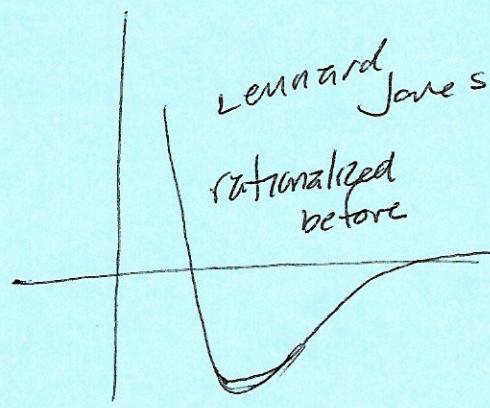


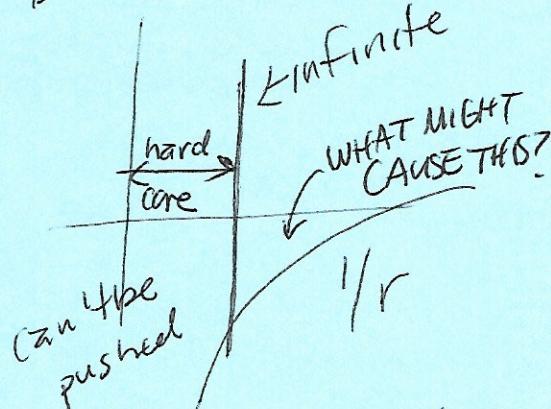
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We have seen the simplest behavior possible for a gas, the ideal gas. What are the smallest modifications we can make to make it more realistic? In particular to make it able to form liquids.

ideal gases don't form liquids



But consider this first



Long-range attraction can be caused by magnetic moment, electronic charge distribution etc.

So now the available volume is $V - Nb$

$$S_{\text{vdW}} = \sum_{i \neq j} u_{ij} = \frac{1}{2} \int d^3x \, d^3y \, n(\vec{x}) \, n(\vec{y}) \, U(\vec{x} - \vec{y})$$

This gives you where b is the excluded volume per particle
total number of part

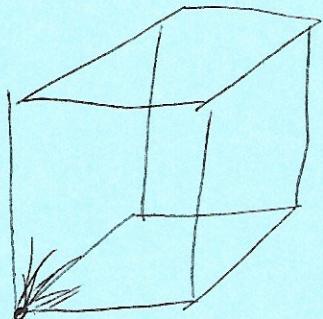
but multiply times density or concentration in space, particles per volume.

over counting whole space for y -particle
for x -particle

An important simplification is $\bar{n}(x) = n$, the concentration at any point is the average concentration, so the concentration is the average. This is called a mean-field approximation, if you are a theoretician you typically start here, although it is not the only thing you could take as average.

Let n be isotropic, then $\Delta U = \frac{1}{2} n^2 \int d^3x d^3y U(x,y)$

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Let start at $0,0$, then $\Delta U = \frac{1}{2} n^2 \int d^3x d^3y U(y)$

~~$$\Delta U = \frac{1}{2} n^2 \int d^3x d^3y \frac{1}{2} n^2$$~~

Volume

$$\Delta U = \frac{1}{2} n^2 V \int d^3y U(y)$$

From $0,0$ to everything else

All space!

$$\Delta U = \frac{1}{2} \frac{N^2}{V} \int d^3y U(y)$$

$$\begin{aligned} \Delta U &= \frac{1}{2} n^2 V (f(2a)) N = \frac{N}{V-Nb} \\ &\Rightarrow n^2 = \frac{-2aU}{2aV} = \sqrt{\frac{U}{Va}} \end{aligned}$$

$$\Delta U = \frac{1}{2} \frac{N^2}{V} (-2a)$$

$$\Rightarrow \Delta U = -\frac{2N^2}{V}$$

KK Eq. 10.37

-2a
because it will
make it pretty in the
future

with $a > 0$, ΔU is attractive

~~$$F = U - \infty, \text{ so } \Delta F \approx \Delta U = -\frac{N^2 a}{V}$$~~
~~$$\text{Also, } F = -Nc \left[\ln \left(\frac{n}{n_Q} \right) - 1 \right] = -Nc \left[\ln \left(\frac{n}{V-Nb} \right) - \ln n_Q + 1 \right]$$~~
~~$$F_{\text{ext}} = -Nc \ln N + \frac{Nc}{V-Nb} + Nc \ln n_Q + 1 = -\frac{N^2 a}{V}$$~~
~~$$\text{ext} = -Nc \left[\frac{V-Nb}{N} n_Q \right] + Nc \ln N$$~~

Before, we derived the free energy for an ideal gas,

$$F_{\text{ideal}} = -N\tau \left[\ln \left(\frac{n_Q}{n} \right) + 1 \right] \quad \begin{matrix} \text{KK Eq. 6.24} \\ \text{KK Eq. 10.34} \end{matrix}$$

$$F_{\text{ideal}} = -N\tau \left[\ln \left(\frac{n_Q V}{N} \right) + 1 \right]$$

Replacing V with $V-Nb$ and adding the adjustment ΔU , we can get the free energy of a less ideal gas, the van der Waals gas.

$$F_{\text{vdW}} = -N\tau \left\{ \ln \left[\frac{n_Q(V-Nb)}{N} \right] + 1 \right\} - \frac{\alpha N^2}{V} \quad \begin{matrix} \text{KK Eq. 10.38} \end{matrix}$$

$$F_{\text{vdW}} = -N\tau \left[\ln n_Q + \ln(V-Nb) - \ln N + 1 \right] - \frac{\alpha N^2}{V}$$

since

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{\partial}{\partial V} \left[N\tau \ln(V-Nb) + \frac{\alpha N^2}{V} \right]$$

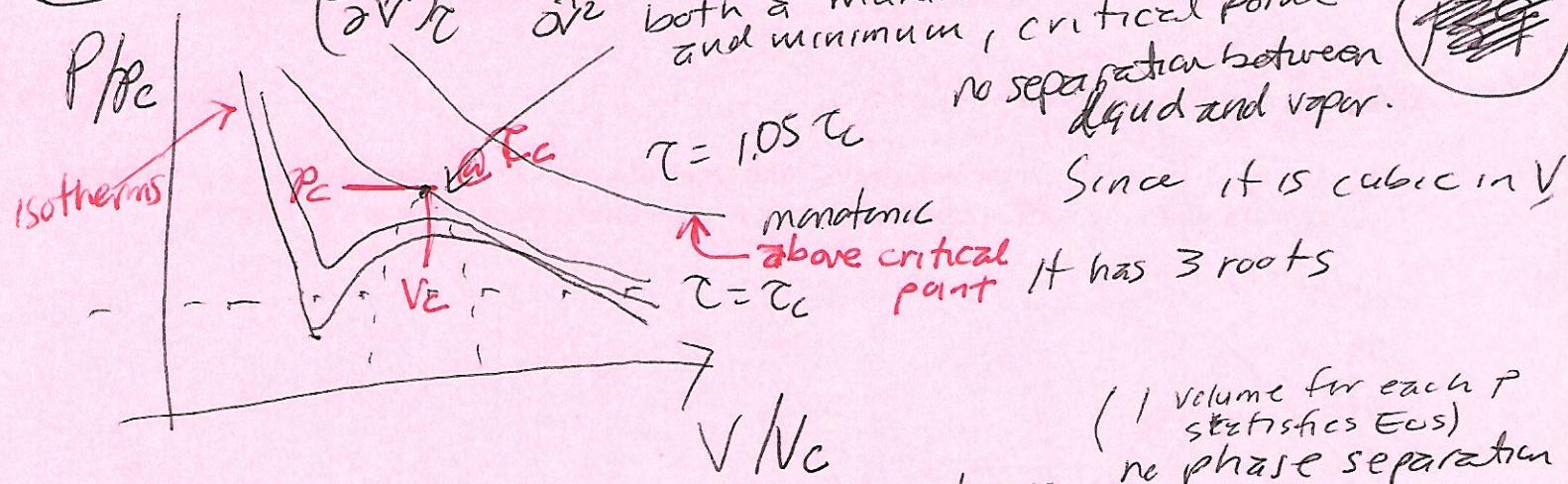
$$P = N\tau \cdot \frac{1}{V-Nb} \cdot 1 - \frac{\alpha N^2}{V^2} = \frac{N\tau}{V-Nb} - \frac{N^2 \alpha}{V^2} \quad \begin{matrix} \text{KK Eq. 10.39} \end{matrix}$$

$$\Rightarrow \boxed{(P + N^2 \alpha / V^2)(V - Nb) = N\tau} \quad \begin{matrix} \text{KK Eq. 10.40} \\ \text{van der Waals equation of state} \end{matrix}$$

c.f. $\uparrow pV = N\tau$ for ideal gas
 effective pressure
 arising from the binding energy

decreased volume

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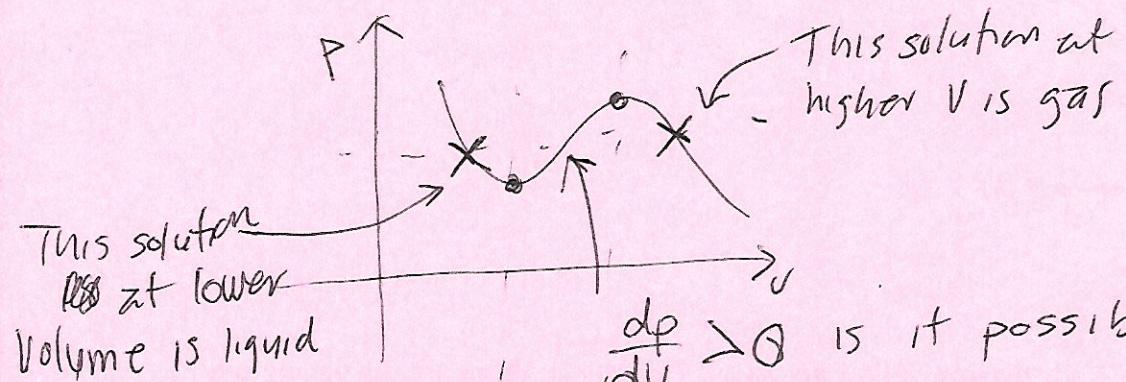
Every $T > T_c$ isotherm is monotonic

Every $T < T_c$ has 3 roots
 $T = T_c$ has 1 solution

(1 volume for each P
 statistics EoS)
 no phase separation

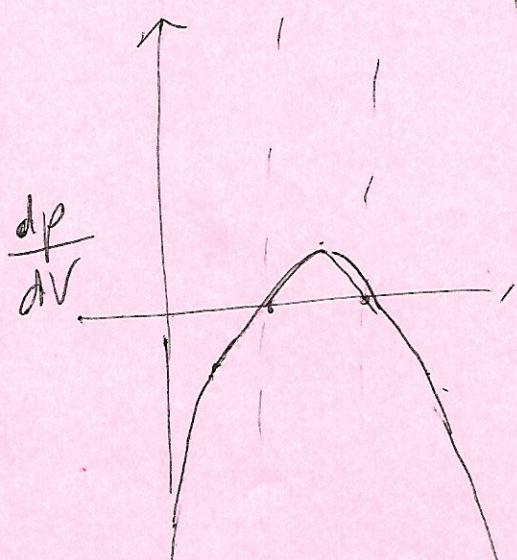
(3 different values of the
 volume solve the EoS)
 (3 solutions are degenerate)

Several points with $\frac{dP}{dV} = 0$



$\frac{dP}{dV} > 0$ is it possible

You increase the pressure and the
 volume increases. Does it make sense?



VdW is the simplest model
 that gives you phase coexistence
 (microscopically)

Take the vdW EoS $\left(P + \frac{N^2 \alpha}{V^2} \right) / (V - Nb) = N \bar{\gamma}$

times $\frac{V^2}{P}$

$$\Rightarrow \left(\frac{V^2 P}{P} + \frac{N^2 \alpha V^2}{P V^2} \right) (V - Nb) = \frac{N \bar{\gamma} V^2}{P}$$

$$\left(V^2 + \frac{N^2 \alpha}{P} \right) (V - Nb) = \frac{N \bar{\gamma} V^2}{P}$$

$$V^3 - V^2 Nb + \frac{N^2 \alpha V}{P} - \frac{N^3 \alpha b}{P} - \frac{N \bar{\gamma} V^2}{P} = 0$$

Cubic equation $\bar{\alpha}x^3 + bx^2 + cx + d = 0$

$$1 V^3 - \left(Nb + \frac{N \bar{\gamma}}{P} \right) V^2 + \frac{N^2 \alpha}{P} V - \frac{N^3 \alpha b}{P} = 0$$

$$\bar{\alpha} = 1$$

$$b = -N \left(b + \frac{\bar{\gamma}}{P} \right)$$

$$c = N^2 \frac{\alpha}{P}$$

$$d = -N^3 \frac{\alpha b}{P}$$

It is the critical isotherm, so T_c

In the degenerate case there is only 1 solution, so V_c

$$(V - V_c)^3 = 0 (V - V_c)^2 (V - 2V_c) = (V^2 - 2VV_c + V_c^2)(V - V_c)$$

$$= V^3 - V^2 V_c - 2V^2 V_c + 2V V_c^2 + V_c^2 V - V_c^3$$

$$= V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3$$

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$$\Rightarrow \cancel{P} + V_c^3 = + N^3 \frac{ab}{P}$$

d)

$$c) 3V_c^2 = N^2 \frac{a}{P}$$

$$b) +3V_c = + N \left(b + \frac{a}{P} \right)$$

$$a) 1 = 1$$

because we are at the critical point, V_c , P_c , T_c

WHAT IS THE CRITICAL ~~B~~ VOLUME?

$$\frac{V_c^3}{3V_c^2} = \frac{\frac{N^3 ab}{P}}{\frac{N^2 a}{P}} = \frac{N^3 ab P}{N^2 a P} = Nb = \frac{1}{3} V_c$$

extensive to intensive

$$\Rightarrow \underline{V_c = 3Nb}$$

The total volume occupied by the particles is Nb , so density is high

WHAT IS THE CRITICAL PRESSURE?

$$P_{c\cancel{a}} \cancel{3P_c V_c^2 = N^2 a}$$

$$P_c = \frac{N^2 a}{3V_c^2} = \frac{N^2 a}{3(3Nb)^2} = \frac{N^2 a}{27N^2 b^2} = \frac{a}{27b^2}$$

WHAT IS THE CRITICAL TEMPERATURE?

$$3V_c = Nb + \frac{NT_c}{P_c} \Rightarrow P_c(3V_c - Nb) = T_c = \frac{a}{27b^2} (9Nb - Nb)$$

$$T_c = \frac{8Nb a}{27Nb^2} = \frac{8a}{27b^2} //$$

a, b are not directly measured in an experiment,
but V, P, T are.

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$$\frac{1}{V_c} \left(P + \frac{N^2 a}{V^2} \right) \left(V - Nb \right) = N\tau \cdot \frac{1}{V_c}$$

$$\frac{1}{P_c} \left(P + \frac{N^2 a}{V^2} \right) \left(\frac{V}{V_c} - \frac{Nb}{V_c} \right) = \frac{N\tau}{V_c} \cdot \frac{1}{P_c}$$

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

$$\left(\frac{P}{P_c} + \frac{V_c^2}{V^2} \cdot \frac{N^2 a}{V_c^2 P_c} \right) \left(\frac{V}{V_c} - \frac{Nb}{V_c} \right) = \frac{N\tau_c}{V_c P_c} \quad \frac{\tau}{\tau_c}$$

$\frac{P}{P_c}, \frac{V}{V_c}, \frac{\tau}{\tau_c}$ are dimensionless quantities, call them $\hat{P}, \hat{V}, \hat{\tau}$

$$\left[\hat{P} + \left(\frac{1}{\hat{V}} \right)^2 \frac{N^2 a}{V_c^2 P_c} \right] \left[\hat{V} - \frac{Nb}{V_c} \right] = \frac{N\tau_c}{V_c P_c} \quad \hat{\tau}$$

$$V_c^2 P_c = \frac{9N^2 b^2 a}{27b^2} = \frac{9N^2 a}{27 \cdot 3} = \frac{N^2 a}{3}$$

$$\left[\hat{P} + \left(\frac{1}{\hat{V}} \right)^2 \frac{N^2 a}{\frac{N^2 a}{3}} \right] \left[\hat{V} - \frac{Nb}{3Nb} \right] = \frac{N\tau_c}{V_c P_c} \quad \hat{\tau}$$

$$\frac{T_c}{V_c P_c} = \frac{\frac{8a}{27b}}{\frac{3Nb^2}{27b^2}} = \frac{8 \cdot 27 \alpha b^2}{3 \cdot 27 \alpha b^2 N} = \frac{8}{3N}$$

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$$\left(\hat{P} + \frac{3}{\hat{V}^2}\right) \left(\hat{V} - \frac{1}{3}\right) = N \cdot \frac{8}{3N} \hat{T}$$

$$\boxed{\left(\hat{P} + \frac{3}{\hat{V}^2}\right) \left(\hat{V} - \frac{1}{3}\right) = \frac{8}{3} \hat{C}}$$

KK Eq. 10.44

Law of corresponding states

Not as good though because

~~Claussius-Claperyon comes~~

from first principles, pure physics, working s. thermodynamics axioms while 10.44 comes from a phenomenological model

kind of Claussius-Claperyon in the sense that it is valid irrespective of the microscopic

$$F_{\text{total}} = F_s + F_R \text{ should be minimal, so } dF_{\text{total}} = dF_s + dF_R = 0$$

$$\frac{dV}{dP} \left[\left(\frac{\partial F_s}{\partial V} \right)_T - \left(\frac{\partial F_R}{\partial V} \right)_T \right] = 0 = -P_s - (-P_R) = -P_s + P_R = 0$$

mechanical equilibrium

$$\Rightarrow P_R = P_s$$