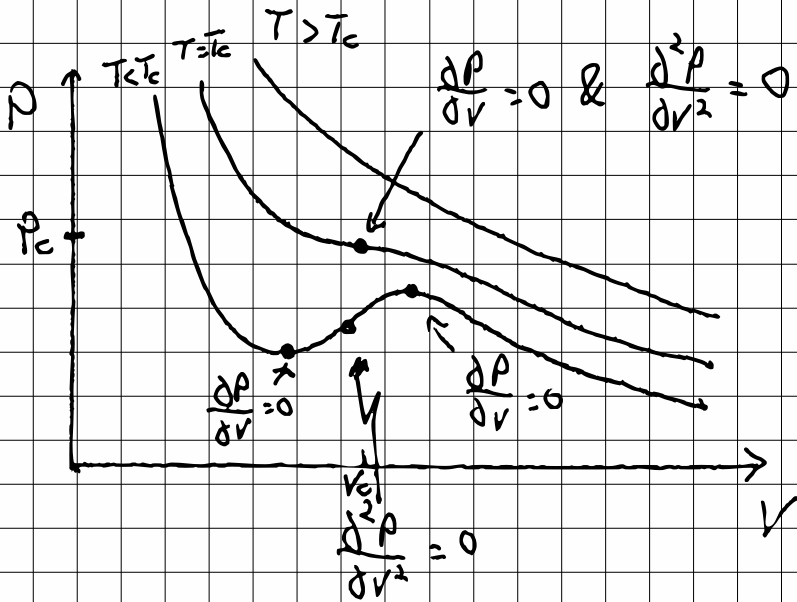


Lecture 6

Van der Waals gas, cont.

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



T_c is determined from the conditions

$$\left(\frac{\partial P}{\partial V}\right)_{T_c, N} = 0 \quad \& \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c, N} = 0$$

Using $P = \frac{Nk_B T}{V-Nb} - a \left(\frac{N}{V}\right)^2$ we have

$$\frac{\partial P}{\partial V} = - \frac{Nk_B T}{(V-Nb)^2} + 2a \frac{N^2}{V^3} \stackrel{\text{at } T=T_c}{=} 0$$

$$\Rightarrow Nk_B T V^3 = 2aN^2(V-Nb)^2 \quad (*)$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{2Nk_B T}{(V-Nb)^3} - \frac{6aN^2}{V^4} = 0$$

$$\Rightarrow 2Nk_B T V^4 = 6aN^2(V-Nb)^3 \quad (**)$$

Divide (**) by (*):

$$2V = 3(V-Nb) \Rightarrow \underline{V_c = 3Nb}$$

$$(*) : k_B T_c = \frac{2aN}{V_c^3} (V_c - Nb)^2 = \frac{2aN(2Nb)^2}{(3Nb)^3}$$

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

$$P_c = \frac{N \frac{8}{27} \frac{a}{b}}{2Nb} - a \left(\frac{N}{36N} \right)^2$$

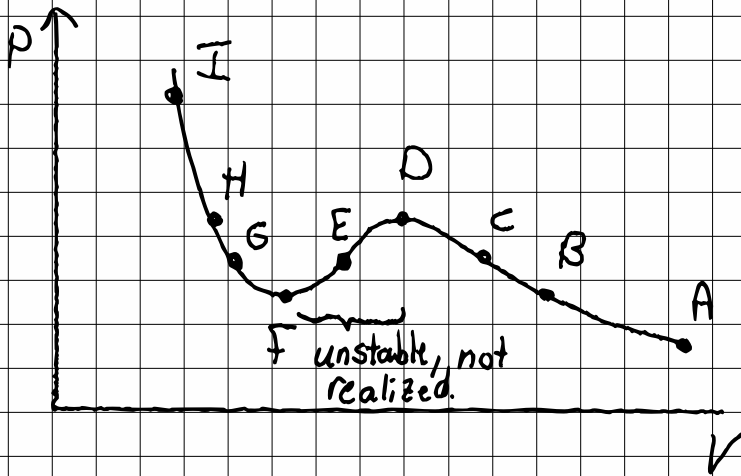
⇓

$$P_c = \frac{4}{27} \frac{a}{b^2} - \frac{a}{b^2} \frac{8}{9 \cdot 3} = \frac{a}{27b^2}$$

$$\frac{P_c V_c}{N k_B T} = \frac{\frac{a}{27b^2} \cdot 36N}{N \frac{8}{27} \frac{a}{b}} = \frac{3}{8}$$

indep. of
a & b.
(ideal gas, this)
ratio = 1

Below T_c ($T < T_c$)



$$\text{Stability: } \left(\frac{\partial^2 F}{\partial V^2} \right)_{T, N} > 0$$

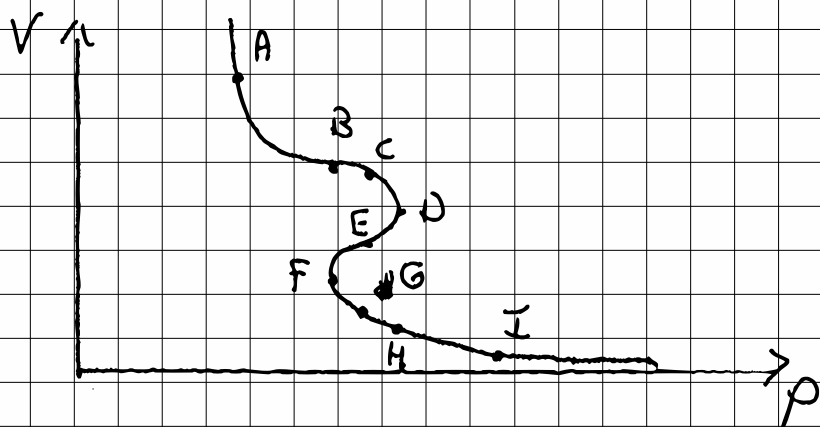
$$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial V} \right)_{T, N} = - \left(\frac{\partial p}{\partial V} \right)_{T, N} > 0$$

-p

$$\Rightarrow \left(\frac{\partial p}{\partial V} \right) < 0 \quad : \text{ Violated between F-D}$$

the Assumption of homogeneity breaks down
The homogeneous solution is unstable on F-D

Flip axes:



In the region B-H there three possible values of V for each p (Except at F & D where there are two possible values)

The middle solution D-F is unstable, so it is not realized, but there are still two solutions to choose between.

Which one is the TD stable state?

Stable state at p & T (and N):

Gibbs free energy should be minimized.

Calculate G , $G = U - TS + PV$

vdW gas is extensive: $U = TS - PV + \mu N$

$\Rightarrow G = \mu N$ so if we can calculate μ we have G .

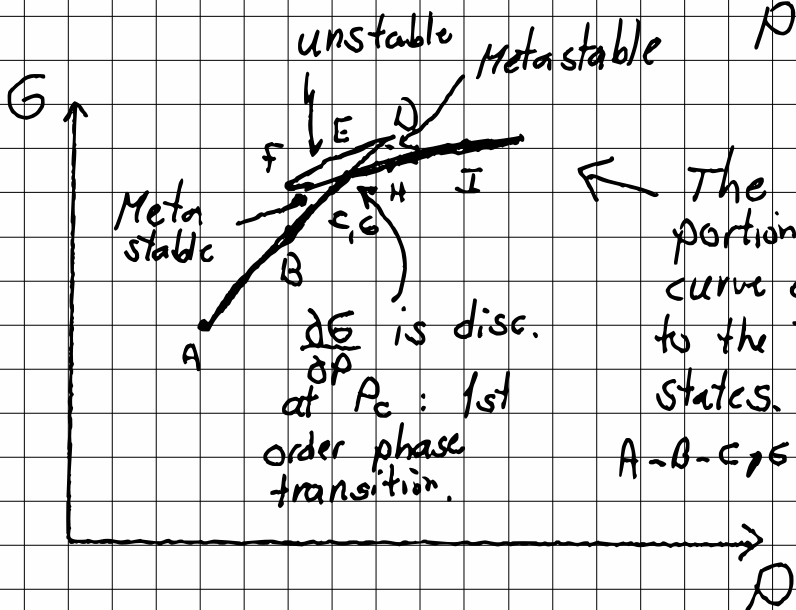
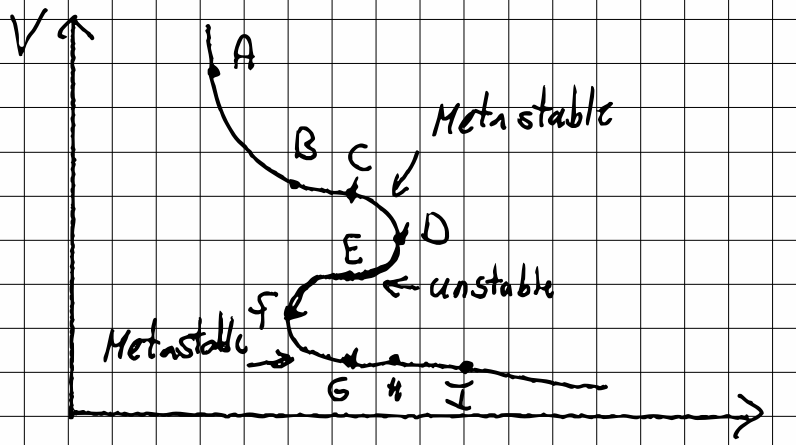
Gibbs-Duhem rel (from extensivity)

$$d\mu = -\left(\frac{S}{N}\right)dT + \frac{V}{N}dP$$

for constant Temp: $d\mu = \frac{V}{N}dP$

or $dG = VdP$

$\Rightarrow G = \int VdP \leftarrow$ area under the V - P curve



A → D : G increases as more and more area is under the curve

D → F : $dP < 0$, and so area under D → F is subtracted

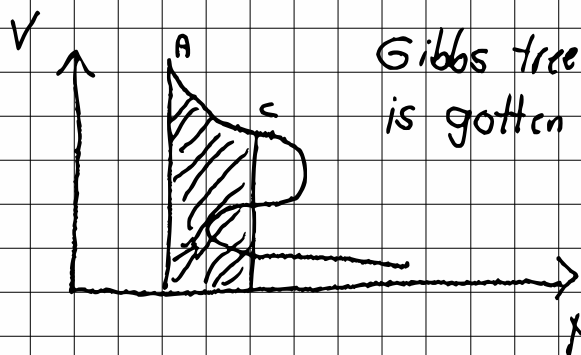
F → I : G increases again, but slowly

At points C & G Gibbs free energy are equal, and so there are two phases that coexists.

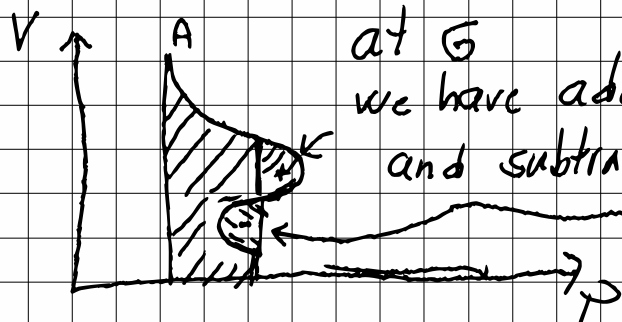
$$V = \left(\frac{\partial G}{\partial P} \right)_{T, N}$$

Since the slope of G at points C & G are different, there are two volumes V_C & V_G

Maxwell construction



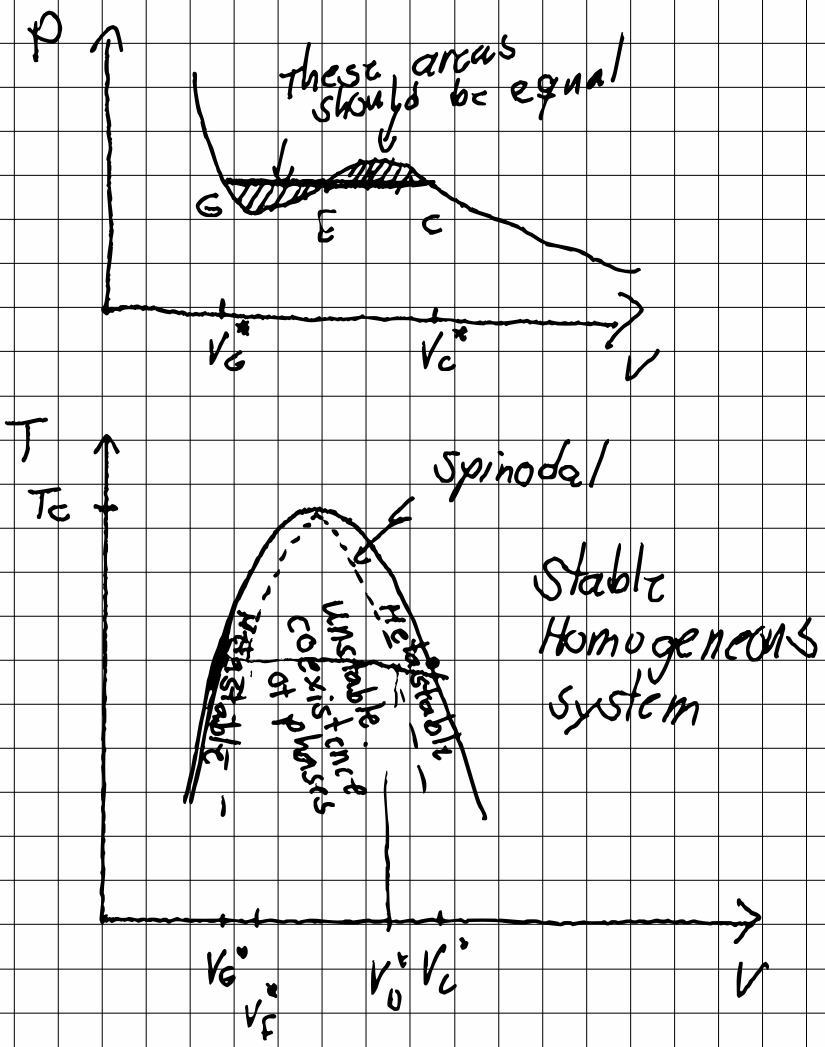
Gibbs free energy at C is gotten by the shaded area



at G we have added this and subtract

So for $G(P_e) = G(P_0)$ these areas must be equal.

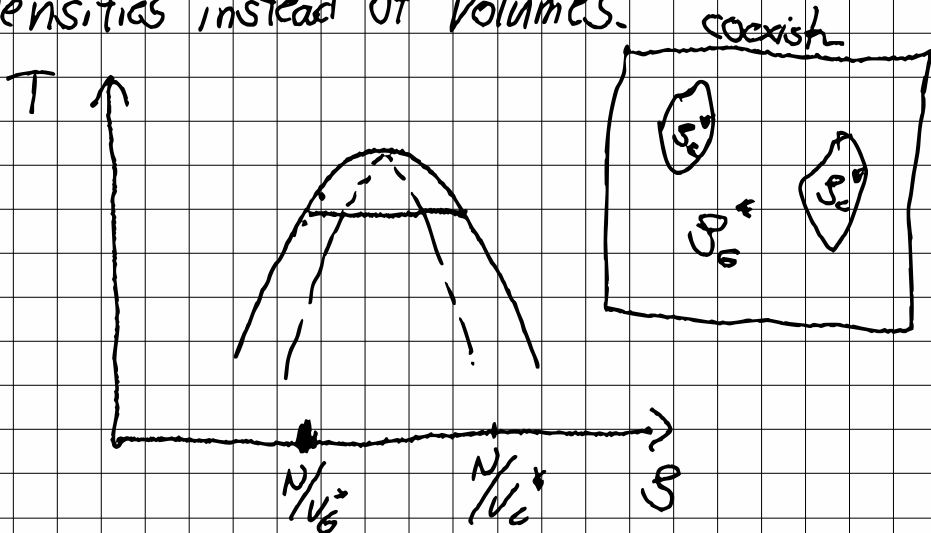
Flip axes again



Coexistence region: Two pure phases, one with volume V_0^* and another with volume V_c^* coexists.

Metastable region: System is homogeneous but can be brought into the coexistence by finite fluctuations.

It is perhaps easier to think about densities instead of volumes.



C-phase: V_c , volume frach.: $X_c = \frac{V_c}{V}$

G-phase: V_G , " $X_G = \frac{V_G}{V}$

$$V_c + V_G = V \Rightarrow X_c + X_G = 1$$

Total number of particles:

$$N = V_c \cdot \rho_c^* + V_G \cdot \rho_G^*$$

Average density: $\rho = \frac{N}{V}$

$$\Rightarrow \rho = X_c \rho_c^* + X_G \rho_G^*$$

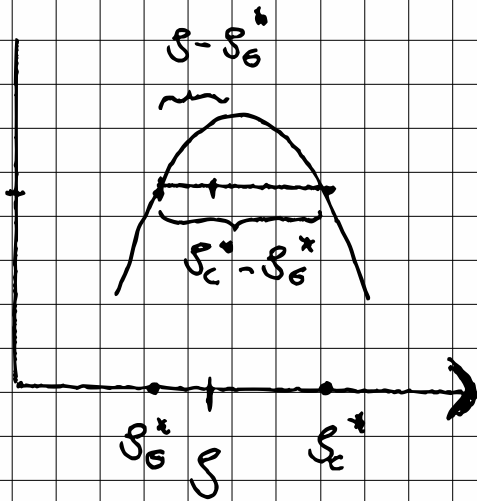
set $X_G = 1 - X_c$ and solve for X_c

~~X_c~~

$$\rho = X_c \rho_c^* + (1 - X_c) \rho_G^*$$

$$\Rightarrow X_c = \frac{\rho - \rho_G^*}{\rho_c^* - \rho_G^*}$$

Lever rule:

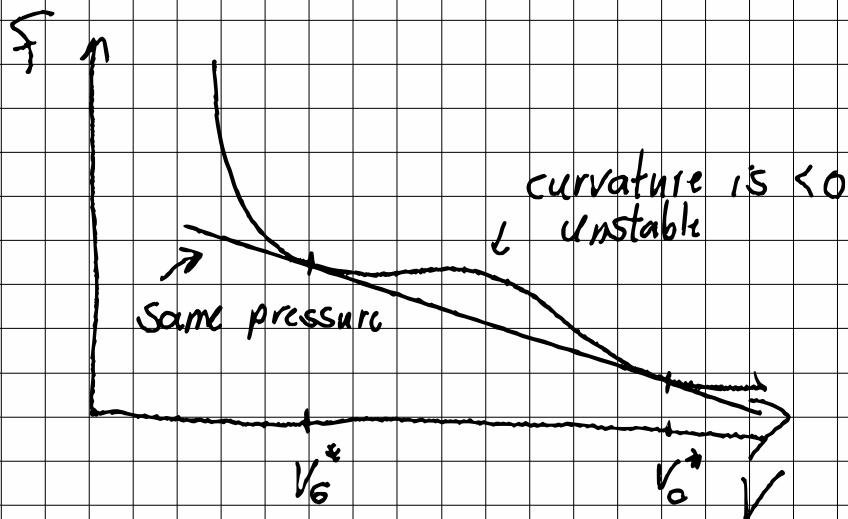


$$\text{so } X_c = \frac{S - S_G^y}{S_C^x - S_G^x}$$

If S is close to S_G^y then X_c is small.

Alternatively:

If we had plotted F vs V
 We would get something like the
 following for $T < T_0$



$$P = - \left(\frac{\partial F}{\partial V} \right)_{T, N}$$

Finding the coexistence pressure this
 way is called "the tangent construction"
 (it replaces the Maxwell construction)