# Van der Waals equation – series expansion

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \wedge \qquad PV = ZRT$$

**Replace all instances of $V$ by $ZRT/P$:**

$$\left[P + \frac{aP^2}{(RTZ)^2}\right]\left(\frac{RTZ}{P} - b\right) = RT$$

**Multiply by $Z^2/P$:**

$$\left[Z^2 + \frac{aP}{(RT)^2}\right]\left(\frac{RTZ}{P} - b\right) = \frac{RTZ^2}{P}$$

**Multiply by $P/RT$:**

$$\left[Z^2 + \frac{aP}{(RT)^2}\right]\left(Z - \frac{bP}{RT}\right) = Z^2$$

$$Z^3 - \frac{bP}{RT}Z^2 + \frac{aP}{(RT)^2}Z - \frac{abP^2}{(RT)^3} = Z^2$$

$$\boxed{Z^3 - \left[\frac{bP}{RT} + 1\right]Z^2 + \frac{aP}{(RT)^2}\cdot Z - \frac{abP^2}{(RT)^3} = 0} \qquad (1)$$

**Taking the limit $P \to 0$**

$$\lim_{P\to 0}\left(Z^3 - \left(\frac{bP}{RT} + 1\right)Z^2 + \frac{aP}{(RT)^2}Z - \frac{abP^2}{(RT)^3}\right) = \left(\lim_{P\to 0} Z\right)^3 - \left(\lim_{P\to 0} Z\right)^2 = 0$$

$$\longrightarrow \boxed{\lim_{P\to 0} Z = 1} \ \checkmark \qquad (2)$$

**Differentiating w.r.t. $P$:**

$$3Z^2\left(\frac{\partial Z}{\partial P}\right)_T - Z^2\left(\frac{b}{RT}\right) - 2Z\left(\frac{bP}{RT} + 1\right)\left(\frac{\partial Z}{\partial P}\right)_T + \frac{aZ}{(RT)^2} + \frac{aP}{(RT)^2}\left(\frac{\partial Z}{\partial P}\right)_T - \frac{2abP}{(RT)^3}$$

**Taking the limit $P \to 0$ and using (2):**

$$3\left(\frac{\partial Z}{\partial P}\right)_T\Big|_{P=0} - \frac{b}{RT} - 2\left(\frac{\partial Z}{\partial P}\right)_T\Big|_{P=0} + \frac{a}{(RT)^2} = 0$$

$$\boxed{\left(\frac{\partial Z}{\partial P}\right)_T\Big|_{P=0} = \frac{1}{RT}\left(b - \frac{a}{RT}\right)} \qquad (3)$$

**So: (Taylor expansion):** $Z = 1 + \left(\frac{\partial Z}{\partial P}\right)_T\Big|_{P=0} P + O(P^2)$

From (3); multiplying by $RT$:

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