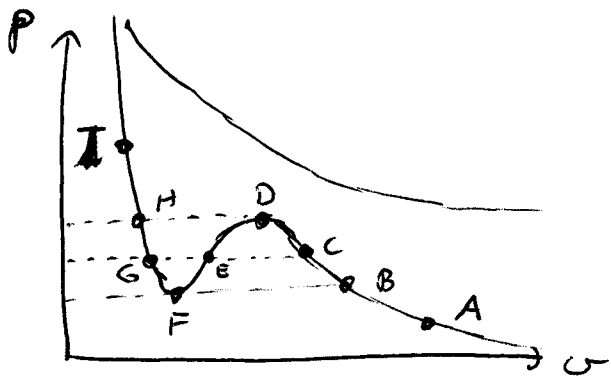


July 4

Van der Waals equation

$$(P + \frac{an^2}{V^2})(V - nb) = nRT$$

$$\rightarrow v^3 - (b + \frac{RT}{P})v^2 + \frac{a}{P}v - \frac{ab}{P} = 0$$



T high: ideal gas $RT = Pv$

T low: can have up to three solutions for v at given (P, T)

between D and F $(\frac{\partial P}{\partial v})_T > 0 \Rightarrow K_T < 0$

contradicts stability criterion!

→ the van der Waals isotherms are unphysical!

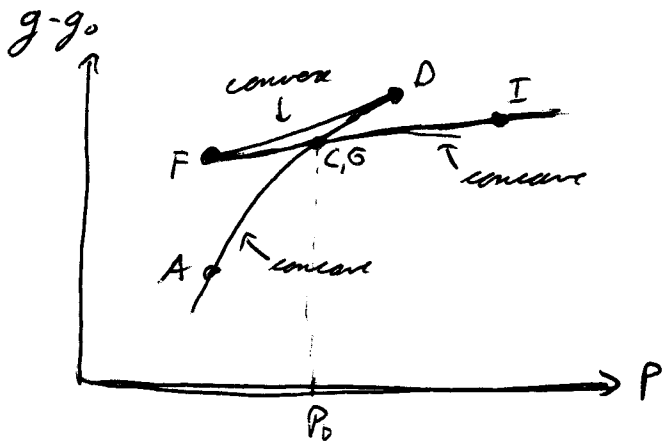
How to fix it?

Look at Gibbs free energy:

$$dg = -sdt + v dP$$

along isotherm $dT = 0$

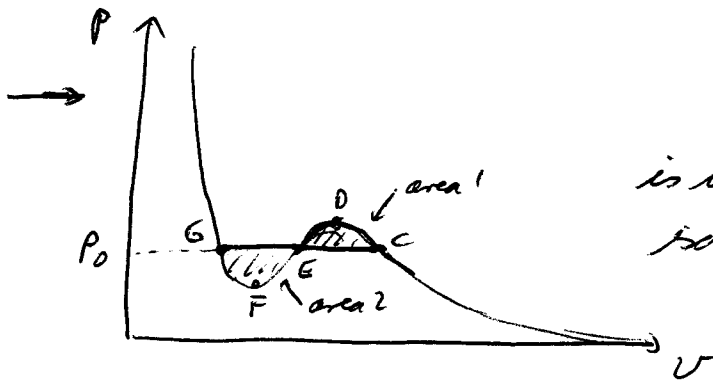
$$\Rightarrow g = g_0 + \int_{P_0}^P v(P) dP$$



Gibbs free energy must be minimal in equilibrium for each $P \Rightarrow$

$$g \text{ follows } \begin{cases} A-D & P < P_0 \\ F-I & P > P_0 \end{cases}$$

In order for g to be constant between points C and G, P must be constant



is the physically correct isotherm

what is P_0 ?

g has the same value at point C and point G

$$\rightarrow 0 = \int_{P_C}^{P_G} v(P) dP = \int_{P_C}^{P_0} v(P) dP + \int_{P_0}^{P_E} v(P) dP + \int_{P_E}^{P_F} v(P) dP + \int_{P_F}^{P_G} v(P) dP$$

$$\rightarrow \int_{P_C}^{P_0} v(P) dP - \int_{P_E}^{P_0} v(P) dP = \int_{P_F}^{P_E} v(P) dP - \int_{P_F}^{P_G} v(P) dP$$

$$\rightarrow \text{area 1} = \text{area 2}$$

The physical isotherm is obtained from the van der Waals isotherm by inserting a line of constant pressure such that two areas between the van der Waals isotherm and the constant pressure line are equal.

"Maxwell construction"

What happens along the constant pressure line?

There is the coexistence of two phases at the same pressure, a liquid (low volume) and a gas (high volume) phase.

volume of the ^{liquid} phase at P_0 : $V_l = V_0$

volume of the gas phase at P_0 : $V_g = V_0$

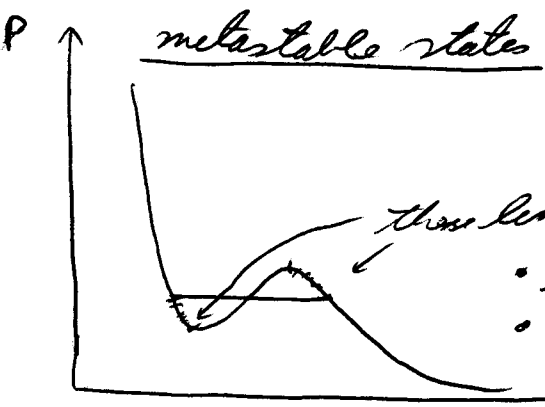
volume of a mixture with mole fraction x_l and x_g

$$V_{\text{mix}}(x_l + x_g) = V_{\text{mix}} = x_l V_l + x_g V_g$$

$$\Rightarrow \frac{x_l}{x_g} = \frac{V_g - V_{\text{mix}}}{V_{\text{mix}} - V_l}$$

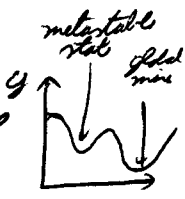
skipped

"Levee rule"



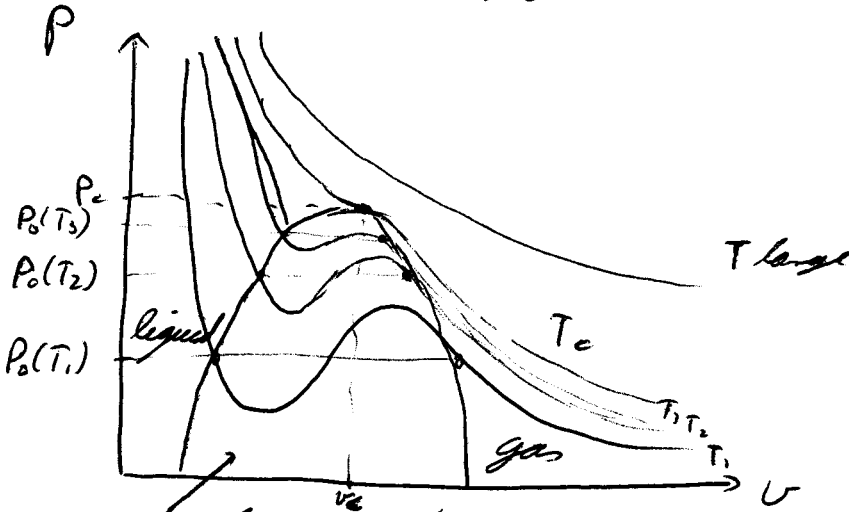
these lines are "metastable states"

- they are stable $(\frac{\partial P}{\partial V}) < 0$
- they are not the global minimum of the Gibbs free energy
- they can be prepared for very clean samples



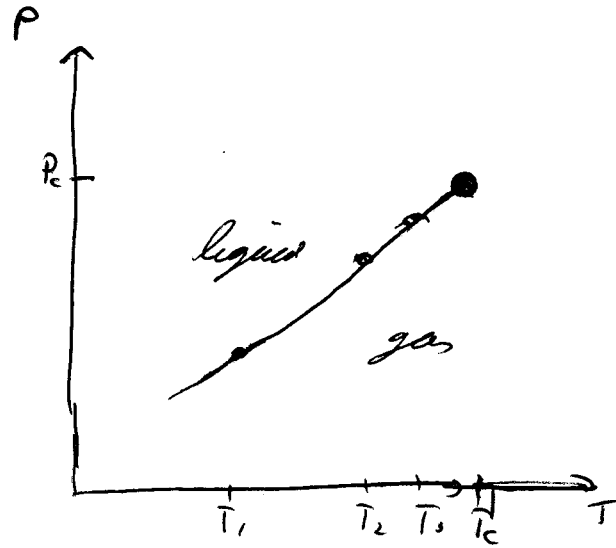
What happens as we vary T?

each T $\xrightarrow{\text{Maxwell construction}}$ $P_0(T)$



coexistence region

\rightarrow phase transition line



for some temperatures the isotherm does not have a coexistence region any more
 \rightarrow critical temperature T_c

at T_c the minimum and the maximum of the isotherm coalesce

$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\rightarrow -\frac{RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0$$

$$\frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4} = 0$$

$$\frac{4aV_c}{V_c^3(V_c-b)} = \frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4} \Rightarrow 4aV_c = 6a(V_c-b) \Rightarrow 2V_c = 6b \Rightarrow V_c = 3b$$

$$T_c = (v_c - b)^2 \frac{2a}{v_c^3 R} = \frac{8al^2}{27l^3 R} = \frac{8a}{27lR}$$

$$P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} = \frac{8a}{27l \cdot 2l} - \frac{a}{9l^2} = \frac{a}{27l^2}$$

$$\boxed{v_c = 3l \quad T_c = \frac{8a}{27lR} \quad P_c = \frac{a}{27l^2}}$$

Introduce reduced variables $\bar{P} = \frac{P}{P_c}$, $\bar{T} = \frac{T}{T_c}$, $\bar{v} = \frac{v}{v_c}$

$$\left(\bar{P} + \frac{a \cancel{27} l^2}{v^2 a} \right) \left(\bar{v} - \frac{l}{3l} \right) = R \frac{T \cancel{27} l^2}{3l \cdot a} = \frac{8}{3} \bar{T}$$

$$\rightarrow \left(\bar{P} + \frac{3}{\bar{v}^2} \right) (3\bar{v} - 1) = 8 \bar{T}$$

no a, b any more

→ All gases obey the same equation if they are the same distance from their respective critical points.

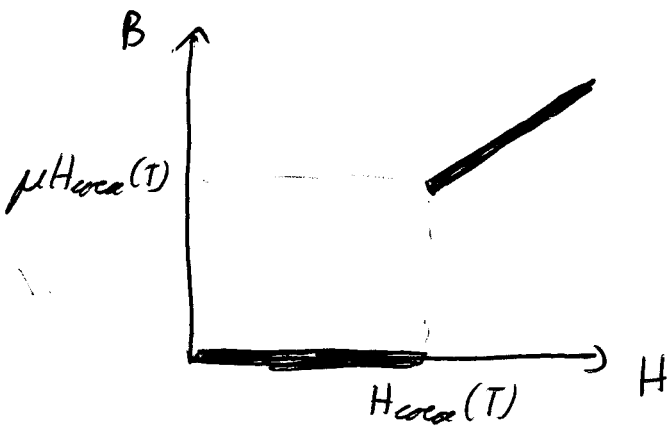
"law of corresponding states"

II.4.2 Superconductors

At low temperatures substances can become perfect diamagnets, i.e. $\mu = 0$. In this "superconducting" state current flows without dissipation.

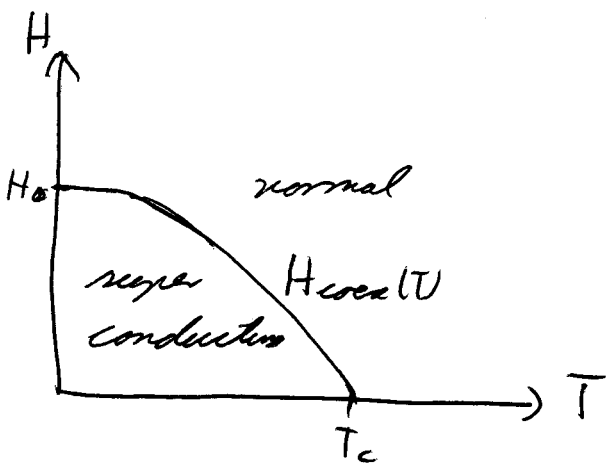
Superconductivity is a quantum mechanical effect.

Phase diagram



$$B = \begin{cases} 0 & \text{if } H < H_{cox}(T) \\ \mu H & \text{if } H > H_{cox}(T) \end{cases}$$

f. ΔU [B = μ(H + M)]



empirical $H_{cox}(T) \approx H_0 \left(1 - \frac{T^2}{T_c^2}\right)$

f. law of corresponding states

↓ 1/4

along coexistence line

$$dg_s = dg_n \Rightarrow -S_n dT - B_n dH = -S_s dT - B_s dH$$

$$\begin{aligned} \Rightarrow S_n - S_s &= (B_s - B_n) \left(\frac{dH}{dT}\right)_{cox} \\ &= -\mu_0 H_{cox}(T) \left(\frac{dH}{dT}\right)_{cox} \end{aligned}$$

Clairaut-Clausius equation for superconductors

- first-order transition for $T < T_c$
- continuous transition for $T > T_c$

shipped