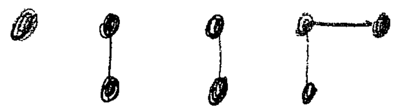
$$\boxed{Q_N(V,T) = \text{sum of all distinct } N\text{-particle graphs}}$$

given $\sum_{l=1}^{N} l m_l = N$ $\qquad$ m_l is the number of l-particle clusters

$m_1 = 1 \quad m_2 = 2 \quad m_3 = 1$

e.g. $N = 8$



$\sum_{l=1}^{N} m_l$ = total # of clusters

Contributions to $Q_N(V,T)$

$\Downarrow$

combinatorial prefactor (i) $$\frac{N!}{(1!)^{m_1}(2!)^{m_2}\cdots} = \frac{N!}{\prod_{l=1}^{N}(l!)^{m_l}}$$ assigning N particles to $\sum_l m_l$ clusters

cluster integral contribution (ii) $$\prod_{l=1}^{N} \frac{[\text{sum of the values of all possible } l\text{-particle clusters}]^{m_l}}{m_l!}$$

$$= \prod_{l=1}^{N} \left(b_l\, l!\, V\right)^{m_l} \frac{1}{m_l!}$$

(summation restricted to $\sum_l m_l l = N$)

$$Q_N(T,V) = \sum_{\{m_l\}}{}' \frac{N!}{\prod_{l=1}^{N}(l!)^{m_l}} \cdot \prod_{l=1}^{N} \frac{(b_l\, l!\, V)^{m_l}}{m_l!} =$$

$$= N! \sum_{\{m_l\}}{}' \prod_{l=1}^{N} \frac{(b_l V)^{m_l}}{m_l!}$$

$$Z_N = \frac{1}{\lambda^{3N}} \sum_{\{m_\ell\}}{}' \prod_\ell \frac{(b_\ell V)^{m_\ell}}{m_\ell!} \qquad \left(\sum_{\ell=1}^{N} \ell m_\ell = N \right)$$

$z = e^{\beta\mu}$

$$Z_G(z,T,V) = \sum_{N=0}^{\infty} z^N Z_N(T,V)$$

(grand-canonical ensemble)

$$= \sum_{N=0}^{\infty} z^N \frac{1}{\lambda^{3N}} \sum_{\{m_\ell\}}{}' \prod_\ell \frac{(b_\ell V)^{m_\ell}}{m_\ell!}$$

for unrestricted sum

$$\sum_{N=0}^{\infty} \underbrace{\sum_{\{m_\ell\}}{}'}_{\text{restricted sum}} \rightarrow \underbrace{\sum_{\{m_\ell\}}}_{\text{unrestricted sum}}$$

$$= \sum_{m_1,m_2,m_3,\dots} \left[\prod_{\ell=1}^{\infty} (z^\ell)^{m_\ell} \left(\frac{1}{\lambda^{3\ell}}\right)^{m_\ell} \frac{(b_\ell V)^{m_\ell}}{m_\ell!} \right] =$$

$$= \sum_{m_1,m_2,\dots} \left[\prod_{\ell=1}^{\infty} \frac{(z^\ell \lambda^{-3\ell} b_\ell V)^{m_\ell}}{m_\ell!} \right] =$$

$$= \prod_{\ell=1}^{\infty} \sum_{m_\ell=0}^{\infty} \frac{\left[(z\lambda^{-3})^\ell b_\ell V\right]^{m_\ell}}{m_\ell!} = \prod_{\ell=1}^{\infty} \exp\left\{(z\lambda^{-3})^\ell b_\ell V\right\}$$

$z = e^{\beta\mu}$

$$\phi(\mu,T,V) = -kT \ln Z_G \qquad \text{(grand potential)}$$

$$PV = -\phi(\mu,T,V) = kTV \sum_{\ell=1}^{\infty} \left(\frac{z}{\lambda^3}\right)^\ell b_\ell$$

$$\boxed{\frac{P}{kT} = \sum_{\ell=1}^{\infty} \left(\frac{z}{\lambda^3}\right)^\ell b_\ell}$$

$$N = z\left(\frac{\partial}{\partial z} \ln Z_G\right)_{T,V} = \boxed{V \sum_{\ell=1}^{\infty} \ell \left(\frac{z}{\lambda^3}\right)^\ell b_\ell}$$

$$\boxed{\begin{aligned} \frac{P}{kT} &= \sum_{l=1}^{\infty}\left(\frac{z}{\lambda^3}\right)^l b_l \quad (1a) \\ n &= \sum_{l=1}^{\infty} l\left(\frac{z}{\lambda^3}\right)^l b_l \quad (1b) \end{aligned}}$$

cluster expansion of classical gas

$$\boxed{\frac{P}{kT} = n + B_2(T)n^2 + B_3(T)n^3 + \dots}$$

virial expansion

$n = \frac{N}{V}$ (particle density)

$B_j(T)$: virial coefficients

From (1b)

$$n = \sum_{l=1}^{\infty} l\, t^l b_l \qquad \left(t \equiv \frac{z}{\lambda^3}\right)$$

would need: $t = c_1 n + c_2 n^2 + c_3 n^3 + \dots$

("inverse" of (1b)) series expansion in n

Determine c_j:

$$n = (c_1 n + c_2 n^2 + c_3 n^3)b_1 + 2(c_1^2 n^2 + 2c_1c_2 n^3)b_2 + 3c_1^3 n^3 b_3 + \sigma(n^4)$$

$$n = c_1 b_1 n + (c_2 b_1 + 2c_1^2 b_2)n^2 + (c_3 b_1 + 4c_1c_2 b_2 + 3c_1^3 b_3)n^3 + \sigma(n^4)$$

$$c_1 = \frac{1}{b_1} = \frac{1}{1} = 1 \qquad (b_1 = 1)$$

$$c_2 = -2b_2$$

$$c_3 = -4(-2b_2)b_2 - 3b_3 = 8b_2^2 - 3b_3$$

Thus, using (1a) now, and using the results for c_j:

$$\frac{P}{kT} = \left(c_1 n + c_2 n^2 + c_3 n^3\right) b_1 + \left(c_1^2 n^2 + 2 c_1 c_2 n^3\right) b_2 + c_1^3 n^3 b_3 + o(n^4)$$

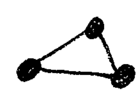
$$= c_1 b_1 n + \left(c_2 b_1 + c_1^2 b_2\right) n^2 + \left(c_3 b_1 + 2 c_1 c_2 b_2 + c_1^3 b_3\right) n^3 + o(n^4)$$

$$= n + \left(-2 b_2 + b_2\right) n^2 + \left(8 b_2^2 - 3 b_3 + 2(-2b_2) b_2 + b_3\right) n^3 + o(n^4)$$

$$= n - b_2 n^2 + \left(4 b_2^2 - 2 b_3\right) n^3 + o(n^4)$$

$$B_2(T) = - b_2 = -\frac{1}{2} \int f(x)\, d^3x$$

$$B_3(T) = 4 b_2^2 - 2 b_3 = -\frac{1}{3} \iint f(x) f(y) f(|\vec{x} - \vec{y}|)\, d^3x\, d^3y$$



$\vdots$

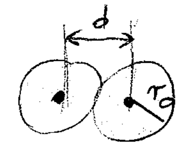
virial coefficients: : only "irreducible" clusters contribute

$\ell \geq 2$ $$B_\ell(T) = -\frac{(\ell - 1)}{\ell!\, V} \times (\text{sum of all irreducible } \ell\text{-particle clusters})$$

Evaluation of the virial coefficient, $B_2(T)$

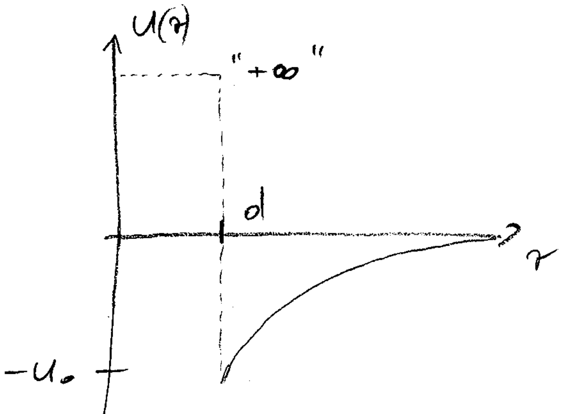
model potential:

$$U(r) = \begin{cases} \infty & r \leqslant d (= 2r_0) \\ -u_0\left(\dfrac{d}{r}\right)^6 & r > d \end{cases}$$



$d = 2r_0$

hard core with weak attractive



Mayer function:

$$f(r) = e^{-\beta U(r)} - 1.$$

$$f(r) = \begin{cases} -1 & r \leqslant d \\ e^{\frac{u_0}{kT}\left(\frac{d}{r}\right)^6} - 1 & r > d \end{cases}$$

assuming $\dfrac{u_0}{kT} \ll 1 \Rightarrow$ $$f(r) = \begin{cases} -1 & r \leqslant d \\ \dfrac{u_0}{kT}\left(\dfrac{d}{r}\right)^6 & r > d \end{cases}$$

$$B_2(T) = -\frac{1}{2}\int_0^\infty f(r)\, 4\pi r^2\, dr = -\frac{1}{2}\left\{ \int_0^d (-1)\, 4\pi r^2\, dr + \left(\frac{u_0}{kT}\right)\int_d^\infty \left(\frac{d}{r}\right)^6 4\pi r^2\, dr \right\}$$

$$= 2\pi \frac{d^3}{3} - 2\pi \frac{u_0}{kT} d^6 \frac{1}{3}\frac{1}{d^3} = \frac{2\pi}{3} d^3 \left(1 - \frac{u_0}{kT}\right)$$

$$= \frac{16\pi r_0^3}{3}\left(1 - \frac{u_0}{kT}\right)$$

$$\boxed{B_2 \simeq \frac{16\pi r_0^3}{3}\left(1 - \frac{U_0}{kT}\right)}$$

$$\frac{P}{kT} \simeq \frac{N}{V} + \frac{16\pi r_0^3}{3}\left(1 - \frac{U_0}{kT}\right)\left(\frac{N}{V}\right)^2 \qquad \left(n = \frac{N}{V}\right)$$

$$P \simeq kT\frac{N}{V}\left\{1 + \frac{16\pi r_0^3}{3}\frac{N}{V}\right\} - \frac{16\pi r_0^3}{3}U_0\left(\frac{N}{V}\right)^2$$

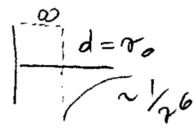
$$\boxed{a \equiv \frac{16\pi r_0^3}{3}U_0} \qquad \boxed{b \equiv \frac{16\pi r_0^3}{3}} = 4 \times \text{molecular volume}$$

$$\left[P + a\left(\frac{N}{V}\right)^2\right] \simeq NkT\frac{1}{V - bN}$$

$$\boxed{\left(P + a\left(\frac{N}{V}\right)^2\right)\left(V - bN\right) \simeq NkT} \qquad \text{V.d.W}$$

Van der Waals Gas

as a result of the cluster expansion
and the virial expansion : $\frac{P}{kT} = n + B_2(T)\, n^2 + \ldots$

and the simple 

potential we

obtained the V.d.W equation of state for the "dilute" interacting gas:

$$\left(P + a\left(\frac{N}{V}\right)^2\right)\left(V - bN\right) = NkT$$

$n = \frac{N}{V}$ (density)

or

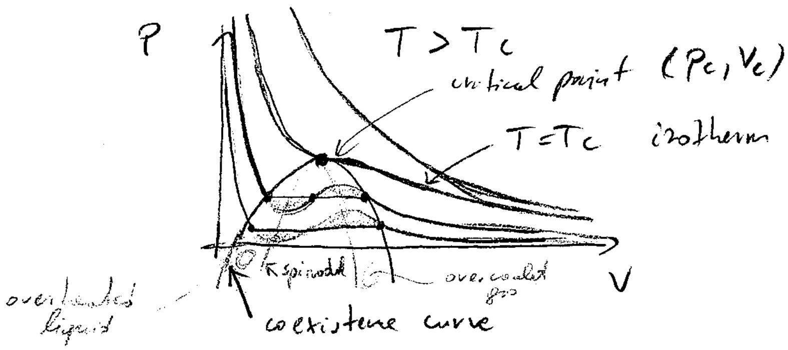
$$\left(P + an^2\right)\left(1 - bn\right) = nkT$$

This approximation (together with keeping only B_2 in the virial expansion)
is justified when $bn \ll 1$
since $b \sim r_0^3$ $\Rightarrow$ $r_0^3 n = \frac{r_0^3}{\ell^3} \ll 1$

$\ell = \left(\frac{V}{N}\right)^{1/3}$ mean interparticle distance

Thus, $\boxed{\frac{r_0^3}{\ell^3} \ll 1}$ means, that the mean interparticle distance, ℓ, has to be much larger than the effective range of interaction, r_0
This is consistent with spirit of the virial expansion
since $B_\ell \sim \left(r_0^3\right)^{\ell - 1}$ $\ell \geq 2$

The V.d.W isotherms



pretend it is "exact":

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

$N = \text{const.}$

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

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

critical point: $\kappa_T \to \infty$

$$\left(\frac{\partial P}{\partial V}\right)_T \to 0$$

for T_c and V_c

$$\begin{cases} \left(\dfrac{\partial P}{\partial V}\right)_{T,N} = -\dfrac{NkT}{(V-Nb)^2} + 2a\dfrac{N^2}{V^3} = 0 \\[2ex] \left(\dfrac{\partial^2 P}{\partial V^2}\right)_{T,N} = \dfrac{2NkT}{(V-Nb)^3} - 6a\dfrac{N^2}{V^4} = 0 \end{cases}$$

$\Leftarrow$ $\boxed{\text{HW excercise}}$

$$\Rightarrow \begin{cases} NkT = 2aN^2\dfrac{(V-Nb)^2}{V^3} \\[2ex] NkT = 3aN^2\dfrac{(V-Nb)^3}{V^4} \end{cases} \Rightarrow 2V = 3(V-Nb) \Rightarrow \boxed{V_c = 3Nb}$$

$$\boxed{kT_c = \frac{8}{27}\frac{a}{b}}$$

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

<u>Note</u>: for $V \lesssim V_c$

$$\frac{N}{V_c}b = \frac{1}{3}$$

$$nb \gtrsim O(1)$$

is <u>not consistent</u> with the basic approximation made along the cluster and virial expansion, i.e. $nb \ll 1$

This yields the unphysical behavior.

Phase Coexistance and Maxwell construction

$\left(\frac{\partial P}{\partial V}\right)_T \leq 0$ should hold in all physical regions

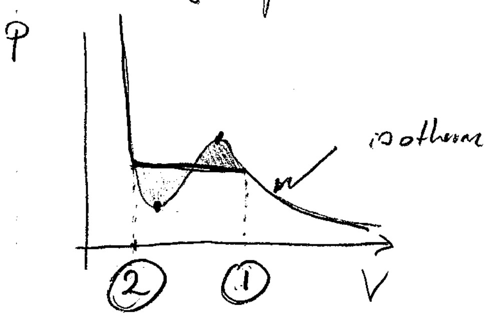
Within the V.d.W approximation, however, $\left(\frac{\partial P}{\partial V}\right)_T > 0$ regions appear, which must be "manually" corrected. This is where the Maxwell construction comes in.

From basic thermodynamics, using the Gibbs free energy per particle (which is equal to the chemical potential μ)

$$\mu(T,P) = \frac{G(T,P,N)}{N} = g(T,P)$$

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP$$ (also from Gibbs-Duhem relation)

coexisting phases must have equal chemical potential (T and P are the same for the two phases)



$$0 = \mu(2) - \mu(1) = \int_1^2 d\mu = \text{along the isotherm} = \frac{1}{N}\int_1^2 V\,dP$$

"equal-area construction"

For $T < T_c$ $\left(\frac{\partial P}{\partial V}\right)_T = 0$: spinodal

Law of Corresponding States

Rescale the V.d.W equation using P_c, V_c, T_c

$$\tilde{T} = \frac{T}{T_c} \qquad \tilde{V} = \frac{V}{V_c} \quad , \quad \tilde{P} = \frac{P}{P_c}$$

$$\left(\tilde{P}P_c + a\left(\frac{N}{\tilde{V}V_c}\right)^2\right)\left(\tilde{V}V_c - Nb\right) = Nk\tilde{T}T_c$$

and $\boxed{V_c = 3Nb \ , \quad kT_c = \frac{8}{27}\frac{a}{b} \ , \quad P_c = \frac{1}{27}\frac{a}{b^2}}$

$$\left(\tilde{P} + \frac{1}{\tilde{V}^2}\frac{aN^2}{V_c^2 P_c}\right)\left(\tilde{V} - \frac{1}{3}\right) = \tilde{T}\frac{NkT_c}{P_c V_c}$$

$$\frac{P_c V_c}{kT_c N} = \frac{3}{8} = 0.375$$

He^4: ≈ 0.31
H_2O : 0.23
Ar: 0.292

$$\boxed{\left(\tilde{P} + \frac{3}{\tilde{V}^2}\right)\left(\tilde{V} - \frac{1}{3}\right) = \frac{8}{3}\tilde{T}}$$

~~universality~~ law of corresponding states

- when expressed in terms of scaled variables, all fluids should exhibit similar behavior.
- this is true, but they won't be the same as the "V.d.W." gas

$\Rightarrow$ concept of <u>universality</u> is very important
(but not described very well by V.d.W eq.)