The van der Waals equation of state

Ideal gas law: $pv = RT$ where $v = N_A V/N$ is the molar volume and $R = N_A k_B = 8.314\ \mathrm{J/mol\cdot K}$ is the gas constant. vdW eqn of state:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

where a and b are constants; $[a] = \frac{\overset{\text{Joule}}{\mathrm{J}} \cdot \overset{\text{liter}}{\ell}}{\mathrm{mol}^2}$, $[b] = \frac{\ell}{\mathrm{mol}}$

The a constant accounts for long-ranged attraction between molecules that drives condensation, and b is an excluded volume accounting for hard cores. So $v_{min} = b$. This can be rearranged as

$$p(T, v) = \frac{RT}{v - b} - \frac{a}{v^2}$$

Q: At fixed T, is this monotonic decreasing in v? Clearly it is decreasing for $v = b + \delta v$ and as $v \to \infty$. In between? Consider the derivative:

$$\frac{\partial p}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$$

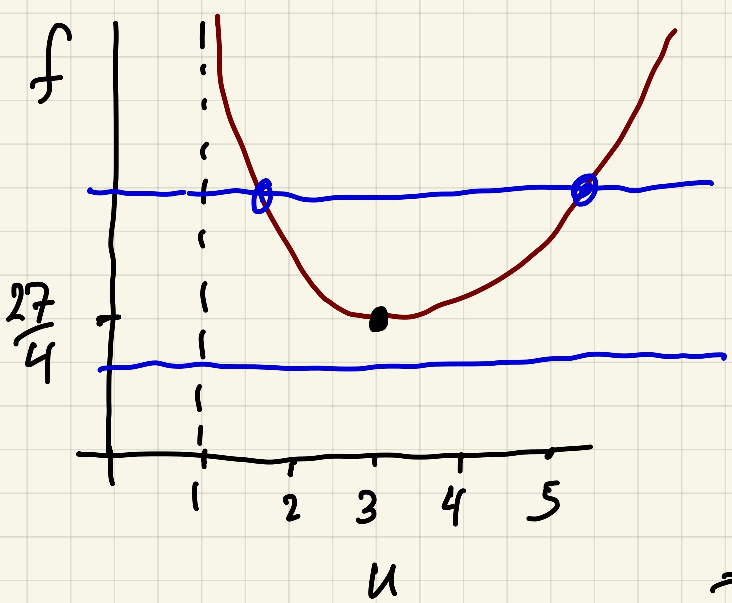
Set this to zero to see if $p(v)$ turns around:

$$\frac{2a}{bRT} = \frac{u^3}{(u-1)^2} \equiv f(u)$$

with $u \equiv v/b$ dimensionless. Now since

$$f'(u) = \frac{3u^2}{(u-1)^2} - \frac{2u^3}{(u-1)^3} = \frac{u^2(u-3)}{(u-1)^3}$$

we see that $f'(u)=0$ has one sol$^{\underline{n}}$ at $u^*=3$, where $f(3) = \frac{27}{4}$.



$$\frac{2a}{bRT} > \frac{27}{4} \Rightarrow 2 \text{ sol}^{\underline{ns}}$$

$$\frac{2a}{bRT} < \frac{27}{4} \Rightarrow 0 \text{ sol}^{\underline{ns}}$$

$$\Rightarrow \frac{2a}{bRT_c} = \frac{27}{4} \Rightarrow T_c = \frac{8a}{27bR}$$

We also have $v_c = u^* b = 3b$ and $p_c = p(T_c, v_c) \Rightarrow$

$$p_c = \frac{a}{27b^2} \quad , \quad v_c = 3b \quad , \quad T_c = \frac{8a}{27bR}$$

These are the coordinates of the <u>critical</u> <u>point</u>.

Expressed in terms of the dimensionless quantities

$$\bar{T} = T/T_c \quad , \quad \bar{p} = p/p_c \quad , \quad \bar{v} = v/v_c$$

we obtain the universal vdW eqn of state

$$\bar{p}(\bar{T}, \bar{v}) = \frac{8\bar{T}}{3\bar{v}-1} - \frac{3}{\bar{v}^2}$$

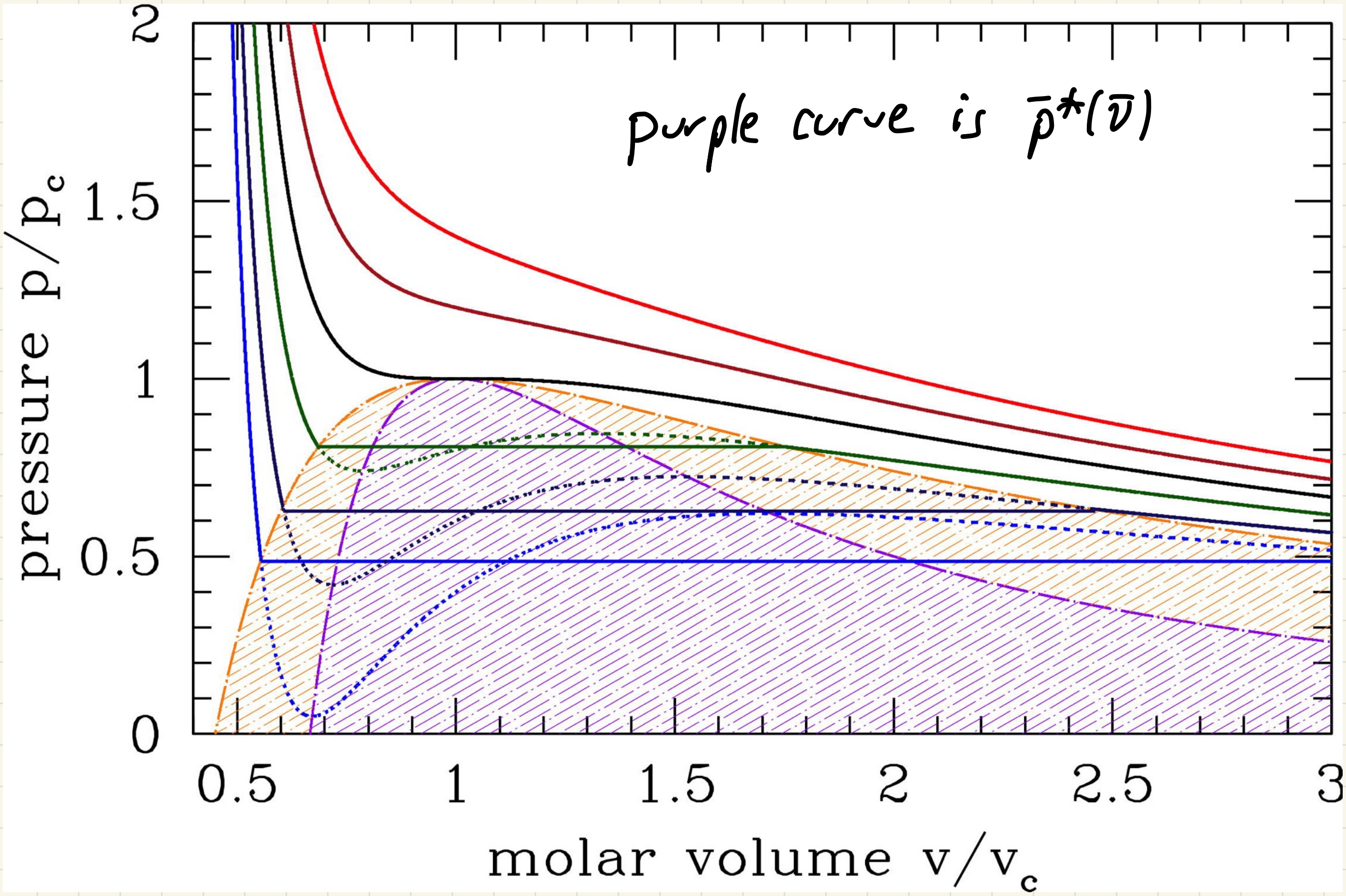
The locus of points in (v,p) plane where $\left.\frac{\partial p}{\partial v}\right|_T = 0$ is then found by setting

$$\left.\frac{\partial p}{\partial v}\right|_T = 0 \Rightarrow \frac{RT}{v-b} = \frac{2a(v-b)}{v^3}$$

and substituting this into vdW:

$$p^*(v) = \frac{RT}{v-b} - \frac{a}{v^2} = \frac{2a}{v^2} - \frac{2ab}{v^3} - \frac{a}{v^2}$$

$$= \frac{a}{v^2} - \frac{2ab}{v^3} \quad \text{i.e.} \quad \bar{p}^*(\bar{v}) = \frac{3\bar{v}-2}{\bar{v}^3}$$



Along $p^*(v)$ the compressibility $\kappa_T = -\frac{1}{v}\frac{\partial v}{\partial p}\Big|_T$ diverges, marking the boundary of thermodynamic stability. Consider the free energy per mole $f = \varepsilon - Ts$. Thermodynamics says

$$dE\Big|_N = T\,dS - p\,dV \Rightarrow \frac{\partial E}{\partial V}\Big|_N = T\frac{\partial S}{\partial V}\Big|_N - p$$

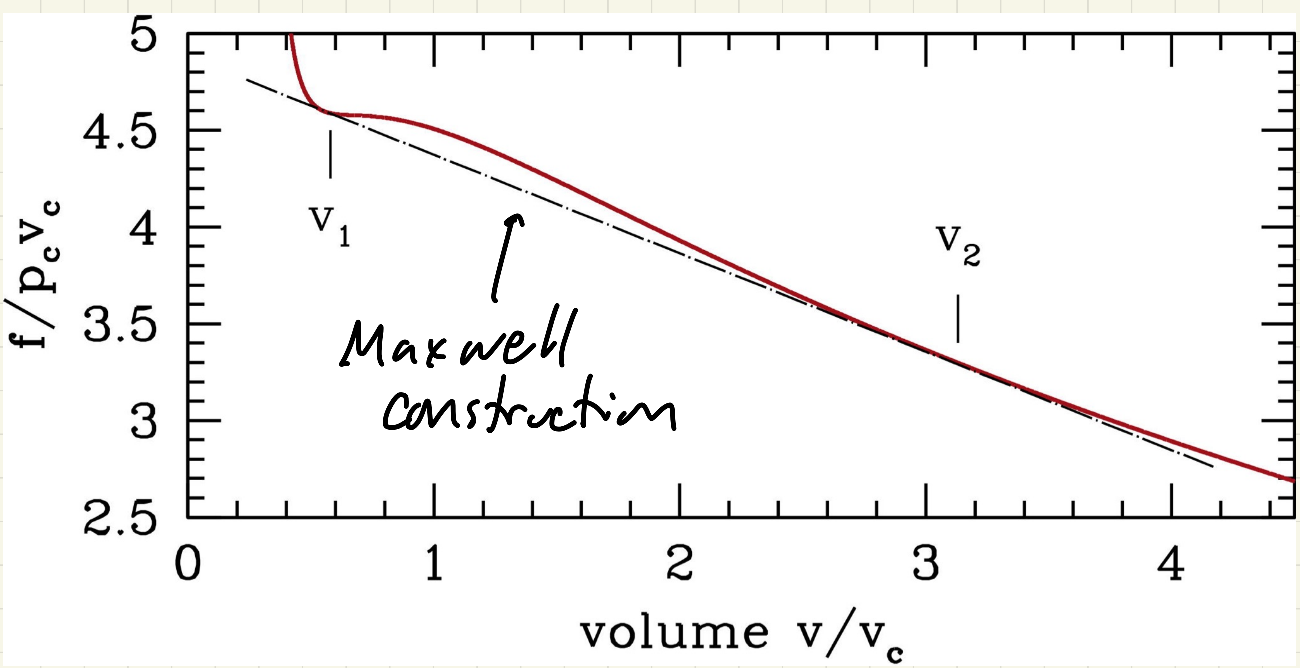
Maxwell rel^{n} from $dF = -S\,dT - p\,dV$: $\frac{\partial S}{\partial V}\Big|_{T,N} = \frac{\partial p}{\partial T}\Big|_{V,N}$

$$\Rightarrow \frac{\partial \varepsilon}{\partial v}\Big|_T = T\frac{\partial p}{\partial T}\Big|_v - p$$

For vdW, then, $\frac{\partial \varepsilon}{\partial v} = \frac{a}{v^2} \Rightarrow \varepsilon = \frac{1}{2} f R T - \frac{a}{v}$
where f is the number of degrees of freedom
occurring quadratically in the Hamiltonian.
We conclude $\varepsilon(T,v) = \frac{1}{2} f R T - \frac{a}{v} \Rightarrow c_v = \frac{\partial \varepsilon}{\partial T} = \frac{1}{2} f R$
Then (see notes eqns 7.10, 11),

$$f(T,v) = \frac{1}{2} f R T \left(1 - \log\left(T/T_c\right)\right) - \frac{a}{v} - RT \log(v-b) - T \overset{\text{const}}{s_0}$$

- Spinodal decomposition : $\frac{\partial^2 f}{\partial v^2} < 0$
- Nucleation : $p(T,v_1) = p(T,v_2) = \frac{1}{v_2 - v_1} \int_{v_1}^{v_2} dv \, p(T,v)$



Maxwell construction: for $v \in [v_1, v_2]$,

$$v = (1-x)v_1 + x v_2$$
$$f = (1-x)f_1 + x f_2$$

In the vicinity of the critical point,

$$\pi \equiv \frac{p - p_c}{p_c} \quad , \quad \epsilon \equiv \frac{v - v_c}{v_c} \quad , \quad t \equiv \frac{T - T_c}{T_c}$$

Then find

$$\pi(\epsilon, t) = \frac{8(1+t)}{2+3\epsilon} - \frac{3}{(1+\epsilon)^2} - 1$$
$$= 4t - 6t\epsilon + 9\epsilon^2 t - \frac{3}{2}\epsilon^3 + \frac{21}{4}\epsilon^4 + \ldots$$

and for $t < 0$ we obtain

$$\epsilon_{L,G} = \mp 2\sqrt{-t} - \frac{5}{18}t + \ldots$$

Eqn of spinodal:

$$0 = \frac{\partial \pi}{\partial \epsilon} = -6t + 18\epsilon t - \frac{9}{2}\epsilon^2 + \ldots$$

which yields $\epsilon = \mp \frac{2}{\sqrt{3}}(-t)^{1/2} + \mathcal{O}(t)$