

3.7 Problems for Chapter 3

3.1 Show that the Joule-Kelvin coefficient is zero for an ideal gas.

The Joule-Kelvin coefficient is given by

$$\mu_J = \frac{1}{c_p} \left\{ T \left. \frac{\partial V}{\partial T} \right|_p - V \right\}.$$

For an ideal gas we have $pV = NkT$, so upon differentiating:

$$\left. \frac{\partial V}{\partial T} \right|_p = \frac{Nk}{p}$$

so that

$$\mu_J = \frac{1}{c_p} \left\{ T \frac{Nk}{p} - V \right\}.$$

And since $pV = NkT$, the bracket is zero. Thus the Joule-Kelvin coefficient is zero.

3.2 Evaluate the constants A , B of Eq. (3.2.15) in terms of the square well potential parameters σ and R .

The square well $B_2(T)$ was given in Eq. (3.2.14):

$$B_2(T) = \frac{2}{3}\pi\sigma^3 R^3 - \frac{2}{3}\pi\sigma^3 (R^3 - 1)e^{\varepsilon/kT},$$

which has the general form of Eq. (3.2.15):

$$B_2(T) = A - Be^{\varepsilon/kT}.$$

We equate the temperature-independent terms and the temperature-dependent terms, giving

$$\begin{aligned} A &= \frac{2}{3}\pi\sigma^3 R^3 \\ B &= \frac{2}{3}\pi\sigma^3 (R^3 - 1). \end{aligned}$$

3.3 Show that the Boyle temperature T_B for the square well gas is given by

$$kT_B = -\varepsilon / \ln(1 - R^{-3}).$$

The square well $B_2(T)$ was given in Eq. (3.2.14):

$$B_2(T) = \frac{2}{3}\pi\sigma^3 R^3 - \frac{2}{3}\pi\sigma^3(R^3 - 1)e^{\varepsilon/kT}.$$

The Boyle temperature T_B is the temperature for which this becomes zero. So

$$R^3 = (R^3 - 1)e^{\varepsilon/kT_B}$$

(which, we note, is independent of σ). This can be manipulated to give

$$\begin{aligned} \frac{\varepsilon}{kT_B} &= \ln\left(\frac{R^3}{R^3 - 1}\right) \\ &= \ln\left(\frac{1}{1 - 1/R^3}\right) \\ &= -\ln(1 - 1/R^3), \end{aligned}$$

so that

$$kT_B = -\varepsilon/\ln(1 - R^{-3}).$$

3.4 For the van der Waals gas show that $T_B = a/bk$ and $T_i = 2a/bk$.

We obtained the second virial coefficient for the van der Waals gas to be (Eq. (3.4.17))

$$B_2(T) = b - \frac{a}{kT}.$$

The Boyle temperature is that for which $B_2(T) = 0$. So setting the above expression to zero gives

$$T_B = \frac{a}{bk}.$$

The inversion temperature is that for which

$$\frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} = 0.$$

Now differentiating $B_2(T)$ gives

$$\frac{dB_2(T)}{dT} = \frac{a}{kT^2}$$

so that we now require to solve

$$\frac{a}{kT^2} = \frac{b}{T} - \frac{a}{kT^2}.$$

This has solution

$$T_i = \frac{2a}{bk}.$$

3.5 The interatomic potential $U(r) = \varepsilon\left(\frac{\sigma}{r}\right)^n$ may be regarded as a “soft sphere” interaction where $1/n$ measures the “softness”.

- (a) Show that when $n \rightarrow \infty$ this reduces to the hard sphere potential.
- (b) Plot $U(r)$ for different n showing the hardening of the potential as n increases.
- (c) The second virial coefficient for particles interacting with this potential is

$$B_2(T) = \frac{2}{3}\pi\sigma^3 \left(\frac{\varepsilon}{kT}\right)^{3/n} \Gamma\left(1 - \frac{3}{n}\right).$$

Show this reduces to the hard sphere case when $n \rightarrow \infty$.

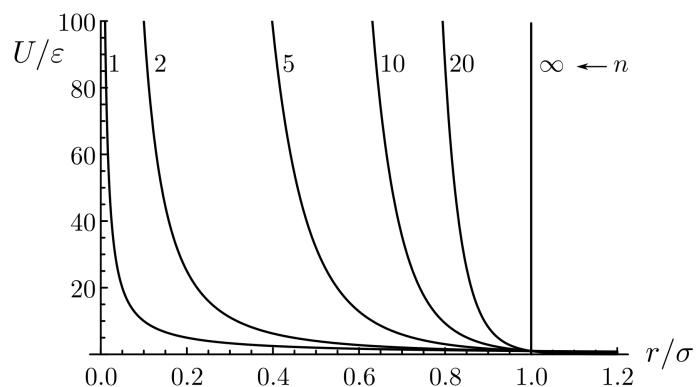
- (d) Sketch the form of this $B_2(T)$ together with the general form for the second virial coefficient. (You might choose the soft sphere case for $n = 12$ and Lennard-Jones $B_2(T)$, and you might plot these over the temperature range $0 < \frac{kT}{\varepsilon} < 20$). They are very different. Explain why.

(a) As (even) n tends to infinity

$$\begin{aligned} \left(\frac{\sigma}{r}\right)^n &\rightarrow \infty && \text{when } r < \sigma \\ \left(\frac{\sigma}{r}\right)^n &\rightarrow 0 && \text{when } r > \sigma, \end{aligned}$$

so that $U(r) = \varepsilon\left(\frac{\sigma}{r}\right)^n$ then corresponds to a hard sphere potential.

(b) The figure shows a plot of $U(r)$ for increasing n .

Figure 3.23: Soft sphere potential for different n parameters

We see the $n \rightarrow \infty$ line is vertical – indicative of a hard sphere.

(c) The second virial coefficient is

$$B_2(T) = \frac{2}{3}\pi\sigma^3 \left(\frac{\varepsilon}{kT}\right)^{3/n} \Gamma\left(1 - \frac{3}{n}\right).$$

As $n \rightarrow \infty$

$$\begin{aligned} \left(\frac{\varepsilon}{kT}\right)^{3/n} &\rightarrow \left(\frac{\varepsilon}{kT}\right)^0 = 1 \\ \Gamma\left(1 - \frac{3}{n}\right) &\rightarrow \Gamma(1) = 1. \end{aligned}$$

So

$$B_2(T) \rightarrow \frac{2}{3}\pi\sigma^3,$$

which is the (temperature-independent) hard sphere result.

(d) The figure shows the $B_2(T)$ for the soft sphere potential and for the Lennard-Jones interaction.

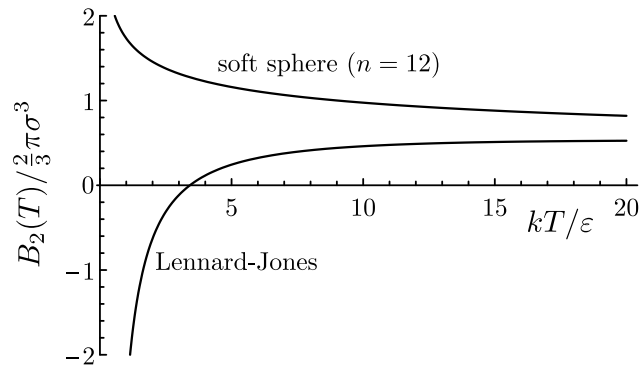


Figure 3.24: $B_2(T)$ for soft sphere potential ($n = 12$) and for Lennard-Jones gas

The Lennard-Jones curve shows the “normal” behaviour: large negative values at low temperatures, increasing through zero and then flattening off at high temperatures. The low temperature negative behaviour is a reflection of the attractive long-distance part of the interaction; the high temperature positive behaviour is a reflection of the short-distance repulsion.

The soft sphere curve is all positive as the interaction is all repulsive. At higher temperatures the more energetic collisions cause the particles to approach closer. This is an “effective” reduction of the particles’ excluded volume.

At even higher temperatures the Lennard-Jones curve will turn over and reduce gently in the same way for the same reason.

- 3.6 For the *hard sphere* gas we saw that the compressibility factor pV/NkT could be expressed as a universal, temperature-independent, function of the density N/V . By noting that, the soft sphere interaction, for a given value of n , the interaction potential scales with a single parameter $\varepsilon\sigma^n$, argue that the soft sphere compressibility factor z may be expressed as a universal function of $N/V T^{3/n}$.

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- 3.7 Show (with the aid of a computer) that for the Lennard-Jones gas

$$T_B = 3.418 \varepsilon/k, \quad T_i = 6.431 \varepsilon/k.$$

The Boyle temperature and the inversion temperature for this gas may be found from their definitions

$$\begin{aligned} B_2(T) = 0 &\quad \rightarrow \quad T_B \\ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} = 0 &\quad \rightarrow \quad T_i \end{aligned}$$

It is convenient to work in dimensionless reduced units: $b_2 = B_2/(\frac{2}{3}\pi\sigma^3)$ and $t = kT/\varepsilon$. Then for the Lennard-Jones gas b_2 is specified as

$$b_2 = \sqrt{2\pi} t^{-1/4} H_{1/2}(-t^{-1/2}).$$

The Boyle temperature is found from the zero of this function. Numerical evaluation of the root gives

$$t_B = 3.418.$$

To obtain the inversion temperature we must examine

$$\frac{db_2}{dt} - \frac{b_2}{t} = \frac{\sqrt{\pi}}{2\sqrt{2}} t^{-1/4} \left[2t^{-1/2} H_{-1/2}(-t^{-1/2}) - 5H_{1/2}(-t^{-1/2}) \right].$$

The inversion temperature is found from the zero of this function. Numerical evaluation of the root gives

$$t_i = 6.431.$$

Converting back to real quantities then gives

$$T_B = 3.418 \varepsilon/k, \quad T_i = 6.431 \varepsilon/k$$

as required.

3.8 For a general inter-particle interaction potential $U(r)$ we may define an *effective* temperature-dependent hard core dimension σ_{eff} by $U(\sigma_{\text{eff}}) = kT$.

- (a) What is the interpretation of this definition?
- (b) At high temperatures only the *repulsive* part of the interaction is relevant.

Show that for the (repulsive part of the) Lennard-Jones 6 – 12 potential, σ_{eff} is given by

$$\sigma_{\text{eff}} = \sigma \left(\frac{4\varepsilon}{kT} \right)^{1/12}.$$

- (c) The previous result corresponds to an *effective volume* $v_{\text{eff}} = \frac{2}{3}\pi\sigma_{\text{eff}}^3$ so that $v_{\text{eff}} = \frac{2}{3}\pi\sqrt{2}(\varepsilon/kT)^{1/4}$. Compare this with the high temperature limit of the Lennard-Jones B_2 . Discuss the similarities.
- (d) You might care to carry out the calculation of σ_{eff} and v_{eff} for the full Lennard-Jones potential, comparing the high temperature expansion of v_{eff} with the high temperature expansion of the Lennard-Jones B_2 .

(a) In a potential $U(r)$, particles with a thermal energy kT will be able to approach each other to a separation σ_{eff} . At this separation all kinetic energy will be lost to the repulsive potential; they cannot get closer. In this respect σ_{eff} is a measure of the *effective size* of the particles.

(b) The repulsive part of the Lennard-Jones potential is

$$U_{\text{rep}}(r) = 4\varepsilon \left(\frac{\sigma}{r}\right)^{12}$$

so equating this to kT we obtain

$$\sigma_{\text{eff}} = \sigma \left(\frac{4\varepsilon}{kT}\right)^{1/12}.$$

(c) We have an *effective volume*

$$v_{\text{eff}} = \frac{2}{3}\pi\sigma^3 \times \sqrt{2} \left(\frac{\varepsilon}{kT}\right)^{1/4}.$$

We saw, in Eq. (3.2.21) that the high temperature limit of the Lennard-Jones B_2 is

$$B_2(T) \sim \frac{2}{3}\pi\sigma^3 \times \frac{2\pi}{\Gamma(1/4)} \left(\frac{\varepsilon}{kT}\right)^{1/4}.$$

(Numerical values: $\sqrt{2} = 1.414$, $2\pi/\Gamma(1/4) = 1.733$).

We learned from the hard core potential, the square well potential and the Sutherland potential, that in the high temperature limit the second virial coefficient corresponds to the excluded volume. We have, here, a way of relating the excluded volume to the inter-particle potential. So here we see a convenient way of relating the high temperature behaviour of B_2 to the repulsive part of $U(r)$.

(d) Using “full” L-J potential we find

$$\begin{aligned}\sigma_{\text{eff}} &= \sigma 2^{1/6} \left\{ \frac{\varepsilon}{kT} \left(\sqrt{\frac{kT}{\varepsilon} + 1} \right) - 1 \right\}^{1/6} \\ &= \sigma 2^{1/6} \left(\frac{\varepsilon}{kT} \right)^{1/12} \left\{ 1 - \frac{1}{6} \left(\frac{\varepsilon}{kT} \right)^{1/2} + \dots \right\}\end{aligned}$$

and

$$\begin{aligned}\sigma_{\text{eff}}^3 &= \sigma^3 2^{1/2} \left\{ \frac{\varepsilon}{kT} \left(\sqrt{\frac{kT}{\varepsilon} + 1} \right) - 1 \right\}^{1/2} \\ &= \sigma^3 2^{1/2} \left(\frac{\varepsilon}{kT} \right)^{1/4} \left\{ 1 - \frac{1}{2} \left(\frac{\varepsilon}{kT} \right)^{1/2} + \dots \right\} \\ &= \sigma^3 \left\{ \sqrt{2} \left(\frac{\varepsilon}{kT} \right)^{1/4} - \frac{1}{\sqrt{2}} \left(\frac{\varepsilon}{kT} \right)^{3/4} + \dots \right\}\end{aligned}$$

so that v_{eff} is then

$$v_{\text{eff}} = \frac{2}{3} \pi \sigma^3 \times \left\{ \sqrt{2} \left(\frac{\varepsilon}{kT} \right)^{1/4} - \frac{1}{\sqrt{2}} \left(\frac{\varepsilon}{kT} \right)^{3/4} + \dots \right\}.$$

The leading term is exactly that calculated from just the repulsive part of the Lennard-Jones potential and the powers of T are the same as those in the high temperature expansion of $B_2(T)$.

3.9 Derive the second virial coefficient expression for the Joule-Kelvin coefficient $\mu_J = \frac{2T}{5k} \left\{ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} \right\}$, and find the inversion temperature for the square well potential gas in the limit $R \rightarrow \infty, \varepsilon \rightarrow 0$. (The full expression for T_i will be found in Problem 3.14.)

In the limit of small $B_2(T)$ we have the equivalent expression for the virial expansion

$$V = \frac{NkT}{p} + NB_2(T).$$

And we have

$$\mu_J = \frac{1}{c_p} \left\{ T \left. \frac{\partial V}{\partial T} \right|_p - V \right\}.$$

So differentiating the expression for V gives

$$\left. \frac{\partial V}{\partial T} \right|_p = \frac{Nk}{p} + N \frac{dB_2(T)}{dT}.$$

We substitute this into the expression for μ , to give

$$\mu_J = \frac{NT}{c_p} \left\{ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} \right\}.$$

Now for an ideal gas the heat capacity at constant volume is given by

$$c_p = \frac{5}{2}Nk$$

and we adopt this as an acceptable approximation in this weakly interacting case. We then obtain the result

$$\mu_J = \frac{2T}{5k} \left\{ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} \right\}.$$

The second virial coefficient for the square well gas is given by

$$B_2(T) = \frac{2}{3}\pi\sigma^3 \{1 - (R^3 - 1)(e^{\varepsilon/kT} - 1)\}.$$

To find the inversion temperature we require to solve the equation

$$\frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} = 0$$

for T . Now using the square-well expression for $B_2(T)$ will result in a complicated equation. A numerical solution can be found if R is specified, or an approximate solution may be found. We shall look for a solution for the inversion temperature in the (realistic) limiting case where there is a long-range, but weak interaction. In other words we are considering the case where R is large and ε is small. When R is very much greater than unity then $B_2(T)$ may be approximated by

$$B_2(T) = \frac{2}{3}\pi\sigma^3 \{1 - R^3(e^{\varepsilon/kT} - 1)\}$$

and if ε is small then we may expand the exponential so that

$$B_2(T) = \frac{2}{3}\pi\sigma^3 \left\{ 1 - \frac{R^3\varepsilon}{kT} \right\}.$$

This expansion is valid for temperatures T much greater than ε/k . This will be justified *a posteriori*.

This expression for $B_2(T)$ is actually equivalent to that obtained for the van der Waals gas; the general behaviour is

$$B_2(T) = b - \frac{a}{kT}.$$

We can then quote the result (derived in the previous Problem)

$$\begin{aligned} T_i &= \frac{2a}{bk} \\ &= \frac{2}{k} R^3 \varepsilon. \end{aligned}$$

This satisfies the requirement on the expansion of the exponential, that $kT \gg \varepsilon$ since R is assumed to be large.

3.10 Show (with the aid of a computer) that for the Sutherland gas

$$T_B = 1.171 \varepsilon/k, \quad T_i = 2.251 \varepsilon/k.$$

The Boyle temperature and the inversion temperature for this gas may be found from their definitions

$$\begin{aligned} B_2(T) = 0 &\quad \rightarrow \quad T_B \\ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} = 0 &\quad \rightarrow \quad T_i \end{aligned}$$

It is convenient to work in dimensionless reduced units: $b_2 = B_2/(\frac{2}{3}\pi\sigma^3)$ and $t = kT/\varepsilon$. Then for the Sutherland gas b_2 is specified as

$$b_2 = e^{1/t} - \sqrt{\pi} t^{-1/2} \operatorname{Erfi}(t^{-1/2}).$$

The Boyle temperature is found from the zero of this function. Numerical evaluation of the root gives

$$t_B = 1.171.$$

To obtain the inversion temperature we must examine

$$\frac{db_2}{dt} - \frac{b_2}{t} = \frac{3}{2} \sqrt{\pi} t^{-3/2} \operatorname{Erfi}(t^{-1/2}) - t^{-1} e^{1/t}$$

The inversion temperature is found from the zero of this function. Numerical evaluation of the root gives

$$t_i = 2.251.$$

Converting back to real quantities then gives

$$T_B = 1.171 \varepsilon/k, \quad T_i = 2.251 \varepsilon/k$$

as required.

- 3.11 Compare the square well and the van der Waals expressions for the second virial coefficient. Show that they become equivalent when the range of the square well potential tends to infinity while its depth tends to zero.

The square well second virial coefficient is given by

$$B_2^{\text{sq}}(T) = \frac{2}{3} \pi \sigma^3 \{1 - (R^3 - 1) (e^{\varepsilon/kT} - 1)\}$$

while that for the van der Waals equation is

$$B_2^{\text{VW}}(T) = b - \frac{a}{kT}.$$

When ε is small the exponential of the square well second virial coefficient can be expanded:

$$B_2^{\text{sq}}(T) \approx \frac{2}{3} \pi \sigma^3 \left\{ 1 - (R^3 - 1) \left(\frac{\varepsilon}{kT} + \frac{1}{2} \left(\frac{\varepsilon}{kT} \right)^2 + \dots \right) \right\}$$

at the same time the range of the well become large so that the 1 may be neglected in comparison with the R^3 . Then

$$B_2(T) \approx \frac{2}{3} \pi \sigma^3 \left\{ 1 - R^3 \left(\frac{\varepsilon}{kT} + \frac{1}{2} \left(\frac{\varepsilon}{kT} \right)^2 + \dots \right) \right\}.$$

In the limit that $\varepsilon \rightarrow 0, R \rightarrow \infty$, while $R^3 \sigma$ remains finite this then becomes

$$B_2(T) \approx \frac{2}{3} \pi \sigma^3 \left\{ 1 - R^3 \frac{\varepsilon}{kT} \right\}.$$

And this has the form of the square well second virial coefficient, where

$$b = \frac{2}{3} \pi \sigma^3, \quad a = \frac{2}{3} \pi \sigma^3 R^3 \varepsilon$$

Thus we have shown that the second virial coefficient of van der Waals equation of state is equivalent to that arising from the square well interaction in the limit of a long-range but weak attraction.

Table 3.4: Second virial coefficient of xenon

$T(\text{K})$	$B_2(\text{cm}^3/\text{mol})$
273.16	-154.74
298.16	-130.21
323.16	-110.62
348.16	-95.04
373.16	-82.13
423.16	-62.10
473.16	-46.74
573.16	-25.06
673.16	-10.77
773.16	-0.13
873.16	7.95
973.16	14.22

3.12 Some measurements of the second virial coefficient $B_2(T)$ for xenon at high temperatures are given in Table 3.4.

If you assume that the interaction between two xenon atoms has the form of the square well potential, what can you deduce about the potential's parameters σ , ε and R ?

The $B_2(T)$ data points are plotted against temperature in Fig. 3.25. If you have access to a non-linear regression app then you can fit the square well $B_2(T)$ expression

$$\begin{aligned}
 B_2(T) &= \frac{2}{3}\pi\sigma^3 \{R^3 - (R^3 - 1)e^{\varepsilon/kT}\} \\
 &= B_2^{\text{hs}} \{R^3 - (R^3 - 1)e^{\varepsilon/kT}\}.
 \end{aligned}$$

through the points. This is the red curve.

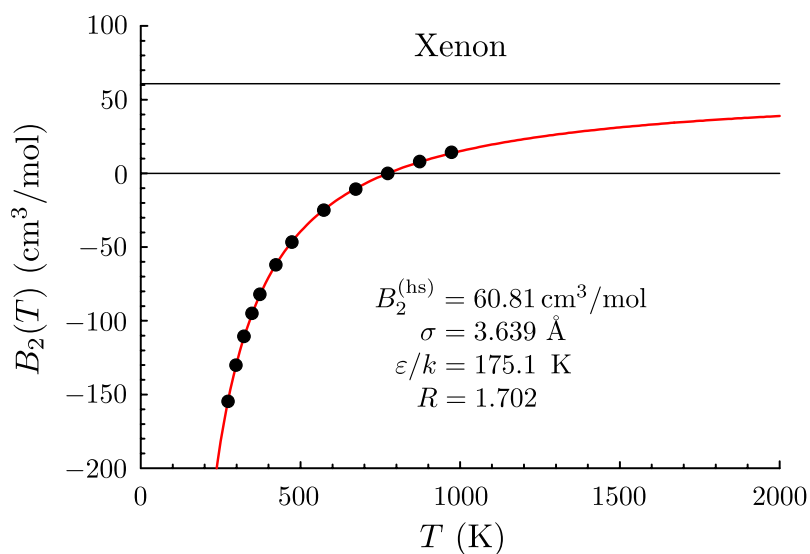


Figure 3.25: Fit of square well expression through xenon B_2 data points.

The fit parameters are

$$\begin{aligned}
 B_2^{\text{hs}} &= 60.81 \text{ cm}^3/\text{mol} \\
 \sigma &= 3.639 \text{ \AA} \\
 \epsilon/k &= 175.1 \text{ K} \\
 R &= 1.702
 \end{aligned}$$

as shown in the figure. This is a complete answer to the problem.

But what if you don't have access to non-linear curve fitting software? A plot of the B_2 data against $1/T$ is shown in Fig. 3.26 together with a linear regression *quadratic* fit through the data. You should have access to linear regression software; if not, it is fairly straightforward to write the code.

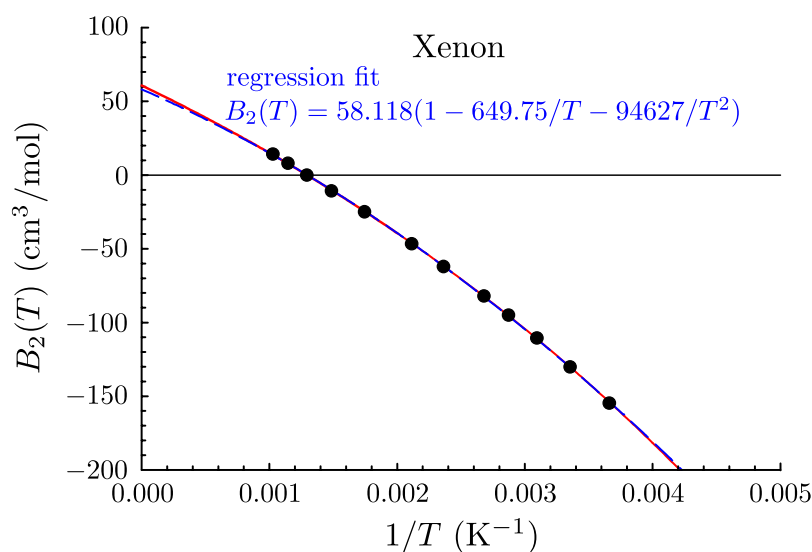


Figure 3.26: Fit of square well expression through xenon data points.

The quadratic fit through these data, the dashed blue line) is found to be

$$B_2(T) = 58.118 \left[1 - 649.75 \frac{1}{T} - 94627 \frac{1}{T^2} \right]$$

which should be compared with the high temperature expansion of the square well B_2

$$B_2(T) = B_2^{\text{hs}} \left[1 - (R^3 - 1) \frac{\varepsilon}{kT} - \frac{(R^3 - 1)}{2} \left(\frac{\varepsilon}{kT} \right)^2 + \dots \right]$$

By equating the coefficients we find

$$B_2^{\text{hs}} = 58.12 \text{ cm}^3/\text{mol}$$

$$\varepsilon/k = 291.3 \text{ K}$$

$$R = 1.48.$$

The hard sphere intercept may be expressed

$$\begin{aligned} B_2^{\text{hs}} &= 58.12 \text{ cm}^3/\text{mol} \\ &= 58.12 \times 10^{-6} \text{ m}^3/\text{mol} \\ &= 58.12 \times 10^{-6} / N_A \text{ m}^3/\text{particle} \\ &= 9.65 \times 10^{-29} \text{ m}^3/\text{particle}. \end{aligned}$$

Then since

$$\sigma = \frac{2}{3} \pi \sigma^3$$

we find σ to be

$$\begin{aligned}\sigma &= 3.59 \times 10^{-10} \text{ m} \\ &= 3.59 \text{ \AA}.\end{aligned}$$

These are *reasonable* approximations to the parameters of the square well potential.

Finally, consider the Boyle temperature. For the square well potential this is given by Eq. (3.2.16):

$$T_B = \frac{-\varepsilon/k}{\ln(1 - R^{-3})}.$$

The experimental points indicate clearly that T_B is close to 773 K. This would be a good input to determining the square well potential parameters. For the parameters determined by the second order $1/T$ expansion we note that T_B would be predicted to be 789.8 K.

The point is that B_2^{hs} and T_B can be determined quite well from the data. We need one further piece of information to determine the *three* parameters of the square well potential.

- 3.13 From the expression for the second virial coefficient, Eq. (3.2.2), show that if the interaction potential has a *universal* form $U(r) = \varepsilon u(r/\sigma)$ — in other words $u(x)$ is the same for different species, where just the scaling parameters ε and σ differ — then $B_2(T)$ also has a universal form.

Start from Eq. (3.2.2)

$$\begin{aligned}B_2(T) &= 2\pi \int_0^\infty r^2 [e^{-U(r)} - 1] dr \\ &= 2\pi \int_0^\infty r^2 [e^{-\varepsilon u(r/\sigma)} - 1] dr\end{aligned}\tag{3.7.1}$$

. Change variables to $x = r/\sigma$, $t = kT/\varepsilon$. Then

$$B_2(T) = -2\pi\sigma^3 \int_0^\infty x^2 [e^{-u(x)/t} - 1] dx.$$

Now the integral depends only on t – call this $f(t)$. So B_2 may be expressed

$$B_2(T) = -2\pi\sigma^3 f(t)$$

or

$$B_2(T) = -2\pi\sigma^3 f(kT/\varepsilon).$$

Thus other words $B_2(T)$ is the same for different species, where just the scaling parameters ε and σ differ; so $B_2(T)$ has a universal form.

3.14 Show that the inversion temperature T_i for the square well gas is given by

$$kT_i = \varepsilon / \{W [e/(1 - R^{-3})] - 1\}$$

where $W[\]$ is the Lambert W-function.

(The Lambert W-function $W[y]$ is the solution to the equation $y = We^W$. It is implemented in *Mathematica* as `LambertW[y]`.)

The square well $B_2(T)$ was given in Eq. (3.2.14):

$$B_2(T) = \frac{2}{3}\pi\sigma^3 R^3 - \frac{2}{3}\pi\sigma^3 (R^3 - 1)e^{\varepsilon/kT}.$$

The inversion temperature T_i is the temperature for which

$$\frac{dB_2(T)}{dT} - \frac{B_2(T)}{T}$$

becomes zero.

For the square well $B_2(T)$

$$\frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} = \left(\frac{\varepsilon}{kT}\right)^2 \left[(R^3 - 1) \left(1 + \frac{kT}{\varepsilon}\right) e^{\varepsilon/kT} - R^3 \frac{kT}{\varepsilon} \right].$$

So setting this to zero gives T_i as the solution to

$$(R^3 - 1) \left(1 + \frac{kT_i}{\varepsilon}\right) e^{\varepsilon/kT_i} = R^3 \frac{kT_i}{\varepsilon}$$

or

$$\left(1 + \frac{\varepsilon}{kT_i}\right) e^{\varepsilon/kT_i} = \frac{1}{1 - R^{-3}}.$$

This has solution

$$kT_i = \varepsilon / \{W [e/(1 - R^{-3})] - 1\}$$

where $W[\]$ is the Lambert W-function.

3.15 In Problems 3.3 and 3.14 the Boyle temperature and the inversion temperature for the hard sphere gas were obtained:

$$kT_{\text{B}} = -\varepsilon / \ln(1 - R^{-3}).$$

$$kT_{\text{i}} = \varepsilon / \{W[e/(1 - R^{-3})] - 1\}.$$

(a) Plot these (with the aid of a computer) and comment on the behaviours in the vicinity of $R = 1$.

(b) Plot the ratio $T_{\text{i}}/T_{\text{B}}$ as a function of R . Comment on the behaviour in the vicinity of $R = 1$ and in the limit $R \rightarrow \infty$.

(a) The plot was made using *Mathematica*.

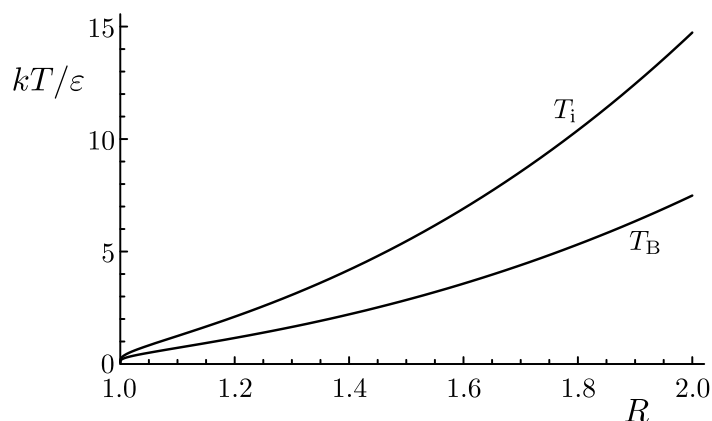


Figure 3.27: Boyle temperature and inversion temperature for a square well potential gas as a function of the range R

As $R \rightarrow 1$ both T_{i} and T_{B} go to zero, but in a non-analytic way. They go down to zero with very high slope. The point is that when $R \rightarrow 1$ the width of the attractive “well” shrinks to zero; we have no attractive part, only the hard core repulsion.

(b) The plot was made using *Mathematica*.

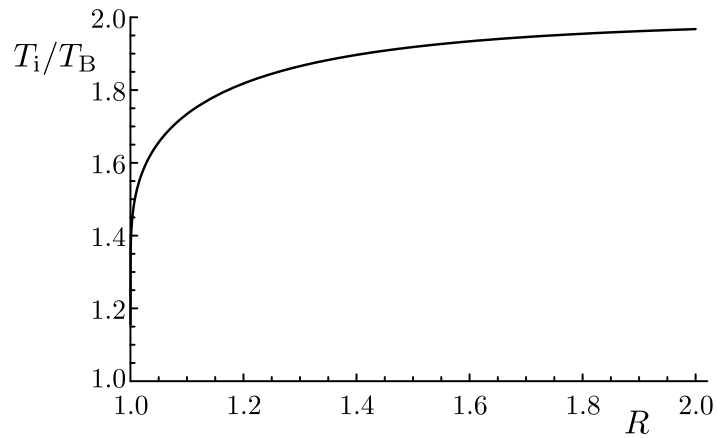


Figure 3.28: Ratio T_i/T_B for a square well potential gas as a function of the range R

As $R \rightarrow 1$ both T_i and T_B go to zero. The ratio goes to unity; this may be understood from the graphical determination of T_i and T_B , considering the way $B_2(T)$ varies as $R \rightarrow 0$ (it approaches the hard core behaviour).

As $R \rightarrow \infty$ the ratio T_i/T_B goes to 2. This is the same as that for the van der Waals gas, Eq. (3.4.18). This is consistent with the idea that the van der Waals gas is equivalent to the square well potential gas in the limit $R \rightarrow \infty$, Problem 3.11.

- 3.16 (a) From the van der Waals partition function expression Eq. (3.4.3), show that the internal energy of a van der Waals gas may be written

$$\frac{E}{N} = \frac{3}{2}kT - a\frac{N}{V}.$$

- (b) Using the relation $pV = \frac{2}{3}E$, Eq. (2.1.35), would give

$$p = \frac{NkT}{V} - \frac{2}{3}a\frac{N^2}{V^2}.$$

This is different from the van der Waals equation of state. Explain.

- (c) Obtain the heat capacity at constant volume C_V for the van der Waals gas. How does this compare with the C_V of an ideal (classical) gas?

- (a) The expression for z , Eq. (3.4.3), is

$$z = \frac{V - V_{\text{ex}}}{\Lambda^3} e^{-\langle E \rangle/kT}$$

so the logarithm of this is

$$\begin{aligned}\ln z &= \ln(V - V_{\text{ex}}) - 3 \ln \Lambda - \frac{\langle E \rangle}{kT} \\ &= \ln(V - V_{\text{ex}}) - \frac{3}{2} \ln \left(\frac{2\pi\hbar^2}{mkT} \right) - \frac{\langle E \rangle}{kT}.\end{aligned}$$

The internal energy is found using Eq. (1.4.23), which we write in slightly different form as

$$E = NkT^2 \left. \frac{\partial \ln z}{\partial T} \right|_{V,N}.$$

Upon differentiating we obtain

$$\frac{\partial \ln z}{\partial T} = \frac{3}{2} \frac{1}{T} + \frac{\langle E \rangle}{kT^2}$$

so that

$$E = \frac{3}{2}NkT + N\langle E \rangle.$$

Or, since $\langle E \rangle = -a\frac{N}{V}$,

$$\frac{E}{N} = \frac{3}{2}kT - a\frac{N}{V} \quad (3.7.2)$$

as required.

(b) As stated, using the relation $pV = \frac{2}{3}E$ would give

$$p = \frac{NkT}{V} - \frac{2}{3}a\frac{N^2}{V^2},$$

whereas the van der Waals equation of state gives

$$p = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2}.$$

These are clearly incompatible: our equation has no excluded volume, Nb , repulsive contribution and it also has the wrong coefficient for the a attractive contribution. The explanation is that the relation $pV = \frac{2}{3}E$ is applicable only to *non-interacting* gases.

(c) Since

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V$$

it follows, from differentiating Eq. (3.7.2), that

$$C_V = \frac{3}{2}Nk.$$

This is the *same* as the C_V of an ideal (classical) gas. So the van der Waals accommodation of the inter-particle interaction has no consequence for C_V (but it does for C_p [?]). Moreover its consequence for the internal energy is to reduce it from the ideal gas value by a temperature-independent constant (the mean field energy).

- 3.17 In Section 3.1.1 we saw that the partition function for an interacting gas may be expressed as $Z = Z_{\text{id}}Q$ where Z_{id} is the partition function for a non-interacting gas and Q is the configuration integral. Explain why the partition function of a *hard sphere* gas might be approximated by

$$Z = Z_{\text{id}} \left(\frac{V - Nb}{V} \right)^N.$$

The interaction is the (infinite) hard sphere repulsion. This has the effect of excluding the “hard sphere volume” from the volume integral in the partition function. So the ideal gas partition function

$$Z_{\text{id}} = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N$$

becomes

$$Z = \frac{1}{N!} \left(\frac{V - Nb}{\Lambda^3} \right)^N,$$

where the excluded volume, proportional to the number of particles, is written as Nb . From these it follows that

$$Z = Z_{\text{id}} \left(\frac{V - Nb}{V} \right)^N.$$

- 3.18 (a) Show that the approximate partition function for the hard sphere gas in the previous question leads to the equation of state $p(V - Nb) = NkT$. This is sometimes called the Clausius equation of state. Give a physical interpretation of this equation.

(b) Show that the first few virial coefficients are given by $B_2(T) = b$, $B_3(T) = b^2$, $B_4(T) = b^3$, etc. These virial coefficients are independent of temperature. Discuss whether this is a fundamental property of the hard sphere gas, or whether it is simply a consequence of the *approximated* partition function.

(a) To find the equation of state we must differentiate $kT \ln Z$ with respect to volume. Now the logarithm of approximate partition is

$$\ln Z = \ln Z_{\text{id}} + N \ln(V - Nb) - N \ln V.$$

For the ideal gas partition function we have

$$\ln Z_{\text{id}} = N \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{Ve}{N} \right],$$

which may be written as

$$\ln Z_{\text{id}} = N \ln V + \text{terms independent of } V.$$

Then

$$\ln Z = N \ln(V - Nb) + \text{terms independent of } V$$

as the $N \ln V$ terms cancel. We then have for the pressure

$$p = kT \left. \frac{\partial \ln Z}{\partial V} \right|_{T,N} = \frac{NkT}{V - Nb},$$

so that

$$p(V - Nb) = NkT$$

as required.

The physical interpretation of this is as an the equation of state for an ideal gas, but with a reduced volume available, because of the finite volume of the (otherwise noninteracting) particles.

(b) In order to find the virial coefficients we must expand p/kT in powers of N/V . Now

$$\frac{p}{kT} = \frac{N}{V - Nb}.$$

(Observe that the right hand side is independent of temperature, so we know that the virial coefficients will be temperature-independent before we start.)

We write p/kT as

$$\frac{p}{kT} = \frac{N}{V} \left(1 - b\frac{N}{V}\right)^{-1}$$

and this is then expanded as

$$\frac{p}{kT} = \frac{N}{V} \left(1 + b\frac{N}{V} + b^2 \left(\frac{N}{V}\right)^2 + b^3 \left(\frac{N}{V}\right)^3 + \dots\right).$$

From this we identify directly

$$B_2(T) = b, B_3(T) = b^2, B_4(T) = b^3, \text{ etc.}$$

The argument about excluded volume in obtaining the partition function for the hard sphere gas is an approximation. In reality imposing the boundary condition $|q_i - q_j| > \sigma$ for all i and j is more complex. However, by examining the structure of the configuration integral

$$Q_N = \frac{1}{V^N} \int e^{-(\sum_{i<j} U(q_i, q_j))/kT} d^{3N}q$$

we note that the exponent is independent of temperature since U/kT is either zero or infinite. Thus Q_N is independent of temperature and from this it follows that the virial coefficients will be temperature-independent. In other words, the virial coefficients for the hard sphere gas will be temperature-independent, irrespective of any approximations made.

[A full calculation of the virial coefficients of the hard sphere gas gives

$$B_2(T) = b, \quad B_3(T) = \frac{5}{8}b^2, \quad B_4(T) = 0.29b^3$$

where $b = 2\pi\sigma^3/3$.

So the precise values of the virial coefficients are not quite those predicted from the approximated Clausius equation of state.]

- 3.19 The one-dimensional analogue of the hard sphere gas is an assembly of rods constrained to move along a line (the Tonks model). For such a gas of N rods of length l confined to a line of length L , evaluate the

configuration integral Q . Show that in the thermodynamic limit the equation of state is

$$f(L - Nl) = NkT$$

where f is the force, the one dimensional analogue of pressure.

Comment on the similarities and the differences from the hard sphere equation of state mentioned in Problem 3.18 (Clausius equation) and the van der Waals equation of state.

In one dimension the configuration integral is given by

$$Q_N = \frac{1}{L^N} \int e^{-(\sum_{i < j} U(x_i, x_j)/kT)} dx_1 dx_2 \dots dx_N.$$

This may be simplified through the change of variables $X_i = x_i - x_{i-1}$. This gives

$$Q_N = \frac{1}{L^N} \int e^{-(\sum_i U(X_i)/kT)} dX_1 dX_2 \dots dX_N$$

with an appropriate choice of boundary conditions (cyclic boundary conditions). But in this form the integrals over the different variables are independent; the exponential, and thus the integral, can be factorized. And since the integral over each X will be the same, we obtain

$$Q_N = \left(\frac{1}{L} \int e^{-U(X)/kT} dX \right)^N.$$

When $X > l$ we have $U = 0$ so that the exponential is unity. And when $X < l$ then U is infinite so that the exponential is zero. So in this case the excluded volume argument holds true and

$$\int e^{-U(X)/kT} dX = L - Nl$$

so that

$$Q_N = \left(\frac{L - Nl}{L} \right)^N.$$

The partition function for the ideal one-dimensional gas is

$$Z_{\text{id}} = \frac{1}{N!} \left(\frac{L}{\Lambda} \right)^N.$$

Then using the calculated configuration integral the partition function is

$$Z = \frac{1}{N!} \left(\frac{L - Nl}{\Lambda} \right)^N.$$

The logarithm of Z is

$$\ln Z = N \ln(L - Nl) + \text{terms independent of } L.$$

The force in the one dimensional gas is given by

$$f = kT \left. \frac{\partial \ln Z}{\partial L} \right|_{T,N}$$

and thus we find

$$f = \frac{NkT}{L - Nl}$$

or

$$f(L - Nl) = NkT.$$

This is the 1d analogue of the Clausius equation of state for the hard sphere gas in 3d. However this is an exact equation of state; the Clausius equation is an approximation. The van der Waals equation is similar. But in that case the long-distance attractive interactions also are taken into account by modifying the pressure.

- 3.20 Estimate the van der Waals parameters a and b in terms of the Lennard-Jones parameters σ and ε .

In the van der Waals approach to the equation of state the repulsive and the attractive parts of the inter-particle interaction were treated separately. We will use this method to see how the two parameters of the van der Waals equation can be estimated in terms of the two parameters of the Lennard-Jones inter-particle interaction potential.

The repulsion is strong; particles are correlated when they are very close together. We accounted for this by saying that there is zero probability of two particles being closer together than σ . Then, as in the hard core discussion of Section 3.2.2, the region of co-ordinate space is excluded, and the form of the potential in the excluded region ($U(r)$ very large) does not enter the discussion. Thus just as in the discussion of the hard core model, the excluded volume will be

$$V_{\text{ex}} = \frac{2}{3} N \pi \sigma^3.$$

The attractive part of the potential is weak. Here there is very little correlation between the positions of the particles; we therefore treat their distribution as approximately uniform. The mean interaction for a single pair of particles $\langle E_p \rangle$ is then

$$\begin{aligned}\langle E_p \rangle &= \frac{1}{V} \int_{\sigma}^{\infty} 4\pi r^2 U(r) dr \\ &= \frac{1}{V} \int_{\sigma}^{\infty} 4\pi r^2 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right\} dr \\ &= -\frac{32\pi\sigma^3}{9V} \varepsilon.\end{aligned}$$

Now there are $N(N-1)/2$ pairs, each interacting through $U(r)$, so neglecting the 1, the total energy of interaction is $N^2 \langle E_p \rangle / 2$. This is shared among the N particles, so the mean energy per particle is

$$\begin{aligned}\langle E \rangle &= \langle E_p \rangle N/2 \\ &= -\frac{16\pi\sigma^3}{9} \frac{N}{V} \varepsilon.\end{aligned}$$

In the van der Waals equation it is the derivative of this quantity we require. Thus we find

$$N \frac{d\langle E \rangle}{dV} = \frac{16}{9} \pi \sigma^3 \left(\frac{N}{V} \right)^2 \varepsilon. \quad (3.7.3)$$

These results give the correct assumed N and V dependence of the parameters used in the previous section. So finally we approximate the van der Waals parameters a and b as

$$\begin{aligned}a &= \frac{16}{9} \pi \sigma^3 \varepsilon \\ b &= \frac{2}{3} \pi \sigma^3.\end{aligned}$$

- 3.21 Show that the leading term in the expansion of $g(n)$, of Eq. (3.6.8), is in n^2 i.e. show that there is no linear term.

The virial expansion is, Eq. (3.6.9),

$$\frac{p}{kT} = \frac{N}{V} + B_2 \left(\frac{N}{V}\right)^2 + B_3 \left(\frac{N}{V}\right)^3 + \dots$$

We may compare this with Eq. (3.6.8), which we write as

$$\frac{p}{kT} = \frac{N}{V} + g(N/V)$$

This shows that $g(N/V)$ is the series

$$g(N/V) = B_2 \left(\frac{N}{V}\right)^2 + B_3 \left(\frac{N}{V}\right)^3 + \dots$$

It follows that the leading term of $g(N/V)$ is in $(N/V)^2$, and that there is no linear term.

- 3.22 Evaluate the sum $\sum_{n=1}^{\infty} n(n+3)y^n$ required in the derivation of the Carnahan and Starling hard sphere equation of state, Eq. (3.6.18). Hint: you know the sum of the convergent geometric progression $\sum_{n=0}^{\infty} y^n = \frac{1}{1-y}$. The trick of differentiation with respect to y will “bring down” an n into the sum.

Let us denote

$$S_0 = \sum_{n=0}^{\infty} y^n = \frac{1}{1-y}$$

and denote

$$S_1 = \sum_{n=0}^{\infty} ny^n, \quad S_2 = \sum_{n=0}^{\infty} n^2y^n.$$

Then

$$\frac{dS_0}{dy} = \sum_{n=0}^{\infty} ny^{n-1} = \frac{1}{y} \sum_{n=0}^{\infty} ny^n = \frac{1}{y} S_1.$$

Also

$$\frac{d^2S_0}{dy^2} = \sum_{n=0}^{\infty} n(n-1)y^{n-2} = \frac{1}{y^2} \sum_{n=0}^{\infty} n(n-1)y^n = \frac{1}{y^2} S_2 - \frac{1}{y^2} S_1.$$

But

$$\frac{dS_0}{dy} = \frac{1}{(1-y)^2}, \quad \frac{d^2S_0}{dy^2} = \frac{2}{(1-y)^3}.$$

Then collecting our information:

$$S_1 = y \frac{dS_0}{dy} = \frac{y}{(1-y)^2}$$

$$S_2 = y^2 \frac{d^2S_0}{dy^2} + S_1 = \frac{2y^2}{(1-y)^3} + \frac{y}{(1-y)^2} = \frac{y(1+y)}{(1-y)^3}.$$

We require to evaluate

$$\sum_{n=1}^{\infty} n(n+3)y^n$$

where the sum goes from $n = 1$ to $n = \infty$. But the n factor in the sum means that we can take the sum from $n = 0$ to $n = \infty$ since the $n = 0$ term makes no contribution. So the required sum may be written

$$\sum_{n=1}^{\infty} n(n+3)y^n = S_2 + 3S_1.$$

Then from the S_1 and S_2 evaluated above, we find

$$\sum_{n=1}^{\infty} n(n+3)y^n = \frac{2y(2-y)}{(1-y)^3}$$

as stated in Eq. (3.6.18).

3.23 Eq. (3.6.26) gives the 3-2 Padé approximation to the hard sphere equation of state based on knowledge of the first six virial coefficients. Use *Mathematica* to expand this expression in powers of y .

- Show that the expansion is consistent with the first six reduced virial coefficients (Table 3.2).
- Compare the higher order terms with those given from the Carnahan and Starling equation of state and compare both with the values corresponding to the Clisby and McCoy virial coefficients.

Comment on whether (in your opinion) the 3-2 Padé or the Carnahan and Starling is the better equation of state.

We enter the polynomial of Eq. (3.6.26) into *Mathematica*

$$poly = \frac{1.27735y^3 + 2.45153y^2 + 1.81559y + 1}{1.18916y^2 - 2.18441y + 1}$$

and then ask it to perform a series expansion:

Series[poly, {y, 0, 10}]

whereupon it gives the output.

$$\begin{aligned} poly = & 1 + 4.y + 10.y^2 + 18.3648y^3 + 28.2247y^4 + 39.8156y^5 + 53.4099y^6 + \\ & + 69.3221y^7 + 87.9148y^8 + 109.607y^9 + 134.882y^{10} + O(y^{11}) \end{aligned}$$

(a) The first six reduced virial coefficients correspond to β_2 to β_6 of Table 3.2 and terms up to y^5 of the above series. The agreement of these coefficients is good, and they start to differ for higher terms.

(b) The Table below shows the true (calculated) virial coefficients with the Carnahan Starling values (Table 3.3), augmented with the coefficients calculated from the 3-2 Padé above.

	True value	C+S value	3-2 Padé
B_2/b	= 1	1	1
B_3/b^2	= 0.625	0.625	0.625
B_4/b^3	= 0.28694950	0.28125	0.28695
B_5/b^4	= 0.11025200	0.10937500	0.110253
B_6/b^5	= 0.03888198	0.03906250	0.0388824
B_7/b^6	= 0.01302354	0.01318359	0.0130395
B_8/b^7	= 0.00418320	0.00427246	0.00423108
B_9/b^8	= 0.00130940	0.00134277	0.00134147
B_{10}/b^9	= 0.00040350	0.00041199	0.00041812
B_{11}/b^{10}	= 0.00012300	0.00012398	0.00012863
B_{12}/b^{11}	= 0.00003700	0.00003672	0.00003917

Table 3.5: Carnahan and Starling's hard sphere virial coefficients