1) We have used quantum mechanical expressions for the translational, rotational, and vibrational energy to calculate the partition function. The translational partition function can be and was calculated classically. The expression for the classical partition function for one dimensional translation within a box of length a is:

\[ q_{trans} = \frac{1}{c} \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} e^{-E(p)/k_BT} dp \]

where \( E(p) = \frac{p^2}{2m} \), p=mv is the momentum, and c is a constant.

a) Perform the integrals and evaluate the classical partition function for one dimensional translation.

b) Compare the expression in part a to the expression that was obtained in the lecture and in the text using the quantum mechanical particle in the box model for translation. Based on this comparison, determine the constant c.

c) Discuss the physical meaning of the constant c. Hint: Statistical argument require a countable number of states.

2) It is common to tabulate the ratios \( \Theta_v = \frac{h}{k_B} \) and \( \Theta_R = \frac{\hbar^2}{2I_k_B} \) so that the single particle partition functions for vibration and rotation can be written as:

\[ q_{rot} = \sum_{J=0}^{\infty} (2J + 1)e^{-\Theta_R J / T} \] \[ q_{vib} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\Theta_v / T} \]

a) Show that the vibrational contribution to the energy is

\[ U_{vib} = Nk_B \left( \frac{\Theta_v}{2} + \frac{\Theta_v}{e^{\Theta_v / T} - 1} \right) \]

Hint: Recall that \( q_{vib} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\Theta_v / T} = e^{-\Theta_v / 2T} \sum_{n=0}^{\infty} e^{-n\Theta_v / T} = \frac{e^{-\Theta_v / 2T}}{1 - e^{-\Theta_v / T}} = e^{-\Theta_v / 2T} \left( 1 - e^{-\Theta_v / T} \right)^{-1} \)

Then use \( U_{vib} = Nk_B T^2 \frac{\partial \ln q_{vib}}{\partial T} = \frac{Nk_B T^2}{q_{vib}} \frac{\partial q_{vib}}{\partial T} \) and remember the chain rule for differentiation...

b) Show that the vibrational heat capacity is
\[ C_v = N k_B \left( \frac{\Theta_v}{T} \right)^2 \frac{e^{\Theta_v/T}}{\left( e^{\Theta_v/T} - 1 \right)^2} \]

c) For H\(^2\) \(\Theta_v = 6215 K\) and for I\(^2\) \(\Theta_v = 310 K\). Calculate the vibrational energies and heat capacities for H\(^2\) and I\(^2\) and 300K and 1000K. How well do these numbers agree with the predictions of the equipartition principle?

d) For H\(^2\) and I\(^2\) at 300K and 1000K, calculate the fraction of molecules not in the ground vibrational state.
   Hint: Calculate the fraction in the ground state, and from this number deduce the fraction not in the ground state.

3) Consider the dimerization of sodium vapor:
\[ 2Na(g) \rightleftharpoons Na_2(g) \]
For Na\(_2\) \(\Theta_v = 229 K, \Theta_r = 0.221 K, \varepsilon_D = 72.3 kJ/mol\).

   a) Calculate the translational partition functions \(q_{trans}\) for Na and Na\(_2\) at T=1000K
   Hint: See example 23.2

   b) Calculate the rotational and vibrational partition functions for Na\(_2\) at T=1000K.
   State any assumptions you make and justify them.
   Hint: See examples 23.5 and 23.7

   c) Calculate the total partition functions for Na and Na\(_2\) at T=1000K. Assume the ground electronic state for Na is doubly degenerate i.e. \(g_{0,Na} = 2\), and \(g_{0,Na_2} = 1\)
   and assume only the ground electronic states are populated.
   Hint: see equation 23.59 and example 23.16

   d) Calculate the equilibrium constant for the dimerization of sodium vapor at T=1000K. Assume the volume \(V=1 m^3\). In your calculation treat the equilibrium constant as a ratio of number densities \(N/V\).
   Hint: see example 23.16

4) Use the Sackur-Tetrode equation to:
   a) Calculate the entropy of one mole of argon gas at a temperature of 300K and a pressure of 1 atm. Assume argon behaves ideally.

   b) Using the Sackur-Tetrode equation, calculate the entropy change \(\Delta S\) when one mole of argon changes its temperature from 300K to 1000K. Assume the volume remains constant and that argon behaves ideally.

   c) Using the Sackur-Tetrode equation, calculate the entropy change \(\Delta S\) when one mole of argon changes its volume from 1m\(^3\) to 10m\(^3\). Assume the temperature remains constant.