Law of corresponding states [tln30]

Use the critical-point values, p_c, V_c, T_c, ρ_c, for the thermodynamic variables and introduce reduced quantities:

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

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

Experimentally:

Guggenheim plot of liquid-vapor coexistence curves:

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

Theoretically:

Van der Waals equation: $\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT.$

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: $p_c = \frac{a}{27b^2}, \quad V_c = 3nb, \quad T_c = \frac{8a}{27bR}.$

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