Classical non-ideal gas

The Mayer cluster expansion

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

Assume pairwise interactions

\[ H = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} u_{ij} \]

where \( u_{ij} = u(r_{ij}) \)

\[ Q_N = \frac{1}{N! h^{3N}} \left( \prod_{k=1}^{N} d^3r_k \prod_{i<j} d^3p_{ij} \right) e^{-\beta \left( \sum_{k=0}^{N} \frac{p_k^2}{2m} + \sum_{i<j} u_{ij} \right)} \]

counts all pairs

\[ Q_N = \frac{1}{N! h^{3N}} Z_N \]

where configuration integral \( Z_N \)

\[ Z_N = \left( \prod_{k=1}^{N} d^3r_k \right) e^{-\beta \sum_{i<j} u_{ij}} \]

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

when \( u_{ij} = 0 \) (no interaction) \( Z_N = V^N \)

\[ Q_N = \frac{V^N}{N! h^{3N}} \] as found before for ideal gas
Define \( f_{ij} = e^{-\beta u(r)} - 1 \)

typical pair interaction behaves as:
\( u(r) \to \infty \) as \( r \to 0 \) repulsive core
\( u(r) \to 0^- \) as \( r \to \infty \) attractive tail
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 \( r \in \) range of interaction

\[ \Rightarrow \text{expect } \int f(r) \, dr \ll \int dr \]

\[ \Rightarrow \text{expand in } f \]

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

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

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

\[
\begin{array}{c}
1 \quad 3 \quad 5 \\
6
\end{array}
= \int d^3r_1 \cdots d^3r_6 \; f_{12} f_{34}
\]

\[
\begin{array}{c}
1 \quad 3 \\
2 \quad 4 \quad 5 \\
6
\end{array}
= \int d^3r_1 \cdots d^3r_6 \; f_{12} f_{35} f_{46} f_{36} f_{45}
\]

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 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

\[
\begin{array}{c}
1 \quad 3 \\
2 \quad 4
\end{array}
= \int d^3r_1 \cdots d^3r_4 \; f_{13} f_{24} f_{14} f_{24}
\]

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 coordinate positions of the $l$ particles into a center of mass coordinate and $l-1$ relative coordinates. The integral over the center of mass coordinate gives $V$ since the integrand is independent of center of mass position (depends only on relative displacement between particles). The integrals over the relative coordinates give finite amount due to the factors $f_{ij}$ which vanish as we exceed the range of the interaction.

\[
I = \int d^3r_1 \cdots d^3r_2 f_{13} f_{24} f_{14} f_{23}
\]

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

\[
\vec{r}_{13} = \vec{r}_1 - \vec{r}_3 \\
\vec{r}_{24} = \vec{r}_2 - \vec{r}_4 \\
\vec{r}_{14} = \vec{r}_1 - \vec{r}_4
\]

\[
\Rightarrow \vec{r}_{23} = \vec{r}_{24} - \vec{r}_{14} + \vec{r}_3
\]

Define cluster integral

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

factor $V$ so that $b_2 \to \text{const as } V \to \infty$

factor $A^3(l-1)$ so that $b_2$ is dimensionless
We will show that one can express all the terms in the configuration integral $Z_N$ in terms of the $b_k$. 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 $b_k$.

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**

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

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

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

There is only one possible way to make a 2-cluster?

$$l=3 \quad b_3 = \frac{1}{3! V \lambda^6} \left[ \int \int \int \right]$$

4 possible ways to make a 3-cluster?

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

Each of these three has same numerical value - just relabel integration vars
\[ b_3 = \frac{1}{6 V A \lambda^6} \left[ 3 \sqrt{\int d^3 \tau_2 d^3 \tau_3 \frac{f_{12} f_{23}}{f_{12} f_{13} f_{23}}} + \int d^3 \tau_1 d^3 \tau_2 d^3 \tau_3 \frac{f_{12} f_{13} f_{23}}{f_{12} f_{13} f_{23}} \right] \times \left[ \int d^3 \rho f(\rho) \right]^2 \]

\[ = 2 \left[ \frac{1}{2 \lambda^3} \int d^3 \rho f(\rho) \right]^2 + \frac{1}{6 V \lambda^6} \int d^3 \tau_1 d^3 \tau_2 d^3 \tau_3 \frac{f_{12} f_{13} f_{23}}{f_{12} f_{13} f_{23}} \]

\[ \overline{\tau}_{12} = \overline{\tau}_1 - \overline{\tau}_2 \]
\[ \overline{\tau}_{23} = \overline{\tau}_2 - \overline{\tau}_3 \]
\[ \overline{\tau}_{13} = \overline{\tau}_1 + \overline{\tau}_{23} \]

\[ b_3 = 2 b_2^2 + \frac{1}{6 \lambda^6} \int d^3 \tau_1 d^3 \tau_2 d^3 \tau_3 f(\overline{\tau}_{12}) f(\overline{\tau}_{23}) f(\overline{\tau}_{12} + \overline{\tau}_{23}) \]

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All \( N \)-particle graphs factor into a set of disjoint \( l \)-clusters.

For example: \( N = 6 \) particles

\[
\begin{array}{c}
1 \quad 3 \quad 5 \\
2 \quad 4 \quad 6
\end{array}
\]

has \( \{ 2 \text{ 1-clusters} \} \) \( \{ 2 \text{ 2-clusters} \} \)

\[
\begin{array}{c}
1 \quad 3 \quad 5 \\
2 \quad 4 \quad 6
\end{array}
\]

has \( \{ 1 \text{ 2-cluster} \} \)

\[
\begin{array}{c}
1 \quad 3 \quad 5 \\
2 \quad 4 \quad 6
\end{array}
\]

has \( \{ 1 \text{ 4-cluster} \} \)

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

\[
\sum_{l=1}^{N} l m_l = N \quad \text{since} \quad l = \# \text{ particles in } \ l \text{-cluster}
\]
Denote \( S^{\{m_i\}} = \text{sum of all graphs that are divided into the particular distribution of } l\)-clusters given by the numbers \( \{m_i\} \).

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:

\[
\begin{align*}
\textbf{1} & \quad \boxed{3} \quad \boxed{5} \\
\text{2} & \quad \boxed{4} \quad \boxed{6} \\
\end{align*}
\]

\[
\begin{align*}
\textbf{1} & \quad \boxed{3} \quad \boxed{5} \\
\text{2} & \quad \boxed{4} \quad \boxed{6} \\
\end{align*}
\]

as well as many others!

\textbf{Example} \( N=9 \) particles \( \circ \circ \circ \circ \circ \circ \circ \circ \circ \)

\( m_1=1 \quad m_2=1 \quad m_3=2 \)

for above decomposition \( \{m_i\} \)

\[ S^{\{m_i\}} = \sum P^{m_1} [\circ - ]^{m_2} [\circ + \Delta + \Lambda + \Delta ]^{m_3} \]

sum over all possible ways to group the \( N \) particles into the specified \( \{m_i\} \) \( l \)-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 N = 9

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

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 doesn't matter so divide by 2.

In general the number of ways to divide N particles in a given grouping \([m_1, m_2, \ldots, m_e]\) of e-clusters is

\[
\frac{N!}{\prod_{e=1}^{\infty} \left[ (l!)^{m_e} \frac{m_e!}{m_e!} \right]} = \frac{N!}{\prod_{e=1}^{\infty} \left[ (l!)^{m_e} \frac{m_e!}{m_e!} \right]}
\]
\begin{align*}
\sum E_{\text{me}^3} &= \sum_{e=1}^{N} \left( \frac{N!}{\prod_{e=1}^{N} (e!)^{m_e} m_e!} \right) \prod_{e=1}^{N} \Gamma \left( \frac{1}{2} \alpha^2 \frac{b e}{V^3} \right) \prod_{e=1}^{N} \left( \frac{2^{3} e^{3} \lambda \beta}{m_e^3} \right)^{m_e} \\
&= N! \prod_{e=1}^{N} \left( \frac{2^{3} e^{3} \lambda \beta}{m_e^3} \right)^{m_e} \\
\sum_{e=1}^{N} E_{\text{me}^3} &= N! \prod_{e=1}^{N} \left( \frac{2^{3} e^{3} \lambda \beta}{m_e^3} \right)^{m_e} \\
Z_N &= \sum_{\sum e} \sum E_{\text{me}^3} = N! 2^{3N} \sum_{\sum e} \left[ \frac{N!}{\prod_{e=1}^{N} (e!)^{m_e} m_e!} \left( \frac{2^{3} e^{3} \lambda \beta}{m_e^3} \right)^{m_e} \right] \\
\sum_{e} \sum E_{\text{me}^3} &= N! \prod_{e=1}^{N} \left( \frac{2^{3} e^{3} \lambda \beta}{m_e^3} \right)^{m_e} \\
\Omega_N &= \frac{1}{N! 2^{3N}} Z_N = \sum_{\sum e} \left[ \prod_{e=1}^{N} \left( \frac{2^{3} e^{3} \lambda \beta}{m_e^3} \right)^{m_e} \right] \\
\text{Grand partition function} \quad \zeta &= \sum_{N=0}^{\infty} Z_N \Omega_N = \prod_{e} Z^e = \prod_{e} \left( \frac{2^{3} e^{3} \lambda \beta}{m_e^3} \right)^{m_e} \\
&= \sum_{N=0}^{\infty} \sum_{\sum e} \prod_{e=1}^{N} \left( \frac{2^{3} e^{3} \lambda \beta}{m_e^3} \right)^{m_e} \\
&\uparrow \quad \text{constraint} \quad \sum_{e} e m_e = N \\
&\text{sum over all } N
\end{align*}
Once we lift the constraint on $N$ by summing over it, we can now sum over all values of the $m_i$ independently.

\[ L = \sum_{m_1=0}^{\infty} \sum_{m_2=0}^{\infty} \left[ \frac{1}{m_1!} \left( \frac{V}{3} \sum b_1 \right)^{m_1} \right] \left[ \frac{1}{m_2!} \left( \frac{V}{3} \sum b_2 \right)^{m_2} \right] \]

\[ = \prod_{e=1}^{\infty} \left\{ \sum_{m=0}^{\infty} \frac{1}{m!} \left( \frac{V}{3} \sum b_2 \right)^{m} \right\} \frac{b_2}{e^2} \frac{1}{\sqrt{\pi}} \]

\[ (1) \quad \frac{P}{k_B T} = \frac{1}{V} \ln L = \frac{1}{V} \sum_{e=1}^{\infty} b_2 \zeta^e \]


By going to the grand canonical ensemble, we replace the dependence on $N/V$, the density, with a dependence instead on fugacity $\zeta$. If we wish to return to finding an expansion for $P/n$ in terms of density rather than $\zeta$, we need to find the relation between $n$ and $\zeta$.

This is given by

\[ (2) \quad \frac{f}{V} = \frac{m}{V} = \frac{1}{V} \frac{\partial \ln L}{\partial \zeta} = \frac{1}{V} \sum_{e=1}^{\infty} e b_2 \zeta^e \]

In principle, we wish to eliminate $\zeta$ between eqs (1) and (2) to get an expansion for $P/n$ in terms of the density $\rho$.\]