Real Gas – Van der Waals Equation & Related Results (Long Answer)

1) Why ideal gas fails

- **Ideal gas assumptions:** point molecules, no intermolecular forces, equation $PV = nRT$.
- **Reality:**
  (i) **Attraction** between molecules reduces the measured pressure.
  (ii) **Finite size** of molecules reduces the free volume.
  Therefore we must correct both P and V.

2) Derivation of Van der Waals (VdW) equation

(A) Pressure correction (attractive forces → a)

Consider n moles in volume V (number density $\rho = n/V$). Due to attractions, molecules near the wall are pulled inward, so the **measured** pressure P is less than the ideal-gas pressure P_{ideal}.

Mean-field estimate: missing pressure ΔP is proportional to the square of density:

$$\Delta P \propto \rho^2 \quad \Rightarrow \quad \Delta P = \frac{an^2}{V^2},$$

$$P_{\text{ideal}} = P + \frac{an^2}{V^2}.$$

(B) Volume correction (finite size → b)

The centers of molecules cannot access the entire container; only the **free volume** $V_{\text{free}} = V - nb$ is available, where b is the **excluded volume per mole**.

(C) Putting the two corrections into the ideal gas law

$$P_{\text{ideal}} V_{\text{free}} = nRT \quad \Rightarrow \quad \left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT.$$

$$\boxed{\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT}$$

3) Excluded volume b (hard-sphere derivation)

- Model each molecule as a hard sphere of radius r.
- For two spheres, the center of one cannot enter a sphere of radius $2r$ around the other.
  Excluded volume **per pair**:

$$V_{\text{excl,pair}} = \tfrac{4}{3}\pi(2r)^3 = 8\left(\tfrac{4}{3}\pi r^3\right).$$

$$v_{\text{excl},1} = \tfrac{1}{2}V_{\text{excl,pair}} = 4\left(\tfrac{4}{3}\pi r^3\right).$$

$$\boxed{b = N_A\, v_{\text{excl},1} = 4\,N_A\left(\frac{4}{3}\pi r^3\right) = 4 \times (\text{actual molecular volume per mole})}$$

4) Critical constants (T_c, P_c, V_c) for a VdW gas

Start with one-mole form:

$$P(V_m, T) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}.$$

$$\left(\frac{\partial P}{\partial V_m}\right)_T = 0, \qquad \left(\frac{\partial^2 P}{\partial V_m^2}\right)_T = 0.$$

From (1): $$\frac{RT}{(V_m - b)^2} = \frac{2a}{V_m^3}.$$

From (2): $$\frac{2RT}{(V_m - b)^3} = \frac{6a}{V_m^4} \Rightarrow \frac{RT}{(V_m - b)^3} = \frac{3a}{V_m^4}.$$

Divide the second identity by the first:

$$\frac{1}{V_m - b} = \frac{3}{2} \cdot \frac{1}{V_m} \Rightarrow V_{m,c} - b = \frac{2}{3} V_{m,c} \Rightarrow \boxed{V_{m,c} = 3b}.$$

Back into (1):

$$\frac{RT_c}{(3b - b)^2} = \frac{2a}{(3b)^3} \Rightarrow \frac{RT_c}{(2b)^2} = \frac{2a}{27b^3} \Rightarrow \boxed{T_c = \frac{8a}{27Rb}}.$$

Finally,

$$P_c = \frac{RT_c}{V_{m,c} - b} - \frac{a}{V_{m,c}^2} = \frac{R\left(\frac{8a}{27Rb}\right)}{2b} - \frac{a}{9b^2} = \frac{4a}{27b^2} - \frac{a}{9b^2} = \boxed{\frac{a}{27b^2}}.$$

Critical compressibility factor:

$$Z_c = \frac{P_c V_{m,c}}{RT_c} = \frac{\frac{a}{27b^2} \cdot 3b}{R \cdot \frac{8a}{27Rb}} = \boxed{\frac{3}{8} = 0.375}.$$