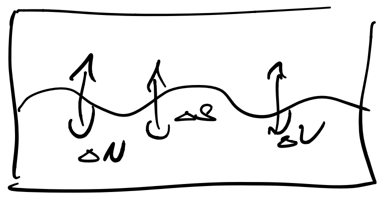


$\Delta U > 0$

$$\rightarrow \left.\frac{\partial^2 U}{\partial X^2}\right|_{Y,Z} > 0$$

$X = \{S, N, V\}$

gen. force

$$\left.\frac{\partial T}{\partial S}\right|_{N,V} > 0 \; ; \; -\left.\frac{\partial p}{\partial V}\right|_{S,N} > 0 \; ; \; \left.\frac{\partial \mu}{\partial N}\right|_{S,V} > 0$$

gen displ.

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V > 0 \; ; \; \kappa_S = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_{S,N} > 0$$

Same for F, G, H:

Show $G(T, p, N)$

$\Rightarrow \Delta G > 0$ MINIMUM WRT EXTENSIVE STATE VARIABLES NOT FIXED BY EXTERNAL CONSTRAINTS.

$$\rightarrow \left.\frac{\partial^2 G}{\partial N^2}\right|_{p,T} > 0 \quad \rightarrow \left.\frac{\partial \mu}{\partial N}\right|_{pT} > 0$$

$$\frac{\partial^2 G}{\partial T^2}\Big|_{p,N} = -\frac{\partial S}{\partial T}\Big|_{p,N} = -\frac{C_p}{T} < 0$$

BECAUSE
$C_p > 0$

$$F(T, V, N) \Rightarrow \kappa_T > 0 \;;\; \frac{\partial \mu}{\partial N}\Big|_{T,V} > 0$$

$$H(S, p, N) \Rightarrow C_p > 0 \;;\; \frac{\partial \mu}{\partial N}\Big|_{S,p} > 0$$

$$\frac{T}{V\kappa_S C_V} > \frac{\alpha^2 T^2}{C_V^2 \kappa_T}$$

$$C_V > \frac{\kappa_S}{\kappa_T}\alpha^2 T V$$

$$C_p - C_V = \frac{\alpha^2 T V}{\kappa_T} \rightarrow C_V > \frac{\kappa_S}{\kappa_T}(C_p - C_V)$$

$$C_p - C_V > 0 \quad (+) \; C_V > 0$$

$$\rightarrow C_p > C_V > 0$$

$$\kappa_T - \kappa_S = \frac{VT\alpha^2}{C_p} > 0$$

$$\kappa_T > \kappa_S > 0$$

SUMMARY: $\left.\frac{\partial y}{\partial X}\right|_{\substack{\text{not } y \\ \text{not } x}} > 0$

WHERE (y, X) ARE CONJUGATE GENERALIZED FORCE/DISPACEMENT PAIR.

$$\rightarrow \frac{\partial X}{\partial y} = \frac{1}{\frac{\partial y}{\partial X}} > 0$$

1. 4.

---

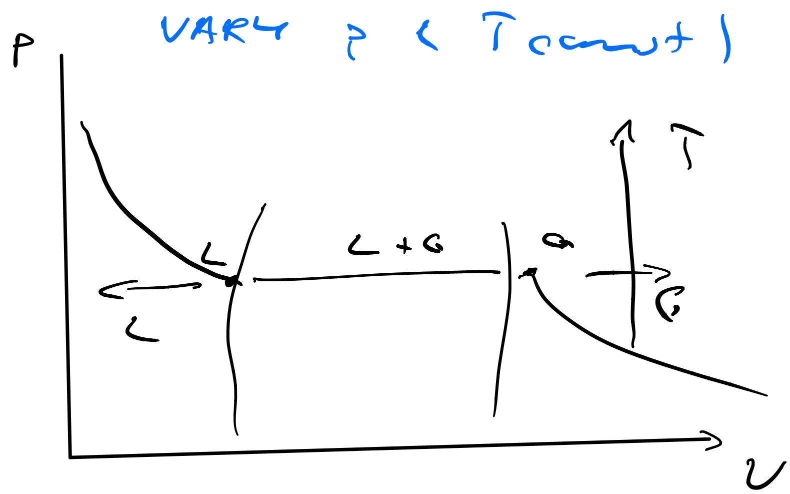
5. Maxwell $\Rightarrow$ 2 p. deriv

$\rightarrow$ connect in Triple product rule

$$\underbrace{(\ \ )(\ \ )}_{\substack{\text{given by} \\ \text{claims} \\ >0}}\underbrace{(\ \ )}_{\text{stability } >0} = -1$$

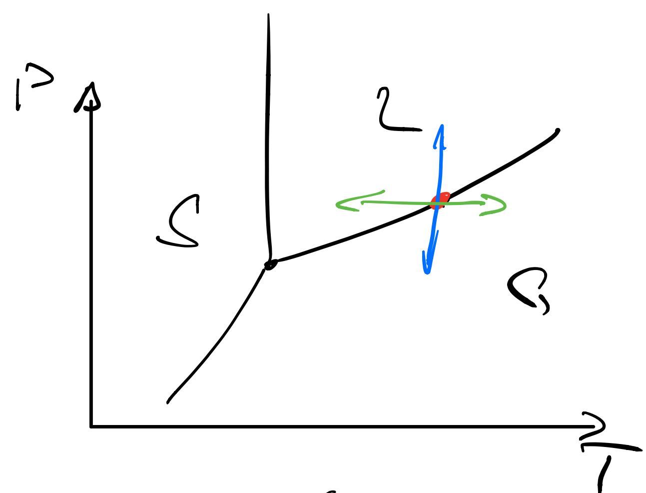
5. false.

$$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_{p} \gtrless 0$$

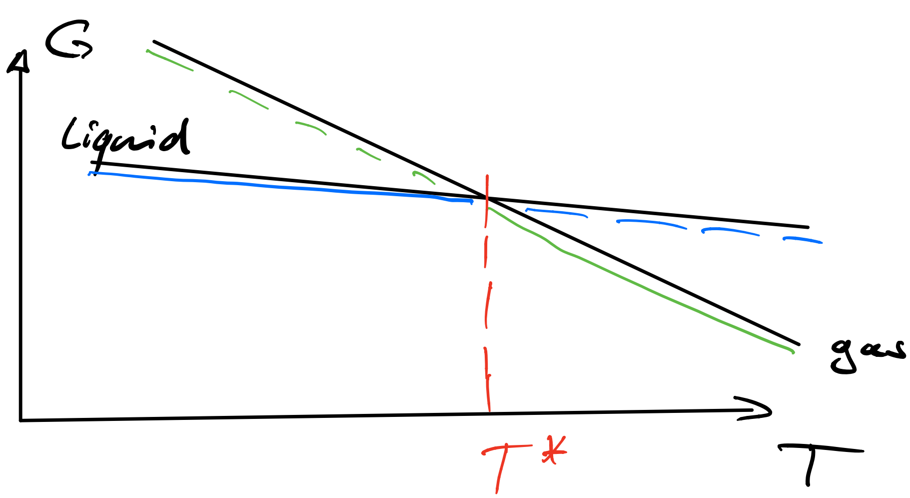


CONSIDER VARYING T HOLDING

p, N CONSTANT



p, T, N → G(T, p, N)



$$-\frac{\partial G}{\partial T} = S \longrightarrow S_{gas} > S_{liquid}$$

$N = \text{const}$, system is extensive

$$G = \mu N \rightarrow G_L = G_g$$

$$\rightarrow \mu_L = \mu_g$$

CALCULATE CHANGE IN ENTROPY

$$\Delta S = \int \frac{đQ}{T} \underset{T = T^* = \text{const}}{=} \frac{1}{T^*} \int đQ = \frac{Q}{T^*} = \frac{L \cdot N}{T^*}$$

L: Latent heat per particle.

$$L = \frac{\Delta S \cdot T^*}{N}$$

MODEL OF A PHASE TRANSITION

IDEAL GAS $pV = NkT$

no phase transition

good approximation to DILUTE REAL GASES

REAL GASES: STARTING FROM IDEAL GAS AND ADD CORRECTIONS IN POWERS OF DENSITY $n = \frac{N}{V}$:

$$p = kT\left(\frac{N}{V}\right)$$
$$= kT\frac{N}{V}\left(1 + B_2(T)\frac{N}{V} + B_3(T)\left(\frac{N}{V}\right)^2 + \dots\right)$$

known as VIRIAL expansion.

$B_n(T)$: VIRIAL COEFFCIENTS.

→ SIMPLE APPROXIMATION FOR A REAL GAS

$$pV = NkT$$

1) $V \to V - V_{excl.}$

↳ from finite size of molecules

$$V_{excl} \propto N \cdot b$$

2) ATTRACTIVE INTERACTION BETWEEN PARTICLES

potential energy per particle DUE TO THE ATTRATION

$$u_{attr} \propto \frac{N}{V}$$ — more nearby molecules

$$U_{att} \propto N u_{attr}$$
$$= -aN \cdot \frac{N}{V} = -a\frac{N^2}{V}$$
$a > 0$

$$p_{attr} = -\frac{\partial U}{\partial V}\bigg|_{N,S} = -\left(-a\frac{N^2}{V}\right)\left(-\frac{1}{V}\right)$$

$$= -a\frac{N^2}{V^2}$$

$$p = \frac{NkT}{V-Nb} + p_{attr}$$

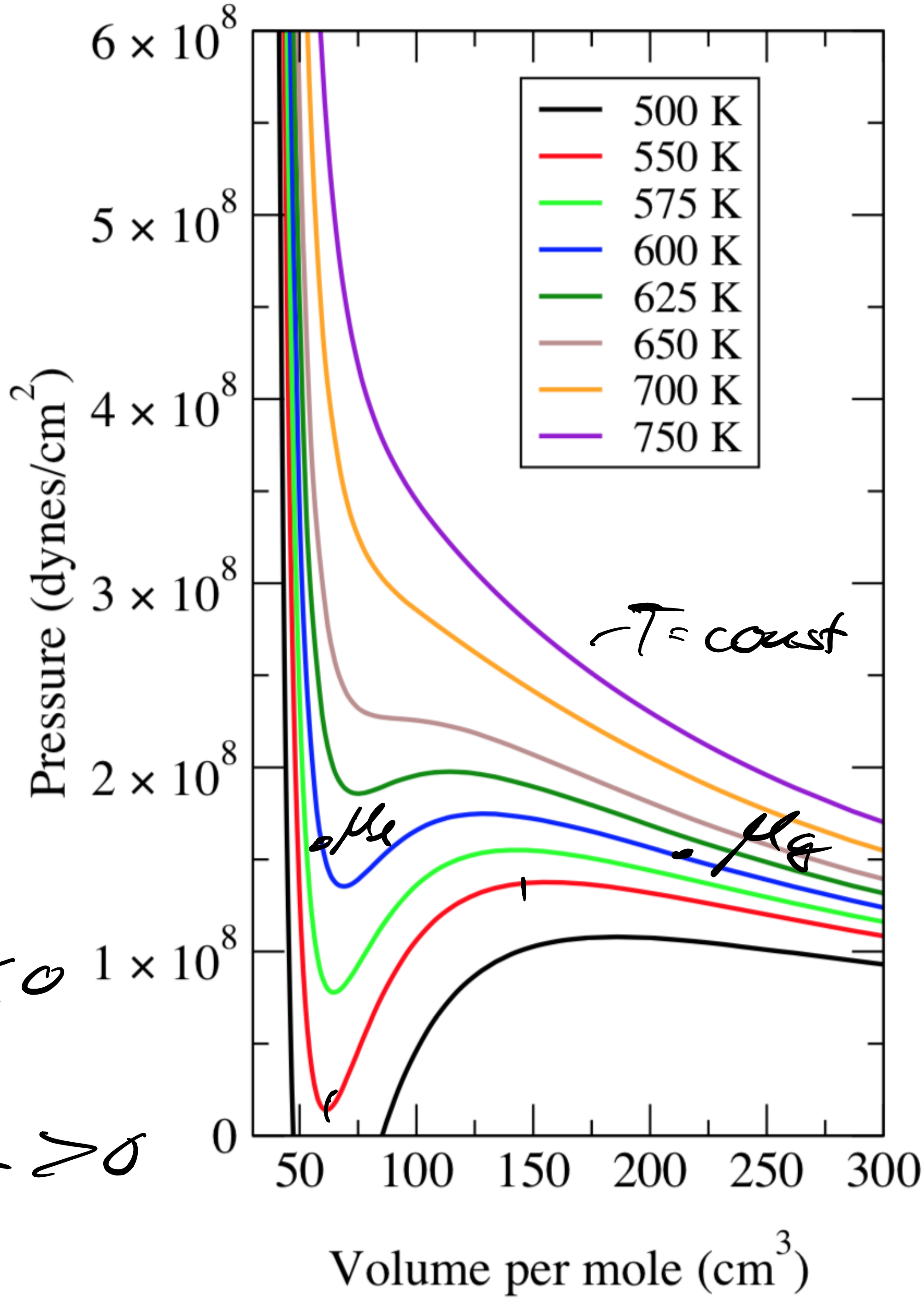
$$\Rightarrow \boxed{\left(p + \frac{aN^2}{V^2}\right)(V-Nb) = NkT}$$

van der Waals EOS

Quiz 5, due 5pm, Tuesday 4/21

1. Intro to van der Waaals EOS

Do problems 11.1 and 11.2 a) (not b) in EOPC.



$$\frac{\partial P}{\partial V} < 0$$

$$\rightarrow \kappa_T > 0$$

MAXWELL CONSTRUCTION

$$\mu_l(V_l) = \mu_g(V_g) \qquad | \cdot N$$

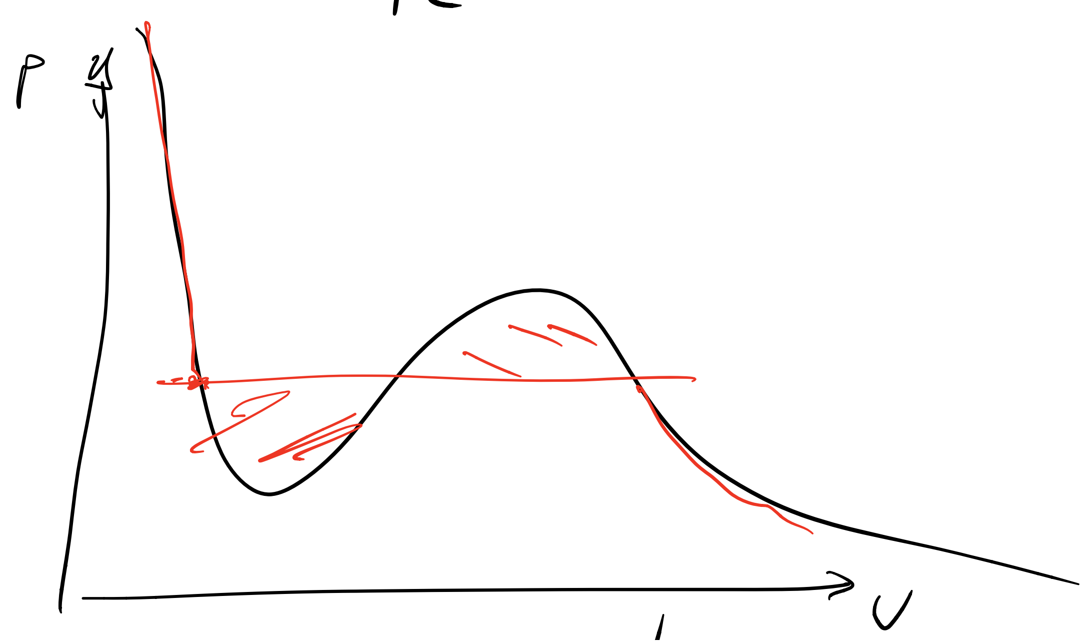
$$G_l(V_l) = G_g(V_g)$$

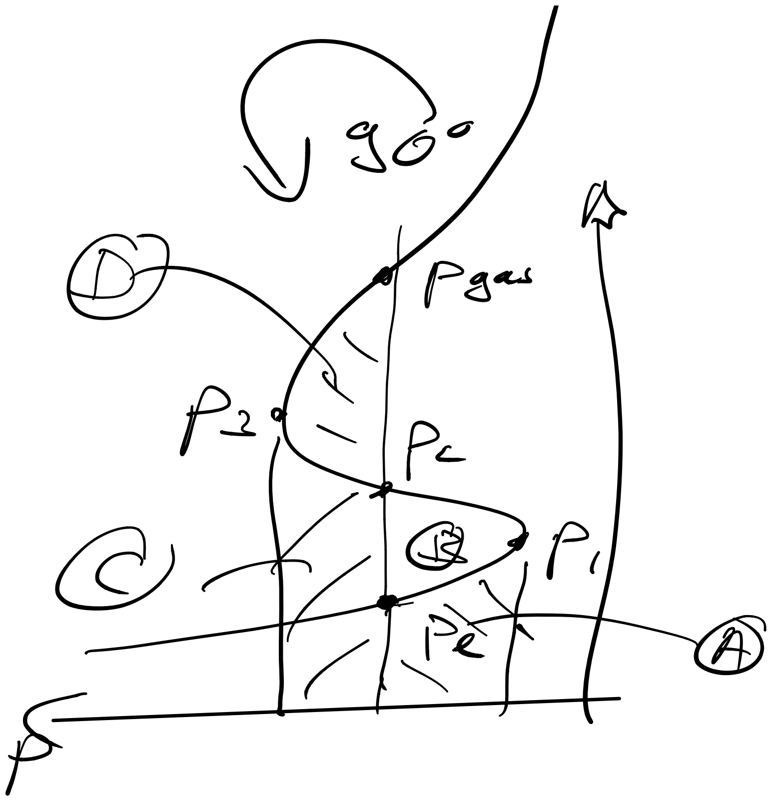
$$dG = -S\,dT + V\,dp + \mu\,dN$$

$T = \text{const}$, $N = \text{const}$

$$dG = +V\,dp$$

$$\Delta G = \int_{G_l}^{G_l} dG = \int_{p_l}^{p_g} V\,dp$$





$$\int_{p_e}^{p_g} V\,dp = \int_{p_e}^{p_1} V\,dp + \int_{p_1}^{p_2} V\,dp + \int_{p_2}^{p_3} V\,dp + \int_{p_3}^{p_g} V\,dp$$

$$-\cancel{A} \qquad +\cancel{A}+B \qquad \cancel{C} \qquad -\cancel{C} \qquad -D$$

$$|\text{Area } B| \doteq |\text{Area } D|$$

$\equiv$ Maxwell construction