Virial expansion for the equation of state

$v = \frac{1}{n} = \frac{V}{N}$ 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

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

- low density or high temperature

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

To get the a_ℓ use:

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

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

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

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

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

$a_1 = 1$

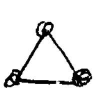
$a_2 = -b_2 = -\frac{1}{2\lambda^3}\int d^3r\ f(r)$

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

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

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

$\uparrow$

a_3 involves only the graph 

can show in general that only irreducible 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

$$a_\ell = -\frac{(\ell-1)}{\ell}\,\beta_{\ell-1}$$

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

---

Return to first non-trivial correction to ideal gas

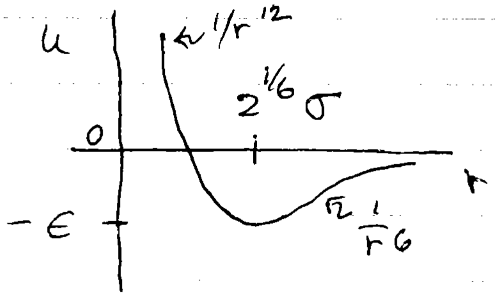
$$a_2 = -\frac{1}{2\lambda^3}\int d^3r\, f(\vec r) = \frac{2\pi}{\lambda^3}\int_0^\infty dr\, r^2\left(1-e^{-\beta u(r)}\right)$$

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

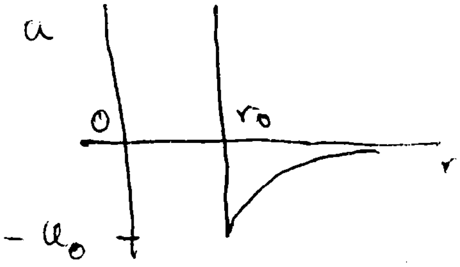
For Argon

$\frac{\epsilon}{k_B} \simeq 120°K$

$\sigma \simeq 3.4$ Å



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



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

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

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

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

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

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

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

↑ 2nd virial coefficient

or

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

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

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

von der Waal's equation of state

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

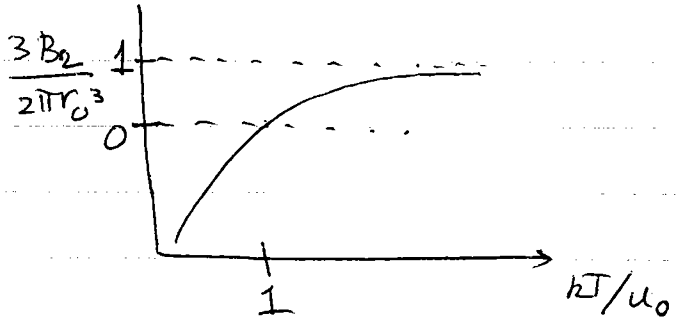
v_0 is "molar volume" — where $v_0 = \underline{\pi r_0^3}$ vol of sphere of diameter

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

$\Rightarrow$



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

Alternate derivation of van der Waals equ of state

(derived by van der Waals long before Mayer expansion)

In ideal gas law $pV = Nk_BT$

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

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

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

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

$$V_{free} = V - \underbrace{Nb}_{\text{excluded volume}} \qquad b \propto \text{volume occupied by one molecule}$$

Using $P_{kinetic}$ and V_{free} in ideal gas law gives

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

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

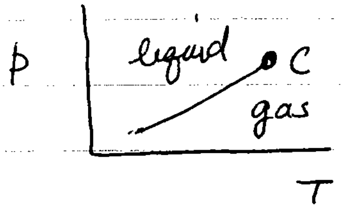
$$\left(p + a\left(\frac{N}{V}\right)^2\right)\left(\frac{V}{N} - b\right) = k_B T$$

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

van der Waals equ of state

van der Waals Theory of Liquid-Gas phase transition

phase diagram



along phase boundary is only place can have coexisting regions of liquid and gas

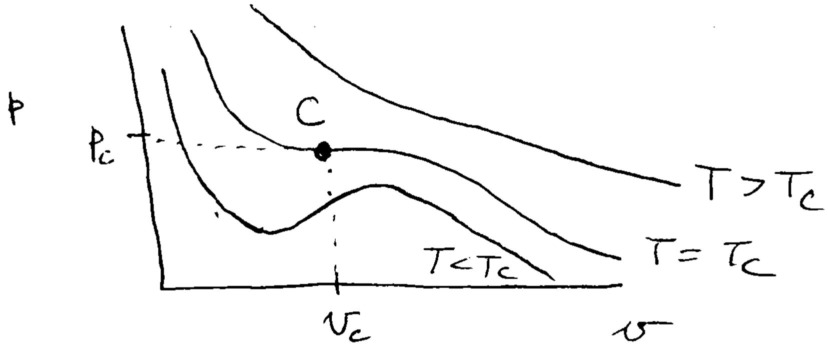
Liquid-Gas phase transition

if one crosses the liquid-gas phase boundary, there is a discontinuous change in particle density. This change in density vanishes continuously as the point C is approached. C is called the liquid-gas "critical end point". The liquid-gas phase boundary ends at C. For T or P above C, there is no distinction between liquid and gas.

van der Waal's equ of state

$$\left(p+\frac{a}{v^2}\right)(v-b)=k_BT \qquad a,b>0$$

Isotherms (p-v curves at constant T) look like



There exists a critical isotherm T_c such that

For $T>T_c$, $dp/dv<0$ monotonic decreasing $p(v)$

At $T=T_c$ first appearence of a point on isotherm with $\left(\frac{\partial p}{\partial v}\right)_T = 0$ this will turn out to be the critical point.

For $T<T_c$ isotherms are not monotonic – there is a region where $\left(\frac{\partial p}{\partial v}\right)_T > 0$.

Recall: isothermal compressibility

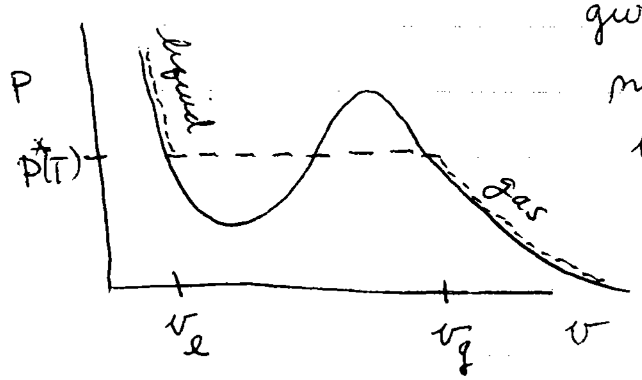
$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = -\frac{1}{v}\,\frac{1}{(\partial p/\partial v)_T}$$

For $T>T_c$, $\kappa_T>0$ everywhere

For $T=T_c$, $\kappa_T\to\infty$ at the point C

For $T<T_c$, $\kappa_T<0$ when $\frac{\partial p}{\partial v}>0$ this is unphysical region – leads to thermodynamically unstable system. we will see that this is region of phase coexistence between liquid and gas

For $T<T_c$ the van der Waals isotherm when viewed as giving $v(p,T)$ becomes multi valued – ie three values of v for fixed p and T within some region of p. We will see that the physical system follows an isotherm that is given by the dashed line. It jumps from v_ℓ to v_g at a given pressure $p^*(T)$. This $p^*(T)$



will be the location of the liquid gas phase boundary, $\frac{1}{v_\ell} - \frac{1}{v_g}$ gives the discontinuity in density at $p^*(T)$. The flat line between v_ℓ and v_g is coexistence region where system can be a mixture of both liquid and gas phases, with average specific volume v s.t. $v_\ell < v < v_g$.

As $T \to T_c^-$, $\left(\frac{1}{v_\ell} - \frac{1}{v_g}\right) \to 0$, $v_\ell, v_g \to v_c$ and $p^*(T) \to p_c$

$\Rightarrow$ C is the critical end point of the liquid-gas phase boundary.

For $T < T_c$ as $T \to T_c^-$ we see that the local max and local min of $p(v,T)$ both merge to the common pt C. $\Rightarrow$ C is an inflection point. $\frac{\partial^2 p}{\partial v^2} = 0$ at C.

Use $\left(\frac{\partial p}{\partial v}\right)_{T_c} = \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$ to determine the location of C.

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

$$\left.\begin{aligned}
\frac{dp}{dv} &= \frac{-k_B T}{(v-b)^2} + \frac{2a}{v^3} = 0 \quad \Rightarrow \quad k_B T = 2a\,\frac{(v_c-b)^2}{v_c^3} \\
\frac{d^2p}{dv^2} &= \frac{2k_B T}{(v-b)^3} - \frac{6a}{v^4} = 0 \quad \Rightarrow \quad k_B T = 3a\,\frac{(v_c-b)^3}{v_c^4}
\end{aligned}\right\} \quad 2a = 3a\,\frac{(v_c-b)}{v_c}$$

$$2v_c = 3v_c - 3b \quad \Rightarrow \quad \boxed{v_c = 3b}$$ critical specific volume

$$\Rightarrow \quad k_B T_c = 2a\,\frac{(v_c - b)^2}{v_c^3} = \frac{2a(3b-b)^2}{(3b)^3} = \frac{2a(4b^2)}{27b^3}$$

$$\boxed{k_B T_c = \frac{8}{27}\,\frac{a}{b}}$$

$$p_c = \frac{k_B T_c}{v_c - b} - \frac{a}{v_c^2} = \frac{8}{27}\,\frac{a}{b}\left(\frac{1}{3b-b}\right) - \frac{a}{(3b)^2}$$

$$= \frac{8}{27}\,\frac{a}{b}\,\frac{1}{2b} - \frac{a}{9b} = \left(\frac{4}{27} - \frac{1}{9}\right)\frac{a}{b^2}$$

$$\boxed{p_c = \frac{1}{27}\,\frac{a}{b^2}}$$

Define $\bar{p} = \frac{p}{p_c}$, $\bar{T} = \frac{T}{T_c}$, $\bar{v} = \frac{v}{v_c}$

Then

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

$$\Rightarrow \left(p_c \bar{p} + \frac{a}{v_c^2 \bar{v}^2}\right)\left(v_c \bar{v} - b\right) = k_B T_c \bar{T}$$

$$\left(\frac{1}{27}\,\frac{a}{b^2}\,\bar{p} + \frac{a}{9b^2\bar{v}^2}\right)\left(3b\bar{v} - b\right) = k_B\left(\frac{8}{27}\,\frac{a}{b}\right)\bar{T}$$

$$\frac{1}{27}\,\frac{a}{b^2}\left(\bar{p} + \frac{3}{\bar{v}^2}\right)(3b)\left(\bar{v} - \frac{1}{3}\right) = \frac{8}{27}\,\frac{a}{b}\,k_B \bar{T}$$

$$\Rightarrow \boxed{\left(\bar{p} + \frac{3}{\bar{v}^2}\right)\left(\bar{v} - \frac{1}{3}\right) = \frac{8}{3}\,k_B \bar{T}}$$

Law of Corresponding states.

Also:
$$\frac{p_c v_c}{k_B T_c} = \frac{1}{27}\frac{a}{b^2}\frac{3b}{\left(\frac{8}{27}\right)\left(\frac{a}{b}\right)} = \frac{3}{8} = 0.375$$

universal # for all gases obeying van der Waals eqn of state

gas	T_c (K)	$\frac{p_c v_c}{k_B T_c}$
Ne	44.8	0.305
Ar	150.7	0.292
Kr	209.4	0.290
Xe	289.8	0.288
N_2	126.0	0.292
O_2	154.3	0.292
CO	133.0	0.294
CH_4	190.3	0.289