0. If you are rusty on series and limits M&S 3-22, C-3, C-4, and C-10 might be helpful, but I won’t collect or grade these exercises.)

- **M&S 3-22**: Evaluate \( S = \sum_{i=0}^{2} \sum_{j=0}^{1} i^j j^i \) by summing over \( j \) first then over \( i \). Now obtain the same result by writing \( S \) as a product of two separate summations.

\[
S = \sum_{i=0}^{2} \sum_{j=0}^{1} i^j j^i = \sum_{i=0}^{2} (x_0^0 + x_1^1) = (x_0 + x_1 + x_2) + (x_1 + x_2 + x_3) = x^0 + 2x^1 + 2x^2 + x^3
\]

Alternatively,

\[
S = \sum_{i=0}^{2} \sum_{j=0}^{1} i^j j^i = \sum_{i=0}^{2} \sum_{j=0}^{j} i^j = (x^0 + x^1 + x^2)(x^0 + x^1) = x^0 + 2x^1 + 2x^2 + x^3.
\]

- **M&S C-3**: Write out the expansion of \( f(x) = (1+x)^{1/2} \) through the quadratic term.

Using the Maclaurin expansion of this function about \( x=0 \) requires:

\[
(f)_{x=0} = (1+x)^{1/2} = 1
\]

\[
\left( \frac{df}{dx} \right)_{x=0} = \left( \frac{1}{2} (1+x)^{-1/2} \right)_{x=0} = \frac{1}{2}
\]

\[
\left( \frac{d^2f}{dx^2} \right)_{x=0} = \left( -\frac{1}{2} \cdot \frac{1}{2} (1+x)^{-3/2} \right)_{x=0} = -\frac{1}{4}
\]

so

\[
f(x) = 1 + \frac{1}{2} x - \frac{1}{8} x^2 + ...
\]

- **M&S C-4**: Evaluate the series \( S = \sum_{n=0}^{\infty} \exp\left\{ -\left( n + \frac{1}{2} \right) \beta \nu \right\} \)

Letting \( x = e^{-\beta \nu} \) this series can be expressed: \( S = x^{1/2} \sum_{n=0}^{\infty} x^n = \frac{x^{1/2}}{1-x} \)

Reinstating \( e^{-\beta \nu} = x \) one obtains the final result:
\[ S = \frac{e^{-\beta h/2}}{1 - e^{-\beta h}} \]

- **M&S C-10**: Evaluate the limit of \( f(x) = \frac{e^{-x} \sin^2 x}{x^2} \) as \( x \to 0 \).

Expanding each factor in a Maclaurin series:

\[
f(x) = \frac{1}{x^2} \left( 1 - x + \frac{1}{2} x^2 + \ldots \right) \left( x - \frac{1}{6} x^3 + \ldots \right)^2
\]

\[
= \frac{1}{x^2} \left( 1 - x + \frac{1}{2} x^2 + \ldots \right) \left( x^2 - \frac{1}{3} x^4 + \ldots \right)
\]

Multiplying these out one finds the lowest order in \( x \) to be

\[ f(x) = \frac{1}{x^2} (1)(x^2) + \ldots \]

so \( f(x) \to 1 \) as \( x \to 0 \).

---

1. **M&S 3-16**: Show that if a partition function is of the form \( Q(N, V, T) = \frac{[q(V, T)]^N}{N!} \) and if \( q(V, T) = f(T)V \), then the ideal-gas equation of state results.

The relation between pressure and \( Q \) is:

\[
P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T}
\]

For \( Q \) of the form specified above \( \ln Q = N \ln q - \ln N! = N \{ \ln f(T) + \ln V \} - \ln N! \) or \( \ln Q = N \ln V + \) (terms independent of \( V \)). Therefore

\[
P = k_B T \frac{\partial}{\partial V} (N \ln V) = \frac{Nk_B T}{V}.
\]
2. A toy model for a dimerization equilibrium is to consider two identical particles confined to the sites of a 1d lattice of M cells of volume $v_{cell}$. At most one particle can occupy any given cell. Assume that there are only two energy levels for this system: a ground state with energy $\varepsilon_0 = 0$, which pertains if the two particles share adjacent sites (i.e. form a dimer), and an excited state with $\varepsilon_1 = \varepsilon$ when they do not ($\varepsilon > 0$).

(a) What is the canonical partition function $Q_2(M, \beta) \equiv Q(N = 2, V = Mv_{cell}, \beta)$ for such a system?

(b) What are the probabilities of finding the particles in dimer, $p_{dimer}$, and monomer states, $p_{monomer}$?

(c) Derive expressions for the energy, heat capacity, and pressure for this system.

(d) Plot the dimer probability, energy, heat capacity, and pressure as a function of temperature for a system having $M = 5$ cells. In order to display the temperature dependence of this model in a general way, work with the dimensionless quantities:

$$U = \frac{U}{\varepsilon}, \quad C_V = \frac{C_V}{k_B} \quad \text{and} \quad P = \frac{v_{cell}^M}{k_BT} P$$

Rewrite your expressions for energy, heat capacity, and pressure in this dimensionless form as functions of the scaled (inverse) temperature variable $x$ and plot $p_{dimer}(x)$, $U(x)$, $C_V(x)$, and $P(x)$.

(e) Discuss (and attempt to rationalize) the behavior of the model in the limits $k_BT/\varepsilon << 1$ and $k_BT/\varepsilon >> 1$.

[Hint: The number of ways that N indistinguishable objects can be placed in M distinguishable locations is given by

$$W(N, M) = \frac{M!}{N!(M-N)!}$$

(a) In general, the canonical partition function can be written as a sum over energy levels:

$$Q(N, V, \beta) = \sum_{\text{energy levels } i} g_i \exp(-\beta \varepsilon_i)$$

with energies $\varepsilon_i$ and degeneracies $g_i$. The system described above has only two energy levels characterized by:

ground level (dimer): $\varepsilon_0 = 0 \quad g_0 = M - 1$ (2-2a)

excited level (monomers): $\varepsilon_1 = \varepsilon \quad g_1 = \frac{1}{2} (M-2)(M-1)$ (2-2b)

I derived these degeneracies using the following argument. The number of adjacent positions that can be occupied by a pair of particles in a system of M cells is M-1, so $g_0 = M-1$. The total number of ways of arranging 2 identical particles in the M cells is:
The degeneracy of the excited level is just

\[ g_1 = W(2, M) - g_0 = \frac{1}{2}M(M - 1) - (M - 1) = \frac{1}{2}(M - 2)(M - 1) \]

The partition function is then:

\[ Q_2(M, \beta) = (M - 1)\{1 + \frac{1}{2}(M - 2)\exp(-\beta\epsilon)\} \]  

(I’ve replaced \( V \) with \( M \) as the argument of \( Q \) in recognition of the fact that here \( V = Mv_{\text{cell}} \) and written \( Q_2(M, \beta) \equiv Q(N = 2, M, \beta) \) to denote that \( N \) is not variable in this system, i.e. that our expressions are specific for a system of 2 particles.

(b) The probability of finding the system in any level \( i \) is \( p_i = g_i\exp(-\beta\epsilon_i)/Q \). For the “dimer” level in this problem the probability is:

\[ p_{\text{dimer}} = \frac{2}{2 + (M - 2)\exp(-\beta\epsilon)} \]  

(2-4a)

and for monomer states:

\[ p_{\text{monomer}} = \frac{(M - 2)\exp(-\beta\epsilon)}{2 + (M - 2)\exp(-\beta\epsilon)} \]  

(2-4b)

(c) The general relations between the thermodynamic (average) quantities of interest and \( Q \) can be written:

\[ U = \langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N, V} = -\left(\frac{\partial \ln Q_2}{\partial \beta}\right)_M \]  

(2-5)

\[ C_V = \left(\frac{\partial U}{\partial T}\right)_{N, V} \quad \text{or} \quad C_V/k_B = \beta^2\left(\frac{\partial^2 \ln Q}{\partial \beta^2}\right)_{N, V} = \beta^2\left(\frac{\partial^2 \ln Q_2}{\partial \beta^2}\right)_M \]  

(2-6)

\[ P = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N, \beta} = k_B T \left(\frac{\partial \ln Q_2}{\partial M}\right)_{\beta} \]  

(2-7)

In the last member of each of these expressions, I’ve specialized to the case at hand without actually evaluating the expression. Now inserting \( Q_2(M, \beta) \) and performing the differentiations:
\[ U = -\left( \frac{\partial \ln Q_z}{\partial \beta} \right)_M \]
\[ = -\frac{1}{Q_z} \left( \frac{\partial Q_z}{\partial \beta} \right)_M \]
\[ = -\frac{1}{Q_z} \{ \frac{1}{2} (M-1)(M-2)(-\varepsilon) \exp(-\beta \varepsilon) \} \]
\[ = \frac{1}{2} (M-2) \exp(-\beta \varepsilon) \varepsilon \]
\[ 1 + \frac{1}{2} (M-2) \exp(-\beta \varepsilon) \]

or
\[ U = \frac{(M-2) \exp(-\beta \varepsilon) \varepsilon}{2 + (M-2) \exp(-\beta \varepsilon)} = p_{\text{mon}} \varepsilon \]

(2-8)

In the rightmost part of Eq. 2-8 I’ve noted that, because we’ve defined the dimer energy to be zero, the average energy is simply the probability of the system being in a monomer state times the monomer energy \( \varepsilon \).

To evaluate the heat capacity, it seemed easiest to use the 1st member of Eq. (2-6) and differentiate Eq. (2-8):

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_M = -k_B \beta^2 \left( \frac{\partial U}{\partial \beta} \right)_M \]
\[ = -k_B \beta^2 \left( \frac{1}{2} \frac{(M-2) \exp(-\beta \varepsilon) \varepsilon}{1 + \frac{1}{2} (M-2) \exp(-\beta \varepsilon)} \right)_M \]
\[ = -k_B \beta^2 \left( \frac{-\frac{1}{2} (M-2) \exp(-\beta \varepsilon) \varepsilon^2}{1 + \frac{1}{2} (M-2) \exp(-\beta \varepsilon)} - \frac{1}{[1 + \frac{1}{2} (M-2) \exp(-\beta \varepsilon)]^2} \right) \]
\[ = \frac{k_B \beta^2 \varepsilon^2 [\frac{1}{2} (M-2) \exp(-\beta \varepsilon)]}{[1 + \frac{1}{2} (M-2) \exp(-\beta \varepsilon)]^2} \left( 1 + \frac{1}{2} (M-2) \exp(-\beta \varepsilon) - \frac{1}{[1 + \frac{1}{2} (M-2) \exp(-\beta \varepsilon)]^2} \right) \]

or
\[ C_v / k_B = \frac{\beta^2 \varepsilon^2 [(M-2) \exp(-\beta \varepsilon)]}{[2 + (M-2) \exp(-\beta \varepsilon)]^2} \]

(2-9)

The pressure is a bit simpler,
\[ P = \frac{k_B T}{v_{\text{cell}}} \left( \frac{\partial \ln Q_2}{\partial M} \right) \beta 
\]
\[ = k_B T \frac{1}{Q_2} \frac{1}{\partial M} \left[ (M-1) + \frac{1}{2} (M-1)(M-2) \exp(-\beta \epsilon) \right] \beta 
\]
\[ = k_B T \frac{1}{Q_2} \left[ 1 + \frac{1}{2} (2M-3) \exp(-\beta \epsilon) \right] \]

or

\[ P = \frac{k_B T}{v_{\text{cell}} (M-1)} \frac{2 + (2M-3) \exp(-\beta \epsilon)}{[2 + (M-2) \exp(-\beta \epsilon)]} \quad (2-10) \]

It is interesting to note that this expression for the pressure can be written in terms of dimer and monomer probabilities (Eq. 2-4) as

\[ P = \frac{k_B T}{v_{\text{cell}} (M-1)} \left( P_{\text{dimer}} + \frac{2M-3}{2(M-2)} 2P_{\text{monomer}} \right) \quad (2-11) \]

In the limit of large \( M \)

\[ P \rightarrow \frac{k_B T}{V} \left( P_{\text{dimer}} + 2P_{\text{monomer}} \right) = \frac{k_B T}{V} N_{\text{ind}} \quad (2-12) \]

where \( N_{\text{ind}} \) is the number of “independent” particles in the system (1 when the system is in a dimer state and 2 when the system is in a monomer state). Thus, this system in the dilute limit follows an ideal-gas law as long as one counts particles in this manner.

(d) In reduced form, the dimer and monomer probabilities, and thermodynamic quantities can be expressed:

\[ P_{\text{dimer}}(x) = \frac{2}{2 + (M-2)e^{-x}} \quad \quad \quad \quad \quad \quad P_{\text{monomer}}(x) = 1 - P_{\text{dimer}}(x) = \frac{(M-2)e^{-x}}{2 + (M-2)e^{-x}} \quad (2-13) \]

\[ \tilde{U}(x) = \frac{(M-2)e^{-x}}{2 + (M-2)e^{-x}} = P_{\text{monomer}}(x) \quad (2-14) \]

\[ \tilde{C}_V(x) = \frac{x^2 (M-2)e^{-x}}{[2 + (M-2)e^{-x}]^2} \quad (2-15) \]

\[ Z(x) = \frac{M}{2(M-1)} \frac{2 + (2M-3)e^{-x}}{[2 + (M-2)e^{-x}]} \quad (2-16) \]

I evaluated these functions using an Excel worksheet. Plots of these functions, in both logarithmic and linear \( x \) representations, are shown on the following page.
Fig. 2-1: Dimer and Monomer Probs.

Probability

\( x = \frac{\varepsilon}{k_B T} \)

\[ \begin{array}{c|c|c|c|c|c|c}
\hline
\text{Probability} & 0.0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
\hline
\text{dimer} & 0.1 & 0.2 & 0.3 & 0.4 & 0.5 & 0.6 \\
\text{monomer} & 0.9 & 0.8 & 0.7 & 0.6 & 0.5 & 0.4 \\
\hline
\end{array} \]

Fig. 2-2: Thermodynamic Functions

Heat Capacity

Energy

Pressure

\[ \frac{U}{\varepsilon}, \frac{C_V}{k_B} \]

\[ \begin{array}{c|c|c|c|c|c|c}
\hline
\text{Pressure} & 0.0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
\text{Z} & 0.5 & 0.6 & 0.7 & 0.8 & 0.9 & 1.0 \\
\hline
\end{array} \]
(e) In the low temperature limit \( k_B T \ll \varepsilon \) or \( x \ll 1 \):

\[
e^{-x} \rightarrow 0
\]

\[
Q \rightarrow (M - 1) = 9
\]

\[
p_{\text{dimer}} \rightarrow 1 \quad p_{\text{monomer}} \rightarrow 0
\]

\[
\frac{U}{\varepsilon} = p_{\text{monomer}} \rightarrow 0
\]

\[
C_v \rightarrow 0
\]

\[
\frac{PV}{Nk_B T} \rightarrow \frac{M}{2(M - 1)} = 0.5
\]

In this limit only dimer states are populated. The energy is zero (because we defined the dimer energy to be zero) and the pressure is approximately that of an ideal gas of dimers. The heat capacity is zero because monomer states are “inaccessible”.

In the high-temperature limit \( k_B T \gg \varepsilon \) or \( x \gg 1 \):

\[
e^{-x} \rightarrow 1
\]

\[
Q \rightarrow \frac{1}{2} M (M - 1) = W(2, M) = 45
\]

\[
p_{\text{dimer}} \rightarrow \frac{M - 1}{W(2, M)} = \frac{2}{2 + (M - 2)} = 0.2 \quad p_{\text{monomer}} \rightarrow 0.8
\]

\[
\frac{U}{\varepsilon} = p_{\text{monomer}} \rightarrow \frac{(M - 2)}{2 + (M - 2)} = 0.8
\]

\[
C_v \rightarrow 0
\]

\[
\frac{PV}{Nk_B T} \rightarrow \frac{M}{2(M - 1)} \left( \frac{2 + (2M - 3)}{2 + (M - 2)} \right) = 1.05
\]

In this limit all states are equally likely. The pressure is approximately that of an ideal gas of monomers. The heat capacity is again zero because energy cannot be added to the system in thermal equilibrium (once the states are completely randomized energy addition causes a population inversion, which is a non-thermal situation).
3. M&S 3-11, 3-14+: The partition function for a monatomic van der Waals gas is

$$Q(N, V, T) = \frac{1}{N!} \left( \frac{2\pi m k_B T}{h^2} \right)^{3N/2} \left( V - Nb \right)^N \exp \left( \frac{aN^2}{Vk_B T} \right)$$

where $a$ and $b$ are the van der Waals constants.

(a) Derive an expression for the energy of a monatomic van der Waals gas.

(b) Calculate the heat capacity of a monatomic van der Waals gas and compare your result with that of a monatomic ideal gas.

(c) Show that the pressure derived from this partition function provides the proper mechanical equation of state for the van der Waals fluid.

(a) Use the expression for the relation between $U$ and $Q$,

$$U = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$\ln Q$ can be written:

$$\ln Q = \ln N! + \frac{3}{2} N \ln \left( \frac{2\pi m k_B T}{h^2} \right) + N \ln(V - Nb) + \frac{aN^2}{Vk_B T}$$

$$= \ln N! + \frac{3}{2} N \ln \left( \frac{2\pi m k_B}{h^2} \right) + \frac{3}{2} N \ln T + N \ln(V - Nb) + \frac{aN^2}{Vk_B T}$$

$$= \frac{3}{2} N \ln T + \frac{aN^2}{Vk_B T} + \text{(terms independent of } T)$$

Thus

$$U = k_B T^2 \frac{\partial}{\partial T} \left( \frac{3}{2} N \ln(T) + \frac{aN^2}{Vk_B T} \right) = k_B T^2 \left( \frac{3N}{2T} - \frac{aN^2}{Vk_B T^2} \right)$$

or

$$U = \frac{3}{2} N k_B T - \frac{aN^2}{V}$$

The first term in this expression is energy of the monatomic ideal gas. The second term describes the effect of attractive interactions present in the vdw fluid.

(b) The heat capacity is simply

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N} = \frac{3}{2} N k_B$$

The constant volume heat capacity of the van der Waals fluid is identical to that of the ideal gas. This identity may seem puzzling, given the fact that molecules of a van der Waals fluid do
interact. It occurs because in this model the attractive interactions are not a function of temperature at constant volume and they therefore have no effect on \( C_V \). The constant pressure heat capacity, \( C_P \), would, however, differ from that of an ideal gas. The infinitely hard repulsive interactions in the vdW fluid do not affect \( U \), \( C_V \), or \( C_P \) because at any finite temperature, configurations in which molecules overlap have zero probability and do not contribute directly to the average properties.

(c) Pressure is calculated from: 

\[
P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T}
\]

Writing \( \ln Q = N \ln(V - Nb) + (aN^2/Vk_BT) + \text{(terms independent of } V) \), this derivative is easily evaluated:

\[
P = k_B T \frac{\partial}{\partial V} \left[ N \ln(V - Nb) + \frac{aN^2}{Vk_BT} \right] = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2}
\]

If one chooses \( N = N_A \) for the number of molecules, this expression can be written in terms of molar quantities as:

\[
P = \frac{RT}{V-b'} - \frac{a'}{V^2}
\]

where \( b' = N_A b \) and \( a' = N_A^2 a \). Thus, one does obtain the vdW equation of state from this partition function, as expected.