1 Second virial coefficient

Starting from the partition function (for a system of pairwise additive interactions)

$$Z = \int e^{-\beta \sum_{ij} v(r_{ij})} d\mathbf{r}_1 \dots \mathbf{r}_N = \int \prod_{ij} e^{-\beta v(r_{ij})} d\mathbf{r}_1 \dots \mathbf{r}_N$$

and summing and subtracting one to $e^{-\beta v(r_{ij})}$

$$Z = \int \prod_{ij} \left(e^{-\beta v(r_{ij})} - 1 + 1 \right) d\mathbf{r}_1 \dots \mathbf{r}_N = \int \prod_{ij} \left(f_{ij} + 1 \right) d\mathbf{r}_1 \dots \mathbf{r}_N$$

where we have defined the Mayer function $f_{ij} \equiv e^{-\beta v(r_{ij})} - 1$. The Mayer function vanishes beyond the interaction range and is equal to minus 1 when v(r) diverges.

Expanding the product one can now write Z as

$$Z == \int d\mathbf{r}_1 \dots \mathbf{r}_N [1 + (f_{12} + f_{13} + \dots) + (f_{12}f_{13} + f_{12}f_{14} + \dots) + \dots]$$

If the density is small, then the probability that in the same region of space distinct Mayer functions are different from zero is negligible and one can stop the sum to the first term obtaining

$$Z = \int d\mathbf{r}_{1}...\mathbf{r}_{N} + \frac{N(N-1)}{2} \int d\mathbf{r}_{1} d\mathbf{r}_{2} f_{12} \int d\mathbf{r}_{3}... \int d\mathbf{r}_{N} = V^{N} + V^{N-2} \frac{N(N-1)}{2} \int d\mathbf{r}_{1} d\mathbf{r}_{2} f_{12} = V^{N} + V^{N-1} \frac{N(N-1)}{2} \int d\mathbf{r}_{12} f_{12}(r_{12}) = V^{N} \left(1 + \frac{N(N-1)}{2V} \int d\mathbf{r}_{12} f_{12}(r_{12})\right)$$

Taking the log and expanding around one

$$\ln Z = N \ln V + \frac{N(N-1)}{2V} \int d\mathbf{r_{12}} f_{12}(r_{12})$$
(1)

To evaluate the equation of state

$$\beta P = -\frac{\partial\beta F}{\partial V} = \frac{\partial\ln Z}{\partial V} = \frac{N}{V} - \frac{N(N-1)}{2V^2} \int d\mathbf{r_{12}} f_{12}(r_{12})$$

which for large N gives

$$\frac{\beta P}{\rho} = 1 + \rho B_2$$

where B_2 is

$$B_2(T) = -\frac{1}{2} \int d\mathbf{r_{12}} f_{12}(r_{12}) = -\frac{4\pi}{2} \int r_{12}^2 dr_{12} f_{12}(r_{12}) = -2\pi \int r_{12}^2 dr_{12} f_{12}(r_{12})$$

and it is named second virial coefficient.

If we would have retained one additional term $((f_{12}f_{13} + f_{12}f_{14} +))$ we would have to terms of the type $f_{12}f_{13}$ and terms of the type $f_{12}f_{34}$, one involving 3 connected particles and one involving two groups of two different particle. If we focus on the terms with three particles we also miss the $f_{12}f_{13}f_{32}$ contribution.

Let's look at these terms. Terms of the type $f_{12}f_{13}$ appears N(N-1)(N-2)/3! times. All other particles contribute only with a V^{N-3} term. Going to relative positions (respect to particle one) introduces another V term. Hence, we should add to Eq. 1 a contribution

$$\frac{N(N-1)(N-2)}{3!V^2} \int d\mathbf{r_{12}} d\mathbf{r_{13}} f_{12}(r_{12}) f_{13}(r_{13})$$

whose derivatives respect to volume adds to the pressure a term

$$-\rho^3 \frac{2}{3!} \int d\mathbf{r_{12}} d\mathbf{r_{13}} f_{12}(r_{12}) f_{13}(r_{13})$$

and to $\beta P/\rho$ a term

$$\rho^2 B_3^1(T) \quad B_3^1(T) = \frac{2}{3!} \int d\mathbf{r_{12}} d\mathbf{r_{13}} f_{12}(r_{12}) f_{13}(r_{13})$$

A similar density factors also arises from the $f_{12}f_{13}f_{32}$ contribution and, in a density expansion, should thus be added to $B_3^1(T)$, producing

$$B_3^2(T) = B_3^1(T) + \frac{2}{3!} \int d\mathbf{r_{12}} d\mathbf{r_{13}} f_{12}(r_{12}) f_{13}(r_{13}) f_{23}(r_{23})$$