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 \( u_{ij} = u(r_{ij}^{-\gamma}) \)

\[ Q_N = \frac{1}{N! \lambda^{3N}} \left( \prod_k \int d^3 r_k \int d^3 p_k \right) e^{-\beta \left( \sum_i \frac{P_i^2}{2m} + \sum_{i < j} u_{ij} \right)} \]

\( N \) counts all pairs

\[ Q_N \approx \frac{1}{N! \lambda^{3N}} Z_N \]

where configuration integral \( Z_N \)

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

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

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

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

typical pair interaction behaves as
\( u(r) \to \infty \) as \( r \to 0 \) repulsive \( \cos \),
\( u(r) \to 0^{-} \) as \( r \to \infty \) attractive \( \sin \),
minimum at \( r_0 \) of depth \( u_0 \).

\[ f(r) \to 0 \quad \text{as} \quad r \to \infty \]
\[ f(r) \to -1 \quad \text{as} \quad r \to 0 \]

\( f(r) \) is non-zero only for \( r \leq \) range of interaction
\[ \Rightarrow \text{expect} \int f(r) \, dr \ll \int dr \]
\[ \Rightarrow \text{expand in } f \]

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

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

To each term in the above expansion we can associate a graph. In each such graph each particle \( i \) a vertex each factor \( f_{ij} \)
is a bond.
For example: \( N = 6 \) particles

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

\[
\int d^3r_1 \cdots d^3r_6 \; f_{12} f_{34} f_{56}
\]

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

\[
\int d^3r_1 \cdots d^3r_6 \; f_{12} f_{35} f_{46} f_{36} f_{45}
\]

The sums in \( \mathbb{Z}_N \) 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:

\[
\begin{align*}
1 & \quad 3 \\
2 & \quad 4
\end{align*}
\]

\[
\int d^3r_1 \cdots d^3r_4 \; f_{13} f_{24} f_{14} f_{23}
\]

as 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 coordinates of the l particles with 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:

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

Define:

\[
\overline{R} = \sum_{i=1}^{l} \frac{r_i - \overline{r}_i}{4}
\]

\[
\overline{r}_{13} = \overline{r}_1 - \overline{r}_3
\]

\[
\overline{r}_{24} = \overline{r}_2 - \overline{r}_4
\]

\[
\overline{r}_{14} = \overline{r}_1 - \overline{r}_4
\]

\[
I = \int d^3\overline{R} \int d^3r_1 \int d^3r_2 \int d^3r_3 \int d^3r_4 f(\overline{r}_{13}) f(\overline{r}_{24}) f(\overline{r}_{14}) f(\overline{r}_{24} - \overline{r}_{14} + \overline{r}_{23})
\]

Define cluster integral:

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

Factor V so that \( b_e \to \text{const} \) as \( V \to \infty \)

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 $b_k$. 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.

\textbf{Example 5}

\begin{align*}
 l = 1 & \quad b_1 = \frac{1}{\sqrt{2}} \left[ \begin{array}{c} 0 \\ 0 \end{array} \right] = \frac{1}{\sqrt{2}} \int d^3 r_1 = 1 \\
 l = 2 & \quad b_2 = \frac{1}{2!} \sqrt{\lambda} a^3 \left[ \begin{array}{c} 0 \\
 1 \\
 2 \\
 3 \end{array} \right] = \frac{1}{2!} \sqrt{\lambda} a^3 \int d^3 r_1 d^3 r_2 \ f_{12} \\
 & \quad = \frac{1}{2!} \int d^3 r \ f(r) \\
 \text{there is only one possible way to make a 2-cluster} \\
 l = 3 & \quad b_3 = \frac{1}{3!} \sqrt{\lambda} a^6 \left[ \begin{array}{c} 1 \\
 2 \\
 3 \\
 1 \\
 2 \\
 3 \\
 1 \\
 2 \\
 3 \end{array} \right] \\
 \text{4 possible ways to make a 3-cluster} \\
 & \quad = \frac{1}{3!} \sqrt{\lambda} a^6 \left[ \int d^3 r_1 d^3 r_2 d^3 r_3 \ (f_{12} f_{23} + f_{12} f_{13} + f_{13} f_{23} + f_{12} f_{13} f_{23}) \right] \\
 \text{each of these three has same numerical value - just relabel integration vars.}
\end{align*}
\[ b_3 = \frac{1}{\sqrt{\lambda^2}} \left[ \frac{3}{2} \Gamma \left( \frac{3}{2} \right) \int \frac{d^3 \bar{n}_2}{2} \right] \left( f_{12} f_{23} + f_{13} f_{12} f_{23} \right) \left[ \int d^3 f \right]^2 \]

\[ = 2 \left[ \frac{1}{2} \int d^3 f \right]^2 + \frac{1}{6 \pi^2} \int d^3 \bar{n}_1 d^3 \bar{n}_2 d^3 \bar{n}_3 f_{12} f_{13} f_{23} \]

\[ \bar{n}_2 = \bar{n}_1 - \bar{n}_2 \]
\[ \bar{n}_{23} = \bar{n}_2 - \bar{n}_3 \]
\[ \bar{n}_3 = \bar{n}_1 + \bar{n}_2 \]

\[ b_3 = 2 b_2^2 + \frac{1}{6 \lambda^2} \int d^3 \bar{n}_1 d^3 \bar{n}_2 d^3 \bar{n}_3 f(\bar{n}_2) f(\bar{n}_{23}) f(\bar{n}_1 + \bar{n}_2) \]

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

For example: \( N = 6 \) particles

\[ \begin{array}{ccc}
1 & 3 & 5 \\
2 & 4 & 6
\end{array} \]

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

\[ \begin{array}{ccc}
1 & 3 & 5 \\
2 & 4 & 6
\end{array} \]

has \( \{ 1 \ \text{2-cluster} \} \)
\( \{ 1 \ \text{4-cluster} \} \)

In general an \( N \)-particle graph can have \( \sum l m_l = N \) since \( l = \# \) particles in \( l \)-cluster.
Denote \( S \{ \text{me}^{\ell} \} = \text{sum of all graphs that are divided into the particular distribution of } \ell\text{-clusters given by the numbers } \{ \text{me}^{\ell} \} \)  

For \( N=6 \), for example, \( S \{ \text{me}=1, m_4=1 \} \) is the sum over all graphs which have 1 2-cluster and 1 4-cluster, it would include the following four graphs:

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

as well as many others!

Example \( N=9 \) particles:

\[
\text{for above decomposition } \{ \text{me}^{\ell} \}, \\
S \{ \text{me}^{\ell} \} = \sum \left[ \begin{array}{c}
\bullet \\
m_1 = 1
\end{array} \right]^{m_1} \left[ \begin{array}{c}
\circ \circ \\
m_2 = 1
\end{array} \right]^{m_2} \left[ \begin{array}{c}
\circ \circ \circ \\
m_3 = 2
\end{array} \right]^{m_3}
\]

sum over all possible ways to group the \( N \) particles into the specified \( \{ \text{me}^{\ell} \} \) \( \ell\)-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 No. 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, doesn't matter which of the two 3-clusters is chosen first
But the order of these does not matter so divide by 2.

In general, the number of ways to divide \( N \) particles in a given grouping \( \{m_e\} \) of \( l \)-clusters is

\[ \frac{N!}{\prod_{e=1}^{\infty} \left( \frac{l!}{m_e!} \right)^{m_e}} \]

\[ \frac{1}{[1 \times (2!)^{m_2} \cdots (l!)^{m_l} \cdots]} \]

\[ \frac{1}{[m_1! \cdot m_2! \cdots m_e! \cdots]} \]
\[ S \{ e_m^3 \} = \left\{ \frac{N!}{\prod_{l=1}^{N} (l!)^{m_e}} \right\} \times \prod_{l=1}^{N} \left( \frac{\alpha^{3(l-1)} b_e}{m_e!} \right) \]

| Contribution from graphs of all \( l \)-clusters |

\[ = N! \prod_{l=1}^{N} \left( \frac{\alpha^{3(l-1)} b_e}{m_e!} \right) \]

\[ Z_N = \sum \left\{ S \{ e_m^3 \} = N! \alpha^{3N} \sum \left[ \prod_{l=1}^{N} \left( \frac{(be \frac{V}{\alpha^3})^{m_e}}{m_e!} \right) \right] \right\} \]

where \( \sum \) is over only \( e_m^3 \) such that \( \sum_{e} l m_e = N \)

and we used \( \prod_{l} (\alpha^3 e)^{m_e} = \prod_{l} \alpha^{3 l m_e} = \alpha^{3 \sum_{e} l m_e} = \alpha^{3N} \)

\[ \alpha_N = \frac{1}{N! \alpha^{3N} Z_N} = \sum \left[ \prod_{l=1}^{N} \left( \frac{(be \frac{V}{\alpha^3})^{m_e}}{m_e!} \right) \right] \]

**Grand partition function**

\[ \mathcal{Z} = \sum_{N=0}^{\infty} Z^N \alpha_N \]

\[ = \sum_{N=0}^{\infty} \sum_{e_m^3}^{\prime} \prod_{l=1}^{N} \left( \frac{(be \frac{Z^2 V}{\alpha^3})^{m_e}}{m_e!} \right) \]

\[ \uparrow \quad \text{Constraint} \quad \sum_{e} l m_e = N \]

\[ \text{sum over all } N \]
Once we lift the constraint on \( N \) by summing over it, we can now sum over all values of the \( m \) independently:
\[
\mathcal{L} = \sum_{m_1 = 0}^{\infty} \sum_{m_2 = 0}^{\infty} \left[ \frac{1}{m_1!} \left( \frac{V}{3} z b_1 \right)^{m_1} \right] \left[ \frac{1}{m_2!} \left( \frac{V}{3} z^2 b_2 \right)^{m_2} \right] = \prod_{e=1}^{\infty} \left\{ \sum_{m=0}^{\infty} \frac{1}{m!} \left( \frac{V}{3} z b_e \right)^m \right\} = \prod_{e=1}^{\infty} e^{\frac{b_e z^e V}{\lambda^3}}
\]

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

"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 \( f \) in terms of density rather than \( z \), we need to find the relation between \( n \) and \( z \).

This is given by
\[
\frac{f}{V} = m = \frac{N}{V} = \frac{1}{V} \frac{\partial \ln \mathcal{L}}{\partial z} = \frac{1}{\lambda^3} \sum_{e=1}^{\infty} b_e z^e
\]

(2) \( \frac{f}{V} = \frac{N}{V} = \frac{1}{V} \frac{\partial \ln \mathcal{L}}{\partial z} = \frac{1}{\lambda^3} \sum_{e=1}^{\infty} e b_e z^e \)

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