

Virial expansion for the equation of state

$$v = \frac{1}{n} = \frac{V}{N} \quad \text{specific volume}$$

$$\frac{p v}{k_B T} = \sum_{l=1}^{\infty} a_l(T) \left(\frac{\lambda^3}{v}\right)^{l-1}$$

virial expansion

a_l depend only on T

$\frac{\lambda^3}{v} = \lambda_m^3$ is small parameter

- low density or

high temperature

For ideal gas, right hand side must = 1

To get the a_l use:

$$\frac{\left(\frac{p}{k_B T}\right)}{\left(\frac{1}{v}\right)} = \frac{\frac{1}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l}{\frac{1}{\lambda^3} \sum_{l=1}^{\infty} l b_l z^l} = \sum_{l=1}^{\infty} a_l \left(\frac{\lambda^3}{v}\right)^{l-1}$$

$$= \sum_{l=1}^{\infty} a_l \left(\sum_{n=1}^{\infty} n b_n z^n\right)^{l-1}$$

$$\frac{b_1 z + b_2 z^2 + b_3 z^3 + \dots}{b_1 z + 2b_2 z^2 + 3b_3 z^3 + \dots} = a_1 + a_2 (b_1 z + 2b_2 z^2 + 3b_3 z^3 + \dots) + a_3 (b_1 z + 2b_2 z^2 + 3b_3 z^3 + \dots)^2 + \dots$$

$$b_1 z + b_2 z^2 + b_3 z^3 + \dots = a_1 (b_1 z + 2b_2 z^2 + 3b_3 z^3 + \dots) + a_2 (b_1 z + 2b_2 z^2 + 3b_3 z^3 + \dots)^2 + a_3 (b_1 z + 2b_2 z^2 + 3b_3 z^3 + \dots)^3 + \dots$$

equate the coefficients of z^l terms on either side
order by order

$$z^1: b_1 = a_1 b_1 \Rightarrow \boxed{a_1 = 1} \quad \text{since } b_1 \neq 0$$

$$z^2: b_2 = 2a_1 b_2 + a_2 b_1^2 \Rightarrow a_2 = -b_2/b_1^2 = -b_2$$

$$\boxed{a_2 = -b_2}$$

$$z^3: b_3 = 3a_1 b_3 + 4a_2 b_1 b_2 + a_3 b_1^3 \\ = 3b_3 - 4b_2^2 + a_3$$

$$\boxed{a_3 = 4b_2^2 - 2b_3}$$

similarly $\boxed{a_4 = -20b_2^3 + 18b_2 b_3 - 4b_4}$

$$a_1 = 1$$


$$a_2 = -b_2 = -\frac{1}{2\lambda^3} \int d^3r f(r)$$

$$a_3 = 4b_2^2 - 2b_3 \quad \text{recall } b_3 = 2b_2^2 + \frac{1}{6\lambda^6} \int d^3r d^3r' f(r) f(r') \\ \times f(r+r')$$

$$= 2(2b_2^2 - b_3)$$

$$= -\frac{1}{3\lambda^6} \int d^3r d^3r' f(r) f(r') f(r+r')$$



a_3 involves only the graph 

can show in general that only irreducible graphs enter the calculation of a_2 . These are graphs that cannot be separated into disjoint groups unless one cuts ~~more~~ two or more bonds.

One can show

$$a_2 = -\frac{(l-1)}{l} \beta_{l-1}$$

where $\beta_{l-1} = \frac{1}{(l-1)! \lambda^{3(l-1)} V} \times (\text{sum of all irreducible } l\text{-clusters})$

Return to first non-trivial correction to ideal gas

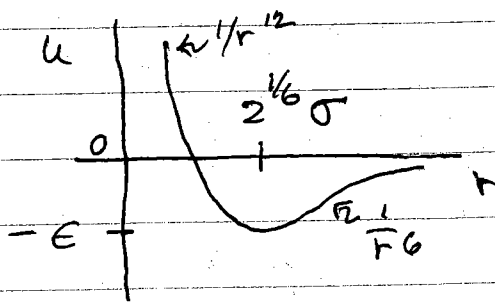
$$a_2 = -\frac{1}{2\lambda^3} \int d^3r f(\vec{r}) = \frac{2\pi}{\lambda^3} \int_0^\infty dr r^2 (1 - e^{-\beta u(r)})$$

Lennard-Jones interaction $u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$

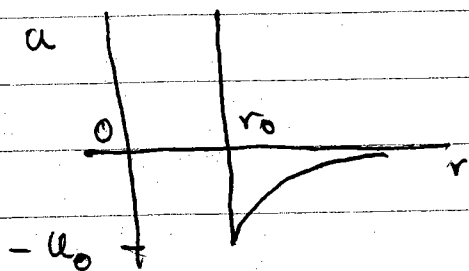
For Argon

$$\frac{\epsilon}{k_B} \approx 120^\circ\text{K}$$

$$\sigma \approx 3.4 \text{ \AA}$$



approx L-J by $u(r) = \begin{cases} -u_0 \left(\frac{r_0}{r}\right)^6 & r \geq r_0 \text{ weak attractive} \\ +\infty & r < r_0 \text{ impenetrable core} \end{cases}$



$$a_2 = \frac{2\pi}{\lambda^3} \left\{ \int_0^{r_0} r^2 dr + \int_{r_0}^{\infty} dr r^2 \left[1 - e^{+\beta u_0 (r_0/r)^6} \right] \right\}$$

for $\frac{u_0}{k_B T} \ll 1$ true at room temp $\frac{u_0}{k_B} \sim 100^\circ K$

$$1 - e^{+\beta u_0 (r_0/r)^6} \approx -\frac{u_0}{k_B T} \left(\frac{r_0}{r}\right)^6$$

$$\int dr \frac{r^2}{r^6} = \int \frac{dr}{r^4} = -\frac{1}{3r^3}$$

$$a_2 \approx \frac{2\pi}{\lambda^3} \left[\frac{r_0^3}{3} - \frac{u_0}{k_B T} \frac{r_0^3}{3} \right] = \frac{2\pi r_0^3}{3\lambda^3} \left[1 - \frac{u_0}{k_B T} \right]$$

$$\frac{p v}{k_B T} = 1 + a_2 \left(\frac{\lambda^3}{v}\right)^2 = 1 + \frac{2\pi r_0^3}{3v} \left(1 - \frac{u_0}{k_B T}\right)$$

$$\Rightarrow p = \frac{k_B T}{v} \left(1 + \frac{B_2(T)}{v}\right) \quad B_2 = \frac{2\pi r_0^3}{3} \left(1 - \frac{u_0}{k_B T}\right)$$

↑ 2nd virial coefficient

or

$$p = \frac{k_B T}{v} + k_B T \frac{2\pi r_0^3}{3v^2} - k_B T \frac{2\pi r_0^3}{3v^2} \frac{u_0}{k_B T}$$

$$\left(p + \frac{2\pi r_0^3 u_0}{3v^2} \right) = \frac{k_B T}{v} \left(1 + \frac{2\pi r_0^3}{3v} \right) \approx \frac{k_B T}{v} \frac{1}{\left(1 - \frac{2\pi r_0^3}{3v} \right)}$$

$$\Rightarrow \left(p + \frac{a}{v^2} \right) (v - b) = k_B T \quad \boxed{\text{van der Waal's equation of state}}$$

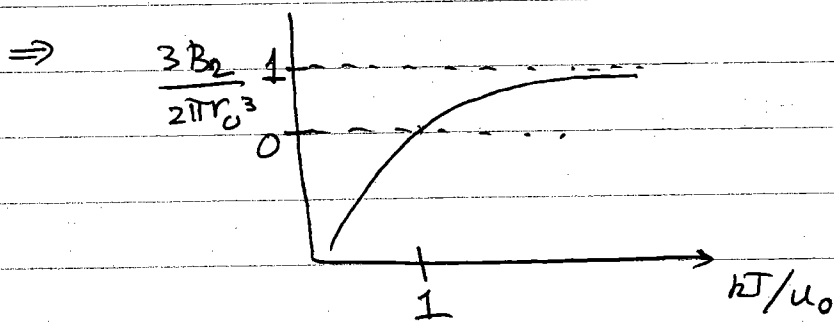
with $a = \frac{2\pi r_0^3 u_0}{3}$, $b = \frac{2\pi r_0^3}{3} = 4 v_0$

v_0 is "molar volume" — where $v_0 = \frac{\pi r_0^3}{6}$ vol of sphere of diameter r_0 .

above derivation assumes $b \ll v$ i.e. dilute gas
mean particle spacing $\gg r_0$

In this approx, a and b are T independent.
This would not be true using a more realistic $u(r)$

Within this approx we had $B_2 = \frac{2\pi r_0^3}{3} \left(1 - \frac{u_0}{k_B T}\right)$



for Lennard Jones potential see Fig 9.2 in Pathria
for B_2 vs T , good agreement for all but the
lightest mass gases, Ar, N_2 , CH_4 , Ne

Alternate derivation of van der Waals eqn of state

(derived by van der Waals long before Mayer expansion)

In ideal gas law $pV = Nk_B T$

p is the pressure of the kinetic energy of the molecules
 V is the volume that the molecules can move around in.

For an interacting gas, the total energy is kinetic plus interaction. The average interaction energy one expects to be $\propto -\left(\frac{N}{V}\right)N$ since each of the

N particles interacts with ~~some~~ the other particles within a certain distance $\sim r_0$ of it. The number of such particles is proportional to the particle density $\left(\frac{N}{V}\right)$. The pressure is proportional to the energy per volume, hence the total pressure is

$$P = P_{\text{kinetic}} - a\left(\frac{N}{V}\right)^2$$

\leftarrow from interactions

$$\text{or } P_{\text{kinetic}} = P + a\left(\frac{N}{V}\right)^2$$

The volume the particles can move in is the "free volume" which equal to the total volume minus the volume the particles themselves occupy

$$V_{\text{free}} = V - Nb$$

$b \propto$ volume occupied by one molecule
 \leftarrow excluded volume

Adding using Primitive and V_{free} in ideal gas law gives

$$P_{primitive} V_{free} = N k_B T$$

$$\left(P + a \left(\frac{N}{V} \right)^2 \right) (V - Nb) = N k_B T$$

$$\left(p + a \left(\frac{N}{V} \right)^2 \right) \left(\frac{V}{N} - b \right) = k_B T$$

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

van der Waals
equ of state