③ Assume $u_{ij}(|\vec{r}_i - \vec{r}_j|) \equiv u_{ij}(r_{ij})$

depends only on distance between molecules, not on orientation. (angles)

$$Z_c = \frac{1}{V^N} \underbrace{\int d^3r_1 \cdots d^3r_N}_{3N \text{ integrals}} \prod_{\text{pairs}} e^{-\beta u_{ij}(r_{ij})}$$

Define Mayer f function

Joseph Mayer

$$e^{-\beta u_{ij}(r_{ij})} \equiv 1 + f_{ij}(r_{ij})$$

$$\prod_{\text{pairs}} e^{-\beta u_{ij}(r_{ij})} = \prod_{\text{pairs}} \left[1 + f_{ij}(r_{ij})\right]$$

$$= (1 + f_{12})(1 + f_{23})(1 + f_{13})(1 + f_{14}) + \cdots$$

$$= 1 + (f_{12} + f_{23} + f_{13} + f_{14} + \cdots) + (f_{12}f_{13} + f_{12}f_{34} + f_{13}f_{24} + \cdots)$$

share index

no index in common

$$= 1 + \sum_{\text{pairs}} f_{ij} + \sum_{\substack{\text{distinct} \\ \text{pairs}}} f_{ij} f_{kl} + \cdots$$

$$Z_c = \frac{1}{V^N}\int d^3r_1 \cdots d^3r_N \Big(\underset{①}{1} + \underset{②}{\sum_{\text{pairs}} f_{ij}} + \underset{③}{\sum_{\text{pairs}} f_{ij} f_{kl}} + \cdots \Big)$$

① $\dfrac{1}{V^N}\displaystyle\int d^3r_1 \cdots d^3r_N \, 1 = \dfrac{V^N}{V^N} = 1$

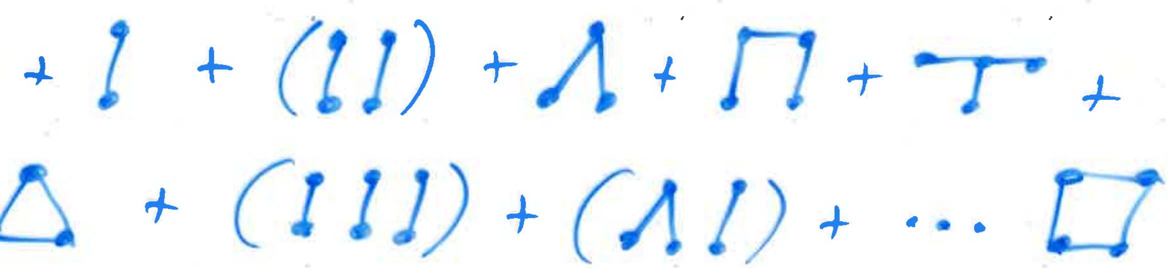
pre ② $\dfrac{1}{V^N}\displaystyle\int d^3r_1 \cdots d^3r_N \, f_{12}(r_{12}) = \dfrac{V^{N-2}}{V^N}\displaystyle\int d^3r_1 d^3r_2 \, f_{12}(r_{12})$

② $\dfrac{N(N-1)}{2}\dfrac{1}{V^2}\displaystyle\int d^3r_1 d^3r_2 \, f_{12}(r_{12}) \equiv$ 

③  $= \dfrac{N(N-1)(N-2)(N-3)}{8\,V^4}\displaystyle\int d^3r_1 \cdots d^3r_4 \, f_{12} f_{34}$

$\left(\int d^3r_1 d^3r_2 f_{12}\right)\left(\int d^3r_3 d^3r_4 f_{34}\right)$

 $= \dfrac{N(N-1)(N-2)}{2\;V^3}\displaystyle\int d^3r_1 d^3r_2 d^3r_3 \, f_{12} f_{23}$

$Z_c = 1 +$ 

parentheses ⟹ disconnected

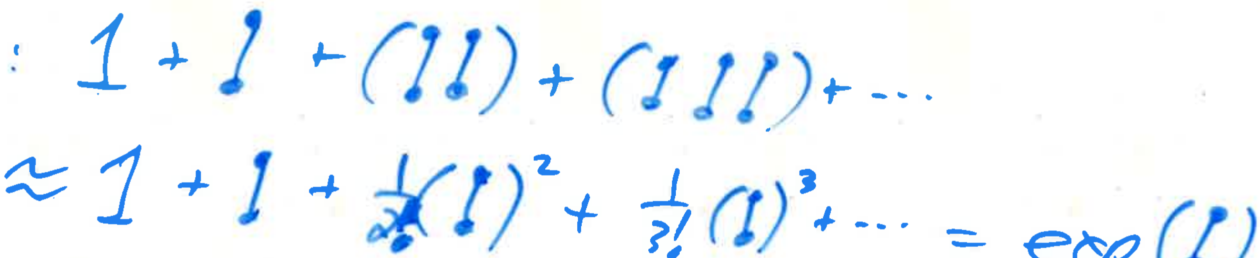
other ⟹ connected

every possible diagram occurs once in the sum.

- 2 or more dots per diagram
- any number of lines coming from a dot 
- one line per pair of dots 

Problem:  $> 1 \Rightarrow$ need lots of terms before the symmetry factor win.

Solution:



with approximation $N \approx N-1 \approx N-2 \approx N-3 \ldots$

disconnected diagrams exponentiate.

If we keep Next-order terms (as well as leading order), the exp() will include diagrams like  and  and ...

Proof?

Cut to the chase:

1PI