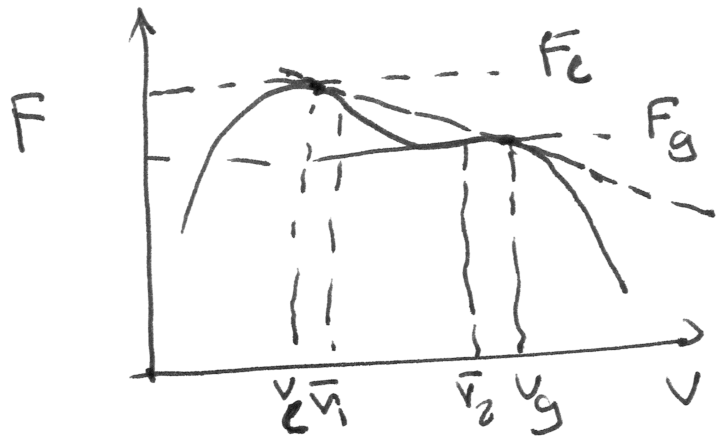
$\Rightarrow$ common pressure of both phases $\Rightarrow P = \dfrac{F_e - F_g}{V_g - V_e}$ (9)

$\Rightarrow$ at equilibrium Gibbs free energy is minimized

$$\frac{\partial G}{\partial V} = \frac{\partial F}{\partial V} + P = 0 \Rightarrow P = -\frac{\partial F}{\partial V}$$

$\Downarrow$ $\Downarrow$

we can find V_e, V_g and F_e, F_g

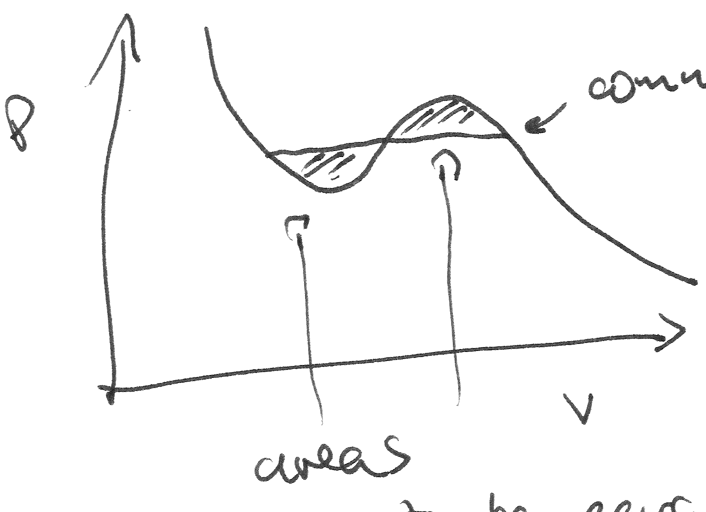


$\Rightarrow$ slope of tangent line gives common pressure

- consider integral

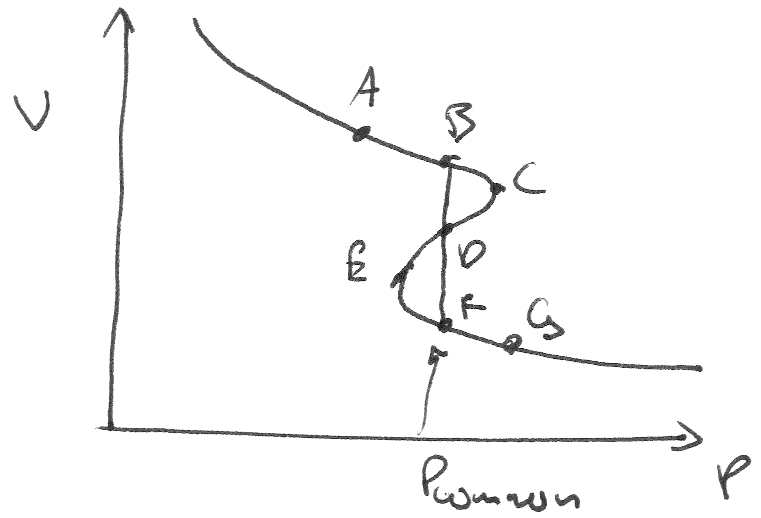
$$\int_{V_e}^{V_g} \left(\frac{\partial F}{\partial V} + P\right) dV = F + PV \Big|_{V_e}^{V_g} = \underbrace{F_g + PV_g - F_e - PV_e}_{\text{Gibbs free energy difference between gas-liquid} \Rightarrow 0}$$

$\Downarrow$



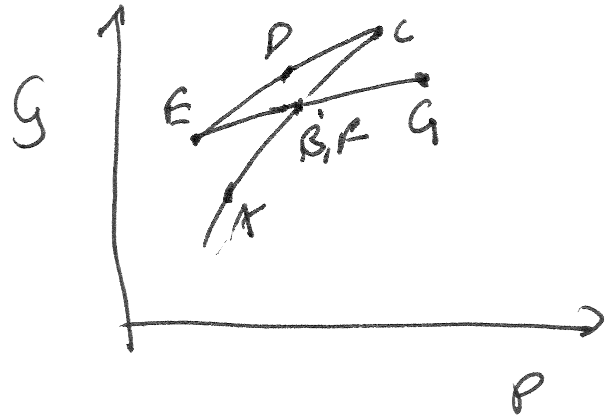
$\Rightarrow$ Maxwell equal area construction

- can also arrive via another way
  → consider plot v vs. P



$G = \int v\,dP$ for an isotherm

let's integrate v dP

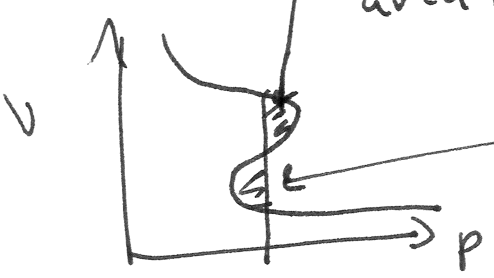


B, F same Gibbs free energy

- equal area construction arises because

$$\int_B^C v(P)\,dP + \int_C^D v(P)\,dP + \int_D^E v(P)\,dP + \int_E^F v(P)\,dP = 0$$

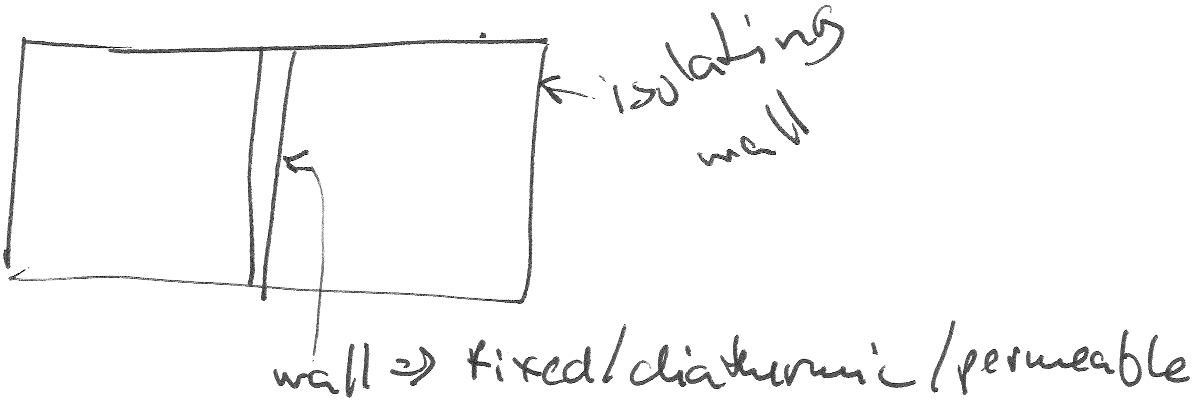
$$\underbrace{\int_D^C v(P)\,dP - \int_B^C v(P)\,dP}_{\text{area 1}} = \underbrace{\int_E^D v(P)\,dP - \int_E^F v(P)\,dP}_{\text{area 2}}$$



for $\Delta G = 0 \Rightarrow$ area 1 = area 2

Now consider two systems which can exchange heat and particles

$\Rightarrow$ T_0, μ_0 $\Rightarrow$ equilibration



this can be a reasonable model for a solid-gas phase transition (sublimation) $\Rightarrow$ the volume of the solid does not change appreciably

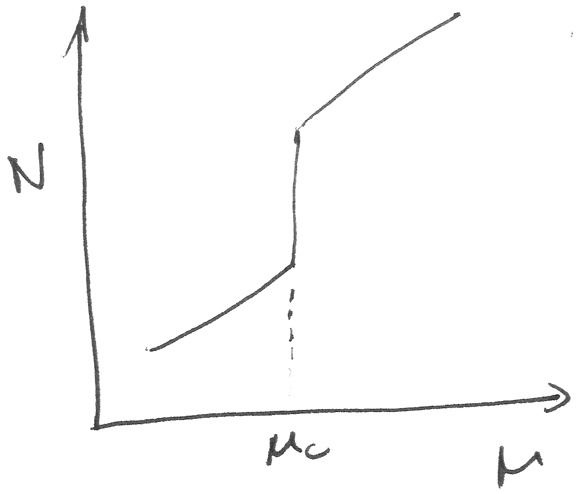
* in this case we have: $\Omega(T_0, \mu_0)$ = equal in both phases

$$d\Omega = -S\,dT - p\,dV - N\,d\mu$$

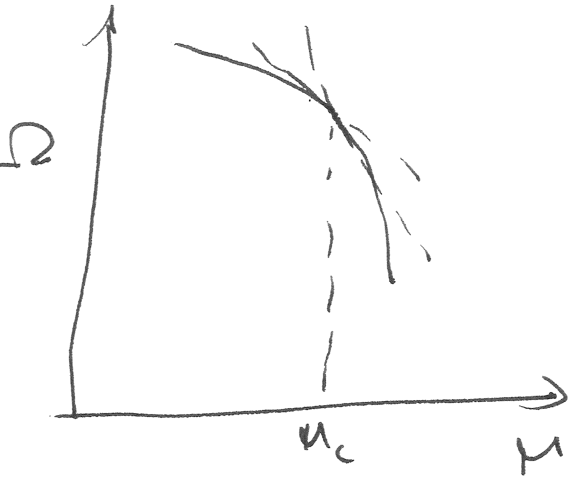
$\Rightarrow$ at fixed T, V $\Rightarrow$ $N = -\left.\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$

stability condition $\frac{\partial N}{\partial \mu} = -\left.\frac{\partial^2 \Omega}{\partial \mu^2}\right)_{T,V} > 0$

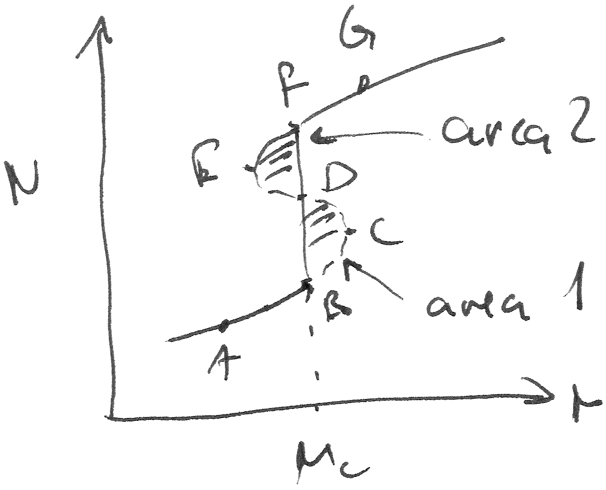
(Ω concave in μ)



$\Rightarrow$



equal area construction proceeds as before



area 1: $\int_D^C N d\mu - \int_B^C N d\mu$

area 2: $\int_E^F N d\mu - \int_E^D N d\mu$

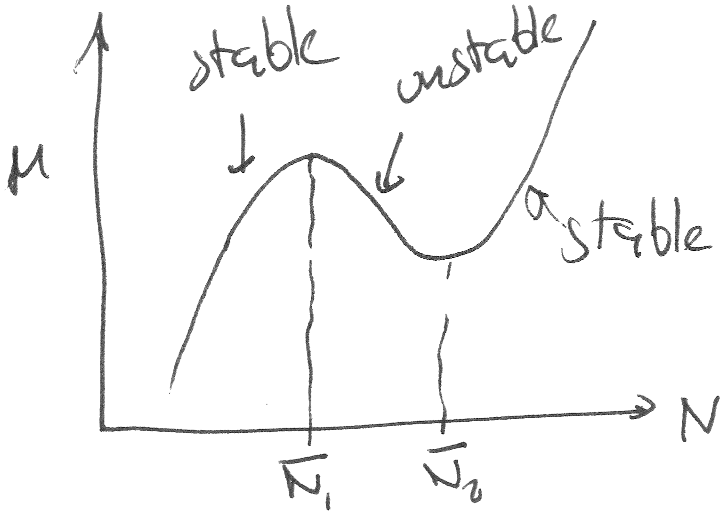
areas equal means Ω does not change across phase transition

$$\int_D^C N d\mu - \int_B^C N d\mu = \int_E^F N d\mu - \int_E^D N d\mu$$

$$-\int_B^D N d\mu - \int_D^F N d\mu = -\int_B^F N d\mu = 0$$

$$\boxed{\Omega_B = \Omega_F}$$

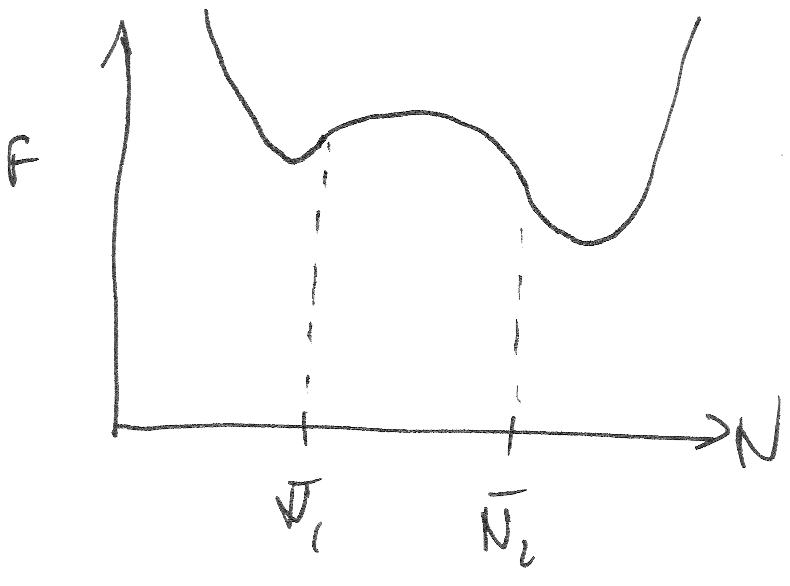
can also consider μ - N plot



$\bar{N}_1, \bar{N}_2$ - inflection points of Helmholtz free energy

$$dF = -SdT - pdV + \mu dN$$

$$\mu = \left.\frac{\partial F}{\partial N}\right)_{T,V} \qquad \left.\frac{\partial \mu}{\partial N}\right)_{T,V} = \left.\frac{\partial^2 F}{\partial N^2}\right)_{T,V}$$ (= 0 for inflection points)

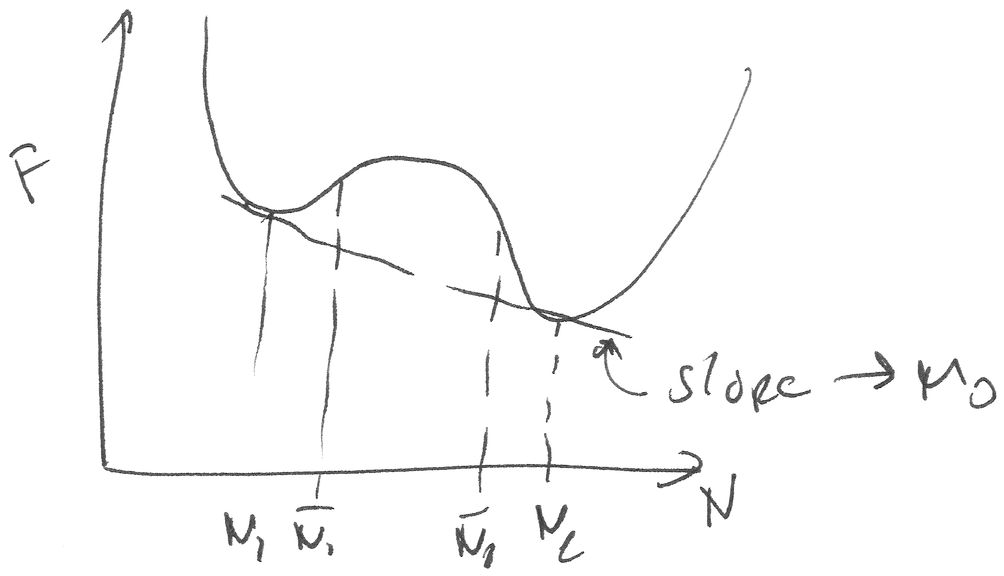


for stable regions F is convex in N

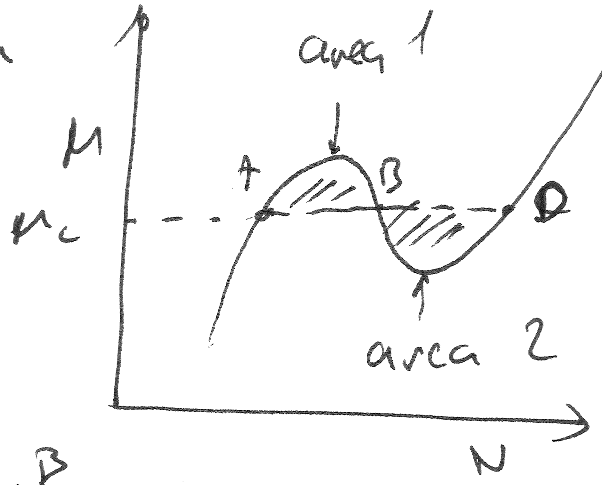
equilibrium N_1, N_2 are found by

$$\frac{\partial F}{\partial N_1} = \frac{\partial F}{\partial N_2} = \mu_0$$ (μ is common to both phases)

$$\Omega_1 = \Omega_2 \Rightarrow F_1 - \mu N_1 = F_2 - \mu N_2$$



equal area



area 1: $\int_A^B \mu \, dN - \mu_c (N_B - N_A) = \int_A^B (\mu - \mu_c) dN$

area 2: $\mu_c (N_D - N_B) - \int_B^D \mu \, dN = \int_B^D (\mu_c - \mu) dN$

$$\rightarrow \quad \int_A^D (\mu - \mu_c) dN = 0$$

since $\mu = \frac{\partial F}{\partial N}$ we have

$$F_D - \mu_c N_D - F_A + \mu_c N_A = 0$$

$$\Downarrow$$

$$\boxed{\Omega_D = \Omega_A}$$

- can also consider

$$F = Vf \cdot \qquad f = f(n) \qquad n = N/V$$

instead of F ⇒ obtain info about pressure

$$dF = -S\,dT - p\,dV + \mu\,dN \qquad\qquad \frac{\partial n}{\partial V} = -\frac{N}{V^2}$$

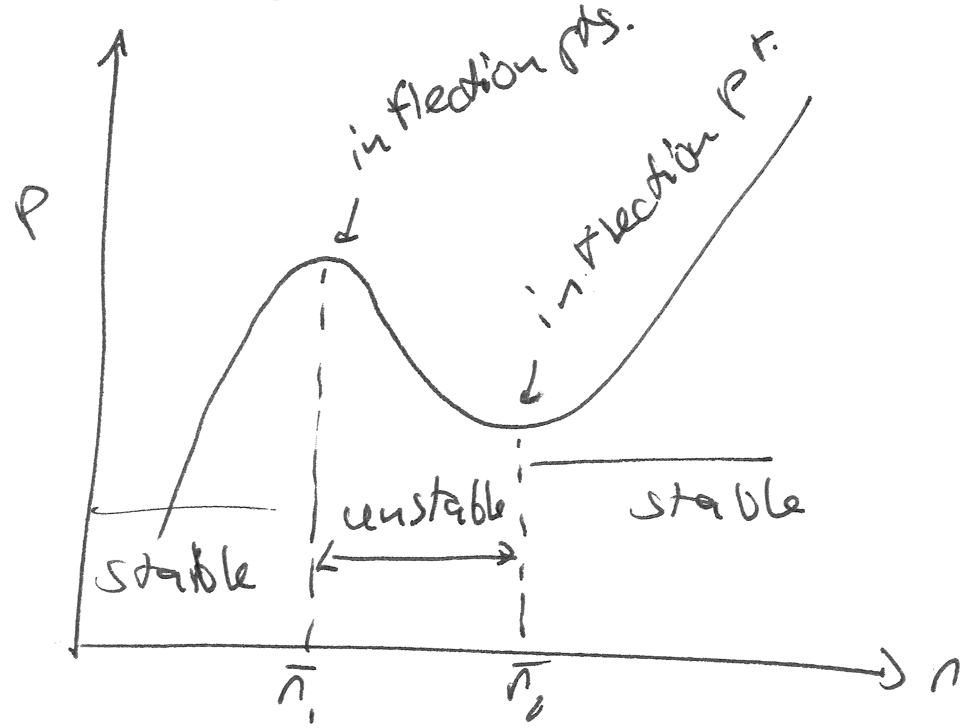
$$p = -\frac{\partial F}{\partial V}\Big)_{T,N} = -f - V\frac{\partial f}{\partial n}\frac{\partial n}{\partial V} = nf' - f$$

$$p = -nf' - f$$

stability ⇒ $-v\dfrac{\partial p}{\partial v}\Big)_T = n\dfrac{\partial p}{\partial n}\Big|_T = n^2 f'' > 0$

$$n^2 \frac{\partial \mu}{\partial n} > 0$$

$$\mu = \frac{\partial F}{\partial N}\Big)_{T,V} = V\frac{\partial f}{\partial n}\frac{\partial n}{\partial N} = f' \Rightarrow \frac{\partial \mu}{\partial n} = f'' > 0$$



For the first example (which uses the Gibbs free energy)

One can use $F = N f(v)$ $\quad v = \frac{V}{N}$

$$dF = -S\,dT - p\,dV + \mu\,dN$$

$$p = -\left.\frac{\partial F}{\partial V}\right)_{T,N} = -N \frac{\partial f(v)}{\partial v}\frac{\partial v}{\partial V} = -f'(v)$$

$$\mu = \left.\frac{\partial F}{\partial N}\right)_{T,V} = f(v) + N\frac{\partial f(v)}{\partial v}\frac{\partial v}{\partial N}$$

$$= f(v) - v f'$$

$$\frac{\partial \mu}{\partial v} = f' - f' - v f'' = -v f''$$

$$\frac{\partial p}{\partial v} = -f'' \Rightarrow \text{stability: } -\frac{1}{v}\frac{\partial v}{\partial p} = \chi_T > 0$$

$$\Rightarrow f'' > 0$$