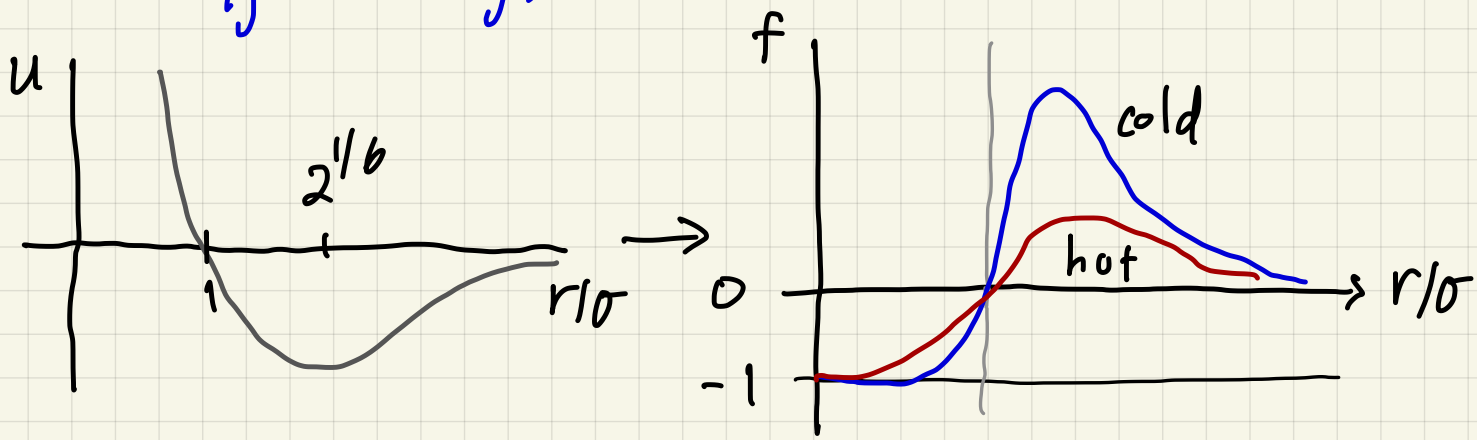
Mayer Cluster Expansion

This is fun. Let $f(r) \equiv e^{-\beta u(r)} - 1$ so

$$Q_N(T,V) = \frac{1}{N!}\int d^d x_1 \cdots \int d^d x_N \prod_{i<j} (1+f_{ij})$$

with $f_{ij} = f(r_{ij})$.



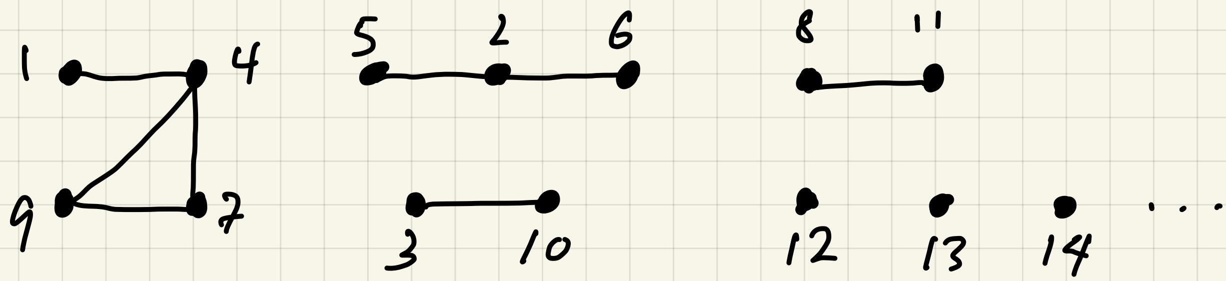
Now $\prod_{i<j}(1+f_{ij}) = 1 + \sum_{i<j} f_{ij} + \sum_{i<j} \sum_{\substack{k<l \\ (i,j)\neq(k,l)}} f_{ij} f_{kl} + \cdots$ (*)

$2^{N(N-1)/2}$ terms since each (i,j) pair can either be present with an f_{ij} factor or not, and there are $\frac{1}{2}N(N-1)$ distinct pairs.

Arrange each term into products over links connected in clusters:

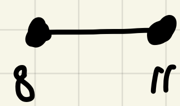
Note $f_{ij} \to 0$ as $r_{ij} \to \infty$. (Assume integrable.)

$$(f_{1,4} f_{4,7} f_{4,9} f_{7,9})(f_{2,5} f_{2,6})(f_{3,10})(f_{8,11})$$

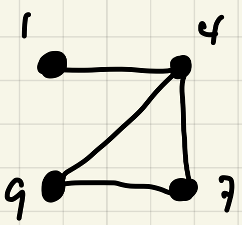


Thus each term in the sum in (*) may be expressed as a graph, and each such graph has a numerical value given by a product of the values of all its component subgraphs:

$= 1$



$= \int d^d x_8 \, d^d x_{11} \, f_{8,11}$



$= \int d^d x_1 \, d^d x_4 \, d^d x_7 \, d^d x_9 \; f_{1,4} f_{4,7} f_{4,9} f_{7,9}$

Now the value of any graph depends only on its structure and not any choice of labels. Consider an un-labeled N-vertex graph and let

$$m_\gamma = \# \text{ of subgraphs of type } \gamma$$

n_γ = # vertices in γ

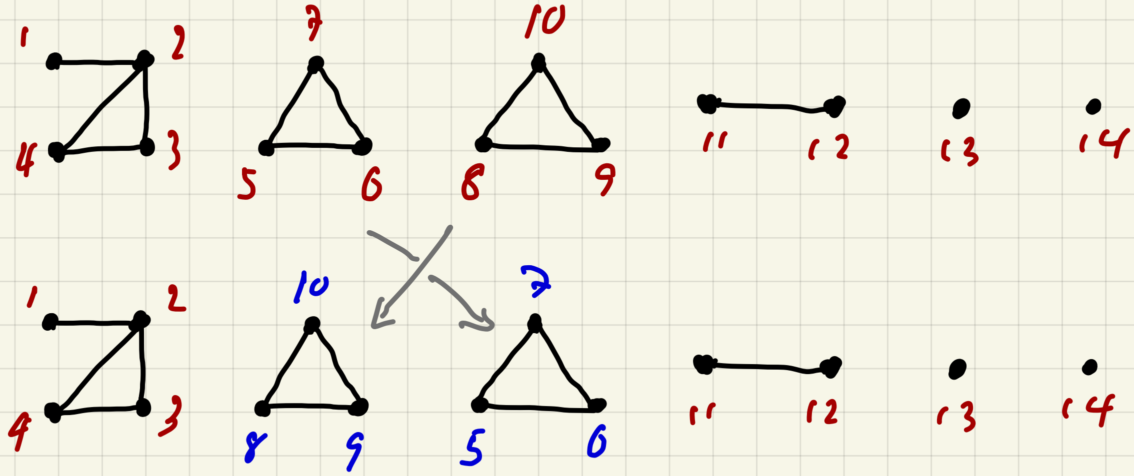
Then we must have $N = \sum_\gamma m_\gamma n_\gamma$

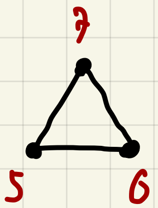
where the sum is over all possible subgraphs.

We now ask: How many ways are there of assigning labels $\{1, \ldots, N\}$ to the vertices? We might suspect $N!$, but this is too big, and for two reasons:

(i) Permuting labeled identical subgraphs yields the same graph.

(ii) There may be permutations of the labels within a subgraph which leave the subgraph unchanged.





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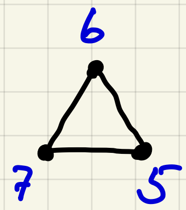


$$= \int d^d x_5 \, d^d x_6 \, d^d x_7 \; f_{5,6} \, f_{6,7} \, f_{5,7}$$

The number of ways we can interchange identical unlabeled subgraphs is $\prod_\gamma m_\gamma!$

The number of permutations of a given subgraph labeling which leaves the product $\prod_{\langle i,j \rangle \in \gamma} f_{ij}$ invariant is the symmetry factor of the subgraph, S_γ.

Thus, the # of ways we can relabel the vertices of a given graph is

$$\# \text{ labelings} = \frac{N!}{\prod_\gamma m_\gamma! \prod_\gamma S_\gamma^{m_\gamma}}$$ and

$$Z(T,V,N) = \sum_{\{m_\gamma\}} \prod_\gamma \frac{1}{m_\gamma!} \left(\frac{V b_\gamma(T)}{\lambda_T^d} \right)^{m_\gamma} \delta_{N, \sum_\gamma m_\gamma n_\gamma}$$

where

$$b_\gamma(T) = \frac{1}{S_\gamma} \int \frac{d^d x_1}{\lambda_T^d} \cdots \int \frac{d^d x_{n_\gamma - 1}}{\lambda_T^d} \prod_{i<j}^{\gamma} f_{ij}$$

$$= \mathcal{O}(V^0) \quad \text{(intensive)}$$

GCE :

$$\Xi(T, V, \mu) = e^{-\beta \Omega(T, V, \mu)}$$

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

$$= \prod_\gamma \sum_{m_\gamma = 0}^{\infty} \frac{1}{m_\gamma} \left(\frac{V e^{n_\gamma \beta \mu} b_\gamma(T)}{\lambda_T^d} \right)^{m_\gamma}$$

$$\Xi(T, V, \mu) = \exp\left(\frac{V}{\lambda_T^d} \sum_\gamma z^{n_\gamma} b_\gamma(T) \right)$$

Thus,

$$\Omega(T, V, \mu) = -\frac{V k_B T}{\lambda_T^d} \sum_\gamma z^{n_\gamma} b_\gamma(T)$$

We then have:

$$p(T, z) = k_B T \lambda_T^{-d} \sum_\gamma z^{n_\gamma} b_\gamma(T)$$

$$n(T, z) = \lambda_T^{-d} \sum_\gamma n_\gamma z^{n_\gamma} b_\gamma(T)$$

As we did with quantum ideal gases,

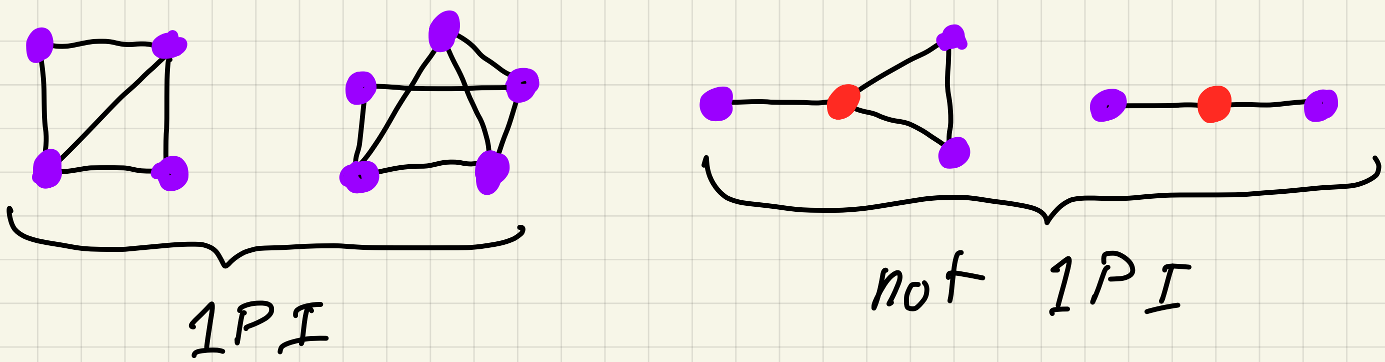
$$n(T,z) \xrightarrow[\text{invert}]{} z(T,n) \longrightarrow p(T, z(T,n)) = p(T,n)$$

$$p(T,n) = n k_B T \left(1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots\right)$$

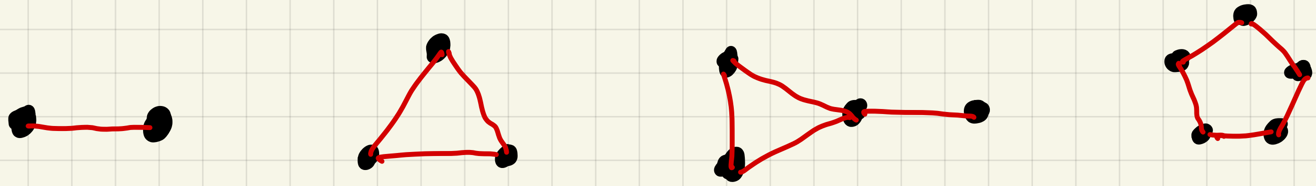
This is the virial expansion of the eqn of state. Diagrammatic rules for $B_k(T)$:

$$B_k(T) = -(k-1)\, \lambda_T^{(k-1)d} \sum_{\gamma \in \Gamma_k} b_\gamma(T)$$

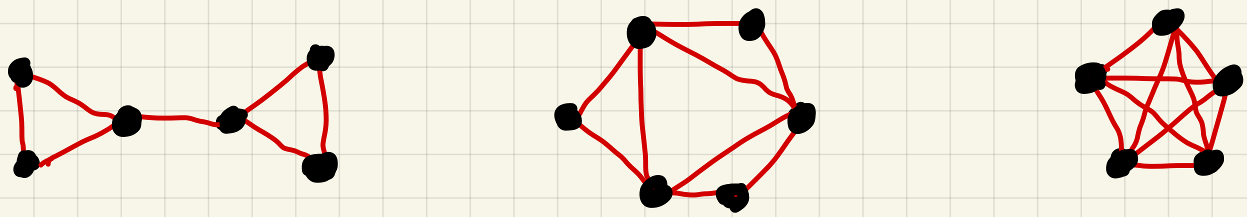
where Γ_k = set of all 1-particle irreducible (1PI) k-site clusters. A 1PI cluster is one which remains connected if any one of its sites and all that site's connecting links are removed.



Subgraph symmetry factors:



$s=2$ $s=6$ $s=2$ $s=10$



8 6 120

Lowest order expansion:

$$B_2(T) = -\lambda_T^3\, b_{\bullet\!-\!\bullet}(T) = -\frac{1}{2}\int d^d r\, f(r)$$

$$B_3(T) = -2\lambda_T^6\, b_{\triangle}(T) = -\frac{1}{3}\int d^d r \int d^d r'\, f(r) f(r') f(|\vec{r}-\vec{r}'|)$$

Hard spheres: $f(r) = \begin{cases} -1 & \text{if } r \leq a \\ 0 & \text{if } r > a \end{cases}$

$$B_2(T) = \frac{2\pi}{3} a^3, \quad B_3(T) = \frac{5\pi^2}{18} a^6$$