Problem set 2

Due October 27, 2026

1. Given the probability-based formula for entropy learned in today's lecture

$$S = -k_B \sum_{i=1}^{Z} P_i \ln P_i$$

where P_i is the Boltzmann probability of the unique microstate i (non-degenerate, occupancy 1),

   (a) Demonstrate that if all microstates have the same energy the entropy reaches maximum when the microstates have the same probability (are uniformly distributed).

   Hint: Apply the Lagrange multiplier method constraining the sum of probabilities to 1.

   (b) Express the entropy in terms of a sum over degenerate states (indexed with uppercase letters), state I having degeneracy g_I and probability P_I. Demonstrate that the entropy reaches maximum when the probability of each degenerate state is proportional to its degeneracy.

2. For a two-state system with ground and excited state labelled '0' and 'e', degeneracies g_0 and g_e, respectively, and the energy difference $E_e - E_0 = \varepsilon$,

   (a) Derive the formulas for the populations of the ground and the excited states, express them in terms of reduced temperature $T^* = k_B T/\varepsilon$ and draw the populations for $g_e = 100 g_0$.

   (b) Derive the formula for the average energy and the heat capacity of the system either by differentiation or by direct calculation of the mean energy and energy variance, respectively.

   (c) Demonstrate that the energy expressed in the units of ε, $E^* = E/\varepsilon$, and the heat capacity expressed in Boltzmann constant units, $C_V^* = C_V/k_B$, depend only on the reduced temperature and the ratio of the degeneracy of the excited to the ground state, g_e/g_0.

(d) Plot E^* and C_V^* in T^* and comment on the dependence of these quantities on the reduced temperature for $g_e/g_0 = 100$. Show both plots in one graph to facilitate the analysis.

3. The partition function of a monoatomic gas at a low pressure (so that intermolecular interactions do not need to be considered), consisting of N atoms, with volume V and absolute temperature T (a canonical ensemble) in the classical limit is expressed as given below

$$Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3N}{2}} \left(\frac{Ve}{N}\right)^N$$

where m is the mass of a gas molecule, k_B is the Boltzmann constant, h is the Planck constant, and $e = 2.718\ldots$ is the Euler number.

(a) Derive the formulas for (i) the energy, (ii) heat capacity at constant volume and (iii) the pressure of the gas.

Hint: Obtain a formula for $\ln Q$, then use the formulas for the logarithms of a product, a quotient, and an exponential expression to separate the respective terms of $\ln Q$ that depend only on one variable of state. Then use the formulas learned in today's lecture to compute the respective derivatives of $\ln Q$.

(b) Compare formula (i) with that for the average energy of an ideal gas from the kinetic theory of monoatomic gases.

(c) Based on formula (iii) derive the equation of state (the Clapeyron equation) of an ideal gas.