

## Physics 112 - Intro to Statistical and Thermal Physics - Spring 2023

### Problem Set 08

Due Friday, April 7 at 11:59 PM (PDT)

*Last Update: April 6, 2023*

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- **Highlighted/Most Relevant Reading for the material on this week's problem set:**

- Schroeder, Sections 7.1

- **Reading for next week:**

- Schroeder, 7.2, 7.3

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## Problem 8.1 - Ionization of Hydrogen

This problem set is all about changing particle numbers! In this first problem we will explore the ionization of hydrogen.

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Let's first consider the thermal *excitation* of a hydrogen atom. The energy levels of an electron bound to hydrogen are given by

$$E_n = -\frac{E_0}{n^2}, \quad E_0 \equiv 13.6 \text{ eV}, \quad n \in \{1, 2, 3, \dots\},$$

where  $n$  is the quantum number for energy and  $E_0$  is the Rydberg unit of energy/the ionization energy of ground state atomic hydrogen. Also recall that the degeneracy of the energy levels in hydrogen are given by  $g(E_n) = 2n^2$ .

(a) Using canonical methods (rather than micro-canonical or grand canonical), determine the relative fraction of hydrogen atoms that are in the  $n = 2$  first excited state vs. the  $n = 1$  ground state as a function of the temperature  $T$ . At what temperature does this fraction reach 1 part in  $10^6$ ? How about 1 part in 1000?

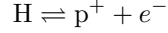
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We can consider the energy levels of an electron in hydrogen as an “internal structure” (in contrast to the “external structure” where we treat the atomic hydrogen as an ideal gas). That is, we can use the states of hydrogen described earlier as the one-particle microstates for calculating an internal one-particle canonical partition function,  $Z_{int,H}$ . You can see from part (a) that if  $T < \sim 10^4$  K (which includes the surface of the sun which is ‘only’ at 5770 K), we can basically assume any atomic hydrogen we have is in the ground state.

(b) **Extra Part** (*Not for Credit*) Argue that in this situation we have  $Z_{int,H} = 2e^{\beta E_0}$ .

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Now let's analyze ionization. We will consider this system to consist of three species: Species 1 is the neutral hydrogen atom H (an electron bound to a hydrogen nucleus). Species 2 is the ionized hydrogen which is just the nucleus, a proton  $p^+$ . Species 3 is the free/unbound electron  $e^-$ . Note that ionization/binding is given by the reaction



Let  $N_H$ ,  $N_p$ , and  $N_e$  be the number of each of the three species present in our system. At fixed temperature and volume the Helmholtz free energy of the system is  $F(T, V, N_H, N_p, N_e)$ . Recall that we can find the chemical potentials for ideal gases via

$$\mu_i = \left( \frac{\partial F}{\partial N_i} \right)_{T, V, N} = -k_B T \ln \left( \frac{V n_{Q,i} Z_{int,i}}{N_i} \right).$$

If we take into account the spin of the free electron we also have  $Z_{int,e} = 2$ . We will make a number of simplifying assumptions. First, we will ignore the electric interactions amongst the electrons and amongst the protons, so that we may treat all three species as non-interacting ideal gases. We will also assume the concentrations of each species are much less than the quantum concentrations. We also approximate  $m_H \approx m_p$ .

(c) Determine the equilibrium relation between the chemical potentials given a system at fixed volume and temperature. Using this equilibrium condition, show that in equilibrium we have

$$\frac{n_p n_e}{n_H} = n_{Q,e} e^{-\beta E_0}.$$

*Hint (highlight to reveal):* [Recall that equilibrium can be determined by minimizing the Helmholtz free energy.]

*Answer (highlight to reveal):* [You should find  $\mu_H = \mu_p + \mu_e$ ]

**Commentary:** The above equation is one form of the **Saha equation**.

Suppose our system starts with  $N$  hydrogen atoms. After equilibration, a fraction  $x$  has ionized so that  $N_H = (1 - x)N$  and  $N_p = N_e = xN$ . Using this we can rewrite the result from (c) as

$$\frac{x^2}{1 - x} = \frac{V n_{Q,e}}{N} e^{-\beta E_0}.$$

We can define the right-hand side as some parameter  $b$  that depends on the concentration  $n \equiv N/V$  and temperature  $T$ . Let's define the dimensionless temperature scale  $T_0$  and dimensionless temperature via

$$\tau \equiv \frac{k_B T}{E_0} = \frac{T}{T_0}.$$

At the solar surface we have temperature  $T = 5770 \text{ K}$  and concentration  $n \approx 10^{20} \text{ m}^{-3}$ .

(d) What is the temperature scale  $T_0$ ? What is  $\tau$  at the surface of the sun? What fraction  $x$  of hydrogen has been ionized at the surface of the sun?

We can get this same result using grand canonical methods. We will ignore spin in this part. Consider a hydrogen which has two possible electron states:

- No electrons (the hydrogen is ionized). This has energy 0.
- One electron (the hydrogen is bound and in the ground state). This has energy  $-E_0$ .

Let the hydrogen be in equilibrium with a reservoir of temperature  $T$  and a gas of electrons with chemical potential  $\mu = -k_B T \ln \left( \frac{n_{Q,e}}{n_e} \right)$ .

(e) Find the relative probability of being ionized-vs-being bound by taking the ratio of the relevant Gibbs factors.

**Commentary:** If we take the relative probability as  $n_p/n_H$ , our answer above recovers the Saha equation from part (c)!

## Problem 8.2 - Grand Factorization

In this problem we will see how to apply the grand canonical ensemble to a simplified version of the two-level paramagnet. Though really what we will be doing is laying the groundwork for quantum statistical mechanics!

Suppose we have an “open” paramagnet system where the number of spins is variable. Our system lives in a reservoir of temperature  $T$  and a gas of free spins with chemical potential  $\mu$ .<sup>1</sup> Suppose our open system can contain at most one spin. Since we will be using  $\mu$  as our chemical potential, let the two different spin states of a single spin be:

$$E_{\uparrow} = -\varepsilon/2, \quad E_{\downarrow} = +\varepsilon/2.$$

Our open system thus contains three possible states:

- No spins.
- One spin in the spin-up state.
- One spin in the spin-down state.

(a) Find the grand canonical partition function  $\Xi$  for this system. Use this to find the average number of particles in the system  $\langle N \rangle$ .

[Note: As a check, we should reasonably expect that our answer will strictly be between 0 and 1 since those are the minimum and maximum possible number of spins in our system given our setup.]

For a specific energy state we define the **occupation number** of the state in a multiple-particle system to be the average number of particles in that energy state. For example, in our system we have two occupation numbers,  $\langle n_{\uparrow} \rangle$  and  $\langle n_{\downarrow} \rangle$ , the average number of particles in the spin-up state and spin-down state, respectively. Mathematically,

$$\langle n_i \rangle = \sum_{n_i=0}^{n_{i,\max}} n_i P(i; n_i),$$

where  $P(i; n_i)$  is the probability that there are  $n_i$  particles in the  $i$ -th energy level. Note that even though part (b) won't be graded you should still give it a shot before moving on to part (c)!

(b) **Extra Part (Not for Credit)** Without explicit calculation, what do you predict the occupation number of the spin-up state will be in the two limits  $T \rightarrow 0$  and  $T \rightarrow \infty$ ?

(c) Using your  $\Xi$  from part (a), find  $P(\uparrow; 1)$ ,  $P(\downarrow; 1)$ ,  $\langle n_{\uparrow} \rangle$ , and  $\langle n_{\downarrow} \rangle$ .

[Note: As a check, you should have  $\langle n_{\uparrow} \rangle + \langle n_{\downarrow} \rangle = \langle N \rangle$ . You can also check your predictions/intuitions from part (b).]

<sup>1</sup>This setup is basically justification for the given features I want us to explore.

Now that we have some of the basics of working with the grand canonical ensemble let's make our system a little more interesting. Suppose instead of allowing at most one spin in our open system, we loosen the restriction to only allowing at most one spin *in each state* in our open system. That is, each state's occupancy must be either 0 or 1. This introduces a fourth microstate,

1. No spins (both occupancies are  $\{n_\uparrow, n_\downarrow\} = \{0, 0\}$ ).
2. One spin in the spin-up state (occupancies  $\{1, 0\}$ ).
3. One spin in the spin-down state (occupancies  $\{0, 1\}$ ).
4. One spin each in the spin-up state and the spin-down state (occupancies  $\{1, 1\}$ ).

(d) Find  $\Xi$  and  $\langle n_1 \rangle$  for this new setup.

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There is something really interesting going on with  $\Xi$  in this case which we will now demonstrate. Suppose that we consider *each energy level of the system as its own subsystem*. That is, we consider just the “spin-up” state as an independent subsystem. This subsystem now has only two possible microstates:

- No spins are in the spin-up state (this is realized by states 1 and 3 in part (d)).
- One spin is in the spin-up state (this is realized by states 2 and 4 in part (d)).

We can find the grand canonical partition function  $\Xi_\uparrow$  for this “single-state” subsystem. Similarly, we consider just the “spin-down” state as a different independent subsystem and find  $\Xi_\downarrow$ . Using this we can determine the occupation numbers directly from the single-state grand canonical partition functions, e.g.

$$\langle n_\uparrow \rangle = k_B T \left( \frac{\partial \ln \Xi_\uparrow}{\partial \mu} \right)_{T, V}. \quad (1)$$

(e) Find the grand canonical partition functions  $\Xi_\uparrow$  and  $\Xi_\downarrow$  for these two subsystems. Show that your answer for  $\Xi$  from part (d) factors into  $\Xi_\uparrow \Xi_\downarrow$ . Finally, calculate  $\langle n_\uparrow \rangle$  using Eq. 1 and show it is equivalent to what you found in (d).

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This will be a nice trick that we will use repeatedly in quantum statistical mechanics - treating each quantum state for the one-particle system as an open system. Let's explore (in not-for-credit/optional parts) two ways we can generalize this: more particles and more states. First, suppose we can have at most *two* of our spins in each state.

(f) **Extra Part (Not for Credit)** Describe the  $3^2 = 9$  different microstates in this system, find the new  $\Xi$ ,  $\Xi_\uparrow$ , and  $\Xi_\downarrow$ , and again show that  $\Xi = \Xi_\uparrow \Xi_\downarrow$ .

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Finally, consider a three-level system where a spin can be in spin-states  $m_s \in \{+1, 0, -1\}$  with energies  $-\varepsilon, 0, +\varepsilon$ , respectively.<sup>2</sup> Let's again have the situation in (d) where each of the three states can be occupied by at most one particle.

(g) **Extra Part (Not for Credit)** Describe the  $2^3 = 8$  different microstates in this system, find the new  $\Xi$ ,  $\Xi_{+1}$ ,  $\Xi_0$ , and  $\Xi_{-1}$ , and show that  $\Xi = \Xi_{+1} \Xi_0 \Xi_{-1}$ .

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<sup>2</sup>We can give these arbitrary energies  $E_{+1}, E_0, E_{-1}$  if we want but this should wind up at least slightly cleaner.

**Commentary:** We will see examples like part (d) and (g) when we deal with **fermionic** system. The condition for us to be able to factor the grand canonical partition function is that our particles have the same energy states and the number of particles in each state is independent of the number of particles in other states. Note that in the case described in part (a) we don't satisfy this since if we have only one particle, filling the lower-energy state automatically means the higher-energy state is empty.

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## Problem 8.3 - DataHub - Adsorption and Hydrogen Storage

When near a surface, gases, liquids, or solutes can potentially **adsorb** onto the surface, which means that molecules bind to specific sites on a surface forming a thin film. For example, carbon filters work via adsorption of dust and smoke particles. In this problem we will explore the adsorption of hydrogen molecules onto a surface.<sup>3</sup> We will start this problem with some theory and then conclude with a DataHub task to numerically approximate our results.

Consider an adsorbing surface having  $N$  sites, each of which can adsorb at most one hydrogen molecule. We will take the energy of an empty site to be 0 and the energy of a site that has adsorbed a hydrogen molecule as  $E = -\varepsilon$ . Note that we assume  $\varepsilon > 0$  ( $E < 0$ ) so it is energetically more favorable for a particle to be adsorbed. The adsorbing sites are in contact with a reservoir of hydrogen gas of chemical potential  $\mu$  and temperature  $T$ .

(a) Find the grand canonical partition function  $\Xi_1$  for a single adsorption site. Use this to find the probability  $p_{\text{ads}}$  that the site has adsorbed a molecule.

Each adsorption site is independent but distinguishable (e.g. by their location) so the probability distribution for the number of occupied sites/adsorbed particles  $n$  is given by a binomial distribution with probability weight  $p_{\text{ads}}$ ,

$$P(n) = p_{\text{ads}}^n (1 - p_{\text{ads}})^{N-n} \binom{N}{n}.$$

We define the **coverage** of sites  $\theta$  as the average fraction of sites that have adsorbed a particle,  $\theta \equiv \langle n \rangle / N$ .

(b) Show that the coverage of the system is  $\theta = (1 + e^{-\beta(\varepsilon + \mu)})^{-1}$ .

*Hint (highlight to reveal):* [What do we know about the mean of a binomial distribution?]

We can express the chemical potential of the hydrogen gas as  $\mu = k_B T \ln \left( \frac{P}{k_B T n_{Q,H}} \right)$ .

(c) **Extra Part** (*Not for Credit*) Show that the coverage can be written in the form

$$\theta = \frac{P}{P + P_0(\varepsilon, T)}; \quad P_0(\varepsilon, T) \equiv k_B T n_{Q,H} e^{-\beta\varepsilon}.$$

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<sup>3</sup>This turns out to be a great way of efficiently storing hydrogen for fuel cells.

Ok, that preliminary theory out of the way, we are ready for the numerical work! You will find the remaining three numerical parts in the link below:

[http://datahub.berkeley.edu/user-redirect/interact?account=ajh38&repo=phy112-001\\_spring\\_2023&branch=main&path=Sp23-112-Hw08-Python](http://datahub.berkeley.edu/user-redirect/interact?account=ajh38&repo=phy112-001_spring_2023&branch=main&path=Sp23-112-Hw08-Python)

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## Not for Credit - DataHub - Maximum Entropy Probability Assignment

Recall that we defined the Gibbs entropy formula for an arbitrary probability distribution  $\{p_{\mathcal{J}}\}$  as

$$S = -k_B \sum_{\mathcal{J}} p_{\mathcal{J}} \ln p_{\mathcal{J}}.$$

I have added a second problem to the data hub, titled “Maximum Entropy Probability Assignment” which explores the idea of maximizing the Gibbs entropy formula under certain constraints. This is a computational version of what we did in the bonus lecture.

