59-240 Lecture 4 Real Gases

- **Molecular Interactions**
  - Low pressure: like a perfect gas
  - Intermediate pressure: Attractive forces
  - High pressure: Repulsive forces
- **Compression factor**
  - $Z = \frac{pV_m}{RT}$
  - Ideal gas: Z=1
  - Interm. pressure: Z<1
  - High pressure: Z>1
  - Different gases have different responses
- **Virial Equations**
  - Power series, empirically measured
  - **Numerical equation**
  - $pV_m = RT(1 + B'p + C'p^2 + \ldots) = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots\right)$
  - Perfect gas: p -> 0
  - p increases: *B* kicks in, linear relation btw *Z* and *p*
  - p high: *C* and higher order terms, not linear
  - Virial equations are **force** equations
- **Boyle Temperature**
  - Temperature at which dZ/dp = 0 as p -> 0
  - $\frac{dZ}{dp} = B' + 2pC' + \ldots \rightarrow B' \text{ as } p \rightarrow 0$
  - Low *T*: dZ/dp < 0, B -ve
  - High *T*: dZ/dp > 0, B +ve
  - Boyle *T*: *B* = 0
- **Principle of Corresponding States**
  - Flat inflection: 2 derivatives equal to zero
  - critical constants are expressed in terms of vdW coefficients
  - reduced variables used to show all gases behave the same
- **van der Waals**
  - $p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$
  - **analytical equation**
  - semiempirical theory
  - experimental observations
  - *nb*: small approximate volume occupied by the molecules
  - *a*: positive proportionality constant (attractive/repulsive forces)
  - vdW loops/Maxwell construction
- **Condensation of CO_2**
  - 20 C example
  - Vapour liquid line
  - 31.04 C example
  - Critical temperature
  - Critical constants, pc, Vc, Tc
  - Supercritical temperature, Tc
- **Virial Coefficients**
  - $pV_m = RT(1 + B'p + C'p^2 + D'p^3)$
  - Methane example