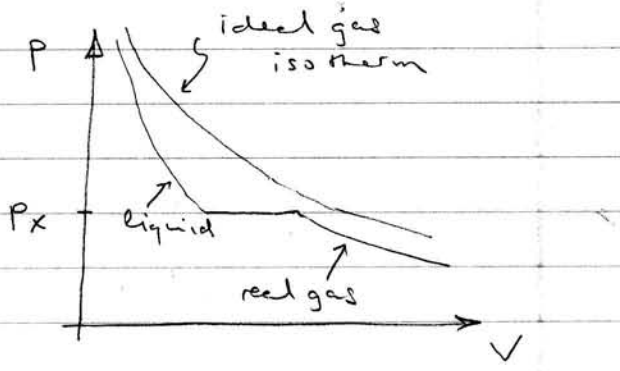
Lecture 21 Van der Waals Model

Last time we discussed phase transitions, especially gas → liquid transition.

Ideal gas law does not capture enough to describe gas → liquid transition.

Eq'n of state: $pV = Nk_BT$

At const. T, as $p \uparrow$ $V \downarrow$ uniformly

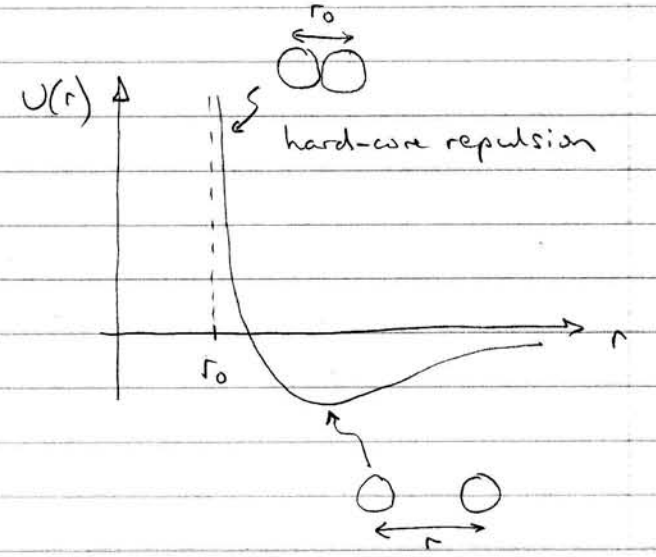


In a real gas, V suddenly drops at some p_x
gas transforms into liquid

To capture this, need to include interactions between gas molecules. Interactions need to be attractive to cause V to drop at gas → liquid transition

The interaction energy between 2 molecules will have the following form

- $U \to 0$ as $r \to \infty$
- $U < 0$ as $r \downarrow$
- $U \to \infty$ as $r \to r_0$



Details unimportant for our level of description

The total energy for a box of N molecules is

$$E_{tot} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} U(|\bar{r}_i - \bar{r}_j|)$$

Kinetic energy

Interaction energy

$\frac{1}{2}$ there to avoid double counting

(Ex: $U(|\bar{r}_1 - \bar{r}_2|) + U(\bar{r}_2 - \bar{r}_1) + \cdots$)

There are $\frac{N(N-1)}{2}$ terms

For ideal gas $U = 0$ and particles are independent and calculating Z is easy.

Here it is very hard because interaction term involves sum over all pairs of molecules (and all their relative positions $r = |\bar{r}_i - \bar{r}_j|$)

To simplify calculation we use Mean Field Method

Here's the idea: instead of calculating interaction between ith molecule and every other molecule $j \neq i$, consider the average interaction energy due to the $j \neq i$ molecules

$$E_i = \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} U(|\bar{r}_i - \bar{r}_j|) \approx \frac{p_i^2}{2m} + \underbrace{\left\langle \frac{1}{2} \sum_{j \neq i} U(|\bar{r}_i - \bar{r}_j|) \right\rangle}_{U_{eff}}$$

So ith molecule sits in an effective potential due to the other molecules collectively

$$U_{eff} = \frac{1}{2} N-1 \langle \varphi(r) \rangle \simeq \frac{N}{2} \int_{r_0}^{\infty} d^3r \frac{\varphi(r)}{V} \equiv -\frac{Na}{V}$$

$N-1$: # of pairs

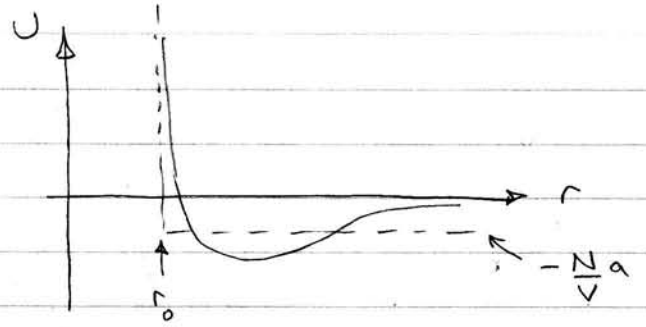
$\langle \varphi(r) \rangle$: interaction potential between pairs

r_0: hard core

Assume $N >>> 1$

$-2a \equiv \int_{r_0}^{\infty} d^3r\ \varphi(r)$ $\quad a>0$. The integral is <0 due to attractive potential $\varphi(r)$

Essentially, we replaced potential with dotted line



$$E_{tot} = \sum_i E_i \cong \sum_i \frac{p_i^2}{2m} - \frac{N^2}{V}a$$

The next thing is to also account for excluded volume due to hard-core model of molecules, so $V \to V - Nb$ where b is volume corresponding to hard-core radius r_0

Now put this into Helmholtz free energy:

$$F_{ideal} = -Nk_BT\left[\ln\left(\frac{n_Q}{n}\right) + 1\right] = -Nk_BT\left[\ln\left(\frac{n_Q V}{N}\right) + 1\right]$$

replace $V \to V - Nb$, $U \to U - \frac{N^2}{V}a$

$$F_{vdw} = -Nk_BT\left[\ln\left(\frac{n_Q(V-Nb)}{N}\right) + 1\right] - \frac{N^2 a}{V}$$

Pressure is given by

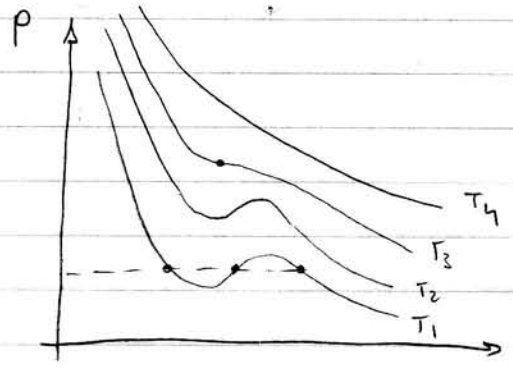
$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V-Nb} - \frac{N^2 a}{V^2}$$

$$\therefore \boxed{\left(p + \frac{N^2 a}{V^2}\right)\left(V - Nb\right) = Nk_BT}$$ Van der Waals model

Reduces to ideal gas $pV = Nk_BT$ when $a = b = 0$

Typical values $b \sim (4\text{Å})^3$, $a \sim 2.5\,\text{eV}\,\text{Å}^3$ but it varies $a(H_2O) \gg a(He)$

What does van der Waals eq'n of state look like?



For T large (T_4), looks like ideal gas.

As T ↓ develops inflection (T_3) then a minimum (T_2, T_1)
⇒ at fixed p, 3 possible values for V?

a, b are material-dependent. It's convenient to put the eq'n of state in a different form.

Define: $p_c = \frac{a}{27b^2}$, $V_c = 3Nb$, $T_c = \frac{8a}{27b}$

and $\hat{p} = \frac{p}{p_c}$, $\hat{V} = \frac{V}{V_c}$, $\hat{T} = \frac{T}{T_c}$

$$\Rightarrow \boxed{\left(\hat{p} + \frac{3}{\hat{V}^2}\right)\left(3\hat{V} - 1\right) = 8\hat{T}}$$ Law of Corresponding states

Rescaled this way, this law is universal. Works pretty well for He, Ne, Kr, Ar, Xe.

p_c, T_c, V_c defined to correspond to inflection point where

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \,, \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 \qquad \text{at } T = T_c \,,\ p = p_c \,,\ V = V_c$$

These are where critical pt. in phase transition occurs

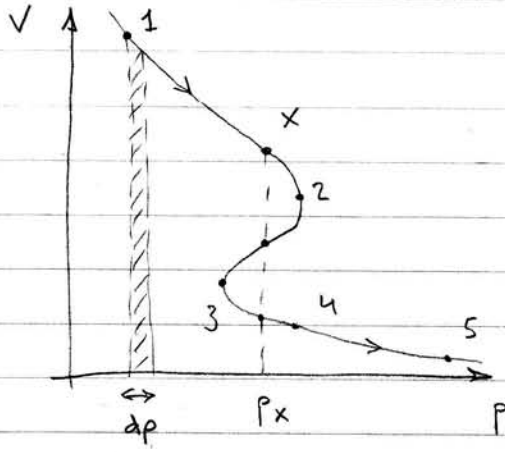
Notice we could write F in terms of natural variables T, V
However, we ultimately want G, because it is minimized
but writing an expression for $G(T,p)$ is difficult
because $V(p)$ is multivalued. We'll do it graphically

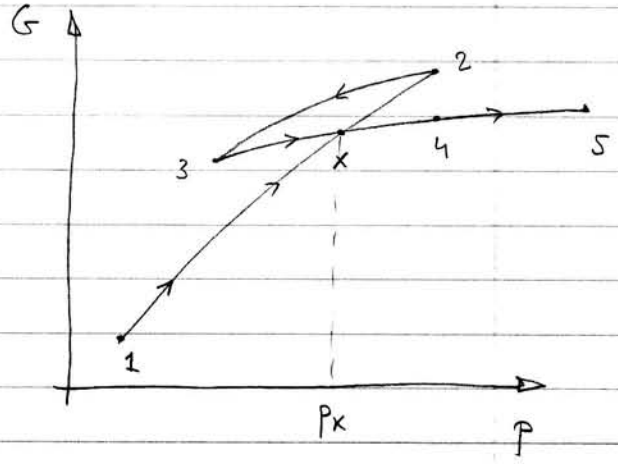
$$dG = -S\cancel{dT}^{\,0} + V dp + \mu\cancel{dN}^{\,0} \qquad \text{for const } T, N$$

$$\therefore \quad G(p) - G(p_1) = \int_{p_1}^{p} V(p')\, dp'$$

i.e. the integral under the curve $V(p)$ (for fixed T)

Consider an isotherm where $V(p)$ is multivalued
Start integrating from 1 → 5

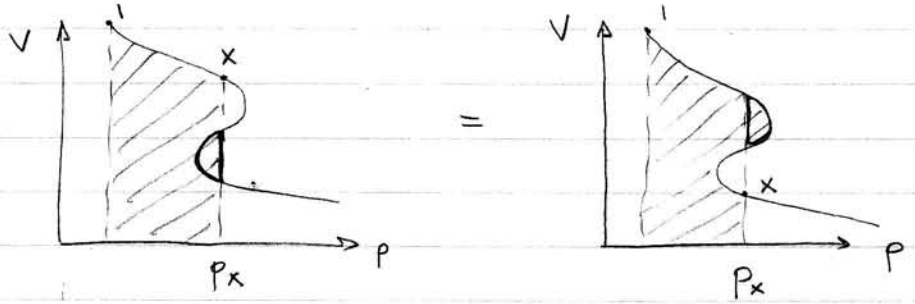




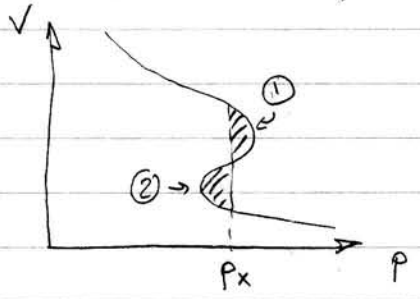
G increases from 1 → x → 2, then decreases for 2 → 3,
increases again 3 → 4 → 5

Pt. x is point where the curves cross

i.e. at p_x

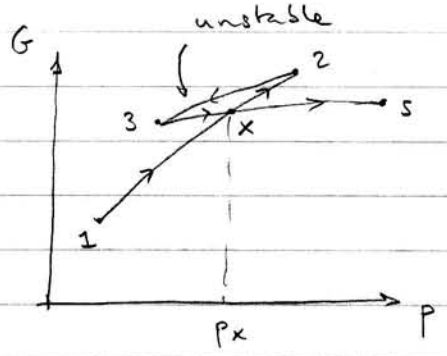


G is the same at p_x : corresponds to pt. at which the 2 highlighted areas are equal



① = ②

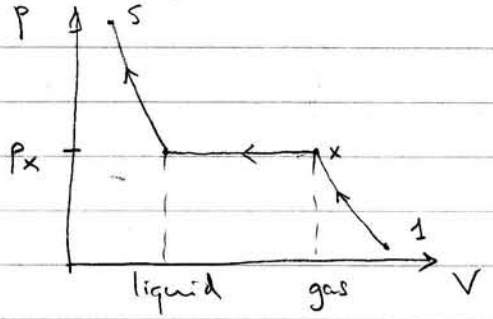
Conclusion is $G(T,p)$ is multivalued



System never explores path $x \to 2 \to 3 \to x$ at equilibrium because G is not minimized.

System follows path $1 \to x \to 5$ instead!

Going back to p-V plot (flipping the axes as is done typically)



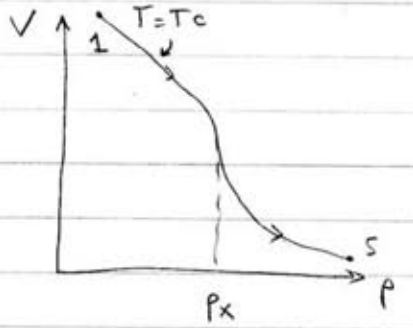
At p_x (called the vapor pressure) V drops rapidly as gas → liquid

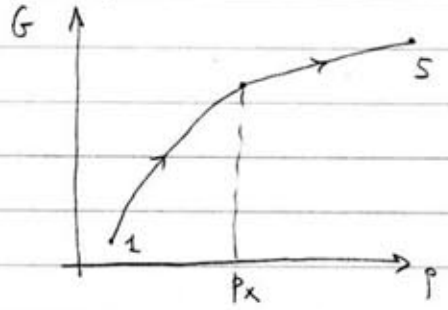
$$V(p_x) = N_{gas} v_{gas} + (N - N_{gas}) v_{liquid}$$

v_{gas}: volume per particle; v_{liquid}: volume per particle

What happens as $T \uparrow$?

At critical temperature T_c $V(p)$ has inflection pt., but it is not multivalued, so G is neither.





Beyond T_c there is no longer a phase transition

Putting it all together: