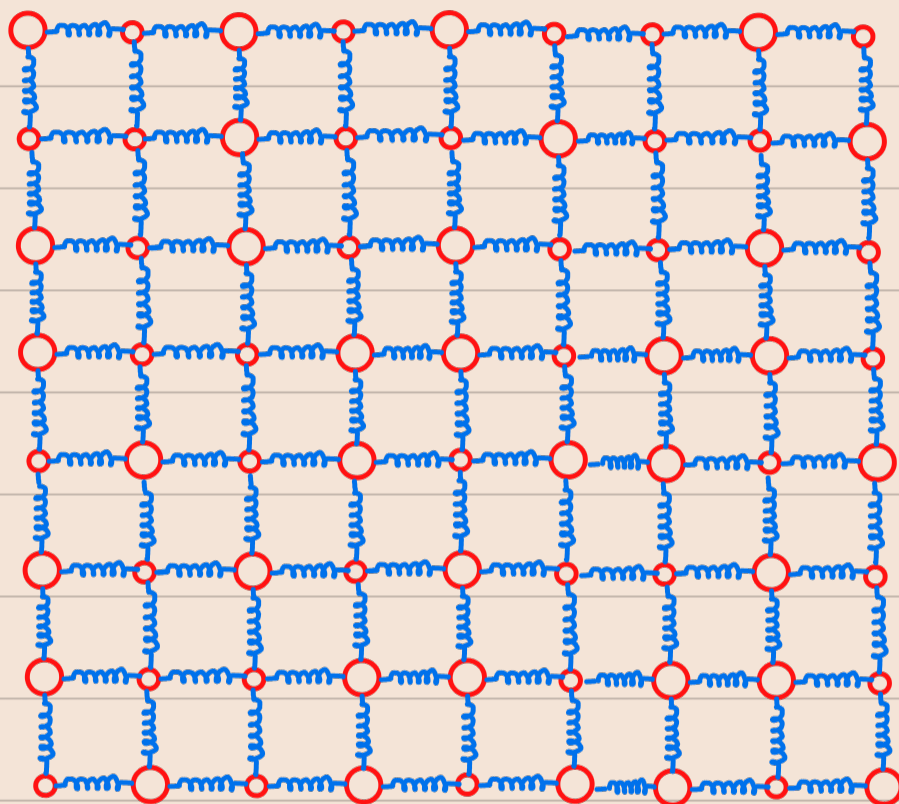


Assignment 2

1) Ions of fluctuating size on lattice



→ Extend
to 3D
to form
Simple
Cubl.

Adjacent ions are connected by a spring with an extension x_{ij} coupled to the state of ions at the nearest neighbour sites ' i ' & ' j '

$$\mathcal{E}(n_i, n_j, x_{ij}) = \frac{1}{2} k x_{ij}^2 + \gamma x_{ij} (n_i + n_j)$$

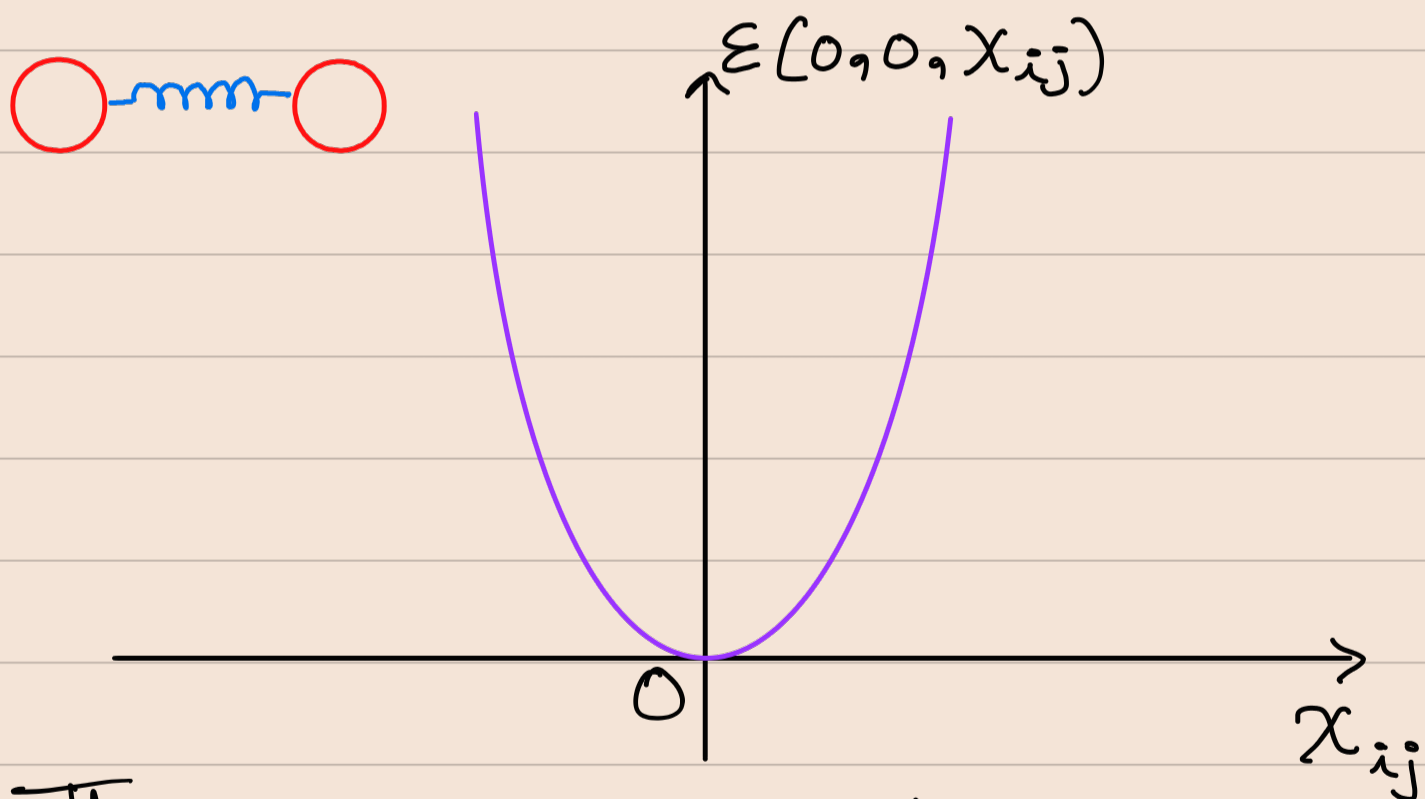
n_i is the indicator function for small ions.

$\{n_i\}$ is a Configuration of ions in the lattice. The total energy of a Configuration is given by

$$E(\{n_i\}, \{x_{ij}\}) = \sum_{\langle ij \rangle} \varepsilon(n_i, n_j, x_{ij})$$

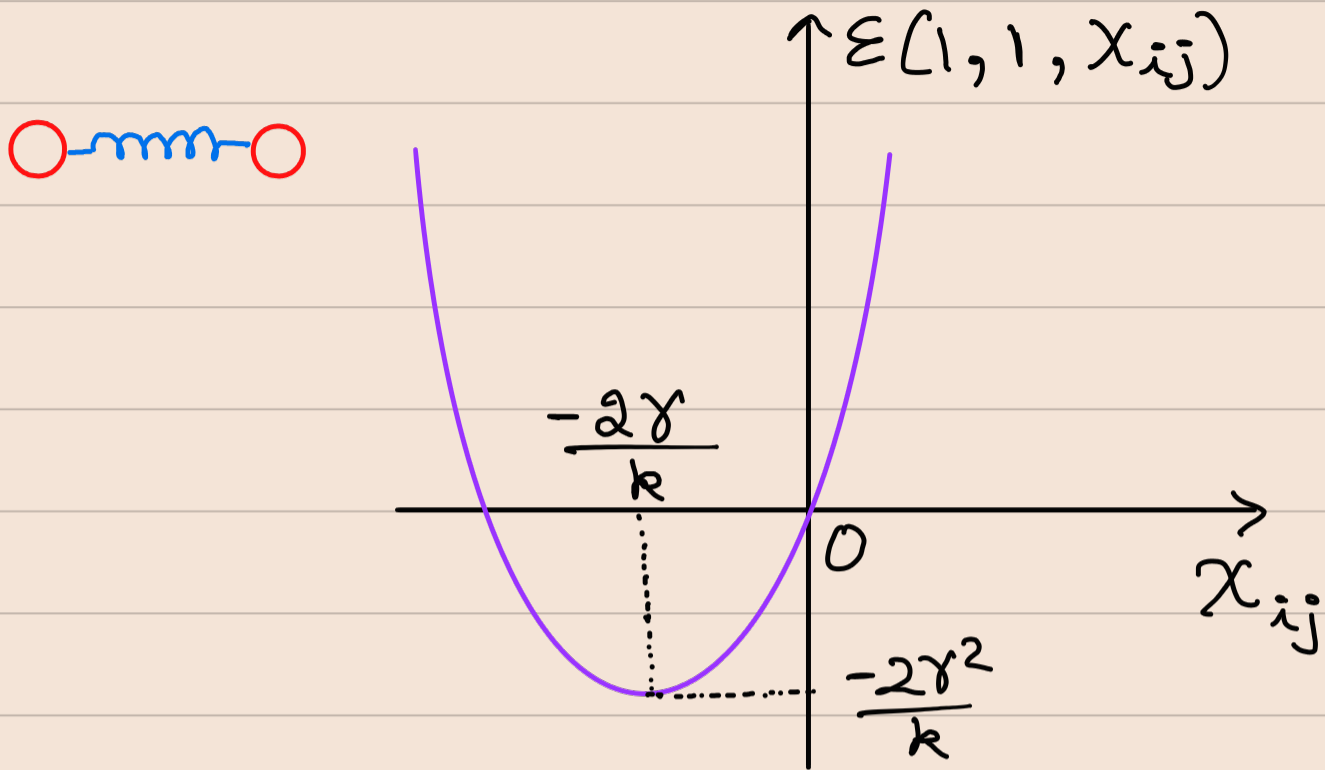
a)

$$(i) \varepsilon(0, 0, x_{ij}) = \frac{1}{2} k x_{ij}^2$$



The minima is at $x_{ij} = 0$. This is Harmonic interaction with a Spring Constant 'k'. The bigger ions tend to be closer together.

$$(ii) \quad \mathcal{E}(1, 1, X_{ij}) = \frac{1}{2} k X_{ij}^2 + 2\gamma X_{ij}$$

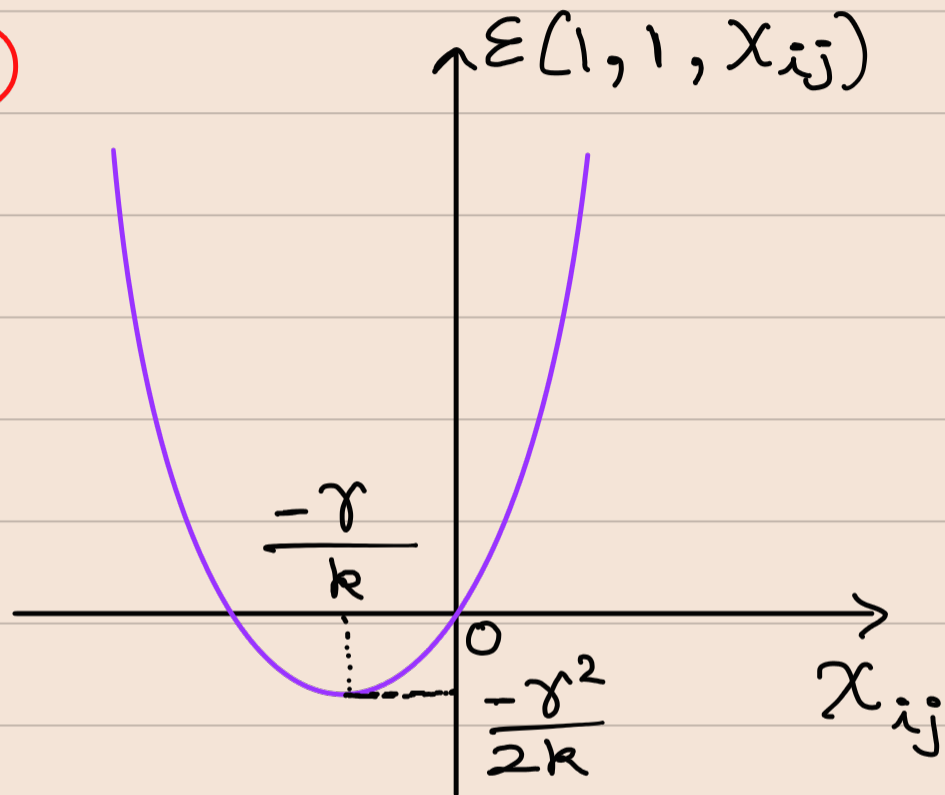


$$X_{ij}^{(\min)} = -\frac{2\gamma}{k}, \quad \mathcal{E}(1, 1, X_{ij}^{(\min)}) = -\frac{2\gamma^2}{k}$$

This is a shifted harmonic well where the equilibrium is at a distance of ' $-\frac{2\gamma}{k}$ ' which minimizes the energy. The smaller ions tend to be at a farther distance away when compared to two bigger ions, But they are more stable than two bigger ions being together.

$$(iii) \quad \mathcal{E}(0, 1, \chi_{ij}) = \mathcal{E}(1, 0, \chi_{ij})$$

$$\mathcal{E}(0, 1, \chi_{ij}) = \frac{1}{2} k \chi_{ij}^2 + \gamma \chi_{ij}$$



This is also a shifted harmonic interaction but with a closer distance as compared to two big ions interaction. Also the reduction in energy is one quarter of two small ion interaction.

b) Let $C: \{n_i\}$ be the configuration of ions in the lattice with the total energy $E(C)$, then the canonical partition function is given by,

$$Z = \int \left(\prod_{\langle ij \rangle} d\chi_{ij} \right) \sum_{\{n_i\}} e^{-\beta E(\{n_i\}, \{\chi_{ij}\})}$$

$$= \int \left(\prod_{\langle ij \rangle} d\chi_{ij} \right) \sum_{\{n_i\}} e^{-\beta \sum_{\langle ij \rangle} \varepsilon(n_i, n_j, \chi_{ij})}$$

$$= \int \left(\prod_{\langle ij \rangle} d\chi_{ij} \right) \sum_{\{n_i\}} \prod_{\langle ij \rangle} e^{-\beta \varepsilon(n_i, n_j, \chi_{ij})}$$

$$= \sum_{\{n_i\}} \int \prod_{\langle ij \rangle} \left[d\chi_{ij} e^{-\beta \varepsilon(n_i, n_j, \chi_{ij})} \right]$$

$$= \sum_{\{n_i\}} \underbrace{\int \prod_{\langle ij \rangle} \left[d\chi_{ij} e^{-\beta \left[\frac{1}{2} k \chi_{ij}^2 + \gamma \chi_{ij} (n_i + n_j) \right]} \right]}_I$$

Consider $\frac{1}{2} k X_{ij}^2 + \gamma X_{ij} (n_i + n_j)$

$$= \frac{1}{2} k \left[X_{ij}^2 + \frac{2\gamma(n_i + n_j)}{k} + \left[\frac{\gamma(n_i + n_j)}{k} \right]^2 - \frac{\gamma^2}{2k} (n_i + n_j)^2 \right]$$

$$= \frac{1}{2} k \left[X_{ij} + \frac{\gamma}{k} (n_i + n_j) \right]^2 - \frac{\gamma^2}{2k} (n_i + n_j)^2$$

Then the integral becomes,

$$I = \int_{-\infty}^{\infty} dX_{ij} e^{-\frac{Bk}{2} \left[X_{ij} + \frac{\gamma}{k} (n_i + n_j) \right]^2} e^{+\frac{B\gamma^2}{2k} (n_i + n_j)^2}$$

$$\Rightarrow I = e^{\frac{B\gamma^2}{2k} (n_i + n_j)^2} \sqrt{\frac{2\pi}{Bk}}$$

Thus Z is,

$$Z = \sum_{\{n_i\}} \prod_{\langle ij \rangle} \left[e^{+\frac{B\gamma^2}{2k} (n_i + n_j)^2} \sqrt{\frac{2\pi}{Bk}} \right]$$

Let N_b be total number of Nearest neighbour bonds, then

$$Z = \left(\frac{2\pi}{\beta k} \right)^{\frac{N_b}{2}} \sum_{\{n_i\}} \prod_{\langle ij \rangle} e^{+\frac{\beta \gamma^2}{2k} (n_i + n_j)^2}$$

$$Z = \left(\frac{2\pi}{\beta k} \right)^{\frac{N_b}{2}} \sum_{\{n_i\}} e^{+\frac{\beta \gamma^2}{2k} \sum_{\langle ij \rangle} (n_i + n_j)^2}$$

$$\text{If } Z_0 = \left(\frac{2\pi}{\beta k} \right)^{\frac{N_b}{2}}$$

$$\& \quad \tilde{E}(\{n_i\}) = \frac{-\gamma^2}{2k} \sum_{\langle ij \rangle} (n_i + n_j)^2$$

$$\text{then } Z = Z_0 \sum_{\{n_i\}} e^{-\beta \tilde{E}(\{n_i\})}$$

$$c) \quad \tilde{E} = \frac{-\gamma^2}{2k} \sum_{\langle ij \rangle} (n_i + n_j)^2$$

$$\text{Let } n_i = \frac{S_i + 1}{2} \Rightarrow S_i = \begin{cases} +1, \text{small} \\ -1, \text{big} \end{cases}$$

$$\Rightarrow n_i + n_j = \frac{S_i}{2} + \frac{S_j}{2} + 1$$

$$(n_i + n_j)^2 = 1 + (S_i + S_j) + \frac{(S_i^2 + S_j^2 + 2S_i S_j)}{4}$$

$$S_i^2 = S_j^2 = 1 \text{ for all 'i'}$$

$$\Rightarrow (n_i + n_j)^2 = \frac{3}{2} + \frac{S_i S_j}{2} + (S_i + S_j)$$

$$\Rightarrow \sum_{\langle i, j \rangle} (n_i + n_j)^2 = \sum_{\langle i, j \rangle} \left[\frac{3}{2} + \frac{S_i S_j}{2} + (S_i + S_j) \right]$$

$$\sum_{\langle i, j \rangle} = \frac{1}{2} \sum_i \sum_{j \in n \cdot n(i)} \quad n \cdot n(i) = \text{Nearest neighbour of 'i'}$$

$$\Rightarrow \frac{1}{2} \sum_i \sum_{j \in n \cdot n(i)} 1 = \frac{6}{2} \sum_i (1) = 3N$$

6 $\rightarrow$ for simple cube

$$\Rightarrow N_b = 3N \rightarrow \text{Total no. of bonds for } N \text{ particles}$$

$$\begin{aligned} \sum_{\langle i, j \rangle} (S_i + S_j) &= 2 \sum_{\langle i, j \rangle} S_i = \sum_i S_i \sum_{j \in n \cdot n(i)} (1) \\ &= 6 \sum_i S_i \end{aligned}$$

$$\Rightarrow \tilde{E} = -\frac{\gamma^2}{2k} \left[\frac{3N_b}{2} + \sum_{\langle ij \rangle} \frac{S_i S_j}{2} + 6 \sum_{\langle ij \rangle} S_i \right]$$

$$\Rightarrow \tilde{E} = -\underbrace{\frac{3\gamma^2 N_b}{4k}}_{\text{Constant}} - \frac{\gamma^2}{4k} \sum_{\langle ij \rangle} S_i S_j - \frac{3\gamma^2}{k} \sum_i S_i$$

Let $J = \frac{\gamma^2}{4k}$, $h = \frac{3\gamma^2}{k}$ & $E_0 = \frac{-3\gamma^2 N_b}{4k}$

$$\Rightarrow \tilde{E} = -J \underbrace{\sum_{\langle ij \rangle} S_i S_j}_{\text{Ising term}} - h \sum_i S_i + \underbrace{E_0}_{\text{Constant Shift}}$$

If we absorb the Constant term into the Z_0 in partition function then

$$\underline{Z = \tilde{Z}_0 e^{-\beta U \{S_i\}}}$$

where $\tilde{Z}_0 = \left(\frac{2\pi}{\beta k} \right)^{\frac{N_b}{2}} e^{\frac{3\beta \gamma^2 N_b}{4k}}$

& $\underbrace{U \{S_i\}}_{\text{Ising like Hamiltonian}} = -J \sum_{\langle i,j \rangle} S_i S_j - h \sum_i S_i$

2) Landau Theory with a cubic Term

$$\Phi(m) = am^2 + bm^4 + cm^3$$

$$b \neq c > 0 \quad \underline{a = A(T - T_0)}$$

a) To find m^* such that $\left. \frac{\partial \Phi}{\partial m} \right|_{m^*} = 0$

$$\Rightarrow 2am_* + 4bm_*^3 + 3cm_*^2 = 0$$

$$\Rightarrow m_* [2a + 4bm_*^2 + 3cm_*] = 0$$

So either $m_* = 0$ or

$$4bm_*^2 + 3cm_* + 2a = 0$$

$$\Rightarrow m_* = \frac{-3c \pm \sqrt{9c^2 - 32ab}}{8b}$$

Thus if $9c^2 - 32ab > 0$
then we have non zero m_* value
that can appear.

$$\Rightarrow 32ab < 9c^2 \Rightarrow a < \frac{9c^2}{32b}$$

But $a = A(T - T_0)$, thus we need $A(T - T_0) < \frac{9c^2}{32b}$ for non zero m_* value

$$\Rightarrow T < T_0 + \frac{9c^2}{32Ab} \quad \left(\text{for more than one root} \right)$$

And if $T > T_0 + \frac{9c^2}{32Ab}$ then

only $m_* = 0$ is the root. Thus

$$T_m = T_0 + \frac{9c^2}{32Ab} \quad \neq \text{ the } m_* \text{ when } T < T_0$$

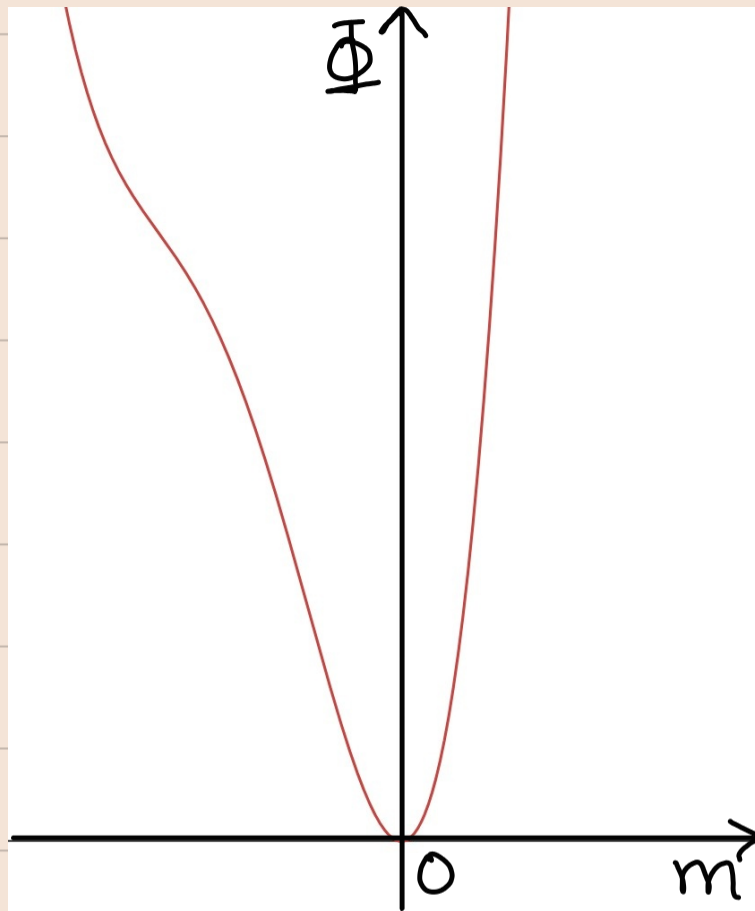
are

$$m_* = 0, \quad \frac{-3c \pm \sqrt{9c^2 - 32ab}}{8b}$$

There are three roots for $\frac{\partial \Phi}{\partial m} \Big|_{m^*} = 0$ when $T < T_m$.

- When $T > T_m$

Here $m^* = 0$ is the only global minima.



Let $m_* = 0, m_+, m_-$ where

$$m_{\pm} = \frac{-3c \pm \sqrt{9c^2 - 32ab}}{8b}$$

$$\left. \frac{\partial^2 \Phi}{\partial m^2} \right|_{m^*} = 2a + 12bm_*^2 + 6cm_*$$

$$m^* = 0 \Rightarrow 2 \left[6bm_*^2 + 3cm_* + a \right]$$

$$\left. \frac{\partial^2 \Phi}{\partial m^2} \right|_{m^*=0} = 2a, \quad \text{Thus when } a > 0 \quad m_*=0 \text{ is minima}$$

But when $a < 0$, $m_*=0$ is maxima

$$\Rightarrow \left. \frac{\partial^2 \Phi}{\partial m^2} \right|_{m^*=m_-} > 0 \quad \text{for any 'a'}$$

(m_- is always some minima)

$$\left. \frac{\partial^2 \Phi}{\partial m^2} \right|_{m^*=m_+} = \begin{cases} +ve \text{ (minima)} & \text{when } a > 0 \\ -ve \text{ (maxima)} & \text{when } a < 0 \end{cases}$$

Thus the value of m^* when new minima just appears when T is lowered than T_m slightly.

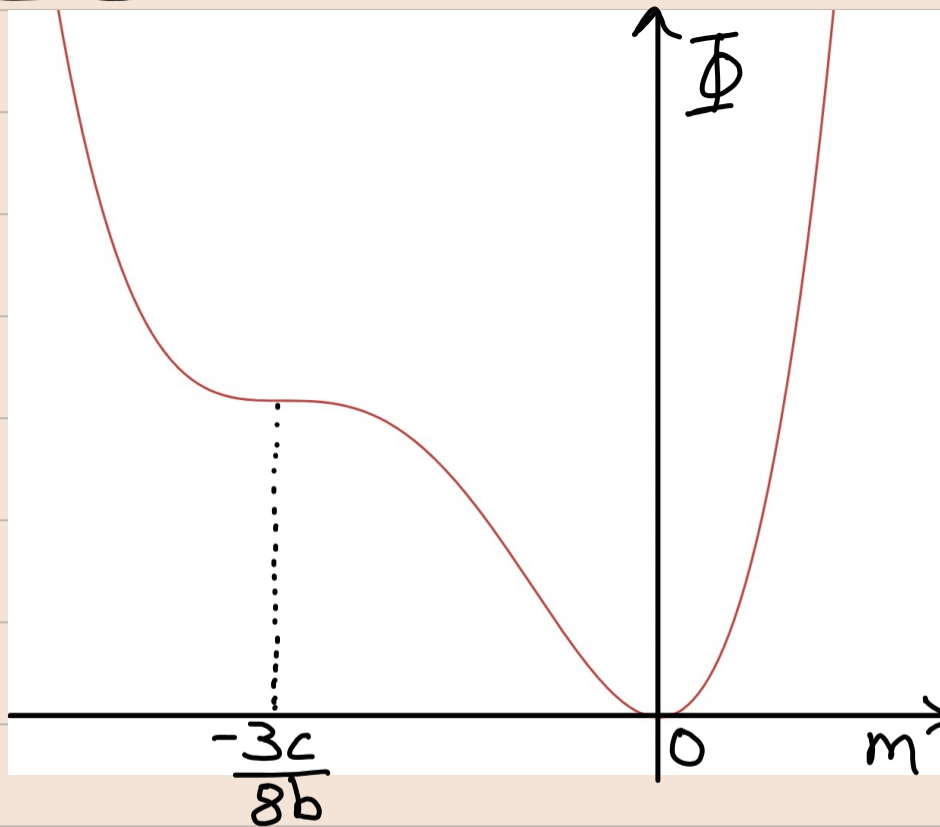
$$\text{So when } T = T_m$$

$$\Rightarrow 9c^2 = 32ab$$

Then $m^*=0 \Rightarrow$ global minima

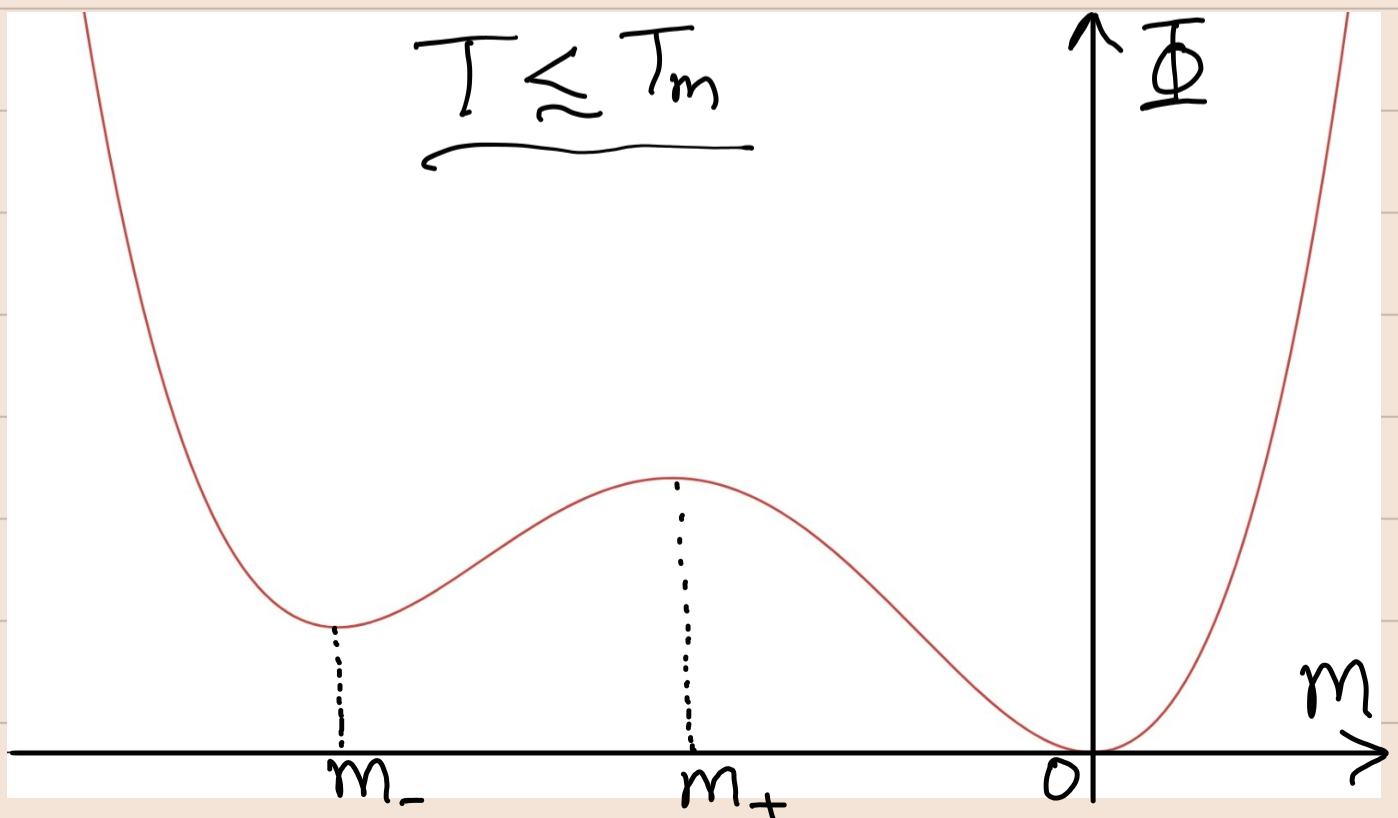
$$\& \quad m^* = -\frac{3c}{8b} \Rightarrow \text{Inflection point}$$

- When $T = T_m$



Thus for $T \lesssim T_m$ $m^* \lesssim -\frac{3c}{8b}$

- When T is just below T_m



To derive the temperature at which $\Phi(m^*) = 0$.

$$\Rightarrow \left. \frac{d\Phi}{dm} \right|_{m^*} = 0 \quad \& \quad \Phi(m^*) = 0.$$

$$\Rightarrow m^* = 0, \quad \frac{-3c \pm \sqrt{9c^2 - 32ab}}{8b}$$

$m^* = 0, m_{\pm}$

• $\Phi(m^* = 0) = 0$ is trivial

• $\Phi(m^* = m_{\pm}) = 0 \quad \& \quad \left. \frac{\partial \Phi}{\partial m} \right|_{m_{\pm}} = 0$

is needed for non trivial solⁿ.

$$\Rightarrow \Phi(m_*) = am_*^2 + bm_*^4 + cm_*^3 = 0$$

$$\& \left. \frac{\partial \Phi}{\partial m} \right|_{m^*} = 2am_* + 4bm_*^3 - 3cm_*^2 = 0$$

$(m_* \neq 0)$

$$\Rightarrow a + bm_*^2 + cm_* = 0$$

$$\& 2a + 4bm_*^2 + 3cm_* = 0$$

$$\Rightarrow 2bm_*^2 + 2cm_* = 4bm_*^2 + 3cm_*$$

$$\Rightarrow 2bm_*^2 = -cm_*$$

$$\Rightarrow m_* = \frac{-c}{2b}$$

$$\Rightarrow m_{\pm} = \frac{-c}{2b}$$

$$\Rightarrow \frac{-3c \pm \sqrt{9c^2 - 32ab}}{8b} = \frac{-c}{2b}$$

$$\Rightarrow -3c \pm \sqrt{9c^2 - 32ab} = -4c$$

$$\Rightarrow \pm \sqrt{9c^2 - 32ab} = -c$$

$\Rightarrow$ only $m_* = m_-$ can satisfy the eqⁿ $\Phi(m_*) = 0$ & $\left. \frac{\partial \Phi}{\partial m} \right|_{m_*} = 0$ simultaneously

$$\Rightarrow 9c^2 - 32ab = c^2$$

$$\Rightarrow 8c^2 - 32ab = 0$$

$$\Rightarrow a = \frac{c^2}{4b} \quad (\text{at } T = T_c)$$

$$\Rightarrow \boxed{T_c = T_0 + \frac{c^2}{4Ab}}$$

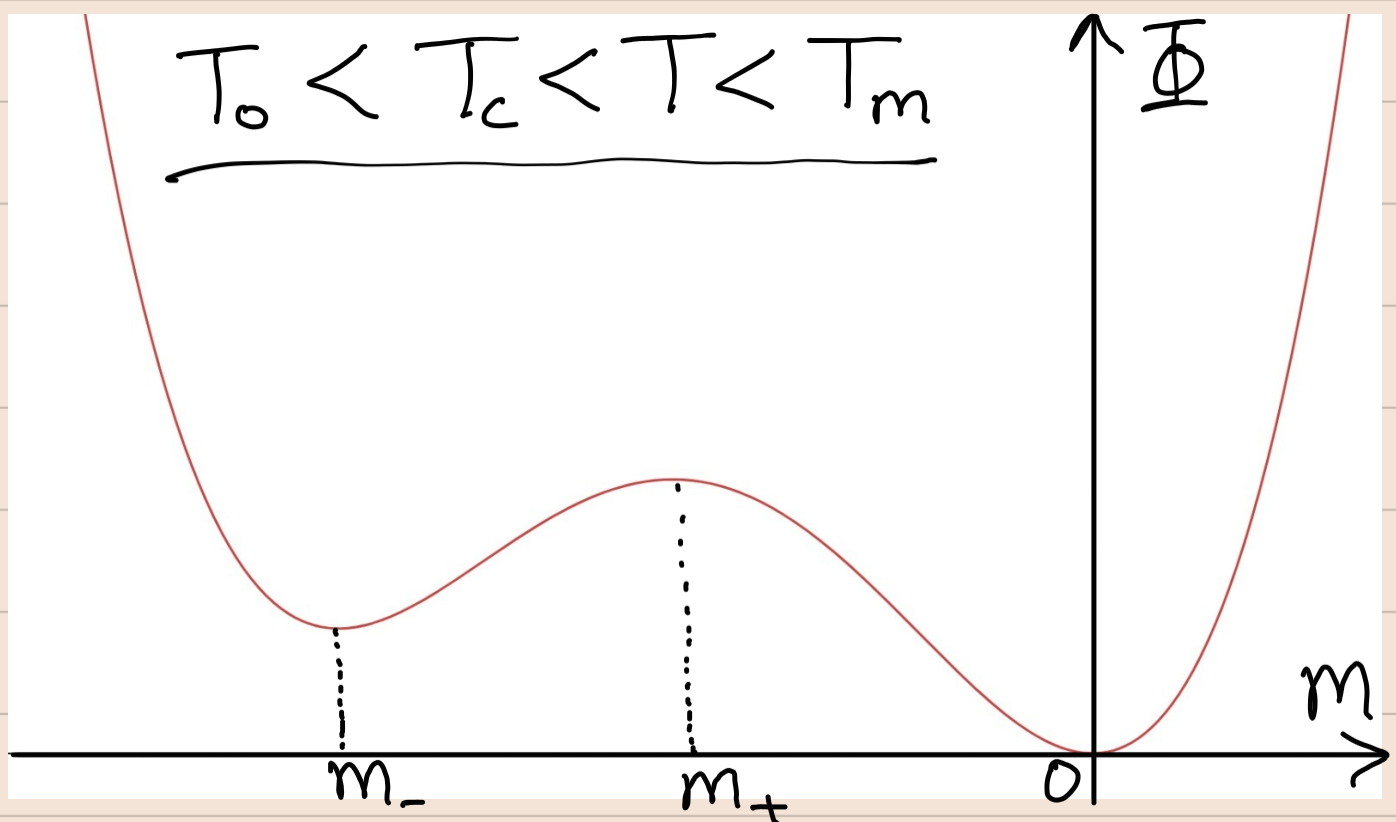
$(m^* = m_+)$ at $T = T_c$ is given by

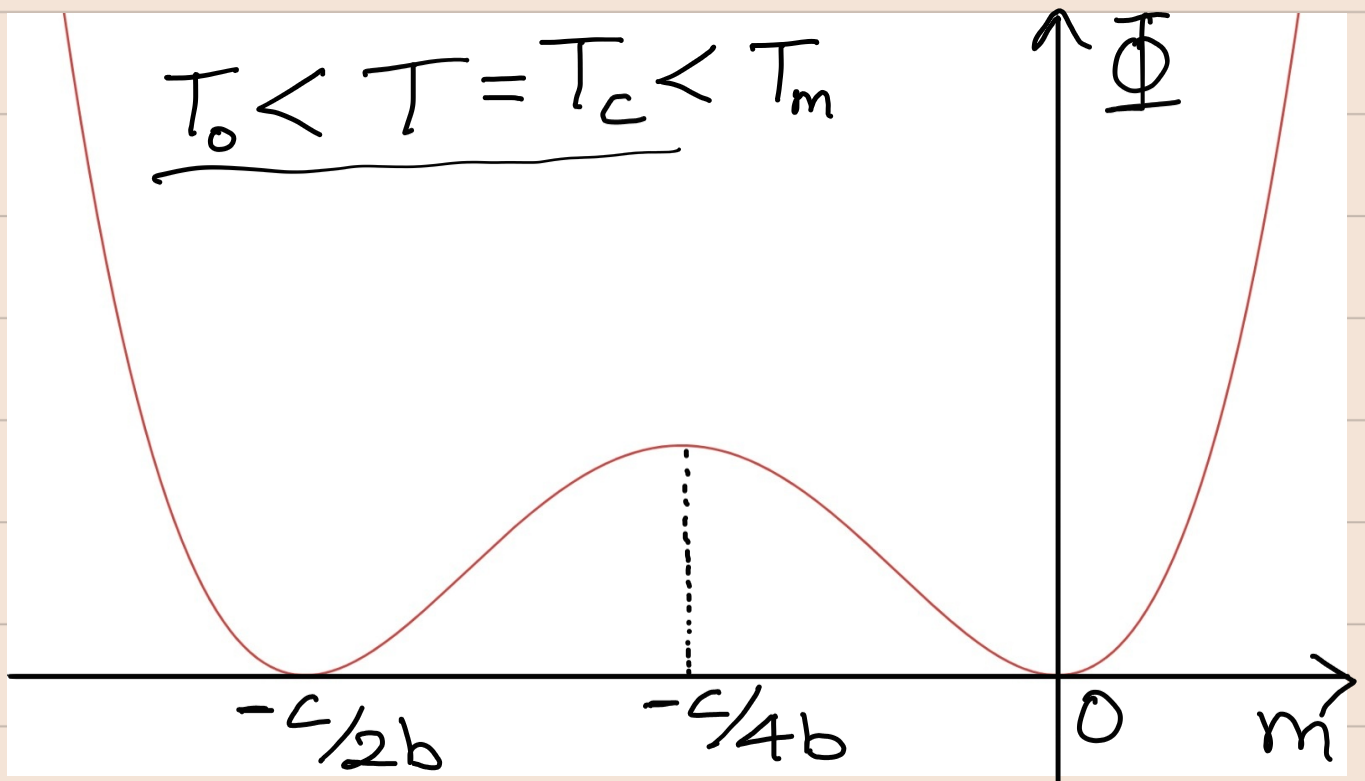
$$(m^* = m_+)_{T=T_c} = \frac{-3c + \sqrt{9c^2 - 32ab}}{8b}$$

$$\Rightarrow a = \frac{c^2}{4b} \Rightarrow 4ab = c^2 \Rightarrow 32ab = 8c^2$$

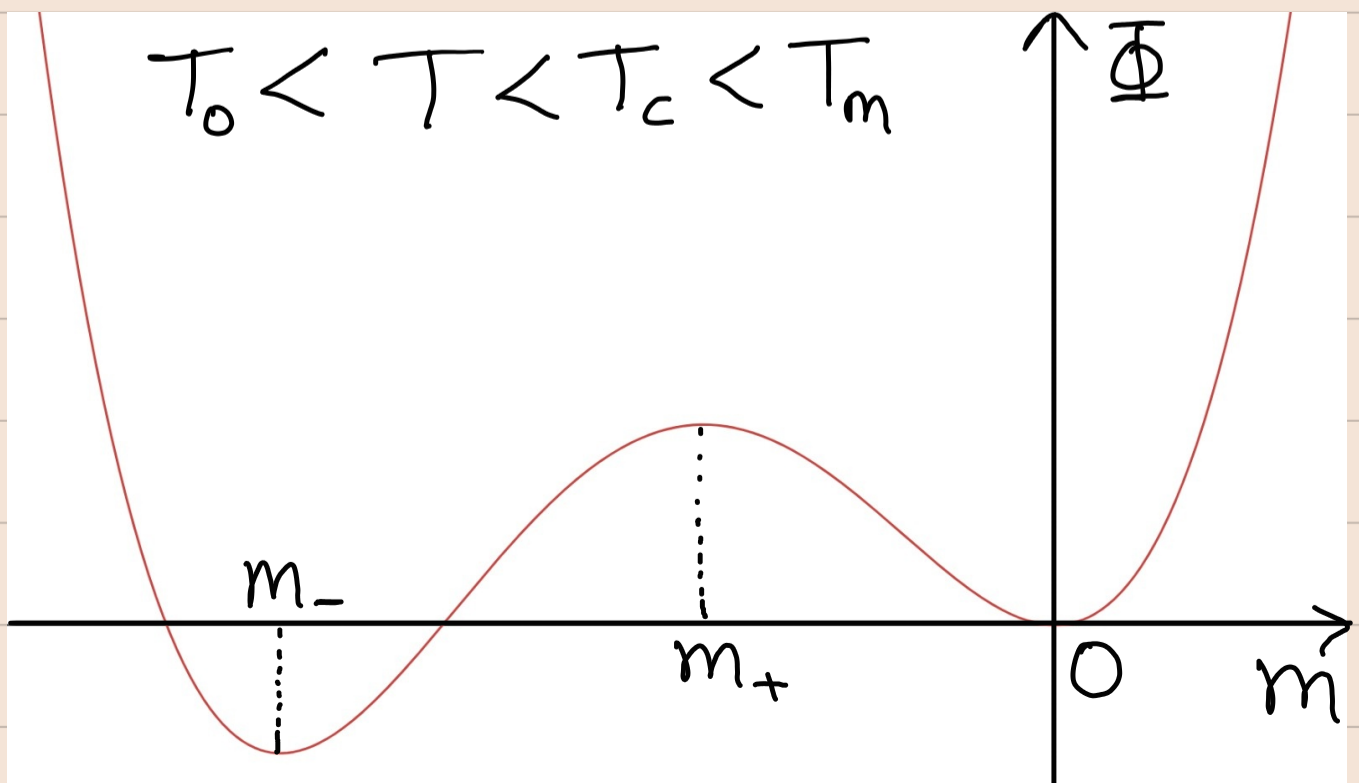
$$\Rightarrow m_+ = \frac{-3c + \sqrt{c^2}}{8b} = \frac{-3c + c}{8b}$$

$$\Rightarrow m_+ = \frac{-c}{4b} \quad (\text{at } T = T_c)$$





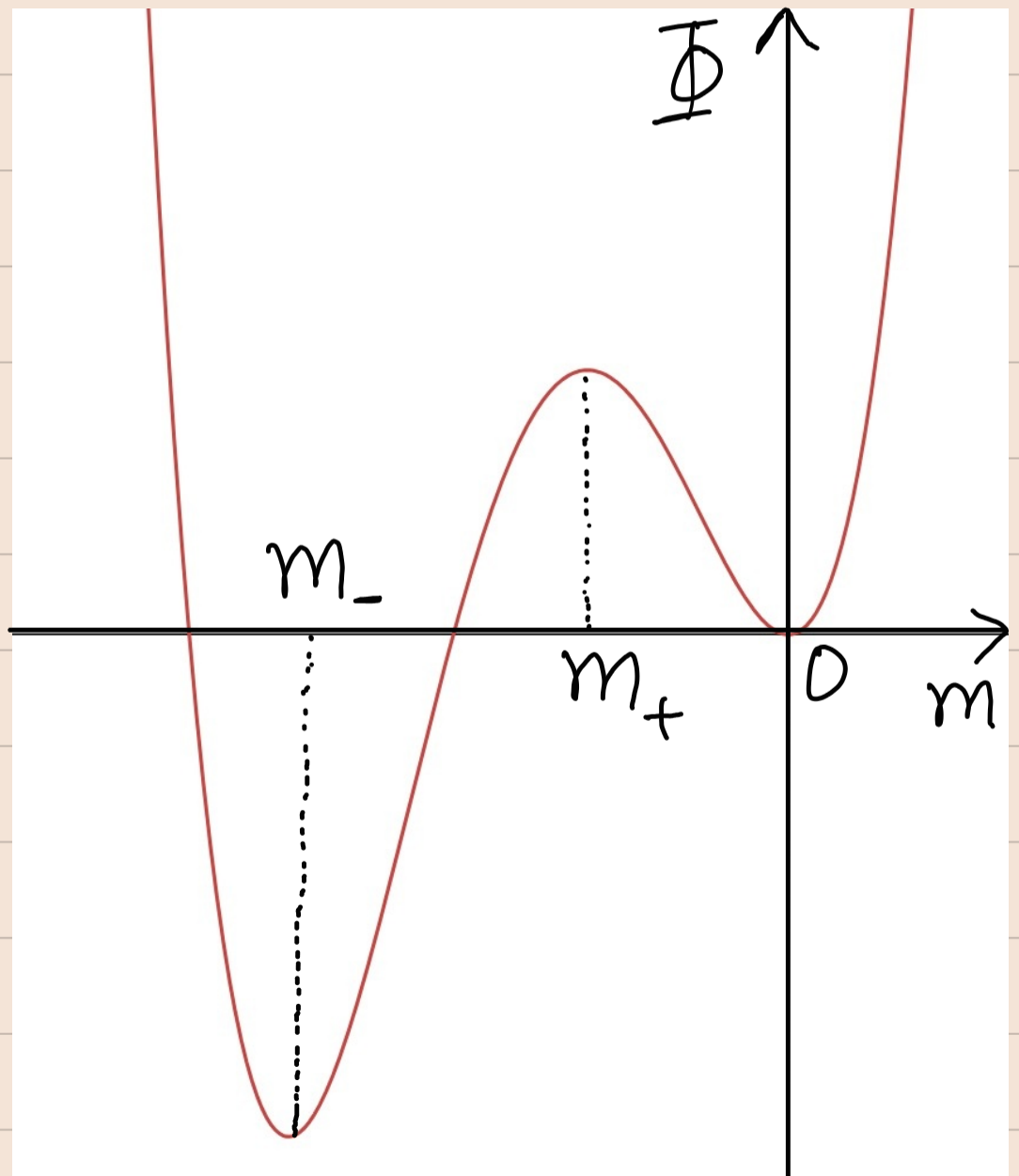
↳ Here is where for the first time more than two equal energy global minima appears. So this is the critical temperature where the global minima changes (abruptly / discontinuous)



- When $T_0 < T < T_c < T_m$

Here $a > 0$, so $m^* = 0$ is a local minima, m_- is a global minima, m_+ is maxima.

$a > 0$



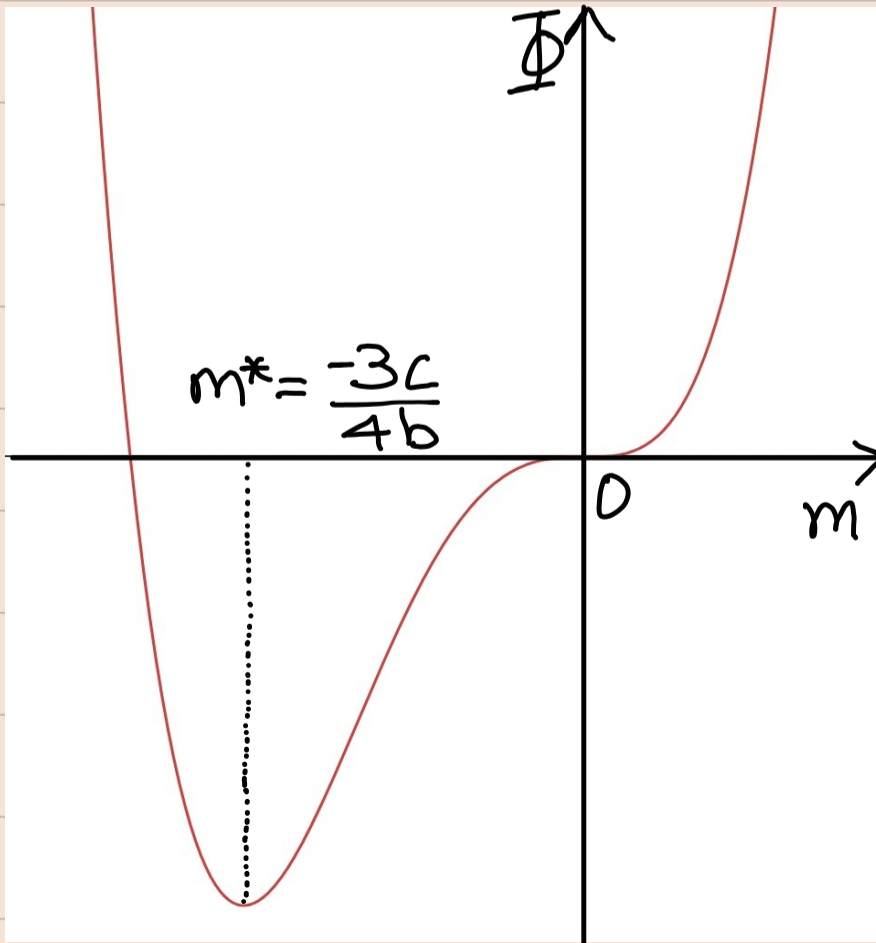
- When $T_0 = T < T_c < T_m$

Here $a = 0$, Thus $m^* = 0$ is an inflexion point.

When $a = 0$, $T = T_0$ &

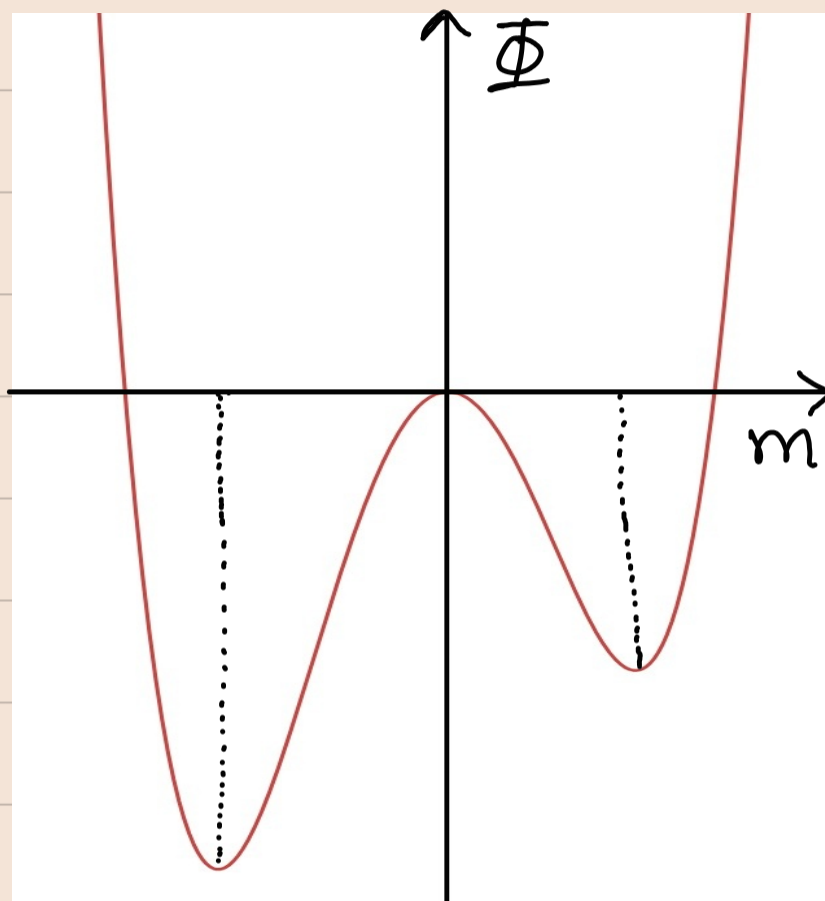
$$\Phi = cm^3 + bm^4$$

$$\Rightarrow \left. \frac{\partial \Phi}{\partial m} \right|_{m^*} = 3cm^2 + 4bm^3 = 0$$
$$\Rightarrow m^* = 0, \frac{-3c}{4b}$$



- When $T < T_0 < T_c < T_m$

Here $a < 0$ thus $m^* = 0$ is a local maxima. m_- is global minima & m_+ is local minima.



$T_m \rightarrow$ Overheating Critical point
 $T_0 \rightarrow$ Overcooling critical point

Ice - Water - Steam phase transition is 1st order phase transition.

In Ice $\leftrightarrow$ Water: $T_0 \rightarrow$ Super cooled water

In Water $\leftrightarrow$ Steam: $T_m \rightarrow$ Super heated water

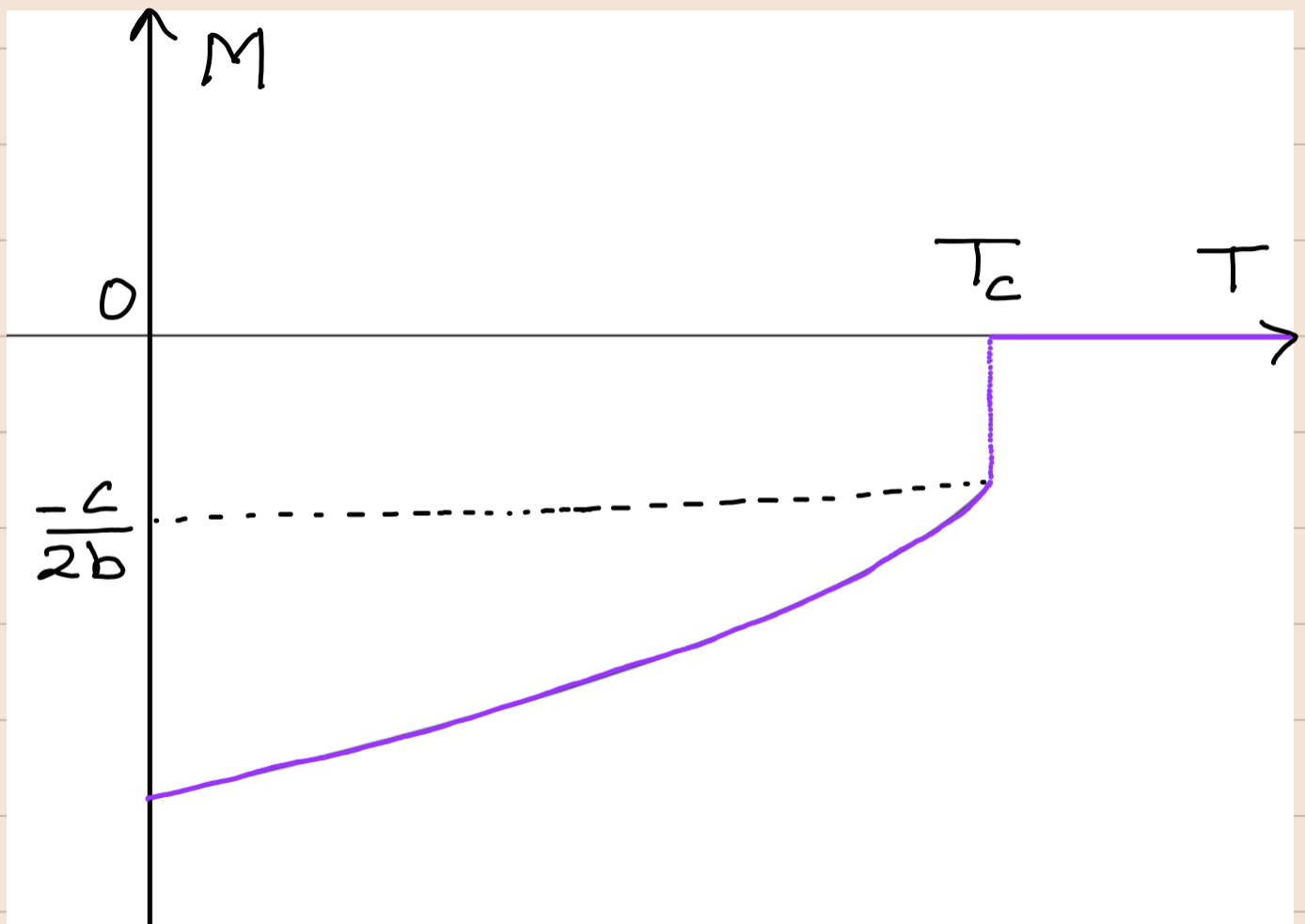
Let M be the global Minimum of Φ . To plot M vs T .

Sol.

$$M = \begin{cases} m_-, & T \leq T_c \\ 0, & T \geq T_c \end{cases}$$

$$M = \begin{cases} \frac{-3c - \sqrt{9c^2 - 32ab}}{8b}, & T < T_c \\ 0, & T > T_c \end{cases}$$

$$T_c = T_0 + \frac{c^2}{4Ab}$$



3)

$$m = B |t|^\beta W_\pm\left(\frac{Dh}{|t|^\Delta}\right)$$

$$\chi(h, t) = \frac{\partial m}{\partial h} = BD |t|^{\beta-\Delta} W'_\pm\left(\frac{Dh}{|t|^\Delta}\right)$$

at $h=0$ $\chi \rightarrow \chi_s(t)$

$$\chi_s = BD |t|^{\beta-\Delta} W'_\pm(0)$$

$$\Rightarrow \chi_s \propto |t|^{\beta-\Delta}$$

But $\chi_s \propto |t|^{-\gamma}$

according to the defⁿ of ' γ '.

$$\Rightarrow \underline{\gamma = \Delta - \beta}$$

Consider the Scaled eqⁿ of state,

$$m = B |t|^\beta W_\pm\left(\frac{Dh}{|t|^\Delta}\right)$$

we know $m \propto h^{1/3}$ at $t=0$.

$\Rightarrow W_{\pm}$ should be such that as $|t| \rightarrow 0$, $W_{\pm}$ should vary as a power law w.r.t its variables such that it can cancel the unwanted 't' dependencies.

$$\Rightarrow W_{\pm} \left(\frac{Dh}{|t|^{\Delta}} \right) \sim \left(\frac{Dh}{|t|^{\Delta}} \right)^{\beta/\Delta} \quad (\text{as } |t| \rightarrow 0)$$

$$\Rightarrow m = |t|^{\beta} \frac{(Dh)^{\beta/\Delta}}{|t|^{\beta}} \quad (|t| \rightarrow 0)$$

$$\Rightarrow m \propto h^{\beta/\Delta} \quad \underline{\text{as } |t| \rightarrow 0}$$

But by defⁿ $m \propto h^{1/2} \quad (t=0)$

$$\Rightarrow \frac{\beta}{\Delta} = \frac{1}{2} \Rightarrow \Delta = 2\beta$$

$$\Rightarrow \underline{\gamma = 2\beta - \beta = \beta(2-1)} \quad \hookrightarrow (1)$$

The Scaling form for the singular part of free energy is,

$$f(h, t) = |t|^{2-\alpha} \mathcal{F}_{\pm} \left[\frac{h}{|t|^{\Delta}} \right]$$

This is Widom's scaling form. $(\Delta = \beta\gamma)$

$$\underbrace{\frac{\partial f}{\partial h}}_m = |t|^{2-\alpha} \left(\frac{1}{|t|^{\beta\gamma}} \right) \mathcal{F}'_{\pm} \left(\frac{h}{|t|^{\beta\gamma}} \right)$$

$$\Rightarrow m = |t|^{(2-\alpha-\beta\gamma)} \mathcal{F}'_{\pm} \left(\frac{h}{|t|^{\beta\gamma}} \right)$$

at $h=0$ we know $m \propto |t|^{\beta}$

$$\Rightarrow \beta = 2 - \alpha - \beta\gamma \quad (2)$$

But $\gamma = \beta(\gamma - 1)$

$$\Rightarrow \beta\gamma = \gamma + \beta \rightarrow \text{Put this in (2)}$$

$$\Rightarrow \beta = 2 - \alpha - \gamma - \beta$$

$$\Rightarrow \underline{\alpha + 2\beta + \gamma = 2}$$

$\hookrightarrow$ Rushbrooke law.

$$\Rightarrow \beta = \left(\frac{2 - \alpha - \gamma}{2} \right)$$

$$\text{By eq}^n (1) \quad \beta = \frac{\gamma}{z-1}$$

$$\Rightarrow \frac{2 - \alpha - \gamma}{2} = \frac{\gamma}{z-1}$$

$$\Rightarrow (2 - \alpha - \gamma)(z-1) = 2\gamma$$

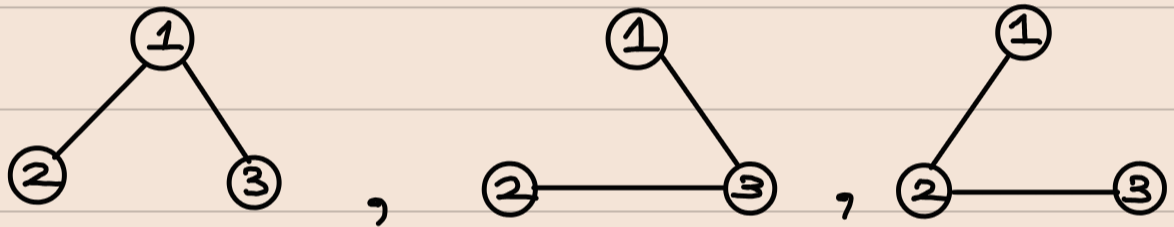
$$\Rightarrow (2 - \alpha - \gamma)z - (2 - \alpha - \gamma) = 2\gamma$$

$$\Rightarrow (2 - \alpha - \gamma)z = 2 - \alpha + \gamma$$

$$\Rightarrow \boxed{z = \frac{2 - \alpha + \gamma}{2 - \alpha - \gamma}}$$

4a) The clusters that contribute to the b_l are the sum of all possible distinct connected graphs of l -particles. We should note that a distinct graph can be equivalently obtained when the bonds b/w the particles is changed but keeping the position of particle fixed.

Eg:

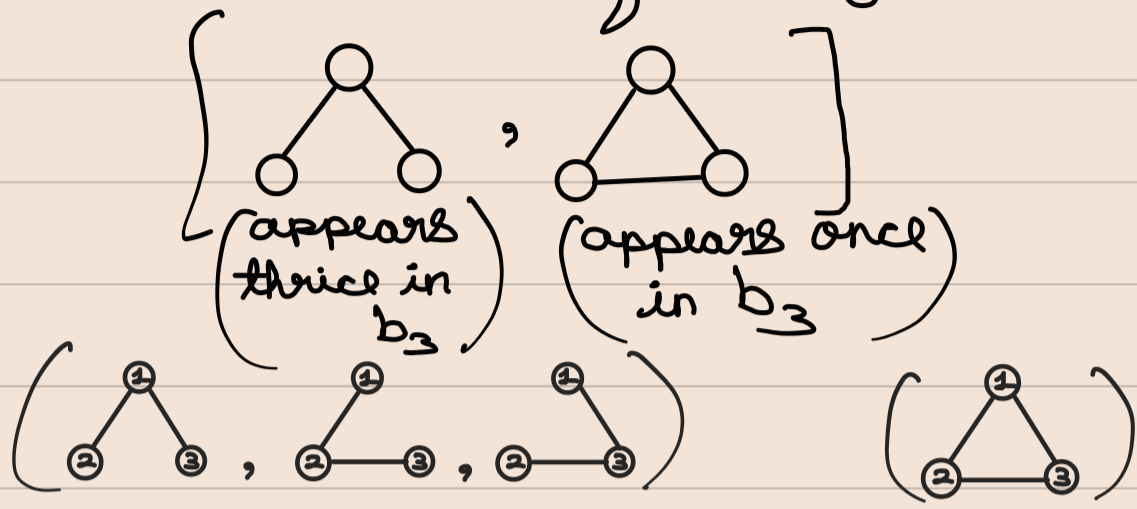


all the above three are distinct.

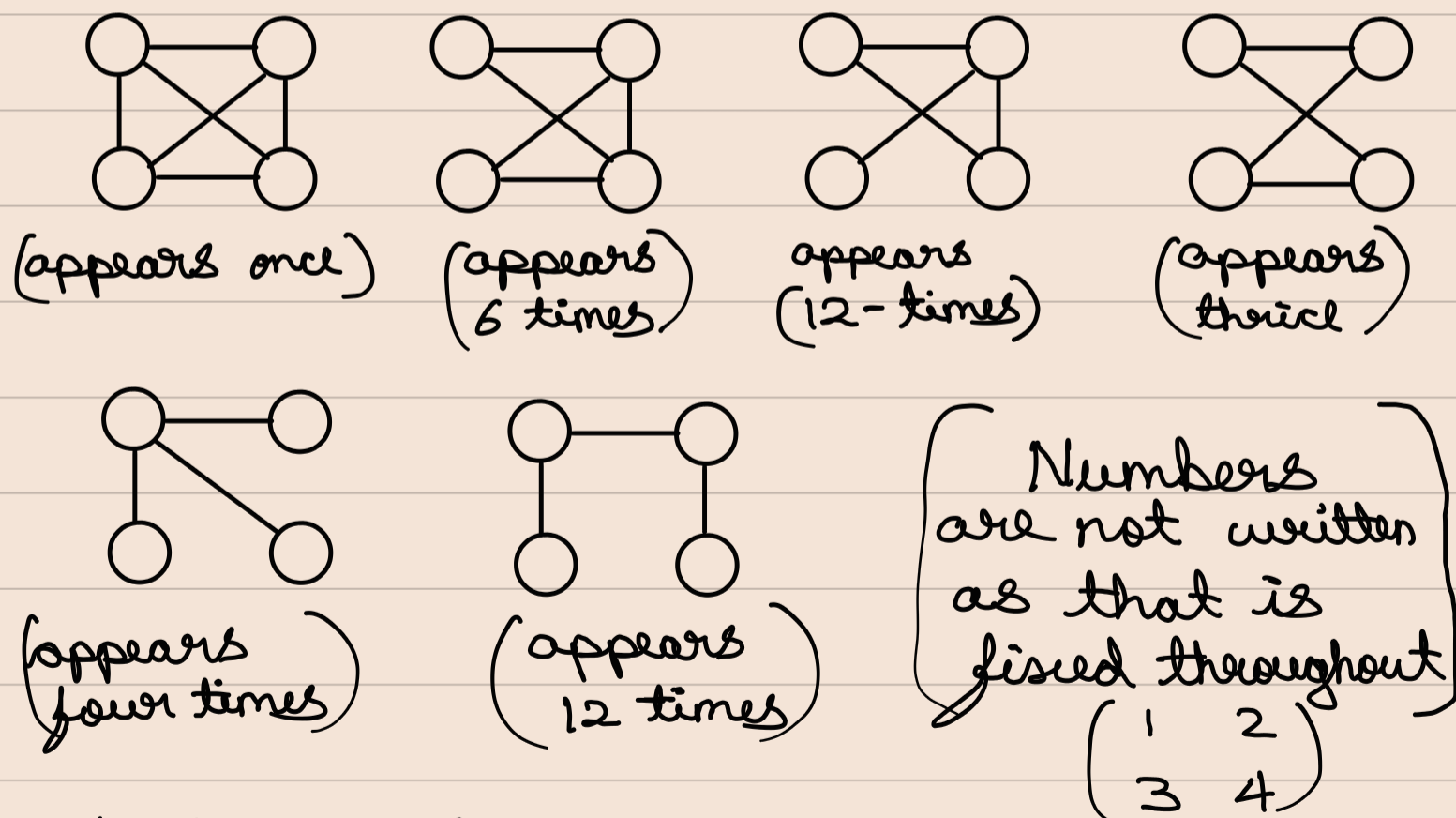
Topologically different clusters

Two l -clusters of same particle size are topologically equivalent if one cluster can be smoothly changed to other without any creation / break of any bonds in the process.

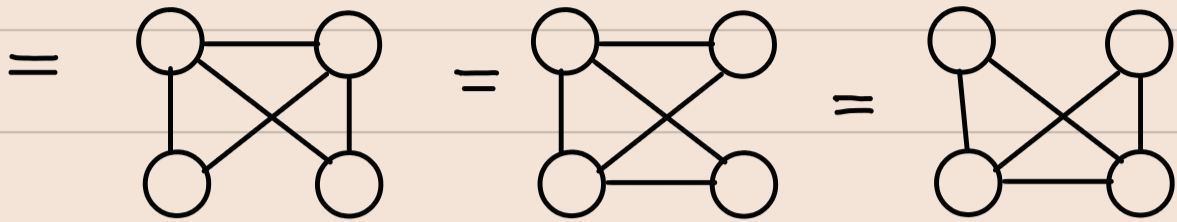
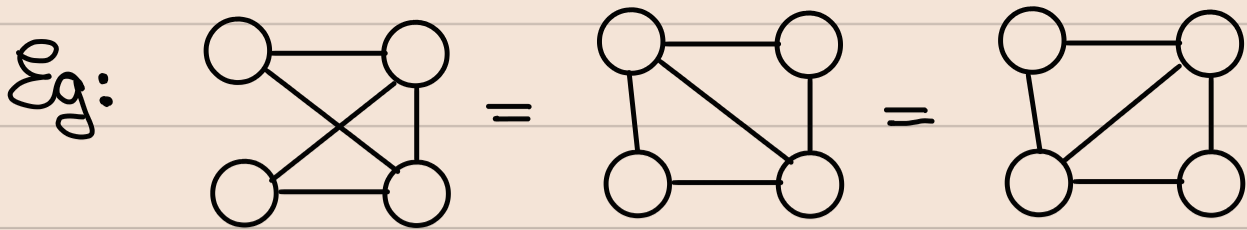
Eg: All possible topologically different 3-clusters are of only two types



All possible topologically different 4-clusters are of 6-types

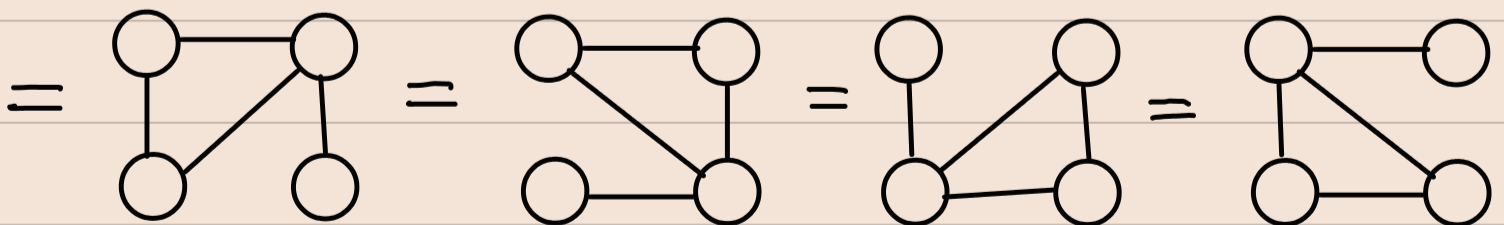
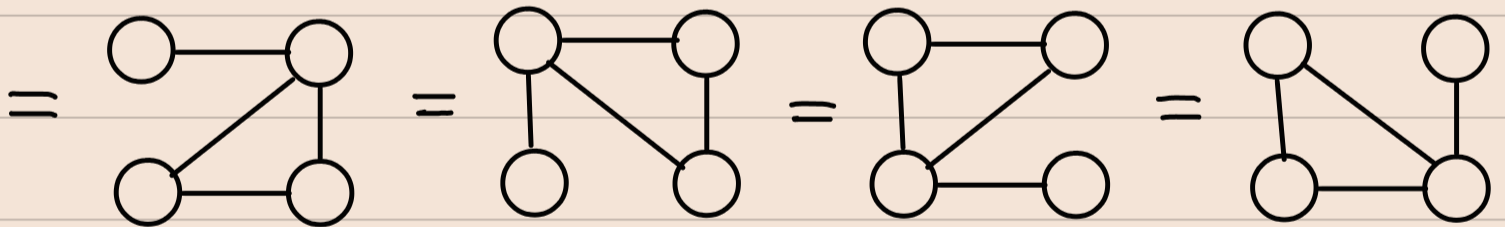
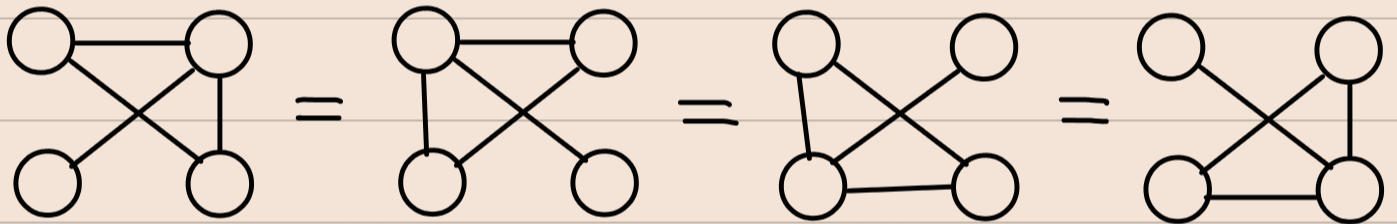


A total of 38 distinct graphs will appear in the expansion of b_4 .



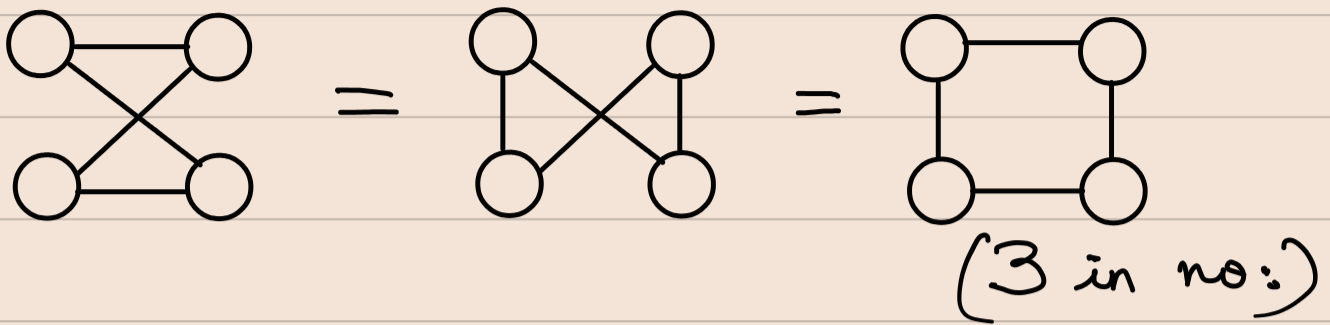
All these are topologically equal
6 in number. (2nd diagram in expansion)

In 3rd diagram above we have (12)

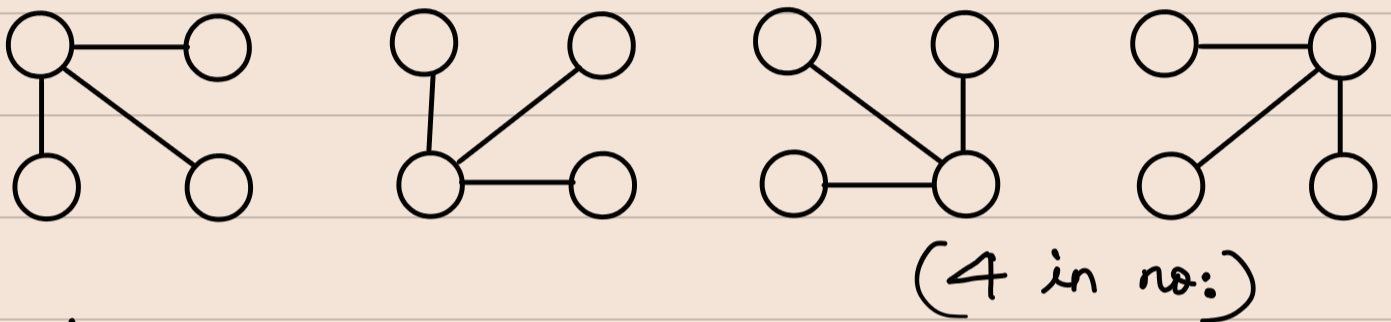


They are all distinct clusters,
but topologically they are same.

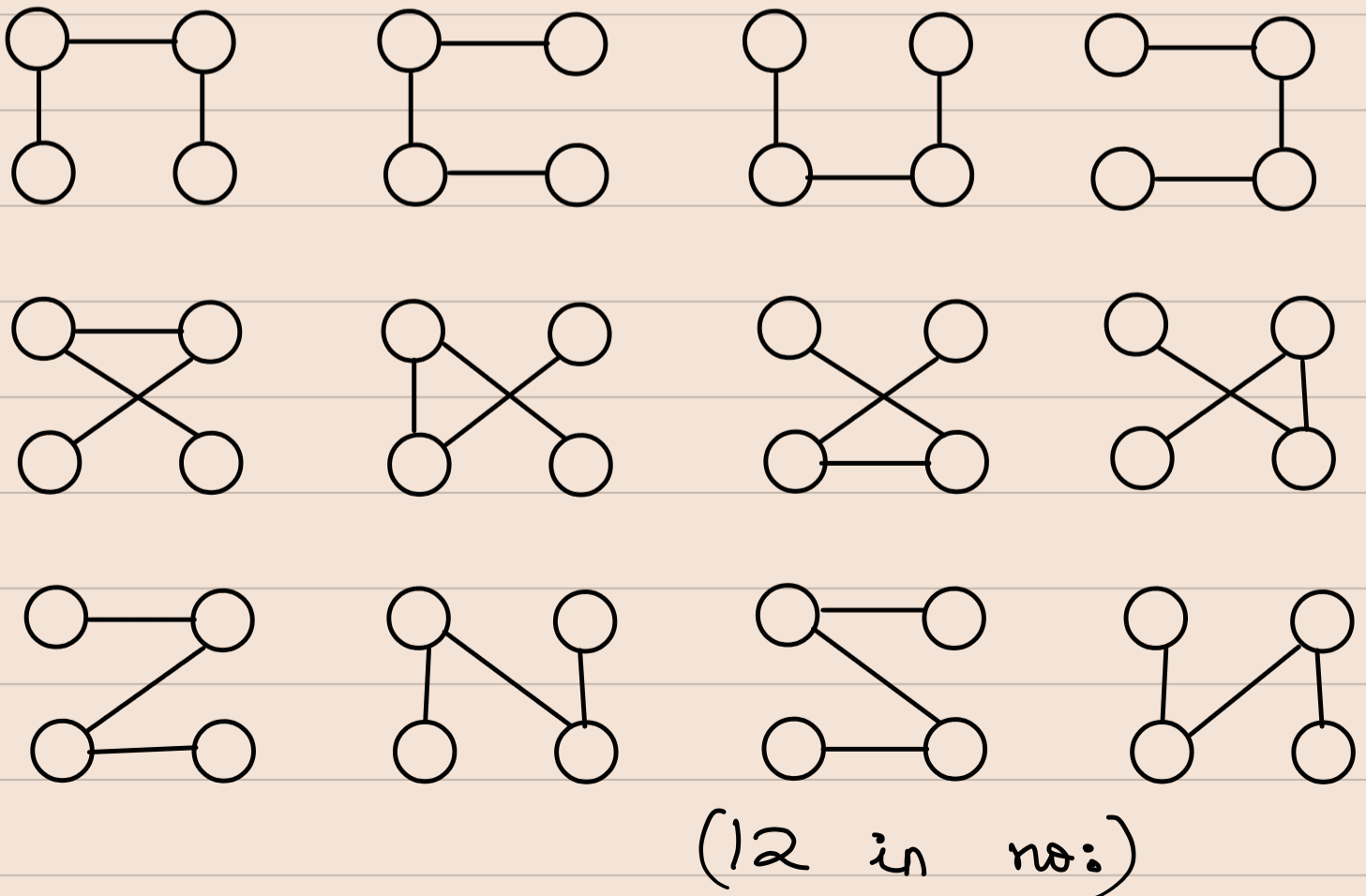
4th diagram in expansion is



5th diagram in expansion is



6th diagram in expansion is



4b) Rods in a 1D Container



$$V_{ij}(|x_i - x_j|) = \begin{cases} \infty, & |x_i - x_j| \leq a \\ 0, & |x_i - x_j| > a \end{cases}$$

$$a_1 = 1 \quad (L \Rightarrow \text{length of container})$$

(1-D volume)

$$a_2 = \frac{-1}{2\lambda L} \left[\begin{array}{c} \circ \\ | \\ \circ \end{array} \right]$$

For 1D

$$a_3 = \frac{-1}{3\lambda^2 L} \left[\begin{array}{ccc} & \textcircled{1} & \\ \textcircled{2} & & \textcircled{3} \\ & \text{---} & \end{array} \right]$$

a_1, a_2 & a_3
are virial
coefficients.

when $x < a$, $f(x) = -1$

when $x > a$, $f(x) = 0$

$$\Rightarrow a_2 = \frac{-1}{2\lambda L} \int_0^L dx_1 dx_2 f_{12}(x_1 - x_2)$$

$$= \frac{-1}{2\lambda} \int_{-L}^L dx f_{12}(x) = \frac{-1}{\lambda} \int_0^L dx f_{12}(x)$$

$$\Rightarrow \boxed{a_2 = \frac{a}{\lambda}}$$

$$a_3 = \frac{-1}{3L\lambda^2} \int_0^L \int_0^L \int_0^L dx_1 dx_2 dx_3 f_{12} f_{13} f_{23}$$

By translational invariance, set x_1 at origin. & vary x_2 & x_3

$$\rightarrow a_3 = \frac{-1}{3\lambda^2} \int_0^L \int_0^L dx_2 dx_3 f(0, x_2) f(x_2, x_3) f(0, x_3)$$

$$f(0, x_2) = -1 \quad \text{when } |x_2| \leq a$$

$$f(0, x_3) = -1 \quad \text{when } |x_3| \leq a$$

$$\& f(x_2, x_3) = -1 \quad \text{when } |x_2 - x_3| \leq a$$

$$\rightarrow a_3 = \frac{-1}{3\lambda^2} \int_{-a}^a dx_2 \int_{-a}^a dx_3 f(|x_2 - x_3|)$$

