Mayer cluster expansion

Interacting classical gas with hard-core repulsion
– [redacted] cluster expansion

In the canonical ensemble, would try to reorganize the series for F in powers of $\frac{N}{V}$

$\Rightarrow$ equation of state $P = -\left(\frac{\partial F}{\partial V}\right)_T$ is organized in "virial expansion"

$$\boxed{\frac{P}{k_B T} = \frac{N}{V}\left[1 + B_2(T)\frac{N}{V} + B_3(T)\left(\frac{N}{V}\right)^2 + \dots\right]}$$

– often used empirically; we want to calculate microscopically [e.g. from the [redacted] reorganized cummulant expansion, $\boxed{B_2(T) = -\frac{1}{2}\int d^3q\,(e^{-\beta v} - 1)}$]

More convenient [redacted] for systematic derivation procedure is [redacted] "cluster expansion" working in the grand canonical ensemble and organizing in [redacted] the "expansion parameter" $f(q_{ij}) = e^{-\beta v(q_{ij})} - 1$ (more precisely, in "fugacity" $e^{\beta\mu}/\lambda^3$)

[redacted]

$$Z_N = \frac{1}{N!\,\lambda^{3N}} \int \prod_i d^3q_i \, e^{-\beta U(\{q_i\})}$$

Grand-canonical partition sum

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N = \sum_{N=0}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^N \frac{1}{N!} S_N$$

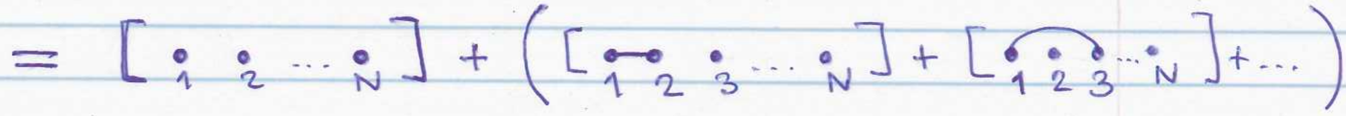
denote as x

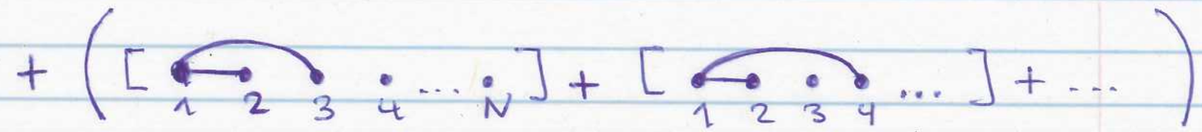
$$S_N = \int \prod_{i=1}^{N} d^3q_i \, e^{-\beta \sum_{i<j} v(q_i - q_j)} = \int d^3q_1 \dots d^3q_N \prod_{i<j}(1 + f_{ij}),$$

$$\boxed{f_{ij} = e^{-\beta v(q_i - q_j)} - 1}$$

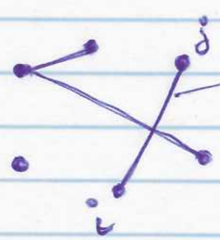
$$S_N = \int d^3q_1 \dots d^3q_N \Big\{ 1 + \left(f_{12} + f_{13} + \dots + f_{1N} + f_{23} + f_{24} + \dots \right)$$

$$+ \underbrace{\left(f_{12} f_{13} + f_{12} f_{14} + \dots \right)}_{(\text{NO } f_{12}^2)} + \dots \Big\} =$$





= Sum of all distinct N-particle graphs

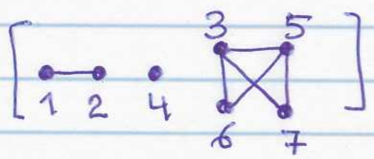


f_{ij} [redacted] pair $\langle ij \rangle$:

connection $\Leftrightarrow$ f_{ij}

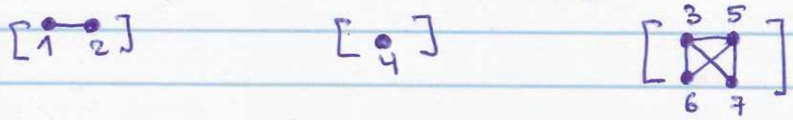
no connection $\Leftrightarrow$ 1

Example: $N = 7$



$$= \int d^3q_1 \dots d^3q_N \; f_{12} \, f_{35} f_{36} f_{37} \, f_{56} f_{57}$$

$$= \int d^3q_1 d^3q_2 \, f_{12} \times \int d^3q_4 \cdot 1 \times \int d^3q_3 \, d^3q_5 \, d^3q_6 \, d^3q_7 \; f_{35} f_{36} f_{37} f_{56} f_{57}$$



$\Rightarrow$ General graph is a product of connected graphs

$$\boxed{ \mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{N!} \text{[redacted]} \left(\frac{e^{\beta\mu}}{\lambda^3} \right)^N \Big(\sum_{\text{arbitrary}} N\text{-particle graphs} \Big) }$$

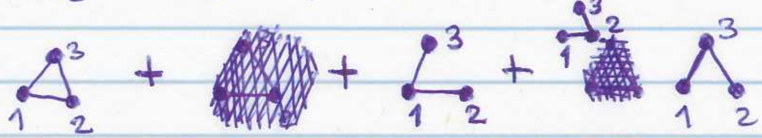
Linked cluster theorem:

"sum of all graphs" = exp(sum of all connected graphs)

$$\boxed{\mathcal{Z} = \exp\left[\sum_{l=1}^{\infty}\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^l \frac{1}{l!}\underbrace{\left(\sum \text{connected } l\text{-particle graphs}\right)}_{=\, b_l}\right]}$$

$b_1 =$  $= \int d^3q_1 = V$

$b_2 =$  $= \int d^3q_1 d^3q_2\, f(\vec{q}_1 - \vec{q}_2) = V\int d^3q\, f(q)$

$b_3 =$  $=$

$$= \int d^3q_1 d^3q_2 d^3q_3\, f(q_1-q_2) f(q_1-q_3) f(q_2-q_3)$$

$$+ 3\int d^3q_1 d^3q_2 d^3q_3\, f(q_1-q_2) f(q_1-q_3) =$$

$$= V\left[\int d^3\tilde{q}_2 d^3\tilde{q}_3\, f(\tilde{q}_2) f(\tilde{q}_3) f(\tilde{q}_3-\tilde{q}_2) + 3\int d^3\tilde{q}_2 d^3\tilde{q}_3\, f(\tilde{q}_2) f(\tilde{q}_3)\right]$$

Remark: * Generally, for any connected cluster, one can change vars to $\underset{i=2,\dots,l}{\tilde{q}_i = q_i - q_1}$; then $\int d^3q_1 \to$ one factor of V.

$$q_i - q_j = \tilde{q}_i - \tilde{q}_j$$

* [graph w disconnected pieces] $\sim V^{\#\text{ of disconnected pieces}}$

HW problem

Remarks: * Grand potential $\Omega = -k_BT \ln \mathcal{Z}$

- can imagine expanding $\underbrace{\text{in terms of}}_{\text{informal series}}$ graphs, but once we do, all disconnected graphs must disappear!

Proof of the linked cluster theorem

$$\boxed{\begin{aligned} S_N &= \sum \left[\text{all distinct } N\text{-particle graphs}\right] = \\ &= \sum_{\substack{\text{"strings of integers"} \geq 0 \\ \{n_1, n_2, \dots\} \\ \text{satisfying } n_1\cdot 1 + n_2\cdot 2 + \dots = N \\ \| \\ \sum_{\ell=1}^{\infty} n_\ell \cdot \ell = N}} \underbrace{b_1^{n_1} b_2^{n_2} \dots}_{\prod_{\ell=1}^{\infty} (b_\ell)^{n_\ell}} \times \underbrace{\frac{N!}{n_1!(1!)^{n_1}\, n_2!(2!)^{n_2} \dots}}_{\frac{N!}{\prod_{\ell=1}^{\infty} n_\ell!(\ell!)^{n_\ell}}} \end{aligned}}$$

$*$ $S_1 = [\bullet] = b_1$

<u>Examples</u>: $*$ $S_2 = [\underset{1}{\bullet}\ \underset{2}{\bullet}] + [\underset{1}{\bullet}\!-\!\underset{2}{\bullet}] = [\bullet][\bullet] + [\overset{\bullet-\bullet}{1\ \ 2}] =$

$$= b_1^2 + b_2$$

$*$ $[\underset{1}{\bullet}\ \underset{2}{\bullet} \dots \underset{N}{\bullet}] \leftrightarrow b_1^N \leftrightarrow$ string $\{N, 0, 0, \dots\}$

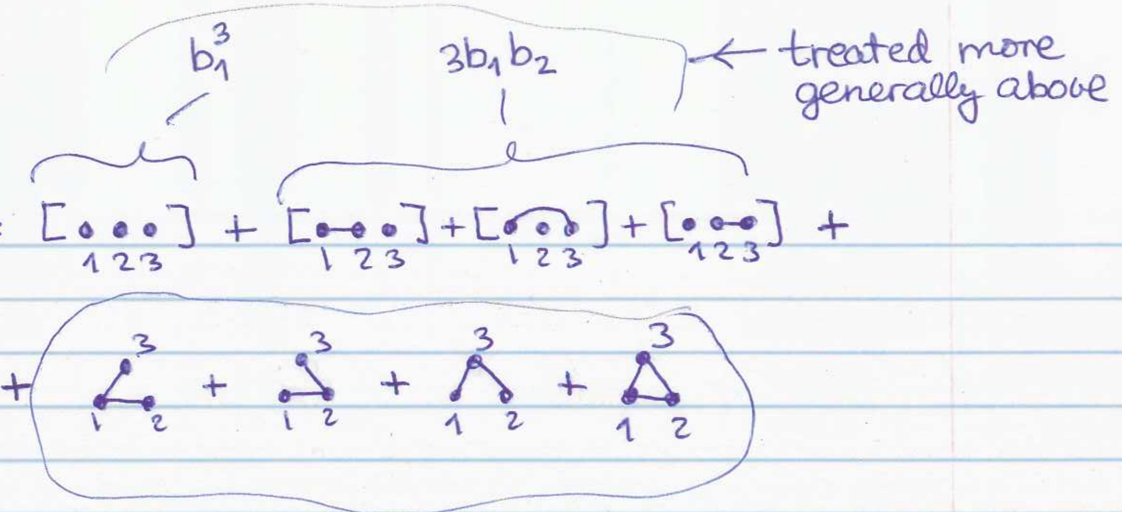
$$W[\swarrow] = \frac{N!}{N!(1!)^N} = 1 \text{ . } \checkmark$$

$*$ $[\underset{1}{\bullet}\!-\!\underset{2}{\bullet}\ \bullet\ \bullet \dots \bullet] + [\underset{1}{\bullet}\frown\bullet\frown\underset{3}{\bullet}\ \bullet \dots] + \dots + [\underset{1}{\bullet}\ \underset{2}{\bullet}\!-\!\underset{3}{\bullet}\ \bullet \dots] + \dots =$

$$= \frac{N(N-1)}{2} b_1^{N-2} b_2$$

string $\{N-2, 1, 0, 0, \dots\}$

$$W[\swarrow] = \frac{N!}{(N-2)!(1!)^{N-2} \cdot 1!(2!)^1} = \frac{N\cdot(N-1)}{2} \checkmark$$

* $S_3 =$ 

$\| \quad b_3$ = sum of connected 3-particle graphs.

* Any $S_N = \left(\begin{array}{l}\text{graphs with several}\\ \text{disconnected components}\end{array}\right) + b_N$

b_N corresponds to string $\{0, 0, \ldots, n_N = 1, \}$

$$W[\ \ ] = \frac{N!}{1!\,(N!)^1} = 1 \ \checkmark$$

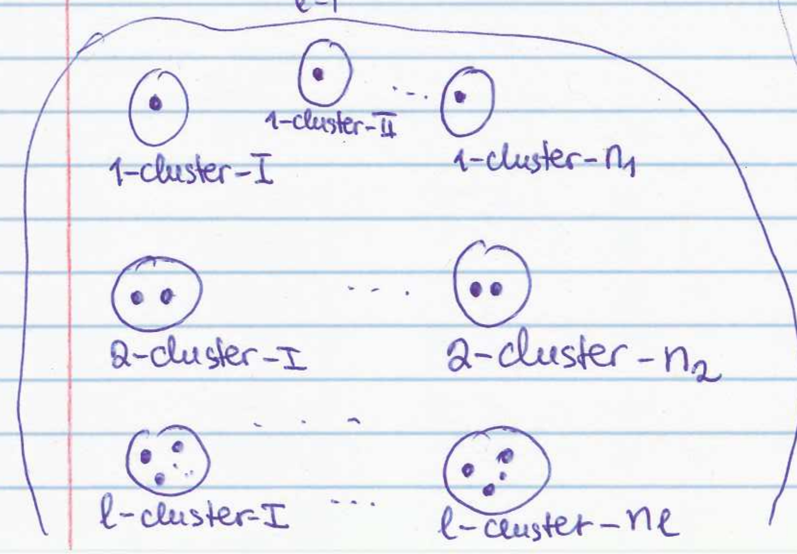
* General case, counting

$$W[\{n_1, n_2, \ldots, n_\ell \ldots\}] = \frac{N!}{\prod_{\ell=1}^{\infty}\left[\underbrace{(\ell!)\,(\ell!)\ldots(\ell!)}_{n_\ell \text{ times}}\right]} \cdot \frac{1}{\prod_\ell (n_\ell!)}$$

$$\sum_{\ell=1}^{\infty} n_\ell \cdot \ell = N$$

- assumes particular "ordering" of ℓ-clusters (ℓ-I, ℓ-II, …, ℓ-n_ℓ)

$\frac{1}{\prod_\ell (n_\ell!)}$ corrects for this assumption



(whether we include $N=0$ or not is not important, since it is $O(1)$ in $\mathcal{Z}$ while everything else has powers of V. convenient to include $N=0 \Leftrightarrow \{\emptyset, \emptyset, \emptyset \dots\}$)

$$\boxed{\mathcal{Z} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^N S_N}$$

$$S_N = \sum_{\substack{\{n_1, n_2, \dots\} \\ \sum_{l=1}^{\infty} n_l \cdot l = N}} \frac{N!}{\prod_{l=1}^{\infty} n_l!\,(l!)^{n_l}} \prod_{l=1}^{\infty} b_l^{n_l}$$

$$= \sum_{\substack{\text{unconstrained} \\ \{n_1, n_2, \dots\} \\ n_i \geq 0}} \prod_{l=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{n_l \cdot l} \frac{b_l^{n_l}}{n_l!\,(l!)^{n_l}}$$

$$\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{n_l \cdot l} \frac{b_l^{n_l}}{n_l!\,(l!)^{n_l}} = \frac{1}{n_l!} \left(\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{l} \cdot \frac{1}{l!} \cdot b_l \right)^{n_l}$$

$$= \prod_{l=1}^{\infty} \exp\left(\left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{l} \cdot \frac{1}{l!} b_l \right) = \boxed{\exp\left[\sum_{l=1}^{\infty} \frac{1}{l!} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{l} b_l \right]}$$

$$-pV = \Omega = -k_B T \ln \mathcal{Z}$$

$$\Rightarrow \boxed{\frac{pV}{k_B T} = \ln \mathcal{Z} = \sum_{l=1}^{\infty} \frac{1}{l!} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{l} b_l}$$

$$\boxed{\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = \sum_{l=1}^{\infty} \frac{1}{(l-1)!} \left(\frac{e^{\beta\mu}}{\lambda^3}\right)^{l} b_l} \Rightarrow \text{solve for } \mu$$

Define $\tilde{b}_l = \dfrac{b_l}{b_1} = \dfrac{b_l}{V}$, $\quad b_l = V \tilde{b}_l$

$$x = \frac{e^{\beta\mu}}{\lambda^3}$$

$$n = \frac{\langle N \rangle}{V} = \sum_{l=1}^{\infty} \frac{1}{(l-1)!} x^l \tilde{b}_l = x + x^2 \tilde{b}_2 + \frac{x^3}{2} \tilde{b}_3 + \ldots$$

$$\frac{P}{k_B T} = \sum_{l=1}^{\infty} \frac{1}{l!} x^l \tilde{b}_l = x + \frac{x^2}{2} \tilde{b}_2 + \frac{x^3}{6} \tilde{b}_3 + \ldots$$

$$\Rightarrow \quad x = n - x^2 \tilde{b}_2 - \frac{x^3}{2} \tilde{b}_3 \ldots$$

Solve iteratively:
(in powers of n)

$$x^{(1)} \approx n$$

$$x^{(2)} \approx n - (x^{(1)})^2 \tilde{b}_2 = n - n^2 \tilde{b}_2$$

$$x^{(3)} \approx n - (x^{(2)})^2 \tilde{b}_2 - \frac{1}{2} (x^{(2)})^3 \tilde{b}_3 =$$

$$= n - (n - n^2 \tilde{b}_2)^2 \tilde{b}_2 - \frac{1}{2} n^3 \tilde{b}_3 =$$

$$= n - n^2 \tilde{b}_2 + \left(2\tilde{b}_2^2 - \frac{1}{2}\tilde{b}_3\right) n^3 + O(n^4)$$

Now equation of state:

$$\frac{P}{k_B T} \approx n - n^2 \tilde{b}_2 + \left(2\tilde{b}_2^2 - \frac{1}{2}\tilde{b}_3\right) n^3 + \frac{1}{2}(n - n^2 \tilde{b}_2)^2 \tilde{b}_2$$

$$+ \frac{n^3}{6} \tilde{b}_3 = n - \frac{1}{2} n^2 \tilde{b}_2 + \left(\tilde{b}_2^2 - \frac{1}{3}\tilde{b}_3\right) n^3 + O(n^4)$$

Virial expansion $\rightarrow$

$$\boxed{\frac{P}{k_B T} = n\left(1 + \underbrace{\left(-\frac{1}{2}\tilde{b}_2\right)}_{B_2(T)} n + \underbrace{\left(\tilde{b}_2^2 - \frac{1}{3}\tilde{b}_3\right)}_{B_3(T)} n^2 + \ldots\right)}$$

$$\boxed{P = n k_B T \left(1 - \sum_{l=2}^{\infty} (l-1) \cdot \frac{1}{l!} \Big(\underbrace{d_l}_{\substack{\text{sum over irreducible} \\ \text{clusters in } b_l}} \Big) \cdot n^{l-1} \right)}$$

$$\left(\ldots \right) = 1 - \frac{1}{2} \tilde{b}_2 n - \frac{1}{3} \left(\tilde{b}_3 - 3 \tilde{b}_2^2 \right) n^2 + \ldots$$