The Mayer Expansion for interacting fluid

\[ \Xi(T,V,\mu) = \sum_{N=0}^{\infty} \exp(\beta \mu N) \mathcal{Z}_N(T,V) = \sum_{N=0}^{\infty} \frac{\exp(\beta \mu N)}{\Lambda_N} Q_N(T,V) = \sum_{N=0}^{\infty} z^N Q_N(T,V) \]

\[ \frac{p}{k_B T} = \frac{1}{V} \ln(\Xi(T,V,\mu)) = \frac{1}{V} \left( zQ_1 + z^3 \left( Q_2 - \frac{1}{2} Q_1^2 \right) + z^4 \left( Q_3 - Q_1 Q_2 + \frac{1}{3} Q_1^3 \right) \right) \]

\[ + z^4 \left( Q_4 - Q_1 Q_3 - \frac{1}{2} Q_2 Q_2 + Q_1^2 Q_2 - \frac{1}{4} Q_1^4 \right) + \ldots \]

\[ \frac{p}{k_B T} = \sum_{i=1}^{\infty} b_i z^i \]

\[ b_1 = \frac{Q_1}{V} = 1 \]

\[ b_2 = \frac{1}{V} \left( Q_2 - \frac{1}{2} Q_1^2 \right) = \frac{1}{2V} \int \int f(r_{12}) d\vec{r}_1 d\vec{r}_2 = \]

\[ = \frac{1}{6V} \int \int \int (3 f(r_{12}) f(r_{23}) + f(r_{12}) f(r_{23}) f(r_{13})) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 = \]

\[ n = z \left( \frac{\partial \beta p}{\partial z} \right) = \sum_{i=1}^{\infty} lb_i z^i \]

Inverting the series for n and substituting into the pressure gives the virial expansion.

\[ \frac{p}{nk_B T} = 1 + B_2 n + B_3 n^2 + B_4 n^3 + \ldots \]

\[ B_2 = -b_2 = -\frac{1}{2V} \int \int f(r_{12}) d\vec{r}_1 d\vec{r}_2 = -\frac{1}{2} \int f(r_{12}) d\vec{r}_{12} = \]

\[ B_3 = -2b_3 + 4b_2^2 = \frac{-2}{6V} \int \int \int f(r_{12}) f(r_{23}) f(r_{13}) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \]

\[ = \frac{-2}{6} \int \int \left( f(r_2) f(r_3) f(r_{23}) d\vec{r}_2 d\vec{r}_3 \right) \]

\[ = -2 \]

Note that the first term in b_3 cancels because that term is the same as \( 2b_2^2 \).

The next order term is
\[ B_4 = -3(\quad + \quad + \quad ) \]
\[ = \frac{-3}{24V} \int \int \int (3f_{12}f_{23}f_{34}f_{41} + 6f_{12}f_{23}f_{41}f_{24} + f_{12}f_{23}f_{34}f_{41}f_{13})d\vec{r}_1d\vec{r}_2d\vec{r}_3d\vec{r}_4 \]

For example for the hard sphere fluid \( f(r) = \begin{cases} -1 & \text{for } r \leq D \\ 0 & \text{for } r > D \end{cases} \). The low order virial coefficients can be calculated exactly. The higher order integrals can be evaluated numerically. The virial expansion of the pressure of the 3D fluid of hard spheres is

\[
\frac{p}{nk_BT} = 1 + 4\eta + 10\eta^2 + 18.36\eta^3 + 28.23\eta^4 + 39.52\eta^5 + 56.5\eta^6 \ldots
\]

where \( \eta = \frac{\pi}{6} nD^3 \) is the volume fraction, i.e. the fraction of the volume \( V \) occupied by the \( N \) spheres. Extrapolation of the series allows for the development of the remarkably accurate Carnahan-Starling equation of state for hard spheres.

\[
\frac{p}{nk_BT} \approx \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}
\]

Similar techniques can be used to develop graph expansions for quantities like the pair correlation function. Exact summations of important classes of graphs can be accomplished in a manner very similar to the Feynman-Dyson graph summations in quantum field theory. For example

\[
g(r_{12}) = \exp(-\beta \phi(r_{12}))\left(1 + \frac{1}{2} r_{12}^2 + \ldots\right)
\]

where the dot is the number density times an integral over position and the lines are f-bonds. This expansion can be recast in terms of exact summations of sets of simpler diagrams that can be well-approximated. For example Perkus-Yevick approximation for a three dimensional fluid of hard spheres of diameter \( D \) gives the following form for the structure factor.

\[
S(k) = \frac{1}{1 - \eta \hat{c}(k)}
\]

where \( n \) is the number density and \( \hat{c}(k) \) is the three dimensional Fourier transform of the function \( c(r) = \alpha + \beta \frac{r}{D} + \gamma \frac{r^3}{D^3} \) for \( r < D \) and \( c(r) \) vanishes for \( r > D \). The coefficients are

\[
\alpha = \frac{-(1 + 2\eta)^2}{(1 - \eta)^4}, \quad \beta = \frac{6\eta(1 + \frac{1}{2}\eta)^2}{(1 - \eta)^4}, \quad \gamma = \frac{-\eta(1 + 2\eta)^2}{2(1 - \eta)^4}. \quad \text{The parameter } \eta \text{ is the volume fraction of spheres and is given by } \eta = \frac{\pi}{6} nD^3. \quad \text{The function } c(r) \text{ is called the direct correlation function. This allows an exact calculation of } S(k). \quad \text{Theory of Simple Liquids} \quad \text{by J.-P. Hansen and I.R. McDonald has a complete treatment of all this.}