Real Gases

- have non-zero volume at low *T* and high *P*
- have repulsive and attractive forces between molecules

short range,
important at high *P*

longer range,
important at moderate *P*

At low pressure, molecular volume and intermolecular forces can often be neglected, i.e. properties → ideal.

Virial Equations

$$P\bar{V} = RT\left[1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \ldots\right] \qquad \bar{V} = V_{\mathrm{m}} = \frac{V}{n}$$

$$P\bar{V} = RT\left[1 + B'P + C'P^2 + \ldots\right]$$

B is the second virial coefficient.

C is the third virial coefficients.

They are temperature dependent.

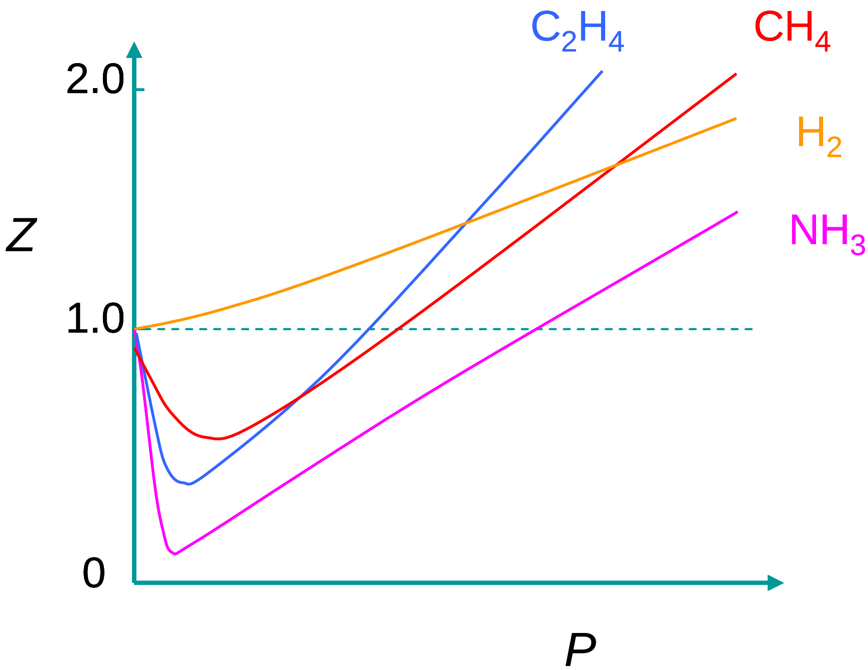
Van der Waals Equation

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

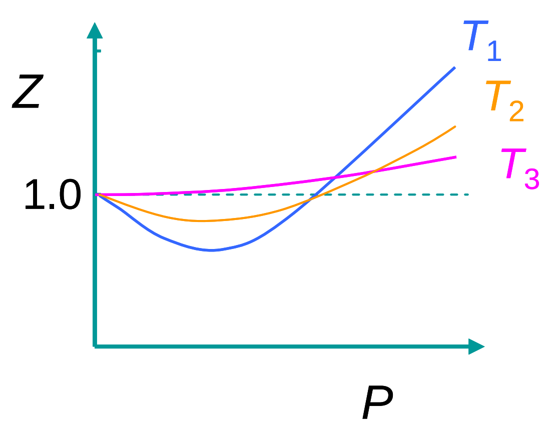
Compressibility Factor

also known as compression factor

$$Z = \frac{P\overline{V}}{RT} = \frac{\overline{V}}{\overline{V}_{\text{ideal}}}$$



The curve for each gas becomes more ideal as $T \rightarrow \infty$



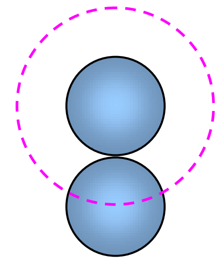
The van der Waals Equation 1

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

Intermolecular attraction
= "internal pressure"

"molecular volume"
≈ excluded volume

$$\tfrac{4}{3}\pi\left(2r\right)^3/2=\tfrac{2}{3}\pi\sigma^3$$



$$P=\frac{RT}{\overline{V}-b}-\frac{a}{\overline{V}^2}$$

$$Z=\frac{P\overline{V}}{RT}=\frac{\overline{V}}{\overline{V}-b}-\frac{a}{RT\overline{V}}$$

$$=1+\frac{1}{RT}\left(b-\frac{a}{RT}\right)P+\frac{a}{\left(RT\right)^3}\left(2b-\frac{a}{RT}\right)P^2+\ldots$$ (boring algebra)

$$\Rightarrow\quad\left(\frac{\partial Z}{\partial P}\right)_T=\frac{1}{RT}\left(b-\frac{a}{RT}\right)+\ldots$$

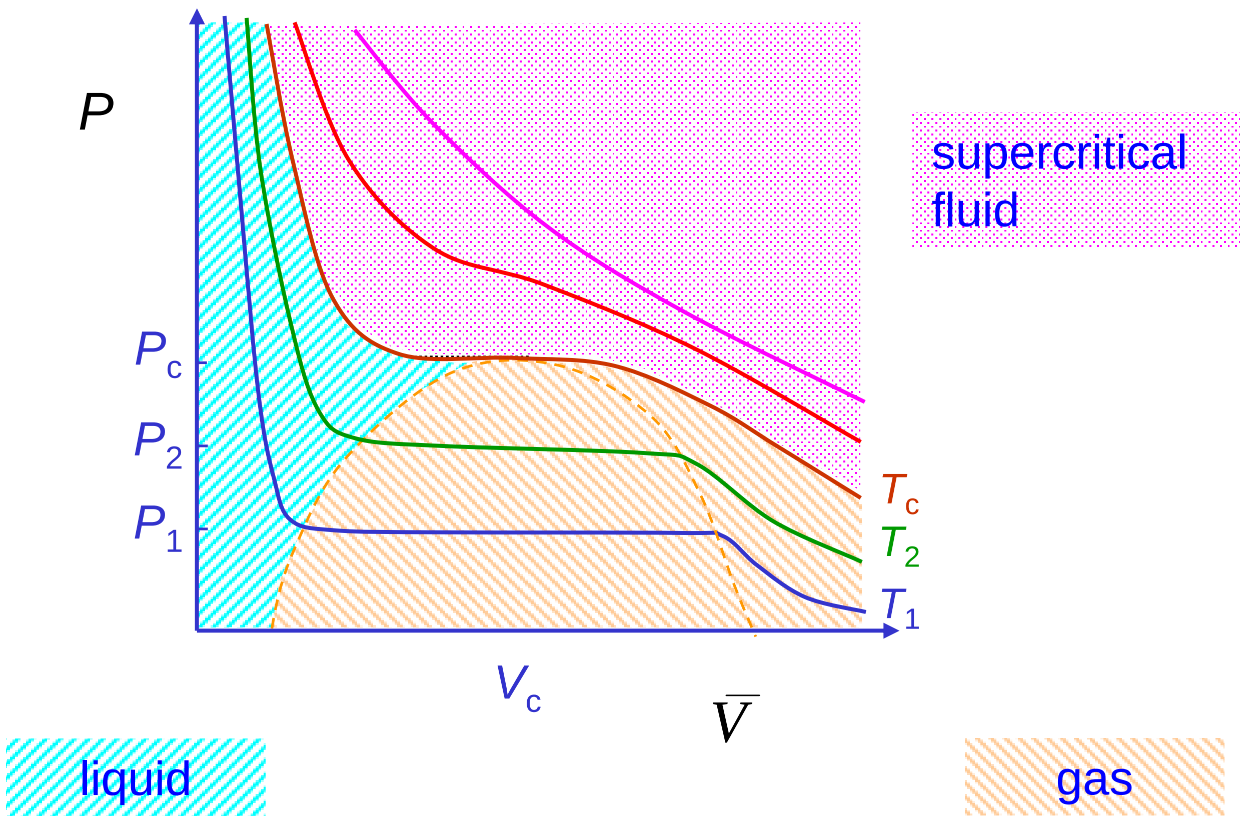
The initial slope depends on *a*, *b* and *T*:

- positive for $b>a/RT$ molecular size dominant
- negative for $b<a/RT$ forces dominant
- zero at $T=a/Rb$ Boyle Temperature

~ ideal behaviour over wide range of *P*

Condensation of Gases

Real gases condense… don’t they?



T_c, P_c and V_c are the critical constants of the gas.

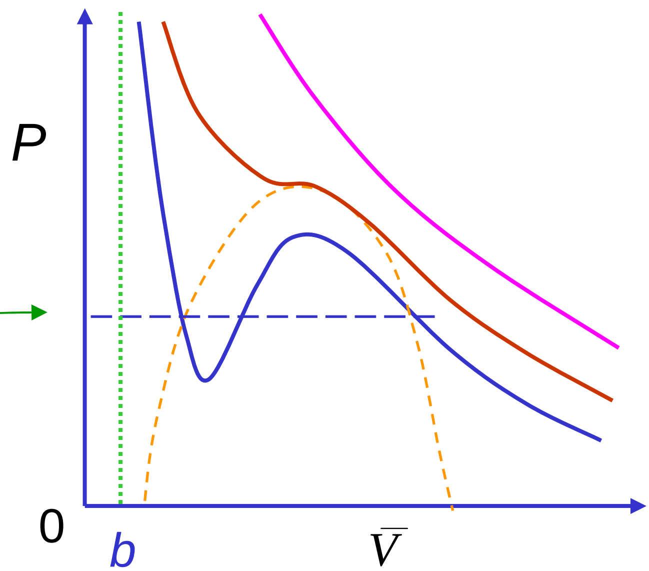
Above the critical temperature the gas and liquid phases are continuous, i.e. there is no interface.

The van der Waals Equation 2

The van der Waals Equation is not exact, only a model.
a and *b* are empirical constant.

$$\bar{V}^3 - \left(b + \frac{RT}{P}\right)\bar{V}^2 + \frac{a}{P}\bar{V} - \frac{ab}{P} = 0$$

The cubic form of the equation predicts 3 solutions



There is a point of inflection at the critical point, so…

slope:

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = -\frac{RT}{(\bar{V}-b)^2} + \frac{2a}{\bar{V}^3} = 0$$

curvature:

$$\left(\frac{\partial^2 P}{\partial \bar{V}^2}\right)_T = \frac{2RT}{(\bar{V}-b)^3} - \frac{6a}{\bar{V}^4} = 0$$

$$\Rightarrow \qquad P_c = \frac{a}{27b^2} \qquad \bar{V}_c = 3b \qquad T_c = \frac{8a}{27Rb}$$

$$Z_c = \frac{P_c\bar{V}_c}{RT_c} = \frac{3}{8} \qquad T_B = \frac{a}{Rb} = \frac{27}{8}T_c$$

The Principle of Corresponding States

Reduced variables are dimensionless variables expressed as fractions of the critical constants:

$$P_r = \frac{P}{P_c} \qquad \bar{V}_r = \frac{\bar{V}}{\bar{V}_c} \qquad T_r = \frac{T}{T_c}$$

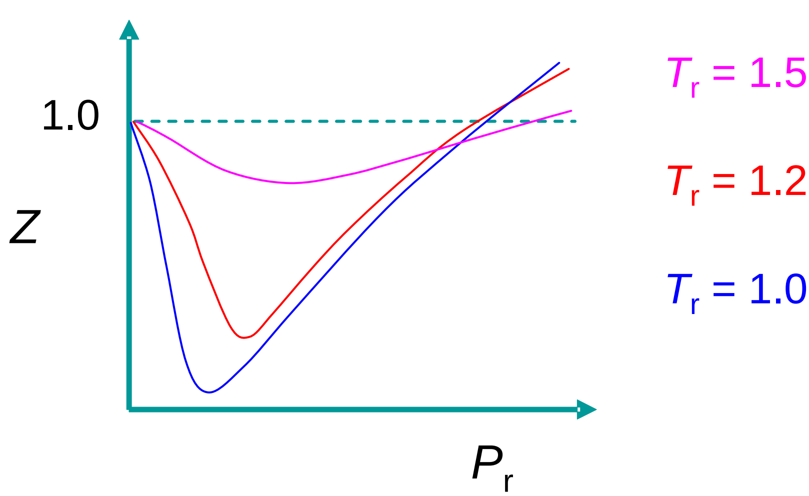
Real gases in the same state of reduced volume and reduced temperature exert approximately the same reduced pressure.

They are in corresponding states.

If the van der Waals Equation is written in reduced variables,

$$\left(P_r + \frac{3}{\bar{V}_r^{\,2}}\right)\left(3\bar{V}_r - 1\right) = 8T_r$$

Since this is independent of *a* and *b*, all gases follow the same curve (approximately).



Properties of Real Gases as $P \to 0$

Real gases have interactions between molecules. These change when the gas is compressed, but …
…they need not go to zero as $P \to 0$.

e.g. consider

$$\left(\frac{\partial Z}{\partial P}\right)_T$$

For an ideal gas:

$$\left(\frac{\partial Z}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{P\bar{V}}{RT}\right) = \frac{\partial}{\partial P}(1) = 0$$

For a real gas:

$$Z = \frac{P\bar{V}}{RT} = 1 + B'P + C'P^2 + \ldots$$

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + \ldots$$

and in the limit:

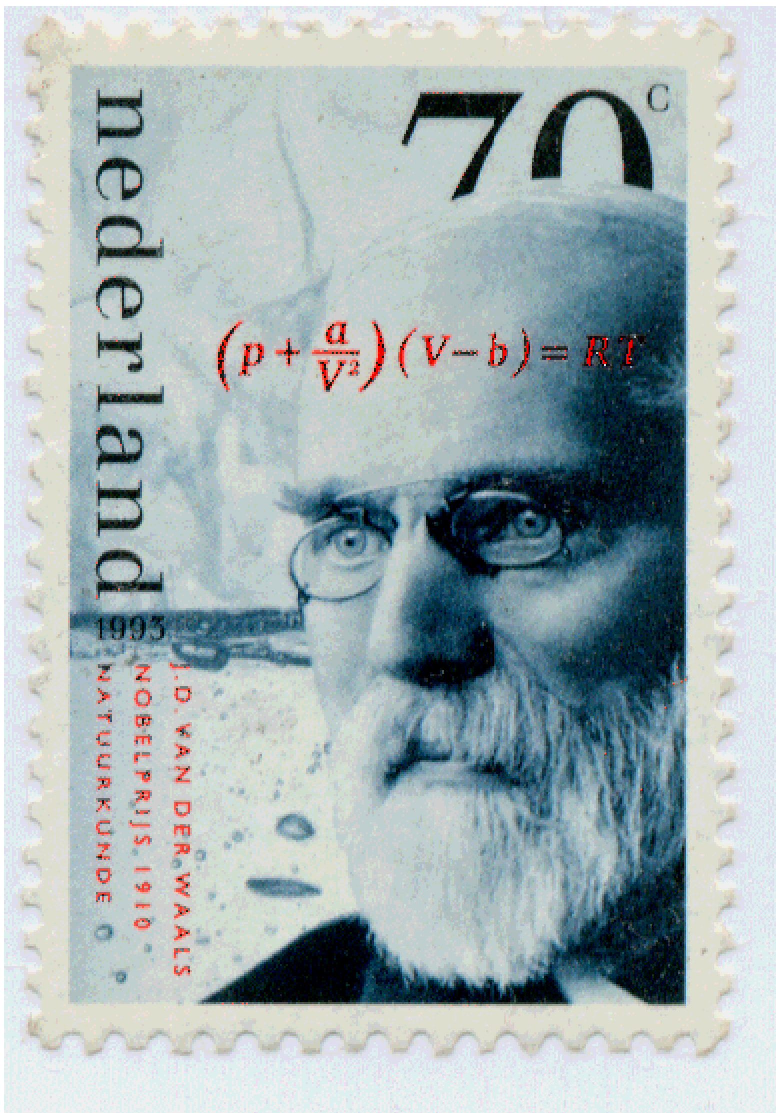
$$\lim_{P \to 0}\left(\frac{\partial Z}{\partial P}\right)_T = B' \neq 0$$

Not all properties of real gases tend to ideal values as $P \to 0$.

van der Waals

Johannes Diderik van der Waals, 1837 - 1923

Nobel Prize in Physics 1910



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