Ph 12 C
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10. Phase Transformations

Homework Chapter 9, Prob. 2, 5
Chapter 10, Prob. 1, 2, 3, 5

Phase transitions: Most active subject of research in modern statistical physics

Basic phenomenon — small change in a variable (e.g. τ) causes large qualitative change in equilibrium configuration

Examples:

- Water (at $p = 1$ atm)
  - ice-liquid at 0°C
  - liquid-steam at 100°C
- Conductor-insulator transition
- onset of
  - Ferromagnetism (iron won't magnetize above critical temp)
  - Superfluidity (2.17°K in He^4)
  - Superconductivity ("High-T_c")

Mathematics:

Hallmark of phase transition is discontinuous behavior (of e.g. density as a function of τ)

$$Z = \sum_{\text{states}} e^{-E_{\text{state}}/\tau}$$

must have discontinuous derivatives

this means that sum must be infinite strictly speaking, phase transitions can occur only for volume $V \to \infty$.
In practice — rounding of discontinuity due to finite volume may be unobservable.

Two things to investigate:

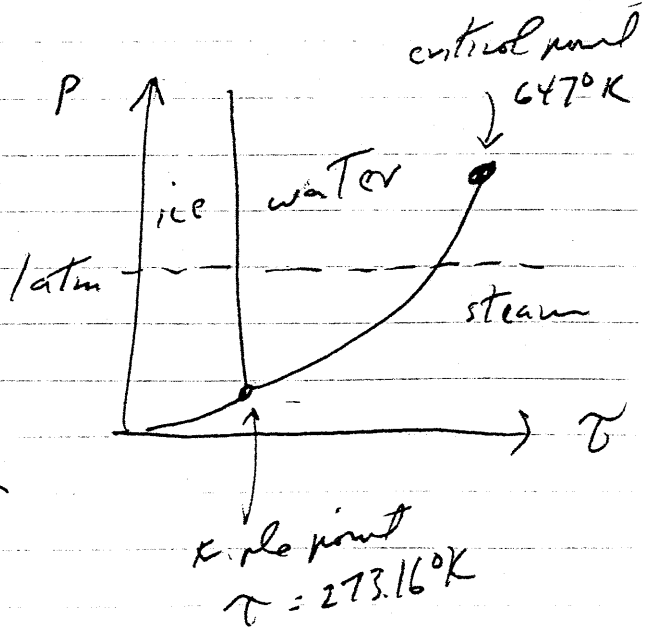
1) How much can we understand about phase transitions using thermodynamics, without worrying about details of a microscopic picture

2) How do we understand phase transitions from a fundamental, microscopic point of view. E.g. calculate τ_{crit}, etc. from first principles

Coexistence of Phases

Example: 3 phases of water

At given pressure, 2 phases can be in stable contact (in equilibrium) only at particular transition temperatures.



Or — fix T and vary available volume —

150 Kerms

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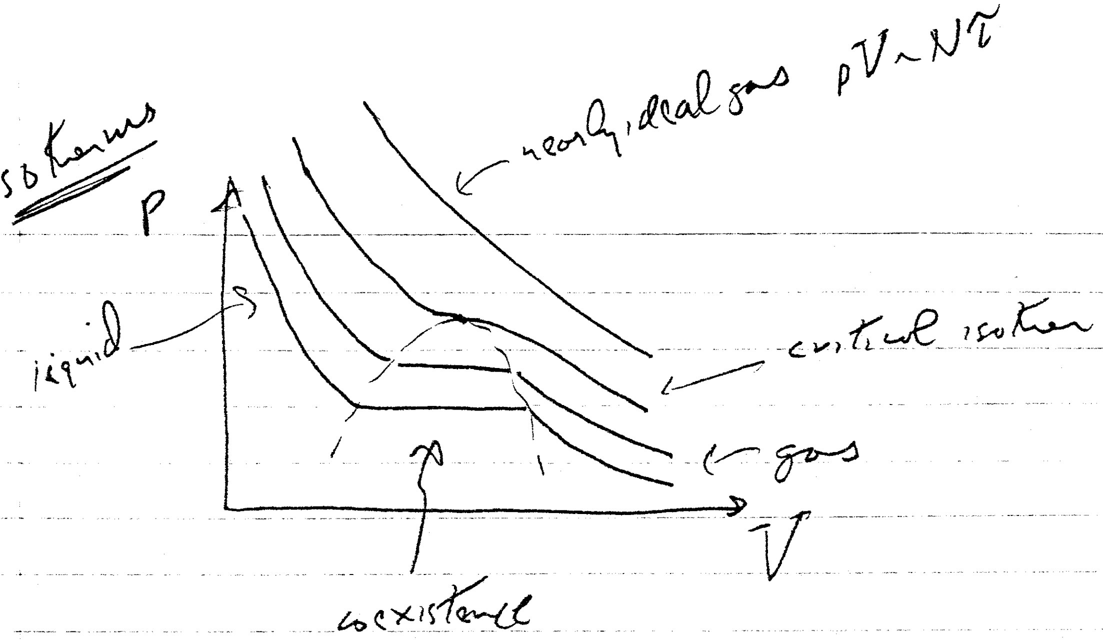
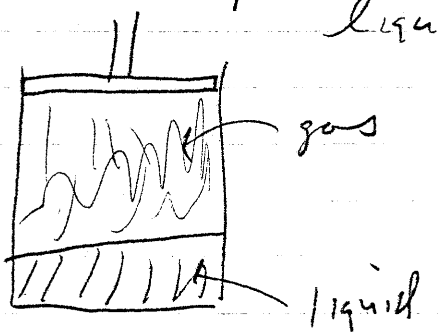


(AT sufficiently high τ (or p) there is no coexistence of liquid and gas)



At given τ, liquid coexists with vapor at a particular pressure

Gas and liquid are in --

Thermal equilibrium (same τ) - or heat would flow

mechanical equilibrium (same p) - or boundary would move / V change

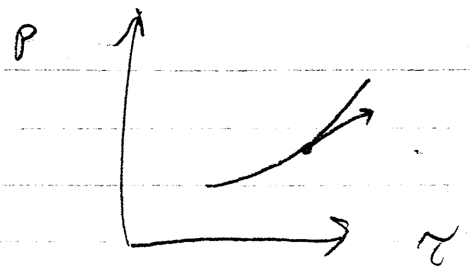
diffusive equilibrium (same μ) or else N flows

Coexistence Curve

How does p at coexistence vary with τ?

$$\mu_\ell(p,\tau) = \mu_g(p,\tau)$$

— one condition determines a curve in p-τ plane. Find slope of the curve.



$$\mu_g(p+dp,\tau+d\tau) = \mu_\ell(p+dp,\tau+d\tau)$$

or $$\left(\frac{\partial\mu_g}{\partial p}\right)_\tau dp + \left(\frac{\partial\mu_g}{\partial\tau}\right)_p d\tau = \left(\frac{\partial\mu_\ell}{\partial p}\right)_\tau dp + \left(\frac{\partial\mu_\ell}{\partial\tau}\right)_p d\tau$$

$$\Rightarrow \left[\left(\frac{\partial\mu_\ell}{\partial\tau}\right)_p - \left(\frac{\partial\mu_g}{\partial\tau}\right)_p\right] d\tau = \left[\left(\frac{\partial\mu_g}{\partial p}\right)_\tau - \left(\frac{\partial\mu_\ell}{\partial p}\right)_\tau\right] dp$$

$$\Rightarrow \left(\frac{dp}{d\tau}\right)_{coex} = \frac{(\partial\mu_\ell/\partial\tau)_p - (\partial\mu_g/\partial\tau)_p}{(\partial\mu_g/\partial p)_\tau - (\partial\mu_\ell/\partial p)_\tau}$$

Recall Gibbs free energy (Chapter 9)

$$G(\tau,p,N) = N\mu(\tau,p)$$

and $\left(\frac{\partial G}{\partial p}\right)_{\tau,N} = V$, $\left(\frac{\partial G}{\partial\tau}\right)_{p,N} = -\sigma$

If we denote $v = V/N$ $s = \sigma/N$ volume and entropy per particle

then $$\left(dp/d\tau\right)_{coex} = \frac{s_g - s_\ell}{v_g - v_\ell}.$$

Can relate Δs to <u>Latent heat</u>

$Q = \tau\Delta\sigma$ or $L = \tau\Delta s$ is amount of heat (per particle) required to boil the liquid

So $$\boxed{\left(\frac{dp}{d\tau}\right)_{coex} = \frac{L}{\tau \Delta v}}$$ the Clausius-Clapeyron eqn (which is well verified)

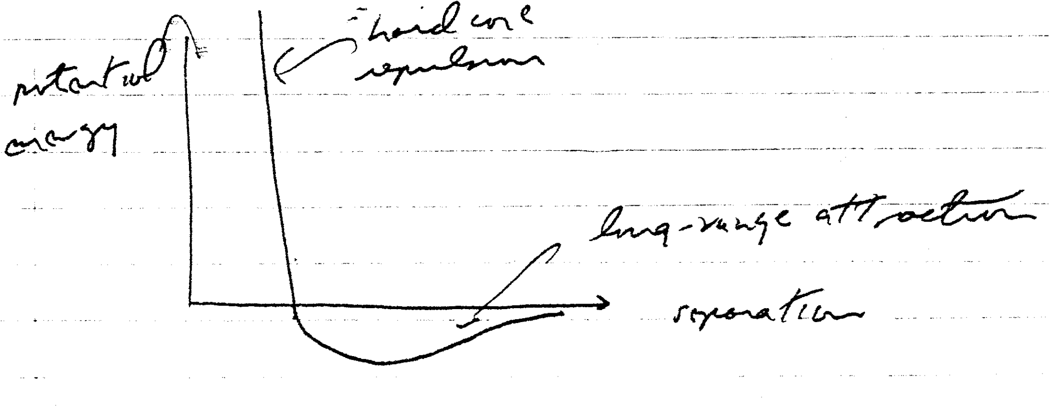
this applies to water-ice transition as well. Note: $\Delta v < 0$ (ice floats)
$\Delta s > 0$ (need heat to melt ice)

Hence $(dp/d\tau)_{coex} < 0$.

pressure *lowers* the coexistence temperature (*unusual*) which is why we can skate on ice.

Van der Waals Equation of State (1873)

We'll consider how interactions among gas molecules modify the ideal gas relation $pV = N\tau$. This will lead us to a crude model of the gas-liquid phase transition.



Effect of the hard core: $V \to V - Nb$
excludes some volume (b = vol. per particle)

Effect of the attraction:

$$U = \sum_{\text{pairs}} V_{\text{pair}} = \frac{1}{2}\int d^3x\, d^3y\, n(\vec{x})\, n(\vec{y})\, V(\vec{x}-\vec{y})$$

Treat density as uniform, $n =$ constant
("Mean field theory" — ignores density fluctuations)

$$= n^2 V \frac{1}{2}\int d^3x\, V(\vec{x}) = -a\, N^2/V$$

Correction to the pressure $p = -\frac{\partial U}{\partial V} = -a\, N^2/V^2$

(attraction $\Rightarrow a > 0$)

So — $pV = \underline{N\tau}$

$$\Rightarrow \boxed{p = \frac{N\tau}{V - Nb} - a\, N^2/V^2}$$

Van der Waals equation

- This is reasonable approximation when gas is close to ideal ($n = N/V$ sufficiently small) But we will use it (<u>without</u> justification) even when corrections to ideal behavior are <u>big</u> (e.g., when gas liquefies)

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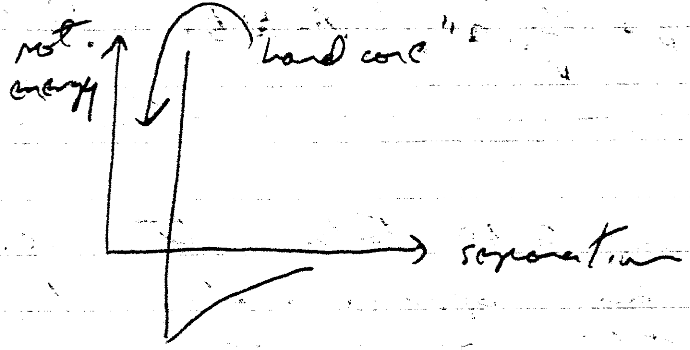
Van der Waals Equation of State

Idealize:



Effect of hard core: excluded volume

$V \to V - Nb \qquad b = $ vol per particle

Effect of attraction

$$\Delta U = \sum_{\text{pairs}<ij>} V_{ij}$$

$$= \frac{1}{2}\int d^3x\, d^3y\; n(\vec{x})\, n(\vec{y})\; V(\vec{x}-\vec{y})$$

"Mean field theory" — treat density n as uniform, ignoring fluctuations

$$= \frac{1}{2} n^2 V \int d^3x\; V(\vec{x}) = -a\frac{N^2}{V}$$

($a > 0$, because pot. energy is negative)

So we write

$$F_{vdW} = F_{ideal}(V - Nb) - a\,N^2/V$$

$$= -N\tau \log\left[n_Q\left(\frac{V-Nb}{N}\right)\right] - aN^2/V$$

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

(over)

1A

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We have

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

van der Waals eqn of state

It is not to be taken too seriously. At best an approximation that applies to sufficiently dilute gas. Without justification, we will apply it to dense gas

For given τ and p, what is V?
Solve a cubic equation

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

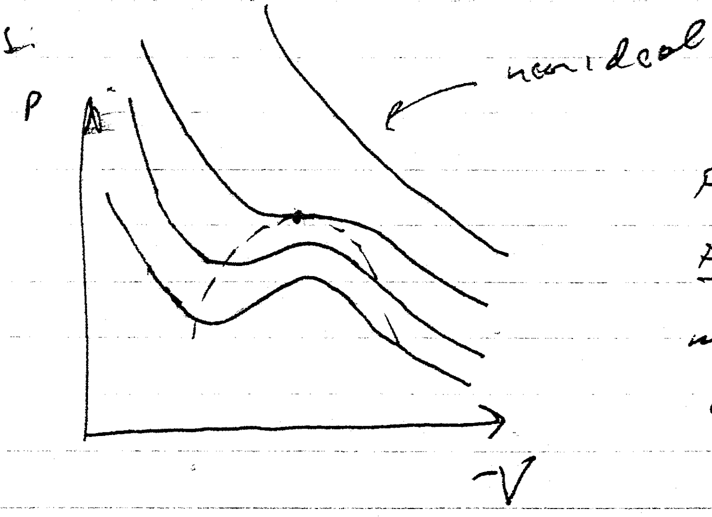
(we multiply vdW eqn by V^2/p)

or $$V^3-\left(Nb+\frac{N\tau}{p}\right)V^2+\frac{N^2a}{p}V-\frac{N^3ab}{p}=0$$

Has either one or 3 real solutions

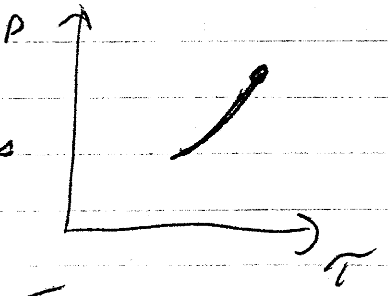
Note: τ large $\Rightarrow$ $V=N\tau/p$ is approx. soln.

Isotherms:



There is critical point where the multivaluedness of V turns on

As we'll soon see, can regard $p_c\ \tau_c$ as end of line of first-order phase transitions in p-τ plane



Lets solve for $p_c\ \tau_c\ V_c$ in terms of N, a, b

At critical point: $(V-V_c)^3=0$

eqn of state has 3 degenerate solutions

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expand: $V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0$

Equate:

① $3V_c = Nb + N\tau_c/p_c$

② $3V_c^2 = \frac{N^2 a}{p_c}$

③ $V_c^3 = \frac{N^3 ab}{p_c}$

Divide ③ by ②: $V_c/3 = Nb$ or $\boxed{V_c = 3Nb}$

(three times excluded volume)

② $\Rightarrow$ $27N^2b^2 = N^2a/p_c$

$\Rightarrow \boxed{p_c = a/27b^2}$

① $\Rightarrow$ $\tau_c = \frac{p_c}{N}(3V_c - Nb) = \frac{a}{27b^2}\,8b = \boxed{\begin{array}{c} 8a/27b \\ = \tau_c \end{array}}$

Now we can eliminate a, b, N and reexpress vdW eqn in terms of V_c p_c τ_c:

$$\left(\frac{V}{V_c} - \frac{Nb}{V_c}\right)\left(\frac{p}{p_c} + \frac{V_c^2}{V^2}\,\frac{N^2 a}{V_c^2 p_c}\right) = \frac{\tau}{\tau_c}\,\frac{N\tau_c}{V_c p_c}$$

$Nb/V_c = \frac{1}{3}$; $\frac{N^2 a}{V_c^2 p_c} = \frac{a}{9b^2}\,\frac{27b^2}{a} = 3$

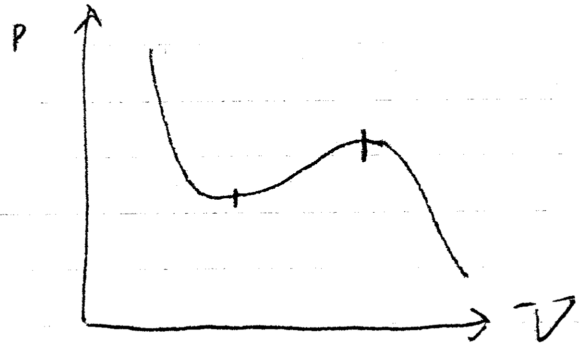
$\frac{N\tau_c}{V_c p_c} = \frac{8a}{27b}\,\frac{1}{3b}\,\frac{27b^2}{a} = 8/3$

We have $$\boxed{\left(\frac{V}{V_c} - \frac{1}{3}\right)\left(\frac{p}{p_c} + 3\left(\frac{V_c}{V}\right)^2\right) = \frac{8}{3}\,\tau/\tau_c}$$

— "The Law of Corresponding States"
correction to ideal gas law takes "universal" form (same for all gases) when expressed in terms of critical values.

Doesn't work all that well, nor should it

The Maxwell Construction



Consider isotherm for $\tau < \tau_c$

There is a regime with $dp/dV > 0$

what is significance of this?
(Note $K_T \equiv -\frac{1}{V}\left(\frac{dV}{dP}\right)_T$ = "compressibility")

Instability

Mathematically: system + reservoir choose volume V to minimize Helmholtz free energy F

so $$dF = \left[\left(\frac{\partial F_{sys}}{\partial V}\right)_\tau - \left(\frac{\partial F_{res}}{\partial V}\right)_\tau\right] dV_{sys} = 0$$

so $p_{sys} = p_{res}$ $\left(p = -\left(\frac{\partial F}{\partial V}\right)_\tau\right)$

But for this to be minimum, need $d^2F \geq 0$

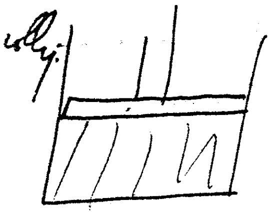
(over)

$$-\frac{\partial}{\partial \bar{V}_{sys}}\left(p_{sys} - p_{res} \right) > 0$$

and $\frac{\partial p_{res}}{\partial V} \approx 0$

so $\boxed{-\frac{\partial p}{\partial V} > 0}$

physically:



If we push a little harder, system pushes back less hard $\Longrightarrow$ it will collapse incidentally, a similar stability criterion applies to heat transfer

$$d\sigma = \left[\left(\frac{\partial \sigma_{sys}}{\partial U}\right)_V - \left(\frac{\partial \sigma_{res}}{\partial U}\right)_V\right] dU_{sys}$$

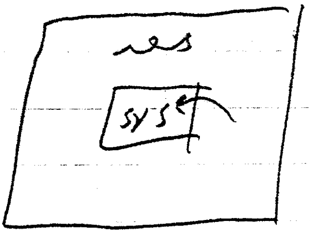
$$= \left(\frac{1}{\tau_{sys}} - \frac{1}{\tau_{res}}\right) dU_{sys} \Rightarrow \tau_{sys} = \tau_{res}$$

But $d^2\sigma \le 0$ needed, if entropy is *maximized*

$$\frac{\partial \tau_{res}}{\partial U} = 0$$

so $\frac{\partial}{\partial U}\frac{1}{\tau} = -\frac{1}{\tau^2}\frac{\partial \tau}{\partial U} = -\frac{1}{\tau^2 C_V} \le 0$

this requires $C_V \ge 0$; heat capacity is positive



physically -- if system has negative heat capacity, heat flow into the system *cools it down*, so *more* heat flows in.

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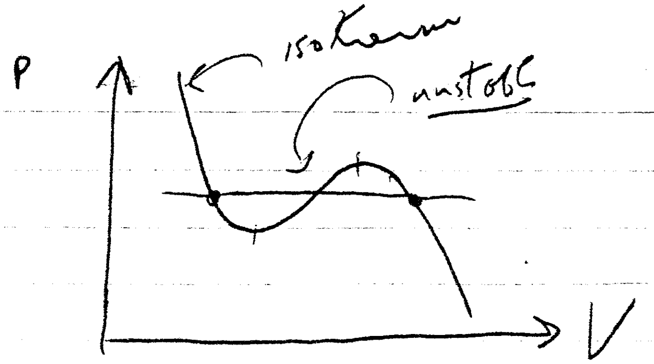
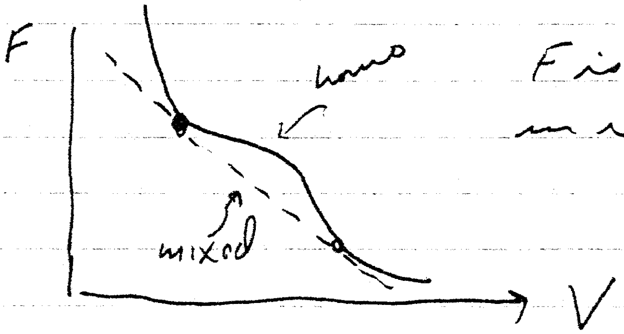
unstable with respect to what? what state does the system prefer to be in?

To see this, consider F as a function of V with τ fixed.

$$F = -\int_{\text{isotherm}} p\, dV \quad (+\text{ constant})$$





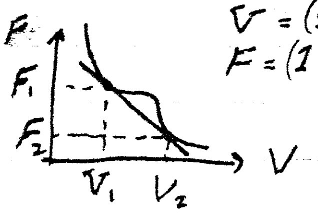
F is concave downward in region where $dp/dV > 0$

Here F is the free energy of homogeneous phase, but we should consider alternative of inhomogeneous phase — i.e. divide available volume into two different phases (at same p and T)

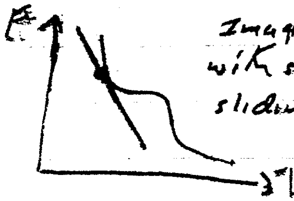
- Equating pressure means same slope for F vs V at both points
- Further F vs V in the mixed phase is a straight line $F = f_1 V_1 + f_2 V_2 = (f_1 - f_2)\Delta V + \text{const}$

↑ free-energy per volume

Where F is concave down, we can get lower F with a mixed phase — and lowest possible F along a line that is tangent to F(V) at two points as shown.

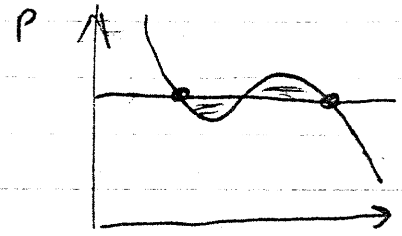


$V = (1-\alpha)V_1 + \alpha V_2$
$F = (1-\alpha)F_1 + \alpha F_2$



Imagine a stick with slope = $-p$ sliding along the curve...

So -- to find value of $p(T)$ at which coexistence occurs, we find slope of this common tangent

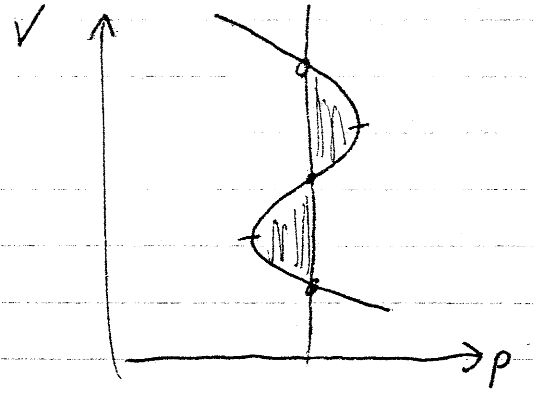


Since $(\Delta F)_{vdW} = (\Delta F)_{mixed}$,

we have $\int (P)_{vdW}\, dV = p \int dV$

this means that regions above and below the horizontal line have equal areas ("Maxwell construction")

Another way to think about this:



Since the two phases are in diffusive equilibrium, they must have same chemical potential

So all gas and all liquid phases have same $G = N\mu$

$$dG = V\,dp \Rightarrow \int V\,dp = 0$$

— again, equal areas

So -- the gas and liquid phases have same G -- but <u>derivatives</u> of G are not the same → Defining property of "First-Order Phase Transition"