ME-351 THERMODYNAMICS AND ENERGETICS II

SPRING 2025

QUESTION 1

The partition function of a monoatomic ideal gas held at constant temperature (T), number of atoms (N) and volume (V) is given by:

$$\mathcal{Z}(N,V,T) = \frac{q^N}{N!}$$

$$q = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V$$

where m is the mass of single atom, k_B is Boltzmann's constant, and h is Planck's constant.

1. List the state variables of the gas that are allowed to fluctuate in this ensemble.
2. Derive an analytical expression for the free energy of the ideal gas. The free energy should be expressed in terms of the variables on the right hand side of the above equations.
3. Is your expression for the free energy of the ideal gas extensive?
4. Derive analytical expressions for $\langle E\rangle$,$\langle p\rangle$,$\langle S\rangle$,and $\langle\mu\rangle$

QUESTION 2

Consider the adiabatic expansion of an ideal gas from V to $2V$

1. What are the variables that are being controlled and allowed to fluctuate in the ensemble you would use to study the expansion of the gas?
2. Express the second law of thermodynamics in this ensemble.
3. Use statistical mechanics to verify the second law of thermodynamics.

You can assume that the number of microstates that are available to the ideal gas in this ensemble (Ω) is proportional to V^N, where V is the volume of the gas and N is the number of atoms in the gas.

QUESTION 3

A system that is subject to boundary conditions of constant temperature (T), number of atoms (N) and volume (V) has several microstates (denoted ν), each with an energy of E_ν. The energy levels are ordered from lowest to highest, i.e. $E_0 < E_1 < \cdots$. Each microstate has a degeneracy given by $\Omega(E_\nu)$. Calculate the entropy of this system at 0K. You can assume that degeneracy of the ground state energy ($\Omega(E_0)$) is proportional to N. Compare the entropy you calculated with the entropy as expected from the third law of thermodynamics.

QUESTION 4

Polymers are substances that consist of repeating subunits called *monomers*. Consider a one-dimensional polymer chain with M monomers. Each monomer can exist in two states. The lowest energy state has energy ϵ_0 while the higher energy state has energy ϵ_1. The polymer chain is held at fixed temperature (T), and number of monomer units (M).

1. Derive an analytical expression for the partition function of this system:
   (a) Write down the expression for the partition function as a sum over microstates. What are the microstates that are accessible to the system?
   (b) In a particular microstate ν, assume that the number of monomers that are in the excited state is denoted n. What is the energy of this microstate? How many microstates are there with this energy?
   (c) Use insights from the previous question to rewrite the mathematical expression for the partition function (denoted $\mathcal{Z}$) and show that:
   $$\mathcal{Z} = \left(\exp\left(-\beta\epsilon_0\right) + \exp\left(-\beta\epsilon_1\right)\right)^M$$
2. What is the probability of sampling a microstate with N excited monomers?