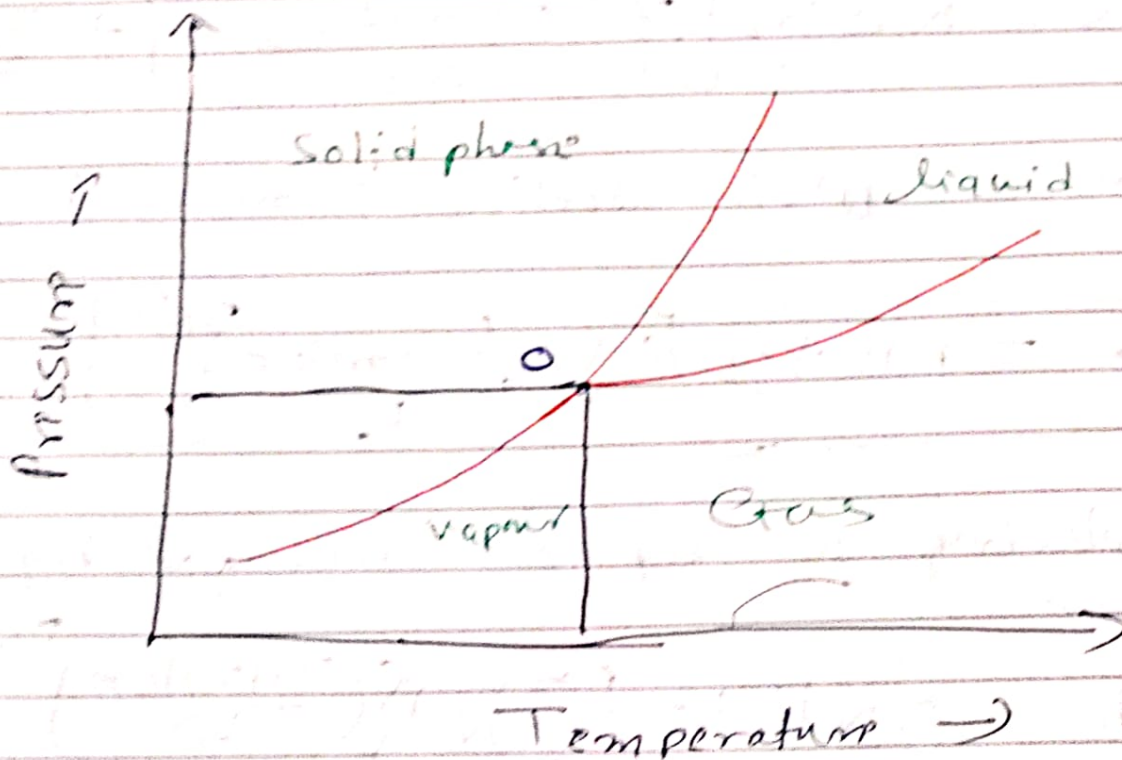


Q. What is phase transition. Differentiate first and second order phase transition.

~~Q. What is phase transition. Differentiate first and second order phase transition.~~

## Phase Transition

Phase transition is when a substance changes from a solid, liquid or gas state to a different state. Every element and substance can transition from one phase to another at a specific combination of temperature and pressure.



this fig point O called triple point

Triple point: - The pressure and temperature such that the solid, liquid and vapor states of the substance can exist simultaneously in equilibrium.

## First Order Phase Transitions

There are some examples of first order phase transition i.e. -

Ice  $\xrightarrow{\text{melting}}$  water

Water  $\xrightarrow{\text{freezing}}$  Ice

Water  $\xrightarrow{\text{boiling}}$  Steam

Steam  $\xrightarrow{\text{condensation}}$  Water

In all this process of changing the state some heat is either evolved (liberated) or absorbed (latent heat).

In First order phase transition the entropy and density (or volume) change. In First order phase transition the Gibbs free energy  $G$  remains constant with respect to temperature and pressure. It is continuous at transition point.

We can see it by Gibb's eqn

Gibb's eqn.

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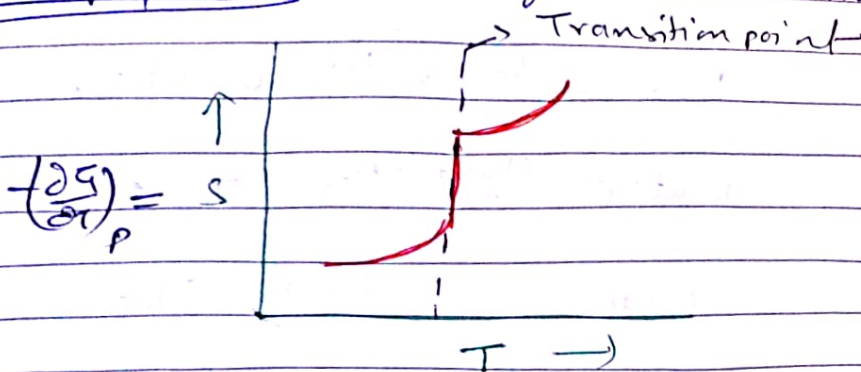
$$G = H - TS$$

we have:

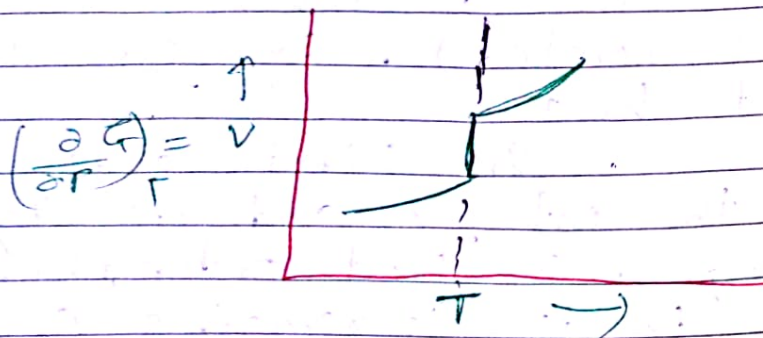
$$V = \left(\frac{\partial G}{\partial P}\right)_T$$

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

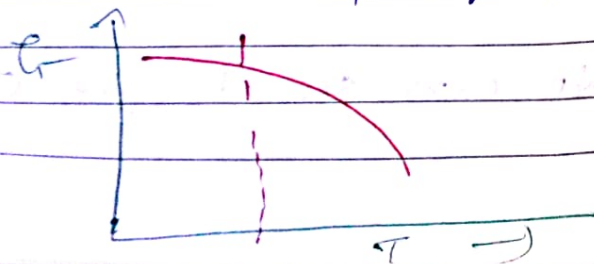
Entropy (S) - changes discontinuously



Volume (V) → changes discontinuously



Gibb's Free energy (G) → does not change discontinuously it means we find continuously graph.



# Second Order Phase Transition (Constant T & P)

.. These transition when during the transition no heat observed or released this transition called second order transition. This transition are smooth transition there is no time gap  
Example

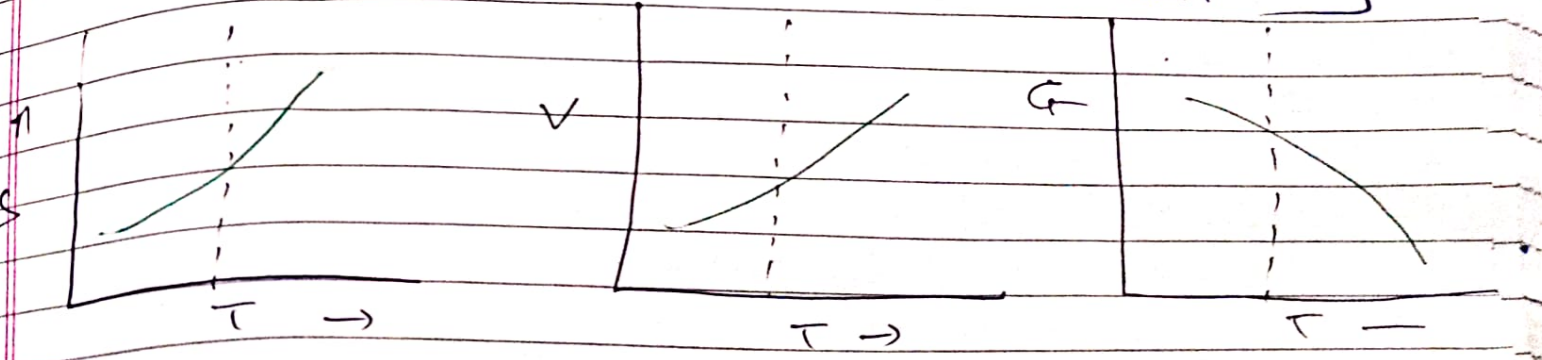
① The transformation of liquid Helium I  $\rightarrow$  to liquid Helium II  
 At a point (2.19 K)

In this transition no evolution or absorption of latent heat during change of states. & density of both liquid helium are same.

Ferromagnetic substance — Paramagnetic substance

(at curie temperature)

This is the main concept of Ising model



Entropy graph continuously

Volume continuously

Gibb's Continuously

heat capacity of substance approaches infinity. Hence the transition from non-ferromagnetic to ferromagnetic state is of second order. It is associated with some kind of change of symmetry of the lattice. For example in ferromagnetism, the symmetry of spins is involved.

It may be noted that the phase transitions of second kind in contrast to ordinary first order phase transition is continuous in the sense that the state of the body changes continuously. Although the symmetry changes discontinuously at the transition point, at each instant, the body belongs to one of the two phases. At a phase transition point of the kind, the bodies in two different states are in equilibrium while at a phase transition point of the second kind, the states of the two phases are the same.

### 13.6 Critical Exponent

It is common experience that when the temperature of a substance is changed, the phase of substance changes. For example water freezes at 273 K and boils at 373 K, both at a fixed pressure of 1 atmosphere. If pressure is changed, these phase changes occur at different temperatures. We can find the pressure and temperature where the substance can exist in either of two phases. For example at  $T = 373$  K and  $P = 1$  atmosphere, water can exist as a high density liquid or a low density vapour. By the addition of latent heat at constant temperature and pressure, liquid is converted into vapour. If temperature is increased, we may get a remarkable new region where liquid and vapour coexist and the density difference between liquid and vapour goes to zero, so that water and steam become indistinguishable. The region where liquid vapour coexistence curve in  $T - P$  diagram terminates is called the critical region. The critical phenomenon describe characteristic behaviour observed in this region surrounding the critical point at  $(T_C, P_C)$ . For water critical point occurs at  $T = 647$  K and  $P = 218$  atmosphere. The surface tension of water because zero at critical temperature.

Critical behaviour has been identified in many systems. In addition to the water-steam system, liquid gas systems generally show critical behaviour where the density difference between liquid and gas phase tends to zero. Other systems showing the critical behaviour are ferromagnets, ferroelectrics binary liquid mixtures, superfluids and super conductors. In many of these systems one phase is ordered and the other phase is disordered. It has become customary for convenience to introduce a parameter which vanishes at critical point and above it called **order parameter**. For example for a liquid-gas system, the order parameter is chosen as the density difference between the liquid and gas phases at given point  $T, P$  on the co-existence curve, which approaches zero according to

$$\rho_L - \rho_v = (T_C - T)^\beta, T < T_C \quad \dots(1)$$

where  $\beta$  is called the critical exponent.

Above the critical temperature the order parameter is zero. For a ferromagnetic system, the order parameter is the homogeneous magnetisation. The source of magnetisation is the spin related magnetism of electrons in the unfilled  $d$  and  $f$  shells of transition metals such as iron, cobalt and nickel. The interaction among electrons and the Pauli's exclusion principle keeps like spins separated. This results to lower energy for parallel spins. Below the critical temperature and in the absence of external magnetic field, the thermodynamically stable state is one in which a significant number of spins is aligned along a common direction, producing a net magnetisation. Above critical temperature the thermal agitations result no residual macroscopic magnetisation if external magnetic field  $H = 0$ . In the critical region above the critical point  $T = T_C, H = 0$ , the macroscopic magnetisation is either quite small or zero depending on whether  $T$  is below or above  $T_C$ . The common linkage between the behaviour of a liquid vapour critical system and a ferromagnetic critical system is the dominance of fluctuations in critical regions.

In addition to critical exponent  $\beta$ , there are several other exponents given below : The critical exponent  $\alpha$  gives a relation for specific heat in the vicinity of critical temperature.

$$c \sim | (T - T_C) |^{-\alpha} \quad \dots(2)$$

The critical exponent  $\gamma$  is related to the critical behaviour of generalised susceptibility.

$$\chi \sim | (T - T_C) |^{-\gamma} \quad \dots(3)$$

The critical exponent  $\delta$  occurs in following two relations :

(a) The relation between external magnetic field and magnetisation at critical temperature

$$H = M^\delta, T = T_C \quad \dots(4a)$$

(b) The relation between pressure and density at critical temperature

$$P - P_C \sim | (\rho - \rho_C) |^\delta, T = T_C \quad \dots(4b)$$

These critical exponents are connected by scaling relations to reduce their independent numbers e.g.,

$$\left. \begin{aligned} \alpha + 2\beta + \gamma &= 2 && \text{Rushbrooke scaling law} \\ \gamma &= \beta(\delta - 1) && \text{Widom scaling law} \end{aligned} \right\} \quad \dots(5)$$

These law were initially derived as inequalities and then were converted to equalities by scaling hypothesis. Several inequalities involving the critical exponents can be derived using thermodynamical stability considerations.

For example specific heat at constant magnetisation  $C_M$  and specific heat at constant magnetic field  $C_H$  for a magnetic system are related as

$$C_H - C_M = T \left( \frac{\partial H}{\partial M} \right)_T \left( \frac{\partial M}{\partial T} \right)_H^2 \quad \dots(6)$$

Thermodynamical stability requirements indicate that  $C_M$  is non-negative

$$\therefore C_H \geq T \left( \frac{\partial H}{\partial M} \right)_T \left( \frac{\partial M}{\partial T} \right)_H^2$$

But susceptibility  $\chi = \left( \frac{\partial M}{\partial H} \right)_T$

$$\therefore C_H \geq \frac{T}{\chi} \left( \frac{\partial M}{\partial T} \right)_H^2$$

For temperatures in the vicinity of critical temperature, we can make use of power law dependence of  $C_H$ ,  $\chi$  and  $M$  on  $(T_C - T)$ , to obtain the inequality

$$(T_C - T)^{-\alpha} \geq A (T_C - T)^{2\beta + \gamma - 2}$$

where  $A$  is a function independent of  $T_C - T$  and  $\alpha$  and  $\gamma$  refer to critical exponents for  $C_H$  and  $\chi$  for  $T < T_C$ .

This gives  $2\beta + \gamma - 2 \geq -\alpha$   
 resulting in Rush boooke inequality  $\alpha + 2\beta + \gamma \geq 2$

### 13.7 Ising Model

The Ising model was set up to investigate the behaviour of substances whose molecule posses a magnetic moment. The model assumes that the significant interaction exists between neighbouring molecules only.

Let there be  $N$  particles arranged in the lattice and also the particles possess spin with a magnetic moment. The spins may be oriented in any of the two possible orientations either up  $A$  or down  $B$ . Let their respective numbers be  $N_+$  and  $N_-$ , so that

$$N_+ + N_- = N$$

Let the interaction energy (which is assumed between nearest neighbours only) of a pair of two adjacent '+'s or of two adjacent '-'s be equal to  $\epsilon$ . The energy of an adjacent  $A$  and  $B$  is taken as zero. Then the energy levels of the system, assuming isotropic interaction, will be given by

$$E(\sigma_i) = -\epsilon \sum_{\langle i, j \rangle} \sigma_i \sigma_j - \mu_B H \sum_i \sigma_i \quad \dots(1)$$

where  $\sigma_i$  is (up)  $+1$  or (down)  $-1$  and  $\mu_B H$  is the interaction energy associated with external magnetic field  $H$ .

For  $\epsilon > 0$  the neighbouring spins tend to be parallel and ferromagnetism is possible. *For stable equilibrium the energy  $E$ , tends to be minimum. Hence the spontaneous configuration of least energy is the completely polarised (ordered) configuration in which all the Ising spins are oriented in the same direction.* The configuration results at absolute zero temperature (i.e.,  $T = 0$ ) when there is no thermal agitation at all. For  $\epsilon < 0$ , the neighbouring spins tend to be antiparallel and antiferromagnetism results.

In equation (1) no distinction is made between  $i$  and  $j$ . The sum over  $\langle i, j \rangle$  has  $\bar{z}(N/2)$  terms, where  $\bar{z}$  is the number of nearest neighbours of a site i.e., coordination number of the lattice and  $N$  is the number of spins.

The partition function, which is essential for determination of thermodynamical quantities, is given by

$$Z = \sum_{(\sigma_i)} e^{-\beta E_i(\sigma_i)} \quad \dots(2)$$

where  $\beta = (1/kT)$  and the sum is taken over  $2^N$  possible combinations of  $N$ -spins.

It is rather difficult to calculate equation (2) exactly. Several approximation methods have been developed. Here we shall give Bragg Williams method which is the simplest.

**Bragg-William's Approximation Method :** This approximation method assumes that the distribution of spins is random. Let  $N_+$  and  $N_-$  be the number of which  $\sigma_i$  is up (or  $+1$ ) and down (or  $-1$ ) respectively.

Then  $\frac{N_+}{N}$  and  $\frac{N_-}{N}$  represents the probability of finding a spin up ( $+1$ ) and down ( $-1$ ) on given lattice site.

Then equation (1) becomes

$$E = -\frac{1}{2} \bar{z} N \epsilon \left[ \left( \frac{N_+}{N} \right)^2 + \left( \frac{N_-}{N} \right)^2 - \frac{2N_+N_-}{N^2} \right] - \mu_B H (N_+ - N_-) \quad \dots(3)$$

where we have assumed  $N_+ > N_-$  in the last term.

The number  $\frac{N_+}{N}$  is a measure of the **long-range order**, as it requires no co-relation between nearest neighbours. It only requires that in the entire lattice only a fraction  $(N_+/N)$  of all the spins are up. If  $(N_+/N)$  is known in the neighbourhood of a given spin, then the same average value is likely to occur everywhere on the entire lattice.

If  $\mu_B$  is the magnetic moment associated with the spin, then the total magnetic moment is

$$M = \mu_B (N_+ - N_-) \quad \dots(4)$$

using

$$\left. \begin{aligned} N &= N_+ + N_- \\ \frac{N_+}{N} &= \frac{1}{2}(1+m), \quad \frac{N_-}{N} = \frac{1}{2}(1-m) \end{aligned} \right\} \dots(5)$$

where  $m = \frac{M}{N\mu_B}$

Then

$$E = -\frac{1}{2} \bar{z} \epsilon N m^2 - \mu_B N m H \dots(6)$$

Here  $m$  is called long-range order parameter,

$$m = \frac{N_+ - N_-}{N} = \frac{2N_+}{N} - 1, \quad -1 \leq m \leq 1$$

The order parameter  $m$  is chosen depending on the problem e.g. it may be magnetisation in a ferromagnetic system or fraction of superconducting electrons in a super conductor or amount of displacement in transitions where atoms are displaced from their positions, in symmetrical phase etc.

The number of arrangements of spins over the  $N$  sites is given by the number of ways of choosing  $N_+$  out of  $N$  i.e.,

$$\Omega_{BW} = \frac{N!}{N_+! (N - N_+)!} \dots(7)$$

From relation between entropy and probability

$$\begin{aligned} S &= k \log \Omega_{BW} \\ &= k \log \left\{ \frac{N!}{N_+! (N - N_+)!} \right\} \end{aligned}$$

As  $N_+ + N_- = N$  i.e.,  $N - N_+ = N_-$ , we have

$$\begin{aligned} S &= k \log_e \left\{ \frac{N!}{N_+! N_-!} \right\} \\ &= k (\log_e N! - \log_e N_+ - \log_e N_-) \end{aligned}$$

Using Stirling approximation  $\log N! = N \log N - N$  we get

$$\begin{aligned} S &= k [N \log_e N - N - N_+ \log_e N_+ + N_+ - N_- \log_e N_- + N_-] \\ &= k [(N_+ + N_-) \log_e N - N_+ \log_e N_+ - N_- \log_e N_-] \\ &= k [N_+ \log_e N + N_- \log_e N - N_+ \log_e N_+ - N_- \log_e N_-] \\ &= -k [N_+ (\log_e N_+ - \log_e N) + N_- (\log_e N_- - \log_e N)] \\ &= -k \left[ N_+ \log_e \frac{N_+}{N} + N_- \log_e \frac{N_-}{N} \right] \end{aligned}$$

i.e.,

$$\begin{aligned} S &= -Nk \left[ \frac{N_+}{N} \log_e \frac{N_+}{N} + \frac{N_-}{N} \log_e \frac{N_-}{N} \right] \\ &= -Nk \left[ \frac{1}{2}(1+m) \log \left( \frac{1+m}{2} \right) + \frac{1}{2}(1-m) \log \left( \frac{1-m}{2} \right) \right] \end{aligned}$$

Helmholtz free energy

$$F = E - TS$$



⇒

$$F = -\frac{1}{2} \bar{z} \epsilon N m^2 - \mu_B N m H - N k T - \log_e 2 \left[ + \frac{1}{2} (1+m) \log_e (1+m) + \frac{1}{2} (1-m) \log_e (1-m) \right]$$

The equilibrium value of  $m$  or  $(N_A - N_B)$  is determined by

$$\frac{\partial F}{\partial m} = 0 \text{ i.e.,}$$

$$-\bar{z} \epsilon N m - \mu_B N H - N k T \left[ \frac{1}{2} \log_e (1+m) + \frac{1}{2} - \frac{1}{2} \log_e (1+m) - \frac{1}{2} \right] = 0 \quad \dots(9)$$

or

$$\log_e \frac{1+m}{1-m} = 2 \frac{\bar{z} \epsilon m + \mu_B H}{k T}$$

$$= 2x \text{ (say) where } x = \frac{\bar{z} \epsilon m + \mu_B H}{k T}$$

It gives well known result of Weiss theory of ferromagnetism

$$m = \frac{M}{N \mu_B} = \frac{e^{2x} - 1}{e^{2x} + 1} = \tanh x \quad \dots(10)$$

For  $H = 0$ , we get an expression for spontaneous magnetic moment as

$$m_S = \tanh(x)_{H=0} = \tanh \frac{\bar{z} \epsilon m_S}{k T}$$

$$m_S = \tanh \frac{T_C m_S}{T}$$

where

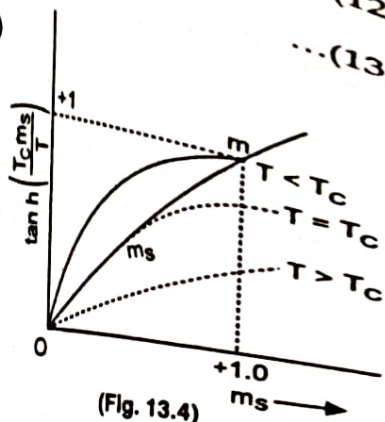
$$T_C = \frac{\bar{z} \epsilon}{k} \text{ is critical temperature} \quad \dots(12)$$

and

$$m_S = \frac{M_S}{H \mu_B} \quad \dots(13)$$

Equation (12) can be solved graphically to obtain  $m_S$  as a function of  $T$  in Bragg-William approximations (fig. 13.4). For this the L.H.S. and R.H.S. are plotted separately as a function of  $T$ . The intercepts of two curves gives the value of  $m$  at temperature of interest. It is clear that the solution is  $m_S = 0$  for  $\frac{T_C}{T} < 1$  and

$m_S = m, 0, -m$  for  $\frac{T_C}{T} > 1$ . But  $m = 0$  is unacceptable because it corresponds to maximum of function  $F$ , instead of minimum. Thus  $m_S = 0$  for  $T > T_C$  and  $m_S = \pm m$  for  $T < T_C$ . The solution  $m_S = \pm m$  occurs because for  $H = 0$ , there is no difference of spin up and down.



(Fig. 13.4)

### 13.8 One Dimensional Ising Model

The one dimensional ising model consists of a chain of  $N$ -spin, each spin interacting only with its two nearest neighbours. In the absence of any external magnetic field, the energy of the configuration specified by  $(\sigma_1, \sigma_2 \dots \sigma_N)$  is given by

$$E_1 = -\epsilon \sum_{i=1}^N \sigma_i \sigma_{i+1} \quad \dots(1)$$

It is convenient to arrange the chain of  $N$ -spins in the form of a ring (fig.), so that  
 $\sigma_{N+1} = \sigma_1$  ... (2)

the partition function is

$$Z = \sum_{\sigma_1 = \pm 1} \dots \sum_{\sigma_N = \pm 1} \exp \left[ \beta \epsilon \left( \sum_{i=1}^N \sigma_i \sigma_{i+1} \right) \right]$$

Now keeping in mind that  $\sigma\sigma'$  can be  $\pm 1$  and so using

$$\exp(c \sigma\sigma') = \begin{cases} e^c & (\sigma\sigma' = 1) \\ e^{-c} & (\sigma\sigma' = -1) \end{cases} \\ = \cosh c + \sigma\sigma' \sinh c$$



(Fig. 13.5)

we get

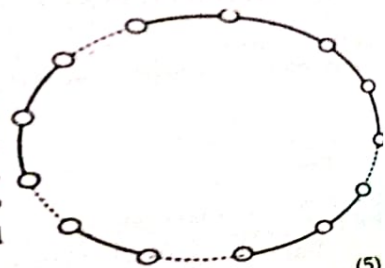
$$Z = \sum_{\sigma_1 = \pm 1} \dots \sum_{\sigma_N = \pm 1} \prod [\cosh \beta\epsilon + \sigma_i \sigma_{i+1} \sinh \beta\epsilon] \dots (3)$$

the expansion of products in (3) gives the sum of terms, each of which is the product of the form

$$(\cosh \beta\epsilon)^{N-s} (\sinh \beta\epsilon)^s (\sigma_i \sigma_{i+1} \dots \sigma_j \sigma_{j+1}) \dots (4)$$

these terms, may be displayed graphically by continuous and dotted links forming the ring. The continuous links correspond to factor  $\sigma\sigma' \sinh \beta\epsilon$  (say) and dotted link to factor  $\cosh \beta\epsilon$ .

At a site when a continuous and a dotted link join, then its spin occurs only once and the sum of two values  $\pm 1$  makes the product zero, while at the other site when two continuous links join its spin occurs squared and gives value  $+1$  because  $\sigma^2 = 1$ . A non-zero contribution occurs when the chain of thick links, if present, has no ends. Thus the only non-zero terms are the first terms  $(\cosh \beta\epsilon)^N$  and the last  $(\sinh \beta\epsilon)^N$ , so their, partition function



(Fig. 13.6)

for

$$Z = 2^N [(\cosh \beta\epsilon)^N + (\sinh \beta\epsilon)^N]$$

$$T \neq 0, \beta\epsilon = \frac{\epsilon}{kT} \neq \infty,$$

$\cosh \beta\epsilon > \sinh \beta\epsilon$ , so we have

$$Z = 2^N (\cosh \beta\epsilon)^N = \left( 2 \cosh \frac{\epsilon}{kT} \right)^N$$

$\therefore$  Helmholtz free energy for the system is

$$F = -kT \log Z = -kT \log_e \left( 2 \cosh \frac{\epsilon}{kT} \right)^N = -NkT \log_e \left( 2 \cosh \frac{\epsilon}{kT} \right)$$

The energy of system

$$E = -T^2 \frac{\partial}{\partial T} \left( \frac{F}{T} \right) = -T^2 \frac{\partial}{\partial T} \left[ -Nk \log_e \left( 2 \cosh \frac{\epsilon}{kT} \right) \right] \\ = NkT^2 \times \frac{1}{\left( 2 \cosh \frac{\epsilon}{kT} \right)} \times \left( 2 \cdot \sinh \frac{\epsilon}{kT} \right) \times \left( -\frac{\epsilon}{kT^2} \right) \\ = -N \epsilon \tanh \frac{\epsilon}{kT}$$

In this case there is no transition temperature.

So one dimensional Ising model can not be ferromagnetic

**13.9. Yang and Lee Theory of Phase Transitions**

The phase transition is basically the result of molecular interactions. Yang and Lee theory is a mathematical description of phase transition keeping in view that a phase transition is simply a singularity or discontinuity in the equation of state :

$$\left. \begin{aligned} P &= \frac{kT}{V} \log Z(z, V) \\ \text{and} \quad \frac{1}{v} &= \frac{1}{V} \frac{\partial}{\partial z} \log Z(z, V) \end{aligned} \right\} \dots(1)$$

where  $V$  is specific volume and  $Z$  is the grand partition function,  $z$  is the fugacity defined as  $z = e^{\mu/kT}$

Both  $P$  and  $V$  are analytic (or regular) functions of  $z$  in complex  $z$ -plane and possess no real roots of the equation  $Z(z, V) = 0$ . This means the zeros of the function  $Z(z, V)$  lie in complex  $z$ -plane, with no root on positive real axis.

When volume  $V$  increases, the number of singularities increases and their positions may shift in the complex  $Z$  plane. When  $V$  is continuously increased and in the limit  $V \rightarrow \infty$ , some of the roots may converge towards the positive real axis. In this limit the equation of state is given by

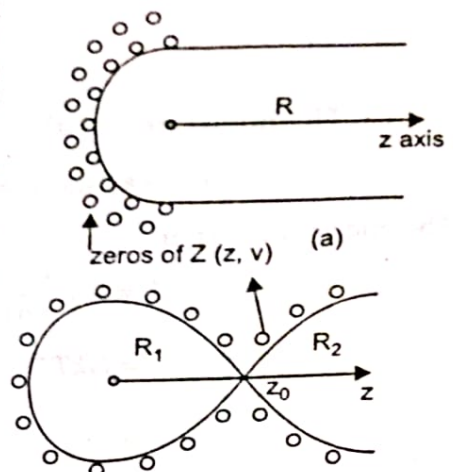
$$\left. \begin{aligned} P &\approx \lim_{V \rightarrow \infty} \left[ \frac{kT}{V} \log Z(z, V) \right] \\ \text{and} \quad \frac{1}{v} &= \lim_{V \rightarrow \infty} \left[ \frac{1}{V} \frac{\partial}{\partial z} \{\log(z, V)\} \right] \end{aligned} \right\} \dots(2)$$

Now it is possible to find the possible singularities in the equation of state; these singularities will represent the phase transitions.

Consider a region  $R$  in complex  $Z$ -plane, containing a segment of real positive  $Z$ -axis and no zero of  $Z(z, v)$  for all values of  $V$ . It is reasonable to think that when  $V \rightarrow \infty$ , the condition  $\frac{\partial p}{\partial V} \leq 0$  holds. In that case, the region under consideration represents single phase (i.e., no phase transition). If there exists a number of overlapping regions, each region will correspond to a phase of the system. Thus to study phase transitions, we have to investigate the behaviour of equation of state when  $z$  goes from one region to another. For such a study the two theorems stated below have extreme importance :

**Theorem I :**  $\lim_{V \rightarrow \infty} \frac{1}{V} \log Z(z, V)$  exists for all values of  $|z| > 0$ . This limit is independent of shape of volume  $V$  and is continuous non-decreasing function of  $z$ . It is assumed that in the limit  $V \rightarrow \infty$ , the surface area of volume considered, increases with increase of  $V$  but no faster than  $V^{2/3}$ .

**Theorem II :** If  $R$  is a region in the complex  $z$ -plane which contains a segment of positive real axis and contains no root of the equation  $Z(z, V) = 0$  for any volume  $V$ , then for all values of  $z$  in



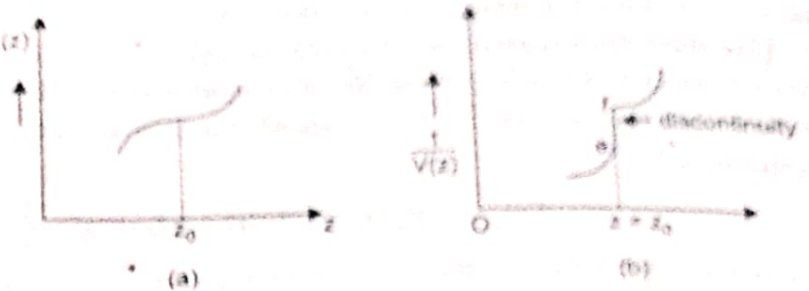
(b)  
(Fig. 13.7)

region  $R$ , the quantity  $\frac{1}{V} \log Z(z, V)$  converges uniformly when  $V \rightarrow \infty$ . This implies that the function  $Z(z, V)$  is an analytic function for all values of  $z$  in region  $R$ .

In view of these theorems we study the possible behaviour of equation of state.

Suppose region  $R$  contains entire positive  $z$ -axis with no zeros, then the system is in single phase. On the other hand if a zero of  $Z(z, V)$  approaches the point  $z_0$  on real positive  $z$ -axis as  $V \rightarrow \infty$ , then there will be two regions  $R_1$  and  $R_2$  in which the theorem II holds.

At  $z = z_0$ ,  $P(z)$  must be continuous, though its first derivative  $\frac{\partial P(z)}{\partial z}$  may be discontinuous.



(Fig. 13.8)

As an example consider the behaviour of system shown in fig. The system possess one phase for  $z < z_0$  and other phase for  $z > z_0$ .

At  $z = z_0$ ,  $\frac{1}{V(z)}$  is discontinuous, thus we obtain the *first order phase transition* because at  $z = z_0$ ,  $P(z)$  is continuous but  $\frac{dP(z)}{dz}$  is discontinuous.

On the other hand if first derivative  $\frac{dP(z)}{dz}$  is continuous but second derivative  $\frac{d^2P(z)}{dz^2}$  is discontinuous at  $z = z_0$ , then we have *second order phase transition*.

Thus an equation of state is capable of exhibiting the phenomenon of phase transition. The phase transition occurs if a root  $z$  of equation  $Z(z, V) = 0$  approaches a real positive  $z$ -axis in the limit  $V \rightarrow \infty$ . The nature of phase transition is governed by the analytic behaviour of  $P(z)$  near such a root of  $z$ .

### 13.10 Landau Theory of Phase Transitions

[Landau gave a systematic theory of phase transitions applicable to a large variety of systems undergoing such transitions. Consider systems at constant volume and temperature, so that their Helmholtz free energy  $F = U - \tau\sigma$  is minimum in equilibrium.] Now question arises  $F$  is minimum with respect to which variable. [For simplicity Landau supposed that the system can be described by a single order parameter  $x$  (say). The parameter may be the magnetisation of a ferromagnetic system, the dielectric polarisation in a ferroelectric system, the fraction of superconducting electrons in a superconductor etc. In thermal equilibrium the order parameter has a certain value  $x = x_0(\tau)$ .

[Landau assumed that  $x$  can be specified independently and the Landau free energy function is

$$F_L(x, \tau) = U(x, \tau) - \tau\sigma(x, \tau) \quad \dots(1)$$

where energy and entropy are taken when the parameter has specified value  $x$  which is not necessarily  $x_0$ . [The equilibrium value  $x_0(\tau)$  is that value of  $x$  at which the Landau function  $F_L$  is

minimum at a given temperature  $\tau$  ( $\tau = kT$ ). The actual Helmholtz free energy  $F(\tau)$  of that system at temperature  $\tau$  is equal to that minimum *i.e.*,

$$F(\tau) = F_L(x_0, \tau) \leq F_L(x, \tau) \text{ if } x \neq x_0 \quad \dots(2)$$

If Landau free energy function  $F_L$  at a given  $\tau$ , is plotted against  $x$ ; then  $F_L$  may have more than one minimum. The lowest of these determine the equilibrium state. In a first order transition the other minimum becomes the lowest minimum if temperature ( $\tau$ ) is increased.

[For most ferromagnetic and ferroelectric systems] the Landau function is an even function of  $x$ ; we restrict ourselves to such systems. [We also assume that the Landau function  $F_L(x, \tau)$  is sufficiently well behaved function of  $x$  and it can be expanded as a power series in  $x$ . For even function of  $x$ ,  $F_L$  may be expressed as]

$$F_L(x, \tau) = f_0(\tau) + \frac{1}{2}f_2(\tau)x^2 + \frac{1}{4}f_4(\tau)x^4 + \dots(3)$$

where  $f_0(\tau), f_2(\tau), f_4(\tau) \dots$  are expansion coefficients] the entire temperature dependence of  $F_L(x, \tau)$  is contained in these coefficients] The simplest example of phase transition occurs when  $f_2(\tau)$  changes sign at a temperature  $\tau_0$ , with  $f_4$  positive and higher terms negligible [For simplicity we assume  $f_2(\tau)$  linear in  $\tau$  over specified temperature range in the form

$$f_2(\tau) = (\tau - \tau_0)\alpha \quad \dots(4)$$

and take  $f_4$  as a constant in that temperature range. With these ideal limitations.

$$F_L(x, \tau) = f_0(\tau) + \frac{1}{2}\alpha(\tau - \tau_0)x^2 + \frac{1}{4}f_4x^4 \quad \dots(5)$$

The assumed equation (4) can not be accurate over a very wide temperature range and it certainly fails at low temperatures because such a linear dependence is not consistent with the third law of thermodynamics.

[For equilibrium value of  $x$ ,  $F_L$  should be minimum. For this we differentiate equation (5) with respect to  $x$  at given  $\tau$  and put equal to zero *i.e.*,

$$\left(\frac{dF_L}{dx}\right)_\tau = 0$$

$$\Rightarrow \left(\frac{\partial F_L}{\partial x}\right)_\tau = (\tau - \tau_0)\alpha x + f_4 x^3 = 0 \quad \dots(6)$$

This gives

$$x = 0 \text{ or } x^2 = (\tau_0 - \tau) \left(\frac{\alpha}{f_4}\right) \checkmark$$

With  $\alpha$  and  $f_4$  positive, the root  $x = 0$  corresponds to the minimum of the free energy function (5) at temperature above  $\tau_0$ ; at this position Helmholtz free energy is

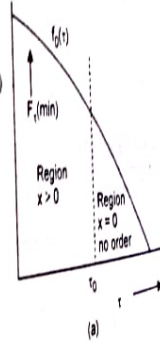
$$F(\tau) = f_0(\tau) \quad \dots(8)$$

The other root of  $x$  given by  $x^2 = \frac{(\tau_0 - \tau)\alpha}{f_4}$  corresponds to the minimum of the free energy function at temperatures below  $\tau_0$ ; at this position the Helmholtz free energy is given by

$$F(\tau) = f_0(\tau) - \left( \frac{\alpha^2}{4f_4} \right) (\tau - \tau_0)^2 \dots (9)$$

The temperature dependence of  $F(\tau)$  for an idealised phase transition of second order is shown in Fig. (a), while the variation of Landau free energy with  $x^2$  is shown in Fig. (b). From fig (b) it is clear that at a temperature below  $\tau_0$ , the equilibrium value of  $x$  gradually increases.

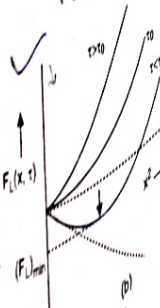
This model describes a phase transition in which the value of order parameter approaching zero continuously as the temperature is increased to  $\tau_0$ . The entropy  $\sigma = - \frac{\partial F}{\partial \tau}$  is continuous at  $\tau = \tau_0$ , so there is no latent heat at transition temperature  $\tau_0$ , such a transition is a second order transition



(Fig. 13.9 a)

**Landau Theory of first order Transition**

The transitions with a non-zero latent heat are called first order transitions. The liquid-gas transformation at constant pressure is a first order phase transition. The first order phase transitions are common in ferroelectric crystals and in metals. The Landau function describes a first order transition when the expansion coefficient  $f_4$  is negative and  $f_6$  is positive.



(Fig. 13.9 b)

$$\text{Let } F_L(x, \tau) = f_0(\tau) + \frac{1}{2} \alpha (\tau - \tau_0) x^2 - \frac{1}{4} |f_4(\tau)| x^4 + \frac{1}{6} f_6 x^6 + \dots (10)$$

The extremum of this function are given by  $\frac{\partial F_L}{\partial x} = 0$

⇒

This gives either  $x = 0$

or

⇒

$$\alpha (\tau - \tau_0) x - |f_4(\tau)| x^3 + f_6 x^5 = 0$$

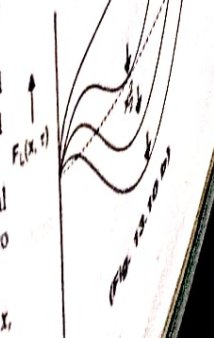
$$x^2 = \frac{|f_4(\tau)| \pm \sqrt{|f_4(\tau)|^2 - 4f_6 \alpha (\tau - \tau_0)}}{2f_6}$$

The plot of Landau function versus  $x^2$  for first order transition is shown in Fig.

At transition temperature  $\tau_0$ , the free energies will be equal for the phases for  $x = 0$  and for  $x$  given by 11 (b) (say  $x = x_2$ ).

The value of transition temperature  $\tau_c$  is not equal to  $\tau_0$  and the first order parameter  $x$  does not go to zero continuously at  $\tau_c$ .

For  $\tau$  below  $\tau_0$ , the minimum is at larger value of  $x$ , but when  $\tau > \tau_0$ , there is a discontinuous change in the position of minimum.



(Fig. 13.10 a)

These results differ from second order transition when  $x$  goes to zero continuously at  $\tau_0 = \tau_c$  moreover a first order transition may show hysteresis as in supercooling or supersaturation but there is no hysteresis effect in second order phase transition.

## EXERCISES

### SHORT ANSWER QUESTIONS

1. What do you mean by triple point ? What is the value of triple point of water ?
2. Is triple factor of a substance unique ? Explain.
3. What are the two factors taken into account to derive the Vanderwaal's equation ? Write Vanderwaal's equation of state.
4. What are the conditions to obtain critical point in Vanderwaal's equation of state ? Express thermodynamic coordinates at critical point in Vanderwaal's equation.
5. Give four characteristics of matter near critical point.
6. What do you mean by first order and second order phase transitions ? Give examples.
7. Write Ehrenfest's equations for phase transitions.
8. What are critical exponents ? Give Rush broove inequality regarding critical exponents.
9. What is Landau function ? What is its value at equilibrium ?
10. Plot curves for Landau function versus variable parameter  $x^2$  for first order transitions and state important characteristics.

### LONG ANSWER QUESTIONS

1. What do you mean by first order and second order phase transitions ? Give a clear distinction between them.
2. Derive Vanderwaal's equation of state and find the thermodynamic coordinates of critical point.
3. What do you mean by the triple point of a substance ? Show that the triple point of a substance is unique.
4. What do you mean by critical exponent ? Introduce various critical exponents known to you ? Are they quite independent ?
5. What are phase transitions of first and second kind? Discuss Ising model for phase transitions of second kind. (Meerut 2003)
6. What do you mean by cooperative phenomenon ? Explain Ising model ? Use Bragg-William approximation method to obtain expressions for entropy and free energy under this model. (Meerut 2006, 2001)
7. Give a brief account of one-dimensional Ising model.
8. What are phase transitions and critical indices ? How Yang and Lee theory may be used to explain phase transition. (Meerut 2005, 2002, 01)
9. Give Landau theory of phase transitions. (Meerut Univ. 2005)
10. Write short notes on :
  - (a) Phase transitions of three matter states (Meerut 2006)
  - (b) Ising model (Meerut 2001)
  - (c) Yang and Lee theory (Meerut 2003)
  - (d) Landau theory (Meerut 2001)

PHASE TRANSITIONS

**MULTIPLE CHOICE QUESTIONS**

Select the right choice

1. Triple point of a substance  
(a) is unique (b) has two values (c) has three values (d) does not exist
2. The correction term  $\frac{a}{V^2}$  in Vanderwall's equation is due to :  
(a) finite size of molecules (b) intermolecular forces (c) surface tension effect (d) all of above
3. The Vanderwaal's gas obey perfect gas equation :  
(a) always (b) at high pressure and low temperatures  
(c) at high pressure and high temperature (d) at low pressure and low temperature
4. Vanderwaal's equation when solved for pressure  $P$  has :  
(a) one root only (b) two roots only (c) three roots only (d) unique value
5. The critical temperature for Vanderwaal's is :  
(a)  $\frac{a}{Rb}$  (b)  $\frac{1}{9} \frac{a}{Rb}$  (c)  $\frac{1}{27} \frac{a}{Rb}$  (d)  $\frac{8}{27} \frac{a}{Rb}$
6. Conversion of boiling water at 1 atmosphere and  $100^\circ\text{C}$  in vapour is :  
(a) zero order phase transition (b) first order phase transition  
(c) second order phase transition (d) third order phase transition
7. Clausius Clapeyon's equation holds for :  
(a) first order phase transition (b) Second order phase transition  
(c) both (a) and (b) (d) neither (a) nor (b)
8. The density and entropy changes suddenly .  
(a) in first order phase transition (b) in second order phase transition  
(c) both in first order and second order phase transitions  
(d) Neither in first order nor in second order phase transitions
9. The first derivative of Giib's function is continuous in :  
(a) first order phase transition (b) second order phase transition  
(c) both in first order and second order phase transitions  
(d) neither in first order not in second order phase transition
10. The Landau function in specified temperature range may be expressed as  $F_L(x, \tau) =$   
(a)  $f_0(\tau) + \alpha(\tau - \tau_0)^2 x^2$  (b)  $f_0(\tau) + \alpha(\tau - \tau_0) x^4$   
(c)  $f_0(\tau) + \alpha(\tau - \tau_0) + \beta(\tau - \tau_0)^2 + \dots$  (d)  $f_0(\tau) + \frac{1}{2} \alpha(\tau - \tau_0)^2 + \frac{1}{4} f_4 x^4$
11. The Landau function for parameter  $x$  at given temperature usually has :  
(a) one root only (b) two roots (c) three roots (d) unique value
12. Landau curves for  $F_L(x, \tau)$  against  $x^2$  meet :  
(a) at  $x = 0$  only (b) at  $x \neq 0$  only (c) both (a) and (b) (d) neither (a) nor (b)

**ANSWERS**

- |        |         |         |         |        |        |        |        |
|--------|---------|---------|---------|--------|--------|--------|--------|
| 1. (a) | 2. (b)  | 3. (b)  | 4. (c)  | 5. (d) | 6. (b) | 7. (a) | 8. (a) |
| 9. (b) | 10. (d) | 11. (b) | 12. (a) |        |        |        |        |