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

### 1) Why ideal gas fails

- ullet 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  $_{V}$ .

$$\square$$
  $\Rightarrow$ 

# 2) Derivation of Van der Waals (VdW) equation

(A) Pressure correction (attractive forces  $\rightarrow a$ )

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

Mean-field estimate: missing pressure  $\Delta P$  is proportional to the square of density:

$$\Delta P \propto 
ho^2 \;\; \Rightarrow \;\; \Delta P = rac{an^2}{V^2},$$

$$P_{ ext{ideal}} = P + rac{an^2}{V^2}.$$

(B) Volume correction (finite size  $\rightarrow b$ )

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

$$\square$$
  $\Rightarrow$ 

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

$$P_{ ext{ideal}} \, V_{ ext{free}} = nRT \quad \Rightarrow \quad \left(P + rac{an^2}{V^2}
ight) (V - nb) = nRT.$$

$$\overline{\left(P+rac{a}{V_m^2}
ight)\,(V_m-b)=RT}$$





# 3) Excluded volume $_b$ (hard-sphere derivation)

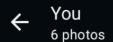
- Model each molecule as a hard sphere of radius  $_{x}$ .
- ullet For two spheres, the center of one cannot enter a sphere of radius  $_{2r}$  around the other. Excluded volume **per pair**:

$$V_{
m excl,pair}=rac{4}{3}\pi(2r)^3=8\left(rac{4}{3}\pi r^3
ight)$$
 .

$$v_{
m excl,1} = rac{1}{2} V_{
m excl,pair} = 4 \left(rac{4}{3} \pi r^3
ight)$$
 .

$$b = N_A \, v_{
m excl,1} = 4 \, N_A \left(rac{4}{3} \pi r^3
ight) = 4 imes ({
m actual \ molecular \ volume \ per \ mole})$$





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

Start with one-mole form:

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

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

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From (1): 
$$\frac{RT}{(V_{2\!\!\!\!/}RT^b)^2}=rac{2a}{V_m^3}$$
  $=rac{RT}{V_m^4}$   $\Rightarrow rac{RT}{(V_m-b)^3}=rac{3a}{V_m^4}$  Divide the second identity by the first:

Divide the second identity by the first:

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

Back into (1):

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

Finally,

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

Critical compressibility factor:

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

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