Phys 344.

Lecture 27.

- Van der Waals equation.

  — A good model for gas-liquid phase transition. (qualitative)

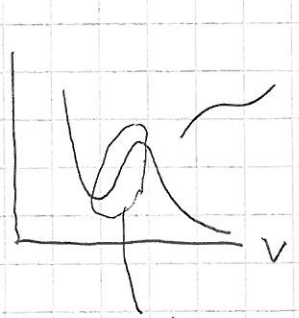
$$P = \frac{NkT}{V-Nb} - \frac{aN^2}{V^2}.$$

Nb — volume correction. ($\propto N$)

$\frac{aN^2}{V^2}$ — long range attraction correction. $\propto$ (# density)^2

- Isothermal lines. T = constant

High T — ideal gas.

low T: 

higher order polynomial.

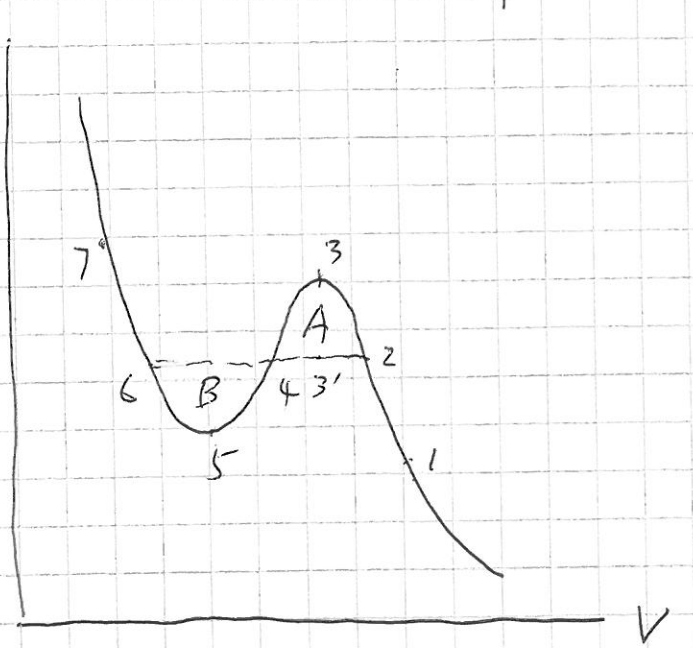
doesn't make sense! $\left(\frac{\partial P}{\partial V}\right)_T \geq 0$.

as $P\uparrow$, $V\uparrow$!

Maxwell showed:

The system actually goes by: $1 \to 2 \to 6 \to 7$.

skipping 3, 5.



① . 3 and 5 are thermodynamically unstable.

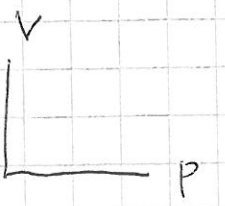
e.g.: $G_{3'} < G_3$. at const T and P.

the system prefers 3'.

② . Where are 2 and 6 ? (why not at a higher or lower P ?)

Maxwell construction: area A = area B.

[Proof]. loop : 2-3-4-5-6-2



$$\int_{loop} dG = 0 = \int_{loop} \left(\frac{\partial G}{\partial P}\right)_T dP = \int_{loop} V dP$$

$$= |\text{Area A}| - |\text{area B}|$$

$$= 0 .$$

OR: one can use the second law:

If A ≠ B.
output work ≠ 0.
only one heat source.

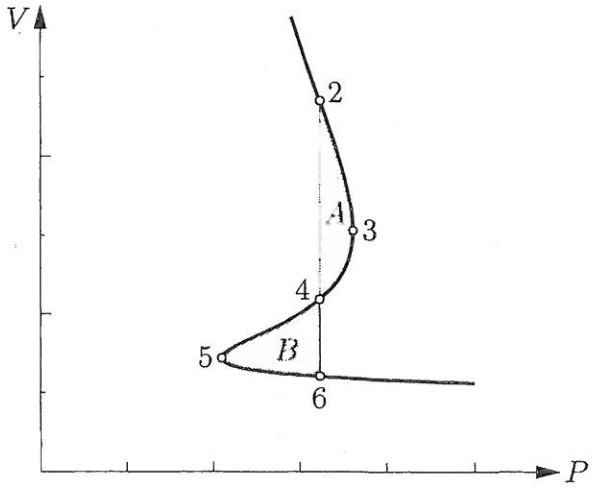


Figure 5.22. The same isotherm as in Figure 5.21, plotted sideways. Regions A and B have equal areas.

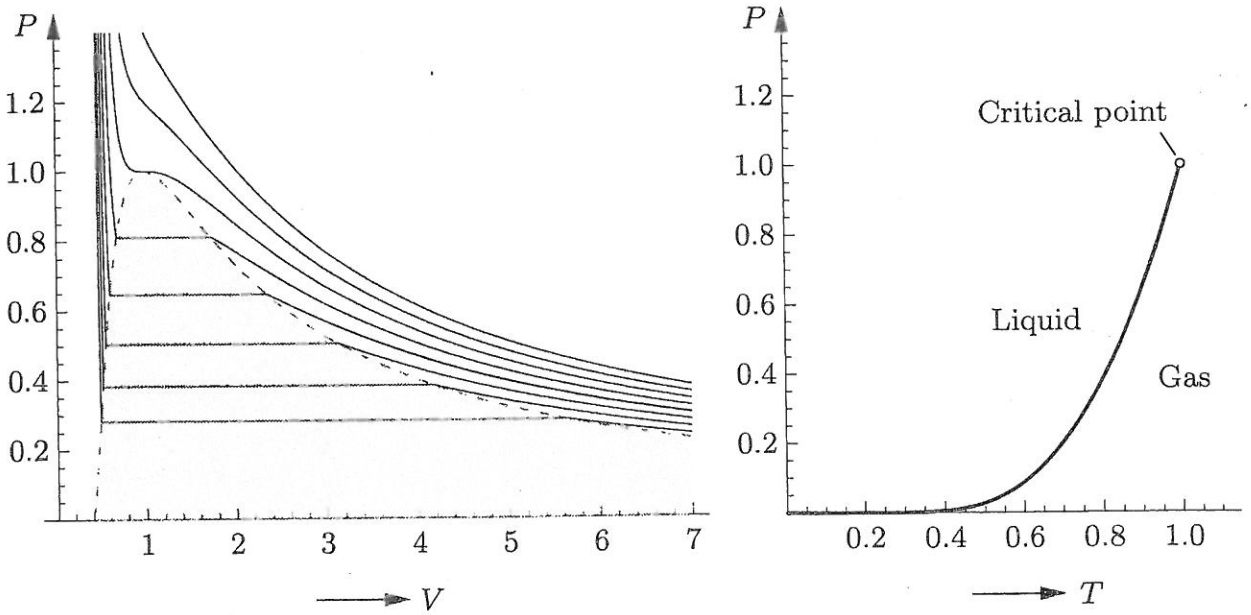


Figure 5.23. Complete phase diagrams predicted by the van der Waals model. The isotherms shown at left are for T/T_c ranging from 0.75 to 1.1 in increments of 0.05. In the shaded region the stable state is a combination of gas and liquid. The full vapor pressure curve is shown at right. All axes are labeled in units of the critical values.

③ Meaning of the horizontal line:

V changes discontinuously. — phase transition!

(density too!)

2 — saturated gas

6 — saturated liquid.

between 2 and 6 — Mixture of liquid + gas.

P — Vapour pressure at T.

④ As Temp increases, along an isotherm, the two points 3 and 5 merge into one. — the critical point.

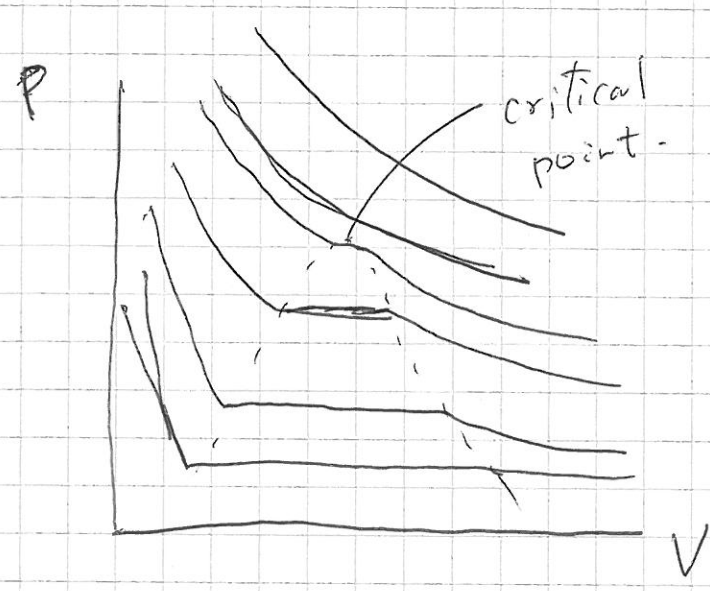
$$\left(\frac{\partial P}{\partial V}\right)_T = 0.$$

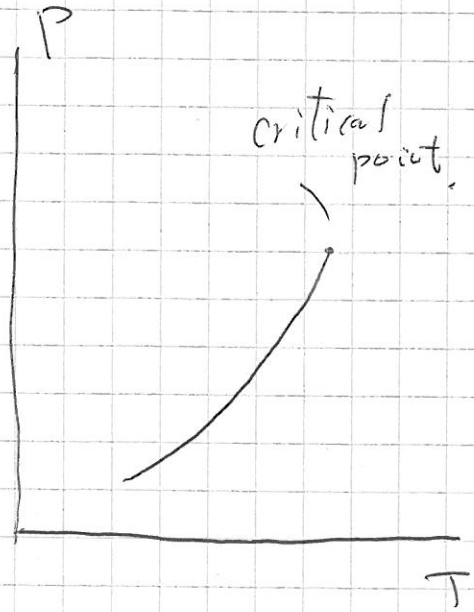
$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0. \quad \text{— neither max nor min.}$$

At the critical point, the difference between liquid and gas disappears. same density, No surface tension, same compressibility.

(at $T > T_c$, we can have gas only)

To find (T, V, P) at the critical point.





$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}.$$

$$\left(\frac{\partial P}{\partial V}\right)_T = 0: \quad -\frac{NkT}{(V-Nb)^2} + \frac{2N^2a}{V^3} = 0 \quad (1)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0: \quad \frac{2NkT}{(V-Nb)^3} - \frac{6N^2a}{V^4} = 0 \quad (2)$$

Solve for V: $\frac{V - Nb}{2} = \frac{V}{3} \Rightarrow V = 3Nb.$

$\therefore \boxed{V_c = 3Nb}$ → plug into (1): $-\frac{NkT_c}{(2Nb)^2} + \frac{2N^2a}{(3Nb)^3} = 0$.

$$\boxed{T_c = \frac{8a}{27bk}}$$

$$\boxed{P_c = \frac{Nk\frac{8a}{27bk}}{3Nb - Nb} - \frac{aN^2}{(3Nb)^2} = \frac{a}{27b^2}}$$