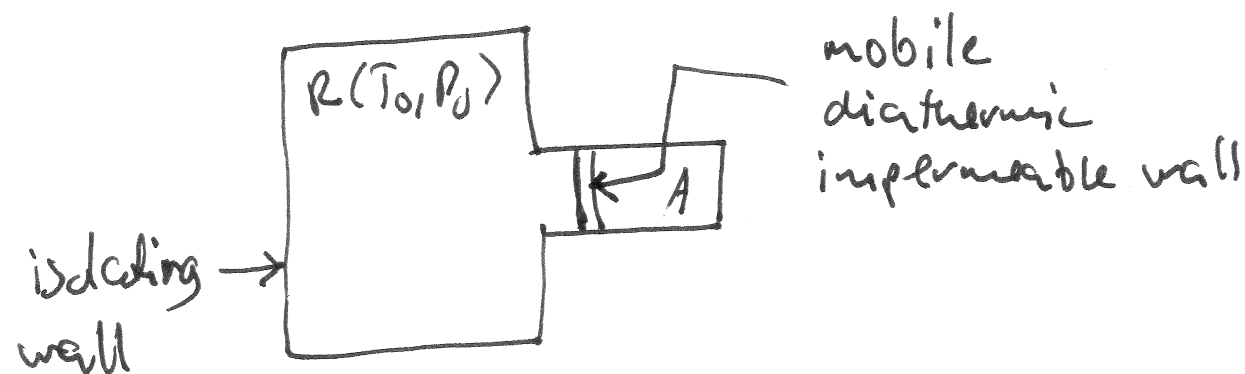


Equilibrium at constant pressure

①

- consider the following setup:



- R - (reservoir) - kept at constant temperature and pressure T_0, P_0

- for any spontaneous process

$$\Delta S_{TOT} = \Delta S + \Delta S_0 \geq 0$$

ΔS_0 - entropy change of reservoir (R)

ΔS - entropy change of system (A)

- if a quantity of heat Q_0 goes from R to A

$$\Delta S_0 = - \frac{Q_0}{T_0} \quad (\text{reservoir temperature does not vary appreciably since } R \gg A)$$

- if A does work on $R \Rightarrow w = -P_0 \Delta V_0$

$$w = P_0 \Delta V_0 = P_0 \Delta V \quad (\text{since } \Delta V_0 = -\Delta V)$$

$$Q_0 = \Delta E + P_0 \Delta V$$

$$\Delta S_{TOT} = \Delta S - \frac{\Delta E}{T_0} - \frac{P_0 \Delta V}{T_0} \geq 0 \Rightarrow T_0 \Delta S - \Delta E - P_0 \Delta V \geq 0$$

$$\Rightarrow \Delta E - T_0 \Delta S + P_0 \Delta V \leq 0 \quad (2)$$

$$\Delta G \leq 0 \rightarrow \boxed{G = E - T_0 S + P_0 V}$$

Gibbs free energy is minimized under these circumstances (T_0, P_0 fixed)

$$\boxed{\Delta G \leq 0}$$

if $\Delta V = 0 \Rightarrow \Delta E - T_0 \Delta S \leq 0$

$$\boxed{F = E - T_0 S}$$

Helmholtz free energy is minimized if T_0, V fixed

$$\boxed{\Delta F \leq 0}$$

F_0 - maximum work that can be supplied by system

$$\Delta S_0 \geq -\Delta S \quad \text{work received by A}$$

$$\Delta E = Q_0 + W$$

$$W = \Delta E - Q_0 \quad \Delta S_0 = -\frac{Q_0}{T_0}$$

~~$$W = \Delta E$$~~

$$\Delta S_0 = \frac{W - \Delta E}{T_0}$$

$$W - \Delta E \geq -T_0 \Delta S$$

$$\boxed{W \leq -\Delta F}$$

Equilibrium and Stability at constant μ (9)

- for phase transitions often more convenient to use another setup: T_0, μ_0 fixed



- particle exchange can take place (from one phase to the other)
- volumes stay constant

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_0 \geq 0$$

reservoir: $\Delta S_0 = \frac{Q_0}{T_0}$

$$Q_0 = T_0 \Delta S_0$$

~~system: $\Delta E = Q + W = \Delta E = Q_0$~~

$$\Delta E_0 = Q_0 + \mu_0 \Delta N_0$$

$$Q_0 = \Delta E_0 - \mu_0 \Delta N_0$$

$$Q_0 = -\Delta E + \mu_0 \Delta N$$

$$T_0 \Delta S - \Delta E + \mu_0 \Delta N \geq 0$$

$$\Delta E - T_0 \Delta S - \mu_0 \Delta N \leq 0$$

can define: $\Omega = E - T_0 S - \mu_0 N$ (grand potential)

$$\text{if } T_0, \mu_0 \text{ held fixed} \Rightarrow \boxed{\Delta \Omega \leq 0}$$

(4)

Ω is minimized at equilibrium

$$d\Omega = dE - TdS - SdT - \mu dN - Nd\mu$$

$$\boxed{d\Omega = -SdT - PdV - Nd\mu}$$

since $\Omega = E - TS - \mu N$

$$\boxed{\Omega = -PV}$$

also $\Omega = F - \mu N$

consider phase equilibria in more detail

1st order phase transitions

$$dG = -SdT + VdP$$

$$\Rightarrow S = - \left. \frac{\partial G}{\partial T} \right|_P \quad V = \left. \frac{\partial G}{\partial P} \right|_T$$

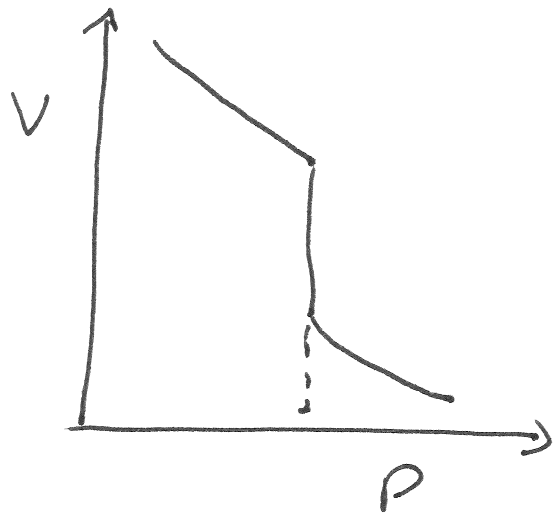
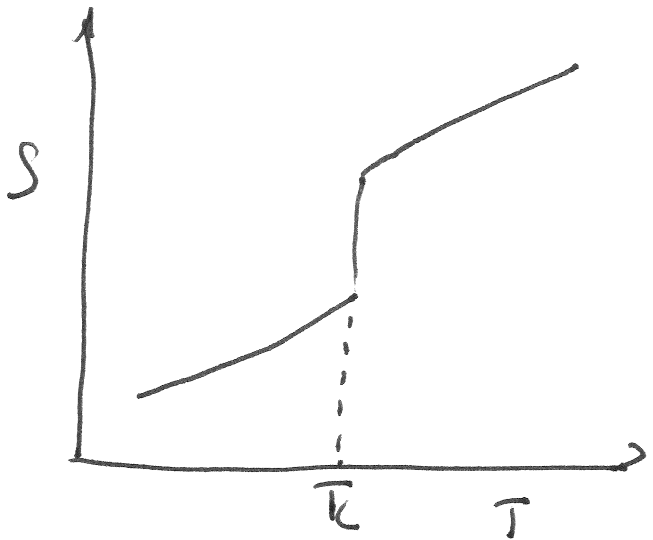
stability condition: remember that G is concave in P and T

$$\Rightarrow \left. \frac{\partial^2 G}{\partial T^2} \right|_P < 0 \Rightarrow - \left. \frac{\partial S}{\partial T} \right|_P < 0$$

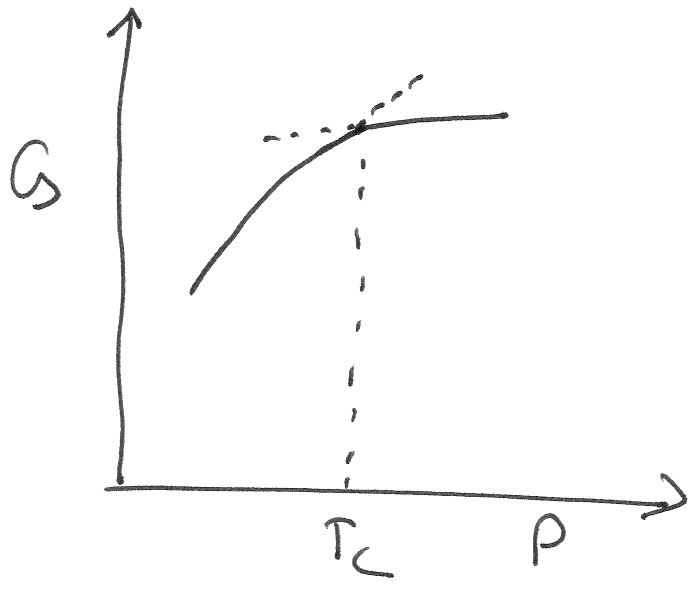
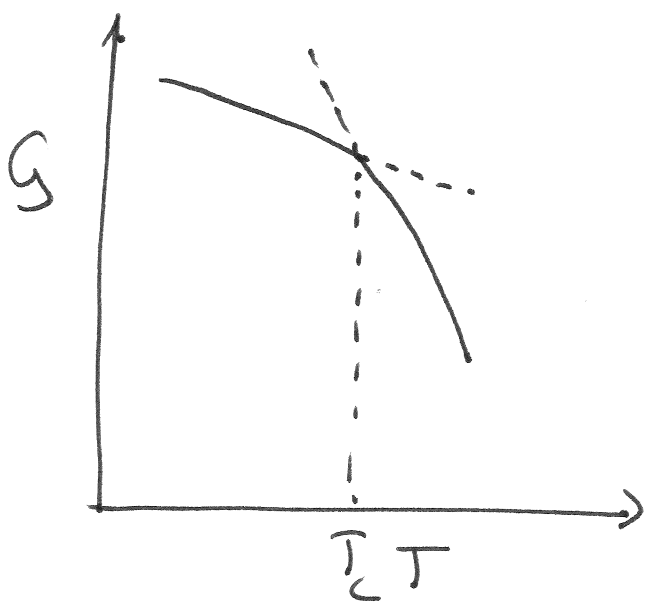
$$\left. \frac{\partial^2 G}{\partial P^2} \right|_T < 0 \Rightarrow \left. \frac{\partial V}{\partial P} \right|_T < 0$$

5

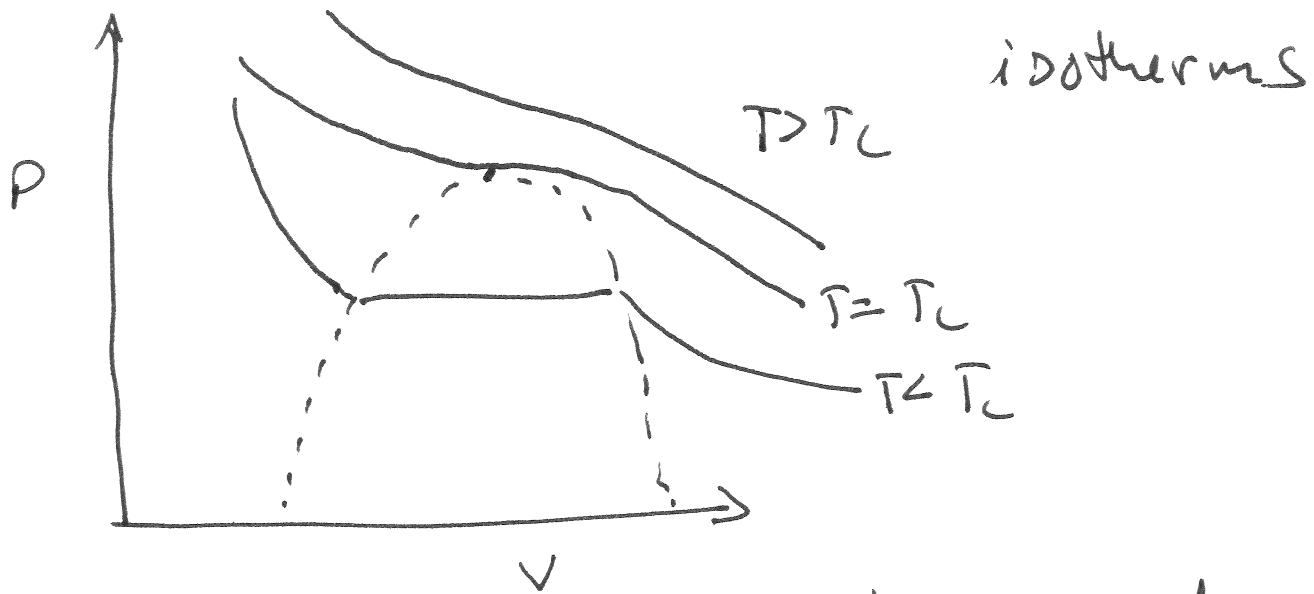
for a 1st order phase transition a discontinuity occurs in S and V at the transition itself (latent heat, volume change)



at T_c the derivatives of G must be discontinuous



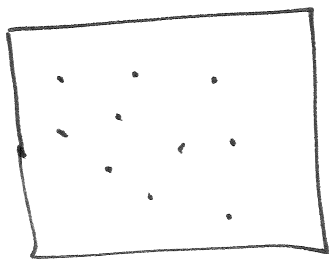
P-V curves for liquid-gas transition (6)



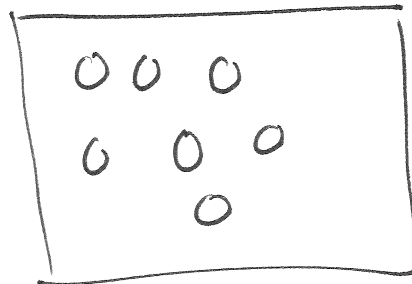
an attempt to reproduce isotherms is the van der Waals equation of state

$$P = \frac{nRT}{v-b} - \frac{a}{v^2} \Rightarrow \begin{matrix} n - \text{density} \\ v - \text{specific volume} \end{matrix}$$

$b \rightarrow$ volume excluded by extent of particles



point particles

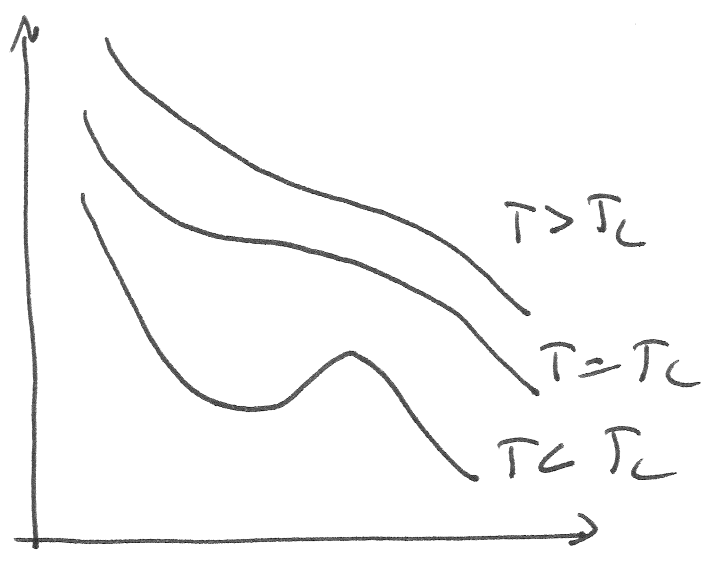


finite particles

\Rightarrow volume b for each particle

$a \rightarrow$ accounts for pair interactions between atoms which reduce the pressure
(at midrange \Rightarrow attractive)

one can plot this equation of state for different temperatures

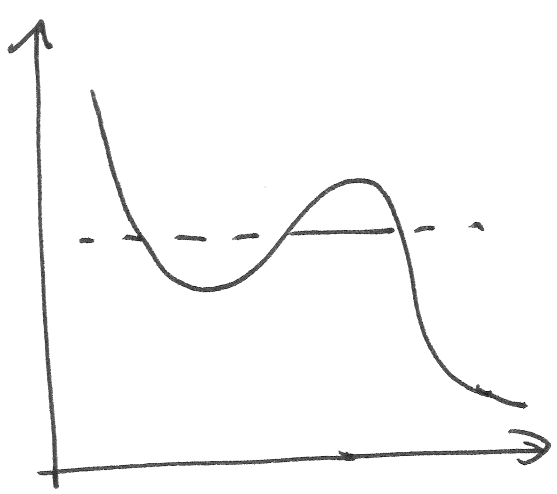


* T_c can be determined by $\frac{\partial P}{\partial V} = 0$ $\frac{\partial^2 P}{\partial V^2} = 0$
 (also $P_{\text{cand}} V_c$)

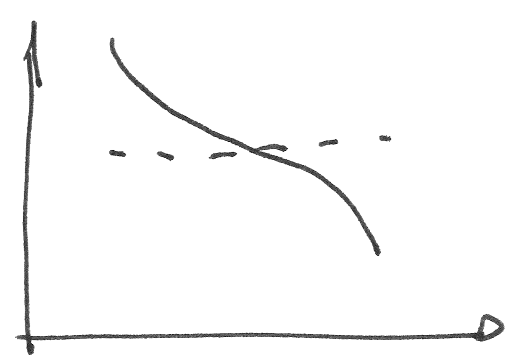
* vdW equation of state can be rearranged to $A v^3 + B v^2 + C v + D = 0$

!!
 equation can have 3 roots maximum

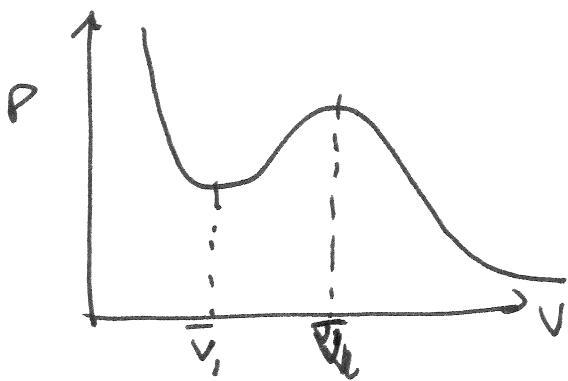
or $T < T_c \Rightarrow 3$ roots



as $T \rightarrow T_c$ roots coalesce into 1



* question: if we have 3 roots \Rightarrow there is an unstable region \Rightarrow what is the common pressure P ? (8)



between \bar{v}_1 and \bar{v}_2
 $\partial P / \partial V > 0 \Rightarrow$ unstable region

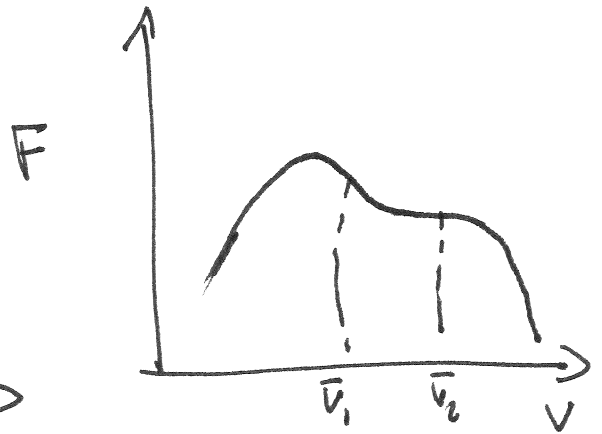
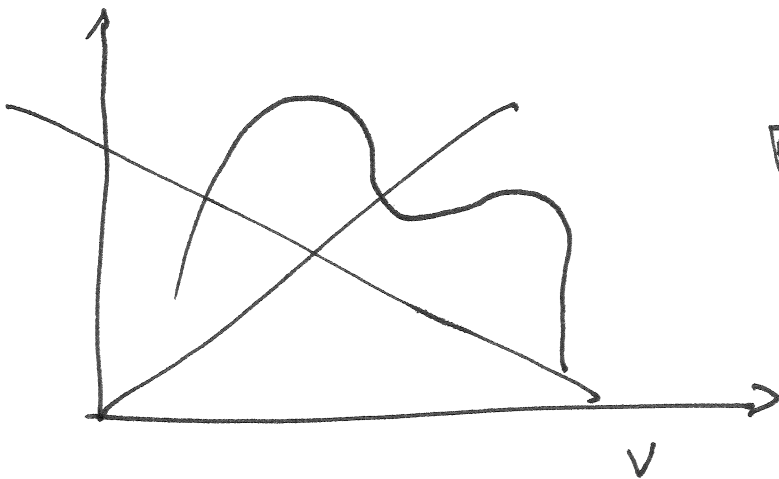
* interesting to consider what Helmholtz free energy looks like \Rightarrow

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

\bar{v}_1 and \bar{v}_2 are inflection points of

Helmholtz free energy

\Rightarrow
$$\left(\frac{\partial^2 F}{\partial V^2} \right)_{\bar{v}_1} = 0 \quad \left(\frac{\partial^2 F}{\partial V^2} \right)_{\bar{v}_2} = 0$$



$G = F + PV$

$G_e = G_g$ at equilibrium

$\Rightarrow G_e = F_e + PV_e = F_g + PV_g$

$\Rightarrow \frac{F_e - F_g}{V_g - V_e} = P$