- The ideal gas law $\left(pV = Nk_BT\right)$ is exact in the limit of no interactions between atoms. A "good approximation" when the density of atoms $\left(\frac{N}{V}\right)$ is small.

- Corrections to ideal gas law are often expressed in terms of a density expansion, known as the "virial expansion".

- In general,

$$\frac{p}{k_BT} = \frac{N}{V} + B_2(T)\frac{N^2}{V^2} + B_3(T)\frac{N^3}{V^3} + \cdots$$

where, $B_j(T)$ are known as the virial coefficients.

- Objective : To compute virial coefficient from first principles. i.e., starting from the knowledge of the underlying potential energy $U(r_{ij})$ between two neutral atoms i and j separated by a distance r_{ij}.

$$\mathcal{H} = \sum_{i=1}^{N} \frac{|\vec{P_i}|^2}{2m} + \sum_{i<j} U(r_{ij}).$$

Notation :- $\begin{cases} \vec{P_i} = \text{momentum of } i^{th} \text{ atom.} \\ p = \text{pressure.} \end{cases}$
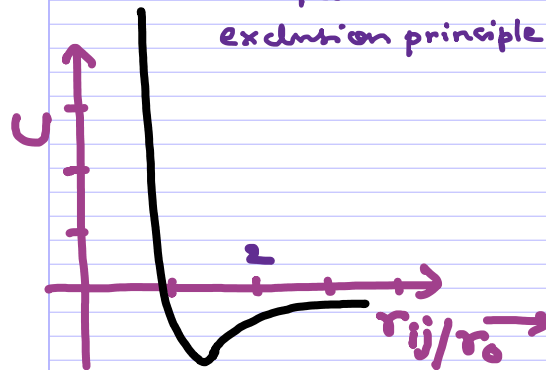
Typical interaction potentials

• Lennard-Jones

$$U(r_{ij}) \sim \left(\frac{r_0}{r_{ij}}\right)^{12} - \left(\frac{r_0}{r_{ij}}\right)^6.$$

Pauli's exclusion principle
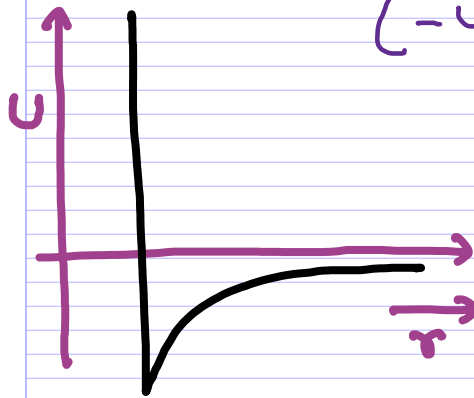
due to fluctuating dipoles of the neutral atoms.

temporary dipole moments

quantum fluctuations

U vs r_{ij}/r_0

• Hard core

$$U(r_{ij}) = \begin{cases} \infty & r < r_0 \\ -U_0\left(\frac{r_0}{r}\right)^6 & r \geqslant r_0. \end{cases}$$

U vs r

$$Z(N,V,T) = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \int \prod_{i=1}^{N} d^3p_i \, d^3q_i \, e^{-\beta H}$$

with $H = \sum_{i=1}^{N} \frac{|\vec{P}_i|^2}{2m} + \sum_{i<j} U(r_{ij})$.

$$\Rightarrow Z(N,V,T) = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{3N}} \left[\int \prod_{i=1}^{N} d^3p_i \, e^{-\beta \sum_{j=1}^{N} \frac{|\vec{P}_j|^2}{2m}} \right]$$

$$\times \left[\int \prod_{i=1}^{N} d^3r_i \, e^{-\beta \sum_{j<k} U(r_{jk})} \right].$$

(Here, $q_i = r_i \, \forall i$)

$$= \frac{1}{N! \, \lambda^{3N}} \int \prod_{i=1}^{N} d^3r_i \, e^{-\beta \sum_{j<k} U(r_{jk})}.$$

where, $\lambda = \sqrt{\dfrac{2\pi\hbar^2}{mk_BT}}$.

(thermal de Broglie wavelength)

A short primer on Mayer function

Mayer function, $f(r) = e^{-\beta U(r)} - 1$.

such that

$f(r) \rightarrow 0$ as $r \rightarrow \infty$.

$\hookrightarrow f(r) \rightarrow -1$ as $r \rightarrow 0$.

Define $f(r_{ij}) = f_{ij}$

$$\therefore Z(N,V,T) = \frac{1}{N! \, \lambda^{3N}} \int \prod_{i=1}^{N} d^3r_i \prod_{j<k} (1 + f_{jk})$$

$$\Rightarrow Z(N,V,T) = \frac{1}{N! \, \lambda^{3N}} \int \prod_{i=1}^{N} d^3r_i \left\{ 1 + \sum_{j<k} f_{jk} + \sum_{\substack{j<k \\ l<m}} f_{jk} f_{lm} + \cdots \right\}$$

$$\underbrace{\phantom{\sum_{j<k} f_{jk}}}_{K}$$

First term in $K \equiv V^N$.

Second term in K has a sum, each element of which is same, such that,

$$\int \prod_{i=1}^{N} d^3r_1 \, f_{12} = V^{N-2} \int d^3r_1 \, d^3r_2 \, f(r_{12})$$

$$= V^{N-1} \int d^3r \, f(r).$$

we make a transformation from

$$\vec{r}_1, \vec{r}_2 \quad \text{to} \quad \vec{r}, \vec{R}$$

where, $\vec{r} = \vec{r}_1 - \vec{r}_2$.

$$\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}.$$

There are $\frac{N(N-1)}{2}$ such pairs $\approx \frac{N^2}{2}$ pairs

(for $N \to 10^{23}$).

$$\therefore \quad Z(N,V,T) = \frac{V^N}{N! \, \lambda^{3N}} \left\{ 1 + \frac{N^2}{2V} \int d^3r \, f(r) + \cdots \right\}$$

$$\underset{\text{"trick"}}{\approx} \frac{V^N}{N! \, \lambda^{3N}} \left[1 + \frac{N}{2V} \int d^3r \, f(r) \right]^N.$$

$$= Z_{ideal} \left[1 + \frac{N}{2V} \int d^3r \, f(r) \right]^N.$$

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

$$\Rightarrow \quad F = -k_B T \ln Z(N, V, T)$$

$$= F_{ideal} - N k_B T \ln \left(1 + \frac{N}{2V} \int d^3r \, f(r) \right)$$

$$\underbrace{\qquad\qquad}_{\approx \frac{N}{2V} \int d^3r \, f(r)}$$

$$\therefore \quad p = -\left(\frac{\partial F}{\partial V} \right)_{N,T} = \frac{N k_B T}{V} - \frac{N^2 k_B T}{2V^2} \int d^3r \, f(r).$$

$$= \frac{N k_B T}{V} \left(1 - \frac{N}{2V} \int d^3r \, f(r) \right).$$

$$\therefore \quad \frac{pV}{N k_B T} = 1 - \frac{N}{2V} \int d^3r \, f(r).$$

Note: $\bullet \; U(r) > 0 \Rightarrow f(r) < 0$
$$\Rightarrow p \text{ increases.}$$

$\bullet \; U(r) < 0 \Rightarrow f(r) > 0$
$$\Rightarrow p \text{ decreases.}$$

Consider a typical potential which is attractive at long distances and repulsive at short distances, e.g., Hard core + van der Waals.

$$\Rightarrow \int d^3r \, f(r) = \int_0^{r_0} (-1) \, d^3r$$
$$+ \int_{r_0}^{\infty} d^3r \left(e^{\beta U_0 \left(\frac{r_0}{r} \right)^6} - 1 \right)$$

At high temperatures,
$$e^{\beta U_0 \left(\frac{r_0}{r} \right)^6} \approx 1 + \beta U_0 \left(\frac{r_0}{r} \right)^6.$$

$$\Rightarrow \int d^3r \, f(r) = -4\pi \int_0^{r_0} r^2 dr + 4\pi \beta U_0 \int_{r_0}^{\infty} \frac{r_0^6}{r^4} dr.$$

$$= \frac{4\pi r_0^3}{3} \left(\frac{U_0}{k_B T} - 1 \right).$$

$$\Rightarrow \quad \frac{pV}{Nk_BT} = 1 - \frac{N}{2V}\left\{ \frac{4\pi r_0^3 U_0}{3k_BT} - \frac{4\pi r_0^2}{3} \right\}$$

$$= 1 - \frac{N}{V}\left(\frac{a}{k_BT} - b \right).$$

$$\text{where,} \quad a = \frac{2\pi r_0^3 U_0}{3} \; ; \; b = \frac{2\pi r_0^3}{3}.$$

$$\therefore \quad \frac{pV}{Nk_BT} = -\frac{Na}{Vk_BT} + \left(1 + \frac{N}{V}b \right).$$

$$\Rightarrow \quad \frac{V}{Nk_BT}\left(p + \frac{N^2a}{V^2} \right) = \left(1 + \frac{Nb}{V} \right).$$

$$\therefore \quad k_BT = \frac{V}{N}\left(p + \frac{N^2a}{V^2} \right)\left(1 + \frac{Nb}{V} \right)^{-1}.$$

$$\underbrace{\qquad\qquad}$$

$$\approx (1 - \frac{Nb}{V})$$

$$\therefore N k_BT = \left(p + \frac{N^2a}{V^2} \right)(V - Nb).$$

$$\Downarrow$$

$$\boxed{\left(p + \frac{N^2a}{V^2} \right)(V - Nb) = Nk_BT}$$
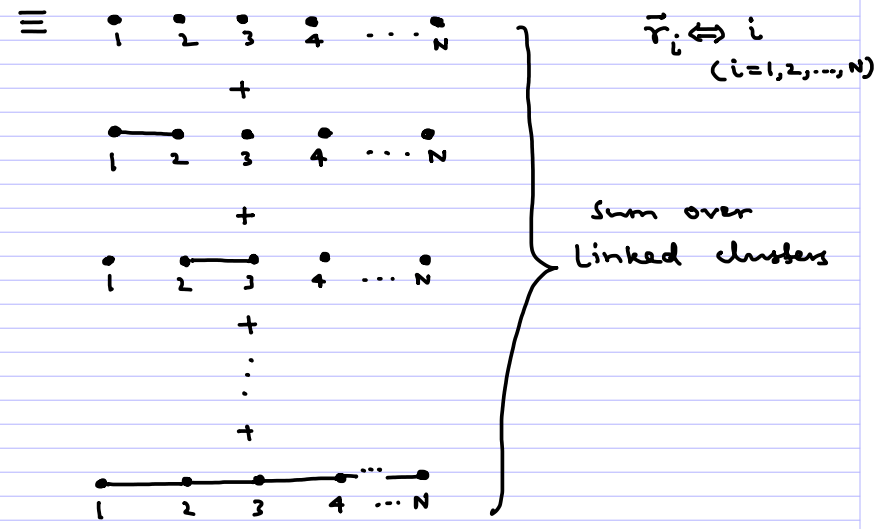
Equation of state for van der Waals gas.

Valid at • low densities.
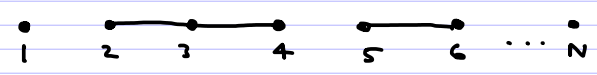   • high temperatures.

Consider the quantity C_N, s.t.,

$$C_N = \int \prod_{i=1}^{N} d^3\vec{r}_i \left(1 + \sum_{i<j} f_{ij} + \sum_{\substack{i<j \\ k<\ell}} f_{ij} f_{k\ell} + \cdots \right)$$

$\underbrace{}_{\text{perturbation series}}$

$\equiv$ $\vec{r}_i \Leftrightarrow i$ $(i=1,2,\ldots,N)$

Sum over Linked clusters

where a typical linked cluster

corresponds to the product

$$\left(\int d^3r_1 \right) \left(\int d^3r_2 \, d^3r_3 \, d^3r_4 \; f_{23} \, f_{24} \right) \left(\int d^3r_5 \, d^3r_6 \; f_{56} \right) \cdots \left(\int d^3r_N \right)$$

The procedure involves enumerating all linked clusters followed by a sum over all contributions.