The cluster expansion

Ideal gas eq of state: $PV = Nk_B T$

Van der Waals eq of state: $(P + an^2)(V - Nb) = Nk_B T$

$n \to N/V$

This is phenomenological

Ideal gas: $P = nk_B T$ okay at low densities. $\to$ interactions unimportant.

Expand P in terms of the density

$$P = nk_B T(1 + a_1 n + a_2 n^2 + \dots)$$

Coefficients a_j are determined by interaction potential.

Van der Waals: $$P = \frac{nk_B T}{(1 - nb)} - an^2 = nk_B T\left(1 + nb - \frac{a}{k_B T} n + n^2 b^2 + \dots\right)$$

$$P = nk_B T(1 + a_1 n + a_2 n^2 + \dots)$$

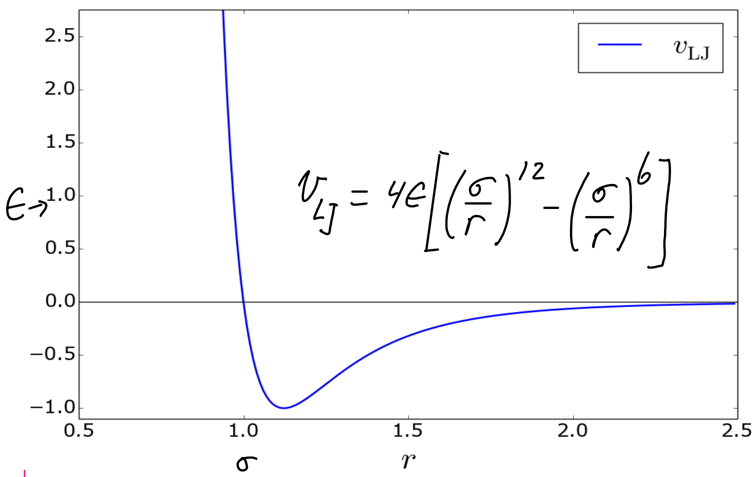
Virial expansion

Our aim is to calculate the coefficients of the n^j from the interaction.

Two-point interactions & Perturbation theory

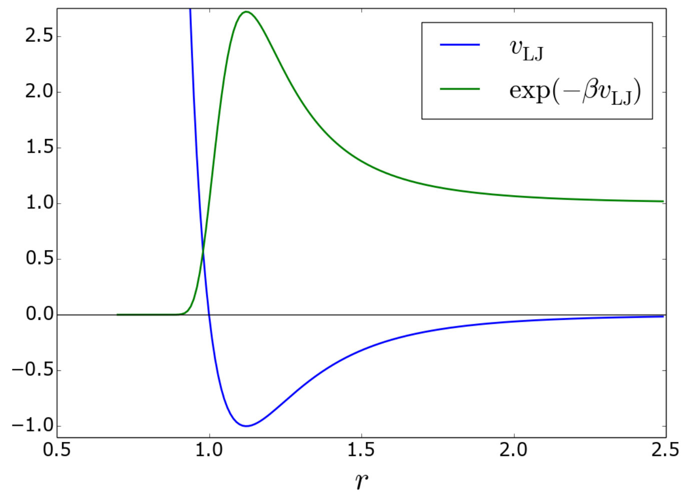
$$U(\underline{r}_1 \dots \underline{r}_N) = \sum_{i<j} v(\underline{r}_i - \underline{r}_j)$$

Scalar particles: $v(\underline{r}_i - \underline{r}_j) = v(|\underline{r}_i - \underline{r}_j|)$



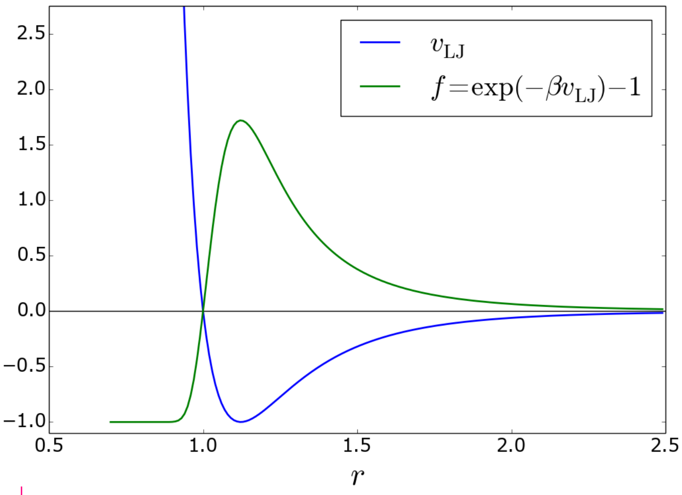
∞ for $r \to 0$
Not suitable for perturbation theory.

What about $e^{-\beta v_{LJ}(r_{ij})}$?



$e^{-\beta v_{LJ}} = 1$ for $r \to \infty$
$\rightarrow$ not suitable for perturbation theory.

Let's try: $e^{-\beta v_{LJ}(r)} - 1$



This seems promising

$$f(r) = e^{-\beta v_{LJ}(r)} - 1$$

is called the Mayer function

$$Z_N = \frac{1}{N!\, h^N} \int e^{-\beta \sum_j \underline{p}_j^2/2m \, - \beta \sum_{j<k} v_{LJ}(r_{jk})} \, d^{3N}p \, d^{3N}r$$

Integrate over $\underline{p}_j$:

$$Z_N = \frac{1}{N!\, \lambda_T^{3N}} \underbrace{\int e^{-\beta \sum_{j<k} v_{LJ}(r_{jk})} \, d^{3N}r}_{Q_N(T,V)} ; \qquad \left(\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \right)$$

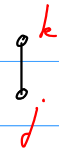
$$e^{-\beta \sum_{j<k} v_{LJ}(r_{jk})} = \prod_{j<k} e^{-\beta v_{LJ}(r_{jk})} =$$

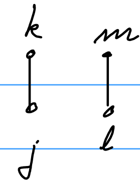
$$\prod_{j<k} \Big(1 + \underbrace{e^{-\beta v_{LJ}(r_{jk})} - 1}_{f_{jk}} \Big) = \prod_{j<k} \left(1 + f_{jk} \right)$$

$$\rightarrow Q_N(T,V) = \int (1+f_{12})(1+f_{34}) \cdots (1+f_{6,23}) \cdots \; d^{3N}r$$

$$= \int \Big(1 + \sum_{j<k} f_{jk} + \sum_{\substack{j<k \\ l<m}}' f_{jk} f_{lm} + \sum_{\substack{j<k \\ l<m \\ i<n}}' f_{jk} f_{lm} f_{in} \cdots \Big) d^{3N}r$$

$\sum\limits_{\text{pairs}}^{\triangledown}$: no two pairs should be identical.

Diagrams: f_{jk} : 

; $f_{jk} f_{lm}$: 

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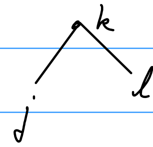
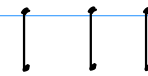
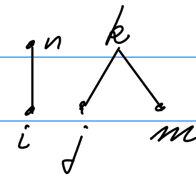
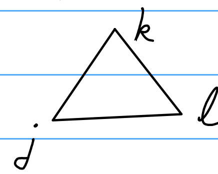
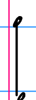
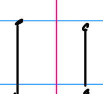
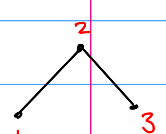
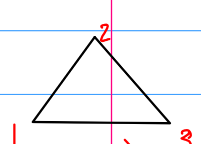
$f_{jk} f_{kl}$: 

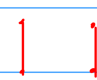
; $f_{jk} f_{lm} f_{in}$ 

$f_{jk} f_{km} f_{in}$: 

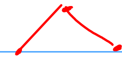
$f_{jk} f_{kl} f_{lj}$: 

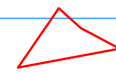
Calculating diagrams:

Diagram	Multiplicity	Factor
	$\frac{N(N-1)}{2}$	$\int f_{12}\, d^3r_1 d^3r_2 = V \int f\, d^3 r \equiv 2V b_2$ $r_1,\ r_2 - r_1 = r$
	$\frac{N(N-1)}{2} \cdot \frac{(N-2)(N-3)}{2} \cdot \frac{1}{2} = \frac{N(N-1)(N-2)(N-3)}{8}$	$\int f_{12} f_{34}\, d^3r_1 \cdots d^3r_4 = V^2 \left(\int f\, d^3r\right)^2 = 4V^2 b_2^2$
	$\frac{N(N-1)(N-2)}{3!} \times 3$	$\int f_{12} f_{23} \underbrace{d^3r_1 d^3r_2 d^3r_3}_{d^3r_2\, d^3r_{21}\, d^3r_{23}} = V \left(\int f\, d^3r\right)^2 = 4V b_2^2$
	$\frac{N(N-1)(N-2)}{3!}$	$\int f_{12} f_{23} f_{31}\, d^3r_1 d^3r_2 d^3r_3 = 3!\, V (b_3 - 2b_2^2)$ $r_{13} = r_{23} - r_{21}$

$$Q_N(T,V) = V^N + V^N \frac{N(N-1)}{V} b_2 + V^N \frac{N(N-1)(N-2)(N-3)}{8V^2} (4b_2^2)$$

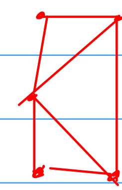
$$+ V^N \frac{N(N-1)(N-2)}{2V^2} 4b_2^2$$ 

$$+ V^N \frac{N(N-1)(N-2)}{V^2} (b_3 - 2b_2^2) + \cdots$$ 

$$= V^N\left(1+\frac{N(N-1)}{V}b_2+\frac{N(N-1)(N-2)(N-3)}{2V^{-2}}b_2^2+\frac{N(N-1)(N-3)}{V^{-2}}b_3\right)$$

$$\Rightarrow Z_N(T,V)=\frac{1}{\lambda^{3N}}\frac{1}{N!}\sum_{\text{diagrams}}\int\prod_{kl} f_{kl}\, d^{3N}r$$

Consider all connected diagrams for j sites.

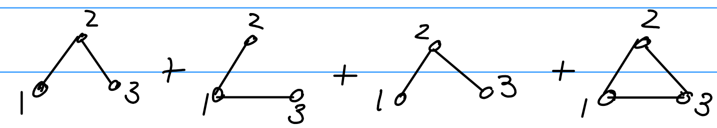


$$\to \sum_{\substack{\text{conn.}\\ \text{diagr}}}\int\prod_{lk\in\text{diagr}} f_{lk}\, d^3r_1\ldots d^3r_j \equiv j!\,V b_j$$

This is the definition of the b_j. $b_1=1$.

Example $j=2$: $| \to V\int f\, d^3r = 2Vb_2$

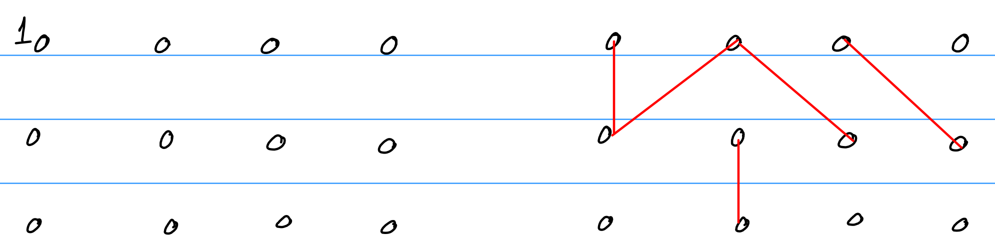
Example: $j=3$:

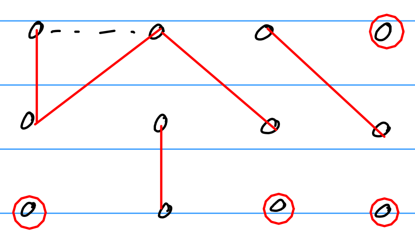


$$=3V\left(\int f d^3r\right)^2+V\int f_1 f_2 f_{12}\, d^3r_1\, d^3r_2$$

$$3V(2b_2)^2+6V(b_3-2b_2^2)=3!\,Vb_3$$

$$Z=\frac{1}{\lambda_T^{3N}}\frac{1}{N!}\sum_{\{m_j\}}\prod_j\frac{N!}{m_j!(j!)^{m_j}}\left(j!\,Vb_j\right)^{m_j}\ ; \quad \sum_j j\, m_j = N$$





We have: 4 clusters of size 1 $m_1=4$
2 clusters " " 2 $m_2=2$
1 cluster of size 4. $m_4=1$

We have:

$$Z = \frac{1}{\lambda_T^{3N}} \frac{1}{\cancel{N!}} \sum_{\{m_j\}} \prod_j \frac{\cancel{N!}\,1}{m_j!\,(j!)^{m_j}} \left(j!\, V b_j\right)^{m_j} ; \quad \sum_{j=1}^{N} j\, m_j = N.$$

Analysis is hampered by the constraint $\sum_{j=1} j \cdot m_j = N$

We relax this constraint by moving to the grand canonical ensemble.

$$\sum_{\text{partionings}} = \sum_{\{m_j\},\, \sum_j j m_j = N} \quad \text{is replaced by} \quad \prod_{j=1}^{\infty} \sum_{m_j=0}^{\infty}$$

For a particular config $\{j, m_j\}$: $N = \sum_j j\, m_j$

$$Z_{gr} = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\{m_j\}_N} \frac{1}{(\lambda_T)^{3N}} \prod_j \frac{1}{(j!)^{m_j} m_j!} (j!\, V b_j)^{m_j}$$

$$= \prod_{j=1}^{\infty} \sum_{m_j=0}^{\infty} \frac{1}{(j!)^{m_j}\, m_j!} \left(\frac{e^{\beta\mu}}{\lambda_T^3}\right)^{j m_j} (j!\, V b_j)^{m_j}$$

$$\mathcal{Z}_{gr} = \prod_{j=1}^{\infty} \sum_{m_j=0}^{\infty} \frac{1}{m_j!\,\cancel{(j!)^{m_j}}} \left[\cancel{j!}\, V b_j \left(\frac{e^{\beta\mu}}{\lambda_T^3} \right)^j \right]^{m_j}$$

$$\prod_{j=1}^{\infty} \exp\left(V b_j \left(\underbrace{\frac{e^{\beta\mu}}{\lambda_T^3}}_{\xi} \right)^j \right)$$

$$\ln \mathcal{Z}_{gr} = \sum_{j=1}^{\infty} V b_j \xi^j \quad ; \quad k_B T \ln \mathcal{Z}_{gr} = PV$$

$$P = k_B T \sum_{j=1}^{\infty} b_j \xi^j = k_B T \left(\xi + b_2 \xi^2 + b_3 \xi^3 + \ldots \right)$$

$\xi = \dfrac{e^{\beta\mu}}{\lambda_T^3}$ but we would like to have P in terms of the density!

$$n = \frac{N}{V} = \frac{\partial \ln \mathcal{Z}_{gr}}{V \partial(\beta\mu)} = \frac{\partial \ln \mathcal{Z}_{gr}}{V \partial \xi} \xi =$$

$$\ln \mathcal{Z}_{gr} = \sum_{j=1}^{\infty} V b_j \xi^j$$

$$\sum_{j=1}^{\infty} j b_j \xi^j = \xi + 2 b_2 \xi^2 + 3 b_3 \xi^3 \ldots = n$$

$$\xi = n + a_2 n^2 + a_3 n^3 + \ldots$$

$$P = k_B T \left(\xi + b_2 \xi^2 + b_3 \xi^3 + \ldots \right)$$

To lowest order: $n = \xi$, i.e. $n = \xi + \mathcal{O}(\xi^2) \Rightarrow \xi^{(1)} = n$

second order: $n = \xi(1 + 2 b_2 \xi) \Rightarrow$

$$\xi = \frac{n}{1 + 2 b_2 \xi} + \mathcal{O}(\xi^3) = n - 2 b_2 \xi n^2 + n(2 b_2 \xi)^2 = n - 2 b_2 n^2 + \mathcal{O}(n^3)$$

$$\xi^{(2)} = n - 2 b_2 n^2$$

$$n = \xi + 2b_2\xi^2 + 3b_3\xi^3 + \dots = \xi(1+2b_2\xi+3b_3\xi^2) + \dots$$

$$\to \xi = \frac{n}{1+2b_2\xi+3b_3\xi^2} = n - 2b_2\xi n - 3nb_3\xi^2 + n(2b_2\xi)^2 + \text{higher order}$$

$$= n - 2b_2(n-2b_2n^2)n - 3b_3n^3 + n(2b_2n)^2 + h.o.t$$

$$= n - 2b_2n^2 - (3b_3 - 8b_2^2)n^3 + h.o.t.$$

$$\xi^{(3)} = n - 2b_2n^2 - (3b_3-8b_2^2)n^3$$

So, to third order in n:

$$P^{(3)} = k_BT\left(\xi^{(3)} + b_2\xi^{(2)2} + b_3\xi^{(1)3}\right) =$$

$$k_BT\left(n - 2b_2n^2 - (3b_3-8b_2^2)n^3 + b_2(n-2b_2n^2)^2 + b_3n^3\right) =$$

$$k_BT\left(n - 2b_2n^2 - (3b_3-8b_2)n^3 + b_2n^2 - 4b_2^2n^3 + b_3n^3\right) + \mathcal{O}(n^4)$$

$$= k_BT\left(n - b_2n^2 + (4b_2^2 - 2b_3)n^3 + \dots\right).$$ virial expansion

Recall: $$\sum_{\substack{\text{conn.}\\ \text{diagr}}} \int \prod_{lk\in \text{diagr}} f_{lk}\, d^3r_1 \dots d^3r_j \qquad j!\,V b_j$$

$$f_{lk} = e^{-\beta v_{LJ}(r_{lk})} - 1$$

Van der Waals: $$P = \frac{nk_BT}{(1-nb)} - an^2 =$$

$$nk_BT\Big(1 + \overbrace{nb - \frac{a}{k_BT}n}^{b_2 = -b + \frac{a}{k_BT}} + n^2b^2 + \dots\Big)$$

$$b_2 = \frac{1}{2}\int\left(e^{-\beta v_{LJ}(r)} - 1\right) d^3r = -\frac{1}{2}\times(\text{excluded volume}) +$$

$$+\frac{1}{2}\int_{|r|>r_c} \beta\, v_{LJ}\, d^3r \quad \rightarrow \quad a = \frac{1}{2}\times \text{integral of the attractive potential.}$$