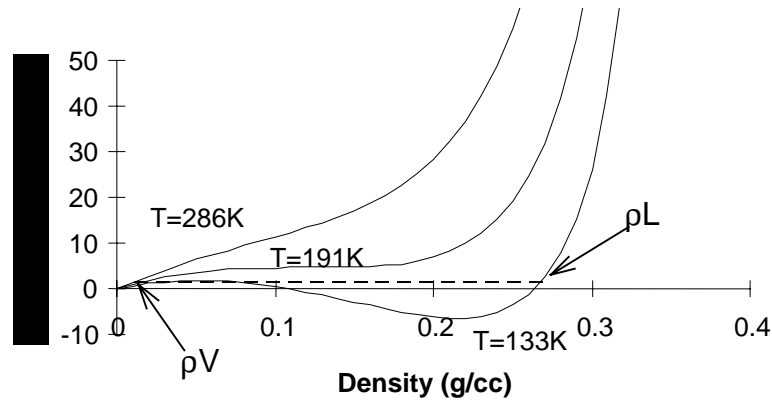# Introductory Chemical Engineering Thermodynamics

**By J.R. Elliott and C.T. Lira**
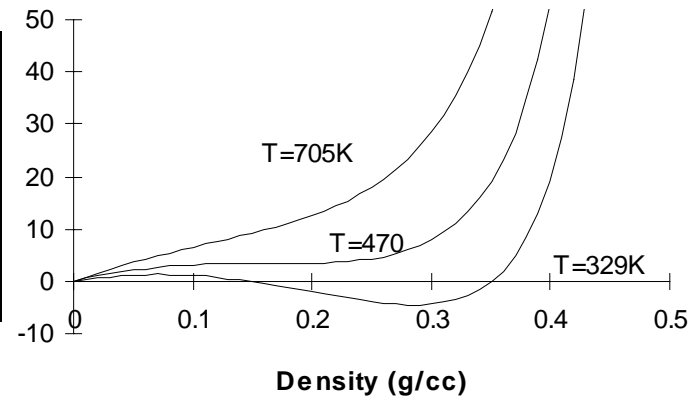
## Chapter 6 - Engineering Equations of State

# II. Generalized Fluid Properties

**The principle of two-parameter corresponding states**



**VdW Pressure (bars) in Methane**  **VdW Pressure (bars) in Pentane**

Critical Definitions:

$T_C$ - critical temperature - the temperature above which no liquid can exist.

$P_C$ - critical pressure - the pressure above which no vapor can exist.

$\omega$ - acentric factor - a third parameter which helps to specify the vapor pressure curve which, in turn, affects the rest of the thermodynamic variables.

Note: at the critical point, $\left(\dfrac{\partial P}{\partial \rho}\right)_T = 0$ and $\left(\dfrac{\partial^2 P}{\partial \rho^2}\right)_T = 0$ at $T_c$ and $P_c$

# II. Generalized Fluid Properties

## The van der Waals (1873) Equation Of State (vdW-EOS)

Based on some semi-empirical reasoning about the ways that temperature and density affect the pressure, van der Waals (1873) developed the equation below, which he considered to be fairly crude. We will discuss the reasoning at the end of the chapter, but it is useful to see what the equations are and how we use them before deriving the details. The vdW-EOS is:

$$Z = 1 + \frac{b\rho}{(1-b\rho)} - \frac{a\rho}{RT} = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT}$$

van der Waals' trick for characterizing the difference between subcritical and supercritical fluids was to recognize that, at the critical point,

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0 \quad \text{at} \quad T_c, \; P_c$$

Since there are only two "undetermined parameters" in his EOS (a and b), he has reduced the problem to one of two equations and two unknowns. Running the calculus gives:
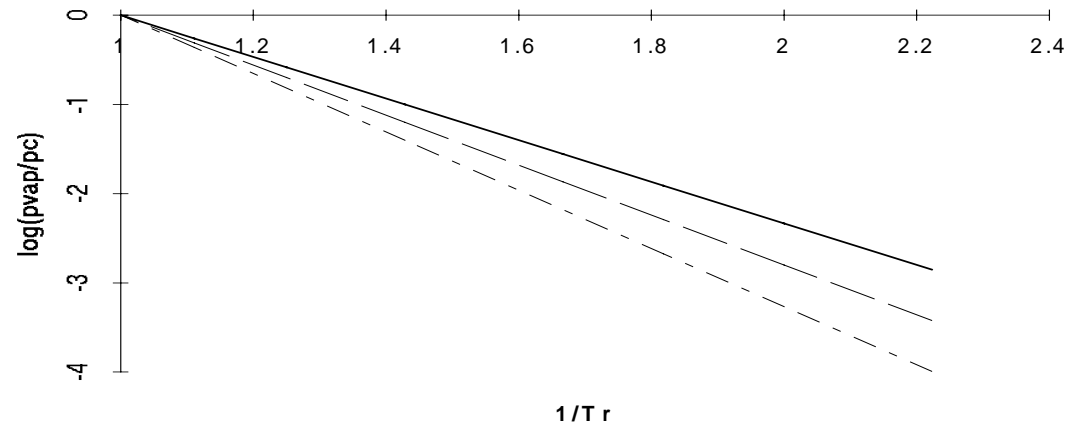$a = 0.475 \, R^2 T_c^2 / P_c; \;\; b = 0.125 \, RT_c / P_c$
The capability of this simple approach to represent all of the properties and processes that we will discuss below is a tribute to the genius of van der Waals.

# II. Generalized Fluid Properties

**The principle of three-parameter corresponding states**

Reduced vapor pressure behavior:



To improve our accuracy over the VdW EOS, we can generate a different set of PVT curves for each family of compounds. We specify the family of compounds via the "third parameter" i.e. $\omega$. Note: The specification of $T_c$, $p_c$, and $\omega$ provides two points on the vapor pressure curve. The key to accurate characterization of the vapor liquid behavior of mixtures of fluids is the accurate characterization of the vapor pressure of pure fluids. VLE was central to the development of distillation technology for the petrochemical industry and provided the basis for most of today's process simulation technology.

# II. Generalized Fluid Properties

## The Peng-Robinson (1976) Equation of State

$$p = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho - b^2\rho^2} \qquad \text{or} \qquad Z = \frac{1}{(1\text{-}b\rho)} - \frac{a}{bRT}\cdot\frac{b\rho}{1+2b\rho - b^2\rho^2}$$

where $\rho$ = molar density = $n/\underline{V}$

By fitting the critical point, where $\partial P/\partial V = 0$ and $\partial^2 P/\partial V^2 = 0$,

$a = 0.457235528\ \alpha R^2 T_c^2/P_c$;  $b = 0.0777960739\ RT_c/P_c$

$\alpha = [1+ \kappa\,(1\text{-}\sqrt{Tr})]^2$ ;  $\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$

$\omega \equiv -1 - \log_{10}(P^{\text{sat}}/P_c)_{Tr\,=0.7} \equiv$ "acentric factor"

$T_c$ , $P_c$ , and $\omega$ are reducing constants according to the principle of corresponding states. By applying Maxwell's relations, we can calculate the rest of the thermodynamic properties $(H,U,S)$ based on this single equation.

# II.  Generalized Fluid Properties

## Solving the Equation of State for Z

$$Z = \cfrac{1}{\left(1 - B/Z\right)} - \cfrac{A}{B} \cdot \cfrac{B/Z}{1 + 2B/Z - (B/Z)^2}$$

$b\rho \equiv B/Z$

where 
$B \equiv bP/RT$
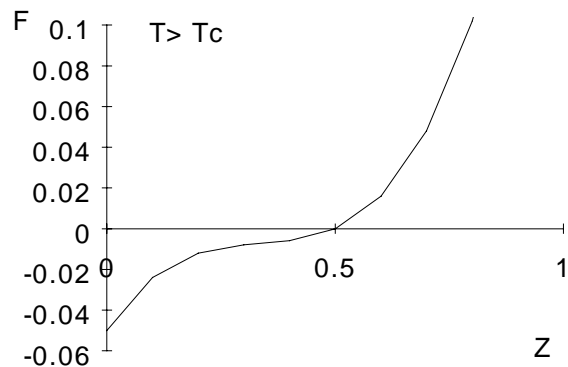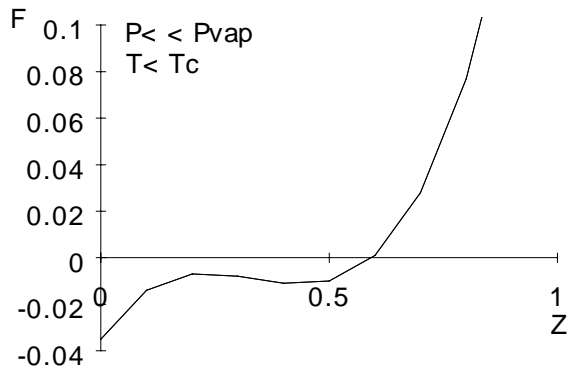
$Z \equiv P/\rho RT$
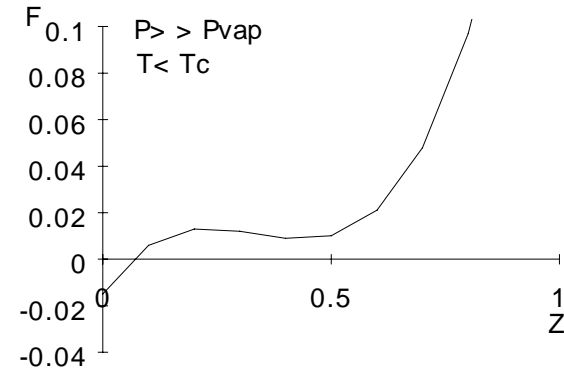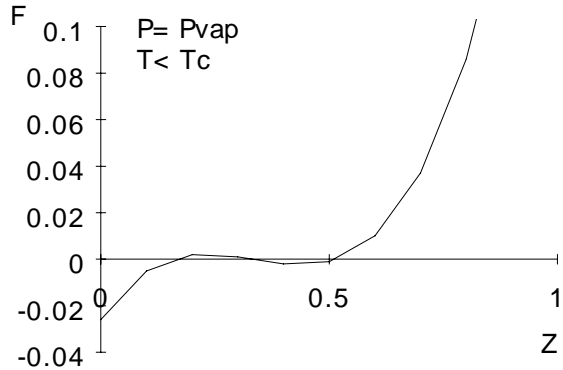
$A \equiv aP/R^2T^2$

Rearranging yields a cubic function in Z

$$Z^3 - (1-B)Z^2 + (A-3B^2-2B)Z - (AB-B^2-B^3) = 0$$

Naming this function F(Z), we can plot F(Z) vs. Z to gain some understanding about its roots

# II. Generalized Fluid Properties

**Solving the Equation of State for Z**

# II.  Generalized Fluid Properties

**Solving the Equation of State for Z (cont.)**

1.  Guess Zold=1 or Zold=0 and compute $F_{old}(Zold)$.
2.  Compute $F_{now}(Z)$ at Z=1.0001 or Z=0.0001
3.  "Interpolate" between these guesses to estimate where F(Z)=0.

   $\Delta Z = (0 - F_{now})*(Znow-Zold)/(F_{now} - F_{old})$.

4.  Set $F_{old}=F_{now}$, Zold=Znow, Znow=Zold+$\Delta$Z
5.  If $|\Delta Z/Znow| < 1.E-5$, print the value of Znow and stop.
6.  Compute $F_{now}(Znow)$ and return to step 3 until step 5 terminates.
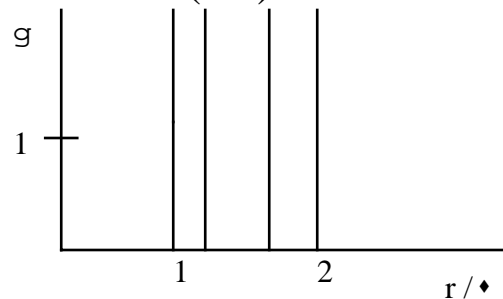
# II. Generalized Fluid Properties

**An Introduction to the Radial Distribution Function**
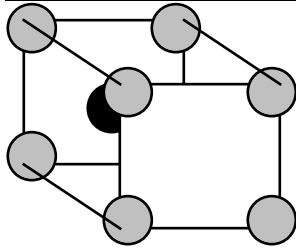


The body centered cubic
unit cell
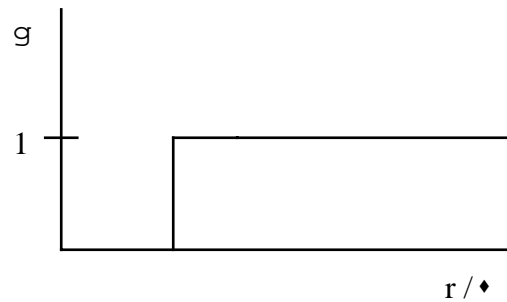
$$Nc = \rho \int_{o}^{R} g(r) \, 4\pi \, r^2 \, dr;$$

where g(r) is our "weighting factor" henceforth referred to as the radial distribution function (rdf).
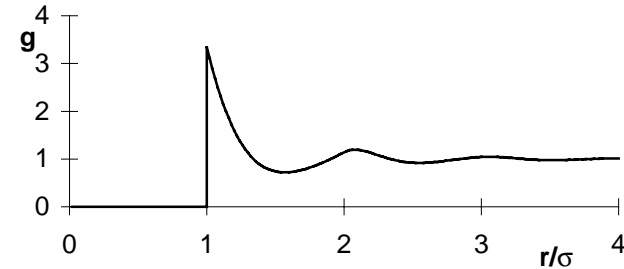


The radial distribution function
for the bcc hard sphere fluid

# An Introduction to the Radial Distribution Function

$$Nc = \rho \int_{o}^{R_o} g(r)\, 4\pi r^2 dr$$
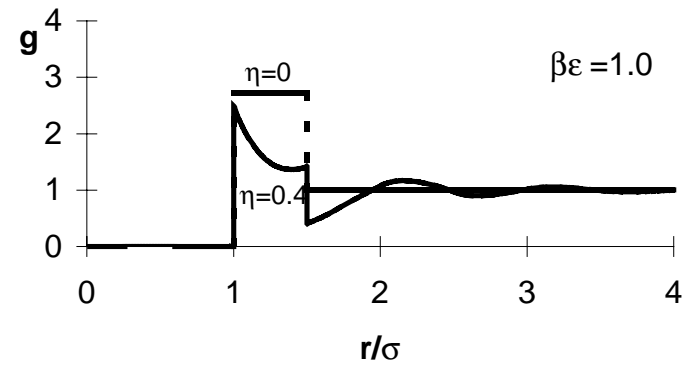
g

1

r / •

**The low density hard-sphere fluid**



**The high density hard sphere fluid**

g

1

r / •
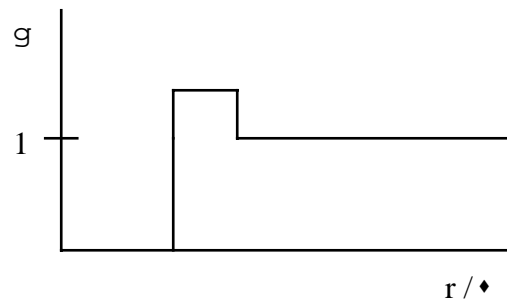
**The low density square-well fluid**



$\eta=0$

$\eta=0.4$

$\beta\varepsilon =1.0$

**The high density square-well fluid**

# II. Generalized Fluid Properties

**The connection from the molecular scale to the macroscopic scale**

**The Energy Equation**

$$\frac{U - U^{id}}{nRT} = \frac{N_A \rho}{2RT} \int_0^\infty N_A u \; g \; 4\pi \; r^2 \; dr$$

**The Pressure Equation**

$$\frac{P}{\rho RT} = 1 - \frac{N_A \rho}{6RT} \int_0^\infty r N_A \left( \frac{du}{dr} \right) g \; 4\pi \; r^2 \; dr$$

$$P / \rho RT = 1 - \frac{N_A \rho}{6RT} \int_0^\sigma r N_A \left( \frac{du}{dr} \right) g \; 4\pi \; r^2 dr \; - \; \frac{N_A \rho}{6RT} \int_\sigma^\infty r N_A \left( \frac{du}{dr} \right) g \; 4\pi \; r^2 dr$$

# II. Generalized Fluid Properties

**The Van der Waals Equation of State**

$$\frac{-N_A\rho}{6RT}\int_{O}^{\sigma} rN_A\left(\frac{du}{dr}\right) g\ 4\pi\ r^2\ dr\ \approx\ \frac{b\rho}{(1-b\rho)} \quad \text{where } b\sim\text{close-packed volume}$$

$$\frac{N_A\rho}{6RT}\int_{\sigma}^{\infty} rN_A\left(\frac{du}{dr}\right) g\ 4\pi\ r^2\ dr\ =\ \frac{\rho N_A\sigma^3 N_A\varepsilon}{6RT}\int_{1}^{\infty} x\left(\frac{du}{dx}\right) g\ 4\pi\ x^2\ dx\ \text{where } x\equiv r/\sigma$$

$$a \equiv \frac{N_A\sigma^3 N_A\varepsilon}{6}\int_{\sigma}^{\infty} x\left(\frac{du/\varepsilon}{dx}\right) g\ 4\pi\ x^2\ dx$$

The resulting equation of state is:

$$Z = 1 + \frac{b\rho}{(1-b\rho)} - \frac{a\rho}{RT} = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT}$$

By fitting the critical point, where $\partial P/\partial V = 0$ and $\partial^2 P/\partial V^2 = 0$,
$a = 0.475\ R^2 T_c^2/P_c;\ \ b = 0.125\ RT_c/P_c$

# II. Generalized Fluid Properties

**Example. From the molecular scale to the continuum**

Suppose that the radial distribution function can be reasonably represented by:

$$g \approx 1 + \frac{b\rho\varepsilon}{kT}\frac{1}{x^4} \qquad \text{where } x \equiv r/\sigma \text{ and } b \equiv {}^{\pi}\!/_{6}\, N_A\sigma^3$$

Derive expressions for the compressibility factors of fluids that can be accurately represented by the square-well potential. Evaluate this expression at $b\rho = 0.2$ and $\varepsilon/kT = 1$.

**Solution**: First read Appendix C then note that, for the square-well potential,

$\exp(-u/kT) = \exp(\varepsilon/kT)\, H(r-\sigma) + [\exp(\varepsilon/kT)-1]\,[1-H(r-1.5\sigma)]$

Taking the derivative of the Heaviside function gives the Dirac delta in two places:

$$Z = 1 + \frac{N_A\rho}{6}\int \left[\delta(r-\sigma)y(r)\exp(\varepsilon/kT) - \delta(r-1.5\sigma)y(r)[\exp(\varepsilon/kT)-1]\right]4\pi r^3 dr$$

$$Z = 1 + \frac{4\pi N_A\rho\sigma^3}{6}\left\{y(\sigma)\exp(\varepsilon/kT) - 1.5^3\, y(1.5\sigma)[\exp(\varepsilon/kT)-1]\right\}$$

Noting that $y(r) \equiv g(r)\exp(u/kT)$ and that $\exp(u/kT)$ is best evaluated inside the well:

$Z = 1 + 4b\rho\, \{\, g(\sigma^+) - 1.5^3[1-\exp(-\varepsilon/kT)]\, g(1.5\sigma^-)\}$      This is true for SW with ***any*** $g(r)$.

For the above expression: $g(\sigma^+) = 1 + b\rho\,\varepsilon/kT$ and $g(1.5\sigma^-) = 1 + 0.198\, b\rho\,\varepsilon/kT$

$Z = 1 + 4b\rho\,\{1 + b\rho\,\varepsilon/kT - 1.5^3[1-\exp(-\varepsilon/kT)](1 + 0.198\, b\rho\,\varepsilon/kT)\}$

$Z = 1 + 4(0.2)\{1+0.2-2.1333*1.0396\} = 0.1858$