

## Classical non-ideal gas

### The Mayer cluster expansion

Need interactions if want to see phase transitions  
(except BE condensation)

Assume pairwise interactions

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{i < j} u_{ij} \quad \text{where } u_{ij} = u(|\vec{r}_i - \vec{r}_j|)$$

↑ counts all pairs

$$Q_N = \frac{1}{N! h^{3N}} \left( \prod_{k=1}^N \int d^3 r_k \int d^3 p_k \right) e^{-\beta \left( \sum_i \frac{p_i^2}{2m} + \sum_{i < j} u_{ij} \right)}$$

easily do  $\vec{p}_i$  integrals as before

$$Q_N \equiv \frac{1}{N! \lambda^{3N}} Z_N$$

where configuration integral  $Z_N$

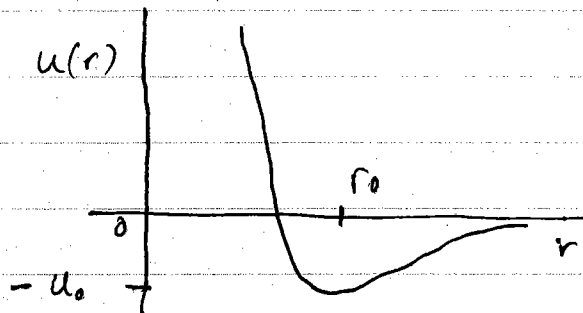
$$Z_N \equiv \left( \prod_k \int d^3 r_k \right) e^{-\beta \sum_{i < j} u_{ij}}$$

$$= \int d^3 r_1 \dots d^3 r_N \prod_{i < j} e^{-\beta u_{ij}}$$

When  $u_{ij} = 0$  (no interaction)  $Z_N = V^N$  and

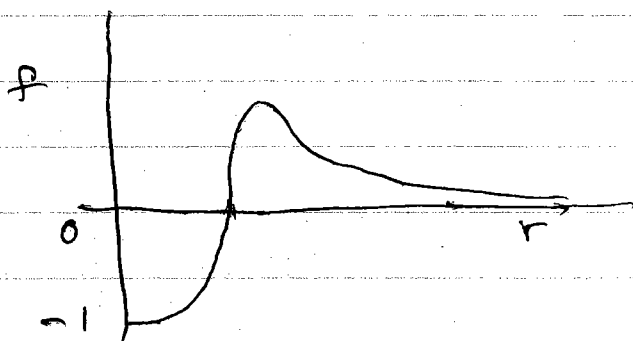
$$Q_N = \frac{V^N}{N! \lambda^{3N}} \quad \text{as found before for ideal gas}$$

Define  $f_{ij} \equiv e^{-\beta u_{ij}} - 1$



typical pair interaction behaves as;  
 $u(r) \rightarrow \infty$  as  $r \rightarrow 0$  repulsive core  
 $u(r) \rightarrow 0^-$  as  $r \rightarrow \infty$  attractive tail

minimum at  $r_0$  of depth  $u_0$



$f(r) \rightarrow 0$  as  $r \rightarrow \infty$

$f(r) \rightarrow -1$  as  $r \rightarrow 0$

$f(r)$  is non zero only for

$r \lesssim$  range of interaction

$\Rightarrow$  expect  $\int f(r) dr \ll \int dr$

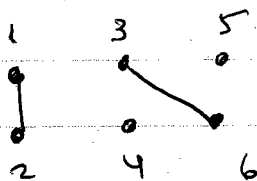
$\Rightarrow$  expand in  $f$

$$Z_N = \int d^3r_1 \dots d^3r_N \prod_{i < j} (1 + f_{ij}) \quad \text{expand the products}$$

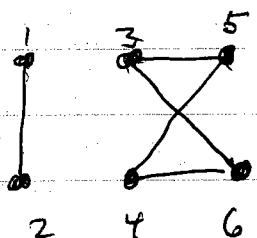
$$= \int d^3r_1 \dots d^3r_N \left[ 1 + \sum_{i < j} f_{ij} + \sum_{\substack{i < j \\ k < l}} f_{ij} f_{kl} + \dots \right]$$

To each term in the above expansion we can associate a graph. In each such graph each particle is a vertex, each factor  $f_{ij}$  is a bond.

For example:  $N=6$  particles



$$= \int d^3r_1 \dots d^3r_6 f_{12} f_{36}$$



$$= \int d^3r_1 \dots d^3r_6 f_{12} f_{35} f_{46} f_{36} f_{45}$$

The sums in  $Z_N$  represent a sum over all such  $N$ -particle graphs.

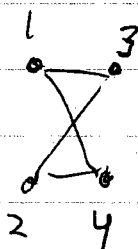
In the last example, we can factor the integrations

$$= \left[ \int d^3r_1 d^3r_2 f_{12} \right] \left[ \int d^3r_3 \dots d^3r_6 f_{35} f_{46} f_{36} f_{45} \right]$$

Such a factorization will always take place for a graph that consists of disconnected clusters.

Therefore we consider specifically now just connected graphs. Define an  $l$ -cluster - a graph of  $l$ -vertices all of which are connected, i.e. cannot separate into disjoint groups without cutting a bond.

for example



$$= \int d^3r_1 \dots d^3r_4 f_{13} f_{24} f_{14} f_{24}$$

is a 4-cluster

Each  $l$ -cluster is proportional to volume  $V$  in the  $V \rightarrow \infty$  limit. To see this, one can always transform the coord positions of the  $l$  particles into a center of mass coord and  $l-1$  relative coords. The integral over the center of mass coord gives  $V$  since the integrand is independent of center of mass position (depends only on relative displacement between particles). The integrals over the relative coords give finite amount due to the factors  $f_{ij}$  which vanish as one exceeds the range of the interaction.

for example  $I = \int d^3r_1 \dots d^3r_4 f_{13} f_{24} f_{14} f_{23}$

define  $\vec{R} = \frac{\vec{r}_1 + \vec{r}_2 + \vec{r}_3 + \vec{r}_4}{4}$

$$\vec{r}_{13} = \vec{r}_1 - \vec{r}_3$$

$$\vec{r}_{24} = \vec{r}_2 - \vec{r}_4$$

$$\vec{r}_{14} = \vec{r}_1 - \vec{r}_4$$

$$\Rightarrow \vec{r}_{23} = \vec{r}_{24} - \vec{r}_{14} + \vec{r}_{13}$$

$$I = \int d^3R \int d^3r_{13} d^3r_{24} d^3r_{14} f(\vec{r}_{13}) f(\vec{r}_{24}) f(\vec{r}_{14}) f(\vec{r}_{24} - \vec{r}_{14} + \vec{r}_{13})$$

Define cluster integral

$$b_e(V, T) \equiv \frac{1}{e!} \frac{1}{V \lambda^{3(l-1)}} \quad (\text{sum of all possible } l\text{-cluster graphs})$$

factor  $V$  so that  $b_e \rightarrow \text{const}$  as  $V \rightarrow \infty$   
 factor  $\lambda^{3(l-1)}$  so that  $b_e$  is dimensionless

We will show that one can express all the terms in the configuration integral  $Z_N$  in terms of the  $b_l$ . Also, in the end we are really interested in the free energy which is related to  $\ln Z_N$ . We will see that  $\ln Z_N$  is expressed directly in terms of the  $b_l$ .

To find all  $l$ -clusters, first write down the  $l$  vertices corresponding to particles 1 to  $l$ . Then draw all possible ways to connect them into a single connected graph.

### Example 5

$$l=1 \quad b_1 = \frac{1}{V} \left[ \overset{1}{\circ} \right] = \frac{1}{V} \int d^3 r_1 = 1$$

$$l=2 \quad b_2 = \frac{1}{2! V \lambda^3} \left[ \overset{1}{\circ} \text{---} \overset{2}{\circ} \right] = \frac{1}{2! V \lambda^3} \int d^3 r_1 \int d^3 r_2 f_{12}$$

$$= \frac{1}{2 \lambda^3} \int d^3 r f(r)$$

there is only one possible way to make a 2-cluster!

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

4 possible ways to make a 3-cluster!

$$= \frac{1}{3! V \lambda^6} \left[ \int d^3 r_1 d^3 r_2 d^3 r_3 \left( f_{12} f_{23} + f_{12} f_{13} + f_{13} f_{23} + f_{12} f_{13} f_{23} \right) \right]$$

each of these three has same numerical value - just relabel integration vars

$$b_3 = \frac{1}{6V\lambda^6} \left[ 3V \int d^3r_{12} d^3r_{23} f_{12} f_{23} + \int d^3r_1 d^3r_2 d^3r_3 f_{12} f_{13} f_{23} \right]$$

$$= \left[ \int d^3r f(r) \right]^2$$

$$= 2 \left[ \frac{1}{2\lambda^3} \int d^3r f(r) \right]^2 + \frac{1}{6V\lambda^6} \int d^3r_1 d^3r_2 d^3r_3 f_{12} f_{13} f_{23}$$

$$\bar{r}_{12} = \bar{r}_1 - \bar{r}_2$$

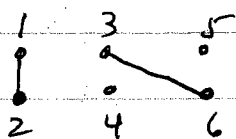
$$\bar{r}_{23} = \bar{r}_2 - \bar{r}_3$$

$$\bar{r}_{13} = \bar{r}_{12} + \bar{r}_{23}$$

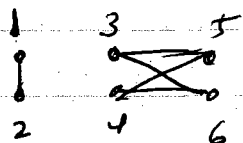
$$b_3 = 2b_2^2 + \frac{1}{6\lambda^6} \int d^3r_{12} d^3r_{23} f(\bar{r}_{12}) f(\bar{r}_{23}) f(\bar{r}_{12} + \bar{r}_{23})$$

all  $N$ -particle graphs factor into a set of disjoint  $l$ -clusters.

For example:  $N=6$  particles



has  $\begin{cases} 2 & 1\text{-clusters} \\ 2 & 2\text{-clusters} \end{cases}$



has  $\begin{cases} 1 & 2\text{-cluster} \\ 1 & 4\text{-cluster} \end{cases}$

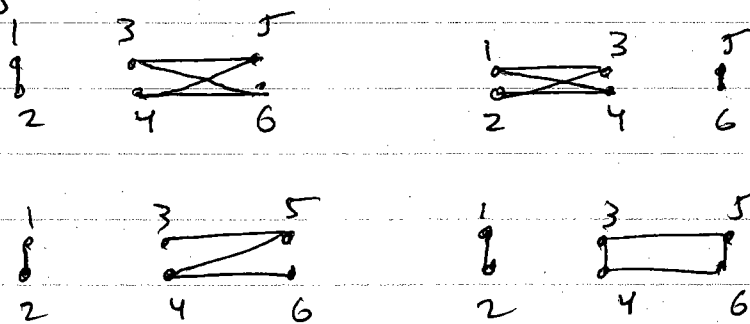
In general an  $N$ -particle graph can have  $m_l$   $l$ -clusters where

$$\sum_{l=1}^N l m_l = N$$

since  $l = \#$  particles in  $l$ -cluster

Denote  $S\{m_l\}$  = sum of all graphs that are divided into the particular distribution of  $l$ -clusters given by the numbers  $\{m_l\}$

For  $N=6$ , for example,  $S\{m_2=1, m_4=1\}$  is the sum over all graphs which have 1 2-cluster and 1 4-cluster. It would include the following four graphs



as well as many others!

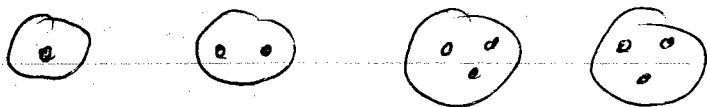
Example  $N=9$  particles 

for above decomposition  $\{m_l\}$ ,

$$S\{m_l\} = \sum_P [\text{isolated}]^{m_1} [\text{edge}]^{m_2} [\text{2-circles} + \text{3-circles} + \text{4-circles} + \text{5-circles}]^{m_3}$$

sum over all possible ways to group the  $N$  particles into the specified  $\{m_l\}$   $l$ -clusters. Each term in this sum gives the same numerical value as one can always relabel the variables of integration to make them look the same.

In this example of  $N=9$



$$9 \times \frac{(8 \times 7)}{2} \times \frac{(6 \times 5 \times 4)}{(3 \times 2)} \times \frac{(3 \times 2 \times 1)}{(3 \times 2)} \times \frac{1}{2} = \frac{9!}{1! 2! (3!)^2 2}$$

↑  
9 ways to pick the particle in the 1-cluster

↑  
8 ways to pick 1st particle of 2-cluster, 7 ways to pick 2nd member of 2-cluster. But the order of these does not matter  $\Rightarrow$  divide by 2.

↑  
doesn't matter which of the two 3-clusters is chosen first

In general the number of ways to divide  $N$  particles in a given grouping  $\{m_l\}$  of  $l$ -clusters is

$$\frac{N!}{[(1!)^{m_1} (2!)^{m_2} \dots (l!)^{m_l} \dots]} \frac{1}{[m_1! m_2! \dots m_l! \dots]}$$

$$= \frac{N!}{\prod_{l=1}^{\infty} [(l!)^{m_l} m_l!]}$$



$$\Rightarrow S\{m_e\} = \left\{ \frac{N!}{\prod_{e=1}^{\infty} (e!)^{m_e} m_e!} \right\} \prod_{e=1}^{\infty} \left[ \frac{e! v \lambda^{3(e-1)} b_e}{m_e!} \right]^{m_e}$$

$\uparrow$  contribution from graph  
of all  $e$ -clusters

$$= N! \prod_{e=1}^{\infty} \frac{(v \lambda^{3(e-1)} b_e)^{m_e}}{m_e!}$$

$$Z_N = \sum'_{\{m_e\}} S\{m_e\} = N! \lambda^{3N} \sum'_{\{m_e\}} \left[ \prod_{e=1}^{\infty} \frac{(b_e \frac{v}{\lambda^3})^{m_e}}{m_e!} \right]$$

where  $\sum'$  is over only  $\{m_e\}$  such that  $\sum_e e m_e = N$

and we used  $\prod_e (\lambda^{3e})^{m_e} = \prod_e \lambda^{3e m_e} = \lambda^{3 \sum_e e m_e} = \lambda^{3N}$

$$Q_N = \frac{1}{N! \lambda^{3N}} Z_N = \sum'_{\{m_e\}} \left[ \prod_{e=1}^{\infty} \frac{(b_e \frac{v}{\lambda^3})^{m_e}}{m_e!} \right]$$

Grand partition function

$$\mathcal{Z} = \sum_{N=0}^{\infty} Z^N Q_N$$

$$\text{we } Z^N = \prod_e (z^e)^{m_e}$$

$$= \sum_{N=0}^{\infty} \sum'_{\{m_e\}} \prod_{e=1}^{\infty} \frac{(b_e z^e \frac{v}{\lambda^3})^{m_e}}{m_e!}$$

$\uparrow$   $\uparrow$  constraint  $\sum_e e m_e = N$   
 sum over all  $N$

Once we lift the constraint on  $N$  by summing over it, we can now sum over all values of the  $m_e$  independently

$$\begin{aligned} \mathcal{Z} &= \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \dots \left[ \frac{1}{m_1!} \left( \frac{V}{\lambda^3} z b_1 \right)^{m_1} \right] \left[ \frac{1}{m_2!} \left( \frac{V}{\lambda^3} z^2 b_2 \right)^{m_2} \right] \dots \\ &= \prod_{e=1}^{\infty} \left\{ \sum_{m=0}^{\infty} \frac{1}{m!} \left( \frac{V}{\lambda^3} z^e b_e \right)^m \right\} = \prod_{e=1}^{\infty} e^{b_e z^e V/\lambda^3} \end{aligned}$$

$$(1) \quad \frac{p}{k_B T} = \frac{1}{V} \ln \mathcal{Z} = \frac{1}{\lambda^3} \sum_{e=1}^{\infty} b_e z^e$$

cluster integrals  $b_e$  are coefficients of Taylor series expansion of  $\frac{p \lambda^3}{k_B T}$  in terms of fugacity  $z$ .

By going to the grand canonical ensemble we replace the dependence on  $N/V$  the density, with a dependence instead on fugacity  $z$ . If we wish to return to find an expansion for  $p$  in terms of density rather than  $z$ , we need to find the relation between  $n$  and  $z$ . This is given by

$$(2) \quad \frac{1}{V} = n = \frac{N}{V} = \frac{1}{V} z \frac{\partial \ln \mathcal{Z}}{\partial z} = \frac{1}{\lambda^3} \sum_{e=1}^{\infty} e b_e z^e$$

In principle we wish to eliminate  $z$  between eqs (1) and (2) to get an expansion for  $\frac{p}{k_B T}$  in terms of the density  $n$ .