Cooperative Phenomena
(Phase Transitions & Ising Model)

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- **Phase Transitions: Brief Introduction**
  - **First Order**
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- **Phase Transitions of the Second kind: Ising model**

- Generally, substances exist in three types of phases: solid, liquid and gas. Phase diagram of a pure substance is shown below.
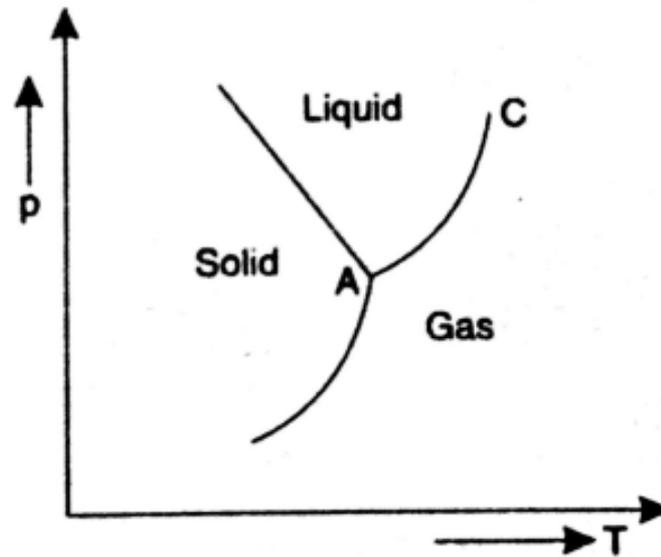
- The three lines separating the phases are called phase equilibrium lines and the common point where all the three phases co-exist in equilibrium with each other is known as *'Triple point'*.

- Consider a system whose phases are in equilibrium and a small change in external conditions results in a certain amount of the substance passing from one phase to another. This is known as phase transition.

- Since, Gibbs free energy is a function of T, P and number of particles (N). So, at constant T and P, Gibbs energy is proportional to the number of particles, i.e.

$$G(T,P,N) = Ng(T,P) \quad \ldots\ldots\ldots(i)$$

Where g(T, P) is Gibbs free energy per particle.

$$G(T, P, N) = \mu N \quad ....(ii)$$

Hence, $\quad \mu = g(T, P) \quad ....(iii)$

First order Phase Transition: Consider a vapor-liquid mixture in equilibrium at vapor pressure P and temperature T.

We know that, $\quad dg = VdP - SdT \quad ....(iv)$

Further, $\quad g = g(P, T)$

$$dg = \left(\frac{\partial g}{\partial P}\right)_T dP + \left(\frac{\partial g}{\partial T}\right)_P dT \quad ....(v)$$

from (iv) and (v), we get

$$\left(\frac{\partial g}{\partial P}\right)_T = V \quad and \quad \left(\frac{\partial g}{\partial T}\right)_P = -S \quad ....(vi)$$

If the derivatives $\left(\partial G/\partial P\right)_{T,N}$ and $\left(\partial G/\partial T\right)_{P,N}$ are discontinuous at the transition point, i.e. V and S have different values in two phases and the transition is called first order phase transition.

In **first order phase transition**-

i. The first order derivatives of Gibbs function change discontinuously.

ii. There is a change in volume, entropy and latent heat.

iii. Density changes discontinuously at transition temperature and pressure.
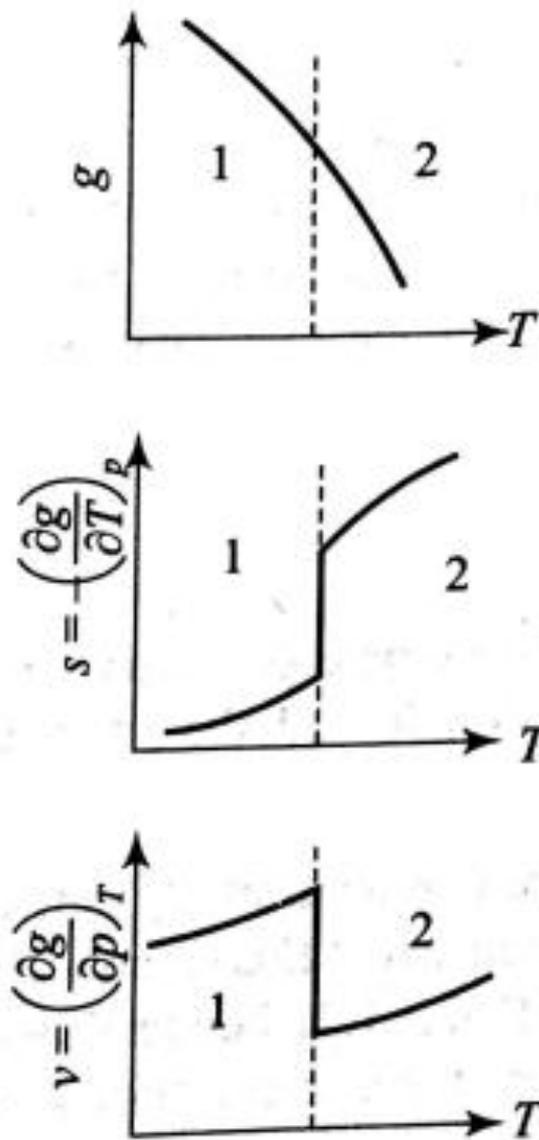
Figure: First Order Phase Transition, Temperature variation of (i) Gibbs function, (ii) Entropy and (iii) volume   [Garg, Bansal & Ghosh]

Second order Phase Transition:

As we found that in first order phase transition, $\left(\partial G/\partial P\right)_{T,N}$ $\left(\partial G/\partial T\right)_{P,N}$ are discontinuous at the transition point. If these derivatives are continuous *but higher order derivatives are discontinuous* at the transition point then the phase transition is known as second order phase transition.

In second order phase transition,

$$\left(\frac{\partial g_1}{\partial T}\right)_P = \left(\frac{\partial g_2}{\partial T}\right)_P \quad and \quad \left(\frac{\partial g_1}{\partial P}\right)_T = \left(\frac{\partial g_2}{\partial P}\right)_T$$

o e.g. transition of liquid He I into liquid He II

o Transition from a non-ferromagnetic state to a ferromagnetic state *(Ising model)*

o A phase transition of second kind in contrast to first order phase transition is continuous in the sense that the *state of the body changes continuously* but discontinuous in the sense that *symmetry of the body changes discontinuously*.

➢ In a phase transition of first kind, the bodies in two different states are in equilibrium, while in a phase transition of second kind, the states of two phases are the same. Second order phase transitions are also called *order-disorder transitions*.
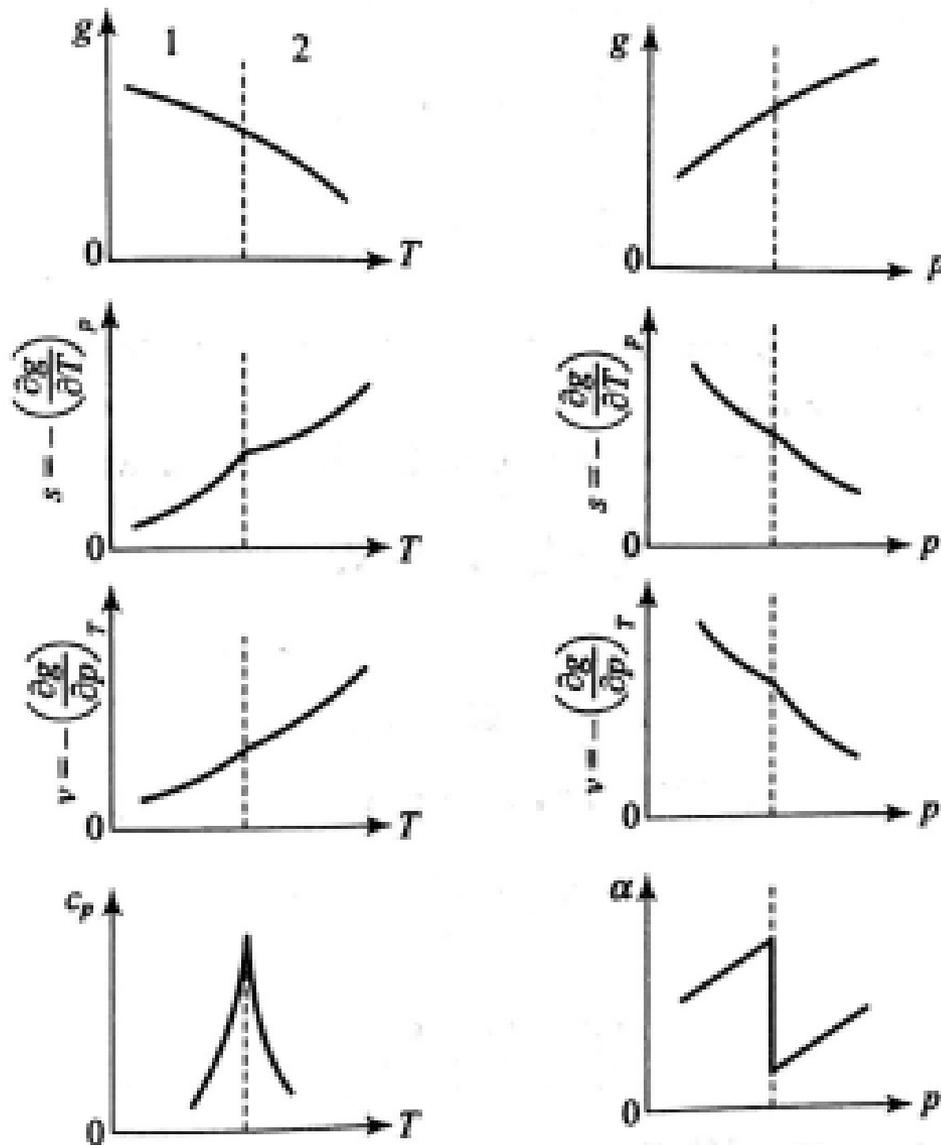
Figure: Second Order Phase Transition, Temperature variation of (i) Gibbs function, (ii) Entropy, (iii) volume and (iv) specific heat

[Garg, Bansal & Ghosh]

Critical Exponent

- It is a matter of common experience that when the temperature of a substance changes, phase of the substance also changes. But the basic problem is to study the behavior of a system in the neighborhood of the critical point.

- As freezing of water takes place at 273 K whereas boiling takes place at 373 K at a fixed pressure of 1 atm. When pressure is changed, phase change occurs at different temperatures.

- If we see the phase diagram of water, at T=373 K and P=1 atm., water exist as a high density liquid or low density vapor.

- But when latent heat is added at constant temperature and pressure, liquid is converted into vapor. If temperature is further increased then a region is observed where density difference between liquid and vapor goes to zero.

- In this region, water and steam become indistinguishable and where liquid-vapor co-existence curve terminates is called the critical region.

- So, besides water-steam system, there are many more systems which show critical behavior, e.g. liquid-gas system, ferromagnets, ferroelectrics, binary alloys, superfluids and superconductors etc.

- In most of the systems one phase is ordered while the other one is disordered.

- Therefore, it is customary to introduce a parameter which vanishes at critical point and above it which is known as order parameter. e.g., for *liquid-gas system, order parameter* is determined by the *density difference* between the liquid and gas phase.

- As T approaches critical temperature T_C, then density difference across the curve varies as –

$$(\rho_L - \rho_V) \sim (T_C - T)^{\beta}$$

where β is called **_critical exponent_**.

Different Critical Exponents

In addition to β, there are also some other critical exponents.

a) **Critical exponent, α:** It is associated with the behavior of specific heat in the vicinity of critical temperature as -

$$C \sim |T - T_c|^{-\alpha}$$

b) Critical exponent, γ: It is related to the critical behavior of generalized susceptibility as –

$$\chi \sim \left| T - T_c \right|^{-\gamma}$$

c) Critical exponent, δ:

i. Relation between external magnetic field and magnetization at critical temperature as –

$$H \sim M^{\delta}, \quad T = T_c$$

ii. Relation between pressure and density at critical temperature as -

$$(P - P_c) \sim \left| \rho - \rho_c \right|^{\delta}, \quad T = T_c$$

- **Scaling relations:**

To reduce the independent number of different exponents, scaling relations are used.

Rushbrooke scaling law: $\alpha+2\beta+\gamma=2$

Widom scaling law: $\gamma=\beta(\delta-1)$

Phase Transitions of the Second Kind: Ising Model

- Consider a ferromagnetic substance like nickel and iron. As $T<T_c$, some of the spins of atoms become spontaneously polarized in the same direction, giving rise to a macroscopic magnetic field.

- As $T>T_c$, then thermal energy makes some of the aligned spins to flip over. Thus, spins get randomly oriented and no net magnetic field is produced.

- The transition from non-ferromagnetic state to ferromagnetic state is called the *phase transition of second kind*. It is associated with some kind of *change in the symmetry of the lattice*. In ferromagnetism, symmetry of spins is involved.

- Ising model assumes the significant interaction between neighboring molecules. In Ising model, the system considered is an array of N-fixed points called lattice sites which form an n-dimensional periodic lattice.

- With each lattice site, a spin variable (s_i) is associated which is a number that is either +1 or -1. If s_i=+1 then it is said to be in *up direction* and if s_i=-1, it is said to have *down spin*.

- A given state of $<s_i>$ specifies a configuration of the whole system whose energy is given by –

$$E_I(s_i) = -\sum_{<i,j>} \varepsilon_{ij} s_i s_j - \mu H \sum_{i=1}^{N} s_i \quad ....(i)$$

where subscript I stands for Ising and the symbol $<i,j>$ represents the nearest-neighbour pair of spins. ε_{ij} is the interaction energy and μH is the interaction energy associated with external magnetic field.

- For an isotropic interaction, $\varepsilon_{ij}=\varepsilon$

$$E_I(s_i) = -\varepsilon \sum_{<i,j>} s_i s_j - \mu H \sum_{i=1}^{N} s_i \quad ....(ii)$$

- $\varepsilon>0$ corresponds to ferromagnetism and $\varepsilon<0$ to antiferromagnetism. In stable equilibrium, the energy E trends to be minimum.

- Therefore, for configuration of least energy, all the atomic spins are completely polarized/ordered in the same direction. Sum over $<i, j>$ constants $\gamma N/2$ terms where γ is the number of nearest neighbours of any given site.

- For the case of ε>0, partition function is given by –

$$Z = \sum_{s_1} \sum_{s_s} \ldots \ldots \sum_{s_N} e^{-\beta E_I(s_i)} \qquad \ldots \ldots (iii)$$

where s_i ranges independently over the values ± 1. There will be 2^N terms in the summation.

Bragg-William's Approximation: Standard Mean Field Approximation

- It was assumed that the distribution of spins is at random. Let on a given site, N_+ be the number of spins for which s_i is $+1$ and N_- be the number of spins for which s_i is -1.

N_+/N is the probability of finding a spins up (+1) and N_-/N is the probability of finding a spin down (-1) on a given lattice site.

from eq^n. (i),

$$E_I = -\frac{1}{2}\gamma N\varepsilon\left[\left(\frac{N_+}{N}\right)^2 + \left(\frac{N_-}{N}\right)^2 - \frac{2N_+N_-}{N^2}\right] - \mu H\left(N_+ - N_-\right) \quad ....(iv)$$

γ is the number of nearest neighbours of a site and $N = N_+ + N_-$ is the number of spins. Assumed $N_+ > N_-$ in the last term.

If magnetic moment associated with the spin is μ_B, then

$$M = \mu_B(N_+ - N_-) \quad ....(v)$$

$$M = \mu_B(N_+ - N + N_+)$$

$$\frac{M}{N\mu_B} = \frac{2N_+}{N} - 1 = m \quad \Rightarrow \frac{N_+}{N} = \frac{1}{2}(1+m) \quad ....(vi)$$

similarly, $\quad \Rightarrow \quad \dfrac{N_-}{N} = \dfrac{1}{2}(1-m) \quad ....(vii)$

$$\frac{2N_+ N_-}{N^2} = \frac{1}{2}(1+m)(1-m) \quad ....(viii)$$

from (vi) and (vii), $\quad N_+ - N_- = mN \quad ....(ix)$

putting the values in eqⁿ. (iv), we get

$$E_I = -\frac{1}{2}\gamma N \varepsilon m^2 - \mu H m N \quad ....(x)$$

Where *m* is a *long-range order parameter* ranging from -1≤m≤+1 represents magnetization in a ferromagnetic system.

Therefore, the number of arrangements of spins over the N sites will be given by the number of ways in which one can pick N_+ things out of N, i.e.

$$W_{BW} = {}^N C_{N_+} = \frac{N!}{N_+!(N-N_+)!} = \frac{N!}{N_+!N_-!}$$

Using Stirling's approx. and after solving above, we get

$$\ln W_{BW} = \ln N! - \ln N_+! - \ln N_-!$$

$$\ln W_{BW} = -\left[N_+ \ln \frac{N_+}{N} + N_- \ln \frac{N_-}{N} \right]$$

$$\ln W_{BW} = -N\left[\frac{1}{2}(1+m)\ln\frac{1}{2}(1+m) + \frac{1}{2}(1-m)\ln\frac{1}{2}(1-m) \right]$$

$$\ln W_{BW} = -N\left[\frac{1}{2}(1+m)\ln(1+m) + \frac{1}{2}(1-m)\ln(1-m) - \ln 2 \right] \quad ......(xi)$$

Now, entropy of the system becomes,

$$S = k \ln W_{BW}$$

$$S = -Nk\left[\frac{1}{2}(1+m)\ln(1+m) + \frac{1}{2}(1-m)\ln(1-m) - \ln 2 \right] \quad ......(xii)$$

Helmholtz free energy is given by – F=E-TS

So, from (x) and (xii), we get

$$F = -\frac{1}{2}\gamma N \varepsilon m^2 - \mu H m N$$

$$-NkT\left[\frac{1}{2}(1+m)\ln(1+m) + \frac{1}{2}(1-m)\ln(1-m) - \ln 2\right] \quad ......(xiii)$$

For equilibrium values of m, $\quad \dfrac{\partial F}{\partial m} = 0$

$$\gamma \varepsilon m + \mu H = kT \ln \frac{(1+m)}{(1-m)}$$

$$\ln \frac{(1+m)}{(1-m)} = \frac{\gamma \varepsilon m + \mu H}{kT} = 2x \quad (say)$$

$$\frac{(1+m)}{(1-m)} = e^{2x} \quad \Rightarrow \quad m = \frac{e^{2x}-1}{e^{2x}+1} = \tanh x \quad ....(xiv)$$

It is well known result of Weiss theory.

- For H=0, spontaneous magnetic moment is –

$$M_s = N\mu_B \tanh \frac{\gamma \varepsilon M_s}{N\mu_B kT} \quad ....(xv)$$

$$m_s = \tanh \frac{T_c m_s}{T} \quad where \quad m_s = \frac{M_s}{N\mu_B} \ \& \ T_c = \frac{\gamma \varepsilon}{k}$$

i. For $\dfrac{T_c}{T} < 1 \implies m_s = 0$

ii. For $\dfrac{T_c}{T} > 1 \implies m_s = m, 0, -m$

m_s=0 is not acceptable as it corresponds to maximum of Helmholtz free energy, instead of minimum. Thus, m_s=0 for T>T_c and m_s=±1 for T<T_c.
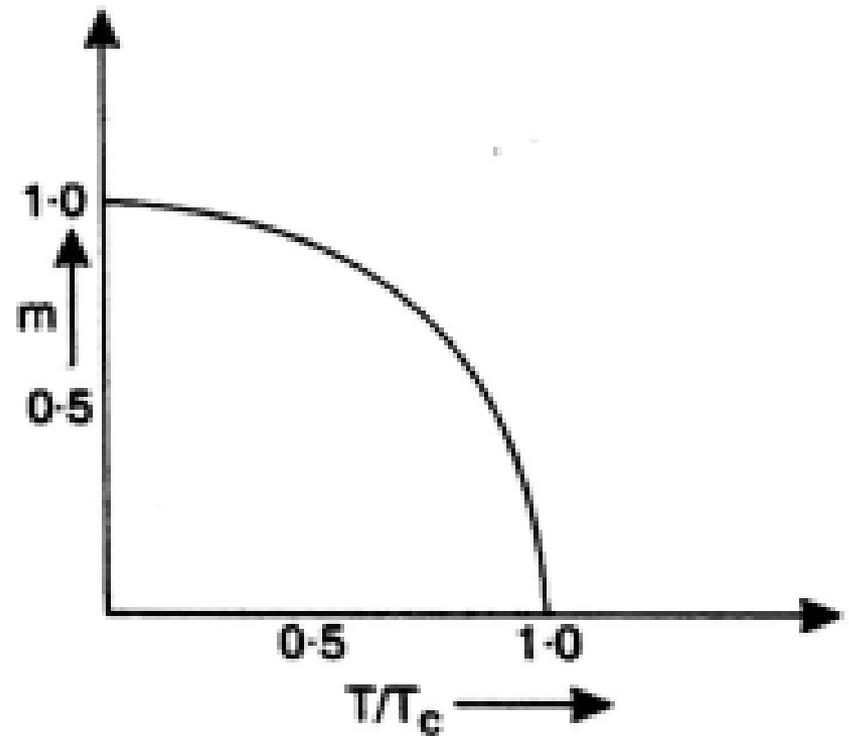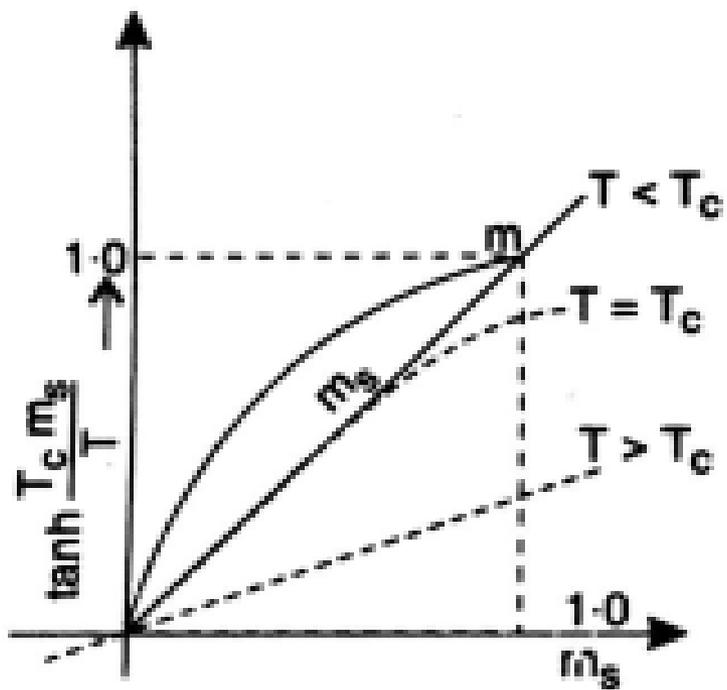
Figure: Plot of saturation magnetization vs temperature

[Gupta & Kumar]

Assignment

1. Solve the problem of One-dimensional Ising model.

2. Write a note on order-disorder in alloys.

References: Further Readings

1. *Elementary Statistical Mechanics* by Gupta & Kumar

2. *Statistical Mechanics* by B.K. Agarwal and M. Eisner

Thank You

For any questions/doubts/suggestions →write at E-mail: neelabh@mgcub.ac.in