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2. **Liquid-Gas Critical Point**

The van der Waals gas is a "simple" modification to the classical ideal gas. Each molecule is assumed to occupy a volume b, so the free volume available to a given molecule is reduced to $(V - Nb)$ for a gas of N molecules in a volume V. There is also an attractive interaction between the molecules, which lowers the energy of the gas, so the Helmholtz free energy of the van der Waals (vdW) gas is:

$$F_{vdW}(N, T, V) = F_{ideal}(N, T, V - Nb) - aN^2/V \ ,$$

where F_{ideal} is the free energy of a classical ideal gas, and $a > 0$ quantifies the attractive interaction.

(a) What is the pressure $p(N, T, V)$ of this van der Waals gas?

(b) If you know the equation of state $p(N, T, V)$ of a more general gas with a liquid-gas critical point, what calculation would you do to locate the critical point, T_c, p_c?

(c) Calculate the critical point T_c, p_c of this van der Waals gas.

a) $F_{vdw}(N,T,V) = F_{ideal}(N,T,V-Nb) - a\frac{N^2}{V} \leftarrow P = -\frac{\partial F}{\partial V}$

$-\frac{\partial F_{vdw}}{\partial V}(N,T,V) = -\frac{\partial F_{ideal}}{\partial V}(N,T,V-Nb) - a\frac{N^2}{V^2}$

$P_{vdw}(N,T,V) = P_{ideal}(N,T,V-Nb) - a\frac{N^2}{V^2} \leftarrow P_{ideal} = \frac{Nk_BT}{V}$

$= \frac{Nk_BT}{V-Nb} - a\frac{N^2}{V^2}$

$$\boxed{P_{vdw} = \frac{Nk_BT}{V-Nb} - a\frac{N^2}{V^2}}$$

b) Phase boundaries occur at the onset of metastable states, which is characterized by an inflection point in the PV-diagram for the critical isotherm. In a first order phase transition (like with the liquid to gas transition), this can be calculated by taking the pressure from the equation of state and setting its first and second derivatives equal to zero. Solving these equations will give you the critical temperature and volume, which you can then plug back into the original equation of state to obtain the critical pressure.

c) $\frac{\partial P}{\partial V} = -\frac{Nk_BT}{(V-Nb)^2} + 2a\frac{N^2}{V^3} \equiv C_1$

$\frac{\partial^2 P}{\partial V^2} = \frac{2Nk_BT}{(V-Nb)^3} - 6a\frac{N^2}{V^4} \equiv C_2$

$\underline{C_1 = 0}$

$2a\frac{N^2}{V^3} = \frac{Nk_BT}{(V-Nb)^2} \rightarrow T_c = \frac{2aN}{k_B}\frac{(V_c-Nb)^2}{V_c^3}$

$\underline{C_2 = 0}$

$3a\frac{N^2}{V^4} = \frac{Nk_BT}{(V-Nb)^3} \rightarrow T_c = \frac{3aN}{k_B}\frac{(V_c-Nb)^2}{V_c^3}\cdot\frac{(V_c-Nb)}{V_c}$

$$T_c = T_c \rightarrow \cancel{\frac{2aN}{k_B}} \frac{\cancel{(V_c - Nb)^2}}{\cancel{V_c^3}} = \cancel{\frac{3aN}{k_B}} \frac{\cancel{(V_c-Nb)^2}}{\cancel{V_c^3}} \cdot \frac{(V_c - Nb)}{V_c}$$

$$\frac{2}{3} = \frac{(V_c - Nb)}{V_c} = 1 - \frac{Nb}{V_c}$$

$$\frac{Nb}{V_c} = \frac{1}{3}$$

$$\boxed{V_c = 3Nb}$$

$$T_c = \frac{2aN}{k_B} \frac{(V_c - Nb)^2}{V_c^3} = \frac{2aN}{k_B} \frac{(2Nb)^2}{(3Nb)^3} = \frac{2a\cancel{N}}{k_B} \frac{4}{27} \frac{1}{\cancel{N}b} = \frac{8a}{27k_B b}$$

$$\boxed{T_c = \frac{8a}{27k_B b}}$$

<u>Back in EoS</u>

$$P_c = \frac{Nk_B}{3Nb - Nb} \cdot \frac{8a}{27k_B b} - a\frac{N^2}{9N^2 b^2} = \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$

$$\boxed{P_c = \frac{a}{27b^2}}$$