Omega_1 f'\,\Omega_1\Omega_2 = f'\,\Omega_2 \qquad \text{.... (7)}$$

Divide equation (7)/(6), we get

$$\frac{\Omega 1}{\Omega 2} = f'(\Omega_2)/\,f'(\Omega_1)$$

$$\Omega_1\, f'(\Omega_1) = \Omega_2\, f'(\Omega_2)$$

$$\Omega\; f'(\Omega) = constant = k$$

$$f'(\Omega_1) = \frac{k}{\Omega}$$

Integrating, $(\Omega) = k\; log\; \Omega + c$

$$S = k\; log\; \Omega + c \qquad \text{....(8)}$$

For a thermo dynamical system at absolute zero Ω=1 and S=0 so that c=0.

$$S = k\; log\; \Omega.$$

This gives the Boltzmann's relation between entropy and probability

(a) Identification of constant 'k'

Consider the expansion of one mole of an ideal gas at pressure p_1 and volume V_1 into an evacuated chamber of volume V_2.

The final pressure is p_2 and the final volume is V_1+ V_2.

The probability of finding one molecule in the first container with volume V_1 is,

$$\frac{V_1}{V_1+V_2}$$

There are N molecules and hence the probability of finding one mole of the gas in the first container with volume V_1 is,

$$\Omega_1 = \left[\frac{V_1}{V_1+V_2}\right]^{N} \qquad \text{....(10)}$$

The probability of finding one mole of the gas in the container has volume V_1+V_2 is

$$\Omega_2 = \left[\frac{V_1+V_2}{V_1+V_2}\right]^N$$

$$= [\,1\,]^N \qquad \text{.....(11)}$$

From Boltzmann relation

$$\Delta S = S_2 - S_1$$

$$= k \log \Omega_2 - k \log \Omega_1$$

$$= \text{k} \log \left(\frac{\Omega 2}{\Omega 1}\right)$$

$$= \text{k} \log \left[\frac{1}{\frac{V_1}{V_1+V_2}}\right]^N$$

$$= \text{k} \log \left[\frac{V_1+V_2}{V_1}\right]^N$$

$$= \log \left[\frac{V_1+V_2}{V_1}\right]^{Nk} \qquad \text{......(12)}$$

The change in entropy when the gas changes from one state with volume V_1 and temperature T_1 to another state with volume V_2 and temperature T_2 is given by,

$$\Delta S = C_v \log \frac{T2}{T1} + \text{R} \log \left[\frac{V_1+V_2}{V_1}\right]$$

For isothermal change $T_2 = T_1$ and hence $C_v \log \frac{T2}{T1} = 0$

$$\Delta S = R \log \left[\frac{V_1+V_2}{V_1}\right]$$

$$= \log \left[\frac{V_1+V_2}{V_1}\right]^R \qquad \text{......(13)}$$

Comparing equation (12) and (13), we get

$$Nk = R$$

$$k = R/N$$

$$= 1.03 \times 10^{-23}\ J/K$$

= Boltzmann‟s constant

2.6 ENTROPY OF AN IDEAL GAS USING MICRO CANONICAL ENSEMBLE

Consider a micro canonical ensemble of a perfect gas. Let there be n point particles with mass m confined in a volume V with total energy u within the energy range δu.

The corresponding volume

$$\Delta\Gamma = \int \mathrm{d}\, q_1 \ldots\ldots\ldots.\, dq_{3n} \int \mathrm{d}\, p_1 \ \ldots\ldots\ldots.\, dp_{3n}$$

$$\int \mathrm{d}\, q_1 \ldots\ldots.\, dq_{3n} = \mathrm{V}^n$$

Hence $\Delta\Gamma = \mathrm{V}^n \int \mathrm{d}\, q_1 \ldots\ldots\ldots.\, dq_{3n}$

The momentum space integral is to be evaluated subject to the constraint of the ensemble

$$u - \delta u \leq u_r \leq u.$$

$$u_r = p_{\,\mathrm{i}}2/2\ .$$

$$u - \delta u \leq 1/2m \sum_{i=1}^{n} {p_i}^2 \leq u$$

The accessible volume in momentum space is the volume of a spherical shell of radius $(2mu)^{1/2}$ and thickness $(\frac{m}{2u})^{1/2}$

The volume of three dimensional sphere of radius 'R' is,

$$\mathrm{V}_3(\mathrm{R}) = \frac{4}{3}\pi\, \mathrm{R}^3$$

$$= \frac{\pi^{3/2}}{\Gamma(\frac{3}{2}+1)}\mathrm{R}^3$$

$$= \frac{\pi^{3/2}}{\left(\frac{3}{2}\right)!}\mathrm{R}^3$$

$$= \mathrm{C}_3\, \mathrm{R}^3$$

$$V_3(R) = \frac{\pi^{f/2}}{\left(\frac{f}{2}\right)!} R^f$$

$$= C_f R^3$$

$$\text{Where} \quad C_f = \frac{\pi^{f/2}}{\left(\frac{f}{2}\right)!}$$

Therefore for 3n dimensional hyper-sphere of radius $(2mu)^{1/2}$, the volume is

$$V_{3n}(R) = \frac{\pi^{3n/2}}{\left(\frac{3n}{2}\right)!} (2mu)^{3n/2}$$

The volume coupled between hyper spheres of radii $(2mu)_{1/2}$ to $[2m\,(u - \delta u)]^{1/2}$ is

$$\int d\,p_1 \ \ldots \ldots \ldots .\, dp_3 = \frac{\pi^{3n/2}}{\left(\frac{3n}{2}\right)!} [(2mu)^{3n/2} \ -\{2m\,(u - \delta u)^{3n/2} \}$$

$$= \frac{\pi^{3n/2}}{\left(\frac{3n}{2}\right)!} [(2mu)^{3n/2} \ -\{1-(1 - \delta u/u)^{3n/2} \}$$

$$= \frac{\pi^{3n/2}}{\left(\frac{3n}{2}\right)!} [(2mu)^{3n/2} \ -\{1 \exp(-\frac{3n}{3} . \frac{\delta u}{u})\}$$

For a macroscopic system 3n = 10^{23} ;

$$\frac{3n}{3} . \frac{\delta u}{u} \quad >> \quad u.$$

And hence we can drop the exponential term.

$$\int d\,p_1 \ \ldots \ldots \ldots .\, dp_3 = \frac{\pi^{3n/2}}{\left(\frac{3n}{2}\right)!} (2mu)^{3n/2}$$

$$\Delta\Gamma = V^n \int d\,q_1 \ldots \ldots \ldots .\, dq_{3n}$$

$$= V^n \frac{\pi^{3n/2}}{\left(\frac{3n}{2}\right)!} (2mu)^{3n/2}$$

According to classical statistical mechanics, the entropy σ in statistical equilibrium is given by,

$$\sigma = log\, \Delta\Gamma$$

$$= \log[\, V^n \frac{\pi^{3n/2}}{\left(\frac{3n}{2}\right)!} (2mu)^{3n/2} \ ]$$

$$= n\, [V\, \pi^{3/2}\, (2\mathrm{mu})^{3n/2}\ -\ (\frac{3n}{2})\, log\, (3n/2)!$$

$$=\ n\, [V\, \pi^{3/2}\, (2\mathrm{mu})^{3n/2}]\ -(\frac{3n}{2})\, log\, (\frac{3n}{2}) + \frac{3n}{2}$$

$$=\ n\, [V\, \pi^{3/2}\, (2\mathrm{mu})^{3n/2}\ ]\ \mathrm{n\, log}\, (\frac{3n}{2})^{3/2} + \frac{3n}{2}$$

$$= n\, log\, [\frac{\mathrm{V}\, \pi^{3/2}\ (2\mathrm{mu})3\mathrm{n}/2}{\left(\frac{3n}{2}\right)^{3/2}}\ ]\ + \frac{3n}{2}$$

$$\sigma =\ [\ \mathrm{V}\ (\frac{4\pi m}{3})^{3/2}\ \ (\frac{u}{n})^{3/2}] +\ \frac{3n}{2}$$

We know that the entropy should not depend on the unit of hyper volume ΔΓ. To make it dimensionless we divide it by h^{3n} .

$$\sigma = log\ [\Delta\Gamma /\ \mathrm{h}^{3n}]$$

$$= n\, log\, [\ \mathrm{V}\ (\frac{4\pi m}{3})^{3/2}\ \ (\frac{u}{n})^{3/2}] +\ \frac{3n}{2}$$

The above equation does not satisfy the additive property and hence to satisfy the additive property we must divide by n!

$$\sigma = log\ [\Delta\Gamma /\ \mathrm{h}^{3n}\, \mathrm{n!}]$$

$$= n\, log\, \frac{[\ \mathrm{V}\ (\frac{4\pi m}{3})^{3/2}\ \ (\frac{u}{n})^{3/2}]}{h^{3n}}\ +\ \frac{3n}{2} -\ log n!$$

$$= n\, log\, \frac{[\ \mathrm{V}\ (\frac{4\pi m}{3})^{3/2}\ \ (\frac{u}{n})^{3/2}]}{h^{3n}}\ +\ \frac{3n}{2} -\ \mathrm{n}\, log\, n\ \ +\ \mathrm{n}$$

$$\sigma = n\, log\, \frac{[\frac{V}{n}\ (\frac{4\pi m}{3})^{3/2}\ \ (\frac{u}{n})^{3/2}]}{h^{3}}\ +\ \frac{5n}{2}$$

This expression satisfies the additive property because instead of V and u we have V/n and u/n. We shall now establish the connection of statistical quantities with corresponding thermodynamic quantities.

2.7 ENTROPY OF MIXING AND THE GIBB'S PARADOX

The partition function of a perfect gas is given by,

$$\mathrm{Z}\ =\ \frac{V}{h^3}\, (2\pi mKT)^{3/2} \qquad \text{---------(1)}$$

The entropy of a perfect gas is given by,

$$S = N\,k \log Z + \frac{3}{2} Nk \quad \text{--------(2)}$$

$$= N\,k \log \left[\frac{V}{h^3} (2\pi m K T)^{3/2}\right] + \frac{3}{2} Nk$$

$$= N\,k \left[\log V + \frac{3}{2} \log m + \frac{3}{2} \log T + C\right] \quad \text{----------(3)}$$

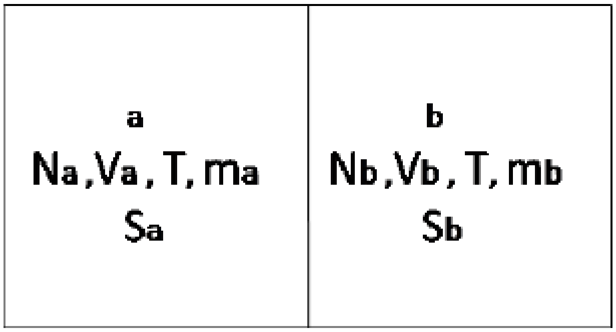
C is a constant term including h, k

The entropy given by equation (3) does not satisfy the additive property and giving paradoxial results.

Explanation

Consider two systems a and b at the same temperature $T_a = T_b = T$

a and b are partitioned by a barrier as shown in figure.



The particles of the two system are identical and distinguishable

The entropies of a and b are given by,

$$S_a = N_a\,k \left[\log V_a + \frac{3}{2} \log m_a + \frac{3}{2} \log T + C\right]$$

$$S_b = N_b\,k \left[\log V_b + \frac{3}{2} \log m_b + \frac{3}{2} \log T + C\right] \quad \text{-------(4)}$$

Here N_a, m_a and V_a represent the number of particles, the mass of each particle and volume of system a.

Here N_b, m_b and V_b represent the number of particles, the mass of each particle and volume of system b.

Entropy is an extensive quantity and satisfies the additive property.

If the entropy given by equation (3) had satisfied the additive property , then by removing partition and allowing the gas molecules to mix freely, the entropy of the joint system would be

$$S_{ab} = S_a + S_b$$

$$= N_a\ k\ [\log V_a + \frac{3}{2}\log m_a + \frac{3}{2}\log T + C] + N_b\ k\ [\log V_b + \frac{3}{2}\log m_b + \frac{3}{2}\log T + C] \quad \text{--------(5)}$$

If the particles of the two system are the same and for convenience we take $V_a = V_b = V$, $N_a = N_b = N$ and $m_a = m_b =$,then the entropy of the individual system be,

$$S_a = S_b$$

$$= N\ k\ [\log V + \frac{3}{2}\log m + \frac{3}{2}\log T + C] \quad \text{-----(6)}$$

Now the entropy of the combined system be,

$$S_{ab} = 2\ [\log V + \frac{3}{2}\log m + \frac{3}{2}\log T + C] \quad \text{-----(7)}$$

Now we shall find actual entropy. Let the partition is removed. Allow the molecules of the gas to mix freely. Now we have a system with 2N particles and volume 2V. Then the entropy of the joint system ab is given by,

$$S_{ab} = 2Nk\ [\log 2V + \frac{3}{2}\log m + \frac{3}{2}\log T + C]$$

$$= 2Nk\ [\log 2V + \frac{3}{2}\log m + \frac{3}{2}\log T + C] + 2\ NK \log 2$$

$$= S_a + + 2\ NK \log 2 \quad \text{-------(8)}$$

Equation (8) is not equal to equation (7), but has an additional factor 2Nk log 2.

Thus by mixing of two gases with each containing N molecules and by removing a partition between them , then the entropy of the joint system increases by 2Nk log 2.

This additional entropy is called entropy of mixing. Thus if we use equation (3) for entropy we got the paradoxial results. This peculiar behavior of the entropy is called Gibb’s paradox.

To resolve Gibb's paradox

Gibbs solved this paradox by considering the two systems with the molecules are identical and distinguishable. If two systems containing same number N are mixed by removing the partition then the diffusion takes place unnoticeably. In this situation N molecules of each system cannot be distinguished in N! ways.

Hence the weight of the configuration

$$W = N! \prod \frac{{g_i}^{ni}}{n_i!}$$

can be replaced by

$$W = \prod \frac{{g_i}^{ni}}{n_i!}$$

$$\text{Log w} = \sum n_i \log g_i \ - \ \sum \log n_i!$$

$$= \sum n_i \log g_i \ - \sum n_i \ \log n_i! \ + \ \sum n_i$$

$$= \sum n_i \log g_i \ - \sum n_i \ \log n_i! \ + \ \text{N}$$

From Maxwell- Boltzmann law

$$n_i = g_i \ e^{-\alpha} e^{-\beta \varepsilon_i}$$

$$\text{Log W}_{\text{max}} = \sum n_i \log g_i \ - \ \sum n_i \log[\, g_i \ e^{-\alpha} e^{-\beta \varepsilon_i}] + N$$

$$= \sum n_i \log g_i \ - \ \sum n_i \log g_i \ - \sum n_i \alpha + \ \sum n_i \, \beta \varepsilon_i + \text{N}$$

$$\text{Log W}_{\text{max}} = \alpha N + \ \beta \ E + N$$

Let us substitute $A = e^{-}$; $ie, \alpha = -\ log\ A$

$$\text{Log W}_{\text{max}} = \ \text{- N log A} + \beta \ E + N$$

$$= \ \text{N} \ \text{- N log A} \ + \ \beta \ E$$

$$= \ \text{N [1 - log A]} + \ \beta \ E$$

$$\text{S} \ = \text{k log W}_{\text{max}}$$

$$= \text{Nk}\,[1 - \log A\,] + \beta\, E\text{k}$$

$$= \text{Nk}\,[1 - \log A\,] + \frac{1}{kT}\frac{3}{2}\,\text{NkT k}$$

$$= \text{Nk}\,[1 - \log A\,] + \frac{3}{2}\,\text{Nk}$$

$$= \text{Nk} - \text{Nk}\,\log A + \frac{3}{2}\,\text{Nk}$$

$$= - \log A + \frac{5}{2}\,\text{Nk}$$

$$= - \text{Nk}\,\log\frac{N}{z} + \frac{5}{2}\,\text{Nk}$$

$$= \text{Nk}\,\log\frac{Z}{N} + \frac{5}{2}\,\text{Nk}$$

$$S = \text{N k}\,\log[\,\frac{V}{h^3}\,\frac{(2\pi mKT)3/2}{N}] + \frac{5}{2}\,\text{Nk}$$

$$= \text{N k}\,\log[\,\frac{V}{N}\,(\frac{(2\pi mKT)}{h^2})^{3/2}] + \frac{5}{2}\,\text{Nk} \qquad \text{-------(9)}$$

The entropy given by this equation satisfies the additive property since here in the argument of logarithm we have V/N in place of V.

In equation (9) replacing N by 2N and V by 2V , the entropy of the combined system be given by,

$$S_{ab} = 2Nk\,[\,\frac{2V}{2N}\,(\frac{(2\pi mKT)}{h^2})^{3/2}] + \frac{5}{2}\,2\text{Nk}$$

$$= 2\,\{\,Nk\,log[\,\frac{V}{N}\,(\frac{(2\pi mKT)}{h^2})^{3/2}] + \frac{5}{2}\,\text{Nk}\,\}$$

$$= 2\,\text{S}$$

$$= S_a + S_b$$

Thus Gibb‟s paradox is resolved .The resolution of Gibb‟s paradox is an example of the success of the quantum theory.

UNIT III

CANONICAL AND GRAND CANONICAL ENSEMBLES

Trajectories and density of states - Liouville’s theorem – Canonical and grand canonical ensembles - Partition function - Calculation of statistical quantities - Energy and density fluctuations

3.1 Trajectories and density of states

The **density of states** (**DOS**) of a system describes the number of allowed modes or states per unit energy range. The density of states is defined as , where $N(E)$ is the number of states in the system of volume whose energies lie in the range from E to E + δE .

$$D(E) = \frac{N(E)}{V}$$

It is mathematically represented as a distribution by a probability density function, and it is generally an average over the space and time domains of the various states occupied by the system. The density of states is directly related to the dispersion relations of the properties of the system. High DOS at a specific energy level means that many states are available for occupation. Generally, the density of states of matter is continuous. In isolated systems however, such as atoms or molecules in the gas phase, the density distribution is discrete, like a spectral density. Local variations, most often due to distortions of the original system, are often referred to as **local densities of states** (LDOSs).

3.2 LIOUVILLE’S THEOREM

Liouville‟s theorem gives information about the rate of change of phase density in the phase space. The theorem may be stated in two parts.

The rate of change of density of phases points in the neighborhood of a moving phase point in the Γ space is zero. This part represents the principle of conservation of density in the phase space.

$$d\rho/dt = 0 \qquad \text{….(1)}$$

Any arbitrary element of volume or extension in phase in the Γ space bounded by a moving surface and containing a number of phase points does not change with time. This part represents the principle of conservation of extension in the phase space.

$$\frac{d}{dt}(\delta\Gamma) = \frac{d}{dt}\left(\prod_i^f dq_i\, dp_i\right) \qquad \text{……..(2)}$$

(i) The principle of conservation of density in the phase space

Consider any arbitrary hyper volume

$$\delta\Gamma = \delta q_1\, \delta q_2 \ldots \ldots .. \delta q_f\, \delta p_1\, \delta p_2 \ldots \ldots .. \delta p_f$$

in the phase space located between

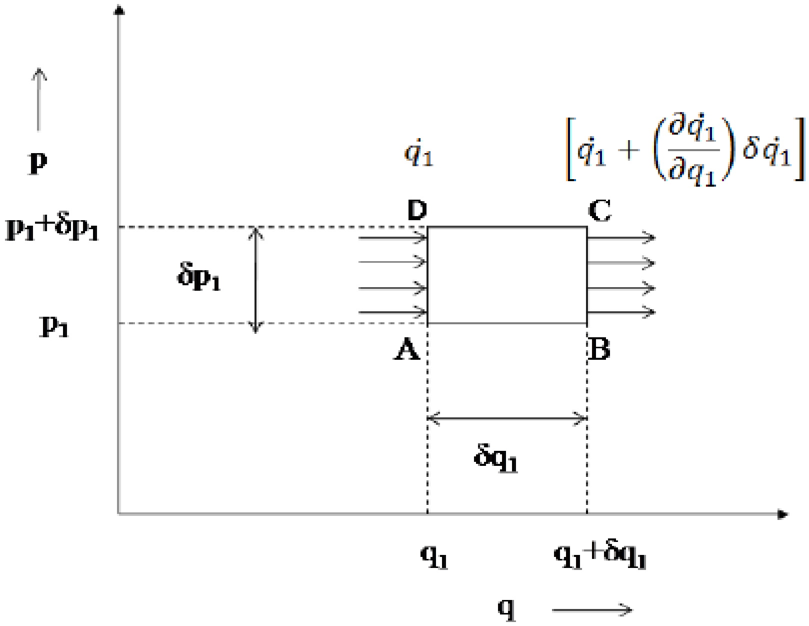
q_1 and $q_1 + \delta q_1 \ldots \ldots \ldots .. q_f$ and $q_f + \delta q_f$,

p_1 and $p_1 + \delta p_1, \ldots \ldots \ldots . p_f$ and $p_f + \delta p_f$.

The number of phase points in this volume element changes with time due to the motion of phase points.

If ρ is the density of phase points, the number of phase points in this volume element at any instant t is ,

$$\delta N = \rho . \delta\Gamma = \rho\delta q_1\, \delta q_2 \ldots \ldots . \delta q_f\, \delta p_1 \delta p_2 \ldots \ldots \ldots \delta p_f \qquad \text{......(3)}$$



$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho . \delta\Gamma)$$

$$= \dot{\rho}\, \delta\Gamma$$

$$= \dot{\rho}\, \delta q_1\, \delta q_2 \ldots \ldots . \delta q_f\, \delta p_1 \delta p_2 \ldots \ldots \ldots \delta p_f \qquad \text{…(4)}$$

This change in the number of phase points in the given hyper volume is due to the difference between the number of phase points entering the hyper volume through any face and the number of those leaving the opposite face per second.

Consider two faces of hyper volume with co-ordinates $q_1$and $q_1 + \delta q_1$. If q_1 is the component of velocity of phase point at $q_1, q_2, \ldots \ldots . q , p_1, p_2, \ldots \ldots \ldots p_f$,then the number of phase points entering the first face AD per second

$$= \rho\dot{q}_1\, \delta q_2 \ldots \ldots . . \ 1 \ldots \ldots . \delta p_f \qquad \ldots.(5)$$

As density ρ changes with change in position and momentum co-ordinates and at the opposite face BC the co-ordinate q_1 changes to $q_1 + \delta q_1$ and the density ρ changes to $(\rho + \frac{\partial \rho}{\partial q_1} \delta q_1)$ at the face BC. The velocity $\dot{q}_1$ changes to ($\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1$) Therefore the number of phase points leaving the opposite face BC at $q_1+\delta q_1$ per second.

$$= (\rho + \frac{\partial \rho}{\partial q_1} \delta q_1)\, (\, \dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1)\, \delta q_2 \ldots \ldots . . \ 1 \ldots \ldots . \delta p_f$$

Neglecting higher order differentials, we get

$$= [\, \rho\, \dot{q}_1 + (\rho\, \frac{\partial \dot{q}_1}{\partial q_1} \delta q_1)\, \delta q_1\,]\ \ \delta q_2 \ldots \ldots . . \ 1 \ldots \ldots . \delta p \ldots\ldots(6)$$

Subtracting (6) from (5) we get the expression for change in the number of phase points per second corresponding to q_1.

$$= -(\, \rho\, \frac{\partial \dot{q}_1}{\partial q_1} + \ \dot{q}_1\, \frac{\partial \rho}{\partial q_1})\, \delta q_1\, \delta q_2 \ldots \ldots . . \ 1 \ldots \ldots . \delta p_f \qquad \ldots\ldots.(7)$$

Similarly, the expression for the change into the number of phase points per second corresponding to p_1 is

$$= -(\, \rho\, \frac{\partial \dot{p}_1}{\partial q_1} + \ \dot{q}_1\, \frac{\partial \rho}{\partial p_1})\, \delta q_1\, \delta q_2 \ldots \ldots . . \ 1 \ldots \ldots . \delta p_f \qquad \ldots\ldots.(8)$$

Since the change in number of phase points per second corresponding to all position and momentum coordinates are like equation (7) and (8), then they are summed up.

The net increase in the number of phase points in the given hyper volume per second is given by,

$$\frac{d}{dt}(\delta N)=-\sum_{i=1}^{f}[\rho\left(\frac{\partial \dot{q}_\iota}{\partial q_i} + \ \frac{\partial \dot{p}_\iota}{\partial q_i}\right) + (\,\dot{q}_\iota \frac{\partial \rho}{\partial q_i} \ + \ \dot{p}_\iota \frac{\partial \rho}{\partial p_i})]\ \delta q_1\, \delta q_2 \ldots \delta q_f \delta p_1 \ldots \qquad ..(9)$$

using equation (4) we get,

$$\frac{\partial\rho}{\partial t} = -\sum_{i=1}^{f}\left[\rho\left(\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i}\right) + \left(\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i}\right)\right] \qquad \text{……(10)}$$

From canonical equation,

$$\frac{\partial\dot{q}_i}{\partial q_i} = \frac{\partial^2 H}{\partial q_i \partial p_i} \qquad \text{and}$$

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

Since the order of differentiation is immaterial i.e,

$$\frac{\partial^2 H}{\partial q_i \partial p_i} = \frac{\partial^2 H}{\partial p_i \partial q_i}$$

We get

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

$$\sum_{i=1}^{f}\left(\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i}\right) = 0 \qquad \text{…..(11)}$$

Now equation (10) becomes

$$\left(\frac{\partial\rho}{\partial t}\right)_{q,p} = -\sum_{i=1}^{f}\left(\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i}\right)$$

$$\left(\frac{\partial\rho}{\partial t}\right)_{q,p} + \sum_{i=1}^{f}\left(\dot{q}_i\frac{\partial\rho}{\partial q_i} + \dot{p}_i\frac{\partial\rho}{\partial p_i}\right) = 0 \qquad \text{……..(12)}$$

This equation represents Liouville‟s theorem

$$\frac{d\rho}{dt}(q_1,\ldots\ldots q_f, p_1,\ldots\ldots p_f, t) = 0$$

$$\text{i.e} \quad \frac{d\rho}{dt} = 0 \qquad \text{……….(13)}$$

This expression represents the principle of conservation of density in phase space.

(ii) The principle of conservation of extension in phase space:

Consider a very small region of hyper volume $\delta\Gamma$ in the Γ space, so that the density of phase points ρ can be taken as uniform throughout the hyper volume. The number of phase points in this hyper volume,

$$\delta N = \rho . \delta\Gamma$$

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho.\delta\Gamma)$$

$$= \frac{d\rho}{dt}\delta\Gamma + \rho\frac{d\delta\Gamma}{dt} \qquad \ldots\ldots\ldots..(14)$$

As each phase point represents a definite system and systems can neither be created nor destroyed, the number of phase points δN must remain fixed.

i.e $$\frac{d}{dt}(\delta N) = 0$$

$$\frac{d\rho}{dt}\delta\Gamma + \rho\frac{d\delta\Gamma}{dt} = 0$$

from equation (14)

$$\frac{d\rho}{dt} = 0$$

$$\rho\frac{d\delta\Gamma}{dt} = 0$$

$$\frac{d\delta\Gamma}{dt} = 0$$

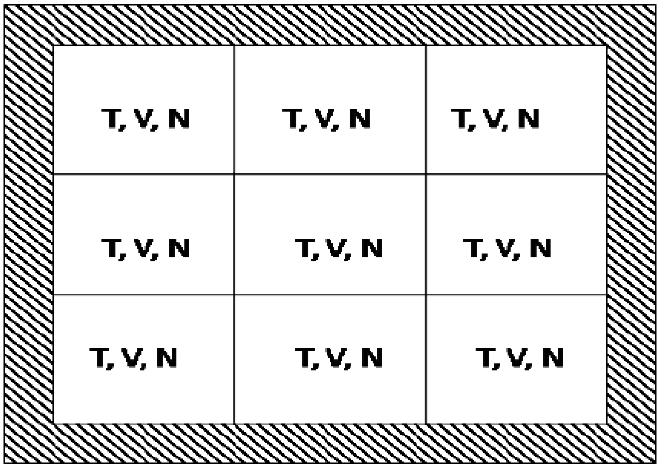
$$\delta\Gamma = constant \qquad \ldots.(15)$$

This expression represents the principle of conservation of extension in the phase space.

3.3 Canonical ensemble

Collection of large number of essentially independent systems with same temperature T, volume V and the number of particles N. All the particles are identical. The individual systems are separated by rigid, impermeable but conducting walls.

Exchange of heat energy between the system takes place. But not the particles. A diagrammatic representation is shown in Figure



3.4 Grand canonical ensemble

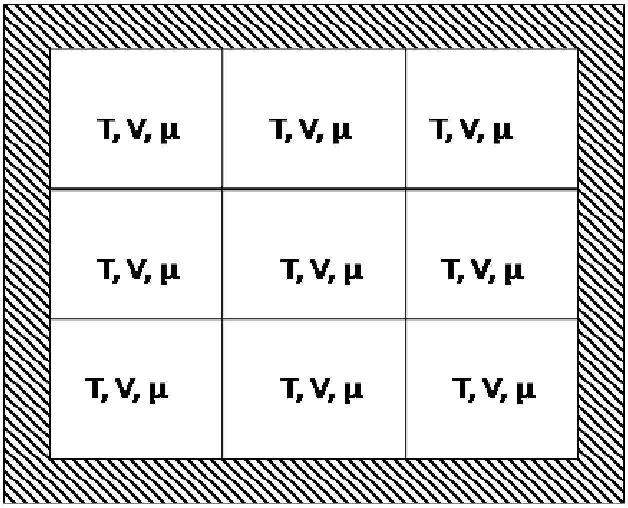
Collection of large number of essentially independent systems with same temperature T, volume V, and the chemical potential μ. All the particles are identical.

The individual systems are separated by rigid, permeable and conducting walls.

Exchange of heat energy as well as the particles between the system takes place.

The state of any ensemble can be completely specified by a large number of phase points in the phase space called ***dust cloud***.

Thus the behavior of an ensemble can be represented by a large number of trajectories (or) phase lines (or) streaming motion of the dust cloud.



3.5 Partition function and thermodynamic function for grand canonical ensemble

In grand canonical ensemble sub system is allowed to exchange energy and the particles with the heat reservoir under the condition,

$$E_s + E_r = E_t \, and \, n_s + n_r = n_t \qquad \text{….(1)}$$

, n_s→ the energy and the number of particles of the sub system.

, n_r→the energy and the number of particles of the heat reservoir.

, n_t→the energy and the number of particles of the total system.

The probability distribution (n) is given by,

$$(n)= \exp\left[\Omega + n\mu - E /\right] \qquad \text{….(2)}$$

Ω→grand potential

μ→chemical potential

The grand partition function is defined as,

$$\mathcal{Z} = \exp(-\Omega/\tau) \text{ ….(3)}$$

$$= \sum e^{\mu n/\tau} \int e^{E/\tau} \, d\Gamma(n) \qquad \text{(classical)}$$

$$= \sum_n \sum_i \exp\left(\mu_n - E_{n,i}\right)/\tau \qquad \text{(quantum)}$$

$$\mathcal{Z} = \sum_n e^{\mu n} \, Z_n$$

$$Z_n = \sum_i e^{-E/\tau} \, d\Gamma(n) \qquad \text{(classical)}$$

$$= \sum_i e^{-E_{n,i}/\tau} \qquad \text{(quantum)}$$

is the canonical partition function .

i.e *the grand partition function $\mathcal{Z}$ is the sum of canonical partition functions Z_i* for ensemble with different n′ s *with weighing factor* $e^{-\mu n/\tau}$.

From equation (3) the partition function is given by,

$$\mathcal{Z} = \exp(-\Omega/\tau)$$

$$\Omega = -\tau \log \mathcal{Z} \qquad \text{….(4)}$$

The entropy σ may be written as,

$$\sigma = \log \Delta\Gamma$$

$$= \log\left[\frac{1}{\rho(\bar{n},\bar{E})}\right]$$

$$= -\,(\Omega + \bar{n}\,\mu - \bar{E})\,/\tau$$

$$= -\,\Omega + \bar{n}\,\mu - U\,/\tau \qquad \text{….(5)}$$

$$\tau\,\sigma = -\,(\Omega + \bar{n}\,\mu - U)$$

$$U - \tau\,\sigma = (\Omega + \bar{n}\,\mu)$$

Helmholtz free energy $F = U - \tau\,\sigma$ ….(6)

$$= \Omega + \bar{n}\,\mu \qquad \text{….(7)}$$

$$G = F + pV \qquad \text{….(8)}$$

$$= U - \tau\,\sigma + pV \text{ ….(9)}$$

$$dG = dU - \tau d\,\sigma - \sigma\,d\tau + pdV + Vdp$$

But $dU = \tau d\,\sigma - pdV + \mu dn$

Hence $dG = \tau d\,\sigma - pdV + \mu dn - \tau d\,\sigma - \sigma\,d\tau + pdV + Vdp$

$$= \mu dn - \sigma\,d\tau + Vdp$$

$$\left(\frac{dG}{dn}\right)_{\tau,p} = \mu \qquad \text{………(10)}$$

Hence $G = \mu n$ for fixed p and η.

In this case $G = \mu\bar{n}$

$$\Omega + \bar{n}\,\mu + pV = \bar{n}\,\mu$$

$$\Omega = -pV$$

$$F + pV = \mu\bar{n} \qquad \text{….(11)}$$

$$U - \tau\,\sigma + pV = \mu\bar{n}$$

$$U - \tau\,\sigma - \Omega = \mu\bar{n}$$

$$U - \tau\,\sigma - \mu\bar{n} = \Omega \qquad \text{….(12)}$$

$$d\Omega = dU - \tau d\,\sigma - \sigma\, d\tau - \mu d\bar{n} - \bar{n}\, d\mu$$

$$= \tau d\,\sigma - pdV + \mu d\bar{n} - \tau d\,\sigma - \sigma\, d\tau - \mu d\bar{n} - \bar{n}\, d\mu$$

$$= -pdV - \sigma\, d\tau - \bar{n}\, d\mu \quad \text{….(13)}$$

$$P = -\left(\frac{d\Omega}{dV}\right)_{\tau,\mu}$$

$$\sigma = -\left(\frac{d\Omega}{d\tau}\right)_{V,\mu}$$

$$\bar{n} = -\left(\frac{d\Omega}{d\mu}\right)_{\tau,V}$$

From the above three relations we can evaluate thermodynamic quantities for the grand canonical ensemble

3.6 ENERGY AND DENSITY FLUCTUATIONS IN ENSEMBLES:

(a) Canonical ensemble

In canonical ensemble the systems are in thermal equilibrium with the heat reservoir and so energy fluctuations take place.

For canonical ensemble partition function

$$Z = \sum_i e^{-\beta E_i} \quad \text{---------(1)}$$

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

$$\frac{\partial z}{\partial \beta} = \sum_i e^{-\beta E_i}\,(-E_i)$$

$$= E_i \sum_i e^{-\beta E_i}$$

$$\sum_i E_i e^{-\beta E_i} = -\frac{\partial z}{\partial \beta}$$

Mean energy $\bar{E} = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$

$$= \frac{\sum_i E_i e^{-\beta E_i}}{Z}$$

$$\bar{E} = -\frac{1}{z}\frac{\partial z}{\partial \beta} \qquad \text{--------(2)}$$

$$\sum_i {E_i}^2 e^{-\beta E_i} = \frac{\partial^2 z}{\partial^2 \beta}$$

$$\overline{E^2} = \frac{\sum_i {E_i}^2 e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$= \frac{\sum_i {E_i}^2 e^{-\beta E_i}}{Z}$$

$$\overline{E^2} = -\frac{1}{z}\frac{\partial^2 z}{\partial \beta^2} \qquad \text{-----------(3)}$$

Using equation (2)

$$\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial}{\partial \beta}\left(-\frac{1}{z}\frac{\partial z}{\partial \beta}\right)$$

$$= -\frac{\partial}{\partial \beta}\left(\frac{1}{z}\frac{\partial z}{\partial \beta}\right)$$

$$= -\left[\frac{1}{z}\frac{\partial^2 z}{\partial \beta^2} - \frac{1}{z^2}\left(\frac{\partial z}{\partial \beta}\right)^2\right]$$

$$= -\left[\overline{E^2} - (\bar{E})^2\right]$$

$$= -(\overline{\delta E})^2 \qquad \text{----------(4)}$$

The molar heat at constant volume

$$C_v = \left(\frac{\partial E}{\partial T}\right)_\text{v}$$

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

$$= -(\overline{\delta E})^2\left(-\frac{1}{KT^2}\right)$$

$$C_v = (\overline{\delta E})^2\left(\frac{1}{KT^2}\right) \qquad \text{--------(5)}$$

$$(\overline{\delta E})^2 = KT^2\, C_v$$

$$\overline{\delta E} = \mathrm{T}\,(\mathrm{K}C_v)^{1/2} \qquad \text{-------(6)}$$

The energy fluctuation is measured by the ratio

$$\frac{\Delta E}{E} = \frac{\sqrt{(\overline{\delta E})^2}}{\bar{E}}$$

$$= \frac{\mathrm{T}\,(\mathrm{K}C_v)^{1/2}}{\bar{E}} \qquad \text{------(7)}$$

For large values of T, C_v and E are proportional to the number of molecules N and hence fluctuation is proportional to $N^{-1/2}$.

For an ideal gas

$$\bar{E} = \mathrm{NkT} \quad \text{and} \quad C_v = \mathrm{Nk}$$

$$\frac{\Delta E}{E} = \frac{T}{NkT}\,[\mathrm{kNk}]^{1/2}$$

$$= \frac{N^{1/2}}{N}$$

$$= N^{-1/2} \qquad \text{--------(8)}$$

For a macroscopic system N = 10^{22}.

So the fluctuations are very small in the order 10^{-11}.

Therefore in canonical ensemble the distribution of energies is so peaked about the ensemble average energy that in practice regarded as a micro canonical ensemble.

(b) Grand canonical ensemble

In grand canonical ensemble the fluctuations take place in concentration as well as energy. The energy fluctuation can be calculated as for canonical ensemble.

For Grand canonical ensemble the partition function

$$\mathcal{Z} = \sum_{n,i} e^{(n\mu - E_{n,i})/\tau} \quad \frac{n}{\tau} \qquad \text{--------(9)}$$

$$\frac{\partial Z}{\partial \mu} = \frac{1}{\tau}\sum_{n,i} n\, e^{(n\mu - E_{n,i})/\tau}$$

$$\sum_{n,i} n\, e^{(n\mu - E_{n,i})/\tau} = \tau\,\frac{\partial Z}{\partial \mu}$$

Mean concentration

$$\bar{n} \;=\; \frac{\sum_{n,i} n\, e^{(n\mu - E_{n,i})/\tau}}{\sum_{n,i}\; e^{(n\mu - E_{n,i})/\tau}}$$

$$= \frac{\sum_{n,i} n\, e^{(n\mu - E_{n,i})/\tau}}{z}$$

$$\bar{n} \;= \frac{\tau}{z}\frac{\partial Z}{\partial \mu} \qquad \text{--------(10)}$$

$$\frac{\partial^2 z}{\partial \mu^2} \;=\; \frac{1}{\tau^2}\sum_{n,i} n^2\; e^{(n\mu - E_{n,i})/\tau}$$

$$\sum_{n,i} n^2\; e^{(n\mu - E_{n,i})/\tau} = \;\tau^2\,\frac{\partial^2 z}{\partial \mu^2}$$

$$\bar{n}^2 \;=\; \frac{\sum_{n,i} n^2\, e^{(n\mu - E_{n,i})/\tau}}{\sum_{n,i}\; e^{(n\mu - E_{n,i})/\tau}}$$

$$= \;\frac{\sum_{n,i} n^2\, e^{(n\mu - E_{n,i})/\tau}}{z}$$

$$\bar{n}^2 \;= \tau^2\,\frac{\partial^2 z}{\partial \mu^2}$$

$$\frac{\partial \bar{n}}{\partial \mu} \;=\; \frac{\partial}{\partial \mu}\left[\frac{\tau}{z}\frac{\partial Z}{\partial \mu}\right]$$

$$= \frac{\tau}{z}\frac{\partial^2 z}{\partial \mu^2} \;-\; \frac{\tau}{z^2}\left(\frac{\partial Z}{\partial \mu}\right)^2$$

$$\tau\frac{\partial \bar{n}}{\partial \mu} \;=\; \frac{\tau^2}{z}\frac{\partial^2 z}{\partial \mu^2} \;-\; \frac{\tau^2}{z^2}\left(\frac{\partial Z}{\partial \mu}\right)^2$$

$$\tau\frac{\partial \bar{n}}{\partial \mu} \;=\; -(\,\overline{\delta n}\,)^2 \qquad \text{--------(12)}$$

For an ideal classical gas

$$\bar{n} = \; e^{\mu/\tau}\,\mathrm{V}\,\left(\frac{2\pi m\tau}{h^2}\right)^2$$

$$\frac{\partial \bar{n}}{\partial \mu} = \frac{1}{\tau} e^{\mu/\tau} \text{V} (\frac{2\pi m\tau}{h^2})^2$$

$$\frac{\partial \bar{n}}{\partial \mu} = \frac{1}{\tau} \bar{n}$$

$$\tau \frac{\partial \bar{n}}{\partial \mu} = \bar{n}$$

$$(\overline{\delta n})^2 = \bar{n}$$

$$\sqrt{(\overline{\delta n})^2} = \sqrt{\bar{n}}$$

The concentration fluctuation is measured by the ratio

$$\frac{\Delta n}{n} = \frac{\sqrt{(\overline{\delta n})^2}}{\bar{n}}$$

$$= \frac{\sqrt{\bar{n}}}{\bar{n}}$$

$$\text{pV} = \bar{n} \text{ kT}$$

$$\frac{\Delta n}{n} = [\frac{kT}{pV}]^{1/2}$$

Smaller of the volume greater is the fractional fluctuation

UNIT IV

CLASSICAL AND QUANTUM STATISTICS

Density matrix - Statistics of ensembles - Statistics of indistinguishable particles - Maxwell-Boltzmann statistics - Fermi-Dirac statistics – Ideal Fermi gas – Degeneracy - Bose-Einstein statistics - Plank radiation formula - Ideal Bose gas - Bose-Einstein condensation

4.1 THE DENSITY MATRIX

A pure quantum state of a system is represented by a single eigenvector ψ_α When the system is described by non-negative probabilities p_α, p_β ……for being in states ψ_α, ψ_β……… a statistical approach is necessary.

A pure classical state is represented by a single moving point in phase space, that have definite value of coordinates $q_{1,}\ q_{2,}$ ……………..$q_{f,}$ and canonical momenta $p_{1,}\ p_2$ …..p_f. at each instant of time. The statistical state can be described by a non-negative density function

$$f(q_{1,}\ q_{2,}\ \ldots\ldots q_{f,}\ \ p_{1,}\ p_2\ \ldots p_f)$$

The probability that the system is found in the interval $dq_1,,\ldots dq_f\ldots\ dp_1\ldots dp_f$ at time *t* is

$$\rho(dq_1,,\ldots dq_f\ldots\ dp_1\ldots dp_f)$$

The quantum analogue of the classical density function is known as density operator.

We know that operators can be expressed by matrices and hence the density operator expressed as matrix is known as density matrix.

The density matrix expresses the result of taking quantum mechanical matrix elements and ensemble averages in the same operation.

Consider an ensemble consisting of *N* systems in the normalized states

$$\psi_i, i = 1, ,2,3.....N$$

Let ω_i be the probability that an assembly will be in the state ψ_i.

We then define the density matrix in the{ ψ_i } representation as

$$\rho_{ij} = \omega_i\, \delta_{ij} \qquad \text{---------(1)}$$

Suppose now we wish to calculate the probability that if a measurement is made on an observable whose operator is $\hat{A}$ having Eigen functions $\emptyset_i$, the result will be the Eigen value a_n corresponding to the Eigen function $\emptyset_i$.

If the assembly is in the state ψ_i and we express ψ_i as a linear combination of the $\emptyset_i$ we obtain

$$\psi_i \sum_j c_{ij} \emptyset_j \qquad \text{----------(2)}$$

The probability that a measurement of $\hat{A}$ will give a_n is then simply $c_{in} * c_{in}$. But the probability that the assembly is in the state ψ_i is ω_i. Therefore the probability that the measurement of A will yield a_n is just

$$\sum \omega_i \, c_{in} * c_{in} = \sum_i \sum_j \omega_i \, \delta_{ij} c_{in} * c_{in}$$

$$= \sum_i \sum_j \rho_{ij} \, c_{in} * c_{in}$$

$$= \sum_i \sum_j c_{in} * c_{in} \int \psi_i * \hat{\rho} \; \psi_j \, \mathrm{dq}$$

$$= \int (\textstyle\sum_i c_{in} \, \psi^*) \, \hat{\rho} \, (\textstyle\sum_i c_{in} \, \psi^*) \, \mathrm{dq}$$

$$= \int \psi_n * \hat{\rho} \; \psi_n \, \mathrm{dq} \qquad \text{---------(3)}$$

Therefore the probability that the measurement on $\hat{A}$ will give a_n is just

$$\int \emptyset_n * \hat{\rho} \; \emptyset_n \, \mathrm{dq} = \rho_{nn}{}' \qquad \text{----------(4)}$$

Now suppose we wish to calculate the average value of A. This will be simply

$$\langle \bar{\hat{A}} \rangle = \sum a_n \, \rho_{nn}{}'$$

$$= \sum_n \int \emptyset_n \, \hat{\rho} \; a_n \emptyset_n \, \mathrm{dq}$$

$$= \sum_n \int \emptyset_n * \hat{\rho} \; \widehat{A_n} a_n \emptyset_n \, \mathrm{dq}$$

$$= \text{Trace } [\hat{\rho} \, \hat{A}]$$

We note that the average $\langle \bar{\hat{A}} \rangle$ is a double average, quantum mechanical average and a statistical mechanical average

4.2 Statistics of indistinguishable particle

By indistinguishable particles we mean that if the position and spin coordinates of two of them are interchanged, there is no physical way of measuring that a change has been made. In classical mechanics identical particles do not lose their individuality despite the identity of their physical properties . If a pair of particles is completely equivalent even then it is possible to identify them by the continuity of their trajectories because this property enables an observer to follow each particle.

This is due to the fact that their wave packets do not overlap, and the particles move in separate, distinguishable continuous orbits.

As an example, consider the molecules in a gas at N.T.P.

Molecular density = 10^{19} mole./cm.^{2}

Volume available to each molecule = 10^{-19} cm.^{3}

Molecular radius = 10^{-8} cm.

Molecular volume = 10^{-24} cm.^{3}

Because the molecule is smaller than the volume available, we can identify every molecule of the gas. The molecules are thus *distinguishable*.

The situation is quite different in quantum mechanics as follows at once from the uncertainty principle. Due to the uncertainty principle, the concept of the path ceases to have any meaning. If the path of an electron is exactly known at a given instant, its coordinates have no definite values even at an infinitely close subsequent instant. By localising and numbering the identical particles at some instant, at some other instant we cannot say which of particle arrived at that point. In quantum mechanics there is no way of keeping track of each particle separately when the wave functions of two identical particles overlap. Thus in quantum mechanics there is, in principle, no possibility of separately following each of a number of similar particles and thereby distinguishing them.

As an example, we consider the conduction electrons of a metal:

Density of electrons = 10^{22} per cm^3

Volume available to each electron = 10^{-22} cm^3

Momentum $p_x = (2mE)^{l/2}$ for 1 eV. = 0.5×10^{-19} erg-sec cm^{-1}

Uncertainty in position $\Delta x = h/p_x = 13 \times 10^{-8}$ cm.

Volume of conduction electron = $(13 \times 10^{-8})^3$ cm^3 =2×10^{-21} cm^3.

Comparing the volume of conduction electron to the volume available, we conclude that the electron wave functions overlap considerably and hence they are *indistinguishable.*

Thus we have two categories of particles:

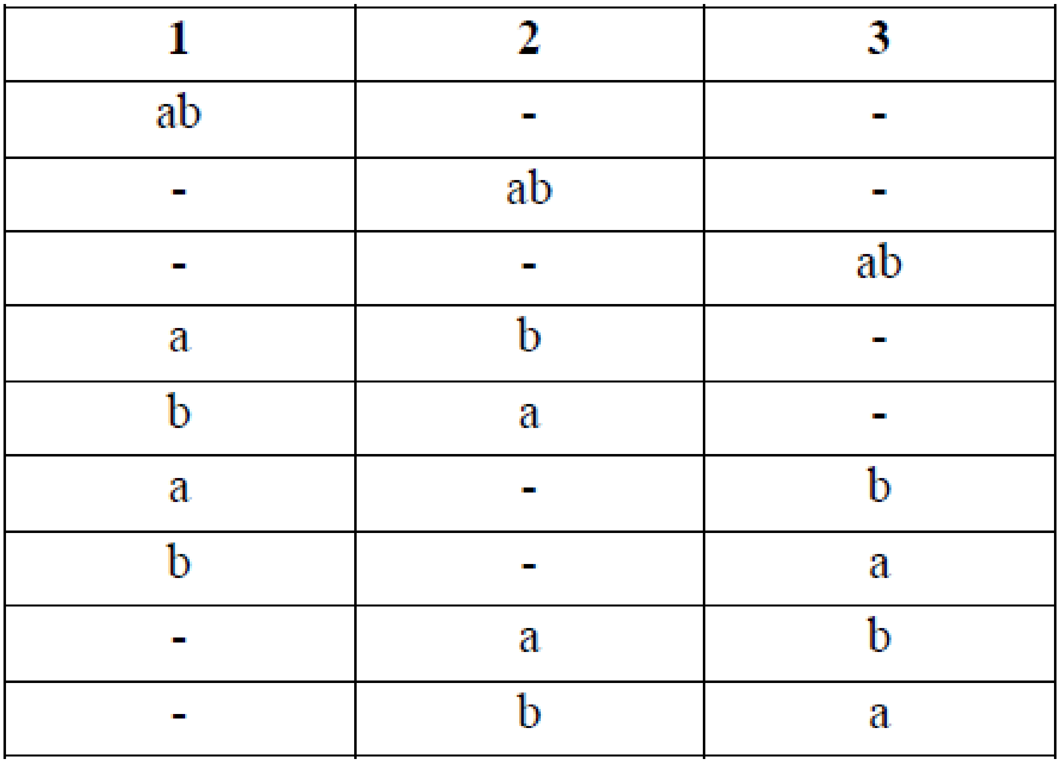
(i) Classical, which are identical but distinguishable.

(ii) Quantum, which are identical and indistinguishable.

When quantum particle density is low, *i.e.*, uncertainty is small in comparison to the volume available, the particles obey classical statistics otherwise we use quantum statistics.

4.3 Maxwell –Boltzmann statistics

The particles are considered distinguishable and any number of particle can be any one state.



1	**2**	**3**
ab	-	-
-	ab	-
-	-	ab
a	b	-
b	a	-
a	-	b
b	-	a
-	a	b
-	b	a

Total states $3^2 = 9$ possible states for the whole gas.

4.4 Fermi-Dirac statistics

Particles are indistinguishable , i.e b = a

1	2	3
a	a	-
a	-	a
-	a	a

3 possible states for the whole gas.

$$\text{Let } \varepsilon = \frac{\text{probability that the two partcles are found in the same state}}{\text{probability that the two particle are found in different states}}$$

Thus for the three cases,

$$\varepsilon_{M-B} = 3/6 = 1/2$$

$$\varepsilon_{B-E} = 3/3 = 1$$

$$\varepsilon_{F-D} = 0/3 = 0$$

Thus in B-E statistics, there is a greater tendency for the particles to bunch together in the same states in comparison to M-B statistics. On the other hand, in the F-D statistics, there is a greater relative tendency to particles to remain apart in different states than there is in classical statistics.

Consider a system having n identical and indistinguishable particles. These particles be divided into quantum groups such that there are $n_1, n_2, \ldots, n_i, \ldots$ number of particles with energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$ respectively.

g_i be the number of eigen states in the i^{th} level.

Conditions

Particles are identical and indistinguishable Particles obey Pauli‟s exclusion principle. Hence each cell contains 0 (or) 1 particle. Obviously $g_i \geq$.

The total number of particles in the system is constant.

$$N = \sum n_i \quad = constant$$

The total energy of the system is constant

$$\mathrm{E} = \sum n_i \, \epsilon_i \quad = constant$$

4.5 IDEAL FERMI GAS

Consider a perfect Fermi-Dirac gas of n Fermions. These particles be divided into quantum groups such that there are $n_1, n_2, \ldots, n_i, \ldots$ number of particles with energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$ respectively. g_i be the number of eigen states in the i^{th} level.

For the most probable distribution

$$n_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i+1}}$$

here $\alpha = \frac{-\mu}{kT}$, $\beta = \frac{1}{kT}$

$$= \frac{g_i}{\frac{1}{A}e^{\alpha+\beta\epsilon_i+1}}$$

where, A = $e^{-\alpha}$

α may be positive or negative.

The constant α can be determined by the condition

$$\mathrm{n} = \sum n_i \ = \sum \frac{g_i}{e^{\alpha+\beta\epsilon_i+1}}$$

$$= \frac{g_i}{\frac{1}{A}e^{\alpha+\beta\epsilon_i+1}} \qquad \text{---------(1)}$$

Since the particles in a box are normal size and the translational levels are closely spaced and hence now the summation is replaced by integration.

The number of particle states $g\ p\ dp$ between momentum p and p+dp is given by

$$= g_s \frac{4\pi p^2 dp}{\frac{h^3}{V}}$$

$$= g_s \frac{4\pi V p^2 dp}{h^3}$$

g_s = degenaracy factor = $(2s + 1)$

$$\text{Now } g\,(p)\,dp = g_s \frac{4\pi V p^2 dp}{h^3} \qquad \text{------}(2)$$

Then equation (1) can be rewritten as

$$n\,(p)\,dp = \frac{g(p)dp}{e^{\alpha+\beta\epsilon_i+1}}$$

$$= g_s \frac{4\pi V p^2 dp}{h^3} \frac{1}{e^{\alpha+\beta\epsilon_i+1}} \qquad \text{------}(3)$$

$$\varepsilon = \varepsilon_i = \frac{p^2}{2m}$$

$$p^2 = 2m\,\varepsilon$$

$$2\text{pdp} = 2m\,d\varepsilon$$

$$\text{dp} = \frac{m}{p}\,d\varepsilon$$

$$= \frac{m}{\sqrt{2m\,\varepsilon}}\,d\varepsilon$$

$$=(\frac{m}{2\varepsilon})^{1/2}\,d\varepsilon$$

Now equation (3) becomes

$$n\,(\varepsilon)\,d\varepsilon = g_s \frac{4\pi V}{h^3}(2m\,\varepsilon)\,(\frac{m}{2\varepsilon})^{1/2}\,d\varepsilon \frac{1}{e^{\alpha+\beta\epsilon_i+1}}$$

$$= \frac{4\pi m V}{h^3}(2m\,\varepsilon)^{1/2} \frac{d\varepsilon}{e^{\alpha+\beta\epsilon_i+1}} \qquad \text{---------}(4)$$

$$\frac{\varepsilon}{kT} = \text{x}$$

$$\varepsilon = kTx$$

$$d\varepsilon = kTdx$$

$$n\,(\varepsilon)\,d\varepsilon \;=\; g_s\frac{4\pi mV}{h^3}(2m\mathrm{kTx}\,)^{1/2}\,\frac{\mathrm{kTdx}}{e^{\alpha+\beta\epsilon_i+1}}$$

$$=g_s\frac{V}{h^3}(2m\mathrm{kTx}\,)^{3/2}\frac{2}{\sqrt{\pi}}\,\frac{x^{1/2}\mathrm{dx}}{e^{\alpha+\beta\epsilon_i+1}}$$

The total number of particles is given by

$$\mathrm{n}=\int_0^\infty g_s\;\frac{V}{h^3}\left(2m\mathrm{kTx}\,\right)^{3/2}\;\frac{2}{\sqrt{\pi}}\;\frac{x^{1/2}\mathrm{dx}}{e^{\alpha+\beta\epsilon_i+1}}$$

$$=\;g_s\;\frac{V}{h^3}\left(2m\mathrm{kTx}\,\right)^{3/2}\;\frac{2}{\sqrt{\pi}}\int_0^\infty\;\frac{x^{1/2}\mathrm{dx}}{e^{\alpha+\beta\epsilon_i+1}}$$

$$\mathrm{n}=g_s\;\frac{V}{h^3}\left(2m\mathrm{kTx}\,\right)^{3/2}\;\;f_1(\alpha) \qquad \text{----------(6)}$$

where $f_1(\alpha)=\frac{2}{\sqrt{\pi}}\int_0^\infty\;\frac{x^{1/2}\mathrm{dx}}{e^{\alpha+\beta\epsilon_i+1}}$

The total energy is given by

$$\mathrm{E}=\int_0^\infty \varepsilon\;\mathrm{n}\;(\varepsilon\,)\mathrm{d}\varepsilon$$

$$=\int_0^\infty \mathrm{kTx}\;\;g_s\;\frac{V}{h^3}\left(2m\mathrm{kTx}\,\right)^{3/2}\;\frac{2}{\sqrt{\pi}}\;\frac{x^{1/2}\mathrm{dx}}{e^{\alpha+\beta\epsilon_i+1}}$$

$$=g_s\;\frac{V}{h^3}\left(2m\mathrm{kTx}\,\right)^{\frac{3}{2}}\frac{2}{\sqrt{\pi}}\quad\int_0^\infty\;\frac{x^{3/2}\mathrm{dx}}{e^{\alpha+\beta\epsilon_i+1}}$$

$$=\;\frac{3}{2}\,g_s\;\frac{V}{h^3}\left(2m\mathrm{kTx}\,\right)^{\frac{3}{2}}\frac{4}{3\sqrt{\pi}}\quad\int_0^\infty\;\frac{x^{3/2}\mathrm{dx}}{e^{\alpha+\beta\epsilon_i+1}}$$

$$=\;\frac{3}{2}\,g_s\;\frac{V}{h^3}\mathrm{kT}\;\left(2m\mathrm{kT}\,\right)^{\frac{3}{2}}\,f_2(\alpha) \qquad \text{--------(8)}$$

$$f_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}dx}{e^{\alpha+\beta\epsilon_i+1}}$$

$f_1(\alpha)$ and $f_2(\alpha)$ must be evaluated for both positive and negative values of α.

Now we introduce the Fermi-Dirac distribution function $f(\varepsilon)$ defined by,

$$f(\varepsilon) = \frac{n(\varepsilon)}{g(\varepsilon)}$$

$$= \frac{1}{e^{\alpha+\beta/kT+1}}$$

$$= \frac{1}{e^{(\varepsilon-\varepsilon_F)/kT+1}} \qquad \text{----------(10)}$$

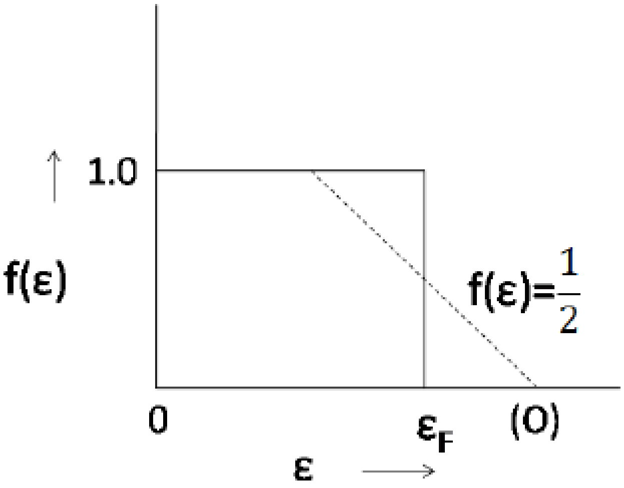
$$\text{Where } \alpha = -\frac{\mu}{kT} = -\frac{\varepsilon_F}{kT}$$

At T=0 K, $f(\varepsilon) = 1 \quad for \quad \varepsilon < \varepsilon_F(0)$

$= 0 \quad for \quad \varepsilon > \varepsilon_F(0)$

$= ½ \quad for \quad \varepsilon = \varepsilon_F$

This is shown in the figure.



ε_F is determined by the condition that the total number of particles is constant at a given temperature T.

The number of fermions in the energy range between ε and $\varepsilon + d\varepsilon$ is given by,

$$n(\varepsilon)\, d\varepsilon = \int f(\varepsilon)\, g(\varepsilon)\, d\varepsilon$$

$$= \frac{4\pi mV}{h^3}(2m)^{1/2} \frac{\varepsilon^{3/2}}{e^{(\varepsilon-\varepsilon_F)/kT+1}} \qquad \text{-----(11)}$$

At absolute zero, all states with $0 < \varepsilon < \varepsilon_F(0)$ are completely filled and all states with $\varepsilon > (0)$ are empty.

ε_F at T=0 K i.e. ε_F (0) is determined by,

$$n = \int_0^{\varepsilon_F(0)} n(\varepsilon)\, d\varepsilon$$

$$= \int_0^{\varepsilon_F(0)} f(\varepsilon)\, g(\varepsilon)\, d\varepsilon$$

$$= \int_0^{\varepsilon_F(0)} g(\varepsilon)\, d\varepsilon$$

$$= \int_0^{\varepsilon_F(0)} g_s \frac{4\pi mV}{h^3}(2m)^{1/2} \varepsilon^{1/2} d\varepsilon$$

$$= g_s \frac{4\pi mV}{h^3}(2m)^{1/2} \int_0^{\varepsilon_F(0)} \varepsilon^{1/2} d\varepsilon$$

$$= g_s \frac{4\pi mV}{h^3}(2m)^{1/2} [\frac{2}{3} \varepsilon_F(0)^{3/2}]$$

$$[\varepsilon_F(0)]^{3/2} = \frac{3n}{4\pi V g_s} \frac{h^3}{(2m)^{1/2}}$$

$$\varepsilon_F(0) = \frac{h^3}{(2m)} [\frac{3n}{4\pi V g_s}]^{2/3} \qquad \text{--------(12)}$$

This gives the Fermi-energy at T= 0K.

For particles with spin equal to 1/2, g_s=2 ie, one particle with spin up and another with spin down. Now we define Fermi temperature T_F as,

$$T_F = \frac{\varepsilon_F(0)}{k}$$

$$= \frac{h^2}{(2mk\,)}\,[\frac{3n}{4\pi V g_s}]^{2/3}$$

$$\rho = \frac{mn}{V}$$

$$\frac{n}{V} = \frac{\rho}{m}$$

$$T_F = \frac{h^2}{(2mk\,)}\,[\frac{3\rho}{4\pi m g_s}]^{2/3}$$

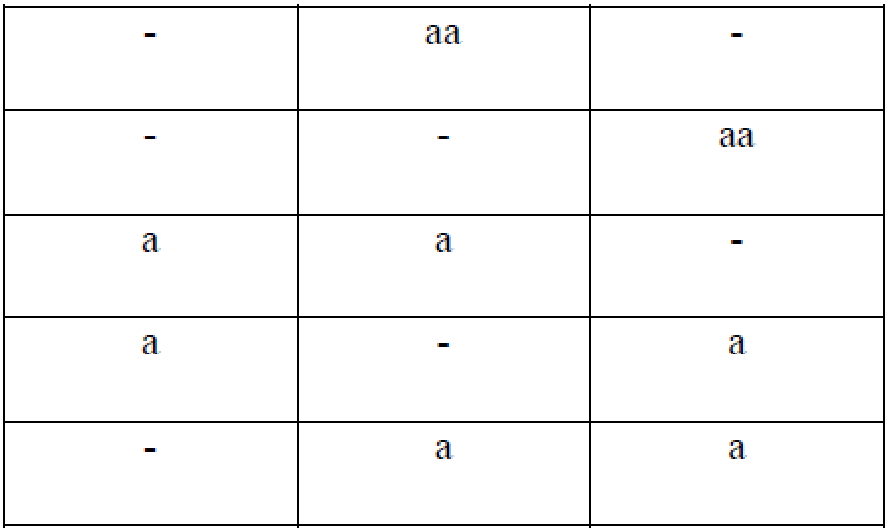
$$\boldsymbol{T_F = \frac{h^2}{(2m^{5/3}k\,)}\,[\frac{3\rho}{4\pi g_s}]^{2/3}}$$

$T << T_F$	strong degeneracy	α is negative
$T > T_F$	weak degeneracy	α is positive
$T >> T_F$	non degeneracy	α is positive

4.6 Bose-Einstein statistics:

Particles are indistinguishable and no more than one particle can be in any one state.

1	2	3
aa	-	-



-	aa	-
-	-	aa
a	a	-
a	-	a
-	a	a

3+3 = 6 possible states for the whole gas.

Consider a system having n identical and indistinguishable particles. These particles be divided into quantum groups such that there are $n_1, n_2, \ldots, n_i, \ldots$ number of particles with energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$ respectively.

g_i be the number of eigen states in the i^{th} level.

4.7 Ideal Bose gas

Consider a perfect Bose-Einstein gas of n bosons. These particles be divided into quantum groups such that there are $n_1, n_2, \ldots, n_i, \ldots$ number of particles with energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$ respectively.

g_i be the number of eigen states in the i^{th} level.

For the most probable distribution

$$n_i = \frac{g_i}{e^{\alpha+\beta\epsilon_i-1}}$$

here $\alpha = \frac{-\mu}{kT}$, $\beta = \frac{1}{kT}$

$$= \frac{g_i}{\frac{1}{A}e^{\beta\epsilon_i-1}}$$

where, A = $e^{-\alpha}$

Since the number of particles cannot be negative, we must always have

$$n_i \geq 0 \ , \quad \frac{1}{A}e^{\beta\epsilon_i} \geq 0$$

The constant α can be determined by the condition

$$\text{n} = \sum n_i = \sum \frac{g_i}{e^{\alpha+\beta\epsilon_i-1}}$$

$$= \frac{g_i}{\frac{1}{A}e^{\beta\epsilon_i-1}} \qquad \text{---------(1)}$$

Since the particles in a box are normal size and the translational levels are closely spaced and hence now the summation is replaced by integration.

The number of particle states $g\ p\ dp$ between momentum p and p+dp is given by

$$= g_s \frac{4\pi p^2 dp}{\frac{h^3}{V}}$$

$$= g_s \frac{4\pi V p^2 dp}{h^3}$$

g_s = degeneracy factor = 1

$$\text{Now } g\ (p)\ dp = g_s \frac{4\pi V p^2 dp}{h^3} \qquad \text{------(2)}$$

Then equation (1) can be rewritten as

$$n\ (p)\ dp = \frac{g(p)dp}{e^{\alpha+\beta\epsilon_i-1}}$$

$$= g_s \frac{4\pi V p^2 dp}{h^3} \frac{1}{e^{\alpha+\beta\epsilon_i-1}} \qquad \text{------(3)}$$

$$\varepsilon = \varepsilon_i = \frac{p^2}{2m}$$

$$p^2 = 2m\,\varepsilon$$

$$2p\mathrm{d}p = 2m\,d\varepsilon$$

$$\mathrm{d}p = \frac{m}{p}\,d\varepsilon$$

$$= \frac{m}{\sqrt{2m\,\varepsilon}}\,d\varepsilon$$

$$=\left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon$$

Now equation (3) becomes

$$n\,(\varepsilon)\,d\varepsilon = \frac{4\pi V}{h^3}(2m\,\varepsilon)\left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon\,\frac{1}{e^{\alpha+\varepsilon/kT-1}}$$

$$= \frac{4\pi mV}{h^3}(2m\,\varepsilon)^{1/2}\,\frac{d\varepsilon}{e^{\alpha+\varepsilon/kT-1}} \qquad \text{---------(4)}$$

$$\frac{\varepsilon}{kT} = \mathrm{x}$$

$$\varepsilon = kTx$$

$$d\varepsilon = kTdx$$

$$n\,(\varepsilon)\,d\varepsilon = \frac{4\pi mV}{h^3}(2m\mathrm{kTx})^{1/2}\,\frac{\mathrm{kTdx}}{e^{\alpha+x-1}}$$

$$=\frac{V}{h^3}(2m\mathrm{kTx})^{3/2}\,\frac{2}{\sqrt{\pi}}\,\frac{x^{1/2}\mathrm{dx}}{e^{\alpha+x-1}}$$

The total number of particles is given by

$$n = \int_0^\infty \frac{V}{h^3}\left(2m\mathrm{kTx}\right)^{3/2} \frac{2}{\sqrt{\pi}} \frac{x^{1/2}\mathrm{dx}}{e^{\alpha+x-1}}$$

$$= \frac{V}{h^3}\left(2m\mathrm{kTx}\right)^{3/2} \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}\mathrm{dx}}{e^{\alpha+x-1}}$$

$$n= \frac{V}{h^3}\left(2m\mathrm{kTx}\right)^{3/2} \; f_1(\alpha) \qquad \text{----------(6)}$$

where $f_1(\alpha) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{1/2}\mathrm{dx}}{e^{\alpha+x-1}}$ -----------(7)

The total energy is given by

$$E = \int_0^\infty \varepsilon\, n\,(\varepsilon\,)\mathrm{d}\varepsilon$$

$$= \int_0^\infty \mathrm{kTx} \;\; \frac{V}{h^3}\left(2m\mathrm{kTx}\right)^{3/2} \frac{2}{\sqrt{\pi}} \frac{x^{1/2}\mathrm{dx}}{e^{\alpha+x-1}}$$

$$= \frac{V}{h^3}\left(2m\mathrm{kTx}\right)^{\frac{3}{2}} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}\mathrm{dx}}{e^{\alpha+x-1}}$$

$$= \frac{3}{2}\frac{V}{h^3}\left(2m\mathrm{kTx}\right)^{\frac{3}{2}} \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}\mathrm{dx}}{e^{\alpha+x-1}}$$

$$= \frac{3}{2}\frac{V}{h^3}\mathrm{kT}\left(2m\mathrm{kT}\right)^{\frac{3}{2}} f_2(\alpha) \qquad \text{--------(8)}$$

$$f_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}\mathrm{dx}}{e^{\alpha+x-1}}$$

For $A < 1, f_1(\alpha)\; and\; f_2(\alpha)$ may be evaluated as follows:

$$f_1(\alpha) = \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{\frac{1}{2}}\mathrm{dx}}{e^{\alpha+x-1}}$$

$$= \frac{2}{\sqrt{\pi}}\int_0^\infty \frac{x^{\frac{1}{2}}\mathrm{dx}}{\left(\frac{e^x}{A}-1\right)}$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty x^{\frac{1}{2}} (\frac{e^x}{A} - 1)^{-1} dx$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty x^{\frac{1}{2}} A\, e^{-x} (1 - A\, e^{-x})^{-1} dx$$

$$= \frac{2}{\sqrt{\pi}} \int_0^\infty x^{\frac{1}{2}} A\, e^{-x} (1 + Ae^{-x} + A^2 e^{-2x} + \cdots .) dx$$

$$= \frac{2}{\sqrt{\pi}} [\int_0^\infty x^{\frac{1}{2}} A\, e^{-x} dx + \int_0^\infty x^{\frac{1}{2}} A^2 e^{-2x} dx +]$$

$$= \frac{2}{\sqrt{\pi}} [\sqrt{\frac{\pi}{2}} [\mathrm{A} + \frac{A^2}{2^{\frac{3}{2}}} + \frac{A^3}{3^{\frac{3}{2}}} + \ldots\ldots\ldots]]$$

$$f_1(\alpha) = \sum_{r=1}^{\infty} \frac{A^r}{r^{\frac{3}{2}}} \qquad \text{----------(10)}$$

Similarly $f_2(\alpha) = \frac{4}{3\sqrt{\pi}} \int_0^\infty \frac{x^{3/2}\mathrm{dx}}{e^{\alpha+x-1}}$

$$f_2(\alpha) = \sum_{r=1}^{\infty} \frac{A^r}{r^{\frac{5}{2}}} \qquad \text{------------(11)}$$

Now,

$$\mathrm{n} = \frac{V}{h^3} (2m\mathrm{kTx})^{3/2} \; f_1(\alpha)$$

$$= \frac{V}{h^3} (2m\mathrm{kTx})^{3/2} \; [\mathrm{A} + \frac{A^2}{2^{\frac{3}{2}}} + \frac{A^3}{3^{\frac{3}{2}}} + \ldots\ldots\ldots] \qquad \text{-------(12)}$$

$$\mathrm{E} = \frac{3}{2} \frac{V}{h^3} \mathrm{kT} \, (2m\mathrm{kT})^{\frac{3}{2}} f_2(\alpha)$$

$$\mathrm{E} = \frac{3}{2} \frac{V}{h^3} \mathrm{kT} \, (2m\mathrm{kT})^{\frac{3}{2}} \; [\mathrm{A} + \frac{A^2}{5^{\frac{3}{2}}} + \frac{A^3}{5^{\frac{3}{2}}} + \ldots\ldots\ldots] \qquad \text{-----(13)}$$

$$\frac{E}{n} = \frac{3}{2} \mathrm{kT} \, [\mathrm{A} + \frac{A^2}{5^{\frac{3}{2}}} + \frac{A^3}{5^{\frac{3}{2}}} + \ldots\ldots\ldots] \quad [\mathrm{A} + \frac{A^2}{2^{\frac{3}{2}}} + \frac{A^3}{3^{\frac{3}{2}}} + \ldots\ldots\ldots]^{-1}$$

$$= \frac{3}{2}\ \mathrm{kT}\ [\mathrm{A} + \frac{A^2}{5^{\frac{3}{2}}} + \frac{A^3}{5^{\frac{3}{2}}} + \ldots\ldots\ldots] \quad [\mathrm{A} + \frac{A^2}{2^{\frac{3}{2}}} + \frac{A^3}{3^{\frac{3}{2}}} + \ldots\ldots\ldots]^{-1}$$

$$= \frac{3}{2}\ \mathrm{kT}\ [1 - \frac{A}{2^{\frac{5}{2}}} + \frac{A^2}{3^{\frac{5}{2}}} + \ldots\ldots\ldots] \qquad \text{-------(14)}$$

The value of α (or) A can be determined by equation (6) as

$$\mathrm{n} = \frac{V}{h^3}(2\pi m\mathrm{kT})^{3/2}\ f_1(\alpha)$$

$$f_1(\alpha) = \frac{n}{V}\frac{h^3}{(2\pi m\mathrm{kT})^{3/2}}$$

Here $f_1(\alpha)$ is directly proportional to particle density n/v and inversely proportional to temperature as $T^{3/2}$.

For $A << 1, f_1(\alpha) = A$

$$\mathrm{A} = \frac{n}{V}\frac{h^3}{(2\pi m\mathrm{kT})^{3/2}} \qquad \text{---------(15)}$$

Obviously A would be small for high temperatures (low density).

4.8 Bose-Einstein condensation:

The degeneracy parameter A is given by,

$$\mathrm{A} = \frac{n}{V}\frac{h^3}{(2\pi m\mathrm{kT})^{\frac{3}{2}}} \qquad \text{--------(1)}$$

And $$n = \frac{V}{h^3}(2\pi m\mathrm{kT})^{\frac{3}{2}}\ f_1(\alpha) \qquad \text{---------(2)}$$

If the particle density is increased or the temperature is decreased then A increases. Now the behaviour of perfect gas departs from the classical perfect gas. This is due to the fact that the velocities of the particles are subjected to quantum statistics.

The gas under this condition is said to be degenerate gas and A is called the degeneracy parameter.

′A′ contains three variables n/V - the particle density , m - mass of each boson and T - temperature of the gas.

The degeneracy criterion will be based on the magnitude

$$\frac{\mathrm{n/V}}{(mT)^{1/2}}$$

Thus the degree of degeneracy will be large when T is low, n/V is large and m is small.

For low energy values A=1 and α=0.

Then$[f_1(\alpha)]_{max} = f_1(0)$

$$= 1+\frac{1}{2^{\frac{3}{2}}}+\frac{1}{2^{\frac{3}{2}}}+\text{.........}]$$

$$= 2.612$$

$$\text{now}\quad \left(\frac{n}{V}\right)_{\mathrm{mqx}} = \frac{(2\pi m\mathrm{kT})^{\frac{3}{2}}}{h^3}\, 2.612 \qquad \text{-----------(4)}$$

Equation (4) corresponds to the limiting case of Bose-Einstein degeneration.

The solution of equation (2) can exist for

$$\frac{n}{V} > \frac{(2\pi m\mathrm{kT})^{\frac{3}{2}}}{h^3}\, 2.612 \qquad \text{-----------(5)}$$

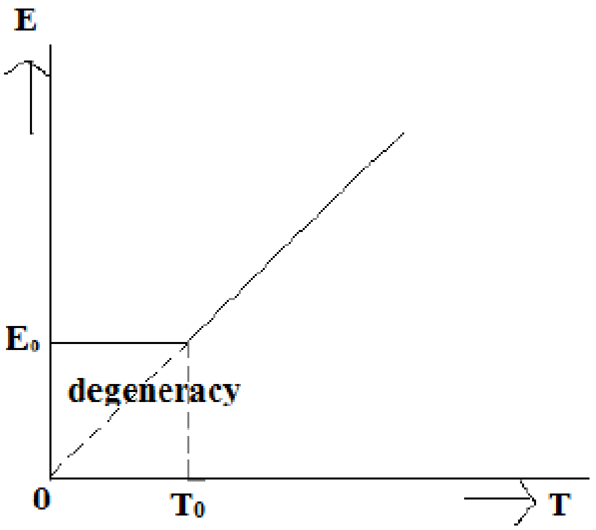
n/v can be alternatively expressed in terms of critical temperature T_o defined as

$$\frac{n}{V} = \frac{(2\pi m\mathrm{k}T_0)^{\frac{3}{2}}}{h^3}\, 2.612 \qquad \text{----------(6)}$$

$$(2\pi m\mathrm{k}T_0)^{\frac{3}{2}} = h^3\,\frac{n}{V}\,\frac{1}{2.612}$$

$$2\pi m\mathrm{k}T_0 = h^2\left(\frac{n}{V}\,\frac{1}{2.612}\right)^{\frac{3}{2}}$$

$$T_0 = \frac{h^2}{2\pi m\mathrm{k}}\left(\frac{n}{V}\,\frac{1}{2.612}\right)^{\frac{3}{2}}$$



T_0 is the lower temperature for which a solution of equation (2) is possible.

There is no solution for $T < T_0$ i.e. the degeneracy starts at T_0.

A graph is drawn between the energy E and temperature T of the gas. Why there is no solution for $T < T_0$. This is because we have assumed continuous distribution and replaced the summation by integration. But at low temperature, the number of particles begins to crowd into lower energy levels. Hence a large number of particles may occupy the ground state $\varepsilon_0 = 0$.

The number of particles between the energy range ε and $\varepsilon + d\varepsilon$ is given by,

$$n\,(\varepsilon)\,dp = \frac{g\,(\varepsilon)dp}{e^{\alpha+\varepsilon/kT-1}} \qquad \text{--------(8)}$$

$$g\,(\varepsilon)\,d\varepsilon = \frac{4\pi mV}{h^3}(2m\,\varepsilon)^{1/2}\,\mathrm{d}\,\varepsilon \qquad \text{----------(9)}$$

For ground state actually $\varepsilon_0 = 0 \ and\ g\,(\varepsilon)\ = 1\ but\ not\ g\,(\varepsilon) = 0$

For $\varepsilon \neq 0$ and $g(\varepsilon) \neq 0$, the distribution given by equation (8) is correct.

But for $\varepsilon = 0$, $g\,(\varepsilon) = 0$ the law gives incorrect result.

For a single state, $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i-1}}$

$$\varepsilon_i = \varepsilon_0 = 0$$
$$g_i = (\varepsilon) = 1$$

$$n = n_0 = \frac{1}{e^{\alpha}-1} \qquad \text{-------------------(10)}$$

This gives the number of particles in the ground state.

Now the total number of particles for the degenerate gas,

$$n = n_0 + \int n(\varepsilon)\, d\varepsilon$$

$$= n_0 + \int_0^\infty \frac{4\pi m V}{h^3}(2m\,\varepsilon)^{1/2}\ \frac{\varepsilon^{1/2}}{e^{\alpha+\varepsilon/kT-1}}\, d\,\varepsilon$$

$$= n_0 + n' \qquad \text{---------(11)}$$

$$n' = \int_0^\infty \frac{4\pi m V}{h^3}(2m\,\varepsilon)^{1/2}\ \frac{\varepsilon^{1/2}}{e^{\alpha+\varepsilon/kT-1}}\, d\,\varepsilon$$

$$n' = \frac{V}{h^3}\ (2\pi m k T)^{3/2}\quad f_1(\alpha)$$

From equation (6)

$$\frac{n}{V} = \frac{(2\pi m k T_0)^{\frac{3}{2}}}{h^3}\ 2.612$$

$$\frac{V}{h^3}\ (2\pi m k T)^{\frac{3}{2}} = n\ \frac{1}{2.612}$$

Now

$$n' = n\ \left(\frac{T}{T_0}\right)^{3/2}\ \frac{f_1(\alpha)}{2.612} \qquad \text{---------(14)}$$

As $f_1(\alpha) < f_1(0)$, n' acquires its maximum value when $\alpha = 0$.

Hence $f_1(\alpha) = 2.612$ for maximum value.

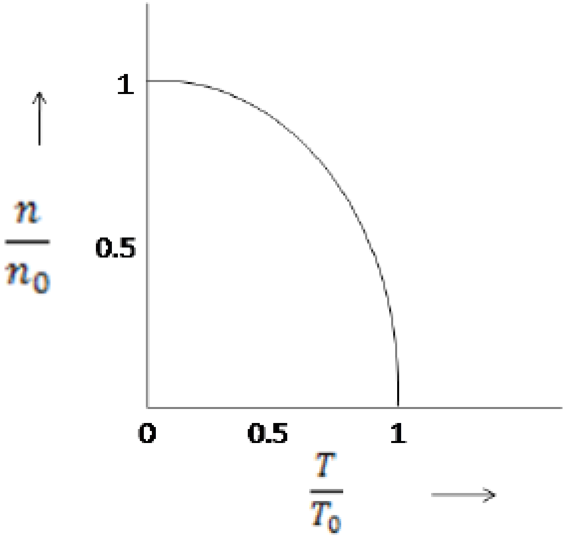
$$n' = n\ \left(\frac{T}{T_0}\right)^{3/2} \qquad for\ T < T_0$$

$$n = n_0 + n'$$

$$n = n_0 + n\ \left(\frac{T}{T_0}\right)^{\frac{3}{2}}$$

$$n_0 = n - n\ \left(\frac{T}{T_0}\right)^{\frac{3}{2}}$$

$$n_0 = n\ \left[1 - \left(\frac{T}{T_0}\right)^{\frac{3}{2}}\right] \qquad for\ T < T_0. \qquad \ldots(15)$$



n_0 gives the number of particles condensed in the ground state. When the temperature is lowered below T_0, the number of particles in the ground state rapidly increases. This rapid increase in the population of the ground state below the critical temperature T_0 for a Bose - Einstein gas is called Bose – Einstein condensation.

Obviously T_0 depends on the particle density n/V. Equation (15) is plotted in figure which represents the fraction of particles condensed in the ground state $for\ T < T_0$.

At the ground state $\varepsilon = 0$, the particles condensed in the ground state do not contribute to the energy.

For above T_o, $\alpha \neq 0$ there is negligible number of particles in the ground state and the gas is said to be classical or non - degenerate gas.

Example: For Helium T_0 can be calculated to have the value 3.12 K.

Therefore the degeneration and condensation of Helium must start at 3.12 K. But experimental observation shows that the condensation of Helium starts at 2.19 K.

i.e. the lambda point transition observed in liquid helium at 2.19 K is essentially a Bose-Einstein condensation.

UNIT V

REAL GAS, ISING MODEL AND FLUCTUATIONS

Cluster expansion for a classical gas - Virial equation of state – Calculation of the first Virial coefficient in the cluster expansion - Ising model - Mean-field theories of the Ising model in three, two and one dimensions - Exact solutions in one dimension. Correlation of space-time dependent fluctuations - Fluctuations and transport phenomena - Brownian motion - Langevin's theory - Fluctuation-dissipation theorem - The Fokker-Planck equation

5.1 Cluster expansion for a classical gas:

Monoatomic gas whose potential energy is given by a sum of two particle interaction u_{ij}. The Hamiltonian of the system is then given by

$$H = \sum_i (\frac{{p_i}^2}{2m}) + \sum_{i<j} u_{ij} \qquad (1)$$

The potential u_{ij} is a function of the relative position vector r_{ij} (= r_j - r_i) .

The partition function of the system would be given by

$$Q_n (V,T) = \frac{1}{N! h^{3N}} \int \exp \{-\beta \sum_i (\frac{{p_i}^2}{2m}) - \beta \ \sum_{i<j} u_{ij}\} \, d^{3N}p \ d^{3N}r \text{ ---(2)}$$

Integrating over the momenta of the particles

$$Q_n (V,T) = \frac{1}{N! \lambda^{3N}} \int \exp \{ -\beta \ \sum_{i<j} u_{ij}\} \, d^{3N}p \ d^{3N}r$$

$$= \frac{1}{N! \lambda^{3N}} \ Z_n (V,T) \qquad \text{--------(3)}$$

Where λ is the mean thermal wavelength of the particles, with the function Z_n (V,T) stands for the space coordination r_1, r_2 , r_3,.... R_N

$$Z_n (V,T) = \int \exp \{ -\beta \ \sum_{i<j} u_{ij}\} \ d^{3N}r$$

$$= \int \prod_{i<j} e^{-\beta u_{ij}} \ d^{3N}r \qquad \text{---------(4)}$$

The function Z_n (V,T) is the configuration integral of the system.

For a gas of non-interacting particles, the integrand in (4) is unity, then we have

$$Z_n{}^{(0)}(\mathrm{V,T}) = \mathrm{V}^{\mathrm{N}}$$

$$and$$

$$Q_n{}^{(0)}(\mathrm{V,T}) = \frac{V^N}{N!\lambda^{3N}}$$

To treat the non-ideal case we introduce, after Mayer, the two-particle function f_{ij} , defined by the relationship.

$$\mathrm{F}_{ij} = e^{-\beta u_{ij}} - 1 \qquad \text{-------------(6)}$$

The absence of interactions, the function f_{ij} is identically zero, in the presence of interactions, it is nonzero but sufficiently high temperatures it is quite small in comparison with the unity.

A typical plot of the functions u_{ij} and f_{ij} is shown in figure

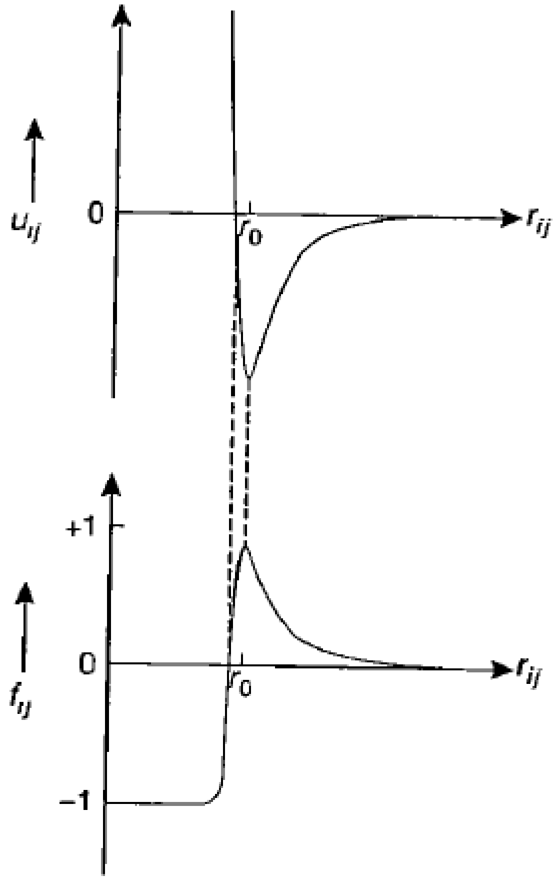
I. The function f_{ij} is everywhere bounded and

II. It becomes negligibly small as the inter particle r_{ij} becomes large in comparison with the effective range r_0 of the potential.

To evaluate the configuration integral(4) we expand its integrand in ascending powers of the function f_{ij}

$$\mathrm{Z_n\,(V,T)} = \int \prod_{i<j}(1+f_{ij})\, d^3r_1 \ldots.\, d^3r_N$$

$$= \int [1 + \sum f_{ij} + \sum f_{ij}f_{kl} + \cdots..]\; d^3r_1 \ldots.\, d^3r_N \qquad \text{------(7)}$$



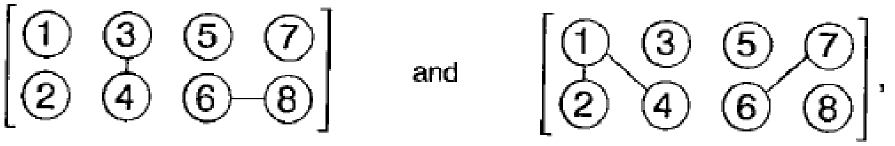
A convenient way of numerating various terms in (7) is to associate each term with a corresponding N-particle graph. For instance, is N were 8, the terms

$$t_A = \int f_{34}\, f_{68}\, d^3r_1 \ldots .\, d^3r_8$$

and

$$t_B = \int f_{12}\, f_{14}\, f_{67} d^3r_1 \ldots .\, d^3r_8 \qquad \text{-------(8)}$$

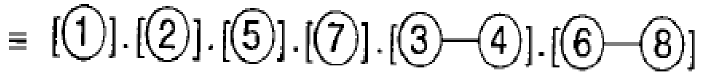
In the expansion of the configuration integral Z_8 could be associated with the 8-particle graph



(9)

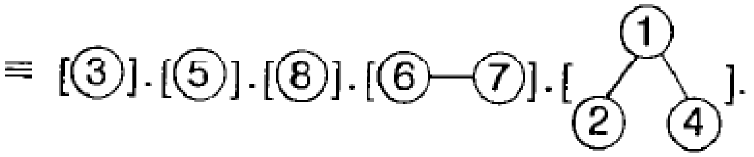
A closer look at the terms t_A and t_B suggests that we better regrad these terms as suitable factorized, that is

$$t_A = \int d^3r_1 \int d^3r_2 \int d^3r_5 \int d^3r_7 \int f_{34}\, d^3r_3 d^3r_4 \int f_{68}\, d^3r_6 d^3r_8$$



(10)

$$t_B = \int d^3r_3 \int d^3r_5 \int d^3r_8 \int f_{12} f_{14}\, d^3r_1 d^3r_2 d^3r_4 \int f_{67}\, d^3r_6 d^3r_7$$



(11)

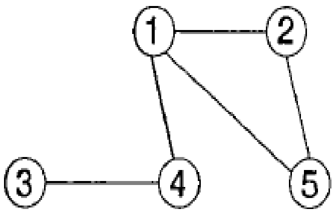
The term t_A in the expansion of the integral Z_8 represents a configuration in which there are four 'clusters' of two particles.

Term t_B represents a 'configuration' in which there are three 'clusters' of one particle.

Cluster cannot be decomposed into simpler graph inasmuch as the corresponding term cannot be factorized into simpler terms.

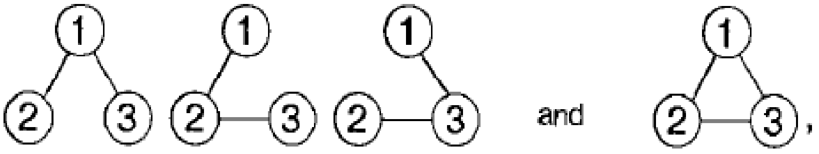
$$\int (f_\alpha\, f_\beta \ldots\ldots f_\lambda)\, d^3r_1 \ldots .\, d^3r_N \qquad \text{--------(12)}$$

$$Z_n\ (V,T) = \text{sum of all distinct N-particle graphs ------(13)}$$



$$\equiv \int f_{12} f_{14} f_{15} f_{25} f_{34}\, d^3r_1 \ldots d^3r_5. \qquad ,(14)$$

A group of *l* particles (*l* = 1 or 2) can lead to variety of *l* – clusters, some of which may be equal in value.



(15)

In view of the variety of ways in which an *l* cluster can appear, we may introduce the notion of the cluster integral b_1 defined by

$$b_l\,(V,T) = \frac{1}{l!\lambda^{3(l-1)}V}\ \text{X (the sum of all possible } l \text{ clusters) ------(16)}$$

Some of the simpler cluster integrals are

$$b_1 = \frac{1}{V}[\textcircled{1}] = \frac{1}{V}\int d^3r_1 \equiv 1, \tag{17}$$

$$\begin{aligned} b_2 &= \frac{1}{2\lambda^3 V}[\textcircled{1}\!-\!\!-\!\textcircled{2}] = \frac{1}{2\lambda^3 V}\iint f_{12}\, d^3r_1\, d^3r_2 \\ &\approx \frac{1}{2\lambda^3}\int f_{12}\, d^3r_{12} = \frac{2\pi}{\lambda^3}\int_0^\infty f(r)r^2\,dr \\ &= \frac{2\pi}{\lambda^3}\int_0^\infty (e^{-u(r)/kT}-1)r^2\,dr, \end{aligned} \tag{18}$$

$$\begin{aligned} b_3 &= \frac{1}{6\lambda^6 V} \times [\text{sum of the clusters (15)}] \\ &= \frac{1}{6\lambda^6 V}\int (\underbrace{f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23}} + f_{12}f_{13}f_{23})\, d^3r_1\, d^3r_2\, d^3r_3 \\ &\approx \frac{1}{6\lambda^6 V}\left[3V\iint f_{12}f_{13}\, d^3r_{12}\, d^3r_{13} + V\iint f_{12}f_{13}f_{23}\, d^3r_{12}\, d^3r_{13}\right] \\ &= 2b_2^2 + \frac{1}{6\lambda^6}\iint f_{12}f_{13}f_{23}\, d^3r_{12}\, d^3r_{13}. \end{aligned} \tag{19}$$

N- particles graph will consist of a number of clusters of which, m_1 are 1 – clusters, m_2 are 2-clusters m_3 are 3- clusters and so on.

$$\sum_{l=0}^{N} l m_i = N \qquad \text{-------------(20)}$$

It represent the ‘collection of graphs’ the sum total of which may be denoted by symbol $S\{m_l\}$.

$$Z_n\,(V,T) = \sum S\{m_l\} \qquad \text{----------(21)}$$

Case (i) straightforward factor of

Case (ii) if all *l* clusters were unique in their formation.

For case (i) we obtain a straight forward factor of

$$\frac{N!}{(1!)^{m_1}(2!)^{m_2}\ldots\ldots} = \frac{N!}{\prod_i (l!)^{m_l}} \qquad \text{---------(22)}$$

Production of combinatorial factor (22) with 'the value of any one graph in set-up'

The corresponding correction factor being

$$\prod_l (1/m_l!) \qquad \text{-----------(24)}$$

A little reflection now shows that case(ii) is completely and correctly taken care of if we replace the product of the expression(23) and (24)

$$\prod_l (the\ sum\ of\ values\ of\ all\ possible\ l - clusters)^{m_l}/m_l!) \qquad \text{------(25)}$$

Equation (16) may be written as

$$\prod_{l=1}^{\infty}\{(b_l l!\, \lambda^{3(l-1)} V)^{m_l} \frac{1}{m_l!}\} \qquad \text{----------(26)}$$

Obtain the configuration integral

$$\mathrm{Z_n(V,T)} = \mathrm{N!}\, \lambda^{3N} \sum [\prod_{m_l}\{b_l \frac{V}{\lambda^3})^{m_l} \frac{1}{m_l!}\}] \qquad \text{------------(27)}$$

The partition function is written as

$$\mathrm{Z(z,V,T)} = \sum_{N=0}^{\infty} z^N Q_N(V,T) \qquad \text{----------(28)}$$

Move over to the grand partition function of the system,

Substituting for Q_n (V,T) from (29)

$$\mathrm{Z(z,V,T)} = \sum_{m1,m2,\ldots=0}^{\infty}[\prod_{l=1}^{\infty}\{(b_l z' \frac{V}{\lambda^3})^{m_l} \frac{1}{m_l!}\}]$$

$$= \prod_{l=1}^{\infty}[\sum_{ml=0}^{\infty}\{\left(b_l z' \frac{V}{\lambda^3}\right)^{m_l} \frac{1}{m_l!}\right\}$$

$$= \exp\, [\sum_{l=1}^{\infty}\{\left(b_l z' \frac{V}{\lambda^3}\right)\}] \qquad \text{----------(29)}$$

$$1/v \ln Z = \frac{1}{\lambda^3}\sum_{l=1}^{\infty}(b_l z')\}$$

$$\frac{P}{kT} = \lim_{v\to\infty}(\frac{1}{V}\ln Z)$$

$$= \frac{1}{\lambda^3}\sum_{l=1}^{\infty}(b_l z')\}$$

$$\frac{N}{V} = \lim_{v\to\infty}\left(\frac{z}{V}\frac{\partial \ln Z}{\partial z}\right)$$

$$= \frac{1}{\lambda^3}\sum_{l=1}^{\infty}(l b_l z')\} \qquad \text{--------(30)}$$

Equation (29) and (30) constitute the famous cluster expansion of the Mayer-Ursell formalism. Eliminating the fugacity parameter z among these equations, we obtain the equation of the state of the system.

5.2 Virial equation of state:

Since $a_1 \equiv 1$, the lowest order virial coefficient that need to consider here is a_2 which is given by

$$a_2 = - b_2 = \frac{2\pi}{\lambda^3}\int_0^{\infty}(1 - e^{-u(r)/kT})r^2\, dr \qquad \text{---------(1)}$$

u (r) being the potential energy of interparticle interaction

$$u(r) = 4\,\varepsilon\,[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}\ ] \qquad \text{-----------(2)}$$

For most practical purposes, the precise form of the repulsive part of the potential is not very important. It may as well be replaced by the crude approximation

$$u(r) = +\infty \text{ for } r < r_0 \qquad \text{-------------(3)}$$

$$u(r) = -u_0\,(r_0/r)^6 \quad (r \geq r_0) \qquad \text{-----------(4)}$$

The potential given by expression (3) and (4) my used if one is only interested in a qualitative assessment of the situation and not in a quantitative comparison between theory and experiment.

Substituting (3) and (4) into (1)

$$a_2 = \frac{2\pi}{\lambda^3}\,[\int_0^{\infty} r^2 dr + \int_{r_0}^{\infty}(1 - \exp\,[\,(\frac{u_0}{kT})(\frac{r_0}{r})^6]r^2\, dr \qquad \text{--------(5)}$$

$$a_2 \approx \frac{2\pi {r_0}^3}{3\lambda^3}\ (1 - \frac{u_0}{kT}) \qquad \text{-------------(6)}$$

Substituting (6) into the expansion we get first-order improvement on the ideal gas law,

$$p \approx \frac{kT}{v}\{1+\frac{2\pi {r_0}^3}{3\lambda^3}\ (1 - \frac{u_0}{kT}\} \qquad \text{------7(a)}$$

$$\approx \frac{kT}{v}\{1+\frac{B_2(T)}{v}\ \} \qquad \text{------7(b)}$$

Where $$B_2 = a_2\lambda^3 = \frac{2\pi {r_0}^3}{3}\ (1 - \frac{u_0}{kT}) \qquad \text{------(8)}$$

$$P + \frac{2\pi {r_0}^3 u_0}{3v^2} \approx \frac{kT}{v}\{1+\frac{2\pi {r_0}^3}{3v}\} \approx \quad \frac{kT}{v}\{1+\frac{2\pi {r_0}^3}{3v}\}^{-1}$$

Which readily leads to the van der waals equation of state

$$(P + \frac{a}{v^2})\quad (v\text{-}b) \cong kT \qquad \text{-----------(9)}$$

Where $a = \frac{2\pi {r_0}^3 u_0}{3}$, $\quad b = \frac{2\pi {r_0}^3}{3} = 4\ v_0$ ----------(10)

The parameter b in the van der waals equation of state is exactly four time the actual molecular volume

$$B_2{}' = 2\pi \int_0^\infty (1 - e^{-u\prime(r\prime)/T\prime})r'^2\, dr' \qquad \text{--------(11)}$$

$$U'(r') = [(\frac{1}{r\prime})^{12} - 2(\frac{1}{r\prime})^6\ ] \qquad \text{-----------(12)}$$

5.3 Ising model

The Ising model was invented to describe the physical system of a ferromagnet and especially its behavior at the critical point T_C. In order to describe the system, its thermodynamic quantities are derived from the partition function

$$z = \sum_s \exp(-\beta E(s)) \qquad \text{----------(1)}$$

Here, the sum is over all possible micro-states s, E(s) is the energy of the corresponding micro-state s and _β= 1/(k_BT). The energy of a micro-state E(s) is given in the model by the energy of a certain configuration σ of the magnetic moments

$$E(\sigma) = E_0(J, \sigma) + E_1(B, \sigma)$$

$$= E_0(J, \sigma) - B \sum_{i=1}^{N} \sigma_i \qquad \text{-------(2)}$$

Here, the first term represents the energy due to the molecular interaction with bond strength J. The second term corresponds to the energy of the system in an external applied magnetic field ~B parallel to the preferred axis whereas here and in the following the Bohr magneton is equal to unity. The free energy per site f in the thermodynamic limit can be calculated by

$$f(B,T) = - k_B T \lim_{N\to\infty} \frac{1}{N} \ln (Z(B)) \qquad \text{----------(3)}$$

The magnetization M of the system is given by the average of the magnetic moments σ_i per site:

$$M(B,T) = \frac{1}{N} \langle \sigma_1 + \cdots .. \sigma_N \rangle$$

$$= \frac{1}{N} \frac{1}{Z} \sum \langle \sigma_1 + \cdots .. \sigma_N \rangle \exp(-\beta E_0(J, \sigma)) - B \sum_{i=1}^{N} \sigma_i \qquad \text{----(4)}$$

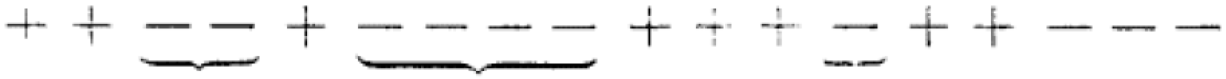
Using equation (3), the magnetization can be calculated as the derivative of the free energy f per site with respect to the magnetic field strength B:

$$M = - \frac{\partial}{\partial B} f(B,T) \qquad \text{----------(5)}$$

5.3 One-dimensional Ising model

Ising's original solution for the linear chain assumes a configuration of N elements with σ_1 positive and σ_2 negative σ_i-values such that

$$N = V_1 + V_2 \qquad \text{-------------(6)}$$



Further, the groups of connected lattice sites with σ_i= - 1 that are embedded by lattice sites with σ_i= +1 are counted by the variable s and shown in figure by the curved brackets. The variable δ is either 0 or 1, depending on whether the chain ends on the right with σ_i= +1 or σ_i= -1. All possibilities to arrange a fixed number of σ_1 positive and σ_2 negative lattice sites such that the chain always starts with a positive lattice site on the left are given by

$$\binom{\nu_1 - 1}{s} \cdot \binom{\nu_2 - 1}{s + \delta - 1}. \quad \text{------------(7)}$$

Here, the first binomial coefficient counts the possibilities to choose the s gaps between the v_1 positive lattice sites. The second binomial coefficient in equation (7) counts the possibilities to distribute the v_2 negative lattice sites on s + δ positions in the chain.

If the linear chain starts with a negative lattice site instead of a positive one on the left side, the number of possible configurations can be obtained from equation (7) by replacing v_1 with v_2 and vice versa:

$$\binom{\nu_2 - 1}{s} \cdot \binom{\nu_1 - 1}{s + \delta - 1}. \quad \text{-------------(8)}$$

The energy E_0 for a system of two neighboring magnetic moments in this approach is considered to be zero if the moments are aligned. If the magnetic moments of two neighboring lattice sites point in opposite direction, the energy of those two lattice sites is ". This way, for a configuration σ_i of certain s and δ, the energy becomes

$$E_0(\sigma_i) = (2s + \delta) \,.\, \varepsilon \quad \text{---------(9)}$$

The energy E_1 of the system corresponding to the magnetic energy of the system in an external applied magnetic field $\underset{B}{\rightarrow}$ is

$$E_1 = (v_2 - v_1) B \quad \text{--------(10)}$$

Combining equations (7), (8), (9) and (10), the partition function Z is obtained as

$$Z = \sum_{\nu_1,\nu_2,s,\delta} \left\{ \binom{\nu_1 - 1}{s}\binom{\nu_2 - 1}{s + \delta - 1} + \binom{\nu_2 - 1}{s}\binom{\nu_1 - 1}{s + \delta - 1} \cdot \cdot e^{-\beta((2s+\delta)\varepsilon + (\nu_2 - \nu_1)B)} \right\}. \quad \text{-------(11)}$$

In equation (11), the sum is over all possible values of the considered variables under the condition of (6). In order to solve this sum, the original approach of E. Ising considers following function

$$F(x) = \sum_{N=0}^{\infty} Z(N)\, x^N \quad \text{--------(12)}$$

where x is a variable without physical meaning and Z(N) is regarded as function only depending on the number of lattice sites N. The calculation of (12) gives

$$F(x) = \frac{2x[\cos\alpha - (1-\exp(-\beta\varepsilon))x]}{1-2\cos\alpha . x + (1-\exp(-2\beta\varepsilon))x^2} \qquad \text{----------(13)}$$

with $\alpha = \beta$B. By partial fraction decomposition, (13) is developed in orders of x and the coefficients corresponding to x^N are

$$Z(N) = c_1\left(\cos(\alpha) + \sqrt{\sin^2(\alpha) + e^{\frac{-2\varepsilon}{k_B T}}}\right)^N + c_2\left(\cos(\alpha) - \sqrt{\sin^2(\alpha) + e^{\frac{-2\varepsilon}{k_B T}}}\right)^N . \qquad \text{-----(14)}$$

The coefficients c_1 and c_2 do not enter into the solution since c_1 (2)= O(1) for all α and the second term $\left(\cos(\alpha) - \sqrt{\sin^2(\alpha) + e^{\frac{-2\varepsilon}{k_B T}}}\right) < 1$ vanishes for large N. In this way according to (5), the magnetization M of the one-dimensional ferromagnet is

$$M = \frac{N\sin\alpha}{\sqrt{\sin^2\alpha + e^{\frac{-2\varepsilon}{k_B T}}}} \qquad \text{------(15)}$$

For the external magnetic field $\vec{B}$ becoming zero, it is clear that $\alpha \to 0$ and the magnetization M therefore vanishes. This implies that the spontaneous magnetization M_0 is zero at any temperature and the Ising model therefore shows no phase transition in one dimension.

This result can also be understood qualitatively by following argument if the linear chain of molecules would be in an ordered state, i.e. all magnetic moments point in the same direction, at finite temperature T, there could always occur a flip of one of the magnetic moments due to thermal fluctuations.

A flip of one magnetic moment somewhere in the middle of the chain would allow the magnetic moments on one side or the other to entirely flip simultaneously since the Ising model considers only next neighbor interaction. Hence, in one dimension, a single flip of a magnetic moment can break the communication between one half of the chain and the other and therefore lead to a disordered state even at low (but finite) temperature T.

Using equations (3) and (5) yields the magnetization M as

$$M(H,T) = \frac{e^{k_1}\sinh(H)}{\sqrt{e^{2k_1}\sinh^2(H) + e^{-2k_1}}}$$

5.4Two-dimensional Ising model

The transfer matrix formalism yielded the partition function Z of the one-dimensional Ising model by finding the transfer matrix V and determining its largest eigenvalue. The transfer matrix V in one dimension is decomposed into the matrices V_1 and V_2:

$$V_1 = \begin{bmatrix} e^{K_1} & e^{-K_1} \\ e^{-K_1} & e^{K_1} \end{bmatrix}, \; V_2 = \begin{bmatrix} e^{H} & 0 \\ 0 & e^{-H} \end{bmatrix}.$$

--------------(1)

These matrices (1) can be expressed in terms of the Pauli matrices 1, τ^x, $\tau^y$and τ^z by

$V_1 = 1.\, e^{k1} + \tau^x\, e-^{k1}$ ----------(2)

And

$V_2 = 1.\, \cosh(H) + \tau^z \sinh(H)$ ------(3)

For all Pauli matrices and τ^i any number a

$\text{Exp}(a\tau^z) = 1 \cosh(a) + \tau^i \sinh(a)$ --------(4)

is valid. Using (4), V_1 and V_2 can be rewritten as

$V_1 = (2 \sinh(2k_1))^{1/2} \exp(k_1^{*}\tau^x)$ and

$V_2 = \exp(H\tau^z)$ -------(5)

The formulation of the decomposition matrices V_1 and V_2 of the one dimensional transfer matrix in terms of Pauli matrices τ^i allows for the generalization to the two dimensional lattice. For the Ising model in two dimensions, here, two different bond strengths J_1 and J_2 within the lattice are considered (see figure) which is the reason why the lattice is called a rectangular lattice instead of a square lattice ($J_1 = J_2$). In two dimensions, one has to sum over 2^M possible configurations of each row instead of the two possible orientations of the magnetic moment. Therefore, the decomposition matrices V_1 and V_2 (5) in two dimensions become

$V_1^{(2)} = (2 \sinh(2k_1))^{M/2} \exp(k_1^{*} \sum \tau_m{}^x)$ and --------(6)

$V_2 = \exp(H \sum \tau_m{}^x)$ -------(7)

where the $\tau_m{}^i$ are no longer the Pauli matrices, but the direct product

$\tau_m{}^x = 1 \times \ldots\ldots \times 1 \times \tau^i \times 1 \times \ldots\ldots \times 1$ --------(8)

with the Pauli matrix τ^i at the m-th position. In two dimensions not only the molecular interaction between the N rows but also the interaction between the M columns has to be taken into account. This is done by $V_3^{(2)}$

$$V_1^{(2)} = \exp (k_2 \sum \tau_m{}^z \ \tau_{m+1}{}^z) \qquad \text{-----(9)}$$

the matrices $V_1^{(2)}$, $V_2^{(2)}$ and $V_3^{(2)}$ are $2^M \times 2^M$ matrices that yield the transfer matrix $V^{(2)}$ for the two-dimensional Ising model as

$$V^{(2)} = (V_2^{(2)} V_3^{(2)})^{1/2} V_1^{(2)} (V_2^{(2)} V_3^{(2)})^{1/2}$$

The partition function is obtained immediately as

$$Z = \operatorname{tr} [V^{(2)}]^N \qquad \text{-----(10)}$$

Although the formulation of the partition function by the transfer matrix formalism is finished, the exact result still has to be calculated.

5.5 Brownian motion - Langevin’s theory

Consider the simplest case of a ‘free’ Brownian particle, surrounded by a fluid environment; the particles is assumed to be free in the sense that it is not acted upon by any other force except the one arising from the molecular bombardment.

The equation of motion of the particle will be

$$M \frac{dv}{dt} = Z(t) \qquad \text{----------(1)}$$

Where M mass of the particle, v(t) particle velocity, f(t) force acting upon the particle by virtue of the impacts from the fluid molecule.

$$M \frac{dv}{dt} = -\frac{v}{B} + F(t)$$

$$\overline{F(t)} = 0 \qquad \text{----------(2)}$$

Taking the ensemble average of (2) we obtain

$$M \frac{d}{dt} \langle v \rangle = -\frac{1}{B} \langle v \rangle \qquad \text{---------(3)}$$

Whence

$$\langle v(t) \rangle = v(0) \exp \left(-\frac{t}{\tau}\right) \qquad \text{--------(4)}$$

$$\tau = \text{MB}$$

The mean drift velocity of the particle decays, at a rate determined by the relaxation time τ to the ultimate value zero.

Dividing (2) by the mass of the particle, we obtain an equation for the instantaneous acceleration,

$$\frac{dv}{dt} = -\frac{v}{\tau} + F(t)$$

$$\overline{A(t)} = 0 \qquad \text{----------(5)}$$

The scalar product of(5) with the instantaneous position r of the particle and take the ensemble average of the product.

$$\frac{d^2}{dt^2}\langle r^2\rangle + \frac{1}{\tau}\frac{d}{dt}\langle r^2\rangle = 2\langle v^2\rangle \qquad \text{-------(6)}$$

V^2 is replaced by 3kT/M. the result is

$$\langle r^2\rangle = \frac{6kT\tau^2}{M}\{\frac{t}{\tau} - (1 - \exp(-\frac{t}{\tau}))\} \qquad \text{-----(7)}$$

First time derivative is vanish, we observe that t << τ

$$\langle r^2\rangle \approx \frac{3kTt^2}{M}$$

$$= \langle v^2\rangle \quad t^2 \qquad \text{-----------(8)}$$

$$\text{r} = \frac{v}{t} \qquad \text{---------(9)}$$

For t >> τ

$$\langle r^2\rangle \approx \frac{3kT\tau}{M} \text{ t} = (6\text{BkT})\text{t} \qquad \text{-------(10)}$$

Relationship between the coefficient of diffusion D and the mobility B

$$\text{D} = \text{BkT} \qquad \text{---------(11)}$$

If we consider a particle of chare e and mass m moving in a viscous fluid under the influence of an external electric field of intensity E, then the ‘coarse-grained ’ motion of the particle will be determined by the equation,

$$\text{M}\frac{d}{dt}\langle v\rangle = -\frac{1}{B}\langle v\rangle \quad + \text{eE} \qquad \text{-------(12)}$$

From equation (11)

$$D = \frac{kT}{e}\ \mu \qquad \text{---------(13)}$$

Replace the time variable t in equation (5) by u, multiply both sides of the equation by exp(u/ τ) rearrange and integrate over du between the limits u = 0, and u=t,

$$V(t) = v(0)e^{-t/\tau} + e^{-t/\tau}\int_0^t e^{u/\tau}\ A(u)du \qquad \text{--------(14)}$$

The average drift velocity is given by the first term from (14)

$$A(u) = 0$$

$$\langle v(t)\rangle = v(0)e^{-t/\tau} \qquad \text{----------(15)}$$

From equation (14)

$$\langle v^2(t)\rangle = v^2(0)e^{-\frac{2t}{\tau}} + 2e^{-\frac{2t}{\tau}}\left[v(0)\int_0^t e^{\frac{u}{\tau}}\ A(u)du\right] +$$

$$e^{-\frac{2t}{\tau}}\iint_0^t e^{\frac{u_1+u_2}{\tau}}\quad A(u_1)A(u_2)du_1du_2 \qquad \text{----------(16)}$$

I. In stationary ensemble the function k(u_1,u_2) depends only on the time interval (u_2 – u_1). Denoting this interval by the symbol s, we have

$$K(u_1, u_1 + s) = \langle A(u_1).A(u_1+s)\rangle = k(s) \qquad \text{-------(17)}$$

II. The quantity K(0) which is identically equal to the mean square value of the variable A at time u_1 must be positive definite.

$$K(0) = \text{constant} > 0 \qquad \text{----------(18)}$$

III. For any value of s, the magnitude of the function K(s) cannot exceed K(0).

$$|K(s)| \le K(0)\quad for\ all\ s \qquad \text{-----------(19)}$$

IV. The function K(s) is symmetric about the values s = 0.

$$K(-s) = K(s) = K\,|(s)|) \qquad \text{--------(20)}$$

V. As s become large in comparison with the characteristic time τ* the values A(u_1) and A (u_1+s) become uncorrelated

$$K(s) = \langle A(u_1).A(u_1+s)\rangle \to \langle A(u_1).A(u_1+s)\rangle = 0 \text{ ----(21)}$$

Double integral appear in equation (16)

$$I = \iint_0^t e^{\frac{u_1+u_2}{\tau}}\quad K(u_2 - u_1)du_1du_2 \qquad \text{------(22)}$$

Changing over to the variables

$$S = \frac{1}{2}(u_1 + u_2)$$

$$S = (u_2 - u_1) \qquad \text{---------(23)}$$

$$I = \int_0^{t/2} e^{2s/\tau}\, ds \int_{-2s}^{+2s} K(s)\, ds + \int_{t/2}^{t} e^{2s/\tau}\, ds \int_{-2(t-s)}^{+2(t-s)} K(s)\, ds \qquad \text{-----(24)}$$

$$I = C \int_0^t e^{2s/\tau}\, ds$$

$$= C\,\frac{\tau}{2}(e^{2t/\tau} - 1) \qquad \text{------(25)}$$

Here

$$C = \int_{-\infty}^{\infty} K(s) ds \qquad \text{--------(26)}$$

Substituting (25) into (16) we get

$$\langle v^2(t)\rangle = v^2(0)e^{-\frac{2t}{\tau}} + C\,\frac{\tau}{2}(e^{2t/\tau} - 1) \qquad \text{--------(27)}$$

t→ ∞ , $\langle v^2(t)\rangle$ must tend to equipartition value 3kT/M

$$C = 6kT/M\,\tau \qquad \text{----------(28)}$$

$$\langle v^2(t)\rangle = v^2(0) + \{\frac{3kT}{M} - v^2(0)\}(1-(e^{2t/\tau}) \qquad \text{-------(29)}$$

Substituting (29) into the right hand side of (6) we obtain the representative description of the manner in which the quantity $\langle r^2\rangle$ varies with t,

$$\frac{d^2}{dt^2}\langle r^2\rangle + \frac{1}{\tau}\,\frac{d}{dt}\langle r^2\rangle = 2\langle v^2(0)\rangle e^{2t/\tau} + \frac{6kT}{M}(1-e^{2t/\tau}) \qquad \text{------(30)}$$

With solution

$$\langle r^2\rangle = v^2(0)\tau^2\,(1-e^{2t/\tau})^2 - \frac{3kT}{M}\tau^2\,(1-e^{t/\tau})(3-e^{t/\tau}) + \frac{6kT}{M}\tau \qquad \text{---(31)}$$

The solution (31) satisfies the initial conditions that both $\langle r^2\rangle$ and its first time derivative vanishes at t=0.

5.7 The Fokker-Planck equation:

Consider the behavior of a dynamical variable, such as position r (t) or the velocity v(t) of a Brownian particle, from the point of view of fluctuations in the value of the variable.

The displacement x (t) of the given set of particles along the x-axis .

At any time t, let f (x,t) dx be the probability x and x+dx. The function f(x,t) must satisfy the normalization condition

$$\int_{-\infty}^{\infty} f(x,t)dx = 1 \qquad \text{---------(1)}$$

The master equations is

$$\frac{\partial f(x,t)}{\partial t} = \int_{-\infty}^{\infty} \{-f(x,t)W(x,x') + f(x',t)W(x',x)\}dx' \qquad \text{----(2)}$$

$$\frac{\partial f(x,t)}{\partial t} = \frac{f - f_0}{\tau} \qquad \text{--------(3)}$$

Where W(x,x') dx'δt denote the probability that in a short interval of time δt a particle having displacement x makes a 'transition' to having a displacement between x' and x'+dx'.

Which has proved to be very useful first approximation for studying problems related to transport phenomena. f_0 denotes the equilibrium distribution function, τ is the relaxation time that determines the rate at which the fluctuations in the system drive it to a state of equilibrium.

The transition probability function W(x,x') is sharply peaked around the value x'=x and falls rapidly to zero away from x. denoting interval (x'-x) by ξ may write,

$$W(x,x') \to W(x;\ \xi)$$

$$W(x',x) \to W(x'; -\xi) \qquad \text{-----------(4)}$$

Expand the right-hand side of (s as) Taylor series around ξ =0. Terms up to second order only,

$$\frac{\partial f(x,t)}{\partial t} = -\frac{\partial}{\partial x}\{\mu_1(x)f(x,t)\} + \frac{1}{2}\frac{\partial^2}{\partial x^2}\{\mu_2(x)f(x,t)\} \qquad \text{------(5)}$$

Where $\mu_1(x) = \int_{-\infty}^{\infty} \xi^2 \, W(x;\xi)$

$$= \frac{\langle \delta x \rangle}{\delta t} = \langle v_x \rangle \qquad \text{--------(6)}$$

$$\mu_2(x) = \int_{-\infty}^{\infty} \xi^2 \, W(x;\xi)$$

$$= \frac{\langle(\delta x)^2\rangle}{\delta t} \qquad \text{------ (7)}$$

Equation (5) is called Fokker – Planck equation which occupies a classic place in the field of Brownian motion and fluctuations.