Exercise 1 Boltzmann vs Gibbs Definition of Entropy

In the lecture, we have seen two possible definitions of the entropy. The first one, often called Boltzmann entropy, is given by

$$S_{\text{Boltzmann}} = k_B \log \Omega, \tag{1}$$

where Ω is the number of possible states. The second one is called Gibbs entropy, and is given by

$$S_{\text{Gibbs}} = -k_B \sum_x P(x) \log P(x), \tag{2}$$

where the sum over x is a sum over all possible states of the system, and $P(x)$ is the probability of being in that state. The goal of this exercise is to make sure that we understand the relation between these two.

(a) We begin with a system which can have $\Omega = 2$ possible states, which we call state 1 and state 2. These could be the outcomes of a coin flip (Heads or Tails), or in materials science, the magnetic moment of an atom (spin up and spin down). What is the Boltzmann entropy of this system?

(b) We now assume that the two states have probabilities of $P(1) = P(2) = \frac{1}{2}$. Calculate the Gibbs entropy of this system, and check that it agrees with the entropy obtained in the previous part.

(c) Now assume that $P(1) = \frac{1}{3}$ and $P(2) = \frac{2}{3}$. Compute S_{Gibbs}. Is it bigger or smaller than in part (b)?

(d) Let $P(1) = 1$ and $P(2) = 0$. Compute S_{Gibbs}. If we interpret entropy as “lack of information”, how does this result make sense? *Hint*: Use the convention $0 \cdot \log 0 = 0$.

(e) We now assume that $P(1) = p$ and $P(2) = 1 - p$ are the two probabilities. Show that the Gibbs entropy is maximal when $p = \frac{1}{2}$. In other words, the state satisfying the equiprobability axiom is the state of maximal Gibbs entropy. *Hint*: It is enough to just make a plot of the entropy as a function of p. If you want to be more exact, try to calculate the maximum of this function.

(f) We now consider a system with $\Omega = 6$ possible states (remember when we rolled dice in lab 1). Assuming that $P(1) = P(2) = \cdots = P(6) = \frac{1}{6} = \frac{1}{\Omega}$, calculate both the Gibbs and Boltzmann entropies and show that they agree.

(g) Generalize this to the case where there are Ω possible states, each with a probability $\frac{1}{\Omega}$. Conclude that the Gibbs entropy is a generalization of the Boltzmann entropy to the case where the probabilities do not need to be the same.

Exercise 2 Relations between Partition Functions and Thermodynamic Potentials

In general, the expectation value of a quantity f is defined as

$$\langle f \rangle = \sum_x f(x) P(x) \tag{3}$$

We can use this for the special case $f(x) = \log P(x)$ to write the Gibbs entropy as

$$S_{\text{Gibbs}} = -k_B \langle \log P \rangle \tag{4}$$

This form is very useful to obtain relations between the partition functions and thermodynamic potentials.

(a) We begin with the canonical ensemble, where the probability of a state is given by

$$P(x) = \frac{1}{Z}e^{-\beta E(x)} = \frac{1}{Z}e^{-\beta E}. \tag{5}$$

Show that

$$\langle \log P \rangle = -\log Z - \beta \langle E \rangle \tag{6}$$

Hint: You should NOT explicitly write out the expectation values as $\langle f \rangle = \sum_x \ldots$. Instead, you can just use that $\langle f + g \rangle = \langle f \rangle + \langle g \rangle$. Note that the partition function Z is just a constant number, which is why we do not need to write $\langle Z \rangle$.

(b) Using the Gibbs definition of entropy, show that

$$-k_B T \log Z = \langle E \rangle - TS = A, \tag{7}$$

where $A = E - TS$ is the macroscopic Helmholtz free energy.

(c) Moving to the isothermal-isobaric ensemble with variables (T, p, N), the probability is given by

$$P(x) = \frac{1}{\Delta}e^{-\beta(E(x)+pV(x))} = \frac{1}{\Delta}e^{-\beta(E+pV)}, \tag{8}$$

where Δ is the normalization constant, called the isothermal-isobaric partition function. Note that the probabilities now run over states x with different volumes $V(x)$. Using similar steps as before, show that

$$-k_B \log \Delta = \langle E \rangle - TS + p\langle V \rangle = G, \tag{9}$$

where $G = E - TS + pV$ is the macroscopically defined Gibbs free energy.

(d) Finally, using the grand canonical ensemble with variables (T, V, μ), the probability is given by

$$P(x) = \frac{1}{\Xi}e^{-\beta(E(x)-\mu N(x))} = \frac{1}{\Xi}e^{-\beta(E-\mu N)}, \tag{10}$$

where Ξ is the grand canonical partition function. Show that

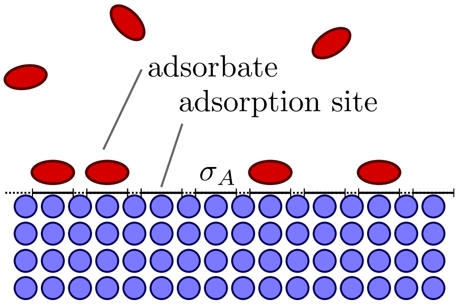
$$-k_B T \log \Xi = \langle E \rangle - TS - \mu \langle N \rangle \tag{11}$$

In thermodynamics, we futher can show that $E = TS - pV + \mu N$, from which it follows that $E - TS - \mu N = -pV$. Combine this to show that

$$k_B T \log \Xi = pV \tag{12}$$

Exercise 3 Langmuir adsorption isotherm

In 1916, Irving Langmuir presented his model for the adsorption of species onto simple surfaces. Langmuir was awarded the Nobel Prize in 1932 for his work concerning surface chemistry. He hypothesized that a given surface has a certain number of equivalent sites to which a species can "stick", either by physisorption or chemisorption.



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In the Langmuir adsorption model, the following assumptions are made for the adsorption of a molecule of one type (A) onto a solid surface:

- The surface containing the adsorbing sites is perfectly flat plane with no corrugations (assume the surface is homogeneous).
- The adsorbing gas adsorbs into an immobile state.
- All adsorption sites are equivalent.
- Each site can hold at most one molecule of A (monolayer coverage only).
- There are no interactions between adsorbate molecules on adjacent sites.

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(a) What is the total number of ways $\Omega(M)$ of arranging M identical molecules onto N surface sites?

(b) We fix the number of absorption sites N, and consider the number M of adsorbed molecules to be the variable particle number (what we usually called N when talking about the grand canonical ensemble). Write down the grand canonical partition function for given temperature T, the absorption energy ϵ of each molecule onto the surface, and chemical potential μ. *Hint:* The naive definition of the grand canonical partition function is

$$\Xi = \sum_{x} e^{-\beta(E(x)-\mu N(x))}, \tag{13}$$

where x runs over all possible microstates, which we can now write as

$$\Xi = \sum_{M=0}^{N} \sum_{x'} e^{-\beta(E(x')-\mu N(x'))}, \tag{14}$$

where the sum over x' only runs over those states where there are M adsorbed molecules. Begin by showing that we can write this as

$$\Xi = \sum_{M=0}^{N} \Omega(M) e^{-\beta(E(M)-\mu M)}, \tag{15}$$

where $\Omega(M)$ is the number of ways to arrange the M atoms onto the N surface sites.

(c) What is the probability $P(M)$ of having M molecules adsorbed on a surface with N sites?

(d) In (c), what is the number of molecules M^* that is most likely to be absorbed on the surface? *Hint*: Instead of maximizing the probability $P(M)$, one can maximize $\log P(M)$ (why?). Use Stirling's approximation.

(e) We define now the fraction of the surface sites covered as $\theta(M) = \frac{M}{N}$. Taking the chemical potential of the molecules to be equal to that of an ideal gas, i.e. $\exp \frac{\mu}{k_B T} = \frac{P}{P_0}$ (where P_0 is constant), show that

$$\theta(M^*) = \frac{M^*}{N} = \frac{1}{\exp \frac{(\epsilon - \mu)}{k_B T} + 1} = \frac{P}{P_0 \exp \frac{\epsilon}{k_B T} + P} \tag{16}$$

which provides us a formula for the (most likely) surface coverage as a function of the tempeature T and pressure p.

The End.