

Overview Chapter 7

$$P = RT/V$$

Ideal Gas Equation of State

Van der Waals Equation of State

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{Cubic Equation of State} \quad a = \frac{27(RT_c)^2}{64 P_c} \quad b = \frac{RT_c}{8P_c}$$

$$Z \equiv \frac{PV}{RT}$$

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}$$

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \dots \quad \text{Virial Equation of State}$$

$$B(T) = b - \frac{a}{RT}$$

Peng-Robinson Equation of State (PREOS)

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

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a}{bRT} \cdot \frac{b\rho}{1+2b\rho-b^2\rho^2}$$

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad \text{Cubic Equation of State}$$

Solve cubic equations (3 roots)

ENGINEERING EQUATIONS OF STATE FOR PVT PROPERTIES

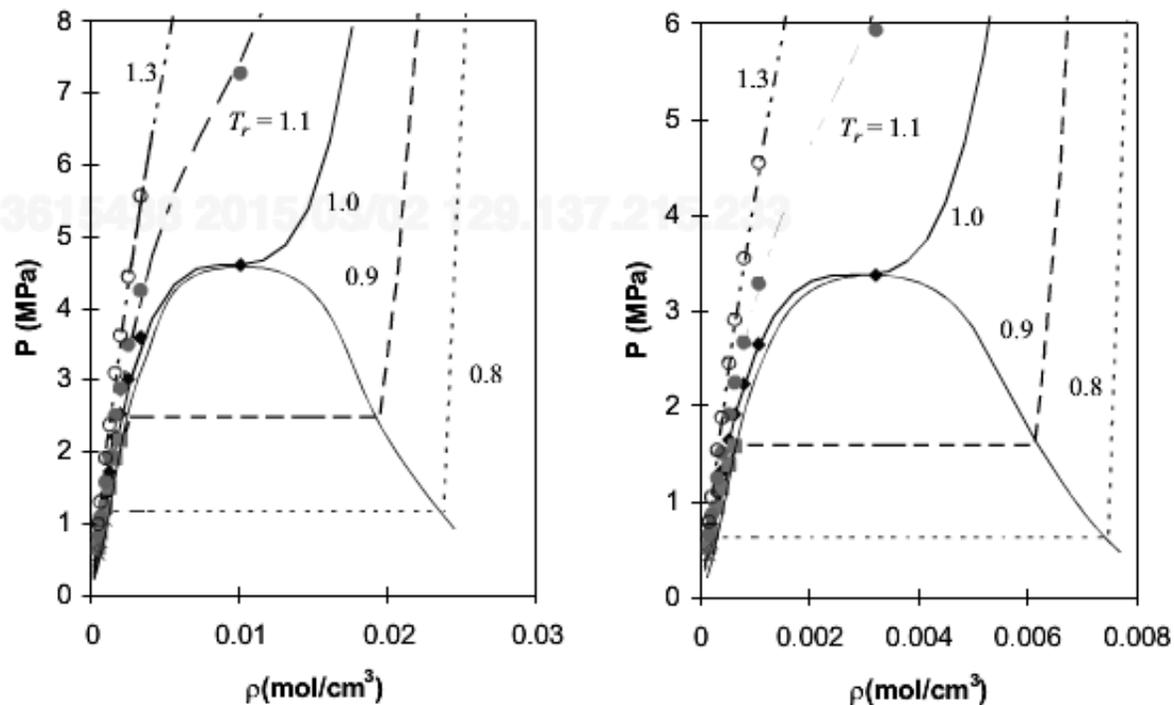


Figure 7.1 Comparison of the $P\rho T$ behavior of methane (left) and pentane (right) demonstrating the qualitative similarity which led to corresponding states' treatment of fluids. The lines are calculated with the Peng-Robinson equation to be discussed later. The phase envelope is an approximation sketched through the points available in the plots. The smoothed experimental data are from Brown, G.G., Saunders Jr., M., and Smith, R.L., 1932. *Ind. Eng. Chem.*, 24:513. Although not shown, the Peng-Robinson equation is not particularly accurate for modeling liquid densities.

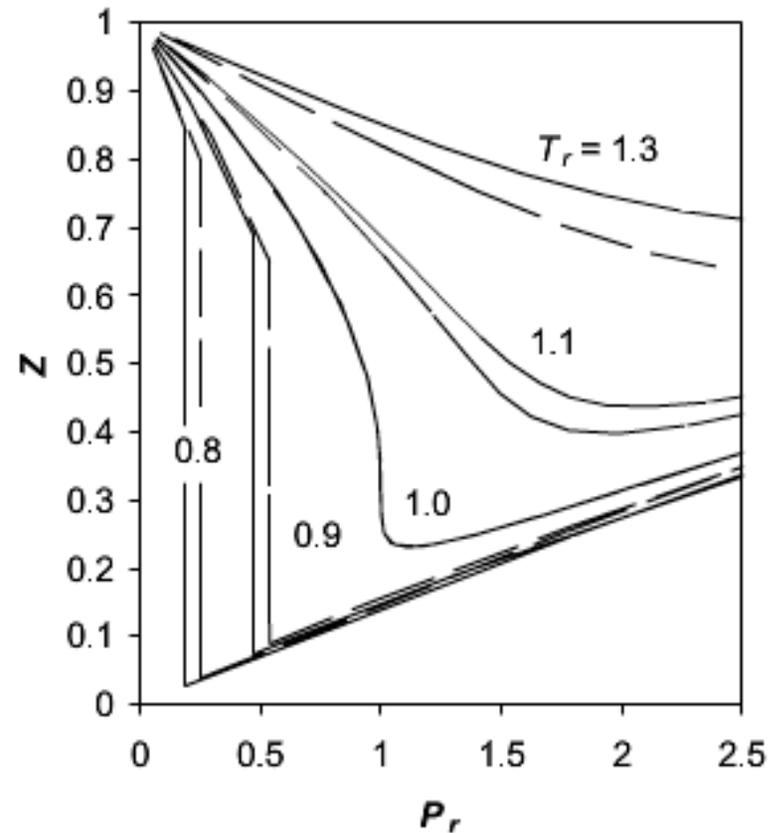


Figure 7.2 The Peng-Robinson lines from Fig. 7.1 plotted in terms of the reduced pressure at $T_r = 0.8, 0.9, 1.0, 1.1,$ and $1.3,$ demonstrating that critical temperature and pressure alone are insufficient to accurately represent the P - V - T behavior. Dashed lines are for methane, solid lines for pentane. The figure is intended to make an illustrative point. Accurate calculations should use the compressibility factor charts developed in the next section.

$$Z \equiv \frac{PV}{RT}$$

7.1  The compressibility factor.

Arrhenius Behavior

$$P_{\text{sat}} \sim \exp(-E_a/kT)$$

$$\text{Log}(P) \sim 1/T$$

Slope is an activation energy for P_{sat}

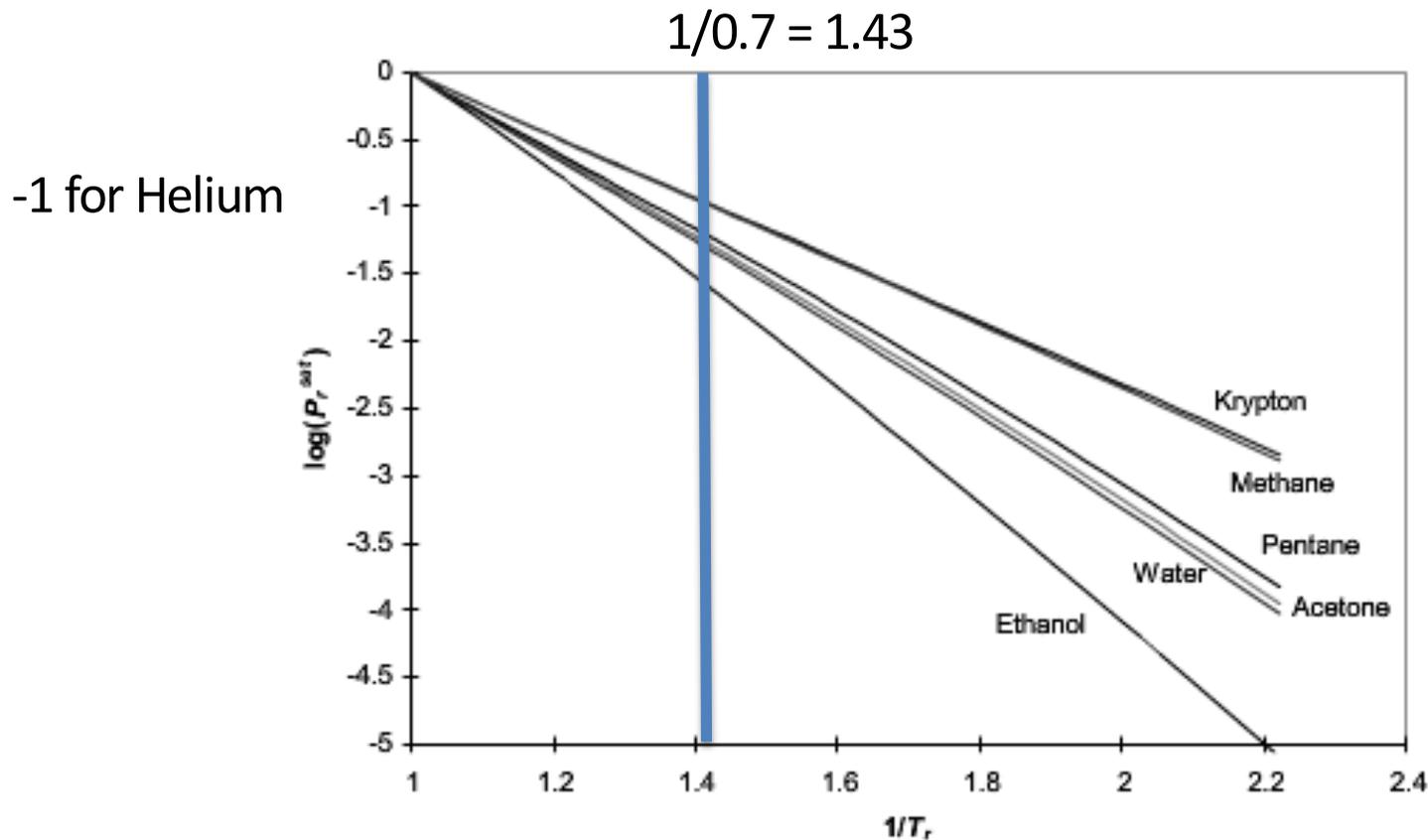


Figure 7.3 *Reduced vapor pressures plotted as a function of reduced temperature for six fluids demonstrating that the shape of the curve is not highly dependent on structure, but that the primary difference is the slope as given by the acentric factor.*

nearly linear, the slopes are different. In fact, we may characterize this slope with a third empirical parameter, known as the acentric factor, ω . The **acentric factor** is a parameter which helps to specify the vapor pressure curve which, in turn, correlates the rest of the thermodynamic variables.²

$$\omega \equiv -1 - \log_{10} \left(\frac{P^{sat}}{P_c} \right) \Bigg|_{T_r = 0.7} \quad \equiv \text{acentric factor} \quad 7.2$$

Acentric factor

From Wikipedia, the free encyclopedia



This article has multiple issues. Please help [improve it](#) or discuss these issues on the [talk page](#). [hide]

- This article **needs additional citations for verification**. (November 2013)
- This article **possibly contains original research**. (March 2011)

The **acentric factor** ω is a conceptual number introduced by [Kenneth Pitzer](#) in 1955, proven to be very useful in the description of matter.^[1] It has become a standard for the phase characterization of single & pure components. The other state description parameters are [molecular weight](#), [critical temperature](#), [critical pressure](#), and [critical volume](#). The **acentric factor** is said to be a measure of the non-sphericity (centricity) of molecules.^[2]

It is defined as:

$$\omega = -\log_{10}(p_r^{\text{sat}}) - 1, \text{ at } T_r = 0.7.$$

where $T_r = \frac{T}{T_c}$ is the [reduced temperature](#), $p_r^{\text{sat}} = \frac{p^{\text{sat}}}{p_c}$ is the [reduced pressure saturation of vapors](#).

For many monatomic fluids

$$p_r^{\text{sat}} \text{ at } T_r = 0.7.$$

is close to 0.1, therefore $\omega \rightarrow 0$. In many cases, $T_r = 0.7$ lies above the [boiling temperature](#) of gases at atmosphere pressure.

Values of ω can be determined for any fluid from $\{T_r, p_r\}$, and a vapor measurement from $T_r = 0.7$, and for many liquid state matter is tabulated into many thermodynamical tables.

The definition of ω gives zero-value for the [noble gases argon](#), [krypton](#), and [xenon](#). ω is almost exactly zero for other spherical molecules.^[2]

Experimental data yields compressibility factors for all fluids that are correlated by the same curves when Z ([compressibility factor](#)) is represented as a function of T_r and p_r . This is the basis premises of [three-parameter theorem of corresponding states](#):

All fluids at any ω -value, in $\{T_r, p_r\} = \text{const.}$ conditions, have about the same Z -value, and same degree of convergence.^[citation needed]

Values of some common gases [edit]

Molecule	Acentric Factor ^[3]
Acetylene	0.187
Ammonia	0.253
Argon	0.000
Carbon Dioxide	0.228
Decane	0.484
Helium	-0.390
Hydrogen	-0.220
Krypton	0.000
Neon	0.000
Nitrogen	0.040
Nitrous Oxide	0.142
Oxygen	0.022
Xenon	0.000

! Pitzer correlation.

$$Z = Z^0 + \omega Z^1$$

7.3

$$\omega \equiv -1 - \log_{10} \left(\frac{P^{sat}}{P_c} \right) \Bigg|_{T_r = 0.7} \quad \equiv \text{acentric factor}$$

7.2

$$Z \equiv \frac{PV}{RT}$$

7.1 ! The compressibility factor.

7.3. Generalized Compressibility Factor Charts

P - V - T behavior can be generalized in terms of T_c , P_c and ω . The original correlation was presented by Pitzer, and is given in the form

$$Z = Z^0 + \omega Z^1$$

7.3

! Pitzer correlation.

$$Z = Z^0 + \omega Z^1$$

7.3

Kenneth S. Pitzer



$$\omega \equiv -1 -$$

7.2

$$Z \equiv$$

! The compressibility factor.

CalTech
Berkeley
Rice
Stanford

7.3. Generalized

P-V-T behavior presented by Pitzer.

ation was

7.3

$$Z = Z^0 + \omega Z^1$$

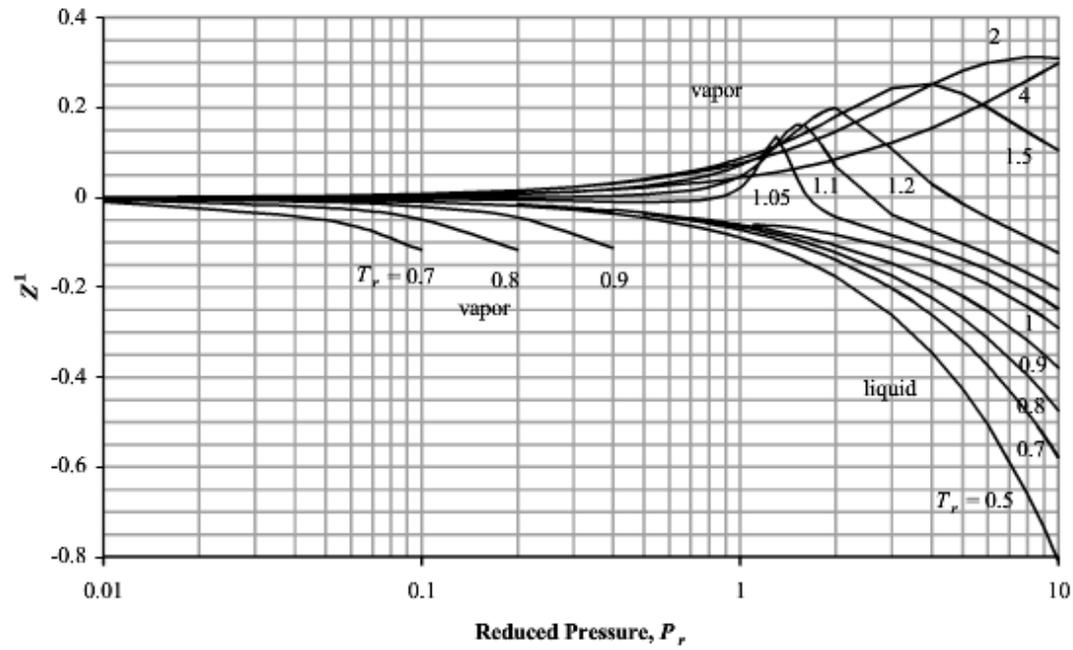
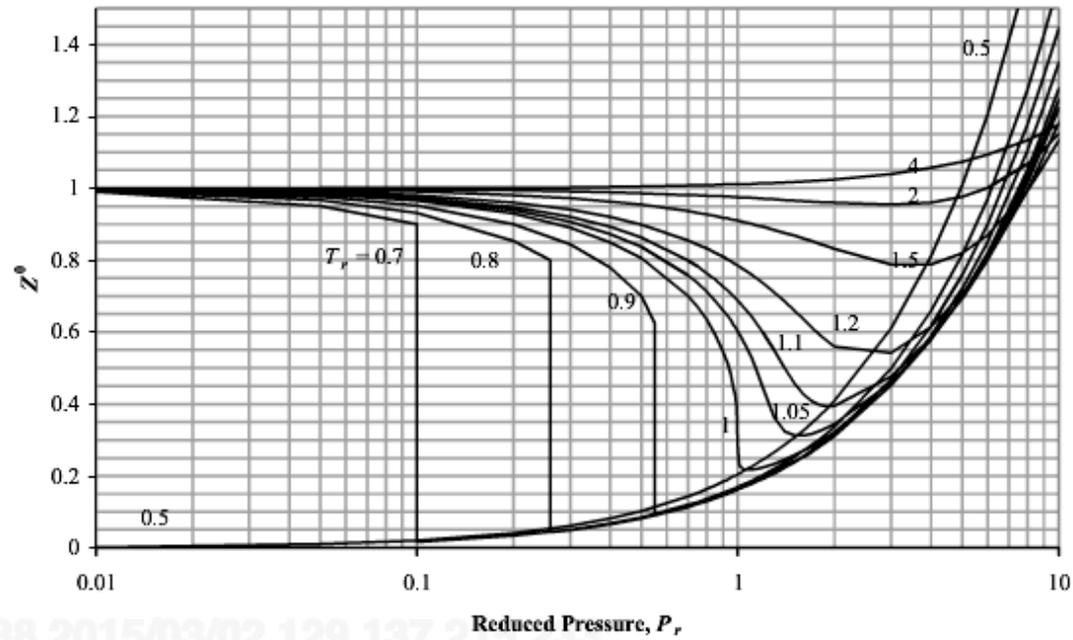


Figure 7.4 Generalized charts for estimating the compressibility factor. (Z^0) applies the Lee-Kesler equation using $\omega = 0.0$, and (Z^1) is the correction factor for a hypothetical compound with $\omega = 1.0$. Note the semilog scale.

Example 7.1 Application of the generalized charts

Estimate the specific volume in cm^3/g for carbon dioxide at 310 K and (a) 8 bar (b) 75 bar by the compressibility factor charts and compare to the experimental values² of 70.58 and 3.90, respectively.

Solution: $\omega = 0.228$ and $T_r = 310/304.2 = 1.02$ for both cases (a) and (b), so,
(a) $P_r = 8/73.82 = 0.108$; from the charts, $Z^0 = 0.96$ and $Z^1 = 0$, so $Z = 0.96$.

$$V = ZRT/(P \cdot MW) = (0.96 \cdot 83.14 \cdot 310)/(8 \cdot 44) = 70.29, \text{ within } 0.4\% \text{ of the experimental value.}$$

(b) $P_r = 75/73.82 = 1.016 \approx 1.02$; Note that the compressibility factor is extremely sensitive to temperature in the critical region. To obtain a reasonable degree of accuracy in reading the charts, we must interpolate between the reduced temperatures of 1.0 and 1.05 which we can read with more confidence.

$$\text{At } T_r = 1.0, Z^0 = 0.22 \text{ and } Z^1 = -0.08 \text{ so } Z = 0.22 + 0.228 \cdot (-0.08) = 0.202$$

$$\text{At } T_r = 1.05, Z^0 = 0.58 \text{ and } Z^1 = 0.03, \text{ so } Z = 0.58 + 0.228 \cdot (0.03) = 0.587$$

Interpolating, $Z = 0.202 + (0.587 - 0.202) \cdot 2/5 = 0.356$

$V = ZRT/(P \cdot MW) = (0.356 \cdot 83.14 \cdot 310)/(75 \cdot 44) = 2.78$, giving 29% error relative to the experimental value.

7.4 THE VIRIAL EQUATION OF STATE

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \dots \quad 7.4$$

$$Z = 1 + B(P/RT) \quad 7.5$$

where B is a function of T . Note that Eqn. 7.5 indicates that Z varies linearly with pressure along an isotherm. Look back at Fig. 7.4 and notice that the region in which linear behavior occurs is limited, but in general, the approximation can be used at higher reduced pressures when the reduced temperature is higher. The virial equation can be generalized in reduced coordinates as given by Eqns. 7.6–7.9.⁵ Eqn. 7.10 checks for restriction of the calculation to the linear Z region.

! Virial equation. B is known as the second virial coefficient, and it is a measure of the slope of the Z -chart isotherms in the linear region.

$$Z = 1 + (B^0 + \omega B^1)P_r/T_r \quad \text{or} \quad Z = 1 + BP/RT \quad 7.6$$

$$\text{where } B(T) = (B^0 + \omega B^1)RT_c/P_c \quad 7.7$$

$$B^0 = 0.083 - 0.422/T_r^{1.6} \quad 7.8$$

$$B^1 = 0.139 - 0.172/T_r^{4.2} \quad 7.9$$

$$\text{Subject to } T_r > 0.686 + 0.439P_r \text{ or } V_r > 2.0 \quad 7.10$$

developed to render the Pitzer correlation in terms of computer-friendly equations. The Lee-Kesler equation was used to generate Fig. 7.4.

$$Z = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^3} + \frac{E_0}{T_r^3 V_r^2} \left(E_1 + \frac{E_2}{V_r^2} \right) \exp\left(-\frac{E_2}{V_r^2} \right) \quad 7.11$$

Why Virial Expansion?

1) In situations where you want simple derivatives of P , V or Z in density.

Density fluctuations can be observed at zero angle scattering (light, neutrons, X-rays) as the inverse of the isothermal compressibility, $\kappa_T = -1/V (dV/dP)_T$, so the first derivative of P as a function of ρ , which is $B_2(T)$, can be easily measured. This can also be measured in an osmotic pressure measurement using a semipermeable membrane.

2) $B_2(T)$ can be calculated from an integral of the potential energy $u(r)$ between atoms/particles, from quantum or molecular or coarse grain theory.

$$B = 2\pi N_A \int_0^\infty \left(1 - \exp\left(-\frac{u}{kT}\right)\right) r^2 dr \quad 7.59$$

3) $B_2(T)$ can be calculated from the radial distribution function, from simulations and measurements.

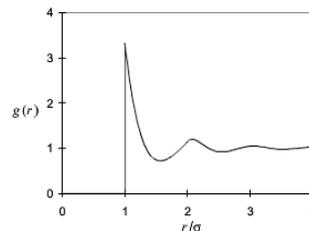


Figure 7.13 The radial distribution function for the hard-sphere fluid at a packing fraction of $\eta = 0.4$.

Example 7.2 Application of the virial equation

Estimate the specific volume in cm^3/g for carbon dioxide at 310 K and (a) 8 bar (b) 75 bar by the virial equation and compare to the experimental values of 70.58 and 3.90, respectively.

Solution: $\omega = 0.228$ and $T_r = 310/304.2 = 1.02$ for both cases (a) and (b), so,

$$B^0 = 0.083 - 0.422/1.02^{1.6} = -0.326$$

$$B^1 = 0.139 - 0.172/1.02^{4.2} = -0.0193$$

$$B(T)P_c/RT_c = (B^0 + \omega B^1) = (-0.326 + 0.228 \cdot (-0.0193)) = -0.3304$$

$$(a) P_r = 8/73.82 = 0.108; \text{ so } Z = 1 + (B^0 + \omega B^1)P_r/T_r = 1 - 0.3304 \cdot 0.108/1.02 = 0.965$$

$V = ZRT/(P \cdot MW) = (0.965 \cdot 83.14 \cdot 310)/(8 \cdot 44) = 70.66$, within 0.1% of the experimental value.

$$(b) P_r = 75/73.82 = 1.016; \text{ applying Eqn. 7.10, } 0.686 + 0.439 \cdot 1.016 = 1.13 > T_r = 1.02. \text{ Therefore, the virial equation may be inaccurate using only the second virial coefficient.}$$

7.5 CUBIC EQUATIONS OF STATE

The van der Waals Equation of State

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2 \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT}$$

7.12  Van der Waals EOS.

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

$$a \equiv \frac{27R^2T_c^2}{64P_c} \quad ; \quad b \equiv \frac{RT_c}{8P_c} \quad 7.13$$

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}$$

7.14  The van der Waals equation

No acentric factor



From *Concepts in Thermal Physics*

Express the van der Waals equation of state in terms of a virial expansion and hence find the Boyle temperature in terms of the critical temperature.

Solution:

The van der Waals equation of state can be rewritten as

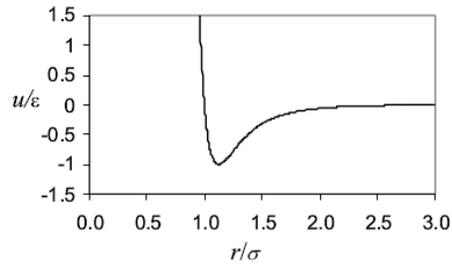
$$pV = \frac{RT}{V-b} + \frac{a}{V^2} = \frac{RT}{V} \left(1 - \frac{b}{V}\right)^{-1} + \frac{a}{V^2}, \quad (26.41)$$

and using the binomial expansion, the term in brackets can be expanded into a series, resulting in

$$\frac{pV}{RT} = 1 + \frac{1}{V} \left(b - \frac{a}{RT}\right) + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \dots, \quad (26.42)$$

which is in the same form as the virial expansion in eqn 26.40 with

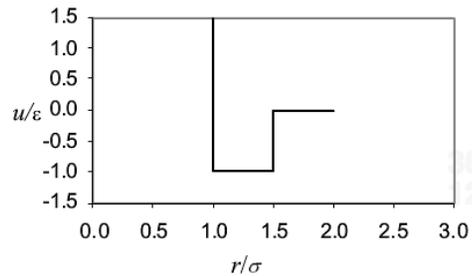
$$B(T) = b - \frac{a}{RT}. \quad (26.43)$$



The Lennard-Jones potential.

$$u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

Note that $\epsilon > 0$ is the depth of the well, and σ is the distance where $u(r) = 0$.

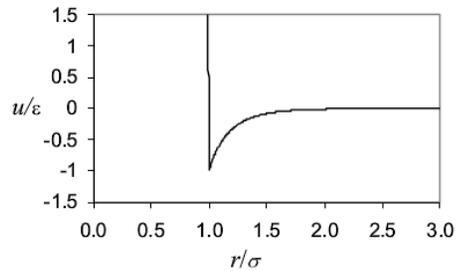


The square-well potential for $\lambda = 1.5$.

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\epsilon & \text{if } \sigma < r \leq \lambda\sigma \\ 0 & \text{if } r > \lambda\sigma \end{cases}$$

$$B = 2\pi N_A \int_0^{\infty} \left(1 - \exp\left(-\frac{u}{kT}\right)\right) r^2 dr$$

7.59



The Sutherland potential.

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\epsilon(\sigma/r)^6 & \text{if } r > \sigma \end{cases}$$

Figure 1.1 Schematics of three engineering models for pair potentials on a dimensionless basis.

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1 - b\rho} - \frac{a\rho}{RT}$$

7.14  The van der Waals equation

Van der Waals Equation as a Cubic EOS

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$V^3P - V^2(bP + RT) + Va - ab = 0$$

$$V = \frac{ZRT}{P}$$

$$\frac{Z^3(RT)^3}{P^2} - \frac{Z^2(RT)^2}{P} \left(b + \frac{RT}{P} \right) + \frac{ZRTa}{P} - ab = 0$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

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

The Peng-Robinson Equation of State

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}$$

! The Peng-Robinson EOS.

Note that a is a temperature-dependent parameter, not a constant. Note the dependence on the acentric factor.

The Peng-Robinson equation of state (EOS) is given by:

$$P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2} \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a}{bRT} \cdot \frac{b\rho}{1+2b\rho-b^2\rho^2} \quad 7.15$$

where $\rho = \text{molar density} = n/V$, b is a constant, and a depends on temperature and acentric factor,⁷

$$a \equiv a_c \alpha; \quad a_c \equiv 0.45723553 \frac{R^2 T_c^2}{P_c} \quad b \equiv 0.07779607 R \frac{T_c}{P_c} \quad 7.16$$

$$\alpha \equiv [1 + \kappa(1 - \sqrt{T_r})]^2 \quad \kappa \equiv 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad 7.17$$

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a}{bRT} \cdot \frac{b\rho}{1+2b\rho-b^2\rho^2} \quad 7.19$$

$$\frac{da}{dT} = \frac{-a_c \kappa \sqrt{\alpha T_r}}{T}$$

7.18

$$Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}$$

7.14

! The van der Waals equation

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2 \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT}$$

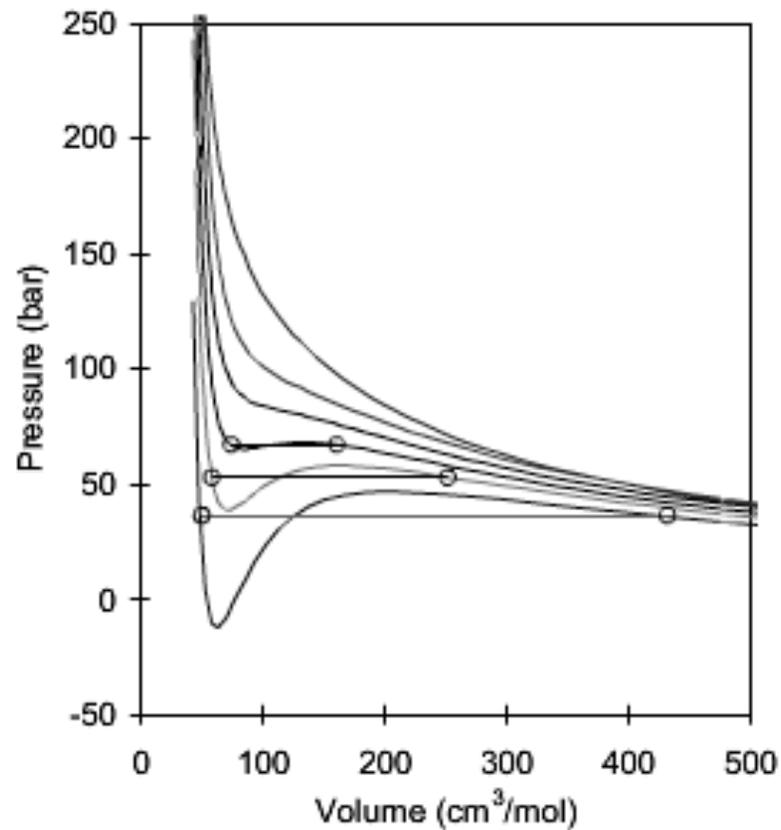


Figure 7.5 Illustration of the prediction of isotherms by the Peng-Robinson equation of state for CO_2 ($T_c = 304.2 \text{ K}$) at 275 K, 290 K, 300 K, 310 K, 320 K, and 350 K. Higher temperatures result in a high pressure for a given volume. The “humps” are explained in the text. The calculated vapor pressures are 36.42 bar at 275 K, 53.2 bar at 290 K, and 67.21 bar at 300 K.

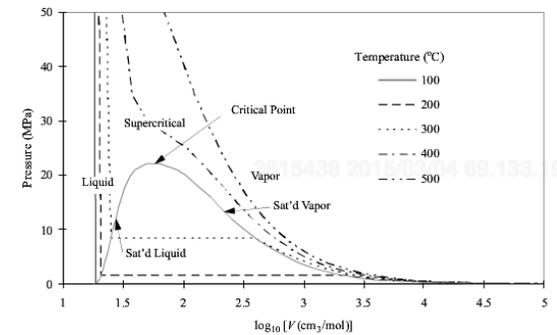


Figure 1.4 P - V - T behavior of water at the same temperatures used in Fig. 1.3. The plot is prepared from the steam tables in Appendix E.

7.6 SOLVING THE CUBIC EQUATION OF STATE FOR Z

Dimensionless form for equations of state

$$Z = PV/RT = P/\rho RT \quad 7.20$$

Defining dimensionless forms of the parameters

$$A \equiv aP/R^2T^2 \quad 7.21$$

$$B \equiv bP/RT \quad 7.22$$

results in the lumped variables

$$b\rho = B/Z; \quad a\rho/RT = A/Z \quad 7.23$$

The Peng-Robinson equation of state becomes

$$Z = \frac{1}{(1 - B/Z)} - \frac{A}{B} \cdot \frac{B/Z}{1 + 2B/Z - (B/Z)^2} \quad 7.24$$

Rearranging the dimensionless Peng-Robinson equation yields a cubic function in Z that must be solved for vapor, liquid, or fluid roots:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad 7.25$$

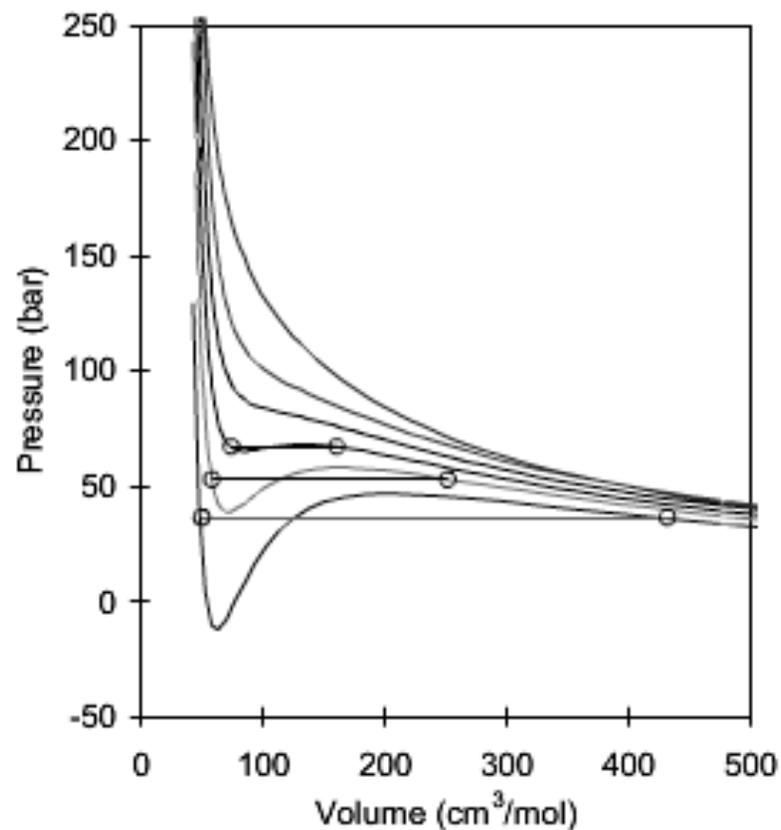


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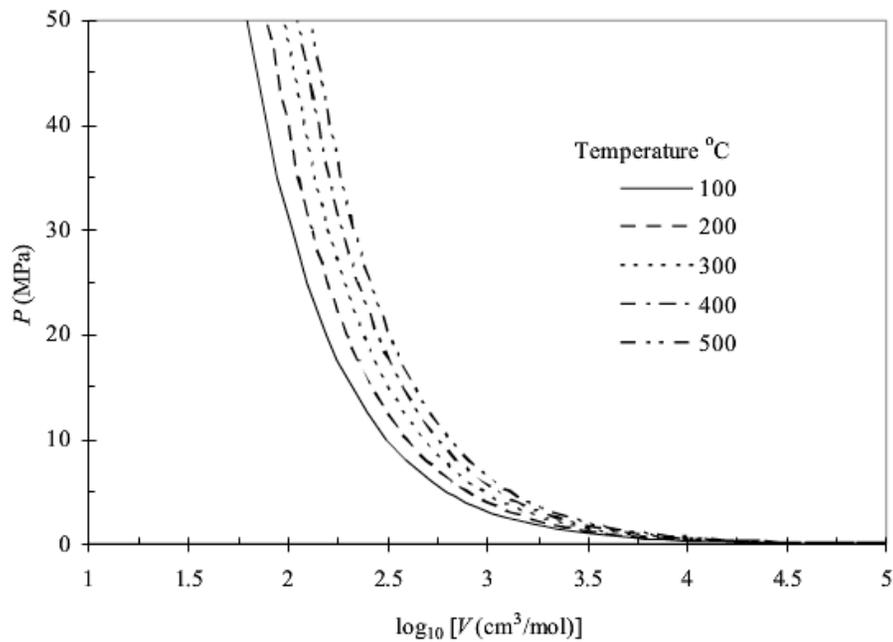


Figure 1.3 Ideal gas behavior at five temperatures.

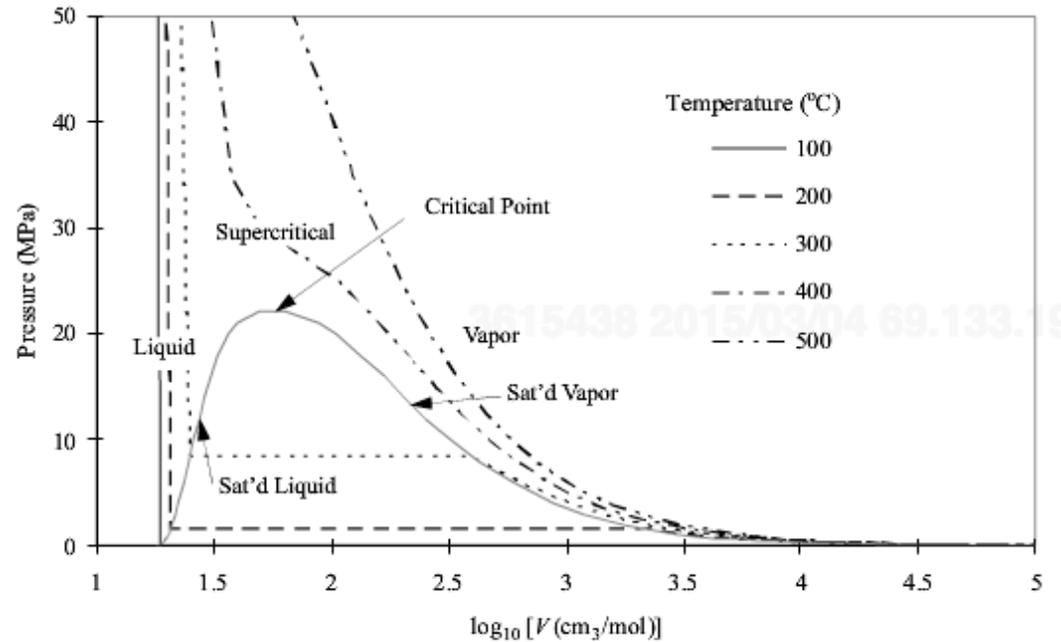
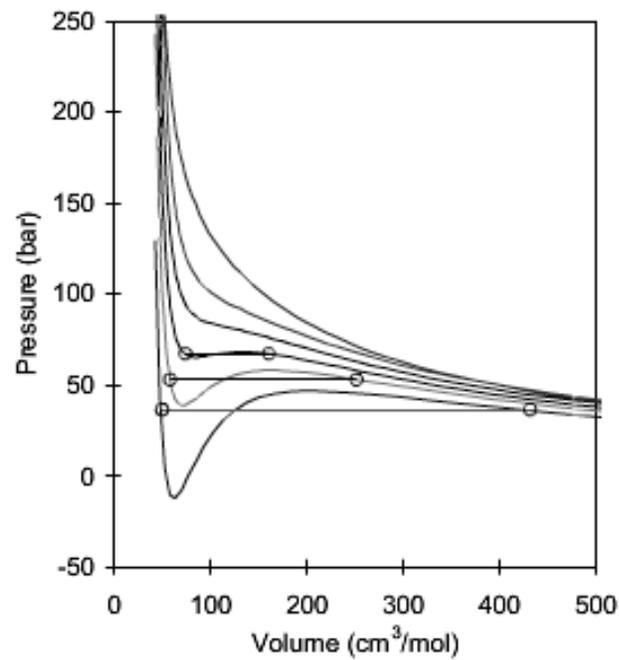


Figure 1.4 P - V - T behavior of water at the same temperatures used in Fig. 1.3. The plot is prepared from the steam tables in Appendix E.



$$F(Z) = Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad 7.25$$

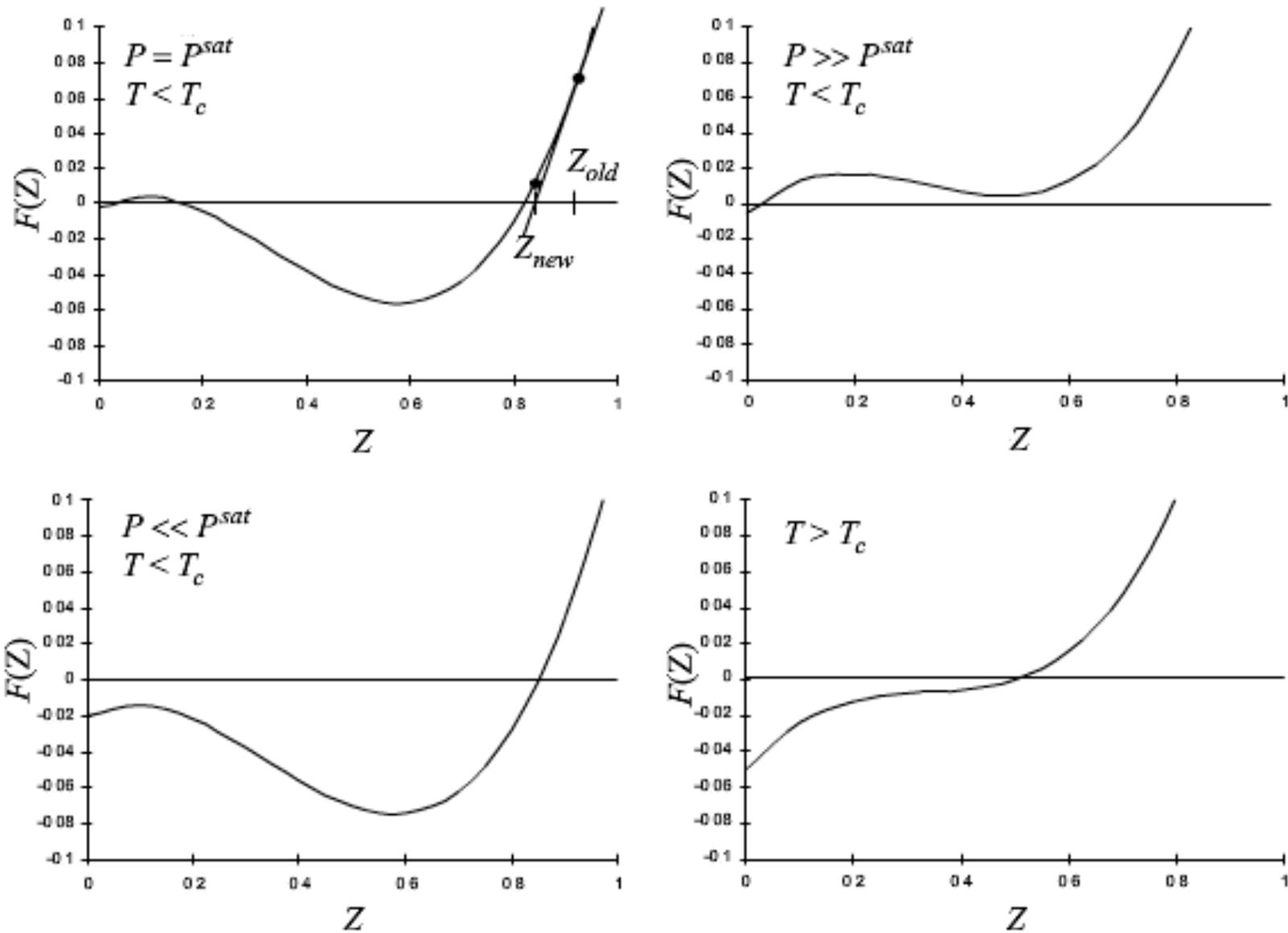


Figure 7.6 Comparison of behavior of cubic in Z for the Peng-Robinson equation of state at several conditions. The labels Z_{new} and Z_{old} in the upper left are described in the iterative description in Appendix B.

Methods of Solving the Cubic Equation

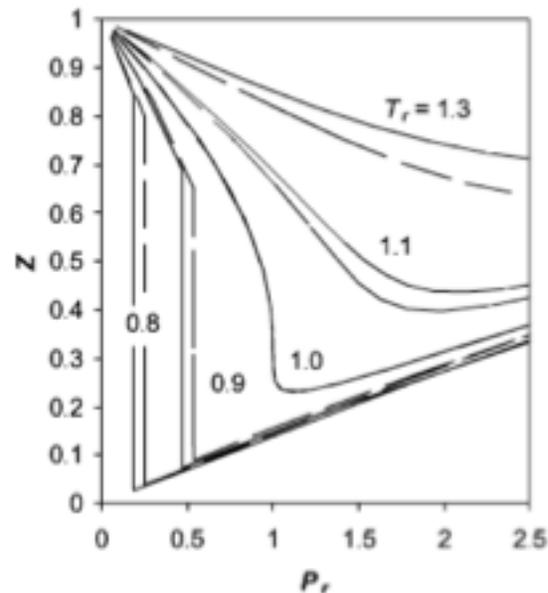
Engineering applications typically specify P and T , and require information about V . Solution of the equation of state in terms of Z is preferred over solution for V , and we can subsequently find V using

$$V = ZRT/P \quad 7.26$$

The value of Z often falls between 0 and 1. (See Fig. 7.4 on page 257.) V often varies from 50–100 cm^3/mole for liquids to near infinity for gases as P approaches zero. It is much easier to solve for

Iterative Method

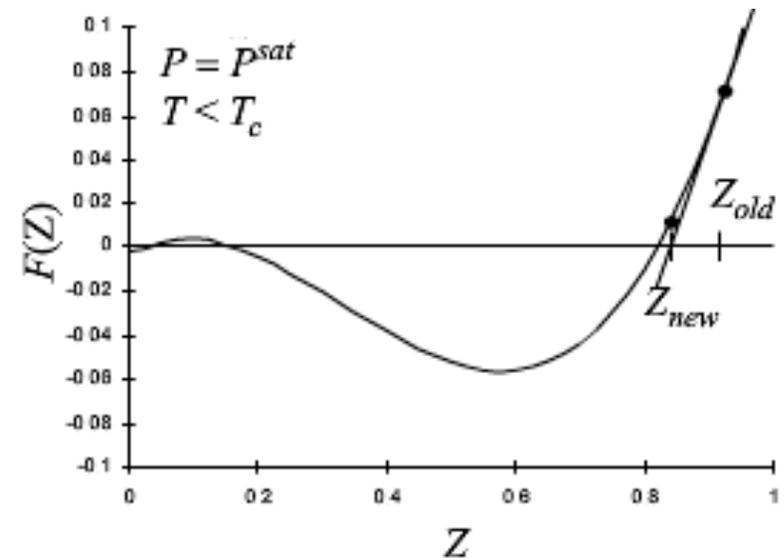
The Newton-Raphson method is described in Appendix B. The Newton-Raphson method uses an initial guess along with the derivative value to rapidly converge on the solution.



Iterative Method

The Newton-Raphson method is described in Appendix B. The Newton-Raphson method uses an initial guess along with the derivative value to rapidly converge on the solution.

$$Z^3 + a_2Z^2 + a_1Z + a_0 = F$$



We seek the value of Z where $F = 0$. Suppose we have made an initial guess Z_{old} which gives a value F_{old} , as shown in the upper-left graph in Fig. 7.6 on page 265. We are seeking a value of Z that results in $F = 0$. If F_{old} is the current value, and if we use the derivative of F as a linear approximation of the function behavior, then $0 = m \cdot Z_{\text{new}} + b$, (where the slope m can be calculated analytically from Eqn. B.37 as $dF/dZ = (3Z^2 - 2(1 - B)Z + (A - 3B^2 - 2B))$). Since the current point is on the same line, we may also write $F_{\text{old}} = m \cdot Z_{\text{old}} + b$. Taking the difference we get $0 - F_{\text{old}} = m \cdot (Z_{\text{new}} - Z_{\text{old}}) + (b - b)$ or rearranging, $-F_{\text{old}}/m + Z_{\text{old}} = Z_{\text{new}}$. Since $m = (dF/dZ)$, we have $Z_{\text{new}} = Z_{\text{old}} - F/(dF/dZ)$. The procedure can be repeated until the answer is obtained. A summary of steps is:

1. Guess $Z_{\text{old}} = 1$ or $Z_{\text{old}} = 0$ and compute $F_{\text{old}}(Z_{\text{old}})$.
2. Compute dF/dZ .
3. Compute $Z_{\text{new}} = Z_{\text{old}} - F/(dF/dZ)$.
4. If $|\Delta Z/Z_{\text{now}}| < 1.E - 5$, print the value of Z_{now} and stop.
5. Compute $F_{\text{new}}(Z_{\text{new}})$ and use this as F_{old} . Return to step 3 until step 4 terminates.

Note that an initial guess of $Z = 0$ converges on the smallest real root. An initial guess of $Z = 1$ almost always converges on the largest real root. At very high reduced pressures, an initial guess greater than one is sometimes required since the compressibility factor can exceed one (see Fig. 7.4 on page 257).

Analytical Solution

The other choice we have for solution of the cubic is to analytically obtain the roots as detailed in Appendix B. The method varies depending on whether one or three roots exist at the pressure of interest. Solutions are implemented in a spreadsheet (Preos.xlsx) or a MATLAB script (Preos.m). MATLAB includes a polynomial root finder, so the statement `Zvals=roots([1 a2 a1 a0])` results in both real and imaginary roots. The argument in the “roots” function is the vector of coefficients for the polynomial in Z . In MATLAB, the indexes of the real roots can be found with `index=find(imag(Zvals)==0)` followed by selecting the real parts of the roots using `Zreal=real(Zvals(index))`.



Preos.xlsx uses the procedures from Appendix B and shows the intermediate calculations.

Example 7.3 Peng-Robinson solution by hand calculation

Perform a hand calculation of the real roots for argon at 105.6 K and 0.498 MPa.

Solution: This example is available online and provides an example of hand calculation at the same conditions as the next example.

<http://chethermo.net/sites/default/files/doc/supp/SuppExcel.pdf>

S-A.1. ADVANCED FEATURES IN EXCEL

Using Solver with Excel

Excel includes an “add-in” feature called Solver which can be used to solve single or multiple equations. The installation of the feature is optional. If it is installed, it will be listed under the **Data** ribbon in the Analysis group. A related feature is called **Goal Seek...**, but it is less powerful since it can only solve a single objective function. (Goal Seek is found under Data ribbon (Data Tools group)>What if analysis...). If Solver is not installed, use online help or find some directions at <http://chethermo.net> in the section for Software Tutorials.

To solve an equation for a single variable, Goal Seek or Solver can be used. We will use Solver since it is the more general tool, and use of Goal Seek is simple if desired, once Solver has been used. **If you are using Solver with a spreadsheet that has been protected, it must first be unprotected using Review ribbon>Unprotect....**

Suppose we wish to solve

$$x^2 + 2x = 1$$

Although the solution may be quickly found by the quadratic formula, a spreadsheet will be created to illustrate the technique that can be applied to more complex problems.

1. Create the following table, entering the labels in column *A* and the initial guess of 0 for *x* in cell *B1*.

	A	B
1	x	0
2	F(x)	

2. Enter the following formula in cell B2: `=B1^2 + 2*B1 - 1`. (Note that you may click on cell B1 rather than typing the name as you enter the formula.)
3. Start Solver from the **Data** ribbon>Analysis Group. The Solver window will pop up as shown below in Figure S-A.1. The objective function (Target cell) is entered in the top entry box. For this example, enter B2 (or click in the entry box, then click in B2). The radio buttons permit the objective cell to be maximized, minimized, or set to a specific value. In this example, select “Equal to: Value of:” and put the number 0 in the entry box. The **Options...** button controls the convergence criteria, but we won’t use that now. (For more information on the options, search online help). The next entry box specifies the cells to adjust in the search for the objective function. For this example, enter B1. (For multiple cells you can drag the mouse over the cell ranges.)
4. Click on **Solve**. Look closely at the information box that pops up when Solver has finished. Since numerical techniques are used, Solver may have difficulty finding a solution for poor initial guesses or poorly defined objective functions, and the box notifies of problems in this event. However, we are solving a simple example here, and the answer is quickly found. The answer should be 0.414.

Example 7.4 The Peng-Robinson equation for molar volume

Find the molar volume predicted by the Peng-Robinson equation of state for argon at 105.6 K and 4.96 bar.

Solution: The critical data are entered from the table on the back flap of the text.

Preos.xlsx output is shown below. The state is in the three-root region, because the cells for the one-root region are labeled #NUM! by Excel. Many of the intermediate calculations are also shown. The volumes are 27.8, 134, and 1581 cm³/mole. The lower value corresponds to the liquid volume and the upper value corresponds to the vapor. Note that Z is close to zero for the liquid and close to one for the vapor.

The output from the Preos.m MATLAB script is also shown below. Though the default output does not include intermediate values, they may be obtained by removing the “;” at the end of any code line and rerunning the script.

Output from Preos.m:

```
argon Tc(K)= 150.9 Pc(MPa)= 4.898 w = -0.004
T(K)= 105.600000 P(MPa)= 0.496000
Zvals =
    0.8971
    0.0759
    0.0157
Z= 0.897123 0.015681
V(cm^3/mol)= 1588.066740 27.758560
fugacity (MPa)= 0.449384 0.449903
Hdep (J/mol)= -222.933032 -6002.507074
```

Peng-Robinson Equation of State (Pure Fluid)

Properties			
Gas	T _c (K)	P _c (MPa)	w
ARGON	150.9	4.898	-0.004

Current State		Roots		fugacity MPa
T (K)	P (MPa)	Z	V cm ³ /gmol	
105.6	0.496			
answers for three root region		0.897123	1588.067	0.449384
		0.075938	134.4247	
		0.015681	27.75856	0.449909
& for 1 root region		#NUM!	#NUM!	#NUM!

Stable Root has a lower fugacity

Spreadsheet protected, but no password used.

Intermediate Calculations			
R(cm ³ MPa/molK)	8.314472		
T _r	0.699801	a (MPa cm ³ /gmol ²)	
P _r	0.101266	165184.2	
	0.368467	b (cm ³ /gmol)	
	1.124086	19.92796	
fugacity ratio	A	0.10628	
	0.998832	B	0.011258

To find vapor pressure, or saturation temperature, see cell A28 for instructions

Peng-Robinson Equation of State (Pure Fluid)

Spreadsheet protected, but no password used.

Properties			
Gas	T _c (K)	P _c (MPa)	
ARGON	150.9	4.898	-0.004

Current State		Roots		
T (K)	105.6	Z	V	fugacity
P (MPa)	0.496		cm ³ /gmol	MPa
answers for three root region		0.897123	1588.067	0.449384
		0.075938	134.4247	
		0.015681	27.75856	0.449909
& for 1 root region		#NUM!	#NUM!	#NUM!

Stable Root has a lower fugacity

Intermediate Calculations			
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P _r	0.101266	165184.2	
	0.368467	b (cm ³ /gmol)	
	1.124086	19.92796	
fugacity ratio	A	0.10628	
	0.998832	B	0.011258

To find vapor pressure, or saturation temperature, see cell A28 for instructions

Solution to Cubic $Z^3 + a_2Z^2 + a_1Z + a_0 = 0$

a ₂	a ₁	a ₀	p	q
-0.988742	0.083385	-0.001068	-0.242486	-0.045187

$$R = q^3/4 + p^3/27 = -1.76E-05$$

If Negative, three unequal real roots,

If Positive, one real root

Method 1 - For region with one real root

P	Q	Root to equation in x
#NUM!	#NUM!	#NUM!

Solution methods are summarized in the appendix of the text.

Method 2 - For region with three real roots

m	3q/pm	3 ^{1/3} p	1	Roots to equation in x		
0.568607	0.983181	0.183666	0.061222	0.567542	-0.253642	-0.3139

Example 7.5 Application of the Peng-Robinson equation

Estimate the specific volume in cm^3/g for carbon dioxide at 310 K and (a) 8 bars (b) 75 bars by the Peng-Robinson equation and compare to the experimental values of 70.58 and 3.90, respectively.¹

Solution: $\omega = 0.228$, $T_c = 304.2$, $P_c = 73.82$, $MW = 44$ g/gmol,

(a) $Z = 0.961$

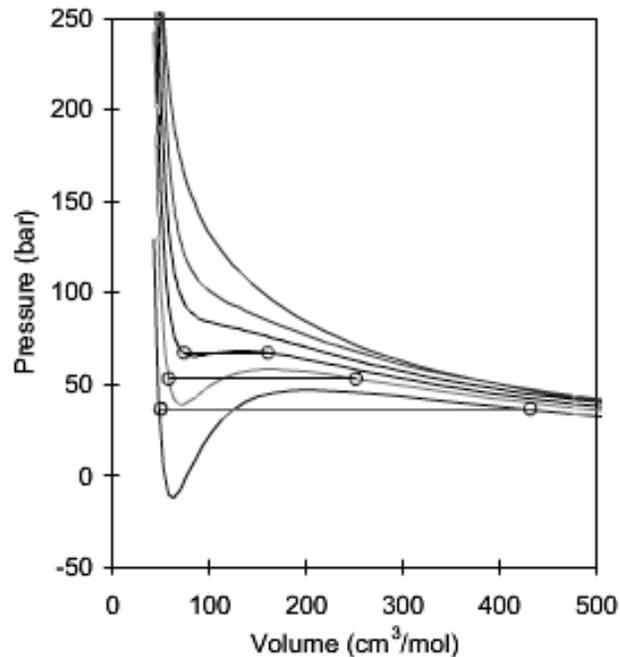
$$V = ZRT/(P \cdot MW) = (0.961 \cdot 83.14 \cdot 310)/(8 \cdot 44) = 70.37, \text{ within } 0.3\% \text{ of the experimental value.}$$

(b) $Z = 0.492$

$$V = ZRT/(P \cdot MW) = (0.492 \cdot 83.14 \cdot 310)/(75 \cdot 44) = 3.84 \text{ giving } 1.5\% \text{ error relative to the experimental value.}$$

Determining Stable Roots

sents the phase that will exist at equilibrium. When three roots are found, the most stable root has the lower **Gibbs energy** or **fugacity**. At phase equilibrium, the Gibbs energy and fugacity of the roots will be equal. Fugacity is closely related to the Gibbs energy and will be described in Chapter 9, but we will begin to use the calculated values before we explain the calculation procedures completely. When three roots exist, the center root is thermodynamically **unstable** because the derivative of pressure with respect to volume is positive, which violates our common sense, and is shown



dition for equilibrium between vapor and liquid roots occurs when the horizontal line on the P - V diagram is positioned such that the area enclosed above the line is exactly equal to the area enclosed below the line. Even though the enclosed areas have different shapes, imagine moving this line up and down until it looks like the areas are equal. The dots in the figure are the predictions of the saturated liquid and vapor volumes, and form the phase envelope. The parts of the isotherms that are between the saturated vapor and saturated liquid roots are either **metastable** or **unstable**.

idly to the equilibrium state. The boundary between the metastable and unstable states is known as the **spinodal** condition, predicted by the EOS by the maximum and minimum in the humps in sub-critical isotherms. We will discuss more details about characterizing proper fluid roots when we

7.7 IMPLICATIONS OF REAL FLUID BEHAVIOR

Example 7.6 Derivatives of the Peng-Robinson equation

Determine $\left(\frac{\partial P}{\partial T}\right)_V$, $\left(\frac{\partial C_V}{\partial V}\right)_T$, and $\left(\frac{\partial U}{\partial V}\right)_T$ for the Peng-Robinson equation.

Solution: The derivatives $(\partial U/\partial V)_T$ and $(\partial C_V/\partial V)_T$ have been written in terms of measurable properties in Examples 6.6 and 6.9, respectively, and have been evaluated for an ideal gas. The analysis with the Peng-Robinson model provides more realistic representation of the properties of real substances. Beginning with the same analytical expressions set forth in the referenced examples, a key derivative is obtained for the Peng-Robinson equation,

$$P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R\rho}{1-b\rho} - \frac{\rho^2}{1+2b\rho-b^2\rho^2} \frac{da}{dT}$$

$$a = a_c \alpha; \quad a_c = 0.45723553 \frac{R^2 T_c^2}{P_c}$$

which approaches the ideal gas limit: $\lim_{\rho \rightarrow 0} \left(\frac{\partial P}{\partial T}\right)_V = R\rho = \frac{R}{V}$. The volume dependence of C_V is obtained by the second derivative:

$$\alpha = [1 + \kappa(1 - \sqrt{T_r})]^2$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{-T\rho^2}{1+2b\rho-b^2\rho^2} \frac{d^2 a}{dT^2} = \frac{-\rho^2}{1+2b\rho-b^2\rho^2} \frac{a_c \kappa}{2} \left(\frac{\kappa}{T_c} + \frac{\sqrt{\alpha T_r}}{T} \right)$$

which approaches the ideal gas limit of zero at low density,

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

$$b = 0.07779607R \frac{T_c}{P_c}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = \frac{\rho^2}{1+2b\rho-b^2\rho^2} \left[a - \frac{da}{dT} \right] = \frac{\rho^2 a_c}{1+2b\rho-b^2\rho^2} [\alpha + \kappa \sqrt{\alpha T_r}],$$

which also approaches the ideal gas limit of zero at low density. We have thus shown that C_V depends on volume. To calculate a value of C_{V^*} first we determine $C_{V^*}^{ig} = C_{V^*}^{ig} - R$, where $C_{V^*}^{ig}$ is the heat capacity tabulated in Appendix E. Then, at a given $\{P, T\}$, the equation of state is solved for ρ . The resultant density is used as the limit in the following integrals, noting as $V \rightarrow \infty$, $\rho \rightarrow 0$, and $dV = -d\rho/\rho^2$: This method is used for departures from ideal gas properties in Chapter 8.

$$C_v - C_{V^*}^{ig} = \int_V^{\infty} \left(\frac{\partial C_V}{\partial V}\right)_T dV = \left(\frac{d^2 a}{dT^2}\right) \int_0^{\rho} \frac{T\rho^2}{1+2b\rho-b^2\rho^2} \frac{d\rho}{\rho^2} = \frac{T}{2\sqrt{2}b} \left(\frac{d^2 a}{dT^2}\right) \ln \left[\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho} \right]$$

$$\text{where } \left(\frac{d^2 a}{dT^2}\right) = \frac{a_c \kappa}{2T_c^2 T_r} \left[\kappa + \frac{\sqrt{\alpha}}{T_r} \right]$$

7.7 IMPLICATIONS OF REAL FLUID BEHAVIOR

Example 6.6 Accounting for T and V impacts on energy

Derive an expression for $\left(\frac{\partial U}{\partial V}\right)_T$ in terms of measurable properties. (a) Evaluate for the ideal gas. (b) Evaluate for the van der Waals equation of state, $P = RT/(V - b) - a/V$.

Solution: Beginning with the fundamental relation for dU ,

$$dU = TdS - PdV$$

Applying the expansion rule

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T \quad 6.45$$

Using a Maxwell relation and a basic identity

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad 6.46$$

(a) For an ideal gas, $P = RT/V$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}, \quad \left(\frac{\partial U}{\partial V}\right)_T^{ig} = \frac{RT}{V} - P = 0 \quad (\text{ig})$$

Thus, internal energy of an ideal gas does not depend on volume (or pressure) at a given T .

(b) For the van der Waals equation,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}; \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) = \frac{a}{V^2} \quad (\text{ig})$$

Example 6.9 Volumetric dependence of C_V for ideal gas

Determine how C_V depends on volume (or pressure) by deriving an expression for $(\partial C_V / \partial V)_T$. Evaluate the expression for an ideal gas.

Solution: Following hint #1 and applying Eqn. 4.30:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

By the chain rule:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_T + T \frac{\partial}{\partial V} \left[\left(\frac{\partial S}{\partial T}\right)_V \right]_T$$

Changing the order of differentiation:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \frac{\partial}{\partial T} \left[\left(\frac{\partial S}{\partial T}\right)_V \right] = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

For an ideal gas, $P = RT/V$, we have $\left(\frac{\partial P}{\partial T}\right)_V$ in Example 6.6:

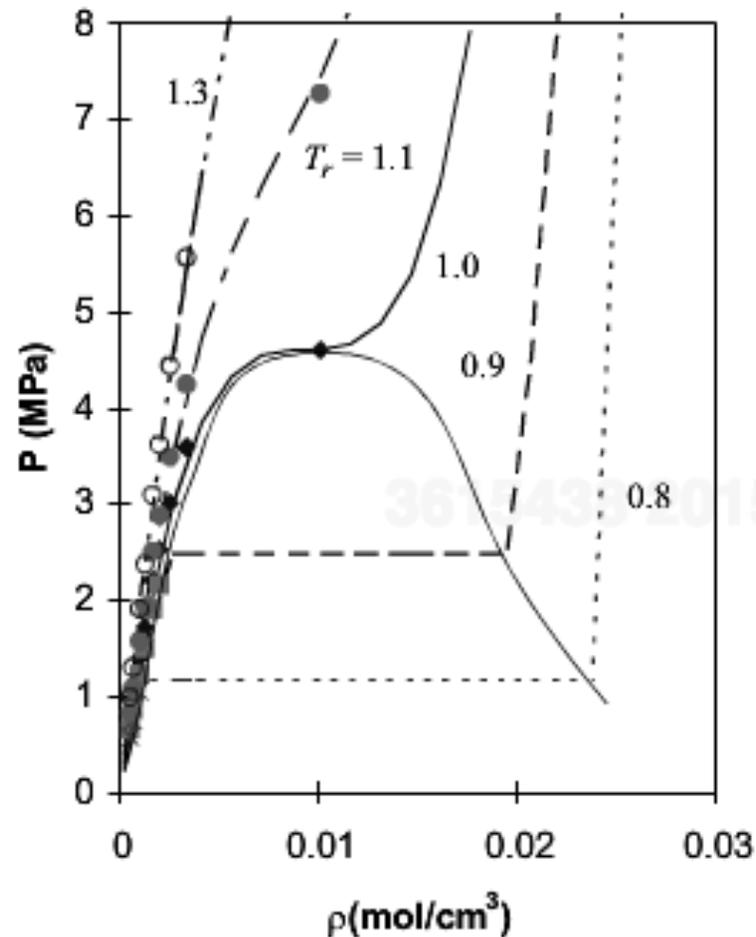
$$\frac{\partial}{\partial T} \left[\left(\frac{\partial P}{\partial T}\right)_V \right] = \frac{\partial}{\partial T} \left(\frac{R}{V} \right) = 0 \quad (\text{ig}) \quad 6.51$$

Thus, heat capacity of an ideal gas does not depend on volume (or pressure) at a fixed temperature. (We will reevaluate this derivative in Chapter 7 for a real fluid.)

7.8 MATCHING THE CRITICAL POINT

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0 \quad \text{at } T_c, P_c \quad 7.27$$

Solve for a and b
in Van der Waals
Eqn. for instance



$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2 \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT}$$

7.12  Van der Waals
EOS.

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

ture of the critical point: The vapor and liquid roots are exactly equal at the critical point (and the spurious middle root is also equal). We can apply this latter insight by specifying that $(Z - Z_c)^3 = 0 = Z^3 - 3Z_c Z^2 + 3Z_c^2 Z - Z_c^3 = Z^3 - a_2 Z^2 + a_1 Z - a_0$ (Appendix B). Equating the coefficients of these polynomials gives three equations in three unknowns: Z_c , A_c and B_c .

$$Z^3 - (3Z_c)Z^2 + (3Z_c^2)Z - (Z_c^3) = 0 \quad \text{B.51}$$

If we compare Eqn. B.51 with Eqn. B.36 at the critical point, we find

$$-a_2 = 3Z_c; \quad a_1 = 3Z_c^2; \quad -a_0 = Z_c^3 \quad \text{B.52}$$

$$Z^3 + a_2 Z^2 + a_1 Z + a_0 = 0 \quad \text{B.36}$$

This is solved in appendix B2 p. 822

Thus, the van der Waals equation predicts a universal value of $Z_c = 0.375$. Plugging this into Eqn. B.56, we find

$$b = \frac{RT_c}{8P_c} \quad \text{B.58}$$

and into Eqn. B.54,

$$a = \frac{27(RT_c)^2}{64 P_c} \quad \text{B.59}$$

ture of the critical point: The vapor and liquid roots are exactly equal at the critical point (and the spurious middle root is also equal). We can apply this latter insight by specifying that $(Z - Z_c)^3 = 0 = Z^3 - 3Z_c Z^2 + 3Z_c^2 Z - Z_c^3 = Z^3 - a_2 Z^2 + a_1 Z - a_0$ (Appendix B). Equating the coefficients of these polynomials gives three equations in three unknowns: Z_c , A_c , and B_c .

Example 7.7 Critical parameters for the van der Waals equation

Apply the above method to determine the values of Z_c , A_c , and B_c for the van der Waals equation.

Solution: Rearranging the equation in terms of A_c and B_c we have:

$$0 = Z^3 - (1 + B_c)Z^2 + A_c Z - A_c B_c = 0 = Z^3 - 3Z_c Z^2 + 3Z_c^2 Z - Z_c^3$$

By comparing coefficients of Z^n : (1) $Z_c = (1 + B_c)/3$; (2) $A_c = 3Z_c^2$; (3) $A_c B_c = Z_c^3$.

Substituting A_c into the last equation, we have: $3Z_c^2 B_c = Z_c^3 (1 + B_c)/3$.

Cancelling the Z_c^2 and solving we have $B_c = 1/8 = 0.125$. The other equations then give $Z_c = 0.375$ and $A_c = 27/64$.

The solution is especially simple for the van der Waals equation, but the following procedure can be adapted for any cubic equation of state:

1. Rearrange the equation of state into its cubic form: $Z^3 - a_2 Z^2 + a_1 Z - a_0$.
2. Guess a value of Z_c (e.g., $Z_c \sim 1/3$).
3. Solve the equivalent of expression (1) for B_c .
4. Solve the equivalent of expression (2) for A_c .
5. Solve the equivalent of expression (3) for Z_c .
6. If $Z_c = \text{guess}$, then stop. Otherwise, repeat.

7.9 THE MOLECULAR BASIS OF EQUATIONS OF STATE: CONCEPTS AND NOTATION

It is feasible to develop equations of state based solely on fitting experimental data. If the fit is insufficiently precise for a given application, simply add more parameters. We see evidence of this approach in the Peng-Robinson equation, where temperature and density dependencies are added to the parameter “ a ” in order to fit vapor pressure and density better. A more extensive example of this approach is evident in the 32 parameter Benedict-Webb-Rubin equation that forms the basis of the Lee-Kesler model. The IAPWS model of H₂O is representative of the current state of this approach. It is the basis of the steam tables in Appendix E.

Since about 1960, computers have made it feasible to simulate macroscopic properties based on a specified intermolecular potential. With this tool, the procedure is clear: (1) Specify a potential model for a given molecule, (2) simulate the macroscopic properties, (3) evaluate the deviations between the simulated and experimental properties, (4) repeat until the deviations are minimized. This procedure is straightforward but tedious. Each simulation of $Z(T,\rho)$ can take an hour or so.

7.9 THE MOLECULAR BASIS OF EQUATIONS OF STATE: CONCEPTS AND NOTATION

The original BWR equation [\[edit\]](#)

$$P = \rho RT + \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right) \rho^2 + (bRT - a) \rho^3 + \alpha a \rho^6 + \frac{c \rho^3}{T^2} (1 + \gamma \rho^2) \exp(-\gamma \rho^2)$$

The BWRS equation of state [\[edit\]](#)

A modification of the Benedict–Webb–Rubin equation of state by Professor Kenneth E. Starling of the University of Oklahoma:^[3]

$$P = \rho RT + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \rho^2 + \left(bRT - a - \frac{d}{T} \right) \rho^3 + \alpha \left(a + \frac{d}{T} \right) \rho^6 + \frac{c \rho^3}{T^2} (1 + \gamma \rho^2) \exp(-\gamma \rho^2)$$

ρ = the **molar density**.

Values of the various parameters for 15 substances can be found in Starling's *Fluid Properties for Light Petroleum Systems*..^[3]

The Modified BWR equation (mBWR) [\[edit\]](#)

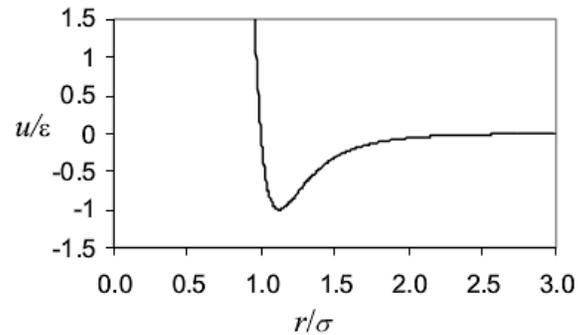
A further modification of the Benedict–Webb–Rubin equation of state by Jacobsen and Stewart:^[4]

$$P = \sum_{n=1}^9 a_n \rho^n + \exp(-\gamma \rho^2) \sum_{n=10}^{15} a_n \rho^{2n-17}$$

where:

$$\gamma = 1/\rho_c^2$$

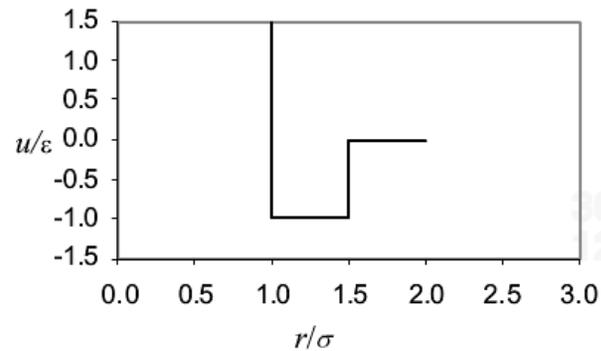
7.9 THE MOLECULAR BASIS OF EQUATIONS OF STATE: CONCEPTS AND NOTATION



The Lennard-Jones potential.

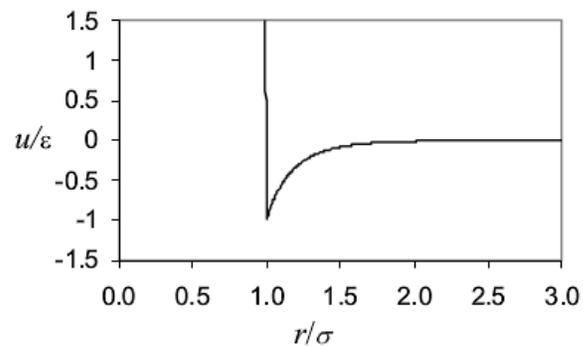
$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

Note that $\varepsilon > 0$ is the depth of the well, and σ is the distance where $u(r) = 0$.



The square-well potential for $\lambda = 1.5$.

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\varepsilon & \text{if } \sigma < r \leq \lambda\sigma \\ 0 & \text{if } r > \lambda\sigma \end{cases}$$



The Sutherland potential.

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\varepsilon(\sigma/r)^6 & \text{if } r > \sigma \end{cases}$$

Figure 1.1 Schematics of three engineering models for pair potentials on a dimensionless basis.

How do molecular parameters relate to EOS

e.g. VDW EOS

VDW EOS

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2$$

PR EOS

$$P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2}$$

Molar volume and b

$$v_{mol} = 4\pi r^3/3 = 4\pi(\sigma/2)^3/3 = \pi\sigma^3/6; \quad N_A v_{mol} = b \quad 7.28$$

Example 7.8 Estimating molecular size

Example 7.4 shows that $b = 19.9 \text{ cm}^3/\text{mol}$ for argon. Estimate the diameter (nm) of argon according to the Peng-Robinson model.

Solution: $N_A \pi \sigma^3/6 = 19.9 \text{ cm}^3/\text{mol}$; $\sigma^3 = 6(19.9 \text{ cm}^3/\text{mol})(1 \text{ mol}/602(10^{21}) \text{ molecules})(10^{21} \text{ nm}^3/\text{cm}^3)/\pi$. Thus, $\sigma^3 = 6(19.9)/(602\pi) = 0.06313 \text{ nm}^3$; $\sigma = (0.06313)^{1/3} = 0.398 \text{ nm}$.

Packing factor (0 to 1) $\eta_P = \rho b = b/V$

VDW EOS

$$Z = 1/(1-\eta_P) - (a/bRT)\eta_P$$

So, a/b is attractive energy in J/mole

$$a/b = N_A \epsilon$$

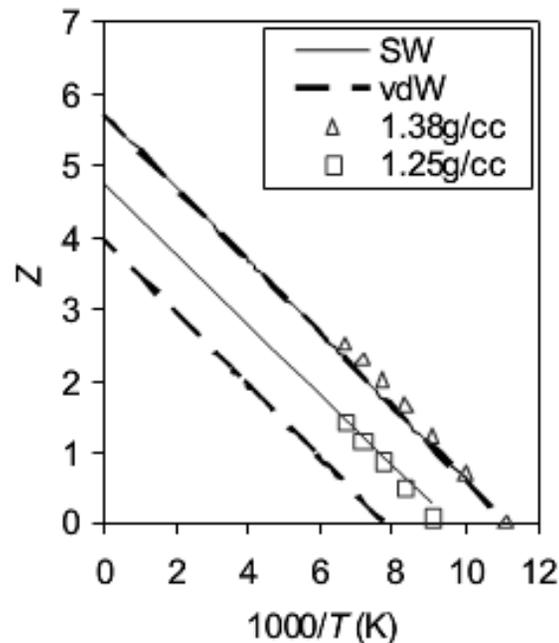
$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2$$

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

$$Z_0 = 1/(1-b\rho)$$

Repulsive Interactions

$$Z = PV/RT = P/\rho RT$$



Slope in 1/T Due to Attractive Interactions

Figure 7.7 Compressed liquid argon. Experimental data from NIST WebBook. Dashed lines characterize the van der Waals model and solid lines correspond to molecular simulation of the square-well model with $\lambda = 1.7$. The manner of fitting the molecular parameters (a and b or ϵ and σ) is described in Example 7.9.

Corresponding States in Molecular Dimensions

As engineers, we would like to get results faster. One idea is to leverage the principle of corresponding states. We know that ϵ has dimensions of J/molecule, so $N_A\epsilon$ has dimensions of J/mol. Therefore, $RT/(N_A\epsilon)$ would be dimensionless and serve in similar fashion to the usual reduced temperature, T/T_c . Similarly, the molecular volume, v_{mol} has dimensions of $\text{cm}^3/\text{molecule}$ and $N_A v_{mol}$ has dimensions of cm^3/mol . Therefore, $N_A v_{mol} \rho$ would be dimensionless and serve in very similar fashion to the usual reduced density, ρ/ρ_c . Another idea would be to tabulate the dimensionless properties from the simulation at many state points, then interpolate, similar to the steam tables. The interpolating equations might even resemble traditional equations of state in form and speed. The difference would be that they retain the connection between the nanoscopic potential model and macroscopic properties. In other words, we can engineer our equations of state to be consistent with specific potential models by expressing our “reduced” temperature and density using molecular dimensions. Then the principle of corresponding states can be applied to match the ϵ and σ for a particular molecule in the same way that we match a and b parameters in the van der Waals model.

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2 \qquad P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2}$$

$$v_{mol} = 4\pi r^3/3 = 4\pi(\sigma/2)^3/3 = \pi\sigma^3/6; \quad N_A v_{mol} = b \qquad 7.28$$

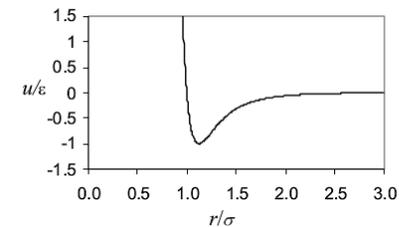
Example 7.8 Estimating molecular size

Example 7.4 shows that $b = 19.9\text{cm}^3/\text{mol}$ for argon. Estimate the diameter (nm) of argon according to the Peng-Robinson model.

Solution: $N_A \pi \sigma^3/6 = 19.9 \text{ cm}^3/\text{mol}$; $\sigma^3 = 6(19.9\text{cm}^3/\text{mol})(1\text{mol}/602(10^{21})\text{molecules})(10^{21} \text{ nm}^3/\text{cm}^3)/\pi$. Thus, $\sigma^3 = 6(19.9)/(602\pi) = 0.06313 \text{ nm}^3$; $\sigma = (0.06313)^{1/3} = 0.398 \text{ nm}$.

equation includes $(1-b\rho)$ in the denominator, forcing divergence as this limit is approached. The prevalence of this combined variable suggests that we give it a special symbol and name, $\eta_P = b\rho = b/V$, the packing efficiency (aka. **packing fraction**).¹⁰

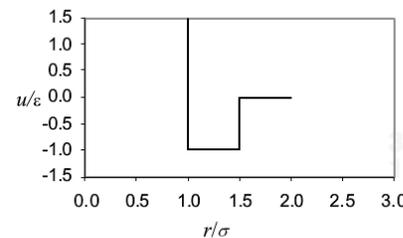
Finally, we should consider the square-well energy parameter, ε , and the van der Waals parameter, a . Applying Eqn. 7.13 indicates that the dimensions of the “ a ” parameter are $\text{J}\cdot\text{cm}^3/\text{mol}^2$. We can rewrite the van der Waals equation as $Z = 1/(1-\eta_P) - (a/bRT)\eta_P$. In this format, it is clear that the combination of variables “ a/b ” represents an attractive energy in J/mol . In other words, $a/b \sim N_A\varepsilon$. Another shortcut for quickly transforming from the macro scale to the nano scale is to recognize that $\varepsilon/k = N_A\varepsilon/R$ and both have dimensions of absolute temperature, K . In this context, the combination of variables $\varepsilon/kT = \beta\varepsilon$ is an especially convenient characterization of dimensionless reciprocal temperature, where $\beta=1/kT$.



The Lennard-Jones potential.

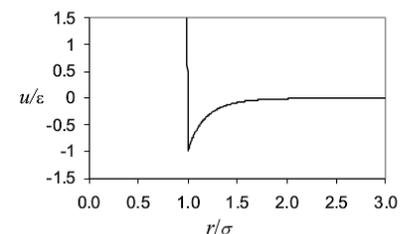
$$u(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$$

Note that $\varepsilon > 0$ is the depth of the well, and σ is the distance where $u(r) = 0$.



The square-well potential for $\lambda = 1.5$.

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\varepsilon & \text{if } \sigma < r \leq \lambda\sigma \\ 0 & \text{if } r > \lambda\sigma \end{cases}$$



The Sutherland potential.

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\varepsilon(\sigma/r)^6 & \text{if } r > \sigma \end{cases}$$

Figure 1.1 Schematics of three engineering models for pair potentials on a dimensionless basis.

Example 7.9 Characterizing molecular interactions

Based on Fig. 7.7, trend lines indicate y -intercept values of, roughly, 5.7 and 4.7 when fit to the isochoric PVT data for argon at 1.38g/cm^3 and 1.25 g/cm^3 , respectively. Similarly, the x -intercepts are roughly 11.2 and 9.5, respectively. Use these values to estimate the EOS parameters.

(a) Estimate the values of a and b at 1.38 g/cm^3 according to the van der Waals model.

(b) Predict the values of x - and y - intercepts at 1.25 g/cm^3 using the a and b from part (a).

(c) Suppose the square-well simulation data can be represented by:

$$Z = 1 + 4 \eta_P / (1 - 1.9 \eta_P) - 15.7 \eta_P \beta \epsilon / (1 - 0.16 \eta_P)$$

Estimate the values of σ and ϵ/k at 1.38g/cm^3 and predict the x - and y -intercepts at 1.25 g/cm^3 .

Solution:

(a) At 1.38g/cm^3 , y -intercept, $Z_0 = 1/(1 - \eta_P) = 5.7 \Rightarrow \eta_P = 1 - 1/5.7 = 0.825 = b\rho$.

$$b = 0.825 \cdot 39.9(\text{g/mol})/1.38(\text{g/cm}^3) = 23.9\text{ cm}^3/\text{mol}.$$

At the x -intercept, $0 = 5.7 - (a/bRT) \cdot \eta_P = 5.7 - (a/bRT) \cdot 0.825 \Rightarrow a/bRT = 5.7/0.825 = 6.91$.

Using the x -intercept to determine temperature, $1000/T = 11.2 \Rightarrow T = 1000/11.2 = 89.3\text{K} \Rightarrow$

$$a = 23.9(8.314)89.3(6.91) = 123\text{ kJ}\cdot\text{cm}^3/\text{mol}^2.$$

(b) At 1.25 g/cm^3 , $\eta_P = 23.9(1.25)/39.9 = 0.7487 \Rightarrow Z_0 = 1/(1 - \eta_P) = 4.0 = y$ -intercept.

At the x -intercept, $0 = 4.0 - 123000/(23.9RT) \cdot 0.7487 = 4.0 - 463/T \Rightarrow T = 463/4 = 116$.

Therefore, the x -intercept is $1000/T = 1000/116 = 8.6$. These x - and y - intercepts form the basis for the dashed line in Fig. 7.7 at 1.25 g/cm^3 . The prediction of the van der Waals model is poor.

(c) The procedure for finding σ and ϵ/k is similar. At the 1.38g/cm^3 ,

$$Z_0 = 1 + 4 \eta_P / (1 - 1.9 \eta_P) = 5.7 \Rightarrow \eta_P (4 + 4.7 \cdot 1.9) = 4.7 \Rightarrow \eta_P = 0.363 = b\rho$$

$$b = 0.363 \cdot 39.9/1.38 = 10.5\text{ cm}^3/\text{mol} = N_A \pi \sigma^3 / 6 \Rightarrow \sigma = 0.322\text{ nm}$$

At the x -intercept, $0 = 5.7 - 15.7(0.363)\beta\epsilon/(1 - 0.16 \cdot 0.363) \Rightarrow \beta\epsilon = 0.942$;

$$1000/T = 11.2 \Rightarrow T = 1000/11.2 = 89.3\text{K} \Rightarrow \epsilon/k = (0.942)89.3 = 84.1\text{ K}$$

At 1.25 g/cm^3 , following the same procedure:

$$\eta_P = 10.5(1.25)/39.9 = 0.329 \Rightarrow Z_0 = 1 + 4\eta_P/(1 - \eta_P) = 4.5 = y\text{-intercept}.$$

At the x -intercept, $0 = 4.5 - 15.7(0.329)\beta\epsilon/(1 - 0.16 \cdot 0.329) = 4.5 - (5.452)\beta\epsilon \Rightarrow \beta\epsilon = 0.827$

$\Rightarrow T = 84.1/0.827 = 102$. Therefore, the x -intercept is $1000/T = 1000/102 = 9.8$. These x - and y -intercepts form the basis for the solid line in Fig. 7.7 at 1.25 g/cm^3 , and the prediction is quite good.

Molecular Simulations for EOS

Collision of two particles in 2D

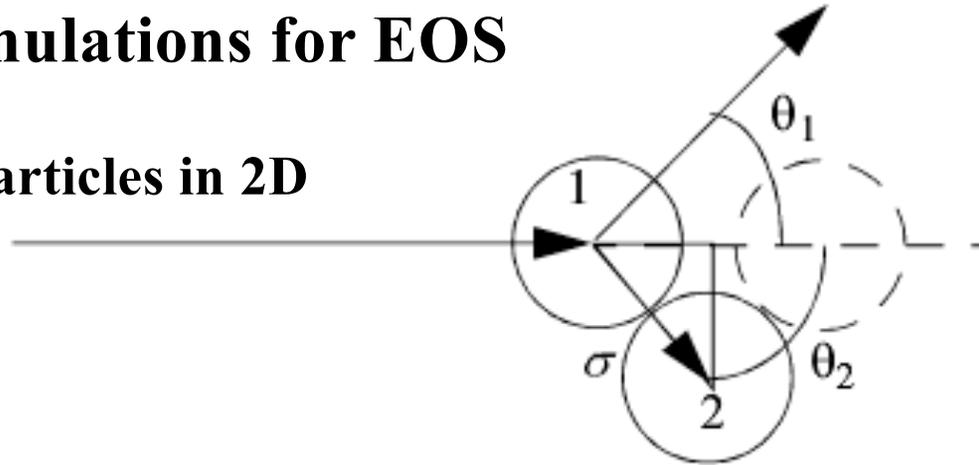


Figure 7.8 *Molecular collision in 2D. The dashed disk is a disk image that will be discussed in the text.*

$$m_1 (v_1^o)^2 = m_1 v_1^2 + m_2 v_2^2 \quad \text{Kinetic energy conserved (elastic)} \quad 7.29$$

$$m_1 v_1^o = m_1 v_1 \cos \theta_1 + m_2 v_2 \cos \theta_2 \quad \text{x-momentum conserved} \quad 7.30$$

$$0 = m_1 v_1 \sin \theta_1 + m_2 v_2 \sin \theta_2. \quad \text{y-momentum conserved} \quad 7.31$$

$$\sin \theta_2 = (y_2^c - y_1^c) / \sigma \quad 7.32$$

$$\theta_1 - \theta_2 = 90^\circ \text{ (Note that } \theta_2 < 0 \text{.)} \quad 7.33$$

$$v_2 = v_1^o \cos \theta_2; v_1 = \sqrt{(v_1^o)^2 - v_2^2}; v_2 \sin \theta_2 = -v_1 \sin \theta_1 \quad 7.34$$

$$t_i^E = (L - x_i - \sigma/2) / v_{i,x} \quad 7.35$$

Example 7.10 Computing molecular collisions in 2D

Let the diameters of two disks, σ , be 0.4 nm, the masses be 16 g/mole, and the length of the square box, L , be 5nm. Start the disks at [1.67 1.67], [3.33 3.33] and initial velocities (nm/ps): [0.167 0.222], [-0.167 -0.222] where 1 nm = 10^{-9} m and 1ps = 10^{-12} s. Note that the gas constant 8.314 J/mol-K = 8.314 kg-nm²/(ns²-mol-K) = 8.314(10^{-6}) kg-nm²/(ps²-mol-K).

- Compute the temperature (K).
- Compute the collision times with the walls.
- Compute the collision times with the disks. Which event occurs first?
- Compute the velocity vectors (m/s) after the first collision event.

Solution:

- $T_{2D} = M_w \langle v^2 \rangle / (2R)$; $\langle v^2 \rangle = (0.167^2 + 0.222^2 + 0.167^2 + 0.222^2) / 2 = 0.07717$
 $T_{2D} = (0.016 \text{ kg/mol}) (0.07717 \text{ nm}^2/\text{ps}^2) / (2 \cdot 8.314 (10^{-6}) \text{ kg-nm}^2/(\text{ps}^2\text{-mol-K})) = 89\text{K}$
- The collision time with the walls depends on the wall being approached. Note that the molecular coordinate will be within $0.5\sigma = 0.2$ nm of the wall coordinate when a wall collision occurs. Disk1 is approaching the north wall and east wall (using superscripts to denote geographic directions), the collision times are $t_1^N = (4.8 - y_1^0) / v_{1,y} = (4.8 - 1.67) / 0.333 = 9.40\text{ps}$, $t_1^E = (4.8 - x_1^0) / v_{1,x} = (4.8 - 1.67) / 0.222 = 14.1\text{ps}$. Similarly, $t_2^S = (0.2 - y_2^0) / v_{2,y} = (0.2 - 1.67) / (-0.222) = 6.62\text{ps}$; $t_2^W = (0.2 - x_2^0) / v_{2,x} = (0.2 - 3.33) / (-0.111) = 28.2\text{ps}$. Molecule 2 collides with the south wall first among wall collisions.
- Translating by Eqn.7.36, $x_2' = y_2' = 3.33 - 1.67 = 1.66$. Translating the velocities to make molecule 2 stationary: $v_{1,x}' = 0.167 - (-0.167) = 0.334$, $v_{1,y}' = 0.444$. Using Eqn. 7.37, $\phi_1 = \tan^{-1}(v_{1,y}' / v_{1,x}') = \tan^{-1}(0.444 / 0.334) = 53.13^\circ$. $\phi_2 = \tan^{-1}(1.66 / 1.66) = 45^\circ$. $r_2' = 1.66(2)^{1/2} = 2.35\text{nm}$. $x_2'' = 2.35 \cos(45 - 53.13) = 2.326$; $y_2'' = 2.35 \sin(45 - 53.13) = -0.332$. Since $|y_2''| < \sigma$, these molecules do collide. By Eqn. 7.40, $\theta_2 = \sin^{-1}(-0.332 / 0.4) = -56.10^\circ$. Then, $x_1^{c'} = 2.326 - 0.4 \cos(-56.10) = 2.103$; noting $v_{1,x}'' = (0.334^2 + 0.444^2)^{1/2} = 0.5556$. $t_{12}^c = 2.103 / 0.556 = 3.78$ ps. So the intermolecular collision occurs first.
- Computing the velocities after collision requires Eqn. 7.34, noting by Eqn. 7.33 that $\theta_1 = 90 - 56.10 = 33.9$. $v_2 = v_1'' \cos \theta_2 = 0.5556 \cos(-56.10) = 0.3099$, $v_1 = (0.5556^2 - 0.3099^2)^{1/2} = 0.4612$. Also note that Eqn. 7.34 gives only the magnitude of the velocity and we are still in the reference frame of Fig. 7.8. Rotating to the original reference frame: $v_{1,x}^f = v_1 \cos(\phi_1 + \theta_1) = 0.4607 \cos(33.9 + 53.13) = 0.0239$. $v_{1,y}^f = 0.4607 \sin(33.9 + 53.13) = 0.4605$; $v_{2,x}^f = v_{2,x}^0 + v_{1,x}^0 - v_{1,x}^f = -0.167 + 0.167 - 0.0239 = -0.0239$. $v_{2,y}^f = -0.222 + 0.222 - 0.4605 = -0.4605$. Finally, we update all the positions to the time of the collision. $x_1^f = [1.67 + 0.167 \cdot 3.78 \quad 1.67 + 0.222 \cdot 3.78] = [2.301 \quad 2.514]$; $x_2^f = [3.33 - 0.167 \cdot 3.78 \quad 3.33 - 0.222 \cdot 3.78] = [2.695 \quad 2.486]$. From this point, the procedure for the next collision is exactly the same.

In retrospect, a major oversimplification of this problem deserves comment. By restricting the system to two particles, it is necessary that the components of velocity be equal and opposite in sign. Otherwise, the system itself would have a net velocity. You should not mistake this equality as a general result. If there were three particles, for example, the velocities would sum to zero, but the individual magnitudes could vary quite substantially.

Analyzing MD Results

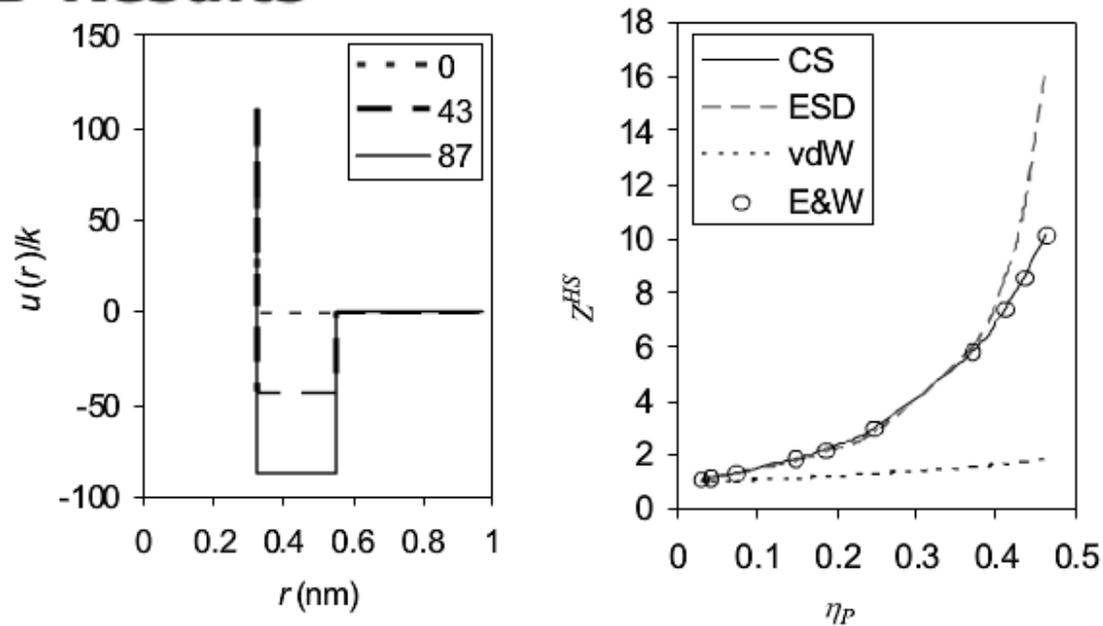


Figure 7.9 (a) The hard-sphere potential as a special case of the square-well model; (b) results of DMD simulations for the hard-sphere potential compared to simulation data of Erpenbeck and Wood cited in the text.

The results of hard-sphere simulations by Erpenbeck and Wood¹⁶ are presented in Fig. 7.9(b). Three equations of state are compared to the simulation results: the van der Waals model, the Carnahan-Starling model, and the ESD model. These models are listed below, along with another called the Scott model.

$$Z^{HS} = 1/(1 - \eta_P); \text{ the van der Waals model} \quad 7.45$$

$$Z^{HS} = (1 + 2\eta_P)/(1 - 2\eta_P); \text{ the Scott model} \quad 7.46$$

$$Z^{HS} = 1 + 4\eta_P/(1 - 1.9\eta_P); \text{ the ESD model} \quad 7.47$$

$$Z^{HS} = 1 + 4\eta_P(1 - \eta_P/2)/(1 - \eta_P)^3; \text{ the Carnahan-Starling model} \quad 7.48$$

Example 7.11 Equations of state from trends in molecular simulations

Use the 3D DMD module at Etonica.org to characterize the trends of the attractive contributions for argon with $\lambda = 1.7$ at densities of 1.25 and 1.38 g/cm³ assuming a diameter of 0.323 nm and $\epsilon/k = 87$ K. Use the results to obtain a cubic equation of state.

Solution: It is straightforward to set a diameter of 0.323 nm, $N_A \epsilon = 87 \cdot 8.314 = 723$ J/mol, MW = 40, and $\lambda = 1.7$. For purposes of this problem, we assume the ESD form suffices over the density range of interest with the objective of obtaining a cubic equation.

The next step is to simulate the full potential and solve for the attractive contribution by subtraction. Fig. 7.7 suggests that a linear function in $\beta\epsilon$ should suffice, and we know that the attractive contribution increases with density. These observations suggest an equation of state of the form

$$Z = 1 + 4 \eta_P / (1 - 1.9 \eta_P) - z_{11} \eta_P \beta\epsilon,$$

where z_{11} designates a constant corresponding to first order in both η_P and $\beta\epsilon$. By regressing the slope of the attractive contribution at the two given densities, we can characterize z_{11} as a function of density. We can also infer the zero density limit of z_{11} from the second virial coefficient as $z_{11}(0) = 4(\lambda^3 - 1) = 15.7$. The results of these characterizations give $z_{11} = 16.3$ at $\eta_P = 0.333$ and 17.0 at $\eta_P = 0.367$. In order to obtain a cubic equation, we must restrict our attention to equations of the form,

$$z_{11} = z_{11}(0) / (1 - z_{12} \eta_P).$$

Plotting $z_{11}(0)/z_{11}$ and fitting a trendline gives $z_{12} = 0.16$ and the final model is,

$$Z = 1 + 4 \eta_P / (1 - 1.9 \eta_P) - 15.7 \eta_P \beta\epsilon / (1 - 0.16 \eta_P)$$

This fit of the attractive trend is crude, but it would be difficult to improve given the constraints imposed by the cubic form. This leaves the door open to future improvements beyond the cubic form. The approach would be similar, however.

7.11 THE MOLECULAR BASIS OF EQUATIONS OF STATE: ANALYTICAL THEORIES

The Energy Equation

$$U - U^{ig} = \frac{N_A \rho}{2} \int_0^{\infty} N_A u g(r) 4\pi r^2 dr \quad 7.49$$

$$\frac{U - U^{ig}}{RT} = \frac{N_A \rho}{2} \int_0^{\infty} \frac{N_A u}{RT} g(r) 4\pi r^2 dr \quad 7.50$$

where u is the pair potential and $g(r) \equiv$ the radial distribution function

The Pressure Equation

$$P = \rho RT - \frac{\rho^2 N_A^2}{6} \int_0^{\infty} r \left(\frac{du}{dr} \right) g(r) 4\pi r^2 dr \quad 7.51$$

$$\frac{P}{\rho RT} = 1 - \frac{\rho N_A}{6} \int_0^{\infty} \frac{N_A r}{RT} \left(\frac{du}{dr} \right) g(r) 4\pi r^2 dr \quad 7.52$$

An Introduction to the Radial Distribution Function

The Fluid Structure of an Ideal Gas

Consider a fluid of point particles surrounding a central particle. What is the number of particles in a given volume element surrounding the central particle? Since they are point particles, they do not

$$dN_V = N \frac{dV}{V} \quad (\text{ig) 7.53}$$

where dN_V is the number of particles in the volume element, N is the total number of particles in the total volume, V is the total volume, dV is the size of the volume element, and $dN_V = N_A \rho dV$

If we would like to know the number of particles within some spherical neighborhood of our central particle, then,

$$dV = 4\pi r^2 dr$$

where r is the radial distance from our central particle,

$$N_c = \int_0^{N_c} dN_V = N_A \int_0^{R_o} \rho 4\pi r^2 dr \quad (\text{ig) 7.54}$$

where R_o defines the range of our spherical neighborhood, N_c is the number of particles in the neighborhood (coordination number).

The Fluid Structure of a Low-Density Hard-Sphere Fluid

$$N_c = N_A \rho \int_0^{R_o} g(r) 4\pi r^2 dr \quad 7.55$$

$$N_c = \int_0^{N_c} dN_V = N_A \int_0^{R_o} \rho 4\pi r^2 dr \quad (\text{ig}) 7.54$$

where $g(r)$ is our average “weighting function,” called the radial distribution function. The radial distribution function is the number of atomic centers located in a spherical shell from r to $r + dr$ from one another, divided by the volume of the shell and the bulk number density.

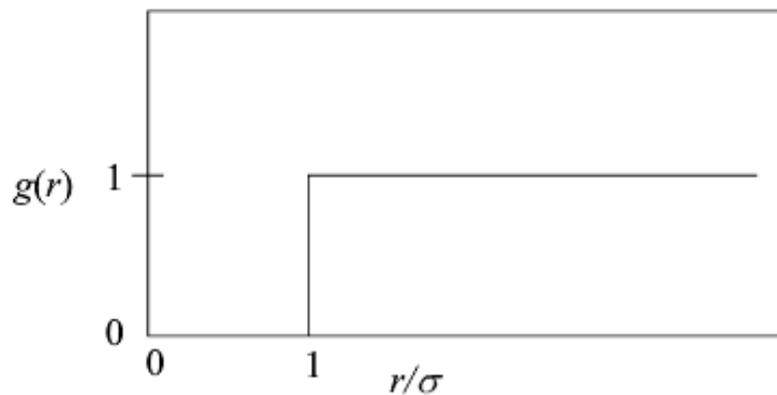


Figure 7.11 The radial distribution function for the low-density hard-sphere fluid.

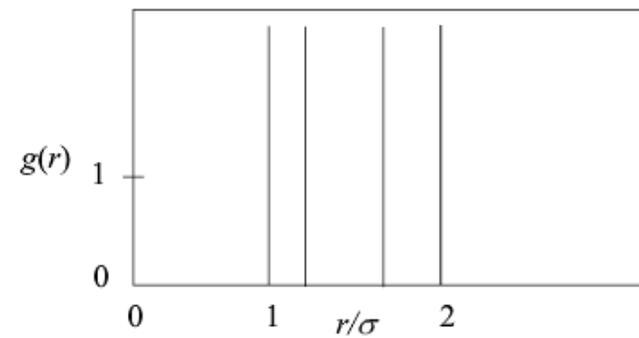


Figure 7.12 The radial distribution function for the bcc hard-sphere fluid.

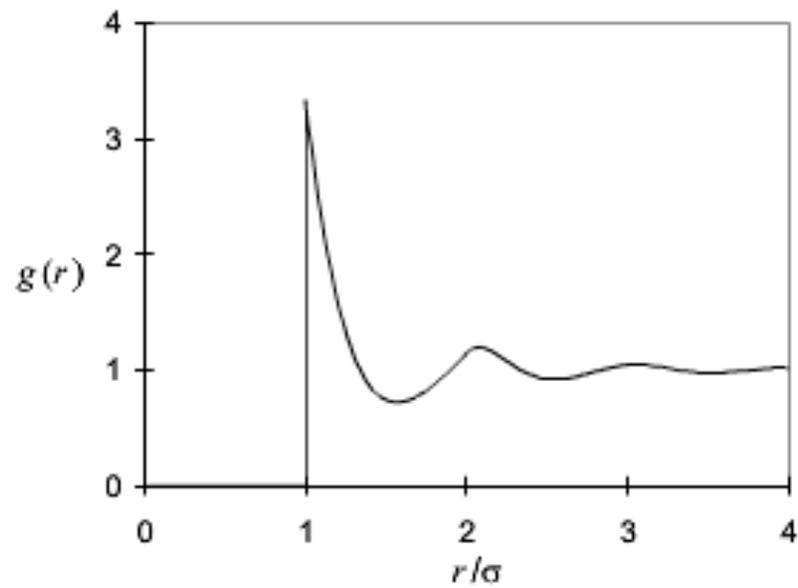
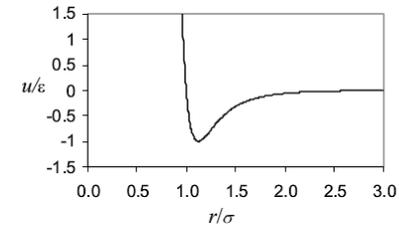


Figure 7.13 *The radial distribution function for the hard-sphere fluid at a packing fraction of $b\rho = 0.4$.*

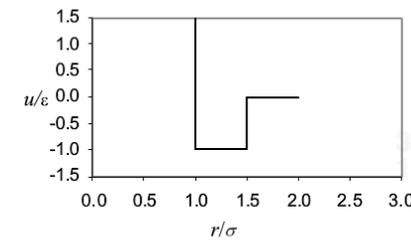
The Structure of Fluids in the Presence of Attractions and Repulsions

$$\lim_{\rho \rightarrow 0} g(r) = \exp\left[-\frac{u(r)}{kT}\right]$$

7.57

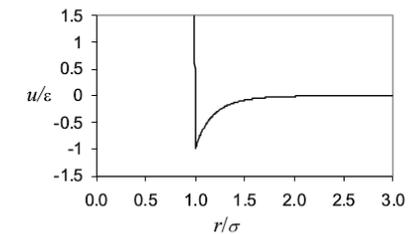


The Lennard-Jones potential.
 $u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$
 Note that $\epsilon > 0$ is the depth of the well, and σ is the distance where $u(r) = 0$.



The square-well potential for $\lambda = 1.5$.

$$u(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\epsilon & \text{if } \sigma < r \leq \lambda\sigma \\ 0 & \text{if } r > \lambda\sigma \end{cases}$$



The Sutherland potential.
 $u(r) = \begin{cases} \infty & \text{if } r \leq \sigma \\ -\epsilon(\sigma/r)^6 & \text{if } r > \sigma \end{cases}$

Figure 1.1 Schematics of three engineering models for pair potentials on a dimensionless basis.

The Virial Equation

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \dots \quad 7.58$$

$$B = 2\pi N_A \int_0^\infty \left(1 - \exp\left(-\frac{u}{kT}\right)\right) r^2 dr \quad 7.59$$

Example 7.12 Deriving your own equation of state

Appendix B shows how the following equation can be derived to relate the macroscopic equation of state to the microscopic properties in terms of the square-well potential for $\lambda = 1.5$.

$$Z = 1 + \frac{4\pi N_A \rho \sigma^3}{6} \{g(\sigma^+) - 1.5^3 [1 - \exp(-\varepsilon/kT)g(1.5\sigma^-)]\} \quad 7.60$$

Apply this result to develop your own equation of state with a radial distribution function of the form:

$$g(x) = \frac{\exp(-u/kT)}{(1 - 2b\rho/x^6)(1 + 2Sb\rho/x^6)} \quad 7.61$$

where $x = r/\sigma$, $b = \pi N_A \sigma^3/6$, and S is the “Student” parameter. You pick a number for S , and this will be your equation of state. Evaluate your equation of state at $\varepsilon/kT = 0.5$ and $b\rho = 0.4$.

Solution: At first glance, this problem may look outrageously complicated, but it is actually quite simple. We only need to evaluate the radial distribution function at $x = 1$ and $x = 1.5$ and insert these two results into Eqn. 7.60.

$$g(\sigma^+) = \frac{\exp(\varepsilon/kT)}{(1 - 2b\rho)\{1 + 2Sb\rho\}} \quad 7.62$$

$$g(1.5\sigma^-) = \frac{\exp(\varepsilon/kT)}{(1 - 0.176Sb\rho)\{1 + 0.176Sb\rho\}} \quad 7.63$$

$$Z = 1 + \frac{4b\rho}{1 - 2b\rho} \frac{\exp(\varepsilon/kT)}{1 + 2Sb\rho} - \frac{13.5b\rho[\exp(\varepsilon/kT) - 1]}{(1 - 0.176b\rho)(1 + 0.176Sb\rho)} \quad 7.64$$

Supposing $S = 3$, $Z(0.5, 0.4) = 1 + 4 \cdot 0.4 \cdot 1.649 / (0.2 \cdot 2.4) - 13.5 \cdot 0.4 \cdot 0.648 / (0.789 \cdot 1.211) = 2.83$.

Congratulations! You have just developed your own equation of state. Have fun with it and feel free to experiment with different approximations for the radial distribution function. Hansen and McDonald^a describe several systematic approaches to developing such approximations if you would like to know more.