Virial expansion for the equation of state

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

$$\frac{pv}{k_B T} = \sum_{\ell=1}^{\infty} a_\ell(T) \left(\frac{\lambda^3}{v}\right)^{\ell-1}$$

virial expansion

a_ℓ depend only on T

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

— low density or

high temperature

For ideal gas, right hand side must $= 1$

To get the a_ℓ use:

$$\frac{\left(\frac{p}{k_B T}\right)}{\left(\frac{1}{v}\right)} = \frac{\frac{1}{\lambda^3} \sum_{\ell=1}^{\infty} b_\ell z^\ell}{\frac{1}{\lambda^3} \sum_{\ell=1}^{\infty} \ell b_\ell z^\ell} = \sum_{\ell=1}^{\infty} a_\ell \left(\frac{\lambda^3}{v}\right)^{\ell-1}$$

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

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

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

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

z^1: $b_1 = a_1 b_1 \Rightarrow \boxed{a_1 = 1}$ since $b_1 = 1$

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

$a_1 = 1$

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

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

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

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

              $\uparrow$

       a_3 involves only the graph $\triangle$

can show in general that only _ireducible_ graphs
enter the calculation of a_l. These are graphs
that _cannot be separated into disjoint groups unless_
one cuts ~~more~~ _two or more_ bonds.

One can show

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

where $\beta_{l-1} = \dfrac{1}{(l-1)! \, \lambda^{3(l-1)} V} \times$ (sum of all ireducible
l-clusters)


Return to first non-trivial correction to ideal gas

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

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

For Argon

$\dfrac{\epsilon}{k_B} \simeq 120°K$

$\sigma \simeq 3.4 \, Å$
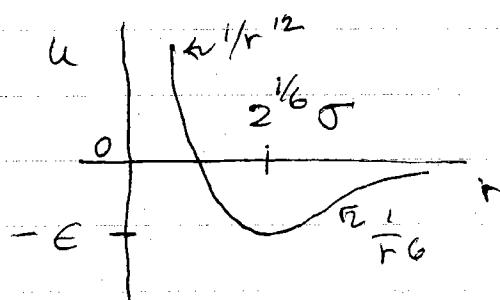
approx L-J by $\quad u(r) = \begin{cases} -u_0 \left(\dfrac{r_0}{r}\right)^6 & r \gg r_0 \quad \text{weak attraction} \\[2mm] +\infty & r < r_0 \quad \text{impenetrable core} \end{cases}$
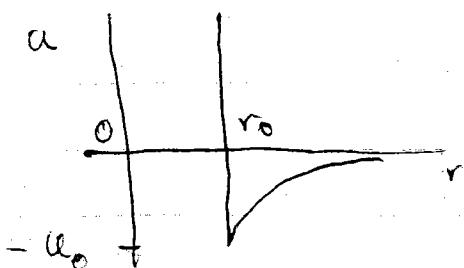
$$a_2 = \frac{2\pi}{\lambda^3} \left\{ \int_0^{r_0} r^2 dr + \int_{r_0}^{\infty} dr \, r^2 \left[1 - e^{+\beta u_0 (r_0/r)^6} \right] \right\}$$

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

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

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

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

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

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

$$\underset{\text{2nd virial coefficient}}{\Big\lfloor}$$

or

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

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

$$\Rightarrow \left(p + \frac{a}{\upsilon^2}\right)(\upsilon - b) = k_B T \qquad \boxed{\begin{array}{l}\text{von der Waal's}\\ \text{equation of state}\end{array}}$$

with $a = \frac{2\pi r_0^3 u_0}{3}$, $b = \frac{2\pi r_0^3}{3} = 4 \upsilon_0$

υ_0 is "molar volume" —   where $\upsilon_0 = \frac{\pi r_0^3}{6}$ vol of sphere of diameter r_0

above derivation assumes $b \ll v$ ie 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 $B_2 = \dfrac{2\pi r_0^3}{3}\left(1 - \dfrac{u_0}{k_B T}\right)$

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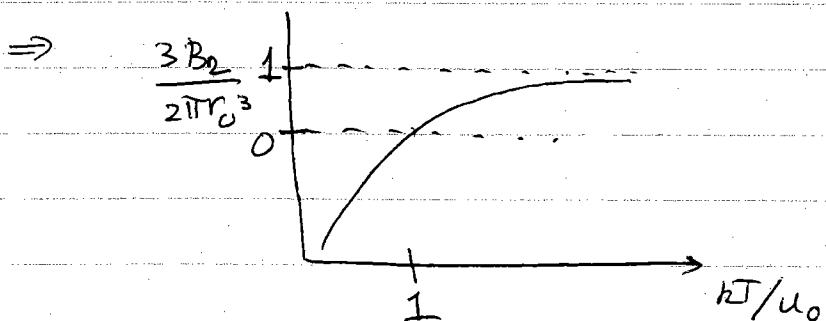
for Lenard Jones potential see Fig 9.2 in Pathria
for B_2 vs T. good agreement for all but the
lightest mass gases , Ar, N_2, CH_4, Ne