Lecture 7

Phase transitions

Last time, developed Clausius-Clapeyron relation

\[ P \begin{array}{c}
I \\
\text{I} \\
\text{II} \\
\text{II}
\end{array} \]

\[ P_{co}(T) \]

\[ \left( \frac{\partial P}{\partial T} \right)_{coex} = \frac{\Delta H}{T \Delta V} = \frac{L}{T \Delta V} \]

\[ \Delta H = \text{enthalpy of transition} \]

\[ = \text{heat that must be added to system to drive all particles from I to II} \]

\[ = H_{II} - H_{I} \]

\[ \Delta V = V_{II} - V_{I} = \text{difference in volume for all particles in state II vs state I (at this P+T)} \]

Here \( N \)

\[ = \text{total # of particles} \]

\[ = N_{I} + N_{II} \]

\[ \begin{align*}
L & = \frac{\Delta H}{N} = \text{latent heat} \\
\nu & = \frac{\Delta V}{N} = \text{difference in volume/particle between phases} \\
\end{align*} \]

\[ L \approx \text{specific volume} \]

This is for \( P=0 \) system

More generally,

\[ \left( \frac{\partial V}{\partial T} \right)_{P=0} = -\frac{\Delta H}{T \Delta X} \]

But if \( \text{II is a gas} \), \( I = \text{solid or liquid} \)

...
First, expect \( V_\Pi \gg V_\frac{1}{2} \)

so \( \Delta V = V_\Pi \quad \Delta V \approx V_\Pi \)

Also, if gas is close to ideal, \( V_\Pi \approx \frac{NkT}{p} \)

So \( \left( \frac{dp}{dT} \right)_{co} = \frac{PL}{kT^2} \)

Integrate: \( \frac{dp}{p} = \frac{L}{k} \frac{dT}{T^3} \)

\( \ln p = -\frac{L}{k} \frac{1}{T} + \text{const} \)

\[ P(T) = P_0 e^{-\frac{L}{kT}} \]

Gives vapor pressure of phase I
- exp. dependence on \( T \)

Breaks down near critical point:

\( L \) depends on \( T \)
\( \to 0 \) as \( T \to T_c \)

Also \( \Delta V \to 0 \) too

So can say a fair bit about \( P/T \) relation
But can use other variables too:

Diagram in $P$-$V$ plane:

For given $P \neq P_c$, could have liquid at low $V$, gas at high $V$

or mixture in between

Add isotherms:

For $T > T_c$, approximately ideal gas

For $T < T_c$, move from liquid to gas at const $P,T$

$\Rightarrow V$ no longer determined by $P,T$!

So how is $V$ determined?
Depends on fraction of particles in two phases

Relation is straightforward:

Define \( x_l = \frac{N_l}{Z} \), \( x_g = \frac{N_g}{N} \) : mole fractions

(liquid) \hspace{2cm} (gas)

Phases have specific volumes \( V_l, V_g \)

(These have to come from eqn of state)

Then \( V_{\text{total}} = V_l + V_g \)

\[ = N_l V_l + N_g V_g \]

\[ = N x_l V_l + N x_g V_g \]

Or \( \frac{V_{\text{total}}}{N} = x_l V_l + x_g V_g \)

So given \( x_l, x_g \), get \( V \)

Or given \( V \), solve for

\[ x_l = \frac{V_g - V}{\Delta V} \]

\[ x_g = 1 - x_l = \frac{V - V_l}{\Delta V} \]

\( \Delta V = V_g - V_l \)

If not given \( x \) or \( V \), not enough information to specify system.
To go further, need eqn of state.

Ideal gas has no phase transition. Consider van der Waals gas.

In terms of specific volume, \((P + \frac{a}{v^2})(v-b) = kT\)

or \(Pv^3 - (Pb+kT)v^2 + av - ba = 0\)

cubic eqn in \(v\): expect 3 roots for given \(P, T\)

But often only one is real.

Plot \(P\) vs \(v\), various \(T\).

For \(T<T_c\) and \(P<P_c\), see 3 possible \(v\)'s for each \((P, T)\).

Above \(P_c\) or \(T_c\), only one solution.

See that at critical point, \(\left(\frac{\partial P}{\partial v}\right)_T = 0 = \left(\frac{\partial^2 P}{\partial v^2}\right)_T\)

Use this to find \(T_c, P_c\).
\[ P = \frac{kT}{u-b} - \frac{a}{u^2} \]

\[
\left( \frac{\partial P}{\partial u} \right)_T = - \frac{kT}{(u-b)^2} + \frac{2a}{u^3} = 0 \Rightarrow \frac{u^3}{(u-b)^2} = \frac{2a}{kT}
\]

\[
\left( \frac{\partial^2 P}{\partial u^2} \right)_T = \frac{2kT}{(u-b)^3} - \frac{6a}{u^4} = 0 \Rightarrow \frac{u^4}{(u-b)^3} = \frac{3a}{kT}
\]

Divide:
\[
\frac{u}{u-b} = \frac{3}{2}
\]

\[ 2u = 3u - 3b \Rightarrow u_c = 3b \]

\[ kT_c = 2a \cdot \frac{(u-b)^2}{u^3} = 2a \cdot \frac{(2b)^2}{(3b)^3} \]

\[ kT_c = \frac{8a}{27b} \]

and
\[ P_c = \frac{kT_c}{u_b} - \frac{a}{u^2} = \left( \frac{8a}{27b} \right) \frac{1}{2b} - \frac{a}{b^2} \]

\[ = \frac{a}{b^2} \left( \frac{4}{27} - \frac{2}{27} \right) \]

\[ P_c = \frac{1}{27} \frac{a}{b^2} \]

Can rewrite eqn of state in terms of \( \bar{P} = \frac{P}{P_c} \), etc.

Get
\[ (\bar{P} + \frac{3}{u^2})(3\bar{u} - 1) = 8\bar{T} \]

\[ \Rightarrow a \& b \text{ drop out!} \]

All van der Walls gases are equivalent in reduced units.

True to good approximation for most real gases
Now, for $T < T_c$ have $P$

Have region where $\frac{d\rho}{d\nu} > 0$

$\Rightarrow$ Unstable:

Suppose small element of fluid $\delta U$ increased

Then $P$ in that element would increase

$\Rightarrow$ cause size to increase further

Expansion runs away

$\Rightarrow$ form bubble in liquid

Similarly if $\delta U$ decreases, $P$ goes down

$\Rightarrow$ form droplet in vapor

So curve as drawn isn't really right

Should be:

$P$

$P_{cc}$

pure liquid

coexistence

metastable states

pure gas

$P$ remains constant in coexistence region
But how do we know where to draw line?

Use method called Maxwell construction

Know that in equilibrium, $G$ is minimized

$$dG = -SdT + UdT$$

On isotherm, $dT = 0$, so

$$G = \int_{T_{\text{fixed}}}^{T} \mu dT$$

Draw $U(P)$:

Between 2 & 6, $G$ is multivalued

But want smallest possible value
So observe

\[ G \]

\[ \rho \]

Location of 2 & 6 determined by \( G(2) = G(6) \)

\[ G(6) - G(2) = \int_{P_2}^{P_6} U \, dP = 0 \]

= area enclosed

\[ U \]

Can't solve analytically, but can integrate numerically to locate transition points

Summary: For given \( T \), find onset of transition by locating points in liquid + gas states where \( G(P, \text{V}_L) = G(P, \text{V}_g) \)

Can locate points by equalizing area enclosed by coexistence line & eqn of state