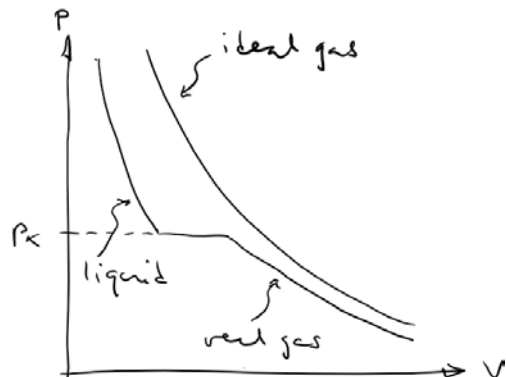## Lecture 20 – Van der Waals model

LAST TIME: We discussed phase transformations, especially the liquid-gas transition, but we didn't explain <u>why</u> this happens.

Ideal gas law does not capture enough physics to describe phase transitions

The equation of state $pV = Nk_BT$ predicts that at constant T, V decreases as p increases <u>uniformly</u>

In a real gas, V <u>suddenly</u> drops at some p_x. Gas condenses into liquid.

TODAY: Non-ideal gases

To capture condensation, we need to include interactions between gas molecules. Interactions must be <u>attractive</u> to cause sudden condensation.

In general, the interaction potential between 2 molecules will depend on their relative distance (we'll ignore orientation effects, etc.):

$$\varepsilon_{tot} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{pairs} \varphi\left(\left|\vec{r}_i - \vec{r}_j\right|\right)$$

$$\uparrow \qquad\qquad \uparrow$$

Kinetic energy Interaction energy

Question 1: How terms in the interaction energy sum, i.e. distinct pairs of particles, are there?

The sum over pairs is $\varphi_{12} + \varphi_{13} + \cdots \varphi_{1N} + \varphi_{23} + \varphi_{24} \cdots \varphi_{2N} + \cdots \varphi_{N-1,N}$ (where $\varphi_{ij} \equiv \varphi\left(\left|\vec{r}_i - \vec{r}_j\right|\right)$).

So there are $N(N-1)/2$ terms (which is also "N choose 2")

Note that we can write the sum in a symmetric way:

$$\sum_{pairs} = \sum_{i=1}^{N}\sum_{\boxed{j=i+1}}^{N} = \frac{1}{2}\sum_{i=1}^{N}\sum_{\substack{j=1 \\ i \neq j}}^{N}$$

The ½ is there to avoid double counting (e.g. $\varphi\left(\left|\vec{r}_1 - \vec{r}_2\right|\right) = \varphi\left(\left|\vec{r}_2 - \vec{r}_1\right|\right)$ etc.)

Writing the classical partition function for this non-ideal gas:

$$Z_{tot} = \frac{1}{h^N N!} \int d^3\vec{p}_1 \int d^3\vec{p}_2 \cdots \int d^3\vec{p}_N \int d^3\vec{r}_1 \int d^3\vec{r}_2 \cdots \int d^3\vec{r}_N \exp\left[-\beta\left(\sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i,j(i\neq j)} \varphi_{ij}\right)\right]$$

$$= \frac{1}{N!}\underbrace{\left(\int \frac{d^3\vec{p}_i}{2\pi\hbar} e^{-\beta p_i^2/2m}\right)^N}_{n_Q(T)} \int d^3\vec{r}_1 \int d^3\vec{r}_2 \cdots \int d^3\vec{r}_N \exp\left(-\frac{\beta}{2}\sum_{i,j(i\neq j)} \varphi\left(|\vec{r}_i - \vec{r}_j|\right)\right)$$

The *N*! is for the indistinguishability of the particles. (Note: for an ideal gas, $\varphi = 0$, the integrals in *r* give V^N, and we recover the expression we derived in Lect. 5.)

Evaluating Z_{tot} is extremely hard because the interaction energy involves the relative positions $|\vec{r}_i - \vec{r}_j|$. We will use an approximation method.

KEY CONCEPT: mean field theory
To simplify the calculation we use the idea of a <u>mean field</u> – instead of calculating the interaction between molecule *i* and every other molecule $j \neq i$, let's consider the <u>average</u> interaction energy due to the $j \neq i$ molecules:

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

So, the *i*-th molecule sits in an <u>effective potential</u> due to the other molecules collectively. Z_{tot} is now much simpler to write:

$$Z_{tot} = \frac{1}{N!}\left(n_Q(T)\int d^3\vec{R} \, e^{-\beta U_{eff}}\right)^N$$

where *R* is the coordinate of the single molecule.

To evaluate the integral, we need to make an educated guess on U_{eff}.

A realistic pairwise interaction potential accounts for attraction between molecules, also repulsion due to the non-zero size of the molecules (i.e. "hard core repulsion"):

- $\varphi(R) < 0$, i.e. attractive, over range of *R*
- $\varphi(R) \rightarrow 0$ as $R \rightarrow \infty$
- $\varphi(R) \rightarrow +\infty$, i.e. repulsive, for $R < R_0$ shorter than the hard core radius of the molecule
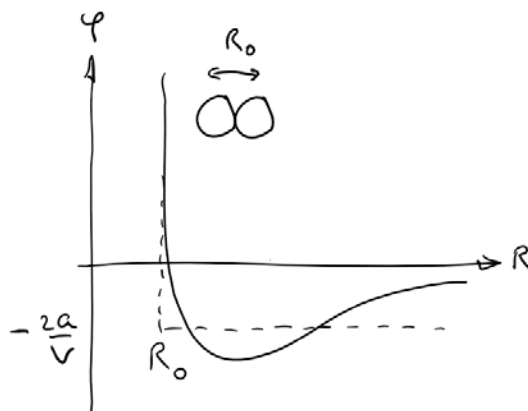
The exact details beyond this will not matter.

Let's simplify further. In the integral over space, there will be regions where $U_{eff} \to \infty$ and $e^{-\beta U_{eff}} \to 0$ corresponding to where the other particles are. Therefore, the integrand is non-zero only in the volume V <u>minus</u> the volume excluded by the other particles $V_x = (N-1)b \approx Nb$ (for $N \gg 1$) where b is the hard-core volume of one particle (and related to R_0).

To estimate the integral, we also make the "smooth potential" approximation, replacing U_{eff} by its average over space, assuming a uniform density of particles n:

$$\overline{\varphi} = \int d^3\vec{R}\, \underbrace{n(R)}_{\frac{N}{V}}\varphi(R) = -\frac{1}{V}\underbrace{\int_{R_0}^{\infty} 4\pi R^2 dR \left|\varphi(R)\right|}_{2a} \equiv -\frac{2a}{V}$$

which must be negative since the interaction is attractive. (Essentially we replace the potential in the figure above with the dotted line). Also, for $N \gg 1$

$$U_{eff} = \left\langle \frac{1}{2}\sum_{j \neq i}\varphi\left(\left|\vec{r}_i - \vec{r}_j\right|\right)\right\rangle = \frac{N-1}{2}\langle\varphi\rangle \approx \frac{N}{2}\langle\varphi\rangle \quad \text{so} \quad \overline{U}_{eff} \approx -\frac{Na}{V}$$

So, the integral is approximated as $\int d^3\vec{R}\, e^{-\beta U_{eff}} \approx (V-Nb)e^{+\beta Na/V}$ and

$$Z_{tot} \approx \frac{1}{N!}\left(n_Q(V-Nb)e^{+\beta Na/V}\right)^N$$

Question 2: From the partition function Z_{tot} determine a) the Helmholtz free energy and b) the pressure the non-ideal gas generates.

a) We get the Helmholtz free energy F from Z_{tot}:

$$F_{vdW} = -k_B T \ln Z_{tot} = -Nk_B T \ln n_Q(V-Nb) + k_B T \ln N! - \frac{N^2 a}{V}$$

$$= -Nk_B T \ln n_Q(V-Nb) + Nk_B T \ln N - Nk_B T - \frac{N^2 a}{V}$$

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

Note that this is simply the ideal gas free energy with two modifications: $V \to V - Nb$ to account for the excluded volume from the hard cores of the molecules, and $-N^2 a/V$ to account for the attractive interaction potential.
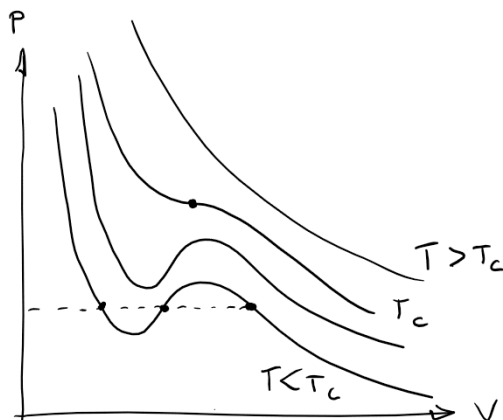
b) We get the pressure p from F:

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

KEY CONCEPT: Reordering the terms above, we get the <u>van der Waals equation of state</u>

$$\left(p+\frac{N^2a}{V^2}\right)(V-Nb)=Nk_BT$$

which reduces to the ideal gas equation of state when $a = 0 = b$, as expected.

Typical values for a and b are: $b \sim (4 \text{ Å})^3$, $a \sim 2.5$ eV Å^3 varying for different gases

What does the van der Waals equation of state look like? Plot isotherms in p-V space

For large T, isotherms look similar to ideal gas equation of state $p = Nk_BT/V$

As T decreases, the curves develop an inflection. At one fixed p, there are 3 possible volumes. This is regime where phase transformation occurs.

Crossover occurs at $T = T_C$ where

$$\left(\frac{\partial p}{\partial V}\right)_{T,N}=0 \text{ and } \left(\frac{\partial^2 p}{\partial V^2}\right)_{T,N}=0$$

This is the <u>critical point</u> – $p = p_C$, $V = V_C$, and $T = T_C$ – which are functions of a and b

Note: Since a and b are material dependent parameters, it is possible to normalize p, V, and T to give a universal equation of state (you will show this in your homework):

$$\left(\hat{p}+\frac{3}{\hat{V}^2}\right)(3\hat{V}-1)=8\hat{T}$$

where $\hat{p}$, $\hat{V}$, and $\hat{T}$ are the normalized variables. This is called the <u>Law of Corresponding States</u>. Works pretty well for noble gases (He, Ne, Kr, Ar, Xe).

KEY CONCEPT: Maxwell construction
Ultimately we want G_{vdw} because it is minimized at equilibrium. Writing an expression for G in terms of its natural variables T, p is tricky because $V(p)$ is multivalued. We'll do it graphically.

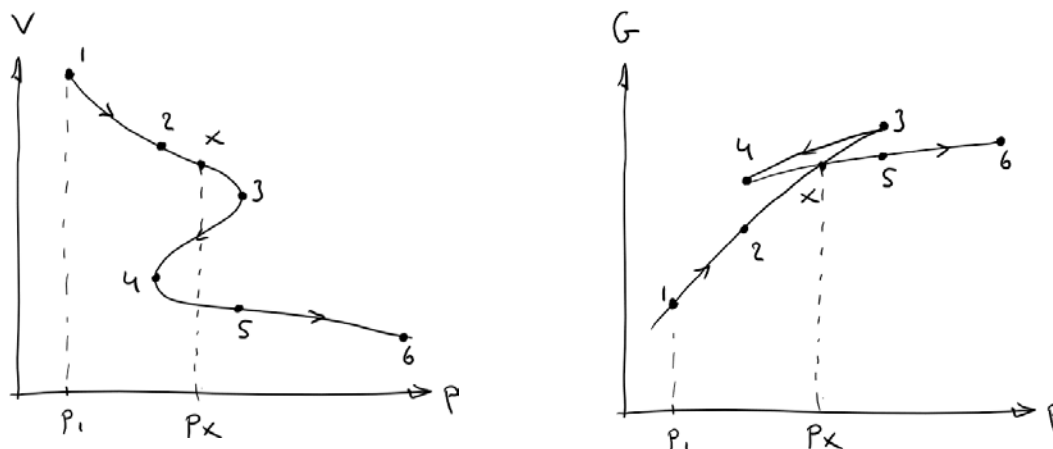For each isotherm (i.e. constant T curve):

$$dG =-S\,dT +Vdp+ \mu\,dN$$

(N is also constant)

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

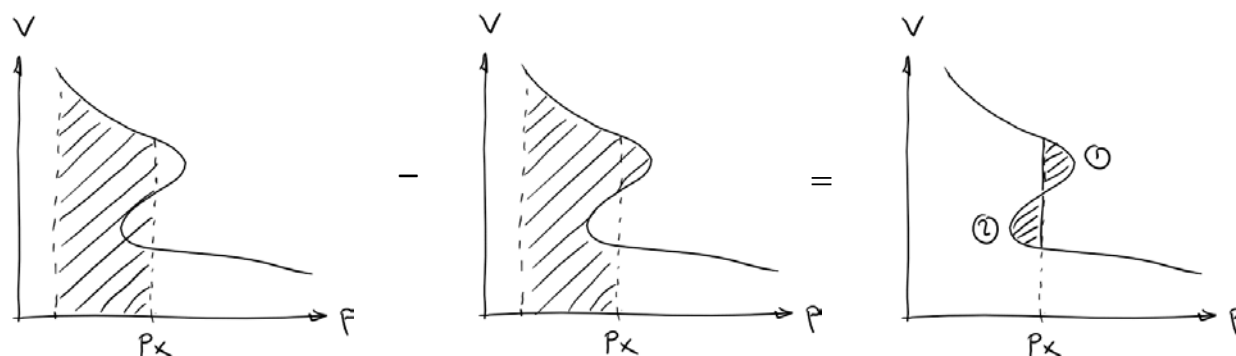This is the integral of a $V(p)$ isotherm starting at some pressure p_1:

Integrating an isotherm from a small pressure p_1 to a large one p_6:

G increases from $1 \to 2 \to x \to 3$, decreases from $3 \to 4$, then increases again from $4 \to 5 \to 6$.

Note that G is <u>multivalued</u> and the curve of G vs. p crosses itself at point x

At what pressure p_x does this happen?


First pass: $2 \to x$ Second pass: $4 \to x$ Difference

p_x is at a point where the 2 highlighted areas ① and ② in the lobes of $V(p)$ are <u>equal</u>. This graph is called the <u>Maxwell construction</u>.

Because G must be minimized, the system never explores path $x \to 3 \to 4 \to x$ at equilibrium. Instead the system follows $1 \to 2 \to x \to 5 \to 6$.

Note that the slope $\left(\partial G / \partial p \right)_{T,N} = V$ is discontinuous at point x, so the volume of the gas changes discontinuously at p_x.
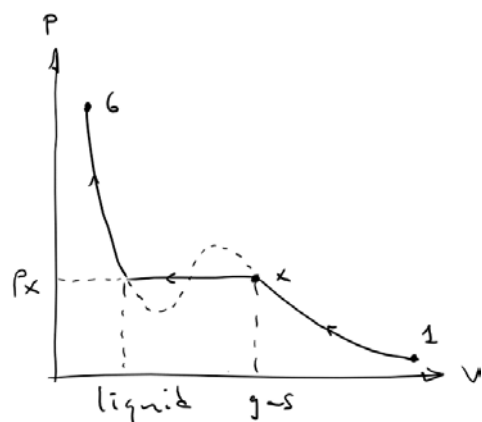
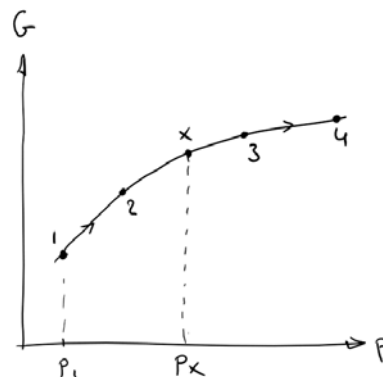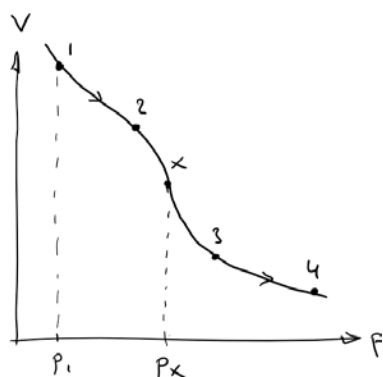Going back to the *p-V* plot:

At $p_x(T)$, called the <u>vapor pressure</u> and determined from the Maxwell construction, the volume drops suddenly as the gas condenses into a liquid:

$$V(p_x) = N_g v_g + (N - N_g)v_\ell$$

where v_g and v_ℓ are volumes per molecule.

Question 3: Draw *G* vs. *p* at the critical temperature *T* = *Tc*.

At the critical temperature, $V(p)$ is no longer multivalued, so neither is its integral *G*.

Note that the slope $(\partial G / \partial p)_{T,N} = V$ is continuous at point *x*

Putting it all together:

There is a coexistence region in *p-V* where liquid and gas phases coexist and interconvert.

For *T* > *Tc* there is no phase transition, and liquid and gas phases are indistinguishable.