Van der Waals Equation of State
-Simple Example of Coexistence

Hard Spheres (HW1)

\[ P(V-Nb) = NkT \]

- To lowest order in \( p = N/V \)
- Equation of State
- \( b = \frac{\pi}{6} r^3 = \frac{4}{3} \) [Volume of sphere] = \( \frac{1}{2} \) [Volume of Excluded Part]

Attracting hard spheres

\[ H = \sum_{i=0}^{N} \frac{P_i}{2m} + \sum_{i=1}^{N} \sum_{j=1}^{N} V(r_{ij}) \]

\[ V(r) \]

Lennard Jones

\[ U_0 \left( \left( \frac{d_0}{r} \right)^{12} - 2 \left( \frac{d_0}{r} \right)^6 \right) \]

Sutherland

\[ V(r) = \begin{cases} \infty & r < d_0 \\ U_0 \left( \frac{d_0}{r} \right)^6 & r > d_0 \end{cases} \]

How does attraction change equation of state, to lowest order in \( p = N/V \)?
Forces on atoms balance inside (distance \(\gg\) do)

\(\langle\text{Pressure on Wall}\rangle = \langle\text{Imbalance of forces on atoms near wall}\rangle\)

\[\Delta F = \text{Change in forces on wall} \quad \text{(assuming to lowest order in } p \text{ that atoms don't rearrange)}\]

\[\Delta F = \text{Net attraction missing due to atoms outside wall}\]

\[\frac{(P + \frac{\Delta F}{A})(V - Nb)}{NkT} = \frac{p^2 U_0 d_0^3 A}{V^2 a} \quad \text{Define } a = \frac{N^2}{V^2 a A}\]

\[\Delta F = (p d_0 A) (p d_0^3) \left(\frac{U_0}{d_0}\right) \sim p^2 U_0 d_0^3 A\]

\[\frac{(P + \frac{M^2}{V})a}{(V - Nb)} = NkT\]

\text{Van der Waals Equation of State}

\[a = \frac{3\pi}{3} d_0^3 U_0 \quad \text{for Sutherland potential small } p\]

\[\text{Fit } a, b \text{ to experiment often}\]
What criterion determines the vapor pressure?
At what pressure does H_2O convert from gas to liquid?
Maxwell Construction

At coexistence, the Gibbs Free energies must be equal.

\[ G_L = G_g \]

Can we derive a formula for the change in \( G \) along the curve?

\[ dG = -SdT + VdP + \mu dN \]

\[ \left. \frac{dG}{dP} \right|_{T,N} = V \]

\[ \Delta G = \int_{P_1}^{P_2} V(P) \, dP \]

\[ = \int_{P_{min}}^{P_{max}} V(P) \, dP + \int_{P_{min}}^{P_{max}} V(P) \, dP + \int_{P_{min}}^{P_{max}} V(P) \, dP \]

\[ = \text{Area difference} \]

\( P_{vapor} \) determined by equating areas between vapor pressure & the isotherms above. 