PHYS 301: Thermodynamics and Statistical Mechanics
Solutions to Problem Set #6

February 25, 2026

Question 1: Deriving Ensembles from the Maximum Entropy Principle

We want to find the probability distribution $p(n)$ that maximizes the Gibbs entropy:

$$S = -k_B \sum_n p(n) \ln p(n) \tag{1}$$

subject to different macroscopic constraints. To do this, we use the method of Lagrange multipliers.

(a) The Microcanonical Ensemble

Constraint: The system is restricted to a set of accessible states, all of which have the same fixed energy E. The only constraint on the probabilities over these accessible states is the normalization condition:

$$\sum_n p(n) = 1 \implies \sum_n p(n) - 1 = 0 \tag{2}$$

Maximization: We construct the Lagrangian function $\mathcal{L}$ by subtracting the constraint (multiplied by a Lagrange multiplier α) from the entropy (divided by k_B for convenience):

$$\mathcal{L} = -\sum_n p(n) \ln p(n) - \alpha \left(\sum_n p(n) - 1 \right) \tag{3}$$

To maximize the entropy, we take the partial derivative of $\mathcal{L}$ with respect to a specific probability $p(m)$ and set it to zero. Using the property $\frac{\partial p(n)}{\partial p(m)} = \delta_{nm}$:

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial p(m)} &= -\sum_n \left[\frac{\partial p(n)}{\partial p(m)} \ln p(n) + p(n) \frac{1}{p(n)} \frac{\partial p(n)}{\partial p(m)} \right] - \alpha \sum_n \frac{\partial p(n)}{\partial p(m)} \\ &= -\sum_n \left[\delta_{nm} \ln p(n) + \delta_{nm} \right] - \alpha \sum_n \delta_{nm} \\ &= -\ln p(m) - 1 - \alpha = 0 \end{aligned} \tag{4}$$

Solving for $p(m)$:

$$\ln p(m) = -1 - \alpha \implies p(m) = e^{-1-\alpha} \tag{5}$$

This shows that $p(m)$ is a constant, completely independent of the state m. If there are Ω total accessible microstates at energy E, the normalization constraint requires:

$$\sum_{m=1}^{\Omega} p(m) = \sum_{m=1}^{\Omega} \text{constant} = \Omega \cdot p(m) = 1 \implies p(m) = \frac{1}{\Omega} \tag{6}$$

This proves that the entropy is maximized when **all accessible states are equally likely**, which is the definition of the **microcanonical ensemble**.

Recovering Boltzmann Entropy: Substituting $p(n) = 1/\Omega$ back into the Gibbs entropy formula:

$$\begin{aligned} S &= -k_B \sum_{n=1}^{\Omega} \left(\frac{1}{\Omega}\right) \ln\left(\frac{1}{\Omega}\right) \\ &= -k_B \ln\left(\Omega^{-1}\right) \sum_{n=1}^{\Omega} \frac{1}{\Omega} \\ &= k_B \ln(\Omega) \cdot (1) \end{aligned} \tag{7}$$

$$\boxed{S = k_B \ln \Omega} \tag{8}$$

This demonstrates that the Gibbs entropy precisely coincides with the Boltzmann entropy for an isolated system.

(b) The Canonical Ensemble

Constraints: The system can exchange energy with a reservoir, meaning the energy of individual microstates E_n can vary, but the *average* energy $\langle E \rangle$ is fixed. We now have two constraints:

$$\text{1. Normalization: } \sum_n p(n) - 1 = 0 \tag{9}$$

$$\text{2. Average Energy: } \sum_n p(n)E_n - \langle E \rangle = 0 \tag{10}$$

Maximization: We introduce two Lagrange multipliers, α for the normalization constraint and λ for the energy constraint:

$$\mathcal{L} = -\sum_n p(n) \ln p(n) - \alpha \left(\sum_n p(n) - 1\right) - \lambda \left(\sum_n p(n)E_n - \langle E \rangle\right) \tag{11}$$

Taking the derivative with respect to $p(m)$ and setting it to zero:

$$\frac{\partial \mathcal{L}}{\partial p(m)} = -\ln p(m) - 1 - \alpha - \lambda E_m = 0 \tag{12}$$

Solving for $p(m)$:

$$\ln p(m) = -1 - \alpha - \lambda E_m \implies p(m) = e^{-1-\alpha} e^{-\lambda E_m} \tag{13}$$

Let the constant $e^{-1-\alpha} \equiv 1/Z$. Then the probability distribution is:

$$p(m) = \frac{1}{Z} e^{-\lambda E_m} \tag{14}$$

Applying the normalization constraint $\sum_m p(m) = 1$ requires that $Z = \sum_m e^{-\lambda E_m}$. This is exactly the form of the **canonical ensemble**.

Evaluating the Lagrange Multiplier λ: To prove that λ is proportional to the inverse temperature, we substitute our probability distribution back into the Gibbs entropy:

$$\begin{aligned} S &= -k_B \sum_n p(n) \ln\left(\frac{e^{-\lambda E_n}}{Z}\right) \\ &= -k_B \sum_n p(n)(-\lambda E_n - \ln Z) \\ &= k_B \lambda \sum_n p(n) E_n + k_B \ln Z \sum_n p(n) \\ S &= k_B \lambda \langle E \rangle + k_B \ln Z \end{aligned} \tag{15}$$

Now, take the total differential dS. Note that Z is a function of λ and the fixed energy levels E_n:

$$dS = k_B \lambda d\langle E \rangle + k_B \langle E \rangle d\lambda + k_B d(\ln Z) \tag{16}$$

We evaluate $d(\ln Z)$:

$$d(\ln Z) = \frac{\partial \ln Z}{\partial \lambda} d\lambda = \frac{1}{Z}\left(\sum_n -E_n e^{-\lambda E_n}\right) d\lambda = -\langle E \rangle d\lambda \tag{17}$$

Substituting this back into the expression for dS:

$$dS = k_B \lambda d\langle E \rangle + k_B \langle E \rangle d\lambda - k_B \langle E \rangle d\lambda = k_B \lambda d\langle E \rangle \tag{18}$$

$$\implies \frac{\partial S}{\partial \langle E \rangle} = k_B \lambda \tag{19}$$

From the thermodynamic definition of temperature, we know that $\frac{\partial S}{\partial \langle E \rangle} = \frac{1}{T}$. Equating the two expressions yields:

$$k_B \lambda = \frac{1}{T} \implies \boxed{\lambda = \frac{1}{k_B T} \equiv \beta} \tag{20}$$

Thus, the Lagrange multiplier λ for the average energy constraint is exactly the inverse temperature parameter β.