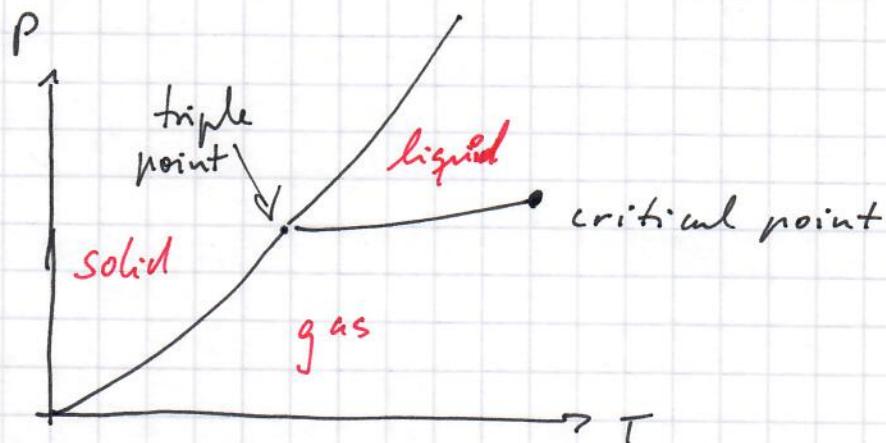


Section 2.1 of text:

115

Phase transitions and phase diagrams

Typical / generic phase diagram



The gas-liquid transition line extends from the triple point to the critical point, at which the properties of the gas and the liquid become indistinguishable and thus the phase transition disappears.

At most (T, P) : the equilibrium state of the substance is a single uniform phase (solid, liquid, or gas).

Single-phase states are separated by two-phase coexistence curves.

Note:

116

It is impossible to compute the phase diagram of a substance using the laws of thermodynamics

→ The equilibrium phase at given P and T depends on the microscopic structure of the substance.

However:

Thermodynamics can do something (it tells us about slope of coexistence curve)

Consider gas-liquid condensation curve.

At any (T, P) point on the curve, a two-phase system composed of gas and liquid could remain at equilibrium within a single container.

Obviously: temperatures and pressures in two phases must be equal.

Moreover, along condensation curve: $\mu_L = \mu_G$

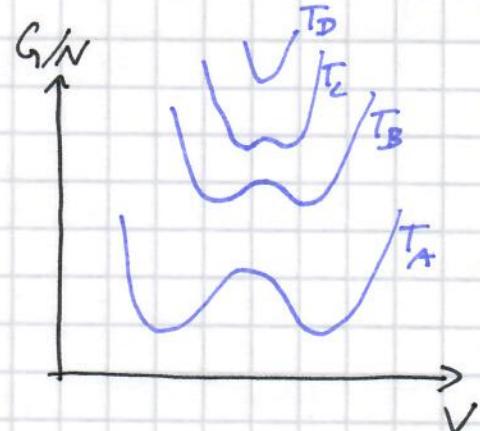
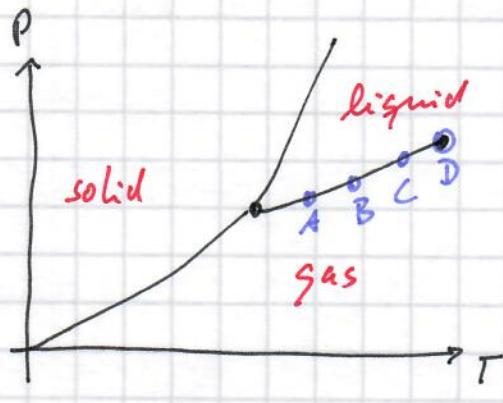
equal chem. potentials!

But we also know:

$$\text{Gibbs free energy } G(T, P, N) = \mu N$$

How does G/N look like?

G/N : Gibbs free energy
(per particle)



For points A, B, C: The two minima of G/N correspond to the coexistence of the gas and liquid phases.

As we move from A to B to C, the two phases become more alike.

"critical point"

At the terminus of the liquid-gas coexistence curve, the two phases become indistinguishable.

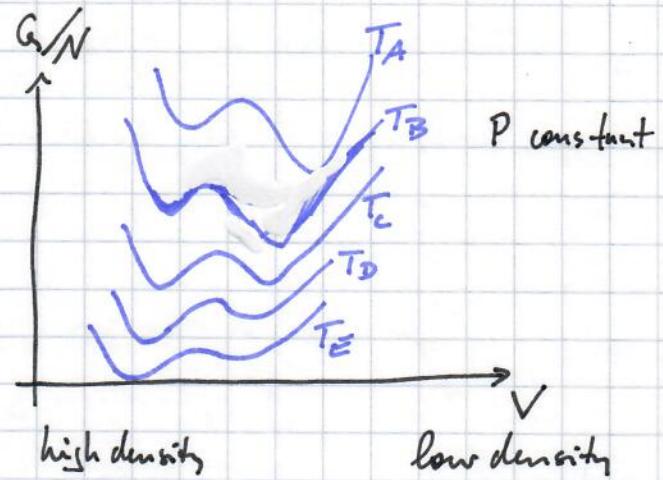
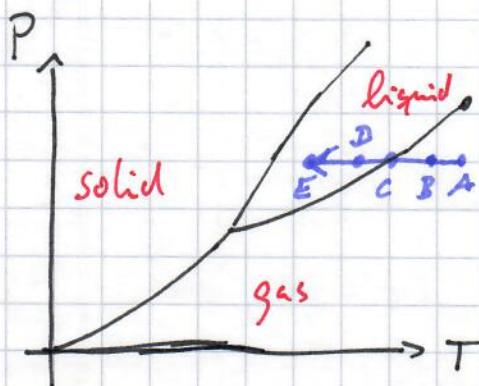
At the critical point, the first-order transition degenerates into a more complicated

transition (or more subtle tran-

118

sition), namely a second-order transition.

Let's look at the Gibbs free energy for a different "trajectory":



The temperature T_c is the transition temperature.

The "high density phase" is stable below the transition temperature.

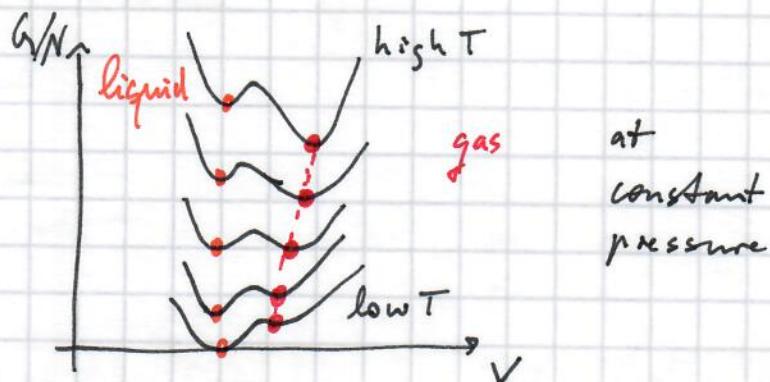
The "low density phase" is stable above the transition temperature.

If the vapor is cooled very gently through the transition temperature, the system finds itself in a state that had been absolutely

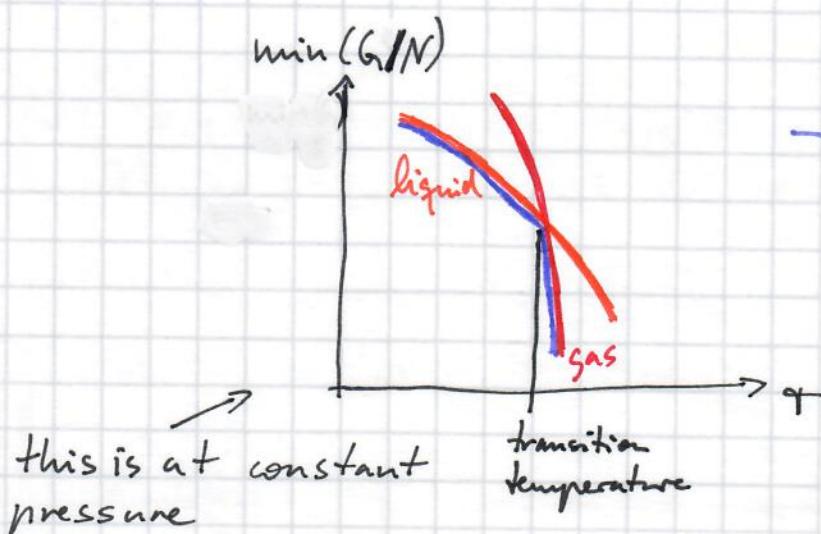
stable but that is now metastable. Sooner or later a fluctuation within the system will "discover" the truly stable state, forming a nucleus of condensed liquid.

→ nucleus then grows rapidly and entire system suddenly undergoes the transition

Let's plot the minimum of G/N as a function of T :



↑
plot from
previous
page



— "true" Gibbs
free energy
(per particle)

The shift of the equilibrium state from one local minimum to the other constitutes a first-order phase transition, induced either by a change in temperature or by a change in some other thermodynamic parameter.

The two states between which a first-order phase transition occurs are distinct, occurring at separate regions of the thermodynamic configuration space.

From the previous plot, we readily see (L liquid; G gas):

$$\left(\frac{\partial (\mathcal{G}/N)_L}{\partial T} \right)_{P,T=T_c} \neq \left(\frac{\partial (\mathcal{G}/N)_G}{\partial T} \right)_{P,T=T_c}$$

In fact: $\left(\frac{\partial (\mathcal{G}/N)_L}{\partial T} \right)_{P,T=T_c} - \left(\frac{\partial (\mathcal{G}/N)_G}{\partial T} \right)_{P,T=T_c}$

discontinuity!
in derivative!

$$= - \left[\left(\frac{S}{N} \right)_L - \left(\frac{S}{N} \right)_G \right]_{T=T_c} < 0$$

$\left(\frac{\partial S}{\partial T} \right)_{P,N} = -S$ read off graph

[12]

It is more convenient to write :

$$\left(\frac{\partial}{\partial T} \left((\mathcal{G}_N)_L - (\mathcal{G}_N)_G \right) \right)_P = - \left[\left(\frac{S}{N} \right)_L - \left(\frac{S}{N} \right)_G \right]$$

at $T = T_c$

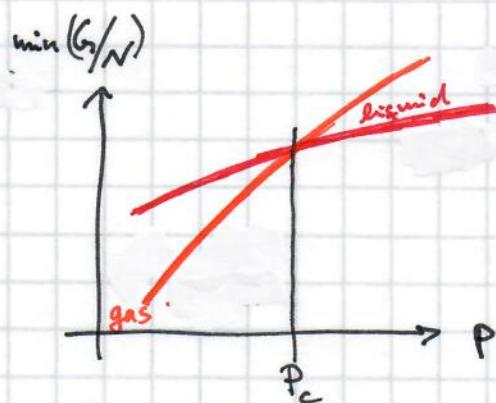
Similarly, we can write :

$$\left(\frac{\partial}{\partial P} \left((\mathcal{G}_N)_L - (\mathcal{G}_N)_G \right) \right)_T = \left(\frac{V}{N} \right)_L - \left(\frac{V}{N} \right)_G$$

at $P = P_c$

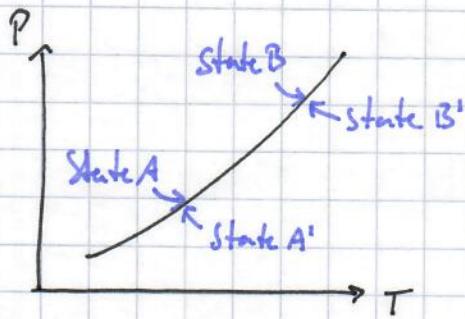
↑

also referred to
as vapor pressure



at constant
temperature

Let's look at this in $P-T$ diagram:



States A and A' are on the coexistence curve
but they correspond to different phases.

Similarly for states B and B' .

$$P_B - P_A = P_{B'} - P_{A'} = dP \text{ (infinitesimal)}$$

$$T_B - T_A = T_{B'} - T_{A'} = dT \text{ (infinitesimal)}$$

Slope of curve is $\frac{dP}{dT}$

Phase equilibrium: $\mu_A = \mu_{A'}$

$$\mu_B = \mu_{B'}$$

$$\Rightarrow \mu_B - \mu_A = \mu_{B'} - \mu_{A'} \quad (*)$$

$$\text{But } \mu_B - \mu_A = -s dT + v dP$$

$$s = S/N, v = V/N$$

$$\text{and } \mu_{B'} - \mu_{A'} = -s' dT + v' dP$$

s, s' : entropies per particle
 v, v' : volume per particle

* becomes: $-s dT + v dP = -s' dT + v' dP$

$$\text{or } (s' - s) dT = (v' - v) dP$$

$$\text{or } \frac{dP}{dT} = \frac{\Delta s}{\Delta v}$$

slope of coexistence curve

discontinuities associated w/ phase transition

$$\Delta s = s' - s$$

discontinuity of entropy

$$\Delta v = v' - v$$

discontinuity of volume

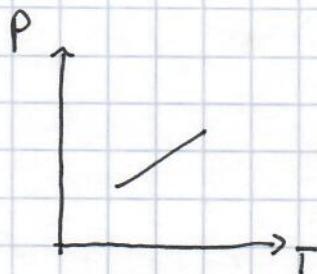
Define: $\ell = T \Delta s$ (ℓ : latent heat at first-order phase transition)

$$\Rightarrow \frac{dP}{dT} = \frac{\ell}{T \Delta v}$$

$$\frac{dP}{dT} = \frac{l}{T \Delta v}$$



obtained from
experiment

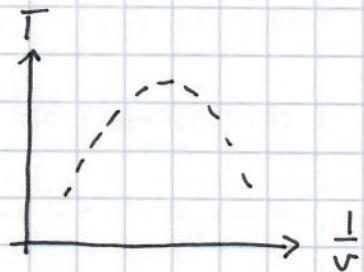


slope can be
measured



Δv can also be measured

e.g.:



(more on this when we
discuss the vdW
gas...)



can be used to measure l

$$\left\{ \frac{dP}{dT} = \frac{l}{T \Delta V} \right\}$$

Clapeyron equation

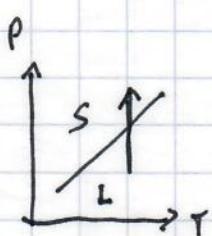
E.g.: solid - liquid transition with

$s_L > s_s$ (positive latent heat)

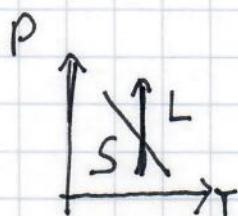
$v_L > v_s$ (positive difference of volume)

$$\Rightarrow \frac{dP}{dT} > 0$$

So: increase of pressure at constant temperature tends to drive the system to more dense (solid) phase



an increase in temperature at constant pressure drives the system to the more entropic (liquid) phase



On the other hand: if $s_L > s_s$ & $v_L < v_s$,

$$\text{then } \frac{dP}{dT} < 0$$

increase of P (T const) tends to drive the system to the more dense liquid phase.

Simple approximations for liquid-gas transition:

Sometimes called Clapeyron-Clausius approximation

- assume $V_L \ll V_G$

$$\Rightarrow \frac{dP}{dT} \approx \frac{l}{T V_G}$$

- assume validity of ideal gas law

$$PV_G = NkT$$

$$\Rightarrow \frac{dP}{dT} \approx \frac{lP}{kT^2}$$

Rewrite: $\frac{dP}{P} \approx \frac{l}{k} \frac{dT}{T^2}$

$$-d\left(\frac{1}{T}\right)$$

Assuming l is constant, we can integrate:

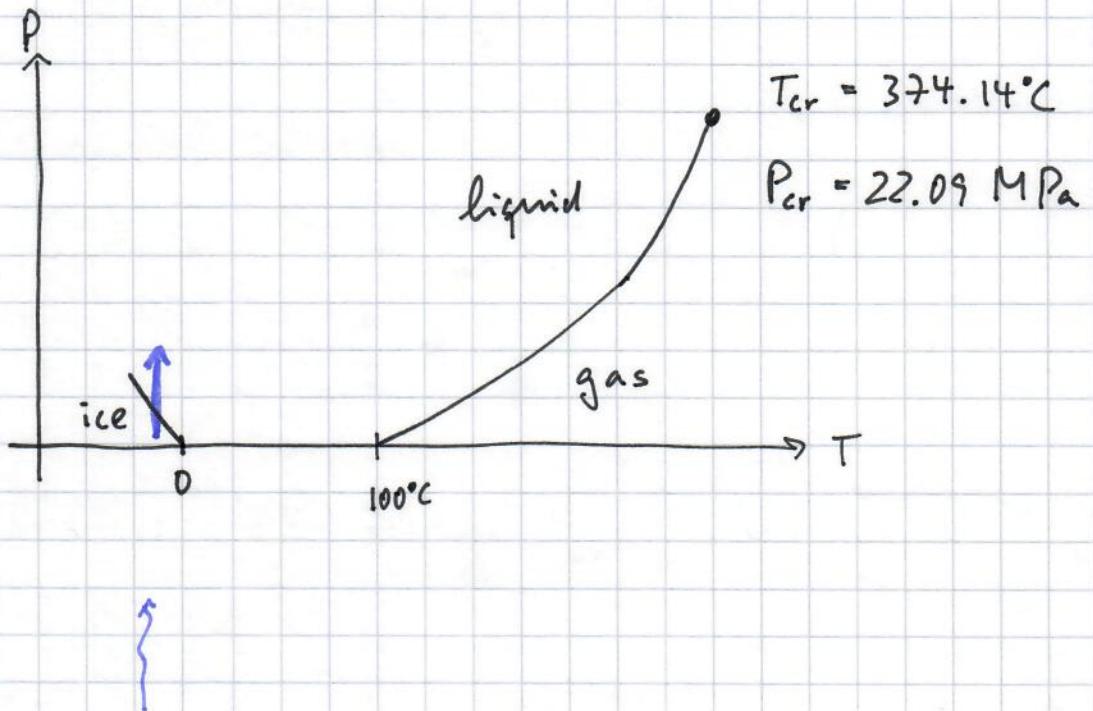
$$\log P = \text{const} - \frac{l}{k} \frac{1}{T}$$

This suggests that one should plot
 $\log P$ versus $1/T$

also called condensation curves

Let's think about ice skating:

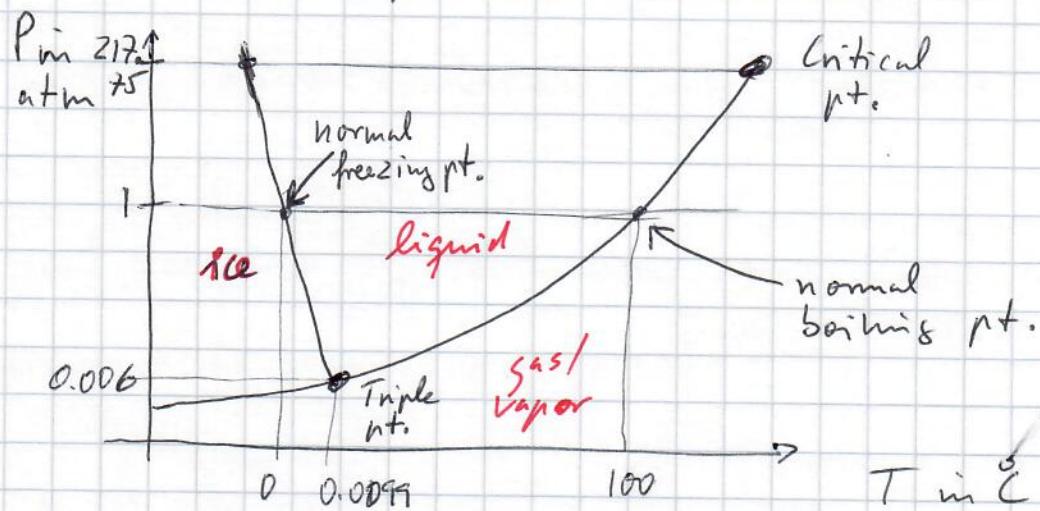
Phase diagram of water



the pressure applied to the ice directly beneath the blade of the skate shifts the ice across the solid-liquid coexistence curve (vertically upward), providing a lubricating film of liquid on which the skate slides.

126a

More complete phase diagram of H_2O :

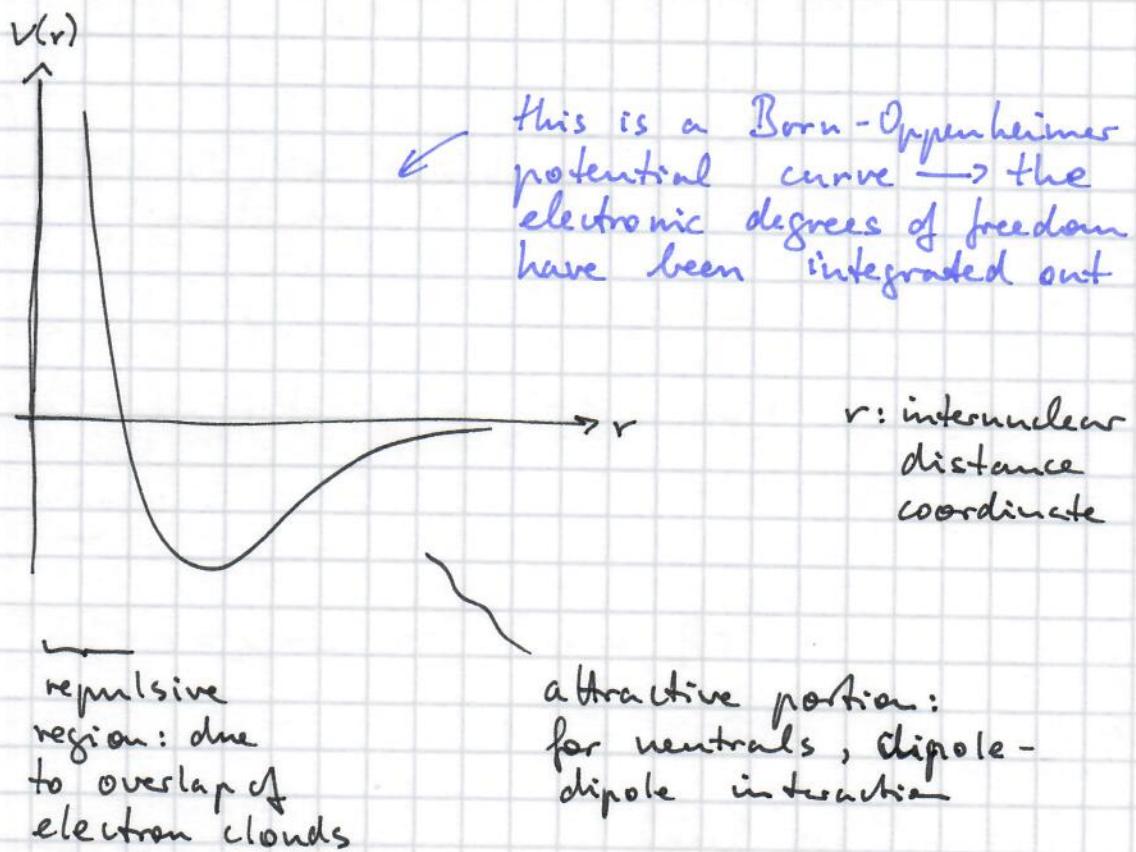


2.3 Van der Waals equation of state (see also Sec. 7.8)

The ideal gas equation of state has limitations.

Real atoms and molecules interact!

How does a typical interaction potential look like?



Simplistic functional form: $V(r) = V_0 \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^6 \right]$

referred to as Lenard-Jones potential

V_0 : units of energy

σ : units of length

We will not (it's hard!!!) treat the problem microscopically.

Instead, we will use an empirical E-O-S that describes the vdW (van der Waals) gas quite well.

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

van der Waals E-O-S

a, b are substance specific constants

Physical interpretation of " $-b$ " and " $-\frac{a}{v^2}$ " corrections:

$$\text{let } b=a=0 \Rightarrow P v = RT$$

$$P V = NRT$$

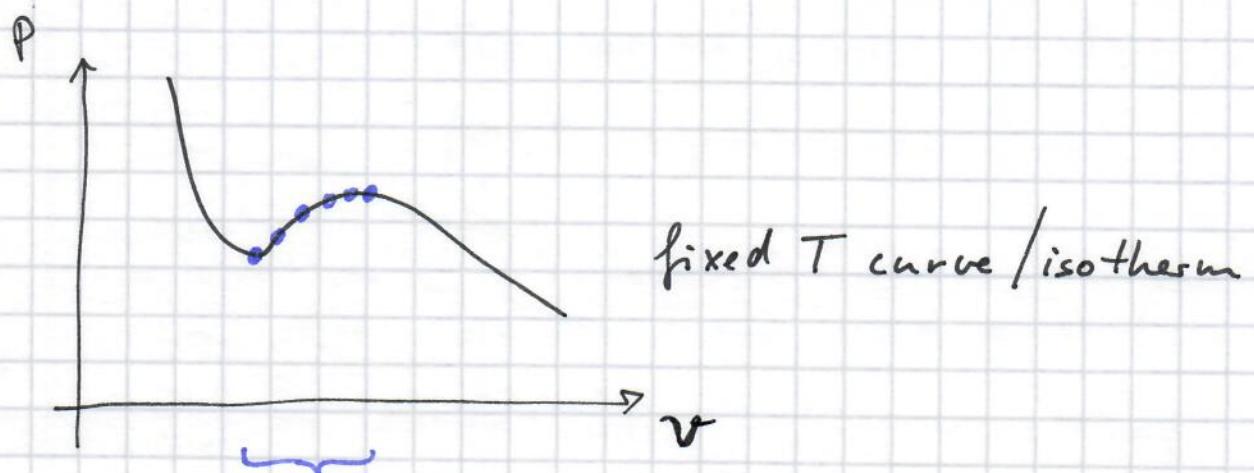
ideal gas law is recovered!

We can think of the $-b$ term as accounting for the fact that the particles are not point particles (repulsive portion of the potential curve). b : "excluded volume per particle"

We can think of the $-\frac{\alpha}{v^2}$ term as accounting for the attractive portion of the portion of the potential: $v^{-2} \propto N^2 \Rightarrow$ we have $N(N-1)/2$ pairwise interactions.

α : measures interatomic or intermolecular attraction

Let's look at the P-v diagram:



we increase
the volume
and the pressure
goes up

\Rightarrow unphysical

$$\left(\frac{\partial P}{\partial V}\right)_T > 0$$

Stability requires $\left(\frac{\partial P}{\partial V}\right)_T < 0$

$$\text{and } K_T > 0$$

see HW

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

isothermal compressibility

Something is wrong ☹

Nevertheless: van der Waals used proposed E-O-S to explain the existence of a critical point (P_c, V_c, T_c) for the gas - liquid phase transition.

↳ this critical point had been found experimentally in 1869

vander Waals was awarded Nobel Prize in 1910

Also: van der Waals used E-O-S to derive "Law of corresponding states" (1880) :

All gases satisfy a universal equation of state once their variables are expressed in terms of dimensionless parameters.

see
page 134

Something is right ☺

What's the fix?

Two more comments:

- b turns out to depend on v and T
 → we will explore this more when we discuss the virial expansion (approximate small parameter expansion)
- van der Waals viewed the qualitative agreement between his theory and experiment as a major victory for the "atomistic theory of matter" (recall, this was at the turn of the century → think about where quantum theory was at...).

Let's start thinking about the "fix":

The E-O-S can be rewritten as:

$$Pv^3 - (Pb + \gamma T)v^2 + av - ab = 0$$

Cubic equation in $v \rightarrow$ three roots

Let's use the additional constraints:

$$\left(\frac{\partial P}{\partial v}\right)_T = 0$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0$$

Mathematically, this means that we are looking for v , P , and T such that the three roots coincide.

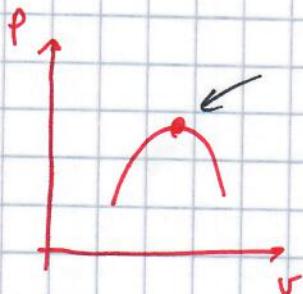
Said differently, we are looking for ^{values} ~~all~~ of the thermodynamic variables such that the $P-v$ curve has no "turn around points".



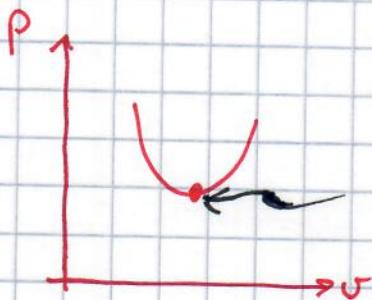
this will become clear
in Fig. on page 136a

132a

Add-on to p. 132:

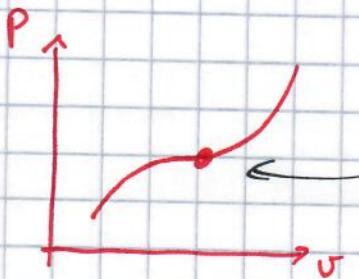


$$\frac{\partial P}{\partial v} = 0 \quad \& \quad \frac{\partial^2 P}{\partial v^2} < 0$$



$$\frac{\partial P}{\partial v} = 0 \quad \& \quad \frac{\partial^2 P}{\partial v^2} > 0$$

How about $\frac{\partial P}{\partial v} = 0$ & $\frac{\partial^2 P}{\partial v^2} = 0$?!



$$\frac{\partial P}{\partial v} = 0 \quad \& \quad \frac{\partial^2 P}{\partial v^2} = 0$$

Physically: The $\left(\frac{\partial P}{\partial v}\right)_T = 0$ condition implies

133

$$k_T \rightarrow \infty$$

The three conditions give us a set of parameters: (v_c, P_c, T_c)

this is the critical point!

We can use v_c, P_c , and T_c to write down the vdW EoS in dimensionless form

Solving the three equations:

$$\left(\frac{\partial P}{\partial v}\right)_T = \frac{-kT}{(v-b)^2} + \frac{2a}{v^3} \stackrel{!}{=} 0 \Rightarrow kT = \frac{3a}{v^4} (v-b)^3$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2kT}{(v-b)^3} - \frac{6a}{v^4} \stackrel{!}{=} 0 \Rightarrow kT = \frac{2a}{v^3} (v-b)^2$$

setting the 2 r.h.s.'s equal

$$\Rightarrow \frac{3a}{v^4} (v-b)^3 = \frac{2a}{v^3} (v-b)^2$$

↓

$$v_c = 3b$$

$$\text{Plug } v_c = 3b \text{ into } kT = \frac{2a}{v^3} (v-b)^2$$

$$\Rightarrow kT_c = \frac{8a}{27b}$$

$$\text{Plug } v_c = 3b \text{ and } kT_c = \frac{8a}{27b} \text{ into } P = \frac{kT}{v-b} - \frac{a}{v^2}$$

$$\Rightarrow P_c = \frac{a}{27b^2}$$

$$(v_c, kT_c, P_c) = \left(3b, \frac{8a}{27b}, \frac{a}{27b^2} \right)$$

determines the critical point.

Also, this set of values can be used to rewrite the E-O-S in dimensionless form.

$$\frac{P}{P_c} = \frac{\frac{8}{kT_c} \frac{kT}{v-b}}{3 \frac{v}{v_c} - 1} - \frac{3}{\left(\frac{v}{v_c}\right)^2}$$

$$\text{or } \tilde{P} = \frac{P}{P_c} ; \quad \tilde{T} = \frac{kT}{kT_c} ; \quad \tilde{v} = \frac{v}{v_c}$$

$$\Rightarrow \tilde{P} = \frac{8 \tilde{T}}{3 \tilde{v} - 1} - \frac{3}{\tilde{v}^2}$$

How do we get this (or: are the original and scaled E-O-S's truly equal)?

$$\text{Start w/ } P = \frac{kT}{v-b} - \frac{a}{v^2}$$

divide both sides by $\frac{a}{27b^2}$

$$\frac{P}{\frac{a}{27b^2}} = \frac{\frac{kT}{a}}{\frac{a}{27b^2}(v-b)} - \frac{\frac{a}{a}}{\frac{a}{27b^2} v^2}$$

$$\underbrace{\frac{8kT}{a}}_{27b^2} \underbrace{b\left(\frac{3v}{3b} - 1\right)}$$

$$\underbrace{\frac{3}{\left(\frac{v}{3b}\right)^2}}$$

$$\underbrace{\frac{\frac{8kT}{a}}{27b^2}}_{\frac{3v}{3b} - 1}$$

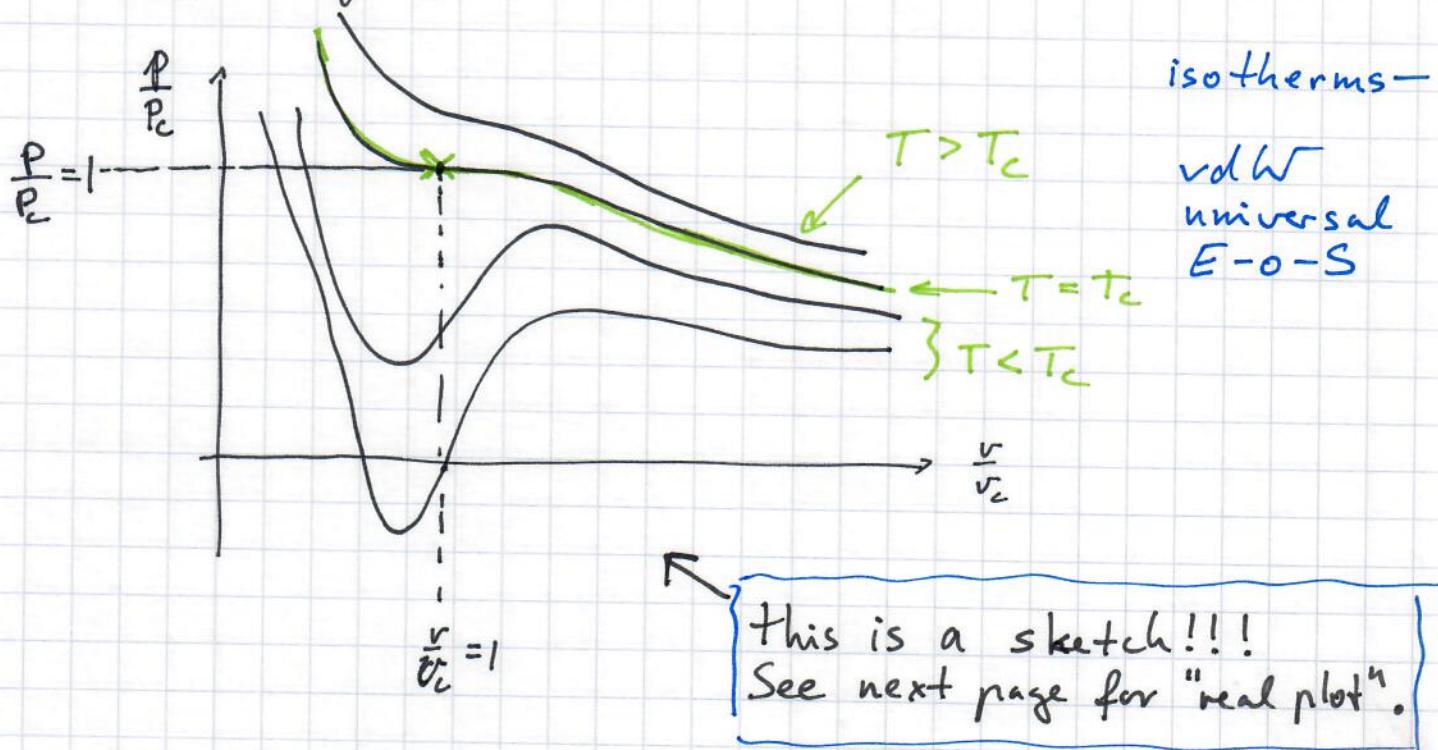
$$\Rightarrow \frac{P}{P_c} = \frac{\frac{8kT}{a}}{\frac{3v}{3b} - 1} - \frac{3}{\left(\frac{v}{v_c}\right)^2}$$



so: it all checks

out!

The reformulation in terms of scaled dimensionless parameters constitutes van der Waals' law of corresponding states.



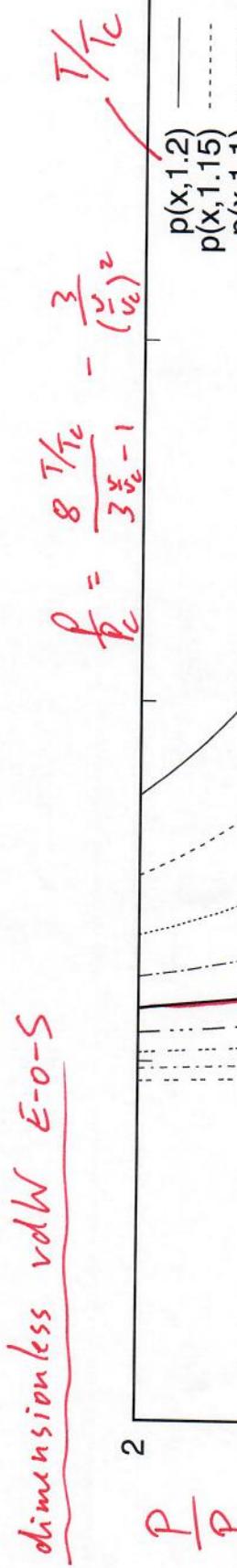
Still: we are dealing with negative compressibility region and negative pressure region

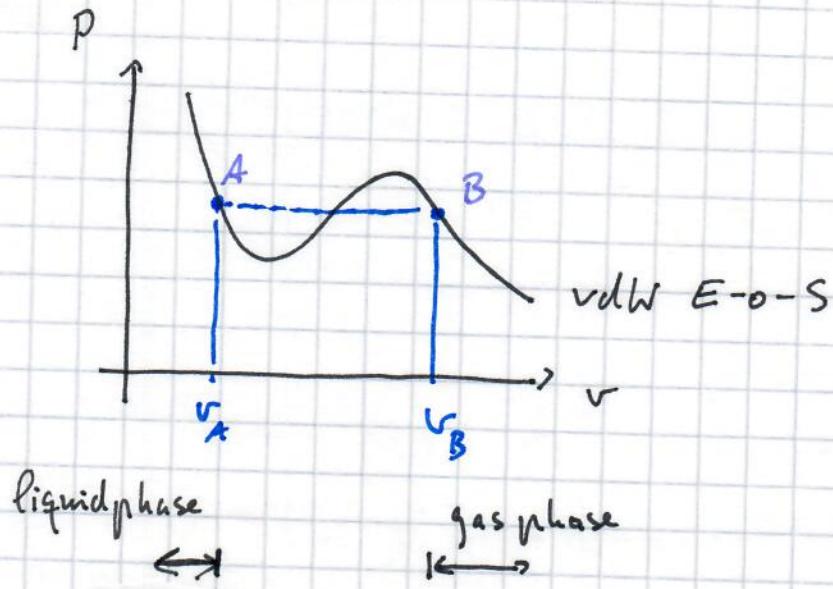
↳ both unphysical!

"fix" to coexistence region is provided by Maxwell construction.

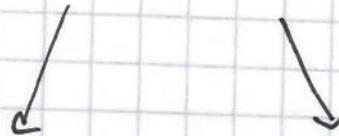
Enforce $\mu_A = \mu_L$ when the two phases co-exist.

136 a





Maxwell construction connects A and B by a horizontal line



$$(v_A, P_A, T_A)$$

$$(v_B, P_B, T_B)$$

$$v_A \neq v_B$$

$$P_A = P_B$$

$$T_A = T_B$$

$P_A = P_B$ is determined by non-local condition:

$$P_A (v_B - v_A) = \int_A^B P(v, T) dv$$

plug in vdW E-o-S

work along the
isobar

integrated work
along the vdW loop

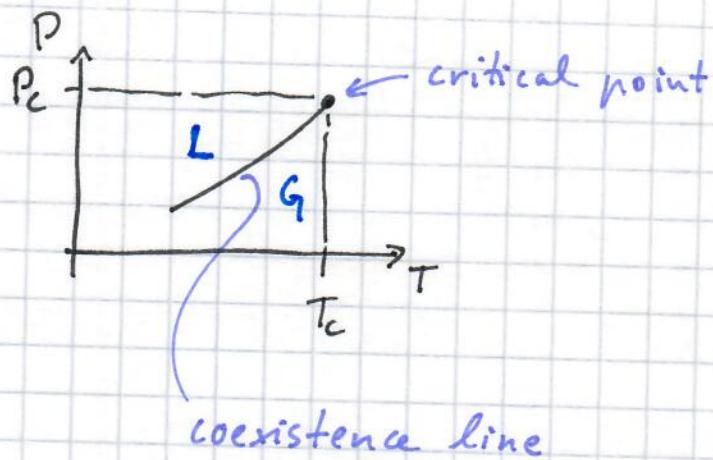
→ this fixes $\mu_A = \mu_B$, allowing the free interchange of molecules or atoms between the liquid at A and the gas at B at constant pressure and temperature.

There is some weirdness to Maxwell's construction:
It uses the unphysical portion of the vdW EoS to construct what the "true" behavior should be.

What happens when $T > T_c$?

The iso therm s decrease monotonically with v .

↳ there is no way to distinguish the liquid and the gas phase

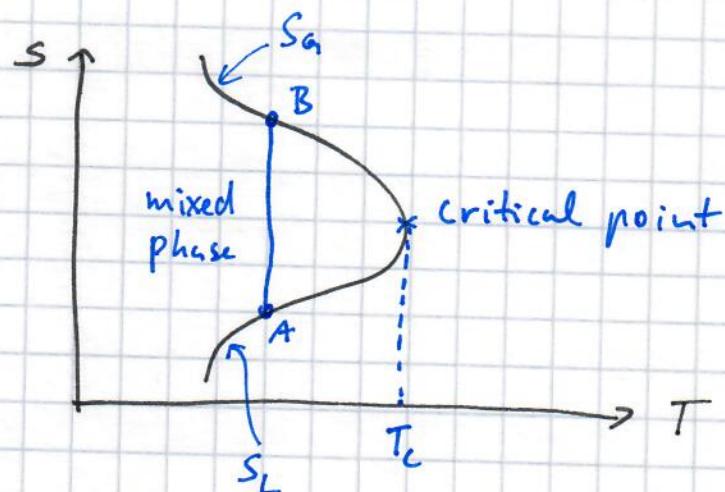


L139

Let's go back to Clapeyron equation:

$$\frac{dP}{dT} = \frac{\ell}{T \Delta v} = \frac{T (s_g - s_L)}{T \Delta v} = \frac{s_g - s_L}{v_g - v_L}$$

$$\ell = T (s_g - s_L)$$



At the critical point : $\Delta v \rightarrow 0$

$$\frac{dP}{dT} \text{ finite}$$

$\Rightarrow \ell$ must go to zero

note: this applies only to phase transition that connects two "fluid phases" !

Moreover: the two fluid phases must be,
of one and the same material.

Important note: in this discussion, a
gas is considered a
special type of fluid