3.7 Problems for Chapter 3

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

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

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

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

3.4 For the van der Waals gas show that $T_\mathrm{B} = a/bk$ and $T_\mathrm{i} = 2a/bk$.

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

(a) Show that when $n \to \infty$ 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 $n \to \infty$.

(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.

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 $N/VT^{3/n}$.

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

$$T_{\mathrm{B}} = 3.418\,\varepsilon/k, \quad T_{\mathrm{i}} = 6.431\,\varepsilon/k.$$

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

(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

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

(c) The previous result corresponds to an *effective volume* $v_{\mathrm{eff}} = \frac{2}{3}\pi\sigma_{\mathrm{eff}}^3$ so that $v_{\mathrm{eff}} = \frac{2}{3}\pi\sqrt{2}(\varepsilon/kT)^{1/4}$. 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.

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

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

$$T_{\mathrm{B}} = 1.171\,\varepsilon/k, \quad T_{\mathrm{i}} = 2.251\,\varepsilon/k.$$

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.

Table 3.4: Second virial coefficient of xenon

T(K)	B_2(cm^3/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?

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.

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

$$kT_\mathrm{i} = \varepsilon \big/ \left\{ W\left[e/(1-R^{-3})\right] - 1 \right\}$$

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]`.)

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

$$kT_{\mathrm{B}} = -\varepsilon/\ln\left(1 - R^{-3}\right).$$
$$kT_{\mathrm{i}} = \varepsilon\Big/\left\{W\left[e/(1 - R^{-3}\right] - 1\right\}.$$

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

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

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?

3.17 In Section 3.1.1 we saw that the partition function for an interacting gas may be expressed as $Z = Z_{\mathrm{id}}Q$ 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

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

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.

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.

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

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.

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.

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.

(a) Show that the expansion is consistent with the first six reduced virial coefficients (Table 3.2).

(b) 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.