

19/02/25

Lecture 13

Cluster & Virial Expansion of Interacting gaseous systems

The canonical ensemble partition function for interacting gas is,

$$Q(N, V, T) = \frac{Z_N^{(c)}(V, T)}{\lambda^{3N} N!}$$

where $\lambda = \frac{h}{\sqrt{2m\pi k_B T}}$ = thermal de Broglie wavelength

And $Z_N^{(c)}(V, T)$ is the Configurational integral that depends on the instantaneous position or configuration of entire system. It is given by,

$$Z_N^{(c)}(V, T) = \int d^{3N} \mathbf{r} e^{-\beta U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)}$$

The potential energy is a function of all the particle's position & can be approximated to pair-interactions $V_{ij}(\vec{r}_i, \vec{r}_j)$

$V_{ij}(\vec{r}_i, \vec{r}_j)$ is the interaction between the particles 'i' & 'j' with position $\vec{r}_i$ & $\vec{r}_j$.
Then $U(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_N)$ is a sum of all possible pair interactions.

$$\Rightarrow U = V_{12} + V_{13} + V_{14} + \dots + V_{1N} \\ + V_{23} + V_{24} + \dots + V_{2N} \\ + V_{34} + \dots + V_{3N} \\ + \dots + V_{N-1,N} \left. \begin{array}{l} \frac{N(N-1)}{2} \\ \text{terms} \\ \text{are} \\ \text{present} \end{array} \right\}$$

$$\Rightarrow U = \sum_{i < j} V_{ij} = \frac{1}{2} \sum_{i \neq j} V_{ij}$$

The configurational can be written as,

$$Z_N = \int d^{3N} \mathbf{r} e^{-\beta \sum_{i < j} V_{ij}}$$

$$\Rightarrow Z_N = \int d^{3N} \mathbf{r} \prod_{i < j} e^{-\beta V_{ij}}$$

We define the Mayer's f -function as

$$f_{ij} = e^{-\beta V_{ij}} - 1$$

$$\Rightarrow Z_N = \int d^{3N} \mathbf{r} \prod_{i < j} (1 + f_{ij})$$

Now $\prod_{i < j} (1 + f_{ij})$ can be written as,

$$\prod_{i < j} (1 + f_{ij}) = \left[\begin{aligned} &(1 + f_{12})(1 + f_{13})(1 + f_{14}) \cdots (1 + f_{1N}) \\ &\times (1 + f_{23})(1 + f_{24}) \cdots (1 + f_{2N}) \\ &\times (1 + f_{34}) \cdots (1 + f_{3N}) \times \cdots (1 + f_{N-1,N}) \end{aligned} \right]$$

$$\Rightarrow \prod_{i < j} (1 + f_{ij}) = 1 + \sum (\text{2-particle connections}) + \sum (\text{3-particle connections}) + \dots$$

- All 2-particle connections are just $f_{12}, f_{13}, \dots$ so, 2 particle connections are given by $\sum_{i < j} f_{ij}$ which has ${}^N C_2 = \frac{N(N-1)}{2}$ distinct terms in it.

- All 3-particle connections are given by $f_{12} f_{13}, f_{12} f_{14}, \dots, f_{12} f_{1N}, f_{12} f_{23}, f_{12} f_{24}, \dots, f_{12} f_{2N}, \dots, f_{12} f_{N-1,N},$
 $f_{13} f_{14}, f_{13} f_{15}, \dots, f_{13} f_{1N}, f_{13} f_{23}, f_{13} f_{24}, \dots, f_{13} f_{2N}, \dots, f_{13} f_{N-1,N}$
 $\dots, f_{1N} f_{23}, f_{1N} f_{24}, \dots, f_{2N}, \dots, f_{1N} f_{N,N-1},$
 $f_{23} f_{24}, \dots, f_{23} f_{2N}, f_{23} f_{34}, \dots, f_{23} f_{3N}, \dots$
 $\dots, f_{N-2,N-1} f_{N-1,N}, f_{N-2,N-1} f_{N-1,N}$

It has ${}^N C_3 = \frac{N(N-1)(N-2)}{3 \times 2}$ terms in it.

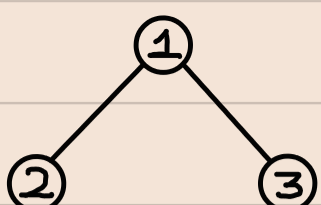
- So we have $1, 2, 3, 4, \dots, l, \dots, N$ particle connections which has ${}^N C_l$ terms in it.

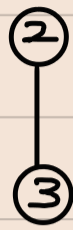
$$\Rightarrow Z_N = \int d^{3N}x \left[1 + \sum_{i < j} f_{ij} + \sum_{i < j < p < q} f_{ij} f_{pq} + \dots \right]$$

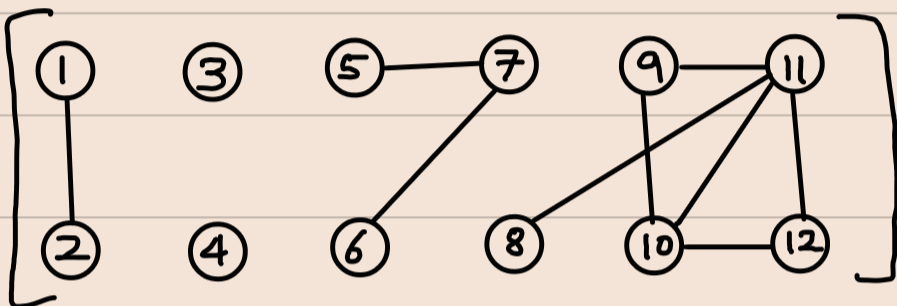
The more intuitive & useful way of writing the configuration integrals is through particle graphs.

An ' n ' particle graph is a collection of ' n ' distinct circles numbered $1, 2, 3, \dots, n$ with any number of lines joining the same number of distinct pairs of circles.

A pair is represented by greek letters $\alpha, \beta, \dots$ so on. If the graph has distinct pairs $\alpha, \beta, \gamma, \dots$ joined by lines, then it represents the term $\int d^{3N}x f_\alpha f_\beta f_\gamma \dots$ which appears in the expansion of Z_N .

Eg:  $= \int d^3x_1 d^3x_2 d^3x_3 f_{12} f_{13}$

 $= \int d^3x_2 d^3x_3 f_{23}$

 will represent

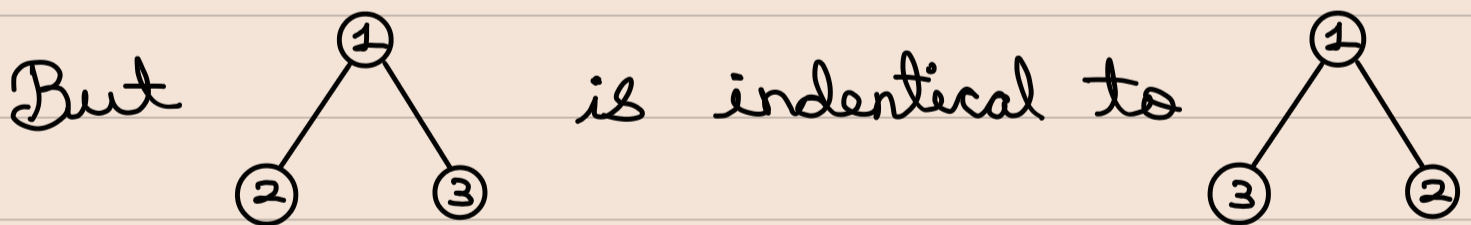
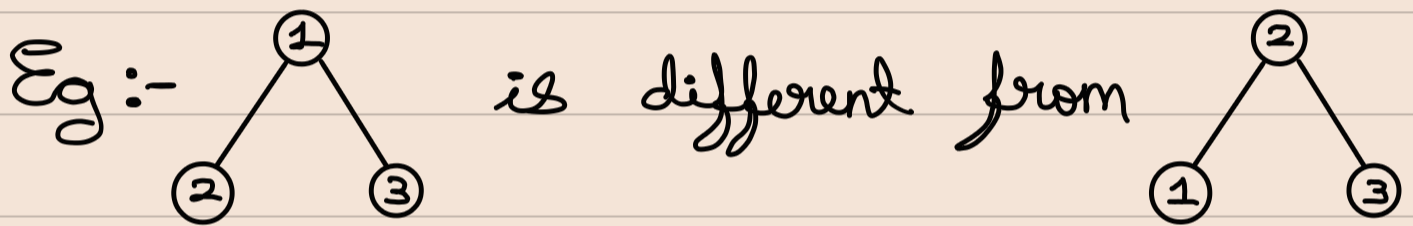
$\int d^3x_1 d^3x_2 \dots d^3x_{12} f_{12} f_{57} f_{67} f_{9,10} f_{8,11} f_{9,11} f_{10,11} f_{11,12} f_{10,12}$

This also equivalent to the integral

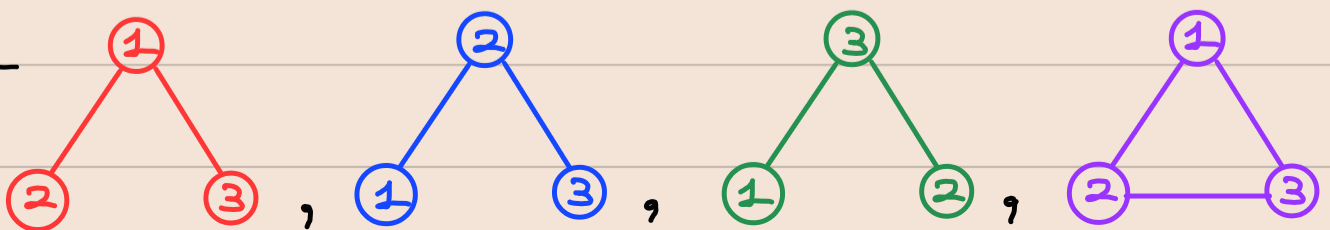
$[\textcircled{3}] \cdot [\textcircled{4}] \cdot [\textcircled{1}-\textcircled{2}] \cdot \left[\begin{array}{c} \textcircled{5} - \textcircled{7} \\ \textcircled{6} \end{array} \right] \left[\begin{array}{c} \textcircled{9} - \textcircled{11} \\ \textcircled{8} - \textcircled{10} \\ \textcircled{10} - \textcircled{12} \\ \textcircled{11} - \textcircled{12} \end{array} \right]$

Where each factor corresponds to a connected graph where every circle is attached to atleast one line & every circle is directly or indirectly attached to all other circles.

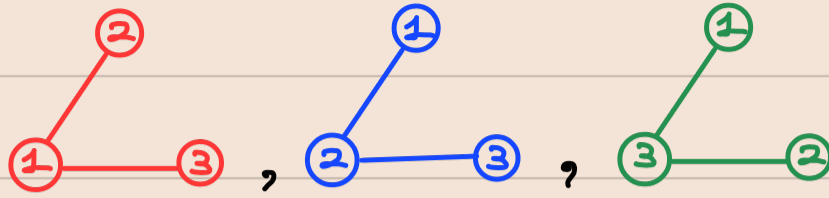
Note: If the set of distinct pairs $\{\alpha, \beta, \gamma, \dots\}$ is joined by lines in a given graph, it is different from another graph where the pairing is $\{\alpha', \beta', \gamma', \dots\}$ even if it looks the same & has same numerical value for the integral.



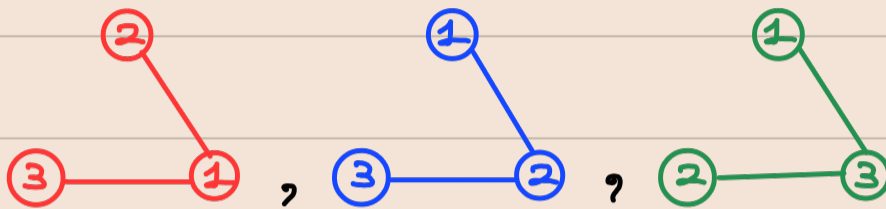
Thus all possible distinct graphs for three connected particles ①, ② & ③ are



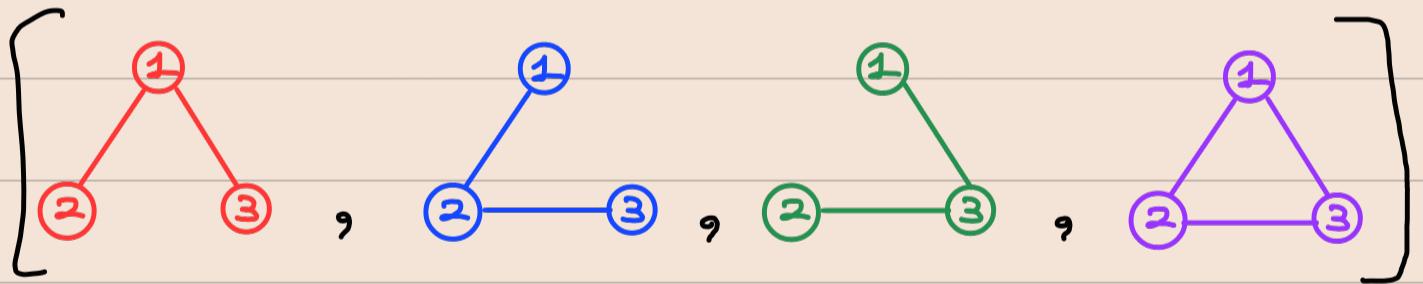
But the first three graphs in the above set is exactly identical to



And also identical to the set



Another way of writing all possible distinct graphs for three connected particles ①, ② & ③ is



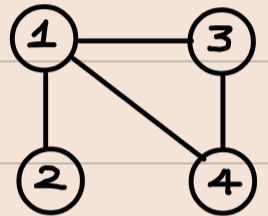
This way of fixing particle's position & then changing the bond configuration is useful & has an added advantage of removing unnecessary repetition.

Thus there are four distinct 3-particle graph.

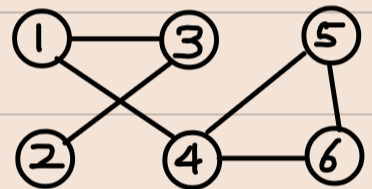
Cluster

An ' l '-cluster is defined as an ' l ' particle connected graph where all the ' l ' particles are connected to to all other particles directly or indirectly.

Eg: This is a 4-cluster



This is a 6-cluster



Cluster integral ' $b_l(V, T)$ '

It is defined as,

$$b_l(V, T) = \frac{\text{Sum of all distinct } l\text{-clusters}}{l! \lambda^{3(l-1)} V}$$

The denominator is chosen such that $b_l(V, T)$ is dimensionless and $\lim_{V \rightarrow \infty} b_l(V, T)$ is a finite number.

$$b_1 = \frac{1}{V} [\textcircled{1}] = \frac{1}{V} \int d^3x_1 = 1$$

$$b_2 = \frac{1}{2! \lambda^3 V} [\textcircled{1} - \textcircled{2}] = \frac{1}{2 \lambda^3 V} \int d^3x_1 d^3x_2 f_{12}$$

If $f_{12}(\vec{x}_1, \vec{x}_2)$ is a function of $\vec{x}_{12}$ given by $\vec{x}_1 - \vec{x}_2$ then we can change the dummy variable $\vec{x}_1 \rightarrow \vec{x}_2 + \vec{x}_{12}$ where $\vec{x}_2$ is constant w.r.t $\vec{x}_{12}$.

$$\Rightarrow d^3x_1 = d^3x_{12} \Rightarrow b_2 = \frac{1}{2 \lambda^3 V} \int d^3x_{12} d^3x_2 f_{12}(\vec{x}_{12})$$

$$\int d^3x_2 = V \Rightarrow b_2 = \frac{1}{2 \lambda^3} \int d^3x_{12} f_{12}(\vec{x}_{12})$$

$$b_3 = \frac{1}{3! \lambda^6 V} \left[\begin{array}{c} \textcircled{1} \\ \diagup \quad \diagdown \\ \textcircled{2} \quad \textcircled{3} \end{array} + \begin{array}{c} \textcircled{1} \\ \diagup \quad \text{---} \quad \diagdown \\ \textcircled{2} \quad \textcircled{3} \end{array} + \begin{array}{c} \textcircled{1} \\ \text{---} \quad \diagdown \\ \textcircled{2} \quad \textcircled{3} \end{array} + \begin{array}{c} \textcircled{1} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \textcircled{2} \quad \textcircled{3} \end{array} \right]$$

$$= \frac{1}{3! \lambda^6 V} \int d^3x_1 d^3x_2 d^3x_3 \left[f_{12} f_{13} + f_{12} f_{23} + f_{13} f_{23} + f_{12} f_{13} f_{23} \right]$$

$$\begin{array}{c} \textcircled{1} \\ \diagup \quad \diagdown \\ \textcircled{2} \quad \textcircled{3} \end{array} = \int d^3x_1 d^3x_2 d^3x_3 f_{12} f_{13} \\ = \int d^3x_1 d^3x_{12} d^3x_{13} f_{12}(\vec{x}_{12}) f_{13}(\vec{x}_{13})$$

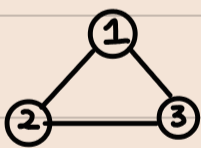
$$\Rightarrow \underline{\text{Diagram 1}} = V \int d^3x_{12} d^3x_{13} f_{12}(x_{12}) f_{13}(x_{13})$$

$$\begin{aligned} \text{Diagram 2} &= \int d^3x_1 d^3x_2 d^3x_3 f_{12} f_{23} \\ &= \int d^3x_{12} d^3x_2 d^3x_{23} f_{12}(x_{12}) f_{23}(x_{23}) \end{aligned}$$

$$\Rightarrow \underline{\text{Diagram 3}} = V \int d^3x_{12} d^3x_{23} f_{12}(x_{12}) f_{23}(x_{23})$$

$$\begin{aligned} \text{Diagram 4} &= \int d^3x_1 d^3x_2 d^3x_3 f_{13} f_{23} \\ &= \int d^3x_{13} d^3x_{23} d^3x_3 f_{13}(x_{13}) f_{23}(x_{23}) \end{aligned}$$

$$\Rightarrow \underline{\text{Diagram 5}} = V \int d^3x_{13} d^3x_{23} f_{13}(x_{13}) f_{23}(x_{23})$$

To evaluate  we need to go to the centroid coordinate system $\vec{R} = \frac{\vec{x}_1 + \vec{x}_2 + \vec{x}_3}{3}$

$$\vec{r} = \vec{x}_1 - \vec{x}_2 \quad \& \quad \vec{r}' = \left(\frac{\vec{x}_1 + \vec{x}_2}{2} \right) - \vec{x}_3$$

The jacobian of transformation is 1.

$$\text{Thus } d^3x_1 d^3x_2 d^3x_3 = d^3R d^3r d^3r'$$

$$\Rightarrow f_{12} \rightarrow f(\vec{r}), \quad f_{13} = f(\vec{r}_1 - \vec{r}_3) \\ = f\left[\vec{r}_1 + \vec{r}' - \frac{\vec{r}_1}{2} - \frac{\vec{r}_2}{2}\right]$$

$$\Rightarrow f_{13} = f\left[\vec{r}' + \frac{\vec{r}_1 - \vec{r}_2}{2}\right] = f_{13}\left(\vec{r}' + \frac{\vec{r}}{2}\right)$$

$$\& \quad f_{23} = f_{23}(\vec{r}_2 - \vec{r}_3) = f_{23}\left[\vec{r}_2 + \vec{r}' - \left(\frac{\vec{r}_1 + \vec{r}_2}{2}\right)\right]$$

$$\Rightarrow f_{23} = f_{23}\left[\vec{r}' - \frac{\vec{r}}{2}\right]$$

$$\Rightarrow \triangle_{123} = \int d^3r_1 d^3r_2 d^3r_3 f_{12} f_{13} f_{23}$$

$$= \int d^3R d^3r d^3r' f_{12}(r) f_{13}\left(\vec{r}' + \frac{\vec{r}}{2}\right) f_{23}\left(\vec{r}' - \frac{\vec{r}}{2}\right) \\ \hookrightarrow \text{gives Volume term}$$

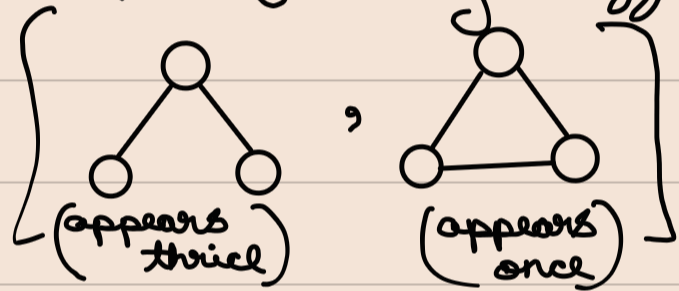
$$\Rightarrow \triangle_{123} = V \int d^3r d^3r' f_{12}(r) f_{13}\left(\vec{r}' + \frac{\vec{r}}{2}\right) f_{23}\left(\vec{r}' - \frac{\vec{r}}{2}\right)$$

$$b_3 = \frac{1}{3! \lambda^6} \left[\int d^3r_{12} d^3r_{13} f_{12}(r_{12}) f_{13}(r_{13}) \right. \\ + \int d^3r_{12} d^3r_{23} f_{12}(r_{12}) f_{23}(r_{23}) \\ + \int d^3r_{13} d^3r_{23} f_{13}(r_{13}) f_{23}(r_{23}) \\ \left. + \int d^3r d^3r' f_{12}(r) f_{13}\left(\vec{r}' + \frac{\vec{r}}{2}\right) f_{23}\left(\vec{r}' - \frac{\vec{r}}{2}\right) \right]$$

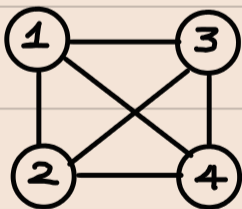
Topologically different clusters

Two clusters of same size are said to be topologically same if one cluster can be smoothly changed to another without creating or breaking any bonds. Also the value of the integral they represent are same.

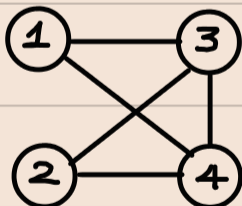
Eg: • All possible topologically different 3-clusters are



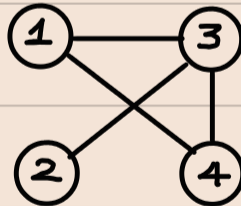
• All possible topologically different 4-clusters are of 6-types



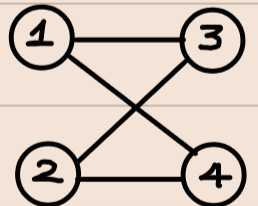
(appears once)



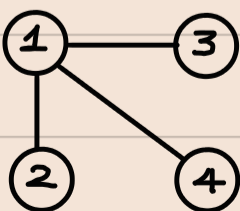
(appears 6 times)



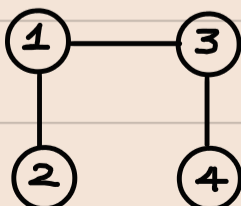
appears (12-times)



(appears thrice)



(appears four times)



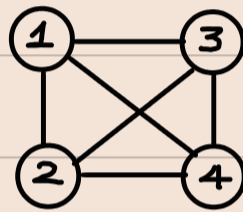
(appears 12 times)

If numbers are not written then it is

1	2
3	4

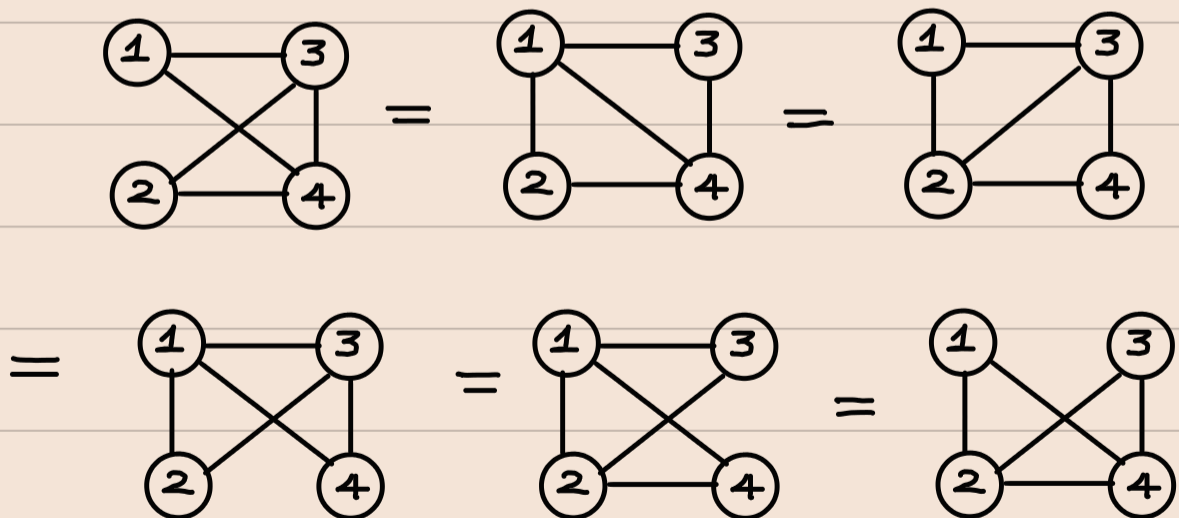
In the diagrammatic expansion of b_4 the diagrams that appear in the sum can be grouped in terms of their topology.

(i) The diagram where all the bonds are connected appears once which is given by

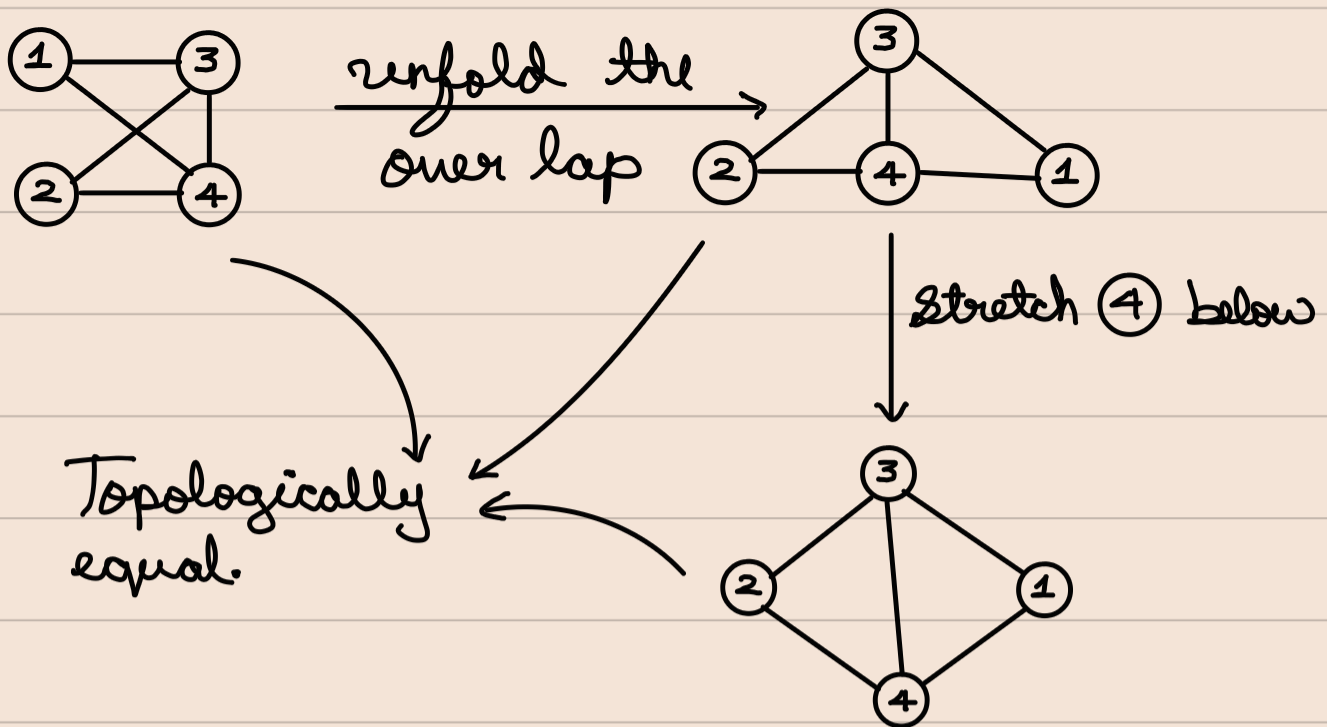


(appears once)

(ii) The diagrams with 5 bonds are

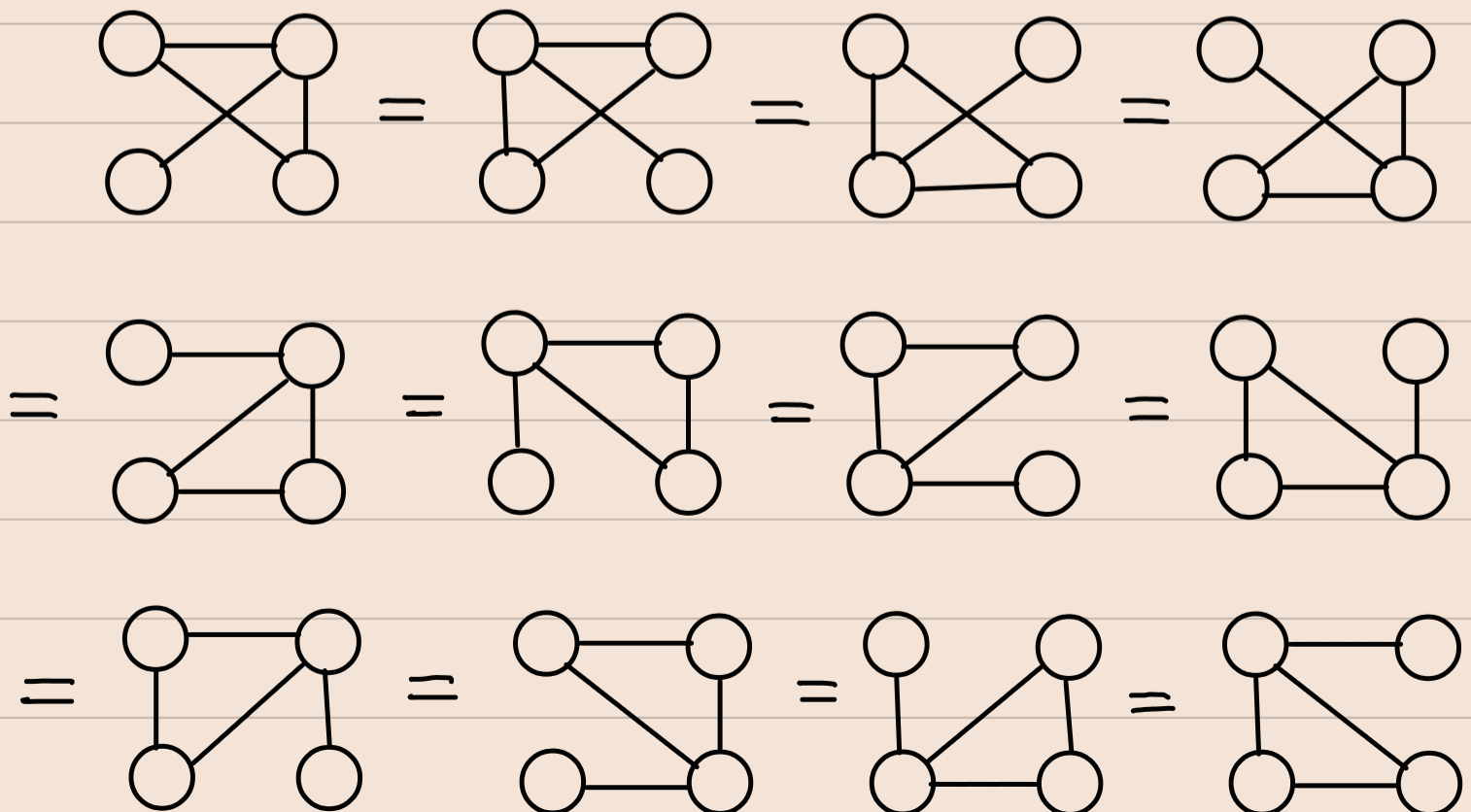


They are all distinct clusters, but topologically they are the same.
(2nd diagram in expansion)

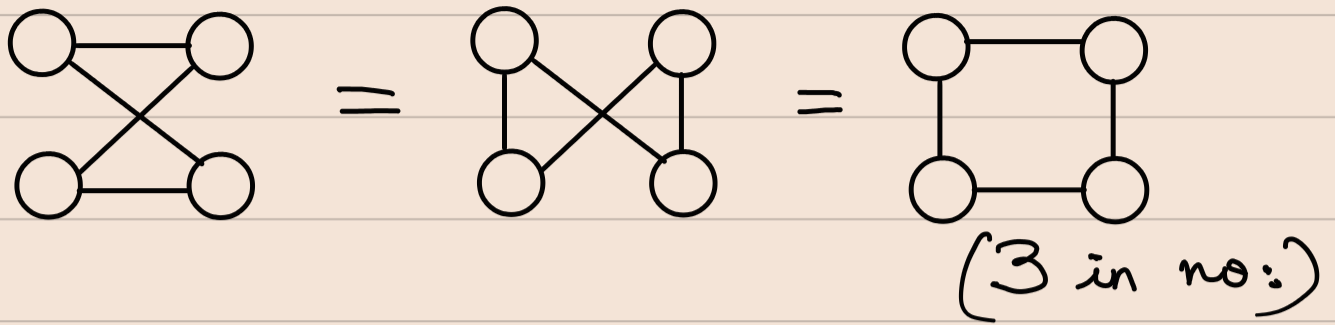


So Even though there are topologically six different 4-clusters, there are 38 distinct 4-clusters.

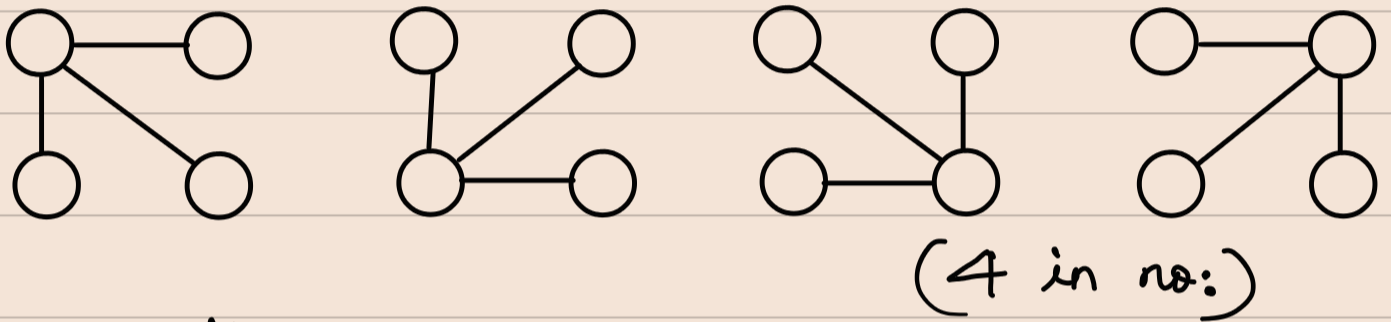
(iii) 3rd diagram in b_4 expansion are



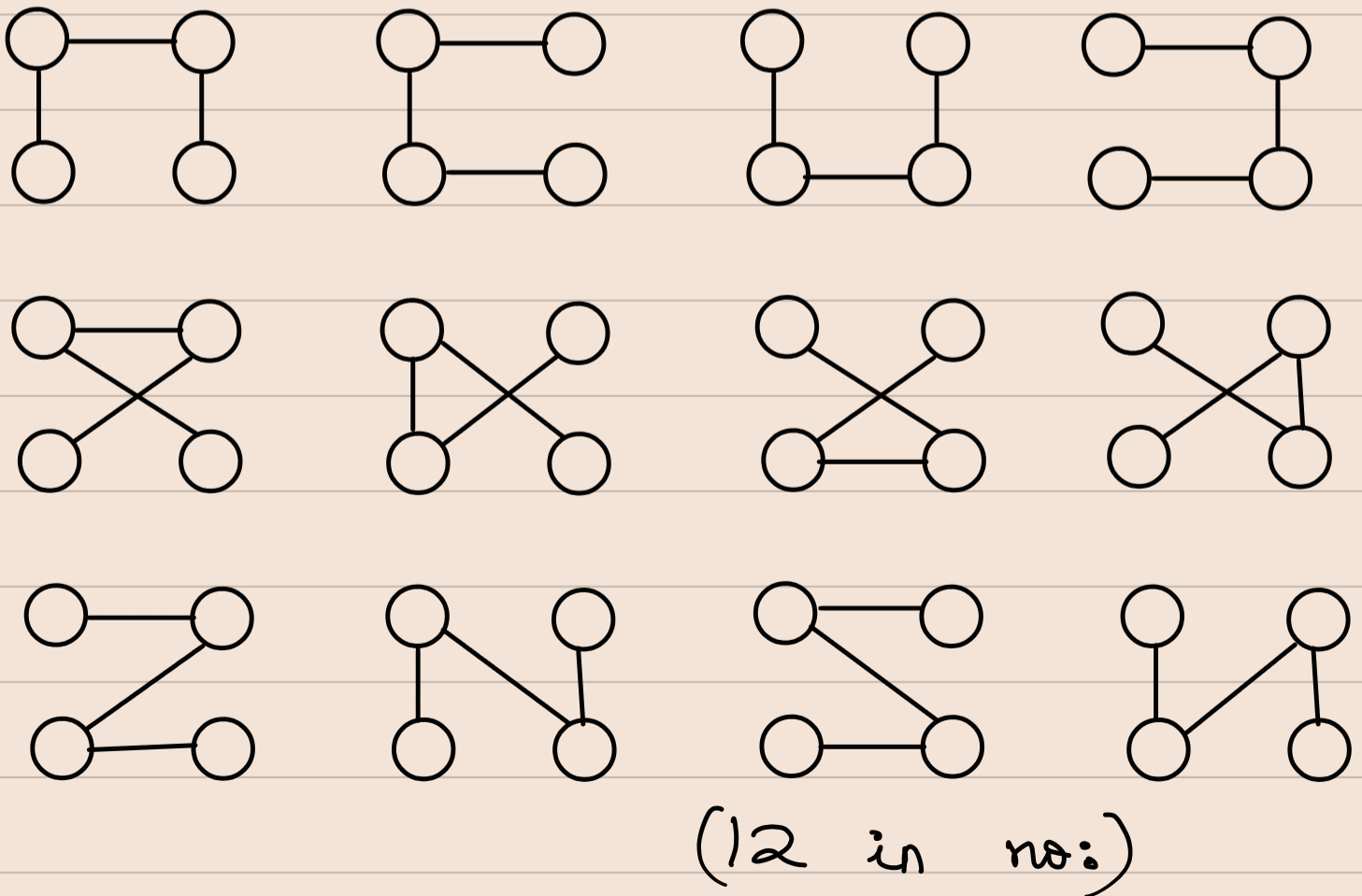
(iv) 4th diagram in expansion is



(v) 5th diagram in expansion is



(vi) 6th diagram in expansion is



Thus we can equivalently write

$$b_4 = \frac{1}{4! \lambda^4 V} \left[\begin{array}{ccc} \begin{array}{c} \text{Graph 1: } 1-2, 1-3, 1-4, 2-3, 2-4, 3-4 \\ +6 \end{array} & \begin{array}{c} \text{Graph 2: } 1-2, 1-3, 1-4, 2-3, 3-4 \\ +12 \end{array} & \begin{array}{c} \text{Graph 3: } 1-2, 1-3, 1-4, 2-4, 3-4 \\ +12 \end{array} \\ \\ \begin{array}{c} \text{Graph 4: } 1-2, 1-3, 2-3, 2-4, 3-4 \\ +3 \end{array} & \begin{array}{c} \text{Graph 5: } 1-2, 1-3, 1-4, 2-3, 2-4 \\ +4 \end{array} & \begin{array}{c} \text{Graph 6: } 1-2, 1-3, 1-4, 2-3, 3-4 \\ +12 \end{array} \end{array} \right]$$

With this convention we can write that the configurational integral Z_N as the sum of all distinct 'N' graphs.

$$\Rightarrow Z_N = \text{Sum of all distinct } N \text{ Particle graphs}$$

(Note: Above statement doesn't need the graphs to be all connected)

Eg: Consider the system of $N=3$ particles. Z_3 is given by

$$Z_3 = \int d^3x_1 d^3x_2 d^3x_3 (1+f_{12})(1+f_{13})(1+f_{23})$$

$$Z_3 = \int d^3x_1, d^3x_2, d^3x_3 \left[1 + f_{12} + f_{13} + f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23} \right]$$

$$= \left[\begin{array}{ccc} \textcircled{1} & & \\ \textcircled{2} & & \textcircled{3} \end{array} \right] + \left[\begin{array}{ccc} \textcircled{1} & & \\ \textcircled{2} & \diagup & \textcircled{3} \end{array} \right] + \left[\begin{array}{ccc} \textcircled{1} & & \\ \textcircled{2} & & \textcircled{3} \diagdown \end{array} \right] + \left[\begin{array}{ccc} \textcircled{1} & & \\ \textcircled{2} & \text{---} & \textcircled{3} \end{array} \right]$$

$$+ \left[\begin{array}{ccc} & \textcircled{1} & \\ \textcircled{2} & \diagup \quad \diagdown & \textcircled{3} \end{array} \right] + \left[\begin{array}{ccc} & \textcircled{1} & \\ \textcircled{2} & \diagup & \textcircled{3} \text{---} \end{array} \right] + \left[\begin{array}{ccc} & \textcircled{1} & \\ \textcircled{2} \text{---} & & \textcircled{3} \diagdown \end{array} \right] + \left[\begin{array}{ccc} & \textcircled{1} & \\ \textcircled{2} & \text{---} & \textcircled{3} \diagup \diagdown \end{array} \right]$$

$\rightarrow Z_{N=3} = \text{Sum of all distinct 3 particle graphs}$

We can also write Z_4 as

$$Z_4 = \int d^3x_1, d^3x_2, d^3x_3, d^3x_4 \left[(1+f_{12})(1+f_{13})(1+f_{14})(1+f_{23}) \times (1+f_{24})(1+f_{34}) \right]$$

It has $2^6 = 64$ terms in the expansion which can be written diagrammatically as,

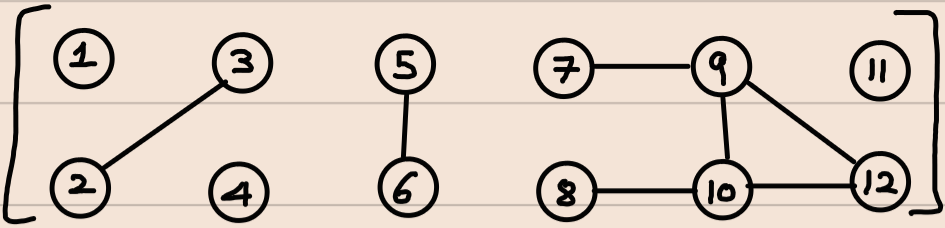
$$\begin{aligned}
Z_4 = & \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ \textcircled{2} & \textcircled{4} \end{array} \right] + 6 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ | & \\ \textcircled{2} & \textcircled{4} \end{array} \right] + 12 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ | & \text{---} \\ \textcircled{2} & \textcircled{4} \end{array} \right] \\
& + 3 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ | & | \\ \textcircled{2} & \textcircled{4} \end{array} \right] + 4 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ | & / \\ \textcircled{2} & \textcircled{4} \end{array} \right] + 12 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ | & \text{---} \\ \textcircled{2} & \textcircled{4} \end{array} \right] \\
& + 4 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ | & \backslash \\ \textcircled{2} & \textcircled{4} \end{array} \right] + 3 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ / & \backslash \\ \textcircled{2} & \textcircled{4} \end{array} \right] + 12 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ / & \backslash \\ \textcircled{2} & \textcircled{4} \end{array} \right] \\
& + 6 \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ / & \backslash \\ \textcircled{2} & \textcircled{4} \end{array} \right] + \left[\begin{array}{cc} \textcircled{1} & \textcircled{3} \\ / & \backslash \\ \textcircled{2} & \textcircled{4} \end{array} \right]
\end{aligned}$$

To handle the integral when 'N' is very large, we need to group the terms efficiently. One way is to define the cluster integrals.

Any 'N' particle graph is a product of a number of clusters of which m_l of them are l-clusters. Consider an

N-particle graph, it may not be fully connected. So it can be written as a product of clusters which has m_l - number of l-clusters.

Eg: Consider a $N=12$ graph



Here for

$l=1$	$m_1=3$
$l=2$	$m_2=2$
$l=3$	$m_3=0$
$l=4$	$m_4=0$
$l=5$	$m_5=1$

for $l=6,7,8,9,10,11,12 \rightarrow m_l=0$.

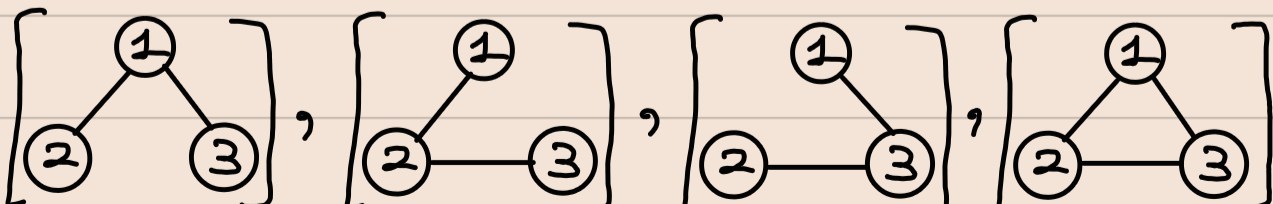
$\Rightarrow \{m_l\} = \{3, 2, 0, 0, 1, 0, 0, 0, 0, 0, 0, 0, 0\}$

now
$$\sum_{l=1}^N l m_l = 1 \times 3 + 2 \times 2 + 5 \times 1$$

$$= 3 + 4 + 5 = 12 = N$$

If a set $\{m_l\}$ that satisfies $\sum_{l=1}^N l m_l = N$ is given, it will not uniquely specify the graph. Since an l -cluster can be written in many ways.

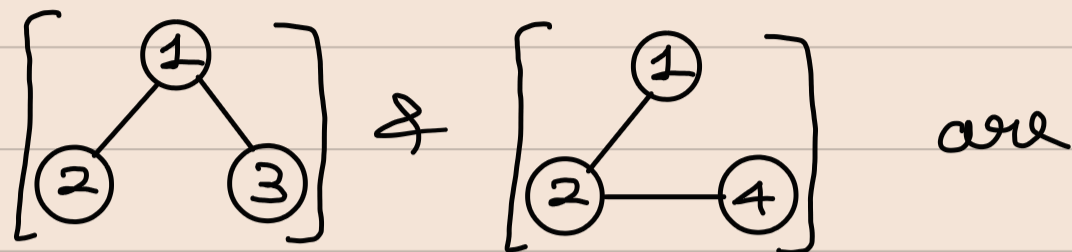
Eg:



all represents 3-cluster.

And also there are many ways to assign which particle belong to which cluster.

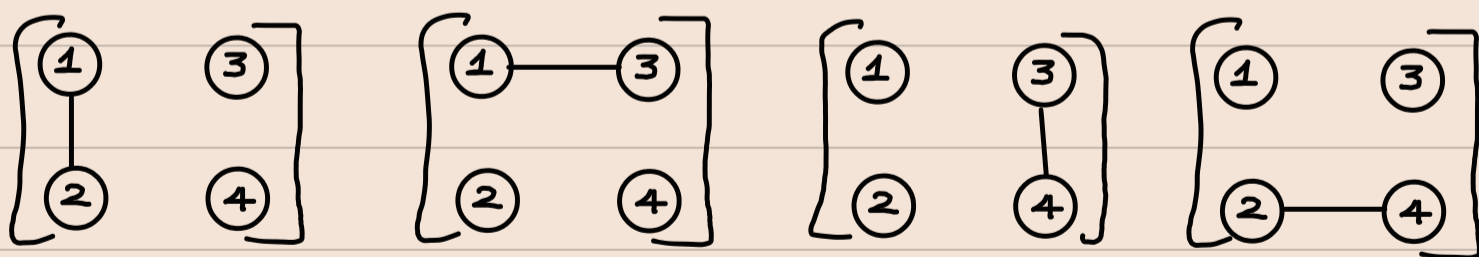
Eg:



also possible 3-clusters.

Thus given a set $\{m_i\}$, it actually represents a collection of graphs. Eg: $\{m_i\} = \{2, 1\}$, it is a 4-particle graph ($1 \times 2 + 2 \times 1$)

$\{2, 1\}$ represents



The sum of all the graphs corresponding to $\{m_i\}$ is denoted by $S\{m_i\}$.

Eg:

$$S\{2, 1\} = \left(\begin{array}{|c|c|} \hline \textcircled{1} & \textcircled{3} \\ \hline \textcircled{2} & \textcircled{4} \\ \hline \end{array} \right) + \left(\begin{array}{|c|c|} \hline \textcircled{1} - \textcircled{3} & \\ \hline \textcircled{2} & \textcircled{4} \\ \hline \end{array} \right) + \left(\begin{array}{|c|c|} \hline \textcircled{1} & \textcircled{3} \\ \hline \textcircled{2} & \textcircled{4} \\ \hline \end{array} \right) + \left(\begin{array}{|c|c|} \hline \textcircled{1} & \textcircled{3} \\ \hline \textcircled{2} - \textcircled{4} & \\ \hline \end{array} \right) + \dots$$

there could be other terms of Particles 5, 6, ... if they exist

Then the claim is,

$$Z_N = \sum_{\{m_\ell\}} S\{m_\ell\}$$

$\sum_{\{m_\ell\}} =$ Sum over all possible Configuration of $\{m_\ell\}$ which satisfy $\sum_\ell l m_\ell = N$

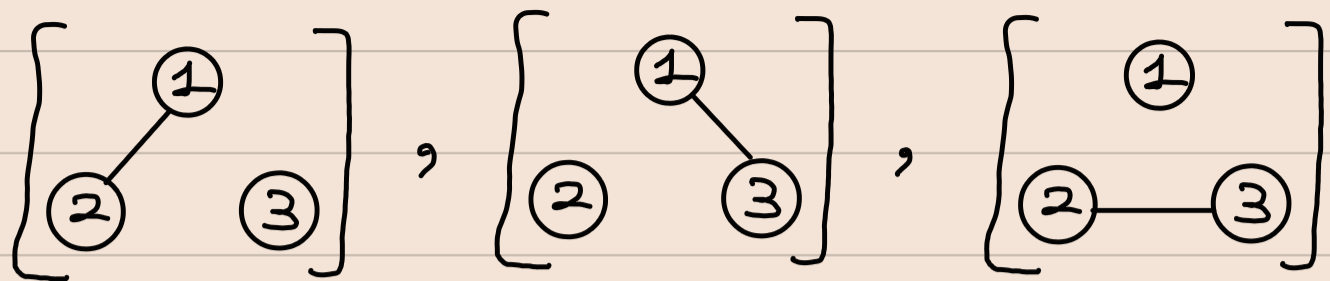
Eg:- Consider three particle $N=3$ System.

Then possible l -values is $l=1, 2, 3$, then $\{m_\ell\}$ will always have '3' elements. And the possible value of $\{m_\ell\}$ are $\{3, 0, 0\}$, $\{1, 1, 0\}$, $\{0, 0, 1\}$

• $\{3, 0, 0\}$ corresponds to

$$\left(\begin{array}{|c|c|} \hline \textcircled{1} & \\ \hline \textcircled{2} & \textcircled{3} \\ \hline \end{array} \right) = \int d^3x_1 d^3x_2 d^3x_3 (1) = V^3$$

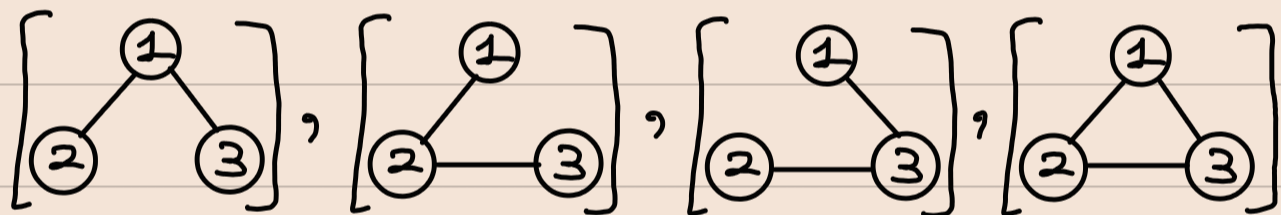
• $\{1, 1, 0\}$ corresponds to



$$S(\{1, 1, 0\}) = \int d^3x_1 d^3x_2 d^3x_3 (f_{12} + f_{13} + f_{23})$$

$$= V^2 \left[\int d^3x_{12} f_{12} + \int d^3x_{13} f_{13} + \int d^3x_{23} f_{23} \right]$$

• $\{0, 0, 3\}$ corresponds to



$$S(\{0, 0, 3\}) = \int d^3x_1 d^3x_2 d^3x_3 (f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23})$$

Now $S(\{3, 0, 0\}) + S(\{1, 1, 0\}) + S(\{0, 0, 3\})$ is just the Z_3 given by

$$Z_3 = \int d^3x_1 d^3x_2 d^3x_3 (1 + f_{12})(1 + f_{13})(1 + f_{23})$$

$$Z_3 = \int d^3x_1 d^3x_2 d^3x_3 \left[1 + f_{12} + f_{13} + f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23} \right]$$

Cluster expansion of Partition function

To get cluster expansion of $Q_N(V, T)$ we first need to address the expansion of $S\{m_e\}$. $\{m_e\} = \{m_1, m_2, m_3, \dots\}$ which satisfy $\sum_e m_e = N$.

$\{m_1, m_2, m_3, \dots\}$ is nothing but
 $= \underbrace{\{[O][O] \dots [O]\}}_{m_1 \text{ factors}} \times \underbrace{\{[O-O][O-O] \dots [O-O]\}}_{m_2 \text{ factors}}$

$\times \underbrace{\left\{ \begin{array}{c} \text{[Diagram 1: V-shape]} \\ \text{[Diagram 2: Zig-zag]} \\ \text{[Diagram 3: Triangle]} \\ \dots \\ \text{[Diagram 4: Square]} \end{array} \right\}}_{m_3 \text{ factors}}$
 $\times \dots$ So on.

Note: We need to fill the numbers $1, 2, \dots, N$ also in these N -number of circles. We have many possible permutations of these numbers which will be defined by some set $\{m_e\}$. Then if we add up all possibilities then we obtain $S\{m_e\}$.

$$\Rightarrow S\{m_l\} = \sum_P [O]^{m_1} [O-O]^{m_2} \times \left[\begin{array}{c} \text{graph 1} \\ + \text{graph 2} \\ + \text{graph 3} \\ + \text{graph 4} \end{array} \right]^{m_3} \times \dots \text{so. on.}$$

$$\Rightarrow S\{m_l\} = \sum_P \prod_{l=1}^N \left[\text{sum of all distinct } l\text{-cluster graphs} \right]^{m_l}$$

$\sum_P \Rightarrow$ extends over all distinct ways of numbering the circles from 1 to N.

Note that the numerical value of the integral is independent of the numbering of circles.

Eg: $\left(\begin{array}{c} \text{graph 1} \\ \text{all permutation} \end{array} \right) = \left(\begin{array}{c} \text{graph 2} \\ \text{all permutation} \end{array} \right)$

Their integral numerical value is same.

Since different numbering of circles won't alter value of the below

$$\left[\prod_{l=1}^N \left(\text{Sum of all distinct } l\text{-cluster graphs} \right) \right]^{m_l} \Rightarrow \text{It is independent of Permutation.}$$

Thus $S\{m_l\}$ is equal to the no: of terms in the sum $\sum_P$ multiplied with value of any one term in any one numbering order.

i.e.

$$S\{m_l\} = \underbrace{\left[\prod_{l=1}^N \left(\text{Sum of all distinct } l\text{-cluster graphs} \right) \right]^{m_l}}_{\text{In any one order of numbering}} \sum_P (1)$$

Now the task is to find $\sum_P (1)$.

Observe that:

a) There are m_l clusters & the permutation of m_l clusters will not give any new graph.

b) In sum over all l -clusters, the permutation of l -particles within the sum will not lead a new graph.

Thus the value of $\sum_P (1)$ is

$$N!$$

$$\underbrace{[(1!)^{m_1} (2!)^{m_2} (3!)^{m_3} \dots]}_{\text{Degeneracy due to internal permutation of } l\text{-particles.}} \underbrace{[(m_1!)(m_2!)(m_3!) \dots]}_{\text{Degeneracy due to Permutation of } l\text{-clusters}}$$

$N! \rightarrow$ Total ways of arranging the particles.

We get the value of any one term as,

$$[O]^{m_1} [O-O]^{m_2} \left[\begin{array}{c} \text{V-shape} + \text{Z-shape} + \text{U-shape} + \text{triangle} \end{array} \right]^{m_3}$$

$\times \dots \text{so on.}$

$$[O] = 1! \vee b_1$$

$$[O-O] = 2! \lambda^3 \vee b_2$$

$$\left[\begin{array}{c} \text{V-shape} + \text{Z-shape} + \text{U-shape} + \text{triangle} \end{array} \right] = 3! \lambda^6 \vee b_3$$

$$\Rightarrow S\{m_l\} = \frac{N! (v b_1)^{m_1} (2! \lambda^3 v b_2)^{m_2} (3! \lambda^6 v b_3)^{m_3} \dots}{[(2!)^{m_2} (3!)^{m_3} \dots] (m_1!)(m_2!)(m_3!) \dots]}$$

$$= \frac{N! (\lambda^0 v b_1)^{m_1} (\lambda^3 v b_2)^{m_2} (\lambda^6 v b_3)^{m_3} \dots}{(m_1!)(m_2!)(m_3!) \dots}$$

$$\Rightarrow S\{m_l\} = N! \prod_{l=1}^N \frac{[\lambda^{3(l-1)} v b_l]^{m_l}}{m_l!}$$

$$\Rightarrow Z_N = N! \sum_{\{m_l\}} \prod_{l=1}^N \frac{[\lambda^{3(l-1)} v b_l]^{m_l}}{m_l!}$$

The canonical partition function is

$$Q_N(V, T) = \frac{1}{N! \lambda^{3N}} Z_N$$

$$\Rightarrow Q_N(V, T) = \sum_{\{m_l\}} \prod_{l=1}^N \frac{\cancel{\lambda^{3l m_l}}}{\cancel{\lambda^{3N}} \lambda^{3 m_l}} \frac{(v b_l)^{m_l}}{m_l!}$$

$$\Rightarrow Q_N(V, T) = \sum_{\{m_l\}} \prod_{l=1}^N \frac{1}{m_l!} \left(\frac{v b_l}{\lambda^3} \right)^{m_l}$$

The above result is tough to calculate because of the restriction given by $\sum_l l m_l = N$. But it is easier to find the grand partition function $\mathcal{Z}(T, V, \mu)$.

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} e^{\beta \mu N} Q_N(V, T)$$

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{\{m_l\}} \underbrace{\delta\left(N - \sum_{l=1}^N l m_l\right)}_{\text{restriction}} \prod_{l=1}^N \frac{1}{m_l!} \left(\frac{V b_l}{\lambda^3}\right)^{m_l}$$

$$= \sum_{\{m_l\}} \underbrace{\sum_{N=0}^{\infty} e^{\beta \mu N} \delta\left(N - \sum_{l=1}^N l m_l\right)}_{\text{Perform } N\text{-sum - '}\delta\text{' is used up.}} \prod_{l=1}^N \frac{1}{m_l!} \left(\frac{V b_l}{\lambda^3}\right)^{m_l}$$

$$\Rightarrow \mathcal{Z}(T, V, \mu) = \sum_{\{m_l\}} e^{\beta \mu \sum_l l m_l} \prod_l \frac{1}{m_l!} \left(\frac{V b_l}{\lambda^3}\right)^{m_l}$$

Let $z = e^{\beta \mu} \Rightarrow \text{fugacity}$

$$\Rightarrow \mathcal{Z}(T, V, \mu) = \sum_{\{m_l\}} \frac{1}{m_l!} \prod_l \left[\frac{z^l V b_l}{\lambda^3} \right]^{m_l}$$

The cluster expansion of eqⁿ of state is got by finding $\log [Z(T, V, \mu)]$

$Z(T, V, \mu)$ can be expanded as

$$= \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \sum_{m_3=0}^{\infty} \dots \left[\frac{z^1 V b_1}{\lambda^3} \right]^{m_1} \left[\frac{z^2 V b_2}{\lambda^3} \right]^{m_2} \left[\frac{z^3 V b_3}{\lambda^3} \right]^{m_3} \dots$$

$m_1! \quad m_2! \quad m_3!$

Here $m_1, m_2, \dots$ are dummy indices

$$\Rightarrow Z(T, V, \mu) = \prod_{l=1}^{\infty} \sum_{m_l=0}^{\infty} \frac{1}{m_l!} \left[\frac{z^l V b_l}{\lambda^3} \right]^{m_l}$$

$$Z(T, V, \mu) = \prod_{l=1}^{\infty} \exp \left[\frac{z^l V b_l}{\lambda^3} \right]$$

$$\Rightarrow Z(T, V, \mu) = \exp \left[\sum_{l=1}^{\infty} \left(\frac{z^l V b_l}{\lambda^3} \right) \right]$$

$$\Rightarrow \log [Z(T, V, \mu)] = \sum_{l=1}^{\infty} \left(\frac{z^l V b_l}{\lambda^3} \right)$$

$$\Rightarrow \frac{\log [Z(T, V, \mu)]}{V} = \frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l$$

But $PV = k_B T \log [Z(T, V, \mu)]$

$$\Rightarrow \frac{P}{k_B T} = \frac{1}{\lambda^3} \sum_{l=0}^{\infty} b_l z^l$$

$\hookrightarrow$ Cluster expansion for eqⁿ of state.
where,

$$b_l(V, T) = \frac{\text{Sum of all distinct } l\text{-clusters}}{l! \lambda^{3(l-1)} V}$$

Consider the definition of the g.c. partition function,

$$Z = \sum_{N=0}^{\infty} z^N Q_N(V, T)$$

$$z = e^{\beta \mu}$$

$$\frac{\partial Z}{\partial z} = \sum_{N=0}^{\infty} N z^{N-1} Q_N(V, T)$$

$$\Rightarrow z \frac{\partial Z}{\partial z} = \sum_{N=0}^{\infty} N z^N Q_N(V, T)$$

$$\Rightarrow \frac{z}{Z} \frac{\partial Z}{\partial z} = \langle N \rangle$$

$$\Rightarrow 3 \frac{\partial \ln(Z)}{\partial 3} = \langle N \rangle$$

$$\ln(Z) = \frac{PV}{k_B T}$$

$$\Rightarrow 3 \frac{\partial}{\partial 3} \left(\frac{PV}{k_B T} \right) = \langle N \rangle$$

$$\Rightarrow 3 \frac{\partial}{\partial 3} \left(\frac{P}{k_B T} \right) = \frac{\langle N \rangle}{V} = \frac{1}{v}$$

Volume per Particle

$$\Rightarrow \frac{1}{v} = 3 \frac{\partial}{\partial 3} \left[\frac{1}{\lambda^3} \sum_{l=0}^{\infty} b_l 3^l \right]$$

$$\Rightarrow \boxed{\frac{1}{v} = \frac{1}{\lambda^3} \sum_{l=0}^{\infty} l b_l 3^l}$$

Thus the two equations given by

$$\frac{P}{k_B T} = \frac{1}{\lambda^3} \sum_{l=0}^{\infty} b_l 3^l \quad \& \quad \frac{1}{v} = \frac{1}{\lambda^3} \sum_{l=0}^{\infty} l b_l 3^l$$

forms a parametric set of equations where '3' acts as a parameter.