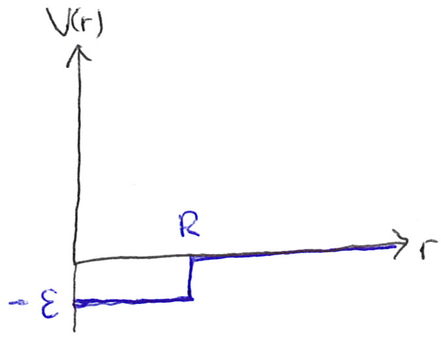
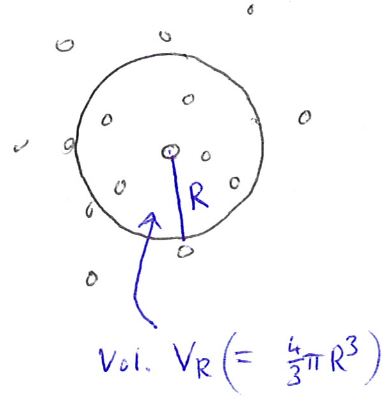
Origin of a/V^2 term in Van der Waals' equation

Assume

$$V(r) = -\varepsilon \quad r<R$$
$$\quad\;\; = 0 \quad r>R$$





No. molecules in V_R $= \dfrac{N V_R}{V}$ (N = total no. molecules)

$\Rightarrow$ PE per molecule $= -\dfrac{\varepsilon N V_R}{V}$

$\Rightarrow$ Total PE $= -\dfrac{\varepsilon N^2}{2}\dfrac{V_R}{V}$ ——— (1)

to avoid double counting

PE is −ve $\Rightarrow$ molecules are pulled into gas (like surface tension)

$\rightarrow$ effective additional negative pressure P_{eff}

$$\rightarrow \quad \underbrace{P}_{\text{measured}} = \underbrace{P_0}_{\text{"true"}} + \underbrace{P_{eff}}_{\text{due to intermolecular attractions}} \quad \text{——— (2)}$$

Consider expansion of gas from $V \rightarrow V + dV$

work done against P_{eff} = change in PE

$$\Rightarrow \quad -P_{eff}\, dV = \frac{\varepsilon N^2}{2}\frac{V_R}{V^2}\, dV \quad (\text{from (1)})$$

$$\Rightarrow \quad P_{eff} = -\frac{\varepsilon N^2}{2}\frac{V_R}{V^2}$$

$$= -\frac{a}{V^2}$$

substitute in (2)

$$\rightarrow \quad \underline{P_0 = P + a/V^2}$$