

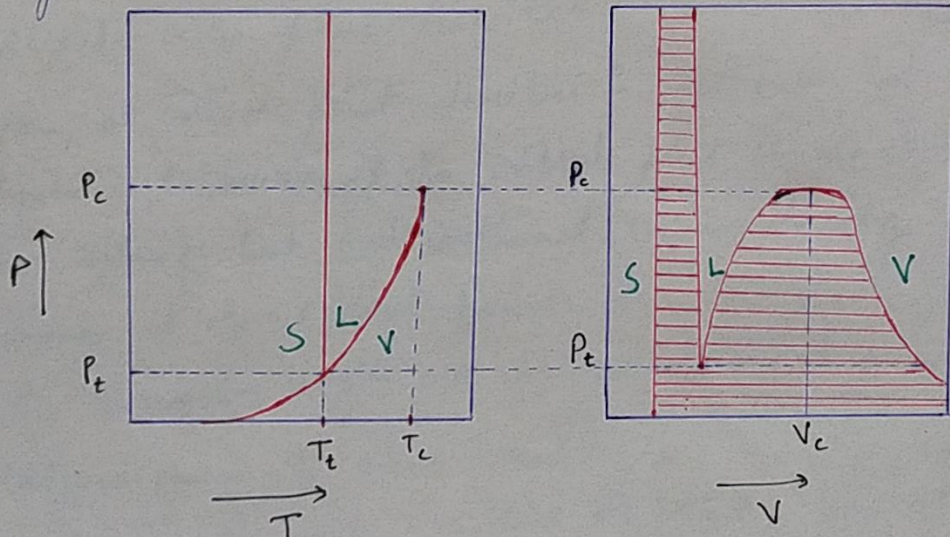
## PHASES, PHASE DIAGRAM & PHASE TRANSITIONS

Matter (materials) exist in variety of phases, depending on thermodynamic parameters such as temperature, pressure, magnetic field and so on.

Thermodynamic phases are regions in the phase diagram where the thermodynamic properties are analytic functions of the thermodynamic parameters.

The evolution of different phases of the material can be obtained by varying thermodynamic parameters can be displayed in the phase diagram.

Phase transitions are points, lines or surfaces in the phase diagram where the thermodynamic properties are nonanalytic.



(164)

The lines in the phase diagram connecting different phases are called phase co-existence lines or first order phase transition lines.

Thermodynamic densities are discontinuous across co-existence lines  $\left(\frac{V}{N}, \frac{S}{N}, \frac{U}{N}\right)$  or across first-order phase transition lines. The slope of the co-existence lines in the P-V phase diagram depend on the latent heat of the transition & the specific volumes of the co-existing phases.

Now, the L-V co-existence line ends at critical point & the discontinuity in density ends at the critical point. That means, all densities are continuous for T & P through the critical point. That is why critical points are called continuous transition or sometimes second-order phase transition.

Now, at critical point density is continuous but thermodynamic behaviour at the critical point is non-analytical. En. specific heat and isothermal compressibility both diverge at the critical point.

The correlation length also diverges at critical point.

Different kind of phase transitions  
Condensation of gases, melting of solids, ferromagnetism, anti-ferromagnetism, order-disorder transition, superconducting

transition, superfluid transition of He I  $\rightarrow$  He II

### Order of Phase Transition :-

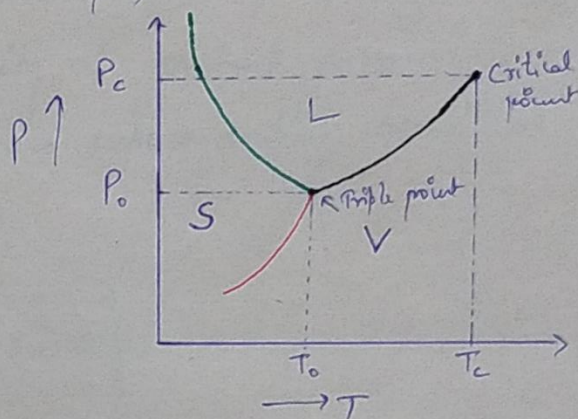
Let us understand it from the perspective of phase diagram of water (easy example)

Co-existence phase line

S and V  $\rightarrow$  sublimation curve (1<sup>st</sup> order)

S and L  $\rightarrow$  melting curve (1<sup>st</sup> order)

L & V  $\rightarrow$  evaporation curve (1<sup>st</sup> order)



The phase transition in the above P-T diagram are described by Gibbs free energy  $G(T, P, N)$ .

$G(T, P, N)$  changes continuously across the phase boundary when the transition is of first order. But entropy  $S$  & volume  $V$ , given by  $S = -\left(\frac{\partial G}{\partial T}\right)_P$ ,  $V = \left(\frac{\partial G}{\partial P}\right)_T$  are

discontinuous.

For second order phase transition,  $G$  is continuous. So is

$S$  &  $V$ .

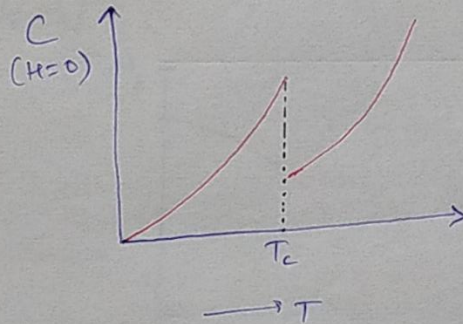
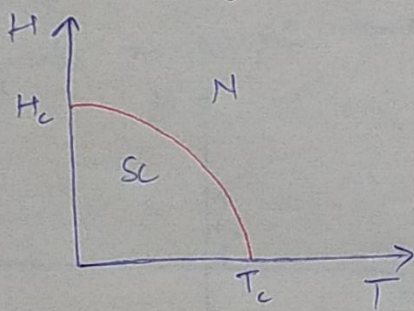
But discontinuities in second order derivatives of  $G$  occur.

$$\text{i.e. } C_p = T \left(\frac{\partial S}{\partial T}\right)_P = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_P$$

isothermal compressibility  $k_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial P^2} \right)_T$

thermal expansion coefficient  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right) = \frac{1}{V} \frac{\partial^2 G}{\partial T \partial P}$

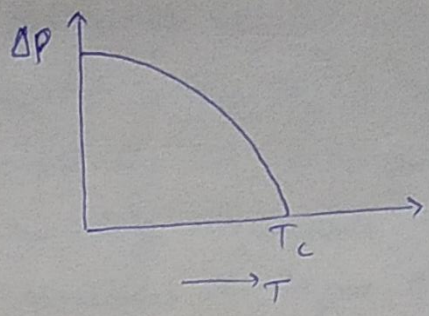
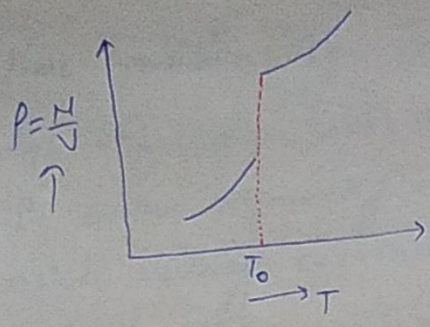
The discontinuity in the heat capacity is reflected as a jump in heat capacity at constant pressure. As we observe in normal  $\rightarrow$  superconducting transitions which is of 2<sup>nd</sup> order.



Density Jumps:

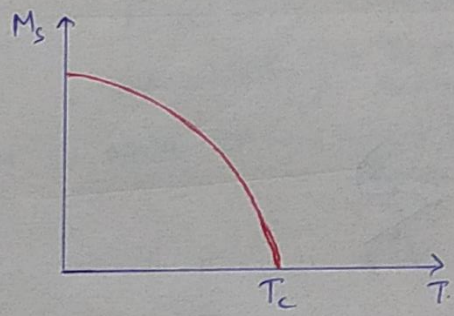
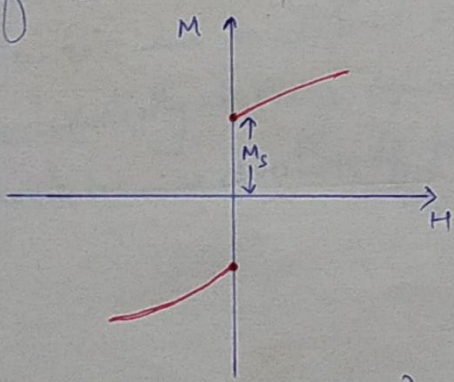
Consider a fluid system for which the volume  $V = \left( \frac{\partial G}{\partial P} \right)_T$  shows a finite discontinuity  $\Delta V$  at 1<sup>st</sup> order phase transition, such as the liquid-gas line below the critical point. The corresponding densities, particle density  $\rho = \frac{N}{V}$  is then likewise discontinuous.

The density jump  $\Delta \rho$  diminishes along the liquid-gas transition line, when the temperature is increased until it is vanishing at  $T_c$ . The transition becomes continuous at  $T = T_c$ .



Spontaneous Magnetic Ordering

The magnetization  $M$  of a magnetic compound is in part induced by an external magnetic field and in part due to the spontaneous ordering i.e. by the alignment of the microscopic moments.



$$M = -\left(\frac{\partial G}{\partial H}\right)_T$$

$$dG = -SdT - MdH$$

The magnetization  $M$  is discontinuous when spontaneous ordering is present. i.e. when transition is 1<sup>st</sup> order. By increasing the temperature ( $T \rightarrow T_c$ ), the jump  $2M_s$  decreases until spontaneous ordering disappears and the phase transition becomes second order at  $T = T_c$ .

Phase transition often involve the development of some type of order with an associated symmetry breaking. The broken symmetry is described by an order parameter which usually increases on moving deeper into the ordered phase, and which measures the degree of order as the phase transition proceeds. The order parameter is a physical observable, usually related to a first derivative of  $G$ .

- Broken Symmetry
- Magnetism → direction of magnetization
  - Water-ice → translational symmetry
  - Superconductivity → Gauge symmetry
  - Ferroelectric → direction of polarization

- Order Parameter
- Ferro-mag → Magnetization
  - Ferroelectricity → Polarization
  - Superconductivity → SC order parameter
  - Water-ice → translational distance

EXCHANGE INTERACTION:-

Exchange interactions are nothing but the electrostatic interaction, arising because charges of the same sign cost energy when they are close together and save energy when they are apart.

Origin :- Consider a simple system of two electrons with spatial coordinate  $r_1$  &  $r_2$ . With corresponding wave fun  $\psi_a(r_1)$  &  $\psi_b(r_2)$ . The wave function for the joint state can be represented by joint wave fun

$\psi_a(r_1) \psi_b(r_2)$ . However, this joint wave fun does not follow (obey) exchange symmetry i.e  $\psi_a(r_1) \psi_b(r_2)$  is not multiple same as  $\psi_a(r_2) \psi_b(r_1)$ .

Therefore, we will make use of symmetric or anti-symmetric product state.

$$\psi_S = \frac{1}{\sqrt{2}} [\psi_a(r_1) \psi_b(r_2) + \psi_a(r_2) \psi_b(r_1)] \chi_S \quad \text{--- (i)}$$

Spin part

$$\psi_T = \frac{1}{\sqrt{2}} [\psi_a(r_1) \psi_b(r_2) - \psi_a(r_2) \psi_b(r_1)] \chi_T \quad \text{--- (ii)}$$

Spatial part

For electron the overall wave fun must be antisymmetric, so if spatial part is symmetric, spin part is antisymmetric (singlet state) & " " " " anti " , spin " " symmetric (triplet state)

The energy of two possible state will be

$$E_S = \int \psi_S^* \hat{H} \psi_S \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad \text{--- (iii)}$$

$$E_T = \int \psi_T^* \hat{H} \psi_T \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad \text{--- (iv)}$$

where spin part ( $\chi_S, \chi_T$ ) are normalized.

So, the difference between two energy (iii) can be written as

$$E_S - E_T = 2 \int \psi_a^*(r_1) \psi_b^*(r_2) \hat{H} \psi_a(r_1) \psi_b(r_2) \, d\mathbf{r}_1 \, d\mathbf{r}_2 \quad \text{--- (v)}$$

The effective Hamiltonian of the system can be written as (50)

$$\hat{H} = \underbrace{\frac{1}{4}[E_S + 3E_T]}_{\text{constant term}} - \underbrace{(E_S - E_T) S_1 \cdot S_2}_{\text{Spin dependent term}} \quad \text{vi} \quad \text{where}$$

$$S_1 \cdot S_2 = -\frac{3}{4} \quad \uparrow\uparrow$$

$$S_1 \cdot S_2 = \frac{1}{4} \quad \uparrow\downarrow$$

Now the exchange constant,  $J$  is defined as

$$J = \frac{E_S - E_T}{2} = \int \psi_a^*(r_1) \psi_b^*(r_2) \hat{H} \psi_a(r_1) \psi_b(r_2) dr_1 dr_2 \quad \text{vii}$$

Now, the spin dependent term in the effective Hamiltonian can be written as.

$$\hat{H}^{\text{spin}} = -(E_S - E_T) S_1 \cdot S_2$$

$$\hat{H}^{\text{spin}} = -2J S_1 \cdot S_2 \quad \text{viii}$$

If  $J > 0$ , then  $E_S > E_T$  i.e. singlet state has higher energy than the triplet state. Thus triplet state is favoured.

If  $J < 0$ , then  $E_S < E_T$ , i.e. singlet state is favoured.

Interaction expressed in (viii) can be applied to neighbouring spins. So we can write

$$\hat{H} = - \sum_{\substack{n,n \\ (i,j)}} J_{ij} S_i \cdot S_j \quad \text{ix}$$

factor of 2 is omitted because the summation include each pair twice.

Eq. (ix) is called Heisenberg Model.

Heisenberg Model can also be written as.



$$\hat{H} = -J \sum_{i>j} J_{ij} S_i \cdot S_j \quad \text{--- (x)}$$

where  $i>j$  avoids 'double counting'. And the summation  $\sum_{i>j}$  is sum over nearest neighbours.

Here the spins  $S_i$  are 3-dimensional vectors. Also, the  $\sum$  can be taken over a lattice of 1, 2 or 3-dimensions.

The dimensionality of spins is designated with  $D$   
 & " " " lattice " " "  $d$ .

However, if we fix the direction of spins i.e. if we fix  $D$ , to be along z-direction only. Now, the spins are allowed to move up or down only. Then, the effective Hamiltonian become

$$\hat{H} = -J \sum_{ij} S_i^z S_j^z \quad \text{--- (xi)}$$

The above eq. represents Ising Model, here  $D=1$  (i.e.  $\pm z$  direction) and  $d$  could be 1, 2 or 3 dimension.

In order to investigate magnetic response of the system, if we subject system to external magnetic field along  $\pm z$  direction. Then Hamiltonian become.

$$\hat{H} = -J \sum_{ij} S_i^z S_j^z - \mu B \sum_i S_i^z \quad \text{--- (xii)}$$

Once our Hamiltonian is constructed, the Partition function <sup>(15)</sup> can be written as

$$Q_N(\beta, T) = \sum_{S_1^z} \sum_{S_2^z} \dots \sum_{S_N^z} \exp(-\beta \hat{H})$$

$$= \sum_{S_1^z} \sum_{S_2^z} \dots \sum_{S_N^z} \exp\left(\beta J \sum_{ij} S_i^z S_j^z + \beta \mu B \sum_i S_i^z\right)$$

(xiii)

Helmholtz free energy

$$A(\beta, T) = -kT \ln Q_N(\beta, T)$$

$$U(\beta, T) = -T^2 \frac{\partial}{\partial T} \left( \frac{A}{T} \right)$$

$$C(\beta, T) = \frac{\partial U}{\partial T}$$

$$\beta \bar{M}(\beta, T) = \mu \left( \overline{\sum_i S_i^z} \right) = \left( \frac{-\partial A}{\partial B} \right) = \frac{1}{\beta} \left( \frac{\partial \ln Q_N}{\partial B} \right)_T = \left( \frac{\partial A}{\partial B} \right)_T$$

(xiv)

### 1D ISING MODEL:-

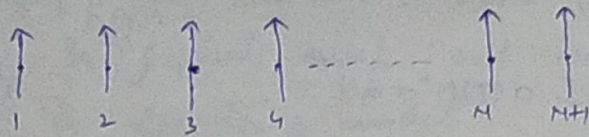
In 1D Ising model, we know  $D=1$  (spin has only one direction) &  $d=1$  (dimension of lattice).

So, consider a chain of  $N+1$  spins (i.e.  $N$  bonds b/w neighbouring spins). The Hamiltonian can be written as

$$H = -J \sum_{i=1}^N S_i^z S_{i+1}^z \quad \text{--- (A)}$$

if  $J > 0$ , so that the ground state is obtained by having all adjacent spins lined up ferromagnetically.

The energy of ground state for  $S_i^z = \frac{1}{2}$  will be  $-NJ/2$ .



Now, imagine creating a defect anywhere on this chain. To create a defect amount of energy required would be  $J$ . A defect means reversing the spin of one ising spin from favourable to unfavourable direction. However, creation of this single defect will have corresponding increase in entropy  $S = k \ln N$  ( $\because$  the defect could be created at any position).

Now, as  $N \rightarrow \infty$ ,  $S$  becomes infinite. The corresponding free energy  $F = E - TS$  will become  $-\infty$  as long as  $T$  is not zero. This means for  $T > 0$ , the defect can spontaneously form & we will never have long range order in 1D ising chain.

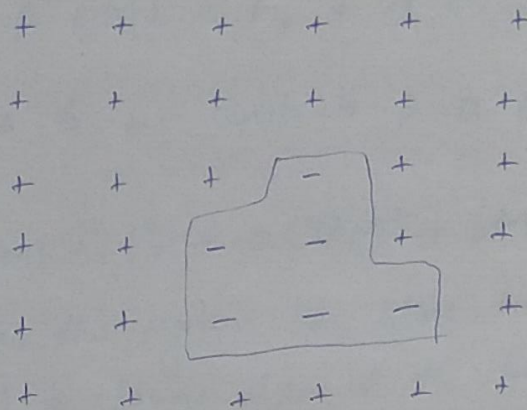
2D Ising Model :- In 2D Ising model, we consider

$D=1$  &  $d=2$ .

In 2D Ising model, establishment of magnetic order above below a transition temperature. i.e long range order is possible in it. This is because both the energy & entropy gain of creating a defect increases comparable to each other. This means entropy does not increase overwhelming by work to energy as it is in 1D Ising model.

which means defect creating creation leads to existence of the critical temp. and hence phase transition exist in 2D Ising model

(156)



The energy & entropy of the down spin (-) defect scale with the perimeter of the defect boundary.

## Landau Theory Of Phase Transition

As we know order parameter helps to capture phase transition. Its value is zero & above phase transition & finite below ( $< T_c$ ) phase transition. Landau emphasizes the importance of the order parameter & suggested that for a given system, its critical behaviour can be determined by expanding its free energy in powers of order-parameter.

To easily understand the theory, let us implement this theory in the case of ferromagnetic material. We know this material is ferromagnetic below  $T_c$  & paramagnetic above  $T_c$ . And the order parameter for para-ferro transition is magnetization  $M$ .

Now, the value of  $M$  for up or down spins will be <sup>(1sr)</sup> same, so we will expand free energy in even powers of  $M$  (order parameter).

i.e.  $F(M) = F_0 + aM^2 + bM^4 + \dots$  (A)

where  $F_0$  &  $b$  are constants &  $a$  is a fn of temp.  
i.e.  $a(T)$

$$F(M) = F_0 + a(T)M^2 + bM^4 \quad \text{--- (B)}$$

Now, we know this system has phase transition, so we allow  $a(T)$  to change sign at the transition temp.  $T_c$ .  
Just near the transition, we write  $a(T) = a_0(T - T_c)$   
where  $a_0$  is a positive constant.

Now, to find the ground state, we differentiate  $F$  w.r.t  $M$  & set to zero. (B)

$$\text{i.e. } \frac{\partial F}{\partial M} = 2a(T)M + 4bM^3 = 0$$

$$\Rightarrow M(2a(T) + 4bM^2) = 0$$

$$\text{i.e. } M=0 \quad \text{or} \quad 2a(T) + 4bM^2 = 0$$

L(C)

$$M^2 = \frac{-a(T)}{2b} = \frac{-a(T - T_c)}{2b}$$

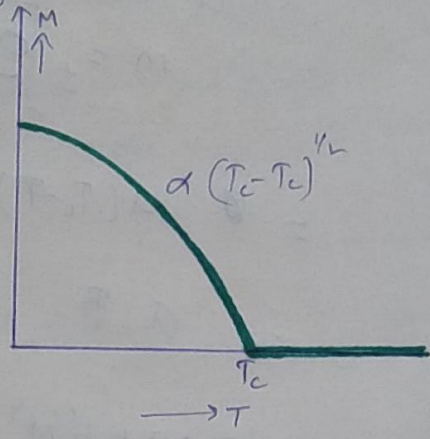
$$M^2 = \frac{a(T_c - T)}{2b}$$

$$M = \pm \sqrt{\frac{a(T_c - T)}{2b}} \quad \text{--- (D)}$$

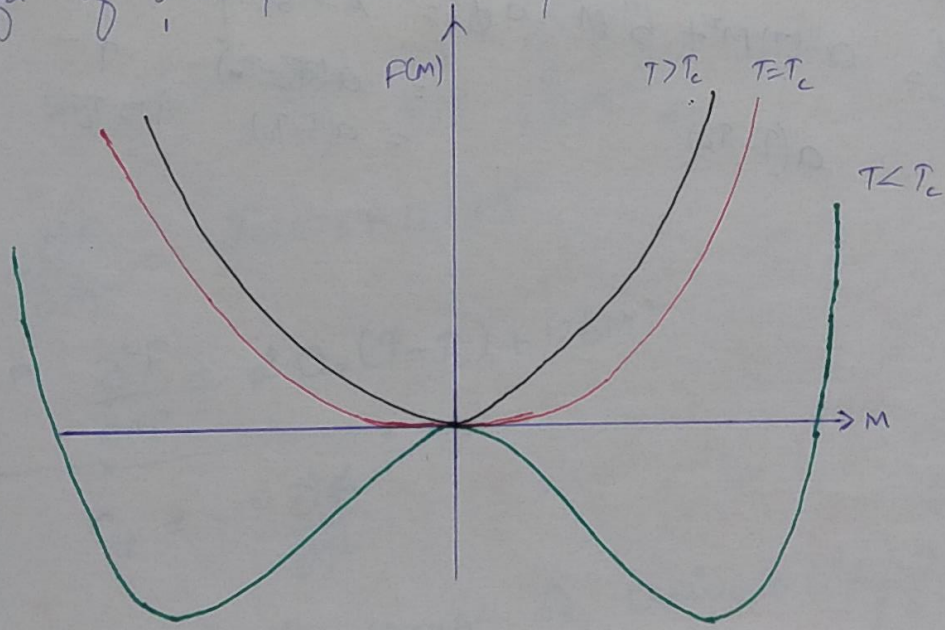
Now, the condition (C) will be true only when  $T > T_c$   
∴ order parameter has value zero <sup>at</sup> above  $T_c$ .

Condition (D) says that it will be valid only for  $T < T_c$ . i.e below  $T_c$  magnetization varies with temp as  $M \propto (T_c - T)^{1/2}$ .

Hence, the magnetization behaviour as a fun of temp is depicted as. we we look closely,  $M \rightarrow 0$  at  $T \rightarrow T_c$



The behaviour of free energy as a fun of order parameter is depicted as below



Now, we can explain behaviour of susceptibility & heat capacity (157)

we know  $\chi = \frac{\partial M}{\partial H}$  or  $\chi^{-1} = \frac{\partial H}{\partial M}$  where  $H$  is applied magnetic field

If  $H$  is the applied magnetic field, to include its effect into Landau theory, we can write

$$F = F_0 + a(T)M^2 + bM^4 - HM$$

Now  $\frac{\partial F}{\partial M} = 0$

we get  $\frac{\partial a(T)M + 4bM^3 - H}{\partial M} = 0$

$$\left(\frac{\partial F}{\partial M}\right)_{H=0} - H = 0$$

we can write  $\chi^{-1} = \frac{\partial H}{\partial M} = \left(\frac{\partial^2 F}{\partial M^2}\right)_{H=0}$

$$\frac{\partial^2 F}{\partial M^2} = 2a(T) + 12bM^2$$

$$\text{or } \frac{\partial^2 F}{\partial M^2} = 2a_0(T - T_c) + 12bM^2$$

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||ly  $C_p = -T \frac{\partial^2 \phi}{\partial T^2}$

Q What is the concept of universality?