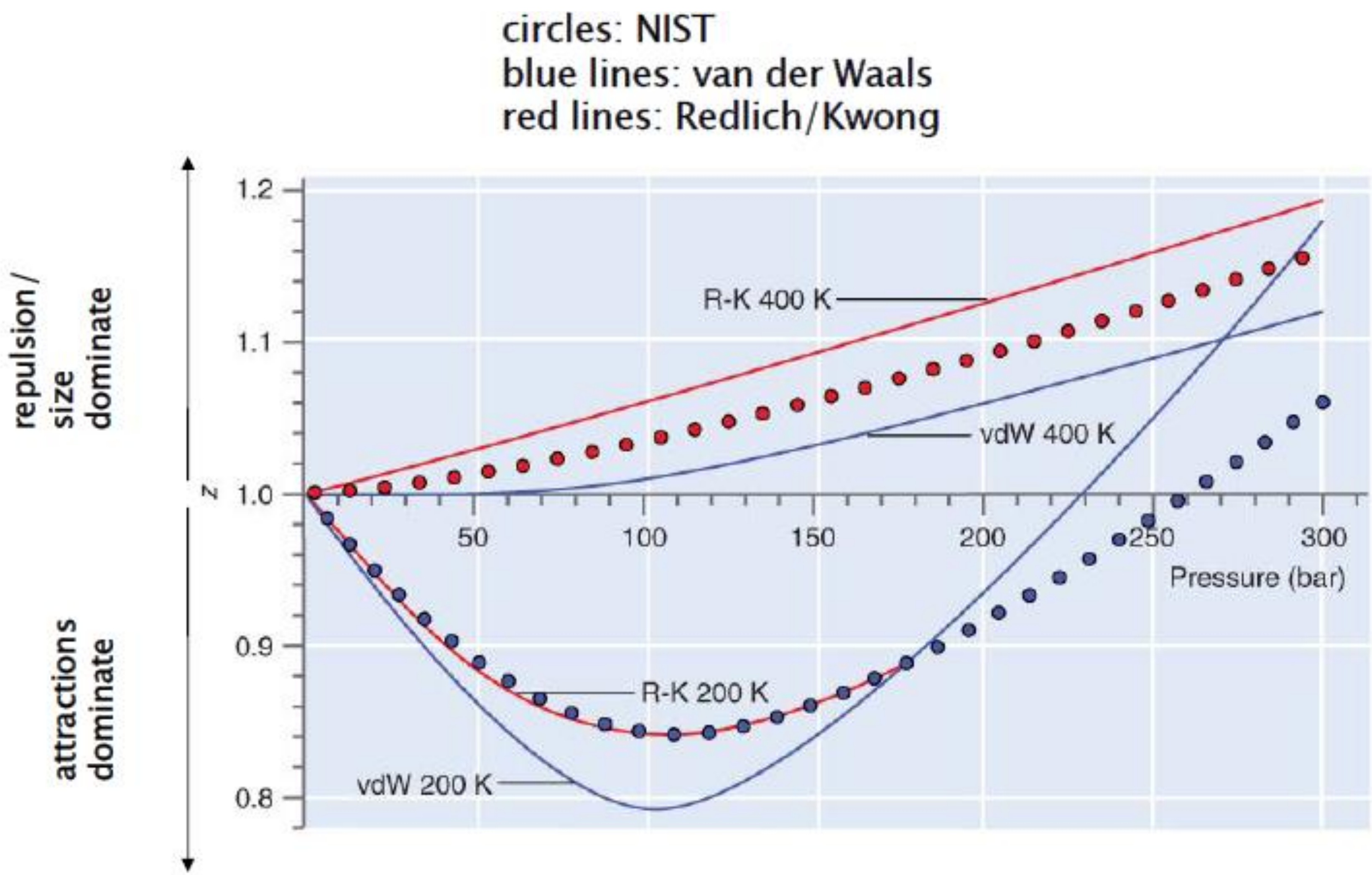
EOS

Compressibility factor (z)

- $z = \frac{Pv}{RT}$
  - z=1 for ideal gas
  - z<1: real gas has smaller volume than ideal gas at same T&P
  - z>1: real gas has larger volume than ideal gas at same T&P
- $z_c = \frac{P_c v_c}{RT_c}$
  - compressibility factor at critical point
  - $z_{c,\text{simple gases}} \approx 0.29$
  - $z_{c,vdw} = 0.375$
  - $z_{c,RK} = 0.333$

	z_c		z_c
Argon	0.291	Methane	0.286
N2	0.292	Ethane	0.279
O2	0.288	Propane	0.276
H2	0.303	Benzene	0.268
CO2	0.274	Methanol	0.221
Water	0.229	Ethanol	0.241

N_2 at 200 & 400K



Cubic EOS

- **3 parameters**
  - a: attraction, b: size, ω = acentric factor
  - Soave-Redlich-Kwong
    - $P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)}$

    $\alpha = (1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)\left(1 - \sqrt{T/T_c}\right))^2$
  - Peng-Robinson
    - $P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)+b(v-b)}$

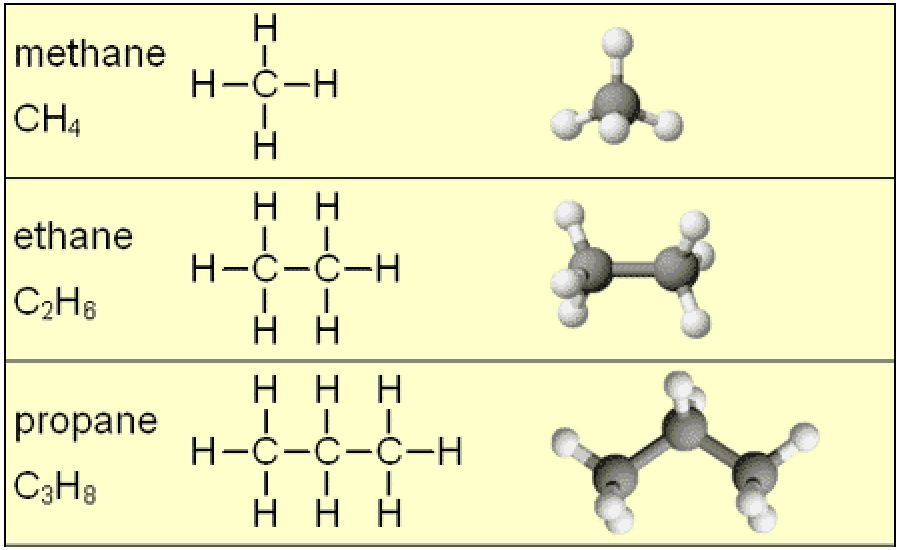
    $$\alpha = \left[1 + \kappa\left(1 - \sqrt{T/T_c}\right)\right]^2$$

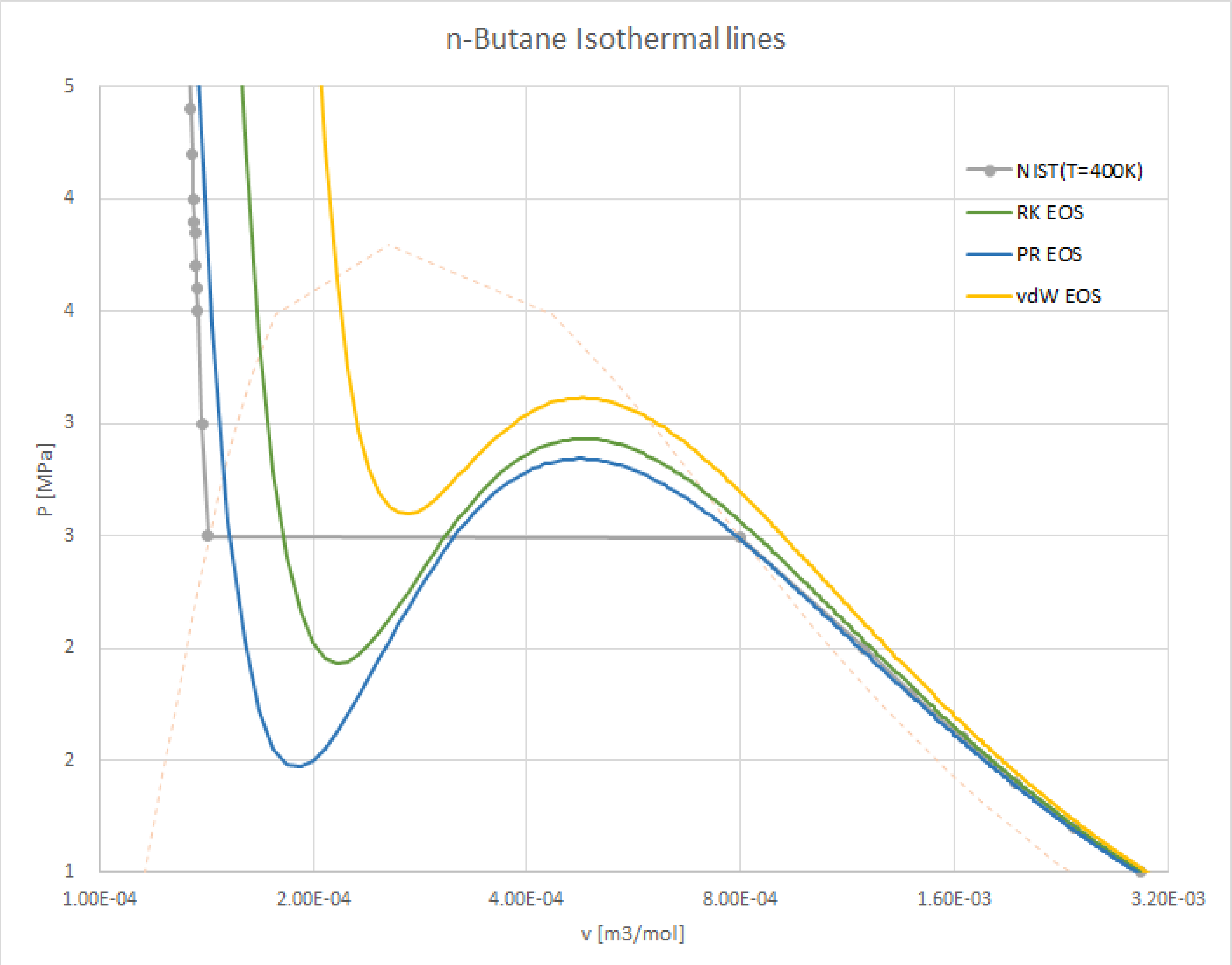
    $$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

Acentric Factor

- How much non-spherical a molecule is
- Typically zero for spherical molecules "simple fluids"

	ω
Argon	0
Xenon	0
Methane	0.012
Ethane	0.100
Propane	0.152
CO2	0.224
Water	0.345





n-Butane Isothermal lines
5
4
4
3
3
2
2
1
P [MPa]
1.00E-04
2.00E-04
4.00E-04
8.00E-04
1.60E-03
3.20E-03
v [m3/mol]
NIST(T=400K)
RK EOS
PR EOS
vdW EOS

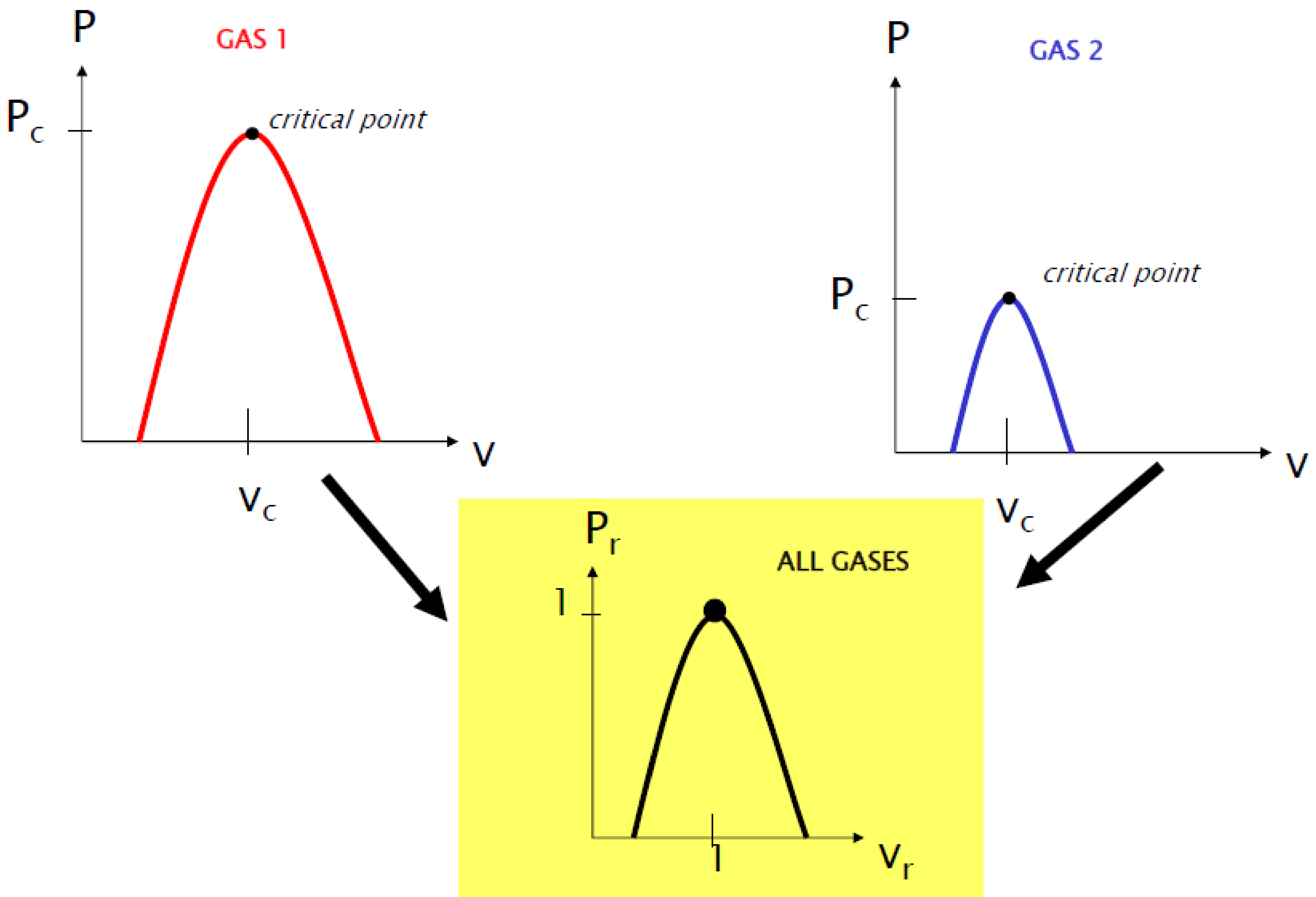
Theory of Corresponding States

- All fluids at the same reduced temperature and reduced pressure have the same compressibility factor z.
- Reduced T, P, v: ratio to critical point values
  - $T_r = \frac{T}{T_c}, P_r = \frac{P}{P_c}, v_r = \frac{v}{v_c}$
  - At the critical point, $T_r = P_r = v_r = 1$

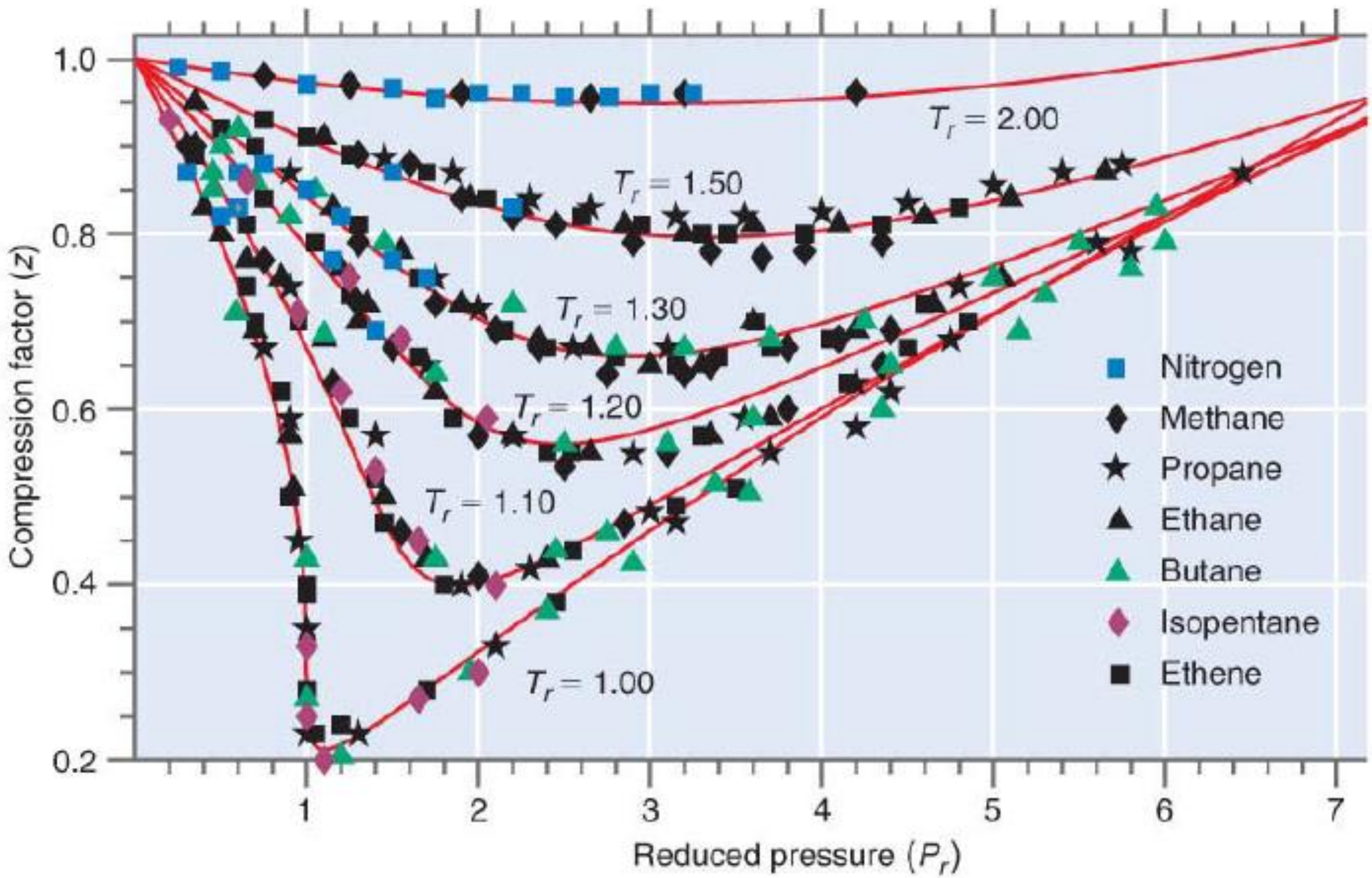
Reduced form of EOS

- VdW
  - $P = \frac{RT}{v-b} - \frac{a}{v^2}$
  - z_{VdW}=Pv/RT=f(T,v,a,b)
  - $a = \frac{27}{64}\frac{(RT_c)^2}{P_c},\ b = \frac{(RT_c)}{8P_c}$
  - $P_r = \frac{8Tr}{3v_r - 1} - \frac{3}{{v_r}^2}$ (4.23)
  - Now z_{VdW}=Pv/RT=f(T_r, v_r)

Theory of Corresponding States



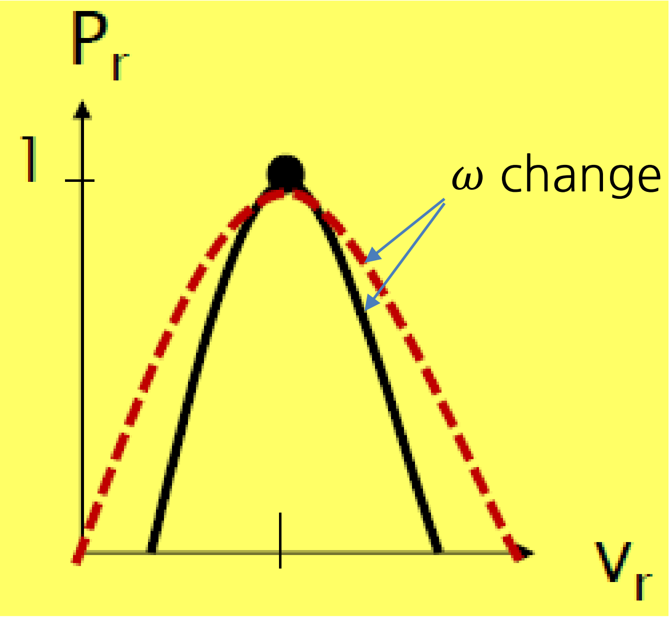
Theory of Corresponding States



Theory of Corresponding States (3 parameters)

- **Lee-Kessler**
  - Modified theory of corresponding states
  - $z = f(T_r, v_r)$ ➡ $z = f(T_r, v_r, \omega)$
  - $z = z^0(T_r, P_r) + \omega z^1(T_r, P_r)$

Simple fluid term | Correction term



  - You can use generalized compressibility chart!
  - (Figure 4.13&4.14)

$z^{(0)}$ vs P_r based on LK EOS (F4.13)

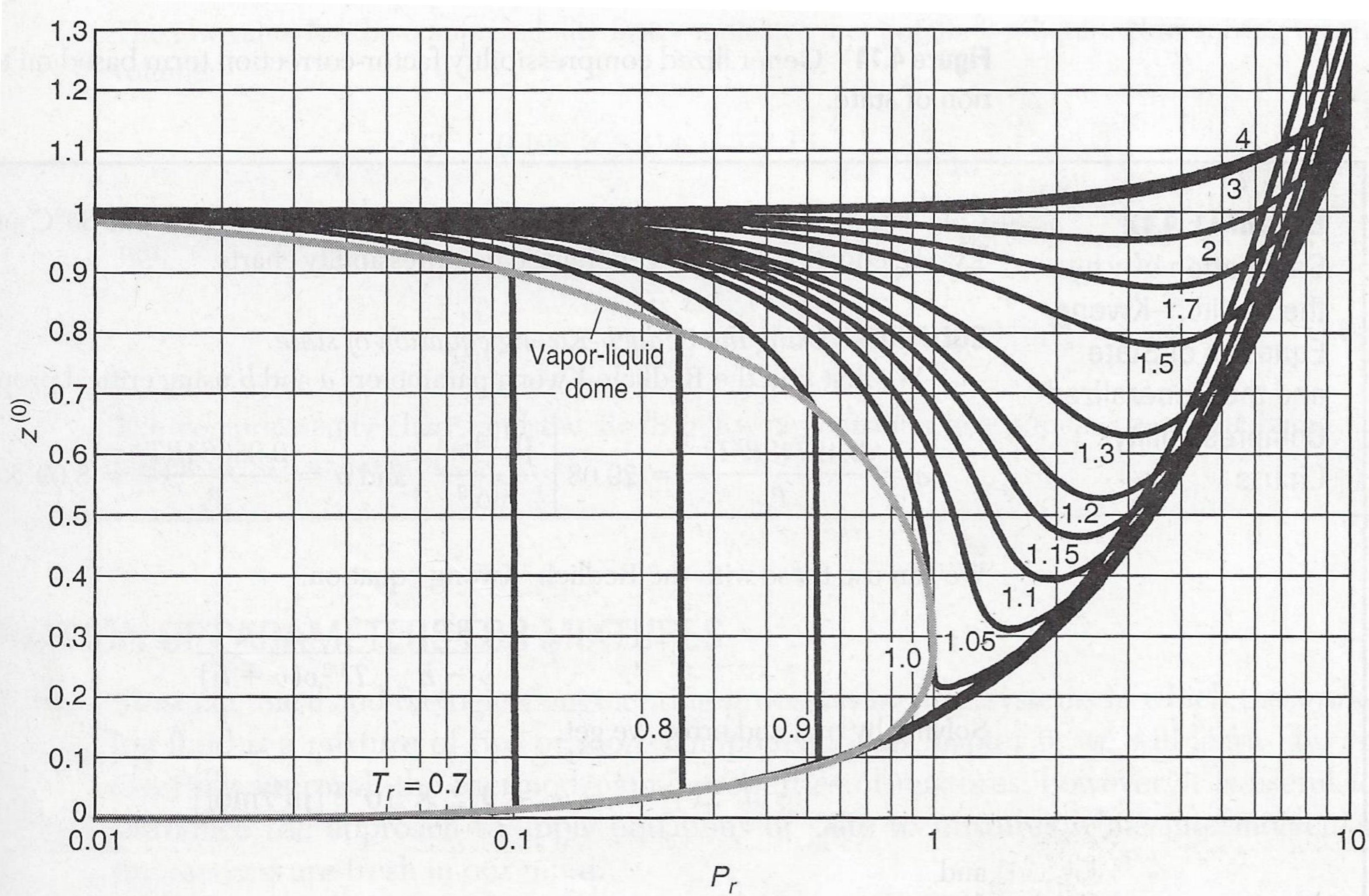


Figure 4.13 Generalized compressibility factor—simple fluid term. Based on the Lee–Kesler equation of state.

$z^{(1)}$ vs P_r based on LK EOS (F4.13)

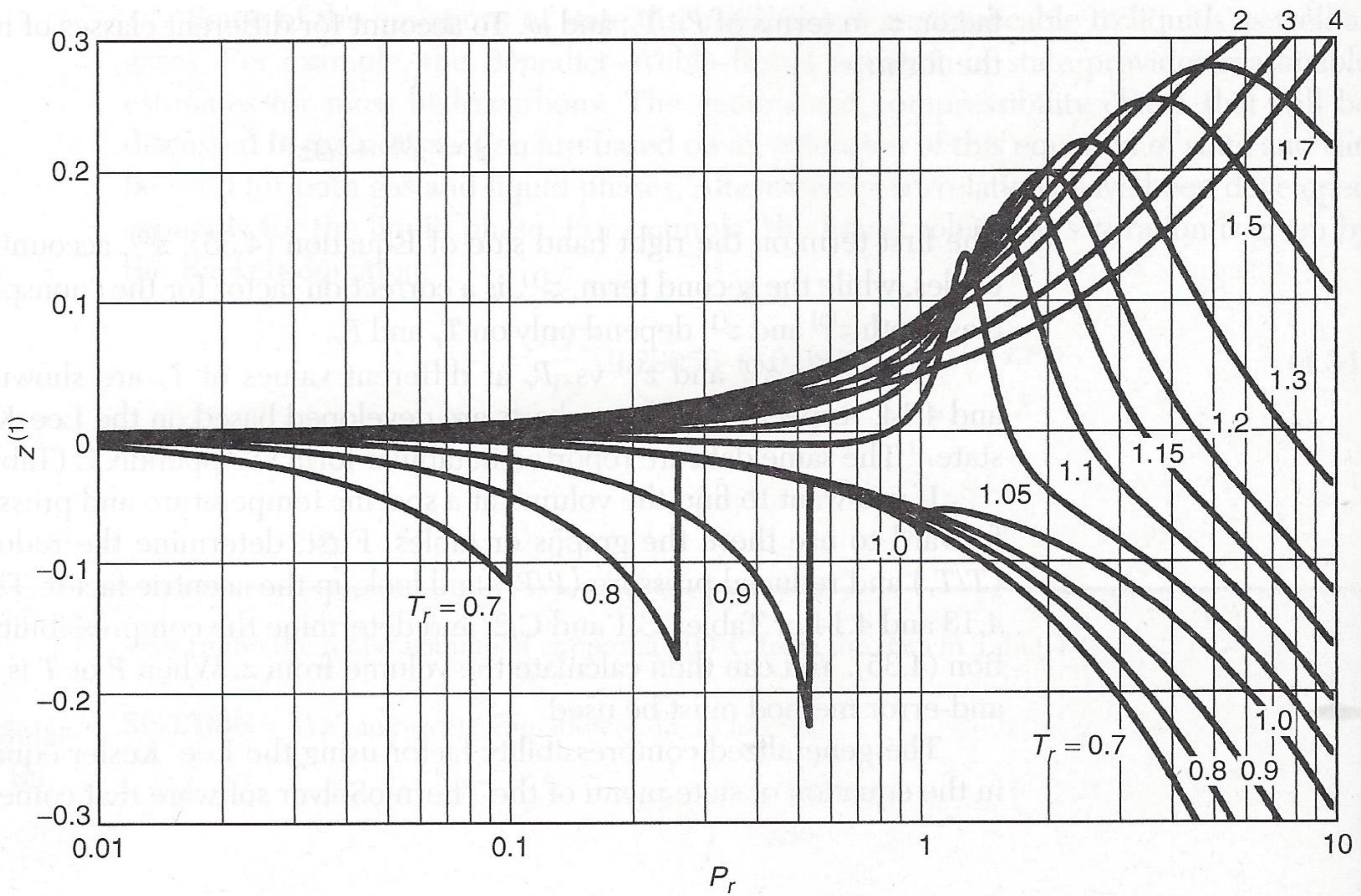
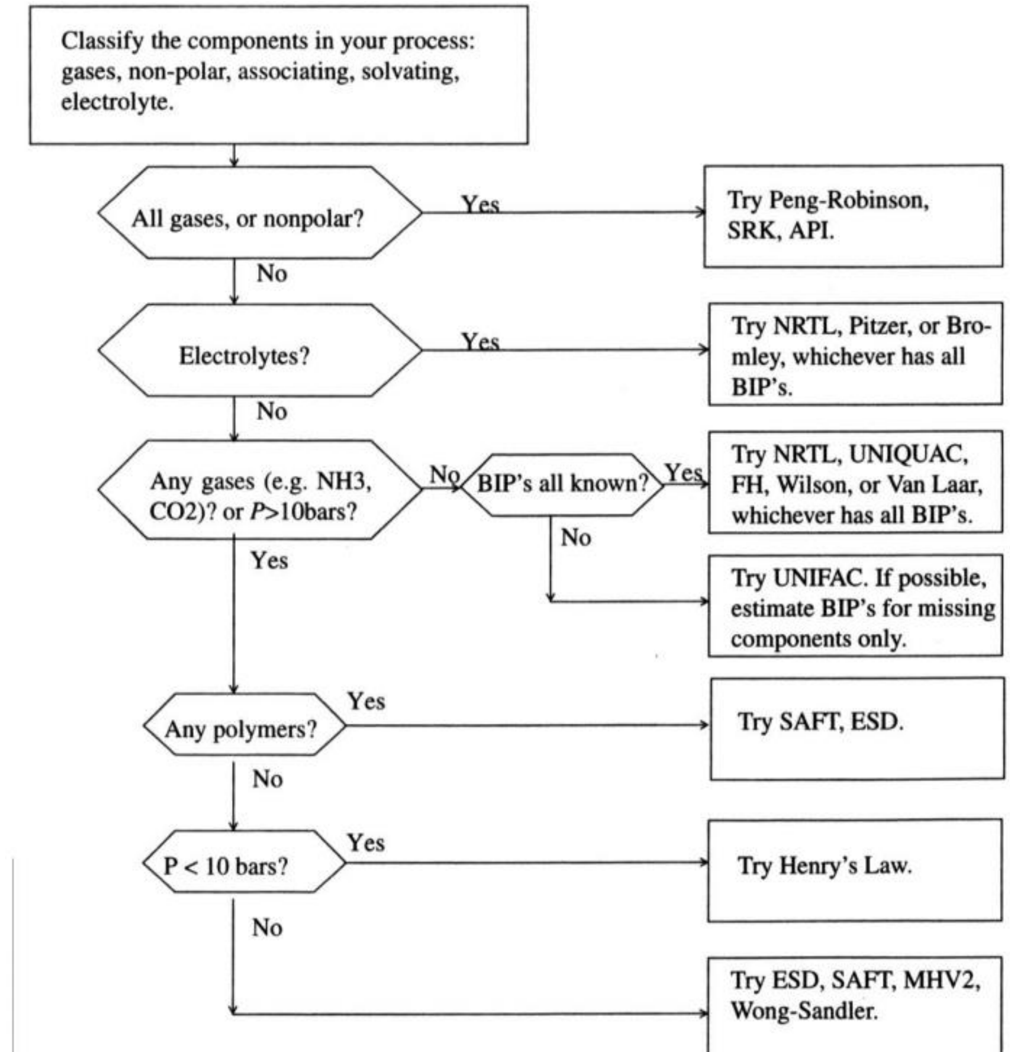


Figure 4.14 Generalized compressibility factor-correction term based on the Lee-Kesler equation of state.

A guide to select a method of calculation for thermodynamic properties



BIP: mean binary interaction parameters

[Elliot and Lira, "introduction to Chemical Engineering Thermodynamics", Prentice Hall, 1999].

EOS for Mixture

Mixing Rule

$$a_{mix} = \sum_i \sum_j y_i y_j a_{ij}, \qquad a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$$

$$b_{mix} = \sum_i y_i b_i$$

*Homework, ex4.13 has an calculation error

RK EOS

$$P = \frac{RT}{v - b} - \frac{a}{\sqrt{T}v(v + b)}$$

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

$$P = \frac{RT}{v - b_{mix}} - \frac{a_{mix}}{\sqrt{T}v(v + b_{mix})}$$

$$a_{mix} = \sum_i \sum_j y_i y_j a_{ij}, \qquad a_{ij} = \sqrt{a_i a_j}(1 - k_{ij})$$

$$b_{mix} = \sum_i y_i b_i$$

For component i

$$a_i = 0.42748 \frac{R^2 T_{c,i}^{2.5}}{P_{c,i}}, \qquad b_i = 0.08664 \frac{RT_{c,i}}{P_{c,i}}$$

Ex 4.12, 4.13