⊙ Non ideal classical gas

monatomic gas (N identical particles of mass m) in volume V at temperature T

T is sufficiently high
$n = N/V$ ~ sufficiently low } classical limit

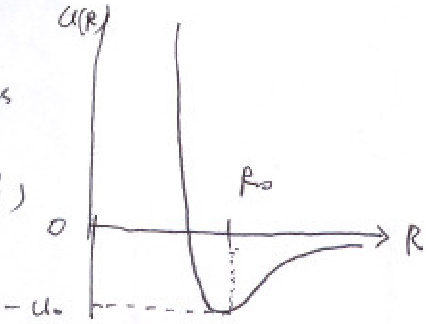
$$H = K + U$$

$$K = \frac{1}{2m}\sum_{j=1}^{N} \vec{p}_j^{\,2} \quad \text{. kinetic}$$

$$U = \frac{1}{2}\sum_{j=1}^{N}\sum_{\substack{k=1 \\ j\neq k}}^{N} u_{jk} \quad \text{interaction between particles}$$

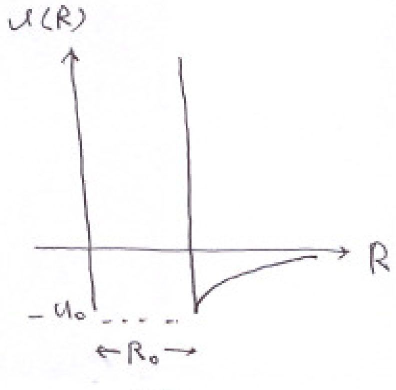
$u_{jk} \longrightarrow$ semi empirical potential " Lennard - Jones ' potential"

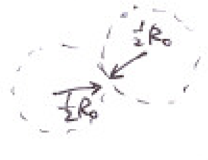
$$u(R) = u_0\Big[\underbrace{\Big(\frac{R_0}{R}\Big)^{12}}_{\text{exclusion.}} - \underbrace{2\Big(\frac{R_0}{R}\Big)^{6}}_{\substack{\text{van der Waals} \\ \text{attraction} \\ \text{(dipole moment)}}}\Big]$$



$\downarrow$ further simplification

$$u(R) = \begin{cases} \infty & R < R_0 \\ -u_0\Big(\frac{R_0}{R}\Big)^{s} & R > R_0 \end{cases}$$





" weakly interacting hard sphere with radius $\frac{1}{2}R_0$ "

$$Z = \frac{1}{N!}\int \frac{1}{h^{3N}} \prod_{i=1}^{N} d^3\vec{p}_i\, d^3\vec{r}_i \quad e^{-\beta(K+U)}$$

$$= \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}N} Z_U \quad , \quad Z_U = \int d^3\vec{r}_1 \cdots d^3\vec{r}_N \; e^{-\beta U(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)}$$

note : $\beta \to 0$ (high temperature) $\Rightarrow$ $Z_U \to V^N$

($\because e^{-\beta U} \to 1$)

ideal gas case

— mean potential energy

$$\bar{U} = \frac{1}{2}N(N-1)\,\bar{u} \simeq \frac{1}{2}N^2\bar{u}$$

$$\bar{u} = \bar{u}_{jk} = \frac{\int e^{-\beta u_{jk}(r_{jk})}\, u_{jk}(r_{jk})\, d^3\vec{r}_{jk}}{\int e^{-\beta u_{jk}(r_{jk})}\, d^3\vec{r}_{jk}}$$

$\vec{r}_{jk} = \vec{r}_j - \vec{r}_k$

$u_{jk}(\vec{r}_{jk}) = u_{jk}(r_{jk})$

$$= -\frac{\partial}{\partial\beta}\ln\int e^{-\beta u(r)}\, d^3r$$

drop index j, k

$u(r) \sim$ small except for small r

$$\Rightarrow e^{-\beta u(r)} \simeq 1$$

$$\Rightarrow \int e^{-\beta u(r)}\, d^3\vec{r} = \int 1 + (e^{-\beta u} - 1)\, d^3\vec{r} = V + I(\beta)$$

$$I(\beta) = \int (e^{-\beta u} - 1)\, d^3\vec{r} = \int_0^\infty 4\pi r^2 (e^{-\beta u} - 1)\, dr$$

$$\Rightarrow \bar{u} = -\frac{\partial}{\partial\beta}\left[\ln V + \ln\left(1 + \frac{I}{V}\right)\right]$$

$\frac{I}{V} \ll 1$

$$\simeq -\frac{\partial}{\partial\beta}\frac{I}{V}$$

$$\Rightarrow \bar{U} = -\frac{1}{2}\frac{N^2}{V}\cdot\frac{\partial I}{\partial\beta}$$

$$\bar{U} = -\frac{\partial}{\partial\beta}\ln Z_U \Rightarrow \ln Z_U(\beta) = \ln Z_U(\beta=0) - \int_0^\beta \bar{U}(\beta')\, d\beta'$$

$Z_U(\beta=0) = V^N$

$$= N\ln V + \frac{1}{2}\frac{N^2}{V} I(\beta)$$

- Equation of state, virial expansion

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = \frac{1}{\beta}\frac{\partial \ln Z_u}{\partial V}$$

$$\Rightarrow \beta\bar{p} = \frac{N}{V} - \frac{1}{2}\frac{N^2}{V^2} I$$

※ $\beta\bar{p} = \frac{\bar{p}}{kT} = n + B_2(T)\, n^2 + B_3(T)\, n^3 + \cdots\cdots$

$n = \frac{N}{V}$.

"virial expansion"

$B_i \sim$ virial coefficient

(remember $n \to$ very small in classical limit)

$$B_2 = -\frac{1}{2} I$$

$$= -2\pi \int_0^\infty \left(e^{-\beta u(R)} - 1\right) R^2 dR$$

use $u(R) = \begin{cases} \infty & (R < R_0) \\ -u_0\left(\frac{R_0}{R}\right)^s & (R > R_0) \end{cases}$

$$\Rightarrow B_2 = 2\pi \int_0^{R_0} R^2 dR - 2\pi \int_{R_0}^{\infty} \left(e^{-\beta u} - 1\right) R^2 dR$$

assume high temperature $\beta u_0 \ll 1$

$$\Rightarrow B_2 = \frac{2\pi}{3} R_0^{\,3} - 2\pi \beta u_0 \int_{R_0}^{\infty} \left(\frac{R_0}{R}\right)^s R^2 dR$$

$$= \frac{2\pi}{3} R_0^{\,3}\left(1 - \frac{3}{s-3}\frac{u_0}{kT}\right)$$

↓ assume $s > 3$.

$$= b' - \frac{a'}{kT}.$$

$a' \propto u_0 R_0^{\,3}$

$$\Rightarrow \frac{\bar{p}}{kT} = n + \left(b' - \frac{a'}{kT}\right) n^2$$

assume: $b' n \ll 1$ (dilute)

$$\Rightarrow \bar{p} + a' n^2 = nkT\,(1 + b'n) \simeq \frac{nkT}{1 - b'n}$$

$$\Rightarrow (\bar{p} + a'n^2)\left(\frac{1}{n} - b'\right) = kT$$

→ "Van der Waals eq"

(※ see also Reif section 10.5)

$n = \frac{N}{V} = \frac{N_a}{v}$ ← Avogadro's #

$$\Rightarrow \left(\bar{p} + \frac{a}{v^2}\right)(v - b) = RT.$$