Law of corresponding states

Use the critical-point values, \( p_c, V_c, T_c, \rho_c \), for the thermodynamic variables and introduce reduced quantities:

\[
\bar{p} = \frac{p}{p_c}, \quad \bar{V} = \frac{V}{V_c}, \quad \bar{T} = \frac{T}{T_c}, \quad \bar{\rho}_l = \frac{\rho_l}{\rho_c}, \quad \bar{\rho}_g = \frac{\rho_g}{\rho_c}.
\]

Empirical fact: Near the critical point, the relations between (reduced) thermodynamic quantities are universal.

Experimentally:

Guggenheim plot of liquid-vapor coexistence curves:

\[
\frac{1}{2}(\bar{\rho}_l + \bar{\rho}_g) \simeq 1 + \frac{3}{4}(1 - \bar{T}), \quad \bar{\rho}_l - \bar{\rho}_g \simeq \frac{7}{2}(1 - \bar{T})^{1/3}.
\]

Theoretically:

Van der Waals equation: \( (p + \frac{a n^2}{V^2})(V - n b) = n R T \).

Critical point condition: \( \left( \frac{\partial p}{\partial V} \right)_T = \left( \frac{\partial^2 p}{\partial^2 V} \right)_T = 0 \).

Critical-point values: \( p_c = \frac{a}{27 b^2}, \quad V_c = 3 n b, \quad T_c = \frac{8 a}{27 b R} \).

VdW equation in reduced units: \( \left( \bar{p} + \frac{3}{\bar{V}^2} \right)(3 \bar{V} - 1) = 8 \bar{T} \).