Real Gas

$$\frac{P}{K_B T} = \frac{1}{v} + B\frac{1}{v^2} + C\frac{1}{v^3} + \dots$$ Virial expansion

$$v = \frac{V}{N}$$

$$B, C, \dots = B(T), C(T), \dots$$

$$\left(P + \frac{a}{v^2}\right)(v - b) = K_B T$$ van der waals equation

a and $b > 0$ Phenomenological parameter

$a \longrightarrow$ Small atractive potential

$b \longrightarrow$ Impenetriability of matter.

$$\frac{P}{K_B T} = -\frac{a}{K_B T v^2} + \frac{1}{v - b}$$

$$\frac{1}{v-b} = \frac{1}{v}\left(1 - \frac{b}{v}\right)^{-1} = \frac{1}{v}\left[1 + \frac{b}{v} + \left(\frac{b}{v}\right)^2 + \left(\frac{b}{v}\right)^3 + \left(\frac{b}{v}\right)^4 + \dots\right]$$

$$= \frac{1}{v} + \frac{b}{v^2} + \frac{b^2}{v^3} + \frac{b^3}{v^4} + \frac{b^4}{v^5} + \dots$$

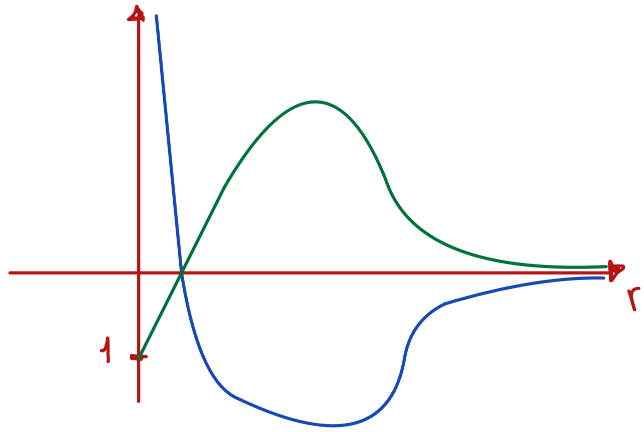
then,

$$\frac{P}{K_B T} = \frac{1}{v} + \left(b - \frac{a}{K_B T}\right)\frac{1}{v^2} + b^2\frac{1}{v^3} + \dots$$

$$Q_N = \int d^3\vec{r}_1 \cdots \int d^3\vec{r}_N \exp\left[-\beta \sum_{i<j} V(|\vec{r}_i - \vec{r}_j|)\right]$$

$$= \left(\prod_{i=1}^{N} \int d^3\vec{r}_i\right) \prod_{i<j} \exp(-\beta V_{ij})$$ $V_{ij} := V(|\vec{r}_i - \vec{r}_j|)$

$$= \left(\prod_{i=1}^{N} \int d^3\vec{r}_i\right) \prod_{i<j} (1 + f_{ij})$$ $f_{ij} := \exp(-\beta V_{ij}) - 1$



If V is small $\quad f_{ij} \simeq 1 + (-\beta V_{ij}) - 1 = -\beta V_{ij}$

$$\prod_{i<j}(1+f_{ij}) = 1 + \sum_{i<j} f_{ij} + \dots$$

therefore,

$$Q_N = V^N + V^{N-2}\sum_{i<j}\int d^3\vec{r}_j \int d^3\vec{r}_j\, f_{ij} + \dots$$

$$\ln(Q_N) - N\ln(V) = \ln\left\{ 1 + \frac{1}{V^2}\sum_{i<j}\int d^3\vec{r}_i \int d^3\vec{r}_j\, f_{ij} + \dots \right\}$$

$$= \frac{1}{V^2}\sum_{i<j}\int d^3\vec{r}_i \int d^3\vec{r}_j\, f_{ij} + \dots$$

$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4}$

$$= \frac{1}{2}N(N-1)\frac{1}{V^2}\int d^3\vec{r}_1 \int d^3\vec{r}_{12} + \dots$$

$$\approx \frac{1}{2}N^2\frac{1}{V^2}\underbrace{\iiint d^2R}_{V}\iiint d^3r\, f(r)$$

$$= \frac{1}{2}\frac{N^2}{V}4\pi\int_0^\infty f(r)\,r^2\,dr$$

We know that

$$z = \frac{1}{N!}\frac{1}{h^{3N}}Z_c = \frac{1}{N!}\left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} Q_N$$

$$\frac{1}{N}\ln(z) \approx \frac{3}{2}\ln\left(\frac{2\pi m}{\beta h^2}\right) + \frac{1}{N}\ln(Q_N) - \ln(N) + 1$$

$$f(T,v) \approx -\frac{3}{2}K_BT\ln(T) - K_BT\ln(v) - K_BTc$$

$$-\frac{1}{2}K_BT\frac{1}{v}\int_0^\infty 4\pi r^2 f(r)dr$$

$$p = -\left(\frac{\partial f}{\partial v}\right)_T \approx \frac{K_BT}{v} - \frac{K_BT}{2v^2}\int_0^\infty 4\pi r^2 f(r)dr$$

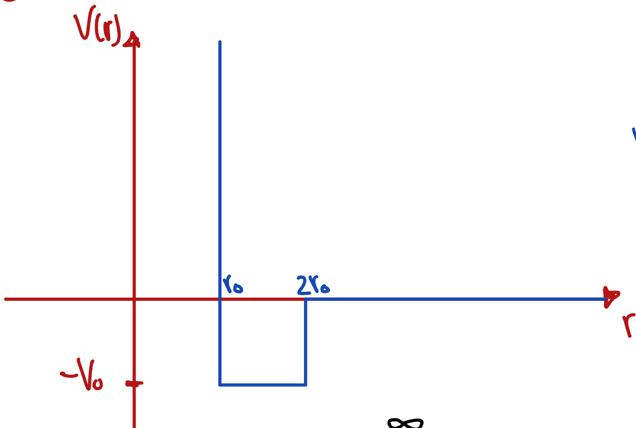
Then,

$$\frac{p}{K_BT} = \frac{1}{v} + B\frac{1}{v^2} + \dots$$

where,

$$B = -2\pi\int_0^\infty r^2 f(r)dr$$

Example:



$$V(r) = \begin{cases} \infty & ;\ 0 < r < r_0 \\ -V_0 & ;\ r_0 < r < 2r_0 \\ 0 & ;\ 2r_0 < r \end{cases}$$

$$B = -2\pi\int_0^\infty r^2\left[\exp(-\beta V(r)) - 1\right]dr$$

$$= -2\pi\left[-\frac{r^3}{3}\Big|_0^{r_0} + \frac{r^3}{3}\left(\exp(\beta V_0) - 1\right)\Big|_{r_0}^{2r_0}\right]$$

$$= \frac{2\pi r_0^3}{3} - \frac{14\pi r_0^3}{3}\left(\exp(\beta V_0) - 1\right)$$

If V_0 is small

$$B \to \frac{2\pi r_0^3}{3} - \frac{14\pi r_0^3}{3}\frac{V_0}{K_BT}$$

but $B = b - \frac{a}{K_BT}$, then $a = \frac{14\pi r_0^3 V_0}{3}$ and $b = \frac{2\pi r_0^3}{3}$.