Homework 4.

C The conditions for the critical point are

$$\left.\frac{\partial p}{\partial v}\right|_T = 0 \qquad \left.\frac{\partial^2 p}{\partial v^2}\right|_T = 0 \qquad \text{working} \quad p = \frac{8t}{3v-1} - \frac{3}{v^2}$$

$$\frac{\partial p}{\partial v} = -\frac{8t}{(3v-1)^2}3 + \frac{6}{v^3} = 0 \qquad \frac{24t}{(3v-1)^3} = \frac{6}{v^3(3v-1)} \qquad (1)$$

$$\frac{\partial^2 p}{\partial v^2} = \frac{8t \times 18}{(3v-1)^3} = \frac{18}{v^4} = 0 \qquad \frac{144t}{(3v-1)^3} = \frac{18}{v^4} \qquad (2)$$

$$\frac{(1)}{(2)} \quad \frac{1}{6} = \frac{1}{3}\frac{v}{(3v-1)} \rightarrow \quad \frac{3v}{2} - \frac{1}{2} = v$$

$$\Rightarrow \boxed{v = 1}$$

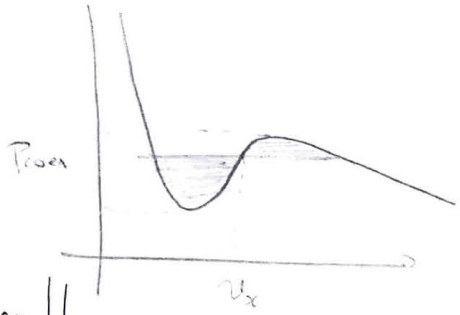
Then from (1) $\frac{24t}{2^{32}} = \frac{6}{x} \Rightarrow \boxed{t = 1}$ and from vdw eq

$$p = \frac{8}{2} - 3 = 1 \qquad \boxed{p = 1}$$

D

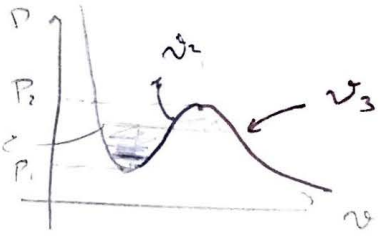
2 Maxwell constructions

$$\int_1^x dp\, v = -\int_x^2 dp\, v$$



Clearly the easiest way to compute the integrals is as an integral in dv

But if we insist to do it in dp we could find equations $v_1(p), v_2(p), v_3(p)$ and the values p_1, p_2



and $$\int_1^x dp\, v = \int_{p_1}^{p_{coex}} (v_2(p) - v_1(p))\, dp \quad v_1$$

$$\int_x^2 dp\, v = \int_{p_{coex}}^{p_2} (v_3(p) - v_2(p))\, dp$$

II Comparison to water.

$$t_{exp} = \frac{373,15}{647} \approx 0,577 = t \checkmark$$

$$P_{exp} = \frac{101,325\ kPa}{22,064\ mPa} = \frac{101.325}{22.064} \times 10^{-3} = 4,59 \times 10^{-3}$$

$$\boxed{P_{exp} = 0.00459} \neq 0,069064$$

The density of liquid water is $1\ g/cm^3$ and watter mass is $18,0153\ g/mol$ Hence a mol of water occupies $18,0153\ cm^3$

$$\Rightarrow \boxed{V_{1\,exp} = 18,0153\ cm^3}$$

The density of water vapor is $0.804\ g/L$ and its molarity is the same so a mol of water occupies $\frac{L}{0.804\,g} \times 18,0153\ g$.

$$= 22,407\ L = 22.407\ cm^3$$

$$\boxed{V_{2\,exp} = 22.407\ cm^3}$$

Then $v_{i\,exp} = \frac{18,0153\ cm^3}{R \cdot 647K / 22,064\ MPa} = \boxed{0,0739 = v_{i,exp}}$

$$\boxed{v_{2\,exp} = 91.9}$$

Hence the discrepancies are around one order of magnitude

III Beyond Van-Der Waals theory

It is reasonable to believe that every influence of the boundary will scale as the boundary over Boundary effect $\propto D^2$ where D is some linear dimension characterizing the system. While Bulk contributions $\propto D^3$ Hence for big enough systems we may neglect the boundary.

If we had two bubbles of radius r_1, r_2

$$V = V_1 + V_2 = \pi (r_1^2 + r_2^2)$$

The surface energy will be $F = 2\pi\gamma (r_1 + r_2)$

while if we had a single bubble of radius $r = \sqrt{r_1^2 + r_2^2}$ ($V = \pi r^2 = \pi (r_1^2 + r_2^2)$) the surface energy will be

$$F_0 = 2\pi\gamma r = 2\pi\gamma \sqrt{r_1^2 + r_2^2} \leq 2\pi\gamma (r_1 + r_2) = F_2$$

Hence as the systems looks to minimize F the bubbles will come together to minimize the free energy

D
→ The stripe just demands to add a constant contribution to the free energy due to the free energy of the boundary layer.
→ The 2 in 1 shows that in a small region for $v > v_1$ we have negative pressure. This would mean that when just a small part of the system has make a phase transition to state 2 there is a force inwards in the system.

This called Laplace pressure