Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 2.3

Gas-Liquid PV Diagrams
The temperature above which a gas cannot be liquefied is called the critical temperature ($T_c$). As $T$ approaches $T_c$, the curves flatten. At $T < T_c$ there are horizontal regions where gas and liquid co-exist.
Non-ideal Cubic Equations of State

van der Waals EOS

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

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

Redlich-Kwong and Peng-Robinson are also cubic and show similar behavior
\[ \overline{V}^3 - \left( b + \frac{RT}{P} \right)\overline{V}^2 + \frac{a}{P} \overline{V} - \frac{ab}{P} = 0 \]

As a cubic equation, there are 3 real roots for temperatures below \( T_c \), which come closer and closer together and ultimately merge to a single, triply degenerate root at \( T = T_c \), \( P = P_c \), and \( V = V_c \).

At that point:
\[ \left( \overline{V} - \overline{V}_c \right)^3 = 0 \]
Solution for the Critical Isotherm

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

Valid for \( T = T_c \): \[ \bar{V}^3 - 3\bar{V}_c \bar{V}^2 + 3\bar{V}_c^2 \bar{V} - \bar{V}_c^3 = 0 \]

Implies: \[ 3\bar{V}_c = b + \frac{RT_c}{P_c} \quad 3\bar{V}_c^2 = \frac{a}{P_c} \quad \bar{V}_c^3 = \frac{ab}{P_c} \]

which yields: \[ \bar{V}_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27bR} \]

...and that’s how van der Waals equation of state parameters are determined! From best fitting to the critical point observables for individual gases.
Critical Compressibility

There is an apparent correspondence between different “real” gases that is entirely independent of the van der Waals equation of state.

\[
\frac{P_c \bar{V}_c}{RT_c} = 1 \left( \frac{a}{27b^2} \right) (3b) \left( \frac{27bR}{8a} \right) = 0.375!
\]