Classical non-ideal gas

The Mayer cluster expansion

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

Assume pairwise interaction

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

$\uparrow$ counts all pairs

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

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

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

where configuration integral Z_N

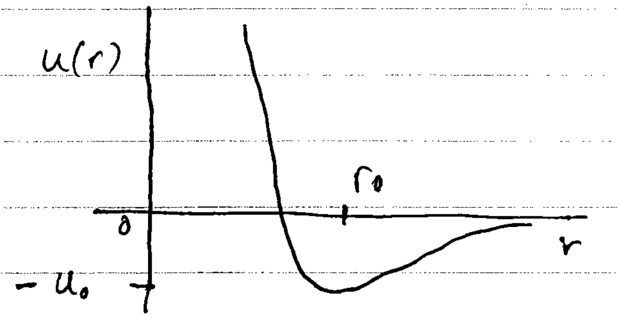
$$Z_N \equiv \left(\prod_k \int d^3r_k \right) e^{-\beta \sum_{i<j} u_{ij}}$$

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

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

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

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

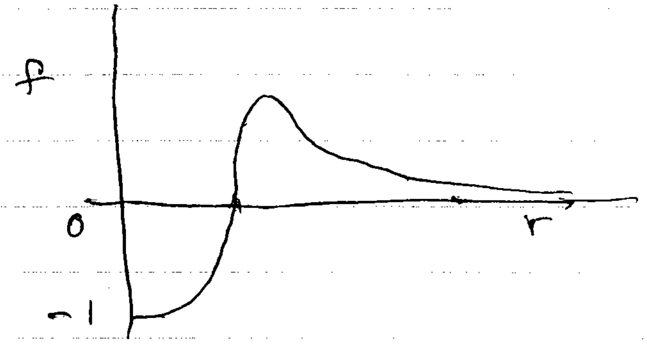


typical pair interaction behaves as:

$u(r) \to \infty$ as $r \to 0$ repulsive cor

$u(r) \to 0^-$ as $r \to \infty$ attractive tai

minimum at r_0 of depth u_0



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

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

$f(r)$ is non zero only for $r \lesssim$ range of interaction

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

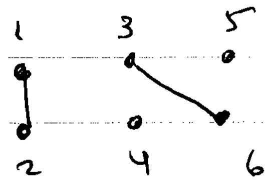
$\Rightarrow$ expand in f

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

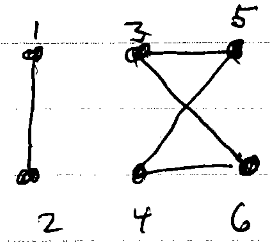
$$= \int d^3r_1 \cdots d^3r_N \left[1 + \sum_{i<j} f_{ij} + \sum_{\substack{i<j \\ k<l}} f_{ij} f_{kl} + \cdots \right]$$

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



$$= \int d^3r_1 \cdots d^3r_6 \; f_{12} \, f_{36}$$



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

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

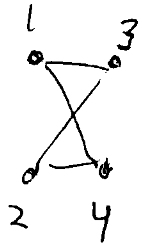
In the last example, we can factor the integrations

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

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

Therefore we consider specifically now just <u>connected</u> graphs. Define an <u>l-cluster</u> - a graph of l-vertices all of which are connected, ie cannot separate into disjoint groups without cutting a bond.

for example



$$= \int d^3r_1 \cdots d^3r_4 \; f_{13} \, f_{24} \, f_{14} \, f_{24}$$

is a 4-cluster

Each l-cluster is proportional to volume V in the $V \to \infty$ 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 $I = \int d^3r_1 \cdots d^3r_4 \; f_{13} f_{24} f_{14} f_{23}$

$$\text{define} \quad \vec{R} = \frac{\vec{r}_1 + \vec{r}_2 + \vec{r}_3 + \vec{r}_4}{4} \qquad \begin{aligned} \vec{r}_{13} &= \vec{r}_1 - \vec{r}_3 \\ \vec{r}_{24} &= \vec{r}_2 - \vec{r}_4 \\ \vec{r}_{14} &= \vec{r}_1 - \vec{r}_4 \\ \Rightarrow \quad \vec{r}_{23} &= \vec{r}_{24} - \vec{r}_{14} + \vec{r}_{13} \end{aligned}$$

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

Define <u>cluster integral</u>

$$b_l(V,T) \equiv \frac{1}{l!} \frac{1}{\underset{\nearrow}{V} \lambda^{3(l-1)}} \text{ (sum of all possible } l\text{-cluster graph}$$

factor V so that $b_l \to$ const as $V \to \infty$

factor $\lambda^{3(l-1)}$ so that b_l 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.

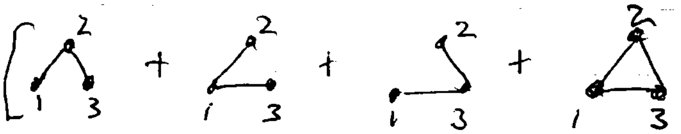
<u>Examples</u>

$\ell = 1$ $\quad b_1 = \frac{1}{V}\Big[$  $\Big] = \frac{1}{V}\int d^3r_1 = \underline{1}$

$\ell = 2$ $\quad b_2 = \frac{1}{2!V\lambda^3}\Big[$  $\Big] = \frac{1}{2!V\lambda^3}\int d^3r_1 \int d^3r_2\, f_{12}$

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

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

$\ell = 3$ $\quad b_3 = \frac{1}{3!V\lambda^6}\Big[$  $\Big]$

~~4~~ possible ways to make a 3-cluster

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

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

$$b_3 = \frac{1}{6V\lambda^6}\Big[3V\underbrace{\int d^3\bar{r}_{12}\, d^3r_{23}\, f_{12} f_{23}}_{=\left[\int d^3r\, f(r)\right]^2} + \int d^3r_1\, d^3r_2\, d^3r_3\, f_{12} f_{13} f_{23}$$

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

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

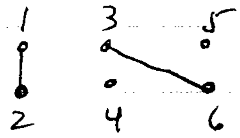
$\bar{r}_{23} = \bar{r}_2 - \bar{r}_3$

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

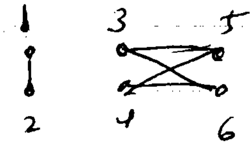
$$b_3 = 2b_2^2 + \frac{1}{6\lambda^6}\int d^3r_{12}\, d^3r_{23}\, f(\bar{r}_{12})\, f(\bar{r}_{23})\, f(\bar{r}_{12} + \bar{r}_{23})$$

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

For example: $N = 6$ particles



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



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

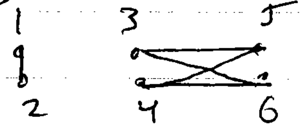
In general an N-particle graph can have m_ℓ ℓ-clusters where

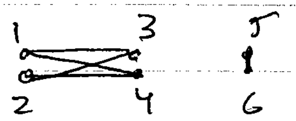
$$\sum_{\ell=1}^{N} \ell m_\ell = N$$

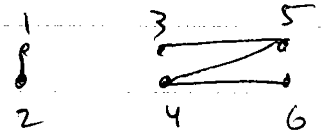
since ℓ = # particles in ℓ-cluster

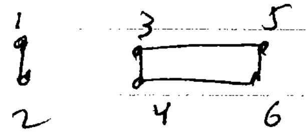
Denote $S\{m_\ell\}$ = sum of all graphs that are divided into the particular distribution of ℓ-clusters given by the numbers $\{m_\ell\}$

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,



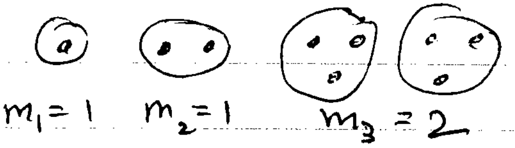






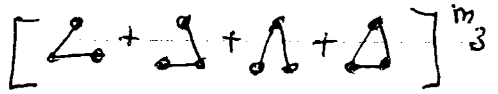
as well as many others!

<u>Example</u> $N=9$ particles



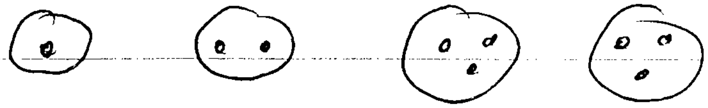
for above decomposition $\{m_\ell\}$,

$$S\{m_\ell\} = \sum_{P} [\circ]^{m_1} [\circ\!-\!\circ]^{m_2} [\quad]^{m_3}$$



↑ sum over all possible ways to group the N particles into the specified $\{m_\ell\}$ 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



$$9 \times \frac{(8\times7)}{2} \times \frac{(6\times5\times4)}{(3\times2)} \times \frac{(3\times2\times1)}{(3\times2)} \times \frac{1}{2} = \frac{9!}{1!\,2!\,(3!)^2\,2}$$

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 ⇒ divide by 2.

doesnt matter which of the two 3-clusters is chosen first

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

$$\frac{N!}{\left[(1!)^{m_1}(2!)^{m_2}\cdots(\ell!)^{m_\ell}\cdots\right]}\,\frac{1}{\left[m_1!\,m_2!\cdots m_\ell!\cdots\right]}$$

$$= \frac{N!}{\prod_{\ell=1}^{\infty}\left[(\ell!)^{m_\ell}\,m_\ell!\right]}$$

$$\Rightarrow \quad S\{m_\ell\} = \left\{ \frac{N!}{\prod_{\ell=1} (\ell!)^{m_\ell} m_\ell!} \right\} \prod_{\ell=1}^{N} \Big[\underbrace{\ell!\, V \lambda^{3(\ell-1)}}\, b_\ell \Big]^{m_\ell}$$

↑ contribution from graph of all ℓ-clusters

$$= N! \prod_{\ell=1}^{N} \frac{\left(V \lambda^{3(\ell-1)} b_\ell\right)^{m_\ell}}{m_\ell!}$$

$$Z_N = \sum_{\{m_\ell\}}{}' S\{m_\ell\} = N!\, \lambda^{3N} \sum_{\{m_\ell\}}{}' \left[\prod_{\ell=1}^{N} \frac{\left(b_\ell \frac{V}{\lambda^3}\right)^{m_\ell}}{m_\ell!} \right]$$

where $\sum'$ is over only $\{m_\ell\}$ such that $\sum_\ell \ell m_\ell = N$

and we used $\prod_\ell (\lambda^{3\ell})^{m_\ell} = \prod_\ell \lambda^{3\ell m_\ell} = \lambda^{3\sum_\ell \ell m_\ell} = \lambda^{3N}$

$$Q_N = \frac{1}{N!\, \lambda^{3N}} Z_N = \sum_{\{m_\ell\}}{}' \left[\prod_{\ell=1}^{N} \frac{\left(b_\ell \frac{V}{\lambda^3}\right)^{m_\ell}}{m_\ell!} \right]$$

Grand partition function

$$\mathcal{L} = \sum_{N=0}^{\infty} z^N Q_N \qquad \text{use } z^N = \prod_\ell (z^\ell)^{m_\ell}$$

$$= \sum_{N=0}^{\infty} \sum_{\{m_\ell\}}{}' \prod_{\ell=1}^{N} \frac{\left(b_\ell z^\ell \frac{V}{\lambda^3}\right)^{m_\ell}}{m_\ell!}$$

↑ ↑ constraint $\sum_\ell \ell m_\ell = N$

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_ℓ independently

$$\mathcal{Z} = \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \cdots\cdots \left[\frac{1}{m_1!}\left(\frac{V}{\lambda^3} z b_1\right)^{m_1}\right]\left[\frac{1}{m_2!}\left(\frac{V}{\lambda^3} z^2 b_2\right)\right]^{m_2} \cdots$$

$$= \prod_{\ell=1}^{\infty}\left\{\sum_{m=0}^{\infty} \frac{1}{m!}\left(\frac{V}{\lambda^3} z^\ell b_\ell\right)^m\right\} = \prod_{\ell=1}^{\infty} e^{b_\ell z^\ell V/\lambda^3}$$

$$(1) \quad \frac{p}{k_BT} = \frac{1}{V}\ln \mathcal{Z} = \frac{1}{\lambda^3}\sum_{\ell=1}^{\infty} b_\ell z^\ell$$

cluster integrals b_ℓ are coefficients of Taylor series expansion of $\frac{p\lambda^3}{k_BT}$ 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

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

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