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

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

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

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

$$V_{free} = V - \underbrace{Nb}_{\text{excluded volume}}$$

$b \propto$ volume occupied by one molecule

~~[illegible]~~ Using P_{kinetic} and V_{free} in ideal gas law gives

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

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

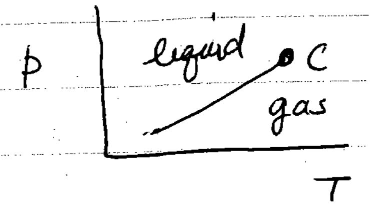
$$\left(p + a\left(\frac{N}{V}\right)^2\right)\left(\frac{V}{N} - b\right) = k_B T$$

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

van der Waals
equ of state

van der Waals Theory of Liquid-Gas phase transition

phase diagram



Liquid-Gas phase transition

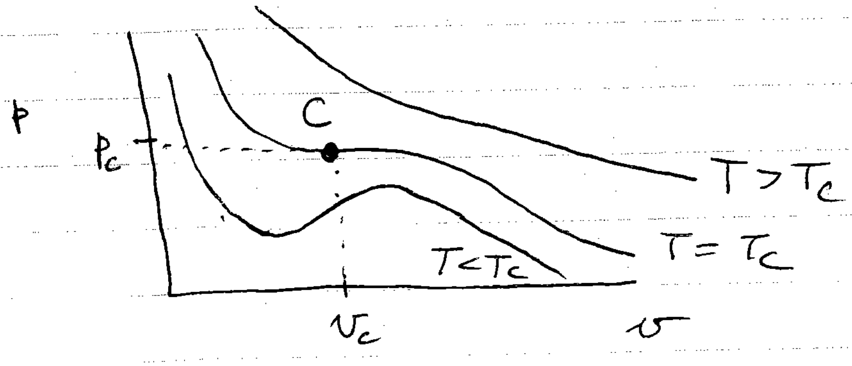
if one crosses the liquid-gas phase boundary, there is a discontinuous change in particle density. This change in density vanishes continuously at the point C is approached. C is called the liquid-gas "critical end point". The liquid-gas phase boundary ends at C. For T or P above C, there is no distinction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

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

van der Waal's equ of state

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

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 <u>not</u> monotonic - there is a region where $\left(\frac{\partial p}{\partial v}\right)_T > 0$.

Recall: isothermal compressibility

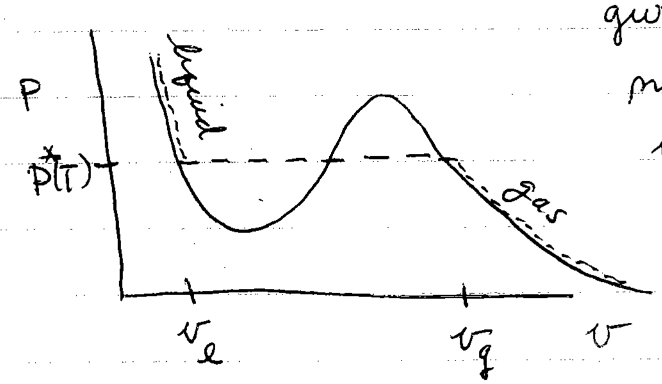
$$\kappa_T = \frac{-1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T = \frac{-1}{v}\,\frac{1}{(\partial p/\partial v)_T}$$

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 vander 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.

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

$$\frac{dp}{dv} = \frac{-k_B T}{(v-b)^2} + \frac{2a}{v^3} = 0 \Rightarrow k_B T = 2a\,\frac{(v_c-b)^2}{v_c^3}$$

$$\frac{d^2p}{dv^2} = \frac{2k_B T}{(v-b)^3} - \frac{6a}{v^4} = 0 \Rightarrow k_B T = 3a\,\frac{(v_c-b)^3}{v_c^4}$$

$$\left.\right\} \; 2a = 3a\,\frac{(v_c-b)}{v_c}$$

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

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

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

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

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

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

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

Then

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

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

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

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

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

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

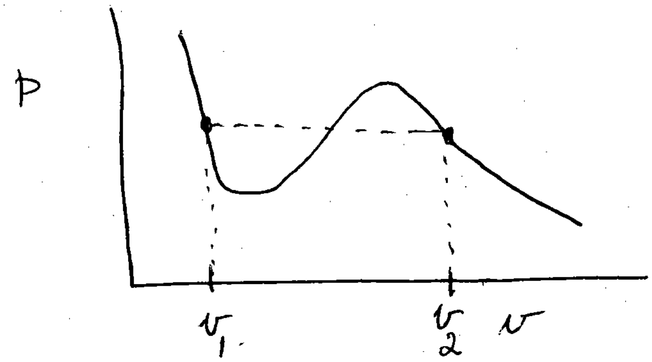
gas	T_c (K)	$\frac{p_c v_c}{k_B T_c}$
Ne	44.8	0.305
Ar	150.7	0.292
Kr	209.4	0.290
Xe	289.8	0.288
N_2	126.0	0.292
O_2	154.3	0.292
CO	133.0	0.294
CH_4	190.3	0.289

Law of corresponding states: If scale p, v, T by values at critical point to get $\bar{p}, \bar{v}, \bar{T}$, then isotherms in terms of $\bar{p}, \bar{v}, \bar{T}$ are independent of a and b - will be the same for any gas.

Now consider $T < T_c$ we want to determine the coexisting values of v_ℓ and v_g that the physical system will have.

Two ways to do this

① Maxwell Construction



Gibbs free energy $G(T,p,N) = \mu N$

$$dG = -SdT + Vdp + \mu dN$$
$$= \mu dN + N d\mu$$
$$\Rightarrow d\mu = -\left(\frac{S}{N}\right)dT + v\,dp$$

↖ Gibbs-Duhem relation

along isotherm $dT = 0$

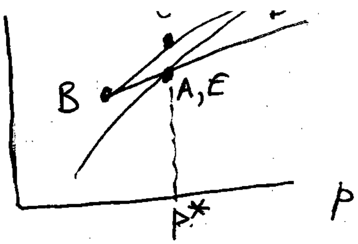
$$\Rightarrow d\mu = v\,dp$$

Now at liquid-gas coexistence, the condition for chemical equilib $\Rightarrow \mu_\ell = \mu_g$

$$\Rightarrow \int_1^2 d\mu = \mu_2 - \mu_1 = \int_1^2 v\,dp = 0 \quad \text{if}$$

v_1 is v_ℓ and v_2 is v_g for coexisting v_ℓ and v_g

graph of $\int v\,dp \rightarrow \mu = \frac{G}{N}$



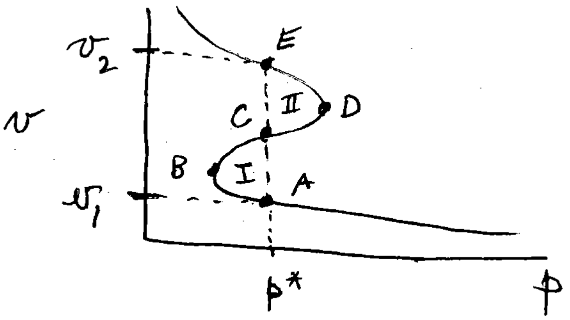
$\frac{G}{N}$ has cusp at p^*

$\frac{d\,G/N}{dp} = v$ is discontinuous at p^*

physical G/N is concave envelope

So $\int_1^2 v\,dp = 0$ determines $v_\ell = v_1$, $v_g = v_2$

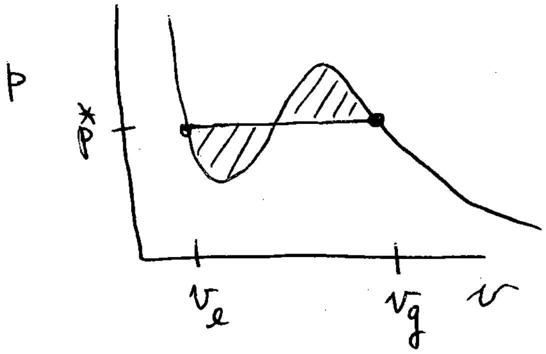
To see the geometric meaning of this



$$\int_1^2 v\,dp = \int_A^B v\,dp + \int_B^C v\,dp + \int_C^D v\,dp + \int_D^E v\,dp$$

$$= \text{area}_{I} - \text{area}_{II}$$

So we get condition of "equal areas"



v_ℓ and v_g determined by the cord at constant p^* such that area above cord = area below cord

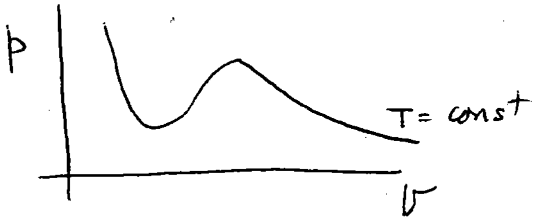
② Consider Helmholtz free energy

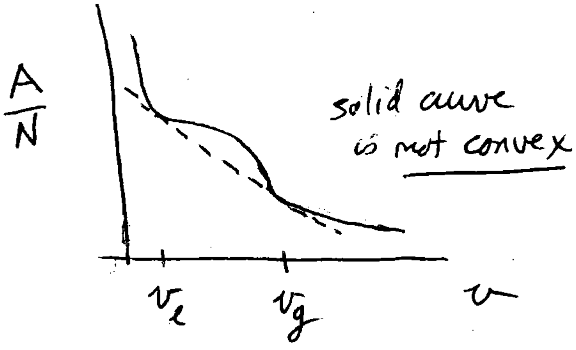
$A(T,V)$ fixed N

$dA = -S\,dT - p\,dV$

$A = -\int p\,dV$ along isotherm

$A/N = -\int p\,dv$





solid curve is not convex

$$p = -\frac{\partial A}{\partial V} = -\frac{\partial A}{N\,\partial v}$$

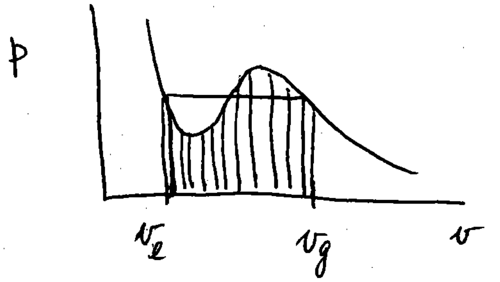
p must be const from v_ℓ to v_g and A should be convex

$\Rightarrow$ coexistence is given by dashed line

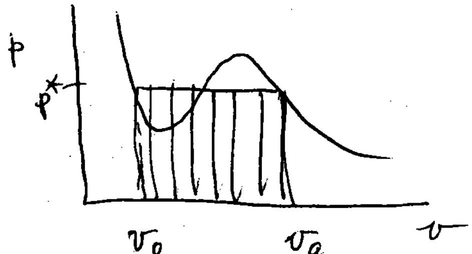
$$p^* = \frac{-\left[\left(\frac{A}{N}\right)_g - \left(\frac{A}{N}\right)_l\right]}{(v_g - v_l)}$$

coexistence pressure is slope of dashed line

$$p^*(v_g - v_l) = -\left[\left(\frac{A}{N}\right)_g - \left(\frac{A}{N}\right)_l\right] = +\int_l^g p\,dv$$

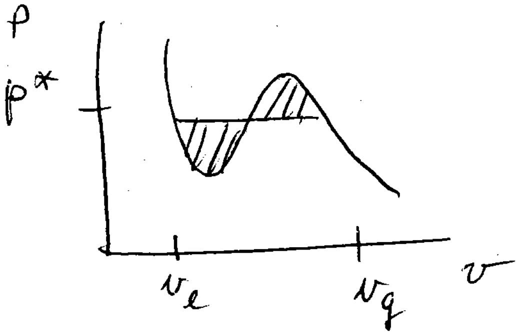


Shaded area is $\int_l^g p\,dv$



shaded area is $p^*(v_g - v_l)$

The two areas are equal only if



the shaded area above p^* equals shaded area below p^*

The locus of points $v_l(T)$, $v_g(T)$ in $p-v$ plane as T varies is called the coexistence curve.