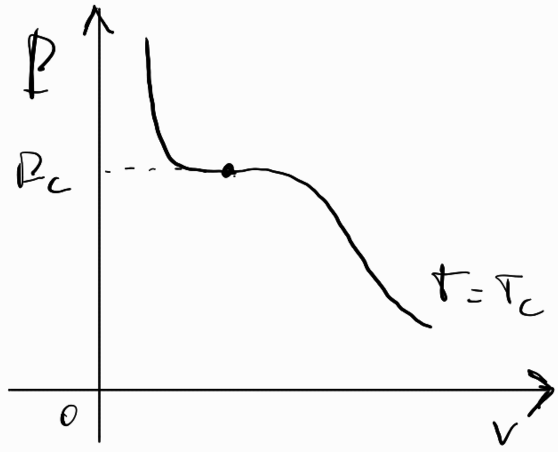
Critical parameters in a VdW system

$$P = \frac{k_B T}{v - b} - \frac{a}{v^2}$$



- 1^{st} method (Analytical)

Impose inflection point condition

$$\begin{cases} \dfrac{\partial P}{\partial v} = 0 \\ \dfrac{\partial^2 P}{\partial v^2} = 0 \end{cases}$$

$$\begin{cases} \dfrac{-k_B T_c}{(v-b)^2} + \dfrac{2a}{v^3} = 0 \\ \dfrac{2 k_B T_c}{(v-b)^3} - \dfrac{6a}{v^4} = 0 \end{cases}$$

$$\begin{cases} 2V\, k_B T_c v^3 = 2a (v-b)^2\, 2V \\ 2 k_B T_c v^4 = 6a (V-b)^3 \end{cases}$$

$$4a (V-b)^2 V = 6a (V-b)^3$$

$$2V = 3(V-b) \longleftrightarrow V = 3b \equiv V_c$$

Then, we first find T_c from the 1^{st} derivative:

$$k_B T_c V_c^3 = 2a (V_c - b)^2$$

$$k_B T_c = \frac{2a \; 4b^2}{27 b^3} = \frac{8a}{27b}$$

And finally P_c:

$$P_c = \frac{k_B T_c}{V_c - b} - \frac{a}{V_c^2} = \frac{k_B T_c}{2b} - \frac{a}{9b^2} = \frac{4a}{27b^2} - \frac{a \cdot 3}{9b^2 \cdot 3} = \frac{a}{27b^2}$$

So in the end:

$V_c = 3b \qquad k_B T_c = \frac{8a}{27b} \qquad P_c = \frac{a}{27b^2}$

Note: $\frac{P_c V_c}{k_B T_c} = \frac{3}{8} = 0{,}375$