The van der Waals gas

Assuming that from the notes you can write the partition function as

$$Z = \frac{1}{N!}\lambda^{-3N}\left\{V^N + \frac{N(N-1)}{2}V^{N-2}\int d^3x_1 d^3x_2 f_{12}\right\}$$

where $f_{12} = f(|x_1 - x_2|)$ depends only on the separation between $\mathbf{x_1}$ and $\mathbf{x_2}$. This suggests a change of variable to center of mass coordinates.

Write $x = (\mathbf{x_1} - \mathbf{x_2})/\mathbf{2}$ and $r = \mathbf{x_1} - \mathbf{x_2}$. Then,

$$\int d^3x_1 d^3x_2 f_{12} \longrightarrow V \int d^3r\left(e^{-\beta V(r)} - 1\right)$$

where $e^{-\beta V(r)} - 1 = f(r)$.

Writing,

$$\begin{aligned} Z &= \frac{1}{N!}\lambda^{-3N}\left\{V^N + \frac{N^2V^{N-1}}{2}\int d^3r f(|r|)\right\} \\ &= \frac{1}{N!}\lambda^{-3N}V^N\left\{1 + \frac{N^2}{2V}\kappa(\beta, a, L)\right\} \end{aligned}$$

where $\kappa(\beta, a, L) = 4\pi\int r^2 dr f(|r|) = 4\pi\int r^2 dr(e^{-\beta V(|r|)} - 1)$. This integral can be evaluated to give $\kappa(\beta, a, L) = -A + B\beta$ with $A = 4\pi a^3/3, B = \frac{4\pi}{3}((a+L)^3 - a^3)V_0$. Then writing,

$$\begin{aligned} F &= \frac{-1}{\beta}\ln Z \\ &= \frac{-1}{\beta}\ln\left\{Z^0\left(1 + \frac{N^2}{2V}\kappa(\beta)\right)\right\} \end{aligned}$$

where $Z^0 = \lambda^{-3N}V^N/N!$ is the partition sum for the perfect gas. Assuming that V_0 and a are small so that $N^2\kappa/2V \leq 1$. Then,

$$F \sim \frac{-1}{\beta}\ln Z^0 - \frac{1}{\beta}\cdot\frac{N^2\kappa}{2V} = -\frac{1}{\beta}\ln Z^0 - \frac{1}{\beta}\frac{N^2}{2V}(-A + B\beta).$$

The equation of state for a gas with interactions of this type is

$$P = -\left(\frac{\delta F}{\delta V}\right)_T = \frac{NkT}{V} - \frac{N^2}{2\beta V^2}(-A + B\beta)$$

which, substituting the expression for A and B, gives,

$$P = \frac{NkT}{V} + \left(\frac{N^2 A}{2V^2}\right) \cdot kT - \frac{N^2 B}{2V^2}$$

or

$$\left(P + \frac{N^2 B}{2V^2}\right)\left(V - \frac{NA}{2}\right) = NkT.$$

This is the van der Waals equation of state. It describes a realistic gas a low density with a shallow attractive potential ($\frac{N^2 \kappa}{2V} \leq 1$).