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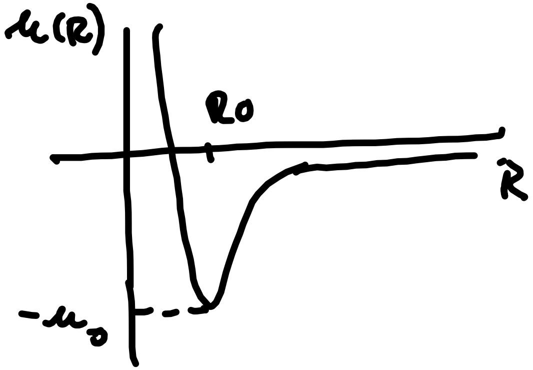
Last time:

Non-ideal gas (weakly interacting particles).

Assumptions: $\frac{N}{V}$ small , T high

Intermolecular potential.



Lennard-Jones potential

$$u(R) = u_0 \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^{6} \right]$$

$$U = \frac{1}{2} \sum_{\substack{j=1 \\ j \neq k}}^{N} \sum_{k=1}^{N} u_{jk}$$

Let's calculate Z for the gas.

We can use the M-B limit of the quantum mechanical distribution

$$Z = \frac{1}{N!}\int \cdots \int e^{-\beta(K+U)} \frac{d^3p_1 \ldots d^3p_N \, d^3r_1 \ldots d^3r_N}{h^{3N}}$$

$$= \frac{1}{h^{3N} N!} \underbrace{\int \cdots \int e^{-\beta K(p_i)} d^3p_1 \ldots d^3p_N}_{\left(\sqrt{\frac{2\pi m}{\sqrt{\beta}}}\right)^{3N}} \underbrace{\int \cdots \int e^{-\beta U} d^3r_1 \ldots d^3r_N}_{Z_U}$$

Then

$$Z = \frac{1}{N!}\left(\frac{2\pi m}{\hbar^2 \beta}\right)^{\frac{3}{2}N} Z_U$$

Z_U will be calculated as a series expansion in powers of $N/V = n$.

- Simplest way: useful to obtain the first term in the expansion – we will see a more general method later.

If $U = 0$ or $\beta \to 0 \to$ high T

$$Z_U = V^N$$

Also:

$$\bar{U} = \frac{\int e^{-\beta U} \, U \, d^3r_1 \cdots d^3r_N}{Z_U} = -\frac{\partial \ln Z_U(\beta)}{\partial \beta}$$

$$\therefore \ln Z_U(\beta) = \underbrace{N \ln V}_{\text{for } \beta = 0} - \int_0^{\beta} \bar{U} \, d\beta' \qquad (5)$$

$\to 0$ for $\beta = 0$

Notice that

$$U = \frac{1}{2} \sum_{\substack{j=1 \\ j \neq k}}^{N} \sum_{k=1}^{N} u_{jk}$$

if $u_{jk} \equiv \bar{u}$ then

$$\bar{U} = \frac{1}{2} \bar{u} \, N(N-1) \overset{N>>1}{\approx} \frac{1}{2} \bar{u} N^2 \qquad (3)$$

If we consider that when we focus on a pair of molecules $\langle jk \rangle$ the other molecules do not interact with them (very weak interactions) then the other molecules act like a heat bath for $\langle jk \rangle$:

$$P(\bar{R}) = e^{-\beta u(R)} d^3R$$

probability that j and k are separated by a distance R.

$\bar{R} = \bar{r}_j - \bar{r}_k$

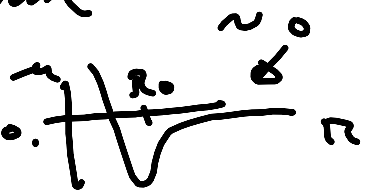
$R = |\bar{R}|$.

then

$$\bar{u} = \frac{\int e^{-\beta u} u \, d^3R}{\int e^{-\beta u} d^3R} = -\frac{\partial}{\partial \beta} \ln \underbrace{\int e^{-\beta u} d^3R}_{\text{over } V} \quad (1)$$

Notice that $u \approx 0$ in most of the volume

Then $e^{-\beta u} \approx 1$ everywhere except at $R \approx R_0$.



Then

$$\int e^{-\beta u}\, d^3R = \int \left[1 + (e^{-\beta u} - 1)\right] d^3R =$$

$$= \underbrace{\int_V d^3R}_{V} + \underbrace{\int_V (e^{-\beta u} - 1)\, d^3R}_{I} = V + I = V\left(1 + \frac{I}{V}\right) \quad (2)$$

$u(\vec{R}) \equiv u(R)$

$$I = \int_V (e^{-\beta u} - 1)\, d^3R = \underbrace{4\pi}_{\int d\Omega} \int_0^\infty (e^{-\beta u} - 1)\, R^2\, dR$$

Since $I \ll V$

Replace ② in ① then:

$\ln(1+x) \simeq x$

if $x \ll 1$

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

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

$$= 0 - \frac{\partial}{\partial \beta}\frac{I}{V} = -\frac{1}{V}\frac{\partial I}{\partial \beta} \qquad (4)$$

In 3 we found that $\overline{U} = \frac{1}{2} N^2 \bar{u}$

then replacing 4 in 3:

$$\overline{U} = -\frac{1}{2}\frac{N^2}{V}\frac{\partial I}{\partial \beta} \qquad (6)$$

Then (replacing 6 in 5):

$$\ln Z_U(\beta) = N \ln V + \int_0^\beta \frac{1}{2}\frac{N^2}{V}\frac{\partial I}{\partial \beta'}\, d\beta' =$$

$$= N \ln V + \frac{1}{2}\frac{N^2 I(\beta)}{V} \qquad (7)$$

Equation of state:

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

→ all the V dependence is here.

(6.5.12)

using ⑦

$$\beta \bar{p} = \frac{\bar{p}}{kT} = \underbrace{\frac{N}{V}}_{n} - \frac{1}{2}\underbrace{\frac{N^2}{V^2}}_{n^2} I(\beta)$$

In general

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

Virial expansion

$B_1 = 1$

B_i : Virial coefficients

$B_i = 0 \quad \forall\, i > 1$ for ideal gas.

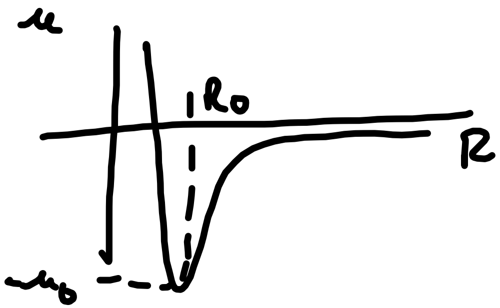
If n is not too large it is enough considering B_2. Let's calculate B_2:

We found that $B_2 = -\frac{1}{2} I(\beta)$

$$B_2 = -\frac{1}{2} I(\beta) = -\frac{1}{2} 4\pi \int_0^\infty \left(e^{-\beta u} - 1\right) R^2 \, dR =$$

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

To evaluate the integral we need to make an assumption about $u(R)$:



- If $R \ll R_0 \Rightarrow u \gg 1$

  $e^{-\beta u} - 1 < 0$

  In this region the contribution to the integrand is negative.

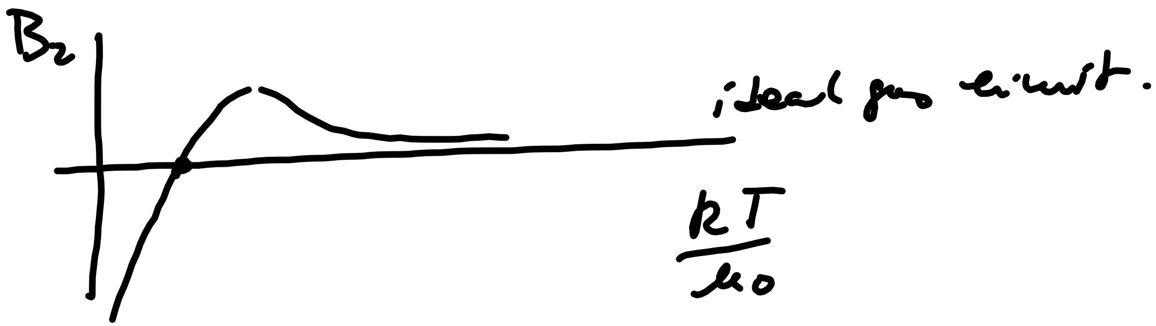
- For $R \gg R_0 \Rightarrow u < 0 \therefore e^{-\beta u} - 1 > 0$

  positive contribution to the integrand

Then

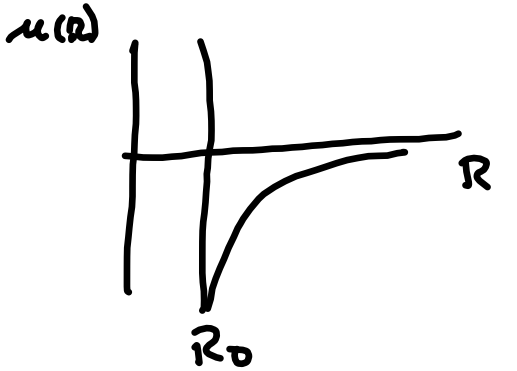
$B_2 < 0$ for high $p \Rightarrow$ low T

$B_2 > 0$ for low $p \Rightarrow$ high T



Van der Waals approximation:

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



s is in general 6 (see homework)

but $s > 3$ works.

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

$$-2\pi \int_{R_0}^\infty \left(e^{+\beta u_0 \frac{R_0^s}{R^s}} - 1\right) R^2 \, dR =$$

$$= \frac{2\pi}{3} R_0^{\,3} - 2\pi \int_{R_0}^{\infty} \beta u_0 \frac{R_0^{\,s}}{R^s} R^2 \, dR =$$

$$e^{-\beta u} \simeq 1 - \beta u \quad \text{if } \frac{u_0}{RT} << 1$$

$$3 - s$$

$$e^{-\beta u} - 1 \simeq -\beta u$$

$$= \frac{2\pi}{3} R_0^{\,3} - 2\pi \beta u_0 R_0^{\,s} \int_{R_0}^{\infty} R^{2-s} \, dR =$$

$$- \frac{1}{s-3} \frac{1}{R^{s-3}} \Big|_{R_0}^{\infty}$$

$$= \frac{2\pi}{3} R_0^{\,3} - \frac{2\pi \beta u_0 R_0^{\,s}}{(s-3) R_0^{\,s-3}} = \underbrace{\frac{2\pi}{3} R_0^{\,3}}_{b} \left(1 - \frac{\overset{1}{\cancel{3}} \beta u_0}{(s-3)} \right) =$$

if $a' = \frac{3}{s-3} b' n_0$ then

$$B_2 = b' - \frac{a'}{kT}$$

Then in the equation of state we obtain:

$$\frac{\bar{p}}{kT} = n + B_2 n^2 = n + \left(b' - \frac{a'}{kT}\right) n^2$$

Then

$$\bar{p} = nkT + n^2 (b'kT + a')$$

if $b'n << 1$

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

Then

$$(p + a' n^2)(1 - b' n) = n k T$$

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

$$\left(p + \frac{\overbrace{a' N_a^2}^{a}}{v^2}\right)\left(\frac{v}{N_a} - b'\right) = kT$$

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

$$n = \frac{N}{V} = \frac{N}{\nu v} = \frac{N_a \cancel{\nu}}{\cancel{\nu} v} = \frac{N_a}{v}$$

$$\left(p + \frac{a}{v^2}\right)\left(v - \underbrace{N_a b'}_{b}\right) = \underbrace{N_a k}_{R} T$$

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

van der Waals eq.