CORRESPONDING STATES

Dimensional analysis of thermodynamic properties

Cubic EOS - e.g. vdW $P = \frac{RT}{V-b} - \frac{a}{V^2}$

[P]: [energy/volume] [R]: [energy/(mol K)] [T]: [K]

[b]: [volume/mole] [a]: same as PV^2: $\frac{[\text{energy}]\times[\text{volume}]}{[\text{mole}]^2}$

Characteristic volume per mole: b
" molar energy: a/b
} 2 parameters

Define dimensionless quantities $P^* = \frac{Pb}{a/b} = \frac{Pb^2}{a}$;

$T^* = \frac{RT}{a/b} = \frac{RTb}{a}$; $V^* = \frac{V}{b}$

All thermodynamic quantities should now be expressible as universal dimensionless functions for any fluid following the vdW EOS:

e.g. $P = \frac{RT}{V-b} - \frac{a}{V^2} \Rightarrow \frac{Pb^2}{a} = \frac{RTb}{a(V/b-1)} - \frac{b^2}{V^2} \Rightarrow$

$$P^* = \frac{T^*}{V^*-1} - \frac{1}{(V^*)^2}$$

recall $b = \frac{RT_c}{8P_c}$ $a = \frac{27R^2T_c^2}{64P_c}$

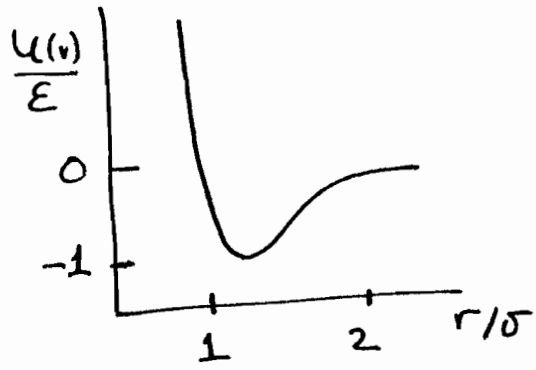
$$\rightarrow P_c^* = \frac{P_c b^2}{a} = \frac{P_c R^2 T_c^2 64 P_c}{64 P_c^2 27 R^2 T_c^2} \Rightarrow P_c^* = \frac{1}{27}$$

Similarly, $T_c^* = \frac{RT_c b}{a} = \frac{R^2 T_c^2 64 P_c}{8P_c \cdot 27 R^2 T_c^2} = \frac{8}{27}$; $V_c^* = 3$

Even if we did not know the exact form of the equation of state for a system, if the intermolecular interactions have similar functional forms, the same principles apply -

E.g. LJ potential

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



ε: energy parameter
σ: size parameter

All systems following this potential have the same dimensionless critical parameters, triple point, vapor pressure of solid or liquid phase etc, using:

$$T^* = \frac{k_B T}{\varepsilon} \qquad V^* = \frac{V}{N_A \sigma^3}$$

Another example: simple model for 1:1 molten salts

$$u(r) = \frac{e^2}{4\pi\varepsilon_0 r^2} \quad r \geq \sigma$$
$$\infty \quad r < \sigma$$

} hard spheres + Coulombic
e: electron charge

$$T^* = \frac{k_B T \cdot 4\pi\varepsilon_0 \sigma}{e^2} \qquad V^* = \frac{V}{N_A \sigma^3}$$

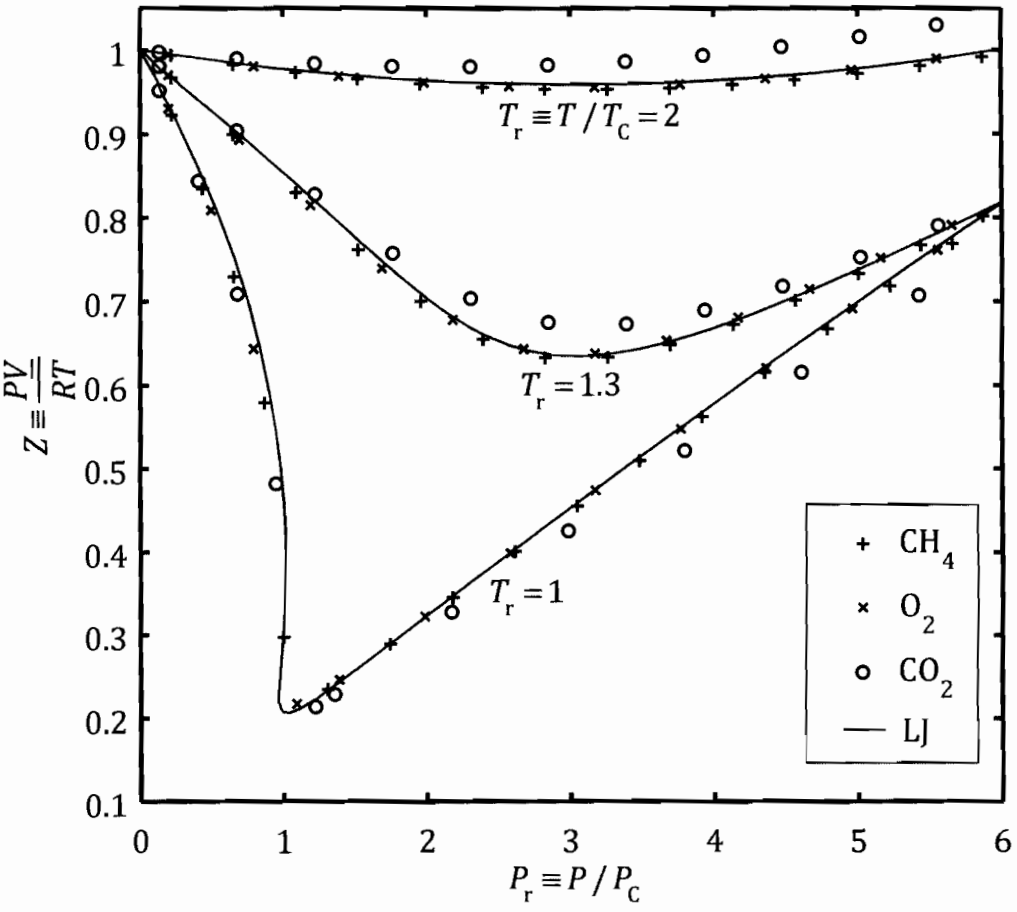
For real substances, the form of the intermolecular potential is not known precisely; however, an energy + size scale can be obtained from the critical parameters. Define reduced properties

$$T_r \equiv \frac{T}{T_c} \qquad P_r \equiv \frac{P}{P_c} \qquad V_r = \frac{V}{V_c}$$

Two-parameter corresponding states hypothesis:

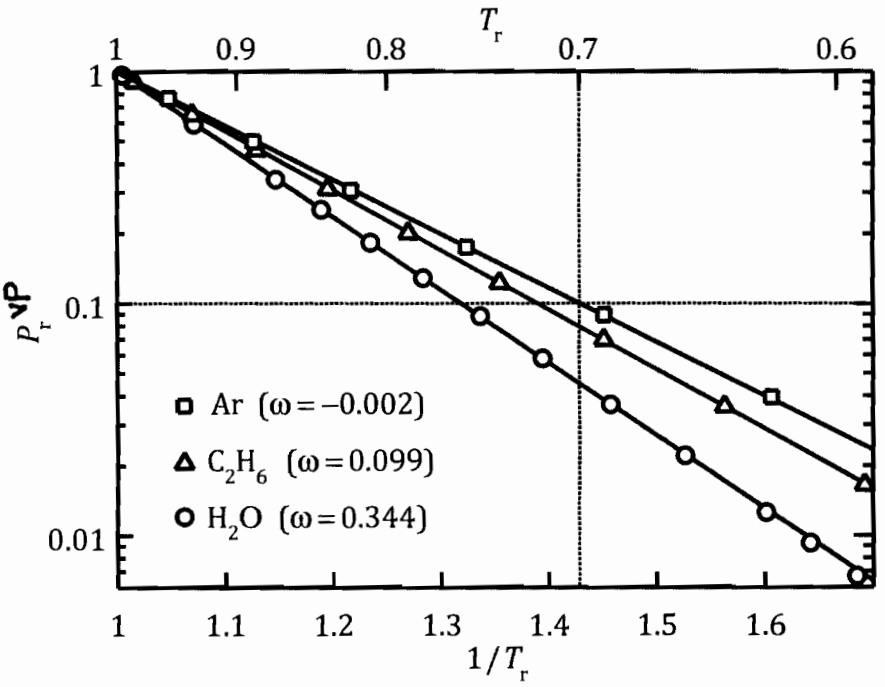
$$Z = \frac{PV}{RT} = f(T_r, P_r) \text{ or } (T_r, V_r)$$ – good for non-polar, spherical

CO_2 deviates significantly



For polar or non-spherical molecules, additional parameters (beyond 2) are needed.

A very useful such parameter was proposed by Pitzer ~1955 to describe different dependence of vapor pressure on temperature



$$\omega \equiv \log_{10}\left[\frac{P_c}{P^{VP}(T_r=0.7)}\right] - 1$$

then $Z = f(T_r, P_r, \omega)$ ← 3-parameter Corresponding States