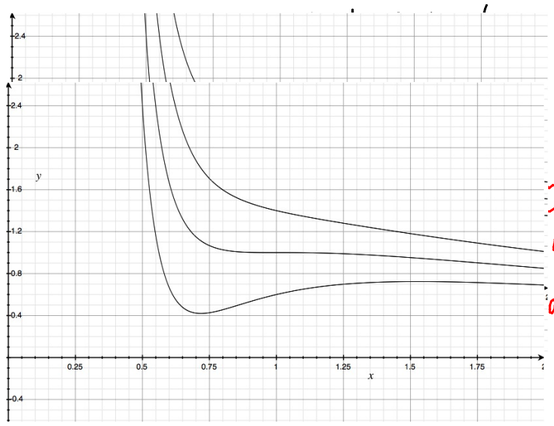
Van der Waals model



impossible
for finite size
molecule b

$$V_{min} = Nb$$

$$P(V - Nb) = NkT$$

- there are short-range attractive forces between molecules in a gas (van der Waals forces)

Imagine all molecules frozen in place, so only energy is a potential energy due to these attractive forces

e.g. ⊕ ⊖

$PE = k\frac{qq}{r} < 0$

Suppose I double density of particles $\frac{N}{V}$

each molecule has twice as many neighbors & twice the PE

⊕ & ⊖ PE becomes more negative

$PE_{1\ molecule} \sim \frac{N}{V}$

$$PE_{gas} \sim N\,PE_{1\ molecule} \sim \frac{N^2}{V}$$

$$PE = -a\frac{N^2}{V} = U$$

$$P_{\substack{due\ to \\ PE}} = -\frac{dU}{dV} = -\frac{d}{dV}\left(-a\frac{N^2}{V}\right) = -a\frac{N^2}{V^2}$$

$$P_{total} = P_{\substack{ideal \\ gas}} - a\frac{N^2}{V^2}$$

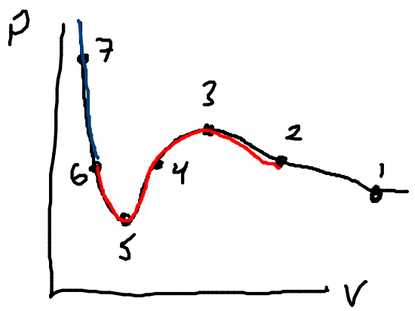
$$P = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2}$$

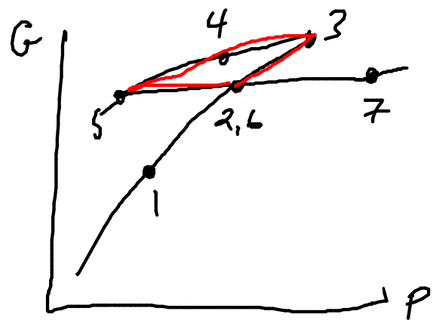
$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NkT$$

van der Waals model

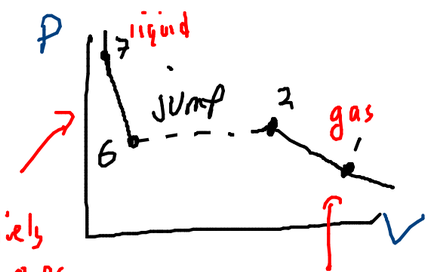
a & b are free parameters which depend on the type of gas

Fig. 5-21 in Schroeder





Unstable - does not appear in reality

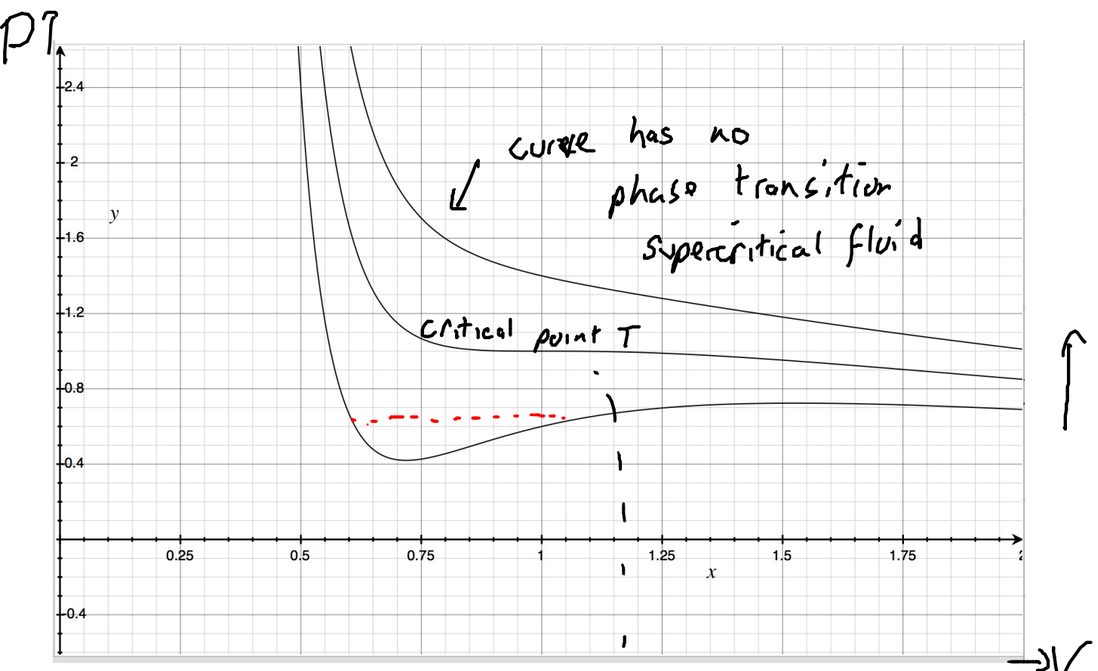


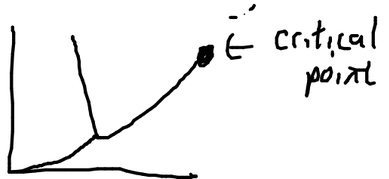
volume is relatively constant over changes in pressure

smaller slope - volume more responsive to pressure

as you lower pressure, volume suddenly jumps to a (much) higher value

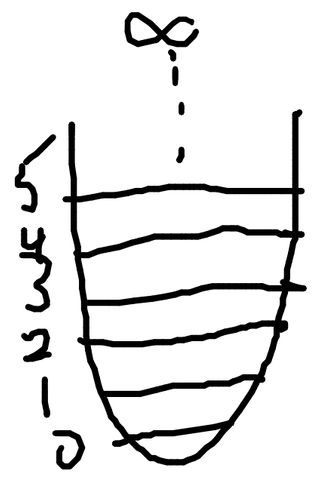
- phase change from a liquid to a gas





Chapter 6

Consider a single harmonic oscillator in QM



What is probability that this oscillator is in its ground state?

- if all states were equally likely,

$$P = \frac{1}{\infty} = 0.$$

- if energy conserved, (no energy in or out).

If H.O. is in the ground state, $P = 100\%$
if not, $P = 0\%$

. if oscillator can exchange energy with its environment,

now it gets interesting.