

Statistical Physics II – Soumyabrata Saha

Scaling Laws :-

Scale invariant functions do not change their overall properties when the argument is increased or decreased by an arbitrary factor.

In general, scale invariant functions are defined by

$$f(bx) \propto f(x)$$

The proportionality constant is some function of b and thus, we have

$$f(bx) = c(b)f(x)$$

Taking the natural logarithm, we get

$$\ln[f(bx)] = \ln[c(b)] + \ln[f(x)]$$

Let us define, $g(\ln x) = f(x)$. Thus, we get

$$\begin{aligned}\ln\{g[\ln(bx)]\} &= \ln[c(b)] + \ln[g(\ln x)] \\ \Rightarrow \ln[g(\ln x + \ln b)] - \ln[g(\ln x)] &= \ln[c(b)] \\ \Rightarrow \frac{\ln[g(\ln x + \ln b)] - \ln[g(\ln x)]}{\ln b} &= \frac{\ln[c(b)]}{\ln b}\end{aligned}$$

Taking the R.H.S. as k which is constant independent of x , we can write the above as

$$\frac{d[\ln g(\ln x)]}{d(\ln x)} = k$$

Integrating and taking $\ln a$ as the constant of integration, we get

$$\begin{aligned}\ln g(\ln x) &= k \ln x + \ln a = \ln ax^k \\ \Rightarrow \ln f(x) &= \ln ax^k \\ \Rightarrow f(x) &= ax^k \\ \therefore f(x) &\sim x^k\end{aligned}$$

The scale invariant function is a monomial of degree k .

For an arbitrary scale factor b , we have

$$\begin{aligned}f(bx) &= a(bx)^k = b^k ax^k \\ \Rightarrow f(bx) &= b^k f(x) \\ \therefore f(bx) &\sim x^k\end{aligned}$$

Let $f(1) = c$ be known. Then, we have for instance

$$f\left(\frac{1}{2}\right) = \left(\frac{1}{2}\right)^k c$$

$$f(\sqrt{2}) = (\sqrt{2})^k c$$

$$f(2) = 2^k c$$

$$f(2^2) = (2^2)^k c$$

Thus, if $f(x)$ known at $x = 1$, it can be calculated for other values of x .

If the value of a scale invariant function is known at a particular point, then the values of the function is known at all other points.

Case I :-

We can have scale invariant functions as a limiting case from a more general functional form.

Let us take a function of the form,

$$f(x) = Ax^k + Bx^{k+k_1} + Cx^{k+k_2} + Dx^{k+k_3} + \dots$$

Here, $0 < k_1 < k_2 < k_3 < \dots$

For $x \rightarrow 0$, we have

$$f(x) \approx Ax^k$$

$$\therefore f(x) \sim x^k$$

The function becomes scale invariant when x is very small.

The scale invariance in physical phenomena is given by power laws.

Case II :-

We can also have scale invariant functions where we get a scale dependent shift after the argument is scaled by a factor.

Let us take a function of the form of

$$f(x) = cx^2 + dx = c \left(x^2 + 2 \cdot x \cdot \frac{d}{2c} + \frac{d^2}{4c^2} \right) - \frac{d^2}{4c}$$

$$\Rightarrow f(x) = c \left(x + \frac{d}{2c} \right)^2 - \frac{d^2}{4c}$$

Taking $X = x + d/2c$, we get

$$f(X) = cX^2 - \frac{d^2}{4c}$$

Scaling the variable X to bX , we have

$$f(bX) = c(bX)^2 - \frac{d^2}{4c} = b^2 cX^2 - \frac{d^2}{4c} = b^2 \left(cX^2 - \frac{d^2}{4c} \right) + b^2 \cdot \frac{d^2}{4c} - \frac{d^2}{4c}$$

$$\Rightarrow f(bX) = b^2 f(X) + (b^2 - 1) \frac{d^2}{4c}$$

Thus, $f(X)$ is scale invariant with scaling exponent 2 and a scale dependent shift which is equal to $(b^2 - 1) d^2 / 4c$.

In other words, $f(x)$ is scale invariant after finding the suitable scaling variable equal to $X = x + d/2c$ and allowing for a scale dependent shift of f .

We can now write, for $f(x) = \ln x$

$$f(bx) = \ln(bx) = \ln x + \ln b$$

$$\Rightarrow f(bx) = f(x) + \ln b$$

This shows that the log functions are scale – invariant with an exponent equal to 0 and a scale dependent shift equal to $\ln b$.

$$\lim_{k \rightarrow 0} \frac{x^k - 1}{k} = \lim_{k \rightarrow 0} \frac{x^k \cdot \ln x - 0}{1} = \left(\lim_{k \rightarrow 0} x^k \right) \ln x$$

$$\Rightarrow \lim_{k \rightarrow 0} \frac{x^k - 1}{k} = \ln x$$

The above result shows that natural logarithms are a special case of the power law functions with the exponent being equal to 0.

Scale invariant power laws – Example I :-

From Kepler's law, the orbital time period is related to radius of the circular orbit as

$$T^2 \propto R^3$$

$$\Rightarrow T \sim R^{3/2}$$

This result comes because of the inverse square law from Newton's law of gravitation.

Scale invariant power laws – Example II :-

Phase velocity of wave = c , Acceleration due to gravity = g , Depth of water = h , Wavelength = λ , and Density of water = ρ

Using dimensional analysis, we get

$$c = g^m \lambda^n h^p \rho^q$$

$$\Rightarrow [LT^{-1}] = [LT^{-2}]^m [L]^n [L]^p [ML^{-3}]^q = [L^m T^{-2m}] [L^n] [L^p] [M^q L^{-3q}]$$

$$\Rightarrow [M^0 L^1 T^{-1}] = [M^q L^{m+n+p-3q} T^{-2m}]$$

Comparing the exponents, we have

$$q = 0$$

$$-2m = -1 \Rightarrow m = \frac{1}{2}$$

$$m + n + p - 3q = 1 \Rightarrow n + p = \frac{1}{2} \Rightarrow p = \frac{1}{2} - n$$

Taking $n \equiv k$, we get

$$c = g^{1/2} \cdot \lambda^k \cdot h^{1/2-k} \cdot f\left(\frac{h}{\lambda}\right)$$

Here, $f\left(\frac{h}{\lambda}\right)$ is a dimensionless quantity.

No other functional form can be written using g , h , λ and ρ , that is dimensionless.

In the large wavelength limit i.e. $\frac{h}{\lambda} \rightarrow 0$, c must be independent of λ .

Thus, we must have for $x \rightarrow 0$

$$f(x) \sim x^k$$

$$\Rightarrow c = g^{1/2} \cdot \lambda^k \cdot h^{1/2-k} \cdot \left(\frac{h}{\lambda}\right)^k \cdot f(0) = g^{1/2} \cdot h^{1/2} \cdot f(0)$$

$$\Rightarrow c \sim h^{1/2}$$

The phase velocity of the wave varies as the square root of the depth of water.

Liquid – Gas Phase Transition :-

Below T_C i.e. $T < T_C$ — Fix temperature, T — Increase density, ρ — From gaseous phase to liquid phase — Must pass through a mixed phase of gas and liquid.

Above T_C i.e. $T > T_C$ — Fix temperature, T — Increase density, ρ — From gaseous phase to liquid phase — Continuous transition — No mixture of phases.

Start from below T_C in the gaseous phase — Raise temperature, T above T_C — Keep temperature, T fixed — Decrease density, ρ — Lower temperature, T below T_C — End in the liquid phase.

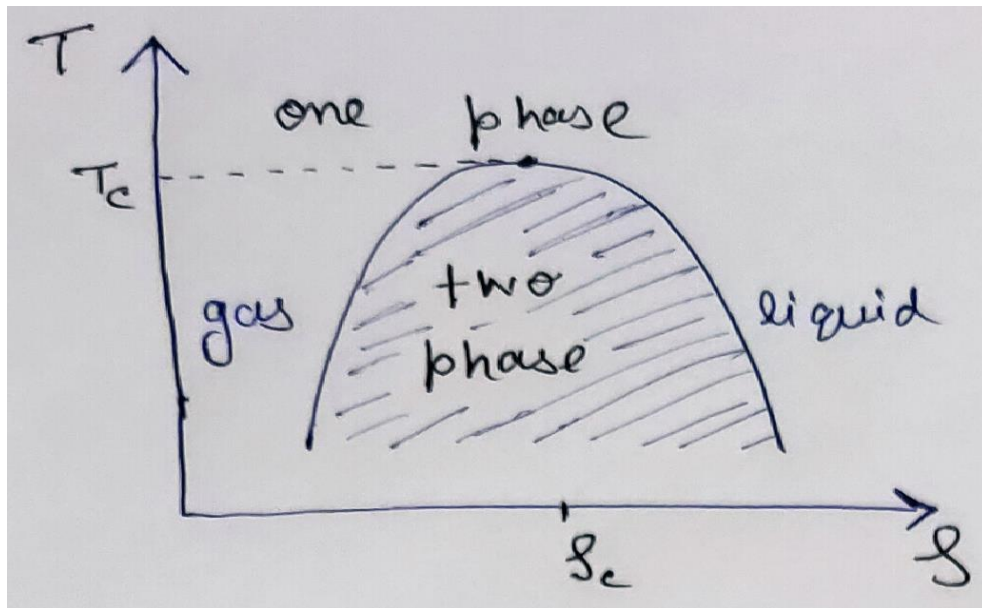
For sulphur hexafluoride (Ref. – M. Ley-Koo and M. S. Green, *Phys. Rev. A* [1977])

$$|\rho_+ - \rho_-| \propto (T_C - T)^{0.327 \pm 0.006}$$

For Helium – 3 (Ref. – C. Pittman, T. Doiron and H. Meyer, *Phys. Rev. B* [1979])

$$|\rho_+ - \rho_-| \propto (T_c - T)^{0.321 \pm 0.006}$$

Here, ρ_+ and ρ_- are the densities on the two branches of the coexistence curve.



Paramagnet – Ferromagnet (or Antiferromagnet) Phase Transition :-

For zero external magnetic field, at high temperature, all possible directions of the spin are equally likely.

The system is in a paramagnetic phase and the net magnetic moment of the system equal to zero.

For zero magnetic field, below a certain temperature (T_c = critical temperature), the spins begin to align in a certain direction.

The system exhibits a net magnetization and is in a ferromagnetic phase.

The magnetization of the system is zero for temperature above the critical point and becomes non – zero as the temperature goes below the critical value.

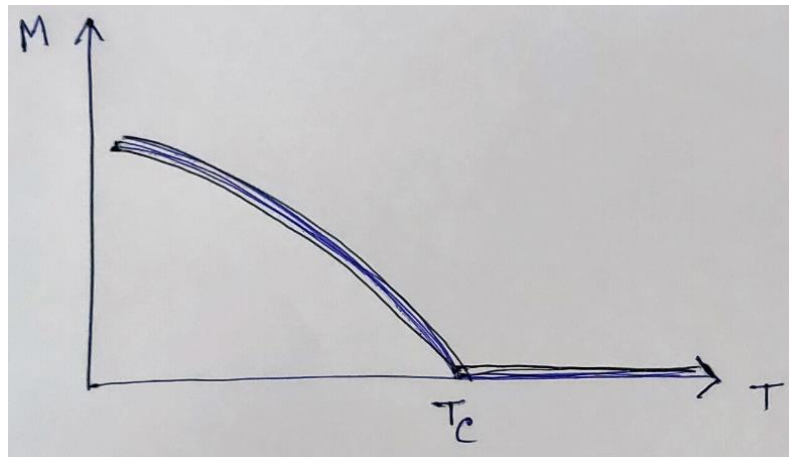
The magnetization increases continuously as the temperature is reduced from the critical point.

In an Ising ferromagnet, the energy of the system is lowered if the spins in the neighboring points are aligned in the same direction i.e. the neighboring spins are parallel to each other.

In an Ising antiferromagnet, the energy of the system is lowered if the spins in the neighboring points are aligned in the opposite direction i.e. the neighboring spins are anti – parallel to each other.

In the three-dimensional Ising antiferromagnet $DyAlO_3$, the magnetization is (Ref. – L. M. Holmes, L. G. Van Uitert and G. W. Hull, *Sol. State Commun.* [1971]),

$$M \propto (T_c - T)^{0.311 \pm 0.006}$$

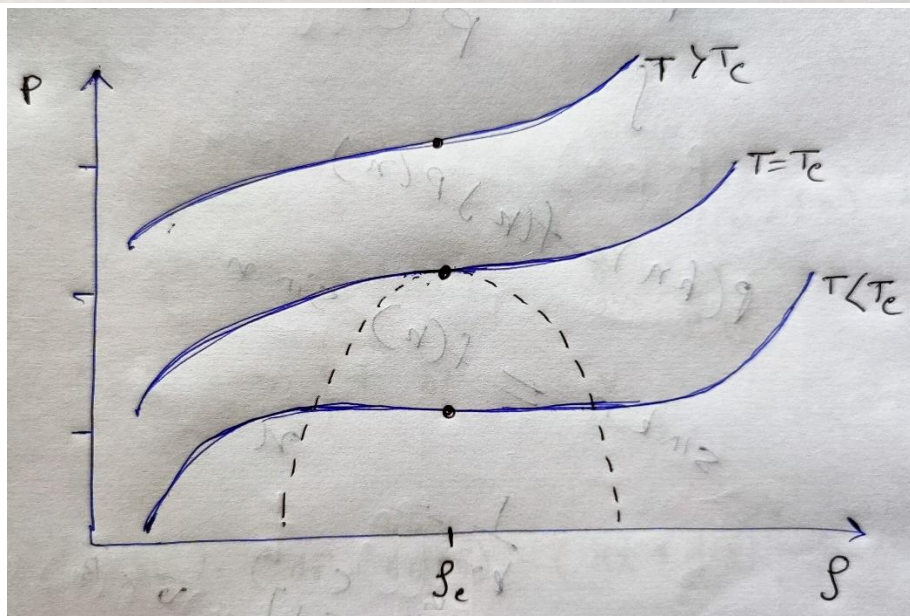
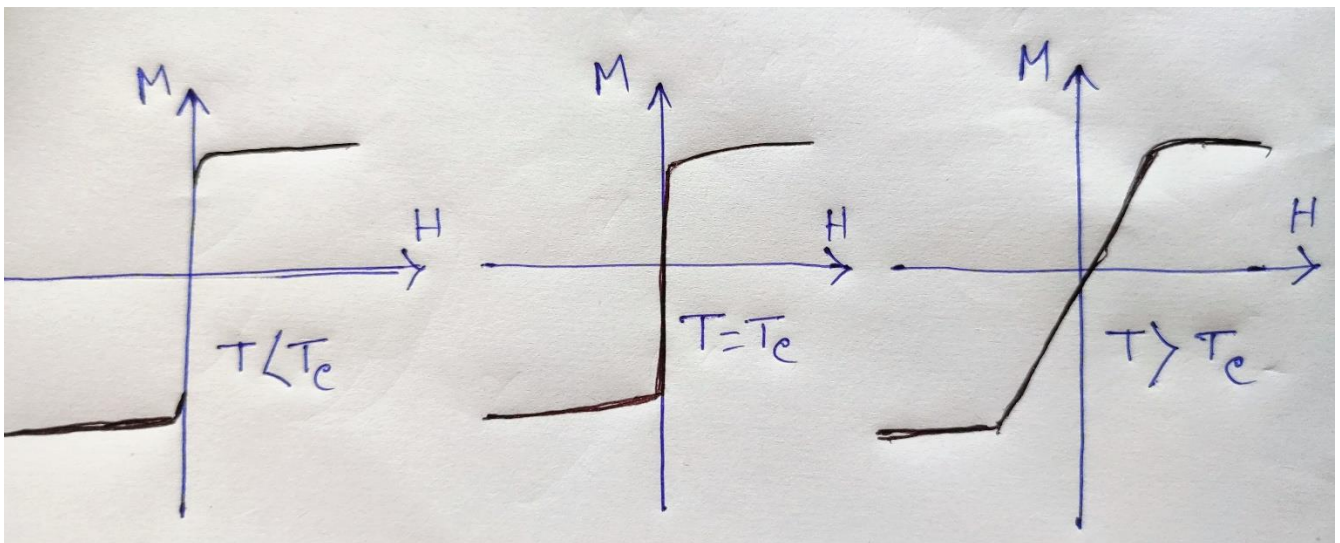


Order parameter :-

The order parameter is equal to zero in one particular phase while it has a non – zero value in the other phase.

For liquid – gas phase transitions $\rho_{liquid} - \rho_{gas}$ i.e. the difference in the densities of the two phases is taken as the order parameter.

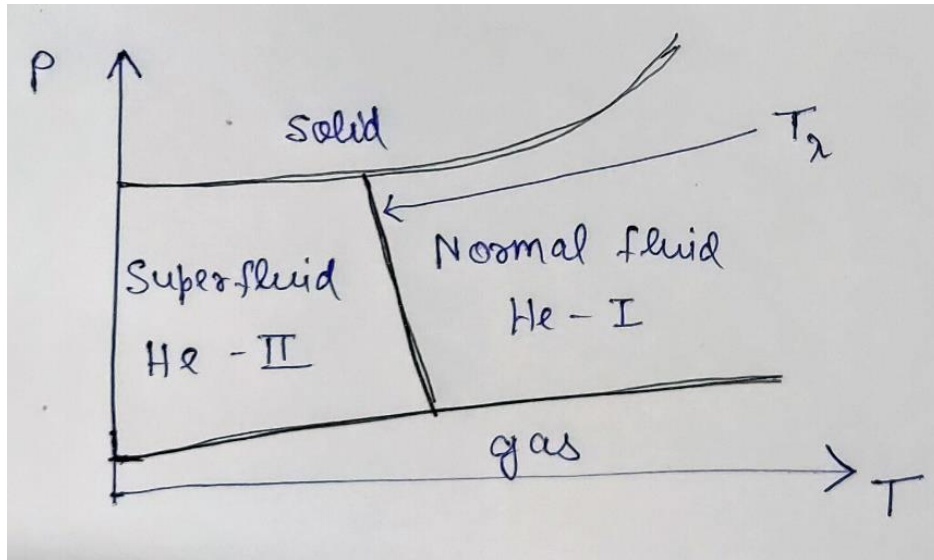
For magnetic phase transitions, the magnetization (M) is taken as the order parameter.



Here, $\rho - \rho_c \equiv M$ and $P - P_c \equiv H$.

Superfluid phase transition in Helium – 4 :-

Within a range of pressure between zero and twenty five atmospheres, liquid helium undergoes a continuous phase transition to superfluid helium at a temperature of about two kelvins.



Very close to the transition temperature, the specific heat varies as (Ref. – J. A. Lipa and T. C. P. Chiu, *Phys. Rev. Lett.* [1983])

$$C \propto |T - T_\lambda|^{0.013 \pm 0.003}$$

The specific heat does not diverge because of the positive value of the critical exponent.

For $T > T_\lambda$

$$C \approx A_+ \ln(T - T_\lambda) + B_+$$

For $T < T_\lambda$

$$C \approx A_- \ln(T_\lambda - T) + B_-$$

Here A_+ , B_+ , A_- and B_- are constants.

There is a discontinuity in the specific heat across the transition temperature but no divergence in its value.

Self – avoiding random walk :-

The random walker cannot land in the same point more than once i.e. the random path cannot intersect itself.

In three dimensions, the root mean square distance after $N \rightarrow \infty$ steps is (Ref. – J. P. Cotton, *J. Physique Lett.* [1980])

$$R \propto N^{0.586 \pm 0.004}$$

This model applies to isolated polymer chain in solution because more than one molecule in the polymer cannot be at the same point.

Some important questions :-

- I) Why do phase transitions occur?
- II) How can we determine the phase diagram as the external parameters are changed?
- III) How can we calculate the critical exponents associated with phase transitions?
- IV) Why do we see universality in different set of phenomena?

Mean field theories (where a physical variable is replaced by its average value) like the Landau theory of phase transitions, break down near the critical point as the fluctuations grow infinitely large.

Near a critical point, the equation of state for magnetic systems (developed by Benjamin Widom) is analogous to that of a fluid (developed by Van der Waals).

Leo Kadanoff suggested that near a critical point, the system looks similar at all length scales.

The critical exponents of thermodynamic quantities behave independently for different systems.

Partition function, free energy and thermodynamic limit :-

Ω is the sample region that denotes the system of our interest and L denotes the characteristic linear dimensions of the system.

$V(\Omega) \propto L^d$ and $S(\Omega) \propto L^{d-1}$ denote the volume and the surface area of the specified region respectively. Here, d represents the dimensionality of the system.

$$H_{\Omega} = -k_B T \sum_n K_n \Theta_n$$

$$\Rightarrow -\beta H_{\Omega} = \sum_n K_n \Theta_n$$

K_n determines the coupling constants and Θ_n determines the various combinations of the degrees of freedom of the system.

K_n are the external parameters such as temperature, magnetic field or exchange interaction parameter.

The partition function is given as

$$Z[\{K_n\}] = Tr(e^{-\beta H_{\Omega}})$$

Here, Tr operation refers to summing over all the degrees of freedom of the system.

The free energy is given as

$$F[\{K_n\}] = -k_B T \ln[Tr(e^{-\beta H_\Omega})]$$

$$\Rightarrow F_\Omega = -k_B T \ln Z_\Omega$$

The quantities $\partial F_\Omega / \partial K_n$, $\partial^2 F_\Omega / \partial K_n^2$ and $\partial^2 F_\Omega / \partial K_m \partial K_n$ provide the information about the thermodynamics of the system.

The free energy for a finite system can be written as

$$F_\Omega[\{K_n\}] = V(\Omega)f_b[\{K_n\}] + S(\Omega)f_s[\{K_n\}] + \mathcal{O}(L^{d-2})$$

The bulk free energy per unit volume is given by

$$f_b[\{K_n\}] = \lim_{V(\Omega) \rightarrow \infty} \frac{F_\Omega[\{K_n\}]}{V(\Omega)}$$

The surface free energy per unit volume is given by

$$f_s[\{K_n\}] = \lim_{S(\Omega) \rightarrow \infty} \frac{F_\Omega[\{K_n\}] - V(\Omega)f_b[\{K_n\}]}{S(\Omega)}$$

The free energy for a system defined on a lattice with N number of lattice sites can be written as

$$F_\Omega[\{K_n\}] \sim N(\Omega)f_b[\{K_n\}]$$

The bulk free energy per unit site is then given by

$$f_b[\{K_n\}] = \lim_{N(\Omega) \rightarrow \infty} \frac{F_\Omega[\{K_n\}]}{N(\Omega)}$$

The above three conditions define the thermodynamic limit.

The concepts of phase transitions and critical phenomena are only defined in the thermodynamic limit.

Thermodynamic limit for power law interactions :-

Let the interaction potential (either for masses or charges) be given by

$$U(r) = \frac{A}{r^n}$$

The total energy of a spherical system with radius R is defined as

$$E(R) = \frac{1}{2} \int d^d r. d^d r'. \rho(\vec{r}). U(\vec{r} - \vec{r}'). \rho(\vec{r}')$$

The integration is carried out in the region specified by Ω .

Assuming uniform density, we get

$$E(R) = \frac{1}{2} \rho^2 \int d^d r. d^d r'. \frac{1}{|\vec{r} - \vec{r}'|^n}$$

Taking $\vec{r} = R\vec{x}$ and $\vec{r}' = R\vec{y}$, we get

$$\begin{aligned} E(R) &= \frac{1}{2} \rho^2 \int R^d d^d x. R^d d^d y. \frac{1}{|R\vec{x} - R\vec{y}|^n} \\ &= \frac{1}{2} \rho^2 R^{2d-n} \int d^d x. d^d y. \frac{1}{|\vec{x} - \vec{y}|^n} \end{aligned}$$

The integral is a constant independent of R and is taken to be equal to C .

The energy per unit volume is given by

$$E_b = \frac{E(R)}{V(R)} = \frac{\frac{C\rho^2}{2} R^{2d-n}}{V_d R^d} = \frac{C\rho^2}{2V_d} R^{d-n}$$

Here V_d is the volume of the d dimensional unit sphere.

$$E_b \sim R^{d-n}$$

For $R \rightarrow \infty$, the thermodynamic limit is well – defined iff E_b does not diverge i.e. when

$$d - n < 0$$

$$\Rightarrow n > d$$

Phase diagram :-

The system hamiltonian is given by $\sum_{n=1}^D K_n \Theta_n$ where $\Theta_1, \Theta_2, \dots, \Theta_D$ are the possible combinations of the degrees of the freedom of the system.

K_1, K_2, \dots, K_D are the coupling constants which denote the axes of the D dimensional phase diagram.

The set of all points where the bulk free energy is non – analytic can combine to form a point or a line, a plane or a hyperplane and so on.

The possible loci of non – analyticity of $f_b[\{K_n\}]$ are points, lines, planes, hyperplanes and so on, with dimensions given by $D_S = 0, 1, 2, 3, \dots$ respectively.

Define codimension for each possible locus of non – analytic $f_b[\{K_n\}]$ as $C = D - D_S$.

C is an invariant quantity i.e. changing D (by adding or removing a coupling constant K_n) will change D_S by the same number.

Phase boundary :-

Phase boundary separates two distinct phases in the phase diagram.

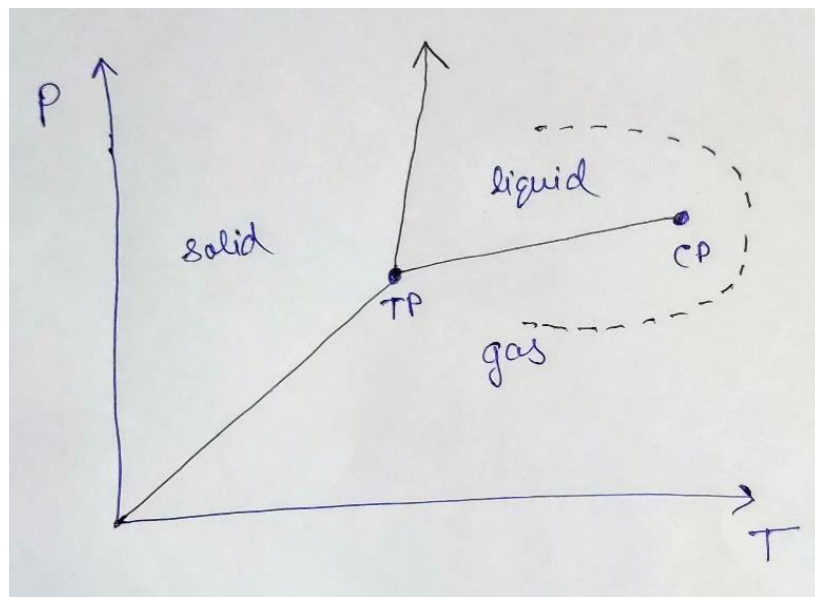
If $C = 1$, the singular locus denotes a phase boundary.

Triple point and critical point are given by singular locus with $C = 0$.

There may exist a particular path that goes from one side of the phase boundary to the other but along which $f_b[\{K_n\}]$ is analytic.

For transitioning from fluid to solid, the system must undergo phase transition.

For transition from liquid to gas, the system can follow a path such that no singularities in the thermodynamic quantities are encountered.



Types of phase transition :-

$f_b[\{K_n\}]$ is continuous everywhere for all systems in general.

Either one or more than one of $\partial f_b[\{K_n\}]/\partial K_i$ is discontinuous across the phase boundary. This is called a first order phase transition.

All of $\partial f_b[\{K_n\}]/\partial K_i$ is continuous across the phase boundary. This is called a continuous phase transition.

Paul Ehrenfest denoted a phase transition to be of the n-th order if the n-th order derivative of the free energy becomes discontinuous.

Ehrenfest's classification of phase transition is incorrect since in the so – called 'second order' phase transitions, the second order derivative of the free energy i.e. the specific heat is actually diverging and not discontinuous.

Correlation length :-

The correlation length determines the range of statistical fluctuations in space for a measurable physical quantity.

It tells us how far in space are the measurable quantities related to one another.

ξ diverges to infinity when the temperature reaches the critical point as $\xi \approx \xi_0 t^{-2/3}$.

Here, $t = |T - T_c|/T_c$ is the reduced temperature that measures the deviation of the temperature of the system from the critical point.

ξ_0 is the correlation length when the system is very far away from the critical point.

Finite size effects :-

In a system of finite size (characteristic dimension of the system = L), the correlation length, ξ cannot exceed L .

As the system temperature comes closer to T_c , ξ diverges and becomes greater than the system's characteristic length, L .

The behavior of the real system deviates from that of the ideal (infinitely large) system described by the thermodynamic limit of f_b .

Take $\xi_0 \approx 10\text{\AA}$ and $L = 1\text{cm}$. Thus,

$$\begin{aligned} L &\approx \xi_0 t^{-2/3} \\ \Rightarrow 1\text{cm} &\approx (10^{-7}\text{cm})t^{-2/3} \\ \Rightarrow t^{-2/3} &\approx 10^7 \\ \Rightarrow t &\approx 10^{-21/2} \\ \Rightarrow \frac{|T - T_c|}{T_c} &\approx 10^{-21/2} \\ \Rightarrow T - T_c &\approx \pm 10^{-21/2} T_c \\ \Rightarrow T &\approx (1 \pm 10^{-21/2}) T_c \end{aligned}$$

The difference between the real temperature of the system and the critical temperature is virtually non – existent.

The deviation of the system's behavior from the ideal thermodynamic limit is negligible.

Phase transition models :-

Ising model, Heisenberg model, Potts model, Baxter model and F model are used in statistical mechanics.

Construct a model that represents the real system as accurately as possible by fine tuning the parameters of the model to match with the experimental results.

Construct a model that captures the essential parts of the system with minimal assumptions and focuses only on the physically relevant results.

The Ising model :-

The degrees of freedom are the classical spin variables that can represent either an up state or a down state given by

$$S_i = \pm 1$$

Here, i denotes the label of the site that runs as $1, 2, \dots, N(\Omega)$.

The total number of possible states are $2^{N(\Omega)}$.

The Hamiltonian is given by

$$H = - \sum_i \mathcal{H}_i S_i - \sum_{i,j} J_{ij} S_i S_j - \sum_{i,j,k} K_{ijk} S_i S_j S_k - \dots$$

\mathcal{H}_i is the external magnetic field that interacts with individual spins.

J_{ij} is the exchange interchange that couples two spins together.

K_{ijk} is the exchange interchange that couples three spins together.

$$F_\Omega[T, \{\mathcal{H}_i\}, \{J_{ij}\}, \{K_{ijk}\}, \dots] = -k_B T \ln[Tr(e^{-\beta H_\Omega})]$$

Here,

$$Tr(e^{-\beta H_\Omega}) = \sum_{S_1=\pm 1} \sum_{S_2=\pm 1} \dots \sum_{S_{N(\Omega)}=\pm 1} (e^{-\beta H_\Omega}) = \sum_{\{S_i\}=\pm 1} (e^{-\beta H_\Omega})$$

The partition function is given by

$$Z_\Omega[T, \{\mathcal{H}_i\}, \{J_{ij}\}, \{K_{ijk}\}, \dots] = \sum_{n=1}^{2^{N(\Omega)}} \exp(-\beta E_n)$$

E_n is the energy of the n^{th} state and is a linear combination of the coupling constants i.e. \mathcal{H}, J, K, \dots

Thus, Z_Ω and hence, F_Ω is analytic everywhere.

For the thermodynamic limit to exist we must have (Ref. – C. Domb and M. S. Green, *Phase Transitions and Critical Phenomena Vol. 1* [1972])

$$\sum_{j, (j \neq i)} |J_{ij}| < \infty$$

In general, if the two spin interaction has the form

$$J_{ij} = \frac{A}{|\vec{r}_i - \vec{r}_j|^n}$$

The thermodynamic limit exists if $n > d$, where d is the dimensionality of the system.

For nearest neighbor interactions ($J_{ij} = 0$ for $j \neq i \pm 1$) with the same interaction strength (J), we have

$$\sum_{j, (j \neq i)} |J_{ij}| = \sum_{j=(i-1), (i+1)} |J_{ij}| = \sum_{j=(i-1), (i+1)} J = 2J < \infty$$

The hamiltonian for the nearest neighbor Ising model is given as

$$H = -\mathcal{H} \sum_i S_i - J \sum_{\langle ij \rangle} S_i S_j$$

The external magnetic field is taken to be uniform in space.

If $\mathcal{H} > 0$, the spins tend to point up to lower the energy of the system.

If $\mathcal{H} < 0$, the spins tend to point down to lower the energy of the system.

In both cases, the spins tend to align parallel to the external magnetic field.

If $J > 0$, the system is ferromagnetic as the spins tend to align parallel to another.

If $J < 0$, the system is anti-ferromagnetic as the spins tend to align anti-parallel to another.

In the absence of the external magnetic field, we have

$$H = -J \sum_{\langle ij \rangle} S_i S_j$$

The hamiltonian remains unchanged if the spins in all the lattice sites are switched i.e. the spin up particles are transformed into spin down particles and vice- versa.