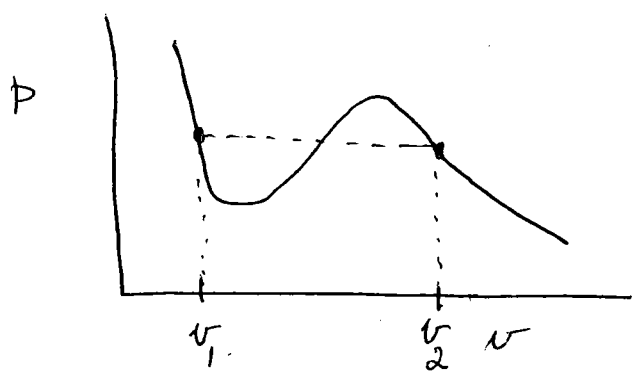
Law of corresponding states: if scale p, v, T by values at critical point to get $\bar{p}, \bar{v}, \bar{T}$, then isotherms in terms of $\bar{p}, \bar{v}, \bar{T}$ are independent of a and b - will be the same for any gas.

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 $dT = 0$

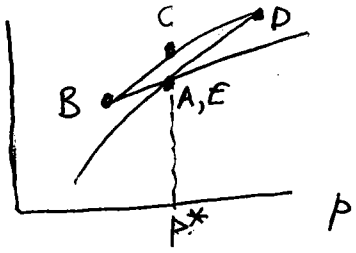
$$\Rightarrow d\mu = v dp$$

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



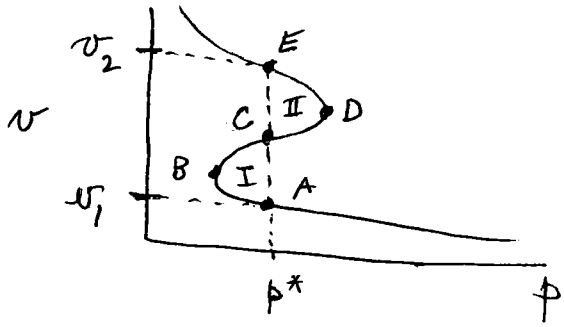
$\frac{G}{N}$ has cusp at p^*

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

physical G/N is concave envelope

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

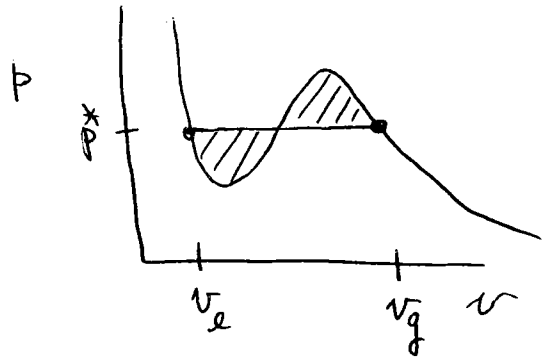
To see the geometric meaning of this



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

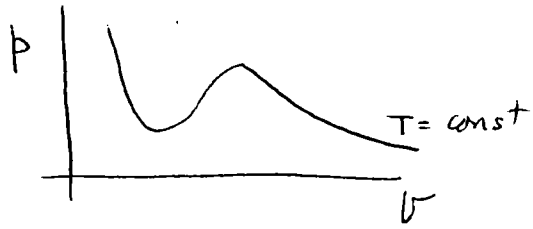
$$= \text{area}_{\mathrm{I}} - \text{area}_{\mathrm{II}}$$

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

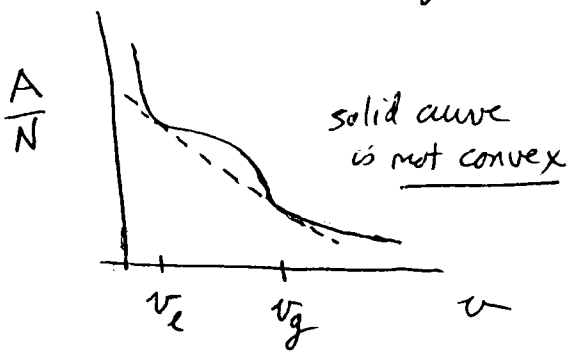
② Consider Helmholtz free energy $A(T,V)$ fixed N



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

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

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



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

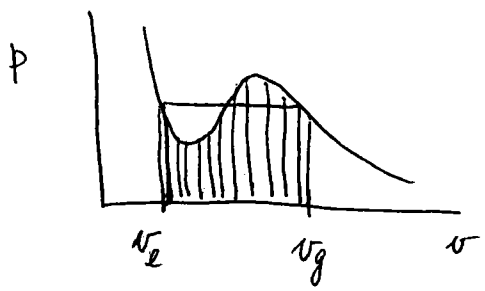
p must be const from v_ℓ to v_g and A should be convex

$\Rightarrow$ coexistence is given by

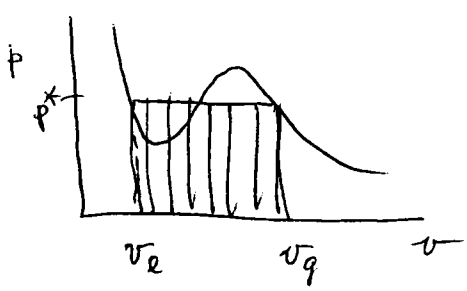
$$p^* = \frac{-\left[\left(\frac{A}{N}\right)_g - \left(\frac{A}{N}\right)_\ell\right]}{(v_g - v_\ell)}$$

coexistence pressure is slope of dashed line

$$p^*(v_g - v_\ell) = -\left[\left(\frac{A}{N}\right)_g - \left(\frac{A}{N}\right)_\ell\right] = +\int_\ell^g p\,dv$$

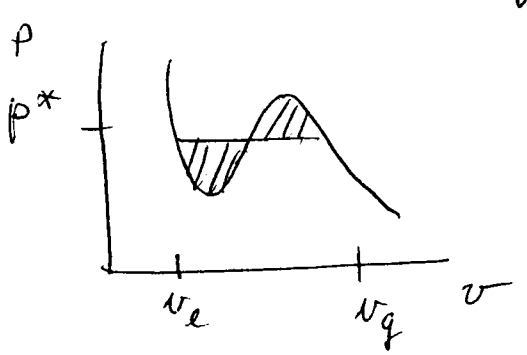


shaded area is $\int_\ell^g p\,dv$



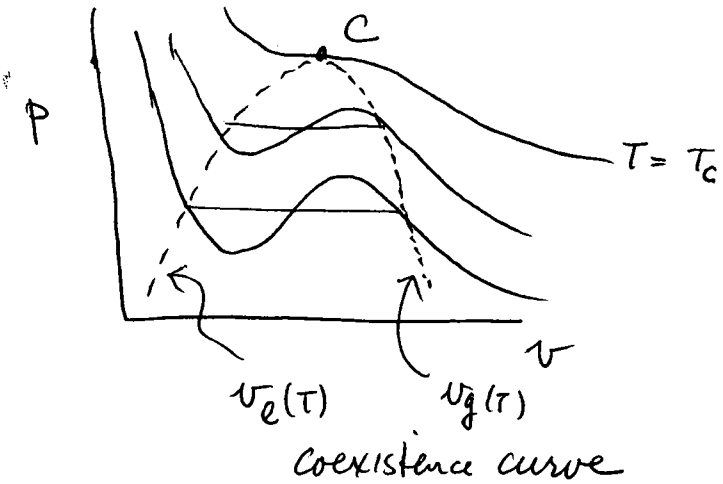
shaded area is $p^*(v_g - v_\ell)$

The two areas are equal only if



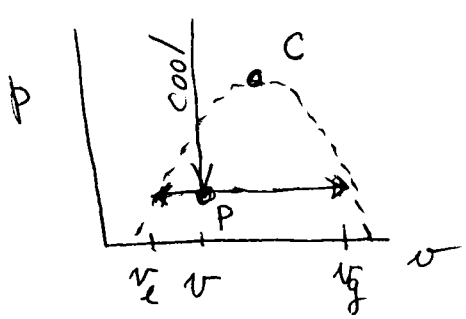
the shaded area above p^* equals shaded area below p^*

The locus of points $v_\ell(T)$, $v_g(T)$ in p-v plane as T varies is called the <u>coexistence curve</u>.



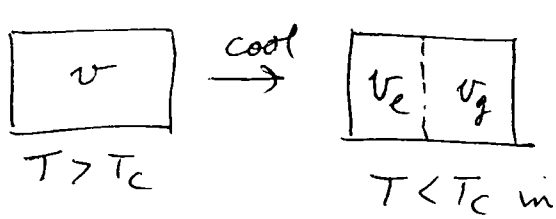
Region of p-v plane under coexistence curve is the <u>coexistence region</u>. Region in which system can coexist as both liquid and gas

Coexistence region is also called the <u>phase separation</u> region. If sit at a fixed density $n = 1/v$ that lies within coexistence region for some range of $T < T_c$, Then cool system into coexistence region to point P,

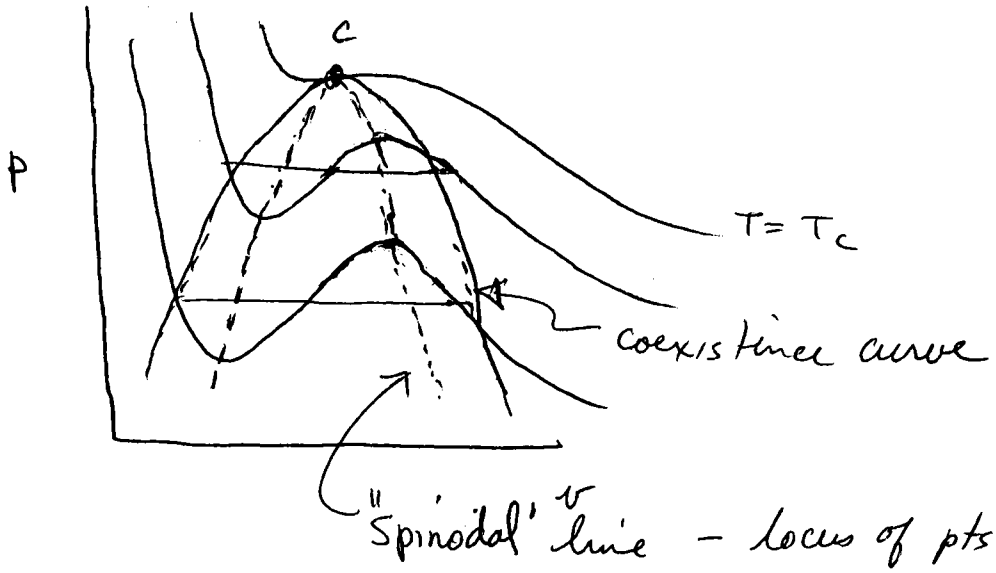


the system can no longer exist at a uniform density $1/v$. It will split up in a part with density $1/v_e$ and a part with density $1/v_g$ such that <u>average</u> density remains $1/v$

The minimum energy state will be one in which the domain wall separating the liquid + gas is minimum, so one gets



the system "phase separates" into a region of liquid and a region of gas



"Spinodal" line – locus of pts where $\frac{dp}{dv} = 0$

van der waals suggested that states between coexistence curve and spinodal line are metastable single phase regions

<u>Law of corresponding states</u> ⇒ when expressed in the scaled variables $\bar{p}, \bar{v}, \bar{T}$, the coexistence curves of all gases should collapse to a universal curve. Expt results give a good agreement with this prediction, but near c the coexistence curve does <u>not</u> agree too well with the van der Waals prediction

see Fig 3.20 of Pluschke + Bergersen