1. Isobaric ensemble.
Consider the following Laplace transformation of the canonical partition function:

\[ Y(T,p,N) = \frac{1}{\Lambda^3} \int_0^\infty dV \exp(-\beta p V) Z(T,V,N) \]

Write the isobaric partition function as

\[ Y(T,p,N) = \frac{1}{\Lambda^3} \int_0^\infty dV \exp(-\beta p V - \beta F(T,V,N)) \]

Show that this can be approximated by expanding about the maximum of the argument of the exponential to quadratic order. Show that logarithm of the isobaric partition function is proportional to the Gibbs free energy

\[ G = F + pV \]

Show that extra logarithmic terms are unimportant in the thermodynamic limit \( N \rightarrow \infty \). Show that

\[ G = N\mu(T,p) \]

Evaluate the isobaric partition function in closed form for the classical monatomic ideal gas with

\[ Z(T,V,N) = \frac{V^N}{N! \Lambda^N(T)} \]

Show that you obtain the correct ideal gas equation of state. Show the chemical potential \( \mu \)

is related to the density by

\[ n = \frac{e^\mu}{\Lambda^3} \]

Show the gas is classical if the chemical potential is sufficiently negative and the gas approaches the quantum limit as the chemical potential approaches zero from below. Wave your hands to explain why the chemical potential should be negative for an ideal gas.

2. The classical Hamiltonian for a chain of \( N \) particles of mass \( m \) connected in one dimension along a line with \( N \) harmonic springs is

\[ H = \sum_{j=1}^N \frac{p_j^2}{2m} + \frac{1}{2} m \omega_0^2 \sum_{j=1}^N (x_j - x_{j-1} - a)^2 \]

where \( a \) is the equilibrium length of each spring and \( k = m \omega_0^2 \) is the spring constant of each spring.

\[ \begin{pmatrix} x_1 & x_2 & x_3 & x_4 & x_5 & x_6 \end{pmatrix} \]

a) Show that the \( N \)-particle partition function

\[ Z_N = \frac{1}{\hbar^N} \int d^N p \int d^N x \exp(-\beta H) \]

can be partially factorized

\[ Z_N = \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{N/2} Q_N \]

Note, no \( N! \) factor is needed for indistinguishability since the particles cannot change places.

Show the configurational partition function can be written as follows:

\[ Q_N = \int d^N x \exp \left( -\frac{1}{2} \beta m \omega_0^2 \sum_{j=1}^N (x_j - x_{j-1} - a)^2 \right) = \int d^N u \exp \left( -\frac{1}{2} \beta m \omega_0^2 \sum_{j=1}^N (u_j - u_{j-1})^2 \right) \]
where \( x_j = ja + u_j \). The quantity \( u_j \) represents the deviation from the \( T=0 \) mechanical equilibrium position of mass \( j \) at position \( ja \).

b) Show that the \( N \) configurational integrals can be evaluated by starting at the \( N \)th integral and working your way back, i.e.

\[
Q_N = \left( \frac{2\pi k_B T}{m\omega_0^2} \right)^{\frac{1}{2}} Q_{N-1}
\]

Use this to show that the \( N \)-particle partition function can be written

\[
Z_N = \left( \frac{k_B T}{\hbar\omega_0} \right)^N.
\]

Determine the free energy. Interpret the internal energy and heat capacity in terms of the number of quadratic degrees of freedom.

c) Show that even at non-zero temperature the average position of each mass is the same as the \( T=0 \) mechanical equilibrium position, i.e. show \( \langle u_j \rangle = 0 \) for all \( j=1,\ldots,N \).

d) Calculate the variance of the position of the first mass \( \langle u_1^2 \rangle \) using an argument similar to the partition function calculation, i.e. show all integrals in numerator and denominator of the average cancel except for the integral involving \( u_1 \).

Next show that the variances along the chain are related by

\[
\langle u_j^2 \rangle = \left( \frac{k_B T}{m\omega_0^2} \right) + \langle u_{j-1}^2 \rangle.
\]

Describe the implications for this for deviation of the \( j \)th particle from its equilibrium position. Mass and spring models are often invoked to describe solids. Does this model display the properties you would ascribe to a solid?

3. The rotational kinetic energy of a diatomic molecule is given by

\[
H_{\text{rotation}} = \frac{1}{2} I 
\]

where \( L \) is the angular momentum operator and

\[
I = \mu a^2
\]

is the moment of inertia. The rotational kinetic energy eigenvalues and degeneracies are

\[
\varepsilon_i = \frac{\hbar^2}{2I} (l + 1) \quad \text{and} \quad g_i = 2l + 1 \quad \text{so the rotational partition function is}
\]

\[
Z_{\text{rotation}} = \sum_{l=0}^{\infty} (2l + 1) \exp \left( -\frac{\beta \hbar^2 l(l+1)}{2I} \right) = \sum_{l=0}^{\infty} (2l + 1) \exp \left( -\beta \varepsilon_i (l + 1) \right).
\]

The sum cannot be done in closed form.

a) Derive approximations that work in the low temperature limit and the high temperature limit. Write the rotational contributions to the internal energy and heat capacity in terms of sums over the rotation eigenvalues. Numerically evaluate and plot \( \frac{U}{N\varepsilon} \) and \( \frac{C}{Nk_B} \) as functions of \( \frac{k_B T}{\varepsilon} \). Explain the low temperature and the high temperature behaviors and show the results agree with your low temperature approximations.

b) Evaluate the crossover temperature scale \( \frac{\varepsilon}{k_B} \) for the case for hydrogen gas \( H_2 \). Since hydrogen atoms are identical, the molecule has special quantum symmetries that depend on the total nuclear spin. The nuclear spins interact very weakly so hydrogen gas can be analyzed as a mixture of two components: ortho-hydrogen with total nuclear spin 1 and para-hydrogen with total nuclear spin 0. The two partition functions are
\[ Z_{\text{para}} = \sum_{l=\text{even}}^{\infty} (2l + 1) \exp\left( \frac{-\beta \hbar^2 l (l + 1)}{2l} \right) = \sum_{l=\text{even}}^{\infty} (2l + 1) \exp(-\beta \epsilon_l (l + 1)) \]

and

\[ Z_{\text{ortho}} = 3 \sum_{l=\text{odd}}^{\infty} (2l + 1) \exp\left( \frac{-\beta \hbar^2 l (l + 1)}{2l} \right) = \sum_{l=\text{odd}}^{\infty} (2l + 1) \exp(-\beta \epsilon_l (l + 1)) \]

Numerically evaluate and plot \( \frac{U}{N\epsilon} \) and \( \frac{C}{Nk_B} \) as functions of \( \frac{k_B T}{\epsilon} \) for each species.

4. Consider the following grand partition function.

\[ \Xi(T, V, \mu) = \left( 1 + z^{\frac{V}{\Lambda^3}} \right)^{\frac{V}{\epsilon}} \left( 1 + z^{\frac{\alpha V}{\Lambda^3}} \right) \]

where \( z = e^{\beta \mu} \), \( \Lambda \) is the thermal DeBroglie wavelength, \( V \) is the sample volume and \( \alpha \) is a dimensionless positive constant. Show that in the low density limit the pressure reduces to the ideal gas equation of state. Show that a first-order phase transition occurs as the pressure increases. Show the pressure is the same in both phases at the transition but the density is discontinuous across the transition. Determine the density change and the latent heat of the transition. Show that transition pressure as a function of temperature obeys the Clausius-Clapyron equation.