1 The Mayer Linked Cluster Expansion

1, The Grand Canonical Ensemble is

\[ Z(\mu, V, T) = \sum_{N=0}^{\infty} z^N Z(N, V, T) \]  

(1)

Therefore the mean particle number is

\[ \langle N \rangle = \frac{\sum_{N=0}^{\infty} N z^N Z}{\sum_{N=0}^{\infty} z^N Z} = \frac{\partial \ln Z}{\partial \ln z} \]

(2)

The \( z = e^{\beta \mu} \) is fugacity. The pressure \( P \) is

\[ P(\mu, V, T) = \frac{kT}{V} \ln Z \]

(3)

So

\[ \frac{\langle N \rangle}{V} = \frac{1}{v} = \frac{z}{V} \frac{\partial}{\partial z} \ln Z \]

(4)

Therefore

\[ \frac{1}{v} = \frac{1}{V} \frac{\partial}{\partial \ln z} \left( \frac{PV}{kT} \right) = kT \frac{\partial}{\partial \mu} \left( \frac{PV}{kT} \right) \]

(5)

or in \( P(v, T, \mu) \)

\[ P(v, T, \mu) = kT \int \frac{\partial(\beta \mu)}{v} \]

(6)

2, For the classical, the grand partition function is

\[ Z(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{z}{\lambda^3} \right)^N Q_N \]

(7)

where

\[ Q_N = \int \prod_{i=1}^{N} d^3r \exp[-\sum_{i<j} \beta U(|r_{ij}|)] \]

\[ \lambda = \sqrt{\frac{2\pi \hbar^2}{mk_B T}} \]

(8)
For pairwise interaction $U(r_{ij})$, we define $f_{ij} = \exp(-\beta U(|r_{ij}|)) - 1$ and write

$$Q_N = \int \prod_{i=1}^{N} d^3 r_i \prod_{i<j} (1 + f_{ij})$$

$$= \int \prod_{i=1}^{N} d^3 r_i (1 + \sum_{i<j} f_{ij} + \sum_{i<j,k<l} f_{ij} f_{kl} + \cdots) \quad (9)$$

For a given term in the series, let $n_l$ be the number of $l$-clusters. Note that $n_l$ satisfy $N = \sum_l n_l$. Summing over all such sets $\{n_l\}$, we can write

$$Q_N = \sum_{\{n_l\}} \frac{N!}{\prod_l n_l! (l!)^{n_l}} \quad (10)$$

where

$$W(\{n_l\}) = \frac{N!}{\prod_l n_l! (l!)^{n_l}} \quad (11)$$

is the number of times terms with $\{n_l\}$ appear in $Q_N$. It follows that the grand partition function is

$$Z(\mu, V, T) = \sum_{N=0}^{\infty} \sum_{\{n_l\}} \frac{1}{N!} \left( \frac{z}{\lambda_T^3} \right)^N \frac{N!}{\prod_l n_l! (l!)^{n_l}} \prod_l b_l^{n_l}$$

$$= \sum_{\{n_l\}} \left( \frac{z}{\lambda_T^3} \right)^{\sum_l n_l} \prod_l \frac{b_l^{n_l}}{n_l! (l!)^{n_l}}$$

$$= \prod_l \sum_{n_l=0}^{\infty} \frac{1}{n_l!} \left( \frac{z b_l}{\lambda_T^3 l!} \right)$$

$$= \exp \left( \sum_l \frac{z b_l}{\lambda_T^3 l!} \right) \quad (12)$$

Hence from

$$P(\mu, V, T) = \frac{kT}{V} \ln Z$$

$$= \frac{kT}{V} \sum_l \frac{b_l}{\lambda_T^3 l!} z^l \quad (13)$$

we see that the pressure written as a series expansion in powers of $z$ has contribution only from the linked diagrams.

3. To the third order we have

$$P = \frac{kT}{\lambda_T^3} \sum_{l=1}^{\infty} b_l z^l = \frac{kT}{\lambda_T^3} (b_1 z + b_2 z^2 + b_3 z^3 + \cdots) \quad (14)$$
\[ b_1 = 1 \]
\[ b_2 = \frac{1}{2\lambda_2^2 V} \int d^3x_1 d^3x_2 f_{12} = \frac{1}{2\lambda_2^2 V} \int d^3x_1 d^3x_2 \left( e^{-\beta U(|x_1 - x_2|)} - 1 \right) \]
\[ b_3 = \frac{1}{3\lambda_0^2 V} \int d^3x_1 d^3x_2 d^3x_3 (f_{12} f_{13} + f_{12} f_{23} + f_{12} f_{13} f_{23}) = \frac{1}{6\lambda_0^2 V} \int d^3x_1 d^3x_2 d^3x_3 \left( e^{-\beta (U_{12} + U_{13} + U_{23})} - e^{-\beta U_{12}} - e^{-\beta U_{13}} - e^{-\beta U_{23}} + 2 \right) \]

Therefore insert \( P \) here
\[ PV = kT \ln Z \]

The exponential functions are analytic, so are the products of exponentials \( e^a e^b = e^{a+b} \). So \( z \) is analytic in \( z \). Furthermore, the exponential function \( e^{\alpha x} \) has no zeros for \( x > 0 \), provided that \( \alpha > 0 \).

5. The derivative of the pressure with respect to \( z \) is
\[ \frac{\partial}{\partial z} P(\mu, V, T) = \frac{kT \frac{\partial \ln Z}{\partial z}}{V} \]
\[ = \frac{kT}{V} \frac{1}{Z} \frac{\partial Z}{\partial z} \]
\[ = \frac{kT}{V} \frac{\langle N \rangle}{z} \]
\[ > 0 \]

which means that the pressure is monotonically increasing with respect to \( z \). Similarly
\[ \frac{\partial}{\partial z} \left( \frac{1}{v} \right) = \frac{1}{V} \frac{\partial}{\partial z} \left( \frac{z}{Z} \frac{\partial Z}{\partial z} \right) \]
\[ = \frac{1}{V} \frac{\partial}{\partial z} \left( \frac{1}{Z} \sum_{N=1}^{\infty} N z^N Z_N \right) \]
\[ = \frac{1}{zV} (\langle N^2 \rangle - \langle N \rangle^2) \]
\[ \geq 0 \]

So \( 1/v \) is also monotonically increasing function of \( z \).

6. We know
\[ \frac{P}{kT} = \frac{1}{\lambda_T^2} \sum_{l=1}^{\infty} b_l z^l \]
\[ \frac{1}{v} = \frac{1}{\lambda_T^2} \sum_{l=1}^{\infty} lb_l z^l \]

As \( V \to \infty \), \( b_l \to b_l \)
Therefore

\[ \frac{PV}{kT} = \sum_{m=0}^{\infty} a_m \left( \sum_{n=1}^{\infty} n \bar{b}_n z^n \right)^m = \sum_{l=1}^{\infty} \frac{\bar{b}_l z^l}{\sum_{l=1}^{\infty} \bar{b}_l z^l} \]  

(21)

Therefore

\[ \sum_{m=0}^{\infty} a_m \left( \sum_{n=1}^{\infty} n \bar{b}_n z^n \right)^{m+1} = \sum_{l=1}^{\infty} \bar{b}_l z^l \]

\[ = a_0 (\bar{b}_1 z + 2\bar{b}_2 z^2 + \cdots) + a_1 (\bar{b}_1 z + 2\bar{b}_2 z^2 + \cdots)^2 + a_2 (\bar{b}_1 z + 2\bar{b}_2 z^2 + \cdots)^3 + \cdots \]  

(22)

Therefore

\[ z^1 : \bar{b}_1 = a_0 \bar{b}_1 \]

\[ z^2 : \bar{b}_2 = 2a_0 \bar{b}_2 + a_1 \bar{b}_1^2 \]

\[ z^3 : \bar{b}_3 = 3\bar{b}_3 + 4a_1 \bar{b}_1 \bar{b}_2 + a_2 \bar{b}_1^3 \]  

(23)

Therefore

\[ a_0 = 1, a_1 = -\bar{b}_2, a_2 = 4\bar{b}_2^2 - 2\bar{b}_3 \]  

(24)

7,

\[ a_1 = -\bar{b}_1 = -\frac{1}{2\lambda^3} \int d^3r \int d^3r_{12} (e^{-\beta u_{12}} - 1) \]

\[ = -\frac{1}{2\lambda^3} \int_0^\infty 4\pi r^2 dr (e^{\beta u_0 r^6} - 1) - \int_0^\infty 4\pi r^2 dr \]

\[ = \frac{2\pi}{3\lambda^3} \left( a^3 - \frac{U_0 r_0^6}{kT a^3} \right) \]  

(25)

2 Statistical Mechanics of a Lattice Gas

1 The grand partition function

\[ Z = \sum_{N=0}^{\infty} z^N Z_N \]  

(26)

where \( Z_N \) is the canonical partition function. Consider the \( M \times M \) lattice by summing over the position \((n, m)\) for each particle \( 1 \cdots N \) of the gas and by summing over the pairs to account for all the configurations, where our Boltzmann term is the usual

\[ U_{ij} = \begin{cases} \infty, & i=j \\ -U_0, & i \text{ and } j \text{ are nearest neighbours} \\ 0, & \text{else} \end{cases} \]  

(27)

The summation can be normalized by \( N! \) and by \( a^{3N} \),

\[ e^{-\beta U(r_{ij})} \approx 1 + f_{ij} \]  

(28)
Therefore

\[ Q_N = \sum_{r_1} \sum_{r_2} \sum_{r_3} e^{-\beta \sum_{\text{pairs}} U(r_{ij})} \]

\[ = \sum_{r_1} \sum_{r_2} \cdots \sum_{r_N} (1 + (f_{12} + f_{13} + \cdots) + (f_{12}f_{13} + \cdots) + \cdots) \]  \hspace{1cm} (29)

Each term can be represented by a graph with \(N\) points in the following way

\[ = (\sum_{1,2} f_{12}) (\sum_{2,3,4} f_{23}f_{34}) \cdots \]  \hspace{1cm} (30)

where \(\sum'_{(1,2,\ldots)}\) is the sum over all configurations which link particles 1, 2, \cdots with the restriction that no two particles are on the same site.

Each graph can be written as a product of connected graphs, i.e. in the form

\[ \prod_{l=1}^{N} ((l!M^2b_l)^{a_l}) \]  \hspace{1cm} (31)

where \(a_l\) is the number of \(l\)-connected subgraphs and \(b_l\) is defined as

\[ b_l = \frac{1}{M^2l!} \{\text{sum of all possible } l\text{-connected graphs}\} \]  \hspace{1cm} (32)

With these definitions, the configurational sum in the grand partition function can be written as

\[ \sum_{a_l} \sum_{P_N} \prod_{l=1}^{N} ((l!M^2b_l)^{a_l}) \]  \hspace{1cm} (33)

where \(\sum_{P_N}\) is the sum over all permutations of the \(N\) particle labels which lead to the same graph.

Putting this back in the the grand partition function

\[ Z = \sum_{N=0}^{\infty} z^N \sum_{\{a_l\}} \sum_{N=0}^{N} (M^2b_l)^{a_l} \]

\[ = \sum_{a_1=0}^{\infty} \sum_{a_2=0}^{\infty} \cdots \sum_{a_l=0}^{\infty} \frac{1}{a_1!} (M^2b_1z)^{a_1} \]

\[ = \exp \left( \sum_{l=1}^{\infty} M^2b_1z^l \right) \]  \hspace{1cm} (34)

2)

\[ F = -kT \ln Z = -kT \sum \frac{z^l b_l}{l!} \]

\[ = -kT \left( b_1z + \frac{b_2}{2}z^2 + \frac{b_3}{6}z^3 + \frac{b_4}{24}z^4 + \cdots \right) \]  \hspace{1cm} (35)
Figure 1: The calculation of $b_3$ and $b_4$

\[ b_1 = 1 \]
\[ b_2 = \frac{1}{2M^2} \sum_{(1,2)} f_{12} = 2(e^{\beta U_0} - 1) \]
\[ b_3 = \frac{1}{6M^2} (3 \sum_{(1,2,3)} f_{12} f_{23} + \sum_{(1,2,3)} f_{12} f_{23} f_{13}) \]
\[ = 2(e^{\beta U_0} - 1)^2 \]
\[ b_4 = \frac{3M^2}{24M^2} 18(e^{-\beta U_0} - 1) = \frac{9}{4}(e^{-\beta U_0} - 1) \]  \( (36) \)

3) As before it is true that $\ln Z = \frac{PL^2}{kT}$ and $n = \frac{\partial (\ln Z)}{\partial \ln z}$

\[ P = \frac{kT}{a_0^2} \sum_{l=1}^{\infty} b_l z^l \]  \( (37) \)

The specific volume

\[ \frac{1}{v} = \frac{1}{a_0^2} \sum_{l=1}^{\infty} lb_l z^l \]  \( (38) \)

Therefore

\[ \frac{PL^2}{kT} = \sum_{l=1}^{\infty} a_l(T) \left( \frac{a_0^2}{L^2} \right)^{l-1} \]  \( (39) \)

This is similar to the interacting gas example, so

\[ a_1 = b_1 = 1 \]
\[ a_2 = -b_2 = -2(e^{\beta U_0} - 1) \]
\[ a_3 = 4b_2^2 - 2b_3 = 16(e^{\beta U_0} - 1)^2 - 4(e^{\beta U_0} - 1) \]
\[ a_4 = -20b_2^3 + 18b_2 b_3 - 3b_4 \]
\[ = -160(e^{-\beta U_0} - 1)^3 + 72(e^{-\beta U_0} - 1)^2 - \frac{27}{4}(e^{-\beta U_0} - 1) \]  \( (40) \)

So $\alpha = N a_0^2$

This was determined by taking the lattice spacing $a_0$ and dividing it by the specific volume. It does not depend on the de Broglie wavelength because this system is not governed by quantum mechanics and no kinetic energy considered with the translational DOF.